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PHOTOINDUCED ELECTRON TRANSFER
IN CHROMOPHORE-QUENCHER COMPLEXES
DESIGNED FOR METAL CENTERED
CHEMISTRY

DAVID ROBERT McDONALD

A thesis submitted to the Faculty of Graduate Studies
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Ottawa-Carleton Chemistry Institute
Carleton University
Ottawa, Ontario

May 1996

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PHOTOINDUCED ELECTRON TRANSFER IN CHROMOPHORE-
QUENCHER COMPLEXES DESIGNED FOR METAL CENTERED
CHEMISTRY

submitted by

DAVID R. McDONALD, B.Sc.

in partial fulfilment of the requirements
for the degree of Doctor of Philosophy

Chair, Chemistry Department

Thesis Supervisor

External Examiner

Carleton University

May 1996

ABSTRACT

A series of photoredox active ligands and the analogous non-photoredox active ligands have been synthesized and characterised by UV/visible, ^1H NMR, ^{13}C NMR, FTIR, mass spectroscopy and elemental analysis. The photoredox active ligands are based on the 2,3-dicyanohydroquinone chromophore which has been protected and functionalized with ligating moieties. Molecular models of the potential chromophore ligands were prepared and steric strain upon the molecules in different coordination environments was used to choose a chromophore ligand for preparation of complexes. The chromophore ligand, 4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline (CL) was chosen for quenching experiments and preparation of complexes. The corresponding ligand, 1,3-bis((3'-pyridylmethyl)imino)isoindoline (L) which lacks the diether functionalities responsible for the strong visible fluorescence of CL but contains the same ligating moieties was used as a blank for both photophysical studies and for the preparation of analogous non-quencher complexes. Attempts to synthesize the deprotected hydroxylated version of CL which is expected to be a reversible two electron donor in the excited state were also carried out.

Picosecond transient absorption spectroscopy of the ligand was carried out in acetonitrile at 298 K in order to determine the absorption spectrum of the ligand excited state (CL^*), the protonated ligand excited state (CLH^*) and the cation radical (CL^+). The excited state displays no detectable absorptions in the 425 nm to 675 nm range investigated whereas the protonated excited state exhibits a broad absorption from 575 nm to 650 nm ($\epsilon \approx 700$) resulting from a very rapid ($\tau < 50$ ps) and efficient protonation from trace water due to the enhanced basicity of the excited state. Emission lifetime measurements were used to determine the lifetimes of the neutral and protonated excited state as $3.81 \pm .04$ ns and $10.4 \pm .3$

ns respectively. Intermolecular quenching studies of the ligand have shown that the cation radical ($\text{CL}^{\bullet+}$) displays a maximum at 475 nm ($\epsilon \simeq 6000$). Picosecond transient absorption spectra of **L** in acetonitrile and under similar conditions used for the intermolecular quenching studies of **CL** displays a lack of any visible transient that can be assigned to the excited state or a radical.

The chromophore–quencher complexes, $\text{Cu}^{\text{(II)}}(\text{CL})(\text{CF}_3\text{SO}_3)_2$, $\text{Cu}^{\text{(II)}}(\text{CL})(\text{H}_2\text{O})_2(\text{CF}_3\text{SO}_3)_2$ and a non–chromophore–quencher complex $\text{Cu}^{\text{(II)}}(\text{L})(\text{H}_2\text{O})(\text{CF}_3\text{SO}_3)_2$ were synthesised and characterized. Intramolecular electron transfer from the $n-\pi^*$ excited state of the photoredox active ligand to the $\text{Cu}^{\text{(II)}}$ metal acceptor occurs in less than 20 ps for $\text{Cu}^{\text{(II)}}(\text{CL})(\text{CF}_3\text{SO}_3)_2$ and 30 ps for $\text{Cu}^{\text{(II)}}(\text{CL})(\text{H}_2\text{O})_2(\text{CF}_3\text{SO}_3)_2$ as shown by emission lifetime measurements and transient absorption spectroscopy. Back electron transfer occurs at a rate of $4.9 \times 10^9 \text{ s}^{-1}$ and $4.0 \times 10^9 \text{ s}^{-1}$ in $\text{Cu}^{\text{(II)}}(\text{CL})(\text{CF}_3\text{SO}_3)_2$ and $\text{Cu}^{\text{(II)}}(\text{CL})(\text{H}_2\text{O})_2(\text{CF}_3\text{SO}_3)_2$ respectively. Intramolecular electron transfer quenching was found to be only 21 % efficient in $\text{Cu}^{\text{(II)}}(\text{CL})(\text{CF}_3\text{SO}_3)_2$ due to a competitive process of ligand excited state protonation to form a non–redox active species.

Irradiation of the reference complex, $[\text{Zn}^{\text{(II)}}(\text{CL})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$, in acetonitrile failed to display the characteristic cation radical but did however exhibit stimulated emission at 485 nm on the 50 ps time scale. Observation of the cation radical spectrum was not expected due to the formation of a thermodynamically unstable $\text{Zn}^{\text{(I)}}$ complex.

The chromophore–quencher complex $[\text{Co}^{\text{(III)}}(\text{CL})_3](\text{CF}_3\text{SO}_3)_3$ was prepared from pentamminecobalt(III)triflate and an excess of ligand by a photo–reaction that is greatly accelerated in the presence of trace amounts of triflic acid. Picosecond transient absorption spectroscopy of the final product displayed the formation of the cation radical in the 20 ps time regime.

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List of Symbols

a	a constant in mathematical expressions or it represents an ammine (NH_3) ligand in chemical formula of complexes
α	distance in excess of centre to centre distance
A	used to designate an acceptor of an electron or energy
b	y-intercept of a fitted line
β	constant to normalize distance dependence of electron transfer
C	Coulomb
c	speed of light = $2.997925 \times 10^8 \text{ m s}^{-1}$
CL	used to designate a redox active chromophore containing ligand
D	used to designate a donor of an electron or energy
δ	shift in ppm from TMS standard (NMR spectra)
e	charge on the electron = $1.60219 \times 10^{-19} \text{ C}$
Δe	number of electrons transferred during electron transfer
E	energy in Joules
E.A.	electron affinity in Volts
ΔE	electrochemical driving force in Volts
E^{ox}	oxidation potential in Volts
E_{O}	reduction potential in Volts vs N.H.E. of the species being oxidized
E^{red}	reduction potential in Volts
E_{r}	reduction potential in Volts vs N.H.E. of the species being reduced
E^*	excited state potential in Volts
E^{oo}	energy of zeroth energy level in Volts
$E_{1/2}$	half-wave reduction potential in Volts
ϵ_0	vacuum permittivity = $8.854188 \times 10^{-12} \text{ J}^{-2} \text{ C}^{-2} \text{ m}^{-1}$
ϵ	dielectric constant of solvent

F	Faraday constant = $9.64846 \times 10^4 \text{ C mol}^{-1}$
ΔG	thermodynamic driving force
$\Delta G^\ddagger$	activation energy
h	Planck's constant = $6.62618 \times 10^{-34} \text{ J s}$
ΔH	enthalpy
η	viscosity in centipoise
I	ionic strength
I.P.	ionization potential in Volts
i	i th component in a series
j	j th component in a series
k_b	Boltzmann's constant = $1.38066 \times 10^{-23} \text{ J K}^{-1}$
k_f	rate of forward electron transfer
k_b	rate of back electron transfer
k_{et}	rate of electron transfer
k_q	quenching rate constant
K	equilibrium constant
λ	reorganizational energy
L	Avogadro constant = $6.02205 \times 10^{23} \text{ mol}^{-1}$
L	used to designate a ligand that is not photo-redox active
Λ_m	Molar conductance in $\text{ohm}^{-1} \text{cm}^2 \text{M}^{-1}$
m	slope of a fitted line
M^+	molecular ion in mass spectroscopy
MeCN	acetonitrile
μ	dipole moment in Debye
n	number of electrons transferred (Nernst equation)
n	refractive index

NMP	N-methylpyrrolidinone
ν	frequency in units of energy
$\bar{\nu}$	frequency in cm^{-1}
$\nu_{0,0}$	frequency of 0,0 electronic transition
$\Delta\text{O.D.}$	change in optical density
ω_p	work required to separate products
ω_r	work required to bring reactants together
P	used to designate a product
Q	charge in Coulombs
R	used to designate a reactant
RMS	statistical error on a fitting function calculated as the square root of the sum of squared deviations from the mean value (Root Mean Square). For the molecular models discussed in Appendix A, this corresponds to the differences between the ideal user-defined structure and the final minimized structure using a procedure based solely on geometrical optimization.
s	singlet energy level
t	time
t	triplet energy level
$t_{1/2}$	half-life of emission decay = $(\ln 2)/k$
TBAH	tetrabutylammonium hexafluorophosphate
TBAT	tetrabutylammonium tetrafluoroborate
τ	emission decay lifetime
τ_f	fluorescence emission lifetime
τ_{CSS}	lifetime of a charge separated state
ϕ	quantum yield for quenching
ϕ^0	quantum yield in the absence of quenching

ϕ_f	static fluorescence quantum yield
ϕ_p	quantum yield for product formation
x	the fixed variable in a line fit
y	the dependent variable in a line fit
3AMP	3-aminomethylpyridine

1. INTRODUCTION

The study of photoinitiated charge separated states has received much attention in the past two decades.¹⁻²⁰ This is in part due to an ongoing interest in the mechanism of long range electron transfer in photosynthetic reaction centers and model systems and a marked increase in the availability of laser techniques capable of measuring the rates of these very fast events. The properties of the excited state or states responsible for electron transfer and the kinetics of electron or energy transfer from these states to ground state species and subsequent electron transfer reactions are most often studied. The results are most often interpreted by the use of classical or quantum mechanical theories of electron transfer. The rates of electron transfer are usually correlated to such factors as the separation of donor and acceptor, the thermodynamic driving force and inverted region behavior, inner and outer sphere reorganizational energies and the orientation of donor and acceptor.¹ Relatively few studies deal with the design of a chromophore-quencher complex in which the photoinduced charge separated state may exhibit metal centered chemistry and therefore be exploited for the purpose of developing new types of photocatalysts.

A chromophore-quencher complex with this unique design consists of a photoredox active organic chromophore bound to a metal site quencher. Excitation of the chromophore results in intramolecular electron transfer to or from the metal ion and the generation of a charge separated state. This is due to the fact that excited state species are superior electron donors and acceptors as compared to the corresponding ground state systems. More specifically, their excited oxidation potentials are lowered and their excited state reduction potentials are increased relative to those of the ground state.

The literature on intramolecular electron transfer quenching in donor-acceptor systems includes several studies on purely organic systems as well as

a few on coordination complexes. Studies that have been carried out on purely organic donor-acceptor systems include electron transfer quenching of pulse radiolysis generated biphenyl radical anion², pyrene³, anthracene³, 1,4-dimethoxyanthrene⁴ and porphyrin⁵ excited states. MLCT based excited states have been shown to be quenched intramolecularly by either interligand electron transfer⁶, intraligand electron transfer⁷ or metal reduction by a donor ligand not associated with the MLCT state.⁸ Few studies have shown definitively the intramolecular quenching of an organic chromophore excited state by a metal ion. One such study⁹ involves electron transfer from a porphyrin based excited state to a Ru(III) polypyridyl quencher covalently linked exocyclic to the porphyrin. Another study¹⁰ has shown that the first excited singlet state of the anthryl chromophore can be quenched by a Co(III) cage complex provided that the link between the two species is sufficiently large enough to eliminate an energy transfer interaction involving the short lived Co(III) triplet state. This energy transfer process has been previously shown¹¹ in $[(\text{NH}_3)_5\text{Co(III)(TSC)}]^{2+}$ (TSC is trans-4-stilbene-carboxylate) where it was concluded that intramolecular excitation energy transfer from the excited state of the chromophore to a low-lying nonspectroscopic triplet LMCT state is responsible for the observed photoreduction of Co(III). More recently, a similar Co(III) system was investigated¹² using a naphthyl group as the chromophore and efficient electron transfer quenching was observed at large distances across a flexible peptide spacer with an inverse distance relationship. This suggested that a hydrogen bonding interaction between the peptide and a coordinated ammonia ligand allowed the donor and acceptor to interact more closely via through space electron transfer.

The use of an organic chromophore centered on the ligand offers several advantages over metal centered chromophores. Organic chromophores generally have much higher absorptivities and would thus be more efficient photocatalysts.

Generally a chromophore which is pseudo-stable as a radical is desired and many such organic chromophores exist. The different bonding and substitutional properties of the metal (M/M^+) couple would be accessible for chemistry without affecting the nature of the chromophore. The chromophore used in this study is an alkoxy derivative of the highly fluorescent 2,3-dicyanohydroquinone molecule which has been cyclized to form a substituted diiminoisoindole chromophore and then functionalized with methylpyridyl moieties to facilitate coordination to a metal ion and eliminate ground state coupling of the chromophore and metal. The choice of metal ion used to form a chromophore quencher complex which exhibits intramolecular electron transfer must ensure that the complex formed does not possess a CT transition with sufficient spectral overlap with the chromophore emission to quench the excited state by an energy transfer mechanism. Additionally, the complex must be thermodynamically and photochemically stable enough to be isolated in pure form.

A description of the necessary conditions to be satisfied in order to prepare a chromophore quencher complex which possesses the desired aforementioned properties will be discussed. In this study, transient absorption spectroscopy, fluorometric titrations and emission lifetime measurements revealed that excited state protonation phenomena can compete efficiently with electron transfer reducing charge separated state yields by more than 75 % in complexes with adjacent aquo ligands. The lifetimes of the charge separated states formed by these complexes are of the order of a few hundred picoseconds being too short to carry out even simple substitution reactions. Synthetic modifications of the ligand can be used in future work to enhance the efficiency of formation and increase the lifetime of the charge separated state so that the chemistry of the reduced metal site quencher can be explored.

1.1 DEACTIVATION OF EXCITED STATES

The absorption (A) of a photon of visible or ultraviolet light of suitable energy by most singlet ground state (S_0) organic chromophores leads to the formation of a singlet excited state species, (S_n). Triplet excited state species (T_n) may also be formed directly (A_T) under certain circumstances such as in the presence of heavy atoms or a high pressure of molecular oxygen²¹, but this is a spin forbidden process and generally has a very small probability under normal circumstances. The excited state species may then be deactivated or lose its electronic excitation energy via a number of different photophysical or photochemical processes as outlined in the energy level diagram shown in figure 1. Photophysical deactivation processes include radiative processes such as fluorescence (F) and phosphorescence (P). Fluorescence is emission from a singlet excited state to a singlet ground state and generally occurs at rates of 10^6 to 10^{12} s^{-1} (μs to ps range of lifetimes). Phosphorescence is emission from a triplet excited state to a singlet ground state and usually occurs at much slower rates of 10^{-1} to 10^6 s^{-1} (10 s to μs range of lifetimes) due to the change in spin multiplicity that is required for this process.

Nonradiative photophysical deactivation of the excited state may also occur through the processes of internal conversion (IC) and intersystem crossing (ISC). Internal conversion is a process which occurs without a change in spin multiplicity and include transitions from vibrationally excited to vibrational ground states and from electronic excited states to a lower energy electronic state. During internal conversion the excitation energy is lost to the surroundings in the form of heat via vibrational and rotational motion. Internal conversion within a single electronic state state is usually called vibrational relaxation and occurs quite rapidly with rates of 10^{12} s^{-1} . Internal conversion between different electronic states however is a normally a much slower process and follows the energy gap law in that the larger

Figure 1.1

Qualitative energy level diagram and excited state deactivation processes

the energy gap, the slower will be the rate of internal conversion. Typical rates of internal conversion are usually less than 10^5 s^{-1} and as such, do not normally compete appreciably with fluorescence and intersystem crossing.

Intersystem crossing is a process which occurs with a change in spin multiplicity and may occur from an excited singlet state to a lower energy excited triplet state or from an excited triplet state to a lower energy singlet state. The rate for this process is quite variable being affected by heavy atoms and molecular structure but it generally will follow the energy gap law for compounds of similar structure being as high as 10^{11} s^{-1} for compounds with a small singlet-triplet energy gap to as low as 10^6 s^{-1} for compounds with a large singlet-triplet energy gap.

In addition, so-called delayed fluorescence may occur from the S_1 state under certain circumstances such as when the T_1 and S_1 state are very close in energy and repopulation of this state may occur via additional intersystem crossing from the T_1 to the S_1 state. This type of fluorescence typically has lifetimes of the order of μs and vanishes at low temperature as it is a thermally activated process.

Both singlet excited states and triplet excited states may also be deactivated by the interaction of this state with another state of suitable energy which may or may not be affiliated with the same molecular species through the process of quenching (Q). Quenching is a general term that includes both intramolecular and intermolecular energy transfer, electron transfer and photochemical reactions.

1.2 QUENCHING MECHANISMS

1.2.1 Energy Transfer

Energy transfer quenching of excited state species may occur via two different mechanisms which may be distinguished by their distance dependence. These are radiative energy transfer which is often²¹ referred to as "trivial" energy

transfer and radiationless energy transfer which may be further subdivided into whether it occurs via a Coulombic interaction or an exchange interaction.

The rate of radiative energy transfer is inversely related to the square root of the separation distance between the excited state species and the quencher. This type of energy transfer may be appreciable when the overlap between the quencher absorption spectrum and the excited state emission spectrum is large. The rate of radiative energy transfer may be calculated²² as:

$$k_{\text{rad}} = \phi_e [Q] \epsilon_Q J \quad 1.1$$

where ϕ_e is the quantum yield of emission, $[Q]$ is the concentration of quencher, ϵ_Q is the extinction coefficient of the quencher at the emission wavelength and J is the integrated overlap of the emission and quencher absorption given by;

$$J = \int_0^\infty I_D \epsilon_Q d\nu \quad 1.2$$

where the experimental emission curve (I_D) and experimental absorption spectrum of the quencher (ϵ_Q) have been plotted on an energy scale and normalized so that complete overlap corresponds to $J = 1$.

Coulombic energy transfer occurs when the oscillating dipole of the excited state donor species (D) is in resonance with or coupled to the dipole of the acceptor (A) and is often referred to as the induced dipole mechanism. The interaction energy between these dipoles is related to the magnitude (μ) and the separation distance between them (R) and Forster²³ has shown that the rate of coulombic energy transfer (k_{coul}) is related to the square of this interaction energy by:

$$k_{\text{coul}} \rightarrow E^2 \approx \frac{\mu_D^2 \mu_A^2}{R_{DA}^6} \quad 1.3$$

Experimentally, the rate of Coulombic energy transfer may be calculated from:

$$k_{\text{coul}} = k \frac{\kappa^2 k_d^0}{R_{DA}^6} J(\epsilon_A) \quad 1.4$$

where k is a constant related to index of refraction and concentration, κ^2 is a term

relating the orientation of the dipoles in space and is often set equal to 2/3 for a random distribution of donor and acceptor in solution, k_d^0 is the radiative lifetime of the donor, R_{DA} is the separation between donor and acceptor and $J(\epsilon_A)$ is the spectral overlap integral integrated over both the frequency and acceptor extinction coefficient as follows:

$$J(\epsilon_A) = \int_0^\infty I_D \epsilon_A d\nu d(\epsilon_A) \quad 1.5$$

where the parameters are the same as those defined for equation 1.2. It has more recently²⁴ been proposed that radiative and Coulombic energy transfer may be interpreted as limiting conditions of a unified theory in which the $1/R^6$ dependence vanishes leaving only a $1/R^2$ term related to the radiative mechanism when R becomes large (150 nm or more).

Energy transfer by an exchange interaction or the collisional mechanism as it is also known involves the direct interaction of the donor and acceptor by contact. Dexter²⁵ has proposed that the rate of energy transfer by an electron exchange interaction (k_{exch}) is given by

$$k_{\text{exch}} = K J \exp(-2R_{DA}/L) \quad 1.6$$

where K is related to the specific orbital interactions, J is a spectral overlap integral normalized with respect to ϵ_A , R_{DA} is the donor acceptor separation distance and L is their van der Waal radii. This theory predicts that k_{exch} is not related to the spectral properties of the acceptor and that the rate will drop off as $\exp(-2R_{DA}/L)$ which limits its effectiveness to 5 to 10 Å whereas the magnitude of k_{coul} may still be significant at distances exceeding 30 Å²¹.

1.2.2 Electron Transfer

Excited electronic states may also be quenched by the process of thermal electron transfer to an acceptor or from a donor moiety of suitable energy. This is quite different from an optical charge transfer in which an electron or a charge

comparable to an electron²⁶ is transferred during the light absorption process (i.e. a vertical transition from one potential energy surface to another). Examples of the latter optical electron transfer process include ligand to metal (LMCT), metal to ligand (MLCT) and intraligand (LLCT) charge transfer absorptions of inorganic complexes, intervalence (IT) charge transfer absorptions in bimetallic complexes, charge transfer (CT) absorptions in donor-acceptor type molecules or complexes and ion pair charge transfer (IPCT) absorptions which can sometimes be observed in halide or complex ion salts of inorganic complexes.

Through the experimental work of Taube and others²⁷ in the 1950s on intermolecular electron transfer reactions of complex ions and theoretical work by Marcus in the 50s and 60s and others later on, several theoretical expressions were derived in order to calculate the rates of electron transfer (k_{et}) reactions. The most notable classical theoretical treatments all possess a similar free energy relationship²⁸ based on reaction rate theory, namely:

$$k_{et} = A \exp(-\Delta G^\ddagger/RT) \quad 1.7$$

and differ in how the pre-exponential factor (A) and the activation barrier ($\Delta G^\ddagger$) are defined. The first of such expressions is the classical treatment put forth by Marcus²⁹ (Hush³⁰ developed a theory similar to that of Marcus to explain electrode reactions) where electron transfer is dealt with in terms of nuclear coordinates and electrostatic potentials of the reactants and is related to the free energy change (ΔG) upon electron transfer and the reorganizational energy (λ) by:

$$k_{et} = \frac{k_b T}{h} \left(\kappa \exp\left\{-\left[\frac{(\lambda + \Delta G)^2}{4\lambda RT}\right]\right\} \right) \quad 1.8$$

where κ is the probability of a system in the transition state being converted to products and is equal to 1 for an adiabatic reaction in which a single potential energy surface for reactants and products is assumed, λ is the total reorganizational energy required to move all nuclei of the inner and outer sphere to their appropriate

position after electron transfer and is equal to:

$$\lambda = \lambda_{\text{in}} + \lambda_{\text{out}} \quad 1.9$$

where λ_{in} is the sum of all the inner sphere bond angle and length changes for the reactants and products and is given by:

$$\lambda_{\text{in}} = (1/2) \sum F_j \Delta Q_j^2 \quad 1.10$$

where F_j is the average force constant of the j th normal mode of the reactant and product and ΔQ_j is the displacement from the equilibrium position of the j th mode.

λ_{out} may be considered as the repolarization energy of the solvent configuration and when the solvent is treated as a dielectric continuum, is given by:

$$\lambda_{\text{out}} = \frac{(\Delta e)^2}{4 \pi \epsilon_0} \left(\frac{1}{2 a_1} + \frac{1}{2 a_2} - \frac{1}{r_{12}} \right) \left(\frac{1}{D_{\text{op}}} - \frac{1}{D_s} \right) \quad 1.11$$

where a_1 and a_2 are the radii of the reactants, Δe is the number of electrons transferred, r_{12} is $a_1 + a_2$, D_{op} is the optical dielectric constant of the medium and is equal to n^2 and D_s is the static dielectric constant of the medium. The most striking feature of equation 1.8 is that the rate of electron transfer is predicted to reach a maximum value when $\Delta G = \lambda$ and then become slower as the driving force for electron transfer is increased thereafter. This is known as the inverted region and is shown on figure 1.2.

In the inverted region in which ΔG becomes larger than λ , the classical treatments predict a much more rapid fall off in rate with increasing exothermicity than what is observed experimentally. In addition, classical approaches fail to explain the observation of electron transfer in weakly coupled systems ($\kappa \ll 1$), at very low temperatures and usually do not accurately describe the rather rapid rates of electron transfer that are found in many biological systems with very large distances between redox pairs. For these systems, semiclassical or quantum mechanical treatments that take into account electronic coupling and electron and nuclear tunneling effects often give a better correlation between theory and

Figure 1.2

Plot of electron transfer rate as a function of thermodynamic driving force. For the classical treatment, electron transfer is considered as adiabatic. For the semiclassical treatment, the curve is similar to that of reference 33, figure 6, curve C, except higher electronic coupling ($H_{rp} = 0.0075$ eV) has been used so that the curves intersect at $-\Delta G = \lambda = 1$ eV.

experiment. Some approaches treat the Frank–Condon factor classically and the electronic factor quantum mechanically whereas others treat the outer sphere reorganizational energy classically and both the inner sphere reorganizational energy and the electronic factor quantum mechanically and may be considered as semiclassical.

For nonadiabatic electron transfer in which only weak electronic coupling between the two redox sites exists, the electronic factor (κ) is less than 1 and equation 1.8 may be rewritten as:

$$k_{\text{et}} = \frac{4 \pi^2}{h} [V_{\text{DA}}]^2 [\text{FC}] \quad 1.12$$

where V_{DA} is the electronic factor and is given by an expression resembling:

$$V_{\text{DA}} = H_{\text{AB}}^0 \exp[-\beta\{r - \alpha\}] \quad 1.13$$

where H_{AB}^0 is the electronic coupling matrix element, r is the centre to centre distance between the redox sites, α is the sum of the radii of the redox active sites and β is a coefficient which describes the distance dependence of the electronic coupling and is typically found to be 10 to 20 nm⁻¹.³¹ FC is the Frank–Condon term and contains the free energy, reorganizational energy and temperature dependent terms as before and is defined as:

$$\text{FC} = \left(\frac{1}{4 \pi \lambda \text{RT}} \right)^{1/2} \exp \left\{ - \left[\frac{(\lambda + \Delta G)^2}{4 \lambda \text{RT}} \right] \right\} \quad 1.14$$

where λ is defined the same as in equation 1.9, 1.10 and 1.11.

Jortner and others³² have treated electron transfer purely quantum mechanically to arrive at much more complicated expressions such as:

$$k_{\text{et}} = 2\pi |H_{\text{ab}}|^2 / h^2 \omega \exp[-S(2\bar{\nu} + 1)] \times I_p \{ 2S[\bar{\nu}(\bar{\nu} + 1)]^{1/2} \} [(\bar{\nu} + 1/\bar{\nu})^p]^{1/2} \quad 1.15$$

where the energies S (inner sphere reorganization) and p (driving force) have been quantized, the outer sphere reorganization energy has been assumed to be zero in this particular example and $\bar{\nu}$ ($= [\exp(h\omega/kT) - 1]^{-1}$) is the quantized energy of a

intramolecular vibrational mode of frequency ω that was found to be strongly coupled to the electron transfer event.

It may be concluded that the semiclassical treatments provide an adequate correlation between experimental and calculated electron transfer rates in most cases. In contrast to the purely classical treatments, they display little or no temperature dependence at low temperature and high driving force and often predict an almost linear decrease in $\ln(k_{et})$ with increasing driving force in the inverted region. A comparison of the variation in electron transfer rate with driving force is shown in figure 1.2 for the classical treatment and a semiclassical quantum mechanical based treatment. Also shown by a horizontal dashed line is a typical organic solvent diffusion rate limit of $10^{10} \text{ s}^{-1}\text{M}^{-1}$ that may cause a levelling of the rate of intermolecular electron transfer in bimolecular systems with a value of ΔG in excess of λ . Intramolecular systems do not suffer from this limitation and in fact, Miller, Calcaterra and Closs^{2a} first provided experimental observation of inverted region behaviour for the intramolecular electron transfer quenching of a pulse-radiolysis generated biphenyl radical.

1.3 DESIGN OF A CHROMOPHORE-QUENCHER COMPLEX

Intermolecular quenching processes are bimolecular and compete with the unimolecular radiative and nonradiative excited state decay processes. In a system in which bimolecular quenching is occurring, the ratio of quantum efficiencies in the absence and presence of quencher can be related to the concentration of quencher by the following expression known as the Stern-Volmer relation²²:

$$\phi^0/\phi = 1 + k_q \tau [Q] \quad 1.16$$

where ϕ^0 and ϕ are the quantum efficiencies for the particular radiative, nonradiative or photochemical decay process under investigation in the absence of quencher and in the presence of quencher, k_q is the Stern-Volmer quenching rate

constant which is the sum of the rates of quenching by all mechanisms, τ is the lifetime of the excited state species being quenched and $[Q]$ is the concentration of quencher.

Using equation 1.16, the relationship between quencher concentration, lifetimes and quenching constants can be determined for any combination of values. For bimolecular quenching the fastest reactions normally occur at the diffusion rate limiting value of $10^{10} \text{ M}^{-1}\text{s}^{-1}$. Singlet excited state species normally have lifetimes of the order of 10^{-8} to 10^{-10} s and as can be seen on table I, in this range the concentration of quencher must be 10^{-2} or more for 50% of the excited state species to be quenched and more than 1 molar for 99% of the excited state species to be quenched. Excited triplet state species will however be quenched efficiently at much lower concentrations of quencher as the lifetimes for these species are substantially longer than singlet excited states.

For intramolecular quenching processes such as in the case of intramolecular electron transfer quenching in donor-bridge-acceptor type systems shown in scheme 1,

Scheme 1

the process is no longer diffusion controlled and unimolecular rate constants of as high as 10^{12} s^{-1} are often found. In this case, the rate of quenching becomes concentration independent at low to moderate concentrations and large k_q and

Table I Quenching relationships between $[Q]$, τ_f , k_q and ϕ/ϕ^0 a,b

a		[Q].50				[Q].99				
		$k_q \rightarrow$	10^9	10^{10}	10^{11}	10^{12}	10^9	10^{10}	10^{11}	10^{12}
		τ (sec) $\downarrow$	bimolecular		unimolecular		bimolecular		unimolecular	
typical singlet states	10^{-10}		10	1	10^{-1}	10^{-2}			10	1
	10^{-9}		1	10^{-1}	10^{-2}	10^{-3}		10	1	0.2
	10^{-8}		10^{-1}	10^{-2}	10^{-3}	10^{-4}	10	1	10^{-1}	10^{-2}
typical triplet states	10^{-5}		10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
	10^{-4}		10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-3}	10^{-4}	10^{-5}	10^{-6}
	10^{-3}		10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-4}	10^{-5}	10^{-6}	10^{-7}

b		ϕ/ϕ^0 for intramolecular singlet excited state quenching				
		$\tau_f \rightarrow$	1 ns	5 ns	10 ns	100 ns
		$k_q \downarrow$				
	10^{12}		1000	5000	10^4	10^5
	10^{11}		100	500	1000	10^4
	10^{10}		10	50	100	1000
	10^9		1	5	10	100
	10^8		0.1	0.5	1	10

- a** for table Ia, $[Q]$ is the concentration of added quencher (moles/litre) $[Q].50$ and $[Q].99$ are the $[Q]$ required to quench 50% and 90% of the excited state species respectively

$$[Q].50 = 1/(\tau_f \times k_q) \text{ and } [Q].99 = 99/(\tau_f \times k_q)$$

τ is the lifetime of the quenched excited state

τ_f is the fluorescence lifetime of quenched excited state

Adapted in part from reference 21

- b** for table Ib, the quenching efficiency is given by

$$\phi/\phi^0 = k_q \times \tau_f$$

equation 1.16 is no longer applicable. The relative ratio of quenched to unquenched species is now simply given by:

$$\phi/\phi^0 = k_q/(k_r + k_{nr}) \quad 1.17$$

where ϕ^0 , ϕ and k_q are defined as before and $(k_r + k_{nr})$ is equal to $1/\tau$ in the absence of quenching. From table Ib, it can be seen that high quenching efficiencies may be obtained for quenching of typical singlet excited states having lifetimes greater than 1 ns.

These particular type of systems in which a chromophore excited state (D^* or A^*) is quenched intramolecularly by a different ground state acceptor (A) or donor (D) moiety associated with the same molecule or complex are called chromophore-quencher complexes. When the quenching mechanism is via electron transfer (i.e. electron transfer is much more rapid than energy transfer or photochemical reaction of the excited state), then k_q in equation 1.17 becomes k_{et} (or k_{for} in scheme 1) and may be calculated according to any of the aforementioned treatments.

In order to calculate the thermodynamic driving force for electron transfer, the redox potential of the chromophore excited state (E^*) and the redox potential of the quencher ground state must be known. The former is calculated³⁴ from the energy of the excited state involved ($E_{0,0}$) and the appropriate ground state oxidation (E_{ox}^0) or reduction (E_{red}^0) potential by:

$$E_{ox}^* = E_{ox}^0 - E_{0,0} \quad 1.18$$

$$E_{red}^* = E_{red}^0 + E_{0,0} \quad 1.19$$

depending on whether the excited state is quenched oxidatively or reductively. The thermodynamic driving force for electron transfer is then given by:

$$\Delta G^0 = -nF(\Delta E^0) \quad 1.20$$

where n is the number of electrons transferred, F is Faraday's constant and ΔE^0 is the difference in redox potentials between the excited state being quenched and the

quencher. It can be seen from equations 1.18 and 1.19 that the excited state species will be both a better electron donor (more negative E_{ox}^* , D^* in the case of scheme 1) and a better electron acceptor (more positive E_{red}^* , A^* in the case of scheme 1). Depending on whether the quencher is an electron acceptor (A) or an electron donor (D), ΔE^0 can be calculated according to either:

$$\Delta E^0 = E_{(D^+/D^*)}^* + E_{(A/A^-)}^0 \quad 1.21$$

when the chromophore excited state (D^*) is quenched oxidatively by the ground state acceptor (A), or:

$$\Delta E^0 = -E_{(A^*/A^-)}^* + E_{(D^+/D)}^0 \quad 1.22$$

when the chromophore excited state (A^*) is quenched reductively by the ground state donor (D).

As can be seen in scheme 1, once the charge separated state is formed, it may undergo rapid back electron transfer (k_{back}) to form the ground state species before a reaction (k_p) to form products may occur. The driving force for this process is given by the difference in the oxidation potential of the reduced acceptor ($E_{(A/A^-)}^0$) and the reduction potential of the oxidized donor ($E_{(D^+/D)}^0$) by:

$$\Delta E_{back}^0 = E_{(A/A^-)}^0 - E_{(D^+/D)}^0 \quad 1.23$$

Thus equations 1.20, 1.12 and an estimated value²¹⁷ of λ may be used to calculate k_{back} and if the assumption that $k_{for} \gg (k_r + k_{nr})$ is made, the lifetime of the charge separated state (τ_{CSS}) may be determined. This is defined as the time required for the concentration of charge separated state species to fall to 1/e of its maximum value and may thus be calculated as:

$$\tau_{CSS} = (\ln 2)/(k_{back} + k_p) \quad 1.24$$

where k_p is the rate of reaction of the charge separated state to form products. In the case where the chromophore quencher complex contains a metal acceptor site and the intention is to use this reduced metal site for further reaction, the upper limit on k_p may be considered to be about 10^8 s^{-1} , which is the rate of some of the

fastest ligand substitution reactions³⁶.

Based on these equations, several generalizations can be made about how to achieve efficient electron transfer quenching in these chromophore-quencher complexes and whether or not the charge separated state will have a sufficiently long lifetime to carry out subsequent chemical reactions. The first is that the forward electron transfer reaction must be made sufficiently exothermic so that the back electron transfer is in the inverted region and hence slower so that an appreciable concentration of charge separated species may be formed. The probability of metal quencher site reaction may also be enhanced by rapidly removing the oxidized or reduced chromophore site by reaction with added sacrificial electron donors or acceptors or by more elegant strategies^{1b}. The rate of electron transfer must also be rapid enough so that the excited state species is not deactivated by simple photophysical processes. In order to accomplish this, the electronic coupling between the excited state chromophore and the quencher site must be maximized while still providing very little or no electronic coupling in the ground state. Another more indirect method to achieve this is to provide a mechanism for the energy of the excited state to be channeled efficiently into the triplet manifold via intersystem crossing and then intramolecularly quench this longer lived triplet state.

1.3.1 Chromophores

The selection criteria for the chromophore functionality of the chromophore quencher complex should be based on many factors related to its spectral and redox properties. The first factor is whether the excited state to be quenched should be singlet or triplet in multiplicity. Many metal complexes have low energy ligand field states of triplet character that are usually reactive in terms of decomposition by ligand dissociation.^{36,37} The initial purpose of this study was to design stable

chromophore quencher complexes that may be used as photocatalysts via metal-centred chemistry and not simply undergo ligand dissociation. Therefore the chromophore was chosen with the intention of quenching its first excited singlet state.

A second factor that must be considered is the energy, emission lifetime and quantum yield of emission of the singlet excited state. The energy should be high enough so that the forward electron transfer rate from this state to (or from) the ground state quencher is near the maximum and the back electron transfer rate is in the inverted region. The energy should also be low enough so as to not overlap with intense charge transfer bands of the metal complex. Metal complexes typically³⁸ exhibit intense charge transfer absorption bands in the ultraviolet region ($\lambda < 400$ nm) of the spectrum and some even exhibit these bands at lower energies (400 nm to 500 nm). As a consequence of this, excited state energies ($E_{0,0}$) of 2.0 eV to 3.1 eV would be desirable for the chromophore and this should be used first to eliminate possible candidate chromophores. Table II lists the singlet excited state energies and other spectral and redox properties for several chromophores. In many of the simple aromatic systems, the excited state energy is well into the ultraviolet (> 3.1 eV) and are thus not good choices. One exception that may be considered is the highly fluorescent ($\phi_f = 1$) 9,10-diphenylanthracene molecule with an excited state energy of 3.16 eV and a lifetime of 8.8 ns.

The lifetime of the excited state (τ_f) should be long enough so that the excited state may be quenched by electron transfer but yet short enough so that nonradiative photophysical deactivation processes are not dominant. An indication of the extent of deactivation by fluorescence versus deactivation by all other photophysical pathways is given by the fluorescence quantum yield (ϕ_f). A chromophore which satisfies the above $E_{0,0}$ criteria and possesses a lifetime in excess of 1 ns and a quantum yield for fluorescence in excess of 0.5 should make a suitable

Table II Spectral and redox properties of several chromophores^a

chromophore	E^{ox}	E^{red}	E_{00}	$E^*(D)$	$E^*(A)$	τ_f	ϕ_f	ref.
benzene	2.42	-2.50	4.71	-2.29	2.15	35	0.11	21,34b 44, 46
naphthalene	1.78	-2.29	3.93	-2.15	1.64	105	0.38	21,34b 44, 46
1-chloronaphthalene		(-1.7)	3.89		2.2	2.4	0.014	46, 47
1-bromonaphthalene	2.09	-1.16	3.87	-1.78	2.71	0.075	0.004	46, 47
1-iodonaphthalene		-0.72	(3.8)		3.08		<0.001	21, 47
anthracene	1.33	-1.71	3.27	-1.94	1.56	5.5	0.46	34b, 43, 48
* 9,10-diphenylanthracene	1.46	-1.94	3.16	-1.94	1.22	8.8	1.0	21, 34b
* 9,10-dichloroanthracene	1.28		3.08	-1.80		15.4	0.56	21, 34b
pyrene	1.40	-1.85	3.44	-2.17	1.59	190	0.7	21,34b 44, 46
* perylene	1.09	-1.43	2.83	-1.74	1.40	5.6	1.0	21,34b 39, 46
coronene	1.47	-1.83	2.89	-1.42	1.06	320	0.23	46
biphenyl	1.93	-2.31	4.16	-2.23	1.85	16.0	0.15	46,47
triphenylene	1.79	-2.22	3.62	-1.83	1.40	500	0.1	21,34b 44
Photo-oxidants								
acridine		-1.38	3.27		1.89	0.35	0.008	46
* 9-aminoacridine		(-0.8)	2.90		(2.1)	15.3	0.99	21, 46
Acridine Orange		-1.08	2.47		1.39	3.4	0.4	34b, 46
indole		(-1.7)	4.16		(2.5)	4.6	0.42	46
isoquinoline		-1.98	3.88		1.90	0.25	0.012	46
isoquinolinium-ClO ₄		(-1.1)	3.71		(2.6)	25	0.94	42
Photo-reductants								
1,4-dibutoxy-2,3-dicyanobenzene	1.5		3.85	-2.35		8.1	0.62	b
2,3-dicyano-p-hydroquinone	1.4		4.1	-2.5		(7)	(0.2)	b
* (2,3-dicyano-p-hydroquinone) ²⁻	(0.25)		3.06	(-2.8)		3.6	0.77	b
1,4-dimethoxybenzene	1.58		4.11	-2.53		2.7	0.21	41, 46
1,4-dimethoxynaphthylene	1.34	(-2.3)	3.78	-2.44	1.48	4.78	0.33	45, 47
phenothiazine	0.77		3.35	-2.58		1.5	0.027	41, 46
H ₂ TPPorphyrin	1.35		1.89	-0.54		13.6	0.11	34b, 46
* ZnTPPorphyrin	1.10		2.07	-0.97		2.7	0.04	34b, 46
* MgTPPorphyrin	0.95		2.02	-1.07		9.2	0.15	34b, 46

a) All electrochemical values (E^{ox} , E^{red} , E^*) have been converted to Volts vs. NHE (using V vs SCE + .242, V vs Fc/Fc⁺ + .4, V vs Ag^{0/+} +.45 or V vs Hg pool -.29), E_{00} is in eV and fluorescence lifetimes (τ_f) are in ns. ϕ_f is fluorescence quantum yield. Values used are for acetonitrile solvent when available. Values in parentheses are estimated. See text for details.

b) from this study

choice. Referring to table II, the chromophores marked with an asterik appear to satisfy these conditions and may be considered as good candidates.

In cases where the data is not available in the literature and the suitability of a particular chromophore is to be checked, one may estimate $E_{0,0}$ from the high energy tail of the fluorescence spectrum. The fluorescence lifetimes may be estimated to within $\pm 20\%$ in the absence of suitable equipment for direct measurement by comparing the fluorescence emission intensity in the absence of oxygen to that of the same solution exposed to air.⁴⁹ The ratio is related to the lifetime by a Stern–Volmer type of relationship similar to equation 1.16,:

$$I_f^0/I_f = 1 + \tau k_q [Q] \quad 1.25$$

where I_f^0 and I_f are the fluorescence intensities in the absence and presence of air respectively, τ is the mean lifetime in the absence of air, k_q is the rate constant for oxygen quenching and $[Q]$ is the concentration of dissolved oxygen in the solvent. In general, ratios of 1 to 2 are obtained for compounds having lifetimes in the 2 to 15 ns range. Exceptions to this general rule do exist and relative insensitivity to oxygen quenching is observed for the so-called "nonalternant" aromatic systems in which one or more of the ring systems contain an odd number of atoms. One such member of this group is fluoranthene and its derivatives where the S_1 to T_1 energy gap of 0.8 eV is less than the energy difference between the ground (T_0) and first excited state (S_1) of molecular oxygen. If the ratio obtained is in large excess of 2, then this compound is very susceptible to triplet quenching and should not be considered.

1.3.2 Quenchers

The choice of metal quencher site is governed by two main factors. The first is that there should be little spectral overlap between the chromophore emission spectrum and the quencher absorption spectrum as this would lead to energy transfer quenching of the excited state. As can be seen in table III, most inorganic

Table III Spectral properties of several complexes^a

complex	CT bands ^b	LF bands	ref.
Ti ^{III} Cl ₃ (py) ₃	< 350	599 (<1)	50
[V ^{III} Cl ₄ (py) ₂]	< 400	634 (<2)	51
Cr ^{III} (NH ₃) ₆	< 350	653 (<2) 464 (1.5) 351 (1.4)	38
Cr ⁰ (CO) ₄ (en)	337 (3.73)	423 (3.12)	52
Mo ⁰ (CO) ₄ (en)	306 (4.00)	395 (3.23)	52
Mo ⁰ (CO) ₄ (bpy)	540, 483 (3.5)	397	53
W ⁰ (CO) ₄ (en)	301 (3.92)	450 (2.6) 397 (3.15)	52
cis-W ⁰ (CO) ₄ (py) ₂	367 (3.81), 413 (3.90)	460 sh	54,55
cis-[(NH ₃) ₄ Ru ^{II} (py) ₂]	410 (3.90), 375 (3.81)	400 to 460 (c)	56
cis-[(bpy) ₂ Ru ^{II} (py) ₂]	460 (3.96)	420 to 500 (c)	57
Co ^{III} (NH ₃) ₆	< 300	769 (.2) 472 (1.7) 338 (1.7)	38,58
Co ^{III} (en) ₃	< 300	730 (.3) 571 (sh) 464 (1.9) 338 (1.7)	38,58
Co ^{III} (bpy) ₃	< 400	430	38,58
Co ^{II} (py) ₆	< 380	485, 510, 540, 1149	59
cis[Co ^{III} (oxalate) ₂ (py) ₂]	< 350	565 (2.24) 392 (2.34)	60
cis-[Co ^{III} (cyclen)Cl ₂]	< 350	520 (2.30) 390 (2.23)	61
cis-[Rh ^{III} (cyclen)Cl ₂]	< 300	365 (2.73) 302 (2.63)	61
cis-[Ir ^{III} (py) ₂ Cl ₄]	313 (3.7), 263 (4.0)	464 (1.3)	62
Ni ^{II} (py) ₆	< 350	370, 607, 743, 985 (<1)	63
Ni ^{II} (diketonate) ₂ (3pic) ₂	333 to 400	969 (.95) 575 (1.11)	64
Cu ^{II} (picO) ₂ (H ₂ O) ₂	375	550 to 650	65
Cu ^{II} -(N-heterocycles)	250 to 330	400 to 850	66
cis-Pt ^{II} Cl ₂ (py) ₂	287 (3.71)	366 (1.45)	67
Ag ^{II} (py) ₂ NO ₃	< 350	not applicable	68
Au ^{III} (py) ₂ Cl ₃	< 400	not applicable	69
Zn ^{II} (py) ₂ (NO ₃) ₂	< 350	not applicable	70

a Values listed are of wavelength maxima in nm, log ϵ in parenthesis when given. See text for discussion.

b For many complexes, the CT band energies were not listed or the spectrum was only recorded down to a certain wavelength. In these cases, only a limit is specified.

c The ligand field bands are not observed due to more intense charge transfer bands. An estimated range of ligand field energies have been given.

complexes possess ligand field based transitions in the visible region of the spectrum. Energy transfer by both a radiative and a Coulombic mechanism would be very low due to the low extinction coefficient of these ligand field transitions. Energy transfer to a ligand field excited state by an exchange mechanism would also be inefficient due to the change in symmetry and multiplicity required for this process.

Charge transfer bands of metal complexes do have appreciable extinction coefficients and will therefore be quite capable of quenching excited state species by both the radiative and Coulombic energy transfer mechanisms. Although the energies of charge transfer bands are difficult to predict, if the oxidation state, spin-state and stereochemistry surrounding the metal ion is known, then it may be possible to estimate this energy using the optical electronegativity concept of Jorgensen⁷¹. The energy of the lowest energy charge transfer transition (ν_{CT}) is given by:

$$\nu_{CT} = 30,000 \text{ cm}^{-1} (\chi_{\text{opt}}(\text{ligand}) - \chi_{\text{opt}}(\text{metal})) \quad 1.26$$

where $\chi_{\text{opt}}(\text{ligand})$ is the optical electronegativity of the ligand and is related to its ionization potential and $\chi_{\text{opt}}(\text{metal})$ is the optical electronegativity of the metal and is related to its electron affinity.

Some general trends that have been observed are that the $\chi_{\text{opt}}(\text{metal})$ values tend to increase across a transition series and down a transition row for a given configuration and oxidation state and tend to increase for a given metal with increasing oxidation state. In the case of ligands, the $\chi_{\text{opt}}(\text{ligand})$ values tend to increase as the electronegativity of the donor atom increases and are slightly larger if it is a σ -orbital involved as opposed to a π -orbital. For LMCT bands, the $\chi_{\text{opt}}(\text{ligand})$ and thus ν_{CT} values follow an order similar to the nephelauxetic series.⁷² For MLCT bands, a low value of $\chi_{\text{opt}}(\text{ligand})$ is required (< 1.5 to 1.8) and values of ν_{CT} tend to follow an opposite trend being related to the electron

affinity of the donor atom. The problem becomes much more complex when several different ligands are in the coordination sphere and it is therefore worthwhile to look at a series of many complexes with similar ligand environments to arrive at a range of possible charge transfer band energies. This has been carried out for copper(II) complexes of N-heterocycles and is included in table III.

The second main factor that will govern the choice of coordination environment around the metal quencher site is the ability of the ligating functionality to stabilize or at least remain coordinated to two adjacent oxidation states of a metal ion. A caveat of this is that for single electron transfers, the metal must possess two adjacent formal oxidation states that are accessible electrochemically. Thus the use of Pt(II) or Pd(II) complexes can be ruled out. As the goal here is to design a complex in which metal centred chemistry is possible without loss of the chromophore containing ligand (i.e. to form a true photocatalyst⁷³), it will be necessary that the reduced and oxidized metal site have different labilities toward the reactant and product molecules of the photocatalytic cycle. This will depend on the mechanism of the reaction (coupling versus abstraction, etc...) and is beyond the scope of this discussion. Thus for the purpose of electron transfer quenching of a remote excited state species, the ligating moieties at the metal quencher coordination site should possess both π -accepting ability and σ -donation ability when the ligands are monodentate. In addition, multidentate or macrocycle ligands which lack π -acceptor properties can function well provided that they are not redox active with respect to the two metal oxidation states that are sought.⁷⁴ The choice will depend to a large extent on the synthetic strategy used but in general, nitrile, phosphine or N-heterocycle monodentate ligands or amine and ether macrocycles should satisfy this condition.

1.3.3 Spacers or bridges

Figure 3 displays several spacers that have been used by other researchers in the field for the purpose of separating the donor and acceptor functionality in organic donor–acceptor type complexes. The first seven entries may be considered as flexible spacers whereas the last three may be considered as rigid spacers. The use of simple flexible linkages such as methylene or amide functionalities is attractive from a synthetic point of view in addition to the fact that the donor and acceptor site can be placed within a few bond lengths of each other. The concern with flexible linkages is that they may provide a means for the donor and acceptor to come into close contact when the spacer is large and interact by through space electron transfer. A concern with rigid spacers is that the donor and acceptor may be locked into a geometry in which the electronic coupling between the two sites is unfavourable.⁸¹ The use of a single methylene unit as a bridge was expected to reduce the potential negative effect of these factors. The use of two or three methylene units could probably also be accommodated, provided the ligating functionality was able to provide some steric restrictions to close contact.

1.3.4 Chromophore–Quencher Complex

The preceding conditions must now be applied to the design of a complete system which starts with the selection of the chromophore. As shown in table II, the dianion of 2,3–dicyano–p–hydroquinone satisfies the necessary conditions of a suitable chromophore with a singlet excited state energy of 3.06 eV, fluorescence lifetime of 3.6 ns and a fluorescence quantum yield of 0.77. It would be expected to be a photo–reductant with an excited state oxidation potential of –2.8 V vs N.H.E. This chromophore was also selected because it was believed that in the dianion form, it may function as a chemically reversible two electron reservoir for multielectron processes via the semiquinone intermediate.⁸²

		reference
polymethylene		75
polyphenyl		75
polycyclohexyl		75
4-methylpyridyl		76
bicyclo[2.2.2]octane		77
amide		78
diamide		78
cyclopentyl		79
tricyclo[4.3.0.0.2,5]		79
tritypceno		80

Figure 1.3

Various bridge spacers used in donor-bridge-acceptor type molecules

The synthetic strategy to form a ligand from this chromophore is outlined in scheme 2.

Scheme 2

The experimental details of this scheme and others are discussed in chapter 2. The reactive hydroxy groups of the chromophore must first be protected so that they are not involved in any of the subsequent reactions. The use of n -butoxy groups was found to be convenient and helped to increase the solubility of the intermediates in organic solvents. Cyclization of the ortho dinitrile group to form an isoindole with

two reactive imine groups exocyclic to the ring was expected to provide us with a considerable amount of synthetic flexibility in terms of spacer and ligating group attachment.

An aminomethylpyridine (3-aminomethylpyridine is shown in scheme 2) or virtually any primary amine with a suitable ligating functionality then reacts with these imine groups to form a bidentate photoredox active ligand. In this case the methylene group is expected to provide the required decoupling between the ground state chromophore and the metal quencher site. The series of ligands with the aminomethyl group at the 2, 3 and 4 positions of the pyridine were prepared characterized and ball and stick molecular models were built to ascertain which could form bis chelated complexes. Both the 3 and 4-substituted derivatives appeared able to accommodate bis chelation of an octahedral coordination environment and the 3 substituted derivative appeared to be capable of bis chelation in a tetrahedral coordination environment. Molecular modelling software was later used to confirm what was observed with the ball and stick models and this is found in appendix A.

At this point, the chromophore was found to have suitable redox and spectral properties to form a chromophore-quencher complex. The excited state energy was found to be -1.86 V, the fluorescence lifetime was found to be in the range of 5 to 10 ns with a quantum yield greater than 0.5. Further synthetic steps were planned such as removing the *n*-butoxy groups to form a dianionic ligand and changing the nature of the ligating groups. Initial studies in this area are discussed in chapter 3.

Attempts were then carried out to form a chromophore-quencher complex with this ligand and several metal and metal complex ions. A chromophore-quencher complex suitable for study was prepared by the reaction of this ligand with copper(II) triflate in acetonitrile or ethanol. The reaction of this chromophore with

most metal and metal complex ions resulted in either decomposition of the ligand such as in the case of tungsten(0) or molybdenum(0) carbonyls or rapid further reaction of the initially formed complex such as in the case of tetramminecobalt(III) ion or the complex formed was too photosensitive to be properly characterized such as in the case of bis(bipyridyl)ruthenium(II) and tetraammineruthenium(II) or (III) complexes. These experiments are summarized in chapters 3.3 and 3.4 and the results of quenching experiments with the copper(II) complexes are discussed in chapter 5.

2. Experimental.

2.1 Reagents.

2,3-dicyano-1,4-hydroquinone, ammonium hexafluorophosphate, 1,3-diiminoisoindoline, n-bromobutane, methyl iodide, dimethylsulphate, 1,3-diaminopropane, dibromoethane, p-benzoquinone, tetraphenylarsonium chloride, methyl viologen dichloride, pyrene, fluorene, m-dinitrobenzene, nitrobenzene, bipyrazine, benzophenone, quinine sulphate, 2-aminomethylpyridine, 3-aminomethylpyridine, 4-aminomethylpyridine, tetraheptylammonium chloride, 3-aminopropylimidazole, trifluoromethanesulphonic acid, tetraethylammonium chloride, tetrabutylammonium bromide and copper turnings were obtained from Aldrich. NaS_2O_6 was obtained from BDH. $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ was obtained from Aldrich or Johnson Matthey. $\text{Co(II)(CH}_3\text{COO)}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Co(II)Cl}_2 \cdot 6\text{H}_2\text{O}$ were obtained from Fisher. NH_3 , oxygen, nitrogen and argon were obtained from Air Products. Caledon HPLC grade acetonitrile was used for fluorescence spectroscopy, cyclic voltammetry and picosecond transient absorption spectroscopy. Reagent grade solvents used were distilled and dried when required.⁸³ $\text{Cu}(\text{CF}_3\text{SO}_3)_2 \cdot n\text{H}_2\text{O}$ was prepared as previously⁸⁴ and methyl viologen dihexafluorophosphate was prepared by metathesis of the hydrochloride with ammonium hexafluorophosphate in water. Pentaamminecobalt(III)triflate⁸⁵, pentaamminecobalt(III)chloride⁸⁶, pentaamine-pyridylcobalt(III)triflate⁸⁷, pentaammineruthenium(III)chloride⁸⁸, pentaamine-ruthenium(III)triflate⁸⁹, pentaammineaquoruthenium(II)chloride⁹⁰, cis-tetra-amminedichlororuthenium(III)chloride⁹¹, cis-tetraamminedibromoruthenium(III)-bromide⁹² and cis-tetraamminediaquoruthenium(III)triflate⁹³ were prepared as previously described.

2.2 Synthesis.

Tetraphenylarsonium salt of 2,3-dicyano-1,4-dihydroxybenzene (1 or

DCHQ) was prepared in a glove box using vacuum dried reagents and solvents dried as previously described⁸³ and degassed by 5 freeze/pump/thaw/argon purge/pump cycles. All solvents and reagents were then transferred to the glove box under vacuum to avoid the inclusion of oxygen. 1.0 g of sodium hydroxide (25 mmol) and 1.0 g of 2,3-dicyanohydroquinone (6.3 mmol) were dissolved in 20 mL of water at room temperature. This was extracted with 3–25 mL aliquots of a 75 mL toluene solution containing 4.0 g of tetraheptyl ammonium chloride (8 mmol). The organic phase was shaken with magnesium sulphate, filtered and then evaporated by passing dry argon through the solution. The oily orange–brown residue that remains was then dissolved in a minimum of acetonitrile (ca 5 mL) at room temperature. This solution was filtered and added to a filtered solution of 1.8 g of tetraphenylarsonium chloride in 10 mL of acetonitrile with rapid stirring. The light orange precipitate that forms immediately was filtered and rinsed with toluene. Recrystallization from 5:1 acetonitrile:toluene affords long orange needles after several hours. These were washed with a minimum of cold 4:1 acetonitrile:toluene, 5 mL of diethyl ether and then transferred under argon to the vacuum line where they were dried for 16 hours at room temperature to give orange needles. Yield, 1.61 g (28%), mp 142 °C dec; Anal. Calcd for $C_{56}H_{42}N_2O_2As_2 \cdot 2H_2O$: C, 70.00; H, 4.83; N, 2.92. Found: C, 69.75; H, 4.60; N, 2.92. UV–visible spectra (MeCN), λ in nm (log ϵ): 410 (3.89)

They are air sensitive and should be stored under argon or nitrogen and protected from light exposure as they will decompose to a bright red solid, presumably containing small amounts of the semiquinone as shown by changes in the electronic spectrum. A bright red solution of the semiquinone can be generated in–situ by the addition of excess potassium iodide to an acetonitrile solution of the dianion. Attempts to isolate pure green crystals of the semiquinone proved to be futile.

UV–visible spectra for the semiquinone (MeCN), λ in nm (log ϵ): 415 (3.48), 440 (3.61), 470 (3.60), 555 (3.41) and 595 (3.39)

1,4-di-n-butoxy-2,3-dicyanobenzene (2)

In the initial phases of synthesis, methyl groups were used to protect the dihydroxy groups of the hydroquinone dianion by a procedure that used sodium hydroxide as the base and dimethylsulphate as the alkylating agent. This procedure gave only moderate yields of 50–60 % and the reaction required periods of several days with heating, nitrogen purge and mechanical stirring. These conditions were required because in order to dialkylate the dianion the temperature had to be increased (i.e. only monoalkylated product was formed if the same reaction was carried out at room temperature), the dianion was oxidized slowly in aqueous base at elevated temperature so nitrogen was purged into the reaction vessel in order to maintain an inert atmosphere above the solution and the product was virtually insoluble in water and rapidly precipitated out causing magnetic stir bars to seize up.

The use of this precursor, 1,2-dicyano-3,6-dimethoxybenzene for subsequent reaction to form the diimine (4), and the ligands 11 and 12 and complexes of these ligands proved to be very difficult as the reactants displayed very poor solubility in most common organic solvents. The n-butyl moiety was found to be a more convenient protecting group as all the subsequently formed products displayed high solubility in common organic solvents. However, the analogous alkylating procedure employing di-n-butylsulphate was similarly difficult due to the same reasons as previously mentioned for the dimethyl derivative in addition to the fact that the di-n-butylsulphate was prepared from sulfuryl chloride and di-n-butylsulfite (which in turn was prepared from n-butanol and thionyl chloride) and vacuum distilled. In an effort to avoid this, a new procedure was developed that was based on phase-transfer catalysis principles⁹⁴ and the final version of this procedure that was used for large scale synthesis is described by method a. It was discovered later that selective dealkylation of the di-n-butoxy derivative was very

difficult and the dimethylated derivative would have to be used. A convenient alkylation procedure employing methyl iodide as alkylating agent, dimethylformamide as solvent, potassium carbonate as the base and ambient conditions was found in the literature⁹⁵ so that the dimethylsulphate procedure could be avoided. This procedure was also found to be readily applicable to formation of the di-*n*-butyl derivative. This latter procedure was much simpler than method **a** due to the shorter time required, the product could be more easily isolated and purified and chlorinated solvents were not required. This procedure is described by method **b**.

a) 16.0 g of 2,3-dicyanohydroquinone (0.1 mol) was added to a mixture of 75.5 mL *n*-bromobutane (0.90 mol), 21.0 g of tetra-*n*-butylammoniumbromide (0.07 mol) and 35.0 g of NaOH (0.90 mol) in 1100 mL of 1:1 water:methylene chloride and the resulting mixture was rapidly stirred at 2400 r.p.m. and 25°C for 7 days. The solution was transferred to a 2 L separatory funnel and the organic phase was drawn off. The aqueous phase was washed with three 150 mL portions of methylene chloride and the washings were added to the organic phase. The organic phase was washed with 200 mL each of water and 1.0 M NaCl and then filtered through 25 g of MgSO₄. This was evaporated to dryness and transferred to a 500 mL medium frit funnel where the white precipitate was washed with three 400 mL portions of water to remove any residual ammonium salt. The solid was allowed to air dry overnight and was recrystallized from ethanol followed by vacuum drying at 110°C for 10 hours to give shiny white platelets. Yield, 22.6 g (83%), mp 182–3 °C; ¹H NMR (CDCl₃) 7.21 (s, 2 H), 4.08 (t, 4 H), 1.82 (quint, 4 H), 1.52 (sext, 4 H), 0.98 (t, 6 H); ¹³C NMR (CDCl₃) 155.2, 118.4, 113.1, 105.2, 69.9, 30.9, 19.0, 13.7. Mass spectrum by chemical ionization with diethyl ether displays major peaks at 273 (M+1), 301 (M+29), 331 (M+59) and 347 (M+75)

b) **2** was prepared analogously to the dimethyl ether.⁹⁵ 9.6 g of

2,3-dicyanohydroquinone (0.06 mol) was added to a mixture of 38.5 mL *n*-bromobutane (0.36 mol) and 20.7 g of K_2CO_3 (0.15 mol) in 200 mL of DMF and the resulting suspension was rapidly stirred at 25°C for 120 hours. The solution was poured into 500 mL of water, filtered and the flocculant white precipitate was washed with 2 L of water. Recrystallization from ethanol followed by vacuum drying at 110°C for 10 hours gave shiny white platelets. Yield, 14.7 g (90%), mp 182–3 °C; 1H NMR ($CDCl_3$) and ^{13}C NMR ($CDCl_3$) were identical to **a**). Anal. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.76; H, 7.18; N, 10.43.

(1H NMR and ^{13}C NMR in App. B, pp. 217 and 218)

4,7-di-*n*-butoxy-1,3-diiminoisoindoline (**3**) was prepared in a similar manner to 1,3-diiminoisoindoline.⁹⁶ 8.6 g of **2** (0.032 mol) and 0.2 g of sodium metal (0.008 mol) were dissolved in 500 mL of methanol and the resulting solution was refluxed. Ammonia was bubbled into the solution until saturated and then continuously at a very slow rate (approximately 20–40 cc/min) while the solution was refluxed for 12 days. The solution was then cooled to –15 °C and the product filtered off. Recrystallization from 1:1 acetone:diethyl ether followed by vacuum drying for 12 hours at 25°C afforded off-white needles. Yield, 7.5 g (81%), mp 228 °C (dec); 1H NMR ($CDCl_3$) 8.19 (br s, 2 H), 7.16 (s, 1 H), 6.92 (s, 2 H), 4.07 (t, 4 H), 1.83 (quint, 4 H), 1.51 (sext, 4 H), 0.98 (t, 6 H); ^{13}C NMR ($CDCl_3$) 167.4, 149.3, 120.8, 115.9, 68.5, 31.1, 19.3, 13.8. Anal. Calcd for $C_{16}H_{23}N_3O_2$: C, 66.41; H, 8.01; N, 14.52. Found: C, 65.86; H, 7.88; N, 14.26. Mass spectrum by chemical ionization with diethyl ether displays major peaks at 290 ($M+1$) and 348 ($M+59$). Mass spectrum by electron ionization displays only minor contribution from molecular ion at 289 (0.8 intensity relative to 100 for peak at 246)

(1H NMR and ^{13}C NMR in App. B, pp. 220 and 221)

4,7-dimethoxy-1,3-diiminoisoindoline (4) was prepared in an analogous manner to the di-*n*-butoxy derivative, **3**. 5.4 g of 1,2-dicyano-3,6-dimethoxy-benzene⁹⁵ (0.029 mol) and 0.1 g of sodium metal (0.004 mol) were dissolved in 550 mL of methanol and the resulting solution was refluxed. Ammonia was bubbled into the mixture until saturated and then continuously at a very slow rate while the solution was refluxed for 14 days. The ammonia inlet tube had to be periodically cleared of precipitated product. The solution was then cooled to -15°C and the product filtered off. Recrystallization from 2:1 acetone:methanol followed by vacuum drying for 10 hours at 25°C afforded tan coloured needles. Yield, 5.77 g (97%), mp 222°C (dec); ^1H NMR (CD_3OD) 7.23 (s, 2 H), 3.97 (s, 6 H), 3.3 (m, 3 H); ^{13}C NMR (CD_3OD) 168.5, 149.1, 118.5, 116.1, 56.0. Anal. Calcd for $\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_2 \cdot \text{H}_2\text{O}$: C, 53.76; H, 5.82; N, 18.82. Found: C, 54.64; H, 5.79; N, 18.72. Mass spectrum by electron ionization displays molecular ion at 205 (relative intensity of 70.0) and $\text{M}-1$ at 204 (relative intensity of 100.0). (^1H NMR and ^{13}C NMR in App. B, pp. 226 and 227)

1,3-bis((3'-pyridylmethyl)imino)isoindoline (5 or L) was prepared similarly to other 1,3-disubstituted isoindolines.⁹⁷ 20 mL of 3-aminomethylpyridine (0.15 mol) was vacuum distilled (2 torr, 90°C) into a flask containing 2.07 g of 1,3-diiminoisoindoline (0.015 mol) and 90 mL of anhydrous ethanol. The solution was slowly heated to reflux. The NH_3 produced was removed by the application of vacuum or an argon purge at 10 min. intervals for the first hour. The solution was refluxed for a further 4 hours and then cooled. The solution was poured into 600 mL of rapidly stirred water and placed in the refrigerator for 2 hours. The flocculant pale yellow suspension was filtered, washed with 500 mL of water and allowed to air dry overnight. The fine yellowish powder can be recrystallized from chloroform with hexanes added to the cloud point. The light

yellow needles were collected by filtration and vacuum dried at 25 °C for 12 hours to give fine pale yellow needles which are hygroscopic. Yield, 4.36 g (89%), mp 165–6 °C; ^1H NMR (CDCl_3 , not shown) 8.64 (s, 2 H), 8.48 (s, 2 H), 7.77 (d, 2 H), 7.43 (s, 2 H), 7.23 (mult, 3 H), 6.79 (s, 2 H), 5.02 (br s, 4 H); ^1H NMR (d_6 -DMSO) 9.36 (s, 1 H), 8.67 (s, 2 H), 8.50 (s, 2 H), 7.83 (m, 4 H), 7.55 (m, 2 H), 7.37 (br s, 2 H), 5.00 (br d, 4 H); ^{13}C NMR (CDCl_3) 168.6, 149.7, 149.6, 148.3, 136.9, 136.5, 130.4, 123.7, 121.9, 50.3(cis), 44.9(trans). Anal. Calcd for $\text{C}_{20}\text{H}_{17}\text{N}_5$: C, 73.37; H, 5.23; N, 21.39. Found: C, 73.17; H, 5.20; N, 21.72. Mass spectrum by chemical ionization with diethyl ether displays $M+1$ ion at 328 (relative intensity of 100.0) and $M+59$ ion at 386 (relative intensity of 14.3).

(^1H NMR and ^{13}C NMR in App. B, pp. 234 and 235)

1,3-bis((4'-pyridylmethyl)imino)isoindoline (6) was prepared from 1,3-diiminoisoindoline and 4-aminomethylpyridine by a similar method to that used for 5. Yield, 84%, mp 170 °C (dec); ^1H NMR (CDCl_3) 8.51 (d, 4 H), 7.69 (s, 2 H), 7.49 (s, 2 H), 7.31 (d, 4 H), 5.00 (br s, 4 H); ^{13}C NMR (CDCl_3) 168.7, 149.9, 149.6, 138.5, 130.5, 123.2, 121.6, 50.0. Anal. Calcd for $\text{C}_{20}\text{H}_{17}\text{N}_5$: C, 73.37; H, 5.23; N, 21.39. Found: C, 73.02; H, 5.23; N, 21.73. Mass spectrum by chemical ionization with diethyl ether displays $M+1$ ion at 328 (relative intensity of 100) and $M+59$ ion at 386 (relative intensity of 16.8).

(^1H NMR and ^{13}C NMR in App. B, pp. 236 and 237)

1,3-bis((2'-pyridylmethyl)imino)isoindoline (7) was prepared from 1,3-diiminoisoindoline and 2-aminomethylpyridine by a similar method to that used for 5. Yield, 67%, mp 254 °C (dec); ^1H NMR (CDCl_3) 7.85 (d, 2 H), 6.80 (multi, 10 H), 4.70 (br s, 4 H), 4.30 (s, $\approx$ 2 H from H_2O); ^{13}C NMR (CDCl_3) 166.7, 158.8, 148.8, 137.0, 136.8, 130.1, 122.6, 122.0, 120.5, 52.6(cis), 56.3(trans). Anal.

Calcd for $C_{20}H_{17}N_5 \cdot 0.75H_2O$: C, 70.31; H, 5.46; N, 20.50. Found: C, 70.33; H, 5.39; N, 20.61. Mass spectrum by chemical ionization with diethyl ether displays $M+1$ ion at 328 (relative intensity of 100) and $M+59$ ion at 386 (relative intensity of 19.2).

(1H NMR and ^{13}C NMR in App. B, pp. 231 and 232)

4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline (8 or CL) was prepared similarly to 5. 20 mL of 3-aminomethylpyridine (0.15 mol) was vacuum distilled (2 torr, 90 °C) into a flask containing 4.22 g of 3 (0.015 mol) and 90 mL of anhydrous ethanol. The solution was slowly heated to reflux. The ammonia gas which formed was removed by the application of vacuum and an argon purge at 15 min. intervals for the first 3 hours. The solution was refluxed for a further 9 hours and then cooled. The solution was poured into 600 mL of rapidly stirred water and placed in the fridge for 2 hours. The flocculant pale yellow suspension was filtered and washed with 500 mL of water. Vacuum drying at 25 °C for 16 hours produces a green glassy mass, which can be ground to a powder and recrystallized from diethyl ether to give a yellow to light green powder which is very hygroscopic. Yield, 4.40 g (64%), mp 67 °C (dec); 1H NMR ($CDCl_3$) 8.69 (s, 2 H), 8.52 (d, 2 H), 7.90 (d, 2 H), 7.27 (t, 2 H), 6.94 (s, 2 H), 5.04 (s, 4 H), 4.14 (t, 4 H), 1.78 (quint, 4 H), 1.40 (sext, 4 H), 0.90 (t, 6 H); ^{13}C NMR ($CDCl_3$) 166.9, 149.7, 149.5, 148.7, 148.4, 135.7, 123.4, 118.4, 116.6, 69.1, 49.6, 31.2, 19.2, 13.8. Anal. Calcd for $C_{28}H_{33}N_5O_2 \cdot 0.5H_2O$: C, 70.11; H, 7.00; N, 14.60. Found: C, 70.10; H, 6.85; N, 14.59. Mass spectrum by chemical ionization with diethyl ether displays $M+1$ ion at 472 (relative intensity of 71.5). Other characteristic peaks are observed at 500 ($M+29$, 1.2 rel. int.), 530 ($M+59$, 6.0 rel. int.) and 544 ($M+73$, 4.0 rel int.). (1H NMR and ^{13}C NMR in App. B, pp. 243 and 244)

4,7-di-n-butoxy-1,3-bis((4'-pyridylmethyl)imino)isoindoline (9) was prepared from **3** and 4-aminomethylpyridine by a similar procedure as **8**. After vacuum drying at 25 °C, a hygroscopic yellow green powder is obtained. Yield, 4.02 g (58%), mp 89 °C (dec); ¹H NMR (CDCl₃) 8.54 (d, 4 H), 7.37 (d, 4 H), 7.24 (s, 1 H), 6.91 (s, 2 H), 4.98 (s, 4 H), 4.10 (t, 4 H), 1.80 (quint, 4 H), 1.47 (sext, 4 H), 0.93 (t, 6 H); ¹³C NMR (CDCl₃) 167.0, 149.0, 149.0, 148.7, 125.6, 122.6, 116.6, 68.9, 49.6 (br), 31.1, 19.2, 13.8. Anal. Calcd for C₂₈H₃₃N₅O₂: C, 71.31; H, 7.05; N, 14.85. Found: C, 70.31; H, 6.85; N, 14.75. Mass spectrum by chemical ionization with diethyl ether gives M+1 ion at 472 (relative intensity, 48.2), M+29 ion at 500 (relative intensity, 0.9), M+59 ion at 530 (relative intensity, 4.7) and M+73 ion at 544 (relative intensity, 3.1).

(¹H NMR and ¹³C NMR in App. B, pp. 245 and 246)

4,7-di-n-butoxy-1,3-bis((2'-pyridylmethyl)imino)isoindoline (10) was prepared from **3** and 2-aminomethylpyridine by a similar procedure as **8**. After recrystallization from 7:1 water:methanol, filtration and vacuum drying at 25 °C, a pink orange powder is obtained. This compound turns red within a few hours when exposed to air. Yield, 48%, mp 105 °C (dec); ¹H NMR (CDCl₃) 8.56 (d, 2 H), 7.60 (multi, 4 H), 7.19 (t, 2 H), 6.91 (s, 2 H), 5.16 (s, 4 H), 4.13 (t, 4 H), 1.90 (quint, 4 H), 1.59 (sext, 4 H), 0.99 (t, 6 H); ¹³C NMR (CDCl₃) 166.8, 159.1, 148.8, 148.7, 136.4, 127.2, 122.1, 121.7, 116.2, 69.0, 52.6 (br), 31.4, 19.3, 14.0. Anal. Calcd for C₂₈H₃₃N₅O₂·H₂O·O₂: C, 64.48; H, 6.76; N, 13.43. Found: C, 65.02; H, 6.57; N, 13.56. Mass spectrum by chemical ionization with diethyl ether gives M+1 ion at 472 (relative intensity, 100), M+29 ion at 500 (relative intensity, 0.9), M+59 ion at 530 (relative intensity, 11.7) and M+73 ion at 544 (relative intensity, 2.6).

(¹H NMR and ¹³C NMR in App. B, pp. 240 and 241)

4,7-dimethoxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline (11) was prepared from **4** and 3-aminomethylpyridine similarly to **8**. Vacuum drying at 25 °C for 16 hours gives a pale yellow powder. Yield, 78%, mp 168 °C (dec); ¹H NMR (CDCl₃) 8.68 (s, 2 H), 8.48 (d, 2 H), 7.77 (d, 2 H), 7.22 (t, 2 H), 6.91 (s, 2 H), 5.02 (br s, 4 H), 3.90 (s, 6 H); ¹³C NMR (CDCl₃) 167.8, 149.7, 149.3, 148.6, 148.4, 135.9, 123.1, 118.9, 115.0, 56.4, 51.6. Anal. Calcd for C₂₂H₂₁N₅O₂: C, 68.20; H, 5.46; N, 18.08. Found: C, 67.51; H, 5.53; N, 17.71. Mass spectrum by chemical ionization with diethyl ether displays M+1 ion at 388 (relative intensity, 57.8), M+29 ion at 416 (relative intensity, 0.9), M+59 ion at 446 (relative intensity, 5.2) and M+73 ion at 460 (relative intensity, 2.6). (¹H NMR in App. B, p. 249)

4,7-dimethoxy-1,3-bis((4'-pyridylmethyl)imino)isoindoline (12) was prepared from **4** and 4-aminomethylpyridine similarly to **8**. Vacuum drying at 25 °C for 16 hours gives a pale green powder. Yield, 75%, mp 121 °C (dec); ¹H NMR (CDCl₃) 8.52 (d, 4 H), 7.32 (d, 4 H), 7.24 (s, 1 H), 6.97 (s, 2 H), 5.00 (s, 4 H), 3.95 (s, 6 H), 1.66 (br s due to H₂O, 4 H); ¹³C NMR (CDCl₃) 166.9, 149.7, 149.3, 148.9, 125.5, 122.8, 115.1, 56.3, 49.8 (br). Anal. Calcd for C₂₂H₂₁N₅O₂·2H₂O: C, 62.35; H, 5.90; N, 16.53. Found: C, 59.86; H, 4.83; N, 15.69. Mass spectrum by chemical ionization with diethyl ether displays M+1 ion at 388 (relative intensity, 100), M+29 ion at 416 (relative intensity, 1.9), M+59 ion at 446 (relative intensity, 9.8) and M+73 ion at 460 (relative intensity, 3.4). (¹H NMR and ¹³C NMR in App. B, pp. 250 and 251)

4,7-dimethoxy-1,3-bis((3'-propyl-N-imidazolyl)imino)isoindoline (13) was prepared from **4** and 3-aminopropylimidazole similarly to **8**. Vacuum drying at 25 °C for 16 hours produces a light green powder which is hygroscopic. Yield,

18%, mp 113–6 °C (dec); ^1H NMR (d_6 -DMSO) 7.70 (s, 2 H), 7.24 (s, 2 H), 7.10 (s, 2 H), 6.89 (s, 2 H), 4.05 (t, 4 H), 3.86 (s, 6 H), 2.07 (quint, 4 H); ^{13}C NMR (d_6 -DMSO) 168.0, 137.4, 135.5, 129.5, 128.4, 119.4, 56.2, 44.3, 32.2. Anal. Calcd for $\text{C}_{22}\text{H}_{27}\text{N}_7\text{O}_7\cdot\text{H}_2\text{O}$: C, 60.12; H, 6.65; N, 22.31. Found: C, 56.84; H, 6.87; N, 23.08. Although the elemental analysis of this ligand was poor, it is included as the elemental analysis of the copper complex prepared from this ligand gave very good results. (^1H NMR and ^{13}C NMR in App. B, pp. 252 and 253)

The synthesis of 4,7-dihydroxy-1,3-bis((3'-pyridylmethyl)imino)-isoindoline (14) was attempted using a procedure based on dealkylation of the dimethoxy derivative 11, using in-situ generated iodotrimethylsilane⁹⁸ The NMR spectra of the isolated final product was consistent with a fully demethylated derivative. However, elemental analysis revealed unacceptably low carbon and nitrogen content thus suggesting the presence of a salt. 0.76 g of 11 (1.0 mmol) and 1.05 g of NaI (7 mmol) were dissolved in 25 mL of anhydrous acetonitrile under nitrogen. The yellow solution becomes colloidal after about 5 minutes. 0.88 mL (7 mmol) of chlorotrimethylsilane was added dropwise with stirring to give an orange slightly colloidal solution. The solution was stirred in the dark at room temperature for a further 72 hours. The solid material was filtered off and extracted in a Soxhlet extractor with diethyl ether until the extractions were very light yellow in colour. This was evaporated to dryness and the residue was dissolved in a minimum of methanol and chromatographed through 100–200 mesh silica using 4:1 methanol:chloroform as an eluent. After evaporation, the residue was recrystallized from methanol. Upon cooling, orange crystals separated from solution. These were collected by filtration, rinsed with 5 mL of cold methanol and vacuum dried at room temperature for 12 hours to give orange crystals. Yield, 0.14 g (39%), mp 110 °C changes to red coloured crystals which melt at 188–9 °C (dec); ^1H NMR (CD_3OD)

8.61 (br s, 2 H), 8.44 (br s, 2 H), 7.89 (d, 2 H), 7.39 (t, 4 H), 5.06 (br s, 2 H), 4.76 (br s, 4 H), 4.01 (s, 2 H); ^{13}C NMR (d_6 -acetone) 173.6, 151.9, 146.0, 145.7, 142.7, 135.8, 126.8, 121.9, 119.7, 57.4; Anal. Calcd for $\text{C}_{20}\text{H}_{17}\text{N}_5\text{O}_2$: C, 66.84; H, 4.77; N, 19.49. Found: C, 41.84; H, 3.93; N, 10.97. The poor elemental analysis obtained for this compound is discussed further in chapter 3.1. (^1H NMR in App. B, p. 254)

2.3 Synthesis of Complexes.

$\text{Co}^{(\text{III})}(\text{NH}_3)_4(\text{L})(\text{CF}_3\text{SO}_3)_3$. 0.85 g (1.4 mmol) of $[\text{Co}^{(\text{III})}(\text{NH}_3)_5(\text{CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)_2$ and 0.49 g (1.5 mmol) of **5** were each dissolved in 20 mL of acetone and a drop of triflic acid was added to the latter solution in order to bring the "pH" of each solution to about 5 as indicated by litmus paper. The solutions were mixed and stirred at room temperature for 48 hours. The pink solution was poured into rapidly stirred diethyl ether and the colloidal pink precipitate was collected by filtration. The brownish-pink tar was redissolved in 50 mL of acetone and 40 mL of diethyl ether was diffused into the solution in the refrigerator. The light pink precipitate was filtered off, rinsed with 20 mL of diethyl ether and vacuum dried for 12 hours at room temperature to afford a pale pink powder. Yield, 0.24 g (18%). ^1H NMR (d_6 -DMSO) 10.0 (br s, 2 H), 9.97 (br s, 2 H), 7.77 (d, 2 H), 7.48 (s, 2 H), 7.28 (mult, 3 H), 6.86 (s, 2 H), 5.14 (br s, 4 H), 3.70 (br s, cis NH_3 6 H), 3.48 (br s, trans NH_3 6 H); IR (KBr pellet): Characteristic ligand bands at $3209\text{ cm}^{-1}(\text{w})$, $1653\text{ cm}^{-1}(\text{m})$, $1617\text{ cm}^{-1}(\text{s})$, $1490\text{ cm}^{-1}(\text{m})$, $1437\text{ cm}^{-1}(\text{m})$ and $722\text{ cm}^{-1}(\text{m})$. Ionic triflate at $1272\text{ cm}^{-1}(\text{s})$. Coordinated ammonia at $3350\text{ cm}^{-1}(\text{m})$; UV/Visible spectroscopy (MeCN), λ in nm (log ϵ): 229 (3.97), 266 (3.71), 306 (4.18), 325 (sh, 3.27), 525 (0.80). (^1H NMR in App. B, p. 257)

$\text{Co}^{(\text{III})}(\text{CL})_3(\text{CF}_3\text{SO}_3)_3$. 0.36 g (0.76 mmol) of **8** was dissolved in 20 mL of dry acetone and a drop of triflic acid was added to make the "pH" as indicated by litmus paper approximately 5 to 6. 0.15 g (0.25 mmol) of $[\text{Co}^{(\text{III})}(\text{NH}_3)_5(\text{CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)_2$ was dissolved in 10 mL of dry acetone and this was added to the solution of **8**. The brownish orange solution was purged with acetone saturated nitrogen and stirred at room temperature for 65 hours while being exposed to fluorescent white light. The reaction mixture was poured into 200 mL of rapidly stirred diethyl ether to precipitate a brown tar. This was rinsed with diethyl ether and vacuum dried for 12 hours at room temperature to give a fine brownish orange powder. This was recrystallized three times from methanol with diethyl ether diffusion, followed by a diethyl ether rinse and 12 hours of room temperature vacuum drying to afford small golden cubes. Yield, 0.08 g (16%). ^1H NMR (d_6 -DMSO) 10.01 (br s, 2 H), 9.98 (br d, 2 H), 8.80 (br s, 1 H), 7.77 (t, 2 H), 7.73 (d, 2 H), 7.52 (s, 2 H), 5.13 (br s, 4 H), 4.31 (t, 4 H), 1.76 (quint, 4 H), 1.35 (sext, 4 H), 0.88 (t, 6 H); IR (KBr pellet) – Characteristic ligand bands at $1677\text{ cm}^{-1}(\text{m})$, $1605\text{ cm}^{-1}(\text{s})$, $1500\text{ cm}^{-1}(\text{m})$, $1431\text{ cm}^{-1}(\text{m})$, $712\text{ cm}^{-1}(\text{m})$. Ionic triflate at $1279\text{ cm}^{-1}(\text{s})$; UV/Visible spectroscopy (MeOH) λ in nm (log ϵ) 207 (4.57), 233 (4.35), 248 (sh, 4.30), 286 (4.28), 365 (sh, 3.76), 419 (4.04). Anal. Calcd for $\text{C}_{87}\text{H}_{99}\text{N}_{15}\text{O}_{15}\text{S}_3\text{F}_9\text{Co}$: C, 54.40; H, 5.16; N, 10.94. Found: C, 54.28; H, 5.31; N, 10.85. (^1H NMR in App. B, p. 259)

$\text{Co}^{(\text{III})}(\text{CL})_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$. 0.22 g of $\text{Co}^{(\text{II})}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.9 mmol) was dissolved in 85 mL of 4:1 ethanol:water and the pH was adjusted to 5 with dilute acetic acid. This was added rapidly with stirring to a solution of 1.50 g of **8** (3.2 mmol) in 140 mL of ethanol with the pH previously adjusted to 5 by the dropwise addition of glacial acetic acid. 0.2 g of activated charcoal was added and the solution was aspirated with air for 30 hours. The solution was filtered into a round

bottom flask and evaporated to near dryness. This was redissolved in a minimum of water and filtered into a saturated solution of 2.5 g of NH_4PF_6 in 12 mL of water. The precipitate was collected by filtration and rinsed with cold water, air dried for several hours and then rinsed with diethyl ether. This impure PF_6 salt was then dissolved in a minimum of acetone and filtered. A solution of 5.0 g of tetrabutylammonium chloride in 20 mL 5:1 acetone:water was filtered and added to the acetone solution of the complex. After several hours in the freezer, a precipitate was obtained which was filtered off, redissolved in 1:1 acetone:water and allowed to slowly evaporate in the dark at room temperature. Long greenish yellow needles were obtained after a few days. These were filtered off, rinsed with cold methanol then diethyl ether and vacuum dried at room temperature for 16 hours to give pale green needles. Yield, 0.75 g (54%). ^1H NMR identical to the triflate salt; IR (KBr pellet): Characteristic ligand bands at $1673\text{ cm}^{-1}(\text{m})$, $1597\text{ cm}^{-1}(\text{s})$, $1499\text{ cm}^{-1}(\text{m})$, $1426\text{ cm}^{-1}(\text{m})$ and $713\text{ cm}^{-1}(\text{m})$. No evidence of PF_6 at 844 cm^{-1} in the spectrum; UV/Visible spectroscopy (H_2O), λ in nm ($\log \epsilon$): 203 (5.05), 233 (4.74), 246 (sh, 4.69), 270 (sh, 4.61), 285 (4.65), 365 (sh, 4.16), 419 (4.38); Visible spectroscopy (MeCN) λ in nm ($\log \epsilon$) 597 (2.32), 640 (2.35), 680 (2.36), 697 (sh, 2.30); Anal. Calcd for $\text{C}_{84}\text{H}_{105}\text{N}_{15}\text{O}_9\text{Cl}_3\text{Co}$: C, 61.74; H, 6.48; N, 12.85. Found: C, 61.51; H, 6.74; N, 12.72.

$[\text{Co}^{(\text{III})}(\text{CL})_3](\text{PF}_6)_3$. a) The above chloride salt was converted back to the hexafluorophosphate salt by dissolving in a minimum of water and filtering slowly into a saturated solution of NH_4PF_6 in water. The precipitate was then recrystallized from acetone with diethyl ether diffusion. Two subsequent recrystallizations from acetone/diethyl ether and methylene chloride/diethyl ether were carried out in order to remove traces of free ligand present. Fine bright yellow needles precipitated out of solution and were collected by filtration. They were

rinsed with cold methanol, then diethyl ether and vacuum dried at room temperature for 16 hours.

b) The procedure for the chloride was followed starting from the acetate but the hexafluorophosphate salt initially obtained was recrystallized three times from methanol or acetone with diethyl ether diffusion instead of being converted to a chloride salt. Small yellow cubes were obtained when methanol was used and clusters of fine yellow needles were obtained when acetone was used. In both cases, the precipitate was collected by filtration, rinsed with diethyl ether and vacuum dried for 16 hours at room temperature.

Both of the above procedures were repeated many times and gave very similar analytical results. Yields, (18 to 43 %). ^1H NMR was identical to the triflate salt; IR (KBr pellet): Characteristic ligand bands at $1677\text{ cm}^{-1}(\text{m})$, $1605\text{ cm}^{-1}(\text{s})$, $1501\text{ cm}^{-1}(\text{m})$, $1428\text{ cm}^{-1}(\text{m})$ and $713\text{ cm}^{-1}(\text{m})$. Ionic PF_6^- at $844\text{ cm}^{-1}(\text{vs})$; UV/Visible spectroscopy (MeCN), λ in nm ($\log \epsilon$): 205 (4.99), 233 (4.68), 246 (sh, 4.60), 268 (sh, 4.51), 285 (4.56), 365 (sh, 4.02), 419 (4.31); Elemental analysis consistently suggested the presence of 1 to 3 % free ligand mixed with the complexes. Typical elemental analysis follow: Anal. Calcd for $\text{C}_{84}\text{H}_{99}\text{N}_{15}\text{O}_6\text{P}_3\text{F}_{18}\text{Co}$: C, 52.86; H, 5.23; N, 11.01. Found (a): C, 53.84; H, 5.45; N, 11.16; Found (b): C, 54.25; H, 5.39; N, 11.34.

$[\text{Ru}^{(\text{II})}(\text{L})(\text{NH}_3)_4](\text{PF}_6)_2$. 0.125 g (0.50 mmol) of $\text{cis}-[(\text{NH}_3)_4\text{Ru}^{(\text{III})}\text{Cl}_2]\text{Cl}$ was dissolved in 7 mL of water and the solution was purged with argon for 20 minutes. This was transferred under vacuum to a flask containing 5.0 g of freshly prepared zinc amalgam and the solution was stirred for 30 minutes in the dark at room temperature. A solution 0.166 g (0.51 mmol) of 5 in 8 mL of slightly acidified methanol ($\text{pH} = 5$ using 0.1 N HCl) was degassed by several freeze, pump, thaw cycles followed by the application of an argon purge for several minutes. This

solution was added under vacuum to the ruthenium containing solution and the resulting solution was stirred at room temperature in the dark for 30 minutes. The filters to be used for isolating the crude Ru(II) complex were rinsed with 5 ml of pH 6 phosphate buffer solution followed by a very dilute HPF_6 rinse just prior to being used. The volume of the solution of complex was reduced to about 8–10 mL by the application of vacuum and then filtered into a cold solution of 2.0 g NH_4PF_6 in 7 mL of water which was made just slightly acidic ($\text{pH} = 6$) by the addition of a small amount of HPF_6 . The resulting suspension was stirred for 10 minutes and then collected on a medium frit filter. The yellow precipitate was rinsed with 2 mL of cold water ($\text{pH} = 6$ by the addition of a trace of HPF_6) followed by 10 mL of diethyl ether. The precipitate was vacuum dried for 12 hours at room temperature and then recrystallized by dissolving in a minimum (4 mL) of very dry acetone and diffusing diethyl ether into the solution at room temperature for 1 day in the dark. The precipitate was collected on a medium frit filter, rinsed with 10 mL of diethyl ether and vacuum dried for 16 hours to give a fine yellow powder. Yield, 0.16 g (72 %) Note that if at any time during the isolation and recrystallization of the complex, it comes into contact with glassware that has not been made slightly acidic, then the yellow complex becomes dark brown almost immediately. All attempts to prepare the corresponding complex with **6**, **8(CL)** or **9** by this method or a similar route starting from the Ru(II) complex, $[(\text{NH}_3)_5\text{Ru}^{\text{(II)}}(\text{H}_2\text{O})](\text{PF}_6)_2$ were unsuccessful and gave brown solids which had ^1H NMR spectra indicative of a ligand reaction.

^1H NMR (d_6 -acetone) 9.18 (s, 2 H), 8.86 (s 2 H), 7.97 (d, 2H), 7.79 (m, 2 H), 7.40 (br s, 2 H), 7.28 (s, 2 H). 5.10 (br s, 4 H), 3.17 (s, 6 H), 2.75 (s, 6 H); IR (KBr pellet): Characteristic ligand bands at $1616\text{ cm}^{-1}(\text{s})$, $1506\text{ cm}^{-1}(\text{m})$, $1435\text{ cm}^{-1}(\text{m})$ and $713\text{ cm}^{-1}(\text{m})$. Ionic PF_6 at $838\text{ cm}^{-1}(\text{vs})$ Coordinated NH_3 at $3369\text{ cm}^{-1}(\text{m})$; UV/Visible spectroscopy (MeCN), λ in nm ($\log \epsilon$): 205 (3.93), 228 (3.98), 261 (4.12), 304 (4.13), 320 (sh, 3.26), 411 (3.03). Based on the lack of observation of a

"clean" ^1H NMR spectra, elemental analysis on this complex was not carried out.

(^1H NMR in Chap. 3, p. 80)

$\text{Ru}^{(\text{III})}(\text{CL})(\text{NH}_3)_4](\text{PF}_6)_3$. Attempts to prepare the $\text{Ru}(\text{III})$ complexes of **6**, **8**(CL) or **9** directly from the $\text{Ru}(\text{III})$ triflate complex, $[(\text{NH}_3)_5\text{Ru}^{(\text{III})}(\text{CF}_3\text{SO}_3)]-(\text{CF}_3\text{SO}_3)_2$ also resulted in the formation of brown solids and as a result, synthetic approaches involving the substitution of a coordinated ammine ligand were abandoned. a) 0.23 g of $\text{cis}-[(\text{NH}_3)_4\text{Ru}^{(\text{III})}(\text{H}_2\text{O})_2](\text{CF}_3\text{SO}_3)_3$ was dissolved in 4 mL of methanol and a solution of 0.18 g of **8** in 2 mL of methanol was added with rapid stirring. A precipitate forms after about 1 minute and the solution was continually stirred for a further 30 minutes. The precipitate was filtered off and rinsed with 10 mL of diethyl ether. The bright yellow powder was then dissolved in 10 mL of water and filtered into a solution of 3.5 g of NH_4PF_6 in 6 mL of water to give a precipitate immediately. This was stirred at room temperature for a further hour and then on ice for 30 minutes. The precipitate was filtered off and rinsed with cold water, diethyl ether and vacuum dried for 12 hours at room temperature. All attempts to recrystallize the PF_6 salt or precipitate a BF_4 or tetraphenylborate salt of this complex resulted in the formation of oils.

b) The same procedure was followed to form the impure triflate salt. This was dissolved in a minimum of water and loaded onto a column of Sephadex SP-C25-120. Elution with 1 M NaCl gives one smeared out band which appears to be at least three different species as determined by UV/visible spectroscopy. The middle fraction displayed the expected spectrum for the complex and was therefore collected, the volume reduced by rotary evaporation and filtered into a saturated solution of NaBF_4 in water. The powdery precipitate collected was found to have the same column characteristics as the impure triflate salt prior to column chromatography suggesting that perhaps the complex reacts on the column.

Zn(CL)(H₂O)₂(ClO₄)₂. A solution of 0.35 g of Zn(ClO₄)₂·6H₂O (0.9 mmol) in 25 mL of acetone was added dropwise to a stirred solution of 0.63 g of CL (1.3 mmol) in 50 mL of acetone. The light yellow precipitate that forms immediately was collected by filtration and recrystallized twice from acetonitrile with diethyl ether diffusion. The light yellow microcrystalline powder was rinsed with diethyl ether and vacuum dried at room temperature for 16 hours. Yield, 0.40 g (61%). ¹H NMR (d₃-acetonitrile) 8.90 (br s, 1 H), 8.72 (s 2 H), 8.49 (s, 2H), 8.09 (d, 2 H), 7.58 (t, 2 H), 7.29 (s, 2 H), 5.05 (br s, 4 H), 4.25 (t, 4 H), 1.77 (quint, 4 H), 1.41 (sext, 4 H), 0.92 (t, 6 H); IR (KBr pellet): coordinated H₂O at 3524 cm⁻¹(s), ionic ClO₄, ν₃ at 1098 cm⁻¹(s), ν₄ at 929 cm⁻¹(w); UV/Visible spectroscopy (MeCN), λ in nm (log ε): 200 (4.01), 231 (3.66), 243 (sh, 3.61), 269 (3.52), 284 (3.52), 297 (sh, 3.38), 365 (sh 3.01), 419 (3.29). Anal. Calcd for C₂₈H₃₇N₅O₁₂Cl₂Zn: C, 43.57; H, 4.83; N, 9.07. Found: C, 43.67; H, 4.47; N, 9.04. (¹H NMR in App. B, p. 255 and 256)

Cu(CL)(CF₃SO₃)₂. 1.03 g of Cu(CF₃SO₃)₂·nH₂O (2 mmol based on n=6) was added to a solution of 1.06 g of CL (2 mmol) in 140 mL of ethanol. The solution was stirred in the dark at 25 °C for 42 hours. Filtration of the light green precipitate followed by 2 recrystallizations from acetonitrile with diethyl ether diffusion gave olive needles. These were rinsed with diethyl ether and vacuum dried at 110 °C for 8 hours. Yield, 0.56 g (27%). IR (KBr pellet): coordinated CF₃SO₃, ν₄ at 1220 cm⁻¹(s), 1241 cm⁻¹(s), 1282 cm⁻¹(s); UV/Visible spectroscopy (MeCN), λ in nm (log ε): 200 (4.44), 235 (4.15), 246 (4.14), 270 (4.03), 283 (4.02), 294 (sh, 3.90), 367 (sh, 3.45), 420 (3.83), 568 (1.82). Anal. Calcd. for C₃₀H₃₃N₅O₈S₂F₆Cu: C, 43.24; H, 3.99; N, 8.40. Found: C, 43.87, H, 4.13; N, 8.56.

$\text{Cu}(\text{CL})(\text{H}_2\text{O})_2(\text{CF}_3\text{SO}_3)_2$ can be isolated if diethyl ether is diffused into the reaction mixture filtrate from the above complex. Filtration, rinsing with diethyl ether and vacuum drying at 110°C for 8 hours gave pale green crystals. Yield, 0.29 g (12%). IR (KBr pellet): coordinated CF_3SO_3 , ν_4 at $1223\text{ cm}^{-1}(\text{s})$, $1245\text{ cm}^{-1}(\text{s})$, $1281\text{ cm}^{-1}(\text{s})$, coordinated H_2O at $3491\text{ cm}^{-1}(\text{s})$; UV/Visible spectroscopy (MeCN), λ in nm (log ϵ): 200 (4.56), 233 (4.33), 243 (sh, 4.30), 270 (4.24), 282 (sh, 4.21), 294 (sh, 4.09), 365 (sh, 3.72), 414 (3.93), 616 (1.79), 840 (1.28). Anal. Calcd. for $\text{C}_{30}\text{H}_{37}\text{N}_5\text{O}_{10}\text{S}_2\text{F}_6\text{Cu}$: C, 41.45; H, 4.29; N, 8.06. Found: C, 41.51; H, 4.13; N, 8.10.

$\text{Cu}(\text{L})(\text{H}_2\text{O})(\text{CF}_3\text{SO}_3)_2$. 1.61 g of $\text{Cu}(\text{CF}_3\text{SO}_3)_2 \cdot n\text{H}_2\text{O}$ (3.4 mmol based on $n=6$) was added to a solution of 1.25 g of L (3.8 mmol) in 180 mL of 95 % ethanol. The pale blue slurry was stirred at 25°C for 20 hours and collected by filtration. The precipitate was placed in 10:1 acetonitrile:water and heated gently until the solid dissolved and the solution became dark blue. The solution was cooled, filtered and diethyl ether was diffused into the filtrate. Dark blue crystals deposited after two days. These were rinsed with diethyl ether and vacuum dried for 16 hours at room temperature. Yield, 0.65 g (27%). IR (KBr pellet): coordinated CF_3SO_3 , ν_4 at $1226\text{ cm}^{-1}(\text{s})$, $1249\text{ cm}^{-1}(\text{s})$, $1278\text{ cm}^{-1}(\text{s})$, coordinated H_2O at $3532\text{ cm}^{-1}(\text{s})$; UV/Visible spectroscopy (MeCN), λ in nm (log ϵ): 229 (3.93), 263 (3.68), 308 (4.11), 320 (sh, 3.21), 579 (1.72). Anal. Calcd for $\text{C}_{22}\text{H}_{19}\text{N}_5\text{O}_7\text{S}_2\text{F}_6\text{Cu}$: C, 37.37; H, 2.71; N, 9.90. Found: C, 37.43; H, 3.11; N, 10.04.

$\text{Cu}(\text{13})(\text{H}_2\text{O})(\text{CF}_3\text{SO}_3)_2$. A solution of 0.81 g of $\text{Cu}(\text{CF}_3\text{SO}_3)_2 \cdot n\text{H}_2\text{O}$ (1.7 mmol based on $n=6$) in 5 mL of acetonitrile was added to a solution of 0.73 g of 13 (1.7 mmol) in 15 mL of acetonitrile. The solution was stirred in the dark at 25°C for 4 hours. Filtration of the mixed olive and bright green precipitate followed by 2 recrystallizations from acetonitrile with diethyl ether diffusion gave small olive

cubes. These were rinsed with diethyl ether and vacuum dried at 110 °C for 8 hours. Yield, 0.38 g (25%). IR (KBr pellet): coordinated CF_3SO_3 , ν_4 at 1220 $\text{cm}^{-1}(\text{s})$, 1241 $\text{cm}^{-1}(\text{s})$, 1282 $\text{cm}^{-1}(\text{s})$; UV/Visible spectroscopy (MeCN), λ in nm ($\log \epsilon$): 219 (4.32), 245 (sh, 4.16), 268 (4.26), 285 (sh, 4.18), 301 (3.94), 366 (3.52), 420 (3.77), 597 (1.87). Anal. Calcd. for $\text{C}_{24}\text{H}_{29}\text{N}_7\text{O}_9\text{S}_2\text{F}_6\text{Cu} \cdot \text{H}_2\text{O}$: C, 35.98; H, 3.65; N, 12.24. Found: C, 35.45, H, 3.64; N, 12.51.

2.4 Physical Measurements. UV-vis spectra were recorded on a Cary 5 spectrophotometer. Fluorescence spectra were recorded on a Perkin-Elmer 204-S Fluorescence spectrometer. Fluorescence quantum yields were calculated using a 5×10^{-3} M quinine sulfate in 1 N H_2SO_4 solution ($\phi = 0.508$) as a standard⁹⁹. Quantum yields were corrected¹⁰⁰ for the difference in refractive index between the standard and the solution being measured. Infrared spectra of sample KBr pellets and Nujol mulls were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. FT-IR spectra of the copper complexes in acetonitrile solution were recorded on the same instrument in a 0.025 mm cell with freshly polished NaCl windows. The solutions were injected into the cell immediately prior to recording the spectra as a delay of more than a few minutes results in the formation of other complexes as indicated by a change in the colour of the solution. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 200 MHz or a Bruker AMX 400 MHz NMR spectrometer. Cyclic voltammetry was performed using a BAS Model CV-27 Cyclic Voltammograph. Details of the electrochemical cell have been previously described.¹⁰¹ Experiments were performed in dry acetonitrile¹⁰² (0.1 M tetrabutylammonium hexafluorophosphate, TBAH or 0.1 M tetrabutylammonium tetrafluoroborate, TBAF), at 25 °C, with a three-electrode system consisting of a platinum-disk working (BAS 1.6 mm diameter), platinum-wire counter and silver wire quasi-reference electrodes. Ferrocene ($E^\circ = 400$ mV vs NHE) was used as an

internal reference.¹⁰³ Potentiometric titrations were carried out on 0.1 M solutions of ligand or complex with no added salts. For solutions in acetonitrile:water mixtures, two concentrations of either standard NaOH (0.1 M and 1×10^{-3} M) or standard HCl (5×10^{-3} and 1×10^{-4} M) in this solvent were used to calibrate the pH meter as liquid junction potentials or another more suitable reference compound were not available. Mixtures of sodium oxalate and oxalic acid were used to reference the pH in methanol and methanol:water mixtures.¹⁸¹ pK_a was then determined from either the inflection points on the plots of pH versus titrant volume and in some cases from the x-intercept of a plot of the differential with respect to pH. Picosecond transient absorption spectroscopy was performed at The Canadian Centre for Picosecond Laser Flash Photolysis of which a detailed description of the laser system has been given.¹⁰⁴ A passively mode-locked Nd:YAG laser provided ≈ 30 -ps (fwhm) pulses (2–3 mJ/pulse) at 355 nm for excitation and two YAG amplifiers and a solution of phosphoric acid in D_2O was used to generate a probe continuum. A schematic of the experimental setup used to obtain the transient absorption spectra is shown in figure 2.1.

Figure 2.1 Schematic diagram of laser system used to record the transient absorption spectra. a) C.W. laser for alignment, b) MS 400 Rear Mirror @ MRC MR at 1064 mm, c) SF 408-07 with Nd:YAG 7 mm x 90 mm (OSG), d) PF 302 Pulse Slicer, e) Rejected Pulse Detector, f) SF 410-07 with 7 x 115 mm Nd:YAG (Amp.), g) SF 410-07 with 9.35 x 115 mm Nd:YAG (Amp.), h) SF 320-16 with 5.48 x 210 mm Nd:Si glass (Amp.), i) Frequency Doubler Type II, j) Frequency Tripler, k) Continuum Generator, m) 355 nm Energy Detector, n) Energy Ratio Meter, o) Continuum Splitter, p) Sample Holder
 adapted from figure courtesy of Mr. K. Daneshmandi

Emission lifetimes were determined by exciting the sample with a 30 ps (fwhm) pulse (0.2 mJ/pulse) at 355 nm from the passively mode-locked Nd:YAG laser. The emission was passed through a 400 nm cut off filter and appropriate neutral density filters before entering a Hamamatsu C979 Temporal Disperser and a C1000 Streak Camera. A C1097 Delay Unit was used to trigger the camera between 1 and 8 ns from the excitation pulse by splitting the beam and passing a portion of the pulse into a Hamamatsu C1083 Photodiode. A schematic of the experimental setup used to obtain the emission lifetimes is shown in figure 2.2.

Figure 2.2 Schematic diagram of equipment setup for emission lifetime measurements. a) Hamamatsu C979 Temporal Disperser, b) Hamamatsu C1000 Streak Camera, c) Hamamatsu C1083 Photodiode, d) Hamamatsu C1097 Delay Unit, e) Hamamatsu C1098 Temporal Analyzer, f) Hamamatsu C1000 Camera Control, g) Monitor, h) Strip chart recorder or digital computer, i) 200 μ J 355 nm laser pulse, j) beam splitter, k) 400 nm cutoff filter, l) neutral density filter, m) sample

3.0 Results and Discussion

3.1 Physical Characterization

3.1.1 Characterization of the Ligands

Characterization of the dianion of 2,3-dicyano-1,4-benzoquinone was limited to electronic and fluorescence spectroscopy due to its instability toward decomposition to the semiquinone in air. This is discussed in some detail in chapter 4. Elemental analysis of the tetraphenylarsonium salt gave acceptable results.

The infrared and NMR spectral data for all of the precursors and ligands are summarized in tables IV and V respectively. Interpretation of these tables may be simplified by referring to the labelled structural diagram shown in appendix G (which is the last page of the thesis). The infrared spectra were of KBr pellets of the samples and the NMR spectra were recorded in CDCl_3 and chemical shifts reported are referenced to an internal TMS reference except where otherwise noted. The infrared, NMR and mass spectra may be found in appendix B. The tentative assignment of the relevant bands in the infrared spectra and resonances in the NMR spectra were determined by comparison with molecules of similar structure and by reference to the extensive literature on organic and heterocyclic compounds.¹⁰⁵⁻¹⁰⁷

The IR spectrum of the di-*n*-butoxy orthodinitrile (2) is shown in figure B.1 (p. 216). Most notable in the spectrum is the nitrile stretching frequency which occurs at 2227 cm^{-1} and the series of three sharp peaks in the aliphatic C-H region (2957 , 2926 and 2868 cm^{-1}) which are characteristic of *n*-butyl groups. In addition, the strong C-O stretching modes are visible at 1070 and 1272 cm^{-1} . Many other significant bands are observed which include aliphatic bending modes, aromatic overtones and ring breathing modes as well as out-of-plane and in-plane rocking modes. The ^1H NMR spectrum (figure B.3, p. 217) consists of a singlet in the aromatic region with a chemical shift of 7.21 ppm due to the two protons on the benzene. In the aliphatic region, four different protons are found as a triplet at 4.08

Table IV IR spectral data for ligands and precursors^{a,b}

Assignment	2	3	2b*	4	5	6	7	8	9	10	11	12
imine N=H		3440m		3446m								
indole N-H		3305m		3348m	3202m	3205m	3182m	3414m	3390m	3360m	3420m	3415m
aromat. C-H	nr	3080w	3094w	3088w	3070w	3090w	nr	3085w	nr	nr	3090w	3084w
pyridyl C-H					3052w 3025w	3043w	3048w 3021w	3048w 3018w	3035w 3007w	3045w 3019w	3049w	3050w 3023w
alkyl C-H	2957w	2930m	2995m	2941m	2925m	2920m	2922m	2956m	2940m	2940m	2932m	2936m
	2926m	2870w	2888w		2860w			2905w	2875w	2855w	2835w	2836w
	2868w	2760w	2772w					2874w				
	2804w											
C=N nitrile	2227m		2228m									
C=N imine		1645s		1647m	1657m	1655m	1658m	1654m	1657m	1653m	1652w	1654w
C=C benzene	1617m	1610m	1605m	1617m	nr	1590s	nr	1625m	1622m	1612s	nr	1622m
C=N & C=C pyridyl ring stretch					1576s 1484m 1425s	1555m nr 1407s	1579s 1469m 1423m	1567s 1466w 1422w	1560s 1490m 1410m	1575s 1555s 1476s	1572s 1466m 1429w	1591m 1576s 1491m 1414s
	1272s 1070s	1258s 1064s	1279s 1058s	1267s 1048s				1271s 1081s	1250s 1061s	1270s 1079s	1275s 1074s	1279m 1069s
C-O stretch												

^a All values are in cm^{-1} . Samples prepared as KBr pellets.

^b Assignments are tentative only. See text for a discussion of the infrared data.

* 2b is the ortho-dicyano precursor of 4.

nr Peak was not resolved but is evident by asymmetric shape or shoulder of nearby band.

Table V**a) ^1H NMR data for ligands and precursors from Appendix G^a**

pos.	rel. int.	2	3	2b ^b	4	5	6	7 ^c	8	9	10 ^c	11	12
3	[2]					7.83m	7.69b	7.85d					
4	[2]	7.21s	6.92s	7.16s	7.23s	7.37b	7.49b	6.80m	6.88s	6.91s	6.91s	6.91s	6.97s
R5	[4]	4.08t	4.07t						4.06t	4.10t	4.13t		
R6	[4]	1.82q	1.83q						1.75q	1.80q	1.90q		
R7	[4]	1.52x	1.51x						1.41x	1.47x	1.59x		
R8	[6]	0.98t	0.98t	3.92s	3.97s				0.90t	0.93t	0.99t	3.90s	3.95s
9	[4]					5.0bd	5.00s	4.70b	5.01bs	4.98s	5.16s	5.02b	5.00s
11	[2] ^d					7.83m	7.31d	6.8m	7.82d	7.37d	7.6m	7.77d	7.32d
12	[2] ^d					7.55m	8.51d	6.8m	7.25t	8.54d	7.19t	7.22t	8.52d
13	[2]					8.50s		6.8m	8.50d		7.6m	8.48d	
14	[2]					8.67s		7.65d	8.72s		8.56d	8.68s	
H _a	[1]		7.16s		3.3m*	9.36	e	e	e	e	e	7.15	e
H _b	[2]		8.19b		3.3m*								

b) ^{13}C NMR data for ligands and precursors from Appendix G

pos.	2	3	2b ^b	4	5	6	7	8	9	10	11	12
1	155.2	167.4	155.5	168.5	168.6	168.7	166.7	166.9	167.0	166.8	166.9	167.4
2	105.2	120.8	102.4	118.5	123.7	123.2	122.6	123.4	122.6	127.2	123.2	122.8
3	113.1	149.3	113.6	149.1	136.9	138.5	137.0	149.7	148.7	148.7	149.7	148.9
4	118.4	115.9	119.7	116.1	130.4	130.5	130.1	116.6	116.6	116.2	115.0	115.1
R5	69.9	68.5						69.1	68.9	69.0		
R6	30.9	31.1						31.2	31.1	31.4		
R7	19.0	19.3						19.2	19.2	19.3		
R8	13.7	13.8	57.2	56.0				13.8	13.8	14.0	56.3	56.3
9					50/45	50.0	53/56	49.6	49.6b	52.6b	51.8	49.8b
10					149.6	149.9	158.8	148.7	149.0	159.1	148.6	149.3
11					136.5	121.6	136.8	135.7	125.6	136.4	135.9	125.5
12					121.9	149.6	120.5	118.4	149.6	121.7	118.9	149.7
13					148.3		122.0	143.4		122.1	148.4	
14					149.7		148.8	149.5		148.8	149.3	

- a** Structures & assignments (pos.) for C and H may be found in appendix G. Numbers in [] of column 2 of table a) are expected relative proton integrations. Observed [] were within 10% of expected except where noted. Lower case letters designate multiplicity: s=singlet, d=doublet, t=triplet, q=quintet, x=sextet, m=multiplet, b=broad singlet. All spectra recorded in CDCl_3 and referenced to solvent, except **4** which was only sufficiently soluble in CD_3OD and ^1H NMR spectrum of **5** which was in d_6 -DMSO.
- b** 2b is the ortho-dicyano precursor of **4**.
- c** overlapping multiplet of [9] for **7** and [4] for **10** at $\delta = 6.8$ (7) or 7.6 (10) ppm
- d** For **6**, **9** and **12**, by symmetry the integrations for protons 11 and 12 are 4.
- e** resonance either could not be identified or could not be differentiated from CHCl_3 peak.
- *** total integration is greater than [3], possibly includes exchanging water or methanol.

ppm, a quintet at 1.82 ppm, a sextet at 1.52 ppm and another triplet at 0.98 ppm with corresponding integrations of 2:2:2:3, relative to the aromatic proton with an integration of 1. The aliphatic protons are shifted downfield in the order listed from the terminal methyl group to the methylene adjacent to the ether oxygen. The ^{13}C NMR as shown in figure B.4 (p. 218) and summarized in table Vb (column 2) displays eight different resonances with four each in the aromatic and aliphatic regions. The proton and carbon NMR spectra are rather simple and are consistent with a plane of symmetry bisecting the molecule. This symmetry is also observed in subsequent derivatives thus simplifying the interpretation of NMR spectra.

The mass spectrum (figure B.5, p. 219) was obtained by chemical ionization with diethyl ether and is therefore expected to display intense mass abundances at $M+75$, $M+59$, $M+29$, $M+15$ and $M+1$ due to secondary ion formation by collision with the common diethyl ether primary ions, the protonated ether ion, the ether ion less a methyl group, ethyl radicals, methyl radicals and protons respectively.¹⁰⁸ The spectrum does indeed display all of these peaks with the $M+75$, $M+29$ and $M+1$ peaks at 273, 301 and 347 being the most intense. No attempt was made to identify the various fragments observed in the spectrum as this is beyond the scope of this study.

At this point, many attempts were carried out to form the ligands 5 through 10 directly from the orthodinitrile using procedures analogous to those of Elvidge and Linstead.¹⁰⁹ Refluxing *n*-butanol was first used as a solvent but the aminomethylpyridines were found to decompose at this temperature. Ethanol and *n*-propanol were also tested as solvents with and without added CaCl_2 as a catalyst¹¹⁰ with little success. It became evident at this point that in order to synthesize the chromophore ligands with methylpyridyl functionalities, the diiminoisoindoline precursor would have to be prepared and isolated.

Initial attempts to cyclize the orthodinitrile **2** with ammonia were carried out in liquid ammonia at 100 °C and 120 psi in a steel hydrogenation bomb type apparatus¹¹¹ but only low yields of less than 10 % were achieved after several days of reaction. In addition, the teflon gaskets were prone to leakage and the reaction vessel required depressurization, both of which resulted in the release of ammonia gas into the laboratory thus creating a hazardous condition requiring temporary evacuation. The procedure⁹⁶ outlined in chapter 2 was carried out at atmospheric pressure in ammonia saturated methanol with an ammonia purge and a catalytic amount of sodium metal added. The active catalyst is in fact sodium methoxide and the reaction mechanism involves cyclization to form 1-imino-3-methoxy-isoindoline¹¹² followed by displacement of the methoxy group by ammonia.

The IR spectrum of the diiminoisoindoline (**3**) derivative shown in figure B.2 (p. 216) has the characteristic n-butyl pattern in addition to two different types of N-H stretches found at 3440 cm⁻¹ and 3305 cm⁻¹, corresponding to the imino and indole groups respectively. The relatively intense peak at 1645 cm⁻¹ has been assigned to the imine C=N stretch by reference to similar compounds.¹¹³ The sharpness of the peaks are greatly reduced as this spectrum was recorded on a conventional scanning spectrophotometer.

The NMR spectra of **3** shown in figures B.7 and B.8 (p. 220 and 221) are quite similar to those found for **2** in the aliphatic regions. An additional broad resonance in the ¹H NMR spectrum at 8.19 ppm has been assigned to the imino protons as it has a relative integration of 2. The indole proton was not identified in the spectral range examined for this compound and many of the subsequently formed compounds and is believed to be undetectable because of nuclear quadrupolar broadening from the nitrogen nucleus as is observed for pyrrole derivatives.¹¹⁴ The ¹³C NMR resonances assigned to carbons 1, 2 and 3 in the aromatic region may experience a higher chemical shift due to inductive effects from

the extended π -system and carbon 4 may experience a slightly lower chemical shift than in 2 due to its remote location from the additional π -system.¹¹⁵ The exact mechanism by which these shifts occur is complex and beyond the scope of this study.¹¹⁶ The tentative assignments are based mainly on the assumptions that carbon-13 resonance intensities follows the order primary > secondary > tertiary and chemical shifts increase with the electronegativity of the substituents attached to the carbon for a given hybridization.¹¹⁷ More sophisticated 2-D NMR experiments could be carried out to definitively identify which resonances are associated with each carbon.

The mass spectrum of 3 is shown in figure B.6 (p. 219). The spectrum acquired by electron ionization (upper curve) displayed only a very minor contribution with a relative intensity of 0.8 % for the molecular ion at 289. Chemical ionization with diethyl ether produced a spectrum with the major peak at 290 due to the $M + 1$ ion.

The analogous methoxy derivatives of 2 and 3 (i.e. 2b and 4) displayed very similar IR spectra (figures B.9 and B.10, p. 222) with the nitrile stretch of 2b appearing at 2228 cm^{-1} and the imine stretch of 4 appearing at 1647 cm^{-1} . The electron ionization mass spectra (figures B.11 and B.12, p. 223) of 2b and 4 display molecular ions at 188 and 204 with relative intensities of 74 % and 70 % as compared to the most intense peaks. The NMR spectra (figures B.13 to B.16, p. 224 to 227) were almost identical to the *n*-butoxy derivatives in the aromatic region as expected. In the aliphatic region, the four resonances of the *n*-butyl groups were replaced by a single resonance due to the methyl group appearing at 3.9 to 4 ppm and 56 to 57 ppm for the ^1H and ^{13}C NMR spectra respectively. It is interesting to note that the imine protons in 4 appear at 3.3 ppm in CD_3OD compared to 8.19 ppm for 3 in CDCl_3 . In addition the relative integration for this resonance is three which suggests that the indole proton (Ha) may possibly be undergoing rapid

exchange with the imine protons in CD_3OD .¹¹⁸

Commercially available 1,3-diiminoisoindoline may be converted to ligands 5, 6 and 7 by an ammonia condensation reaction with the meta, para and ortho substituted series of aminomethylpyridines. Care must be taken to vacuum distill the aminomethylpyridines below 100°C as decomposition was observed above this temperature. The temperature must be raised slowly with intermittent application of vacuum to remove the ammonia liberated followed by argon purge to raise the pressure and thus avoid bumping of the reaction mixture. For one of the preparations of 7, the temperature was not raised and the solution was only stirred at room temperature for several days. The isolated product was the monosubstituted derivative of which a ^{13}C NMR spectrum was obtained and is shown in figure B.21 (p. 230). This provides a synthetic route to asymmetric multidentate ligands which may be attractive for further studies of electronic coupling effects in ligands of this type or to tune the metal coordination site for specific catalytic activity.

The infrared spectra of 5, 6 and 7 are shown in figures B.17 to B.19 (p. 228 and 229) and summarized in table IV. Of note is the absence of the ether C—O stretch that is observed in all the other compounds as strong peaks around 1270 cm^{-1} and 1060 cm^{-1} . A few additional weak bands in the aromatic C—H stretching region around 3040 cm^{-1} have been assigned to the pyridyl groups. An attempt was made to identify all of the major peaks using observations on methylpyridines¹¹⁹ and the related ligands 8 through 12 but with a lack of isotope substituted derivatives, the overlap of several bands made this task very difficult.

The mass spectra by chemical ionization of 5, 6 and 7 shown in figures B.20, B.24 and B.25 (p. 229 and 233) all exhibit the $M + 1$ ion as the most intense peak with the $M + 59$ peak also evident. The ^1H and ^{13}C NMR spectra of these three ligands (figures B.22, B.23, B.26, B.27, B.28 and B.29, p. 231, 232 and 234 to

237) all exhibit typical substituted pyridyl resonance patterns¹²⁰ and possess a pattern of resonances that suggest that the molecules exist in a near symmetric conformation with a plane of symmetry through the centre of the molecule. The only exception to this are the methylene protons which appears as a broad doublet in 5, a broad singlet in 7 and a sharp singlet in 6 at approximately 5 ppm. This may be rationalized in terms of cis-trans isomerization of this group about the imine nitrogen which would cause broadening or splitting of this peak depending on the rate of interconversion. This is further shown by the additional carbon resonances in the ¹³C NMR spectra in the 50 ppm region for 5 and 7.

Characterization of ligands 8 to 12 was carried out in the same manner as for the so-called "nonchromophore" ligands 5, 6 and 7. The infrared spectra shown in figures B.30, B.31, B.32, B.42 and B.43 (p. 238, 239 and 247) displayed many features similar to the the nonchromophore ligands with the addition of peaks associated with the alkoxy groups. Mass spectra were acquired by chemical ionization (figures B.33, B.36, B.37, B.44 and B.45, p. 239, 242 and 248) and displayed the M + 1 ion at 472 for 8, 9 and 10 and at 388 for the methoxy derivatives, 11 and 12. The ¹H and ¹³C NMR spectra (figures B.34, B.35, B.38, B.39, B.40, B.41, B.46, B.47, B.48 and B.49, p. 240, 241, 243 to 246 and 249 to 252) all displayed resonance patterns characteristic of a plane of symmetry bisecting the molecule. In addition, only one resonance due to the methylene protons and carbon are observed on the ¹H NMR and ¹³C NMR spectra of these ligands suggesting that the alkoxy substituents at the 4 and 7 position provide sufficient steric hindrance to cis-trans isomerization about the imine nitrogens.

Ligand 13 was prepared from 4 and 3-aminopropyl-N-imidazole by the same procedure as that used for the methylpyridyl containing ligands. The addition of two more methylene units to the spacer was expected to slow the rates of both the forward and back electron transfer by one to two orders of magnitude as a result

of both increasing separation and reduced electronic coupling.¹²¹ The imidazoles were assumed to be roughly equivalent to the pyridyls and were used because of their commercial availability.

The NMR spectra of the dimethoxy derivative, 13 (figures B.52 and B.53, p. 255 and 256) displayed a resonance pattern consistent with a plane of symmetry bisecting the molecule. The methoxy groups at the 4 and 7 position presumably provide sufficient steric hindrance to cis-trans isomerization even when the more flexible propylimidazolyls are attached to the imines at positions 1 and 3.

As discussed in chapter 1, the dianion form of the chromophore is expected to have more attractive properties in terms of excited state redox potential, chemical reversibility and two electron donor capability. Several attempts to dealkylate the *n*-butoxy ligand, 8, using various procedures found in the literature¹²² were to no avail. Methyl groups are generally much easier than butyl groups to remove and therefore subsequent attempts to form the dianion version of the chromophore ligand started with the dimethoxy ligand, 11. A procedure based on the use of in-situ generated iodotrimethylsilane⁹⁸ gave the most encouraging results and is outlined in chapter 2. The ¹H NMR spectrum for the isolated product of this procedure is shown in figure B.54 (p. 257). The methylene protons appear at 4.76 ppm in CD₃OD and the hydroxy protons appear at 4.01 ppm. The additional resonance appearing as a broad singlet at 5.06 is due to residual protons from water associated with the solvent as determined by a reference spectrum of the solvent alone. The absence of any resonance¹²³ due to the methoxy groups at 3.6 ppm suggests that the dealkylation was complete. The ¹³C NMR data supports this further with only one carbon resonance observed in the aliphatic region at 57.4 ppm. Unfortunately, elemental analysis of this product gave low values for C, H and N suggesting the presence of a salt impurity. The use of a stoichiometric amount of sodium iodide in the preparation or a more sophisticated purification procedure may

alleviate this problem in future work.

3.2 Structure of the Complexes

From molecular models (see Appendix A) of the ligands **5** (or **L**), **6**, and **7** in different coordination environments, it became apparent that these ligands may function as mono or bidentate neutral ligands coordinating a metal ion in either a mono or bis pyridyl fashion or if the indole is deprotonated, the ligand may function as a tridentate anionic ligand.

In the case of **7** in which the 2-pyridyl nitrogen is slightly facing the indole, the most favourable coordination geometries were as either a tridentate anionic ligand, a bidentate ligand coordinating through one pyridyl and one imine or a bidentate ligand coordinating through both pyridyls with the indole ring at an almost right angle to the coordination plane. Early attempts to prepare a Cu(II) complex of this ligand led to the formation of poorly characterized insoluble brown salts that displayed a dramatic reduction in the intensity of the imine C=N stretch and a broad featureless electronic spectrum both indicative of polymer formation. It is for this reason that no further attempts were made to prepare complexes of this ligand or the analogous di-*n*-butoxy derivative, **10**.

Of the two remaining ligands, **5** and **6**, the most favourable coordination environments were obtained in the case of the 3-substituted derivative, **5**. When an octahedral or a tetrahedral coordination environment is imposed on these two ligands, the total RMS error on the final structure is less for **5**. In addition, the optimized model geometries exhibits less than 0.01 Å of non-coplanarity in the pyridine rings in the case of **5** as compared to values greater than 0.13 Å for **6**. Similar calculations with ligand **5** coordinated in tetragonally distorted octahedral and square pyramidal geometries also gave optimized structures with small perturbations from ideal geometries.

3.3 Synthesis and Characterization of the Complexes

Shown in figure B.55 (p. 258) is the FTIR spectrum of the Co(III)tetraammine derivative of the ligand 5 (or hereby known as L), $[a_4(L)Co(III)](TFMS)_3$ (where TFMS signifies the triflate or trifluoromethanesulphonate anion). The spectrum contains similar C—H stretching frequencies as the free ligand shown in figure B.18 (p. 228) with the addition of partially overlapping strong N—H stretch vibrations. The fingerprint regions are very similar with the addition of the intense ν_3 stretch of ionic triflate at 1200 cm^{-1} .

When the same synthetic procedure was used to form the analogous complex with the chromophore ligand, 8 (or hereby known as CL), the small golden cubes that were obtained in very small yield ($< 2\%$) after several recrystallizations exhibited no spectral peaks in either the infrared (figure B.56, p. 256) or 1H NMR (figure B.57, p. 259) spectrum to indicate the presence of amine ligands. In addition, the 1H NMR spectrum displays a downfield shift for the two pyridyl protons (labelled e and f) adjacent to the nitrogen which is consistent with bis pyridyl coordination. The broad peak just above the baseline at 8.8 ppm with an integration of 1 (labelled a) is believed to be due to the indole proton. Elemental analysis of this compound indicated that the complex was in fact a tris chelated cobalt(III) complex of CL and a proposed mechanism for its' formation is postulated in chapter 6.

A photochemical reaction involving the initially formed monodentate pyridyl coordinated pentaamminecobalt(III) complex was suspected. The reaction between the pentaamminecobalt(III) triflate ion and the ligand was therefore studied by UV—visible spectroscopy. Figure 3.1 displays the spectra obtained when a solution of these is irradiated with 405 nm light for varying periods of time. The growth in the absorption at 435 nm and the accompanying reduction in intensity at 255 nm after 5 seconds is due to protonation and coordination of the ligand. The

growth of the ligand associated bands of the resulting complex in the 230 to 290 nm range occurs quite rapidly and is essentially complete after just 15 seconds.

In an effort to prepare larger quantities of this complex for further study, the procedure was repeated using a 3:1 ligand to Co ratio and exposing the reaction mixture to visible light. Yields of 10 to 20 % could be obtained by this technique after several recrystallizations. Further synthetic routes starting from a Co(II) salt gave much higher yields of 50 % or more for the chloride and 20 to 45 % for the hexafluorophosphate salt of this complex. The ^1H NMR spectra of these salts were very similar to the triflate and are not included. The infrared spectra of the chloride and hexafluorophosphate are shown in figures B.58 and B.59 (p. 260).

The coordination geometries of both copper and zinc complexes are quite extensive and an idea of these geometries can be inferred by reference to the infrared (table VI) and electronic spectra (figure 3.2) of the complexes as well as their electrochemical properties (chapter 5.1).

The solid state infrared spectra of the three copper complexes (figures B.61, B.62 and B.63, p. 262 and 263) and the zinc complex (figure B.60, p. 261) display several common features. The pyridine ring C-H stretching vibrations that appear at 3048 cm^{-1} and 3018 cm^{-1} for CL and 3052 cm^{-1} and 3025 cm^{-1} for L are shifted to higher energies in all four complexes. The pyridine C=C stretching mode that appears at 1567 cm^{-1} and 1572 cm^{-1} for CL and L respectively is also shifted by 35 to 45 cm^{-1} in the complexes. Both of these shifts are known¹²⁴ to be indicative of coordination of pyridines. Additional shifts are expected for the out-of-plane and the in-plane pyridine ring bending modes which occur in the range 1020 to 1030 cm^{-1} and 625 to 640 cm^{-1} respectively. In the zinc complex {hereby referred to as ZnCL-H2}, the in-plane ring bending mode is shifted to 657 cm^{-1} but in all the copper complexes, this mode and the out-of-plane mode are obscured by other more intense absorptions.

Figure 3.1 UV-visible spectra of photolysis of $[(\text{NH}_3)_5\text{Co}(\text{III})(\text{CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)_2$ in methanol in the presence of excess CL with added trace triflic acid.

Table VI IR spectral data for metal complexes and free ligands^{a,b}

Proposed Assignment	5 (L)	CuL-H	8 (CL)	CuCL	CuCL-H2	ZnCL-H2
H ₂ O O-H		3532m			3491m	3524m
indole N-H	3202m	3300m	3414m	3283m	3288m	3316m
phenyl C-H	3070w	not resolved	3085w	not resolved	not resolved	not resolved
pyridine C-H	3052w 3025w	3089w 3064w	3048w 3018w	3084w 3049w	3089w not resolved	3080w 3060w
C=N imine	1657m	1644mw	1654m	1641m	1639m	1639m
C-C & C=N pyridyl	1576s 1484w 1425m	1581s 1488m 1441m	1567s 1466w 1422w	1601s 1500ms 1442mw	1597s 1469ms 1443mw	1602s 1499m 1440mw
C-C indole	1529s	1526m	1524m	hidden	hidden	hidden
py-CH ₂ -ox or	1425s	1431m	1422m	1442m	1443m	1440m
ether CO str			1273s 1081s	hidden 1066ms	hidden 1065ms	1272m hidden
indole NH oop	801s	806m	803w	810m	806m	810w
pyridine ip	1188m 1116s 1040m	1195m 1094m not resolved	1188w hidden 1040m	1195m 1095w hidden	not resolved 1105w hidden	1198w hidden hidden
pyridine oop	777s 708s	759w 711m	782m 711s	752w 711w	756w 710m	753w 704m
pyridine ring	1020m	968w	1029m	974w	970w	972w
CF ₃ SO ₃ ν ₄ CF ₃		1278s		1282s	1281s	
CF ₃ SO ₃ ν ₄ CF ₃		1249s		1241s	1245s	
CF ₃ SO ₃ ν ₄ CF ₃		1226s		1220s	1223s	
CF ₃ SO ₃ ν ₃ SO ₃		1162s		1162s	1162s	
CF ₃ SO ₃ ν ₂ SO ₃		1032s		1029s	1030s	
CF ₃ SO ₃ S-C str		759w		752m	756m	
CF ₃ SO ₃ ν ₃ SO ₃		638s		637s	638s	
ClO ₄ ν						1098s
ClO ₄ ν ₁						929w
ClO ₄ ν ₂						623ms

^a All values are in cm⁻¹. Samples prepared as KBr pellets.

CuL-H is Cu(L)(H₂O)(TFMS)₂, CuCL is Cu(CL)(TFMS)₂, CuCL-H2 is Cu(CL)(H₂O)₂(TFMS)₂ and ZnCL-H2 is Zn(CL)(H₂O)₂(ClO₄);

Many absorption bands have been omitted for simplicity. See individual spectra in Appendix B.

^b not resolved refers to bands that appear as shoulders or asymmetry in a neighbouring band and hidden refers to weak or medium bands that fall at the same frequency as a more intense anion band.

Figure 3.2 UV-Visible spectra of a) $\text{Li}(\text{Cl})_2\text{Cu}(\text{H}_2\text{O})_2\text{Cu}(\text{CF}_3\text{SO}_2)_2$,
 b) $\text{Li}(\text{Cl})_2\text{Cu}(\text{CF}_3\text{SO}_2)_2$, c) $\text{Li}(\text{Cl})_2\text{Cu}(\text{H}_2\text{O})_2\text{Cu}(\text{CF}_3\text{SO}_2)_2$ and d) $\text{Li}(\text{Cl})_2\text{Cu}(\text{H}_2\text{O})_2\text{Zn}(\text{ClO}_2)_2$
 in acetone/nitile at $1 \times 10^{-4} \text{ M}$.

2

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PRECISIONSM RESOLUTION TARGETS

The indole N—H bending mode at 1490 cm^{-1} is relatively unchanged in the complexes as is the ether C—O stretch at 1064 cm^{-1} which can only be observed in the copper triflate complexes due to the intense perchlorate absorption of the zinc complex. In addition, the indole N—H stretching mode observed at around 3400 cm^{-1} in the free ligands (figures B.18 and B.31, p. 228 and 238) is still observed in the complexes although it is shifted by 120 cm^{-1} to lower frequencies. A possible explanation for this shift may be a hydrogen bonding interaction with the oxygen atoms of the counterions which would in effect weaken the N—H bond and shift the band to lower frequencies in the same manner as is observed for intramolecular hydrogen bonding effects in ortho—carbonyl—substituted phenols.¹²⁵

The infrared data suggests that the ligands are coordinated in a bidentate manner through both pyridine moieties in all of the complexes.

In the solid state, all three copper complexes are coordinated by either mono or bidentate triflate anions. This is evident from the splitting of the ν_4 SO_3 symmetric and asymmetric stretching modes which occur at 1280 cm^{-1} (s) and 1232 cm^{-1} (m) in the ionic Na salt.¹²⁶ These are split into three intense peaks of almost equal intensity and this has been previously ascribed to lowering of the symmetry of the CSO_3 group from C_{3v} symmetry to Cs symmetry in $\text{Cu(II)(CF}_3\text{SO}_3)_2$ ¹²⁷ and other $\text{Cu(II)(N-heterocycle)}$ triflate complexes.¹²⁸

Some insight into the structure of the copper complexes in solution can be gained by the use of solution IR spectra and electronic spectra. Figures B.64, B.65 and B.66 (p. 263 and 264) are the FTIR spectra for a 0.25 mm NaCl cell containing neat acetonitrile, an acetonitrile solution of hexaaquocopper(II)triflate and an acetonitrile solution of the $[(\text{CL})\text{Cu(II)}](\text{TFMS})_2$ complex respectively. The IR spectra of the $[(\text{CL})\text{Cu(II)}](\text{TFMS})_2$ at 0.01 M in acetonitrile solution displays only two ν_4 SO_3 modes at 1272 cm^{-1} (s) and 1225 cm^{-1} (w) similarly to the hexaaquocopper complex in solution and the aforementioned sodium salt in the solid

state. The other two copper complexes exhibit this same characteristic of ionic triflate anion when their IR spectra are recorded in acetonitrile solution. In addition, the spectrum of the diaquo Cu complex, $[(\text{CL})(\text{H}_2\text{O})_2\text{Cu}(\text{II})](\text{TFMS})_2$ appears almost identical to the anhydrous Cu complex, $[(\text{CL})\text{Cu}(\text{II})](\text{TFMS})_2$ in acetonitrile solution with the appearance of an enhanced absorption around 3500 cm^{-1} presumably due to coordination of residual water from both the solvent and NaCl windows.

The water molecules associated with the two copper complexes, $[(\text{L})(\text{H}_2\text{O})\text{Cu}(\text{II})](\text{TFMS})_2$ and $[(\text{CL})(\text{H}_2\text{O})_2\text{Cu}(\text{II})](\text{TFMS})_2$ and the zinc complex appear to be coordinated to the metal ions due to the appearance of a sharp O—H stretch around 3500 cm^{-1} . This cannot be differentiated from lattice water on this basis alone¹²⁹ and the three low intensity librational modes of coordinated water are not observed due to the overlap of more intense ligand related absorptions. However, electronic spectra of the copper complexes, shown in figure 3.1 inset, suggest that the water is coordinated in the copper complexes. For the zinc complex, the perchlorate anions are of T_d symmetry as shown by the presence of ν_3 at 1098 cm^{-1} and ν_4 at 623 cm^{-1} which is consistent with ionic ClO_4^- .¹³⁰ The weak ν_1 mode expected in the 930 to 945 cm^{-1} range is hidden by more intense ligand related modes. Tetrahedral geometry is common for zinc complexes and should be the most stable configuration for a d^{10} group IIb metal¹³¹, although 5-coordinate trigonal bipyramidal and square pyramidal are also common when an anionic ligand is present.¹³² This suggests that the zinc complex is tetrahedral with a bidentate bis-pyridyl ligand and two water molecules occupying the four available coordination sites. In acetonitrile solution the coordinated water may be expected to exchange rapidly with solvent due to the rather large rate constant for this process.¹³³ However, the Zn^{2+} ion prefers coordination of a hard σ -donor ligand such as water over a soft π -acceptor ligand like acetonitrile when no anions are

coordinated to the metal. The fact that the diaquo complex is isolated by recrystallization from acetonitrile solution provides indirect evidence to support this hypothesis.

The electronic spectrum of $[(\text{CL})\text{Cu}(\text{II})](\text{TFMS})_2$ in acetonitrile displays one ligand field transition at 568 nm ($\epsilon=66$) as shown in figure 3.2 inset. For $\text{CuN}_4\text{-o}$ chromophores the suggested¹³⁴ stereochemistry for a single unresolved band of this energy is tetragonally distorted octahedral. In the case of $[(\text{CL})(\text{H}_2\text{O})_2\text{Cu}(\text{II})](\text{TFMS})_2$, the band at 616 nm with a shoulder at 840 nm suggests a square based pyramidal structure. For $[(\text{L})(\text{H}_2\text{O})\text{Cu}(\text{II})](\text{TFMS})_2$, one broad band at 579 nm also suggests a tetragonally distorted octahedral structure. These suggested stereochemistries are based on a comparison with Cu chromophores with only nitrogen containing ligands.⁶⁶ If the effect of coordinated water and coordinated acetonitrile solvent is taken into account, then CuN_6 , CuN_3O_2 and CuN_5O chromophores may be expected for the three complexes in solution. The variation in ligand field stabilization energy for the mixed nitrogen/oxygen containing chromophores versus the nitrogen containing one would be very small and the proposed geometries of the complexes would remain essentially the same but with a little added distortion due to the inequivalence of the ligands surrounding the metal ion.

3.4 Strategies Toward Other Complexes

Many synthetic strategies were tested using the 4-pyridyl derivative, **6** and either aquopentaammineruthenium(II) or cis-diaquotetraammineruthenium(II) and the photoactive n-butoxy substituted derivative, **9** and either of the Ru(II) precursors or a Ru(III) precursor, cis-diaquotetraammineruthenium(III). Complexes prepared from both of the Ru(II) precursors displayed an asymmetric coordination environment as shown by doubling of the ligand related peaks in the ^1H NMR

spectrum and the addition of two new types of protons in the spectrum at 4.4 and 7.3 ppm. These additional protons with approximate integrations of one each are consistent with an imine bond shift that may come about via a mechanism similar to that observed for cis coordinated 2-aminopyridine derivatives of Ru(II).¹³⁵ These complexes also displayed two broad absorptions in the visible region at 480 nm and 570 nm which were unexpected since the ligand spectrum has its lowest energy absorption at 420 nm and the two MLCT bands of the Ru-pyridine chromophore are expected at 410 nm and 375 nm by analogy to similar cis-bismonopyridyl complexes.¹³⁶ The quasi-reversible ($\Delta E_p = 140$ mV) cyclic voltammogram of this complex gave a higher than expected $E_{1/2}$ for the Ru(II/III) couple. This data is summarized in table VII where this complex is labelled as a complex of 9' to indicate that the ligand has reacted in the complex.

It is believed that during formation of the bidentate Ru(II) complex, the Ru(II)-pyridyl bonds could obtain additional stability by the displacement of electron density from the para-directing 4-pyridyl group to the exocyclic methylene group. This in turn would be followed by a shift in the imine bond and a proton transfer to the indole 3 position carbon, with the overall reaction represented by scheme III.

Scheme III

The electrochemical and UV-visible data for several ruthenium(II/III)

couples and the related 2-aminomethylpyridine complex are summarized in table VIIb. By analogy to the $\text{cis-[a}_4\text{Ru(II/III)(py)}_2\text{]}$ (where $\text{a} = \text{NH}_2$) couple listed, a bispyridyl coordinated chromophore quencher complex of ligands 5, 8, or 9 is expected to have a Ru(II/III) redox couple in the 0.5 V vs N.H.E. range. Additionally, it may be expected that the energy of the LMCT bands of the Ru(III) complex would be much higher than the excited state energy of the chromophore thus eliminating the possibility of energy transfer quenching.

Molecular models of this imine-bond shifted compound display a more ideal octahedral geometry about the metal ion with the π -plane of the pyridyls in the correct position for Ru(II) $d\pi$ -backbonding. With the unreacted symmetrical ligand, either both pyridyls must be skewed at an angle of approximately 45 degrees or one has to be fully rotated so that the pyridyl π -plane is almost parallel to the Ru(II) d -orbitals. It seems very unlikely that ideal octahedral coordination geometries could be obtained with this ligand due to the severe steric strain that must be placed upon the imine-methylene-pyridyl linkage for complex formation.

It was originally thought that this reactivity of the coordinated ligand could be circumvented by preparing the Ru(III) chromophore quencher complex directly from the less π -donating Ru(III) ion by direct substitution in a labile cis-diaquo complex. Attempts to prepare this complex were similar to that used to prepare the Ru(III) complex of 8 (or CL). For the resulting Ru(III) complex with 9, a yellow complex with an electronic spectrum that is a composite of the free ligand and the LMCT bands of the complex, $\text{cis-dipyridyltetraammineruthenium(III)}$ was expected but instead a brown complex similar to that obtained for the Ru(II) complexes with two broad absorptions in the visible region (≈ 470 nm with a shoulder around 575 nm) was isolated. Upon further investigation, this complex displayed many properties similar to that obtained above for the Ru(II) complex although its' NMR spectrum was substantially broadened due to a paramagnetic impurity. In this

Table VII Summary of Characterization data for ruthenium complexes of **5**, **8** and **9** and related literature complexes.^{a,b}

a) IR and ¹H NMR data

complex	IR data (ν in cm^{-1})	¹ H NMR δ in ppm [integration]	ref.
this study			
5	$\nu_{\text{N-H}}$ 3202, $\nu_{\text{C=N}}$ 1484	-CH ₂ - 5.0 [4], py 7.2-8.6 [8]	c
$[\text{a}_4\text{Ru}^{\text{II}}(\text{5})](\text{PF}_6)_2$	$\nu_{\text{N-H}}$ 3277, $\nu_{\text{C=N}}$ 1485	no data	c
$[\text{a}_5\text{Ru}^{\text{II}}(\text{5}')](\text{PF}_6)_2$	$\nu_{\text{N-H}}$ 3241, $\nu_{\text{C=N}}$ 1470 & 1515	-CH ₂ - 5.0 [2], -CH-N 4.3 [1] N=CH- and py 7.2-8.9 [9]	c
9	$\nu_{\text{N-H}}$ 3390, $\nu_{\text{C=N}}$ 1490	-CH ₂ - 5.0 [4], py 7.2-8.6 [8]	c
$[\text{a}_4\text{Ru}^{\text{II}}(\text{9}')](\text{PF}_6)_2$	no data	-CH ₂ - 5.1 [2], -CH-N 4.4 [1] N=CH- 7.3 [1], py 7.3-8.7 [8]	c
literature ligand rxn.			
$[\text{a}_4\text{Ru}^{\text{II}}(\text{2AMpy})](\text{PF}_6)_2^{\text{d}}$	no data	-CH ₂ - 3.93, py 7.7-8.4	124
$[\text{a}_4\text{Ru}^{\text{II}}(\text{2IMpy})](\text{PF}_6)_2^{\text{d}}$	no data	=CH- 9.08, py 7.1-8.8	124

b) Electrochemical and UV/visible data

complex	$\text{Ru}^{\text{II/III}}$ $E_{1/2}$	UV/vis (MLCT and LMCT only)	ref
this study			
$[\text{a}_4\text{Ru}^{\text{II}}(\text{5})](\text{PF}_6)_2$	0.585	412 (4.06), 372 (3.92)	c
$[\text{a}_4\text{Ru}^{\text{II}}(\text{Cl})](\text{PF}_6)_2$	0.575	e	c
$[\text{a}_4\text{Ru}^{\text{II}}(\text{9}')](\text{PF}_6)_2$	0.765	557, 442, 380	c
$[\text{a}_4\text{Ru}^{\text{II}}(\text{5}')](\text{PF}_6)_2$	0.771	580, 450, 360-375(sh)	c
cis- $[\text{a}_4\text{Ru}^{\text{II}}(\text{4CH}_3\text{py})_2](\text{PF}_6)_2$	0.565	408 (4.01), 362 (3.8)	c
cis- $[\text{a}_4\text{Ru}^{\text{II}}(\text{3CH}_3\text{py})_2](\text{PF}_6)_2$	0.545	406 (4.02), 355 (3.81)	c
Ru(II)/III couples			
$[\text{a}_6\text{Ru}^{\text{II}}]^{2+}$		400 (1.48), 275 (2.80)	125
$[\text{a}_6\text{Ru}^{\text{III}}]^{3+}$		320 (2.00), 275 (2.68)	125
$[\text{a}_5\text{Ru}^{\text{II}}(\text{py})]^{2+}$	0.300	407 (3.89)	126
$[\text{a}_5\text{Ru}^{\text{III}}(\text{py})]^{3+}$		262 (3.66), 253 (3.66)	125
cis- $[\text{a}_4\text{Ru}^{\text{II}}(\text{py})_2]^{2+}$	0.505	410 (3.90), 375 (3.81)	127
cis- $[\text{a}_4\text{Ru}^{\text{III}}(\text{py})_2]^{3+}$		261 (3.84), 254 (3.86)	128
literature ligand rxn.			
$[\text{a}_4\text{Ru}^{\text{II}}(\text{2AMpy})](\text{PF}_6)_2^{\text{e}}$	+0.295	414 (6.3), 248 (5.8)	124
$[\text{a}_4\text{Ru}^{\text{II}}(\text{2IMpy})](\text{PF}_6)_2^{\text{e}}$	+0.565	520 (6.1), 378 (4.4), 267 (7.5)	124

- a IR data of KBr pellets, ¹H NMR spectra of d₆-DMSO solutions of ligands and d₆-acetone solutions of complexes, both referenced to internal TMS.
b $E_{1/2}$ of $\text{Ru}^{\text{II/III}}$ couple measured in acetonitrile as described in chapter 2, UV/vis absorption spectra measured in acetonitrile or water,
c this study
d 2AMpy is 2-aminomethylpyridine, 2IMpy is 2-iminomethylpyridine
e band is a composite of MLCT and ligand centered bands

latter case it is believed that either photoreduction of the metal has occurred, leading to the aforementioned imine bond shift or that some type of concerted LMCT induced ligand decomposition/metal reduction has occurred. In the latter case, a mechanism involving energy transfer quenching of the ligand excited state may even be possible. At this point, the use of the 4-pyridyl substituted ligands was ceased as the systems produced were reactive and this made successful synthesis of a stable complex that could be studied photophysically seem unlikely.

In addition, much effort was put forth to prepare the Ru(II)tetraammine complexes of **5** and **8** and the Ru(III)tetraammine complex of **8** so they will be described briefly here. Ruthenium(II) complexes of these two ligands are susceptible to a similar ligand reaction as observed for ligands **6** and **9**. However, as described in chapter 2.3, the ligand reaction may be suppressed in this case by the addition of trace acids suggesting that the ligand reaction is base promoted. In figure 3.3, the UV/visible spectra of the tetraammineruthenium(II) complex of **5** (or **L**) is shown to be quite similar to the spectrum of cis-bis(3-aminomethylpyridine)tetraammine-ruthenium(II) with MLCT bands appearing at 412 nm and 372 nm. The ruthenium(III) complex may be prepared either by controlled potential electrolysis of this ruthenium(II) complex or directly from the cis-diaquo ruthenium(III) precursor as outlined in chapter 2.3 for the ruthenium(III) complex of **CL**. Cyclic voltammetry of the Ru^(III) complex gives one quasi-reversible ($\Delta E_p = 110$ mV) wave in the expected range at -0.585 V vs N.H.E. as shown in figure 3.4a. The ¹H NMR spectrum of one such complex is shown by figure 3.6 (p. 80) to display a loss of symmetry associated with the aforementioned ligand reaction.

If the procedure used to form the Ru^(II) complex of **L** is repeated using the photo-active ligand **8** (or **CL**), only brown compounds indicative of ligand reaction could be isolated. Synthetic preparations starting from the cis-diaquo ruthenium(III) precursor as described in chapter 2.3 did however give a compound

Figure 3.3

UV-visible spectra of acetonitrile solutions of
a) $\text{cis-}[(\text{NH}_3)_4(3\text{-aminopyridine})_2\text{Ru(II)}](\text{PF}_6)_2$ at $3.2 \times 10^{-5} \text{ M}$
and b) $[(\text{NH}_3)_4\text{Ru(II)(L)}](\text{PF}_6)_2$ at $4.2 \times 10^{-5} \text{ M}$

that had the expected properties of the desired chromophore quencher complex. The complex seems to photoreact during purification by column chromatography to give a product that appears to be a mixture of three complexes. The UV/visible spectra of the column fractions collected during purification are shown in figure 3.5. The middle spectrum is that expected for the desired $\text{Ru}^{(\text{III})}$ complex of CL. If this compound is isolated and chromatographed, it again displays the same behaviour as the impure mixture. Cyclic voltammetry of this mixture does in fact display the presence of three redox active complexes as shown by figures 3.4b,c,d. By analogy to the $\text{Ru}^{(\text{III})}$ complex of L, the middle redox wave at -0.575 V vs N.H.E. has been assigned to the $[(\text{NH}_3)_4\text{Ru}^{(\text{III})}\text{CL}]^{3+}$ complex with the other two waves probably being due to photosubstituted products. Further attempts to isolate this complex in pure form were to no avail and thus abandoned.

During the course of the synthetic work required to obtain a suitable chromophore-quencher complex, several other metal ions and complex ions were reacted with either L or CL. These include $\text{Ni}(\text{II})$ perchlorate which gave a bright red product upon reaction with a very complicated NMR spectrum indicating loss of symmetry upon coordination and/or ligand reaction. Thermal reaction of L with tungsten or chromium carbonyls resulted in ligand decomposition. Photochemical reaction with these same complexes at room temperature gave bright orange solutions which turned brown immediately upon exposure to air. Reaction with bis(bipyridyl)bis(acetonitrile)ruthenium(II) apparently gave the desired product based on electronic spectra which could not be isolated as it readily lost CL during purification.

Also planned were further modifications to the ligand, either by extending the length of the methylene spacer to ethyl, propyl and butyl spacers¹⁴⁰ or changing the ligating functionalities to bipyridyls¹⁴¹ or triphenylphosphines¹⁴².

Figure 3.4 Cyclic voltammograms in 0.1 M TBAH acetonitrile solutions of:
 a) $[(\text{NH}_3)_4\text{Ru}^{\text{III}}(\text{L})](\text{PF}_6)_2$ (1.0×10^{-3} M) from +0.1 to -0.85 V vs N.H.E. and $[(\text{NH}_3)_4\text{Ru}^{\text{III}}(\text{CL})](\text{PF}_6)_2$ (1.0×10^{-3} M) from
 b) +0.3 to -0.5 V vs N.H.E.
 c) +0.3 to -0.68 V vs N.H.E.
 d) +0.7 to -1.0 V vs N.H.E. showing Fc/Fc⁺ internal reference
 A Pt working and counter electrode and a Ag reference electrode were used. Scan speed = 100 mV/s.

Figure 3.5 UV/visible spectra of column fractions during attempted purification of $[(\text{NH}_3)_4\text{Ru}^{\text{III}}(\text{Cl})]^{3+}$ by column chromatography on Sephadex SP-C25 120. (see text for details) a) start of band, b) middle of band, c) end of band

Figure 3.6

200 MHz ^1H NMR spectrum of (tetraammine)(1,3-bis((3'-pyridylmethyl)imino)-isoindoline)ruthenium(II)hexafluorophosphate $((\text{NH}_3)_4\text{Ru}(\text{L})(\text{PF}_6)_2)$ in d_6 -acetone. Many impurities due to diethyl ether, acetone and water.

4. CHROMOPHORE EXCITED STATE.

4.1 Electronic and Fluorescence Spectra.

The properties of the chromophore, 1,2-dicyano-3,6-dihydroxybenzene are dependent on whether the molecule is a fully protonated, a mono deprotonated anion or a fully deprotonated dianion molecule. The fully protonated form is moderately soluble in common organic solvents and almost insoluble in water at a pH below 8. The first hydroxyl moiety is deprotonated at a pH of about 9–10 and at a pH of 12.5 the second hydroxyl is deprotonated to form the dianion. As discussed in chapter 3, it is necessary to protect these hydroxyl moieties prior to cyclization of the ortho nitriles so that they do not participate in any of the subsequent base catalysed reactions that the molecule must undergo in order to form the chromophore ligand. This functionalization of the hydroxyls has a profound effect upon both the chemical and photophysical properties of the chromophore.

Alkylation of the hydroxyl moieties enhances the solubility of the chromophore in common organic solvents and renders it almost totally insoluble in aqueous solution. The sensitivity of the chromophore towards decomposition in air is also eliminated. This decomposition is believed to be an oxidation of photoexcited hydroquinone dianion by molecular oxygen to form the semiquinone as evidenced by the appearance of several peaks at 415, 440, 470, 555 and 595 nm in the visible spectrum corresponding to the presence of semiquinone¹⁴³ in samples of the dianion that had been exposed to air for extended periods of time. This reaction occurs within minutes for solid samples of the tetraphenylarsonium salt of the dianion that have not been completely dried of organic solvents. The reaction which is characterized by a colour transformation from golden-orange to a bright red was not observed in samples of sodium, potassium or ammonium salts of the dianion.

The insensitivity of the dialkoxy derivatives toward decomposition in air

also meant that subsequent preparative steps could be carried out in the presence of oxygen, simplifying both synthetic manipulation and characterization.

The absorption spectra of both the sodium salt and the tetraphenylarsonium salt of the dianion are shown in figure 4.1a. They both exhibit a peak in the visible region centered at 410 nm ($\log \epsilon = 3.89$). The large absorption due to the two tetraphenylarsonium cations in the UV region obscures the spectrum of the dianion below 350 nm. In the spectrum of the sodium salt, a small shoulder at around 320 nm and a broad intense peak at 238 nm are observed. The small shoulder at 320 nm may be due to an impurity in the original 2,3-dicyanohydroquinone or a partially base hydrolyzed derivative as it is not observed in any of the subsequently formed derivatives. Recrystallization of samples of the sodium salt results in a sporadic variation in the intensity of this peak relative to the other two¹⁴⁴ which lends support to the supposition that it is due to some form of impurity. The cause of this absorption was not explored any further as it was not observed in the spectra of the dialkoxy derivative prepared by either the phase transfer method employing NaOH at room temperature as the base or the heterogeneous method which employed K_2CO_3 as the base. This low energy absorption gives rise to an emission near 500 nm as shown in figure 4.2.

The absorption spectrum of 1,3-diiminoisoindoline, also shown in figure 4a displays one relatively low intensity peak at 295 nm ($\log \epsilon = 3.60$) and two more intense absorptions at higher energy. Based on the intensity and energy of the low energy peak¹⁴⁵, the band is assigned to an electronic transition between a non-bonding molecular orbital and a π^* molecular orbital. The derivative lacking this diiminoisoindoline structure, (2) also displays a low energy transition at 349 nm that based on similar arguments must be assigned to a transition from a non-bonding orbital centered on the ether oxygen to a π^* molecular orbital. It is this latter transition that corresponds to the absorption at 365 nm in the

Figure 4.1 UV-visible spectra of

- a) 1,2-dicyano-3,6-dihydroxybenzene in 0.1 M NaOH H₂O solution,
 *— tetraphenylarsonium salt of the 1,2-dicyano-3,6-dihydroxybenzene dianion (1) in acetonitrile
 — 1,3-diiminoisoindoline in acetonitrile
- b) -.-.- 1,4-di-n-butoxy-2,3-dicyanobenzene (2) in acetonitrile,
 --- 4,7-di-n-butoxy-1,3-diiminoisoindoline (3) in acetonitrile,
 — 4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)-imino)isoindoline (8) in acetonitrile
- All concentrations are 1×10^{-4} M

Table VIII UV/visible data^a for ligands and precursors^b

1	2	3a	3	5	8	assignment
c	210 (4.81)	218 (4.48)	210 (4.58) d		204 (4.85)	π, π^*
	227 (4.91)	247 (4.11)	226 (4.69)	226 (4.73)	223 (4.71)	π, π^*
				263 (4.50)	262 (4.45)	π, π^*
				298 (4.09) d	268 (4.45)	π, π^*
				321 (4.07) d	282 (4.37)	π, π^*
410 (3.89)	349 (4.09)	295 (3.60)	354 (4.09)			
			410 (3.65) d		367 (4.06)	nb, π^* e
					418 (3.87) d	nb, π^* f

a) data in nm, log ϵ in $M^{-1}cm^{-1}$ in parenthesis

- b) 1 is tetraphenylarsonium salt of 2,3-dicyano-3,6-dihydroxybenzene
 2 is 1,4-di-n-butoxy-2,3-dicyanobenzene
 3 is 4,7-di-n-butoxy-1,3-diiminoisoindoline
 3a is 1,3-diiminoisoindoline
 5 or L is 1,3-bis((3'-pyridylmethyl)imino)isoindoline
 8 or CL is 4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline

All samples were approximately 10^{-4} M acetonitrile solutions

- c) off-scale due to intense tetraphenylarsonium absorptions
 d) shoulder
 e) due to neutral form
 f) due to protonated form

Figure 4.2 Uncorrected fluorescence spectra of a) 1,2-dicyano-3,6-dihydroxybenzene in 0.1 M NaOH, b) tetraphenylarsonium salt of the 1,2-dicyano-3,6-dihydroxybenzene dianion (1) in acetonitrile solutions of 2×10^{-5} M concentration. Excitation wavelength = 365 nm, 10 nm monochromator bandpass

Figure 4.3 Uncorrected fluorescence spectra of a) 1,4-di-n-butoxy-2,3-dicyanobenzene (2) in acetonitrile, b) 4,7-di-n-butoxy-1,3-diminoisindoline (3) in acetonitrile, c) 4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)imino)isindoline (8) in acetonitrile solutions of 2×10^{-5} M concentration. Excitation wavelength = 365 nm, 10 nm monochromator bandpass

subsequently formed dialkoxy derivatives, 3 and 8 as shown in figure 4.1b. It is this absorption at 365 nm that leads to the formation of a redox active excited state in 8 (or CL).

An additional low energy absorption is also present on both of the diiminoisoindoline derivatives (3 and 8) but is absent from the spectrum of the orthodinitrile (2). This absorption is due to a protonated form of these molecules and gives rise to an emission at 485 nm as shown in figure 4.3 and summarized in table IX. This will be discussed further in the next section.

The absorption spectra of the three derivatives which lack the dialkoxy moieties are shown in figure 4.4. All three spectra are quite similar with the $nb-\pi^*$ absorption appearing at 325 to 330 nm and no appreciable absorption above 365 nm. As emission spectra and transient absorption spectra have been recorded in this study using 365 nm excitation, these molecules should provide suitable spectroscopic blanks. Emission from these molecules is not observed when excited with 365 nm radiation. Excitation of less than 340 nm is required to observe any substantial amount of emission from these derivatives.

The absorption spectra of the three dialkoxy derivatives in which the substitution position on the methylpyridyls have been changed are shown in figure 4.5. No significant differences are observed for the $\pi-\pi^*$ transitions below 300 nm. The spectra of both the 2- and 3-substituted derivatives, 10 and 8, exhibit an additional lower energy absorption at 418–420 nm that has been assigned to the corresponding $nb-\pi^*$ transition of the protonated ligand. The 4-substituted derivative displays only a broadened absorption in neutral acetonitrile but this band is resolved upon addition of either triflic or acetic acid or by recording the spectrum in mixed solvents of water with acetonitrile, DMSO, alcohols or NMP. The assignment is therefore based on an analogy with a similar observation of a red shifted absorption in acidic solution of other basic organic chromophores¹⁴⁶,

Figure 4.4 UV-visible spectra of 1×10^{-3} M acetonitrile solutions of a) 1,3-bis(2'-pyridylmethyl)imino)isoindoline (7), b) 1,3-bis(3'-pyridylmethyl)imino)isoindoline (5) c) 1,3-bis(4'-pyridylmethyl)imino)isoindoline (6).

Figure 4.5 UV-visible spectra of 1×10^{-4} M acetonitrile solutions of a) 4,7-di-n-butoxy-1,3-bis((2'-pyridylmethyl)imino)isoindoline (10), b) 4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline (8), c) 4,7-di-n-butoxy-1,3-bis((4'-pyridylmethyl)imino)isoindoline (9).

Figure 4.6 Uncorrected fluorescence spectra of a) 4,7-di-n-butoxy-1,3-bis((2'-pyridylmethyl)imino)isoindoline (10), b) 4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline (8), c) 4,7-di-n-butoxy-1,3-bis((4'-pyridylmethyl)imino)isoindoline (9) in acetonitrile solutions of 2×10^{-5} M concentration. Excitation wavelength = 365 nm, 10 nm monochromator bandpass.

Figure 4.7 UV-visible and uncorrected fluorescence emission spectra of 1×10^{-4} M solutions of 4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline (8) as a function of solvent a) THF, b) diethyl ether, c) acetone, d) ethanol

Table IX Emission spectral data for ligands and precursors^a

i)

solvent ^b	emission wavelength in nm (static quantum yields) ^c			
	1	2	3	8
MeCN	477 (0.62)	379 (0.79)	408 (0.31)	419 (0.15)
			481 (0.21)	485 (0.71)

ii)

solvent ^b	fluorescence emission lifetime ^d			
	1	2	3	8
MeCN	8.1 ns	3.6 ns	1) 90 ps 2) 130 ps	3.8 ns
MeCN + H ₂ O		3.5 ns	1.3 ns	9.2 ns
MeCN + HOAc		3.8 ns	10.0 ns	10.4 ns
MeCN + TEA ^e		94 ps	60 ps	260 ps

- a) 1 is tetraphenylarsonium salt of 2,3-dicyano-3,6-dihydroxybenzene
 2 is 1,4-di-n-butoxy-2,3-dicyanobenzene
 3 is 4,7-di-n-butoxy-1,3-diiminoisoindoline
 8 or CL is 4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline

b) MeCN is acetonitrile, HOAc is acetic acid, TEA is triethylamine

c) Excitation wavelength was 365 nm, concentration of 10^{-5} M in acetonitrile
 Static quantum yields (Φ_f corrected) were determined as described in
 appendix C.

d) 365 nm excitation, emission monitored above 400 nm by use of a 400 nm
 high bandpass cutoff and suitable neutral density filters used between
 sample cell and streak camera. Concentrations as noted in Appendix D.
 Errors on lifetimes are typically less than 2 % by comparison of several
 single lifetime measurements on the same sample.

e) Quenching is observed for solutions containing triethylamine. See appendix D

the acid-base behaviour of the absorption and by comparison of the fluorescence spectra of the three compounds that are shown in figure 4.6. The 2-substituted derivative, 10 displays only one emission at 495 nm which is due to a protonated excited state whereas the 3-substituted derivative, 8 and the 4-substituted derivative, 9 display two emissions at 486 and 419 nm and 480 and 415 nm respectively. From the ^1H NMR spectra and elemental analysis of the three compounds, a full water molecule is associated with 10, half a water molecule with 8 and no water is associated with 9. The relative emission intensities follow the reverse trend increasing from 10 to 8 to 9 which is expected for a process in which radiationless decay pathways involving internal conversion are reduced as a result of increased rigidity in the molecule¹⁴⁷ due to water complexation. The fact that no high energy emission is observed in 10 and that a low energy absorption is not observed in 9 suggests that the excited state is a much stronger base than the ground state which is quite common for compounds of this type.¹⁴⁸

The solvent dependence of the nb, π^* based absorptions and emissions of both the neutral and protonated chromophore ligand, 8 was also examined and is shown in figure 4.7 for a few of the solvents that could be rigorously dried and is summarized in table IX for all the solvents studied. In solvents that could be made sufficiently anhydrous such as alkanes and ethers, only one absorption around 360 nm ($\log \epsilon = 4$) and one emission around 415 nm (quantum yield = 0.2) is observed due to the unprotonated neutral ligand. If scrupulous care was taken to eliminate exposure to air, ethyl acetate, acetone and ethanol were also able to be dried sufficiently⁸³ to eliminate the absorption due to the protonated form. However, in ethanol the long wavelength emission is observed if the excitation wavelength used to irradiate the sample is above 450 nm. The use of this low energy excitation removes the possibility of creating excited state neutral ligand and lends evidence for a specific H-bonding interaction with the alcoholic proton in the ground state.

Table XSpectral data for CL as a function of solvent^a

solvent	UV/visible data		Fluorescence data for CL		Fluorescence data for CLH+	
	wavelength/nm	log E	emission max/nm	relative intensity	emission max/nm	relative intensity
n-hexane	359	4.14	416	0.23	c	c
cyclohexane	b	b	409	0.17	c	c
diethyl ether	350	4.11	411	0.18	c	c
ethyl acetate	355	4.22	413	0.22	c	c
tetrahydrofuran	355	4.14	416	0.2	c	c
methylene chloride	359	4.02	422	0.22	481	0.3
acetone	357	3.88	415	0.23	c	c
ethanol	364	3.86	431	0.38	481	0.4
acetonitrile	359	4.06	419	0.19	486	0.22

a) CL is 4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline

UV visible data recorded from 300 nm to 500 nm at concentrations of 1×10^{-4} M to 3×10^{-4} MFluorescence data recorded with excitation wavelength at 365 nm, concentration of 10^{-5} M

b) not recorded

c) not observed

The specific H-bonding interaction is further supported^{148d} by lack of a typical emission energy versus solvent polarity type of relationship which is usually observed for excited states that possess an appreciably different dipole moment than the ground state.¹⁴⁹ The absence of a large Stokes shift also suggests that the ground state is extensively hydrogen bonded¹⁵⁰ and this is supported by the observation of a slightly decreased Stokes shift in ethanol, where the emission maximum is 481 nm for the protonated ligand and 431 nm for the neutral ligand. This latter effect is also observed in studies of the transient absorption spectra of **8** to be discussed later.

Acetonitrile and methylene chloride were the most difficult solvents to dry as compared to the alkanes and ethers. The observation of both absorptions and emissions in these solvents suggested that the residual water concentrations after drying was comparable to the concentration of the ligand itself. However, the solubilities of both the free ligand and the complexes in these solvents made their use very convenient as well as other considerations such as the ability to carry out cyclic voltammetry and the availability of precursor reference spectra in acetonitrile solutions. In both of these solvents, the emission due to the protonated form of the ligand (**8**), hereafter referred to as CLH⁺ is more intense than that due to the neutral ligand, CL[•] with a ratio of approximately 1.15:1 and 1.35:1 for acetonitrile and methylene chloride respectively. A further increase in the ratios can be observed as water is added to the samples up to a ratio about 2:1 for 1:1 water:acetonitrile and 3:1 for water-saturated methylene chloride. The difference between the ratios in the two solvents may be ascribed to a difference of both the pK_a and pK_a⁺ for this ligand in these solvents.¹⁵¹

4.2 Protonation Equilibria

The chromophore ligand has several basic functionalities which include the

imino and indole nitrogens and the pyridyl groups with typical pK_a values in the range 10–14¹⁵², 2–3¹⁵³ and 3.7–6¹⁵⁴ respectively. Thus it is not surprising that under quite mild conditions, the ligand may be protonated to some degree in the ground state and to a different extent in the excited state due to the change in electron density at the basic or acidic site on the molecule upon excitation¹⁵⁵. Generally, pyridines and imines become stronger bases in the excited state^{155a} and indoles (or pyrroles) become stronger acids^{155b,c}.

Figure 4.8 shows the effect of pH on the UV–visible spectrum of the chromophore ligand in 4:1 acetonitrile:water. In "neutral" solution in which no acid or base has been added, the pH of the solution was found to be 8.99 for this solvent mixture and 8.67 for neat methanol.¹⁵⁶ A typical¹⁵⁷ bathochromic shift is observed with decreasing pH which is indicative of protonation at a site on the molecule directly coupled to the chromophore. Potentiometric titration of both the chromophore ligand (CL) and the nonchromophore ligand (L), shown in figure 4.9 display two distinct protonation steps occurring at similar pH values for both compounds. The first occurs at a pH of 10 and another occurs at a pH of 5.7. A pK_a of 5.5 is what would be expected for protonation of a pyridyl moiety and in fact values of $5.67 \pm .18$ and $5.82 \pm .05$ were determined for CL and L respectively. The former protonation step occurring with pK_a 's of $9.4 \pm .4$ and $9.95 \pm .26$ for CL and L respectively, can only be assigned to protonation of the imines as the indole is far too acidic to be protonated at this pH.

A similar pH dependence is observed for CL in the copper complex, CuCL as shown in figure 4.10. The useful pH range is limited by complex decomposition via pyridyl protonation at pHs below 5.5 and by loss of an isobestic point above a pH of 9.3. Within this pH range the reversible protonation of the ligand can be observed as an increase in the absorbance at 419 nm at the expense of the 367 nm absorption quite similarly to that observed for the free ligand shown in figure 4.8

Figure 4.8 UV-visible spectra of 1×10^{-4} M solution of Cl^- in 4:1 acetonitrile:water as a function of pH. pH was adjusted by the addition of 1 N HCl or 1 N NaOH.

Figure 4.9 Potentiometric titration of L and CL in 4:1 acetonitrile:water

Figure 4.10 UV-visible spectra of 1×10^{-4} M solution of $(\text{Cl})\text{Cu}(\text{II})(\text{CF}_3\text{SO}_3)_2$ in 4:1 acetonitrile:water as a function of pH. pH was adjusted by the addition of 1 N HCl or 1 N NaOH in 4:1 acetonitrile:water.

with a slightly higher extrapolated pKa of 9.4 versus the 8.99 value for the free ligand. In this solvent mixture one may expect to form the diaquo copper complex (CuCL-H_2) rather rapidly and the enhanced acidity of the coordinated ligand may therefore be due to the greater acidity of water bound to a M^{2+} ion as is observed for aqueous copper(II) solutions.¹⁵⁸

The fluorescence spectra of CL in 4:1 acetonitrile:water as a function of pH are shown in figure 4.11. The ligand is a weak base in acetonitrile:water solution with a pKa of $8.99 \pm .06$ as determined by spectroscopic titration shown in figure 4.8. At this pH, the emission spectrum consists of a large emission at 486 nm ($\phi_{486} = 0.12$) with a much smaller shoulder at 419 nm ($\phi_{419} = 0.04$). Both of these emissions are due to singlet-singlet transitions as shown by their insensitivity to oxygen quenching even under 1 atm. of O_2 . As the pH of the solution is raised, the intensity of the 486 nm band decreases and the intensity of the 419 nm band increases until at a pH of 11.5, no 486 nm emission is detectable and only the higher energy emission with $\phi_{419} = 0.15$ is visible. At lower pHs below 7.0, only the low energy emission is observed but the quantum yield increases dramatically to 0.71. This lower energy emission has been assigned to emission from a protonated excited state of the ligand. The site of protonation in this protonated excited state is most likely to be the imine nitrogen as this is partially protonated in the ground state. The pKa* may be estimated using a Forster cycle analysis¹⁵⁹ which is based on the energy gap between the ground and excited state forms of the chromophore. This is given by:

$$\text{pKa}^* = \text{pKa} + (0.625/T)(\nu_b - \nu_a) \quad 4.1$$

where ν_b is the energy of the first electronic excited state ($\nu_{0,0}$) of the neutral chromophore and ν_a is the energy of the first electronic excited state of the protonated chromophore. From figure 4.11, ranges for these energies may be estimated as $\nu_b = 377\text{--}380$ nm or $26,525\text{--}26,315$ cm^{-1} and $\nu_a = 420\text{--}440$ nm or

Figure 4.11 Fluorescence spectra of CL in 4:1 acetonitrile:water as a function of pH. Concentration = 2×10^{-5} M. Excitation wavelength = 365 nm, monochromator bandpass = 10 nm. pH adjusted by addition of 1.0 N HCl or 1.0 N NaOH. pH values are: a) 13.48, b) 11.30, c) 9.38, d) 9.27, e) 9.02, f) 7.39, g) 6.91. At pH's from 6.91 to 2.3, no further change was detected and all spectra overlap with curve g.

23,809–22,727 cm^{-1} . This gives an average value for the pK_a^* of $15.6 \pm .9$ when both the upper and lower estimates of the $\nu_{0,0}$ are considered.

Conversely, the pK_a^* may be determined experimentally as 10.5 from the inflection point in the fluorimetric titration curve shown in figure 4.12. If the protonation phenomena in the excited state occurs much more rapidly than the fluorescence, then a pseudoequilibrium is established and the inflection point on the fluorimetric titration curve gives a close estimate of the pK_a^* .¹⁶⁰ The rates of protonation and deprotonation of the excited state are of the order of $10^{10} \text{ M}^{-1}\text{s}^{-1}$ in neutral solutions whereas the rates of emission are of the order of 10^8 s^{-1} and therefore the value of the pK_a^* obtained from the titration curve is an acceptable estimate of the actual pK_a^* . Precise measurements of pK_a^* 's involve the use of some type of dynamic analysis¹⁶¹ and detailed calculations are further complicated by inner filter effects on both of the emission spectra¹⁶² and the time resolved spectra and lifetime measurements.¹⁶³

The large increase in quantum yield upon protonation contradicts the energy gap law for radiationless transition rates and probably results from a more structurally constrained molecule upon protonation. This would reduce the vibrational and rotational modes responsible for radiationless deactivation of the excited state. As previously mentioned, the absence of a large Stokes shift suggests that the ground state is extensively hydrogen bonded and this is supported by the observation of a slightly decreased Stokes shift in hydrogen bonding solvents such as ethanol. The addition of ions such as Na^+ to a solution of the chromophore ligand in acetonitrile increases the emission of the protonated excited state at the expense of the deprotonated excited state emission. The effect of added ions enhancing the rate of solvent assisted protonation has been previously observed in azaphenanthrenes.¹⁶⁴

Figure 4.12 Fluorometric titration of CL and CLH⁺ in 4:1 acetonitrile:water

4.3 Concentration and Oxygen Quenching

If the concentration of the ligand is increased in acetonitrile to more than 5×10^{-3} M, self-absorption effects decrease the intensity of the 486 nm emission and completely eliminates the 419 nm emission. The concentration dependence of the emission and the calculation of corrected fluorescence spectra and quantum yields are dealt with in more detail in appendix C.

Oxygen quenching of both excited state singlets¹⁶⁵ and triplets^{166,167} is well known and manifests itself as either a reduction in emission intensity as the oxygen concentration is increased or complete lack of emission in samples exposed to air. A study of this type is shown in figure 4.13 for the DCHQ dianion (1) and the chromophore ligand, 8, both in acetonitrile solutions of approximately 2×10^{-5} M concentration. The same sample was used for all the points of each compound on the curves starting at a partial pressure of oxygen of 0 torr by first degassing the sample (in a specially designed inert atmosphere cell) by several freeze-pump-thaw cycles followed by an argon purge up to atmospheric pressure. In subsequent samples, a measured pressure of oxygen was allowed to equilibrate with the sample for 30 minutes prior to measuring the emission intensity at 477 or 419 nm respectively for 1 and CL. A slightly higher oxygen pressure was then added, equilibrated and the emission measured and this procedure was repeated until 1 atm. of oxygen was in equilibrium with the sample. The chromophore ligand 8 (or CL) displays no reduction in emission intensity up to an oxygen partial pressure of 600 torr with only a 20 % reduction in intensity at 750 torr of oxygen. As a result of this observation, all subsequent emission studies of CL were carried out in air saturated solutions as there was no fear of excited state depopulation by triplet state oxygen quenching for this system.

Figure 4.13 Effect of oxygen on the relative emission intensity of the tetraphenylarsonium salt of the 1,2-dicyano-3,6-dihydroxybenzene dianion in acetonitrile (**DCHQ dianion**) and the chromophore ligand, 4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline in acetonitrile (**CL**). Excitation at 365 nm, monochromator bandpass = 10 nm. Both at a concentration of 2×10^{-5} M.

4.4 Emission Lifetime Measurements.

A study of substitution effects upon the emission lifetimes was carried out for the dianion (DCHQ or 1), the di-*n*-butoxy ether (2), the diiminoisoindoline (3) and the chromophore ligand (CL or 8). A few shortcomings were later noted in the way in which the lifetimes were recorded but with the facility in Montreal and a lack of time, the experiments could not be repeated. The first is that the emission was filtered using a 400 nm cutoff filter and is a composite of the emission from both the neutral and protonated excited states. The use of bandpass filters to look at both the neutral excited state emission and the protonated excited state emission separately would have provided a much clearer interpretation of the results. Emission lifetimes measured on solutions of 1, 2, 3 and 8 with triethylamine added as a base displayed very rapid decays with lifetimes in the 100 ps to 1 ns range suggesting that some type of quenching process was occurring. Efficient and rapid photoreduction of n,π^* triplet states by triethylamine is known to occur by both a hydrogen atom abstraction mechanism¹⁶⁸ and by a charge-transfer mechanism.¹⁶⁹ A detailed study of the behaviour of the chromophore in the presence of triethylamine is beyond the scope of this study and these results have therefore been included in appendix D as well as some preliminary experiments in other solvents and with related ligands.

A complete list of all lifetimes measured can be found in appendix D and a short list of the results for 1, 2, 3 and 8 can be found in Table IX. The maximum radiative lifetimes in the absence of non-radiative decay and quenching can be calculated according to the method outlined by Turro¹⁷⁰. The calculated radiative lifetime (k_e^0) for an excited singlet state can be calculated from the integrated absorption band responsible for populating this state which in this case is the lowest energy $n\pi^*$ transition, according to:

$$k_e^0 = 3 \times 10^{-9} \bar{\nu}_0^2 \int \epsilon d\bar{\nu} \cong \bar{\nu}_0^2 f \quad 4.2$$

where $\bar{\nu}_0$ is the energy corresponding to the maximum wavelength of absorption in cm^{-1} , $\int \epsilon d\bar{\nu}$ is the integration over the absorption band and f is the oscillator strength of the absorption. In the case of **3** and **8**, this calculation is further complicated by the presence of an overlapping absorption due to the protonated form. Therefore, equation 4.2 may be further approximated as

$$k_e^0 \equiv 1/\tau^0 \approx 10^4 \epsilon_{\text{max}} \quad 4.3$$

for absorption bands with a half-band width of the order of 3000 cm^{-1} which is typical for most organic chromophores at room temperature with absorption maxima near 400 nm in the visible or near UV region. This will therefore yield values of k_e^0 that are slightly low for **2**, slightly high for **1** and the protonated species 3H^+ and CLH^+ and approximately correct for **3** and **8**. Shown in table XI is a comparison values of τ^0 calculated according to equation 4.3 with experimentally determined values.

Figure 4.14 shows the emission lifetime, least squares exponential fit and residuals plot for **1** in acetonitrile. The observed lifetime of $8.08 \pm 0.29 \text{ ns}$ is reduced substantially from the calculated radiative lifetime of 12.9 ns. The poor agreement between the calculated and experimental value is an indication of additional decay pathways. Without an experimental lifetime for the T_1 state, only a composite rate constant for all nonradiative processes can be calculated according to:

$$\tau_f = 1/(k_e^0 + k_{\text{nr}}) \text{ where } k_{\text{nr}} = k_{\text{isc}} + k_{\text{ic}} + k_{\text{q}}[\text{Q}] \quad 4.4$$

This gives a value of $4.6 \times 10^7 \text{ s}^{-1}$ for k_{nr} which is greater than that predicted¹⁷¹ for an internal conversion process from the S_1 state to the S_0 state. The rate of internal conversion may be estimated from $k_{\text{ic}} \approx 10^{13} f_{\nu}$ where f_{ν} is a function of the energy gap between the zeroth vibrational levels of the state undergoing internal conversion¹⁷². For an energy gap of 67 kcal/mol ($\nu_{00} = 425 \text{ nm}$), a maximum rate of $k_{\text{ic}} < 10^7 \text{ s}^{-1}$ would be expected.¹⁷³

Oxygen quenching of the excited triplet state would be inefficient at

Table XI Comparison of Calculated^a and Observed Radiative Lifetimes^b

	1	2	3	3H ⁺	CL	CLH ⁺
Calculated	12.9 ns	8.1 ns	8.1 ns	22.4 ns	8.7 ns	13.5 ns
Observed	8.08 ± .29 ns	3.61 ± .03 ns	1) 89 ± 4 ps 2) 134 ± 3 ps 3) 1.25 ± .02 ns	9.97 ± .43 ns	3.81 ± .04 ns	10.4 ± .3 ns

a) Calculated according to equation 4.2 and assumptions described in text

b) 1 is tetraphenylarsonium salt of 2,3-dicyano-3,6-dihydroxybenzene

2 is 1,4-di-n-butoxy-2,3-dicyanobenzene

3 is 4,7-di-n-butoxy-1,3-diiminoisoindoline

CL is 4,7-di-n-butoxy-1,3-bis((3'-pyridyl)methyl)aminoisoindoline

Observed lifetimes were recorded with 365 nm excitation and emission monitored above 400 nm by use of a 400 nm high pass cutoff and suitable neutral density filters used between sample cell and streak camera.

Concentrations as noted in Appendix D

Figure 4.14 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for tetraphenylarsonium salt of DCHQ²⁻ (I) in acetonitrile : 5.0×10^{-3} M; streak camera speed at 26.66 ps/channel

depopulating the singlet state with $k_q[\text{O}_2] \simeq 4.5 \times 10^5 \text{ s}^{-1}$. Therefore, even in the presence of internal conversion, intersystem crossing is the dominant nonradiative pathway in 1 with a k_{isc} of approximately $4 \times 10^7 \text{ s}^{-1}$ which would be slightly less than the experimental value of k_{nr} .

The emission decay, exponential fit and residuals for 2 in acetonitrile are shown in figure 4.15. From the fit of the data, an emission decay rate of $2.77 \pm .02 \times 10^8 \text{ s}^{-1}$ or a lifetime of $3.61 \pm .03 \text{ ns}$ is found. A shorter lifetime is to be expected for this compound relative to 1 on the basis that the maximum calculated radiative lifetime is shorter. This factor alone cannot explain the magnitude of the reduction in the observed radiative rate, even if the rate of intersystem crossing is similar to that in 1 with a rate of $4 \times 10^7 \text{ s}^{-1}$. With the total nonradiative rate calculated as $1.54 \times 10^8 \text{ s}^{-1}$ according to equation 4.3 and the rate for quenching by oxygen estimated to be far less than in 1¹⁷⁴, the major deactivation pathway must be via internal conversion. The rate for internal conversion, k_{ic} may be estimated¹⁷² as approximately 10^6 s^{-1} in a similar manner to 1. Depopulation of the S_1 state should be relatively unaffected by this process, but the addition of promoter vibrations to the molecule greatly enhance internal conversion processes by acting as "loose bolts" or "free rotors"¹⁷⁵. In this particular case, the additional vibrational and rotational modes associated with the added n-butyl groups must be efficient at promoting internal conversion processes in this molecule.

The observed quantum yield for fluorescence in 2 of 0.79 as listed in table IX is thus in error by as much as 40 % and is probably closer to 0.45 as determined by the emission lifetime measurement. There are many reasons for disagreement between quantum yields determined statically and dynamically and these are discussed in greater detail in appendices C and D. The major factor operative here is the enhanced scattering and stray light detection when the emission monochromator with a 10 nm bandpass is set at 379 nm which is only 14 nm from the

Figure 4.15 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for 1,4 di n butoxy 2,3 dicyanobenzene (2) in acetonitrile, 5.0×10^{-3} M, streak camera speed at 26.66 ps/channel

excitation wavelength of 365 nm. The emission lifetime on the other hand was measured using a 400 nm cutoff filter and would not be affected by this effect.

The large mismatch of quantum counter excitation and emission wavelength versus **2** would cause the measured quantum yield to be slightly high. Self-quenching effects in the other derivatives appears to cancel out much of this quantum counter mismatch factor. In this molecule that argument cannot be used for the following reason. All the other compounds studied have emission maxima above 400 nm which is closer to the 461 nm emission maximum of the quantum counter quinine bisulphate and therefore the overestimate of the static ϕ_f due to the nonlinear detector response is less. Additionally, self-quenching processes have been observed for **1**, **3** and **8** at concentrations above 5×10^{-5} M which would reduce the observed static ϕ_f and tend to cancel out some of the error due to the nonlinear detector response. In order to avoid this complication, reported static ϕ_f (table IX i) were measured at 1×10^{-5} M in the case of **3** and **8** and 5×10^{-7} M in the case of **1** and compared to ϕ_f measured at concentrations where self-quenching was observed. Differences of up to 60 % were noted for the measured static quantum yields when this was carried out. The maximum measured static quantum yields are listed in table IX i and they were subsequently found to be within 15 % of those estimated using the kinetic data (table IX ii) except for in the case of **2**. That reported for **2** was measured at 1×10^{-5} M and was found to be relatively insensitive to self-quenching over the concentration range 10^{-6} to 10^{-4} M.

The emission lifetime, exponential fit and residuals for **3** are shown in figures 4.16 and 4.17 for the fast component measured with a streak camera speed of 2.67 ps/channel at 0.01 M concentration and the slower component measured with a streak camera speed of 11.11 ps/channel at 2.8×10^{-4} M concentration respectively. The emission decay rates from these figures are $1.12 \pm .05 \times 10^{10} \text{ s}^{-1}$ and $7.46 \pm .17 \times 10^9 \text{ s}^{-1}$ which translate into emission lifetimes of $89 \pm 4 \text{ ps}$ and $134 \pm 3 \text{ ps}$

Figure 4.16 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for 4,7-di-n-butoxy-1,3-diiminoisoindoline(**3**) in acetonitrile, 1.0×10^{-2} M, streak camera speed at 2.67 ps/channel

Figure 4.17 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for 4,7-di-n-butoxy-1,3-diimino-indoline (**3**) in acetonitrile, 2.8×10^{-4} M, streak camera speed at 11.11 ps/channel

respectively. It should also be noted that the slower lifetime reported may be slightly high as evidenced by the positive tail on the residuals plot for figure 4.17. The similarity in lifetimes precluded the use of deconvolution methods to obtain more accurate decay rates for this molecule.¹⁷⁶ Initially, the entire data set for figure 4.16 was fit to a biexponential function but the fit converged to a composite fast decay of 100 ± 13 ps and a slow decay of several hundred ns due to the baseline so an iterative process was used in order to reduce the magnitude of the residuals and the error on the fits to less than 6 %. For figure 4.17, the least squares analysis was therefore carried out on the data 5 short lifetimes (450 ps) after the incident pulse in order to reduce the effect of the shorter lifetime. This data was then scaled to figure 4.16 using the intensity of the data 4 to 5 long lifetimes (535 to 670 ps) from the incident pulse, extrapolated to time zero and subtracted from the decay in figure 4.16 prior to fitting this data. The least squares fit of the fast decay component was then carried out using only the initial decay component corresponding to approximately 1 short lifetime. By this method, it is believed that the reported decay rates are accurate to within 3 % for the fast component and within 10 % for the slow component. The "goodness of fit" for the slow component is also shown in figure 4.17 (residuals vs time) to be less than ideal, displaying a trend which suggests that the reported rate for this decay is slightly high, probably as a result of a deficiency in the fitting function.¹⁷⁷

As shown previously, the radiative lifetime calculated for this molecule and its protonated form are 8.1 ns and 22.4 ns respectively. The dramatic reduction in lifetimes is difficult to rationalize in terms of non-radiative deactivation processes involving intersystem crossing or internal conversion alone. Therefore an interpretation of these rather rapid emission decays must invoke an argument based upon two different quenching processes. For the decay of 89 ± 4 ps observed in figure 4.16 at rather high concentration, the most likely mechanism would be

intermolecular quenching of excited state 3 by ground state 3. This type of self quenching process has been observed previously for several types of indole compounds.¹⁶⁰ In the case of the longer lifetime of 134 ± 3 ps observed in figure 4.17 for a more dilute solution, this process would be reduced substantially and some form of intramolecular quenching process must be operative. This may be by either intramolecular charge-transfer quenching of the excited phenyl ether by the diiminoindole moiety¹⁷⁸ or intramolecular proton-transfer quenching of the excited state by an imino proton.¹⁷⁹ In this particular case the latter proton-transfer quenching process is favoured as the phenyl ether and diiminoindole groups would be rather strongly coupled in the ground state and there is no evidence of a large excited state dipole moment as would be expected for an intramolecular charge-transfer process. This would manifest itself as a dependence of fluorescence wavelength maxima versus solvent polarity¹⁴⁸ which is not observed with this molecule. A more detailed photophysical study of this compound would be warranted in order to identify the exact mechanism of excited state decay.

The emission lifetime, least squares fit and residuals for the chromophore ligand CL in acetonitrile are shown in figure 4.18. The observed radiative decay rate is $2.62 \pm .03 \times 10^8 \text{ s}^{-1}$ which corresponds to an emission lifetime of $3.81 \pm .04$ ns. This is less than half of the calculated radiative lifetime of 8.7 ns and gives a total nonradiative decay rate of $1.5 \times 10^8 \text{ s}^{-1}$. Of this, the rate of intersystem crossing in CL may be estimated as having a maximum value of $5 \times 10^7 \text{ s}^{-1}$ by analogy to that previously calculated for 1 and 2. The rate of internal conversion may be expected to be greater than in 1 due to the addition of the methylpyridyls which would act as additional free rotors capable of promoting internal conversion processes. This yields a rate of internal conversion in this molecule of the order of $1 \times 10^8 \text{ s}^{-1}$. Normally, rates of internal conversion are not able to compete favourably with fluorescence or intersystem crossing. Exceptions occur¹⁸⁰ when S_1 undergoes a photochemical

Figure 4.18 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for CL in acetonitrile, 2.8×10^{-4} M, streak camera speed at 26.66 ps/channel

deactivation process, S_1 and S_0 undergo a surface crossing and when the energy difference between S_1 and S_0 is less than 50–60 kcal/mole. A surface crossing may be suspected in this particular case as there is no evidence for photochemical deactivation and the S_1 – S_0 energy difference is of the order of 75 kcal/mole.

The addition of water to acetonitrile solutions of CL also has a profound effect upon the emission lifetime (figure 4.19). The decay rate was found to be 2.5 times slower at $1.08 \pm .03 \times 10^8 \text{ s}^{-1}$ corresponding to a lifetime of $9.24 \pm .21 \text{ ns}$ as compared to $3.81 \pm .04 \text{ ns}$ for the ligand in neat acetonitrile (figure 4.18). When a stronger proton donor is added such as acetic acid, which has a pK_a of 22.3 in acetonitrile as compared to water ($\text{pK}_a > 28$)¹⁸¹, the emission decay rate decreases further to $9.58 \pm .28 \times 10^7 \text{ s}^{-1}$ (lifetime = $10.44 \pm .30 \text{ ns}$) as shown in figure 4.20. This is in much better agreement with the calculated radiative lifetime for the protonated form of CL which was determined to be 13.5 ns (table XI). The reduction in this discrepancy between the calculated and observed radiative lifetimes as compared to the neutral ligand (i.e. 3.81 ns vs 8.7 ns) may be attributed to the reduction in internal conversion processes that was noted earlier to explain the dramatic increase in quantum yield that accompanies protonation. In addition, the rate of intersystem crossing must be reduced substantially from the estimated value of $5 \times 10^7 \text{ s}^{-1}$ found for CL as the total nonradiative decay rate is only $2 \times 10^7 \text{ s}^{-1}$.

Figure 4.19 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for 4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline (CL) in 20:1 acetonitrile:water, 2.8×10^{-4} M, streak camera speed at 26.66 ps/channel

Figure 4.20 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for 4,7 di n butoxy 1,3 bis(3'-pyridylmethyl)imino)sandoline (CL₁) in 20:1 acetonitrile:acetic acid, 2.8×10^{-4} M, streak camera speed at 26.66 p./channel

4.5 Excited State Spectrum.

Transient absorption spectra of the ligand in acetonitrile are shown in figures 4.21, 4.22, 4.23 and 4.24 at concentrations of 2.12×10^{-4} M, 5.0×10^{-4} M, 1.0×10^{-3} M and 5.0×10^{-3} M respectively. In figure 4.21, the solution is so dilute that only the Raman absorptions of the acetonitrile solvent and a small broad absorption spanning the entire spectrum are observed regardless of the delay after the excitation pulse. In figure 4.22, a broad absorption of low intensity centered at 525 nm grows in rapidly in less than 50 ps and persists for more than 5 ns in the dilute solution. As the concentration of the solution is increased by a factor of two as shown in figure 4.23, the broad absorption is reduced after 5 ns and only an absorption centered around 475 nm remains. The 50 ps short time delay spectrum at even higher concentrations displays an even further reduction in the intensity of the broad band and the absorption previously at 475 nm after 5 ns is further blue shifted to 460 nm in figure 4.24. The 525 nm band appears to be due to the protonated excited state of the ligand for several reasons. Namely, as the concentration of the solution is increased, the effect of trace water on the absorption spectrum would be reduced and the intensity of this absorption would decrease accordingly as shown in the series of figures from 4.21 to 4.24 due to the unavailability of protons. Figure 4.25 shows that when excess water is present, the intensity of this band increases dramatically although it appears to shift to a longer wavelength of 625 nm. The emission at 485 nm due to protonated excited state cancels out some of the protonated excited state absorption and this therefore shifts the band maximum to longer wavelength.

This absorption is situated at about 590 nm in methanol (figure 4.26) where protons are available for protonation of the excited state but the enhanced emission from the protonated chromophore is not as large. In this particular case, the chromophore may be expected to be less protonated in the ground state prior to

Figure 4.21 Transient absorption spectrum of CL (2.12×10^{-4} M in acetonitrile).

Figure 4.22 Transient absorption spectrum of CL (5.0×10^{-4} M in acetonitrile)

Figure 4.23 Transient absorption spectrum of CL (1.0×10^{-3} M in acetonitrile)

Figure 4.24 Transient absorption spectrum of CL (5.0×10^{-3} M in acetonitrile)

Figure 4.25 Transient absorption spectrum of CL (4.8×10^{-3} M in 20% acetonitrile/water)

Figure 4.26 Transient absorption spectrum of CL (1.0 x 10⁻³ M in methanol)

light absorption than in the case of acetonitrile:water due to the smaller autodissociation constant of methanol versus water. However, it was previously shown from fluorescence spectra and emission lifetime measurements that the ground state is involved in some type of specific hydrogen bonding interaction with alcoholic solvents. If the rate of protonation and deprotonation in methanol is on the same time scale as the emission, then a dynamic equilibrium between the neutral and protonated excited states would be created that would reduce the emission intensity of the protonated species substantially as many of these species would lose their proton prior to emission. This would therefore explain both the reduced emission intensity or negative absorbance change due to the protonated form in methanol and the apparently longer lifetime of the neutral excited state species. More experimental data would be required in order to determine accurate rates of protonation and deprotonation for the excited state chromophore in methanol.

The higher energy absorption at 460 nm observed after 5 ns in figure 4.24 may be due to a small amount of self quenched ligand (ie. $CL^+ \cdot CL^-$) as self quenching is observed at this concentration. Another possibility is that it is some form of excimer (CL_2^*) as it would be expected to have an absorption occurring more red shifted compared to the monomer emission of 419 nm. A protonated excimer (ie. CL_2H^+) would be expected to be substantially red shifted beyond 485 nm where the emission due to the protonated monomer occurs. Intermediate between these extremes would be some type of solvent mediated excimer formation where the solvent may be trace amounts of water in the acetonitrile. Nevertheless, the intensity of this absorption is quite low (absorbance change of 0.05) and regardless of its source would not be expected to interfere with the interpretation of quenching spectra.

4.6 Cation Radical Spectrum

The redox potential of both the neutral and protonated excited state can be estimated from the energy of the high energy tail of the respective emission spectra ($\nu_{0,0}$) and the $E_{1/2}^{\text{ox}}$ for the $\text{CL}^{\cdot/0}$ and $\text{CLH}^{2\cdot/+}$ couples. The emission spectra were found to tail off at 380 nm (3.26 V.) and 447 nm (2.77 V.) for CL and CLH^+ respectively as shown in figure 4.11 (curves a and i). Cyclic voltammetry of the chromophore ligand in acetonitrile displays one broad irreversible oxidation peak around +1.5 V vs NHE and one irreversible reduction peak at -1.7 V vs NHE, both of approximately the same area as shown in figure 4.27a. As the scan rate was increased, the oxidation peak shifted anodically and became ill-defined as the scan rate was reduced. Irreversible redox peaks should vary linearly with the square root of the scan rate over a certain range and should follow the relationship¹⁸²:

$$(E_p)_2 - (E_p)_1 = \{(RT)/(\alpha n_a F)\} \ln(\nu_1/\nu_2)^{1/2} \quad 4.5$$

where E_p are the measured peak potentials in volts, R is the gas constant, F is Faraday's constant, T is temperature in K, ν is the scan or voltage sweep rate, α is the transfer coefficient which is typically in the range 0.3 to 0.7 and n_a is the number of electrons transferred in the rate controlling step. The oxidation potential of the neutral chromophore ligand can be estimated from the intercept of a plot of peak potential vs the square root of the scan rate such as is shown in figure 4.27b. The oxidation potential can be estimated as +1.40 V. vs. NHE from this plot. It is expected to be less than the value of +1.58 V. vs. NHE reported for *p*-dimethoxybenzene.¹⁸³ The slope of a plot of the above relationship which is not shown gives a value of 3.13×10^{-21} moles for the slope ($= \alpha n_a$, $\alpha_{\text{max}}=1$) which means either several oxidations are occurring concurrently ($n_a > 6.023 \times 10^{23} \text{ e}^-/\text{mol}$) or a reaction between the oxidized ligand and the electrode is occurring. The latter situation is suggested by the loss of anodic current intensity in the ligand oxidation peak when successive scans are made from 0.0 volts to +1.55 V versus N.H.E.

Figure 4.27 a) Cyclic voltammogram of 4,7-di-*n*-butoxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline (4L) (1.0×10^{-3} M) in 0.1 M tetrabutylammonium tetrafluoroborate acetonitrile solution. Pt working and counter electrode. Ag reference electrode. Internally referenced against the ferrocene/ferrocenium ion redox couple. Scan speed = 100 mV/s for shown CV.
b) Effect of varying scan speed on the position of the ligand oxidation

without cleaning of the working electrode in between scans.

Attempts to obtain the oxidation potential of the protonated chromophore ligand by adding glacial acetic acid to an acetonitrile solution were to no avail. Nothing was observed up to the anodic limit of 2.1 V. and therefore a limiting value of +2.1 V. will be used for subsequent calculations of the protonated excited state redox potential.

The redox potentials of the excited states may then be calculated according to:

$$E_{\text{CL}}^{+/*} = E_{\text{CL}}^{\text{ox}} - \nu_{0,0} = 1.40 - 3.26 = -1.86 \text{ V. for CL}$$

and

$$E_{\text{CLH}}^{2+/*} = E_{\text{CLH}}^{\text{ox}} - \nu_{0,0} = (> 2.1) - 2.77 = (> -0.67 \text{ V.}) \text{ for CLH}^*$$

Using these values, the driving force for electron transfer from the neutral excited state to methyl viologen dication (MV^{2+}) which has a half-wave reduction potential of -0.448 V. vs NHE ¹⁸⁴ may be calculated according to¹⁸⁵:

$$\Delta E = E_{1/2}^{\text{red}}(\text{A}) - E_{\text{D}}^{+/*} + w(p) - w(r) \quad 4.6$$

where $w(p)$ is the work term related to the products and is approximately 0.03 V for two unipositive ions, $w(r)$ is the work required to bring the reactants together and is zero when one of the reactants is uncharged. The driving force for electron transfer from CL^* to MV^{2+} is then equal to +1.44 V whereas electron transfer quenching of the protonated excited state is thermodynamically favourable by less than +0.25 V..

Figure 4.28 shows transient absorption spectra of intermolecular electron transfer quenching of CL^* by methyl viologen dication (MV^{2+}). The spectra show the transient absorption spectrum expected¹⁸⁶ for the reduced quencher $\text{MV}^{\bullet}$, with an absorption maximum at 607 nm ($\epsilon = 13,900$)¹⁸⁷ with two less intense shoulders and a tail into the UV. An additional band also appears at 480 nm ($\epsilon = 6,100$) which has been assigned to the cation radical of the chromophore ligand ($\text{CL}^{\bullet+}$). A steady state concentration of both species is established on the nanosecond time

Figure 4.28 Transient absorption spectrum of CL ($2.5 \times 10^{-3} \text{ M}$) and methylviologen dihexafluorophosphate ($2.0 \times 10^{-2} \text{ M}$) in acetonitrile.

regime because diffusion of the positively charged products away from each other in solution occurs much more rapidly than the back electron transfer process. This appears as a growth in the entire spectrum from 1 ns to 10 ns. On a much slower time scale of minutes as is shown in figure 4.29, only the spectrum of the reduced methylviologen quencher is observed to grow in.

Intermolecular electron transfer quenching of the chromophore excited state by p-benzoquinone with a reduction potential of -0.31 V. vs. NHE in acetonitrile¹⁸⁸ is favourable by an estimated $+1.53$ V whereas quenching of the protonated excited state is again only favourable by a maximum of $+0.26$ V. Figure 4.30 shows the transient absorption spectra obtained for this system at 50 ps, 5 ns and 10 ns following the excitation pulse. The spectra consist of an absorption at 430 nm ($\epsilon = 7,400$) due to the p-benzoquinone anion radical which tails off toward the red, giving no absorption beyond 450 nm.¹⁸⁹ This leaves an additional absorption centered at 480 nm ($\epsilon = 6,000$) which can only be assigned to the ligand cation radical spectrum. The rate of electron transfer has been calculated as $6 \times 10^7 \text{ s}^{-1}$ and at the concentrations used here, the efficiency is about 70 %. For the slower back electron transfer process, all that can be determined on this time scale is that the rate is less than $5 \times 10^7 \text{ s}^{-1}$.

Intermolecular electron transfer quenching of the chromophore excited state with $[(\text{NH}_3)_5\text{Co}(\text{py})]^{3+}$ with a reduction potential of $+0.05$ V. vs NHE¹⁹⁰ is favourable by $+1.94$ V in the case of CL^* and less than $+0.75$ V in the case of CLH^* . Figure 4.31 shows the transient absorption spectra obtained 50 ps and 5 ns following the excitation pulse for a solution, 0.023 M in $[(\text{NH}_3)_5\text{Co}(\text{py})]^{3+}$ and 9.1×10^{-4} M in CL. The 50 ps spectrum displays a large broad absorption at 625 nm due the protonated ligand and a large negative absorption at 495 nm due to the enhanced emission from the protonated ligand. In addition, a small absorption can be seen at about 460 nm which is suspected to be due to the radical cation. It is blue

Figure 4.29 Visible spectrum of sequential irradiation a solution of 4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline (CL) (2.5×10^{-3} M) and methylviologen dhexafluorophosphate (2.0×10^{-2} M) in acetonitrile. Bottom curve at $t=0$, each successive curve at $t=1, 2, 5, 10, 15$ and 20 minutes. Illuminated with a 250 W projector lamp passed through a 400 nm cutoff filter and a 5cm water cell. Sample temperature thermostatted to 25 ± 1 deg. C.

Figure 4.30 Transient absorption spectrum of CL (2.5×10^{-3} M) and p-benzoquinone (0.1 M) in acetonitrile

Figure 4.31 Transient absorption spectrum of **CL** (9.1×10^{-4} M) and $[(\text{NH}_3)_5\text{Co}(\text{py})]^{3+}$ (2.3×10^{-2} M) in acetonitrile

shifted and of very low intensity due to the interference from the large emission. Unfortunately the growth and decay of the radical cation cannot be determined from this data. Nevertheless, quenching rates can be evaluated under similar conditions as shown by the Stern–Volmer plot in figure 4.32. A slope of $433 \pm 26 \text{ M}^{-1}$ ($= k_q \tau$) is obtained which corresponds to a quenching rate constant of $1.1 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ when an emission lifetime of 3.8 ns is used ($k_q = 4.33 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ if $\tau = 10 \text{ ns}$ is used). The quencher must be associated with the chromophore in the ground state prior to excitation in order to account for the extremely rapid quenching rate as this is beyond the diffusion rate limit for this solvent.¹⁹¹

Figure 4.32 Stern-Volmer plot of 4,7-di-*n*-butoxy-1,3-bis((3'-pyridyl-methyl)imino)isoindoline (CL) ($9.1 \times 10^{-4} \text{ M}$ in acetonitrile) fluorescence quenching by $[(\text{NH}_3)_5\text{Co}(\text{py})]^{3+}$

For intermolecular electron transfer quenching of CL^* by $[\text{Co}(\text{III})(\text{bpy})_3]^{3+}$, the process is favourable by about +2.25 V.¹⁹² and the transient absorption spectra are shown in figure 4.33. At 1 ns after the excitation pulse, only absorptions due to the ligand cation radical at 475 nm and the protonated excited state at 625 nm

are visible due to the lack of absorption of the reduced quencher, $[\text{Co(II)(bpy)}_3]^{2+}$ in the visible region.¹⁹³ The cation radical grows in at $1 \times 10^9 \text{ s}^{-1}$ and then decays at a rate of $7 \times 10^7 \text{ s}^{-1}$. At these concentrations, the efficiency of electron transfer was found to be 39 %. The absorption appearing at 510 nm in the spectrum recorded after 10 ns may be due to a Co(II) substitution product or a chromophore photo-product. It may even be possible that the protonated excited state is quenched by the easily reduced $[\text{Co(III)(bpy)}_3]^{3+}$ quencher by a slower process due to the smaller driving force of less than 0.9 V. for this redox pair. In this case the protonated radical dication would be the source of this absorption but this will require further studies to positively identify the origin of this absorption.

In summary, the cation radical consists of a single absorption centered at 480 nm with an extinction coefficient of $6100 \text{ M}^{-1}\text{cm}^{-1}$ as determined from the transient absorption spectra of intermolecular quenching (see Appendix F for detailed calculations). In addition, the protonated excited state of the chromophore ligand consists of a single broad absorption centered at 625 nm with an extinction coefficient of $600 \text{ M}^{-1}\text{cm}^{-1}$. Intramolecular quenching of the chromophore excited state is thus expected to occur very rapidly (ca. 10^{11} s^{-1}) in the chromophore quencher complexes producing a cation radical spectrum which decays at a slower rate than it is formed. This process should compete with the slower process of excited state protonation but both will be evident as it was not possible to obtain sufficiently anhydrous acetonitrile.

Figure 4.33 Transient absorption spectrum of CL (1.67 × 10⁻³ M) and [Co(bpy)₃]³⁺ (4.1 × 10⁻² M) in acetonitrile

5. INTRAMOLECULAR ELECTRON TRANSFER QUENCHING IN Cu(II) COMPLEXES

Chapter 3 described many of the difficulties encountered in attempting to prepare and characterize complexes of the chromophore ligand coordinated to cobalt(III) metal site quenchers. The available data on these complexes and some speculation as to their intramolecular quenching behaviour is deferred until chapter 6. In this chapter, intramolecular electron transfer quenching of the chromophore excited state by copper(II) metal site quenchers is discussed.

5.1 Electrochemical Studies

Copper complexes impose some challenges in terms of interpreting electron transfer rates as a function of thermodynamic driving force. This is mainly due to the difficulty in obtaining half wave reduction potentials for these complexes as many undergo ligand loss and/or substitution upon reduction to the Cu(I) species and subsequently display irreversible behaviour in their cyclic voltammograms. As a result of this, reduction potentials were determined by extrapolating the scan rate dependence of the observed peak potentials to very high scan rates where the effect of ligand substitution would be minimal. In addition, the use of Pt working electrodes is known to often result in only the observation of a Cu(II/0) reduction and so Au and Pb electrodes were used because of their superior behaviour for cathodic processes in acetonitrile.¹⁹⁴ The electrochemical behaviour of the ligand coordinated to a zinc ion was examined first in order to differentiate the effects of coordination to a metal ion from effects due to the behaviour of the complexes in solution.

Figure 5.1 is a cyclic voltammogram of the zinc complex of the chromophore ligand (ZnCl-H₂) recorded in acetonitrile (0.1 M TBAT, Pt working electrode) at a scan rate of 100 mV/s. The voltage scale has been converted to volts

Figure 5.1 Cyclic voltammogram of diaquo(4,7-di-*n*-butoxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline)-zinc(II) perchlorate (**ZnCL-H2**) (1.0×10^{-3} M) in 0.1 M tetrabutylammonium tetrafluoroborate acetonitrile solution. Pt working and counter electrode. Ag reference electrode. Internally referenced against the ferrocene/ferrocenium ion redox couple. Scan speed = 100 mV/s for shown CV.

Figure 5.2 Cyclic voltammogram of aquo(1,3-bis((3'-pyridylmethyl)imino)isoindoline)-copper(II) triflate (**CuL**) (1.0×10^{-3} M) in 0.1 M tetrabutylammonium tetrafluoroborate acetonitrile solution. Pt working and counter electrode. Ag reference electrode. Internally referenced against the ferrocene/ferrocenium ion redox couple. Scan speed = 100 mV/s for shown CV.

versus NHE by comparison with an internal reference of the ferrocene/ferrocenium ion couple. The irreversible anodic peak at +1.75 V is due to the ligand oxidation which appears at approximately 1.5 V for the free ligand (figure 4.27, p. 124) at the same scan rate. The small stabilization of the ligand toward oxidation may in part be due to the cationic nature of the complex with which it is coordinated.¹⁹⁵ An irreversible peak is observed at -0.80 V with a higher integrated current than the anodic peak. Based on the current intensity and the voltage of the peak,¹⁹⁶ it has been assigned to a two electron reduction of the zinc(II) ion with the coordinated ligand.

For the aquo copper complex ($\text{CuL}-\text{H}$) of the reference ligand, L, the ligand oxidation peak is not observed up to the anodic limit of this electrode/electrolyte system as shown in figure 5.2. An irreversible peak of high current intensity is observed at -1.30 V with a distinct shoulder at -1.18 V. The shoulder is suspected of being due to a two electron reduction of copper(II) to copper(0). The peak at -1.30 V then corresponds to reduction of the free ligand on the copper metallized electrodes. Upon reversal of the voltage sweep, two oxidation peaks are observed at -0.26 and -0.09 V which are suggested to correspond to one electron oxidations of the copper(0) and copper(I) acetonitrile solvate complexes.

For the anhydrous chromophore quencher complex, denoted as CuCL , the ligand oxidation wave cannot be observed in the cyclic voltammogram (figure 5.3) up to the anodic limit shown. An irreversible cathodic peak is observed at -0.98 V which is due to a two electron reduction of copper(II) and a quasi-reversible cathodic peak is observed at -1.65 V which has been assigned to reduction of the ligand. The subsequent oxidation of the reduced ligand during reversal of the voltage sweep is shown to give rise to a peak of smaller intensity in contrast to that observed for the free ligand under the same conditions as shown in chapter 4, figure 4.27, p. 124. This quasi-reversible behaviour is observed in methylene chloride

Figure 5.3 Cyclic voltammogram of (4,7-di-n-butoxy-1,3-bis(3'-pyridylmethyl)imino)isoindoline)-copper(II)triflate (CuCl) ($1.0 \times 10^{-3} \text{ M}$) in 0.1 M tetrabutylammonium tetrafluoroborate acetonitrile solution. Pt working and counter electrode. Ag reference electrode. Internally referenced against the ferrocene/ferrocenium ion redox couple. Scan speed = 100 mV/s for shown CV.

Figure 5.4 Cyclic voltammogram of (4,7-di-n-butoxy-1,3-bis(3'-pyridylmethyl)imino)isoindoline)-copper(II)triflate (CuCl) ($1.0 \times 10^{-3} \text{ M}$) in 0.1 M tetrabutylammonium tetrafluoroborate methylene chloride solution. Pt working and counter electrode. Ag reference electrode. Internally referenced against the ferrocene/ferrocenium ion redox couple. Scan speed = 100 mV/s for shown CV.

(figure 5.4) and when a gold working electrode (figure 5.5) is used and may be due to enhanced stability of the reduced ligand on a copper coated electrode surface. As the voltage sweep becomes further positive, two ill-resolved peaks can be observed at -0.54 and $+0.08$ V. These peaks are absent from the cyclic voltammogram recorded in methylene chloride (figure 5.4) and are therefore ascribed to oxidation of the Cu(0) and Cu(I) acetonitrile solvate complexes. The broadness of the peaks and the appearance of an additional broad cathodic peak at -0.18 V when the voltage is cycled back in the negative direction lend support to this.

If a gold working electrode is used as shown in figure 5.5, then two irreversible one electron reductions corresponding to the Cu(II/I) and Cu(I/0) couples can be observed. If the cathodic voltage is limited to less than -1.2 V, then these couples appear as almost quasi-reversible peaks. In figure 5.5, the voltage was swept to -2.0 V to include the ligand reduction and therefore upon voltage sweep reversal, small peaks corresponding to the oxidation of the acetonitrile solvate complexes are observed. An appreciable amount of copper remains on the gold electrode as shown by the large stripping peak at $+0.97$ V.

Figure 5.6 displays the cyclic voltammogram of this complex in acetonitrile using a lead working electrode. The voltage range is quite limited due to oxidation of the electrode at $+0.6$ V¹⁹⁴ and reduction of surface oxides at -1.4 V¹⁹⁷. However, two distinct quasi-reversible redox couples can be observed at -0.54 and -0.89 V which have been assigned to the Cu(II/I) and Cu(I/0) couples respectively. Cu(II/I) couples in the range -0.46 to -0.88 V generally correspond to redox processes in which both the Cu(II) and Cu(I) species exhibit nonplanar geometries about the copper ion.¹⁹⁸ Negative reduction potentials for Cu(II/I) couples and large separations between the cathodic and anodic waves also imply that a reduction in coordination number occurs upon reduction.¹⁹⁹ A coordination number of 4 is common for Cu(I) complexes of strong π -acceptors such as pyridine¹⁹⁹ and a

Figure 5.5 Cyclic voltammogram of (4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline)-copper(I)triflate (CuCl) ($1.0 \times 10^{-3} \text{ M}$) in 0.1 M tetrabutylammonium tetrafluoroborate acetonitrile solution. Au working electrode. Pt counter electrode. Ag reference electrode. Internally referenced against the ferrocene/ferrocenium ion redox couple. Scan speed = 100 mV/s for shown CV.

Figure 5.6 Cyclic voltammogram of (4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline)-copper(I)triflate (CuCl) ($1.0 \times 10^{-3} \text{ M}$) in 0.1 M tetrabutylammonium tetrafluoroborate acetonitrile solution. Pb working electrode. Pt counter electrode. Ag reference electrode. Internally referenced against the ferrocene/ferrocenium ion redox couple. Scan speed = 100 mV/s for shown CV.

coordination number of 6 has been proposed (chapter 3.3) for the tetragonally distorted octahedral Cu(II) complex much in agreement with this observation.

The Cu(II/I) and Cu(I/0) couples of the diaquo chromophore copper(II) complex (denoted as **CuCL-H2** in table XI) are observed at -0.75 and -0.93 V as shown in figure 5.7. The difference in potentials versus the complex lacking coordinated water must be related to the effect that this has on the geometry and composition of the Cu(I) coordination sphere. The copper stripping peak is observed at -0.10 V with a small shoulder at $+0.10$ V presumably due to the Cu(I/II) oxidation.

The aquo copper(II) complex of ligand 13 was also studied by cyclic voltammetry and is shown in figure 5.8. The observation of two quasi-reversible waves with peak reduction potentials of -0.43 and -0.72 V and peak to peak separations²⁰⁰ of 460 and 220 mV have been assigned to the Cu(II/I) and Cu(I/0) couples respectively by analogy with **CuCL** and **CuCL-H2**. The differences in redox potentials may be ascribed to a small increase in the stability of the Cu(I) complex relative to the Cu(II) complex due to the imidazoles²⁰¹ and the additional flexibility of this ligand.

Figure 5.7 Cyclic voltammogram of diaquot(4,7-dimethoxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline)-copper(II)triflate ($\text{Cu(14H}_2\text{)}$) ($1.0 \times 10^{-3} \text{ M}$) in 0.1 M tetrabutylammonium tetrafluoroborate acetonitrile solution. Pt working and counter electrode. Ag reference electrode. Internally referenced against the ferrocene/ferrocenium ion redox couple. Scan speed = 100 mV/s for shown CV.

Figure 5.8 Cyclic voltammogram of aquo(4,7-dimethoxy-1,3-bis((3'-propyl-N'-imidazolyl)imino)isoindoline)-copper(II)triflate (Cu(13H)) ($1.0 \times 10^{-3} \text{ M}$) in 0.1 M tetrabutylammonium tetrafluoroborate acetonitrile solution. Pt working and counter electrode. Ag reference electrode. Internally referenced against the ferrocene/ferrocenium ion redox couple. Scan speed = 100 mV/s for shown CV.

Table XII Electrochemical data for complexes^{a, b}

Assignment	5 (L)	CuL-H	8 (CL)	CuCL	CuCL-H2	Cu(13)H	ZnCL-H2
$E_{\text{Ligand}^{+}/0}$ cathodic							
$E_{\text{Ligand}^{0}/-}$ anodic	c	c	+1.45	d	d	d	+1.94
$E_{\text{Cu}^{II/I}}$ anodic	-1.48	-1.30	-1.60	-1.65	d	-1.28	d
$E_{\text{Cu}^{I/O}}$ anodic				-0.50 e	-0.75	-0.43 h	
$E_{\text{Cu}^{II/O}}$ anodic				-0.83 e	-0.93	-0.72 h	
$E_{\text{Cu}^{I/O}}$ cathodic		-1.18		-0.98			
$E_{\text{Cu}^{II/I}}$ cathodic		-0.26 f		-0.54 f			
$E_{\text{Cu}^{II/O}}$ cathodic				+0.12 e	(+0.10) g		
$E_{\text{Zn}^{II/O}}$ anodic		-0.09 f		-0.09 f	-0.10		
							-0.80

- a All potentials are peak potentials in V. vs N.H.E. at the lowest scan rates where the peaks are visible. Conditions are described in chapter 2. Pt working electrode used except where noted.
- b CuL-H is $\text{Cu(L)(H}_2\text{O)(TFMS)}_2$, CuCL is Cu(CL)(TFMS)_2 , CuCL-H2 is $\text{Cu(CL)(H}_2\text{O)}_2(\text{TFMS})_2$
- c Cu(13)H is $\text{Cu(13)(H}_2\text{O)(TFMS)}_2$ and ZnCL-H2 is $\text{Zn(CL)(H}_2\text{O)}_2(\text{ClO}_4)_2$.
- d not observed in potential limits of electrode/electrolyte system.
- e interference from trace water precludes observation
- f using a Au working electrode, also CuO/II at -0.07 V, a cathodic peak can be observed at -0.50 V vs N.H.E. with a Pt working electrode if the voltage sweep is limited to 0 to -0.7 V.
- g may be due to acetonitrile solvate complex
- h as a shoulder on cathodic side of stripping peak
- h quasi-reversible with peak separation of 460 and 220 mV for II/I and I/O couples

5.2 Photophysical Studies

The fluorescence spectrum for the zinc complex as shown in figure 5.9a shows only the 485 nm emission due to the protonated excited state. The lack of observation of any emission due to the neutral ligand suggests that either the coordinated ligand has a higher pK_a^* than the free ligand or that protonation of the coordinated ligand is much more efficient because of the close proximity of coordinated or associated water molecules. The pK_a^* of the coordinated ligand for the CuCL complex has been estimated as 10–11 from fluorometric titration. This is in the same range as the free ligand which has a pK_a^* of 10.5. The pK_a^* of ZnCL–H₂ is expected to be quite similar and this suggests that enhanced efficiency of protonation is responsible for the lack of observation of emission from the neutral excited state. The quantum yield for fluorescence has also increased slightly from 0.71 to 0.78 but this may be attributed to the increased rigidity of the ligand when coordinated to a metal ion and the subsequent loss in vibrational and rotational non-radiative deactivation pathways of the excited state. For the CuCL complex, again only the 486 nm emission is observed but it is of much lower intensity with a quantum yield of 0.03. The UV–visible and emission spectral data for these complexes are summarized in tables XIII and XIV respectively.

The dramatic loss in fluorescence intensity may be due to quenching by one or more of several different mechanisms.²⁰² These include (i) electronic energy transfer, (ii) electron transfer, (iii) a chemical reaction involving atom transfer, (iv) exciplex formation, (v) spin-catalyzed deactivation and (vi) the external heavy atom effect. In cases where the observed rate constants are greater than 10^7 s^{-1} , consideration of only the electron and energy transfer processes is warranted.²⁰³ Both the radiative and radiationless (or Coulombic) energy transfer mechanisms require spectral overlap between the emission of the donor and the absorption of the acceptor.²⁴ The lowest energy LMCT transition for the copper–pyridyl complexes

Figure 5.9

Apparent fluorescence spectra of a) $(\text{ClO}_4)_2\text{Zn}(\text{II})(\text{ClO}_4)_2$,
 b) $(\text{ClO}_4)_2\text{Cu}(\text{II})(\text{CF}_3\text{SO}_3)_2$, c) $(\text{ClO}_4)_2\text{Cu}(\text{II})(\text{CF}_3\text{SO}_3)_2$,
 d) $(\text{CF}_3\text{SO}_3)_2\text{Cu}(\text{II})(\text{CF}_3\text{SO}_3)_2$. All solutions are 1×10^{-5} M
 in acetonitrile. Excitation wavelength = 365 nm. Solvent = monochromator
 bandpass

Table XIII

UV/Visible spectral data for complexes^a

Assignment	ϵ (L)	CuL-H	8 (CL)	CuCl	CuCl-H2	ZnCl-H2
π, π^* ^c	226 (4.73)	229 (3.93)	204 (4.85)	200 (4.63)	200 (4.56)	200 (4.01)
π, π^* ^c			223 (4.71)	235 (4.15)	233 (4.33)	231 (3.66)
π, π^* ^c			262 (4.45)	246 (4.14)	243* (4.30)	243* (3.61)
π, π^* ^c	263 (4.50)	263 (3.68)	268 (4.45)	270 (4.03)	270 (4.24)	269 (3.52)
π, π^* ^c			282 (4.37)	282* (4.02)	282* (4.21)	284 (3.52)
π, π^* ^c	298* (4.09)	308 (4.11)		294* (3.90)	293* (4.09)	297* (3.38)
π, π^* ^c	321* (4.07)	320* (3.21)				
nb, π^* ^d			367 (4.06)	367* (3.45)	365* (3.72)	365* (3.01)
nb, π^* ^e			418* (3.87)	420 (3.83)	414 (3.93)	419 (3.29)
d, d ^f		579 (1.72) ^b		568 (1.82) ^b	616 (1.79) ^b	
d, d ^f					840 (1.28) ^b	

^a wavelength in nm. (log ϵ), for 1×10^{-4} M solutions in acetonitrile.CuL-H is Cu(L)(H₂O)(TFMS)₂, CuCL is Cu(CL)(TFMS)₂, CuCL-H2 is Cu(CL)(H₂O)₂(TFMS)₂ and ZnCL-H2 is Zn(CL)(H₂O)₂(ClO₄)₂^b 1×10^{-2} M solution^c ligand centred transitions^d due to neutral form of ligand, see chapter 4^e due to protonated form of ligand, see chapter 4^f ligand field transition

* an unresolved shoulder

Table XIVEmission spectral data for copper and zinc complexes^{a, b}

	8 (CL)	CuCL	CuCL-H2	Cu(13)H f)	ZnCL-H2
	fluorescence emission spectra				
Φ_F (CL) c)	0.15	0.00	0.00	0.00	0.00
Φ_F (CLH ⁺) c)	0.71	0.03	0.22	0.13	0.92
	fluorescence emission lifetimes				
τ_F (CL) c)	$3.81 \pm .04$ ns	22.4 ± 2.2 ps	25.6 ± 1.1 ps	$80.7 \pm .8$ ps	
τ_F (CLH ⁺) c)		$4.64 \pm .06$ ns	4.2 ± 0.1 ns		$9.93 \pm .29$ ns
τ_F (CLH ⁺) d)	9.24 ± 21 ns	$6.41 \pm .12$ ns			5.61 ± 13 ns
τ_F (CLH ⁺) e)	10.4 ± 3 ns	$6.77 \pm .11$ ns	$7.45 \pm .18$ ns		9.07 ± 25 ns
	transient absorption spectroscopy				
$\tau_{et}(\text{forward})$ c)		15 ± 5 ps	21 ± 1 ps		
$\tau_{et}(\text{back})$ c)		294 ± 8 ps	360 ± 20 ps		
τ_{CLH^+} c)		4 ± 3 ns	$5 \pm$ ns		

a Taken in part from Appendix D. Φ_F are fluorescence quantum yields at 10^{-5} M. τ_F are emission lifetimes and τ_{et} 's and τ_{CLH^+} are lifetimes for the forward and back electron transfers and the protonated excited state as determined by transient spectroscopy.

b CuCL is CuCL(TFMS)₂, CuCL-H2 is CuCL(H₂O)₂(TFMS)₂, Cu(13)H is Cu(13, H₂O)(TFMS)₂ and ZnCL-H2 is ZnCL(H₂O)₂(ClO₄)₂.

c in neat acetonitrile, d) in 20% acetonitrile/water, e) in 20% acetonitrile/water and

f for 13 and 13H⁺, λ_{exc} occurs at 416 nm and 480 nm with $\Phi_F = 0.12$ and 0.58 , respectively.

prepared in this study cannot be resolved from the more intense ligand bands but is expected to occur in the 250 nm to 330 nm region by analogy with other Cu(II)-N-heterocycle complexes⁶⁶ thus eliminating the possibility that energy transfer is operative here. Energy transfer to a ligand field excited state by an exchange mechanism²¹ would be very inefficient due to the change in symmetry and multiplicity required and has been estimated²⁰⁴ at $2 \times 10^{-4} \text{ s}^{-1}$ for this system. Intramolecular electron transfer quenching of the neutral ligand excited state is the only mechanism available to account for the observed results and this competes with deactivation by protonation of the neutral excited state to give a lower energy non-redox active protonated excited state.

The fluorescence spectra of CuCL and CuCL-H₂ in acetonitrile (figure 5.9) show that the neutral chromophore ligand excited state is quenched in both the CuCL complex and in the CuCL-H₂ complex. Emission lifetime measurements of the zinc complex shown in figure 5.10, reveal that the lifetime of the zinc complex is $10.2 \pm 1.6 \text{ ns}$ which is longer than the $3.8 \pm 0.4 \text{ ns}$ found for the chromophore ligand but quite comparable to the $9.6 \pm 0.6 \text{ ns}$ observed for the ligand in 4:1 acetonitrile:water which has been assigned to the protonated chromophore excited state. Figure 5.11 shows the picosecond transient absorption spectra recorded for the zinc complex at 50 ps and 5 ns following the excitation pulse. No evidence for the formation of the ligand cation radical is observed and in fact the zinc complex displayed stimulated emission from the protonated excited state at 485 nm on the 50 ps time scale as evidenced by a substantially higher emission from the complex in the presence of the probe pulse. Therefore it can be concluded that the behaviour of the zinc complex is indicative of an efficient proton transfer quenching of the higher energy neutral excited state by complex associated water molecules.

In the case of Cu(CL), the driving force for electron transfer to form the Cu(I) species has been estimated²⁰⁵ as 1.36 V. and this may be a low estimate

Figure 5.10 a) Fluorescence emission lifetime, b) least square fit of data and c) residual. (CT fit for $(\text{CT})(\text{H}_2\text{O})_2/\text{Zn}(\text{H})(\text{ClO}_4)_2$ in acetonitrile $6.40 \times 10^{-5} \text{ M}$, total concentration of 0.001 g/l (channel 1).

Figure 5.11 Transient absorption spectra of $(\text{Cl})(\text{H}_2\text{C})_2\text{Zn}(\text{H})(\text{ClO}_4)_2$ ($2.12 \times 10^{-4} \text{ M}$) in acetonitrile

because a cathodic ligand oxidation peak potential and an anodic Cu(II) reduction peak potential were used in the calculation. The emission decay in figure 5.12 displays a very short component with a lifetime of 22 ± 2 ps and a much slower component with a lifetime of 4.6 ± 0.1 ns may be observed if the streak camera speed is reduced to 26.66 ps/channel as in figure 5.13. When the concentration of the complex is reduced from 0.01 M to 2×10^{-4} M as shown in figure 5.14, only the slow component is observed with a longer lifetime of 8.7 ± 0.2 ns. On the basis of these observations, the slow component has been assigned to emission from the protonated excited state of the chromophore because it becomes more prevalent as the concentration of the complex is reduced

Picosecond transient absorption spectra for this complex (figure 5.15) display the rapid formation of the chromophore cation radical absorption at 475 nm. This absorption is of slightly larger intensity at 20 ps following excitation as it is when the 30 ps duration excitation and the probe continuum pulse are passed through the sample simultaneously, labelled 0 ps on the figure. This means that when the sample has been exposed to half of the excitation pulse or about 15 ps (ie. 0 ps curve), most of the cation radical has been formed and all of the cation radical is formed within 5 ps after the excitation pulse ends (ie. 20 ps curve). This gives a rate of formation for the cation radical of between $5 \times 10^{10} \text{ s}^{-1}$ and $1 \times 10^{11} \text{ s}^{-1}$ or in 10 to 20 ps much in agreement with the 22 ± 2 ps component of the emission decay curve. The efficiency of this electron transfer process has been calculated as 21 % as shown in appendix F. The cation radical then decays at a rate of $2.4 \times 10^9 \text{ s}^{-1}$ ($\tau = 294$ ps) presumably by back electron transfer to form the Cu(II) complex. Back electron transfer has a driving force²⁰⁶ of 1.90 V. which would be well into the inverted region^{1,2,11,207,208} by analogy with other systems.²⁰⁹ The decay of the broad absorption at 625 nm is compared to the 475 nm absorption in figure 5.16 and it is evident that the two absorptions are from a different species. The 625 nm

Figure 5.12 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for $(\text{Cl})_2\text{Cu}(\text{DCl})_2\text{SO}_3$ in acetonitrile (1.0×10^{-2} M), fast component at a streak camera speed of 2.67 ps/channel

Figure 5.13 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for $(\text{CL})\text{Cu}(\text{II})(\text{CF}_3\text{SO}_3)_2$ in acetonitrile (1.0×10^{-2} M); slow component at a streak camera speed of 26.66 ps/channel

Figure 5.14 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for $(\text{C}_6\text{H}_5)_3\text{C}(\text{D})(\text{C}_6\text{H}_5)_2\text{SO}_3^-$ in acetonitrile (2.0×10^{-3} M), streak camera speed of 26.66 ps/channel

Figure 5.15 Transient absorption spectra of $(\text{CL})\text{Cu}(\text{II})(\text{CF}_3\text{SO}_3)_2$ ($1.15 \times 10^{-4} \text{ M}$) in acetonitrile

absorption is due to the protonated excited state and was found to decay with a lifetime of 7 ± 2 ns. There is a large uncertainty in this value due to the low extinction coefficient for this absorption coupled with the relatively high level of noise on the spectra in this region. By analogy with the chromophore ligand and the zinc complex, this absorption due to the protonated excited state would be expected to have a lifetime of the order of 9 to 11 ns. However, the 7 ± 2 ns value is in fair agreement with the 4.6 ± 0.1 ns and 8.7 ± 0.2 ns values found by emission lifetime measurements of a more concentrated solution (1×10^{-2} M, figure 5.13) and a more dilute solution (2×10^{-4} M, figure 5.14) respectively. This variation in the lifetime of the long component as a function of concentration can be explained if the scheme shown in scheme IV is considered.

Scheme IV

Based on the rates of electron transfer and protonation, it is evident that this can be considered a coupled system⁴⁸ and therefore the value of the long component is actually dependent on the concentration of the various excited states formed. This in turn is related to the initial concentrations, pKa's and extinction coefficients at 355 nm of the ground state species, the proton concentration in solution and the

a)

b)

Figure 5.16 a) Change in optical density versus time at 475 nm and 625 nm, from figure 5.19 and b) $\ln(\text{absorbance change})$ versus time from a)

intensity of the excitation pulse. Additional data as a function of concentration, pH and excitation energy is required to solve these complex equilibria.

In figure 5.17, the emission lifetime is shown for a 20:1 acetonitrile:water solution of this complex and only a slow decay with a lifetime of $6.41 \pm .12$ ns is observed with little evidence for a faster decay of the order of 20 ps. This means that both protonation of the ground and excited state ligand in this complex is much more efficient than the electron transfer pathway. In this case, one or more of the solvent molecules represented by S in scheme IV may be a coordinated water molecule that would more easily facilitate protonation of the excited state.

Transient absorption spectra were also recorded at higher concentrations of 0.05 M to rule out the possibility that the observed quenching was due to an intermolecular process. The decay of the cation radical was unchanged by this and the decay of the protonated excited state became more uncertain due to added spectral noise and thermal lensing effects. Transient absorption of the non-chromophore quencher complex, CuL-H (figure E.9) displayed no observed transients in the 425 to 675 nm range, thus eliminating the possibility that the observed cation radical spectrum was due to a LMCT band. By analogy with a number of Cu(I) complexes with nitrogen ligands, any MLCT bands due to the reduced metal would also be expected to be higher in energy than the observed 425 nm limit of the current spectra.

Transient absorption spectra of the CuCL complex recorded in methanol are shown in figure 5.18 at 50 ps, 500 ps, 5 ns and 10 ns after the pump pulse. The spectra are quite different than those recorded in acetonitrile with the appearance of a large negative absorbance change centred at 480 nm due to the enhanced emission from the protonated ligand. The magnitude of this negative absorbance is followed quite closely by the positive absorption at 325 nm due to the protonated excited state. The small peak at 470 nm on the 50 ps spectrum has been assumed to be due

Figure 5.17 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for (CL)Cu(II)(CF₃SO₃)₂ in 20:1 acetonitrile-water (9.5×10^{-3} M), streak camera speed of 26.66 ps/channel

Figure 5.18 Transient absorption spectra of $(\text{CL})\text{Cu}(\text{II})(\text{CF}_3\text{SO}_3)_2$ ($1.0 \times 10^{-3} \text{ M}$) in methanol

to the presence of a small amount of ligand cation radical. Based on this assumption and using the method outlined in appendix F, an electron transfer efficiency of 9 % has been calculated for this complex in methanol

In the CuCl-H2 complex the driving force for forward electron transfer has now been reduced slightly to 1.11 V²¹⁰ and accompanying this is a slightly decreased rate for the forward process. From figure 5.19, only a fast component with a lifetime of 26 ± 1 ps ($k = 3.8 \times 10^{10} \text{ s}^{-1}$) is observed. The reduced number of photon counts and the lack of an appreciable amount of slow emission decay due to the protonated ligand suggests that much of the protonation of the coordinated ligand occurs in the ground state prior to sample irradiation as the protonated ligand absorbs strongly at 420 nm (ν_2 in scheme IV) as opposed to 367 nm (ν_1 which is close to the 355 nm excitation pulse) for the neutral ligand. If reference is made to scheme IV, then the equilibrium lies to the upper left (i.e. $[(S)_n\text{Cu}^{(II)}\text{ClH}^+]^{3+}$) prior to excitation of the sample. Upon excitation, a large portion of this species must be rapidly deprotonated to form neutral excited state ligand species which are subsequently quenched by intramolecular electron transfer. The fluorescence spectrum of CuCl-H2 (figure 5.9, excitation wavelength = 365 nm) does in fact display an emission at 485 nm due to the protonated form of the ligand thus supporting this mechanism. Figure 5.20 displays transient absorption spectra for a similar solution of this complex. The radical cation grows in less than 100 ps and then decays with a lifetime of 360 ± 20 ps. The protonated excited state grows in less than 100 ps and is much more intense relative to the radical cation than it is in figure 5.15 for the anhydrous complex. The decay of this species is roughly 5 ± 1 ns with an added uncertainty due to the high noise level of the spectra from the enhanced emission at 485 nm. Attempts to correct the spectra for this emission were unsuccessful but an upper limit on the efficiency of electron transfer can be estimated as 17 %. The slower rates of electron transfer can be accounted for by

Figure 5.19 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for $(\text{CF}_3\text{H}_2\text{O})_2\text{Cu}(\text{DB}(\text{CF}_3\text{SO}_2)_2)$ in acetonitrile (5.0×10^{-3} M); streak camera speed of 2.67 ps/channel

Figure 5.20 Transient absorption spectra of $(\text{ClEt}_2\text{O})_2\text{CuIICl} \cdot \text{SO}_3$ at $0.5 \times 10^{-4} \text{ M}$ in acetonitrile

Figure 5.21 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for $(13)(\text{H}_2\text{O})_2\text{Cu}(\text{II})(\text{CF}_3\text{SO}_3)_2$ in acetonitrile (9.0×10^{-4} M); streak camera speed of 2.67 ps/channel

considering the thermodynamic driving force. For the forward process the driving force is less by about 0.25 V. due to the inability of water ligands to stabilize the Cu(I) state and for the reverse process the driving force is higher²¹¹ by 0.25 V. for the same reason. The slower rate associated with this back electron transfer process confirms that free energies for electron transfer in this system greater than 1.1 V. display the inverse dependence on driving force typical for inverted region behaviour. The lower efficiency of electron transfer and apparently longer lifetime of the protonated excited state can be accounted for by the more efficient protonation from coordinated water molecules in this complex.

Figure 5.21 displays the emission lifetime, least squares fit and residuals for the aquo copper complex of ligand 13 in acetonitrile. An emission lifetime of 81 ± 1 ps was obtained for this complex with no evidence of a long component due to emission from the protonated excited state observed under these conditions. Time was not available to carry out transient absorption studies of this complex but with a driving force estimated²¹² at +1.43 V for electron transfer quenching of the chromophore excited state and the similarity to the previously discussed copper complexes, this is presumed to be the quenching mechanism here. If the bisimidazolyl coordinated metal quencher site is assumed to be approximately equivalent to that in the bipyridyl coordination site in the previously discussed copper complexes, then equation 1.13 may be used to determine a value of β for this system. Values of 0.34 and $0.59 \text{ \AA}^{-1}$ are obtained for a through bond ($\approx 5 \text{ \AA}$) and through space ($\approx 3 \text{ \AA}$) electron transfer process respectively. For nonadiabatic electron transfer in covalently linked donor-acceptor pairs, typical values of β have been estimated to be of the order of 1 and $2 \text{ \AA}^{-1}$ for through bond and through space electron transfer respectively.³¹ Further studies of this and similar complexes would be very interesting.

Figure 5.21 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for $(13)(\text{H}_2\text{O})_2\text{Cu}(\text{II})(\text{CF}_3\text{SO}_3)_2$ in acetonitrile (9.0×10^{-4} M); streak camera speed of 2.67 ps/channel

6. Co(III) CHROMOPHORE QUENCHER COMPLEXES.

6.1 $(\text{NH}_3)_4\text{Co(III)}$ complexes.

Several attempts were carried out to prepare the bispyridyl coordinated tetraamminecobalt(III) complex of the chromophore ligand by an analogous technique to that used for the non-chromophore ligand noted in chapter 2, page 41. Acetone or sulfolane solutions of the chromophore ligand and the very labile pentaamminecobalt(III) triflate complex⁸⁵ were first made slightly acidic (to a "pH" of approximately 5–6) by the addition of trace amounts of triflic acid. The two solutions were then mixed and stirred at room temperature for times ranging from minutes to several days. The resulting brown complex was precipitated from solution by the addition of a five-fold volume of diethyl ether to the rapidly stirred solution. The precipitate was then isolated by vacuum filtration, redissolved in a minimum of acetone, filtered and placed in a sealed container with an adjacent beaker of diethyl ether and the ether was allowed to diffuse into the acetone solution of the impure complex at room temperature or in the refrigerator for times varying from hours to days. Recrystallization of the complex was also carried out in acetonitrile, anhydrous methanol and absolute ethanol by a similar technique. The resulting microcrystalline precipitates that deposited were then isolated by filtration and vacuum dried at room temperature. In all cases, precautions were taken to carry out all manipulations in a dark room including the preparation of analytical samples for ^1H NMR, FTIR and UV-visible spectroscopy. Spectral absorptions on the FTIR and ^1H NMR spectra displayed features characteristic of a large degree of ammine ligand loss depending on the length of the reaction and number of manipulations carried out. Elemental analysis was carried out on a sample of small golden cubes which were isolated from one of the methanol/diethyl ether solutions. The analysis confirmed that the isolated complex was in fact a tris chelated cobalt complex of the chromophore ligand. X-ray crystal structure determination was also

attempted on this sample. However, the crystals proved to be unsuitable.

Based on the observation of this very rapid reaction as shown in figure 3.2 and the absence of amines in the isolated product, a mechanism of sequential ammine loss from a 5-coordinate Co(II) complex is proposed.²¹³ This is shown in figure 6.1 in which the excited state of the coordinated ligand is oxidatively quenched by Co(III) to form a charge separated state consisting of a radical cation and a very labile Co(II) quencher site. This may then undergo rapid ammine loss in the presence of trace acid before back electron transfer can occur.

6.2 Co(III)(CL)₃ complexes.

As shown in chapter 2, the triflate salt of [(CL)₃Co(III)]³⁺ was found to give a better elemental analysis than the chloride or hexafluorophosphate salts and was therefore studied in more detail. Cyclic voltammetry of this complex was carried out in 0.1 M tetrabutylammonium hexafluorophosphate acetonitrile solution using a platinum working electrode as shown in figure 6.2

Figure 6.2 Cyclic voltammogram of [(CL)₃Co(III)](CF₃SO₃)₃ (1.0×10^{-3} M) in 0.1 M tetrabutylammonium hexafluorophosphate acetonitrile solution. Pt working and counter electrode. Ag reference electrode. Internally referenced against the ferrocene/ferrocenium ion redox couple. Scan speed = 100 mV/s.

Figure 6.1

Proposed mechanism for the formation of $[(\text{CL})_3\text{Co}^{(\text{III})}]^{3+}$ from photolysis of $[(\text{NH}_3)_5\text{Co}^{(\text{III})}(\text{CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)_2$ in the presence of excess CL in acetone with added trace triflic acid.

The irreversible ligand oxidation and ligand reduction are observed with peak potentials of +1.45 and -1.16 V respectively. The additional cathodic peak at -0.76 V has been assigned to the Co(III/II) couple. The rather large negative value for this couple²¹⁴ may be ascribed to an increased steric restriction toward formation of a tetrahedral Co(II) species due to steric constraints imparted on the complex by the ligands. A similar effect is observed²¹⁵ for the Ni(III/II) couple in complexes with macrocyclic ligands where the Ni(III) complex becomes more difficult to reduce to the square planar Ni(II) complex as the octahedral coordination sphere becomes more rigid due to increasing denticity of the macrocycle.

Table XV lists a summary of the ¹H NMR, UV-visible and electrochemical data for the triflate, chloride and hexafluorophosphate salts of this complex and the related tetraamminecobalt(III) complex of the non-chromophore ligand. The latter complex exhibits proton resonances in the 2.5 to 4 ppm range due to the cis and trans ammine ligands and both complexes exhibit a single resonance at 5 ppm due to the methylene protons. In addition, a weak ligand field transition may be observed in [a₄Co(III)(L)] (where a = NH₃) at 521 nm that is not easily observed in the tris ligated complexes due to the tail of the intense band at 419 nm. The Co(III/II) couple for this complex is found at -0.95 V suggesting that it is the rigidity of the ligand and not its' bulkiness that leads to a more negative Co(III) reduction potential.

Fluorescence emission quenching of this complex in which the ligand to metal ion ratio is 3:1 displayed a nonlinear excitation intensity dependence making interpretation very difficult. This was further complicated by large self absorption effects due to the protonated ligand even at 5×10^{-5} M concentrations. However, no emission due to the neutral ligand excited state could be observed suggesting that either quenching was occurring or the excited state species were protonated completely as in the case of the zinc complex.

Table XV ^1H NMR, UV-visible and electrochemical data for CL, L, $[\text{Co}(\text{III})(\text{CL})_3]\text{X}_3$ and $[\text{a}_4\text{Co}(\text{III})(\text{L})](\text{CF}_3\text{SO}_3)_3^a$

complex or ligand	^1H NMR data δ (vs TMS) [integration]	UV-vis data λ/nm (log ϵ)	Echem data ^b E_p / V vs NHE
CL	6.94 singlet [2] phenyl 7.24 singlet [1] NH 7.27 triplet [2] 7.90 doublet [2] 8.52 doublet [2] 8.69 singlet [2]	204 (4.85) 223 (4.71) 262 (4.45) 268 (4.45) 282 (4.37) 367 (4.06) 418 (3.87)	$E^{\text{ox}}_{(\text{L}^+/\text{L})}$ +1.45 $E^{\text{red}}_{(\text{L}/\text{L}^-)}$ -1.60
$[\text{Co}(\text{III})(\text{CL})_3](\text{CF}_3\text{SO}_3)_3$	7.51 singlet [2] phenyl 8.8 broad singlet [1] NH 7.77 triplet [2] 7.73 doublet [2] 9.98 doublet [2] 10.01 singlet [2]	207 (4.57) 233 (4.35) 248 (4.30) 286 (4.28) 365 (3.76) 419 (4.04)	$E^{\text{ox}}_{(\text{L}^+/\text{L})}$ +1.45 $E^{\text{red}}_{(\text{Co}(\text{III})/\text{Co}(\text{II}))}$ -0.76 $E^{\text{red}}_{(\text{L}/\text{L}^-)}$ -1.16
$[\text{Co}(\text{III})(\text{CL})_3]\text{Cl}_3$	7.56 singlet [2] phenyl 7.86 triplet [2] 7.76 doublet [2] 9.99 doublet [2] 10.32 singlet [2]	203 (5.05) 233 (4.74) 246 (4.69) 270 (4.61) 285 (4.65) 365 (4.16) 419 (4.38)	c
$[\text{Co}(\text{III})(\text{CL})_3](\text{PF}_6)_3$	7.51 singlet [2] phenyl 8.8 broad singlet [1] NH 7.77 triplet [2] 7.73 doublet [2] 9.99 doublet [2] 10.04 singlet [2]	205 (4.99) 233 (4.68) 246 (4.60) 268 (4.51) 285 (4.56) 365 (4.02) 419 (4.31)	c
L	7.43 singlet [2] phenyl 6.79 br singlet [2] phenyl 7.23 multiplet [2] 7.77 doublet [2] 8.48 singlet [2] 8.64 singlet [2]	226 (4.73) 263 (4.50) 298 (4.09) sh 321 (4.07) sh	$E^{\text{ox}}_{(\text{L}^+/\text{L})}$ c $E^{\text{ox}}_{(\text{L}/\text{L}^-)}$ -1.48
$[\text{a}_4\text{Co}(\text{III})(\text{L})](\text{TFMS})_3$	7.54 singlet [2] phenyl 6.85 singlet [2] phenyl 8.9 broad singlet [1] NH 7.25 multiplet [2] 7.83 doublet [2] 9.96 singlet [2] 10.01 singlet [2]	205 (4.8) 229 (4.6) 268 (4.6) 304 (4.2) sh 320 (4.1) sh 521 (1.8)	$E^{\text{ox}}_{(\text{L}^+/\text{L})}$ c $E^{\text{ox}}_{(\text{Co}(\text{III})/\text{Co}(\text{II}))}$ -0.95 $E^{\text{red}}_{(\text{L}/\text{L}^-)}$ d

- a ^1H NMR from d_6 -DMSO solutions (aromatic and indole N-H region listed only), UV-vis data recorded in acetonitrile except for $[\text{Co}(\text{III})(\text{CL})_3]\text{Cl}_3$ which was recorded in water, electrochemical data obtained in acetonitrile as described in text except for $[\text{a}_4\text{Co}(\text{III})(\text{L})](\text{TFMS})_3$ which was recorded in methylene chloride
- b E_{peak} measured only as all ligands and cobalt complexes displayed irreversible electrochemistry
- c not observed up to anodic limit of solvent/electrolyte system
- d not observed up to cathodic limit of methylene chloride solvent
- e not measured

Fluorescence emission lifetime measurements were carried out on both the cobalt and zinc complex in methanol and are shown in figures 6.3 and 6.4. The cobalt complex does not exhibit a rapid emission decay component as seen in the copper complexes. The emission decays with a lifetime of 6.98 ± 0.15 ns as compared to 8.19 ± 0.21 ns for the zinc complex under similar conditions. The protonated ligand emission is dominant and most likely precludes observation of a rapid decay component. Additional experiments in which narrow bandpass filters are used to isolate the emission from the protonated excited state and the neutral excited state would aid in the interpretation of this system.

Transient absorption spectra of the cobalt complex in acetonitrile were recorded 20 ps and 100 ps after the pump pulse. These spectra, shown in figure 6.5 are dominated by a large positive absorbance change at 625 nm due to the protonated ligand and a large negative absorbance change at 485 nm due to the enhanced emission from this same species. In addition, a small absorption can be seen on the 20 ps spectrum at 485 nm that may be due to the ligand cation radical. This is similar to the behaviour of the copper complex in methanol as shown in figure 5.19. Further studies are required to definitively prove the involvement of the ligand cation radical and hence show that intramolecular electron transfer is the quenching mechanism operative in this case.

Figure 6.3 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for $[(\text{CL})_3\text{Co}(\text{III})](\text{CF}_3\text{SO}_3)_3$ in methanol (2.0×10^{-3} M); streak camera speed of 26.66 ps/channel

Figure 6.4 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for $(\text{CL})(\text{H}_2\text{O})_2\text{Zn}(\text{II})(\text{ClO}_4)_2$ in methanol ($2.0 \times 10^{-3} \text{ M}$): streak camera speed of 26.66 ps/channel

Figure 6.5 Transient absorption spectra of $[(\text{CL})_3\text{Co}(\text{III})](\text{CF}_3\text{SO}_3)_2$ ($1.0 \times 10^{-3} \text{ M}$) in acetonitrile

7. Conclusion

It has been shown definitively that a charge separated state involving an oxidized organic chromophore and a reduced metal acceptor can be produced by intramolecular electron transfer provided that the redox and spectroscopic properties of the chromophore quencher complex have been appropriately designed in. In order for a system of this type to be useful for photocatalytic applications, several conditions must be satisfied²¹⁶:

- i) dissociation of the photo-active ligand does not occur.
- ii) both the excited state and the subsequent charge separated state are not quenched by an energy transfer mechanism.
- iii) H^+ and H^- transfer on the ligands are slow compared to electron transfer.

The system prepared for this study fulfills the first two requirements but proton transfer to the chromophore excited state occurs much too rapidly in these complexes for charge separation to be efficient. This can be circumvented in future complexes by avoiding the use of basic iminium functionalities on the chromophore ligand. Another factor not considered above is that the lifetime of the charge separated state is too short at 300 ps to carry out a chemical reaction at the metal center. On this time scale, even trivial ligand dissociation is not competitive with back electron transfer. To facilitate the formation of a prolonged charge separated state, the back electron transfer rate must be reduced and the most convenient method to delay this inverted region process would be to increase the thermodynamic driving force. This can be easily accomplished by dealkylating the *n*-butoxy moieties on the chromophore to form a hydroquinone-like chromophore. The resulting ligand would have a significantly higher excited state redox potential of approximately 2.8 V. and in addition would function as a chemically reversible 2 e^- reservoir. Other methods to vary the thermodynamics in this system involve

changing the photoredox properties of the chromophore by covalent attachment of electronegative moieties or the redox properties of the metal quencher site by appropriate ligand perturbation.

8.0

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$$k_q \approx \frac{1}{\tau \times [O_2]} = k_0 + g_1 k_d P_1 + g_3 k_d P_3$$

$$= \frac{1}{9} k_d \{k_{et}/(k_{et} + k_d)\} + \frac{1}{3} k_d \{k_{isc}/(k_{isc} + k_d)\}$$

- where k_0 is the triplet radiative decay rate which is negligible, g_1 and g_3 are spin statistical factors, k_d is the diffusion controlled rate constant and P_1 and P_3 are the probabilities of oxygen quenching per encounter by energy transfer (P_1) and intersystem crossing (P_3). Therefore maximum rates for triplet quenching by energy transfer, triplet quenching by intersystem crossing and singlet quenching should be $1/9(k_d)$, $1/3(k_d)$ and k_d respectively where k_d is typically $3 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ for most organic solvents.
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191. According to Smoluchowski^{191b}, this type of transient quenching due to rapid reaction of excited state species and quencher in close proximity should lead to an upward curvature in the Stern-Volmer plot. This is given by:

$$k_t = 4\pi D_{ab} R_0 N' [1 + \{R_0 / (\pi D_{ab} t)^{1/2}\}]$$

where D_{ab} is the sum of diffusional coefficients for each species determined by the Stokes-Einstein equation, R_0 is the sum of the molecular radii, N' is Avagadro's number divided by 1000 and $R_0 / (\pi D_{ab} t)^{1/2}$ is the transient term in the equation. In cases where R_0 is large or D_{ab} is small such as the case here, the transient term becomes significant especially at short times.

The lack of observation of upward curvature on the Stern–Volmer plot may be due to the limited concentration range under which it spans.

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212. $\Delta E^* = E_r(\text{Cu}^{2+/+}) - E_o(\text{CL}^{+/*}) = -0.43 - (-1.86) = +1.43 \text{ V}$.
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For CL, B2PI and HQPVP, the following rates (in s^{-1}) are calculated:

	CL	B2PI	HQPVP
$k_{\text{obs}} =$	2.63×10^8	2.71×10^8	3.02×10^8
$k_{\text{isc}} =$	5×10^7	5×10^7	$> 5 \times 10^7$

	CL	B2PI	HQPVP
$k_r =$	1.1×10^8	$\geq 1.2 \times 10^8$	$\geq 2 \times 10^8$
$k_{ic} =$	1×10^8	$< 1 \times 10^8$	$< 5 \times 10^7$

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versus pathlength travelled from the front of the sample cell to the back in radial space. Ignoring additional losses due to reflection and refraction, this leads to a reduction of approximately 65 %. Therefore the two factors would be reduced as follows:

$$\text{total reduction} = 39 \% = 2x + (0.65)x$$

which gives $x = 14.7$, so the effective sample volume would be reduced by $2x$ or 29.4 % (≈ 29 %) and the effective number of incident pump photons would be reduced by $0.65x$ or 9.6% ($\approx 10\%$).

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APPENDIX A

Molecular Models of ligands in different coordination environments

In order to gain a better understanding of the factors that influence the stability of both the coordinated ligands and complexes, molecular models of the 2-, 3- and 4-methylpyridyl derivatives of the chromophore in different coordination environments were calculated using a commercially available modelling program. Chem3DTM by Cambridge Scientific Computing, Inc. was used to determine both the chelate ring geometry and coordination environment for ligands 5, 6 and 7 ligating either an octahedral or a tetrahedral metal ion in a bis(pyridyl) mode. In addition, the geometry of ligand 5 and 7 coordinating an octahedral metal ion in a tridentate, bis(pyridyl)-indole mode was also examined as this mode of coordination seemed feasible by the proximity of the indole nitrogen to the pyridyls.

As a crystal structure of the ligands or the complexes were not available, the structural data for the closely related ligand, bis-1,3-(2-pyridylimine)-isoindoline²¹⁷ was used for optimization of the ligand structure and a typical metal-pyridine nitrogen bond distance of 200 pm with ideal octahedral or tetrahedral geometry was used for optimization of the complexes. In the case of the tetragonally distorted octahedral geometry that may be expected for many copper(II) complexes, a combination of one axial and one equatorial ligating pyridyl was used with nitrogen-copper bond lengths of 240 pm and 200 pm respectively. For the square pyramidal copper(II) complex, the ligand was again coordinated in an axial-equatorial mode with axial and equatorial copper-nitrogen bond lengths of 210 pm and 200 pm respectively. In addition, the trans equatorial positions were assumed to be at an angle of 165 degrees to each other as is found for many^{66,218} copper(II) complexes that possess this geometry as opposed to the ideal 180 degrees expected for a true square pyramidal structure.

All of the structures were minimized for structural error using a limiting

RMS gradient change of 0.100. Limiting values less than this led to exceedingly long computations as well as final RMS errors on the structures that were only 0.5 to 1 % less than the values listed in table XVI. In table XVI, chelate ring geometry was defined by three parameters, namely the indole-C/imine-N/methylene-C and imine-N/methylene-C/pyridyl-C bond angles and the pyridine ring deformation which is defined as the average amount of non-coplanarity in each of the pyridine rings. For the complexes, an additional set of parameters was defined that characterize the coordination environment around the metal and include the metal-nitrogen bond lengths and the average cis and trans (to pyridine) ligand bond angles as noted. Ligands 5, 6 and 7 which contain hydrogens at the 4,7 position were used for all the structural minimizations as the inclusion of methoxy or n-butoxy groups was found to have no effect on the final RMS error and made observation of several of the model figures to be difficult.

For all three free ligands, chelate ring geometries were found to be within 1 or 2 % of the ideal values and the pyridine ring deformation was found to be nil in all three cases. The RMS error on the final structural models was found to be approximately 12 % in all three cases.

For the 3-substituted ligands (5, 8 and 11), an octahedral or tetragonally distorted octahedral coordination environment with RMS errors of less than 12 % were found to be preferred over both tetrahedral and square pyramidal geometries which have RMS errors of 16.3 and 16.0 % respectively. It should be noted however that the pyridine ring deformation was found to be quite low (< 10 pm) for this ligand in all of the bis-pyridyl ligated complexes and the coordination environment was typically within 1 % of that expected. Refer to figures A.1, A.2, A.9 and A.10 and table XVI for details of the structures.

For the 4-substituted ligands (6, 9 and 12), both a tetrahedral and an octahedral bis-pyridyl geometry may be accommodated but a rather large

deformation of 131 pm and 155 pm respectively must be imparted on the pyridine rings in order for this ligand to coordinate. This can be easily seen in figures A.4 c,d and A.5 c,d where a large puckering of both of the pyridine rings is observed. A similar result was obtained for this ligand using ball and stick molecular models in which severe strain was imparted on the chelate ring in order to force a bis-pyridyl coordination environment. If the position of one of the imine bonds is shifted closer to the pyridyl group, then most of the ring deformation is lost and bis-pyridyl coordination seems more feasible (not shown, average RMS error = 13.1 %, average pyr ring def. = 14 pm). This was discussed previously in section 3.4 on earlier work with ruthenium(II) complexes and ligands 6 and 9.

Although the 2-substituted ligands (7 and 10) were prepared mainly to aid in the characterization of the other ligands, molecular models of complexes of these ligands coordinated to an octahedral or tetrahedral symmetry metal site reveal that this ligand can easily coordinate in both geometries. The use of this ligand for chromophore-quencher complexes was however negated as it was feared that the indole nitrogen would be in very close proximity to the metal ion and may coordinate to form a tridentate type complex in which the electronic ground states of both the chromophore and metal quencher site were strongly coupled. As can be seen in table XVI and figure A.8, this tridentate coordination can be easily accommodated by this ligand with little additional strain imparted on the chelate ring geometry and only small perturbations to the coordination environment around the metal. For comparison, tridentate coordination of the 3-substituted ligand (5), shown in figure A.3, results in large deviations of the chelate ring geometry from ideal and a very large RMS error on the structurally minimized model of more than 60 %.

Table XVI Optimized geometries for ligands and ligands coordinated to metals in different coordination environments^a

ligand ^b	chelate ring geometry ^c			coordination environment			RMS
	parameter	ideal	model	parameter	typical	model	Error
5, 8 or 11	$\angle \text{C=N-CH}_2$ $\angle \text{N-CH}_2\text{-py}$ Pyr ring def	120 109.47 0	119.85 110.53 0.000 Å				12.176
6, 9 or 12	$\angle \text{C=N-CH}_2$ $\angle \text{N-CH}_2\text{-py}$ Pyr ring def	120 109.47 0	118.36 110.08 0.000 Å				11.978
7 or 10	$\angle \text{C=N-CH}_2$ $\angle \text{N-CH}_2\text{-py}$ Pyr ring def	120 109.47 0	121.25 110.42 0.000 Å				12.270
complex							
5, 8 or 11 bis(pyridyl) Oh	$\angle \text{C=N-CH}_2$ $\angle \text{N-CH}_2\text{-py}$ Pyr ring def	120 109.47 0	119.75 109.91 0.000 Å	$\angle \text{cis py-py}$ $\angle \text{trans py-X}$ M-N	90 180 2.00 Å	91.19 179.45 2.000 Å	11.892
5, 8 or 11 bis(pyridyl) Td	$\angle \text{C=N-CH}_2$ $\angle \text{N-CH}_2\text{-py}$ Pyr ring def	120 109.47 0	121.57 104.26 0.009 Å	$\angle \text{cis py-py}$ $\angle \text{adj py-X}$ M-N	109.47 109.47 2.00 Å	109.09 109.58 2.001 Å	16.328
5, 8 or 11 Octahedral (tridentate) bis(pyridyl)indole	$\angle \text{C=N-CH}_2$ $\angle \text{N-CH}_2\text{-py}$ Pyr ring def	120 109.47 0	134.31 102.99 0.155 Å	$\angle \text{cis py-py}$ $\angle \text{trans py-X}$ $\angle \text{trans indole-X}$ M-pyridine M-indole	90 180 180 2.00 Å 2.20 Å	90.51 177.88 175.78 1.990 Å 2.229 Å	60.958
6, 9 or 12 bis(pyridyl) Oh	$\angle \text{C=N-CH}_2$ $\angle \text{N-CH}_2\text{-py}$ Pyr ring def	120 109.47 0	119.27 109.47 0.131 Å	$\angle \text{cis py-py}$ $\angle \text{trans py-X}$ M-N	90 180 2.00 Å	90.43 180.00 2.000 Å	16.746
6, 9 or 12 bis(pyridyl) Td	$\angle \text{C=N-CH}_2$ $\angle \text{N-CH}_2\text{-py}$ Pyr ring def	120 109.47 0	119.47 110.06 0.157 Å	$\angle \text{cis py-py}$ $\angle \text{adj py-X}$ M-N	109.47 109.47 2.00 Å	107.74 109.83 2.000 Å	16.764
7 or 10 bis(pyridyl) Oh	$\angle \text{C=N-CH}_2$ $\angle \text{N-CH}_2\text{-py}$ Pyr ring def	120 109.47 0	118.37 109.78 0.003 Å	$\angle \text{cis py-py}$ $\angle \text{trans py-X}$ M-N	90 180 2.00 Å	91.06 179.57 2.001 Å	12.039
7 or 10 bis(pyridyl) Td	$\angle \text{C=N-CH}_2$ $\angle \text{N-CH}_2\text{-py}$ Pyr ring def	120 109.47 0	120.65 108.70 0.014 Å	$\angle \text{cis py-py}$ $\angle \text{adj py-X}$ M-N	109.47 109.47 2.00 Å	108.12 109.97 1.999 Å	12.138
7 or 10 Octahedral (tridentate) bis(pyridyl)indole	$\angle \text{C=N-CH}_2$ $\angle \text{N-CH}_2\text{-py}$ Pyr ring def	120 109.47 0	119.63 112.55 0.010 Å	$\angle \text{cis py-py}$ $\angle \text{trans py-X}$ $\angle \text{trans indole-X}$ M-pyridine M-indole	90 180 180 2.00 Å 2.20 Å	93.95 176.77 176.11 1.999 Å 2.198 Å	19.843
5, 8 or 11 bis(pyridyl) to Cu(II) tetrag. distorted Oh (axial-equatorial)	$\angle \text{C=N-CH}_2$ $\angle \text{N-CH}_2\text{-py}$ Pyr ring def	120 109.47 0	119.69 108.91 0.005 Å	$\angle \text{cis py-X}$ $\angle \text{trans py-X}$ $\angle \text{axN-eqN}$ M-N axial M-N equatorial	90 180 90 2.40 Å 2.00 Å	89.97 179.89 90.70 2.400 Å 2.000 Å	11.912
5, 8 or 11 bis(pyridyl) to Cu(II) square pyramidal (axial-equatorial)	$\angle \text{C=N-CH}_2$ $\angle \text{N-CH}_2\text{-py}$ Pyr ring def	120 109.47 0	120.26 104.33 0.000 Å	$\angle \text{cis py-X}$ $\angle \text{trans py-X}$ $\angle \text{axN-eqN}$ M-N axial M-N equatorial	90 165 97.5 2.10 Å 2.00 Å	88.98 164.52 97.65 2.103 Å 2.002 Å	16.025

a) Using Chem3DTM by Cambridge Scientific Computing, Inc. b) Oh is an octahedral and Td is a tetrahedral coordination environment. See text for details. c) These 3 values give an indication as to the amount of steric strain that is imparted on the chelate ring by the act of coordination. Pyr ring def is the average amount of non-coplanarity in the C and N atoms of both pyridine rings.

a perpendicular to indole

b coordination sphere

c through one py-metal plane

d through other py-metal plane

Figure A.1

Molecular model of 1,3-bis((3'-pyridylmethyl)imino)isoindoline in a bis-pyridyl bidentate octahedral coordination environment.

a perpendicular to indole **b** coordination sphere **c** through one py-metal plane **d** through other py-metal plane **Figure A.2**

Molecular model of 1,3-bis((3'-pyridylmethyl)imino)isoindoline in a bis-pyridyl bidentate tetrahedral coordination environment.

a perpendicular to indole

b coordination sphere

c through one py-metal plane

d through other py-metal plane

Figure A.3

Molecular model of 1,3-bis((3'-pyridylmethyl)imino)isoindoline in a bis-pyridyl, mono-indole tridentate octahedral coordination environment.

a perpendicular to indole

b coordination sphere

c through one py-metal plane

d through other py-metal plane

Figure A.4

Molecular model of 1,3-bis((4'-pyridylmethyl)imino)isoindoline in a bis-pyridyl bidentate octahedral coordination environment.

a perpendicular to indole

b coordination sphere

c through one py-metal plane

d through other py-metal plane

Figure A.5

Molecular model of 1,3-bis((4'-pyridylmethyl)imino)isoindoline in a bis-pyridyl bidentate tetrahedral coordination environment.

a perpendicular to indole

b coordination sphere

c through one py-metal plane

d through other py-metal plane

Figure A.6

Molecular model of 1,3-bis((2'-pyridylmethyl)imino)isoindoline in a bis-pyridyl bidentate octahedral coordination environment.

a perpendicular to indole

b coordination sphere

c through one py-metal plane

d through other py-metal plane

Figure A.7

Molecular model of 1,3-bis((2'-pyridylmethyl)imino)isoindoline in a bis-pyridyl bidentate tetrahedral coordination environment.

Figure A.8

Molecular model of 1,3-bis((2'-pyridylmethyl)imino)isoindoline in a bis-pyridyl, mono-indole tridentate octahedral coordination environment.

a perpendicular to indole

b coordination sphere

c through one py-metal plane

d through other py-metal plane

Figure A.9

Molecular model of 1,3-bis((3'-pyridylmethyl)imino)isoindoline in an axial-equatorial bis-pyridyl tetragonally distorted octahedral coordination environment.

Figure B.17 Infrared spectrum of 1,3-bis((2'-pyridylmethyl)imino)isoindoline (7) (KBr pellet). Absorption at 2300 cm^{-1} due to atmospheric CO_2 .

Figure B.18 Infrared spectrum of 1,3-bis((3'-pyridylmethyl)imino)isoindoline (5 or L) (KBr pellet). Absorption at 2300 cm^{-1} due to atmospheric CO_2 .

APPENDIX B

Figures B.1 to B.67 (IR, MS and NMR spectra)

Figure B.1 Infrared spectrum of 1,4-di-n-butoxy-2,3-dicyanobenzene (2) (KBr pellet)

Figure B.2 Infrared spectrum of 4,7-di-n-butoxy-1,3-diiminoisoindoline (3) (KBr pellet)

Figure B.3

200 MHz ^1H NMR spectrum of 1,4-di-n-butoxy-2,3-dicyanobenzene (2) in CDCl_3 . CHCl_3 impurity resonance at 7.09 ppm.

Figure B.4

200 MHz ^{13}C NMR spectrum of 1,4-di-n-butoxy-2,3-dicyanobenzene (2) in CDCl_3 . CDCl_3 resonance at 77.06 ppm.

Figure B.5 C.I. mass spectrum of 1,4-di-n-butoxy-2,3-dicyanobenzene (2)

Figure B.6 E.I. and C.I./ether mass spectrum of 4,7-di-n-butoxy-1,3-diiminoisoindoline (3)

Figure B.7

200 MHz ^1H NMR spectrum of 4,7-di-*n*-butoxy-1,3-diiminoisoindoline (**3**) in CDCl_3 . CHCl_3 impurity resonance at 7.12 ppm.

Figure B.8

200 MHz ^{13}C NMR spectrum of 4,7-di-n-butoxy-1,3-diiminoisoindoline (3) in CDCl_3 . CDCl_3 resonance at 77.12 ppm.

Figure B.9 Infrared spectrum of 1,2-dicyano-3,6-dimethoxybenzene (2b) (KBr pellet)

Figure B.10 Infrared spectrum of 1,3-diimino-4,7-dimethoxyisoindoline (4) (KBr pellet). Absorption at 2300 cm^{-1} due to atmospheric CO_2 .

Figure B.11 E.I. mass spectrum of 1,2-dicyano-3,6-dimethoxybenzene (2b)

Figure B.12 E.I. mass spectrum of 1,3-diimino-4,7-dimethoxyisindoline (4)

Figure B.13 200 MHz ^1H NMR spectrum of 1,2-dicyano-3,6-dimethoxybenzene (2b) in CDCl_3 . CHCl_3 and H_2O impurity resonances at 7.24 and 1.53 ppm.

Figure B.14 200 MHz ^{13}C NMR spectrum of 1,2-dicyano-3,6-dimethoxybenzene (2b) in d_6 -DMSO. DMSO resonance at 39.5 ppm.

Figure B.15

200 MHz ^1H NMR spectrum of 1,3-diimino-4,7-dimethoxyisoindoline (**4**) in CD_3OD . CD_3OH impurity resonance 4.88.

Figure B.16

200 MHz ^{13}C NMR spectrum of 1,3-diimino-4,7-dimethoxyisoindoline (4) in d_6 -DMSO. DMSO resonance at 39.5 ppm.

Figure B.17 Infrared spectrum of 1,3-bis((2'-pyridylmethyl)imino)isoindoline (7) (KBr pellet). Absorption at 2300 cm^{-1} due to atmospheric CO_2 .

Figure B.18 Infrared spectrum of 1,3-bis((3'-pyridylmethyl)imino)isoindoline (5 or L) (KBr pellet). Absorption at 2300 cm^{-1} due to atmospheric CO_2 .

Figure B.19 Infrared spectrum of 1,3-bis((4'-pyridylmethyl)imino)isoindoline (6) (KBr pellet)

Figure B.20 C.I./ether mass spectrum of 1,3-bis((2'-pyridylmethyl)imino)isoindoline (7)

Figure B.21

200 MHz ^{13}C NMR spectrum of 1-imino-3-(2'-pyridylmethylimino)-isoindoline in d_6 -DMSO. DMSO resonance at 39.1 ppm.

Figure B.22 100 MHz ^1H NMR spectrum of 1,3-bis((2'-pyridylmethyl)imino)isoindoline (7) in CDCl_3 . H_2O impurity resonance at 4.2, ppm.

Figure B.23

200 MHz ^{13}C NMR spectrum of 1,3-bis((2'-pyridylmethyl)imino)-isoindoline (7) in CDCl_3 . CDCl_3 resonance at 77.0 ppm.

Figure B.24 C.I./ether mass spectrum of 1,3-bis((3'-pyridylmethyl)imino)isoindoline (5 or L)

Figure B.25 C.I./ether mass spectrum of 1,3-bis((4'-pyridylmethyl)imino)isoindoline (6)

Figure B.26

200 MHz ^1H NMR spectrum of 1,3-bis((3'-pyridylmethyl)imino)isoindoline (5 or L) in d_6 -DMSO. H_2O impurity resonance at 3.44 ppm.

Figure B.27 200 MHz ^{13}C NMR spectrum of 1,3-bis((3'-pyridylmethyl)imino)-isoindoline (S or L) in CDCl_3 . CDCl_3 resonance at 77.1 ppm.

Figure B.28

200 MHz ^1H NMR spectrum of 1,3-bis((4'-pyridylmethyl)imino)isoindoline (6) in CDCl_3 . Impurity gives doublets at 8.75 and 7.61 ppm.

Figure B.29 200 MHz ^{13}C NMR spectrum of 1,3-bis((4'-pyridylmethyl)imino)isoindoline (6) in CDCl_3 . CDCl_3 resonance at 77.1 ppm.

Figure B.30 Infrared spectrum of 4,7-di-n-butoxy-1,3-bis((2'-pyridylmethyl)imino)-isoindoline (**10**) (KBr pellet)

Figure B.31 Infrared spectrum of 4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)imino)-isoindoline (**8** or **CL**) (KBr pellet). Absorption at 2300 cm^{-1} due to atmospheric CO_2 .

Figure B.32 Infrared spectrum of 4,7-di-n-butoxy-1,3-bis((4'-pyridylmethyl)imino)-isoindoline (9) (KBr pellet). Absorption at 2300 cm^{-1} due to atmospheric CO_2 .

Figure B.33 C.I./ether mass spectrum of 4,7-di-n-butoxy-1,3-bis((2'-pyridylmethyl)imino)-isoindoline (10)

Figure B.34

200 MHz ^1H NMR spectrum of 4,7-di-n-butoxy-1,3-bis((2'-pyridylmethyl)-imino)-isoindoline (10) in CDCl_3 .

Figure B.35

200 MHz ^{13}C NMR spectrum of 4,7-di-n-butoxy-1,3-bis((2'-pyridyl)methyl)-imino)isoindoline (10) in CDCl_3 . CDCl_3 resonance at 77.1 ppm.

Figure B.36 C.I./ether mass spectrum of 4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)imino)-isoindoline (8 or CL)

Figure B.37 C.I./ether mass spectrum of 4,7-di-n-butoxy-1,3-bis((4'-pyridylmethyl)imino)-isoindoline (9)

Figure B.38

200 MHz ^1H NMR spectrum of 4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)-imino)isoindoline (8 or CL) in CDCl_3 .

Figure B.39

200 MHz ^{13}C NMR spectrum of 4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)-imino)isoindoline (8 or CL) in CDCl_3 . CDCl_3 resonance at 77.1 ppm.

Figure B.40

200 MHz ^1H NMR spectrum of 4,7-di-n-butoxy-1,3-bis((4'-pyridylmethyl)imino)isoindoline (9) in CDCl_3 . CHCl_3 impurity resonance at 7.24 ppm.

Figure B.41

200 MHz ^{13}C NMR spectrum of 4,7-di-n-butoxy-1,3-bis((4'-pyridylmethyl)imino)isoindoline (**9**) in CDCl_3 . CDCl_3 resonance at 77.5 ppm.

Figure B.42 Infrared spectrum of 4,7-dimethoxy-1,3-bis((3'-pyridylmethyl)imino)-isoindoline (11) (KBr pellet)

Figure B.43 Infrared spectrum of 4,7-dimethoxy-1,3-bis((4'-pyridylmethyl)imino)-isoindoline (12) (KBr pellet)

Figure B.44 C.I./ether mass spectrum of 4,7-dimethoxy-1,3-bis(3'-pyridylmethyl)imino-indoline (11)

Figure B.45 C.I./ether mass spectrum of 4,7-dimethoxy-1,3-bis(4'-pyridylmethyl)imino-indoline (12)

Figure B.46

200 MHz ${}^1\text{H}$ NMR spectrum of 4,7-dimethoxy-1,3-bis((3'-pyridylmethyl)imino)isondoline (**11**) in CDCl_3 . CHCl_3 impurity resonance at 7.24 ppm.

Figure B.47

200 MHz ^1H NMR spectrum of 4,7-dimethoxy-1,3-bis((4'-pyridylmethyl)imino)isoindoline (**12**) in CDCl_3 . CHCl_3 impurity resonance at 7.24 ppm.

Figure B.48

200 MHz ${}^1\text{H}$ NMR spectrum of 4,7-dimethoxy-1,3-bis((4'-pyridylmethyl)-imino)isoindoline (**12**) in CDCl_3 . CDCl_3 resonance at 77.0 ppm.

Figure B.49 200 MHz ^1H NMR spectrum of 4,7-dimethoxy-1,3-bis((3'-propyl-N'-imidazolyl)-imino)isoindoline(14) in d_6 -DMSO. DMSO and H_2O resonances at 2.6 and 3.4 ppm.

Figure B.50

400 MHz ^{13}C NMR spectrum of 4,7-dimethoxy-1,3-bis((3'-propyl-N'-imidazolyl)imino)isoindoline(14) in d_6 -DMSO. DMSO resonance at 39.5 ppm.

Figure B.51

200 MHz ^1H NMR spectrum of an impure sample of 4,7-dihydroxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline (15) in CD_3OD .

Figure B.52

200 MHz ${}^1\text{H}$ NMR spectrum of diaquo(4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)imino)isoundoline)zinc(II)perchlorate (ZnCL-H_2) in d_6 -DMSO.

Figure B.53

200 MHz ^1H NMR spectrum of diaquo(4,7-di-n-butoxy-1,3-bis(3'-pyridylmethyl)iminoisoindolin-2-yl)zinc(II)perchlorate ($\text{ZnCL}\cdot\text{H}_2$) in d_3 MeCN

Figure B.54

200 MHz ${}^1\text{H}$ NMR spectrum of (tetraammine)(1,3-bis((3'-pyridylmethyl)imino)isomdoline)cobalt(III)triflate $((\text{NH}_3)_4\text{Co}(\text{L})(\text{CF}_3\text{SO}_3)_3)$ in d_6 -DMSO.

Figure B.55 Infrared spectrum of (1,3-bis((3'-pyridylmethyl)imino)isoindoline)-tetraamminecobalt(III)triflate ($[\text{CoL}_4](\text{CF}_3\text{SO}_3)_3$) (KBr pellet)

Figure B.56 Infrared spectrum of tris(4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline)cobalt(III)triflate ($(\text{Co}(\text{CL})_3(\text{CF}_3\text{SO}_3)_3)$) (KBr pellet)

Figure B.57

200 MHz ${}^1\text{H}$ NMR spectrum of tris(4,7-di-n-butoxy-1,3-bis((3'-pyridyl)methylamino)isondoline)cobalt(III)triflate ($\text{Co}(\text{Cl})_3(\text{CF}_3\text{SO}_3)_3$) in d_6 -DMSO.

Figure B.58 Infrared spectrum of tris(4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)-imino)isoindoline)cobalt(III)chloride ($\text{Co}(\text{Cl})_3\text{Cl}_3$) (KBr pellet)

Figure B.59 Infrared spectrum of tris(4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)-imino)isoindoline)cobalt(III)hexafluorophosphate ($\text{Co}(\text{Cl})_3(\text{PF}_6)_3$) (KBr pellet)

Figure B.60

Infrared spectrum of diaquo(4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)-imino)isoindoline)copper(II)triflate (CuCL-H₂) (KBr pellet)

Figure B.61 Infrared spectrum of aquo(1,3-bis((3'-pyridylmethyl)imino)isoindoline)copper(II)triflate ($\text{CuL} \cdot \text{H}_2\text{O}$) (KBr pellet)

Figure B.62 Infrared spectrum of (4,7-dibutyl-1,3-bis((3'-pyridylmethyl)imino)isoindoline)copper(II)triflate (CuL) (KBr pellet)

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PM-1 3½"x4" PHOTOGRAPHIC MICROCOPY TARGET
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Figure B.63 Infrared spectrum of diaquo(4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline)zinc(II)perchlorate ($\text{ZnCl} \cdot \text{H}_2$) (KBr pellet)

Figure B.64 Infrared spectrum in a 0.25 mm NaCl cell of neat acetonitrile blank for figures B.65 and B.66

Figure B.65 Infrared spectrum in a 0.25 mm NaCl cell of an acetonitrile solution of hexaaquocopper(II)triflate

Figure B.66 Infrared spectrum in a 0.25 mm NaCl cell of (4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline)copper(II)triflate (CuCl)

APPENDIX C

Calculation of corrected fluorescence spectra and quantum yields.

A method to calculate corrected fluorescence spectra is outlined that is based upon the suggestions advocated by Demas and Crosby. They suggest that corrected emission spectra be presented in units of relative quanta per unit frequency interval versus a linear energy scale. For reasons of simplicity and familiarity, the emission spectra shown in chapters 4 and 5 are of the uncorrected recorded data and are in the form of relative emission intensity versus wavelength. This technique is not compulsory for the presentation of spectra but is necessary for the determination of meaningful quantum yields. A comprehensive review of the topic is given by Demas and Crosby²¹⁹.

Quantum yields can be determined using standard solid scatterers such as MgO films, various solution scatterers, integrating spheres, photodiode quantum counters or by comparison with compounds of known quantum yield. All of the quantum yields calculated herein were determined by the latter technique using a 5×10^{-3} M quinine bisulphate in 0.1 N sulphuric acid solution as the quantum yield standard. Several precautions must be observed when determining quantum yields by this method such as the spectral distribution of the excitation source and resulting different incident light intensity, different refractive indices of the sample and standard solution, concentration related effects such as reductions in emission intensity due to self absorption and differences in the emission distribution of the sample and reference.

The spectral distribution of the Xenon lamp used for the fluorescence intensity measurements is similar to that shown in figure C.1, upper curve.²²⁰ The lower curve corresponds to the spectral output of a cool (or low pressure) source in which the atomic emission lines are enhanced relative to the broad background emission. The standard quinine bisulphate solution used has a "best" value for its'

Spectrum of 350 W xenon lamp.

Figure C.1 Spectral output of a typical Xenon lamp
 (after C. A. Parker, "Photoluminescence of Solutions",
 Elsevier Publishing Company, Amsterdam, 1968)

quantum yield of 0.546 for 365 nm excitation at 25°C.²¹⁹ All of the fluorescence measurements recorded using this excitation wavelength require no correction for incident light intensity. Fluorescence emission measurements recorded using an excitation wavelength of 415 nm were corrected for the greater incident light intensity at this wavelength by multiplying by a factor equivalent to the ratio of the intensity at 365 nm divided by the intensity at 415 nm.

$$\begin{aligned} \text{light intensity correction} &= J_{365} / J_{415} \\ &= \frac{1.4 \times 10^7 \text{ Einstein s}^{-1} \text{ ster}^{-1}}{3.3 \times 10^7 \text{ Einstein s}^{-1} \text{ ster}^{-1}} \\ &= 0.424 \end{aligned}$$

The different refractive indices of the standard solution and sample solution was corrected for in the following manner according to Demas and Crosby²¹⁹. The Xenon lamp was assumed to be a continuous point source and internal reflection was ignored. According to Snell's law,

$$I_1 = I_0 (n_1^2 / n_0^2)$$

where I_1 is the incident intensity through the sample, I_0 is the intensity through the quartz cell window and n_1 and n_0 are the respective refractive indices of the two media. It can be easily shown that if

$n_1 < n_0$, then I_1 is larger than I_0 and if

$n_1 > n_0$, then I_1 is smaller than I_0

Therefore, if the incident light intensity passing through the reference and the sample are compared, the I_0 and n_0 components due to the quartz cell factor out leaving

$$I_s = I_r (n_s^2 / n_r^2)$$

where I_s is the incident light intensity on the sample and I_r is the incident light intensity on the reference. In the case of an acetonitrile sample solution, n_s is 1.342

and for the reference 0.1 N H_2SO_4 solution, n_r is 1.334 which means $n_s > n_r$ and the incident light intensity would be about 1 % higher on the sample as compared with the reference solution. The subsequent emission from the sample or reference are less intense and cannot be considered a point source so the corresponding correction to the emission intensity is rather small and will be considered as negligible in this case. As a result of this, the measured quantum yields in acetonitrile were reduced by a factor of 1 %.

Of the other solvents used, the respective increases to the incident light intensity and the resulting reductions that should be applied to the measured quantum yields are 3 % for diethyl ether, 4 % for ethanol, 6 % for hexane and ethyl acetate, 11 % for THF and 14 % for cyclohexane and methylene chloride. Of the solvents used for emission measurements, only in methanol is the magnitude of the incident light intensity on the sample reduced by 2 % as compared to the reference. For this case, the measured quantum yield should be increased by 2 % to account for the apparent less intense excitation source.

The emission distribution for the sample and the standard may often be substantially different and must be accounted for.^{219,221} If self absorption is negligible, then the rate of emission in quanta/sec, Q is given by:

$$Q = I_0 (2.303\epsilon c l) \phi_f$$

and is equal to the total area under the emission curve. For two solutions of sample (s) and reference standard (r) measured under the same conditions (λ_{ex} , $\epsilon c l$, solvent, etc.), the ratio of the rates of emission should be equal to the ratio of the fluorescence quantum yields:

$$Q_s/Q_r = \phi_s/\phi_r$$

As many of the emission measurements were recorded as peak emission intensities (I), a correction for the area to peak height ratio of the emission (A) must be used to correct for this source of error. This leads to:

$$\phi_s = \phi_r (I_s/I_r)(A_r/A_s)$$

where A_r/A_s is equal to 0.76 in the case of quinine bisulphate and CL.

The last correction to the emission intensity that must be made is due to the concentration of the sample solution. Figure C.2 shows plots of the normalized emission intensity versus logarithm of concentration for the dianion, CL and CLH^+ in acetonitrile. The emission intensity has been normalized by dividing all of the emission intensities for a given compound by the maximum emission intensity recorded for that compound so that the three species can be compared to each other on one graph. The data was then replotted as normalized emission intensity divided by concentration versus the logarithm of concentration in order to highlight the concentration ranges under which quenching or self absorption processes are operative.

The dianion displays only an almost constant increase in intensity with increasing concentration but if the emission intensity is divided by the concentration a maximum is observed at a concentration of 3×10^{-7} M. As the concentration is increased beyond this, some type of efficient self quenching process is believed to be occurring. Simple self absorption quenching would be expected to be negligible at this concentration but perhaps self aggregation or some other chemical effect is enhancing this process. For the purpose of determining quantum yields, a concentration of 3×10^{-7} M was used as the effect of self quenching would be minimal while the emission intensity signal was large enough to be at least 90 % larger than the background signal.

In the case of the chromophore ligand and its protonated form a gradual shift from the protonated form to the neutral form is observed as the concentration is increased. This is due simply to the reduced concentration of residual water in the acetonitrile relative to the concentration of the ligand. The emission intensity per concentration of the neutral form reaches a maximum value at a concentration of

Figure C.2 Normalized fluorescence intensity as a function of concentration. Solvent is acetonitrile.

Figure C.3 Fluorescence intensity/concentration versus concentration. Solvent is acetonitrile.

5×10^{-5} M and is reduced by further increases in concentration as a result of self absorption quenching. For these two species, quantum yields were determined at concentrations of 5×10^{-5} M and 5×10^{-6} M for the neutral and protonated forms respectively with appropriate reductions applied to the concentration values due to the formation of the other species. The quantum yields for compounds 2 and 3 were determined at concentrations of 1×10^{-5} M where self absorption effects are expected to be negligible.

APPENDIX D

Summary of Emission Lifetime Measurements and Least Squares Fits

Table XVII. Rates, lifetimes and intercepts from least squares fit of emission data to $\ln(\text{photon counts})$ vs time for ligands and complexes for experimental conditions described in table XVIII^a

sample	k_1/s^{-1}	τ	b
1	$4.464 \pm .442 \times 10^{10}$	22.4 ± 2.2 ps	$10.63 \pm .56$
2	$2.153 \pm .029 \times 10^8$	$4.64 \pm .06$ ns	$4.562 \pm .011$
3	$1.144 \pm .027 \times 10^8$	$8.74 \pm .21$ ns	$5.482 \pm .012$
4	$1.224 \pm .029 \times 10^8$	$8.17 \pm .19$ ns	$5.272 \pm .013$
5	$1.098 \pm .028 \times 10^8$	$9.11 \pm .23$ ns	$5.109 \pm .012$
6	$5.864 \pm .315 \times 10^{10}$	17.1 ± 0.9 ps	$13.72 \pm .51$
7	$6.279 \pm .477 \times 10^{10}$	15.9 ± 1.2 ps	$13.93 \pm .73$
8	$1.560 \pm .028 \times 10^8$	$6.41 \pm .12$ ns	$5.124 \pm .012$
9	$1.751 \pm .025 \times 10^8$	$5.71 \pm .08$ ns	$5.216 \pm .010$
10	$1.477 \pm .025 \times 10^8$	$6.77 \pm .11$ ns	$5.483 \pm .009$
11	$2.623 \pm .025 \times 10^8$	$3.81 \pm .04$ ns	$5.261 \pm .008$
12	$1.082 \pm .025 \times 10^8$	$9.24 \pm .21$ ns	$4.725 \pm .010$
13	$9.580 \pm .277 \times 10^7$	$10.44 \pm .30$ ns	$5.212 \pm .012$
14	$3.831 \pm .074 \times 10^9$	261 ± 5 ps	$5.610 \pm .030$
19	$2.767 \pm .022 \times 10^8$	$3.61 \pm .03$ ns	$5.231 \pm .010$
20	$2.868 \pm .032 \times 10^8$	$3.49 \pm .04$ ns	$5.949 \pm .014$
21	$2.622 \pm .028 \times 10^8$	$3.81 \pm .04$ ns	$5.484 \pm .012$
22	$1.063 \pm .016 \times 10^{10}$	94.1 ± 1.4 ps	$6.961 \pm .044$
23	$1.122 \pm .046 \times 10^{10}$	89.1 ± 3.7 ps	$6.588 \pm .103$
24	$7.463 \pm .167 \times 10^9$	134 ± 3 ps	$12.61 \pm .08$
25	$8.026 \pm .120 \times 10^8$	$1.25 \pm .02$ ns	$6.083 \pm .032$
26	$1.003 \pm .043 \times 10^8$	$9.97 \pm .43$ ns	$5.496 \pm .020$
27	$1.665 \pm .058 \times 10^{10}$	60.1 ± 2.1 ps	$9.635 \pm .195$

sample	k_1 / s^{-1}	τ	b
28 ^b	$1.665 \pm .089 \times 10^9$	601 ± 32 ps	$7.857 \pm .139$
	$1.674 \pm .042 \times 10^8$	$5.97 \pm .15$ ns	$5.334 \pm .021$
29 ^b	$1.500 \pm .030 \times 10^9$	667 ± 13 ps	$7.542 \pm .138$
	$1.744 \pm .044 \times 10^8$	$5.73 \pm .14$ ns	$5.268 \pm .022$
30	$1.076 \pm .026 \times 10^8$	$9.29 \pm .22$ ns	$5.263 \pm .011$
31	$9.532 \pm .345 \times 10^9$	105 ± 4 ps	$6.078 \pm .078$
32	$1.152 \pm .022 \times 10^9$	868 ± 17 ps	$6.073 \pm .039$
33	$1.237 \pm .045 \times 10^8$	$8.08 \pm .29$ ns	$4.675 \pm .020$
37	$3.908 \pm .166 \times 10^{10}$	25.6 ± 1.1 ps	$15.00 \pm .45$
38	$1.007 \pm .029 \times 10^8$	$9.93 \pm .29$ ns	$5.127 \pm .012$
39	$1.781 \pm .041 \times 10^8$	$5.61 \pm .13$ ns	$5.640 \pm .018$
40	$1.103 \pm .031 \times 10^8$	$9.07 \pm .25$ ns	$5.390 \pm .013$
41	$3.020 \pm .038 \times 10^8$	$3.31 \pm .04$ ns	$5.382 \pm .016$
42	$1.717 \pm .032 \times 10^8$	$5.82 \pm .11$ ns	$5.800 \pm .014$
43	$6.160 \pm .283 \times 10^8$	$1.62 \pm .07$ ns	$5.513 \pm .067$
44	$2.709 \pm .029 \times 10^8$	$3.69 \pm .04$ ns	$5.811 \pm .012$
45	$2.010 \pm .037 \times 10^8$	$4.98 \pm .09$ ns	$5.737 \pm .016$
46	$1.239 \pm .013 \times 10^{10}$	80.7 ± 0.8 ps	$6.239 \pm .020$
47	$3.450 \pm .076 \times 10^8$	$2.90 \pm .06$ ns	$5.561 \pm .033$
48	$1.221 \pm .031 \times 10^8$	$8.19 \pm .21$ ns	$5.629 \pm .013$
49	$1.432 \pm .030 \times 10^8$	$6.98 \pm .15$ ns	$5.555 \pm .012$
50	$1.342 \pm .033 \times 10^8$	$7.45 \pm .18$ ns	$5.473 \pm .014$
51	$2.752 \pm .033 \times 10^8$	$3.63 \pm .04$ ns	$5.439 \pm .015$
52	$4.538 \pm .126 \times 10^9$	220 ± 6 ps	$8.776 \pm .126$
53	$1.079 \pm .011 \times 10^{10}$	92.7 ± 0.9 ps	$7.307 \pm .031$
54	$1.297 \pm .031 \times 10^8$	$7.71 \pm .18$ ns	$5.528 \pm .013$
55	$1.373 \pm .036 \times 10^8$	$7.28 \pm .19$ ns	$5.138 \pm .016$

^a Data was fitted to the equation $\ln(\text{photon counts}) = -k(\text{time}) + b$, using the curve fitting routine in a commercially available software package entitled "SigmaPlot" which is distributed by Jandel Corporation. A description of the samples is given in table XVIII

^b The slow component was fitted first using only data points estimated to be 5 lifetimes from the start of τ_{fast} to the end of the decay curve.

This fit was then used to correct the more accurate fit of the fast component data to the equation $\ln(\text{photon cts}) = -(k_{\text{fast}} + k_{\text{slow}})t + b_{\text{fast}}$

Table XVIII. Sample description for emission lifetime measurements reported in table XVII

sample	description ^{a,b}
1	Cu(CL)(TFMS) ₂ , 1 x 10 ⁻² M in acetonitrile, short lifetime
2	Cu(CL)(TFMS) ₂ , 1 x 10 ⁻² M in acetonitrile, long lifetime
3	Cu(CL)(TFMS) ₂ , 2 x 10 ⁻⁴ M in acetonitrile
4	Cu(CL)(TFMS) ₂ , 2 x 10 ⁻⁴ M in acetonitrile + 2 drops H ₂ O
5	Cu(CL)(TFMS) ₂ , 2 x 10 ⁻⁴ M in acetonitrile + 2 drops HOAc
6	Cu(CL)(TFMS) ₂ , 2 x 10 ⁻⁴ M in acetonitrile + 2 drops TEA
7	Cu(CL)(TFMS) ₂ , 1 x 10 ⁻² M in acetonitrile + 2 drops TEA
8	Cu(CL)(TFMS) ₂ , 1 x 10 ⁻² M in acetonitrile + 2 drops H ₂ O
9	Cu(CL)(TFMS) ₂ , 1 x 10 ⁻² M in acetonitrile + 2 drops methanol
10	Cu(CL)(TFMS) ₂ , 1 x 10 ⁻² M in acetonitrile + 2 drops HOAc
11	CL, 2.8 x 10 ⁻⁴ M in acetonitrile
12	CL, 2.8 x 10 ⁻⁴ M in acetonitrile + 2 drops H ₂ O
13	CL, 2.8 x 10 ⁻⁴ M in acetonitrile + 2 drops HOAc
14	CL, 2.8 x 10 ⁻⁴ M in acetonitrile + 2 drops TEA
19	2, 5.0 x 10 ⁻³ M in acetonitrile
20	2, 5.0 x 10 ⁻³ M in acetonitrile + 2 drops H ₂ O
21	2, 5.0 x 10 ⁻³ M in acetonitrile + 2 drops HOAc
22	2, 5.0 x 10 ⁻³ M in acetonitrile + 2 drops TEA
23	3, 1.0 x 10 ⁻² M in acetonitrile, short lifetime
24	3, 1.0 x 10 ⁻² M in acetonitrile, long lifetime
25	3, 1.0 x 10 ⁻² M in acetonitrile + 2 drops H ₂ O
26	3, 1.0 x 10 ⁻² M in acetonitrile + 2 drops HOAc
27	3, 1.0 x 10 ⁻² M in acetonitrile + 2 drops TEA
28	CL, 2.0 x 10 ⁻⁴ M in methanol
29	CL, 2.0 x 10 ⁻⁴ M in methanol + 2 drops H ₂ O
30	CL, 2.0 x 10 ⁻⁴ M in methanol + 2 drops HOAc
31	CL, 2.0 x 10 ⁻⁴ M in methanol + 2 drops TEA
32	CL, $\approx$ 4.0 x 10 ⁻⁵ M in hexanes ^c
33	DCHQ(Ph ₄ As) ₂ , 0.5 M in acetonitrile ^d
37	Cu(CL)(H ₂ O) ₂ (TFMS) ₂ , 9 x 10 ⁻⁴ M in acetonitrile
38	Zn(CL)(H ₂ O) ₂ (ClO ₄) ₂ , 4 x 10 ⁻⁴ M in acetonitrile
39	Zn(CL)(H ₂ O) ₂ (ClO ₄) ₂ , 4 x 10 ⁻⁴ M in acetonitrile + 2 drops H ₂ O

- 40 $\text{Zn}(\text{CL})(\text{H}_2\text{O})_2(\text{ClO}_4)_2$, 4×10^{-4} M in acetonitrile + 2 drops HOAc
- 41 HQPVP, 5.0×10^{-3} M in acetonitrile
- 42 15, $\approx 4.0 \times 10^{-3}$ M in acetonitrile^c
- 43 14, 3.0×10^{-3} M in acetonitrile
- 44 B2PI, 4.0×10^{-3} M in acetonitrile
- 45 $\text{Cu}(\text{HQPVP})\text{Br}$, 2.0×10^{-3} M in acetonitrile^f
- 46 $\text{Cu}(14)(\text{H}_2\text{O})(\text{TFMS})_2$, 5.0×10^{-3} M in acetonitrile^f
- 47 $\text{Cu}(\text{B2PI})\text{Br}$, 7.5×10^{-3} M in acetonitrile^f
- 48 $\text{Zn}(\text{CL})(\text{H}_2\text{O})_2(\text{ClO}_4)_2$, 2.0×10^{-3} M in methanol
- 49 $\text{Co}(\text{CL})_3(\text{TFMS})_3$, 2.0×10^{-3} M in methanol
- 50 $\text{Cu}(\text{CL})(\text{H}_2\text{O})_2(\text{TFMS})_2$, 9×10^{-4} M in acetonitrile + 2 drops HOAc
- 51 $\text{Zn}(\text{HQPVP})(\text{ClO}_4)_2$, 4.0×10^{-3} M in acetonitrile^f
- 52 $\text{Zn}(\text{B2PI})(\text{ClO}_4)_2$, 2.4×10^{-3} M in acetonitrile^f
- 53 $\text{Co}(\text{CL})_3(\text{TFMS})_3$, 2.0×10^{-3} M in methanol + 2 drops TEA
- 54 $\text{Co}(\text{CL})_3(\text{TFMS})_3$, 2.0×10^{-3} M in methanol + 2 drops H_2O
- 55 $\text{Co}(\text{CL})_3(\text{TFMS})_3$, 2.0×10^{-3} M in methanol + 2 drops HOAc
- a TEA is triethylamine, HOAc is acetic acid, TFMS is trifluoromethylsulphonate salt, HQPVP is 4,7-dihydroxy-1,3-bis(2'-pyridylimino)isoindoline from previous studies, B2PI is 4,7-di-n-butoxy-1,3-bis(2'-pyridylimino)isoindoline from previous studies
- b sample volume was 10 ml initially and 10.1 ml with added TEA, HOAc or H_2O (i.e. 1 %/vol or 0.002 M), all samples prepared in air
- c limited due to poor solubility, estimated from weight of undissolved solid
- d tetraphenylarsonium salt of DCHQ, best elemental analysis
- e on impure sample, estimated from elemental analysis assuming impurity is a salt as suggested by NMR
- f complex not well characterized

Errors on Emission lifetime measurements

Error values listed in table XVII are standard deviations of the data from the individual line fits. Duplicate measurements and calculations were carried out on samples 20 and 30 to give rates of $2.887 \times 10^8 \text{ s}^{-1}$ and $1.070 \times 10^8 \text{ s}^{-1}$ respectively. These values are within 1 % of those listed in table XVII. The average values (mean $\pm$ 3 sigma) for these two samples is therefore $2.88 \pm .03 \times 10^8 \text{ s}^{-1}$ and $1.07 \pm .01 \times 10^8 \text{ s}^{-1}$ respectively. The other reported values may be expected to be accurate to within 2 % and are therefore reported to 3 significant figures.

Emission lifetime of CL in other solvents

In methanol the chromophore ligand exhibits both a fast decay and a slow decay component as shown in figure D.1. The fast component has a decay rate of $1.67 \pm .09 \times 10^9 \text{ s}^{-1}$ (or a lifetime of $601 \pm 32 \text{ ps}$) and the slow component has a decay rate of $1.67 \pm .04 \times 10^8 \text{ s}^{-1}$ (or a lifetime of $5.97 \pm .15 \text{ ns}$). The fit of the slower component included only data points that were estimated to be at least 5 of the fast lifetimes from the start of the fast decay. The slow decay rate was then used in a biexponential equation to determine the fast decay rate. The fits obtained in this manner are judged to be fairly good as evidenced by the small magnitude and randomness of the residuals.

The slow component is assigned to the decay of the neutral chromophore excited state as was the case in acetonitrile. The decrease in the decay rate as compared to in acetonitrile is believed to be due to a reduction in the degree of internal conversion brought about by specific solvent hydrogen bonding interactions with the pyridyl moieties, the imine nitrogens and the indole nitrogen and/or proton. In the absence of specific solvent interactions, the rate would be expected to be the same as in acetonitrile as both solvents have very similar donor numbers and dielectric constants.²²²

Figure D.1 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for CL in methanol, 2.4×10^{-4} M, streak camera speed at 26.66 ps/channel

Figure D.2 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for CL in hexanes, 6.0×10^{-5} M, streak camera speed at 26.66 ps/channel

The fast decay component may be due to some form of self quenching process induced by ligand aggregation. In hexanes where the solubility of the ligand is poor and aggregate formation would be expected, only one fast component with a decay rate of $1.15 \pm .02 \times 10^9 \text{ s}^{-1}$ (lifetime = $868 \pm 17 \text{ ps}$) is observed. This is shown in figure D.2 for a hexanes solution that was saturated with respect to ligand concentration at room temperature. This suggests that in hexanes, all of the chromophore ligand exists in aggregates as no slow component is observed. The more rapid fluorescence decay for this species in methanol versus hexanes is not surprising as this trend was observed for indole in methanol and n-hexane.²²³

Emission lifetimes of related species

The dihydroxy and di-n-butoxy derivatives of the chromophore containing 2-pyridyl ligating moieties instead of 3-methylpyridyl groups were also investigated as these may provide some insight into the influence of the molecules rigidity upon the deactivation of the excited state and in particular, the internal conversion process. In the di-n-butoxy derivative, only the 2-pyridyl moieties would be "less freely rotating" due to intramolecular hydrogen bonding with the indole proton. In the dihydroxy derivative, the flexible alkyl groups are absent and replaced with a proton that may be directly involved in hydrogen bonding to the surrounding solvent, thus further decreasing the available vibrational deactivation modes.

The emission lifetime, exponential fit and residuals for these two molecules in acetonitrile are shown in figures D.3 and D.4 for the dihydroxy and di-n-butoxy derivative respectively. The dihydroxy derivative displays an emission decay rate of $3.02 \pm .04 \times 10^8 \text{ s}^{-1}$ (lifetime = $3.31 \pm .04 \text{ ns}$) and the di-n-butoxy derivative displays an emission decay rate of $2.71 \pm .03 \times 10^8 \text{ s}^{-1}$ (lifetime = $3.69 \pm .04 \text{ ns}$). CL was shown previously in chapter 4.2 to have a fluorescence lifetime of 3.81 ns which was shorter than expected and was ascribed to enhanced internal conversion. Both of the

Figure D.3 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for 4,7-dihydroxy-1,3-bis((2'-pyridyl)imino)isoindoline in acetonitrile, 5.0×10^{-3} M, streak camera speed at 26.66 ps/channel

Figure D4 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for 4,7-di-n-butoxy-1,3-bis((2'-pyridyl)imino)isoindoline in acetonitrile, 4.0×10^{-3} M, streak camera speed at 26.66 ps/channel

more rigid derivatives display shorter emission lifetimes in contrast to what may be expected on the basis of this argument alone. It is therefore evident that the electronic structure of both the excited state and ground state of these molecules are perturbed substantially by functionalization. The similarity between the rates for the two derivatives may suggest that it is mainly the interaction between the pyridyls and the indole that is responsible for this perturbation. However, much of this electronic effect in the hydroxy derivative may be effectively cancelled out by a reduction in internal conversion due to specific solvent interactions and alkyl loss. In order to account for the anomalous higher decay rate in the hydroxy derivative as compared to the *n*-butoxy derivative, a minimum radiative rate for the hydroxy derivative of at least $2 \times 10^8 \text{ s}^{-1}$ may be assigned²²⁴ if the intersystem crossing rate is assumed to be unaffected and the internal conversion rate is at most $1.0 \times 10^8 \text{ s}^{-1}$.

To elucidate further on this point, the dimethoxy derivative of the chromophore with 3-propyl-*N*-imidazolyl ligating groups was prepared and investigated. In this derivative, the effect of replacing a methylene with a propylene linkage is not expected to effect the chromophore's electronic states but should increase the rate of internal conversion due to the additional vibrational modes. The substitution of methoxy groups for *n*-butoxy groups should partially oppose the increase in internal conversion processes due to the propylene linkages and may be expected to have only a small effect on the electronic states of the chromophore. The imidazolyls can be considered to be approximately equivalent to the pyridyl groups in their remote location as very little coupling would occur across this rather long saturated linkage.

The emission lifetime, exponential fit and residuals for this compound in acetonitrile is shown in figure D.5. The observed decay rate for the 3-propyl-*N*-imidazolyl derivative was found to be $6.16 \pm .28 \times 10^8 \text{ s}^{-1}$ (lifetime = $1.62 \pm .07 \text{ ns}$) which is more than twice the decay rate observed for the chromophore

Figure D.5 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for 4,7-dimethoxy-1,3-bis((3'-propyl-N'-imidazolyl)imino)isoindoline in acetonitrile, 6.0×10^{-3} M, streak camera speed at 26.66 ps/channel

Figure D.6 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for 4,7-di-hydroxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline in acetonitrile, 5.0×10^{-3} M, streak camera speed at 26.66 ps/channel

ligand, CL. This large enhancement in rate may be ascribed to both an increase in the extent of internal conversion occurring in this molecule and an increase in the radiative rate due to perturbations of the electronic states. The proportions of the excited state decay rate that are due to the internal conversion and radiative decay pathways cannot be distinguished without further study.

Figure D.6 displays the emission lifetime, exponential fit and residuals for an impure sample of the dihydroxy derivative of CL. The absence of unassigned proton or carbon NMR resonances as well as elemental analysis suggest that the impurity is a salt. In the case of this derivative, a slower decay rate of $1.72 \pm .03 \times 10^8 \text{ s}^{-1}$ (lifetime = $5.82 \pm .11 \text{ ns}$) is observed. Internal conversion processes are reduced due to the absence of the n-butoxy groups and the radiative rate may also be reduced due to perturbations of the excited and ground state electronic configurations. The total of these two decay rates may be estimated as $1.2 \times 10^8 \text{ s}^{-1}$ which means both rates are less than 10^8 s^{-1} and of similar magnitude to the rate of intersystem crossing. The possibility of exploring the photochemistry of the triplet state of this compound therefore becomes experimentally feasible and the mechanism by which this excited state is intramolecularly quenched should be quite different than that of CL. This is beyond the scope of this study but would make for an interesting follow up project.

Emission lifetimes in the presence of base, acid or water

In order to study the photophysical properties of the chromophore alone in the absence of the protonated form, the aliphatic amine, triethylamine was added to solutions of the chromophore in acetonitrile. The emission lifetime, fit and residuals for this solution is shown in figure D.7 to have a very rapid decay rate of $3.83 \pm .07 \times 10^9 \text{ s}^{-1}$ which corresponds to a lifetime of $261 \pm 5 \text{ ps}$. This is an order of magnitude shorter than expected for the neutral chromophore and may be attributed to some

Figure D.7 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for 4,7-di-n-butoxy-1,3-bis((3'-pyridylmethyl)imino)isoindoline in 20:1 acetonitrile:triethylamine, 2.8×10^{-4} M, streak camera speed at 2.67 ps/channel

type of quenching process²²⁵ and the most likely mechanism would be via sensitized triethylamine oxidation.²²⁶ Unfortunately, a suitable base could not be found that did not influence the excited state properties in some manner. All ionic bases undergo some form of specific solvation or even coordination resulting in an enhanced emission similar to the protonated form or the zinc complex discussed in chapter 5 and no organic base could be found that did not quench the fluorescence to some degree.²²⁷

Protonation of the orthodinitrile precursor, (2) was not observed under similar experimental conditions as that used for the chromophore ligand. For example, the observed emission lifetimes in 20:1 acetonitrile:water and 20:1 acetonitrile:acetic acid calculated from figures D.8 and D.9 are $3.49 \pm .04$ ns and $3.81 \pm .04$ ns respectively. These lifetimes are not significantly different from the value of $3.61 \pm .03$ ns found in neat acetonitrile solution and shown in figure 4.10. This is not a surprising result considering this molecule lacks the imino functionalities that seem to be responsible for this behaviour in the chromophore ligand.

The diiminoisoindoline derivative (3), however does display this increase in emission lifetime with protonation. Figure D.10 shows the lifetime, fit and residuals obtained in 20:1 acetonitrile:water solution. An emission lifetime of $1.25 \pm .02$ ns is obtained which is about an order of magnitude greater than the two fast decays (89 and 134 ps) observed in neat acetonitrile. This is still much shorter than the calculated radiative lifetime of 22.4 ns calculated for this compound. It is reasonable to assume that the added water preferentially solvates this molecule and reduces the amount of self-aggregation and self-quenching that was proposed to explain the rapid biexponential decay. As acetic acid is added to the solution, a large increase in the emission lifetime is observed which is consistent with protonation of the excited state similar to in CL. The emission lifetime, fit and residuals for 3 in 20:1

Figure D.8 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for 1,4-di-n-butoxy-2,3-dicyanobenzene in 20:1 acetonitrile:water, 5.0×10^{-3} M, streak camera speed at 26.66 ps/channel

Figure D.9 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for 1,4-di-*n*-butoxy-2,3-dicyanobenzene in 20:1 acetonitrile:acetic acid, 5.0×10^{-3} M, streak camera speed at 26.66 ps/channel

Figure D.10 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for 4,7-di-n-butoxy-1,3-diiminoisoindoline in 20:1 acetonitrile:water, 0.01 M, streak camera speed at 26.66 ps/channel

Figure D.11 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for 4,7-di-n-butoxy-1,3-diiminoisoindoline in 20:1 acetonitrile:acetic acid .001 M, streak camera speed at 26.66 ps/channel

acetonitrile:acetic acid, shown in figure D.11, yields an emission lifetime of $9.97 \pm .43$ ns which is more in line with that expected by analogy to CL. Evident on the rather noisy lifetime trace is the appearance of some growth midway through the measurement. It is unknown if this is a real phenomena or if it is an experimental artifact. It may be due to a growth in the concentration of protonated form on the ns time scale via protonation of the already formed excited state. This means that the excited state pKa of this molecule is much less than that determined for CL (which was 10.5) which did not display this dynamic protonation phenomena.

The chromophore exhibits quite different behaviour in wet methanol as compared to wet acetonitrile solutions as evidenced by the biexponential lifetime decay shown in figure D.12. This behaviour is almost identical to that observed in dry methanol where the fast and slow components decayed with lifetimes of 601 ± 32 ps and $5.97 \pm .15$ ns. Here the corresponding lifetimes were found to be slightly increased for the short component to 667 ± 13 ps and slightly decreased for the slow component to $5.73 \pm .14$ ns. The fast decay was previously ascribed to some form of self quenching process induced by ligand aggregation. No significant conclusions can be drawn from the small increase in lifetime in the absence of further studies. The small increase in the lifetime of the slower component which is due to the neutral excited state chromophore can be explained on the basis of an increase in the dielectric constant or polarity of the solvent mixture as compared to methanol alone. This increase in polarity of the solvent medium would alter the specific interactions in the excited state and thus change the solvent relaxation energy²²⁸ for this molecule.

Figure D.13 displays the emission lifetime, exponential fit and residuals for a 20:1 methanol:acetic acid solution of CL. The behaviour in this case is similar to in acidic acetonitrile giving a decay rate of $1.076 \pm .026 \times 10^8 \text{ s}^{-1}$ (lifetime = $9.29 \pm .22$ ns) which is just slightly faster than the rate obtained for the protonated ligand

Figure D.12 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for CL in 20:1 methanol:water, 2.0×10^{-4} M, streak camera speed at 26.66 ps/channel

Figure D.13 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for CL in 20:1 methanol:acetic acid, 2.0×10^{-4} M, streak camera speed at 26.66 ps/channel

in acetonitrile ($10.44 \pm .30$ ns). The difference in the two emission lifetimes can be assigned to a small decrease in internal conversion deactivation in methanol as a consequence of some remaining specific solvent hydrogen bonding interactions between the solvent and locations on the ligand not involved in protonation.

Figure D.14 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for $(\text{CL})(\text{H}_2\text{O})_2\text{Zn}(\text{II})(\text{ClO}_4)_2$ (**ZnCL-H2**) in 20:1 acetonitrile:water (3.8×10^{-4} M); streak camera speed of 26.66 ps/channel

Figure D.15 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for $(\text{CL})(\text{H}_2\text{O})_2\text{Zn}(\text{II})(\text{ClO}_4)_2$ in 20:1 acetonitrile:acetic acid (3.8×10^{-4} M); streak camera speed of 26.66 ps/channel

Figure D.16 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for $\text{ClCu(II)(CF}_3\text{SO}_3)_2$ in 20:1 acetonitrile:water (1.9×10^{-4} M); streak camera speed of 26.66 ps/channel

Figure D.17 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for (CL)Cu(II)(CF₃SO₃)₂ in 20:1 acetonitrile:acetic acid (1.9×10^{-4} M); streak camera speed of 26 66 ps/channel

Figure D.18 a) Fluorescence emission lifetime. b) least squares fit of data and c) residuals of fit for $(\text{Cl})\text{Cu}(\text{II})(\text{CF}_3\text{SO}_3)_2$ in 20:1 acetonitrile:methanol ($9.5 \times 10^{-3} \text{ M}$); streak camera speed of 26.66 ps/channel

Figure D.19 a) Fluorescence emission lifetime, b) least squares fit of data and c) residuals of fit for $(\text{Cl})\text{Cu}(\text{II})(\text{CF}_3\text{SO}_3)_2$ in 20:1 acetonitrile:acetic acid ($9.5 \times 10^{-4} \text{ M}$), streak camera speed of 26.66 ps/channel

APPENDIX E

Transient Absorption Spectra Blanks

The transient absorption spectra of neat acetonitrile 50 ps and 5 ns after the pump pulse are shown in figures E.1 and E.2. The middle curve is the average spectrum and the upper and lower curves are the 2 sigma limits. A sharp negative absorptive change due to a Raman band of acetonitrile is observed at 440 nm and a less intense overtone is observed at 510 nm. The spectra for neat methanol (figures E.3 and E.4) display no significant spectral changes in the region of interest. The spectra of methyl viologen in acetonitrile (figures E.5 and E.6) and $[(\text{NH}_3)_5\text{Co(III)(py)}]^{3+}$ in acetonitrile (figure E.7) display only the intense negative absorbance change at 440 nm due to the Raman band of acetonitrile. Hexaaquocopper(II) triflate in acetonitrile (figure E.8) displays both Raman bands of acetonitrile. The spectrum of the copper complex with the "nonchromophore" ligand, L (figure E.9) shows evidence for a small absorption tail in the blue end of the spectrum. This may be a tail of a ligand to metal charge transfer band in the ultraviolet region or by analogy to the chromophore ligand, it may be an absorption due to the protonated form of the ligand.

Figure E.1 Transient absorption spectrum of neat acetonitrile 50 ps after the pump pulse

Figure E.2 Transient absorption spectrum of neat acetonitrile 5 ns after the pump pulse

Figure E.3 Transient absorption spectrum of neat methanol 50 ps after the pump pulse

Figure E.4 Transient absorption spectrum of neat methanol 5 ns after the pump pulse

Figure E.5 Transient absorption spectrum of methyl viologen (1.36×10^{-2} M in acetonitrile)

Figure E.6 Transient absorption spectrum of p-benzoquinone (3.05×10^{-2} M in acetonitrile)

Figure E.7 Transient absorption spectrum of $[(\text{NH}_3)_5\text{Co}^{\text{III}}(\text{py})]^{3+}$ (2.57×10^{-2} M in acetonitrile)

Figure E.8 Transient absorption spectrum of $[(\text{H}_2\text{O})_6\text{Cu}(\text{III})]^{2+}$ (3.36×10^{-2} M in acetonitrile)

Figure E.9 Transient absorption spectrum of $[(L)(H_2O)Cu(III)]^{2+}$ (1.0×10^{-3} M in acetonitrile)

APPENDIX F

Transient Spectra Actinometry and Electron Transfer Efficiencies

The molar extinction coefficients of the excited states formed and the number of photons incident on the sample must be known in order to calculate electron transfer efficiencies under the experimental conditions used. These quantities can be estimated from measurements of the laser energy but this will inevitably lead to overestimated values as the overlap of the pump and probe pulse is not 100 %. One useful spectroscopic actinometer for this purpose is the lowest triplet-triplet absorption of benzophenone which is shown in figure F.1, 50 ps after excitation of a 3.7×10^{-2} M acetonitrile solution with the pump pulse.

Excitation of either the singlet $nb-\pi^*$ or singlet $\pi-\pi^*$ states is followed by efficient intersystem crossing to the triplet manifold with unity quantum yield in 5 to 15 ps, depending on the solvent and excitation wavelength used.²²⁹ Internal conversion to the lowest lying triplet state is also known to occur within 50 ps.²³⁰ The molar extinction coefficient of the lowest lying singlet $nb-\pi^*$ transition of benzophenone at the excitation wavelength of 355 nm has been determined as $85 \text{ M}^{-1}\text{cm}^{-1}$ ²³¹ for the 0.0367 M solution used and the extinction coefficient of the T_1-T_2 transition at 525 nm is previously known as $6100 \text{ M}^{-1}\text{cm}^{-1}$.²³² If several assumptions are made in determining the number of probe and pulse photons incident on the sample, the ratio of excited triplet state benzophenone molecules absorbing probe radiation to the total number of molecules excited by the pulse can be determined. This in turn can be used as an actinometer to scale all the other spectra to as the efficiency of this process is known to be 100%.

The number of molecules exposed to the excitation pulse can be estimated as:

$$(\text{pulse sample vol.}) \times [\text{benzophenone}] = \{\text{beam area} \times \text{path length}\} \times [\text{benzophenone}]$$

where the beam diameter is 1.5 mm, path length is 0.2 cm, angle of incidence on the

Figure F.1 Transient absorption spectrum of benzophenone, 50 ps after excitation with the pump pulse (3.7×10^{-2} M in acetonitrile)

sample cell is $\approx 15^\circ$ (assumed = 0°) and concentration is 0.0367 M

$$\begin{aligned}
 &= \{(\pi (0.075 \text{ cm})^2) \times (0.2 \text{ cm})\} \times (0.0367 \text{ M} \times 6.023 \times 10^{23}) \\
 &= (3.5 \times 10^{-3} \text{ cm}^3) \times (2.21 \times 10^{19} \text{ molecules/cm}^3) \\
 &= 7.74 \times 10^{16} \text{ molecules exposed to the incident pulse}
 \end{aligned}$$

The number of photons absorbed is then equal to:

(number of incident photons) $\times$ (percentage of light absorbed)

where the number of photons for a 2.06 mJ, 355 nm pulse is

$$\begin{aligned}
 &\{2.06 \times 10^{-3} \text{ J}\} / \{(28,169 \text{ cm}^{-1} / 8.06573 \times 10^3 \text{ cm}^{-1} / \text{eV}) \times 1.6021 \times 10^{-19} \text{ J/eV}\} \\
 &= 3.68 \times 10^{15} \text{ photons}
 \end{aligned}$$

and the percentage of light absorbed can be determined from Beer's law as

$$\begin{aligned}
 \% \text{ Absorbed} &= 100 \% - \% \text{ transmitted} \\
 &= 100(1 - 10^{\epsilon bc}) = 100(1 - 10^{\exp(85 \text{ M}^{-1}\text{cm}^{-1} \times 0.2 \text{ cm} \times 0.0367 \text{ M}))} \\
 &= 79.4 \% \approx 80 \%
 \end{aligned}$$

Thus 80 % of the incident photons are absorbed or 2.9×10^{15} photons.

The number of excited state molecules can also be determined since the singlet state initially formed vibrationally relaxes in about 5 ps, intersystem crossing to the triplet manifold occurs in about 30 ps with unit quantum yield and the pulse width is 30 ps. For the spectrum recorded 50 ps after the pulse we can therefore assume that 100 % of the excited molecules exist in the T_1 state which has an $\epsilon = 6100 \text{ M}^{-1}\text{cm}^{-1}$ for the observed absorption of 1.02 at 525 nm. The number of excited state molecules formed can thus be calculated as:

$$\begin{aligned}
 \text{number of excited molecules} &= [T_1] \times L \times \text{Volume} \\
 &= \{1.02 / (6100 \text{ M}^{-1}\text{cm}^{-1} \times 0.2 \text{ cm}) \times 10^{-3} / \text{cm}^3\} \times 6.023 \times 10^{23} \text{ mol./M} \times 3.5 \times 10^{-3} \text{ cm}^3 \\
 &= 1.76 \times 10^{15} \text{ molecules excited}
 \end{aligned}$$

The number of excited state molecules divided by the estimated number of photons

absorbed gives an indication of the efficiency at which initially formed pump pulse excited state molecules absorb the delayed probe pulse radiation;

$$= (1.76 \times 10^{15} \text{ excited molecules} / 2.9 \times 10^{15} \text{ photons}) \times 100 \%$$

$$= 60.7 \% \approx 61 \% \text{ efficiency}$$

This calculated efficiency is expected to be less than 100 %, due mainly to the approximation that the overlap of the incident pump photon flux and incident probe photon flux is unity. This efficiency can be used to give a more accurate value for both the incident pump photon flux and the sample volume irradiated by both pulses that can be used in subsequent calculations. If we assume that the sample volume is overestimated by twice the factor that the incident number of photons are and make a correction for sample absorption²³³, then they can be reduced by factors of 71 % and 90 % respectively.

$$\text{Effective sample volume} = 3.5 \times 10^{-3} \text{cm}^3 \times 0.71 = 2.5 \times 10^{-3} \text{cm}^3$$

$$\text{Effective incident \# of pump photons} = 3.68 \times 10^{15} \times 0.90 = 3.3 \times 10^{15}$$

Extinction Coefficient of Radical Cation (CL^{•+})

The spectrum of intermolecular electron transfer quenching of the excited state of CL by methylviologen dication, MV²⁺ (similar to figure 4.40) can be used²³⁴ to determine the molar extinction coefficient of the absorption at 475 nm due to the radical cation of the chromophore ligand. The extinction coefficient of the 607 nm absorption due to the oxidized quencher, MV^{•+} is known from spectroelectrochemical studies²³⁵ to be 13,900. The change in absorbance of 0.134 for this band is due also in part by the absorption of the unquenched protonated excited state of the ligand. This quantity has been reduced by using appropriate concentrations whereby almost 100 % of the excited state molecules formed are quenched (see Table I in chapter 1).

The amount of $MV^{\bullet+}$ formed can then be determined by Beer's Law:

$$\begin{aligned} [MV^{\bullet+}] &= A_{607} / (\epsilon_{607} \times b) \\ &= 0.134 / (13,900 \text{ M}^{-1}\text{cm}^{-1} \times 0.2 \text{ cm}) \\ &= 4.8 \times 10^{-5} \text{ M} \end{aligned}$$

This can then be used to determine the extinction coefficient at 475 nm due to the cation radical of the chromophore as neither $MV^{\bullet+}$ or MV^{2+} absorb at this wavelength.

$$\begin{aligned} \epsilon_{475} &= A_{475} / ([MV^{\bullet+}] \times b) \\ &= 0.058 / (4.8 \times 10^{-5} \text{ M} \times 0.2 \text{ cm}) \\ &= 6040 \text{ M}^{-1}\text{cm}^{-1} \end{aligned}$$

Similar calculations can be carried out for the other two spectra at 5 and 10 ns to give values of 6400 and 6050. A pseudo steady state is created as the positively charged products rapidly diffuse away from each other before back electron transfer can occur and results in a growth in the entire spectrum over time. The best value for the extinction coefficient of the 475 nm chromophore radical cation absorption is $6100 \pm 200 \text{ M}^{-1}\text{cm}^{-1}$.

Intermolecular Electron Transfer Efficiency of p-benzoquinone

A similar procedure may be used for spectra of quenching by p-benzoquinone (p-BQ) with an extinction coefficient of $7,400 \text{ M}^{-1}\text{cm}^{-1}$ for the radical anion absorption at 430 nm.²³⁶

$$\begin{aligned} [p\text{-BQ}^{\bullet-}] &= A_{430} / (\epsilon_{430} \times b) \\ &= 0.19 / (7,400 \text{ M}^{-1}\text{cm}^{-1} \times 0.2 \text{ cm}) \\ &= 1.4 \times 10^{-4} \text{ M} \end{aligned}$$

This may then be used to determine the electron transfer efficiency of this quenching process as follows:

The concentration of radical cation formed can be calculated from the absorbance change at 475 nm and the molar extinction coefficient.

$$\begin{aligned}
 [\text{CL}^{\bullet+}] &= A_{475} / (\epsilon_{475} \times b) \\
 &= 0.156 / (6100 \text{ M}^{-1}\text{cm}^{-1} \times 0.2 \text{ cm}) \\
 &= 1.3 \times 10^{-4} \text{ M}
 \end{aligned}$$

The number of chromophore radical cation molecules formed is then,

$$\begin{aligned}
 \text{Number of quenched CL molecules} &= [\text{CL}^{\bullet+}] \times L \times \text{volume} \\
 &= 1.3 \times 10^{-4} \text{ M} \times 6.023 \times 10^{23} \text{ molecules/mole} \times 10^{-3} \text{ l/cm}^3 \times 2.5 \times 10^{-3} \text{ cm}^3 \\
 &= 2.0 \times 10^{14} \text{ radical cation molecules formed}
 \end{aligned}$$

The quantity of excited state molecules formed can also be calculated from the effective laser power, effective sample volume and chromophore concentration.

$$\text{Average laser power} = 2.63 \text{ mJ}$$

$$\text{Effective laser power} = 4.7 \times 10^{15} \times 0.90 = 4.2 \times 10^{15} \text{ photons}$$

$$\begin{aligned}
 \text{Number of ground state molecules} &= \text{effective volume} \times \text{concentration} \\
 &= 2.5 \times 10^{-3} \text{ cm}^3 \times 1 \times 10^{-3} \text{ M} \times 6.023 \times 10^{23} \text{ molecules/mole} \times 10^{-3} \text{ l/cm}^3 \\
 &= 1.5 \times 10^{15} \text{ ground state molecules}
 \end{aligned}$$

At 355 nm, 80 % of the ground state molecules absorb photons from the incident pump pulse.

$$\begin{aligned}
 \text{Number of excited state molecules} &= 0.80 \times \# \text{ of ground state molecules} \\
 &= 0.80 \times 1.5 \times 10^{15} \\
 &= 1.2 \times 10^{15} \text{ excited state molecules}
 \end{aligned}$$

The electron transfer efficiency is then equal to the ratio of quenched to excited state molecules,

$$\begin{aligned}\text{Electron transfer efficiency} &= 2.0 \times 10^{14} / 1.2 \times 10^{15} \\ &= 0.17 \text{ or } 17 \%\end{aligned}$$

Extinction Coefficient of Protonated Excited State (CLH⁺)

The extinction coefficient of the protonated excited state can be determined from the absorbance change on the transient spectra recorded in 20:1 acetonitrile:water solution where approximately 45 % of the excited state molecules formed are protonated (pH = 9.8, see figure 4.8) and no quenching processes are operative. These spectra are shown in figure 4.25 and the spectrum recorded 5 ns after the pump pulse will be used as this is where the maximum change is observed. The band is found at 525 nm in acetonitrile but as water is added or if the spectra are recorded in methanol, the enhanced emission from at 485 nm distorts the spectra and the band appears at 625 nm. For this reason, the error on the extinction coefficient for this band may be as high as 20 %.

$$\begin{aligned}\epsilon_{625} &= A_{625} / ([\text{CLH}^+] \times l) \\ &= 0.24 / ([4.8 \times 10^{-3} \text{ M} \times 0.45] \times 0.2 \text{ cm}) \\ &= 600 \text{ M}^{-1}\text{cm}^{-1}\end{aligned}$$

Intramolecular Electron Transfer Efficiency in Copper Complexes

A similar procedure can be used to determine the electron transfer efficiencies of the copper chromophore quencher complexes using the transient absorption spectra of the Cu(CL)(TFMS)₂ complex in acetonitrile (figure 5.19) and methanol (figure 5.25) and the Cu(CL)(H₂O)₂(TFMS)₂ complex in acetonitrile (figure 5.27).

From figure 5.19, the maximum absorption change due to formation of the radical cation is 0.16 and occurs 20 ps after the pulse. The pump pulse width is 30 ps which means that the pulse has completely passed through the sample after 15

ps. With the excited state lifetime known to be 22.4 ± 2.2 ps from emission lifetime measurements and the lifetime of the charge separated state at 294 ± 8 ps from the decay of this absorption, one can surmise that this maximum observed is slightly reduced from the total number of radical cations formed. This absorption change at 20 ps after the pump pulse can however be used if a correction for depletion of this species by the back electron transfer process and for incomplete formation from the excited state are made. Also evident on the three figures is the formation of protonated chromophore excited state which can be shown to be the major factor that reduces the electron transfer efficiency from 100 %.

The number of photons absorbed by the sample volume can first be determined from the laser power of 2.22 mJ and the optical density of the solution at 365 nm of 2.4 ($A = \epsilon bc = 10500 \text{ M}^{-1}\text{cm}^{-1} \times 0.2 \text{ cm} \times 1.15 \times 10^{-3} \text{ M}$, i.e. essentially 100 % of the incident light is absorbed):

From the previous calculation for benzophenone, where a laser power of 2.06 mJ translated into an effective number of incident pump photons of 3.3×10^{15} ;

$$\begin{aligned}\text{Effective number of pump photons} &= 2.22 \text{ mJ} / 2.06 \text{ mJ} \times 3.3 \times 10^{15} \\ &= 3.6 \times 10^{15} \text{ incident photons}\end{aligned}$$

$$\begin{aligned}\text{Number of ground state molecules} &= \text{effective volume} \times \text{concentration} \\ &= 2.5 \times 10^{-3} \text{ cm}^3 \times 1.15 \times 10^{-3} \text{ M} \times 6.023 \times 10^{23} \text{ molecule/mole} \times 10^{-3} \text{ l/cm}^3 \\ &= 1.73 \times 10^{15} \text{ ground state molecules}\end{aligned}$$

$$\begin{aligned}\# \text{ of excited state molecules} &= \% \text{ light absorbed} \times \# \text{ ground state mol.} \\ &= 100 \% \times 1.73 \times 10^{15} \text{ ground state molecules} \\ &= 1.73 \times 10^{15} \text{ excited state molecules}\end{aligned}$$

Note: At this optical density and incident laser power, 100 % of the ground state molecules in the effective sample volume would absorb at least one photon during the pump pulse duration. This means that single excited state formation is complete in about half of the duration of the pump pulse and the possibility of forming double

excited species exists. These double excited species will be ignored in the following calculations.

The concentration of radical cations formed can then be compared to the concentration of excited state molecules formed to give an indication of the electron transfer efficiency. The concentration of radical cations observed will be inherently lower than the total concentration of radical cations formed because of complexes that have not yet undergone electron transfer and charge separated state complexes that have already undergone back electron transfer. These two factors can be accounted for using the observed rates of both the forward ($k_{et} = 4.46 \times 10^{10} \text{ s}^{-1}$) and back ($k_{et} = 3.40 \times 10^9 \text{ s}^{-1}$) electron transfer reactions.

The concentration of radical cations observed is:

$$\begin{aligned} [\text{CL}^{\bullet}] &= A_{475} / (\epsilon_{475} \times b) \\ &= 0.160 / (6100 \text{ M}^{-1}\text{cm}^{-1} \times 0.2 \text{ cm}) \\ &= 1.31 \times 10^{-4} \text{ M} \end{aligned}$$

Assuming that the formation of the charge separated state is a first order process, then the total concentration of radical cations that would be formed in the absence of back electron transfer after a certain time (t), $[\text{CL}^{\bullet}]_t$ can be determined as follows:

$$d[\text{CL}^{\bullet}]/dt = k_f[\text{CL}^*] - k_p[\text{CL}^*][\text{H}^{\bullet}]$$

which if protonation ($k_p[\text{CL}^*][\text{H}^{\bullet}]$) is ignored and the rate equation is integrated and rearranged, yields:

$$[\text{CL}^{\bullet}]_t = [\text{CL}^*] \times (1 - e^{-k_f t})$$

The effect of the back electron transfer process 20 ps after the pump pulse can then be factored in as:

$$d[\text{CL}^{\bullet}]/dt = -k_b[\text{CL}^{\bullet}]$$

to give:

$$[CL^+]_t = [CL^+]_0 \times (e^{-k_b t})$$

If $[CL^+]$ is assumed to be equal to $[CL^+]_0$ then these two expressions can then be combined to yield:

$$[CL^+]_{20} = [CL^+] \times \{(1 - e^{-k_f t})e^{-k_b t}\}$$

That may be solved to give the expected concentration of radical cations 20 ps after the pump pulse in the absence of depopulation by protonation:

$$\begin{aligned} [CL^+]_{20} &= 1.15 \times 10^{-3} \times \{(1 - e^{-(4.46 \times 10^{10})(2 \times 10^{-11})})e^{-(3.4 \times 10^9)(2 \times 10^{-11})}\} \\ &= 6.34 \times 10^{-4} \text{ M} \end{aligned}$$

The concentration of observed radical cation species divided by the concentration expected will give an indication of the electron transfer efficiency in this complex.

$$\begin{aligned} \text{Electron transfer efficiency} &= (1.31 \times 10^{-4} \text{ M} / 6.34 \times 10^{-4} \text{ M}) \times 100 \% \\ &= 21 \% \end{aligned}$$

The low electron transfer efficiency is believed to be mainly due to the high susceptibility of this ligand toward excited state protonation which was neglected in this calculation.

The same procedure may be carried out on the $Cu(CL)(TFMS)_2$ complex in methanol and the $Cu(CL)(H_2O)_2(TFMS)_2$ complex in acetonitrile to give electron transfer efficiencies of 9 % and 17 % respectively

Appendix G

Structure of precursors and ligands

1 (or DCHO) $R = (\text{phenyl})_4\text{As}^+$

2 $R = \overset{R5}{\text{CH}_2}-\overset{R6}{\text{CH}_2}-\overset{R7}{\text{CH}_2}-\overset{R8}{\text{CH}_3}$

2b $R = \overset{R8}{\text{CH}_3}$

3 $R = \overset{R5}{\text{CH}_2}-\overset{R6}{\text{CH}_2}-\overset{R7}{\text{CH}_2}-\overset{R8}{\text{CH}_3}$

4 $R = \overset{R8}{\text{CH}_3}$

5 (or L) $R = -\text{H}$, $X = \overset{9}{\text{CH}_2}-\overset{10}{\text{C}_6\text{H}_4}-\overset{11}{\text{N}}-\overset{12}{\text{C}_6\text{H}_4}-\overset{13}{\text{CH}_2}-\overset{14}{\text{N}}$

6 $R = -\text{H}$, $X = \overset{9}{\text{CH}_2}-\overset{10}{\text{C}_6\text{H}_4}-\overset{11}{\text{N}}-\overset{12}{\text{C}_6\text{H}_4}-\overset{13}{\text{CH}_2}-\overset{14}{\text{N}}$

7 $R = -\text{H}$, $X = \overset{9}{\text{CH}_2}-\overset{10}{\text{C}_6\text{H}_4}-\overset{11}{\text{N}}-\overset{12}{\text{C}_6\text{H}_4}-\overset{13}{\text{CH}_2}-\overset{14}{\text{N}}$

8 (or CL) $R = \overset{R5}{\text{OCH}_2}-\overset{R6}{\text{CH}_2}-\overset{R7}{\text{CH}_2}-\overset{R8}{\text{CH}_3}$, $X = \overset{9}{\text{CH}_2}-\overset{10}{\text{C}_6\text{H}_4}-\overset{11}{\text{N}}-\overset{12}{\text{C}_6\text{H}_4}-\overset{13}{\text{CH}_2}-\overset{14}{\text{N}}$

9 $R = \overset{R5}{\text{OCH}_2}-\overset{R6}{\text{CH}_2}-\overset{R7}{\text{CH}_2}-\overset{R8}{\text{CH}_3}$, $X = \overset{9}{\text{CH}_2}-\overset{10}{\text{C}_6\text{H}_4}-\overset{11}{\text{N}}-\overset{12}{\text{C}_6\text{H}_4}-\overset{13}{\text{CH}_2}-\overset{14}{\text{N}}$

10 $R = \overset{R5}{\text{OCH}_2}-\overset{R6}{\text{CH}_2}-\overset{R7}{\text{CH}_2}-\overset{R8}{\text{CH}_3}$, $X = \overset{9}{\text{CH}_2}-\overset{10}{\text{C}_6\text{H}_4}-\overset{11}{\text{N}}-\overset{12}{\text{C}_6\text{H}_4}-\overset{13}{\text{CH}_2}-\overset{14}{\text{N}}$

11 $R = \overset{R8}{\text{OCH}_3}$, $X = \overset{9}{\text{CH}_2}-\overset{10}{\text{C}_6\text{H}_4}-\overset{11}{\text{N}}-\overset{12}{\text{C}_6\text{H}_4}-\overset{13}{\text{CH}_2}-\overset{14}{\text{N}}$

12 $R = \overset{R8}{\text{OCH}_3}$, $X = \overset{9}{\text{CH}_2}-\overset{10}{\text{C}_6\text{H}_4}-\overset{11}{\text{N}}-\overset{12}{\text{C}_6\text{H}_4}-\overset{13}{\text{CH}_2}-\overset{14}{\text{N}}$

13 $R = \overset{R8}{\text{OCH}_3}$, $X = \overset{9}{\text{CH}_2}-\overset{10}{\text{CH}_2}-\overset{11}{\text{CH}_2}-\overset{12}{\text{N}}-\overset{13}{\text{C}_6\text{H}_4}-\overset{14}{\text{N}}$

14 $R = -\text{OH}$, $X = \overset{9}{\text{CH}_2}-\overset{10}{\text{C}_6\text{H}_4}-\overset{11}{\text{N}}-\overset{12}{\text{C}_6\text{H}_4}-\overset{13}{\text{CH}_2}-\overset{14}{\text{N}}$

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