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Synthesis and Characterization of Novel Organometallic and Organic Electrochromic Materials

by

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**A thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfillment of
the requirements for the degree of
Doctor of Philosophy**

Department of Chemistry

**Carleton University
Ottawa, Ontario
September 2001**

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**Synthesis and Characterization of Novel Organometallic
and Organic Electrochromic Materials**

Submitted by
Pierre Desjardins, B.Sc.

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

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September 10, 2001

This thesis is dedicated to my wife

Michelle, my son Marc, my parents in-law

Stephen and Elaine Conrad and

my parents Leo and Therese.

Abstract

With the proliferation of the internet, new fiberoptic high-bandwidth data transmission systems are needed to both keep up with current growth in demand for service as well as expand the system in anticipation of future communication needs. Our group is engaged in the development of new materials for optical switching and modulation as well as optical waveguide applications. This research project involved the structure-function study of the electrochromic behaviour of dinuclear azodicarbonyl (ADC) ruthenium complexes and 1,8-naphthalimides. This understanding of the structural parameters necessary to elicit a specific wavelength or electrical potential will allow the rational design of new materials and devices with specific optoelectronic properties.

A series of ADC ruthenium complexes were synthesized and characterized using X-ray crystallography; uv-vis-NIR, NMR, and IR spectroscopy; and cyclic-voltammetry. This was followed by the study of a series of 1,8-naphthalimides, where acceptor strength of the substituent was increased systematically. The spectral and electrochemical behaviour was characterized and this data was also rationalized in terms of the Hammett parameter.

The final stage of the project was the development of ADC Ruthenium oligomers and polymers. The oligomeric complexes were essentially ADC dimers bridged by various fragments, such as phenyl, butyl, ethenyl, and ethynyl. The electronic coupling between individual ADC dinuclear fragments and the electrochromic behaviour of these oligomers and polymers were characterized.

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"I want to know gods thoughts, the rest are details."

... *Albert Einstein*

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Glossary

ACN	-	Acetonitrile
ADC	-	Azodicarbonyl
ATO	-	Antimony doped Tin Oxide (conductive and electrochromic)
CE	-	Colouration efficiency
CT	-	Charge Transfer
DMAc	-	<i>N,N</i> -dimethylacetamide
DMF	-	<i>N,N</i> -dimethylformamide
DMSO	-	Dimethylsulphoxide
EC	-	Electrochromic
ECD	-	Electrochromic Device
EtOH	-	Ethanol
IT	-	Intervalence Charge Transfer
ITO	-	Indium doped Tin Oxide (conductive)
LMCT	-	Ligand-to-Metal Charge Transfer
MLCT	-	Metal-to-Ligand Charge Transfer
MMCT	-	Metal-to-Metal Charge Transfer
MS	-	Mass Spectrometry (CI=chemical ionization, EI=electron impact, FAB=fast atomic bombardment, and ESI=electrospray ionization)
NIR	-	Near Infrared Region
NMP	-	<i>N</i> -methylpyrrolidone
NMR	-	Nuclear Magnetic Resonance (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, and <i>J</i> =coupling constant)
OTTLE	-	Optically Transparent Thin Layer Electrochemical (cell)

PANI	-	Polyaniline
TBAH	-	tetrabutylammonium hexafluorophosphate
TEA	-	Triethylamine
VOA	-	Variable Optical Attenuator

Basic Principles

Electrochromic devices (ECD's) are increasingly attracting attention as new alternatives for information display and active signage applications, “smart” windows for energy conserving architectural transparencies, “smart” or “Night Vision Safety” mirrors and NIR attenuation for fiberoptic communication. The heart of an ECD is an electrochromic material that can express variable chromatic behaviour with variations in oxidation state. The diagram in figure I.1 shows a typical layered device consisting of one or two transparent electrodes, typically indium tin oxide (ITO) coated glass, within which are sandwiched two dissimilar electrochromic (EC) materials separated by a gel or solid electrolyte.

Figure I.1: Basic solid-state electrochromic display device¹.

Electrochromism has predominantly been studied in organic dyes, conducting organic polymers, transition metal oxides, metal containing polymers and mixed oxide transition metal salts. EC materials can be subdivided by the mode of colouring as either cathodic or anodic. Generally, an anodically colouring material switches upon oxidation, whereas a cathodically colouring material does so upon reduction. Furthermore, the electrochromic process may be viewed as a doping of the material either by injection or removal of charge from the material, shown in scheme I.1. Concomitant with this doping, a new colour is exhibited by the material, the precise nature and mechanism of which will be left to a latter part of this chapter when examples of the more significant electrochromic materials will be discussed in some detail. It should be noted however that this subdivision is not a rigid boundary for classification of specific materials. It is more appropriate to realize that it is dependant, within a specific device arrangement, upon the initial and final state being switched. For instance, if a device incorporates an initially cathodically doped tungsten oxide then switching will involve an anodic process. As well, as has been shown by Sapp *et al*², derivatives of polythiophene can be made to be both cathodically and anodically colouring.

Cathodic Doping

Colour 1 Colour 2

Anodic Doping

Colour 1 Colour 2

Scheme I.1

Figure I.2: Operating principle of (A) Solution, (B) Solution/Solid Hybrid, and (C) Solid-State device configurations³.

The typical electrochromic device can be solid state, but also fully solution and combination solid/solution devices have been explored as is shown in figure I.2. In any

case, a device will consist of at least two active materials and an electrically conductive material laminated upon two non-conducting supports. The two active materials, one cathodically and the other anodically colouring, ideally should possess complimentary colouring characteristics. Conceptually, complimentary implies that each material should possess spectroscopically similar behaviour upon redox switching as is shown in figure I.8. This, however, may not always be possible and so an alternative may be to have one or both materials assume a bleached state electrochemically complimentary to a coloured state of the other. Yet another possibility worth noting would be to couple an electrochromic material of interest with one that remains transparent irrespective of its oxidation state, such as the transition metal-cerium oxide thin films of Azens *et al*⁴, thereby rendering mute any concerns regarding colour matching.

In the literature the characterization of an EC material is most often presented as the culmination of electrochemical and spectral analysis performed on it in isolation. Organic materials, for instance, are often evaluated in solution by cyclic voltammetry and in-situ spectroelectrochemical analysis. Cyclic voltammetry (CV), where the material is dissolved in solution with an electrolyte, utilizes a three-electrode system, which includes a working (Pt, C, or Au), counter (Pt) and reference (often SCE, Ag/Ag⁺ or pseudo-silver) electrodes. In-situ spectroelectrochemical analysis of solution samples is performed in an optically transparent thin layer electrochemical or OTTLE cell⁵, in which the working electrode is constructed of a semitransparent gold mesh and placed such that it intersects the analysing beam of the spectrometer. The cell pictured in figure

I.3 and used in the current work, incorporates a silver wire pseudo-reference and platinum wire counter electrode.

Conversely analysis of solid samples, typically polymeric or insoluble materials, is performed with the material mounted on the working electrode. In CV experiments, for instance, the material is coated on the working electrode, which is then immersed into an electrolyte solution along with a counter and reference electrode. In-situ spectroelectrochemical studies, similarly, involve mounting the material on the working electrode, in this case on optically transparent conductive support. This is then inserted in an optical cell or cuvette containing electrolyte solution as well as ancillary electrodes (counter and reference) as is shown in figure **IV.7**.

However, discovery of the spectral versus electrochemical behaviour is not the only in-situ technique applied to materials in the thin film. Once the chromism is known for a variety of oxidation states it is often desirable to measure the stability and efficiency of the electrochromic switching. This is done by applying repeated square wave potential steps across one redox couple or if no well defined couple exists, to different levels of injected charge (figure **I.4**).

Figure I.3: Schematic Diagram of OTTLE Cell showing the three electrodes; (a) gold mesh working electrode, (b) gold mesh counter electrode and (c) silver wire pseudo-reference electrode.

The colouration efficiency and the trend in both the current and optical transmittance amplitude over time are important parameters to be extracted from experiments such as the one shown in figure I.4. If, for instance, a material is unstable to repeated redox switching the transmittance differential at some arbitrary wavelength and the current amplitude will decrease over time as the material denatures. As well, if the coulombic efficiency, which is the expression of the current symmetry of the redox process, is not 100% then on each cycle a small percentage of one state may remain even at a potential that favours the formation of an alternate redox state.

Figure I.4: Electrical and optical (@ 490 nm) responses at 2s pulse period and 8s pulse period of poly(dithieno-3,2-b:2',3'-d-thiophene)⁶.

Colouration efficiency (CE)⁷ is determined by taking the ratio of the optical change ($\Delta OD @ \lambda$) at some characteristic wavelength versus the charge per unit area (Q_d) of film converted. This determination is mainly applied to experiments involving materials in the solid state regardless of whether a solution or solid-state electrolyte is used. It is calculated using equation 1, by determining the film area and integrating the current-time trace generated by the potential pulse, and combining with the $\Delta OD(\lambda)$ determined from the ratio of the bleached and coloured transmittance. Selected CE data are presented in table I.1, it should be noted that the higher the number the more efficient

the colouration and that this parameter is most meaningful when measuring a material between a highly coloured and bleached state since it is taken at one wavelength.

$$CE(\lambda) = \Delta OD(\lambda) / Q_d \quad \text{Equation 1}$$

$$\Delta OD(\lambda) = \log[T_b(\lambda) / T_c(\lambda)] \quad \text{Equation 2}$$

Table I.1: Selected CE for EC materials taken from the literature.

anodic EC/cathodic EC	λ (nm)	CE (cm ² /C)
Poly(3,6-bis(3,4-ethylenedioxythiophene)- <i>N</i> -methylcarbazole)/Poly(2'-hexadecyl-3,4-ethylenedioxythiophene) ^a	650	1413
Poly(4,4'-dipentoxy-2,2'-bithiophene) ^b	620	95
Poly(pyrrole)/ Poly(3,4-ethylenedioxythiophene) ^b	640	360
Amorphous WO ₃ ^c	633	115
Prussian blue ^d	633	68

^a Sapp *et al*²; ^b De Paoli *et al*⁸; ^c Faugnan *et al*⁹; ^d Tada *et al*¹⁰

Electrochromic Materials

Tungsten Oxide

Of the materials studied thus far, perhaps none has been the subject of more studies than tungsten trioxide. Since the discovery in 1969¹¹ of the electrochromism of tungsten oxide, many studies have been conducted on this material; the reader is directed to the pertinent reviews¹²⁻¹⁷ and some works¹⁸⁻²⁴.

The electrochromism is known to result from the incorporate charge-balancing (i.e. H^+ or Li^+) cations and electrons to form the blue W^{VI} - W^V mixed oxide complex, thereby classifying it, in principle, as a cathodically colouring material. In the case of Li^+ cations the electrochemical reaction can be written as in equation 3.

Colouration is reversible between the W^{VI} and mixed valence $W^{VI}W^V$ states, however reduction beyond this point results in the irreversible formation of the metallic “bronze” state. In the mixed oxide form, colouration results from an intervalence charge transfer between adjacent sites, imparting a deep blue colour to films of the material. The fully oxidized W^{VI} is typically light blue and transparent, any colouration present being due to small amounts of the mixed oxide state. The spectrum of amorphous tungsten oxide is given in figure I.5, showing a very broad band encompassing the entire visible but also the NIR and near uv.

Films of WO_3 are made in a variety of ways, including vacuum thermal, chemical vapour deposition, electrochemical oxidation of tungsten metal, RF-/DC-sputtering and sol-gel methods⁷. Of these methods, it is suggested that sputtering is best suited for producing large-scale films, of use in electrochromic windows¹⁴. Quality differences

between the individual techniques appear to be minimal and one should note that though differences in morphology have been observed, good quality electrochromic films have been made from all methods. As has been suggested, the choice of methodology is influenced more by application. In the work of Monk *et al*²⁵⁻²⁷ electrochemical techniques were used to produce WO₃, NiO, CoO, and MoO₃ host films incorporating of a dopant metal oxide which included different combinations of the afore mentioned materials to tune the chromism, thereby tailoring the film to fit specific applications.

In recent times, some have begun to look at ways of imparting 3D structure to the metal oxide films beyond the amorphous or crystalline morphologies resulting from the simple deposition methods mentioned earlier. Cheng *et al*²⁸, in a recent work reports of a mesoporous tungsten oxide film on ITO glass substrate, which is made via the combination of tungsten hexachloride with a triblock copolymer called Pluric P₁₂₃. This method differs from other mesoporous materials²⁹ as a non-ionic and arguably non-amphiphilic material provides the template. Comparisons with a sol-gel derived tungsten oxide were made, and although there were similarities in the XRD pattern, the mesoporous material had BET surface areas ~8 times higher. As well, the N₂ isotherm data and TEM imaging suggested the presence of pores, albeit not ordered, possessing pore diameters of 40 to 60 Å. Electrochromic response of the mesoporous film was found to be superior to that of the sol-gel prepared amorphous WO₃, showing both faster response times and higher CE values, which the authors attribute to the greater porosity and concomitantly superior electrolyte penetration.

Figure I.5: Spectra of amorphous WO_3 film: neutral (—) and reduced (---).

film was 370 ± 50 nm on 25 Ω Nesa[®] Glass³⁰.

Several recent patents regarding the manufacture of improved tungsten thin films underscore the importance of film morphology and composition upon the function of the electrochromic material. The mesoporous WO_3 material of Balkus *et al*³¹, analogous to that of Cheng *et al*²⁸, except that a more traditional patterning material, a quaternary amine amphiphile (hexadecyltrimethylammonium chloride), was used as the template. As well, the invention of Babinec *et al*³², describing a superior method for making, via thermal vacuum vapour deposition, transition metal oxide thin films of W, Ni, V, Mo, Ru, Ir, and Ti incorporating an alkali metal where the oxidation level of the transition metal is between 2 and 3.2. CE for one lithiated tungsten oxide example of this

invention was $\sim 30 \text{ cm}^2/\text{C}$, and it was able to cycle 11000 prior to failure which, according to the author, was one and one half times that of a normal tungsten oxide film.

Prussian Blue

Another mixed oxide transition metal material Prussian blue (PB) represents one example of a major class of mixed oxide polynuclear hexacyanometallates³³. The complex bears the formula $[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6]^-$ and the blue colouration arises from an intervalence charge transfer band centred to 690 nm. The complex can adopt a variety of oxidation states from the fully oxidized $\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}$, which is brown in colour and known as Prussian brown (PX), to the fully reduced $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ state known as Prussian white (PW) or Everitt's Salt which is transparent³⁴. Another intermediate state, known as Prussian green or Berlin Green, is a non-distinct mixed oxide state between PB and PX and is believed to encompass a continuum of compositions between these two limiting compositions in thin films³⁵. The spectra, shown in figure I.6, shows the band shape in the uv-vis-NIR range for the four distinct compositions of these iron cyanide salts.

Figure I.6: Spectra of (i) PB - blue, (ii) PW - transparent, (iii-v) PG – green, (vi) PX – yellow³⁵.

The redox mechanism resulting in the various oxidation states is given in scheme I.2^{30, 35, 36}. It should be noted from this that the material can be considered either cathodically or anodically colouring depending upon which initial and final state is being electrochemically switched. In any case, the Prussian series of states, possessing one colourless and three coloured states is considered polyelectrochromic. Films of this material have been made via the electrochemical reduction of a solution containing $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}$ and Fe^{III} ions or by electroless deposition via a sacrificial electrode³⁷⁻⁴².

Scheme I.2

Though the bulk of the study of PB, as with all other electrochromic materials, has been relegated to conductive glass or polymer surfaces, recently some authors have looked to the feasibility optical switching within a paper medium. This would, if successful, lead to novel printing methods or perhaps new active markings for secure documents. In recent works by Mortimer *et al*⁴³ and Monk *et al*⁴⁴ this was explored and, though electrochemical switching is reversible the PB tended to migrate out of the paper matrix. Methyl viologen and tungsten oxide were also found to be responsive, while remaining within the paper matrix and so were deemed to be more suitable for producing electrochromic paper.

Viologen

Methyl viologen is one of many diquaternized *N*-substituted 4,4'-bipyridylum salts^{36, 45, 46} that have been studied for their electrochromic properties. Viologen

possess three accessible redox states, shown in scheme I.3, the dication, radical cation and neutral quinoid like reduced state. The dication state is colourless, whereas the radical cation is intensely coloured due to an intermolecular charge transfer transition. The colour of the radical can be tuned by appropriate choice of the nitrogen substituent, aryl substituents for instance impart a green hue to the radical while alkyl substituents give a blue/violet colour. This is due to changes in the orbital bandgap (E_g) of the ring system arising from changes in charge distribution.

Scheme I.3

The spectra for the *N*-hexyl derivative, taken at potential steps from the dication to the radical cation, are given in figure I.7. The spectra also show strong influence from dimer formation, a common observance in the spectrum of the radical resulting from

intermolecular spin pairing. This spin pairing results in a blue shift of the major intramolecular charge transfer transition concomitant with the creation of a new low energy band.

Figure 1.7: In-situ electrochemical generation of the radical cation from the dication *N,N'*-dihexyl-4,4'-bipyridylium dibromide³⁶.

Some effort has been made to affix viologen to a solid substrate, or at the very least reduce its solubility. According to Mortimer^{36, 46} this has been accomplished by adding bulky substituents that result in the overall reduction in the solubility of the compound in protic solvents. Another method is to immobilize the viologen fragment by

modifying the alkyl groups such that they are capable of bonding to a substrate, examples of which are given by Cummins *et al*⁴⁷, and others⁴⁸⁻⁵¹. In this study Cummins reports the generation of an ultrafast electrochromic window based upon a viologen-modified nanostructured TiO₂ mounted on F-doped tin oxide coated glass. The viologen species, possessing phosphate groups capable to hydrogen bonding to TiO₂ is shown as the final product in scheme I.4. Switching times were reported to be as fast as 250 ms, with a colouration efficiency of 270 cm²C⁻¹ and the device was stable through 10⁴ cycles. Furthermore, in the coloured state the device was a blue-red, a combination of the viologen and nanostructured phenothiazine modified SnO₂.

Scheme I.4

Conductive Polymers

Many studies have been conducted regarding the electrochemistry, electrical conductivity of the doped state and electrochromism of the conductive polymers, such as

polyaniline, polypyrrole and polythiophene, and so the reader is directed to the pertinent reviews^{6, 36, 46, 52-55}.

Polyaniline is one of the oldest known conductive polymer and was first discovered in 1862 by Letherby⁵⁶, known as aniline black, was an important material for dyeing and printing. PANI⁵⁷⁻⁶⁶, mainly produced by the chemical or electrochemical oxidation of aniline, can exist in three distinct forms depending upon the oxidation state. It is known that polyaniline exhibits polyelectrochromism, expressing colours such as transparent yellow, green, dark blue, and black or dark purple (see Scheme I.5)^{36, 67, 68}. These colours correspond to the leucoemeraldine (fully reduced), emeraldine base and emeraldine salt (polaronic partially oxidized) and pernigraniline (fully oxidized), respectively.

The leucoemeraldine (fully reduced) form possesses only benzenoid centred $\pi \rightarrow \pi^*$ transitions and, since no long-range electronic conjugation exists in the polymer these transitions appear in the uv at ~326 nm, and the material is colourless. At the other extreme is the pernigraniline (fully oxidized) form in which exist equal quantities of benzenoid and quinoid rings resulting in three uv-vis spectral bands at ~270 nm, 326 nm and 564 nm. The long wavelength band responsible for the near black intense purple colour is believed to be due to a charge transfer⁶⁹ transition involving the benzenoid and quinoid ring systems. Again, the uv bands are localized $\pi \rightarrow \pi^*$ transitions of the quinoid and benzenoid units respectively, analogous to the leucoemeraldine form.

Scheme 1.5

The intermediate oxidation state has relatively complicated spectra, dependent upon the pH, dominated by the presence of charge carriers (polarons and bipolarons) in the polymer. Two forms of the polymer exist in this oxidation state, which have a proposed 3:1 benzenoid to quinoid composition and are labelled the emeraldine base (EB) and the protonated emeraldine salt (ES). The visible spectra of the EB form closely matches that of the pernigraniline form since they both contain similar functional units, the only difference observed is with respect to the band at 2.2 eV, which is red-shifted to 2.0 eV or 620 nm⁷⁰ accounting for the blue colour of this state. The ES form possesses visible and NIR bands at 450 nm, 830 nm, and 1240 nm, the latter of which is assigned to

the intrachain free-carrier excitation. As well, the band at 450 nm is the ‘polaron’ band while the transition at 830 nm is the excitonic band⁶⁹⁻⁷¹.

It has been found that electrochemically deposited films of PANI are only stable electrochromic materials between the leucoemeraldine and emeraldine states, as at potentials above 0.8 V the electrochemistry is not reversible⁶⁴. Potential cycling above 0.8 V results in a new couple at ~ 0.5 V which increases in intensity with potential cycling attributable to the appearance of a decomposition product, which Genies *et al*^{58, 59, 62} has been able to determine is cross-linking of the polymer⁶². In non-aqueous solutions, this middle couple reaches a maximum concomitant with complete loss of the other two couples and can be cycled with no apparent loss of intensity. However, under aqueous acid conditions, this couple reaches a maximum then also decays over time, due to degradation of the polymer to hydroquinone, which has a redox couple at 0.5 V⁶³.

In addition to the electrochemical limitation of PANI, poor structural control leading to wide variations in the properties, and poor solubility have prevented the commercialization of this polymer in EC devices. Effort has been directed at developing synthetic protocols to produce more structurally controlled and soluble PANI^{36, 72-75} derivatives. However, these modifications have not removed the underlying electrochemical instability of PANI above 0.8 V.

Recently, however, similar EC behavior has been observed in oligomeric polyaniline, and thus some effort has been directed toward preparing such systems as EC materials. Although these oligomers do not produce stable films and are subject to similar poor solubility, such structures can be incorporated into a well-behaved polymer system, thereby producing uniform, electrochemically stable, and behaviorally predictable films. Shacklette *et al*⁶³ successfully prepared dimeric and tetrameric aniline in order to model the electrochemical behavior of PANI. Electrochemical studies of these molecules were performed and it was shown that they possessed fully reversible electrochemical behavior, unlike PANI. Furthermore, in-situ spectroelectrochemical studies of the tetramer demonstrated that it also possessed similar polychromic behavior as PANI. In other studies by Wang *et al*^{76, 77} an aniline trimer was grafted into a polyimide, with the result of producing a material with excellent solubility that, produced good quality films on ITO, showed fully reversible electrochemical behavior above the 0.8 V PANI boundary and exhibited the same electrochromism as other oligoaniline derivatives.

Polypyrrole, polythiophene and the analogues such as polycarbazole represent another class of conjugated polymer that exhibit electrochromism^{6, 36, 46, 78}. Typically these systems are mainly p-doping (oxidation) or anodically coloring as they are unstable toward n-doping (reduction). Films of these polymers are generally made via chemical or electrochemical oxidation of the monomer, as shown in scheme 1.6, producing the p-

doped conductive form of the polymer, which can then be reduced to produce the neutral or undoped polymer.

Scheme I.6

The doping process, as shown in Scheme I.7 for polypyrrole and polythiophene, involves the oxidation of the polymer with concomitant insertion of charge balancing anions. Oxidation of the polypyrrole produces a colour change from yellow (neutral) to blue-violet (doped), while that of polythiophene is from red to blue.

Scheme 1.7

In the case of polypyrrole however, the yellow state is known to be susceptible to oxygen degradation. To some extent this has been improved by the preparation of the polymer in the presence of an amphiphilic anions⁷⁹⁻⁸¹, or by preparation of composites with anionic polyelectrolytes⁸²⁻⁸⁸. As well, the addition of substituents in the nitrogen or carbon 3,4 positions has been shown to improve the stability⁸⁹, regioselectivity^{90, 91}, and the morphology of the resulting polymers^{8, 92}. The work of Jelle *et al*⁹³, for instance, showed poly(*N*-methylpyrrole) possessed stability toward repeated electrochemical switching and good CE (64 cm² C⁻¹), when combined in a device incorporating a poly(thiophene) derivative. In another study, Schottland⁸⁹ produced highly stable films of poly(3,4-alkyldioxypyrrole) materials capable of being electrochemically switched up to 40,000 times.

In addition to improvements in stability and morphology, the nature of these substituents can be used to tune the chromism and electrochemistry of the polymer, as has been shown with polythiophene³⁶. The incorporation of an electron-donating substituent(s) into the ring, for instance tends to decrease the oxidation potential of the polymer by raising the energy of the HOMO level. At the same time, the LUMO level is not overtly perturbed, and so the effect is to reduce the differential energy of the HOMO-LUMO levels thereby resulting in a red shift in all spectral bands for all oxidation states. In a paper by Gustaffsson-Carlberg et al⁹⁴, this concept was studied in some detail with a series of polythiophenes in which the substituent in the 3 position was varied between cyclohexane and 4-octylbenzene. The $\pi \rightarrow \pi^*$ transition onset, and hence the band-gap (E_g), decreased from 2.4 to 1.8 eV between the cyclohexyl to the 4-octylbenzyl substituent. Further comparisons to poly(3,4-ethyldioxythiophene)⁹⁵ with an E_g of 1.6 eV and polythiophene at 2.1 eV⁴⁶, shows the degree to which the optical properties can be varied.

Many other studies of 3,4 substituted polythiophenes⁹⁶⁻¹⁰² have been done which show similar behaviour and, in addition, other benefits are realized such as higher stability, faster response times, and greater processability due to greater solubility and lower crystallinity inherent with alkyl substituted systems. As well, the n-doping characteristics of modified polythiophenes have been investigated and, while it is true that unsubstituted polythiophene is unstable toward n-doping, polymers with electron withdrawing substituents are stable to reduction^{36, 103}. A good example of such a

derivative is the p- and n-dopable poly(cyclopenta[2,1-*b*;4,3-*b'*]dithiophen-4-(cyano,nonafluorobutylsulfonyl)-methylidene)⁹⁹ material.

Various derivatives of polypyrrole and polythiophene have been reported that should be classed as new polymers and discussed separately. Such materials as polycarbazole or copolymers of thiophene and various other monomers are a novel group of analogous polymers with new and interesting behaviours. Polycarbazole, for instance, has been shown to be a highly stable fast switching electrochromic material in a study by Verghese *et al*⁷⁸, possessing lifetimes of $>10^4$ cycles on ITO and switching times in range of 100 ms. As well, examples of thiophene containing copolymers can be found in the works of Sotzing *et al*^{104, 105}, Sapp *et al*¹⁰⁶, and Beggiato *et al*¹⁰⁷, of these interesting low E_g (i.e. 1.1 to 1.3 eV) poly(Th-CNV-EDOT) and poly(BEDOT-CNV) were prepared.

As previously mentioned, the concept of band gap (E_g) tunability¹⁰⁸ is significant in terms of the construction of complimentary devices as by judicious choice of materials² one can optimize the device properties. For instance, in the work of Sapp *et al*², both high and low E_g polythiophene derivatives are combined in a device such that the neutral state of one is spectrally complimentary to the p-doped (oxidized) state of the other, shown schematically in figure 1.8. Devices constructed via this principle achieved good CE values, for example the dual polymer [PBEDOT-NCH₃Cz]-[PEDOT-C₁₆H₃₃] device at 1413 cm²/C.

Figure I.8: Schematic diagram of dual complimentary polymer ECD².

Metallic Complexes

Transition metal complexes as well as their polymeric analogues are potentially useful electrochromic materials, as they typically possess low energy bands within the visible and NIR region. These transitions arise as a result of charge transfer transitions involving the metal centre and one or more of the ligands comprising the complex, these can include MLCT and LMCT transitions.

One system explored are the metal containing polymers, an example of which is the study of Shagisultanova *et al*¹⁰⁹, who prepared polymer films electrochemically from [Pd(bis(salicaldehyde)-1,2-propylenediamine)] and [Pd(bis(salicaldehyde)-1,3-propylenediamine)]. Though no chemical structure was given for the polymer, they were able to produce films of the materials that were then found to reversibly switch between the emerald green oxidized state to the yellow reduced state. However, most of the metal containing polymer systems mentioned in this review would possess some form of electrochromism, whether the major transitions are MLCT or LMCT in origin, as these transitions are generally within the visible range and sensitive to metal oxidation state. Others, such as Benzo-15-crown-5 ether-vinyl-bipyridyl containing systems of Beer *et al*¹¹⁰, the 2,2'-bipyridyl system of Rasmussen *et al*¹¹¹, and the polypyridyl complex polymers of Leasure *et al*¹¹² all exhibit electrochemically switchable chromism.

Two recent novel studies regarding the application of dinuclear metal complexes as electrochromics are those of Lee *et al*¹¹³, referring to a dinuclear ferrocenyl oxomolybdenum(V) conjugated bridged system (figure I.9) and Cowen *et al*¹¹⁴, referring to a 2,2'-dithienyl-5,5'-diphenol bridged molybdenum complex (figure I.10). Both of these materials possess strong NIR bands and were developed for possible application in optical data communication. The complex of Cowen *et al*¹¹⁴ is of particular interest as it possesses a strong MMCT transition at 1310 nm for the mixed valence oxidation state, and is the first example of the intervalence charge transfer transition of mixed valence dinuclear complexes being exploited in this way. In this

study the electrochromic device was an all-liquid cell in which ITO coated glass was used as the electrodes. They found that up to 50 dB switching was possible between the bleached and coloured state, corresponding to an absorbance change of *ca.* 0 to 5.

Figure I.9: Ferrocenylphenol-[Mo(O)(Tp)Cl₂] complex of Lee *et al*¹¹³.

Figure I.10: VOA material reported by Cowen *et al*¹¹⁴.

Electrochromic Display Devices

Many devices have been constructed^{2, 8, 18, 19, 47, 93, 108, 115-127}, some to evaluate materials, never meant for commercialization, others that have been patented and still others commercialized. A search on Delphion¹²⁸ that lists US patents from 1971 onward, for instance, shows 458 patents have been filed on the subject of electrochromic devices exemplary of the interest in this field. Most devices share a common construction theme, as shown in figure I.1, where one or more electrochromic materials are sandwiched between two electrically conductive and, in some cases, transparent electrodes with either a solid, gel or solution electrolyte filling the middle space and serving to maintain electrical conduction through the device. In this section a few of the more novel examples will be reviewed in order to communicate the flavour of this branch of material science and engineering.

According to Granqvist's review¹, there are four distinct device applications of electrochromic devices. These are shown graphically in Figure I.11 and, essentially, comprise variable transmission, variable reflectance, information display, and variable emittance surfaces. In this section, the first three classes will be discussed as they have direct relevance to the materials discussed thus far and the overall theme of this work.

Figure 1.11: The principles of four different applications of electrochromic devices¹.

In recent reviews by Rauh *et al*³ and Czandema *et al*¹²⁹, the design requirements of commercial devices are discussed. Issues such as uv degradation, thermal cycling and manufacturing issues, with respect to the quality of electroactive films and purity of constituent materials, can all affect the operation and durability of a device. Smart windows, used to control solar heating in architectural applications, and smart mirrors, used to reduce headlight glare during night driving, must be designed such as to minimize effects of thermal cycling and uv degradation. Furthermore, relative to other devices based on alternate established technology and user expectation, devices must perform

adequately and be cost competitive to be viewed as effective and advantageous. The design criteria, which suggest limits for cycle life, spectral range and temperature durability, for displays, mirrors and windows, are given in table I.2.

Table I.2: Comparative features of electrochromic devices³.

	Display	Mirror	Window
Area (cm ²)	1-50	150	10 ⁴ -10 ⁸
Cycles	10 ⁶ -10 ⁸	10 ⁵	10 ⁴
Switching speed (s)	0.1-10	1-10	10-10 ⁴
Charge/cycle (mC/cm ²)	2-20	2-20	20-40
Life (yr.)	>5	>5	10-20
Color	Variable	Neutral	Neutral
Spectral range (nm)	400-700	400-700	350-2000
Open circuit memory (s)	>10 ⁴	>10 ⁴ to <5	>10 ⁴ to 0
Temperature (°C)	0-50	-40-80	-20-80
MFG. cost (\$/cm ²)	0.1	0.01	10 ⁻³

One application, as suggested by Granqvist, is the reflective device, which has been commercialized as the so-called “Night Vision Safety” mirror by the Gentex Corporation. The first NVS mirror, however, was commercialized more than ten years ago by Nissan as described in their 1988 patent¹³⁰, and employed WO₃ as the cathodic and a triphenylamine polymer as the anodic electrochromic material. These devices are currently supplied to most major automobile companies, and can be added as an option on higher-end vehicles. One example of this device, as described in the 1998 Patent of Gentex¹²², employs an all-liquid cell with solvated anodic and cathodic electrochromic materials. The device operates, much as is shown in figure I.2(A), utilizing a viologen derivative as the cathodically colouring and a phenazine derivative as the anodically

colouring material, likely selected from a host of compounds, developed by Gentex and patented¹³¹. Furthermore, the device is externally powered while control is achieved via sensors positioned fore and aft to prevent colouring during daylight except at night and in response to elevated light levels from vehicle headlights.

An interesting example of a self-powered window device can be found in the patent of Byker *et al*¹³². This device in one embodiment couples a p-n silicon photovoltaic cell as the power source, which is held within the void between and in electrical contact with the two opposing electrodes comprising the window. As well, a solution electrolyte containing 5,10-dihydro-5,10 dimethylphenazine, as the anodic material, and 1,1'-di(phenylpropyl)-4,4'-dipyridinium difluoroborate as the cathodic material, produces the desired colouring in response to external light levels. Furthermore, although the all solution example is one embodiment, the authors leave it open for exploration of thin film electrochromics with the possibility of solid or gel electrolytes.

Finally, the works of Coleman *et al*¹³³ and Liu *et al*¹³⁴ present a novel method for producing electrochromic display devices via a simple printing technology. These devices do not employ a sandwich configuration with opposing electrodes as in traditional devices, but an interdigitated electrode approach, wherein the electrodes are side-by-side and face up on the substrate. In the Coleman device, the counter and working electrodes were printed in a pattern using conductive silver or carbon inks. This

was followed by application of a conductive metal oxide (ATO-TiO₂) in a polymer binder upon which the electrochromic layer is applied followed by application of a gelled electrolyte. The device functions, it appears, by virtue of the fact that different sections of the conductive metal oxide layer, and hence the electrochromic material, are exposed to differing potential. The apparent short circuit in the cross section shown in figure I.12, is not an issue, according to the authors, if the interelectrode spacing is significantly larger than the thickness of the of the metal oxide layer and the electrolyte conductivity is high enough to maximize current flow along the desired path. The electrochromic layer in this design may be virtually any small molecule (i.e. viologen), metal oxide or conductive polymer, and devices incorporating polyaniline and Prussian blue were demonstrated.

Figure I.12: Interdigitated electrode electrochromic device¹³⁴.

The device of Liu *et al*¹³⁴, is similar in that the same technique is used to construct the device, however the electrochromic material in this case is ATO. In this device the authors produce a nanostructured ATO material, which was found to be a high contrast electrochromic material. The devices thus prepared, and shown in figure I.13 configured as an information display, were reported to exhibit excellent contrast, although no explicit mention of cycling speed or cycle life was made.

Figure I.13: Word display from Liu *et al*¹³⁴.

Rationale and Objectives

The research project undertaken and reported herein was conceived to examine molecular systems that possessed electrochromism, with particular attention to finding systems possessing NIR electrochemically switchable chromism in the range of 1550 nm (3rd transmission window). The reader is directed to figure I.14, which shows graphically the three transmission windows of silica optical waveguide materials. It should also be noted that, even if a material may not have a transition within the 3rd transmission window, correspondence with either of the other two windows may also be useful. The primary reason for selecting the 3rd window is justified in considering the obvious benefits in terms of power consumption and signal clarity gained as the total attenuation of the fibre is minimal in this region.

The results reported here were for the electrochemical, structural and spectroscopic investigation of the 1,8-naphthalimide and the dinuclear ruthenium complexes of azodicarbonyl (ADC) systems. Although the former material has been the subject of several studies as a fragment incorporated into polymer systems^{135, 136}, the latter has never, to our knowledge, been explored for its electrochromic properties. Our objectives, therefore, in this project were;

1. *Gain a better appreciation of the interplay of electronic configuration and the electrochemical and spectroscopic properties of both systems under study.*
2. *Develop polymeric materials suitable for the construction of prototype electrochromic devices.*
3. *Study the electrochromism with respect to stability, a critical issue for commercial application.*

Figure I.14: Graphical representation of NIR optical transmission profile.

Model Compound Studies

With respect to the first objective the studies conducted on these materials encompassed a QSAR study of model systems. These model studies, described in chapters 2 and 3, comprised the synthesis of a series of compounds in which certain functional groups were varied according to the donor potential in order to assess the perturbation upon the model system. In the case of the 1,8-naphthalimide system, this included placing electron withdrawing substituents on the naphthalene ring in the 4 and 5 positions, whereas for the azodicarbonyl complexes both electron withdrawing and donating substituents were introduced on the carbonyl carbons of the bridging ligand.

Azodicarbonyl Complexes

To begin, the literature is replete with studies of dinuclear metal complexes, in fact, since the Creutz-Taube ion was first characterized¹³⁷⁻¹³⁹ many groups have devoted a great deal of effort toward understanding the interplay of ligand and metal structure with respect to the strength and nature of the metal-metal interaction in such systems¹⁴⁰⁻¹⁶¹. Briefly, in these systems the bridging ligand mediates electronic coupling between the two metals, the strength of which is generally dependant upon the degree of delocalization within the bridge and the degree to which these delocalized orbitals are energy matched to that of the metal centres. Spectroscopically these systems, in addition to possessing the normal metal-ligand and ligand-metal charge transfer

transitions (MLCT and LMCT, *resp.*) of coordination complexes, they also possess a metal-metal charge transfer (MMCT) transition associated with the mixed valence species. Furthermore, coupling between the metals tends to stabilize the complex to further oxidation after the 1st oxidation of one of the metal centres. In symmetric complexes this results in a splitting of the oxidation potentials of each metal for the same change in the formal oxidation state, whereas otherwise the oxidation potentials would be coincidental (scheme I.8) in a complex where the metals are electronically isolated.

Scheme I.8

In considering an appropriate system to investigate, it was decided to focus upon the dinuclear complexes of ruthenium. To justify this, we considered that the synthetic chemistry of ruthenium is well developed¹⁶², dinuclear ruthenium complexes comprise the largest group of such complexes¹⁶³ and many of the strongly coupled complexes possess NIR MMCT transitions. As well, that spectroscopy and electrochemistry of these complexes is well understood, and thus provides a good context by which the current work can be rationalized. The rutheniumbisbipyridyl bridged

complex of R,R'-azodicarbonyldiruthenium, previously studied by Kaim¹⁶⁴⁻¹⁶⁶, possess two non-degenerate Ru(II) → Ru(III) redox couples in ACN with large K_c values, evidence of strong metal-metal coupling. Furthermore, in addition to the MLCT and LMCT transitions associated with the [Ru(II)-Ru(II)] and [Ru(III)-Ru(III)] oxidation states, these complexes possess strong MMCT transitions in the NIR. A representative example would be the $[\{Ru(bpy)_2\}_2 \mu-(adc-OC_2H_5)]^{2+}$ (diethyl azodicarboxylate) complex which possesses strong bipyridyl centred MLCT ($d(Ru^{II}) \rightarrow \pi^*(bpy)$) around 520 nm, ADC centred LMCT ($\pi[(adc-OC_2H_5)_2] \rightarrow d(Ru^{III})$) at 900 nm, and MMCT ($dRu^{II} \rightarrow dRu^{III}$) at 1420 nm. For electrochromic applications, therefore, this material shows promise as it possesses strong and electrochemically selectable visible (MLCT and LMCT) and NIR (MMCT) chromism.

In determining a research direction we considered the proximity of the two one-electron couples present in the adc system. As it was desirable to exploit the mixed valence MMCT transition for optical switching applications, it was our intent to explore the possibility of increasing the difference between the redox couples in order to enhance selectivity of the mixed valence state. Therefore, we propose that, given the fact that the adc complex amounts to two fused 5-membered rings, the effect of a substituent imposed upon each ring should be greatest upon the metal within the ring system with which it is associated. Combining both electron withdrawing and donating substituents, one associated with each ring system, should then shift the potential at which each metal centre is oxidized in electrochemically opposite directions as shown in scheme I.9.

Y = Electron Withdrawing Substituent

X = Electron Donating Substituent

Scheme I.9

The second part of the model research involved exploring the possibility of extending the adc system to dimeric complexes. This was done for two reasons, as a prelude to producing polymeric adc systems but also to attempt to modify the electrochemical behaviour of the system. In considering the later, we suggest that if the degree of communication between individual adc fragments within a macromolecular construct could be enhanced then the result would be to further split the position at which each ruthenium redox couple occurs. As with the dinuclear complexes, this would have the affect of shifting sequentially the redox potentials for each metal, and in the case of a dimer, extending the electrochemical range at which mixed valence behaviour exists, as shown graphically in scheme I.10.

Scheme I.10

Naphthalimide

With respect to the naphthalimide systems we cite the literature which has shown that aromatic fused ring systems such as naphthalene and perylene have previously been studied for their fluorescence and luminescence for light emitting applications¹⁶⁷⁻¹⁹³, photosensitizer for photovoltaic applications¹⁹⁴⁻²⁰² and semiconductor behaviour for electronic applications²⁰³⁻²⁰⁶. Furthermore, the di- and tetracarboxylic anhydrides and imides, electrochemically functionalised derivatives of these materials, have also attracted some attention as a novel group of electrochromic materials^{135, 136, 167, 172, 201, 207-212}. These aromatic imide and anhydride systems typically possess 1 or 2 one-electron redox couples cathodic to NHE and, upon reduction from the neutral to the radical anion or dianion, possess distinct uv-visible transitions for each oxidation state.

Furthermore, in the case of the tetracarboxylic anhydride derivatives, incorporation into a polymer is relatively straightforward using known imide chemistry and produces materials with good physical properties^{135, 136, 173, 174, 213}.

In a recent study Viehbeck *et al*²¹⁴ have shown, with a series of diimides in which the imide substituent was varied, a strong dependence exists between the donor potential of the substituent and the potential of both the first and second reduction couple. Furthermore, the compounds showed large wavelength differences between the major absorbance in the neutral and radical anion state, significant to display applications where maximizing contrast is desirable. A specific example is the *N,N'*-dibutyl-1,4,5,8-naphthalenetetracarboxdiimide, for which the neutral adduct exhibited only $\pi \rightarrow \pi^*$ transitions and was red in colour, while the radical anion possessed a series of visible bands between 471 and 754 nm and was violet.

It is obvious from the literature that the naphthalimide system possesses some electrochromism although few studies have been conducted focusing upon this nature. It was therefore of interest to our group to further explore this system and discover the nature of the link between the electronic environment within the ring system and the electrochemical and spectral properties. We suggest that the incremental addition of electron donating and withdrawing substituents should produce a predictable and incremental shift in the redox potential and that this can be correlated with some

substituent parameter set such as Hammett. Of specific interest is the behaviour under the influence of withdrawing substituents, which has not been fully explored thus far.

Polymeric Systems

In order to make solid-state thin film devices it was felt that polymeric analogues to the dinuclear complexes had to be developed. Therefore in the second phase of the research, analogous polymeric derivatives will be produced in order to assess the concordance of the properties with those expressed by the model compounds. It is our belief that if, for instance, complexation of a polyhydrazine system can be achieved the properties of the resulting polymer should correlate with that of the dinuclear complexes if the spacer between the resulting adc residues is saturated. We suggest this as the spacer and polymer matrix in general would essentially behave as a solid solvent. Previous works by Mohammed *et al*²¹⁵, discussed in more detail in chapter IV, suggests that it is possible to complex polyhydrazine with various metal fragments and produce a system which displays both spectral and electrochemical activity.

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Introduction

In this study several derivatives of 1,8-naphthalimide were prepared in order to probe the effect of incremental reduction of electron density within the naphthalene ring system upon the electrochemical and spectroscopic properties. Several questions were ventured in the inception of this work, namely, how does the 1st and 2nd redox couple vary with naphthalene substituent donor potential and, if a relationship exists, can this be exploited to produce a material with low potential optical switching.

Secondly, we desired to probe how the spectroscopic properties varied with substituent and oxidation state. Here, we wished to know whether the affect of various electron-withdrawing substituents would produce a blue shift in the principal $\pi \rightarrow \pi^*$ absorbance band as indicated by the work of Grabtchev *et al*¹. This affect would be consistent with the E_g variation observed for other kinds of conjugated systems as a result of varying degrees of stabilization in the π bonding molecular orbital (HOMO). For instance, when the electron density is reduced as a result of the withdrawal of electron density from the ring system the HOMO orbital level is stabilized such that the energy differential between HOMO and LUMO is increased.

The results obtained in such a study should be useful to design new electrochromic materials based upon the 1,8-naphthalimide system. The substituent

moieties introduced into the naphthalimide system within this study are shown in figure

II.1.

Figure II.1: 4,5-X,Y-1,8-naphthalimide derivatives.

Results and Discussion

Synthesis: All compounds were prepared from the corresponding acid anhydrides, in reasonably high yield and in acceptable purity directly without any further purification.

The imidization reaction was performed under relatively mild conditions and clearly represents a convenient approach to derivatization of the naphthalimide system. This compares well with that employed by Viehbeck³, in which the compounds were prepared in DMAc at 125 °C.

It should be noted that method A (page 76), reported here for the first time, was an improvement over existing synthetic routes, of which method B (page 77) is representative. By conducting the imidization under acidic conditions, the alkyl amine can be sufficiently deactivated in order to prevent nucleophilic displacement of the naphthyl substituent while not preventing attack of the anhydride group.

The synthesis of the diphenylsulphide and diphenylsulphone derivatives was carried via nucleophilic aromatic substitution of the dintronaphthalic anhydride as shown in scheme II.1.

Scheme II.1

Electrochemistry: In all naphthalimide derivatives at least one quasi-reversible redox couple assignable to the one electron reduction of the imide carbonyl carbon was observed. In the case of compounds II.2, II.4, and II.8, a second couple was observed at

more cathodic potential. Comproportionation constants (k_c) were calculated and compared for all compounds possessing two redox couples. The numerical value of such a quantity is a measure of the stability of the radical species toward further reduction as influenced by the first. The greatest values were derived for the phenylsulphone-substituted compounds while the lowest values came from the nitro compounds. This being said, one must consider that the spacing of the two redox couples is affected by the relative ease with which the second redox centre is reduced in isolation as well as the overall conjugation of the system, which facilitates charge density distribution.

Comparison of our results with those of the amine substituted naphthalimides of Viehbeck³ and the phthalimide of Mazur⁴ show these compounds possess k_c values (i.e. 10^7 to 10^{12}) in the same range as the phenylsulphone-substituted compounds (10^7 - 10^9) reported here. It is most probable that the redox mechanism of the Viehbeck and Mazur imides involves two sequential one-electron reductions of the imide carbonyls, where the high k_c values are due to electrostatic repulsion between the two adjacent anionic carbanions. Consequently, by analogy it may be that the redox mechanism does not involve the substituent for the phenylsulphone-substituted compounds, but is most likely entirely imide based. However, given the rather low k_c (10^4 - 10^6) in the case of the nitro-substituted compounds and that reduction of the nitro substituent would likely be more favourable, it is most probable that in this case the second reduction is substituent based.

Table II.1: Electrochemical Data for *N*-butyl-4-*X*-5-*Y*-naphthalimide Compounds.

Compound #: X, Y	Solvent	${}^1E^0$ (mV) ^{a,b}	${}^2E^0$ (mV) ^a	ΔE (mV) ^a [k_c] ^c	σ^d
II.1: H, H	DMF	-1110			0
	ACN	-1110			
II.2: SO ₂ Ph, SO ₂ Ph	DMF	-410	-960	550 [2.1 X 10 ⁹]	1.36
	ACN	-370	-840	470 [9.2 X 10 ⁷]	
II.3: SPh, SPh	DMF	-870			0.14
	ACN	-860			
II.4: NO ₂ , NO ₂	DMF	-210	-560	350 [8.6 X 10 ⁵]	1.56
	ACN	-180	-460	280 [5.6 X 10 ⁴]	
II.5: Cl, H	DMF	-970			0.23
	ACN	-950			
II.6: SO ₂ Ph, H	DMF	-680			0.68
	ACN	-690	-1160	470 [9.2 X 10 ⁷]	
II.7: SPh, H	DMF	-950			0.07
	ACN	-940			
II.8: NO ₂ , H	DMF	-380	-790	410 [8.9 X 10 ⁶]	0.78
	ACN	-360	-670	310 [1.8 X 10 ⁵]	
II.9: Cl, Cl	DMF	-830			0.46
	ACN	-760			

^a referenced to NHE, averaged for the anodic and cathodic peak potentials at a scan rate of 200 mV/s; ^b performed in solutions with 0.1 M TBAH; ^c $\text{Log}(k_c) = |{}^2E^0 - {}^1E^0|/0.059$; ^d values of σ_p used and for compounds II.2, II.3, II.4, and II.9 $\sigma = 2\sigma_p$.

Figure II.2: Cyclic voltammogram of II.4 in DMF with 0.1 M TBAH.

Across the series, the E^0 potential of both couples are shifted anodically in ACN versus DMF and, as the electron withdrawing potential of the naphthalene substituent increases, the E^0 potential is also shifted anodically. These results can be rationalized by considering the destabilizing influence toward reduction of lowering the electron density within the naphthylimide system. To better quantify this observation, the Hammett substituent terms (σ)² were plotted against the 1st redox couple position of the compounds, shown in the plot of figure II.3. For this study, the linear combination of σ_p parameters was used cumulatively to estimate the effect of the substituents. The plots show a strong correlation for the disubstituted, but not so for the monosubstituted derivatives. As well, the line slopes, which are comparable between the solvents, are

greater for the monosubstituted derivatives over the disubstituted, indicating a greater sensitivity with a single substituent versus that of two substituents.

Where systems expressed a second redox couple (compounds **II.2**, **II.4**, **II.6** and **II.8**), no Hammett correlation was observed, which may be partial confirmation of the redox assignments made earlier in the text. The reasoning to account for this suggests that a correlation is impossible if the redox event is centred upon the substituent for which the Hammett parameter has been assigned. Furthermore, since it seems reasonable to suggest that the mechanism invoked to account for the second redox couple is different depending upon the specifics of the system under study, no correlation should be expected.

Comparison with similar systems, such as the *N*-butylphthalimide (${}^1E^0 = -1139$ mV) and *N*-butyl-4-aminonaphthalimide (${}^1E^0 = -1210$ mV) of Viehbeck³ or the *N*-ethyl-4-aminonaphthalimide (${}^1E^0 = -1144$) and *N*-ethyl-4-methoxynaphthalimide (${}^1E^0 = -1164$) of Martin⁵, place this work in some perspective. Specifically, for the naphthalimide systems, the introduction of an electron donating group shifts the ${}^1E^0$ potential cathodically compared to the unsubstituted system and suggests a continuum in the substituent effect.

Figure II.3: Plots of $^1E^0$ potentials versus Hammett parameter. (A) in ACN and (B) in DMF.

Uv-vis-NIR Spectroscopy: The uv-vis-NIR spectra were collected in both ACN and DMF for the neutral, radical anion and dianion. The neutral form of the compounds possessed only uv bands in the range of 230 and 358 nm, which can be assigned to the π

→ π^* transitions normally observed for such systems^{3, 6, 7}. The radical anion, in addition to the uv bands red shifted by approximately 10 and 20 nm, also possessed visible charge transfer (CT) bands in the range of 400 to 860 nm. A surprising result was the low energy CT transition between 1158 and 1177 nm for compound **II.4**. The uv bands, attributable to $\pi \rightarrow \pi^*$, possessed extinction coefficients of approximately 30000 to 40000 $M^{-1}cm^{-1}$, while the CT transitions ranged from approximately 1300 to 10000 $M^{-1}cm^{-1}$. The long wavelength uv transitions (300 to 400 nm), however, had extinction coefficients in the same range as those of the visible CT transitions, which suggest similar origin. The dianion form showed similarly complex spectral structure to that of the radical anion. In this case, for **II.4** a new transition at 931-948 is observed with almost identical intensity as that of the band 1158-1177 observed for the radical form.

Generally, there appeared to be a red shift in the primary uv bands for this series, which is inconsistent with observations for other systems and our expectations. It was believed that as a result of the stabilizing influence of an electron withdrawing substituent the HOMO orbital energy should be reduced, thereby increasing the $\pi \rightarrow \pi^*$ energy and the band-gap (E_g). Although the difference is nominal across the series it nonetheless indicates that simply decreasing the electron density within the ring system does not necessarily lead to increased stabilization. What we may be observing here could be a loss of aromaticity, which might be leading to an overall destabilization of the ring system.

Figure II.4: Uv-vis-NIR of in-situ electrochemical generation of $A^{\bullet}$ and $A^{2\bullet}$ of II.4 in DMF utilizing the OTTLE cell.

Of note is the spectral simplicity of II.2. In DMF, only one band is observed for all states of the compound, while in ACN two are observed for the neutral and radical forms only. It has been suggested that resonance interactions⁶ play a key role in the observed spectral structure, however in this case such resonance behaviour is less likely due to loss of planarity imposed by the bulky $-\text{SO}_2\text{Ph}$ groups. To show this, the optimized geometry for both the nitro and phenylsulphone systems were determined using AM1 semi-empirical method (i.e. performed on an Intel PIII with PC Spartan *Plus* v1.0). The dihedrals along the C9-C10-C5-C6 carbons of compound 2 were determined to be almost twice (18.9°) that of the dinitro (10.6°) compound, while the unsubstituted naphthalimide had a dihedral angle of $<0.1^\circ$.

Table II.2: Electronic Spectral Data^{a,b} for *N*-butyl-4-X-5-Y-naphthalimide Compounds.

Compound #: X, Y	Solvent ^c	Neutral	1-	2-
II.1: H, H	DMF	334(4.08)	270(4.02), 318(3.70) 419(3.96), 489(3.40) 800(3.17)	
	ACN	234(4.67), 331(4.09) 345(4.06)	234(4.45), 375(3.70) 416(3.68), 466(3.56)	
II.6: SO ₂ Ph, H	DMF	337(4.14), 350(4.10)	319(4.02), 480(3.74) 817(2.76)	
	ACN	233(4.53), 335(4.16) 350(4.12)	313(4.01), 416(3.53) 508(3.63), 809(2.69)	319(4.03), 362(3.88) 418(3.70)
II.2: SO ₂ Ph, SO ₂ Ph	DMF	359(4.01)	483(3.59)	480(3.65)
	ACN	242(4.39), 356(3.97)	254(4.31), 357(3.92)	490(3.73)
II.8: NO ₂ , H	DMF	350(4.01)	318(3.93), 338(3.81) 471(3.99), 558(3.87) 775(3.58), 853(3.68)	317(3.95), 338(3.78) 480(3.84), 563(3.75)
	ACN	348(4.02)	338(3.77), 442(3.60) 554(3.37), 842(3.25)	426(3.72)
II.4: NO ₂ , NO ₂	DMF	350(4.05)	273(4.18), 348(3.84) 520(4.13), 575(3.95) 1158(3.25)	267(4.25), 287(4.21) 478(4.02), 931(3.54)
	ACN	237(4.48), 345(4.07)	271(4.08), 343(3.90) 518(4.07), 575(3.87) 1177(3.14)	332(3.93), 447(3.86) 948(3.03)

^a $\lambda(\log \epsilon)$; ^b extinction coefficients determined using a 1 cm quartz cell in pure solvent; ^c spectroelectrochemical experiments performed using the OTTLE cell with solvent TBAH concentration of 0.1M.

Table II.3: Perceived colours of the neutral, radical anion (1-), and dianion (2-) oxidation states of selected naphthalimides taken in DMF.

Compound #: X, Y	Neutral	1-	2-
II.1: H, H	Pale yellow	Pale green	
II.6: SO ₂ Ph, H	Pale yellow	Light brown	
II.2: SO ₂ Ph, SO ₂ Ph	Yellow	Dark green	Green-brown
II.8: NO ₂ , H	Brown	Violet	Red-violet
II.4: NO ₂ , NO ₂	Brown	Violet	Deep violet

Colour and contrast are important parameters to be considered in developing electrochromic materials for display purposes. Therefore the colours for **II.1**, **II.2**, **II.4**, **II.6** and **II.8** were explored for all oxidation states in DMF and are presented in table **II.3**. The compounds showing the least contrast between neutral and radical forms were **II.1**, **II.2** and **II.6**, not surprising given the low wavelength differential for the major absorption bands, which ranged from 84 to 143 nm. The others in the series showed more pronounced colour changes and had correspondingly higher λ differentials ranging between 122 and 172 nm. Those compounds having a second reduction couple showed

only a deepening of the colour expressed in the radical form when further reduced to the dianion.

Table II.4: Optical band-gap (E_g) Energies of selected naphthalimides from spectral data measured in ACN.

Compound #: X,Y	E_g (eV) ^a	$^1E^0$ (mV) ^{b,c}
II.1: H, H	3.41	-1110
II.6: SO ₂ Ph, H	3.28	-690
II.2: SO ₂ Ph, SO ₂ Ph	3.02	-370
II.8: NO ₂ , H	2.97	-360
II.4: NO ₂ , NO ₂	3.14	-180

^a from the $\pi \rightarrow \pi^*$ onset energy; ^b referenced to NHE, averaged for the anodic and cathodic peak potentials at a scan rate of 200 mV/s; ^c performed in solution with 0.1 M TBAH.

Optical bandgap values were derived for the neutral states of compounds II.1, II.2, II.4, II.6, and II.8 and were compared to the $^1E^0$ potentials (table II.4 and figure II.5). While these values give the energy difference between the π and π^* (HOMO and LUMO) levels of the systems, they should also indicate their relative stabilities. As has been indicated in an earlier discussion regarding the band-gap dependence of conducting polymers, the influence of electron withdrawing substituents stabilizes the π level thereby

resulting in an increase in E_g and anodic shift in the reduction potential. However, if this were true the plot should show an inverse concordance between the $E_{1/2}$ potential and E_g but the results show little or no correlation between band gap energy and ${}^1E^0$ and no trend appears to be evident.

Figure II.5: Optical band gap versus ${}^1E^0$ for neutral *N*-butyl-4-X-5-Y-naphthalimide compounds ($r^2 = 0.71$).

Conclusions

The materials generally behaved as expected, that is, with increasing electron withdrawing potential of the substituent(s) the 1st redox potential was shifted anodically. The shift in redox potential was correlated with that of the Hammett parameter set and

the results indicated that the potential did indeed correlate well for the disubstituted but not the monosubstituted compounds.

Of note was the discovery of a long wavelength NIR band for the dinitro derivative. The possible basis for this transition was given as an internal charge transfer transition involving the radical carbonyl and nitro substituent. As a basis for this rational we cite the literature as transitions of this nature have previously been observed in 4-nitroaniline and 4-nitrophenylcyanamide derivatives^{7, 8}. The position of the band and the fact that it is only observed for the radical anion form is promising in terms of the possible use of this system in NIR optical switching applications.

The lack of any reasonable explanation in the literature for the lack of any correspondence of the ${}^2E^0$ with the Hammett term led us to suggest that the mechanism for the redox behaviour of these systems may be dependant upon the redox behaviour of the substituent. This proposal was based upon a comparison of the comproportionation constants, which is an indicator of resistance to further reduction of the radical anion. This, as well as the apparently poor correlation of the 1st redox couple of the monosubstituted compounds, suggests further study is necessary.

Experimental

Measurements

^1H and ^{13}C NMR spectra were recorded on Varian Gemini 200 and Bruker AMX-400 spectrometers using deuterated chloroform (CDCl_3), acetone (acetone-d_6), and dimethylsulfoxide (DMSO-d_6) as solvents. The chemical shifts are reported in δ (ppm) relative to tetramethylsilane as internal standard. IR spectra were performed on KBr mull of the compound and collected with a Bomem Michelson-100 FTIR. Melting points were measured on a Fisher-Jones melting point apparatus and are uncorrected. The University of Ottawa Regional Mass Spectrometry Centre performed the low-resolution EI mass spectroscopy and peaks are reported as m/z (% intensity relative to the base peak).

Uv-vis-NIR spectrophotometric and electrochemical measurements were taken in spectroscopic grade acetonitrile (ACN) and *N,N'*-dimethylformamide (DMF) using a Perkin Elmer Lambda 900 uv-vis-NIR and BAS 100 B/W, respectively.

Tetrabutylammonium hexafluorophosphate (TBAH) was used as the supporting electrolyte for all electrochemical measurements, at an approximate concentration of 0.1M. Solvents were used as received, however the TBAH was recrystallized from MeOH/EtOH and dried under vacuum at 110°C prior to use. Spectroelectrochemical generation of the $\text{RA}^\cdot$ (radical anion) and DA^{2-} (dianion) oxidation states of the compounds were performed using an optically transparent thin layer electrochemical cell (OTTLE). The internal

standard used to determine the position of the $E_{1/2}$ potentials for the complexes was $\text{Fe}(\text{Cp})_2$ (Aldrich, used as received) which has an $E_{1/2}$ (vs. NHE) potential in ACN of +666 mV and +643 mV in DMF⁹. Cyclic voltammetry was performed using a BAS C3 cell stand, samples were degassed with argon and stirred continuously between recordings. Quantitative spectroscopy was performed in the pure solvent, using a 1 cm quartz cell, and analyte concentrations in the range of 4×10^{-5} to 3×10^{-4} molar.

Reagents and Synthesis

All naphthalimide derivatives were synthesised by Dr. Liviu Dinescu from reagents obtained from commercial sources (Aldrich) and used without further purification unless otherwise stated. Dimethylformamide (DMF) was distilled from BaO under reduced pressure and stored over molecular sieves. 4,5-Dinitro-¹⁰, 4-phenylthio-¹¹, 4-phenylsulfonyl-¹² and 4,5-dichloronaphthalic^{13, 14} anhydrides were synthesized according to known procedures and were shown to have the expected physical and spectral properties.

4,5-Diphenylthionaphthalic anhydride: Under a N_2 atmosphere, 1.5 g (13.6 mmol) of thiophenol and 3.5g (42.67 mmol) of anhydrous sodium acetate were added to a solution of 4,5-dinitronaphthalic anhydride (1.96 g, 6.8 mmol) in 15 mL of dry DMF. The mixture was stirred vigorously at room temperature for 24 hours. The mixture was diluted with 50 ml of cold water and the precipitate formed was filtered and washed

several times with cold water. Purification by crystallization from glacial acetic acid gave 2.6 g of product (92%) as a yellow solid: m.p. 192-193 °C; ¹H NMR (200 MHz, acetone-d₆) δ 7.46-7.57 (m, 6H), 8.34 (d, *J* = 8.0 Hz, 1H).

4,5-Diphenylsulfonylnaphthalic anhydride: 0.2 g (0.48 mmol) of 4,5-

Diphenylthionaphthalic anhydride was refluxed for 3 hours in a solution of 2 mL H₂O₂ (30% in water) and 5 mL of glacial acetic acid. The mixture was diluted with 30 mL of cold water and the precipitate formed was filtered and washed several times with cold water. The compound was further purified by crystallization from aqueous acetic acid to give 0.15 g of product (65%) as light yellow crystals: m.p. 176-180 °C; ¹H NMR (200 MHz, acetone-d₆) δ 7.43-7.70 (m, 5H), 8.55 (d, *J* = 8.0 Hz, 1H), 8.63 (d, *J* = 8.0 Hz, 1H).

N-Butylnaphthylimides: These were prepared using two methods:

Method A was applied to naphthalic anhydrides having chloro and nitro substituents in the 4 and 5 positions, which can be displaced via nucleophilic aromatic substitution by the aliphatic amine. The following procedure is representative for Method A: 1.0 g (3.5 mmol) of 4,5-dinitronaphthalic anhydride and 0.38 g (5.21 mmol) of *n*-butylamine were heated for 3 hours at 80 °C in mixture of 9 mL DMF and 1 mL glacial acetic acid. The mixture was poured in 20 mL of a solution of hydrochloric ethanol (5%) and upon the slow evaporation of the solvent brown crystals precipitated, which were filtered and dried (1.02 g, 85%).

Method B was applied to naphthalic anhydrides having substituents in the 4 and 5 positions other than chloro and nitro. The following procedure is representative for Method B: 0.5 g (1.21 mmol) of 4,5-diphenylthionaphthalic anhydride was refluxed for 1h in a solution of 0.26 g (3.55 mmol) *n*-butylamine in 6 mL absolute ethanol. Upon cooling to room temperature, yellow crystals precipitated, which were filtered and dried to give 0.41 g (72%) of imide **2.3**.

N-Butyl-naphthylimide (**II.1**): m.p. 95-98 °C; ¹H NMR (200 MHz, acetone-d₆) δ 0.96 (t, *J* = 8.0 Hz, 3H), 1.32-1.50 (m, 2H), 1.62-1.76 (m, 2H), 4.16 (t, *J* = 8.0 Hz, 2H), 7.85 (t, *J* = 6.0 Hz, 2H), 8.38 (t, *J* = 6.0 Hz, 2H), 8.54 (t, *J* = 6.0 Hz, 2H); MS (EI, *m/z*) calcd. For C₁₆H₁₅NO₂ 253.1, found 253 (M⁺, 95).

N-Butyl-4,5-diphenylsulfonylnaphthylimide (**II.2**): m.p. 140-142 °C; ¹H NMR (200 MHz, acetone-d₆) δ 0.91 (t, *J* = 8.0 Hz, 3H), 1.31-1.45 (m, 2H), 1.54-1.70 (m, 2H), 4.05 (t, *J* = 8.0 Hz, 2H), 7.42-7.70 (m, 10H), 8.49 (d, *J* = 8.0 Hz, 2H), 8.57 (d, *J* = 8.0 Hz, 2H); MS (EI, *m/z*) calcd. for C₂₈H₂₃NO₆S₂ 533.1, found 533 (M⁺, 20).

N-Butyl-4,5-diphenylthionaphthylimide (**II.3**): m.p. 136-138 °C; ¹H NMR (200 MHz, CDCl₃) δ 0.94 (t, *J* = 6.0 Hz, 3H), 1.32-1.48 (m, 2H), 1.53-1.78 (m, 2H), 4.12 (t, *J* = 6.0 Hz, 2H), 7.34-7.49 (m, 12H), 8.32 (d, *J* = 8.0 Hz, 2H); MS (EI, *m/z*) calcd. for C₂₈H₂₃NO₂S₂ 469.1, found 469 (M⁺, 100).

N-Butyl-4,5-dinitronaphthylimide (II.4): m.p. 136-140 °C; ^1H NMR (200 MHz, acetone- d_6) δ 0.96 (t, $J = 8.0$ Hz, 3H), 1.37-1.50 (m, 2H), 1.66-1.80 (m, 2H), 4.16 (t, $J = 8.0$ Hz, 2H), 8.68 (d, $J = 8.0$ Hz, 2H), 8.85 (d, $J = 8.0$ Hz, 2H); MS (EI, m/z) calcd. for $\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_6$ 343.1, found 343 (M^+ , 24).

N-Butyl-4-chloronaphthylimide (II.5): m.p. 88-91 °C; ^1H NMR (200 MHz, acetone- d_6) δ 0.96 (t, $J = 8.0$ Hz, 3H), 1.31-1.50 (m, 2H), 1.60-1.78 (m, 2H), 4.11 (t, $J = 8.0$ Hz, 2H), 7.99 (t, $J = 8.0$ Hz, 2H), 8.46 (d, $J = 8.0$ Hz, 1H), 8.60 (d, $J = 8.0$ Hz, 2H); MS (EI, m/z) calcd. $\text{C}_{16}\text{H}_{14}\text{ClNO}_2$ 287.1, found 287 (M^+ , 78).

N-Butyl-4-phenylsulfonylnaphthylimide (II.6): m.p. 180-182 °C; ^1H NMR (200 MHz, acetone- d_6) δ 0.94 (t, $J = 8.0$ Hz, 3H), 1.31-1.49 (m, 2H), 1.60-1.78 (m, 2H), 4.11 (t, $J = 8.0$ Hz, 2H), 7.58-7.70 (m, 3H), 7.93-8.14 (m, 3H), 8.59-8.80 (m, 3H), 9.10 (d, $J = 8.0$ Hz, 1H); MS (EI, m/z) calcd. for $\text{C}_{22}\text{H}_{19}\text{NO}_4\text{S}$ 393.1, found 393 (M^+ , 96).

N-Butyl-4-phenylthionaphthylimide (II.7): m.p. 89-90 °C; ^1H NMR (200 MHz, acetone- d_6) δ 0.95 (t, $J = 8.0$ Hz, 3H), 1.30-1.49 (m, 2H), 1.60-1.78 (m, 2H), 4.09 (t, $J = 8.0$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 1H), 7.49-7.59 (m, 5H), 7.90 (t, $J = 8.0$ Hz, 1H), 8.34 (d, $J = 8.0$ Hz, 1H), 8.55-8.68 (m, 2H); MS (EI, m/z) calcd. for $\text{C}_{22}\text{H}_{19}\text{NO}_2\text{S}$ 361.1, found 361 (M^+ , 88).

N-Butyl-4-nitronaphthylimide (II.8): m.p. 163-165 °C; ^1H NMR (200 MHz, acetone- d_6) δ 0.96 (t, $J = 8.0$ Hz, 3H), 1.32-1.52 (m, 2H), 1.60-1.78 (m, 2H), 4.12 (t, $J = 8.0$ Hz, 2H), 8.09 (t, $J = 8.0$ Hz, 1H), 8.51 (d, $J = 8.0$ Hz, 1H), 8.64-8.75 (m, 3H); MS (EI, m/z) calcd. for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4$ 298.1, found 298 (M^+ , 100).

N-Butyl-4,5-dichloronaphthylimide (II.9): m.p. 165 °C; ^1H NMR (200 MHz, CDCl_3) δ 0.96 (t, $J = 8.0$ Hz, 3H), 1.32-1.51 (m, 2H), 1.60-1.79 (m, 2H), 4.14 (t, $J = 8.0$ Hz, 2H), 7.87 (d, $J = 8.0$ Hz, 2H), 8.52 (d, $J = 8.0$ Hz, 2H); MS (EI, m/z) calcd. for $\text{C}_{16}\text{H}_{14}\text{Cl}_2\text{NO}_2$ 321.0, found 321 (M^+ , 65).

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Introduction

The novel complexes reported herein were synthesised from a series of symmetric and asymmetric hydrazide ligands produced by the reaction of various acid chloride, acid anhydrides or isocyanates with hydrazine or a hydrazide. The complexes were prepared in order to determine their thermal stability, spectroscopic and electrochemical behaviour as the electron density within the bridging ligand is varied and the electrochemical kinetics of the 1st redox couple were determined. Therefore, herein is reported the synthesis and characterization of a series of novel dinuclear [$\{\text{Ru}(\text{bpy})_2\}_2\mu\text{-R}_2\text{-adc}\](PF₆)₂, [$\{\text{Ru}(\text{bpy})_2\}_2\mu\text{-R, ph-adc}\](PF₆)₂, [$\{\text{Ru}(\text{bpy})_2\}_2\mu\text{-R, CH}_3\text{Oph-adc}\](PF₆)₂, [$\{\text{Ru}(\text{bpy})_2\}_2\mu\text{-R, R'-adc}\](PF₆)₂, complexes, where “R” and “R'” were selected between strongly electron withdrawing (i.e. nitrophenyl and trifluoromethyl) to strongly electron donating (i.e. *N,N*-dimethylamino and *N*-propylamino). The complexes synthesised as part of this study are indicated in scheme III.1 below and the synthetic method in scheme III.3.$$$$

Scheme III.1

Furthermore, several tetranuclear and one pentanuclear complex were prepared. This was done as a synthetic prelude to polymeric materials in order to probe the synthesis beyond the dinuclear case. At the same time, the bridge, in this case referring to the connecting moiety between each dinuclear complex, was varied between the saturated butyl to the fully unsaturated acetylene (scheme III.2). To our knowledge, this is the first series of complexes of this kind ever constructed, and was done in order to probe the effect of inter-complex coupling on the electrochemistry and spectroscopy of the linked dinuclear complexes.

Scheme III.2

Results and Discussion

Synthesis: Ligand preparation was generally high yield and performed under mild conditions. The high solubility of the product 1,2-dicarbonylhydrazine products in THF was advantageous in purification where an acid chloride was utilized in the synthesis as the HCl by-product was removed easily as the $TEA \cdot HCl$. In these cases, NMR spectra of

the crude complexes were generally devoid of peaks indicative of starting material and so recrystallization was not necessary. In the case of the 1-benzoyl-2-trifluoroacetylhydrazine, evaporation of the solvent was sufficient to produce a product with acceptable purity. Finally, the low solubility of the 1-benzoyl-2-(*N*-propylcarbamyl)hydrazine allowed separation of the product by direct filtration followed by THF washing to remove residual reactants.

Scheme III.3

Preparation of the dinuclear complexes was generally high yield (cp. 70% crude). Column chromatography on alumina produced between 2 and 3 separate chromatographic bands, corresponding to the $\text{Ru}^{\text{II}}\text{Ru}^{\text{II}}$ (purple, 1st), $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$ (yellow, 2nd)

and $\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}$ (green, 3rd) oxidation states of the complex. In some cases it was possible to isolate both the $\text{Ru}^{\text{II}}\text{Ru}^{\text{II}}$ and $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$ complexes, however the $\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}$ chromatographic bands were very faint in all cases and were not mobile under the prevailing column conditions.

The preparation of the tetranuclear and pentanuclear complexes was conducted in the same manner as that of the dinuclear. Column chromatography was used to purify the complexes and, as in the case of the dinuclear, several bands emerged corresponding to the lowest through to the highest total oxidation state of the complex. The difference, broadly speaking, was that the yield of the majority band was very low and the band movement through the column was relatively slow. This was likely due to the higher charge associated with these complexes in the lowest oxidation state, which increased the strength of the association interaction between the complex and the alumina packing. As a partial solution to this, the WA-I alumina packing was partially deactivated from activity grade I to activity grade III by the addition of 6% (w/w) water.

X-Ray Crystal Data: The structure of the complex was similar to other azodicarbonyl complexes^{1, 2}. The x-ray data is presented in table III.1 (and Appendix 1) and the ortep diagram of the complex is shown in figure III.1.

The features of this complex are much the same as that of the $[\{\text{Rh}(\text{CO})_2\}_2 \mu\text{-benzoylazodicarbonyl}]^2$. The geometry around ruthenium is essentially octahedral with the only deviations arising from constraints placed upon the bipyridine and bridging ligands. The 3 planar bidentate ligands were nearly orthogonal with angles ranging from 83.6 to 89.8 degrees.

The bridging azodicarbonyl ligand appeared to be nearly planar and the distance between the metal centres was 4.671 Å, which was intermediate to that of the Cu and Rh analogues at 4.819 and 3.347 Å^{1, 2}. The bond lengths between the nitrogen and oxygen of the bridge and ruthenium were 2.084 and 2.038 Å, similar to the Rh analogue² but shorter than those of the copper analogue. This can be attributed to the greater degree of $d\pi \rightarrow \pi^*$ back-bonding associated with second row transition metals versus that of first

row. Furthermore, bond lengths within the bridge, specifically the C28-O1 and C28-N5, were intermediate between the single and double bond lengths indicating extended conjugation across the molecule.

Table III.1: Crystal data and selected bond lengths and angles for $\{[\text{Ru}(\text{bpy})_2]_2\mu\text{-Ph, CH}_3\text{-adc}](\text{BF}_4)_2$ (III.7).

A. Crystal Data			
Formula	$\text{C}_{49}\text{H}_{40}\text{B}_2\text{F}_8\text{N}_{10}\text{O}_2\text{Ru}_2$	$V, \text{\AA}^3$	5017(1)
Formula wt.	1176.67	Z	4
$a, \text{\AA}$	25.684(4)	Density (calcd), g cm^{-3}	1.558
$b, \text{\AA}$	12.086(2)	Space Group	C2/c
$c, \text{\AA}$	17.625(3)	$\lambda (\text{Mo K}\alpha) \text{\AA}$	0.71073
$\beta, \text{deg.}$	113.507(2)	R_I	0.0669
B. Selected bond lengths ($\text{\AA}$)			
Ru-O1	2.038(7)	N5-N5a	1.468(14)
Ru-N5	2.084(8)	O1-C28	1.298(11)
Ru-N1	2.058(9)	C28-N5	1.306(11)
Ru-N2	2.081(11)	C28a-C27	1.70(3)
Ru-N3	2.018(8)	C28-C26	1.441(13)
Ru-N4	2.020(10)	Ru-Ru ^a	4.671
C. Selected bond angles (deg.)			
N4-Ru-N3	78.9(4)	O1-C28-N5	123.8(9)
N1-Ru-N2	78.3(4)	C28-N5-N5a	111.8(9)
O1-Ru-N5a	77.9(3)	N5-N5a-Ru	111.7(7)
N3-Ru-N1	89.8(3)	N4-Ru-N5a	89.7(3)
N2-Ru-O1	83.6(3)		

^a calculated using ORTEP III software.

MS, NMR and IR Spectroscopy: MS spectroscopy was used to validate proposed structures of all ligands and complexes synthesised. In the case of the metal complexes this was, other than uv-vis-NIR and electrochemical methods, the only validation of the proposed formula as both the NMR and IR spectroscopy of the

complexes was not informative. Interpretation of the MS spectra involved both correlation of mass and peak pattern, as ruthenium has seven naturally occurring isotopes. Simulation of fragments with both single and multiple metal constituents using Isopro 3.0 produced distinctive mass patterns, which could be correlated with those observed in the mass spectra.

With respect to the NMR, a small residual of oxidized paramagnetic complex made it impossible to make even rudimentary assignments as it resulted in a great degree of peak overlap and the generally poor spectra.

Thermal Analysis: All dinuclear complexes in this series exhibited relatively high thermal stability (see table III.2), with typical decomposition temperatures (at 5% weight loss under N₂ atmosphere) in the range of 257 to 400 °C. This stability was surprising but not entirely unexpected in light of the tight binding to be expected between ruthenium and the three bidentate (i.e. two bipyridyl and azodicarbonyl) chelates capable of engaging in both σ -donor and π^* -acceptor bonding interactions.

The tetra- and pentanuclear complexes generally showed the same stability except the ethylene and acetylene bridged systems, which had markedly lower decomposition temperatures.

Table III.2: Thermal gravimetric analysis data for $\{[Ru(bpy)_2]_2 \mu\text{-R, R'-adc}\}^{n+}$ complexes.

(Complex #) R, R'	Decomposition Temperature (5% wt. Loss, °C)
(III.1) Ph, Ph	397
(III.2) CH ₃ OPh, CH ₃ OPh	400
(III.3) NO ₂ Ph, NO ₂ Ph	369
(III.4) NH(C ₃ H _{7-n}), NH(C ₃ H _{7-n})	278
(III.5) Ph, CH ₃ OPh	360
(III.6) Ph, CF ₃	377
(III.7) Ph, CH ₃	373
(III.8) Ph, NO ₂ Ph	350
(III.9) Ph, N(CH ₃) ₂	311
(III.10) Ph, NH(C ₃ H _{7-n})	257
(III.11) CH ₃ OPh, CF ₃	400
(III.12) CH ₃ OPh, CH ₃	400
(III.13) CH ₃ OPh, NO ₂ Ph	360
(III.14) CH ₃ OPh, N(CH ₃) ₂	334
(III.15) CH ₃ OPh, NH(C ₃ H _{7-n})	311
(III.16) NO ₂ Ph, NH(C ₃ H _{7-n})	313

Differential scanning calorimetry was performed on selected dinuclear and tetranuclear complexes to probe for the presence of transitions indicative of either melting or softening due to inter- or intra-molecular motion. The complexes analyzed were $\{[Ru(bpy)_2]_2 \mu\text{-CH}_3\text{OPh, NH(C}_3\text{H}_7\text{-n)-adc}\}(PF_6)_2$ (III.15), $\{[Ru(bpy)_2]_2 \mu\text{-CH}_3\text{OPh, NO}_2\text{Ph-adc}\}(PF_6)_2$ (III.13), and $\{[Ru(bpy)_2]_2 \mu\text{-NO}_2\text{Ph, NH(C}_3\text{H}_7\text{-n)-adc}\}(PF_6)_2$ (III.16) as well as the butyl, ethenyl, and acetylene bridged tetranuclear complexes. Of all of the complexes analyzed no transitions were observed, with the exception of the acetylene bridged tetranuclear complex. This complex showed a melting endotherm at 68 °C, which was in agreement with the melting point found visually.

Table III.3: Thermal gravimetric analysis data for $\{[Ru(bpy)_2]_4 \mu\text{-R-bisbenzoyl}ad\text{c}](PF_6)_4$ tetranuclear complexes.

(Complex #) R	Decomposition Temperature (5% wt. Loss, °C)
(III.17)	360
(III.18)	235
(III.19)	102
(III.20)	400
(III.21)	364

Cyclic voltammetry: All dinuclear complexes exhibited two quasi-reversible one-electron redox couples, anodic to NHE, associated with the ruthenium metal centres and, in some complexes only, two reversible cathodic couples associated with the bipyridine ligands. The electrochemical data for the metal redox couples, along with comproportionation constants k_c , are tabulated in table III.4 while a typical cyclic voltammogram is presented in figure III.2.

Figure III.2: Cyclic voltammogram of $[\{Ru(bpy)_2\}_2\mu\text{-Ph, NO}_2\text{Ph-adc}]^{n+}$ (III.8) in ACN (0.1 M TBAH) at a scan rate of 200 mV/s.

The trend over the series showed that as the average donor strength of the substituent increased the $E_{1/2}$ potential was shifted cathodically. It was observed, in all cases, that both metal redox couples were effected nearly equally by the various substituents, the only affect being a slight drop in the $\Delta E_{1/2}$ over the series with increasing donor strength. The most conspicuous exceptions were the $[\{Ru(bpy)_2\}_2\mu\text{-R, NH(C}_3\text{H}_7\text{-n)-adc}]^{n+}$ complexes, which had the largest $\Delta E_{1/2}$ values. This can be attributed to the presence of the 2° amine group that may provide extra stabilization to the mixed valence complex through a resonance mechanism involving deprotonation (scheme III.4). In support of this mechanism it should be noted that the magnitude of $\Delta E_{1/2}$ indicates the

stability of the mixed valence species and so it was believed that these systems must gain stability via a mechanism not available to any of the other complexes studied.

Furthermore, the appearance of a C=N str. at 1582 cm^{-1} and the loss of intensity of the N-H bending mode at 1538 cm^{-1} in the IR of the mixed valence state for the $[\{\text{Ru}(\text{bpy})_2\}_2\mu\text{-Ph, NH}(\text{C}_3\text{H}_7\text{-n})\text{-adc}]^{n+}$ (3.10) complex (see figure III.3), would appear to support this claim.

Scheme III.4

Figure III.3: IR spectra of $[\{\text{Ru}(\text{bpy})_2\}_2\mu\text{-Ph, NH}(\text{C}_3\text{H}_7\text{-n})\text{-adc}]^{n+}$ (III.10).

Table III.4: Electrochemical data^a for $\{[Ru(bpy)_2]_2\mu-R, R'-adc\}(PF_6)_2$ complexes taken in ACN (0.1 M TBAH).

(Complex #) R, R'	¹ E _{1/2} (p-p) ^e		² E _{1/2} (p-p) ^e		ΔE	k_c^d
	NHE ^b	Ag/Ag ⁺ ^c	NHE ^b	Ag/Ag ⁺ ^c		
(III.1) Ph, Ph	800(74)	290	1380(77)	870	580	6.4×10^9
(III.2) CH ₃ OPh, CH ₃ OPh	760(79)	530	1330(114)	1100	570	4.3×10^9
(III.3) NO ₂ Ph, NO ₂ Ph	930(61)	680	1510(85)	1260	580	6.4×10^9
(III.4) NH(C ₃ H _{7-n}), NH(C ₃ H _{7-n})	330(120)	-40	920(130)	550	590	9.5×10^9
(III.5) Ph, CH ₃ OPh	790(112)	310	1360(112)	880	570	4.3×10^9
(III.6) Ph, CF ₃	970(103)	560	1540(103)	1130	570	4.3×10^9
(III.7) Ph, CH ₃	730(96)	300	1330(96)	900	600	1.4×10^{10}
(III.8) Ph, NO ₂ Ph	880(162)	460	1480(155)	1060	600	1.4×10^{10}
(III.9) Ph, N(CH ₃) ₂	650(133)	140	1150(128)	640	500	2.9×10^8
(III.10) Ph, NH(C ₃ H _{7-n})	590(82)	90	1220(87)	720	630	4.5×10^{10}
(III.11) CH ₃ OPh, CF ₃	960(85)	570	1520(106)	1130	560	2.9×10^9
(III.12) CH ₃ OPh, CH ₃	740(77)	260	1320(84)	840	580	6.4×10^9
(III.13) CH ₃ OPh, NO ₂ Ph	850(69)	410	1420(84)	980	570	4.3×10^9
(III.14) CH ₃ OPh, N(CH ₃) ₂	630(84)	130	1080(64)	580	450	4.1×10^7
(III.15) CH ₃ OPh, NH(C ₃ H _{7-n})	560(74)	70	1170(79)	680	610	2.1×10^{10}
(III.16) NO ₂ Ph, NH(C ₃ H _{7-n})	660(120)	310	1300(130)	950	640	6.6×10^{10}

^aFrom cyclic voltammetry performed at 200 mV/s scan rate. ^bPotentials E in mV vs. NHE reference. ^cPotentials E in mV vs. silver pseudo-reference. ^d $k_c = 10^{[16.91\Delta E] 50,54}$. ^epeak-peak separation in mV.

The tetranuclear complexes showed between two and four distinct metal centered redox couples. For the butyl, phenyl, and bipyridyl-bridged complexes two, presumably two electron couples were observed in the cv. These can be assigned to the 1st and 2nd one electron Ru^{II} ↔ Ru^{III} couples of each of the linked dinuclear adc complexes. It is relatively simple to rationalize the result for the butyl, as this is a saturated bridge and lacks any degree of conjugation and so there is little expectation of coupling³. The phenyl and bipyridyl-bridged systems should have shown some coupling however, referring to the crystal structure of the $\{[Ru(bpy)_2]_2\mu-Ph, CH_3-adc\}^{2+}$ (III.7) complex, the phenyl ring is orthogonal to the planar adc bridge thus precluding effective π overlap.

In the case of the ethenyl and acetylene bridged complexes, between three and four redox couples were observed. Speaking on a case-by-case basis, the ethenyl bridged system showed four redox couples that appeared as two closely spaced pairs at approximately the same position as that of the other tetranuclear complexes. Each couple appeared to possess the same current magnitude and can be assigned to four one-electron couples. The comproportionation constants for the 1st/2nd and 3rd/4th redox couples were smaller by several orders of magnitude than between the 2nd and 3rd couples and can be assigned to the splitting of the 1st and 2nd redox couples of each adc fragment. Whereas the separation between the 2nd and 3rd couple, which were in the same range as that of the 1st and 2nd couples of the dinuclear complexes, can be assigned to the same separation of each adc moiety. This difference, indicative of differential between the coupling within the adc fragments and that between each fragment, shows that though some coupling exists between the two fragments mediated by the ethenyl bridge, it has much less strength than that mediated by the adc bridge.

The acetylene bridged complex exhibited three redox couples, which by current density estimation, were assigned as two one-electron couples (1st and 2nd couple) and one two-electron couple (3rd couple). The 1st redox couple is assigned to the $\text{Ru}^{\text{II}}\text{Ru}^{\text{II}} \leftrightarrow \text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$ couple of one adc fragment, the second assigned to the $\text{Ru}^{\text{II}}\text{Ru}^{\text{II}} \leftrightarrow \text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$ of the other fragment, while the third to two coincidental one electron redox couples of both fragments $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}} - \text{Ru}^{\text{II}}\text{Ru}^{\text{III}} \leftrightarrow \text{Ru}^{\text{III}}\text{Ru}^{\text{III}} - \text{Ru}^{\text{III}}\text{Ru}^{\text{III}}$.

$$E_{p,a} - E_{p,c} = 59/n \text{ mV}$$

Equation 1

Table III.5: Electrochemical data^a for $\{[\text{Ru}(\text{bpy})_2]_4 \mu\text{-R-dibenzoyladc}\}(\text{PF}_6)_4$ tetranuclear complexes taken in ACN (0.1 M TBAH^b).

(Complex #) R	E ¹ (p-p)	E ² (p-p)	E ³ (p-p)	E ⁴ (p-p)	ΔE	k _c ^c
(III.17)	770 (60)	1340 (80)	-	-	570	4.3 X 10 ⁹
(III.18)	890	980	1540	1570	90 560	33 2.9 X 10 ⁹
(III.19)	780 (60)	1370 (80)	1550 (90)	-	30 590	3.2 9.5 X 10 ⁹
(III.20)	850	1440	-	-	180 590	1.1 X 10 ³ 9.5 X 10 ⁹
(III.21)	940	1530			590	9.5 X 10 ⁹

^aFrom cyclic voltammetry performed at 200 mV/s scan rate. Potentials E in mV vs. NHE.

^bTBAH=tetrabutylammonium hexafluorophosphate. ^ck_c=10^{[16.91ΔE] 50,54}

In the analysis of the electrochemistry, the peak-peak separation for the oxidation and reduction waves of each couple was examined. Generally, for the dinuclear complexes, even as the scan rate is reduced to 50 mV/s the separation was greater than the Nernst predicted 59 mV^{4, 5} given in equation 1. The results showed that the first redox couple deviated less than that of the second couple and, as the scan rate was increased between 50 and 250 mV/s, the deviation from kinetic reversibility decreased as would be expected for quasi-reversibility. Furthermore, for only two of the dinuclear complexes, namely the $\{[\text{Ru}(\text{bpy})_2]_2 \mu\text{-(NO}_2\text{Ph)}_2\text{-adc}\}(\text{PF}_6)_2$ (III.3) (i.e. 60 mV at both 200 and 50 mV/s), and $[\text{Ru}(\text{bpy})_2]_2 \mu\text{-Ph}_2\text{-adc}\}(\text{PF}_6)_2$ (III.1) (i.e. 60 mV at 50 mV/s), did

the 1st redox couple separation appear to indicate reversible behaviour as the scan rate was adjusted. It was therefore not possible to make assignments as to the number of electrons involved in each redox process from the peak-peak separations directly for all complexes. Lastly, with regard to the acetylene bridged tetranuclear complex, the peak-peak separation was greater for the 3rd redox couple (90 mV) than the 1st couple (60 mV), therefore the assignment of the 3rd couple being a two-electron process is based solely upon the differential peak intensities.

Table III.6: Electrochemical kinetic data for $\{[Ru(bpy)_2] \mu-R, R'-adc\}(PF_6)_2$ complexes taken in ACN (0.1 M TBAH^b).

(Complex #) R,R'	I_{lim} (μA)	D (cm^2/s)	k_s (cm/s)	v_s (mole/s)	Switching Speed (s/cm^2)
(III.5) CH ₃ OPh, Ph	0.862	3.7×10^{-5}	0.61	2.9×10^{-9}	70
(III.8) NO ₂ Ph, Ph	0.329	1.8×10^{-5}	0.033	4.1×10^{-10}	500
(III.10) NH(C ₃ H ₇ -n), Ph	0.431	1.8×10^{-5}	0.084	1.3×10^{-9}	150

In order to quantify the optical switching speed of this material, the non-homogeneous electron transfer kinetics were measured using the method of Nicholson and Shain^{6, 7} (see table III.6). Briefly, in this method, the diffusion controlled limiting current for the 1st (i.e. $Ru^{II}Ru^{II} \leftrightarrow Ru^{II}Ru^{III}$) redox couple is measured and from this the diffusion coefficient for the species is calculated using equation 2. This is then combined with the current function (ψ)^{4, 6} (equation 3) to generate the rate constant (k_s) in terms of cm/s. The reaction velocity (v_s) in mole/s was then calculated by multiplying by the area of the electrode and the concentration of the analyte. Furthermore, though the kinetics of

this material have not been measured previously, comparison with the results for $[\text{Co}(\text{bpy})_3]^{2+/3+}$ charge transfer rate constants measured by Pyati *et al*⁷, showed that the magnitude does not appear to be unreasonable. Additionally, it was found that the velocity varied by approximately an order of magnitude for the three compounds measured, however since no kinetic argument can be made to account for the trend in the results this variation might simply be within the systemic uncertainty for the method.

$$D = \frac{i_{\text{lim}}}{4nFrC} \quad \text{Equation 2}$$

$$k_s = \psi \sqrt{\pi a D} \quad \text{Equation 3}$$

The velocity was not a useful indicator of actual switching speed in the solid state therefore the time necessary to switch between 0 and 2 OD at 1550 nm was calculated. This calculation was accomplished by assuming the probable density of a film of this material was equal to that of the crystallized complex taken from the x-ray analysis. The film thickness parameter was then adjusted to be sufficient to produce the desired optical density for the NIR MMCT band in the coloured state. The results, which should be interpreted as merely a boundary condition, indicate that in order to achieve full attenuation would require on the order of 1 to as much as 10 minutes.

Lastly, to better rationalize the substituent affect, a correlation was sought between the donor capacity of the substituent and both the spectroscopic and

electrochemical results. It seemed prudent to employ Hammett parameters for the various side groups as they have been compiled for many fragments and provide a direct measure of electron donor potential. The work of others⁸⁻¹⁰ has shown that strong correlations exist for metal bipyridyl complexes.

The plot in figure III.4 shows the correlation between the average Hammett (σ^*) for the two substituents and both the 1st and 2nd metal redox couples of the dinuclear complexes. It should be noted that in deriving a suitable correlation it was necessary to take the average total Hammett. The plot clearly shows a strong correlation between Hammett parameter and electrochemical properties, which is significant to note since it shows that each metal is approximately equally perturbed by both substituents. This is reasonable in light of the strongly delocalised nature of the ADC system and the fact that the mean through bond distance between the carbonyl carbons and each metal is nearly equal.

Figure III.4: Average Hammett versus $E_{1/2}$ for $[\{\text{Ru}(\text{bpy})_2\}_2\mu\text{-R, R'-adc}]^{n+}$ complexes. Correlations were performed by linear regression using Sigmaplot 5.0.

Uv-vis-NIR: Band assignments for similar ADC complexes have already been published¹¹ and so the more pronounced features of the spectroscopy will be dealt with here. With respect to the dinuclear complexes, the 2+ ($\text{Ru}^{\text{II}}\text{Ru}^{\text{II}}$) oxidation state exhibited two absorption bands associated with the $d(\text{Ru}^{\text{II}}) \rightarrow \pi^*(\text{bpy})$ MLCT transitions at ca. 520 and 360 nm. Over the series there is a slight decrease overall in the MLCT band energy of approximately 850 cm^{-1} with increasing donor strength of the substituent R,R'.

Figure III.5: Uv-vis-NIR spectra of $\{[Ru(bpy)_2]_2\mu\text{-Ph, NO}_2\text{Ph-adc}\}^{n+}$ (III.8) in ACN (0.1 M TBAH) using the OTTLE cell.

Oxidation to the 3+ ($Ru^{II}Ru^{III}$) mixed valence state blue shifts the bpy centred MLCT by about 3000 cm^{-1} , although the higher energy transition is not observed and is likely masked by the intense bpy centred $\pi \rightarrow \pi^*$ transitions. As well, an intense near infrared band appears, associated with the MMCT transition ($d\pi(Ru^{II}) \rightarrow d\pi(Ru^{III})$), between 1100 to 1800 nm. The MMCT band is blue shifted as the donor potential of substituent is increased, which can be rationalized in a hole transfer regime as indicated by the work of Kaim¹² and shown schematically in scheme III.5. Overall the effect of increasing the electron density in the bridge is to destabilize the Ru^{II} donor orbital thus increasing the energy gap between donor and acceptor metal.

Scheme III.5

For the $4+$ ($\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}$) oxidation state, in addition to the bpy $\pi \rightarrow \pi^*$ transitions, an intense band between 800 and 950 nm was observed, which is assigned to the ADC centred LMCT $\pi[(\text{adc-X, Ph})^{2-}] \rightarrow d\text{Ru}^{\text{III}}$ transition.

Table III.7: Electronic spectral data^a for $[\{\text{Ru}(\text{bpy})_2\}_2\mu\text{-R}_2\text{-adc}]^{n+}$ in ACN.

(Complex #) R	n	$\text{Ru}^{\text{n}}/\text{Ru}^{\text{m}^b}$	$\lambda_{\text{max}}(\log \epsilon)$
(III.1) Ph	2	II/II	245(4.96), 294(4.92), 356(4.29), 518(4.19)
	3	II/III	243(4.72), 292(4.88), 432(4.10), 1590(4.13)
	4	III/III	250(4.80), 306(4.65), 317(4.66), 808(4.14)
(III.2) CH_3OPh	2	II/II	290(4.67), 354(4.24), 520(4.13)
	3	II/III	289(4.65), 440(3.86), 1593(3.84)
	4	III/III	303(4.47), 850(3.87)
(III.3) NO_2Ph	2	II/II	288(4.69), 348(4.25), 507(4.19)
	3	II/III	288(4.63), 430(3.87), 1629(3.83)
	4	III/III	305(4.43), 315(4.42), 779(3.76)
(III.4) $\text{NH}(\text{C}_3\text{H}_7\text{-n})$	2	II/II	288(5.01), 454(4.17)
	3	II/III	287(5.03), 451(4.18), 685(3.63), 795(3.60), 1119(3.43)
	4	III/III	286(4.97), 441(4.11), 639(3.72), 792(3.71)
	5	III/III	305(4.81), 642(3.37)

^a Wavelengths in nm and molar extinction coefficients ϵ in $\text{M}^{-1}\text{cm}^{-1}$; ^b Ruthenium oxidation states.

Table III.8: Electronic spectral data^a for $\{[Ru(bpy)_2]_2\mu-R, R'-adc\}^{2+}$ in

ACN.

R, R'	<i>n</i>	Ru ^{II} /Ru ^{III} ^b	$\lambda_{max}(\log \epsilon)$
(III.5) Ph, CH ₃ OPh	2	II/II	244(4.69), 294(4.88), 354(4.25), 519(4.16)
	3	II/III	244(4.70), 291(4.84), 434(4.08), 1590(4.07)
	4	III/III	247(4.72), 284(4.65), 824(3.97)
(III.6) Ph, CF ₃	2	II/II	244(4.67), 353(4.28), 498(4.21)
	3	II/III	244(4.68), 287(4.86), 425(4.08), 1655(4.04)
	4	III/III	244(4.73), 304(4.77), 311(4.77)
(III.7) Ph, CH ₃	2	II/II	245(4.65), 292(4.93), 350(4.24), 522(4.18)
	3	II/III	243(4.65), 291(4.88), 431(4.03), 1557(4.08)
	4	III/III	248(4.74), 306(4.60), 316(4.61), 812(4.12)
(III.8) Ph, NO ₂ Ph	2	II/II	245(4.66), 293(4.91), 352(4.25), 513(4.18)
	3	II/III	245(4.68), 290(4.84), 429(4.05), 1612(4.07)
	4	III/III	249(4.76), 304(4.63), 801(3.93)
(III.9) Ph, N(CH ₃) ₂	2	II/II	245(4.67), 354(4.23), 519(4.13)
	3	II/III	244(4.66), 441(4.08), 1378(3.77)
	4	III/III	245(4.68), 281(4.80), 911(4.02)
(III.10) Ph, NH(C ₃ H ₇ - <i>n</i>)	2	II/II	246(4.66), 348(4.20), 521(4.12)
	3	II/III	244(4.66), 291(4.90), 429(4.02), 1246(3.71)
	4	III/III	248(4.70), 281(4.74), 363(4.01), 631(3.55), 943(4.01)
(III.11) CH ₃ OPh, CF ₃	2	II/II	242(4.67), 354(4.24), 499(4.16)
	3	II/III	245(4.67), 428(4.04), 1639(3.91)
	4	III/III	251(4.78), 304(4.74), 311(4.74)
(III.12) CH ₃ OPh, CH ₃	2	II/II	245(4.69), 348(4.23), 523(4.15)
	3	II/III	244(4.78), 446(4.10), 1556(4.04)
	4	III/III	251(4.75), 304(4.65), 820(4.12)
(III.13) CH ₃ OPh, NO ₂ Ph	2	II/II	244(4.67), 288(4.93), 458(4.06)
	3	II/III	243(4.59), 285(4.79), 1600(3.54)
	4	III/III	246(4.52), 283(4.55), 319(4.44), 805(3.78)
(III.14) CH ₃ OPh, N(CH ₃) ₂	2	II/II	244(4.66), 288(4.95), 351(4.16)
	3	II/III	244(4.65), 288(4.95), 450(4.14), 1354(3.58)
	4	III/III	245(4.62), 285(4.92), 387(3.98), 419(3.97), 909(3.92)
(III.15) CH ₃ OPh, NH(C ₃ H ₇ - <i>n</i>)	2	II/II	245(4.65), 289(4.95), 346(4.15), 455(4.10)
	3	II/III	244(4.65), 288(4.94), 449(4.10), 1253(3.57)
	4	III/III	246(4.65), 285(4.88), 929(3.91)
(III.16) NO ₂ Ph, NH(C ₃ H ₇ - <i>n</i>)	2	II/II	245(4.65), 288(4.97), 455(4.13)
	3	II/III	244(4.62), 286(4.94), 427(4.10), 1224(3.05)
	4	III/III	244(4.64), 284(4.86), 425(4.03), 907(2.96)
	5*	III/III	243(4.63), 284(4.69), 424(4.21)

^a Wavelengths in nm and molar extinction coefficients ϵ in M⁻¹cm⁻¹; ^b Ruthenium oxidation states.

Table III.9: Electronic spectral data^a for $\{[Ru(bpy)_2]_4 \mu\text{-R-dibenzoyladc}\}^{n+}$ tetranuclear complexes in ACN.

(Complex #) R	n	Ru ^k /Ru ^l -Ru ^m /Ru ⁿ ^b	$\lambda_{\max}(\log \epsilon)$
(III.17)	4	II/II-II/II	245(4.92), 293(5.20), 348(4.49), 520(4.43)
	6	II/III-II/III	242(4.93), 291(5.11), 434(4.46), 1510(4.38)
	8	III/III-III/III	248(5.00), 304(4.87), 316(4.86), 802(4.48)
(III.18)	4	II/II-II/II	245(4.92), 288(5.20), 358(4.49), 464(4.48), 508(4.46)
	6	II/III-II/III	244(4.91), 288(5.16), 449(4.46), 1645(4.22)
	8	III/III-III/III	246(4.97), 303(4.92), 801(4.12)
(III.19)	4	II/II-II/II	244(4.46), 287(4.86), 452(3.99)
	5	II/III-II/II	243(4.47), 287(4.81), 449(4.06), 1579(3.63)
	6	II/III-II/III	248(4.56), 304(4.55), 809(3.55)
	8	III/III-III/III	247(4.59), 305(4.58), 797(3.53)
(III.20)	4	II/II-II/II	294(5.15), 357(4.52), 518(4.44)
	6	II/III-II/III	290(5.11), 431(4.31), 1575(4.31)
	8	III/III-III/III	306(4.90), 316(4.90), 798(4.30)
(III.21)	6	II/II-II/II	289(5.32), 458(4.47)
	8	II/III-II/III	288(5.25), 435(4.47), 1619(4.19)
	10	III/III-III/III	313(5.15)

^a Wavelengths in nm and molar extinction coefficients ϵ in $M^{-1}cm^{-1}$; ^b Oxidation states for Ruthenium in ADC fragment.

As with the electrochemical data, the correlation of the MMCT transition with the Hammett substituent term was sought. The shift, in terms of wavelength, for this band was more pronounced than that of the visible MLCT and LMCT transitions. A strong correlation between the major MMCT NIR band energies (eV) and Hammett was not found, however, in our study. The plot of σ_T^* versus MMCT band energy (figure III.6) shows a correlation (r^2) of 0.72 which indicates that, though a trend is present, the relationship between the substituent nature and the observed perturbation in this system is more involved than a simple correlation can account for.

Table III.10: Hammett substituent parameters^a and MMCT bandenergies^b taken in ACN for [$\{\text{Ru}(\text{bpy})_2\}_2\mu\text{-R, R'-adc}\]^{n+}$.

(Complex #) R,R'	σ_T^*	MMCT
(III.1) Ph,Ph	0.05	0.7798
(III.2) CH ₃ OPh,CH ₃ OPh	-0.03	0.7783
(III.3) NO ₂ Ph,NO ₂ Ph	0.51	0.7612
(III.4) NH(C ₃ H ₇ -n),NH(C ₃ H ₇ -n)	-0.85	1.108
(III.5) Ph,CH ₃ OPh	0.01	0.7798
(III.6) Ph,CF ₃	0.51	0.7492
(III.7) Ph,CH ₃	-0.10	0.7965
(III.8) Ph,NO ₂ Ph	0.28	0.7692
(III.9) Ph,N(CH ₃) ₂	-0.47	0.8999
(III.10) Ph,NH(C ₃ H ₇ -n)	-0.40	0.9936
(III.11) CH ₃ OPh,CF ₃	0.47	0.7565
(III.12) CH ₃ OPh,CH ₃	-0.14	0.7969
(III.13) CH ₃ OPh,NO ₂ Ph	0.24	0.7750
(III.14) CH ₃ OPh,N(CH ₃) ₂	-0.51	0.9159
(III.15) CH ₃ OPh,NH(C ₃ H ₇ -n)	-0.44	0.9896
(III.16) NO ₂ Ph,NH(C ₃ H ₇ -n)	-0.17	1.013

^a Hammett values taken from Hansch et al¹³, $\sigma_T^* = (\sigma_T^X + \sigma_T^Y)/2$;where $\sigma_T = \sigma_p + \sigma_m$. ^b Energies in eV. Figure III.6: Correlation of average Hammett (σ^*) and MMCT band energy ($r^2 = 0.72$).

The tetranuclear and pentanuclear complexes showed much the same spectroscopy as that of the dinuclear complexes. In the case of the butyl and phenyl bridged complexes, the position of the NIR MMCT transition was nearly the same as that of the comparable $[\{\text{Ru}(\text{bpy})_2\}_2 \mu\text{-Ph, CH}_3\text{-adc}](\text{PF}_6)_2$ (III.7) and $[\{\text{Ru}(\text{bpy})_2\}_2 \mu\text{-Ph}_2\text{-adc}](\text{PF}_6)_2$ (III.1) complexes, although a slight blue shift was evident. These complexes, including the pentanuclear $\text{Ru}(\text{bpy})_3$ bridged complex had the same nature as that of the dinuclear adc complexes, indicating no electronic communication existed between the individual dinuclear ADC fragments.

An anomalous result was derived for the acetylene-bridged complex as it possessed the mixed valence MMCT transition for only the 5+ ($[\text{Ru}^{\text{II}}\text{-Ru}^{\text{III}}]\text{-}[\text{Ru}^{\text{II}}\text{-Ru}^{\text{II}}]$) oxidation state. Strangely, no such NIR spectroscopic behaviour was observed for the 6+ ($[\text{Ru}^{\text{II}}\text{-Ru}^{\text{III}}]\text{-}[\text{Ru}^{\text{II}}\text{-Ru}^{\text{III}}]$) or double mixed valence state, and the spectra for the 6+ and 8+ ($[\text{Ru}^{\text{III}}\text{-Ru}^{\text{III}}]\text{-}[\text{Ru}^{\text{III}}\text{-Ru}^{\text{III}}]$) oxidation states were essentially the same, exhibiting what appeared to be LMCT transitions at approximately 800 nm. This indicates that the electrochemistry may be more complex than simply a progression from ($[\text{Ru}^{\text{II}}\text{-Ru}^{\text{II}}]\text{-}[\text{Ru}^{\text{II}}\text{-Ru}^{\text{II}}]$) to ($[\text{Ru}^{\text{II}}\text{-Ru}^{\text{III}}]\text{-}[\text{Ru}^{\text{II}}\text{-Ru}^{\text{II}}]$) then to ($[\text{Ru}^{\text{II}}\text{-Ru}^{\text{III}}]\text{-}[\text{Ru}^{\text{II}}\text{-Ru}^{\text{III}}]$) and finally to ($[\text{Ru}^{\text{III}}\text{-Ru}^{\text{III}}]\text{-}[\text{Ru}^{\text{III}}\text{-Ru}^{\text{III}}]$). A possible rational for this spectral behaviour may be that the double mixed valence state undergoes charge redistribution to form $[\text{Ru}^{\text{II}}\text{-Ru}^{\text{II}}]\text{-}[\text{Ru}^{\text{III}}\text{-Ru}^{\text{III}}]$ which would not be expected to possess an MMCT transition as that of the dinuclear adc complex.

Conclusions

The complexes presented herein proved to be relatively simple to synthesize, behaved generally as expected, possessed strong visible and NIR bands, and were thermally stable. We rationalized both the spectroscopy and electrochemistry in terms of the Hammett substituent parameter and found the best correlation occurred when comparison was made with the average of the total σ terms for each substituent. This correlation indicated that each metal appears to be affected equally by each substituent in the system. This was accounted for by considering that the metal-substituent distance is nearly the same for both substituents, coupled with the fact that there exists a high degree of delocalisation within the bridging ligand, this can be rationalized.

The tetranuclear complexes exhibited some interesting behaviour attributed to the degree of coupling between the individual adc fragments. Firstly, the systems within which the adc fragments were isolated exhibited the same behaviour as that of the dinuclear complexes. However, where the spacer was varied to an ethenyl system, weak splitting consistent with that proposed was observed. However, with respect to the acetylene-bridged system, the results were somewhat anomalous as, rather than the predicted four one-electron couples, three couples were observed comprised of two one-electron and one two-electron couples. Furthermore, the spectroscopy of the two accessible mixed valence states of this material indicated that oxidation of the first $[\text{Ru}^{\text{II}}-\text{Ru}^{\text{III}}]-[\text{Ru}^{\text{II}}-\text{Ru}^{\text{II}}]$ resulted in a bleaching of the MMCT transition. Though an adequate

explanation for the electrochemical behaviour has not been offered, the disappearance of the mixed valence state was attributed to an internal comproportionation. The results, therefore, indicate that both unexpected and interesting new behaviours result from the intercoupling of strongly coupled systems and is deserving of further research.

Kinetic measurements performed on a selected group of the dinuclear complexes indicated that the electrochemical switching speed may not be adequate for NIR modulation applications. This being said, however, reference to table I.2 would indicate that these materials might be adequate for other applications where speed is not crucial.

Experimental

Measurements

Uv-vis-NIR spectrophotometric and electrochemical measurements were taken in spectroscopic grade acetonitrile using a Perkin Elmer Lambda 900 uv-vis-NIR and BAS 100 B/W, respectively. NMR spectra were taken in DMSO- d_6 for the bridging ligands and in CD₂Cl₂ for the complexes and performed on a Bruker AMX-400 and Varian Gemini 200. IR spectra were performed on KBr mull of the compound and collected with a Bomem Michelson-100 FTIR. Spectroelectrochemical generation of the Ru^{II}Ru^{III} and Ru^{III}Ru^{III} oxidation states of the complexes were performed using an OTTE¹⁴ cell (see chapter I). The internal standard used to determine the position of the E_{1/2} potentials

for the complexes was $\text{Co}(\text{Cp})_2\text{PF}_6$ (98%, Aldrich) with an $E_{1/2}$ (vs. NHE) potential of -664 mV^{15} (in ACN) and -589 mV^{15} (in DMF). Cyclic voltammetry was performed using a BAS C3 cell stand, samples were degassed with argon and stirred continuously between recordings. The X-ray crystal structure determination was performed on a 1K Siemens Smart/CCD using Mo-K α radiation ($\lambda=0.71073 \text{ \AA}$) at 238 K. Thermal analysis was performed on Sieko TG/DTA 220 under a 200 cc/min. flow of dry, high purity N_2 gas. Differential scanning calorimetry was performed on a Sieko DSC 220C under a 50 cc/min. flow of dry, high purity N_2 gas.

Melting points were measured on a Fisher-Jones melting point apparatus and are uncorrected. The University of Ottawa Regional Mass Spectrometry Centre performed the low-resolution EI, FAB and ESI mass spectroscopy and peaks are reported as m/z (% intensity relative to the base peak).

Reagents and Synthesis

All reagents and solvents utilized in preparing the bridging adc ligands and complexes were used as received. Spectroscopic grade acetonitrile was used to perform both the quantitative uv-vis-NIR spectroscopy and cyclic voltammetry, however it was necessary to distill it over P_2O_5 in order to perform the spectroelectrochemical experiments in the OTTLE cell. The dibenzoylhydrazine was purchased from Aldrich.

All ligands were synthesized from the appropriate hydrazide and an appropriate acid chloride, acid anhydride or isocyanate. The specific synthetic environment was varied to permit reasonable yields, however generally they were produced in THF with a stoichiometric amount of triethylamine (TEA) added to remove the by-product HCl.

All ruthenium complexes were synthesized via the procedure of Kaim¹², using $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ prepared according to the method of Sullivan¹⁶ from $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (Aldrich). The general synthetic approach for the dinuclear complexes was to combine 0.38 mmol (200 mg) $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ with 0.19 mmol of the dicarboxylhydrazine ligand and 40 mg NaOH or 100 mg Na_2CO_3 in 80 mL of 5:1 $\text{H}_2\text{O}/\text{EtOH}$. The mixture was then refluxed for approximately 14 hours under ambient atmosphere, after which it was cooled to room temperature, and the product was precipitated by the addition of excess NH_4PF_6 . The crude product was then isolated by filtration, dried under vacuum, and then purified via column chromatography using WA-I acid alumina (chromatography grade, Sigma) and ACN (reagent grade, Aldrich) as the mobile phase.

Dinuclear Ruthenium ComplexesLigand Precursor Compounds*4-methoxybenzoylhydrazine:*

10 g (60.2 mmol) of methyl-4-methoxybenzoate was dissolved into 40 mL of toluene, upon which 40 mL hydrazine hydrate was added, and the mixture was stirred vigorously for 24 hours. The crude product precipitated and was filtered and washed with cold water and ether. Yield of the crude product was 9.0g (90%). (FTIR $\nu(\text{C}=\text{O})$ 1618 cm^{-1} , $\nu(\text{NH})$ 3332 cm^{-1} ; ^1H NMR (200 MHz, d_6 -DMSO) δ 3.80 (s,3H), 4.44 (s,2H), 6.99 (d,2H), 7.81 (d,2H), 9.64 (s,1H); MS (EI, m/z) calcd. for $\text{C}_8\text{H}_{10}\text{N}_2\text{O}_2$ 166.07, found 166 (M^+ , 13.2); mp 140-142 °C)

Ligand synthesis*1,2-di(4-methoxybenzoyl)hydrazine:*

2.6 g (15.2 mmol) of 4-methoxybenzoyl chloride was combined with 0.4 g (7.99 mmol) of hydrazine hydrate in 50 mL of THF with 2.0 g of TEA and stirred at room temperature for 1 hour. The product was precipitated in methanol, filtered and recrystallized from ethanol/DMF. Yield of the crude product was 2.1 g (90%). (FTIR $\nu(\text{C}=\text{O})$ 1597 cm^{-1} , $\nu(\text{NH})$ 3218 cm^{-1} ; ^1H NMR (200 MHz, d_6 -DMSO) δ 3.84 (s,6H), 7.06 (d,4H), 7.93

(d,4H), 10.32 (s,2H); MS (EI, m/z) calcd. for $C_{16}H_{16}N_2O_4$ 300.11, found 300 (M^+ , 7.1); mp 229-230 °C)

1,2-di(4-nitrobenzoyl)hydrazine:

7.8 g (42.0 mmol) of 4-nitrobenzoyl chloride was combined with 1.0 g (19.9 mmol) of hydrazine hydrate in 100 mL THF with 10 g TEA and stirred at room temperature for 1 hour. The product was precipitated in methanol, filtered and dried under vacuum overnight. Yield of the crude product was 1.7 g (26%). (FTIR $\nu(C=O)$ 1705, 1656 cm^{-1} , $\nu(NH)$ 3291, 3202 cm^{-1} ; 1H NMR (200 MHz, d_6 -DMSO) δ 8.22 (d,4H), 8.42 (t,2H), 11.10 (s,2H); MS (EI, m/z) calcd. for $C_{14}H_{10}N_4O_6$ 330.06, found 330 (M^+ , 2.7); mp 275-276 °C)

1,2-di(N-propylcarbamyl)hydrazide:

3.6 g (42.3 mmol) of n-propylisocyanate was combined with 1.0 g (19.9 mmol) of hydrazine hydrate in 50 mL of THF and stirred for 4 hours. The product precipitated directly from THF, filtered to remove the reaction solvent and dried over night under vacuum. Yield of the crude product was 3.5 g (88%). (FTIR $\nu(C=O)$ 1660 cm^{-1} , $\nu(NH)$ 3292, 3202 cm^{-1} ; MS (EI, m/z) calcd. for $C_8H_{18}N_4O_2$ 202.14, found 202 (M^+ , 3.6); mp 262-264 °C)

1-acetyl-2-benzoylhydrazine:

1.5 g (11.2 mmol) of benzoylhydrazide was dissolved in 40 mL THF. While agitating, to this solution was added 1.11 g (11.0 mmol) TEA followed by the slow addition of 0.86 g (11.0 mmol) of acetyl chloride. TEA·HCl formed almost immediately and was removed by filtration. The filtrate was then rotary evaporated to remove the solvent and dried under vacuum overnight yielding 1.1 g (55% yield) of crude product. Recrystallization from EtOH/H₂O afforded a white, crystalline product. (FTIR $\nu(\text{C}=\text{O})$ 1702, 1647 cm^{-1} , $\nu(\text{NH})$ 3199 cm^{-1} ; ^1H NMR (200 MHz, d_6 -DMSO) δ 1.94 (s, 3H), 7.54(m, 3H), 7.88 (d, 2H), 9.91 (s, 1H), 10.31 (s, 1H); MS (EI, m/z) calcd. for $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_2$ 178.2, found 178.1 (M^+ , 6.1); mp 172-174 °C).

1-benzoyl-2-trifluoroacetylhydrazine:

1.5 g (11.2 mmol) benzoylhydrazide and 2.0 g (9.3 mmol) of trifluoroacetic anhydride were added to 20 mL of THF. After the solution cooled to room temperature, the crude product was isolated by rotary evaporation. Yield was 1.9 g (73%). (FTIR $\nu(\text{C}=\text{O})$ 1715, 1678, 1630 cm^{-1} , $\nu(\text{NH})$ 3226 cm^{-1} ; ^1H NMR (200 MHz, d_6 -DMSO) δ 9.55 (m, 3H), 9.90 (d, 2H), 10.81 (s, 1H), 11.65 (s, 1H); MS (EI, m/z) calcd. for $\text{C}_9\text{H}_7\text{N}_2\text{O}_2\text{F}_3$ 232.2, found 232 (M^+ , 12.9); mp 153-154 °C).

1-benzoyl-2-(N,N-dimethylcarbamyl)hydrazine:

Synthesis and isolation were the same as the 1-acetyl-2-benzoylhydrazine, using 1.5 g (11.2 mmol) benzoylhydrazide, 1.2 g (11.2 mmol) dimethylcarbamyl chloride and 1.11 g

TEA. Yield of the crude product was 0.9 g (39%). (FTIR $\nu(\text{C}=\text{O})$ 1663, 1604 cm^{-1} , $\nu(\text{NH})$ 3218 cm^{-1} ; ^1H NMR (200 MHz, d_6 -DMSO) δ 2.90 (s,6H), 7.50 (m,3H), 7.90 (d,3H), 8.45 (s,1H), 10.05 (s,1H); MS (EI, m/z) calcd. for $\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}_2$ 207.2, found 207.1 (M^+ , 13.2); mp 199-201 $^\circ\text{C}$)

1-benzoyl-2-(N-propylcarbonyl)hydrazine:

1.5 g (11.2 mmol) benzoylhydrazide and 1.0 g (11.7 mmol) n-propylisocyanate were combined in 20 mL of THF. The product precipitated from solution almost immediately and after waiting approx. 30 minutes to ensure that the reaction had reached completion, the product was isolated by filtration, the residue was washed with THF and diethyl ether. Yield of the crude product was 1.87 g (75%). (FTIR $\nu(\text{C}=\text{O})$ 1670, 1635 cm^{-1} , $\nu(\text{NH})$ 3338, 3276 cm^{-1} ; ^1H NMR (200 MHz, d_6 -DMSO) δ 0.85 (t,3H), 1.40 (m,2H), 3.05 (m,2H), 6.50 (s,1H), 7.55 (m,3H), 7.85 (s,1H), 7.95 (d,2H), 10.10 (s,1H); MS (EI, m/z) calcd. for $\text{C}_{11}\text{H}_{15}\text{N}_3\text{O}_2$ 221.3, found 221.1 (M^+ , 2.7); mp 172-174 $^\circ\text{C}$)

1-benzoyl-2-(4-nitrobenzoyl)hydrazine:

1.5 g (11.2 mmol) of benzoylhydrazide was dissolved in 20 mL of water and 2.0 g (10.8 mmol) 4-nitrobenzoyl chloride was dissolved in 20 mL of toluene. The two solutions were then combined and vigorously agitated for 10 hours. The product precipitated and was isolated by filtration to yield 2.6 g (81%) of the crude product. (FTIR $\nu(\text{C}=\text{O})$ 1683, 1645, 1605 cm^{-1} , $\nu(\text{NH})$ 3347, 3241 cm^{-1} ; ^1H NMR (200 MHz, d_6 -DMSO) δ 7.57 (m,3H),

7.93 (m,2H), 8.16 (d,2H), 8.38 (d,2H), 10.69 (s,1H), 10.91 (s,1H); MS (EI, m/z) calcd. for $C_{14}H_{11}N_3O_4$ 285.3, found 285.1 (M^+ , 4.7); mp 254-256 °C).

1-benzoyl-2-(4-methoxybenzoyl)hydrazine:

Synthesis and isolation were the same as the 1-acetyl-2-benzoylhydrazine, using 1.5 g (11.2 mmol) benzoylhydrazide, 1.9 g (11.1 mmol) 4-methoxybenzoyl chloride and 1.11 g of TEA. Yield of the crude product was 2.9 g (97%). (FTIR $\nu(C=O)$ 1667, 1631, 1607 cm^{-1} , $\nu(NH)$ 3205 cm^{-1} ; 1H NMR (200 MHz, d_6 -DMSO) δ 5.13 (s,3H), 8.36 (d,2H), 8.86 (m,3H), 9.23 (d,4H) 11.72 (d,2H); MS (EI, m/z) calcd. for $C_{15}H_{14}N_2O_3$ 270.3, found 270 (M^+ , 5.1); mp 201-202 °C).

1-(4-methoxybenzoyl)-2-(4-nitrobenzoyl)hydrazine:

1.8 g (10.8 mmol) 4-methoxybenzoylhydrazine was suspended in 25 mL water and combined with 2.0 g (10.8 mmol) of 4-nitrobenzoyl chloride dissolved in 25 mL of toluene. The mixture was then refluxed for 2 hours, cooled to room temperature followed by precipitation of the product in methanol. Yield of the crude product was 3.2 g (94%). (FTIR $\nu(C=O)$ 1609, 1591, 1558 cm^{-1} , $\nu(NH)$ 3200 cm^{-1} ; 1H NMR (200 MHz, d_6 -DMSO) δ 3.85 (s,3H), 7.08 (d,2H), 7.94 (d,2H), 8.17 (d,2H), 8.39 (d,2H), 10.53 (s,1H), 10.84 (s,1H); MS (EI, m/z) calcd. for $C_{15}H_{13}N_3O_5$ 315.09, found 315 (M^+ , 2.3); mp 256-258 °C)

1-(4-methoxybenzoyl)-2-trifluoroacetylhydrazine:

Synthesis and isolation were the same as the 1-benzoyl-2-trifluoroacetylhydrazine, using 1.8 g (10.8 mmol) 4-methoxybenzoylhydrazine and 2.0 g (9.5 mmol) trifluoroacetic anhydride. Yield of the crude product was 2.4 g (85%). (^1H NMR (200 MHz, d_6 -DMSO) δ 3.85 (s,6H), 7.08 (d,4H), 7.89 (d,4H), 10.68 (s,2H); MS (EI, m/z) calcd. for $\text{C}_{10}\text{H}_9\text{F}_3\text{N}_2\text{O}_3$ 262.06, found 262 (M^+ , 8.0); mp 147-148 $^\circ\text{C}$)

1-acetyl-2-(4-methoxybenzoyl)hydrazine:

To 40 mL of THF were added 1.8 g (10.8 mmol) 4-methoxybenzoylhydrazine, 0.9 g (11.5 mmol) of acetyl chloride and 1.1 g TEA. The reaction mixture was stirred for 1 hour, followed by evaporation of half of the THF. The product was precipitated in methanol, filtered and dried over night under vacuum. Yield of the product was 2.14 g (95%). (FTIR $\nu(\text{C}=\text{O})$ 1685, 1608, 1572 cm^{-1} , $\nu(\text{NH})$ 3257 cm^{-1} , ^1H NMR (200 MHz, d_6 -DMSO) δ 1.92 (s,3H), 3.83 (s,3H), 7.03 (d,2H), 7.87 (d,2H), 9.83 (s,1H), 10.15 (s,1H); MS (EI, m/z) calcd. for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3$ 208.08, found 208 (M^+ , 6.7); mp 146-148 $^\circ\text{C}$)

1-(N,N-dimethylcarbamyl)-2-(4-methoxybenzoyl)hydrazine:

Synthesis and isolation were the same as the 1-acetyl-2-benzoylhydrazine, using 1.8 g (10.8 mmol) of 4-methoxybenzoylhydrazine, 1.2 g (11.1 mmol) of dimethylcarbamyl chloride and 1.1 g TEA. Yield of the product was 1.5 g (59%). (FTIR $\nu(\text{C}=\text{O})$ 1655, 1632, 1609 cm^{-1} , $\nu(\text{NH})$ 3206 cm^{-1} ; ^1H NMR (200 MHz, d_6 -DMSO) δ 2.87 (s,6H), 3.83

(s,3H), 7.03 (d,2H), 7.87 (d,2H), 8.36 (s,1H), 9.91 (s,1H); MS (EI, m/z) calcd. for $C_{11}H_{15}N_3O_3$ 237.11, found 237 (M^+ , 8.3); mp 218-220 °C)

1-(4-methoxybenzoyl)-2-(N-propylcarbamyl)hydrazine:

Synthesis and isolation were the same as the 1-benzoyl-2-(N-propylcarbamyl)hydrazine, using 1.3 g (7.8 mmol) 4-methoxybenzoylhydrazine and 0.9 g (10.5 mmol) of n-propylisocyanate. Yield of the crude product was 1.8 g (92%). (FTIR $\nu(C=O)$ 1649, 1609 cm^{-1} , $\nu(NH)$ 3299 cm^{-1} ; MS (EI, m/z) calcd. for $C_{12}H_{17}N_3O_3$ 251.13, found 251 (M^+ , 1.6); mp 176-179 °C)

1-(4-nitrobenzoyl)-2-(N-propylcarbamyl)hydrazine:

Synthesis and isolation were the same as the 1-benzoyl-2-(N-propylcarbamyl)hydrazine, using 2.0 g (11.0 mmol) of 4-nitrobenzoyl hydrazine and 1.0 g (11.0 mmol) n-propylisocyanate. Yield of the crude product was 2.7 g (92%). (FTIR $\nu(C=O)$ 1656, 1643, 1606 cm^{-1} , $\nu(NH)$ 3290 cm^{-1} ; 1H NMR (200 MHz, d_6 -DMSO) δ 0.85 (t,3H), 1.42 (q,2H), 3.01 (q,2H), 6.63 (s,1H), 7.98 (s,1H), 8.14 (d,2H), 8.36 (d,2H), 10.48 (s,1H); MS (EI, m/z) calcd. for $C_{11}H_{14}N_4O_4$ 266.10, found 266 (M^+ , 1.0); mp 235-237 °C)

Symmetric Complexes*[{Ru(bpy)₂}₂μ-Ph₂adc](PF₆)₂ (III.1):*

Synthesis and purification were performed in the manner described previously, using 200 mg (0.38 mmol) Ru(bpy)₂Cl₂·2H₂O, 46 mg (0.19 mmol) dibenzoylhydrazide, and 40 mg NaOH. Yield of the purified product was 46%. (MS (FAB, m/z) calcd. for ([{Ru(bpy)₂}₂μ-Ph₂adc](PF₆))⁺ C₅₄F₆H₄₂N₁₀O₂PRu₂ 1210.1, found 1210.1 (M⁺, 1.0)).

[{Ru(bpy)₂}₂μ-CH₃OPh₂adc](PF₆)₂ (III.2):

Synthesis and purification were performed in the manner described previously, using 200 mg (0.38 mmol) Ru(bpy)₂Cl₂·2H₂O, 57 mg (0.19 mmol) 1,2-di(4-methoxybenzoyl)hydrazine, and 40 mg NaOH. Yield of the purified product was 49%. (MS (FAB, m/z) calcd. for ([{Ru(bpy)₂}₂μ-(CH₃Oph)₂adc](PF₆))⁺ C₅₆F₆H₄₆N₁₀O₄PRu₂ 1271.1, found 1271.2 (M⁺, 0.4)).

[{Ru(bpy)₂}₂μ-(NO₂Ph)₂adc](PF₆)₂ (III.3):

Synthesis and purification were performed in the manner described previously, using 200 mg (0.38 mmol) Ru(bpy)₂Cl₂·2H₂O, 63 mg (0.19 mmol) 1,2-di(4-nitrobenzoyl)hydrazine, and 40 mg NaOH. Yield of the purified product was 57%. (MS (FAB, m/z) calcd. for ([{Ru(bpy)₂}₂μ-(NO₂Ph)₂adc](PF₆))⁺ C₅₄F₆H₄₀N₁₂O₆PRu₂ 1301.1, found 1301.0 (M⁺, 1.8)).

[{Ru(bpy)₂}₂μ-(C₃H₇-n)HN₂adc](PF₆)₂ (III.4):

Synthesis and purification were performed in the manner described previously, using 200 mg (0.38 mmol) Ru(bpy)₂Cl₂·2H₂O, 33 mg (0.19 mmol) 1,2-di(*N*-propylcarbonyl)hydrazine, and 40 mg NaOH. Yield of the purified product was 44%. (MS (FAB, *m/z*) calcd. for ([{Ru(bpy)₂}₂μ-((C₃H₇-n)HN)₂adc](PF₆))⁺ C₄₈F₆H₄₈N₁₂O₂PRu₂ 1172.1, found 1172.0 (M⁺, 1.0)).

Asymmetric Complexes

[{Ru(bpy)₂}₂μ-Ph, CH₃OPh-adc](PF₆)₂ (III.5):

Synthesis and purification were performed in the manner described previously, using 200 mg (0.38 mmol) Ru(bpy)₂Cl₂·2H₂O, 48 mg (0.19 mmol) 1-benzoyl-2-(4-methoxybenzoyl)hydrazine, and 40 mg NaOH. Yield of the purified product was 43%. (MS (FAB, *m/z*) calcd. for ([{Ru(bpy)₂}₂μ-Ph, CH₃OPh-adc](PF₆))⁺ C₅₅F₆H₄₄N₁₀O₃PRu₂ 1240.1, found 1240.0 (M⁺, 1.4)).

[{Ru(bpy)₂}₂μ-Ph, CF₃-adc](PF₆)₂ (III.6):

Synthesis and purification were performed in the manner described previously, using 200 mg (0.38 mmol) Ru(bpy)₂Cl₂·2H₂O, 44 mg (0.19 mmol) 1-benzoyl-2-trifluoroacetylhydrazine, and 106 mg Na₂CO₃. Yield of the purified product was 58%. (MS (FAB, *m/z*) calcd. for [{Ru(bpy)₂}₂μ-Ph, CF₃-adc](PF₆)⁺ C₄₉F₉H₃₇N₁₀O₂PRu₂

1202.0, found 1201.3 (M^+ , 0.1); [$\{Ru(bpy)_2\}_2\mu\text{-ph, CF}_3\text{-adc}\}^+ C_{49}F_3H_{37}N_{10}O_2Ru_2$ 1057.0, found 1057.7 (M^+ , 0.7).

[$\{Ru(bpy)_2\}_2\mu\text{-Ph, CH}_3\text{-adc}\}(PF_6)_2$ (III.7):

Synthesis and purification were performed in the manner described previously, using 200 mg (0.38 mmol) $Ru(bpy)_2Cl_2 \cdot 2H_2O$, 34 mg (0.19 mmol) 1-acetyl-2-benzoylhydrazine, and 40 mg NaOH. Yield of the purified product was 57%. (MS (FAB, m/z) calcd. for ($[\{Ru(bpy)_2\}_2\mu\text{-Ph, CH}_3\text{-adc}\}(PF_6)]^+ C_{49}F_6H_{40}N_{10}O_2PRu_2$ 1148.0, found 1148.1 (M^+ , 4.3)).

[$\{Ru(bpy)_2\}_2\mu\text{-Ph, NO}_2\text{Ph-adc}\}(PF_6)_2$ (III.8):

Synthesis and purification were performed in the manner described previously, using 200 mg (0.38 mmol) $Ru(bpy)_2Cl_2 \cdot 2H_2O$, 54 mg (0.19 mmol) 1-benzoyl-2-(4-nitrobenzoyl)hydrazine, and 40 mg NaOH. Yield of the purified product was 44%. (MS (FAB, m/z) calcd. for ($[\{Ru(bpy)_2\}_2\mu\text{-Ph, NO}_2\text{Ph-adc}\}(PF_6)]^+ C_{54}F_6H_{41}N_{11}O_4PRu_2$ 1255.1, found 1255.9 (M^+ , 9.8)).

[$\{Ru(bpy)_2\}_2\mu\text{-Ph, N(CH}_3)_2\text{-adc}\}(PF_6)_2$ (III.9):

Synthesis and purification were performed in the manner described previously, using 200 mg (0.38 mmol) $Ru(bpy)_2Cl_2 \cdot 2H_2O$, 39 mg (0.19 mmol) 1-benzoyl-2-(*N,N*-dimethylcarbamyl)hydrazine, and 40 mg NaOH. Yield of the purified product was 43%.

(MS (FAB, m/z) calcd. for $([\{Ru(bpy)_2\}_2\mu\text{-Ph, N(CH}_3)_2\text{-adc}](PF_6))^+$ $C_{50}F_6H_{43}N_{11}O_2PRu_2$ 1177.1, found 1177.1 (M^+ , 1.1);).

$[\{Ru(bpy)_2\}_2\mu\text{-Ph, NH(C}_3\text{H}_7\text{-n)-adc}](PF_6)_2$ (III.10):

Synthesis and purification were performed in the manner described previously, using 200 mg (0.38 mmol) $Ru(bpy)_2Cl_2 \cdot 2H_2O$, 42 mg (0.19 mmol) 1-benzoyl-2-(*N*-propylcarbamyl)hydrazide, and 40 mg NaOH. Yield of the purified product was 41%.

(MS (FAB, m/z) calcd. for $([\{Ru(bpy)_2\}_2\mu\text{-Ph, NH(C}_3\text{H}_7\text{-n)-adc}](PF_6))^+$ $C_{51}F_6H_{44}N_{11}O_2PRu_2$ 1190.1, found 1190.2 (M^+ , 6.4)).

$[\{Ru(bpy)_2\}_2\mu\text{-CH}_3O\text{Ph, CF}_3\text{-adc}](PF_6)_2$ (III.11):

Synthesis and purification were performed in the manner described previously, using 200 mg (0.38 mmol) $Ru(bpy)_2Cl_2 \cdot 2H_2O$, 50 mg (0.19 mmol) 1-(4-methoxybenzoyl)-2-trifluoroacetylhydrazide, and 106 mg Na_2CO_3 . Yield of the purified product was 50%.

(MS (FAB, m/z) calcd. for $([\{Ru(bpy)_2\}_2\mu\text{-CH}_3O\text{Ph, CF}_3\text{-adc}](PF_6))^+$ $C_{50}F_9H_{41}N_{10}O_3PRu_2$ 1233.0, found 1233.0 (M^+ , 5.6)).

$[\{Ru(bpy)_2\}_2\mu\text{-CH}_3O\text{Ph, CH}_3\text{-adc}](PF_6)_2$ (III.12):

Synthesis and purification were performed in the manner described previously, using 200 mg (0.38 mmol) $Ru(bpy)_2Cl_2 \cdot 2H_2O$, 40 mg (0.19 mmol) 1-acetyl-2-(4-methoxybenzoyl)hydrazide, and 106 mg Na_2CO_3 . Yield of the purified product was

70%. (MS (FAB, m/z) calcd. for ([{Ru(bpy)₂}₂μ-CH₃OPh, CH₃-adc](PF₆))⁺

C₅₀F₆H₄₄N₁₀O₃PRu₂ 1179.1, found 1178.9 (M⁺, 5.1)).

[{Ru(bpy)₂}₂μ-CH₃OPh, NO₂Ph-adc](PF₆)₂ (III.13):

Synthesis and purification were performed in the manner described previously, using 200 mg (0.38 mmol) Ru(bpy)₂Cl₂·2H₂O, 60 mg (0.19 mmol) 1-(4-methoxybenzoyl)-2-(4-nitrobenzoyl)hydrazide, and 40 mg NaOH. Yield of the purified product was 30%. (MS (FAB, m/z) calcd. for ([{Ru(bpy)₂}₂μ-CH₃OPh, NO₂Ph-adc](PF₆))⁺ C₅₅F₆H₄₅N₁₁O₅PRu₂ 1286.1, found 1286.1 (M⁺, 19.7).

[{Ru(bpy)₂}₂μ-CH₃OPh, N(CH₃)₂-adc](PF₆)₂ (III.14):

Synthesis and purification were performed in the manner described previously, using 200 mg (0.38 mmol) Ru(bpy)₂Cl₂·2H₂O, 45 mg (0.19 mmol) 1-(*N,N*-dimethylcarbamyl)-2-(4-methoxybenzoyl)hydrazide, and 40 mg NaOH. Yield of the purified product was 32%.

(MS (FAB, m/z) calcd. for ([{Ru(bpy)₂}₂μ-CH₃OPh, N(CH₃)₂-adc](PF₆))⁺

C₅₁F₆H₄₇N₁₁O₃PRu₂ 1208.1.2, found 1208.0 (M⁺, 12.3)).

[{Ru(bpy)₂}₂μ-CH₃OPh, NH(C₃H₇)-adc](PF₆)₂ (III.15):

Synthesis and purification were performed in the manner described previously, using 200 mg (0.38 mmol) Ru(bpy)₂Cl₂·2H₂O, 48 mg (0.19 mmol) 1-(4-methoxybenzoyl)-2-(*N*-propylcarbamyl)hydrazide, and 40 mg NaOH. Yield of the purified product was 32%.

(MS (FAB, m/z) calcd. for ([{Ru(bpy)₂}₂μ-CH₃OPh, NH(C₃H₇-n)-adc](PF₆))⁺

C₅₂F₆H₄₉N₁₁O₃PRu₂ 1222.1, found 1222.0 (M⁺, 6.9)).

[{Ru(bpy)₂}₂μ-NO₂Ph, NH(C₃H₇-n)-adc](PF₆)₂ (III.16):

Synthesis and purification were performed in the manner described previously, using 200 mg (0.38 mmol) Ru(bpy)₂Cl₂·2H₂O, 51 mg (0.19 mmol) 1-(4-nitrobenzoyl)-2-(*N*-propylcarbamyl)hydrazine, and 40 mg NaOH. Yield of the purified product was 29%.

(MS (FAB, m/z) calcd. for ([{Ru(bpy)₂}₂μ-NH(C₃H₇-n), NO₂Ph-adc](PF₆))⁺

C₅₁F₆H₄₆N₁₂O₄PRu₂ 1236.1, found 1236.0 (M⁺, 24.8)).

Tetranuclear Ruthenium Complexes

Ligand Precursor Compounds

Acetylenoyldihydrazide:

4 g (23.5 mmol) of diethyl acetylenedicarboxylate were dissolved in 40 mL of toluene, to which was added 20 mL hydrazine hydrate. The mixture was refluxed for 2 hours, cooled to room temperature and then the volume was reduced by half via rotary evaporation. Finally the product was precipitated in ethanol. Yield of the crude product was 3.17 g (95%). (FTIR ν(C≡C) 1244 cm⁻¹, ν(C=O) 1646, 1591, 1528 cm⁻¹, ν(NH) 3300, 3259 cm⁻¹; ¹H NMR (400 MHz, d₆-DMSO) δ 5.70 & 5.98 (broad, 6H); ¹³C NMR

(100.6 MHz, d_6 -DMSO) δ 87.0 (d), 160.7 (d); MS (EI, m/z) calcd. for $C_4H_6N_4O_2$ 142.1, found 142 (M^+ , 93.2); mp dec. 270 °C)

Dihydrazide Ligands:

1,4-(dibenzoylhydrazine)acetylendicarboxylate:

In 30 mL of THF, 1.0 g (7.0 mmol) of acetylenoyl dihydrazide, 2.1 g (15 mmol) of benzoyl chloride and 1.5 g (15 mmol) of TEA were added and stirred for 2 hours. The mixture was then evaporated to half volume on a rotary evaporator and added quickly to 300 mL of vigorously stirring CH_3OH to precipitate the product. The yellow precipitate was isolated by filtration and dried under vacuum overnight. Yield of the crude product was 250 mg (42%). (FTIR $\nu(C\equiv C)$ 1244 cm^{-1} , $\nu(C=O)$ 1758, 1632 cm^{-1} , $\nu(NH)$ 3210 cm^{-1} ; 1H NMR (200 MHz, d_6 -DMSO) δ 7.58; ^{13}C NMR (50.3 MHz, d_6 -DMSO) δ 128.18, 129.25, 132.61, 133.26, 166.56; MS (EI, m/z) calcd. for $C_{18}H_{14}N_4O_4$ 350.1, found 358 (M^+ , 0.2); mp 185-187 °C)

dibenzoylhydrazineisophthalate:

In 40 mL of THF, 1.0 g (4.9 mmol) of isophthaloyl chloride, 1.3 g (9.5 mmol) benzoic hydrazide, and 1.0 g (9.9 mmol) of TEA were combined and stirred at room temperature for 4 hours. The mixture was then evaporated to half volume on a rotary evaporator and added quickly to 300 mL of vigorously stirring CH_3OH to precipitate the product. The white precipitate was isolated by filtration and dried under vacuum overnight. Yield of

the crude product was 1.9 g (96%). (FTIR $\nu(\text{C=O})$ 1682, 1642, 1600 cm^{-1} , $\nu(\text{NH})$ 3219 cm^{-1} ; ^1H NMR (200 MHz, d_6 -DMSO) δ 7.59 (m, 7H), 7.97 (d, 4H), 8.16 (d, 2H), 8.53 (s, 1H), 10.69 (s, 4H); MS (EI, m/z) calcd. for $\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_4$ 402.1, found 402 (M^+ , 6.4); mp $>300^\circ\text{C}$)

1,4-(dibenzoylhydrazine)fumarate:

In 40 mL of THF, 1.0 g (6.5 mmol) of fumaryl chloride, 1.8 g (13 mmol) of benzoic hydrazide, and 1.5 g (15 mmol) of TEA were combined and stirred for 2 hours. The mixture was then evaporated to half volume on a rotary evaporator and added quickly to 300 mL of vigorously stirring CH_3OH to precipitate the product. The light brown precipitate was isolated by filtration and dried overnight under vacuum. Yield of the crude product was 2.0 g (87%). (FTIR $\nu(\text{C=O})$ 1600 cm^{-1} , $\nu(\text{NH})$ 3189 cm^{-1} ; ^1H NMR (200 MHz, d_6 -DMSO) δ 7.15 (s, 2H), 7.59 (m, 6H), 7.96 (d, 4H), 10.64 (s, 2H), 10.69 (s, 2H); MS (EI, m/z) calcd. for $\text{C}_{18}\text{H}_{16}\text{N}_4\text{O}_4$ 352.1, found 355 (M^+ , 0.01); mp $>300^\circ\text{C}$)

1,6-(dibenzoylhydrazine)adipate:

In 40 mL THF, 1.0 g (5.7 mmol) of adipicdihydrazide, 1.6 g (11 mmol) of benzoyl chloride, and 1.2 g (12 mmol) of TEA were combined and stirred for 2 hours at room temperature. The mixture was then filtered to remove the precipitated $\text{TEA}\cdot\text{HCl}$, followed by evaporation of the solvent via rotary evaporation. The product was then washed with water and CH_3OH to remove any residual reactants and $\text{TEA}\cdot\text{HCl}$ salt, and dried overnight under vacuum. Yield of the crude product was 2.0 g (91%). (FTIR

$\nu(\text{C}=\text{O})$ 1668, 1599, 1574 cm^{-1} , $\nu(\text{NH})$ 3207 cm^{-1} ; ^1H NMR (200 MHz, d_6 -DMSO) δ 1.64 (m, 4H), 2.23 (m, 4H), 7.54 (m, 6H), 7.89 (d, 4H), 9.88 (s, 2H), 10.32 (s, 2H); MS (EI, m/z) calcd. for $\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_4$ 382.2, found 382 (M^+ , 6.2); mp 244-246 $^\circ\text{C}$

Complexes

$[\{\text{Ru}(\text{bpy})_2\}_4 \mu\text{-(1,6-(dibenzoylhydrazine)adipate})](\text{PF}_6)_4$ (III.17):

Synthesis and purification were performed in the manner described previously for dinuclear complexes, using 200 mg (0.38 mmol) $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, 30.0 mg (0.095 mmol) 1,6-(dibenzoylhydrazine)adipate, 100 mg Na_2CO_3 . Yield of the purified product was 30%. (MS (ESI, m/z) calcd. for $([\{\text{Ru}(\text{bpy})_2\}_4 \mu\text{-(1,6-(dibenzoylhydrazine)adipate})](\text{PF}_6)_2)^{2+}$ $\text{C}_{100}\text{F}_{12}\text{H}_{82}\text{N}_{20}\text{O}_4\text{P}_2\text{Ru}_4$ 1161.0, found 1161.4 (M^+ , 14.07)).

$[\{\text{Ru}(\text{bpy})_2\}_4 \mu\text{-(1,4-(dibenzoylhydrazine)fumarate})](\text{PF}_6)_4$ (III.18):

Synthesis and purification were performed in the manner described previously for dinuclear complexes, using 200 mg (0.38 mmol) $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, 33.0 mg (0.095 mmol) 1,4-(dibenzoylhydrazine)fumarate, and 100 mg Na_2CO_3 . Yield of the purified product was 33%. (MS (ESI, m/z) calcd. for $([\{\text{Ru}(\text{bpy})_2\}_4 \mu\text{-(1,4-(dibenzoylhydrazine)fumarate})](\text{PF}_6)_2)^{2+}$ $\text{C}_{98}\text{F}_{12}\text{H}_{76}\text{N}_{20}\text{O}_4\text{P}_2\text{Ru}_4$ 1146.0, found 1146.6 (M^+ , 1.18)).

[{Ru(bpy)₂}₄ μ-(1,4-dibenzoylhydrazineacetylendicarboxylate)](PF₆)₄ (III.19):

Synthesis and purification were performed in the manner described previously for dinuclear complexes, using 200 mg (0.38 mmol) Ru(bpy)₂Cl₂·2H₂O, 33.3 mg (0.095 mmol) 1,4-(dibenzoylhydrazine)acetylendicarboxylate, and 100 mg Na₂CO₃. Yield of the purified product was 50%. (MS (ESI, m/z) calcd. for ([{Ru(bpy)₂}₄ μ-(1,4-dibenzoylhydrazineacetylendicarboxylate)](PF₆)₂ (CH₃OH)₄)²⁺ C₁₀₂F₁₈H₉₀N₂₀O₈P₃Ru₄ 1209.1, found 1210.8 (M⁺, 0.02); ([{Ru(bpy)₂}₄ μ-(1,4-dibenzoylhydrazineacetylendicarboxylate)](CH₃OH)₄)⁴⁺ C₁₀₂H₉₀N₂₀O₄Ru₄ 532.6, found 532.7 (M⁺, 3.04).

[{Ru(bpy)₂}₄ μ-(Dibenzoylhydrazineisophthalate)](PF₆)₄ (III.20):

Synthesis and purification were performed in the manner described previously for dinuclear complexes, using 200 mg (0.38 mmol) Ru(bpy)₂Cl₂·2H₂O, 38.6 mg (0.095 mmol) dibenzoylhydrazineisophthalate, and 100 mg Na₂CO₃. Yield of the purified product was 19%. (MS (ESI, m/z) calcd. for ([{Ru(bpy)₂}₄ μ-(Dibenzoylhydrazineisophthalate)](PF₆)₂)²⁺ C₁₀₂F₁₂H₇₈N₂₀O₄P₂Ru₄ 1171.0, found 1171.5 (M⁺, 2.37)).

Pentanuclear Ruthenium ComplexesLigand Precursor Compounds*5,5'-dimethyl-2,2'-bipyridine:*

Using the method of Sasse¹⁷, 300 mL of 3-picoline was added to 125 g of freshly degassed and dried Raney Nickel catalyst. The mixture was then allowed to reflux for 48 hours, and once cooled to room temperature the picoline was decanted. To increase the yield the Raney Nickel was flushed several times with benzene. The picoline and benzene solutions were combined and the solvent evaporated to give the crude product. The crude yield of product was 58 g. Recrystallization was from ethanol with a yield of purified product 70% versus crude. (¹H NMR (200 MHz, d₆-DMSO) δ 2.31 (s, 3H), 7.65 (d, 1H), 8.26 (d, 1H), 8.42 (s, 1H); ¹³C NMR (50.3 MHz, CDCl₃) δ 18.6, 120.6, 133.3, 138.7, 140.8, 154.0; MS (EI, m/z) calcd. for C₁₂H₁₂N₂ 184.1, found 184 (M⁺, 100); mp 114-115 °C)

5,5'-dicarboxy-2,2'-bipyridine:

Synthesis was via the method of Bos et al¹⁸ scaled down to use 5 g (27.1 mmol) of 5,5'-dimethyl-2,2'-bipyridine. The yield of crude diacid was 2.6g (40%). (MS (EI, m/z) calcd. for C₁₂H₈N₂O₄ 244.0, found 244 (M⁺, 2.3); mp >300 °C)

5,5'-dichlorocarbonyl-2,2'-bipyridine:

1 g (4.1 mmol) of 5,5'-dicarboxy-2,2'-bipyridine was added to 15 mL thionyl chloride and refluxed for 3 hours. The reflux was followed by removal of the thionyl chloride via distillation, then addition of hot toluene. The product formed fine crystals from toluene upon cooling with a yield of 600 mg (52%). (FTIR $\nu(\text{C=O})$ 1727 cm^{-1} ; $\nu(\text{C-Cl})$ 848, 867 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 8.55 (d,1H), 8.69 (d,1H), 9.37 (s,1H); MS (EI, m/z) calcd. for $\text{C}_{12}\text{H}_6\text{Cl}_2\text{N}_2\text{O}_2$ 280.0, found 280 (M^+ , 19.9); mp 208-210 $^\circ\text{C}$).

Dihydrazide Ligand*5,5'-(2,2'-dibenzoylhydrazine)dicarbonyl-2,2'-bipyridine:*

In 20 mL of THF, 200 mg (0.71 mmol) of 5,5'-dichlorocarbonyl-2,2'-bipyridine, 194 mg (1.4 mmol) of benzoic hydrazide, and 144 mg (1.4 mmol) of TEA were combined and stirred, under reflux, for 12 hours. The mixture was then evaporated to half volume on a rotary evaporator. The product was then precipitated by addition to 300 mL of vigorously stirring CH_3OH and isolated by filtration. Yield of the crude product was 218 mg (64%). (FTIR $\nu(\text{C=O})$ 1589, 1577 cm^{-1} ; $\nu(\text{N-H})$ 3208 cm^{-1} ; ^1H NMR (200 MHz, d_6 -DMSO) δ 7.57 (m,6H), 7.96 (d,4H), 8.48 (d,2H), 8.64 (d,2H), 9.24 (s,2H), 10.68 (s,2H), 10.90 (s,2H); MS (EI, m/z) calcd. for $\text{C}_{26}\text{H}_{20}\text{N}_6\text{O}_4$ 480.2, found 481 (M^+ , 0.1); mp >300 $^\circ\text{C}$).

Complex

$[\{Ru(bpy)_2\}_5 \mu-(5,5'-(2,2'-dibenzoylhydrazine)dicarbonyl-2,2-bipyridine)](PF_6)_6$

(III.21):

Synthesis and purification were performed in the manner described previously for dinuclear complexes, using 200 mg (0.38 mmol) $Ru(bpy)_2Cl_2 \cdot 2H_2O$, 37 mg (0.076 mmol) 5,5'-(2,2'-dibenzoylhydrazine)dicarbonyl-2,2-bipyridine, 100 mg Na_2CO_3 . Yield of the purified product was 14%. (MS (ESI, m/z) calcd. for $([\{Ru(bpy)_2\}_5 \mu-(5,5'-(2,2'-dibenzoylhydrazine)dicarbonyl-2,2-bipyridine)](PF_6)_3)^{3+}$ $C_{126}F_{18}H_{96}N_{26}O_4P_3Ru_5$ 992.9, found 992.0 (M^+ , 0.22)).

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Introduction

The incorporation of a metal fragment into a polymer is not new, many examples exist in the literature, of significance are the systems incorporating the 2,2'-bipyridyl¹⁻⁹, and the ferrocenyl containing systems¹⁰⁻¹³, as well as many systems which contain pendant metal fragments¹⁴⁻²¹. Two categories exist; those, which possess a continuous organic backbone with a ligand incorporated into the backbone and so are also organic polymers in the absence of a metal, and those in which the metal forms an integral link in the backbone. The former class of polymers can be made in a variety of ways depending upon the nature of the constituents, but generally follow one of two approaches. The first involves initially preparing an organic polymer containing some ligand fragment followed by subsequent metal introduction essentially following the same philosophy as preparing a complex. Conversely, the second approach involves the preparation of a metal complex containing a polymerizable ligand(s), and so in this case metal complex synthesis precedes polymer formation. Typical examples of the prior method are the 2,2'-bipyridyl containing polymers of Yu⁷, Tokura³, Wang¹, and Maruyama⁸, whereas the poly(phenylene sulfide)s and poly(phenylene oxide)s of Abd-El-Aziz *et al*²² and de Denus *et al*²³ are representative examples of the later method.

The polymers in which the metal is incorporated into the backbone can also be prepared by a variety of methods. The ROP method utilized by Manners *et al*^{12, 13}

constitutes one method of preparing well defined polymer materials incorporating a [1]ferrocenophane. As well, these polymers can be formed by the combination of metal ion with that of an A-A monomer, typically containing two bi- and tri-dentate ligand units. Representative examples of this would be the rod-like oligomers of Grosshenny *et al*^{24, 25} or the high molecular weight polymers of Kelch *et al*^{2, 4}.

Figure IV.1: (a) Polyimide(s) and Polyester(s) of Yu *et al*⁷, (b)

Poly(ferrocenyldimethylsilane)s of Ni *et al*¹², (c) Poly(phenylene

sulfide)s and Poly(phenylene oxide)s of Abd-El-Aziz *et al*²², (d)

Ruthenium coordination polymer of Kelch *et al*^{2, 4}.

In conceiving this mode of the research it was our intention to preserve as much as possible the dinuclear complex properties in the polymer system as much as possible. Having discovered the work of Mohamed *et al*²⁶, in which he prepared metallized films from a series of wholly aromatic polyhydrazines at room temperature in DMAc by combination of the polymers with salts of Cu(II), Ag(I), Ni(II), Pb(II), Fe(III), and Cd(II), we endeavoured to synthesis a series of four aromatic and aliphatic polyhydrazines as shown in figure IV.2. Subsequent to isolation of the polymer, the metallization could be conducted in the same manner as that of the complexes in chapter III, thus this approach is akin to that of Yu⁷ given earlier. The polymers thus made would be expected to exhibit similar properties as the dinuclear complexes as these materials should be simply an extension of the dimeric azodicarbonyl complexes reported in chapter III. We report herein the synthesis and characterization, including the electrochromic switching stability in the solid state of these polymer systems.

Results and Discussion

Synthesis: The polymers were synthesised from equimolar quantities of each monomer in NMP via the method of Frazer *et al*^{27, 28}. The polymers, shown in figure IV.2, were colourless, and were found to be sparingly soluble in DMF, ACN and to an extent DMSO. Only the fully aliphatic derivatives were sufficiently soluble in DMSO to permit viscosity measurements. Inherent viscosities were measured for the Poly(adipic hydrazine) (IV.5) and poly(adipic, 1,6-carbamylhexyl hydrazine) (IV.8) and were found

to be 0.139 and 0.262 respectively, which when compared to those of Higashi *et al*²⁹, showed that they were of low molecular weight.

Synthesis of the poly($\{\text{Ru}(\text{bpy})_2\}_2\text{-adc}$) was performed in the same manner as that of the dinuclear complexes as early experimentation revealed that the polyhydrazines were freely soluble in weak aqueous base solutions. The metal containing polymers were isolated as brilliantly purple coloured solids. Purification of the polymers was not performed as initial trials showed that all of the materials were trapped within the alumina stationary phase and deactivation of the alumina packing did not appreciably improve elution.

Figure IV.2: Hydrazine polymers.

Figure IV.3: Polymeric azodicarbonyl ruthenium complexes.

Thermal Analysis: Thermal analysis was performed in the same manner as that used for the dinuclear and tetranuclear complexes. The results, summarized in table IV.1, show the decomposition temperatures for the polyhydrazines and polyazodicarbonyl ruthenium complexes. No trend is observed in the results, however generally the polyhydrazines were less stable than the polyazodicarbonyl ruthenium complexes, except for the IV.4 vs. the IV.8 case. Studies by Frazer *et al*²⁷, have revealed that aliphatic polyhydrazines undergo dehydration above 150 °C to yield a cyclic oxydiazole as shown in scheme IV.1. This certainly accounts for the low apparent decomposition temperature of the polyhydrazines versus that of the polyazodicarbonyl ruthenium complexes, however it does not account for the unusually high decomposition temperature of IV.4.

Scheme IV.1

Table IV.1: Thermal gravimetric analysis data for all polymers.

Polymer	Decomposition Temperature (5% wt. Loss, °C)
IV.1	148
IV.2	89
IV.3	87
IV.4	251
IV.5	202
IV.6	204
IV.7	208
IV.8	209

DSC experiments were run on all polymers from 30 °C to ~10 °C below the thermal decomposition temperature, however no peaks indicative of a phase change were observed.

Electrochemistry: Electrochemistry was performed on only the polyazodicarbonyl ruthenium complexes as films on a Pt disk electrode. The cv trace showed two quasi-reversible couples, similar to the dinuclear complexes, attributable to the two one-electron couples per dinuclear adc fragment in the polymer.

Table IV.2: Electrochemical data for polymer complexes in solid state on Pt disk electrode in CHCl_3 (with 0.1 M TBAH).

Complex	1 st $E_{1/2}$ ^a (p-p) ^b	2 nd $E_{1/2}$ ^a (p-p) ^b	ΔE (mV)	^c K_c
IV.5	310(210)	920(270)	610	2.1×10^{10}
IV.6	450(180)	1040(222)	590	9.5×10^9
IV.7	310(260)	930(240)	620	3.0×10^{10}
IV.8	120(75)	730(100)	610	2.1×10^{10}

^a All redox couples in mV versus silver pseudo-reference electrode at 10 mV/s scan rate. ^b Peak to peak separation for each redox couple in mV. ^c $K_c = 10^{(16.91\Delta E)/30, 31}$.

Table IV.3: Electrochemical switching of polymer complexes on Pt disk electrode (BAS 2013, 1.6 mm dia.) in CHCl_3 (with 0.1 M TBAH).

Polymer	Switching Period (ms)	Total Time (hrs) (Cycles)	Initial Charge $\mu\text{C}/\text{cm}^2$	Medial Charge $\mu\text{C}/\text{cm}^2$	Final Charge $\mu\text{C}/\text{cm}^2$
IV.5	1200	16.7 (50000)	184	241	258
IV.6	2400	22.7 (34000)	241	80	63
IV.7	2400	16 (24000)	262	93	57
IV.8	1200	21.7 (65000)	78	76	69

The peak-to-peak separations for both couples ranged between 75 and 272 mV.

The magnitude of this separation was generally higher versus the dinuclear complexes and can be attributed to lower kinetics due to the uptake and expulsion of electrolyte from the film. The movement of electrolyte, particularly counterion, into and out of the film is necessary for charge balancing and generally controls the electrochemical rate. An anomalous result was derived for IV.8, which showed peak-peak separations of the same

magnitude as that of the solution dinuclear and tetranuclear complexes may simply be due to a much thinner film, as we will see from the switching trials.

Figure IV.4: CV of polymer IV.5 in the solid state on a Pt disk electrode in CHCl_3 at a scan rate of 20 mV/s (with 0.1 M TBAH).

In order to measure long term switching stability, the polymer films were subjected to repeated switching between the reduced or $-\text{[Ru}^{\text{II}}\text{Ru}^{\text{II}}\text{]}-$ and the mixed valence $-\text{[Ru}^{\text{II}}\text{Ru}^{\text{III}}\text{]}-$ state at a frequency ranging from 1.2 to 2.4 s. The choice of frequency was made based upon the relative speed at which the redox current minimized. Results for the trials are displayed in table IV.3 along with total charge per unit area of

electrode taken from the integration, with respect to time, of the current trace initially, at the middle and finally the end of the experiment. The results show a small degree of change over time for **IV.8** only, an increase of nearly a factor of two for **IV.5** and a significant drop in electrochemical response for **IV.6** and **IV.7**, the latter likely being a result of film delamination.

Uv-vis-NIR: Spectra for all polymers in the reduced, mixed valence and oxidized form were taken in-situ with the polymer mounted on ITO coated glass, and exhibited similar peak patterns as that observed for the dinuclear complexes. This is consistent with the presence of isolated adc fragments within a saturated polymer where no electronic interaction between the dinuclear ADC fragments exists.

Table IV.4: Spectral data for polymeric complexes on ITO glass.

Polymer	λ_{max} (nm)		
	-(2,2)-	-(2,3)-	-(3,3)-
IV.5^a	353, 518	451, 1521	315, 463, 830
IV.5^b	350, 520	454, 657, 1532	457, 810
IV.6^a	455, 516	452, 647, 1585	452, 805
IV.7^b	351, 463, 513	450, 1576	454, 809
IV.8^b	460	455, 579, 1188	460, 910

Electrolyte: ^a THF with 0.1 M TBAH, ^b CHCl₃ with 0.1 M TBAH.

The data for all polymers, taken utilizing a liquid electrolyte solution made up of 0.1 M TBAH in CHCl₃, is given in table **IV.4**. The solvent choice here was made purely on the basis of differential solubility expressed by the polymers. All polymers were found to be insoluble in CHCl₃, and so the majority were evaluated spectroscopically

using TBAH solutions of this solvent as the electrolyte. The data for IV.5 showed only a slight solventochromic shift in the major spectral bands and so it was concluded that data derived in either solvent would be, for all intents and purposes, equivalent. It was, however, necessary to evaluate some of the polymers in THF since, for long term switching trials, delamination of the ITO layer occurred during repeated electrochemical switching of the films in CHCl_3 .

Figure IV.5: Spectroelectrochemical spectra for polymer IV.5 on ITO in CHCl_3 with 0.1 M TBAH.

It was felt that a measure of the extinction coefficients might indicate the level of metal incorporation within the polymers. By choosing the bands characteristic of the

ADC complex, such as the MLCT or bipyridyl $\pi \rightarrow \pi^*$ transitions, this may be accomplished assuming the extinction coefficients are not significantly affected by the metal environment.

The extinction coefficients for the $[\text{Ru(II)}]d\pi \rightarrow [\text{bpy}]\pi^*$ MLCT bands at ca. 450 to 520 nm were generally lower compared to those found for the dinuclear complexes. In the case of the IV.7 and IV.8 this is not as clear from the numbers presented in the table IV.5, however referring to figure IV.4, these systems contain two adc fragments per repeat unit. Therefore, accounting for this the two have $\log(\epsilon)$ values of 3.93 and 3.84 for the IV.7 and IV.8 (*resp.*). The observed differential in extinction may be the result of differences in environment of each metal complex, however, if this is attributable to incomplete complexation of the polymer it would indicate, on average, that only 53% of the possible hydrazine dicarbonyl sites are complexed in the polymer versus the dinuclear complexes. However, if we then compare these with that of the acetylene bridged tetranuclear complex, which possesses the lowest ϵ values of all the complexes, the number of sites probably complexed raises to well over 100%. Therefore, the most likely cause of this discrepancy is differential metal environment, which would lead to a conclusion that all of the available hydrazine dicarbonyl sites are occupied by $\text{Ru}(\text{bpy})_2$ fragments.

Table IV.5: Quantitative spectral data for polymeric complexes in ACN.

Polymer	$\lambda_{\max}(\text{nm})$	$\epsilon (\text{M}^{-1}\text{cm}^{-1})$	$\log(\epsilon)$
IV.5	245	26300	4.42
	289	54600	4.74
	350	9000	3.95
	516	7500	3.88
IV.6	244	29900	4.48
	288	54600	4.74
	454	7600	3.88
IV.7	244	68000	4.83
	289	127300	5.10
	457	16900	4.23
IV.8	244	63700	4.80
	290	122200	5.09
	455	13700	4.14

Figure IV.6: Polymer IV.5 solid state switching on ITO/glass in THF with 0.1 M TBAH.

A solid state, long term optical switching experiment was conducted using ITO coated glass as the substrate and THF/0.1M TBAH as the electrolyte (i.e. same experimental set-up as was used for spectral studies), in order to evaluate the stability of the films to withstand repeated bleach-colour cycling. Polymer IV.5 turned out to be the only material, which formed films stable toward dissolution over the full length of the experiment. Given this polymer IV.5 was then spin cast onto ITO and cycled between – 200 mV and 600 mV, which switched the material electrochemically between the reduced $\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}}$ and mixed valence $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ states. The period of the switching was 4 s with each potential being held for 2 s and timebase absorbance at 1550 nm were taken for 120 s at intervals through the experiment initially, at 9 hours and finally at 19 hours. Figure IV.6 shows the optical switching data taken by the spectrometer, and the results of the trial are given in table IV.6.

The colouration efficiency (CE) was calculated according to the method of Sapp *et al*³² using equation 1 and 2. The results show that the CE value increases over the first half of the experiment and drops slightly over the second half. The values themselves, however, are comparable to those of Sapp *et al*³² for a series of PEDOT dual polymer solid state ECD's and are several orders of magnitude higher than those for WO_3 or Prussian blue. Furthermore, the observed trend over the experiment is a result of swelling within the film, which results in greater void space within the polymer matrix augmenting charge transport, thus decreasing resistance of the film and increasing CE. Over time however, this swelling can result in a reduction in the electrical contact

between the film and the ITO surface, which would account for the reduction in the CE in the later half of the experiment.

$$CE(\lambda) = \frac{\Delta OD(\lambda)}{Q_d} \quad \text{Equation 1}$$

$$\Delta OD(\lambda) = \log[T_b(\lambda)/T_c(\lambda)] \quad \text{Equation 2}$$

Table IV.6: Optical switching data for polymer IV.5 in THF with 0.1 M TBAH.

Time	%T _b /%T _c	Δ%T	Q _p (μC)	area (cm ²)	Q _d (μC/cm ²)	ΔOD (x10 ⁻²)	CE (cm ² /C)
Initial	79/74	5	180	3	60	2.84	470
9 Hrs. (8100 cycles)	68/63	5	160	3	53	3.32	630
19 Hrs. (17100 cycles)	69/65	4	130	3	43	2.59	600

Conclusions

The polymers constructed, though seemingly low molecular weight produced reasonably good films on ITO coated glass. The thermal stability was excellent and, as with the dimeric butyl and isophthalyl bridged tetranuclear complexes, exhibited similar spectroscopic and electrochemical behaviour as the dinuclear model complexes.

Synthetically, these materials were prepared using the same simple methods as used for producing the dinuclear complexes.

Long term switching trials in the solid state indicated good chemical stability of the material and comparable colouration efficiencies as other well-established electrochromic materials. Further research is necessary, however to discover a way to stabilize the films against dissolution in the electrolyte solution for application in solution/solid hybrid devices.

Experimental

Measurements

Electrochemical and spectroscopic measurements were taken in the solid state by casting thin films of the polymer on either platinum disk electrode (BAS 2013 MF, 1.6 mm diameter) or ITO coated glass. The ITO coated glass was pretreated by first cleaning it by momentarily dipping it in concentrated H_2SO_4 , followed by rinsing with deionized water and drying under a stream of Argon. The clean ITO surface was then treated with a 2% solution of 3-aminopropyltriethoxysilane (99%, Aldrich) in toluene via spin coating, followed by air drying for 1 hour, and finally coating with a solution of the polymer in DMF/ CHCl_3 . The polymer coating on ITO was then allowed to air dry for several hours prior to testing.

Cyclic voltammetry measurements were made in precisely the same manner as has been described previously, with the following exceptions. The solvent used was

spectroscopic grade CHCl_3 with 0.1 M TBAH. The reference and counter electrodes were silver wire and platinum wire, respectively. No internal standard, such as FeCp_2 or $[\text{CoCp}_2]\text{PF}_6$ used in the characterization of all small molecule materials, were used as the working electrode was completely coated with the polymer being characterized, therefore the electrochemical measurements are reported versus the pseudo silver electrode.

Spectroelectrochemical and switching experiments were performed with polymer coated on ITO and mounted within a 1 cm quartz cuvette (figure IV.7). The cuvette was also fitted with a platinum wire counter electrode and silver wire pseudo reference electrode. Sufficient electrolyte solution, THF or CHCl_3 with 0.1 M tetrabutylammonium hexafluorophosphate, was then added to the cell in order to make good contact with all electrodes and fully flood the spectrometer light path.

Figure IV.7: Spectroelectrochemical experimental set-up.

Reagents and Synthesis

All ligands were synthesized from the appropriate hydrazide and either the appropriate diacid chloride, dihydrazide or diisocyanate. Reagents include phthaloyl dichloride (Aldrich), hydrazine hydrate (Aldrich), adipic dihydrazide (98%, Aldrich), adipoyl chloride (98%, Aldrich), 1,6-diisocyanohexane (98%, Aldrich), *N*-methylpyrrolidone (NMP) (97%, Aldrich), and *N,N*-dimethylformamide (DMF) (99.8, Aldrich).

All polymer metal coordination complexes were synthesized in the same manner as that of the dinuclear and polynuclear complexes. The general synthetic approach was to combine 0.38 mmol (200 mg) $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ with 0.19 mmol (w.r. hydrazide fragment) of the carboxylhydrazine polymer and 100 mg Na_2CO_3 in 80 mL of 5:1 $\text{H}_2\text{O}/\text{EtOH}$. The mixture was then refluxed for approximately 14 hours under ambient atmosphere, after which it was cooled to room temperature, and the product was precipitated by the addition of excess NH_4PF_6 . The crude product was then isolated by filtration, and dried under vacuum.

Ligand Precursor Compounds

Isophthalic dihydrazide:

To 20 mL hydrazine hydrate was added 1.0 g (4.9 mmol) of phthaloyl chloride. The mixture was stirred for 1 hour, followed by precipitation of the product from CH_3OH .

The yield of the product was 0.9 g (94%). (FTIR $\nu(\text{C}=\text{O})$ 1665 cm^{-1} , $\nu(\text{NH})$ 3290 cm^{-1} ; ^1H NMR (200 MHz, d_6 -DMSO) δ 4.60 (s,4H), 7.56 (t,1H), 7.97 (d,2H), 8.31 (s,1H), 9.88 (s,2H); MS (EI, m/z) calcd. for $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$ 194.2, found 194 (M^+ , 30.2); mp 227-230 $^\circ\text{C}$)

Polyhydrazine Ligands

Poly(adipic hydrazine)(IV.1):

To 30 mL of NMP were added 1.74 g (10 mmol) of adipic dihydrazide and 1.83 g (10 mmol) of adipoyl chloride. The mixture was allowed to stir overnight at room temperature, under N_2 , followed by precipitation of the product in 300 mL of vigorously stirring CH_3OH . The product was isolated by filtration and dried overnight under vacuum. Yield of the crude polymer was 1.7 g (61%). (FTIR $\nu(\text{C}=\text{O})$ 1600 cm^{-1} , $\nu(\text{NH})$ 3216 cm^{-1} ; ^1H NMR (200 MHz, d_6 -DMSO) δ 1.5 (s,4H), 2.1(s,4H), 9.7 (s,2H))

Poly(isophthalic hydrazine)(IV.2):

Synthesis was the same as for poly(adipic hydrazine), except with 15 mL NMP, 0.99 g (5 mmol) of isophthalic dihydrazide, 1.02 g (5 mmol) of isophthaloyl chloride. Yield of the crude polymer was 1.4 g (69%). (FTIR $\nu(\text{C}=\text{O})$ 1649 cm^{-1} , $\nu(\text{NH})$ 3235 cm^{-1} ; ^1H NMR (200 MHz, d_6 -DMSO) δ 7.7 (t, 1H), 8.2 (d,2H), 8.5 (s,1H), 10.8 (s,2H))

Poly(adipic, isophthalic hydrazine)(IV.3):

Synthesis was the same as for poly(adipic hydrazine), except with 1.74 g (10 mmol) of adipic dihydrazide and 2.03 g (10 mmol) isophthaloyl chloride. The yield of the crude polymer was 2.6 g (69%). (FTIR $\nu(\text{C=O})$ 1654 cm^{-1} , $\nu(\text{NH})$ 3241 cm^{-1} ; ^1H NMR (200 MHz, d_6 -DMSO) δ 1.6 (s, 4H), 2.4 (s, 4H), 7.6 (t, 1H), 8.1 (d, 2H), 8.2 (s, 1H), 9.9 (s, 2H), 10.4 (s, 2H))

Poly(adipic, 1,6-carbamylhexyl hydrazine)(IV.4):

In 15 mL DMF was added 523 mg (3 mmol) of adipic hydrazide and 505 mg (3 mmol) of 1,6-diisocyanohexane. The polymer, which precipitated from the reaction mixture, was isolated by filtration and dried overnight under vacuum. Yield of the crude polymer was 0.8 g (78%). (FTIR $\nu(\text{C=O})$ 1654 cm^{-1} , $\nu(\text{NH})$ 3353, 3224 cm^{-1} ; ^1H NMR (200 MHz, d_6 -DMSO) δ 1.4 (m, 12H), 2.1 (s, 4H), 3.0 (m, 4H), 6.3 (s, 2H), 7.6 (s, 2H), 9.4 (s, 2H))

Complexes*Poly([Ru(bpy)₂]₂ μ -(adipic adc)](PF₆)₂)(IV.5):*

The synthesis was performed in the manner described previously for dinuclear complexes, using 200 mg (0.38 mmol) Ru(bpy)₂Cl₂·2H₂O, 35 mg (0.25 mmol w.r. repeat unit) poly(adipic hydrazine), and 100 mg Na₂CO₃. Yield of the polymer was 215 mg (87% based on reacted polymer). (FTIR $\nu(\text{C=O})$ 1605 cm^{-1} , $\nu(\text{P-F})$ 830 cm^{-1})

Poly([{Ru(bpy)₂}₂ μ-(isophthalic adc)](PF₆)₂)(IV.6):

The synthesis was performed in the manner described previously for dinuclear complexes, using 200 mg (0.38 mmol) Ru(bpy)₂Cl₂·2H₂O, 35 mg (0.22 mmol w.r. repeat unit) poly(isophthalic hydrazine), and 100 mg Na₂CO₃. Yield of the crude polymer was 218mg (88% based on reacted polymer). (FTIR ν(C=O) 1605 cm⁻¹, ν(P-F) 841 cm⁻¹)

Poly([{Ru(bpy)₂}₄ μ-(adipic, isophthalic adc)](PF₆)₄)(IV.7):

The synthesis was performed in the manner described previously for dinuclear complexes, using 200 mg (0.38 mmol) Ru(bpy)₂Cl₂·2H₂O, 30 mg (0.099 mmol w.r. repeat unit) poly(adipic, isophthalic hydrazine), and 100 mg Na₂CO₃. Yield of the crude polymer was 230 mg (95% based on reacted polymer). (FTIR ν(C=O) 1605 cm⁻¹, ν(P-F) 842 cm⁻¹)

Poly([{Ru(bpy)₂}₄ μ-(adipic, 1,6-carbamylhexyl adc)](PF₆)₄)(IV.8):

The synthesis was performed in the manner described previously for dinuclear complexes, using 200 mg (0.38 mmol) Ru(bpy)₂Cl₂·2H₂O, 33 mg (0.097 mmol w.r. repeat unit) poly(adipic, 1,6-carbamylhexyl hydrazine), and 100 mg Na₂CO₃. Yield of the crude polymer was 137 mg (56% based on reacted polymer). (FTIR ν(C=O) 1605 cm⁻¹, ν(N-H) 3326 cm⁻¹, ν(P-F) 841 cm⁻¹)

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Summary

In this research we have successfully derivatized both the dinuclear ruthenium azodicarbonyl and 1,8-naphthalimide in order to probe the effect of substituent donor/acceptor potential on the electrochemistry and spectroscopy. Furthermore, in the case of the ADC complexes, tetranuclear dimeric and polynuclear analogues were also prepared and studied. The results revealed that the donor potential of the substituent has a profound, but predictable, effect on the properties of these systems. Additionally, for the ADC systems, scale-up from small molecule to macromolecular analogues did not adversely affect the properties and was accomplished without the necessity of altering the synthetic methodology.

With respect to the naphthalimide system, the results of derivatization were generally in accordance with known principles, that is, the greater the withdrawing potential of the substituent the greater the anodic shift in the electrochemistry. This is contiguous with the results, by others, for donor substituent derivatized naphthalimides. An unexpected result, in the case of the dinitro-substituted compound, was the discovery of an extraordinarily low energy NIR band for the radical anion. This band can, tentatively, be attributed to an intramolecular CT transition involving the radical imide and nitro substituent.

The results for the dinuclear complexes generally conformed to those of others who have studied these systems. One result that was novel was the determination, for the first time, of the crystal structure of the ruthenium analogue. The structure was compared to those of the rhodium and copper analogues, and found to be similar in that the ADC bridge system was planar in all cases.

The tetranuclear complexes were dimeric analogues of the dinuclear ADC. In the series, the bridging fragment between individual adc dinuclear fragments was varied such that the degree of electronic coupling varied from negligible (i.e. alkyl) to strong (i.e. acetylene). The results proved to be more complex than was expected. Firstly, one would expect concomitant with an introduction of coupling between two symmetric metal centres, splitting in the redox couples for each metal. This would translate, in the case of two strongly coupled dinuclear complexes, to a further splitting of the redox potentials for each metal centre commensurate with the degree of coupling. For the alkyl versus the ethenyl bridged systems this appears to be true, however not so for the acetylene bridged system. The nature of this discrepancy and others, such as the lack of mixed valence behaviour in the acetylene system after the second one electron couple, is still under investigation. It has been suggested that an internal comproportionation may be responsible for the unusual spectroscopic behaviour of the acetylene system, however this rationalization has some profound issues. These include; the lack of an MLCT transition for the $[\{\text{Ru}^{\text{II}}\text{Ru}^{\text{II}}\}-\{\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}\}]$, such a reorganization would seem to be contrary to the optimum stability for the system which favours a mixed-valence state

based on the k_c magnitude, and the apparent two-electron oxidation of the $\text{Ru}^{\text{II}}\text{Ru}^{\text{II}}$ ADC fragment which should experience at least some splitting based upon the precedence of the dinuclear systems.

The polymeric systems proved to be relatively simple to prepare and formed reasonably good films on ITO and platinum in spite of their obvious low molecular weight, as determined by viscosity measurements. Electrochemical and spectroscopic studies showed that the behaviour observed for the dinuclear complexes was preserved in the polymeric derivatives. Furthermore, the materials exhibited excellent chemical stability in long term switching experiments. As well, the NIR band, important in terms of optical switching for data communication, appeared to possess similar intensity to that of the dinuclear complexes. Finally, the colouration efficiencies (CE), determined for the polymeric materials at 1550 nm, were in the range of other electrochromic materials discussed in chapter 1. Given the large contrast in the colours exhibited, the optical density of the NIR transition and excellent CE, it should be concluded that these materials represent a promising novel class of electrochromics suitable for both optical data communication and display applications.

Appendix I

X-Ray Crystallographic Data for $[\{\text{Ru}(\text{bpy})_2\}_2 \mu\text{-ph,CH}_3\text{-adc}](\text{BF}_4)_2$

Table 1. Crystal data and structure refinement for ww002.

Identification code	ww002
Empirical formula	C ₄₉ H ₄₀ B ₂ F ₈ N ₁₀ O ₂ Ru ₂
Formula weight	1176.67
Temperature	238(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 25.684(4) Å alpha = 90 deg. b = 12.086(2) Å beta = 113.507(2) deg c = 17.625(3) Å gamma = 90 deg.
Volume	5017(1) Å ³
Z, Calculated density	4, 1.558 Mg/m ³
Absorption coefficient	0.682 mm ⁻¹
F(000)	2360
Crystal size	0.2 x 0.2 x 0.2 mm
Theta range for data collection	1.73 to 21.00 deg.
Limiting indices	-25 ≤ h ≤ 23, 0 ≤ k ≤ 12, 0 ≤ l ≤ 17
Reflections collected / unique	19729 / 2704 [R(int) = 0.0854]
Completeness to theta = 21.00	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.928078 and 0.667591
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2704 / 0 / 349
Goodness-of-fit on F ²	1.006
Final R indices [I > 2sigma(I)]	R1 = 0.0669, wR2 = 0.1949
R indices (all data)	R1 = 0.0905, wR2 = 0.2135
Largest diff. peak and hole	0.899 and -1.116 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ww002. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ru	3345(1)	2813(1)	1275(1)	68(1)
O(1)	2770(3)	1666(6)	1297(4)	79(2)
N(1)	3898(4)	2295(10)	2428(6)	92(4)
N(2)	3729(4)	1458(7)	982(6)	80(3)
N(3)	3884(4)	4048(7)	1315(5)	69(2)
N(4)	2993(4)	4098(8)	1633(5)	77(3)
N(5)	2286(4)	2063(6)	-83(5)	60(2)
C(1)	4023(8)	2886(15)	3111(9)	150(8)
C(2)	4388(8)	2404(16)	3900(10)	136(7)
C(3)	4586(9)	1310(20)	3905(11)	152(8)
C(4)	4455(7)	793(17)	3209(12)	152(8)
C(5)	4107(5)	1220(11)	2383(10)	97(5)
C(6)	3655(6)	1112(10)	225(9)	96(4)
C(7)	3835(7)	79(12)	54(11)	116(5)
C(8)	4086(8)	-596(16)	683(14)	139(6)
C(9)	4195(6)	-343(11)	1461(11)	102(4)
C(10)	4008(5)	713(12)	1613(8)	91(4)
C(11)	4360(5)	3968(11)	1160(7)	88(4)
C(12)	4709(5)	4866(13)	1226(9)	99(4)
C(13)	4582(6)	5847(13)	1448(8)	99(4)
C(14)	4115(6)	5982(11)	1622(7)	91(4)
C(15)	3775(4)	5037(10)	1557(6)	68(3)
C(16)	2516(6)	4039(13)	1787(8)	102(4)
C(17)	2311(7)	4919(15)	2058(10)	127(6)
C(18)	2563(8)	5969(15)	2142(10)	147(7)
C(19)	3058(7)	6001(11)	2006(8)	118(5)
C(20)	3250(5)	5103(10)	1725(6)	81(4)
C(21)	1598(6)	418(9)	582(10)	57(9)
C(22)	1329(5)	-573(12)	607(9)	60(5)
C(23)	1578(6)	-1574(9)	552(10)	87(7)
C(24)	2095(6)	-1585(9)	473(11)	95(8)
C(25)	2364(5)	-595(11)	448(11)	79(7)
C(26)	2115(6)	406(9)	503(10)	54(8)
C(27)	1841(13)	610(20)	580(20)	63(9)
C(28)	2357(5)	1497(8)	582(6)	71(3)
B	5752(6)	7745(13)	1325(9)	78(4)
F(1)	5436(6)	8484(16)	770(8)	256(8)
F(2)	5674(5)	6729(10)	1085(10)	236(8)
F(3)	6291(4)	8022(7)	1551(7)	154(4)
F(4)	5582(5)	7880(6)	1949(6)	142(4)

Table 3. Bond lengths [Å] and angles [deg] for ww002.

Ru-N(4)	2.020(10)
Ru-N(3)	2.018(8)
Ru-O(1)	2.038(7)
Ru-N(1)	2.058(9)
Ru-N(5) #1	2.084(8)
Ru-N(2)	2.081(11)
O(1)-C(28)	1.298(11)
N(1)-C(1)	1.324(19)
N(1)-C(5)	1.420(16)
N(2)-C(6)	1.336(15)
N(2)-C(10)	1.388(15)
N(3)-C(15)	1.337(13)
N(3)-C(11)	1.359(15)
N(4)-C(16)	1.357(15)
N(4)-C(20)	1.360(13)
N(5)-C(28)	1.306(11)
N(5)-N(5) #1	1.468(14)
N(5)-Ru#1	2.084(8)
C(1)-C(2)	1.45(2)
C(2)-C(3)	1.41(3)
C(3)-C(4)	1.30(2)
C(4)-C(5)	1.466(19)
C(5)-C(10)	1.417(19)
C(6)-C(7)	1.405(17)
C(7)-C(8)	1.32(2)
C(8)-C(9)	1.32(2)
C(9)-C(10)	1.426(18)
C(11)-C(12)	1.382(16)
C(12)-C(13)	1.329(18)
C(13)-C(14)	1.363(18)
C(14)-C(15)	1.413(15)
C(15)-C(20)	1.493(15)
C(16)-C(17)	1.357(19)
C(17)-C(18)	1.41(2)
C(18)-C(19)	1.38(2)
C(19)-C(20)	1.364(17)
C(21)-C(22)	1.3900
C(21)-C(26)	1.3900
C(22)-C(23)	1.3900
C(23)-C(24)	1.3900
C(24)-C(25)	1.3900
C(25)-C(26)	1.3900
C(26)-C(28)	1.441(13)
C(27)-C(28)	1.70(3)
B-F(2)	1.288(17)
B-F(3)	1.322(15)
B-F(1)	1.334(19)
B-F(4)	1.345(16)
N(4)-Ru-N(3)	78.9(4)
N(4)-Ru-O(1)	95.7(4)
N(3)-Ru-O(1)	174.4(4)
N(4)-Ru-N(1)	98.3(4)
N(3)-Ru-N(1)	89.8(3)
O(1)-Ru-N(1)	89.7(3)
N(4)-Ru-N(5) #1	89.7(3)

N(3)-Ru-N(5)#1	103.2(3)
O(1)-Ru-N(5)#1	77.9(3)
N(1)-Ru-N(5)#1	165.9(3)
N(4)-Ru-N(2)	176.5(3)
N(3)-Ru-N(2)	101.7(4)
O(1)-Ru-N(2)	83.6(3)
N(1)-Ru-N(2)	78.3(4)
N(5)#1-Ru-N(2)	93.5(3)
C(28)-O(1)-Ru	114.0(6)
C(1)-N(1)-C(5)	125.8(13)
C(1)-N(1)-Ru	123.7(12)
C(5)-N(1)-Ru	110.5(8)
C(6)-N(2)-C(10)	114.8(11)
C(6)-N(2)-Ru	127.0(8)
C(10)-N(2)-Ru	117.2(9)
C(15)-N(3)-C(11)	116.6(10)
C(15)-N(3)-Ru	116.3(7)
C(11)-N(3)-Ru	127.0(9)
C(16)-N(4)-C(20)	117.1(11)
C(16)-N(4)-Ru	125.0(9)
C(20)-N(4)-Ru	117.9(8)
C(28)-N(5)-N(5)#1	111.8(9)
C(28)-N(5)-Ru#1	135.8(7)
N(5)#1-N(5)-Ru#1	111.7(7)
N(1)-C(1)-C(2)	119.0(19)
C(3)-C(2)-C(1)	118.2(18)
C(4)-C(3)-C(2)	119.3(19)
C(3)-C(4)-C(5)	127(2)
N(1)-C(5)-C(10)	121.5(11)
N(1)-C(5)-C(4)	111.2(16)
C(10)-C(5)-C(4)	127.2(16)
N(2)-C(6)-C(7)	124.3(12)
C(8)-C(7)-C(6)	117.5(16)
C(7)-C(8)-C(9)	124.1(18)
C(8)-C(9)-C(10)	117.0(14)
N(2)-C(10)-C(9)	122.4(12)
N(2)-C(10)-C(5)	109.0(13)
C(9)-C(10)-C(5)	128.5(14)
N(3)-C(11)-C(12)	122.2(13)
C(13)-C(12)-C(11)	119.9(13)
C(12)-C(13)-C(14)	121.0(13)
C(13)-C(14)-C(15)	117.1(13)
N(3)-C(15)-C(14)	123.2(11)
N(3)-C(15)-C(20)	115.6(9)
C(14)-C(15)-C(20)	121.2(12)
C(17)-C(16)-N(4)	122.5(12)
C(16)-C(17)-C(18)	121.1(13)
C(19)-C(18)-C(17)	115.1(15)
C(20)-C(19)-C(18)	122.0(13)
C(19)-C(20)-N(4)	121.7(11)
C(19)-C(20)-C(15)	126.9(11)
N(4)-C(20)-C(15)	111.3(10)
C(22)-C(21)-C(26)	120.0
C(23)-C(22)-C(21)	120.0
C(22)-C(23)-C(24)	120.0
C(25)-C(24)-C(23)	120.0
C(24)-C(25)-C(26)	120.0
C(25)-C(26)-C(21)	120.0
C(25)-C(26)-C(28)	127.6(10)
C(21)-C(26)-C(28)	112.0(10)

O(1)-C(28)-N(5)	123.8(9)
O(1)-C(28)-C(26)	113.1(10)
N(5)-C(28)-C(26)	119.5(10)
O(1)-C(28)-C(27)	115.8(14)
N(5)-C(28)-C(27)	119.8(14)
C(26)-C(28)-C(27)	28.1(10)
F(2)-B-F(3)	110.3(13)
F(2)-B-F(1)	115.3(16)
F(3)-B-F(1)	108.0(13)
F(2)-B-F(4)	109.0(12)
F(3)-B-F(4)	111.5(13)
F(1)-B-F(4)	102.6(13)

Symmetry transformations used to generate equivalent atoms:
 #1 -x+1/2,-y+1/2,-z

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ww002.
The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Ru	75(1)	74(1)	41(1)	5(1)	8(1)	-28(1)
O(1)	87(5)	85(5)	43(4)	13(4)	1(4)	-33(4)
N(1)	86(7)	119(9)	47(6)	5(6)	0(5)	-64(7)
N(2)	75(6)	63(6)	80(7)	38(6)	8(5)	-8(5)
N(3)	74(7)	76(6)	42(5)	5(4)	8(4)	-17(5)
N(4)	85(7)	93(7)	52(5)	-17(5)	25(5)	-39(6)
N(5)	78(6)	54(5)	42(5)	0(4)	17(4)	-24(4)
C(1)	157(15)	200(18)	56(9)	26(10)	3(9)	-107(14)
C(2)	136(15)	151(14)	82(11)	15(11)	3(10)	-73(13)
C(3)	146(17)	200(20)	72(11)	18(13)	5(11)	-76(16)
C(4)	95(11)	197(18)	120(14)	94(14)	-2(10)	-34(12)
C(5)	70(8)	72(9)	134(13)	52(9)	26(8)	-15(7)
C(6)	116(11)	72(9)	93(10)	27(7)	36(8)	3(7)
C(7)	126(13)	82(10)	124(12)	29(9)	31(10)	18(9)
C(8)	120(14)	132(15)	158(17)	-28(14)	48(14)	1(12)
C(9)	89(10)	67(9)	129(13)	21(9)	23(9)	-2(7)
C(10)	76(9)	114(12)	73(8)	-9(8)	20(7)	-26(8)
C(11)	62(8)	94(9)	94(9)	28(7)	17(7)	9(7)
C(12)	46(7)	103(10)	126(11)	32(9)	10(7)	-23(8)
C(13)	72(9)	99(11)	100(10)	7(8)	8(8)	-43(8)
C(14)	98(10)	93(9)	76(8)	-18(6)	27(7)	-39(8)
C(15)	60(7)	86(8)	51(6)	-13(5)	14(5)	-40(6)
C(16)	114(11)	128(11)	80(9)	-28(8)	56(8)	-50(9)
C(17)	128(13)	172(16)	118(12)	-57(11)	87(11)	-65(12)
C(18)	175(16)	173(16)	146(14)	-99(13)	120(13)	-71(14)
C(19)	175(15)	101(10)	110(10)	-61(9)	91(11)	-63(10)
C(20)	100(9)	90(9)	60(7)	-35(6)	38(7)	-45(8)
C(21)	38(17)	90(20)	56(13)	-11(12)	30(13)	7(14)
C(22)	63(13)	49(12)	73(13)	-14(10)	31(11)	-27(11)
C(23)	95(18)	70(16)	118(19)	-13(14)	64(16)	-55(14)
C(24)	130(20)	49(13)	140(20)	-7(14)	91(19)	-10(14)
C(25)	103(18)	26(11)	140(20)	-3(11)	82(17)	8(11)
C(26)	36(16)	90(20)	29(10)	10(10)	7(12)	-25(13)
C(27)	40(20)	64(16)	67(18)	23(13)	3(14)	-11(15)
C(28)	93(8)	54(6)	49(6)	5(5)	11(6)	-30(6)
B	61(9)	101(11)	74(9)	5(8)	30(8)	-16(8)
F(1)	185(12)	410(20)	129(9)	100(12)	13(8)	70(14)
F(2)	205(11)	191(10)	420(20)	-187(13)	234(14)	-99(10)
F(3)	84(6)	153(8)	203(10)	26(7)	36(6)	-35(5)
F(4)	228(11)	96(6)	143(8)	-21(5)	118(8)	-36(6)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ww002.

	x	y	z	U(eq)
H(1A)	3877	3605	3085	180
H(2A)	4489	2808	4395	163
H(3A)	4811	965	4407	183
H(4A)	4598	71	3237	182
H(6A)	3471	1592	-222	115
H(7A)	3779	-123	-488	140
H(8A)	4193	-1300	571	166
H(9A)	4387	-837	1894	122
H(11A)	4456	3280	1002	105
H(12A)	5036	4783	1115	119
H(13A)	4818	6456	1485	119
H(14A)	4022	6673	1779	110
H(16A)	2321	3362	1703	122
H(17A)	1994	4826	2192	153
H(18A)	2408	6603	2280	176
H(19A)	3267	6662	2110	142
H(21A)	1429	1095	619	68
H(22A)	980	-565	661	73
H(23A)	1397	-2243	569	105
H(24A)	2264	-2262	436	114
H(25A)	2713	-603	394	95
H(27A)	1557	1014	703	94
H(27B)	2008	42	996	94
H(27C)	1663	266	39	94

Table 6. Observed and calculated structure factors for mw002

h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
2	0	0	1692	1174	49	13	7	0	424	362	31	-15	3	1	659	635	13	-13	7	1	107	155	107	-6	0	2	2170	2468	132
4	0	0	2884	3030	24	15	7	0	649	637	22	-13	3	1	1213	1205	10	-11	7	1	312	255	29	-4	0	2	4344	3798	44
6	0	0	1945	1601	17	17	7	0	140	237	139	-11	3	1	450	431	12	-9	7	1	93	81	92	-2	0	2	3901	4041	42
8	0	0	1019	952	11	19	7	0	151	214	151	-9	3	1	807	845	9	-7	7	1	51	59	51	0	0	2	826	996	29
10	0	0	1381	1590	14	0	8	0	0	63	1	-7	3	1	1807	1831	13	-5	7	1	858	926	9	2	0	2	2955	3196	31
12	0	0	787	826	12	2	8	0	292	245	24	-5	3	1	480	439	9	-3	7	1	203	30	36	4	0	2	2772	2906	29
14	0	0	846	760	15	4	8	0	458	479	11	-3	3	1	1540	1572	12	-1	7	1	627	639	11	6	0	2	116	46	86
16	0	0	499	491	21	6	8	0	105	31	105	-1	3	1	1143	1468	79	1	7	1	455	411	10	8	0	2	1167	1230	16
18	0	0	887	914	35	8	8	0	262	305	27	-1	3	1	614	802	8	3	7	1	601	573	9	10	0	2	1807	1763	20
20	0	0	508	494	53	10	8	0	168	118	108	3	3	1	1851	1784	13	5	7	1	184	221	29	12	0	2	368	379	22
22	0	0	244	261	129	12	8	0	0	58	1	5	3	1	1363	1412	10	7	7	1	290	242	20	14	0	2	1618	1672	20
1	1	0	260	139	5	14	8	0	139	192	138	7	3	1	398	384	13	9	7	1	182	264	56	16	0	2	918	884	33
3	1	0	1959	1893	15	16	8	0	167	107	96	9	3	1	1297	1377	12	11	7	1	233	130	43	18	0	2	0	119	1
5	1	0	2413	2471	18	1	9	0	411	384	22	11	3	1	1630	1595	14	13	7	1	159	142	79	20	0	2	564	447	49
7	1	0	382	338	12	3	9	0	928	859	11	13	3	1	0	13	1	15	7	1	217	59	68	22	0	2	439	406	68
9	1	0	735	729	10	5	9	0	440	423	16	15	3	1	1189	1208	13	17	7	1	0	26	1	-23	1	2	173	174	143
11	1	0	474	470	11	7	9	0	442	360	19	17	3	1	597	646	20	-18	8	1	223	313	62	-21	1	2	92	50	92
13	1	0	132	153	44	9	9	0	550	588	22	19	3	1	75	47	74	-16	8	1	508	503	25	-19	1	2	0	131	1
15	1	0	253	276	23	11	9	0	294	290	45	21	3	1	65	106	65	-14	8	1	349	254	38	-17	1	2	126	112	70
17	1	0	217	194	49	13	9	0	418	278	30	-22	4	1	78	78	77	-12	8	1	381	377	33	-15	1	2	603	555	12
19	1	0	133	18	132	15	9	0	579	537	35	-20	4	1	111	178	111	-10	8	1	655	661	17	-13	1	2	404	423	12
21	1	0	244	269	79	0	10	0	512	483	24	-18	4	1	414	435	23	-8	8	1	248	214	31	-11	1	2	456	427	11
23	1	0	75	70	74	2	10	0	25	41	24	-16	4	1	761	791	13	-6	8	1	592	657	13	-9	1	2	898	939	8
0	2	0	2240	1768	24	4	10	0	208	110	40	-14	4	1	94	128	93	-4	8	1	1379	1391	14	-7	1	2	2827	2715	17
2	2	0	718	590	6	6	10	0	164	203	61	-12	4	1	297	350	21	-2	8	1	162	166	40	-5	1	2	411	363	12
4	2	0	1232	1308	8	8	10	0	230	283	49	-10	4	1	1265	1229	10	0	8	1	1119	1127	14	-3	1	2	224	121	14
6	2	0	1418	1536	10	10	10	0	155	30	100	-8	4	1	194	110	26	2	8	1	1255	1285	10	-1	1	2	1367	1662	11
8	2	0	1015	1067	9	12	10	0	160	137	101	-6	4	1	1565	1599	11	4	8	1	449	502	12	1	1	2	1031	974	8
10	2	0	1505	1580	11	1	11	0	0	23	1	-4	4	1	1699	1784	14	6	8	1	688	705	10	3	1	2	839	870	9
12	2	0	1223	1303	10	3	11	0	560	443	16	-2	4	1	70	140	70	8	8	1	822	802	19	5	1	2	987	1126	9
14	2	0	80	55	80	5	11	0	269	315	44	0	4	1	1528	1529	11	10	8	1	168	129	90	7	1	2	848	888	9
16	2	0	462	471	19	7	11	0	492	375	26	2	4	1	262	193	16	12	8	1	497	441	26	9	1	2	565	577	10
18	2	0	914	935	16	9	11	0	286	275	44	4	4	1	164	117	25	14	8	1	220	264	59	11	1	2	98	70	98
20	2	0	0	202	1	0	12	0	206	247	57	6	4	1	1323	1311	10	16	8	1	209	258	65	13	1	2	630	606	11
22	2	0	0	227	1	2	12	0	0	112	1	8	4	1	1498	1493	11	-15	9	1	202	291	68	15	1	2	702	696	16
1	3	0	291	264	17	4	12	0	139	97	138	10	4	1	139	130	55	-13	9	1	0	76	1	17	1	2	150	137	150
3	3	0	1441	1351	10	-23	1	1	259	260	76	12	4	1	758	725	12	-11	9	1	226	252	54	19	1	2	198	176	135
5	3	0	481	467	9	-21	1	1	431	451	42	14	4	1	912	968	12	-9	9	1	236	279	53	21	1	2	112	69	111
7	3	0	696	619	8	-19	1	1	1170	1223	13	16	4	1	445	410	24	-7	9	1	63	23	63	-24	2	2	21	31	21
9	3	0	1006	886	9	-17	1	1	175	171	54	18	4	1	132	191	131	-5	9	1	165	189	47	-22	2	2	232	271	52
11	3	0	1272	1216	10	-15	1	1	1164	1145	11	20	4	1	217	224	52	-3	9	1	283	252	27	-20	2	2	681	690	15
13	3	0	925	906	11	-13	1	1	817	807	10	-21	5	1	0	96	1	-1	9	1	196	109	44	-18	2	2	208	252	47
15	3	0	646	769	13	-11	1	1	364	389	14	-19	5	1	565	487	19	1	9	1	341	277	24	-16	2	2	912	876	11
17	3	0	391	353	22	-9	1	1	184	214	24	-17	5	1	483	437	23	3	9	1	186	150	47	-14	2	2	1222	1302	11
19	3	0	222	263	54	-7	1	1	1811	1784	11	-15	5	1	160	80	60	5	9	1	138	169	62	-12	2	2	493	472	12
21	3	0	0	92	1	-5	1	1	897	783	7	-13	5	1	568	567	16	7	9	1	266	289	53	-10	2	2	624	595	10
23	3	0	0	28	1	-3	1	1	2690	2874	17	-11	5	1	246	214	23	9	9	1	65	165	65	-8	2	2	2499	2391	17
0	4	0	745	839	20	-1	1	1	4074	5166	48	-9	5	1	566	530	9	11	9	1	268	342	49	-6	2	2	220	264	28
2	4	0	326	283	13	3	1	1	2094	2562	22	-7	5	1	1548	1698	11	13	9	1	171	113	89	-4	2	2	6760	6359	43
4	4	0	1190	1278	9	5	1	1	2923	2835	83	-5	5	1	1055	1125	10	15	9	1	0	80	1	-2	2	2	402	395	11
6	4	0	1823	1913	13	7	1	1	1655	1749	12	-3	5	1	802	799	10	-14	10	1	473	405	29	0	2	2	220	132	19
8	4	0	510	432	10	9	1	1	128	104	33	-1	5	1	563	565	25	-12	10	1	241	262	54	2	2	2	1289	1107	17
10	4	0	707	691	9	11	1	1	1207	1210	9	1	5	1	171	141	21	-10	10	1	557	523	22	4	2	2	2311	2444	77
12	4	0	959	943	12	13	1	1	1714	1684	12	3	5	1	227	211	19	-8	10	1	104	101	103	6	2	2	375	349	13
14	4	0	206	163	41	15	1	1	70	5	69	5	5	1	1061	1145	9	-6	10	1	432	448	16	8	2	2	1255	1385	11
16	4	0	535	558	16	17	1	1	1033	1104	14	7	5	1	330	301	14	-4	10	1	638	556	14	10	2	2	1431	1393	11
18	4	0	610	590	19	19	1	1	752	799	16	9	5	1	386	3													

Table 6. Observed and calculated structure factors for m002

h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
-18	4	2	146	124	79	-4	8	2	129	112	95	-6	2	3	84	76	83	-8	6	3	672	728	10	5	11	3	0	27	1
-16	4	2	443	445	20	-2	8	2	223	146	31	-4	2	3	117	219	53	-6	6	3	971	955	12	7	11	3	279	336	44
-14	4	2	1216	1131	13	0	8	2	278	197	22	-2	0	3	298	229	15	-4	6	3	303	322	15	-2	12	3	249	221	39
-12	4	2	105	151	104	2	8	2	515	543	11	0	2	3	1218	1089	9	-2	6	3	961	910	10	-24	0	4	565	548	24
-10	4	2	1347	1255	11	4	8	2	178	143	35	2	2	3	394	436	13	0	6	3	1082	1139	9	-22	0	4	499	454	27
-8	4	2	2191	2174	15	6	8	2	207	229	38	4	4	3	1091	1117	10	2	6	3	206	218	23	-20	0	4	536	559	21
-6	4	2	199	161	19	8	8	2	292	311	34	6	6	3	240	234	31	4	6	3	1380	1393	10	-18	0	4	1014	1017	15
-4	4	2	1650	1806	14	10	8	2	178	148	61	8	8	3	329	343	24	6	6	3	749	794	10	-16	0	4	233	229	41
-2	4	2	792	802	16	12	8	2	392	279	35	10	10	3	654	653	8	8	6	3	842	804	14	-14	0	4	778	645	19
0	4	2	192	214	22	14	8	2	0	79	1	12	12	3	690	633	15	10	6	3	1071	1067	15	-12	0	4	623	641	20
2	4	2	337	367	11	16	8	2	53	116	53	14	14	3	312	288	34	12	6	3	679	639	18	-10	0	4	908	1087	13
4	4	2	783	903	8	-15	9	2	203	106	70	16	16	3	278	256	38	14	6	3	163	176	83	-8	0	4	2517	2505	26
6	4	2	488	433	8	-13	9	2	156	294	99	18	18	3	204	208	113	16	6	3	530	507	21	-6	0	4	497	545	21
8	4	2	1635	1665	14	-11	9	2	794	698	20	20	20	3	230	241	84	18	6	3	79	183	79	-4	0	4	266	183	30
10	4	2	452	447	13	-9	9	2	88	47	87	-23	3	3	462	455	19	-19	7	3	312	309	42	-2	0	4	437	367	15
12	4	2	141	62	71	-7	9	2	750	738	13	-21	3	3	128	79	127	-17	7	3	0	1	1	0	0	4	5960	5803	50
14	4	2	949	891	16	-5	9	2	457	401	20	-19	3	3	148	82	81	-15	7	3	166	100	79	2	0	4	2230	2126	17
16	4	2	577	605	21	-3	9	2	104	96	104	-17	3	3	325	305	28	-13	7	3	112	82	112	4	0	4	2668	2663	28
18	4	2	174	220	70	-1	9	2	1435	1460	28	-15	3	3	844	883	11	-11	7	3	178	142	41	6	0	4	2971	2824	31
20	4	2	383	378	44	1	9	2	1238	1302	11	-13	3	3	553	623	12	-9	7	3	289	299	23	8	0	4	1479	1439	18
-21	5	2	224	310	60	3	9	2	538	502	15	-11	3	3	1956	2007	14	-7	7	3	200	49	42	10	0	4	1377	1373	17
-19	5	2	564	599	19	5	9	2	628	641	15	-9	3	3	2293	2245	16	-5	7	3	276	194	27	12	0	4	1179	1166	17
-17	5	2	444	412	21	7	9	2	395	386	26	-7	3	3	2047	1979	15	-3	7	3	206	218	28	14	0	4	231	187	157
-15	5	2	46	79	46	9	9	2	119	27	118	-5	3	3	2303	2229	17	-1	7	3	217	200	22	16	0	4	658	556	43
-13	5	2	674	687	13	11	9	2	577	539	22	-3	3	3	1791	1962	15	1	7	3	379	408	13	18	0	4	541	517	57
-11	5	2	385	330	16	13	9	2	365	393	36	-1	3	3	845	796	8	3	7	3	112	122	55	20	0	4	232	334	155
-9	5	2	223	213	21	-14	10	2	66	46	66	1	3	3	1647	1727	26	5	7	3	316	311	19	-25	1	4	0	53	1
-7	5	2	2022	1914	15	-12	10	2	290	272	39	3	3	3	170	102	25	7	7	3	94	80	94	-23	1	4	73	76	72
-5	5	2	2600	2596	20	-10	10	2	245	333	49	5	3	3	442	484	7	9	7	3	376	336	26	-21	1	4	182	181	50
-3	5	2	408	392	14	-8	10	2	79	19	79	7	3	3	1690	1786	36	11	7	3	285	235	38	-19	1	4	0	14	1
-1	5	2	702	729	8	-6	10	2	208	213	38	9	3	3	1086	1127	20	13	7	3	276	270	40	-17	1	4	13	39	13
1	5	2	1491	1546	10	-4	10	2	272	283	30	11	3	3	579	624	18	15	7	3	147	152	95	-15	1	4	153	119	44
3	5	2	56	21	56	-2	10	2	234	264	34	13	3	3	989	1020	15	17	7	3	152	167	101	-13	1	4	265	241	23
5	5	2	1596	1605	12	0	10	2	361	301	24	15	3	3	515	503	22	-18	8	3	449	364	30	-11	1	4	538	552	10
7	5	2	736	728	8	2	10	2	479	513	21	17	3	3	336	337	34	-16	8	3	167	216	87	-9	1	4	780	725	9
9	5	2	685	611	11	4	10	2	276	331	43	19	3	3	509	466	35	-14	8	3	349	368	29	-7	1	4	744	691	11
11	5	2	1092	1099	15	6	10	2	68	180	68	-22	4	3	111	72	110	-12	8	3	526	478	22	-5	1	4	529	509	11
13	5	2	840	884	15	8	10	2	0	161	1	-20	4	3	238	256	40	-10	8	3	81	84	81	-3	1	4	403	314	13
15	5	2	119	35	118	10	10	2	336	305	36	-18	4	3	539	565	18	-8	8	3	804	826	14	-1	1	4	1914	1852	17
17	5	2	316	348	35	12	10	2	74	134	74	-16	4	3	0	58	1	-6	8	3	604	604	15	1	1	4	4536	4440	27
19	5	2	420	452	28	-11	11	2	475	450	28	-14	4	3	1180	1235	11	-4	8	3	593	640	18	3	1	4	1286	1278	9
-20	6	2	410	397	33	-9	11	2	108	15	108	-12	4	3	166	149	40	-2	8	3	1165	1197	12	5	1	4	405	369	10
-18	6	2	427	430	31	-7	11	2	469	425	26	-10	4	3	1564	1448	12	0	8	3	1094	1127	10	7	1	4	383	344	11
-16	6	2	121	128	121	-5	11	2	480	350	16	-8	4	3	1833	1837	16	2	8	3	123	113	65	9	1	4	93	88	92
-14	6	2	368	280	28	-3	11	2	147	61	60	-6	4	3	1875	1843	13	4	8	3	1465	1486	12	11	1	4	352	295	26
-12	6	2	166	171	52	-1	11	2	108	14	108	-4	4	3	614	592	14	6	8	3	327	326	26	13	1	4	353	360	27
-10	6	2	326	326	16	1	11	2	283	281	30	-2	4	3	1004	942	11	8	8	3	595	547	18	15	1	4	345	378	55
-8	6	2	215	224	21	3	11	2	132	187	132	0	4	3	314	209	14	10	8	3	481	521	21	17	1	4	182	202	182
-6	6	2	455	449	11	5	11	2	382	359	32	2	4	3	513	480	8	12	8	3	351	375	27	19	1	4	99	70	98
-4	6	2	110	147	93	7	11	2	329	303	37	4	4	3	1500	1543	11	14	8	3	97	98	97	-24	2	4	379	384	31
-2	6	2	751	817	11	-4	12	2	319	317	26	6	4	3	1538	1601	12	-17	9	3	0	123	1	-22	2	4	427	387	24
0	6	2	564	599	9	-2	12	2	183	242	55	8	4	3	620	663	11	-15	9	3	0	64	1	-20	2	4	321	298	31
2	6	2	830	883	8	0	12	2	0	49	1	10	4	3	1449	1452	16	-13	9	3	75	112	75	-18	2	4	908	880	11
4	6	2	249	228	20	2	12	2	0	62	1	12	4	3	997	1032	15	-11	9	3	128	226	128	-16	2	4	84	107	83
6	6	2	234	181	21	-25	1	3	0	80	1	14	4	3	112	105	112	-9	9	3	153	174	60	-14	2	4	236	201	26
8	6	2	279	248	25	-23	1	3	444	515	28	16	4	3	642	624	19	-7	9	3	294	270	32	-12	2	4	1747	1764	12
10	6	2	347	345	26	-21	1	3	542	564	19	18	4	3	122	137	121												

Table 6. Observed and calculated structure factors for ww002

h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
7	3	4	92	28	92	13	7	4	144	153	103	-8	2	5	471	511	14	-6	6	5	1080	1075	14	-12	0	6	511	499	17
9	3	4	1285	1287	15	15	7	4	506	495	20	-6	2	5	741	706	9	-4	6	5	1087	1184	27	-10	0	6	79	98	78
11	3	4	1096	1041	15	-18	8	4	0	6	1	-2	2	5	567	507	8	-2	6	5	764	724	10	-8	0	6	1779	1895	17
13	3	4	328	359	34	-16	8	4	202	127	54	-4	2	5	450	364	9	0	6	5	1143	1174	10	-6	0	6	611	497	14
15	3	4	435	406	25	-14	8	4	198	240	63	0	0	2	963	989	8	2	6	5	1102	1105	11	-4	0	6	2493	2569	22
17	3	4	299	242	61	-12	8	4	0	46	1	2	2	5	2268	2290	39	4	6	5	91	128	91	-2	0	6	2201	2390	20
19	3	4	214	228	95	-10	8	4	366	329	23	4	4	2	760	832	7	6	6	5	959	974	13	0	0	6	1554	1527	15
-24	4	4	297	283	35	-8	8	4	0	41	1	6	6	2	746	730	10	8	6	5	1287	1302	14	2	0	6	4043	3896	35
-22	4	4	140	57	88	-6	8	4	162	109	66	10	2	5	221	198	27	10	6	5	322	315	33	4	0	6	1650	1543	13
-20	4	4	311	325	31	-4	8	4	178	23	43	12	2	5	718	698	15	12	6	5	441	394	25	6	0	6	519	491	11
-18	4	4	0	101	1	-2	8	4	179	104	46	14	2	5	224	185	49	14	6	5	466	456	24	8	0	6	1204	1166	17
-16	4	4	573	555	14	0	8	4	0	75	1	14	2	5	470	467	23	16	6	5	0	17	1	10	0	6	839	800	16
-14	4	4	167	196	46	2	8	4	155	5	56	16	2	5	353	319	56	-21	7	5	67	130	67	12	0	6	319	262	117
-12	4	4	1454	1374	12	4	8	4	272	165	30	18	2	5	129	135	128	-19	7	5	171	67	74	14	0	6	988	950	39
-10	4	4	979	913	11	6	8	4	98	16	97	-23	3	5	101	38	101	-17	7	5	243	175	48	16	0	6	932	747	40
-8	4	4	1060	1050	10	8	8	4	177	76	56	-21	3	5	186	153	63	-15	7	5	120	209	120	18	0	6	214	138	214
-6	4	4	2881	2908	21	10	8	4	275	235	38	-19	3	5	157	74	83	-13	7	5	193	159	51	-25	1	6	21	130	21
-4	4	4	722	724	10	12	8	4	115	58	115	-17	3	5	436	471	18	-11	7	5	335	293	24	-23	1	6	0	69	1
-2	4	4	567	604	9	14	8	4	53	155	53	-15	3	5	324	330	21	-9	7	5	238	171	35	-21	1	6	0	6	1
0	4	4	528	667	10	-17	9	4	0	123	1	-13	3	5	1929	1860	13	-7	7	5	186	209	46	-19	1	6	0	53	1
2	4	4	557	603	8	-15	9	4	452	467	30	-11	3	5	337	395	18	-5	7	5	269	330	26	-17	1	6	447	409	18
4	4	4	823	851	10	-13	9	4	355	279	28	-9	3	5	1541	1439	12	-3	7	5	97	123	97	-15	1	6	210	220	32
6	4	4	939	925	11	-11	9	4	185	277	63	-7	3	5	1520	1486	13	-1	7	5	272	227	26	-13	1	6	171	143	36
8	4	4	90	141	89	-9	9	4	505	467	16	-5	3	5	1270	1222	10	1	7	5	201	18	32	-11	1	6	745	718	12
10	4	4	801	834	25	-7	9	4	429	350	23	-3	3	5	851	800	8	3	7	5	271	191	24	-9	1	6	458	393	15
12	4	4	1074	1133	33	-5	9	4	152	173	64	-1	3	5	879	913	9	5	7	5	156	123	63	-7	1	6	343	369	14
14	4	4	0	179	1	-3	9	4	1066	1169	14	-1	3	5	209	244	24	7	7	5	322	268	27	-5	1	6	616	580	9
16	4	4	449	442	28	-1	9	4	699	710	13	5	3	5	455	540	11	9	7	5	253	277	36	-3	1	6	891	1004	13
18	4	4	209	235	89	-1	9	4	675	753	13	5	3	5	1761	1866	13	11	7	5	213	182	50	-1	1	6	1143	1046	9
-23	5	4	118	164	117	3	9	4	1037	926	15	7	3	5	266	286	18	13	7	5	43	43	43	1	1	6	340	299	11
-21	5	4	369	379	29	5	9	4	97	78	96	9	3	5	1391	1366	16	15	7	5	21	34	21	3	1	6	1170	1075	8
-19	5	4	118	53	118	7	9	4	472	444	22	11	3	5	798	775	15	-18	8	5	180	242	66	5	1	6	601	650	8
-17	5	4	502	524	22	9	9	4	371	416	33	13	3	5	141	39	140	-16	8	5	455	394	24	7	1	6	507	515	10
-15	5	4	945	947	11	11	9	4	170	179	69	15	3	5	775	772	17	-14	8	5	229	100	49	9	1	6	119	145	57
-13	5	4	228	254	30	-14	10	4	341	341	41	17	3	5	358	308	50	-12	8	5	406	431	23	11	1	6	148	57	88
-11	5	4	931	1039	10	-12	10	4	77	48	76	19	3	5	0	66	1	-10	8	5	744	717	13	13	1	6	352	410	53
-9	5	4	1459	1502	11	-10	10	4	195	181	54	-24	4	5	268	258	40	-8	8	5	264	229	30	15	1	6	145	46	145
-7	5	4	730	634	11	-8	10	4	299	312	30	-22	4	5	125	20	124	-6	8	5	577	597	16	17	1	6	149	112	148
-5	5	4	1116	1103	13	-6	10	4	327	378	29	-20	4	5	237	166	46	-4	8	5	933	966	12	-24	2	6	66	14	66
-3	5	4	1567	1741	20	-4	10	4	86	107	86	-18	4	5	101	152	101	-2	8	5	412	341	20	-22	2	6	140	135	76
-1	5	4	657	669	9	-2	10	4	100	113	100	-16	4	5	531	509	16	0	8	5	1082	1073	13	-20	2	6	499	506	18
3	5	4	387	368	10	0	10	4	148	234	65	-14	4	5	751	669	12	2	8	5	1382	1342	14	-18	2	6	376	376	21
5	5	4	879	737	8	2	10	4	54	6	54	-12	4	5	611	649	12	4	8	5	220	95	46	-16	2	6	1074	1072	10
7	5	4	482	548	8	4	10	4	80	72	80	-10	4	5	1530	1548	13	6	8	5	862	860	13	-14	2	6	1433	1453	11
9	5	4	1184	1181	14	6	10	4	199	216	60	-8	4	5	917	973	10	8	8	5	699	662	15	-12	2	6	340	214	19
11	5	4	1049	1096	15	8	10	4	299	240	40	-6	4	5	1032	932	10	10	8	5	167	140	56	-10	2	6	1963	1862	16
13	5	4	567	570	21	10	10	4	141	81	141	-4	4	5	1206	1234	16	12	8	5	380	368	22	-8	2	6	1710	1804	14
15	5	4	0	31	1	-11	11	4	173	189	90	-2	4	5	834	812	10	-17	9	5	200	163	75	-6	2	6	191	176	24
17	5	4	786	714	17	-9	11	4	529	451	19	0	4	5	835	980	9	-15	9	5	131	218	130	-4	2	6	1401	1467	10
19	5	4	167	167	75	-7	11	4	480	382	20	2	4	5	463	525	11	-13	9	5	0	29	1	-2	2	6	746	782	7
-22	6	4	342	307	39	-5	11	4	199	223	47	4	4	5	638	735	9	-11	9	5	326	320	26	0	2	6	721	709	8
-20	6	4	460	451	24	-3	11	4	285	341	31	6	4	5	641	532	15	-9	9	5	288	340	30	2	2	6	1849	1756	12
-18	6	4	273	236	41	-1	11	4	0	23	1	8	4	5	1112	1031	15	-7	9	5	0	90	1	4	2	6	2126	2213	13
-16	6	4	470	466	25	1	11	4	98	65	97	10	4	5	396	395	28	-5	9	5	115	65	114	6	2	6	429	437	10
-14	6	4	150	145	98	3	11	4	473	378	24	12	4	5	601	558	19	-3	9	5	290	276	30	8	2	6	1193	1282	12
-12	6	4	339	325	24	5	11	4	222	167	55	14	4	5	453	518	26	-1	9	5	114	180	113	10	2	6	1020	892	15
-10	6	4	585	567	13	-25	1	5	236	242	52	16	4	5	157	153	86	1	9	5	280	257	30						

Table 6. Observed and calculated structure factors for w002

h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
-14	4	6	1042	934	12	10	8	6	100	67	99	-3	3	7	918	981	8	-18	8	7	431	343	27	-16	2	8	424	456	18
-12	4	6	145	79	56	12	8	6	171	168	54	-1	3	7	315	329	13	-16	8	7	257	318	43	-14	2	8	513	446	14
-10	4	6	1152	1084	12	-17	9	6	435	328	26	1	3	7	1550	1563	11	-14	8	7	432	461	25	-12	2	8	1800	1859	16
-8	4	6	1291	1398	10	-15	9	6	0	97	1	3	3	7	1096	1040	14	-12	8	7	514	455	23	-10	2	8	302	278	24
-6	4	6	273	243	14	-13	9	6	370	397	29	5	3	7	435	420	13	-10	8	7	43	48	43	-8	2	8	871	899	9
-4	4	6	1150	1217	10	-11	9	6	494	419	17	7	3	7	1343	1446	13	-8	8	7	487	540	18	-6	2	8	935	921	9
-2	4	6	1123	1254	10	-9	9	6	191	158	47	9	3	7	476	494	17	-6	8	7	451	303	20	-4	2	8	854	877	10
0	4	6	515	479	11	-7	9	6	311	335	29	11	3	7	854	829	16	-4	8	7	248	278	32	-2	2	8	1320	1272	10
2	4	6	1002	1010	9	-5	9	6	552	541	16	13	3	7	653	611	18	-2	8	7	897	895	13	0	2	8	2284	2304	13
4	4	6	616	682	10	-3	9	6	264	186	33	15	3	7	164	116	163	0	8	7	558	603	15	2	2	8	1795	1850	11
6	4	6	55	42	54	-1	9	6	872	791	13	-24	4	7	0	114	1	2	8	7	522	563	20	4	2	8	862	945	8
8	4	6	1005	1036	12	1	9	6	511	430	22	-22	4	7	118	138	117	4	8	7	1250	1265	16	6	2	8	1666	1593	13
10	4	6	437	394	25	3	9	6	642	635	17	-20	4	7	451	400	28	6	8	7	609	544	17	8	2	8	361	360	22
12	4	6	125	119	125	5	9	6	627	634	17	-18	4	7	268	312	40	8	8	7	182	98	52	10	2	8	790	778	14
14	4	6	595	583	19	7	9	6	490	485	20	-16	4	7	419	476	17	10	8	7	473	480	19	12	2	8	799	750	17
16	4	6	190	206	122	9	9	6	0	4	1	-14	4	7	954	986	11	-17	9	7	59	50	59	14	2	8	89	9	89
-23	5	6	384	432	31	-14	10	6	191	106	59	-12	4	7	577	579	12	-15	9	7	211	195	54	16	2	8	412	377	45
-21	5	6	0	47	1	-12	10	6	194	176	69	-10	4	7	810	715	10	-13	9	7	278	259	36	-25	3	8	0	46	1
-19	5	6	479	430	27	-10	10	6	371	418	22	-8	4	7	1087	1142	11	-11	9	7	176	185	54	-23	3	8	101	130	101
-17	5	6	143	138	95	-8	10	6	310	349	30	-6	4	7	880	827	8	-9	9	7	102	122	101	-21	3	8	245	340	34
-15	5	6	393	431	24	-6	10	6	106	59	105	-4	4	7	732	771	8	-7	9	7	138	84	77	-19	3	8	120	82	120
-13	5	6	1036	1134	15	-4	10	6	86	78	86	-2	4	7	1769	1789	13	-5	9	7	41	148	40	-17	3	8	485	477	17
-11	5	6	592	621	16	-2	10	6	162	110	60	0	4	7	401	439	15	-3	9	7	188	222	51	-15	3	8	372	364	20
-9	5	6	101	43	100	0	10	6	480	557	21	2	4	7	198	143	30	-1	9	7	575	564	15	-13	3	8	98	107	98
-7	5	6	1578	1593	12	2	10	6	225	263	47	4	4	7	518	518	12	1	9	7	404	370	25	-11	3	8	692	707	18
-5	5	6	1206	1277	16	4	10	6	102	151	102	6	4	7	865	908	12	3	9	7	174	129	59	-9	3	8	1332	1363	10
-3	5	6	743	717	9	6	10	6	70	48	70	8	4	7	542	570	19	5	9	7	0	62	1	-7	3	8	869	905	10
-1	5	6	642	630	10	-9	11	6	321	219	26	10	4	7	894	905	13	7	9	7	0	4	1	-5	3	8	468	468	12
1	5	6	1085	1139	9	-7	11	6	233	284	39	12	4	7	702	671	18	-12	10	7	390	307	22	-3	3	8	967	995	9
3	5	6	47	30	47	-5	11	6	483	423	25	14	4	7	251	250	42	-10	10	7	75	63	74	-1	3	8	123	121	43
5	5	6	1287	1332	13	-3	11	6	54	158	54	16	4	7	485	462	37	-8	10	7	244	304	31	1	3	8	576	651	9
7	5	6	803	721	13	-1	11	6	543	478	19	-23	5	7	82	62	82	-6	10	7	463	380	21	3	3	8	806	728	10
9	5	6	0	12	1	1	11	6	413	397	29	-21	5	7	417	398	29	-4	10	7	83	132	83	5	3	8	230	207	29
11	5	6	635	578	18	-25	1	7	0	11	1	-19	5	7	272	207	49	-2	10	7	856	717	13	7	3	8	407	354	20
13	5	6	566	604	19	-23	1	7	494	497	17	-17	5	7	354	305	30	0	10	7	403	430	25	9	3	8	999	1004	14
15	5	6	186	153	61	-21	1	7	306	339	29	-15	5	7	292	271	38	2	10	7	147	91	77	11	3	8	362	355	24
-22	6	6	0	94	1	-19	1	7	271	273	31	-13	5	7	46	46	46	4	10	7	270	296	36	13	3	8	186	213	57
-20	6	6	603	538	20	-17	1	7	958	933	11	-11	5	7	656	639	16	-7	11	7	218	298	44	15	3	8	297	191	55
-18	6	6	416	397	31	-15	1	7	1125	1141	10	-9	5	7	1263	1205	13	-5	11	7	254	268	39	-24	4	8	251	231	47
-16	6	6	266	276	37	-13	1	7	649	587	12	-7	5	7	430	397	16	-3	11	7	196	87	48	-22	4	8	312	309	38
-14	6	6	418	348	23	-11	1	7	1111	1062	12	-5	5	7	740	833	9	-1	11	7	112	35	111	-20	4	8	89	97	89
-12	6	6	183	126	62	-9	1	7	1105	1103	9	-3	5	7	668	721	10	-24	0	8	194	250	70	-18	4	8	148	43	84
-10	6	6	746	760	15	-7	1	7	68	94	67	-1	5	7	304	284	20	-22	0	8	425	364	34	-16	4	8	219	242	48
-8	6	6	520	429	15	-5	1	7	2030	2095	13	1	5	7	741	760	10	-20	0	8	758	716	17	-14	4	8	489	412	20
-6	6	6	613	585	11	-3	1	7	811	823	9	3	5	7	250	227	24	-18	0	8	1143	1024	17	-12	4	8	1021	1022	12
-4	6	6	412	336	18	-1	1	7	815	833	8	5	5	7	194	171	43	-16	0	8	387	408	26	-10	4	8	516	459	14
-2	6	6	425	469	13	1	1	7	3535	3583	20	7	5	7	564	592	15	-14	0	8	434	375	30	-8	4	8	173	157	33
0	6	6	135	121	45	3	1	7	1687	1666	12	9	5	7	297	344	29	-12	0	8	913	1003	19	-6	4	8	1145	1095	11
2	6	6	320	328	20	5	1	7	1250	1208	9	11	5	7	183	196	50	-10	0	8	321	232	29	-4	4	8	315	328	15
4	6	6	252	303	30	7	1	7	981	1046	9	13	5	7	343	342	30	-8	0	8	283	281	28	-2	4	8	1173	1127	9
6	6	6	203	198	43	9	1	7	847	767	11	15	5	7	35	73	35	-6	0	8	961	935	13	0	4	8	1138	1248	10
8	6	6	646	729	15	11	1	7	587	581	32	-22	6	7	0	71	1	-4	0	8	1685	1842	16	2	4	8	497	433	12
10	6	6	396	381	23	13	1	7	856	780	28	-20	6	7	442	465	27	-2	0	8	1321	1275	46	4	4	8	467	485	14
12	6	6	164	86	74	15	1	7	206	278	139	-18	6	7	0	118	1	0	0	8	1802	1905	17	6	4	8	701	712	19
14	6	6	160	97	78	17	1	7	0	195	1	-16	6	7	255	300	41	2	0	8	344	314	22	8	4	8	81	109	81
-21	7	6	0	77	1	-24	2	7	0	79	1	-14	6	7	869	953	16	4	0	8	996	1016	13	10	4	8	580	595	16
-19	7	6	520	589	23	-22	2	7	0	39	1	-12	6	7	715	716	17	6	0	8	1571	1621	14	12	4				

Table 6. Observed and calculated structure factors for m002

h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
-2	6	8	164	203	51	-8	2	9	304	286	20	-15	7	9	305	320	37	-16	2	10	862	929	13	-11	7	10	557	449	18
0	6	8	369	421	18	-6	2	9	759	694	9	-13	7	9	0	38	1	-14	2	10	815	771	14	-9	7	10	589	605	15
2	6	8	111	12	111	-4	2	9	0	36	1	-11	7	9	216	154	55	-12	2	10	71	37	70	-7	7	10	658	653	14
4	6	8	382	383	23	-2	2	9	155	123	39	-9	7	9	168	41	57	-10	2	10	1030	883	10	-5	7	10	535	611	15
6	6	8	381	354	24	0	2	9	277	266	18	-7	7	9	284	378	28	-8	2	10	1096	1174	10	-3	7	10	164	91	52
8	6	8	65	18	65	2	2	9	812	861	8	-5	7	9	465	435	18	-6	2	10	467	427	13	-1	7	10	900	949	13
10	6	8	337	303	26	4	2	9	560	596	11	-3	7	9	193	45	50	-4	2	10	1558	1580	13	1	7	10	920	905	16
12	6	8	217	261	39	6	2	9	726	645	13	-1	7	9	220	189	39	-2	2	10	1245	1290	10	3	7	10	0	40	1
-19	7	8	438	365	28	8	2	9	590	522	13	-1	7	9	242	187	45	0	2	10	188	222	30	5	7	10	846	846	17
-17	7	8	376	459	26	10	2	9	127	165	106	3	7	9	457	488	23	2	2	10	1338	1419	11	7	7	10	517	520	18
-15	7	8	888	915	16	12	2	9	209	206	53	5	7	9	0	15	1	4	2	10	1141	1216	11	-16	8	10	142	246	113
-13	7	8	451	467	26	14	2	9	255	267	67	7	7	9	239	179	33	6	2	10	350	331	21	-14	8	10	247	146	43
-11	7	8	171	282	76	-23	3	9	253	185	40	9	7	9	0	59	1	8	2	10	653	643	13	-12	8	10	143	133	109
-9	7	8	700	708	13	-21	3	9	56	111	55	-18	8	9	254	343	46	10	2	10	489	464	15	-10	8	10	108	60	108
-7	7	8	192	151	36	-19	3	9	559	529	16	-16	8	9	573	578	19	12	2	10	147	182	147	-8	8	10	126	106	91
-5	7	8	494	478	15	-17	3	9	127	179	103	-14	8	9	410	331	27	-23	3	10	0	107	1	-6	8	10	336	341	24
-3	7	8	1043	1064	13	-15	3	9	627	594	14	-12	8	9	125	271	125	-21	3	10	0	8	1	-4	8	10	139	124	66
-1	7	8	465	447	18	-13	3	9	1208	1189	13	-10	8	9	407	331	23	-19	3	10	514	525	20	-2	8	10	116	61	115
1	7	8	698	719	13	-11	3	9	508	538	15	-8	8	9	0	44	1	-17	3	10	451	484	20	0	8	10	222	190	45
3	7	8	1064	1078	17	-9	3	9	1071	1125	10	-6	8	9	639	579	14	-15	3	10	332	292	24	2	8	10	140	193	90
5	7	8	544	622	26	-7	3	9	1090	1121	10	-4	8	9	677	677	15	-13	3	10	636	657	20	4	8	10	73	164	72
7	7	8	427	414	24	-5	3	9	132	137	47	-2	8	9	99	10	99	-11	3	10	449	472	18	6	8	10	111	79	110
9	7	8	526	613	18	-3	3	9	1611	1619	10	0	8	9	622	682	17	-9	3	10	679	668	11	-13	9	10	156	197	88
11	7	8	53	24	53	-1	3	9	1493	1498	11	2	8	9	826	862	17	-7	3	10	933	879	10	-11	9	10	457	404	24
-18	8	8	99	87	98	1	3	9	473	502	12	4	8	9	121	75	120	-5	3	10	811	831	10	-9	9	10	0	45	1
-16	8	8	244	178	57	3	3	9	99	160	83	6	8	9	551	557	21	-3	3	10	257	137	23	-7	9	10	533	540	15
-14	8	8	259	228	41	5	3	9	1105	1151	13	8	8	9	354	385	27	-1	3	10	602	578	10	-5	9	10	494	455	15
-12	8	8	88	137	87	7	3	9	0	35	1	-15	9	9	73	150	72	1	3	10	637	601	11	-3	9	10	111	67	110
-10	8	8	293	195	31	9	3	9	718	737	14	-13	9	9	0	72	1	3	3	10	0	56	1	-1	9	10	491	474	21
-8	8	8	95	12	94	11	3	9	310	348	27	-11	9	9	102	14	102	5	3	10	783	787	12	1	9	10	329	408	30
-6	8	8	88	82	88	13	3	9	164	103	75	-9	9	9	0	191	1	7	3	10	397	349	19	3	9	10	124	9	123
-4	8	8	210	294	43	-24	4	9	190	256	69	-7	9	9	0	110	1	9	3	10	96	189	96	-8	10	10	0	11	1
-2	8	8	360	337	25	-22	4	9	208	231	51	-5	9	9	189	254	35	11	3	10	521	521	21	-6	10	10	198	208	40
0	8	8	114	138	113	-20	4	9	82	46	82	-3	9	9	213	223	38	-22	4	10	253	265	37	-4	10	10	160	190	49
2	8	8	300	321	33	-18	4	9	123	171	123	-1	9	9	128	125	128	-20	4	10	254	237	40	-23	1	11	498	490	17
4	8	8	350	334	27	-16	4	9	408	414	26	1	9	9	204	155	51	-18	4	10	366	346	31	-21	1	11	251	256	33
6	8	8	58	64	57	-14	4	9	78	36	77	3	9	9	201	165	51	-16	4	10	101	49	101	-19	1	11	346	323	28
8	8	8	109	111	109	-12	4	9	490	581	18	5	9	9	0	17	1	-14	4	10	583	495	27	-17	1	11	755	792	17
-15	9	8	513	510	28	-10	4	9	990	1026	11	-10	10	9	379	388	24	-12	4	10	129	117	128	-15	1	11	897	856	15
-13	9	8	340	277	30	-8	4	9	228	223	25	-8	10	9	363	265	23	-10	4	10	710	672	14	-13	1	11	417	356	23
-11	9	8	112	50	112	-6	4	9	1569	1514	12	-6	10	9	419	443	20	-8	4	10	1050	1068	11	-11	1	11	575	606	13
-9	9	8	360	373	24	-4	4	9	1266	1231	9	-4	10	9	535	496	16	-6	4	10	330	275	19	-9	1	11	335	355	21
-7	9	8	450	316	17	-2	4	9	110	173	57	-2	10	9	117	21	117	-4	4	10	1056	1091	10	-7	1	11	358	266	19
-5	9	8	487	519	20	0	4	9	608	575	11	0	10	9	308	321	35	-2	4	10	610	570	11	-5	1	11	1541	1563	11
-3	9	8	828	769	13	2	4	9	1017	1049	11	-24	0	10	220	220	57	0	4	10	77	98	76	-3	1	11	1026	1068	10
-1	9	8	160	132	78	4	4	9	313	276	29	-22	0	10	350	352	33	2	4	10	569	562	13	-1	1	11	499	481	12
1	9	8	487	520	20	6	4	9	559	521	16	-20	0	10	571	567	22	4	4	10	352	454	19	1	1	11	1713	1755	12
3	9	8	618	630	17	8	4	9	690	643	15	-18	0	10	176	101	77	6	4	10	331	333	27	3	1	11	477	495	16
5	9	8	288	312	33	10	4	9	0	21	1	-16	0	10	1523	1515	22	8	4	10	460	560	17	5	1	11	497	443	15
7	9	8	185	237	57	12	4	9	462	441	18	-14	0	10	857	776	21	10	4	10	277	299	29	7	1	11	819	776	17
-12	10	8	129	170	104	-23	5	9	316	244	40	-12	0	10	222	222	50	12	4	10	106	67	106	9	1	11	687	635	25
-10	10	8	122	134	122	-21	5	9	284	263	42	-10	0	10	115	185	115	-21	5	10	104	176	104	11	1	11	556	540	30
-8	10	8	51	77	50	-19	5	9	365	329	29	-19	5	10	1550	1652	16	-19	5	10	276	317	42	-24	2	11	0	29	1
-6	10	8	145	189	75	-17	5	9	34	69	33	-6	0	10	434	361	19	-17	5	10	113	167	112	-22	2	11	141	204	98
-4	10	8	124	132	123	-15	5	9	302	301	34	-4	0	10	1876	1936	18	-15	5	10	147	124	71	-20	2	11	218	283	40
-2	10	8	343	408	30	-13	5	9	639	538	15	-2	0	10	1490	1533	16	-13	5	10	551	583	18	-18	2	11	260	272	35
0	10	8	269	307	36	-11	5	9	315	308	27	0	0																

Table 6. Observed and calculated structure factors for w002

h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
11	3	11	328	356	49	-6	0	12	1126	1147	15	-1	5	12	91	136	91	-16	4	13	58	178	57	-4	2	14	897	864	13
-22	4	11	72	128	71	-4	0	12	616	730	17	1	5	12	309	322	24	-14	4	13	163	140	71	-2	2	14	619	611	14
-20	4	11	0	83	1	-2	0	12	1003	1070	15	3	5	12	521	512	16	-12	4	13	640	672	15	0	2	14	43	111	43
-18	4	11	195	139	60	0	0	12	1207	1210	15	5	5	12	229	234	29	-10	4	13	618	651	15	2	2	14	938	1001	14
-16	4	11	331	347	34	2	0	12	312	326	46	7	5	12	429	419	18	-8	4	13	153	185	58	4	2	14	937	946	16
-14	4	11	460	470	22	4	0	12	103	50	102	-20	6	12	84	17	84	-6	4	13	720	765	16	-21	3	14	0	45	1
-12	4	11	260	257	35	6	0	12	949	972	32	-18	6	12	405	231	29	-4	4	13	667	650	16	-19	3	14	202	200	57
-10	4	11	569	526	16	8	0	12	474	436	50	-16	6	12	0	33	1	-2	4	13	101	136	101	-17	3	14	89	31	88
-8	4	11	1022	1035	12	10	0	12	698	664	36	-14	6	12	218	164	57	0	4	13	476	488	16	-15	3	14	490	469	19
-6	4	11	299	314	22	-23	1	12	0	6	1	-12	6	12	318	336	33	2	4	13	352	351	20	-13	3	14	406	415	23
-4	4	11	432	368	17	-21	1	12	62	66	62	-10	6	12	436	374	25	4	4	13	82	35	81	-11	3	14	244	324	39
-2	4	11	863	906	11	-19	1	12	104	29	104	-8	6	12	0	7	1	-9	4	13	687	617	13	-9	3	14	206	184	47
0	4	11	424	402	18	-17	1	12	0	22	1	-6	6	12	379	381	23	-19	5	13	155	15	78	-7	3	14	583	572	16
2	4	11	145	75	60	-15	1	12	0	32	1	-4	6	12	564	508	16	-17	5	13	0	46	1	-5	3	14	509	560	17
4	4	11	508	537	25	-13	1	12	103	39	103	-2	6	12	162	124	55	-15	5	13	141	111	90	-3	3	14	0	18	1
6	4	11	240	226	30	-11	1	12	147	121	63	0	6	12	320	283	27	-13	5	13	422	414	22	-1	3	14	490	515	17
8	4	11	376	480	19	-9	1	12	353	343	23	2	6	12	145	129	65	-11	5	13	329	299	27	1	3	14	256	236	31
10	4	11	519	466	17	-7	1	12	364	309	21	4	6	12	227	285	35	-9	5	13	188	239	56	3	3	14	309	345	27
-21	5	11	447	370	22	-5	1	12	201	186	35	6	6	12	291	310	29	-7	5	13	826	791	15	5	3	14	571	594	19
-19	5	11	178	55	63	-3	1	12	328	305	20	-17	7	12	207	397	55	-5	5	13	334	279	30	-20	4	14	57	102	57
-17	5	11	246	138	42	-1	1	12	430	459	16	-15	7	12	756	681	18	-3	5	13	262	288	36	-18	4	14	245	220	40
-15	5	11	411	372	25	1	1	12	131	153	79	-13	7	12	0	53	1	-1	5	13	327	329	26	-16	4	14	110	153	109
-13	5	11	173	228	71	3	1	12	31	13	31	-11	7	12	518	523	21	1	5	13	0	69	1	-14	4	14	625	598	15
-11	5	11	635	655	14	5	1	12	321	309	36	-9	7	12	526	549	18	3	5	13	301	297	24	-12	4	14	106	50	105
-9	5	11	727	668	13	7	1	12	0	68	1	-7	7	12	315	325	26	5	5	13	215	281	33	-10	4	14	518	535	18
-7	5	11	232	232	37	9	1	12	155	75	155	-5	7	12	433	385	19	-18	6	13	169	218	87	-8	4	14	767	691	15
-5	5	11	790	808	13	-24	2	12	331	357	29	-3	7	12	607	677	15	-16	6	13	202	136	49	-6	4	14	137	128	137
-3	5	11	666	631	13	-22	2	12	342	287	28	-1	7	12	154	210	63	-14	6	13	125	156	125	-4	4	14	589	572	20
-1	5	11	198	183	36	-20	2	12	309	343	37	1	7	12	388	451	23	-12	6	13	705	741	14	-2	4	14	349	339	27
1	5	11	475	498	17	-18	2	12	572	546	21	3	7	12	844	807	14	-10	6	13	536	542	19	0	4	14	162	134	57
3	5	11	59	40	58	-16	2	12	192	199	73	-14	8	12	85	209	85	-8	6	13	85	41	85	2	4	14	404	391	24
5	5	11	250	307	31	-14	2	12	312	260	33	-12	8	12	54	22	54	-6	6	13	390	472	24	4	4	14	450	410	18
7	5	11	509	512	17	-12	2	12	972	1023	11	-10	8	12	244	266	34	-4	6	13	695	730	13	-19	5	14	294	277	34
9	5	11	391	365	22	-10	2	12	166	181	50	-8	8	12	98	140	97	-2	6	13	133	15	91	-17	5	14	249	229	40
-20	6	11	301	400	38	-8	2	12	1038	1026	11	-6	8	12	33	3	32	0	6	13	566	566	16	-15	5	14	0	88	1
-18	6	11	449	441	27	-6	2	12	1139	1129	13	-4	8	12	0	14	1	2	6	13	530	523	17	-13	5	14	492	505	18
-16	6	11	0	135	1	-4	2	12	551	602	13	-2	8	12	113	114	113	-15	7	13	183	103	71	-11	5	14	515	542	20
-14	6	11	701	637	19	-2	2	12	689	723	13	0	8	12	86	43	85	-13	7	13	279	218	34	-9	5	14	251	251	37
-12	6	11	186	175	63	0	2	12	1108	1194	15	-23	1	13	153	73	61	-11	7	13	289	224	35	-7	5	14	757	824	18
-10	6	11	578	563	18	2	2	12	316	288	25	-21	1	13	277	327	33	-9	7	13	142	161	90	-5	5	14	268	300	36
-8	6	11	869	934	16	4	2	12	786	820	14	-19	1	13	733	663	17	-7	7	13	116	126	116	-3	5	14	126	152	126
-6	6	11	520	532	16	6	2	12	812	829	12	-17	1	13	56	97	56	-5	7	13	201	176	40	-1	5	14	304	377	38
-4	6	11	471	474	18	8	2	12	291	273	51	-15	1	13	673	613	18	-3	7	13	0	8	1	1	5	14	444	374	20
-2	6	11	852	975	12	10	2	12	606	585	27	-13	1	13	728	706	14	-1	7	13	0	65	1	-16	6	14	190	196	56
0	6	11	655	622	16	-23	3	12	185	205	56	-11	1	13	319	313	26	1	7	13	0	3	1	-14	6	14	310	185	29
2	6	11	188	179	40	-21	3	12	137	205	98	-9	1	13	840	807	11	-10	8	13	444	432	22	-12	6	14	128	171	127
4	6	11	704	695	16	-19	3	12	0	10	1	-7	1	13	1236	1244	11	-8	8	13	164	56	61	-10	6	14	105	64	104
6	6	11	525	528	15	-17	3	12	305	284	37	-5	1	13	61	38	60	-6	8	13	188	238	43	-8	6	14	341	302	29
8	6	11	242	269	36	-15	3	12	357	464	34	-3	1	13	907	907	10	-4	8	13	522	455	18	-6	6	14	91	81	91
-19	7	11	268	228	44	-13	3	12	0	44	1	-1	1	13	530	612	16	-22	0	14	176	198	81	-4	6	14	343	326	29
-17	7	11	0	26	1	-11	3	12	538	525	17	1	1	13	185	150	48	-20	0	14	282	285	57	-2	6	14	167	226	58
-15	7	11	386	237	29	-9	3	12	569	570	13	3	1	13	757	752	14	-18	0	14	0	15	1	0	6	14	0	9	1
-13	7	11	0	240	1	-7	3	12	292	272	25	5	1	13	939	944	16	-16	0	14	651	652	27	-13	7	14	277	344	38
-11	7	11	189	132	60	-5	3	12	608	649	12	7	1	13	142	21	141	-14	0	14	651	555	20	-11	7	14	474	450	24
-9	7	11	261	291	35	-3	3	12	1034	989	12	-22	2	13	0	92	1	-12	0	14	243	251	53	-9	7	14	147	176	87
-7	7	11	282	237	29	-1	3	12	314	320	25	-20	2	13	150	95	93	-10	0	14	935	892	17	-7	7	14	487	481	20
-5	7	11	19																										

Table 6. Observed and calculated structure factors for wu002

h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
-11	3	15	775	741	14	-11	5	15	420	380	25	-2	0	16	650	672	23	-4	2	16	0	120	1	-11	5	16	374	419	29
-9	3	15	304	289	35	-9	5	15	388	327	26	0	0	16	1130	1042	20	-2	2	16	491	484	19	-9	5	16	507	505	22
-7	3	15	215	217	45	-7	5	15	95	92	95	-19	1	16	0	8	1	0	2	16	888	866	17	-7	5	16	73	77	72
-5	3	15	481	474	18	-5	5	15	441	416	23	-17	1	16	0	183	1	-17	3	16	214	266	50	-15	1	17	575	579	17
-3	3	15	511	457	16	-3	5	15	287	296	37	-15	1	16	175	217	53	-15	3	16	83	187	83	-13	1	17	682	622	13
-1	3	15	442	378	20	-1	5	15	59	74	58	-13	1	16	98	94	97	-13	3	16	179	137	54	-11	1	17	112	87	112
1	3	15	677	699	15	-12	6	15	258	202	39	-11	1	16	0	31	1	-11	3	16	257	285	42	-9	1	17	303	275	29
-18	4	15	0	181	1	-10	6	15	280	304	37	-9	1	16	164	168	52	-9	3	16	218	217	45	-7	1	17	509	495	18
-16	4	15	0	77	1	-8	6	15	540	566	20	-7	1	16	208	201	42	-7	3	16	192	173	56	-5	1	17	0	36	1
-14	4	15	211	244	42	-6	6	15	192	179	56	-5	1	16	0	64	1	-5	3	16	263	274	38	-14	2	17	234	200	41
-12	4	15	120	116	120	-4	6	15	387	414	29	-3	1	16	181	178	52	-3	3	16	517	496	16	-12	2	17	165	222	57
-10	4	15	253	255	42	-18	0	16	576	631	30	-1	1	16	64	42	64	-1	3	16	56	61	56	-10	2	17	152	163	85
-8	4	15	732	739	16	-16	0	16	277	260	46	-18	2	16	333	360	37	-16	4	16	328	336	28	-8	2	17	0	57	1
-6	4	15	350	356	27	-14	0	16	476	359	26	-16	2	16	105	89	105	-14	4	16	164	116	59	-6	2	17	286	246	31
-4	4	15	427	394	22	-12	0	16	804	816	18	-14	2	16	437	428	22	-12	4	16	456	416	25	-13	3	17	332	295	33
-2	4	15	350	396	31	-10	0	16	562	553	20	-12	2	16	633	637	15	-10	4	16	215	208	50	-11	3	17	0	25	1
0	4	15	195	135	57	-8	0	16	492	463	21	-10	2	16	200	174	44	-8	4	16	254	254	41	-9	3	17	241	262	41
-15	5	15	276	215	32	-6	0	16	547	523	20	-8	2	16	427	367	20	-6	4	16	505	486	22	-7	3	17	427	399	21
-13	5	15	30	26	29	-4	0	16	0	58	1	-6	2	16	403	373	22	-4	4	16	361	289	28						