Synthesis, Characterization and Application of Ruthenium-Containing Polymers

Xianguo Wu, M.Sc.

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

August 2008

© Copyright

Library and
Archives Canada

Published Heritage
Branch

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque et
Archives Canada

Direction du
Patrimoine de l'édition

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence

ISBN: 978-0-494-43915-9

Our file Notre référence

ISBN: 978-0-494-43915-9

NOTICE:

The author has granted a non-exclusive license allowing Library and Archives Canada to reproduce, publish, archive, preserve, conserve, communicate to the public by telecommunication or on the Internet, loan, distribute and sell theses worldwide, for commercial or non-commercial purposes, in microform, paper, electronic and/or any other formats.

The author retains copyright ownership and moral rights in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

AVIS:

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque et Archives Canada de reproduire, publier, archiver, sauvegarder, conserver, transmettre au public par télécommunication ou par l'Internet, prêter, distribuer et vendre des thèses partout dans le monde, à des fins commerciales ou autres, sur support microforme, papier, électronique et/ou autres formats.

L'auteur conserve la propriété du droit d'auteur et des droits moraux qui protègent cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

In compliance with the Canadian Privacy Act some supporting forms may have been removed from this thesis.

Conformément à la loi canadienne sur la protection de la vie privée, quelques formulaires secondaires ont été enlevés de cette thèse.

While these forms may be included in the document page count, their removal does not represent any loss of content from the thesis.

Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant.

Abstract

Near-infrared (NIR) light covers the wavelength from 750 nm to 2500 nm. Materials, interacting or emitting light in this region, have drawn increasing interests due to their unique electrical and optical properties. In theory, electrochromic (EC) materials which can reversibly change their absorption at telecommunication wavelengths (980, 1330 and 1550 nm) at different oxidation states are potentially useful in optical switching and attenuation. The device application requires these NIR materials be incorporated as thin films.

This thesis research focuses mainly on the synthesis, characterization and application of a series of dicarbonylhydrazine ruthenium complexes and polymers. Different strategies have been applied to the synthesis of NIR-active film-forming materials: crosslinking the functionalized ruthenium complexes, complexation of ligand polymers and polymerization of the ruthenium complex monomers.

Crosslinking of the functionalized dendric DCH-Ru complex is a simple way to form the films with high resistance to solvents and thermal degradation. All the complex polymers in the mixed-valence state show intense and broad absorption in the NIR region. Direct polymerization of the DCH-Ru monomers produces the complex polymers with controlled molecular weights, compositions and good solubility for film casting. The application of these complex polymers in electrochromic variable optical attenuator devices has been demonstrated. A high dynamic range of optical attenuation of 30 dB at 1550 nm has been achieved with a hybrid device using a dendric DCH-Ru complex in solution and WO₃ thin film as complimentary NIR electrochromic materials.

Acknowledgements

Pursuing a Ph.D is a struggling time in my life. Without the help from so many people, this work could not be done.

First of all, I like to thank my supervisor, Dr. Zhiyuan Wang, for all of his guidance, understanding and support throughout my graduate study. What I have learned from him will benefit the rest of life.

Second, I want to thank those old students who have left this lab. They treated me like their brothers. Whenever I needed help, they would give out their hands without my asking. Their care and love was especially important to me when I was alone at that time. And my thanks also go to the people currently in this lab. Although they are younger, they are just like most others who worked in this lab before. As a student in organic chemistry, I have to spend a lot of time in purifying stuff. But most people from this lab don't need to be purified. They would try what they could to help others. The list of the name could be too long, but the names have already stored in my memory.

And there are many others out of this lab I need to thank. I can't forget to thank the technicians working on NMR and MS at Carleton U. and Ottawa U. They have done a lot of work to help me to finish my job.

Finally, I thank my wife and my parents for their support all the time.

Table of Contents

Abstract.....	I
Acknowledgements.....	II
Table of Contents.....	III
List of Figures.....	VI
List of Schemes.....	X
List of Tables.....	XI
List of Abbreviations.....	XII
Chapter I Introduction to Near-Infrared Materials and Applications	1
I.1. Near-Infrared Active Metal Oxides	2
I.2. Near-Infrared Active Organic Compounds.....	3
I.3. Near-Infrared Active Polymers.....	10
I.4. Near-Infrared Active Metal Complexes.....	16
I.5. Electrochromic Variable Optical Attenuator (ECVOA).....	24
I.6. Rationale and Objectives	25
References.....	27
Chapter II Design, Synthesis and Application of [G]-1 DCH-Ru Complexes	34
II.1 Introduction	34
II.2 Synthesis and Characterization of [G]-1 DCH-Ru complexes.....	36
II.3 Electrochemical Properties.....	38
II.4 UV-vis-NIR Spectroscopic Properties	41
II.5 NIR Electrochromic Variable Optical Attenuator.....	42
II.5.1 Single-Layer Device.....	42

II.5.2 Hybrid Single-Layer Device	44
II.6 Conclusion.....	48
II.7 Experimental Section	48
References.....	54
Chapter III Synthesis and Characterization of Biurea-Ruthenium Complex.....	57
III.1 Introduction.....	57
III.2 Results and Discussion	60
III.2.1 Complex Monomer	60
III.2.1.1 Synthesis and Characterization	61
III.2.1.2 Electrochemical Properties	61
III.2.1.3 Spectroelectrochemical Properties.....	62
III.2.2 Complex Dimer.....	62
III.2.2.1 Synthesis and Characterization	63
III.2.2.2 Electrochemical Properties	66
III.2.2.3 Spectroelectrochemical Properties.....	67
III.2.3 Polymer Complex	71
III.2.3.1 Synthesis and Characterization.....	71
III.2.3.2 Electrochemical Properties	73
III.3 Conclusion	74
III.4 Experimental Section.....	75
References.....	79
Chapter IV Ru-Containing Polymers by Suzuki Cross-Coupling Polymerization.....	81
IV.1 Introduction.....	81

IV.2	Design and Synthesis of AB monomers	84
IV.2.1	DCH-based AB-type Monomer	84
IV.2.2	Biurea-based AB-type Monomer.....	87
IV.3	AA-BB copolymers	89
IV.3.1	Synthesis and Characterization of Poly(DCH-Ru-alt-triglycol).....	90
IV.3.2	Synthesis and Characterization of Poly(fluorene-co-DCH-Ru)	93
IV.3.3	Solution Property	96
IV.3.4	Electrochemical characterization.....	99
IV.3.5	UV-vis-NIR Spectroscopic Study.....	101
IV.3.6	Photoluminescent and Electroluminescent Properties.....	103
IV.3.7	Thermal Properties.....	109
IV.3.8	Electrochromic Properties	110
IV.4	Conclusion	112
IV.5	Experimental Section.....	113
	References.....	127
	Appendix.....	134
	Appendix.....	134

List of Figures

Figure I.1. Absorption of WO ₃ films under different reduction potential.	3
Figure I.2. Examples of NIR electrochromic polymers.	11
Figure I.3. Evolution of energy levels with p-doping (top) and n-doping (bottom) in a conjugated polymer with non-degenerated ground states.	13
Figure I.4. Spectroelectrochemistry for PEDOT film on ITO.	14
Figure I.5. Spectroelectrochemistry of a thin PEDOP film (a: -0.887 V, j: -0.37 V). ...	14
Figure I.6. [$\{Ru(bpy)_2\}_2 \mu\text{-}Ph_2dch\}^{2+}$ (L.21): general structure, typical CV and absorption spectra in three different oxidation states.	23
Figure I.7. Concept design of transmissive ECVOA.	25
Figure II.1. IR spectra of ligands II.1-5 (KBr pallets).	38
Figure II.2. CV of II.4-Ru (R = Ph) in 0.1 M TBAH/ACN (scanning rate of 200 mv/s). 39	
Figure II.3. Relationship between the total Hammett parameter and redox potentials (E_1 , E_2).	40
Figure II.4. UV-vis-NIR spectra of DCH-Ru complex 2d (R = Ph) at different oxidation states.	41
Figure II.5. NIR ECVOA device configuration.	45
Figure II.6. The X-ray pattern of ITO/WO ₃ and blank ITO glass.	45
Figure II.7. The relation between the applied voltage and attenuation at 1550 nm of device A: ITO / WO ₃ / Fc / ITO (■) and B: ITO / WO ₃ / DCH-Ru / ITO (●).	46
Figure II.8. The transmittance vs time curves of devices A and B under 2.0V.	47
Figure III.1. Cyclic voltammogram of monomer complex (III.1-Ru) in 0.1 M	

TBAH/ACN (200 mV/s).....	61
Figure III.2. Spectroelectrochemical spectrum of monomer complex (III.1-Ru) in 0.1M TBAH/ACN solution.....	62
Figure III.3. IR spectra of dimer ligand (III.2) and its complex (III.2-Ru).	63
Figure III.4. ^1H and ^{13}C NMR spectra of dimer ligand (III.2).	64
Figure III.5. ESI-MS spectrum of dimer complex (III.2-Ru).	65
Figure III.6. Cyclic voltammogram of dimer complex (III.2-Ru) in 0.1M TBAH/ACN solution.	66
Figure III.7. Spectroelectrochemical spectra of dimer complex (III.2-Ru) in 0.1M TBAH/ACN solution.	68
Figure III.8. ^1H NMR and ^{13}C NMR spectra of polymer ligand (III.3).	72
Figure III.9. Cyclic voltammogram of complex polymer (III.3-Ru) in 0.1M TBAH/ACN solution.	74
Figure IV.1. IR spectra of ligands IV.2 and IV.3 (KBr pellet).	85
Figure IV.2. ^1H NMR spectra of IV.2 and IV.3 in $\text{DMSO}-d_6$	85
Figure IV.3. Calculated geometric structure of $[\{\text{Ru}(\text{bpy})_2\}_2 \mu\text{-Ph}_2\text{dch}]^{2+}$ by Spartan ES as a model compound for $[\text{IV.3-Ru}]^{2+}$	87
Figure IV.4. Calculated geometric structure of $[\{\text{Ru}(\text{bpy})_2\}_2 \mu\text{-(NHPh)}_2\text{dch}]^{2+}$ as a model compound for $[\text{IV.10-Ru}]^{2+}$ by Spartan ES.	89
Figure IV.5. IR spectra of compound IV.11 and its complex IV.11-Ru.....	91
Figure IV.6. ^{13}C NMR spectrum of monomer IV.11-Ru.	91
Figure IV.7. IR spectra of starting monomers IV.16, IV.17 and IV.11-Ru and product IV.20 in KBr.	94

Figure IV.8. ^1H NMR spectrum (300 MHz, $\text{DMSO}-d_6$) of IV.20.	95
Figure IV.9. Reduced viscosities as a function of polymer concentration in DMF without or with salt (0.01M NH_4PF_6) at 30 °C: (B) IV.18, salt free;(X) IV.18, with salt; (!) IV.19, salt free; (∇) IV.19 with salt; (,)IV.20, salt free; (–) IV.20, with salt.	97
Figure IV.10. GPC traces of DCH-Ru copolymers using 2 mM NH_4PF_6 in DMF as n eluant : 1) IV.18, 2) IV.19, 3) IV.20.	99
Figure IV.11. Cyclic voltammograms of monomers and copolymers IV.18, IV.19 and IV.20 in 0.1M TBAH/ACN solution at room temperature (polymers are coated on electrode).	100
Figure IV.12. UV-vis-NIR spectra of starting monomers and copolymer products. in ACN at a concentration of 0.020 mg/ml.	102
Figure IV.13. Fluorescent spectra of fluorene ($\lambda_{\text{ex}} = 280$ nm, inserted figure) and PFO (inserted figure, $\lambda_{\text{ex}} = 330$ nm) in toluene and Ru copolymers in ACN at c = 2.14×10^{-5} M ($\lambda_{\text{ex}} = 330$ nm): (a) fluorene; (b) PFO; (c) IV.18; (d) IV.19; (e) IV.30.	104
Figure IV.14. PL spectra of three copolymers in ACN at c = 0.10 mg/mL.	106
Figure IV.15. EL spectra of LED devices containing polymers IV.18, IV.19 and IV.20 with a configuration of ITO/polymer/Au.	108
Figure IV.16. EL performance of copolymer IV.20 in film at a thickness of 80 nm: (a) current vs time; (b) brightness (radiance) vs time.	109
Figure IV.17. TGA traces of PFO and three copolymers.	110
Figure IV.18. Current (dot line) and transmission (solid line) changes of IV.20 film	

(thickness: 325 ± 5 nm) at 1600 nm at a constant potential of + 600 mV
 and - 600 mV in 0.1M TBAH/THF. 111

Figure IV.19. Change of transmittance at 1600 nm of the film of copolymer IV.20 film

(thickness: 325 ± 5 nm) coated on ITO glass (electrolyte: 0.1 M
 $\text{NH}_4\text{PF}_6/\text{THF}$) as a function of switching speed (5s, 10s and 20s); pulse
 potentials: ± 600 mV..... 112

List of Schemes

Scheme III.1. (a) Poly(2,2'-bipyridine-5,5'-diyl), (b) Copolymer with quarter(3-octylthiophene), (c) Copolymer with benzobisoxazole, (d) Polyamides, (e) Polyesters.	58
Scheme III.2. General reaction routes to prepare (a) polyhydrazides and (b) polybiurea.	58
Scheme III.3. Structures of monomer, dimer and polymer complexes and their ligands.	59
Scheme III.4. Proposed oxidation mechanism of NH group in $[\{Ru(bpy)_2\}_2\mu\text{-Ph, NH(C}_3\text{H}_7\text{-n)dch}](PF_6)_2$	69
Scheme III.5. Proposed redox process of dimer complex (III.2-Ru).	70
Scheme IV.1. Accepted mechanism of Suzuki-coupling reaction.	81
Scheme IV.2 General representation of SPC with the AA/BB-type or AB-type polymerization. X and Y represent aromatic units, typically benzene derivatives.	83
Scheme IV.3. Synthesis of Ru-containing polymer by Suzuki cross-coupling Polymerization.	83
Scheme IV.4. Synthesis of AB ligand and the complex.	84
Scheme IV.5. Synthesis of Biurea-based AB-type ligand.	88
Scheme IV.6. Synthesis of monomer IV.11-Ru complex and BB monomer IV.14.	90
Scheme IV.7. Suzuki cross-coupling polymerization of IV.11-Ru and IV.14.	93
Scheme IV.8. Preparation of poly(fluorene-co-DCH-Ru) by Suzuki cross-coupling in ACN at a concentration of 0.020 mg/ml.	94

List of Tables

Table I.1. Organic NIR-absorbing and electrochromic compounds.....	4
Table I.2. Examples of dinuclear metal complexes with MMLC-related NIR	
Absorption.....	19
Table I.3. Examples of dinuclear metal complexes with IVCT-related NIR.....	21
Table II.1. Syntheses of 1,3,5-benzenetris(2'-substituted carbohydrazides) II.1-5 and the	
corresponding DCH-Ru complexes II.(1-5)-Ru.	37
Table II.2. Electrochemical oxidative potentials of complexes in 0.1M TBAH/ACN	
solution (scanning rate of 200 mv/s).....	39
Table II.3. Optical data of complexes at different oxidative states.	42
Table III.1. Electrochemical data of monomer and dimer complexes.....	70
Table III.2. Spectroelectrochemical data of three complexes.....	70
Table IV.1. Intrinsic viscosity and GPC data of copolymers IV.18, IV.19 and IV.20. ...	97
Table IV.2. Electrochemistry data ^a of monomers and copolymers taken in 0.1M	
TBAH/ACN.	101
Table IV.3. Photophysical properties of monomer 11 and three copolymers in A.	103
Table IV.4. Measured Ru content by colorimetric method.	103
Table IV.5. Thermal stability results of PFO and copolymers IV.18, IV.19 and IV.20	
under N ₂	110

List of Abbreviations

PDQ	Pentacenediquinone
CAN	Acetonitrile
BPA	4,4'-Isopropylidenediphenol
BPY	Bipyridine
CB	Conducting Band
CE	Color efficiency
CV	Cyclic Voltammetry
DCH	Dicarbonylhydrazine
DMF	N,N-dimethylformamide
DMF	N,N-dimethylformamide
DMSO	Dimethylsulphoxide
DMSO- <i>d</i> ₆	Deuterated Dimethylsulfoxide
DSC	Differential scanning calorimetry
EC	Electrochromic
ECVOA	Electrochromic Aariable Optical Attenuator
Fc	Ferrocene
GPC	Gel Permeation Chromatography
HOMO	Highest Occupied Molecular Orbital
ICP	Inductively Coupled Plasma
ITO	Indium Doped Tin Oxide
LMCT	Ligand-to-Metal Charge Transfer
LUMO	Lowest Unoccupied Orbital

LVCT	Intervalence Charge Transfer
MLCT	Metal-to-Ligand Charge Transfer
MMCT	Metal-to-Metal Charge Transfer
NHE	Normal Hydrogen Electrode
NIR	Near-Infrared
PDA	N,N'-diphenyl-1,4-phenylenediamine
PDBF	Poly(dibenzofulvene)
PDEQ	Poly(5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline)
PEDOP	Poly(3,4-ethylenedioxy pyrrole)
PEDOT	Poly(3,4-ethylenedioxy thiophene)
PSS	Poly(styrene sulfonate)
SPC	Suzuki polycondensation
TBAH	Tetra-n-butylammonium Hexafluorophosphate
TEAP	Tetraethylammonium Perchlorate
TG	thermogravimetry
THF	Tetrahydrofuran
TMS	Tetramethylsilane
V ₂ O ₅	Vanadium Oxide
VB	Valence Band
VOA	Variable optical attenuator
WDM	Wavelength-Division Multiplexing
WO ₃	Tungsten Oxide

Chapter I Introduction to Near-Infrared Materials and Applications

The infrared part of the electromagnetic spectrum covers the range from roughly 300 GHz (1 mm) to 400 THz (750 nm). It can be divided into three parts: Far-infrared, Mid-infrared and Near-infrared.

Far-infrared, from 300 GHz (1 mm) to 30 THz (10 μm). The lower part of this range may also be called microwaves. This radiation is typically absorbed by so-called rotational modes in gas-phase molecules, by molecular motions in liquids, and by phonons in solids. The wavelength range from approximately 200 μm up to a few mm is often referred to as "sub-millimetre" in astronomy, reserving far infrared for wavelengths below 200 μm .

Mid-infrared, from 30 to 120 THz (10 to 2.5 μm). Hot objects (black-body radiators) can radiate strongly in this range. It is absorbed by molecular vibrations, where the different atoms in a molecule vibrate around their equilibrium positions. This range is sometimes called the *fingerprint region* since the mid-infrared absorption spectrum of a compound is very specific for that compound.

Near-infrared, from 120 to 400 THz (2,500 to 750 nm). Physical processes that are relevant for this range are similar to those for visible light. Visible light (and near-infrared light) is typically absorbed and emitted by electrons in molecules and atoms that move from one energy level to another. The light we see with our eyes is really a very

small portion of the electromagnetic spectrum. A rainbow shows the optical (visible) part of the electromagnetic spectrum; infrared (if you could see it) would be located just beyond the red side of the rainbow with ultraviolet appearing just beyond the violet end.

Materials, either inorganic or organic, interacting or emitting light in this region have drawn increasing interests because their electric and optical properties are unique and suitable for a number of applications in photonics^{1,2}, optical communications³, biotechnology⁴, spacecraft thermal control and military application⁵. For example, auto-fluorescence and absorption from tissue and water are minimized in the near-infrared region, and the NIR light penetrates deeper into tissues and causes less damage to the cells⁶. In telecommunication, the wavelengths of 980, 1300 and 1500 nm are desirable because silica-based optical fibres have a minimum optical loss for data transmission.

This chapter covers a brief historical review on some important classes of NIR materials and application in variable optical attenuators, and finally the rationale and objectives for this thesis research.

I.1. Near-Infrared Active Metal Oxides

Metal oxides such as tungsten oxide (WO_3)⁷ and vanadium oxide (V_2O_5)⁸, can become NIR-absorbing when being reduced. The thin film of the reduced WO_3 or V_2O_5 absorbs broadly in the NIR region, also called “cathodically colored” in the NIR region. The absorbance in the NIR region is associated to the degree of reduction or ion insertion coefficient and as well film morphology⁹. As shown in figure I.1, the WO_3 film absorbs weakly around 400 nm, but strongly from 400 to 1600 nm upon reduction¹⁰. However,

some inherent drawbacks, such as high cost for film preparation and long switching time¹¹, limit these materials for large-scale film production and industrial applications.

Figure I.1. Absorption of WO₃ films under different reduction potentials.

I.2. Near-Infrared Active Organic Compounds

Organic NIR-absorbing or electrochromic materials include mainly organic dyes and conducting polymers. Compared to inorganic NIR materials, organic materials are readily to be modified to have a wide range of the electrical/optical properties, easy to process, and cost effective¹². Applications in optical recording, display, laser printer, laser filter, infrared photography and medical applications have been realized. The existing reviews cover mainly the NIR-absorbing organic materials with the maximum absorptions below 1000 nm¹³⁻¹⁵. Thus, the following review will focus on those exhibiting the long-wavelength NIR absorption and electrochromism (1000 – 2000 nm).

*Near-Infrared Dyes***Table I.1. Organic NIR-absorbing and electrochromic compounds.**

No.	Structure	Radical state	λ_{max} (log ϵ) ^a	solvent	Ref.
I.1			1615 (4.34)		
		cation	1572 (4.45)	CH ₂ Cl ₂	17
			1312 (4.48)		
I.2		cation	1120 (< 4)	H ₂ O	19
I.3			1140 (3.59) - 1700	(H ₂ O)	20
		anion	~ 1300	(film)	30
I.4		anion	1560 (4.20)	DMF	21
I.5		anion	1335 (4.50)	DMF	
I.6		anion	1305 (4.49)	THF	22

I.7		anion or dianion	1345, 1180	CH ₃ CN	23 24
I.8		cation	1000, 1150	CH ₃ CN	16
I.9		cation	1000, 1630	CH ₂ Cl ₂	27
I.10		neutral	1230 - 1260 (3.67 - 3.53)	CH ₂ Cl ₂	28

X = O, N-CH₂-Ph^a λ_{max} in nm, ϵ in M⁻¹cm⁻¹.

NIR-absorbing organic molecules generally have π -conjugated structures, such as phthalocyanine, naphthalocyanine, polymethine, phenylmethane, quinone and azo dyes. However, only those that can undergo reversible redox reaction are suitable for electrochromic application. NIR electrochromism is more likely observed in molecules with relatively stable radicals generated during the redox reaction, either cationic radicals or anionic radicals¹⁶.

Intense NIR absorption arising from the radical cations is likely obtained in the electron-efficient systems when oxidized or from dicationic salts when reduced. Examples of the former are systems containing two π – bridged triphenylamines (**I.1**, Table I.1)¹⁷. They can reversibly undergo two one-electron oxidation processes to form radical monocations and dications. Their radical monocations are characterized by an intense and sharp band at 734 nm and a broad (covering from 1000 to over 2500 nm) and relatively intense ($\epsilon > 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) intervalence charge-transfer (IVCT) band in the NIR region, which is attributed to a photoinduced intramolecular electron-transfer between the two redox centers. The spectroelectrochemistry of dendric hexaarylbenzene containing six triarylamine has also been studied by Nöll, showing the absorbance of the radical trication being about one order of magnitude lower than those of bistriarylamine¹⁸. Viologens, 1,1'-disubstituted-4,4'-bipyridinium salts, are a family of parent dications. Although the electrochromism of their radical cations has mostly been studied in the visible region for display application^{13, 15}, a weak NIR absorption ($\epsilon < 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) at 1120 nm has also been reported for 1-methyl-1'-alkyl-substituted viologens when the alkyl group is long enough ($n = 16$ or 18) (**I.2**, Table I.1)¹⁹. The observed NIR absorption is due to the radical dimers formed in one-electron reduction.

On the other hand, intense NIR absorption is also observed in electron-deficient conjugated systems including aromatic imides, quinones and Schiff base cryptans when reduced. The Miller group did extensive research and found that the molecular stacking plays an important role in NIR absorption of the radical anions such as disodium *N,N*-bis(p-sulfonatophenyl)naphthalenedicarboximide (**I.3**, Table I.1)²⁰. In *N,N*-dimethylformamide (DMF), it existed as a monomeric radical anion, and no absorption

above 800 nm was observed. In water, it formed π -stacked radical dimers and a relatively intense band appeared at 1140. With higher π -stacking aggregates in brine, the absorption band was further shifted to 1700 nm. They also studied the electrochromic properties of the anion radicals of diquinone compounds. Semiquinones **I.4** and **I.5** (Table I.1)²¹ were found to absorb intensely and sharply at 1560 nm and 1335 nm in DMF solution, respectively, which was ascribed to $\pi^* - \pi^*$ excitations from the delocalized anions. Both compounds have two reversible redox couples at less negative potentials, originating from two one-electron reactions, $X \leftrightarrow X^{\cdot-}$ and $X^{\cdot-} \leftrightarrow X^{2-}$. The absorption bands varied with electron-donating or electron-withdrawing substituents, a blue shift for the former and a red shift for the latter. Strong NIR absorption peaking at 1305 nm in tetrahydrofuran (THF) with a shoulder was also observed in an organoboron compound, 4,4'-bis(dimesitylboryl)biphenyl (**I.6**, Table I.1),²² when reduced to anion radical, which was assigned to $\pi^* - \pi^*$ transition, i.e. SOMO to LUMO. Another type of compound in this class is Schiff base cryptand (**I.7**, Table I.1), which can be electrochemically²³ or chemically²⁴ reduced to form monoanion, dianion and trianion. Its reduction is not quite reversible due to the presence of several chemical equilibria. Both the monoanion and dianion showed the same spectra in the visible and NIR region with absorption at 1345 nm plus a shoulder at 1180 nm, which behaved similar to the single strand $(CH_3)_2CH-N=CH-meta-C_6H_4CH=N-CH(CH_3)_2$.

Cyanines are a type of conjugated system that contains neutral nitrogen and positively charged nitrogen in their parent states. Thus, they can produce radicals in both one-electron reduction and one-electron oxidation, and both radicals are expected to display long-wavelength absorption in long-length cyanine²⁵. However, the redox

reversibility highly depends on their structures, and relatively intense long-wavelength absorption is only observed in the radical cations, due to their higher stability than the opposite radical anions. Closed-shell polymethine cyanines are well-known for their systemic shift of the absorption with the extension of the polymethine chains. A number of cationic cyanine salts have been reported to absorb intensely at 1000 - 2000 nm^{25, 26}. However, the NIR electrochromism involving the radicals has not received much interest, probably due to lower absorptions restricted in the region below 1000 nm and the decreased stability of the radical ions with long polymethine chains. Relatively intense absorption at longer wavelength was reported in the mixed cyanine system. The violene/cyanine compound (**I.8**, Table I.1)¹⁶ displayed a broad band at 800 – 1300 nm when reduced to radical cation. The squaraine-based cyanine (**I.9**, Table I.1)²⁷, is featured with a donor-bridge-acceptor structure. Its radical cation, resulting from single-electron oxidization, revealed an intense and sharp band at 1000 nm and a broad and less intense band at ~1630 nm due to the intramolecular electron transfer. The cyclic voltammograms of both cyanines showed two reversible one-electron oxidation waves with a one-electron reduction wave with limited reversibility for the latter cyanine.

Some molecules containing a strong donor and an acceptor linked by a non-conjugated spacer show contrary electrochromic behavior and are less studied in comparison with the conjugated organic systems. A representative example is the σ -bond-bridged diad system (**I.10**, Table I.1)²⁸, having trialkyltetrathiafulvalene as a strong π -donor and trinitrofluoren-9-dicyanomethylene as a strong π -acceptor. Such a system has a very low energy gap between highest occupied molecular orbital (HOMO) and lowest unoccupied orbital (LUMO) (about 0.3 eV) and in solution displays relatively intense

NIR absorption bands peaking at 1230 – 1260 nm in the neutral state. Both ester- and amide-bridged systems showed high electrochemical reversibility, especially for the latter. The NIR absorption bands disappeared after being reduced or oxidized to the radicals, resulting from the loss of donor or acceptor ability.

Nevertheless, there are two major problems associated with ionic organic dyes for electrochromic applications: aggregation and instability of radicals. The aggregation of radicals in solution causes complication in understanding of their electrochemical and spectral properties²⁹. One of the solutions to the aggregation problem is to absorb dyes onto a solid surface like a silver halide crystal in order to make the aggregation process irreversible. However, this could make the fabrication of electrochromic devices quite inconvenient. An alternative solution is to stabilize the radicals with ionic polymers to form films.³⁰ However, the films formed are highly anisotropic in NIR absorption, and the film sizes are determined by the area of the electrodes used. Another major problem is the instability of the radical ions formed in redox reactions, especially for radical anions. They easily undergo degradation in air because of their high reactivity towards oxidation, therefore the redox reactions have to be carried out with protection of inert gases and at low temperatures, e.g. -20 °C³¹. As for radical cations of cyanines, some of them can undergo rapid dimerization to form stable dication products, which makes the electrochemical process irreversible^{32, 33}. Although this problem can be partially fixed through structural modification, such as substituting the methine carbons with bulky alkyl groups³⁴, the NIR electrochromic property for cyanines are rarely reported.

1.3. Near-Infrared Active Polymers

The advantage of polymers over small organic molecules is their ease to form films by solution processes for application in devices. Polymeric electrochromic materials that are active in the NIR region can be divided into two categories: non-conjugated polymers and conjugated polymers. The non-conjugated electrochromic polymers are generally constructed from electrochromic chromophores by incorporating into or grafting onto polymer backbones. Viologens are a popular class of chromophores used to build non-conjugated electrochromic polymers, owing to their ease to undergo nucleophilic substitution reaction with high yields. For example, viologen can be incorporated into a polymer backbone by the reactions of equimolar 4,4'-bipyridyl and α,α' -dibromo-p-xylene in dry acetonitrile (poly(xylyl viologen), Figure I.2)³⁵. Viologens can also be easily grafted to chlorinated poly(oxyethylene)³⁶ and polymeric microspheres³⁷ with controllable degrees of functionalization. However, the electrochromic properties of these viologen polymers are usually restricted within the UV-vis spectral region. Recently, Nakano and Yade reported that the oxidized oligo- and poly(dibenzofulvene) (PDBF, Figure I.2)³⁸, made from anionic polymerization of 1,1-diphenylethylene, displayed intense and broad absorption bands centered from 1400 nm to 1600 nm depending on the degree of polymerization. The authors ascribed the NIR absorption to the intramolecular charge resonance of π -stacked structure. Unfortunately, the oxidization of such polymers is irreversible, which makes them not suitable for NIR electrochromic applications. Our lab recently synthesized a series of polymers containing NIR electrochromic chromophore, pentacenediquinone (PDQ), by copolymerization of bis(4-fluorophenyl)sulfone, 4,4'-isopropylidenediphenol (BPA) and 1,8-

dinitropentacenediquinone. Similar to pentacenediquinone, the resulting poly(PDQ-BPS-co-BPA) (Figure I.2) displayed two absorption bands in N,N-dimethylformamide (DMF) peaking at 1170 and 1396 nm when reduced to radical anions. In the solid state, their absorption intensities varied with respect to the thicknesses of films as well as the molar ratios of PDQ in polymers. Although these polymers behave high thermal stability (degradation temperature > 375 °C), high electrochemical reversibility for the first two reduced steps and long-term stability for their anion radicals (no optical loss for 7 days), their optical contrasts need to be improved and switching time needs to be reduced for use in optical attenuators in the NIR region.

Figure I.2. Examples of NIR electrochromic polymers.

In a conjugated polymer, the lowest-energy optical transition is directly related to its bandgap, i.e., the lowest energy required for electronic excitation from the valence band (VB) (highest occupied band) to the conducting band (CB) (lowest unoccupied band). The optical transition relies on the structure of the conjugated polymer (intrinsic bandgap) as well as the doping level. For conjugated polymers, doping is generally referred to the process of oxidation (“p-doping”) or reduction (“n-doping”) with ion

insertion or expulsion of counter ions, although the latter is less common than the former due to the increased instability at the reduced state. As a result, all conjugated polymers are potentially electrochromic materials. The doping process is depicted in figure I.3.³⁹ Considering a conjugated polymer with non-degenerated ground states, which is the case for most aromatic conjugated polymers, either p-doping or n-doping will create new energy levels (polaron and bipolaron) between the valence band (highest occupied band) and the conducting band (lowest unoccupied band), which will give rise to the appearance of low-energy transitions. With the increase of the doping level, the original bandgap (difference of the energy level of the conducting band and the valence band) will be replaced by a lower bandgap. At a high doping level, the bipolaron bands will overlap with the π bands to produce metallic-like states. Experimentally, the bandgap of a conjugated polymer is determined by the onset of the absorption band (“optical bandgap”) or the difference of the onset electrochemical potential for oxidation and for reduction (“electrochemical bandgap”). As a result, the reduction in bandgap will shift the absorption to higher wavelengths, which makes conjugated polymers able to achieve electrochromism in the long-wavelength region. On the other hand, as the shift in absorbance owing to doping is limited, the position of the shifted absorption band is highly dependent on the absorbance of a conjugated polymer at its undoped state (intrinsic bandgap). Hence, a long wavelength absorption in the visible region at the neutral state is required for a conjugated polymer to achieve absorption in the NIR region at the doped state. In other words, intrinsically low-bandgap polymers with $E_g \leq 1.8 - 1.9$ eV ($\sim 650 - 700$ nm)⁴⁰ are desired to realize NIR electrochromism once being doped.

Figure I.3. Evolution of energy levels with p-doping (top) and n-doping (bottom) in a conjugated polymer with non-degenerated ground states.

Conjugated polymers have been studied as electrochromic materials, owing to their several advantages, such as high colouration efficiency, low switching time⁴¹⁻⁴², availability of multiple colours in the same material^{43,44}, fine tunability of the band gap⁴⁵ and film-forming property⁴⁶. However, NIR electrochromism was only considered as an accompanied phenomenon as most of the studies focused on their electrochromic properties and applications in the visible region^{14, 15, 47-49}.

Polyaniline displays absorption maximum at ~1900 nm at its emeraldine state (a partially oxidized state) with intensity and peak values depending on the applied potentials and the degree of protonation, which is attributed to the transition of VB to the lowest polaron level^{50,51}. The fully reduced or oxidized state shifts the absorption band to higher energy but with relatively broad absorption in the above region, i.e. a relatively low optical contrast in the NIR region, which diminishes the value of polyaniline as an active material for NIR display and optical attenuation. The band gap of polyaniline is

easily changed through structural modification, because the introduction of substituents onto the nitrogen generally reduces the conjugation of the polymer chains, resulting in a blue shift of the absorption band⁵² or phenyl ring⁵³.

Figure I.4. Spectroelectrochemistry for PEDOT film on ITO.

Figure I.5. Spectroelectrochemistry of a thin PEDOP film (a: -0.887 V, j: -0.37 V).

p-Doped polythiophene shows broad absorption from 1000 to 2500 nm⁵⁴, as well as good environmental stability at both the p-doped and neutral state⁵⁵. However, due to its rigid structure it is insoluble in most solvents and is not easily to be processed. This problem can be solved by introduction long-chain, or bulky, or polar groups, or

incorporating it with surfactants like poly(styrene sulfonate) (PSS)^{56, 57}. The structural modification also varies the band gaps of the polymers and hence the absorption wavelengths at their doped states. A representative is poly(3,4-ethylenedioxythiophene) (PEDOT), which was first developed by Bayer AG⁵⁸ and studied in detail for its electrochromic property by the Reynolds' group. The doped PEDOT is more stable under ambient conditions than the neutral PEDOT. As shown in Fig. I.4¹⁵, the polymer absorbs at 621 nm (2.0 eV) in the neutral state (-0.93 V) due to a $\pi - \pi^*$ interband transition. When being oxidized, the decrease in absorption in the visible region is accompanied by the increase in absorption at ~ 1.25 and ~ 0.80 eV due to the formation of polaronic charge carriers. Further oxidization results in bipolarons with the enhanced NIR absorption at 0.80 eV, which matches one of the telecommunication wavelengths of 1550 nm.

The p-doped polypyrrole film has the NIR absorption band peaking at ~ 1240 nm⁵⁹ and can undergo an electrochromic switch with a fast stepping time (~ 100 ms)⁴⁷. However, the electrochromic property of polypyrrole is not fully exploited, mainly due to the degradation of the film during redox process¹³. The substituted polypyrroles with a higher stability have been obtained. An interesting example is poly(3,4-ethylenedioxythiopyrrole) (PEDOP) (Figure I.5), which has a lower bandgap (2.0 eV)^{60, 61} than polypyrrole (2.7 eV)⁶². Its film displays a dual electrochromism in both visible and NIR regions similar to PEDOT with a lower energy transition at ~ 0.77 eV (1600 nm). Because of its low oxidization potential (-0.15 to +0.05 V vs SCE), it shows a high stability under ambient conditions in the doped state.

A great number of low bandgap copolymers based on thiophene and EDOT have also been prepared⁶⁴⁻⁶⁵, and some of them display excellent electrochromic properties in

the NIR region, such as poly(5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline) (PDEQ)⁶⁶. Being commercially available, PEDOT is at present the most desirable material for NIR electrochromic device application, although there is a cost issue for its monomer⁶⁷.

I.4. Near-Infrared Active Metal Complexes

NIR-absorbing metal complexes have gained much attention owing to some unique features such as electrochromism, large extinction coefficient, easy modification of the ligands, good solubility and processability. Mono- and multi-nuclear complexes have been reported with absorptions in the NIR region.

For mono-nuclear complexes to absorb close to the NIR region, it generally requires a large planar ligand system for electrons to delocalize to a large extent to achieve low-energy $\pi - \pi^*$ transfer. Nickel-dithiolene complexes are one of the few types of mono-nuclear complexes whose absorption can be tuned to match the telecommunication wavelengths. 1,2-Dithiolene is a bidentate ligand consisting of two sulfur atoms connected via an unsaturated carbon-carbon backbone. Since the first report on nickel-dithiolene complexes by Schrauzer and Mayweg in 1962⁶⁸, metal-dithiolene complexes have drawn much attention for use as NIR dyes, mostly in lasers⁶⁹ and photocurrent detectors⁷⁰, conducting and magnetic materials⁷¹. It has been found that the absorption maxima of the nickel dithiolene complexes can go up to 1500 nm or even

beyond by increasing the electron-donating ability of the substituents and the coplanarity of the ligand⁶⁹. For example, the N,N'-diethyl-6,6'-tetrahydroquinoxalyl substituted dithiolato nickel has the absorption maximum approaching 1370 nm in dichloromethane (1440 nm in dimethylsulphoxide), compared to that of unsubstituted complex at 720 nm in hexane. The NIR-absorption can also be reversibly switched between the bleached and colored state, respectively⁷². However, introduction of highly electron-rich groups tend to cause some problems, such as photochemical instability, low yield and difficulty in purification, which hampers their applications as NIR electrochromic materials.⁶⁹

N,N'-diethyl-6,6'-tetrahydroquinoxalyl substituted dithiolato nickel

A large number of dinuclear complexes with conjugated bridging ligands have been found to have absorption maxima in the NIR region, covering the both telecommunication wavelengths of 1.3 μm and 1.55 μm . Organic dinuclear or multinuclear complexes are more common to be NIR electrochromic, with the low-energy transition mainly arising from the charge-transfer between metal and ligand (MLCT or LMCT depending on the relative energy levels of empty and occupied orbitals of metals and ligands) or intervalence charge transfer (IVCT) between metals via the bridging ligand.

Speaking on electrochemistry, MLCT or LMCT generally depends on their relative ease to undergo oxidation. Apparently, more easily oxidized ligand should favour

metal to ligand charge transfer. The MLCT-type example complexes and their spectral data associated with electrochemical reactions are shown in table I.2. The dioxolene-based dinuclear ruthenium complex $[\mathbf{I.11}]^{3+}$ (sq-q) (Table I.2), resulting from ligand-centred oxidation (0.06 V vs Fc/Fc⁺), displays a transition at 1225 nm ($\epsilon \sim 4.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), which is ascribed to Ru(II) to sq-q MLCT transitions. This transition is absent in its fully reduced state $[\mathbf{I.11}]$ and fully oxidized state $[\mathbf{I.11}]^{4+}$ ⁷⁴. The derivate of **I.11** with larger size of dendric hexahydroxytriphenylene (**I.12**) as bridging ligand appears less favorable to achieve high contrast in the NIR region. $[\mathbf{I.12}]^{3+}$ (sq-sq-sq) has large overlapping in absorption with other two oxidized states, $[\mathbf{I.12}]^{4+}$ (sq-sq-q) and $[\mathbf{I.12}]^{5+}$ (sq-q-q) over 800 nm. It has to undergo a 3e-oxidization to convert to $[\mathbf{I.12}]^{6+}$ (q-q-q) to minimize the overlapping at 1170 nm and a high driving potential of 1.03 eV vs. SCE is required⁷⁵. On the other hand, more easily oxidized metal should favour ligand to metal charge transfer. In dinuclear tris(pyrazolyl)-borate-molybdenum complexes, metal molybdenum is easier to be oxidized, resulting in highly intense ligand to metal charger transfer (LMCT) transition. A variety of biphenolate bridging ligands have shown intense NIR absorption at Mo(V)/Mo(VI) states mainly due to Mo(VI) to ligand LMCT⁷⁶. The most remarkable complex among them is 4,4'-[2,2'-bithiophene]-5,5'-diylbiphenolate bridged product $[\mathbf{I.13}]^+$ which has a very intense transition at 1360 nm ($\epsilon \sim 3.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), close to one of the telecommunication wavelengths. This transition is absent in its $[\mathbf{I.13}]^0$ (Mo(V)/Mo(V)) state. A solution-based optical attenuator with this product reaches a high dynamic range of 50 dB with a good reversibility⁷⁷, although the switching time is as long as in minutes.

Table I.2. Examples of dinuclear metal complexes with MLCT and LMCT-related NIR absorption.

No.	Structures and redox reaction	Oxidation potential	$\lambda_{\max}$ (log ϵ), Solvent	Ref.
I.11		0.06 V vs. Fc/Fc ⁺	1080 (4.57), CH ₂ Cl ₂	74
I.12		1.03 V vs. SCE	1170 (4.60), ACN	75
I.13		0.44 V vs. Fc/Fc ⁺	1,360(3.47), CH ₂ Cl ₂	76

^a $\lambda_{\max}$ in nm, ϵ in M⁻¹cm⁻¹.

As for the IVCT-related NIR absorption, it is generally seen with dinuclear metal complexes in which the two metals exist in the two different oxidation states with relatively strong electronic interaction.⁷³ When there is a strong inner sphere interaction between the two metals, the mixed-valence state is more stable, rather than

disproportionating to the isovalent states. In addition, IVCT in mixed-valence state, or a charge transfer from metal donor (lower oxidization state) to metal acceptor (higher oxidization state) via the bridging ligand, requires a lower energy compared to the one the isovalent state. Experimentally, the stability of the mixed-valence state can be evaluated by the separation between the redox couples in electrochemistry. Considering a mixed-valence complex M^{II}/M^{III} , the comproportionation constant K_c (equilibrium constant) can be expressed by:

$$K_c = [M^{II}/M^{III}]^2 / ([M^{II}/M^{II}][M^{III}/M^{III}]). \quad (1)$$

K_c is determined from electrochemical data according to the Nernst equation:

$$\Delta G = -RT(\ln K_c) = -nF(\Delta E), \quad (2)$$

where ΔE is the separation between the two redox potentials, R is universal gas constant, F is Faraday constant, n is the number of electrons transferred in the cell reaction or half-reaction. It is apparent that a large potential separation will lead to the more stable mixed-valence state. On the other hand, the magnitude of interaction, or coupling constant (J), is largely determined by the true electron-transfer distance (r in Å), as well as the extinction coefficient of the IVCT band (ϵ in $M^{-1}cm^{-1}$), the width at half-height of the IVCT band ($\nu_{1/2}$ in cm^{-1}) and the energy of the IVCT band maximum (E in cm^{-1}), which is generally expressed as^{78, 79}:

$$J = 2.05 \times 10^{-1} (\epsilon \nu_{1/2} \cdot E)^{0.5} / r. \quad (3)$$

As pointed out by Ward, the energy of IVCT relies largely on K_c and J : when the interaction (J) is high and K_c is large, the IVCT appears at low energy with high intensity.

Table I.3. Examples of dinuclear metal complexes with IVCT-related NIR absorption.

No.	Structures	$\lambda_{\max}$ (), Solvent	K_c	J (cm^{-1})	Ref.
I.14		1570 (3.70), D2O	3×10^6	3300	80
I.15		1500 (3.62), D2O	8×10^4	855	84, 85
I.16^b		2000 (4.15), CH_2Cl_2	350	830	81
I.17^c		1520, ACN	1×10^5	3200	82
I.18^c		1936 (4.34), ACN	690	1020	
I.19^c		1650 (3.82), ACN	16	600	89
I.20^c		1214 (3.34), ACN	6	330	

^a $\lambda_{\max}$ in nm, ϵ in $\text{M}^{-1}\text{cm}^{-1}$.

^b Tterpy = 4'-(4-tolyl)-2,2':6',2''-terpyridine.

^c byp = 2,2'-bipyridyl

Since the discovery of $[(\text{NH}_3)_5\text{Ru-pyrazine-Ru}(\text{NH}_3)_5]^{5+}$ by Creutz and Taube (Creutz-Taube ion)⁸⁰, a great number of dinuclear ruthenium complexes with low-energy IVCT at mixed-valence states have been prepared⁷³. Some active in the range of telecommunication wavelengths are selected and listed in table I.3. All the complexes in table I.3 show relatively strong low-energy transition over 1220 nm in the mixed-valence state. Among them, **[I.16]**³⁺ displays the lowest energy transition around 2000 nm with the highest extinction coefficient ($\epsilon = 14000 \text{ M}^{-1} \text{ cm}^{-1}$)⁸¹. The Creutz-Taube ion (**[I.14]**⁵⁺) and 2,3,5,6-tetra-2-pyridinylpyrazine bridged dinuclear ruthenium complex **[I.17]**⁵⁺ displays absorption maxima around 1550 nm with very high coupling constant ($3200 - 3300 \text{ cm}^{-1}$)⁸², which are more considered as valence-delocalized complexes (Robin and Day class III)^{73, 83}. With the extension of the length of pyrazine bridge, e.g. by insertion S-S bond between two pyridines in **I.15**^{84, 85}, the metal-metal interaction drops to a much lower value (from 3200 to 855) which is accompanied with the decrease in comproportionation constant and a blue shift of the low-energy transition. This trend is more clearly shown in a series of dinuclear ruthenium complexes **I.18**, **I.19** and **I.20**⁸⁶. With the separation of the two metals further by inserting phenyl rings, both coupling constant and comproportionation constant decrease to lower values with optical transition being shifted to a higher energy. As pointed by Ward, the change in metal-metal interaction (1020 to 330, 3 folds) seems to be less affected by the increase of the distance than the change in comproportionation constant (690 to 6, 115 folds).

L.21 (Figure I.6) represents another type of mixed-valence dinuclear ruthenium complexes. It was first prepared Kaim et al.⁸⁷ and further developed by Desjardins et al. from our lab⁸⁸. **[L.21]**²⁺ is simply prepared from the reaction of $\text{cis-Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$

and a dicarbonylhydrazine (dch) ligand in a basic condition and easily separated by column chromatography. It can undergo two reversible one-electron oxidation reactions result in $[\text{L.21}]^{3+}$ and $[\text{L.21}]^{4+}$ with a large $\Delta E > 0.45 \text{ V}$ ($K_c > 5 \times 10^7$). The mixed-valence $[\text{L.21}]^{3+}$ complexes display intense ($\epsilon > 7000 \text{ M}^{-1} \text{ cm}^{-1}$) and broad (half-width $> 1250 \text{ cm}^{-1}$) absorption in the NIR region, which is absent when reduced to $[\text{L.21}]^{3+}$ state or further oxidized to $[\text{L.21}]^{4+}$ state. Their IVCT is little solvent dependent but highly substituent dependent. An electron donor causes a blue shift of the transition, while an electron acceptor brings a red shift to the transition. By finely tuning the substituents, e.g. $\text{R} = \text{CH}_3$, an intense ($\epsilon = 9300 \text{ M}^{-1} \text{ cm}^{-1}$) IVCT band at 1550 nm can be achieved, which matches one of the telecommunication wavelengths. Not useful only for tuning the optical transition, the change of R group gives a possibility to introduce other functional groups for polymerization. These features, plus the stability in the air and towards thermal degradation, have made DCH-based dinuclear ruthenium complexes attractive electrochromic materials for NIR optical attenuation and other applications.

Figure I.6. $[\{\text{Ru}(\text{bpy})_2\}_2 \mu\text{-Ph}_2\text{dch}]^{2+}$ (L.21): general structure, typical CV and absorption spectra in three different oxidation states.

I.5. Electrochromic Variable Optical Attenuator (ECVOA)

Electrochromic (EC) materials that change the absorption in the NIR region, in particular at telecommunication wavelengths, are useful for applications in optical communication, such as variable optical attenuators (VOA). A VOA is a device that can attenuate the intensity or power level of an input optical beam to produce an output optical beam with controlled intensity. It is an essential component in telecommunication system involving the wavelength-division multiplexing (WDM) technology because it can flatten signal variations caused by changes in source power, amplifier gain and other components^{89 - 91}. Various types of VOA devices have been developed and operate in different mechanisms, such as sliding-block mechanical devices⁸⁹ and thermo-optic systems^{90, 91}.

A new concept transmissive VOA has been proposed⁹², which is based on the use of NIR electrochromic materials to absorb or attenuate the NIR light and thus called electrochromic variable optical attenuator (ECVOA, Figure I.7). It composes one NIR electrochromic material coated on a transparent electrode like indium doped tin oxide (ITO) glass with opposite electrochromic behavior (DCH-Ru and WO_3), separated by a thin layer of gel electrolyte. When electrons are injected to the cathodically electrochromic material (WO_3), it will under to reduction to turn “colored” at 1550 nm. At the same time, the anodically electrochromic material (DCH-Ru) will undergo oxidation to become “colored” and thus the light will be absorbed or attenuated. By switching the bias, both materials change to the “bleached” states and the light will then be allowed to pass. Compared to some known VOAs, advantages of ECVOA include possible integration with other optical devices on one planar substrate, low-cost

fabrication, low operation voltage (e.g., 2 V) and large dynamic range of attenuation (e.g., 10-50 dB). For commercial application of ECVOA, electrochromic materials should have the following features: high contrast ratio (percent transmittance change between bleached and colored state) at the telecommunication wavelengths, high color efficiency, low cost in preparation, good processibility, fast switching time and long-time stability.

Figure I.7. Concept design of transmissive ECVOA.

I.6. Rationale and Objectives

Although the DCH-based dinuclear ruthenium complexes have shown some good properties as NIR electrochromic materials, they are still not suitable for application in solid devices. Thus, by incorporating DCH-Ru active component in the film-forming polymers, applications of these NIR electrochromic materials in solid devices should be realized. Accordingly, this research will mainly focus on exploration of different ways of incorporating the DCH-Ru complexes into various polymeric systems. Three strategies for making DCH-Ru film-forming materials can be envisioned: doping DCH-Ru into crosslinked polymer host, complexation with DCH-containing polymers and

polymerization of functionalized DCH-Ru monomers. Therefore, the objectives of this research are:

1. To prepare [G]-1 dendric DCH ligands and their ruthenium complexes with a higher ruthenium content in order to improve the extinction coefficient at 1550 nm and to study the electronic/optical properties-structure relationships;
2. To evaluate the attenuation performance of ECVOA based on [G]-1 dendric DCH-Ru complexes;
3. To prepare and study polymeric DCH-Ru complexes though polymeric ligand containing hydrazinedicarboxamide (-NH-DCH-NH-);
4. To synthesize the DCH-Ru polymers from A-B and AA-BB types of monomers and to evaluate optical attenuation of the resulting polymers at 1550 nm.

References

1. Yang, R. Q.; Tian, R. Y.; Yan, J. A.; Zhang, Y.; Yang, J.; Hou, Q.; Yang, W.; Zhang, C.; Cao, Y. *Macromolecules* **2005**, 38, 244.
2. Brabec, C. J.; Winder, C.; Sariciftci, N. S.; Hummelen, J. C.; Dhanabalan, A.; van Hal, P. A.; Janssen, R. A. J. *Adv. Funct. Mater.* **2002**, 12(10), 709.
3. McDonagh, M. A.; Bayly, S. R.; Riley, D. J.; Ward, M. D.; McCleverty, J. A.; Cowin, M. A.; Morgan, C. N.; Varrazza, R.; Penty, R. V.; White, I. H. *Chem. Mater.* **2000**, 12, 2523.
4. Hilderbrand, S. A.; Kelly, K. A.; Weissleder, R.; Tung, C. H. *Bioconjugate Chem.* **2005**, 16, 1275.
5. Chandrasekhar, P.; Zay, B. J.; McQueeney, T.; Scara, A.; Ross, D.; Birur, G. C.; Haapanen, S.; Kauder, L.; Swanson, T.; Douglas, D. *Synth. Met.* **2003**, 135–136, 23.
6. Tung, C.; Lin, Y.; Moon, W.; Weissleder, R. *ChemBioChem* **2002**, 3, 784.
7. Greenberg, C. B. *Thin Solid Films* **1994**, 251, 81.
8. Anaissi, F. J.; Demets, G. J. F.; Toma, H. E. *ElectroChem. Commun.* **1999**, 1, 332.
9. Wang, Z. Y.; Zhang, J. D.; Wu, X. G.; Birau, M.; Yu, G. M.; Yu, H. A.; Qi, Y. H.; Desjardins, P.; Meng, X. S.; Gao, J. P.; Todd, E.; Song, N. H.; Bai, Y. W.; Beaudin, A. M. R.; LeClair, G. *Pure Appl. Chem.* **2004**, 76(7–8), 1435.
10. Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. *Electrochromism: Fundamentals and Application*, VCH Weinheim, **1995**.
11. Somani, P. R.; Radhakrishnan, S. *Mater. Chem. Phys.* **2002**, 77, 117.
12. Wolff, J. J.; Wortmann, R. *Adv. Phys. Org. Chem.* **1999**, 32, 121.
13. Mortimer, R. J. *Chem. Soc. Rev.* **1997**, 26, 147.

14. Mortimer, R. J. *Electrochim. Acta* **1999**, 44, 2971.
15. Mortimer, R. J.; Dyer, A. L.; Reynolds, J. R. *Displays* **2006**, 27, 2.
16. Hünig, S.; Kemmer, M.; Wenner, H.; Perepichka, I. F.; Bäuerle, P.; Emge, A.; Gescheid, G. *Chem. Eur. J.* **1999**, 5(7), 1969.
17. Lambert, C.; Nöll, G. *J. Am. Chem. Soc.* **1999**, 121, 8434.
18. Lambert, C.; Nöll, G. *Chem. Eur. J.* **2002**, 8(15), 3467.
19. Lee, C.; Lee, Y. M.; Moon, M. S.; Park, S. H.; Park, J. W.; Kim, K. G.; Jeon, S. H. *J. Electroanal. Chem.* **1996**, 416, 139.
20. Penneau, J. F.; Stallman, B. J.; Kasai, P. H.; Miller, L. L. *Chem. Mater.* **1991**, 3, 791.
21. Almlöf, J.; Jozefiak, T. H.; Feyereisen, M. W.; Miller, L. L. *J. Am. Chem. Soc.* **1990**, 112, 1206.
22. Fiedler, J.; Zali, S. T.; Klein, A.; Hornung, F.; Kaim, W. *Inorg. Chem.* **1996**, 35, 3039.
23. Demol, F.; De Backer, M. G.; Levillain, E.; Sauvage, F. X. *Spectrochim. Acta A* **2001**, 57, 1611.
24. Ichimura, A. S.; Xie, Q.; Szajek, L. P.; Lema, J.; Burns, A.; Huang, R. H.; Jackson, J. E.; Dye, J. L.; Demol, F.; Sauvage, F. X.; De Backer, M. G. *J. Phys. Chem. A* **2000**, 104, 3038.
25. Fabian, J.; Nakazumi, H.; Matsuka, M. *Chem. Rev.* **1992**, 92, 1197.
26. Fabian, J. *J. Prakt. Chem.* **1991**, 333(2), 197.
27. Bulschel, M.; Ajayaghosh, A.; Arunkumar, E.; Daub, J. *Org. Lett.* **2003**, 5(17), 2975.

28. Perepichka, D. F.; Bryce, M. R.; Batsanov, A. S.; McInnes, E. J. L.; Zhao, J. P.; Farley, R. D. *Chem. Eur. J.* **2002**, 8(20), 4656.
29. Lenhard, J. R.; Hein, B. R. *J. Phys. Chem.* **1996**, 100, 17287.
30. Miller, L. L.; Zhong, C. J.; Kasai, P. *J. Am. Chem. Soc.* **1993**, 115, 5982.
31. Ichimura, A. S.; Xie, Q.; Szajek, L. P.; Lema, J.; Burns, A.; Huang, R. H.; Jackson, J. E.; Dye, J. L.; Demol, F.; Sauvage, F.-X.; DeBacker, M. G. *J. Phys. Chem. A* **2000**, 104, 3038.
32. Lenhard, J. R.; Parton, R. L. *J. Am. Chem. Soc.* **1987**, 109, 5808.
33. Parton, R. L.; Lenhard, J. R. *J. Org. Chem.* **1990**, 55, 49.
34. Lenbard, J. R.; Cameron, A. D. *J. Phys. Chem.* **1993**, 97, 4916.
35. Akahoshi, H.; Toshima, S.; Itaya, K. *J. Phys. Chem.* 1981, 85, 818.
36. Zhang, S. S.; Sha, Q. Q. *Solid State Ionics* **1993**, 59, 179.
37. Ryu, J.-H.; Shin, D.-O.; Suh, K.-D. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, 43, 6562.
38. Nakano, T.; Yade, T. *Chem. Lett.* **2008**, 37(3), 258.
39. Moliton, A.; Hiorns, R. C. *Polym. Int.* **2004**, 53, 1397.
40. Unur, E.; Jung, J. H.; Mortimer, R. J.; Reynolds, J. R. *Chem. Mater.* **2008**, 20, 2328.
41. Kumar, A.; Welsh, D. M.; Morvant, M. C.; Piroux, F.; Abboud, K. A.; Reynolds, J. R. *Chem. Mater.* **1998**, 10, 896.
42. Sapp, S. A.; Sotzing, G. A.; Reynolds, J. R. *Chem. Mater.* **1998**, 10, 2101.
43. Thompson, B. C.; Schottland, P.; Zong, K.; Reynolds, J. R. *Chem. Mater.* **2000**, 12, 1563.
44. Sonmez, G.; Meng, H.; Wudl, F. *Chem. Mater.* **2003**, 15, 4923.

45. Roncali, J. *Chem. Rev.* **1997**, 97, 173.
46. Sonmez, G.; Shen, C. K. F.; Rubin, Y.; Wudl, F. *Angew. Chem. Int. Ed.* **2004**, 43, 1497.
47. Hyodo, K. *Electrochim. Acta* **1994**, 39(2), 265.
48. Somani, P.; Mandale, A. B.; Radhakrishnan, S. *Acta Mater.* **2000**, 48, 2859.
49. Mortimer, R. J.; Sonmez, G. *Chem. Commun.* **2005**, 5251.
50. Li, Y. F.; Yan, B. Z.; Yang, J.; Cao, Y.; Qian, R. Y. *Synth. Met.* **1988**, 25, 79.
51. Monkman, A. P.; Bloor, D.; Stevens, G. C.; Stevens, J. C. H.; Wilson, P. *Synth. Met.* **1989**, 29(1), E277.
52. Watanabe, A.; Mori, K.; Iwabuchi, A.; Iwasaki, Y.; Nakamura, Y.; Ito, S. *Macromolecules* **1989**, 22, 3521.
53. Mortimer, R. J. *J. Mater. Chem.* 1995, 5, 969.
54. Chung, T. C.; Kaufman, J. H.; Heeger, A. J.; Wudl, F. *Phys. Rev. B* **1984**, 30(2), 702.
55. Tourillon, G.; Garnier, F. *J. Electrochem. Soc.* **1983**, 130(10), 2042.
56. Leclerc, M.; Faid, K. *Adv. Mater.* **1997**, 9(14), 1087.
57. Chan, H. S. O.; Ng, S. C. *Prog. Polym. Sci.* **1998**, 23(7), 1167.
58. Reference 9a in Groenendaal, L. B.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Mater.* **2000**, 12(7), 481.
59. Kanazawa, K. K.; Diaz, A. F.; Gill, W. D.; Grant, P. M.; Street, G. B.; Gardini, G. P.; Kwak, J. F. *Synth. Met.* **1986**, 3, 329.
60. Gaupp, C. L.; Zong, K.; Schottland, P.; Thompson, B. C.; Thomas, C. A.; Reynolds, J. R. *Macromolecules* **2000**, 33, 1132.

61. Schottland, P.; Zong, K.; Gaupp, C. L.; Thompson, B. C.; Thomas, C. A.; Giurgiu, I.; Hickman, R.; Abboud, K. A.; Reynolds, J. R. *Macromolecules* **2000**, 33, 7051.
62. Reference 27, 28 in Walczak, R. M.; Reynolds, J. R. *Adv. Mater.* **2006**, 18, 1121.
63. Walczak, R. M.; Reynolds, J. R. *Adv. Mater.* **2006**, 18, 1121.
64. Roncali, J. *Macromol. Rapid Commun.* **2007**, 28, 1761.
65. Bundgaard, E.; Krebs, F. C. *Sol. Energy Mater. Sol. Cells* **2007**, 91, 954.
66. Durmus, A.; Gunbas, G. E.; Toppare, L. *Chem. Mater.* **2007**, 19, 6247.
67. Groenendaal, L. B.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Mater.* **2000**, 12(7), 481.
68. Schrauzer, G. N.; Mayweg, V. P. *J. Am. Chem. Soc.* **1962**, 84, 3221.
69. Mueller-Westerhof, U. T.; Vance, B.; Yoon, D. I. *Tetrahedron* **1991**, 47, 909.
70. Aragoni, M. C.; Arca, M.; Cassano, T.; Denotti, C.; Devillanova, F. A.; Isaia, F.; Lippolis, V.; Natali, D.; Nitti, L.; Sampietro, M.; Tommasi, R.; Verani, G. *Inorg. Chem. Commun.* **2002**, 5, 869.
71. Robertson, N.; Cronin, L. *Coord. Chem. Rev.* **2002**, 227, 93.
72. Deplano, P.; Mercuri, M. L.; Pintus, G.; Trogu, E. F. *Comments Inorg. Chem.* **2001**, 22(6), 353.
73. Ward, M. D. *Chem. Soc. Rev.* **1995**, 24, 121.
74. Joulié, L. F.; Schatz, E.; Ward, M. D.; Weber, F.; Yellowlees, L. J. *J. Chem. Soc. Dalton Trans.* **1994**, 799.
75. Barthram, A. M.; Cleary, R. L.; Kowallick, R.; Ward, M. D. *Chem. Commun.* **1998**, 2695.
76. Bayly, S. R.; Humphrey, E. R.; de Chair, H.; Paredes, C. G.; Bell, Z. R.; Jeffery, J.

- C.; McCleverty, J. A.; Ward, M. D.; Totti, F.; Gatteschi, D.; Courric, S.; Steele, B. R.; Screttas, C. G. *J. Chem. Soc., Dalton Trans.* **2001**, 1401.
77. McDonagh, A.; Bayly, S. R.; Riley, D. J.; Ward, M. D.; McCleverty, J. A.; Cowin, M. A.; Morgan, C. N.; Varrazza, R.; Penty, R. V.; White, I. H. *Chem. Mater.* **2000**, 12, 2523.
 78. Allen, C. C.; Hush, N. S. *Prog. Inorg. Chem.* **1967**, 8, 357.
 79. Hush, N. S. *Prog. Inorg. Chem.* **1967**, 8, 391.
 80. Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, 95, 1086.
 81. Laye, R. H.; Couchman, S. M.; Ward, M. D. *Inorg. Chem.* **2001**, 40, 4089.
 82. Colin, J.-P.; Lainé, P.; Launay, J.-P.; Sauvage, J.-P.; Sour, A. *J. Chem. Soc. Chem. Commun.* **1993**, 434.
 83. Fürholz, U.; Joss, S.; Bürgi, H. B.; Ludi, A. *Inorg. Chem.* **1985**, 24, 943.
 84. Moreira, I. S.; Franco, D. W. *J. Chem. Soc. Chem. Commun.* **1992**, 450.
 85. Moreira, I. S.; Franco, D. W. *Inorg. Chem.* **1994**, 33, 1607.
 86. Beley, M.; Chodorowski-Kimmes, S.; Collin, J.-P.; Lainé, P.; Launay, J.-P.; Sauvage, J.-P. *Angew Chem. Int. Ed. Eng.* **1994**, 33, 1775.
 87. Kaim, W.; Kasack, V.; Binder, H.; Roth, E.; Jordanov, J. *Angew. Chem., Int. Ed. Eng.* **1988**, 27, 1174.
 88. Qi, Y. H.; Desjardins, P.; Wang, Z. Y. *J. Opt. A Pure Appl. Opt.* **2002**, 4, S273.
 89. Barber, B.; Giles, C. R.; Askuk, V.; Ruel, R.; Stulzl, L.; Bishop, D. *IEEE Photonics Technol. Lett.* **1998**, 10, 1262.
 90. Kawai, T.; Koga, M.; Okuno, M.; Kitoh, T. *Electron. Lett.* **1998**, 34, 264.
 91. Jin, Y. S.; Lee, S. S.; Son, Y. S. *Electron. Lett* **1999**, 35, 916.

92. Qi, Y. H.; Wang, Z. Y. *Macromolecules* **2003**, 36, 3146.

Chapter II Design, Synthesis and Application of [G]-1 DCH-Ru Complexes

II.1 Introduction

A variable optical attenuator (VOA) is a device that can attenuate the intensity of an input optical beam to produce an output optical beam with controlled intensity¹⁻³. It's a key component in wavelength-division multiplexing (WDM) technology, in which multiple wavelengths are multiplexed on a single optical fiber. Development of VOA operated in the NIR region, especially at 1310 nm and 1550 nm, has drawn a great deal of research in fibre-optic telecommunications, in which silica fibers are used to transmit optical data with a minimal optical loss. NIR VOA devices have been fabricated based on various mechanisms such as electrochromic⁴, micro-electro mechanic^{5,6}, liquid crystal⁷⁻⁹ and thermo-optic^{10,11} attenuators. Among these VOA devices, electrochromic VOA (ECVOA) has the advantages of low driving voltage, ease of fabrication, ease of integration in optical fiber system and a minimum amount of moving parts, which can meet the current challenges to fabricate low-power consuming, flexible, lightweight and inexpensive VOA devices.

EC materials which are active in the NIR region are thus of interest to be explored. Due to the low density, higher color contrast, thermal stability and electrochemical stability upon cycling, NIR-active organic EC materials, typically conducting polymers like poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives, can well serve this purpose. However, most interest in EC materials has been directed to optical change in the visible region with the applications as tunable windows¹², variable-reflectance

mirrors¹³ and EC displays¹⁴, etc. Only recently did the PEDOT-based ECVOA begin to be reported from our group and other groups¹⁵⁻¹⁷.

As one group of NIR-active materials, metal complexes, especially dinuclear and polynuclear complexes, also received much attention in this field for several reasons. Firstly, reversible electrochromism is the intrinsic feature for most metal complexes. Secondly, they exhibit high color contrast in the NIR region upon oxidation or reduction. Thirdly, their redox potentials are generally lower than 3 V. Fourthly, the absorption band can be well controlled by structural modification. Finally, they can form high-quality thin films, with proper structural modification or polymerization, on electrodes. The reported NIR electrochromic metal complexes include ruthenium dioxolene complexes¹⁸, tris(pyrazolyl)borato-molybdenum complexes¹⁹ and mixed-valence dinuclear ruthenium complexes²⁰⁻²².

It's known that dinuclear metal complexes with a significant metal-metal electronic coupling can show an intervalence charge transfer (IVCT) transition, or metal-to-metal charge transfer (MMCT) transition, from the metal donor to the metal acceptor²³. This transition often occurs in the long-wavelength region due to the low energy transition. The early work by Kaim et al. shows that the mixed-valence dinuclear ruthenium complexes based on dicarbonylhydrazine (DCH) and 2,2'-bipyridine (bpy) ligands are highly electrochromic in the NIR region^{20, 21}, which makes them excellent candidates for use as NIR electrochromic materials in devices. Extensive studies on the novel dinuclear ruthenium complexes (DCH-Ru) have been carried out in our group in the past few years. A series of dinuclear DCH-Ru complexes bearing various donor and acceptor groups have been prepared²⁴. DCH-Ru complexes with weak electron-donating

substituents (e.g., phenyl, alkyl, and phenoxy) are proposed to be the most promising materials for use in variable optical attenuator (VOA) for their strong electrochromism at the telecommunication band of 1550 nm.

In this chapter, a series of [G]-1 (hexanuclear) DCH-Ru complexes having a benzene core are proposed. The synthesis, property and ECVOA application of a series of [G]-1 DCH-Ru complexes are described. Some advantages are expected from the dendric structure. The most desirable feature of such a dendric structure should be the capability to undergo cross-linking reaction to produce good films with high resistance to solvent and thermal degradation if a reacting group is attached to each end. A slightly higher molar extinction coefficient is expected compared to monomeric dinuclear ruthenium species due to the slightly higher ratio of ruthenium content to the overall molecular weight. In addition, rapid ion transportation is expected in a crosslinked film due to its larger free volume, which will allow for a faster switching in VOA.

II.2 Synthesis and Characterization of [G]-1 DCH-Ru complexes

The [G]-1 ligands **II.1-5** were synthesized according to a previous procedure,²⁵ from the reaction of 1,3,5-benzenetricarboxylic acid trichloride with three equivalents of the corresponding hydrazides in 53-85% yield (Table II.1). The corresponding hexanuclear ruthenium complexes were prepared using the similar procedure in literature²¹, by reacting *cis*-Ru(bpy)₂Cl₂·2H₂O with a [G]-1 ligand under a basic condition in methanol/water (Table II.1). The complexes were purified by column chromatography on acidic aluminum oxide with acetonitrile as the eluent and 45 - 56% yield was obtained.

Table II.1. Syntheses of 1,3,5-benzenetris(2'-substituted carbohydrazides) II.1-5 and the corresponding DCH-Ru complexes II.(1-5)-Ru.

Ligand	R	Yield %	M.P. / °C	Complex	Yield %
II.1	-C ₅ H ₁₀ OH	53	218-219	II.1-Ru	45
II.2	-PhOCH ₃	85	180-182	II.2-Ru	55
II.3	-PhOH	61	284-286	II.3-Ru	50
II.4	-Ph	75	307-309	II.4-Ru	56
II.5	-PhNO ₂	72	217-218	II.5-Ru	48

The structures of the ligands were characterized by IR, 1H NMR and ^{13}C NMR.

As shown in figure II.1, the IR bands at around 3250 cm^{-1} , 1650 cm^{-1} and $1600 - 1500\text{ cm}^{-1}$ are assigned to N-H, C=O and aromatic C=C, respectively. The IR spectra of the corresponding ruthenium complexes show the absence of the N-H stretch at 3250 cm^{-1} . The new band at 840 cm^{-1} is from the P-F stretching vibration of the PF_6^- counter ion. The peaks of carbonyl carbons of these ligands in the ^{13}C NMR spectra appear in the range 171.1 - 164.9 ppm and the chemical shift of C-2 in ligand **II.1** (structures in Table II.1)

exhibits a strong dependence on the nature of the substituent R. Due to the highest electron-donating ability, the C-2 has the highest chemical shift at 171.1 ppm.

Figure II.1. IR spectra of ligands II.1-5 (KBr pellets).

II.3 Electrochemical Properties

CV experiments were performed in 0.1M TBAH/acetonitrile solution at a scanning rate of 200 mV/s and the representative result of **II.4-Ru** was shown in figure II.2. The electrochemical data for the DCH-Ru complexes, along with comproportionation constants K_c are given in table II.2, and a representative cyclic voltamogram (CV) of **II.4-Ru** (R = Ph) is shown in figure II.2. Each dendritic complex exhibits two quasi-reversible redox couples in the positive potential region like a dinuclear DCH-Ru complex, which can be assigned to two three-electron oxidation steps: $3(\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}}) \rightarrow 3(\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}) \rightarrow 3(\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}})$. This result suggests there is no electron delocalization among the three dinuclear-complex moieties. As the average donor strength of the substituent decreases, both the first (E_1) and second half-wave oxidation potentials (E_2) shift anodically. The

difference between two oxidation potentials (ΔE), also an indicator of the stability of the mixed-valence species, is not greatly affected by the substituents because of the synchronous shifts of E_1 and E_2 . However, ΔE values do show a dropping trend over the series with the increasing donor strength.

Figure II.2. CV of II.4-Ru ($R = \text{Ph}$) in 0.1 M TBAH/ACN (scanning rate of 200 mv/s).

Table II.2. Electrochemical oxidative potentials of complexes in 0.1M TBAH/ACN solution (scanning rate of 200 mv/s).

Complex	R	E_1/mV	E_2/mV	$\Delta E/\text{mV}$	K_c^a	δ^*
II.1-Ru	$\text{C}_5\text{H}_{10}\text{OH}$	597	1183	586	8.1×10^9	-0.18
II.2-Ru	$p\text{-PhOMe}$	620	1182	562	3.1×10^9	-0.09
II.3-Ru	$p\text{-PhOH}$	631	1235	604	1.6×10^{10}	-0.06
II.4-Ru	Ph	645	1238	593	1.1×10^{10}	-0.02
II.5-Ru	$p\text{-PhNO}_2$	747	1369	622	3.2×10^{10}	0.25

^a $K_c = 10^{16.91\Delta E}$

The relationship between the oxidation potential and the electron-donating strength of constituents can be depicted by employing the Hammett parameter as it provides a direct measurement of the strength of an electron donor²⁶. The Hammett parameters are calculated according to the following equation:

$$\sigma^* = {}^1\sigma_p + {}^2\sigma_p \quad (1)$$

where ${}^1\sigma_p$ and ${}^2\sigma_p$ are the Hammett parameters of the substituent R and R', respectively.

As approximation, the phenyl core was served as one substituent. The calculated σ^* values are listed in table 2 and the plots of σ^* value vs E_1 and E_2 are shown in figure II.3. The plot clearly shows a linear dependence of the electrochemical properties of [G]-1 DCH-Ru complexes on Hammett parameters like dinuclear DCH-Ru complexes²⁴. Hence, by selecting proper substituent, the [G]-1 DCH-Ru complex with the desired ΔE can be achieved.

Figure II.3. Relationship between the total Hammett parameter and redox potentials (• E_1 , ○ E_2).

II.4 UV-vis-NIR Spectroscopic Properties

The electronic spectra of a representative [G]-1 DCH-Ru complex (**II.4-Ru**) at different oxidation states in acetonitrile (ACN) with tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte are shown in figure II.4, and the spectroelectrochemical data of the five complexes are listed in table II.3.

Figure II.4. UV-vis-NIR spectra of DCH-Ru complex 2d (R = Ph) at different oxidation states in 0.1 M TBAH/ACN.

At $\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}}$ state, the absorption bands around 350 nm and 510 nm are assigned to $d(\text{Ru}^{\text{II}}) \rightarrow \pi^*(\text{bpy})$, metal-to-ligand charge transfer (MLCT) transitions. When oxidized to $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$, a broad (from 1000 nm to over 2000 nm) and intense ($10^4 \text{ M}^{-1} \text{ cm}^{-1}$) appears with peak values ranging from 1540 to 1616 nm, which is attributed to the intervalence transitions, either from metal-to-metal charge transfer (MMCT) transition (localized situation) or different combinations of metal-centered molecular orbitals (delocalized situation)²¹. Due to the little bathochromic shift and high intensity of the NIR band, this transition has been largely attributed to a delocalized situation²¹. It is also

noticed that the absorption maximum of this band shifts to a shorter wavelength upon increasing the donor effect of the substituent, which can be explained by the hole transfer mechanism proposed by Kaim²¹. The effect of increasing the electron density in the bridge is to destabilize Ru^{II} and stabilize Ru^{III}, resulting in the increase of the energy gap between donor and acceptor metals. At Ru^{III}/Ru^{III} state, the bands around 800 nm are assigned to DCH-centred $\pi(\text{DCH})^{2-} \rightarrow d(\text{Ru}^{\text{III}})$, ligand-to-metal charge transfer (LMCT) transition.

As shown in table II.3, the DCH-Ru complexes with weak donating-strength substituent (**II.1-5**) can all be considered as the suitable materials for use in ECVOA as the maxima of their MMCT bands are close to the telecommunication wavelength of 1550 nm.

Table II.3. Optical data of complexes at different oxidative states.

Complex	R	$\lambda_{\text{max}} / \text{nm} (\log [\epsilon / \text{M}^{-1}\text{cm}^{-1}])$		
		Ru ^{II} /Ru ^{II}	Ru ^{II} /Ru ^{III}	Ru ^{III} /Ru ^{III}
II.1-Ru	C ₅ H ₁₀ OH	353(4.42), 510(4.36)	448(4.20), 1540(4.10)	804(4.10)
II.2-Ru	<i>p</i> -PhOMe	362(4.50), 502(4.37)	456(4.30), 1579(4.12)	817(3.96)
II.3-Ru	<i>p</i> -PhOH	354(4.42), 505(4.31)	428(4.21), 1600(4.12)	809(3.99)
II.4-Ru	Ph	353(4.49), 517(4.39)	450(4.32), 1590(4.17)	809(3.99)
II.5-Ru	<i>p</i> -PhNO ₂	354(4.43), 497(4.37)	455(4.28), 1616(4.12)	793(3.84)

II.5 NIR Electrochromic Variable Optical Attenuator

II.5.1 Single-Layer Device

Compared to previously studied dinuclear DCH-Ru complexes²⁴, [G]-1 DCH-Ru complexes have some similar properties such as strong NIR absorption around 1550 nm,

large K_c ($\sim 1 \times 10^{10}$) and relative low potential (450 – 600 mv vs NHE) for the first oxidation. They possess relatively higher molar extinction coefficient and are capable of forming a crosslinked network, which make them readily applicable in a solid device.

A simple single-layer ECVOA device was fabricated by cross-linking **II.1-Ru** with triisocyanate to form a film on an ITO electrode. The crosslinked film was inert to common organic solvents such as acetone, acetonitrile and DMF without noticeable leaching after 24 hours. The crosslinked film (thickness = 400 ± 10 nm) displays the same electrochemical and electrochromic behaviors as its dendritic complex. In a cell, the crosslinked film coated on ITO glass was switched between + 700 mv to + 1200 mv versus silver electrode in 0.1 M TBAH/ACN solution.

Typically, two parameters, attenuation and switching time, are used to evaluate the performance of an ECVOA. Attenuation is the transmittance difference between bleached and colored state, which is calculated by the equation (2):

$$A = 10 \times \log(T_b/T_c) \quad (2)$$

where A is the attenuation in dB, T_b is the transmittance of the bleached state and T_c is the transmittance of the colored or NIR-absorbing state. Switching speed is the time required to achieve the conversion between the two states. At a switching speed of 2 s for 90% conversion, a maximum attenuation of 2.0 dB at 1550 nm was achieved, which translates to an intrinsic attenuation value of 4.9 dB/ m for the film. When the switching speed was set at 3s, a full conversion was reached, leading to a maximum attenuation of 2.7 dB or 6.8 dB/ m for the film.

Color efficiency (CE) is another key parameter to evaluate an EC device. It is determined by the injected/ejected charge per unit electrode area (ΔQ) and the change in

optical density (ΔOD) during a redox step of the device. The CE at the specified wavelength is expressed as²⁷:

$$CE(\lambda) = \Delta OD(\lambda) / \Delta Q = \log(T_b/T_c) / \Delta Q \quad (2)$$

A high CE value means that the device can provide a large optical modulation with a small charge insertion or ejection. It is a crucial parameter for practical EC devices because long-term cycling stability may be enhanced by using a lower charge insertion or ejection rate. The electrochromic efficiency at 1550 nm of the crosslinked film was measured to be 238 cm²/C. This value is higher than some known electrochromic materials²⁸.

II.5.2 Hybrid Single-Layer Device

For practical applications, the attenuation range of a VOA is required to be more than 20 dB. A single layer device based on the film of **II.1-Ru** is thus not suitable for its low intrinsic attenuation power (6.8 dB/ μ m). Although a thicker film can increase the attenuation range, it will result in a lower switching speed due to longer ion diffusion time. A solution is to combine a cathodic coloring material with the anodic [G]-1 DCH-Ru material to form a double-layer device. Tungsten oxide (WO₃) is a suitable cathodic EC material with a long-term stability, broad NIR absorption and high coloration efficiency²⁹. However, the low CE of thin film of [G]-1 DCH-Ru complex can not match the high CE and high charge density of polycrystalline thin film of WO₃³⁰. Hence, we designed a hybrid single-layer device with WO₃ on an electrode and the ruthenium complex in an electrolyte solution to solve the problem of mismatch.

Figure II.5. NIR ECVOA device configuration.

The configuration of the hybrid ECVOA device is shown in figure II.5. Complex **II,4-Ru** was selected for its highest molar extinction coefficient ($1.41 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). The electrolyte solution was made of 0.1 M LiClO₄ in propylene carbonate (PC). For a comparison, a NIR-inactive EC material, ferrocene (Fc), was also used in another ECVOA device. The WO₃ film can be made by electrodeposition, sol-gel, CVD, vacuum vapor deposition and sputtering methods³¹. The WO₃ coated ITO glass was made by vacuum vapor deposition. Figure II.6 shows the X-ray pattern of WO₃ on ITO glass and blank ITO glass. The three peaks at 21.3°, 30.3° and 35.3° belong to the (200), (201), (221) planes of WO₃ film, which is in line with reference for polycrystalline WO₃³².

Figure II.6. The X-ray pattern of ITO/WO₃ and blank ITO glass.

Figure II.7. The relation between the applied voltage and attenuation at 1550 nm of device A: ITO / WO₃ / Fc / ITO (■) and B: ITO / WO₃ / DCH-Ru / ITO (●).

Figure II.7 illustrates the relation between the applied voltage and the optical attenuation at 1550 nm of devices A (ITO / WO₃ / Fc / ITO) and B (ITO / WO₃ / DCH-Ru / ITO). Ferrocene was used as a blank reference to show the effect of DCH-Ru on device performance because it has no NIR absorption. Under 0.5 V, the attenuation of devices A and B is 1.3 dB and 0.7 dB, respectively. They are almost the same because under 0.5 V, the [G]-1 DCH-Ru complex can not be electrochemically oxidized to its Ru^{II}/Ru^{III} state that has NIR absorption at 1550 nm. When the applied voltage is higher than 0.5 V, the attenuation ranges of both devices increase with the increase of voltage until they reach a plateau above 2.0 V where the attenuations of device A and B are 19.1 dB and 30.0 dB, respectively. These results demonstrate that the operation voltage of the device should not be lower than 2.0 V and the attenuation power of device B is about 50% larger than that of the ferrocene-containing device A. The transmittance vs time

curves of devices A and B under 2.0 V are shown in figure II.8. Both devices reach full response within 100 s and give the attenuation of 19.1 dB and 30.0 dB, respectively. The response times for both devices to reach 90% of total conversion are 2.5 s and 5.4 s, respectively.

The injected charge was measured to be 7.81×10^{-2} C and 2.97×10^{-2} C for devices A and B, respectively. With the active area of 1.2 cm^2 for each device, the charge densities are calculated to be $6.51 \times 10^{-2} \text{ C/cm}^2$ and $2.48 \times 10^{-2} \text{ C/cm}^2$ for devices A and B, respectively. Accordingly, with the measured ΔOD (at 1550 nm) of 1.91 and 3.01, the color efficiency of devices A and B are calculated to be $29.2 \text{ cm}^2/\text{C}$ and $121.2 \text{ cm}^2/\text{C}$, respectively. This shows that the ruthenium complex as a counter electrode NIR EC material contributes to larger optical attenuation and higher color efficiency in device B. The stability and reversibility of device B is evaluated by the long-term attenuating ability. After 18 cycles, the dynamic attenuation range dropped 9%, but kept steady afterwards.

Figure II.8. The transmittance vs time curves of devices A and B under 2.0V.

Because the electrochemical reduction of DCH-Ru complex is faster than electrochemical oxidation for this “rechargeable battery type of device”, the reduction voltage should be lower than the oxidation voltage. Otherwise, the time for electrochemical oxidation or NIR-color bleaching will be very long (several hours) and the device will show a poor reversibility.

II.6 Conclusion

In this work, a series of [G]-1 DCH-Ru complexes with excellent NIR electrochromic (~1550 nm) properties have been obtained. A fine tuning of the electrochemical and optical properties of the complexes has been achieved by changing the electron-donating nature of the substituents. The electrochemical properties that are affected by the substituents are correlated well using the Hammett parameters. Two electrochromic VOA devices (simple and hybrid single-layer devices) have been demonstrated. The higher dynamic range of optical attenuation of the hybrid device indicates that the mismatch of the charge density between WO_3 and the crosslinked DCH-Ru complex film can be largely reduced by using relatively high concentration of DCH-Ru complex in solution. In a hybrid ECVOA, a dynamic attenuation range as high as 30 dB has been obtained.

II.7 Experimental Section

Materials

All the chemicals were purchased from Sigma–Aldrich Canada Ltd. and used as supplied. Spectroscopic grade acetonitrile was used in the UV–vis–NIR spectroscopy

and cyclic voltammetric measurements. *Cis*-Ru(bpy)₂Cl₂·2H₂O was prepared according to the literature method.³³ ITO glass was purchased from Delta Technology Company.

Synthesis of 6-Hydroxyhexanoic Hydrazide

To a solution of hydrazine hydrate (5 mL, 0.1 mol) in DMF (5 mL) was added ϵ -caprolactone (5.5 mL, 0.05 mol) dropwise at room temperature. After stirring for 1 h, the resultant white precipitate was collected by filtration and washed with hot acetone twice to give a white powder (5.8 g, 81% yield). mp 115-116 °C; ¹H NMR (200 MHz, DMSO-*d*₆): δ /ppm 8.90 (s, 1H), 4.35 (tri, 1H, *J* = 6.6 Hz), 4.12 (s, 2H), 3.36 (tri, 2H), 1.98 (tri, 2H, *J* = 7.5 Hz), 1.42 – 1.26 (m, 6H). IR (KBr, cm⁻¹): 3311 ($\nu_{\text{N-H}}$), 1642 ($\nu_{\text{C=O}}$), 1536.6 ($\nu_{\text{N-H}}$); MS (ESI, *m/z*) found (nature of the peak, relative intensity): 147 (*M* + H⁺, 44).

General procedure for the preparation of [G]-1 ligands II.1-5

To a solution of one of the acid hydrazides (0.03 mol) and potassium carbonate (4.2 g, 0.03 mol) in 160 ml of water-THF (3:1) was added a solution of 1,3,5-benzenetricarboxylic acid trichloride (2.66 g, 0.01 mol) in THF (20 mL) with stirring. The reaction mixture was stirred for 1 - 3 h. The resulting solid was collected by filtration, washed with water and dried. Recrystallization from dimethylsulfoxide-water (1:1 in volume) gave the products as white powders.

1,3,5-Benzenetricarboxylic tris[2-(6-hydroxyhexano)hydrazide] (II.1)

IR (KBr, cm⁻¹): 3221 ($\nu_{\text{N-H}}$), 2937, 2862 ($\nu_{\text{C-H}}$), 1649 ($\nu_{\text{C=O}}$), 1612 ($\nu_{\text{C=C}}$), 1055 ($\nu_{\text{C-O}}$);

¹H NMR (300 MHz, DMSO-*d*₆) δ /ppm: 10.57 (s, 3H), 9.98 (s, 3H), 8.50 (s, 3H), 4.37 (s,

3H), 3.39 (tri, 6H, $J = 6$ Hz), 2.20 (tri, 6H, $J = 6$ Hz), 1.56 (m, 6H), 1.44 (m, 6H), 1.35 (m, 6H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ/ppm : 171.9, 164.9, 133.8, 130.0, 61.1, 33.8, 32.7, 25.6, 25.5; MS (ESI, m/z) found (nature of the peak, relative intensity): 595 ($\text{M} + \text{H}^+$, 1.2).

1,3,5-Benzenetricarboxylic tris[2-(4-Methoxybenzoyl)hydrazide] (**II.2**)

IR (KBr, cm^{-1}): 3255 ($\nu_{\text{N-H}}$), 1647 ($\nu_{\text{C=O}}$), 1608, 1500 ($\nu_{\text{C=C}}$), 1259 ($\nu_{\text{C-O}}$); m.p. ; ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ/ppm : 10.78(s, 3H), 10.51 (s, 3H), 8.64 (s, 3H), 7.94 (d, 6H, $J = 9$ Hz), 7.07(d, 6H, $J = 9\text{Hz}$), 3.84 (s, 9H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ/ppm : 165.7, 165.5, 162.6, 134.1, 130.1, 129.9, 125.0, 114.2, 55.9; MS (ESI, m/z) found (nature of the peak, relative intensity): 655 ($\text{M} + \text{H}^+$, 0.2).

1,3,5-Benzenetricarboxylic tris[2-(4-hydroxybenzoyl)hydrazide] (**II.3**)

IR (KBr, cm^{-1}): 3254 ($\nu_{\text{N-H}}$), 1647 ($\nu_{\text{C=O}}$), 1608, 1502 ($\nu_{\text{C=C}}$), 1267 ($\nu_{\text{C-N}}$); ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ/ppm : 10.73 (s, 3H), 10.38 (s, 3H), 10.25 (s, 3H), 8.63 (s, 3H), 7.82 (d, 6H, $J = 6$ Hz), 6.86 (d, 6H, $J = 6$ Hz); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ/ppm : 165.9, 165.5, 161.2, 134.1, 130.1, 130.0, 123.5, 115.5; MS (ESI, m/z) found (nature of the peak, relative intensity): 613 ($\text{M} + \text{H}^+$, 0.7).

1,3,5-Benzenetricarboxylic tris[2-benzoylhydrazide] (**II.4**)

IR (KBr, cm^{-1}): 3255 ($\nu_{\text{N-H}}$), 1649 ($\nu_{\text{C=O}}$), 1608, 1502 ($\nu_{\text{C=C}}$), 1267 ($\nu_{\text{C-N}}$); ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ/ppm : 10.87 (s, 3H), 10.67 (s, 3H), 8.66 (s, 3H), 7.96 (d, 6H, $J = 7.2$ Hz), 7.52 – 7.60 (m, 9H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ/ppm : 166.2, 165.4, 134.0,

132.9, 132.4, 130.2, 129.0, 128.0; MS (ESI, m/z) found (nature of the peak, relative intensity): 565 ($M + H^+$, 2.3).

1,3,5-Benzenetricarboxylic tris[2-(4-nitrobenzoyl)hydrazide] (**II.5**)

IR (KBr, cm^{-1}): 3254 ($\nu_{\text{N-H}}$), 1653 ($\nu_{\text{C=O}}$), 1600 ($\nu_{\text{C=C}}$), 1525, 1350 ($\nu_{\text{N-O}}$), 1263 ($\nu_{\text{C-N}}$); ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ /ppm: 11.03 (s, 6H), 8.67 (s, 3H), 8.40 (d, 6H, $J = 9$ Hz), 8.18 (d, 6H, $J = 9$ Hz); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ /ppm: 165.3, 164.7, 149.9, 138.5, 130.4, 129.5, 124.3; MS (ESI, m/z) found (nature of the peak, relative intensity): not found.

General procedure for the preparation of [G]-1 DCH-Ru complexes II.(1-5)-Ru

To a solution of [G]-1 ligand (0.063 mmol) and sodium carbonate (50 mg, 0.5 mmol) in a mixture of water/ethanol (5/1 v:v, 80 ml) were added 3 equivalents of *cis*- $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (0.20 g, 0.38 mmol) with stirring. The solution was heated to reflux for 48 h under argon. After cooling to room temperature, 1.00 g of ammonium hexafluorophosphate in 40 mL of water was added to afford red dark precipitate. The precipitate was filtered off, redissolved in acetone (20 mL) and precipitated into diethyl ether. The product was further purified by column chromatography with acetonitrile on acidic alumina and dried under vacuum.

Measurements

The NMR spectra were obtained at room temperature on a Varian Gemini 200 and a Bruker AMX-400 NMR spectrometer, using deuterated dimethylsulfoxide (DMSO- d_6) as solvents with 1% tetramethylsilane (TMS) as an internal standard. The chemical shifts were reported in δ (ppm) to TMS. IR spectra were recorded using KBr pellets of the compound and collected with an ABB Bomem Michelson-100 FT-IR spectrometer.

Cyclic voltammetry (CV) was performed using a BAS100B/W electrochemical station interfaced and monitored with a PC computer. The standard three-electrode configuration was composed by a platinum as working electrode, a platinum wire as counter electrode, and a silver wire as reference electrode. The silver pseudo-reference electrode was calibrated with a ferrocene/ferrocenium (Fc/Fc^+) redox couple, and the potentials were reported respect to the normal hydrogen electrode (NHE). tetra-*n*-butylammonium hexafluorophosphate (TBAH) in acetonitrile (0.1 M) as a supporting electrolyte was used for all electrochemical measurements. All the solutions were deoxygenated with argon prior to electrochemical measurements.

Spectroelectrochemical measurements were carried out by combining the electrochemical station with a Perkin Elmer Lambda 900 UV-vis-NIR spectrometer. The optical attenuation was monitored at 1550 nm. Spectroelectrochemistry in solutions was performed using an OTTLE cell.³⁴

Fabrication of Hybrid and Single-layer ECVOA Devices

The WO_3 film was vacuum deposited onto clean ITO glass under dynamic vacuum of 10^{-4} Pa. The film thickness is controlled by quartz oscillator to be about 300

nm. Then the film was annealed at 450 °C for 30 minutes to form a polycrystalline film. The structure of film was characterized by X-ray diffraction.

The optical attenuator is of transmittance type and fabricated as follows: The ITO/WO₃ glass and a clean ITO glass were assembled together with clips and a 125 μ m polyethylene sheet as spacer. Then the solution of ferrocene (Fc) or ruthenium complex (1.0 mM) was injected into the cell gap. The ECVOA device was characterized using BAS100B/W electrochemistry workstation and Perkin Lambda 900 UV-vis-NIR spectrometer. The spectrometer was used to measure the change of transmittance of the device under square wave or constant voltage applied by electrochemistry workstation.

References

1. Kawai, T.; Koga, M.; Okuno, M.; Kitoh, T. *Electron. Lett.* **1998**, 34, 263.
2. Barber, B.; Giles, C. R.; Askyuk, V.; Ruel, R.; Stulzl, L.; Bishop, D. *IEEE Photo. Technol. Lett.* **1998**, 10, 1262.
3. Jin, Y. S.; Lee, S. S.; Son, Y. S. *Electron. Lett.* **1998**, 35, 916.
4. Cowin, M. A.; Varrazza, R.; Morgan, C.; Penty, R. V.; White, I. H.; McDonagh, A. M.; Bayly, S.; Riley, J.; Ward, M. D.; McCleverty, J. A. *Trends Opt. Photonics* **2001**, 54, WR6/1.
5. Barber, B.; Giles, C. R.; Askyuk, V.; Ruel, R.; Stalz, L.; Bishop, D. *IEEE Photon. Technol. Lett.* **1998**, 10, 1262.
6. Ford, J. E.; Walker, J. A.; Greywall, D. S.; Goossen, K. W. *J. Lightwave Technol.* **1998**, 16, 1663.
7. Fan, Y. H.; Lin, Y. H.; Ren, H.; Gauza, S.; Wu, S. T. *Appl. Phys. Lett.* **2004**, 84, 1233.
8. Wu, Y. H.; Lin, Y. H.; Lu, Y. Q.; IDE, M.; Suguro, A.; Hosaka, Y.; Katsunuma, A.; Takahashi, K.; Shiraishi, A. *Opt. Review* **2004**, 11, 132.
9. Ren, Q. W.; Fan, Y. H.; Wu, J. R.; Wu, S. T. *Proc. SPIE* **2005**, 5936, 59360J/1.
10. Kawai, T.; Koga, M.; Okuno, M.; Kitoh, T. *Electron. Lett.* **1998**, 34, 264.
11. Lee, S. S.; Jin, Y. S.; Son, Y. S. *J. Lightwave Technol.* **1999**, 17, 2556.
12. Cui, H. N. ; Costa, M. F.; Teixeira, V.; Porqueras, I.; Bertran, E. *Surf. Sci.* **2003**, 532,1127.
13. Mortimer, R. J. *Chem. Soc. Rev.* **1997**, 26,147.
14. Pages, H.; Topart, P.; Lemordant, D. *Electrochim Acta* **2001**, 46, 2137.

15. Zhang, J. D.; Yu, H. A.; Wu, X. G.; Wang, Z. Y. *Opt. Mater.* **2004**, 27, 265.
16. Vergaz, R.; Barrios, D.; Sanchez-Pena, J. M.; Vazquez, C. Pozo-Gonzalo, C.; Mecerreyes, D.; Pomposo, J. *Proc. SPIE* **2005**, 5840, 389.
17. Grenier, C. R. G.; Reynolds, J. R. *Adv. Funct. Mater.* **2007**, 17, 1480.
18. Joulié, L. F.; Schatz, E.; Ward, M. D.; Weber, F.; Yellowlees, L. J. *J. Chem. Soc. Dalton Trans.* **1994**, 5, 799
19. Harden, N. C.; Humphrey, E. R.; Jeffery, J. C.; Lee, S. M.; Marcaccio, M.; McCleverty, J. A.; Rees, L. H.; Ward, M. D. *J. Chem. Soc. Dalton Trans.* **1999**, 15, 2417
20. Kaim, W.; Kasack, V.; Binder, H.; Roth, E.; Jordanov, J. *Angew. Chem., Int. Ed. Engl.* **1988**, 27, 1174.
21. Kasack, V.; Kaim, W.; Binder, H.; Jordanov, J.; Roth, E. *Inorg. Chem.* **1995**, 34, 1924.
22. Ward, M. D. *Chem. Soc. Rev.* **1995**, 24, 121.
23. Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, 95, 1086.
24. Qi, Y.; Desjardins, P.; Wang, Z. Y. *J. Opt. A: Pure Appl. Opt.* **2002**, 4, S273.
25. Tashtoush, H.; Subaihi, R.; Al-Talib, M. *Magn. Reson. Chem.* **1997**, 35, 549.
26. Hansch, C.; Leo, A. and Taft, R. W. *Chem. Rev.* **1991**, 91, 165.
27. Bange, K.; Gambke, T. *Adv. Mater.* **1990**, 2, 10.
28. Schwendeman, I.; Hwang, J.; Welsh, D. M.; Tanner, D. B.; Reynolds, J. R. *Adv. Mater.* **2001**, 13, 634.
29. Wang, Z. Y.; Zhang, J.; Wu, X.; Birau, M.; Yu, G.; Yu, H.; Qi, Y.; Desjardins, P.; Meng, X.; Gao, J. P.; Todd, E.; Song, N.; Bai, Y.; Beaudin, A. M. R.; LeClair, G.

- Pure Appl. Chem.* **2004**, 76, 1435.
30. Qi, Y. H.; Wang, Z. Y., *Macromolecules* **2003**, 36, 3146.
 31. Granqvist, C. G. *Electrochimica Acta* **1999**, 44, 3005.
 32. Sun, H. T.; Cantalini, C.; Lozzi, L.; Passacantando, M.; Santucci, S.; Pelino, M.
Thin Solid Films **1996**, 287, 258.
 33. Sullivan, B.; Salmon, D.; Meyer, T. *Inorg. Chem.* **1978**, 17, 3334.
 34. Kejecik, M.; Danek, M.; Hartl, H. J. *J. Electroanal. Chem.* **1991**, 317, 179.

Chapter III Synthesis and Characterization of Biurea-Ruthenium Complex Monomers, Dimers and Polymers

III.1 Introduction

A ligand polymer refers to a linear or branched polymer that is able to form complexes with metals. By complexation of ligand polymers, the complex polymers will have the physical, chemical and mechanical properties imparted by the metal complex and the polymer. Depending on the position of the ligand fragment in polymer, metal complexes can be introduced into a polymer chain as part of the main chain or pendent groups¹. As incorporation of metal complex in polymer main chain will greatly change photophysical properties of the polymer, the metal complex polymers generally find applications in optoelectronics such as OLED, transistors and solar cells.

As the complexation of a metallic compound with a ligand polymer can be conducted in the same manner as that to form a small complex, much effort of the research on this type of polymers has focused on the design of ligand polymers. The well known ligand has is widely used in metal-containing polymers is 2,2'-bipyridyl. Some of 2,2'-bipyridyl ligand polymers are shown in scheme III.1²⁻⁶. Bipyridyl ruthenium complexes are widely used and incorporated into polymers.

As for the DCH ligand we are interested in, it can be found as a component in a large number of potential ligand polymers, such as polyhydrazides^{7,8} and polybiureas⁹. The former can be prepared by treating the same molar equivalents of hydrazine or a dihydrazide and an acid chloride in *n*-methyl-2-pyrrolidone (NMP); the latter can be prepared from hydrazine and a diisocyanate (Scheme III.2).

Scheme III.1. (a) Poly(2,2'-bipyridine-5,5'-diyl),² (b) Copolymer with quarter(3-octylthiophene),³ (c) Copolymer with benzobisoxazole,⁴ (d) Polyamides,⁵ (e) Polyesters.⁶

Scheme III.2. General reaction routes to prepare (a) polyhydrazides and (b) polybiurea.

Aliphatic DCH-Ru polymers have been prepared from polyhydrazides in our lab¹⁰. Good films and high color efficiencies have been achieved from those polymers. However, due to their aliphatic structures, their thermal decomposition temperatures (5% wt. loss) are below 210 °C, which limits the use of these materials in high-temperature applications.

In this thesis work, the ligand polymers based on the aromatic biurea unit will be investigated (Scheme III.2). By design, the complex polymers are expected to have high thermal stability than those based on aliphatic hydrazides. Second, the fragment between each two DCH-Ru units may be oxidized to a conjugated bridge for electron/charge delocalization. Third, oxidation of the central diaminophenylene bridge may produce another electrochromic moiety in the product. Such potential properties make biurea-containing atomic polymers highly interesting to be explored. In addition to the polymer ligand, two model compounds, the monomer and dimer complexes were also designed.

Scheme III.3. Structures of monomeric, dimeric and polymeric complexes and their Ligands.

III.2 Results and Discussion

III.2.1 Complex Monomer

III.2.1.1 Synthesis and Characterization

The ligand, 1,6-diphenylbiurea, was synthesized by reacting two equivalents of phenyl isocyanate with 1 equivalent of hydrazine hydrate in THF. Its IR spectrum is characterized by strong bands at 3298 and 3222 cm^{-1} due to the two different NH groups. The C=O bending mode is found at 1670 cm^{-1} . In the ^1H NMR spectrum, the peaks at 8.79 and 7.98 ppm are assigned to the two biurea protons; those at 7.50, 7.25 and 6.95 ppm are ascribed to the protons from benzenes. In addition, five peaks in the ^{13}C NMR spectrum at 156.5, 140.1, 128.9, 122.1 and 119.0 ppm further confirm the structure.

The monomeric complex was prepared and purified following the procedure described previously. This complex appeared to be easily oxidized in the air, resulting in a low yield (10 %) for the product in the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ state. Its ^1N NMR spectrum was not obtained due to the existence of the paramagnetic Ru^{III} species.

III.2.1.2 Electrochemical Properties

The electrochemical properties were examined by cyclic voltammetry (CV). The CV in figure III.1 reveals three oxidation couples. The first two quasi-reversible couples at 0.22 and 0.78 V (vs. NHE) are assigned to the successive one-electron oxidation of the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}}$ to $\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}$. Because of the presence of two electron donors, oxidation potentials of the DCH-Ru moiety are quite low, making their $\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}}$ and $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ states unstable under ambient conditions. The one at the highest potential (~ 1.0 V) is due to the oxidation of the NH groups attached to benzenes. This value is comparable to the

oxidation potential of the amino group in diphenylamine (0.63 vs. SCE). This suggests that unlike the amide's NH, the NH adjacent to the DCH-Ru fragment has some characteristic of the amino group¹¹. As the radical cation of the NH is not stabilized, this redox process is almost irreversible.

Figure III.1. Cyclic voltammogram of monomer complex (III.1-Ru) in 0.1 M TBAH/ACN (200 mV/s).

III.2.1.3 Spectroelectrochemical Properties

The UV-vis-NIR absorption of the monomeric complex at different oxidation states was measured in an OTTLE cell. Similar to other DCH-Ru complexes¹², at the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}}$ state **III.1-Ru** has the two absorption bands at 502 nm and 389 nm which are assigned to $d(\text{Ru}^{\text{II}}) \rightarrow \pi^*(\text{bpy})$ MLCT transitions (Figure III.2). Oxidation to the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ state (potential = 300 mV) shifts the bpy centred MLCT transition and results in the appearance of a broad NIR band ($\lambda_{\text{max}} = 1273$ nm) from intervalence transitions. At

the $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ state (potential = 900 mV), an intense band at 840 nm was observed, which is assigned to the DCH-centred $\pi(\text{DCH})^{2-} \rightarrow d\text{Ru}^{\text{III}}$ LMCT transition.

Figure III.2. Spectroelectrochemical spectrum of monomer complex (III.1-Ru) in 0.1M TBAH/ACN solution.

III.2.2 Complex Dimer

To better evaluate the contribution of the central bridge (*p*-phenylenediamine) to the band gap and electronic communication during redox reactions, a dimeric ligand (**III.2**) is designed. With an aniline fragment attached to the ends of the DCH moiety, it would be an ideal dimeric ligand. However, the absence of two electron-donating NH moieties will increase the oxidation potentials of the complex dimer, making it less unstable and easier to be purified.

III.2.2.1 Synthesis and Characterization

The dimeric ligand was synthesized in one step by reacting 2 equivalents of 4-methoxybenzohydrazide with 1 equivalent of 1,4-phenylenediisocyanate in anhydrous THF at room temperature. The product showed high purity and could be used without further purification. The complex dimer was prepared following the method described before, resulting in a yield of 40% after purification by column chromatography.

In the IR spectra (Figure III.3), the absorption of N-H stretching mode appears as a shoulder of the broad band from water, locating at 3274 cm^{-1} . The C=O and C=C stretching modes are found at 1664 cm^{-1} and $1500\sim 1600\text{ cm}^{-1}$, respectively. The structure was further confirmed by ^1H and ^{13}C NMR spectra as shown in figure III.4 and all the protons and carbons were assigned.

Figure III.3. IR spectra of dimeric ligand (III.2) and its complex (III.2-Ru).

The complex dimer was prepared following the procedure described previously. As shown by the IR spectra, the carbonyl absorption band at 1664 cm^{-1} from the dimer ligand disappears from its ruthenium complex (III.2-Ru) due to the electron

delocalization on $[\text{DCH}]^{2-}$ moieties. Upon oxidation (10% H_2O_2), the N-H bending mode at 1537 cm^{-1} in **III.2-Ru** disappears. The results suggest the NH groups on central bridge are prone to oxidation under proper conditions.

Figure III.4. ^1H and ^{13}C NMR spectra of dimer ligand (**III.2**).

The ^1H NMR spectrum of the complex dimer shows highly overlapped peaks for aromatic protons and N-H protons due to the coexistence of several stereoisomers, making them very difficult to be assigned. The integral ratio of those protons to the protons on the methoxy groups was calculated to be 13.2:1, which is close to the expected value of 13:1. In addition, the peak from the methoxy protons in the complex

was found to shift to a lower field ($\delta = 3.82$ ppm) than that in the ligand ($\delta = 2.05$ ppm), indicating a weaker electron acceptor of the DCH-Ru moiety than the DCH counter part in the dimeric ligand.

Figure III.5. ESI-MS spectrum of complex dimer (III.2-Ru).

The formation of the target dimer complex is supported by the results of electrospray ionisation mass spectrometry (ESI-MS) (Figure III.5), in which the expected signals of monocation ($[M-PF_6]^+$, $m/z = 2257.0$), dicationa ($[M-2PF_6]^{2+}$, $m/z = 1217.0$), trication ($[M-3PF_6]^{3+}$, $m/z = 761.1$) and tetracation ($[M-4PF_6]^{4+}$, $m/z = 534.8$) are well resolved. The purity of the dimer complex was evaluated by inductively coupled plasma (ICP) analysis. The content of ruthenium in the complex was found to be 13.8% which is slightly lower than the expected value of 14.8%.

III.2.2.2 Electrochemical Properties

Cyclic voltammogram of complex dimer **III.2-Ru** shows two reversible oxidation couples as shown in figure III.6. The tiny waves above 1.40 eV are probably from some impurities. If the diaminophenylene bridge and the DCH-Ru units exist as an isolated entity, there should be in total four reversible oxidation couples, or two from each component. However, only two oxidation couples appear.

Figure III.6. Cyclic voltammogram of dimer complex (**III.2-Ru**) in 0.1M TBAH/ACN solution.

Considering the amino characteristic of the amide groups in the complex dimer, *N,N'*-diphenyl-1,4-phenylenediamine (PDA) was taken as a reference for comparison. The first (E_1) and the second (E_2) half-wave potential and the redox potential splitting (ΔE) of PDA are 0.32 - 0.24 V, 0.75 - 0.87 and 0.43 - 0.53 V (vs. NHE), respectively, in ACN with tetraethylammonium perchlorate (TEAP) as supporting electrolyte^{13, 14}. While the corresponding potentials found in the complex dimer are 0.41 V, 0.99 V and 0.48 V, respectively, which are close to the values of PDA. Therefore, it is reasonable to believe

that the two types of the redox waves overlap at each oxidation step. If this is true, the anodic shift of the oxidation compared to PDA can be attributed to the stabilization of electron-deficient DCH-Ru moiety during oxidation.

III.2.2.3 Spectroelectrochemical Properties

This assumption of the oxidation behaviour was supported by the spectroelectrochemical properties of the dimer complexes. Figure III.7 shows the absorption spectra during the electrochemical oxidation of complex dimer **III.2-Ru** in an OTTLE cell. At zero potential, it displays two intense bands at 338 and 521 nm which are attributed to $d(\text{Ru}^{\text{II}}) \rightarrow \pi^*(\text{bpy})$ MLCT. The central bridge is expected to absorb below 320 nm, outside of the spectral range of interest. Under an applied potential of 0.40 V, the two DCH-Ru species are expected to oxidize to the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ states according to CV data. A broad band appears in the NIR region ($\lambda_{\text{max}} = 1312$ nm), which is assigned to the MMLC of the DCH-Ru moiety. In addition, a shoulder accompanying the NIR band around 850 nm is assigned to the IVCT of the partially formed radical cations of *p*-phenylenediamine. For PDA, this absorption shows at about 710 nm¹³. The red shift is attributed to the decreased donor effect of the DCH-Ru moieties when oxidized to the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ state. The similar trend has been reported in the PDA-type of compounds substituted with the electron-withdrawing groups¹³. With the further increase of the potential but lower than the potential to oxidize DCH-Ru to the $\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}$ state, the absorption maximum of the NIR band shifted slightly to a higher wavelength (1345 nm) without changing the intensity, which is attributed to the decrease of the electron-donating strength of the oxidized NH groups. The position of the shoulder did not change,

but the intensity increased. These results suggest that the oxidation of the central bridge occurs at a relatively higher potential than the DCH-Ru^{II} unit.

Figure III.7. Spectroelectrochemical spectra of complex dimer (III.2-Ru) in 0.1M TBAH/ACN solution.

The oxidation mechanism of the NH groups could be argued. As proposed by Desjardins¹⁵, at the Ru^{II}/Ru^{III} state, the NH group in [$\{\text{Ru}(\text{bpy})_2\}_2\mu\text{-Ph, NH}(\text{C}_3\text{H}_7\text{-n})\text{-dch}\}(\text{PF}_6)_2$] can be reversibly oxidized by the neighboured Ru^{III}, resulting in the formation of C=N double bond and reduced Ru^{II}/Ru^{II} (Scheme III.4). However, this is not the case for the complex dimer, because Otherwise, the IVCT band from the delocalized radical cation of the central bridge would have been observed.

Scheme III.4. Proposed oxidation mechanism of NH group in $\{[Ru(bpy)_2]_2\mu\text{-Ph, NH(C}_3\text{H}_{7-n}\text{)dch}\}(\text{PF}_6)_2$.

When the potential increased to 800 mV, the intensity of the NIR band started to drop, indicating that the oxidation reaction from the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ to $\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}$ states began to take place. The NIR band shifted to a longer wavelength of 1610 nm due to the further decrease of the electron-donating strength of the central bridge. Under this intermediate state, the absorption band at 870 nm can be attributed to two portions. One is from $\pi(\text{DCH})^{2-} \rightarrow d(\text{Ru}^{\text{III}})$, or LMCT, around 800 - 900 nm for typical DCH-Ru complexes¹³. The other is from the unconverted radical cationic bridge, observed at 640 nm as a shoulder. When the potential reaches 1.00 V, the NIR band disappeared and the intensity of the LMCT got further increase, indicating a complete conversion from the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ to $\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}$ state. The LMCT band also shifted to a lower wavelength of 840 nm from 800 mV to 900 mV, which can be ascribed to the increased electron-deficiency of dicationic bridge. This change is consistent to the substituent effect observed in dinuclear DCH-Ru systems¹² and our dendric complexes discussed in chapter 2. The shoulder at ~650 nm

shifted slightly to 630 nm and reached its maximum intensity at 0.90 V, still about 100 nm longer compared to that in the dicationic PDA.

Based on the results from CV and spectroelectrochemistry, the oxidation process of the dimer complex can be described as two reversible three-electron steps as shown in scheme III.4. At each oxidation step, DCH-Ru and *p*-phenylenediamine moiety take place nearly simultaneously. The electrochemical and spectroelectrochemical data of complex monomer (**III.1-Ru**) and dimer (**III.2-Ru**) are summarized in tables III.1 and III.2.

Scheme III.5. Proposed redox process of complex dimer (III.2-Ru).

Table III.1. Electrochemical data of monomer and dimer complexes.

Complex	E_1/mV	E_2/mV	E_3/mV	$\Delta E^a/\text{mV}$	K_c
III.1-Ru	219	776		557	2.6×10^9
III.2-Ru	405	989	~ 1000	584	7.5×10^9

^a $\Delta E = E_2 - E_1$

Table III.2. Spectroelectrochemical data of three complexes.

Complex	$\lambda_{\text{max}} / \text{nm} (\log [\epsilon / \text{M}^{-1}\text{cm}^{-1}])$		
	$\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}}$	$\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$	$\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}$
III.1-Ru	389(3.84),	453(3.97), 1273(3.70)	540(3.67),
	502(3.95)		938(4.07)
III.2-Ru	338(4.50),	420(4.14), 850(3.72),	840 (4.10)
	521(4.27)		

III.2.3 Polymer Complex

III.2.3.1 Synthesis and Characterization

The polybiurea ligand was prepared in DMSO by treating stoichiometric quantities of *p*-phenylenediisocyanate with hydrazine hydrate. The resulting product appeared to be a gel in the solvent due to the strong interchain hydrogen-bonding interactions. The IR spectrum of the product appears similar to that of ligand monomer, showing N-H stretching at 3240 cm^{-1} and C=O stretching at 1664 cm^{-1} .

For each repeating unit, three major peaks at 8.66, 7.87 and 7.37 ppm are found in the ^1H NMR spectrum (Figure III.8) and assigned to the two identical protons on the NH groups between the two carbonyl groups and the two identical protons on NH groups attached to benzene, and the four identical protons on benzene, respectively. In the ^{13}C NMR spectrum, three peaks are found at 156.1, 134.1 and 119.2 ppm, which are attributed to the two identical carbons from the carbonyl groups, two identical carbons on benzene attached to the NH groups and four identical carbons on benzene, respectively.

It is also noticed that two small peaks appearing in the ^1H NMR spectrum. One is close to the peak of water and the other one is located beside the peaks from the biurea group. They are highly possible from the hydrazide groups at the ends of polymer chains. The difference between the integral ratio between the actual value (1:1.5) and the expected value (1:2) is largely due to the incomplete integration of the NH_2 groups as part of the peak is shielded by the broad peak from water. According to the integral ratio of the protons on repeating unit and the protons from end groups, the number-average molecular (M_n) weight of the product could be calculated for low-molecular-weight polymers. Assuming that the polymer chains have the same hydrazide group at the chain

ends, the average degree of polymerization is calculated to be about 11, equal to a M_n of 2.1×10^3 . However, this molecular weight does not represent the whole sample, because the sample is only partially dissolved in the solvent (DMSO- d_6). Even at a higher temperature (330 K) during the NMR experiment, a large amount of the sample remained insoluble.

Figure III.8. ^1H NMR and ^{13}C NMR spectra of polymer ligand (III.3).

Thermal properties of the ligand polymer were analyzed by differential scanning calorimetry (DSC) and thermogravimetry (TG). Due to its highly rigid structure, no

glass-transition temperature was found. The onset temperature for 5% weight loss was found to be 320 °C for the ligand polymer by TG, indicating a relatively high thermal stability.

The complexation reaction of the ligand polymer with a ruthenium complex was carried out in DMF, in order to fully solve the ligand polymer. The final product was precipitated in water containing NH_4PF_6 salt. Like the complex monomer, the complex polymer appeared to be readily oxidized in the air during workup. The product as dark blue solids could not be purified by column chromatography as it is strongly absorbed by alumina.

III.2.3.2 Electrochemical Properties

As shown by CV (Figure III.9), the product did not achieve the desired ratio of complexation since the oxidation waves from DCH-Ru moieties (less than 1000 mV) are weak. The ruthenium content analyzed by ICP is only 11.8%, which is lower than the expected value of 15.5%. The oxidation around 1.00 V is likely from the single nuclear ruthenium complex incorporated into the polymer backbone. The reason for incomplete complexation is mainly due to the stiffness of the polymer chains. As the each incorporation will increase the rigidity of the polymer chain, the lack of rotation just prevent the polymer chain from further complexation.

Figure III.9. Cyclic voltammogram of complex polymer (III.3-Ru) in 0.1M TBAH/ACN solution.

III.3 Conclusion

We have designed and synthesized three biurea-containing ligands, in the forms of monomer, dimer and polymer. The complex dimer serves as a good model to study the electrochemical property related to the structural details. As predicted, the NH group shows some amino characteristics after the complexation of the DCH moieties. The electrochemical properties of the central diaminophenylene bridge and the DCH-Ru moiety are quite similar and can still be successfully explored and studies by spectroelectrochemistry. The complexation of the ligand polymer could not produce the fully complexed polymers, due to the stiffness of the polymer backbone. Therefore, a new method is needed to make DCH-Ru-containing polymers.

II.4 Experimental Section

Materials

All reagents and solvents utilized in synthesis and measurement were used as received. *cis*-Ru(bpy)₂Cl₂·2H₂O was prepared according to the literature method.¹⁷

Measurements

¹H and ¹³C NMR spectra were recorded on Bruker AMX-400 and Varian 300 MHz NMR spectrometers using deuterated dimethylsulfoxide (DMSO-d₆) as solvents with 1% tetramethylsilane (TMS) as an internal standard. The chemical shifts were reported in δ (ppm) to TMS. IR spectra were taken on an ABB Bomem MB-100 FTIR in KBr

UV-vis-NIR spectroscopic and electrochemical measurements were taken using spectroscopic grade acetonitrile (ACN) or N,N-dimethylformamide (DMF) on a Perkin Elmer Lambda 900 UV-vis-NIR and BAS 100 B/W, separately.

Inductively coupled plasma (ICP) analysis of ruthenium was done at the Institute of Chemistry, Chinese Academy of Sciences, Beijing, China.

N, N'-diphenyl-1,2-Hydrazinedicarboxamide (**III.1**)

To a solution of phenylisocyanate (1.19 g, 10.0 mmol) in THF (20 mL) was added dropwise a solution of hydrazine hydrate (55%, 0.30 g, 5.0 mol) in THF (5 mL) with stirring. The solution was kept stirring for 1 h after the completion of addition. The resulting precipitate was collected by filtration, washed with water and dried to give

white powder (0.98 g, 73% yield). M. p. 240–241 °C; IR (KBr, cm^{-1}): 3298, 3222 ($\nu_{\text{N-H}}$), 3095 ($\nu_{\text{C-H}}$), 1670 ($\nu_{\text{C=O}}$), 1596, 1546, 1448 ($\nu_{\text{NC=C}}$); ^1H NMR (300 MHz, $\text{DMSO-}d_6$): 8.79 (s, 2H), 7.98 (s, 2H), 7.50 (d, 4H, $J = 7.2$ Hz), 7.25 (t, 4H, $J = 7.2$ Hz), 6.95 (t, 2H, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ/ppm : 156.5, 140.1, 128.9, 122.1, 119.0; MS (ESI, m/z) found (nature of the peak, relative intensity): 271 ($\text{M} + \text{H}^+$, 2.3).

N,N'-(1,4-phenylene)bis(4-methoxybenzoylsemicarbazide) (**III.2**)

To a solution of 4-methoxybenzohydrazide (0.83 g, 5.0 mmol) in THF (20 mL) was added dropwise a solution of 1,4-phenylene diisocyanate (0.40 g, 2.5 mol) in anhydrous THF (5 mL) with stirring. The solution was kept stirring for 2 h after the completion of addition. The resulting precipitate was collected by filtration, washed with water and dried to give white powder (1.17 g, 95% yield). $T_d > 330$ °C; IR (KBr, cm^{-1}): 3274 ($\nu_{\text{N-H}}$), 1664 ($\nu_{\text{C=O}}$), 1606, 1564, 1506 ($\nu_{\text{C=C}}$); ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ/ppm : 10.13 (s, 2H), 8.71 (s, 2H), 8.04 (s, 2H), 7.90 (d, 4H, $J = 6.6$ Hz), 7.35 (s, 4H), 7.03 (d, 4H, $J = 6.6$ Hz), 3.82 (s, 6H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ/ppm : 165.8, 161.8, 155.8, 134.0, 129.3, 124.6, 119.0, 113.5; MS (ESI, m/z) found (nature of the peak, relative intensity): 494 ($\text{M} + \text{H}^+$, 0.6).

Poly(1,4-phenylene-1,6-biurea) (**III.3**)

To a solution of 1,4-phenylene diisocyanate (1.60 g, 10 mmol) in DMSO (15 mL) was added dropwise a solution of hydrazine hydrate (55%, 0.58 g, 10 mmol) in DMSO (5 mL). The solution was kept stirring after the completion of addition. The resulting

product was precipitated in methanol, filtered, washed with methanol and dried to give white powder (1.88 g, 98% yield). Td > 320 °C; IR (KBr, cm⁻¹): 3240 (ν_{N-H}), 1664 (ν_{C=O}), 1514 (ν_{C=C}); ¹H NMR (300 MHz, DMSO-*d*₆): 8.66 (s, 2H), 7.87 (s, 2H), 7.37 (s, 4H); ¹³C NMR; (100 MHz, DMSO-*d*₆) δ/ppm: 156.1, 134.1, 119.2.

General procedure for the preparation of DCH-Ru complexes

The ruthenium complexes were synthesized via the procedure of Kaim.¹⁶ The general synthetic procedure was to combine 0.38 mmol (200 mg) Ru(bpy)₂Cl₂•2H₂O with 0.19 mmol of the *dicarboxylhydrazine fragment* and 40 mg NaOH or 100 mg Na₂CO₃ in 80 mL of 5:1 H₂O/EtOH (v:v). The mixture was then refluxed for approximately 14 hours under argon. After cooling to room temperature, 1.00 g of tetra-*n*-butylammonium hexafluorophosphate (TBAH) in 40 mL of water was added to afford red dark precipitate. The precipitate was filtered off, redissolved in acetone (20 mL) and precipitated into diethyl ether. The product was further purified by column chromatography with acetonitrile on acidic alumina and dried under vacuum.

(III.2-Ru)

IR (KBr, cm⁻¹): 1602, 1506 (ν_{C=C}); 1539 (ν_{N-H}); ¹H NMR (300 MHz, DMSO-*d*₆): 9.22 – 5.51, (m, 78H), 2.85 (s, 6H); MS (ESI, m/z) found (nature of the peak, relative intensity):

2257.0 ($[\text{M-PF}_6]^+$, < 0.1), 1217.0 ($[\text{M-2PF}_6]^{2+}$, 5.10), 761.1 ($[\text{M-3PF}_6]^{3+}$, 58.50), 534.8 ($[\text{M-4PF}_6]^{4+}$, 0.32).

References

1. Ciardelli, F.; Tsuchida, E.; Wöhrle, D. *Macromolecule–Metal Complexes*, Springer-Verlag, **1996**.
2. Yamamoto, T.; Yoneda, Y.; Maruyama, T. *J. Chem. Soc. Chem. Commun.* **1992**, 1652.
3. Trouillet, L.; De Nicola, A.; Guillerez, S. *Chem. Mater.* **2000**, 12, 1611.
4. Yu, S. C.; Gong, X.; Chan, W. K. *Macromolecules* **1998**, 31, 5639.
5. Yu, S. C.; Chan, W. K. *Macromol. Rapid. Commun.* **1997**, 18, 213.
6. Yu, S. C.; Chan, W. K. *Macromolecules* **2000**, 33, 3259.
7. Frazer, A. H.; Wallenberger, F. T. *J. Polym. Sci. Part A: Polym. Chem.* **1964**, 2, 1137.
8. Frazer, A. H.; Wallenberger, F. T. *J. Polym. Sci. Part A: Polym. Chem.* **1964**, 2, 1147.
9. Campbell, T. W.; Foldi, V. S.; Farago, J. *J. Appl. Polym. Sci.* **1959**, 11(5), 155.
10. Desjardins, P.; Wang, Z. Y. *ACS Symp. Ser.* **2005**, 888, 51.
11. D'Aprano, G.; Leclerc, M.; Zotti, G. *Synth. Met.* **1996**, 82, 59.
12. Kasack, V.; Kaim, W.; Binder, H.; Jordanov, J.; Roth, E. *Inorg. Chem.* **1995**, 34, 1924.
13. Nishiumi, T.; Nomura, Y.; Chimoto, Y.; Higuchi, M.; Yamamoto, K. *J. Phys. Chem. B* **2004**, 108, 7992;
14. Aprano, G. D.; Leclerc, M.; Zotti, G. *Synth. Metals* **1996**, 82, 59.
15. Desjardins, P. *Synthesis and Characterization of Novel Organometallic and Organic Electrochromic Materials*, PhD dissertation, Carleton University, **2001**, 91.
16. Kaim, W.; Kasack, V. *Inorg. Chem.* **1990**, 29, 4696.

17. Sullivan, B.; Salmon, D.; Meyer, T. *Inorg. Chem.* **1978**, 17, 3334.

Chapter IV Ru-Containing Polymers by Suzuki Cross-Coupling Polymerization

IV.1 Introduction

The Suzuki reaction, also called Miyaura-Suzuki reaction, is the palladium(0)-catalysed cross-coupling between an aryl- or vinyl- boronic acid and an aryl- or vinyl-halide in the presence of a base, which was first discovered by Akira Suzuki et al in 1979¹. The accepted mechanism is shown in scheme IV.1, which involves oxidative addition of the halide substrate to give a Pd(II) intermediate, followed by a transmetallation, and a final reductive elimination that regenerates the catalyst²⁻⁴. The transmetallation is thought to be facilitated by base-mediated formation of the tetracoordinate boronate anion which is more electrophilic than the free boronic acid⁵.

Scheme IV.1. Accepted mechanism of Suzuki-coupling reaction.

This reaction is not restricted to boronic acids (or their esters) and halides. Potassium trifluoroborates^{6,7}, organoboranes⁸⁻¹¹ and fluorosulfonates¹² can also be used in place of boronic acids. Some pseudohalides, for example triflates¹³⁻¹⁶ may also be used as coupling partners. Several reviews on the Suzuki reaction have been published.¹⁷⁻²¹

Because of low catalyst loading (typically 0.5 mol %), potential recycling of the catalyst, high productivity, low energy consumption, mild conditions, low waste production, and safe solvents, the application of the Suzuki reaction has been widespread from the synthesis of small molecular, natural products^{22,23} and pharmaceutical drugs^{24,25} to various polymers^{26,27}.

As stated above, the Suzuki reaction offers several advantages to make it satisfy the requirements for condensation polymerization. If the two starting materials contain bifunctional bromo and boronic acid (or boronic acid ester) groups, the cross-coupling reaction can in principle lead to the formation of a linear polymer. Thus, such a reaction can be deemed to be a Suzuki cross-coupling polymerization (also called as Suzuki polycondensation, SPC), which is a typical step-growth polymerization, as shown in scheme IV.2. The boronic acid or boronic acid ester and the halide can be present in the same monomer (AB-type) or in different monomers (AA/BB-type). In 1988, the Suzuki cross-coupling reaction was successfully applied in making poly(p-2,5-di-n-hexylphenylene) (PPP derivate) by the Schlüter group at the Max-Planck Institute for Polymer Research in Mainz²⁶. Since then, much effort has been made to utilize this reaction as a powerful synthetic tool in modern polymer chemistry. A variety of aromatic polymers have been prepared through this cross-coupling polymerization, such as chelating polymers²⁸⁻²⁹, hyperbranched polymers³⁰⁻³⁶, dendrimers^{37,38}, amphiphilic copolymers³⁹⁻⁴¹, polyelectrolytes^{42,43}, main-chain chiral polymers⁴⁴⁻⁴⁷, poly(arylene vinylene)s and poly(arylene ethynylene)s⁴⁸⁻⁵¹.

AA/BB-approach **AB-approach**

Scheme IV. 2. General representation of SPC with the AA/BB-type or AB-type polymerization. X and Y represent aromatic units, typically benzene derivatives.

The Suzuki cross-coupling polymerization is also useful in producing metal-containing polymers with the luminescent and redox-active properties typically through AA/BB-type approach⁵²⁻⁵⁵. An example is the alternating copolymer containing a ruthenium-bipyridine metal complex and 1,4-phenylene unit produced by the Klemm group (Scheme IV.3)⁵⁶.

Scheme IV.3. Synthesis of Ru-containing polymer by Suzuki cross-coupling Polymerization.

In this chapter, two synthetic approaches, i.e., AB- and AA-BB-type polymerizations are described for the synthesis of a novel series of polymers containing a

dinuclear ruthenium complex moiety by SPC. In addition, polymer modification is described through the introduction of short poly(ethylene glycol) fragments in order to increase the ion transport property of the Ru-containing polymer and other properties.

IV.2 Design and Synthesis of AB monomers

IV.2.1 DCH-based AB-type Monomer

The simplest AB ligand based on 1,2-dicarbonylhydrazide (DCH) should have the structure of **IV.2** or **IV.3** (Scheme IV.4) with bromophenyl and borophenyl attached to the DCH separately.

Scheme IV.4. Synthesis of AB ligand and the complex

As shown in scheme IV.4, this ligand can be prepared by reacting 4-bromobenzhydrazide and 4-bromobenzoyl chloride (**IV.1**)⁵⁷. Moreover, the product obtained in an aqueous medium is different from the one under anhydrous condition. The latter kept the boronic acid ester group from the reactant with a m.p. of 249 – 251 °C, while the former was a hydrolyzed boronic acid product (no m.p. detected owing to the decomposition). The structural difference in the product is elucidated by IR and ^1H NMR.

In figure IV.1, the absorption band of the methyl group at $\sim 2900\text{ cm}^{-1}$ from **IV.3** disappears for **IV.2**. In comparison of the ^1H NMR spectra of these two products (Figure IV.2), the missing of the methyl peaks at 1.37 ppm for **IV.2** indicates a nearly complete hydrolysis of the boronic acid ester under aqueous conditions.

Figure IV.1. IR spectra of ligands **IV.2** and **IV.3** (KBr pellet).

Figure IV.2. ^1H NMR spectra of **IV.2** and **IV.3** in $\text{DMSO-}d_6$.

The corresponding complexes **IV.2-Ru** and **IV.3-Ru** were prepared according to the procedure of Kaim⁵⁸, reacting *cis*-Ru(bpy)₂Cl₂·2H₂O with ligands **IV.2** and **IV.3** separately under a basic condition in the mixture of methanol/water. During the purification of the complexes derived from this AB-type ligand by column chromatography on basic aluminum oxide, the ester also tends to be hydrolyzed to the acid. Thus, **IV.3-Ru** should be a better choice for polymerization. However, the SPC of **IV.3-Ru** didn't produce high molecular weight polymer according to the low viscosity ($\eta_{inh} = 0.08$ dL/g, $c = 0.5$ g/dL) of the product.

The unsuccessful polymerization is likely to be caused by the steric hindrance instead of the reactivity of the monomer complex. In the catalytic cycle of Suzuki reaction, oxidative addition is generally a rate-determining step¹⁷. Considering the electron-withdrawing nature of the DCH fragment in ligand **IV.3**, the corresponding Ru complex should be ready to undergo oxidative addition. According to the calculated geometric structure of $\{[Ru(bpy)_3]_2 \mu\text{-}Ph_2dch\}^{2+}$ (a model compound for **[IV.3-Ru]²⁺**) presented in figure IV.3, the phenyl ring and bipyridyl group is almost face-to-face parallel, which is likely to cause more steric hindrance when the two phenyl rings are connected. Thus, structural modification of ligand **IV.3** is necessary by pushing phenyl rings away from the dipyriddy groups.

Figure IV.3. Calculated geometric structure of $[\{Ru(bpy)_2\}_2 \mu\text{-}Ph_2dch]^{2+}$ by Spartan ES as a model compound for $[IV.3\text{-}Ru]^{2+}$.

IV.2.2 Biurea-based AB-type Monomer

Compared to ligand **IV.2**, the only change in ligand **IV.10** (Scheme IV.5) is the insertion of the -NH- moiety between the DCH and phenyl groups, aiming at reducing steric hindrance from the dipyridyl groups. Another purpose is to alter the redox property of the complex polymer. Compound **IV.6** was prepared according to a known procedure⁵⁹, starting from 4-bromoaniline (**IV.4**). After deprotection by the Pd/C catalyzed hydrogenation, the boronic acid salt (**IV.5**) was then converted to its ester (**IV.6**) through a solid phase reaction with pinacol followed by the formation of the urethane (**IV.7**) with phenyl chloroformate⁶⁰. Upon reacting with excess hydrazine hydrate, compound **IV.8** was obtained in 69% yield, which was then reacted with 4-bromophenyl isocyanate to afford **IV.10**. The corresponding **IV.10-Ru** was prepared by using the same procedure as for ligand **IV.3**.

Scheme IV.5. Synthesis of Biurea-based AB-type ligand.

As shown in figure IV.4, the phenyl groups in the calculated geometric structure of $[\{ Ru(bpy)_2 \}_2 \mu-(NHPh)_2 dch]^{2+}$ (a model compound for $[IV.10-Ru]^{2+}$) are not parallel to any of the bipyridyl group, and they stick out more compared to those in $[\{ Ru(bpy)_2 \}_2 \mu-Ph_2 dch]^{2+}$. Such difference should reduce the steric hindrance of **IV.10-Ru** during polymerization. But, the viscosity of the product didn't give any increase against the starting monomer even when the reaction time was extended to 24 hrs. The low reactivity of **IV.10-Ru** may be caused by the relatively high electron-donating effect of the $-NH-$

group attached to the phenyl ring. As we have discussed in previous chapter, after the formation of complex, the withdrawing ability of the carbonyl group is highly reduced to leave the -NH- group with high electron density, which makes **IV.10-Ru** less active in the step of oxidative-addition compared to electron-withdrawing group¹⁷.

Figure IV.4. Calculated geometric structure of $[Ru(bpy)_3]_2 \mu-(NHPh)_2 dch]^{2+}$ as a model compound for **[IV.10-Ru]²⁺** by Spartan ES.

IV.3 AA-BB copolymers

In the AA/BB approach, the DCH-Ru monomer can start with dibromo- or diboronic acid functional groups. However, it will take extra steps to synthesize a diboronic DCH ligand than a dibromo- DCH ligand. In addition, the relative inert biromo- DCH-Ru complex is easier to be purified by column chromatography. Thus, in the AA/BB approach, we decided to polymerize a dibromo- DCH-Ru monomer with other diboronic acid or ester monomers, not the inverse.

IV.3.1 Synthesis and Characterization of Poly(DCH-Ru-alt-triglycol)

DCH-Ru monomer **IV.11-Ru** was prepared from the complexation of AA ligand (**IV.11**) with *cis*-Ru(bpy)₂Cl₂·2H₂O according to the method by Kaim⁵⁸ in 73% yield after purification by column chromatography (Scheme IV.14). The TLC result on alumina plate only gave one spot (eluent: ACN).

Scheme IV.6. Synthesis of monomer IV.11-Ru complex and BB monomer IV.14.

By comparing the IR spectra (Figure IV.5) of the complex (**IV.1-Ru**) to its ligand (**IV.11**), the major difference is the disappearance of the N-H band at 3200 cm⁻¹ and the appearance of a P-F band at 841 cm⁻¹. The ¹³C NMR spectrum of **IV.11-Ru** (Figure IV.6) shows 29 peaks with 2 different carbonyl peaks at 175.2 and 175.0 ppm separately, which

indicates the presence of two diastereomers. In the dinuclear DCH-Ru complex, ruthenium metal center can possess right-handed or left-handed chirality (Δ or Λ), respectively. For a symmetrical DCH-Ru complex, there exist a meso ($\Delta\Delta$) and two enantiomeric isomers ($\Delta\Delta$ and $\Lambda\Lambda$). For each diastereomer, there will be 25 resonance peaks in the ^{13}C NMR spectrum. As a result, there should be totally 42 peaks in the ^{13}C NMR spectrum. Due to the signal overlapping, only 39 peaks are seen in figure IV.6. This finding is consistent to that of its structural isomer of oxamide-Ru complexes studied in our lab⁶¹.

Figure IV.5. IR spectra of compound IV.11 and its complex IV.11-Ru.

Figure IV.6. ^{13}C NMR spectrum of monomer IV.11-Ru.

Compound **IV.14** is the ester derivative of its boronic acid **IV.13** that was synthesized according to a known procedure⁶² from its precursor **IV.12** and purified by flash column chromatography (eluant: hexane/ether = 2/1) (Scheme IV.14). Compound **IV.12** was obtained in 75% yield by refluxing 4-bromophenol with 1,2-bis(2-chloroethoxy)ethane in n-butanol with the presence of KOH⁶³. Refluxing **IV.13** and pinacol in toluene gave the BB monomer **IV.14** in quantitative yield.

The polymerization was carried out in degassed DMF at 100 °C with K₂CO₃ as a base and Pd(PPh₃)₄ as a catalyst (Scheme IV.7). The inherent viscosity of the polymerization product was found to be 0.25 dL/g (c = 5 mg/mL), suggesting the formation of an oligomer. The IR spectrum of this product shows a band at 840 cm⁻¹ for the P-F stretching from PF₆⁻, a band at 1631 cm⁻¹ from -CON- (18 cm⁻¹ lower than the carbonyl group in the ligand), two bands at 2925 cm⁻¹ and 2861 cm⁻¹ for the methylene moiety and a band at 1264 cm⁻¹ for the ether linkage from monomer **IV.14**. The boron-aryl absorbance at 1144 cm⁻¹ in the starting compound **IV.14**⁶⁴ was not observed in the product. The integrals of its ¹H NMR spectrum give the expected numbers of the different protons: 48 protons between 6.36 and 9.34 ppm from all the benzene rings, 4 protons at 4.15, 3.80 and 3.66 ppm for each methylene moieties. The cyclic voltammogram spectrum of the oligomer shows two reversible pairs of oxidation couples starting at 0.45 V and 1.00 V which is 50 mV lower than those of the starting monomer **IV.11-Ru**.

Scheme IV.7. Suzuki cross-coupling polymerization of IV.11-Ru and IV.14.

IV.3.2 Synthesis and Characterization of Poly(fluorene-co-DCH-Ru)

Poly(9-alkylfluorene)s are highly fluorescent in solution and in the solid-state⁶⁵. Rigid-rod polyfluorene has a tendency to form excimer aggregates, which leads to a red-shifted emission to long wavelength (> 500 nm)⁶⁶. Its emission spectrum overlaps well with the MLCT absorption (360 - 520 nm) of DCH-Ru, thus the copolymers could be a good model for energy-transfer study. Herein, we chose commercially available 9,9-dioctylfluorene-2,7-bis(trimethylborate) (**IV.16**) as a monomer and 9,9-dioctyl-2,7-dibromofluorene (**IV.17**) and DCH-Ru monomer **IV.11-Ru** (Scheme IV.8). The two octyl side chains in **IV.16** are expected to impart the solubility to the polymers. The molar feed ratios of **IV.11-Ru** to the total starting monomers are 0.50, 0.44, 0.22 and 0.11, respectively. Except for the ratio at 0.11, the polymerization at all the other feed ratios produced high-molecular-weight copolymers according to the viscosity data. Polyfluorene is non-polar and soluble in toluene, chloroform and THF. When the molar feed ratio to the total starting monomers is lower than 0.22, the product was not polar enough to be soluble in DMF, which was obtained only in low molecular weight.

Scheme IV.8. Preparation of poly(fluorene-co-DCH-Ru) by Suzuki cross-coupling polymerization.

Figure IV.7. IR spectra of starting monomers IV.16, IV.17 and IV.11-Ru and product IV.20 in KBr.

The polymer structures were characterized by IR and ^1H NMR. The broad band from 3700 cm^{-1} to 3100 cm^{-1} in the IR spectrum is from the water in the KBr pellet. By comparing the IR spectra (Figure IV.7) of the product (**IV.20**) and the starting monomers

(**IV.11-Ru**, **IV.16** and **IV.17**), we can see that for the product, the band at 2848 – 2952 cm^{-1} ($\nu_{\text{C-H}}$) is from **IV.16** and **IV.17**, and the bands at 1633 cm^{-1} ($\nu_{\text{C=O}}$) and 844 cm^{-1} ($\nu_{\text{P-F}}$) are from **IV.11-Ru**. The ^1H NMR spectrum of **IV.20** in figure IV.8 shows the aromatic protons from fluorene and DCH-Ru moieties at 6.38 - 9.44 ppm (m, 46H) and aliphatic protons at 2.13 ppm (s, 3H), 1.04 ppm (s, 21H) and 0.62 ppm (s, 10H). The integrals of the ^1H NMR spectra of **IV.19** and **IV.20** also give the numbers of protons close to the calculated values according to the feed ratios. Unfortunately, it's difficult to use the ^1H NMR data to calculate the degree of polymerization for these polymers due to the overlaps of the resonance signals of the methyl end-capped group and the octyl groups at ~ 2.4 ppm.

Figure IV.8. ^1H NMR spectrum (300 MHz, $\text{DMSO-}d_6$) of **IV.20**.

IV.3.3 Solution Property

In the polymer backbone, each DCH-Ru unit bears two positive charges. Therefore, these polymers were expected to behave like polyelectrolytes. The reduced viscosities, η_{red} , of polymers **IV.18I**, **V.19I** and **V.20** containing a different amount of DCH-Ru were measured at 30 °C and shown in figure IV.9 as a function of polymer concentration in DMF. For each polymer solution without the addition of salt (NH_4PF_6), we observed a pronounced polyelectrolyte effect, i.e., the reduced viscosity increases with the decrease of concentration, because of the long-range electrostatic interactions. Under low ionic strength conditions, this observed increase of the reduced viscosity upon dilution can be described by the Fuoss-Strauss equation⁶⁷:

$$\eta_{\text{red}}^{-1} = c/\eta_{\text{sp}} = 1/[\eta] + (B/[\eta])c^{1/2} \quad (1)$$

where, c is concentration, η_{sp} is specific viscosity, $[\eta]$ is intrinsic viscosity, and B is a constant reflecting the interaction of polyelectrolytes. This equation can be used to estimate intrinsic viscosity ($[\eta]$) by plotting (c/η_{sp}) vs. $c^{1/2}$. A more accurate way to measure $[\eta]$ is to add salt to the polyelectrolyte solution to suppress the polyelectrolyte effect by screening out electrostatic interactions. In the presence of 0.01 M NH_4PF_6 , the reduced viscosity of each polymer solution can be fitted by a straight line. Thus, the intrinsic viscosities are 0.69, 1.06 and 0.70 mL/g for polymer **IV.18**, **IV.19** and **IV.20**, respectively (Table IV.1).

Figure IV.9. Reduced viscosities as a function of polymer concentration in DMF without or with salt (0.01M NH_4PF_6) at 30 °C: (B) IV.18, salt free; (X) IV.18, with salt; (!) IV.19, salt free; (∇) IV.19 with salt; (,) IV.20, salt free; (–) IV.20, with salt.

Table IV.1. Intrinsic viscosity and GPC data^b of copolymers IV.18, IV.19 and IV.20.

Compound	$[\eta]^a / (\text{dL} / \text{g})$	$\overline{M}_w / \text{kD}$	$\overline{M}_n / \text{kD}$	PDI
IV.18	0.69	45660	20310	2.25 (95.0%) ^c
		2640	2360	1.12 (5.0%) ^c
IV.19	1.06	4490	2840	1.58 ^c
IV.20	0.70	2690	2030	1.32 ^c

^a intrinsic viscosity. ^b DMF solvent relative to polystyrene standards. ^c $[\text{NH}_4\text{PF}_6] = 2 \text{ mM}$.

The molecular weight measurement was carried out on gel permeation chromatography (GPC) with polystyrene as standards. Unfortunately, under the normal conditions, elution with CHCl_3 or DMF, often gives uninterpretable results for polyelectrolytes, especially for those containing charged metals, due to the strong interaction between these polymers and the packing materials in GPC column (e.g.,

polystyrene/divinyl benzene crosslinked beads). Addition of a salt in the eluent is proven to be effective to break up such interaction and useful in obtaining the more realistic chromatogram for metal-containing polymers⁶⁸.

The GPC traces of the copolymers are illustrated in figure IV.10. We first used 1 mM NH_4PF_6 in DMF as an eluent. This solvent system could only elute polymer **IV.18** which has the lowest total metal charges among the three polymers. When the concentration of NH_4PF_6 was increased to 2 mM, copolymer **IV.19** and **IV.20** were also able to be eluted. The GPC data are shown in Table IV.1. For copolymer **IV.18**, the small shoulder peak at longer retention time indicates the presence of low molecular weight oligomers with a portion of 5.00% according to the integral of the peak. Because of the significant structural difference between the Ru-containing copolymers and polystyrene standard, only the apparent molecular weights of a series of polymers with similar structures can be obtained⁶⁹, in addition to the polydispersity index (PDI). PDI is defined by the ratio of $\overline{M}_w / \overline{M}_n$, where $\overline{M}_w$ and $\overline{M}_n$ are the weight- and number-average molecular weight of the sample, respectively. By comparing the PDI data of the three polymers in table IV.1, **IV.20** turns out to have the lowest polydispersity index and also the lowest $\overline{M}_w$.

Figure IV.10. GPC traces of DCH-Ru copolymers using 2 mM NH_4PF_6 in DMF as an eluant : 1) IV.18, 2) IV.19, 3) IV.20.

IV.3.4 Electrochemical characterization

The cyclic voltammograms of the monomers (**IV.11-Ru** and **IV.16**) and copolymers **IV.18**, **IV.19** and **IV.20** were illustrated in figure IV.11 and the electrochemistry data are presented in Table IV.2. The cyclic voltammogram of low-molecular-weight **IV.20** (trace 3 in Figure IV.11) bears two pairs of reversible oxidation peaks owing to the dinuclear Ru component and one irreversible peak from the fluorene part. The 1st redox couple is assigned to $\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}} \leftrightarrow \text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$, and the 2nd redox couple is assigned to $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}} \leftrightarrow \text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}$. The oxidation potentials of these two couples are very close to those of the starting monomer **IV.11-Ru**, which suggests that the interaction between two dinuclear units through fluorene moiety is too weak, and there is no conjugation through the fluorene spacer. Therefore, the three polymers show only two redox couples from the DCH-Ru fragment and the positions are very close in cyclic voltammograms despite their different chain structures. Meanwhile, the oxidation potential of the fluorene part is anodically shifted with respect to the starting monomer **IV.16** (1.56 V vs. 1.49V vs. NHE). This is because the electron-deficient $\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}$

moiety tends to lower both the HOMO and LUMO of fluorene, making it more difficult to oxidize. Like other polyelectrolytes, the solubility of these polymers decreases with the increase of the ionic strength, which makes it difficult to carry out the electrochemical studies in a 0.1M electrolyte/ACN or DMF solution for those high-molecular-weight polymers. Thus, these polymers were coated on a Pt-disc electrode (1 mm diameter) for electrochemical work. The two cycles of CV for copolymer **IV.18** are fully repeatable, while for copolymer **IV.19** and **IV.20**, compared to the 1st cycle of CV, the 2nd cycle shows a large drop regarding the current intensity due to partial dissolution of the coated polymers in the electrolyte solution.

Figure IV.11. Cyclic voltammograms of monomers and copolymers **IV.18, **IV.19** and **IV.20** in 0.1M TBAH/ACN solution at room temperature (polymers are coated on electrode).**

Unlike **IV.19** and **IV.20**, each showing only one oxidation peak for the fluorene moiety in CV at a relatively higher oxidation potential (~1.60 V), polymer **IV.18** shows multiple oxidation peaks for its fluorene fragments at lower potentials (1.24-1.57 V). This

difference can be attributed to the formation of relative longer oligofluorene fragments on the polymer chains. Compared to single fluorene molecule, the HOMO energy level is higher in fluorene oligomers, making it easier to oxidize.

Table IV.2. Electrochemistry data^a of monomers and copolymers taken in 0.1M TBAH/ACN.

compound	$E_1^{\text{ox}} / \text{V}$	$E_2^{\text{ox}} / \text{V}$	$E_3^{\text{ox}} / \text{V}$	$\Delta E_{2-1} / \text{V}$	k_c^c
IV.16	\	\	1.45	\	\
IV.11-Ru	0.52	1.05	\	0.55	2.0×10^9
IV.20 oligomer	0.48	1.05	1.60	0.57	4.35×10^9
IV.18	0.50	1.06	1.24-1.57	0.56	3.0×10^9
IV.19	0.51	1.06	1.61	0.55	2.0×10^9
IV.20	0.51	1.06	1.60	0.55	2.0×10^9

^a Scanning rate = 200 mV/s, Potentials E vs NHE.

^b TBAH = tetrabutylammonium hexafluorophosphate.

^c $k_c = \exp(nFAE/RT) = 10^{16.91AE}$, T = 298 K

IV.3.5 UV-vis-NIR Spectroscopic Study

Figure IV.12 shows the UV-vis spectra of monomer **IV.11-Ru** and three copolymers in acetonitrile and the data are presented in Table IV.3. For monomer **IV.11-Ru**, the strong absorption band at about 300 nm is attributed to the intraligand $\pi \rightarrow \pi^*$ (bpy) transitions. The broad absorption bands at 357 nm and 524 nm are assigned to typical spin-allowed metal-to-ligand charge-transfer (MLCT) transitions. For copolymer **IV.18**, **IV.19** and **IV.20**, they all show two absorption peaks at about 300 nm and 525 nm, while the absorption peak around 360 nm is blue-shifted for **IV.19** and **IV.20** and red-shifted

for **IV.18** due to different spectral overlapping. Fluorene monomer has strong UV absorption lower than 320 nm, while the absorption maximum of polyfluorene is around 380 nm. In **IV.19** and **IV.20**, the polymer chain structure is close to alternating to make the spectral overlapping happen between the DCH-Ru and the fluorene moieties, resulting in a blue-shift to ~345 nm. For copolymer **IV.18**, there exists longer oligofluorene fragments, which make the spectral overlapping between the DCH-Ru and the oligofluorenes red-shift to 375 nm.

Figure IV.12. UV-vis-NIR spectra of starting monomers and copolymer products. in ACN at a concentration of 0.020 mg/ml.

As the intensity of the absorption band at 525 nm is associated with MLCT of DCH-Ru fragment and the position is almost the same in both the monomer complex and the copolymers, it's feasible to use a colorimetric method for the detection of the Ru content in polymers. Within a 3 % error, the measured data (Table IV.4) are in a good agreement with those as calculated from the feed ratios.

Table IV.3. Photophysical properties of monomer 11 and three copolymers in ACN.

Compound	Absorption $\lambda_{\text{max}}/\text{nm}$ [$\log(\epsilon/\text{M}^{-1}\text{cm}^{-1})$]	Assignment	Emission $\lambda_{\text{max}}/\text{nm}$	
			$\lambda_{\text{ex}} = 320 \text{ nm}$	$\lambda_{\text{ex}} = 560 \text{ nm}$
IV.11-Ru	297 (4.76)	$\pi \rightarrow \pi^*$	790	418
	357 (IV.24), 524 (4.17)	MLCT		
IV.18	298 (4.36)	$\pi \rightarrow \pi^*$	790	408
	375 (4.49), 525 (3.54)	MLCT		
IV.19	298 (4.62)	$\pi \rightarrow \pi^*$	790	403
	347 (IV.55), 525 (3.87)	MLCT		
IV.20	297 (4.70)	$\pi \rightarrow \pi^*$	790	418
	345 (4.54), 525 (3.92)	MLCT		

Table IV.4. Measured Ru content by colorimetric method.

copolymer	molar ratio in feed	Calculated Ru	Measured Ru
	IV.11-Ru:IV.16: IV.17	wt%	wt%
IV.18	0.22: 0.50: 0.28	7.4	7.9
IV.19	0.44: 0.50: 0.06	11.0	11.0
IV.20	0.50: 0.50: 0	11.6	11.6

IV.3.6 Photoluminescent and Electroluminescent Properties

The photoluminescent spectra ($\lambda_{\text{ex}} = 320 \text{ nm}$) of the three copolymers (**IV.18**, **IV.19** and **IV.20**) were obtained in ACN at a concentration of $2.14 \times 10^{-5} \text{ M}$ for each and are shown in figure IV.13. For **IV.20**, its maximum quantum yield in solution was obtained at a concentration of $2.14 \times 10^{-5} \text{ M}$ by adjusting the concentration, which suggests that at a lower concentration, the quenching of the PL is mainly through intrachain energy transfer; while at a higher concentration, both intrachain and interchain

energy transfer will take place. Quantum yields of the copolymers, relative to poly(9,9'-dioctylfluorene) (**PFO**), were determined by the following equation⁷⁰:

$$\phi_2 = \phi_1(I_2/I_1)(n_2/n_1)^2(1-10^{-A_1})/(1-10^{-A_2}) \quad (2)$$

where ϕ is the emission quantum yield of an unknown or a reference compound, I is the integral of the emission intensity (area under the emission maximum), A is the absorbance at λ_{ex} in a 1-cm cell, and n is the refractive index of the solvent.

Figure IV.13. Fluorescent spectra of fluorene ($\lambda_{ex} = 280$ nm, inserted figure) and **PFO** (inserted figure, $\lambda_{ex} = 330$ nm) in toluene and Ru copolymers in ACN at $c = 2.14 \times 10^{-5}$ M ($\lambda_{ex} = 330$ nm): (a) fluorene; (b) **PFO**; (c) **IV.18**; (d) **IV.19**; (e) **IV.30**.

It's clear that in comparison with **PFO** (inserted figure in Figure 3.13), the fluorescent quenching is evident even at the lowest loading of monomer **IV.11-Ru** for **IV.18** which has a relative quantum yield of 1.58 % to **PFO**. For **IV.20** in which the molar ratio of fluorene to DCH-Ru is 1:1, its relative quantum yield to **PFO** in ACN

drops to 0.53%. In addition, the PL spectra of the copolymers show a blue-shift with the increase of DCH-Ru content in polymer. This is because with a higher Ru content, the polyfluorene segments become shorter. When the fluorene content is equal to that of DCH-Ru, the PL of the fluorene segments will be similar to that of fluorene alone at 330 nm (trace a in Figure IV.13), since there is no conjugation between fluorene units through DCH-Ru units. Thus, the emission at about 400 nm from both **IV.19** and **IV.20** is most likely from the tailing of fluorene unit. Due to the strong intra- and interchain quenching, no PL at around 400 nm was detected in the solid state for all the three polymers. Copolymer **IV.18** gave nearly a complete emission from oligofluorene fragments in the polymer chain with a maximal emission at 419 nm. According to the relationship between the wavelength of the maximal fluorescent and the length of oligofluorenes⁷¹, the average length of the oligofluorene in copolymer **IV.18** is 5 ~ 6 repeating units.

As a chromophore in the polymer, the DCH-Ru unit can also emit when being excited at the wavelength of its MLCT band. The room-temperature PL spectra obtained at the excitation wavelength of 560 nm are depicted in figure IV.14. All the copolymers give the same maximal peaks as the monomer complex **IV.11-Ru** at 780 nm, which is assigned to a spin-forbidden metal-to-ligand charge-transfer (³MLCT) transition^{72,73}.

Figure IV.14. PL spectra of three copolymers in ACN at $c = 0.10$ mg/mL.

For the potential application in light-emitting diodes (LEDs), both the PL and EL (electroluminescence) properties are required for the device design. The EL of Ru(II) complexes is ascribed to electro-generated chemiluminescence (ECL) with a process described as the following equations⁷⁴:

In a ECL device, holes are injected from the anode into the t_{2g} orbital of Ru, while electrons are injected from the cathode into the π^* orbital of the ligands. These electrogenerated species hop through the film, until they meet in a single molecule and form excited cations. The deactivation of these radical cations results in the generation of light.

With the functions of an efficient hole/electron transporter and a light-emitter, a single-layer ECL device can be fabricated from Ru^{II} complex⁷⁵. The electrochemical

process in the ECL device leaves it independent of the work functions of the electrodes. Thus, more air-stable metal like Au can be used as an electrode.

To demonstrate EL of the three complex copolymers, a simple single-layer diode device was fabricated with the structure of ITO/copolymer/Au. All the copolymers can form good films with a thickness of 80 ~ 100 nm on ITO anode by spin-coating. A layer of gold (130 nm) as a cathode is deposited onto the polymer layer under a pressure of 3×10^{-7} Torr. The EL spectra shown in figure IV.15 for all the copolymers are similar to their PL spectra with a maximal peak at about 790 nm due to MLCT transition. The temporal evolution of the current and radiance of the device based on **IV.20** is shown in figure IV.15 under different forward bias voltages. Upon application of a voltage, the current rapidly increases to a steady-state value, while the radiance initially follows the current but then decays exponentially with time, which is similar to other ruthenium complex based devices reported in the literature⁷⁶⁻⁷⁸. Compared to DCH-Ru pendant polymers⁷⁹, the main-chain copolymer **IV.20** responds 4 times faster (20s vs 100s) to reach maximum emission under the similar conditions: the voltage (5V), the Ru content (11.6% vs 10.6%) and film thickness (~80 nm). This is likely due to the higher ionic conductivity of **IV.20**.

Figure IV.15. EL spectra of LED devices containing polymers IV.18, IV.19 and IV.20 with a configuration of ITO/polymer/Au.

The solid-state LED devices based on the copolymer **IV.20** operate in a mechanism similar to that for electrochemical cells. Unlike organic LED requiring low work function cathodes (e.g., Ca), the devices containing redox ruthenium complex polymers can be made with an air-stable Au cathode. Upon applying a voltage, the counterions (PF_6^-) accumulate near the anode and deplete near the cathode, causing a lowering of the barriers for hole and electron injection and thus an increase in the current. When the anion distribution is in equilibrium at the electrodes, as dictated by the applied bias and the Coulombic interactions with the ionic and electronic charge in the device, a steady state is reached. It is believed that in the steady state the applied voltage drops at the contacts, and the holes and electrons move within the device by diffusion only^{76,77}. A higher voltage facilitates the accumulation of the PF_6^- ions at the anode, resulting in a faster device turn-on (Figure IV.16). The previous study⁷⁹ found that the external

quantum efficiency (EQE) of the devices for polymers with the DCH-Ru groups showed a similar tendency as the EL radiance changed with time. Both the EL radiance and EQE began to decay after the current was up to the steady state and decayed faster under higher voltages. Using copolymers having less ruthenium content (**IV.18**), much weaker EL was obtained.

Figure IV.16. EL performance of copolymer IV.20 in film at a thickness of 80 nm:

(a) current vs time; (b) brightness (radiance) vs time.

IV.3.7 Thermal Properties

The thermal stability of all the three copolymers and **PFO** was measured by thermogravimetric analysis (TGA) under nitrogen as assessed by the onset temperature for 5% weight loss. All the polymers were found to be quite stable at the temperatures up to 405 °C (Figure IV.17 and Table IV.5). Differential scanning calorimetry (DSC) was also done on the copolymers at a flow rate of 10 °C/min. No glass transition temperatures were detected for either of the copolymers, indicating the rigidity of the polymer backbone.

Figure IV.17. TGA traces of PFO and three copolymers.

Table IV.5. Thermal stability results of PFO and three copolymers under N₂.

Polymer	PFO	IV.18	IV.19	IV.20
T _d / °C ^a	426	400	405	385

^a temperature for 5% weight loss in nitrogen assessed by TGA with a flow rate of 10 °C / min

IV.3.8 Electrochromic Properties

The electrochromic (EC) properties of the copolymers were evaluated as a thin film on ITO glasses. With the highest Ru content, polymer **IV.20** was expected to achieve the highest optical attenuation at 1600 nm for a given thickness. In a three-electrode system, ITO glass acts as a working electrode, Pt as a counter electrode and Ag as a reference electrode. The oxidation and reduction potentials are set at +600 mv and -600 mv, respectively. At a time-based mode, both CV and UV-vis-NIR methods can be used to monitor the redox process of the polymer film (Figure IV.18). For a film with a thickness of 325 ± 5 nm, the oxidation process was found to be much slower than the reduction process (20s vs 3s), indicating that the slow oxidation process will prolong the

time to reach high attenuation degree. This result was also observed for films with lower or higher thickness.

Figure IV.18. Current (dot line) and transmission (solid line) changes of IV.20 film (thickness: 325 ± 5 nm) at 1600 nm at a constant potential of + 600 mV and - 600 mV in 0.1M TBAH/THF.

According to Street's study on polypyrrole-coated electrode⁸⁰, charge compensation during reduction is favored by diffusion of the electrolyte cation into the polymer and not the anion in the polymer into solution. His study suggests that in our experiment, diffusion of anion (PF_6^-) from solution into polymer is much slower than diffusion of cation (NBu_4^+) from solution into polymer. The optical attenuation (dB) at 1600 nm was calculated from the equation:

$$\text{Attenuation} = 10\log(T_b/T_c) \quad (3)$$

where T_b and T_c are the bleached and colored state of the film, respectively. The measurements were done in a 0.1 M $\text{NH}_4\text{PF}_6/\text{THF}$ solution under the pulse potentials of ± 600 mV at different switching speeds. The traces are shown in Figure IV.19. The attenuation ranges were calculated to be 1.27, 2.92 and 3.77 dB at the switching speeds of

5s, 10s, and 20s, respectively. The attenuation range at a switching speed of 20s corresponds to an intrinsic attenuation value of 11.6 dB/ μm . Compared to the thinner film ($200 \pm 5 \text{ nm}$) at the same switching speed (10s), thicker film had a higher attenuation range (2.92 dB vs 1.74 dB), but the attenuation property regarding the thickness is very close (8.98 dB vs 8.7 dB). There was no noticeable optical loss for the film at bleached state after 30 cycles at all the three switching speeds.

Figure IV.19. Change of transmittance at 1600 nm of the film of copolymer IV.20 film (thickness: $325 \pm 5 \text{ nm}$) coated on ITO glass (electrolyte: 0.1 M $\text{NH}_4\text{PF}_6/\text{THF}$) as a function of switching speed (5s, 10s and 20s); pulse potentials: $\pm 600 \text{ mV}$.

IV.4 Conclusion

In conclusion, we synthesized a series of dinuclear DCH-Ru based main-chain polymers by Suzuki-coupling polymerization through AA/BB approach. These polymers bear both the properties from single molecule DCH-Ru, such as NIR electrochromicity, NIR photoluminescence, NIR electroluminescence, and reversible redox behavior, and

general polymeric properties like good film formation. These polymers are highly thermally stable and behave like polyelectrolytes in solution. Compared to the method to prepare such DCH-Ru main-chain polymers by complexation of the corresponding DCH polymer ligand and *cis*-Ru(byp)₂Cl₂·2H₂O, the current method provided several advantages: (1) easy purification of the polymer products; (2) easy control of the molecular weight by changing the reaction time; (3) easy modification of the polymer structure by choosing proper comonomers. These polymers will be very useful in broad fields, such as reductants detection, NIR marker, NIR electrochromic device, and NIR photovoltaic device, etc.

IV.5 Experimental Section

Materials

All reagents and solvents utilized in synthesis and measurement were used as received.

Measurements

¹H and ¹³C NMR spectra were recorded on Bruker AMX-400 and Varian 300 MHz NMR spectrometers using deuterated chloroform (CDCl₃), acetone (acetone-d₆) and dimethylsulfoxide (DMSO-d₆) as solvents with 1% tetramethylsilane (TMS) as an internal standard. The chemical shifts were reported in δ (ppm) to TMS.

IR spectra were taken on an ABB Bomem MB-100 FTIR in KBr pellets or films coated on a salt plate. Uv-vis-NIR spectrophotometric and electrochemical measurements were taken in spectroscopic grade acetonitrile (ACN) or dimethylformide

(DMF) using a Perkin Elmer Lambda 900 uv-vis-NIR and BAS 100 B/W, separately. The photoluminescent (PL) tests were done on a Shimadzu RF-1501 fluorescence spectrophotometer with a range of 300 nm to 800 nm and a PTI QuantaMaster Bench-top continuous spectrofluorometer with a range from 180 nm to 1700 nm. The polymer film for PL test is made from casting a DMF solution on an ITO glass.

The EI and ESI mass spectroscopy were performed in the University of Ottawa Regional Mass Spectrometry Centre and reported as m/z (% intensity relative to the base peak). Melting points were measured on a Fisher-Jones melting point apparatus without any correction.

Spectroelectrochemical generation of $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ and $\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}$ oxidation states of the complexes were completed in an OTTLE cell. The redox potentials were measured vs. NHE with ferrocene as an internal standard.

Viscosity measurements were carried out at 30 °C (± 0.1 °C) using Ubbelohde viscosimeters. Measurements in the presence of added salt were carried out by dissolving the polymer in 0.01 M NH_4PF_6 /DMF solution. Flow times were measured with an accuracy of (± 0.2 s). Every determination was repeated three times to check the reproducibility. GPC measurements were performed on a Perkin Elmer system with an NCI-900 network chromatography interface, an isocratic LC-250 pump, a series 200 refractive index detector, a LC-101 oven and a Polymer Laboratories PLgel 5 μm Mixed-D column. The oven temperature was kept at 50°C during the tests. A solution of 1.0 and 2.0 mM NH_4PF_6 in DMF was used as an eluent at a flow rate of 1.0 mL/min. Molecular weights were calculated against polystyrene standards.

General Procedure for Suzuki Cross-Coupling Polymerization

To a glass tube were added 0.5 part of diboronic acid ester compound, **a** part of monomer complex **IV.11-Ru**, **b** part of dibromo- compound ($0.5 + \mathbf{a} + \mathbf{b} = 1$), 0.4 % part of palladium(0) catalyst and DMF in a weight/volume ratio of 10 %. After the stirred mixture was bubbled by argon for 10 mins, 1.25 parts of K_2CO_3 were added to the solution at room temperature. The mixture was kept stirring at $100\text{ }^\circ\text{C}$ overnight under the protection of argon before the reaction was stopped by adding 0.1 part of 4-methylphenylboronic acid followed by adding 0.1 mL of bromobenzene with a interval of 2 hrs. Then the mixture was cooled to room temperature, and the product was precipitated in 75 mL of methanol containing 5 times amount of NH_4PF_6 . The product was filtered out, washed by methanol and deionic water, and dried at reduced pressure to give polymers in high yields.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxazolidin-2-yl)benzoyl chloride (IV.1)

To a solution of 1.0 g (4.0 mmol) of pinacol protected 4-carboxyphenylboronic acid in 5 mL freshly distilled chloroform were added 3.0 mL (41 mmol) of thionyl chloride and a few drops (about 0.1 mL) of *N,N*-dimethylformamide. The solution was heated to reflux for 2 hrs. The reaction solution was then allowed to cool to room temperature and was concentrated on a rotary evaporator under reduced pressure. To the residue was added 8 mL of chloroform and the resulting solution was concentrated again. This procedure was repeated two more times to remove residual thionyl chloride. The

crude material was dried under vacuum and was obtained as an off-white solid (1.06 g, 99 % yield). The product was used right away for the next reaction.

4-(2-(4-Bromobenzoyl)hydrazinecarbonyl)phenylboronic acid pinacol ester (IV.2)

To a solution of 1.08 g (0.50 mmol) of 4-bromobenzoic hydrazide and 0.40 g (0.50 mmol) of pyridine in 20 mL of anhydrous THF was added dropwise 1.33g (0.50 mmol) of freshly prepared 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic chloride in 5 mL of anhydrous THF while stirring. Solvent was removed under reduced pressure after the mixture was kept stirring overnight. The solid was then filtered out, washed by distilled water three times and recrystallized from THF/hexane to provide 1.30 g (58 % yield) of the product as a white solid. M.p. 249-251 °C; IR (KBr pellet, cm^{-1}): 3423 (H_2O), 3222 ($\nu_{\text{N-H}}$), 2979, 2925, 2853 ($\nu_{\text{C-H}}$, aliphatic), 1652 ($\nu_{\text{C=O}}$), 1602, 1552 ($\nu_{\text{C=C}}$), 1396 ($\nu_{\text{C-N}}$), 1363 ($\nu_{\text{B-O}}$); ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ /ppm: 11.01 (s, 1H), 10.96 (s, 1H), 7.88 (d, 2H, $J = 8.0$ Hz), 7.84 (d, 2H, $J = 8.0$ Hz), 7.68 (d, 2H, $J = 8.0$ Hz), 7.58 (d, 2H, $J = 8.0$ Hz), 1.29 (s, 12H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ /ppm: 166.4, 165.5, 135.0, 134.6, 134.2, 132.1, 130.0, 127.3, 126.8, 126.2, 84.5, 25.2; MS found (nature of the peak, relative intensity): 446 (M^+ with ^{81}Br , 0.6), 444 (M^+ with ^{79}Br , 0.5), 428 ($[\text{M-H}_2\text{O}]^+$ with ^{81}Br , 99.1), ($[\text{M-H}_2\text{O}]^+$ with ^{79}Br , 98.5).

4-(2-(4-Bromobenzoyl)hydrazinecarbonyl)phenylboronic acid (IV.3)

To a solution of 0.82 g (3.1 mmol) of 4-bromobenzhydrazide in 20 mL water/THF (3:1) with 0.33g (3.1 mmol) Na_2CO_3 were added dropwise a solution of 0.66 g (3.1 mmol) of freshly prepared 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic chloride in 5 mL of anhydrous THF while stirring. After addition, the mixture was kept stirring for 4 hrs. The solid was then filtered, washed with distilled water and dried under vacuum. The desired product was obtained as a white powder (0.76 g, 65 % yield). $T_d > 260\text{ }^\circ\text{C}$ (m.p. was not observed); IR (KBr pellet, cm^{-1}): 3423 (H_2O), 3222 ($\nu_{\text{N-H}}$), 1640 ($\nu_{\text{C=O}}$), 1602, 1552 ($\nu_{\text{C=C}}$), 1402 ($\nu_{\text{C-N}}$), 1371 ($\nu_{\text{B-O}}$); ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ/ppm : 10.60 (s, 1H), 10.52 (s, 1H), 8.24 (s, 2H), 7.88 (m, 6H), 7.75 (d, 2H, $J = 9.0\text{ Hz}$); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ/ppm : 166.4, 165.4, 138.7, 134.5, 134.2, 132.1, 130.0, 126.8, 126.2; MS (EI, m/z) not found.

4-Bromo-N,N-dibenzylaniline (IV.4)

To a mixture of 17.2 g (100 mmol) of 4-bromoaniline and 16.0 g (151 mmol) of Na_2CO_3 in 100 mL of DMF was added 35.9 g (210 mmol) of benzyl bromide dropwise while stirring with the protection of argon. The mixture was kept stirring at $100\text{--}100\text{ }^\circ\text{C}$ overnight and then poured into 400 mL of ice-water, washed with distilled water and cold

methanol, and dried under reduced pressure at 50 °C. The product was obtained as white crystals in needles (32.3 g, 92% yield). M.p. 126–127 °C (124–127 °C)⁹⁰; IR (neat, cm⁻¹): 3085, 3062, 3028 ($\nu_{\text{C-H}}$, aromatic), 2925, 2861 ($\nu_{\text{C-H}}$, aliphatic), 1591, 1496, 1450 ($\nu_{\text{C=C}}$); ¹H NMR (300 MHz, CDCl₃) δ /ppm: 7.67 (d, 2H, J = 9.0 Hz), 7.38-7.25 (m, 10H), 6.78 (d, 2H, J = 6.0 Hz), 4.70 (s, 4H); ¹³C NMR (75 MHz, CDCl₃) δ /ppm: 136.4, 136.2, 128.7, 127.1, 126.7, 111.7, 83.2, 78.5, 53.8; MS calcd.: 352.3; EI m/z found (nature of the peak, relative intensity): 351 (M⁺ with ⁸¹Br, 37.4), 353 (M⁺ with ⁷⁹Br, 36.8).

Cyclotrimeric 4-(N,N-dibenzylamino)-phenyl-boronic anhydride (IV.5)

To a solution of 30.0 g (85.2 mmol) of 4-bromo-N,N-dibenzylaniline in 180 mL of anhydrous THF cooled to -78 °C was added 37.5 mL (94.5 mmol) of a 2.5 M hexyllithium in hexane solution dropwise in 30 mins with stirring. This solution was transferred to 23.7 mL of (102.9 mmol) of triisopropyl borate and stirred under -78 °C for a further 1 h. The bath was removed and the solution was warmed to room temperature naturally and kept stirring overnight. The concentrated product was mixed with 225 mL of ethyl acetate and 86 mL of water. The organic phase was separated, dried over sodium sulfate and concentrated. The solid product was suspended in 50 mL of hexane, filtered off and washed with 110 mL of ethyl acetate. The filtrate was concentrated to afford 16.3 g (18.0 mmol, 63%) desired product as a white solid. M.p. 192-193 °C; IR (neat, cm⁻¹): 3420 (H₂O), 3089, 3062, 3032 ($\nu_{\text{C-H}}$, aromatic), 2979, 2929 ($\nu_{\text{C-H}}$, aliphatic), 1600, 1506,

1451 ($\nu_{C=C}$, aromatic), 694 (ν_{B-O} , boroxine)⁹¹; 1H NMR (75 MHz, $CDCl_3$) δ /ppm: 8.05 (d, 1H, $J = 9.0$ Hz), 7.37-7.20 (m, 11H), 6.86-6.77 (m, 2H), 4.77 (s, 2H), 4.71 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ /ppm: 152.2, 138.0, 137.3, 129.3, 128.8, 127.1, 126.7, 111.5, 53.9; MS (ESI, m/z) found (nature of the peak, relative intensity): 1016.4 ($[M+H_3O]^+$, 0.10).

4-Aminophenylboronic acid hydrochloride (IV.6)

To a solution of 6.28 g (7.0 mmol) of trimeric 4-(N,N-dibenzylamino)-phenylboronic anhydride in 50 mL of methanol were added 126 mg of Pd/C (10%) and 1.0 mL of hydrochloric acid and shaken at room temperature under hydrogen atmosphere (10-40 psi) for 3 hrs until the pressure stopped changing. The catalyst was then filtered off and the filtrate was concentrated at reduced pressure. The desired product was collected as a white solid. (3.45 g, 95% yield). This product was used for the next step of reaction without further purification. Td > 230 °C (m.p. was not observed).

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl) aniline hydrochloride (IV.7)

To a mortar were added 3.56 g (20.5 mmol) of 4-aminophenylboronic acid hydrochloride and 2.83 (24.2 mmol) of pinacol and milled for 10 mins. After heating in vacuum at 52 °C for 2 hrs, the mixture was washed with ethyl ether and dried in vacuum to give the desired product as a white solid (5.18 g, 98% yield). The sample without HCl

used for IR and NMR test was prepared by adding diluted sodium bicarbonate to adjust the PH = 8. The precipitate was filtered off and dried in vacuum. $T_d > 300\text{ }^{\circ}\text{C}$ (m.p. was not observed); IR (neat, cm^{-1}): 3450, 3357 ($\nu_{\text{N-H}}$), 3043 ($\nu_{\text{C-H}}$, aromatic), 2974 ($\nu_{\text{C-H}}$, aliphatic), 1629 ($\nu_{\text{N-H}}$), 1603 ($\nu_{\text{C=C}}$), 1360 ($\nu_{\text{B-O}}$, ester); ^1H NMR (150 MHz, CDCl_3) δ/ppm : 7.64 (d, $J = 6.0$ Hz), 6.68 (d, $J = 6.0$ Hz) 3.85 (s, 2H), 1.34 (s, 12H); ^{13}C NMR (75 MHz, CDCl_3) δ/ppm : 148.0, 136.44, 114.7, 83.4, 24.9; MS (ESI, m/z) found (nature of the peak, relative intensity): 220.2 ($[\text{M}-\text{Cl}]^+$, 47.2).

Phenyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenylcarbamate (IV.8)

To a mixture of 1.36 g (5.3 mmol) of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline hydrochloride suspended in 150 mL of anhydrous dichloromethane were added 0.84 g (10.6 mmol) of pyridine and 0.83 g of phenyl chloroformate (5.3 mmol). The mixture was stirred overnight till TLC (1:1 = hexane: ether) analysis showed the consumption of all starting materials. The solution was washed with saturated sodium bicarbonate (20 mL $\times$ 3), water (20 mL $\times$ 3) and brine (20 mL $\times$ 3) before it was concentrated. The residue was dried at reduced pressure to give the product as colorless needles (1.17 g, 65% yield). M.p. $184\text{ }^{\circ}\text{C}$; IR (neat, cm^{-1}): 3321 ($\nu_{\text{N-H}}$, amide), 3051 ($\nu_{\text{C-H}}$, aromatic), 2982, 2929 ($\nu_{\text{C-H}}$, aliphatic), 1728 ($\nu_{\text{C=O}}$), 1606, 1401 ($\nu_{\text{C=C}}$), 1587 ($\nu_{\text{N-H}}$, amide), 1361 ($\nu_{\text{B-O}}$, ester) 1196, 1142 ($\nu_{\text{C-O}}$, ester); ^1H NMR (300 MHz, CDCl_3) δ/ppm : 7.81 (d, 2H, $J = 9.0$ Hz), 7.43 (m, 4H), 7.28 (d, 1H, $J = 9.0$ Hz), 7.21 (d, 2H, $J = 9.0$ Hz), 7.08 (s, 1H), 1.37 (s, 12H); ^{13}C NMR (75 MHz, CDCl_3) δ/ppm : 151.5, 150.5, 143.0,

140.0, 136.0, 129.4, 125.8, 121.7, 117.6, 83.8, 24.9; MS (EI, m/z) found (nature of the peak, relative intensity): 339 (M^+ , 2.1).

N-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-hydrazinecarboxamide (**IV.9**)

To a solution of 0.27 g (7.6 mmol) of 85% hydrazine hydrate in 10 mL of methanol was added 1.20 g (3.5 mmol) of compound **IV.7**. The mixture was heated to reflux for 3 hrs where the complete conversion of the starting compound was checked by TLC (1:1 = hexane: ether). The solution was then cooled down to 0 °C to promote crystallization. The product was washed by chilled ethyl ether and methanol to give 0.68 g (69%) of colorless crystal in needles. M.p. 188 °C; IR (neat, cm^{-1}): 3347, 3317 ($\nu_{\text{N-H}}$, amide), 3108 ($\nu_{\text{C-H}}$, aromatic), 2979, 2929 ($\nu_{\text{C-H}}$, aliphatic), 1682 ($\nu_{\text{C=O}}$), 1606, 1511 ($\nu_{\text{C=C}}$), 1580, 1534 ($\nu_{\text{N-H}}$, amide), 1397 ($\nu_{\text{C-N}}$), 1360 ($\nu_{\text{B-O}}$, ester); ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.76(s, 1H), 7.55 (s, 4H), 7.50 (s, 1H), 4.37 (s, 2H), 1.28 (s, 12H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 157.0, 142.8, 136.0, 135.2, 116.9, 83.2, 24.6; MS (EI, m/z) found (nature of the peak, relative intensity): 277 (M^+ , 8.2).

N-(4-Bromophenyl)-*N'*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,2-hydrazinedicarboxamide (**IV.10**)

To a stirred solution of 1.35 g (4.9 mmol) of compound **IV.9** in 30 mL of dry THF was added dropwise 0.97 g (4.9 mmol) of 4-bromophenyl isocyanate in 10 mL of dry THF at 0 °C. After stirring at 0 °C for 30 mins, the mixture was warmed to room temperature and kept stirring for 3 hrs. The precipitate was then filtered off, washed by dry THF and dried at reduced pressure to yield 2.2 g (96%) product as white powder. M.p. 243 °C; IR (KBr, cm^{-1}) 3450 (H_2O), 3292 ($\nu_{\text{N-H}}$), 3101 ($\nu_{\text{C-H}}$), 2982, 2939 ($\nu_{\text{C-H}}$, aliphatic), 1670 ($\nu_{\text{C=O}}$), 1598, 1547, 1490 ($\nu_{\text{C=C}}$), 1402 ($\nu_{\text{C-N}}$), 1363 ($\nu_{\text{B-O}}$, ester); ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ /ppm: 8.96 (s, 1H), 8.95 (s, 1H), 8.08 (s, 1H), 8.06 (s, 1H), 7.57 (d, 2H, $J = 8.4$ Hz) 7.51 (t, 4H), 7.42 (d, 2H, $J = 8.8$ Hz), 1.27 (s, 12H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ /ppm: 155.8, 155.64, 142.58, 139.08, 135.96, 135.17, 121.1, 120.4, 117.3, 113.2, 83.2, 24.6; MS (EI, m/z) found (nature of the peak, relative intensity): 474 (M^+ with ^{79}Br , 0.2) and 476 (M^+ with ^{81}Br , 0.1).

1,2-Bis(4-bromobenzoyl)hydrazine (IV.11)

To a solution of 80 mL of THF/ H_2O (1:1) with 0.25 g (5.0 mmol) of hydrazine monohydrate and 0.53 g of Na_2CO_3 (5.0 mmol) was added 2.20 g (10.0 mmol) of 4-bromobenzoyl chloride in one portion. The stirring started immediately and continued for 1 hr at room temperature. Then the mixture was heated to 40°C and kept stirring for 4 hrs before it's cooled down to room temperature. The solvent was removed at reduced pressure. The white precipitate was collected by filtration and washed with distilled water 3 times. The crude product was purified by recrystallization and the desired product was

obtained as white crystal in plates (1.32g, 67% yield). M.p. 286°C (lit. 284-286 °C)⁹²; IR (KBr, cm⁻¹): 3440 (H₂O), 3203 ($\nu_{C=C}$), 3024 (ν_{C-H}), 1647 ($\nu_{C=O}$), 1601, 1560, 1499, 1464($\nu_{C=C}$), 1265 (ν_{C-N}); ¹H NMR (300 MHz, DMSO-*d*₆) δ /ppm: 10.64, (s, 2H), 7.86 (d, 4H, J = 9.0 Hz), 7.75 (d, 4H, J = 9.0 Hz); ¹³C NMR (75 MHz, DMSO-*d*₆) δ /ppm: 165.4, 132.1, 132.0, 130.0, 126.2; MS (EI, m/z) found (nature of the peak, relative intensity): 380 ([M-H₂O]⁺, 79.4).

[{Ru(bpy)₂}μ-(BrPh)₂-dch](PF₆)₂ (IV.11-Ru)

To a solution of 0.40 g of IV.11 (1.0 mmol) and 0.53 g (5.0 mmol) of Na₂CO₃ in 150 mL of EtOH/H₂O (1:2) was added 1.04 g (2.0 mmol) of *cis*-Ru(bpy)₂Cl₂·2H₂O. The mixture was refluxed overnight under argon and the product was precipitated by adding 5.00 g of NH₄PF₆ in 50 mL of H₂O after the solution was cooled to room temperature. The crude product was purified by chromatography with grade III acid alumina as stationary phase and 1:1 acetonitrile:toluene as starting eluent. After the yellow band was washed out of the column, the eluent was changed to H₂O/acetonitrile (5:95) and the purple band was collected. The solution was concentrated and the product was reprecipitated by adding NH₄PF₆ aqueous solution, filtered out, washed with water and dried at reduced pressure to give 1.12g (73%) of desired product. IR (KBr, cm⁻¹): 3433 (H₂O), 3055 (ν_{C-H} , aromatic), 2952, 2926, 2853 (ν_{C-H} , aliphatic), 1607 ($\nu_{C=N}$), 1578, 1481 ($\nu_{C=C}$), 829 (ν_{P-F}); ¹H NMR (300 MHz, DMSO-*d*₆) δ /ppm: 9.28 (d, 1H, J = 5.4 Hz), 9.17

(d, 1H, $J = 5.1$ Hz), 8.90 (d, 1H, $J = 5.1$ Hz), 8.73 (d, 1H, $J = 8.4$ Hz), 8.64 (m, 2H), 8.54 (d, 2H, $J = 8.1$ Hz), 8.49 (d, 2H, $J = 8.1$ Hz), 8.32-8.08 (m, 8H), 7.81 (t, 2H, $J_1 = J_2 = 7.8$ Hz), 7.18-7.12 (t, 4H), 6.91-6.82 (m, 6H), 6.47 (d, 2H, $J = 8.1$ Hz), 6.24 (s, 2H); ^{13}C NMR (75 MHz, DMSO- d_6) δ /ppm: 175.2, 175.0, 158.4, 158.3, 158.2, 158.0, 157.9, 152.6, 152.5, 152.0, 151.6, 151.5, 151.4, 151.0 (d), 149.5, 137.2, 127.0 (d), 136.7, 136.5, 136.4, 134.3, 133.9, 133.8, 130.9, 130.8, 128.8, 128.2, 127.5, 127.2, 126.8, 126.3, 124.4, 124.2, 124.0, 123.9, 122.2, 122.0. MS calcd.: 1513.9 ($\text{C}_{54}\text{H}_{40}\text{Br}_2\text{F}_{12}\text{N}_{10}\text{O}_2\text{P}_2\text{Ru}_2$); ESI m/z found (nature of the peak, relative intensity): 1368.8 ($[\text{M-PF}_6]^+$, 0.25), 612.1 ($[\text{M-2PF}_6]^{2+}/2$, 28.83).

1,8-Bis(4-bromophenoxy)-3,6-dioxaoctane (IV.12)

To a solution of 9.34 g of *p*-bromophenol in 16 mL of dimethyl sulfoxide (DMSO) was added 2.16 g of sodium hydroxide and was stirred at 60°C for 2 hrs under nitrogen. A solution of 2.25 g 1,2-bis(2-chloroethoxy)ethane in 108 mL of degassed DMSO was then added dropwise at 60 °C and the resulting mixture was kept stirring at 90°C overnight. When it was cooled to room temperature, 100 mL of water was added to the mixture to yield a pale brown precipitate. The crude product was isolated by filtration, and recrystallized from methanol to yield 4.53 g (82%) of desired product was white crystals. M.p. 73 °C (lit. 70 °C)⁹³; IR (neat, cm^{-1}): 3096, 3066 ($\nu_{\text{C-H}}$, aromatic), 2929, 2876 ($\nu_{\text{C-H}}$, aliphatic), 1591, 1488, 1453 ($\nu_{\text{C=C}}$), 1246, 1127, 1062 ($\nu_{\text{C-O}}$, ether); ^1H NMR (300MHz, CDCl_3) δ /ppm: 7.38 (d, 2H, $J = 9.0$ Hz), 6.81 (d, 2H, $J = 9.0$ Hz), 4.11 (t, 2H, $J = 3.0$ Hz), 3.87 (t, 2H, $J = 3.0$ Hz), 3.76 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ /ppm:

157.9, 132.24, 116.5, 113.1, 70.9, 68.7, 67.7; MS (EI, m/z) found (nature of the peak, relative intensity): 460 (M^+ , 26.8).

1,8-Bis(2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)-3,6-dioxaoctane

(IV.14)

To a stirred solution of 3.68 g of dibromide compound **IV.12** in 100 mL of anhydrous THF at -75°C under argon was added dropwise 12.8 mL (32 mmol) of 2.5 M n-butyllithium solution in hexane over 15 mins. After the mixture was maintained for 2 hrs at the same temperature, it was transferred over 15 mins into a 40 mL of trimethyl borate (0.352 mol) in 100 mL of dry THF solution through a tubing bridge at -75°C . The temperature was gradually raised over 3 hrs to room temperature after maintaining at low temperature for another hour. An excess of trimethyl borate was decomposed by the addition of 80 mL of 2 M HCl at 0°C , and then the mixture was stirred at room temperature for 24 hrs. The solvent was removed under reduced pressure, and the precipitate was filtered by suction. After washed with H_2O (5×80 mL) and hexane (5×50 mL), it was recrystallized from methanol-water to afford 2.38 g (76%) of 4,4'-(ethane-1,2-diylbis(oxy))bis(4,1-phenylene)diboronic acid (**IV.13**) as white solid.. The final pinacol-protected product was obtained in 99% yield by refluxing one equivalent of compound **IV.13** and two equivalent of pinacol in toluene for 4 hrs.. M.p. $94-96^{\circ}\text{C}$; IR (neat, cm^{-1}): 3040 ($\nu_{\text{C-H}}$, aromatic), 2977, 2929, 2876 ($\nu_{\text{C-H}}$, aliphatic), 1605, 1515 ($\nu_{\text{C=C}}$), 1362 ($\nu_{\text{B-O}}$, ester), 1249, 1061 ($\nu_{\text{C-O}}$, ether), 1146 ($\nu_{\text{B-C}}$); ^1H NMR (300 MHz, CDCl_3)

δ/ppm : 7.75 (d, 2H, $J = 9.0$ Hz), 6.91 (d, 2H, $J = 9.0$ Hz), 4.16 (t, 2H, $J = 2.5$ Hz), 3.88 (d, 2H, $J = 2.5$ Hz), 3.76 (s, 2H), 1.35 (s, 12H); ^{13}C NMR (75 MHz, CDCl_3) δ/ppm : 161.4, 136.5, 129.4, 114.0, 83.56, 70.9, 69.8, 67.3, 24.9; MS (EI, m/z) found (nature of the peak, relative intensity): 554 (M^+ , 21.2).

Poly(triglycolbiphenyl-alt-DCH-Ru) (IV.5)

IR (acetonitrile, cm^{-1}) 3078, 3030 ($\nu_{\text{C-H}}$, aromatic), 2925, 2868 ($\nu_{\text{C-H}}$, aliphatic), 1602, 1511 ($\nu_{\text{C=C}}$), 1264, 1245 ($\nu_{\text{C-O}}$, ether), 840 ($\nu_{\text{P-F}}$); ^1H NMR (300MHz, $\text{DMSO}-d_6$) δ/ppm : 9.43-6.36 (m, 48H), 4.15 (s, 4H), 3.80 (s, 4H), 3.66 (s, 4H).

poly(fluorene-alt-DCH-Ru) (IV.20)

IR (acetonitrile, cm^{-1}) 3078, 3030 ($\nu_{\text{C-H}}$, aromatic), 2930, 2853 ($\nu_{\text{C-H}}$, aliphatic), 1628 ($\nu_{\text{C=N}}$), 1602, 1499 ($\nu_{\text{C=C}}$), 840 ($\nu_{\text{P-F}}$); ^1H NMR (300MHz, $\text{DMSO}-d_6$) δ/ppm : 6.38 - 9.44 (m, 46H), 2.13 (s, 3H), 1.04 (s, 21H) and 0.62 (s, 10H).

References

1. Miyaoura, Norio; Yamada, Kinji; Suzuki, Akira *Tetrahedron Lett.* **1979**, 20, 3437.
2. Miyaoura, N.; Yamada, K.; Suginome, H.; Suzuki, A.; *J. Am. Chem. Soc.* **1985**, 107, 972.
3. Smith, G. B.; Dezeny, G. C.; Hughes, D. L.; King, A. O.; Verhoeven, T. R. *J. Org. Chem.* **1994**, 59, 8151.
4. Moreno-Manas, M.; Pérez, M.; Pleixats, R. *J. Org. Chem.* **1996**, 61, 2346.
5. Martin, A. R.; Yang, Y. *Acta Chem. Scand.* **1993**, 47, 221.
6. Molander, G. A.; Bernardi, C. R. *J. Org. Chem.* **2002**, 67, 8424.
7. Molander, G. A.; Dehmelt, F. *J. Am. Chem. Soc.* **2004**, 126, 10313.
8. Miyaoura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, 11, 513.
9. Miyaoura, N.; Suginome, H.; Suzuki, A. *Tetrahedron* **1983**, 39, 3271.
10. Miyaoura, N.; Ishiyama, T.; Sasaki, H.; Ishikawa, M.; Sato, M.; Suzuki, A. *J. Am. Chem. Soc.* **1989**, 111, 314.
11. Miyaoura, N.; Ishiyama, T.; Ishikawa, M.; Suzuki, A. *Tetrahedron Lett.* **1986**, 27, 6369.
12. Roth, G. P.; Fuller, C. E. *J. Org. Chem.* **1991**, 56, 3493.
13. Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, 109, 5478.
14. Martorell, G.; Garcia-Raso, A.; Saa, J. M. *Tetrahedron Lett.* **1990**, 31, 2357.
15. Ohe, T.; Miyaoura, N.; Suzuki, A. *Synlett* **1990**, 221.
16. Fu, J. M.; Snieckus, V. *Tetrahedron Lett.* **1990**, 31, 1665.
17. Suzuki, A. *Pure Appl. Chem.* **1991**, 63, 419.

17. Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, 95, 2457.
18. Suzuki, A. *J. Organometallic Chem.* **1999**, 576, 147.
19. Bellina, F.; Carpita, A.; Rossi, R. *Synthesis* **2004**, 15, 2419.
20. Kotha, S.; Lahiri, K.; Kashinath, D. *Tetrahedron* **2002**, 58, 9633.
21. Corbet, J. P.; Mignani, G. *Chem. Rev.* **2006**, 106, 2651.
22. Chemler, S. R.; Trauner, D.; Danishefsky, S. J. *Angew. Chem., Int. Ed.* **2001**, 40, 4544.
23. Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, 44, 4442.
24. De Vries, J. G.; De Vries, A. H. M.; Tucker, C. E.; Miller, J. A. *Innovations in Pharm. Tech.* **2001**, 01, 125.
25. Yasuda, N. *J. Organo. Chem.* **2002**, 253, 279.
26. Rehahn, M.; Schlüter, A. D.; Wegner, G.; Feast, W. J. *Polymer* **1989**, 30, 1060.
27. Schlüter, A. D. *J. Polym. Sci. Part A: Poly. Chem.* **2001**, 39, 1533.
28. Zhen, H.; Luo, C.; Yang, W.; Song, W. Y.; Du, B.; Jiang, J. X.; Jiang, C. Y.; Zhang, Y.; Cao, Y. *Macromolecules* **2006**, 39, 1693.
29. Zhen, H. Y.; Jiang, C. Y.; Yang, W.; Jiang, J. X.; Huang, F.; Cao, Y. *Chem. Eur. J.* **2005**, 11, 5007.
30. Li, Z. A.; Di, C. A.; Zhu, Z. C.; Yu, G.; Li, Z.; Zeng, Q.; Li, Q. Q.; Liu, Y. Q.; Qin, J. *G. Polymer* **2006**, 47, 7889.
31. Wu, C. W.; Lin, H. C. *Macromolecules* **2006**, 39, 7232.
32. Xin, Y.; Wen, G. A.; Zeng, W. J.; Zhao, L.; Zhu, X. R.; Fan, Q. L.; Feng, J. C.; Wang, L. H.; Wei, W.; Peng, B.; Cao, Y.; Huang, W. *Macromolecules* **2005**, 38, 6755.
33. Liu, X. M.; Lin, T. T.; Huang, J. C.; Hao, X. T.; Ong, K. S.; He, C. B.

- Macromolecules* **2005**, 38, 4157.
34. Fei, Z. P.; Li, B. S.; Bo, Z. S.; Lu, R. *Org. Lett.* **2004**, 6, 4703.
 35. Li, J.; Bo, Z. S. *Macromolecules* **2004**, 37, 2013.
 36. Bo, Z. S.; Schlueter, A. D. *Chem. Commun.* **2003**, 18, 2354.
 37. Bo, Z. S.; Schluter, A. D. *Chem. Eur. J.* **2000**, 6, 3235.
 38. Fu, Y. Q.; Li, Y.; Li, J.; Yan, S. K.; Bo, Z. S. *Macromolecules* **2004**, 37, 6395
 39. Bo, Z. S.; Zhang, C. M.; Severin, N.; Rabe, J. P.; Schlueter, A. D. *Macromolecules* **2000**, 33, 2688.
 40. Kandre, R. M.; Kutzner, F.; Schlaad, H.; Schluter, A. D. *Macromol. Chem. Phys.* **2005**, 206, 1610.
 41. Li, A. Y.; Chang, J. Y.; Wang, K. Q.; Lu, L. D. *Adv. Mater. Res.* **2006**, 11-12, 371
 42. Huang, F.; Hou L. T.; Wu H. B.; Wang X. H.; Shen, H. L.; Cao, W.; Yang, W.; Cao, Y. *J. Am. Chem. Soc.* **2004**, 126, 9845.
 43. Huang, F.; Hou, L. T.; Shen, H. L.; Yang, R. Q.; Hou, Q.; Cao, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, 44, 2521.
 44. Nehls, B. S.; Galbrecht, F.; Brauer, D. J.; Lehmann, C. W.; Scherf, U.; Farrell, T. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, 44, 5533.
 45. Hu, Q. S.; Katayama, H.; Nagao, M.; Nishimura, T.; Matsui, Y.; Fukuse, Y.; Wakioka, M.; Ozawa, F. *Macromolecules* **2006**, 39, 2039.
 46. Vitharana, D.; Liu, G. Y.; Jain, V.; Wagaman, M. W.; Zhang, L.; Lee, T. R.; Pu, L. *Macromolecules* **1996**, 29, 1082.
 47. Hu, Q. S.; Vitharana, D.; Liu, G. Y.; Jain, V.; Pu, L. *Macromolecules* **1996**, 29, 5075.
 48. Grigoras, M.; Antonoaia, N. C. *Polymer Int.* **2005**, 54, 1641.

49. Zhu, Z. G.; Swager, T. M. *J. Am. Chem. Soc.* **2002**, *124*, 9670.
50. Koch, F.; Heitz, W. *Macromol. Chem. Phys.* **1997**, *198*, 1531.
51. Bao, Z.; Chen, Y.; Cai, R.; Yu, L. *Macromolecules* **1993**, *26*, 5281.
52. Ng, P. K.; Wong, W. T.; Chan, W. K. *Macromol. Rapid Comm.* **1997**, *18*, 1009.
53. Pautzsch, T.; Klemm, E. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 2911.
54. Dinakaran, K.; Chou, C. H.; Hsu, S. L.; Wei, K. H. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4838.
55. Liu, S. J.; Zhao, Q.; Chen, R. F.; Deng, Y.; Fan, Q. L.; Li, F. Y.; Wang, L. H.; Huang, C. H.; Huang, W. *Chem. Eur. J.* **2006**, *12*, 4351.
56. Frank, W.; Pautzsch, T.; Klemm, E. *Macromol. Chem. Phys.* **2001**, *202*, 2535.
57. DiCesare, N.; Lakowicz, J. R. *Chem. Commun.* **2001**, *19*, 2022.
58. Kaim, W. and Kasak, V. *Inorg. Chem.* **1990**, *29*, 4696.
59. Meudt, A.; Lehnemann, B.; Scherer, S.; Kalinin, A.; Snieckus, V. US7196219.
60. Cui, J. J. WO2004076412.
61. Rastegar, M. F.; Todd, E. K.; Tang, H. D.; Wang, Z. Y. *Org. Lett.* **2004**, *6*, 4519.
62. Deng, G.; James, Tony D.; Shinkai, S. *J. Am. Chem. Soc.* **1994**, *116*, 4567.
63. Tashiro, M.; Sumida, T.; Fukata, G. *J. Org. Chem.* **1980**, *45*, 1156.
64. Gerrard, W. *The Organic Chemistry of Boron*; Academic Press: London/New York, 1961.
65. Klämer, G.; Lee, J. I.; Davey, M. H.; Miller, R. D. *Adv. Mater.* **1999**, *11*, 115.
66. Bliznyuk, V. N.; Carter, S. A.; Scott, J. C.; Klärner, G.; Miller, R. D.; Miller, D. C. *Macromolecules* **1999**, *32*, 361.
67. Fuoss, R. M.; Strauss, U. P. *J. Polym. Sci.* **1948**, *3*, 603.

68. Meier, M. A. R.; Lohmeijer, B. G. G.; Schubert, U. S. *Macromol. Rapid Commun.* **2003**, 24, 852.
79. Rader, H. J.; Spickerman, J.; Kreyenschmidt, M.; Mullen, K. *Macromol. Chem. Phys.* **1996**, 197, 3285.
70. Jones, W. E., Jr.; Bignozzi, C. A.; Chen, P.; Meyer, T. J. *Inorg. Chem.* **1993**, 32, 1167.
71. Jo, J.; Chi, C. Y.; Hoyer, S.; Wegner, G.; Yoon, D. Y. *Chem. Eur. J.* **2004**, 10, 2681.
72. Constable, E. C.; Housecroft, C. E.; Schofield, E. R.; Encinas, S.; Armaroli, N.; Barigelletti, F.; Flamigni, L.; Figgemeier, E.; Vos, J. G. *Chem. Commun.* **1999**, 10, 869.
73. Benniston, A. C.; Harriman, A.; Lawrie, D. J.; Mayeux, A. *Phys. Chem. Chem. Phys.* **2004**, 6, 51.
74. Fahnrich, K. A.; Pravda, M.; Guilbault, G. G. *Talanta* **2001**, 54, 531.
75. Elliott, C. M.; Pichot, F.; Bloom, C. J.; Rider, L. S. *J. Am. Chem. Soc.* **1998**, 120, 6781.
76. Kikuchi, D.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **1998**, 63, 6023;
77. Bloxham, J.; Moody, C. J.; Slawin, A. M. Z. *Tetrahedron* **2002**, 58, 3709.
78. Barbieri, A.; Ventura, B.; Barigelletti, F.; Nicola, A.; Quesada, M.; Ziessel, R. *Inorg. Chem.* **2004**, 43, 7359.
79. Wang, S.; Li, X. Z.; Xun, S. D.; Wan, X. H.; Wang, Z. Y. *Macromolecules* **2006**, 39, 7502.
80. Kaufman, J. H.; Kanazawa, K. K.; Street, G. B. *Phys. Rev. Lett.* **1984**, 53, 2461.

Summary

In this research we have successfully developed DCH-Ru-containing polymeric materials through the methods of crosslinking dendric DCH-Ru complexes and polymerization of DCH-Ru complex dibromide monomer with other diboronic acid monomers. The resulting products contain the NIR electrochromic properties from DCH-Ru fragments as well as good film-formtion properties because of their high molecular weights, which make them suitable for NIR electrochromic variable optical attenuator in solid device. An intrinsic dynamic attenuation of 11.6 dB has been obtained from one of the copolymers, which is comparable to the highest value reported so far in conducting polymers. Also they are easy for purification and quite stable in the ambient condition. A high dynamic attenuation of 30 dB has also been reached in a single-layer hybrid ECVOA device.

For solid-state DCH-Ru complexes, further improvement of the intrinsic attenuation is still possible from DCH-Ru polymers with higher Ru content than the copolymer we have made. Considering the AA-BB approach, replacing the fluorene fragment in boronic acid with much lower molecular-weight ones like 1,4-phenyl unit can largely increase the Ru content in the final polymeric product. The modification on dipyriddy parts to make them polymerizable could be another approach to increase the Ru content. In addition, complexes containing metals other than ruthenium with high molar extinguishing coefficient in the NIR region should also be considered for further enhancing the attenuation ability and decreasing the high cost of the raw ruthenium complex. Asymmetric Nickel-dithiolenes could be taken as such candidate metal complexes by the introduction of large donating and withdrawing groups at each side,

which could highly improve the stability of the products to electrochemical reaction and degradation, making them excellent NIR electrochromic materials.

Appendix

^1H and ^{13}C Spectra of Ligands and Complexes

1,3,5-Benzenetricarboxylic tris[2-(6-hydroxyhexano)hydrazide]] (II.1)

1D carbon with proton decoupling

1,3,5-Benzenetricarboxylic tris[2-(4-Methoxybenzoyl)hydrazide] (II.2)

1D proton

1D carbon with proton decoupling

1,3,5-Benzenetricarboxylic tris[2-(4-hydroxybenzoyl)hydrazide] (II.3)

1,3,5-Benzenetricarboxylic tris[2-benzoylhydrazide] (II.4)

1D carbon with proton decoupling

1,3,5-Benzenetricarboxylic tris[2-(4-nitrobenzoyl)hydrazide] (II.5)

1D carbon with proton decoupling

1D carbon with proton decoupling

```
Current Data Parameters
NAME      David-980811-1
EXPNO     1
PROCNO    1
```

```

F2 - Acquisition Parameters
Date_ 20080811
Time 18.48
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 32768
SOLVENT DMSO
NS 512
DS 4
SWH 18028.846 Hz
FIDRES 0.550297 Hz
AQ 0.2088159 sec
RG 250
DN 27.733 used
DE 6.00 used
TE 295.4 K
D1 2.00000000
d11 6.00000000
DELTA 1.88923333 sec
FQ9 1

```

```
***** CHANNEL f1 *****
NAME          110
PI              9.50 10000
PUL            -1.00  20
SPIN           75.4803248  000
```

```

***** CHANNEL 12 *****
CP2PRG2      wait:16
RXC2          IN
PCPRG2       100.00  0.000000
PL2          0.00  0.00
PL12         10.42  0.00
PL13         21.34  0.00
SFC2         300.157006  0.00

```

```

F2 - Processing parameters
ST          32768
SP          75.4727788 MB
WIZW       ZW
SDB         0
LB          1.00 Hz
GB          0
PC          1.40

```

4-(2-(4-Bromobenzoyl)hydrazinecarbonyl)phenylboronic acid pinacol ester (IV.2)

1D proton

1D carbon with proton decoupling

N-(4-Bromophenyl)-*N'*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,2-hydrazinedicarboxamide (**IV.10**)

1,2-Bis(4-bromobenzoyl)hydrazine (IV.11)

Current Data Parameters
NAME XSM
EXPNO 8
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060312
Time 17.22
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 32768
SOLVENT DMSO
NS 16
DS 2
SWH 4189.179 Hz
FIDRES 0.128846 Hz
AQ 2.6477664 sec
RG 228
DM 80.800 usec
DE 6.00 usec
TE 294.6 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
SFO1 300.1518535 MHz

F2 - Processing parameters
SI 32768
SF 300.1500000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D carbon with proton decoupling

Current Data Parameters
NAME XSM 2
EXPNO 9
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060312
Time 18.04
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 32768
SOLVENT DMSO
NS 500
DS 4
SWH 18028.846 Hz
FIDRES 0.550197 Hz
AQ 0.9088159 sec
RG 181
DM 27.733 usec
DE 6.00 usec
TE 297.9 K
D1 2.00000000 sec
d11 0.20000000 sec
DELTA 1.89999998 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.50 usec
PL1 -1.00 dB
SFO1 75.4803248 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.42 dB
PL13 21.34 dB
SFO2 300.1512006 MHz

F2 - Processing parameters
SI 32768
SF 75.4727380 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

$[\{ Ru(bpy)_2 \} \mu-(BrPh)_2-dch] (PF_6)_2$ (IV.11-Ru)

1D proton

1D carbon with proton decoupling