

**SPECTROSCOPIC CHARACTERIZATION OF  
DNA-MEDIATED CHARGE TRANSFER**

Thesis by  
Christopher R. Treadway

In Partial Fulfillment of the Requirements  
for the Degree of  
Doctor of Philosophy

California Institute of Technology

Pasadena, California

2003

(Defended September 4, 2002)

## Acknowledgements

The research outlined in the thesis below would not have been possible without the inspiration and help provided by people too numerous to mention. At the risk of this becoming a rambling Oscar acceptance speech, however, those notable people are as follows. I am indebted to Professor Jacqueline K. Barton for giving me the opportunity to do research in an exciting field. Jackie was always available to discuss matters great or small, and her willingness to allow me to pursue the study of topics outside my areas of expertise was a big factor in my decision to choose her as a research advisor. Upon joining Jackie's group I was introduced to her secretary Maureen Renta. Mo deserves all the credit for keeping the group running efficiently and making sure graduate students are not burdened with too many administrative tasks.

My thesis committee is also in need of special recognition. I thank Professor Harry B. Gray for serving as Chairman and for being one of the most personable and entertaining people in the chemistry world. My decision to attend Caltech was based in large part on the two hours Harry took out of his busy schedule to spend with me during my visit to campus as a senior in college. My choice of research topics was greatly influenced by the work of Professor Rudolph A. Marcus. Rudy gave a seminar detailing his work on electron transfer at the University of Illinois when I was a sophomore. Since starting research at Caltech he has been very helpful in shaping our group's ideas about electron transfer through DNA. Professor Jonas C. Peters was the last faculty member to join my committee. Jonas came on board in time for my fourth-year meeting, as he was appointed to the Caltech faculty after I started graduate school (I remember reading articles he was publishing as a graduate student at M.I.T.). His expertise has helped us overcome several problems we have encountered trying to synthesize new molecules.

Many Barton group members, past and present, provided their time and knowledge to help me learn new ideas and collect data. Professor Shana O. Kelley was kind enough to take me under her wing and put up with an endless barrage of questions

and requests. Without her my first few years of graduate school would have been a much bigger hurdle. Drs. R. Erik Holmlin and Peter J. Dandliker imparted to me their knowledge of inorganic and organic synthesis, respectively. Professor Marilena Fitzsimons Hall patiently showed me how to use new instruments and remained calm when I nearly burned down the lab. Drs. Daniel B. Hall and Megan E. Nuñez spent many hours teaching me to run gels. Despite their excellent tutelage, I could not be convinced to come over to the Dark Side (hardcore biochemistry, not the *Star Wars* rogue Jedi organization). Professor Eric D. A. Stemp readily dispensed his knowledge of photochemistry and photophysics in addition to spending countless hours helping me with laser experiments. I also owe him a big thanks for introducing me to such fine culinary treasures as Donut Man, Señor Fish, In-N-Out, Dodger Dogs, and Dr. Hoggly Woggly's Tyler Texas BBQ.

For my first project in the Barton group, Professor Sonya Franklin was a great collaborator. She and Pratip Bhattacharya took many NMR spectra and were always willing to discuss research or other mundane matters. It was a pleasure to collaborate on a review article with Professor Michael G. Hill. Mike also provided many simplified explanations of phenomena too complex for my fried brain to comprehend. For one year I was assisted by Viktor Alekseyev, a talented undergraduate student at Caltech. My best wishes go out to him as he toils through graduate school at Stanford. Drs. Matthias Pascaly, Matthias M. Manger, and Alexander Schnyder donated various ligands and metal complexes for some of the studies detailed in this thesis. Drs. Jennifer Kisko and Henrik Junicke provided synthetic advice in addition to serving as faithful Napster co-conspirators. Dr. Jae Yoo took several EPR spectra, and for this I might consider forgiving him for being a PAC-10 fan. Drs. Olav Schiemann and Melanie N. O'Neill were collaborators on the 2-aminopurine project; how they remained so chipper and supportive in the face of my constant grouchiness will forever remain a great unsolved mystery. Dr. Elizabeth Boon Carrico and Dr. Kimberly Copeland donated a lot of time

teaching me how to use various instruments. This does not, however, excuse the fact that they are Duke fans. I might change my mind if they promise to root for the Fighting Illini, knowing full well that any Blue Devils' fan could never cheer for the Tar Heels.

My last few years in the Barton group were a lot of fun thanks to Sarah Delaney and Jonathan R. Hart. Sarah ran several gels for me and was always willing to lend a sympathetic ear. Her attempts to get me to eat more healthy foods, however, were not successful (although I did begin to see merit in taking Flinstones vitamins). Ketchup is a fruit, and pickles are vegetables! Jonathan was my collaborator in synthesizing the now infamous phen\*. He also served as my 24/7, on-call tech support. I thank him for that and for the ongoing dialogue we share about technology-related issues.

Other members of the Caltech community have assisted me at various times over the past several years. The Laboratory for Molecular Sciences, spearheaded by Professor Ahmed H. Zewail, provided access to ultrafast lasers that allowed two of my research projects to flourish. Drs. Chaozhi Wan and Torsten Fiebig were instrumental obtaining and interpreting laser data. The Beckman Institute Laser Resource Center (BILRC), under the guidance of Dr. Jay Winkler, also gave me access to fast lasers for spectroscopy experiments. I thank Dr. Randy Villahermosa from the Gray group for keeping the lasers running and helping me obtain data. The Grubbs group is probably glad that I am graduating. I may have spent enough time there to become an honorary group member. Dr. Todd Younkin, Dr. Melanie Sanford, and Christopher W. Bielawski deserve special recognition. They were kind enough to listen to my ramblings and assist me with several syntheses.

It would have been a challenge to survive the graduate school experience without the support of many good friends. My technology investing cohorts (Jon Samardzich, Bo Kolody, Drake Shining, Andy Abplanalp, and Michael Reynolds, among others) have provided a steady stream of information and entertainment for the last few years. Jon was kind enough to invite me into the Pasadena Fire Department's inner circle; hopefully

I changed their minds about the mad scientists over at Caltech. Bo might be the only professor in the country more cynical than his graduate students, and his sense of humor could always bring a smile to my face. I hope some of Drake's street smarts rubbed off on me, and I hope his music results in all the success and happiness he could ever want. Andy deserves a Ph.D. for being able to pronounce his last name. I'll thank him with a steak and cerveza when this ordeal is over. Mike has been a great friend and mentor. Even though our technology project never really got past the initial stages, I learned a great deal. I am very thankful for his contributions around the Holidays meant to make me feel like I was home with family and friends instead of stuck in the lab doing research.

Friends from places near and far played a large part in my happiness as a struggling grad student in Pasadena. A few weeks before moving to California, I took part in the marriage of a lifelong friend, Michael Shawn Anderson, to his new wife Jammie Dyan Anderson. Their welcoming me home and acceptance as a third wheel every Christmas and Memorial Day is something I will always cherish. Equally important, they understand the necessity to dine on the fine meals served up by Benny's Pizza. Following Mike's wedding I got reacquainted with another longtime friend, Rebecca Dawn Langdon. She made every visit home a memorable one. The letters we exchanged, while not exactly Pulitzer Prize-winning material, were some of the most entertaining literature penned in the last several decades. I thank her for reminding me that work isn't everything, and it is healthy to have fun. The card she sent before my candidacy exam is a classic example. I wish her all the best with Jake Prokop as they continue their lives in Florida.

Many folks in California helped make my brief stay in the state a pleasant one. Dr. Sunday Ann Brooks made sure I ventured out to see the famous sites in Los Angeles, and I enjoyed the many weekends of partying made possible by her and her friends at UC-Riverside. My roommate for the past three years, Christopher W. Bielawski,

provided much entertainment in addition to chemistry knowledge. I am sure we would have both graduated much sooner were it not for our obsession with the Internet and our stock portfolios. I also thank Chris and Professor Janis Louie for providing free meals every time I took my car into the shop for repairs, which was quite often for the Pontiac Grand Prix known as CALTEC 1. It has been a pleasure getting to know Sarah Frantom over the last year. She was able to understand my obsession with McDonald's and college football. That still does not, however, excuse the fact that she is a Michigan fan. Go Illini! Finally, I owe a huge debt to Dr. Todd Ross Younkin and his wife Wendy. Todd befriended me during my first year of graduate school, and our philosophies on life, work, and college football have produced a great friendship. It was a lot of fun partying with him while he was here. He also was instrumental in getting me a job at Intel, and for that I will be forever grateful. I look forward to spending time with him and his wife upon moving to Portland. With any luck, they might forget the debauchery that took place at their wedding reception in Orlando, Florida, in July 2001.

The biggest thanks of all goes out to my family. Their support and encouragement certainly makes things easier during trying times. I hope I have made them proud. They will most certainly be glad to know that I am finally finishing my education and starting life in the real world.

## Abstract

The DNA double helix, in addition to serving as a carrier of genetic information, provides a well-characterized molecular  $\pi$  stack through which charge transfer may be examined. Previous biochemical, photophysical, and electrochemical experiments have established that efficient charge transfer through DNA is mediated by the DNA base stack. To investigate the rates and efficiencies of that process we examined the spectroscopy of a series of DNA duplexes modified with a variety of photo- and redox-active moieties. Further, we examined the interactions and redox chemistry of a series of metallointercalators possessing high oxidation potentials with DNA.

The dynamics of photoinduced charge transfer through DNA were examined as a function of distance for a series of duplexes modified with 7-deazaguanine and a covalently attached ethidium chromophore. Over donor-acceptor distances of 10–17 Å, the dynamics of charge transfer were found to be distance independent. The observed decay times corresponding to charge transfer could be grouped into two components: (1) injection of charge into the DNA base stack, a process taking place on the 5-picosecond timescale, and (2) a correlated charge transfer rate corresponding to the reorientation of ethidium within the duplex, a process taking place on the 75-picosecond timescale. This study was the first definitive demonstration of the important role reactant dynamics play in DNA-mediated charge transfer.

Using the modified bases 2-aminopurine and 7-deazaguanine, intrastrand charge transfer through DNA was investigated. The photooxidation of guanine and 7-deazaguanine by 2-aminopurine was found to take place on the picosecond timescale. Charge transfer rates and quenching yields were also found to depend on the driving force for the reaction and the composition of the intervening base stack. These experiments again demonstrated that charge migration through the DNA  $\pi$  stack is a fast and efficient process.

The photooxidation of 7-deazaguanine by a ruthenium(II) intercalator in DNA was examined. Photoinduced charge transfer efficiencies over 7–14 Å were found to be shallow and dependent upon the chirality of the covalently attached metallointercalator. Nanosecond to subnanosecond decay rates were measured, and the spectroscopic signature of a charge transfer intermediate was observed.

A series of ruthenium(II) intercalators with high oxidation potentials was created. The spectroscopy of these complexes in the absence and presence of DNA was examined and compared to the well-known molecular “light switch” type complexes. Redox reactivity of the compounds with DNA did not correlate directly with oxidation potential and was found to be dependent on DNA binding and luminescence quenching abilities. Low-temperature EPR experiments revealed generation of long-lived radical species by the complexes in frozen DNA. These results demonstrated that redox potential may not be used as a sole predictor of reactivity with the base stack of DNA.

Finally, the binding of ruthenium(II) and rhodium(III) intercalators to DNA was investigated with CD and NMR spectroscopies. Data confirmed that metallointercalators do not preferentially bind next to each other along the double helix. Hence, direct contact of reactants cannot be used to explain fast and efficient charge transfer between metallointercalators bound noncovalently to DNA.

These studies have provided direct measurements of the dynamics of DNA-mediated charge transfer. Importantly, the stacking and dynamics of the reactants and DNA bases were found to affect the observed charge transfer behavior. These parameters, in addition to many others, must be included in any adequate description of the migration of charge through the DNA  $\pi$  stack.



## Table of Contents

Acknowledgements	ii
Abstract	vii
Table of Contents	ix
List of Figures	xiii
List of Tables	xvii
<b>Chapter 1: Introduction Charge Transfer and Charge Transport</b>	<b>1</b>
<b>Through the DNA Double Helix</b>	
1.1 Introduction	2
1.2 Basic Electron Transfer Theory	4
1.3 Approaches to Study Long-Range Charge Transport Through DNA	10
1.3.1 Probes and assemblies	10
1.3.2 Biochemical measurements of oxidative damage	14
1.3.3 Photophysical studies of DNA-mediated charge transfer	15
1.3.4 Electrochemistry using DNA films	16
1.4 Parameters Explored in Characterizing DNA Charge Transport	17
Chemistry	
1.4.1 Perturbations to the $\pi$ stack in studies of photoinduced charge transport	17
1.4.2 The effects of stacking and dynamics on DNA charge transport	21
1.4.3 Electrochemical measurements of stacking perturbations	26
1.4.4 Energetics of donors and acceptors	29
1.5 Current Focus	32
1.6 References	34
<b>Chapter 2: Spectroscopy of Ethidium/7-Deazaguanine-Modified DNA Duplexes</b>	<b>39</b>
2.1 Introduction	40
2.2 Experimental Section	42

2.3 Results and Discussion	44
2.3.1 Ethidium-nucleotide interactions and charge transfer	44
2.3.2 Ethidium/7-deazaguanine DNA duplexes and charge transfer	49
2.4 Conclusions	65
2.5 References	66
<b>Chapter 3: Spectroscopy of 2-Aminopurine/7-Deazaguanine-Modified DNA Duplexes</b>	68
3.1 Introduction	69
3.2 Experimental Section	72
3.3 Results and Discussion	74
3.3.1 Steady-state spectroscopic investigations of intrastrand charge transfer	74
3.3.2 Time-resolved spectroscopic investigations of intrastrand charge transfer	82
3.4 Conclusions	88
3.5 References	89
<b>Chapter 4: Synthesis and Spectroscopy of Ruthenium(II)/7-Deazaguanine-Modified DNA Assemblies</b>	91
4.1 Introduction	92
4.2 Experimental Section	95
4.3 Results and Discussion	101
4.3.1 Synthesis of ruthenium-DNA conjugates	101
4.3.2 Steady-state spectroscopy of Ru/G and Ru/Z conjugates	107
4.3.3 Time-resolved spectroscopy of Ru/G and Ru/Z conjugates	114
4.4 Conclusions	125
4.5 References	126

<b>Chapter 5: Synthesis and Characterization of Ruthenium Intercalators with High Redox Potentials and Their Chemistry with DNA</b>	128
5.1 Introduction	129
5.2 Experimental Section	132
5.3 Results	140
5.3.1 UV-visible spectroscopy	140
5.3.2 Redox properties	142
5.3.3 Spectroscopic properties in the absence and presence of DNA	143
5.3.4 Reactivity in the presence of DNA	153
5.4 Discussion	165
5.4.1 Redox properties	165
5.4.2 Spectroscopic properties in the absence of DNA	165
5.4.3 Spectroscopic properties in the presence of DNA	166
5.4.4 Reactivity with DNA	167
5.5 Conclusions	169
5.6 References	170
<b>Chapter 6: Spectroscopy of Ruthenium(II) and Rhodium(III) Intercalators Bound Noncovalently to DNA</b>	172
6.1 Introduction	173
6.2 Experimental Section	177
6.3 Results and Discussion	179
6.3.1 Circular dichroism	179
6.3.2 Redox properties	186
6.3.3 Binding of Ru and Rh' to the DNA decamer	198
6.3.4 Time-resolved emission studies of photoinduced electron transfer on the DNA decamer	199
6.4 Conclusions	201

6.5 References

206

**Chapter 7: Summary and Conclusions**

210

## List of Figures

### Chapter 1

1.1 Schematic illustration of the DNA double helix	3
1.2 Illustration of a Rh(III) modified duplex with 5'-GG-3' sites up to 200 Å away	4
1.3 Reaction coordinate diagram and couplings for electron transfer	7
1.4 Assemblies in which long-range charge transport was demonstrated	12
1.5 Illustration of duplex DNA self-assembled monolayers on gold	14
1.6 Assemblies highlighting the importance of stacking to charge transfer in DNA	18
1.7 Effect of protein binding on long-range guanine oxidation	20
1.8 Ethidium, guanine, and 7-deazaguanine structures and reactivity	22
1.9 Structures, reactivity, and stacking of modified bases in DNA	24
1.10 Distance dependence of electron transfer through DNA-modified electrodes	26
1.11 Incorporation of a mismatch in DNA-modified gold electrodes	27
1.12 Energetics and coupling involved in various charge transfer mechanisms	31

### Chapter 2

2.1 Structure and potential of ethidium	40
2.2 Structures and potentials of guanine and 7-deazaguanine	41
2.3 Electron transfer cycle between ethidium and 7-deazaguanine	42
2.4 Stern-Volmer plot of ethidium fluorescence quenching	45
2.5 Transient absorption spectra of ethidium with dGTP and dZTP	45
2.6 NMR spectra of ethidium with dZTP	48
2.7 Distance dependence of ethidium luminescence quenching by Z in DNA	50
2.8 Single photon counting data for Et/G and Et/Z duplexes	51
2.9 Synthesis of Et-DNA conjugates	52
2.10 MALDI-TOF mass spectrum of an Et-DNA conjugate	52
2.11 UV-visible spectra of Et/G and Et/Z duplexes	53

2.12	Fluorescence spectra of Et/G and Et/Z duplexes	55
2.13	Transient absorption of Et/G and Et/Z duplexes	56
2.14	Fluorescence anisotropy of Et/G and Et/Z duplexes	59
2.15	Fluorescence up-conversion of Et/G and Et/Z duplexes	60
2.16	Polyacrylamide gel showing the ethidium intercalation site in DNA duplexes	62

### Chapter 3

3.1	Structure and potential of 2-aminopurine	69
3.2	Spectral properties of 2-aminopurine	70
3.3	Structures and potentials of guanine, inosine, and 7-deazaguanine	71
3.4	Electron transfer cycle between 2-aminopurine and guanine	71
3.5	Distance dependence of Ap/G and Ap/Z intrastrand charge transfer	77
3.6	Distance and sequence dependences of Ap/Z intrastrand charge transfer	79
3.7	Dependence of charge transfer on the oxidation potential of the base donor	82
3.8	Transient absorption decays for Ap/G duplexes	84
3.9	Transient absorption decays for Ap/Z duplexes	84
3.10	Plots of charge transfer rate vs. distance for Ap/G and Ap/Z duplexes	87

### Chapter 4

4.1	Structure and potential of $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$	93
4.2	Structures and potentials of guanine and 7-deazaguanine	93
4.3	Electron transfer cycle between 7-deazaguanine and $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$	94
4.4	Structure of $[\text{Ru}(\text{phen})(\text{phen}')\text{dppz}]^{2+}$	102
4.5	Synthesis of Ru-DNA conjugates	104
4.6	Structure of the four diastereomers of $[\text{Ru}(\text{phen})(\text{phen}')\text{dppz}]^{2+}$	105
4.7	Circular dichroism spectra of Ru-DNA conjugates	106
4.8	Sequences of Ru-DNA conjugates	107

4.9	Fluorescence spectra of Ru/G and Ru/Z duplexes	109
4.10	Distance dependences of charge transfer in Ru/Z DNA duplexes	111
4.11	Structure of $[\text{Ru}(\text{bpy})_2(\text{bpy}')^{2+}]^{2+}$	112
4.12	Fluorescence spectra of $[\text{Ru}(\text{bpy})_2(\text{bpy}')^{2+}]^{2+}$ -DNA conjugates	113
4.13	Time-resolved fluorescence of $\Lambda 1$ -Ru-DNA conjugates	115
4.14	Time-resolved fluorescence of $\Lambda 2$ -Ru-DNA conjugates	116
4.15	Time-resolved fluorescence of $\Delta 1$ -Ru-DNA conjugates	117
4.16	Time-resolved fluorescence of $\Delta 1$ -Ru-DNA conjugates	118
4.17	Fluorescence and transient absorption of Ru/G and Ru/Z duplexes	121
4.18	Transient absorption spectrum of a $\Delta 3$ -Ru/Z duplex	122
4.19	Transient absorption spectra for a variety of $[\text{Ru}(\text{phen})_2\text{dppz}]$ species	123

## Chapter 5

5.1	Flash-quench cycle for <i>in situ</i> generation of Ru(III)	131
5.2	Structures of several dppz-based Ru(II) intercalators	132
5.3	UV-visible spectrum of $[\text{Ru}(5,5'\text{-CF}_3\text{bpy})_2\text{dppz}]^{2+}$ in water	141
5.4	UV-visible titration of $[\text{Ru}(5,5'\text{-CF}_3\text{bpy})_2\text{dppz}]^{2+}$ with calf thymus DNA	144
5.5	Fluorescence spectra of $[\text{Ru}(4,4'\text{-CF}_3\text{bpy})_2\text{dppz}]^{2+}$	146
5.6	Fluorescence spectra of $[\text{Ru}(5,5'\text{-CF}_3\text{bpy})_2\text{dppz}]^{2+}$	147
5.7	Fluorescence spectra of $[\text{Ru}(5,5'\text{-F}_2\text{bpy})_2\text{dppz}]^{2+}$	148
5.8	Fluorescence spectra of $[\text{Ru}(4,4'\text{-CHO}\text{bpy})_2\text{dppz}]^{2+}$	149
5.9	Fluorescence spectra of $[\text{Ru}(5,5'\text{-CF}_3\text{bpy})(\text{phen})\text{dppz}]^{2+}$	150
5.10	Stern-Volmer quenching plots for various Ru(II) intercalators	154
5.11	Gel demonstrating oxidative damage to DNA by Ru(III)	155
5.12	Gel demonstrating oxidative damage to DNA by Ru(III)	156
5.13	EPR of $[\text{Ru}(5,5'\text{-CF}_3\text{bpy})_2\text{dppz}]^{2+}$ with several polynucleotides	158
5.14	EPR of $[\text{Ru}(5,5'\text{-F}_2\text{bpy})_2\text{dppz}]^{2+}$ with several polynucleotides	159

5.15 EPR of $[\text{Ru}(4,4'\text{-CHObpy})_2\text{dppz}]^{2+}$ with several polynucleotides	160
5.16 Transient absorption of $[\text{Ru}(5,5'\text{-CF}_3\text{bpy})_2\text{dppz}]^{2+}$ with polynucleotides	158
5.17 Transient absorption of $[\text{Ru}(5,5'\text{-F}_2\text{bpy})_2\text{dppz}]^{2+}$ with polynucleotides	159
5.18 Transient absorption of $[\text{Ru}(4,4'\text{-CHObpy})_2\text{dppz}]^{2+}$ with polynucleotides	160

## Chapter 6

6.1 Structures of Ru(II) and Rh(III) intercalators and a DNA decamer duplex	176
6.2 Circular dichroism spectra of Ru and Rh in the presence of calf thymus DNA	180
6.3 Circular dichroism spectra of Ru and Rh in the presence of poly d(AT)	182
6.4 Circular dichroism spectra of Ru as a function of Rh in poly d(AT)	185
6.5 Imine region 2-D NOESY NMR of Ru and Rh' with a DNA decamer duplex	188
6.6 Cytosine region 2-D NOESY NMR of Ru and Rh' with a DNA decamer duplex	189
6.7 Imine region 1-D $^1\text{H}$ NMR for Ru and Rh' with a DNA decamer duplex	190
6.8 Schematic of equilibrium binding of Ru and Rh' to a DNA decamer duplex	192
6.9 Emission decays of Ru +/- Rh' with a DNA decamer duplex	200



**List of Tables****Chapter 2**

2.1 Transient absorption lifetimes for ethidium with dGTP and dZTP	46
2.2 Emission, melting temperature, and polarization for Et/G and Et/Z duplexes	54
2.3 Transient absorption lifetimes for Et/G and Et/Z duplexes	57
2.4 Emission data for mismatch containing Et/G and Et/Z duplexes	64

**Chapter 3**

3.1 Melting temperature data for Ap/I, Ap/G, and Ap/Z duplexes	75
3.2 Luminescence quenching data for Ap/G, and Ap/Z duplexes	76
3.3 Sequence dependent luminescence quenching data for Ap/Z duplexes	78
3.4 Effect of intervening bases on Ap/Z intrastrand charge transfer	80
3.5 Transient absorption decay times for Ap/I, Ap/G, and Ap/Z duplexes	83
3.6 Luminescence quenching yields for selected Ap/Z duplexes	86

**Chapter 4**

4.1 Mass spectrometry data for Ru-DNA conjugates	104
4.2 Fluorescence data for Ru/G and Ru/Z duplexes	110
4.3 Fluorescence lifetime data for Ru/G and Ru/Z duplexes	119
4.4 Comparison of charge transfer decay times in Et/Z, Ap/Z, and Ru/Z duplexes	124

**Chapter 5**

5.1 UV-visible spectra parameters for various Ru(II) intercalators	142
5.2 Electrochemical parameters for various Ru(II) intercalators	143
5.3 Hypochromism upon binding of various Ru(II) intercalators	145
5.4 Fluorescence parameters for various Ru(II) intercalators	151
5.5 Fluorescence lifetimes of various Ru(II) intercalators	153

**Chapter 6**

6.1 Chemical shift data for Ru and Rh' with a DNA decamer duplex	194
6.2 Luminescence lifetimes of Ru +/- Rh and Rh' with a DNA decamer duplex	199