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Synthesis and Optical Properties of Four Oligothiophene-Ruthenium Complexes and Synthesis of a Bidentate Ligand for C-F Bond Activation

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SYNTHESIS AND OPTICAL PROPERTIES OF FOUR OLIGOTHIOPHENE-RUTHENIUM COMPLEXES AND SYNTHESIS OF A BIDENTATE LIGAND FOR C-F BOND ACTIVATION

by

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GRADUATE COMMITTEE APPROVAL

of a thesis submitted by

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ABSTRACTS

SYNTHESIS AND OPTICAL PROPERTIES OF FOUR OLIGOTHIOPHENE-RUTHENIUM COMPLEXES AND SYNTHESIS OF A BIDENTATE LIGAND FOR C-F BOND ACTIVATION

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Chapter 1

Photovoltaic cells and fluorescence sensing are two important areas of research in chemistry. The combination of photon-activated electron donors with electron acceptors provides a strong platform for the study of optical devices.

A series of four oligothiophene-ruthenium complexes has been synthesized. Variation in oligothiophene length and bipyridine substitution allowed comparison of these variables on electronic properties. The longer oligothiophenes display lower energy absorption and emission compared to the shorter ones. Aromatic conjugation appears more complete with para-, rather than meta-, substitution. Oligothiophenes and $Ru(bpy)_3^{2+}$ are highly fluorescent individually, but fluorescence is quenched when connected.

Chapter 2

Bonds of carbon to fluorine are among the strongest single bonds. Single bonds between carbon and hydrogen are also very strong and are ubiquitous. The ability to manipulate these bonds is of great interest to chemists.

Two tungsten metal complexes, [6-(perfluorophenyl)bipyridyl] tetracarbonyltungsten and [6-(phenyl)bipyridyl]tetracarbonyltungsten, were prepared for mechanistic C-F and C-H bond activation studies, respectively. These compounds were synthesized through Stille and Suzuki coupling of commercial reagents. Ligands were then bound to tungsten to form the tetracarbonyl complexes.

ACKNOWLEDGMENTS

I would like to thank the Department of Chemistry and Biochemistry at Brigham Young University for funding and Dr. Roger Harrison for his training, help, and patience during this research. I thank the contributors to the University for its existence. I thank my parents for their sacrifice and encouragement which enabled me to arrive at this point. I thank my wife, for her commitment and love, which brings light into my life.

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Abstract

A series of four oligothiophene-ruthenium complexes have been synthesized through multiple Stille couplings. Variation in oligothiophene length and bipyridine substitution allowed comparison of these variables on electronic properties. The longer oligothiophenes display lower energy absorption and emission compared to the shorter ones. Aromatic conjugation appears more complete with para-, rather than meta-, substitution. Oligothiophenes and $Ru(bpy)_3^{2+}$ are highly fluorescent individually, but fluorescence is quenched when connected.

1.1. Introduction

1.1.1. Light Activated Systems

Photovoltaic cells and fluorescence sensing are two important areas of research in chemistry. The need for clean and renewable energy sources has increased interest in solar power. Photovoltaic cells based on organic components provide the possibility of inexpensive devices. Fluorescence sensing has been shown to be a very sensitive method for detection of many analytes.[1] One of the applications of fluorescent sensors involves the identification of harmful compounds in water.

In both photovoltaic and fluorescence sensing systems, a photon of light is absorbed, which creates an excited state in the system. Energy, sometimes in the form of an electron, is then transferred from the excited donor group to an acceptor group of lower energy. In the case of solar cells, an electron must be channeled to perform work.

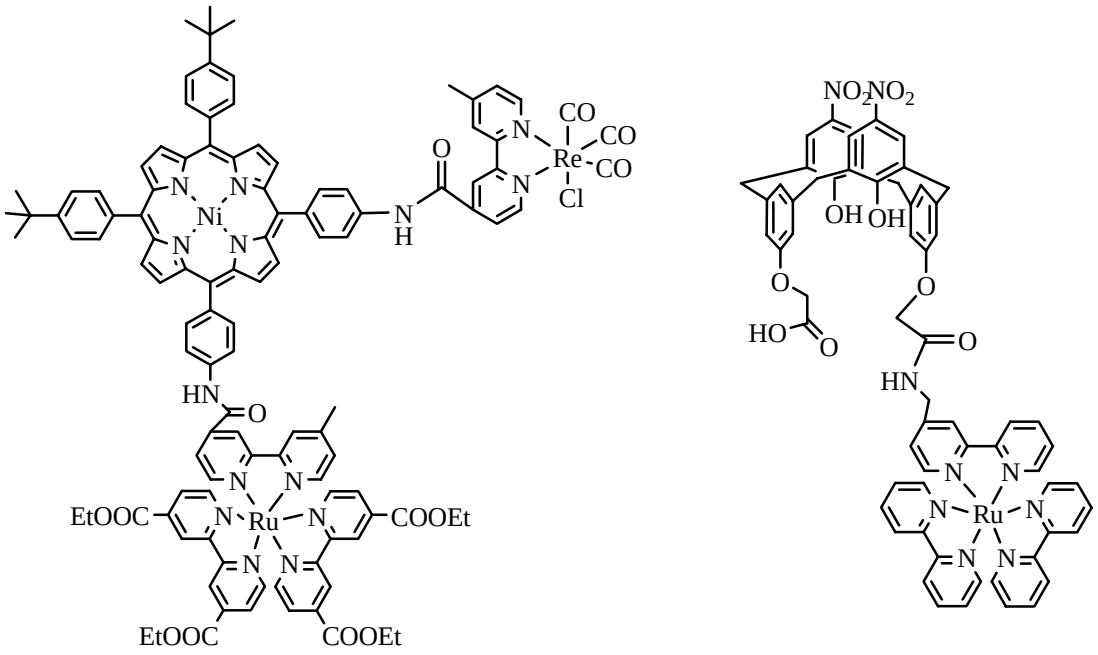
In fluorescent systems, the transferred energy or electron stimulates the emission of a photon of light with its wavelength being determined by the presence or absence of a given analyte. Our interest is currently focused in fluorescent systems, although possible applications include photovoltaic cells.

In the following sections we will acquaint the reader with a variety of donor-linker-acceptor systems.

1.1.2. Light-Activated Electron Donor Groups

Several research groups use Ru complexes as a source of photo-excited electrons for molecular devices. One group is exploring the possibility of organic circuitry in solar cells.[2-4] In their systems, ruthenium polypyridyl complexes are bound to TiO_2 surfaces through carboxylic acid groups on the ligands. One of the keys to solar cell function is an efficient quantum yield (ϕ) for electron transfer between the sensitized metal center and the semiconductor surface. Quantum yield is a measurement of how frequently an excitation event leads to an electron being injected into the semiconductor. One factor that is being studied for its affect on ϕ is the distance required for the excited electron to jump between Ru and the semiconductor.[2]

Another important step for solar cell function is the regeneration of the ground state Ru complex by reduction. A general mechanism for the process employed by Meyer et al. involves reduction of I_2 at a platinum electrode followed by oxidation of I^- to $I^\bullet$ by Ru^{3+}.[3] While this process must be efficient, it must not compete with the charge injection into the semiconductor surface. It was found that a similar process mediated by I_3^- might be too fast for complexes with only moderately fast injection rates.[4]

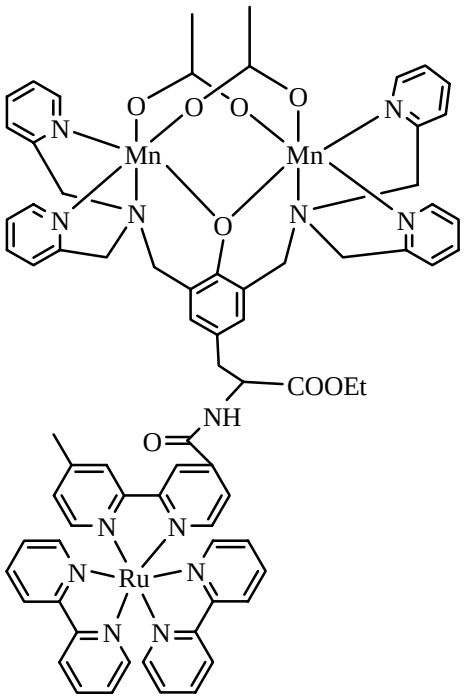


1 **2**

Figure 1.1. Metal triad compound **1**[5] and calixarene sensor complex **2**.[6]

Sun et al. synthesized and studied a ruthenium-zinc porphyrin-rhodium triad (**1**) to understand the interplay between the three light active groups (Figure 1.1).[5] They found that each group absorbed and emitted similarly to their respective control groups except that the ruthenium metal to ligand charge transfer (MLCT) emission was only half as intense as in the standard. This, they conclude, indicates that there is some energy or electron transfer between ruthenium and the Zn-porphyrin. Rhenium did not seem to communicate electronically in this complex.

Maestri et al. synthesized Ru-bipyridyl complexes bearing macrocyclic calixarenes, such as **2** (Figure 1.1).[6] These particular calixarenes had been shown to coordinate lanthanide cations, specifically Nd^{3+}, Tb^{3+} and Eu^{3+}. Complex **2** was dissolved in solutions containing one of the lanthanides and Ru fluorescence was measured and compared to the standard. The effects of each ion on fluorescence varied.



3

Figure 1.2. Photosystem II mimic system **3**.[7]

Neodymium(III) strongly quenched Ru fluorescence, while Tb^{3+} increased emission intensity. Europium(III) both quenched and increased emission, depending upon the specific complex studied. These effects were not attributed to electron transfer, but rather to energy transfer and to large electric fields created around Ru by the coordinated cations. The lack of electron transfer is not surprising due to the lack of conjugation between the lanthanides and the metal complex.

Akermark et al. developed system **3** with some similarity to the active site of the photosystem (PS) II enzyme in chlorophyll (Figure 1.2).[7] Their goal was to study the electron transfer from one or two manganese atoms to a photooxidized ruthenium center. A complete circuit was envisioned with the use of methyl viologen to accept the excited electron from Ru and transport it to Mn. They were able to determine that this actually

occurred in competition with the direct return of the electron from methyl viologen to ruthenium. The electron transfer between Mn and Ru occurs despite a minimal amount of conjugation between the metal centers.

McCusker et al. thoroughly studied a series of 4,4'-diphenyl-2,2'-bipyridine ligands bound to Ru^{2+}.[8, 9] It was shown that in the ground state, the phenyl rings are canted relative to the metal-bound bipyridine. Reduction of the ligand, through MLCT, causes the phenyl rings to lie co-planar with the bipyridine due to the lower energy associated with charge delocalization.

1.1.3. Linking and Accepting Groups

For a molecule to function as a linker between the electron donor and acceptor it must have several favorable properties. A primary requirement is that it be able to conduct electricity. Another is that its available orbitals overlap with those of the donor and acceptor such that an electron can be transferred. Finally, the chemistry required to covalently attach the donor, linker, and acceptor must be known. Oligothiophenes fulfill these three requirements. Whereas polymers are linked monomers of imprecise number, oligomers are shorter chains of a known number of monomers. Depending on the application, oligothiophenes can behave as electron donors or as linkers.

In the 1970's it was discovered that polyacetylenes conduct electricity.[10] From that discovery, the field of conducting polymers emerged. One of the most studied of conducting polymers is polythiophene.[11,12] Polythiophenes display advantages over silicon semiconductors in terms of environmental stability, cost, weight, and flexibility.

For organic molecules, the band gap between HOMO and LUMO determines the relative conducting, semiconducting, or insulating properties of the molecule. As molecular or atomic orbitals overlap, the band gap decreases, increasing conductivity. This principle has been extensively applied in conjugated aromatic systems to produce organic semiconductors. The HOMO-LUMO gap for individual aromatic molecules is too large to act as a semiconductor, but when linked into oligomers or polymers the electrical properties become favorable.

Thiophene is an electron rich aromatic ring. Photooxidation of poly- or oligothiophene can be a source of current in an electronic device. Orbital conjugation in polythiophenes, with conjugation extending over many rings, provides a band gap energy consistent with that of semiconductors. Maximum conjugation length has been difficult to measure and most estimates range from 10 to 20 thiophene rings. Modifying functional groups can induce n- or p-type doping. In addition, when excited by an electrical current, polythiophenes can emit light of tunable wavelengths.

The study of oligothiophenes has evolved in parallel with that of polythiophenes. Oligothiophenes are developed both as models for and monomers of the polymers. Polymer properties can be tuned by a variety of factors, including small structural modifications of the monomer units. Interest in the properties of oligothiophenes themselves has also been great. One of their useful properties is the ability to form self-assembled monolayers (SAMs) onto surfaces (Figure 1.3). These well-ordered monolayers provide even conduction properties across the surface on which the compound was laid. The most common metal onto which SAMs have been laid is gold.

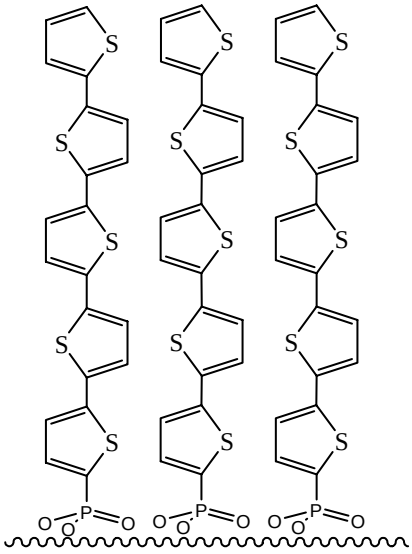


Figure 1.3. Oligothiophenes bound to a surface through phosphonic acid moieties.

Recently there have been studies involving oligothiophene on gold,[13] silicon,[14] indium tin oxide (ITO)[15] and CdSe nanocrystals.[16]

Schwartz et al. synthesized tetrathiophene and attached a phosphonic acid group.[14] This was laid on a silicon surface and examined using AFM and X-ray reflectivity. They found that the compound formed a tightly packed SAM which thoroughly covered the surface. In another instance Schwartz et al.[15] attached the same oligothiophene to an ITO surface to study its effect on hole injection into the solid during electron transfer. They found that with the phosphonic acid ligand the oligothiophene was orthogonal to the surface.

Frechet et al. also used a phosphonic acid ligand, but used it to attach ter- and pentathiophene oligomers to CdSe nanocrystals.[16] Fluorescence measurements showed that with terthiophene (T_3) as the ligand, the fluorescence quantum yield for the nanocrystal increased, whereas with pentathiophene (T_5) attached, it was completely quenched. They proposed the relative HOMO and LUMO energy levels as shown in

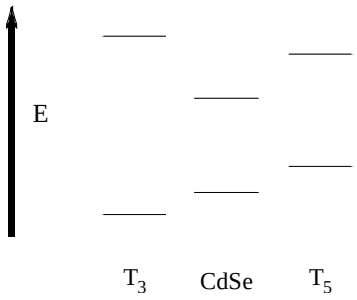


Figure 1.4. Relative representation of proposed boundary orbital energy.[16]

Figure 1.4. Fluorescence quenching was described as follows: when CdSe is excited, an electron jumps to the LUMO; an electron from the HOMO of T_5 drops to the half-filled CdSe orbital, which inhibits CdSe fluorescence. Increased CdSe fluorescence in the T_3 complex was described as follows: When a T_3 electron is excited it can fall into the CdSe LUMO. An electron from the CdSe HOMO drops to fill the T_3 orbital. This leaves a hole into which the remaining excited electron can drop, releasing a photon of light.

In addition to metals, oligothiophenes have been extensively studied in conjunction with one or more other optically interesting groups, such as fullerenes,[17-25] porphyrins,'' ferrocenes, or other ligand-coordinated transition metals, especially Ru.[26-31,33,34] In the cases where oligothiophenes are used as linkers between groups, they may be thought of as molecular wires. The main interest in these molecules lies in photon-induced electron promotion. All of the above mentioned groups absorb visible light. This means that they all have LUMOs of low enough energy to be readily accessible. The relative energies of the empty orbitals dictate if the electron will jump between functionalities. Electron transfer implies the formation of a charge separated state. Promotion and manipulation of this charge separation is a focus of study. If the charge separation is effective, and if the induced current can be made to do work before

regenerating the ground state system, then a solar power cell may be possible with that system.

Ito et al. have demonstrated electron transfer from ferrocene[19] and a porphyrin[20] through oligothiophenes to a fullerene. They have also employed a porphyrin-oligothiophene-fullerene triad as an ion sensor by attaching a crown-ether moiety between adjacent thiophenes. The attachment is made in such a way that when an ion becomes bound in the crown ether, the connected thiophenes are forced into an orthogonal orientation, decreasing the conjugation between the porphyrin and the fullerene. Thus, ion concentration may be measured by decreasing fluorescence emission.

1.1.4. Oligothiophene-Ruthenium Complexes

Electronic communication between oligothiophene and Ru complexes is our area of interest. This subset of ruthenium and thiophene chemistry is also of interest.[27-34] One system that has been thoroughly studied is a symmetric bipyridine-thiophene backbone linked by ethynyl spacers. Ruthenium was the primary metal involved, although Re and Os were also used. Figure 1.5 displays several of these compounds.

The first studies[27] involved complexes linked through single thiophenes, such as **4**. Cyclic voltammetry (CV) and UV-Visible spectroscopy indicated that the metal centers were electronically isolated from each other, despite the backbone being fully conjugated.

A later study[28] employed compound **5**. Once again, intercomponent interaction was low. The metals behaved independently of each other and of the bridging ligand. Cyclic voltammetry measurements showed initial oxidation centered on the

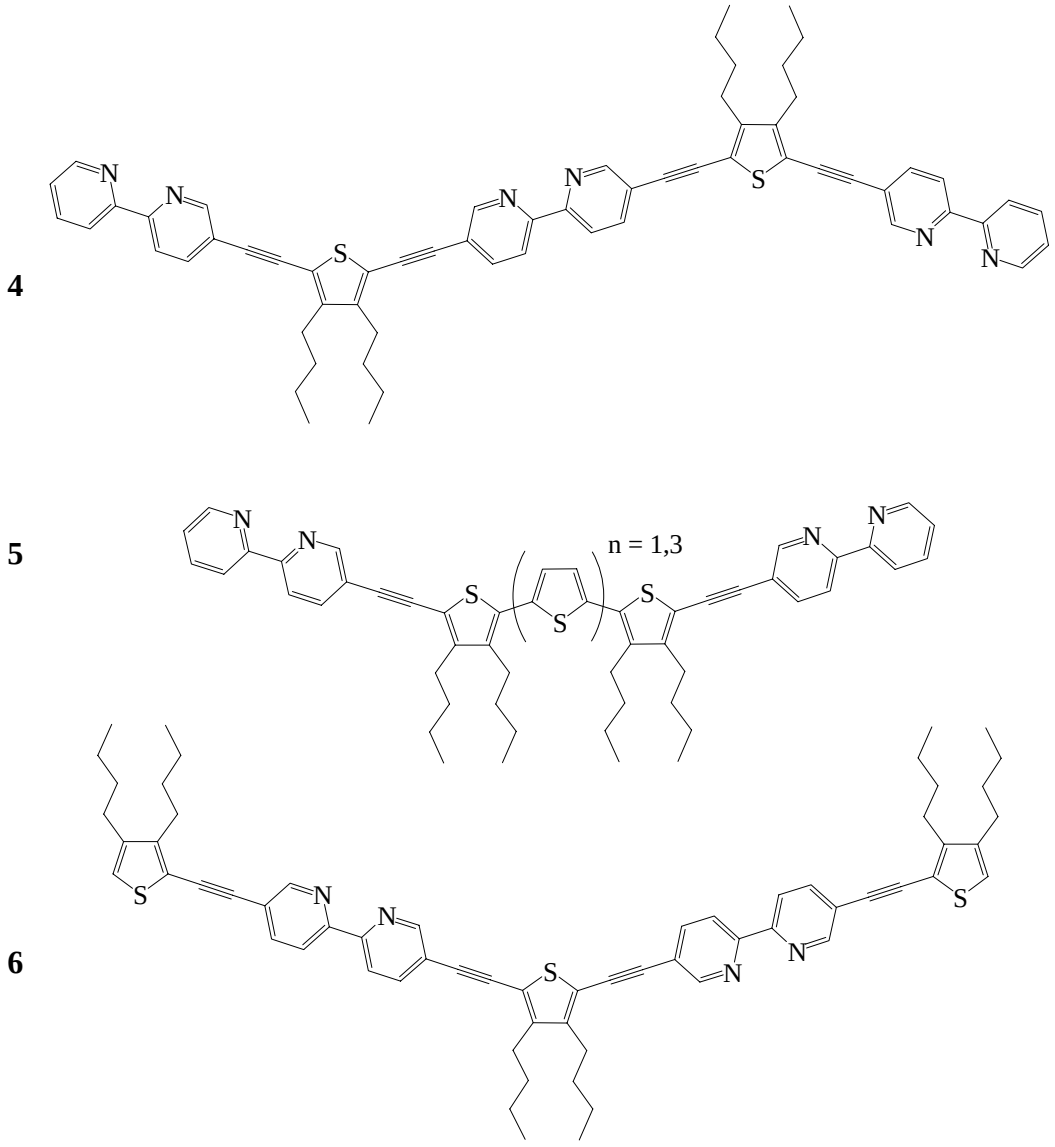


Figure 1.5 Conjugated molecules **4**, **5**, and **6**.

oligothiophene (considered an electron rich species) followed by Ru(II) oxidation to Ru(III). The reductions were located on the electron-poor bipyridyl ligands. The only evidence of interaction between the metals and the oligothiophene was in luminescence measurements. As is common with oligothiophene structures, the conjugated backbones were highly absorbent and fluorescent with emission quantum yields on the order of 10%.

Once metals were bound, however, the strong π to π* fluorescence was strongly quenched, leaving only weak MLCT emission bands.

The most recent studies employed **6**. This is a single thiophene system with the metals moved to the interior of the chain. Heterometallic systems employing Ru, Os and Re were used to study energy transfer between metal centers. As before, the CV data showed no connection between the metal centers. The absorbance spectra are similar for the homonuclear ruthenium and osmium complexes, except for a small low energy shoulder in the Os complex. This is ascribed to the enhanced intersystem crossing due to the spin-orbit coupling caused by the larger atom. Absorbance spectra of heteronuclear complexes were inconclusive concerning intermetallic interaction. The luminescence spectra again showed quenching of the strong backbone fluorescence with metal coordination.

Another well-researched system consists of two $Ru(bpy)_3$ complexes covalently bound directly by an oligothiophene (Figure 1.6).[32] Optical and electrochemical studies concluded that although the metal centers were directly linked, they still did not communicate electronically unless they were separated by only a single thiophene. This was determined by observing that with a single thiophene there were two single electron oxidations for Ru. With longer oligothiophenes there was only one 2-electron oxidation. Other conclusions from this research agreed with the general findings: more extended oligothiophenes stabilize charge, bipyridine is conjugated with the oligothiophene, and the complex's MLCT redshifts versus $Ru(bpy)_3^{2+}$.

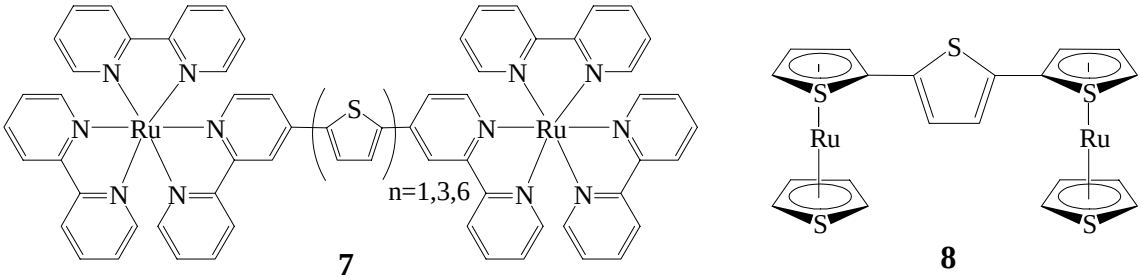


Figure 1.6. Ru diad complex **7**[32] and η^6 complex **8**.[34]

An unusual attachment of Ru or Os to an oligothiophene chain was reported by Mann et al.[33,34] Prior to their studies it was known that metal ions could bind η^6 to a single thiophene, but this was never applied to oligothiophenes.[34] They found that Ru and Os each bind to the terminal thiophene of an oligothiophene. An example of this is **8**, shown in Figure 1.6. This effectively removes the coordinated thiophene from conjugation. Although the complexes were thoroughly studied by several NMR methods and CV, UV-Vis and fluorescence measurements were not reported.

A potentially important aspect of Ru-oligothiophene chemistry is the position of attachment of oligothiophene to the complexing bipyridine. The two commonly studied positions are 4 and 5 (Figure 1.7).[8,9,26,30,35] It is often stated that substitution at the 4 position allows conjugation of oligothiophene to Ru without conjugation to the bipyridine. It is also stated that substitution at the 5 position allows complete conjugation between the bipyridine and oligothiophene. This concept is easily understood in theoretical terms by resonance structures. Experimental study on the practical extent of this effect in terms of polymers and oligomers appears to be lacking.

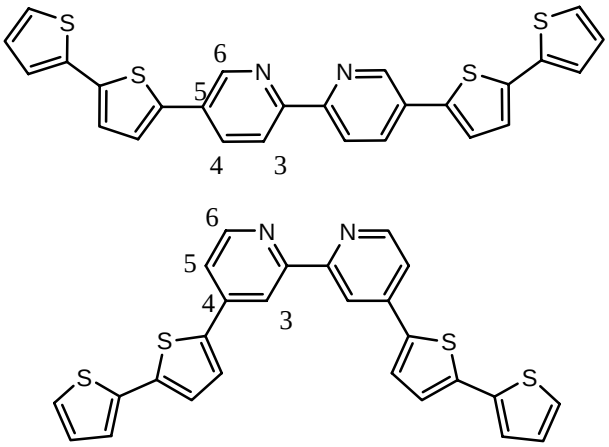


Figure 1.7. 5,5'-bis(bithienyl)bipyridine **9** and 4,4'-bis(bithienyl)bipyridine **10**.[26,30]

The most significant studies to articulate the experimental difference between 4- and 5-position substitution are those of Swager et al.[26,30] Compounds **9** and **10** (Figure 1.7) were polymerized. The Ru complexes of **9** and **10** were also polymerized. A comparison of the conductivity of each polymer demonstrated that in the 5-substituted complex the metal centers were electronically isolated. The polymer of **9** displayed similar conductivity with or without Ru. The polymer of **10** gave no detectable conductivity. With Ru present, however, the polymer of **10** was conductive at voltages corresponding to the redox potentials of Ru. This demonstrates that a conjugated path through the polymer was created by the addition of Ru.

Absorbance measurements indicate that there is partial conjugation with both **9** and **10**, but that conjugation is more complete with **9**. The UV-Vis measurements for bipyridine and bithiophene are 283 nm and 303 nm, respectively. If there were no interaction between the bipyridine and bithiophene moieties then we would expect to see the same two absorptions in the spectra of **9** and **10**. This is not the case. The maximum absorptions for **9** and **10** are 396 nm and 361 nm, respectively. It is observed that

conjugation is present in both compounds, which is indicated by a single lower energy absorption. Compound **9**, substituted in the 5-position, exhibits a greater degree of conjugation as indicated by the longer π to π^* absorption wavelength.

Because of steric crowding, substitution at the 6-position is of less interest. However, in light of the current topic it is interesting to note that there does appear to be good conjugation between oligothiophene and phenanthroline substituted at the ortho position.[36,37]

1.1.5. Synthesis

Thiophenes respond well to standard aryl coupling and substitution methods. Regioselectivity is easily controlled. The C2 proton is the most acidic of thiophene. Thus, bases such as LDA and n-BuLi can be used to deprotonate at the 2-position in preparation for transmetallation with tin or boron reagents. Halogenation also occurs preferentially at the 2-position. Oligomers are generally attached in a 2,2' fashion.

The most common method for construction of oligothiophenes is metal-catalyzed aryl cross coupling. For direct thiophene connection, Stille and Kumada coupling have been employed the most, but the non-toxic Suzuki coupling is becoming more commonly used. Many functional groups have been attached to thiophene.[16,19,20,31,38,39,40]

The main difficulty encountered during the synthesis of oligothiophenes is the insolubility of extended, unfunctionalized chains. Most researchers prefer to attach functional groups to the 3-position of the thiophene to increase oligomer solubility. The only disadvantage to this practice is that interaryl steric interactions might force non-planarity, which decreases conjugation. Generally, it appears that only large groups

interfere with conjugation. Some smaller groups, such as short alkyl chains, actually increase conductivity in polythiophenes.[11] This increase results from increased order in the polymer, and thus does not affect oligomers.

1.1.6 Proposed Goal

Our goal is the synthesis of oligothiophene-ruthenium complexes in preparation for CdSe nanoparticle binding. A general representation of our proposed compounds is shown in Figure 1.8. Ruthenium was to be complexed with bipyridine, which would in

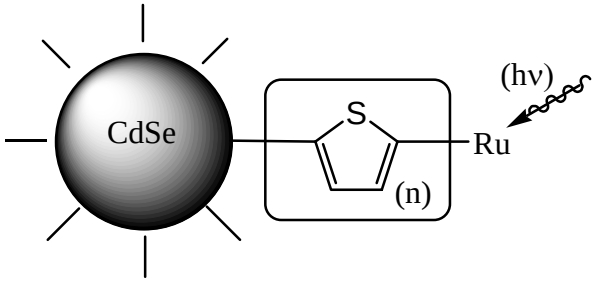


Figure 1.8. Proposed CdSe-oligothiophene-ruthenium complex.

turn be covalently bound to the oligothiophene. The oligothiophenes would be attached at both the 4- and 5-positions on bipyridine to compare the electronics of the different positions. We estimated that a tetrathiophene linker would provide optimal electronic properties. Bithiophene linker compounds would also be prepared to study the differences in oligothiophene length. Phosphonic acid was chosen as the connecting group between the oligothiophene and the nanoparticle because of its metal binding properties. Incorporating these characteristics, we targeted compounds **11**-**14** for synthesis (Figure 1.9). To our knowledge, this would be the first example of an asymmetric

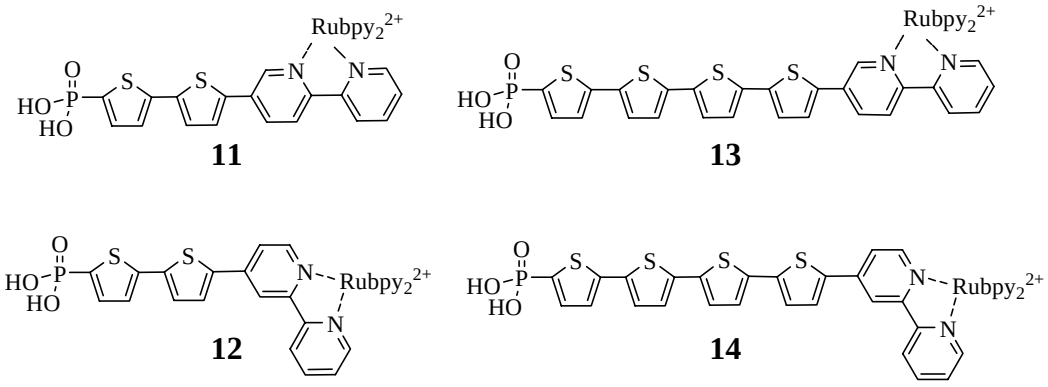


Figure 1.9. Target oligothiophene-Ru complexes **11**-**14**.

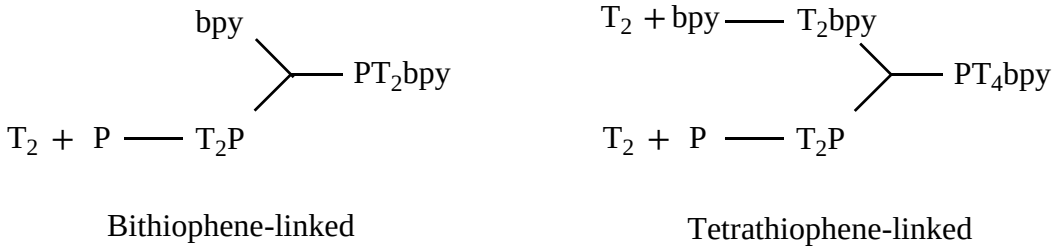
oligothiophene-ruthenium complex. Attachment to CdSe nanoparticles would present the first example of communication between ruthenium and CdSe nanocrystals.

1.2. Results and Discussion

1.2.1. Synthesis

Synthesis of the oligomer backbones was approached in a convergent manner using known chemistry as shown in Scheme 1.1.

Scheme 1.1

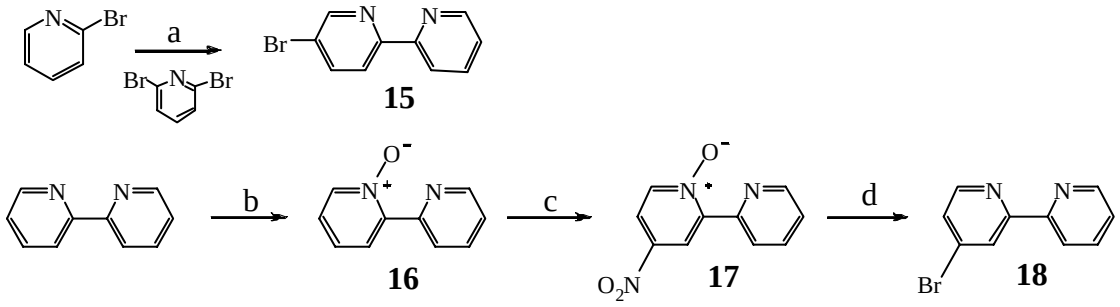


Bithiophene-linked

Tetrathiophene-linked

Abbreviations: T_n is oligothiophene of length n, P is diethylphosphonate, bpy is bipyridine. All attachments to thiophene are made at C2.

Scheme 1.2



Reagents: (a) (1) n-BuLi, Bu_3SnCl; (2) 2,5-dibromopyridine, $Pd(PPh_3)_4$; (b) MMPP; (c) con. H_2SO_4, con. HNO_3; (d) (1) acetyl bromide; (2) PBr_3.

We began by preparing the bipyridines for the donor complexes. Scheme 1.2 outlines the synthetic pathway to 5- and 4-bromobipyridines (**15** and **18**, respectively). Compound **15** was made according to the literature procedure with only minor modifications to the isolation.[41]

Compound **18** was made with variations to multiple procedures.[42-44] Effective procedures for the synthesis of bipyridine N-oxide from bipyridine have been reported using m-chloroperoxybenzoic acid (mCPBA), however we chose to use magnesium monoperoxyphthalate (MMPP) as it is less toxic and less expensive. Although the yield was lower than that shown using mCPBA, the excess bpy is recoverable. One reference to the use of MMPP for bipyridine oxidation was found, but the procedure appeared more complex than necessary.[42] The use of glacial acetic acid did not seem necessary in light of other N-oxidation reactions with MMPP, and evaporating acetic acid directly is difficult. A simple trial with ethanol as the solvent showed the same percent conversion

to the N-oxide as with acetic acid. It was also found that **16** could be separated from unreacted starting material by a simple extraction followed by flash chromatography.

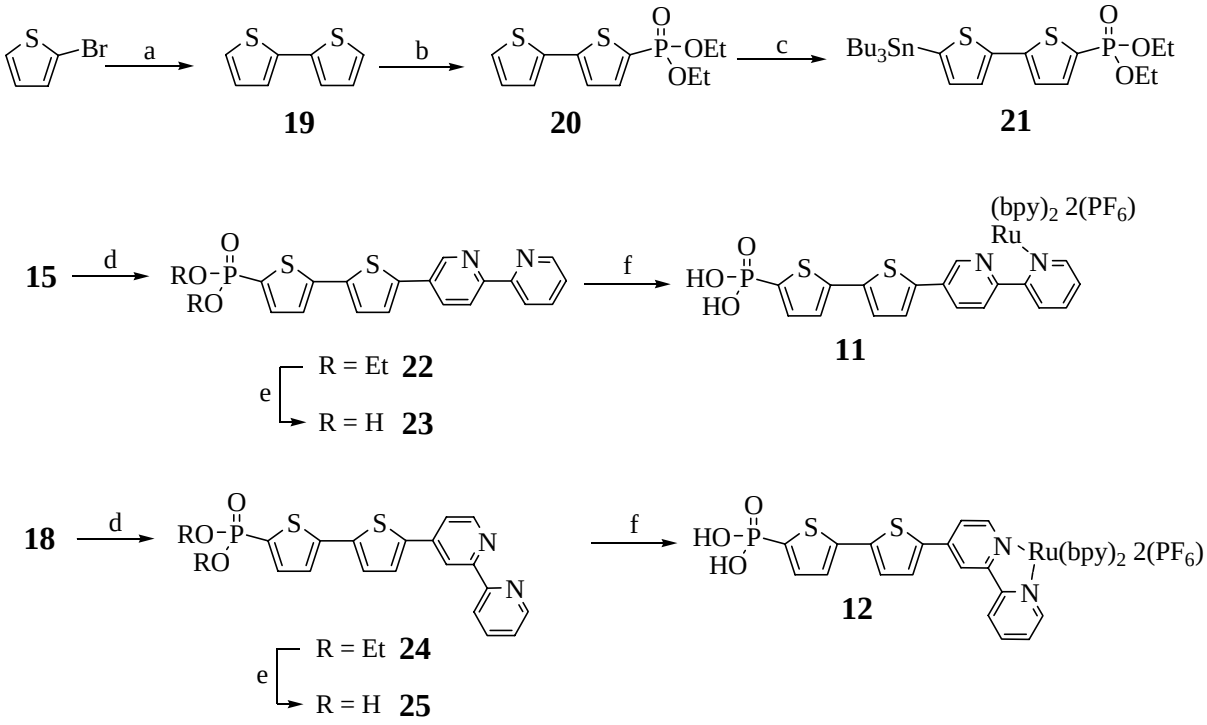
Several reported procedures for the synthesis of nitro compound **17** use fuming sulfuric and nitric acids and produce only 30-40% yields. The best published yield for the synthesis of **17** is less than 50%[43] and we were not able to reproduce even that yield. Our new procedure gives yields of 45-50%. Careful control of the temperature and rate of nitric acid addition prevented dinitration.

The transformation from **17** to **18** was made according to the literature procedure.[44] Acetyl bromide was added to replace the nitro group and PBr_3 effected the removal of the oxide. We found that purification of the product could be simplified to an extraction with $CHCl_3$ followed by sublimation.

We will first discuss the synthesis of the compounds incorporating the bithiophene linkers. Scheme 1.3 displays the synthesis of bithiophene triads **11** and **12**. With the bromobipyridines in hand, the next step is to prepare the bithiophene linker. Bithiophene (**19**) is commercially available, but the synthesis is simple and efficient. 2-Bromothiophene is used to make both coupling partners in a Kumada cross coupling. Catalysis is efficient, with only 0.25 mol% $PdCl_2$(dppf) required for quantitative yields. Sublimation yields pure **19**.

Before connecting bithiophene with bipyridine, we added the phosphorus group to bithiophene. The phosphoric acid is protected as the diethylphosphonate during the coupling sequence. Compound **20** was made according to the literature procedure with the bithienyllithiate performing nucleophilic attack on diethylchlorophosphonate.[40] The literature reference uses such a small amount of solvent that the lithiated compound

Scheme 1.3. Synthesis of bithiophene-Ru complexes **11** and **12**.[a]



[a]Reagents: (a) (1) Mg(s); (2) 2-bromothiophene, $PdCl_2$(dppf); (b) (1) n-BuLi; (2) $(EtO)_2P(O)Cl$; (c) (1) LDA; (2) Bu_3SnCl; (d) **21**, $Pd(PPh_3)_4$; (e) (1) TMSBr; (2) H_2O; (f) (1) $RuCl_2bpy_2$, NaOH; (2) KPF_6.

precipitates from solution and forms a thick slush. This inhibits the diethylchlorophosphonate from mixing properly and encourages decomposition pathways. The use of more solvent results in a significant increase in yield.

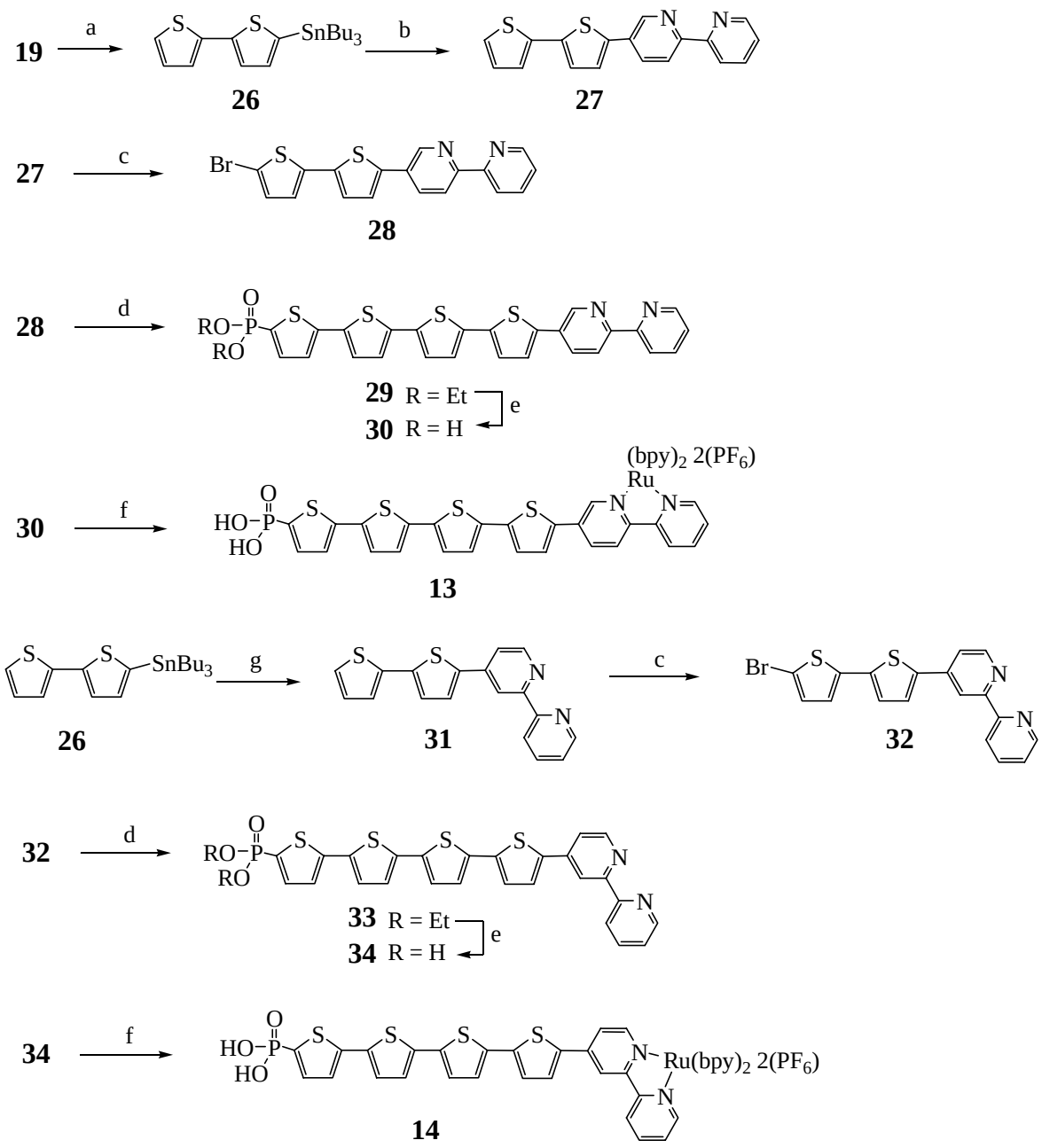
The Stille coupling partner, **21**, was formed from **20** by deprotonation with lithium diisopropylamide (LDA) followed by transmetallation with tributyltin chloride. We were not able to duplicate the published yield for **21**.[40] It is supposed that LDA is used as the base instead of n-butyllithium because the increased steric bulk reduces the likelihood of nucleophilic attack on the phosphorus.

With tributyltin coupound **21** and bromobipyridines **15** and **18**, we were ready to connect the two. Stille coupling provided the backbone for the bithiophene compounds. The ethyl groups on the phosphonate were cleaved by substitution with trimethylsilyl bromide (TMSBr) followed by hydrolysis to the acids.[16,45] These compounds, **23** and **25**, are insoluble in most solvents except DMSO and basic water.

Ruthenium was readied for attachment by preparing the dichlorobis(2,2'-bipyridyl)ruthenium ($RuCl_2bpy_2$) complex according to the literature procedure.[46] Final complexes **11** and **12** are prepared by refluxing $RuCl_2bpy_2$ with **23** or **25**, respectively, in slightly basic water. The base improves the solubility of the phosphonic acid compounds and ensures deprotonation of the pyridyl nitrogens. After the reaction is complete, the product is precipitated by acidification and the Cl^- counter-ion is exchanged for PF_6^-. Originally DMF was used during the isolation, but it was very difficult to completely remove it under vacuum. Acetonitrile is a fitting replacement for DMF.

It was assumed that after construction of the tetrathiophene moiety, one might functionalize each terminus of the chain in sequence as was done with the bithiophene-based compounds. It was found, however, that tetrathiophene was too insoluble to make the subsequent reactions feasible. At this point it was determined that bithiophene units would need to be functionalized separately, followed by coupling to form the tetrathiophene-linked compounds. Scheme 1.4 displays the synthetic approach.

Scheme 1.4. Synthesis of tetrathiophene-Ru complexes **13** and **14**.[a]



[a]Reagents: (a) (1) n-BuLi; (2) Bu_3SnCl; (b) **15**, $Pd(PPh_3)_4$; (c) NBS; (d) **21**, $Pd(PPh_3)_4$; (e) (1) TMSBr; (2) H_2O; (f) (1) $RuCl_2bpy_2$, NaOH; (2) KPF_6; (g) **18**, $Pd(PPh_3)_4$.

For the synthesis of the tetrathiophene-linked compounds, **21** represents half of the final product backbone. The other half was begun by forming the tributyltin adduct of bithiophene and coupling with the desired bromobipyridine. This was done by following a published procedure.[30] In our hands the yields of **27** and **31** were poor and purification was difficult. Bromination was accomplished in nearly quantitative yields with NBS. In the future, much less solvent could be used than we did for the bromination.

The backbone was assembled by Stille coupling between **21** and **28** or **32**. Compounds **29** and **33** were isolated by filtration due to their relative insolubility. The ethyl groups were cleaved by reaction with TMSBr. Yields appeared to be high, although we were unable to characterize them due to their insolubility in all common solvents.

Ruthenium was added using the same method as that used for the bithiophene compounds. Reaction times were nearly ten times longer for the tetrathiophenes because of the insolubility of the acid compounds.

From a synthetic standpoint, the only significant difference between 4- and 5-substituted compounds is that compounds in the 5-position are noticeably less soluble than those in the 4-position.

$Ru(bpy)_3(PF_6)_2$ was synthesized for use as a standard when measuring the optical properties of the oligothiophene-ruthenium complexes. Refluxing water with $RuCl_3$ and bipyridine did not yield any of the desired product. After addition of DMF and continued refluxing the product was formed. After having synthesized it by this procedure, several references in the literature were found.[47,48] A reducing agent is required for this reaction and it appears that both ethanol and DMF are suitable reducing agents.

For future nanocrystal studies, bithienylphosphonic acid was synthesized from **20**. Because a homogeneous mixture formed between **20** and TMSBr the reaction was probably complete in much less time than was allowed.

1.2.2. General Theory

Complexes of ruthenium have been known for decades and continue to be studied.[2-9,49-51] When ruthenium is bound to aromatic ligands, such as bipyridine or phenanthroline, a metal to ligand charge transfer (MLCT) transition becomes available. This MLCT absorption is responsible for the intense orange to red color of the complexes. Figure 1.10 displays an approximate orbital diagram for $Rubpy_3^{2+}$ taken from a work by Lytle and Hercules.[49] The symmetry of the complex is best described as D_3 because of a small splitting of the t_{2g} orbitals which has been attributed to covalency in the bonding.[48] The absorption spectrum of $Ru(bpy)_3PF_6$ is shown in Figure 1.11, with an inset showing the relevant absorption and emission spectra. Here we will only discuss the

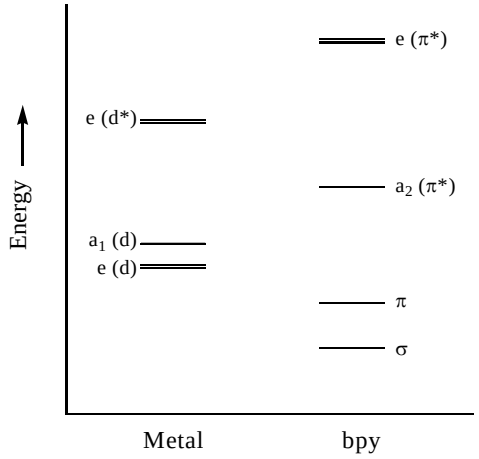


Figure 1.10. Relative orbital energy levels for $Rubpy_3^{2+}$.

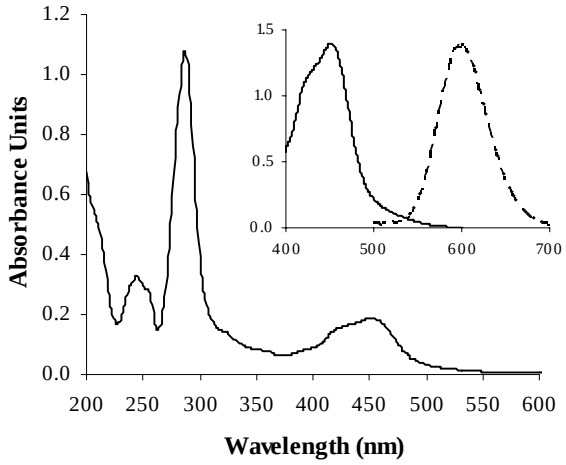


Figure 1.11. Absorbance spectrum on $Ru(bpy)_3^{2+}$ in acetonitrile. Inset shows an expansion of the absorption spectrum (solid line) with the emission (dashed line).

most prominent spectral features. Previous studies have identified the peaks at 244, 287, and 450 nm as the e(d) to e(π*) (MLCT), π to a_2(π*), and e(d) to a_2(π*) (MLCT) respectively. The shoulders on the MLCT absorptions have been described as vibronic in origin.

The emission wavelengths are significantly red-shifted (ca. 150 nm) with respect to absorption. Researchers believe that the emission is due to charge transfer fluorescence. However, significant spin-orbit coupling exists, which, through singlet to triplet conversion, may permit other emissive decay pathways.

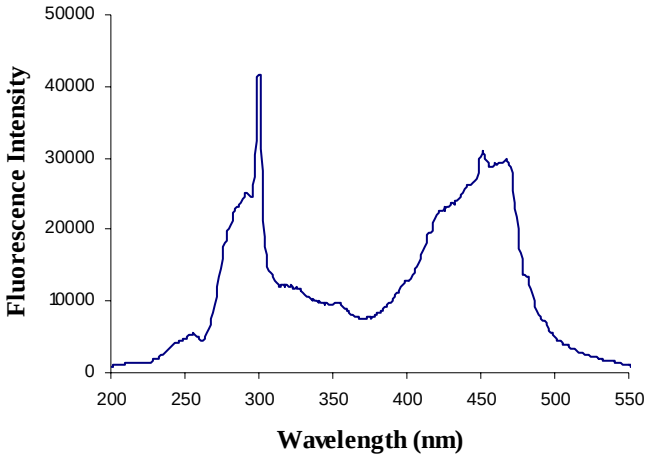


Figure 1.12. Excitation spectrum of $Ru(bpy)_3^{2+}$ with emission at 600 nm.

Scanning excitation wavelengths for emission at 600 nm (Figure 1.12) provides another interesting point. Excitation into the π to π* absorption band results in the same fluorescence emission as excitation of the MLCT absorption. This affirms the assumption that the most prominent CT transition is due to the e(d) to $a_2(\pi^*)$ absorption. This also indicates that orbital coupling is sufficient to allow facile electron transfer from the metal d orbital to the bipyridyl π HOMO. This is necessary to create a hole for the excited electron to fall into. Since the quantum efficiencies of emission are comparable at the two absorption wavelengths, we can assume that the e(d) to π transition is fast relative to emission.

1.2.3. Optical studies

Absorbance and emission measurements were taken to understand: (1) the effect of the phosphonic acid moiety on electronics; (2) relative orbital energy levels between bi- and tetrathiophene compounds; (3) the difference between 4- and 5-position

substitution on bipyridine; and (4) orbital overlap and electronic communication between Ru and oligothiophene.

Table 1.1 displays the relevant UV-visible absorption data. In order to compare spectra that were taken in different solvents, **31** and **27** were dissolved separately in acetonitrile and DMSO. A red shift of 5 and 7 nm, respectively, was found on going to the more polar solvent. This shows that the absorbances are fairly similar whether measured in DMSO or acetonitrile.

Table 1.1. Spectral Properties of Oligothiophenes and Oligothiophene-Ruthenium Complexes[a]

	absorption					emission
Compounds	λ_{max} (ε_{max})					λ_{max}
11	244 (27000)	287 (78000)	397 (41000)			445
12	245 (34000)	288 (75000)	384 (32000)	466 (28000)		436
13	245 (32000)	288 (75000)	365[c]	446 (52000)		486
14	245 (38000)	289 (75000)	385[c]	437 (49000)	478 (46000)	507/530
22	237 (12000)	261 (10000)	365 (43000)			416/437
23[b]			377 (32000)			449
24	241	274	359			
25[b]			363 (28000)			452
27	238 (12000)	289 (12000)	363 (45000)			445
27[b]			374 (53000)			454
29[b]			432 (22000)			503
31	242 (19000)	282 (16000)	357 (28000)			430
31[b]			362 (24000)			436
33	241 (23000)	274 (25000)	420 (57000)			486/508
Tetrathiophene	254 (8000)		393 (20000)			450/478
$Ru(bpy)_3(PF_6)_2$	244 (29000)	287 (95000)		450 (16000)		600
$RuCl_2bpy_2$	242	298	376	550		

[a]Dissolved in acetonitrile unless otherwise noted. Concentrations are 0.01 mM. [b]Dissolved in DMSO. [c]Shoulder.

To measure the effect of the phosphonic acid moiety on absorbance and emission, **31** and **27** were compared to **25** and **23**, respectively. DMSO was chosen for the

measurements as it is the only solvent which will dissolve all four compounds. The absorbance maxima were very similar, the acids are red-shifted one and three nanometers for the 4- and 5-position compounds, respectively. A greater difference is seen in the emission spectra. While fluorescence intensity and peak shape were coincident, the emission frequency shifted substantially. Unfortunately the shift was not consistent. Compound **25** emitted at 16 nm lower energy than **31**, while **23** came at 5 nm higher energy than **27**. This variation seems anomalous and more work will be necessary to clarify the situation. In terms of intramolecular electronic communication, we do not predict that the phosphonic acid will have any influence.

Spectral features of the oligothiophenes are in line with reported results for similar compounds. Low peaks in the region of 240 nm are assigned to individual thiophene absorption.[32] A lower energy peak is found between 275 and 290 nm, which results from residual bipyridine absorption. In the region of 350-430 is found the π to π^* transition for the entire ligand. Emission due to excitation of the π to π^* transition is very intense. Emission maxima are generally shifted 70-80 nm relative to the absorption.

Increased conjugation results in a decrease in energy required for electron excitation. Applying this general statement, we see that substitution off of the 5-position results in a higher degree of conjugation between the oligothiophene and bipyridine segments, although the difference in λ_{max} is only about 10 nm. Interestingly, the difference appears greater in DMSO than acetonitrile.

Another interesting observation may be made by comparing 5,5'- and 4,4'-bis(bithienyl)bipyridines **9** and **10** to 5- and 4-tetrathienylbipyridines **29** and **33**, respectively. Each has a bipyridine with four thiophene rings attached in comparable

positions, but **9** and **10** have two thiophene-pyridine connections, whereas **29** and **33** have only one. The absorptions of **9** and **10** are red-shifted 30-50 nm relative to **29** and **33**. We may thus conclude that conjugation across a thiophene-pyridine connection is significantly less than that of a direct thiophene-thiophene link. This comes as no surprise, as we expect that orbital overlap is at a maximum when the energy and size of the adjacent orbitals are the same. Thiophene, being electron rich, will have boundary orbitals of different energy than that of pyridine, which is electron poor.

The absorbance spectra of the four ruthenium-oligothiophene complexes are shown in Figure 1.13. Some aspects of the spectra are similar. The uneven peak around 250 nm is a combination of the π to π^* transition of individual thiophenes and the e(d) to e(π^*) MLCT. The strong signal at 290 nm is assigned to bipyridine, comprising the one attached to oligothiophene and the two ancillary bipyridines on Ru.

Each spectrum also requires individual consideration. 4-Substituted bithiophene compound **12** displays two low energy peaks. The first, at 384 nm, appears to be the π to π^* signal but red shifted. This effect is common to all Ru complexes of this type and has been ascribed to the "donor-acceptor" nature of the system.[30] The second peak, at 466 nm can be assigned to the MLCT localized on the oligothiophene-substituted bipyridine. The red-shift of 16 nm relative to bipyridine $Ru(bpy)_3^{2+}$ is explained by the greater stabilization of the negative charge on the extended ligand.

The spectrum of tetrathiophene compound **14** is very similar to that of **12** with the exception of the expected red shift. The magnitude of the π to π^* signal shift is similar to the equivalent difference between the metal-free oligothiophenes **24** and **33**. On the other

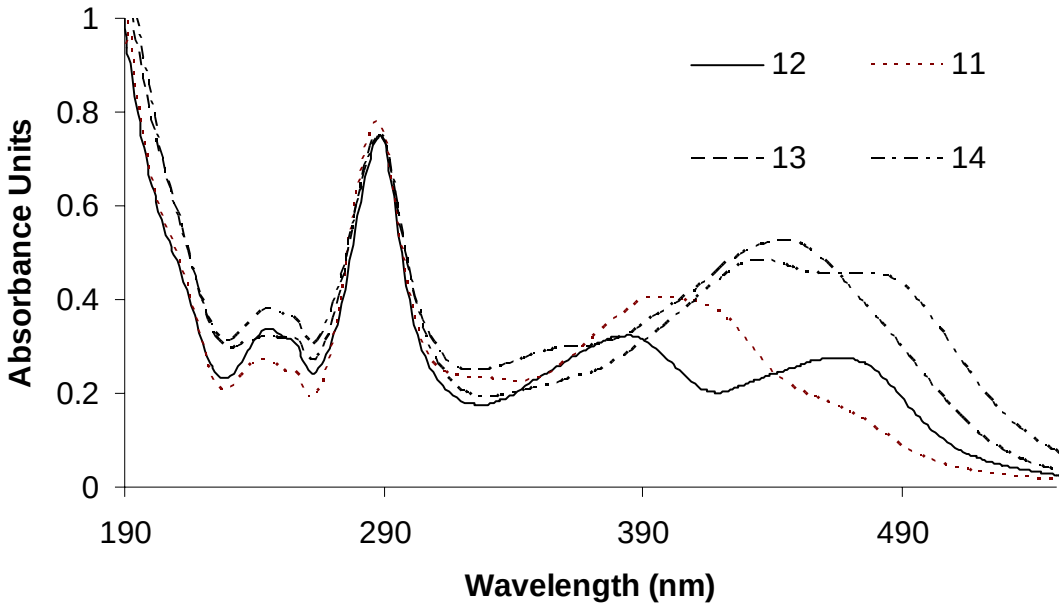


Figure 1.13. Absorbance spectra for all four Ru-complexed oligothiophenes. Concentrations were normalized to 0.01 mM in acetonitrile.

hand, the MLCT band is only moderately shifted. These two observations tend to confirm the assignment of the peaks.

The spectra of 5-substituted compounds **11** and **13** are more difficult to assign. The low energy portion of the spectra are dominated by what may be assigned as the π to π* transition. A low shoulder is visible for bithiophene **11** which corresponds to the MLCT wavelength, but it is not clear why the absorption coefficient has decreased. In the case of tetrathiophene **13** there is not a visible shoulder. This may be partially explained by overlap of the strong π to π* signal on the MLCT. There also seems to be a drop in intensity of the MLCT.

The emission spectra of the complexes show a dramatic quenching of both the oligothiophene and $Ru(bpy)_3^{2+}$ fluorescence. This effect is common to such

complexes.[27,28] The strongest emissions for **11** and **12** are found by exciting at 365 nm and collecting at 400 nm. The maximum fluorescence of compounds **13** and **14** is found by exciting at 400 nm and recording emission at 500 nm. These very weak emissions are quite similar to those of the free ligands. This either indicates that trace amounts of free ligand are present, or that the ligand emissions have not been entirely quenched.

As nearly all of the energy emission appears to be dissipated nonradiatively, we cannot discuss possible electron or energy transfer mechanisms. We are left to assume that enough closely spaced molecular orbitals have been formed to allow vibrational decay from the excited to ground state.

Future studies on these compounds will include the determination of emission quantum efficiency and the measurement of oxidation and reduction potentials by CV. Coordination of these compounds to CdSe nanocrystals through phosphate binding will also be performed and electron transfer will be studied.

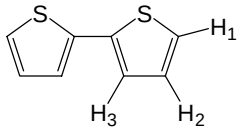
1.3. Conclusion

Oligothiophene-ruthenium complexes **11**-**14** were synthesized by aryl coupling and metal coordination. Emission studies reveal extensive metal-ligand communication which is indicated by fluorescence quenching. Comparison of 4- and 5-substituted bipyridines shows that conjugation with attached thiophene occurs most effectively through the 5-position while the 4-position communicates with the metal.

1.4. Experimental

General

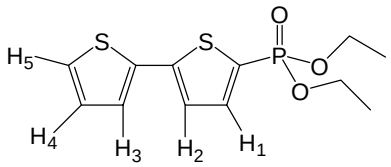
All starting materials were purchased from commercial sources and used as received. Solvents were passed through a solvent drying system with activated alumina columns. All NMR spectra were recorded on 300 or 500 MHz Varian Oxford spectrometers. Proton and ^{13}C NMR spectra were referenced to TMS or residual solvent signals. ^{31}P NMR signals were referenced to an external sample of 85% H_3PO_4. Mass spectra (including exact mass) were recorded on an Agilent ESI-TOF mass spectrometer. Compounds were prepared for UV-Vis analysis by preparing 0.01 mM solutions in acetonitrile or DMSO. UV-Vis spectra were analyzed on an HP 8453 spectrometer. Fluorescence measurements were made on a Photon Technology International Bryte Box. Melting points were found with a Mel-Temp apparatus from Laboratory Devices and are uncorrected. Column chromatography was done with silica gel with a mesh size of 60-200.



2,2'-bithiophene (19, T_2)

A 250 mL, 3-neck, round bottom flask containing a stir bar and Mg powder (2.76 g, 113.6 mmol) was oven dried. After cooling the flask, 125 mL dry ether was added and the flask was purged with N_2. The inert atmosphere was maintained throughout the reaction. Bromothiophene (7.35 mL, 75.9 mmol) was added by syringe and the reaction

was heated to reflux briefly to initiate the reaction. The reaction refluxed for 1 hr, then was cooled in an ice bath. The cooled solution was transferred by cannula to a second flask which contained bromothiophene (7.40 mL, 76.4 mmol), and $NiCl_2$(dppp) (0.417 g, 1.0 mol%) in 125 mL dry ether at 0 ºC. The new solution was stirred and allowed to warm to room temperature overnight. The reaction was quenched with 1 M HCl. Insoluble solids were removed by filtering through celite. The layers were separated and the organic layer was extracted once with water (50 mL). The combined aqueous fractions were extracted once with ether (50 mL). The combined organics were dried over $MgSO_4$, filtered and evaporated. The resulting oil (12.1 g, 72.8 mmol, 96%) was clean by NMR. Sublimation resulted in a white crystalline solid (m.p. 31.5-32 ºC). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.20 ($H_{1,3}$, dd, 2H, J = 0.5, 4.75 Hz), 7.17 ($H_{1,3}$, dd, 2H, J = 1.0, 3.5 Hz), 7.01 (H_2, dd, 2H, J = 5.25, 3.75 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 137.643, 128.017, 124.600, 124.011. HRMS (ESI-TOF) calcd for $C_8H_6S_2$ $(M+H)^+$: 166.9984, found: 166.9982.

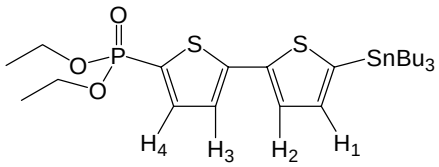


Diethyl 2,2'-bithien-5-ylphosphonate (20, T_2P)

Synthesized according to the literature procedure except with more solvent.[40]

To 200 mL of dry THF under N_2 in a Schlenk flask was added 2.57 g bithiophene (15.5 mmol) and the solution was cooled to -78 ºC. n-Butyllithium (9.8 mL, 15.7 mmol) was added by syringe and the solution was stirred for 1 hr. Diethylchlorophosphate (2.70

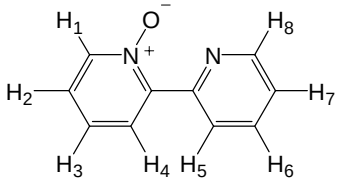
mL, 18.7 mmol) was then added and the resulting yellow/gold solution was allowed to warm to room temperature overnight. The reaction was quenched with 1 mL H_2O with no visible reaction. The solvent was removed and the resulting oil was partitioned between water (20 mL) and diethyl ether (50 mL). The layers were separated and the ether layer was washed once with water. The organics were then dried over $MgSO_4$, filtered and concentrated. Crude T_2P was purified by column chromatography through silica gel with ethyl acetate:hexanes (4:1) as eluant. T_2P (4.04 g, 13.4 mmol, 86%) was collected as a green oil. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.54 (H_1, dd, 1H, *J* = 3.5, 8.0 Hz), 7.29 ($H_{3,5}$, dd, 1H, *J* = 1.0, 5.0 Hz), 7.25 ($H_{3,5}$, dd, 1H, *J* = 1.0, 4.0 Hz), 7.20 (H_2, dd, 1H, *J* = 3.5 Hz), 7.04 (H_4, dd, 1H, *J* = 5.0, 4.0 Hz), 4.05-4.25 (OCH_2CH_3, m, 4H), 1.35 (OCH_2CH_3, dt, 6H, *J* = 8.5, 0.5 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 145.62 (C-P *J* = 7.5 Hz), 137.60 (C-P *J* = 10.5 Hz), 136.13, 128.261, 126.49 (C-P *J* = 208.5 Hz), 126.14, 125.39, 124.50 (C-P *J* = 16.5 Hz), 62.89 (C-P *J* = 5.5 Hz), 16.47 (C-P *J* = 6.0 Hz). ^{31}P-NMR ($CDCl_3$, 121 MHz): δ 11.80 (s). HRMS (ESI-TOF) calcd for $C_{12}H_{15}O_3PS_2$ $(M+H)^+$: 303.0273, found: 303.0265.



Diethyl 5'-tributylstannyl-2,2'-bithien-5-ylphosphonate (21, SnT_2P)

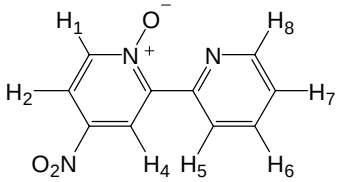
Synthesized according to the literature procedure.[40]

To a Schlenk flask with 5 mL THF under N_2 was added diisopropylamine (0.225 mL, 1.61 mmol). The solution was cooled to -78 ºC and n-BuLi (0.92 mL, 1.47 mmol) was added dropwise. After stirring for 15 minutes the LDA solution was warmed to room temperature and transferred by syringe to a Schlenk flask containing T_2P (0.42 g, 1.4 mmol) in 20 mL dry THF under N_2 at -78 ºC. The solution immediately went black. After stirring cold for 1 hour, Bu_3SnCl (0.43 mL, 1.6 mmol) was added and the solution was left to stir and warm to room temperature overnight. The medium red and clear solution was evaporated and 50 mL hexanes was added to the residue and the mixture was stirred vigorously for 45 minutes. Precipitated salts were removed by filtering through celite and the filtrate was concentrated. NMR analysis of the resulting light yellow oil showed SnT_2P (0.59 g, 1.0 mmol, 72%) and unreacted T_2P (0.10 g). The Stille reagent may be used directly, or after purifying by column chromatography through silica with hexanes:ethyl acetate (3:1) as eluant. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.54 (H_4, dd, 1H, *J* = 3.5, 8.0 Hz), 7.37 (H_2, d, 1H, *J* = 3.5 Hz), 7.20 (H_3, dd, 1H, *J* = 3.5, 3.5 Hz), 7.09 (H_1, d, 1H, *J* = 3.5 Hz), 4.20-4.10 (OCH_2CH_3, m, 4H), 1.61-1.53 ($SnCH_2CH_2CH_2CH_3$, m, 6H), 1.41-1.28 ($SnCH_2CH_2CH_2CH_3$ and OCH_2CH_3, m, 12H), 1.16-1.10 ($SnCH_2CH_2CH_2CH_3$, m, 6H), 0.91 ($SnCH_2CH_2CH_2CH_3$, t, 9H, *J* = 7.0 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 145.81 (C-P *J* = 7.5 Hz), 141.15, 138.97, 137.61 (C-P *J* = 10.5 Hz), 136.31, 126.34, 125.29 (C-P *J* = 209.5 Hz), 123.97 (C-P *J* = 17.5 Hz), 62.64 (C-P *J* = 5.5 Hz), 28.94, 27.24, 16.30 (C-P *J* = 7.0 Hz), 13.67, 10.93. ^{31}P-NMR ($CDCl_3$, 121 MHz); δ (ppm): 12.14 (s). HRMS (ESI-TOF) calcd for $C_{24}H_{41}O_3PS_2Sn$ $(M+H)^+$: 593.1330, found: 593.1329.



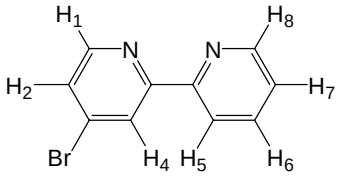
2,2'-bipyridine N-oxide (16, O-bpy)

To 600 mL of ethanol was added bipyridine (30.04 g, 192 mmol) and MMPP (38.59 g, 78.0 mmol), and the mixture was stirred and refluxed for 5 hours. Evaporation of the solvent produced a gummy solid. This was stirred vigorously in 600 mL $CHCl_3$ for 1 hour after which the insoluble material was filtered out and discarded. The solvent was again evaporated. The unreacted bipyridine (14.4 g, 92.4 mmol) was removed by column chromatography (370 g silica gel, ethyl acetate) after which pure O-bpy was flushed off with 20% methanol in ethyl acetate. The product was isolated (13.48 g, 78.3 mmol, 50% based on MMPP) as a brown oil. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 9.02 (d, 1H, J = 8.0 Hz), 8.74 (dm, 1H, J = 4.0 Hz), 8.32 (m, 1H), 8.26 (t, 1H, J = 5.0 Hz), 7.90 (ddd, 1H, J = 2.0, 8.0, 8.0 Hz), 7.46-7.42 (m, 3H). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 150.86, 150.25, 136.92, 128.48, 126.65, 125.90, 125.37, 125.14. HRMS (ESI-TOF) calcd for $C_{10}H_8N_2O$ $(M+Na)^+$: 195.0529, found: 195.0527.



4-nitro-2,2'-bipyridine N-oxide (17, O-bpy-NO_2)

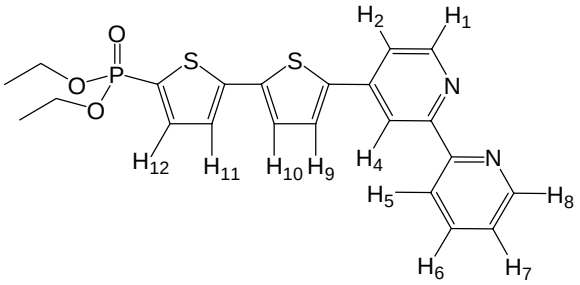
O-bpy **16** (4.48 g, 26.0 mmol) was dissolved in 50 mL conc. H_2SO_4 and the mixture was stirred and heated to 100 ºC. Concentrated nitric acid (6 mL) was dripped in overnight. After 12 hours an additional 5 mL HNO_3 was added over 5 hours. The temperature was maintained for a further 2 hours. After cooling, the solution was poured into ~50 g of ice. The solution was cooled in an ice bath while 81 g NaOH dissolved in a minimum amount of water was added to render the solution slightly basic. (WARNING! Extremely exothermic reaction!) The solution was extracted with $CHCl_3$ (4 x 50 mL). The combined extracts were washed once with water, then dried over $MgSO_4$, filtered and evaporated. O-bpy-NO_2 (3.38 g, 12.8 mmol, 49%) was isolated as an off-white solid (m.p. 180-184 ºC). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 9.16 (H_4, d, 1H, J = 3.5 Hz), 8.89 (H_5, dm, 1H, J = 8.0 Hz), 8.79 (H_8, dm, 1H, J = 5.0 Hz), 8.36 (H_1, d, 1H, J = 7.5 Hz), 8.07 (H_2, dd, 1H, J = 3.5, 7.5 Hz), 7.88 (H_6, ddd, 1H, J = 2.0, 8.0, 8.0 Hz), 7.44 (H_7, ddd, 1H, J = 1.0, 8.0, 5.0 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 150.07, 147.81, 142.18, 136.92, 125.59, 125.35, 122.86, 119.11. HRMS (ESI-TOF) calcd for $C_{10}H_7N_3O_3$ $(M+H)^+$: 218.0560, found: 218.0560.



4-bromo-2,2'-bipyridine (18, 4-Brbpy)

Synthesized according to the literature procedure.[44]

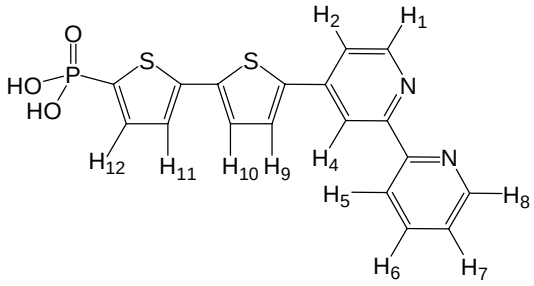
Acetyl bromide (45 mL, 610 mmol) was added to a solution of O-bpy-NO_2 (8.93 g, 41.1 mmol) in 25 mL glacial acetic acid. The mixture was heated to 30 ºC for 0.5 hours during which time a yellow precipitate formed. PBr_3 (31 mL, 330 mmol) was then added and the precipitate redissolved. The solution was heated to reflux for 1.5 hrs. After cooling, the acetic acid was neutralized with NaOH and the solution was extracted with $CHCl_3$ (4 x 50 mL). The organic extracts were dried over $MgSO_4$, filtered, and evaporated. The resulting crude red oil was put under vacuum and heated to 80 ºC. 4-Brbpy (7.46 g, 32 mmol, 78%) sublimed as a white solid (m.p. 51-52 ºC). The later sublimation fractions became yellow due to impurities and were discarded. The major impurity of the yellow fractions appeared to be 4-nitro-2,2'-bipyridine. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.67 (H_8, dm, 1H, J = 5.0 Hz), 8.62 (H_4, d, 1H, J = 2.0), 8.46 (H_1, d, 1H, J = 5.5 Hz), 8.38 (H_5, d, 1H, J = 8.0 Hz), 7.81 (H_6, ddd, 1H, J = 2.0, 7.5, 7.5 Hz), 7.46 (H_2, dd, 1H, J = 2.0, 5.5 Hz), 7.32 (H_7, ddd, 1H, J = 1.0, 7.5, 5.0 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 157.51, 154.86, 149.97, 149.36, 137.16, 134.07, 126.99, 124.62, 124.41, 121.48. HRMS (ESI-TOF) calcd for $C_{10}H_7N_2Br$ $(M+H)^+$: 234.9865, found: 234.9866.



Diethyl 5'-(2,2'-bipyridin-4-yl)-2,2'-bithien-5-ylphosphonate (24, 4-PT$_2$bpy)

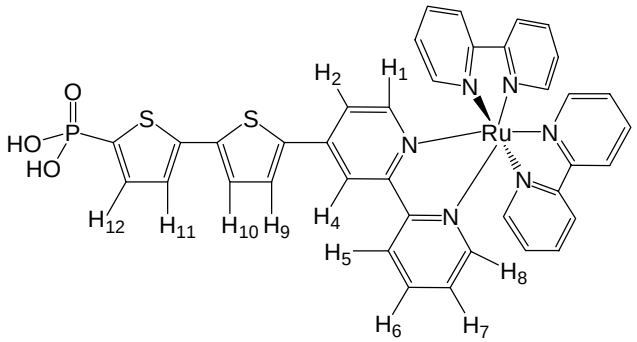
TinT$_2$P (1.7 g, 2.9 mmol) was dissolved in 30 mL dry toluene under N_2. 4-Brbpy (0.9 g, 4 mmol) and Pd(PPh$_3$)$_4$ (0.17 g, 5 mol%) were added and the solution was heated to reflux for 48 hours. After cooling, the solution was extracted with 20 mL water, then 20 mL of saturated NH_4Cl. The combined aqueous fractions were extracted with toluene (2 x 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered and evaporated. The resulting crude orange oil was chromatographed on silica with hexanes:ethyl acetate (1:1) followed by ethyl acetate. 4-PT$_2$bpy (0.55 g, 1.2 mmol, 42%) was collected as an orange viscous oil with ~90% purity as determined by NMR. This was used without further purification. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 8.73 (H_8, dm, 1H, *J* = 5.0 Hz), 8.68 (H_1, d, 1H, *J* = 5.5 Hz), 8.63 (H_4, d, 1H, *J* = 1.5 Hz), 8.42 (H_5, d, 1H, *J* = 8.0 Hz), 7.85 (H_6, ddd, 1H, *J* = 2.0, 8.0, 8.0 Hz), 7.59 (H_{10}, d, 1H, *J* = 4.0 Hz), 7.59 (H_{12}, dd, 1H, *J* = 3.5, 8.5 Hz), 7.48 (H_2, dd, 1H, *J* = 2.0, 5.0 Hz), 7.35 (H_7, ddd, 1H, *J* = 1.0, 7.5, 5.5), 7.29 (H_9, d, 1H, *J* = 4.0 Hz), 7.28 (H_{11}, dd, 1H, *J* = 3.5, 3.5 Hz), 4.11-4.25 (O*C*H_2CH$_3$, m, 4H), 1.37 (OCH$_2$C*H*$_3$, t, 6H, *J* = 7.0 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 157.05, 155.83, 149.99, 149.31, 137.65 (C-P *J* = 11.0 Hz), 137.11, 128.72, 128.56, 127.01 (C-P *J* = 209.5), 126.64, 126.34, 124.95 (C-P *J* = 16.5 Hz), 124.13, 121.38, 119.61, 117.04, 62.96 (C-P *J* = 5.5 Hz), 16.44 (C-P *J* = 6.5 Hz). ^{31}P-NMR ($CDCl_3$, 121

MHz); δ (ppm): 11.45 (s). HRMS (ESI-TOF) calcd for $C_{22}H_{21}N_2O_3PS_2$ $(M+Na)^+$: 479.0623, found: 479.0624. UV-Vis: λ_{max} (nm): 241, 274, 358.



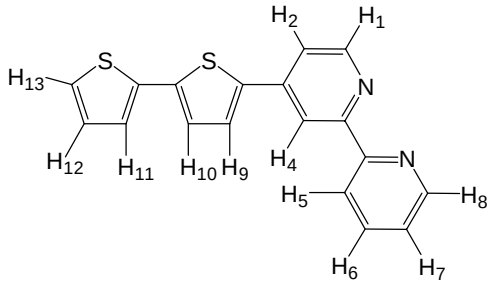
5'-(2,2'-bipyridin-4-yl)-2,2'-bithien-5-ylphosphonic acid (25, 4-APT$_2$bpy)

4-PT$_2$bpy (0.45 g, 0.99 mmol) was added to a Schlenk flask and thoroughly degassed with N_2. Trimethylsilyl bromide (TMSBr) (1.0 mL, 7.6 mmol) was added through a septum. The resultant slurry was stirred overnight under N_2. The reaction was quenched with water and stirred vigorously. The solid was filtered out and washed with acetone. 4-APT$_2$bpy (0.39 g, .97 mmol, 99%) was collected as an orange powder (m.p. 232-237 ºC). ^{1}H-NMR (DMSO, 500 MHz): δ 8.80 (H_8, d, 1H, J = 4.5 Hz), 8.75 (H_1, d, 1H, J = 5.0 Hz), 8.70 (H_4, d, 1H, J = 0.5 Hz), 8.57 (H_5, d, 1H, J = 8.0 Hz), 8.14 (H_6, ddd, 1H, J = 1.0, 8.0, 8.0 Hz), 8.06 (H_9, d, 1H, J = 4.0 Hz), 7.91 (H_2, dd, 1H, J = 1.5, 5.0 Hz), 7.64 (H_7, ddd, 1H, J = 1.0, 6.0, 6.0 Hz), 7.61 (H_{10}, d, 1H, J = 4.0 Hz), 7.52 (H_{11}, dd, 1H, J = 3.5, 3.5 Hz), 7.42 (H_{12}, dd, 1H, J = 3.5, 8.5 Hz). ^{13}C-NMR (DMSO, 125 MHz): Unavailable due to insufficient solubility. ^{31}P-NMR (DMSO, 121 MHz): δ 5.20 (s). HRMS (ESI-TOF) calcd for $C_{18}H_{13}N_2O_3PS_2$ $(M+H)^+$: 401.1780, found: 401.0176. UV-Vis (H_2O/OH^-): λ_{max} (nm): 238 (ε = 13000), 278 (ε = 13000), 363 (ε = 31000).



[5'-(2,2'-bipyridin-4-yl)-2,2'-bithien-5-ylphosphonic acid]bis(bipyridyl)ruthenium(II) hexafluorophosphate (12, 4-APT$_2$bpyRu)

To 25 mL H_2O was added 4-APT$_2$bpy (0.199 g, 0.499 mmol), $RuCl_2bpy_2$ (0.264 g, 0.545 mmol), and NaOH (24.4 mg, 0.61 mmol). The mixture was refluxed for 2.5 hours. After cooling, the mixture was acidified with about 1 mL 1 M HCl and filtered to remove unreacted starting material. KPF_6 in 10 mL H_2O (0.49 g, 2.7 mmol) was added, which precipitated a red solid. The mixture was filtered through a medium fritted filter. 4-APT$_2$bpyRu (0.410 g, 0.371 mmol, 74%) was washed with ether and dried (m.p. 232-237 ^oC). ^{1}H-NMR (DMSO, 500 MHz): δ 9.14 (d, 1H, *J* = 8.5 Hz), 9.08 (d, 1H, *J* = 2.0 Hz), 8.88-8.85 (m, 4H), 8.24-8.16 (m, 6H), 7.90 (d, 1H, *J* = 2.5 Hz), 7.77-7.74 (m, 4H), 7.71 (dd, 1H, *J* = 2.0, 6.0 Hz), 7.66 (d, 1H, *J* = 3.5 Hz), 7.62 (d, 1H, *J* = 6.5 Hz), 7.57-7.53 (m, 5H), 7.49 (dd, 1H, *J* = 3.0, 3.0 Hz), 7.42 (dd, 1H, *J* = 3.5, 8.0 Hz). ^{13}C-NMR (DMSO, 125 MHz): Unavailable due to insufficient solubility. ^{31}P-NMR (DMSO, 121 MHz): δ 5.12 (s). HRMS (ESI-TOF) calcd for $C_{38}H_{29}N_6O_3PS_2Ru$ $(M)^{2+}$: 407.0256, found: 407.0256. UV-Vis: λ_{max} (nm): 245 (ε = 34000), 288 (ε = 75000), 384 (ε = 32000), 466 (ε = 28000).

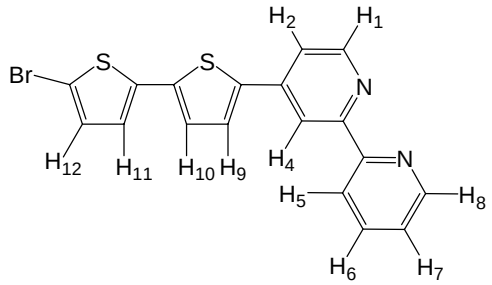


5-(2,2'-bipyridin-4-yl)-2,2'-bithiophene (31, 4-T_2bpy)

Synthesized according to the literature procedure.[30]

Bithiophene (2.00 g, 12.0 mmol) was dissolved in 50 mL dry THF under N_2 and the solution was cooled to -78 ºC. n-BuLi (7.5 mL, 12 mmol) was added dropwise, and the solution was stirred for 1 hr with continued cooling. Tributyltin chloride (3.9 mL, 14 mmol) was added in one aliquot and the mixture was left to stir and warm to room temperature overnight. The solvent was evaporated and 50 mL dry toluene was added. The precipitate was removed by vacuum filtration under air. The solution was returned to a Schlenk flask and purged with N_2. 5-Brbpy (2.77 g, 11.8 mmol) and $Pd(PPh_3)_4$ (0.40 g, 2.9 mol%) were added and the solution was heated to reflux for 72 hours. The solvent was evaporated and the solid was taken up in 200 mL CH_2Cl_2 and 50 mL 2 M NaOH. The layers were separated and solid impurities were removed by filtration through celite. The filter was washed with CH_2Cl_2 until the filtrate ran pale. The solvent was evaporated and the solid was chromatographed with silica and 1% methanol in ethyl acetate. 4-T_2bpy (1.50 g, 4.7 mmol, 40%) was collected as a brown solid (m.p. 108-113 ºC) which was clean to NMR. Sublimation yields a pure yellow solid, with only a small amount of material is lost to decomposition. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 8.72 (H_8, dm, 1H, *J* = 4.0 Hz), 8.64 (H_1, d, 1H, *J* = 4.5 Hz), 8.62 (H_4, dm, 1H, *J* = 2.0 Hz), 8.43 (H_5, ddd, 1H, *J* = 8.0, 1.0, 1.0 Hz), 7.82 (H_6, ddd, 1H, *J* = 2.0, 7.5, 7.5 Hz), 7.55 (H_9, d, 1H, *J* = 4.0 Hz),

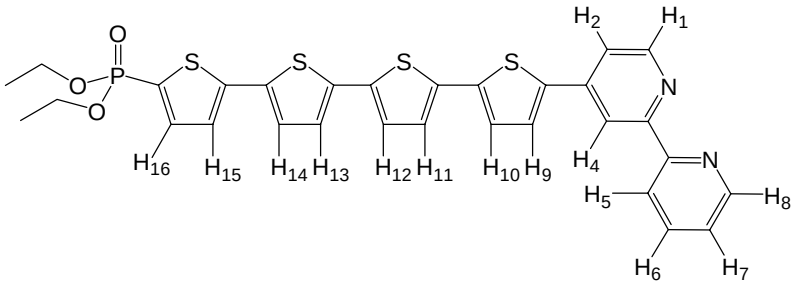
7.46 (H_2, dd, 1H, *J* = 2.0, 5.5 Hz), 7.32 (H_7, ddd, 1H, *J* = 1.0, 7.5, 5.0 Hz), 7.27-7.25 (H_{11+13}, m, 2H), 7.20 (H_{10}, d, 1H, *J* = 3.5 Hz), 7.05 (H_{12} dd, 1H, *J* = 5.0, 4.0 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 157.15, 156.20, 150.01, 149.41, 142.28, 140.18, 139.45, 137.12, 137.11, 128.22, 126.56, 125.37, 124.98, 124.59, 124.09, 121.48, 119.64, 117.08. HRMS (ESI-TOF) calcd for $C_{18}H_{12}N_2S_2$ $(M-H)^+$: 321.0515, found: 321.0516. UV-Vis: λ_{max} (nm): 242 (ε = 19000), 282 (ε = 16000), 357 (ε = 28000).



5-bromo-5'-(2,2'-bipyridin-4-yl)-2,2'-bithiophene (32, 4-BrT_2bpy)

To 200 mL of 1:1 $CHCl_3$:acetic acid was added 4-T_2bpy (1.00 g, 3.12 mmol) and N-bromosuccinamide (NBS) (0.56 g, 3.14 mmol). The reaction was heated to 60 ºC and was maintained at that temperature for 15 minutes before cooling. The mixture was poured into 50 mL of water and the layers were separated. The aqueous layer was extracted with $CHCl_3$ (2 x 50 mL) and the combined organic extracts were washed with $K_2CO_{3\,(aq)}$ until neutral. The organic layer was then dried over $MgSO_4$, filtered and evaporated. 4-BrT_2bpy (1.20 g, 3.00 mmol, 96%) was collected as an orange solid (m.p. 137-141 ºC, with partial decomposition). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.72 (H_8, dm, 1H, *J* = 4.0 Hz), 8.64 (H_1, dd, 1H, *J* = 5.0, 1.0 Hz), 8.60 (H_4, dm, 1H, *J* = 2.0 Hz), 8.42 (H_5, ddd, 1H, *J* = 8.0, 1.0, 1.0 Hz), 7.83 (H_6, ddd, 1H, *J* = 2.0, 8.0, 8.0 Hz), 7.53 (H_9, d,

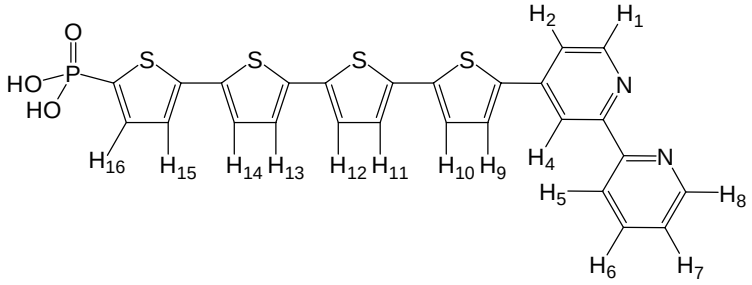
1H, *J* = 4.0 Hz), 7.44 (H_2, dd, 1H, *J* = 3.0, 5.0 Hz), 7.33 (H_7, dd, 1H, *J* = 1.0, 8.0, 5.0), 7.12 (H_{10}, d, 1H, *J* = 4.0 Hz), 7.00 ($H_{11,12}$, d, 1H, *J* = 4.0 Hz), 6.97 ($H_{11,12}$, d, 1H, *J* = 4.0 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 157.05, 155.97, 150.00, 149.34, 141.98, 140.50, 138.51, 138.18, 137.17, 131.03, 126.56, 125.13, 124.57, 124.16, 121.44, 119.60, 117.00, 112.06. HRMS (ESI-TOF) calcd for $C_{18}H_{13}N_2O_3PS_2$ $(M+H)^+$: 398.9620, found: 398.9621.



Diethyl 5’’’-(2,2’-bipyridin-4-yl)-2,2’-5’,2’’-5’’,2’’’-tetrathien-5-ylphosphonate (33, 4-PT$_4$bpy)

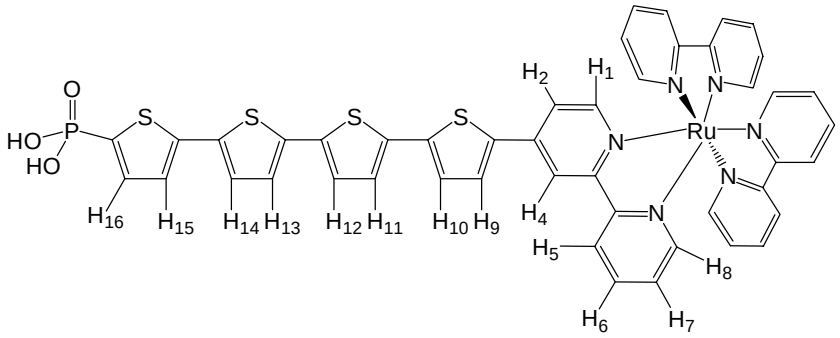
To 25 mL dry toluene under N_2 in a Schlenk flask was added TinT$_2$P (1.02 g, 1.72 mmol), 4-BrT$_2$bpy (0.715 g, 1.79 mmol) and $Pd(PPh_3)_4$ (0.101 g, 5.1 mol%). The solution was heated to reflux and stirred for 72 hours. After cooling, the mixture was poured into 100 mL hexane, which precipitated a red/orange solid (m.p./dec. ~150 ºC). 4-PT$_4$bpy (0.877 g, 1.41 mmol, 82%) was collected by filtration and washed with hexanes. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 8.72 (H_8, dm, 1H, *J* = 5.0 Hz), 8.66 (H_1, d, 1H, *J* = 5 Hz), 8.63 (H_4, d, 1H, *J* = 2.0 Hz), 8.44 (H_5, d, 1H, *J* = 8.0 Hz), 7.83 (H_6, ddd, 1H, *J* = 2.0, 7.5, 7.5 Hz), 7.57 (H_9, d, 1H, *J* = 4.0 Hz), 7.55 (H_{16}, dd, 1H, *J* = 8.5, 3.5 Hz), 7.47 (H_2, dd, 1H, *J* = 2.0, 5.5 Hz), 7.34 (H_7, ddd, 1H, *J* = 1.0, 8.0, 5.0 Hz), 7.22 (H_{10}, d, 1H, *J* = 4.0

Hz), 7.20 (H_{15}, dd, 1H, J = 3.0, 3.0 Hz), 7.18 ($H_{11\text{-}14}$, d, 2H, J = 4.0 Hz), 7.14 ($H_{11\text{-}14}$, d, 1H, J = 7.0 Hz), 7.13 ($H_{11\text{-}14}$, d, 1H, J = 6.5 Hz), 4.22-4.12 (OCH_2CH_3, m, 4H), 1.37 (OCH_2CH_3, t, 6H, J = 7.0 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 157.09, 156.03, 150.04, 149.41, 142.07, 140.44, 138.76, 137.55, 137.21, 136.44, 136.36, 126.72, 126.18, 125.10, 124.87, 124.18, 121.47, 119.60, 117.02. ^{31}P-NMR ($CDCl_3$, 121 MHz): δ 11.63 (s). HRMS (ESI-TOF) calcd for $C_{30}H_{25}N_2O_3PS_4$ $(M+2H)^{2+}$: 311.0316, found: 311.0316. UV-Vis: λ_{max} (nm): 241 (ε = 22000), 276 (ε = 25000), 420 (ε = 57000).



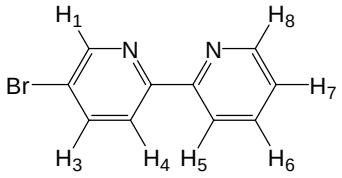
5’’’-(2,2’-bipyridin-4-yl)-2,2’-5’,2’’-5’’,2’’’-tetrathien-5-ylphosphonic acid (34, 4-APT$_4$bpy)

4-PT$_4$bpy (0.152 g, 0.245 mmol) was placed in a Schlenk flask under N_2 and TMSBr (1.0 mL, 7.6 mmol) was added by syringe. The slurry was left to stir overnight. Some TMSBr had evaporated leaving the slurry thick. One milliliter $CHCl_3$ was added, followed by 1 mL acetonitrile. The reaction was then quenched with water and a precipitate formed. 4-APT$_4$bpy (0.123 g, 89% if pure) was washed extensively with acetonitrile then dried. NMR and MS spectra were not recorded due to the insolubility of the product in all common solvents. Dec. ~245 ºC.



[5’’’-(2,2’-bipyridin-4-yl)-2,2’-5’,2’’-5’’,2’’’-tetrathien-5-ylphosphonic acid]bis(bipyridyl)ruthenium(II) hexafluorophosphate (14, 4-APT$_4$bpyRu)

To 30 mL H_2O in a round bottom flask was added 4-APT$_4$bpy (76.2 mg, 0.135 mmol), $RuCl_2bpy_2$ (66.0 mg, 0.136 mmol), and NaOH (5 mg, 0.1 mmol). The mixture was heated to reflux for 16 hours. After cooling, the mixture was filtered through celite to remove unreacted starting material. The solid was washed with basic water until the filtrate ran pale. KPF_6 (0.20 g, 1.1 mmol) in 5 mL H_2O was added to the filtrate with no result. 10 mL 1 M HCl was added, which caused a red/orange solid to precipitate from solution. The solid was collected by centrifugation and washed once with water. The solid was then suspended in acetonitrile and transferred to a round bottom flask. The solvents were evaporated, which left 4-APT$_4$bpyRu (0.109g, 0.086 mmol, 64%) as a red solid (m.p./dec. >190 ºC). ^{1}H-NMR (DMSO, 500 MHz): δ 9.17 (H_5, d, 1H, *J* = 8.0), 9.09 (s, 1H), 8.86 (m, 4H), 8.24-8.15 (m, 6H), 7.90 (d, 1H, *J* = 5.5 Hz), 7.76-7.73 (m, 4H), 7.68 (d, 1H, *J* = 6.5 Hz), 7.61 (d, 2H, *J* = 5.0 Hz), 7.56-7.53 (m, 5H), 7.48 (d, 1H, *J* = 4.0 Hz), 7.42-7.37 (m, 5H). ^{13}C-NMR (DMSO, 125 MHz): Unavailable due to insufficient solubility. ^{31}P-NMR (DMSO, 121 MHz): δ 5.32 (s) HRMS (ESI-TOF) calcd for $C_{46}H_{33}N_6O_3PS_4Ru$ $(M)^{+2}$: 489.0134, found: 489.0135. UV-Vis: λ_{max} (nm): 245 (ε = 33000), 289 (ε = 60000), 438 (ε = 34000), 476 (ε = 33000).

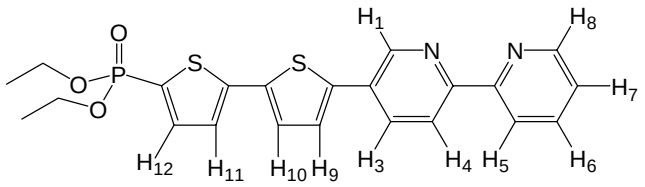


5-bromo-2,2'-bipyridine (15, 5-Brbpy)

Synthesized according to the literature procedure.[41]

A solution of 2-bromopyridine (6.55 g, 41.5 mmol) in 80 mL dry ether under N_2 was cooled to -78 ºC. n-BuLi (28.0 mL, 45.0 mmol) was added dropwise. After 2 hours of continued cooling tributyltin chloride (12 mL, 45 mmol) was added dropwise. The reaction was left to stir and warm to room temperature over night. The solvent was evaporated and 50 mL dry hexanes was added. The slurry was stirred for 0.5 hours. The precipitate was removed by filtration under N_2. The hexanes were evaporated to a deep red/orange oil. 2,5-dibromopyridine (9.1 g, 38.4 mmol) was added, followed by dry xylenes (75 mL). The solution was purged by bubbling with N_2 for 50 minutes. $Pd(PPh_3)_4$ (0.41 g, 0.9 mol%). The reaction was heated to 120 ºC for 24 hours and was then poured into 200 mL 2 M NaOH. The layers were separated and the aqueous layer was extracted with toluene (3 x 30 mL). The combined organic fractions were dried over $MgSO_4$, filtered and evaporated. The residual oil was chromatographed on silica with 3:1 hexanes:CH_2Cl_2 progressing to pure CH_2Cl_2 as eluant. 5-Brbpy (6.5 g, 28 mmol, 72%) was then collected as an off-white solid (m.p. 72-74 ºC). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 8.71 (H_1, d, 1H, J = 2.0 Hz), 8.66 (H_8, dd, 1H, J = 5.0, 1.0 Hz), 8.36 (H_5, d, 1H, J = 8.5 Hz), 8.31 (H_4, d, 1H, J = 8.5 Hz), 7.92 (H_3, dd, 1H, J = 2.5, 9 Hz), 7.80 (H_6, ddd, 1H, J = 2.0, 7.5, 7.5 Hz), 7.31 (H_7, ddd, 1H, J = 1, 5 Hz, 7.5 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ

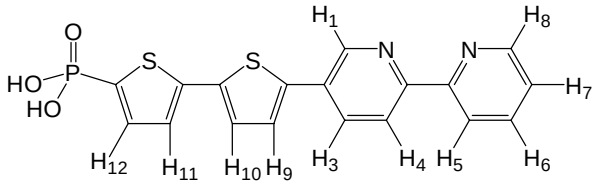
155.29, 154.75, 150.32, 149.39, 139.62, 137.15, 124.15, 122.47, 121.29, 121.11. HRMS (ESI-TOF) calcd for $C_{10}H_7N_2Br$ $(M+H)^+$: 234.9865, found: 234.9862.



Diethyl 5'-(2,2'-bipyridin-5-yl)-2,2'-bithien-5-ylphosphonate (22, 5-PT$_2$bpy)

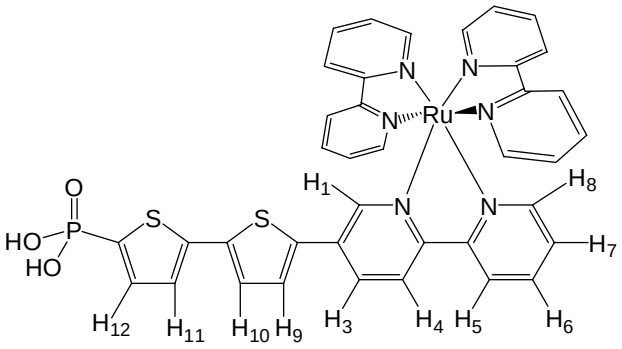
To 20 mL dry toluene under N_2 was added TinT$_2$P (0.88 g, 1.5 mmol), 5-Brbpy (0.350 g, 1.49 mmol) and $Pd(PPh_3)_4$ (0.089 g, 5.1 mol%). The solution was refluxed for 72 hours. Toluene was evaporated and the solid was chromatographed on silica with ethyl acetate as the eluent. The product was recovered and left under vacuum to remove volatile impurities. 5-PT$_2$bpy (0.57 g, 1.2 mmol, 81%) was collected as a slightly sticky yellow solid. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.93 (H_1, dm, 1H, *J* = 3.0 Hz), 8.69 (H_8, dm, 1H, *J* = 5.0 Hz), 8.44 ($H_{4,5}$, d, 1H, *J* = 8.5 Hz), 8.42 ($H_{4,5}$, d, 1H, *J* = 7.0), 7.98 (H_3, dd, 1H, *J* = 2.5, 8.5 Hz), 7.82 (H_6, ddd, 1H, *J* = 2.0, 8.0 Hz), 7.58 (H_{12}, dd, 1H, *J* = 3.5, 8.0 Hz), 7.37 (H_9, d, 1H, *J* = 3.5 Hz), 7.32 (H_7, ddd, 1H, *J* = 1.0, 7.5, 5.0), 7.28 (H_{10}, d, 1H, *J* = 3.0 Hz), 7.26 (H_{11}, dd, 1H, *J* = 3.5, 3.5 Hz), 4.25-4.09 (m, 4H), 1.37 (t, 6H, *J* = 7.0 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 155.62, 155.34, 149.39, 146.13, 144.96 (d, *J* = 8.0 Hz), 140.82, 137.69 (d, *J* = 11.0 Hz), 137.09, 136.50 (d, *J* = 3.0 Hz), 133.57, 129.71, 126.67 (d, *J* = 210.0 Hz), 126.40, 125.35, 124.71 (d, *J* = 17.0 Hz), 123.97, 121.20, 121.18. ^{31}P-NMR ($CDCl_3$, 121 MHz): δ 11.56 (s) HRMS (ESI-TOF) calcd for

$C_{22}H_{21}N_2O_3PS_2$ $(M+Na)^+$: 479.0623, found: 479.0623. UV-Vis: λ_{max} (nm): 238 (ε = 13000), 260 (ε = 11000), 365 (ε = 43000).



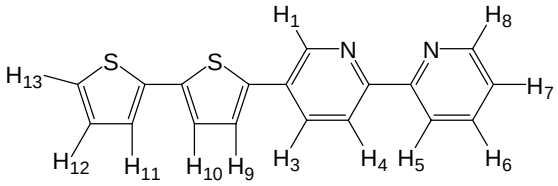
5'-(2,2'-bipyridin-5-yl)-2,2'-bithien-5-ylphosphonic acid (23, 5-APT$_2$bpy)

To 5-PT$_2$bpy (0.479 g, 1.05 mmol) under N_2 was added TMSBr (1.0 mL, 7.6 mmol). The slurry was stirred for 2.5 hours before being quenched with water. Excess water was removed under vacuum. Acetone was added and the slurry was stirred vigorously and then filtered. The solid was washed with acetone and methanol until the filtrate ran colorless. The bright orange solid (m.p. 218-221 ºC) was dried and collected (0.335 g, 0.77 mmol, 73%). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 9.07 (H_1, d, 1H, *J* = 2.5 Hz), 8.74 (H_8, d, 1H, *J* = 4.5 Hz), 8.47 ($H_{4,5}$, d, 1H, *J* = 2.5, Hz), 8.46 ($H_{4,5}$, d, 1H, *J* = 2.5 Hz), 8.27 (H_3, dd, 1H, *J* = 2.5 Hz, 8.5 Hz), 8.07 (H_6, ddd, 1H, *J* = 8.0, 8.0, 0.5 Hz), 7.78 (H_9, d, 1H, *J* = 4.0 Hz), 7.55 (H_{12}, t, 1H, 6.0 Hz), 7.52 (H_{10}, d, 1H, *J* = 4.0 Hz), 7.43-7.39 ($H_{7,11}$, m, 2H). ^{13}C-NMR (DMSO, 125 MHz): Unavailable due to insufficient solubility. ^{31}P-NMR (DMSO, 121 MHz): δ 5.36 (s). HRMS (ESI-TOF) calcd for $C_{18}H_{13}N_2O_3PS_2$ $(M+H)^+$: 401.0178, found: 401.0177. UV-Vis (DMSO): λ_{max} (nm): 377 (ε = 32000).



[5'-(2,2'-bipyridin-5-yl)-2,2'-bithien-5-ylphosphonic acid]bis(bipyridyl)ruthenium(II) hexafluorophosphate (11, 5-APT$_2$bpyRu)

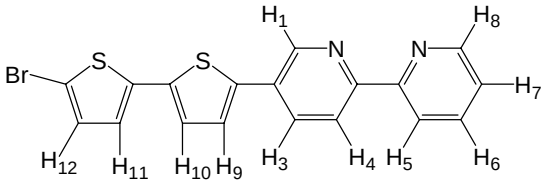
To 25 mL H_2O was added 5-APT$_2$bpy (0.204 g, 0.510 mmol), $RuCl_2bpy_2$ (0.249 g, 0.514 mmol), and NaOH (21.3 mg, 0.533 mmol). The mixture was refluxed for 3 hours. After cooling, the mixture was acidified with 1 M HCl and filtered to remove unreacted starting material. KPF_6 (0.427 g, 2.32 mmol) in 10 mL water was added which precipitated a red solid. The solid was collected by centrifugation. It was then dissolved in acetone, transferred to a round bottom flask and evaporated dry. 5-APT$_2$bpyRu (0.490 g, 0.444 mmol, 87%) was collected as a red/brown solid (dec. >180 ºC). ^{1}H-NMR (DMSO, 500 MHz): δ 8.91-8.84 (m, 6H), 8.46 (d, 1H, *J* = 8.0 Hz), 8.28 (dd, 1H, *J* = 8.0, 8.0 Hz), 8.21-8.16 (m, 4H), 7.94 (d, 1H, *J* = 5.0 Hz), 7.85 (d, 1H, *J* = 5.0 Hz), 7.77-7.74 (m, 3H), 7.66-7.61 (m, 2H), 7.56-7.52 (m, 5H), 7.46 (d, 1H, *J* = 4.0 Hz), 7.38 (dd, 1H, *J* = 3.5, 7.5 Hz), 7.35 (d, 1H, *J* = 3.0 Hz). ^{13}C-NMR (DMSO, 125 MHz): Unavailable due to insufficient solubility. ^{31}P-NMR (DMSO, 121 MHz): δ 4.83 (s) HRMS (ESI-TOF) calcd for $C_{38}H_{29}N_6O_3PS_2Ru$ $(M)^{+2}$: 407.0256, found: 407.0264. UV-Vis: λ_{max} (nm): 244 (ε = 27000), 287 (ε = 78000), 397 (ε = 41000).



5-(2,2'-bipyridin-5-yl)-2,2'-bithiophene (27, 5-T_2bpy)

Bithiophene (2.00 g, 12.0 mmol) was dissolved in 50 mL dry THF under N_2 and the solution was cooled to -78 ºC. n-BuLi (7.5 mL, 12 mmol) was added dropwise, and the solution was stirred for 1 hr with continued cooling. Tributyltin chloride (3.9 mL, 14 mmol) was added in one aliquot and the mixture was left to stir and warm to room temperature overnight. The solvent was evaporated and 50 mL dry toluene was added. The precipitate was removed by vacuum filtration under air. The solution was returned to a Schlenk flask and purged with N_2. 5-Brbpy (2.76 g, 11.7 mmol) and $Pd(PPh_3)_4$ (0.41 g, 2.9 mol%) were added and the solution was heated to reflux for 72 hours. The solvent was evaporated and the solid was taken up in 200 mL CH_2Cl_2 and 50 mL 2 M NaOH. The layers were separated and solid impurities in the organic layer were removed by filtration through celite. The solid was washed with CH_2Cl_2 until the filtrate ran pale, then the solid was discarded. The solvent was evaporated and the residual solid was chromatographed with silica and 0.5% methanol in ethyl acetate increasing to 2% methanol. 5-T_2bpy (1.47 g, 4.6 mmol, 39 %) was collected as a brown solid (m.p. 145-148 ºC) which was clean by NMR. Sublimation yields a pure yellow solid, but some material is lost to decomposition. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 8.94 (H_1, d, 1H, J = 2.0 Hz), 8.69 (H_8, d, 1H, J = 4.0 Hz), 8.43 ($H_{4,5}$, m, 2H), 7.99 (H_3, dd, 1H, J = 2.5, 8.5 Hz), 7.83 (H_6, ddd, 1H, J = 1.5, 7.5, 7.5 Hz), 7.36 (H_9, d, 1H, J = 4.0 Hz), 7.32 (H_7, ddd, 1H, J = 1.0 Hz, 6.5, 5.0 Hz), 7.25 ($H_{11,13}$, dd, 1H, J = 1.0, 5.0 Hz), 7.24 ($H_{11,13}$, dd, 1H, J = 1.0,

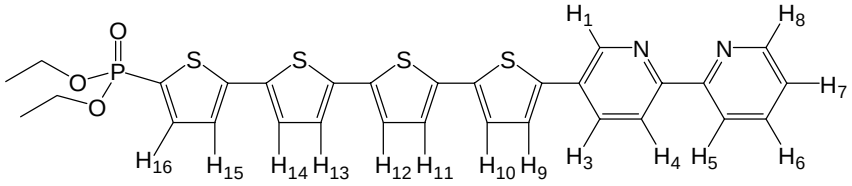
3.5 Hz), 7.20 (H_{10}, d, 1H, *J* = 3.5 Hz), 7.05 (H_{12}, dd, 1H, *J* = 5.0, 3.5 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 155.82, 154.98, 149.42, 146.08, 139.10, 138.32, 137.09, 133.43, 130.16, 128.15, 125.19, 125.06, 124.96, 124.29, 123.89, 121.20, 121.17. HRMS (ESI-TOF) calcd for $C_{18}H_{12}N_2S_2$ $(M+H)^+$: 321.0515, found: 321.0513. UV-Vis: λ_{max} (nm): 238 (ε = 12000), 258 (ε = 14000), 287 (ε = 11000), 363 (ε = 45000).



5-bromo-5'-(2,2'-bipyridin-5-yl)-2,2'-bithiophene (28, 5-BrT_2bpy)

To 200 mL of 1:1 $CHCl_3$:HOAc was added 5-T_2bpy (1.00 g, 3.12 mmol) and NBS (0.56 g, 3.14 mmol). The reaction was heated to 60 ºC and was maintained at that temperature for 15 minutes before cooling. The mixture was poured into 50 mL of water and the layers were separated. The aqueous layer was extracted with $CHCl_3$ (2 x 50 mL) and the combined organic extracts were washed with K_2CO_3(aq) until neutral. The organic layer was then dried over $MgSO_4$, filtered and evaporated. 4-BrT_2bpy (1.21 g, 3.00 mmol, 96%) was collected as an orange solid (m.p. 175-179 ºC, with partial decomposition). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.92 (H_1, dm, 1H, *J* = 2.5 Hz), 8.69 (H_8, dm, 1H, *J* = 3.5 Hz), 8.43 (H_4, dd, 1H, *J* = 0.5 Hz, 8.5 Hz), 8.42 (H_5, ddd, 1H, *J* = 1.0 Hz, 1.0 Hz, 8.5 Hz), 7.97 (H_3, dd, 1H, *J* = 2.5 Hz, 8.5 Hz), 7.83 (H_6, ddd, 1H, *J* = 2.0 Hz, 8.0 Hz, 8.0 Hz), 7.34 (H_9, d, 1H, *J* = 4.0 Hz), 7.32 (H_7, ddd, 1H, *J* = 1.5, 7.5, 5.5 Hz), 7.13 (H_{10}, d, 1H, *J* = 4.0 Hz), 7.02 ($H_{11,12}$, d, 1H, *J* = 4.0 Hz), 6.97 ($H_{11,12}$, d, 1H, *J* = 4.0 Hz).

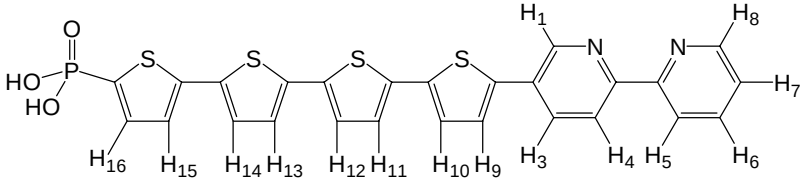
^{13}C-NMR ($CDCl_3$, 125 MHz): δ 155.84, 155.26, 149.48, 146.18, 139.71, 138.66, 137.24, 137.15, 133.56, 131.01, 130.00, 125.25, 124.38, 123.98, 121.28, 121.25, 111.76. HRMS (ESI-TOF) calcd for $C_{18}H_{11}N_2S_2Br$ $(M-H)^+$: 398.9620, found: 398.9619.



Diethyl 5’’’-(2,2’-bipyridin-5-yl)-2,2’-5’,2’’-5’’,2’’’-tetrathien-5-ylphosphonate (29, 5-PT$_4$bpy)

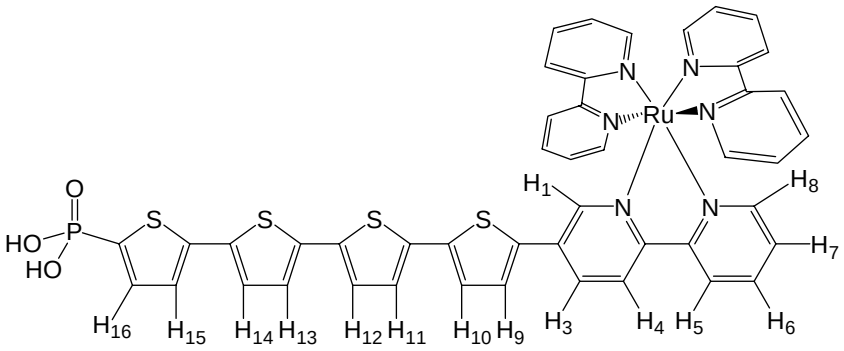
TinT_2P (2.6 g, 4.4 mmol) and BrT_2bpy (1.15 g, 2.9 mmol) were dissolved in 90 mL dry toluene under N_2. $Pd(PPh_3)_4$ (0.17 g, 5 mol%) was added, and the mixture was heated to reflux for 16 hours. The reaction mixture was poured into 200 mL hexanes and a precipitate was allowed to form for several minutes. The solid was collected by filtration and the filtrate was discarded. The solid was then dissolved in THF and the residual solid was removed by filtering through celite and was discarded. The THF solution was evaporated to an orange/brown sticky solid which was stirred vigorously in ~100 mL ether for 0.5 hours. The dry solid 5-PT$_4$bpy (0.77 g, 1.2 mmol, 41 %) was collected by filtration (dec. ~200 ºC). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 8.93 (H_1, d, 1H, *J* = 2.5 Hz), 8.69 (H_8, dm, 1H, *J* = 2.5), 8.43 ($H_{4,5}$, dd, 2H, *J* = 8.5, 8.5 Hz), 7.98 (H_3, dd, 1H, *J* = 8.5, 2.5 Hz), 7.83 (H_6, ddd, 1H, *J* = 7.75, 7.75, 2.0 Hz), 7.56 (H_{16}, dd, 1H, *J* = 8.5, 4.0 Hz), 7.36 (H_9, d, 1H, 3.5 Hz), 7.31 (H_7, ddd, 1H, *J* = 1.0, 7.0, 5.0 Hz), 7.21 (H_{10}, d, 1H, *J* = 3.5 Hz), 7.20 (H_{15}, dd, 1H, *J* = 3.0, 3.0 Hz), 7.18 ($H_{11\text{-}14}$, d, 1H, *J* = 3.5 Hz), 7.16 ($H_{11\text{-}}$

$_{14}$, d, 1H, *J* = 3.5 Hz), 7.13 ($H_{11\text{-}14}$, d, 1H, *J* = 4.0 Hz), 7.12 ($H_{11\text{-}14}$, d, 1H, *J* = 3.0 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 155.86, 155.21, 149.50, 146.18, 139.62, 137.79, 137.72, 137.16, 136.60, 136.10, 135.00, 133.53, 130.07, 126.18, 125.69, 125.39, 125.18, 125.12, 125.04, 124.81, 124.55, 124.42, 123.98, 121.30, 121.26, 63.01 (C-P *J* = 5.5 Hz), 16.53 (C-P *J* = 6.0 Hz). ^{31}P-NMR ($CDCl_3$, 121 MHz): δ 11.44 (s). HRMS (ESI-TOF) calcd for $C_{30}H_{25}N_2O_3PS_4$ $(M+H)^+$: 621.0558, found: 621.0559. UV-Vis (DMSO): λ_{max} (nm): 432 (ε = 22000).



5’’’-(2,2’-bipyridin-5-yl)-2,2’-5’,2’’-5’’,2’’’-tetrathien-5-ylphosphonic acid (30, 5-APT$_4$bpy)

5-PT$_4$bpy (0.213 g, 0.343 mmol) was placed in a Schlenk flask under N_2. TMSBr (1.0 mL, 7.6 mmol) was added by syringe. The slurry was stirred for 16 hours. Some of the TMSBr evaporated, leaving the slurry thick. This was dissolved in 3 mL $CHCl_3$ then quenched with water. The slurry was filtered with difficulty then washed with acetonitrile and dried. Dark red 5-APT$_4$bpy (0.155 g, 0.27 mmole, 80% if pure) is insoluble in all common solvents. Dec. ~250 ºC.



[5’’’-(2,2’-bipyridin-5-yl)-2,2’-5’,2’’-5’’,2’’’-tetrathien-5-ylphosphonic acid]bis(bipyridyl)ruthenium(II) hexafluorophosphate (13, 5-APT$_4$bpyRu)

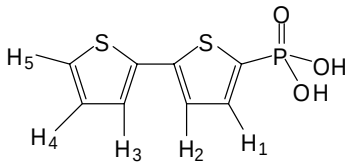
To 25 mL of water in a round bottom flask was added 5-APT$_4$bpy (0.147 g, 0.26 mmol), $RuCl_2bpy_2$, (0.13 g, 0.27 mmol), and NaOH (17 mg, 0.425 mmol). The mixture was refluxed for 4 hours. After cooling, a solution of KPF_6 (0.29 g, 1.6 mmol) in 10 mL 0.3 M HCl was added and a red precipitate formed. The solid was collected by centrifugation and the mother liquor was decanted. The solid was dissolved in DMF, collected in a round bottom flask and the DMF was evaporated. 0.252 g (76%, 0.20 mmol) 5-APT$_4$bpyRu was collected as a red/black solid (dec. ~210 ºC). ^{1}H-NMR (DMSO, 500 MHz): δ 8.93 (d, 1H, *J* = 8.5 Hz), 8.90-8.85 (m, 5H), 8.47 (d, 1H, *J* = 8.5 Hz), 8.32 (t, 1H, *J* = 8.0 Hz), 8.22-8.16 (m, 4H), 7.97 (m, 1H), 7.88 (d, 1H, *J* = 5.5 Hz), 7.78 (m, 2H), 7.75 (d, 1H, *J* = 5.5 Hz), 7.66 (t, 1H, *J* = 6.5 Hz), 7.61 (s, 1H), 7.56 (m, 5H), 7.46 (d, 1H, *J* = 3.5 Hz), 7.42 (d, 1H, *J* = 3.5 Hz), 7.40-7.38 (m, 4H), 7.36 (d, 1H, *J* = 3.5 Hz). ^{13}C-NMR (DMSO, 125 MHz): Unavailable due to insufficient solubility. ^{31}P-NMR (DMSO, 121 MHz): δ 4.83 (s). HRMS (ESI-TOF) calcd for $C_{46}H_{33}N_6O_3PS_4Ru$ $(M)^{+2}$: 489.0134, found: 489.0136. UV-Vis: λ_{max} (nm): 245 (ε = 32000), 288 (ε = 75000), 446 (ε =52000).

5,5'-dibromo-2,2'-bithiophene (Br_2T_2)

This compound is an intermediate in the synthesis of tetrathiophene. The use of tetrathiophene was abandoned due to insolubility.

To 25 mL of 1:1 $CHCl_3$:acetic acid was added bithiophene (0.963 g, 5.79 mmol) and NBS (2.06 g, 11.6 mmol). The reaction was heated to reflux for 30 minutes. Upon cooling, voluminous white flakes precipitated out of solution. The solid was collected by filtration and the filtrate set aside. The solid was then washed on the filter with large amounts of methanol and then with 15 mL of ether. The solid was collected and vacuumed dry to yield a first fraction of Br_2T_2.

The methanol and ether filtrate was evaporated and the solid residue was added to the original reaction mother liquor. Water was added to the mother liquor until the layers separated. The organic layer was extracted with water (2 x 20 mL) and then with 1 M NaOH (2 x 20 mL). The organic extracts were then dried over $MgSO_4$, filtered through celite, and evaporated. The resulting solid was recrystallized in hexanes. This solid was added to the first fraction of solid to yield 1.69 g Br_2T_2 (5.22 mmol, 90.2 %, m.p. 145-147 ºC). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 6.96 (d, 2H, *J* = 4.0 Hz), 6.84 (d, 2H, *J* = 4.0 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 137.99, 130.87, 124.36, 111.73.



2,2'-bithien-5-ylphosphoric acid (T_2PA)

T_2P (0.27 g, 0.89 mmol) was placed in a Schlenk flask under N_2. TMSBr (0.90 mL, 6.8 mmol) was added by syringe. The solution was stirred for 18 hours. 1 M NaOH was added to the solution to quench it. The mixture was partitioned between 1 M NaOH and ether. The layers were separated and the aqueous layer was extracted again with ether. The aqueous layer was then rendered acidic with 1 M HCl, whereupon the product precipitated as a white solid (dec. 192 ºC). T_2PA was collected by filtration and washed with ether. 0.189 g (0.77 mmol, 87%). ^{1}H-NMR (DMSO, 500 MHz): δ 7.55 (H_1, d, 1H, *J* = 5.0 Hz), 7.35 (H_2, d, 1H, *J* = 3.5 Hz), 7.30 (H_3, dd, 1H, *J* = 3.5, 7.5 Hz), 7.27 (H_5, t, 1H, *J* = 3.5 Hz), 7.09 (H_4, dd, 1H, *J* = 3.5, 4.5 Hz). ^{13}C-NMR (DMSO, 125 MHz): δ 140.63 (C-P *J* = 7.0 Hz), 136.30 (C-P *J* = 195.0 Hz), 136.01, 133.46 (C-P *J* = 10.0 Hz), 128.40, 125.98, 124.62, 124.08 (C-P *J* = 15.0 Hz). ^{31}P-NMR (DMSO, 121 MHz): δ 4.90 (s). HRMS (ESI-TOF) calcd for $C_8H_7O_3PS_2$ $(M+H)^+$: 246.9647, found: 246.9645.

Tris(2,2'-bipyridyl)ruthenium(II) hexafluorophosphate

$RuCl_3 \cdot 0.82\ H_2O$ (0.151 g, 0.682 mmol) and bipyridine (0.421 g, 2.70 mmol) were combined in 20 mL H_2O and the mixture was heated to reflux for 24 hours. During this time the color changed to blue-green. DMF (1 mL) was added and reflux was continued for 72 hours. The color became dark red. The solution was cooled to room temperature and KPF_6 (0.70 g, 3.8 mmol) in 5 mL H_2O was added. An orange precipitate formed

immediately. The mixture was stirred for 2 minutes and then filtered. The solid was washed with 10 mL water and 25 mL THF and allowed to dry. ^{1}H-NMR (DMSO, 500 MHz): δ 8.84 (d, 6H, *J* = 8.0 Hz), 8.18 (ddd, 6H, *J* = 1.0, 7.5, 7.5 Hz), 7.74 (d, 6H, *J* = 5.0 Hz), 7.54 (ddd, 6H, *J* = 1.0, 6.5, 6.5 Hz). ^{13}C-NMR (DMSO, 125 MHz): δ 156.54, 151.20, 137.91, 127.88, 124.47. HRMS (ESI-TOF) calcd for $C_{30}H_{24}N_6Ru$ $(M)^{+2}$: 285.0547, found: 285.0552. UV-Vis: λ_{max} (nm): 244 (ε = 28000), 287 (ε = 95000), 451 (ε = 16000).

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Chapter 2: Bipyridyl-Tungsten Complexes for C-F and C-H Activation

Abstract

Tungsten metal complexes, [6-(perfluorophenyl)bipyridyl]tetracarbonyltungsten (**4**) and [6-(phenyl)bipyridyl]tetracarbonyltungsten (**6**) were prepared for mechanistic C-F and C-H bond activation studies, respectively. Ligands were synthesized through Stille and Suzuki coupling of commercial reagents followed by metal binding.

2.1. Introduction

Carbon-fluorine bonds are the strongest single covalent bonds to carbon. Fluorine imparts useful properties on the molecular and macroscopic scales due to its strong bond to carbon and high hydrophobicity. Chemists are interested in being able to make and break these bonds selectively. A thorough review of C-F activation was published by Kiplinger et al.[1] and a more recent review focused on activation by the Pt group metals.[2]

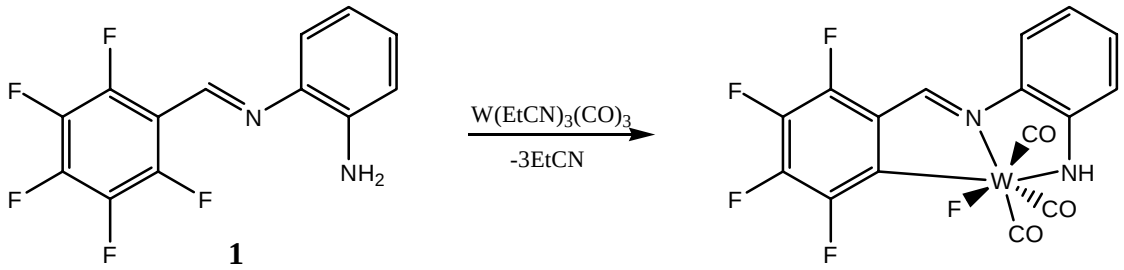
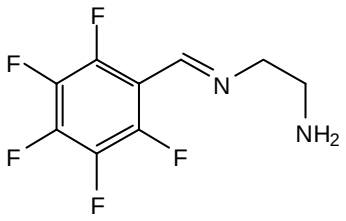


Figure 2.1. Oxidative C-F addition on an activated tungsten complex.

The first examples of facile transition metal insertion into a C-F bond were made by the Richmond group.[3] A Schiff base reaction between phenylenediamine and pentafluorobenzaldehyde provided **1**, a bidentate ligand tethered to the pentafluoro ring (Figure 2.1). This chelating ligand was bound to tricarbonyltungsten and at room temperature the tungsten inserted into the C-F bond forming a metalacyclopentane. The authors identify several factors that aid the oxidative addition step. First, the attachment of the perfluoro ring to a chelating ligand provides a fixed close proximity between the fluorine and the metal. Second, the amine ligands help create an electron rich metal center, which encourages oxidative addition.

2



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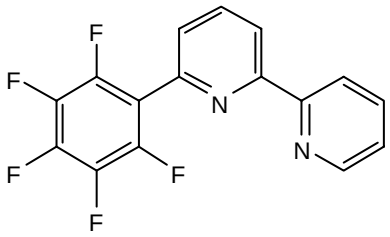
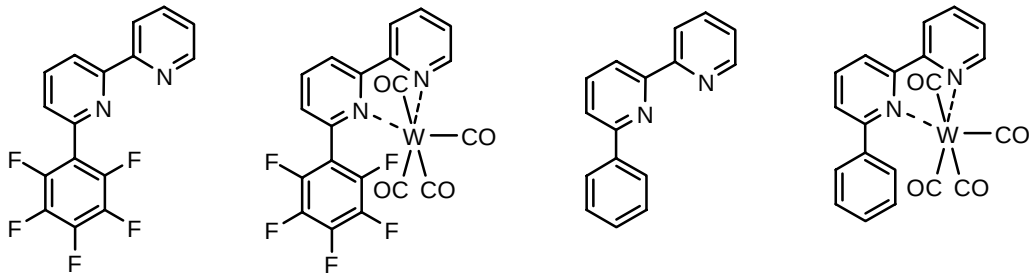


Figure 2.2. C-F activation targets.

To study the mechanism of C-F bond activation, Asplund and co-workers have proposed studying related compounds **2** and **3**. (Figure 2.2). These ligands are to be bound to tungsten carbonyl complexes. They propose to monitor the CO stretching frequencies using femtosecond IR spectroscopy. Infrared stretches of metal carbonyls are very sensitive to the oxidation state of the metal and are easily monitored. The oxidation state of the metal is determined by the ligand environment. Studying C-F activation by femtosecond IR monitoring of CO stretches would allow us to monitor the reaction mechanism in terms of the ligands bound. This information would give clues about which ligands are coordinated during the activation. In order for these studies to be accurate, an

open coordination site must be created at a precisely determined moment. In the original C-F oxidative addition studies, the open site was produced thermally at room temperature. For the proposed studies the precursor complex is a ligand-$W(CO)_4$ complex. A pulse of energy from a laser dissociates a CO, leaving an open site for oxidative addition. IR measurements begin from the moment of the laser pulse and continue as the transition states form. These studies have been performed[4] on **2**, and are proposed for **3**. A comparable C-H activating ligand, **5**, was also desired. This paper details the synthesis of ligands **3** and **5**, and their respective tetracarbonyl tungsten complexes, **4** and **6**.



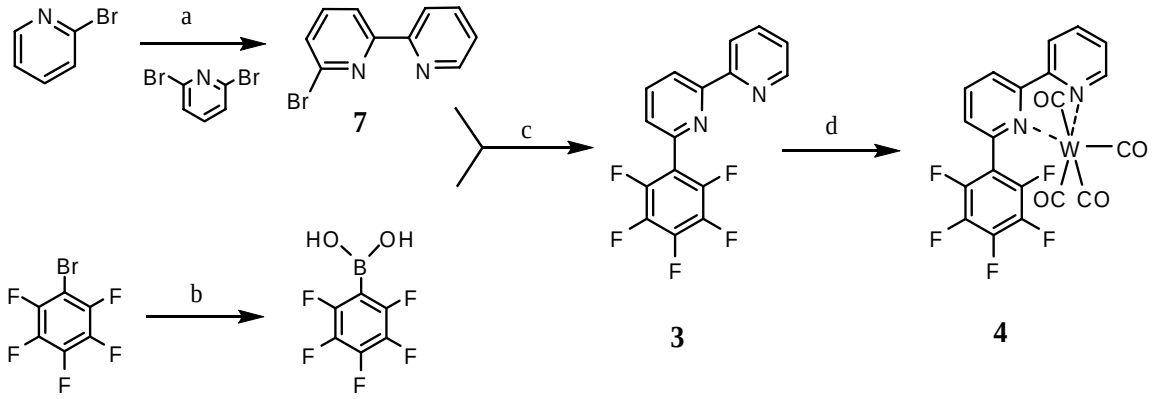
3 **4** **5** **6**

Figure 2.3. Target complexes **3** and **5** and their respective tungsten complexes, **4** and **6**.

2.2. Results and Discussion

A brief inspection of the target complexes **4** and **6** would indicate that simple Suzuki or Stille coupling might be used to produce the ligands in two steps. Metal coordination could then be achieved by reaction with $W(CO)_6$ according to the literature for similar compounds. It was found, however, that aryl coupling to bipyridine was not straight forward. The synthesis of both target compounds is described below.

Scheme 2.1. Synthesis of [6-(perfluorophenyl)-2,2'-bipyridine]tetracarbonyltungsten **(4)**.



Reagents: (a) (1) n-BuLi; (2) Bu_3SnCl; (3) 2,6-dibromopyridine, $Pd(PPh_3)_4$; (b) (1) Mg; (2) $B(OMe)_3$; (3) HCl; (c) tBuOK, tBuOH, Ag_2O, $Pd(PPh_3)_4$; (d) $W(EtCN)_3(CO)_3$.

Scheme 2.1 outlines the synthesis of tungsten complex **4**. 6-bromo-2,2'-bipyridine, **7**, is a known compound and was synthesized according to a modification of the literature procedure.[5] The use of trimethyltin chloride in place of tributyltin chloride might have improved the yield.[6]

A first attempt to couple **7** to C_6F_5Br was made by forming the tributyltin adduct of bpy followed directly by $Pd(PPh_3)_4$ mediated coupling with C_6H_5Br. This reaction entirely failed to produce **3**. It was decided that the oxidative addition/transmetallation roles should be switched.

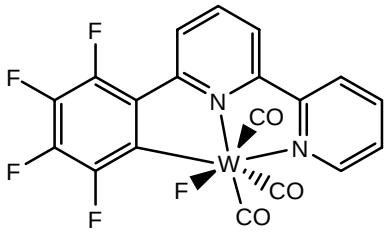
Perfluorophenyl boronic acid **8** was also synthesized according to the literature,[7] with a single modification. The crude yield was very good, as in the literature, but only a moderate yield was recovered from the recrystallization. We supposed that heating at refluxing toluene temperature might cause anhydride formation with loss of water by

evaporation. The dehydration product might remain soluble in the solvent. To circumvent this problem water was added to toluene before the recrystallization to keep the temperature down and discourage dehydration. The yield of **8** improved from 51% to 62% with this alteration, although the supposed decomposition products were never identified in the mother liquor. The white crystalline material that cocrystallized with **8** dissolves in hot water, so the water layer should be removed while the recrystallizing solution is still hot.

As others have found to be the case, the subsequent Suzuki coupling was difficult. Following a similar procedure in the literature,[8] the coupling was hastened with Ag_2O. Potassium *t*-butoxide was used as the base. The reaction temperature and time were adjusted to produce the maximum yield while minimizing the unwanted nucleophilic aromatic substitution reaction with the base. The product was obtained in moderate yields as stable yellow crystals.

Synthesis of $W(EtCN)_3(CO)_3$ was very difficult, despite the simple procedure.[9] All glassware must be rigorously dry and oxygen free. Satisfactory results were only obtained if propionitrile was distilled from fresh CaH_2 prior to each use. $W(EtCN)_3(CO)_3$ is air sensitive as a solid and decomposes instantly in solution.

The reaction of **3** with $W(CO)_6$ in refluxing xylenes failed to produce **4**. Unidentifiable decomposition products were all that was recovered. Fortunately, **4** was produced as an unforeseen byproduct of another reaction. During an attempt to make the oxidative addition product **9** thermally, by the reaction of **3** with $W(EtCN)_3(CO)_3$, it was noticed that the reaction produced **4** with some **3**

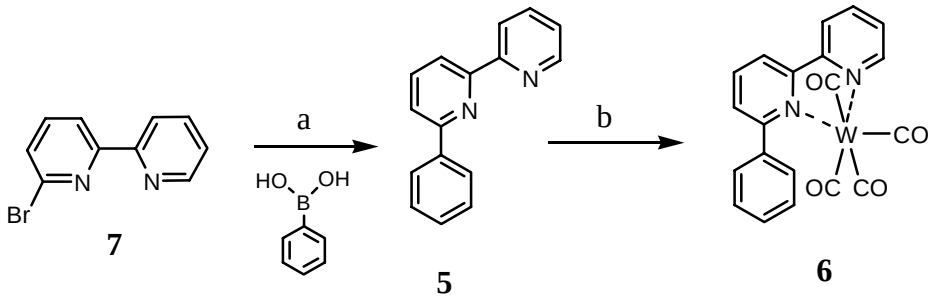


9

present. Compound **3** was removed by rinsing with hexanes. Complex **4** is stable as a solid, but decomposes slowly in solution. Crystals could not be grown for X-ray analysis due to this instability. Attempts to synthesize compound **9** were unsuccessful and were abandoned.

We found that an analogous compound for C-H activation (**6**) could be readily synthesized and might provide an interesting comparison with **4**. Scheme 2.2 displays the reaction sequence for the synthesis of **6**.

Scheme 2.2. Synthesis of **6**.



Reagents: (a) phenylboronic acid, K_2CO_3, Ag_2O, $Pd(PPh_3)_4$; (b) $W(CO)_6$.

A synthesis of ligand **5** was previously reported in the literature.[10] It was made through a cyclization reaction involving a complex precursor. With **7** in hand and phenylboronic acid readily available, we attempted the Suzuki coupling. Reaction under normal Suzuki conditions gave poor yields after heating at 80 ºC in DMF for 5 days. The addition of Ag_2O improved the reaction dramatically, producing good yields after heating for one hour at 85 ºC. Silver oxide is a common accelerant for Suzuki reactions. It is assumed to aid the transmetallation step.[11]

Target compound **6** was produced without difficulty by applying a related procedure for the synthesis of $W(CO)_4$bpy.[12] Single crystals were grown by vapor diffusion.

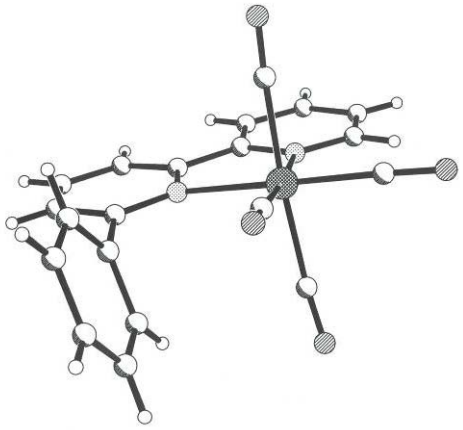


Figure 2.3. X-ray crystal structure of **6**

We see from the crystal structure of **6** (Figure 2.3) that the pendent phenyl ring is canted about 70º relative to the bipyridine in the solid state. In the ^{19}F NMR of **4** we see three well defined peaks, indicating fluorine equivalence in the ortho and meta positions. As steric interactions between the pendent ring and the adjacent carbonyl appear to inhibit free rotation, it should be assumed that the ring oscillates in the solution phase, being, on average, perpendicular to the plane of the bipyridine. As the NMR signals are well defined, it is apparent that this oscillation occurs rapidly at room temperature compared to the NMR timescale.

Femtosecond IR studies are underway.

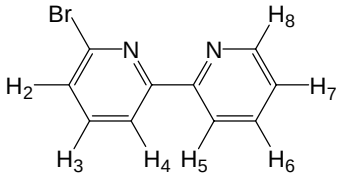
2.3. Conclusion

Ligands 6-(F_5Ph)bpy (**3)** and 6-Phbpy (**5)** were synthesized through modified Suzuki coupling. The tungsten complex of **5** was formed by thermal displacement of two carbonyls on $W(CO)_6$. The complex of **3** required the use of the activated complex $W(EtCN)_3(CO)_3$ and fortuitous disproportionation. There appears to be free rotation of the pendent phenyl ring, despite the adjacent carbonyl.

2.4. Experimental

General

Unless otherwise stated, all starting materials were purchased from commercial sources and used as received. Solvents were dried by passing them through a solvent drying system with activated alumina columns. All NMR spectra were recorded on 300 or 500 MHz Varian spectrometers. Proton and ^{13}C NMR spectra were referenced to TMS or residual solvent signals. ^{19}F NMR signals were referenced to an external sample of $CFCl_3$. Mass spectra (including exact mass) were recorded on an Agilent ESI-TOF mass spectrometer. IR spectra were taken on a Thermo Nicolet Avatar 360 FT-IR. Melting points were found with a Mel-Temp apparatus from Laboratory Devices. Column chromatography was done with silica gel with a mesh size of 60-200.

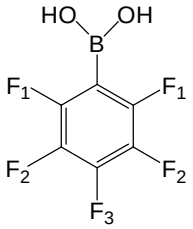


6-bromo-2,2'-bipyridine (7)

Synthesized according to the literature procedure.[5]

A solution of 2-bromopyridine (3.0 mL, 31 mmol) in 50 mL dry THF under N_2 was cooled to -78 ºC. n-BuLi (21.0 mL, 33.6 mmol) was dripped in over 10 minutes. After 1 hour of continued cooling Bu_3SnCl (9.2 mL, 34 mmol) was added dropwise. The reaction was left to stir and warm to room temperature over night. The solvent was evaporated under reduced pressure and 50 mL dry hexanes was added. The slurry was stirred for 0.5 hours. The precipitate was removed by filtration under N_2. The hexanes were evaporated

to a deep orange oil. Dry xylenes (80 mL) was added, followed by 2,6-dibromopyridine (7.3 g, 31 mmol) and $Pd(PPh_3)_4$ (0.505 g, 1.4 mol %). The reaction was heated to 120 ºC for 72 hours and was then poured into 100 mL 3 M NaOH. The layers were separated and the aqueous layer was extracted with toluene (3 x 30 mL). The combined organic fractions were extracted once with 20 mL H_2O, dried over $MgSO_4$, filtered and evaporated. The resultant red/brown oil was purified by column chromatography through silica with toluene as eluant. This was followed by sublimation at 85 ºC under vacuum. The first waxy fraction was discarded. 6-Brbpy (2.54 g, 10.8 mmol, 35%) was then collected as a white crystalline solid. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 8.67 (H_8, dm, 1H, *J* = 5.0 Hz), 8.41 (H_5, dm, 1H, *J* = 8.0 Hz), 8.38 (H_2, dd, 1H, *J* = 6.5, 1.0 Hz), 7.82 (H_6, ddd, 1H, *J* = 7.5, 7.5, 1.5), 7.68 (H_3, dd, 1H, *J* = 7.5, 7.5 Hz), 7.50 (H_4, dd, 1H, *J* = 7.5, 1.0 Hz), 7.33 (H_7, ddd, 1H, *J* = 7.5, 4.5, 1.5). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 157.534, 154.675, 149.425, 141.796, 139.447, 137.238, 128.201, 124.486, 121.694, 119.910. HRMS (ESI-TOF) calcd for $C_{10}H_7N_2Br$ $(M+H)^+$: 234.9865, found: 234.9863.

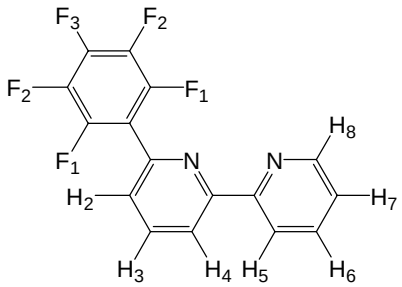


Perfluorophenylboronic acid (8)

Synthesized according to the literature procedure.[7]

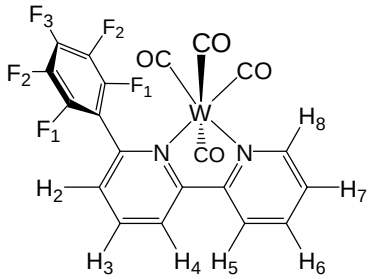
A 250 mL 3-neck flask was oven dried with a stirbar and Mg powder (1.49 g, 61.3 mmoles). 125 mL dry ether was added under argon. C_6F_5Br (9.471 g, 38.35 mmoles) was

added and the mixture was heated to initiate reaction. The heat was removed and the reaction refluxed on its own for 1.5 hrs. The mixture was then refluxed by heating for a further 20 minutes. During this time, a 1 L Schlenk flask was dried, filled with 150 mL dry ether and $B(OMe)_3$ (5.50 mL, 48.4 mmoles), and was cooled to 0 ºC. The Grignard solution was cannulated into the receiving flask and the combined solutions were stirred cold for 1 hr. The cold bath was removed and the reaction was stirred another hour. The reaction was quenched with 150 mL of 1 M HCl. The layers were separated and the aqueous layer was extracted with water (2 x 50 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and evaporated to a light brown solid. The solid was recrystallized from 20:1 toluene:water after cooling in a refrigerator for 1.5 hrs. The solid, $C_6F_5B(OH)_2$ (4.58 g) was filtered out as fine light brown needles, and was washed with petroleum ether. A second recrystallization produced 0.716 g more product mixed with white crystal clusters which were easily removed by hand. The combined mass was 5.04 g (23.9 mmoles, 62.2%). ^{1}H-NMR (acetone-d^6, 500 MHz): δ 8.25 (s). ^{13}C-NMR ($CDCl_3$, 125 MHz): Not recorded due to extensive C-F splitting. ^{19}F-NMR ($CDCl_3$, 282 MHz); δ (ppm): -133.38 (F_1, dd, 2F), -155.49 (F_3, t, 1F), -164.25 (F_2, dt, 2F). Splitting patterns are distinct, but coupling is not consistent. Nevertheless, coupling constants appear to be similar to literature values.[7]



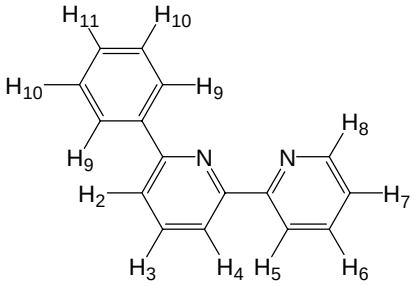
6-(perfluorophenyl)-2,2'-bipyridine (3)

To 60 mL dimethoxyethane was added (in order): 6-Brbpy (1.125 g, 4.79 mmoles), $C_6F_5B(OH)_2$ (1.359 g, 6.41 mmoles), t-BuOH (2 mL), Ag_2O (2.149 g, 9.27 mmoles), $Pd(PPh_3)_4$ (0.8483 g, 15.3 mole %), and t-BuOK (1 g, 8.91 mmoles). After addition of t-BuOK the flask was immediately fitted with a reflux condenser and was plunged into an oil bath that was preheated to 90-100 ºC. After exactly 30 minutes the reaction was quenched with excess water. The layers were separated and the aqueous layer was extracted multiple times with EtOAc. The combined organic layers were dried, filtered, and evaporated to give a yellow oily solid. Column chromatography with 1:1 EtOAC:Hex provided clean product, which may then be recrystallized in hexane to remove any unwanted S_NAr byproduct. Pure **3** (0.878 g, 2.7 mmol, 57%) was collected as yellow crystals (m.p. 174-180 ºC). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.69 (H_8, dm, 1H, *J* = 5.0 Hz), 8.50 (H_2, dd, 1H, *J* = 1.0, 7.5 Hz), 8.43 (H_5, dd, 1H, *J* = 1.0, 7.0 Hz), 7.96 (H_3, dd, 1H, *J* = 8.0, 8.0 Hz), 7.82 (H_6, ddd, 1H, *J* = 2.0, 8.0, 8.0 Hz), 7.49 (H_4, dd, 1H, *J* = 1.0, 7.5 Hz), 7.33 (H_7, ddd, 1H, *J* = 1.0, 7.5, 5.0 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 156.96, 155.71, 149.46, 137.88, 137.27, 125.90, 124.35, 121.66, 121.25. Carbons split by fluorine were not visible. ^{19}F-NMR ($CDCl_3$, 282 MHz): δ -143.80 (F_1, dd, 2F), -154.82 (F_3, t, 1F), -162.73 (F_2, dt, 2F). Coupling is uneven. See comment for **8**. HRMS (ESI-TOF) calcd for $C_{16}H_7N_2F_5$ $(M+H)^+$: 323.0602, found: 323.0604.



[6-(perfluorophenyl)-2,2'-bipyridine]tetracarbonyltungsten (4)

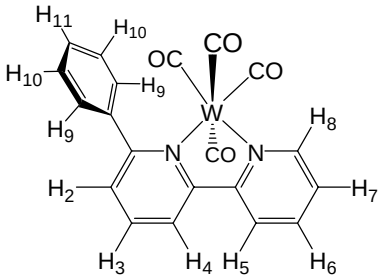
To a dried Schlenk flask was added **3** (0.06 g, 0.2 mmol) and $W(EtCN)_3(CO)_3$ and the flask was thoroughly degassed under N_2. Dry THF (5 mL) was added by syringe and a deep blue/green color formed immediately. The solution was stirred for 72 hours then heated to 55 ºC for 2 hours. Crude **4** (35 mg, 0.06 mmol, 30%) was collected by filtration. If **3** is present, it removed by dissolving in hexanes and filtering to collect **4** as a dark solid. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 9.35 (H_8, dm, 1H, *J* = 5.5 Hz), 8.30 (H_2, d, 1H, *J* = 8.0 Hz), 8.11 (H_5, d, 1H, *J* = 8.0 Hz), 8.10 (H_3, dd, 1H, *J* = 7.5, 8.0 Hz), 8.01 (H_6, dd, 1H, *J* = 8.0, 8.0 Hz), 7.53 (H_4, d, 1H, *J* = 7.5 Hz), 7.45 (H_7, dd, 1H, *J* = 6.5, 7.0 Hz). ^{19}F-NMR ($CDCl_3$, 282 MHz): δ -141.51 (F_1, m, 2F), -151.95 (F_3, m, 1F), -161.20 (F_2, m, 2F).



6-phenyl-2,2'-bipyridine (5)

To 50 mL of DMF was added 6-Brbpy (0.500 g, 2.13 mmoles), phenylboronic acid (0.399 g, 3.27 mmoles), potassium carbonate (0.594 g, 4.3 mmoles), Ag_2O (0.994 g, 4.29

mmoles), and $Pd(PPh_3)_4$ (0.124 g, 5 mole %). The mixture was purged with N_2 for 10 min then the reaction flask was plunged into an oil bath which was preheated to 85 ºC. The purge was discontinued after 30 min. After heating for 1 hr the reaction was complete as monitored by GC-MS. After cooling, the mixture was filtered through a celite pad. The filtrate was partitioned between H_2O and CH_2Cl_2 then extracted with H_2O (2 x 20mL). The organic extracts were collected then extracted once with water (20 mL), dried over $MgSO_4$, filtered, and evaporated. Column chromatography with 10:1 Hex:EtOAc produced **5** as an off-white flakey solid (0.375 g, 76%, m.p. 79-82 ºC). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 8.67 (dm, 1H, *J* = 5.5 Hz), 8.63 (dm, 1H, *J* = 8.0 Hz), 8.37 (dd, 1H, *J* = 1.0, 7.5 Hz), 8.15 (d, 1H, *J* = 1.5 Hz), 8.14 (d, 1H, *J* = 1.0 Hz), 7.86 (dd, 1H, *J* = 8.0, 8.0 Hz), 7.82 (ddd, 1H, *J* = 2.0, 8.0, 8.0 Hz), 7.75 (dd, 1H, *J* = 1.0, 8.0 Hz), 7.50 (dt, 2H, *J* = 1.5, 6.0, 6.0 Hz), 7.44 (d, 1H, *J* = 7.5 Hz), 7.30 (ddd, 1H, *J* = 1.0, 7.5, 5.5 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 156.551, 156.484, 155.859, 149.213, 139.471, 137.875, 137.031, 129.190, 128.892 (2C), 127.096 (2C), 123.916, 121.464, 120.462, 119.455. HRMS (ESI-TOF) calcd for $C_{16}H_{12}N_2$ $(M+H)^+$: 233.1073, found: 233.1075.



[6-phenyl-2,2'-bipyridine]tetracarbonyltungsten (6)

$W(CO)_6$ (49 mg, 0.14 mmoles) and 6-phbpy (32 mg, 0.14 mmoles) were dissolved in 2 mL dry xylenes and the solution was purged with N_2 for 5 minutes before being heated to reflux under N_2. The reaction was heated for 2 hours, then cooled to RT and placed in a freezer for 15 min. (6-phbpy)$W(CO)_4$ (46 mg, 0.087 mmoles, 62%) precipitated and was collected by filtration and washed with hexanes. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 9.35 (H_8, d, 1H, *J* = 4.5 Hz), 8.17 (d, 2H, *J* = 8.0 Hz), 8.01 (H_3, dd, 1H, *J* = 8.0, 7.5 Hz), 7.98 (H_6, ddd, 1H, *J* = 1.5, 8.0, 7.5 Hz), 7.57-7.53 (m, 5H), 7.40 (H_7, ddd, 1H, *J* = 1.5, 8.0, 4.5 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 217.33, 210.47, 201.90 (2C), 164.57, 157.03, 156.56, 153.36, 142.37, 137.05, 137.02, 129.92, 128.75 (2C), 128.37 (2C), 127.14, 125.85, 123.21, 121.00. IR ($CHCl_3$ solution, cm^{-1}): 2006 (sharp, medium), 1893 (sharp, strong), 1882 (sharp, strong), 1828 (sharp, medium).

2.5. References

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