

C500 Report

# Towards Mixed-Valent Molecular Wires

Submitted by

Kumar Parimal

Under the supervision of

Professor Amar H. Flood



Department of Chemistry  
Indiana University, Bloomington  
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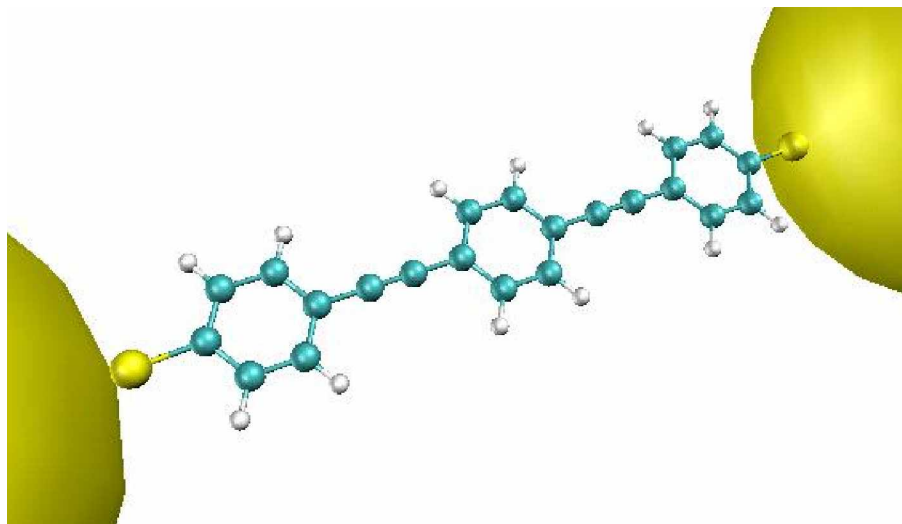
## Abstract

A series of binuclear ruthenium(II) complexes based on the bridging ligand 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz), that can form mixed-valent states, have been designed to incorporate thiol functionality allowing the self-assembly onto gold electrodes for studies in molecular electronics. Cyanation, the first step toward a variety of bptz ligands, has been optimized for reaction yield to 55%. Two bptz ligands, 3,6-bis(5-methyl-2-pyridyl)-1,2,4,5-tetrazine (5Me<sub>2</sub>bptz) and 3,6-bis(4-methyl-2-pyridyl)-1,2,4,5-tetrazine (4Me<sub>2</sub>bptz) have been prepared with modest yields (<20%). An alternative high yielding (~80%) route to these ligands has been proposed. A reaction to test benzylic bromination using 2-bromo-5-methylpyridine has been performed prior to bromination of the two benzylic groups of the bptz-based ligands. The Raman spectra of 5Me<sub>2</sub>bptz and 4Me<sub>2</sub>bptz and their precursor subunits, 2-cyano-5-methylpyridine and 2-cyano-4-methylpyridine have been recorded with 514.5 and 785 nm excitation in order to assign the observed Raman bands to either the pyridyl or tetrazine ring systems. Self-assembled monolayer of a model compound, pentaammineruthenium(II) (pic-SP)<sup>2+</sup> (pic-SP is a propionitrile protected 4-mercaptopycolyl ligand, 4-(3-thiopropionitrile)-picolyl) were prepared and preliminary electrochemical characterization suggest monolayers form slowly in both dilute MeCN solution and when using NaHCO<sub>3</sub> as an *in situ* deprotecting reagent.

# Towards Mixed-Valent Molecular Wires

## Introduction

The objective of this work is to design, synthesize and characterize molecular wires by building on the chemical knowledge established from the 1970s on the Creutz-Taube ion (CT ion) and the more general area of mixed-valent chemistry. Such molecular wires may have potential as interconnects in the electronics industry (Figure 1)<sup>1</sup> as well as providing fundamental studies on charge transfer and transport through electrode-molecule-electrode system. Thiol-terminated, rigid polypyridine diruthenium mixed-valent complexes will be used to direct the formation of self-assembled monolayers (SAMs) of molecular wires on gold electrodes on account of the fact that thiols confer high adsorbability onto gold surfaces.



**Figure 1.** A thiol terminated molecule sandwiched between two gold electrodes.

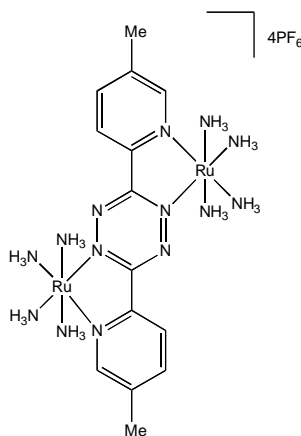
The surface-based electrochemistry, surface-enhanced Raman spectroscopy (SERS) and electrical conductivity measurement of the complexes and the SAMs will be studied. Ultimately, these systems will be used for the formation and testing of a single molecule nano-electrode.

The first part of this study involves the design and synthesis of a molecule that has a conjugated  $\pi$  system. The flow of electrons through the mixed-valent molecules considered here can be tuned and controlled by means of –

- (a) conjugation within the molecular backbone,
- (b) stabilization of polypyridine-based LUMOs by coordination with electropositive metal centers,
- (c) introduction of metal-based  $d\pi$  HOMOs into the frontier orbital region

and for the specific class of mixed-valent compounds based on 3,6-bis-(2-pyridyl)-1,2,4,5-tetrazine (bptz) (Scheme 1) studied here, the  $\pi$ -accepting tetrazine subunit may lead to delocalization of the  $d\pi$ -HOMO and  $\pi^*$  LUMO on account of  $d\pi-\pi^*$  back-bonding, a factor which will also contribute towards shifting the energy bands and modulating conjugation.

**Scheme 1.** Diruthenium-bptz complex



Considerable interest has developed over the past few years towards the use of small molecules as active components of electronic circuitry – the field is known as molecular scale electronics or molecular electronics. The research in this field may provide a pathway to high-density nanoelectronic devices. This pathway involves the development of a molecular memory device based on reversible switching of a molecule between two conducting states in response to a trigger, such as an applied voltage.<sup>1</sup> Experiments to date have examined a multitude of molecules conducting in parallel or in some cases transport through single molecules. The latter includes molecules probed in a two terminal geometry using electrically controlled “break junctions” or alternatively scanning probes, as well as three terminal single-molecule transistors. These are made to characterize carbon nanotubes, fullerenes and conjugated molecules, some of which are diluted in a less-conducting molecular layer. Transistors from a single molecule transition metal complex has been designed where electron transport occurs through well defined charge states of a single atom.<sup>2</sup> The ultimate goal of molecular electronics is to understand fundamentally and therefore, to design rationally electrical devices in which their properties are determined by the molecule.

The synthesis and characterization of thiophene bound SAMs on gold surfaces have been reported.<sup>4</sup> The characterization was done by X-ray photoelectron spectroscopy (XPS), angle-resolved XPS and ellipsometry. Their studies show that the density of the SAMs depends on the length of the molecules. Longer linear molecules tend to form denser SAMs. Molecules of benzene-1,4-dithiol were self assembled onto two facing gold electrodes of a break junction to form a statically stable gold/sulfur-aryl-sulfur/gold system.<sup>5</sup> The system allowed the direct observation of charge transport through the molecular monolayer. This study provided a quantitative measurement of conductance through a single molecule, which is a fundamental step in the emerging area of molecular electronics.

Relevant to the present research dinuclear mixed-valence complexes were synthesized and assembled on boron-doped silicon surfaces (redox site density was calculated as  $1.6 \times 10^{13} \text{ cm}^{-2}$ ).<sup>7</sup> The measurement of AC capacitance of the film for two similar compounds demonstrated that the molecular design can be used to tailor the properties of the device. External electric field control of the position of the electron in a mixed-valence complex makes it possible to use these complexes for Quantum Cellular Automata (QCA), a computational paradigm which is based on encoding binary information in the charge configuration of quantum dot cells. Mixed-valence compounds contain metal centers which, at least in a formal sense, can exist in more than one oxidation state. One of the continuing themes in mixed-valence chemistry is the effect of electronic delocalization on the mixed-valence properties. In metal complexes, delocalization can be varied by making changes in the metal, the bridging ligand, the ancillary ligands, the solvent and the

temperature. Electronic delocalization is promoted by mixing the electronic donor and acceptor wave functions. If the electronic coupling is sufficient, there is a complete blending of oxidation states and the odd electron once produced chemically, electrochemically or photochemically is delocalized over both sites.<sup>8</sup> The mixed-valence complexes are organized into three main classes according to the Robin and Day classification scheme<sup>9</sup>.

Class I : no coupling between redox sites and no electron transfer.

Class II : weak coupling between redox sites and electron transfer depends upon thermal activation.

Class III : strong coupling between redox centers and activation less electron transfer between two sites.

Since the late 1960s many mixed-valence complexes have been prepared, of which the  $\mu$ -pyrazine bridged ruthenium dimer by Creutz and Taube<sup>10</sup> and the cyclopentadienyl linked biferrocenium cation by Cowan and co-workers<sup>11</sup> were two of the first. Symmetrical as well as asymmetrical mixed-valence complexes of ruthenium and iron has been reported by Fehlner.<sup>7</sup> Various transition metal mixed-valence complexes has been reported by Kaim<sup>12</sup> among others and extensive reviews are available in the literature.<sup>8</sup> Our interest lies at extending these studies from the solution and into new environment to the interface of hard materials that lies between molecules and electronics.

## **Objective**

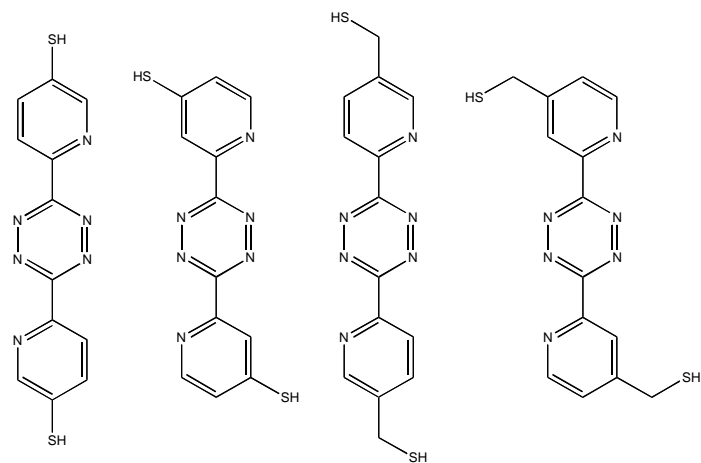


The primary target is to synthesize polypyridine ligands with thiol groups or protected thiol groups at the terminal axial positions for the SAM formation. Synthetic strategies will be based on known ligands<sup>12</sup> and will be developed further still, to not only accommodate thiol functionality, but also to direct coordination towards the pyridyl nitrogens and away from the potentially monodentate sulfur atoms. The first target is a bipyridyl tetrazine (bptz) ligand with thiol group along the axis of the ligand (Scheme 2).

The thiol group can be attached to the pyridine ring either directly or by using the methylene linkage to attach the thiol group to the picolyl ring system (Scheme 2). Also the position of the linkage can be varied at the pyridine ring. Our objective is to synthesize four different kinds of ligands based on the reported bptz ligand depending on position of linkage (3- or 4-) and the manner of attachment of thiol functionality (directly conjugated or with broken conjugation). Subsequently each of these ligands will be co-ordinated to redox-active metal moieties such as  $\{\text{Ru}(\text{NH}_3)_4\}^{2+}$ , in order to obtain the mixed-valent systems. The properties of the complexes will be studied, where three structural parameters can be changed

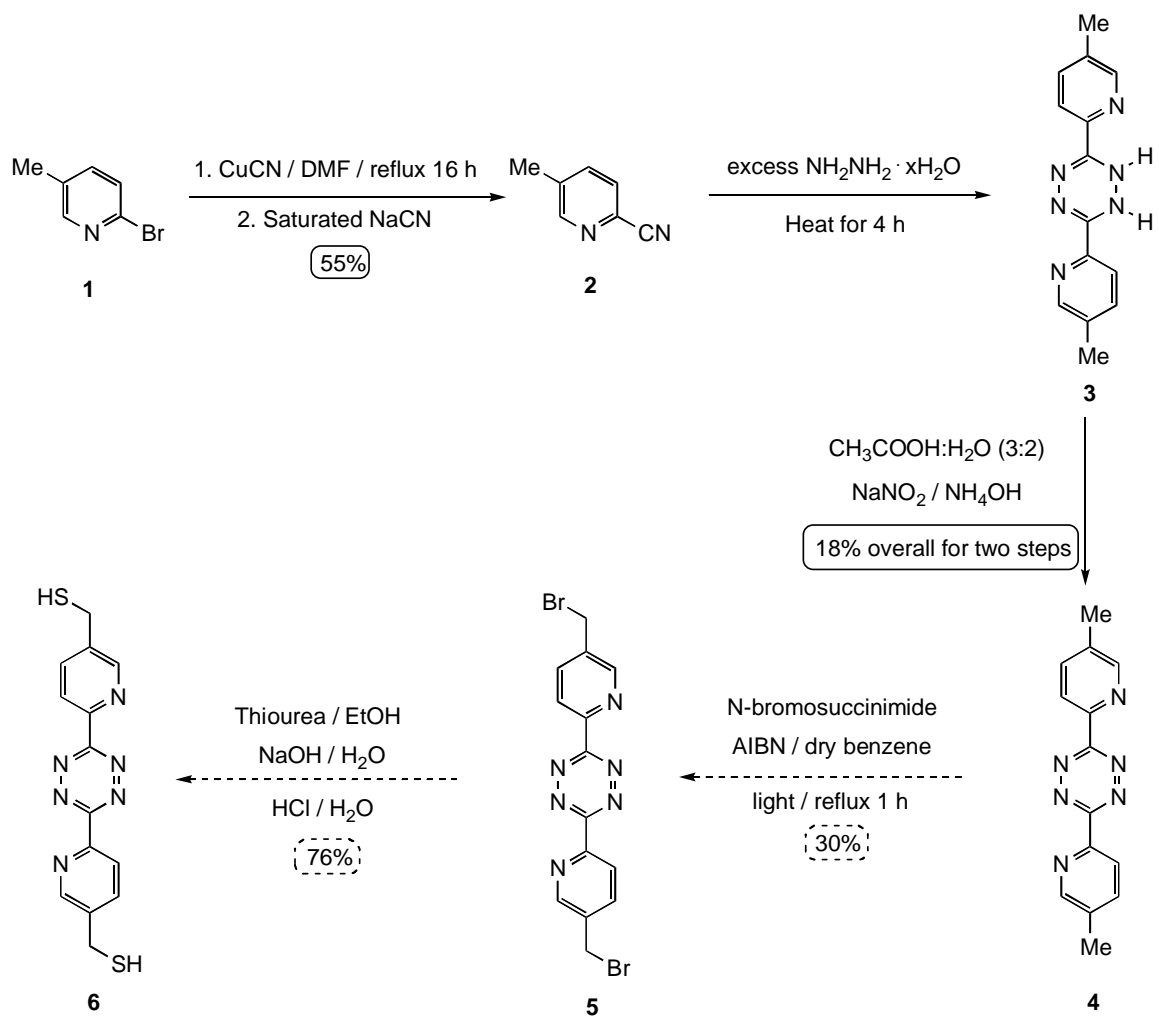
1. The position of the thiol functionality
2. The mode of attachment of the thiol functionality
3. The metal centers having different redox potential.

**Scheme 2.** Bptz based target ligands

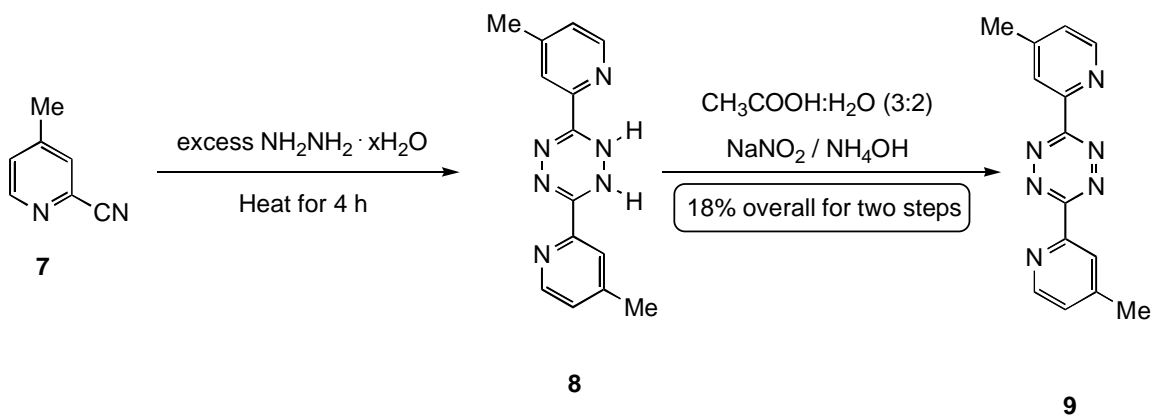


The synthetic scheme to be followed is outlined in (Scheme 3-6).<sup>12-18, 22-24</sup>

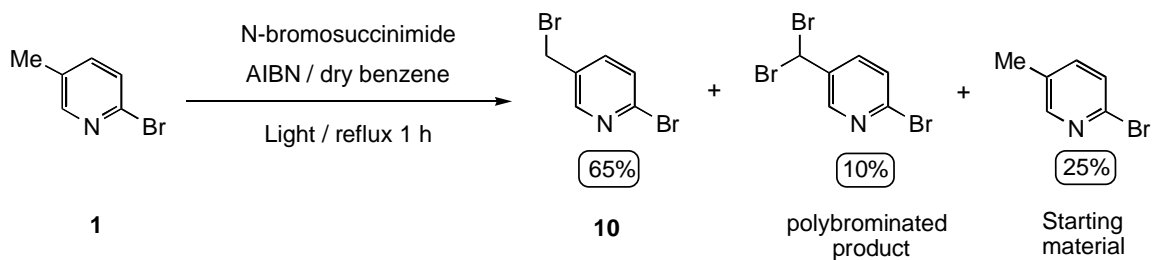
**Scheme 3.** Proposed synthesis of the 3,6-bis-(5-methylthiol-2-pyridine)-1,2,4,6-tetrazine ligand. (Yields in brackets refer to expectations based on literature values and the dotted arrows indicate reaction not completed)



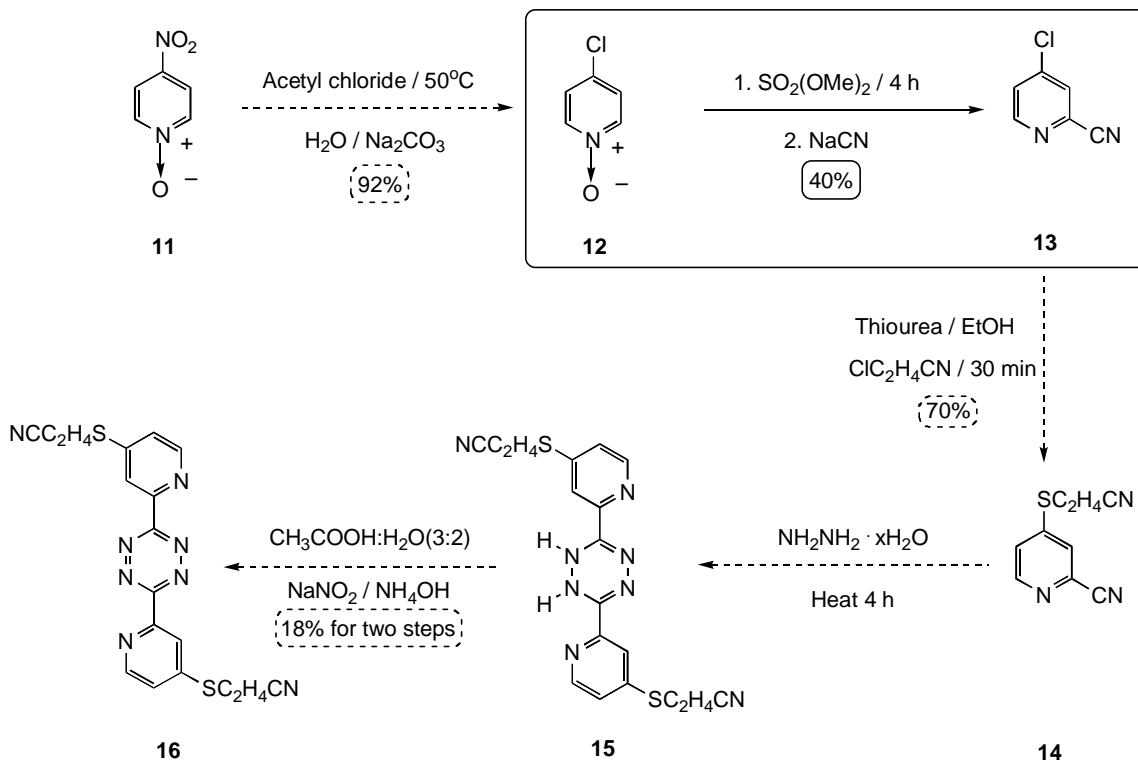
**Scheme 4.** Proposed synthesis of the 3,6-bis-(4-methyl-2-pyridine)-1,2,4,5-tetrazine ligand. (Yields in brackets refer to expectations based on literature values)



**Scheme 5.** Bromination of 2-bromo-5-methylpyridine as a test reaction for benzylic bromination



**Scheme 6.** Proposed synthesis of the directly conjugated dithiols bptz ligand



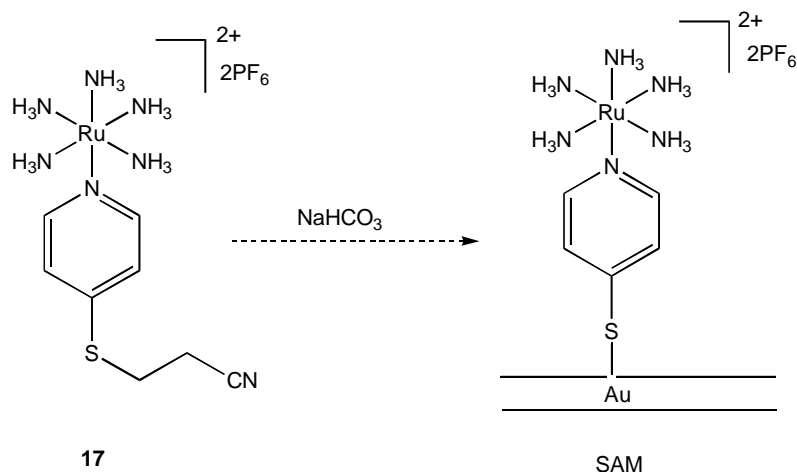
The synthesized products will be characterized by various standard techniques including  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR, UV-Vis-NIR spectroscopy and mass spectrometry. Microanalyses will be carried out and single crystals will be grown for X-ray crystallography studies.

Our next job is to self assemble these molecules on the gold surface and study their properties by electrochemistry and spectroscopy. The electronic properties of the molecular wires will be investigated using a combination of electrochemistry, UV-Vis-NIR absorption spectroscopy, fluorescence and resonance Raman spectroscopy. Each technique provides a complementary picture that will allow the energy levels and the sizes and shapes of the HOMO and LUMO to be characterized. These experimental data will be complimented by computational studies.

Furthermore, these solution-studies, particularly the Raman spectroscopy provides signatures that can be observed in SAMs on gold electrodes. The resonance Raman enhances the vibrational bands. SERS will be recorded for the SAMs. It will have the same fingerprint region but the signals will be enhanced. SER spectra will be compared with the solution phase vibrational spectra and with the electrochemistry data. Our initial target is to analyze the solution and solid state Raman spectra of the molecule and assign the fingerprint region. Once the molecules are assembled on the gold we can compare the spectra with the solution / solid-state spectra.

Towards these targets compound, a thio compound pentaammineruthenium(II) (pic-SP)<sup>2+</sup> (pic-SP is a propionitrile protected 4-mercaptopycolyl ligand, 4-(3-thiopropionitrile)-picolyl)<sup>27</sup>, **17** was used to make SAM (Scheme 7) and the electrochemistry of the SAMs were recorded. The Raman spectra of the methyl substituted bptz ligands were recorded and the vibrational frequencies were assigned according to the literature.

**Scheme 7.** Self assembly on the gold surface



## Results and Discussion

*Synthesis:* Each of the bptz-based ligand (Scheme 2) rely upon the preparation of a substituted 2-cyanopyridine precursor. Towards these ends the cyanation was investigated in various ways using either CuCN<sup>1,2</sup> or NaCN as the cyanide source. The main problem with using CuCN is the tentative formation of a copper complex with the pyridine product. The green color of the products from these reactions indicated the complex formation. The synthesized substituted 2-cyanopyridine can act both as a electron  $\sigma$  donor as well as an electron  $\pi$  acceptor ligand. The lone pair of electrons on the nitrogen can donate to the metal while the empty  $\pi^*$  orbital of 2-cyanopyridine is available to accept the electrons by back donation from the metal  $d\pi$  orbitals. Based on prior works where KCN has been used to remove the ligand from the copper, the green compound was washed with saturated NaCN solution from which a white compound was obtained and its identity confirmed by <sup>1</sup>H NMR and IR spectroscopy and by mass spectrometry. Attempts to use NaCN as a cyanide source or to use pyridine as a competitive coordinating solvent for the CuCN reagent were not successful.

The methyl substituted bptz analogs were prepared in two steps from the corresponding 4- and 5- methyl substituted 2-cyanopyridines. The dihydro intermediate compounds, **3** and **8** (Scheme 3 and 4) , prepared by the condensation of substituted 2-cyanopyridine with hydrazine hydrate, were isolated as a yellow solid, it was used without further purification. Both bis-(methylpyridine)tetrazines, **4** and **9** were generated by reduction using sodium nitrite. Formation of the tetrazine core from the 2-cyanopyridine precursors is one of the early steps in the proposed scheme towards the dithiol ligands and the yield of the reaction is low (<20%). Hence an alternate way to synthesize the tetrazine with higher yields (~80%) has been identified that relies upon a copper catalyst to improve the yield. The authors claim that the higher yields of the reaction between cyanobenzene and hydrazine depends on the substitution pattern of a methyl group. The substitution at the *meta* and *para* position with respect to the cyano group increases the yield compared to the unsubstituted cyanobenzene. Furthermore, the reaction works effectively (80%) with 2-cyanopyridine. Considering the above two factors we assume that the formation of bptz ligands using a copper catalyst from methyl substituted 2-cyanopyridines will provide a higher yields.

The next step in the proposed reaction scheme is a benzylic *di*bromination of the methyl substituted bptz (Scheme3). In order to test the reaction benzylic *mono*bromination was carried out on a related, 2-bromo-5-methylpyridine. A mixture of products were obtained including starting material, monobromo product and the dibromo product. These products were identified by the <sup>1</sup>H NMR. indicating that the monobromo is the major product with a 65 % yield followed by the starting material (25 %) and the dibromo as the minor



component (10 %). This result suggest that under similar conditions, bromination of the dimethyl substituted bptz ligand should favor a *dibromo* product over polybrominated and underbrominated ones. Literature values show that bromination of dimethyl substituted compounds gives yields of 30 % of *dibromo* products.

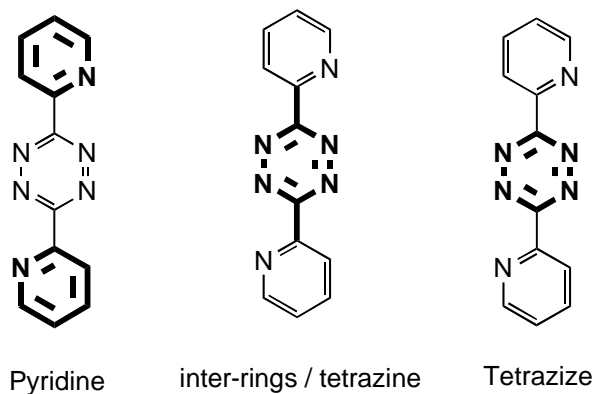
*Self-Assembled Monolayers:* To study the ability of tetraammineruthenium(II) compounds to self assemble onto gold electrode a SAM of **17** was prepared. The SAM formation was investigated in two different ways. Firstly the molecules were assembled by thermodynamic process by assuming that the sulfur–gold bond is thermodynamically favored over sulfur–carbon bond thus the molecules self assemble on gold by self deprotection. Secondly we deprotected the thiol functionality and self assemble the molecules on gold *in situ*. The preliminary results suggest that the deprotection gives a better result. These SAMs were studied by cyclic voltammetry. Cyclic voltammograms were recorded at different scan rates (Figure 2). For a SAM, an increase in the scan rate show a linear increase in the peak current value (Figure 3).



*Raman Spectroscopy:* The other technique to study the SAMs is Raman spectroscopy. Raman spectra were recorded for the methyl-substituted bptz ligands, **4** and **9** and their corresponding precursors **2** and **7**. The Raman spectrum was recorded by excitation with 514.5 nm, which will be pre-resonance Raman spectrum while one recorded by excitation with 785 nm will be normal Raman spectrum. Based on the UV-vis of the similar kind of system we can say that these wavelengths are non-resonant wavelengths. The data was used to assign the observed Raman bands to either the pyridyl or tetrazine ring systems.

The Raman spectra of the methyl substituted bptz ligands show strong bands at 1579, 1486, 1435, 1306  $\text{cm}^{-1}$  for 3,6-bis(5-methyl-2-pyridine)-1,2,4,5-tetrazine and at 1593, 1557, 1450, 1306  $\text{cm}^{-1}$  for 3,6-bis(4-methyl-2-pyridine)-1,2,4,5-tetrazine. The peaks around 1450  $\text{cm}^{-1}$  can be assigned to the tetrazine ring stretches, the peaks at higher frequencies around 1550  $\text{cm}^{-1}$  can be assigned to the pyridyl rings and the peak at 1306  $\text{cm}^{-1}$  can be assigned to the inter-ring stretching and tetrazine (Scheme 8). These values are assigned on the basis of works reported<sup>26</sup> on the Raman spectra of bptz ligand and its complexes.

**Scheme 8 .** Different vibrations in a bptz molecule



## Experimental

Starting materials have been obtained from Sigma Aldrich and Alfa Aesar and used as received. All the starting materials and the products are found to be air and moisture stable. Solvents were dried for some reactions by standard procedures reported in the literature. For the workup, the solvents were used without any further purification. The column chromatography was done by using silica gel 150 (mesh 100-200). The melting points were measured in glass capillaries and were reported uncorrected.  $^1\text{H}$  NMR was recorded on 400 MHz Varian Inova NMR Spectrometer. Infrared spectra were recorded on Nicolet 510P FT-IR spectrometer as KBr diluted thin pellets in solid state. The solid state Raman spectrum was recorded on Renishaw inVia Raman Microscope with Argon laser for 514.5 nm and diode laser for 785 nm. The electrochemistry was carried out using a Princeton Applied Research potentiostat/galvanostat Model 263A with silver wire as a reference electrode, platinum wire as a counter electrode and a coiled gold wire with the self assembled molecules on it as a working electrode.

### **2-Cyano-5-methylpyridine (2)**

2-Bromo-5-methylpyridine (0.5g, 2.9 mmol) was added to CuCN (0.3g, 3.0 mmol) in DMF (15 mL). The reaction mixture was refluxed under nitrogen at 120°C for 16 h. The progress of the reaction was monitored by TLC and a dark brown precipitate was observed at the end of the reaction. The reaction mixture was poured into water (50 mL), the precipitate was filtered and the residue was washed with saturated NaCN solution and the resulting crude yellow product was extracted into ethyl acetate. Additional product was extracted from the filtrate with ethyl acetate. The crude product was purified by

column chromatography (SiO<sub>2</sub>, EtOAc:hexane 4%:96%) to yield **2** as white crystalline solid (0.2 g, 55 %). m.p. 72-73°C; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD, ppm) δ = 8.527 (s, 1H, Ar-H), 7.803-7.783 (d, 1H, *J* = 8 Hz, Ar-H), 7.736-7.716 (d, 1H, *J* = 8 Hz, Ar-H), 2.414 (s, 3H, Me); IR (KBr, cm<sup>-1</sup>) ν<sub>CN</sub> = 2231.

#### **3,6-bis(5-methyl-2-pyridine)-1,2,4,5-tetrazine (4)**

2-Cyano-5-methylpyridine (0.4g, 3.4 mmol) was added to an excess of hydrazine hydrate (10 mL) and the reaction mixture was refluxed for 4 h generating a yellow precipitate. The reaction was allowed to cool and the excess hydrazine was removed under vacuum and the product, dihydro tetrazine was taken to the next step without further purification. The yellow compound was dissolved in 3:2 mixture of CH<sub>3</sub>COOH:H<sub>2</sub>O (15 mL) and cooled to 0°C. A freshly prepared 5.2 M sodium nitrite solution was added dropwise to the reaction mixture with vigorous stirring until the solution changes to a red color. The reaction mixture was neutralized by addition of ammonium hydroxide (30%) to give pink precipitate. The product was filtered and rinsed with water and methanol to give pure compound. Crystals of the pure compound, **4** were grown in CHCl<sub>3</sub> (0.05g, 18 %), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ = 8.809 (s, 2H, Ar-H), 8.655-8.635 (d, 2H, *J* = 8 Hz, Ar-H), 7.822-7.803 (d, 2H, *J* = 7.6 Hz, Ar-H), 2.501 (s, 6H, Me).

#### **3,6-Bis-(4-methyl-2-pyridine)-1,2,4,5-tetrazine (9)**

The preparation of **9** followed the same procedure as for **4** starting from 2-cyano-4-methylpyridine (0.2g, 1.7 mmol) to yield pure compound, **9** (0.02g, 10 %). <sup>1</sup>H NMR (400

MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 8.741-8.729 (d, 2H,  $J$  = 4.8 Hz, Ar-H), 8.661 (s, 2H, Ar-H), 7.599-7.587 (d, 2H,  $J$  = 4.8 Hz, Ar-H), 2.602 (s, 6H, Me).

### **2-bromo-5(methylbromide)pyridine (10)**

2-Bromo-5-methylpyridine (0.1g, 0.58 mmol), NBS (0.1g, 0.58 mmol, recrystallized from hot water) and AIBN (0.009g, 0.058 mmol) was added to a flask and was dried under vacuum. Dry benzene (5 mL) was introduced to the flask through a syringe. The reaction mixture was refluxed by using a 200 watt incandescent lamp for 1 h. The progress of the reaction was monitored by TLC. The mixture was cooled to RT and filtered. The filtrate was dried and the NMR was recorded in CD<sub>3</sub>OD which show three different compounds *i.e.*, starting compound, monobromo product, **10** and the dibromo product. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD, ppm)  $\delta$  = 2.258 (s, 3H, CH<sub>3</sub>), (s, 2H, CH<sub>2</sub>Br), 7.100 (s, 1H, CHBr<sub>2</sub>), 8.135 (s, 1H, Ar-H, starting material), 7.511-7.490 (d, 1H,  $J$  = 8.4 Hz, Ar-H, starting material), 7.436-7.415 (d, 1H, Ar-H,  $J$  = 8.4 Hz, starting material), 8.359 (s, 1H, Ar-H, monobromo product), 7.740-7.713 (d, 1H,  $J$  = 10.8 Hz, Ar-H, monobromo product), 7.550-7.529 (d, 1H,  $J$  = 8.4 Hz, Ar-H, monobromo product), 8.485 (s, 1H, Ar-H, dibromo product), 7.981-7.960 (d, 1H,  $J$  = 8.4 Hz, Ar-H, dibromo product), 7.632-7.611 (d, 1H,  $J$  = 8.4 Hz, Ar-H, dibromo product).

### **2-cyano-4-chloropyridine (13)**

4-Chloropyridine N-oxide (0.2g, 1.5 mmol) was dissolved in dimethyl sulfate (0.15 mL, 1.7 mmol) and the mixture was heated at 65°C for 4 h during which time the color changes from white to brown. The reaction mixture was cooled to RT and NaCN (0.15g, 3.1 mmol) in water (2 mL) was added and the product was extracted into ethyl acetate. Purification by column chromatography (SiO<sub>2</sub>, hexane) gave a mixture of two products. The mixture was dissolved in hexane and kept in refrigerator to crash out the product, **13** as crystalline solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 8.614-8.600 (d, 1H, *J* = 5.6 Hz, Ar-H), 7.694 (s, 1H, Ar-H), 7.530-7.516 (d, 1H, *J* = 5.6 Hz, Ar-H).

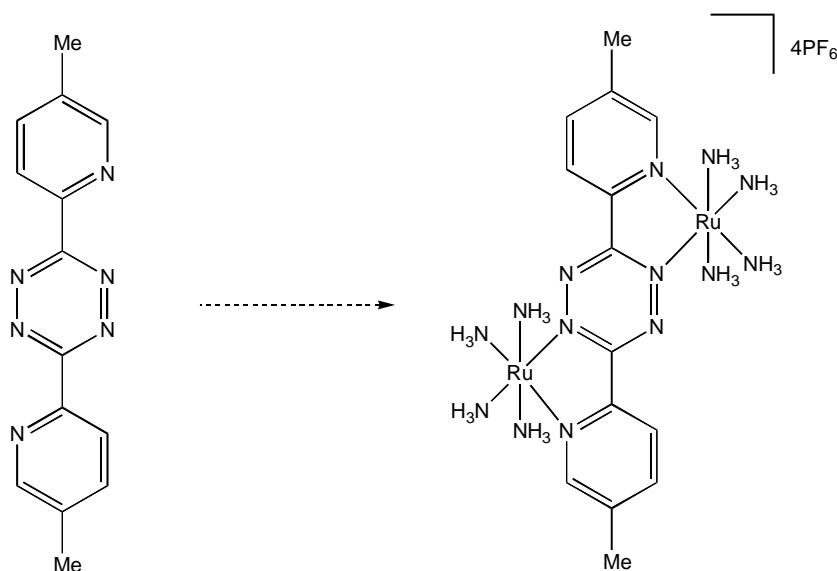
### Self-assembled monolayer

Coiled gold wires were cleaned in piranha solution (5 min, 3:1 H<sub>2</sub>SO<sub>4</sub>: H<sub>2</sub>O<sub>2</sub>, ~80°C). The wires were then rinsed with milliQ water to remove the acid, sonicated for 5 min in milliQ water to remove any residual physisorbed acid and washed with milliQ water. The wires were then rinsed with MeCN two times. The wires were soaked in a dilute solution (0.5 mM, MeCN) of the thiocompound, **17**. Cyclic voltammetry was carried out on the wires after soaking for 15 min, 1 and 16 h. Formation of the SAMs was also investigated by deprotecting the thiol functionality. An equimolar amount of sodium bicarbonate was used to deprotect the ethylcyano protecting group allowing the molecules to self assemble onto the gold wire *in situ*. The cyclic voltammetry was carried out for the monolayers after soaking in the solution for 45 min and 20 h.

### Future Work

After synthesizing and characterizing the target ligands, the further studies involve the complexation<sup>18</sup> of these ligands with metal moieties to obtain the molecular wires. The metal moieties are selected on the basis of the correct size and the right redox potential of the metal center. For example  $\{\text{Ru}(\text{NH}_3)_4\}^{2+}$  presents a smaller coordination sphere and a stabilized  $\text{Ru}^{\text{III/II}}$  oxidation potential on account of the strong  $\sigma$ -donor properties of the amine ligands. By contrast,  $\{\text{Ru}(\text{bpy})_2\}^{2+}$  is larger and has a less stable  $\text{Ru}^{\text{III/II}}$  oxidation state change. Our target is to prepare and characterize the molecular wires with various oxidation states including one with mixed valence states. The flow of electrons through these wires may be mediated by metal-to-metal charge transfer (MMCT) interactions involving an intervalence transition (IT) through the rearranged molecular orbitals. The HOMO–LUMO energy gap and their redox energies can be tuned in these molecules by changing the auxillary ligands. The auxillary ligands also play a role in controlling the geometric and steric factors. The metal center is selected on the basis of its stability under thermal conditions and in the solution phase.

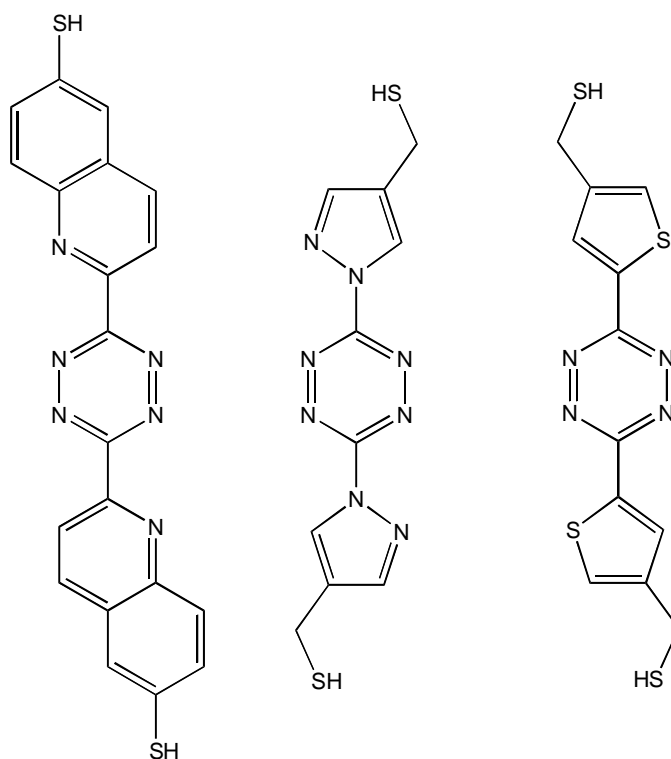
**Scheme 9.** Synthesis of diruthenium complex





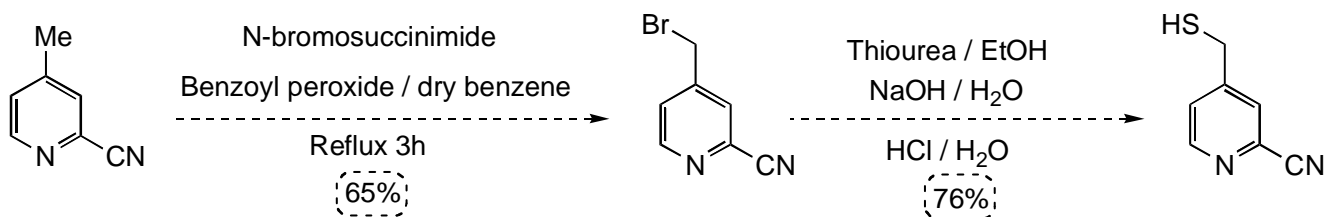
The metals that will satisfy the conditions will be selected. The potential metals to be used are iron, ruthenium and osmium. Our target is to form complexes of the four target ligands mentioned earlier with the three metals and compare the electrochemical properties of the expected twelve complexes. In addition we can modify our ligand by varying the length of the backbone or by changing the coordinating centers of the ligand (Scheme 10).

**Scheme 10. Some modified ligand system**

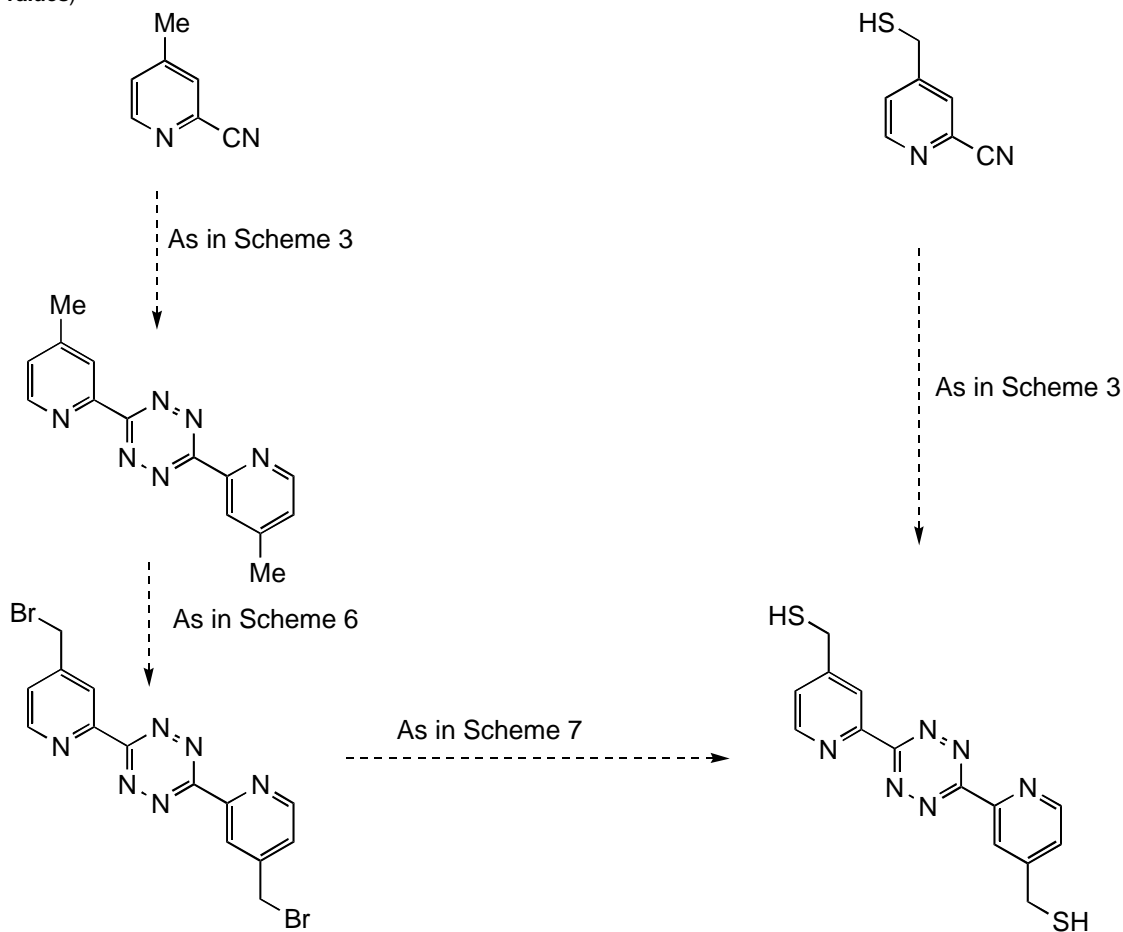


An alternate synthetic scheme to synthesize thiol-terminated btpz is been outlined in (Scheme 11 and 12).<sup>15, 19–21, 24</sup>

**Scheme 11. Synthesis of methyl-thio pyridine. (Yields in brackets refer to expectations based on literature values)**



Scheme 12. Synthesis of thiol terminated tetrazine. (Yields in brackets refer to expectations based on literature values)



The next target of the project is to characterize the electrical properties of SAMs of molecular wires. The molecular wires will be self assembled on gold electrodes to form SAMs. The surface studies of these resulting nano-electrodes will be studied both spectroscopically and electrochemically again by Raman spectroscopy and cyclic voltammetry to show how the molecules behave under bias. These ‘half-devices’ employing SAMs serve as practical stepping stones to full devices in which there is no solvent. Simple devices will be made in order to characterize the conductance properties of molecular wires simultaneously with Raman spectroscopic measurements and thus providing a rational link back to solution.

## Conclusion

A series of binuclear ruthenium(II) complexes based on the thiol terminated bptz ligands, that can form mixed-valent states, have been designed which can be self-assembled onto gold electrodes for studies in molecular electronics. Cyanation, the first step toward a variety of bptz ligands, has been optimized for reaction yield to 55%. Two bptz ligands, **4** and **9** have been synthesized with modest yield (<20%). An alternative high yielding (~80%) route to these ligands has been proposed. To test the benzylic bromination, a test reaction was performed on a similar compound, 2-bromo-5-methylpyridine prior to bromination of the two benzylic groups of the bptz-based ligands. The Raman spectra of the two methyl substituted bptz ligands, **4** and **9** have been recorded with 514.5 and 785 nm excitation in order to assign the Raman bands. Self-assembled monolayer of a model thiocompound, **17** were prepared and the electrochemical studies suggest monolayers form slowly in both dilute MeCN solution and when using NaHCO<sub>3</sub> as an *in situ* deprotecting reagent.

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