

Synthesis and Electrochemical Response of Bis(terpyridine) Metal Complex Nanowires with Thiophene Linkers

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Abstract

The research focuses on studying the electrochemical response of the bis(terpyridine) metal complex nanowires composed of a new bridging ligand, α,ω -bis(terpyridyl)-bithiophene containing a thiophene linker. The prepared nanowires were analyzed by cyclic voltammometry and potential step chronoamperometry (PSCA) to determine surface coverage and confirm stoichiometry of prepared wire.

I. INTRODUCTION

Surface-modified electrodes have attracted considerable attention as targets for the development of novel functional materials. Among different surface modification methods, self assembled monolayers (SAM) have various advantages, including facile and ubiquitous solution processes, and the spontaneous ordering of adsorbates to form dense, ordered, and robust monolayers[1]. Bis(terpyridine) metal complex wires are fabricated by bottom up method[2] through formation of self assembled multilayers (Figure 1).

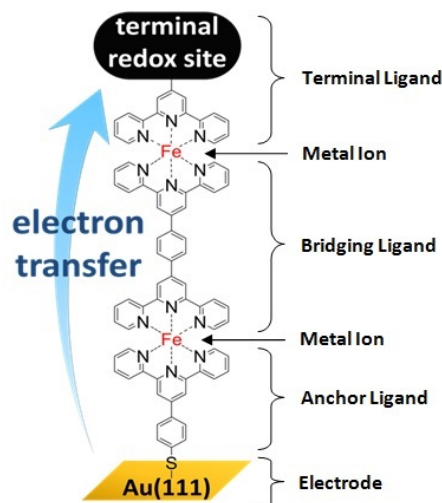


Figure 1: Basic structure of bis(terpyridine) metal complex wire

I.1 Structure

The bis(terpyridine) metal complex wires are constructed upon an elec-

trode such as highly conducting metal or semiconductor. The first wire element is anchoring ligand, which attaches to electrode surface. The second element is metal ion which is often a transition metal ion that forms coordination complexes with ligands. The third element is bridging ligand which can influence the wire length. The wire is terminated by terminal ligand which contains a redox-active site. All the coordination complexes in wire attain an octahedral geometry. All ligands used are terpyridine ligands.

I.2 Characteristics

The characteristic feature of bis(terpyridine) metal complex wire is its superior, long range electron transport ability which can be explained by sequential hopping mechanism[1] (Figure 2). When a suitable potential is applied, metal ion closest to electrode gets oxidized hereby transferring electron to electrode. This creates hole at the metal ion site, which triggers the oxidation of next metal ion, transferring the electron from the metal ion to hole. This process continues and finally, terminal redox site gets oxidized, and an efficient electron transfer takes place. Continuous conjugation promotes electron transfer between redox sites.

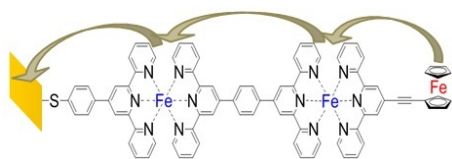


Figure 2: Sequential Electron Hopping

The electron transfer rate is given by the following equation:

$$k = k^0 \exp(-\beta^d d) \quad (1)$$

where

k = electron transfer rate constant

k^0 = zero distance rate constant

d = wire length

β^d = attenuation factor

Intra-wire electron transfer takes place in the wire and sequential hopping provides it long range electron transfer ability.

I.3 Effect of Bridging Ligand

Effect of bridging ligand on the electron transfer rate can be studied by comparing β^d values (from equation 1). Three types of metal bis(terpyridine) wires were studied, each having a different bridging ligand and (Figure 3).

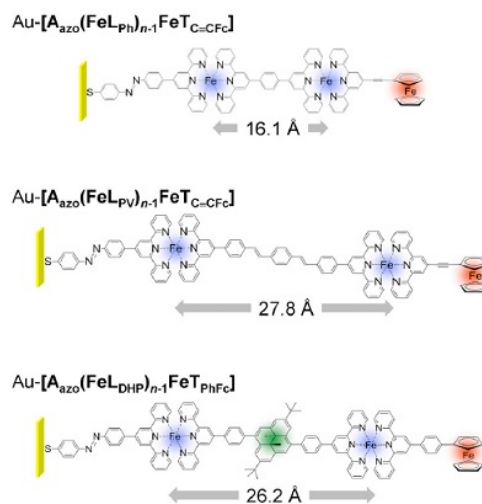


Figure 3: Metal bis(terpyridine) wires with different bridging ligands A,B & C

The β^d values of the three wires followed the relation:

$$\beta_B^d > \beta_A^d > \beta_C^d \quad (2)$$

β^d depends upon the distance between consecutive metal ions. β^d of B is larger than that of A because of deceleration in electron hopping process due to increasing distance. On the contrary, β^d of C is the smallest, though distance between metal ions in B and C are comparable, because of the presence of a redox active moiety in between two metal complexes which explicitly participates in either, electron hopping or facilitates electron hopping.

I.4 New Bridging Ligand

As mentioned above, the chemical structure of bridging ligands strongly affects the electron transfer ability of the wires. In this study, I focused on the new bridging ligand, α,ω -bis(terpyridyl)bithiophene, to fabricate molecular wires with superior electron transport ability (Figure 4). This ligand is advantageous because firstly, it has a highly conjugated system, which can facilitate electron transfer between redox sites.

Secondly, presence of bithiophene linker generates a possibility of it acting as a redox active site, thereby increasing electron transfer rate through the wires. Lastly, the ligand exhibits fluorescence which emerges the possibility of the wires being used for

photochemical applications.

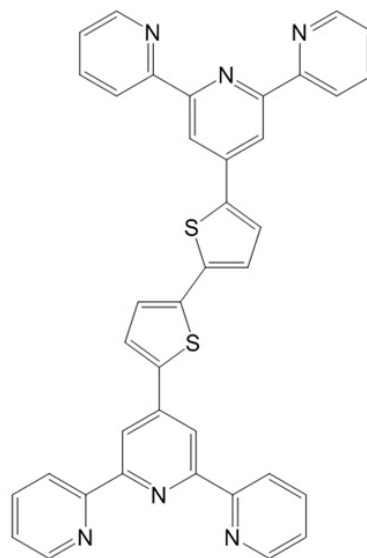


Figure 4: Chemical structure of α,ω -bis(terpyridyl)bithiophene

II. EXPERIMENTAL SECTION

Synthesis of Bridging Ligand

Preparation of bridging ligand is illustrated schematically in Figure 5.

II.1 Preparation of Kröhnke Salt

To a solution of 2-acetylpyridine (5 g, 41.45 mmol) in 50 ml of pyridine was added I₂ (11.5 g, 45.4 mmol) and heated to 100° C for 3 hours. Upon cooling to room temperature, the black precipitate was filtered through Buchner funnel, copiously washed with Et₂O, and air dried. The black solid was recrystallized from hot EtOH and filtered through a Buchner funnel. The solid was dried in vacuo to yield 7.31 g of black crystalline salt[3]. Yield: 56.1%

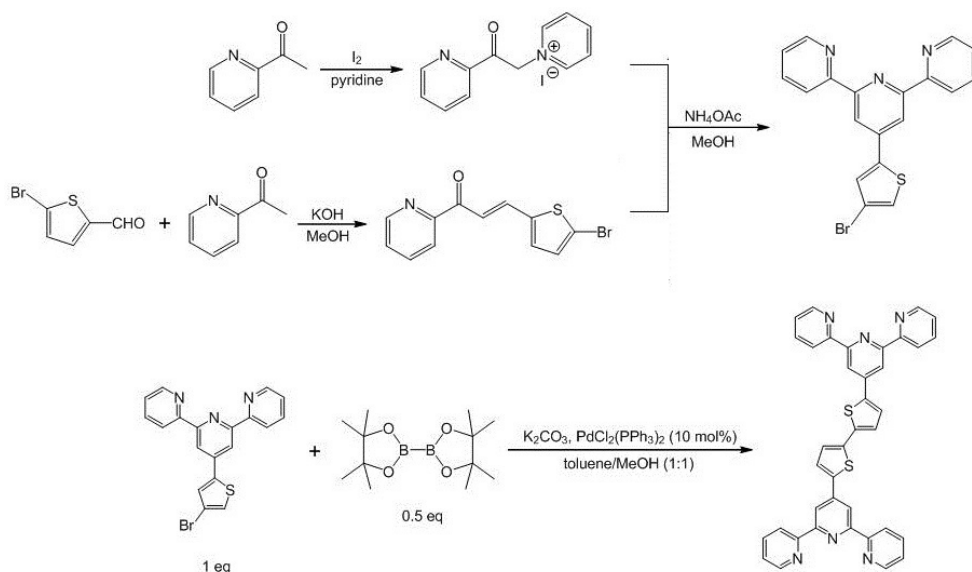


Figure 5: Schematic representation of synthesis of α, ω -bis(terpyridyl)bithiophene

II.2 Preparation of 4'-(2-(5-Bromo)thienyl)-2,2':6',2''-terpyridine

Potassium hydroxide (1.2 g, 21 mmol) was dissolved in methanol (20 ml). The solution was cooled at 0° C in ice water bath. 2-Acetylpyridine (1.3 g, 11 mmol) was added and dissolved in the reaction mixture. 5-Bromo-2-thiophenecarbaldehyde (2.0 g, 11 mmol) was added slowly into the solution. The reaction was stirred for 3 hours at 0° C. The reaction mixture was extracted with CH₂Cl₂ and then dried over MgSO₄. The solvent was removed by reduced pressure. The yellow solid of 3-(5-bromo-thiophen-2-yl)-1-pyridin-2-yl-propenone obtained was used for the next step without purification and mixed with N-[2-oxo-2-(2-(4-methoxycarbonylpyridyl))ethyl]pyridinium iodide (Kröhnke salt) (3.5 g, 11 mmol) and ammonium acetate (3.3 g, 43 mmol)

were dissolved in methanol (30 ml). The reaction was refluxed under N₂ for 5 h. The reaction mixture was cooled down to room temperature. The green precipitate was formed and collected by vacuum filtration. The precipitate was washed with cooled methanol (3 x 20 ml) and recrystallized from acetonitrile to give 1.79 g of light brown solid[4]. Yield: 41.3%

II.3 Synthesis of α, ω -bis(terpyridyl)bithiophene

4'-(2-(5-Bromo)thienyl)-2,2':6',2''-terpyridine (258 mg, 0.656 mmol), bis-(pinacolato)-diboran (83 mg, 0.328 mmol) and K₂CO₃ (120 mg, 0.868 mmol) was dissolved in a degassed toluene/methanol mixture (5 ml, 1:1), then Pd(PPh₃)₂Cl₂ (46 mg) was added and the reaction mixture was kept under stirring for 18 hours at 100°C. The mixture was diluted with toluene (20 ml), water was added (20 ml) and the

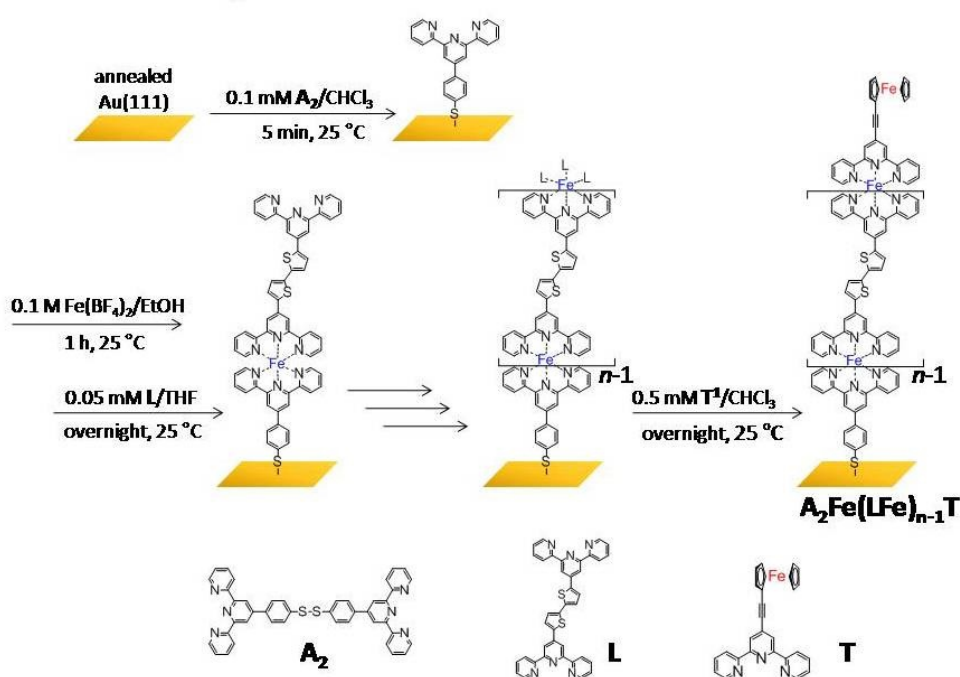


Figure 6: Schematic representation of bottom-up fabrication method for synthesis of $Au-[AFe(LFe)_{n-1}T]$

formed two-phase system was filtered. The obtained greenish sediment was dissolved in a large amount of hot THF, filtered and solvent was evaporated to obtain the desired product[5]. Yield: 14.2%

Product was confirmed by 1H NMR spectroscopy.

III. SYNTHESIS OF NANOWIRES

Au/mica plates (Au with a thickness of 100 nm was deposited on natural mica) were used for preparation of wires. Prior to use, the surface was annealed with a hydrogen flame. This treatment gave an Au(111)-like surface comprising Au single-crystal grains hundreds of nanometer wide. Schematic illustration of fabrication

of the wires is provided in Figure 6. The bottom-up construction was initiated with the fabrication of a SAM consisting of anchor ligand (A), by immersing an Au/mica plate into a 0.1 mM solution of disulfide A_2 in chloroform for 5 min (Step 1). The modified plate was then rinsed with solution of $Fe(BF_4)_2$ in ethanol for 1 hour, followed by washing with water and ethanol, and drying under nitrogen flow (Step 2). To complete the $Fe(tpy)_2$ motif, the metal-terminated surface was immersed in a 0.05 mM solution of bridging ligand (L) in THF overnight, accompanied by washing with THF and drying under a nitrogen flow (Step 3). Steps 2 and 3 were repeated $n-1$ times. To terminate the extension of the metal complex wire, the plate was subjected to Step 2 again, and then immersed in a 0.5 mM so-

lution of redox-active terminal ligand (T) in chloroform overnight, washed with chloroform, and dried under a nitrogen flow (Step 4)[6].

IV. ELECTROCHEMICAL MEASUREMENTS

The electrochemical measurements were carried out by using a Au/mica (electrode area: 0.264 cm^2) working electrode covered by the metal complex film, a Pt wire counter electrode, and an Ag/Ag⁺ (10 mM AgClO₄ in 0.1 M *n*Bu₄NClO₄-MeCN) reference electrode in a standard one-compartment cell. Cyclic voltammetry and PSCA were performed by using ALS 650DT electrochemical analyzers. All experiments were carried out in 1 M *n*Bu₄ClO₄/CH₂Cl₂ argon atmosphere[6].

V. RESULTS AND DISCUSSION

In cyclic voltammograms of 3 layered wire (Figure 7), two reversible redox peaks assigned to terminal ferrocene (0.28 V vs. Ag/Ag⁺) and Fe(tpy)₂ (0.90 V) were observed. Also, by the integration of the faradic current of these redox species, surface coverage was calculated. For a 2 layered wire, surface coverage for ferrocene and Fe(tpy)₂ were $1.82 \times 10^{-10} \text{ mol/cm}^2$ and $1.64 \times 10^{-10} \text{ mol/cm}^2$ respectively, and for 3 layered wire, it was $1.48 \times 10^{-10} \text{ mol/cm}^2$ and $2.83 \times 10^{-10} \text{ mol/cm}^2$ respectively. For 2 layered wire the ratio of surface coverage of Fe(tpy)₂ to Fc should be 2:1 in ideal case, confirming the presence of two

Fe units for every Fc unit. However, the experimental ratio was 0.9:1 for 2 layered wire. Similarly, for 3 layered wire the ideal ratio should be 3:1 but the experimental ratio was 1.9:1. This deviation could be attributed to the uneven wire length, resulting from the partial complexation of bridging ligand..

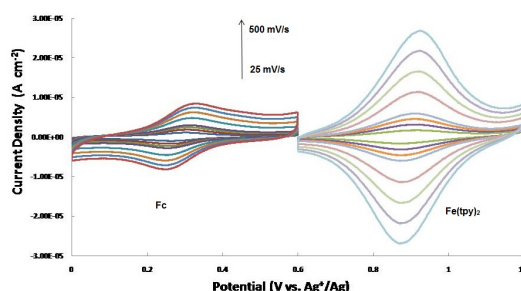


Figure 7: Cyclic voltammograms of Au-[AFe(LFe)₂T] at scan rate = 25, 50, 75, 100, 200, 300, 400 and 500 mV/s

The peak current (both anodic and cathodic) were plotted against the scan rate for Fe(tpy)₂ and ferrocene (Figure 8). The linear relationship between peak currents and scan rates, suggests that the linear Fe(tpy)₂ molecular wires were immobilized on the gold surface, and their bottom-up extension was successful.

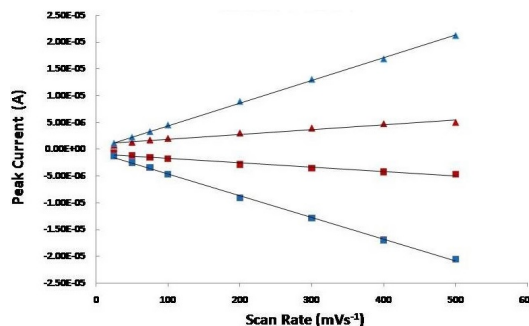


Figure 8: Peak currents vs. scan rate, for positive (triangle) and negative (square) peak of Ferrocene (Red) and Fe(tpy)₂ (Blue)

Chronoamperometric analysis was also done but no substantial result was inferred from the analysis because of uneven length of wires.

VI. PERSPECTIVE

The preparation of wires of uneven lengths could be due to several factors. Major factor responsible for this behavior is very low solubility of new bridging ligand in solvents used for wire preparation. Alkyl groups can be attached to the ligands in order to increase van der Waals interaction and hence increase solubility[5]. Moreover, other solvents which can dissolve the bridging ligand effectively will allow us to fabricate molecular wires easily. Also, carrying out reaction at high temperature can be effective for facilitating complexation between bridging ligand and Fe which can lead to uniform wire growth.

VII. CONCLUSION

The research was basically focused on the development of a new bridging ligand for the high electron transfer within bis(terpyridine) metal complex wire. The bridging ligand was successfully synthesized and nanowires containing bridging ligand were prepared. Nanowires were analyzed by cyclic voltammometry and PSCA and it was concluded that partial complexation of the bridging ligand took place, leading to wires of uneven length. Several factors responsible for this behavior were asserted and new

ways for dealing with enhancing complexation of bridging ligand to form multilayered wire were proposed.

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