Synthesis and Redox Behavior of Biferrocenyl-Functionalized Ruthenium(II) Terpyridine Gold Clusters

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Spectroscopic and electrochemical characterizations of ferrocene- and biferrocene-functionalized terpyridine octanethiolate monolayer-protected clusters were investigated. The electrochemical measurements of Ru2+/3+ coordinated with 4-ferrocenyl-2,2'-6,2''-terpyridine and 4-biferrocenyl-2,2'-6,2''-terpyridine complexes were dominated by the Ru2+/3+ oxidation potentials, indicating that there is an interaction between the Ru2+ and Fe3+ metal centers. The coordination of the Ru2+ metal center with 4-ferrocenyl-2,2'-6,2''-terpyridine and 4-biferrocenyl-2,2'-6,2''-terpyridine leads to an intense [(d(π)π)Ru] → [(d(π)π)Ru](π*terpy)] transition in the visible region. The [(d(π)π)Ru] → [(d(π)π)Ru](π*terpy)] transition observed at ~510 nm revealed that there was a qualitative electronic coupling between metal centers. The coordination of the Ru2+ transition metal center lowers the energy of the π*terpy orbitals, causing this transition.

Introduction

This paper describes a synthetic pathway to the formation of stable biferroceny-functionalized terpyridine-alkanethiolate monolayer-protected Au clusters (MPCs). It also describes their spectroscopic and electrochemical characterizations. The investigation of alkanethiolate Au-based monolayers includes examples of ferrocenyl alkanethiols (Fc(CH2)nSH, Fc = (C5H5)Fe(C5H4) ),1-3 carbonyl-functionalized ferrocenyl alkanethiols (FcCO(CH2)nSH and FcCO2(CH2)nSH),4-12 and carbonyl-functionalized biferrocenyl alkanethiols (BifcCO(CH2)nSH, Bifc = (C5H5)2Fe(C5H4) ). Very recently, we have reported ferrocenyl alkanethiol (Bifc(CH2)nSH) Au-based monolayers.16

The pioneering studies of electroactive self-assembled monolayers (SAMs) of ferrocene-terminated alkanethiols coadsorbed with unsubstituted n-alkanethiols on evaporated gold films were reported by Chidsey.4,17 Monolayers containing low concentrations (mole fraction yFe ≤ 0.25) of alkanethiols linked to ferrocene by a polar ester group (FcCO2(CH2)nSH) coadsorbed with CH3(CH2)nSH (n = 7, 9, 11) showed thermodynamically ideal surface electrochemistry. At low mole fractions, Chidsey suggested that the ferrocene groups were homogeneous and noninteracting. At higher mole fractions of the electroactive thiol in the adsorption solution, the resulting cyclic voltammograms broadened, developed an asymmetry, and finally developed an additional set of peaks as the amount of ferrocene was increased. Chidsey suggested that the breakdown of the thermodynamically ideal behavior of this system is probably due to a combination of interactions between ferrocene sites and the inhomogeneity of those sites at higher surface contractions. The use of ferrocene-terminated thiols (Fc(CH2)nSH) in which the ferrocene is attached directly to the polymethylene chain without a polar ester group led to broadened electrochemical features, even at the lowest fraction (yFe = 0.05) examined. This highly nonideal behavior at low surface coverage suggested a strong interaction between the ferrocene groups, which was perhaps due to aggregation.

Following the report by Brust et al. on the synthesis of gold clusters stabilized by monolayers of alkanethiolate ligands,18,19 Murray et al. launched an investigation of...
their synthesis to find the core size and the chemical, electrochemical, structural, and physical properties in ferrocenyl alkaneolthiolate Au clusters.\textsuperscript{8–12} The voltammetric results showed that ferrocenyl alkaneolthiolate Au clusters not only exhibited ferrocene electrochemistry but also exhibited a double layer charging phenomenon analogous to that of a metal electrode/solution interface. The cyclic voltammetry (CV) results revealed that the physisorption of clusters acted as tiny electrodes on the working electrode. Recently, the design of new bis-2,2′:6′,2″-terpyridine (terpy–terpy) ligands created by connecting two terpyridine (terpy) moieties via a rigid spacer attached to their 4′-position shows a surge in interest, owing to their great utility in the field of molecular electronics. As artificial photosynthesis,\textsuperscript{20–24} The terpy–terpy ligands that have been prepared and used further to make dinuclear transition metal complexes are illustrated in Chart 1.\textsuperscript{25–28}

Numerous studies on transition metal 2,2′:6′,2″-terpyridine (terpy) complexes exhibiting luminescence from metal-to-ligand charge-transfer (MLCT) excited states have been reported. The complexes formed between terpy and Ru\textsuperscript{2+} are normally weakly luminescent at room temperature, but attaching a functionalized group at the 4′-position provides the desired emission. It has been shown that if the Ru\textsuperscript{2+} terpy complex substituted an alkenylene group at the 4′-position of the terpy moiety, it could possess a room-temperature luminescence lifetime ($\tau_L = 565$ ns) 1000-fold longer than that of the Ru(terpy)$_2$\textsuperscript{2+} complex ($\tau_L = 0.56$ ns) in deoxygenated CH$_3$CN at 25 °C.\textsuperscript{31}

The preparation of 4′-ferrocenyl-2,2′:6′,2″-terpyridine (fcterpy) was reported,\textsuperscript{39,40} and cyclic voltammetric measurements of its Ru\textsuperscript{2+} metal complexes ([Ru(terpy)(fcterpy)]\textsuperscript{2+} and [Ru(fcterpy)$_2$]\textsuperscript{2+}) indicated that the Ru\textsuperscript{2+/3+} and ferrocenium/ferrocene redox couple at ~1.3 and ~0.6 V versus Ag/AgCl, respectively. Due to the fact that electronic coupling between the Ru\textsuperscript{2+} and ferrocenyl center is small, attachment of a ferrocene moiety to the 4′-position of terpy has minimal influence on the electrochemical properties in comparison with its monomeric components.\textsuperscript{41} In addition to the $\pi_{terpy}$–$\pi_{terpy}$ absorptions (240–280 nm) and the d$_{Ru-terpy}$ MLCT absorption (~480 nm), the [Ru(terpy)(fcterpy)]\textsuperscript{2+} and the [Ru(fcterpy)$_2$]\textsuperscript{2+} complexes exhibited an unusual [(d($\pi$fc)\textsuperscript{2}$\rightarrow$ d($\pi$fc)$\pi_{terpy}$ Ru)]$\pi_{terpy}$ Ru MLCT absorption at ~510 nm.\textsuperscript{41}

Very recently, our interest in the design of molecular electronic wire has focused on how to arrange the redox-active subunits. It is hoped that it will be possible to control transfer or store information along the wire. We have prepared a series of molecular wires derived from terpyridines bridged by a ferrocenyl spacer.\textsuperscript{42} Due to the $\pi_{terpy}$–$\pi_{terpy}$ transition, the binuclear biferrocene appears to be promising bridge that could ensure fast and quantitative transfer of energy within the array. We recognized that the biferrocene ligand usually employed in mixed-valence chemistry was not readily applicable to structural variations and would be a very good system for systematic work. The spectroscopic measurements for mixed-valence biferrocenium showed that electron transfer in this system was quite easy.\textsuperscript{33}
Rotello’s research group has recently synthesized nanoparticles bearing terpyridine ligands and studied their self-assembly using a variety of transition metals. The present paper describes the first step in the preparation of 4-ferrocenyl-2,2′,6′,2″-terpyridine and 4′-biferrocenyl-2,2′,6′,2″-terpyridine ruthenium(II) terpyridyl-octanethiolato complexes (1 and 2 in Scheme 1) and studies of the self-assembly of 1 and 2 chemisorbed on Au nanoparticles. Expansion of this study to the synthesis of molecular wire assembled on a gold surface is underway and will be reported in due course.

Experimental Section

General Information. The preparations involving air-sensitive materials were carried out by using standard Schlenk techniques under an inert atmosphere of N2. Chromatography was performed on neutral Al2O3 (act. III). Dried CH2Cl2 and THF were distilled from P2O5 and Na, respectively. Samples of Ru(DMSO)4Cl2,45 dibromobiferrocene,46 and 4-ferrocenyl-2,2′,6′,2″-terpyridine were prepared according to the literature procedure. All other chemicals used were reagent grade and used as received. Ferrocene- and biferrocene-functionalized terpyridine octanethiolatemonolayer-protected clusters (MPCs 3 and 4) were prepared as illustrated in Scheme 1. Octanethiolated Au MPCs (AuC8) were prepared as described by Murray.11

Synthesis of Biferrocenecarboxaldehyde. At −78 °C, 4.7 mL of n-BuLi (1.6 M in hexane, 7.2 mmol) was added under nitrogen to the dried THF (30 mL) solution of dibromobiferrocene (1.80 g, 28 mmol). The resulting solution was stirred at −78 °C for 1 h. DMF (0.25 mL) was then added, and the solution was stirred at −78 °C for 1 h. Water was then added, and the mixture was extracted with CHCl3. The combined extracts were dried over MgSO4 and concentrated by means of a rotary evaporator. The residue was then chromatographed on Al2O3 (act. III). Elution with hexan/CH2Cl2 (1/1) gave the desired compound with a yield of 28%. Anal. Calcd for C21H18Fe2O9H2O: C, 60.62; H, 4.84.

Synthesis of Dichloro(DMSO)(4′-biferrocenyl-2,2′,6′,2″-terpyridine)Ru(II). An ethanol solution (10 mL) of Ru(DMSO)Cl2 (0.140 g, 0.29 mmol) and fcterpy[Ru(DMSO)Cl2] (0.126 g, 0.3 mmol) was refluxed for 15 h under N2. After cooling to room temperature, the precipitate was collected by filtration and the crude product was washed with ether several times. The crude product was used without any further purification. The yield was ~72%. 1H NMR (DSMO-d6): δ 3.86 (dd, 2H, Cp), 3.89 (s, 5H, Cp), 4.38 (dd, 2H, Cp), 4.54 (dd, 2H, Cp), 4.69 (dd, 4H, Cp), 5.33 (dd, 2H, Cp), 7.78 (dd, 2H, Py), 8.17 (dd, 2H, Py), 8.61 (s, 2H, Py), 8.75 (dd, 2H, Py), 9.01 (dd, 2H, Py). Mass spectrum (ESI-M): m/z at m/z 850.

Synthesis of Dichloro(DMSO)(4′-biferrocenyl-2,2′,6′,2″-terpyridine)Ru(II). An ethanol solution (10 mL) of Ru(DMSO)Cl2 (0.140 g, 0.29 mmol) and fcterpy[Ru(DMSO)Cl2] (0.126 g, 0.3 mmol) was refluxed for 15 h under N2. After cooling to room temperature, the precipitate was collected by filtration and the crude product was washed with ether several times. The crude product was used without any further purification. The yield was ~72%.

Synthesis of 8(2,2′,6′,2″-terpyridine-4-yl)octanethiol. Functionalized terpy thiol was prepared through a similar synthetic route described in the literature with some slight modifications.44 Briefly, the 1,8-diiodoacetone was converted to 8(2,2′,6′,2″-terpyridine-4-yl)-1-iodoacetone by treatment with 4′-hydroxy-terpyridine and K2CO3 in acetonitrile, and the resulting solution was then refluxed for 24 h. The halide group was then replaced by treatment with NaSH in THF and refluxed for 8 h under N2 to create the desired terpy thiol.

Synthesis of 1. The ferrocene thiol derivative 1 (illustrated in Scheme 1) was prepared by reacting terpy thiol (21.5 mg, 0.022 mmol) and fcterpy[Ru(DMSO)Cl2] (29.5 mg, 0.044 mmol) in ethanol (50 mL) and refluxing the resulting solution for 48 h under N2. After cooling to room temperature, the volume of the solution was reduced by one-half using a rotary evaporator. A saturated aqueous solution of NH4PF6 (2 mL) was then added to this dark-colored solution to produce a violet precipitate. The violet precipitate was washed several times with ethanol and purified by chromatography. Elution with ultrapure water as eluent with the desired compound with a yield of 32%. Anal. Calcd for C50H38Fe2N4O4P: FeN2O (tetrakis(acetylacetonate)) RuS2-2H2O: C, 49.62; H, 3.92; N, 5.99; P, 3.28; S, 2.62. Found C, 49.76; H, 3.92; N, 5.99; P, 3.28.

Synthesis of 4′-Biferrocenyl-2,2′,6′,2″-terpyridine (biferrocenyl-terpyridine). The biferrocenyl-terpyridine was prepared in a fashion similar to that of the tetracyclop.40 Anal. Calcd for C50H38Fe2N4O4P: FeN2O (tetrakis(acetylacetonate)) RuS2-2H2O: C, 67.85; H, 4.68; N, 6.79. Found: C, 68.53; H, 4.57; N, 6.54. 

Acknowledgments

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at 138 °C. When the color of this solution changed from brown to dark red, the solution was heated further at 110 °C for an additional 5 h. The change in color also included a size evolution. The solvent was removed in a rotary evaporator (under 50 °C) followed by washing several times with ethanol and acetone. The Au MPCs created by using the heating treatment had average core diameters of approximately 4.5 nm (measured by transmission electron microscopy (TEM)).

**Synthesis of Au MPCs 3 and 4.** A mixture containing octanethiol-modified Au clusters (50 mg) and derivative 1 or 2 (10 mg) in a 5 mL toluene/CH₂Cl₂ (3:7) solution was stirred at room temperature for 48 h. The solvent was removed under a vacuum. The resulting product was cleaned by washing with hexane and acetone, and it was then suspended in acetone and isolated with a centrifuge. This procedure was repeated several times in order to obtain purified modified Au MPCs.

**Electrochemical Measurements.** Cyclic voltammetry was performed using a BAS 100W system. The reference electrode was Ag/AgCl in a saturated KCl solution. The CV measurements were carried out in a standard three-compartment cell under N₂ at 25 °C equipped with a Pt counter electrode, glassy carbon working electrode, and Ag/AgCl reference electrode in a CH₂Cl₂/CH₃CN (3:7) solution containing a 0.1 M (n-C₄H₉)₄NPF₆ elec-

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trolyte. Under these conditions, ferrocene showed a reversible redox process at $E_{1/2} = 0.44 \text{ V}$.  

**Physical Methods.** The $^{1}H$ and $^{13}C$ NMR spectra were run on a Varian UNITY INOVA-500 spectroscope. The UV spectra were obtained with a Hitachi U-4000 spectroscope. Transmission electron microscopy was performed in a Philips CM-200 TWIN TEM microscope. The nanoparticles dissolved in CH$_2$Cl$_2$ solution were then dropped into a 200 mesh carbon-coated copper grid sample holder, followed by natural evaporation at room temperature. 

**Results and Discussion**

In the following sections, the characterization data of MPCs using TEM, UV-vis, and NMR techniques are discussed first, followed by the electrochemical measurements of MPCs.

**Characterizations of MPCs 3 and 4.** The biferrocenyl MPCs were characterized by using several techniques: TEM for particle size and shape, UV-vis for particlesize, and NMR for adsorption of biferrocenyl thiols.

TEM Imaging. The Au MPCs have 2.2 $\pm$ 0.7 nm average core diameters estimated by TEM. The ~2 nm particles were used to induce size and shape evolution with heating treatment. The Au MPCs with heating treatment have 4.5 $\pm$ 0.3 nm core diameters estimated by TEM. The TEM imaging of biferrocenyl-functionalized MPCs showed an average core size of 4.5 $\pm$ 0.2 nm. A representative TEM micrograph is shown in Figure 1. The particle sizes appear uniform with a narrow distribution.

UV-Vis Measurement. Optically, both intensity and energy of the surface plasmon (SP) resonance bands of nanoparticles have been known to be strongly dependent on size. Figure 2 shows a set of UV-vis spectra of 3 and 4. The spectrum for the 4.5 nm octanethiolate MPCs showed an identifiable SP band at 515 nm. The shape and position of this band are in agreement with those previously reported. Spectra of biferrocenyl thiocarbamate MPCs exhibited a significant change in the intensity for the SP band at 520 nm. The feature of the SP band is in agreement with those obtained for 4–6 nm Au nanoparticles.

NMR Spectroscopic Analysis. The solution NMR technique has been used to confirm an important question, which was whether the organic shell was functionalized by 1 and 2. Figure 3 shows the $^{13}C$ NMR spectra for the AuC$_8$, ferrocene-functionalized MPCs 3 and biferrocenyl-functionalized MPCs 4. The high field (10–40 ppm) peaks in Figure 3 established the resonances as coming from the phenyl and terpyridine groups in an octanethiol. The confirmation of the functionalization came from the low field peaks at 60–80 ppm and 110–170 ppm, which were established as the resonances of the ferrocenyl and terpyridine groups, respectively. It was interesting to note that the biferrocenyl alkane thiocarbamate gave sharper NMR signals at room temperature in comparison with the octanethiolate MPCs. It is suggested that the faster electron relaxation caused by the Fe centers decreases the efficiency of the nuclear relaxation mechanism, lengthening $T_1$ for the nucleus and causing the line to appear sharper.

**Electrochemical Measurements.** The electrochemical parameters for 1–4 and related compounds obtained from the CV are summarized in Table 1. The voltammograms of 3 and 4 are shown in Figure 4. As expected, the redox behavior of 1–4 was dominated by the Ru$^{2+}$/Ru$^{3+}$ redox couple (E$_{1/2}$ at $\approx 1.3 \text{ V}$), the Fe$^{2+}$/Fe$^{3+}$ redox couple (E$_{1/2}$ at $\approx 0.6$ and $\approx 0.9 \text{ V}$), and the terpy/terpy$^\ast$/terpy$^{2\ast}$ redox couple (E$_{1/2}$ at ca. $-1.2$ and ca. $-1.4 \text{ V}$). Making a comparison of the E$_{1/2}$ values of Ru$^{2+}$-coordinated ferrocenylterpy and biferrocenylterpy* (1 and 2) with the corresponding ferrocenylterpy and biferrocenylterpy free ligand revealed that there was a qualitative exchange of information within the array. The negative shift of the E$_{1/2}$ values ($-0.02 \text{ V}$) for the terpyferrocenyl/terpyferro- cenium redox couples upon the coordination of Ru$^{2+}$ with free ferrocenylterpy and biferrocenylterpy ligands indicated that there was an interaction between Ru$^{2+}$ and Fe$^{2+}$ centers. Furthermore, there was an appreciable variation ($\approx 0.05 \text{ V}$) detected in the potentials associated with free ferrocenylterpy and biferrocenylterpy ligands.

![Figure 1. TEM imaging of biferrocene-functionalized MPCs 4.](image_url)

Table 1. CV Data of 1–4 and Related Compounds with a Scan Rate of 100 mV s$^{-1}$

<table>
<thead>
<tr>
<th>Compd$^a$</th>
<th>$\text{Ru center}$</th>
<th>$\text{Fe center}$</th>
<th>$\text{terpy center}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{1/2}$ (V)$^b$</td>
<td>$\Delta E_{1/2}$ (mV)$^c$</td>
<td>$E_{1/2}$ (V)$^b$</td>
</tr>
<tr>
<td>fc</td>
<td>0.46</td>
<td>70</td>
<td>0.28</td>
</tr>
<tr>
<td>bifc</td>
<td>0.45</td>
<td>73</td>
<td>&lt; -1.7</td>
</tr>
<tr>
<td>fctpy</td>
<td>1.28</td>
<td>121</td>
<td>0.62</td>
</tr>
<tr>
<td>bifctpy</td>
<td>1.33</td>
<td>119</td>
<td>0.48</td>
</tr>
<tr>
<td>1</td>
<td>1.32</td>
<td>90</td>
<td>0.68</td>
</tr>
<tr>
<td>3</td>
<td>1.37</td>
<td>77</td>
<td>0.58</td>
</tr>
<tr>
<td>4</td>
<td>1.37</td>
<td>77</td>
<td>0.58</td>
</tr>
</tbody>
</table>

$^a$ fc, ferrocenyl; bifc, biferrocenyl; fctpy, 4-ferrocenyl-2,2′,6,6′-terpyridine; bifctpy, 4-biferrocenyl-2,2′,6,6′-terpyridine. $^b$ All half-wave potentials are referred to the Ag/AgCl electrode in CH$_2$Cl$_2$/CH$_3$CN (3:7). $^c$ Peak to peak separation between the resolved reduction and oxidation wave maxima. $^d$ Peak separation between two redox waves.

with the Ru$^{2+}$/Ru$^{3+}$ redox couples for 1 and 2. This was possible due to the back-bonding of the Fe$^{2+}$ metal center to the terpy ligand. Furthermore, the decreasing of the $\Delta E_{1/2}$ value from 0.43 V in biferrocenylterpyridine to 0.38 V in 2 indicates that the magnitude of Fe–Fe interaction changed significantly on the coordination of the Ru$^{2+}$ ion. The zero-point energy difference between the two vibronic states of biferrocenylterpy was similar to that of 2, which was reasonable in terms of the similar environmental effect. Consequently, the smaller value of $\Delta E_{1/2}$ in 2 gave an indication of smaller Fe–Fe interactions. A comparison of $E_{1/2}$ values of 3 and 4 with the corresponding $E_{1/2}$ values of 1 and 2 revealed a positive shift of potential on the chemisorption of 1 and 2 on the surface.

Biferrocene takes a two-step one-electron redox process with the formation of the mixed-valence state. Nishihara reported\cite{13-15} the electrochemical properties of the SAMs of BifcCO(CH$_2$)$_n$SH on Au electrodes and of BifcCO(CH$_2$)$_n$SH-modified Au clusters. The BifcCO(CH$_2$)$_n$SH-modified Au cluster underwent a two-step one-electron redox process in CH$_2$Cl$_2$ solution. However, the shape of the voltammogram changed gradually during the potential scans, and it finally converted into one broad redox wave. However, this is not what was observed for 3 and 4. Repeat scanning did not change the voltammograms of 3 and 4, showing that these MPCs were stable to electrochemical cycling. For 3 and 4, the redox waves were symmetric. They also had a small splitting between the oxidation and reduction waves for Fe$^{2+}$/Fe$^{3+}$ and terpy/terpy$^2-$ redox couples. Furthermore, the peak current was proportional to the scan rate ($\nu$). This was in contrast to the $\nu^{1/2}$ dependence observed for Nernstian waves of diffusing species. These factors were all consistent with most of the current arising from reaction of an adsorbed layer of MPCs.

As given in Table 1, the $\Delta E_{p}$ values of the various redox centers correspond to the standard electron-transfer rate constants; thus, the larger the $\Delta E_{p}$, the smaller the electron-transfer rate constant.\cite{20} Another interesting finding was that the $\Delta E_{p}$ value of the second redox wave (terpy/terpy$^2-$ redox couple; $E_{1/2}$ at $-1.42$ V for 3 and at $-1.36$ V for 4) was always greater than that of the first terpy/terpy$^-$ redox wave ($E_{1/2}$ at $-1.20$ V for 3 and at $-1.10$ V for 4). As the charge density of the terpy moiety increases, the electron-transfer rate constant would be expected to decrease. However, the first Fe$^{2+}$/Fe$^{3+}$ redox wave at 0.58 V for 4 showed a larger $\Delta E_{p}$ value (42 mV) than the second Fe$^{2+}$/Fe$^{3+}$ redox wave at 0.89 V ($\Delta E_{p} = 23$ mV). In the case of 4, there were two ferrocenyl groups at different distances removed from the electrode. The key questions that arose from this observation were as follows: First of all, which ferrocenyl group is the first to be electrochemically oxidized? Also, by what mechanism does this oxidation occur? From the electron-withdrawing effect of terpy substituents and the smaller electron-transfer rate constant (larger $\Delta E_{p}$ value) for the first Fe$^{2+}$/
Fe$^{3+}$-redox couple in 4 ($E_{1/2}$ at 0.58 V), it would be suggested that the first oxidation in 4 occurs at the free ferrocenyl moiety (at a distance further removed from the electrode).

The mechanism is illustrated schematically in Figure 5 (mechanism a). One possible mechanism by which such an oxidation process could occur is called “electron hopping” and is illustrated schematically in Figure 5 (mechanism b). For a direct electron-transfer mechanism, the oxidation process has been initiated through appropriate control of the electrode potential, and the ferrocenyl moiety sitting further removed from the electrode surface becomes oxidized. Initially, the ferrocenyl site sitting directly on the electrode surface is still in the unoxidized Fe$^{2+}$ state. However, electron hopping cannot be excluded as a possible mechanism. As shown in Figure 5 (mechanism b), the ferrocenyl moiety sitting directly on the electrode surface was oxidized. Electrons can hop from the unoxidized ferrocenyl site to the Fe$^{3+}$ site at the electrode surface. Electron hopping occurs via a well-known electron self-exchange chemical process. Theoretically, the magnitude of the electronic coupling between two ferrocenyl sites plays an important role in determining the possibility of the electron hopping mechanism. It has been reported that there is a strong electronic interaction between the two Fe sites in mixed-valence biferrocenium salts. Biferrocene exhibited strong interactions between the metal orbitals and the $\pi$ system of the Cp rings, and electron delocalization could possibly have been caused by metal–ligand orbital overlap. An intervalence transition band in the NIR region has been observed for mixed-valence biferrocenium salts. The more positive shift of the first redox potential from 0.48 V in 2 to 0.58 V in 4 upon the chemisorption on the surface revealed the possible existence of the electron hopping mechanism.

In our previous report, the standard rate constant of the second Fe$^{2+}$/Fe$^{3+}$ redox wave was always greater than that of the first Fe$^{2+}$/Fe$^{3+}$ redox wave for a biferrocenyl-octanethiolate monolayer on an Au(111) surface. Theoretically, the interaction between the two centers would be expected to lead to a smaller standard rate constant for the second Fe$^{2+}$/Fe$^{3+}$ redox wave as the charge density of the biferrocenyl moiety increased. In the existence of the stronger Fe–Fe interaction, the oxidation potential of the second wave shifted to the higher voltage. The reduction potential of the second wave shifted to the lower voltage when the charge density of the biferrocenyl moiety caused by the oxidation of one of the ferrocenyl moieties increased. In other words, to explain the greater electron-transfer rate constant for the second Fe$^{2+}$/Fe$^{3+}$ redox wave in the case of the biferrocenyl-octanethiolate monolayer
on the Au(111) surface, the intramolecular electron hopping mechanism may have played a more important role in determining the magnitude of the electron-transfer rate constant. As shown in Figure 5, the ferrocenyl moiety that was sitting closer to the electrode surface became oxidized initially based on the electron-donating effect of octyl substituents. Electrons could then hop from the unoxidized ferrocenyl site to the Fe3+ site.

UV–Visible Spectroscopy. The UV–visible spectral data of 1–4 and relevant compounds are summarized in Table 2. The visible absorption bands at 325 nm (ε = 51 M-1 cm-1) and 440 nm (ε = 87 M-1 cm-1) of ferrocene were assigned to the 1A1g → 1Eg and 1A1g → 1Eg d-d transitions, respectively.51-53 In comparison with ferrocene, the absorption band at 450 nm (ε = 570 M-1 cm-1) for biferrocene was red-shifted, and the molar absorptivity was considerably enhanced. Attachment of a terpy to the ferrocene and biferrocene moieties had a significant influence on the d-d transitions. The visible bands at 459 nm (ε = 910 M-1 cm-1) for terpy and at 460 nm (ε = 2230 M-1 cm-1) for biferrocene were red-shifted relative to the ferrocene and biferrocene, which was consistent with the electron-withdrawing character of terpy.52,53

As shown in Table 2, the visible spectra for compounds 1 and 2 were dominated by 1ε(dp)[3] → 1ε(dp)[p*terpyR] MLCT absorption bands at ~480 nm. These were assigned by analogy to the well-documented MLCT transitions found for [Ru(terpy)][PF6]2.54 (478 nm; ε = 14 000 M-1 cm-1), [Ru(terpy)(fcterpy)][PF6]2.54 (487 nm; ε = 15 000 M-1 cm-1), and [Ru(fcterpy)][PF6].54 (482 nm; ε = 15 000 M-1 cm-1).

As shown in Figure 6, broad structureless absorption bands at 510 nm (ε = 16 000 M-1 cm-1) for 1 and 510 nm (ε = 9700 M-1 cm-1) for 2 are apparent in the visible absorption spectra. In the case of Ru2+ transition metal complexes containing ferrocenyl moieties, an intense broad structureless band in the 520 nm region has been observed.21,41,57 For the [Ru(terpy)(fcterpy)]2+ and [Ru(fcterpy)]2+ compounds, bands at 515 nm (ε = 256 M-1 cm-1) and 526 nm (ε = 15 000 M-1 cm-1) were apparent.41 This band is assigned to the 1ε(dp)[p*terpyRu] → 1ε(dp)[p*terpyRu] transition.21 The intensity of this transition changes with the number of ferrocenyl substituents, and it disappears upon the oxidation of ferrocene. In this study, this band was not present in the parent compounds (fcterpy and biferrocenyl), but the coordination with Ru2+ metal centers in compounds 1 and 2 led to an intense transition in the visible region. The 1ε(dp)[p*terpyRu] → 1ε(dp)[p*terpyRu] transition observed at ~510 nm revealed that there was a qualitative electronic coupling between the Ru2+ and Fe3+ centers. The coordination of two Ru2+ transition metal centers lowered the energy of the p*terpy orbitals giving the 1ε(dp)[p*terpyRu] → 1ε(dp)[p*terpyRu] transition.

Conclusion

We have prepared functionalized 1-terpyridyl)ferrocene and 1-terpyridyl)bisferrocene ligands. Spectroscopic data show that the use of suitable metal ions such as Ru2+ will prove to be versatile in building molecular self-assembled monolayers on gold clusters. The potential shift of the E1/2 values associated with Ru2+/Ru3+ and Fe2+/Fe3+ redox couples and the decreasing of the ΔE1/2 value for the Fe2+/Fe3+ redox couples upon the coordination of the Ru2+ ion with free terpyridylferrocene and terpyridyliberrocene ligands indicated that there was an interaction between the Ru2+ and Fe3+ centers. Furthermore, the 1ε(dp)[p*terpyRu] → 1ε(dp)[p*terpyRu] transition observed at ~510 nm in 1 and 2 reveals that there is a qualitative electronic coupling between the Ru2+ and Fe3+ centers. Compounds of 4-ferrocenyl-2,2',6,2'-terpyridine and 4-biferrocenyl-2,2',6,2'-terpyridine potentially have the capability to coordinate transition metals, demonstrating their versatility in molecule assembly and the generation of various composites.

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