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Transition-Metal Tris-Bipyridines Containing Three Dithienylcyclopentenes: Synthesis, Photochromic, and Electrochromic Properties

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Designed prototype molecules for making a three-terminal single-molecule device, star-shaped Fe^{II}, Co^{II}, and Ru^{II} tris-bipyridine complexes containing three dithienylcyclopentenes, have been synthesized and characterized. All complexes displayed reversible photochromic behavior when irradiated with UV or visible light. The open form of these complexes could be cyclized electrochemically as revealed by cyclic voltammetric studies and bulk electrolysis experiments.

Introduction

Because of their appealing photophysical and electrochemical properties, transition-metal polypyridine complexes have been widely employed in building nanoscale molecular architectures to perform light and redox-related functions.[1] These materials have recently gained renewed interest in the form of applications as molecular wires for molecular electronics, including single-molecule devices.[2] Dithienylethene derivatives are one of the most intensively studied photochromic materials, which can "switch" a molecule between a nonconjugated "open" form and a conjugated "closed" form by irradiation with specific wavelengths of light.[3] In most cases, they display high photoreversibility, good fatigue resistance, and thermal irreversibility. Recent studies on the photochromic properties and conductivity switching of dithienylethene derivatives attached to an electrode surface show promise for these materials to be used in solid state devices.[4]

To meet the demand for miniaturization of electronic components, we have recently begun investigating the construction of transition-metal polypyridines-based architectures which display reversibly switchable properties. A series of linear molecules composed of transition-metal bisterpyridines and photochromic dithienylcyclopentenes have been designed and synthesized.[5] The photochromic and electrochromic behaviors of those molecules were found to be highly dependent on the metal species and the arrangement of different components. We report, herein, the synthesis as well as photochromic and electrochromic properties of iron, cobalt, and ruthenium tris-bipyridines **1**−**3** containing three switchable arms (Figure 1). It should be mentioned that a great number of photochrome-metal hybrids have been documented in the literature,[6] and

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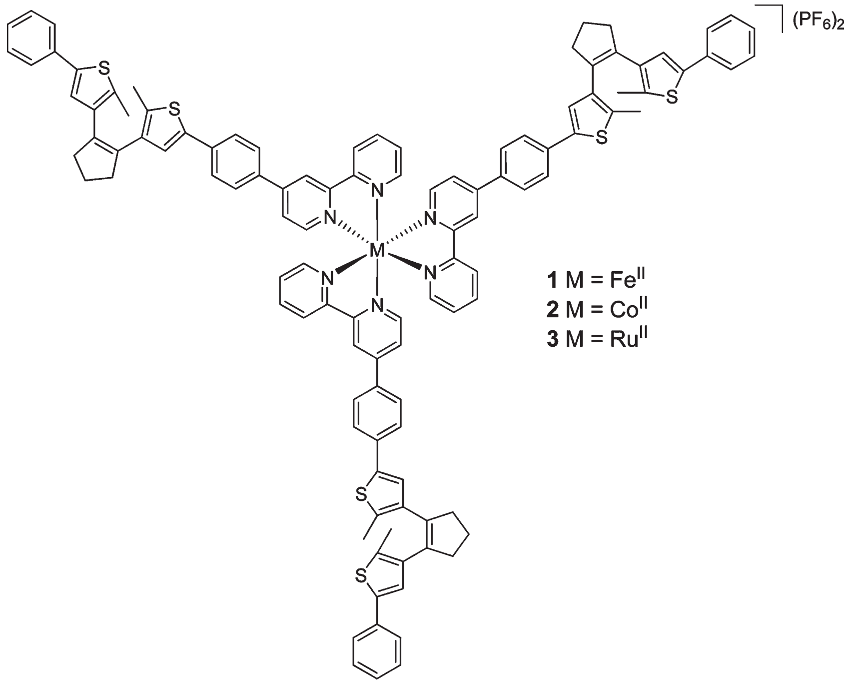


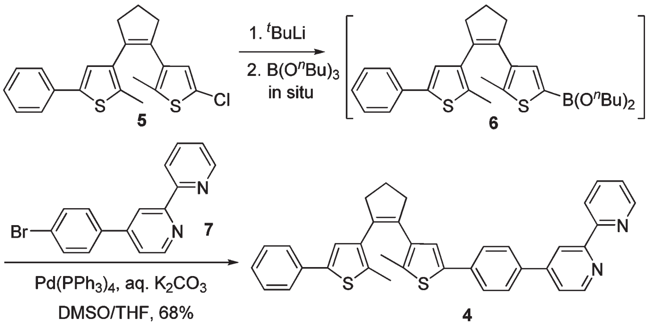
Figure 1. Transition-metal tris-bipyridines **1**−**3**.

many of them display both photochromic and electrochromic behaviors. Among them, transition-metal polypyridine complexes containing one or multi dithienylethene units have received much attention.[7] These complexes have been studied in switching luminescence, controlling electron transfer, modulating metal−metal communication, or constructing integrated memories or logic gates. However, few of them have dealt with their application to molecular electronics.[7c,7l] We believe that transition-metal complexes **1**−**3** could be used as the basis of three-terminal electronic devices[8] after attaching anchoring groups such as pyridine, thiolate, or isocyanide. The three side arms would be bound to source, drain, and gate electrodes, respectively, in a typical field-effect transistor (FET) configuration, with the metal center in the middle of the single molecular device. Electronic conduction through source and drain could be modulated by the reversible and stable redox states of the metal center and/or the open/closed forms of the dithienylethene bridges.

Results and Discussion

Synthesis. To prepare these complexes, we first synthesized the corresponding bipyridine (bpy) ligand **4** with a pendant dithienylcyclopentene unit, as outlined in Scheme 1. The known monochloride **5** was first lithiated with *t*-BuLi,[5b,9] followed by the addition of tributyl borate to give the monoboronic ester **6**. A Suzuki coupling between **6** and the bpy-containing phenyl bromide **7**[10] afforded the desired ligand **4** in moderate yield (68%). Direct complexation of $FeCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, and $Ru(DMSO)_4Cl_2$ with three equiv of **4** yielded **1**−**3**, respectively. Judging from the indistinct peaks from their ^1H NMR spectra, we believe these complexes were obtained as a mixture of all possible fac and mer isomers. However, this problem could be precluded if a 4,5-diazafluorene-derived[11] dithienylethene ligand were used, which will be a target of future work.

Scheme 1. Synthesis of the Dithienylcyclopentene-Containing Bipyridine Ligand **4**



Electronic Absorption and Photochromic Behaviors. The UV/vis absorption spectra of **1**−**4** were recorded (Figure 2). The spectrum of ligand **4**, in its open form, shows two bpy-based bands at 244 and 286 nm (Figure 2a). The shoulder at 335 nm is assigned to the $S_0 \rightarrow S_1$ transition of the dithienylcyclopentene unit. The small band at 550 nm is most likely from a small amount of the closed isomer present. However, this could not be removed with visible light. After irradiation at 330 nm for 10 min, the colorless solution turned purple, and a broad peak, centered at 545 nm, emerged. This suggests that an efficient open-to-closed isomerization of the dithienylethene unit takes place.[3,5,7] The corresponding

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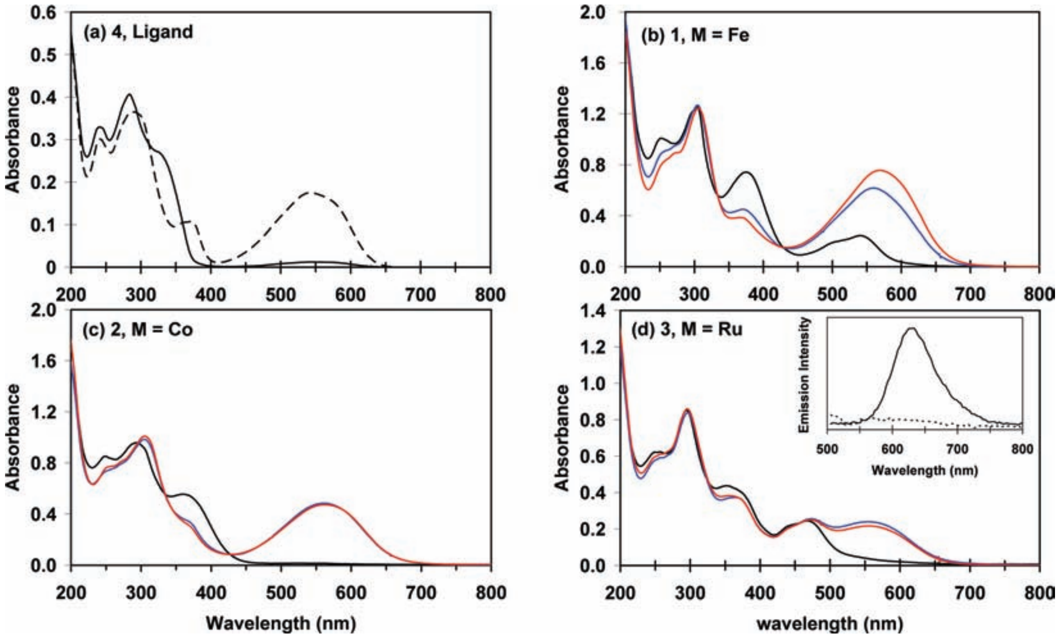

Figure 2. UV/vis absorption spectral changes of **1**−**4** at a concentration of 1 × 10^{-5} M. (a) Spectra of ligand **4** in *n*-hexane before (solid line) and after (dashed line) irradiation to the photostationary state (pss) at 330 nm for 10 min. (b) Spectra of Fe-complex **1** in acetonitrile before (black) and after (blue) irradiation to pss at 350 nm for 8 h. Red: spectrum of all-closed isomer of **1**. (c) Spectra of Co-complex **2** in acetonitrile before (black) and after (blue) irradiation at 350 nm for 10 min to the pss. Red: spectrum of all-closed isomer of **2**. (d) Spectra of Ru-complex **3** in acetonitrile before (black) and after irradiation at 350 nm for 10 min (blue) or at 470 nm for 15 min (red) to the pss. Inset: emission spectral change of **3** in acetonitrile at a concentration of 1 × 10^{-5} M before (solid line) and after irradiation at 350 nm to the pss (dashed line). The excitation wavelength was 450 nm.

^{1}H NMR analysis showed a quantitative conversion to the closed form (see the Supporting Information). The closed form underwent the reversible conversion back to the open form after irradiation at 500 nm for 10 min.

The open-to-closed photoisomerization of the Fe^{II} complex **1** also proceeds, albeit with a much longer response time. The open isomer of **1** displays a typical $S_0 \rightarrow S_1$ transition of the dithienylcyclopentene unit at 378 nm and a metal-to-ligand-charge-transfer (MLCT) band at 543 nm. It is evident that, when the solution was irradiated at 350 nm for 8 h to the photostationary state (pss) (blue line in Figure 2b), the $S_0 \rightarrow S_1$ transition of the dithienylcyclopentene unit decreased significantly and a broad absorption band between 440 and 700 nm was concomitantly enhanced. Given the large number of multidithienylethene systems that have only one subunit being photoactive,[12] it would be necessary to determine the conversion efficiency of the open-to-closed isomerization of **1**. For this purpose,[13] an all-closed isomer of Fe-complex **1** was prepared from the closed isomer of ligand **4**, which was obtained by UV irradiation of its open isomer to the pss as described above. The absorption spectrum of this all-closed isomer at the same concentration is shown in red in Figure 2b. By comparing the absorbance of the red and blue traces at 600 nm, it is clear that around 70% of the open ligand in Fe-complex **1** has been cyclized upon UV irradiation to the pss.

In comparison to the slow photoconversion kinetics of the Fe^{II} complex **1**, the open isomer of the Co^{II} complex **2** was quickly transformed into the corresponding closed isomer upon irradiation at 350 nm for 10 min (blue in Figure 2c). A broad and intense band between 440 and 700 nm was observed, which originates from the $S_0 \rightarrow S_1$ transition of the closed dithienylcyclopentene unit. Using a similar method, an all-closed isomer of the Co^{II} complex **2** was prepared, and its absorption spectrum is shown in red in Figure 2c. It appears that most of the open dithienylethene units in **2** have been cyclized upon UV irradiation, which indicates that all three dithienylethene units are photoactive. The significantly sluggish photoconversion kinetics of the Fe^{II} complex **1**, in contrast to that of the Co^{II} complex **2**, may be caused by energy transfer from the dithienylethene unit to the low-energy ^{3}MC (metal centered, M = Fe^{II}) or ^{3}MLCT levels; while the Co^{II}-polypyridine complexes have no intense MLCT or d-d bands in the visible region. It is worth noting that, in the studies of azobenzene-conjugated transition-metal bisterpyridine complexes by Nishihara and co-workers,[14] Co^{II} complexes exihibited much more efficient trans-to-cis photoisomerization than the Fe^{II} analogue as well. When irradiated with visible light (470 nm), the closed form of the Co^{II} complex **2** underwent partially reversible photoisomerization back to the corresponding open forms (25−30%, Figure S9 in the Supporting

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(13) NMR spectral analysis is used in many other cases to estimate the conversion efficiency (see references 3 and 7). However, because of the presence of many possible isomers in our complexes, we were unable to obtain useful information for this purpose. We believe that the comparison of the absorption spectra of the all-closed isomer and the complex in the pss provides at least a qualitative, if not quantitative, sense of the conversion efficiency of different complexes. This method is also used in the case of the Co^{II} complex **2**, in which NMR data becomes even more complicated because of its paramagnetic nature.

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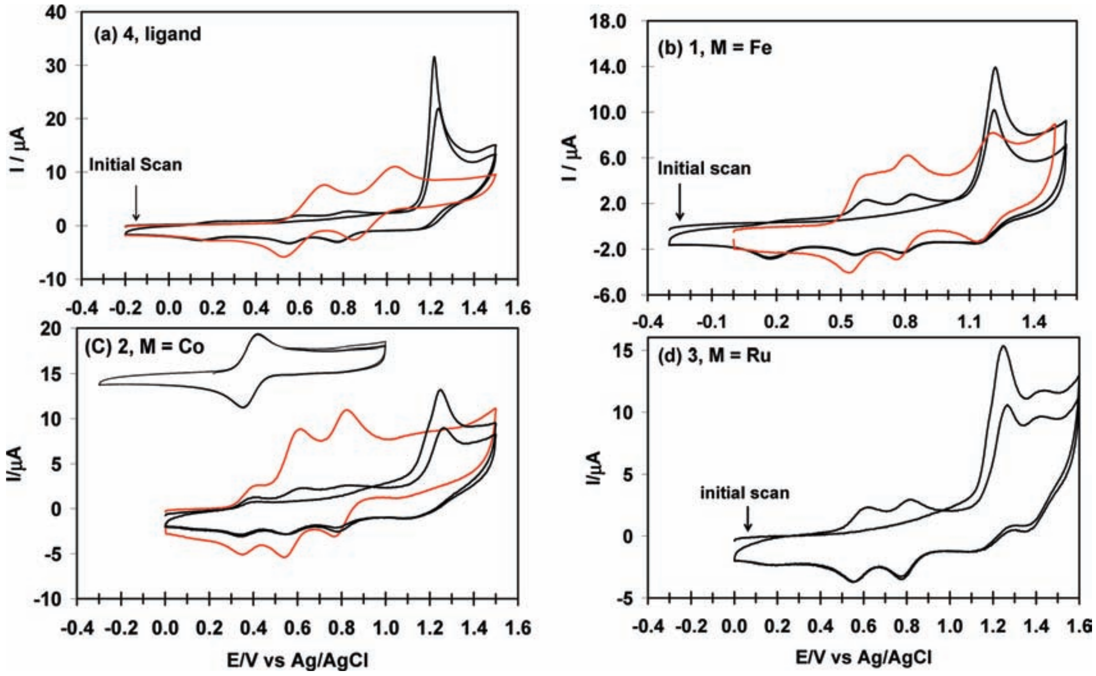

Figure 3. CV of (a) ligand **4** (2.0 mM in dichloromethane), red: closed isomer of **4**, (b) Fe^{II} complex **1** (0.3 mM), red: all-closed isomer of **1** (0.5 mM), (c) Co^{II} complex **2** (0.3 mM), red: all-closed isomer of **2** (0.5 mM), and (d) Ru^{II} complex **3** (0.3 mM) in acetonitrile containing 0.1 M Bu_4NClO_4 as the supporting electrolyte at a scan rate of 100 mV/s. The working electrode is a glassy carbon; the counter electrode is a Pt wire and the reference electrode is Ag/AgCl in saturated NaCl.

Information). In term of its stability, we did not observe any spectral changes after 10 h at room temperature in the dark. However, the closed form was gradually converted to the open form after heating at 70 °C over 20 h (Figure S10 in the Supporting Information), which, in turn, could be recyclized upon UV irradiation to the pss. Considering the relatively low efficiency of the photoinduced reopening transformation, the thermo-induced closed-to-open isomerization provides an alternative to reopen the closed form.

The photophysical properties of the Ru^{II}-containing complex **3** are different from those of **1** and **2**. Its ring-closure reaction can be sensitized either by the dithienylethene unit at 350 nm (blue line in Figure 2d), or by the MLCT band at 470 nm (red line in Figure 2d). As determined by ^1H NMR analysis (see the Supporting Information), 67% of the dithienylethene units are closed in the pss. This indicated that only two of the three dithienylethene units are photoactive. However, further experiments are needed to confirm this assertion. Sensitization of the dithienylethene unit by the MLCT band is likely a result of the intramolecular energy transfer from the triplet MLCT state to the dithienylethene-centered triplet state.[7a,15] However, cyclization of the Fe^{II}-containing complex **1** could not be triggered through irradiation of its MLCT band. It should also be noted that the emission of $[Ru(bpy)_3]^{2+}$ is completely quenched by the closed dithienylethene units (Inset, Figure 2d), which is again caused by the intramolecular energy transfer from ^{3}MLCT to the dithienylethene-centered triplet state.

Electrochemical Properties and Electrochromic Behavior. The electrochemical behavior of dithienylethene derivatives has received a great deal of attention.[16] The proper combination of substituents on the thienyl rings, and experimental conditions, can facilitate the electrochemical cyclization and cycloreversion reactions, making these materials electrochromic in addition to photochromic.[16] The electrochemical properties and isomerization reactions of ligand **4** and complexes **1**−**3** were studied by cyclic voltammetric (CV) analysis in dichloromethane and acetonitrile solutions, respectively. In the initial anodic scan of the free ligand **4** (Figure 3a), an irreversible wave, related to the oxidation of the two thienyl units at +1.22 V (vs Ag/AgCl), was observed. This was followed by two new reversible waves centered at +0.79 and +0.57 V in the reverse scan and subsequent scans. The latter two waves are in agreement with the stepwise oxidation of the two thienyl rings of the closed form of **4** (red line, Figure 3a).[5,16] All of these results suggest that an electrochemically induced cyclization of **4** occurred after oxidation of the thienyl rings.[5,16] Similar CV profiles were found when ligand **4** was coordinated to Fe^{II}, Co^{II}, or Ru^{II} ions (Figures 3b−d), with the metal centered redox couple at +1.18 ($Fe^{II/III}$), +0.36 ($Co^{II/III}$), and +1.38 V ($Ru^{II/III}$), respectively. The inset to Figure 3c shows the redox wave of $Co^{II/III}$ across the potential

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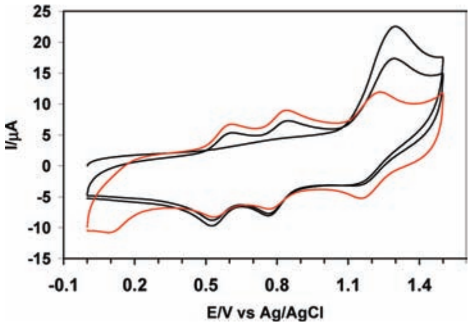

Figure 4. Change in CV profile of the Fe^{II} complex **1** (0.3 mM) upon electrolysis at +1.3 V vs Ag/AgCl. Black: before electrolysis. Red: after electrolysis. The working electrode is a glassy carbon disk (d = 3 mm) for the CV measurement and a high surface area graphite rod (d = 6 mm) for the electrolysis experiment; the counter electrode is a Pt wire and the reference electrode is Ag/AgCl in saturated NaCl.

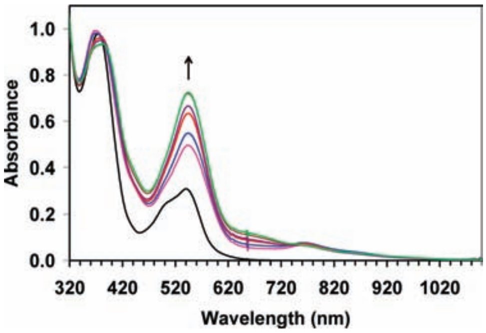

Figure 5. UV/vis absorption spectrum change of the Fe^{II} complex **1** (0.16 M) upon electrolysis of an acetonitrile solution containing 0.1 M of Bu_4NClO_4 at +1.2 V vs Ag/AgCl for 0.5, 1, 2, 4, 7, 10 min, respectively. The working electrode is an ITO-coated glass plate, the counter electrode is a Pt wire, and the reference electrode is Ag wire. A thin UV cell (l = 2 mm) was used in these experiments.

window from −0.3 V to +1.0 V, which clearly indicates that no electrochemical cyclization occurs except when the potential is scanned beyond +1.25 V. CV profiles of the all-closed isomer of the Fe^{II} **1** and Co^{II} complexes **2** are also shown for comparison (red lines in Figures 3b and 3c). It is interesting and puzzling that the Fe^{II} complex shows roughly a 1:1 peak ratio of the ligand-related response to the metal-related one; while this ratio is much higher in the case of the Co^{II} complex. Their differential pulse voltammetric (DPV) analyses, shown in Figures S6 and S7 in the Supporting Information, also yielded similar results. Further experiments are ongoing to address this difference, and will be reported elsewhere. The synthesis of the all-closed isomer of Ru^{II} complex **3** was not attempted, because of the visible light sensitivity and the harsh reaction conditions required.

The electrochemical ring closing reaction was further probed by electrolysis experiments and spectroelectrochemistry. Upon electrolysis of an acetonitrile solution of the open isomer of the Fe^{II} complex **1** at +1.3 V versus Ag/AgCl, the irreversible wave at +1.18 V, from the open isomer, disappeared (red line in Figure 4). Three redox waves corresponding to the oxidation of the two thienyl groups and the Fe^{II} center in the closed isomer, respectively, were observed. The change in the UV/vis spectrum of the open isomer of the Fe^{II} complex **1** at +1.2 V is shown in Figure 5. It is evident that a broadband around 550 nm is enhanced significantly, and the band at 360 nm decreased slightly, which is in agreement with the formation of the closed isomer. The emergence of a small new band at 760 nm could be assigned to a dicationic species generated after the electrochemically induced ring-closure of the dithienylethene part[16g] because this peak is also evident after holding the potential at +1.0 V during the spectroelectrochemical experiment of all-closed isomer of the Fe^{II} complex **1** (see Figure S8 in the Supporting Information).

Conclusions

In summary, a series of star-shaped transition-metal complexes with three dithienylcyclopentene-containing arms have been prepared and characterized. These complexes, especially the Co^{II} complex **2**, displayed attractive photochromic and electrochromic behaviors as determined from photoirradiation experiments and electrochemical analysis. Work is underway to prepare similar complexes with anchoring groups at the end of each arm to study them in break junctions and other devices.[17]

Experimental Section

Electronic Absorption and Emission Spectra and Irradiation Experiments. All optical ultraviolet−visible (UV/vis) absorption spectra were obtained using an HP 8453 diode array spectrometer at room temperature, with standard 1.0 cm quartz cells. The emission spectra were recorded on a Fluorolog 2 series spectrofluorometer of Spex industries, Inc. All samples were N_2-saturated before measurement. Irradiation experiments were carried out using a 200 W Mercury Xenon lamp as the light source, and the specific wavelength was selected with a monochromator.

Electrochemical Measurements. All cyclic voltammograms (CV) were taken using an Epsilon BAS CV-27 potentiostat. Three-compartment electrochemical cells (separated by medium-porosity sintered glass disks) with provision for gas purging were employed. All joints were standard taper so that all compartments could be hermetically sealed with Teflon adapters. A glassy carbon electrode with a diameter of 3 mm was used as a working electrode. The electrode was polished prior to use with 1 μm diamond paste (Buehler) and rinsed thoroughly with water and acetone. A large area platinum wire coil was used as the counter electrode. All potentials are referenced to a saturated Ag/AgCl electrode without regard for the liquid junction potential. All measurements were carried out at a scan rate of 100 mV/s, in 0.1 M of Bu_4NClO_4 (TBAP) as the supporting electrolyte.

Synthesis. All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Dry tetrahydrofuran was distilled from Sodium/benzophenone, and other solvents (analytical grade) were used without further purification. NMR spectra were recorded in the designated solvent on a Varian 300 or Varian 400 spectrometer. Spectra are reported in ppm values from residual protons of the deuterated solvent for ^1H NMR (7.26 ppm for chloroform and 1.92 ppm for acetonitrile) or from solvent carbon for ^{13}C NMR (77.00 ppm for chloroform). MALDI-TOF positive ion data were obtained with a Waters MALDI micro MX mass spectrometer run in reflection mode. HRMS-ESI data were obtained

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(17) (a) Park, J.; Pasupathy, A. N.; Goldsmith, J. I.; Soldatov, A. V.; Chang, C.; Yaish, Y.; Sethna, J. P.; Abruña, H. D.; Ralph, D. C.; McEuen, P. L. *Thin Solid Films* **2003**, *438−439*, 457. (b) Weibel, N.; Grunder, S.; Mayor, M. *Org. Biomol. Chem.* **2007**, *5*, 2343. (c) Joachim, C.; Gimzewski, J. K.; Aviram, A. *Nature* **2000**, *408*, 541. (d) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791.

with a Q-Tof Ultima mass spectrometer by Mass Spectrometry Center, SCS, University of Illinois. Elemental analysis was done by Robertson Microlit Laboratories, Madison, NJ. The preparation of monochloride **5** has been described previously.[5b,9] 4-(*p*-Bromophenyl)-2,2′-bipyridine **7** was prepared according to known procedures with slight modifications[9] (see the Supporting Information).

4-(4-(5-Methyl-4-(2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)thiophen-2-yl)phenyl)- 2,2′-bipyridine (4). To a solution of **5** (710 mg, 2.0 mmol) in tetrahydrofuran (THF, 30 mL) were added 1.5 mL of 1.7 M *t*-butyllithium (2.5 mmol) in *n*-pentane at room temperature. After 15 min, 1.0 mL of tributyl borate (4.0 mmol) was added. After stirring for another hour, the resulting reddish solution was used directly for the following reaction. To another Schlenk flask filled with 40 mL of degassed DMSO were added bpy ligand **7** (560 mg, 1.8 mmol) and $Pd(PPh_3)_4$ (22 mg, 0.02 mmol). After stirring for 15 min, 10 mL of 2.0 M saturated aqueous sodium carbonate solution (20 mmol) and 1.0 mL of ethylene glycol were added. The solution was stirred for another 15 min under bubbling, before the temperature was raised to 60 °C. To the mixture was then added the above prepared reddish solution in one portion. The mixture was stirred at 80 °C for 24 h. After cooling, 100 mL of ethyl acetate were added to dilute the mixture, followed by washing with water (30 mL × 2) and brine. Flash column chromatography on neutral alumina (ethyl acetate/hexane, 1:2) of the concentrated residue afforded 700 mg of **4** as a solid (68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.01 (s, 3H, Me), 2.05 (s, 3H, Me), 2.10 (m, 2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{CH_2}$), 2.87 (m, 4H, $\mathrm{C}\mathit{H_2}\mathrm{CH_2C}\mathit{H_2}$), 7.06 (s, 1H, CH), 7.13 (s, 1H, CH), 7.23 (m, 1H), 7.34 (m, 3H), 7.53 (m, 3H), 7.62 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.85 (td, J = 7.8, 1.5 Hz, 1H), 8.46 (d, J = 8.1 Hz, 1H), 8.72 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.37 (Me), 14.43 (Me), 22.91 ($\mathrm{CH_2}\mathit{CH_2}\mathrm{CH_2}$), 38.37 (2C, $\mathit{CH_2}\mathrm{CH_2}\mathit{CH_2}$), 118.38, 121.03, 121.15, 123.69, 123.82, 124.50, 125.17 (2C), 125.58 (2C), 126.88, 127.37 (2C), 128.55, 128.70 (2C), 132.07, 134.33, 134.38, 134.75, 135.13, 135.17, 136.26, 136.51, 136.83, 138.63, 139.63, 148.40, 149.04, 149.55, 155.97, 156.50. HRMS-ESI calcd. for $[M+H]^+$ ($C_{37}H_{31}N_2S_2$) 567.1938, found 567.1929.

Fe^{II} Complex 1. To a solution of ligand **4** (130 mg, 0.23 mmol) in 4 mL of dichloromethane was added a solution of $FeCl_2 \cdot 4H_2O$ (14 mg, 0.07 mmol) in 6 mL of methanol. The mixture was stirred at room temperature for 1 h. Then, an excess of NH_4PF_6 (200 mg, dissolved in 4 mL of methanol) was added. The brown precipitate was collected after filtration and washed with methanol and ether (110 mg, 77%). ^{1}H NMR (300 MHz, CD_3CN): δ 2.04 (s, 9H, 3Me), 2.08 (s, 9H, 3Me), 2.12 (m, 6H, $\mathrm{3CH_2}\mathit{CH_2}\mathrm{CH_2}$, overlapped with residual peak of solvent), 2.87 (t, J = 7.5 Hz, 12H, $\mathrm{3C}\mathit{H_2}\mathrm{CH_2C}\mathit{H_2}$), 7.17 (s, 3H, 3CH), 7.22−7.88 (m, 42H), 8.17 (m, 3H), 8.70−8.88 (m, 6H). MALDI-MS: 1757.71 for $[M - 2PF_6 + 2H]$ (calcd 1757.50), 1190.65 $[M - 2PF_6 - \text{ligand } \mathbf{4} + 2H]$ (calcd 1190.32). Anal. Calcd for $C_{111}H_{90}F_{12}FeN_6P_2S_6 \cdot 2H_2O$: C, 64.03; H, 4.55; N, 4.04. Found: C, 63.82; H, 4.25; N, 4.14. UV/vis (CH_3CN): λ_{max} (nm)/ε (10^5 M^{-1} cm^{-1}) 253 (1.01), 307 (1.26), 378 (0.74), 501 (0.19), 543 (0.24, MLCT).

Co^{II} Complex 2. To a solution of ligand **4** (130 mg, 0.23 mmol) in 4 mL of dichloromethane was added a solution of $CoCl_2 \cdot 6H_2O$ (17 mg, 0.07 mmol) in 6 mL of methanol. The mixture was stirred at room temperature for 30 min. Then, an excess of NH_4PF_6 (200 mg, dissolved in 4 mL of methanol) was added. The green precipitate was collected after filtration and washed with methanol and ether (115 mg, 80%). MALDI-MS: 1190.50 for $[M - 2PF_6 - \text{ligand } \mathbf{4} - H]$ (calcd 1190.30). UV/vis (CH_3CN): λ_{max} (nm)/ε (10^5 M^{-1} cm^{-1}) 251 (0.86), 296 (0.96), 369 (0.53). Anal. Calcd for $C_{111}H_{90}F_{12}CoN_6P_2S_6 \cdot 2H_2O$: C, 63.93; H, 4.54; N, 4.03. Found: C, 63.97; H, 4.22; N, 4.22.

Ru^{II} Complex 3. Under a nitrogen atmosphere, a mixture of ligand **4** (30 mg) and $Ru(DMSO)_4Cl_2$[18] (8 mg) in 5 mL of ethylene glycol was heated at 110 °C for 5 h in the dark. After cooling to room temp, an excess of NH_4PF_6 (100 mg, dissolved in 5 mL of water) was added. The red-orange precipitate was collected after filtration and washed with water and ethyl ether, followed by recrystallization from a mixture of acetonitrile/ethyl ether to give 30 mg of **3** (79% yield). ^{1}H NMR (300 MHz, CD_3CN): δ 2.04 (s, 9H, 3Me), 2.08 (s, 9H, 3Me), 2.20 (m, 6H, $\mathrm{3CH_2}\mathit{CH_2}\mathrm{CH_2}$, overlapped with residual peak of solvent), 2.88 (t, J = 7.5 Hz, 12H, $\mathrm{3C}\mathit{H_2}\mathrm{CH_2C}\mathit{H_2}$), 7.17 (s, 3H, 3CH), 7.22−7.88 (m, 42H), 8.12 (m, 3H), 8.74 (m, 6H). MALDI-MS: 1944.1 $[M - PF_6 - H]$ (calcd 1944.4), 1798.3 $[M - 2PF_6 - 2H]$ (calcd 1798.4), 1231.6 $[M - 2PF_6 - \text{ligand } \mathbf{4} - 3H]$ (calcd 1231.1). UV/vis (CH_3CN): λ_{max} (nm)/ε (10^5 M^{-1} cm^{-1}) 252 (0.62), 300 (0.84), 357 (0.43), 377 (0.39), 477 (0.25, MLCT). HRMS-ESI calcd. for $[M - 2PF_6 - 2H]^{2+}$ ($C_{111}H_{88}N_6RuS_6$) 900.2311, Found: 900.2289.

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Supporting Information Available: Synthetic procedure for 4-(*p*-bromophenyl)-2,2′-bipyridine **7**, UV/vis absorption data, electrochemical data, and the method to determine the open-to-closed conversion efficiency of ligand **4** and Ru^{II} complex **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) $Ru(DMSO)_4Cl_2$ was prepared to according to known procedures: Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204.