Inorg. Chem. **2009**, *48*, 991−999

Inorganic Chemistry
Article

Dithienylcyclopentenes-Containing Transition Metal Bisterpyridine Complexes Directed toward Molecular Electronic Applications

Yu-Wu Zhong, Neus Vila, Jay C. Henderson, and Héctor D. Abruña*

Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301

Received August 20, 2008

There is continuing interest in the design and synthesis of functional materials for applications in molecular electronics and information storage. Of particular interest are systems that can provide multiple means for controlling transport through well-defined and stable electronic and/or redox states. We report herein the synthesis and characterization of a system containing transition-metal complexes along with dithienylethene (DTE) units so as to achieve photo and redox control of transport. A facile synthetic methodology was developed to assemble and couple metal terpyridine (M-tpy) complexes with the photochromic DTE unit in a linear structure with M-DTE-M or DTE-M-DTE arrangements, with emphasis on the latter series. The photochromic properties of these assemblies were examined by monitoring the changes in their UV/vis spectra upon irradiation at specific wavelengths capable of triggering the open/closed isomerization in the DTE units. Their electrochromic properties were studied via cyclic voltammetry and controlled potential electrolysis experiments. Complexes **10** (PhDTE-Fe-DTEPh) and **11** (PhDTE-Co-DTEPh) with phenyl-ending groups were found to be both photochromic and electrochromic, so they represent excellent candidates for further elaborations. The Fe(II)-containing complex **8** (ClDTE-Fe-DTECl) with chloride-ending groups was photochromically inactive but could undergo the electrochemically induced open-to-closed isomerization. On the contrary, the electrochromically inactive complex **9** (ClDTE-Co-DTECl) underwent cyclization under ultraviolet irradiation.

Introduction

Transition-metal polypyridine complexes have been well studied for constructing macromolecular assemblies and molecular wire prototypes.[1] In this sense, metal terpyridine (M-tpy) complexes are particularly attractive because of their high stability, accessibility of multiple stable redox states, and the easy and reliable formation of linear structures via functionalization at the 4′-position of the tpy ligand. Among them, those containing ruthenium, osmium, cobalt, and iron centers have received the most attention.[2] Recent investigations introduced molecular switch functions into these structures, which may exhibit multiple stable states in response to external stimuli.[3] For example, Nishihara and co-workers constructed a number of transition metal-polypyridine complexes bearing azobenzene derivatives and carried out a systematic study of their *trans*/*cis* isomerization and the concurrent change of the photophysical and electrochemical properties.[4] They found that the type of metal

---

* To whom correspondence should be addressed. E-mail: hda1@cornell.edu.

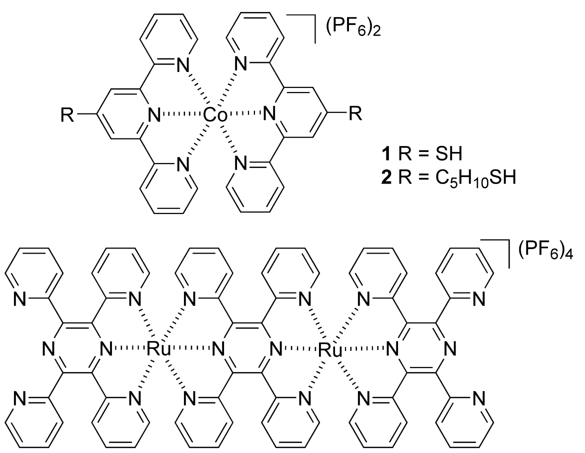
(1) (a) Schubert, U. S.; Eschbaumer, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2892. (b) Harriman, A.; Ziessel, R. *Chem. Commun.* **1996**, 1707. (c) Balzani, V.; Juris, A.; Venturi, M. *Chem. Rev.* **1996**, *96*, 759. (d) Barigelletti, F.; Flamigni, L. *Chem. Soc. Rev.* **2000**, *29*, 1. (e) Ziessel, R. *Synthesis* **1999**, 1839. (f) Balzani, V.; Juris, A. *Coord. Chem. Rev.* **2001**, *211*, 97.

(2) (a) Constable, E. C. *Chem. Soc. Rev.* **2007**, *36*, 246. (b) Medlycott, E. A.; Hanan, G. S. *Chem. Soc. Rev.* **2005**, *34*, 133. (c) Baranoff, E.; Collin, J.-P.; Flamigni, L.; Sauvage, J.-P. *Chem. Soc. Rev.* **2004**, *33*, 147. (d) Torieda, H.; Yoshimura, A.; Nozaki, K.; Sakai, S.; Ohno, T. *J. Phys. Chem. A* **2002**, *106*, 11034. (e) Torieda, H.; Nozaki, K.; Yoshimura, A.; Ohno, T. *J. Phys. Chem. A* **2004**, *108*, 4819. (f) Baitalik, S.; Wang, X.-Y.; Schmehl, R. H. *J. Am. Chem. Soc.* **2004**, *126*, 16304. (g) Constable, E. C.; Dunphy, E. L.; Housecroft, C. E.; Kylberg, W.; Neuburger, M.; Schaffner, S.; Schofield, E. R.; Smith, C. B. *Chem.—Eur. J.* **2006**, *12*, 4600. (h) Eryazici, I.; Moorefield, C. N.; Newkome, G. R. *Chem. Rev.* **2008**, *108*, 1834.

(3) (a) Habuchi, S.; Ando, R.; Dedecker, P.; Verheijen, W.; Mizuno, H.; Miyawaki, A.; Hofkens, J. *Proc. Natl. Acad. Sci.* **2005**, *102*, 9511. (b) Saha, S.; Stoddart, J. F. *Chem. Soc. Rev.* **2007**, *36*, 77. (c) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72.

(4) (a) Nishihara, H. *Bull. Chem. Soc. Jpn.* **2005**, *77*, 407. (b) Yutaka, T.; Kurihara, M.; Kubo, K.; Nishihara, H. *Inorg. Chem.* **2000**, *39*, 3438. (c) Yutaka, T.; Mori, I.; Kurihara, M.; Mizutani, J.; Kubo, K.; Furusho, S.; Matsumura, K.; Tamai, N.; Nishihara, H. *Inorg. Chem.* **2001**, *40*, 4986. (d) Yutaka, T.; Mori, I.; Kurihara, M.; Mizutani, J.; Tamai, N.; Kawai, T.; Irie, M.; Nishihara, H. *Inorg. Chem.* **2002**, *41*, 7143. (e) Yutaka, T.; Mori, I.; Kurihara, M.; Mizutani, J.; Tamai, N.; Nishihara, H. *Inorg. Chem.* **2003**, *42*, 6306.

10.1021/ic801588y CCC: $40.75



1 R = SH
2 R = $C_5H_{10}SH$

3

Figure 1. Complexes used in single-molecule devices.

species, the valence state of the metal center, counterion, and the solvent all played an important role in determining the extent of the *trans*/*cis* isomerization.

We have long been involved in the study of M-tpy based macromolecular complexes and coordination polymers, including their preparation, film formation and characterization, and application in catalysis and device fabrication.[5] Our recent work has focused on the development of single-molecule electronic devices incorporating M-tpy complexes designed so that electron transport occurs through well-defined charge states of the metal center and/or the ligand.[6] Another advantage of using the M-tpy complexes is that the linear geometries between the 4,4′-substituents on the bis-tpy ligand guarantees a good connection to the source and drain electrodes of a single-molecule device in a field-effect transistor (FET) geometry. Among molecules examined (Figure 1), complexes **2** and **3** have shown coulomb blockade effects, while Kondo-assisted tunneling was observed for complex **1** bearing shorter linkers. The next step is to introduce a photochromic DTE unit into these complexes and devices, aiming to modulate the electronic conductivity of the molecular assembly by irradiating with a specific wavelength of light and/or changing the charge states of the metal centers as schematically represented in Figure 2.

As pioneered by Irie and co-workers,[7] the photochromic DTE derivatives have been widely used in constructing small, supra-, and polymeric functional materials.[8] Simple irradiation of a DTE derivative under ultraviolet light converts the open form to the closed form; while the reversible closed-to-open isomerization can be achieved by irradiating with visible light (cf. Figure 2). The octatetraene structure in the closed form, which is highlighted in red in Figure 2, makes it more conjugated than the corresponding open isomer. On the basis of this, the DTE derivatives can be used to switch and control various physical and chemical properties. Additionally, their high fatigue resistance, thermal irreversibility, and short response time also contribute to making them particularly attractive switching materials for optical storage and optoelectronics.

Considering the importance of transition metals for building supramolecular structures and functional materials, a number of metal-polypyridine complexes with a bridging or pendant DTE unit have been reported in studies of the luminescence switch, controlled electron transfer, or metal−metal communication.[9] However, M-tpy complexes containing DTE units have not been well investigated, in part, because of the synthetic difficulties and their inferior photophysical properties relative to the metal-bipyridine complexes. In a previous communication,[10] we reported the synthesis and preliminary studies of the photochromic and electrochromic properties of complexes **4**−**7** (Figure 3), which are composed of a linear M(tpy)-dithienylethene-M(tpy) assembly (abbreviated as M-DTE-M hereafter, M = Ru, Os, Fe, and Co). The open forms of Ru-DTE-Ru and Fe-DTE-Fe were found to be inert to ultraviolet photo irradiation but could be cyclized electrochemically as revealed by cyclic voltammetric studies. On the contrary, Co-DTE-Co underwent efficient photo- but not electrochemical cyclization. The corresponding Os^{II} complex **5** was neither photochromic nor electrochromic. These complexes were studied as the prototype compounds and potential candidates for future device applications. However, some issues still need to be addressed before they can be put into devices. During the preparation of the Fe^{II} and Co^{II}-containing complexes **6** and **7**, we found the presence of

---

(5) (a) Flores-Torres, S.; Hutchison, G. R.; Stoltzberg, L. J.; Abruña, H. D. *J. Am. Chem. Soc.* **2006**, *128*, 1513. (b) Bernhard, S.; Takada, K.; Díaz, D. J.; Abruña, H. D.; Mürner, H. *J. Am. Chem. Soc.* **2001**, *123*, 10265. (c) Bernhard, S.; Goldsmith, J. I.; Takada, K.; Abruña, H. D. *Inorg. Chem.* **2003**, *42*, 4389. (d) Storrier, G. D.; Takada, K.; Abruña, H. D. *Inorg. Chem.* **1999**, *38*, 559. (e) Blasini, D. R.; Flores-Torres, S.; Smilgies, D.-M.; Abruña, H. D. *Langmuir* **2006**, *22*, 2082.

(6) (a) Park, J.; Pasupathy, A. N.; Goldsmith, J. I.; Chang, C.; Yaish, Y.; Petta, J. R.; Rinkoski, M.; Sethna, J. P.; Abruña, H. D.; McEuen, P. L.; Ralph, D. C. *Nature* **2002**, *417*, 722. (b) Unpublished results about compound **3**. See recent studies on single-molecule devices using M-tpy complexes: (c) Seo, K.; Konchenko, A. V.; Lee, J.; Bang, G. S.; Lee, H. *J. Am. Chem. Soc.* **2008**, *130*, 2553. (d) Tang, J.; Wang, Y.; Klare, J. E.; Tulevski, G. S.; Wind, S. J.; Nuckolls, C. *Angew. Chem., Int. Ed.* **2007**, *46*, 3892.

(7) (a) Irie, M.; Uchida, K. *Chem. Lett.* **1995**, 899. (b) Takeshita, M.; Choi, C. N.; Irie, M. *Chem. Commun.* **1997**, 2265. (c) Irie, M.; Mohri, M. *J. Org. Chem.* **1988**, *53*, 803. (d) Gilat, S. L.; Kawai, S. H.; Lehn, J. M. *Chem.*—*Eur. J.* **1995**, *1*, 275. (e) Tsivgoulis, G. M.; Lehn, J. M. *Angew. Chem., Int. Ed.* **1995**, *34*, 1119.

(8) (a) Irie, M. *Chem. Rev.* **2000**, *100*, 1685. (b) Tian, H.; Yang, S. *Chem. Soc. Rev.* **2004**, *33*, 85. (c) Wigglesworth, T. J.; Myles, A. J.; Branda, N. R. *Eur. J. Org. Chem.* **2005**, 1233. (d) Tian, H.; Yang, S. *Chem. Commun.* **2007**, 781.

(9) (a) Jukes, R. T. F.; Adamo, V.; Hartl, F.; Belser, P.; De Cola, L. *Inorg. Chem.* **2004**, *43*, 2779. (b) Jukes, R. T. F.; Adamo, V.; Hartl, F.; Belser, P.; De Cola, L. *Coord. Chem. Rev.* **2005**, *249*, 1327. (c) Fraysse, S.; Coudret, C.; Launay, J.-P. *Eur. J. Inorg. Chem.* **2000**, 1581. (d) Ngan, T.-W.; Ko, C.-C.; Zhu, N.; Yam, W.-W. *Inorg. Chem.* **2007**, *46*, 1144. (e) Lee, J. K.-W.; Ko, C.-C.; Wong, K. M.-C.; Zhu, N.; Yam, W.-W. *Organometallics* **2007**, *26*, 12. (f) Matsuda, K.; Takayama, K.; Irie, M. *Chem. Commun.* **2001**, 363. (g) Norsten, T. B.; Branda, N. R. *Adv. Mater.* **2001**, *13*, 347. (h) Fernández-Acebes, A.; Lehn, J.-M. *Chem.*—*Eur. J.* **1999**, *5*, 3285. (i) Aubert, V.; Guerchais, V.; Ishow, E.; Hoang-Thi, K.; Ledoux, I.; Nakatani, K.; Le Bozec, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 577. (j) Qin, B.; Yao, R.; Zhao, X.; Tian, H. *Org. Biomol. Chem.* **2003**, *1*, 2187. (k) Qin, B.; Yao, R.; Tian, H. *Inorg. Chim. Acta* **2004**, *357*, 3382.

(10) Zhong, Y.-W.; Vila, N.; Henderson, J. C.; Flores-Torres, S.; Abruña, H. D. *Inorg. Chem.* **2007**, *46*, 10470.

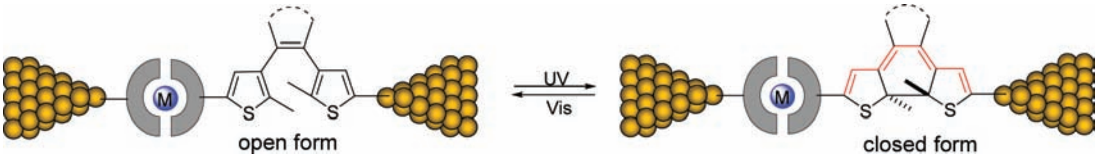
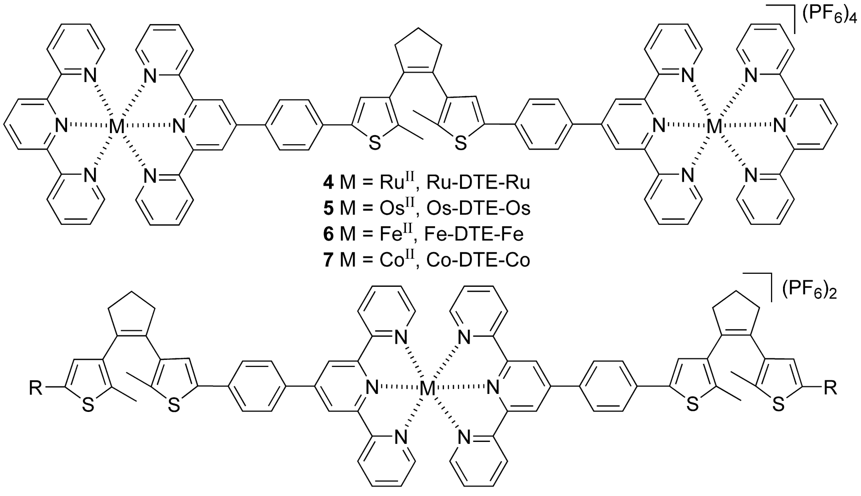


Figure 2. Single-molecule device with a photochromic switch.



4 M = Ru^{II}, Ru-DTE-Ru
5 M = Os^{II}, Os-DTE-Os
6 M = Fe^{II}, Fe-DTE-Fe
7 M = Co^{II}, Co-DTE-Co

8 M = Fe^{II}, R = Cl, ClDTE-Fe-DTECl
9 M = Co^{II}, R = Cl, ClDTE-Co-DTECl
10 M = Fe^{II}, R = Ph, PhDTE-Fe-DTEPh
11 M = Co^{II}, R = Ph, PhDTE-Co-DTEPh

Figure 3. Dithienylcyclopentene-containing transition M-tpy complexes.

some impurities resulting from ligand exchange reactions,[11] as identified from MALDI-MS analysis.[12] However, previous studies revealed that the combination of DTE with Fe- or Co(tpy) complexes showed much better photochromic properties than that with Ru- or Os(tpy) complexes, **4** and **5**. Although the open-to-closed isomerization occurred for Co-DTE-Co **7**, it was unable to undergo the reversible opening reaction. Moreover, none of the complexes were both photochromic and electrochromic, which is our ultimate design objective.

Another series of complexes, **8**−**11**, composed of the same building blocks as the M-DTE-M series but in an arrangement of dithienylethene-M(tpy)-dithienylethene (abbreviated as DTE-M-DTE hereafter, M = Fe and Co) were subsequently investigated. These complexes are designed such that a linear conformation similar to that of M-DTE-M complexes is retained; however, the DTE-M-DTE complexes have two identical tpy ligands around the metal center, thus circumventing the ligand exchange issues. More importantly, their physical properties could be easily tuned by changing the terminal R groups at the two ends of the ligand since they are close to the functional DTE units. For example, these R groups have been shown to modulate the absorption maxima of the $S_0 \rightarrow S_1$ transition of the closed-ring DTE unit by over 150 nm.[13] Terminal R groups, such as pyridine, thiolate, or isocyanide, can also be used to assist their assembly onto electrode surfaces.[14] We describe herein the design, synthesis, electrochemistry, and photophysical properties of these complexes. A comparison of the synthetic approach, photochromic behavior, and electrochemical properties between the M-DTE-M and DTE-M-DTE series will also be presented.

Results and Discussion

Synthesis. The dithenylcyclopentene unit developed by the Feringa group[13,15] was selected to be incorporated into our molecules, since they display good photochromic properties and can be obtained with ease. All of the compounds were prepared starting from a known bischloride **12** (Scheme 1). Complexes **4** and **5** containing the Ru or Os metal centers were obtained through the Suzuki coupling between **13** or **14** with a bisboronic ester generated in situ from **12**, since the high stability of **13** or **14** made them compatible with

---

(11) The fast ligand exchange rate has been well known in many Fe(II) and Co(II)-containing complexes: (a) Goral, V.; Nelen, M. I.; Eliseev, A. V.; Lehn, J.-M. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 1347. (b) Constable, E. C.; Housecroft, C. E.; Kulke, T.; Lazzarini, C.; Schofield, E. R.; Zimmermann, Y. *J. Chem. Soc., Dalton Trans.* **2001**, 2864. (c) Hogg, R.; Wilkins, R. G. *J. Chem. Soc.* **1962**, 341.

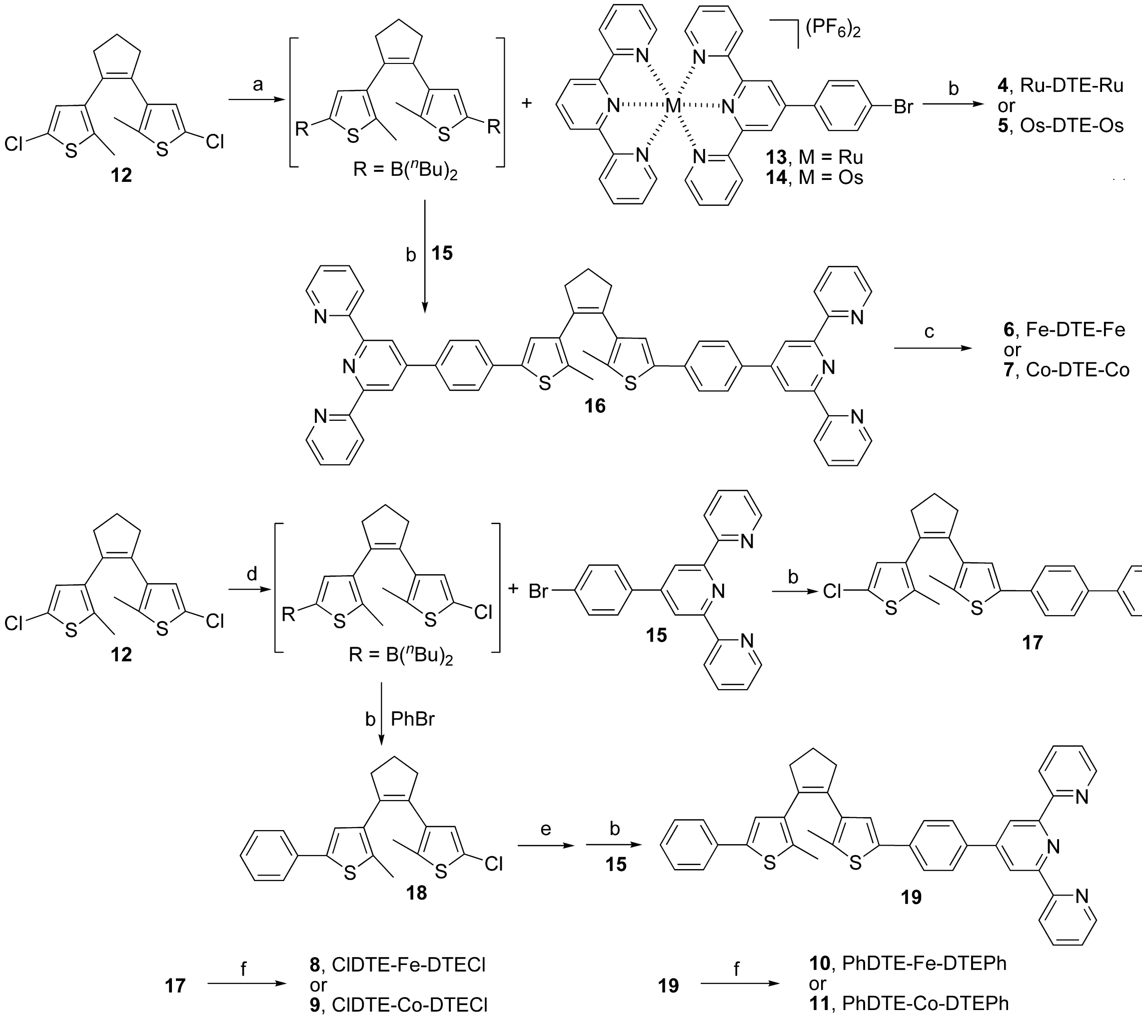
(12) For example, in the MALDI-MS spectrum of Co-DTE-Co **7**, a peak at 1807.6 was detected which was in accordance with a ligand-exchange product (**16**)Co(**16**).

(13) (a) Lucas, L. N.; de Jong, J. J. D.; van Esch, J. H.; Kellogg, R. M.; Feringa, B. L. *Eur. J. Org. Chem.* **2003**, 155. (b) Irie, M.; Sakemura, K.; Okinaka, M.; Uchida, K. *J. Org. Chem.* **1995**, *60*, 8305. (c) Gilat, S. L.; Kawai, S. H.; Lehn, J.-M. *Chem. Commun.* **1993**, 1439.

(14) Auditore, A.; Tuccitto, N.; Marzanni, G.; Quici, S.; Puntoriero, F.; Campagna, S.; Licciardello, A. *Chem. Commun.* **2003**, 2494.

(15) Lucas, L. N.; van Esch, J. H.; Kellogg, R. M.; Feringa, B. L. *Chem. Commun.* **1998**, 2313.

Scheme 1. Synthesis of Dithienylcyclopentene-Containing Transition-Metal Complexes[a]



[a] Reaction conditions: (a) *n*-BuLi (2.0 equiv); then B(OBu)$_3$. (b) Pd(PPh$_3$)$_4$, aq. Na$_2$CO$_3$, DMSO/THF. (c) (tpy)FeCl$_2$ or (tpy)CoCl$_2$, then NH$_4$PF$_6$. (d) *n*-BuLi (1.0 eq.); then B(OBu)$_3$. (e) *t*-BuLi (1.0 equiv); then B(OBu)$_3$. (f) FeCl$_2$·4H$_2$O or CoCl$_2$·6H$_2$O, then NH$_4$PF$_6$.

the relatively harsh reaction conditions.[16] In the synthesis of **6** or **7**, a bis-tpy ligand **16**, containing the dithenylcyclopentene unit was first prepared from a similar Suzuki coupling between **12** and **15**,[17] and then complexed with individual metals.

A similar synthetic strategy was used to synthesize the DTE-M-DTE complexes **8**−**11**, however, benefiting from a selective monolithiation reaction of the bischloride **12** in high yield.[13a] Thus, compound **12** was first monolithiated with 1.0 equiv of *n*-BuLi, followed by treatment with boronic acid tributyl ester to provide the intermediate monoboronic ester, which then reacted with 1.0 equiv of the tpy ligand **15**[17] to give the monotpy ligand **17**. Alternatively, the bischloride **12** was subjected to two consecutive Suzuki couplings first with bromobenzene, and then the tpy ligand **15** to give ligand **19**. It is worth noting that the Cl−Li exchange reaction of substrate **18** was achieved with 1.0 equiv of *t*-BuLi instead of *n*-BuLi. Straightforward reactions between **17** or **19** with FeCl$_2$ or CoCl$_2$ provided the desired complexes **8**−**11** in good yields (70%−90%).

Electronic Absorption and Photochromic Behaviors. The absorption spectra of ligands **16**, **17**, and **19** and complexes **4**−**11** were recorded. Their photochromic behaviors were studied by monitoring the changes in their absorption spectra upon irradiation with a specific wavelength of light in a 1 cm cell. These results are summarized in Table 1.

Ligand **17**, in its open form, showed three peaks at 240, 285, and 328 nm (Figure 4a). The former two peaks were assigned to the tpy-based transitions, and the peak at 328 nm was due to the $S_0 \rightarrow S_1$ transition of the dithenylcyclopentene unit. After irradiation at 320 nm for 5 min, the peak at 328 nm decreased and a broad peak centered at 500 nm emerged. Such behavior is characteristic of the formation of the closed-form of DTE derivatives,[13,15] since the closed form is more conjugated than the open form with greater electron delocalization resulting in a red shift of the $S_0 \rightarrow S_1$ transition. As estimated from ^{1}H NMR analysis, ap-

---

(16) See some examples of palladium-mediated cross-couplings involving transition-metal polypyridine complexes: (a) Tzalis, D.; Tor, Y. *Chem. Commun.* **1996**, 1043. (b) Fang, Y.-Q.; Polson, M. I. J.; Hanan, G. S. *Inorg. Chem.* **2003**, *42*, 5. (c) Aspley, C. J.; Williams, J. A. G. *New J. Chem.* **2001**, *25*, 1136.

(17) Wang, J.; Hanan, J. S. *Synlett* **2005**, 1251.

Table 1. UV/vis Absorption Maxima and the Molar Absorption Coefficients of Compounds Studied[a]

	λ_{max}/nm (ε/10^5 M^{-1} cm^{-1})			
compound	Tpy-based	$S_0 \rightarrow S_2$[b]	$S_0 \rightarrow S_1$[b]	MLCT
12[c]			240	
12 (closed)[c]		276	444	
16	292 (0.78)		340 (0.67)	
16 (closed)	285 (0.81) 316 (0.72)	386 (0.15)	570 (0.33)	
17	240 (0.18) 285 (0.16)		328 (0.13)	
17 (closed)	252 (0.17) 285 (0.18)		500 (0.042)	
19	285 (0.37)		328 (0.24)	
19 (closed)	280 (0.35)	378 (0.075)	550 (0.13)	
4	310 (3.1)		370 (1.0)	489 (1.4)
5	313 (3.5)		360 (1.4)	489 (1.4) 666 (0.32)
6	322 (1.3)		376 (0.72)	567 (0.56)
7	283 (0.67) 319 (0.69)		388 (0.30)	519 (0.03)
7 (closed)	283 (0.67) 318 (0.77)		600 (0.15)	*d*
8	286 (0.20) 324 (0.19)		374 (0.14)	575 (0.11)
9	281 (0.73) 317 (0.59)		388 (0.44)	529 (0.04)
9 (closed)	288 (0.78) 318 (0.71)		534 (0.20)	*d*
10	286 (1.05) 319 (0.91)		375 (0.53)	574 (0.43)
10 (closed)	286 (1.05) 321 (0.92)		*d*	*d*
11	285 (1.96) 314 (1.59)		391 (0.89)	530 (0.09)
11 (closed)	287 (1.81) 315 (1.94)	373 (0.61)	580 (1.00)	*d*

[a] All spectra were recorded in a conventional 1.0 cm quartz cell at a concentration of 1×10^{-5} M in acetonitrile except **16** in THF, **17** and **19** in *n*-hexane. [b] Dithienylcyclopentenes-based transitions. [c] See ref 13a. [d] The transition could not be differentiated because of overlap.

proximately 55% of the sample underwent the open-to-closed conversion. Further irradiation led to decomposition of the sample.

The absorption spectra of ligand **19** are shown in Figure 4b. It displays similar peaks to **17** at 285 and 328 nm. After irradiation at 320 nm for 5 min, the colorless solution turned deep pink. The $S_0 \rightarrow S_1$ transition of the DTE unit in the closed form shifted from 328 to 550 nm, and a peak at 378 nm was assigned to its $S_0 \rightarrow S_2$ transition. The corresponding ^{1}H NMR analysis confirmed a quantitative open-to-closed conversion. Subsequent irradiation at 520 nm gave rise to a decoloration of the solution, indicating the reversible closed-to-open isomerization. Solutions of compounds **12**,[13] **17**, **19**, and **16**[10] in the closed form exhibited pale pink, pink, deep pink, and purple colors, respectively, and the $S_0 \rightarrow S_1$ transitions of the DTE units were centered at 444, 500, 550, and 570 nm, respectively. This demonstrates that the attachment of aryl groups, capable of delocalizing π-electrons to the DTE derivatives, gives rise to better photochromic properties and a distinct red-shift of their absorption spectra in the closed form. Similar phenomena have been previously found on some other DTE derivatives by other groups.[18]

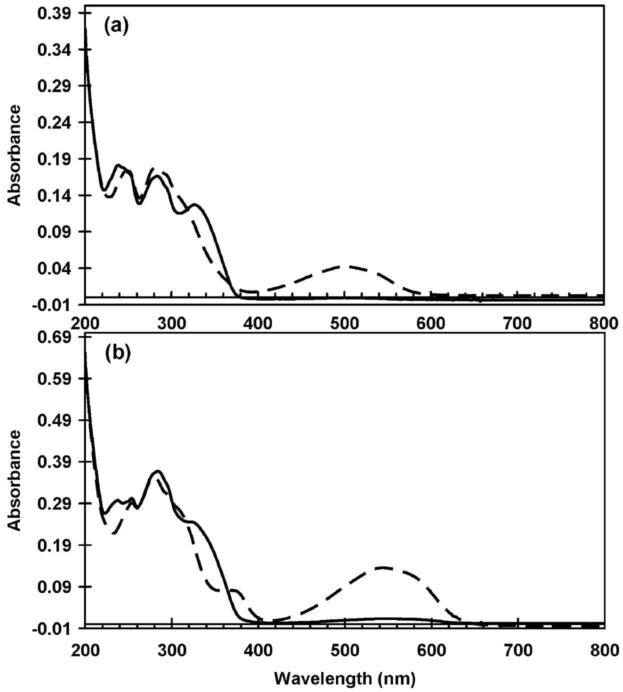


Figure 4. UV/vis absorption spectra of (a) **17** and (b) **19** at a concentration of 1×10^{-5} M in *n*-hexane before (solid line) and after (dashed line) irradiation at 320 nm for 5 min to the photostationary state.

Given our earlier results,[10] it came as no surprise that the iron-containing complex, **8**, did not show any sign of open-to-closed isomerization under UV irradiation. It appears that the low energy MLCT band at 574 nm can quench the excited S_1 state of the DTE unit (Figure 5a). The same is true for the M-DTE-M complexes containing the Ru, Os, and Fe metal centers.[10] However, the closed-form formation of complex **10** did indeed take place, as was evident from the spectral change upon irradiation at 380 nm for 10 h (Figure 5b). The extent of conversion efficiency has not been determined because of the slow response and the overlap of signals in the ^{1}H NMR spectrum.

The cobalt-containing complexes **9** and **11** showed much better photochromic properties than **8** and **10** (Figure 6). After irradiation of an acetonitrile solution of **9** at 350 nm for 3 h, the peak at 388 nm decreased, while a broad peak centered at 534 nm emerged, indicating formation of the closed-isomer. In spite of the paramagnetic nature of the cobalt (II) center, its ^{1}H NMR analysis was achieved, and it showed a 40% photoconversion. On the other hand, a quantitative open-to-closed conversion took place for complex **11** with two phenyl groups at the distal positions, after irradiation at 380 nm for 4 h. The $S_0 \rightarrow S_1$ transition of the DTE unit shifted to 580 nm. The cycloreversion reaction could also be triggered by irradiation at 600 nm. After comparing the absorption spectra of complexes **9** or **11** with their corresponding uncoordinated ligands **17** or **19** (Figure 4) in the closed from, we find a considerable red-shift of the $S_0 \rightarrow S_1$ transition of the DTE unit after complexation with metals, indicating the electron-withdrawing properties of the conjugated metal centers.

---

[18] (a) Irie, M.; Eriguchi, T.; Takada, T.; Uchida, K. *Tetrahedron* **1997**, *53*, 12263. (b) Chen, Y.; Zeng, D. X.; Fan, M. G. *Org. Lett.* **2003**, *5*, 1435. (c) de Jong, J. J. D.; Lucas, L. N.; Hania, R.; Pugzlys, A.; Kellogg, R. M.; Feringa, B. L.; Duppen, K.; van Esch, J. H. *Eur. J. Org. Chem.* **2003**, 1887.

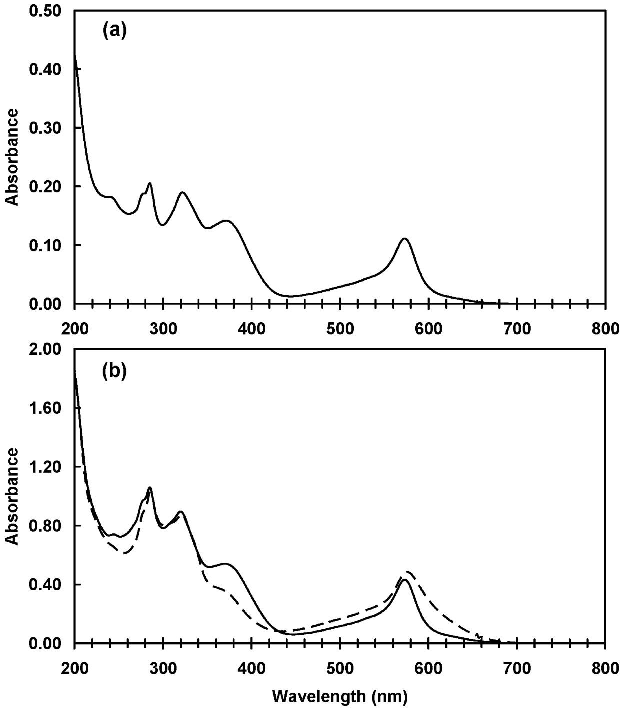


Figure 5. UV/vis absorption spectra of the Fe-containing complexes (a) **8** and (b) **10** at a concentration of 1 × 10^{-5} M in acetonitrile before (solid line) and after (b, dashed line) irradiation at 380 nm to the photostationary state.

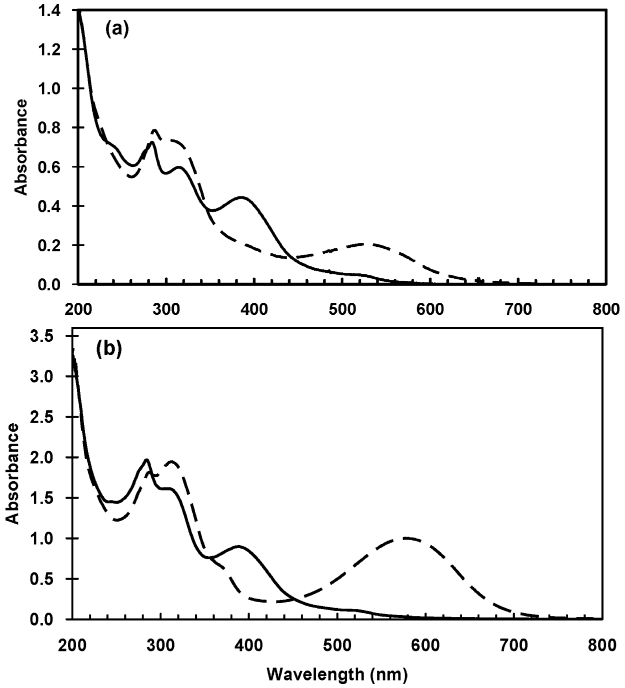


Figure 6. UV/vis absorption spectra of the Co-containing complexes (a) **9** and (b) **11** at a concentration of 1 × 10^{-5} M in acetonitrile before (solid line) and after (dashed line) irradiation at 350 nm for 3 h (for **9**) or at 380 nm for 4 h (for **11**) to the photostationary state.

Table 2. Electrochemical Data of Investigated Compounds[a]

compound	metal-based	DTE-based
4	1.35 ($Ru^{II/III}$)	1.22[b]
4 (closed)	*c*	0.54, 0.75
5	0.98 ($Os^{II/III}$)	1.31[b]
6	1.23 ($Fe^{II/III}$)	1.22[b]
6 (closed)	*c*	0.60, 0.81
7	0.39 ($Co^{II/III}$), −0.61 ($Co^{I/II}$)	
17		1.40[b]
19		1.26[b]
19 (closed)		0.57, 0.80
8	1.20 ($Fe^{II/III}$)	1.35[b]
8 (closed)	*c*	0.40, 0.65
9	0.37 ($Co^{II/III}$)	1.35[b]
10	1.24 ($Fe^{II/III}$)	1.19[b]
10 (closed)	1.21 ($Fe^{II/III}$)	0.58, 0.80
11	0.38 ($Co^{II/III}$), −0.60 ($Co^{I/II}$)	1.22[b]
11 (closed)	*c*	0.60, 0.83

[a] All measurements were carried out at a 0.3 mM concentration of the corresponding complex in acetonitrile, Ag/AgCl reference electrode, glassy carbon as the working electrode, platinum wire as the counter electrode, at a scan rate of 100 mV/s, and in 0.1 M Bu_4NClO_4 as the supporting electrolyte. Unless otherwise noted, the potential was reported as the $E_{1/2}$ value. [b] Irreversible, $E_{\text{anodic.}}$ [c] The redox potential was not determined.

Electrochemical Properties and Electrochromic Behavior. In addition to their well-studied photochromic properties, the DTE derivatives also possess very interesting electrochemical properties. Depending on the substitution patterns, these compounds can undergo electrochemical cyclization and cycloreversion reactions once the thienyl units are oxidized.[19] This provides an alternative stimulus, other than light, with which to alter the molecular switch state. Moreover, the electrochemical and electrochromic properties could be modulated by the metal centers present in the same molecules.[20] As reported in previous studies,[19] the electrochemical cyclization of DTE derivatives can be probed by cyclic voltammetric (CV) analysis. The appearance of two one-electron redox waves in the reverse and subsequent scans after the oxidation of the thienyl groups was characteristic of the ring-closure reaction. We carried out a detailed CV analysis of the M-DTE-M and DTE-M-DTE complexes and the uncoordinated ligands to investigate their electrochemical and electrochromic behaviors. The data are summarized in Table 2.

On the basis of its CV profile (Figure 7a), ligand **17** did not show any sign of electrochemical cyclization after the oxidation of the thienyl groups at +1.40 V versus Ag/AgCl since the first and second scans remained virtually unchanged. However, the attachment of a phenyl group, ligand **19**, made a significant difference (Figure 7b). In the initial anodic scan, an irreversible wave at +1.26 V was observed, which was ascribed to the oxidation of the two thienyl units of the open form. Subsequently, two new reversible waves at +0.80 and +0.57 V appeared in the reverse and subsequent scans, which were in agreement with the stepwise oxidation of the two thienyl rings of the closed form.[19] This indicated that the electrocyclization occurred during the reverse scan and thereafter. The peak at +0.12 V was due

---

(19) (a) Browne, W. R.; de Jong, J. J. D.; Kudernac, T.; Walko, M.; Lucas, L. N.; Uchida, K.; van Esch, J. H.; Feringa, B. L. *Chem.—Eur. J.* **2005**, *11*, 6414. (b) Browne, W. R.; de Jong, J. J. D.; Kudernac, T.; Walko, M.; Lucas, L. N.; Uchida, K.; van Esch, J. H.; Feringa, B. L. *Chem.—Eur. J.* **2005**, *11*, 6430. (c) Moriyama, Y.; Matsuda, K.; Tanifuji, N.; Irie, S.; Irie, M. *Org. Lett.* **2005**, *7*, 3315. (d) Guirado, G.; Coudret, C.; Hliwa, M.; Launay, J.-P. *J. Phys. Chem. B* **2005**, *109*, 17445. (e) Peters, A.; Branda, N. R. *J. Am. Chem. Soc.* **2003**, *125*, 3404. (f) Peters, A.; Branda, N. R. *Chem. Commun.* **2003**, 954. (g) Baron, R.; Onopriyenko, A.; Katz, E.; Lioubashevski, O.; Willner, I.; Wang, S.; Tian, H. *Chem. Commun.* **2006**, 2147.

(20) Guirado, G.; Coudret, C.; Hliwa, M.; Launay, J.-P. *J. Phys. Chem. C* **2007**, *111*, 2770.

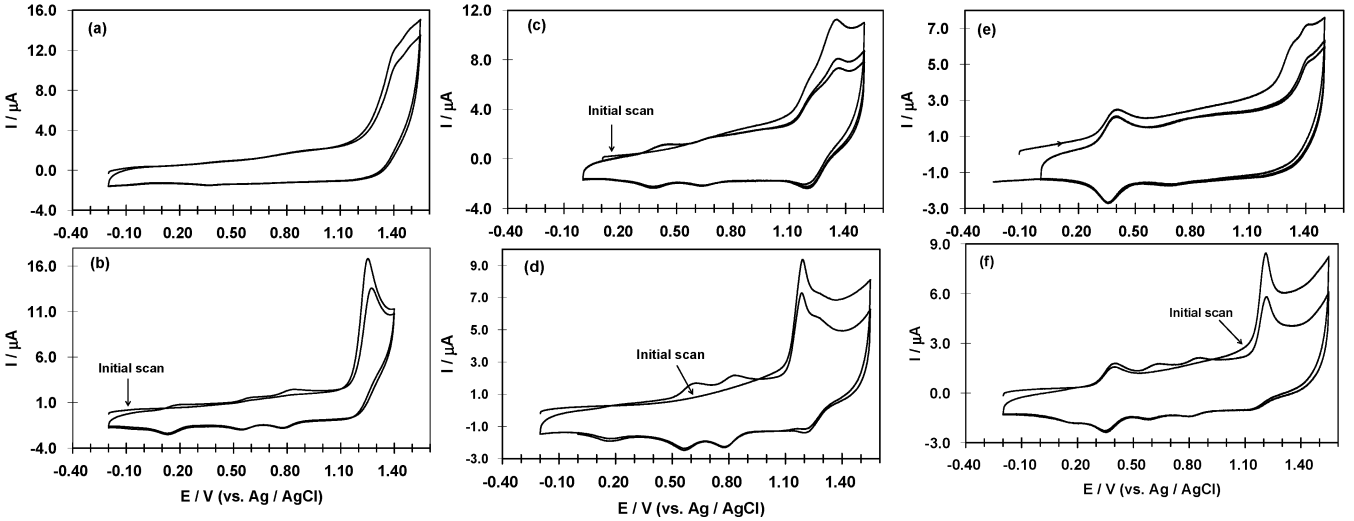


Figure 7. Cyclic voltammetry at a glassy carbon electrode at 0.1 V/s for the ligands (a) **17** and (b) **19**, the Fe-containing complexes (c) **8** and (d) **10**, and the Co-containing complexes (e) **9** and (f) **11** at a concentration of 0.3 mM in acetonitrile containing 0.1 M TBAP as the supporting electrolyte. The counter electrode was a platinum wire.

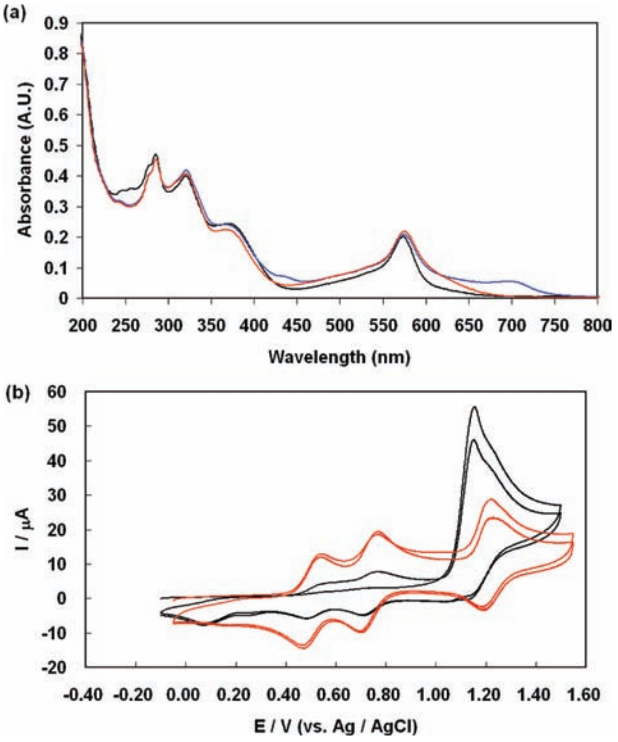


Figure 8. (a) UV/vis absorption spectrum change of the Fe-containing complexes **10** before (black line) and after (blue) electrolysis on a glassy carbon electrode ($d = 3$ mm) of a 0.2 mM acetonitrile solution containing 0.1 M of $TBABF_4$ at 100 mV/s at +1.2 V vs Ag/AgCl. The red line was recorded after re-reduction at +0.2 V under the same conditions. (b) Cyclic voltammetry of **10** before (black line) and after (red) electrolysis at +1.2 V vs Ag/AgCl.

to an unidentified product derived from the electrochemically generated radical cation intermediate.[19a]

Both of the Fe-containing complexes, **8** and **10**, underwent electrochemically induced cyclization (Figures 7c and 7d), with compound **10** proceeding to a larger extent judging approximately from the amplitude of the redox waves in the reverse and subsequent scans. The CV profile of the Co-containing complex **9** (Figure 7e) showed the $Co^{II/III}$ redox peak at +0.37 V and the irreversible oxidation of the thienyl groups at +1.35 V, with no sign of electrochemical ring-closing. Considering that ligand **17** and its corresponding Co complex, **9**, were totally unable to cyclize electrochemically, whereas cyclization did occur for complex **8** after complexation with iron, the introduction of specific metal centers into these systems can be utilized to alter and control their electrochemical properties. Complex **11**, which displayed excellent photochromic properties as described earlier, proved to be a good prototype molecule for molecular electronics applications. Its electrochemical cyclization was also confirmed by similar CV analysis as shown in Figure 7f.

The electrochemical ring closing reaction was further probed by electrolysis experiments. Upon electrolysis of an acetonitrile solution of the open isomer of the Fe-containing complex **10** at +1.2 V (vs Ag/AgCl), the UV/vis spectrum showed an enhancement of the broadband around 570 nm and a slight decrease of the band at 360 nm (Figure 8a), which was in agreement with the formation of the closed isomer (cf. Figure 5b). The emergence of a new band at 700 nm could be assigned to the radical cationic intermediate of **10** in the open-to-closed isomerization reaction. This band disappeared again upon re-reduction at +0.20 V. The change in the voltammetric profile of **10** upon electrolysis at +1.2 V (vs Ag/AgCl) is shown in Figure 8b. The irreversible wave at +1.16 V, from the open isomer, disappeared and three one-electron redox waves corresponded to the oxidation of the two thienyl groups and the Fe^{II} center in the closed isomer, respectively.

Conclusions

In summary, a series of dithienylcyclopentenes containing transition metal bis-terpyridine complexes, including M-DTE-M and DTE-M-DTE arrangements, have been designed and synthesized. Their linear conformation and tunable redox and photochromic properties make them promising candidates for single-molecule device applications. By comparison, the DTE-M-DTE compounds appear more promising than the M-DTE-M series. They can be prepared in high purity and quantities because of their molecular symmetry and easy availability of the starting materials. The Ph-ending molecules **19**, **10**, and **11** generally displayed superior photochromic and electrochromic properties than the Cl-ending molecules **17**, **8**, and **9**. Interestingly, the Fe- and Co-containing molecules **10** and **11** are both photochromic and electrochromic. Studies on the dithienylethene derivatives deposited on an electrode surface or bridged between two electrodes have been recently reported.[21] These reports indicate the high potential of the dithienylethene derivatives for electric conductivity modulation in single-molecule devices. The work on the preparation of similar complexes with anchoring groups to study them in break junctions[22] is underway.

Experimental Section

UV/vis Absorption Measurements and Irradiation Experiments. All optical ultraviolet−visible (UV/vis) absorption spectra were obtained using a HP 8453 diode array spectrometer at room temperature in denoted solvents, with a conventional 1.0 cm quartz cell. 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 voltammetry was taken using an Epsilon BAS CV-27 potentiostat. Three-compartment electrochemical cells (separated by medium-porosity sintered glass disks) with provision for gas addition was 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 0.3 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 with a 0.3 mM concentration of the corresponding complex in acetonitrile at a scan rate of 100 mV/s, in 0.1 M of Bu_4NClO_4 (TBAP) as the supporting electrolyte.

Synthesis. The synthesis of complexes **4**−**7** and ligand **16** have been described in a previous publication.[10] Compounds **12**,[13] **15**,[17] and **18**[23] were prepared according to literature reports. 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. MALDI-TOF positive ion data were obtained with a Waters MALDI micro MX mass spectrometer run in reflection mode. HRMS-ESI data were obtained with a Q-Tof Ultima mass spectrometer by Mass Spectrometry Center, SCS, University of Illinois.

Cl-DTE-tpy (17). To a solution of **12** (165 mg, 0.50 mmol) in THF (8.0 mL) were added 0.31 mL of 1.6 M *n*-butyllithium (0.50 mmol) in *n*-hexane at room temperature. Fifteen minutes later, 0.40 mL of tributyl borate (1.5 mmol) were added. After stirring for 1 h, the resulting reddish solution was used directly for the following addition. To another Schlenk flask filled with 30 mL of degassed DMSO were added **15** (180 mg, 0.50 mmol) and $Pd(PPh_3)_4$ (22 mg, 0.02 mmol). After stirring for 15 min, 2.5 mL of 2 M aqueous sodium carbonate solution (5.0 mmol) and 0.30 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 toluene were added to dilute the mixture, followed by washing with water (20 mL × 2) and brine. Flash column chromatography on alumina (ethyl acetate/hexane, 5/1) of the concentrated residue afforded 203 mg of **17** as a foamy solid in a yield of 67%. ^1H NMR (300 MHz, $CDCl_3$): δ 1.91 (s, 3H, Me), 2.02 (s, 3H, Me), 2.00−2.15 (m, 2H, $CH_2\mathit{CH_2}CH_2$), 2.76 (t, $J = 7.2$ Hz, 2H, $C\mathit{CH_2}$), 2.84 (t, $J = 7.2$ Hz, 2H, $C\mathit{CH_2}$), 6.65 (s, 1H, CH), 7.10 (s, 1H, CH), 7.33−7.37 (m, 2H), 7.62 (d, $J = 8.1$ Hz, 2H), 7.85−7.92 (m, 4H), 8.67 (d, $J = 8.1$ Hz, 2H), 8.74 (d, $J = 6.6$ Hz, 2H, overlapped), 8.75 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.13 (Me), 14.38 (Me), 22.80 ($CH_2\mathit{CH_2}CH_2$), 38.25 ($C\mathit{CH_2}$), 38.35 ($C\mathit{CH_2}$), 118.21, 121.22, 123.68, 124.22, 124.95, 125.47, 126.71, 127.18, 127.53, 128.79, 133.16, 133.76, 134.94, 135.05, 136.45, 136.55, 136.70, 138.97, 148.94, 155.73, 156.03. HRMS-ESI: calcd for $[M + H]^+$ ($C_{36}H_{29}N_3S_2Cl$) 602.1491, found 602.1485. The CH peaks of the thienyl rings in the ^1H NMR spectrum of the open and closed form displayed two singlets at 6.65, 7.10 and 5.96, 6.47, respectively, which allowed us to determine the open-to-closed conversion efficiency.

Ph-DTE-tpy (19). This compound was prepared from a similar Suzuki coupling as described above from the substrate **18** and tpy ligand **15** in a yield of 78%, except that *t*-BuLi was used instead of *n*-BuLi for the Cl−Li exchange step. ^1H NMR (300 MHz, $CDCl_3$): δ 2.04 (s, 3H, Me), 2.05 (s, 3H, Me), 2.00−2.15 (m, 2H, $CH_2\mathit{CH_2}CH_2$), 2.87 (m, 4H, $\mathit{CH_2}CH_2\mathit{CH_2}$), 7.09 (s, 1H, CH), 7.16 (s, 1H, CH), 7.23−7.36 (m, 5H), 7.53 (d, $J = 7.2$ Hz, 2H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.80−7.89 (m, 4H), 8.64−8.76 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.37 (Me), 14.40 (Me), 22.90 ($CH_2\mathit{CH_2}CH_2$), 38.37, 124.03, 125.22, 125.55, 127.05, 127.27, 129.04, 133.50, 133.98, 134.64, 134.73, 135.37, 135.53, 136.59, 140.06. HRMS-ESI: calcd. for $[M + H]^+$ ($C_{42}H_{34}N_3S_2$) 644.2194, found 644.2194. The CH peaks of the thienyl rings in the ^1H NMR spectrum of the open and closed form displayed two singlets at 7.09, 7.16, and 6.43, 6.52 respectively, which allowed us to determine the open-to-closed conversion efficiency.

$[Fe(Cl\text{-}DTE\text{-}tpy)_2](PF_6)_2$ (8). To a solution of ligand **17** (66 mg, 0.11 mmol) in 4.0 mL of dichloromethane was added a solution of $FeCl_2 \cdot 4H_2O$ (10 mg, 0.05 mmol) in 2.0 mL of methanol. The mixture was stirred at room temperature for 1 h. Then an excess of NH_4PF_6 (200 mg) was added. The brown precipitate was collected after filtration and washed with methanol and ether (70 mg, 90%). ^1H NMR (300 MHz, CD_3CN): δ 1.98 (s, 6H, 2Me), 2.08−2.20 (m, 4H, overlapped) 2.11 (s, 6H, 2Me), 2.84 (t, $J = 6.3$ Hz, 4H, $2C\mathit{CH_2}$), 2.91 (t, $J = 6.9$ Hz, 4H, $2C\mathit{CH_2}$), 6.80 (s, 2H, 2CH), 7.08−7.13 (m, 4H), 7.22 (d, $J = 5.4$ Hz, 4H), 7.41 (s, 2H, 2CH), 7.91−7.99 (m, 8H), 8.34 (d, $J = 8.4$ Hz, 4H), 8.64 (d, $J =$

---

(21) (a) Katsonis, N.; Kudernac, T.; Walko, M.; van der Molen, S. J.; van Wess, B. J.; Feringa, B. L. *Adv. Mater.* **2006**, *18*, 1397. (b) Areephong, J.; Browne, W. R.; Katsonis, N.; Feringa, B. L. *Chem. Commun.* **2006**, 3930. (c) He, J.; Chen, F.; Liddell, P. A.; Andréasson, J.; Straight, S. D.; Gust, D.; Moore, T. A.; Moore, A. L.; Li, J.; Sankey, O. F.; Lindsay, S. M. *Nanotechnology* **2005**, *16*, 695. (d) Duliæ, D.; van der Molen, S. J.; Kudernac, T.; Jonkman, H. T.; de Jong, J. J. D.; Bowden, T. N.; van Esch, J.; Feringa, B. L.; van Wess, B. J. *Phys. Rev. Lett.* **2003**, *91*, 207402. (e) Whalley, A. C.; Steigerwald, M. L.; Guo, X.; Nuckolls, C. *J. Am. Chem. Soc.* **2007**, *129*, 12590.

(22) 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.

(23) Kudernac, T.; De Jong, J. J.; Van Esch, J.; Feringa, B. L.; Duliæ, D.; Van Der Molen, S. J.; Van Wees, B. J. *Mol. Cryst. Liq. Cryst.* **2005**, *430*, 205.

7.8 Hz, 4H), 9.21 (s, 4H). MALDI-MS: 1258 $[M - 2PF_6]^{2+}$. Anal. Calcd for $C_{72}H_{56}Cl_2FeF_{12}N_6P_2S_4$: C, 55.78; H, 3.64; N, 5.42. Found: C, 56.07; H, 3.71; N, 5.53.

$[Co(Cl\text{-}DTE\text{-}tpy)_2](PF_6)_2$ (9). To a solution of ligand **17** (42 mg, 0.07 mmol) in 4.0 mL of dichloromethane was added a solution of $CoCl_2 \cdot 6H_2O$ (7.1 mg, 0.03 mmol) in 2.0 mL of methanol. The mixture was stirred at room temperature for 30 min. Then an excess of NH_4PF_6 (200 mg) was added. The orange precipitate was collected after filtration and washed with methanol and ether (42 mg, 85%). ^{1}H NMR (300 MHz, CD_3CN): δ 2.36 (s, 6H, 2Me), 2.40 (m, 4H, overlapped), 2.47 (s, 6H, 2Me), 3.10 (m, 4H, 2C*CH*$_2$), 3.36 (m, 4H, 2C*CH*$_2$), 7.16 (s, 2H, 2CH), 8.67 (s, 2H, 2CH), 9.00−9.50 (m, 8H), 13.72 (s, 4H), 32.37 (s, 4H), 41.84 (s, 4H), 53.98 (s, 4H), 92.00 (br, 4H). MALDI-MS: 1261 $[M - 2PF_6]^{2+}$. Anal. Calcd for $C_{72}H_{56}Cl_2CoF_{12}N_6P_2S_4$: C, 55.67; H, 3.63; N, 5.41. Found: C, 55.57; H, 3.54; N, 5.33. The CH peaks of the thienyl rings in the ^{1}H NMR spectrum of the open and closed form displayed two singlets at 7.16, 8.17 and 6.37, 8.19 respectively, which allowed us to determine the open-to-closed conversion efficiency.

$[Fe(Ph\text{-}DTE\text{-}tpy)_2](PF_6)_2$ (10). To a solution of ligand **19** (71 mg, 0.11 mmol) in 4.0 mL of dichloromethane was added a solution of $FeCl_2 \cdot 4H_2O$ (10 mg, 0.05 mmol) in 2.0 mL of methanol. The mixture was stirred at room temperature for 1 h. Then an excess of NH_4PF_6 (200 mg) was added. The brown precipitate was collected after filtration and washed with methanol and ether (76 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.11 (s, 6H, 2Me), 2.14 (s, 6H, 2Me), 2.00−2.15 (m, 4H, 2CH$_2$*CH*$_2$CH$_2$, overlapped), 2.95 (m, 8H, 2*CH*$_2$CH$_2$*CH*$_2$), 7.08−7.44 (m, 18H), 7.60 (d, $J = 7.2$ Hz, 4H), 7.91−8.00 (m, 8H), 8.33 (d, $J = 8.4$ Hz, 4H), 8.63 (d, $J = 7.8$ Hz, 4H), 9.21 (s, 4H). MALDI-MS: 1342.3 $[M - 2PF_6]^{2+}$.

$[Co(Ph\text{-}DTE\text{-}tpy)_2](PF_6)_2$ (11). To a solution of ligand **19** (70 mg, 0.11 mmol) in 6.0 mL of dichloromethane was added a solution of $CoCl_2 \cdot 6H_2O$ (12 mg, 0.05 mmol) in 3.0 mL of methanol. The mixture was stirred at room temperature for 30 min. Then an excess NH_4PF_6 (200 mg) was added. The orange precipitate was collected after filtration and washed with methanol and ether (57 mg, 71%). ^{1}H NMR (300 MHz, CD_3CN): δ 2.43 (s, 6H, 2Me), 2.50 (m, 4H, overlapped) 2.61 (s, 6H, 2Me), 3.24 (m, 4H, 2C*CH*$_2$), 3.42 (m, 4H, 2C*CH*$_2$), 7.50 (m, 2H, Ph), 7.64 (m, 6H, overlapped, 4H from Ph, 2H from 2CH), 7.94 (d, $J = 7.8$ Hz, 4H, Ph), 8.76 (s, 2H, 2CH), 9.25−9.40 (m, 8H), 13.78 (s, 4H), 32.41 (s, 4H), 42.05 (s, 4H), 54.06 (s, 4H), 92.20 (br, 4H). The CH peaks of the thienyl rings in the ^{1}H NMR spectrum of the open and closed form displayed two singlets at 7.64, 8.76, and 6.92, 8.48, respectively, which allowed us to determine the open-to-closed conversion efficiency.

Acknowledgment. We thank the NSF/NIRT program (Grant CHE-0403806) for funding support. This work was also supported by Cornell Center for Materials Research (CCMR).

Supporting Information Available: NMR spectra of newly prepared compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

IC801588Y