Inorg. Chem. **2007**, *46*, 10470–10472

Inorganic Chemistry
Communication

Dinuclear Transition-Metal Terpyridine Complexes with a Dithienylcyclopentene Bridge Directed toward Molecular Electronic Applications

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

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

Received September 11, 2007

A series of dinuclear metal terpyridine (M-tpy; M = Ru, Os, Fe, and Co) complexes with a photochromic dithienylethene bridge were designed and synthesized through either a convergent or a divergent approach. The open forms of the complexes containing Ru^{II} and Fe^{II} centers were found to be inert to ultraviolet photoirradiation but could be cyclized electrochemically as revealed by a cyclic voltammetric study. On the contrary, the Co^{II} complex underwent efficient photochemical but not electrochemical cyclization. The corresponding Os^{II} complex was neither photochromic nor electrochromic.

Stimulated by their potential application in molecular electronics and information storage, chemists have been devoted to the design and synthesis of smart materials that may perform a molecular switch function.[1] Upon response to external stimuli, these materials can exhibit both "on" and "off" states, which modulate both their chemical and physical properties. Among these materials, the photochromic dithienylethene derivatives have received much attention as switch materials mainly because of their good fatigue resistance and thermal irreversibility.[2] Simple irradiation with a specific wavelength of light can "switch" the molecule between a nonconjugated open form and a conjugated closed form.

Recently, we[3] have been involved in the development of single molecular electronic devices incorporating transition-metal terpyridine (M-tpy) complexes designed so that electron transport occurs through well-defined charge states of the metal center. The M-tpy complexes were selected because of their appealing photophysical and electrochemical properties.[4] The reliable formation of a linear structure via functionalization at the 4′ position of the tpy ligand helps to form a good connection between two electrodes. We are now interested in introducing the photochromic dithienylethene unit into these structures by aiming to control the conductivity of the molecular wire through both photo- and electrochemical switching. The photochromic properties and conductivity switching of dithienylethene derivatives attached on an electrode surface have been studied recently;[5] however, the incorporation of transition-metal complexes into these devices to enhance electron transport remains unexplored.

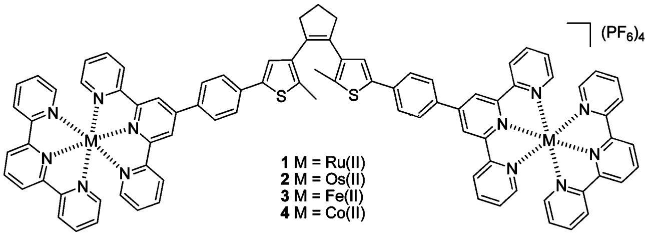


Figure 1. Dinuclear complexes studied.

The prototype molecules for our purposes are the dinuclear M-tpy complexes **1**−**4** bearing a dithenylcyclopentene bridge (Figure 1). Subsequently, anchoring groups such as pyridine, thiolate, or isocyanide will be attached onto the two distal positions of the complexes, and the whole molecules will be used in single-molecule devices. It should be noted that a number of metal polypyridine complexes with a bridging or pendant dithienylethene unit have been reported in studies of the luminescence switch, controlled electron transfer, or metal−metal communication.[6] However, the M-tpy complexes containing the dithienylethene unit have not been well investigated partially because of the synthetic difficulties and

---

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

(1) (a) Nishihara, H. *Bull. Chem. Soc. Jpn.* **2005**, *77*, 407. (b) Habuchi, S.; Ando, R.; Dedecker, P.; Verheijen, W.; Mizuno, H.; Miyawaki, A.; Hofkens, J. *Proc. Natl. Acad. Sci.* **2005**, *102*, 9511. (c) Saha, S.; Stoddart, J. F. *Chem. Soc. Rev.* **2007**, *36*, 77. (d) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72.

(2) (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.

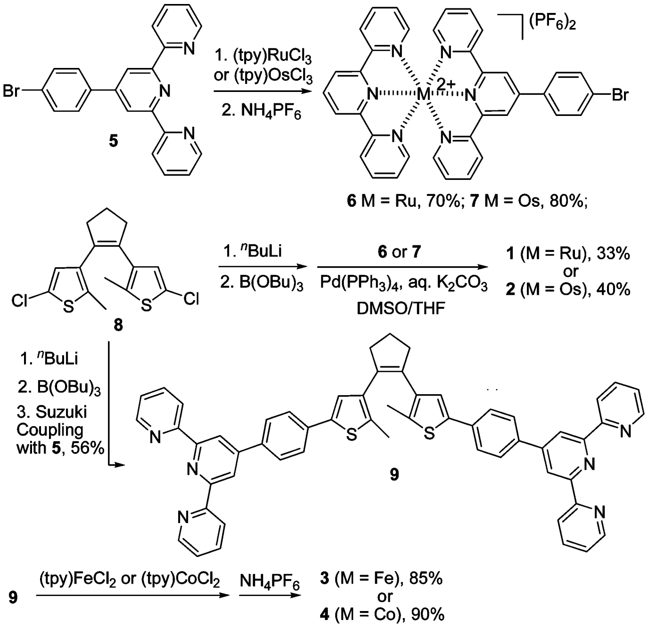
(3) Park, J.; Pasupathy, A. N.; Goldsmith, J. I.; Chang, C.; Yaish, Y.; Petta, J. R.; Rinkoski, M.; Sethna, J. P.; Abruña, H. D.; McEuen, P. L.; Ralph, D. C. *Nature* **2002**, *417*, 722.

(4) (a) Constable, E. C. *Chem. Soc. Rev.* **2007**, *36*, 246. (b) Schubert, S. S.; Eschbaumer, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2892. (c) Harriman, A.; Ziessel, R. *Chem. Commun.* **1996**, 1707. (d) Balzani, V.; Juris, A.; Venturi, M. *Chem. Rev.* **1996**, *96*, 759. (e) Barigelletti, F.; Flamigni, L. *Chem. Soc. Rev.* **2000**, *29*, 1.

(5) (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.

10.1021/ic701784b CCC: $37.00

Scheme 1. Synthesis of Dinuclear Complexes **1**−**4**



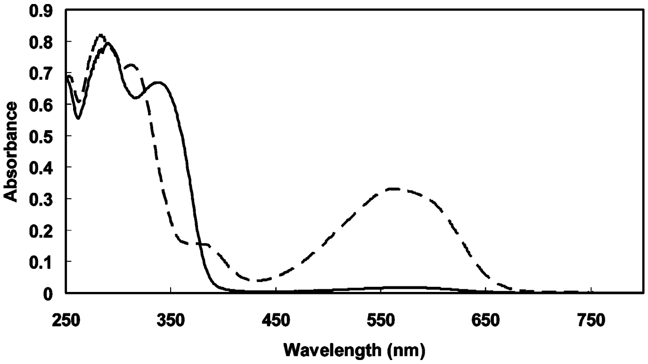


Figure 2. UV/vis absorption of open (solid line) and closed (dashed line) forms of **9** at a concentration of 1 × 10^{-5} M in THF.

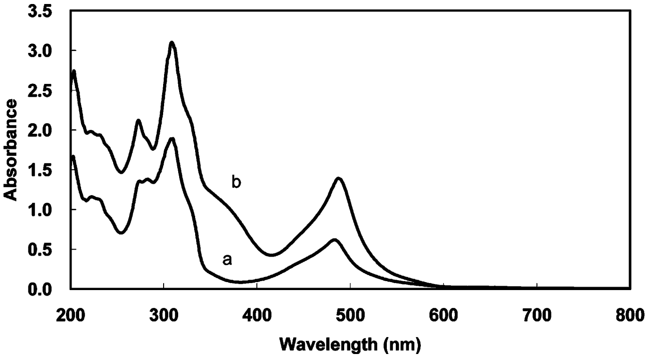


Figure 3. UV/vis absorption spectra of (a) the monoruthenium complex **6** and (b) bisruthenium complex **1** at a concentration of 1 × 10^{-5} M in acetonitrile.

their inferior photophysical properties relative to the metal bipyridine complexes. On the other hand, for single-molecular device applications, the M-tpy complexes are particularly attractive because of their well-defined geometries, which for 4′,4′ substituents ensure a linear assembly. We describe herein the synthesis, characterization, and preliminary study of the photochromic and electrochromic properties of complexes **1**−**4**.

As outlined in Scheme 1, complexes **1**−**4** were synthesized through either a convergent or a divergent strategy. Ru^{II}- and Os^{II}-containing complexes **1** and **2** were synthesized using a Suzuki coupling between a bisboronic ester generated in situ from bischloride **8**[7] and the corresponding mononuclear complexes **6** and **7**,[8] which were prepared from the known tpy derivative **5**[9] with Ru(tpy)Cl$_3$ and Os(tpy)Cl$_3$. Because of the fast ligand exchange rate of Fe^{II} and Co^{II} complexes, we decided to run the metal−ligand complexation reaction in the last step through a divergent manner. In this approach, the bisterpyridine ligand **9** with the dithenylcyclopentene bridge was first obtained after Suzuki coupling between **5** and the same bisboronic ester mentioned above. Direct complexation of **9** with 2 equiv of Fe(tpy)Cl$_2$ and Co(tpy)Cl$_2$ gave **3** and **4**, respectively.

The UV/vis absorption spectra of the above compounds were recorded. The C_2-symmetric ligand **9** in its open form showed two peaks at 292 and 340 nm (Figure 2), which was assigned to the tpy-based transition and the $S_0 \rightarrow S_1$ transition of the dithenylcyclopentene unit, respectively. After irradiation at 320 nm for 5 min, the colorless solution turned purple, and a broad peak centered at 570 nm appeared. Such behavior is characteristic of the closed-form formation of dithienylethene derivatives[6a,7a] because 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. The corresponding ^{1}H NMR analysis confirmed a quantitative open-to-closed conversion (see the Supporting Information). After irradiation at 520 nm, decoloration of the solution occurred because of the reversible closed-to-open isomerization.

The monoruthenium complex **6** and bisruthenium complex **1** showed similar peaks below 340 nm (ligand-based transitions) and singlet metal-to-ligand charge-transfer (^{1}MLCT) bands around 480 nm, while the molar absorption coefficient of **1** was approximately twice that of **6** (Figure 3). This suggests that no significant metal−metal communication between two ruthenium centers exists. The clear shoulder at 370 nm in **1** is assigned to the $S_0 \rightarrow S_1$ transition localized on the dithienylethene unit. When **1** was irradiated with UV light (250, 300, or 350 nm) for at least 4 h, no distinct change in its absorption spectrum was evident. This indicated that **1** failed to undergo cyclization under UV irradiation. The same phenomena were observed for the bisosmium complex **2** and bisiron complex **3** (see the Supporting Information).

---

(6) (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) Qin, B.; Yao, R.; Zhao, X.; Tian, H. *Org. Biomol. Chem.* **2003**, *1*, 2187. (j) Qin, B.; Yao, R.; Tian, H. *Inorg. Chim. Acta* **2004**, *357*, 3382.

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

(8) Aspley, C. J.; Williams, J. A. G. *New J. Chem.* **2001**, *25*, 1136.

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

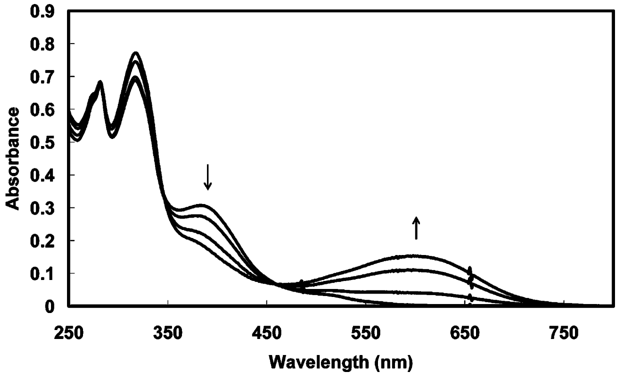


Figure 4. UV/vis absorption spectral change of **4** at a concentration of 1×10^{-5} M in acetonitrile upon irradiation at 350 nm for 2 h. The spectra were collected at 0, 30, 90, and 120 min, respectively.

We also noticed that complexes **1**−**3** all have an intense MLCT band in the visible region, which could quench the S_1 excited state of the central dithienylethene unit and lead to a failure to close. With this in mind, we turned to the bis-Co^{II} complex **4**, which only has very weak bands above 450 nm. The open-to-cyclized photoisomerization of the bis-Co^{II} complex **4** did indeed take place, which was evidenced by a significant decrease of the band at 370 nm and the emergence of a new absorption band between 460 and 750 nm upon irradiation at 350 nm (Figure 4). Because of the paramagnetic properties of the Co^{II} complex, it is difficult to determine the relative ratio of the two forms by ^{1}H NMR analysis. When irradiated with visible light ($\lambda > 500$ nm), the complex did not undergo reversible photoisomerization.

The electronic properties and isomerization reactions of these complexes were further studied by cyclic voltammetric (CV) analysis. A detailed electrochemical study of dithenylcyclopentene derivatives has been conducted by the Feringa group.[10] They found that a proper combination of substituents on the thienyl rings and experimental conditions could facilitate the electrocyclization and cycloreversion. In the initial anodic scan of the bis-Ru^{II} complex **1** (Figure 5a), an irreversible wave at +1.22 V (vs Ag/AgCl) slightly before the Ru^{III}/Ru^{II} redox wave was observed and was ascribed to the oxidation of the two thienyl units of the open form. After that, two new reversible waves at +0.54 and +0.75 V appeared in the reverse and subsequent scans. These two waves were in agreement with the stepwise oxidation of the two thienyl rings of the closed form of **1**. This indicated that the electrocyclization occurred in the diffusion layer during the reverse scan and thereafter. The same was true for the bis-Fe^{II} complex **3** (Figure 5b), with similar oxidation potentials for the thienyl rings. However, the electrocyclization was not observed in the bis-Os^{II} complex **2** and the bis-Co^{II} complex **4** (see the Supporting Information). It seems that the oxidation of the metal centers (Os^{III}/Os^{II}, +0.99 V; Co^{III}/Co^{II}, 0.39 V) before the oxidation of the thienyl rings in the corresponding open isomer prevents the electrochemical cyclization.

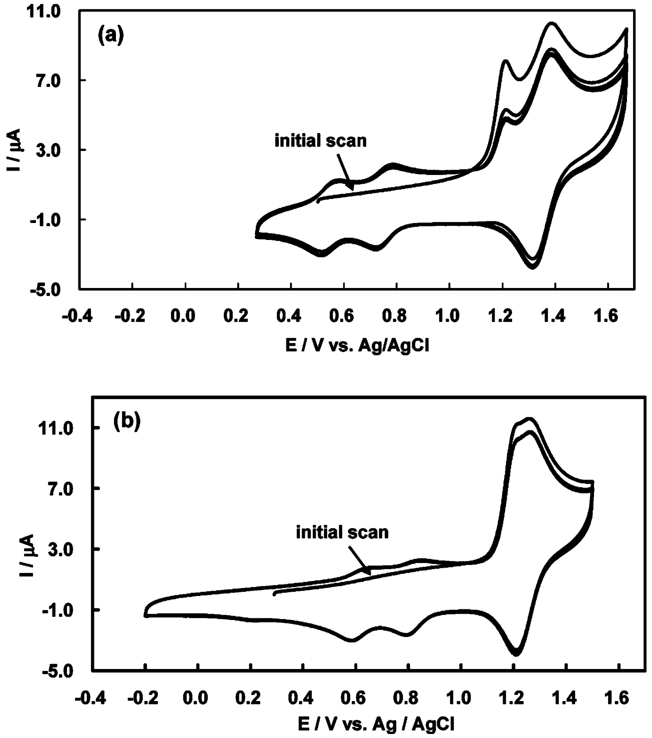


Figure 5. CV of (a) **1** and (b) **3** at a concentration of 0.3 mM in acetonitrile containing 0.1 M Bu$_4$NClO$_4$ as the supporting electrolyte at a scan rate of 100 mV/s. The working electrode is a glassy carbon; the counter electrode is a Pt wire.

In summary, four potential candidates for molecular electronic applications containing a dithienylcyclopentene bridge and two M-tpy moieties at the distal positions were designed and synthesized. The photophysical and electrochemical properties of these molecules can be easily tuned by a simple change of the metal centers and peripheral substituents. Initial studies showed that efficient photocyclization occurred for the bis-Co^{II} complex, while molecules with two Ru^{II} or Fe^{II} centers were subject to electrochemical but not photochemical cyclization. Noteworthy is the influence of different metal species for the cis/trans isomerization in the azo-containing M-tpy complexes that have been demonstrated by the Nishihara group.[11] Future work will focus on the preparation of complexes with anchoring groups in order to study them in break junctions and other devices.[12]

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

Supporting Information Available: Synthetic procedures and characterization, UV/vis spectra, CV analysis of newly prepared compounds, and determination method for the open-to-closed conversion efficiency of bis-tpy ligand **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC701784B

---

(10) (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.

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

(12) 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**, *457*, 438.