Inorg. Chem. **2004**, *43*, 2779–2792

Inorganic Chemistry
Article

Photochromic Dithienylethene Derivatives Containing Ru(II) or Os(II) Metal Units. Sensitized Photocyclization from a Triplet State

Ron T. F. Jukes,[†] Vincenzo Adamo,[§] František Hartl,[†] Peter Belser,[§] and Luisa De Cola*[,†,‡]

Molecular Photonic Materials, Institute of Molecular Chemistry, University of Amsterdam,
Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands, Amsterdam Nanocenter,
Kruislaan 407, 1098 SJ Amsterdam, The Netherlands, and Institute of Inorganic Chemistry,
University of Fribourg, Pérolles CH-1700, Fribourg, Switzerland

Received November 18, 2003

Efficient photocyclization from a low-lying triplet state is reported for a photochromic dithienylperfluorocyclopentene with Ru(bpy)$_3$ units attached via a phenylene linker to the thiophene rings. The ring-closure reaction in the nanosecond domain is sensitized by the metal complexes. Upon photoexcitation into the lowest Ru-to-bpy ^{1}MLCT state followed by intersystem crossing to emitting ^{3}MLCT states, photoreactive ^{3}IL states are populated by an efficient energy-transfer process. The involvement of these ^{3}IL states explains the quantum yield of the photocyclization, which is independent of the excitation wavelength but decreases strongly in the presence of dioxygen. This behavior differs substantially from the photocyclization of the nonemissive dithienylperfluorocyclopentene free ligand, which occurs from the lowest ^{1}IL state on a picosecond time scale and is insensitive to oxygen quenching. Cyclic voltammetric studies have also been performed to gain further insight into the energetics of the system. The very high photocyclization quantum yields, far above 0.5 in both cases, are ascribed to the strong steric repulsion between the bulky substituents on the dithienylperfluorocyclopentene bridge bearing the chelating bipyridine sites or the Ru(bpy)$_3$ moieties, forcing the system to adopt nearly exclusively the reactive antiparallel conformation. In contrast, replacement of both Ru(II) centers by Os(II) completely prevents the photocyclization reaction upon light excitation into the low-lying Os-to-bpy ^{1}MLCT state. The photoreaction can only be triggered by optical population of the higher lying ^{1}IL excited state of the central photochromic unit, but its yield is low due to efficient energy transfer to the luminescent lowest ^{3}MLCT state.

Introduction

In recent years much research effort has been devoted to the development of photochromic materials, that is, systems that can be converted reversibly from one form into another upon light excitation.[1−3] The interest in these compounds stems from their potential application in molecular electronics and information storage.[4−7] One of the most promising classes of photochromic materials are diarylethenes with attached thiophene rings (i.e., dithienylethenes), whose photochromic properties were first described by Irie and Mohri in 1988.[8] Among important features of this class of molecules are the good fatigue resistance, fairly high photocyclization quantum yields, high reversibility of the forward and reverse photoprocesses triggered by irradiation with light of different wavelengths, and thermal stability of the products.[9] In some cases it has been possible to quantitatively transform the system from one form to the other.[10−12]

---

* Author to whom correspondence should be addressed. E-mail: ldc@science.uva.nl.

[†] University of Amsterdam.

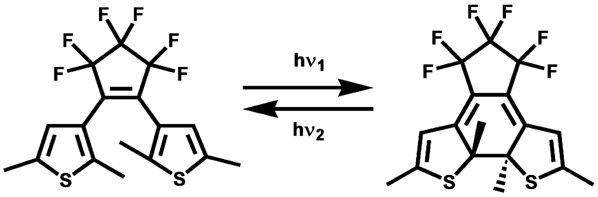
[‡] Amsterdam Nanocenter.

[§] University of Fribourg.

(1) Crano, J. C.; Guglielmetti, R. J. *Organic Photochromic and Thermochromic Compounds*; Kluwer: Dordrecht, 1999; Vol. 1.
(2) Feringa, B. L. *Molecular Switches*; Wiley-VCH: Weinheim, 2001.
(3) Dürr, H.; Bouas-Laurent, H. *Photochromism: Molecules and Systems*; Elsevier: Amsterdam, 2003.
(4) Irie, M. E., Ed. Special edition on "Photochromism: memories and switches". *Chem. Rev.* **2000**, *100* (5).
(5) Joachim, C.; Gimzewski, J. K.; Aviram, A. *Nature* **2000**, *408*, 541−548.
(6) Raymo, F. M. *Adv. Mater.* **2002**, *14*, 401−414.
(7) Balzani, V.; Credi, A.; Venturi, M. *Chem. Phys. Chem.* **2003**, *4*, 49−59.
(8) Irie, M.; Mohri, M. *J. Org. Chem.* **1988**, *53*, 803−808.
(9) Irie, M. *Chem. Rev.* **2000**, *100* (5), 1685−1716.
(10) Irie, M. *Tetrahedron* **1997**, *53*, 12263−12271.
(11) Gilat, S. L.; Kawai, S. H.; Lehn, J. M. *Chem. Eur. J.* **1995**, *1*, 275−284.

10.1021/ic035334e CCC: $27.50

Scheme 1



One of the most commonly investigated groups of dithienylethenes is that based on dithienylperfluorocyclopentene.[9,13−18] The photoreactivity of this kind of molecule is depicted in Scheme 1. The cyclized form of a dithienylethene is usually referred to as closed (Scheme 1, right) and the noncyclized form as open (Scheme 1, left). Considerable effort has been devoted to determine the exact mechanism of the photocyclization for this class of compounds. Theoretical calculations show that upon excitation of the open form to the S_1 state, a barrierless transition takes place to a transient state in which the molecule is strongly distorted.[16,19−21] From this state, the ring closure is favored over decay to the ground state of the open molecule. As the path is barrierless, the process occurs on a very short time scale, typically within 10 ps or less.[9] The photocyclization reaction is generally considered to be restricted to the singlet state. Little attention, limited so far to a single case,[22] has been devoted to the role, in the cyclization reaction, of the low-lying triplet excited states populated either by intersystem crossing from the dithienylethene singlet excited state or by photosensitization. However, the system studied by Xu et al.[22] proved not to be reactive from such a triplet state.

It should be noted that in the open form a dithienylethene molecule can exist in two conformations: (i) parallel, in which the two thiophene rings are in the mirror symmetry; (ii) antiparallel, in which the rings are in the C_2 symmetry.[9] According to the Woodward−Hoffmann rules,[23] the photocyclization reaction can only occur in the antiparallel conformation. For unsubstituted dithienylethenes, the ratio of molecules in the parallel and antiparallel conformations is close to 1:1 and the cyclization quantum yield therefore cannot exceed 0.5.[9] The antiparallel conformation ratio can be favored and the photoreaction enhanced by, for example, attaching bulky groups to the thiophene rings of dithienylethenes,[16,24,25] incorporating the dithienylethene in a polymer backbone,[26] or fixing the molecules in a crystal lattice.[27,28] The existence of the two conformations, only one of which being reactive, has been used as an explanation for the occurrence of both emission and photocyclization from the same sample, even though the time scales of the two processes are completely different. It is assumed that the molecules in the antiparallel conformation all undergo photocyclization, while those in the nonreactive parallel conformation are luminescent.[24,29]

The photocycloreversion is significantly less efficient than the photocyclization, in most cases the quantum yield values typically not exceeding 0.1,[9] although exceptions have been reported.[30−32]

Apart from promoting the photocyclization, the functionalization of the photochromic unit is also important for other reasons, such as tuning the absorption properties to excite the molecule at a desired wavelength or creating a system that can be used for information storage. In many cases, reading out the stored information with light that electronically excites the photochromic compounds causes the information to be lost. A number of different methods to achieve a nondestructive readout have been suggested, such as locking the system in one state[33] or observing changes in optical rotation,[34,35] refractive index,[36] emission,[14,29,37,38] or infrared absorption.[39]

In substituted dithienylethenes the different parts of the molecule are often considered as independent components. The electronic interaction between the parts is then not taken into account in advance, despite the fact that several examples exist where the substituents cause a strong decrease or even

---

(12) Irie, M.; Sakemura, K.; Okinaka, M.; Uchida, K. *J. Org. Chem.* **1995**, *60*, 8305−8309.
(13) Fernández-Acebes, A.; Lehn, J. M. *Chem. Eur. J.* **1999**, *5*, 3285−3292.
(14) Myles, A. J.; Branda, N. R. *Adv. Funct. Mater.* **2002**, *12*, 167−173.
(15) 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**, 1887−1893.
(16) Ern, J.; Bens, A. T.; Martin, H. D.; Kuldova, K.; Trommsdorff, H. P.; Kryschi, C. *J. Phys. Chem. A* **2002**, *106*, 1654−1660.
(17) Krayushkin, M. M.; Stoyanovich, F. M.; Zolotarskaya, O. Y.; Yarovenko, V. N.; Bulgakova, V. N.; Zavarzin, I. V.; Martynkin, A. Y. *Russ. Chem. Bull.* **2002**, *51*, 2097−2099.
(18) Shim, S. D.; Joo, T. H.; Bae, S. C.; Kim, K. S.; Kim, E. Y. *J. Phys. Chem. A* **2003**, *107*, 8106−8110.
(19) Ern, J.; Bens, A. T.; Martin, H. D.; Mukamel, S.; Schmid, D.; Tretiak, D.; Tsiper, E.; Kryschi, C. *J. Lumin.* **2000**, *87−89*, 742−744.
(20) Hania, P. R.; Telesca, R.; Lucas, L. N.; Pugzlys, A.; Esch, J. v.; Feringa, B. L.; Snijders, J. G.; Duppen, K. *J. Phys. Chem. A* **2002**, *106*, 8498−8507.
(21) Guillaumont, D.; Kobayashi, T.; Kanda, K.; Miyasaka, H.; Uchida, K.; Kobatake, S.; Shibata, K.; Nakamura, S.; Irie, M. *J. Phys. Chem. A* **2002**, *106*, 7222−7227.
(22) Xu, B. A.; Huang, Z. N.; Jin, S.; Ming, Y. F.; Fan, M. G.; Yao, S. D. *J. Photochem. Photobiol., A* **1997**, *110*, 35−40.
(23) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970.
(24) Ern, J.; Bens, A. T.; Martin, H. D.; Mukamel, S.; Tretiak, S.; Tsyganenko, K.; Kuldova, K.; Trommsdorff, H. P.; Kryschi, C. *J. Phys. Chem. A* **2001**, *105*, 1741−1749.
(25) Krayushkin, M. M.; Stoyanovich, F. M.; Zolotarskaya, O. Y.; Chernoburova, E. I.; Makhova, N. N.; Yarovenko, V. N.; Zavarzin, I. V.; Martynkin, A. Y.; Uzhinov, B. M. *Chem. Heterocycl. Compd.* **2002**, *38*, 165−176.
(26) Stellacci, F.; Bertarelli, C.; Toscano, F.; Gallazzi, M. C.; Zotti, G.; Zerbi, G. *Adv. Mater.* **1999**, *11*, 292−295.
(27) Shibata, K.; Muto, K.; Kobatake, S.; Irie, M. *J. Phys. Chem. A* **2002**, *106*, 209−214.
(28) Pu, S. Z.; Zhang, F. S.; Sun, F.; Wang, R.; Zhou, X. H.; Chan, S. K. *Tetrahedron Lett.* **2003**, *44*, 1011−1014.
(29) Yagi, K.; Soong, C. F.; Irie, M. *J. Org. Chem.* **2001**, *66*, 5419−5423.
(30) Nakayama, Y.; Hayashi, K.; Irie, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 202−207.
(31) Uchida, K.; Matsuoka, T.; Kobatake, S.; Yamaguchi, T.; Irie, M. *Tetrahedron* **2001**, *57*, 4559−4565.
(32) Morimitsu, K.; Kobatake, S.; Nakamura, S.; Irie, M. *Chem. Lett.* **2003**, *32*, 858−859.
(33) Kawai, S. H.; Gilat, S. L.; Ponsinet, R.; Lehn, J. M. *Chem. Eur. J.* **1995**, *1*, 285−293.
(34) Yamaguchi, T.; Uchida, K.; Irie, M. *J. Am. Chem. Soc.* **1997**, *119*, 6066−6071.
(35) Fernández-Acebes, A. *Chirality* **2000**, *12*, 149−152.
(36) Tanio, N.; Irie, M. *Jpn. J. Appl. Phys.* **1994**, *33*, 1550−1553.
(37) Norsten, T. B.; Branda, N. R. *J. Am. Chem. Soc.* **2001**, *123*, 1784−1785.
(38) Cho, H.; Kim, E. *Macromolecules* **2002**, *35*, 8684−8687.
(39) Uchida, K.; Saito, M.; Murakami, A.; Nakamura, S.; Irie, M. *Adv. Mater.* **2003**, *15*, 121−125.

a complete loss of the photochromic behavior.[13,40] Even though some studies have been performed to clarify the exact effect of certain substituents,[12,29,31] a more general understanding of the way the photochromic unit interacts with the other components of the molecule is crucial for the development of dithienylethenes that are suited for practical applications.

In this study we describe in detail the syntheses, characterization, and electrochemical, photophysical, and photochemical properties of a series of photochromic compounds containing either free chelating ligands or chelated metal complex units. In particular, the dithienylperfluorocyclopentene chromophoric unit is connected through a phenylene linker to 2,2′-bipyridine (bpy) or to the well-known Ru(bpy)$_3$[41] or Os(bpy)$_3$ moieties. We will show that it is possible to sensitize the photocyclization reaction by exciting the ruthenium units. As reported herein, we find that the photoreaction occurs from the triplet excited state of the dithienylethene unit and that the efficiency of the cyclization reaction can be extremely high.

Experimental Section

All reactions were carried out under an argon atmosphere. Solvents were distilled from appropriate drying agents. Perflurocyclopentene was purchased from Fluorochem and tetrakis(triphenylphosphine)palladium(0) from Strem. 4-(4-Bromophenyl)-[2,2]′-bipyridine (**2**) was synthesized using a modified procedure of Montalti et al.[42,43] The 3-bromo-2-methyl-5-thiopheneboronic acid (**3**) was prepared following a published procedure.[11] The precursor metal complex [Ru(bpy)$_2$Cl$_2$]·2H$_2$O was obtained as described in the literature.[44]

4-[4-(4-Bromo-5-methyl-thiophen-2-yl)-phenyl]-2,2′-bipyridine, 4. Tetrahydrofuran (16 mL) and argon-saturated aqueous 2 M sodium carbonate (16 mL) were added to a mixture of 4-(4-bromophenyl)-2,2′-bipyridine (**2**) (1.52 g, 4.89 mmol), 3-bromo-2-methyl-5-thiopheneboronic acid (**3**) (0.90 g, 4.07 mmol), and [Pd(PPh$_3$)$_4$] (141 mg, 0.12 mmol). The resulting two-phase system was refluxed under an argon atmosphere for 24 h and then cooled to room temperature. The white precipitate of ligand **4** was collected by filtration, washed with acetone, and dried in vacuo to afford a white powder. Yield 1.2 g, 72%. mp = 172 °C. ^{1}H NMR [400 MHz, CDCl$_3$]: $\delta = 2.42$ (s, 3H, CH_3(15)), 7.17 (s, 1H, H−C(12)), 7.33 (dd, 1H, $^{3}J = 4.8$ $^{4}J = 1.3$, H−C(5′)), 7.53 (d, 1H, $^{3}J = 5.2$, $^{4}J = 1.8$, H−C(5)), 7.61 (d, 2H, $^{3}J = 8.6$, $^{4}J = 2.0$, H−C(8) and H−C(8′)), 7.77 (d, 2H, $^{3}J = 8.6$, $^{4}J = 2.0$, H−C(9) and H−C(9′)), 7.84 (t, 1H, $^{3}J = 7.8$, $^{4}J = 1.8$, H−C(4′)), 8.46 (d, 1H, $^{3}J = 7.8$, H−C(3′)), 8.69 (d, 1H, $^{3}J = 5.8$, $^{4}J = 1.0$, H−C(6)), 8.70 (s, 1H, H−C(3)), 8.71 (d, 1H, $^{3}J = 5.1$, $^{4}J = 0.5$, H−C(6′)). ^{13}C NMR [100 MHz, CDCl$_3$]: $\delta = 15.0$ (C(15)), 110.2 (C$_{\text{quat.}}$), 118.7 (C(3)), 121.3 (C(5)), 121.4 (C(3′)), 124.0 (C(5′)), 125.9 (C(9) and C(9′)), 126.2 (C(12)), 127.7 (C(8) and C(8′)), 134.3 (C$_{\text{quat.}}$), 134.4 (C$_{\text{quat.}}$), 137.1 (C(4′)), 140.2 (C$_{\text{quat.}}$), 137.3 (C$_{\text{quat.}}$), 148.6 (C$_{\text{quat.}}$), 149.2 (C(6′)), 149.7 (C(6)), 155.9 (C$_{\text{quat.}}$), 156.6 (C$_{\text{quat.}}$). FAB^{+}-MS, *m*/*z*: 407 [M]$^{+}$. Anal. Calcd for C$_{21}$H$_{15}$BrN$_2$S (407.33): C, 61.92; H, 3.71; N, 6.88. Found: C, 62.44; H, 3.64; N, 6.67.

1-{5-[4-(4-[2,2′-Bipyridyl])phenylene]-2-methylthien-3-yl}-perfluorocyclopentene, 6. To a clear solution of **4** (300 mg, 0.74 mmol) in tetrahydrofuran under an argon atmosphere at −78 °C, 1.6 M butyllithium in hexane (0.48 mL, 0.77 mmol) was added slowly while the mixture turned dark. After 30 min, perfluorocyclopentene (**5**) (100 μL, 0.74 mmol) was added through a cold syringe as fast as possible. The mixture was stirred in the dark for 1 h and then warmed to room temperature. The reaction was quenched by addition of 1 M HCl (1.5 mL). The organic solvent was removed under vacuum. After neutralization with aqueous sodium bicarbonate, the product was extracted with 3 × 25 mL dichloromethane and washed with 2 × 10 mL saturated aqueous sodium bicarbonate. The combined organic extracts were dried on Na$_2$SO$_4$, filtered, and evaporated under vacuum. The product was chromatographed over silica gel with dichloromethane/diethyl ether (1:1) to yield a brown powder. Recrystallization from diethyl ether afforded a beige powder. Yield 120 mg, 31%. ^{1}H NMR [400 MHz, CDCl$_3$]: $\delta = 2.50$ (d, 3H, $^{3}J = 3.5$, CH_3(15)), 7.32 (s, 1H, H−C(12)) 7.35 (d, 1H, $^{3}J = 5.0$, H−C(5′)), 7.55 (dd, 1H, $^{3}J = 5.0$, $^{4}J = 1.7$, H−C(5)), 7.66 (d, 2H, $^{3}J = 8.3$, H−C(9) and H−C(9′)), 7.79 (d, 2H, $^{3}J = 8.3$, H−C(8) and H−C(8′)), 7.84 (t, 1H, $^{3}J = 8.1$, $^{4}J = 1.8$, H−C(4′)), 8.46 (d, 1H, $^{3}J = 8.1$, H−C(3′)), 8.69 (s, 1H, H−C(3)), 8.71 (d, 1H, $^{3}J = 5.0$, H−C(6)), 8.73 (d, 1H, $^{3}J = 5.5$, H−C(6′)). ESI-MS, *m*/*z*: 521.09 [M]$^{+}$.

1,2-Bis(5-(4′-(4″-[2,2′]bipyridinylphenyl)-2-methylthiophen-3-yl))perfluorocyclopentene, 1o. To a clear solution of **4** (1.00 g, 2.46 mmol) in tetrahydrofuran at −78 °C under an argon atmosphere, butyllithium (1.6 M in hexane, 1.6 mL, 2.52 mmol) was added slowly while the mixture became dark. After 30 min, perfluorocyclopentene (**5**) (165 μL, 1.23 mmol) was added through a cold syringe as fast as possible. The mixture was then stirred in the dark for 1.5 h and then warmed to room temperature. The reaction was stopped by addition of 1 M HCl (5 mL). The organic solvent was removed under vacuum. After neutralization with aqueous sodium bicarbonate, the product was extracted with 3 × 25 mL dichloromethane and washed with 2 × 10 mL saturated aqueous sodium bicarbonate. The combined organic extracts were dried on Na$_2$SO$_4$, filtered, and evaporated under vacuum. The product was chromatographed over alumina with hexane/ethyl acetate (4:1) to yield a green-brown powder. Recrystallization from diethyl ether afforded a beige powder. Yield 150 mg, 15%. ^{1}H NMR [400 MHz, CDCl$_3$]: $\delta = 2.02$ (s, 3H, CH_3(15)), 7.32 (dd, 1H, $^{3}J = 4.8$, H−C(5′)), 7.35 (s, 1H, H−C(12)), 7.53 (d, 1H, $^{3}J = 5.0$, $^{4}J = 1.8$, H−C(5)), 7.65 (d, 2H, $^{3}J = 8.3$, H−C(9) and H−C(9′)), 7.79 (d, 2H, $^{3}J = 8.3$, H−C(8) and H−C(8′)), 7.83 (t, 1H, $^{3}J = 8.1$, $^{4}J = 1.8$, H−C(4′)), 8.45 (d, 1H, $^{3}J = 8.1$, H−C(3′)), 8.68 (d, 2H, $^{3}J = 6.8$, H−C(6)), 8.71 (s, 1H, H−C(3)), 8.72 (d, 2H, $^{3}J = 7.3$, H−C(6′)). ^{13}C NMR [100 MHz, CDCl$_3$]: $\delta = 15.04$ (C(15)), 21.71 (C(16), C(17), C(18)), 119.06 (C(3)), 121.65 (C(3′)), 121.72 (C(5)), 123.40 (C(12)), 124.26 (C(5′)), 126.52 and 126.46 (C(9) and C(9′)), 128.16 (C(8) and C(8′)), 134.41 (C$_{\text{quat.}}$), 137.38 (C(4′)), 138.07 (C$_{\text{quat.}}$), 141.88 (C$_{\text{quat.}}$), 142.30 (C$_{\text{quat.}}$), 148.76 (C(3)), 149.59 (C(6) and C(6′)), 150.16 (C$_{\text{quat.}}$), 156.49 (C$_{\text{quat.}}$), 157.22 (C$_{\text{quat.}}$). MS (FAB^{+}): *m*/*z* 829.2 [M + H]$^{+}$. HRMS (ESI): *m*/*z* [M + H]$^{+}$ calcd for C$_{47}$H$_{31}$F$_6$N$_4$S$_2$: 829.1889. Found: 829.1888.

[Ru(4)(bpy)$_2$](PF$_6$)$_2$, Ru(4). A solution of **4** (60 mg, 147 μmol) and [Ru(bpy)$_2$Cl$_2$]·2H$_2$O (84 mg, 161 μmol) in 20 mL of methoxyethanol was refluxed for 17 h under an argon atmosphere. The solvent was removed under vacuum and the residue was treated with an aqueous solution of 10% NH$_4$PF$_6$. The precipitate was collected by filtration and washed with water. The crude product

---

(40) Osuka, A.; Fujikane, D.; Shinmori, H.; Kobatake, S.; Irie, M. *J. Org. Chem.* **2001**, *66*, 3913−3923.

(41) Adamo, V.; Belser, P. *Chimia* **2003**, *57*, 169−172.

(42) Montalti, M.; Wadhwa, S.; Kim, W. Y.; Kipp, R. A.; Schmehl, R. H. *Inorg. Chem.* **2000**, *39*, 76−84.

(43) Querol, M.; Bozic, B.; Salluce, N.; Belser, P. *Polyhedron* **2003**, *22*, 655−664.

(44) Lay, P. A.; Sargeson, A. M.; Taube, H. In *Inorganic Syntheses*; Shreeve, J. M., Ed.; Wiley: New York, 1986; Vol. 24, p 292.

was purified by plate chromatography (SiO_2) using a mixture of acetonitrile/methanol/water/saturated solution of potassium nitrate (60:5:5:0.5) as eluent. The main red band was scratched out and isolated with a 1% NH_4PF_6/acetone solution as solvent. After water was added, the organic solvent was removed, and an orange-red powder was recovered by filtration. Yield 129 mg, 79%. ^{1}H NMR [400 MHz, CD_3OD]: $\delta = 2.44$ (s, 3H, CH_3(15)), 7.37 (s, 1H, H−C(12)), 7.52 (m, 5H, H−C(5′), *H*−C(5″), *H*−C(5$_b$″), *H*−C(5‴), and *H*−C(5$_b$‴)), 7.80 (m, 8H, *H*−C(5), *H*−C(6), *H*−C(6′), *H*−C(6$_b$″), *H*−C(6‴), *H*−C(6$_b$‴), *H*−C(9), and *H*−C(9′)), 7.97 (m, 3H, *H*−C(6″), *H*−C(8), and *H*−C(8′)), 8.14 (m, 5H, *H*−C(4′), *H*−C(4″), *H*−C(4$_b$″), *H*−C(4‴), and *H*−C(4$_b$‴)), 8.71 (dd, 4H, $^3J = 8.2$, $^4J = 2.15$, *H*−C(3″), *H*−C(3b″), *H*−C(3‴), and *H*−C(3b‴)), 8.90 (d, 1H, $^3J = 8.1$, *H*−C(3′)), 8.97 (d, 1H, $^3J = 1.77$, *H*−C(3)). ^{13}C NMR [100 MHz, $CDCl_3$]: $\delta = 13.8$, 110.5, 118.5, 121.5, 124.6, 124.9, 126.0, 127.1, 127.9, 128.1, 138.2, 151.6, 157.5. MS (ESI): *m/z* 965.03 $[M - 1PF_6]^{1+}$, 411.03 $[M - 2PF_6]^{2+}$. HRMS (ESI): *m/z* $[M - 2PF_6]^{2+}$ calcd for $C_{41}H_{31}BrN_6Ru(102)S$: 411.0262. Found: 411.0263.

[Ru(6)(bpy)$_2$](PF$_6$)$_2$, Ru(6). A solution of **6** (23 mg, 44.2 μmol) and $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (25 mg, 42 μmol) in 10 mL of methoxyethanol was refluxed for 17 h under an argon atmosphere. The solvent was removed under vacuum and the residue was treated with an aqueous solution of 10% NH_4PF_6. The precipitate was collected by filtration and washed with water. The crude product was purified by plate chromatography (SiO_2) using a mixture of acetonitrile/methanol/water/saturated solution of potassium nitrate (60:5:5:0.5) as eluent. The main red band was scratched out and isolated with a 1% NH_4PF_6/acetone solution as solvent. After water was added, the organic solvent was removed, and an orange-red powder was recovered by filtration. Yield 25 mg, 46%. ^{1}H NMR [400 MHz, CD_3OD]: $\delta = 2.54$ (d, 3H, $^3J = 2.7$, CH_3(15)), 7.52 (m, 6H, H−C(12), H−C(5′), *H*−C(5″), *H*−C(5$_b$″), *H*−C(5‴), and *H*−C(5$_b$‴)), 7.85 (m, 8H, *H*−C(5), *H*−C(6), *H*−C(6′), *H*−C(6$_b$″), *H*−C(6‴), *H*−C(6$_b$‴), *H*−C(9), and *H*−C(9′)), 7.95 (d, 1H, $^3J = 5.6$, *H*−C(6″)), 8.01 (d, 2H, $^3J = 8.6$, *H*−C(8), and *H*−C(8′)), 8.13 (m, 5H, *H*−C(4′), *H*−C(4″), *H*−C(4$_b$″), *H*−C(4‴), and *H*−C(4$_b$‴)), 8.71 (dd, 4H, $^3J = 8.0$, $^4J = 2.4$, *H*−C(3″), *H*−C(3b″), *H*−C(3‴), and *H*−C(3b‴)), 8.90 (d, 1H, $^3J = 8.1$, *H*−C(3′)), 8.98 (d, 1H, $^3J = 1.5$, *H*−C(3)). ^{13}C NMR [400 MHz, $CDCl_3$]: $\delta = 13.6$, 120.7, 121.7, 123.4, 124.6, 124.9, 126.5, 128.0, 128.3, 135.5, 138.2, 141.8, 144.8, 149.4, 151.6, 157.5, 157.6, 157.9. MS (ESI): *m/z* 1079.07 $[M - 1PF_6]^{1+}$, 467.07 $[M - 2PF_6]^{2+}$. HRMS (ESI): *m/z* $[M - 2PF_6]^{2+}$ calcd for $C_{46}H_{31}F_7N_6Ru(102)S$: 467.0622. Found: 467.0626.

[{Ru(bpy)$_2$}$_2$(μ-1o)](PF$_6$)$_4$, Ru(μ-1o)Ru. A solution of **1o** (21.5 mg, 0.024 mmol) and $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (27 mg, 0.051 mmol) in 5 mL of methoxyethanol was refluxed for 15 h under an argon atmosphere. The solvent was distilled off under vacuum and the residue was treated with an aqueous solution of 10% NH_4PF_6. The precipitate was collected by filtration and washed with water. The crude product was purified by plate chromatography (SiO_2), using a mixture of acetonitrile/methanol/water/saturated solution of potassium nitrate (40:10:10:1) as eluent. The main orange band was scratched out and isolated with a 1% NH_4PF_6/acetone solution as solvent. After water was added, the organic solvent was removed, and an orange-red powder was recovered by filtration. Yield 24 mg, 40%. ^{1}H NMR [400 MHz, CD_3OD]: $\delta = 2.09$ (s, 6H), 7.52 (m, 12H), 7.84 (m, 16H), 7.96 (d, 2H, $^3J = 5.6$), 8.01 (d, 4H, $^3J = 8.6$), 8.15 (m, 10H), 8.72 (dd, 8H, $^3J = 8.1$, $^4J = 0.8$), 8.91 (d, 2H, $^3J = 8.1$), 8.99 (d, 2H, $^3J = 1.3$). ^{13}C NMR [100 MHz, $CDCl_3$]: $\delta = 14.6$, 30.8, 122.6, 124.9, 125.6, 125.9, 127.3, 127.4, 129.0, 129.3, 136.3, 136.6, 139.2, 142.6, 144.0, 150.4, 152.6, 152.7, 158.5, ÁD 158.7, 158.9. MS (ESI): *m/z* 973.11 $[M - 2PF_6]^{2+}$, 600.42 $[M - 3PF_6]^{3+}$, 414.07 $[M - 4PF_6]^{4+}$. HRMS (ESI): *m/z* $[M - 4PF_6]^{4+}$ calcd for $C_{87}H_{62}F_6N_{12}Ru(102)_2S_2$: 414.0659. Found: 414.0658.

[{Os(bpy)$_2$}$_2$(μ-1o)](PF$_6$)$_4$, Os(μ-1o)Os. A solution of **1o** (15.0 mg, 0.018 mmol) and $[Os(bpy)_2Cl_2]$ (10.4 mg, 0.018 mmol) in 5 mL of methoxyethanol was refluxed overnight under an argon atmosphere. The solvent was distilled off under vacuum and the residue was treated with an aqueous solution of 10% NH_4PF_6. The precipitate was collected by filtration and washed with water. The crude product was purified by plate chromatography (SiO_2), using a mixture of acetonitrile/methanol/water/saturated solution of potassium nitrate (40:10:10:1) as eluent. After isolation and reprecipitation with ammonium hexafluorophosphate, a dark green powder was obtained. Yield 10.5 mg, 24%. ^{1}H NMR [400 MHz, CD_3OD]: $\delta = 2.07$ (s, 6H), 7.43 (m, 10H), 7.57 (s, 2H), 7.77 (m, 12H), 7.85 (m, 6H), 7.98 (m, 14 H), 8.71 (d, 8H, $^3J = 7.5$), 8.90 (d, 2H, $^3J = 8.0$), 8.99 (s, 2H). MS (ESI): *m/z* 1062.17 $[M - 2PF_6]^{1+}$, 659.78 $[M - 3PF_6]^{3+}$, 458.60 $[M - 4PF_6]^{4+}$. HRMS (ESI): *m/z* $[M - 4PF_6]^{4+}$ calcd for $C_{87}H_{62}F_6N_{12}Os(190)Os(192)S_2$: 458.5948. Found: 458.5936.

General Techniques. ^{1}H and ^{13}C NMR spectra were obtained with Varian Gemini-300 (300.075 MHz for ^{1}H and 75.4 MHz for ^{13}C) or Bruker Avance DRX-400 (400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C) spectrometers. Chemical shifts (δ) are given in ppm, using the solvent itself as internal standard. The coupling constants (J) are given in Hertz. The ^{1}H and ^{13}C numbering is depicted in Chart 1.

Mass spectra were recorded on a Vacuum Generators Micromass VG 70/70E (FAB ionization, nitrobenzyl alcohol matrix of the sample) mass spectrometer. ESI and high-resolution mass spectra were recorded on a Brucker FTMS 4.7T BioAPEXII spectrometer.

UV−vis spectra were recorded on a Hewlett-Packard 8453 diode array or Varian Cary 4 spectrophotometers and emission spectra with a Spex 1681 spectrofluorometer. Deaerated solutions were prepared by the freeze−pump−thaw technique on a vacuum line. All emission spectra were corrected for the photomultiplier response. Luminescence quantum yields were determined for optically diluted solutions, using an aerated aqueous solution of $[Ru(bpy)_3]Cl_2$ ($\varphi_{em} = 0.028$)[45] as reference for the **Ru(μ-1o)Ru**, **Ru(μ-1c)Ru**, **Ru(4),** and **Ru(6)** complexes and an aerated solution of $[Os(bpy)_3](PF_6)_2$ in MeCN ($\varphi_{em} = 0.0035$)[46] for the **Os(μ-1o)-Os** complex.

Nanosecond time-resolved absorption spectra were measured using a setup described previously.[47] The irradiation source was a continuously tunable (400−700 nm) Coherent Infinity XPO laser working at 10 Hz (2 ns fwhm). A 50% mirror is used to divide the probe light into a sample and a reference beam, which greatly improves the signal-to-noise ratio. Where necessary, a stock solution was flowed through a cell, so that the probed solution was constantly renewed.

Time-resolved emission studies were performed using the continuously tunable (400−700 nm) Coherent Infinity XPO laser as the excitation source. The emitted light was detected with a streak camera (Hamamatsu C5680-21) equipped with a M 5677 sweep unit.

(Sub)picosecond transient absorption spectra were measured using a setup described in detail in a previous paper.[48] The laser

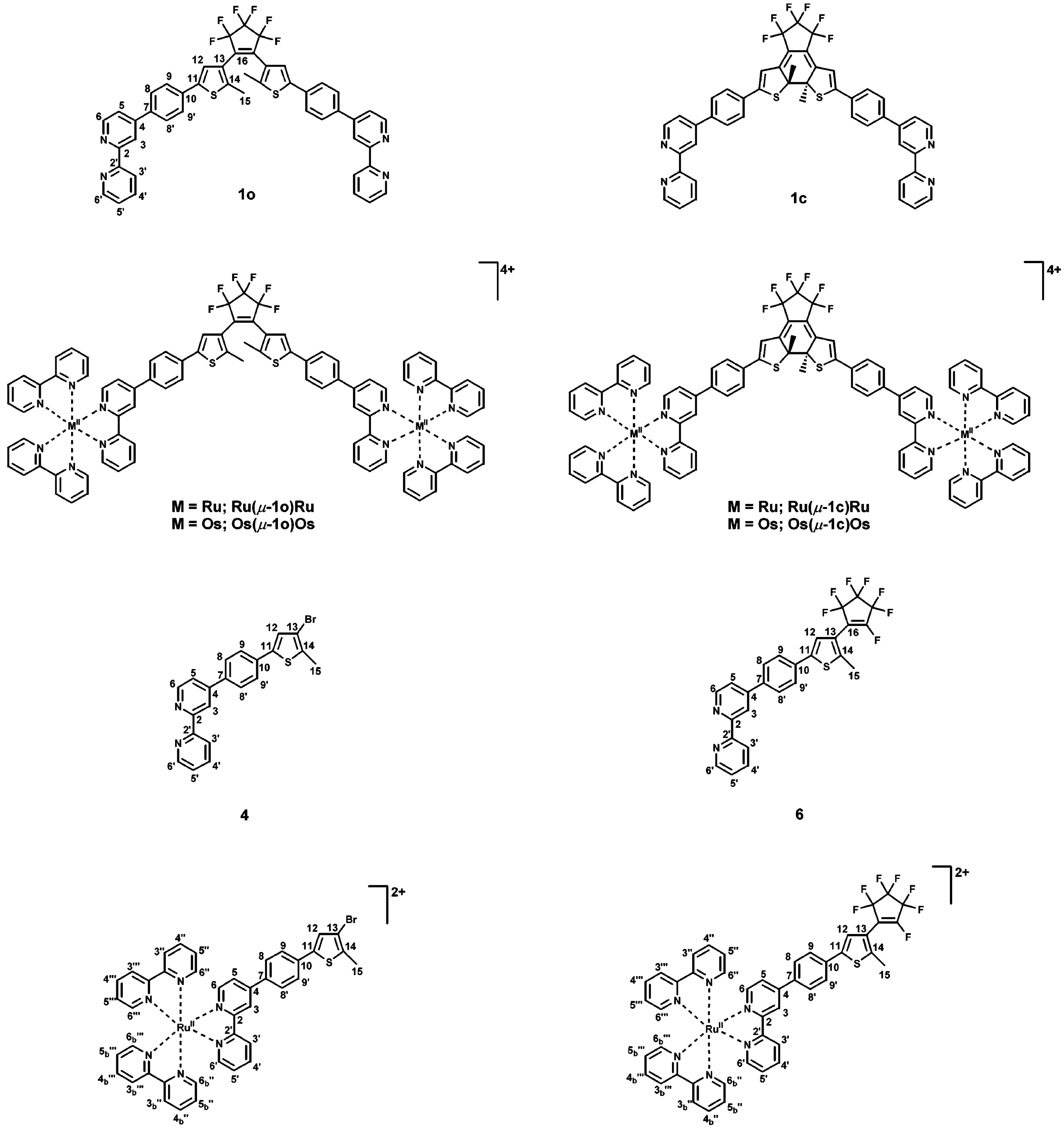
---

(45) Nakamaru, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697−2705.

(46) Frank, M.; Nieger, M.; Vögtle, F.; Belser, P.; Zelewsky, A. v.; De Cola, L.; Balzani, V.; Barigelletti, F.; Flamigni, L. *Inorg. Chim. Acta* **1996**, *242*, 281−291.

(47) Kleverlaan, C. J.; Stufkens, D. J.; Clark, I. P.; George, M. W.; Turner, J. J.; Martino, D. M.; Willigen, H. v.; Vlček, A., Jr. *J. Am. Chem. Soc.* **1998**, *120*, 10871−10879.

Chart 1. Schematic Molecular Structures of the Studied Compounds, with Numbering of ^1H and ^{13}C Positions



1o

1c

M = Ru; Ru(μ-1o)Ru
M = Os; Os(μ-1o)Os

M = Ru; Ru(μ-1c)Ru
M = Os; Os(μ-1c)Os

4

6

Ru(4)

Ru(6)

part is based on a Spectra-Physics Hurrican Ti-sapphire regenerative amplifier system. The full spectrum setup is based on an optical parametric amplifier (Spectra-Physics OPA 800) as a pump. A residual fundamental light from the pump OPA is used for the generation of white light that is detected with a CCD spectrograph. The laser output is typically 5 μJ pulse^{-1} (130 fs fwhm) with a repetition rate of 1 kHz. A circular cuvette ($d = 1.8$ cm, 1 mm, Hellma) with the sample solution was placed in a homemade rotating ball bearing (1000 rpm), to avoid local heating by the laser beam and buildup of a photoproduct.

Photocyclization quantum yields were determined by monitoring the increasing visible absorbance of the photoproduct upon irradiation. The photoconversion was kept below 10%. Absorption at the irradiation wavelength was always >3 to ensure total absorption of the incident light. The medium-pressure Xe lamp of the Spex 1681 spectrofluorometer with a stable monochromatized output served as the irradiation source. The photon flux was determined before and after each measurement, using the Aberchrome 540 and Aberchrome 540P actinometers in toluene.[49]

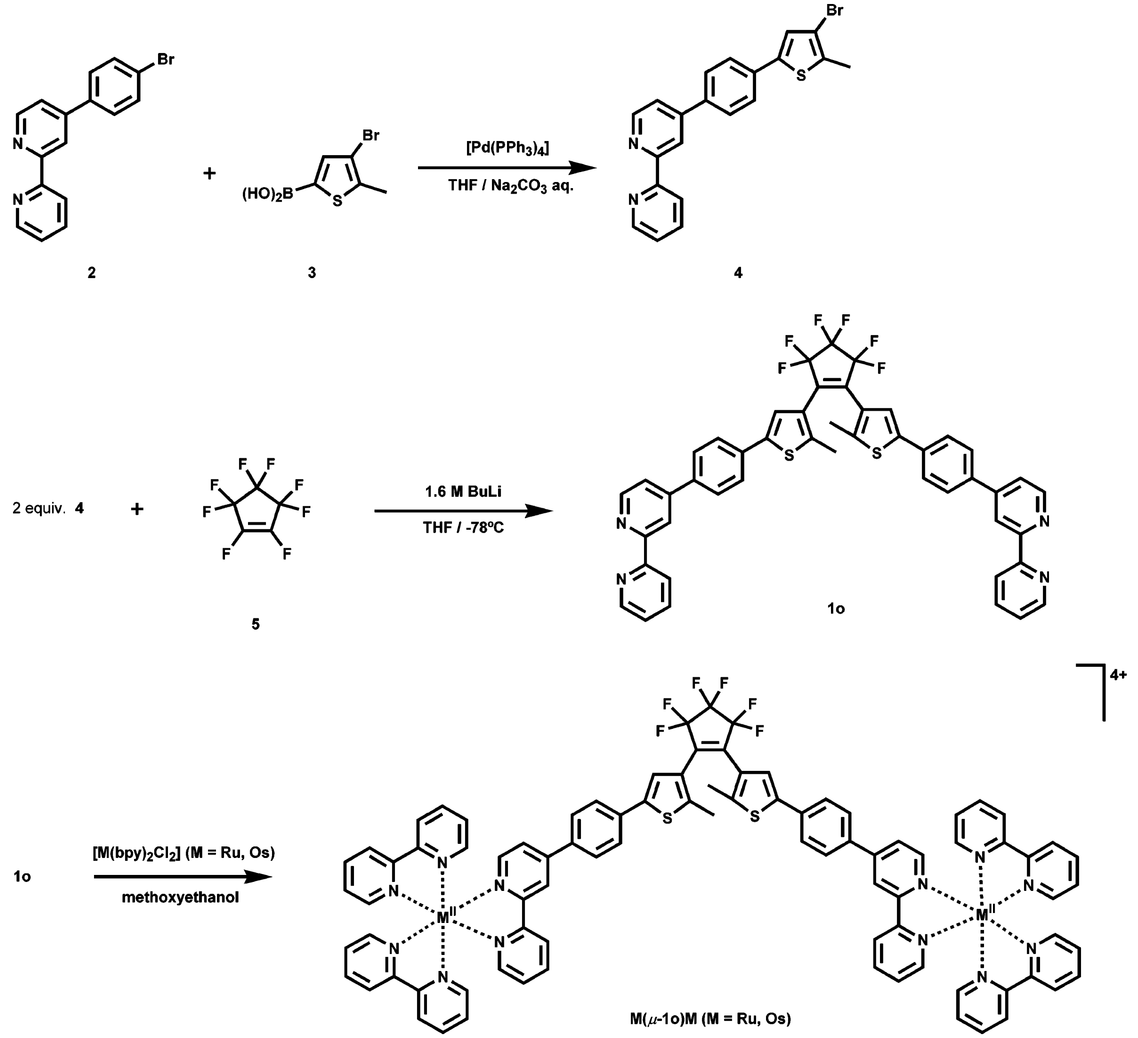
Cyclic and Osteryoung square-wave voltammograms of approximately 10^{-4} M parent compounds in 10^{-1} M Bu_4NPF_6 electrolyte solution were recorded in a gastight single-compartment three-electrode cell equipped with platinum disk working (apparent surface of 0.42 mm^2), coiled platinum wire auxiliary, and silver wire pseudoreference electrodes. The cell was connected to a

---

(48) Campagna, S.; Serroni, S.; Puntoriero, F.; Loiseau, F.; De Cola, L.; Kleverlaan, C. J.; Becher, J.; Sorensen, A. P.; Hascoat, P.; Thorup, N. *Chem. Eur. J.* **2002**, *8*, 4461−4469.

(49) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 341−343.

Scheme 2



computer-controlled PAR Model 283 potentiostat. All redox potentials are reported against the ferrocene/ferrocenium (Fc/Fc$^+$) redox couple used as internal standard.[50,51]

Estimated experimental errors in the reported data are as follows: absorption and emission maxima ±2 nm; emission lifetime ±8%; emission quantum yield ±20%; photocyclization quantum yield ±10%.

Results and Discussion

Syntheses. All investigated compounds are depicted in Chart 1. Two homodinuclear complexes containing either Ru(II) (**Ru(*μ*-1o)Ru**) or Os(II) (**Os(*μ*-1o)Os**) centers, have been synthesized from free ligand **1o**. Model compounds **4**, **6**, **Ru(4)**, and **Ru(6)** have also been prepared and studied. Compounds **4** and **6** can be regarded to represent half of free ligand **1o** and were used as references in the electrochemical study only. Complexes **Ru(4)** and **Ru(6)**, representing approximately half of complex **Ru(*μ*-1o)Ru** were also employed as photophysical references since [Ru(bpy)$_3$]$^{2+}$ proved to be inappropriate for **Ru(*μ*-1o)Ru**. Synthetic details for all the studied compounds are given in the Experimental Section. The general procedure involves the preparation of photoactive dithienylethene bridging ligand **1o** containing two bipyridine chelating sites. Then, this ligand is complexed with precursors [Ru(bpy)$_2$Cl$_2$]·2H$_2$O and [Os(bpy)$_2$Cl$_2$] to obtain the corresponding homodinuclear complexes **Ru(*μ*-1o)Ru** and **Os(*μ*-1o)Os**, respectively (Scheme 2). After isolation of the products as hexafluorophosphate salts, their purification was performed on a preparative plate (SiO$_2$).

A number of studies were carried out on dithienylethenes substituted with metal centers, with the aim to achieve a nondestructive readout. Attempts were made to observe a significant change either in the emission of the metal center[13,14,52] or in the electronic coupling between two metal centers[53] upon photocyclization. The use of metal complexes has the critical advantage that the energy levels, excited-state lifetimes, and redox properties of the metal center can be easily tuned. Furthermore, when different spacers (length, geometry, and electronic nature) are employed to connect the metal units with the photochromic moiety, strongly or

---

(50) Gritzner, G.; Kůta, J. *Pure Appl. Chem.* **1984**, *56*, 461−466.

(51) Pavlishchuk, V. V.; Addison, A. W. *Inorg. Chim. Acta* **2000**, *298*, 97−102.

(52) Norsten, T. B.; Branda, N. R. *Adv. Mater.* **2001**, *13*, 347−349.

(53) Fraysse, S.; Coudret, C.; Launay, J. P. *Eur. J. Inorg. Chem.* **2000**, 1581−1590.

Table 1. UV−Vis Absorption Spectra and Absorption Molar Coefficients of the Investigated Photochromic Compounds in Their Open and Closed Forms[a]

compound	λ_{max}/nm (ϵ_{max}/10^4 M^{-1} cm^{-1})				
1o	239 (4.2)	285 (sh, 4.9)	321 (6.3)		
1c	243 (4.2)	277 (4.0)	331 (4.8), 605 (2.0)	392 (sh, 1.3)	
Ru(μ-1o)Ru	245 (7.4)	288 (15.6)	345 (7.1)		458 (4.2)
Ru(μ-1c)Ru	245 (6.8)	288 (14.9)	328 (sh, 6.5), 614 (3.2)	402 (3.0)	458 (3.8)
Ru(4)	245 (3.1)	289 (6.9)	343 (2.9)		458 (1.9)
Ru(6)	246 (3.9)	288 (7.1)	338 (3.2)		456 (1.9)
Os(μ-1o)Os	246 (7.0), 492 (3.4)	292 (15.1), 590 (0.9)	353 (6.3)		441 (3.6)
Os(μ-1c)Os	246 (6.2), 492 (3.3)	292 (13.9)	331 (sh, 5.7), 618 (3.7)	393 (3.4)	445 (3.1)

[a] In MeCN at 293 K.

weakly interacting systems can be designed. The metal complex substituents might then be used as sensitizers for the photoreaction, shifting the wavelength at which cyclization can be triggered into the visible region. Too strong an electronic coupling, however, may change the properties of the photochromic unit to such an extent that no photoreaction occurs any longer.[13] Therefore, a good balance of the electronic interaction between the chromophoric units must be achieved. To prevent a full electronic delocalization (upon excitation) on the system, we have included a phenylene group as a semiconductive spacer between the dithienylethene unit and the metal complexes (Chart 1). Furthermore, the absorption properties of the compounds are such to allow selective excitation of the different components (see below).

The complexation with either Ru(II) or Os(II) causes big changes in the spectroscopic properties of the compounds compared to the free ligand. For the metal complexes, an absorption band due to a singlet metal-to-ligand charge-transfer transition (^{1}MLCT) is present at a lower energy than the $S_0 \rightarrow S_1$ transition of the photochromic unit in the open state. The S_1 state (^{1}IL), therefore, is not populated upon irradiation into the ^{1}MLCT band. However, Ru(II) and Os(II) complexes show efficient intersystem crossing (ISC) from the ^{1}MLCT to the ^{3}MLCT state, from which the T_1 state (^{3}IL) of the photochromic unit can be populated provided it lies at a lower energy than the ^{3}MLCT state. As only little is known about the energy of the T_1 state of dithienylethenes, we have synthesized both the diruthenium and diosmium complexes that are structurally identical, but differ in energies of their MLCT states.

Upon photocyclization, the properties of the excited states of the dithienylethene moiety change dramatically, resulting in a different photochemical, photophysical, and electrochemical behavior of the open and closed forms. As both metal complex moieties are luminescent and their emission properties depend on the state of the photochromic unit, this could be a way to monitor the photoreaction and to understand its intimate mechanism.

Electronic Absorption and Emission Spectroscopic Properties. UV−vis absorption maxima and corresponding molar absorption coefficients of compounds **1o**, **1c**, **Ru(4)**, **Ru(6)**, **Ru(μ-1o)Ru**, **Ru(μ-1c)Ru**, **Os(μ-1o)Os**, and **Os(μ-1c)Os** are listed in Table 1.

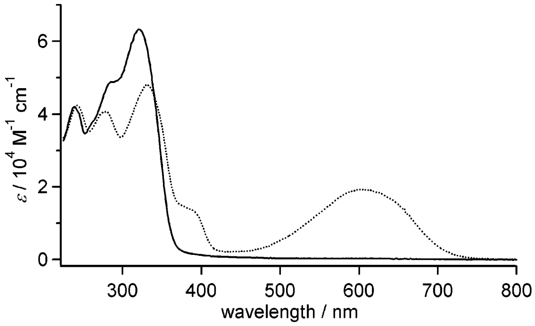


Figure 1. UV−vis spectra of compound **1o** (—) and a solution of **1o/1c** in the photostationary state (···). The latter spectrum corresponds to a 98% photoconversion of **1o** to **1c**, as determined from the corresponding ^{1}H NMR spectrum. Conditions: MeCN, 293 K.

The open form of the uncoordinated ligand **1o** in acetonitrile is colorless. The electronic absorption spectra of **1o** and **1c** in acetonitrile are shown in Figure 1. The absorption maximum at 321 nm corresponds to the $S_0 \rightarrow S_1$ (^{1}IL) transition localized on the photochromic unit, while the shoulder at 285 nm involves the $\pi \rightarrow \pi^*$ transition of the bpy ligands. Upon conversion to the closed form **1c**, the solution turns blue. The cyclization forces the system into a more planar conformation, thereby increasing the conjugation and lowering the energy of the $S_0 \rightarrow S_1$ transition of the photochromic unit.[9] As can be seen in Figure 1, the bpy intraligand transitions are not affected by the cyclization of the central unit, while the $S_0 \rightarrow S_1$ absorption of the dithienylethene moiety shifts from 321 to 605 nm. The bands at 392 and 331 nm are assigned to the $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ transitions, respectively.[19]

Complex **Ru(μ-1o)Ru** in acetonitrile is yellow. The UV−vis spectra of **Ru(μ-1o)Ru** and **Ru(μ-1c)Ru** in this solvent are shown in Figure 2. By comparison with $[Ru(bpy)_3]^{2+}$, the bands at 288 and 458 nm in the spectrum of **Ru(μ-1o)Ru** can be assigned to a ligand-centered transition localized on the bpy ligands and a Ru^{II}-to-bpy charge-transfer (^{1}MLCT) transition, respectively.[54] The MLCT band shifts to slightly lower energy compared to $[Ru(bpy)_3]^{2+}$, as also found for model complexes **Ru(4)** and **Ru(6)** (Table 1), indicating that in the ^{1}MLCT state the charge is localized on the more conjugated substituted bpy ligand (see also section on

---

(54) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85−277.

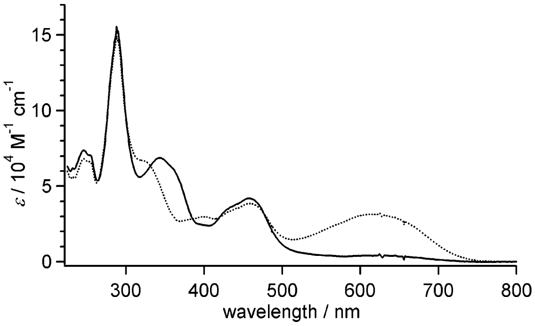


Figure 2. UV−vis spectra of complex **Ru(μ-1o)Ru** (—) and a solution of **Ru(μ-1o)Ru/Ru(μ-1c)Ru** in the photostationary state (···). The latter spectrum corresponds to a 97% photoconversion of **Ru(μ-1o)Ru** to **Ru(μ-1c)Ru**, as determined from the corresponding ^{1}H NMR spectrum. Conditions: MeCN, 293 K.

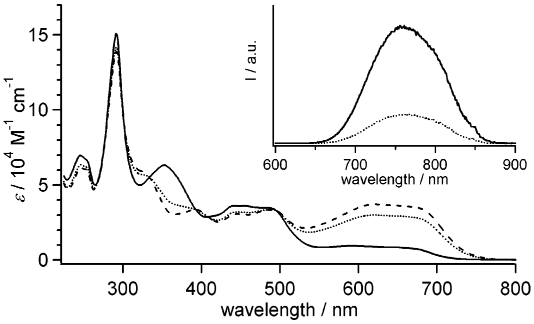


Figure 3. UV−vis spectra of complex **Os(μ-1o)Os** (—) and a solution of **Os(μ-1o)Os/Os(μ-1c)Os** in the photostationary state (···). The latter spectrum corresponds to a 73% photoconversion of **Os(μ-1o)Os** to **Os(μ-1c)Os**, as determined from the corresponding ^{1}H NMR spectrum. The UV−vis spectrum of pure **Os(μ-1c)Os** (- - -) was constructed by extrapolation to 100% photoconversion. Inset: the corresponding decrease in emission of **Os(μ-1o)Os** upon conversion from 100% open form to the photostationary state. Conditions: MeCN, 293 K.

Transient Absorption Spectroscopy). The absorption band at 345 nm corresponds to the $S_0 \rightarrow S_1$ (^{1}IL) transition localized on the central photochromic unit. The electron-withdrawing metal center causes a lowering of the LUMO on the photochromic unit (see also Table 4), resulting in a shift of the corresponding absorption band to a significantly lower energy compared to the free ligand **1o**. Upon irradiation of the solution, conversion to **Ru(μ-1c)Ru** is observed. The band at 345 nm disappears and a new absorption band grows in at 614 nm, giving the solution green color. By analogy to **1c**, the band at 614 nm can be ascribed to the ^{1}IL transition localized on the cyclized dithienylethene. The ^{1}IL$_{\text{bpy}}$ band at 288 nm and the ^{1}MLCT band at 458 nm, which correspond to electronic transitions not localized on the photochromic bridge but on the metal centers, vary only little upon irradiation.

The UV−vis spectra of **Os(μ-1o)Os** and **Os(μ-1c)Os** in acetonitrile are shown in Figure 3. The open osmium complex **Os(μ-1o)Os** exhibits the same kind of absorption bands as the ruthenium complex **Ru(μ-1o)Ru** (Table 1). The spectrum also contains a broad and relatively weak absorption band between 500 and 700 nm, giving the solution green color already when the complex is in the open form. This band can be assigned to partially allowed ^{3}MLCT transitions, typical for $[\text{Os(bpy)}_3]^{2+}$-type complexes. Upon conversion to **Os(μ-1c)Os**, the ^{1}IL band of the closed dithienylethene form arises in the 550−750-nm region and the green color of the solution turns darker.

Table 2. Emission Maxima (λ_{Max}), Lifetimes (τ), and Quantum Yields (φ_{em}) of Investigated Photochromic Complexes **Ru(μ-1o)Ru**, **Os(μ-1o)Os**, and Mononuclear Models **Ru(4)** and **Ru(6)**[a]

		τ/ns		φ_{em}[b]	
compound	λ_{max}/nm	aerated	deaerated	aerated	deaerated
Ru(μ-1o)Ru	630	140	310	0.006 (334) 0.007 (450)	0.014 (334) 0.014 (450)
Os(μ-1o)Os	759	44	62	0.004 (334) 0.004 (450)	0.005 (334) 0.006 (450)
Ru(4)	626	240	2250	0.012 (334) 0.011 (450)	0.095 (334) 0.098 (450)
Ru(6)	626	220	2100	0.013 (334) 0.011 (450)	0.113 (334) 0.121 (450)

[a] In MeCN at $T = 293$ K. [b] Irradiation wavelength (nm) in brackets.

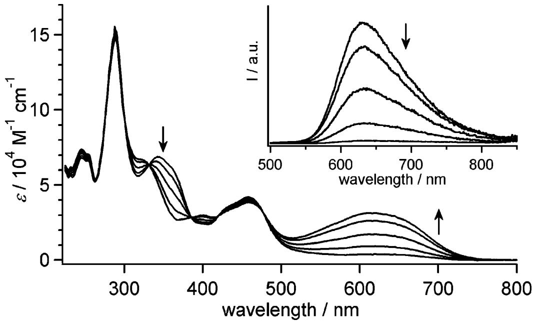


Figure 4. UV−vis spectral changes accompanying the photocyclization of **Ru(μ-1o)Ru** to **Ru(μ-1c)Ru**. Inset: the corresponding decrease in emission of **Ru(μ-1o)Ru**. Conditions: MeCN, 293 K.

Emission spectra and emission lifetimes in acetonitrile solution at room temperature have been recorded for **Ru(μ-1o)Ru** and **Os(μ-1o)Os** and for reference compounds **Ru(4)** and **Ru(6)**. Emission quantum yields have also been determined. The results are summarized in Table 2. No emission could be detected for **1o** and **1c** and the corresponding closed form of the ruthenium and osmium complexes.

Excitation of **Ru(μ-1o)Ru**, either into the ^{1}IL or ^{1}MLCT transitions, results in light emission with a maximum at 630 nm (Figure 4). The broad and featureless emission can be assigned to originate from the ^{3}MLCT state.[54] As normally observed for emission from triplet states, it is quenched by dioxygen and, therefore, for an aerated solution a shorter excited-state lifetime and a lower emission quantum yield are found than for a deaerated solution (Table 2). Both the emission lifetime and quantum yield are independent of the excitation wavelength.

A close comparison with reference complexes **Ru(4)** and **Ru(6)** shows that the excited-state properties of **Ru(μ-1o)Ru** are very different from those of the model compounds. These complexes have been chosen as proper reference, as their bpy substituents closely resemble those in **Ru(μ-1o)Ru**, but they cannot undergo any photocyclization reaction. Therefore, **Ru(4)** and **Ru(6)** should give a good guess of the emission lifetime and quantum yield that would have been found for **Ru(μ-1o)Ru** in the absence of other processes. Their extended bpy(ph) π-system (Chart 1) causes their emission properties to be remarkably different from those of unsubstituted $[Ru(bpy)_3]^{2+}$, showing that the latter complex is not an appropriate reference.

Both **Ru(4)** and **Ru(6)** in deaerated acetonitrile have high emission quantum yields and long excited-state lifetimes. This is the result of a strong delocalization of the excited MLCT state on the substituted bipyridine ligand. This effect has already been described in the literature for $Ru(bpy)_3$-type complexes substituted with phenyl groups in the 4- and 4′-positions.[55,56] Their emission lifetimes and quantum yields exceed those of **Ru(*μ*-1o)Ru** seven to eight times. Provided the emissive states of **Ru(*μ*-1o)Ru**, **Ru(4)**, and **Ru(6)** are very similar, as also demonstrated by their almost identical absorption and emission spectra, this difference can only be explained by the presence of a nonradiative deactivation path for the **Ru(*μ*-1o)Ru**. The fact that the emission lifetime of **Ru(*μ*-1o)Ru** is reduced to the same extent as the emission quantum yield indicates that there is a direct pathway from the emissive state to the reactive state or that both processes occur from the same state. Upon photoconversion of **Ru(*μ*-1o)Ru** to **Ru(*μ*-1c)Ru**, the intensity of the emission diminishes. In the photostationary state the emission quantum yield reaches merely 3% of the original value (Figure 4). The residual emission has the same lifetime as that of the open form, suggesting that a small amount of **Ru(*μ*-1o)Ru** is not converted to **Ru(*μ*-1c)Ru** (see also next section), and that in fact **Ru(*μ*-1c)Ru** is nonemissive.

The emission spectrum in acetonitrile of **Os(*μ*-1o)Os** exhibits a broad structureless band with a maximum at 759 nm (Figure 3, inset), due to the decay of the ^{3}MLCT state. The emission quantum yield and lifetime are almost identical to those reported for $[Os(bpy)_3]^{2+}$ and are independent of the excitation wavelength. Upon conversion of **Os(*μ*-1o)Os** to **Os(*μ*-1c)Os**, the emission intensity decreases and reaches 25% of the original intensity (Figure 3, inset), while the emission lifetime remains the same. Like in the case of the corresponding ruthenium complex, the residual emission is attributed to unconverted molecules **Os(*μ*-1o)Os** (see also next section), and also **Os(*μ*-1c)Os** is considered to be nonemissive.

Photochemical Reactions. To fully understand the emission properties, it is necessary to analyze the photochemical behavior of the systems and to establish which excited states are involved in the conversion of the open forms **1o**, **Ru(*μ*-1o)Ru**, **Os(*μ*-1o)Os** to the closed forms **1c**, **Ru(*μ*-1c)Ru**, **Os(*μ*-1c)Os** and vice versa. The photochemical reactions have been studied in acetonitrile in the presence and absence of dioxygen. The photocyclization reaction can be easily followed by UV−vis absorption and emission spectroscopy since, as already mentioned above, the photophysical properties of the two forms are very different. An almost quantitative conversion of **1o** to **1c** can be achieved by irradiation with UV light. The reverse reaction is triggered by visible light since the closed form has a strong absorption in the 500−700-nm region (Figure 1). The dinuclear ruthenium complex can also be converted almost quantitatively from the open form **Ru(*μ*-1o)Ru** to the closed form **Ru(*μ*-1c)Ru** upon irradiation into the ^{1}IL or ^{1}MLCT bands (Figure 2). Open form **Ru(*μ*-1o)Ru** is slowly recovered upon irradiation of **Ru(*μ*-1c)Ru** into the ^{1}IL band of the photochromic unit (600−750 nm). At shorter wavelength than 600 nm, this band overlaps with the ^{1}MLCT band of **Ru(*μ*-1o)Ru** and, therefore, full photocycloreversion can only be achieved by irradiation with light $\lambda > 600$ nm. Open form **Os(*μ*-1o)Os** can only be converted to closed form **Os(*μ*-1c)Os** by irradiation into the ^{1}IL band at 353 nm (Figure 3). Irradiation into the ^{1}MLCT band at 492 nm does not lead to cyclization. Slow and inefficient photocycloreversion of **Os(*μ*-1c)Os** can be achieved by irradiation into the ^{1}IL band (550−750 nm). Unfortunately, some decomposition of **Os(*μ*-1c)Os** occurs upon the required prolonged irradiation, preventing us from drawing accurate conclusions about the photocycloreversion process of **Os(*μ*-1c)Os**.

The photocyclization of dithienylethenes is not always quantitative since, at a certain moment, equilibrium is established between the two photoactive forms. The photostationary state (PSS) can be analyzed with other spectroscopic tools to determine the exact ratio between the open and closed forms. The most straightforward method is ^{1}H NMR spectroscopy that permits comparison of the relative intensities of selected proton signals. The most suitable signals, showing the largest shifts upon cyclization, are those of the methyl groups on the thiophene rings. In the ^{1}H NMR spectrum of **1o** in $CDCl_3$, only one methyl signal is observed at δ 2.02. Upon irradiation with 334-nm light a new methyl signal grows in for **1c** at δ 2.26. In the PSS, 98% of all the molecules are converted into the closed form **1c**. The methyl signal for **Ru(*μ*-1o)Ru** in CD_3OD can be found at δ 2.09 and for **Ru(*μ*-1c)Ru** at δ 2.26. In the PSS, 97% of all molecules exist as **Ru(*μ*-1c)Ru**. The methyl signals for **Os(*μ*-1o)Os** and **Os(*μ*-1c)Os** in CD_3OD arise at δ 2.07 and 2.25, respectively; their ratio shows that in this case the PSS contains only 73% of **Os(*μ*-1c)Os**. These values are in good agreement with the residual emission found for the complexes upon photocyclization.

An important property common to most dithienylethenes is that both the open and closed forms are thermally stable at room temperature. To test whether this is also the case for **1o**, **Ru(*μ*-1o)Ru**, and **Os(*μ*-1o)Os**, and for **1c**, **Ru(*μ*-1c)Ru**, and **Os(*μ*-1c)Os** (in the photostationary states), their solutions were kept in the dark for several days. No thermal reaction was detected by UV−vis spectroscopy in any of the samples.

The quantum yields of the photocyclization of compounds **1o**, **Ru(*μ*-1o)Ru**, and **Os(*μ*-1o)Os** are given in Table 3. For compounds **1o** and **Ru(*μ*-1o)Ru** the photocyclization quantum yields are independent of the excitation wavelength. In contrast, **Os(*μ*-1o)Os** only converts to **Os(*μ*-1c)Os** upon irradiation into the ^{1}IL band, but remains photostable upon irradiation into the ^{1}MLCT band. The photocyclization quantum yields of **1o** and **Os(*μ*-1o)Os** are insensitive to dioxygen, whereas the quantum yield for **Ru(*μ*-1o)Ru**

---

(55) Cook, M. J.; Lewis, A. P.; McAuliffe, G. S. G.; Skarda, V.; Thomson, A. J.; Glasper, J. L.; Robbins, D. J. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1293−1301.

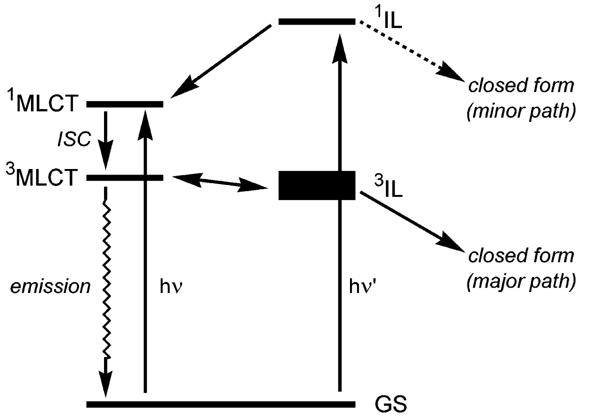
(56) Cook, M. J.; Lewis, A. P.; McAuliffe, G. S. G.; Skarda, V.; Thomson, A. J.; Glasper, J. L.; Robbins, D. J. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1303−1307.

Table 3. Quantum Yields φ_λ[a] for the Photocyclization of Dithienylethene **1o** and Homodinuclear Complexes **Ru(μ-1o)Ru** and **Os(μ-1o)Os**

	φ_{334}		φ_{450}	
compound	aerated	deaerated	aerated	deaerated
1o	0.72	0.74	*b*	*b*
Ru(μ-1o)Ru	0.37	0.88	0.38	0.80
Os(μ-1o)Os	0.0045	0.0041	*c*	*c*

[a] In MeCN at $T = 293$ K; $\lambda_{irr} = 334$ and 450 nm. [b] Compound **1o** does not absorb at 450 nm. [c] No photoreaction.

Scheme 3. Qualitative Energetic Scheme for the Efficient Sensitized Photocyclization of Complex **Ru(μ-1o)Ru**

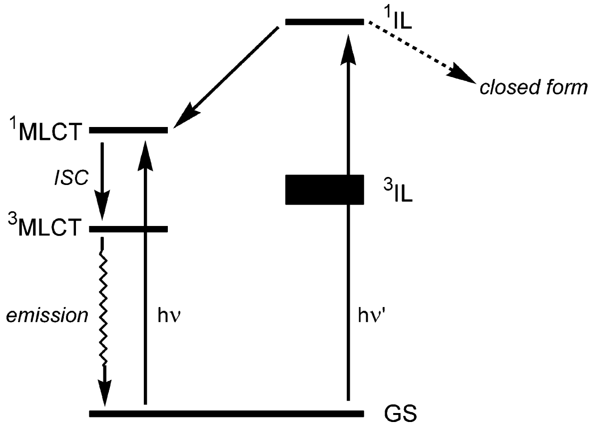


exhibits a strong oxygen dependency (Table 3). As stated earlier, the photocyclization of dithienylethenes is generally described as a barrierless reaction occurring from a singlet excited state on a time scale of picoseconds.[9] Dithienylethene **1o** is nonemissive and has an oxygen-independent photocyclization quantum yield of 0.7. Furthermore, transient absorption spectroscopy shows that **1o** has a sub-nanosecond excited-state lifetime (see below). All these observations are in agreement with the published model. Therefore, we believe that the energetics of **1o** is essentially the same as that of the dithienylethenes described in the literature.[19,21,57]

For dinuclear ruthenium complex **Ru(μ-1o)Ru** in deaerated solution, the photocyclization quantum yield is extremely high and the photochemical reaction is also triggered by irradiation into the ^{1}MLCT band of the Ru(bpy)$_3$ moiety (Table 3). As already stated, the emission quantum yield of this compound is much lower and the excited-state lifetime much shorter than those of the reference complexes. The deactivation pathway of the emitting state must therefore involve the reactive state of the photochromic unit. Analyzing the spectroscopic data, we can conclude that in the case of **Ru(μ-1o)Ru** the photocyclization takes place from a triplet state localized on the photochromic unit (^{3}IL), which is populated by energy transfer from the luminescent ^{3}MLCT state lying at approximately the same or slightly higher energy than the ^{3}IL state. The emission of **Ru(μ-1o)Ru** is therefore quenched by the photoreaction.

Qualitative energetic diagrams for **Ru(μ-1o)Ru** and **Os(μ-1o)Os** are depicted in Schemes 3 and 4, respectively. Precise determination of the energy of the ^{3}IL state of the photochromic unit could not be achieved since ligand **1o** itself is not phosphorescent at low temperatures, not even with a coordinated innocent metal ion such as Zn^{2+}. However, we can easily estimate that the energy of the ^{3}IL state must lie between 1.37×10^4 and 1.62×10^4 cm^{-1}. This can be concluded from the facts that irradiation into the ^{1}MLCT band of diosmium complex **Os(μ-1o)Os** does not lead to photocyclization, and that no quenching of the emission or the excited-state lifetime is observed for this complex. The ^{3}MLCT state of **Os(μ-1o)Os** must therefore lie at a lower energy than the triplet state of the dithienylethene unit (Scheme 4). On the other hand, the emission of complex **Ru(μ-1o)Ru** is quenched, but not completely, by energy transfer from the ^{3}MLCT state to the ^{3}IL state. This is an indication that the energies of the two states are very similar and that, in fact, equilibrium exists between them (Scheme 3).

Scheme 4. Qualitative Energetic Scheme for the Inefficient Photocyclization of Complex **Os(μ-1o)Os**



The photocyclization reaction of **Ru(μ-1o)Ru** is quenched by dioxygen, which implies that the time scale of this process lies in the nanosecond domain. The diffusion-controlled quenching by dioxygen is too slow to play a significant role on a shorter time scale. From these observations the following conclusions can be drawn about the energetics and kinetics of the system. Because of the low driving force for the energy transfer from the ^{3}MLCT state to the ^{3}IL state, this process is expected to be rather slow (although still faster than a few nanoseconds detectable by our nanosecond transient absorption measurement, see later). Back energy transfer should occur since the emission quantum yield is still reasonably high, even with an extremely efficient photocyclization reaction. The photoreaction must also be rather slow (having a rate comparable to that of the emission) in order for the back energy transfer to be able to compete with it. Because of the long-lived-triplet character of this state, the reaction can nevertheless be extremely efficient.

In the literature the possibility of a competition between the emissive and reactive processes, as we report here, had so far been dismissed[24,29] (see Introduction), as the much shorter time scale on which the photocyclization takes place would quench the emission completely. However, in the case of **Ru(μ-1o)Ru** the photocyclization takes place on the nanosecond time scale and, therefore, a parallel occurrence

---

(57) Ern, J.; Bens, A. T.; Martin, H. D.; Mukamel, S.; Schmid, D.; Tretiak, S.; Tsiper, E.; Kryschi, C. *Chem. Phys.* **1999**, *246*, 115−125.

of the emission and photocyclization is very possible. The observation that not only the emission quantum yield but also the emission lifetime is reduced compared to the reference compounds supports this conclusion.

The photocyclization quantum yields, determined for **1o** and a deaerated sample of **Ru(μ-1o)Ru**, significantly exceed 0.5 (Table 3), which is generally considered as the maximum value for this type of photochromic molecule. These results imply that the antiparallel conformation in **1o** and **Ru(μ-1o)Ru** is favored over the parallel conformation. This is the result of the bulky substituents attached to the thiophene rings. In both the parallel and antiparallel conformations, the two thiophene rings twist out of the plane of the cyclopentene ring in order to reduce the steric hindrance between the two methyl groups. In the parallel conformations of **1o**, **Ru(μ-1o)Ru**, and **Os(μ-1o)Os** not only the methyl groups hinder each other but also the two bulky substituents in the 5,5′-positions of the thienyl groups. However, in sharp contrast to **1o** and **Ru(μ-1o)Ru**, the photocyclization quantum yield of compound **Os(μ-1o)Os**, for which the antiparallel conformation should also be strongly favored, is much lower (Table 3). This is due to a fast and efficient energy transfer to the ^{1}MLCT state upon excitation to the ^{1}IL state (Scheme 4). The reason that the cyclization reaction still occurs is that the extremely fast cyclization reaction from the ^{1}IL state[9] is able to compete with the energy transfer.

The fact that the photocyclization quantum yield of **Ru(μ-1o)Ru** in deaerated solvent is higher than that of **1o** can be attributed to (i) increased steric repulsion between the two chains caused by the presence of the bulky Ru(bpy)$_3$ moieties, forcing more molecules to adopt the antiparallel conformation, (ii) differences in the profiles of the excited states, and (iii) a combination of the two factors. The current results do not allow discrimination between these options.

Pico- and Nanosecond Transient Absorption Spectroscopy. To gain more insight into the mechanism and kinetics of the population of the photoreactive state, transient absorption spectroscopic studies were carried out. No nanosecond transient species could be detected for open-form ligand **1o** upon irradiation at 334 nm or for its closed form **1c** upon irradiation at either 334 or 615 nm. From these results we can conclude that the lifetimes of the excited species of **1o** and **1c** are in the sub-nanosecond time domain. This is in agreement with the reported picosecond excited-state lifetimes determined for other dithienylethenes.[9]

The nanosecond transient absorption spectra of mononuclear complexes **Ru(4)** and **Ru(6)** (Figure 5b) are identical to each other and do not depend on the selected irradiation wavelength, viz. 334 or 450 nm. The transient spectra strongly resemble those of excited [Ru(bpy)$_3$]$^{2+}$ and, in particular, [{Ru(bpy)$_2$}$_2$(μ-bpy(ph)$_4$bpy)]$^{2+}$.[58] The transient absorption band around 375 nm is attributed to the absorption of the radical anion bpy$^{\bullet -}$. Around 460 nm we observe the bleach of the MLCT band. Therefore, we can conclude that the lowest excited state of **Ru(4)** and **Ru(6)** has a Ru-to-bpy MLCT character. This is in agreement with the cyclic voltammetric data (see below). The broad feature in the visible region of the transient absorption spectrum is attributed to a high delocalization of the negative charge on the substituted bpy,[56,59] showing that this ligand is involved in the lowest MLCT excited state.

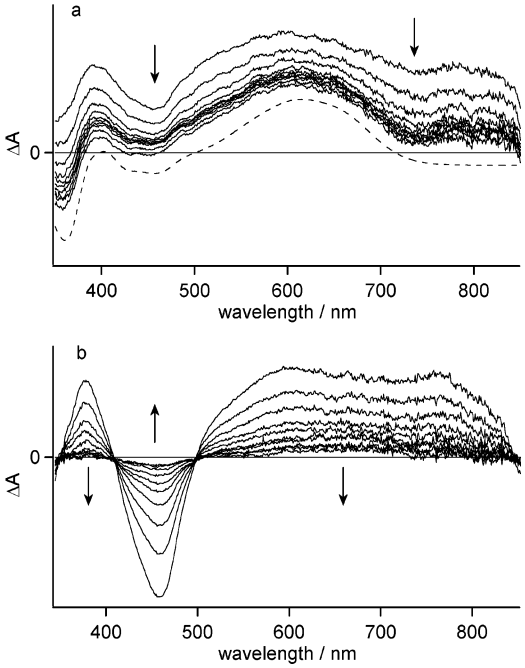


Figure 5. Transient absorption difference spectrum of **Ru(μ-1o)Ru** (a), employing a step size of 50 ns between frames. The dotted line shows the shape of the steady-state difference spectrum between **Ru(μ-1c)Ru** and **Ru(μ-1o)Ru**. Transient absorption difference spectrum of **Ru(6)** (b), employing a step size of 75 ns between frames. Conditions: MeCN, air-equilibrated solution, 293 K, irradiation with 450-nm light.

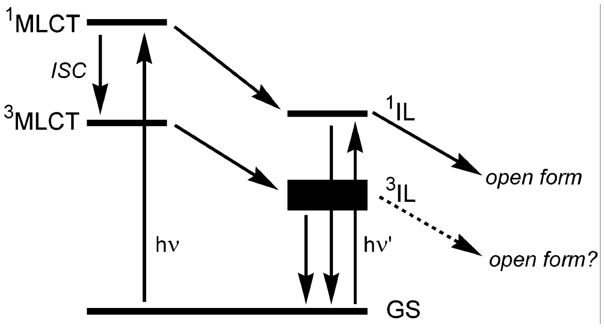
With use of a a flow-through cell, nanosecond transient absorption spectra were recorded for diruthenium complex **Ru(μ-1o)Ru** (Figure 5a). Irradiation at either 334 or 450 nm yielded exactly the same spectrum, showing a broad and structureless absorption over the entire detection range of 300−800 nm. The absence of a bleach of the MLCT band around 460 nm is an indication that the excited state observed on this time scale does not have a Ru-to-bpy charge-transfer character and that in this state the ruthenium center remains in the oxidation state Ru(II). The assignment of the excited state as ^{3}IL, localized on the dithienylethene unit, is therefore most likely. The decay of the transient absorption spectra could not be fitted precisely, for two reasons. First, the absorption increase resulting from the formation of photoproduct **Ru(μ-1c)Ru** is on the same order of magnitude as the decrease due to the depopulation of the excited state. Furthermore, because of the high reactivity of **Ru(μ-1o)Ru**, the buildup of photoproduct **Ru(μ-1c)Ru** in the sample beam could not be completely avoided. Nevertheless, assuming a monoexponential decay, the lifetime of the observed excited state of **Ru(μ-1o)Ru** under aerated conditions has been estimated to lie in the range of 100−200 ns.

---

(58) Welter, S.; Benetti, A.; Brunner, K.; Hofstraat, J. W.; Dong, B.; Chi, L.; Fuchs, H.; De Cola, L. *J. Am. Chem. Soc.*, submitted for publication.

(59) Damrauer, N. H.; Boussie, T. R.; Devenney, M.; McCusker, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 8253−8268.

Scheme 5. Qualitative Energetic Scheme for the Photocycloreversion of Complexes **Ru(μ-1c)Ru** and **Os(μ-1c)Os**



This value has the same order of magnitude as the corresponding emission lifetime. For the deaerated sample, increased photoproduct formation was clearly observed in the transient spectrum.

Attempts to record picosecond transient absorption spectra of **1o** and **Ru(μ-1o)Ru** were not successful since with the current setup we could not avoid a significant buildup of photoproducts **1c** and **Ru(μ-1c)Ru**, respectively, in the sample beam.

The cycloreversion process is much less efficient than the photocyclization. The corresponding quantum yields have not been determined precisely, but they are clearly much lower than those for the photocyclization, not exceeding 0.1. It was therefore possible to record a picosecond transient absorption spectrum of **Ru(μ-1c)Ru**. Upon excitation at 615 nm of a **Ru(μ-1c)Ru** solution, a bleach of the ^{1}IL band in the 550−670-nm region is observed together with structureless transient absorption bands below 550 nm and above 670 nm. The excited state has a lifetime of approximately 2 ps. In agreement with spectra already reported for similar uncomplexed dithienylethenes,[57,60,61] the transient is ascribed to the ^{1}IL state of the bridge in **Ru(μ-1c)Ru** (Scheme 5).

Excitation of **Ru(μ-1c)Ru** with 450-nm light into the lowest ^{1}MLCT transition results in a different transient absorption spectrum (Supporting Information, Figure S1). Within the first 5 ps strong changes can be observed in the spectrum. A transient absorption band grows at ca. 525 nm, while a bleaching appears, centered around 650 nm. A transient absorption band above 700 nm rises within the pulse. After the initial changes, the spectrum does not develop further and the observed excited state decays with a lifetime of 12 ns. The spectrum resembles the one observed upon irradiation at 615 nm, apart from the strong absorption band at 525 nm, which overlaps with the bleaching of the $S_0 \rightarrow S_1$ between 550 and 670 nm, cutting it off at ca. 600 nm. On the basis of this similarity, the relatively long lifetime and the absence of a band for the MLCT band, we ascribe this transient absorption spectrum as being due to the ^{3}IL state of the closed photochromic unit. As we irradiate into the ^{1}MLCT band, this excited state must be populated from the ^{3}MLCT state since, as discussed above, population of the ^{1}IL state results in a decay to the ground state within a few picoseconds, with no observable population of the ^{3}IL state (Scheme 5). The transfer of energy from the ^{3}MLCT state to the ^{3}IL state can account for the initial changes in the spectrum.

Table 4. Electrochemical Data for Selected Compounds under Study[a] and Two Reference Compounds

compound	T/K	$E_{1/2}$/V Ru$^{II/III}$	$E_{1/2}$/V (bpy$^{0/-}$)$_{I}$	$E_{1/2}$/V (bpy$^{0/-}$)$_{II}$	$E_{1/2}$/V (bpy$^{0/-}$)$_{III}$	$E_{p,c}$/V[b]
bpy[c,d]	293		−2.72			
$[Ru(bpy)_3]^{2+}$ [e]	293	+0.89	−1.72	−1.93	−2.18	
4	293					−2.36[f]
Ru(4)	293	+0.86	−1.70	−1.90	−2.17	−2.53
6	293					−2.21[f]
Ru(6)	293	+0.86	−1.70	−1.89	−2.18	−1.86
	208	+0.84	−1.72	−1.90	−2.12	−2.05
1o	293					−2.12[f]
Ru(μ-1o)Ru	293	+0.86	−1.73	−1.90	−2.17	−1.86
	208	+0.84	−1.71	−1.90	−2.13	−2.04
1c	293					−1.37[g]
Ru(μ-1c)Ru	293					−1.27[g]

[a] Redox potentials (V vs Fc/Fc$^+$) were determined from combined cyclic and Osteryoung square-wave voltammetric scans. Conditions: MeCN (unless stated otherwise), Pt disk working microelectrode, $v = 100$ mV s^{-1} (cyclic voltammetry), $f = 30$ Hz (s-w voltammetry). [b] Irreversible reduction localized on the photochromic dithienylethene unit. [c] In THF. [d] Reference 62. [e] Reference 63. [f] Successive reversible reduction of a secondary product found at $E_{1/2} = -2.42$ V for **4** (see Figure 6), −2.45 V for **6**, and −2.47 V for **1o** (see Figure 7). [g] Successive irreversible reduction of a secondary product found at $E_{p,c} = -1.82$ V for **1c** (see Figure 7) and −1.37 V for **Ru(μ-1c)Ru**.

In the nanosecond transient absorption spectrum of **Os(μ-1o)Os** excited with 450-nm light, a clear bleach of the Os-to-bpy ^{1}MLCT band can be observed (Supporting Information, Figure S2). The transient species decays with the same lifetime as the emission. Obviously, this transient spectrum can be ascribed to the ^{3}MLCT excited state, which we had already predicted to be the lowest excited state for **Os(μ-1o)Os**.

Upon irradiation of **Os(μ-1c)Os** into the ^{1}MLCT band with 450-nm light, a transient spectrum very similar to that of **Ru(μ-1c)Ru** is observed, with a lifetime of 10 ns. With the same reasoning as above, this spectrum is ascribed to the ^{3}IL state of **Os(μ-1c)Os**. This shows that when the molecule is in the closed form, the ^{3}IL state is the lowest excited state independent of the metal unit (Scheme 5).

Electrochemistry. Cyclic voltammetric measurements were performed on compounds **1o**, **1c**, **Ru(μ-1o)Ru**, and **Ru(μ-1c)Ru** and on reference compounds **4**, **6**, **Ru(4)**, and **Ru(6)**. For **Ru(μ-1o)Ru** and **Ru(6)**, also square wave voltammetry was employed in order to better resolve the cathodic steps. The corresponding redox potentials are listed in Table 4.

The first reduction wave for ligands **4** (Supporting Information, Figure S3) and **6** are completely irreversible. Taking into account that the reduction of 2,2′-bipyridine and its derivatives is a fully reversible one-electron process,[62] we can conclude that the reduction of **4** and **6** is localized

---

(60) Miyasaka, H.; Araki, S.; Tabata, A.; Takahiro, N.; Mataga, N.; Irie, M. *Chem. Phys. Lett.* **1994**, *230*, 249−254.

(61) Ern, J.; Bens, A. T.; Bock, A.; Martin, H. D.; Kryschi, C. *J. Lumin.* **1998**, *76&77*, 90−94.

(62) Krejčík, M.; Vlček, A. A. *J. Electroanal. Chem.* **1991**, *313*, 243−257.

(63) Sutin, N.; Creutz, C. *Adv. Chem. Ser.* **1978**, *168*, 1−27.

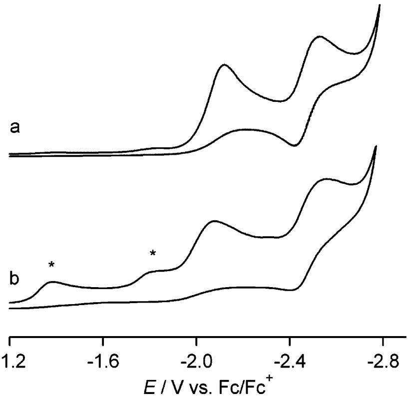


Figure 6. Cyclic voltammograms of compound **1o** (a) and of the same solution after partial photocyclization of **1o** to **1c** (b). Cathodic waves of **1c** marked with asterisks. Conditions: MeCN, 293 K, Pt disk microelectrode, $v = 100$ mV s^{-1}.

on the substituents attached to the bipyridine moiety. The products of the irreversible reduction have not been identified.

Also for ligand **1o** the first reduction wave is irreversible (Figure 6a). Compared to compound **6**, the cathodic peak potential is only slightly less negative (Table 4). The cathodic response indicates that also in this case reduction is not localized on the bipyridine termini, but on the photochromic bridge. Repetition of the voltammetric scan reversed beyond the cathodic wave of **1o** showed that the electrochemical reduction of the bridge did not lead to the formation of the cyclized product **1c**.

For mononuclear complexes **Ru(4)** (Supporting Information, Figure S4) and **Ru(6)** the first reduction wave is fully reversible. The electrode potential compares well with the first reduction of $[Ru(bpy)_3]^{2+}$. Therefore, this wave can be attributed to the reduction of the substituted bipyridine group stabilized by coordination. For **Ru(4)**, the following two reduction waves are also reversible and can be attributed to the ancillary bipyridine ligands, by analogy with $[Ru(bpy)_3]^{2+}$. After these three reversible cathodic steps of **Ru(4)**, an irreversible reduction is also found. For **Ru(6)** already the second reduction wave is irreversible, followed by two reversible bpy-localized steps (Table 4). In analogy with compounds **4** and **6**, the irreversible cathodic waves of **Ru(4)** and **Ru(6)** are assigned to reductions localized on the photochromic unit. The fact that the irreversible wave for **Ru(6)** is found at a less negative potential compared to that for **Ru(4)** is explained by the presence of the withdrawing perfluorocyclopentene moiety. The small difference in the reduction potentials of the irreversible wave ($E_{p,c} = -1.86$ V) and the second reversible wave ($E_{1/2} = -1.89$ V) for **Ru(6)** shows that there is little electronic interaction between the bipyridine and dithienylethene moieties.

The cyclic voltammogram for diruthenium complex **Ru(*μ*-1o)Ru** (Figure 7a) is almost identical to that of **Ru(6)**. Because of the strong overlap between waves in the cyclic voltammagram, the Osteryoung square wave voltammogram of **Ru(*μ*-1o)Ru** was also recorded for better resolution (Figure 7b). The initial reversible reduction wave again belongs to a (ph)bpy-localized step; the lowest excited ^{1}MLCT state, therefore, has a Ru-to-bpy character. However, the irreversible cathodic wave, which has been ascribed to reduction of the photochromic backbone, lies only at a slightly more negative potential. This suggests that an optically inaccessible Ru-to-bridge ^{1}MLCT state exists, at only slightly higher energy than the Ru-to-bpy ^{1}MLCT state. Nothing can be said with certainty about the relative energies of the corresponding ^{3}MLCT states, except that, most likely, they also are close in energy. The possibility that these Ru-to-bridge MLCT states play a role in the photoinduced cyclization of **Ru(*μ*-1o)Ru** therefore cannot be excluded.

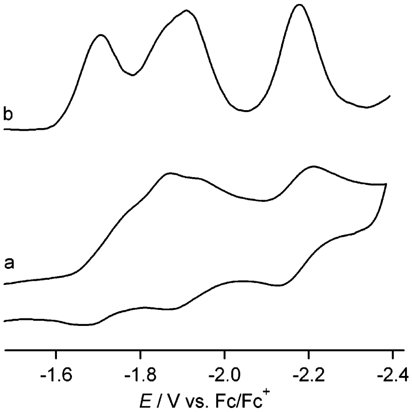


Figure 7. Cyclic (a) and Osteryoung square-wave (b) voltammograms of complex **Ru(*μ*-1o)Ru**. Conditions: MeCN, 293 K, Pt disk microelectrode, $v = 100$ mV s^{-1} (cyclic voltammetry), $f = 30$ Hz (s-w voltammetry).

Photoproducts **1c** and **Ru(*μ*-1c)Ru** were photogenerated in situ within the cyclic voltammetric cell, allowing a straightforward assignment of their cathodic waves. For both **1c** (Figure 6b) and **Ru(*μ*-1c)Ru** the first reduction is irreversible. These waves lie at a considerably less negative potential than those for **1o** and **Ru(*μ*-1o)Ru**. This potential shift can be explained by considering the bridging ligand to be more conjugated in the closed form and, therefore, capable of better accommodation of the added electrons than the open form. This stabilization of the lowest energy level of the bridging ligand by the photocyclization is also reflected in the low-lying ^{1}IL band of the cyclized products (see above).

Conclusions and Perspectives

This work describes syntheses, characterization, and photocyclization behavior of a series of derivatives of dithienylperfluorocyclopentene. By introduction of bulky substituents on the thiophene rings, the antiparallel conformation of the photochromic backbone is favored over the parallel one, thereby increasing the cyclization quantum yield. This results in cyclization quantum yields for **1o** and **Ru(*μ*-1o)Ru** that were unusually high, far above 0.5.

For complex **Ru(*μ*-1o)Ru** the photocyclization reaction occurs both upon excitation to the ^{1}IL state, localized on the photochromic part, and upon excitation to the ^{1}MLCT state at lower energy, localized on the $Ru(bpy)_3$ part, with almost identical quantum yields. Furthermore, strong oxygen quenching of the cyclization reaction was observed. In this case, the photocyclization reaction occurs from the ^{3}IL state that is populated from the ^{3}MLCT state. To the best of our knowledge, this is the first time that it has been proven that photocyclization of dithienylethenes can also occur from a triplet state and that sensitization of the photoreaction by irradiation of an attached metal center is possible. In contrast to the photocyclization reaction from a singlet state, which is known to occur in a few picoseconds, here the reaction occurs on the nanosecond time scale. Equilibrium exists between the ^{3}MLCT and ^{3}IL states, which are close in energy, resulting in a competition between the emissive and reactive processes.

The ^{3}MLCT emissions of both **Ru(*μ*-1o)Ru** and **Os(*μ*-1o)Os** are quenched upon conversion to their respective closed forms **Ru(*μ*-1c)Ru** and **Os(*μ*-1c)Os**. This is due to energy transfer to the lowest excited states of the photochromic unit that are at lower energy than those of the metal center in the closed form.

To achieve a nondestructive readout by means of observing the emission, one would ideally like to construct a dithienylethene system in which the photochromic and luminescent parts can be addressed independently, such that selective excitation would lead to the population of either the photoreactive or the emissive state. Energetically speaking, this means that the reactive levels must lie at a higher energy than the emissive states, while the coupling between the different components must be such that kinetically the photocyclization is favored over energy transfer from the reactive to the emissive state. Upon conversion the lowest excited state must be localized on the photochromic unit and efficiently quench the emission of the luminescent moiety. If a luminophore is used that emits on a much longer time scale than that of the reaction, it should be possible to construct a system where the coupling is such that all of the former conditions are met. However, quenching of the emission in the closed form by population of the photoreactive state will inevitably lead to a photoprocess. To truly achieve nondestructive readout, a nonreactive state must be populated by deactivation of the luminescent state, while direct excitation of the photochromic unit still leads to photocycloreversion. Although one such system has been reported by Branda and co-workers,[14,52] this type of behavior is extremely difficult to predict in advance.

Acknowledgment. We thank the National Swiss Science Foundation for funding through the NFP 47 program. We also thank the EC (contract G5RD-CT-2002-00776, MWFM) for financial support.

Supporting Information Available: Selected transient absorption difference spectra of **Ru(*μ*-1c)Ru** and **Os(*μ*-1o)Os** and cyclic voltammograms of **4** and **Ru(4)**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC035334E