Optical Switching and Fluorescence Modulation Properties of Photochromic Metal Complexes Derived from Dithienylethene Ligands

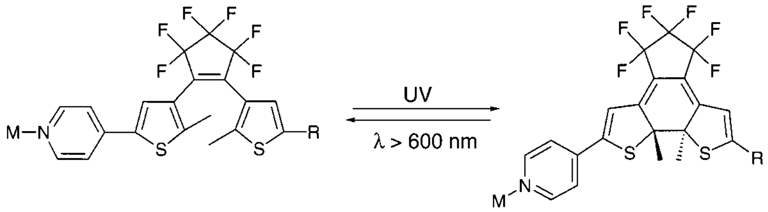
Alvaro Fernández-Acebes and Jean-Marie Lehn*[a]

Abstract: Organic photochromic systems represent a starting point for the preparation of light-triggered molecular switching devices. The novel dithienylethene-tungsten (**1**,**2**), rhenium (**3**,**4**), and ruthenium (**5**) complexes were synthesized from their parent ligands. The biscyano photochromic complexes **14** and **16** were also prepared although their metallic complexes could not be isolated. All the compounds described exhibited pronounced photochromic properties. Irradiation of the open forms of complexes **1**–**4** with UV light resulted in essentially quantitative photocyclization to the deeply colored closed forms; the colorless open forms could be regenerated by irradiation with visible light of $\lambda > 600$ nm. Compounds **1**–**4** were found to display a fluorescence discrimination between their open and closed forms when excited at wavelengths (240 nm) that almost did not affect the state of the system. Finally the closed form of product **5**, prepared from the closed form of its parent ligand, was photochemically stable. Thus, the molecules **1**–**5** represent two kinds of nondestructive read-out models.

Keywords: diarylethenes · luminescence · molecular devices · photochromism · transition metals

Introduction

In the last few years much attention has been devoted to molecular switching processes as they are crucial to the realization of devices that can operate at both molecular and supramolecular levels.[1, 2] This stems from their role in, among others, photoswitchable host–guest events,[3, 4] materials for nonlinear opticals,[5, 10] liquid crystals[2, 6, 8] as well as various optoelectronic devices such as optical memory,[2, 7, 8] photo-optical switching, and display. In particular, molecular units that allow the reversible modulation of a given electronic property, for example, conjugation by an external trigger such as light, are of potential interest as materials for optical data storage. The photochromic materials used for such devices must cope with several requirements[7, 8] to be suitable for a practical device like thermal stability of both forms, low photofatigue, high sensitivity at diode laser wavelength, rapid reponse, and nondestructive read-out capability.



1o $M = W(CO)_5$, $R = N\text{-}[W(CO)_5]pyridyl$ **1c**
2o $M = W(CO)_5$, $R = p\text{-}Phenol$ **2c**
3o $M = [Re(bpy)(CO)_3](CF_3SO_3)$, $R = N\text{-}[Re(bpy)(CO)_3(CF_3SO_3)]pyridyl$ **3c**
4o $M = [Re(bpy)(CO)_3](CF_3SO_3)$, $R = p\text{-}Methoxyphenyl$ **4c**

Figure 1. Photochemical interconversion of compounds **1**–**4** between their open and closed forms.

Dithienylethenes,[3, 4, 9–20] derived in particular from perfluorocyclopentene,[3, 4, 9–19] have been studied to these ends, as they display excellent photochromic properties and low photofatigue. Irradiation of such compounds with light of well-separated wavelengths[9–15] allows the interconversion between a nonconjugated ("open form", colorless) isomer and a conjugated ("closed form", deeply colored) one (Figure 1).

A major problem arises from read-out instability. As a consequence, much activity is presently being directed towards the design of systems with nondestructive read-out capability. Although some alternatives have already been proposed,[11–14, 15a, 15b] further development of new systems is warranted.

In view of the rich variety of properties of some metal ion complexes (light absorption and emission, energy and electron transfer…) it was of interest to study the combination of

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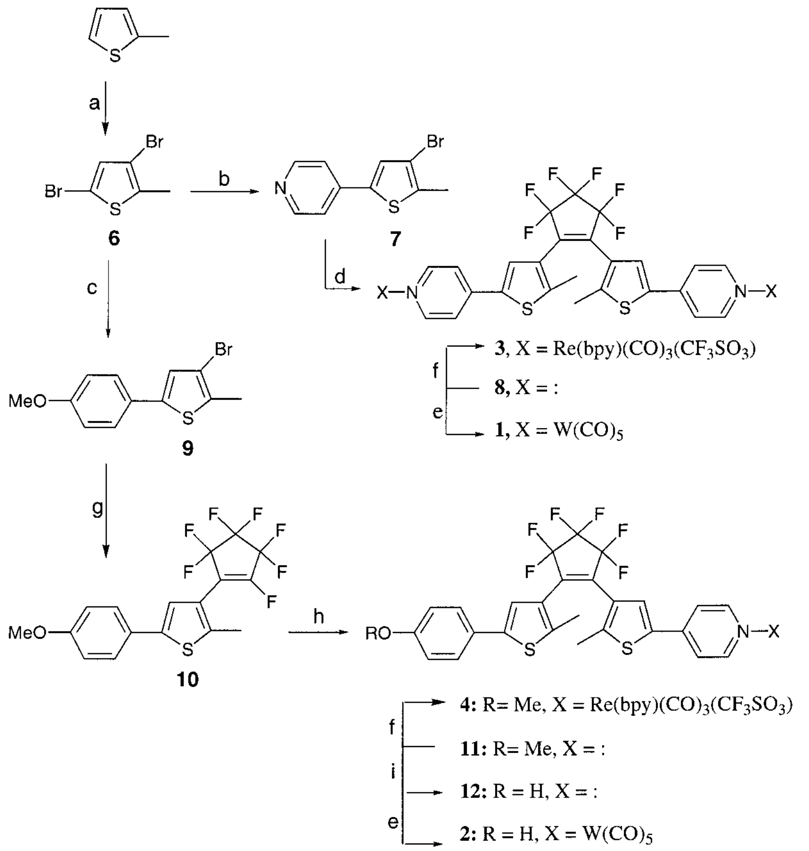
[a] Prof. J.-M. Lehn, Dr. A. Fernández-Acebes
Chimie des Interactions Moléculaires, Collège de France
11 Place Marcelin Berthelot, F-75005 Paris (France)
(UPR No.285 of the CNRS)
Fax: (+33) 1-4427-1356



Scheme 1. Synthesis of the dithienylethene photochromic complexes **1–4**, **8**, **11**, **12**. Reagents and conditions: a) Br_2, AcOH/$CHCl_3$, RT; b) BuLi, $B(OBu)_3$, –78 °C, 2 h and then $[Pd(PPh_3)_4]$, Na_2CO_3, THF, 4-bromopyridine, reflux 12 h; c) BuLi, $B(OBu)_3$, –78 °C, 2 h and then $[Pd(PPh_3)_4]$, Na_2CO_3, THF, 4-bromoanisole, reflux 12 h; d) BuLi, THF, –78 °C, perfluorocyclopentene (0.5 equiv) and 78 °C, RT; e) $[W(CO)_6]$ (1 or 2 equiv), UV irradiation 30 min and addition of **8** (0.5 equiv) or **12** (1 equiv) in THF at RT; f) $[Re(bpy)(CO)_3(CH_3CN)]CF_3SO_3$ (2 equiv from **8** or 1 equiv from **11**), THF, reflux; g) BuLi, THF, –78 °C, perfluorocyclopentene (1 equiv) and 78 °C, RT; h) **7**, BuLi, THF, –78 °C, addition of **10** and 78 °C, RT; i) BBr_3, CH_2Cl_2, reflux 4 h.

metal ion coordination centers with organic photochromic units, especially with respect to the possibility to photomodulate their features.[12, 13, 18, 21] In an earlier communication[13a] we have already reported the photochemical properties of some dithienylethene-tungsten complexes, we herein describe the synthesis and characterization of the novel diarylethene based molecular switches **1–4** (see Scheme 1) bearing metal ion complexes of tungsten, rhenium, and ruthenium as well as their photochromic properties.

Results and Discussion

Synthesis: The synthesis of the photochromic complexes **1–4** is outlined in Scheme 1. The known photochromic compound **8** was prepared from 2-methylthiophene by the described method.[10] Palladium-catalyzed Suzuki coupling of **6** with 4-bromoanisole in aqueous base containing THF gave the thiophene **9** that was then treated with perfluorocyclopentene affording **10**. Subsequent

Abstract in Spanish: *Los fotocromos orgánicos representan un punto de partida para la preparación de sistemas fotomodulables. Los nuevos complejos ditienileténicos derivados de wolframio (**1,2**), renio (**3,4**) y rutenio (**5**) fueron sintetizados a partir de sus correspodiendes ligandos sin metalar. Asímismo, se han preparado los fotocromos bis-ciano **14** y **16** aunque sus complejos metálicos no pudieron ser aislados. Todos los productos descritos presentaron pronunciadas propiedades fotocr-micas. Irradiación de las formas abiertas de los productos **1–4** con luz UV originó esencialmente la fotociclación cuantitativa a la fuertemente coloreada forma cerrada; las formas incoloras abiertas pudieron ser regeneradas a través de la irradiación con luz visible de λ > 600 nm. Los compuestos **1–4** mostraron una discriminación de fluorescencia entre sus formas abiertas y cerradas al ser excitados a longitudes de onda (240 nm) que apenas afectan al estado del sistema. Finalmente, la forma cerrada del producto **5**, preparada a partir de su correspondiente ligando sin metalar cerrado, result- ser fotoqu'micamente estble. Así pues, las moléculas **1–5** representan dos tipos de modelos de lectura no-destructiva.*

Abstract in French: *La mise au point de dispositifs moléculaires commutables par la lumière repose sur l'utilisation de composés organiques photochromes. Dans ce contexte les nouveaux complexes dithiényléthene-tunsgstène (**1,2**), rhénium (**3,4**) et ruthénium (**5**) ont été préparés à partir des ligands libres correspondants. Les nitriles photochromes **14** et **16** ont aussi été préparés mais leur complexes métalliques n'ont pas pu être isolés. Tous les produits décrits présentent des propriétés photochromes très prononcées. L'irradiation des formes ouvertes **1–4** par la lumière UV engendre une photociclisation conduisant quantitativement aux formes fermées très fortement colorées. Il est possible de revenir aux formes ouvertes incolores par irradiation avec de la lumière visible à 600 nm. Les composés **1–4** présentent une discrimination de fluorescence entre leurs formes ouvertes et fermrées quand ils sont excités avec une lumière ayant une longueur d'onde (240 nm) qui n'affecte presque pas l'état du système. La forme fermée du produit **5**, préparée à partir de la forme fermée du ligand non complexé, est photochimiquement stable. Ainsi, les molécules **1–5** représentent deux différents modèles de lecture non-destructive.*

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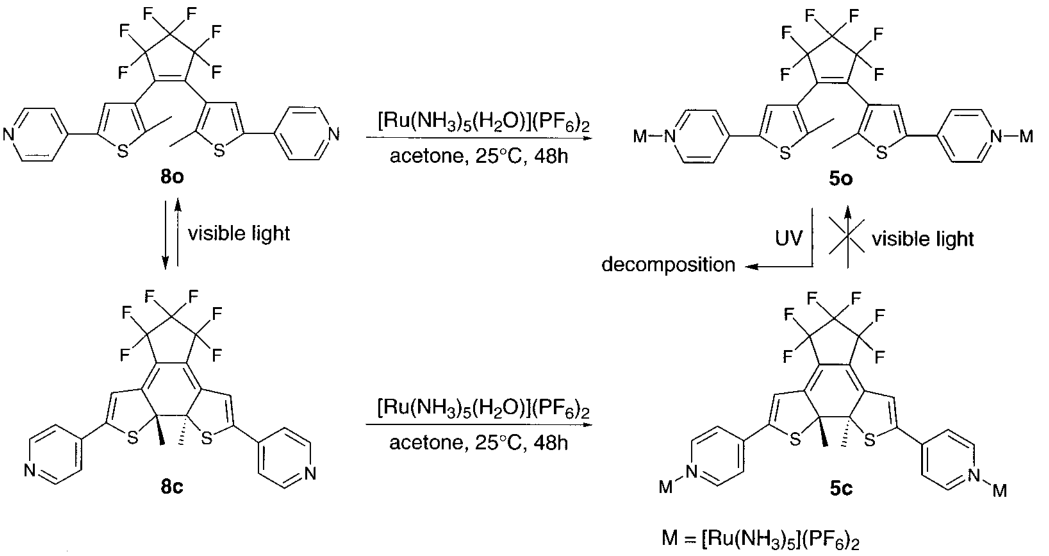
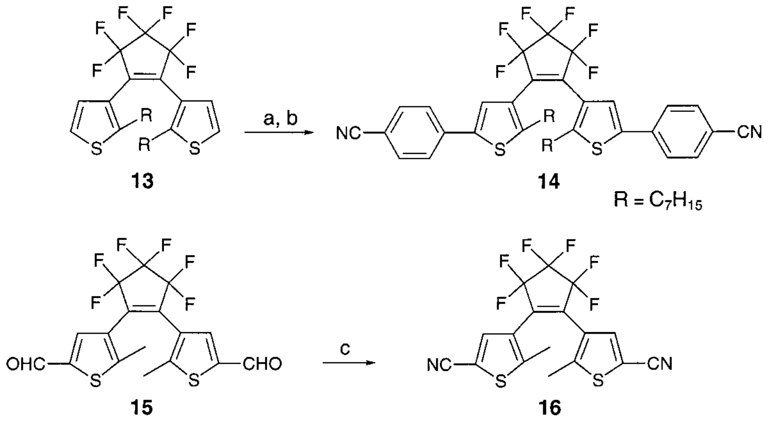


Scheme 2. Synthesis of the dithienylethene photochromic complexes **5o** and **5c** from **8o** and **8c**, respectively.

coupling of **10** with the pyridylthiophene **7** followed by deprotection of the product obtained (**11**) with BBr_3 resulted in the formation of the unsymmetrical photochromic diarylethene **12**. The tungsten complexes **1** and **2** were obtained in good yields (58 and 67 %) by the addition of solutions of **8** and **12** in THF, respectively, to $[W(THF)(CO)_5]$ prepared by the UV irradiation of a solution of $[W(CO)_6]$ in THF with a 150-W Hg lamp.[22, 23] The rhenium complexes **3** and **4** were also obtained in good yields (63 and 48 %, respectively) by refluxing the starting photochromic compounds (**8** and **11**) with $[Re(bpy)(CO)_3(CH_3CN)]CF_3SO_3$ in acetone.[24] Finally, the synthesis of the ruthenium complexes **5o** and **5c** was carried out (Scheme 2) by treating the photochromic complex **8** in either its open form **8o** or its closed form **8c** with two equivalents of $[Ru(NH_3)_5(H_2O)](PF_6)_2$[25] in acetone at ambient temperature for 48 h.

In view of the great affinity of metals like ruthenium(II) for the cyanide ion [29] it was of interest to prepare a new type of molecular switches containing two nitrile groups as well as to explore their applicability as ligands in metal complexation processes. As shown in Scheme 3, the bis-cyano derivative **14** was prepared by palladium-catalyzed Suzuki coupling of **13** with 4-bromobenzonitrile, whereas the photochromic compound **16** was prepared from the bis-aldehyde **15** by a modification of the Schmidt reaction.[30] The reaction of **14o** or **16o** with $[Ru(NH_3)_5(H_2O)](PF_6)_2$, under the same conditions as described for **8**, afforded a yellowish solid whose ^1H NMR spectrum was compatible with the expected structure, however this complex was very unstable and in the presence of light it decomposed quickly. Additional attempts to obtain the corresponding tungsten or rhenium complexes from either **14o** or **16o** were unsuccessful and only starting material was recovered in both cases.



Scheme 3. Synthesis of the bis-cyano dithienylethene photochromic complexes **14** and **16**. Reagents and conditions: a) BuLi, Et_2O/TMEDA; $-78\,^{\circ}C$, $B(OBu)_3$; b) THF, Na_2CO_3, $[Pd(PPh_3)_4]$, 4-bromobenzonitrile; c) NaN_3, H_2SO_4, benzene, RT, 12 h.

Photochromic properties: The UV/Vis spectra of the open **1o**–**5o** and closed **1c**–**5c** forms of compounds **1**–**5** are consistent with the remarkable photochromism demonstrated for diarylethenes of this type.[9–14] As shown in Table 1 the open forms of **1**–**5** show absorptions bands with λ_{max} values between 209 and 378 nm, whereas the highly colored closed forms **1c**–**5c** display a typical broad absorption band in the visible region at wavelengths between 604 nm (**4c**) and 632 nm (**2c**).

The photochemical interconversion properties of compounds **1**–**5** were monitored directly by both ^1H NMR and electronic absorption spectroscopy. The conversion **o**→**c** or **c**→**o** for products **1**–**5** was easily monitored by the relative integrals of the corresponding pairs of proton signals for the two isomers. Selected chemical shift data for both open and closed isomers of **1**–**5** are given in Table 1; in agreement with previous results of our group[10b] photocyclization results in a considerable upfield shift (of up to $\delta = 0.7$) of the thiophenic

Table 1. ^{1}H NMR (200 MHz) and absorption spectral data for the open **1o–5o** and closed **1c–5c** forms of complexes **1–5**.

Compound	^{1}H NMR[a,b] thiophene protons	λ_{max} [nm][c] ($\varepsilon \times 10^{-3}$[cm^{-1}M^{-1}])
1o	7.54 (s)	209 (50)
1c	6.86 (s)	240 (10), 615 (4)
2o	7.12 (s), 7.51 (s)	203 (36), 233 (10)
2c	6.61 (s), 6.84 (s)	239 (16), 632 (4)
3o[d]	7.83 (s)	207 (22), 319 (18)
3c[d]	7.17 (s)	207 (22), 350 (8), 621 (6)
4o[d]	7.34 (s), 7.7–7.9[e]	239 (8)
4c[d]	6.93 (s), 7.52 (s)	361 (6), 604 (4)
5o[d]	7.86 (s)	378 (8)
5c[d]	7.28 (s)	382 (6), 609 (6)

[a] Chemical shifts, δ (multiplicity). [b] In $CDCl_3$ unless otherwise indicated. [c] In $MeOH/H_2O$ (5/1) (**1,2**) or MeOH (**3,4**). [d] In [D$_6$]acetone. [e] Overlapping multiplet.

protons. Conversion to the closed forms of **1o–4o** can be achieved by irradiation at 312 nm (using a standard lamp for visualizing TLC plates, see Experimental Section for details); the colorless open form could then be regenerated by irradiation with visible light of $\lambda >$ 600 nm. Under the low intensity conditions used, irradiation times of about 15 min were sufficient to give conversions of up to 90 %.

The photochromic complex **5** was studied in a similar fashion. Attempts to carry out the photocyclization of **5o** in chloroform failed and a few minutes of UV irradiation resulted in the decomposition of the product. However, it is noteworthy that the closed complex **5c** (obtained from **8c**) is photochemically stable; after irradiation of a solution of **5c** in chloroform with red light of $\lambda >$ 600 nm for 1 h, the presence of the open form **5o** was not detected by ^{1}H NMR spectroscopy. Under the same conditions, the closed forms **1c–4c** were completely decolorized within 10 min.

Switching of fluorescence: The fluorescence displayed by **1–4** and the changes in the luminescence properties can be brought about by photochemical switching between their open and closed forms (Table 2). The closed form of **1** and **2** were found to present strong emissions when excited in the 200–400 nm region. In contrast, the corresponding open forms showed much weaker fluorescence, this effect being especially pronounced for compound **2** (Figure 2). The rhenium complexes **3** and **4** displayed also a fluorescence discrimination (Table 2) when excited in the same region, the emission being in these cases always stronger for the open forms **3o** and **4o**.

Excitation in the absorption bands of **1–4** which allow a fluorescence discrimination, has low photochemical activity and thus affects only little the state of the system. To find out which band was inactive in the closing process, **1–4** were irradiated with light of different wavelengths between 240–350 nm using the monochromator of the fluorimeter. The band at $\lambda = 240$ nm showed low activity in the closing process, (Table 3). The absorptions at 311 and 390 nm, which also displayed fluorescence discrimination, are so active that in comparable conditions 50 % of conversion to the closed forms occurs after a few minutes.

Detailed emission data are available for a variety of [W(CO)$_5$L] type complexes.[26, 27] The first report of emission for any type of metal carbonyl complex concerns a number of

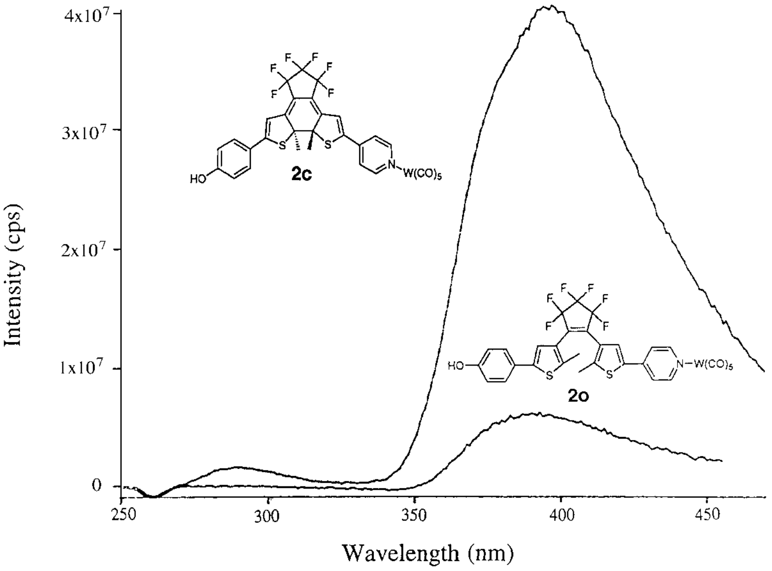


Figure 2. Fluorescence spectra of the closed **2c** and open **2o** forms of **2** (excitation at 240 nm).

Table 2. Relative fluorescence and emission quantum yields for the open **1o–4o** and closed **1c–4c** forms of complexes **1–4**.

Compound	Fluorescence wavelength[a]	Fluorescence intensity[b] (λ of the excitation [nm])	Emission quantum yield ϕ_{em}[d] (λ of the excitation [nm])
1o	382	2.4×10^6 (240); 8.2×10^6 (311)	0.03 (240); 0.04 (311)
1c	382	7.8×10^6 (240); 2×10^7 (311)	0.08 (240); 0.12 (311)
ratio **1c/1o**		3.2 (240); 2.4 (311)	2.7 (240); 3 (311)
2o	400	5.6×10^6 (240); 4.5×10^5 (394)[c]	0.03 (240); 0.01 (394)
2c	400	4.1×10^7 (240); 5×10^6 (394)[c]	0.15 (240); 0.07 (394)
ratio **2c/2o**		7 (240); 11 (394)	5 (240); 7 (394)
3o	372	9.3×10^5 (270); 2.7×10^6 (320)	0.01 (270); 0.04 (320)
3c	372	3.4×10^5 (270); 1.3×10^6 (320)	4×10^{-3} (270); 0.02 (320)
ratio **3o/3c**		2.7 (270); 2.1 (320)	2.5 (270); 2 (320)
4o	368	1.1×10^6 (270); 1×10^7 (315)	0.03 (270); 0.18 (315)
4c	368	3.8×10^5 (270); 5.4×10^6 (315)	0.01 (270); 0.11 (315)
ratio **4o/4c**		2.9 (270); 1.8 (315)	3 (270); 1.6 (315)

[a] Fluorescence detected [nm]. [b] Arbitrary units; $\approx 10^{-4}$ solutions of complexes in $MeOH/H_2O$ (5/1) (**1,2**) or MeOH (**3,4**). [c] Fluorescence observed at 677 when excited at 394 nm. [d] All compounds are referenced to naphthalene in cyclohexane ($\phi_{em} = 0.27$[34]).

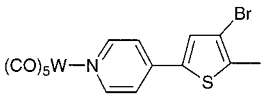
Table 3. Percentage of conversion from the open forms (**1o**–**4o**) to the closed forms (**1c**–**4c**) of complexes **1**–**4** after irradiation at 240 nm.[a]

Compound	Irradiation time 30 s [%]	 2 min [%]	 5 min [%]
1	4	12	
2	< 1	3	7
3[b]	< 1	3	9
4[b]	< 1	2	3

[a] Same conditions as in Table 2; slit used: 1 mm, 4.5 nm. [b] Irradiation at 270 nm.

[$W(CO)_5L$] species (with L is pyridine or other amines) as pure solids in rigid organic glasses at 77 K.[26a, 27b] Matrix isolation studies of [$W(CO)_5L(py)$] have provided data on the fluorescence from substituted metal carbonyls.[27] It is noteworthy that two emission bands ($^3E_a \rightarrow {}^1A_1$ LF phosphorescence and $^1E_a \rightarrow {}^1A_1$ fluorescence) were recorded for a number of [$W(CO)_5(py)$] complexes in either Ar or CH_4 matrices at 12 K. Metal carbonyl complexes were not expected to emit in solution at room temperature because of rapid ligand dissociation and efficient nonradiactive relaxation to the ground state. However, recent investigations concerning room temperature luminescence of {$W(CO)_5$} centers have shown that complexes which possess a MLCT (metal-to-ligand charge-transfer) state as the lowest energy excited state undergo relatively slow radiactive deactivation that can be readily detected under fluid conditions. Hence, only the [$W(CO)_5L$] complexes where L is a pyridine derivative with an electron-withdrawing substituent, exhibit luminescence at room temperature.[22, 27]

The fluorescence shown by the compounds **1** and **2** seems to result from the presence of the thiophene unit attached to the *para* position of the pyridine ring. To investigate this, we have prepared the compounds **17** and **18** in good yields using the procedure described for **1** and **2**. Compound **17** displayed a very strong fluorescence at 365–370 nm when irradiated in the 240–320 nm region, whereas **18**, in agreement with the literature data,[22] was not fluorescent. The corresponding parent ligands present a much weaker fluorescence. On the other hand, mono- and dimetallic species of rhenium such as [(bpy)$Re(CO)_3L$] have been found to possess attractive spectroscopic, photophysical, and electrochemical properties.[31] Such complexes display usually strong fluorescence in room temperature fluid solution.[24, 31, 32] In particular when the ligand is bpy, the emission is consistent with an MLCT origin. In our case, since the rhenium is bonded to two different nitrogen π-donor ligands the fluorescence detected for **3** and **4** could result from two possible excited states: Re →L8MLCT) and Re →L′ (MLCT) (with L = py and L′ = bpy).



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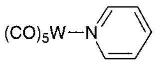

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Chemical locking: Photochromic complexes **5o** and **5c** represent switchable analogues of the dinuclear ruthenium complexes reported by Creutz ant Taube,[25b, 25c] in which two pentaamineruthenium(II) moieties can be either nonconjugated (**5o**) or connected through a conjugated system (**5c**). As described above, these two forms cannot be photointerconverted and may only be prepared from their parent ligands **8o** and **8c**. In terms of applicability in optical memory systems, the photochemical stability of **5c** provides in principle an alternative nondestructive read-out method. It is tempting to suggest a system formed by an adequate solid matrix impregnated with the photochromic complex **8o** in which one might store information by irradiating with UV light. Subsequent treatment of the matrix with a solution of Ru^{II} could result in the transformation of **8** into **5** and therefore in the chemical locking of the stored information. Nondestructive read-out should then be possible using visible light.

Conclusion

The photochromic complexes **1**–**4** act as optical switches presenting a light-triggered fluorescence by excitation of absorption bands that have only little effect on the switching process. The detected fluorescence seems to result from a MLCT. In terms of potential use for optical data storage and readout, compounds **1**–**4** display a fluorescence discrimination between their open and closed forms when excited at wavelengths that almost do not effect the equilibria. This fluorescence switching could be the basis of a nondestructive read-out method. Also photochromic complex **5**, whose closed form (**5c**) is photochemically stable, provides in principle a nondestructive read-out system; since one could use the parent ligand **8** for the storage of information by **8o**,**8c** interconversion and visible light $\lambda > 600$ nm for a nondestructive read-out on complexes **5**, the complexation with Ru may be considered to act as a chemical locking of the information. These various processes are schematically summarized in Figure 3.

Finally, the present results point to the interest of photoswitchable metal complexes with respect to both photochemical behavior and potential optical applications, for instance in three-dimensional optical storage devices.[33] Modulation of their redox properties may also be considered, as well as of photoinduced electron transfer between heterometallic centers.

Experimental Section

General methods: Starting materials were commercially available (Aldrich) and were used without further purification. Perfluorocyclopentene was purchased from Fluorochem-Limited. Compounds **6**,[10] **7**,[10] **8**,[10] **9**,[11] **15**,[10] and **18**[22, 23] have been described. Metal complexes of W,[22, 23] Re,[24] and Ru,[25] were prepared following standard conditions. Reactions were monitored by TLC using aluminum-backed Kieselgel 60_{254} plates and visualized by UV light. Flash column chromatography was performed using either Kieselgel 60 (230–400 mesh) silica gel or aluminum oxide 90 (70–230 mesh). In the case of photochromic complexes, purifications were carried out protected from light with aluminium foil. Colored open forms can be originated for the presence of very low quantities of the closed isomers.

Melting points were determined on an Electrothermal 1A9100 digital apparatus and are uncorrected. ^1H NMR spectra were recorded on a

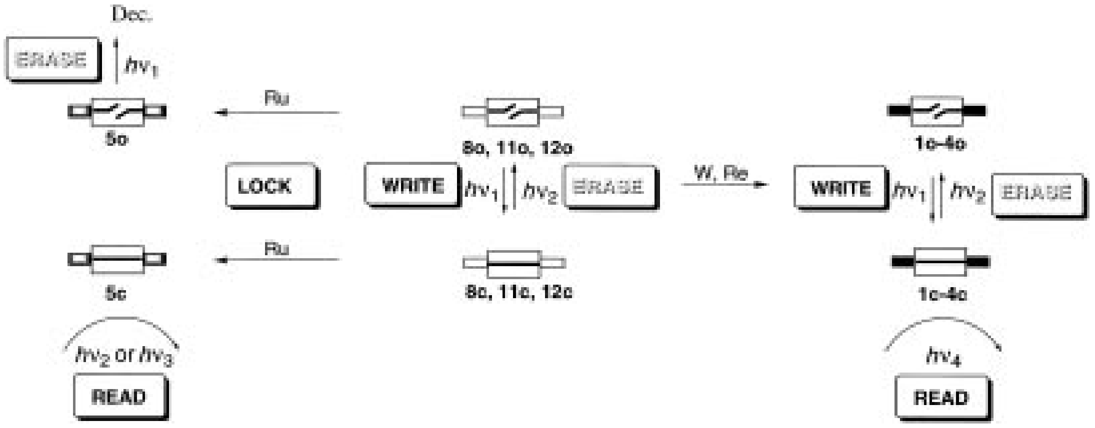

Figure 3. Schematic representation of an erasable optical memory system with nondestructive readout capacity based on the photochromic and luminescence properties of compounds **1**–**5**; $h\nu_1$: UV light; $h\nu_2$, $h\nu_3$: visible light; $h\nu_4$: UV excitation light.

Bruker AM 200SY instrument. ^{1}H NMR spectra were obtained at 200 MHz with the residual proton signals as reference peaks (assigned chemical shifts at $\delta = 7.26$, 2.04 for deuterated chloroform and acetone, respectively); coupling constants (J) are given in Hertz. UV absorption spectra were recorded on a Beckman DU 640 spectrophotometer in spectrograde solvents. UV irradiations were performed (unless otherwise indicated) with standard lamps used for visualizing TLC plates (VL6L; 6W, 312 nm tube power 12 W). For visible irradiations, light from a 300-W tungsten source was passed through a red filter (600 nm) and the samples were placed in a glass chamber maintained at room temperature (RT). Fluorescence emission spectra were recorded in spectrograde solvents on a Spex FluoroMax spectrophotometer equipped with a 150-W ozone-free xenon lamp. Irradiations at different wavelengths in the kinetic experiments of the opening–closing processes were carried out using the monochromator of the fluorimeter. Elemental analysis were performed by the Service Régional de Microanalyse, Université Pierre and Marie Curie (Paris).

1-[5′-(4″-Methoxyphenyl)-2′-methylthien-3′-yl]perfluorocyclopentene (10): Butyllithium (1.6 M in hexanes, 1.8 mL, 2.9 mmol) was slowly added to a stirred solution of the bromothiophene **9** (767 mg, 2.7 mmol) in dry THF (30 mL) at −78 °C under nitrogen atmosphere. After 10 min, perfluorocyclopentene was added and, after an additional 1 h of stirring, the reaction was allowed to warm to ambient temperature. The solvents were then removed in vacuo and the obtained product extracted with CH_2Cl_2 and washed with saturated aqueous sodium hydrogen carbonate. Finally, the combined organic phases were dried, evaporated and the residue chromatographed over silica gel (hexane/CH_2Cl_2 (4:1)). Pure product **10** was thus obtained (408 mg, 38 %) as a colorless solid: m.p. 65–66 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.46$ (d, $J = 3.2$, 3 H), 3.84 (s, 3 H), 6.92 (AB system, $J = 8.8$, 2 H), 7.13 (s, 1 H), 7.47 (AB system, $J = 8.8$, 2 H); $C_{17}H_{11}F_7OS$: calcd C 51.52, H 2.80; found C 51.75, H 2.80.

1-[5′-(4″-Methoxyphenyl)-2′-methylthien-3′-yl]-2-[2‴-methyl-5‴-(pyrid-4^{IV}-yl)-thien-3‴-yl]perfluorocyclopentene (11): Butyllithium (1.6 M in hexane, 1 mL, 1.6 mmol) was slowly added to a stirred solution of 3-bromo-2-methyl-5-(4′-pyridyl)thiophene **(7)** (402 mg, 1.58 mmol) in THF at −78 °C under nitrogen atmosphere. After 10 min, a solution of cyclopentene **10** in tetrahydrofuran was added and the resulting mixture was stirred at −78 °C for an additional hour. The solution was allowed to warm to ambient temperature. HCl (0.5 M, 5 mL) was then added and the solvents removed in vacuo. The residue was extracted with CH_2Cl_2 and washed with saturated aqueous sodium hydrogen carbonate. The combined organic phases were then dried, and evaporated to a brown syrup. Chromatography over silica with CH_2Cl_2/EtOAc (8:1 to 4:1) as the eluent afforded **11** as a yellowish glass (515 mg, 65 %); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.94$ (s, 3 H), 2.00 (s, 3 H), 3.84 (s, 3 H), 6.92 (AB system, $J = 8.8$, 2 H), 7.15 (s, 1 H), 7.41 (AB system, $J = 6.2$, 2 H), 7.46 (AB system, $J = 8.8$, 2 H), 7.48 (s, 1 H), 8.60 (AB system, $J = 6.2$, 2 H); $C_{27}H_{19}F_6NOS_2$: calcd C 58.79, H 3.47, N 2.54; found C 58.19, H 3.54, N 2.54; exact mass calcd for $C_{27}H_{19}F_6NOS_2$: 551.0812, found 551.0811.

1-[5′-(4″-Hydroxyphenyl)-2′-methylthien-3′-yl]-2-[2‴-methyl-5‴-(pyrid-4^{IV}-yl)-thien-3‴-yl]perfluorocyclopentene (12): Boron tribromide (1 M in CH_2Cl_2, 0.9 mL, 0.9 mmol) was added to a solution of **11** (150 mg, 0.27 mmol) in dry CH_2Cl_2 (10 mL) and the reaction was heated to reflux under a nitrogen atmosphere in the dark for 4 h. The reaction was then cooled and extracted with dichloromethane, the combined organic phases were washed with water and evaporated in vacuo yielding an orange solid, which was dissolved in MeOH (5 mL) and aqueous sodium hydroxide (33 % w/w, 5 mL). The resulting mixture was stirred in the dark for 24 h at ambient temperature, and then diluted with water and neutralized with concentrated hydrochloric acid. The resulting suspension was extracted with EtOAc and washed with water. The combined organic phases were dried and the solvent was removed in vacuo yielding a yellow solid. Chromatography over silica gel (CH_2Cl_2/EtOAc (4:1)) afforded **12** (103 mg, 71 %) as a yellow solid. M.p. 220 °C; ^{1}H NMR (200 MHz, [D$_6$]acetone): (open isomer): $\delta = 2.02$ (s, 3 H), 2.10 (s, 3 H), 6.88 (AB system, $J = 8.7$, 2 H), 7.29 (s, 1 H), 7.47 (AB system, $J = 8.7$, 2 H), 7.60 (AB system, $J = 6.2$, 2 H), 7.78 (s, 1 H), 8.58 (AB system, $J = 6.2$, 2 H), 8.64 (s, 1 H); $C_{26}H_{17}F_6NOS_2$: calcd C 58.10, H 3.19, N 2.60; found C 58.37, H 3.45, N 2.47.

1,2-Bis[5′-(4″-cyanophenyl)-2′-methylthien-3′-yl]perfluorocyclopentene (14): 1,2-Bis-(2′-*n*-heptylthiophen-3′-yl)-perfluorocyclopentene (**13**, 534 mg, 1 mmol) (prepared following the described procedure[12]) was dissolved in anhydrous Et_2O (15 mL containing 0.3 mL of TMEDA). To the resulting solution cooled at −78 °C butyllithium (1.6 M in hexane, 0.63 mL, 1 mmol) was added dropwise under nitrogen. Stirring at room temperature was continued for 20 min and then $B(OBu)_3$ (780 mg, 3.4 mmol) was added in one portion. The red-brown solution was stirred for 1 h and then diluted with anhydrous THF (12 mL). This solution was transferred without further purification to a refluxing mixture containing: 4-bromobenzonitrile (1.8 g, 10 mmol), $[Pd(PPh_3)_4]$ (50 mg, 0.043 mmol), Na_2CO_3 (1.9 M, 8 mL), and THF (150 mL), and the resulting two-phase system refluxed overnight. The solvents were then evaporated, extracted with CH_2Cl_2 (2 × 50 mL), washed with H_2O (10 mL), dried over Na_2SO_4 and finally chromatographed over silica gel (hexane/EtOAc (10:1)) affording **14** (200 mg, 35 %) as a white solid. M.p. 124–126 °C; ^{1}H NMR (200 MHz, $CDCl_3$): open isomer: $\delta = 0.78$ (t, $J = 6.8$, 6 H), 0.9–1.3 (m, 20 H), 2.2 (m, 4 H), 7.39 (s, 2 H), 7.66 (s, 4 H), 8.78 (d, $J = 6.7$, 4 H); $C_{41}H_{40}F_6N_2S_2$: calcd C 66.65, H 5.46, N 3.79; found C 66.53, H 5.64, N 3.75.

1,2-Bis(5′-cyano-2′-methylthien-3′-yl)perfluorocyclopentene (16): To a stirred mixture of sodium azide (33 mg, 0.5 mmol) in benzene (10 mL), concentrated sulfuric acid (0.03 mL) was added dropwise while the temperature was maintained at 10–15 °C. Then the bis-aldehyde **15** (51 mg, 0.1 mL) was added at the same temperature. Stirring was continued at room temperature overnight. Excess ice was then added, the two layers were separated, the aqueous layer was extracted with Et_2O, and the ether extracts were added to the benzene layer. The solvents were evaporated and the residue chromatographed over silica gel (CH_2Cl_2/hexane (4:1)) affording **16** (153 mg, 30 %) as a white solid: m.p. 200 °C; ^{1}H NMR (200 MHz, [D$_6$]acetone): open isomer: δ: 2.05 (s, 6 H), 7.94 (s, 2 H); ^{13}C NMR (50 MHz, [D$_6$]acetone): open isomer: δ: 24.7, 119.4, 123.5, 135.6, 148.7, 160.8 (signals of the perfluorocyclopentene ring are coupled with the F); $C_{17}H_8F_6N_2S_2$: calcd C 48.80, H 1.93, N 6.69; found C 48.64, H 2.08, N 6.58; exact mass calcd for $C_{17}H_9F_6N_2S_2$: 419.0111, found: 419.0123.

1,2-Bis[2′-methyl-5′-(*N*-pentacarbonyltungsten(0)pyrid-4″-yl)-thien-3′-yl]-perfluorocyclopentene (1): A stirred solution of $[W(CO)_6]$ (243 mg, 0.69 mmol) in deaerated THF (50 mL) under nitrogen atmosphere was irradiated with a 150-W Hg UV lamp for 30 min at ambient temperature. A solution of **8** (180 mg, 0.34 mmol) in THF (20 mL) was then added to the deep yellow solution, and the resulting mixture was stirred at ambient temperature protected from the light with aluminum foil. After 30 h, the solvents were evaporated and the resulting precipitate washed several times with hexane and dissolved in acetone. Crystallization was carried out by slow diffusion of hexane into the acetone layer. The resulting solid was then filtered and dried in vacuo, to yield the complex **1o** as a dark powder (231 mg, 58%). M.p. > 350 °C (decomp); ^{1}H NMR (200 MHz, $CDCl_3$): open isomer **1o**: $\delta = 2.01$ (s, 6H), 7.35 (d, $J = 6.7$, 4H), 7.54 (s, 2H), 8.78 (d, $J = 6.7$, 4H); closed isomer **1c**: $\delta = 2.20$ (s, 6H), 6.86 (s, 2H), 7.33 (d, $J = 6.7$, 4H), 8.88 (d, $J = 6.7$, 4H); $C_{35}H_{16}F_6N_2O_{10}S_2W_2$: calcd C 35.92, H 1.38, N 2.39; found C 36.05, H 1.27, N 2.34.

1-[5′-(4″-Hydroxyphenyl)-2′-methylthien-3′-yl]-2-[2‴-methyl-5‴-(*N*-pentacarbonyltungsten(0)pyrid-4⁗yl)thien-3‴-yl]perfluorocyclopentene (2): A solution of the photochromic complex **12** (30 mg, 0.05 mmol) in THF (5 mL) was added to $[W(CO)_5(thf)]$ (0.024 M in THF, 0.12 mmol) (prepared as described above), and the reaction was stirred at ambient temperature in the dark under a nitrogen atmosphere. After 30 h the solvents were evaporated and the residue washed repeatedly with hexane. Chromatography over alumina (hexane/EtOAc (4:1)) afforded a dark solid; product **2o** was obtained pure (29 mg, 67%) as a blue powder following crystallization by slow diffusion of hexane into acetone. M.p. > 350 °C (decomp); ^{1}H NMR (200 MHz, $CDCl_3$): open isomer **2o**: $\delta = 2.03$ (s, 3H), 2.05 (s, 3H), 6.82 (d, $J = 8.6$, 2H), 7.12 (s, 1H), 7.32 (d, $J = 6.6$, 2H), 7.41 (d, $J = 8.6$, 2H), 7.51 (s, 1H), 8.71 (d, $J = 6.6$, 2H); closed isomer **2c**: $\delta = 2.16$ (s, 3H), 2.17 (s, 3H), 6.61 (s, 1H), 6.84 (s, 1H), 6.89 (d, $J = 8.6$, 2H), 7.30 (d, $J = 6.6$, 2H), 7.51 (d, $J = 8.6$, 2H), 8.82 (d, $J = 6.6$, 2H); $C_{31}H_{17}F_6NO_6S_2W_1$: calcd C 43.22, H 1.99, N 1.63; found C 43.05, H 1.99, N 1.63.

3-Bromo-2-methyl-5-(*N*-pentacarbonyltungstenpyrid-4′-yl)thiophene (17): A solution of 3-bromo-2-methyl-5-pyridylthiophene (253 mg, 1 mmol) in THF (40 mL) was added to $[W(CO)_5(thf)]$ (0.024 M in THF, 42 mL, 1 mmol) (prepared as described for product **1**) and the reaction was stirred at ambient temperature in the dark under a nitrogen atmosphere. After 72 h, the solvents were evaporated and the residue washed repeatedly with hexane. Chromatography over alumina (hexane/CH_2Cl_2 (3:1)) followed by recrystallization from Et_2O of the obtained residue afforded complex **17** (409 mg, 71%) as an orange solid: M.p. 158–160 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.49$ (s, 3H), 7.31 (d, $J = 6.6$, 2H), 7.40 (s, 1H), 8.73 (d, $J = 6.6$, 2H); $C_{15}H_8BrNO_5SW$: calcd C 31.17, H 1.40, N 2.42; found C 31.21, H 1.55, N 2.40.

1,2-Bis{5′-[*N*-(2″,2‴-bipyridyl)tricarbonylrhenium(I)pyrid⁗-4-yl]-2′-methylthien-3′-yl}perfluorocyclopentane bistrifluorosulfonate (3): A solution of **8** (80 mg, 0.15 mmol) and $[Re(bpy)(CO)_3(CH_3CN)]CF_3SO_3$ (190 mg, 0.31 mmol) in deaerated THF (15 mL) was refluxed under nitrogen atmosphere for 4 h. The solvents were then evaporated and the resulting precipitate washed several times with hexane and finally crystallized from hexane/acetone (5:1) affording complex **3o** (153 mg, 63%) as a blue powder. ^{1}H NMR (200 MHz, [D$_6$]acetone): open isomer **3o**: $\delta = 1.99$ (s, 6H), 7.63 (d, $J = 6.8$, 4H), 7.83 (s, 2H), 8.0 (m, 4H), 8.4–8.5 (m, 8H), 8.76 (d, $J = 8.2$, 4H), 9.46 (d, $J = 5.4$, 4H); closed isomer **3c**: $\delta = 2.13$ (s, 6H), 7.17 (s, 2H), 7.68 (d, $J = 5.4$, 4H), 8.0 (m, 4H), 8.4–8.5 (m, 4H), 8.60 (d, $J = 5.4$, 4H), 8.76 (d, $J = 8.2$, 4H), 9.47 (d, $J = 5.4$, 4H); $C_{53}H_{32}F_{12}N_6O_{12}S_4Re_2$: calcd C 38.03, H 1.93, N 5.01; found C 37.36, H 1.93, N 4.97.

1-[5′-(4″-Methoxyphenyl)-2′-methylthien-3′-yl]-2-{5‴-[*N*-(2^{IV},2^{V}-bipyridyl) tricarbonylrhenium(I)pyrid^{VI}-4-yl]-2‴-methylthien-3‴-yl}perfluorocyclopentene trifluorosulfonate (4): A solution of **11** (20 mg, 0.036 mmol) and $[Re(bpy)(CO)_3(CH_3CN)]CF_3SO_3$ (23 mg, 0.036 mmol) in deaerated THF (10 mL) was refluxed under nitrogen atmosphere for 24 h. The solvents were then evaporated and the residue washed several times with hexane and finally crystallized from Et_2O/acetone (10:1) affording complex **4o** (153 mg, 48%) as a dark powder. This product displayed a limited stability and decomposed after a few days even when stored under nitrogen in the dark. ^{1}H NMR (200 MHz, [D$_6$]acetone): open isomer **4o**: $\delta = 2.0$ (s, 3H, overlapped), 2.19 (s, 3H), 3.82 (s, 3H), 6.97 (d, $J = 8.9$, 2H), 7.34 (s, 1H), 7.55 (d, $J = 8.9$, 2H), 7.7–7.9 (m, 2H), 8.3–8.4 (m, 5H), 8.70 (d, $J = 8.1$, 2H), 8.92 (d, $J = 6.5$, 2H), 9.10 (d, $J = 5.6$, 2H); closed isomer **4c**: $\delta = 2.25$ (s, 3H), 2.26 (s, 3H), 3.90 (s, 3H), 6.93 (s, 1H), 7.08 (d, $J = 8.9$, 2H), 7.52 (s, 1H), 7.8–8.0 (m, 4H), 8.3–8.5 (m, 4H), 8.69 (d, $J = 8.2$, 2H), 8.97 (d, $J = 6.1$, 2H), 9.10 (d, $J = 5.6$, 2H).

1,2-Bis[2′-methyl-5′-(*N*-pentaamineruthenium(II)pyrid-4″-yl)thien-3′-yl)-perfluorocyclopentene bisdihexafluorophosphate (5): A solution of **8o** (50 mg, 0.09 mmol) and $[Ru(NH_3)_5(H_2O)](PF_6)_2$ (86 mg, 0.18 mmol) in deaerated acetone (15 mL) was stirred under nitrogen atmosphere for 72 h. The solvents were then evaporated and the resulting precipitate washed several times with EtOAc and finally crystallized from hexane/acetone (5:1) affording complex **5o** (120 mg, 88%) as a yellowish powder. The same procedure applied to the photochromic complex **8c** afforded **5c** (80%) as a deep blue powder. ^{1}H NMR (200 MHz, [D$_6$]acetone): open isomer: $\delta = 2.02$ (s, 6H), 2.59 (s), 3.19 (s, 6H), 7.51 (d, $J = 6.4$, 4H), 7.86 (s, 2H), 8.80 (d, $J = 6.4$, 4H); closed isomer: $\delta = 2.21$ (s, 6H), 2.66 (s), 3.50 (s), 7.28 (s, 2H), 7.47 (d, $J = 6.8$, 4H), 8.97 (d, $J = 6.8$, 4H); $C_{25}H_{46}F_{30}N_{12}P_4S_2Ru_2$: calcd C 21.24, 3.28, N 11.89; found C 21.45, H 3.27, N 11.84.

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