# Photochromic Switches Incorporated in Bridging Ligands: A New Tool to Modulate Energy-Transfer Processes**

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The thoughful construction of molecular switches has led to a gamut of supramolecular systems that can be used in molecular electronics. These include molecules based on thienylethenes, spiropyrans, fulgides, dithienylphenanthrolines, and diazafluorenes. This article reviews the recent developments made in the synthesis and characterization of all these systems, thereby allowing a comparative study to validate the viability of these switchable molecules on a nanoscale. Also, the drawbacks of each class are demonstrated and, at the same time, the remedies for further improvisation are prescribed. We have made an honest attempt to present an exhaustive account of all the different photochromic switches developed by us hitherto.
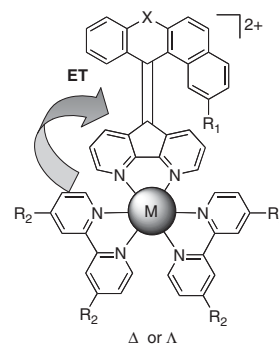
1. Introduction

The design and construction of molecular-level devices is of great scientific interest since it enables the development of new concepts and offers new vistas in the field of applied chemistry, which in turn, are strongly related to nanotechnology and nanoscience.[1] A molecular-level device can be defined as an assembly of molecular components that can achieve specific functions such as light-induced energy/electron transfer, conformational change, or bond breaking/bond making.[2] The clever assembly of molecular building blocks has provided the chemist with powerful tools to build up supramolecular systems of nanoscale dimensions that can approach the level of miniaturization in microelectronics and the length scale of biological systems.[3] This "bottom–up" approach is extremely interesting because it allows tuning of the properties of complex structures at a molecular level, thereby, leading to the construction of controllable molecular devices. Special care must be devoted to the design of systems used in signal generation, processing, and storage, especially because they are able to perform light-induced functions as a consequence of energy/electron-transfer processes. Since light plays a major role, there is a need to design molecular-level systems capable of handling light signals.[4] The aim of the different sections described herein is to highlight the syntheses and photophysical characterization of novel light-driven molecular switches and the prospects of their promising applications in optical data storage, molecular electronics, and molecular-level logic gates.[5]

The general idea behind the construction of our photonic devices is depicted in Figure 1. Two metal complexes (Ru^{II}/Os^{II}) are connected by a wire-type bridging ligand containing two coordinating sites.[6] The two metal centers differ in the energies of their respective excited states. By irradiation into the

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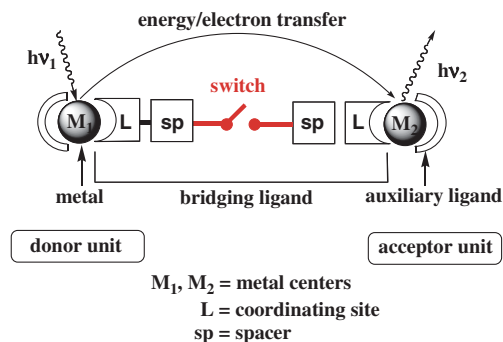
Figure 1. Schematic presentation of a binuclear metal complex containing a switching unit in the bridging ligand.

singlet metal–ligand charge-transfer (^{1}MLCT) absorption band, a driving force is created which induces an energy-transfer process from the higher-lying excited Ru unit via the bridging ligand to the Os complex. Both metal complexes dissipate their individual excited states by emitting light of different wavelengths. By studying the emission properties of the two metal centers, the photophysical behavior of the whole system (the lifetime of each excited state, quantum yield, and rate constant of the energy-transfer process) can be ascertained. As mentioned before, the driving force for the energy-transfer process is provided by the excited-state potential of the two metal complexes. Under such conditions, the rate constant for the process is only influenced by the nature of the bridging ligand. We have developed a series of rigid, wire-type bridging ligands and measured their behavior with respect to the energy-transfer process in the bimetallic compound.[7]

By incorporation of a covalently bound photochromic unit into the bridging ligand, a modulation of the electronic/energetic conductivity through the bridge must be possible. Photochromic units exist in two forms, the open form and the closed form. Normally, π-conjugation of the switching unit is much more pronounced in one of the forms than in the other. Therefore, the energy level of the photochromic unit drops down, inducing a faster rate for the energy-transfer process. The state (ON or OFF) of the photochromic unit can be reversibly changed by irradiation into a characteristic absorption band of either the open or the closed form. The entire system can be monitored by measuring the emission of the Ru/Os center of the molecular device.

Among several switching systems developed by us, we describe herein modified dithienylethene, spiropyran, and fulgimide linkers, all three being efficient photochromic units. Furthermore, we discuss a new class of photochromic molecules incorporated in a phenanthroline-type ligand and, finally, a short overview about a new class of chiroptical switches.

2. Photochromic Dithienylethene Derivatives Containing Ru^{II} and/or Os^{II} Metal Units

In recent years, much research effort has been devoted to the development of photochromic materials, i.e., systems that can be converted reversibly from one form into another upon light excitation.[8–10] One of the most promising classes of photochromic materials is diarylethenes with attached thiophene rings (i.e., dithienylethenes), whose photochromic properties were first described by Irie and Mohri in 1988.[11] Among important features of this class of molecules are 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.[12] In some cases it has been possible to quantitatively transform the system from one form to the other.[13–15]

Dithienylethene derivatives containing the perfluorinated cyclopentene ring as a central part have attracted immense attention of late. Among many other scientific groups, the investigations of Irie,[11–13,15,16] Lehn,[17] Launay,[18] Branda,[19] Munakata,[20] and Effenberger[21] have essentially developed the field of dithienylethene switches. The photoresponsive behavior stems from the ability of the central unit to cyclize upon UV irradiation. The conversion to the "closed" form is, in our case, almost quantitative, and the two forms, open and closed, are thermally stable and can be converted into each other several thousand times. On going from the open to the closed form, the system changes from colorless to blue.

In this study we describe the syntheses, photophysical properties, and photochemical behavior of a series of photochromic compounds containing either a free chelating ligand or a chelated metal-complex unit. In particular, the dithienyl-perfluorocyclopentene chromophoric unit is connected through a phenylene linker to 2,2′-bipyridine (bpy) and to the well-known

Ru(bpy)$_3$[22] or Os(bpy)$_3$ moieties. Two homodinuclear complexes containing either Ru^{II} (**Ru(μ-1o)Ru**) or Os^{II} (**Os(μ-1o)Os**) centers, and a heterodinuclear complex containing Ru^{II} and Os^{II} (**Ru(μ-1o)Os**) have been synthesized from free ligand **1o** (see Scheme 1). The general procedure involves the preparation of the 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**, and the heterodinuclear complex (**Ru((μ-1o)Os**) (Scheme 1).[23] After isolation as hexafluorophosphate salts, the purification of the products is performed on a preparative plate (SiO$_2$).

The complexation with either Ru^{II} or Os^{II} causes big changes in the spectroscopic properties of the compounds compared to the free ligands. For the metal complexes, an absorption band due to a ^{1}MLCT transition is present at a lower energy than the S$_0$→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 from the ^{1}MLCT to the triplet MLCT (^{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 the structurally identical diruthenium and diosmium complexes as well as the heterodinuclear Ru^{II}/Os^{II} complex, wherein all the three complexes differ in the energy 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.[24] As all three metal-complex moieties are luminescent and their emission properties depend on the state of the photochromic unit, this could provide a way to monitor the photoreaction and to understand its intimate mechanism.
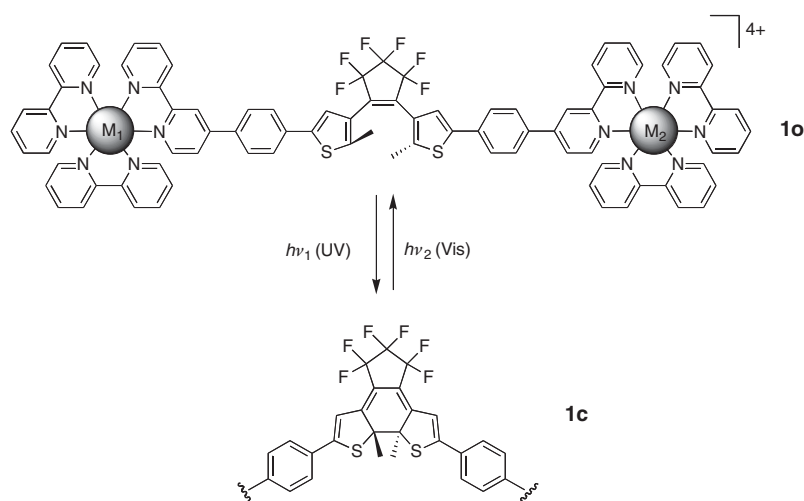
2.1. Electronic Absorption and Emission Spectroscopic Properties

UV-vis absorption maxima and corresponding molar absorption coefficients of compounds **1o**, **1c**, **Ru(μ-1o)Ru**, **Ru(μ-1c)Ru**, **Os(μ-1o)Os**, **Os(μ-1c)Os**, **Ru(μ-1o)Os**, and **Ru(μ-1c)Os** are listed in Table 1.
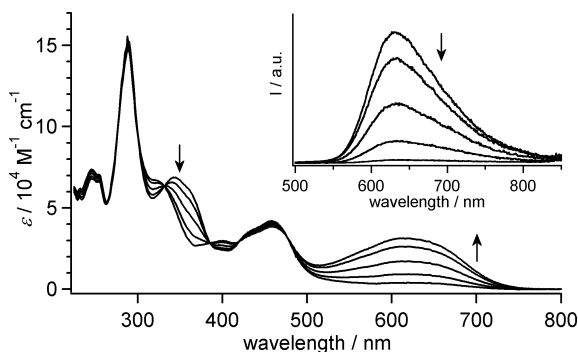
Table 1. UV-vis absorption maxima (λ_{max}) and molar absorption coefficients ($\breve{\alpha}_{max}$) of the investigated photochromic compounds in their open and closed forms [a].

Compound	λ_{max} [nm] ($\breve{\alpha}_{max}$ [10^4 M^{-1} cm^{-1}])
1o	285 (4.9), 321 (6.3)
1c	277 (4.0), 331 (4.8), 392 (sh, 1.3), 605 (2.0)
Ru(μ-1o)Ru	288 (15.6), 345 (7.1), 458 (4.2)
Ru(μ-1c)Ru	288 (14.9), 328 (sh, 6.5), 402 (3.0), 458 (3.8), 614 (3.2)
Os(μ-1o)Os	292 (15.1), 353 (6.3), 441 (3.6), 492 (3.4), 590 (0.95)
Os(μ-1c)Os	292 (13.9), 331 (sh, 5.7), 393 (3.4), 445 (3.1), 492 (3.3), 618 (3.7)
Ru(μ-1o)Os	290 (15.1), 350 (6.5), 456 (3.9), 590 (0.56)
Ru(μ-1c)Os	290 (13.8), 329 (sh, 5.8), 396 (3.1), 457 (3.4), 617 (3.3)

[a] In MeCN, at temperature, T = 293 K; sh = shoulder.

The open form of the uncoordinated ligand **1o** in acetonitrile is colorless. In the electronic absorption spectra of **1o** and **1c** in acetonitrile, the absorption maximum at 321 nm corresponds to the S$_0$→S$_1$ (^{1}IL) transition localized on the photochromic unit, while the shoulder at 285 nm involves the π→π* transition of the bpy ligands. Upon conversion to the closed form of **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$_0$→S$_1$ transition of the photochromic unit.[13] The bpy intraligand transitions are not affected by the cyclization of the central unit, while the S$_0$→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$_0$→S$_2$ and S$_0$→S$_3$ transitions, respectively.[25]

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. In 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.[26] The MLCT band shifts to slightly lower energy compared to [Ru(bpy)$_3$]$^{2+}$, indicating that in the ^{1}MLCT state the charge is localized on the more conjugated substituted bpy ligand. The absorption band at 345 nm corresponds to the S$_0$→S$_1$ (^{1}IL) transition localized on the central photochromic unit. The electron-withdrawing metal center causes a lowering of the lowest unoccupied molecular orbital (LUMO) on the photochromic unit, resulting in a shift of the corresponding absorption band to a significantly lower energy compared to the free ligand **1o**. Upon irra-

Scheme 1. Closing and opening process on the dithienylethene switching unit. *h*: Planck's constant; *v*: frequency of light.

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Figure 2. UV-vis spectral changes observed during the photocyclization of **Ru(μ-1o)Ru** to **Ru(μ-1c)Ru**. Inset: the corresponding decrease in emission of **Ru(μ-1o)Ru**. *I*: intensity; conditions: MeCN, 293 K. (Reprinted with permission from [24]. Copyright 2004, the American Chemical Society.)

diation of the solution, conversion to **Ru(μ-1c)Ru** is observed. The band at 345 nm disappears and a new absorption band grows at 614 nm, giving the solution a green color. In analogy to **1c**, the band at 614 nm can be ascribed to the [1]IL transition localized on the cyclized dithienylethene. The [1]IL$_{bpy}$ 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 a 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 a green color already when the complex is in the open form. This band can be assigned to partially allowed [3]MLCT transitions, typical for [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.
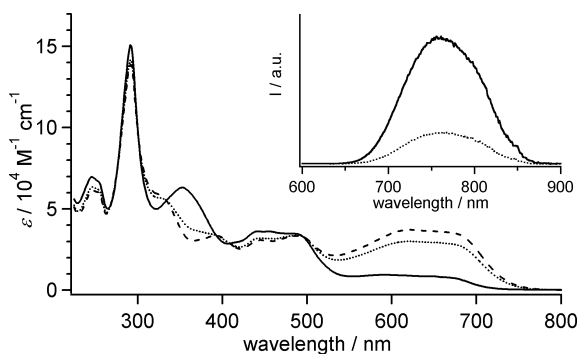
Figure 3. UV-vis spectra of complex **Os(μ-1o)Os** (—) and a solution of **Os(μ-1o)Os/Os(μ-1c)Os** in the photostationary state (·····). The latter spectrum corresponds to a 73 % photoconversion from **Os(μ-1o)Os** to **Os(μ-1c)Os**, as determined from the corresponding ^{1}H NMR spectrum. The UV-vis 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 the 100 % open form (—) to the photostationary state (·····). Conditions: MeCN, 293 K. (Reprinted with permission from [24]. Copyright 2004, the American Chemical Society.)

The electronic absorption spectra of **Ru(μ-1o)Os** and **Ru(μ-1c)Os** in acetonitrile are shown in Figure 4. The absorption spectrum of **Ru(μ-1o)Os** is the average of the absorption spec-
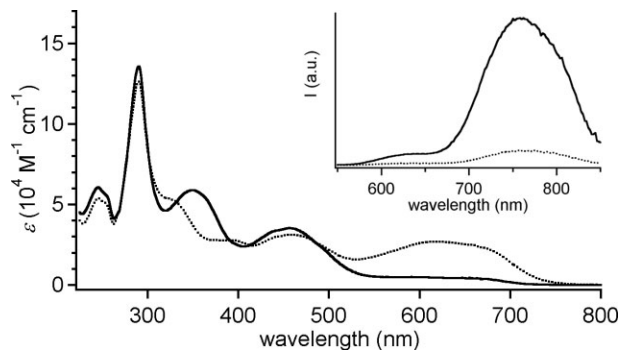
Figure 4. UV-vis spectra of complex **Ru(μ-1o)Os** (—) and mixed **Ru(μ-1o)Os/Ru(μ-1c)Os** in the photostationary state (···) obtained by irradiation with 334 nm light. The latter spectrum corresponds to a 90 % photoconversion from **Ru(μ-1o)Os** to **Ru(μ-1c)Os**, as determined from the corresponding ^{1}H NMR spectrum. Inset: the corresponding decrease in emission of **Ru(μ-1o)Os** (—) caused by conversion to the photostationary state (···). Conditions: MeCN, 293 K.

tra of complexes **Ru(μ-1o)Ru** and **Os(μ-1o)Os**.[24] This suggests that, in the heterometallic complex, the interactions between the Ru-based and Os-based components are weak.

A solution of open-form complex **Ru(μ-1o)Os** in acetonitrile is greenish and becomes a dark green (Fig. 4) upon irradiation. The color change reflects the cyclization of the photochromic unit, leading to a more conjugated system, the closed-form complex **Ru(μ-1c)Os**. At the photostationary state, the ^{1}H NMR spectrum of a sample in CD$_3$OD proves that, upon irradiation with 334 nm light, 90 % of the starting **Ru(μ-1o)Os** complex is converted to the closed form, **Ru(μ-1c)Os**.

Besides the spectral changes occurring in the UV-vis absorption spectrum, dramatic changes are observed in the emission behavior. Emission spectra and emission lifetimes in acetonitrile solution at room temperature have been recorded for **Ru(μ-1o)Ru**, **Os(μ-1o)Os**, and **Ru(μ-1o)Os**. 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 forms 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 619 nm (Fig. 2, inset). The broad and featureless emission can be assigned to originate from the [3]MLCT state.[26] 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.

Ru(bpy)$_3$-type complexes substituted with phenyl groups in the 4- and 4′-positions[27] in deaerated acetonitrile have high emission quantum yields and long excited-state lifetimes. This is the result of strong delocalization of the excited MLCT state

Table 2. Emission maxima (λ_{max}), lifetimes (τ), and quantum yields (φ_{em}) of the investigated photochromic complexes **Ru(μ-1o)Ru**, **Os(μ-1o)Os**, and **Ru(μ-1o)Os** [a].

Compound	λ_{max} [nm]		τ [ns]				φ_{em} [b]			
	Ru	Os	Ru		Os		Ru		Os	
			Aerated	Deaerated	Aerated	Deaerated	Aerated	Deaerated	Aerated	Deaerated
Ru(μ-1o)Ru	630		140	310			0.006 (334)	0.014 (334)		
							0.007 (450)	0.014 (450)		
Os(μ-1o)Os		757			44	62			0.004 (334)	0.005 (334)
									0.004 (450)	0.006 (450)
Ru(μ-1o)Os	630 [c]	758	0.07		0.56 [d]		2×10^{-4} (471)		0.0035 (471)	
			0.61		46					

[a] In MeCN, at $T = 293$ K, all values obtained from single measurements. [b] Excitation wavelength [nm] in brackets. [c] The ruthenium emission appears as a shoulder of the osmium emission band, and the reported emission maximum could merely be estimated. [d] Growth of the emission.

on the substituted bipyridine ligand. Their emission lifetimes and quantum yields exceed those of **Ru(μ-1o)Ru** seven to eight times. This difference can only be explained by the presence of a non-radiative 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 photo-conversion 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 (Fig. 2, inset). 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**, and that, in fact, **Ru(μ-1c)Ru** is non-emissive.

The emission spectrum of **Os(μ-1o)Os** in acetonitrile exhibits a broad structureless band with a maximum at 730 nm (Fig. 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 (Fig. 3, inset), while the emission lifetime remains the same. As in the case of the corresponding ruthenium complex, the residual emission is attributed to unconverted molecules of **Os(μ-1o)Os**, and also **Os(μ-1c)Os** is considered to be non-emissive.

The emission spectrum of **Ru(μ-1o)Os** in aerated acetonitrile (Fig. 4, inset) was recorded upon excitation with 471 nm light, which corresponds to the isoabsorptive wavelength for the Ru-bpy and Os-bpy ^{1}MLCT bands. It shows both ruthenium-based and osmium-based emissions, centered at about 630 and 730 nm, respectively. From comparison of the emission intensities, we can conclude that the ruthenium moiety in **Ru(μ-1o)Os** emits much less than in the homodinuclear complex, while the osmium emission intensity is about 90 % that of **Os(μ-1o)Os** (Table 2). This result reveals that the energy transfer from the ruthenium to osmium centers in **Ru(μ-1o)Os** is very efficient and that the quenching of the ruthenium moiety is in a large part due to the energy transfer, and, in a much smaller part, due to the photoreaction.

The excited-state lifetimes mirror the emission spectra discussed above for the osmium-based component. In fact the osmium excited state lives 46 ns (Table 2), which is essentially identical to the emission lifetime of **Os(μ-1o)Os** (44 ns).[24] The lifetime of the ruthenium emission is strongly reduced compared to **Ru(μ-1o)Ru**. The emission decay is bi-exponential, with components of 0.07 and 0.61 ns. We believe that the longer component is due to the quenched ruthenium unit in the open form and the shorter one is due to a small amount of closed-form ruthenium that is obtained during the measurement upon excitation in the UV region. The energy-transfer process can also be monitored by the rise time of 0.56 ns observed in the osmium decay measurements. This value agrees well with the long decay component (0.61 ns) of the ruthenium emission.

This article summarizes syntheses, characterization, and photocyclization behavior of a series of derivatives of dithienylperfluorocyclopentene. By introducing 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 are 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 high quantum yields. Furthermore, a 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 timescale. An equilibrium exists between the ^{3}MLCT and ^{3}IL states, which are close in energy, resulting in 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, which are at a lower energy than those of the metal center in the closed form.

The bridging unit in the dinuclear metal complex **Ru(μ-1o)Os** (open form) allows an efficient energy transfer from the excited ruthenium to the osmium center. When the switching unit is present in its closed form, the energy level of the dithienyl-ethene unit is below the energy levels of the two metal centers, quenching both emissions. The closed switching unit then acts as a trap for the excited states of both coordinated metal termini.

In order to achieve a non-destructive readout by means of observing the emission, one would ideally like to construct a di-thienylethene system in which the photochromic and lumines-cent parts can be addressed independently, such that selective excitation would lead to the population of either the photo-reactive 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 emis-sive 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 timescale 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. In order to truly achieve non-destruc-tive readout, a non-reactive 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,[28] this type of behavior is extremely difficult to predict in ad-vance.

3. Spiropyran Units Incorporated into Bridging Ligands

Spiropyrans belong to a promising class of photo-chromic materials whose performance is based on the reversible heterolytic cleavage of a C–O bond in the spiro form of the spiropyran switching unit, to generate a highly colored merocyanine form that thermally reverts spontaneously to the closed spiro form.[8–10] As pioneers who have developed in the last few years the spirooxazine and spiropyran photochromic systems, Frank,[29] Gust,[30] Ray-mo,[31] Hurst,[32] and Benniston[33] can be men-tioned among others: Recently, a lot of attention has been focused on the potential application of

these compounds in the development of optical filters and optical recording.[34,35]

Synthesis of the ligand 4bpy-Sp-NO$_2$ (**3**) (see Fig. 5) with one bipyridine moiety attached to the indole part of the spiropyran skeleton, has been described in our previous work.[36] This ligand was used for the preparation of mononuclear metal com-plexes. The mononuclear ruthenium(II) complex [Ru(bpy)$_2$-(4bpy-Sp-NO$_2$)]$^{2+}$ (**4**) and mononuclear osmium(II) complex [Os(bpy)$_2$(4bpy-Sp-NO$_2$)]$^{2+}$ (**5**) have been synthesised by complexation reaction of ligand **3** with the metal precursors [Ru(bpy)$_2$Cl$_2$]·2H$_2$O and [Os(bpy)$_2$Cl$_2$] in ethylene glycol and methoxyethanol, respectively.

The solution of the closed form of ligand **3** in tetrahydrofu-ran (THF) is pale yellow. The absorption maximum at 328 nm is attributed to an actinic band of the switching unit and the one at 273 nm to a $\pi \rightarrow \pi^*$ transition in the bipyridine moiety.

Upon irradiation by UV light at –50 °C, the closed form was converted to the open form and the color of the solution turned blue. A new strong band at 590 nm is a characteristic absorp-tion maximum of the switching unit in the open form. The $\pi \rightarrow \pi^*$ transition in the bipyridine moiety is practically unaf-fected by the opening process (Fig. 5).

The solution of the closed form of complex **4** in THF shows absorption maxima at 291 nm corresponding to a spin-allowed ligand-centered $\pi \rightarrow \pi^*$ transition of the bipyridine ligand (^{1}IL$_{b-py}$), and at 459 nm assigned as a spin-allowed Ru^{II}-to-bipyri-dine charge-transfer transition from Ru^{II} to the bipyridine (^{1}MLCT). The band at 365 nm belongs to the absorption of the switching unit. Upon irradiation by UV light at –50 °C, the closed form converts to the open form. The new strong band at
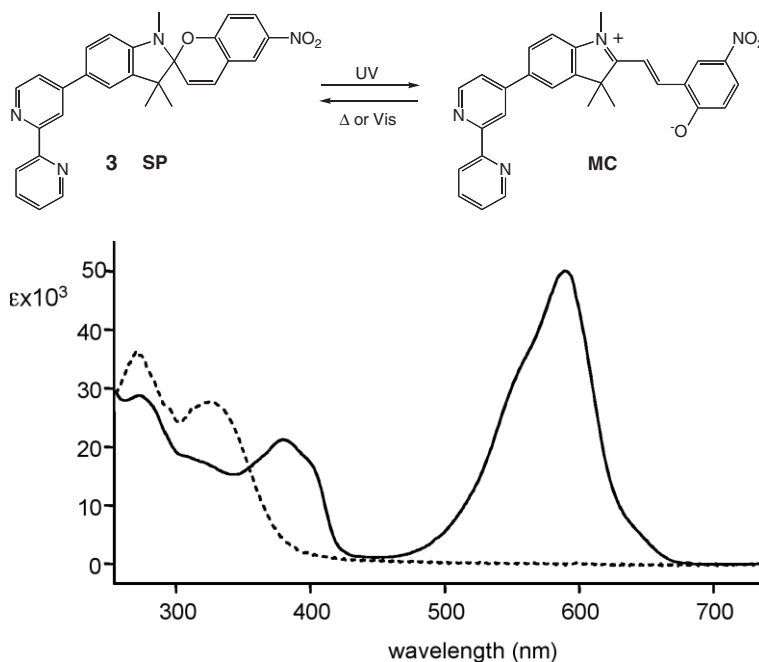
Figure 5. Absorption spectra of 4bpy-Sp-NO$_2$ (**3**; SP) in the closed form (– – –) and 4bpy-Sp-NO$_2$ (MC) converted to the open form (—) to an unknown degree in tetrahy-drofuran (THF) at –50 °C.

603 nm is a characteristic absorption maximum of the switching unit in the open form. The bands, $^1IL_{bpy}$ and ^1MLCT, are not affected by the opening process (Fig. 6). The absorption maximum of the open form shows a blue-shift at lower temperatures: for ligand **3** from 599 to 590 nm, and for complex **4**, from 607 to 603 nm, when the temperature is decreased from 20 to –50 °C.

From the difference in the ring-opening quantum yield between ligand **3** and the corresponding mononuclear metal complexes **4** and **5**, it appears that, upon excitation of the spiropyran unit, efficient energy transfer to the metal center competes with the ring-opening reaction (Table 3).

Decrease in the photochemical ring-opening quantum yield while going from Sp-NO$_2$ (**2**) to 4bpy-Sp-NO$_2$ (**3**) is not quite yet understood (Table 3, φ_{334} aerated). A few reports in the literature state that substitution at certain positions of the spiropyran switching unit influences the photochemical ring opening.[8]

The ring-opening quantum yield of the switching unit decreases going from Sp-NO$_2$ (**2**) to 4bpy-Sp-NO$_2$ (**3**) due to the presence of the bipyridine substituent. In the corresponding ruthenium (**4**) and osmium complexes (**5**), the presence of the transition-metal center decreases the feasibility of the ring-opening process drastically, and the ring-opening quantum yield decreases from 0.078 for ligand **3** to around 0.0065 for the corresponding ruthenium complex **4**.

Synthesis of the heterobinuclear metal complex of the spiropyran switching unit was based on a chemistry-on-the-complex protocol where classic organic and organometallic reactions are performed directly on the metal complex. The ruthenium metal precursor, as the debutant metal entity, binds directly to an aldehyde-functionalized chelating moiety, **6**, and gives the ruthenium mononuclear complex, **7**. A condensation reaction directly introduces a new chelating site on mononuclear metal

Table 3. Ring-opening quantum yields of investigated compounds in THF at –50 °C upon irradiation with 334 nm light with identical molar absorption coefficients for all compounds.

| Compound	ϕ_{334} Aerated
Sp-NO$_2$ (**2**)	0.24
4bpy-Sp-NO$_2$ (**3**)	0.078
Ru(bpy)$_2$-4bpy-Sp-NO$_2$ (**4**)	0.0065
Os(bpy)$_2$-4bpy-Sp-NO$_2$ (**5**)	0.0049

complex, **7**, and yields mononuclear complex, **8**, with a free chelating site. Osmium is then introduced into the newly created chelating site and gives the final heterobimetallic complex, **9** (Fig. 7).

Upon irradiation of the [Ru(bpy)$_2${μ-(4bpy-Sp-phenIm)}-Os(bpy)$_2$]$^{4+}$ complex (**9**) in THF solution at –50 °C by UV light, the intensity of absorption does not change with time. The result remains unchanged upon irradiation at 450 nm at the same temperature. The experiment shows that the closed form of the switching unit in the heterodinuclear complex is inactive and cannot be converted to the open form either by UV light or irradiation at 450 nm. The quenching of the excited state of the switching unit due to the presence of the second metal center cannot be explained in detail, given the present status of our investigation. This behavior is in agreement with the results observed for the mononuclear metal complexes **4** and **5**, for which the decreasing ring-opening quantum yield is due to the presence of the transition metal. In the closed form of the heterobinuclear metal complex, **9**, we observed a slow energy transfer (Ru → Os). The reason for this behavior is the fact that the two halves of the spiropyran unit are orthogonal and, therefore, almost no conductivity exists across the spiropyran.

In contrast to the formerly described dithienylethene switching system, the molecular interrupter on the basis of a spiropy-
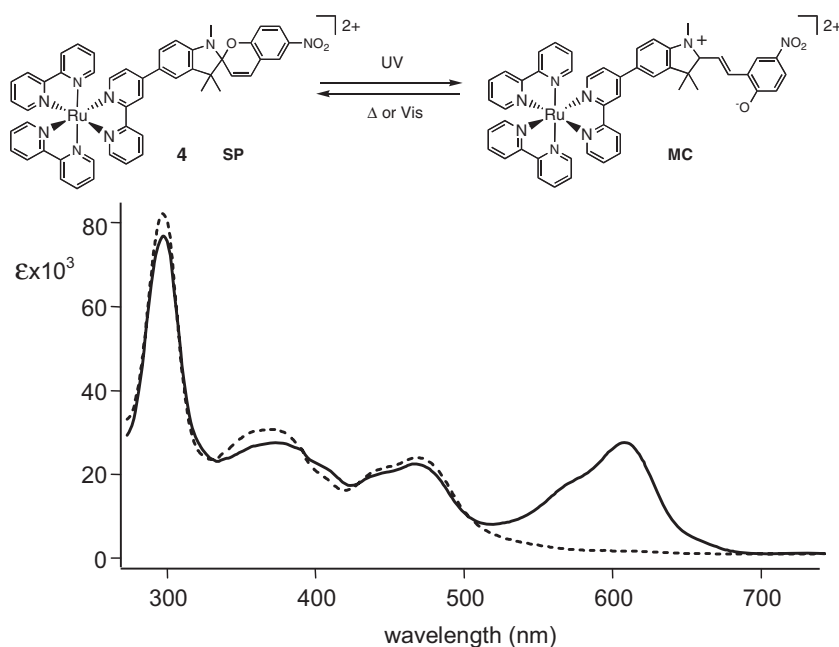
Figure 6. Absorption spectra of Ru(bpy)$_2$-4bpy-Sp-NO$_2$ (**4**; SP) in the closed form (– – –) and Ru(bpy)$_2$-4bpy-Sp-NO$_2$ (MC) converted to the open form (—) to an unknown degree in THF at –50 °C.
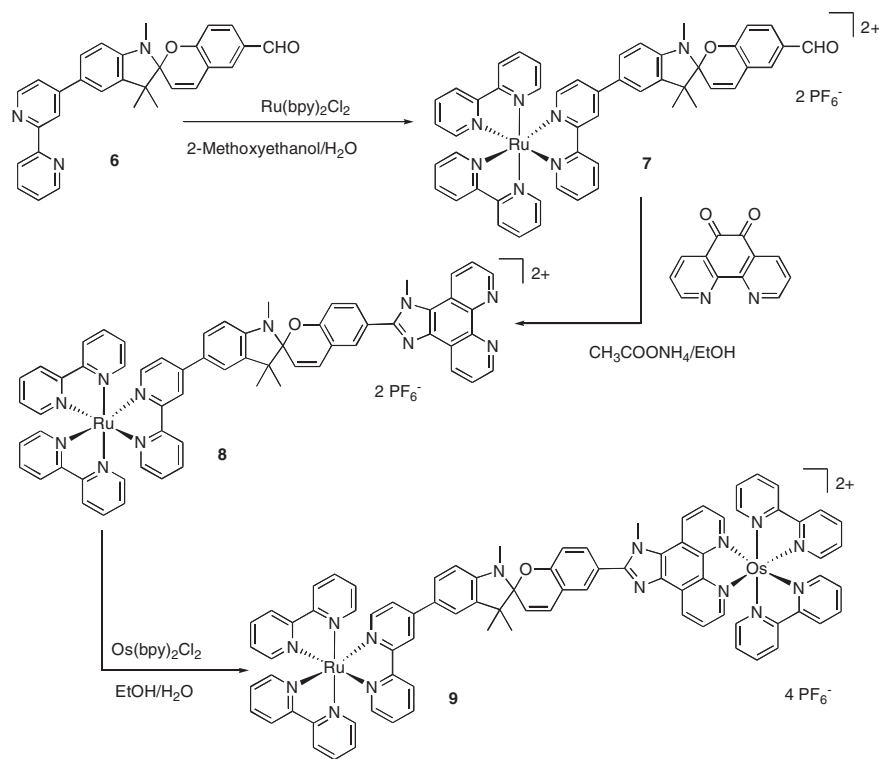
Figure 7. Synthesis of the heterobinuclear spiropyran metal complex [Ru(bpy)$_2$-4bpy-Sp-PhenIm-Os(bpy)$_2$](PF$_6$)$_4$ (**9**).

ran moiety is more promising. Both photoinduced processes, the photochemical opening and closing reaction (ON/OFF state of the interrupter) and the photophysical induced energy (information) transfer, are independent. In the closed form of spiropyran the photoreactivity is observable upon UV irradiation. The emission behavior can be proven upon visible excitation. The energy-transfer process is, in the closed form of the spiropyran switching unit, not very pronounced and corresponds to the closed form of our interrupter. In the more conjugated open form of the spiropyran, the energy of the ^{3}IL state lies between the energy levels of the ruthenium and osmium ^{3}MLCT states. Therefore, an enhanced energy transfer to, and emission intensity from, the osmium moiety must be observed. The open form of the spiropyran moiety corresponds, therefore, to the open form of our interrupter. A continuation of this work will be directed at the synthesis of a new heterobinuclear metal complex, in which the spiropyran unit is connected to the metal centers by short aliphatic chains. This kind of aliphatic connection is envisaged to interrupt the π-conjugation and avoid the quenching of the excited state of the switching unit by the metal centers. Positions of these aliphatic substituents on the switching unit must be chosen with respect to the electronic behavior of the spiropyran switch.

4. Fulgides as Photochromic Switches

Fulgides have been identified as viable photochromic substances for a broad range of applications, including optical memory and switching, due to the thermal stability of both forms of these molecules upon light excitation.[8,10,12] In recent years, a great deal of effort has been devoted to the manipulation of the structure of fulgide molecules in order to control their optical properties. The main contributions to the development of fulgides and related systems have been made by Yokoyama,[37] Heller,[38] Yam,[39] and Effenberger.[40] We describe here the synthesis and photophysical properties of a new fulgide, in its amide form, containing either a free chelating ligand or a chelated metal-complex unit. In particular, the thienyl fulgimide chromophoric unit is connected through a benzylene linker to 2,2′-bipyridine (bpy) or to the well-known Ru(bpy)$_3$ and Re(bpy)(CO)$_3$Cl moieties. The presence of a metal center should control the photochromic behavior of the fulgimide unit, depending on the position of ^{3}IL with respect to the lowest luminescent ^{3}MLCT state. In particular, the photoreaction can only be triggered either by optical population of the higher-lying ^{1}IL excited state of the central photochromic unit or by an efficient energy transfer from the lowest luminescent ^{3}MLCT state.

4.1. Synthesis

The thienyl fulgide (**Z**)-**10** (Scheme 2) was synthesized by Stobbe condensation[41] of 3-acetyl-2,5-dimethylthiophene and dimethylisopropylidenesuccinate, followed by hydrolysis and subsequent cyclization of the resulting diacids with acetylchloride. The 4-(4-aminomethylphenyl)-2,2′-bipyridine, **11**, derivative was prepared by following the procedure described in the literature.[42,43] Treatment of the thienyl fulgide (**Z**)-**10** with precursor **11** in refluxing dichloromethane gave the corresponding succinamic acids by nucleophilic addition of the pri-
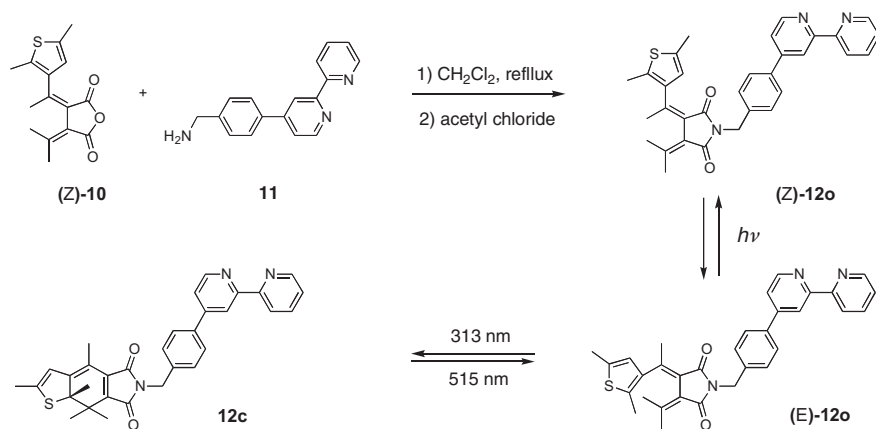
Scheme 2. Preparation protocol for **(E)-12o**.

mary amine to the carbonyl group. The fulgimide in the open form, (**Z**)-**12o**, was isolated in acetylchloride after 2 h in a good yield by intramolecular elimination of a water molecule. The resulting fulgimide was treated with [Re(CO)$_5$Cl] and [Ru(bpy)$_2$Cl$_2$]·2H$_2$O to give the corresponding rhenium(I) and ruthenium(II) complexes in toluene and ethylene glycol, respectively.

4.2. Results and Discussion

The open *Z*-form of the uncoordinated ligand (**Z**)-**12o** in acetonitrile is pale yellow. The electronic absorption spectrum of **12o** (Fig. 8) shows the typical $\pi \rightarrow \pi^*$ transitions of 2,2′-bipyridine (bpy) and the oligophenylene spacer below 300 nm. The shoulder at 335 nm corresponds to the $S_o \rightarrow S_1$ (^{1}IL) transition localized on the photochromic unit. Upon irradiation with UV light ($\lambda = 313$ nm), the pale-yellow solution of **12o** turns bright purple, with a new absorption band rising at 515 nm. The cyclization forces the system into a more planar conformation, thereby increasing the conjugation and lowering the energy of the $S_o \rightarrow S_1$ transition of the photochromic unit. However, the
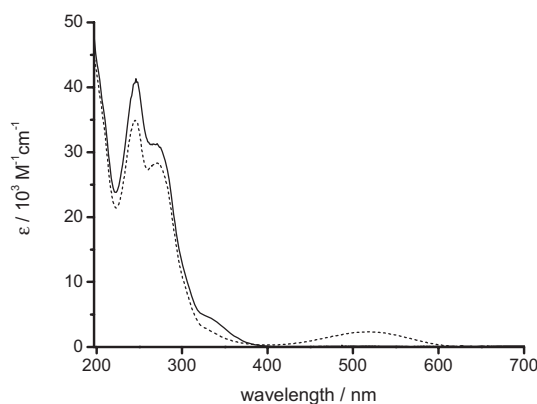
bpy transitions are not affected by cyclization. Furthermore, the closed form corresponds to a photostationary state of **12o** consisting of a mixture of both open and closed forms. The ratio between these two isomers after UV irradiation was determined from the corresponding ^{1}H NMR spectrum.

Complex Re(**12o**) was obtained as a mixture of *E*- and *Z*-isomers in a 1:1 ratio, as determined from the corresponding ^{1}H NMR spectrum. Re(**12o**) in acetonitrile is yellow in the UV-vis spectrum (Fig. 9), the intense absorption bands in the UV region should be associated with the LC and CT transitions centered on the bpy moiety of the ligand **12o**. These bands are likely to obscure the much weaker Re^I-to-bpy charge-transfer absorption (^{1}MLCT) and the $S_o \rightarrow S_1$ transition of the photochromic unit, which appears as an additional tail towards the visible region. The latter absorption band is shifted to lower energy compared to the free ligand **12o** due to the presence of a withdrawing metal center that lowers the energy of the LUMO of the photochromic unit. Upon irradiation with UV light ($\lambda = 300$ nm), the pale-yellow solution of Re(**12o**) turns bright
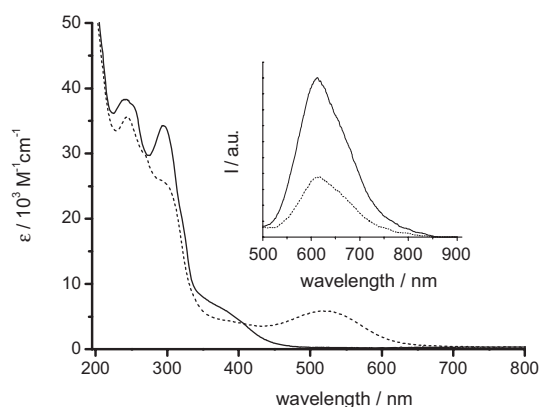

Figure 8. Absorption spectra of compound **12o** (—) and a solution of **12o/12c** in the photostationary state (– – –) produced with 313 nm irradiation. The latter spectrum corresponds to a 75 % photoconversion of **12o** to **12c**, as determined from the corresponding ^{1}H NMR spectrum. Conditions: MeCN, 293 K.

Figure 9. Absorption spectra of compound **Re(CO)$_3$Cl(12o)** (—) and a solution of **Re(CO)$_3$Cl(12o)/Re(CO)$_3$Cl(12c)** in the photostationary state (···) produced with 300 nm irradiation. The latter spectrum corresponds to a 33 % photoconversion of **Re(CO)$_3$Cl(12o)** to **Re(CO)$_3$Cl(12c)**, as determined from the corresponding ^{1}H NMR spectrum. Conditions: MeCN, 293 K. Inset: the corresponding decrease in emission of **Re(CO)$_3$Cl(12o)** upon conversion from 33 % open form (—) to the photostationary state (– – –). Conditions: $\lambda_{exc} = 400$ nm, 293 K.

purple, with a new absorption band appearing at 520 nm (Fig. 9). By analogy to **12o**, the band at 520 nm can be assigned to the ^{1}IL transition localized on the cyclized fulgimide moiety of the ligand. Also, in this case the cyclization does not affect the ^{1}IL$_{bpy}$ and ^{1}MLCT transition bands. The photocyclization is not quantitative, pointing to an equilibrium between the two photoactive forms. The ^{1}H NMR spectrum reveals not only the presence of both open and closed forms (in ratio 1:1), but also the fact that the open form is a mixture of *E*- and *Z*-isomers (in the ratio 1:1). Therefore, the photostationary state contains merely 33 % of Re(**12c**), in agreement with the emission found for the complex upon photocyclization (Figure 9, inset).

Complex Ru(**12o**) was obtained as a mixture of *E*- and *Z*-isomers in the ratio 1:1, as determined from the corresponding ^{1}H NMR spectrum. The complex Ru(**12o**) in acetonitrile is yellow and the UV-vis spectra in this solvent is shown in Figure 10. By comparison with [Ru(bpy)$_3$]$^{2+}$, the absorption bands in the UV-vis spectrum of Ru(**12o**) (Fig. 10) at 288 and 454 nm can be assigned to a ligand-centered transition localized on the bpy ligands, and to Ru^{II}-to-bpy charge-transfer (^{1}MLCT) transition, respectively.[26]

The intense band at 288 nm is likely to obscure the much weaker $S_o \rightarrow S_1$ (^{1}IL) transition localized on the photochromic
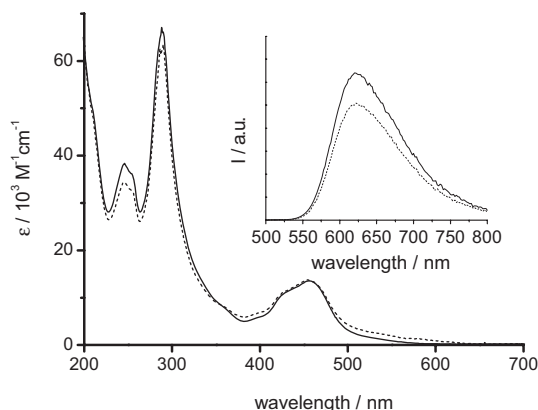
Figure 10. Absorption spectra of compound **Ru(12o)** (—) and a solution of **Ru(12o)**/**Ru(12c)** in the photostationary state (– – –) produced with 300 nm irradiation. Conditions: MeCN, 293 K. Inset: the corresponding decrease in emission of **Ru(12o)** upon conversion from the open (—) to the photostationary state (– – –). Conditions: λ_{exc}= 450 nm, 293 K.

unit, which appears as an additional tail towards the visible region. Upon irradiation with 300 nm light at room temperature, the photochromic response of Ru(**12o**) is weak. A new absorption band appeared at 480 nm as an additional tail (Fig. 10) but the solution color did not change. The small decrease in the intensity of the emission of Ru(**12o**) upon irradiation suggests a photoconversion to the closed form Ru(**12c**), which was too low to be detected by ^{1}H NMR spectroscopy.

4.3. Conclusion

A new photochromic ligand has been synthesized by attaching a fulgide chromophore to 4-(*p*-tolylene)-2,2′-bipyridine. The new ligand and the corresponding ruthenium and rhenium complexes show photochromic behavior of the fulgide unit. Further investigations are under way in order to localize the right position of ^{3}IL transition with respect to the lowest luminescent ^{3}MLCT state.

5. A New Class of Molecular-Switching Systems Based on Dithienyl-phenanthroline Ligands

Most of the dithienylethene-based switching molecules described in the literature need UV light to perform the photocyclization reaction.[12] The use of visible light to perform the cyclization process, similar to that described in Section 2, could avoid photodecomposition processes. For that reason, the Ru(bpy)$_3^{2+}$ moiety could be used as a sensitizer. After irradiation into the ^{1}MLCT band of the ruthenium complex, an energy-transfer process to the switching unit takes place, and induces the photocyclization process.

In addition, as pointed out in Section 2, the drawback of the influence on the state of the switching unit (ON/OFF) by an energy-transfer process from the excited ruthenium complex to the switching part of the bridging ligand can be used to our advantage. As shown in Figure 11, the T-shaped arrangement is ideally suited for an energy/electron transfer along the long axis, as well as a perpendicularly oriented independent photochemical switching process. The photochromic unit can be influenced through an attached metal complex, by an energy-transfer process. The connection between the metal complex and the switch-
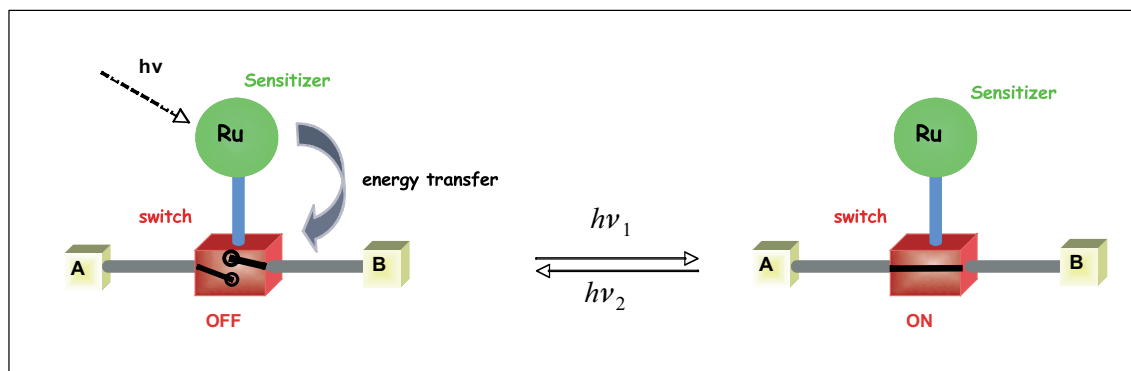
Figure 11. The T-shaped arrangement of a ruthenium sensitizer influencing the state of the switching unit (ON/OFF).

ing unit is achieved by the newly designed bridging ligands depicted in Figure 12. At the same time that we developed our new ligand system incorporated in complex **13**, Yam et al. published the same ligand coordinated in a rhenium complex.[44]
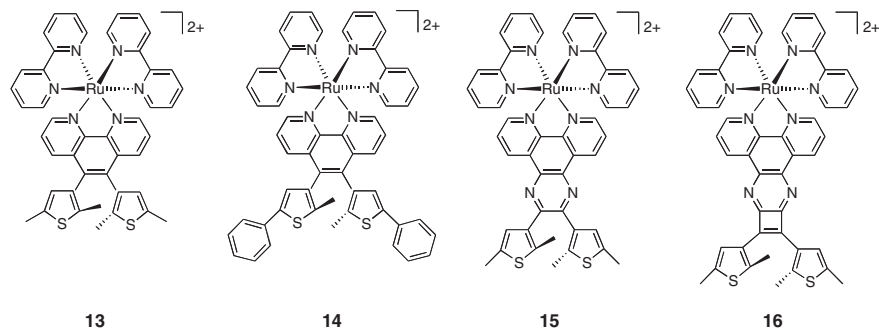
5.1. Synthesis

To get complex **13**, 5,6-dibromo-1,10-phenanthroline was prepared using the protocol described by Mlochowyski.[45] The thienyl moieties were built in by a Suzuki coupling between 3-bromo-2,5-dimethylthiophene and 5,6-dibromo-1,10-phenanthroline. The final complexation producing **13** was performed by the reaction of the new ligand with the precursor compound, $[Ru(bpy)_2Cl_2] \cdot 2H_2O$. The target complex **14** was synthesized in several steps, too. Initial bromination of 2-methylthiophene was followed by Suzuki coupling with iodobenzene. The obtained 2-methyl-3-bromo-5-phenylthiophene was then coupled with 5,6-dibromo-1,10-phenanthroline, yielding the desired ligand system. The final complexation was again performed with $[Ru(bpy)_2Cl_2] \cdot 2H_2O$ in methoxyethanol

Complex **15** was formed by a Friedel–Crafts acylation reaction between 2,5-dimethyl-thiophene and oxalyl chloride to get dithienylethanedione. In parallel, 1,10-phenanthroline was converted to phenanthroline-5,6-dione followed by 5,6-dihydroxylaminophenanthroline and finally into 5,6-diaminophenanthroline.[46] Coupling of the two precursor compounds gave the new ligand that was complexed again with $[Ru(bpy)_2Cl_2] \cdot 2H_2O$. For complex **16**, squaric acid dichloride was prepared by a reaction between squaric acid and oxalyl chloride. To complete the preparation of the metal complex, the same strategy was employed as that used for complex **15**.

### 5.2. Analytical and Photophysical Studies

For complexes **13** and **14**, the protons at the 4- and 7-positions on the phenanthroline unit hinder the free rotation of the thiophene moiety[44] and two sets of methyl signals are observed with NMR spectroscopy. That observation corresponds to the co-existence of two molecules with parallel and antiparallel conformations of the central methyl group; this situation is well known in dithienylethene systems.[47] In this case as well, only the antiparallel conformer can undergo the cyclization reaction, in agreement with the Woodward–Hofmann rule.[48]

After separation of the thienylethene moieties from the phenanthroline part by an incorporated pyrazine unit (complex **15**), the ^{1}H NMR spectrum showed only one methyl signal. This result can be interpreted by assuming that the interconversion between syn- and anti-conformers is fast and unresolved on the ^{1}H NMR time scale. The same applies to the complex **16**.

By irradiation at 450 nm into the ^{1}MLCT band of complexes **13** and **14**, a cyclization reaction takes place (Fig. 13). Thermal back reaction occurs spontaneously at room temperature, which can be simulated by a first-order reaction. The lifetime of the photocyclized ligand in complex **13** is 4.8 min at 25 °C, increasing to 10.3 min for the ligand in complex **14**. The thermal instability is attributed to the gain of aromatic energy[49] by
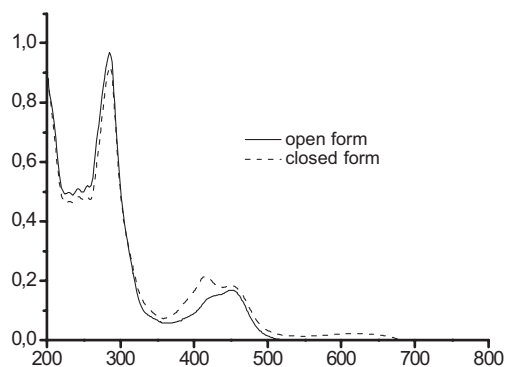
Figure 13. Spectral changes of complex **14** (1.0×10^{-5} M) in acetonitrile upon MLCT excitation at 450 nm.

the reopening process back to the original phenanthroline moiety. Complex **14** exhibits a strong emission band at 608 nm after excitation at 450 nm, which is in stark contrast to other binuclear metal complexes connected to a switching unit.[23,24] The photofatigue resistance was also tested. The photochromic properties of the free ligand disappeared after five cycles, in contrast to the corresponding metal complex that was stable for many cycles. To induce the closing process, light at 254 nm was used. The complex **15** seems to be photoinert.[50] Oxygen reacts with complex **16** during the irradiation process quite rapidly. The mass spectrum of the photo-oxidation product shows an increase in the molecular weight by 32 $g \, mol^{-1}$, the molecular mass of O_2. The structure of the new compound is hitherto unknown.

13 **14** **15** **16**

Figure 12. The synthesized metal complexes with the new dithienyl-phenanthroline ligands.

5.3. Discussion

By combination of a dithienylethene unit with a phenanthroline moiety, a new type of photochromic switch, containing a ruthenium complex as sensitizer, was prepared. Selective irradiation into the ^{1}MLCT band causes photocyclization triggered by energy transfer from the metal center to the photochromic unit. The presence of the metal center increases the photofatigue resistance. The closed forms of compounds **13** and **14** are thermally unstable. The other complexes appear to be photoinert (**15**) or oxygen-sensitive (**16**).

6. 4,5-Diazafluorene-Based Overcrowded Alkene: A New Ligand for Transition-Metal Complexes

Overcrowded bis(tricyclic) aromatic enes (Fig. 14) have been extensively studied as molecular switches since their "helicity" can be inverted by means of circularly polarized light and such a change can be easily monitored by circular dichroism techniques.[51] Besides, it has been proved that a light-induced change in helicity of these molecules can further induce changes in the handedness and pitch of liquid-crystalline materials when used as dopant agents.[52] This kind of system can be used either in a pure diastereomeric form (through a photodestruction process) or as a racemic MP mixture (through a photoenrichment process) as was shown by Feringa and van Delden.[53] To improve the photomodulation of these systems, several synthetic modifications have been introduced. These modifications are mainly oriented towards the increase of encumbrance around the central double bond in order to achieve extremely high overcrowding in the fjord region of these systems.[54]

In this article we wish to present the synthesis of the first overcrowded polycyclic aromatic ene based on a 4,5-diazafluorene moiety which fulfills the steric requirements to create overcrowding in the fjord region and, therefore, helical conformation. Moreover, the introduction of the 4,5-diazafluorene moiety can open the path to photochromic studies of novel compounds based on the use of metallic centers as built-in sensitizers for the photomodulation of the system helicity (see Fig. 14).

By irradiation into the ^{1}MLCT band of the sensitizer, an energy transfer can occur from the metal center to the double bond of the switching unit. Due to the energy transfer to the double bond, a free rotation around the bond can be induced and, therefore, a change in the helicity (M or P) of the system could be observed. Such a photosensitized switching process can be performed with light of wavelength 450 nm and not necessarily, as often described in the literature, of wavelengths in the near-UV region. Therefore, an improvement of photoresistance can be achieved.

Optimization of our novel chiroptical system can be performed in several ways. A change in the X-position character from oxygen to sulfur or carbon atom not only strongly affects the electronic situation, but also causes the sterical stress in the fjord region.[54] The same effect can be observed on increasing the size of the substituent R_1. A change of the metal center, M, opens up another possibility to modify the sensitizer part (M = Os, Ru, Fe, Ir, Rh, or Re). A variation of the substituents, R_2 (donor or acceptor groups), on the two bipyridine-type ligands will ensure that a directed energy transfer from the metal center to the diazafluorene ligand or to the attached double bond occurs. Another, but nevertheless interesting modification, can be studied. In the case of an octahedral metal complex like $[Ru(bpy)_3]^{2+}$, our compounds exist in four different isomeric forms (pairs of diastereomeres), namely Δ(M/P) and Λ(M/P), respectively. We have developed, in our laboratories, different techniques to build up only one of the two chiral metal complexes in a pure form.[55] Adapted to our switching system, the P and the M helical arrangement are no longer mirror images. They change from an enantiomeric mixture to diastereomeric one. Only preliminary results about the photophysical properties of Ru^{II}, Os^{II}, and Re^I complexes with the above-mentioned ligand are presented here.

The syntheses of ligand **17** (see Fig. 14) have been achieved following published procedures.[56] It is well known that the Barton reaction affords an episulfide-type compound, which leads to the desired alkene after sulfur removal, this final step being the most difficult. In our case, heating the starting materials under reflux conditions in toluene for 72 h leads, straightforwardly, to the alkene-type compound without any trace of the episulfide intermediate. The structure of ligand **17** was confirmed by X-ray analysis.

$[Ru(bpy)_2(\mathbf{17})](PF_6)_2$, $[Os(bpy)_2(\mathbf{17})](PF_6)_2$, and $Re(\mathbf{17})(CO)_3Cl$ were prepared by refluxing ligand **17** with the appropriate metal source, viz. $[Ru(bpy)_2Cl_2]\cdot2H_2O$, $[Os(bpy)_2Cl_2]$, and $[Re(CO)_5Cl]$, respectively, for several hours, using methoxyethanol for the ruthenium and osmium complexes and toluene for the rhenium complex formation.[57] The ruthenium and osmium complexes were purified by recrystallization of their hexafluorophosphate salts from acetone/hexane and subsequently from methanol. For the rhenium complex, the purification was achieved by crystallization from toluene/acetone.
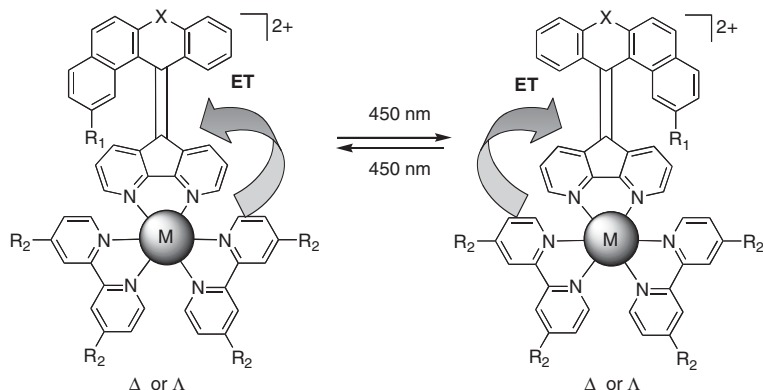
Figure 14. The new chiroptical switching metal complex. The functions X, R_1, R_2, M, and Δ/Λ can be individually modified. We have prepared prototype metal complexes $[Ru(bpy)_2(\mathbf{17})](PF_6)_2$ in a racemic form with X= O, R_1= O–CH$_3$, R_2= H, and M= Ru, Os and Re with the new switching ligand **17**.

UV-vis absorption spectra of ligand **17** and its metal complexes with Ru[II], Os[II], and Re[I] are shown in Figure 15. The absorption spectrum of ligand **17** shows a broad peak at 360 nm corresponding to a ligand-centered (^{1}LC) transition mainly localized in the methoxy-benzo-xanthene part of the molecule. At about 300 nm, a transition associated with the diazafluorene part can be observed. In the UV region of the spectra of the ruthenium and osmium complexes an intense absorption band (280 nm) can be attributed to a ^{1}LC transition within the bpy ligand. Moderately intense ^{1}MLCT bands are observed for both complexes in the 400–500 nm region. In the Os[II] complex, spin–orbit coupling gives rise to a broad and weak absorption at wavelengths higher than 600 nm, corresponding to the forbidden, formally ^{3}MLCT transition. The rhenium complex Re(**17**)(CO)$_3$Cl shows an intense absorption at 370 nm attributed to a ^{1}MLCT transition. This study shows that the possibility of selective irradiation into the metal center exists, which may result in helicity tuning through a triplet–triplet sensitization mechanism.

We have achieved the synthesis of a new molecular system capable of acting as a chiroptical switch. It consists of a switching part and a covalently bound photosensitizer. The switching part was built up by a methoxy-substituted benzo-xanthene unit connected via a double bond to a chelating ligand (4,5-diazafluorene). The new ligand system was attached to different metal complex units (M= Ru, Os, and Re) that can act as photosensitizers. Different activities concerning the chiral resolution and photophysical studies of ligand **17**, and its metal complexes are in progress.

7. Conclusions and Outlook

In the present article, we have shown that the connection of binuclear metal complexes, able to perform energy-transfer processes, with photochromic units leads to interesting supramolecular constructions. It is evident that the prediction of a synthetic pathway for the preparation of a system that works well is not yet possible. The first-described bisthienylethene system works well in the open form, in which an efficient energy-transfer process from the excited donor unit (Ru complex) to the acceptor unit (Os complex) can be observed. On the other hand, in the closed form, the energy level of the photochromic unit drops drastically and it acts as a trap for both the excited metal complexes. Such a system cannot be used as a simple interrupter for energy or information transfer. It influences both sides of the switching unit in the closed form. A second drawback of the system is the fact that the excitation energy (450 nm) needed to close the switching unit is the same as that used to induce the energy transfer in the first place. Therefore, it is essential to differentiate properly the photochemical process of changing the state of the switching unit (ON/OFF) from that of the photoinduced energy/information transfer. This can be achieved by the incorporation of another, energetically low-lying acceptor unit. The energy level of the closed switching unit lies, under such conditions, between the levels of the donor and acceptor units.

The second system containing a spiropyran switching unit is much more promising than that using thienylethene. The state of the switching unit is not influenced by irradiation into the ^{1}MLCT band of the donor unit, which implies that the energy level of the spiropyran unit lies higher than the corresponding donor unit (excited ruthenium complex). In contrast, the heteronuclear metal complex (Ru–spiropyran–Os) with the spiropyran unit in the closed form exhibits remarkable energy-transfer behavior. Unfortunately, the binuclear metal complex in the closed form shows no photochromic activity and cannot be transformed to its open form. An interruption of the π-conjugation between the photochromic unit and the acceptor part by an aliphatic spacer (a –CH$_2$– group) can help recover the photochromic properties of the spiropyran switch.

The final part of the paper describes other switching systems that are in their early stages of investigation. Predictions concerning their respective feasibilities to work as interrupters for energy-transfer processes are not possible for the moment.
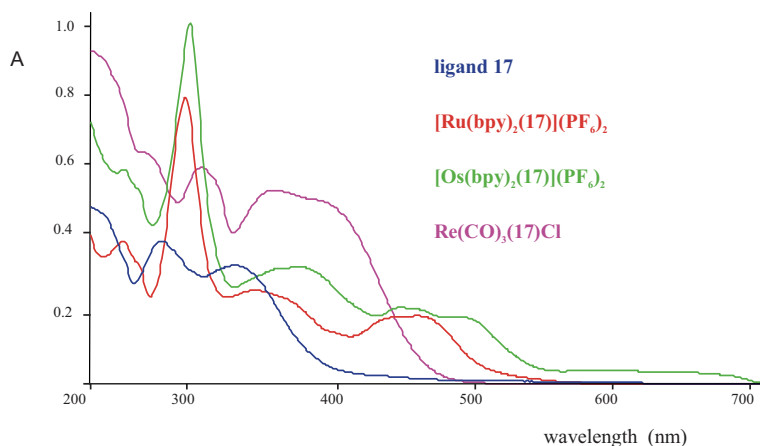
8. Experimental

Details pertaining to the experimental procedures can be found in the Supporting Information.

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Figure 15. UV-vis absorption of ligand **17** and its Ru[II], Os[II], and Re[I] complexes.

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