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# Metal Complexes Featuring Photochromic Ligands

**Véronique Guerchais and Hubert Le Bozec**

**Abstract** Organic photochromic molecules are important for the design of photoresponsive functional materials such as switches and memories. Over the past 10 years, research efforts have been directed towards the incorporation of photoresponsive molecules into metal systems, in order either to modulate the photochromic properties or to photoregulate the redox, optical, and magnetic properties of the organometallic moieties. This chapter focuses on work reported within the last few years in the area of organometallic and coordination complexes containing photochromic ligands. The first part is related to photochromic azo-containing metal complexes. The second part deals with metal complexes incorporating 1,2-dithienylethene (DTE) derivatives. The last three parts are devoted to metal complexes featuring other photochromes such as spiropyran, spirooxazine, benzopyran, and dimethyldihydropyrene derivatives.

**Keywords** Photochromes, Transition metal complexes

**Contents**

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## 1 Introduction

Photochromism, which refers to the reversible color change of a compound with light irradiation, is attracting much attention for the construction of molecular devices. During the past decade there has been a growing interest in the synthesis, properties, and applications of organic photochromic materials [1–5].

Photochromic materials have been the focus of intensive investigations for several decades from both the fundamental and practical points of view for their potential applications to optically rewritable data storage, optical switching, and chemical sensing.... Useful properties that may be photoregulated include luminescence, refractive index, electronic conductance, magnetism, optical rotation, nonlinear optics, redox chemistry.... Photochromic transformations are generally based on unimolecular processes involving the interconversion of two isomers, such as *cis*/*trans* isomerization, ring opening/closing, or intramolecular proton transfer. So far, various types of organic photochromic compounds such as azobenzenes, diarylethenes, fulgides, spirobenzopyrans, and dimethyldihydropyrenes have been developed.

Metal complexes featuring photoresponsive ligands are an interesting alternative to pure organic photochromes. Combining a photochromic moiety with an organometallic or coordination compound will provide new properties deriving from the combination of redox, optical and magnetic properties of the metal complexes with the photochromic reaction.

The aim of the present chapter is to review some recent developments, made in the last 10 years in organometallic and coordination compounds that contain ligands functionalized by organic photochromic units such as azobenzene, dithienylethene (DTE), spiropyran (SP) and spirooxaxine (SO), benzopyran, and dimethyldihydropyrene, respectively. Other known types of photochromic metal complexes based on linkage isomerization of coordinated ligands such as dimethyl sulfoxide and pyridine will not be discussed in this chapter.

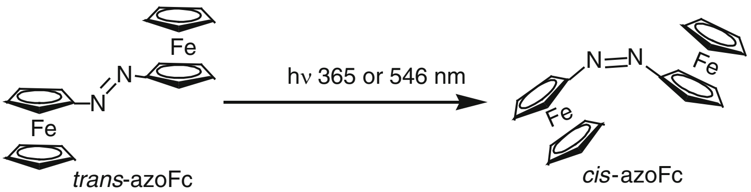
# 2 Photochromic Azo-Containing Metal Complexes

## *2.1 Introduction*

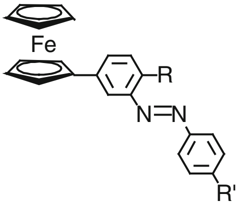
Azobenzene derivatives constitute a family of dyes which are well known for their photochromic properties. The photochemistry of azobenzene derivatives has been extensively studied in solution as well in polymer matrices [6, 7]. These compounds have been widely investigated as promising systems for various applications such as photo-switching devices, optical data storage, holography, and nonlinear optics [8, 9]. Basically, they are characterized by a *trans* to *cis* isomerization of the N=N double bond upon UV light irradiation, and the reverse isomerization can take place by visible light irradiation or by heating, the *trans* form being generally more stable than the *cis* form. Azo-containing transition metal complexes can provide interesting versatile molecular materials because of the combination of the photoisomerization behavior of the azo group with the optical, redox, and magnetic properties of the metal complexes [10–12].

## *2.2 Azoferrocene and Ferrocene–Azobenzene Derivatives*

The synthesis of azoferrocene (azoFc), one of the simplest organometallic analogs of azobenzene, was reported in 1961 by Nesmeyanov [13, 14]. Nishihara et al. examined much later the isomerization behavior of this interesting bimetallic complex [15]. The UV–visible spectrum of *trans*-azoFc in acetonitrile shows two strong absorption bands at 318 and 530 nm assigned to π−π* transition of the azo group and MLCT ($d_{\mathrm{Fe}} \rightarrow \pi^*_{\mathrm{CpN=NCp}}$) transition, respectively. Upon UV irradiation, the π−π* band decreased and a new band appeared at 368 nm, showing isosbestic points. This new band was assigned to the *n*–π* transition of the *cis* isomer. Remarkably, the photoisomerization proceeded upon irradiation in the MLCT band ($\lambda = 546$ nm). This is a rare example of photoisomerization using a much longer wavelength than that of the π−π* band. However, the back *cis*→*trans* reaction could not be observed by either heating or irradiation with visible light.



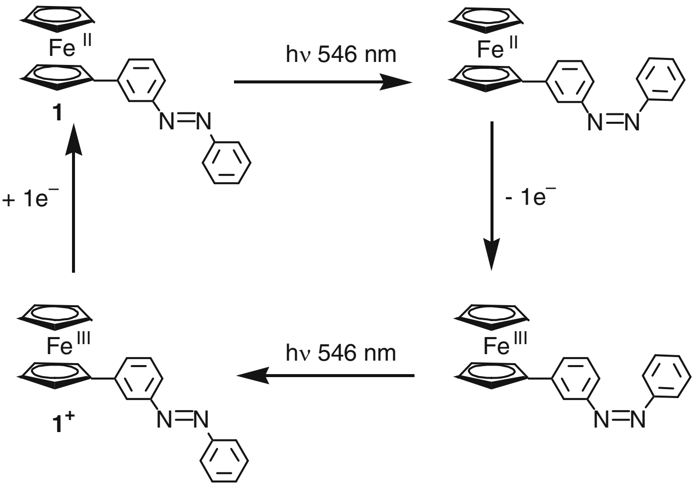
In order to study the photoisomerization using MLCT, Nishihara prepared a series of azobenzene derivatives substituted by a ferrocenyl group at the *meta* position of one phenyl ring [16, 17]. For example, 3-ferrocenylazobenzene **1** showed an interesting redox-conjugated reversible isomerization cycle using a single light.



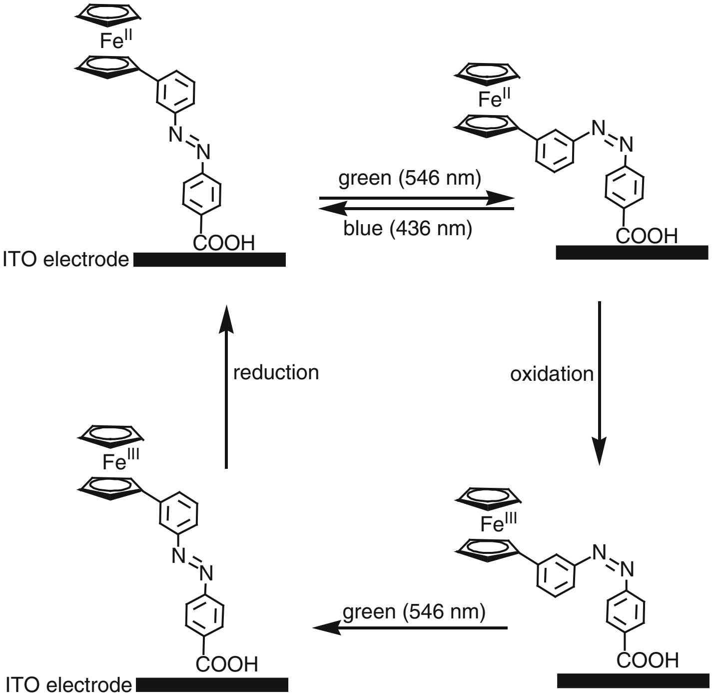
**1** R = H, R' = H
**2** R = Cl, R' = H
**3** R = H, R' = $CO_2H$

Compound **1** displays in acetonitrile a strong azo π–π* band at 318 nm and a weaker MLCT band at 444 nm. The *trans* to *cis* photoisomerization proceeded upon either UV light (320 nm) or green light (546 nm) irradiation, at wavelengths corresponding to the maximum of the π–π* band and to the edge of MLCT band, respectively. The *cis* molar ratio in the photostationary state (PSS) upon UV light and green light irradiation were estimated to be 61% and 35%, respectively. Upon chemical or electrochemical one electron oxidation to the resulting $\mathbf{1}^+$, the MLCT band disappeared, and a new weak ligand-to-metal charge transfer (LMCT) band appeared at 730 nm. This ferrocenium complex showed only *trans* to *cis* photoisomerization with UV light irradiation, whereas the reverse *cis* to *trans* reverse isomerization proceeded by excitation of the *n*–π* band with green light. The different responses to green light between the Fe(II) and Fe(III) states were used to achieve a reversible photoisomerization with a single visible light source by combination with the reversible redox $Fe^{III}/Fe^{II}$ reaction (Scheme 1).

In order to improve the efficiency of photoisomerization with green light, different ferrocenyl azobenzene derivatives were also prepared either by adding substituents on the benzene ring or by changing the position of the ferrocenyl moiety (*ortho*, *meta* or *para*) on the benzene ring [17]. Upon introducing an electron-withdrawing substituent, such as a chloro group in *para* position to the ferrocenyl group (**2**), the *cis* molar ratio at 546 nm light irradiation was increased from 35% (R = H) to 47% (R = Cl). More recently, Nishihara et al. succeeded



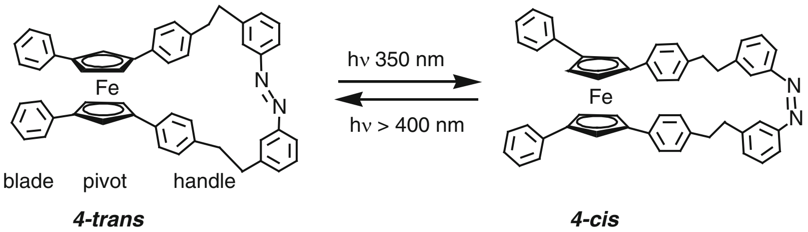
**Scheme 1** Reversible photoisomerization of **1** with single light and redox reaction



**Scheme 2** Schematic representation of the couple redox-single light isomerization of **3**/ITO

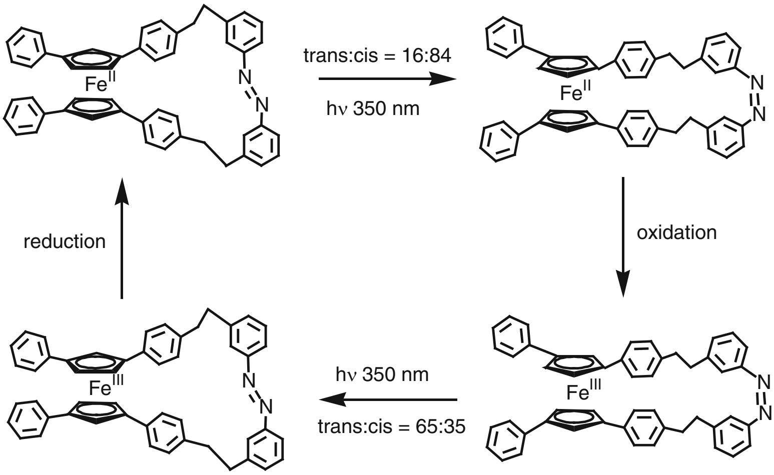
in constructing a single light controllable azobenzene monolayer system by electrochemical oxidation [18]. They synthesized the 3-ferrocenyl-4′-carboxylazobenzene compound **3** containing a carboxylic acid end group, and then prepared a monolayer of **3** on a transparent indium tin oxide (ITO) electrode. The photoswitching behavior of this system was nicely evidenced and, like the parent 3-ferrocenylazobenzene **1** in solution, the single-light photoisomerization cycle of **3**/ITO was achieved by the combination of green light and electrochemical reactions (Scheme 2).

Aida and coworkers have developed novel molecular machines containing a photochromic azobenzene unit and a ferrocenyl moiety. They have designed an interesting "light-driven chiral molecular scissors" **4**, consisting of a tetrasubstituted ferrocene as the pivot part which is able to generate an angular motion, two phenyl groups as the blade moieties, and two phenylene groups as the handle parts strapped by an photoisomerizable azobenzene unit through ethylene linkage [19].

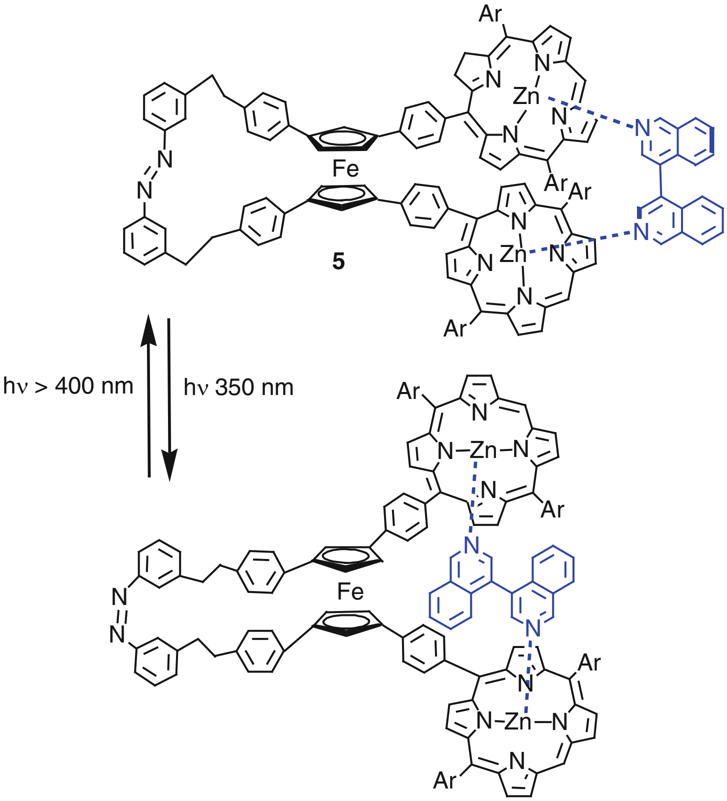


UV light irradiation at 350 nm of a THF solution of the *trans* isomer resulted in a typical *trans* to *cis* isomerization of the azobenzene moiety (89% conversion), whereas irradiation with a visible light gave back to a *trans*/*cis* isomer ratio of 46:54. Absorption, circular dichroism (CD) and $^1$H NMR spectra of an enantiomer of **4** agreed well with the prediction by DFT calculations that the blade parts are opened when the azobenzene unit adopts a *cis* configuration while they are closed in the case of the *trans* isomer. Interestingly, the oxidation state of the ferrocene pivot was found to affect the PSSs of **4** and thus to allow a reversible open–closed motion by use of redox and UV light [20] (Scheme 3).

This concept was then nicely applied by Aida to develop light-powered molecular pliers **5** that can bind and deform guest molecules [21, 22]. They introduced an appropriate guest-binding site – a zinc porphyrin complex – at each cyclopentadienyl ring of the ferrocene. The zinc porphyrin units were found to bind bidentate guests such as 4,4′-biisoquinoline, forming a stable host–guest complex. Upon exposition to UV and visible light, *trans*/*cis* photoisomerization of azobenzene induced mechanical twisting of the guest molecule, which was detected by changes in the CD spectra (Scheme 4).



**Scheme 3** Open/closed motion of **4** induced by redox and UV light

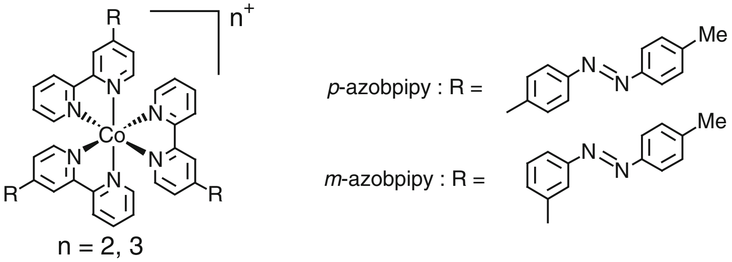


**Scheme 4** Photoisomerization of guest–host molecular pliers upon UV and visible irradiation

## 2.3 *Metal Complexes with Azobenzene-Conjugated Bipyridine Ligands*

### 2.3.1 Tris(bipyridine) Metal Complexes

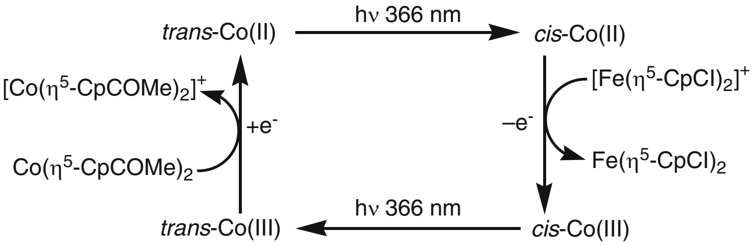
The first example of reversible *trans–cis* isomerization of the azo group achieved through a combination of photoirradiation and a redox cycle between Co(II) and Co (III) was reported by Nishihara [23]. The tris(*p*-azobipy)Co(II) complex used in this system was prepared from 4-tolylazophenyl-2,2′-bipyridine (*p*-azobipy) and $Co^{II}(NO_3)_2$ and characterized by a reversible Co(III)/Co(II) wave at low potential (−0.15 V vs $Fc^+/Fc$ in dichloromethane). The corresponding Co(III) complex was readily obtained upon oxidation of the Co(II) complex with silver triflate. Both Co (II) and Co(III) complexes displayed in UV–visible spectroscopy a strong $\pi-\pi^*$ band due to the azo group at $\lambda = 360$ nm. Upon irradiation, the two complexes showed different behavior: UV light irradiation at 366 nm of a $CH_2Cl_2$ solution of $[Co^{II}(p\text{-azobipy})_3](BF_4)_2$ resulted in a decrease of the $\pi-\pi^*$ band and an increase of the *n*–π* band at ca. 450 nm, in agreement with a typical *trans*-to-*cis* isomerization of the azobenzene moiety (40% conversion at the PSS), whereas irradiation with 438 nm light gave back the *trans* isomer. By contrast, almost no decrease in absorbance of $\pi-\pi^*$ band of $[Co^{III}(p\text{-azobipy})_3](BF_4)_3$ could be observed under UV light irradiation, suggesting a much more effective *cis*-to-*trans* back reaction in the case of the oxidized Co(III) complex. The same behavior was observed in the case of $[Co^{II}(m\text{-azobipy})_3](BF_4)_2$ and $[Co^{III}(m\text{-azobipy})_3](BF_4)_3$ which showed in the PSS 57% and 9% *trans* to *cis* photoconversion, respectively [24].



The difference in *cis* form concentrations between Co(II) and Co(III) was applied for the reversible photoisomerization of the azobenzene moieties upon excitation with a single UV light source and addition of stoichiometric chemical oxidizing and reducing agents, respectively (Scheme 5) [23, 24].

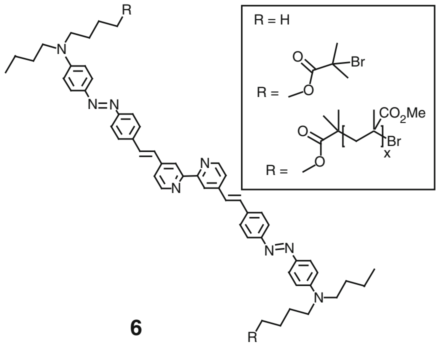
Tris(styrylbipyridine)zinc(II) complexes functionalized by dialkylamino-azobenzene groups have recently been designed by Le Bozec et al. to prepare photoisomerizable star-shaped nonlinear optical polymers **7** [25].

Recent studies have highlighted the potential of bipyridyl metal complexes in the field of nonlinear optics, and high molecular hyperpolarizability *β* values have been reported by our group for octupolar ($D_3$) tris(4,4′-disubstituted-2,2′-bipyridine) metal

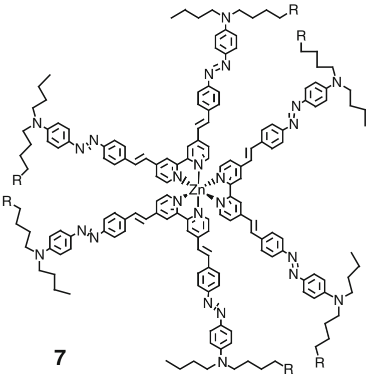


**Scheme 5** Reversible *trans-cis* isomerization of an azo group through a combination of UV light and Co(III)/Co(II) redox change

complexes [26]. Because the traditional electric-field poling-which is the relevant technique for the molecular orientation of dipolar chromophores-is not applicable for octupolar NLO-phores due to the absence of permanent dipole moment, the so-called "all optical poling" technique has been used to induce noncentrosymmetric ordering of multipolar molecules in polymer films. Basically, this method requires the use of polymer matrices containing NLO chromophores featuring photoisomerizable moieties such as an azobenzene group which can undergo reversible *trans*/*cis*/*trans* photoisomerization cycles. In chloroform solution, ligand **6** and complex **7** showed the usual photoisomerization behavior of push-pull azobenzene derivatives [25, 27]. The corresponding photoisomerizable star-shaped polymer was subsequently prepared by atom transfer radical polymerization (ATRP) of methylmethacrylate (MMA). The resulting polymer film also exhibited a photoisomerization behavior typical of azo dyes. Finally, the macroscopic optical molecular orientation of this grafted NLO-polymer film was promoted for the first time using a combined one- and two-photon excitation at 1,064 nm and 532 nm, respectively [28].



**6**



**7**

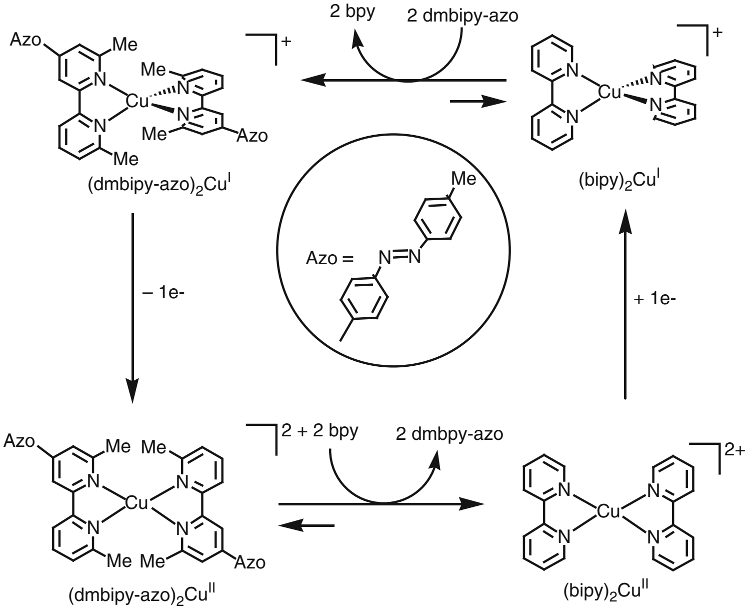
## 2.3.2 Bis(bipyridine) Metal Complexes

The key feature to stabilize pseudotetrahedral Cu(I) complexes of ligands such as 2,2-bipy is the incorporation of substituents α to the imine nitrogen.

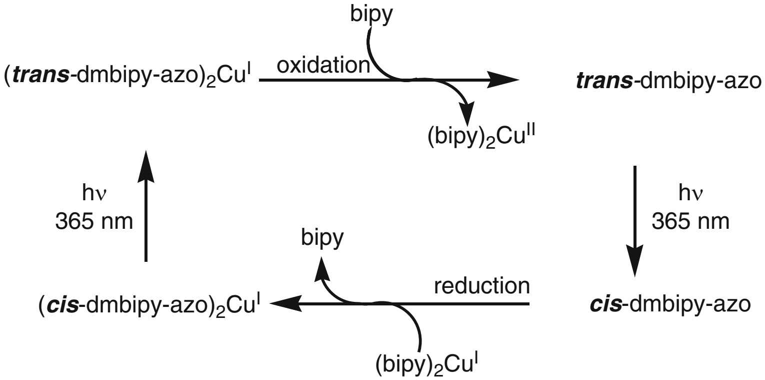
In contrast, in the absence of *ortho* substituents, Cu(I) complexes are readily oxidized to the more stable square planar Cu(II) complexes. Nishihara et al. used this coordination motion to promote the reversible *trans*-*cis* photoisomerization of an azobenzene-attached 6,6′dimethyl-2,2′-bipyridine (dmbipy-azo) with a single light source, by controlling the binding/release reaction of the ligand to copper [29]. Upon irradiation at 365 nm, the free *trans*-dmbipy-azo ligand was almost quantitatively converted to the *cis* isomer. On the other hand, the *cis* molar ratio at PSS were only 18% and 14% for the corresponding Cu(I)and Cu(II) complexes, respectively. A cyclic voltammetry study of $[(\text{dmbipy-azo})_2\text{Cu}]^+$ in the presence of 2 equivalents of 2,2′-bipy also revealed a facile ligand exchange reaction between the two bipyridine ligands, the driving force for this exchange being the difference in coordination geometry between Cu(I)and Cu(II) (Scheme 6).

By combining the dynamic motion of the metal complex with that of the azobenzene ligand, an efficient reversible *trans*–*cis* isomerization of $[(\text{dmbipy-azo})_2\text{Cu}]^+$ upon UV irradiation was observed with an increase of the *cis*/*trans* ratio to 70%. The experiment was performed chemically in the presence of 2 equivalents of bipy with oxidizing and reducing agents (Scheme 7).

This concept of reversible ligand exchange reaction in pseudotetrahedral Cu(I) complexes was also exploited by Nishihara and coworkers to convert

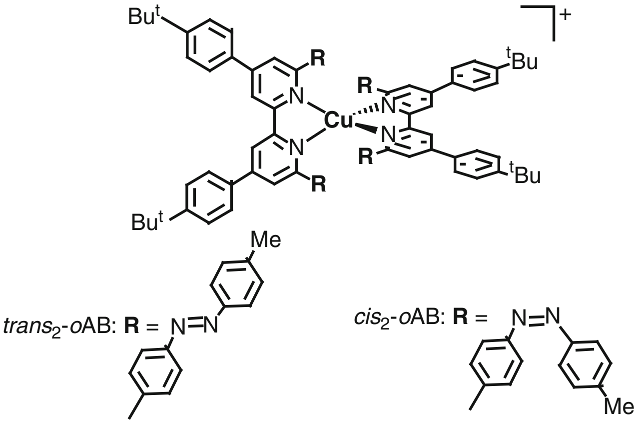


**Scheme 6** Redox-controlled coordination reaction of dmbpy-azo and bpy ligands

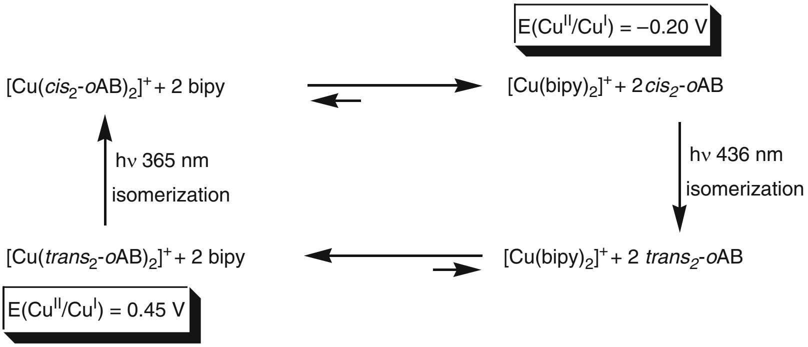


**Scheme 7** Coordination synchronized *trans-cis* photoisomerization of dmbipy-azo driven by Cu(II)/Cu(I) redox change

photon energy into electronic potential energy [30]. They developed a new 2,2′-bipyridine ligand *trans*$_2$-*o*-AB containing two azobenzene moieties at the 6,6′position and prepared the corresponding [Cu(*trans*$_2$-*o*-AB)$_2$]$^+$ and [Cu(*cis*$_2$-*o*-AB)$_2$]$^+$complexes, the latter being formed upon photoisomerization with UV light of the *trans*$_2$-*o*-AB ligand.



Due to interligand π-stacking effect, the coordination structure of [Cu(*trans*$_2$-*o*-AB)$_2$]$^+$ was found to be much more stable than that of [Cu(*cis*$_2$-*o*-AB)$_2$]$^+$. The destabilization of the *cis* isomer was used to drive a ligand exchange reaction between *cis*$_2$-*o*-AB and 2,2′-bipy, and concomitantly to shift the Cu$^{II}$/Cu$^I$ redox potential by ca. 0.6 V. The combination of the *trans*/*cis* photoisomerization of azobenzene with the ligand exchange reaction was nicely applied to construct an

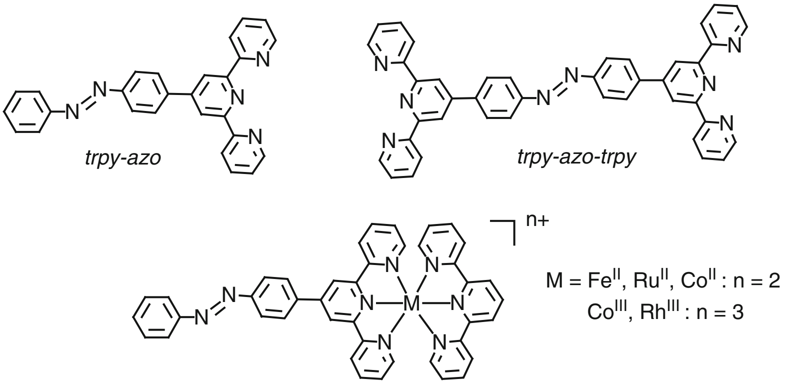


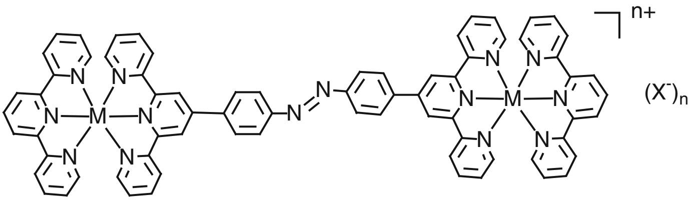
**Scheme 8** Photoelectric conversion induced by a ligand exchange reaction

artificial molecular machine where UV/visible light information can be transformed into an electrode change (Scheme 8).

## 2.4 Metal Complexes with Azobenzene-Conjugated Terpyridine Ligands

The photoisomerization properties of mononuclear and dinuclear transition metal complexes containing azobenzene-conjugated terpyridine ligands (*trpy–azo* and *trpy–azo–trpy*) have been investigated with several $d^6$ (Fe$^{II}$, Ru$^{II}$, Co$^{III}$, Rh$^{III}$) and $d^7$ (Co$^{II}$) metal ions [31–34]. The *trans/cis* photoisomerization behavior was found to be strongly dependent on the nature of the metal, as well on the nature of the counter anion and the solvent. Upon UV irradiation, the monometallic ruthenium complex [(trpy)Ru(*trpy–azo*)]$^{2+}$ underwent *trans* to *cis* photoisomerization to reach a PSS with only 20% of the *cis* form, whereas the bimetallic [(trpy)Ru(*trpy–azo–trpy*) Ru(trpy)]$^{4+}$ did not photoisomerize at all [31, 33]. In contrast, the corresponding mono- and bimetallic Rh(III) complexes were found to isomerize almost totally [32, 33]. The reverse *cis* to *trans* isomerization upon visible light irradiation was





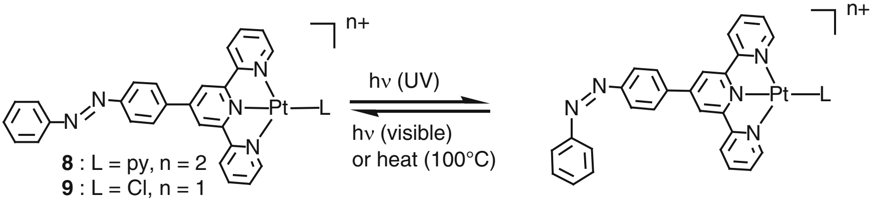
M = $Ru^{II}$, $Co^{II}$ : n = 4
$Co^{III}$, $Rh^{III}$ : n = 6

$X^-$ = $BF_4^-$, $PF_6^-$, $BPh_4^-$

not observed for both rhodium compounds but only upon heating in the dark. The absence of *trans* to *cis* photoisomerization in the case of Ru complexes was attributed to energy transfer from the azo excited state to the low-lying MLCT state. As for Ru complexes, the monometallic Fe complex showed an MLCT band at low energy [$\lambda_{MLCT}$ ($CH_3CN$) = 580 nm], and the *cis* to *trans* photoisomerization behavior was depressed by an energy transfer pathway [34].

Interestingly, the rate of the *trans* to *cis* photoisomerization of Rh complexes was found to depend on the nature of the counter anion: for example, the use of $BPh_4^-$ instead of $PF_6^-$ or $BF_4^-$ resulted in a much faster photoisomerization [32, 33]. This difference was attributed to the larger size of $BPh_4^-$ which prevents strong ion pairing with the complex cation, and consequently reduces the apparent rotor volume, resulting in a faster photoisomerization. The photochemical properties of the mono- and bimetallic $d^7$ Co(II) and $d^6$ Co(III) complexes were also investigated [34]. The Co(III) complexes were easily obtained upon oxidation of the Co(II) compounds with silver salts. The Co(II) complexes exhibit reversible *trans*/*cis*/*trans* photoisomerization of the azo group in propylene carbonate (PC) upon irradiation at 366 nm and 435 nm, respectively. The *cis* to *trans* isomerization is also effective in PC by heating at 90°C. The *trans* to *cis* photoisomerization of the Co(III) complexes also occurred at 366 nm in dichloroethane, although less efficiently than that of Co(II), but the back photoisomerization could not be observed by either visible irradiation or heat. Thus these studies demonstrated the profound influence of the metal center, as well as of the oxidation state on the photochromic behavior of the azobenzene unit.

The photoluminescence switching upon *trans–cis* photoisomerization of the azobenzene moiety of square planar platinum(II) complexes **8** and **9** were investigated by Nishihara and coworkers [35].



**8** : L = py, n = 2
**9** : L = Cl, n = 1

emission OFF ($\lambda_{exc}$ = 450 nm)

emission ON
($\lambda_{exc}$ = 450 nm, $\lambda_{em}$ = 600 nm)

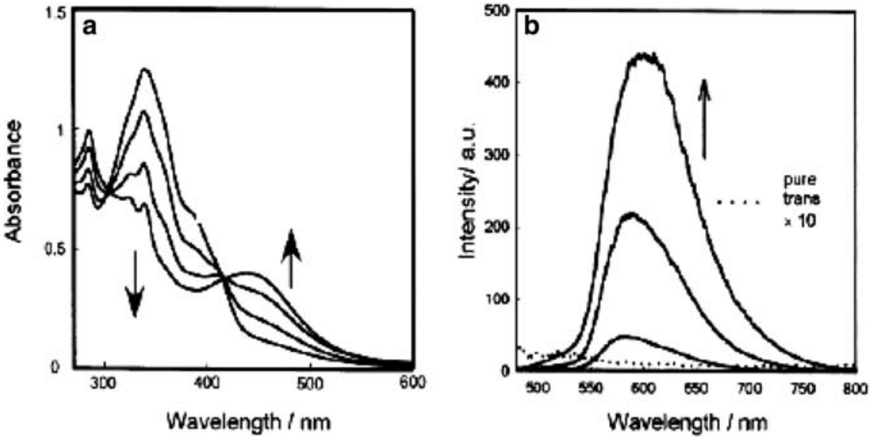


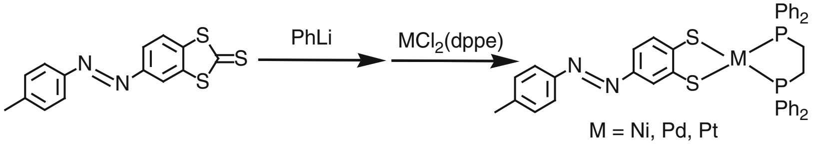
**Fig. 1a** UV–visible absorption change of **9** in propylene carbonate upon irradiation at 366 nm. **b** Emission spectral change of **9** in EtOH–MeOH–DMF at 77 K upon irradiation at 366 nm ($\lambda_{\mathrm{exc}} = 450$ nm) (Reprinted with permission from [35])

Their absorption spectra show at ca. 350 nm characteristic strong azo π−π* bands overlapped with weaker MLCT bands. Upon photoirradiation at 366 nm, efficient *trans* to *cis* photoisomerization occurred as evidenced by the decrease of the π−π* band and the apparition of the azo *n*–π* band at around 450 nm (Fig. 1).

The reverse *cis* to *trans* isomerization was observed either by irradiation with visible light or by heat. No emission in solution at room temperature could be observed for both isomers. In organic glasses at 77 K a dramatic emission spectral enhancement was observed by the *cis–trans* conformation change: whereas the *trans* forms are nonluminescent at excitation wavelength of 450 nm, the *cis* isomers exhibit a red luminescence centered at 600 nm. The long emission lifetime of 40 μs is typical of an $^3$MLCT excited state, probably with mixing of some $^3$π−π* excited state. This OFF/ON switching was interpreted by the nonplanar geometry of the *cis* form and the reduced π-conjugation effect.

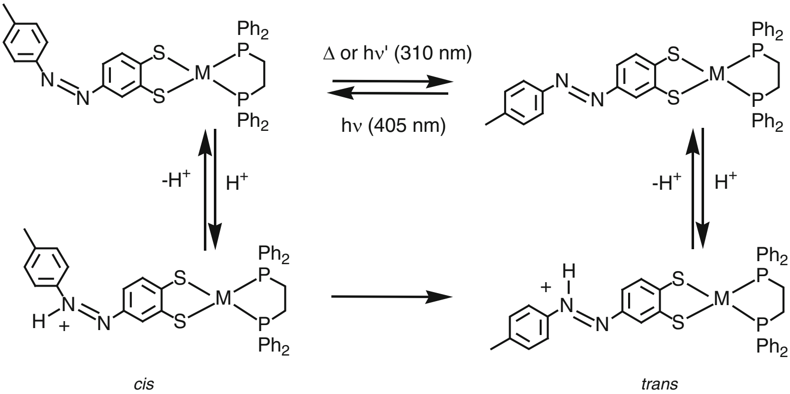
## 2.5 Metalladithiolenes with Azobenzene Groups

Metal dithiolene complexes represent an important class of organometallic molecules which have been widely studied for their interesting properties such as redox activity, conductivity, and magnetism. In order to design new photo-responsive multifunctional compounds, a series of complexes combining metalladithiolenes with azobenzene groups has been described by Nishihara et al. [36–38]. New square planar azobenzodithiolene Ni, Pd, and Pt complexes were prepared from the benzodithiolethione precursor [36, 37].

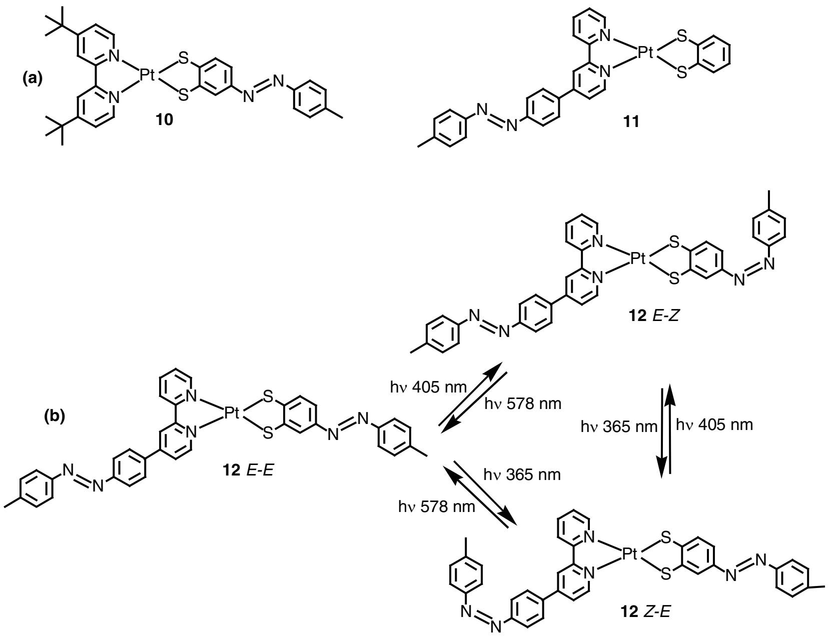


Upon photoirradiation in the π−π* transition band at 405 nm, a decrease of this band was observed, indicating the occurrence of the *trans* to *cis* photoisomerization. A conversion of ca. 40% in PSS was found, according to $^1$H NMR spectroscopic measurements. The back *cis* to *trans* photoisomerization also occurred upon photoirradiation, but unusually by using UV light excitation, with an energy higher than the π−π* transition. The *trans* isomers also underwent a dramatic color change, from yellow to blue–green, upon addition of triflic acid, in agreement with the protonation of the azo moiety. When a slight amount of acid was added to the photogenerated *cis* isomers, an immediate *cis* to *trans* transformation was observed. This "proton-catalyzed" isomerization indicated that the *cis*-protonated form instantly produced the *trans*-protonated form which gave the *trans* isomer after the release of $H^+$. In this isomerization, it was presumed that protonation of the nitrogen atom changed its hybridization from $sp^2$ to $sp^3$, allowing a more facile rotation around the N–N bond (Scheme 9).

Nishihara and coworkers have recently investigated the photoisomerization behavior of platinum(II) complexes **10** and **11** containing an azobenzene on the metaldithiolene side and the bipyridine side, respectively (Scheme 10a) [38]. They also studied the photocontrolled multistability of a platinum complex **12** featuring two azobenzene moieties, one bounded to the dithiolato ligand and the other linked to the bipyridine ligand. All complexes feature strong absorption bands in the UV region, attributed to π−π* transitions of the azobenzene and bipy moieties. Complex **11** also displays at λ 405 nm a band that has been assigned to a MLCT-like transition, from the metalladithiolene (π) to the azobenzene (π*) level. In the lower



**Scheme 9** Photo and proton responses of azobenzodithiolene metal complexes

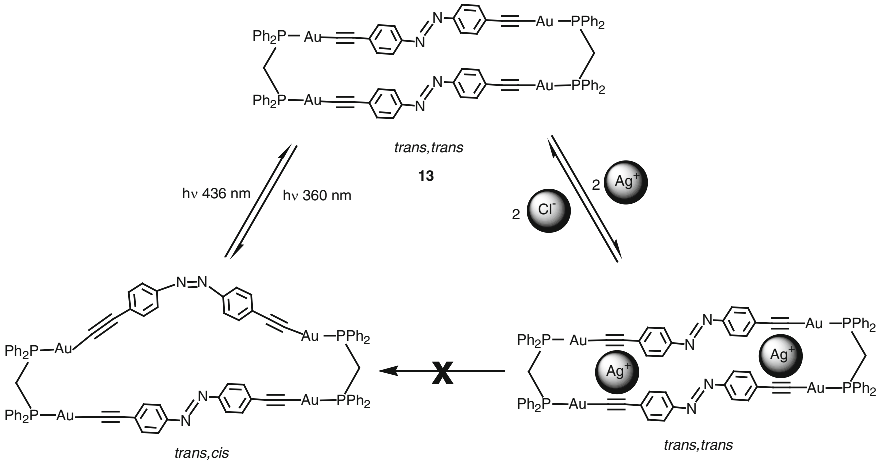


**Scheme 10** (**a**) Chemical structures of complexes **10** and **11** **b** Photoisomerization behavior of **12**

energy region, other bands were observed for both **10** and **11**, attributed as mixed-metal/ligand-to-ligand charge transfer (MMLL'CT) bands [39]. All these assignments were supported by TD-DFT calculations. These two complexes underwent both *trans*/*cis* photoisomerization, but at different wavelengths. For **10**, the *trans* to *cis* isomerization proceeded with a conversion of 45% in PSS, upon irradiation into the MLCT band at 405 nm. The back *cis* to *trans* isomerization occurred by excitation of the MMLL'CT band with 578 nm yellow light. On the other hand, complex **11** displayed *trans* to *cis* photoisomerization upon irradiation with 365 nm UV light (23%conversion in PSS), whereas the reverse isomerization was also observed by irradiation at 578 nm. Interestingly, complex **12** bearing an azobenzene on both the bipy and dithiolate ligands, showed photochromic behavior which was almost the superposition of those of complexes **10** and **11**. Thus, by using three monochromic lights, three out of the four possible states, the exception being the *cis*,*cis*-state, could be reversibly switched (Scheme 10b).

## *2.6 Azobenzene-Containing Metal Alkynyl Complexes*

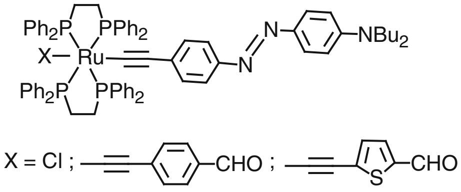
Organometallic alkynyl complexes exhibit a rich coordination chemistry with copper(I), silver(I), and gold(I) ions, and the ability of alkynyl groups to coordinate to metal centers in σ- and π-bonding modes has made them versatile ligands in the



**Scheme 11** "Locking" and "unlocking" mechanism upon addition and removal of $Ag^+$ ions

synthesis of polynuclear metal complexes [40]. Very recently, Yam and coworkers prepared a tetranuclear gold(I) alkynyl phosphine complex **13** containing azobenzene functionalities and demonstrated the generation of a dual-input lockable molecular logic photoswitch [41]. Upon irradiation at 360 nm into the π–π* azo transition, *trans–cis* photoisomerization occurred, and it was estimated that only the *trans,cis* product was formed. The back *cis* to *trans* isomerization proceeded by excitation into the *n*–π* transition at 486 nm. Interestingly, introduction of $Ag^+$ ions to **13** inhibited the photoisomerization process, probably because of π-coordination of adjacent pairs of alkynyls to the $Ag^+$ ions which locks up the *trans* conformation of the azobenzene units. In contrast, upon abstraction of $Ag^+$ with a chloride anion, the photoisomerization process could be restored, showing that photoswitching behavior can be controlled via silver(I) coordination/decoordination (Scheme 11).

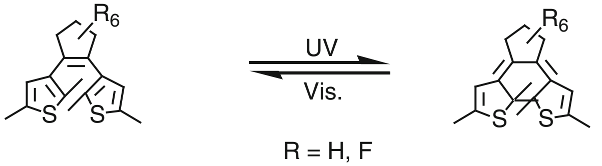
A series of push–pull azobenzene containing ruthenium(II) σ-acetylide NLO-phores have also been prepared recently and their holographic properties, which are based on *trans–cis–trans* photoisomerization cycles of azobenzene, have been investigated in PMMA thin films [42, 43]. Surface relief gratings with good temporal stability were obtained upon short pulse laser irradiation ($\lambda = 532$ nm), showing that these organometallic photochromes are promising candidates for optical data storage applications.



# 3 Metal Complexes Incorporating 1,2-Dithienylethene

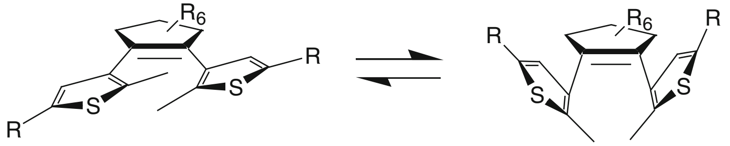
## 3.1 Introduction

Diarylethene (DTE) derivatives that have been used as ligands for incorporation into transition metal complexes have recently received much attention. Coordination of DTE ligands opens up new perspectives for the design of photoswitchable molecules. 1,2-Dithienylcyclopentene and its perfluoro analog have particularly attracted increased interest for their excellent stability and fatigue-resistance properties. Irradiation at appropriate wavelength allows the interconversion of a nonconjugated colorless *open* form to the conjugated, colored, *closed* form [44, 45].



*open non conjugated form* *closed conjugated form*

The open-ring isomer of DTE has parallel and antiparallel conformations which are in dynamic equilibrium. The closing process follows the rules according to Woodward–Hoffmann, in which the photocyclization occurs, via a conrotatory mechanism, only from an antiparallel conformation of the two thienyl rings. For unsubstituted DTE derivatives, the ratio of molecules in the parallel and antiparallel conformations is close to 1:1 and the cyclization quantum yield therefore cannot exceed 0.5. The photoreversion is significantly less efficient than the photocyclization, in most cases the quantum yield values typically not exceeding 0.1.

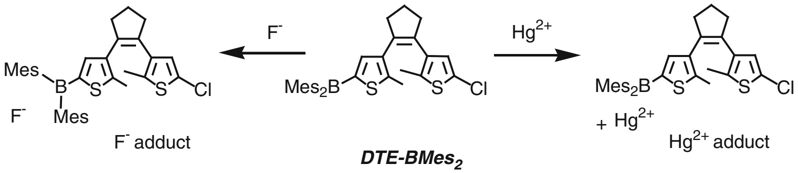


Antiparallel Parallel

## 3.2 Organo-Boron DTE-Based Dithienylcyclopentene

### 3.2.1 Modulation of the Photochromic Properties by Ions

The special binding ability of the organo-boron functionalized 1,2-dithienylcyclopentene DTE-BMes$_2$ with fluoride (tetrammonium fluoride (TBAF)) and mercuric ions (Hg(ClO$_4$)$_2$) allows the modulation of its spectral properties, in its open and PSS states [46].



Upon addition of about 1.5 equivalents of TBAF, the absorption maximum of PSS (generated by irradiation with 365 nm) was blue-shifted from 560 to 490 nm. When about 6 equivalents of Hg(ClO$_4$)$_2$ was added, the absorption maximum of PSS was blue-shifted from 560 to 440 nm. Moreover, the absorption intensity decreased. The modulation mechanism is attributed to the Lewis acid–base interaction between a trivalent boron atom and a fluoride ion, and the complexation interaction between mercury and the sulfur atom (Fig. 2).

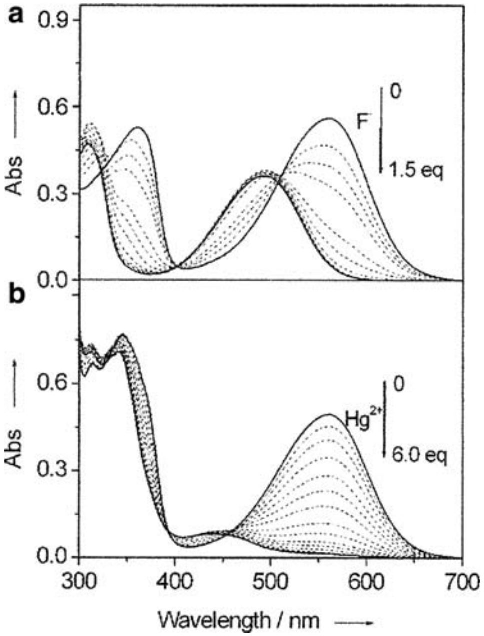
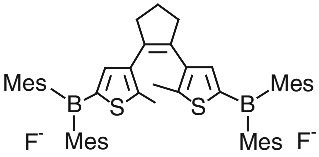


**Fig. 2** Changes in UV–visible absorption spectra of closed-ring DTE–BMes$_2$ (PSS) (5.10$^{-5}$ M) in THF solution upon addition of (**a**) 0–1.5 equivalents TBAF and (**b**) 0–6.0 equivalents of Hg (ClO$_4$)$_2$ (Reprinted with permission from [46])

Similar results were obtained in the case of bis(mesityl)boryl derivative DTE-$(BMes_2)_2$; its fluoride binding property is remarkably selective [47].



***DTE-$(BMes_2)_2$***

### 3.2.2 Up-Conversion Luminescent Switch Based on the Combination of DTE and Rare-Earth Nanophosphors

Up-conversion rare-earth nanophosphors (UCNPs) consisting of certain lanthanide dopants embedded in a crystalline host lattice can convert near infrared (NIR) excitation light into emission at visible wavelengths via the sequential absorption of two or more low energy photons. The hybrid system DTE–$BMes_2$/$LaF_3$:Yb, Ho loaded in PMMA film underwent a reversible photochromic reaction similar to those of the isolated species DTE–$BMes_2$ [48]. What is important is that DTE-$BMes_2$ has no absorption in the NIR region in both the open and PSS states, whereas $LaF_3$:Yb, Ho can emit visible luminescence by excitation at 980 nm, due to the large anti Stokes shift. A highly efficient hybrid nanosystem has been thus achieved via an intramolecular energy transfer process (Fig. 3).

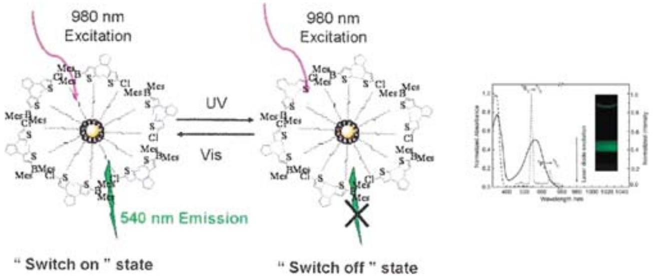
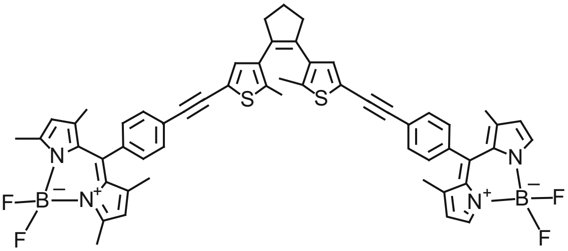


**Fig. 3** UV–visible absorption spectra of DTE–$BMes_2$/$LaF_3$:Yb, Ho-loaded PMMA film before (*dashed line*) and after (*solid line*) irradiation with 365 nm light for 30 min, and the normalized up-conversion luminescence spectra of the prepared film (*dotted line*, $\lambda_{exc} = 980$ nm). *Inset* shows the image of the up-conversion emission of the film. (Reprinted with permission from [48])

### 3.2.3 Fluorescent Bodipy-Based Switches

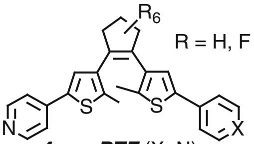
Covalently linked BODIPY dyes (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene) to the photochromic DTE unit allow the formation of new photoswitches that are highly emissive as open-ring isomers and in which the fluorescence is significantly quenched in closed-ring isomers [49]. Switching of the fluorescence is reversible and can be repeated (20 cycles) without significant loss of its intensity. Intramolecular energy transfer from the dye to the closed-ring form of the DTE is suggested to be the mechanism of fluorescence quenching.



## 3.3 *Complexes Incorporating DTE-Based Pyridine, Cyano, or Carboxylate Ligands*

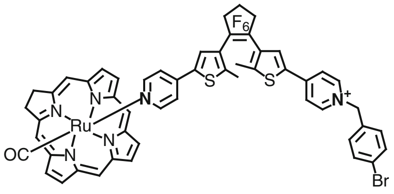
### 3.3.1 Photochromism in Solution

The pyridine derivatives, the *monodentate* 1-(2-methyl-5-phenyl-3-thienyl)-2-(2-methyl-5-(4-pyridyl)-3-thienyl)perfluorocyclopentene and the *bidentate* 1,2-bis (2-methyl-5-(4-pyridyl)-3-thienyl)perfluorocyclopentene, incorporating the DTE moiety as the photochromic unit (4-py-DTE$_f$ [50, 51] and 4-py$_2$-DTE$_f$ [52]) and the nonfluorinated analog (4-py$_2$-DTE) [53] have been coordinated to various transition metals, allowing the change of physical properties of metal complexes.



***4-py$_2$-DTE*** (X=N)
***4-py-DTE*** (X=CH)

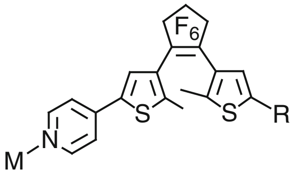
Branda showed that the ability of the pyridine ligand of the pyridinium salt of 4-py$_2$-DTE$_f$ to coordinate to a ruthenium center is modulated by interconverting the compound between its electronically insulated ring-open and electronically connected ring-closed form [54, 55].



***(Ru-TPP)(4-py-DTE$_f$)***

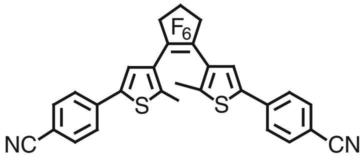
The *open-* and *closed*-ring monocationic DTE-based pyridine ligand exhibits different ability to coordinate the ruthenium porphyrin complex Ru(TTP)(CO)(EtOH) (TTP: *tetra*(4-methylphenylporphyrin)). The axial coordination of the closed-ring isomer of the pyridine complex which is electronically coupled with the pyridinium end group through to the π-conjugated DTE bridge is 1.5 times less effective than that of the related open isomer. This low selectivity is suggested to result from the fact that the free pyridine ring is not completely coplanar with the DTE framework.

Complexes of tungsten, rhenium, and ruthenium of 4-py-DTE$_f$ and 4-py$_2$-DT$_f$ have been developed by Lehn [56, 57]. These complexes exhibit good photochromic properties. A switching of fluorescence between their open and closed forms is observed when excited at 240 nm, a wavelength of irradiation that almost did not affect the state of the molecule.

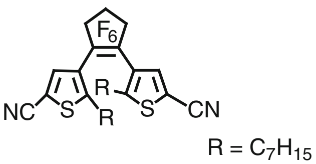


M = W(CO)$_5$, R = *N*-[W(CO)$_5$]pyridyl
M = W(CO)$_5$, R = *p*-phenol
M= [Re(bpy)(CO)$_3$(CF$_3$SO$_3$)],
R = *N*-[Re(bpy)(CO)$_3$(CF$_3$SO$_3$)]pyridyl
M= [Re(bpy)(CO)$_3$(CF$_3$SO$_3$)],
R =*p*-methoxy phenyl
M= [Ru(NH$_3$)$_5$](PF$_6$)$_2$, R = [Ru(NH$_3$)$_5$](PF$_6$)$_2$

The related metal complexes (W, Re, Ru) of the two cyano derivatives DTE–CN and DTE–C$_6$H$_4$–CN were found to be unstable.



***DTE-C$_6$H$_4$-CN***



R = $C_7H_{15}$

***DTE-CN***

The photoresponsive ligand 4-py-$DTE_f$ has been combined with a spin-crossover complex, in order to achieve a molecular bistable spin system. The photoisomerization of the high spin Fe(II) complex Fe(4-py-$DTE_f$)$_4$(NCS)$_2$ allows the modulation of its magnetic properties [58].

### 3.3.2 Photochromism of Metal Complexes in the Single-Crystalline Phase

The photoreactivity of DTE derivatives in the crystalline state is of special interest because of their potential usefulness for holographic and three-dimensional memories. In crystals, molecules are regularly oriented and packed in fixed conformations. In many cases, free rotation is inhibited. Therefore, the photoreactivity in the crystalline phase is dependent on the space for free rotation of the thienyl rings and the conformation formed in the crystal lattice. Several reports on the synthesis of metal complexes of photochromic diarylethenes and their photo-reactivity in the single-crystalline phase or the photoswitching of the coordination structure have been reported. These studies demonstrate that complexation to metal ions does not prohibit the photochromic reactions of the diarylethene units in the single-crystalline phase.

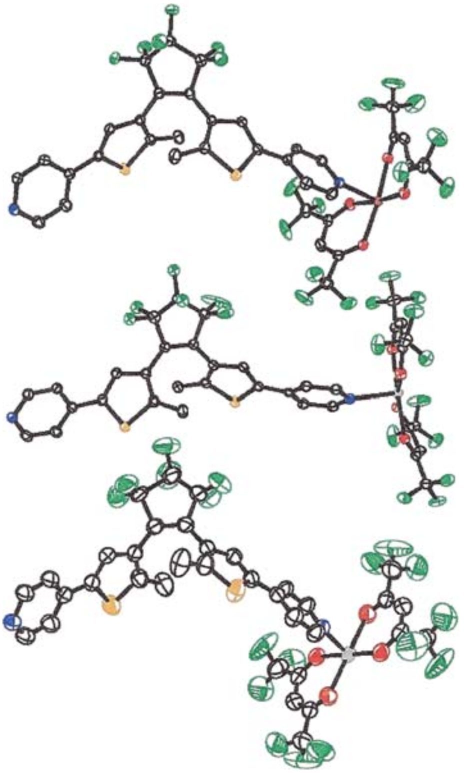
#### Discrete Structure and Coordination Polymers

Metal complexes of monodentate (4-py-$DTE_f$) and bidentate (4-$py_2$-$DTE_f$) photochromic pyridine ligands and M(hfac)$_2$ (Zn(II), Cu(II), Mn(II)) (hfac = hexafluoroacetylacetone) have been synthesized [51]. The bidentate ligand 4-$py_2$-$DTE_f$ leads to the formation of coordination polymers (4-$py_2$-$DTE_f$)M(hfac)$_2$ whereas discrete 1:2 complexes were obtained for the monodentate ligand 4-py-DTE. The chain structure depends on the metal fragments, the complexes adopt a chain-like structure, a zigzag shaped in the case of (4-$py_2$-$DTE_f$)Cu(hfac)$_2$ and (4-$py_2$-$DTE_f$)Zn (hfac)$_2$ and an almost straight chain in the case of (4-$py_2$-$DTE_f$)Mn(hfac)$_2$ (Fig. 4). All photochromic units adopt an antiparallel conformation, in which photocyclization reaction takes place. This process has been monitored by means of polarized absorption spectroscopy.

The complexation of Cu(hfac)$_2$ and the isolated *closed-ring* isomers were performed to afford discrete 2:3 complexes closed-(4-py-$DTE_f$)$_2${Cu(hfac)$_2$}$_3$ and closed-(4-$py_2$-$DTE_f$)$_2$Cu(hfac)$_2$, probably as the result of reduced coordination ability of the pyridine ligand upon ring-closure. Photocyclization process induced a change in the coordination structure, as demonstrated by ESR studies in the case of (4-$py_2$-$DTE_f$)$_2$Cu(hfac)$_2$.

Similar results were obtained in the case of (4-py-DTE)$ZnCl_2$, two pyridines of two different molecules are coordinated to $ZnCl_2$ to form a linear coordination polymer [59]. It is noteworthy that, in this case, the complex adopts a parallel conformation and therefore no photochromism was observed in the crystalline phase.

**Fig. 4** ORTEP drawings of X-ray crystallographic structures of linear chain complexes of the open-ring isomer (50% probability). **a** (4-py$_2$-DTE$_f$)$_2$Zn(hfac)$_2$. **b** (4-py$_2$-DTE$_f$)Mn(hfac)$_2$. **c** (4-py$_2$-DTE$_f$) Cu(hfac)$_2$. Hydrogen atoms are omitted for clarity. Only one repeating unit. (Reprinted with permission from [51])



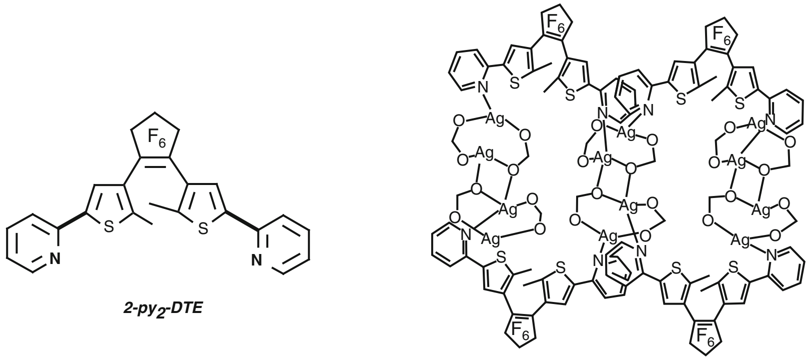


**Fig. 5** One-dimensional double chain structure of [Ag$_2$(2-py$_2$-DTE)][(CF$_3$CO$_2$)]. (Reprinted with permission from [61])

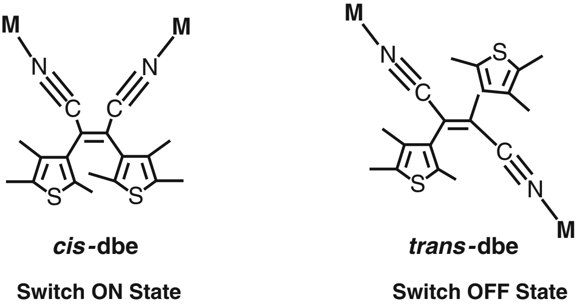
The crystal of the discrete 2:1 complex (4-py$_2$-DTE)$_2$ZnCl$_2$ undergoes photochromic reaction by alternate irradiation with UV and visible light.

The structure and the photoreactivity depend on the substituents of the cyclopentene ring of the DTE unit, perfluorinated or not. Tian observed an enhancement of the photochromism, i.e., a higher quantum yield compared to that of the free ligand by coordination of the 1,2-bis(2-methyl-5(-4-pyridyl)-3-thienyl)*cyclopentene* to $ZnCl_2$ [53]. The structure of the coordination polymer, a zigzag chain, shows that the open-ring of the DTE adopts an antiparallel conformation in the crystal phase [60].

The related derivative 1,2-bis(2-methyl)-5-(**2**-pyridyl)-3-thienyl-perfluorocyclopentene (2-$py_2$-DTE) is able to coordinate Ag(I) ions [61]. Three novel Ag(I) complexes were prepared and all complexes display reversible photogenerated behavior in crystalline phase (Fig. 5).

### 1,2-Dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (*cis*-dbe)

The two cyano groups of 1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (*cis*-dbe) bridge two dimetal carboxylates of Mo(II) or Rh(II), to give a 1D zigzag infinite chain. However, the photochromic properties in crystalline phase are only observed for Mo complexes [62].



In the case of Cu(I) ions, the structure is composed of macrocations $[Cu(cis\text{-}dbe)_2]^+$ in which each metal center is coordinated with one CN group of the four DTE molecules [63]. Each *cis*-dbe bridges two copper(I) ions with two cyano groups, leading to an infinite network of metal cations. This copper coordination polymer shows reversible photochromism in the crystalline phase, whereas no modification is observed for the related $[Cu(trans\text{-}dbe)(THF)(ClO_4)]^+$ which forms a zigzag chain (Fig. 6).

Munakata also investigated the crystallographic structures of silver(I)-*cis*-dbe coordination polymers with five different anions ($CF_3SO_3$, $C_nF_{n+1}CO_2$; $n = 1$–4) which shows different photochromic reactions on the crystalline phase [64]. The differences are attributed to the varied Ag–S distances, controlled by the nature of the counter-anion (Fig. 7). These are the first examples of the metal ions coordinated to the thiophene rings of the DTE core, indicating that the soft Ag(I) ion has a relatively high affinity for sulfur donor atoms.

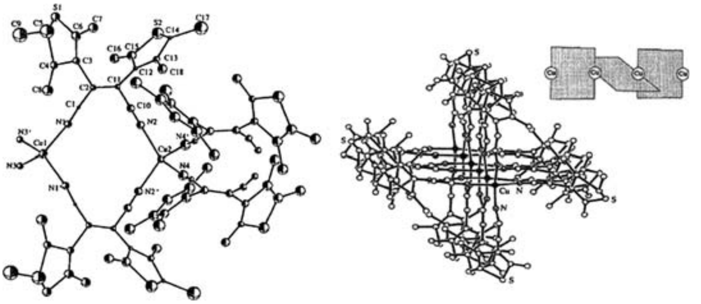
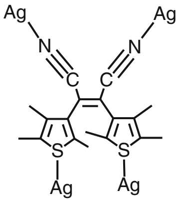


**Fig. 6** **a** Partial molecular structure of [Cu($cis$-dbe)$_2$][ClO$_4$)] showing the twisted ring-opened form of the DTE. **b** A view of the crystal packing showing a one-dimensional array of the metal ions. (Reprinted with permission from [63])



**Ag$_2$*(cis-dbe)***

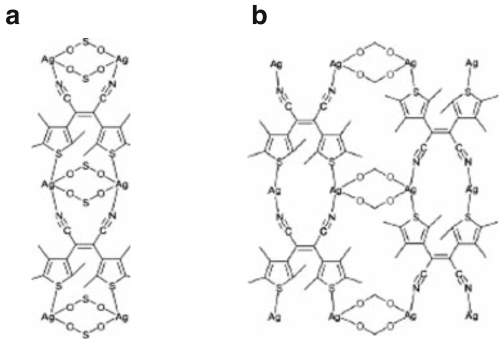
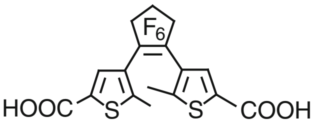


**Fig. 7** Schematic views of (**a**) 1D structure of Ag$_2$(dbe)(CF$_3$SO$_3$)$_2$ and (**b**) 2D sheet structure of Ag$_2$(dbe)(X)$_2$ X = $C_nF_{n+2}CO_2$. (Reprinted with permission from [64])

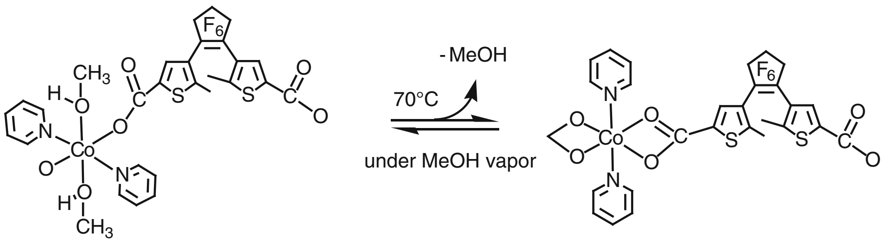
## 1,2-Bis(2-methyl-5-carboxylic acid-3-thienyl)perfluorocyclopentene (DTE-5-CA)

1,2-Bis(2-methyl-5-carboxylic acid-3-thienyl)perfluorocyclopentene (DTE-5-CA), which was first synthesized by Branda [65] and incorporated into polymers, can also be used as a versatile ligand as demonstrated by Munakata [66].



***DTE-5-CA***

In the three complexes [Co(DTE-5-CA)$(py)_2(MeOH)_2$], [Cu(DTE-5-CA)$(py)_3$] (EtOH)$(py)_{1.8}$, and [Zn(DTE-5-CA)(phen)($H_2O$)], DTE-5-CA acts as a bis-monodentate bridging ligand through one of the oxygen atom of each carboxylate group to generate the 1D polymer. The two thienyl rings in all cases adopt antiparallel conformation and the distance between the two reactive carbon atoms are short enough to allow photocyclization in the crystalline phase. The coordination geometry and packing of the compounds significantly affect the photochromic performance.



***Co-DTE-5-CA*-MeOH** ***Co-DTE-5-CA***

The Co(II) complex undergoes a solid-state structural transformation via the liberation of bound MeOH upon heating. Strikingly, the dynamic structural changes do not prohibit the reversible photoisomerization of the MeOH-desolvated form (Co–DTE–5-CA), indicating retention of the framework and excellent stability (Fig. 8).

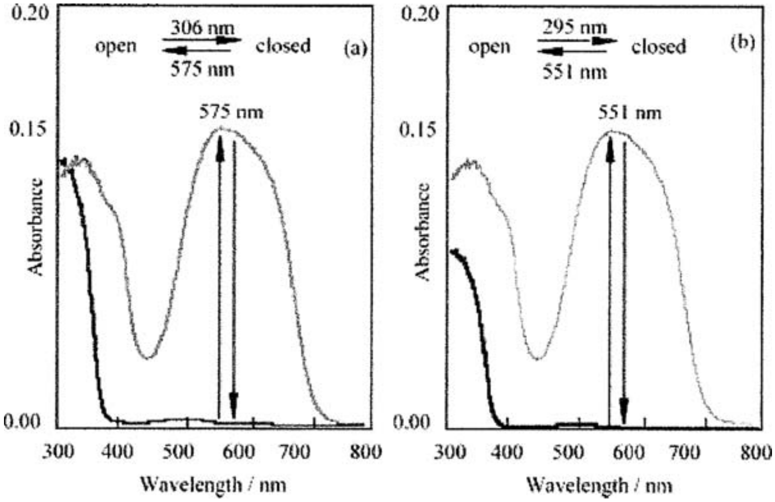
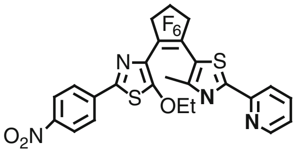


**Fig. 8** Absorption spectral changes of (**a**) Co–DTE–5-CA–MeOH and (**b**) Co–DTE–5-CA in the crystalline phase. (Reprinted with permission from [66])



***dithiazole-py***

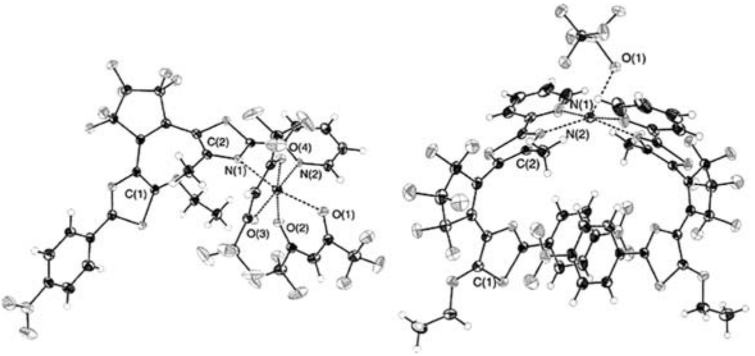


**Fig. 9** ORTEP views of Cu(hfac)$_2$(dithiazole-py) (*left*) and Ag(dithiazole-py)$_2$CF$_3$SO$_3$ (*right*). (Reprinted with permission from [67])

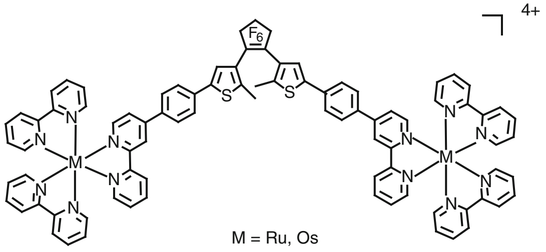
Dithiazolylethene-based derivatives display an (*N*,*N*) chelating site from the pyridyl and thiazolyl fragments allowing the access to the monomeric metal complexes Cu(hfac)$_2$(dithiazole-py), Mn(hfac)$_2$(dithiazole-py), and Ag(dithiazole-py)$_2$CF$_3$SO$_3$ [67] (Fig. 9). None of these complexes display crystalline state photochromism.

## *3.4 Photoregulation of Luminescence*

Among outputs, luminescence emission is considered to be one of the most attractive, owing to the ease of detection and the cheap fabrication of devices in which it is detected. Many examples of fluorescent photochromic molecules have been published, by combining a DTE unit with a fluorophore [4]. Incorporation of the DTE fragment into the ligands of transition-metal polypyridine complexes allows the photoreaction to proceed via a triplet state leading to a photoregulation of phosphorescence.

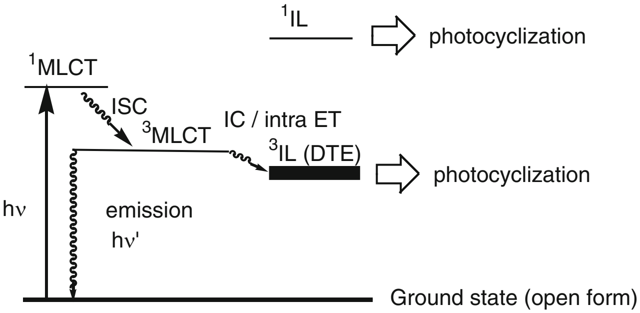
### 3.4.1 Complexes Incorporating DTE-Based Bipyridine Ligand

De Cola reported homo- and heterodinuclear systems in which the metallic fragments [Ru(bipy)$_3$]$^+$ and [Os(bipy)$_3$]$^+$ are bridged by a dithienylperfluorocyclopentene molecular switch, a phenylene group being used as a spacer [68–70].



In these metal systems, De Cola demonstrated that the photochromism can be extended from the UV region in the free ligand to the visible region corresponding to the MLCT transition. The extension of the excitation wavelengths to the visible region to trigger the photochromic reaction allows the use of less destructive visible light sources and is highly desirable. Direct evidence of triplet MLCT photosensibilization of the ring-closing reaction of diarylethene has been reported by means of transient absorption and time-resolved emission studies. The ring-closure reaction is in the nanosecond domain and the quantum yield decreases strongly in the presence of dioxygen. The photosensitization mechanism involving an internal conversion or intramolecular energy transfer from the $^3$MLCT state to the $^3$IL (DTE) state has been demonstrated. Once the $^1$MLCT state is populated, intersystem crossing to the $^3$MLCT state would occur leading to the sensitization of the photochromic reactive $^3$IL(DTE) state that initiates the ring-closure reaction (Scheme 12). This behavior differs substantially from the photocyclization process of the nonemissive DTE free ligand, which occurs from the lowest $^1$IL state on the picosecond timescale and is insensitive to oxygen quenching. Replacement of both Ru(II) centers by Os(II) completely prevents the photocyclization reaction upon light excitation into the lowest-lying $^1$MLCT excited state.

A disadvantage of such system is that, in the trapping state, energy is transferred to the photochromic moiety that can consequently convert to the parent form. Therefore monitoring the occurrence or absence of energy transfer cannot be used as means for nondestructive readout, as the excitation affects the state of the system.



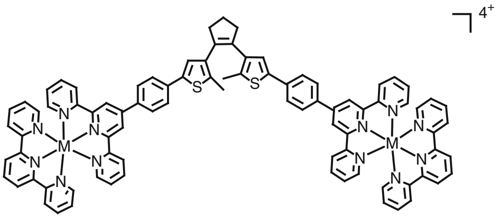
**Scheme 12** Proposed qualitative energetic scheme for photosensitized photochromism by MLCT

The possible quenching by the sensitized photocyclization renders the photoluminescence from the $^3$MLCT state less efficient. Upon conversion to their respective closed form, the $^3$MLCT emission of both Ru(II) and Os(II) complexes are quenched. This is due to an energy transfer to the lowest excited state of the DTE unit that is lower in energy than those of the metal centers in the closed form.

The parent heterodinuclear Ru/Os complex was also investigated. The bridging unit in its open form allows an efficient energy transfer from the excited ruthenium to the acceptor osmium center. When the bridging DTE unit is in its closed form, the energy level IL(*closed*-DTE) drops down and is below of the energy level of the two metal centers, quenching both emissions.

### 3.4.2 Complexes Incorporating DTE-Based Terpyridine Ligand

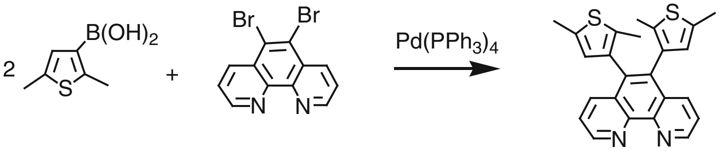
The related dinuclear terpyridine complexes were investigated [71]. The Ru(II) and Fe(II) complexes, in their open forms, were found to be inert to UV irradiation but could be cyclized electrochemically as revealed by a cyclic voltammetry study. In contrast, the bis-Co(II) complex underwent efficient photochemical but not electrochemical cyclization. The corresponding Os(II) complex was neither photochromic nor electrochromic.



M = Ru, Os, Fe, Co

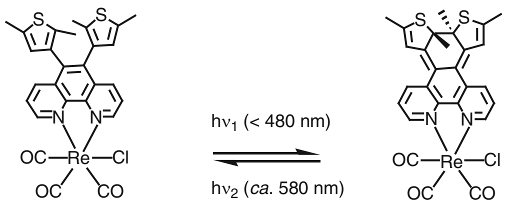
### 3.4.3 Complexes Incorporating DTE-Based Phenanthroline Ligand

Yam reported the synthesis and sensitized photochromic properties of a versatile diarylethene containing 1,10-phenanthroline ligand and their metal complexes (Re [72, 73], Pt [74]). Unlike other studies where the ligand is covalently connected to the DTE unit, phen1 displays an original design in which the ligand itself is part of the dithienyl framework.



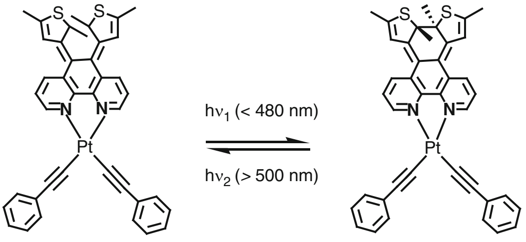
***phen1***

Unlike most other DTE systems, in which rapid interconversion of the two conformers results in a time-average $^1$H NMR signals, the protons at the 4- and 7-positions of the sterically demanding phenanthroline moiety hinder the rotation of the thienyl rings. Thus, the parallel and antiparallel conformations of the free ligand phen1 and the rhenium complex $[Re(CO)_3(phen1)(Cl)]$ (Re-phen1), are distinguished by the presence of two-well resolved sets of $^1$H NMR signals. The structure of the free ligand phen1 shows that two thiophene rings tend to orient themselves perpendicular to the plane of the phenanthroline moiety.



**Re-phen1**

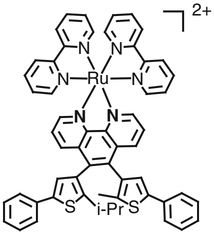
The ligand phen1 has been also used to prepare the bis(alkynyl)platinum complex Pt-phen1. The structure of the two conformers, parallel and antiparallel, has been resolved. This is the first example of X-ray crystal structures in which both isomers of the same photochromic molecule have been determined.



**Pt-phen1**

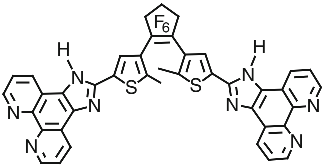
Perturbation of the photochromic and luminescence properties upon coordination to the metal center (Re, Pt) has been observed. A red shift of the absorption band for the closed isomer is attributed to the perturbation of the metal center in the complex. The emission of both phen1(*o*) and M-phen1(*o*) (MLCT) (*o*: open form, *c*: closed form) changes upon conversion to the closed form in the PSS. The strong red-shift of the emission observed for the closed form phen1(*c*) is attributed to the extension of the π-conjugation and has an IL (π→π*) phosphorescence in origin. A close resemblance of the emission of M-phen1(*c*) with that of phen1(*c*) suggests that the IL excited state, lower-lying in energy than that of the MLCT excited state, is the predominant emissive state.

Unlike the symmetrically substituted analogue phen1, the unsymmetrically substituted DTE containing 1,10-phenanthroline ligand phen2 and the corresponding Ru-phen2 exhibit no photochromic properties [75].

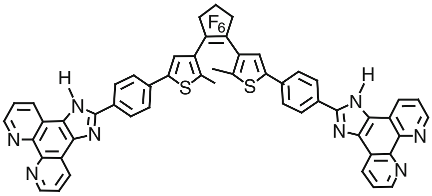


***Ru-phen2***

The diarylethene containing imidazo[4,5-f][1,10]phenanthroline has been synthesized but no examples of metal complexes are reported yet [76]. These ligands are sensitive to both light (UV/visible light irradiation) and chemical stimuli (alkali/acid treatment). A reversible four-state molecular switch has been realized by a single molecule.



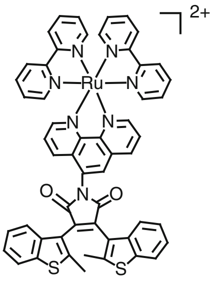
***phen3***



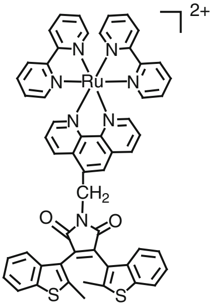
***phen4***

Maleimide Model

The study of a 1,2-bis(2-methylbenzothiophen-3-yl)maleimide model (phen-DAE) and two dyads in which the photochromic unit is coupled via a direct nitrogen–carbon bond (Ru–phen–DAE) or through an interverting methylene group (Ru–phen–$CH_2$–DAE) to a Ru–polypyridine chromophore has provided strong evidence for the participation of triplet state in the photochromic behavior of this class of diarylethenes [77]. Unlike previous studies, evidence of triplet reactivity case is obtained not only for the metal-containing systems but also for the isolated phen-DAE. A complete kinetic characterization has been obtained by ps–ns time-resolved spectroscopy. The experimental results are complemented by a combined ab initio and DFT computational study whereby the potential energy surfaces for ground state and lowest triplet state of the DAE are investigated along the reaction coordinate for photocyclization/cycloreversion.



**Ru-phen-DAE**

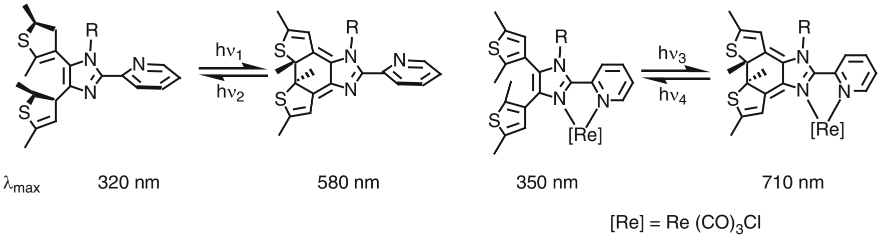


**Ru-phen-$CH_2$-DAE**

### 3.4.4 Near-Infrared Photochromic Behavior (Imidazole–Pyridine)

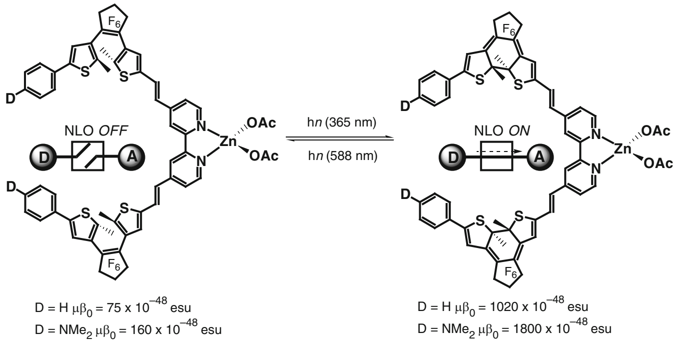
Metal coordination of the DTE derivative and extension of the π-conjugated system through an enhancement of planarity provides an alternative and versatile route to a new class of photochromic compounds that show absorption and reactivity in the NIR region.

The Re(I) complexes featuring a DTE containing 1-aryl-2-(2-pyridyl)imidazole ligand has been demonstrated to exhibit NIR photochromic behavior, with a large red shift in absorption maxima upon photocyclization that has been brought by metal coordination-assisted planarization of the extended π-conjugated system [78].



## 3.5 *Photoswitching of Second-Order NLO Activity*

The NLO properties of metal-containing photochromic ligands have been evaluated by EFISH measurement for the open and PSS closed forms, and for the first time an efficient ON/OFF switching of the nonlinear optical (NLO) response was demonstrated [79]. Most molecules with large NLO activities comprise π-systems unsymmetrically end-capped with donor and acceptor moieties. In order to carry out the photoswitching of the NLO properties, a new type of 4,4′-bis(ethenyl)-2,2′-bipyridine ligands functionalized by a phenyl- and dimethylaminophenyl- DTE groups has been designed. These ligands have allowed the preparation of photochromic dipolar zinc(II) complexes. These molecules underwent an efficient reversible interconversion between a nonconjugated open form and a π-conjugated closed form when irradiated in the UV and visible spectral ranges, respectively.



## 3.6 Photoswitching of a Magnetic Interaction

The first example of a magnetic metal–radical interaction was achieved by the coordination of a DTE (1,2-bis(2-methyl-benzothienyl-3-yl)perfluorocyclopentene) based-1,10-phenanthroline ligand containing a nitronyl nitroxide radical with a Cu(II) ion [80]. Mixing this ligand with [Cu(hfac)$_2$] in toluene led to a hypsochromic shift of the absorption maxima of the closed-ring isomer due to complexation. ESR measurement in toluene of the open-ring isomer of the Cu complex gave a spectrum that is the superposition of the spectra from the nitroxide radical and Cu(II). Photoirradiation gives rise to a new peak due to a large exchange interaction; the exchange interaction difference between open- and closed- isomers was estimated by ESR spectral change to be more than 160-fold (Fig. 10).

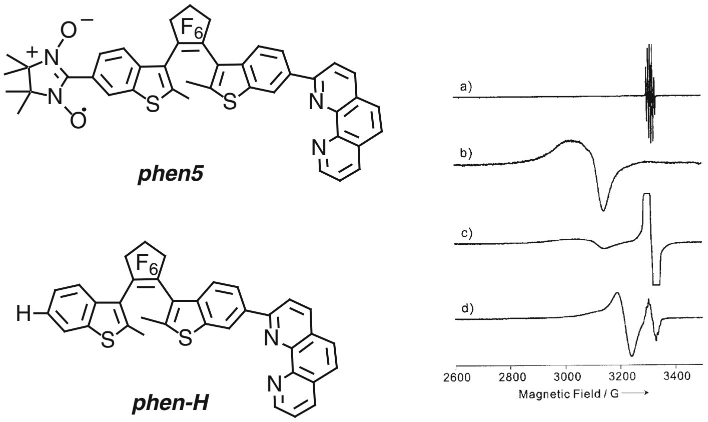
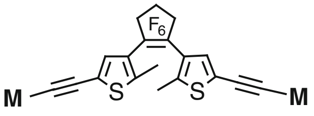


**Fig. 10** X-band ESR spectra in toluene solution at room temperature (9.33 GHz, 1 mW, 2,600–3,500 G region). **a** Spectrum of phen5. **b** Spectrum of Cu(hfac)$_2$(phen-H). **c** Spectrum of Cu(hfac)$_2$ (phen5). **d** Spectrum of closed-Cu(hfac)$_2$(phen5); (in the photostationary state under irradiation with 366 nm light). The spectra were obtained with 0.5 G modulation amplitude for **a**, and with 32 G modulation amplitude for **b**–**d**. The same sample was used for measuring spectra **c** and **d**. (Reprinted with permission from [80])

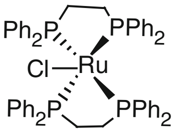
## 3.7 Photo- and Electrochromic Properties of Metal-Based DTE Derivatives

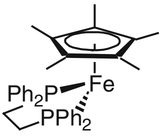
Electron transfer is an appealing process allowing the same transformation as in photochemistry, i.e., cyclization-reopening. In this context, the DTE unit has proven to be useful for the elaboration of photo and/or electrochromic metal-based systems specially devoted to the control of the electronic communication in bimetallic complexes. Organometallic complexes consisting of π-conjugated system bridging two redox active metal centers have proven to be efficient molecular wires (Fig. 11).

The attachment of the iron organometallic moieties [($\eta^5$-$C_5Me_5$)Fe(dppe)] (dppe = diphenylphosphinoethane) at the 5 and 5′-positions of the thiophene rings, using a C≡C as a linker group, improves the efficiency of the photochromic process, compared to that of the free alkyne which is unchanged even after prolongated UV irradiation. The electronic communication performance between the two metal centres could then be switched ON and OFF, as illustrated by the large difference of the $K_C$ (conproportionation constant) values of the two open and closed forms ($K_C$(ON)/$K_C$(OFF) = 39).



M = ($\eta^5$-$C_5Me_5$)Fe(dppe) [81]
Ru(dppe)$_2$(Cl) [82]





The utilization of the ruthenium carbon-rich fragments [Ru(dppe)$_2$(Cl)(C≡C)] gives rise to a light- and electrotriggered switch featuring multicolor electrochromism [82]. Quantitative cyclization occurs upon oxidation at remarkably low potential, far below pure DTE processes that generally occur around 1 V. This is the result of the unique electronic structure of the ruthenium complexes that leads, in radical species, to electronic delocalization on the carbon-rich ligand including the thiophene rings, allowing a radical coupling in the open state to form the more stable closed-ring isomer.

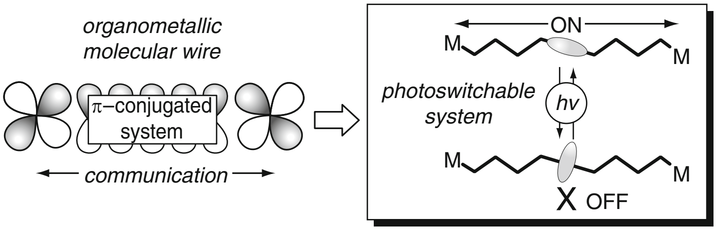
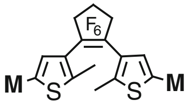


**Fig. 11** Organometallic photoswitchable molecular wires. (Reprinted with permission from [81])

Extension of this work by directly σ-bonding the DTE unit with the redox active metal fragments $M(\eta^5\text{-}C_5H_5)L_2$ (M = Fe, Ru; $L_2 = (CO)_2$, $(CO)(PPh_3)$, dppe) leads to bimodally stimuli-responsive, photo- and pseudoelectrochromic behavior with the remarkable switching factor $K_C(\text{closed})/K_C(\text{open})$ up to $5.4 \times 10^3$ [83].

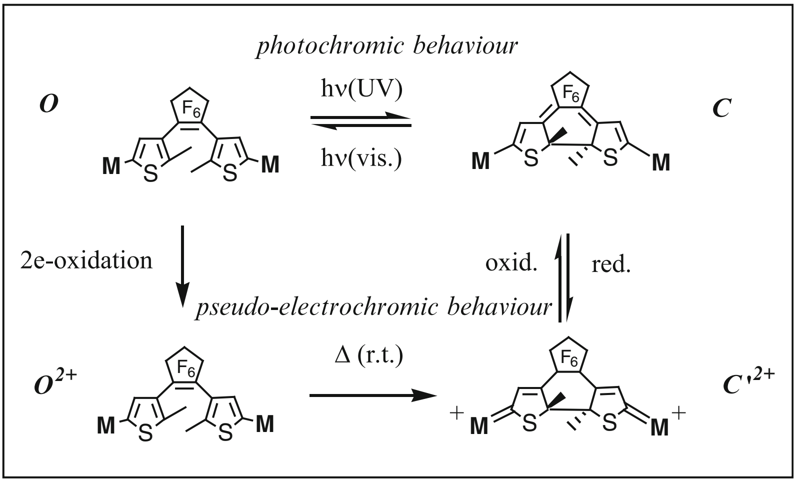


$M = (\eta^5\text{-}C_5H_4)Fe/Ru(CO)_2$

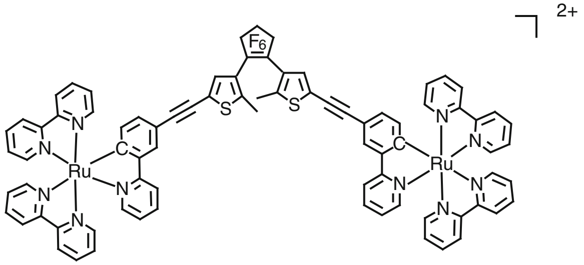
$(\eta^5\text{-}C_5H_4)Fe/Ru(CO)(PPh_3)$

$(\eta^5\text{-}C_5Me_4)Fe(dppe)$

It is noteworthy that the dicationic closed form $C'^{2+}$ is diamagnetic, as a result of the coupling of the radical centers. Its carbene structure has been established on the basis of NMR data and the crystallographic structures of isolated iron $C'^{2+}$species.



The "electrical communication" between metallic sites could be probed by the presence or absence of the intervalence transition when the mixed valence state of the system is formed. Coudret and Launay have demonstrated the ON/OFF switch of the intervalence transition of the dinuclear cyclometallated Ru complex; the mixed valence state is, however, unstable [84].



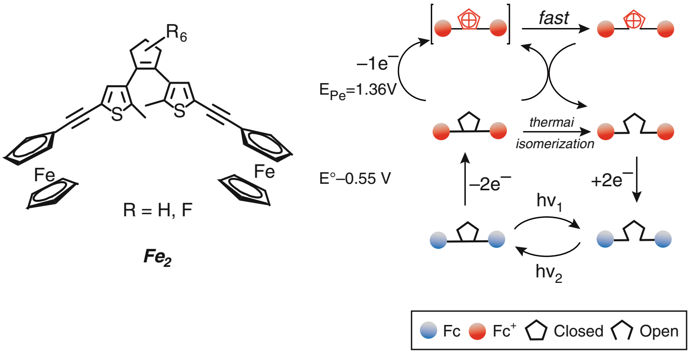
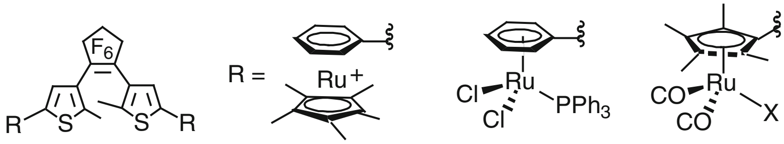


**Fig. 12** Proposed mechanism for the perfluorinated bimetallic $Fe_2$ system. (Reprinted with permission from [85])

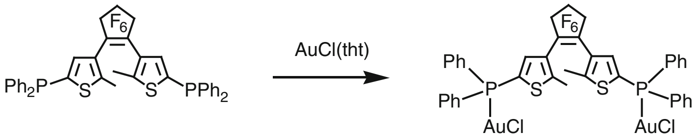
Later on, they investigated the bis(iron) derivative $Fe_2$ and showed that the presence of the ferrocenyl substituent makes possible a quantitative thermal reopening upon partial or complete oxidation of the redox active system without oxidizing the photochromic core [85, 86]. This process is catalytic in electrons in the case of the perhydro-DTE compound. The thermal reopening of neutral DTE unit is facilitated by electron-withdrawing substituent as *gem*-dicyanovinyl (Fig. 12).

## 3.8 Other DTE-Based Metal Complexes

The X-ray crystallographic structures of a series of DTE–organoruthenium complexes, DTE–$(RRuL_m)_n$ ($RRuL_m$ = $(\eta^6\text{-}C_6H_5)Ru(\eta^5\text{-}C_5Me_5)$: $n = 1,2$; $(\eta^6\text{-}C_6H_5)RuCl_2(PPh_3)$: $n = 1, 2$; $(\eta^5\text{-}C_5Me_4)Ru(CO)_2$: $n = 1, 2$) reveal the antiparallel conformation of the two thiophene rings suitable for the photochemical ring-closure. The efficiency of the photochromic process of these DTE–Ru complexes depends on the nature of attached metal fragments. However, no significant photochromic behavior is noticed for the benzofused derivative, and UV irradiation of the arene complexes of $(\eta^6\text{-}C_6H_5)RuCl_2(PPh_3)$ induces the irreversible dissociation of the arene ligand [87].



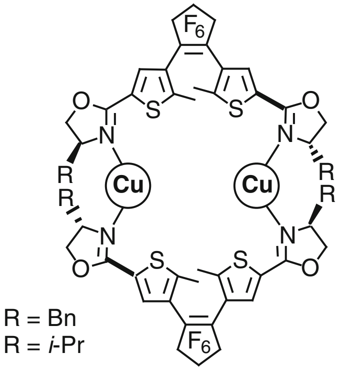
The DTE decorated with phosphine ligands has been coordinated to gold. The electronic differences between the two isomers of the free bis(phosphine) ligand was demonstrated by $^{31}P$ NMR spectroscopy [88].



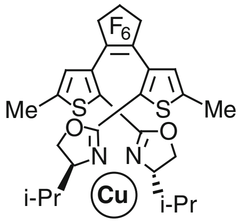
## 3.9 DTE-Based Ligands in Catalysis

Although examples of regulation of catalysis by azobenzene derivatives has been reported – a concept which relies on the changes in molecular geometry that result from the light-induced *cis–trans* isomerization – their successes are limited by the thermal reversibility of the azobenzene derivatives and cannot be used for practical applications. The approach developed by Branda takes advantages of the thermal stability of the DTE derivatives and harness the differences in geometry to regulate metal-catalyzed reactions [89].

The copper(I)-catalyzed cyclopropanation of styrene with ethyldiazoacetate was used as a model reaction.



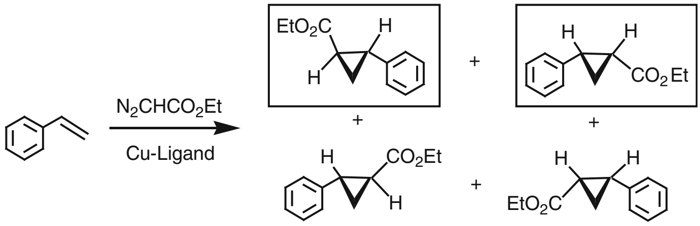
oxazoline rings at the C-2 position



***DTE-5-oxazoline***

oxazoline rings at the C-5 position

When the oxazoline ring is located at position 2 of the two thienyl rings of the DTE, optically pure binuclear helicate, composed of two DTE-based ligands wrapped around two copper centers, is formed. Since this open-ring form is flexible, the isomeric states of compounds do not affect the stereoselectivity of the cyclopropanation when they are used as ligands and neither the enantioselectivity nor the diastereoselectivity is significantly altered.



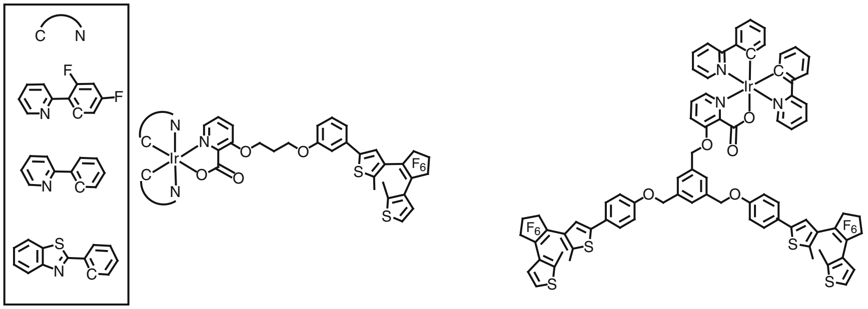
| | | |
|---|---|---|
| *Ring-open* 5-oxazoline DTE | 30% ee | 50% ee |
| *Ring-closed* 5-oxazoline DTE | <5% ee | <5% ee |

Changing the location of the oxazoline units from the “external” position to the internal position (position 5) allows the formation of a monomeric species in which the metal is in a $C_2$-chiral environment. Measurable but low enantioselectivities were observed by using the open-ring form whereas the closed-ring counterpart, isolated after UV irradiation, did not lead to significant stereoselectivity as a result of a more rigid architecture which prevents a suitable coordination site for the metal center.

## 3.10 Multi-DTE Metal Complexes

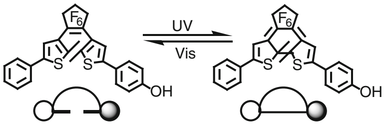
A few examples of metal complexes containing several DTE units have been reported. Generally, like their organic congeners [90–92], the conversion to the fully closed isomer is not observed; this is attributed to intramolecular transfer from the reactive state (open part) to the closed-ring DTE part, the lower-lying excited state.

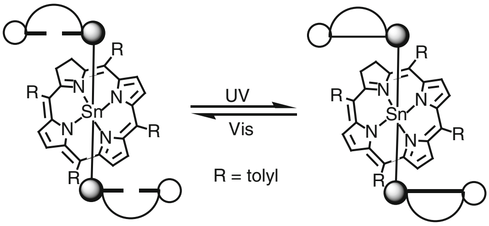
Phosphorescent heteroleptic Ir(III)-based switches were designed and synthesized; an additional enhancement of the phosphorescence modulation has been observed by incorporating two accepting DTE units [93].



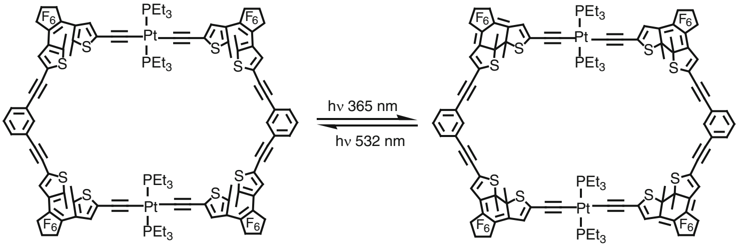
### 3.10.1 DTE-Based Phenolic Ligands (Oxy Anionic Ligands)

The preferential coordination of the tin(IV) porphyrins to oxyanionic ligands has been used for the elaboration of the photochromic fluorophore Sn(TTP)(DTE–Ph–O)$_2$ (TTP: 5,10,15,20-tetratolylporphyrinato) in which two phenolic derivatives of DTE (DTE–Ph–O) are axially coordinated in *trans* position. Small changes of the fluorescence intensity in the luminescence modulation are observed in the PSS [94].





*A Pt macrocycle* containing four DTE units has been described. Upon UV irradiation, two photo-induced cyclization reactions occur. The converted closed isomer Pt(*c*,*o*,*c*,*o*) has been isolated and characterized by $^1$H NMR spectroscopy. The high value of the cyclization quantum yield (0.64) is attributed to the enforced antiparallel conformation in the macrocycle [95].

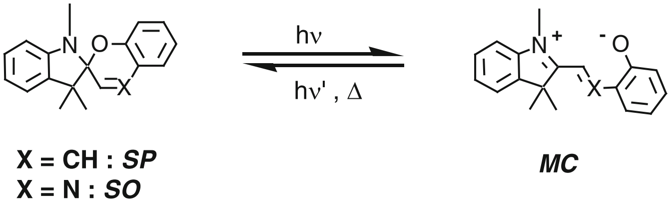


**Pt(*o*,*o*,*o*,*o*)** **Pt(*c*,*o*,*c*,*o*)**

## 4 Photochromic Spiropyran and Spirooxazine-Containing Metal Complexes

### 4.1 Introduction

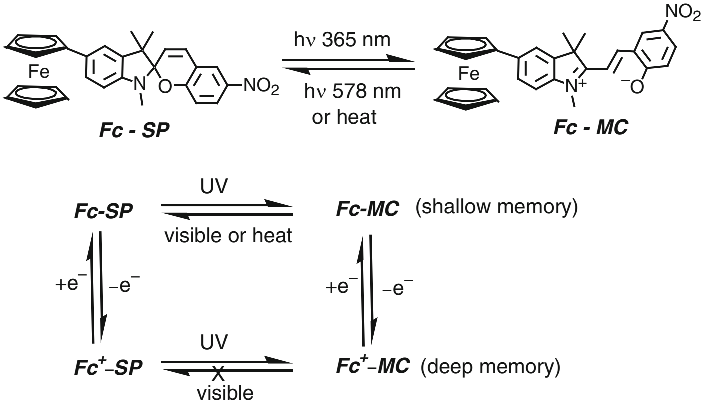
SP/SO are one of the most attractive classes of photochromic molecules and have been extensively studied due to their fatigue resistance and good photostability [96, 97]. The photochromic properties of SP were first recognized by Fischer and Hirshberg in 1952 [98]. The photochromism is attributed to the photochemical cleavage of the spiro C–O bond, forcing the molecule to open up. This ring-opening reaction results in the extension of the π-conjugation in the colored photomerocyanine (MC) form which is thermally unstable and readily reverted by thermal reaction or by absorption of visible-light irradiation (Scheme 13). Numerous studies on the nature of intermediates have been developed, including transient spectroscopy on the nanosecond timescale.



Scheme 13 Photochromic interconversion of a typical spiropyran and spirooxazine

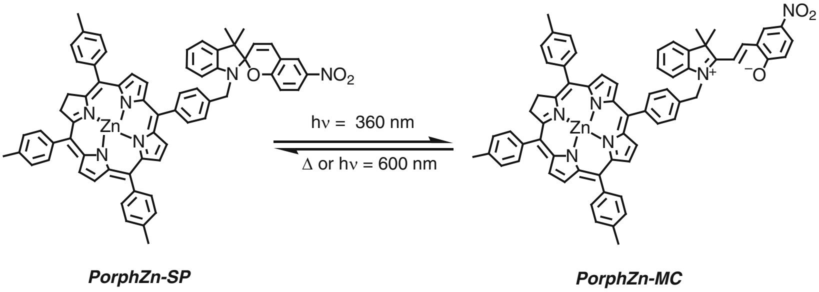
## 4.2 Ferrocenylspiropyran

Nishihara reported the synthesis of a ferrocenylspiropyran compound, and demonstrated that the thermodynamic stability of the MC form can be completely and reversibly switched by a combination of SP/MC photoisomerization and Fc/Fc$^+$ redox cycle [99]. Irradiation of a pale yellow solution of Fc–SP in methanol with UV light (365 nm) afforded a red purple solution ($\lambda_{max} = 530$ nm) ascribed to the open MC form. The MC molar ratio in the PSS was estimated to be 75% in methanol. The $\lambda_{max}$, yield in the PSS and thermodynamic stability were also found to depend on the polarity of the solvent: in dichloromethane the open form ($\lambda_{max} = 578$ nm) was formed in only 56% yield in the PSS, and isomerized to Fc–SP much faster than in methanol at 20°C. Upon chemical one-electron oxidation to the resulting Fc$^+$–SP, two new absorption bands appeared at 515 and 1,250 nm. This ferrocenium complex showed complete SP to MC photoisomerization with UV light irradiation and, unlike Fc–MC which readily isomerized to Fc–SP within few hours at 20 °C or upon visible irradiation, Fc$^+$–MC was stable towards heat and light. The reason for the MC stabilization by Fc$^+$ was not fully clarified, but the large blue shift for Fc$^+$–MC relative to Fc–MC suggested a strong electronic effect of Fc$^+$ as a result of π-conjugation. The reversible photoisomerization and redox cycle was also studied in a polymer matrix and showed the same behavior as that in solution.



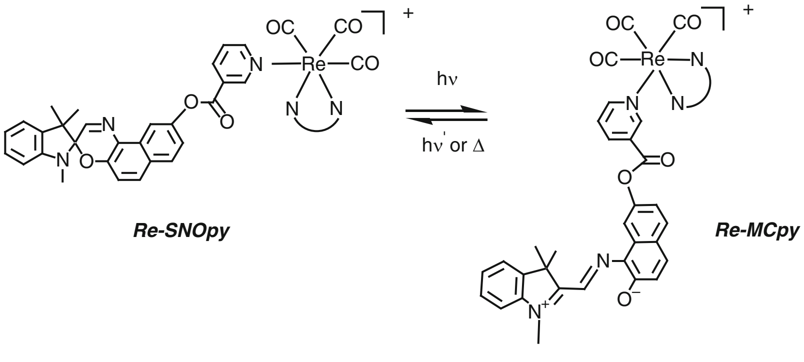
## 4.3 Porphyrin Spiropyran Metal Complexes

Bahr et al. have developed a new dyad by linking a photochromic nitrospiropyran moiety to a zinc ($Porph_{Zn}$–SP) porphyrin [100]. They showed typical photochromic behavior, i.e., conversion to the open merocyanine form upon UV excitation which in turn closes to the spiro form thermally or by irradiation into its visible absorption band. The emission properties of the two forms, $Porph_{Zn}$–SP and $Porph_{Zn}$–MC, were investigated. The fluorescence of the porphyrin is unperturbed by the attached SP moiety in the closed form, whereas the porphyrin first excited singlet state is quenched by the merocyanine with a quantum yield of 0.93, reducing the lifetime from 1.8 ns to 130 ps. The quenching of luminescence was assigned to a singlet–singlet energy transfer. Thus, this photoswitchable quenching phenomenon provides light-activated control of the porphyrin first excited states.



## 4.4 Spiropyran- and Spirooxazine- Containing Polypyridine Metal Complexes

SO are structurally and functionally very similar to SP. A series of rhenium complexes featuring a spironaphthoxazine-based pyridine ligand (SNOpy) $[Re(CO)_3(phen)(SNOpy)]^+$, $[Re(CO)_3(4,4'\text{-}Me_2\text{-bipy})(SNOpy)]^+$, and $[Re(CO)_3(4,4'\text{-}^tBu_2\text{-bipy})$

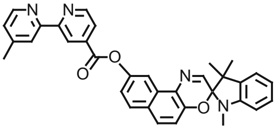


(SNOpy)]$^+$ (SNOpy: 1,3,3-trimethylspiroindoline naphthoxazine-9′-ylnicotinate) have been synthesized and their photochromic behavior demonstrated [101–103].

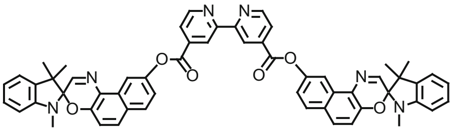
The Re–SNOpy complexes exhibit strong luminescence; the two emission bands are attributed to the ligand-centered (LC) fluorescence and phosphorescence. An assignment as MLCT phosphorescence was ruled out, since the emission energies are insensitive to the diimine ligands, irrespective of their different π* orbital energies. The formation of the MC (Re–MCpy) open form upon MLCT excitation is suggestive of an efficient photosensitization of Re–SNOpy by the MLCT excited state. It is likely that an intramolecular energy transfer from $^3$MLCT to the SNOpy moiety occurs, to give the $^3$SNOpy state, which would either return back to the ground state with emission of light or undergo the ring-opening process to give the colored Re–MCpy form.

The Re–MCpy form is thermally unstable and readily undergoes thermal bleaching which follows first-order kinetics to the closed form. The decoloration rate constant of the Re–MCpy form strongly depends on temperature and on the nature of the solvent used, the zwitterionic Re–MCpy form being more stabilized in polar solvent such as MeOH. This constant decreases, to a small extent, upon addition of $ZnCl_2$; this could be attributed to the stabilization of the Re–MCpy form by the formation a $Zn^{2+}$ complex [101].

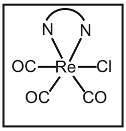
The related 2,2′-bipyridine derivatives have been prepared and incorporated in Re complexes $[Re(CO)_3(Cl)(N,N\text{-SNObipy})]$ [102]. Their X-ray crystal structure reveals an orthogonal arrangement of the indoline and naphthoxazine planes (interplanar angle 88°2″) and a relatively longer spiro C–O bond (1.47 Å), these features are commonly observed in related systems. Unlike the Re–SNOpy complexes $[Re(bipy)(CO)_3(SNOpy)]^+$, Re–SNObipy complexes do not exhibit any photochromism with MLCT excitation. This is probably because the energies of the $^3$MLCT excited state of the complexes estimated from the phosphorescence of the complexes (~166–188 kJ mol$^{-1}$) are insufficient for the sensitization when compared to the triplet excitation states of spironaphthoxazines (~210–225 kJ mol$^{-1}$). The switching of their emission properties ($^3$MLCT to $^3$LC phosphorescence of the merocyanine moiety) upon conversion to the open form has been reported.



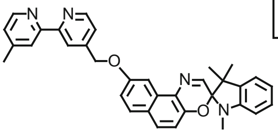
***SNObipy1***



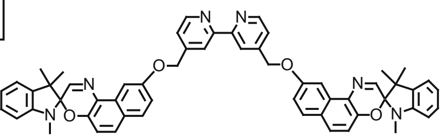
***SNObipy2***



***Re-SNObpy***



***SNObipy3***



***SNObipy4***

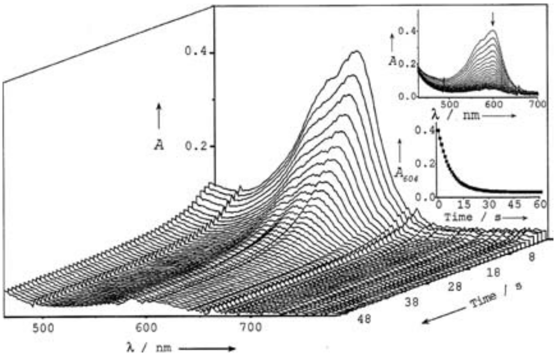
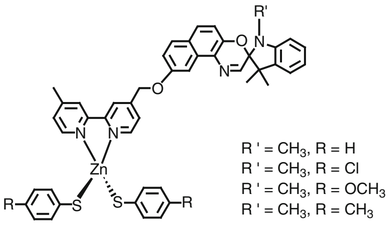


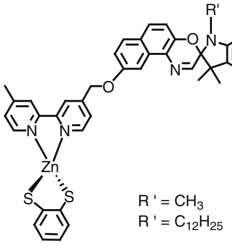
**Fig. 13** Time-dependent UV–visible absorption spectral changes in the open form of Re(CO)$_3$(Cl)(SObpy4) in acetonitrile after excitation at 365 nm. The *inserts* show the overlaid UV–visible absorption spectra at different decay times and the decay trace at the absorption maximum at 604 nm with time. (Reprinted with permission from [102])

The kinetics for the bleaching process (Re–SNObipy to Re–MCbipy) have been determined for both the free ligands and the complexes (Fig. 13).

By incorporating these SNObipy ligands into various metal complex systems, their photochromic properties can be tuned and perturbed without the need for tedious synthetic procedures for the organic framework. As an extension of her work, Yam investigated a series of substituted spironaphtoxazine containing 2,2′-bipyridine and their Zn complexes bis-thiolate [103]. Upon excitation at 330 nm, all the ligands and complexes exhibit photochromic behavior.

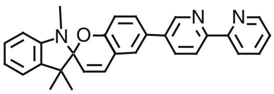


**Zn-SNObipy3**

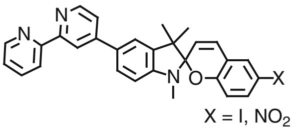


**Zn-SNObipy3**

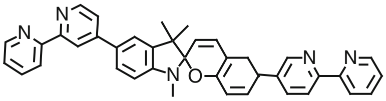
SP or SO units have also been bounded to 2,2′-bipyridine and 1,10-phenanthroline: (1) the bipyridine moiety has been attached either to the pyran part (SPbipy1) or the indoline part (SPbipy2) of the SP skeleton, (2) the bipyridine ligand SPbipy3



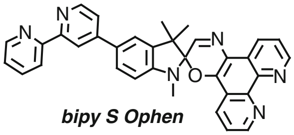
**SP bipy1**



**SP bipy2**



**SP bipy3**

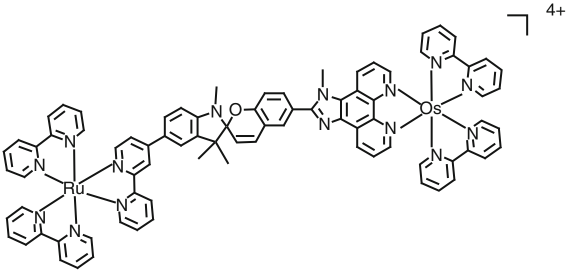


**bipy S Ophen**

bears a bipyridine at each end of the SP skeleton, (3) a phenanthroline-based SO attached to a bipyridine ligand (bipySOphen) [104].

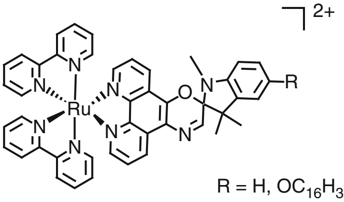
The photophysical, photochemical, and redox properties of mononuclear complexes $[M(bpy)_2(NO_2\text{–}SPbipy)]^{2+}$ (M = Ru, Os) have been investigated [105]. These metallated nitrospiropyran compounds undergo efficient electrochemically induced conversion to the merocyanine open form, by first reducing the closed form and subsequently reoxidizing the corresponding radical anion in two well-resolved anodic steps. Metal complexation of the SP results in a strongly decreased efficiency of the ring-opening process as a result of energy transfer from the reactive excited SP to the MLCT excited state. The lowest excited triplet state of the SP in its open MC form is lower in energy than the excited triplet MLCT level of the $[Ru(bpy)_3]^+$ moiety but higher in energy than for $[Os(bpy)_3]^+$, resulting in energy transfer from the excited ruthenium center to the SP but inversely in the osmium case.

The heterobinuclear complex *Ru–SP–Os* has been synthesized by using the "chemistry-on-the complex" strategy [70]. To the Ru mononuclear complex a free chelating site was introduced, to which the Os moiety was subsequently connected. However, this dinuclear complex was shown to be inactive; no conversion to the open form occurs whatever the irradiation wavelength used (UV or visible (450 nm) light).



***Ru-SP-Os***

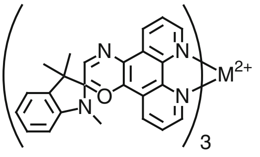
A dramatic increase in the ring-closing rate was observed for the *Ru–R–SOphen* (R = H, $C_{16}H_{33}$) complexes, the effect being attributed to the strong electron-donation ($d_\pi Ru \rightarrow \pi^*(N,N)$) of the organometallic fragment $[Ru(bipy)_2]^{2+}$ [106].



R = H, $OC_{16}H_{33}$

***Ru-R-S Ophen***

A series of $M^{II}$tris(spiro[indolinephenanthrolinoxazine]) (Mn, Fe, Co, Ni, Cu, Zn) have been synthesized, resulting in tunable and significantly increased photoresponsivities (photocolorabilities) [107]. A significant stabilization of the MC form results from metal complexation. An increase in charge density in the oxazine of the molecule leads to destabilization of the MC form Metal complexation is expected to decrease the negative charge density of the oxazine moiety through inductive effects and to increase the charge density through $d_{\pi}\mathrm{M} \rightarrow \pi^*(N,N)$ donation. The increase in MC stability suggests that inductive effects play a dominant role.

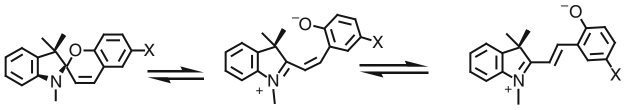


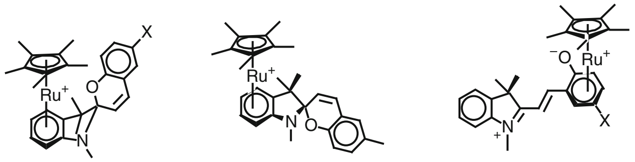
M = Zn, Fe, Co, Mn, Ni, Cu

**M-SOphen**

## 4.5 Diastereomeric Isomerism in $[(\eta^6\text{-spirobenzopyran})\mathrm{Ru}(\mathrm{C_5Me_5})]^+$

$\eta^6$-Coordinated spirobenzopyran complexes are known for ruthenium and chromium. Ruthenium–arene complexes $[(\mathrm{C_5Me_5})\mathrm{Ru}(\eta^6\text{-SP–X})]^+$ (SP–X benzopyran) are formed as two diastereoisomers where complexation occurs in the indoline (A) or dihydrobenzopyran part (B) of the SP–X ligand [108]. UV irradiation of A does not cause any color change, but induces an inversion of the configuration of the chiral spiro carbon atom (A′).





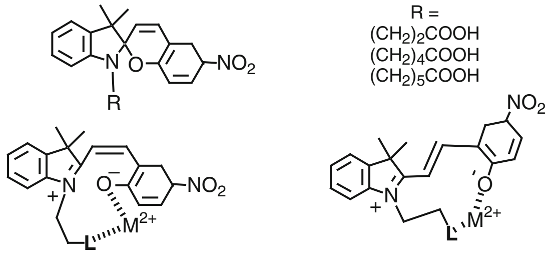
**A** **A'** **B**

($\eta^6$-SP)Cr(CO)$_3$ complexes (A ring adducts) were studied, the ring formation during their synthesis and ring-closing reaction during and after UV irradiation proceeding diastereoselectively to let chromium atom and oxygen atom of the pyran part located on the same side of the indoline ring [109].

## 4.6 Complexes of Spiropyrans with Metal Ions

Intramolecular bidentate metal ion chelation ($\mathrm{Ca^{2+}}$, $\mathrm{Zn^{2+}}$) gives rise to thermally stable SP/MC photoswitches [110, 111]. The addition of $\mathrm{Zn(ClO)_4}$ and $\mathrm{Cu(ClO_4)}$

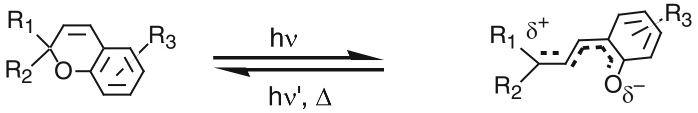
gives rise to the stabilization of two geometric isomers, *cis*-MC and *trans*-MC, via the coordination to the COOH coordinating group attached to the indolino ring. This is the first evidence of the *cis*-MC isomeric form being observable by UV–visible spectrophotometry over a significant period of time [112].



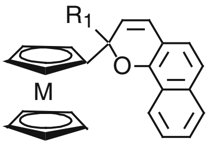
***cis-MC*** ***trans-MC***

## 5 Photochromic Metallocenyl Benzopyran Derivatives

Like SP, benzopyrans are converted under UV irradiation into colored merocyanine forms. The reaction is reversible and the back closure reaction takes place either thermally or upon irradiation in the visible range.



A series of ferrocenyl compounds such as **14** have been prepared and their photochromic properties investigated [113–115]. These studies have shown that the introduction of a ferrocenyl group in the 2-position modifies the photochromic behavior of these compounds, i.e., an extended wavelength range with two absorption bands around 450 and 600 nm for the open form, an increased of the closure kinetic constants and a good resistance to fatigue. More recently, the synthesis and photochromic properties of the corresponding ruthenocenyl **15** and osmocenyl **16** derivatives have been reported. These complexes showed only one absorption band in the visible region near 500 nm, but again an increase of the

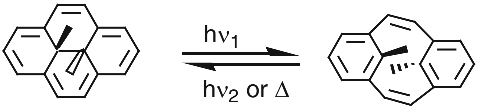


M = Fe: **14**; Ru : **15**; Os : **16**
$R_1$ = Me, Ph

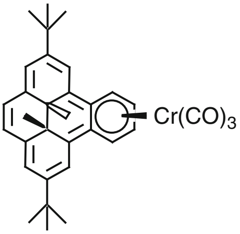
bleaching kinetics, when compared to the parent alkyl- and phenyl-substituted benzopyrans.

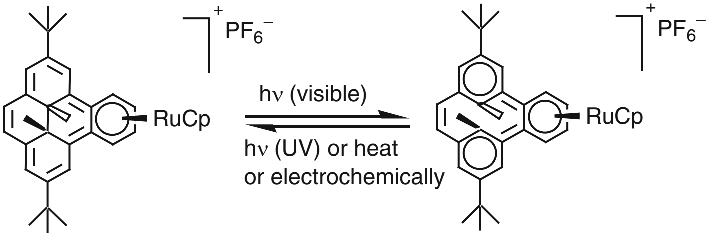
## 6 Dimethyldihydropyrene Metal Complexes

Among the diarylethene family, the dimethyldihydropyrene (DHP)/cyclophanediene (CPD) system is interesting because it is a rare example of negative photochrome, where the thermally stable DHP closed form is colored. Upon irradiation with visible light, DHP is converted to the colorless, open CPD form, and the reverse reaction occurs either photochemically with UV light or thermally [116, 117].

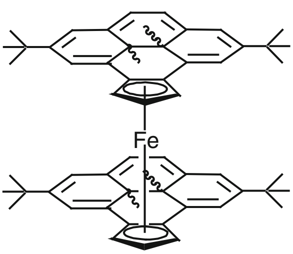


Only a few examples of organometallic complexes featuring DHP derivatives are known. Mitchell and coworkers have recently reported the synthesis and photochromic properties of benzodimethyldihydropyrene chromium tricarbonyl and ruthenium cyclopentadienyl complexes, in which the $Cr(CO)_3$ and $Ru(C_5H_5)^+$ fragments are coordinated to the fused benzene ring [118, 119]. The photochromic behavior of these compounds were studied and found to depend on the nature of the organometallic moieties. Surprisingly, the chromium complex did not show any photoisomerization at all. Conversely, the ruthenium complex was found to photo-open quantitatively, but at 30% of the rate of the uncomplexed parent compound. Interestingly, photo-closing of the CPD to the DHP form occurred either photochemically with UV light, electrochemically on reduction, or thermally.

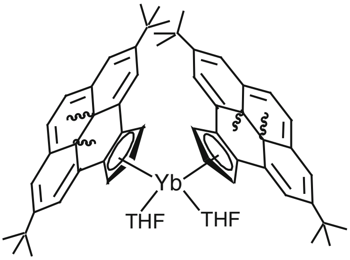




More recently, Mitchell, Berg and coworkers prepared divalent ytterbium and iron metallocenes based on cyclopentadienyl-fused DHP [120]. These complexes were isolated as a mixture of *rac* and *meso* isomers in 3:2 and 1:1 ratio for Fe and Yb, respectively. Their photochemical reactivities were also investigated, and photolysis in the visible at $\lambda > 490$ nm did not result in isomerization to the CPD opened forms, in contrast to the lithium salt LiCpDHP [121].

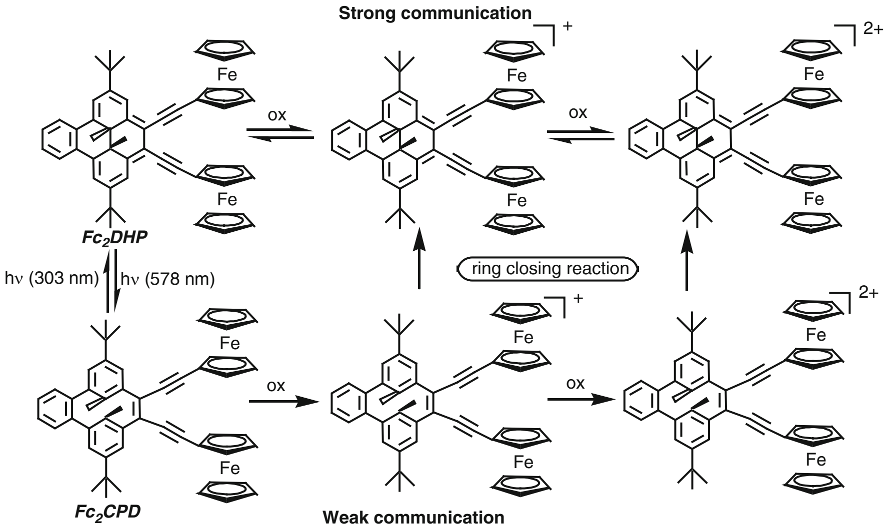


**Fe(CpDHP)$_2$**



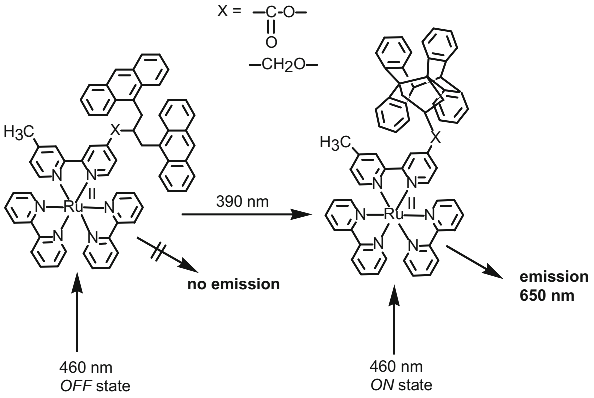
**Yb(CpDHP)$_2$(THF)$_2$**

Very recently, Nishihara and coworkers prepared a bis (ferrocenyl)dimethyldihydropyrene (*Fc$_2$DHP*) in which DHP and metal complexes are connected through an ethynyl moiety [122]. This complex exhibits both reversible DHP/CPD photochromic behavior and photoswitching of the electronic communication the two ferrocene sites. In addition, Fc$_2$CPD also showed a redox-assisted closing reaction of the photogenerated CPD form with oxidation of the ferrocene moieties. This system is unique since the ring-closing is triggered by oxidation of not the DHP unit but the ferrocene moiety.



## 7 Other Photochromic Metal Complexes

A photochromic dianthryl molecule can act as a triplet energy transfer quencher when combining with a ruthenium diimine complex [123]. UV excitation of the systems (X = $CH_2O$, C(O)O) results in a photoinduced cycloaddition of the dianthryl unit, leading to an increase of the luminescence intensity. Near-field optical addressing of this luminescent photoswitcheable system (X = $CH_2O$) as a dopant in PMMA films has been demonstrated [124] (Fig. 14).



This work is based on work previously reported by Belser and De Cola on a Re complex in which the bipyridine ligand incorporates an anthryl derivative [125].

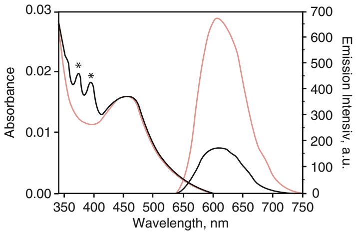
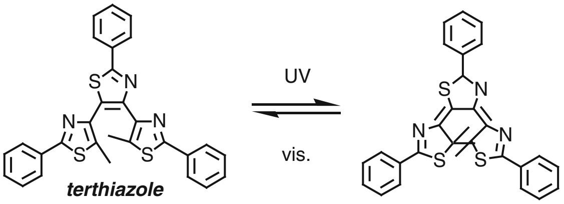


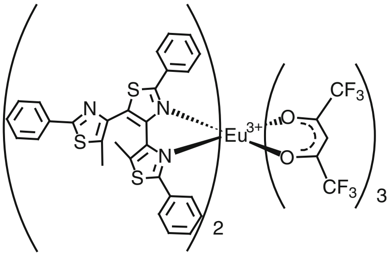
**Fig. 14** *Black lines*: absorption and emission ($\lambda_{exc} = 360$ nm) spectra measured for Ru-anthryl (X = $CH_2O$) for dispersed in a 45 ± 5 nm thick PMMA film. Absorption peaks associated with the dianthryl unit are indicated by *asterisk*. *Red lines*: analogous spectra measured following the formation of the cycloadduct by 400 nm irradiation (10 mW, 5 min) of a ~18 mm diameter circular area of the doped PMMA film. (Reprinted with permission from [124])

## *7.1 Terthiazole Derivatives*

The luminescence of the Eu(III) complex Eu(THIA)$_2$(HFA)$_3$ (THIA: 4,5-bis (5-methyl-2-phenylthiazole) is efficiently quenched when the photochromic ligand THIA is converted from the colorless ring-open form to the closed-ring form upon UV light irradiation, resulting in change of the emission intensity [126].



***terthiazole***
***THIA***



***Eu(THIA)$_2$(HFA)$_3$***

# 8 Conclusion

A number of systems where photoresponsive molecules are used as ligands to form metal complexes, mono- or multimetallic, have been reported during the last decade. Such complexes exist for a wide range of metal centers (Cr, Mo, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pt, Cu, Ag, Au, Zn) and more recently lanthanides (Eu). The photochromic properties of the organic framework were found, in some cases, to be enhanced by complexation and, as its organic counterpart, also effective in single-crystalline phase.

These reports shows that the photochromic properties could be readily tuned by changing the nature of the metal system without modifying the photochromic ligand. Thus, by a rational design of metal centers, ancillary ligands, and counter-anions, photochromic behavior can be controlled or modified. In addition, triplet reaction pathways have been demonstrated, allowing the extension of the excitation wavelengths to lower energies, which are less destructive. Finally, these metal systems allow the photomodulation of various properties such as luminescence, second-order nonlinear optics, and magnetic or electronic interaction for which the presence of the organometallic fragment is crucial for the properties mentioned. These investigations were initiated 10 years ago and yet this field still has to be explored.

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