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Metal-based Photoswitches Derived from Photoisomerization

Shoko Kume · Hiroshi Nishihara (✉)

Graduate School of Science, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku,
113-0033 Tokyo, Japan
nisihara@chem.e.u-tokyo.ac.jp

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Abstract A combination of photochromism and other molecular functionalities is an efficient way to construct novel multi-mode photofunctional molecules. From this perspective, a considerable number of photochromic metal complexes involving photochromic moieties and coordination compounds with unique electronic, magnetic and optical properties have been investigated. One research point of interest in the photochromic complexes focuses on how metal coordination affects the isomerization behavior of the photochromic moiety. Proper molecular structural design can more strongly stabilize a metastable state in support of feasible metal–ligand interactions, improving the thermal durability of the molecular photomemory. Moreover, isomerization can be caused not only by the excitation at the photochromic moiety, but also by the stimulation (light or electron) at the metal complex moiety. The multi-moiety combined response may be able to construct an integrated memory or a logic gate in a single molecule. Another research point of interest focuses on how structural conversion at the photochromic moiety affects electromagnetic properties at the complex moiety. Several studies have shown how photon information/energy is converted to luminescence, an electronic signal, or a magnetic response at the complex moiety. Interactions between multiple complex moieties can also be reversibly tuned with light when the photochromic moiety is used as a spacer between them. Here we review recent studies on the combination of photochromic moieties with coordination compounds, categorizing the research findings according to the structure of the photochromic moieties.

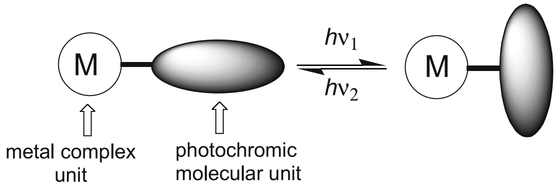
Keywords Metal complex · Multi-mode function · Photochromism

1
Introduction

Photochromic molecules for which the structure – more specifically, the electronic structure and color – changes reversibly in response to photoirradiation have attracted much recent attention because of their possible applications in the area of photon-mode high-density information storage and photo-switching devices. Thus far, many photochromic molecules have been found, including spiropyran, spiroxazine, chromene, fulgide, diarylethene, stilbene, azobenzene, and so on [1]. In the research regarding such compounds, the tuning of their photochromic and other properties by introducing appropriate substituents has been explored, and the development of hybrid materials with polymers and liquid crystals to achieve conversion of photo-signals into other signals has been extensively investigated.

In addition, molecules that can act as devices by themselves have attracted much recent attention in the field of molecular-scale electronics [2]. Such molecules are required to show bi-stable or multi-stable states that can be reversibly interconverted by applying external stimuli such as photons, electrons, protons, and so on. Metal complexes are excellent candidates that have been known to exhibit unique physical properties that can respond to various stimuli from an external field. It is thus an effective approach to make device-performing single molecules from a combination of metal complex units with photochromic molecular units in a single molecule. There are two interesting questions with regard to the photochromic molecule-containing metal complexes (Fig. 1). First, what are the effects of metal complex units on the photo-transformation of the ligand? And second, what are the changes in the physical properties of metal complex units caused by the ligand transformation?

In the present article, we provide an overview of the studies dealing with metal complexes with photochromic ligands. It should be noted that there are certain photochromic metal complexes that show their photochromism



Interest in metal complexes with photochromic ligand(s) is twofold.

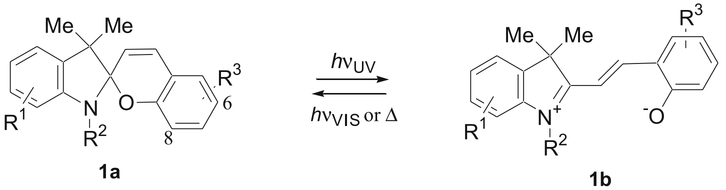
1) Effects of complex units on the isomerization of azo units.
2) Changes in physical properties of the complex by isomerization of the azo units.

Fig. 1 Concept of photochromic molecule-bound metal complexes by a change in the coordination structure or intermolecular interactions, but they will not be included in this review.

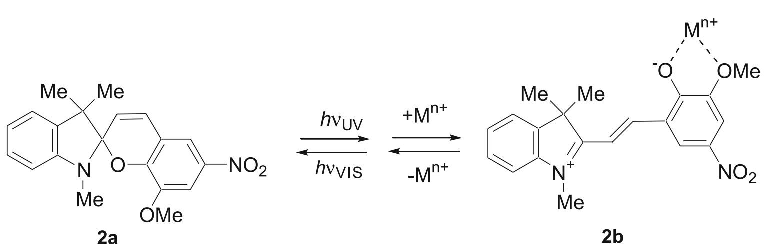
2
Spiropyran-, Spirooxazine-, and Chromene-Attached Complexes

The thermodynamically stable form of spiropyran (**1a**) is almost colorless and has a closed structure of two doubly fused rings. UV light irradiation to this closed form cleaves the C – O bond to give a colored open form, *trans*-merocyanine (**1b**), with extended π-conjugation (*cis*-merocyanine is formed as a short-lived reaction intermediate). Merocyanine **1b** returns to **1a** by visible-light irradiation or by heating. Spirooxazine and chromene undergo similar photochromic reactions between closed and open forms. The thermodynamic stability balance between spiropyran and merocyanine forms is considerably altered by the electronic effects of substituents on the backbone. Among the spiropyran family, spiropyrans with a nitro group at the six-position have been widely employed for the study of photochemistry. It has been found that when a heteroatom (O, N, etc.) is attached to the eight-position, steric hindrance makes it difficult for the closed spiropyran form to bind to a metal ion, but the open form can act as a good chelating ligand [3]. As a result of this finding, numerous studies investigating the relationship between the complexation of *d*- and *f*-transition metal ions and photochromic properties have been carried out.

A spiropyran with a methoxy group at the eight-position, **2a** and its derivatives show a blue shift of the absorption peak when a metal ion is attached to form a chelate complex, **2b** [4, 5]. The type of metal ion has little effect on the wavelength of the absorption maximum, λ_{max}, but it has a strong influence



1a **1b**

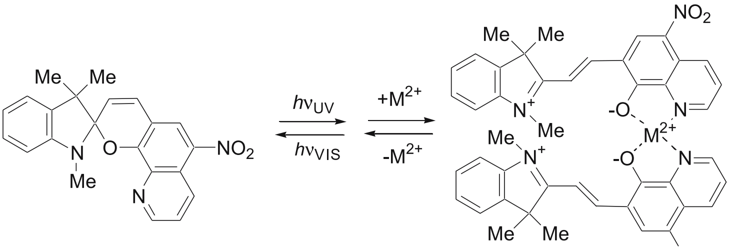


2a **2b**

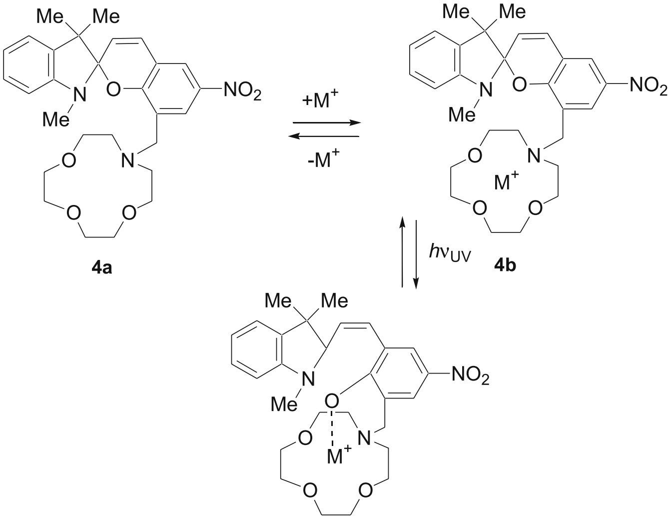
on the stability of the photo-excited state. The photo-reaction mechanism and kinetics upon the complexation of the merocyanine form with metal ions have been analyzed [6, 7].

The coordination ability of the merocyanine form has been utilized for the sensing of heavy metal ions. For example, the $\lambda_{\max}$ of *trans*-merocyanine form of nitroquinospiropyranindoline (**3a**) is 580 nm, which shifts to 518–538 nm by coordinating the N and O atoms to Zn^{2+}, Co^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, or Ni^{2+} ions; the degree of the shift depends on the type of metal ion [8, 9], and this phenomenon has been utilized for application in the selective sensing of metal ions.

The ability to tune the photochromic behavior of crown ether-bound spiropyrans, **4a** and **5a**, by connecting them to metal ions, was investigated by Kimura and his coworkers [10, 11]. This complexation of the crown ether moiety with a metal ion accelerates the transformation from spiropyran, **4b** to merocyanine, **4c**, by light or heat. When this complexation effect is weak, thermodynamic equilibrium favors the spiropyran form, and



3a **3b**



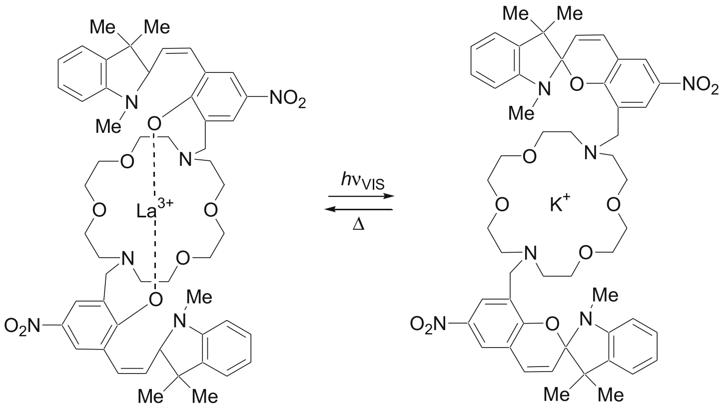
4a **4b**

4c

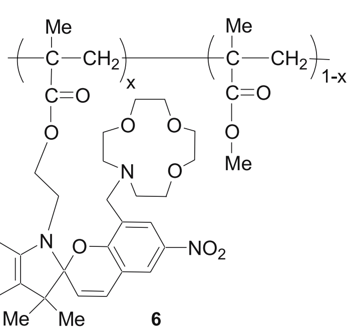
transformation to the merocyanine occurs upon UV light irradiation. On the other hand, when the complexation ability is strong, thermodynamic equilibrium lies further to the merocyanine form and UV light irradiation results in transformation to the spiropyran form. This result implies that the direction of the photoisomerization can be switched by metal coordination. Crowned bis(spiropyran) **5a** causes the coordination metal to change from La^{3+} to K^+ by visible light irradiation leading to merocyanine-to-spiropyran isomerization [11]. Crowned spiropyran vinyl polymers, **6**, also have a photochromic ability to show photoresponsive ion-conducting behavior [12].

5-Ferrocenylspiropyran, **7**, can control the stability of the merocyanine form by changing the oxidation state of the ferrocene moiety [13]. This system works not only in liquid solution but also in a polymer electrolyte.

Spironaphthoxazine with a crown ether, **8**, also shows photochromic behavior that is sensitive to the type of alkali and alkaline earth metal ions [14]. Other derivatives of spiropyran and spirooxazine, **9–12**, which can chelate metal ions were synthesized, and the effects of complexation on their photochromic behavior have been investigated [15–17].



5a **5b**



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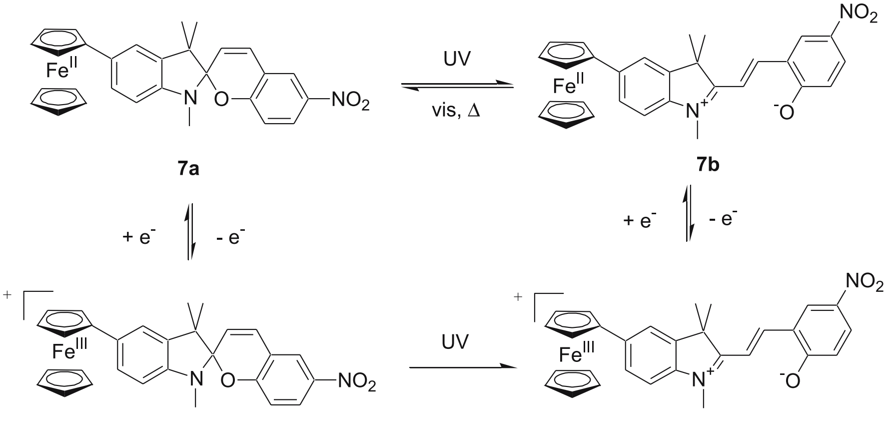
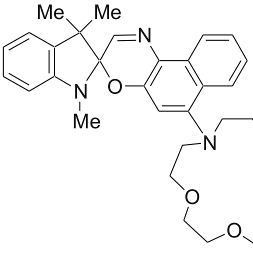


7a **7b**

7c **7d**



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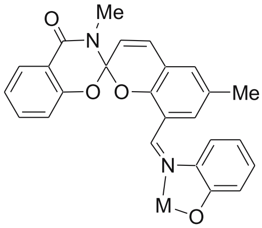

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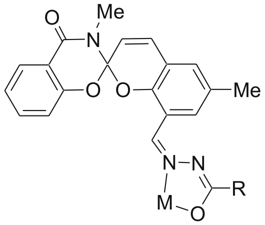

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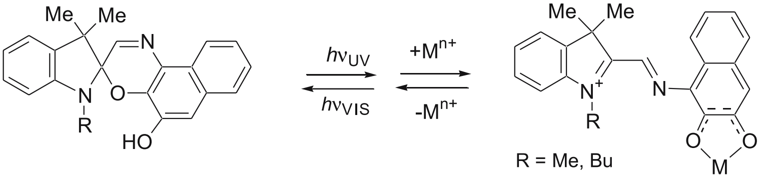
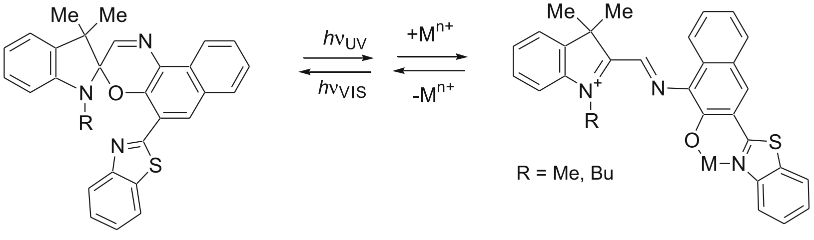
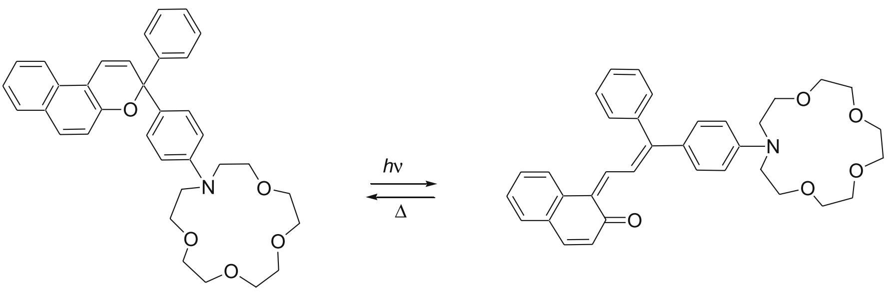


11a **11b**

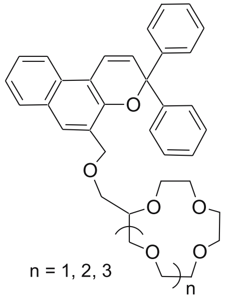


12a **12b**

The effects of the reversible photochromic reaction of an azacrown-containing benzochromene **13** on complex formation with Ca^{2+} in acetonitrile were studied by Ushakov et al. [18]. It was found that both the initial chromene **13a** and its photoinduced merocyanine isomer **13b** are able to form 1 : 1 complexes with Ca^{2+}, and the complexation causes strong spectroscopic shifts, leading to an increase in the dark lifetime of **13b.** The equilibrium constant for the 1 : 1 complexation decreases upon photoinduced ring-opening reaction. Another series of chromene derivatives with crown ethers, **14**, not only show photochromism but also induce aggregation to form the 1 : 2 complex, resulting in the switching of the complex stoichiometry by UV irradiation [19]. Compound **14** also exhibits ion-responsive



13a **13b**



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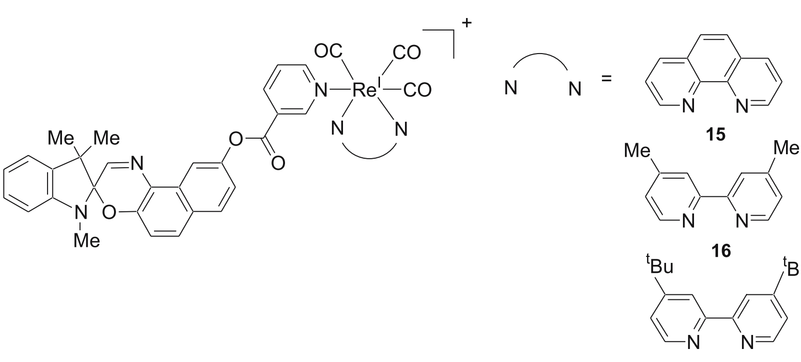
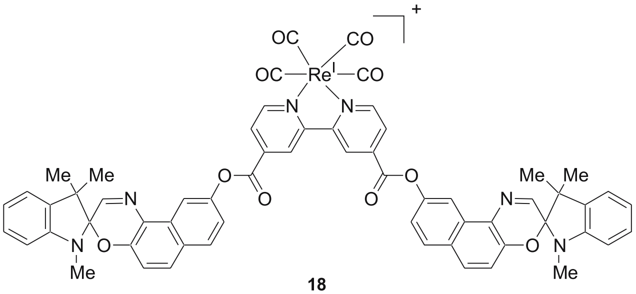


photochromism depending on the metal ion-binding ability of their crown ether moieties.

A series of spironaphthoxazine-containing Re^{I} tricarbonyl diimine complexes, **15–21**, were prepared by Yam and her coworkers [20, 21]. All the



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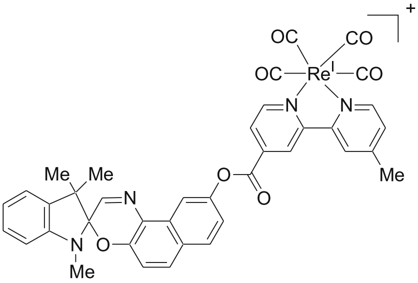

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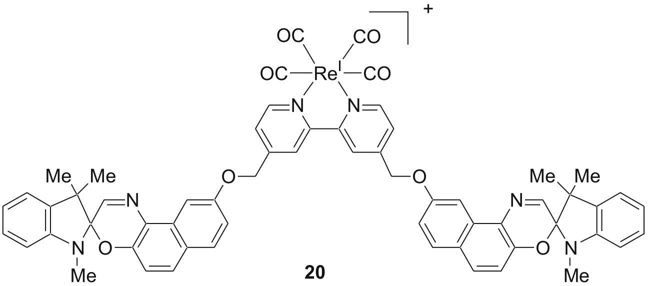

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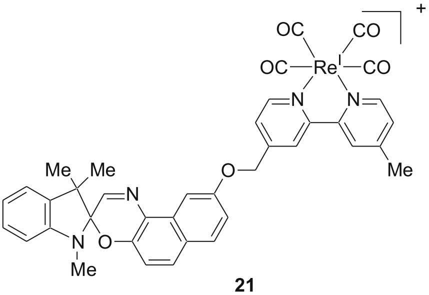

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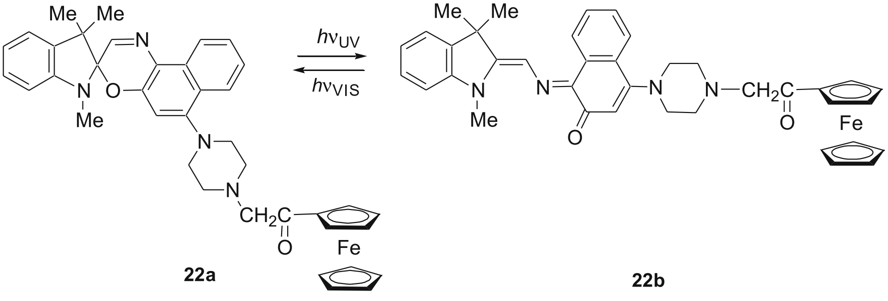


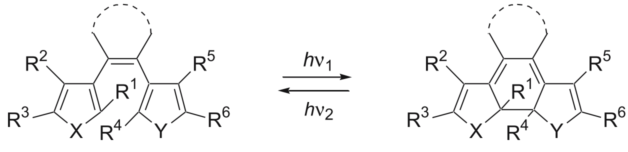
22a **22b**

complexes undergo a photochromic reaction upon irradiation at 365 nm, exciting the $\pi - \pi^*$ transitions, and **15–17** also react upon irradiation at 420 nm, exciting the MLCT ($d\pi \rightarrow \pi^*$ (diimine)) transition [20]. The complexes **18** and **19** exhibit strong ^{3}MLCT phosphorescence at 642 and 600 nm, respectively, in EtOH/MeOH/CH_2Cl_2 glass at 77 K, and this emission band would be switched to LC phosphorescence of the photomerocyanine moiety at 705–710 nm upon conversion to the open form [21].

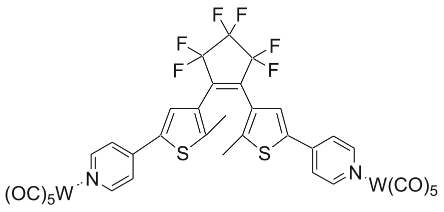
A ferrocene moiety-attached spironaphthoxazine derivative, **22a**, which isomerizes into a thermally stable merocyanine form, **22b**, and its application in rewritable high density optical data storage have been reported by Song et al. [22].

3
Diarylethene-Attached Complexes

Diarylethene, **23a**, found by Irie and Mohri [23], exhibits phototransformation into a closed form, **23b**, and has various advantages, such as high stability, high reversibility, high reproducibility, high quantum yield, and a large difference in λ_{max} between the two forms [24]. Fernández-Acebes and Lehn synthesized W, Re and Ru complexes of pyridyldithienylethenes, **24–28**, and showed their pronounced photochromic properties [25, 26]. Irradiation of the open forms of **24–27** with UV light was found to result in essentially quantitative photocyclization to the closed forms, and the back reaction occurred



23a **23b**



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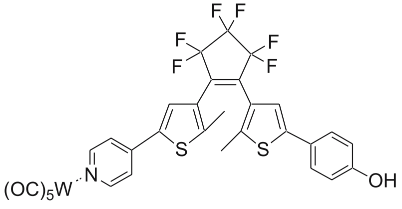

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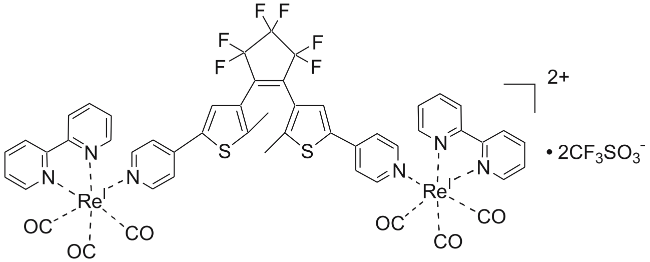

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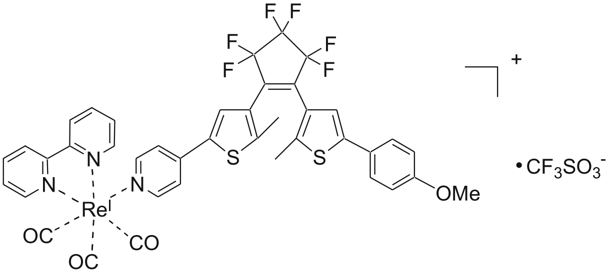

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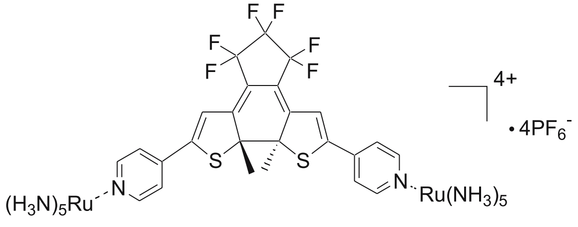

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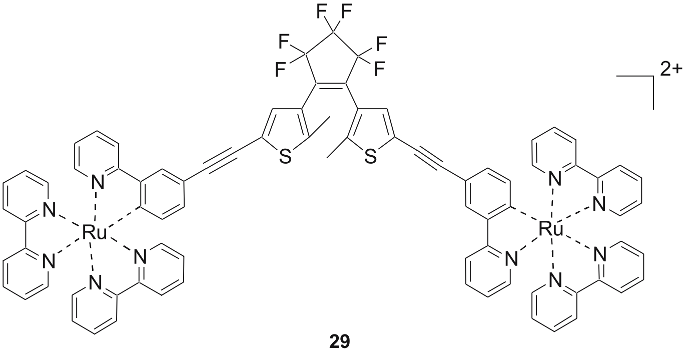
by irradiation with visible light of λ > 600 nm. The complexes display a fluorescence discrimination between their open and closed forms. In contrast, the closed form of a Ru complex, **28**, is photochemically stable.

Fraysse et al. have synthesized a derivative with two ruthenium centers, **29**, and have investigated its photochromic and redox properties [27]. The closed form of this complex is obtained with 254-nm light irradiation in 75%



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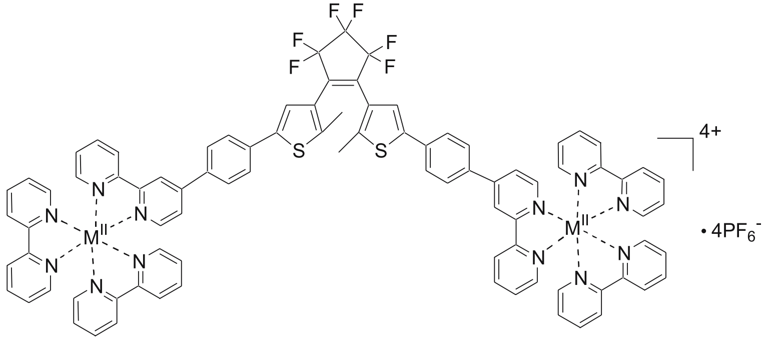
yield. The redox potentials of the Ru^{III}/Ru^{II} couple are almost the same in both open and closed forms (0.53 and 0.52 V vs. SCE, respectively). In the oxidized form of this complex, the open form shows no absorption band in the near-infrared region, whereas the closed form exhibits an intervalence charge transfer (IVCT) band at wavelengths longer than 1000 nm due to the formation of a stable mixed-valence state. This result implies that the electron communication between two metal sites is controlled by the photochemical transformation of the bridging diarylethene moiety. A gradual ring-opening process in the oxidized state of the closed form has also been found.

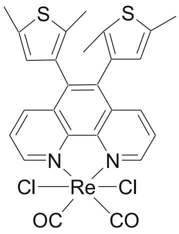
De Cola et al. have found efficient photocyclization from a low-lying triplet state for a diethynylperfluorocyclopentene with $Ru(bpy)_2$ units attached via a phenylene linker to the thiophene rings, **30** [28]. The ring-closure reaction in the nanosecond domain is sensitized by the metal complexes. Upon photoexcitation into the lowest Ru-to-bpy ^{1}MLCT state followed by intersystem crossing to emitting ^{3}MCLT states, photoreactive ^{3}IL states are populated by an efficient energy-transfer process. In contrast, replacement of both Ru^{II} centers by Os^{II} (**31**) completely prevents the photocyclization reaction upon excitation into the low-lying Os-to-bpy ^{1}MLCT state.



30: M = Ru
31: M = Os

Yam and her coworkers have synthesized a Re^I tricarbonyl complex of a photochromic ligand, bis(2,5-dimethyl-3-thienyl)-1,10-phenanthroline, **32**, which shows an expansion of the excitation wavelength region to ca. 480 nm in the visible region, corresponding to the MLCT excitation [29]. The photosensitization mechanism involves an intramolecular energy-transfer process from the ^{3}MLCT to the ^{3}IL state that initiates the ring-closure reaction [30]. Reversible switching of the emissive state by the photochromic reaction has also been demonstrated [29].

Novel Ag^I coordination polymers with a diarylethene derivative, *cis*-dbe, have been synthesized by Munakata et al. [31]. Polymers with a one-dimensional infinite chain structure, **33**, and another with a two-dimensional sheet structure, **34**, were synthesized and their reversible photoreactions with 450 nm and 560 nm light in the solid state were revealed.



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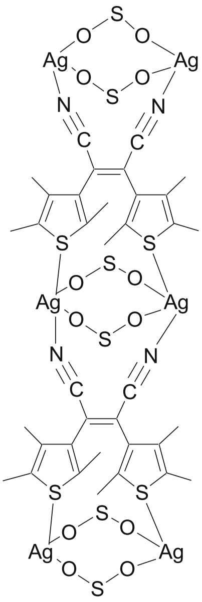

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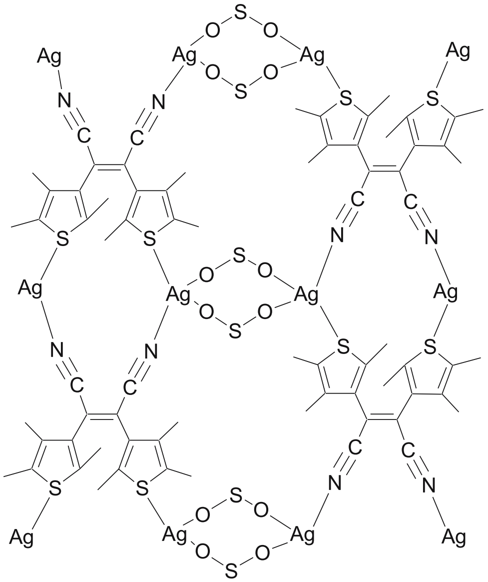

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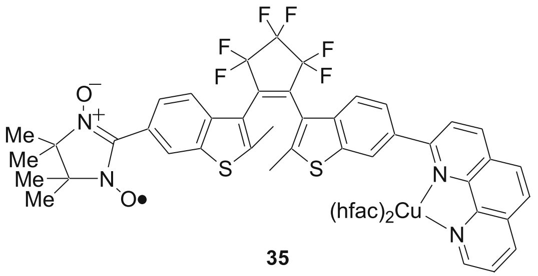
Irie, Matsuda and coworkers have presented photoswitching of an intramolecular spin-exchange interaction between a Cu^{II} ion and a nitroxyl radical by using a metal complex of diarylethene-1,10-phenanthroline ligand, **35** [32]. EPR measurement has shown that a large exchange interaction appears between spins of the nitroxyl radical and Cu^{II} by irradiation with 366 nm light, causing an isomerization from the open to the closed form and creating the largest magnetic photoswitching phenomenon recorded in diarylethene systems. Zn^{II}, Mn^{II}, and Cu^{II} complexes of bidentate and monodentate diarylethene ligands, **36–41**, having polymeric and discrete 1 : 2 complexes, respectively, were synthesized and their photoinduced coordination structural changes were also studied [33]. The reversible change in the EPR spectra of the copper complexes of the bidentate ligand by photoirradiation indicates the photoisomerization-induced change of the coordination structure. The complex composed of $ZnCl_2$ and the monodentate ligand undergoes a photochromic reaction in the crystalline state by alternate irradi-



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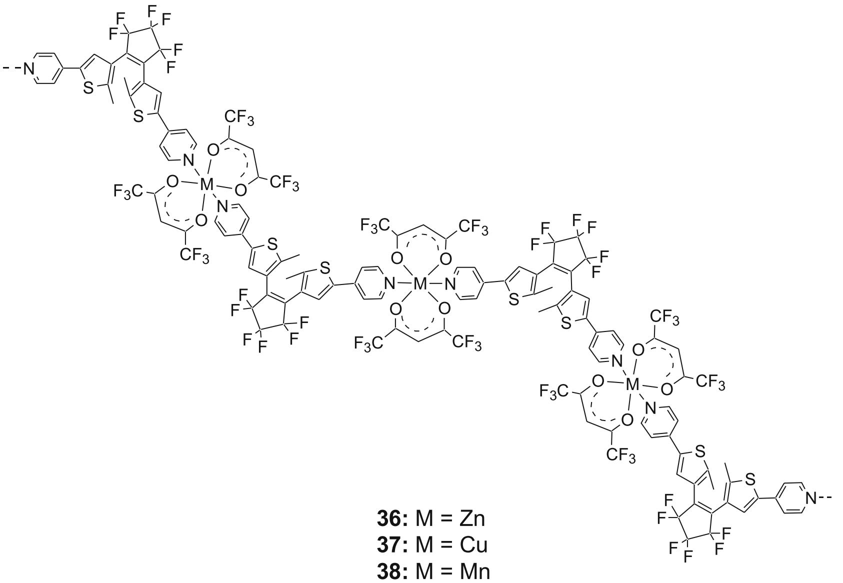
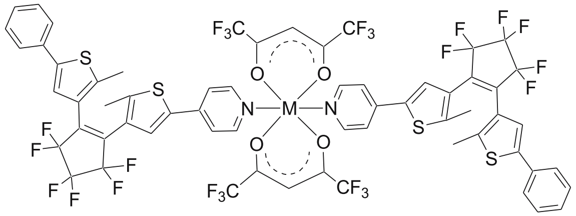
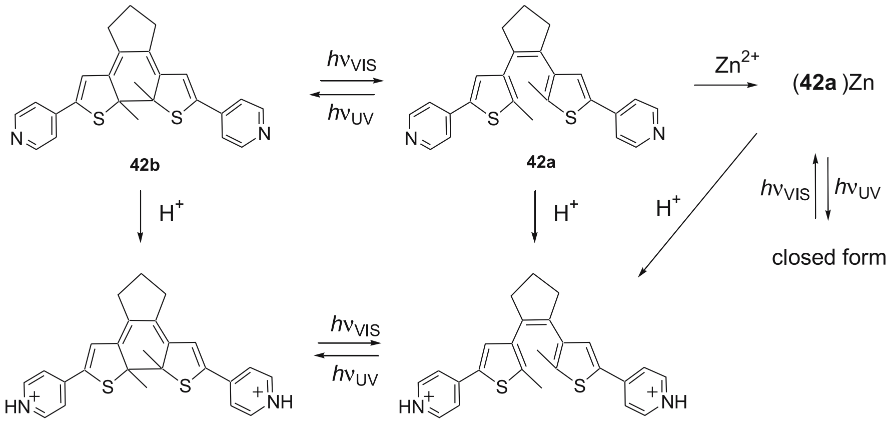


36: M = Zn
37: M = Cu
38: M = Mn



39: M = Zn
40: M = Cu
41: M = Mn

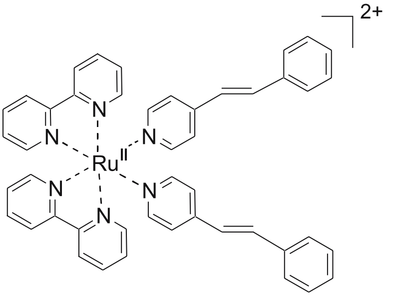


ation with UV and visible light, while crystals of the complex of the bidentate ligand with $ZnCl_2$ show no photoreactivity [34].

Tian et al. have reported that bis(5-pyridyl-2-methylthien-3-yl)cyclopentene ligand **42** shows enhancement of photochromism by complexation with a Zn^{2+} ion [35]. They also found that the fluorescent properties, including the intensity and emission peak wavelengths of the compound, can be reversibly regulated by UV-vis light, Zn^{2+}, and protons [36].

4
Stilbene- and Azobenzene-Attached Complexes

Stilbene and azobenzene cause photoisomerization between trans and cis forms, and their structures are simple enough to provide many derivatives; thus various combinations with transition metals have been reported. Ru^{II} complexes with both trans and cis forms of 4-stilbazole (stpy), $Ru(bpy)_2$(*trans*-stpy) (**43a**) and $Ru(bpy)_2$(*cis*-stpy) (**43b**) have been synthesized by Whitten et al., and the trans/cis ratio ($D_{c/t}$) of each in the photo-



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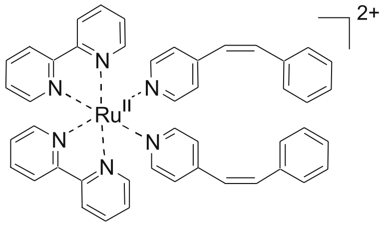
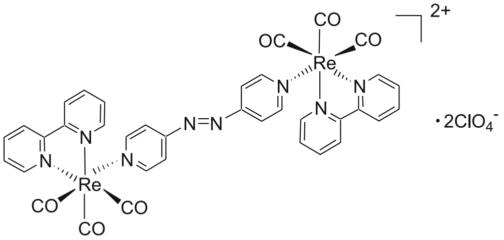


43b

stationary state (PSS) has been examined [37, 38]. A characteristic of these complexes is that they have a metal-to-ligand charge-transfer (MLCT) (d-π^*) transition in the low-energy region around 340–500 nm. The $D_{c/t}$ value is 0.96 on photoirradiation at 313 nm, which is not significantly different from the value of 1.36 for free stpy, because isomerization results from activation of the $\pi - \pi^*$ band. In the complex, trans-to-cis isomerization with $D_{c/t}$ equaling 0.04 is observed in response to photoirradiation at 546 nm, where the free ligand has no absorption. This photoreaction is caused by the MLCT transition.

Light-induced excited spin state trapping (LIESST), in which the spin state of the molecule changes between low and high spin states, is an interesting phenomenon for application to photomagnetic memories. Originally, the subject of photo-activation was the ligand-field (d–d) transition, but recently a ligand-driven light-induced spin change (LD-LISC) has been discovered. In this phenomenon, photo-activation of a transition of a ligand molecule causes a similar spin transition. A complex with a *trans*-stilbene-containing ligand, Fe^{II}(4-*trans*-stpy)$_4$($NCBPh_3$)$_2$ undergoes a thermal low-spin/high-spin transition at 190 K; in contrast, the complex containing the cis-ligand retains a high-spin state at any temperature [39]. Light irradiation to this complex at 140 K at 322 nm causes a trans-to-cis isomerization, and this is reversed by 260-nm irradiation.

Yam et al. have synthesized compounds, **44–49**, in which a luminescent tricarbonyldiiminerhenium(I) unit is bound to a pyridylazo or pyridylvinyl ligand, and they have examined the photochemical and electrochemical properties of these compounds [40–42]. All the complexes except **47** show trans-to-cis isomerization by light irradiation at wavelengths longer than 350 nm. In particular, the quantum yields of the photoreaction are 0.66 and 0.47, respectively, and the cis ratios in PSS are both 74% for 4-(4-nitrostyryl)pyridine (NSP) complexes, **48** and **49**. These values are similar to those of free NSP, which has a quantum yield of 0.81 and a cis ratio of ca. 80%. It is also interesting that the quantum efficiency of photoluminescence in the trans form of a phenylazopyridine complex, **46**, is 7.2×10^{-4}, whereas it increases to 0.027 in the cis form [40, 41]. This result indicates that isomerization



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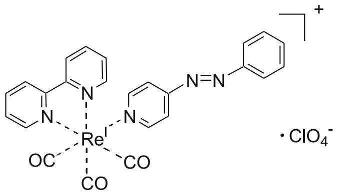

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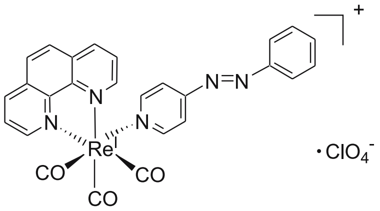

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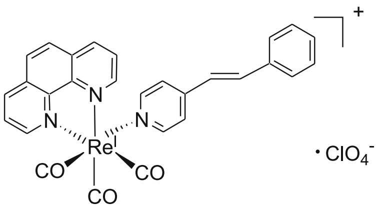

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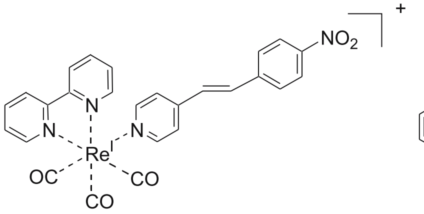

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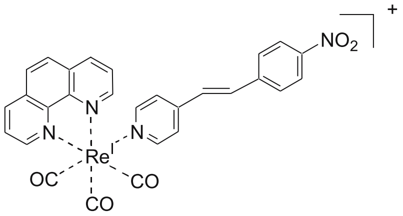
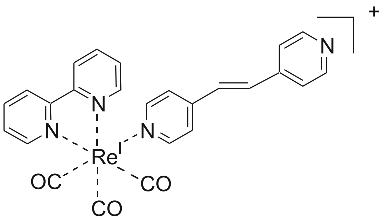


49

switches the photoluminescence property. Gray and his coworkers have also reported photoswithchable luminescence of different tricarbonyldiiminerhenium(I) complexes, **50** [43]. Vlček et al. have analyzed ultrafast excited-state dynamics preceding a ligand trans-cis isomerization of **51** and **52**, concluding that coordination of the styrylpyridine ligand to the Re^I center switches the ligand trans-cis isomerization mechanism from singlet to triplet (intramolec-



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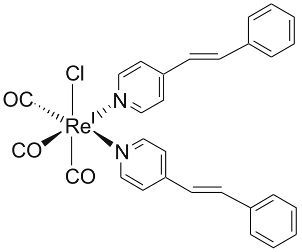

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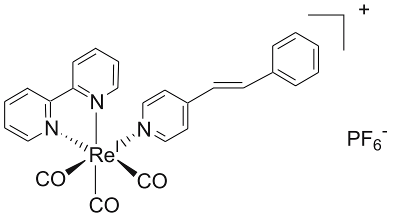
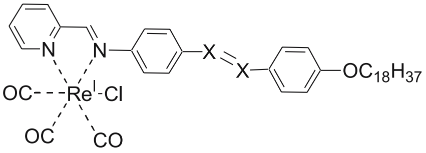


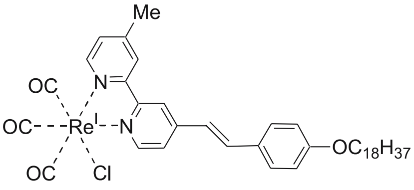
52

ular sensitization) [44]. In the case of **52**, a ^{1}MLCT → ^{3}MLCT intersystem crossing takes place first with a time constant of 0.23 ps, followed by an intramolecular energy transfer from the $\mathrm{Re^I(CO)_3}$-(bpy) chromophore to a ligand ^{3}IL state with a 3.5 ps time constant. Photoisomerization phenomena of $\mathrm{Re^I}$ complexes with long alkyl chains have been investigated by Yam et al. [45]. The isomerization of complex **53** with an azo group is reversed by alternate photoirradiation at 365 and 450 nm light, and that of complex **54** with a stilbene group reverses with alternate photoirradiation at 365 and 254 nm light. Further, it is interesting that complex **55** exhibits isomerization by excitation of the MLCT band at 480 nm. It has been reported that the Langmuir-Blodgett films of these complexes do not show photoisomerization behavior. This inhibition of isomerization is attributed to insufficient free space for the structural change between trans and cis forms to occur.

Tsuchiya has succeeded in controlling intramolecular electron transfer through photoisomerization by employing a molecule in which two tetraphenylporphyrin units (free-base and/or Zn complex) are connected at



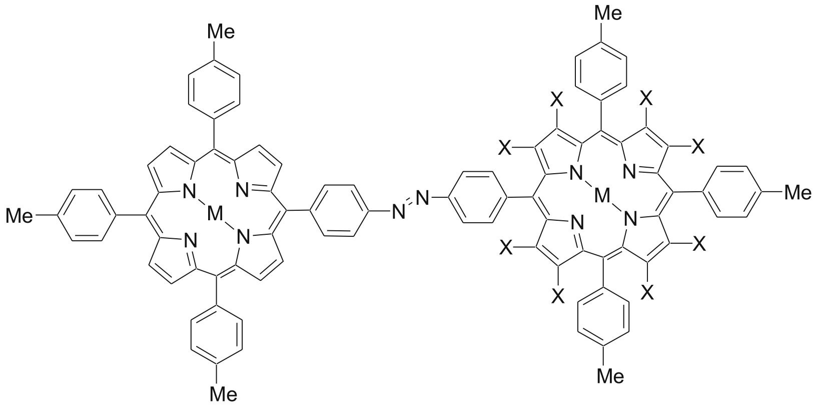
53: X = N, **54:** X = CH



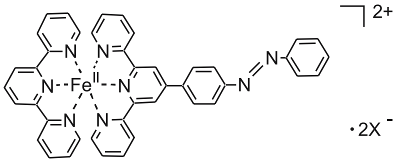
55

the meso-positions [46]. He prepared two types of diporphyrin compounds, one involving an electron-withdrawing F-substituted porphyrin ring, **56** and **57**, and the other involving two regular porphyrin rings, **58** and **59**. By comparing the physical properties of the two types of compounds, he was able to evaluate the electron transfer between donor and acceptor moieties. He has found that both azo-bridged diporphyrins cause trans-to-cis isomerization at wavelengths shorter than 440 nm, and that the reverse cis-to-trans isomerization occurs thermally. Interestingly, the photoluminescence intensity of the donor-acceptor-type diporphyrins, **56** and **57**, decreases with the transformation into the cis form. Since no similar change was observed in **58** or **59**, this phenomenon can be ascribed to intramolecular electron transfer.

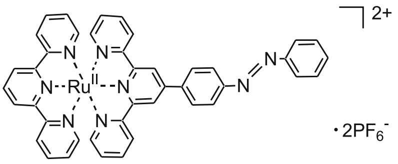
Multi-mode molecular switching properties and functions of azo-conjugated terpyridine complexes of transition metals have been studied [47–49]. The dependences of the photoisomerization behavior on the metal center and its oxidation state were investigated using azobenzene-attached terpyridine complexes of four metals: Fe, Co, Ru, and Rh. As for the Fe^{II} and Ru^{II} complexes, **60–62**, photoisomerization is totally inhibited when UV light irradiation excites the $\pi - \pi^*$ band of the azobenzene moiety in the trans form due to the occurrence of energy transfer from the azobenzene unit to the complex unit [50–53].



56: M = Zn, X = F, **57:** M = H_2, X = F, **58:** M = Zn, X = H, **59:** M = H_2, X = H,



60 X = PF_6, BPh_4



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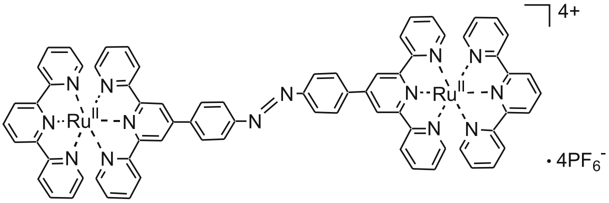
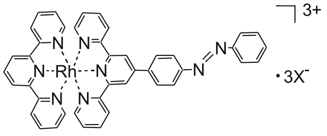


62

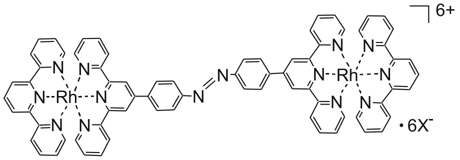
In contrast to the group 8 metal (Fe, Ru) complexes, the group 9 metal (Co, Rh) complexes, **63**–**66**, undergo significant trans-to-cis photoisomerization [50–52], whereas the cis-to-trans photoisomerization, upon excitation of the azo *n*–π^* transition by 430-nm light irradiation, does not occur for any of the mononuclear and dinuclear Rh complexes, **63** and **64**, and their thermal cis-to-trans isomerization proceeds at a much slower rate than that of the free ligands. The quantum yield of the trans-to-cis photoisomerization for **63** and **64** is much smaller than that of organic azobenzenes, and depends strongly on the counterions and solvents.

Otsuki et al. have studied electrochemical and optical properties of Ru^{II} complexes with azobis(2,2′-bipyridine)s [54]. They have found that not only



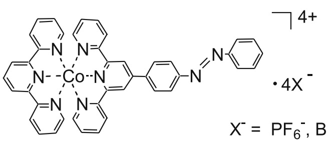
X = BF$_4$, PF$_6$, BPh$_4$

63



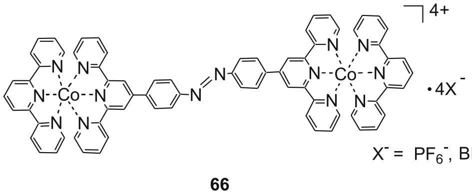
X = BF$_4$, PF$_6$, BPh$_4$,B(C$_6$H$_4$F)$_4$, B[C$_6$H$_3$(CF$_3$)$_2$]$_4$, Cl, Br, I

64



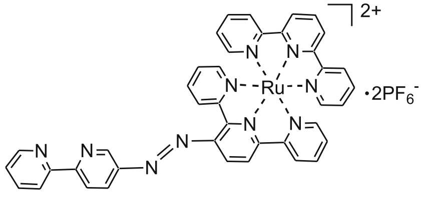
X$^-$ = PF$_6^-$, BPh$_4^-$

65



X$^-$ = PF$_6^-$, BPh$_4^-$

66

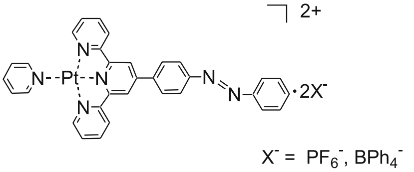


67

the ligands, but also the mononuclear Ru^{II} complex, **67**, isomerize reversibly upon light irradiation, and that the low-energy MLCT state sensitizes the isomerization of the azo moiety in this complex.

Azobenzene-containing Pt^{II} complexes, **68** and **69**, for which the emission properties can be switched by delivering photons, were synthesized. Square-planar Pt^{II} terpyridine complexes are strongly luminescent in the visible region, with several emission modes due to the intra-ligand $\pi-\pi^*$ state, the MLCT state, and states originating from intermolecular π–π or Pt – Pt interactions in the solid state or in fluid solution [55]. UV-vis spectra of **68** and **69** in DMF exhibit an intense azo $\pi-\pi^*$ band of the ligand at 350 nm that overlaps with the less intense MLCT bands of the complex unit, and their photoirradiation using 366-nm light causes trans-to-cis photoisomerization; cis-to-trans isomerization occurs by either photoirradiation with visible light (wavelength > 430 nm) or by heat. The emission at 600 nm was switched on upon trans-to-cis photoisomerization of **68** and **69**. The emission lifetime was measured as 40 μs, indicating that the emission is assignable to ^{3}MLCT origin.

The first example of facile reversible trans-to-cis isomerization of the azo group through a combination of photoirradiation and a redox cycle has been achieved in an azobenzene-attached tris(bipyridine)cobalt system [56–58]. This combination makes possible both forward and backward isomerization in response to irradiation from a single light source (Scheme 1). The Co^{II} complex, **70**$\cdot 2BF_4$, with *trans*-azobenzene moieties affords the cis form in



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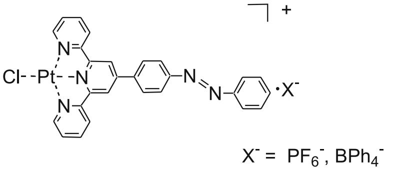

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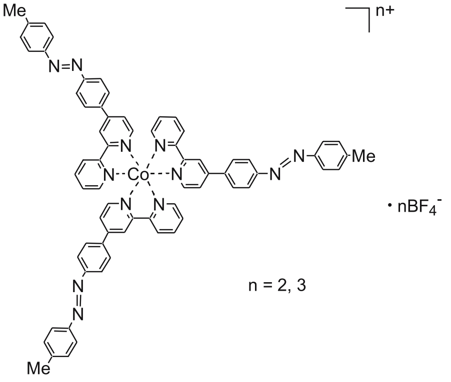

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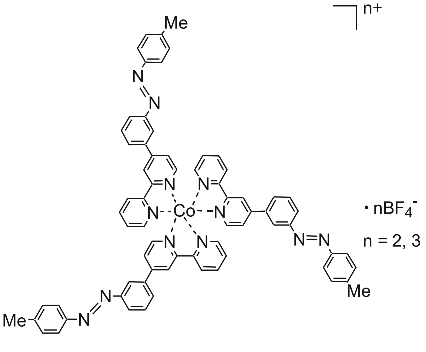

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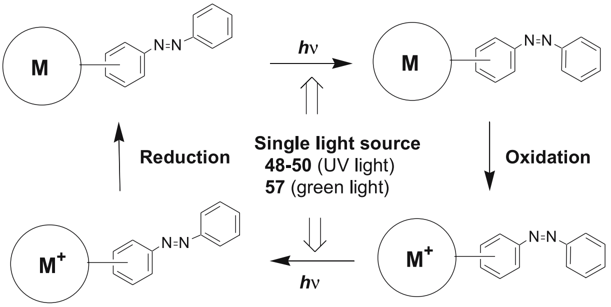
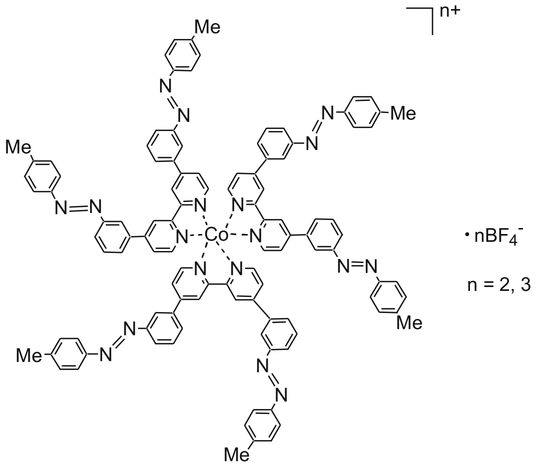


Scheme 1 Reversible isomerization using a single light source and redox reaction

yield of 40% in PSS upon irradiation with 365-nm light in dichloromethane, and the irradiation with 438-nm light causes cis-to-trans isomerization. In contrast, the yield of the cis form in PSS with 365-nm light irradiation for the Co^{III} complex, **70**·$3BF_4$, is only 6% [56].

The redox-coupled photoisomerization cycle shown in Scheme 1 was confirmed by the results of a sequence of experiments involving photoirradiation of Co^{II} species with 365-nm light, chemical oxidation from Co^{II} to Co^{III}, photoirradiation with 365-nm light, and chemical reduction, enabling continuous control of total conversion to the cis form of azobenzene moieties in PSS within a range of 6–40%. The trans-to-cis conversion range is extended to 9–57% by using the redox reaction in the *meta*-substituted cobalt complex, **71**; an efficient reaction was induced by altering the substitution position between the bipyridine and azo moieties, thereby weakening their electronic interaction [57]. A tris(bipyridine)cobalt complex containing six azobenzene moieties, **72**, also shows redox-conjugated reversible photoiso-

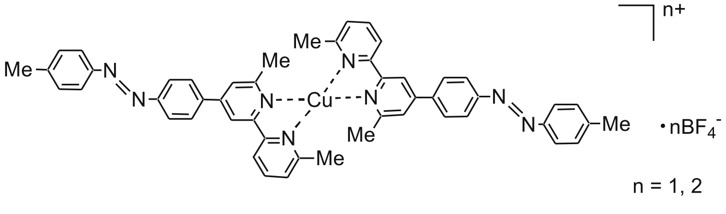


72

merization using UV light with conversion in the range of 9–54%. There is little cooperation among the photochemical structural changes of six azobenzene moieties in **72**, as investigated with ^1H NMR spectroscopy, and each azobenzene moiety is isomerized to a cis-isomer with a random probability of 50% [58]. The femtosecond transient absorption spectra of the ligands and the complexes, **71** and **72**, have suggested that the photo-excited states of the azobenzene moieties in the Co^{III} complexes are strongly deactivated by electron-transfer from the azobenzene moiety to the cobalt center to form an azobenzene radical cation and a Co^{II} center [58].

In contrast to Co, which favors the formation of a hexa-coordinate tris(bipyridine) complex, as noted above, Cu gives a tetra-coordinate bis(bipyridine) complex. The redox reaction of this complex is accompanied by a unique structural conversion of the favored geometry from a tetra-coordinate square planar or a penta- or hexa-coordinate structure of Cu^{II} to a tetra-coordinate tetrahedral structure of Cu^{I}. Based on this property of Cu, a molecularly synchronized system, in which the trans-to-cis and cis-to-trans isomerization of azobenzene-attached bipyridine is controlled by its binding/release reaction to copper driven by a Cu^{II}/Cu^{I} redox change, was constructed with a 6,6′-dimethyl-substituted, azobenzene-attached bipyridine ligand and its Cu complex, **73** [59]. A mixture of a Cu^{I} complex, **73**·BF_4 and 2 equiv of bpy in dichloromethane formed 32% cis isomer by irradiation with 365-nm light, while the cis yield in the UV-light irradiation of the mixture after oxidation to the Cu^{II} state was 70%. These results demonstrate that the isomerization behavior is controllable with a single UV light source and that the ligand's binding/release reaction is reversibly brought about by the Cu^{II}/Cu^{I} redox change (Scheme 2).

Another system constructed based on the unique coordination property of Cu is a "molecular photo-electro transducer", which works in a cyclic manner totally powered by light irradiation [60]. The UV/blue light controlled repetitive motion of azobenzene moieties in 6,6′-bis(4″-tolylazo)-4,4′-bis(4-*tert*-butylphenyl)-2,2′-bipyridine, **74**, causes reciprocal Cu^{I} translocation between two coordination environments in complex **75**, resulting in pumping of the redox potential of Cu^{I} (Scheme 3). Therefore, UV/blue light information can be successfully transformed into an electrode potential change and



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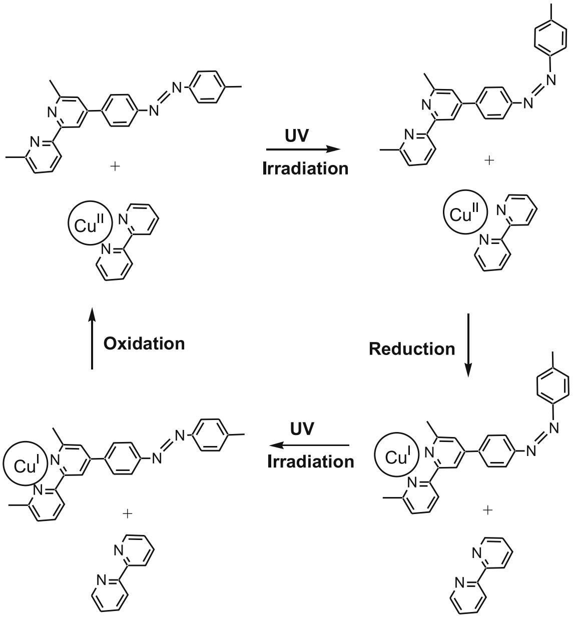
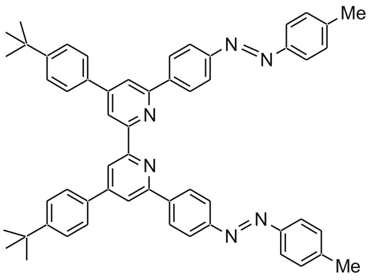


Scheme 2 Reversible isomerization using a single UV light source synchronized with redox and ligand-exchange reactions



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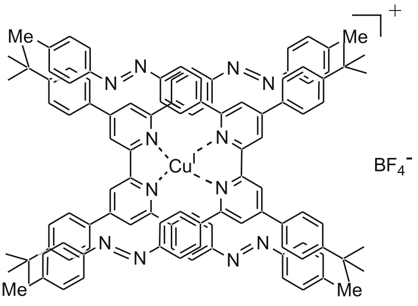
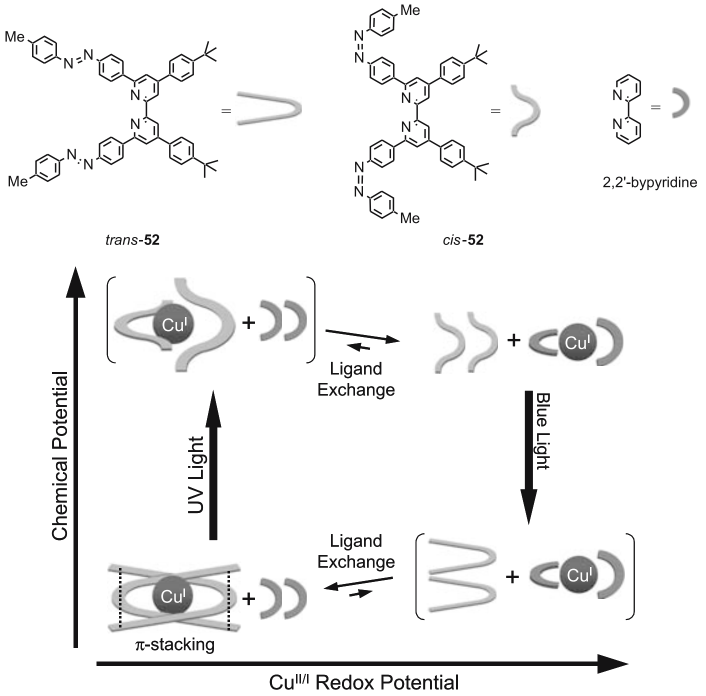


75

positive/negative current response, which is closely related to natural visual transduction both functionally and mechanically.

Unique photoisomerization behavior of ferrocene-bound stilbene, **76**, has been reported by Kunkely and Vogler [61]. Complex **76** shows two long-wavelength absorptions near 570 and 370 nm, which are assigned to metal-to-ligand charge transfer (MLCT) and intra-ligand charge transfer (ILCT) transitions, respectively. MLCT as well as ILCT excitation leads to a trans/cis isomerization at the olefinic double bond.

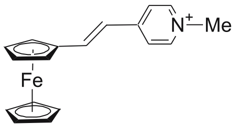
Azoferrocene, **77**, is a π-conjugated ferrocene dimer and one of the simplest analogues of azobenzene, having two redox-active metal complex units.



Scheme 3 A molecular photo-electro transducer

Photoirradiation of **77** in the trans form, *trans*-**77**, in acetonitrile with 365-nm UV light exciting the $\pi - \pi^*$ transition, and also with 546 nm green light exciting the metal-to-ligand charge-transfer (MLCT) transition causes a decrease in the intensity of the $\pi - \pi^*$ band and growth of a new band at 368 nm that shows isosbestic points [62]. It has recently been reported that the presence of trace protons in the photoreaction medium causes an irreversible photoreaction of azoferrocenes [63, 64]. For example, the photoreaction of 4-ferrocenylazophenol (**78**) in ethanol or acetonitrile with a trace amount of water affords a phenylhydrazonocyclopentadiene derivative, indicating that hydrolysis of the photoexcited species has occurred.

3-Ferrocenylazobenzene, **79**, has been found to be a more stable photoisomerization molecular system sensitive to green light. This compound



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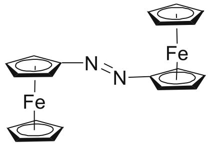

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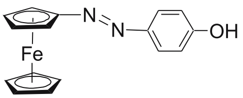

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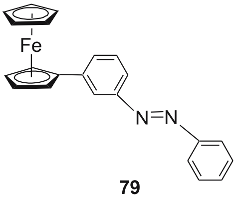
achieves reversible isomerization using a single green light source by combining it with the reversible redox reaction between Fe^{II} and Fe^{III} (Scheme 1) [65].

Trans-**79** (Fe^{II}) shows an azo $\pi - \pi^*$ band at $\lambda_{max} = 318$ nm and a less intense visible band at 444 nm. The trans-to-cis isomerization proceeds through both green (546 nm) and UV (320 nm) light irradiation, whose wavelengths correspond to an edge of the visible band and the maximum in the azo $\pi - \pi^*$ band, respectively. The cis molar ratio reached 35% and 61% in the PSS upon the green-light and the UV-light irradiation, respectively. The quantum yield for the trans-to-cis isomerization, $\Phi_{t\rightarrow c}$, was estimated to be 0.51 for the green light (546 nm), which is much higher than that (0.021) for the UV light (320 nm) and which exceeds that of azobenzene ($\Phi_{t\rightarrow c} = 0.12$ (313-nm excitation)). The MLCT band diminishes in the UV-vis spectrum of *trans*-$\mathbf{79}^+$ (Fe^{III}), so that its photoisomerization occurs with UV-light irradiation but not the green light irradiation. When an acetonitrile solution of *trans*-**79** (Fe^{II}) was irradiated with the green light to reach the PSS (35% cis molar ratio), followed by a chemical oxidation to the Fe^{III} state, thermal isomerization to the trans form proceeded very slowly ($k = 8.7 \times 10^{-4}\ s^{-1}$ at 70 °C), while the green light irradiation into the mixture of *trans*- and *cis*-$\mathbf{79}^+$ (Fe^{III}) promoted a change to reach the all-trans PSS, suggesting that *cis*-$\mathbf{79}^+$ is isomerized to the trans form by excitation of the n–π^* band with the green light.

The photoisomerization behavior and the thermal isomerization behavior of ferrocenylazobenzenes are strongly influenced by the substituents on the benzene rings and by the substitution position of the ferrocenyl moiety on the benzene ring [65, 66] Among the derivatives of **79**, 2-chloro-5-ferrocenylazobenzene exhibits the highest cis molar ratio (47%) in the PSS of green light irradiation. 4- and 2-Ferrocenylazobenzenes, **80** and **81**, also respond to green light in addition to UV light exciting the π–π^* transition but the cis molar ratio in the PSS is lower than that of **79**. The response to green light in **80** and **81** is caused by the MLCT (from Fe d orbital to azo π^* orbital) band excitation, while the character of the MLCT band, as estimated by a TD-DFT calculation, differs for **79** and **80**. The oxidized form of **80** undergoes facile cis-to-trans thermal isomerization. In addition, both **79** and **80** undergo facile protonation and show proton-catalyzed cis-to-trans isomerization.



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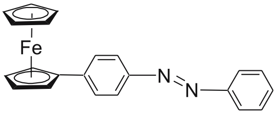

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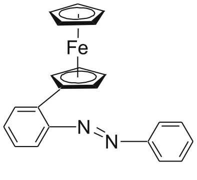
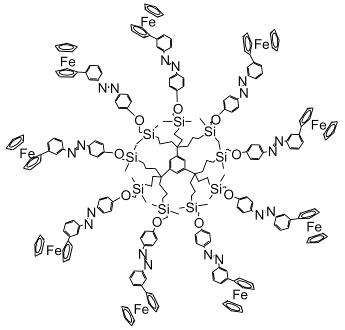
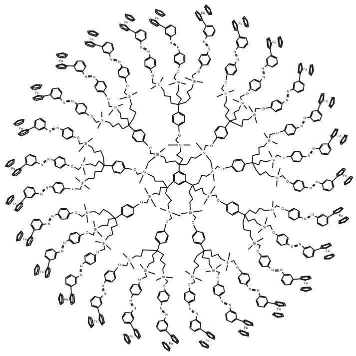


81

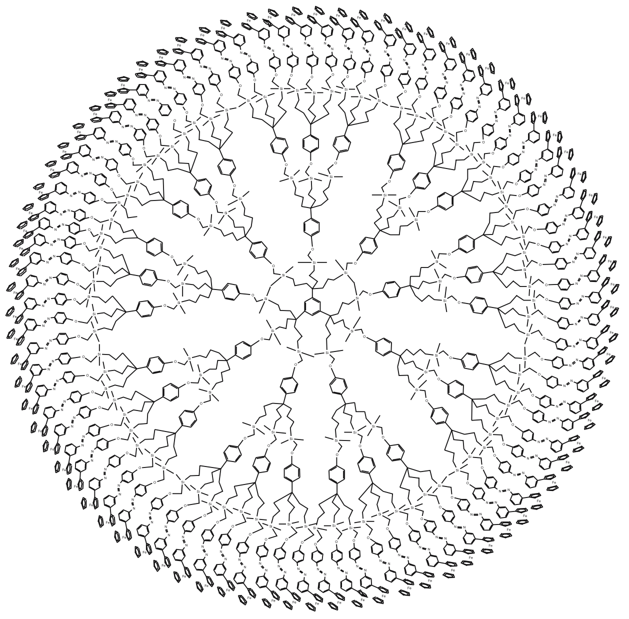
A family of 3-ferrocenylazobenzene-attached dendrimers, 9mer (**82**), 27mer (**83**) and 81mer (**84**), which is the first series of redox-active photochromic dendrimers, exhibit photochromism responding to three different light sources, i.e., 365, 436, and 546 nm lights [67]. Decreases in the size of the dendrimers induced by *trans*-to-*cis* photoisomerization appear and become more significant with increases in the size of the dendrimers up to



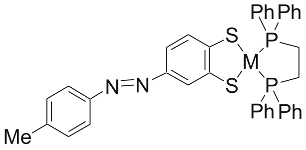
82 (9mer)



83 (27mer)



84 (81mer)



85: M = Ni
86: M = Pd
87: M = Pt

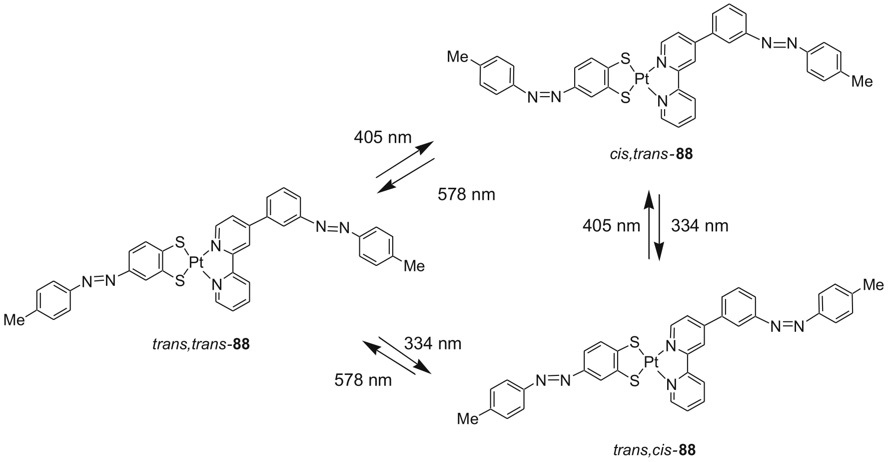
81mer. Electrochemical treatment of the 81mer provides a photo-sensitive and redox-active dendrimer film-coated electrode.

Late transition metal dithiolato complexes possess an aromatic nature, showing reversible redox activity and deep color. The combination of dithiolene complexes of Ni, Pd, and Pt with the azo group, **85–87**, shows reversible photoisomerization and protonation behavior in addition to the protonation-catalyzed cis-to-trans isomerization of the complexes [68, 69] The trans-to-cis isomerization of **85–87** in acetonitrile occurs by irradiation of the transition from metalladithiolene π to azobenzene π^* orbital at $\lambda_{\max} = 405$ nm ($\varepsilon_{\max}$ = ca. 2×10^4 mol^{-1} dm^3 cm^{-1}), whereas the cis-to-trans isomerization proceeds by photoirradiation at 360 nm in **85**, and at 310 nm in both **86** and **87**. Immediate cis-to-trans transformations occur when a slight amount of acid is added to a solution containing *cis*-**85–87**.

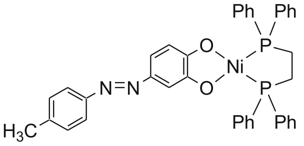
A platinum complex with both an azo-bound dithiolato ligand and an azobenzene-bound bipyridine ligand, **88**, was synthesized [70]. This complex exhibits tri-stability which is reversibly controllable using different energy lights. The *trans,trans*-**88** is converted to *trans,cis*-**88** by 334 nm-light irradiation to excite into the $\pi - \pi^*$ transition of the azobenzene moiety on the bipyridine ligand, and to *cis,trans*-**88** by 405 nm-light irradiation to excite into the π(dithiolene)–π^*(azobenzene) transition of the dithiolato ligand. Both *trans,cis*- and *cis,trans*-forms return to *trans,trans*-**88** by irradiation of the MLCT band with 578 nm light (Scheme 4).

An azo-conjugated catecholato ligand and its nickel complexes, **89** and **90**, were synthesized, and their physical and chemical properties were investigated [71]. The complex with one azo-catecholato ligand, **89**, shows no obvious photo-response, whereas the compound with two azo-catecholato ligands, **90**, causes some photoisomerization. Both complexes show remarkable proton responses.

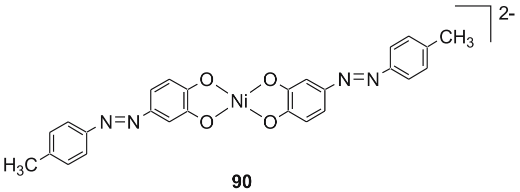
Crown ether-bound styryl dyes have been studied by Fedorova and her coworkers. The photochromic properties of the dyes, **91**, are based on reversible trans-cis isomerization and [2 + 2]-photocycloaddition. They exhibit a strong preference for formation of complexes with heavy metal ions [72]. Due to its specific structure, the betaine-type dye is able to form an “anion-capped” trans-isomer. Intramolecular coordination in the “anion-capped” isomer enhances its stability and causes a sharp deceleration of its dark trans-



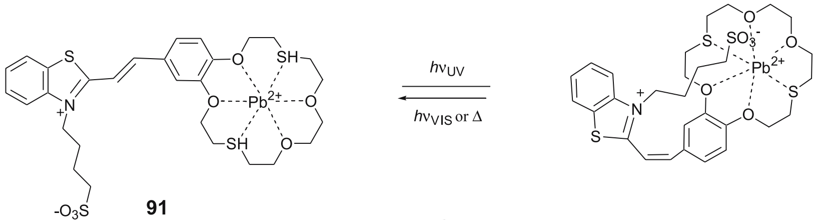
Scheme 4 Tri-stable photochromism with three-color light



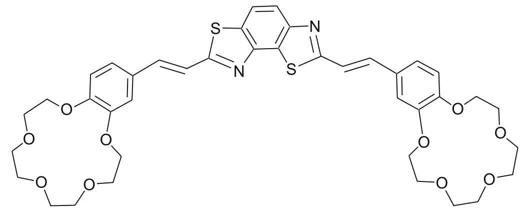
89



90



91



92

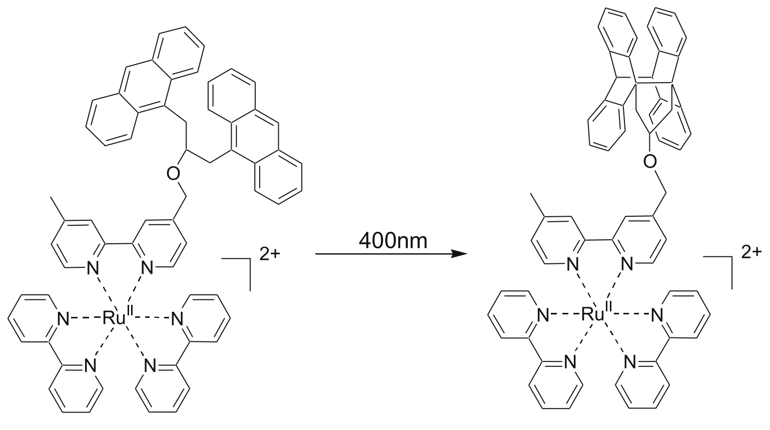
cis isomerization [73]. A large ionochromic effect and fluorescence quenching on complex formation with alkaline-earth metal cations have been found for 2-styrylbenzothiazole containing a phenylazacrown ether moiety. However, considerable distinctions in the spectral properties of the photoisomers and their ability to form a complex were not found [74]. A benzo[1,2-*d*;3,4-*d*′]bisthiazole derivative with two crown ethers, **92**, forms relatively strong

2 : 2 stoichiometric complexes with K^+, among the alkali metal cations, and Ba^{2+}, among the alkaline earth metal cations [75].

Einaga and his coworkers have presented photo-controllable molecular systems, salts of $[M(en)_2][Pt(en)_2Cl_2]^{4+}$ (M^{2+} = Pt^{II}, Pd^{II} and en = ethylenediamine) and 4-[4-(*N*-methyl-*N*-*n*-dodecylamino)phenylazo]benzene sulfonate ions, which have been designed by the self-assembly of chloride-bridged platinum/palladium complexes [76]. Reversible structural changes caused by cis-trans photoisomerization of azo groups in the compounds occur by alternating irradiation of UV and visible light. Visible light irradiation causes a trans-to-cis isomerization of the azo group, leading to the formation of plate-like structures, whereas UV light irradiation causing cis-to-trans isomerization does fragmentation of the assembling structures. This fragmentation brings about reversible changes in the electronic states of the chloride-bridged platinum/palladium complexes; the plate-like structures exhibit CT absorption of chloride-bridged platinum complexes and delocalized Pt^{II}/Pt^{IV} states, while the fragments of the separated complexes exhibit no CT bands.

5
Other Systems Using Organic Photochromic Molecules

Several kinds of organic molecules are known to undergo dimerization or its reverse reaction by photoirradiation. Castellano et al. have shown that the coupling of the irreversible dianthryl photo-dimerization to the Ru^{II} complex emission using **93** permits nondestructive photoluminescence readout of binary information photochemically recorded at the molecular level in a polystyrene matrix [77, 78]. McSkimming et al. have reported an aza-

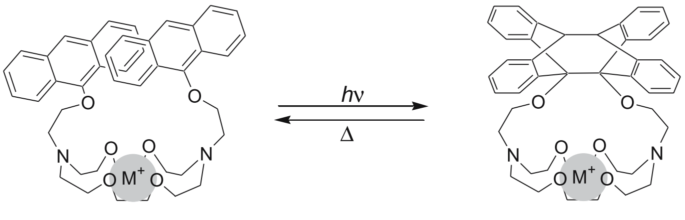


93a **93b**

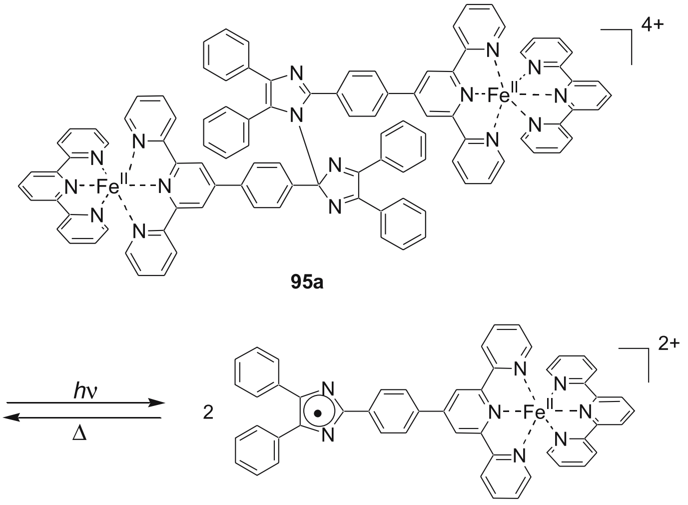
crown ether with anthracene-containing pendant arms, **94**, which shows a reversible intramolecular [$4\pi + 4\pi$] cycloaddition reaction upon irradiation at $\lambda > 300$ nm [79]. This crown ether forms complexes of 1 : 1 stoichiometry with cations, and the above photochromic process is cation-dependent; in particular, the rate of the thermal reverse reaction is decreased by smaller cations and increased by larger cations, especially Rb^+.

A Fe^{II} complex of a photochromic ligand, bis(terpyridyl)hexaarylbiimidazole (bistpy-HABI) **95**, was synthesized, and its photochemical cleavage into a pair of terpyridyltriphenylimidazolyl radicals on irradiation with UV light was studied by Abe and his coworkers [80]. The triplet state of the light-induced radical pair from **95**, as well as that from the free ligand, was confirmed to be a ground state or nearly degenerated with a singlet state. The first observation of a decrease in activation energy of the radical recombination reaction by the formation of a metal-coordinated radical complex was reported.

Kimura et al. have reported a dramatic conformational change of a Crystal Violet derivative with three crown ether moieties, **96**, on its cesium-ion

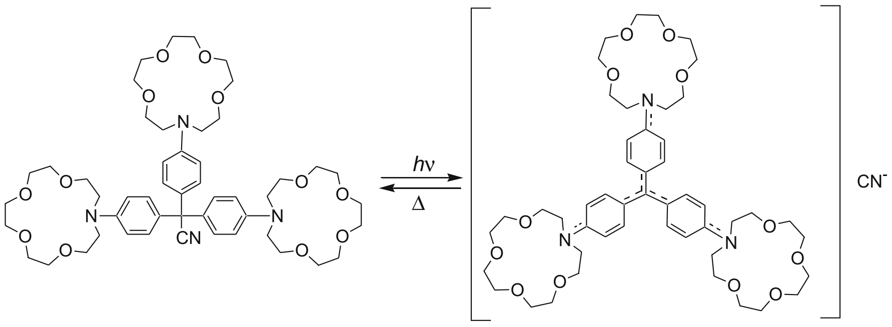


94a **94b**

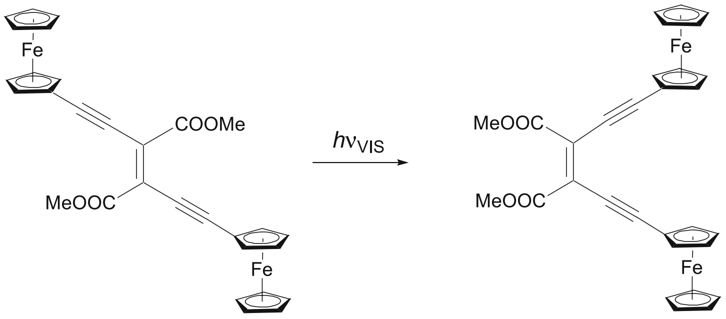


95a

95b



96a **96b**



97a **97b**

complexation, which decelerates the photochemical reaction of the crystal violet [81].

It has been recently reported that the *E*-form of bis(ferrocenylethynyl)-ethane, **97a**, can undergo photoisomerization to the *Z*-form, **97b**, by excitation of a charge transfer band with visible light [82]. This structural change affords a decrease in the "through bond" mixed-valence interaction between two ferrocenes.

6
Concluding Remarks

We have described herein different single-molecule systems combining photochromic molecular units and metal complex units. These systems show unique behaviors that have not been seen in common organic photochromic compounds. Table 1 summarizes such behaviors and phenomena. The findings regarding photochromic metal complexes denote the creation of new types of photo-responsive materials having multi-mode functions via properly designed communication between photochromic molecules and metal complexes. These materials will be useful for the development of chemosen-

Table 1 New functions developed in photochromic metal complexes

Metal complex properties	Developed functions	Refs.
Control of isomerization with a metal complex moiety		
Complexation	Durable memory	[4, 5, 13, 15, 22]
	Positive/negative photochromism	[10]
Ligand exchange	Single-light isomerization	[59]
Redox reaction	Single-light isomerization	[56–59, 65]
CT excitation	Isomerization with low photon energy	[20, 21, 28–30, 37] [38, 54, 61, 65]
	Site-selective isomerization	[70]
Electron donation	Proton-catalyzed isomerization	[68, 69]
Bulkiness	Irreversible isomerization	[50–52]
Tuning of metal complex properties with photoisomerization		
Photoluminescence	Luminescence on/off	[25, 26, 29, 40, 42, 43, 55]
Redox reaction	Photo-electron transfer	[60]
Ligand exchange	Photo-transduction	[60]
Magnetic properties	Spin–spin interaction tuning	[32]
	LD-LISC	[39]
Complexation	Ion sensing	[8, 11, 18, 19, 79]
Mixed valence state	Electron mobility tuning	[27, 82]
	Photo-controlled 1D-chain structure	[76]
Photo-induced electron transfer	Electron mobility tuning	[46, 76]

sors, and also multi-mode switching and information storage systems at the molecular level.

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