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Review

Recent progress of luminescent metal complexes with photochromic units

Yasuchika Hasegawa*, Tetsuya Nakagawa, Tsuyoshi Kawai*

Graduate School of Materials Science, Nara Institute of Science and Technology, Takayama 8916-5, Ikoma, Nara 630-0101, Japan

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ABSTRACT

Photo-responsive molecules have been studied extensively because of their light irradiation abilities that enable modulation of certain physical and chemical properties in emerging molecular electronic and photonic devices. For advanced photonic applications, photochromic metal complexes that have photochromic units as the photo-responsive ligand are highly desirable, as they allow improvement of the photochromic properties and their photo-switching functionality. This article focuses on recent progress in luminescent metal complexes with photochromic units. Luminescence-switching properties of photochromic metal complexes depend on characteristic electronic transitions. The electronic transitions of photochromic metal complexes can be divided into three categories: (1) π–π* transition of the ligand, (2) metal to ligand charge transfer (MLCT) in transition-metal complex, and (3) *f*–*f* transition in lanthanide complex. Luminescence modulation using various metal complexes with photochromic units has been studied extensively in recent years, and various applications for future molecular switching devices are expected in the field of advanced photonics. Based on the literature and our studies on luminescent metal complexes with photochromic units, we report on the recent progress of luminescent metal complexes with photochromic units.

1. Introduction

Photo-responsive molecules and polymers have been studied extensively because of their capability to modulate physical and chemical properties for use as active elements in future devices [1–3]. Considerable interest has been focused on photochromic molecules [4–6], such as azobenzene [7], spiropyrane [8] and diarylethene [4,9–12], which undergo reversible photoisomerization reactions between two isomers upon irradiation of appropriate wavelength. The photo-switching phenomena of photochromic molecules have been studied to control various chemical and physical properties of materials such as emission intensity and wavelength [13–20], refractive index [21–23], electronic conduction [24–31], electrochemical response [32–40], magnetic interactions [41–44] and self-assembling behavior [45–47] of molecules and polymers. Among them, photo-switching and photo-responsive modulation of the emission properties of luminescent molecules with photochromic units is one of the most promising research areas in molecular photo-switches and photo-memory because of their high sensitivity, resolution, contrast and fast response times in luminescence technology [48]. Early studies on the luminescence-switching phenomenon of photochromic diarylethene looked at the simple diarylethene molecule itself and its doping effects on the emission properties of conjugated polymers [13]. Tsuvgoulis and Lehn [14] have attempted to achieve nondestructive readout memory on the basis of luminescence modulation with diarylethene derivatives. A number of luminescent molecules that have photochromic units and organic or inorganic luminescence units have been proposed thus far.

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* Corresponding authors. Tel.: +81 743 72 6171.
E-mail addresses: hasegawa@ms.naist.jp (Y. Hasegawa), tkawai@ms.naist.jp (T. Kawai).

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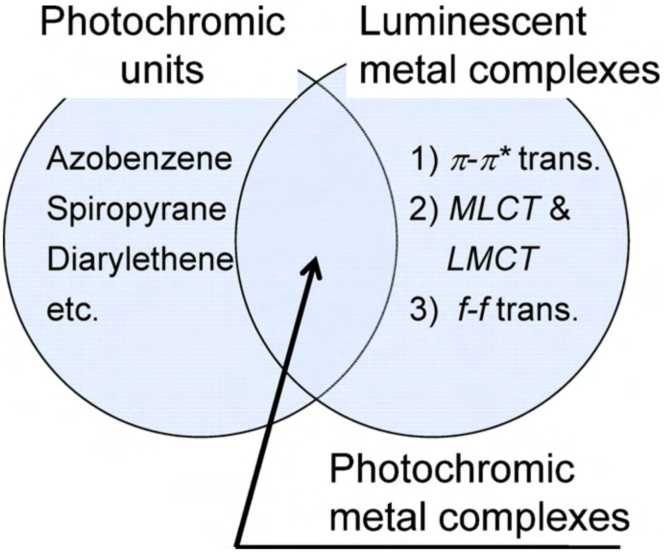

Fig. 1. Research area of luminescent metal complexes with photochromic units.

We focus here on photo-switching modulation of the emission properties of luminescent metal complexes with photochromic units. Luminescent metal complexes that have photochromic units as the photo-responsive ligand are desirable for advanced photonic applications. The first luminescence modulation in a photochromic metal complex has been reported as a metal complex with a photochromic diarylethene unit [49,50]. Luminescence modulation using various metal complexes with photochromic units has been studied extensively in recent years, and various applications for future molecular switching and memory devices are expected. Luminescence-switching characteristics of photochromic metal complexes depend on characteristic electronic transitions in the emission band. They can be classified into three categories: (1) π–π^* transition of the ligand, (2) metal to ligand charge transfer (MLCT) in transition-metal complex, and (3) *f*–*f* transition in lanthanide complex (Fig. 1). In order to achieve reversible control of the electronic transition properties, researchers in related fields have proposed novel strategies, conceptual designs and remarkable structures of photochromic metal complexes based on the nature of their emission transitions.

The authors have reported on control of the electronic transitions of metal complexes with *f*–*f* transition bands, and lanthanide complexes [51,52]. Generally, *f*–*f* electronic transitions of lanthanide complexes are dominated by radiative and non-radiative processes from emitting levels. Radiative rate constants of the lanthanide complexes depend greatly on the geometrical symmetry of the coordination structure. Richardson and Reid have estimated the transition intensity parameters of lanthanide complexes from the ligand field [53,54]. Binnemans has proposed evaluating the transition intensity by using Judd-Ofelt analysis [55]. Since these studies, it has been widely accepted that the radiative transition probability between 4*f* orbitals is enhanced by reducing the coordination structure's geometrical symmetry [56–66]. The emission properties of lanthanide complexes also depend on vibronic properties, which dominate the kinetics of the non-radiative transition processes. According to the energy gap theory, the non-radiative transition processes are promoted by the presence of ligands and solvents with high-frequency vibrational modes [67]. In earlier studies, we have reported on the suppression of radiationless quenching in Nd(III) systems in organic media by introducing diketonato ligands that have C–F bonds with low-vibrational frequency (LVF) such as hexafluoroacetylacetonato (hfa) [68–72]. The LVF ligands that have C–F bonds instead of C–H bonds effectively suppress radiationless transition in the lanthanide complexes. The combination of these photophysical observations and photochromic properties made it possible for us to report on successful reversible luminescence modulation using photochromic lanthanide complexes, recently [73–76].

Based on our studies and the literature on luminescent metal complexes with photochromic units, we report on molecular strategies and recent progress of luminescent metal complexes with photochromic units in this review.

2. Photochromic metal complexes with π–π^* transition band

Studies on control of π–π^* transitions in luminescent metal complexes with photochromic units have been reported, recently. In particular, photochromic metal complexes with luminescent phthalocyanine and tetraazaporphyrin frame-works have been studied intensively because of their characteristic emission properties and switching behavior upon photochromic reactions at room temperature. Luminescent Zn, Pd, Pt phthalocyanine and tetraazaporphyrin with photochromic diarylethene units (Fig. 2a and b) [77–79], axially coordinated Sn porphyrinic dithienylethene (Fig. 2c) [80], a Zn porphyrin with photochromic spiropyrane unit (Fig. 2d) [81] have been reported thus far. The luminescence-switching properties originate from efficient spectroscopic overlapping between the emission band of the metal complex and the absorption band of the colored photochromic units, which is characteristic only in the colored form. The luminescence quenching in the colored states of the photochromic metal complexes is attributed to intramolecular energy transfer from the excited metal complex to the colored photochromic units, which does not occur in the bleached state. Control of π–π^* transition in photochromic metal complexes with luminescent poly-pyridyl frame-works have been also studied. A Pt complex composed of terpyridine with photochromic azobenzene unit shows luminescence switching at 77 K (Fig. 3a) [82]. The emission band at 77 K is attributed to the triplet state of terpyridine π–π^* transition. The luminescence switching might be based on the nonplanar geometry of the *cis* form, as well as the reduced π-conjugation effect, 1) photoinduced electron transfer from the nitrogen lone pair to the emissive unit is inhibited, and/or 2) the triplet state energy of the azo chromophore is higher that of the trans form. It has been also observed that the emission band of Zn complexes composed of dithienylphenanthroline unit in 77 K (Fig. 3b) shift to the red region upon conversion of the open-form to the colored-form in the photostationary state, which is consistent with the reduced HOMO-LUMO energy gap as a result of the extended π-conjugation in the condensed thiophene units upon occurrence of the photocyclization reaction [83].

On the other hand, control of the π–π^* transition in photochromic metal complexes with characteristic ligand structures, Zn complex composed of bis(acrylamidine) with photochromic diarylethene units (Fig. 3c) [84] and Au complex composed of N-heterocyclic carbene ligands (Fig. 3d) [85] has been reported. In the Au complex, the photochromic ligand exhibited a photochromic cyclization reaction upon excitation at 285 nm. The quantum yield for the photocyclization reaction of the Au complex ($\Phi_{O-C} = 0.47$) was found to be improved compared to that of the organic ligand ($\Phi_{O-C} = 0.21$). A higher cyclization quantum yield was ascribed to the coordination of the carbene moiety to the electron-rich d^{10} Au(I) center. In the closed-ring form, this complex showed emission at 660 nm. Metal ion sensing using luminescent spiropyrane units has also been studied extensively [86–88].

3. Photochromic transition-metal complexes with MLCT bands

Transition-metal complexes consisting of the metal M and the aromatic organic ligands L possess a metal to ligand charge trans-

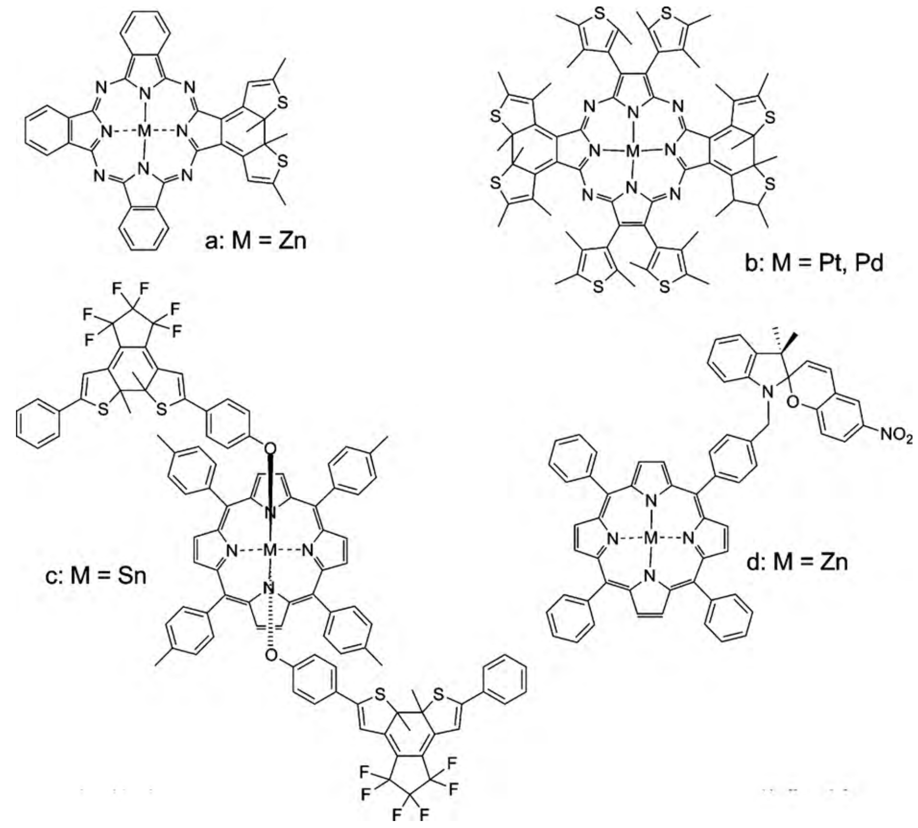

Fig. 2. Chemical structures of photochromic metal complexes with π–π* transition band based on phtalocyanine, tetraazaphorphyrin and porphyrin frame-works.

fer band (MLCT band) and/or a ligand to metal charge transfer band (LMCT band). The energy levels and the photophysical properties of MLCT and LMCT bands can be fine-tuned by careful selection of ligands and metals. Photochromic modulation using control of the energy levels of MLCT and LMCT bands has been achieved using Re complexes with diarylethene units (Fig. 4a) [89,90]. The emission band is assigned as the ^{3}MLCT transition. Upon conversion from open-form to closed-form in the photo-stationary state, the maximum wavelength emission band shifts from 595 nm to 644 nm. The red shift in the emission energies of the closed-form

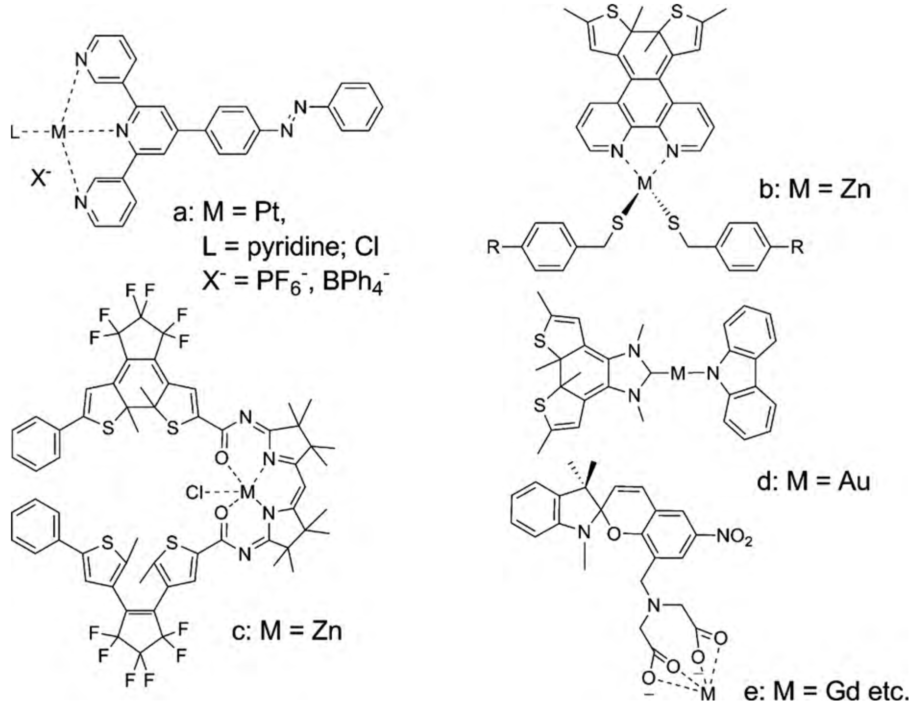

Fig. 3. Chemical structures of photochromic metal complexes with π–π* transition band based on poly-pyridyl and specific frame-works.

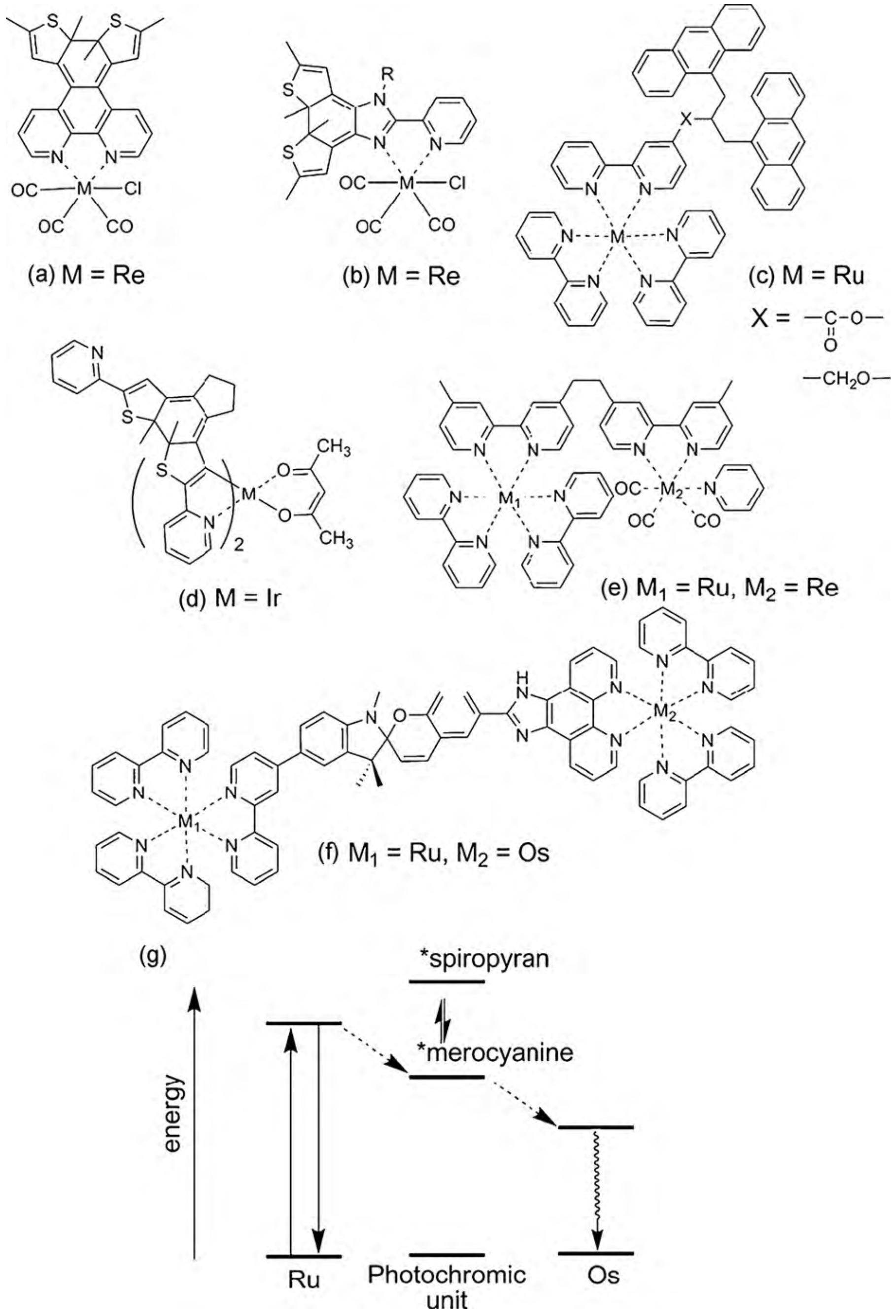

Fig. 4. (a–f) Chemical structures of photochromic transition-metal complexes with MLCT transition band. (g) Energy diagram for the envisaged Ru-spiropyran-Os energy transfer switch.

relative to that of the open-form is in line with the increased extent of π-conjugation upon the photo induced ring-closing reaction. Luminescence switching using Re complexes with extended photochromic ligands has also been reported (Fig. 4b) [91]. This complex showed ^{3}MLCT phosphorescence with a maximum at 570 nm upon excitation at 410 nm at 298 K. The emission intensity of the open-form was larger than that of the closed-form. In the Re complex, NIR photochromic behavior with a red shift in the absorption maxima was observed. This NIR photochromic behavior could be attributed to the planarization of the four heterocyclic rings. On the other hand, the organic ligand systems alone did not show such NIR photochromic behavior.

A Ru(II) complex with a photochromic dianthyl unit has been reported (Fig. 4c) [92]. This complex exhibited a photocycloaddition reaction of the dianthyl unit under irradiation at 390 nm light, in which the cycloaddition complex shows larger MLCT-based emission than the initial complex. Optical recording and luminescence readout of a Ru(II) complex with a photochromic dianthyl unit in PMMA thin films have been also demonstrated by near-field scanning optical microscopy (NSOM) [93]. Localized UV irradiation of this PMMA thin film resulted in photoinduced state switching and a concomitant increase in emission intensity.

In recent studies, photochromic ligands have been exploited to form Ir(III) complexes (Fig. 4d) [94]. Highly emissive Ir complexes were formed with two cyclometalated ligands and a single monoanionic, bidentate ancillary ligand. Because of the strong spin–orbit coupling of 5d ion, the related d^6 Ir complexes show intense phosphorescence at room temperature. The electronic transition for luminescence in these Ir complexes has been ascribed to a mixture of $(MLCT)^3$ and $(\pi-\pi^*)^3$ ligand state. The reported Ir complexes with photochromic diarylethene units show effective luminescence switching based on the photochromic reaction at room temperature. The luminescence switching is caused by spectroscopic overlap between the absorption band of the closed-form of photochromic Ir complex and the emission band of the triplet-state. It is suggested that intramolecular quenching of the triplet-state via energy transfer should be effective only in the closed-form, resulting in a decrease in the emission intensity relative to that is open-form.

Dual luminescence from a mixed-metal complex containing Re(I) and Ru(II) photochromophores has been reported (Fig. 4e) [95]. This complex showed emission at 540 nm and 610 nm, its emission changed little when the solution was irradiated at 355 nm for an extended period (>1 h). Control of the energy transfer process based on luminescent Ru(II) and Os(II) complexes containing photochromic units has also been investigated (Fig. 4f) [96,97]. In these systems, energy transfer from donor Ru(II) complex to acceptor Os(II) complex is reversibly switched “on” and “off” by converting the photochromic part. Ru(II) complex and Os(II) complex are linked by a photochromic spiropyrane bridge, and the donor-bridge-acceptor systems are based on the principle that the lowest lying energy levels of photochromic systems are those between the donor and acceptor, thereby facilitating the energy transfer (Fig. 4g). All optical integrated logic operations, composed of luminescent Ru(II) complex and photochromic spiropyrane, have been also reported [98]. Luminescence switching of transition-metal complexes is expected to open-up new fields of molecular device science.

4. Photochromic lanthanide complex with *f–f* transition bands I

We focus here on photo-switching modulation of the emission properties of lanthanide ions. These ions are the most popular luminescent elements for practical applications, such as luminescent displays, lasers, and optical devices, on the basis of their characteristic 4*f*–4*f* transition processes [99–106]. As practical emission materials, lanthanide complexes have unique characteristics such as narrow emission bands, which enable them to show clear color emissions with high color purity, and a wide variation of emission colors from the visible to near-IR range, depending on the central metal ion. Because lanthanide ion emissions come mainly from electric dipole (ED) transitions in 4*f* orbitals, the emission line wavelengths of lanthanide complexes are insensitive to the nature of ligand and coordination structures. The charge transfer interaction between the lanthanide ion and organic ligands is not major, mainly controlling the MLCT emission in the case of *d*-group metal complexes such as Ru and Os. No marked change in the emission properties of the lanthanide complex with photochromic ligands would be induced by the change in the MLCT interaction. While the emission intensity of the lanthanide complexes has been significantly sensitive to the fine structure of the coordination chemistry [107]. The ED transition of the 4*f* orbitals is intrinsically *La Porté*-forbidden and is markedly sensitive to the asymmetric structure of the coordination field. Thus, the ED transition is expected to achieve photochromic control of the lanthanide complex emission property, provided that the photochromic unit is introduced as the ligand and that the symmetry of the ligand field, or ‘odd parity’ [108,109], is modulated by the photochromic reactions of the ligands.

The photochromic and emission properties of a photochromic lanthanide complex, $Eu(hfa)_3(THIA)_2$ have demonstrated the possibility of photon-mode control of the ED transition probability of photochromic lanthanide(III) complex based on the change of ligand–lanthanide interaction (Fig. 5a). The emission bands are observed at 579 nm, 592 nm, 614 nm, 651 nm, and 698 nm, and are attributed to the *f–f* transitions $^5D_0-^7F_0$ (zero–zero band: forbidden transition), $^5D_0-^7F_1$ (magnetic dipole transition: MD), $^5D_0-^7F_2$ (electric dipole transitions: ED), $^5D_0-^7F_3$ (forbidden transition), $^5D_0-^7F_4$ (electric dipole transitions: ED), respectively. The intensity of the $^5D_0-^7F_1$ (MD) transition is known to be insensitive to the surrounding environment of the Eu(III) ion [110–112]. On the other hand, $^5D_0-^7F_2$ (ED) transition is extremely sensitive to the odd parity of the crystal field [56–66]. The ED transition probability of a Eu(III) complex is, therefore, estimated with the relative intensity ratio of the $^5D_0-^7F_2$ (ED) transition against the $^5D_0-^7F_1$ (MD) transition in the emission spectrum. Thus, the measured emission spectra were normalized with respect to the $^5D_0-^7F_1$ (MD) transition, as shown in Fig. 5b. The normalized emission intensity at $^5D_0-^7F_2$ transition intensity of the colored form was significantly smaller than that of $Eu(hfa)_3(THIA)_2$-O. The decrease in normalized emission intensity of the ED band in the colored form is explained by the decrease of the ED transition probability of the $^5D_0-^7F_2$. The odd parity nature of $Eu(hfa)_3(THIA)_2$-C seems, thus, to be less than that of $Eu(hfa)_3(THIA)_2$-O. The reversible changes of relative emission intensity at 614 nm are also observed by the alternative irradiation cycles of UV ($\lambda = 365$ nm) and visible light ($\lambda > 440$ nm).

Table 1
Emission quantum yields, emission lifetimes and radiative rate constants of $^5D_0-^7F_2$ transition in $Eu(hfa)_3(THIA)_2$-O and $Eu(hfa)_3(THIA)_2$-C at 80 K.

Complex[a]	Φ (%)[b]	τ (ms)	k_r ($\times 10^2$ s^{-1})[c]
$Eu(hfa)_3(THIA)_2$-O	10	0.60	1.7
$Eu(hfa)_3(THIA)_2$-C	7.6	0.50	1.5

The emission quantum yield of Eu(III) complexes was measured by excitation at 465 nm ($^7F_0-^5D_2$). The emission lifetimes of Eu(III) complexes were measured by excitation at 337 nm.

[a] In EtOH/MeOH glass matrix at 80 K.

[b] Estimated from emission peak area between 600 nm and 630 nm.

[c] Radiative rate constant = emission quantum yield/emission lifetime.

In order to analyze the emission quantum yield and the absolute ED transition probability of $Eu(hfa)_3(THIA)_2$-C, the fully colored state was prepared using UV (365 nm) light irradiation at 80 K, at which temperature the photo-cycloreversion reaction does not take place upon irradiation of visible light (Fig. 5c). The emission quantum yields and emission lifetimes of the $^5D_0-^7F_2$ in $Eu(hfa)_3(THIA)_2$-O and $Eu(hfa)_3(THIA)_2$-C are summarized in Table 1. The radiative rate constants of $^5D_0-^7F_2$ transition of $Eu(hfa)_3(THIA)_2$-C and $Eu(hfa)_3(THIA)_2$-O were estimated to be 1.5×10^2 s^{-1} and 1.7×10^2 s^{-1}, respectively. The decrease of about 10% is worth noting from the view point of emission properties of Eu(III) complexes with different ligands [60]. We observed not only the decrease of ED transition intensity but also a significant decrease of the radiative rate constant in $Eu(hfa)_3(THIA)_2$-C.

The ED transition probabilities of a lanthanide(III) complex have been reported by Mason and Richardson to be dominated by (1) statically and (2) dynamically coupled ligand–lanthanide electrostatic interactions [55,53,113,54]. In the static coupling model, the ligand environment is represented in terms of a crystal field which is controlled by a static point charge of the coordinating atoms and their positions. In the dynamic coupling models, meanwhile, the ligand environment is represented in terms of anisotropic polarizabillty of the coordination field which might be affected by charge distribution, existence and position of heavy atoms, and π-conjugation expansion in the ligands.

In order to discuss the origin of the photochromic modulation of the emission properties in the present Eu(III) complex, the geometrical structure and the electrostatic potential surface of the THIA ligand were calculated by quantum chemical calculation based on the density functional theory (DFT) at the 6-31G(d) level (Fig. 6). The

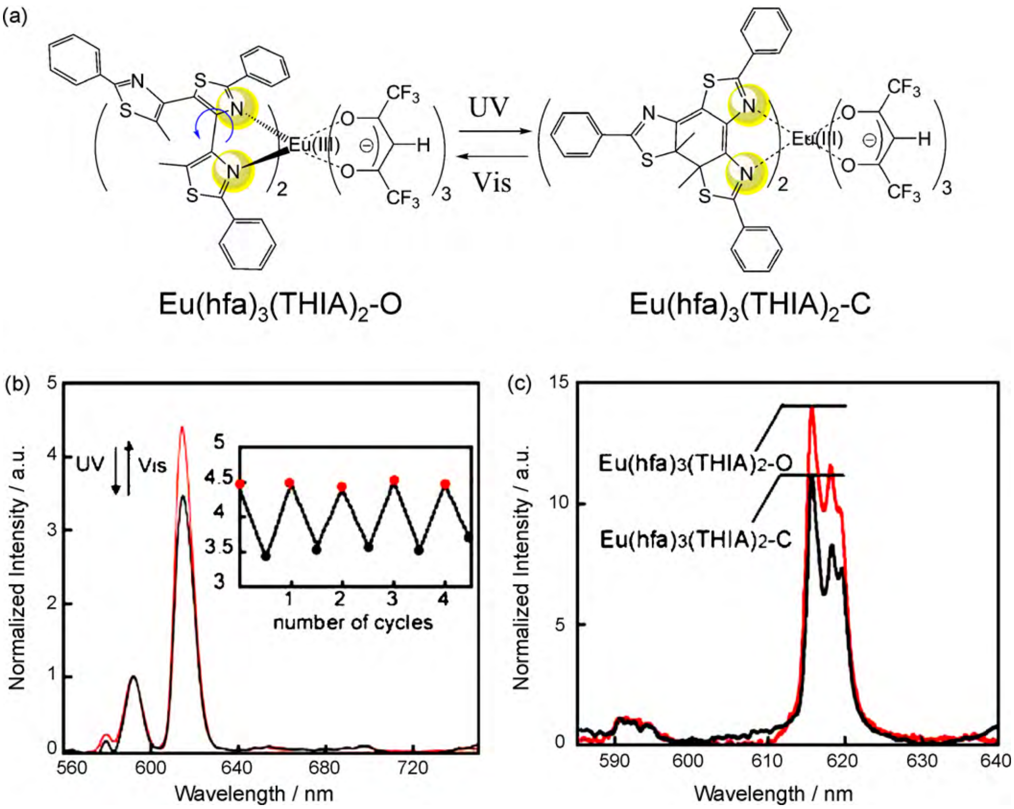

Fig. 5. (a) Photochemical reactions of Eu(hfa)$_3$(THIA)$_2$-O and Eu(hfa)$_3$(THIA)$_2$-O. (b) Normalized emission spectra of Eu(hfa)$_3$(THIA)$_2$-O (red line) and colored photo-stationary state (black line) under 365 nm. (a) In toluene solution at room temperature (excitation at 465 nm) (*Inset*: reversible change of relative emission intensity at 614 nm with the alternative irradiation cycles of UV and visible light). (c) In EtOH/MeOH glass matrics at 80 K: Eu(hfa)$_3$(THIA)$_2$-O (red line) and Eu(hfa)$_3$(THIA)$_2$-C (black line). Emission spectra were normalized at 592 nm ($^5D_0$–$^7F_1$).

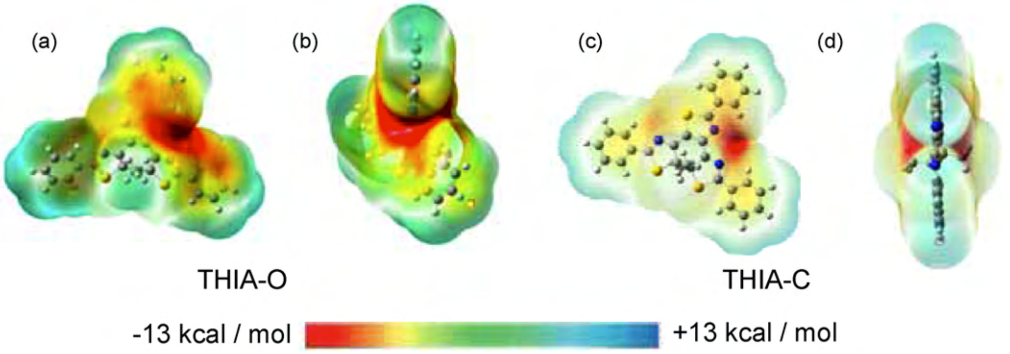

Fig. 6. Electrostatic potential surface of THIA-O [a: front view and b: side view] and THIA-C [c: front view and d: side view].

anisotropic polarizability of THIA-C is smaller than that of THIA-O, which would affect the anisotropic polarizability of the ligand and the ED transition probability [56]. Richardson and co-workers have reported that the anisotropic polarizability influences the ED transition probability in trivalent Eu(ODA)$_3{}^-$ and Eu(DBM)$_3$H$_2$O complexes [114]. The calculated values of polarizabillty for THIA-O and THIA-C at 465 nm were 512 Bohr^3 and 759 Bohr^3, respectively and THIA-C seems to have a larger polarizability and thus larger anisotropic polarizable than those of THIA-O. There is an apparent discrepancy between the results obtained in our study of photochromic ligand polarizability and Richardson's models, which might result from the fact that our DFT calculations are based on free photochromic units. Therefore, effect on the anisotropic polarizability on the change in ED transition probability might not be ruled out for the Eu(hfa)$_3$(THIA)$_2$.

5. Photochromic lanthanide complex with *f–f* transition bands II

Photochromic molecules with attached luminophor are promising photofunctional molecules for luminescent optical memory. However, nondestructive readout capability of photochromic molecules with organic luminophor or transition-metal complexes has not yet been reported. There are two major problems with nondestructive readout. The first is the difficulty in selective excitation in the readout process. This requires that both states of diarylethene have zero absorbance at the luminescence excitation wavelength to avoid the photochromic reaction during the luminescence reading process. The second is related to the luminescence modulation mechanism. Readout is generally based on the quenching of luminescence from

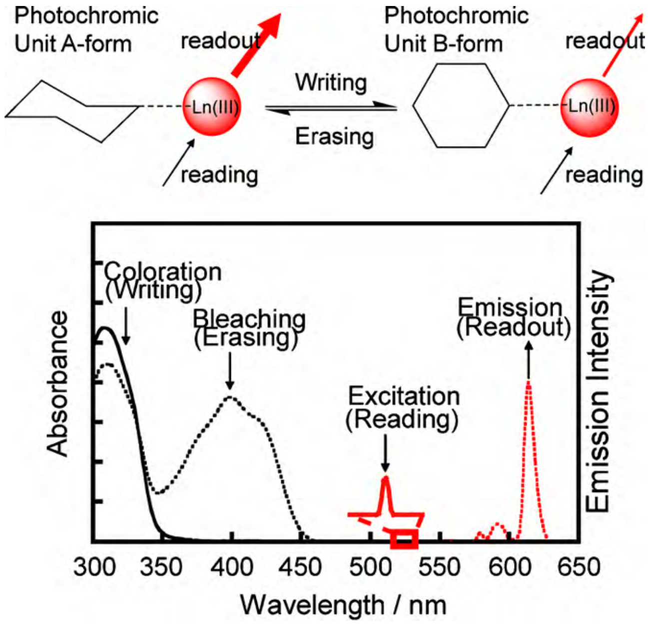

Fig. 7. Schematic representation of transitions of diarylethene (black line) and Eu(III) complex (red line).

an excited luminescent center to the colored state of the diarylethene by an intramolecular Förster resonance energy transfer (FRET) [115–117]. The drawback is that such energy induces photochromic cycloreversion and thus destroys the stored information.

The first problem might be solved by separating the absorption wavelength of both diarylethene isomers, from the excitation and luminescence wavelengths of the luminescent centers. If lanthanide is used as the luminescent center in combination with photochromic diarylethene, the excitation of diarylethenes and lanthanide complexes occurs at their π- and 4*f*-electron systems, respectively. Because there is no overlap in energy or in wavefunction between the two transitions, it is possible to divide the excitation of a diarylethene from the excitation and luminescence of a lanthanide complex.

Table 2
Experimental emission efficiencies, emission lifetimes, radiative rate constants and non-radiative rate constants of Eu-BTFO4-O and Eu-BTFO4-C.

Complex	Φ^a (%)	τ^b (ms)	k_r ($\times 10^2$ s^{-1})	k_{nr} ($\times 10^2$ s^{-1})
Eu-BTFO4-O	16	0.71	2.3	1.2
Eu-BTFO4-C	10	0.68	1.5	1.3

[a] The emission quantum efficiencies of Eu-BTFO4-O and Eu-BTFO4-C in ethyl acetate were evaluated by utilizing Eu(hfa)$_3$(BIPHEPO) as the standard of $\Phi_{Ln} = 0.60$ [60].

[b] The emission lifetimes of Eu-BTFO4-O and Eu-BTFO4-C in ethyl acetate were were measured by excitation at 355 nm.

As suggested in Fig. 7, a photochromic diarylethene with its absorption bands at shorter wavelengths is required to divide the absorption bands from the excitation and emission bands of the Eu(III) complex. From the view point of 'wavelength-divided' luminescence modulation systems, we prepared a photochromic Eu(III) complex with a BTFO4 ligand, whose absorption bands exist at shorter wavelengths due to the stabilization of the HOMO in the closed-ring form (Fig. 8a) [118–120].

The emission spectra of Eu-BTFO4 upon excitation at 526 nm ($^7F_0$–$^5D_1$ transition) are shown in Fig. 8b. The emission intensity at 615 nm was increased upon visible light irradiation. It should be noted that Eu-BTFO4, in both the open- and closed-forms, has no spectroscopic overlap between its absorption and emission bands. Therefore, this change in emission intensity cannot be explained by the photo-switching phenomena based on FRET. Here, the hypersensitive transition, centered at 615 nm, gave rise to the largest change in the Eu(III) emission. Since this transition is highly sensitive to the changes in the local coordination environment [60], we can conclude that such emission intensity changes are directly linked to the changes of the ligand field caused by photochromic reaction. We next studied the kinetic effect on the change of the photophysical properties caused by photochromic reaction. The emission quantum efficiency (Φ_{Ln}) and the emission lifetime (τ_{emi}) of Eu-BTFO4-O and Eu-BTFO4-C were measured to obtain

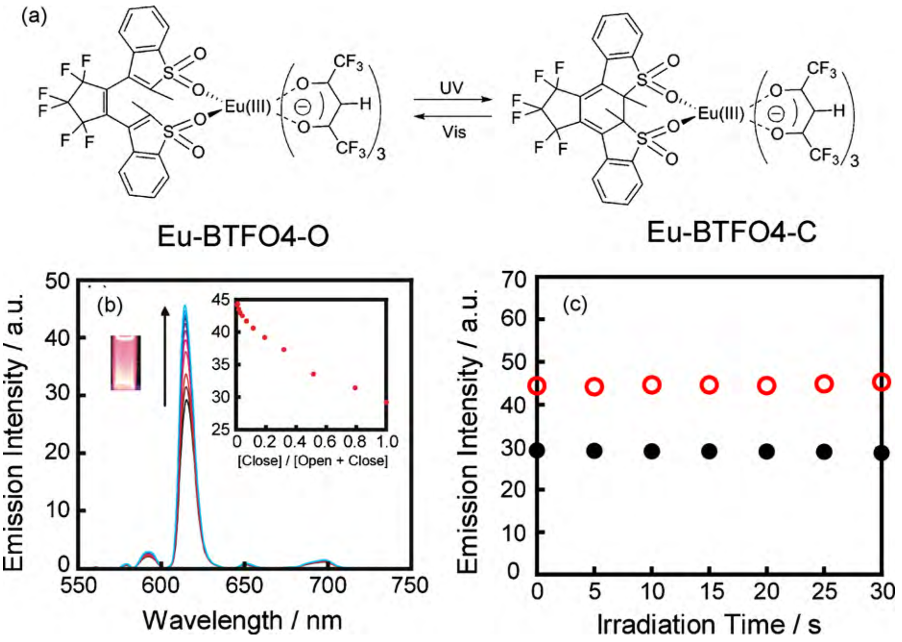

Fig. 8. (a) Photochemical reactions of Eu-BTFO4-O and Eu-BTFO4-C. (b) Emission spectroscopic change of Eu-BTFO4 in ethyl acetate solution upon visible light irradiation ($\lambda > 420$ nm). $\lambda_{ex} = 526$ nm. Inset shows change of emission intensity at 615 nm as a function of conversion ratio of Eu-BTFO4-C. (c) Emission intensity at 615 nm of Eu-BTFO4 in the open-form (○) and in the closed-form (●) plotted versus irradiation time. $\lambda_{ex} = 526$ nm.

the radiative and non-radiative rate constants. The evaluated data are summarized in Table 2. It is clearly shown that the k_{nr} values of the Eu-BTFO4-O and Eu-BTFO4-C are almost the same, which can be affected by back-energy transfer to the sensitizer [121,122] and quenching by ligand vibrations [68–72]. Therefore, these processes appear not to play a major role in the emission intensity change upon the photochromic reaction. Notably, the k_r value of Eu-BTFO4-O is 1.5 times larger than that of Eu-BTFO4-C. The radiative process of the Eu(III) complex is affected by the ligand field related to the electric dipole transition probability [56–66]. Therefore, we conclude that the change of the radiative process plays a major role in the emission intensity change of Eu-BTFO4.

To investigate its nondestructive readout capability, Eu-BTFO4 was irradiated continuously by a 526 nm light in order to induce excitation of the Eu(III) ion in both open- and closed-form complexes. The irradiation did not induce any change in the emission intensity at 615 nm for either form, as shown in Fig. 8c. We also observed no apparent absorption spectroscopic change between the open- and closed-forms, which indicates luminescence modulation with nondestructive readout capability in the present Eu(III) complex.

Recently, control of the intramolecular Förster resonance energy transfer process in luminescent lanthanide complexes with photochromic units has been reported [123,124]. However, nondestructive readout capability of these lanthanide complexes cannot be achieved, because these lanthanide complexes possess spectroscopic overlapping between the emission band from the lanthanide ion and the absorption band of the colored photochromic units. FRET excitation of the colored form is known to induce the photochromic cycloreversion reaction [116]. In contrast, wavelength-divided luminescence modulation for nondestructive readout using a diarylethene with Eu(III) complex is demonstrated here for the first time. The conceptual design and remarkable luminescence modulation for the nondestructive readout provide a significant impact on scientific interests in the area of photofunctional materials science.

6. Conclusions

Modulating luminescence intensity is one of the most promising areas in molecular photo-switches and molecular memory because of the high sensitivity, resolution, contrast and fast response times in luminescence technology. This review illuminates recent progress in the field of luminescent metal complexes with photochromic units. There is potential to make valuable contributations in synthesis, spectroscopy and computation. The concept of luminescence switching using luminescent metal complexes with photochromic units is both experimentally and intellectually challenging as a field of study. There are also obvious applications for these materials in optical devices, photonic memory and photosensing applications. For these reasons, it is hoped that this paper serves as motivation for others to enter this field.

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References

[1] B.L. Feringa, Molecular Switches, Wiley–VCH, Weinheim, 2001.
[2] V. Balzani, M. Venturi, A. Credi, Molecular Devices and Machines—A Journey into the Nanoworld, Wiley–VCH, Weinheim, 2003.
[3] S. Shinkai, Pure Appl. Chem. 59 (1987) 425.
[4] M. Irie, Chem. Rev. 100 (2000) 1683.
[5] G.H. Brown, Photochromism, Wiley–Interscience, New York, 1971.
[6] H. Dürr, H. Bouas-Laurent, Photochromism: Molecules and Systems, Elsevier, Amsterdam, 1990.
[7] G.S. Kumar, D.C. Neckers, Chem. Rev. 89 (1989) 1915.
[8] G. Berkovic, V. Krongauz, V. Weiss, Chem. Rev. 100 (2000) 1741.
[9] M. Irie, M. Mohri, J. Org. Chem. 53 (1988) 803.
[10] M. Irie, Chem. Rev. 100 (2000) 1685, and references therein.
[11] H. Tian, S. Yang, Chem. Soc. Rev. 33 (2004) 85.
[12] H. Tian, S. Wang, Chem. Commun. (2007) 781.
[13] T. Koshido, T. Kawai, K. Yoshino, Synth. Met. 73 (1995) 257.
[14] G.M. Tsuvgoulis, J.-M. Lehn, Angew. Chem. Int. Ed. Engl. 34 (1995) 1119.
[15] T. Norsten, N.R. Branda, J. Am. Chem. Soc. 123 (2001) 1784.
[16] A.J. Myles, N.R. Branda, Macromolecules 36 (2003) 298.
[17] E. Murguly, T.B. Norstern, N.R. Branda, Adv. Mater. 13 (2001) 347.
[18] A. Osuka, D. Fujikane, H. Shinmori, S. Kobatake, M. Irie, J. Org. Chem. 66 (2001) 3913.
[19] K. Yagi, C.F. Soong, M. Irie, J. Org. Chem. 66 (2001) 5419.
[20] G. Jiang, S. Wang, W. Yuan, L. Jiang, Y. Song, H. Tian, D. Zhu, Chem. Mater. 18 (2006) 235.
[21] N. Tanio, M. Irie, Jpn. J. Appl. Phys. 33 (1994) 1550.
[22] T. Kawai, T. Koshido, K. Yoshino, Appl. Phys. Lett. 67 (1995) 795.
[23] M.-S. Kim, H. Maruyama, T. Kawai, M. Irie, Chem. Mater. 15 (2003) 4539, and references therein.
[24] T. Kawai, T. Kunitake, M. Irie, Chem. Lett. 28 (1999) 905.
[25] D. Dulić, S.J. van der Molen, T. Kudernac, H.T. Jonkman, J.J.D. de Jong, T.N. Bowden, J. van Esch, B.L. Feringa, B.J. van Wees, Phys. Rev. Lett. 91 (2003) 207402.
[26] T. Kawai, Y. Nakashima, M. Irie, Adv. Mater. 17 (2005) 309.
[27] T. Kawai, Y. Nakashima, T. Kunitake, M. Irie, Curr. Appl. Chem. 5 (2005) 139.
[28] E. Kim, H.W. Lee, J. Mater. Chem. 16 (2006) 1384.
[29] N. Katsonis, T. Kudernac, M. Walko, S.J. van der Molen, B.J. van Wees, B.L. Feringa, Adv. Mater. 18 (2006) 1397.
[30] M. Ikeda, N. Tanifuji, H. Yamaguchi, M. Irie, K. Matsuda, Chem. Commun. (2007) 1355.
[31] A. Staykov, D. Nozaki, K. Yoshizawa, J. Phys. Chem. 111 (2007) 3517.
[32] T. Kawai, T. Koshido, M. Nakazono, K. Yoshino, Chem. Lett. (1993) 697.
[33] T. Koshido, T. Kawai, K. Yoshino, J. Phys. Chem. 99 (1995) 6110.
[34] S.L. Gilat, S.H. Kawai, J.-M. Lehn, J. Chem. Soc., Chem. Commun. (1993) 1439.
[35] S.L. Gilat, S.H. Kawai, J.-M. Lehn, Chem. Eur. J. 1 (1995) 275.
[36] S.H. Kawai, S.L. Gilat, R. Ponsinet, J.-M. Lehn, Chem. Eur. J. 1 (1995) 285.
[37] S.H. Kawai, S.L. Gilat, J.-M. Lehn, Eur. J. Org. Chem. (1999) 2359.
[38] Y. Moriyama, K. Matsuda, N. Tanifuji, S. Irie, M. Irie, Org. Lett. 7 (2005) 3315.
[39] R. Baron, A. Onopriyenko, E. Katz, O. Lioubashevski, I. Willner, S. Wang, H. Tian, Chem. Commun. (2006) 2147.
[40] B. Gorodetsky, N.R. Branda, Adv. Funct. Mater. 17 (2007) 786.
[41] K. Matsuda, M. Irie, J. Am. Chem. Soc. 122 (2000) 7195.
[42] K. Matsuda, M. Irie, J. Am. Chem. Soc. 122 (2000) 8309.
[43] K. Matsuda, M. Matsuo, S. Mizoguti, K. Higashiguchi, M. Irie, J. Phys. Chem. B 106 (2002) 11218.
[44] N. Tanifuji, M. Irie, K. Matsuda, J. Am. Chem. Soc. 127 (2005) 13344.
[45] J.J.D. de Jong, L.N. Lucas, R.M. Kellogg, J.H. van Esch, B.L. Feringa, Science 304 (2004) 278.
[46] J.J.D. de Jong, P.R. Hania, A. Pagzlys, L.N. Lucas, M. de Loos, R.M. Kellogg, B.L. Feringa, K. Duppen, J.H. van Esch, Angew. Chem. Int. Ed. 44 (2005) 2373.
[47] T. Hirose, K. Matsuda, M. Irie, J. Org. Chem. 71 (2006) 7499.
[48] A.P. de Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, Chem. Rev. 97 (1997) 1515.
[49] A. Fernandez-Acebes, J.-M. Lehn, Adv. Mater. 10 (1998) 1519.
[50] A. Fernandez-Acebes, J.-M. Lehn, Chem. Eur. J. 5 (1999) 3285.
[51] S. Yanagida, Y. Hasegawa, K. Murakoshi, Y. Wada, N. Nakashima, T. Yanamaka, Coord. Chem. Rev. 171 (1998) 461.
[52] Y. Hasegawa, Y. Wada, S. Yanagida, J. Photochem. Photobiol. C Photochem. Rev. 5 (2004) 183.
[53] E.M. Stephens, M.F. Reid, F.S. Richardson, Inorg. Chem. 23 (1984) 4611.
[54] M.T. Devlin, E.M. Stephens, M.F. Reid, F.S. Richardson, Inorg. Chem. 26 (1987) 1208.
[55] S.F. Mason, R.D. Peacock, B. Stewart, Chem. Phys. Lett. 29 (1974) 149.
[56] S.F. Mason, J. Indian Chem. Soc. 63 (1986) 73.
[57] A.F. Kirby, F.S. Richardson, J. Phys. Chem. 87 (1983) 2544.
[58] M. Montalti, L. Prodi, N. Zaccheroni, L. Charbonnière, L. Douce, R. Ziessel, J. Am. Chem. Soc. 123 (2001) 12694.
[59] K. Driesen, P. Lenaerts, K. Binnemans, C. Görller-Walrand, Phys. Chem. Chem. Phys. 4 (2002) 552.
[60] Y. Hasegawa, M. Yamamuro, Y. Wada, N. Kanehisa, Y. Kai, S. Yanagida, J. Phys. Chem. A 107 (2003) 1697.
[61] W. Liu, T. Jiao, Y. Li, Q. Liu, M. Tan, H. Wang, L. Wang, J. Am. Chem. Soc. 126 (2004) 2280.
[62] J.P. Cross, M. Lauz, P.D. Badger, S. Petoud, J. Am. Chem. Soc. 126 (2004) 16278.
[63] P. Nockemann, B. Thijs, N. Postelmans, K.V. Hecke, L.V. Meervelt, K. Binnemans, J. Am. Chem. Soc. 128 (2006) 13658.
[64] K. Nakamura, Y. Hasegawa, H. Kawai, N. Yasuda, N. Kanehisa, Y. Kai, T. Nagamura, S. Yanagida, Y. Wada, J. Phys. Chem. A 111 (2007) 3029.
[65] A. Wada, M. Watanabe, Y. Yamanoi, T. Nankawa, K. Namiki, M. Yamasaki, M. Murata, H. Nishihara, Bull. Chem. Soc. Jpn. 80 (2007) 335.

[66] Y. Hasegawa, S. Tsuruoka, T. Yoshida, H. Kawai, T. Kawai, J. Phys. Chem. A 112 (2008) 803.
[67] G. Stain, E. Würzberg, J. Chem. Phys. 62 (1975) 208.
[68] Y. Hasegawa, Y. Kimura, K. Murakoshi, Y. Wada, T. Yamanaka, J. Kim, N. Nakashima, S. Yanagida, J. Phys. Chem. 100 (1996) 10201.
[69] Y. Hasegawa, K. Murakoshi, Y. Wada, S. Yanagida, J. Kim, N. Nakashima, T. Yamanaka, Chem. Phys. Lett. 8 (1996) 8.
[70] Y. Hasegawa, M. Iwamuro, K. Murakoshi, Y. Wada, R. Arakawa, T. Yamanaka, N. Nakashima, S. Yanagida, Bull. Chem. Soc. Jpn. 71 (1998) 2573.
[71] Y. Hasegawa, T. Ohkubo, K. Sogabe, Y. Kawamura, Y. Wada, N. Nakashima, S. Yanagida, Angew. Chem. Int. Ed. 39 (2000) 357.
[72] Y. Wada, T. Okubo, M. Ryo, T. Nakazawa, Y. Hasegawa, S. Yanagida, J. Am. Chem. Soc. 122 (2000) 8583.
[73] T. Nakagawa, K. Atsumi, T. Nakashima, Y. Hasegawa, T. Kawai, Chem. Lett. 36 (2007) 372.
[74] T. Nakashima, K. Atsumi, S. Kawai, T. Nakagawa, Y. Hasegawa, T. Kawai, Eur. J. Org. Chem. 19 (2007) 3212.
[75] T. Nakagawa, Y. Hasegawa, T. Kawai, J. Phys. Chem. A 112 (2008) 5096.
[76] T. Nakagawa, Y. Hasegawa, T. Kawai, Chem. Commun. 37 (2009) 5630.
[77] Q. Luo, B. Chen, M. Wang, H. Tian, Adv. Funct. Mater. 13 (2003) 233.
[78] H. Tian, B. Chen, H. Tu, K. Müllen, Adv. Mater. 14 (2002) 918.
[79] B. Chen, M. Wang, Y. Wu, H. Tian, Chem. Commun. (2002) 1060.
[80] H.J. Kim, J.H. Jang, H. Choi, T. Lee, J. Ko, M. Yoon, H.-J. kim, Inorg. Chem. 47 (2008) 2411.
[81] J.L. Bahr, G. Kodis, L. Garza, S. Lin, A.L. Moore, T.A. Moore, D. Gust, J. Am. Chem. Soc. 123 (2001) 7124.
[82] T. Yutaka, I. Mori, M. Kurihara, J. Mizutani, N. Tamai, T. Kawai, M. Irie, H. Nishihara, Inorg. Chem. 41 (2002) 7143.
[83] T.-W. Ngan, C.-C. Ko, N. Zhu, V.W.-W. Yam, Inorg. Chem. 46 (2007) 1144.
[84] H. Zhao, U. Al-Atar, T.C.S. Pace, C. Bohne, N.R. Branda, J. Photochem. Photobiol. A Chem. 200 (2008) 74.
[85] V.W.-W. Yam, J.K.W. Lee, C.-C. Ko, N. Zhu, J. Am. Chem. Soc. 131 (2009) 912.
[86] T. Sakata, D.K. Jackson, S. Mao, G. Marriott, J. Org. Chem. 73 (2008) 227.
[87] J. Filley, M.A. Ibrahim, M.R. Nimlos, A.S. Watt, D.M. Blake, J. Photochem. Photobiol. A Chem. 117 (1998) 193.
[88] S. Kumar, C. Chau, G. Chau, A. McCurdy, Tetrahedron 64 (2008) 7097.
[89] V.W.-W. yam, C.-C. Ko, N. Zhu, J. Am. Chem. Soc. 126 (2004) 12734.
[90] C.-C. Ko, W.-M. Kwok, V.W.-W. Yam, D.L. Phillips, Chem. Eur. J. 12 (2006) 5840.
[91] P.H.-M. Lee, C.-C. Ko, N. Zhu, V.W.-W. Yam, J. Am. Chem. Soc. 129 (2007) 6058.
[92] D.S. Tyson, C.A. Bignozzi, F.N. Castellano, J. Am. Chem. Soc. 124 (2002) 4562.
[93] V. Ferri, M. Scoponi, C.A. Bignozzi, D.S. Tyson, F.N. Castellano, H. Doyle, G. Redmond, Nano Lett. 4 (2004) 835.
[94] W. Tan, Q. Zhang, J. Zhang, H. Tian, Org. Lett. 11 (2009) 161.
[95] S.V. Wallendael, D.P. Rillema, J. Chem. Soc., Chem. Commun. (1990).
[96] R.T.F. Jukes, B. Bozic, P. Belser, L. De Cola, F. Hartl, Inorg. Chem. 48 (2009) 1711.
[97] R.T.F. Jukes, B. Bozic, F. Hartl, P. Belser, L. De Cola, Inorg. Chem. 45 (2006) 8326.
[98] S. Silvi, E.C. Constable, C.E. Housecroft, J.E. Beves, E.L. Dunphy, M. Tomasulo, F.M. Raymo, A. Credi, Chem. Eur. J. 15 (2009) 178.
[99] J. Kido, H. Hayase, K. Hongawa, K. Nagai, K. Okuyama, Appl. Phys. Lett. 65 (1994) 2124.
[100] Y. Hasegawa, K. Sogabe, Y. Wada, S. Yanagida, J. Lumin. 101 (2003) 235.
[101] N. Weibel, L.J. Charbonniere, M. Guardigli, A. Roda, R. Ziessel, J. Am. Chem. Soc. 126 (2004) 4888.
[102] G.W. Burdick, R.L. Summerscales, S.M. Crooks, M.F. Reid, F.S. Richardson, J. Alloys Compd. 303–304 (2000) 376.
[103] N. Fatin-Rouge, E. Toth, D. Perret, R.H. Backer, A.E. Merbach, J.-C.G. Büenzli, J. Am. Chem. Soc. 122 (2000) 10810.
[104] S.I. Klink, L. Grave, D.N. Reinhoudt, F.C.M. van Veggel, M.H.V. Werts, F.A.J. Geurts, J.W. Hofstraat, J. Phys. Chem. A 104 (2000) 5457.
[105] J.I. Bruce, R.S. Dickins, L.J. Govenlock, T. Gunnlaugsson, S. Lopinski, M.P. Lowe, D. Parker, R.D. Peacock, J.J.B. Perry, S. Aime, M. Botta, J. Am. Chem. Soc. 122 (2000) 9674.
[106] A. Beeby, S. Faulkner, D. Parker, J.A.G. Williams, J. Chem. Soc., Perkin Trans. 2 (8) (2001) 1268.
[107] G.F. de Sá, O.L. Malta, C. de Malleo Donegá, A.M. Simas, R.L. Longo, P.A. Santa-Cruz, E.F. da Silva jr., Coord. Chem. Rev. 196 (2000) 165.
[108] B.R. Judd, Phys. Rev. 127 (1962) 750.
[109] G.S.J. Ofelt, Chem. Phys. 37 (1962) 511.
[110] C. Görller-Warrand, L. Fluyt, A. Ceulemans, W.T. Carnall, J. Chem. Phys. 95 (1991) 3099.
[111] M.H.V. Werts, R.T.F. Jukes, J.W. Verhoeven, Phys. Chem. Chem. Phys. 4 (2002) 1542.
[112] K. Lunstroot, K. Driesen, P. Nockemann, C. Görller-Walrand, K. Binnemans, S. Bellayer, J.L. Bideau, A. Vioux, Chem. Mater. 18 (2006) 5711.
[113] M.F. Reid, F.S. Richardson, J. Phys. Chem. 88 (1984) 3579.
[114] J.J. Dallara, M.F. Reid, F.S. Richardson, J. Phys. Chem. 88 (1984) 3587.
[115] T. Kawai, T. Sasaki, M. Irie, Chem. Commun. (2001) 711.
[116] T. Fukaminato, T. Sasaki, T. Kawai, N. Tamai, M. Irie, J. Am. Chem. Soc. 126 (2004) 14843.
[117] S.J. Lim, J. Seo, S.Y. Park, J. Am. Chem. Soc. 128 (2006) 14542.
[118] Y.C. Jeong, S.I. Yang, K.H. Ahn, E. Kim, Chem. Commun. (2005) 2503.
[119] Y.C. Jeong, J.P. Han, Y. Kim, E. Kim, S.L. Yang, K.H. Ahn, Tetrahedron 63 (2007) 3173.
[120] T. Fukaminato, M. Tanaka, L. Kuroki, M. Irie, Chem. Commun. (2008) 3924.
[121] G.A. Hebbink, S.I. Klink, P.G.B. Oude Alink, F.C.J.M. van Veggel, Inorg. Chem. Acta 317 (2001) 114.
[122] M. González-Lorenzo, C. Platas-Iglesias, F. Avecilla, C.F.G.C. Geraldes, D. Lmbert, J.-C.G. Bünzli, A. de Blas, T. Rodríguez-Blas, Inorg. Chem. 42 (2003) 6946.
[123] Z. Wang, Y. Ma, R. Zhang, A. Peng, Q. Liao, Z. Cao, H. Fu, J. Yao, Adv. Mater. 21 (2009) 1737.
[124] K. Machitani, Y. Nakahara, K. Kimura, Bull. Chem. Soc. Jpn. 82 (2009) 472.