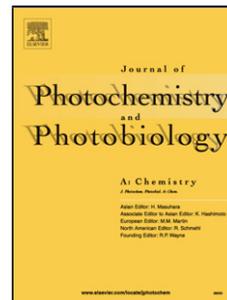


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ABSTRACT: We developed a model dual-light-responsive luminescent lanthanide supramolecular switch. A poly[2]pseudorotaxane was firstly constructed from a dilanthanide metal supramolecular assembly (EuTb·1_{EPO}) and an asymmetric diarylperfluorocyclopentene (**2**), in which EuTb·1_{EPO} exhibits a satisfactory and tunable lanthanide luminescence, while the **2** moiety in the poly[2]pseudorotaxane displays a reversible photochromic process upon light irradiation with an excellent resistance to fatigue. By switching between closed-form and open-form states of **2** using ultraviolet and visible light irradiation alternately, the lanthanide luminescence of poly[2]pseudorotaxane can be quenched and rapidly recovered, that is, the poly[2]pseudorotaxane can be used as switchable controlling unit.

Keywords: supramolecular switch; poly[2]pseudorotaxane; lanthanide luminescence; asymmetric diarylperfluorocyclopentene; stimuli-responsive supramolecular material

1. Introduction

The rapidly increasing responsive materials are now catering for the development of biosensors[1-5], surface materials[6-7], and smart optical switches[8]. Among these addressable smart nanodevices, light-responsive apparatuses possess distinctive advantages for their ability to convert optical signals into versatile output signals[9]. On the other hand, light, as a source of stimulus response, is one of the most widely utilized triggers, owing to its accessibility, spatiotemporal and wavelength-selective precision, clean and waste-free[10-12]. Possessing these enormous advantages, optically responsive materials have become a focus in scientific research in recent years. Photochromic compounds, such as spirooxazines[13-14], spiropyranes[15], azobenzenes[16], and diarylethenes (DAEs)[17-19], have been frequently applied to optical devices for their abilities of reversibly interconverted by light irradiation between two states with significant structural differences. The developing of DAE photochromic compounds has provided an ideal candidate for constructing smart materials owing to they could fulfill the following requirements simultaneously: (1) superb resistance to fatigue, (2) extreme sensitivity, (3) rapid response, (4) remarkable thermally irreversible photochromic behavior, and (5) retaining high reactivity in solid state[20]. DAEs exhibit reversible light-induced cyclization and cycloreversion reactions which cause sufficiently different absorption spectra and subtle geometrical change. As a consequence, the outstanding performance of the DAEs offers great

potential for advancing optoelectronic technologies, optical memories, and fluorescent biological markers. For instance, the covalently junction of DAE photoswitches and graphene electrodes forms single-molecule electrical switch, showing that photochromic molecules with suitable conductive properties and amenable to anchoring to solid-state electrodes can be key components for future photoswitching nanoelectronics with nondestructive readout capability[21]. A method for pairing chirality α -amino acids and naphthalimide chromophore connected to bistable photoresponsive DAE constructs a unique supramolecular helical architecture that can act as a dynamic photoswitch for modulating the morphology, fluorescence, and helicity[22].

The dynamic photoreversibility with modulation of luminescence intensity is one of the most fascinating aims in molecular photoswitches because of the luminescent tunable systems would offer a various of application for biosensors and optical bioimaging. Kim and co-workers developed a water-soluble dendritic nanocluster using the DAE derivative as a crosslinker, and cyanine 3 working as a fluorescence donor molecule. The dye-crosslinked dendritic nanocluster can work as a reversibly photoswitch for fluorescence imaging in vivo, which showed high on-off contrast in living systems[23]. In recent years, lanthanide-based luminescent devices have been considered as a class of popular luminescent materials because of their unique highly desirable physical properties, such as long decay times, large Stokes shifts, and narrow emission in visible and near-infrared regions[24-26]. New multifunction luminescent materials that integration of photochromic DAEs with lanthanide components have exhibited a few remarkable unexpected applications. Lanthanide-doped upconverting nanoparticles were successfully prepared with DAE photoswitches, showing the toggle photochromic DAEs between their two unique optical and structural states by modulating merely the intensity of the 980 nm excitation light[27]. Moreover, the combination of the chiral DAE molecular switch and lanthanide-doped upconverting nanoparticles formed a self-organized helical superstructure exhibiting unprecedented reversible handedness inversion under NIR light irradiation[28]. Lanthanide-luminescence-based materials have been utilized as

an intermediary to furnish the multiple light sources. Correspondingly, fascinating developments are taking place to modulate the luminescent intensity of lanthanide complexes because of their high sensitivity, resolution, and contrast and fast response, which are essential in luminescence technology. The system accompanying with reversible modulation mechanisms would offer a facilitation method of regulating these versatile optical properties. More recently, We successfully constructed some interesting supramolecular devices, such as tris[2]pseudorotaxane[29] and [2]pseudorotaxane[30], revealing an excellent reversible luminescent lanthanide switches in the presence of K^+ or 18-crown-6. Nevertheless, drawbacks, such as the requirement of external additives, hamper their practical application. Therefore, A light-responsive [2]pseudorotaxane was constructed from perfluorocyclopentenodiarylethene and a Eu^{3+} complex of terpyridinyldibenzo-24-crown-8 which can reversibly modulate the Eu^{3+} luminescence by UV and visible-light irradiation[31]. Moreover, several smart devices have been fabricated from lanthanide complexes and DAEs for modulating luminescence intensity of lanthanide complexes by light stimuli, especially those that can be reversibly manipulated[32-33]. However, the developing of luminescent lanthanide molecular photoswitches was still slow and all the system chose the focal items in the single lanthanide metal. Designing the reversible stimuli responsive luminescent dilanthanide switches remain a longstanding challenge. Lately, we prepared a supramolecular assembly via the coordination of a host molecule (**1**) and dilanthanide metal, which could exhibit excellent dilanthanide luminescence with switching function[34]. As part of our continuing research work in lanthanide-luminescence-based materials, we herein described a non-covalently binding method to prepare a poly[2]pseudorotaxane by simple combining an asymmetric diarylperfluorocyclopentene photochromic molecule DAE (**2**) and a dilanthanide metal supramolecular assembly ($EuTb \cdot 1_{EPO}$) (Fig. 1) through the interaction of the dialkylammonium moiety in **2** with the 24C8 ring in $EuTb \cdot 1_{EPO}$ to demonstrate that the Tb^{3+} and Eu^{3+} luminescence can be reversibly and simultaneously regulated by the cyclization and cycloreversion reactions of **2** caused

by alternating UV and visible-light irradiation.

2. Experimental

2.1. Materials

Host **1** and diarylperfluorocyclopentene **2** were prepared according to the literature procedure [30,33]. Tb(OTf)₃, Eu(OTf)₃ were purchased from Aladdin and used without further purification.

2.2. Instrument

UV/vis spectra were measured in a quartz cell (light path 10 mm) on a Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller. NMR spectra were recorded on a Varian Mercury VX400 instrument. The optical switch experiments were carried out using a photochemical reaction apparatus with a 500W Hg lamp. Fluorescence spectra were performed on an F-4500 spectrofluorometer (Hitachi, Tokyo, Japan) equipped with a plotter unit and a quartz cell (1 cm × 1 cm). The slit width was 10 and 10 nm for excitation and emission, respectively.

2.3. Preparation of thin polymer films

The 10 g poly methylmethacrylate (PMMA) was added to 60 mL of CHCl₃ and then stirred until it was completely dissolved into transparent liquid by heating. Then a specified amount (5 wt% of loading) of compound **2** was added to the PMMA solution and stirred well to mix. The solution was poured on to a glass slide and kept in a dark room. After the complete evaporation of the solvent, the PMMA film with compound **2** was obtained. The resulting films were kept in a dark room.

3. Result and discussion

We firstly investigated the optical properties of compounds **1** and **2**. The anthracene (ant) unit within the host molecule **1** could undergo reversibly photooxygenation between ant and endoperoxide (EPO) upon light irradiation or heating. When adding the Ln³⁺ (Tb³⁺, Eu³⁺) ion into EPO-form host molecular **1**_{EPO}, metallosupramolecular assembly was formed. More importantly, it could exhibit excellent lanthanide luminescence. As shown in Fig. S3, coordination of UV-actuated EPO host molecule through terpyridine unit with Tb³⁺ and Eu³⁺ results in Ln·**1**_{EPO} which show green and red emission, respectively. Further, the equimolar Tb³⁺ and Eu³⁺ metal ions are

simultaneously added into **1**_{EPO} solution forming bimetallic EuTb·**1**_{EPO} which shows yellow emission.

The photochromic feature of **2** was then evaluated by UV-vis spectroscopy (Fig. S4). A solution of open-form (OF) **2** initially exhibited negligible absorbance in the range of 450-750 nm. However, drastically increased absorbance was observed after 12s irradiation under UV light (365 nm). The generation of a new absorption peak was centered at ~598 nm with an accompanying isosbestic point at 370 nm, corresponding to UV-triggered formation of closed-form (CF). Then, visible light-actuated CF-to-OF reverse transition was investigated. After 1 min irradiation UV-irradiated solution by visible light (600 nm) led to gradually attenuated CF absorption peak. Undergoing several times repeated experiments, changes in CF absorption intensities were reversible without significant fatigue effect under alternated UV/visible light irradiation. Moreover, it is noteworthy that the photochromic DAE could undergo reversible switchable OF-CF transition upon alternated UV-vis light irradiation in solid materials. Photochromic compound **2** was mixed with PMMA and the mixture thus obtained was subjected to spin-coating. The PMMA film containing DAE **2** displayed excellent photochromic performance, as well as the case study in solution (Fig. 2b). By alternating irradiation with 365 nm/600 nm light, prominently changes in color experienced interconversion of colorless and blue, resulting from the photocyclization of photochromic DAE **2** (Fig. 2b), indicative of utmost importance to their practical applications.

When an equimolar amount of OF-**2** was added to a solution of EuTb·**1**_{EPO}, the luminescence intensity of the complex EuTb·**1**_{EPO} had not significant change (Fig. 4b). Thus, the association with OF-**2** did not significantly alter the luminescent behavior of EuTb·**1**_{EPO}. The association between host **1**_{EPO} and guest **2** was quantitatively investigated by ¹H NMR (Fig. 3). We added the compound OF-**2** to a solution of **1**_{EPO} at an OF-**2**/**1**_{EPO} mixed molar ratio of 1:2. H₄ and H₅ adjacent to the ammonium site on the axle component in **2** were shifted down field ($\Delta\delta = 0.78$ and 0.54 ppm, respectively). This results confirmed the interaction of the secondary ammonium moiety in **2** with the DB24C8 ring in **1**_{EPO}, leading to the formation of the

[2]pseudorotaxane OF-2 \subset 1_{EPO}. Moreover, we attempted to obtain the association constant (K_s) of host 1_{EPO} with guest 2. The photooxygenation of 1 caused a significant change with its conformation from a relatively “planar” structure to a “dihedral” structure (Fig. 6). Therefore, it may be a stoichiometric 1:1 binding ratio between 1_{EPO} and 2 because of the steric hindrance of the “dihedral” structure of the 1_{EPO}, rather than 1:2 binding ratio. So the MALDI-TOF of mixed solution of 1_{EPO} and 2 in a ratio 1:2 was conducted. As shown in Fig. S5, the strong binding affinity and 1:1 stoichiometry was confirmed by the MALDI-TOF spectrum in which a peak at *m/z* 2131.7 attributed to 2 \subset 1_{EPO} was observed. Then the association constant of host 1_{EPO} with guest 2 was measured by the ¹H NMR spectrum. As shown in Fig. S6, the K_s was calculated to be ca. $1 \times 10^3 \text{ M}^{-1}$.

It is well-known that the luminescence switching properties originate from good spectral overlap between the emission band of the metal complex and the absorption band of the colored photochromic unit[35-37]. In the present OF-2 \subset EuTb·1_{EPO} system, the strong emission of complex EuTb·1_{EPO} occurs at 544 nm and 615 nm, while all of the absorption bands of OF-2 occur below 400 nm (Fig. 4a). Therefore, no intermolecular resonance energy transfer (RET) from the Eu³⁺ and Tb³⁺ moiety of EuTb·1_{EPO} to the diheteroarylethene of OF-2 would be expected. However, when OF-2 \subset EuTb·1_{EPO} was exposed to 365 nm UV light, ~60% of the fluorescence intensity at 615 nm was quenched, with an accompanying ~40% of the fluorescence intensity at 544 nm was quenched (Fig. 5a). Moreover, reversibly switchable fluorescence emission of Eu³⁺ and Tb³⁺ could be achieved under alternate UV-vis light irradiation. As shown in Fig. 5b, UV-actuated fluorescence quenching and visible light-actuated fluorescence recovery processes for OF-2 \subset EuTb·1_{EPO} could be repeated for several times without significant fatigue effect under alternated 365 nm/600 nm irradiation, as reflected by reversible changes in Eu³⁺ and Tb³⁺ fluorescence intensities.

Although, the absorption band of closed-form photochromic 2 had an excellent spectral overlap with the emission band of Eu·1_{EPO} and Tb·1_{EPO} (Fig. 4a), the

efficiency of energy transfer from metal complex to photochromic unit was not desirable. We proposed that the low concentration of the guest in solution should be responsible for the unsatisfactory efficiency of energy transfer. On the other hand, the photooxygenation of **1** caused a significant change with its conformation from a relatively “planar” structure to a “dihedral” structure (Fig. 6), and thus decreased the distance between the two crown ether motifs of **1**. Meanwhile, an unexpected conformation changes in the EPO-form **1** can markedly decrease the interaction of the secondary ammonium moiety in **2** with the DB24C8 ring in **1**_{EPO}. As a result, the concentration of complex **2**⊂EuTb·**1**_{EPO} was low, accompanying with partial free guest of DAE **2**. We speculated that the low concentration of the complex **2**⊂EuTb·**1**_{EPO}, should be responsible for the unsatisfactory efficiency of energy transfer from Eu³⁺ and Tb³⁺ to CF-**2**. In addition, we have done contrast experiments used a reference compound 4'-(p-tolyl)-2,2',6',2''-terpyridine (**3**, Scheme S1) lacking the DB24C8 moiety. As shown in Fig. 7, in contrast, reference compound lacking the DB24C8 moiety quenched the fluorescence by only 12% for Tb³⁺ and 15% for Eu³⁺, respectively. The additional experiment results revealed the critical role of the crown ether moiety in facilitating the energy transfer process.

In this system, Eu³⁺ and Tb³⁺ were served as two different donors, DAE as an acceptor. We think that the degrees of quenching different for the Eu³⁺ and Tb³⁺ luminescence may originate from the different spectral overlap. As shown in Fig. 4a, it was found that the spectral overlap almost completely between the emission band of the Eu·**1**_{EPO} and the absorption band of the colored photochromic unit, even the

emission at maxima. Contrastively, the relatively poor spectral overlap was found between the emission band of the $\text{Tb}\cdot\mathbf{1}_{\text{EPO}}$ and the absorption band of the colored photochromic unit. May be the reason why the degrees of quenching different for the Eu^{3+} and Tb^{3+} luminescence.

4. Conclusion

In summary, a poly[2]pseudorotaxane exhibiting photoswitchable and reversible luminescence modulation has been fabricated from supramolecular assembly $\text{EuTb}\cdot\mathbf{1}_{\text{EPO}}$ and an unsymmetrical perfluorocyclopentene **2** (DAE), where $\mathbf{1}_{\text{EPO}}$ is anthracene-endoperoxide-based host molecular. The synthetic host molecule **1**, containing an ant core, could undergo reversible photooxygenation between ant (thermolysis) and EPO ($\lambda = 365$ nm irradiation). Coordination of $\mathbf{1}_{\text{EPO}}$ through tpy with Tb^{3+} and Eu^{3+} results in $\text{Ln}\cdot\mathbf{1}_{\text{EPO}}$ which show green and red emission respectively. Further, the equimolar Tb^{3+} and Eu^{3+} metal ions are simultaneously added into $\mathbf{1}_{\text{EPO}}$ solution forming bimetallic $\text{EuTb}\cdot\mathbf{1}_{\text{EPO}}$ which shows yellow emission, as compared to the unoxidized host molecule **1** with an integrated aromatic conjugation system. As opposed to the Ln^{3+} complexes $\text{Ln}\cdot\mathbf{1}_{\text{EPO}}$, Tb^{3+} and Eu^{3+} ion coordination to the unoxidized host molecule **1** results in fluorescence quenching, respectively. DAE moieties within poly[2]pseudorotaxane undergo phototriggered reversible and bistable photochromism between open-form (OF, $\lambda = 600$ nm irradiation) and closed-form (CF, $\lambda = 365$ nm irradiation) states. The DAE exhibited excellent resistance to fatigue and thermally stable. By utilizing the noncovalent interaction of the dialkylammonium moiety in DAE with the 24C8 ring in $\text{EuTb}\cdot\mathbf{1}_{\text{EPO}}$, the constructed poly[2]pseudorotaxane demonstrated that the bimetallic lanthanide luminescence can be simultaneously and reversibly modulated upon the ring-closing and ring-opening reactions of DAE caused by UV and visible-light irradiation. The dual-light-stimuli-driven luminescent lanthanide supramolecular switch paves the way for their future in multistimulus-responsive supramolecular materials.

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Appendix A. Supplementary data

Compound characterization, and additional figures are provided.

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Figure Caption:

Fig. 1. Structures of host compound **1**, guest compound **2**.

Fig. 2. (a) changes in the chemical structure of **2** upon alternating UV and visible-light irradiation.

(b) Absorption spectra of **2** in PMMA films undergoing photoconversion from OF-to-CF upon exposure to 365 nm light; after 80 s, the maximal change was achieved at 615 nm. Inset: absorbance changes at 615 nm for the observed upon alternating UV (365 nm) and visible-light (600 nm) irradiation in PMMA films and changes in the color of **2** in PMMA films upon alternating UV (365 nm) and visible-light (600 nm) irradiation.

Fig. 3. Partial ^1H NMR spectra (400 MHz, $\text{CD}_3\text{CN}/\text{CDCl}_3 = 1:1$, 298 K) of a) free **2**, b) $\mathbf{1}_{\text{EPO}}$ and 2.0 equiv of **2**, and c) free $\mathbf{1}_{\text{EPO}}$. $[\mathbf{1}_{\text{EPO}}] = 1.0 \text{ mM}$. See Figure 1 for atom labels.

Fig. 4. (a) Absorption spectra (left axis) of the photochromic compounds **2**, open forms (OF) are plotted with blue line and closed forms (CF) with black line, and fluorescence emission (red line and green line, right axis) for the fluorescent of complex $\text{Eu}\cdot\mathbf{1}_{\text{EPO}}$ and $\text{Tb}\cdot\mathbf{1}_{\text{EPO}}$ is also shown. Emission spectra of (b) $\text{EuTb}\cdot\mathbf{1}_{\text{EPO}}$, and in the presence of 1.2 equiv. of OF-**2** in $\text{CH}_3\text{CN}/\text{CHCl}_3$ (1:1, v:v) solution.

Fig. 5. Emission spectra of the $\mathbf{2}\subset\text{EuTb}\cdot\mathbf{1}_{\text{EPO}}$ system (0.1 mM) in $\text{CH}_3\text{CN}/\text{CHCl}_3$ (1:1, v/v) solution: (a) upon UV light irradiation at 365 nm ($\lambda_{\text{ex}} = 320 \text{ nm}$), (b) emission intensity changes at 544 nm and 616 nm upon UV irradiation ($\lambda_{\text{ex}} = 320 \text{ nm}$), (c) Schematic illustration of the light-modulated (irradiation by alternating at 365 and 600 nm) supramolecular switch.

Fig. 6. Reversible structural transformation of host molecular **1** by irradiation at 365 nm and heating.

Fig. 7. Emission spectra of (a) $\text{Eu}\cdot\mathbf{3}$ (b) $\text{Tb}\cdot\mathbf{3}$ (0.01 mM) with **2** after UV irradiation 2 min in $\text{CH}_3\text{CN}/\text{CHCl}_3$ solution (1:1), $\lambda_{\text{ex}} = 320 \text{ nm}$.

Fig. 2.

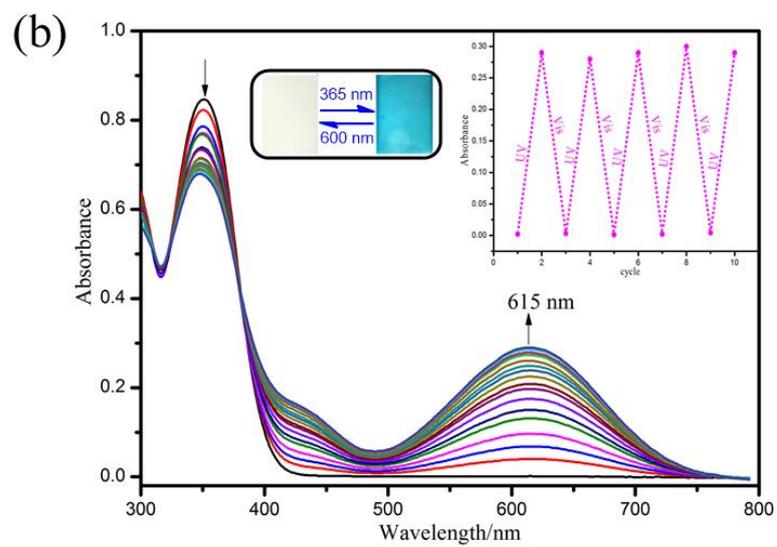
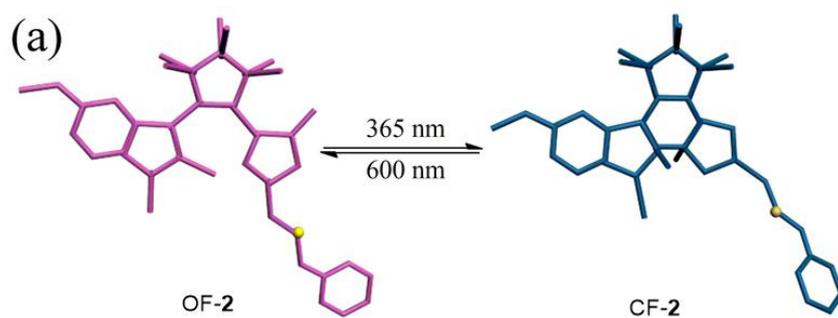


Fig. 3.

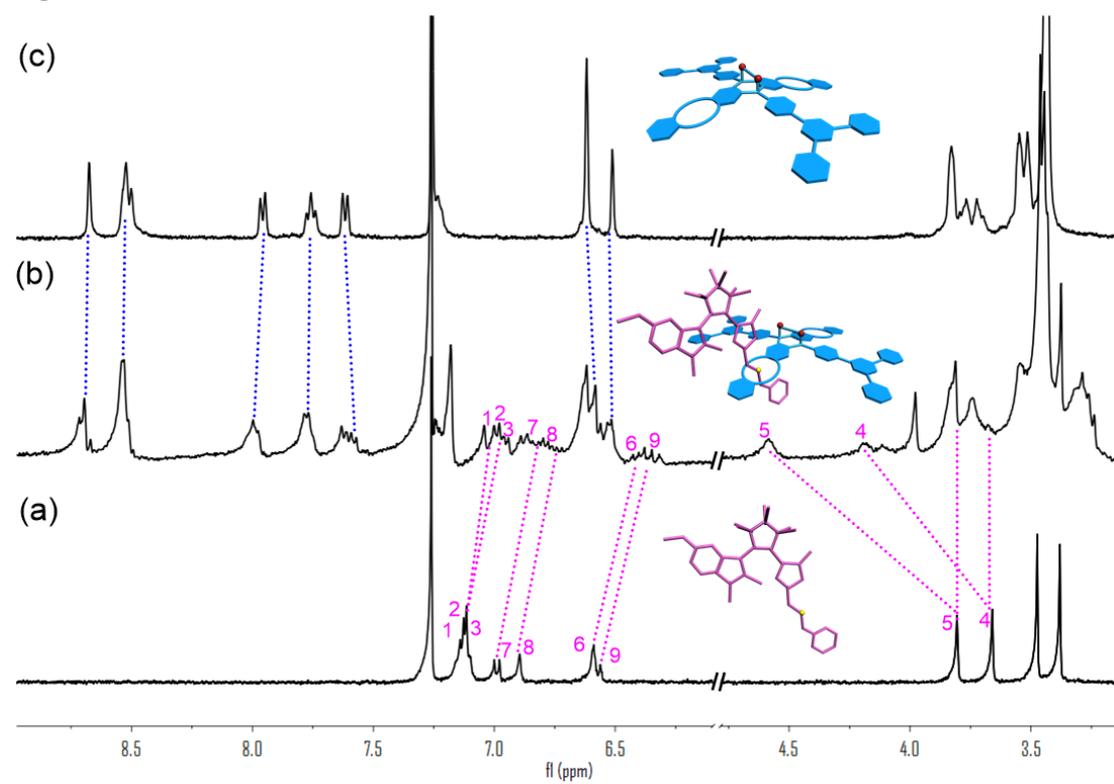


Fig. 4.

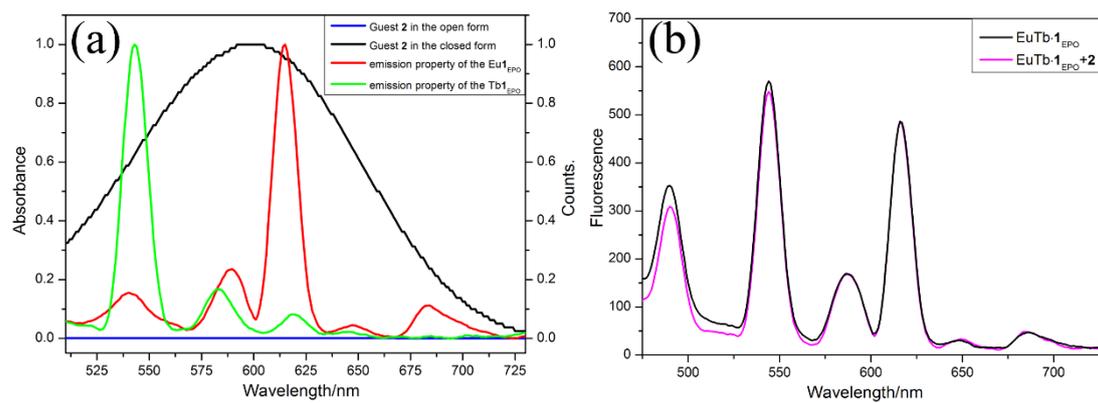


Fig. 5.

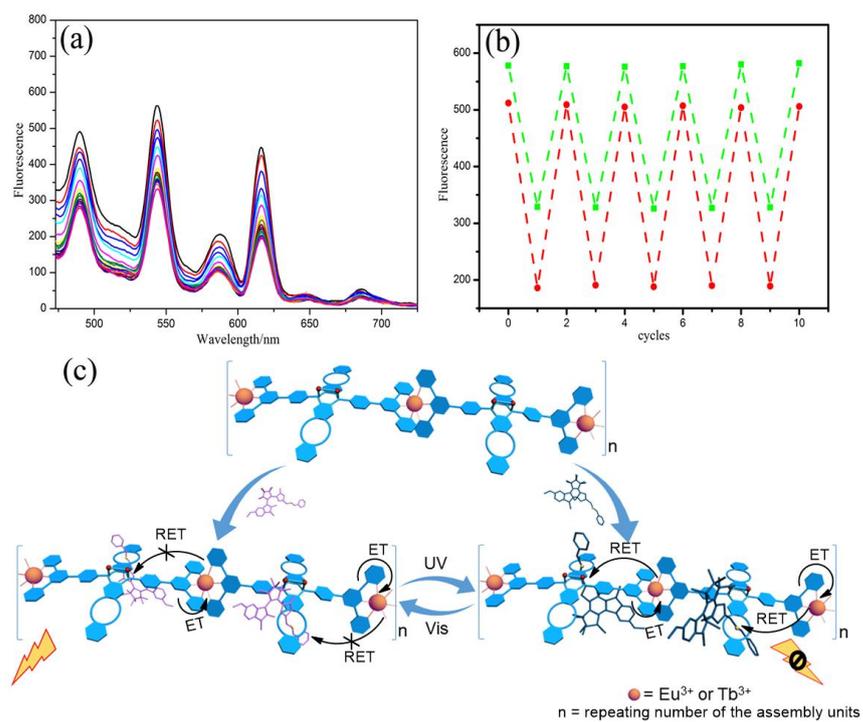


Fig. 6.

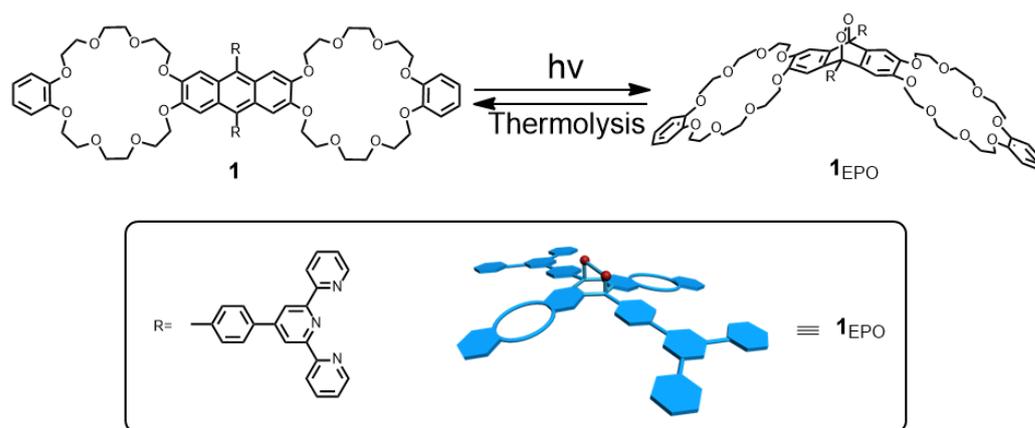


Fig. 7.