

Dual-Stimulus Luminescent Lanthanide Molecular Switch Based on an Unsymmetrical Diarylperfluorocyclopentene

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S Supporting Information

ABSTRACT: A [2]pseudorotaxane formed from an unsymmetrical diarylperfluorocyclopentene (**1**) and a Eu³⁺ complex of terpyridinyldibenzo-24-crown-8 (**2**) revealed excellent reversible lanthanide luminescence switching behavior dual-modulated by host–guest and optical stimuli.

Research on optically modulated smart materials has received much attention because of their potential application to optical switches, optoelectronics, smart surfaces, photoinduced shape-memory polymers, functional vesicles, bio-nanodevices, and molecular machines.¹ Photochromic compounds can be interconverted between two states with different spectroscopic properties using light,² which makes them good candidates for realizing smart optical modulation. Diarylethene derivatives (DAEs) are the most promising optically responsive compounds, featuring notable thermally irreversible photochromic behavior, high photoisomerization quantum yields, and outstanding fatigue resistance.³ On the other hand, lanthanide-luminescence-based devices⁴ are also well-developed because of their unique luminescence properties, such as long-lived excited states, visible-light emission, large Stokes shifts, and narrow emission bandwidths. The integration of photochromic DAEs with luminescent lanthanide components has displayed a few remarkable potential applications, including a photochromic Eu³⁺ complex with a sulfone moiety incorporated in a DAE for a potential optical memory medium with nondestructive readout capability.^{5a} The combination of lanthanide-doped upconverting nanoparticles and DAE photoswitches enables not only optical memory applications^{5b} but also modulation with near-IR light,^{5c,d} offering new opportunities in photodynamic therapy. Photoswitching and photoresponsive modulation of the emission properties of luminescent molecules with photochromic units is one of the promising research areas in molecular photoswitches and photomemory because of their high sensitivity, resolution, and contrast and their fast response, which are essential in luminescence technology.⁶ An interesting example of luminescence from lanthanide-appended rotaxanes and its nonradiative quenching upon binding of a halide in the rotaxane cavity was recently reported.^{6d} However, the reversible optical modulation of the luminescence intensity of lanthanide complexes remains a challenge. We recently constructed some interesting supramolecular devices⁷ in which tris[2]-pseudorotaxane^{7a} and [2]pseudorotaxane^{7b} systems behave as

reversible luminescent lanthanide switches in the presence of K⁺ or 18-crown-6 (18C6).

In this work, we non-covalently combined an unsymmetrical perfluorocyclopentene-based photochromic DAE (**1**) to a Eu³⁺ complex of a dibenzo-24-crown-8 (DB24C8) derivative bearing a terpyridine (tpy) moiety (**2**) (Figure 1) through the interaction

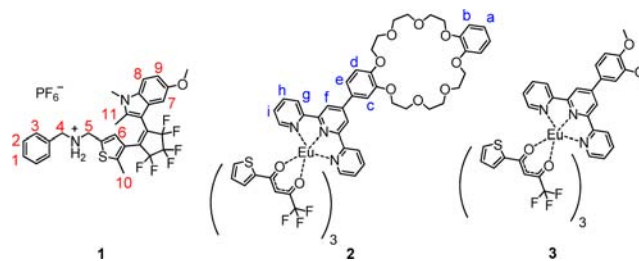


Figure 1. Structures of diarylethene **1**, Eu³⁺ complex **2**, and reference compound **3** without DB24C8.

of the dialkylammonium moiety in **1** with the 24C8 ring in **2** to demonstrate that the Eu³⁺ luminescence can be reversibly modulated by the ring-closing and ring-opening reactions of **1** caused by UV and visible-light irradiation. We introduced an indole chromophore in **1** to lower the excitation energy in order to facilitate resonant energy transfer (RET) from the excited lanthanide ion to one of the isomers of the photochromic switch.⁸ We also introduced a thermally stable thiophene-based unsymmetrical DAE as the RET acceptor in **1**, using perfluorocyclopentene as the central ethene linker because of its resistance to fatigue.

The syntheses of **1**, **2**, and the reference compound **3** are shown in Figure S1 in the Supporting Information. Briefly, **1** was synthesized by condensation of 4-[3,3,4,4,5,5-hexafluoro-2-(5-methoxy-1,2-dimethyl-1H-indol-3-yl)cyclopent-1-enyl]-5-methylthiophene-2-carbaldehyde with benzylamine and subsequent protonation and counterion exchange. The electron-withdrawing property of the perfluoro substituents promoted the cyclization reaction.⁹ Eu³⁺ complex **2** was prepared in 83% yield by the reaction of 4-formyl-DB24C8 with 1-(pyridin-2-yl)ethanone under basic conditions^{10a} followed by complexation of the resulting tpy-appended DB24C8 derivative with europium thenoyltrifluoroacetate [Eu(tta)₃·3H₂O].^{10b}

Compound **1** exhibited reversible and bistable photochromism. UV irradiation (365 nm) of a solution of open-form (OF) **1**

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led to the generation of a new absorption band at ~ 598 nm with an accompanying isosbestic point at 370 nm. Thus, the solution changed from colorless to dark green (Figure 2). Upon visible-

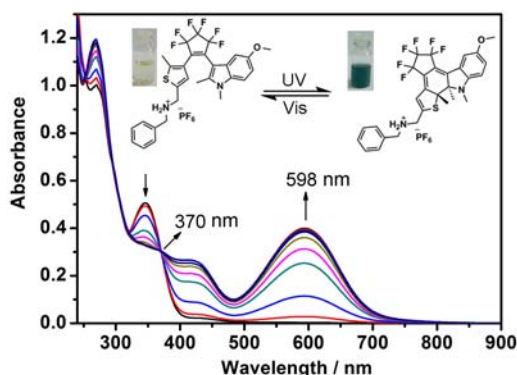


Figure 2. Absorption spectra of **1** (1.0×10^{-5} M) undergoing photoconversion from the initial open form to the closed form upon exposure to 365 nm light; after 2 min, the maximal change was achieved at 598 nm. Inset: changes in the chemical structure and photographic images of **1** upon alternating UV and visible-light irradiation in 1:1 $\text{CH}_3\text{CN}/\text{CHCl}_3$.

light irradiation (614 nm), the dark-green solution of closed-form (CF) **1** returned to colorless (Figure 2). Laser flash photolysis of OF-**1** in 1:1 $\text{CH}_3\text{CN}/\text{CHCl}_3$ showed a transient absorption at ~ 420 nm with a decay lifetime of 650 μs , further confirming the conversion of the DAE moiety from the coplanar OF to the twisted CF.^{9c} CF-**1** maintained its inherently high thermal stability. At an elevated temperature (60 $^\circ\text{C}$), it did not show any sign of thermal ring opening in the dark for at least for 15 h upon monitoring at 614, 485, and 425 nm (Figure S39). The photocyclization quantum yields ($\Phi_{0 \rightarrow c}$) corrected for the active conformer were determined to be 0.38 for **1** and 0.20 for [2]pseudorotaxane **1C2** (Figure S31). Moreover, **1C2** displayed excellent photochromic performance in poly(methyl methacrylate) (PMMA), as was the case in solution (Figure S42).

Significantly, we obtained a single crystal of **1**·Cl by slow evaporation from a $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solution. X-ray crystallographic analysis¹¹ revealed a favorable structure for solid-state photochromism: **1** exclusively adopts the antiparallel conformation (Figure 3a), which is in sharp contrast to the solution-phase behavior, where the antiparallel and parallel conformers coexist, as evidenced by ^1H NMR spectroscopy (Figure S27). Moreover, right-handed helical chains are formed by the hydrogen-bonding interactions linking **1** molecules (Figure S26). The distance between the photocyclizing carbon atoms ($\text{C6} \cdots \text{C20}$) is 3.645 \AA , allowing the photochromic cyclization reaction in the crystal.¹²

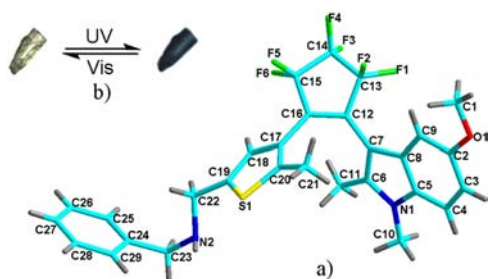


Figure 3. (a) Crystal structure of **1**. (b) Color changes of a single crystal of **1** upon alternating irradiation at 365 and 614 nm.

As in solution, the bulk crystals of **1**·Cl readily underwent the reversible photochromic ring-closing and -opening reactions upon irradiation at 365 and 614 nm, respectively (Figure 3b).

Benefiting from the excellent luminescence properties of Eu^{3+} , complex **2** displayed satisfactory luminescence in solution. When excited at 390 nm, the complex showed five emission peaks, at 580 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_0$), 594 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_1$), 619 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$), 656 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_3$), and 700 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_4$) (Figure S30). The strong fluorescence of **2** may be attributed to intramolecular energy transfer (ET)^{13a,b} from the excited tpy moiety to Eu^{3+} .

When an equimolar amount of compound OF-**1** was added to a solution of **2**, the luminescence intensity of the complex decreased by $\sim 10\%$ as a result of the photoinduced electron transfer (PET) between OF-**1** and **2**.^{7a} Thus, the association with OF-**1** did not significantly alter the luminescent behavior of **2**. In the ^1H NMR spectrum of the equimolar mixture (Figure 4), the

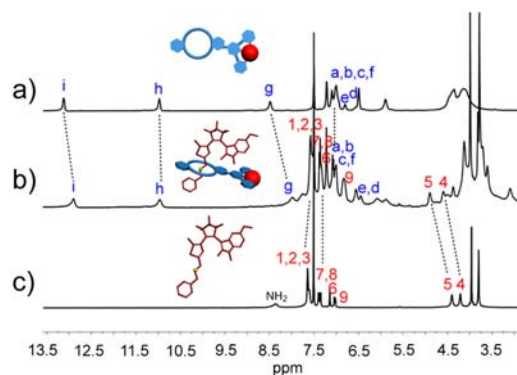


Figure 4. Partial ^1H NMR spectra (400 MHz, 1:1 $\text{CD}_3\text{CN}/\text{CDCl}_3$, 298 K) of (a) free **2**, (b) an equimolar mixture of **2** and **1**, and (c) free **1**. [**1**] = 5.0 mM. See Figure 1 for atom labels.

aromatic protons H_g , H_h , and H_i in **2** were shifted upfield ($\Delta\delta = -0.50$, -0.02 , and -0.22 ppm, respectively), while H_4 and H_5 adjacent to the ammonium site on the axle component in **1** were shifted downfield ($\Delta\delta = 0.38$ and 0.49 ppm, respectively). This observation confirmed the interaction of the secondary ammonium moiety in **1** with the DB24C8 ring in **2**, leading to the formation of the [2]pseudorotaxane OF-**1C2**.

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.¹³ In the present OF-**1C2** [2]pseudorotaxane system, the strongest emission of complex **2** occurs at 619 nm, while all of the absorption bands of OF-**1** occur below 400 nm. Therefore, no intermolecular RET from the Eu^{3+} moiety of **2** to the diheteroarylethene of OF-**1** would be expected. However, when OF-**1C2** was exposed to 365 nm UV light, $\sim 80\%$ of the fluorescence intensity at 619 nm was quenched, with an accompanying decrease in the quantum yield from 0.128 to 0.020 (Figure 5). In addition to the decrease in the steady-state fluorescence, the fluorescence lifetimes of Eu^{3+} in OF-**1C2** [$\tau = 638$ μs (88.68%) and 321 μs (11.32%); Figure S32 top] were dramatically decreased in the [2]pseudorotaxane CF-**1C2** [$\tau = 216$ μs (90.01%) and 371 μs (9.99%); Figure S32 bottom]. These observations jointly indicate the occurrence of the intermolecular RET from the Eu^{3+} donor (D) in **2** to the diheteroarylethene acceptor (A) in CF-**1** because of the perfect energy match between the emission of **2** and the absorption of CF-**1** as well as the short D–A distance. The center-to-center distance between CF-**1** and Eu^{3+} , estimated as 20.2 \AA (Figure

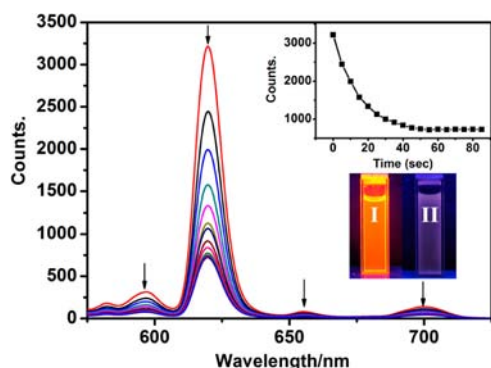


Figure 5. Emission spectra of the **1C2** system (1.0×10^{-5} M) and (upper inset) emission intensity changes at 619 nm upon UV irradiation ($\lambda_{\text{ex}} = 390$ nm) in 1:1 $\text{CH}_3\text{CN}/\text{CHCl}_3$. The lower inset shows the emission color change upon UV irradiation.

S41) using the molecular mechanics (Dreiding force field)-optimized structure of **CF-1C2**, is well within the Förster radius ($R_0 = 30.7$ Å),¹⁴ facilitating RET. In contrast, reference compound **3** lacking the DB24C8 moiety quenched the fluorescence by only 9% (Figure S37), revealing the critical role of the crown ether moiety in facilitating the RET process in **CF-1C2**.

The fluorescence modulation of the **1C2** [2]pseudorotaxane system upon alternating UV and visible-light irradiation is illustrated in Figure 6. After the complex solution was irradiated

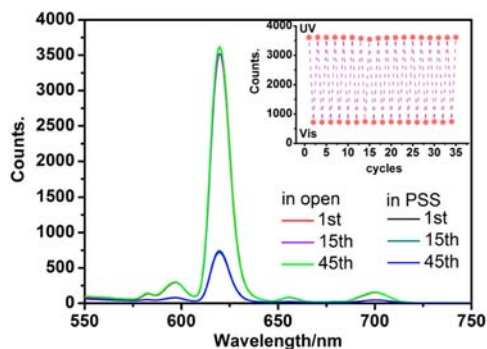


Figure 6. Fluorescence spectra and (inset) intensity changes at 619 nm for the **1C2** system (in 1:1 $\text{CH}_3\text{CN}/\text{CHCl}_3$) observed upon alternating UV (390 nm) and visible-light (619 nm) irradiation. PSS denotes the photostationary state.

with UV light at 365 nm for 5 min, it was immediately moved into the fluorescence spectrometer for emission measurements ($\lambda_{\text{ex}} = 390$ nm). The characteristic fluorescence emission of Eu^{3+} was significantly quenched. However, after visible-light irradiation at 614 nm for 10 min, the fluorescence intensity was totally recovered.

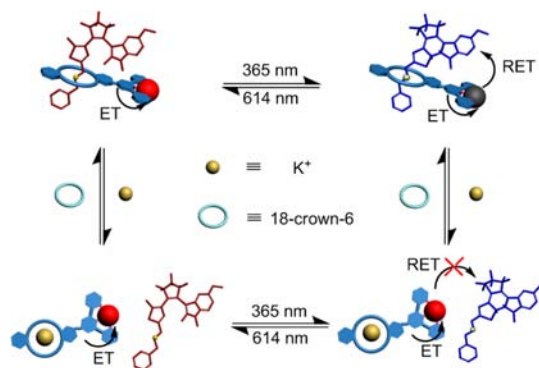
It is well-documented that the assembly/disassembly of [2]pseudorotaxanes based on DB24C8 and dialkylammonium salts can be reversibly manipulated by adding K^+ and 18C6 in series, which has been proved to be a simple and accessible strategy for constructing supramolecular switching systems.^{7,15} The assembly and disassembly of **OF-1C2** were examined by ^1H NMR spectroscopy. As shown in Figure S33, when excess KPF_6 was added to the solution of **OF-1C2**, the methylene protons H_4 and H_5 on the axle component **OF-1** were shifted upfield to the original positions observed for free **OF-1**, suggesting that the dialkylammonium ion of **OF-1** was expelled from the ring of

DB24C8 by K^+ . This is reasonable because the association constant of **DB24C8** with K^+ ($K_a = 7.6 \times 10^3 \text{ M}^{-1}$)¹⁶ is larger than that for the formation of **OF-1C2** ($K_a = 1.2 \times 10^3 \text{ M}^{-1}$)¹⁷ (Figure S38), leading to the dissociation of **OF-1C2** upon addition of K^+ . When **18C6** was added to the above system, the H_4 and H_5 signals returned to the positions for **OF-1C2**, indicating that the [2]pseudorotaxane was regenerated.

Luminescence spectral experiments were also performed to confirm the interaction between **OF-1C2** and KPF_6 . The fluorescence intensity of **2** was slightly enhanced upon addition of KPF_6 (Figure S34), indicating that no RET occurred when **OF-1C2** was disassembled. In sharp contrast, when KPF_6 was added to the solution of **CF-1C2**, the lanthanide emission of this system was gradually recovered (Figure S36), suggesting that the RET process was inhibited as a result of disassembly of the [2]pseudorotaxane. When **18C6** was added to this solution, the lanthanide emission of **2** was quenched via RET from Eu^{3+} to the diheteroarylethene in the regenerated [2]pseudorotaxane.

Upon irradiation of the above-mentioned solution containing **OF-1**, **2**, and KPF_6 at 365 nm for 5 min, the fluorescence intensity was only slightly decreased (Figure S35), revealing that the RET was suppressed when the pseudorotaxane structure was destroyed by the addition of K^+ even when **OF-1** was converted to **CF-1**. Scheme 1 shows the switch modes of the **1C2** system, which exhibits the expected luminescent lanthanide switching behavior.

Scheme 1. Schematic Illustration of the Light-Modulated Molecular Switch



In summary, we have designed and synthesized the host–guest partners **1** and **2** with perfect spectral overlap between the host emission and the guest absorption. The [2]pseudorotaxane **1C2** was readily constructed from Eu^{3+} complex **2** bearing a tpy-DB24C8 moiety as the host and the photochromic DAE **1** containing a dialkylammonium moiety as the guest through complexation of the ammonium moiety of **1** with the DB24C8 moiety of **2**, facilitating the RET process upon the ring-closing reaction of **1** under UV irradiation. Control of the RET process by the alternating UV and visible-light irradiation enabled the reversible on/off switching of the lanthanoid luminescence. Furthermore, the reversible luminescence behavior of the [2]pseudorotaxane system could be manipulated by the successive addition of K^+ as a competitive guest and **18C6** as a competitive host. This dual-stimuli-driven luminescent lanthanide molecular switch possesses two distinctive features: (1) the combination of RET with photochromic switching can provide a highly efficient luminescence switch, and (2) the self-assembled supramolecular scaffold can be disassembled and reassembled

non-covalently to function as a molecular switch. The present results may provide a novel perspective for the design of multistimulus-driven molecular machines and logic gates.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental procedures, additional data, and a CIF. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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- (11) Crystallographic data for **1**: C₂₉H₂₇ClF₆N₂OS, M_r = 601.04, orthorhombic, space group P2₁2₁2₁, a = 6.7922(9) Å, b = 20.030(3) Å, c = 20.030(3) Å, α = β = γ = 90°, V = 2788.9(7) Å³, Z = 4, ρ_{calcd} = 1.431 g/cm³, T = 113(2) K, 29 302 measured reflns, 6613 unique reflns (R_{int} = 0.0468), R₁ = 0.0309, wR₂ = 0.0589 [I ≥ 2σ(I)], GOF = 1.010. CCDC 886318 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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