Reversibly Photoswitchable Supramolecular Assembly and Its Application as a Photoerasable Fluorescent Ink

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A photoswitchable supramolecular assembly was constructed from perfluorocyclopentene diarylethene and $[Ru(bpy)_3]^{2+}$ mediated by the noncovalent association of dialkylammonium with dibenzo-24-crown-8. Possessing the reversible photoisomerization property and a high Förster resonance energy transfer (FRET) efficiency, the resultant supramolecular assembly could efficiently and reversibly switch on/off the luminescence of the $[Ru(bpy)_3]^{2+}$ center upon irradiation by different wavelength light both in solution and in the solid state. Significantly, the characters written with the supramolecular assembly as ink could be reversibly and repeatedly erased and recovered by altering the wavelength of irradiation light.

Recently, the construction of micrometer/nanometer-sized molecular-level machines and devices via a bottom-up approach has attracted growing attention.[1,2] As an important molecular-sized device, supramolecular switches have been widely applied in the fields of anticounterfeiting materials,[3] smart surfaces,[4] drug release,[5] phototunable luminescence materials,[6] cell tracking, and intelligent anticorrosion coatings.[7] Generally, these supramolecular switches are smartly controlled by several kinds of external stimulation, such as chemical stimulus,[8] temperature,[9] electric field,[10] biological molecules,[11] and so on. However, the photocontrol of supramolecular switches still remains as a challenge.[12] Among the various building blocks to construct photocontrolled supramolecular switches, diarylethene derivatives (DAEs) can be reversibly interconverted between closed-ring and open-ring forms by alternating UV and visible light irradiation, with accompanying appreciable changes of polarizability, color, conformation, and spectroscopic property, thus could record input, rewrite, and produce a nondestructive read out of data.[13] In addition, the high photoisomerization quantum yield, good thermally stability, rapid light response, and outstanding fatigue resistance allowed the successful application of DAEs in optical switches, optoelectronics, smart surfaces, photoinduced shape-memory polymers, functional vesicles, bionanodevices, and information storage media.[14] For example, Clever et al. took advantage of the large conformational changes of dithienylethene under UV and visible light to achieve the photocontrolled interconversion between two metal organic frameworks.[15] Feringa and co-workers connected dithienylethene with various chiral functional groups to induce the formation of a chiral supramolecular gel.[16] We also constructed a dual-stimulus [2]pseudorotaxane based on an unsymmetrical diarylperfluorocyclopentene and Eu^{3+}/terpyridinyldibenzo-24-crown-8 complex and revealed an excellent photochemical control of the luminescence of lanthanide.[17]

Here, we report a supramolecular switch constructed via the noncovalent host–guest association between a symmetrical dialkylammonium-modified perfluorocyclopentene diarylethene derivative (**1**) and a $[Ru(bpy)_3]^{2+}$ complex appended with two dibenzo-24-crown-8 (DB24C8) moieties (**2**) (**Scheme 1**). Benefiting from the reversible photoisomerization property of the diarylethene unit in **1** as well as the good photophysical property of the $[Ru(bpy)_3]^{2+}$ center in **2**, the present supramolecular switch could perfectly control the luminescence of **2** and the intermolecular FRET behavior by altering the wavelength of irradiation light in solution and also in the solid state. Crucially, this reversible supramolecular photoswitching system showed excellent performance as a photoerasable fluorescent ink. Thus, the characters written with the supramolecular assembly could be erased and recovered by alternating the irradiation wavelength, and the photocontrolled erase/recover cycles were reversible and repeatable.

Brief synthesis routes to guest **1** and host **2** were shown in Figure S1 (Supporting Information). Guest **1** was obtained in 88% yield through the condensation of **6** with benzylamine, followed by protonation and counterion exchange. Host **2** was prepared in 52% yield through the reaction of mono(4-hydroxymethyl)dibenzo-24-crown-8 (**7**) with *bis*(bromomethyl)-2,2′-bipyridine (**8**), followed by the complexation of $Ru(bpy)_2Cl_2{\cdot}2H_2O$. As shown in **Figure 1**a, the UV–vis spectrum of the open form of **1** (**OF-1**) showed a strong absorption at 301 nm. When the solution of **OF-1** was irradiated with UV light (254 nm, 2 min), the peak at 301 nm gradually decreased in intensity and a new peak appeared at 592 nm, leading to an obvious color change of the solution from colorless to blue. In addition, a clear isosbestic point was observed at 324 nm. These phenomena jointly indicate the transformation of **1** from the open form (**OF-1**) to the closed form (**CF-1**). When the solution of **CF-1** thus obtained was irradiated with visible light (>420 nm, 16 s), the blue solution of **CF-1** returned to colorless and the original UV–vis spectrum of **OF-1** was recovered, indicating the reverse transformation from **CF-1** to **OF-1**. These jointly demonstrate the photoswitched conformational interconversion of **1**, and this interconversion could be repeated several times without any appreciable

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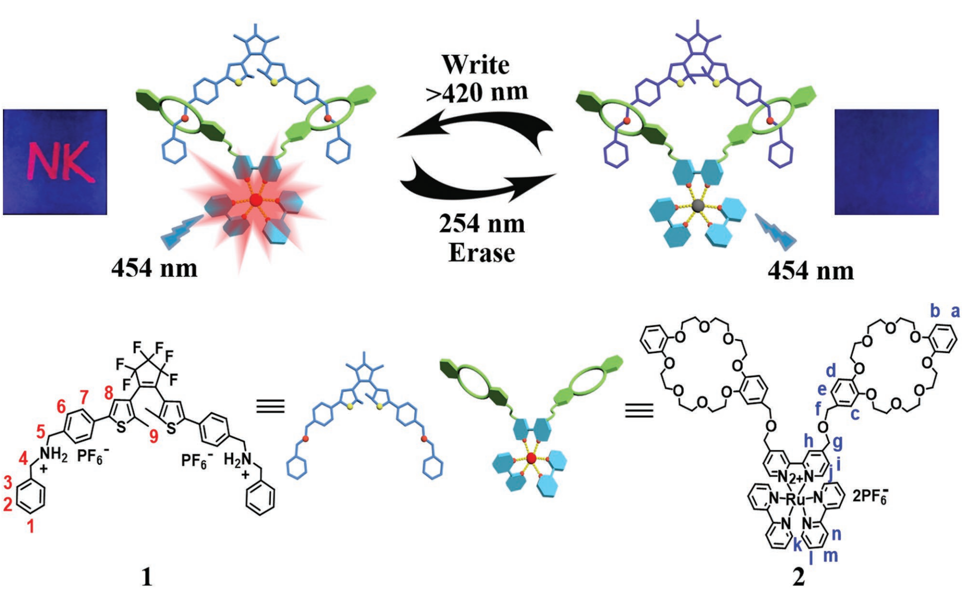

Scheme 1. Schematic illustrations of the reversibly photoswitchable supramolecular assembly as photoerasable fluorescent ink.

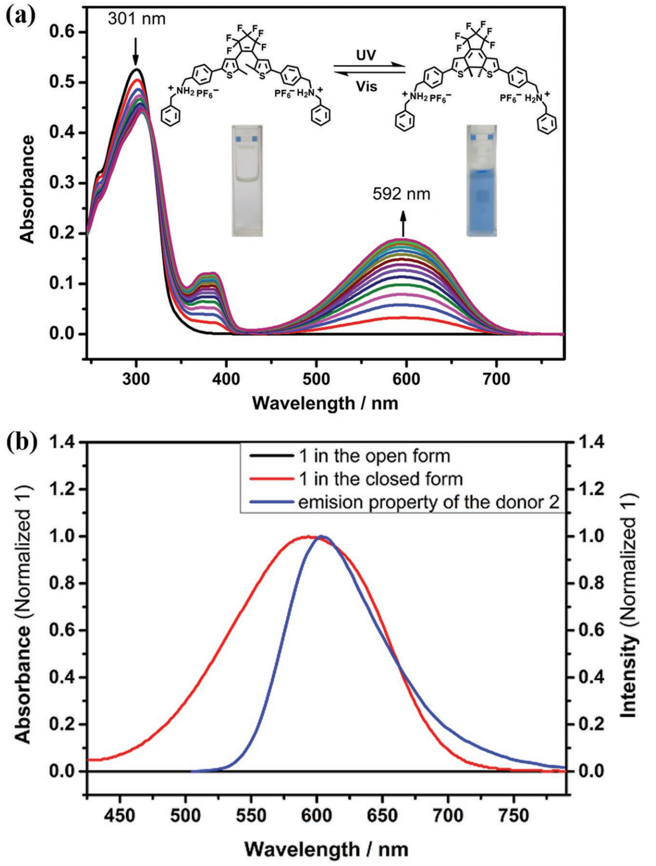

Figure 1. a) UV–vis spectra changes of **1** (2.0×10^{-5} M) in the solution of CH_2Cl_2/CH_3CN (98:2) upon irradiation with 254 nm light for up to 2 min. Inset: changes of the photographic images and the chemical structure of **1** upon alternating UV and visible light irradiation. b) Partial UV–vis spectra (left axis) of **OF-1** (black line) and **CF-1** (red line) and fluorescence emission (blue line, right axis) of **2**.

light fatigue phenomenon (Figure S20, Supporting Information). The ring-closing conversion yield of **1** upon irradiation with UV light (254 nm) was determined to be 95% from the NMR spectral changes (Figure S21, top, Supporting Information), while the closed form quantitatively afforded the open form upon irradiation with visible light (>420 nm) (Figure S21, bottom, Supporting Information). Moreover, guest **1** showed good thermal stability. As monitored by the UV–vis spectrum (Figure S22, Supporting Information), when the solution of **CF-1** was kept at 60 °C in the dark for at least 3.5 h, **CF-1** did not show any sign of thermal ring-opening, demonstrating that **1** is a good P-type photochromic compound. In addition, the guest molecule **1** also displayed excellent reversibility and photochromic performance in another stiff matrix, i.e., poly(methyl methacrylate) (PMMA, M_w = 996 kDa), as was the case in solution (Figure S23, Supporting Information). On the other hand, the UV–vis spectrum of **2** (Figure S24, Supporting Information) showed two characteristic peaks of the $[Ru(bpy)_3]^{2+}$ moiety at 288 and 454 nm. When excited at 454 nm, the fluorescence spectrum of **2** showed a strong emission at λ_{max} = 607 nm. Judging from the emission band of **2**, we deduce that the FRET process can occur only from **2** to **CF-1** due to the significant spectral overlap of the absorption band of **CF-1** with the emission band of **2** over 550 nm (Figure 1b), which is consistent with the previously reported results.[17]

It is well documented that the secondary alkylammonium ion noncovalently associates with DB24C8 through the cooperative N—H···O and C—H···O hydrogen-bonding interactions in less polar solvents[18] and the binding constant reaches up to 10^5 M^{-1} in CH_2Cl_2/CH_3CN (98:2).[2,19] Therefore, the supramolecular assembly $1 \subset 2$ should be readily constructed by mixing both components in a CH_2Cl_2/CH_3CN (98:2) solution. In the ^1H NMR spectrum of an equimolar mixture of **OF-1** and **2** (**Figure** 2c), the benzylic protons (H_4 and H_5) in **OF-1** showed obvious downfield shifts ($\Delta\delta$ = 0.26 ppm for H_4 and 0.33 ppm for H_5), while the aromatic protons (H_2, H_3, and H_6) in **OF-1** shifted to

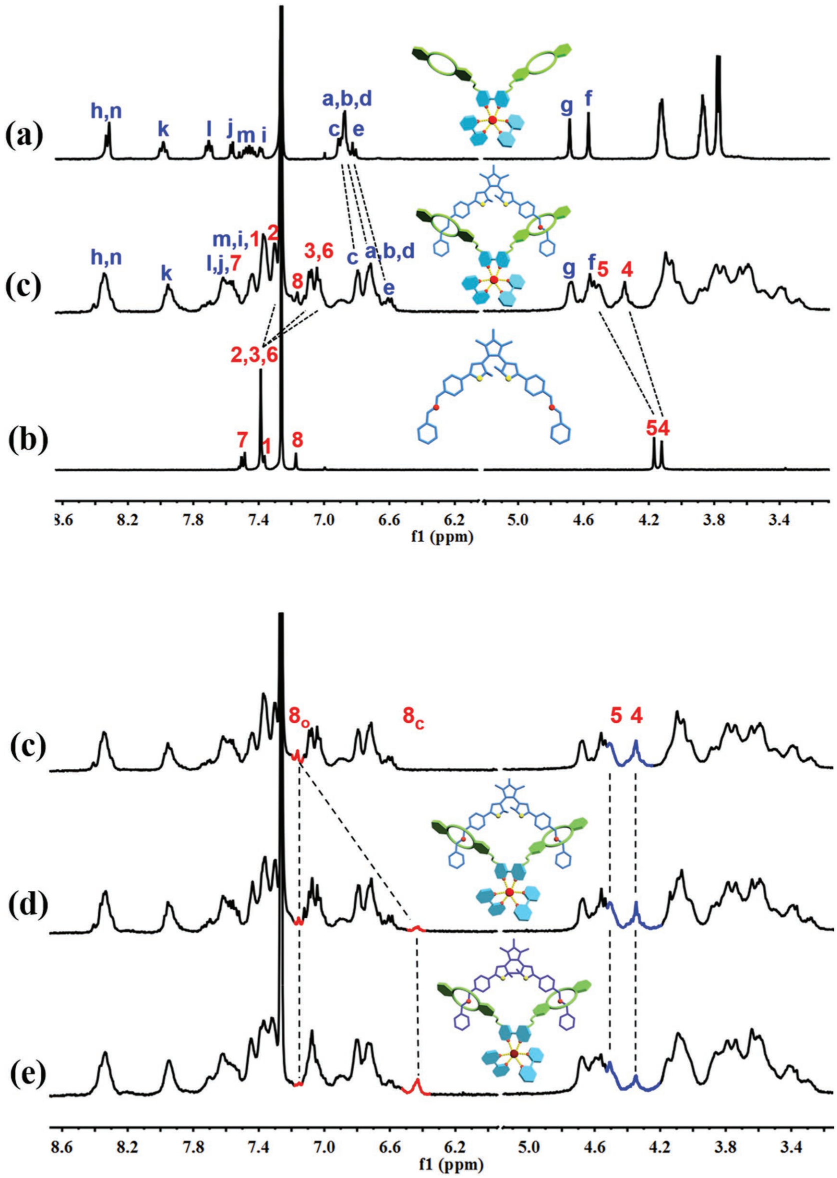

Figure 2. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$ = 98:2, 298 K) of a) free **1**, b) free **2**, c) an equimolar mixture of **OF-1** and **2**, d) sample (c) irradiated at 254 nm for 30 min, and e) sample (c) irradiated at 254 nm for 60 min; [**OF-1**] = [**2**] = 2.0 × 10^{-3} M. In particular, the peaks labeled "8_o" and "8_c" donate H_8 of the open and closed forms of **1**, respectively; for the full proton labeling, see Scheme 1.

the upfield ($\Delta\delta$ = 0.07–0.33 ppm). Also, the aromatic protons (H_a, H_b, H_c, H_d, and H_e) of the DB24C8 moieties in **2** showed appreciable upfield shifts ($\Delta\delta$ = 0.10–0.20 ppm) with accompanying peak splits of the methylene protons in the DB24C8 moieties. And the Job plot (Figure S25, Supporting Information) showed the maximum at a molar fraction of 0.5, indicating the 1:1 stoichiometry between **OF-1** and **2**. Moreover, the electrospray ionization mass spectrum showed only one intense peak at m/z = 1245.1 assignable to [**OF-1** $\subset$ **2**]$^{2+}$ (Figure S26, Supporting Information). These results jointly indicate that the two DB24C8 moieties in **2** are bound to the two secondary dialkylammonium units in **1** to form the supramolecular assembly **OF-1** $\subset$ **2** as illustrated in Scheme 1. In addition, the specific viscosity of the **OF-1** $\subset$ **2** solution linearly increased with an increase of concentration, indicating that no supramolecular polymers formed in the concentration range employed (Figure S27, Supporting Information). Upon irradiation of **OF-1** $\subset$ **2** by UV light (254 nm), no appreciable changes were observed for the NMR signals of aromatic protons excepting the upfield shift of H_8, despite the color change of the solution from yellow to dark brown. Also, the benzylic protons (H_4 and H_5) showed no appreciable shifts, indicating that the association mode of **1** $\subset$ **2** did not change even after the photocyclization of diarylethene group (Figure 2d,e).

It is interesting to further investigate the photoswitchable FRET process in the **1** $\subset$ **2** assembly. Upon association with **OF-1**, the fluorescence intensity of **2** decreased by 13% (Figure S28, Supporting Information), owing to the photoinduced electron transfer between the $[Ru(bpy)_3]^{2+}$ center in **2** and the diarylethene group in **1**.[8] However, upon irradiation with the UV light (254 nm) for up to 5.5 min, the fluorescence intensity of the resultant **OF-1** $\subset$ **2** assembly was gradually quenched by 91% (**Figure 3**a), and the fluorescence quantum yield of the **OF-1** $\subset$ **2** assembly decreased from 0.076 to 0.027 (Table S1, Supporting Information). The apparent ring-closing reaction rate constant (k') was determined to be 8.4 × 10^{-3} s^{-1}, assuming a first-order rate equation (Figure S29, Supporting Information). The fluorescence quenching phenomenon could also be readily recognized by the naked eyes, where the bright red fluorescence of **OF-1** $\subset$ **2** assembly gradually turned dark when the solution was irradiated with UV light (254 nm). Subsequently, the UV-irradiated solution was further irradiated by visible light (>420 nm), the fluorescence color of the solution returned to red (Figure 3a, inset). This is because the UV light (254 nm) irradiation converted the open form (**OF-1**) to the closed form (**CF-1**), and the FRET path from the $[Ru(bpy)_3]^{2+}$ center in **2** (donor) to **CF-1** (acceptor) became open to quench the fluorescence. However, the quenched fluorescence of the **1** $\subset$ **2** assembly was recovered to its original level upon the subsequent irradiation with the visible light (>420 nm, 24 s) because of the reverse photoisomerization from **CF-1** to **OF-1**. Significantly, this cycle could be repeated without fatigue at least ten times (Figure 3b). In addition, the center-to-center distance between **2** and **CF-1** in a geometry-optimized assembly was 14.6 Å (Figure S30, Supporting Information). This value is obviously shorter than the Förster radius (R_0 = 30.7 Å),[20] and the FRET process should be facilitated. The photocontrolled

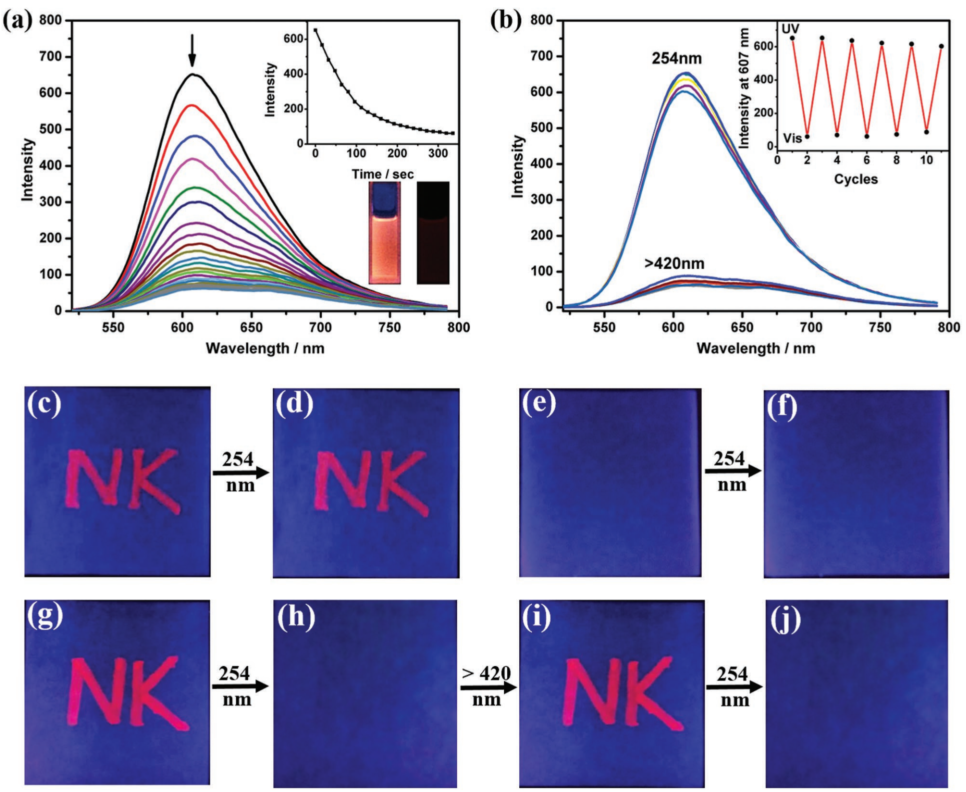

Figure 3. a) Emission spectra of **OF-1** ⊂ **2** (6.0×10^{-5} M) and (inset) emission intensity changes at 607 nm upon irradiation with UV light (254 nm, 5.5 min) ($\lambda_{ex} = 454$ nm) in CH_2Cl_2/CH_3CN (98:2). b) Emission spectra and (inset) intensity changes at 607 nm for the **1** ⊂ **2** assembly in CH_2Cl_2/CH_3CN (98:2) upon alternating UV (254 nm, 5.5 min) and visible-light (>420 nm, 24 s) irradiation at 298 K. c,d) Fluorescence images of characters written by free **2**, observed under 365 nm light. e,f) Fluorescence images of characters written by free **1**, observed under 365 nm light. g–j) Fluorescence images of characters written by the **1** ⊂ **2** assembly before and after irradiated with UV or visible light, observed under 365 nm light.

energy transfer efficiency (E) was evaluated as 90.6%, according to the energy transfer equation.[21]

Additionally in solution, the **1** ⊂ **2** assembly also showed the excellent reversibility and photochromic performance in a PMMA film and in the solid state (Figures S31, S32, and S33, Supporting Information). The energy transfer efficiency in the solid state was >98%, which is higher than that in solution (90.6%). Similarly, the ring-closing reaction (under the comparable irradiation conditions) was slightly accelerated in the solid state ($k'_{solid} = 9.6 \times 10^{-3}$ s^{-1}) than in solution ($k'_{soln} = 8.4 \times 10^{-3}$ s^{-1}), for which the fixed antiparallel conformation of the guest molecule **1** in the solid state is likely to be responsible at least in part (Figure S34, Supporting Information). Although the separate determination of the cyclization quantum yield (Φ_c) in the solid-state sample on paper was not feasible due to the light scattering from the paper surface, the comparable k' values observed in solution and in the solid state imply that the Φ_c values are also comparable to each other, as the apparent rate constant of photoreaction is expressed as $k' = k \cdot I \cdot \varepsilon \cdot \Phi$, where k represents the inherent photochemical reaction rate constant, I the light intensity, ε the molar extinction coefficient at the excitation wavelength, and Φ the photoreaction quantum yield. In order to further confirm the highly efficient ring-open/close reactions, we investigated the photochromic switching behaviors in another stiff medium, i.e., PMMA. Therein, both the guest **1** and assembly **1** ⊂ **2** displayed the excellent reversibility and photochromic performance in the PMMA matrix, as in solution (Figures S23 and S32, Supporting Information).

Benefiting from the good photoswitchable luminescence behaviors, the **1** ⊂ **2** assembly could serve as the photoerasable fluorescence ink. In a typical test, some characters were written with the solution of free **2** or the **OF-1** ⊂ **2** assembly as ink on ordinary white paper, these characters emitted bright red fluorescence upon exposure to the UV light at 365 nm after being dried in air (Figure 3c,g). In a control experiment, the characters written with free **OF-1** showed no appreciable fluorescence under the same condition (Figure 3e). When irradiated with the UV light (254 nm), the characters written with free **OF-1** or **2** did not show any changes in appearance, but the ones written with the **OF-1** ⊂ **2** assembly disappeared (Figure 3h). Interestingly, the erased characters could completely recover upon irradiation with visible light (>420 nm) (Figure 3i), and these photocontrolled erase/recover cycles could be repeated several times. These photoerase/recovery properties will enable the application of the **1** ⊂ **2** assembly as novel anticounterfeiting materials in which the information and the state could be effectively written, concealed, and read out by simply alternating the irradiation with UV and visible light.

In conclusion, we successfully constructed a photocontrollable supramolecular switch from the $[Ru(bpy)_3]^{2+}$ complex bearing two crown ethers as the host moieties, and the photochromic perfluorocyclopentene diarylethene containing two dialkylammonium ions as the guest moieties, through the noncovalent association of a alkylammonium ion with DB24C8. Owing to the reversible photoisomerization property of the dithienylethene unit and the highly efficient FRET between host and guest, the **1** ⊂ **2** assembly could reversibly switch on/off the luminescence of the $[Ru(bpy)_3]^{2+}$ center both in solution and in the solid state by alternating UV and visible light irradiation. As a result, the present supramolecular switch will find applications in the fields of information and state storage media, photocontrolled molecular devices, and reversible erase/rewrite systems.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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