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Photo-controlled chirality transfer and FRET effects based on pseudo[3]rotaxane†

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The use of light to regulate the chirality of supramolecular assemblies in a non-invasive manner remains a challenge. Herein, we report a novel photochromic pseudo[3]rotaxane based on a (R/S)-2,2'binaphthyl secondary ammonium salt guest (2) and anthracenebridged bis(dibenzo-24-crown-8) (1), which features a chirality transfer and fluorescence resonance energy transfer (FRET) from 2 to 1. Benefiting from the photo-oxidation of anthracene, the induced circular dichroism (ICD) signals of (R/S)-2@1 can be switched off/on by irradiation with 365 nm UV light and heating. This noncovalent supramolecular assembly strategy provides us with unique opportunities to design and construct further smart photo-responsive chiral molecular switches.

Owing to its wide applications in advanced materials,¹ such as information memory devices,² chiral sensing systems,³ nonlinear electronic devices⁴ and liquid crystal seeds,⁵ the transfer and control of both chirality and various optical properties have attracted significant attention lately. To date, a major pathway used to realize this is the direct influence implemented by chiral substructures that are covalently bound.⁶ Sometimes, a single asymmetric center may exert a small effect on a prochiral atom at the other end of a long alkyl chain. In addition, noncovalent interactions used in supramolecular chemistry based on chiral templates,⁷ which have facilitated understanding of the mechanism of chiral formation in nature, have paved another route to the transfer of chirality. Some water-soluble charged biopolymers, such as polypeptides,⁸ polysaccharides⁹ and DNA,¹⁰ have been used as templates to bypass the complicated design and synthesis of chiral covalent adducts. For example, Liu et al. have reported a chirality transfer amplified circularly polarized luminescence (CPL) through the co-assembly and weak π - π interaction driven nanohelix of the chiral *N*,*N*'-bis(dodecyl)-L(D)-amine-glutamic diamide derivative donor and achiral 9,10-bis(phenylethynyl)anthracene acceptor.¹¹ Benefiting from supramolecular macrocycle effectively promoted interplay between the chiral donor and achiral acceptor, systems were even found to remember the induced chirality when the chiral building block lost its optical activity.¹² Crown ethers, composed of oxygen atoms linked by alkyl chains have flexible cavities which endow them with a strong binding ability with metal ions and organic ammonium, and are thus reported to be useful in constructing various chiral supramolecular assemblies with specific functions.¹³ Recently, Lee and co-workers prepared and isolated two planar-chiral pillar[5]thiacrown molecules (in-pR-L and in-pS-L). Upon metal complexation stimulus under ClO_4^- or NO_3^- , the in-pS-L suffered a planar chirality inversion to out-pR-L.¹⁴ In addition, we successfully introduced a cholesterol derivative to a photo-responsive azobenzene-bridged bis(dibenzo-24-crown-8) that resulted in a photo-controlled macroscopic chirality transfer from the guest to the host. Furthermore, in order to mimic the multichannels in living organisms, efforts have been taken to construct supramolecular systems with chiral information and energy transfer.¹⁵ Förster resonance energy transfer (FRET) is the mostly commonly used method.¹⁶ In the FRET process, an excited-state donor transfers energy to the ground-state acceptor through nonradiative dipoledipole coupling.¹⁷ The distance of the separation, spectral overlap and relative spatial orientations are crucial to achieving effective FRET. FRET has been used to investigate molecular interactions and used as a ruler to measure the structure of organic biomolecules.18

Although some progress has been made during the past few decades, there still remains some interesting questions that have drawn our attention, such as whether this process can be selectively controlled by external stimuli, and how? Encouraged by our previous works,¹⁹ we proposed that stimuli-responsive supramolecular systems would provide a promising solution. The key to the design of responsive supramolecular systems is the introduction of photochromic molecules.²⁰ These molecules, which can be reversibly switched between two isomeric forms

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such as diarylethene derivatives,²¹ azobenzene,²² spiropyran²³ and anthracene,²⁴ have been widely applied in molecular machines, drug release, and photo-tunable luminescence materials. Furthermore, compared with other various external stimuli, light is the most ideal trigger owing to its low cost, non-invasiveness, ubiquity and the ease of control. Recently, we reported a multistimuli-responsive and photo-controlled supramolecular luminescent gel via an anthracene-bridged bis(dibenzo-24-crown-8) (1) and proved its reversible photooxidation process.²⁵ However, studying and exploring the potential chiral optical properties in supramolecular assemblies is still a great challenge. Herein, we introduced two chiral (R/S)-2,2'-binaphthyl dual secondary ammonium salts (2) to 1 which resulted in a chiral and optical information transfer from the guest to the host. Owing to the strong binding of the crown ether cavity with the secondary ammonium ion group, the supramolecular assembly 2(a)1 was constructed conveniently by mixing 1 and 2. Using ¹H NMR, ¹H-¹H rotating frame Overhauser effect spectroscopy (ROESY), diffusion-ordered NMR spectroscopy (DOSY), fluorescence titration and electrospray ionization mass spectrometry (ESI-MS), we demonstrated that 2@1 was generated in the form of a host and guest 1:1 instead of n:n. The NH_2^+ of the secondary ammonium salt was located in the center of **1**. The π - π noncovalent interaction of the anthracene and binaphthyl group further reduced the distance between the host and guest. Interestingly, the expression of induced chirality in the form of the induced circular dichroism (ICD) signals was photo-controlled, which could be switched off/on using UV light irradiation and heating. Benefiting from the spectral overlap of the emission of 2 and the absorption of 1, the short relative distance and restricted rotation, a strong FRET from 2 to 1 still remained. An illustration of the transfer of ICD and FRET is shown in Scheme 1.

The detailed synthesis process for the (R/S)-2,2'-binaphthyl secondary ammonium salt guest (2) is shown in Scheme S1 (ESI[†]). The guest molecule 2 was obtained in an 80% yield by aldimine condensation, followed by counter ion exchanges. Firstly, the binding modes between 1 and 2 were studied using ¹H NMR and two-dimensional (2D) ROESY spectroscopy, according to our report the binding constant between 1 and secondary ammonium salt group reached $10^6 \text{ M}^{-2.25}$ As shown in Fig. 1, when host 1 and guest (R)-2 were mixed in a 1:1 stoichiometric ratio in $CDCl_3/CD_3CN$ (v:v = 2:1), the ¹H NMR spectrum of (R)-2@1 showed a significant difference to those for 1 and (R)-2, indicating the formation of the supramolecular assembly. Upon complexation, the benzylic protons H_a and H_b in (*R*)-2 showed a significant downfield shift ($\Delta \delta_a = 0.55$ ppm, $\Delta \delta_{\rm b} = 0.31$ ppm), whereas the aromatic protons H_e ($\Delta \delta = 0.11$ ppm), $H_h (\Delta \delta = 0.06 \text{ ppm})$, He ($\Delta \delta = 0.05 \text{ ppm}$) and H_{15-18} in the crown ether 1 shifted upfield. Also, the methylene protons H_{11} and H₁₂ of the DB24C8 moieties in 1 showed appreciable downfield shifts ($\Delta \delta_{11} = 0.19$ ppm, $\Delta \delta_{12} = 0.17$ ppm) accompanying other alkyl protons peak splits. These results jointly indicate that the NH_2^+ of (*R*)-2 was located in the cavities of 1. As expected, the ¹H NMR spectrum of (S)-2@1 exhibited a similar chemical shift to (R)-2@1. In addition, the existing strong nuclear Overhauser



Scheme 1 (a) Chemical structures and proton designations of the chiral guest 2, achiral crown ether host 1 and photo-oxygenation product **1EPO**. (b) Representation of the stimuli-responsive chirality transfer and FRET between the chiral donor 2 and the achiral acceptor 1 in 2@1.



Fig. 1 ¹H NMR spectra (400 MHz, CDCl₃/CD₃CN = 2:1, 298 K, [(*R*)-2] = [1] = 1.0 mM) of: (a) the free guest (*R*)-2; (b) an equimolar mixture of (*R*)-2 and 1; and (c) the free crown ether host **1**. For full proton labeling, see Scheme 1.

effects between (*R/S*)-2 and the crown ether protons in 1 (Fig. S6, ESI[†]) could further indicate the noncovalent interaction between the dibenzo-24-crown-8 (DB24C8) and secondary ammonium ion through the cooperation of the weak C···H···O, N···H···O hydrogen-bonding interactions in CDCl₃/CD₃CN. Referring to our previously reported work,²⁵ the π - π noncovalent interaction between the anthracene and binaphthyl group also made a positive contribution towards the shift of the protons.

 Table 1
 Diffusion coefficients (D) obtained from DOSY measurements

Complex	Diffusion coefficient $(m^2 s^{-1})$	$V_{\rm complex}/V_1$
1	6.27×10^{-10}	1.00
(R)-2	6.25×10^{-10}	1.01
(S)-2	7.76×10^{-10}	0.53
(R)-2 + 1	4.85×10^{-10}	2.16
(S)-2 + 1	$5.18 imes 10^{-10}$	1.77

Obviously, as a typical AA monomer the resulting (R/S)-2 could bind with BB-types to capture 1 in n:n or 1:1. To eliminate the possibility of forming oligomers, we performed DOSY measurements. As shown in Table 1, the measured average diffusion coefficients at a concentration of 1.0 mM of 1, (R)-2 and (S)-2 were 6.27 \times 10⁻¹⁰, 6.25 \times 10⁻¹⁰ and 7.76 \times 10⁻¹⁰, respectively. Upon addition of 1.0 eq. (R)-2 or (S)-2 to 1, the Davg value reached 4.85 \times 10⁻¹⁰ and 5.18 \times 10⁻¹⁰ showing a single diffusion coefficient. According to the Stokes-Einstein equation, the average size of (R/S)-2(a)1 could be estimated by assuming the host-guest complexes as being hydrodynamically spherical. The average volume of (R)-2@1 and (S)-2@1 are 2.16 and 1.77 times larger than that of the crown ether 1, implying that small-size supramolecular assemblies have indeed been formed. Fortunately, the electrospray ionization ESI-MS spectrum showed an intense peak that was assigned to $[(R/S)-2@1]^{2+}$ at m/z = 946.9, which was in accordance with the DOSY NMR results (Fig. S8-S13, ESI†).

Judging from the absorption band of 1 and the emission band of (R/S)-2 (Fig. 2a), we deduced that the efficient energy transfer process could occur from (R/S)-2 to 1. As shown in Fig. 2b, after fixing the concentration of (S)-2 at 0.06 mM, the fluorescence spectrum for (S)-2 showed an intense emission band at 370 nm. Upon gradual addition of 1 to the solution of (S)-2, the fluorescence emission intensity of (S)-2 at 367 nm suffered a significant decrease accompanied by a tremendous increase at 410 nm belonging to the crown ether host 1, when excited at 305 nm UV light. When the ratio of added 1 and the existing (S)-2 in solution reached 1:1, the fluorescence intensity of both components reached a balance point. Of course, the FRET process from (R)-2 to 1 was similar to that of (S)-2 (Fig. S14, ESI[†]). Benefiting from the fluorescence titration experiment, the binding constant in CHCl₃/CH₃CN was determined to be about 5.2×10^4 M⁻¹ (Fig. S15, ESI[†]). In addition,

we also investigated the energy-transfer efficiency of **1** and (R/S)-**2**, as it is a very important index to evaluate the FRET ability. As calculated from Fig. 2b and Fig. S15 (ESI[†]), the energy-transfer efficiencies of (S)-**2**(**a**)**1** and (R)-**2**(**a**)**1** were 84% and 83%, respectively. The similar FRET efficiencies further illustrated the two supramolecular assemblies have the same binding characteristics. Furthermore, the distance between **2** and **1** was calculated to be about 12.61 Å in a geometry-optimized assembly (Fig. S16, ESI[†]), which was shorter than that of the FRET radius (<10 nm).

As the (R/S)-2 have chiral centers and good optical properties, the two guests were characterized using circular dichroism (CD) experiments. As depicted in Fig. S17 (ESI⁺), (S)-2 presented obvious negative Cotton effects at 270-340 nm, and a positive Cotton effect at 340-350 nm corresponding to the UV-vis absorption region of the binaphthalene chromophore (Fig. 3a) assigned to the CT and $n-\pi^*$ transition. The enantiomer (R)-2 presented mirror imaged CD signals while the host 1 showed no CD signals. Interestingly, when mixing (S)-2 or (R)-2 with 1 in a 1:1 ratio, the supramolecular assembly showed ICD signals for 1 in the UV-vis absorption region, suggesting that the handedness could be transferred to the host through the host-guest complexation. As shown in Fig. S21 (ESI[†]), there was no "majority rule" in the system. To our surprise, we found that the ICD signals exhibited by anthracene were opposite to those of (S)-2 or (R)-2 in binaphthyl. The density functional theory (DFT) and timedependent density functional theory (TD-DFT) calculations reveal that this unique phenomenon is the result of longdistance charge transfer transitions being selected by the symmetry of the excited acceptor (detailed process is shown in the ESI[†]). It was well documented that 1 could form stable endoperoxides (EPOs) by trapping a singlet oxygen $({}^{1}O_{2})$ and the reverse process can be actuated under thermolysis. As seen in Fig. S18 (ESI[†]), the ICD spectra of anthracene disappeared and reappeared when (S)-2@1 or (R)-2@1 were irradiated with UV-vis light at 365 nm and heated at 100 °C for 10 h under N₂. A reasonable explanation for this phenomenon may be the structural transformation between 1 and 1EPO which is regulated by light and heating.

In summary, taking advantage of the strong binding affinity of DB24C8 with a secondary ammonium cation, a photo/thermal dual-controlled chirality transfer supramolecular assembly (R/S)-2@1 was successfully constructed, during which the inherent



Fig. 2 (a) Partial normalized spectrum overlap between the absorption of **1** and the emission of (*R*/S)-**2**. (b) Fluorescence spectra of (S)-**2** in CHCl₃/CH₃CN ([(S)-**2**] = 0.06 mM, v/v = 2:1) with the gradual addition of **1** (λ_{ex} = 305 nm).



Fig. 3 (a) UV-vis spectra of 1, (*R*)-2, (*S*)-2, (*R*)-2@1, (*S*)-2@1. (b) Normalized ICD spectra of (*R*)-2@1, (*S*)-2@1 at 350-420 nm by the chiral guest in CHCl₃/CH₃CN at 298 K ([1] = [(*R*)-2] = [(*S*)-2] = 0.3 mM).

chirality of (*R*/*S*)-2 transferred to the host **1**. The induced chirality of the supramolecular assemblies could be reversibly tuned upon light irradiation or heating. Crucially, the assembly pattern of (*R*/*S*)-2 and **1** was confirmed using ¹H NMR, ROESY, DOSY, fluorescence titration and ESI-MS. In addition, a strong FRET process existed between the donor (*R*/*S*)-2 and acceptor **1**. The concept of multi-stimuli responsive handedness transfer will provide deep insights into developing chiral functional materials.

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Conflicts of interest

There are no conflicts to declare.

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