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Noncovalent Bridged Bis(Coumarin-24-Crown-8) Phosphorescent Supramolecular Switch

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A multicolor room temperature phosphorescence (RTP) supramolecular photo-switch encryption film is constructed by the coassembly of coumarin-24-crown-8 (C24C8), diarylethene dicationic alkylammonium derivative (1), rhodamine B (RhB) and poly(vinyl alcohol) (PVA). Benefiting from the tightly binding of C24C8 and secondary alkylammonium ion, 1 formed noncovalent bridged bis(coumarin-24-crown-8), which displayed photo-switchable RTP with green afterglow (more than 5 s) after coassembly with PVA. Especially doping with RhB gave a photo-switchable highly efficient phosphorescence-harvesting system with multicolor through triplet-to-singlet Förster-resonance energy transfer (TS-FRET). The energy transfer efficiency and antenna effect of C24C8+RhB@PVA film reached 88.3% and 62.6 when the donor/acceptor ratio is 50:1, respectively. Therefore, diarylethene noncovalent bridged bis(coumarin-24-crown-8) supramolecular assembly not only displays a multicolor photoluminescence-switch, but also presents a phosphorescent photo-switch with afterglow, which provides a simple and feasible way to construct smart RTP materials through host-guest strategy.

1. Introduction

Supramolecular photoluminescence switch[1] was a current research hotspot, due to their wide applications in optoelectronic devices,[2] information encryption,[3] bioimaging,[4] and so on.[5] In the research progress of supramolecular photoswitches, diarylethene derivatives and crown ethers were usually used as important building elements to constructed supramolecular assembly. Benefiting from the strong binding of benzo-24-crown-8 and secondary alkylammonium ion, many supramolecular photo-switches were constructed by the host-guest interaction of benzo-24-crown-8 derivatives and cationic secondary alkylammonium salts. For example, Liu et.al reported a dual-stimuli driven lanthanide luminescent switch based on the supramolecular assembly of asymmetric diarylperfluorocyclopentene and trivalent europium ion (Eu^{3+}) coordinated terpyridine modified dibenzo-24-crown-8 which can be tuned by both light irradiation and K^+/18-crown-6.[6] Furthermore, they reported a photoreaction driven reversible photoluminescence switch, which was constructed by the coordination of 9,10-diphenylanthracene dibenzo-24-crwon-8 with terpyridine terminal and Eu^{3+}.[7] Yang et.al reported a metal ions actived photo-switch constructed by diarylethene modified azadithiacrownether through alter the electronic energy state of diarylethene.[8] However, most of the photo-switches based on 24-crown-8 were mainly focused on fluorescence, phosphorescent photo-switches with afterglow haven't been report yet to our best knowledge.

Considering that the purely organic room temperature phosphorescence (RTP) with specific features of large Stokes shift, long lifetime showed great potential applications in numerous fields,[9] such as optoelectronic, biological imaging, and anti-counterfeit, it is urgent to develop stimuli-responsive phosphorescent materials. Thus, a lot of efforts were contributed to constructing purely organic RTP materials through enhancing the intersystem crossing (ISC) and restricting nonradiative decay of triplet excitons,[10] such as host-guest doping,[11] crystallization,[12] polymerization,[13] heavy halogen atom[14] and so on. Among them, crown ether host also can emit bright phosphorescence in a crystallization state, and its cavity structure provided a feasible way to construct phosphorescent switches through host-guest interactions. For example, Tang et.al reported a series of phosphorescent materials based on traditional crown ethers whose phosphorescent lifetime can be tuned by K^+ which was used for time-resolved information encryption.[12a] Herein, we reported a reversible phosphorescence-harvesting photo-switch constructed by coumarin-24-crown-8 (**C24C8**), diarylethene bridged di-secondary alkylammonium ion (**1**), rhodamine B (RhB) and poly(vinyl alcohol) (PVA). **C24C8** was chosen as phosphor and host which showed bright RTP at 516 nm with green afterglow after coassembly with PVA. Commercial dye RhB whose absorbance spectrum showed good overlap with the phosphorescence spectrum of **C24C8**@PVA film was selected as an acceptor to constructed multi-color triplet-to-singlet Förster-resonance

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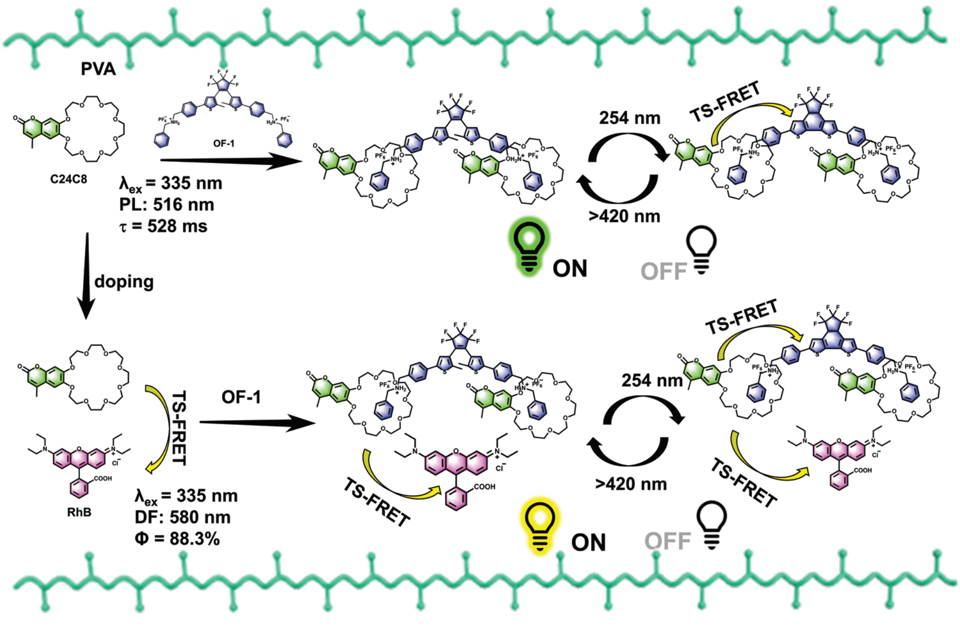

Scheme 1. Schematic diagram of the phosphorescence energy transfer photo-switch (PL: phosphorescent luminescence, DF: delayed fluorescence).

energy transfer (TS-FRET)[15] system with high energy transfer efficiency (Φ) of 88.3%. Then photo-switch molecule **1** was introduced as a guest binding with **C24C8** to construct photo-switchable phosphorescence energy transfer system and used for information encryption with afterglow. The diarylethene noncovalent bridged bis(coumarin-24-crown-8) phosphorescent supramolecular switch based on host-guest strategy provides an easy way to construct stimuli-responsive phosphorescent materials (**Scheme 1**).

2. Results and Discussion

In this work, **C24C8** with coumarin group whose carbonyl can promote the spin-orbit coupling (SOC) of luminophores[16] was synthesized through the route shown in Scheme S1 (Supporting Information) and the corresponding characters were shown in Figures S1–S3 (Supporting Information). To obtain RTP, we coassembly **C24C8** with PVA which was an effective method to obtain amorphous RTP materials.[17] Firstly, the photophysical properties of **C24C8**@PVA were studied through photoluminescence spectra and delayed spectra (delayed 1 ms) at different temperatures. As shown in Figure S5 (Supporting Information), both the intensity of photoluminescence and delayed spectra of **C24C8**@PVA increased with the decline of temperature, which indicated the phosphorescence nature of the emission at 516 nm. To figure out the effect of the dopped ratio on the photophysical properties of **C24C8**@PVA, the steady-state photoluminescence spectra and phosphorescence spectra (delayed 1 ms) of the dopped PVA films with different concentrations of **C24C8** were carried out. As shown in **Figure 1**, both the photoluminescence and phosphorescence increased at first and then descend with the increase of the **C24C8** concentration and reached maximum when the concentration of **C24C8** was 0.15 μM/ml 5% PVA. So the subsequent studies about **C24C8**@PVA films were executed with a doping concentration of 0.15 μM/ml 5% PVA. It can be seen obviously that the **C24C8**@PVA showed maxima of fluorescence emission at 408 nm[18] (Figure 1a) and phosphorescence emission at 516 nm (Figure 1b), respectively. Interestingly, the time-resolved decay curve of **C24C8**@PVA film was measured and showed a lifetime up to 528.03 ms (Figure 1c). Further, the photoluminescence yield of **C24C8**@PVA was measured and calculated as 46.26% (Figure S7, Supporting Information). The luminescence experiments of reference molecule 4-methylesculetin (**ME**) were executed with the dopped concentration of 0.15 μM ml^{-1} 5% PVA. As shown in Figure S6 (Supporting Information), **C24C8**@PVA film showed fluorescence peak at 408 nm and phosphorescence peak at 516 nm, while the PVA film of **ME** showed only fluorescence at 458 nm. We speculated that the phosphorescence was induced by the confinement of cyclizing and hydrogen bindings between ether oxygen chains and PVA. More interestingly, **C24C8** dopped PVA film showed excellent RTP properties, and the bright green afterglow of the film can be seen by the naked eyes after the 365 nm light is turned off for 5 s (Figure 1d).

Considering the strong and excellent RTP property of **C24C8**@PVA film, we choose it as a donor to construct a phosphorescence energy transfer system. RhB is a common commercial dye (λ_{em} = 576 nm, Figure S8, Supporting Information) and its absorbance spectrum showed good overlap with the phosphorescence spectra of **C24C8**@PVA film satisfying the prerequisites of FRET[19] (**Figure 2**a). Then the delayed photoluminescence spectra (delayed 1 ms) and lifetimes of **C24C8**+RhB@PVA films with the increasement of the concentration of RhB were measured. As shown in Figure 2b, a new long-lifetime emission peak at 580 nm appeared even at a 0.05% (donor: acceptor = 2000:1) doping ratio of RhB and enhanced gradually with the addition of RhB accompanying the colors changed from green to yellow (Figure 2e). Meanwhile,

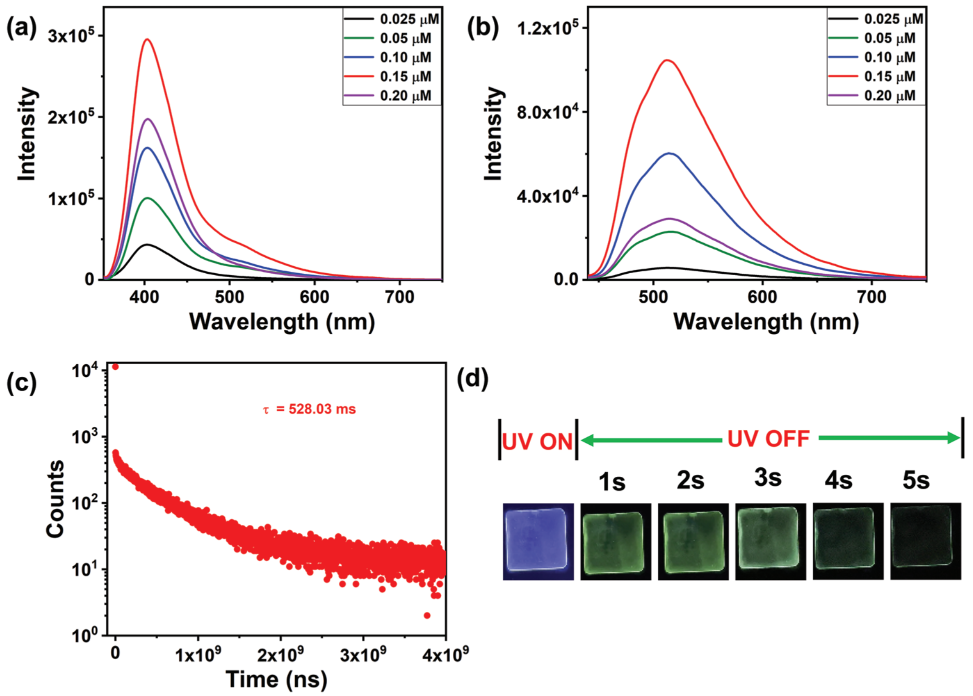

Figure 1. a) Photoluminescence spectra and b) phosphorescence spectra (delayed 1 ms) of **C24C8**@PVA film with different dopped concentrations of **C24C8** (0.025-0.20 μM) in 1 ml PVA (5 wt.%). c) The time-resolved decay curve of **C24C8**@PVA (0.15 μM ml^{-1}). (d) Photos of **C24C8**@PVA (0.15 μM ml^{-1}) were taken under 365 nm lamp before and after the lamp was turned off.

the phosphorescence at 516 nm decreased and generated a blue-shift gradually. A reasonable explanation for the emission of phosphorescence donor at 516 nm showing a blue shift upon increasing the ratio of donor/acceptor (≈20 nm when the ratio of donor/acceptor is up to 50/1) is that the increased molecular aggregation formed gradually with the increasing of the concentration of RhB through electrostatic interactions. And the new peak at 580 nm is similar to the location of the fluorescence peak of RhB in aqueous (Figure S8, Supporting Information) indicated the TS-FRET process from the triplet state of C24C8 to the singlet state of RhB (Figure 6a). The emission of **C24C8**+**RhB@PVA** at 580 nm reached maximum with a ratio of 2% due to the aggregation-causing quenching (ACQ) nature of RhB with a lifetime of 57.8 ms (Figure 2b,d, and Figure S11, Supporting Information). Meanwhile, the phosphorescent lifetime of **C24C8**+**RhB@PVA** at 516 nm reduced from 528.03 ms to 61.9 ms with the increasement of RhB (Figure 2c and Figure S10, Supporting Information), confirming an efficient TS-FRET occurred between **C24C8** and RhB. The energy transfer efficiency (Φ) was calculated as 88.3% (Figure S10, Supporting Information) with a molar ratio of 50:1 (donor: acceptor). Subsequently, the antenna effect was obtained as 62.6 (Figure S9, Supporting Information) indicating the construction of highly efficient phosphorescence-harvesting system.

To obtain a photo-switchable phosphorescence light-harvesting system, a diarylethene bridged di-secondary alkylammonium ion (**1**) was synthesized in open form (**OF-1**) through the route shown in Scheme S2 (Supporting Information) and the ^{1}H NMR spectrum was given in Figure S4 (Supporting Information). First, the photo-isomerization of compound **1** was investigated by ^{1}H NMR spectra. As shown in Figure S12b (Supporting Information), the proton signals (H$_d$, H$_e$, H$_g$, H$_f$, and H$_i$) of **1** shifted to the down field and proton H$_h$ shifted to up field after being irradiated by 254 nm light for 60 minutes meaning the **OF-1** transformed to **CF-1** and the conversion yield was calculated as 93%.[20] Subsequently, irradiation with >420 nm light for 2 minutes, the proton signals of **CF-1** returned to their original positions completely indicating the ring-opening yield was 100%. Further, we investigated the photoreaction of **1** by UV/vis spectra. The acetonitrile solution of **1** showed a sharp absorption peak at 295 nm and bathochromic shifted to 318 nm with a new peak arising at 592 nm accompanying colors changed from colorless to blue after irradiation with 254 nm light (Figure S15a, Supporting Information), indicating the formation of **CF-1**. Subsequently irradiation with >420 nm light, the solution of **CF-1** changed back to colorless and its absorption back to the original position (Figure S15b, Supporting Information). Then the solution of **1** was irradiated with alternative light of 254 nm and >420 nm and the changes of its absorption at 592 nm were recorded in Figure S15d (Supporting Information) indicating good reversibility of photo-isomerization. It is well known that 24 crown 8 could be associates with secondary alkylammonium ion through hydrogen-bonding interactions of N–H…O and C–H…O in solvents with low polarity.[21] The ^{1}H NMR spectrum of the mixture of **OF-1** and **C24C8** with a ratio of 1:2 showed that the coumarin protons (H$_1$, H$_3$, and H$_4$) of **C24C8** showed obvious downfield shifts, while the protons (H$_c$, H$_f$, H$_g$, and H$_h$) of **OF-1** shifted to up field and the protons H$_d$ and H$_e$ shifted to down fields (**Figure 3**). Further, we performed the experiment of 2D ROESY NMR spectrum of **1**$\subset$**C24C8** (Figure S14, Supporting information) indicating that there are

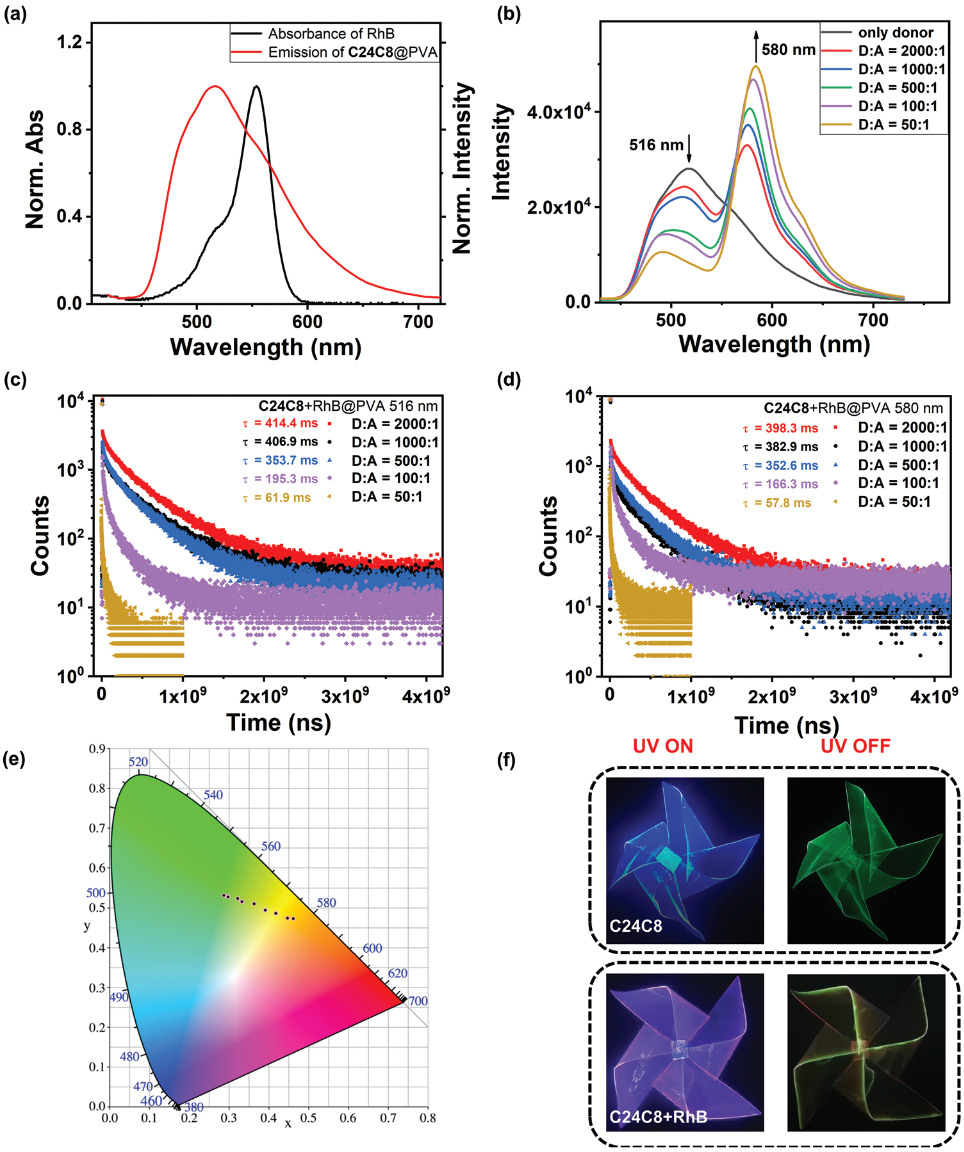

Figure 2. a) Absorbance spectrum (black curve) and phosphorescence spectrum (delayed 1 ms) of **C24C8**@PVA film (red curve). b) Delayed photoluminescent spectra (delayed 1 ms) of **C24C8**+RhB@PVA with different contents of RhB (0%–2%). The time-resolved intensity decay curves of **C24C8**+RhB@PVA films with different contents of RhB (0-2%) were measured at (c) 516 nm and (d) at 580 nm, respectively. e) CIE 1931 chromaticity diagram of **C24C8**+RhB@PVA films with different contents of RhB (0-2%). f) Photos of **C24C8**@PVA and **C24C8**+RhB@PVA films in the shape of pinwheels before and after the 365 nm light was turned off.

NOE correlations between H_3 and H_d, H_3 and H_e, implying the ring of **C24C8** binding on the secondary alkylammonium ion part of **1**. These phenomena indicated that the noncovalent interactions occurred between **1** and **C24C8**. Further, we investigated the photo-isomerization of supramolecular assembly **1⊂C24C8** by ^{1}H NMR spectra and UV/vis spectra. As shown in Figure S13 (Supporting Information), some protons of **1** generated a shift implying the photo-isomerization occurred in supramolecular assembly. Then the reversibility of the photo-isomerization of **1⊂C24C8** was studied by UV/vis spectra. With the irradiation of 254 nm light, a new peak at 592 nm appeared and increased gradually in the absorption spectrum of **1⊂C24C8** (Figure S16a, Supporting Information). Subsequently irradiation with >420 nm light, the absorbance of **1⊂C24C8** at 592 nm decreased until disappeared (Figure S16b, Supporting Information). Then the solution of **1⊂C24C8** was irradiated by alternative 254 nm light and >420 nm light and its absorption at 592 nm was recorded indicating good reversibility (Figure S16d, Supporting Information). All the phenomena indicated that both **1** and supramolecular assembly **1⊂C24C8** showed excellent photo-isomerization and reversibility.

By virtue of the good reversibility of the photo-isomerization of **1**, two photo-switchable phosphorescent energy transfer systems were constructed. As shown in **Figure** 4a and **Figure** 5a, the absorption spectrum of **OF-1⊂C24C8** showed good overlap with both the emission of **C24C8**@PVA and the emission of **C24C8**+RhB@PVA, which satisfied the rule of FRET. Subsequently, the photo-switched emission

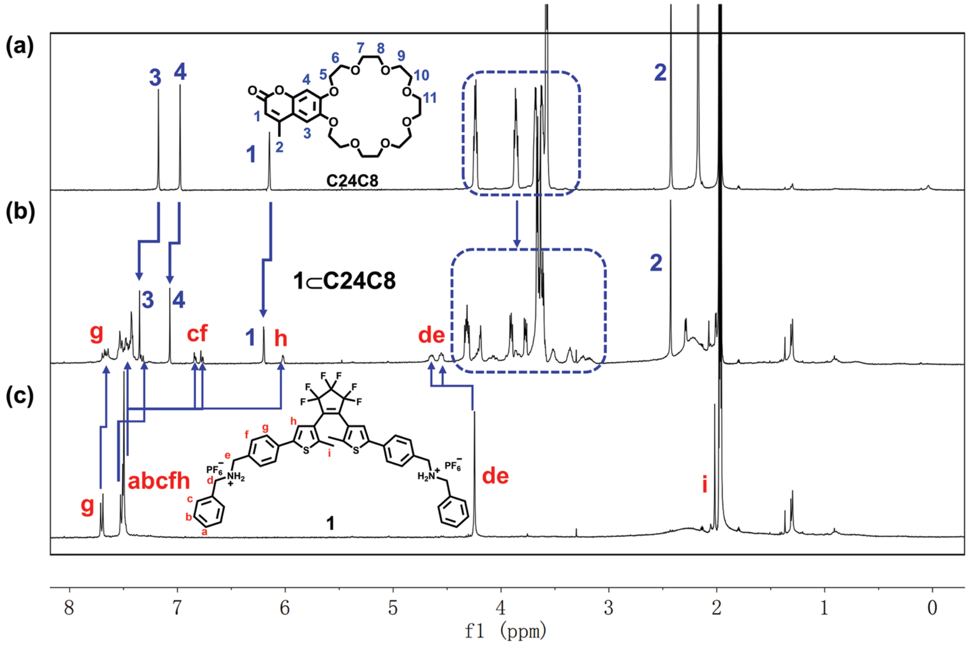

Figure 3. ^{1}H NMR spectra of a) **C24C8**, b) **1⊂C24C8** and c) **1**. ([**C24C8**] = 4 mM, [**1**] = 2 mM, 400 MHz, CD_3CN-*d3*, 298 K).

spectra of **OF-1⊂C24C8**@PVA and **OF-1⊂C24C8**+RhB@PVA films were performed. With the irradiation of 254 nm light, the phosphorescence intensity of **OF-1⊂C24C8**@PVA film decreased and reach a minimum after being irradiated for 90 s (Figure 4b). Then the film was irradiated by >420 nm light for 30 seconds, and its phosphorescence intensity was restored gradually (Figure 4c). Further, the phosphorescence spectra of **OF-1⊂C24C8**@PVA film irradiated by alternative

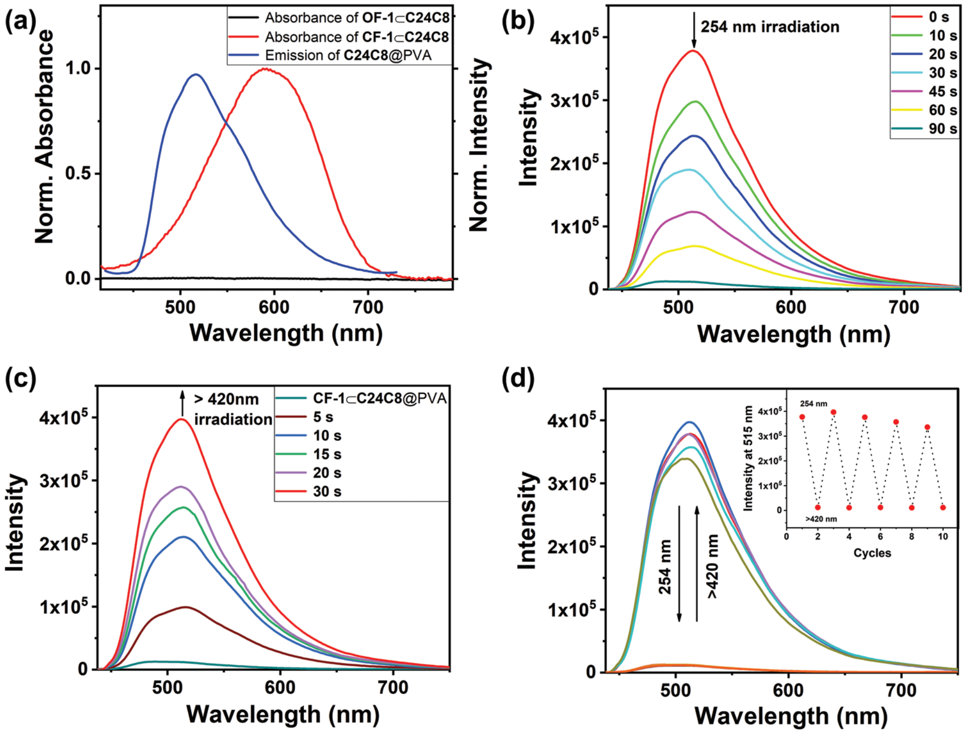

Figure 4. a) Normalized absorbance spectra of **OF-1⊂C24C8** (black curve), **CF-1⊂C24C8** (red curve) and normalized phosphorescence spectrum (delayed 1 ms) of **C24C8**@PVA (blue curve). b) Phosphorescence spectra (delayed 1 ms) of **1⊂C24C8**@PVA irradiated by 254 nm light for different times. c) Phosphorescence spectra (delayed 1 ms) of **CF-1⊂C24C8**@PVA irradiated by >420 nm light for a different time. d) Phosphorescence spectra (delayed 1 ms) of **1⊂C24C8**@PVA irradiated by alternative 254 nm light and >420 nm light. Inset: The changes of phosphorescent intensity at 515 nm.

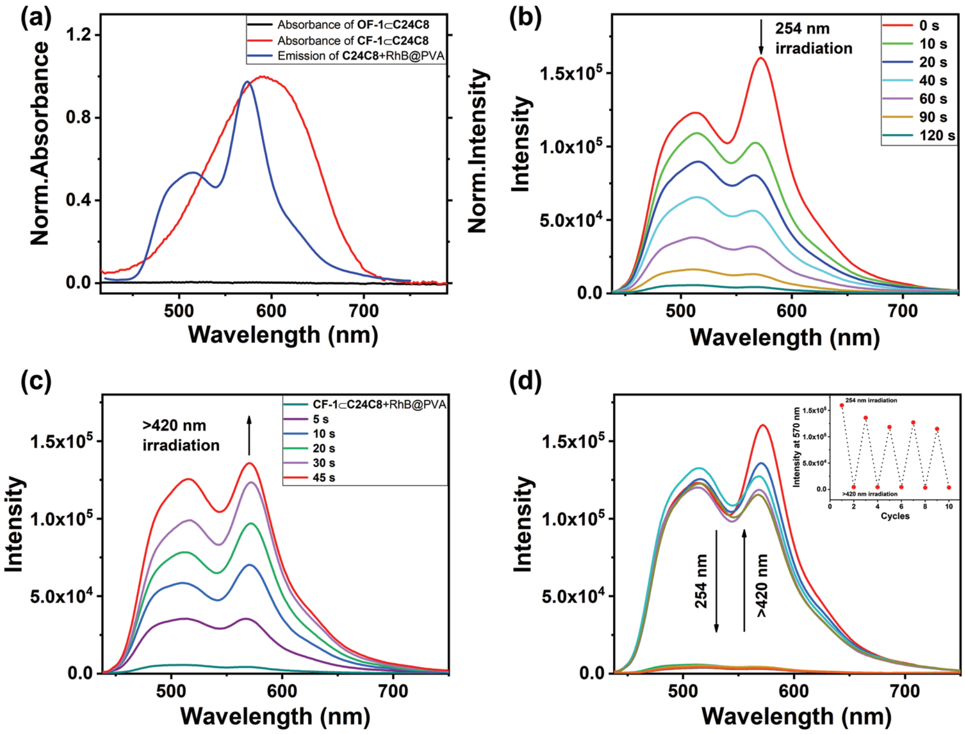

Figure 5. a) Normalized absorbance spectra of **OF-1⊂C24C8** (black curve), **CF-1⊂C24C8** (red curve) and phosphorescence spectrum (delayed 1 ms) of **C24C8**+RhB@PVA (blue curve). b) Phosphorescence spectra (delayed 1 ms) of **1⊂C24C8**+RhB@PVA irradiated by 254 nm light for different times. c) Phosphorescence spectra (delayed 1 ms) of **CF-1⊂C24C8**+RhB@PVA irradiated by >420 nm light for different times. d) Phosphorescence spectra (delayed 1 ms) of **1⊂C24C8**+RhB@PVA irradiated by alternative 254 nm light and >420 nm light. Inset: The changes of phosphorescent intensity at 570 nm.

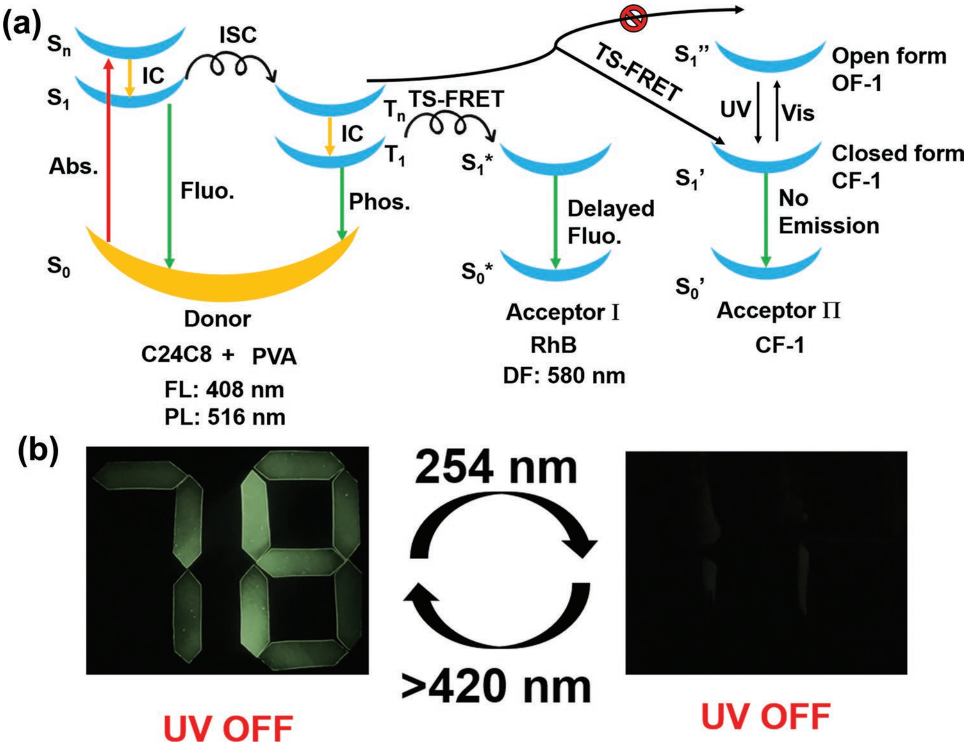

Figure 6. a) Jablonski diagram for understanding the FRET progress. b) Illustration of the components of information "78" and photographs of information encryption based on the photo-switched persistent phosphorescence of **1⊂C24C8**@PVA irradiated by alternative 254 nm light and >420 nm light.

254 nm light and >420 nm light were performed (Figure 4d). As shown in Figure 4d (inset), the phosphorescence intensity at 516 nm was recorded and showed good reversibility. When it comes to **OF-1⊂C24C8**+RhB@PVA film, similar phenomena were observed. With the irradiation with 254 nm light, the photoluminescence intensity of **OF-1⊂C24C8**+RhB@PVA film decreased and reached a minimum after 120 s. Then irradiated by >420 nm light for 45 s, the photoluminescent emission was restored. The photoluminescence spectra of **OF-1⊂C24C8**+RhB@PVA film irradiated by alternative 254 nm light and >420 nm light were given in Figure 5d and the intensity at 570 nm was recorded. All the phenomena indicated that the photo-isomerization of **OF-1⊂C24C8**+RhB@PVA film showed good reversibility. To figure out the progress of the photo-controlled TS-FRET progress, the fluorescence spectra of **1**+RhB@PVA film irradiated by 254 nm light for different times were performed and showed no changes (Figure S17, Supporting Information). The results indicated that neither the open nor closed ring of **1** disturbed the photoluminescence of RhB, confirming that there was no assembly formed between **1** and RhB. It is reasonable to think that TS-FRET occurred between **C24C8** and **CF-1** when **1⊂C24C8**+RhB@PVA film irradiated by 254 nm light (**Figure 6**a) and further caused the decrease of both phosphorescence of **C24C8** and the delayed fluorescence of RhB (Figure 5b).

Benefiting from the RTP nature of **C24C8**@PVA and the reversible photo-isomerization of **1**, **1⊂C24C8**@PVA films were used for information encryption. As shown in Figure 6b, the **1⊂C24C8**@PVA films were used to fabricate number "78". When irradiated by excitation light and turn off, these films presented information of "78" with green afterglow. After irradiating by 254 nm light for several minutes, the afterglow of the information disappeared after the excitation light was turned off. The photo-switched phosphorescence material was successfully used in time-resolved information encryption.

3. Conclusion

In summary, we constructed photo-switchable phosphorescence-harvesting system with excellent reversibility and multicolors emission. In this system, **C24C8** was used as a phosphor by coassembly with PVA and showed bright RTP with green afterglow. RhB was selected as an acceptor to obtain a multicolor phosphorescence-harvesting system with a long lifetime. Diarylethene modified di-secondary alkylammonium ion **1** can bind with **C24C8** to work as a molecular switch which can quench the luminescence of **C24C8** and RhB through TS-FRET from **C24C8** to **1**. Finally, these materials with photo-switchable RTP with afterglow were used for time-resolved information encryption. This work laid the foundation for the construction of phosphorescent photo switches with afterglow through host-guest interaction.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

crown ether, phosphorescence, photo-switch, supramolecular assembly, triplet-to-singlet Förster-resonance energy transfer (TS-FRET)

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