

Room-Temperature Phosphorescence and Reversible White Light Switch Based on a Cyclodextrin Polypseudorotaxane Xerogel

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The development of metal-free room-temperature phosphorescent (RTP) and white-light-emitting supramolecular materials is significant for artificial soft materials. Herein, a polypseudorotaxane xerogel is fabricated by threading a linear brominated aromatic aldehyde polymer into α -cyclodextrin cavities. The xerogel can be excited to produce not only RTP signals based on the xerogel network structure's strong restriction of phosphor vibrations and suppression of the nonradiative relaxation process but also white-light emission at room temperature. Notably, the polypseudorotaxane system possesses excellent fluorescence–phosphorescence dual emission properties and is capable of reversible photoluminescence switching between blue fluorescence emission and white-light emission in the presence and absence of water.

The development of pure organic molecules with room-temperature phosphorescence (RTP) has attracted significant research interest due to their potential applications in light emitting diodes,^[1] chemical sensors,^[2] biological imaging,^[3] photodynamic therapy,^[4] and so forth. In general, two vital factors must be considered when designing pure organic molecules for efficient RTP: the promotion of efficient intersystem crossing (ISC) from singlet to triplet by enhancing the spin–orbit coupling and the suppression of nonradiative relaxation from the triplet to the ground state.^[5] However, the energy of the excited triplet states of organic phosphors is readily dissipated through thermal radiation and collisional deactivation.^[6] As a result, much effort has been devoted to developing organic phosphorescent materials, including crystallization-induced phosphorescence^[7] or embedding phosphors into a rigid matrix.^[2,8] Recently, RTP materials constructed with macrocyclic compounds through host–guest interactions have become a popular research topic in supramolecular chemistry.^[9] Cyclodextrins (CDs),^[10] as an example of an important macrocyclic molecule, can bind

various guest molecules to form stable supramolecular inclusion complexes and enhance the luminescence behavior of luminogens due to its hydrophobic internal cavity.^[11] After Turro's group first reported the RTP of 1-bromonaphthalene and 1-chloronaphthalene induced by cyclodextrin through host–guest interactions in nitrogen-purged aqueous solutions,^[12] several examples of RTP systems based on cyclodextrin were reported by Tian and co-workers.^[9c,13] The most commonly used phosphors/CD supramolecular assembly is α -bromonaphthalene/ β -CD, in which α -bromonaphthalene is included into the CD cavity, resulting in the enhancement of

RTP emission;^[13a,b,d] this is a convenient and efficient approach to the construction of organic RTP materials. The host–guest interactions between cyclodextrin and phosphors not only restrict the vibrations of guest phosphors but also shield them from quenchers and suppress nonradiative relaxation to induce or enhance the RTP emission (Scheme 1).^[14] Considering the advantages of host–guest interaction-induced RTP emission, we present herein a new strategy to fabricate a white-light-emitting polypseudorotaxane xerogel with RTP. There are several advantages in this system: 1) the linear bromobenzaldehyde polymer is threaded into α -CD cavities to construct a supramolecular polypseudorotaxane xerogel by hydrogen bonding and hydrophobic interactions, which provides a protective environment to immobilize phosphors and suppress the nonradiative relaxation process, resulting in phosphorescence emission at 550 nm; 2) compared with the previously reported RTP materials based on cyclodextrin by host–guest interaction, this supramolecular polypseudorotaxane xerogel exhibits excellent fluorescence–phosphorescence dual emission properties and white-light emission at room temperature; 3) the polypseudorotaxane xerogel can reversibly convert its photoluminescence behavior from blue fluorescence emission to white-light emission in response to water.

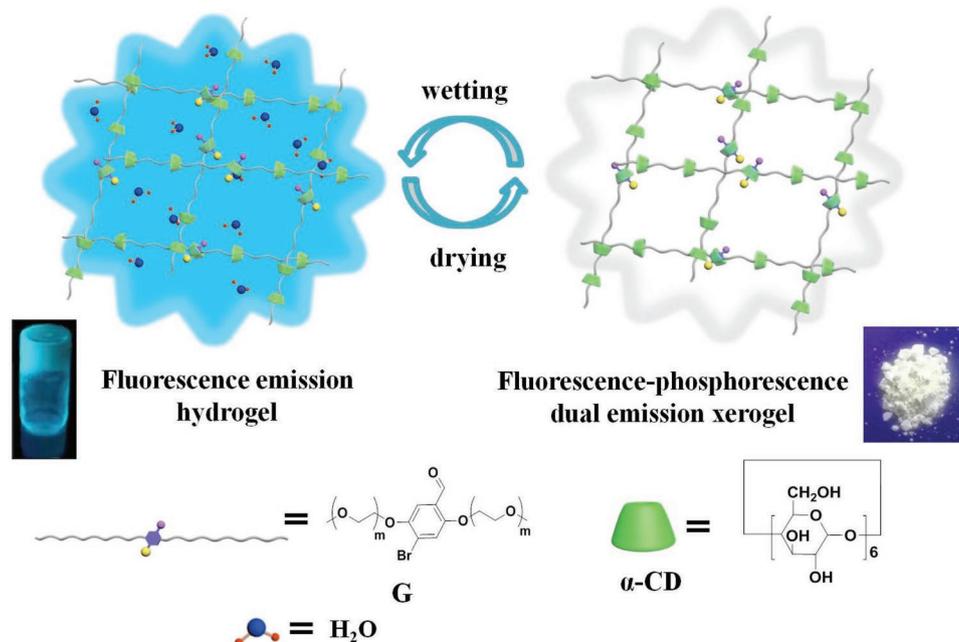
It is well-known that bromobenzaldehyde can generate a triplet state, and the heavy atom effect is able to reinforce ISC to produce efficient phosphorescence emission from purely organic materials by crystal design.^[15] However, its phosphorescence cannot be detected in solution or noncrystalline states. In this work, a new organic phosphor polymer (**G**) with a bromobenzaldehyde core and polyethylene glycol (PEG) side chains was conveniently synthesized. We first investigated the solution-state luminescence properties of **G**, and its ultraviolet

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Scheme 1. RTP and reversible white-light emission switching based on cyclodextrin polypseudorotaxane xerogel.

(UV) absorption and fluorescence spectra are depicted in Figure S7 in the Supporting Information. An aqueous solution of **G** under ambient conditions exhibited blue fluorescence emission at 470 nm with a fluorescence lifetime of 2.5 ns (Figure S8, Supporting Information), but no phosphorescence emission was found. The fluorescence quantum yield of **G** in solution was 10.21% (Figure S9, Supporting Information). Moreover, **G** in the solid state is weakly luminescent, and does not display any visible fluorescence or phosphorescence under an ultraviolet lamp at room temperature (Figure S16, Supporting Information). The weak fluorescence could be attributed to the aggregation-induced quenching of **G** in the solid state, and the low phosphorescence efficiency in the disordered solid state may be due to the vibrational dissipation process. It is well-known that PEG chains can thread into α -CD cavities to construct supramolecular polypseudorotaxane.^[16]

Subsequently, the hydrogelation of α -CD with **G** was easily obtained by mixing the compounds in aqueous solutions under constant stirring overnight (Figure S10, Supporting Information). The critical gelation concentration was measured to be 9 wt%. Because both hydrogen bonding and hydrophobic interactions play significant roles in the formation of the hydrogel, the gel network structure was further formed. The supramolecular hydrogel exhibited strong blue fluorescence emission at 470 nm (Figure 1a). The mechanical properties of the supramolecular hydrogel were also investigated. Figure S11a in the Supporting Information exhibits the plots of storage moduli (G') and loss moduli (G'') with increased oscillation strain. G' was larger than G'' under oscillation strains from 0.01% to 100%, indicating that the supramolecular hydrogel was stable, and the physical crosslinkages remained undamaged. G' was less than G'' when the oscillation strain increased further

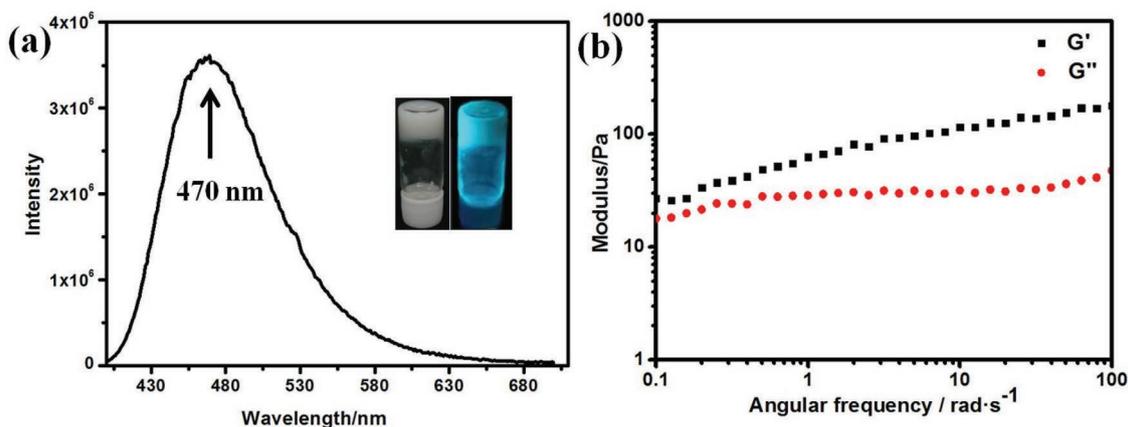


Figure 1. a) The fluorescence emission spectra of supramolecular hydrogel by the threading of **G** chain into α -cyclodextrin cavity. Inset: photographs of hydrogel under natural light (left) and 365 nm light (right). b) The rheological characterization of hydrogel.

demonstrating a gel–sol transition and the destruction of the hydrogel network. From these results, 1% strain was chosen to investigate the storage moduli (G') and loss moduli (G'') of the hydrogel with regards to the oscillation frequency. As shown in Figure S11b in the Supporting Information, G' remained larger than G'' across the range of angular frequency (0.1 – 100 rad s^{-1}), indicating the good stability of this hydrogel. Moreover, steady shear rheological experiments (Figure S11c, Supporting Information) revealed the shear thinning of the supramolecular hydrogel. The viscosity of the hydrogel decreased significantly with an increasing shear rate. The G/α -CD hydrogel was filtered and washed with water to remove any free G or α -CD and then dried to obtain G/α -CD polypseudorotaxane. ^1H NMR (Figure S13, Supporting Information) indicated that five α -CD were threaded through by the bromobenzaldehyde polymer (G). The rotating frame overhauser effect spectroscopy (ROESY) spectrum (Figure S12, Supporting Information) showed a clear correlation between the PEG chains and bromobenzaldehyde of G and the α -CD cavity, indicating the threading of G into the α -CD cavities.

When the hydrogel was freeze-dried, a white-light-emitting xerogel powder was obtained under excitation with 365 nm UV light at room temperature (Figure S10, Supporting Information). Figure 2a shows the steady-state (prompt) photoluminescence spectrum (black line) of the xerogel powder at 295 K. This compound was found to exhibit dual emission bands

peaking near 445 and 550 nm. The red line illustrates the time-resolved (delayed) photoluminescence spectra obtained 0.1 ms after excitation. Under this condition, the delayed spectra showed a single band at 550 nm, revealing that the emission band contains a short-lived emission at 445 nm and a long-lived emission at 550 nm, respectively. To confirm this, time-resolved decay curves at 445 and 550 nm were measured (Figure 2c,d). The emission at 445 nm shows a lifetime in the nanosecond scale (1.56 ns), indicating that it was a fluorescence emission with a fluorescence quantum yield of 3.11%. The emission at 550 nm showed a lifetime in the millisecond scale (2.79 ms), indicating that it was a phosphorescence emission with a corresponding quantum yield of 1.23%. Through the fluorescence–phosphorescence dual emission, the xerogel exhibited bright white-light emission upon 365 nm UV irradiation. The white-light emission quantum yield was 4.34%. Furthermore, the Commission Internationale de l'Éclairage (CIE) coordinates of xerogel were calculated to be 0.27 and 0.28, respectively (Figure 3c). Compared with the weakly luminescent polymer chain G , the polypseudorotaxane xerogel exhibited not only RTP emission but also white-light emission effects. These results demonstrated that construction of the polypseudorotaxane xerogel network structure by hydrogen bonding and hydrophobic interactions provided a protective environment to effectively immobilize the phosphors and suppress the nonradiative relaxation process, which resulted in room-temperature

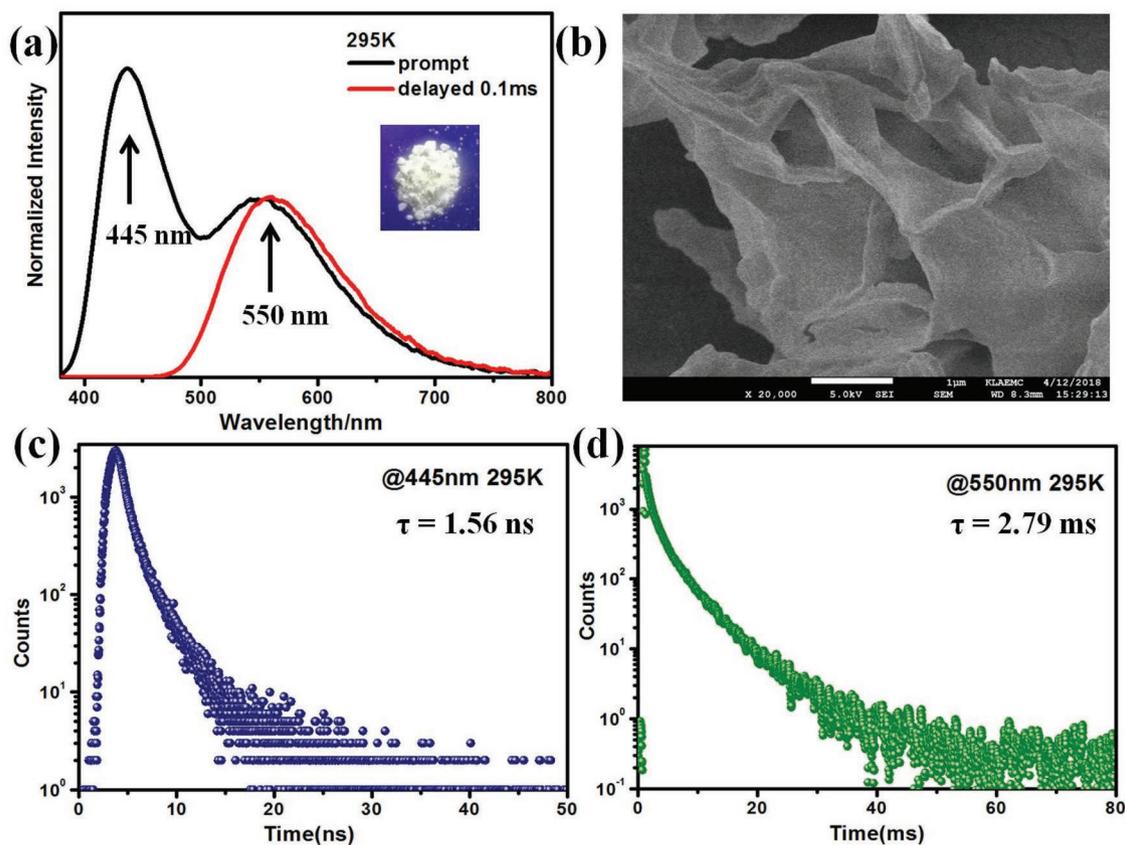


Figure 2. a) The prompt (black line) and delayed (red line, 0.1 ms) photoluminescence spectrum of the xerogel powder at 295 K. Inset: photographs of xerogel powder under 365 nm UV light. b) SEM images of xerogel powder. c) The fluorescence and (d) phosphorescence decay curves of xerogel at 445 and 550 nm, respectively, at 295 K.

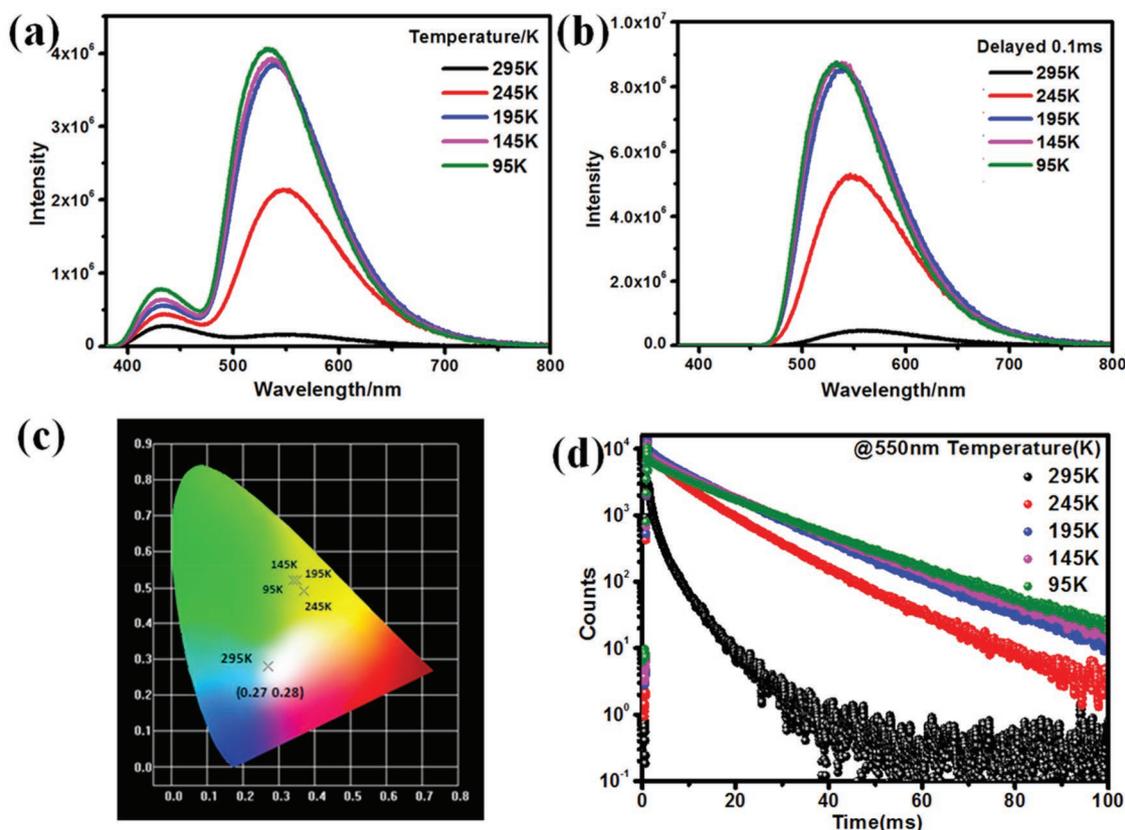


Figure 3. a) The prompt and (b) the delayed photoluminescence spectrum of the xerogel at different temperatures from 295 to 95 K. c) CIE 1993 coordinates of prompt photoluminescence at different temperatures from 295 to 95 K. d) Phosphorescence decay curve of xerogel at 550 nm from 295 to 95 K.

phosphorescence emission. Without the assistance of gelation, the supramolecular complex also possessed fluorescence–phosphorescence dual emission properties (Figure S17, Supporting Information). The host–guest interactions between the bromobenzaldehyde polymer and α -CD also supply a protective environment to enhance RTP emission. However, the simple supramolecular complex has a relatively low phosphorescence emission due to the absence of support for the rigid structures of gels compared to xerogels. Then, we investigated the photoluminescence properties of different ratios of α -CD to bromobenzaldehyde (Figure S21, Supporting Information). The results indicate that α -CD plays an important role in the photoluminescence of bromobenzaldehyde. Subsequently, fluorescence and phosphorescence properties of different length PEG chains with α -CD were studied (Figure S18, Supporting Information). Based on the photoluminescence studies of different PEG chains, the shorter PEG chains in G1 cannot form a hydrogel with α -CD, and the longer PEG chains of G2 with α -CD have relatively weak photoluminescence; therefore, we chose G for further research in this work. These experiments proved that the fluorescence and phosphorescence properties of bromobenzaldehyde polymer G are attributed to the host–guest interactions with α -CD and the rigid gel structure.

To verify the phosphorescence characteristics of the long-lived emission bands at 550 nm, we further investigated the effects of temperature on the phosphorescence emission. By decreasing the temperature from 295 to 95 K, the photoluminescence at

445 and at 550 nm were increased by 3- and 24-fold, respectively (Figure 3a). The time-resolved (delayed) phosphorescence intensity is shown in Figure 3b, measured 0.1 ms after excitation. The tremendous enhancement of phosphorescence intensity was attributed to the suppression of the nonradiative relaxation process of triplets to the ground state at low temperatures. The phosphorescent lifetime further proved this property (Figure 3d). The temperature-dependent emission decay showed a continuous enhancement in the lifetime from 2.79 to 15.99 ms at 295 and 95 K, respectively. The phosphorescence lifetime variation with temperature is summarized in Table S1 in the Supporting Information.

From the abovementioned studies, we can reasonably speculate that the enhancement of phosphorescence emission was induced by two factors: 1) the formation of polypseudorotaxane by the threading of G chains into α -cyclodextrin cavities through host–guest interactions; 2) the rigid gel network structure formed by hydrogen bonding. To evaluate this influence, as a control experiment, cyclodextrin monomer D-glucopyranose was added to an aqueous solution of G. The solid powder weakly illuminated when the solution of this mixture was lyophilized (Figure S16, Supporting Information). This result clearly demonstrated that the host–guest interactions based on cyclodextrin play an important role for the RTP emission. Furthermore, scanning electron microscopy (SEM) images (Figure 2b) of the lyophilized hydrogel indicated the morphological information to be porous lamellar nanosheets,

which were expected to be able to act as scaffolds, enabling the xerogel to produce RTP emission. X-ray powder diffraction (XRD) analysis was carried out to verify the structure of the xerogel (Figure S20, Supporting Information). Compared to the XRD results of α -CD, the peak shape of the gel became blunt, but a sharper peak was observed at $2\theta = 19.7^\circ$ (4.51 Å). This peak indicates that the α -CD/G xerogel system formed a typical hexagonal tubular structure.^[17]

The immobilization of phosphors by the polypseudorotaxane xerogel network structure was demonstrated as a convenient and effective strategy to supply a protective environment to enhance RTP emission. Meanwhile, the hydrogen bonding network structure could be influenced by water, which greatly decreased the RTP intensity. Thus, the xerogel exhibited white-light emission with fluorescence–phosphorescence dual emission, but the hydrogel only showed blue fluorescence emission under 365 nm UV light. Based on this phenomenon, we inferred that the intensity of phosphorescence emission of the xerogel was strongly dependent on the water content. As shown in Figure S22 in the Supporting Information, the phosphorescence intensity decreased as the humidity increased, and recovered after drying. This process could be repeated over several cycles (Figure S23, Supporting Information). We deduced that more water was absorbed by the xerogel at higher humidity, and the absorbed water could influence the hydrogen bonding network structure, in turn accelerating the nonradiative relaxation process, finally resulting in the significant decrease in phosphorescence emission. Consequently, the white-light-emitting xerogel with fluorescence–phosphorescence dual emission readily converted into blue fluorescence by the stimulus response to water and recovered by drying.

Benefitting from the reversible photoluminescence switching, we put the blue fluorescent hydrogel on glass and dried it to obtain a white-light-emitting dry gel under 365 nm UV light. Interestingly, the white-light-emitting dry gel was converted into blue fluorescence when water was applied. Based on the abovementioned behaviors, the characters “NK” were written on the surface of dry gel. The blue fluorescence emission of the characters “NK” could be clearly observed under 365 nm light irradiation (Figure 4a). Similarly, the hydrogel was coated onto the surface of a diode, which engendered blue fluorescence emission. In this case, white-light emission was clearly observed upon the removal of water (Figure 4b). Figure 4c indicates the possible emission switch processes. The bromobenzaldehyde core could provide enhanced spin–orbit coupling, promoting efficient intersystem crossing from S_1 to T_1 . In the xerogel solid state, the α -CD/G polypseudorotaxane host–guest interactions and the rigid gel network structure from hydrogen bonding could restrict the vibration of the phosphor, suppress the vibration dissipation, and enhance the phosphorescence emission from T_1 to ground state. Thus, the xerogel system possessed excellent fluorescence–phosphorescence dual emission properties. In the hydrogel state, the hydrogen bond interactions between α -CD could be broken by water, promoting vibrational motion and quenching the phosphorescence emission, and the hydrogel only emitted strong fluorescence but not phosphorescence. As a result, this water-responsive property could have potential applications for secure image communications, printer inks, and water sensors.

In summary, a new strategy to develop an RTP material was realized using a polypseudorotaxane xerogel, which was constructed by the threading of brominated aromatic aldehyde

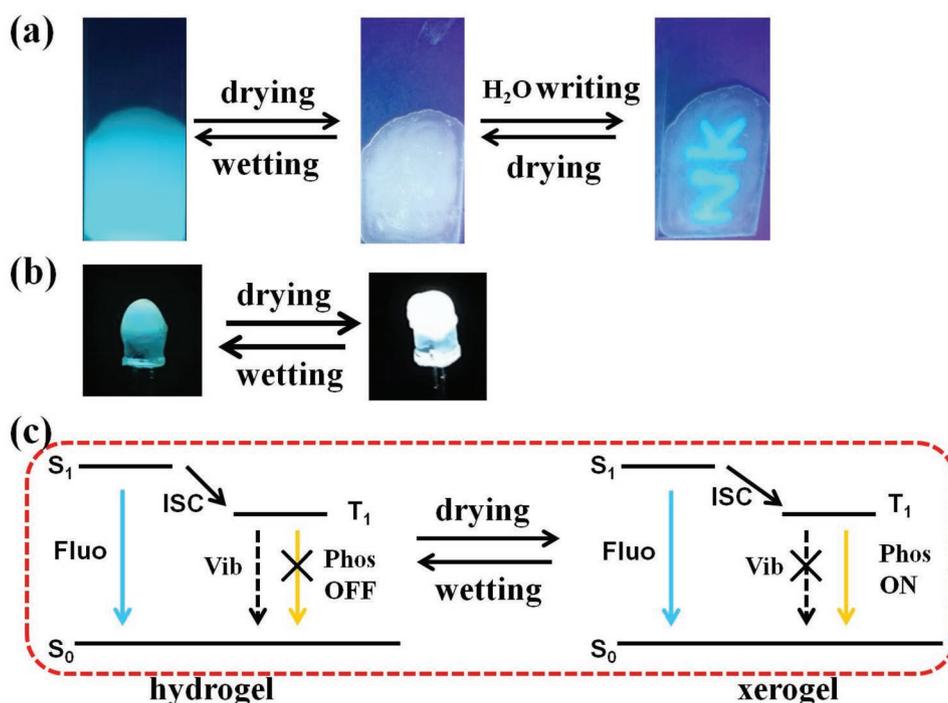


Figure 4. Photographs of (a) hydrogel dropped into the glass before and after drying under 365 nm UV light, and letters written by water before and after drying under 365 nm UV light; (b) hydrogel coated into the surface of the diode before and after drying under 365 nm UV light; (c) schematic illustration of the possible emission switch processes.

polymer (G) linearly into α -cyclodextrin cavities, based on hydrogen bonding and hydrophobic interactions. The polypseudorotaxane and xerogel network possesses a rigid structure that could effectively immobilize the phosphors and restrict the vibrational dissipation, which enable this xerogel to emit RTP. This polypseudorotaxane xerogel is low cost, nontoxic, conveniently prepared, and easily processed. Moreover, this polypseudorotaxane xerogel exhibits excellent fluorescence–phosphorescence dual emission properties with white-light emission at room temperature. Significantly, the polypseudorotaxane xerogel possesses a unique water-responsive property, which leads to reversible photoluminescence switching behavior from blue fluorescence emission to white-light emission. We believe that this innovative strategy has the potential for wide applications in organic luminescent materials or optical devices.

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.

Keywords

α -cyclodextrin, pseudopolyrotaxane xerogel, room-temperature phosphorescence, white-light emission

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