Multicolor luminescent supramolecular hydrogels based on cucurbit[8]uril and OPV derivative†

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Supramolecular hydrogels have received considerable attention because of their various fascinating applications. Herein, an alkyl chain-modified oligo(p-phenylenevinylene) (Py-OPV) derivative was synthesized. When assembled with cucurbit[8]uril, its fluorescence intensity was enhanced without any change in color. However, the molecules underwent J-type dimerization when encased in the cavity of cucurbit[8]uril, which possessed different emission properties based on the monomer. By simply changing the concentration of cucurbit[8]uril, the fluorescence properties of the assemblies were easily altered. In addition, luminescent supramolecular hydrogels were constructed with Py-OPV and cucurbit[8]uril based on the photopolymerization of acrylamide. By embedding the assembly in the polymer to confine it, hydrogels emitting various tones of blue light were easily constructed. The preparation method of such luminescent hydrogels provides a new reference method for the construction of specific luminescent materials.

Introduction

As a unique material between solid and liquid materials, the hydrogel combines the elasticity of solids and the fluidity of liquids, and plays an extremely important role in the field of soft materials research.† Supramolecular assembly, based on the host-guest interactions, provides a new way for constructing such hydrogels with the advantages of simple operation, convenient synthesis and applications in the water phase. Among them, a multiple emission fluorescent hydrogel is a hot topic in the research field. For example, Lin et al. reported an easy-to-make strong white AIE supramolecular polymer as a color tunable photoluminescent hydrogel. Moreover, Liu et al. reported highly swollen hydrogels with tunable white-light emission by supramolecular self-sorting. In addition, Huang et al. reported multifluorescent supramolecular polymeric hydrogels for encoding, reading, and transforming information.†

Moreover, some reports about achieving multiple luminescence emission by supramolecular methods have been reported. Tao et al. reported a facile cucurbit[8]uril-based supramolecular approach to fabricate tunable luminescence materials in aqueous solutions. However, there are few reports about using a single fluorophore to achieve multiple fluorescence emissions for hydrogels. Moreover, our group has reported some supramolecular hydrogels with a variety of properties and uses. Based on the above research results, we tried to make a supramolecular hydrogel with various fluorescence properties. Herein, an alkyl chain-modified amphiphatic oligo(p-phenylenevinylene) (Py-OPV) derivative, 1-methyl-4-((E)-4-((E)-2-(1-octylypyridin-1-ium-4-yl)vinyl)styryl)pyridin-1-ium iodide, was synthesized. When assembled with cucurbit[8]uril, its fluorescence intensity was enhanced without any change in color. However, the molecules proceeded via J-type dimerization when encased in the cavity of cucurbit[8]uril, which emitted at different fluorescence wavelengths from the monomer. By simply changing the concentration of cucurbit[8]uril, the fluorescence properties of the assemblies were easily altered. In addition, a luminescent supramolecular hydrogel was constructed with Py-OPV and cucurbit[8]uril based on the photopolymerization of acrylamide. By embedding the assembly in the polymer to constrain it, hydrogels emitting in various tones of blue light were easily constructed (Scheme 1). The preparation method of such luminescent hydrogels provides a new reference method for the construction of specific luminescent materials.

Results and discussion

The amphiphilic guest Py-OPV that has two positive charges and an octyl tail was synthesized in 67.7% yield (Scheme S1, ESI†), and its CB[8]-mediated supramolecular assembly and luminescence behaviors were investigated. With the increase in the concentration, the optical transmittance of Py-OPV at 480 nm gradually decreased, and the critical aggregation concentration (CAC) of Py-OPV was measured as 0.06 mmol L⁻¹ (Fig. S6 and S7, ESI†). In addition, the fluorescence of free Py-OPV had an
emission maximum at 471 nm (Fig. S8, ESI†), and the emission intensity decreased with the increase in the concentration, probably due to the aggregation-caused quenching (ACQ) effect triggered by the π·π stacking of the Py-OPV skeleton. The host–guest binding and supramolecular assembly of Py-OPV with macromolecular compounds were expected to reduce the ACQ effect and thus enhance the fluorescence intensity of Py-OPV. Herein, CB[7] and CB[8] were selected as the host macromolecular compounds to explore their supramolecular assembly and fluorescence enhancement behaviors towards Py-OPV.

First, the concentration of the aqueous solution of Py-OPV was fixed at 10.0 μmol L⁻¹, and different ratios of the aqueous solution of CB[7] were gradually added to the Py-OPV solution. With the addition of CB[7] (0–3 equiv.), the absorption intensity of Py-OPV at 392 nm gradually weakened with a red shift. Moreover, the absorption at 440 nm was enhanced (Fig. S9, ESI†). This may indicate that Py-OPV molecules were entrapped in the hydrophobic cavities of CB[7], which limited the rotation of Py-OPV and weakened the π·π stacking. When CB[7] was twice the amount of Py-OPV, the enhancement in the absorption intensity at 440 nm tended to be steady, indicating that CB[7] and Py-OPV might be bound in a stoichiometric 2 : 1 ratio (Fig. S10, ESI†), which was further verified by the Job’s plots (Fig. S13, ESI†). In the 1H NMR spectral analysis, it was also observed that the binding sites of CB[7] with Py-OPV were not only in the aromatic regions, but also in the aliphatic regions, leading to the formation of pseudorotaxanes (Fig. S14, ESI†).

The fluorescence properties of the system were also studied. With the addition of CB[7], the fluorescence intensity of Py-OPV increased and was eventually steady (Fig. 1a). This was because more Py-OPV molecules were encapsulated into the hydrophobic cavities of CB[7] in the form of monomeric molecules with enhanced fluorescence. The maximum fluorescence emission peak of the system was still at 471 nm. When CB[7] reached twice the amount of Py-OPV, the increase in the fluorescence intensity tended to be gentle, further demonstrating that CB[7] and Py-OPV were bound in a 2 : 1 mode (Fig. S12, ESI†). However, only the fluorescence intensity was enhanced in this process. There was no change in the emission wavelength, indicating that the fluorescence color of the system remained unchanged. Therefore, we considered switching to CB[8] as the host to try adjusting the emission color of the system.

Since the larger cavity of CB[8] may accommodate two Py-OPV molecules, the binding behavior of CB[8] with Py-OPV was also studied. First, a UV-vis absorption experiment was performed with the concentration of Py-OPV in water fixed at 10.0 μmol L⁻¹ and the proportion of CB[8] gradually increased. A phenomenon similar to that of CB[7] was observed, indicating that CB[8] could also bind Py-OPV via the simple host–guest interactions (Fig. S15, ESI†). In addition, the Job’s plots gave the stoichiometry of 1 : 1 (Fig. S16, ESI†). In the 1H NMR spectral analysis (Fig. 2), when 0.5 equivalent of CB[8] was added, the aromatic region of Py-OPV had a significant shifts, while the aliphatic region had no obvious change. When 1 equivalent of CB[8] was added, the aliphatic region also underwent significant shift and the aromatic region saw the appearance of new peaks. A possible reason might be that for the CB[8]/Py-OPV system, CB[7] and Py-OPV were bound in a 2 : 1 ratio, whereas two CB[7] molecules were respectively bound to the aromatic group and the alkyl chain to form the pseudorotaxane. However, for the CB[8]/Py-OPV system, CB[8] and Py-OPV were bound in the n : n mode, where one CB[8] molecule encapsulated the aromatic groups of the two Py-OPV molecules into its cavity, and the other encapsulated the long alkyl chain to form the supramolecular polymer. In addition, 2D NMR was also performed to investigate the binding mode between Py-OPV and CB[8]. In the ROESY spectrum (Fig. S19, ESI†), the protons of CB[8] showed clear NOE correlations with the protons of both the aromatic region
reports,

The mechanism of the multicolor emission may be

As shown in Fig. 1b, the fluorescence performance of the CB[8]/Py-OPV system was quite different from that of CB[7]/Py-OPV. When CB[8] was gradually added, the fluorescence intensity of Py-OPV at 471 nm decreased, and a new broad peak appearing at 550–650 nm with the fluorescence intensity gradually increasing. This change implied that the fluorescent color of the solution should have a large change with the gradual addition of CB[8]. In order to clearly explore the emission color changes during this process, eleven aqueous solutions with the Py-OPV/CB[8] ratios ranging from 1:0 to 1:1 were prepared. As the proportion of CB[8] increased, the fluorescence color of the system changed gradually in the order of blue, white, light yellow, and light green (Fig. 1c). According to the above experimental phenomena and the literature reports,

The mechanism of the multicolor emission may be

that when two Py-OPV molecules were encapsulated in the cavity of CB[8], they underwent a J-type dimerization, resulting in the bathochromic shift from the blue light of a single Py-OPV molecule to the yellow light of the dimer. With the gradual addition of CB[8], a certain proportion of Py-OPV converted to dimers, and the others remained as monomers. The Py-OPV monomers emitted blue light, while the dimers emitted yellow light. As the Py-OPV:CB[8] ratio reached 1:0.2, the mixed emission color became white because yellow light and blue light could complement each other. When CB[8] was further added, the emission color turned green. In addition, the morphology of the assembly was investigated by SEM. The CB[8]/Py-OPV assembly exhibited a regular three-dimensional diamond-shaped structure with a side length of about 200 nm (Fig. 3b). Moreover, the free Py-OPV formed a linear structure (Fig. 3a), which was quite different from that of CB[8]/Py-OPV.

In order to compare the effects of different macrocycles on the emission color changes, α-cyclodextrin, β-cyclodextrin and sulfonated calix[4]arene were used as control compounds, and their effects on the fluorescence properties of Py-OPV were studied (Fig. S20–S22, ESI†). It could be seen that the fluorescence intensity of Py-OPV slightly decreased with the addition of α-cyclodextrin or β-cyclodextrin but significantly quenched with the addition of sulfonated calix[4]arene. These phenomena demonstrated that only CB[8] could be used to regulate the fluorescence behaviors of Py-OPV and to achieve the multicolor fluorescence emission.

Supramolecular hydrogels have many applications in the scientific fields of research and have attracted considerable attention. Fortunately, the CB[8]/Py-OPV assembly could form a transparent and elastic supramolecular hydrogel based on the photopolymerization of acrylamide. By simply irradiating a mixture of the CB[8]/Py-OPV assembly, acrylamide, N,N-methylenebis(acrylamide), ammonium persulfate and N,N,N′,N′-tetramethylethlenediamine under sunlight for about five minutes, the mixture solution quickly became a transparent hydrogel. In addition, the resultant hydrogel showed good viscoelastic properties and mechanical properties. Fig. S26a (ESI†) shows the plots of storage moduli (G′) and loss moduli (G″) of the hydrogel versus the applied range of external strain at a fixed angular frequency of 10 rad s⁻¹. Under the strain from 0.1% to 110%, G′ and G″ remained nearly unaltered. Besides, G′ was larger than G″, demonstrating that the hydrogel network was very stable and the physical structure remained undamaged. When the strain kept increasing, G′ began to decrease while G″ increased. However, G′ was still larger than G″ even at the strain of 2000%, indicating that the hydrogel was very stable. Then, the viscoelastic region was analyzed. 1% strain was chosen to investigate the colloidal sensitivity to the oscillation frequency. As shown in Fig. S26b (ESI†), G′ and G″ did not undergo any obvious changes within the range of angular frequency (0.1–100 rad s⁻¹). In addition, G′ stayed larger than G″, indicating a good stability of hydrogel towards the oscillation. Moreover, the hydrogel was strong enough that it was not easy to destroy, even with scissors.

Moreover, the hydrogels remained nearly unchanged even after a month in the dark (Fig. S27, ESI†). Besides, the hydrogels were stable in the presence of water (Fig. S28, ESI†). First, the hydrogels were lyophilized to form white solids. Then, they were soaked in water overnight, leading to the recovery of the hydrogels with the initial fluorescence emission. These hydrogels were also very stable to temperature. In order to test their thermal stability, they were soaked in hot water at 80 °C for up to 10 minutes. To our surprise, their shape and fluorescence properties did not exhibit any differences (Fig. S29, ESI†).

Significantly, the CB[8]/Py-OPV hydrogel emitted various tones of blue light by changing the ratio between CB[8] and Py-OPV (Fig. 4a–c). Furthermore, the SEM images (Fig. 4d) of the lyophilized hydrogels provided morphological information.
of the hydrogel made without CB[8] as lamellar nanosheets, while the hydrogel made with 1.0 equiv. of CB[8] were thicker and bigger lamellar nanosheets with numerous holes. This illustrated the addition of CB[8] changed the microstructure of the hydrogel and further changed the fluorescence properties of the hydrogel to some extent.

Experimental

All the reagents and solvents were commercially available and used as received unless otherwise noted. All aqueous solutions were prepared in distilled water. Column chromatography was performed on a 200–300 mesh silica gel. NMR spectra were recorded on a Bruker AV400 instrument. UV/vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer in a quartz cell at 298 K. Steady state fluorescence emission spectra were recorded in a conventional quartz cell at 298 K on a Varian Cary Eclipse equipped with a Varian Cary single-cell Peltier accessory to control the temperature. The fluorescence lifetimes were measured by time-correlated single photon counting on a FLS920 instrument (Edinburgh Instruments Ltd, Livingstone, UK) with a H₂ pulse lamp. The SEM images were recorded on a JEOL JSM-7500F scanning electron microscope, operating at an accelerating voltage of 30 keV.

Synthetic route of Py-OPV (Scheme 2)

Synthesis of A2. Methyl iodide (0.4 g, 2.5 mmol) was added using a syringe to a solution of A1 (1.80 g, 6.3 mmol) in dichloromethane (50 mL), and then the reaction mixture was stirred at 80 °C for 17 h. After cooling, the mixture was filtered, and the solid was washed with dichloromethane, chloroform and distilled water. A yellow solid (0.44 g) was obtained in 46.6% yield after drying under vacuum. ¹H NMR (400 MHz, CD₃OD) δ: 8.73 (d, J = 6.9 Hz, 2H), 8.52 (d, J = 6.4 Hz, 2H), 8.19 (d, J = 6.9 Hz, 2H), 7.94 (d, J = 16.3 Hz, 1H), 7.80 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 6.4 Hz, 2H), 7.59 (d, J = 16.5 Hz, 1H), 7.51 (d, J = 16.2 Hz, 1H), 7.34 (d, J = 16.4 Hz, 1H), 4.32 (s, 3H) ppm. ESI-MS (m/z): calculated for C₁₂₈H₁₉₂N₂⁺: 299.4, found: 299.2.

Synthesis of Py-OPV. 1-Iodoctane (1 mL, 5.5 mmol) was added using a syringe to a solution of A2 (0.20 g, 0.48 mmol) in N,N-dimethylacetamide (10 mL), and then stirred at 150 °C for 2 h. After cooling, the mixture was filtered, and the solid was washed using N,N-dimethylacetamide and diethyl ether. A yellow solid (0.37 g) was obtained in 67.7% yield after drying under vacuum. ¹H NMR (400 MHz, DMSO-d₆) δ: 8.98 (d, J = 6.8 Hz, 2H), 8.89 (d, J = 6.4 Hz, 2H), 8.26 (dd, J = 6.8, 10.0 Hz, 4H), 8.08 (dd, J = 8.0, 15.8 Hz, 2H), 7.88 (s, 4H), 7.67 (d, J = 3.6 Hz, 1H), 7.63 (d, J = 3.6 Hz, 1H), 4.53 (t, J = 7.6 Hz, 2H), 4.27 (s, 3H), 1.95–1.87 (m, 2H), 1.29–1.25 (m, 10H), 0.87 (t, J = 6.4 Hz, 3H) ppm. ¹³C NMR (101 MHz, DMSO-d₆) δ: 152.5, 152.1, 145.2, 144.3, 139.8, 139.5, 136.9, 136.8, 128.8, 124.6, 124.5, 124.1, 123.7, 59.9, 47.1, 31.1, 30.5, 28.4, 28.3, 25.4, 22.1, 13.9 ppm. ESI-MS (m/z): calculated for C₂₉H₂₈N₂⁺: 206.3, found: 206.2. Anal. calcd for C₂₉H₂₈N₂⁺H₂O (684.11): C, 50.89; H, 5.60; N, 4.09. Found: C, 50.69; H, 5.70; N, 4.00.

Preparation of hydrogels

The aqueous solution of Py-OPV (250 µL, 0.1 mM) was added to the aqueous solution of CB[8] (0, 25 µL, 50 µL, 75 µL, 125 µL, 250 µL, and 0.1 mM), and then was added with water to 500 µL. Moreover, acrylamide (0.9384 g, monomers), N,N-methylenebis(acrylamide) (0.564 mg, cross-linkers), ammonium persulfate (1.598 mg, photo initiator) and N,N,N',N'-tetramethylethylenediamine (5 µL, cross-linking accelerator) were dissolved in 6 mL water. After slightly stirring, each 1 mL of the mixture was added into the above assembly solution. Then, after 5 minutes of exposure to sunlight, they became transparent and elastic hydrogels.

Conclusions

In summary, a luminescent supramolecular system was successfully constructed through the host-guest interactions.
mediated by Py-OPV and cucurbit[8]uril, presenting multicolor emission, such as blue, white, yellow and green. Herein, we used only one fluorophore to achieve a variety of fluorescent color transitions. By the simple addition of CB[8] to the aqueous solution of Py-OPV, the optical properties of Py-OPV were easily improved. When CB[7] was the host, the assembly only had an increase in the fluorescence intensity, while its fluorescence emission color could not be adjusted. Furthermore, α-cyclodextrin, β-cyclodextrin, and sulfonated calix[4]arene were respectively selected for the same fluorescence experiment, and the fluorescence had a certain degree of quenching. In addition, luminescent supramolecular hydrogels were constructed with Py-OPV and cucurbit[8]uril based on the photo-polymerization of acrylamide. By embedding the assembly in the polymer to constrain it, hydrogels emitting various tones of blue light were easily constructed. The preparation method of such luminescent hydrogels provides a new reference method for the construction of specific luminescent materials.

Conflicts of interest
There are no conflicts to declare.

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Notes and references