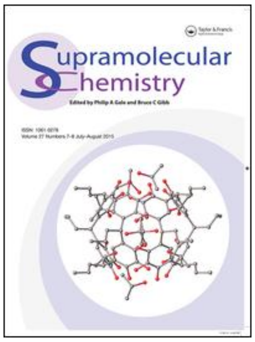

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Adsorption of anionic dyes from water by thermostable supramolecular hydrogel

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ABSTRACT
A supramolecular hydrogel was successfully constructed by the noncovalent association of cucurbit[8]uril (CB[8]) with a tetraphenylethylene (TPE) derivative bearing four monocharged viologens (TPE-4Q). Due to the attractive photophysical behaviours of TPE and its rigid complexation with CB[8], the obtained hydrogel emits bright orange fluorescence and is highly thermostable even at 200 °C. Rheological analyses and microscopic investigations jointly confirm that the supramolecular hydrogel possesses good rheological properties and well-organised lamellar structures. Significantly, the assembly/disassembly process of this supramolecular hydrogel can be efficiently modulated by several external stimuli, including pH, mechanical force and competitive guests. Moreover, as investigated by UV/Vis and fluorescence titrations, this two-dimensional self-assembly can specifically adsorb π-conjugated anionic dyes in water with high adsorption efficiency, mainly through the π-stacking interaction with TPE backbones and the electrostatic interaction with monocharged viologen sites.

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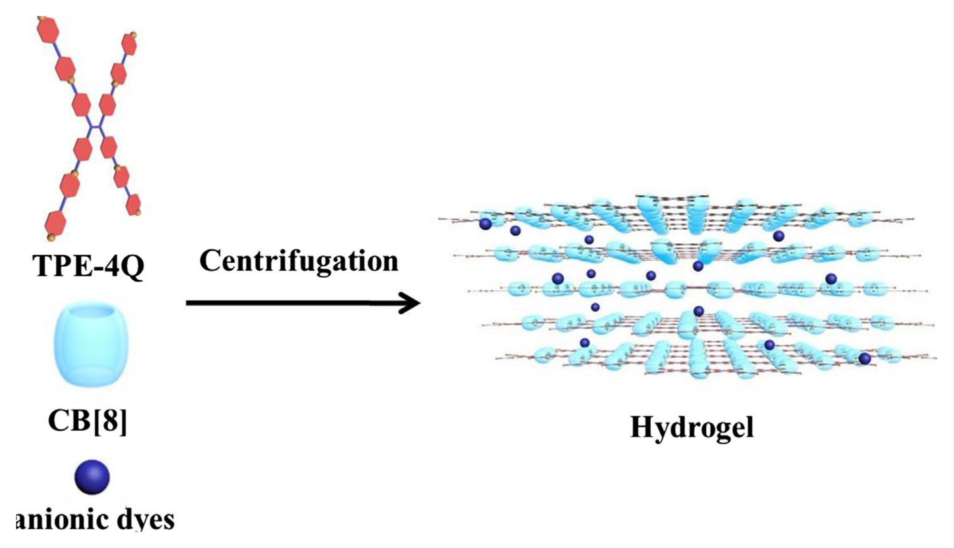
Supramolecular hydrogel; stimuli-responsiveness; cucurbituril; tetraphenylethylene



Introduction

Graphene and its analogues as a star material have aroused a great research interest in miscellaneous fields (*1–3*). Possessing the specific spatial arrangement and large surface area, graphene can exhibit excellent substrate-loading and adsorption capabilities towards various drug molecules, organic dyes and metal complexes mainly through mutual π-stacking interactions (*4–13*). However, there is a general consensus that low water solubility and biocompatibility may impede the graphene-involved binding systems from further practical application. Alternatively, combined, the advantages of useful functionality and easier operability, the solution-phase supramolecular organic frameworks (SOFs) were recently emerged as a new type of two-dimensional (2D) graphene-like materials (*14*). SOFs are mainly constructed by noncovalent interactions of water-soluble macrocycles with functional guest molecules, thus leading to many promising and interesting

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properties and functions. For instance, Zhao et al. (*15*) reported a highly ordered porous SOF monolayer, by which the fluorescence emission of nonemissive components could be greatly enhanced upon rigid organisation with cucurbituril in water–organic mixed solvent.

Supramolecular hydrogels are one of water-based soft materials that have highly variable mechanical properties, which make them increasingly important in biomedical and industrial applications (*16–20*). In particular, macrocycle-based supramolecular hydrogels can form 3D networks through noncovalent connections and have been endowed with switchable responsiveness towards external stimuli (*21–25*). In this work, we fabricated a fluorescent hydrogel based on the host–guest complexation between cucurbit[8]uril(CB[8]) and a positively charged tetraphenylethylene derivative (TPE-4Q) (Scheme 1). The binary complexes intermolecularly arrange themselves into 2D planar networks at relatively higher concentration and then the single layers can stack with each other to form highly thermostable hydrogel with good rheological properties and well-defined structures. Moreover, benefiting from the high cationic density, this supramolecular hydrogel can selectively adsorb *π*-aromatic species and then remove them from water by simple centrifugation. Therefore, such type of hydrogel is expected to be utilised as a functional carrier or separator for wider practical application.

Result and discussion

Formation of the supramolecular hydrogel

It has been already reported that TPE-4Q and CB[8] can form a supramolecular organic framework monolayer in 1:2 molecular ratio during the preparation of our manuscript (*15*). More interestingly, it is found that in our case, a hydrogel could be further formed by the same host and guest components. There are two methods to make such stable and fluorescent supramolecular hydrogels in water. One is to mix TPE-4Q and CB[8] at 1:2 molecular ratio under sonication for 2 h; the other is to centrifuge the solution of TPE-4Q·CB[8]complex for 5 min. The formation of TPE-4Q·CB[8] assembly using centrifugation method can be also monitored by UV/Vis spectroscopy. Before centrifugation, there were two main absorption peaks at 281 and 373 nm, while no obvious absorption was observed in the supernatant after centrifugation, indicating that most of the TPE-4Q·CB[8] complexes were converted to the binary hydrogel and located at the bottom of centrifuge tube (Figures 1 and S1e in the Supplementary Information). Benefiting from CB[8]-induced fluorescence enhancement of TPE-4Q (*15*), the obtained hydrogel could emit orange fluorescence under UV light irradiation at 395 nm (Figure 2(a) and (b)). Moreover, the hydrogel remained stable without any collapse even when placed upside-down for 30 days (Figure 2(c) and (d)).

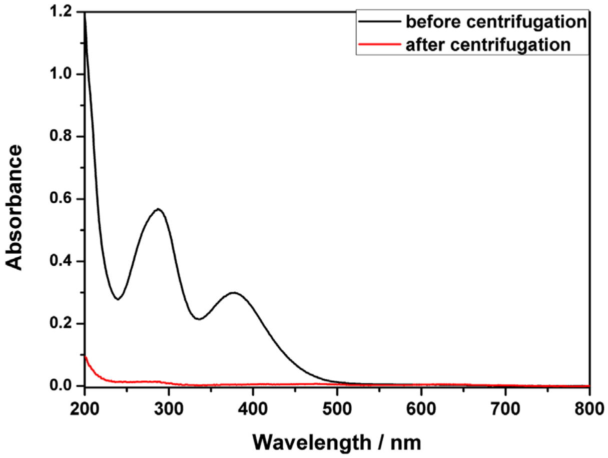


Figure 1. (Colour online) UV/Vis spectra of TPE-4Q·CB[8] assembly before centrifugation and the corresponding supernatant after centrifugation ([TPE-4Q] = 0.01 mM and [CB[8]] = 0.02 mM, 25 °C).

Next, rheological analyses gave more structural information of the TPE-4Q·CB[8] hydrogel. (Figure 3(a) and (b)) shows the plots of the storage moduli (*G*′) and the loss moduli (*G*″) vs. frequency and strain, respectively, in which no obvious change was found within the applied range of angular frequency for *G*′ and *G*″, and the *G*′ value was larger than the *G*″ value, which is a characteristic of stable gel-phase material (*26,27*). Moreover, when the strain was below 0.1%, *G*′ and *G*″ remained essentially constant, but the *G*′ value sharply decreased when the strain was above 0.1%, and it became smaller than *G*″ when the strain was above 0.35%. These phenomena indicate that the hydrogel could be transformed into a thickened liquid under a certain strain force or shaking. In addition, the plots of viscosity and shear stress vs. shear rate were shown in Figure 3(c). It is found that the viscosity decreased as the shear rate increased, corresponding to the type of shear-thinning hydrogel. Moreover, there was no obvious change for *G*′ and *G*″ below 100 °C, while they showed a sudden leap probably due to some water molecules inside the hydrogel vaporising above 100 °C. Nevertheless, it is noteworthy that the *G*′ values were larger than *G*″ with temperature ascending from 25 to 200 °C, indicating that the TPE-4Q·CB[8] hydrogel is highly thermostable in a wide temperature range (Figure 3(d)). The responsiveness of TPE-4Q·CB[8] hydrogel towards strain and temperature was also examined by the mechanical force and high-temperature tests, as described below.

Furthermore, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed to give the visual information of the binary hydrogel. SEM

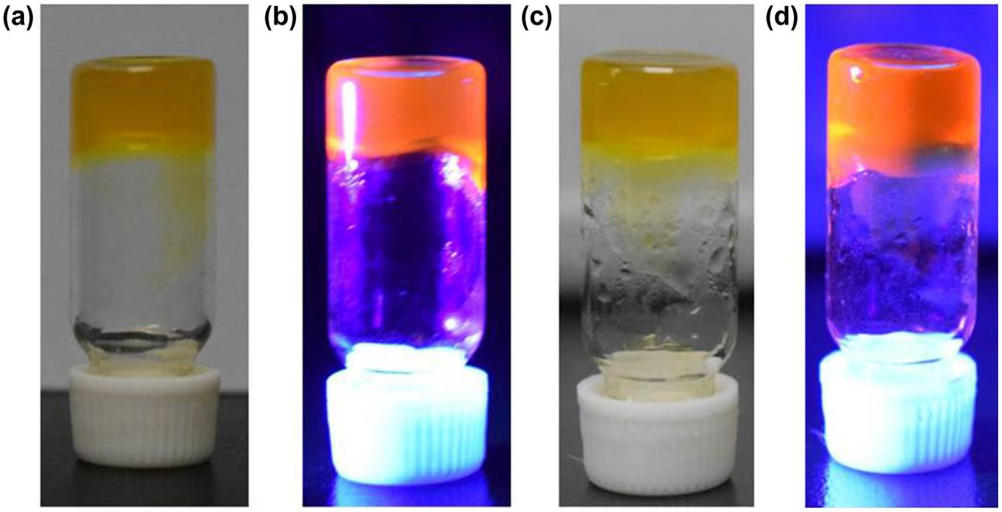


Figure 2. (Colour online) Photographs of hydrogels formed by TPE-4Q (5 mM, 0.5 wt%) and CB[8] (10 mM, 1.3 wt%). (a, b) freshly prepared hydrogel and its orange emission irradiated at 395 nm; (c, d) the corresponding hydrogel formed after 30 days.

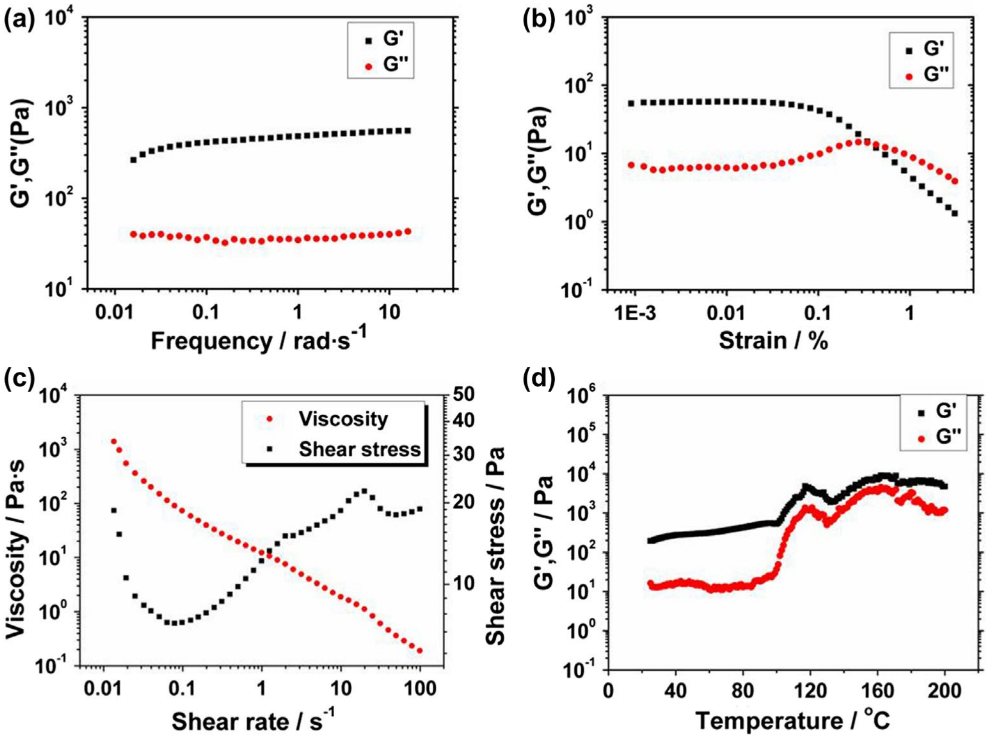


Figure 3. (Colour online) Rheological analyses of the hydrogel formed by CB[8] (10 mM, 1.3 wt%) and TPE-4Q (5 mM, 0.5 wt%). (a) Storage moduli (*G*′) and loss moduli (*G*″) obtained from a frequency sweep at 0.1% strain; (b) *G*′ and *G*″ values obtained from a strain sweep at 1 rad/s frequency; (c) viscosity and shear stress obtained from a shear rate sweep; and (d) *G*′ and *G*″ values obtained from a temperature sweep at 0.1% strain and 1 rad/s frequency.

images show that the cryo-dried and lyophilised sample existed as stacked rhombohedra structure. This morphology demonstrates that the TPE-4Q·CB[8] complex could be extended as rhombohedra particles, which eventually stacked with each other to form lamellar structures and water molecules were entrapped among the layers (Figure 4). Along with the SEM microscopic investigation, the stacked lamellar structures were also observed in the TEM images at the edge of the cryo-dried and lyophilised sample (Figure S2 in the Supplementary Information).

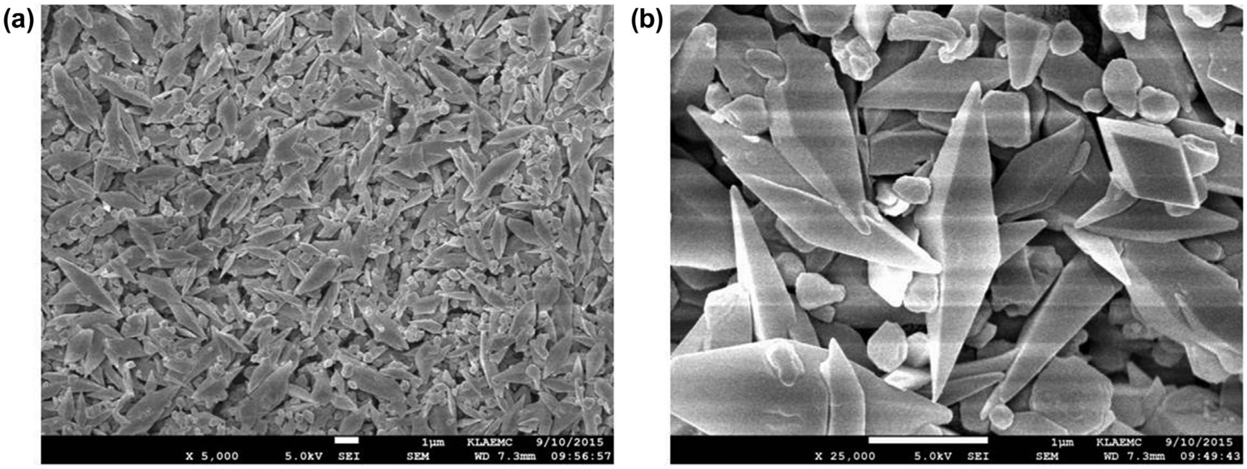


Figure 4. (a) Typical SEM image of cryo-dried and lyophilised TPE-4Q·CB[8] hydrogel and (b) magnified rhombic structures (The scale bars are 200 nm and 1 μm in (a) and (b), respectively).

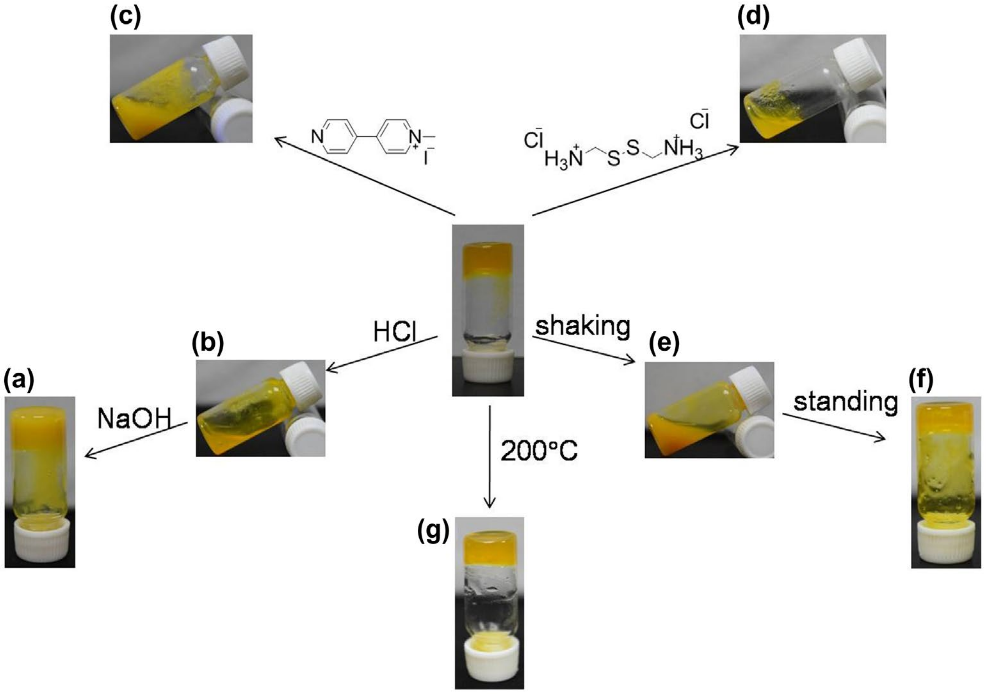


Figure 5. (Colour online) Multistimuli-responsiveness of the supramolecular hydrogel formed by TPE-4Q (5 mM, 0.5 wt%) and CB[8] (10 mM, 1.3 wt%) and its thermal stability at 200 °C.

Multistimuli-responsive behaviours of the hydrogel

The responsiveness to various external stimuli, such as pH, redox and temperature, is the characteristic advantage of supramolecular assembly. Due to the noncovalent molecular binding properties, the obtained TPE-4Q-CB[8] hydrogel showed good responsive capability to pH and competitive guests (Figure 5(a)–(d). That is, when HCl was added, the hydrogel instantly turned to turbid liquid, and it changed back to hydrogel when aqueous NaOH was added to neutralise the excess HCl. Moreover, the hydrogel structure could be irregularly destroyed by adding 1-methyl-4,4′-bipyridinium salt or cystamine dihydrochloride as competitive guest. As discerned from the moduli–strain curve in Figure 3(b), it is accordingly observed that this hydrogel could be changed into thickened liquid by severely shaking and then the hydrogel state was reproduced after standing for 10 min (Figure 5(e) and (f). More significantly, different from other conventional supramolecular hydrogels, the TPE-4Q·CB[8] hydrogel was highly thermostable, and it remained stable even when heated up to 200 °C (Figures 3(d) and 5(g)).

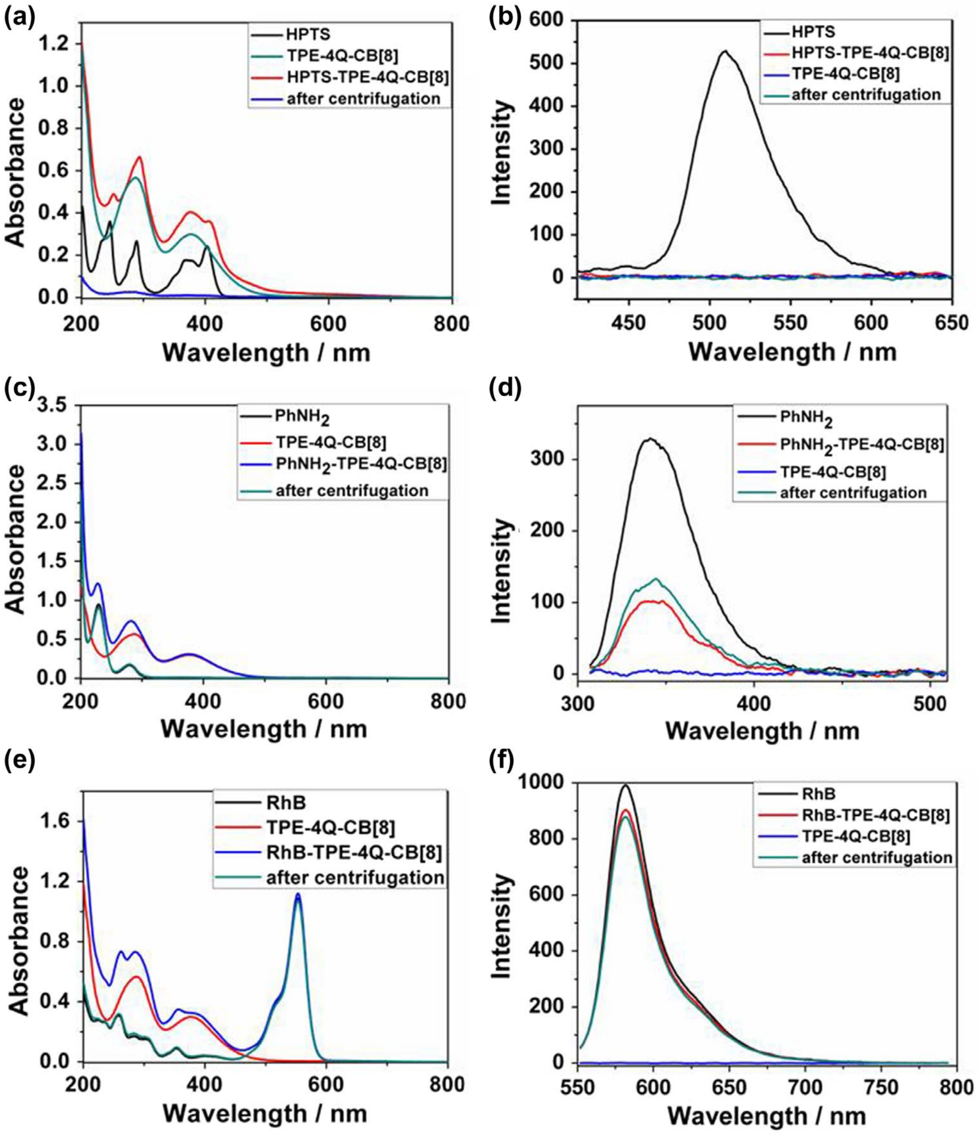
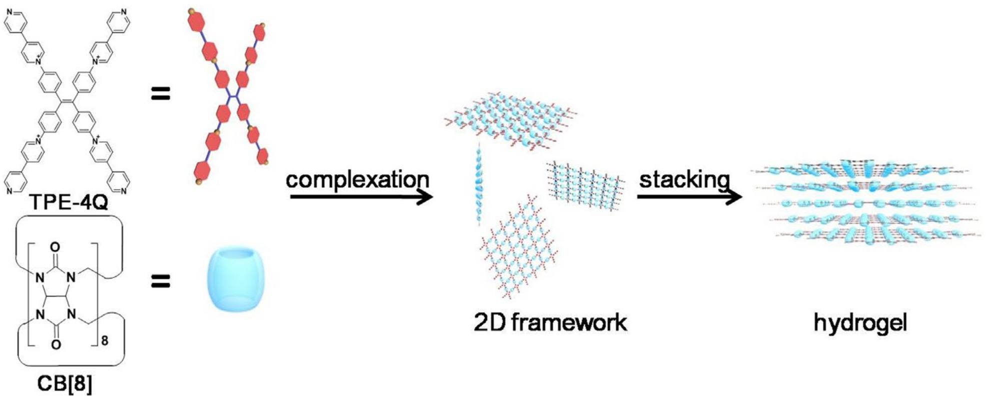


Figure 6. (Colour online) UV/Vis and fluorescence spectra of (a, b) HPTS, (c, d) aniline and (e, f) RhB before and after loading and separation by TPE-4Q·CB[8] hydrogel. ([HPTS] = [aniline] = [RhB] = 0.01 mM, 25 °C).

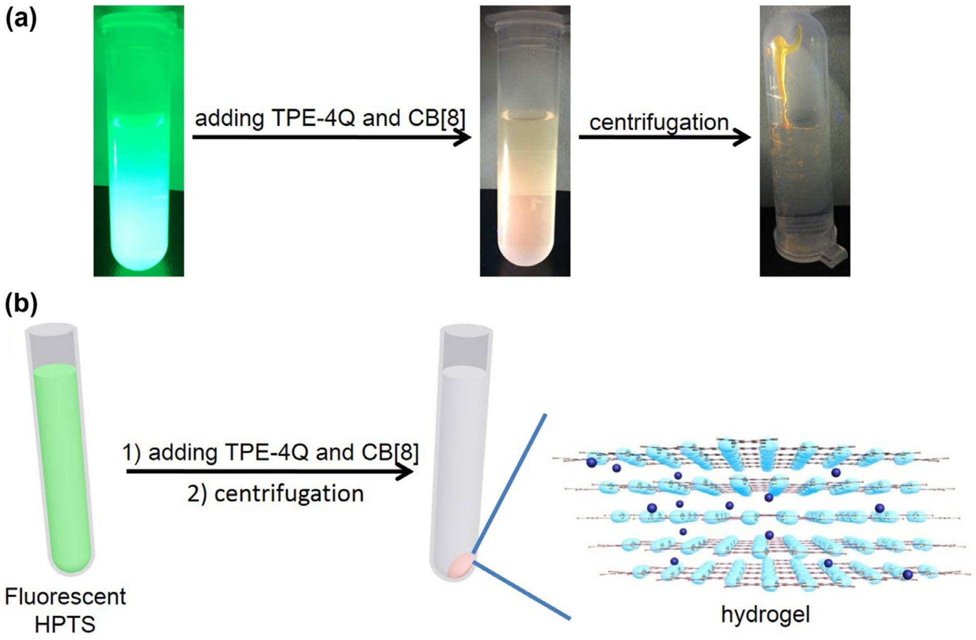
Adsorption of anionic dye by hydrogel

After scrutinising the molecular binding mode of the obtained TPE-4Q·CB[8] assembly, the high density of positive charges inspired us to hypothesise that some appropriate dye molecules may be filled into the 3D skeleton of supramolecular hydrogel via the π-stacking interaction with TPE moieties and the electrostatic attraction with monocharged viologen sites. Therefore, the trisodium salt of 8-hydroxypyrene-1,3,6-trisulfonic acid (HPTS), a π-aromatic molecule with intensive negative charges, was selected as the model substrate in the dye-loading and separating experiments. In addition, the neutral and positively charged substrates, aniline and rhodamine B (RhB), were used as reference to examine the π-conjugation and charge effects in the molecular binding process (Chart 1).

When added into the solution of TPE-4Q·CB[8] complex, the fluorescence of HPTS was seriously quenched, and no absorption peak of HPTS or TPE-4Q was observed in the supernatant after centrifugation (Figure 6(a) and (b)). By comparing the UV/Vis absorption intensity of HPTS at 368 nm before and after centrifugation, it was calculated that nearly 97% HPTS was removed by the TPE-4Q·CB[8] hydrogel. In the case of aniline, although the fluorescence was quenched by 69% in the presence of TPE-4Q·CB[8] complex, the absorption of the supernatant of aniline-loaded sample after centrifugation resembled one of the free aniline in water, suggesting that the hydrogel was formed, but aniline still completely remained in the liquid phase (Figure 6(c) and (d)). In contrast, as for RhB, no spectral change was observed in fluorescence and UV/Vis spectra before and after centrifugation, which is mainly



Scheme 1. (Colour online) Schematic illustration of the formation of TPE-4Q· CB[8] hydrogel.



Scheme 2. (Colour online) (a) Fluorescence emission change of HPTS before andafter centrifugation by TPE-4Q·CB[8] complex and (b) schematicillustration of loading and removal of HPTS by the TPE-4Q·CB[8] hydrogel network

contributed to the much lower loading and removal efficiencies (Figure 6(e) and (f)). Therefore, we can reasonably infer that the highly cationic TPE-4Q·CB[8] hydrogel can efficiently load π-conjugated anionic substrates and remove them from aqueous environment to hydrogel network, while the neutral and cationic substrates cannot be well trapped by TPE-4Q·CB[8] hydrogel because of the rather weak or even unfavourable electro-repulsive interactions. The schematic illustration of selective adsorption of HPTS by TPE-4Q·CB[8] hydrogel is shown in Scheme 2.

Conclusion

In conclusion, a fluorescent supramolecular hydrogel has been prepared for loading anionic dyes in water.

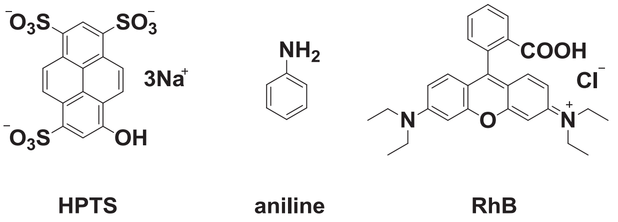


Chart 1. Molecular structures of HPTS, aniline, and RhB used in dye-loading experiments

Different from other conventional hydrogels that are usually formed by 3D entanglement of flexible linear structures, this hydrogel is constructed by stacked lamellar structures, which is confirmed by microscopic investigation. Interestingly, the obtained binary hydrogel possesses multistimuli-responsive properties towards acid–base, competitive guests and mechanical force. Owing to the strong binding between TPE-4Q and CB[8], this supramolecular hydrogel is highly thermostable even at 200 °C. The hydrogel also exhibits brilliant loading and removal capabilities to negatively charged π-aromatic substrates, which may find more potential applications in various fields, e.g. wastewater treatment and environmental surveillance. Further studies on the loading and removal of other functional substrates are currently in progress.

Experimental section

Materials

All the chemical reagents were purchased from commercial resource unless noted. The TPE derivative bearing four monocharged viologens (TPE-4Q) was synthesised by a slight modification. In our case, the 1-(2,4-dinitrophenyl)-[4,4′-bipyridin]-1-ium intermediate was used as hexafluorophosphate salt and the solvent was changed to dimethylsulfoxide in Zincke reaction to achieve a higher solubility and gram-scale preparation. Then, the hexafluorophosphate counterion was converted to chloride salt of TPE-4Q through a standard counterion exchange using tetrabutylammonium chloride in nitromethane. 1-Methyl-4,4′-bipyridinium salt was prepared by the direct reaction of 4,4′-dipyridine with iodomethane in acetonitrile. 1 M HCl and 1 M NaOH were used in acid–base responsiveness experiments.

Measurements

NMR spectroscopy

^{1}H and ^{13}C NMR spectra were recorded on a Brucker AV400 spectrometer.

Fluorescence spectroscopy

Steady-state fluorescence spectra were recorded in a conventional quartz cell (light path 10 mm) on a Varian Cary Eclipse equipped with a Varian Cary single-cell peltier accessory to control temperature. It should be noted that the fluorescence of the TPE-4Q is so weak that it cannot be detected in the dye-loading and separating experiments.

Rheological characterisation

The rheology tests were carried out on an AR 2000ex (TA Instrument) system; 40-mm parallel plates were used during the experiment at the gap of 500 μm. The gel was characterised by the mode of a dynamic frequency sweep in the region of 0.01–10 Hz at the strain of 1%.

UV/Vis spectroscopy

UV/Vis spectra and the optical transmittance were recorded in a quartz cell (light path 10 mm) on a Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller.

TEM microscopy

TEM images were acquired using a Tecnai 20 high-resolution transmission electron microscope operating at an accelerating voltage of 200 keV. The sample for high-resolution TEM measurements was prepared by dropping the solution onto a copper grid. The grid was then air-dried.

SEM microscopy

SEM images were obtained using a Hitachi S-3500 N scanning electron microscope. SEM samples were prepared by direct freezing of the supramolecular hydrogels in liquid nitrogen followed by lyophilisation. The obtained cryo-dried materials were imaged after sputtering.

Supplemental material

Supplemental data for this article can be accessed online here: http://dx.doi.org/10.1080/10610278.2016.1158406

Disclosure statement

No potential conflict of interest was reported by the authors.

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References

(1) Novoselov, K.S.; Geim, A.K.; Morozov, S.V.; Jiang, D.; Zhang, Y.; Dubonos, S.V.; Grigorieva, I.V.; Firsov, A.A. *Science* **2004**, *306*, 666–669.

(2) Novoselov, K.S.; Geim, A.K.; Morozov, S.V.; Jiang, D.; Katsnelson, M.I.; Grigorieva, I.V.; Dubonos, S.V.; Firsov, A.A. *Nature* **2005**, *438*, 197–200.

(3) Allen, M.J.; Tung, V.C.; Kaner, R.B. *Chem. Rev.* **2010**, *110*, 132–145.

(4) Liu, Z.; Sun, X.-M.; Nakayama-Ratchford, N.; Dai, H.-J. *ACS Nano.* **2007**, *1*, 50–56.

(5) Liu, Z.; Robinson, J.T.; Sun, X.-M.; Dai, H.-J.J. *Am. Chem. Soc.* **2008**, *130*, 10876–10877.

(6) Dhar, S.; Liu, Z.; Thomale, J.; Dai, H.-J.; Lippard, S.J. *J. Am. Chem. Soc.* **2008**, *130*, 11467–11476.

(7) Liu, Z.; Cai, W.-B.; He, L.-N.; Nakayama, N.; Chen, K.; Sun, X. M.; Chen, X.-Y.; Dai, H.-J. *Nat. Nanotechnol.* **2007**, *2*, 47–52.

(8) Liu, Z.; Davis, C.; Cai, W.-B.; He, L.-N.; Chen, X.-Y.; Dai, H.-J. *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 1410–1415.

(9) Cherukuri, P.; Gannon, C.J.; Leeuw, T.K.; Schmidt, H.K.; Smalley, R.E.; Curley, S.A.; Weisman, R.B. *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 18882–18886.

(10) Sun, X.-M.; Liu, Z.; Welsher, K.; Robinson, J.T.; Goodwin, A.; Zaric, S.; Dai, H.-J. *Nano Res.* **2008**, *1*, 203–212.

(11) Zhang, L.; Xia, J.; Zhao, Q.; Liu, L.; Zhang, Z. *Small* **2010**, *6*, 537–544.

(12) Yang, Y.; Zhang, Y.-M.; Chen, Y.; Zhao, D.; Chen, J.-T.; Liu, Y. *Chem. Eur. J.* **2012**, *18*, 4208–4215.

(13) Zhang, Y.-M.; Cao, Y.; Yang, Y.; Chen, J.-T.; Liu, Y. *Chem. Commun.* **2014**, *50*, 13066–13069.

(14) Zhang, K.-D.; Tian, J.; Hanifi, D.; Zhang, Y.-B.; Sue, Andrew Chi-Hau; Zhou, T.-Y.; Zhang, L.; Zhao, X.; Liu, Y.; Li, Z.-T. *J. Am. Chem. Soc.* **2013**, *135*, 17913–17918.

(15) Xu, S.-Q.; Zhang, X.; Nie, C.-B.; Pang, Z.-F.; Xu, X.-N.; Zhao, X. *Chem. Commun.* **2015**, *51*, 16417–16420.

(16) Huang, X.; Terech, P.; Raghavan, S.R.; Weiss, R.G. *J. Am. Chem. Soc.* **2005**, *127*, 4336–4344.

(17) Lee, K.-Y.; Mooney, D.J. *Chem. Rev.* **2001**, *101*, 1869–1880.

(18) Langer, R.; Tirrell, D.A. *Nature* **2004**, *428*, 487–492.

(19) Lutolf, M.P. *Nat. Mater.* **2009**, *8*, 451–453.

(20) Harada, A.; Kobayashi, R.; Takashima, Y.; Hashidzume, A.; Yamaguchi, H. *Nat. Chem.* **2011**, *3*, 34–37.

(21) Wang, K.-P.; Chen, Y.; Liu, Y. *Chem. Commun.* **2015**, *51*, 1647–1649.

(22) Wang, Z.; Guo, D.-S.; Zhang, J.; Liu, Y. *Acta Chim. Sinica* **2012**, *70*, 1709–1715.

(23) Zhang, J.; Guo, D.-S.; Wang, L.-H.; Wang, Z.; Liu, Y. *Soft Matter* **2011**, *7*, 1756–1762.

(24) Appel, E.A.; Biedermann, F.; Rauwald, U.; Jones, S.T.; Zayed, J.M.; Scherman, O.A. *J. Am. Chem. Soc.* **2010**, *132*, 14251–14260.

(25) Appel, E.A.; Loh, X.-J.; Jones, S.T.; Biedermann, F.; Dreiss, C.A.; Scherman, O.A. *J. Am. Chem. Soc.* **2012**, *134*, 11767–11773.

(26) Seiffert, S.; Sprakel, J. *Chem. Soc. Rev.* **2012**, *41*, 909–930.

(27) Zhang, Q.; Qu, D.-H.; Ma, X.; Tian, H. *Chem. Commun.* **2013**, *49*, 9800–9802.