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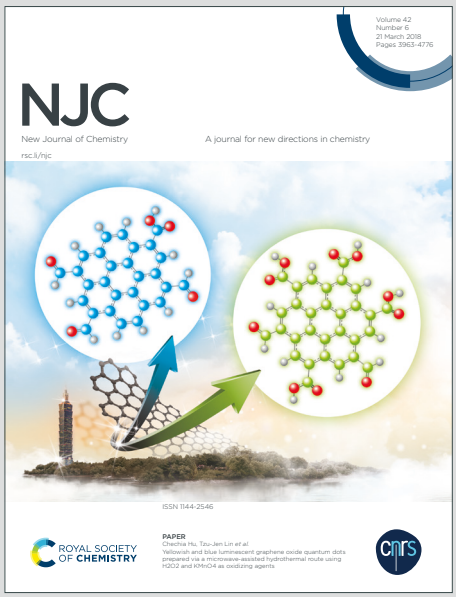

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ARTICLE

Stimuli-responsive supramolecular polymer network based on bi-pillar[5]arene for efficient multiple organic dye contaminants adsorption

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A novel supramolecular polymer networks gel (**NT**) based on bi-pillar[5]arene, which could adsorb and separate organic dyes were efficiently constructed. First, a novel supramolecular gelator, **NBP5** (host), and a tripodal guest, **TG** (guest), were successfully designed and synthesized. Then, host **NBP5** and guest **TG** could construct a stable supramolecular polymer networks gel, **NT**, via π-π interactions, hydrogen bonding interactions and host-guest interactions in DMSO/H_2O solution. Interestingly, **NT** shows multi-responsiveness toward outer stimuli, such as temperature, mechanical, concentration, pH and competitive guest. More importantly, **NT** could carry out adsorption and separation of organic dyes such as methylene blue, crystal violet , methyl orange, orange I, sudan I and sudan Ⅱ by the complex intermolecular interactions. The adsorption rates of this gels for dyes are in the range of 83.15%-97.56%, indicating nice adsorption property. Moreover, the xerogel of **NT** could desorp in ethanol solution, showing good recyclability. The multi-responsiveness and adsorption separation properties are based on the multi-interaction sites that we rationally introduced into the **NT**. Therefore, it is a convenient way for the preparation of supramolecular polymer networks-based multiple functional smart materials.

Introduction

Organic dyes are widely used in industries such as food, paper, cosmetics, pharmaceuticals, leather industries and so on.[1] However, many organic dyes are toxic and even carcinogenic. Toxic dyes can enter the food chain through water bodies, eventually affecting health of human and animal.[2] Moreover, even low concentrations (<1 ppm) of dyes can seriously affect the clarity and oxygen solubility of water bodies. And can also pose significant threats to the ecosystem. Owing to dyes being thermal stability, light stability, stable to oxidizing agents, difficult to degrade and high solubility in water, treatment of organic dyeing wastewater is a major challenge.[3] Currently, numerous methods such as adsorption,[4] chemical oxidation,[5] photolytic degradation,[6] biological treatment[7] and membrane separation[8] have been developed to remove organic dyes from wastewater. Among these methods, adsorption is considered as the most attractive technology because it has the advantages of high feasibility, high efficiency, economic feasibility, fewer by-products, simplicity of operation, high recyclability as well as the wide suitability for diverse dyes.[9] Up to now, many materials such as graphene aerogels (GAs),[10] clay and modified clay,[11] activated carbon,[12] zeolites,[13] synthetic fibers materials,[14] metal organic frameworks[15] and so on, were explored as adsorbents to remove organic dyes from wastewater. However, most of those materials show high adsorption capacity in high concentrated dyes wastewater, but poor efficiency in low concentrated dye wastewater. In addition, the high cost is also a main barrier which limits the practical application of present adsorbents.[16] So it is still a great practical significance to develop cheap and efficient adsorbents.

In the past few decades, supramolecular polymer networks (SPNs) represent a new multi-functional materials that have many potential applications in fields such as sensing,[17] drug delivery,[18] recognition,[19] molecular adsorption,[20] separation[21] and catalysis.[22] Commonly, SPNs is constructed from a large amount of low-molecular weight monomer components through intermolecular non-covalent interactions, including host-guest inclusion interactions,[23] H-bonding interactions,[24] C-H · · · π interactions,[25] π - π stacking interactions,[26] metal coordination interactions,[27] hydrophobic/hydrophilic interactions,[28] electrostatic interactions,[29] Van der Waals[30] and so on. Interestingly, the diversity and dynamic controllability of self-assembling interactions and diverse self-assembly systems affords the SPNs multi-stimuli response properties and flexible nature.[31] Compared with metal-organic frameworks (MOFs),[32] covalent organic frameworks (COFs)[33] other frameworks, SPNs have the merits of easy preparation and functionalization. This makes it an excellent multifunctional materials with unlimited

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development potential in various fields. Although there are many reports on SPNs,[34] it is still a big challenge to construct SPNs with various method of sself-assembly and special functions.

Pillar[*n*]arenes as a new family of macrocyclic host molecules, reported in 2008 by Ogoshi,[35] present unique structures and easily functionalized properties. Importantly, the pillar[*n*]arenes provide rich and diverse supramolecular assembly driving interactions,[36] which could also serve as a new platform to prepare a intriguing supramolecular systems. However, due to the rigid structure of pillar[*n*]arenes and the relatively weak binding capacity, there are only a few reports on the construction of SNPs based on pillar[*n*]arene. This will greatly hinder the development of SPNs based on pillar[*n*]arenes. Therefore, it is a great significance and value to develop a new SNPs based on pillar[*n*]arene.

Inspired by this,[37] we designed and synthesized a bi-pillar[5]arene with multi-interactions sites. The bi-pillar[5]arene was rational introduced into SNPs through the host-guest interactions and intermolecular interactions, as a new supramolecular multi-functional material to develop its potential applications. The design strategy are the following: First, we introduced the acylhydrazone group into pillar[5]arene molecule as fluorophore, hydrogen bonding sites and connecting bridge between the two pillar[5]arene. Then, the object of the tripod structure was introduced to provide a strong assembly complexing ability and a hydrogen bonding sites. Finally, the stable SNPs **NT** were successfully constructed from bi-pillar[5]arene **NBP5** and the guest **TG** in mixed solvent of DMSO/H_2O. Studies have shown that there are host-guest interactions, π - π stacking interactions and intermolecular hydrogen bonding interactions present in **NT**. Due to various intermolecular interactions, **NT** shows strong blue fluorescence emission and multi-stimuli response. Most importantly, the **NT** shows adsorption separation properties for organic dyes pollutants from aqueous solutions. Therefore, this work contributes to the construction of a supramolecular polymer networks based on bi-pillar[5]arene, which has potential application in adsorption of organic dyes.

Results and discussion

At the first, a novel gelator (**NBP5**) decorated with two identical pillar[5]arene tails was first synthesized by rationally connecting two aldehyde functionalization pillar[5]arene moiety group via 2,6-pyridine dihydrazide. The compound **NBP5** and **TG** were characterized by ^{1}H NMR, ^{13}C NMR, ESI mass. (Figure S1-S14).

Then, supramolecular polymer networks **NT** was prepared by dissolving host **NBP5** (7mg) and guest **TG** (0.5mg) in DMSO/H_2O solution (0.1mL), and the temperature is not lower than 43 ℃ followed by cooling to room temperature. After guest **TG** was added to DMSO/H_2O (v : v = 8 : 2) solutions of host **NBP5**, the fluorescence intensity of mixture will be enhanced (Figure S16), which indicated that there are host-guest collaborations between **TG** and **NBP5**.

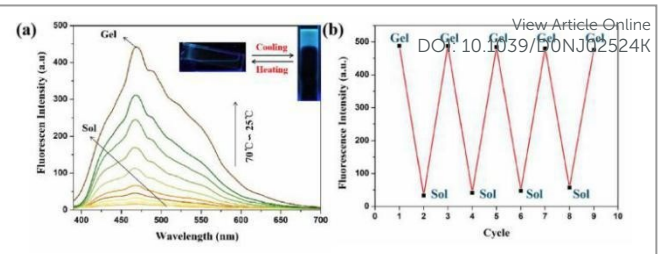

Figure 1 (a) Temperature-dependent fluorescent spectra of **NT** (Sol) and **NT** (Gel) in the DMSO/H_2O solution; (b) Fluorescent "Gel-Sol" cycles of **NT**, controlled by cooling and heating (λ_{ex} =360nm).

Then, supramolecular polymer networks **NT** was prepared by dissolving host **NBP5** (7mg) and guest **TG** (0.5mg) in DMSO/H_2O solution (0.1mL), and the temperature is not lower than 43 ℃ followed by cooling to room temperature. After guest **TG** was added to DMSO/H_2O (v : v = 8 : 2) solutions of host **NBP5**, the fluorescence intensity of mixture will be enhanced (Figure S16), which indicated that there are host-guest collaborations between **TG** and **NBP5**.

Additionally, as shown in Figure 1a, **NT** has weak fluorescence emission in hot DMSO/H_2O ($T>T_{gel}$); however, with the temperature dropping below ($T<T_{gel}$), the blue fluorescence intensity will gradually increase and reached a steady state within short time, which indicated that the fluorescence emission of **NT** was AIE.[38] Meanwhile, the gelation properties of **NT** were explored in various solvents are summarized in Table S1. The critical gel concentration (the lowest amounts of **NBP5** needed to sustain gel formation) of **NT** is determined to 7% (w/v, 10mg·mL^{-1} = 1%). Contemporary, the phase transition temperature (T_{gel}) of **NT** is approximately 40-43 ℃. Moreover, it is interesting to find that **NT** showed reversible transition (gel-sol) in response to temperature and performed many times with small fluorescence efficiency loss (Figure 1b). In addition, the Tyndall effect experiment was carried out to measure the critical aggregation concentration (CAC) of supramolecular aggregates. The critical aggregation concentrations were measured to be 1.0 × 10^{-5}M in DMSO/H_2O (v : v = 8 : 2) binary solution. Meanwhile, we have

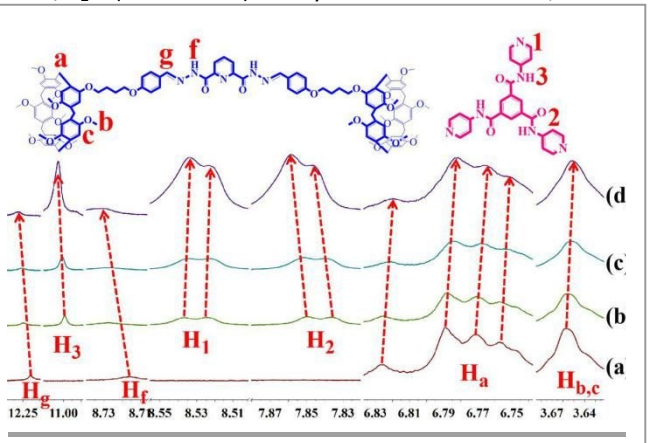

Figure 2 ^{1}H NMR titration spectrum (600 MHz, 298K) of **NBP5** (10.0 mM) in DMSO-d_6 at various equivalents of **TG**: (a) 0 equiv.; (b) 1.0 equiv.; (c) 2.0 equiv.; (d) 4.0 equiv.

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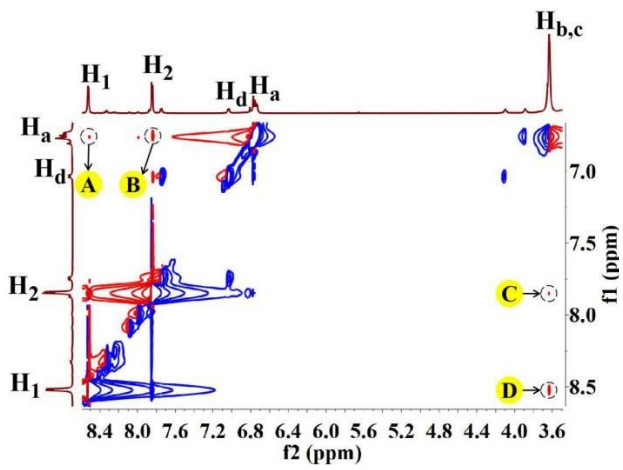


Figure 3 2D NOESY NMR spectrum (600 MHz, 298 K) of 10.0 mM **NBP5** and **TG** in DMSO-d_6 solution.

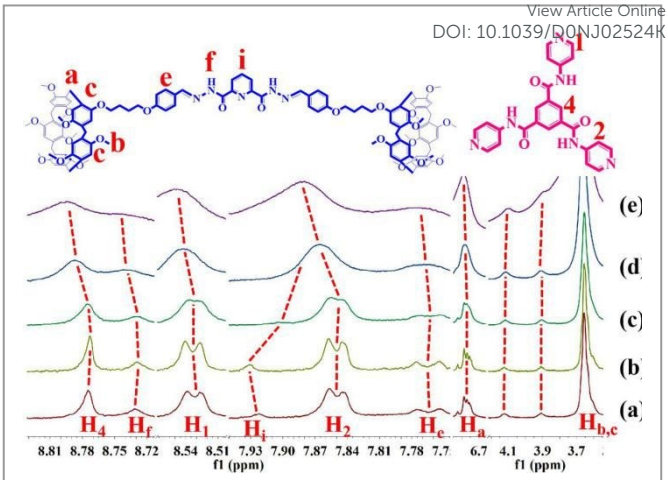


Figure 4 ^{1}H NMR spectra (600MHz, 298 K) of **NT** in DMSO-d_6 at various concentrations: (a) 1.0 mM; (b) 5.0 mM; (c) 10.0 mM; (d)20.0 mM; (e) 40.0 mM.

estimated the association constant (K_a) of the complexation between **NBP5** and **TG** at room temperature in DMSO solution is about 2.14 $\times 10^8 M^{-1}$ according to the absorption titration experiments (Figure S17). Therefore, **NT** gel has potential applications in temperature fluorescent switches.

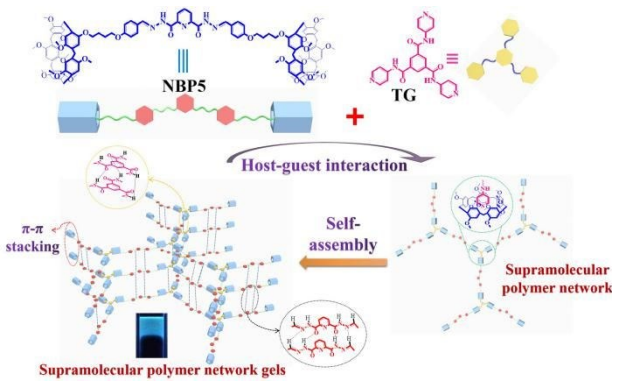
To study the assembly mechanism of **NBP5** and **TG**, ^{1}H NMR titration experiment was carried out (Figure 2). With the increasing amount of **TG**, the signals of protons H_a and $H_{b,c}$ on **NBP5** shifted upfield gradually. What's more, the signals of protons H_1 on **TG** shifted upfield. Meanwhile, the signals of protons H_2 on **TG** shifted downfield. These results confirmed that both the the pyridinium groups of **TG** were partially included in the cavity of **NBP5** through π - π stacking interactions, C-H···π interactions and C-H···O interactions.[39] At the same time, in the corresponding 2D NOESY NMR experiments (Figure 3), there are four correlations (A, B, C and D) were observed between the protons H_a and $H_{b,c}$ on cavity of **NBP5** and the protons H_1 and H_2 on **TG**, which implied the pyridinium groups of **TG** were included into the cavity of bi-pillar[5]arene **NBP5**.

Moreover, from the concentration-dependent ^{1}H NMR spectra (Figure 4), all signal peaks shifted rapidly and became broad at high concentration, which clear confirmed the formation of high-molecular-weight aggregates driven by host-guest interactions between **NBP5** and **TG**.[40]

Moreover, the assembly process of **NBP5** and **TG** was also investigated by the small-angle XRD patterns. As shown in Figure S18, the small-angle XRD patterns of **NBP5** suggested that there was no long-range order in **NBP5**. However, the xerogel of **NT** exhibited well-resolved XRD patterns that were characteristic of the long-range ordering of the molecules. These results verified that **NBP5** and **TG** could assemble into a stable gel. For the xerogel of **NT**, the *d*-spacings of 3.80Å (2θ = 23.08°) confirmed the π-π stacking interactions existed in the assembly process of **NBP5** and **TG**. Moreover, hydrogen bonding interactions also were involved in the stacking process of **NT**. In ^{1}H NMR titration (Figure 2), the signals of protons H_g and H_f on **NBP5** shifted downfield, indicating that there are intermolecular hydrogen bonding interactions between the bi-pillar[5]arene group of adjacent molecules. Meanwhile, the signals of protons H_3 on **TG** shifted downfield, which also could be attributed to the intermolecular hydrogen bonding interactions between the **TG** of adjacent molecules.

In SEM, host **NBP5** showed a flake structure (Figure S19a), guest **TG** showed a rod-like structure (Figure S19b) and **NT** showed a regular porous network structure (Figure S19c), which also supported the idea that **NBP5** and **TG** could assemble into supramolecular polymer networks by π - π stacking interactions, hydrogen bonding interactions and host-guest interactions. According to th above research, we speculated about the possible self-assembly mechanism of supramolecular polymer networks gel **NT**. First, host **NBP5** and guest **TG** could assemble into a novel supramolecular polymer networks through host-guest interactions. Then, the supramolecular polymer networks could form stable supramolecular polymer networks gel **NT** through π-π stacking interactions and intermolecular hydrogen bonding interactions (Scheme 1).

Supramolecular assembly systems become sensitive to the external environment due to the existence of host-guest



Scheme 1 Proposed assemble mechanism of **NT**

interaction, intermolecular hydrogen bonding interactions and π-π stacking interactions in the system.[41] On this foundation, we carefully studied the multi- stimulus response behavior of **NT** (Figure 5). As we all know, the supramolecular host-guest assembly system has a reversible response to temperature.[42] At high temperature, supramolecular assembly system **NT** transforms into a clear and transparent solution. Subsequently, the solution was cooled below the melting temperature, and a light yellow gel formed again and reached a stable state. It is because the host-guest interactions and intermolecular hydrogen bonding interactions will be destroyed at high temperature, resulting in the decomposition and transformation of supramolecular assembly system **NT** into solution.[43]

Simultaneously, the gel **NT** exhibited reversible thixotropic behavior through mechanical stimulation (Figure 5). The vial containing the gel was shaken for 10 seconds, and it was observed that the gel turned into flowing white turbid solutio. And then stand for 5 min, the gel state recovered and remained stable. It shows that gel **NT** has good mechanical response performance. Similarly, this gel **NT** could also achieved reversible gel-sol phase transition several times in the case of concentrate-dilute.[44]

It is known that the pH conditions had a notable effect on the formation of intermolecular hydrogen bonding interactions. The **NT** also showed the corresponding acid-base responsiveness.[45] As shown in Fig. 5, after 5μL triethylamine was added into **NT**, the **NT** gradually collapses and becomes white turbid solution. SEM images also showed that the cross-linked networks of gel **NT** was destroyed, and an irregular massive morphology was observed (Figure S20b). These results suggested that intermolecular hydrogen bonding interactions and π-π stacking interactions have been destroyed. Next, the same amount of CH_3COOH was added into the above turbid solution, the gel returned to its original gel state and remained stable. The SEM image also records the change of the gel system morphology from disordered block morphology to regular microsphere morphology (Figure S20c).

Furthermore, if the competitive guest adiponitrile was added to **NT** at high temperature, the solution could not form gel **NT** after cooling. The fundamental reason was that the guest adiponitrile had stronger competitive binding with bi-pillar[5]arene than **TG**, resulting in **TG** free from the cavity of bi-pillar[5]arene. The SEM also showed the cross-linked networks morphology of **NT** was destroyed and turned to an unordered block structure after addition of adiponitrile (Fig. S20a). Based on the above studies, supramolecular polymer networks gel have great research value as stimuli-responsive materials.[46]

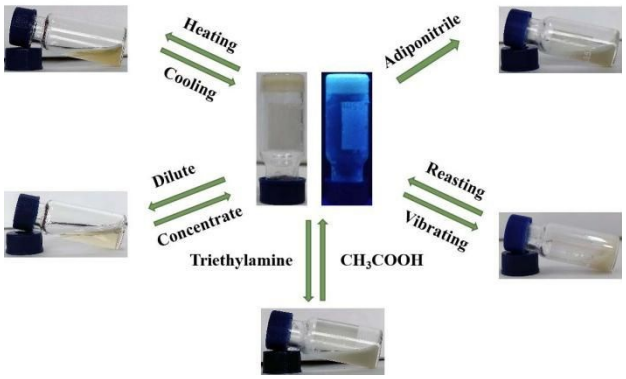


Figure 5 Photographs of gel-sol transitions of gel **NT** triggered by a variety of stimuli.

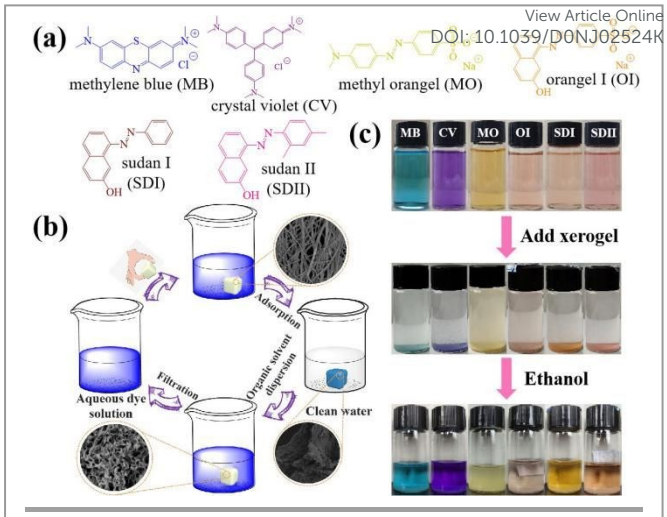


Figure 6 (a) Chemical structures of the organic dyes used to test the adsorption behavior of **NT**; (b) Cartoon representation of adsorption process; (c) The adsorption separation and desorption of various organic dyes by **NT**.

Organic dye contamins that are considered to be poisonous exist everywhere in our daily life. The most urgent task is to remove such dye molecules from effluents. Considering **NT** contains porous network in its structure, the adsorption properties were explored using various dye adsorption and separation experiments in water. As shown in Fig. 6, six organic dyes with different charges, namely, positively charged methylene blue, crystal violet, negatively charged orange, orange I and neutral sudan I, sudan Ⅱ were selected to evaluate the abilities of **NT** in the adsorption and separation of dyes. All the measurements were performed in aqueous solutions at room temperature under constant stirring. The adsorption rate experiments were performed by immersing 1.0mg as-synthesized **NT** powder into 10.0mL of different organic dyes aqueous solutions. During the UV-vis absorbance measurements, in units of 30 minutes, 2.0mL of the upper clear part of the solution was picked up periodically and poured back to the original solution system instantly after the measurement. Changes in the UV-vis spectrum were observed (Figure 7a, Figure S21): the absorbance intensity decreased with immersion time. And the dramatic decolorization changes could be also easily monitored by the naked eye (Figure 6c). After adsorption, assuming a Beer-Lambert relationship between concentration and absorbance intensity (Figure S22),[47] the concentration was calculated by comparing the UV-vis absorbance to the appropriate calibration curve. The removal efficiency of dye was calculated by the following equation:

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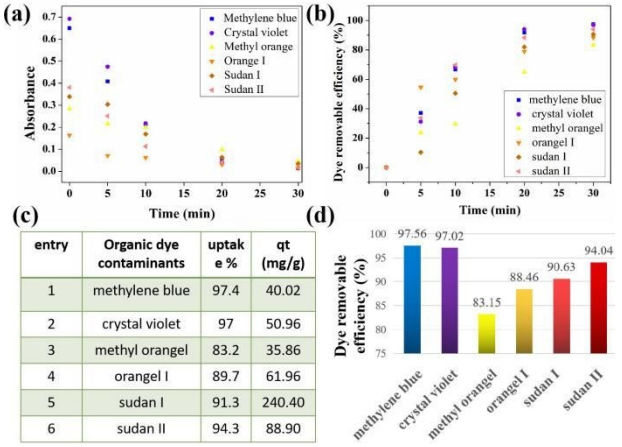

entry	Organic dye contaminants	uptake %	qt (mg/g)
1	methylene blue	97.4	40.02
2	crystal violet	97	50.96
3	methyl orangel	83.2	35.86
4	orangel I	89.7	61.96
5	sudan I	91.3	240.40
6	sudan II	94.3	88.90

Figure 7 (a) The absorbance of each dye changes with time; (b)The time-dependent adsorption efficiency of each organic dye; (c) The equilibrium uptake percentage and amount of organic dye adsorbed per gram of **NT**; (d) the percentage removal efficiency of each organic dye determined after 30 min contact.

(1) where C_0 (mg·L^{-1}) and C_v (mg·L^{-1}) are the initial and residual concentrations of the organic dyes in the stock solutions and filtrates, respectively. And E is the percentage of adsorption.

$$E = \frac{(C_0 - C_v)}{C_0} \times 100\% \quad (1)$$

(2) where C_0 and C_t (mg·L^{-1}) are concentrations of dye in aqueous solution at the beginning, t-time, respectively.[48] The adsorption capacity Q_t (dye removal per gram of **NT** of at time, mg·g^{-1}) and Q_e (dye adsorbed per gram of **NT** at equilibrium, mg·g^{-1}) were calculated according to the following equations:

$$Q_t = \frac{(C_0 - C_t)}{m} \times V \quad (2)$$

$$Q_e = \frac{(C_0 - C_e)}{m} \times V \quad (3)$$

where C_e (mg·L^{-1}) represents concentration of dye in aqueous solution at equilibrium; m (g) is the mass of **NT** and V (L) is the volume of dye solution.[49]

In addition, corresponding plots of the organic dyes removal efficiency as a function of time (Figure 7b) and net percentage of organic dyes removal efficiency (Figure 7d) were constructed. In SEM (Figure S23), after the adsorption, the network structure used disappeared, indicating that there is adsorption behavior between **NT** and dyes. According to these results, the **NT** xerogel shows fast adsorption (5-30min) and high organic dyes removal efficiency (up to 97.56%). In order to compare the adsorption capacity of the gel **NT** and the host **NBP5**, the two powders were added to the same dye solution. After 30 minutes, the dye solution containing **NT** faded, while the dye solution containing host **NBP5** remained unchanged.

Desorption experiment was processed with fresh, completely dye filled **NT** by immersing in organic solvent ethanol and slightly heated for about 20min. With the passage of time, the dye is dispersed in the organic solution ethanol, and the color of the solution changes to the color of the dye.

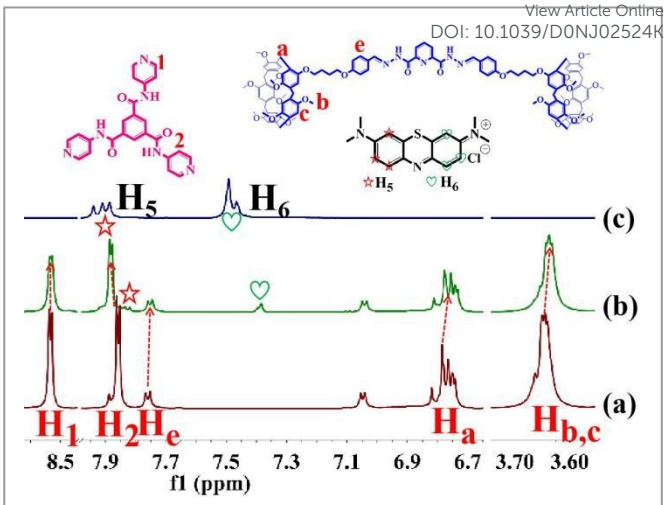

Figure 8 Partial ^{1}H NMR spectra of **NT** in DMSO-d_6 with MB (a) **NT** (b) 3 equiv.; (c) MB**.**

The **NT** powder attached with the color of the dye returns to its original state at an objective speed (Figure 6c). Subsequently, after filtration and vacuum-drying, the **NT** xerogel was recovered. Regardless of reasonable quality loss, **NT** powder can achieve recycling. In addition, the SEM of the regenerated **NT** xerogel still kept up the porous structure, confirming its good stability (Figure S25). This implies that supramolecular polymer networks gel **NT** can be considered potential materials for dye adsorption and selective separation with the merits of convenience, rapidity and environmental friendliness.

The adsorption mechanism of **NT** was also investigated by ^{1}H NMR, 2D diffusion-ordered NMR spectroscopy (2D-NOESY NMR) and scanning electron microscopy (SEM) analysis. Taking MB as an example, as shown in Figure 8, after a serious of MB was added into the **NT** solution (DMSO-d_6), the signals of protons H_5 and H_6 of MB and the signals of protons H_a and $H_{b,c}$ of bi-pillar[5]arene shifted upfield. Meanwhile, the signals of protons H_1 and H_2 of **TG** shifted downfield, which indicating that π - π stacking interactions and hydrogen bonding interactions involved in **NT** and MB. At same time, in the NOESY spectrum (Figure S24), cross-peaks A and B revealed the correlations between the protons signals of MB and those of protons of **NBP5**, indicating that the C-H···π interactions, π-π stacking interactions and electrostatic interactions which existed in MB and the bi-pillar[5]arene groups. Furthermore, the above proposed adsorption mechanism was also supported by SEM. As shown in Figure S25, after adsorption MB into the **NT**, the porous network structures of the **NT** xerogel changed into a irregular block, which could be ascribed to dye molecules that was adsorbed by the **NT** xerogel. According to these mechanism researches, it is clear that the rationally introduced multi-interactions sites such as electrostatic, π · · · π stacking interactions, H-bonding interactions, C-H · · · π interactions, and host-guest inclusion interactions sites. It plays play a vital role in the separation of organic dyes.

Conclusions

In conclusion, a novel supramolecular polymer networks gel **NT** was been successfully constructed by directly assembling bi-pillar[5]arenebased gelator **NBP5** and tripodal guest **TG**. Interestingly, the **NT** exhibited strong aggregation induced emission (AIE) and multi-responsiveness toward outer stimuli, which can facilitate its application as smart material. Importantly, the **NT** xerogels could effectively adsorb and separat various organic dyes from aqueous solution. The removal efficiency towards MB dyes exceeds 97%, and the adsorption exhibits high efficiency at low equilibrium concentration which has big significance to treat practical wastewater. In addition, **NT** xerogels shows excellent application potential in recycling. This original research not only develops a simple, efficient method for the supramolecular polymer networks, but also provides a cheap and sustainable approach for organic dyes separation. We expec that this original research would provide a broad platform for the design and construction of advanced and smart supramolecular materials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Graphical Abstract

Stimuli-responsive supramolecular polymer network based on bi-pillar[5]arene for efficient multiple organic dye contaminants adsorption

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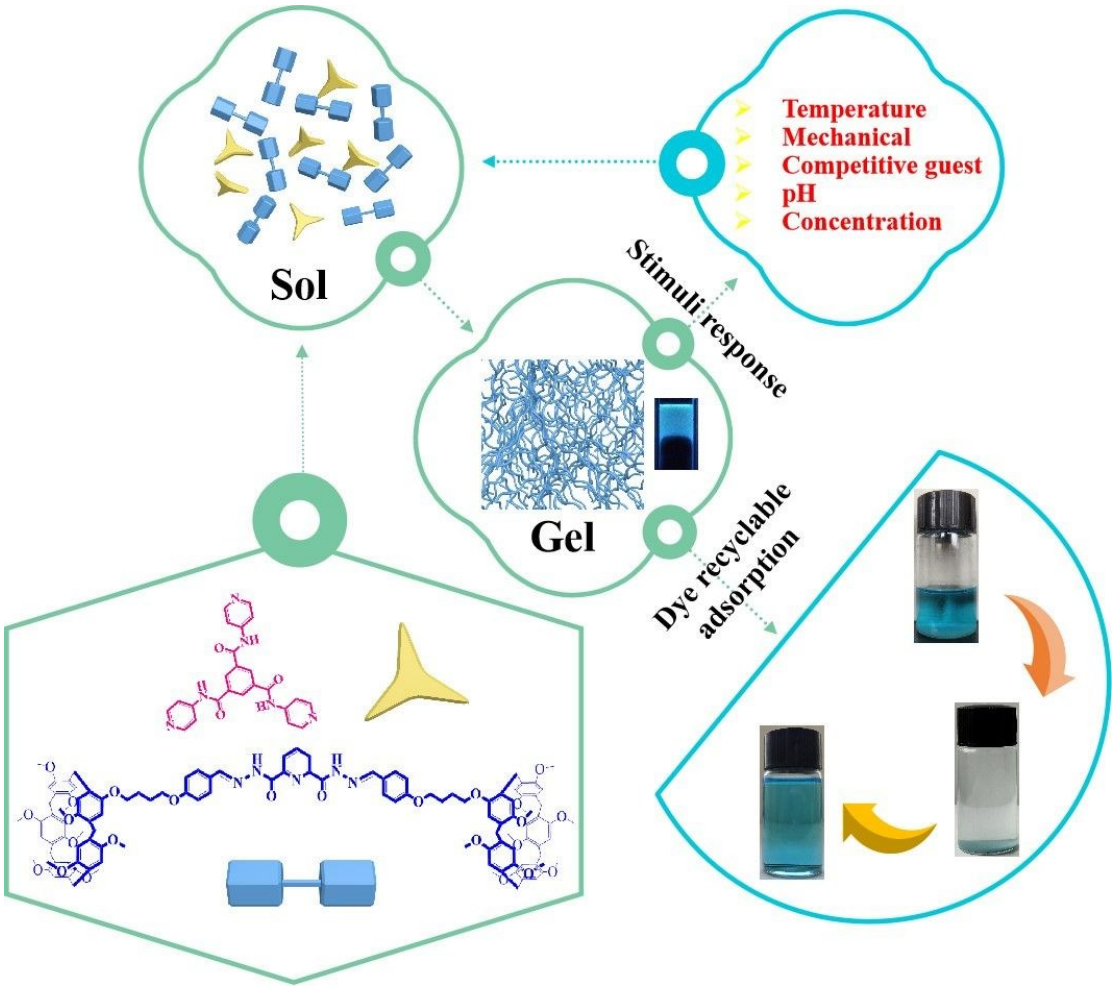

Text:

A novel supramolecular polymer networks gel have been successfully prepared via bi-pillar[5]arene and tripodal guest, which could self-assemble to form a supramolecular polymer networks gel at high concentration, exhibiting multiple stimuli-responsiveness and efficient adsorption of organic dyes in aqueous solution.