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Supramolecular Assembly-Induced Emission Enhancement for Efficient Mercury(II) Detection and Removal

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KEYWORDS: aggregation-induced emission; sensing; nanoparticles; pillar[n]arenes; supramolecular polymer

ABSTRACT: New strategies that can simultaneously detect and remove highly toxic environmental pollutants such as heavy metal ions are still in urgent need. Herein, through supramolecular host-guest interactions, a fluorescent supramolecular polymer has been facilely constructed from a newly designed [2]biphenyl-extended pillar[6]arene equipped with two thymine sites as arms (**H**) and a tetraphenylethylene (TPE)-bridged bis(quaternary ammonium) guest (**G**) with aggregation-induced emission (AIE) property. Interestingly, supramolecular assembly-induced emission enhancement (SAIEE) could be switched on upon addition of Hg^{2+} into the abovementioned supramolecular polymer system to generate spherical-like supramolecular nanoparticles, owing to the restriction of intramolecular rotation (RIR)-related AIE feature of **G**. Significantly, this supramolecular polymer with integrated modalities has been successfully used for real-time detection and removal of toxic heavy metal Hg^{2+} ions from water with quick response, high selectivity, and rapid adsorption rates, which could be efficiently regenerated and recycled without any loss via a simple treatment with Na_2S. The newly developed supramolecular polymer system combines the inherent rigid and spacious cavity of novel extended-pillarene host with the AIE characteristics of TPE-based guest, suggesting a great potential in the treatment of heavy metal pollution and environmental sustainability.

INTRODUCTION

Water pollution arising from heavy metal ions continues to be one of the major problems of environmental concerns, which represents a serious threat to human beings and animals worldwide.[1, 2] Among those heavy metal ions, mercury(II) is considered as one of the most harmful pollutants due to its severe damage to kidney function, immune system, and central nervous system.[3-6] The development of integrative strategy in real-time sensing and rapid removal of mercury ions is of great importance in materials chemistry, chemical engineering, and environmental science. Design and synthesis of effective and economical materials to adsorb and remove mercury ion has attracted numerous attention over the past decades. Notably, a range of porous materials, which include porous silicas,[7] porous organic polymers (POPs),[8,9] covalent organic frameworks (COFs),[10,11] conjugated microporous polymers,[12] conjugated macrocycle polymers,[13] porous aromatic frameworks,[14] and metal organic frameworks (MOFs),[15,16] have been successfully applied in the adsorption of heavy metal ions by virtue of their considerable porous nature. Until mercury emissions can be greatly reduced, it is imperative to develop new modern technologies to decrease and detect the mercury found in the atmosphere and industrial wastewater run-off to offer enhanced protection to the planet and livings.

On the other hand, one appealing feature of supramolecular chemistry lies in its excellent ability in organizing diversified components together for the construction of dynamic and reversible hybrid materials.[17-19] Based on the fascinating directional non-covalent interactions, supramolecular polymers with advanced architectures and attractive stimuli-responsive properties have drawn much attention in the fabrication of smart functional materials for applications in sensing and detection, biomedicine, and organic photoelectronic devices.[20-26] Taking advantage of a wide range of driving forces and upon careful selection of fluorescent building blocks, tailorable supramolecular polymers with desirable morphologies, optical properties, and unique functions could be designed and constructed through noncovalent interactions including the special host-guest inclusion complexation between supramolecular macrocycles and their guests.[27-29] Supramolecular host compounds including crown ethers,[30] cyclodextrins,[31] cucurbit[n]urils,[32] calix[n]arenes,[28, 33, 34] pillar[n]arenes,[35-43] and beyond,[44, 45] have been employed as characteristic building blocks for the construction of multifunctional supramolecular polymeric materials.[46-51] In 2016, we reported a new type of macrocyclic arenes, namely [2]biphenyl-extended pillar[6]arene (BpP6),[52] which possesses a larger cavity and less crowded substituents on the ring backbone as compared with traditional pillar[6]arene, endowing it with favorable binding selectivity towards petrochemicals such as xylene and toluene in the solid single crystals. More recently, we synthesized the first water-soluble derivative of BpP6 as a very promising detection and separation agent for naphthalene sulfonate substrates in water.[53] Along with the abovementioned studies, we would like to selectively tailor the portals of BpP6 with powerful functionalities for in-depth study on their structural diversity and expand their versatile applications by precision fabrication. Although the utilization of fluorescent supramolecular polymers based on macrocyclic arenes in the detection and removal of heavy metal ions especially mercury in wastewaters still remains challenging,[50] we envision that, by a rationale design of proper supramolecular polymer systems that are capable of selectively sequestering and detecting mercury(II) simultaneously with the aid of synthetic macrocyclic arene chemistry, we could satisfy the different demands and complicated requirements in the control of mercury pollution, hopefully with much lower detection limit, quicker response, and better anti-interference ability.

Inspired by the discovery of tight covalent bonds between thymine (T) and mercury ion (T-Hg^{2+}-T bonds) by Ono in 2006,[54] and the recent employment of T-Hg^{2+}-T pairing for ion detection and molecular sensing in DNA,[55, 56] herein, we design and synthesize a new BpP6 derivative bearing two thymine binding sites as flexible arms (**H**), followed by supramolecular assembly with a tetraphenylethylene (TPE)-bridged bis(quaternary ammonium) guest (**G**) capable of aggregation-induced emission (AIE)[57] to give a fluorescent linear supramolecular polymer (**G⊂H**, **Figure 1**). Upon addition of Hg^{2+}, this supramolecular polymer could eventually self-assemble into spherical nanoparticles through the formation of supramolecular network induced by the T-Hg^{2+}-T pairing between Hg^{2+} ions and the arms of **H**, which exhibit strong AIE fluorescence attributing to supramolecular-assembly induced emission enhancement (SAIEE).[47, 58-62] Therefore, a simple supramolecular assembled module strategy has been utilized in the construction of a sensitive "switch-on" fluorescent probe for Hg^{2+} with highly efficient removal performance.

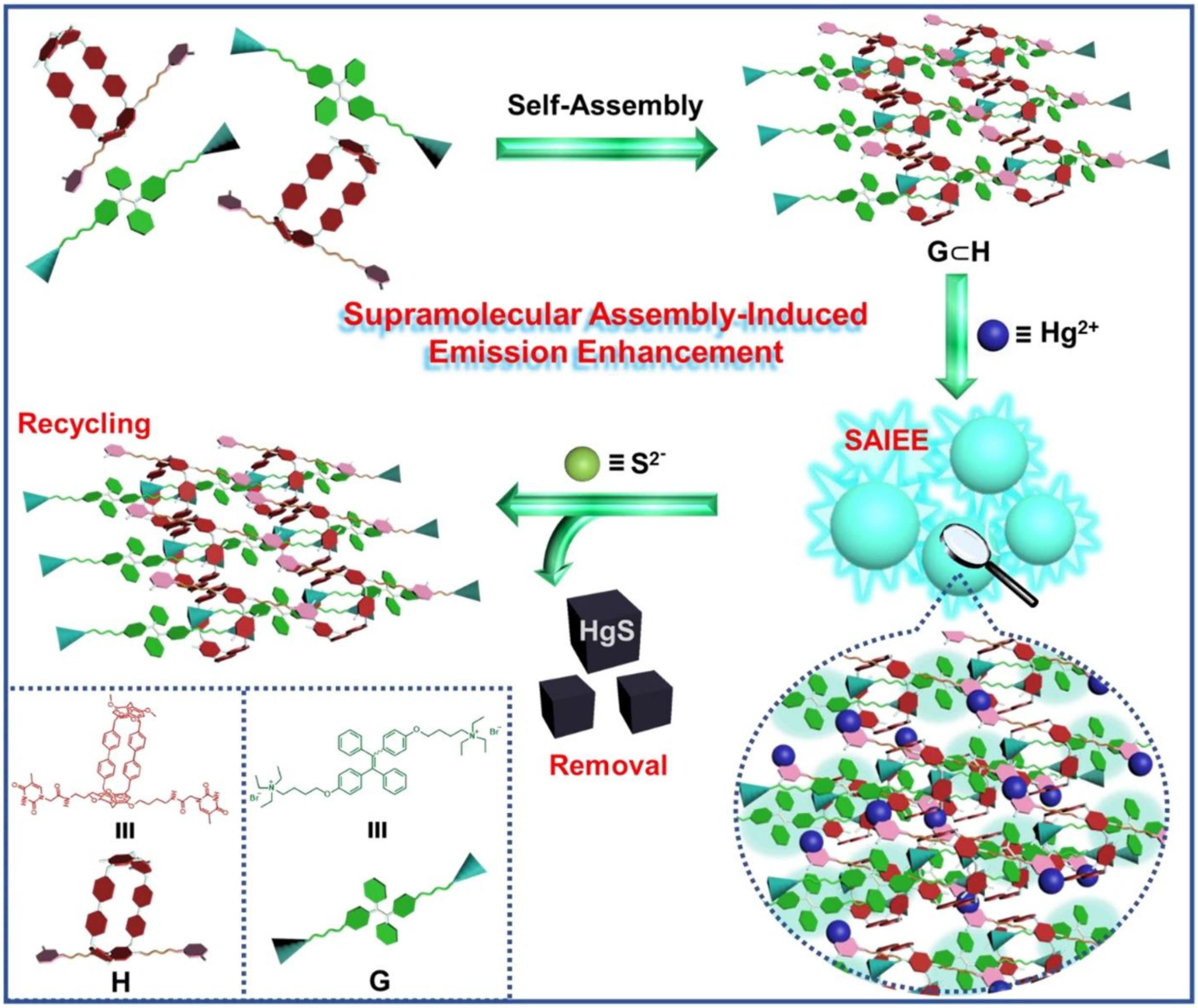
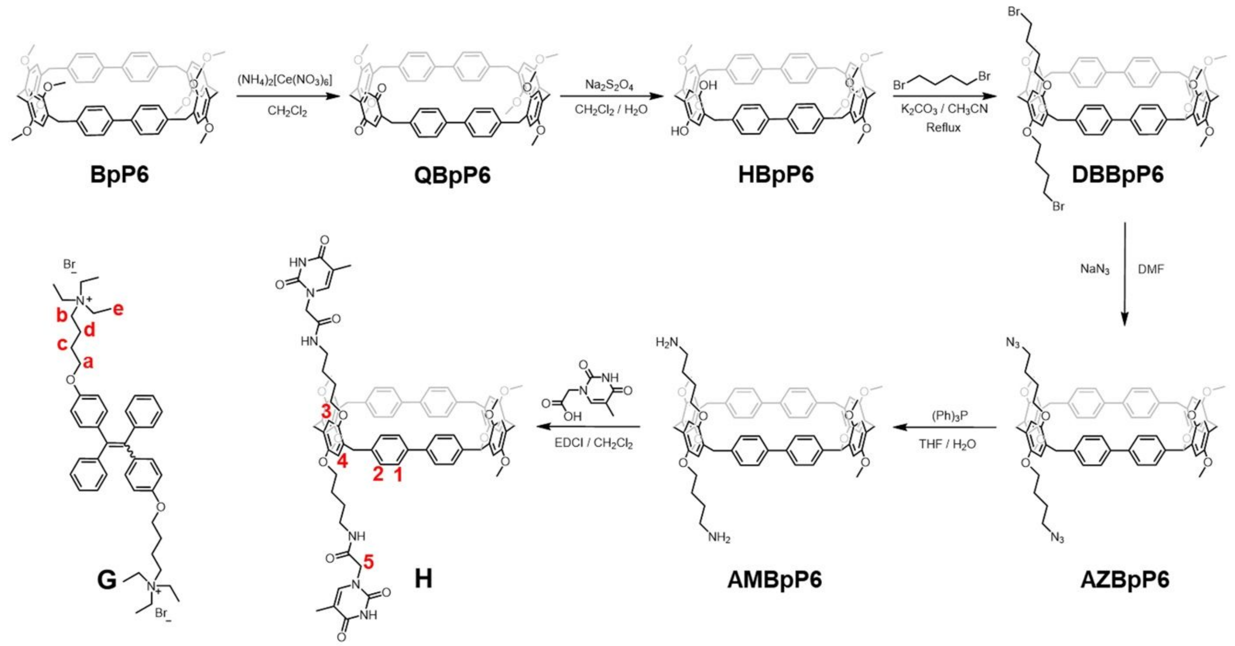


Figure 1. Schematic illustration of the sensing and removal of Hg^{2+} from water based on the "switch-on" fluorescence of the supramolecular polymers (**G⊂H**) and the regeneration-recycling process.

RESULTS AND DISCUSSION

Synthesis of the functional supramolecular macrocycle (H).

The synthetic route to the targeted compound **H** is shown in **Scheme 1**. The starting macrocycle (BpP6) was synthesized according to our published procedure.[52] To realize the tailored terminal functionalization, we first conducted partial oxidation towards single methoxy group within the cyclic ring of BpP6 to give a synthetic intermediate QBpP6 containing one benzoquinone unit, followed by the hydrogenated reduction to afford HBpP6 in a quantitative yield. Thereafter, bromo-functionalized DBBpP6 was obtained through a nucleophilic substitution between HBpP6 and excess 1,4-dibromo butane in the presence of K_2CO_3 with a satisfactory yield. Furthermore, the obtained DBBpP6 was treated with sodium azide in dimethylformamide (DMF) to generate AZBpP6 via nucleophilic substitution in a high yield of 90%, followed by further reduction by PPh_3 through the Staudinger reaction in the mixture solution of tetrahydrofuran and water to produce the intermediate AMBpP6 with a good yield of 50%. Finally, the target **H** was facilely synthesized in a yield of 68% through the condensation of AMBpP6 and thymine derivative as catalyzed by 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI). All the obtained compounds have been verified and fully characterized by ^{1}H NMR, ^{13}C NMR, and MALDI-TOF-MS spectroscopy (**Figure S2-26**).



Scheme 1. Synthetic route to the thymine-functionalized BpP6 derivative **H** and the chemical structure of the TPE-bridged bis(quaternary ammonium) guest **G**.

Supramolecular assembly of H and G mediated by Hg^{2+}.

To rule out the roles of host-guest interactions in the construction of supramolecular polymers, we investigated the related association and binding between macrocyclic **H** and cationic **G** by ^1H NMR spectroscopy. As shown in **Figure 2a**, a fast exchange process on the NMR timescale did take place due to the supramolecular complexation of **H** and **G** in $CDCl_3$ according to the proton NMR spectra of **H**, **G**, and the mixture of **G** and 1.0 equiv. **H**. Upon the addition of **H**, alkyl protons signals of **G** displayed clear upfield shift in sharp contrast with pure **G** ($\Delta\delta$ = -0.12, -0.14, -0.11, -0.13, -0.11 ppm for protons H_a, H_b, H_c, H_d, H_e, respectively), indicating the shielding effect of macrocyclic cavity and the existence of inclusion complexation. With regard to the proton NMR spectrum of **H**, obvious upfield shifts of protons H_1, H_2, H_4 in biphenyl and phenyl and downfield shifts of protons H_3, H_5 further confirmed the host-guest inclusion complexation between the electron-deficient quaternary ammonium groups of **G** and the electron-rich cavity of **H** via electrostatic interactions.

In addition, 2D ROESY NMR spectroscopy was also performed to demonstrate the geometry of **H**. As in **Figure 2b** and **Figure S27**, the ROE correlations were clearly observed due to the π-π and C-H$\cdots\pi$ interactions of the protons H_a, H_b, H_c, H_d, H_e, H_f and H_g at high concentration. However, no ROE correlation between the protons of biphenyl or phenyl and the protons of alkyl chain of **H** has been found, strongly suggesting that no self-inclusion structure existed in **H**. And the same conclusion was also reached based on the ^1H NMR spectra of **H** at different concentrations (**Figure S28**).

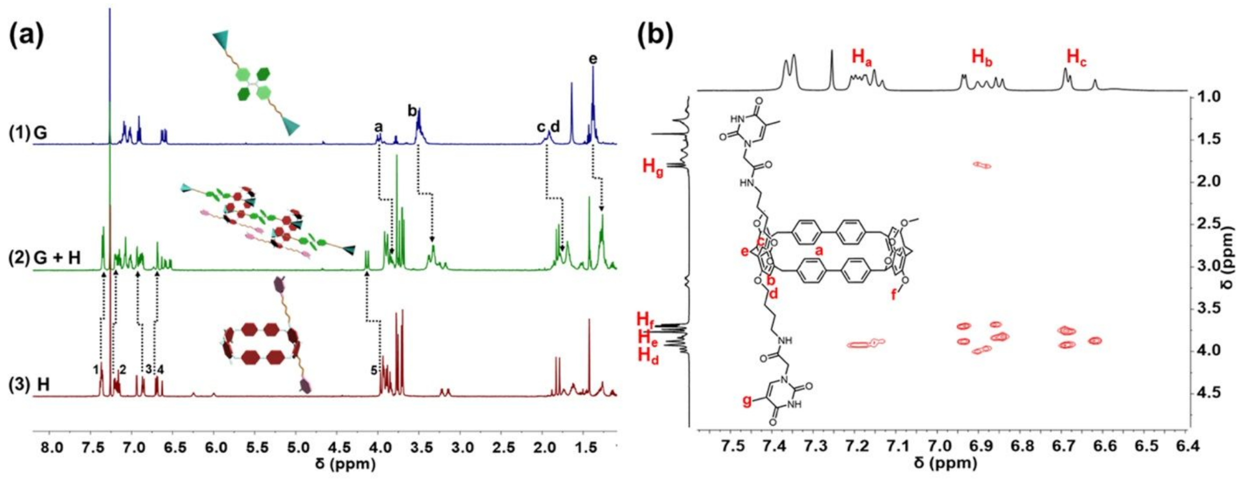


Figure 2. (a) ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K) of (1) **G** (5.0 mM); (2) the equimolar mixture of **G** and **H** (5.0 mM each); (3) **H** (5.0 mM); and (b) Partial 2D ROESY spectrum (400 MHz, $CDCl_3$, 298 K) of **H** (20 mM) with a mixing time of 300 ms.

Moreover, we investigated the binding mode between synthetic macrocycle **H** and quaternary ammonium **G** assisted by the analysis of Job's plot (**Figure S29a**).[63] We anticipate that the larger cavity of **H** holds great potential in stabilizing more than one guest. For the sake of comparison, a counterpart guest molecule **G'**, with only one quaternary ammonium moiety, was synthesized as a control entity. As illustrated in **Figure S29b**, the experimental results of Job's plot analysis support the 1:2 binding mode between **H** and **G'**, so that the related 2:2 binding mode between **H** and **G** could be concluded. Furthermore, ^{1}H NMR titration experiments were carried out to calculate the related association constant (K_a) between **H** and **G'**, which was determined to be 2×10^{3} M^{-1} according to the nonlinear least-squares analysis (**Figure S29c,d**).

In the readily prepared linear polymer **G⊂H**, the thymine arms in **H** possess the binding ability towards Hg^{2+}, which allows the further formation of crosslinked supramolecular network. The related connections could be ascribed to the unique T−Hg^{2+}−T pairings between thymine and Hg^{2+}. In this regard, upon the addition of Hg^{2+}, the host-guest complex underwent an assembled process and afforded the resulting supramolecular assembly (**G⊂H**@Hg^{2+}). Scanning electron microscopy (SEM), transmission electron microscope (TEM) and dynamic light scattering (DLS) measurements have been conducted to characterize the morphology of **G⊂H**@Hg^{2+} (**Figure 3a and Figure S33**). The observed spherical assemblies have an average diameter of around 164 nm, reflecting that the crosslinked aggregates have been created due to the tight binding of T-Hg^{2+}-T pairings in an almost perpendicular direction with respect to the host-guest interactions between **H** and **G**. Herein, we found that the T-Hg^{2+}-T pairings not only connect the pseudorotaxane structures in **G⊂H**, but also cooperatively pull the supramolecular polymer into nanoscaled spherical assemblies. The 2D diffusion-ordered NMR spectroscopy (DOSY) experiments (**Figure S34**) showed that the weight-average diffusion coefficient (*D*) of **H** (2 mM), **G⊂H** (2 mM), and **G⊂H**@Hg^{2+} (2 mM) were 5.99×10^{-10} m^2 s^{-1}, 5.82×10^{-10} m^2 s^{-1}, and 3.78×10^{-10} m^2 s^{-1}, respectively, revealing the formation of supramolecular polymer **G⊂H** and the supramolecular assembly of **G⊂H**@Hg^{2+}.

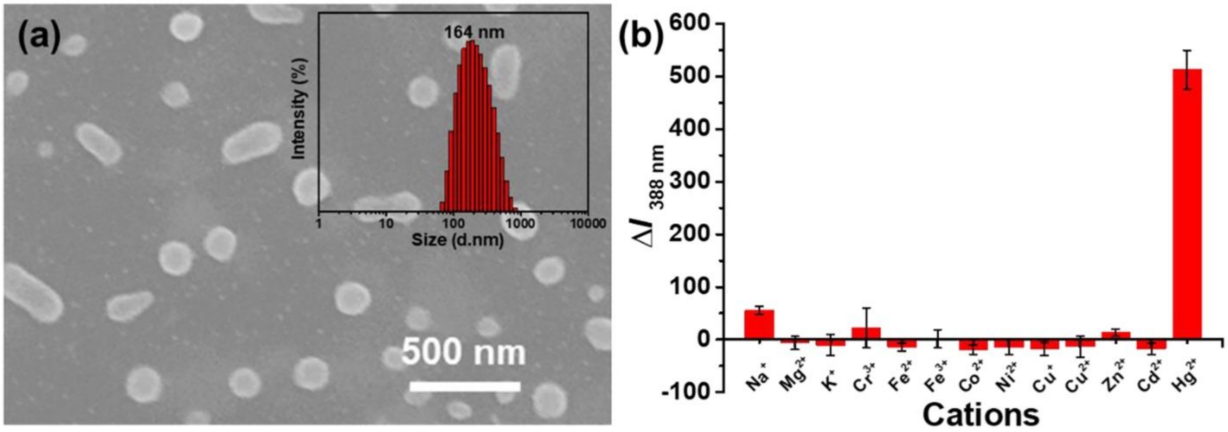


Figure 3. (a) SEM image of **G⊂H**@Hg^{2+}. The insert is the DLS analysis of **G⊂H**@Hg^{2+}; (b) Fluorescence emission (at 388 nm) of **G⊂H** in a mixed solvent of chloroform and acetone (15 μM) with the addition of the aqueous solutions of 1.0 equiv. of different metal ions (15 μM). Conditions: $CHCl_3$/acetone/H_2O (v/v/v = 1:4:495) as solvent; λ_{ex} = 312 nm; slit widths: Ex. 3 nm, Em. 5 nm.

Switch-on fluorescence of supramolecular assembly **$G\subset H@Hg^{2+}$**.

Fluorescent experiments were carried out to investigate the proposed mechanism for fluorescent sensing of **G⊂H** toward Hg^{2+}. Both the TPE derivative **G** and the supramolecular polymer **G⊂H** exhibited negligible or very weak fluorescence in the state of dispersion on account of the free rotation of peripheral phenyl rings and the concomitant nonradiative energy decay in accordance with the pioneer work by Tang and coworkers.[64-67] Regardless of the addition of **H**, **G⊂H** also displayed weak fluorescence. However, once the aqueous solution of $HgCl_2$ was introduced, spherical-shaped supramolecular assembly **G⊂H**@Hg^{2+} was formed and the obvious fluorescence enhancement was switched on upon the irradiation of 312 nm UV light. As shown in **Figure 4a**,**5a**, the strong fluorescence emission and white solid could be observed just by naked eyes. In particular, the formation of spherical-shaped supramolecular assembly **G⊂H**@Hg^{2+} renders the intramolecular rotations within the TPE entities to be restricted, resulting in the switch-on fluorescence due to the effect of SAIEE. Along with the addition of Hg^{2+}, the emission intensity increased sharply and reached the maximum value when the equivalent of Hg^{2+} reached 1.0. These findings strongly support that the supramolecular polymer **G⊂H** could serve as considerable fluorescent probe for sensing toxic heavy metal ion Hg^{2+}.

Moreover, in order to study the anti-interference ability of **G⊂H** against the variation of pH and temperature in response to Hg^{2+}, we preformed the fluorescence measurement experiments under different conditions as presented in **Figure 4b-d**. With an elevated temperature, no obvious change of emission was observed. Similarly, with that case of temperature, the fluorescence emission of **G⊂H**@Hg^{2+} also remained at almost maximum value under different acidic environment. In contrast, significant fluorescence quenching of **G⊂H**@Hg^{2+} was discovered under alkaline conditions, most likely due to the generation of mercuric oxide coming from the reaction between

OH^- and Hg^{2+} and the destruction of the crisscrossed network. Next, the selectivity and specificity of **G⊂H** sensing towards Hg^{2+} was investigated by assessing the fluorescence intensity change by the addition of various metal ions of 1.0 equiv. into the system of **G⊂H** including Na^+, Mg^{2+}, K^+, Cr^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^+, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}, respectively. Other metal ions, despite under identical conditions, were still unfavorable for the switch-on fluorescence as shown in **Figure 3b**. The specific coordination of thymine with Hg^{2+} was recognized as the dominating reason for the formation of crossed-linked network, which endowed **G⊂H** with unique ability in sensing Hg^{2+}.

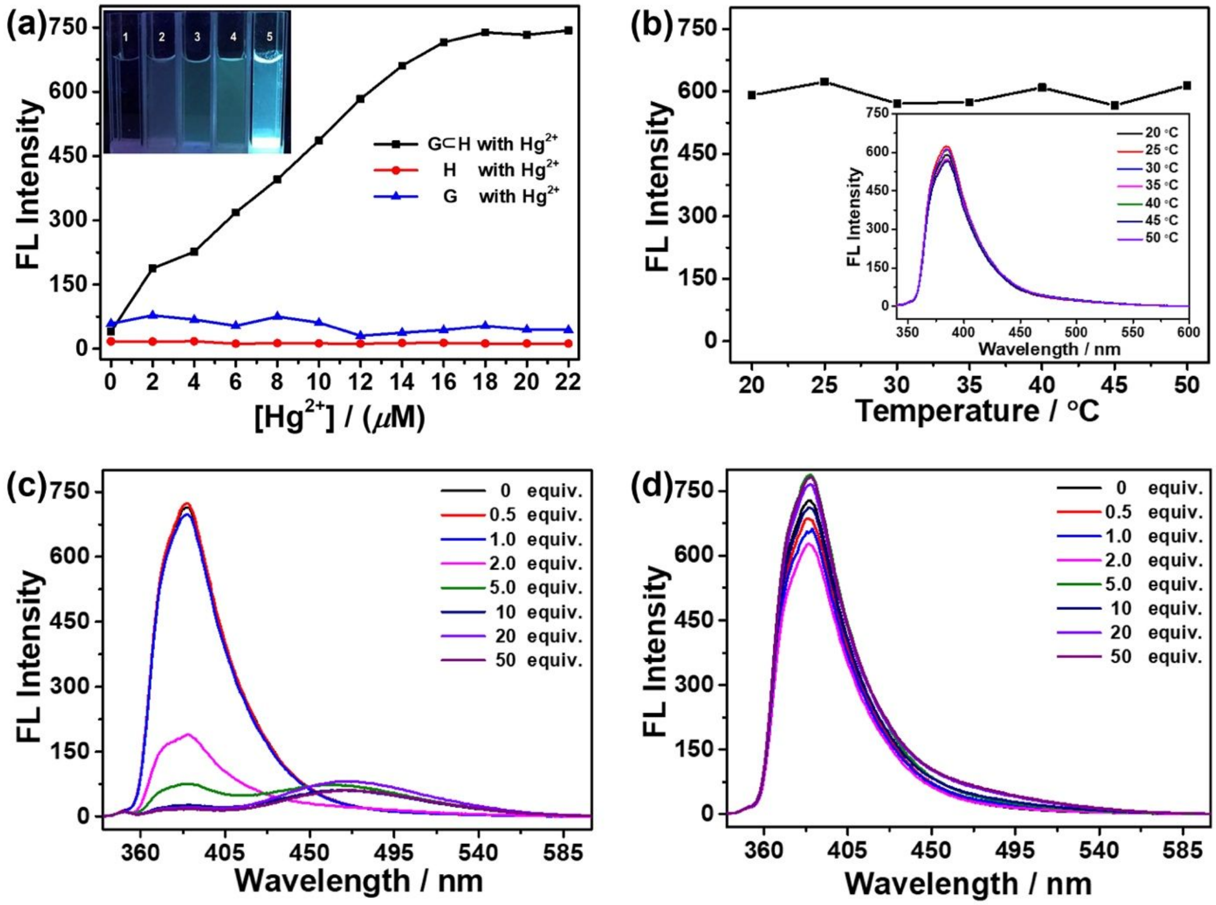


Figure 4. (a) The variation of fluorescence intensity of **G** ⊂ **H**, **H** and **G** (15 μM) with the increasing concentration of Hg^{2+} (from 0 to 22 μM); slit width: Ex. 3 nm, Em. 5 nm. The inset shows the emission of (1) Hg^{2+}; (2) Hg^{2+} + **H**; (3) Hg^{2+} + **G**; (4) **G⊂H**; (5) **G⊂H**@Hg^{2+} under 365 nm UV light irradiation; (b) Fluorescence spectral responses of **G⊂H** + Hg^{2+} (15 μM) towards the variation of temperature; slit width: Ex: 1.5 nm, Em: 3 nm. And the fluorescence spectra of **G⊂H**@Hg^{2+} (15 μM) upon the addition of different amounts of (c) NaOH and (d) HCl aqueous solution (from 0 to 50 equiv.); slit widths: Ex: 3 nm, Em: 5 nm. Conditions: $CHCl_3$/acetone/H_2O (v/v/v = 1:4:495) as solvent; λ_{ex} = 312 nm.

Application in the rapid removal of Hg^{2+}.

In addition to fluorescence sensing toward Hg^{2+}, we also evaluated the performance of **G⊂H** in the applicable removal of Hg^{2+}. Since the supramolecular polymer **G⊂H** exhibited excellent solubility in a mixed solvent of chloroform and acetone, the aqueous solution of Hg^{2+} (30 ppm in 10 mL water) was added into the mixture of **G⊂H** and 0.5 mL chloroform/acetone (v/v = 1:4) (4.5 μM). The apparent white precipitate emerged immediately, indicating the formation of supramolecular assembly **G⊂H**@Hg^{2+}. By virtue of the strong binding of T−Hg^{2+}−T pairings between thymine groups and Hg^{2+}, the supramolecular polymer **G⊂H** tends to form a much hypercross-linked network, which has rendered the obtained materials as versatile absorbents for Hg^{2+}. The mixture was stirred for another 12 h to guarantee the complete adsorption of Hg^{2+} ion, followed by further centrifugation to separate the precipitate from the mother liquid. Then the remaining solution was analyzed by inductively coupled plasma (ICP) for the analysis of residual Hg^{2+}. With the considerable selectivity and strong binding, the supramolecular polymer **G⊂H** displayed remarkable Hg^{2+} removal efficiency that was found to be over 90% and only 2.9 ppm detectable Hg^{2+} existed in the remaining solution. In a simple regeneration treatment, the separated white precipitate **G⊂H**@Hg^{2+} was dissolved in 10 mL chloroform/acetone (v/v = 1:4), followed by the addition of excessive amount of Na_2S, and black HgS solid was produced. After stirring the mixture for another 12 h, the absorbent **G⊂H** was fully regenerated and recycled with centrifugation (**Figure 5a**). Furthermore, another five cycles have been performed within the identical removal procedures, showing that **G⊂H** possesses excellent recyclability (**Figure 5d**). Besides, as shown in **Figure 5b**, with the increasing concentration of Hg^{2+}, the emission exhibited a linear relationship with Hg^{2+} in the range of 0-15 μM. Meanwhile, the detection limit of Hg^{2+} was determined to be 3×10^{-7} M based on 3σ/s, where σ was coming from the standard deviation in 10 blank measurements in **Figure 5c** and s was the slope in **Figure 5b**. All the experimental results clearly demonstrated that supramolecular polymer **G⊂H** could serve as an applicable fluorescence probe and a good absorbent material for sensing and removing Hg^{2+} in water and provided a considerable method in the treatment of mercury ion pollutants with desirable recyclability.

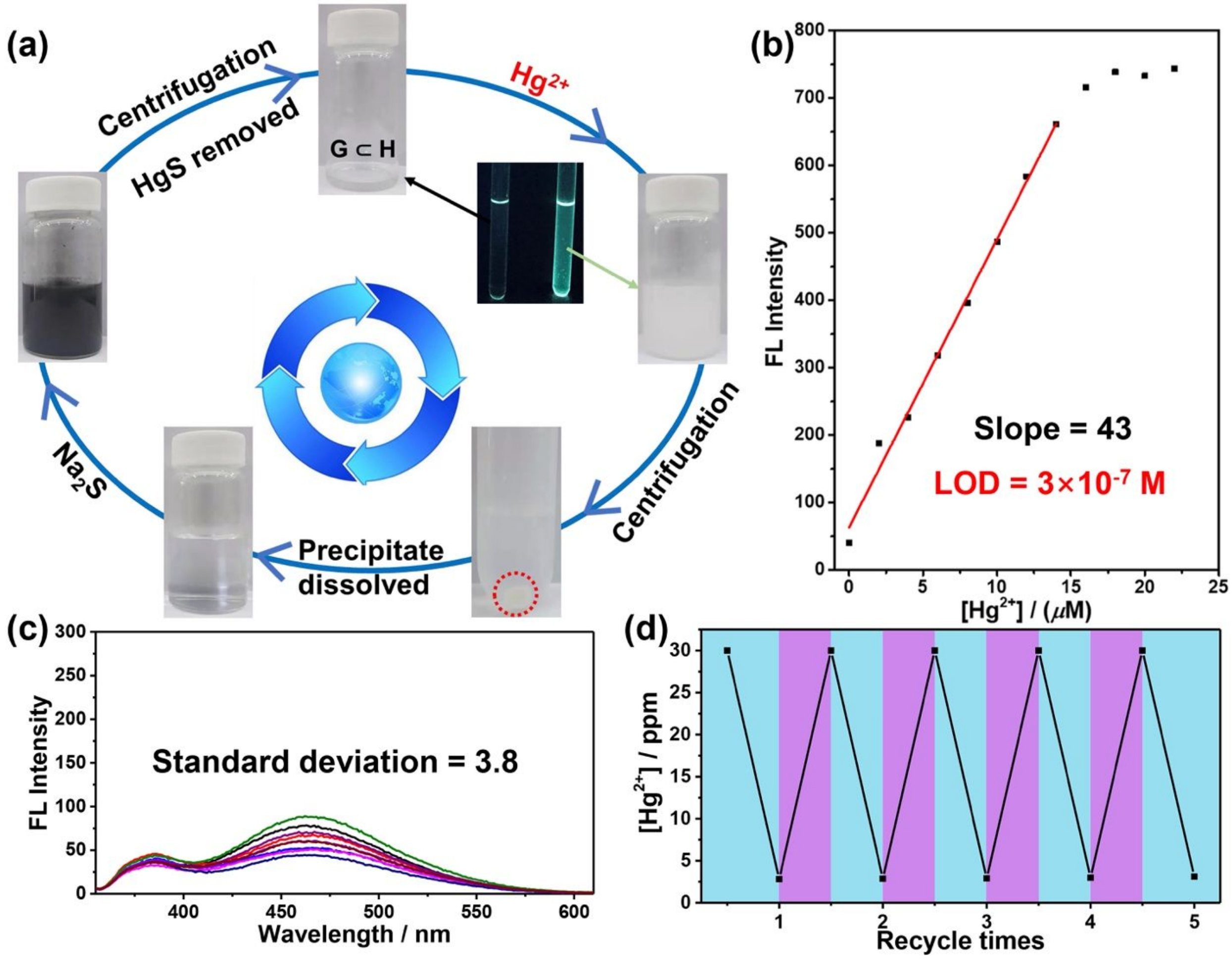


Figure 5. (a) Representative photos during the process of sensing and removal of Hg^{2+} and regeneration of absorbent material (**G⊂H**). (b) The plot of the fluorescence intensity of **G⊂H** at 388 nm against the concentration of Hg^{2+}. λ_{ex} = 312 nm; slit width: Ex. 3 nm, Em. 5 nm; (c) The fluorescence spectra of ten blank measurements of **G⊂H** (15 μM) in $CHCl_3$/acetone/H_2O; Conditions: $CHCl_3$/acetone/H_2O (v/v/v = 1:4:495) as solvent; λex = 312 nm; slit widths: Ex: 3 nm, Em: 5 nm; (d) Recyclable performance of **G⊂H** towards the removal of Hg^{2+}.

CONCLUSION

In summary, we reported on the construction of the first fluorescent supramolecular polymer based on a thymine modified [2]biphenyl-extended version of pillarene host by a simple supramolecular assembly with the aid of an AIEgen-bridged quaternary ammonium guest, and addressed its facile application not only for fluorescent detection of heavy metal ion Hg^{2+} with quick response and high selectivity, but also for efficient removal of Hg^{2+} with rapid adsorption rate and high adsorption capacity. Based on the SAIEE mechanism, the fluorescent emission emerged instantly with the addition of Hg^{2+} due to the tight T-Hg^{2+}-T paring between thymine groups in **H** and Hg^{2+} in the environment and the corresponding formation of the spherical-shaped crosslinked supramolecular assembly **G⊂H**@Hg^{2+}. This work thus combined the AIE effect and the supramolecular module strategy in delivering an applicable method for the selective detection and rapid removal of toxic Hg^{2+}, offering perspective potential in tackling the problem of heavy metal ions pollution for environmental remediation and stimulating new thinking for the sorbent materials design.

ASSOCIATED CONTENT

Supporting Information.

The synthetic routes to **H**, **G** and **G'**. ^{1}H NMR, ^{13}C NMR and MALDI-TOF-MS spectra of the obtained products. Job's plots of **H** with **G** and **H** with **G'**. The NMR titration experiment and association constant figures of **H** with **G**. Fluorescence experiment figures of **H** with Hg^{2+} and **G** with Hg^{2+}. SEM and TEM images of **H** with Hg^{2+} and **G** with Hg^{2+}. The following files are available free of charge. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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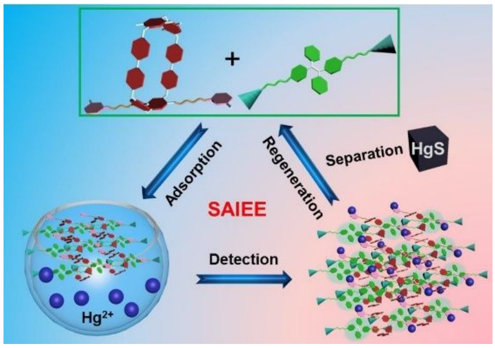
TOC Graphic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Adsorption
Regeneration
Separation
HgS
SAIEE
Detection
Hg^{2+}