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Pillar[5]arene-based supramolecular pseudorotaxane polymer material for ultra-sensitive detection of Fe^{3+} and F^-†

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Recent advancements in ultra-sensitive detection, particularly the Aggregation Induced Emission (AIE) materials, have demonstrated a promising detection method due to their low cost, real-time detection, and simplicity of operation. Here, coumarin functionalized pillar[5]arene (**P5C**) and bis-bromohexyl pillar[5]arene (**DP5**) were successfully combined to create a linear AIE supramolecular pseudorotaxane polymer (**PCDP-G**). The use of **PCDP-G** as a supramolecular AIE polymer material for recyclable ultra-sensitive Fe^{3+} and F^- detection is an interesting application of the materials. According to measurements, the low detection limits of **PCDP-G** for Fe^{3+} and F^- are 4.16×10^{-10} M and 6.8×10^{-10} M, respectively. The **PCDP-G** is also a very effective logic gate and a material for luminous displays.

Introduction

The significance of ultrasensitive response in biological, chemical, and environmental applications has recently attracted a lot of attention.[1–5] Many techniques have been employed up to this point for the crucial guest detection. Liu *et al.*[6] show an ultra-sensitive photodetector based on a graphene/monolayer MoS_2 vertical heterostructure operating at room temperature, while Liao and colleagues[7] present an orthogonal framework for cfDNA cancer monitoring *via* genome-wide mutational integration, enabling ultra-sensitive detection, overcoming the limitation of cfDNA abundance, and empowering treatment optimization in low-disease-burden oncology care. The development of an effective material for the ultra-sensitive response to special guests is still a fascinating task, despite the abundance of approaches that have been described.

Pseudorotaxanes, a type of typical molecular machine built by interlocked molecules,[8] have been greatly implied in drug delivery,[9–11] conducting materials,[12,13] artificial molecular machines,[14] gene delivery,[15,16] functional bioimaging,[17] supra-amphiphiles,[18,19] as well as functional supramolecular systems.[20–23] The supramolecular polymers created from pseudorotaxanes can sense, process, and actuate responses to external change on their own because of the dynamic and reversible nature of noncovalent interactions.[24,25] Due to this characteristic, supramolecular polymers have a considerable advantage over other materials when used as ultrasensitive response material.

Pillar[5]arenes, first reported by Ogoshi,[26] have been the main body of the new-generation macrocyclic ring due to its sophisticated pillar structure with electron-rich cavities, ease of functionalization,[27] and aggregation-inducing properties.[28] Moreover, the pillar[5]arene group provides supramolecular systems with a variety of assembly-driving forces including C–H⋯π, π⋯π and cation⋯π interactions, which can be employed as the primary building block for creating stimuli-responsive supramolecular assembly systems.[29–33] Nowadays, nonporous adaptive crystals,[34–36] chemical sensors,[37–40] catalysis,[41] pseudorotaxanes,[42,43] and supramolecular materials[44,45] have all been made using new supramolecular systems based on functionalized pillar[5]arenes. The development of a novel supramolecular system based on pillar[5]arene for the ultra-sensitive detection of ions is thus of tremendous significance.

In this work, we rationally designed and synthesized a novel pillar[5]arene host **P5C** by joining a pillar[5]arene group and coumarin group *via* a hydrazide group in light of the aforementioned factors and our long-standing interest in supramolecular systems. A novel AIE bi-component supramolecular polypseudorotaxane polymer **PCDP-G** that was created from **P5C** and **DP5** has the potential to be used as an ultra-sensitive luminous material. Our strategies are as follows. Firstly, pseudorotaxanes are formed by one side of the alkyl chain of **DP5** being threaded into the pillar[5]arene cavities of **P5C** and the other being threaded into the pillar[5]arene cavity of **DP5**.

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Secondly, both the coumarin and pillar[5]arene moieties of **P5C** and **DP5** could not only act as π–π interaction sites but also serve as fluorophores. As expected, **P5C** and **DP5** could self-assemble into the stable supramolecular polymer **PCDP-G**. Interestingly, the polymer **PCDP-G** shows strong AIE properties and could ultra-sensitively detect Fe^{3+} and F^-. In addition, the **PCDP-G** could serve as a fluorescent display material as well as an effective logical gateway.

Results and discussion

The synthetic details of pillar[5]arene **P5C** are shown in Scheme S1.† **P5C** and their intermediates have been characterized by ^1H NMR, ^{13}C NMR and ESI mass spectrometry (Fig. S1–S4, ESI†).

At first, the **P5C** and **DP5** could self-assemble into a supramolecular pseudorotaxanes polymer in cyclohexanol solution (Table S1, ESI†). The lowest critical gelation concentration (CGC) is 10% (w/v, 10 mg mL^{-1} = 1%), and the higher gel–sol transition temperature (T_{gel}) is 58–60 °C. Interestingly, the mixture solution of **P5C** and **DP5** in cyclohexanol showed negligible fluorescence ($T > T_{gel}$); with the temperature of the hot cyclohexanol solution cooling below the T_{gel}, the supramolecular pseudorotaxanes polymer **PCDP-G** showed strong yellow fluorescence at 365 nm and reached a steady state within three minutes (Fig. S5, ESI†). Meanwhile, the sol–gel transition process exhibits excellent circularity (Fig. S6, ESI†). These results indicated that the strong yellow fluorescence of **PCDP-G** was induced by aggregation-induced emission (AIE).[46]

The self-assembly mechanism of **PCDP-G** was carefully investigated by ^1H NMR, 2D NOESY NMR and scanning electron microscopy (SEM). As shown in ^1H NMR (Fig. 1 and S7, ESI†), the addition of 1 equiv. **DP5** caused the proton signal peaks H_a, H_b, H_c on **P5C** and H_1, H_2, H_3 on **DP5** to show distinct downfield shifts, respectively, while the proton signal peak H_4 on **DP5** showed an up-field shifts, which implied that one side of the alkyl chain of **DP5** partially threaded into the pillar[5]arene cavity of **P5C** and the other side threaded into the pillar[5]arene cavity of **DP5**. As shown in the 2D NOESY spectra (Fig. S8, ESI†), the correlation peaks A and B between the signals of proton H_4 on **DP5** with $H_{a,c}$ on **P5C** and $H_{1,2}$ on **DP5**, respectively, also evidenced the pseudorotaxanes formed. At the same time, the correlation peaks C of proton H_3 with $H_{1,2}$ on **DP5** and D of proton H_b with $H_{a,c}$ on **P5C** indicated that the pillar[5]arene groups of **P5C** and **DP5** are self-assembled through C–H⋯π interactions, respectively. Moreover, the proton signal peaks H_i, H_j, H_k, H_l, H_m on **P5C** shifted to downfield also supported that the π⋯π interactions of coumarin moieties were present. The π⋯π interactions mechanism is also supported by the peak E correlations of H_f, H_m with H_i, H_l on **P5C**. SEM morphological features of PCDP showed a regular spherical morphology, which also supported the self-assemble process (Fig. S9, ESI†). Therefore, there are firstly formed the supramolecular pseudorotaxanes, and then self-assembly *via* C–H⋯π interactions of the pillar[5]arene groups on **P5C** and **DP5**, respectively, and π⋯π interactions of the coumarin group in the formation of supramolecular pseudorotaxanes in the system (Scheme 1).

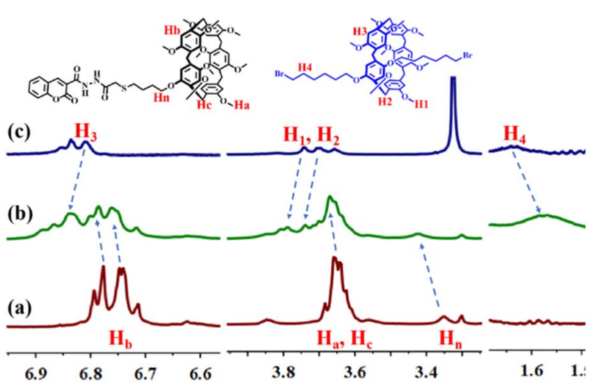
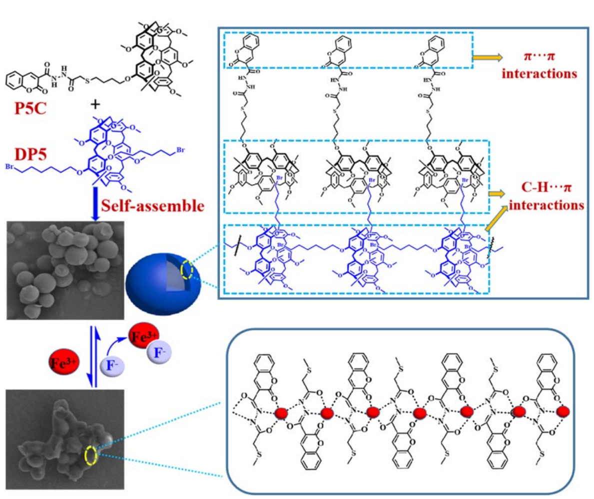


Fig. 1 Partial concentration-dependent ^1H NMR spectra (600 MHz, 298 K) in DMSO-d_6: (a) free **P5C** 10 mg mL^{-1}; (b) **P5C** 10 mg mL^{-1} and **DP5** 10.0 mg mL^{-1}; (c) **DP5** 10.0 mg mL^{-1}.

The fluorescence response abilities of **PCDP-G** toward cations were studied by diffusion with various cations: Cu^{2+}, Co^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, Ca^{2+}, Fe^{3+}, Mg^{2+}, Ba^{2+}, Tb^{3+}, Ag^+, Hg^{2+} and La^{3+} (using their solid perchlorate salts as sources). After addition of above cations (water solution, 0.1 M), only Fe^{3+} caused the fluorescence of **PCDP-G** to quench, and other cations did not show a similar response (Fig. 2), which implied that **PCDP-G** could selectively detect Fe^{3+}. The fluorescence titration of **PCDP-G** for Fe^{3+} was also carefully carried out. Only 0.009 equiv. Fe^{3+} (water solution, 0.1 M) can induce the fluorescence of **PCDP-G** to be quenched (Fig. S10, ESI†). Moreover, according to the fluorescence titration of **PCDP-G** for Fe^{3+} and calculations based on the 3*σ*/*m* method,[47] the lowest detection of the fluorescence spectra change (LOD) of the **PCDP-G** for Fe^{3+} is 4.16×10^{-10} M, which indicated the **PCDP-G** could ultra-sensitively detect Fe^{3+} (Fig. S10 and S11, ESI†).

Furthermore, the successive response properties of the supramolecular metal polymer PCDP-GFe (**PCDP-G** containing 0.01 equiv. Fe^{3+}) towards various anions were further discussed



Scheme 1 The chemical structures, and the self-assemble process of **P5C** and **DP5** for the formation of the supramolecular poly-pseudorotaxane polymer **PCDP-G** as well as the mechanism of **PCDP-G** for fluorescence responses of Fe^{3+} and F^-.

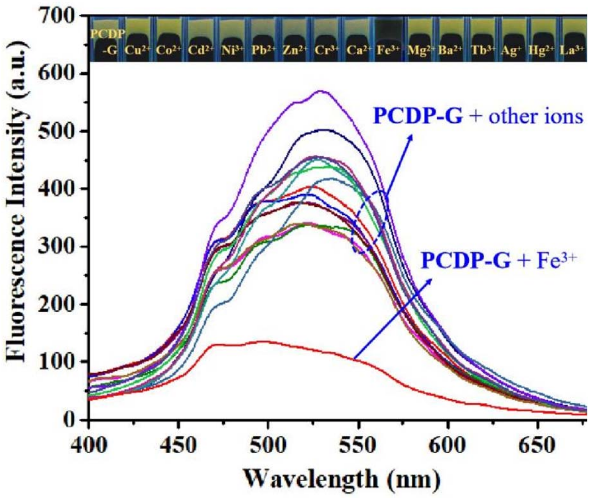


Fig. 2 Fluorescence response of the **PCDP-G** upon addition of various mental aqueous solution ($\lambda_{ex} = 375$ nm) in cyclohexanol system.

by adding aqueous solutions (C = 0.1 M) of various anions, including F^-, Cl^-, Br^-, I^-, ClO_4^-, AcO^-, HSO_4^-, SCN^-, CN^- and N_3^- (for F^-, Cl^-, Br^-, I^-, HSO_4^-, AcO^- and ClO_4^-, using their tetrabutylammonium (TBA) salts; for CN^-, OH^-, N_3^-, SCN^- and S_2^-, using their sodium salts). As shown in Fig. 3, only F^- induced the quenching of the fluorescence of PCDP-GFe changed to yellow, and other anions could not induce any change. These results indicated that PCDP-GFe could selectivity detect F^- in water.

Then, in order to investigate the fluorescent response efficiency of the PCDP-GFe towards F^-, we carried out fluorescence emission titration experiments (Fig. S12, ESI†). After the increasing concentration of F^- was gradually added into the PCDP-GFe, the emission intensity of PCDP-GFe recovered. The limits of the lowest detection of the fluorescence spectra change calculated on the basis of $3\delta/s$ method are 6.8×10^{-10} M (Fig. S13, ESI†), which indicated that the PCDP-GFe could be used for ultra-sensitive detection of F^-. Based on the successive response properties of **PCDP-G** for Fe^{3+} and F^-, we can see that the cyclic fluorescence detection was recyclable at least 3 times (Fig. S14, ESI†). These results illustrate that **PCDP-G** has higher sensitivity when compared with other fluorescence sensors for Fe^{3+} and F^- (Tables S3 and S4, ESI†). Therefore, the supramolecular pseudorotaxanes polymer **PCDP-G** can be used for recyclable ultrasensitive detections of Fe^{3+} and F^-.

The fluorescence response mechanisms of **PCDP-G** were carefully investigated *via* FT-IR and SEM. As shown in the FT-IR spectrum (Fig. 4), the stretching vibration peaks of –NH on **PCDP-G** appeared at 3419 cm^{-1}. After addition of Fe^{3+}, the stretching vibration peaks of –NH shifted to 3455 and 3293 cm^{-1}, and the lactone carbonyl stretching vibration on coumarin moieties at 1722 cm^{-1} got shifted to a lower wave number at 1717 cm^{-1} upon complexation. The results are attributed to the oxygen atom and nitrogen atom in the acylhydrazone-based derivatives having strong coordination abilities with Fe^{3+} and the Fe^{3+} trigger amide tautomerization probably.[48–50] The further addition of F^- induced the stretching vibration peaks of –NH to shift to 3450 cm^{-1} and 3298 cm^{-1}, and the stretching vibration peaks of C=O on coumarin returned to 1720 cm^{-1}. These were attributed to the strong combination of F^- with Fe^{3+}.[51] According to the SEM spectra, the regular spherical morphology of PCDP changed to the cross-linked spherical morphology by adding Fe^{3+} and subsequently changed to the dumbbell pattern. These results also support the above supposition. Therefore, according to these results, the proposed reversible Fe^{3+} and F^- response mechanism is shown in Scheme 1, which is based on coordination interactions and competitive binding processes.

As the **PCDP-G** could act as an Fe^{3+} and F^- controlled "OFF-On-OFF" fluorescence response switch, this inspired us to apply it as a logic gate strategy for the detection of ions. Herein, the sensitization of **PCDP-G** luminescence enabled the design of an

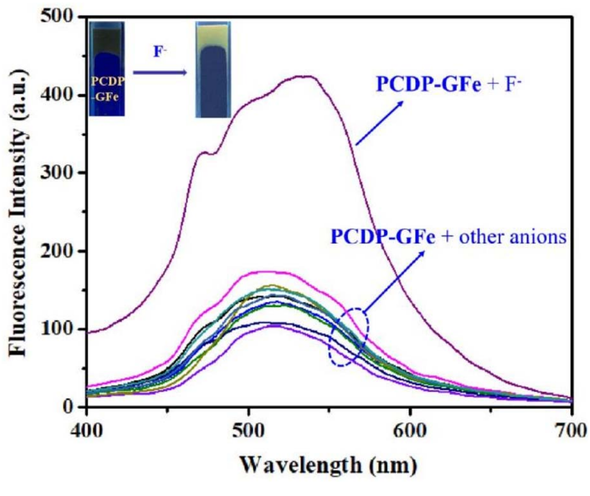


Fig. 3 Fluorescence response of the PCDP-GFe upon addition of various anions aqueous solution ($\lambda_{ex} = 375$ nm) in cyclohexanol system.

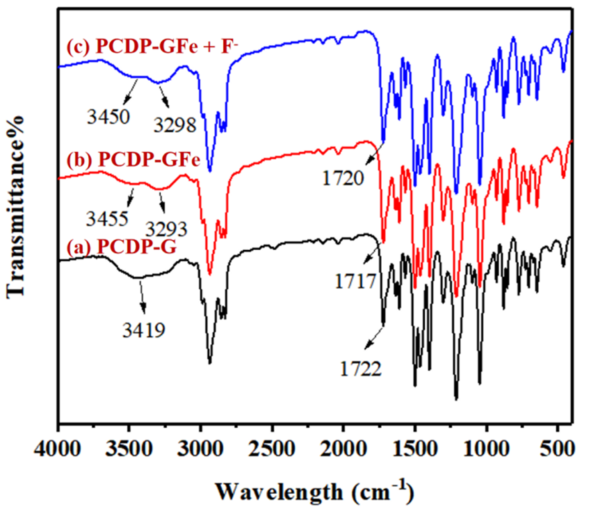
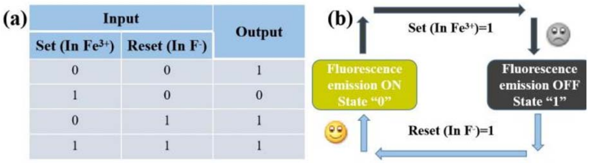


Fig. 4 FT-IR spectra of CPDP-G, CPDP-GFe and CPDP-GFe + F^- complex powdered in KBr disks.



(a)

Input		Output
Set (In Fe^{3+})	Reset (In F^-)	
0	0	1
1	0	0
0	1	1
1	1	1

Fig. 5 Implementation and truth table for IMP logic function using the supramolecular polymer **PCDP-G**.

"IMPLICATION" logic gate. In this logic gate (Fig. 5a and b), the two inputs are Fe^{3+} and F^-; their absence and presence are defined as "0" and "1", respectively. The change in fluorescence intensity of **PCDP-G** acted as an output. The defined "1" and "0" represent the strong fluorescence intensity and weak fluorescence intensity, respectively. When there is no input (0, 0), the output is "1". Similarly, only the Fe^{3+} input (1, 0) caused the fluorescence intensity to be extremely weak, and the output was "0". With only F^- input, there was a strong fluorescence intensity, and the output was "1". When the system was input with Fe^{3+} and F^- together (1, 0), the fluorescence intensity increased and gave an output signal of "1". Therefore, this simple supramolecular polymer material was a potential candidate for the development of new generations of digital devices.

Conclusions

In summary, a novel coumarin-functionalized pillar[5]arene derivative (**P5C**) was successfully synthesized. **P5C** and bis-bromohexyl pillar[5]arene (**DP5**) could form a linear AIE supramolecular poly-pseudorotaxane material (**PCDP-G**) by C–H⋯π and π⋯π stacking interactions, and the **PCDP-G** exhibits strong yellow aggregation-induced emission. Interestingly, **PCDP-G** can be used as an AIE supramolecular polymer material for recyclable ultra-sensitive detection of Fe^{3+} and F^-. The low detection limits of **PCDP-G** for Fe^{3+} and F^- were measured to be 4.16×10^{-10} M and 6.8×10^{-10} M, respectively. Moreover, the fluorescence changes of **PCDP-G** upon the addition of Fe^{3+} and F^- were utilized as an "IMPLICATION" logic gate. The new strategy of preparing supramolecular polymer material with the yellow AIE effect for sensitive detection of Fe^{3+} and F^- may stimulate the development of new approaches to fabricating functional supramolecular materials.

Conflicts of interest

There are no conflicts to declare.

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