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# Pillar[5]arene-based supramolecular pseudorotaxane polymer material for ultra-sensitive detection of Fe<sup>3+</sup> and F<sup>-</sup>†

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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<sup>3+</sup> and F<sup>-</sup> detection is an interesting application of the materials. According to measurements, the low detection limits of PCDP-G for Fe<sup>3+</sup> and F<sup>-</sup> are 4.16 × 10<sup>-10</sup> M and 6.8 × 10<sup>-10</sup> M, respectively. The PCDP-G is also a very effective logic gate and a material for luminous displays.

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## Introduction

The significance of ultrasensitive response in biological, chemical, and environmental applications has recently attracted a lot of attention.<sup>1–5</sup> Many techniques have been employed up to this point for the crucial guest detection. Liu *et al.*<sup>6</sup> show an ultra-sensitive photodetector based on a graphene/monolayer MoS<sub>2</sub> vertical heterostructure operating at room temperature, while Liao and colleagues<sup>7</sup> 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,<sup>8</sup> have been greatly implied in drug delivery,<sup>9–11</sup> conducting materials,<sup>12,13</sup> artificial molecular machines,<sup>14</sup> gene delivery,<sup>15,16</sup> functional bioimaging,<sup>17</sup> supramolecular amphiphiles,<sup>18,19</sup> as well as functional supramolecular systems.<sup>20–23</sup> 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.<sup>24,25</sup> 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,<sup>26</sup> have been the main body of the new-generation macrocyclic ring due to its sophisticated pillar structure with electron-rich cavities, ease of functionalization,<sup>27</sup> and aggregation-inducing properties.<sup>28</sup> 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.<sup>29–33</sup> Nowadays, nonporous adaptive crystals,<sup>34–36</sup> chemical sensors,<sup>37–40</sup> catalysis,<sup>41</sup> pseudorotaxanes,<sup>42,43</sup> and supramolecular materials<sup>44,45</sup> 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  $\pi$ - $\pi$  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  $\text{Fe}^{3+}$  and  $\text{F}^-$ . 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  $^1\text{H}$  NMR,  $^{13}\text{C}$  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,  $10\text{ mg mL}^{-1} = 1\%$ ), and the higher gel–sol transition temperature ( $T_{\text{gel}}$ ) is 58–60 °C. Interestingly, the mixture solution of **P5C** and **DP5** in cyclohexanol showed negligible fluorescence ( $T > T_{\text{gel}}$ ); with the temperature of the hot cyclohexanol solution cooling below the  $T_{\text{gel}}$ , 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).<sup>46</sup>

The self-assembly mechanism of **PCDP-G** was carefully investigated by  $^1\text{H}$  NMR, 2D NOESY NMR and scanning electron microscopy (SEM). As shown in  $^1\text{H}$  NMR (Fig. 1 and S7, ESI†), the addition of 1 equiv. **DP5** caused the proton signal peaks  $\text{H}_{\text{a}}$ ,  $\text{H}_{\text{b}}$ ,  $\text{H}_{\text{c}}$  on **P5C** and  $\text{H}_1$ ,  $\text{H}_2$ ,  $\text{H}_3$  on **DP5** to show distinct down-field shifts, respectively, while the proton signal peak  $\text{H}_4$  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  $\text{H}_4$  on **DP5** with  $\text{H}_{\text{a,c}}$  on **P5C** and  $\text{H}_{1,2}$  on **DP5**, respectively, also

evidenced the pseudorotaxanes formed. At the same time, the correlation peaks C of proton  $\text{H}_3$  with  $\text{H}_{1,2}$  on **DP5** and D of proton  $\text{H}_{\text{b}}$  with  $\text{H}_{\text{a,c}}$  on **P5C** indicated that the pillar[5]arene groups of **P5C** and **DP5** are self-assembled through C–H $\cdots\pi$  interactions, respectively. Moreover, the proton signal peaks  $\text{H}_i$ ,  $\text{H}_j$ ,  $\text{H}_k$ ,  $\text{H}_l$ ,  $\text{H}_m$  on **P5C** shifted to downfield also supported that the  $\pi\cdots\pi$  interactions of coumarin moieties were present. The  $\pi\cdots\pi$  interactions mechanism is also supported by the peak E correlations of  $\text{H}_i$ ,  $\text{H}_m$  with  $\text{H}_i$ ,  $\text{H}_l$  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 $\cdots\pi$  interactions of the pillar[5]arene groups on **P5C** and **DP5**, respectively, and  $\pi\cdots\pi$  interactions of the coumarin group in the formation of supramolecular pseudorotaxanes in the system (Scheme 1).

The fluorescence response abilities of **PCDP-G** toward cations were studied by diffusion with various cations:  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$  and  $\text{La}^{3+}$  (using their solid perchlorate salts as sources). After addition of above cations (water solution, 0.1 M), only  $\text{Fe}^{3+}$  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  $\text{Fe}^{3+}$ . The fluorescence titration of **PCDP-G** for  $\text{Fe}^{3+}$  was also carefully carried out. Only 0.009 equiv.  $\text{Fe}^{3+}$  (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  $\text{Fe}^{3+}$  and calculations based on the  $3\sigma/m$  method,<sup>47</sup> the lowest detection of the fluorescence spectra change (LOD) of the **PCDP-G** for  $\text{Fe}^{3+}$  is  $4.16 \times 10^{-10}\text{ M}$ , which indicated the **PCDP-G** could ultra-sensitively detect  $\text{Fe}^{3+}$  (Fig. S10 and S11, ESI†).

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

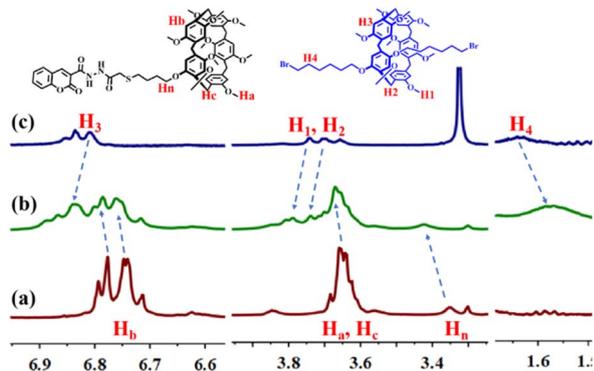
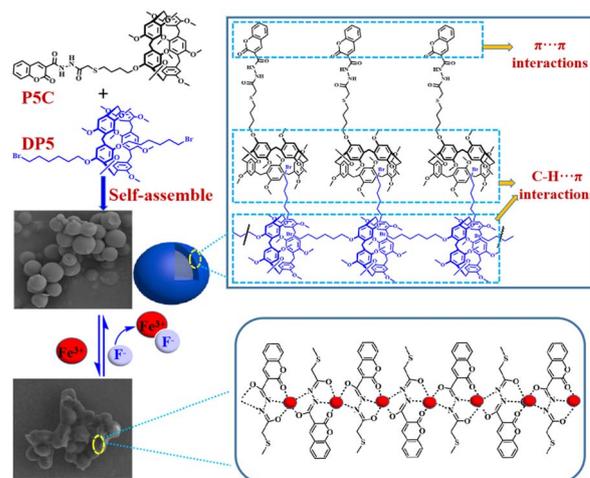


Fig. 1 Partial concentration-dependent  $^1\text{H}$  NMR spectra (600 MHz, 298 K) in  $\text{DMSO}-d_6$ : (a) free **P5C**  $10\text{ mg mL}^{-1}$ ; (b) **P5C**  $10\text{ mg mL}^{-1}$  and **DP5**  $10.0\text{ mg mL}^{-1}$ ; (c) **DP5**  $10.0\text{ mg mL}^{-1}$ .



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  $\text{Fe}^{3+}$  and  $\text{F}^-$ .



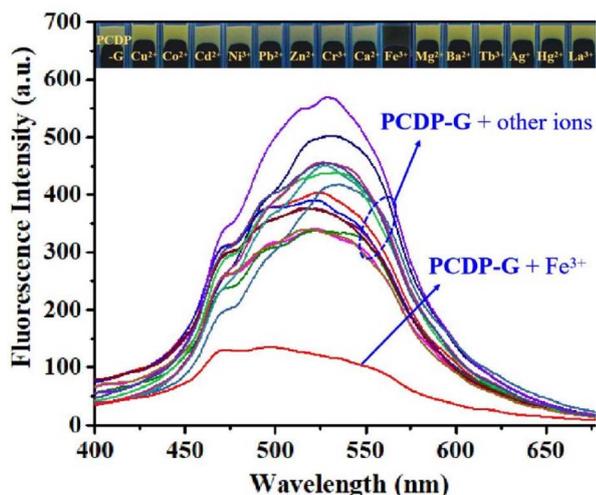


Fig. 2 Fluorescence response of the PCDP-G upon addition of various metal aqueous solution ( $\lambda_{\text{ex}} = 375$  nm) in cyclohexanol system.

by adding aqueous solutions ( $C = 0.1$  M) of various anions, including  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{ClO}_4^-$ ,  $\text{AcO}^-$ ,  $\text{HSO}_4^-$ ,  $\text{SCN}^-$ ,  $\text{CN}^-$  and  $\text{N}_3^-$  (for  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{HSO}_4^-$ ,  $\text{AcO}^-$  and  $\text{ClO}_4^-$ , using their tetrabutylammonium (TBA) salts; for  $\text{CN}^-$ ,  $\text{OH}^-$ ,  $\text{N}_3^-$ ,  $\text{SCN}^-$  and  $\text{S}_2^-$ , using their sodium salts). As shown in Fig. 3, only  $\text{F}^-$  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 selectively detect  $\text{F}^-$  in water.

Then, in order to investigate the fluorescent response efficiency of the PCDP-GFe towards  $\text{F}^-$ , we carried out fluorescence emission titration experiments (Fig. S12, ESI $^\dagger$ ). After the increasing concentration of  $\text{F}^-$  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  $6.8 \times 10^{-10}$  M

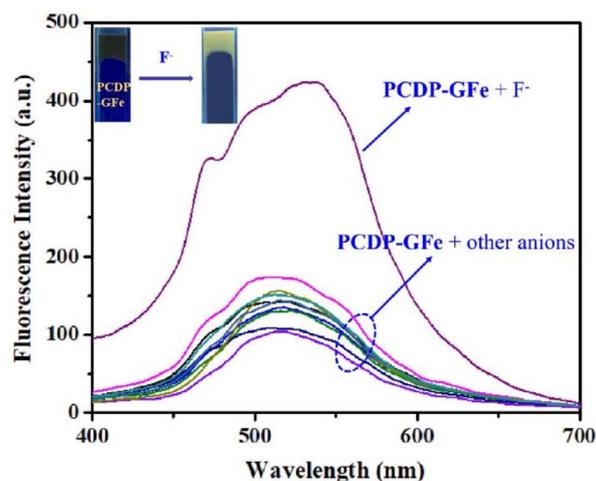


Fig. 3 Fluorescence response of the PCDP-GFe upon addition of various anions aqueous solution ( $\lambda_{\text{ex}} = 375$  nm) in cyclohexanol system.

(Fig. S13, ESI $^\dagger$ ), which indicated that the PCDP-GFe could be used for ultra-sensitive detection of  $\text{F}^-$ . Based on the successive response properties of PCDP-G for  $\text{Fe}^{3+}$  and  $\text{F}^-$ , we can see that the cyclic fluorescence detection was recyclable at least 3 times (Fig. S14, ESI $^\dagger$ ). These results illustrate that PCDP-G has higher sensitivity when compared with other fluorescence sensors for  $\text{Fe}^{3+}$  and  $\text{F}^-$  (Tables S3 and S4, ESI $^\dagger$ ). Therefore, the supramolecular pseudorotaxanes polymer PCDP-G can be used for recyclable ultrasensitive detections of  $\text{Fe}^{3+}$  and  $\text{F}^-$ .

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  $-\text{NH}$  on PCDP-G appeared at  $3419$   $\text{cm}^{-1}$ . After addition of  $\text{Fe}^{3+}$ , the stretching vibration peaks of  $-\text{NH}$  shifted to  $3455$  and  $3293$   $\text{cm}^{-1}$ , and the lactone carbonyl stretching vibration on coumarin moieties at  $1722$   $\text{cm}^{-1}$  got shifted to a lower wave number at  $1717$   $\text{cm}^{-1}$  upon complexation. The results are attributed to the oxygen atom and nitrogen atom in the acylhydrazone-based derivatives having strong coordination abilities with  $\text{Fe}^{3+}$  and the  $\text{Fe}^{3+}$  trigger amide tautomerization probably.<sup>48–50</sup> The further addition of  $\text{F}^-$  induced the stretching vibration peaks of  $-\text{NH}$  to shift to  $3450$   $\text{cm}^{-1}$  and  $3298$   $\text{cm}^{-1}$ , and the stretching vibration peaks of  $\text{C}=\text{O}$  on coumarin returned to  $1720$   $\text{cm}^{-1}$ . These were attributed to the strong combination of  $\text{F}^-$  with  $\text{Fe}^{3+}$ .<sup>51</sup> According to the SEM spectra, the regular spherical morphology of PCDP changed to the cross-linked spherical morphology by adding  $\text{Fe}^{3+}$  and subsequently changed to the dumbbell pattern. These results also support the above supposition. Therefore, according to these results, the proposed reversible  $\text{Fe}^{3+}$  and  $\text{F}^-$  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  $\text{Fe}^{3+}$  and  $\text{F}^-$  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

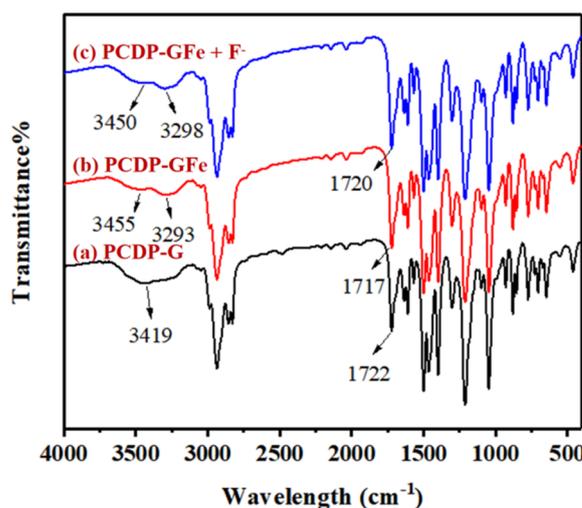


Fig. 4 FT-IR spectra of PCDP-G, PCDP-GFe and PCDP-GFe +  $\text{F}^-$  complex powdered in KBr disks.



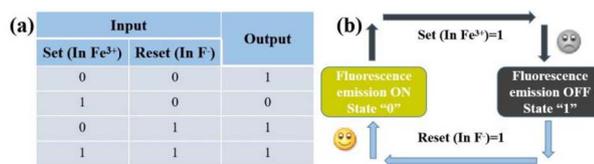


Fig. 5 Implementation and truth table for IMP logic function using the supramolecular polymer PCDP-G.

"IMPLICATION" logic gate. In this logic gate (Fig. 5a and b), the two inputs are Fe<sup>3+</sup> and F<sup>-</sup>; 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<sup>3+</sup> input (1, 0) caused the fluorescence intensity to be extremely weak, and the output was "0". With only F<sup>-</sup> input, there was a strong fluorescence intensity, and the output was "1". When the system was input with Fe<sup>3+</sup> and F<sup>-</sup> 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... $\pi$  and  $\pi$ ... $\pi$  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<sup>3+</sup> and F<sup>-</sup>. The low detection limits of PCDP-G for Fe<sup>3+</sup> and F<sup>-</sup> were measured to be  $4.16 \times 10^{-10}$  M and  $6.8 \times 10^{-10}$  M, respectively. Moreover, the fluorescence changes of PCDP-G upon the addition of Fe<sup>3+</sup> and F<sup>-</sup> 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<sup>3+</sup> and F<sup>-</sup> 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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## Notes and references

- 1 B. Tan, H. Zhao, W. Wu, X. Liu, Y. Zhang and X. Quan, Fe<sub>3</sub>O<sub>4</sub>-AuNPs anchored 2D metal-organic framework nanosheets with DNA regulated switchable peroxidase-like activity, *Nanoscale*, 2017, **9**, 18699–18710.
- 2 H. Li, D.-X. Chen, Y.-L. Sun, Y. B. Zheng, L.-L. Tan, P. S. Weiss and Y.-W. Yang, Viologen-Mediated Assembly of and Sensing with Carboxylatopillar[5]arene-Modified Gold Nanoparticles, *J. Am. Chem. Soc.*, 2013, **135**, 1570–1576.
- 3 M. Sun, R. Bai, X. Yang, J. Song, M. Qin, Z. Suo and X. He, Hydrogel Interferometry for Ultrasensitive and Highly Selective Chemical Detection, *Adv. Mater.*, 2018, **30**, 1804916.
- 4 A. T. Aron, K. M. Ramos-Torres, J. A. Cotruvo Jr and C. J. Chang, Recognition- and Reactivity-Based Fluorescent Probes for Studying Transition Metal Signaling in Living Systems, *Acc. Chem. Res.*, 2015, **48**, 2434–2442.
- 5 L. Wang, N. Wang, J. Wen, Y. Jia, S. Pan, H. Xiong, Y. Tang, J. Wang, X. Yang, Y. Sun, Y. Chen and P. Wan, Ultrasensitive sensing of environmental nitroaromatic contaminants on nanocomposite of Prussian blue analogues cubes grown on glucose-derived porous carbon, *J. Chem. Eng.*, 2020, **397**, 125450.
- 6 Y. Liu, T. Gong, Y. Zheng, X. Wang, J. Xu, Q. Ai, J. Guo, W. Huang, S. Zhou, Z. Liu, Y. Lin, T.-L. Ren and B. Yu, Ultra-sensitive and plasmon-tunable graphene photodetectors for micro-spectrometry, *Nanoscale*, 2018, **10**, 20013–20019.
- 7 A. Zviran, R. C. Schulman, M. Shah, *et al.*, Genome-wide cell-free DNA mutational integration enables ultra-sensitive cancer monitoring, *Nat. Med.*, 2020, **26**, 1114–1124.
- 8 J. E. M. Lewis, P. D. Beer, S. J. Loeb and S. M. Goldup, Metal ions in the synthesis of interlocked molecules and materials, *Chem. Soc. Rev.*, 2017, **46**, 2577–2591.
- 9 S. Loethen, J.-M. Kim and D. H. Thompson, Biomedical Applications of Cyclodextrin Based Polyrotaxanes, *Polym. Rev.*, 2007, **47**, 383–418.
- 10 S. F. Taveira, A. Varela-Garcia, B. S. Souza, R. N. Marreto, M. Martin-Pastor, A. Concheiro and C. Alvarez-Lorenzo, Cyclodextrin-based poly(pseudo)rotaxanes for transdermal delivery of carvedilol, *Carbohydr. Polym.*, 2018, **200**, 278–288.
- 11 Z. Li, N. Song and Y.-W. Yang, Stimuli-Responsive Drug-Delivery Systems Based on Supramolecular Nanovalves, *Matter*, 2019, **1**, 345–368.
- 12 F. Cacialli, J. S. Wilson, J. J. Michels, C. Daniel, C. Silva, R. H. Friend, N. Severin, P. Samori, J. P. Rabe, M. J. O'Connell, P. N. Taylor and H. L. Anderson, Cyclodextrin-threaded conjugated polyrotaxanes as insulated molecular wires with reduced interstrand interactions, *Nat. Mater.*, 2002, **1**, 160–164.
- 13 L. Li, L. He, B. Wang, P. Ge, L. Jing, H. Liu, C. Gong, B. Zhang, J. Zhang and W. Bu, Secondary dialkylammonium salt/crown ether [2]pseudorotaxanes as nanostructured platforms for proton transport, *Chem. Commun.*, 2018, **54**, 8092–8095.



- 14 G. Du, E. Moulin, N. Jouault, E. Buhler and N. Giuseppone, Muscle-like Supramolecular Polymers: Integrated Motion from Thousands of Molecular Machines, *Angew. Chem., Int. Ed.*, 2012, **51**, 12504–12508.
- 15 T. Ooya, H. S. Choi, A. Yamashita, N. Yui, Y. Sugaya, A. Kano, A. Maruyama, H. Akita, R. Ito, K. Kogure and H. Harashima, Biocleavable Polyrotaxane–Plasmid DNA Polyplex for Enhanced Gene Delivery, *J. Am. Chem. Soc.*, 2006, **128**, 3852–3853.
- 16 J. J. Li, F. Zhao and J. Li, Polyrotaxanes for applications in life science and biotechnology, *J. Appl. Microbiol. Biotechnol.*, 2011, **90**, 427–443.
- 17 S. S. Liow, H. Zhou, S. Sugiarto, S. Guo, M. L. S. Chalasani, N. K. Verma, J. Xu and X. J. Loh, Highly Efficient Supramolecular Aggregation-Induced Emission-Active Pseudorotaxane Luminogen for Functional Bioimaging, *Biomacromolecules*, 2017, **18**(3), 886–897.
- 18 X. Chi, X. Ji, D. Xia and F. Huang, A Dual-Responsive Supra-Amphiphilic Polypseudorotaxane Constructed from a Water-Soluble Pillar[7]arene and an Azobenzene-Containing Random Copolymer, *J. Am. Chem. Soc.*, 2015, **137**, 1440–1443.
- 19 X. Chi, G. Yu, X. Ji, Y. Li, G. Tang and F. Huang, Redox-Responsive Amphiphilic Macromolecular [2] Pseudorotaxane Constructed from a Water-Soluble Pillar[5] arene and a Paraquat-Containing Homopolymer, *ACS Macro Lett.*, 2015, **4**, 996–999.
- 20 W. Zhu, W. Li, C. Wang, J. Cui, H. Yang, Y. Jiang and G. Li, CB[8]-based rotaxane as a useful platform for sensitive detection and discrimination of explosives, *Chem. Sci.*, 2013, **4**, 3583–3590.
- 21 L. Ma, R. Tang, Y. Zhou, J. Bei, Y. Wang, T. Chen, C. Ou, Y. Han, C.-G. Yan and Y. Yao, Pillar[5]arene-based [1] rotaxanes with salicylaldehyde as the stopper: synthesis, characterization and application in the fluorescence turn-on sensing of Zn<sup>2+</sup> in water, *Chem. Commun.*, 2022, **58**, 8978–8981.
- 22 Y. Shi, Z. Yang, H. Liu, Z. Li, Y. Tian and F. Wang, Mechanically Linked Poly[2]rotaxanes Constructed via the Hierarchical Self-Assembly Strategy, *ACS Macro Lett.*, 2015, **4**, 6–10.
- 23 Q. Shi, X. Wang, B. Liu, P. Qiao, J. Li and L. Wang, Macrocyclic host molecules with aromatic building blocks: the state of the art and progress, *Chem. Commun.*, 2021, **57**, 12379–12405.
- 24 Z.-Y. Li, Y. Zhang, C.-W. Zhang, L.-J. Chen, C. Wang, H. Tan, Y. Yu, X. Li and H.-B. Yang, Cross-Linked Supramolecular Polymer Gels Constructed from Discrete Multi-pillar[5] arene Metallacycles and Their Multiple Stimuli-Responsive Behavior, *J. Am. Chem. Soc.*, 2014, **136**, 8577–8589.
- 25 K. Yang, Y. Pei, J. Wen and Z. Pei, Recent advances in pillar [n]arenes: synthesis and applications based on host-guest interactions, *Chem. Commun.*, 2016, **52**, 9316–9326.
- 26 T. Ogoshi, S. Kanai, S. Fujinami, T. Yamagishi and Y. Nakamoto, para-Bridged Symmetrical Pillar[5]arenes: Their Lewis Acid Catalyzed Synthesis and Host-Guest Property, *J. Am. Chem. Soc.*, 2008, **130**, 5022–5023.
- 27 T. Ogoshi, T. Yamagishi and Y. Nakamoto, Pillar-Shaped Macrocyclic Hosts Pillar[n]arenes: New Key Players for Supramolecular Chemistry, *Chem. Rev.*, 2016, **116**, 7937–8002.
- 28 J.-F. Chen, G. Meng, Q. Zhu, S. Zhang and P. Chen, Pillar[5] arenes: a new class of AIEgen macrocycles used for luminescence sensing of Fe<sup>3+</sup> ions, *J. Mater. Chem. C*, 2019, **7**, 11747–11751.
- 29 L. Chen, Y. Cai, W. Feng and L. Yuan, Pillararenes as macrocyclic hosts: a rising star in metal ion separation, *Chem. Commun.*, 2019, **55**, 7883–7898.
- 30 H. Zhang, Z. Liu and Y. Zhao, Pillararene-based self-assembled amphiphiles, *Chem. Soc. Rev.*, 2018, **47**, 5491–5528.
- 31 Y. Wang, D. Wang, J. Wang, Ch. Wang, J. Wang, Y. Ding and Y. Yao, Pillar[5]arene-derived covalent organic materials with pre-encoded molecular recognition for targeted and synergistic cancer photo- and chemotherapy, *Chem. Commun.*, 2022, **58**, 1689–1692.
- 32 J.-F. Chen, Q. Lin, Y.-M. Zhang, H. Yao and T.-B. Wei, Pillararene-based fluorescent chemosensors: recent advances and perspectives, *Chem. Commun.*, 2017, **53**, 13296–13311.
- 33 H. Li, Y. Yang, F. Xu, T. Liang, H. Wen and W. Tian, Pillararene-based supramolecular polymers, *Chem. Commun.*, 2019, **55**, 271–285.
- 34 Y. Zhou, K. Jie, R. Zhao, E. Li and F. Huang, Highly Selective Removal of Trace Isomers by Nonporous Adaptive Pillararene Crystals for Chlorobutane Purification, *J. Am. Chem. Soc.*, 2020, **142**(15), 6957–6961.
- 35 Y. Wu, J. Zhou, E. Li, M. Wang, K. Jie, H. Zhu and F. Huang, Selective Separation of Methylfuran and Dimethylfuran by Nonporous Adaptive Crystals of Pillararenes, *J. Am. Chem. Soc.*, 2020, **142**, 19722–19730.
- 36 X. Sheng, E. Li, Y. Zhou, R. Zhao, W. Zhu and F. Huang, Separation of 2-Chloropyridine/3-Chloropyridine by Nonporous Adaptive Crystals of Pillararenes with Different Substituents and Cavity Sizes, *J. Am. Chem. Soc.*, 2020, **142**, 6360–6364.
- 37 J. Wang, M. Cen, J. Wang, D. Wang, Y. Ding, G. Zhu, B. Lu, X. Yuan, Y. Wang and Y. Yao, Water-soluble pillar[4]arene [1]quinone: synthesis, host-guest property and application in the fluorescence turn-on sensing of ethylenediamine in aqueous solution, organic solvent and air, *Chin. Chem. Lett.*, 2022, **33**, 1475–1478.
- 38 C. Li, S. Chen, J. Li, K. Han, M. Xu, B. Hu, Y. Yu and X. Jia, Novel Neutral Guest Recognition and Interpenetrated Complex Formation from Pillar[5]arenes, *Chem. Commun.*, 2011, **47**, 11294–11296.
- 39 X. Shu, J. Fan, J. Li, X. Wang, W. Chen, X. Jia and C. Li, Complexation of Neutral 1,4-Dihalobutanes with Simple Pillar[5]-arenes that is Dominated by Dispersion Forces, *Org. Biomol. Chem.*, 2012, **10**, 3393–3397.
- 40 X. Shu, S. Chen, J. Li, Z. Chen, L. Weng, X. Jia and C. Li, Highly Effective Binding of Neutral Dinitriles by Simple Pillar[5]-arenes, *Chem. Commun.*, 2012, **48**, 2967–2969.



- 41 C. Li, J. Ma, L. Zhao, Y. Zhang, Y. Yu, X. Shu, J. Li and X. Jia, Molecular Selective Binding of Basic Amino Acids by a Water-Soluble Pillar[5]arene, *Chem. Commun.*, 2013, **49**, 1924–1926.
- 42 C. Li, L. Zhao, J. Li, X. Ding, S. Chen, Q. Zhang, Y. Yu and X. Jia, Self-assembly of [2]Pseudorotaxanes Based on Pillar [5]arene and Bis(imidazolium) Cations, *Chem. Commun.*, 2010, **46**, 9016–9018.
- 43 S. Dong, B. Zheng, Y. Yao, C. Han, J. Yuan, M. Antonietti and F. Huang, LCST-Type Phase Behavior Induced by Pillar[5]arene/Ionic Liquid Host-Guest Complexation, *Adv. Mater.*, 2013, **25**, 6864–6867.
- 44 Q. Duan, Y. Cao, Y. Li, X. Hu, T. Xiao, C. Lin, Y. Pan and L. Wang, pH-Responsive Supramolecular Vesicles Based on WaterSoluble Pillar[6]arene and Ferrocene Derivative for Drug Delivery, *J. Am. Chem. Soc.*, 2013, **135**, 10542–10549.
- 45 Z.-D. Tang, X.-M. Sun, T.-T. Huang, J. Liu, B. Shi, H. Yao, Y.-M. Zhang, T.-B. Wei and Q. Lin, Pillar[n]arenes-based materials for detection and separation of pesticides, *Chin. Chem. Lett.*, 2023, **34**, 107698.
- 46 H. Su, W. Luo, J. W. Y. Lam, J. Qian, K. S. Wong and B. Z. Tang, Functionalized AIE nanoparticles with efficient deep-red emission, mitochondrial specificity, cancer cell selectivity and multiphoton susceptibility, *Chem. Sci.*, 2017, **8**, 4634–4643.
- 47 H. N. Kim, W. X. Ren, J. S. Kim and J. Yoon, Fluorescent and colorimetric sensors for detection of lead, cadmium, and mercury ions, *Chem. Soc. Rev.*, 2012, **8**, 3210–3244.
- 48 Z. Liao, Y. Liu, S.-F. Han, D. Wang, J.-Q. Zheng, X.-J. Zheng and L.-P. Jin, A novel acylhydrazone-based derivative as dual-mode chemosensor for Al<sup>3+</sup>, Zn<sup>2+</sup> and Fe<sup>3+</sup> and its applications in cell imaging, *Sensor. Actuator. B*, 2017, **244**, 914–921.
- 49 V. Kumar, A. Kumar, U. Diwan and K. K. Upadhyay, A Zn<sup>2+</sup>-responsive highly sensitive fluorescent probe and 1D coordination polymer based on a coumarin platform, *Dalton Trans.*, 2013, **42**, 13078–13083.
- 50 Š. Budzák and D. Jacquemin, Mechanism of fluorescence switching in one ESIPT-based Al<sup>3+</sup> probe, *J. Phys. Chem. B*, 2016, **120**, 6730–6738.
- 51 W. Zhu, H. Fang, J.-X. He, W.-H. Jia, H. Yao, T.-B. Wei, Q. Lin and Y.-M. Zhang, Novel 2-(hydroxy)-naphthyl imino functionalized pillar[5]arene: a highly efficient supramolecular sensor for tandem fluorescence detection of Fe<sup>3+</sup> and F<sup>-</sup> and the facile separation of Fe<sup>3+</sup>, *New J. Chem.*, 2018, **42**, 11548–11554.

