CHEMISTRY
A European Journal

A Journal of
ChemPubSoc Europe

Accepted Article

Title: Pillar[5]arenes-Based Supramolecular Organic Framework with Multi-Guests Detection and Recyclable Separation Properties

Authors: Qi Lin, Yan-Qing Fan, Peng-Peng Mao, Lu Liu, Juan Liu, You-Ming Zhang, Hong Yao, and Tai-Bao Wei

To be cited as: *Chem. Eur. J.* 10.1002/chem.201705107

Link to VoR: http://dx.doi.org/10.1002/chem.201705107

Supported by
ACES

WILEY-VCH

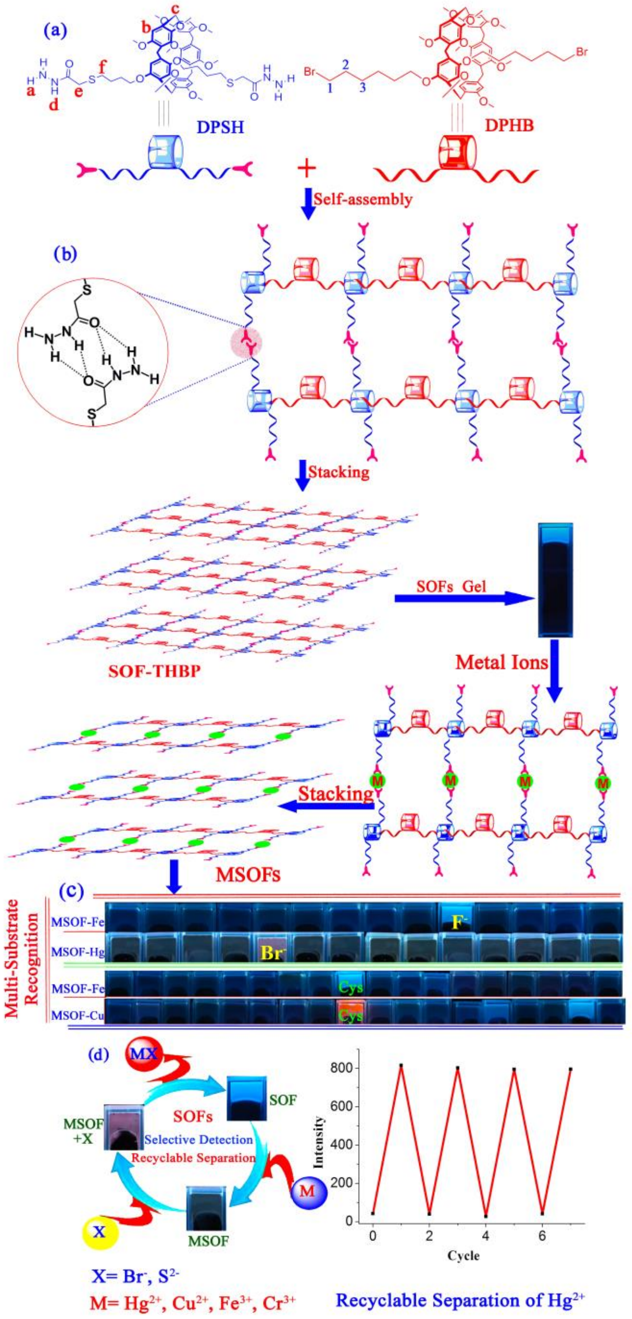
Pillar[5]arenes-Based Supramolecular Organic Framework with Multi-Guests Detection and Recyclable Separation Properties

Qi Lin*[a], Yan-Qing Fan[a], Peng-Peng Mao[a], Lu Liu[a], Juan Liu*[b], You-Ming Zhang[a], Hong Yao[a], Tai-Bao Wei*[a]

Abstract: The selective detection and separation of target ions or molecules is an intriguing issue. Herein, a novel supramolecular organic framework (**SOF-THBP**) was constructed by bis-thioacetylhydrazine functionalized pillar[5]arenes. The **SOF-THBP** shows fluorescent response for Fe^{3+}, Cr^{3+}, Hg^{2+} and Cu^{2+}. The xerogel of **SOF**-**THBP** shows excellent recyclable separation properties for these metal ions and the absorption rates were up to 99.29%. More interestingly, by rationally introduced these metal ions into the **SOF**-**THBP**, a series of metal ions coordinated SOFs (MSOFs) such as **MSOF-Fe**, **MSOF-Hg** and **MSOF-Cu** were constructed. These metal ions coordinated **MSOFs** could selectively and sensitively sense F^-, Br^-, and L-Cys, respectively. The detection limits of these **MSOFs** for F^-, Br^- and L-Cys were about 10^{-8} M. It's a novel and efficient way to approach multi-guest responsive **SOFs**.

Over the past decade, rationally design, synthesis and property developments of supramolecular organic frameworks (SOFs) [1] have attracted a lot of interests due to their versatile applications in many fields, including sensing,[2] separation,[3] gas adsorption and storage,[4] drug delivery,[5] biotechnology,[6] catalysis,[7] and opto/electronic devices.[8] The SOFs are assembled from the molecular building blocks by supramolecular interaction.[9] Benefited on the dynamic and reversible nature of supramolecular interaction,[10] SOFs show many merits such as easy to fabrication, various assemble models and versatile stimuli-response properties.[11] Therefore, SOFs become one of the hottest research fields in materials science.[12]

Moreover, pillar[n]arenes, firstly reported by Ogoshi in 2008,[13] have become a new class of supramolecular host and undergone a rapid development.[14] In addition, pillar[n]arenes have various supramolecular assembly driving forces including C-H···π, π···π, cation···π, hydrophobic/hydrophilic, etc.[13] These properties not only afforded pillar[n]arenes outstanding abilities to selectively bind different kinds of guests,[15] but also provided a novel platform for the construction of various interesting supramolecular systems[13, 14, 16-20] as well as SOFs.[9] However, the reporting on pillar[n]arenes based-SOFs is still very scarce.[11]



Scheme 1. (a) The chemical structures of **DPSH** and **DPHB**; (b) cartoon representation for the formation of the **SOF-THBP**; (c) multi-guest-response properties of **SOF-THBP** and metal ions coordinated **SOFs**; (d) recyclable separation properties of **SOF-THBP**.

In addition, ions and molecules play fundamental roles in chemical, biological, environmental fields,[21] selective detection

---

[a] Qi Lin, Yan-Qing Fan, Peng-Peng Mao, Lu Liu, You-Ming Zhang, Hong Yao, Tai-Bao Wei.
Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education of China, Key Laboratory of Polymer Materials of Gansu Province.
College of Chemistry and Chemical Engineering Northwest Normal University, Lanzhou, 730070, China.
E-mail: linqi2004@126.com; weitaibao@126.com.
[b] Juan Liu
College of Chemical Engineering, Northwest University for Nationalities, Lanzhou, 730070, China.
E-mail: liujuan656@126.com

Supporting information for this article is given via a link at the end of the document.

of special ions/molecules and recyclable separation of toxic ions in environmental are very important.[22] For example, fluoride ion plays important role in bone health, dental health [23] and has potential use for the treatment of osteoporosis.[24, 25] However, excessive intake of fluoride can lead to acute gastric and kidney problems.[26] In addition, heavy metal ions are widely used in industry, while, because of the high toxicity and bioaccumulation, heavy metal ions released into the environment can lead to a wide range of severe diseases [27]. For instance, mercury can cause grisly immunotoxic, genotoxic, and neurotoxic effects, including damages to the central nervous system, endocrine system, kidney, and other organs.[28] Moreover, amino acids play important role in human health [29], for example, L-Cysteine (L-Cys) is one of the sulfhydryl containing small molecular amino acids that play crucial roles in many physiological and pathological processes.[30] Therefore, developing efficient methods for selective detection or separation these important ions and molecules in environmental is essential.[22] Although numerous molecular recognition and separation methods have been reported,[24] the development of supramolecular materials for synchronous detection and separation target guest is still an intriguing challenge.

In view of these and as part of our research interests in molecular recognition [25] and supramolecular functional materials,[11, 17, 26] herein, we report a novel supramolecular organic framework (named **SOF**-**THBP**, Scheme 1) which was based on a host (**DPSH**)-guest (**DPHB**) system and constructed by a novel bis-thioacetylhydrazine functionalized pillar[5]arene (**DPSH**) and a bis-bromohexane functionalized pillar[5]arene (**DPHB**). Interestingly, the xerogel of **SOF-THBP** shows excellent recyclable separation properties for Hg^{2+}, Cr^{3+}, Cu^{2+} and Fe^{3+}. More importantly, the **SOF-THBP** shows fluorescent response for Hg^{2+}, Cr^{3+}, Cu^{2+} and Fe^{3+} in gel states, by rationally introduced these metal ions into the **SOF-THBP**, the obtained metal ions coordinated **SOFs** (named **MSOFs**) could fluorescently sense F^-, Br^-, and L-Cys respectively with specific selectively and high sensitivity.

The novel bis-thioacetylhydrazine functionalized pillar[5]arene derivative (**DPSH**) (Scheme 1a) has been synthesized by rationally connected a pillar[5]arene moiety and two thioacetylhydrazine groups (Scheme S1†). Interestingly, as shown in Scheme 1a, through the collaboration of the guest bis-bromohexane functionalized pillar[5]arene (**DPHB**), the host **DPSH** and the guest **DPHB** could assemble into a novel supramolecular organic framework (**SOF**-**THBP**) in cyclohexanol solution. Interestingly, the **SOF**-**THBP** could form stable gel in cyclohexanol (Scheme 1b and Table S1†), the critical gelation concentration (**CGC**) is 47.5 mM while the gel-sol transition temperature (T_{gel}) is **43~47** °C (Table S1†).

The self-assembly mechanism of the **SOF**-**THBP** were carefully investigated (Scheme 1b) via fluorescence spectra, ^{1}H NMR, IR, XRD and SEM. Firstly, in the fluorescence spectra, as shown in Fig. S11, the host **DPSH** shows fluorescence emission at 456 nm and the guest **DPHB** shows very weak fluorescence emission at 456 nm in cyclohexane solution. While, when the guest **DPHB** was added into the cyclohexane solution of host **DPSH**, the fluorescence emission at 456 nm of **DPSH** shows enhancement. Moreover, with the temperature of the **DPSH** and **DPHB** mixture hot solution dropping below the T_{gel} of **SOF-THBP**, the fluorescence emission at 456 nm shown enhancement and red shift, which indicated that there is host-guest interactions existing between **DPSH** and **DPHB**.

Then, in the host-guest titration ^{1}H NMR spectra (Fig. 1), with the addition of different equivalents **DPHB** to a solution of **DPSH**, the signals of H^1 (3.70 ppm), H^2 (1.76 ppm) and H^3 (1.45 ppm) on **DPHB** show upfield shifts (shifted to 3.62 ppm, 1.57ppm, 1.36 ppm), meanwhile, the H^b (6.78 ppm) and H^c (3.63 ppm) on **DPSH** shown downfield shifts (shifted to 6.84 ppm, 3.79 ppm). These results suggested that the alkyl chains of **DPHB** were threaded into the cavity of **DPSH** via C-H$\cdots\pi$ interactions[31] (Scheme 1b). At same time, in the concentration-dependent ^{1}H NMR spectra of **DPSH** (Fig. S12†), with the increasing of the **DPSH**' s concentration, the signals of H^a (3.63 ppm), H^b (6.78 ppm) and H^d (10.08 ppm) on **DPSH** shown downfield shifts (shifted to 3.71 ppm, 6.81 ppm, 10.13 ppm). Meanwhile, in the corresponding IR spectra (Fig. S13†), the -C=O and -NH vibration absorption peaks of **DPSH** appeared at 1734 and 3460 cm^{-1} respectively, however, in the mixture of **DPSH** and **DPHB**, the -C=O and -NH vibration absorption peaks shifted to 1668 and 3406 cm^{-1}, which indicated that H^a and H^d formed stable intermolecular hydrogen bonds with -C=O on adjacent molecule (Scheme 1b). Therefore, by the collaboration of above mentioned C-H$\cdots\pi$ and intermolecular hydrogen bond interactions, **DPSH** and **DPHB** assembled into the 2D network **SOFs** structure (Scheme 1b).

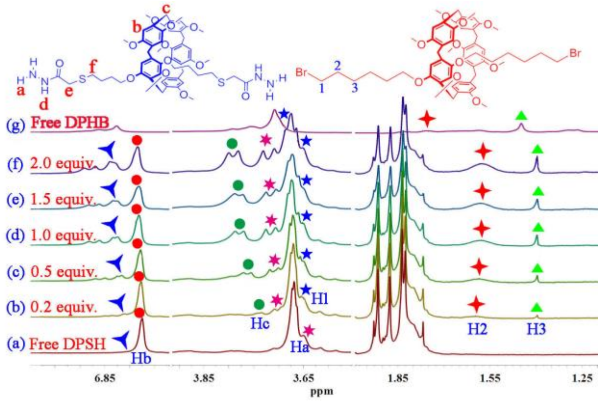


Fig 1. Partial ^{1}H NMR spectra of **DPSH** (9.5×10^{-4} mol/L) in DMSO-d_6 with increasing amounts of **DPHB**, (a) Free **DPSH**; (b)-(f) **DPSH** with increasing amounts of **DPHB**; (g) Free **DPHB** .

Moreover, in the small-angle XRD (Fig. S14†), the XRD patterns of free **DPSH** or **DPHB** show very few diffraction peaks, wich indicated that there is no long-range order in the free **DPSH** or **DPHB**. However, the XRD patterns of the **SOF**-**THBP** xerogel clearly show many typical diffraction peaks indicated the long-range ordering of the assembled-molecules. The *d*-spacing of 3.48 and 3.59 Å at 2θ=25.53 and 24.74° suggested that π-π stacking (Scheme 1b) exists in the 2D networks through the pillar[5]arene groups. Moreover, the *d*-spacing of 3.98Å at 2θ=22.30° also supported the 3D layers structure (Scheme 1c) exists in the **SOF**-**THBP**.

The scanning electron microscope (SEM) also support above proposed assemble mechanism. In the SEM, the **DPSH** exists in amorphous powder (Fig. S15a†), while, upon the addition 1 equiv. of the guest **DPHB**, the **DPSH** and the **DPHB** self-assembled into massive structure (Fig. S15b†), on the other hand, it also testified that **DPSH** formed 3D **SOF** with **DPHB** by self-assembly and host-guest complexation.

Table 1. Adsorption percentage of **SOF-THBP** for Fe^{3+}, Cu^{2+}, Cr^{3+} and Hg^{2+}.

Entry	Ion	Initial concentration (M)	Residual concentration (M)	Adsorption percentage %
1	Hg^{2+}	1×10^{-5}	6.59×10^{-7}	93.41%
2	Cu^{2+}	1×10^{-5}	3.03×10^{-7}	96.96%
3	Fe^{3+}	1×10^{-5}	7.06×10^{-8}	99.29%
4	Cr^{3+}	1×10^{-5}	4.01×10^{-7}	95.99%

In order to evaluate the guests detection and separation properties of the **SOF-THBP**, at first, we carefully investigated the cations response properties by adding and diffusing various metal ions (Mg^{2+}, Ca^{2+}, Cr^{3+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Ba^{2+}, Al^{3+}, La^{3+}, Eu^{3+} and Tb^{3+}) into **SOF-THBP** gels, respectively. Interestingly, as shown in Fig. S16, upon the addition of 1.0 equiv. of Fe^{3+}, Cu^{2+}, Cr^{3+}, or Hg^{2+} into **SOF-THBP**, the fluorescence emission of the **SOF-THBP** was quenched. The lowest fluorescent response concentration of Fe^{3+}, Cr^{3+}, Cu^{2+} and Hg^{2+} for the **SOF-THBP** were determined by fluorescent titrations and calculated on the basis of 3σ/m method [32] (Fig. S17†), which were distribute in the range of 1.0×10^{-6} M to 1.0×10^{-7} M (Table S2†) and indicated the **SOF-THBP** have high sensitivities for above mentioned cations.

Then, the ingestion capacity of the **SOF-THBP** for Fe^{3+}, Cu^{2+}, Cr^{3+} and Hg^{2+} in water were assessed by inductively coupled plasma (ICP) analysis. Xerogel (0.1 mg, 5×10^{-8} mol) was suspended in a dilute aqueous solution of Fe^{3+}, Hg^{2+}, Cr^{3+}, Cu^{2+} (all concentration is about 1×10^{-5} M in 5.0 mL) and stirred for 0.5 h. Then, the suspension was centrifuged at 10000 r/min for 5 min, the precipitate was removed by the way of filtration. Then, the absorbing rate percentage of the **SOF-THBP** for Fe^{3+}, Cu^{2+}, Cr^{3+} and Hg^{2+} in water were assessed by ICP analysis. As shown in Table 1, after the adsorption these cations via xerogel of the **SOF-THBP** in water, the residual concentrations of Fe^{3+}, Cu^{2+}, Cr^{3+} and Hg^{2+} were less than 6.59×10^{-7} M~7.06×10^{-8} M and the absorption rate of the **SOF-THBP** for these cations were up to 93.41%~99.29%. These results indicated that the **SOF-THBP** has excellent adsorption and removal capacities for Fe^{3+}, Cr^{3+}, Hg^{2+} and Cu^{2+} in water. Meanwhile the ingestion capacity of the free **DPSH** or **DPHB** for Fe^{3+}, Cu^{2+}, Cr^{3+} and Hg^{2+} in water were also investigated by ICP analysis. As shown in Table S4 and S5, the adsorption percentages of the free **DPSH** or **DPHB** for these metal ions were lower than the **SOF-THBP**. In addition, a comprehensive comparison of **SOF-THBP** with reported materials on adsorption percentage for Fe^{3+}, Cu^{2+}, Cr^{3+} and Hg^{2+} were listed in Table S6. The results shown that the **SOF-THBP** has strong adsorption ability for these cations.

Furthermore, in order to investigate the recyclability of the **SOF-THBP**, after absorbing above cations, the **SOF-THBP** was extracted by using dichloromethane. Reuse of the recycled **SOF-THBP** showed almost no loss of activities in the capture of these cations (Scheme 1d). These features are of utmost importance for the practical applications of the **SOF-THBP** in the removal of Fe^{3+}, Cu^{2+}, Cr^{3+} and Hg^{2+} in water.

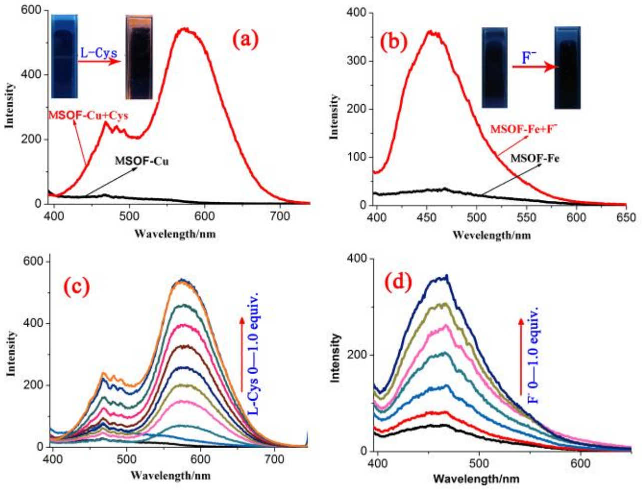


Fig 2. Fluorescence spectra of supramolecular organic framework (in gelated state) (a) **MSOF-Cu** and **MSOF-Cu** + L-Cys; (b) **MSOF-Fe** and **MSOF-Fe + F^-**; (c) The fluorescent titrations of **MSOF-Cu** for L-Cys; (d) The fluorescent titrations of **MSOF-Fe** for F^-.

Due to the **SOF-THBP** shown excellent response and binding properties for Fe^{3+}, Cr^{3+}, Cu^{2+} and Hg^{2+}, we rationally introduced competitive coordination properties by adding these cations into **SOF-THBP** to prepare Fe^{3+}, Cr^{3+}, Cu^{2+} and Hg^{2+} coordinated **SOFs** (**MSOFs**) respectively and named as **MSOF-Fe**, **MSOF-Cu** and so on correspondingly. Interestingly, by the competitive coordination interactions, the different metal ions coordinated **SOFs** (**MSOFs**) shown different guest response properties. Taking **MSOF-Fe** as an example, as shown in Scheme 1c (line 1) and Fig.2, with the addition of water solutions of various anions (F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, N_3^-, SCN^-, S^{2-}, ClO_4^-, CN^-, and OH^-) into the **MSOF-Fe**, only F^- could induce the **MSOF-Fe** emitting the bright blue fluorescence at 456 nm immediately. However, other anions could not induce similar response. Therefore, the **MSOF-Fe** could selectively detect F^- in water. The detection limits of the **MSOF-Fe** for F^- is 6.93×10^{-8} M, which was also determined by fluorescent titrations and calculated on the basis of 3σ/m method [32] (Fig. 2b, S18† and Table S2†). Similar tests were applied to the other metal ions coordinated **SOFs**. As a result, the **MSOF-Hg** could selectively fluorescence “turn-on” sense Br^- (Scheme 1c line 2; and Fig. S19† and S18†), and the detection limits of the **MSOF-Hg** for Br^- is 4.79×10^{-8} M (Fig. S18b† and Table S2†). Moreover, in order to investigate the selectivity of the **MSOF**s for these anions, as shown in Figure S20, the control experiments were carried out under the competition conditions. The coexist competition anions could not induce any interfere in the F^- sensing process for **MSOF-Fe** or Br^- sensing process for **MSOF-Hg**.

Moreover, due to the special importance of amino acids in biological field, we also investigated the recognition profiles of metal ions coordinated **SOFs** toward various amino acids, including L-Phe, L-Gln, L-Ile, L-Thr, L-Glu, L-Ala, L-Ser, L-Met, L-Val, L-Tyr, L-Ary, DL-Asp, L-Pro, L-His, L-Leu, L-Gly and L-Cys (water solution, c = 0.1 M) via similar methods. As a result, the **MSOF-Fe** and **MSOF-Cu** could selectively sense L-Cys (Scheme 1c (line 3 and 4), Fig. 2a, S19a† and S18†) respectively. With the addition of water solutions of various amino acids into these **SOFs**, only L-Cys could induce **MSOF-Fe** emitting a bright blue fluorescence at 453 nm (Fig.S19a†), similarly, as shown in the Scheme1c (line 4), L-Cys could also induce the **MSOF-Cu** emitting a orangered fluorescence at 574 nm (Fig. 2a). The lowest detection limits of **MSOF-Cu** and **MSOF-Fe** for L-Cys is 6.09×10^{-8} and 5.38×10^{-8} respectively (Fig. 2c, S18c† and Table S2†). Moreover, in order to investigate the selectivity of the **MSOF**s for these amino acids, as shown in Figure S21, the control experiments were carried out under the competition conditions. The coexist competition amino acids could not induce any interfere in the L-Cys sensing process for **MSOF-Fe** or L-Cys sensing process for **MSOF-Cu**.

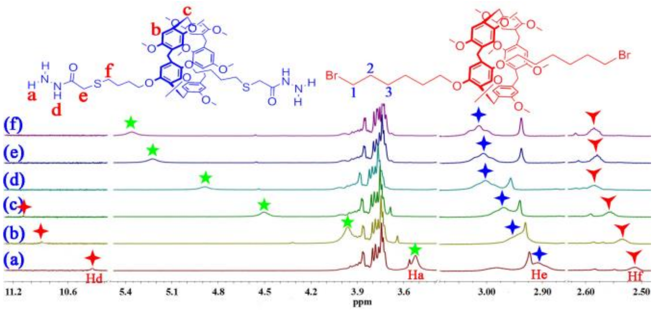


Fig 3. Partial ^{1}H NMR spectra of **SOF-THBP** in DMSO-d_6 with different equivalent Hg^{2+}; (a) Free **SOF** gel; (b) 0.1 equiv.; (c) 0.3 equiv.; (d) 0.5 equiv.; (e) 1.0 equiv.; (f) 2.0 equiv.

Then, the selective possible responsive mechanism of the **SOFs** was carefully investigated by ^{1}H NMR titration and IR spectra. For instance, in the FT-IR of the **SOF-THBP** (Fig. S22†), the stretching vibration absorption of -C=O and -NH groups appeared at 1668 and 3406 cm^{-1}, respectively. While, with the addition of Fe^{3+} into the **SOF-THBP** gel and the formation of Fe^{3+} coordinated **MSOF-Fe**, the -C=O and -NH absorptions shifted to 1676 and 3255 cm^{-1} respectively, which was attributed to the coordination of Fe^{3+} with -C=O and -NH groups in **SOF-THBP** (Fig. S23†). Because at every coordinated point the first thing happens is electron transfer, electron would transfer with coordination between **SOF-THBP** and Fe^{3+}, which induced the fluorescence of **SOF-THBP** gel quenching. After the addition of L-Cys into **MSOF-Fe**, the stretching vibration absorptions of -C=O and -NH recovered to 1667 and 3406 cm^{-1}, respectively (Fig. S22†), which indicated that the L-Cys competitively binds with the Fe^{3+} and the hydrazide group of the **SOF-THBP** released again (Fig. S23†), simultaneously, the fluorescence recovered. Meanwhile, after the addition of F^- into **MSOF-Fe**, the stretching vibration absorptions of -C=O and -NH recovered to 1667 and 3405 cm^{-1}, respectively (Fig. S24†), which indicated that the F^- competitively binds with the Fe^{3+} and the hydrazide group of the **SOF-THBP** released again (Fig. S25†), simultaneously, the fluorescence also recovered.

Similarly, as shown in Figure S26; with the addition of Cr^{3+} into the **SOF-THBP** and the formation of Cr^{3+} coordinated **MSOF-Cr**, the -C=O and -NH stretching vibration absorptions shifted to 1655 and 3426 cm^{-1} respectively, which was attributed to the coordination of Cr^{3+} with -C=O and -NH groups in **SOF-THBP** (Fig. S27†). The coordination procedure also induced the fluorescence of **SOF-THBP** gel quenching.

Moreover, in the FT-IR of the **SOF-THBP** (Fig. S28†), the stretching vibration absorptions C-S-C groups appeared at 1043 cm^{-1}, with the addition of Cu^{2+} and the formation of Cu^{2+} coordinated **MSOF-Cu**, the C-S-C absorptions shifted to 1101 cm^{-1}, meanwhile, the stretching vibration absorption of -C=O and -NH groups shifted to 1738 and 3448 cm^{-1}, respectively, which was attributed to the coordination of Cu^{2+} with -C=O, -NH and C-S-C group in **SOF-THBP** (Fig. S29†). Similarly, the coordination induced the fluorescence of **SOF-THBP** gel quenching. After the addition of L-Cys into **MSOF-Cu**, the stretching vibration absorptions of -C=O, -NH and C-S-C shifted to 1669, 3429 and 1088 cm^{-1}, respectively (Fig. S28†), which indicated that the L-Cys binds with the Cu^{2+} (Fig. S29†), at the same time, the **MSOF-Cu** showed a sudden orange fluorescence emission.

Similarly, in the FT-IR of the **SOF-THBP** (Fig. S30†), with the addition of Hg^{2+} and the formation of Hg^{2+} coordinated **MSOF-Hg**, the stretching vibration absorption of C-S-C and -NH groups shifted to 1049 cm^{-1} and 3406 cm^{-1}, respectively, which was attributed to the coordination of Hg^{2+} with C-S-C and -NH groups in **SOF-THBP** (Fig. S31†). Similarly, the coordination induced the charge transfer and fluorescence of **SOF-THBP** gel quenching. After the addition of Br^- into the **MSOF-Hg**, the stretching vibration absorptions of -NH and C-S-C shifted to 3409 and 1094 cm^{-1}, respectively (Fig. S30†). This result indicated that the Br^- binds with the Hg^{2+} (Fig. S31†), at the same time, and the **MSOF-Hg** showed a red fluorescence emission.

Moreover, the titration ^{1}H NMR spectrum of Hg^{2+} for **SOF-THBP** also supported above mentioned proposed coordination mechanism. As shown in Fig. 3, upon the addition of different equivalent Hg^{2+} (1.0 mol/L) into a solution of **SOF-THBP** (1.9×10^{-2} M) in DMSO-d_6, the signals of H^a (3.52 ppm), H^d (9.85 ppm) H^e (2.91 ppm) and H^f (2.51 ppm) showed downfield shifts (shifted to 5.36 ppm, 11.10 ppm, 3.01 ppm, 2.58 ppm, respectively), which indicated that the Hg^{2+} complexed with **SOF-THBP** through the acylhydrazine group and thioether group on **DPSH**. The ^{1}H NMR titration of Br^- for **MSOF-Hg** was also carried out in DMSO-d_6. With the addition of different equivalent Br^- into a solution of **MSOF-Hg** (Fig. S32†), the signals of H^a (3.88 ppm), H^d (11.05 ppm), H^e (3.30 ppm), H^f (2.12 ppm) showed upfeld shifs (shifted to 3.41 ppm, 10.96 ppm, 3.28 ppm, 1.92 ppm, respectively), which indicated that the Br^- complexed with **MSOF-Hg**.

In summary, a novel supramolecular organic framework (**SOF-THBP**) was constructed by bis-thioacetylhydrazine functionalized pillar[5]arene. The **SOF-THBP** shows multi-guests fluorescent response in gel states. Interestingly, the xerogel of **SOF-THBP** shows excellent recyclable separation properties for Fe^{3+}, Cu^{2+}, Cr^{3+} and Hg^{2+}. More importantly, by rationally introduced these metal ions into the **SOF-THBP**, a series of metal ions coordinated **SOFs** (MSOFs) could be formed, which could selectively and sensitively sense F^-, Br^-, and L-Cys, respectively. It's a novel and efficient way for the development of multi-functional **SOFs** materials for multi-guests detection and recyclable separation.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (NSFC) (No. 21574104; 21161018; 21262032) and the Program for Changjiang Scholars and Innovative Research Team in University of Ministry of Education of China (IRT 15R56).

Keywords: supramolecular organic framework • detection and separation • pillararene • metal ions coordinated SOFs (MSOFs) • self-assembly

[1] M. Pfeffermann, R. Dong, R. Graf, W. Zajaczkowski, T. Gorelik, W. Pisula, A. Narita, K. Müllen, and X. Feng. *J. Am. Chem. Soc.* ***2015**, 137, 14525-14532.*

[2] S. Shanmugaraju, C. Dabadie, K. Byrne, A. J. Savyasachi, D. Umadevi, W. Schmitt, J. A. Kitchenc and T. Gunnlaugsson. *Chem. Sci.* ***2017**, 8, 1535.*

[3] S. Y. Ding, M. Dong, Y. W. Wang, Y. T. Chen, H. Z. Wang, C. Y. Su, and W. Wang. *J. Am. Chem. Soc.* ***2016**, 138, 3031-3037.*

[4] R. S. Patil, D. Banerjee, C. Zhang, P. K. Thallapally, and J. L. Atwood. *Angew. Chem. Int. Ed.* ***2016**, 55, 4523 -4526.*

[5] S. Mitra, H. S. Sasmal, T. Kundu, S. Kandambeth, K. Illath, D. Díaz, and R. Banerjee. *J. Am. Chem. Soc.* ***2017**, 139, 4513-4520.*

[6] E. L. Magnotti, S. A. Hughes, R. S. Dillard, S. Wang, L. Hough, A. Karumbamkandathil, T. Lian, J. S. Wall, X. B. Zuo, E. R. Wright, and V. P. Conticello. *J. Am. Chem. Soc.* ***2016**, 138, 16274-16282.*

[7] T. Ogoshi, N. Ueshima, and T. Yamagishi. *Org. Lett.* ***2013**, 15, 3742-3745***.**

[8] A. Karmakar, R. Illathvalappil, B. Anothumakkool, A. Sen, P. Samanta, A. V. Desai, S. Kurungot, and S. K. Ghosh. *Angew. Chem. Int. Ed.* ***2016**, 55, 10667–10671.*

[9] K. D. Zhang, J. Tian, D. Hanifi, Y. B. Zhang, A. C. H. Sue, T. Y. Zhou, L. Zhang, X. Zhao, Y. Liu, and Z. T. Li. *J. Am. Chem. Soc.* ***2013**, 135, 17913-17918.*

[10] J. Lü, C. Perez-Krap, M. Suyetin, N. H. Alsmail, Y. Yan, S. H. Yang, W. Lewis, E. Bichoutskaia, C. C. Tang, A. J. Blake, R. Cao, and M. Schröder. *J. Am. Chem. Soc.* ***2014**, 136, 12828-12831.*

[11] Y. M. Zhang, B. B. Shi, H. Li, W. J. Qu, G. Y. Gao, Q. Lin, H. Yao and T. B. Wei. *Polym. Chem.,* ***2014**, 5, 4722-4725.*

[12] L. Zhang, X. Zhao, Y. Liu, and Z. T. Li. *J. Am. Chem. Soc.* ***2013**, 135, 17913-17918.*

[13] T. Ogoshi, T. Yamagishi, and Y. Nakamoto. *Chem. Rev.* ***2016**, 116, 7937-8002.*

[14] a) L. l. Yang, X. X. Tan, Z.Q. Wang, and X. Zhang. *Chem. Rev.* ***2015**, 115, 7196-7239.* b) K. Yang, Y. Pei, J. Wen and Z. Pei. *Chem. Commun.* ***2016**, 52, 9316-9326.* c) K. Yang, Y. Chang, J. Wen, Y. Lu, Y. Pei, S. Cao, F. Wang, and Z. Pei. *Chem. Mater.* ***2016**, 28, 1990-1993.*

[15] a) G. C. Yu, K. C. Jie, and F. H. Huang. *Chem. Rev.* ***2015**, 115, 7240-7303.* b) D. H. Qu, Q. C. Wang, Q. W. Zhang, X. Ma, and H. Tian. *Chem. Rev.* ***2015**, 115, 7543-7588.* c) A. J. McConnell, C. S. Wood, P. P. Neelakandan, and J. R. Nitschke. *Chem. Rev.* ***2015**, 115, 7729-7793.*

[26] C. J. Li, L. Zhao, J. Li, X. Ding, S. H. Chen, Q. l. Zhang, Y. H. Yu and X. S. Jia. *Chem. Commun.,* ***2010**, 46, 9016-9018.*

[17] T. B. Wei, J. F. Chen, X. B. Cheng, H. L., B. B. Han, H. Yao, Y. M. Zhang and Q. Lin. *Polym. Chem.,* ***2017**, 8, 2005-2009.*

[18] X. D. Chi, X. F. Ji, D. Y. Xia, and F. H. Huang. *J. Am. Chem. Soc.* ***2015**, 137, 1440-1443.*

[19] I. I. Slowing, J. L. Vivero-Escoto, C. W. Wu, V. S. Y. Lin. *Advanced Drug Delivery Reviews* ***2008**, 60 1278-1288.*

[20] K. I. Shivakumar, Y. C. Yan, C. E. Hughes, D. C. Apperley, K. D. M. Harris, and G. J. Sanjayan. *Cryst. Growth Des.* ***2015**, 15, 1583-1587.*

[21] a) M. Xue, Y. Yang, X. C. Chi, X. Z. Yan, and F. H. Huang. *Chem. Rev.* ***2015**, 115, 7398-7501.* b) K. P. Carter, A. M. Young and A. E. Palmer, *Chem. Rev.* ***2014**, 114, 4564-4601.*

[22] B. O. Okesola and D. K. Smith. *Chem. Soc. Rev.,* ***2016**, 45, 4226-4251.*

[23] a) C. R. Wade, A. E. J. Broomsgrove, S. Aldridge, and F. P. Gabbai. *Chem. Rev.* ***2010**, 110, 3958-3984.* b) Y. Zhou, J. F. Zhang, and J. Yoon. *Chem. Rev.* ***2014**, 114, 5511-5571.*

[24] S. Dong, B. Zheng, F. Wang, and F. H. Huang. *Acc. Chem. Res.* ***2014**, 47, 1982-1994.*

[25] a) Q. Lin, T. T. Lu, J. C. Lou, G. Y. Wu, T. B. Wei and Y. M. Zhang. *Chem. Commun.,* ***2015**, 51, 12224-12227.* b) T. B. Wei, J. F. Chen, X. B. Cheng, H. Li, B. B. Han, Y. M. Zhang, H. Yao and Q. Lin, *Org. Chem. Front.,* ***2017**, 4, 210.* c) Q. Lin, X. Liu, T. B. Wei, Y. M. Zhang. *Chem. Asian J.,* ***2013**, 3015-3021*.

[26] a) Q. Lin, T. T Lu, X. Zhu, T. B. Wei, H. Li, Y. M. Zhang. *Chem. Sci.,* ***2016**, 7, 5341-5346.* b) Q. Lin, B. Sun, Q. P. Yang, Y. P. Fu, X. Zhu, T. B. Wei, and Y. M. Zhang. *Chem. Eur. J.* ***2014**, 20, 11457-11462.*

[27] S. Y. Ding, M. Dong, Y. W. Wang, Y. T. Chen, H. Z. Wang, C. Y. Su, and W. Wang. *J. Am. Chem. Soc. 2016, 138, 3031-3037.*

[28] Q. Sun, B. Aguila, J. Perman, L. D. Earl, C. W. Abney, Y. C. Cheng, H. Wei, N. Nguyen, L. Wojtas, S. Q. Ma. *J. Am. Chem. Soc.* ***2017**, 139, 2786-2793.*

[29] C. E. Paulsen and K. S. Carroll. *Chem. Rev.* ***2013**, 113, 4633-4679.*

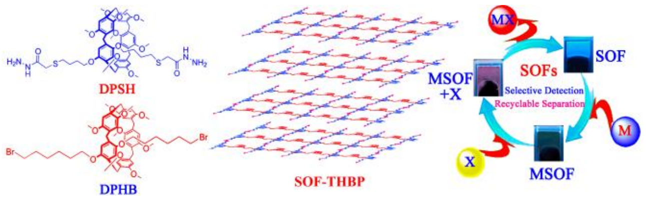
[30] a) E. Krieg, M. M. C. Bastings, P. Besenius, and B. Rybtchinski. *Chem. Rev.* ***2016**, 116, 2414-2477.* b) F. Lecaille, J. Kaleta, and D. Bromme. *Chem. Rev.* ***2002**, 102, 4459-4488.* c) D. W. Zhang, A. Martinez, and J. P. Dutasta. *Chem. Rev.* ***2017**, 117, 4900-4942*

[31] S. A. Reid, S. Nyambo, L. Muzangwa, B. Uhler. *J. Phys. Chem.* ***2013**, 117, 13556-13563.*

[32] Analytical Methods Committee. *Analyst,* ***1987**, 112, 199-204.*

Entry for the Table of Contents

COMMUNICATION



Multi-Functional SOFs: Novel supramolecular organic framework (**SOF-THBP**) was constructed by functionalized pillar[5]arenes. By rationally introduced metal ions into the **SOF-THBP,** a series of metal ions coordinated **SOFs** (MSOFs) were constructed. The **SOF-THBP** shows excellent recyclable separation properties for Cr^{3+}, Hg^{2+}, etc. The MSOFs could selectively and sensitively sense F^-, Br^-, and L-Cys, respectively.

Qi Lin[a], Yan-Qing Fan[a], Peng-Peng Mao[a], Lu Liu[a], Juan Liu*[b], You-Ming Zhang[a], Hong Yao[a], Tai-Bao Wei*[a]*

Page No. – Page No.

Pillar[5]arenes-Based Supramolecular Organic Framework with Multi-Guests Detection and Recyclable Separation Properties