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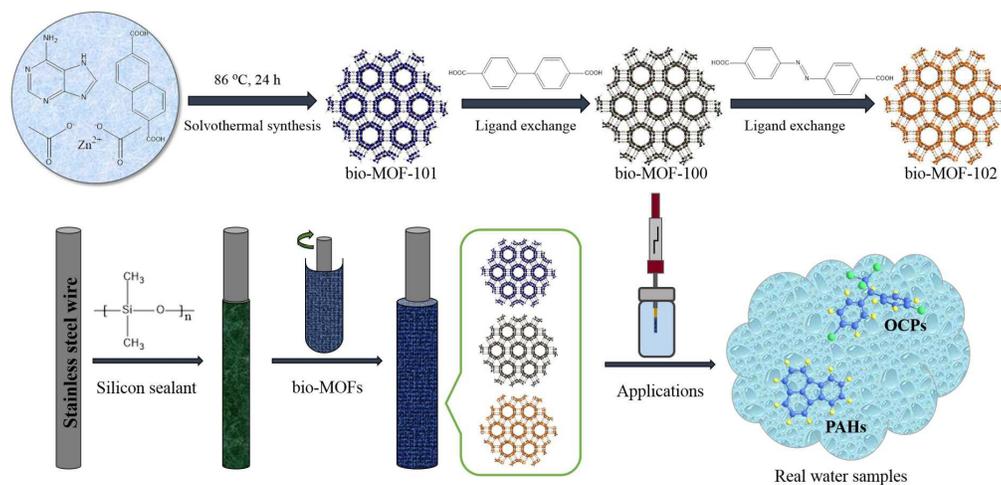
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The stepwise ligand exchange strategy was successfully utilized for the improvement of adsorption ability of a series of bio-MOFs for the first time and the proposed method was applied to the determination of environmental water samples.





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COMMUNICATION

Isorecticular bio-MOFs 100-102 coated solid-phase microextraction fibers for fast and sensitive determination of organic pollutants by pore structure dominated mechanism

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Here we report the successful utilization of the stepwise ligand exchange strategy for the improvement of adsorption ability of a series of bio-MOFs. The fast extraction rate and the different adsorption performances of the three bio-MOFs coatings were dominated by their pore structures.

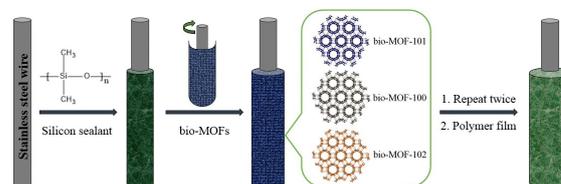
Hierarchical materials are organized by the functional subunits on multiple levels from the molecule scale through the mesoscale.^{1,2} Metal-organic frameworks (MOFs) can be viewed as a kind of hierarchical materials as they are hybrid crystalline compounds composed of organic linkers and metal cations, which link together to form the functional mesostructures.^{3,4} The inorganic-organic hybrid nature then leads to the permanent porosity, high specific surface area and pore volume, out-surface modification and tunable pore size of the MOFs, which result in various applications such as gas-storage, exchange or separation, heterogeneous catalysis, drug delivery and magnetism.^{5,6}

In recent years, MOFs have received more and more attentions in the field of sample preparation and chromatographic separation.⁷⁻¹⁰ Up to date, several MOFs including IRMOF-3,¹¹ MAF-X8,¹² MIL-101(Cr),¹³ MOF-199,¹⁴ ZIF-7 and ZIF8,¹⁵ MIL-53(Al),¹⁶ ZIF-9,¹⁷ MIL-88,¹⁸ MOF-199/GO,¹⁹ MOF-199/CNTs²⁰ and UiO-66,²¹ have been applied as novel coating materials for solid-phase microextraction (SPME)²²⁻²⁵ of various analytes. The prominent adsorption performance of the proposed MOFs-coated SPME adsorbents were mainly come from the porous structure, the high surface area and the conjugated interaction of the materials. In fact, the structure tunable nature of the MOFs makes it possible for the design of the task-specific SPME adsorbents. By varying inorganic/organic components, molecular topologies and organic linkers, ideally novel MOFs with additional feature can be created.²⁶ Unfortunately, although more and more researchers have focused their attention on the rational design and optimization of novel MOFs and the

regulation of pore structures in these materials,²⁷⁻³⁰ the utilization of tunable design strategy for the improvement of adsorption ability is still underdeveloped.

Herein, with the help of stepwise ligand exchange strategy,³ the potential use of the isorecticular bio-MOFs 100-102 as SPME coatings was systematically investigated for the first time in this work. The extraction efficiencies of the bio-MOFs fibers were evaluated by using polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) as the target analytes. The fast and excellent extraction performances of the bio-MOFs-coated SPME fibers were explored by theoretical analysis. To the best of our knowledge, the preparation of a series of isorecticular bio-MOFs with different ligands as SPME adsorbents and the exploration of their extraction mechanisms were firstly reported in this work.

For the fabrication of the bio-MOFs-coated fibers, the neutral silicone sealant was used as the bridging agent with the help of the solidification reaction (see ESI†). The series of isorecticular bio-MOFs 100, 101 and 102 with permanent mesoporosity and pore sizes ranged from 2.1-2.6 nm and BET surface areas ranging from 3222-4410 m² g⁻¹ were synthesized by solvothermal method and stepwise ligand exchange reaction (see ESI†).³⁰ With the ordered mesopores and ultrahigh surface area, these isorecticular bio-MOFs are believed to have superior potential for adsorption applications.



Scheme 1 Schematic demonstration for the fabrication of the bio-MOFs-coated SPME fibers.

As shown in Scheme 1, the stainless steel wire was dipped into the silicone sealant dispersed with *o*-xylene and a thin film of silicone sealant formed on the surface of the wire. The wire was subsequently rotated in the synthesized bio-MOF-101 to get the single-layer coating. Then the single-layer fiber was cured at 150 °C for 30 min to evaporate the dispersing agent and realize the solidification reaction before the next coating procedure. Repeat

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the above procedures for twice and a three-layer bio-MOF-101 fiber was obtained. Finally, the coated wire was dipped into the diluted silicone sealant again to form a thin film of polymer to avoid the flaking of the crystal and create a hydrophobic surface of the coating.^{11,31} The bio-MOF-100 and bio-MOF-102 coatings were fabricated by the same procedures and all of the bio-MOFs coatings possessed a rough surface with a coating thickness of nearly 25 μm (Fig. 1).

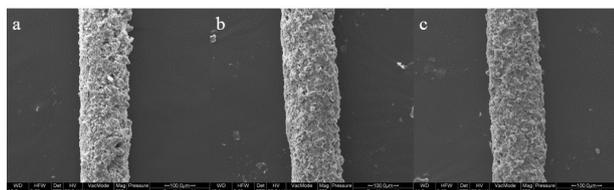


Fig. 1 Scanning electron microscopic images of (a) bio-MOF-101, (b) bio-MOF-100 and (c) bio-MOF-102 fibers.

The typical X-ray diffraction patterns of the as-synthesized bio-MOFs 100-102 were all in good agreement with the simulated ones (Fig. S1, ESI[†]), which indicated the successful synthesis of the isorecticular bio-MOFs. The TGA curves of the bio-MOFs 100-102 exhibited that all of the bio-MOFs could be stable up to 370 $^{\circ}\text{C}$. The high thermostability made bio-MOFs 100-102 to be the favorable materials for preparing SPME fiber coatings.

To evaluate the extraction performance of the self-made fibers, analytes with different polarity, hydrophobicity and size were selected (Fig. S3 and Table S1, ESI[†]) and the commercial 65 μm PDMS/DVB fiber was chosen for the comparison. Before the evaluation, extraction time was optimized to achieve better extraction efficiencies (Fig. S4, ESI[†]). The bio-MOFs 100-102 coatings showed much faster extraction equilibrium (40 min) towards the analytes compared to the commercial fiber (more than 70 min). The reason was that the bio-MOFs 100-102 series possessed mesopores with the size from ~ 2.1 to 2.6 nm,³⁰ which were much larger than the maximum diameters of all the selected analytes (Table S1, ESI[†]). These mesopores allowed the analytes to diffuse through the sorbent at any angle during adsorption process and resulted in more quickly extraction rates.³²

Taking the different thickness of the self-made coatings and the commercial coating into consideration, we used "normalized extraction efficiency"¹² to compare the extraction efficiencies. As shown in Fig. 2, all the bio-MOFs 100-102 coatings showed excellent ability for enrichment of the PAHs and OCPs. Detailedly, bio-MOF-101 coating, bio-MOF-100 coating and bio-MOF-102 coating possessed normalized extraction efficiencies 1.0-17.2, 0.7-22.5 and 1.3-32.0 fold higher than those obtained by PDMS/DVB coating, respectively. Among the three bio-MOFs coatings, bio-MOF-102 coating was the best one for the enrichment of the target analytes with much better extraction efficiencies than those of the other two coatings, which indicated the successful utilization of ligand exchange strategy for the improvement of adsorption ability. Besides, the same extraction experiments were performed with the pure silicone sealant coated fiber and the blank stainless steel wire. The bio-MOFs fibers possessed much better adsorption abilities compared with the pure silicone sealant fiber and the stainless steel wire fiber (Fig. S5, ESI[†]), especially for the large size analytes, which reflected that the outstanding adsorption performance of the self-

made fibers mostly came from the bio-MOFs instead of the silicone sealant or the stainless steel wire.

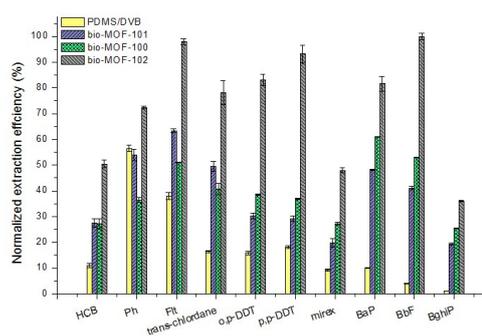


Fig. 2 Comparison of the normalized extraction efficiencies of bio-MOFs coated fibers and the PDMS/DVB fiber. Sample volume, 10 mL; concentration, 6 $\mu\text{g L}^{-1}$ for six OCPs, 5 $\mu\text{g L}^{-1}$ for four PAHs and 2.5 $\mu\text{g L}^{-1}$ for BghiP; extraction time, 40 min for bio-MOFs fibers and 70 min for PDMS/DVB fiber; desorption time, 300 s; desorption temperature, 260 $^{\circ}\text{C}$.

Theoretical analysis was used to explore the adsorption mechanism of the bio-MOFs-coated fibers. The simulated adsorption energies and the adsorption quantities of the three bio-MOFs towards the ten target analytes were carried out by Materials Studio. From the results (Fig. 3), all of the three bio-MOFs showed good affinities for the target analytes and no obvious differences among the three curves were observed. Besides, the bio-MOFs showed better affinities to the PAHs than the OCPs which may probably result from the π - π stacking effect between the adsorbents and the PAHs. The similar adsorption energies of the three bio-MOFs indicated that the three bio-MOFs had the same affinity to each analyte and the different adsorption performances of them were not caused by their affinities to the analytes.

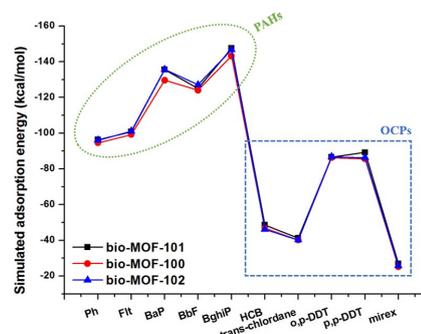


Fig. 3 Simulated adsorption energies of the ten analytes adsorbed by the bio-MOFs 100-102 crystal cells.

However, when we pressed all of the ten analytes into the simulated bio-MOFs crystal cells respectively with the analytes pressures in direct proportion to their concentrations in working solution, we can find that the simulated adsorption quantity of each analyte was mostly relevant to their adsorption amount conducted by SPME. The simulated adsorption quantity of each analyte in bio-MOF-102 crystal cell and the SPME extraction amount of the bio-MOF-102 coating were shown in Fig. 4(a). Obviously, the two curves presented the same trend. From the simulated adsorption quantities of the three bio-MOFs (Fig. 4(b)), bio-MOF-102 exhibited the best adsorption performance to the analytes, which was

consistent with the extraction results shown in Fig. 2. However, the bio-MOF-100 presented better simulated adsorption ability than the bio-MOF-101 while the real extraction results in Fig. 2 showed that they had similar adsorption performance. That was because the as-synthesized bio-MOF-100 in this work had some defects created during the ligand exchange process, which has been reported in the previous works.^{30,33} The bio-MOF-102 was reported to have a high pore volume that exceed $4 \text{ cm}^3 \text{ g}^{-1}$, while the bio-MOF-101 possessing a pore volume of $2.8 \text{ cm}^3 \text{ g}^{-1}$. Due to the defects, the pore volume of the bio-MOF-100 decreased to that was similar to the pore volume of bio-MOF-101. This might be the reason why the bio-MOF-100 coating did not present better extraction performance compared with the bio-MOF-101 coating. In conclusion, the different adsorption performances of the three bio-MOFs coatings were mainly caused by their different abilities to accommodate the target analytes, which was directly relevant to their pore volumes.

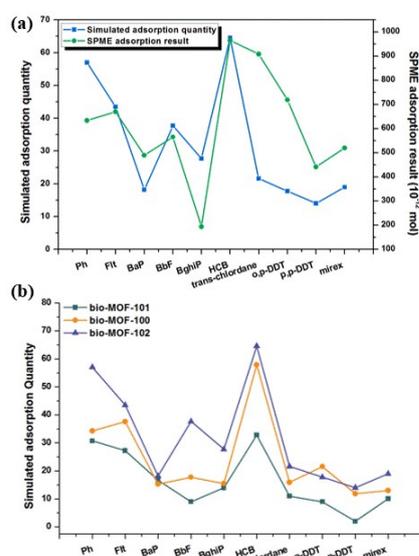


Fig. 4 (a) The simulated adsorption quantities of each analyte in bio-MOF-102 crystal cell and the SPME extraction results of the bio-MOF-102 coating. (b) The simulated adsorption quantities of the bio-MOFs 100-102 crystal cells.

The analytical performances of the bio-MOF-102 fiber which possessed the best extraction ability were listed in Table S2 (see ESI[†]). The method showed wide linear ranges, low LODs and good reproducibilities. The developed method was then applied to the determination of the PAHs and OCPs in environmental water samples including pond water and river water and satisfactory recoveries were achieved (Table S3, ESI[†]).

In summary, the stepwise ligand exchange strategy was successfully utilized for the improvement of adsorption ability of a series of bio-MOFs for the first time in this work. Theoretical analysis indicated that the fast extraction rate and the different adsorption performances of the three bio-MOFs coatings towards the target analytes were dominated by the mesopores and the different pore volumes of the bio-MOFs. This work indicated that MOF materials could be rationally designed to serve as promising adsorbents for SPME and other applications, such as gas-storage, separation and etc.

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Notes and references

- T. Li, J. E. Sullivan and N. L. Rosi, *J. Am. Chem. Soc.* 2013, **135**, 9984.
- W. Gao, W. Yan, R. Cai, L. Meng, A. Salas, X. Wang, L. Wojtar, X. Shi and S. Ma, *Inorg. Chem.* 2012, **51**, 4423.
- D. D. Sante, A. Stroppa, P. Jian and S. Picozzi, *J. Am. Chem. Soc.* 2013, **135**, 18126.
- A. Stroppa, P. Barone, J. M. Perez-Mato and S. Picozzi, *Adv. Mater.* 2013, **25**, 284.
- D. Bradshaw, A. Garai and J. Huo, *Chem. Soc. Rev.* 2012, **41**, 2344.
- O. Shekha, J. Liu, R. Fischer and C. Wöll, *Chem. Soc. Rev.* 2011, **40**, 1081.
- Z. Gu, C. Yang, N. Chang and X. Yan, *Acc. Chem. Res.* 2012, **45**, 734.
- Z. Gu and X. Yan, *Angew. Chem., Int. Ed.* 2010, **49**, 1477.
- N. Chang, Z. Gu and X. Yan, *J. Am. Chem. Soc.* 2010, **132**, 13645.
- C. Yang and X. Yan, *Chinese J. Anal. Chem.* 2013, **41**, 1297.
- J. Zheng, S. Li, Y. Wang, L. Li, C. Su, H. Liu, F. Zhu, R. Jiang and G. Ouyang, *Anal. Chim. Acta* 2014, **829**, 22.
- C. He, J. Tian, S. Liu, G. Ouyang, J. Zhang and X. Chen, *Chem. Sci.* 2013, **4**, 351.
- L. Xie, S. Liu, Z. Han, R. Jiang, H. Liu, F. Zhu, F. Zeng, C. Su and G. Ouyang, *Anal. Chim. Acta* 2015, **853**, 303.
- X. Cui, Z. Gu, D. Jiang, Y. Li, H. Wang and X. Yan, *Anal. Chem.* 2009, **81**, 9771.
- N. Chang, Z. Gu, H. Wang and X. Yan, *Anal. Chem.* 2011, **83**, 7094.
- X. Chen, H. Zang, X. Wang, J. Cheng, R. Zhao, C. Cheng and X. Liu, *Analyst* 2012, **137**, 5411.
- L. Yu and X. Yan, *Chem. Commun.* 2013, **49**, 2142.
- Y. Wu, C. Yang and X. Yan, *J. Chromatogr. A* 2014, **1334**, 1.
- S. Zhang, Z. Du and G. Li, *Talanta* 2013, **115**, 32.
- Z. Zhang, Y. Huang, W. Ding, and G. Li, *Anal. Chem.* 2014, **86**, 3533.
- H. Shang, C. Yang and X. Yan, *J. Chromatogr. A* 2014, **1357**, 165.
- G. Ouyang, D. Vuckovic and J. Pawliszyn, *Chem. Rev.* 2011, **111**, 2784.
- D. Vuckovic and J. Pawliszyn, *Anal. Chem.* 2011, **83**, 1944.
- H. Bagheri, H. Piri-Moghadam and M. Naderi, *Trends Anal. Chem.* 2012, **34**, 126.
- J. Xu, J. Zheng, J. Tian, F. Zhu, F. Zeng, C. Su and G. Ouyang, *Trends Anal. Chem.* 2013, **47**, 68.
- C. Liu, T. Li and N. L. Rosi, *J. Am. Chem. Soc.* 2012, **134**, 18855.
- K. Hu, M. Kurmoo, Z. Wang and S. Gao, *Chem. Eur. J.* 2009, **15**, 12050.
- E. Pardo, C. Train, H. Liu, L. M. Chamoreau, B. Dkhil, K. Boubekeur, F. Lloret, K. Nakatani, H. Tokoro, S. Ohkoshi and M. Verdager, *Angew. Chem., Int. Ed.* 2012, **124**, 8481.
- M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter and M. O'Keeffe, *Science* 2002, **295**, 469.
- T. Li, M. T. Kozłowski, E. A. Doud, M. N. Blakely and N. L. Rosi, *J. Am. Chem. Soc.* 2013, **135**, 11688.
- W. Zhang, Y. Hu, H. Jiang and S. Yu, *J. Am. Chem. Soc.* 2014, **136**, 16978.
- H. Wu, Q. Gong, D. H. Olson and J. Li, *Chem. Rev.* 2012, **112**, 836.
- J. An, O. K. Farha, J. T. Hupp, E. Pohl, J. L. Yeh and N. L. Rosi, *Nat. Commun.* 2012, **3**, 604.