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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

A porous Cd(II)-MOF-coated quartz fiber for solid-phase microextraction of BTEX

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

The utilization of a porous Cd(II)-MOF ($[\text{Cd}(\text{L})_2(\text{ClO}_4)_2] \cdot \text{H}_2\text{O}$) (L = 4-amino-3,5-bis(4-pyridyl-3-phenyl)-1,2,4-triazole) with good thermal/chemical stability for solid-phase microextraction (SPME) is reported. The Cd(II)-MOF thin films are expediently in situ grown on quartz fiber in solution, which exhibit high sensitivity and selectivity towards volatile benzene, toluene, *o*-, *m*-, *p*-xylene, and ethylbenzene (termed as BTEX) aromatics. The limits of detection for BTEX are 0.01-0.001 μgL^{-1} .

Introduction

Solid-phase microextraction (SPME) as a green analysis method,^[1] established by Pawliszyn in the 1990s,^[2] is proven to be an effective and practical analysis method which is widely used in environmental science and life science.^[3] SPME involves absorbing the target analyte from the sample onto a stationary phase coated on the fiber. The stationary phases coated on the fibers in SPME are generally organic polymers,^[4] sol-gel coatings^[5] and immunosorbents.^[6] Some of fiber coatings now are commercially available, including poly(dimethylsiloxane) (PDMS), divinylbenzene (DVB), polyacrylate (PA) Carboxen (CAR) and poly(ethylene glycol) (PEG; Carbowax, CW). On the other hand, metal-organic frameworks (MOFs),^[7] as an important class of hybrid porous materials, exhibit a promising application for molecular adsorption and separation. Therefore, they could be the excellent candidates for preparing new types of extraction fiber coatings for SPME, so the MOFs would be expected to effectively enlarge the applicability of SPME. Compared to the analyte extraction based on the fiber coatings mentioned above, the SPME performed on MOFs-coated fibers, however, has received very limited investigation. Up to date, only a few SPME fiber coatings based on porous MOFs fabricated by hydrothermal or solvothermal approach have been reported.^[8]

It is well known that aromatic compounds such as benzene, toluene, *o*-, *m*-, *p*-xylene, and ethylbenzene (termed as BTEX) are typical volatile organic compounds (VOCs) of great social and environmental significance.^[9] They are widely used in the manufacture of paints, agricultural chemicals, artificial rubber and chemical intermediates, which results in the BTEX species widely existing in water, air, soil and sediments. So their detection, enrichment and degradation have recently become a central interest for chemists.

We have described the preparation and adsorption of a three-

dimensional metal-organic framework of 1 ($[\text{Cd}(\text{L})_2(\text{ClO}_4)_2] \cdot \text{H}_2\text{O}$) (L = 4-amino-3,5-bis(4-pyridyl-3-phenyl)-1,2,4-triazole).^[10] It contains square-like channels with crystallographic dimensions of ca. $11 \times 11 \text{ \AA}$, and it is able to encapsulate C_6 - C_8 aromatics under ambient conditions (Figure 1). The crystals of this Cd(II)-MOF (1) are very stable and retain their single crystallinity till 300°C . The surface area calculated from the N_2 adsorption isotherm was estimated to be $205 \text{ m}^2 \text{ g}^{-1}$ (BET) and $270 \text{ m}^2 \text{ g}^{-1}$ (Langmuir), respectively (Figure S1, Supporting Information). So such porous MOFs might be ideal candidate for SPME fiber coating.

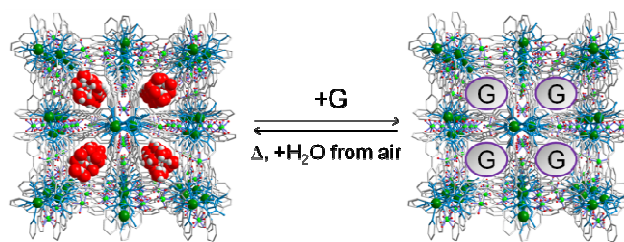


Figure 1. Aromatics adsorption based on Cd(II)-MOF in single-crystal-to-single-crystal fashion (G = benzene, toluene, *o*-, *m*-, *p*-xylene).

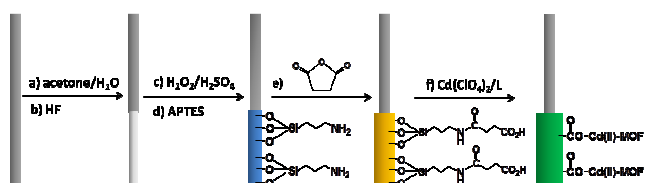
In this contribution, we report a Cd(II)-MOF-coated quartz fiber, as a new SPME device, to absorb, enrich and detect the BTEX species. The SPME fiber coated by the Cd(II)-MOF was easily fabricated by growth of Cd(II)-MOF film on the etched quartz fiber in solution under ambient conditions. Our results demonstrated that the Cd(II)-fiber is very stable in water or humidity environment, and showed excellent performance and very low detection limits in adsorption, enrichment and detection of BTEX species.

Results and Discussion

Fabrication of SPME fibers

The SPME fiber was prepared as following: The quartz fiber (diameter ca. 0.4 mm) was cleaned by acetone and then washed with water to remove the polyimide layer. The cleaned fiber (ca. 1.5 cm) was dipped into HF for 1 min., and then treated with a mixture of H_2O_2 and H_2SO_4 ($v : v = 1 : 3$) for around half an hour to generate hydroxylated surface covered fiber. The obtained fiber was further aminated by immersing the hydroxylated fiber in an EtOH solution of 3-aminopropyltriethoxysilane (APTES)

($V_{\text{APTES}} : V_{\text{EtOH}} = 1 : 15$) for 2 h. The final carboxylated fiber was prepared by dipping the aminated fiber in a saturated EtOH solution of succine anhydride for 3 h. The Cd(II)-MOF coated fiber for SPME was fabricated by immersing the fresh prepared carboxylated fiber into a mixed solution system which is composed of a CH_2Cl_2 (8 mL) solution of L (10 mg) and MeOH (8 mL) solution of $\text{Cd}(\text{ClO}_4)_2$ (12 mg) in a tube at room temperature for 10 h. After that, the Cd(II)-MOF coated fiber was assembled into a 5 μL GC microsyringe to get the SPME device (Scheme 1, the FTIR spectra see Figure S2, Supporting Information).



Scheme 1 Schematic fabrication process of Cd(II)-MOF-coated SPME quartz fiber.

Scan electron micrographs showed that the quartz fiber was uniformly coated by dense and regular Cd(II)-MOF crystals (Figure 2). The thickness of the Cd(II)-MOF coating is around 30 μm (Figure S3, Supporting Information), which is suitable for SPME. So far, the reported MOF-coated fibers are prepared by hydrothermal or solvothermal approach, the Cd(II)-MOF-coated fiber herein is the first example of MOFs-coated SPME device fabricated in solution, which is a more convenient operation approach than those of hydrothermal and solvothermal methods.

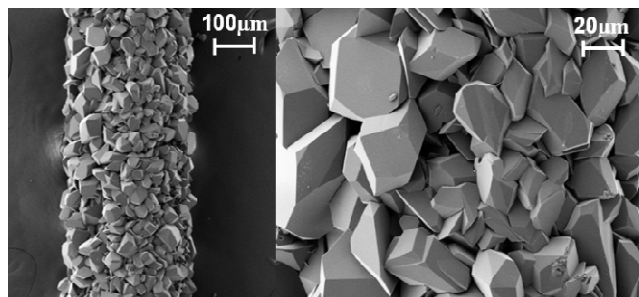


Figure 2. Scan electron micrographs of Cd(II)-MOF grown on quartz fiber.

Stability of Cd(II)-MOF coating

In practice, the target analytes collection or enrichment based on SPME are often carried out in aqueous media or humid atmosphere. In addition, the SPME sometimes performs in relative higher temperature environment. So the stability of MOFs in humid and relative high temperature environments is very important, which would determine if the MOFs are able to be the practical SPME fiber coatings. For examination of the stability of the Cd(II)-MOF coating, the corresponding X-ray powder diffractions were performed under different conditions. As shown in Figure 3, the XRPD patterns performed on the obtained Cd(II)-MOF coatings under different conditions are

identical to that of as-synthesized bulk sample, indicating the fiber coating is very stable in aqueous media, saturated water vapor and even at 250 °C. Therefore, the Cd(II)-coating herein could be a practical material to pick up the target analytes from aqueous media or high humid environment, and even at high temperature.

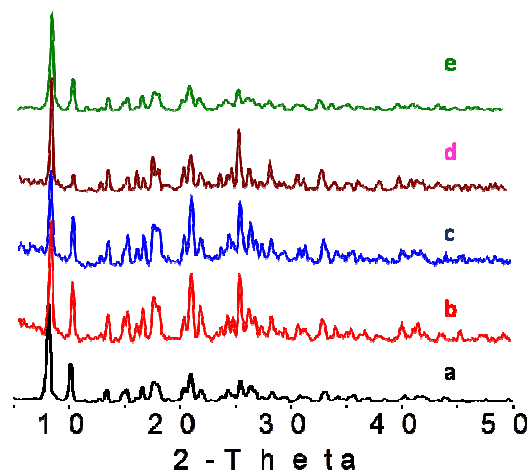
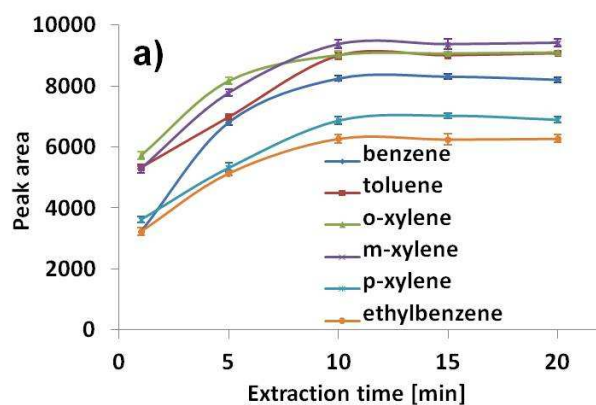


Figure 3. XRPD patterns of Cd(II)-MOF coating: a) Cd(II)-MOF bulk crystals. b) Cd(II)-MOF coating. c) Cd(II)-MOF coating in water for a week. d) Cd(II)-MOF coating in saturated water vapor for a week. e) Cd(II)-MOF coating heated at 250 °C for 30 min.

Optimized experimental parameters of Cd(II)-MOF coating for BTEX

As mentioned above, Cd(II)-MOF shows significant affinity for C_6 - C_8 aromatics, including benzene and alkyl-substituted benzene molecules. It can uptake these aromatic molecules in both liquid and vapor phases to generate G@Cd(II)-MOF ($\text{G} = \text{C}_6$ - C_8 aromatics) via single-crystal-to-single-crystal fashion.¹⁰ On the other hand, the encapsulated guest species can be easily removed by heating with retention of its single crystallinity.¹⁰ So the Cd(II)-MOF framework is rigid and stable during the adsorption and desorption processes, and definitely suitable to be the SPME fiber coating for aromatic analytes determination.



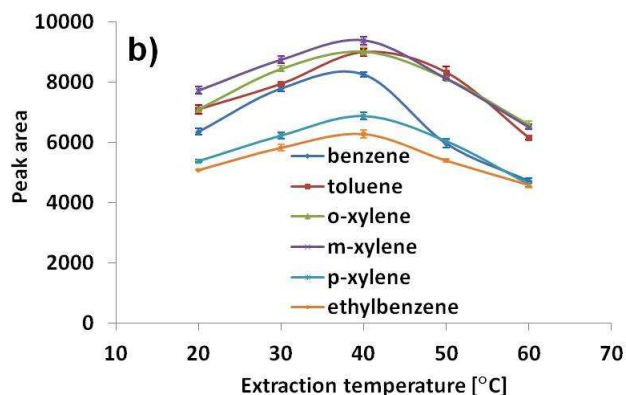


Figure 4. a) The diagram of the extraction time of Cd(II)-MOF coated fiber for benzene, toluene, ethylbenzene, and *o*-, *m*-, *p*-xylene (adsorption temperature, 40°C; desorption temperature, 250°C; desorption time, 15s; sample volume, 20 mL; analytes concentration, 3 μg L⁻¹), in which the chromatographic peak area was plotted against the trial retraction time. b) The diagram of the extraction temperature of Cd(II)-MOF coated fiber for benzene, toluene, ethylbenzene, and *o*-, *m*-, *p*-xylene (desorption temperature, 250°C; desorption time, 15s; sample volume, 20 mL; analytes concentration, 3 μg L⁻¹).

As shown in Figure 4, the BTEX analytes reached their saturated adsorption capacities on Cd(II)-MOF coated fiber in about 10 min., indicating a fast adsorption kinetics of the all the six analytes on Cd(II)-MOF coating. Notably, our previous study revealed that these encapsulated aromatic guests in Cd(II)-MOF could be removed above 40-50°C based on the thermogravimetric analysis (TGA),¹⁰ so the effect of adsorption temperature ranging from 20 to 60°C on extraction efficiency was tested. As indicated in Figure 4, the uptaken amounts increased with increasing temperature for all target aromatic analytes, the loaded amounts, however, began to gradually decrease above 40°C. So the best extraction time based on Cd(II)-MOF coating is 40°C.

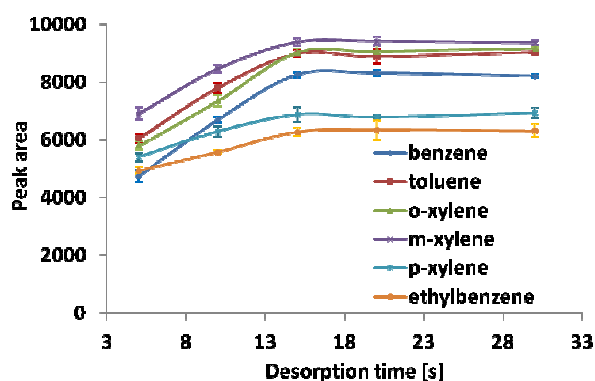


Figure 5. The diagram of the desorption time of Cd(II)-MOF coated fiber for benzene, toluene, ethylbenzene, and *o*-, *m*-, *p*-xylene (adsorption temperature, 40°C; desorption temperature, 250°C; sample volume, 20 mL; analytes concentration, 3 μg L⁻¹).

Besides extraction time and temperature, the desorption time is also an important parameter for practical SPME application. The chosen desorption temperature is 250°C, which briefly depends on the thermal stability of Cd(II)-MOF coating mentioned above. Figure 5 indicates that desorption time is very short at this temperature, and all the loaded analytes can be desorbed in 15s. Undoubtedly, the short desorption time will help to prolong the

lifetime of the injector and the fiber. In addition, the linearity for BTEX has been tested. For benzene, the Cd(II)-MOF-coated fiber exhibited a wide linearity at 2-30 μg L⁻¹ with good correlation coefficients ($R^2 > 0.9998$), and the linearity can be used for 0.5-120 μg L⁻¹ (Figure S4, Supporting Information). Unfortunately, the rest of BTEX have a poor linearity.

In short, the optimized conditions of Cd(II)-MOF coating are: extraction time, 10min; desorption time, 15 s; extraction temperature, 40°C; desorption temperature, 250°C. Under the optimized conditions, the Cd(II)-MOF-coated fiber has a very low detection limits (0.01-0.001 μg L⁻¹) for BTEX species (Table 1). In addition, no decrease of the extraction performance was detected after more than 100 replicated extractions. The observed detection limits and the number of replicated extraction times are equivalent to the reported BTEX MOF-fiber.^{8b}

Table 1. The detection limits for BTEX based on the Cd(II)-MOF-coated quartz fiber

sample	B	TOL	OX	MX	PX	EB
LOD ₁ /μg L ⁻¹	0.01	0.005	0.001	0.001	0.003	0.005

B = benzene, TOL = toluene, OX = *o*-xylene, MX = *m*-xylene, PX = *p*-xylene.

Comparison of the Cd(II)-MOF-coated fiber with commercial available fibers

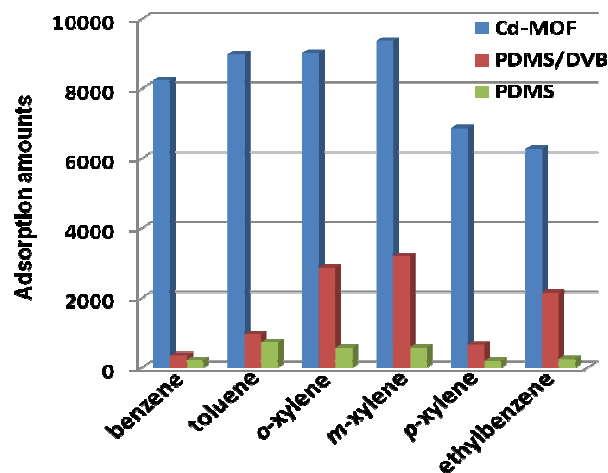


Figure 6. Comparison of the normalized extraction efficiencies of Cd(II)-MOF-coated quartz fibers and commercial SPME fibers (PDMS/DVB and PDMS) for BTEX/ (Experimental conditions: extraction temperature, 40°C; adsorption time, 10 min.; BTEX saturated NaCl solutions, 3 μg L⁻¹).

Compared to the commercial PDMS (100 μm) and PDMS/DVB (65 μm) fibers (PDMS = polydimethylsiloxane, DVB = divinylbenzene), the extraction efficiency of the Cd(II)-MOF-coated fibers is much higher under the same experimental conditions. As shown in Figure 6, Only tiny amounts of the loaded BTEX analytes by PDMS fiber were detected (green column), whereas the amounts of BTEX analytes uploaded on PDMS/DVB fiber obviously increased due to its porous structure

(red column). For *o*-, *m*-xylene and ethylbenzene species, the adsorption capacity of PDMS/DVB fiber is ca. one third of Cd(II)-MOF coated fiber. Compared to commercial SPME fibers, the big difference in extraction efficiency might result from the suitable pore size, highly regular channels of the structure as well as the hydrophobic nature of the Cd(II)-MOF SPME thin films.

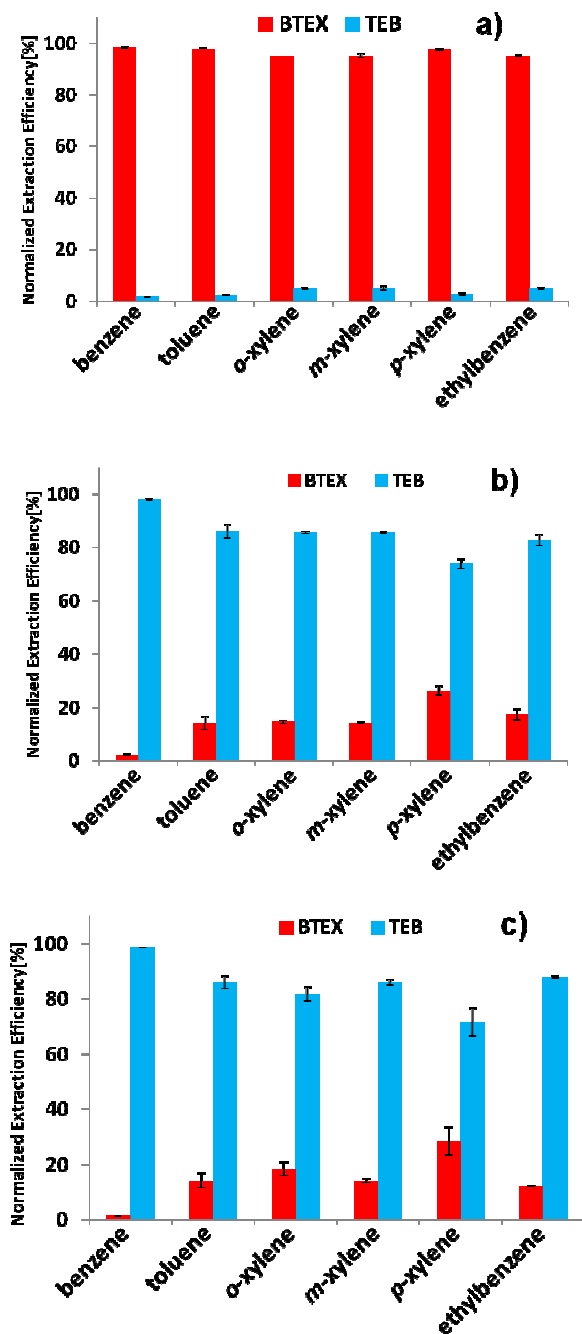


Figure 7. Comparison of the normalized extraction efficiencies of Cd(II)-MOF-coated quartz fibers (a) and commercial SPME fibers PDMS/DVB (b) and PDMS (c) for BTEX and TEB (Experimental conditions: extraction temperature, 40°C; adsorption time, 10 min.; BTEX saturated 15 NaCl solutions, 3 $\mu\text{g L}^{-1}$).

For real SPME fibers, equally important to adsorption capacity is selectivity for capturing specific target analytes in the presence

of other competitors. So the selectivity and anti-interference ability of Cd(II)-MOF coating was examined, because the BTEX 20 samples in analytical practice might contain other kinds of alkyl-substituted aromatic compounds such as 1,3,5-triethylbenzene. When the Cd(II)-MOF-coated fiber was used to pick up the analyte consisting of equimolar amounts of BTEX and 1,3,5-triethylbenzene (TEB), almost no detectable chromatographic 25 peak for TEB was found (Figure 7) under experimental conditions, so the Cd(II)-MOF-coated fiber is able to selectively adsorb of BTEX over TEB substrate. The high adsorption selectivity might be briefly attributed to the strict pore size ($11 \times 11 \text{ \AA}$) limitation of the Cd(II)-MOF. In contrast, the commercial 30 PDMS and PDMS/DVB fibers performed contrary adsorption behaviour in selectivity, and they all displayed higher affinity toward TEB instead of BTEX species.

Detection BTEX analytes in seawater

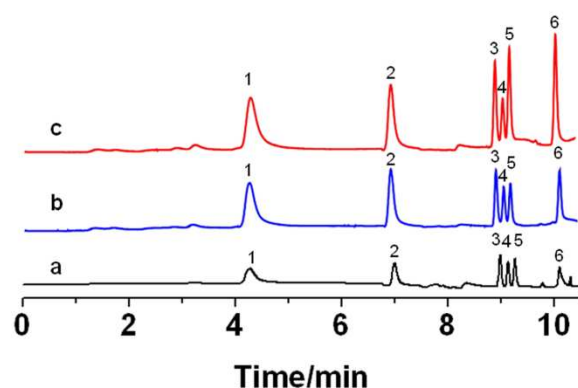


Figure 8. GC chromatograms for (a) sea water. (b) BTEX standard solution (20 ng L^{-1}). (c) spiked sample: 1 benzene; 2 toluene; 3 ethylbenzene; 4 *p*-xylene; 5 *m*-xylene; 6 *o*-xylene.

The seawater sample was collected from Kiaochow bay 40 (Huangdao, China). It was analyzed immediately after sampling without any pre-treatment. After exposure to the seawater sample at 40°C for 30 min., the Cd(II)-MOF-coated fiber was inserted into the GC injector for desorption and analysis. As shown in Figure 8, all six types of BTEX species were detected, and almost 45 no other kinds of aromatics were observed, indicating that the Cd(II)-MOF-coated fiber exhibits an excellent selectivity for BTEX species. As indicated in Table 2, recoveries obtained by spiking 20 ng L^{-1} for benzene, toluene, ethylbenzene, *o*-, *m*-, and *p*-xylene ranged from 82.61-102.06%. The RSD of 2.80-11.15% 50 were obtained from three parallel experiments on the same SPME fiber.

Table 2. Analytical results for the determination of BTEX in seawater sample

Analyte	B	TOL	OX	MX	PX	EB
Concn. (ng L^{-1})	6.28	6.65	12.28	12.71	12.68	6.06
Recovery ^a (%)	96.54	91.44	91.52	82.61	88.54	102.06
RSD ^b (%)	6.72	9.87	2.80	2.52	4.63	11.15

^a Spiked with 20 ng L⁻¹ for each BTEX; ^b n = 3

B = benzene, TOL = toluene, OX = *o*-xylene, MX = *m*-xylene, PX = *p*-xylene.

Conclusions

In summary, we have successfully fabricated a porous Cd(II)-MOF-coated quartz fiber in solution. The obtained Cd(II)-MOF-coated quartz fiber is thermal and chemical stable in aqueous media. Moreover, the Cd(II)-MOF thin films exhibits high sensitivity and selectivity towards volatile benzene, toluene, *o*-, *m*-, *p*-xylene, and ethylbenzene (BTEX) due to its unique porous structure and excellent adsorption properties for BTEX. The limits of detection for BTEX are 0.01-0.001 μg L⁻¹. The Cd(II)-MOF fiber described herein could be a specific SPME detector for BTEX species.

Acknowledgements

We are grateful for financial support from 973 Program (Grant Nos. 2012CB821705 and 2013CB933800), NSFC (Grant Nos. 21271120) and “PCSIRT”.

Notes and references

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- † Electronic Supplementary Information (ESI) available: Experimental section, including instrumentation, chemicals and reagents, GC analysis, SPME procedures and detecting the seawater. See DOI: 10.1039/b000000x/
- A. Spietelun, A. Kloskowski, W. Chrzanowski, J. Namieśnik, *Chem. Rev.* 2013, **113**, 1667.
 - (a) C. L. Arthur, J. Pawliszyn, *Anal. Chem.* 1990, **62**, 2145. (b) C. L. Arthur, L. M. Killam, K. D. Buchholz, J. Pawliszyn, *Anal. Chem.* 1992, **64**, 1960.
 - (a) E. Olkowska, Ż. Polkowska, J. Namieśnik, *Chem. Rev.* 2011, **111**, 5667. (b) G. Ouyang, D. Vuckovic, J. Pawliszyn, *Chem. Rev.* 2011, **111**, 2784.
 - F. Augusto, E. Carasek, R. G. C. Silva, S. R. Rivellino, A. D. Batista, E. Martendal, *J. Chromatogr. A* 2010, **1217**, 2533.
 - A. Kumar, Gaurav, A. K. Malik, D. K. Tewary, B. Singh, *Anal. Chim. Acta* 2008, **610**, 1.
 - W. M. Mullett, J. Pawliszyn, *J. Sep. Sci.* 2003, **26**, 251.
 - (a) J.-R. Li, J. Sculley, H.-C. Zhou, *Chem. Rev.* 2012, **112**, 869. (b) H. Wu, Q. Gong, D. H. Olson, J. Li, *Chem. Rev.* 2012, **112**, 836. (c) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae, J. R. Long, *Chem. Rev.* 2012, **112**, 724.
 - To our knowledge, only 4 research reports related to the MOFs-coated SPME fibers prepared by hydrothermal or solvothermal approach have been recently published: (a) X.-Y. Cui, Z.-Y. Gu, D.-Q. Jiang, Y. Li, H.-F. Wang, X.-P. Yan, *Anal. Chem.* 2009, **81**, 9771. (b) C.-T. He, J.-Y. Tian, S.-Y. Liu, G. Ouyang, J.-P. Zhang, X.-M. Chen, *Chem. Sci.*, 2013, **4**, 351. (c) L.-Q. Yu, X.-P. Yan, *Chem. Commun.* 2013, **49**, 2142. (d) S. Zhang, Z. Du, G. Li, *Talanta* 2013, **115**, 32.
 - (a) D. E. Reusser, J. D. Istok, H. R. Beller, J. A. Field, *Environ. Sci. Technol.* 2002, **36**, 4127. (b) S. B. Hawthorne, D. J. Miller, *Environ. Sci. Technol.* 2003, **37**, 3587. (c) Y. Ueno, T. Horiuchi, T. Morimoto, O. Niwa, *Anal. Chem.* 2001, **73**, 4688.
 - (a) Q.-K. Liu, J.-P. Ma, Y.-B. Dong, *Chem. Eur. J.* 2009, **15**, 10364. (b) Q.-K. Liu, J.-P. Ma, Y.-B. Dong, *J. Am. Chem. Soc.* 2010, **132**, 7005.