Supporting Information

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

*Yan-An Li, Fan Yang, Zhao-Cai Liu, Qi-Kui Liu, Yu-Bin Dong**

Experimental Section

Instrumentation. GC analysis was performed on a 7890A gas chromatograph (Agilent Technologies, CA, USA) equipped with a flame ionization detector (FID) and a split/splitless injector. The GC capillary column (DB-WAX, 30 m length × 0.53 mm i. d. × 1.0 μm) was purchased from the Agilent Technologies. The scanning electron microscopy (SEM) micrographs were recorded on a Gemini Zeiss Supra TM scanning electron microscope. The X-ray diffraction (XRD) experiments were obtained on a D8 ADVANCE X-ray powder diffractometer with CuKa radiation (λ = 1.5405 Å). The Brunauer-Emmett-Teller (BET) surface area of the evacuated Cd-MOF was measured on an ASAP 2020/TriStar 3000 (Micromeritics) using nitrogen adsorption at 77 K.

Chemicals and Reagents. All chemicals used were at least of analytical grade. Hydrogen peroxide aqueous solution (30%), sulfuric acid, hydrofluoric acid, APTES and succine anhydride were purchased from the Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene were purchased from the Alfa Aesar and dissolved in methanol (high performance liquid chromatography grade) to make stock solutions at a concentration of 1 mg/mL for each compound. Working solutions were prepared by step-by-step dilution just before use. A commercial SPME manual holder and the fibers coated with 100 μm of PDMS and 65 μm of PDMS/DVB (Supelco) were used for comparison. The fibers were conditioned in the GC inject port according to the manufacturer.

GC Analysis. In all measurements, the column temperature was maintained at 40°C for 5 min and then programmed at 10°C min^{-1} to the final temperature of 230°C for 7 min. The injector

temperature was set at 250°C. The detector temperature was set at 300°C. The high-purity nitrogen was used as the carrier gas at a flow rate of 60 mL min^{-1}. Hydrogen and air were maintained at flow rates of 30 and 400 mL min^{-1}, respectively.

SPME Procedures: All SPME fibers were pretreated in the GC injection port at 250°C under nitrogen flow for 15 min before use. All the appropriate standard solutions were prepared by diluting the BTEX stock solution (1 mg/mL) with saturated sodium chloride solution. A glass vial (20 mL), the sample container, with a magneton inside was placed on a magnetism msier with a stirring rate of 1500 rpm. Then the needle of the SPME fiber was penetrated the septum of the vial and the coated fiber was exposed to the sample for a period of time at required temperature. After extraction, the fiber was subsequently inserted into the GC injector for desorption and analysis.

Detecting the seawater. The sea water sample was collected from Kiaochow bay (Huangdao, China). It was analyzed immediately after sampling without any pretreatment. Water (10 mL) sample was sealed in a head space vial (20 mL) at 40°C with stirring. The Cd(II)-MOF fiber was exposed to the sample for 30 min. After extraction, the fiber was subsequently inserted into the GC injector for desorption and analysis.

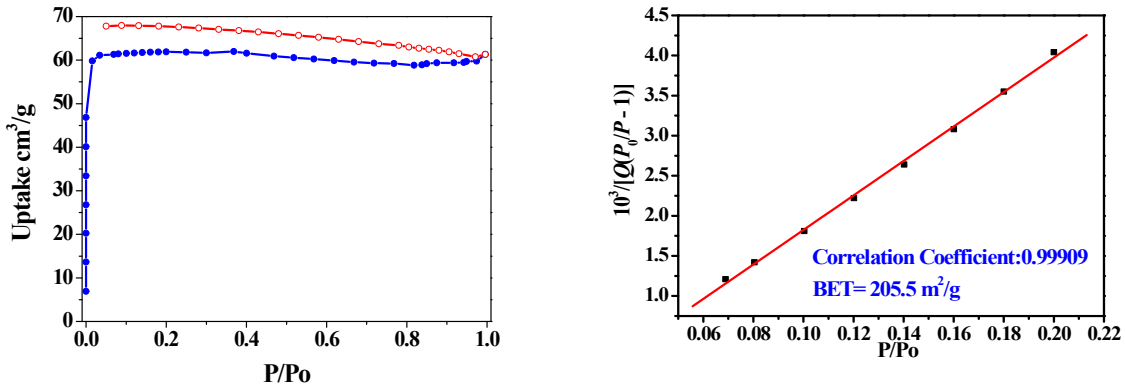

Figure S1. Left: N_2 adsorption isotherms of Cd(II)-MOF collected at 77 K. Right: The Brunauer-Emmett-Teller (BET) plot for Cd(II)-MOF in the chosen range (P/P_0 = 0.07 – 0.20).

The FTIR spectra shows at 3430 cm^{-1} for Si-OH and at 1047 cm^{-1} the broaden and the increase of intensity peak for Si-O-Si confirm the condensations of APTES with Si-OH. The appearance of –COOH characteristic bands at 3500-2500 cm^{-1} and -CO-NH- at 1632 cm^{-1} also demonstrates the successful carboxyl modification of the quartz fiber. For Cd-MOF-coated SPME, the appearance of the characteristic bands of the Cd(II)-MOF indicates the growth of the Cd(II)-MOF on the surface of the quartz fiber.[1]

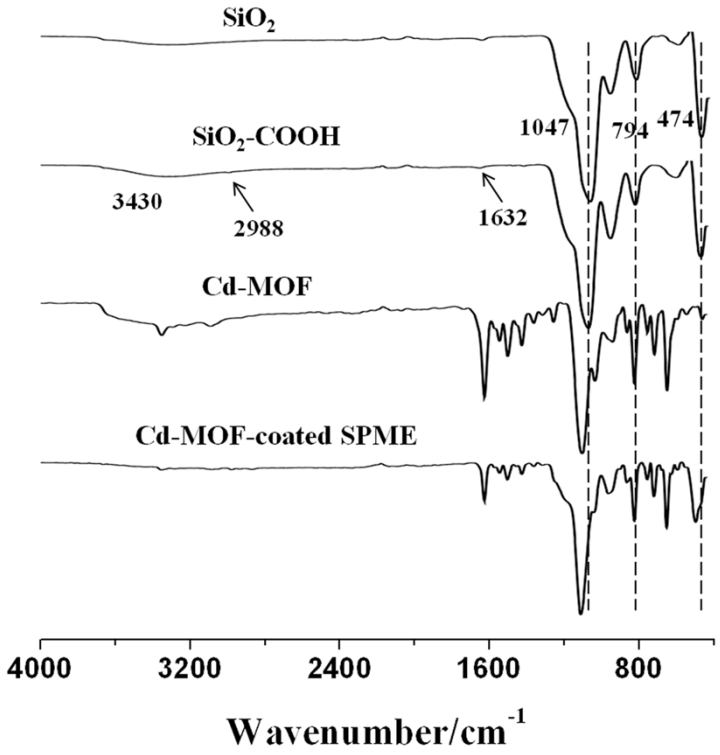

Figure S2. The FTIR spectra of the assembly process of the Cd(II)-MOF coated SPME fiber.

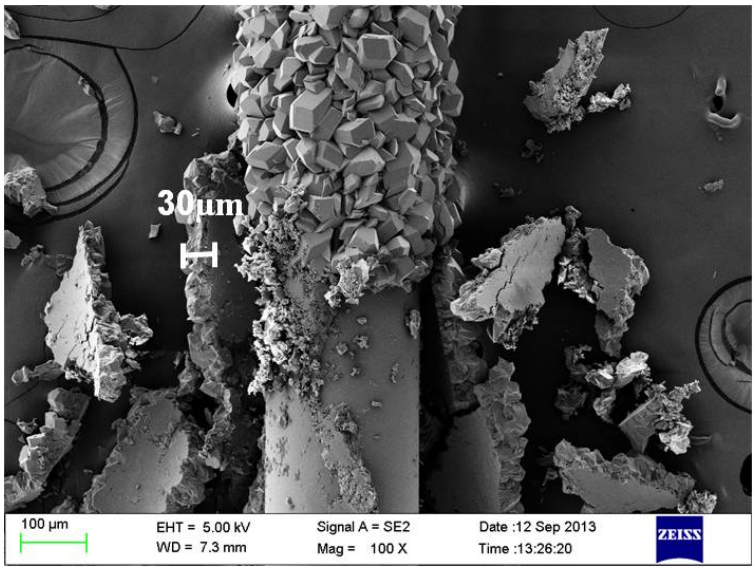

Figure S3. The thickness (~30μm) of the Cd(II)-MOF coated on the SPME fiber.

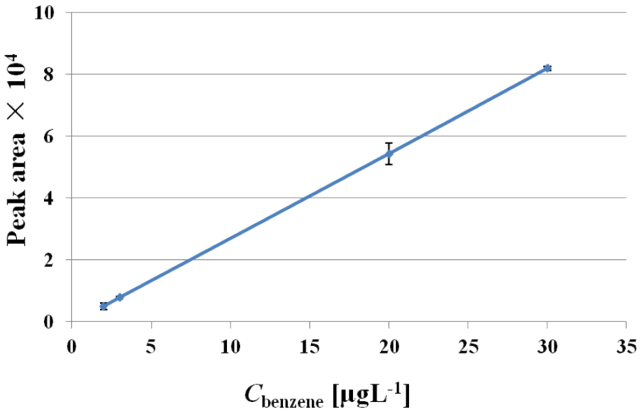

Figure S4. The linearity for benzene.

References

[1] (a) Q.-P. Liu, L.-X. Gao, Z.-W. Gao, L. Yang, *Mater. Lett.* 2007, **61**, 4456; (b) D. J. Macquarrie, Chem. Commun. 1996, 1961; (c) Y.-Y. Fu, C.-X. Yang, X.-P. Yan, *Chem. Eur. J.* 2013, **19**, 13484.