Electronic Supplementary Information for

Covalent bonding of zeolitic imidazolate framework-90 to functionalized silica fiber for solid-phase microextraction

Li-Qing Yu [a, b], *Xiu-Ping Yan** [a]

[a] *Research Center for Analytical Science, College of Chemistry, Nankai University, 94 Weijin Road, Tianjin 300071*

[b] *On leave from College of Chemical and Environmental Sciences, Hebei University, Baoding 071002, China. E-mail: yuliqinghbdx@126.com*

Chemicals and Materials. All chemicals used were at least of analytical grade. $Zn(NO_3)_2 \cdot 4H_2O$ and *N*,*N*-dimethylformamide (DMF) were purchased from Tianjin Standard Science and Technology Co. (Tianjin, China). 4-Nonylphenol (98%), 4-tert-octylphenol (97%), bisphenol A (guarantee-reagent grade), imidazolate-2-carboxyaldehyde (>99%), and 3-aminopropyltriethoxysilane (APTES) (98%) were purchased from Aladdin Reagent Co. (Shanghai, China). The stock solutions of the analytes (1000 mg L^{-1}) were prepared using methanol as the solvent, and stored at 4 °C in darkness. Working standard solutions were prepared by an appropriate dilution of their stock solutions with ultrapure water just before use. Fused-silica hollow fibers (375 μm o.d. × 250 μm i.d., Yongnian Optical Fiber, Handan, China) were used as the substrate to fabricate the ZIF-90 bonded fiber for SPME. A 5 μL GC microsyringe (Shanghai Gaoge Industrial and Trade Co. Ltd., Shanghai, China) was used to assemble the SPME device.

Commercial SPME manual holder and the fibers coated with 85 μm PA and 65 μm PDMS/DVB (Supelco, Bellefonte, PA, USA) were used for

comparison. The fibers were conditioned in the GC inject port according to the manufacturer before use.

Instrumentation and characterization. GC measurements were performed on Thermo Trace Ultra equipped with a flame ionization detector. The GC capillary column (SE-54, 30-m length × 0.53-mm i.d. × 1.0 μm) was purchased from the Lanzhou Institute of Chemical Physics (Lanzhou, China) for all separations. The column temperature was maintained at 160 °C for 2 min and then increased to 280 °C for 5 min at a ramp rate of 10 °C min^{-1}. The injector temperature was 280 °C and the temperature of the flame ionization detector was 300 °C. High-purity nitrogen (99.99%, BOC Gases Co., Tianjin, China) was used as the carrier gas at a flow rate of 20 mL min^{-1}. Hydrogen and air were maintained at flow rates of 30 and 300 mL min^{-1}, respectively. Splitless injections were used throughout the experiments.

The X-ray diffraction (XRD) experiments were recorded on a D/max-2500 diffractometer (Rigaku, Japan) using $Cu_{K\alpha}$ radiation (λ=1.5418 Å). The scanning electron microscope (SEM) images were obtained on a SS-550 scanning electron microscope at 15.0 kV (Shimadzu, Japan). Thermogravimetric analysis (TGA) experiments were performed on a thermal gravimetric analyzer (Rigaku, Japan) from room temperature to 600 °C under N_2. Fourier transform infrared (FT-IR) spectra (4000-400 cm^{-1}) in KBr were recorded on a Magna-560 spectrometer (Nicolet, Madison, WI, USA). BET surface area was measured on an ASAP 2010 micropore physisorption analyzer (Micromeritics, Norcross, GA, USA) using nitrogen adsorption at 77 K in the range $0.02 \leq P/P_0 \leq 0.20$, respectively.

Fabrication of the ZIF-90 Bonded Fiber for SPME. Schematic illustration for fabricating the ZIF-90 bonded fiber is given in Scheme 1. In detail, the following three steps were applied: (a) One fused-silica hollow fiber (3 cm) was heated with a spirit lamp to remove the protective polyimide layer (See inset A in Scheme 1), then dipped into a 1.0 M NaOH solution in a hot water bath (70 °C) for 30 min to break the Si-O-Si bonds to form Si-OH groups.

The pretreated fused-silica fiber was subsequently rinsed with ultrapure water, and dried at room temperature. (b) The hydroxylated fiber was dipped into an APTES solution for 12 h, and put in an oven at 120 °C for 30 min to react with APTES thoroughly. These two operations were repeated twice. The fiber coated with white silanizated APTES layer (See inset B in Scheme 1) was washed with toluene and ethanol, and dried at room temperature. (c) The APTES functionalized fiber was vertically immersed into a Teflon liner, which was filled with a mixture of $Zn(NO_3)_2 \cdot 4H_2O$ (0.07 M) and imidazolate-2-carboxyaldehyde (0.1 M) in DMF solution necessary for ZIF-90 preparation,[44] and heated at 100 °C in oven for 18 h. After solvothermal reaction, the silica fiber coated with orange uniform and dense ZIF-90 layer (See inset C in Scheme 1) was washed with DMF several times, and dried in oven at 60 °C over night for SPME application.

SPME Procedure. To perform the extraction, 10 mL of aqueous standard solution or sample solution containing 1 g NaCl and 0.1M HCl was placed in a 20 mL glass vial. The vial was tightly capped with a butyl rubber stopper wrapped with polytetrafluoroethylene sealing tape. The needle of the SPME device was passed through the septum, and the ZIF-90 bonded fiber was pushed to be exposed to headspace above the solution. The extraction was carried out at 60 °C under stirring at 1200 rpm. After 30-min extraction, the fiber was removed from the vial and immediately transferred into the GC injection port for desorption at 280 °C for 3 min. The fiber was conditioned at 250 °C for 10 min between two extractions.

Determination of Enhancement Factor. The enhancement factor (EF) of a given analyte was determined as the ratio of the sensitivity after SPME to that obtained by direct injection of 1 μL of standard solution.

Real Samples. Local river water samples were collected, and centrifuged at 2000 rpm for 2 min. The supernatants were collected in precleaned glass bottles and analyzed immediately.

A soil sample was collected on campus, air-dried and sieved with a 30

mesh sieve to remove coarse particles. 1 g of the soil sample was dispersed in 10 mL of 0.1M HCl aqueous solution containing 1 g NaCl for subsequent SPME.

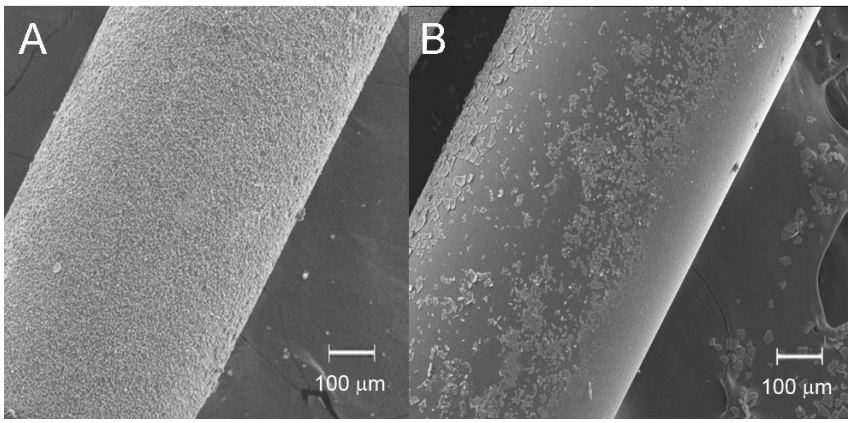

Fig. S1. SEM images of ZIF-90 coating prepared on APTES modified (A) and APTES-free fiber (B).

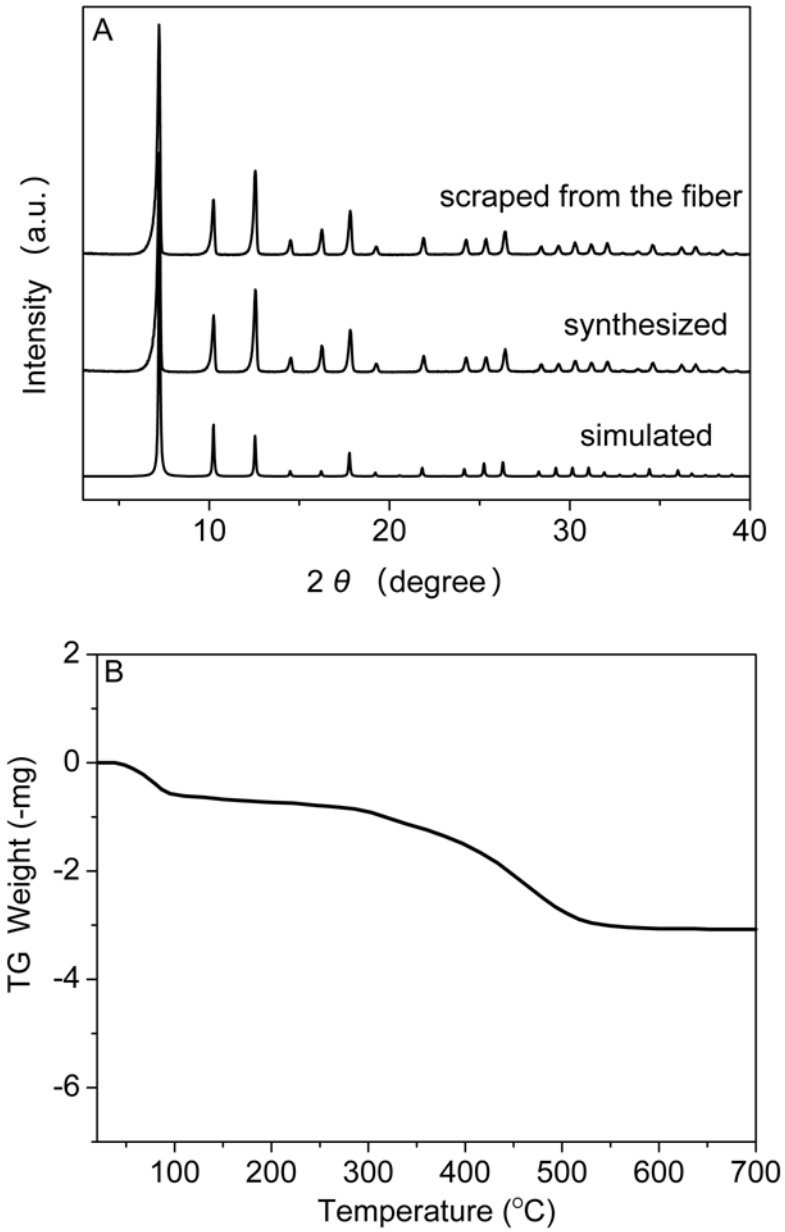

Fig. S2 (A) XRD patterns of simulated ZIF-90 diffraction patterns and the ZIF-90 include as-synthesized and scraped from silica fibers. (B) TG curve of the ZIF-90 powder. Please note that the initial weight loss between 50°C and 100°C resulted from the removal of the solvent methanol trapped within the pores.

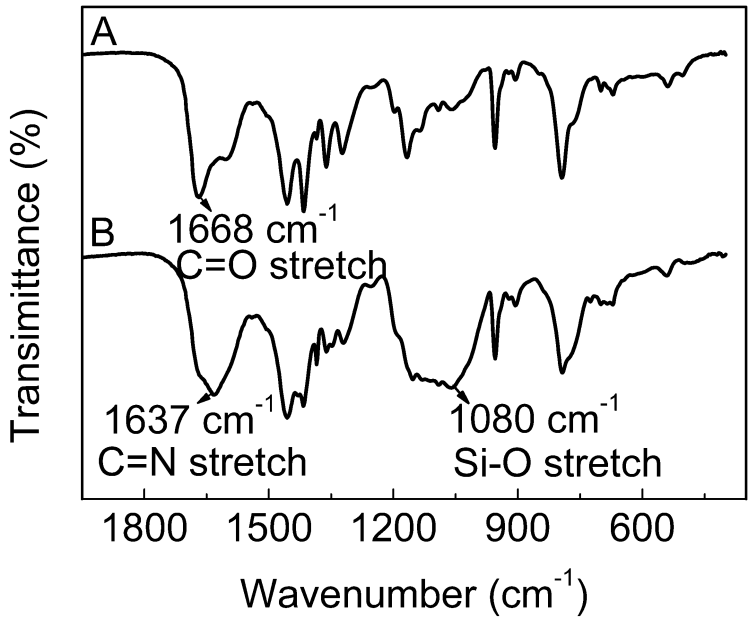

Fig. S3 FT-IR spectra of the as-prepared ZIF-90 crystals (A), and the powder scraped from the fiber (B).

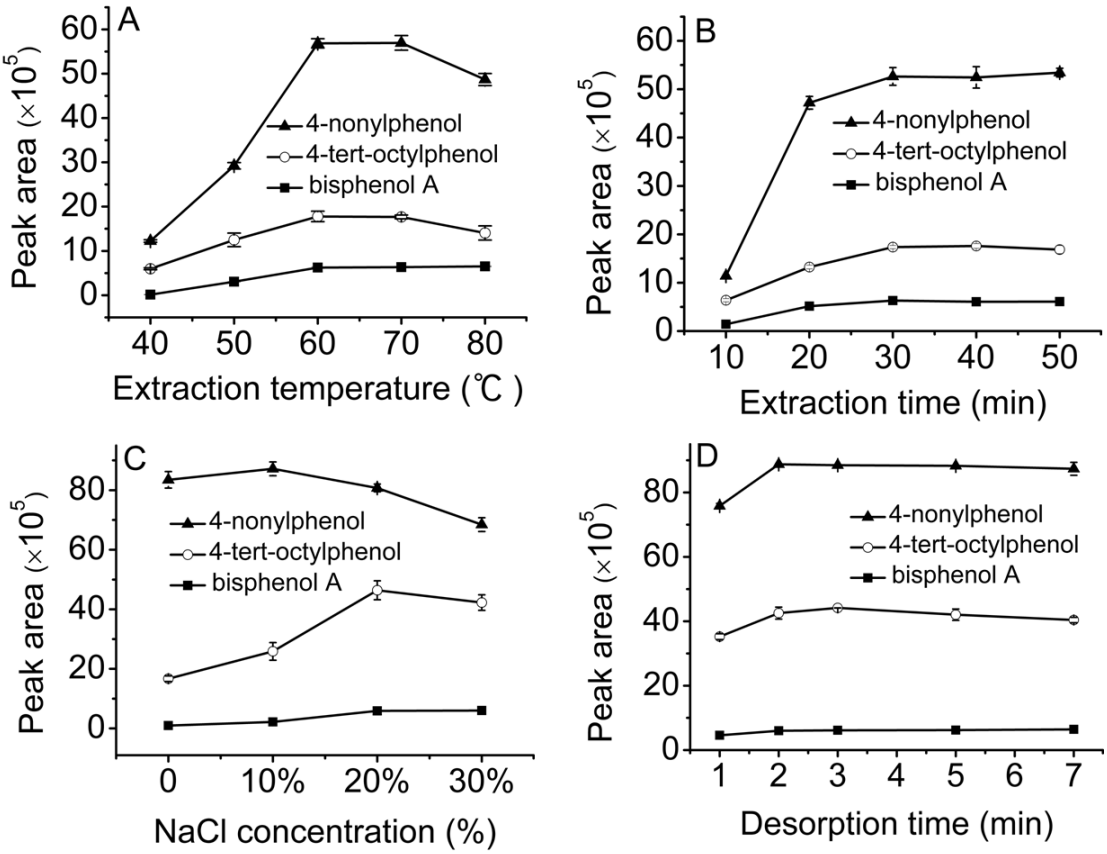

Fig. S4 Effect of the experimental conditions on the peak areas of the phenolic endocrine disruptors (100 μg L^{-1} each) using the ZIF-90 bonded fiber for SPME: (A) Extraction temperature; (B) Extraction time; (C) NaCl concentration ; (D) Desorption time. Errors bars show the standard deviation for triplicate determinations (n = 3).

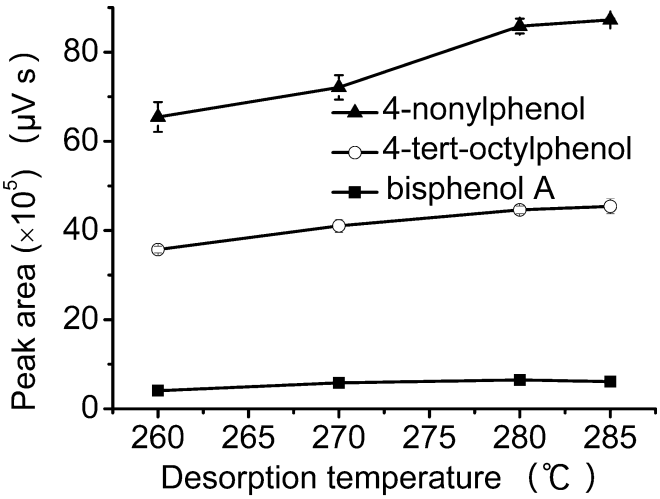

Fig. S5 Effect of desorption temperature on the peak areas of the analytes.

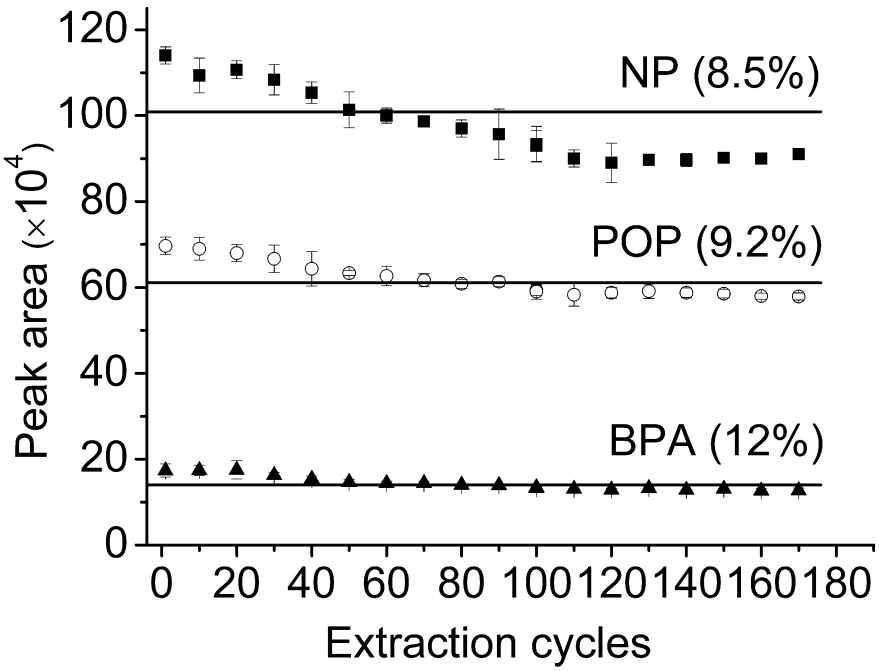

Fig. S6 Robustness of the ZIF-90 coating in water sample for studied APs at concentration of 100 μg L^{-1} by HS-SPME mode. The solid lines and numbers in parentheses represent average values and the pooled RSD (%) values over the 170 extractions, respectively.

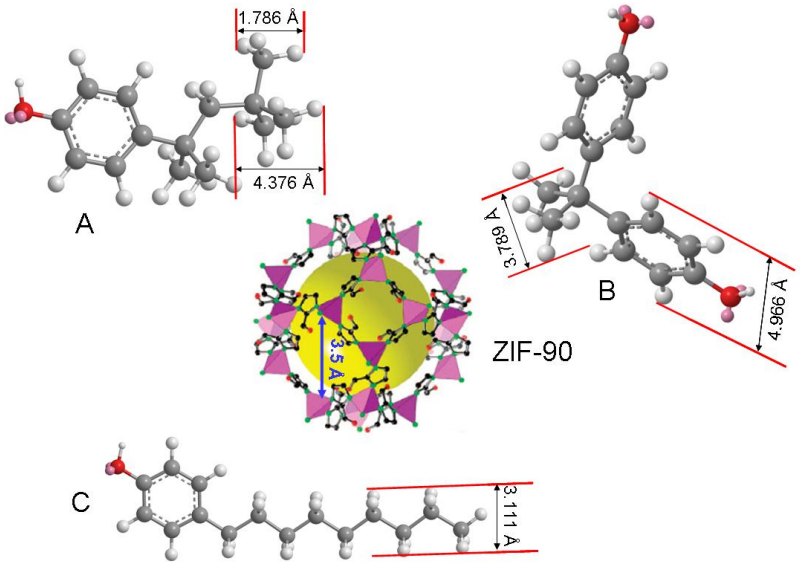

Fig. S7 The molecular 3D structures obtained from Chem 3D Ultra 11.0 on the basis of the energy minimum state using MM2 method. A, 4-tert-octylphenol; B, bisphenol A; C, 4-nonylphenol.

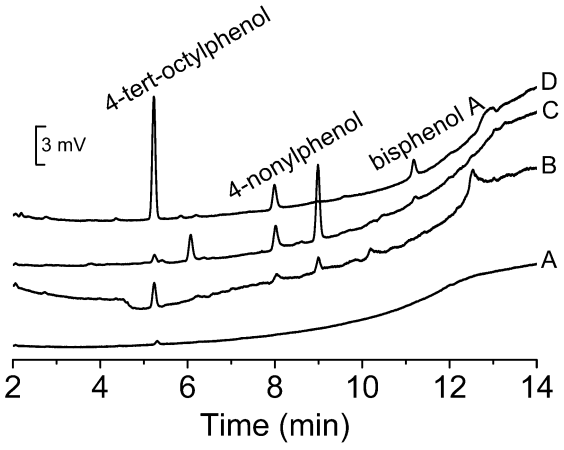

Fig. S8 GC chromatograms for (A) soil sample, (B) river water 1, (C) river water 2, (D) a mixture of the standard solution of 4-nonylphenol, 4-tert-octylphenol, and bisphenol A (1 μg L^{-1} each).

Table S1. Characteristic data of the developed SPME-GC-FID method for the determination of the endocrine disruptors

Analyte	linear range (µg L^{-1})	linearity (r^2)	precision (RSD, n=6) (%)	fiber-to-fiber reproducibility (RSD, n=3) (%)	DLs (ng L^{-1})	QLs (ng L^{-1})
4-nonylphenol	0.1-1000	0.9995	3.1	2.6	34.1	90.9
4-tert-octylphenol	0.1-1000	0.9986	2.8	3.1	28.9	77.1
bisphenol A	1-1000	0.9978	4.0	6.7	196	523

Table S2. Analytical results (Mean ± *s*, *n* = 3) for the determination of the phenolic endocrine disruptors in soil and water samples

analyte	soil sample		river water 1		river water 2	
	concn (ng g^{-1})	recovery[a] (%)	concn (ng L^{-1})	recovery (%)	concn (ng L^{-1})	recovery (%)
4-nonylphenol	< DL	101 ± 3	< QL	102 ± 6	439 ± 42	96 ± 2
4-tert-octylphenol	< QL	89 ± 4	110 ± 9	95 ± 5	< QL	104 ± 5
bisphenol A	< DL	97 ± 2	< DL	101 ± 3	< QL	94 ± 1

[a] Recovery data for spiked 1 µg L^{-1} for 4-nonylphenol, 4-tert-octylphenol and bisphenol A.