Electronic Supplementary Information for

Zeolitic imidazolate frameworks nanocrystals for enrichment and direct detection of environmental pollutants by negative ion surface-assisted laser desorption/Ionization timeof-flight mass spectrometry[†]

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EXPERIMENTAL SECTION

Chemicals and materials.

All chemicals were at least of analytical grade without further treatment before use. Deionized water (18.2 M Ω cm⁻¹) was prepared with a Milli-Q water purification system (Millipore, USA). Sodium formate (99%, NaCO₂H) and Zinc nitrate hexahydrate (99%, Zn(NO₃)₂·6H₂O), 2-Methylimidazole (98%), Benzimidazole (98%) and Imidazolate-2carboxyaldehyde (99%) were purchased from Aladdin Chemisry Co. Ltd (Shanghai, China). Methanol (HPLC grade) and DMF were obtained from Guangfu Fine Chemical Research Institute (Tianjin, China). Bisphenol A (99%, BPA) and Bisphenol B (98%, BPB), Bisphenol F (99%, BPF), Bisphenol AF (98%, BPAF) and Bisphenol S (99%, BPS) were obtained from Aladdin Chemisry Co. Ltd (Shanghai, China). Sodium Chloride (AR, NaCl) was purchased from Dieckmann Chemistry Co. Ltd (Shenzhen, China). Heptadecafluorooctane sulfonic acid potassium salt (PFOS), 1-Nitropyrene (1-NP), 3-Nitrofluoranthene (3-NF), 7-nitrobenz[a]anthracene (7-NBaA), 2,6-Dichlorophenol (2,6-DCP) and 3, 5-Dibromophenol (3,5-DBP) were purchased from Sigma-Aldrich(USA). α -cyano-4-hydroxycinnamic acid (CHCA) was gained from Sigma-Aldrich (USA). 3-Aminoquinoline (3-QA) was purchased from Fluka (Buchs, Switzerland).

Synthesis and characterization of ZIF-7, ZIF-8 and ZIF-90

ZIF-7 nanocrystals were synthesized according to Li *et al* ¹ by stirring at room temperature. A solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.302 g) in 50 mL DMF was added into a solution of benzimidazole (0.769 g) in 50 mL DMF under stirring with a magnetic bar. After keeping at room temperature for 48 h, the ZIF-7 crystals were separated by centrifugation at 10000 rpm for 10 min and then washed with fresh methanol for 3 times. The obtained white solid was dried at 100 °C for 12 h.

ZIF-8 nanocrystals were synthesized by stirring at room temperature according to Cravillon *et al* ². A solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.2933 g) in 20 mL MeOH was rapidly poured into a solution of 2-methylimidazole (0.6489 g) in 20 mL MeOH under stirring with a magnetic bar. After keeping for 1 h, the nanocrystals were obtained. The ZIF-8 crystals were separated by centrifugation at 10000 rpm for 10 min and then washed with fresh methanol for 3 times. The obtained white solid was dried at 100 °C for 12 h.

ZIF-90 nanocrystals were synthesized by stirring at room temperature according to

Thompson *et al*³. A solution of 20 mmol of NaCO₂H and 20 mmol of imidazolate-2carboxyaldehyde in 50 mL of MeOH was heated to 50 °C until it became clear, then cooled it to the room temperature. Another solution of 50 mmol of $Zn(NO_3)_2 \cdot 6H_2O$ in 50 mL ultrapure water was poured into the above solution and then stirred it at room temperature for 1 h. The gained milky mixture was centrifuged at 10000 rpm for 10 min and washed the solid with methanol for three times. The ZIF-90 crystals were dried at 100 °C for 12 h.

XRD, SEM and TEM were employed to characterize the prepared ZIF-7, ZIF-8 and ZIF-90. The XRD patterns were recorded with a D/max-2500 diffractometer using CuKa radiation (λ =1.5418 Å). The scanning electron microscopy (SEM) images were recorded on a LEO 1530 Field Emission SEM. The TEM images were obtained by Tecnai G2 20 S-TWIN Transmission Electron Microscope.

Preparation of analyte solutions

BPA, BPB, BPS, BPF, BPAF and PFOS were respectively dissolved in ACN/H₂O (2/1, v/v) at a concentration of 100 mM as stock solutions and stored at 4 °C in the dark. The work solutions were prepared by step-by-step dilution of the stock solution with ACN/H₂O (2/1, v/v) before use. 1-NP, 3-NF, 7-NBaA, 2,6-DCP and 3,5-DBP were respectively dissolved in dichloromethane at a concentration of 100 μ g mL⁻¹. All analyte solutions were stored at 4 °C for use.

Sewage samples were collected from local river. Firstly, 10 μ L different concentration (20 μ M, 50 μ M and 100 μ M) of BPS was directly added into 1 mL sewage with vibration for 1 min, respectively. And then the BPS was extracted with 500 μ L dichloromethane (DCM) and centrifugated for 10 min at 12000 rpm and discarded the aqueous phase. The organic phase was dried by N₂ and followed by adding 10 μ L ACN/ H₂O into the residue with vibration for 10 s. Finally, 1 μ L mix solution was pipetted onto the MALDI target plate and let it dry.

Sample preparation for MALDI-TOF MS analysis

The CHCA matrix solution was prepared by adding CHCA in a solvent mixture containing ACN and H_2O at a ratio of 2:1(v/v) as saturated solution. 3-Aminoquinoline (3-QA) was prepared by dissolving in ACN/ H_2O (1/1) at a concentration of 10 mg mL⁻¹. The ZIF-7, ZIF-8 and ZIF-90 (1.0 mg mL⁻¹) matrix solutions were prepared by suspending solids in ethanol/ water (1:1, v/v), followed by sonication for 1 h to fully disperse them, respectively.

Three sample preparation methods were tested before MALDI-TOF MS analysis (Figure 1D).

After optimized, the matrix-first method was chosen to be the sample preparation method.

a. Matrix-First Method: 1 μ L of the ZIF-8 solution was deposited first onto the MALDI target and dried in the air. Then, 1 μ L of the BPA solution was deposited onto the matrix spot and dried in the air.

b. Sample-First Method: 1 μ L of the BPA solution was deposited first onto the MALDI target and dried in the air. Then, 1 μ L of the ZIF-8 solution was deposited onto the matrix spot and dried in the air.

c. On Probe Remix: 1 μ L of the ZIF-8 solution was deposited first onto the MALDI target and 1 μ L of the BPA solution was immediately deposited onto the matrix spot before it dried in the air. Then, the mixture dried in the air at room temperature.

Enrichment and analysis of bisphenols with ZIF-7 and ZIF-8

ZIF-7 and ZIF-8 were suspended in ethanol/H₂O (v/v, 1/1) at a concentration of 10 mg mL⁻¹, respectively. After sonication for 10 min, the mixture (5 μ L) was immediately added into 1 mL of BPS solution or river water spiked with 10 μ M BPS. The mixture was then vibrated for 30 s. After standing for 2 h, the mixture was separated by centrifugation at 12000 rpm for 15 min. The supernatant was removed and the ZIFs on which analytes were enriched was resuspended in a 5 μ L solution of ethanol in H₂O (v/v, 1/1) with ultrasonication for 2 min. Finally, 1 μ L of the ZIFs suspension was pipetted onto the sample target. After 10-15 min evaporation of solvent, the sample target was for further analysis by MALDI-TOF MS.

MALDI-TOF MS analysis

MALDI-TOF MS experiments were performed on a Bruker Autoflex II mass spectrometer (Bruker Daltonics, Germany). A pulsed laser (337 nm nitrogen laser) was used for desorption/ionization of samples with a laser attenuator offset of ~70% in negative reflection mode. The RP-MALDI-MS parameters were maintained as follows, the acceleration voltages was 19 kV and delayed extraction was 120 ns and each data of mass spectrum was the average data from 500 individual laser shots. To gain good resolution and signal-to-noise (S/N) ratios, the laser power was adjusted to slightly above desorption/ionization (D/I) threshold energy.

Recoveries experiments

A known amount of standard BPS solution was added into the sewage to gain different concentrations (20 μ M, 50 μ M and 100 μ M) solution and then treated the same as the sample

solution.

Adsorption Experiments

To study the adsorption kinetics, 10 mL of 40 μ g mL⁻¹ of BPS solution in C₂H₅OH / H₂O (v/v, 1/1) was added into a 15 mL centrifugal tube containing 10.0 mg of ZIF-7 or ZIF-8 with vibration for 30 s, respectively. The adsorption was carried out at room temperature and the supernatant was collected at different adsorption times (1 min - 240 min) to determine the unabsorbed BPS.

To study the adsorption capacities of ZIF-7 and ZIF-8, 1 mL of BPS with different concentrations (2 μ g mL⁻¹ - 150 μ g mL⁻¹) in C₂H₅OH / H₂O (v/v, 1/1) was added into 1.5 mL centrifugal tube containing 1.0 mg of ZIF-7 or ZIF-8, respectively. The mixture was then vibrated for 30 s and kept for 2 h at room temperature. After centrifugation at 12000 rpm for 15 min, and the concentration of BPS in the supernatant was determined by HPLC. The equilibrium adsorption capacity (Qe, mg g⁻¹) was calculated according to the following equation.

$$Qe = \frac{(Co - Ce)V}{m}$$

Co is the initial concentration of BPS (μ g mL⁻¹), Ce is the supernatant concentration of BPS (μ g mL⁻¹), V is the volume of BPS solution (mL) and m is the weight of the ZIF-7 or ZIF-8 (mg).



Figure S1. XRD patterns of synthesized ZIF-7 (A), ZIF-8 (B) and ZIF-90 (C) compared with those simulated.



Figure S2. SEM images of prepared ZIF-7 (A) and ZIF-90 (B) and TEM images of ZIF-7 (C) and ZIF-90 (D) nanocrystals.



Figure S3. Optical photographs of different matrix including ZIF-7 (A), ZIF-8 (B) and ZIF-90 (C), CHCA (D), 3-QA (E) in SALDI-TOF MS.



Figure S4. Chemical structures of all the analytes including BPA (A), BPB (B), BPS (C), BPF (D), BPAF (E), 1-NP (F), 3-NF (G), 7-NBaA (H), 2,6-DCP (I), 3,5-DBP (J) and PFOS (K).



Figure S5. Mass spectra of BPA (A, F), BPB (B, G), BPS (C, H), BPF (D, I) and BPAF (E, J) at the concentration of 1 mM with the traditional matrices of 3-QA (A-E) and CHCA (F-J) in negative-ion mode.



Figure S6. SALDI-TOF MS spectra of 200 μ M BPS (A)in different concentration of NaCl and (B) the reproducibility in 500 mM NaCl with ZIF-8 as the matrix in negative-ion mode.



Figure S7. MS signal intensity of BPA reproducibility gained from the same sample spot (A) and from 30 different sample spots (B) with the matrix of ZIF-8 in negative mode. The concentration of BPA was 1.0 mM.



Figure S8. The calibration curves of bisphenols for quantitative determination according to (A) the intensity of [BPA-H]⁻, (B) intensity of [BPB-C₂H₆-H]⁻, (C) intensity of [BPS-H]⁻, (D) intensity of [BPF-H]⁻ and intensity of [BPAF-CF₃H-H]⁻.



Figure S9. Mass spectra of (A) Sewage; (B) 20 µM BPS in spiked sewage; (C) 50 µM BPS in spiked

sewage; (D) 100 μ M BPS in spiked sewage by using ZIF-8 as the matrix in negative ion mode.



Figure S10. Mass spectra of 1-NP (0.4044 mM), 3-NF (0.4044 mM), 7-NBaA (0.3659 mM), 2,6-DCP (1 mM), 3,5-DBP (1 mM) and PFOS (1 mM) with ZIF-7 as the matrix in negative-ion mode.



Figure S11. Mass spectra of 1-NP (0.4044 mM, A), 3-NF (0.4044 mM, B), 7-NBaA (0.3659 mM, C), 2,6-DCP (1 mM, D), 3,5-DBP (1 mM, E) and PFOS (1 mM, F) with 3-QA as the matrix in negative-ion mode.



Figure S12. Mass spectra of 1-NP (0.4044 mM, A), 3-NF (0.4044 mM, B), 7-NBaA (0.3659 mM, C),

2,6-DCP (1 mM, D), 3,5-DBP (1 mM, E) and PFOS (1 mM, F) with CHCA as the matrix in negativeion mode.



Figure S13. (A) The time-dependent adsorption kinetics of BPS (40 μ g mL⁻¹) with different standing time (1 - 240 min); (B) Adsorption isotherms of BPS (2 - 150 μ g mL⁻¹) after standing for 120 min. ZIF-7 and ZIF-8 were used as adsorbents with the concentration of 1 mg mL⁻¹ in 50% C₂H₅OH aqueous solution, respectively.



Figure S14. Mass spectra of different concentration of BPS solution with ZIF-8 as adsorbent and matrix before and after enrichment

_	BPA	BPB	BPS	BPF	BPAF
LOD (ng mL ⁻¹)	1.60	2.50	1.17	2.92	2.98
LOQ (ng mL ⁻¹)	5.28	8.25	3.86	9.64	9.83
R ²	0.9925	0.9918	0.9953	0.9973	0.9947
Calibration range	50-500	50-500	50-500	50-500	50-500
(µM)					

Table S1 The quantitative analysis of bisphenols using ZIF-8 as the matrix.

a. R² represents the square of the linearity related coefficient.

Analytical	LOD	LOQ	Linear range	Analytes	Ref.
Methods					
SPE-HPLC-DAD	0.6-1.1 ng mL ⁻¹	-	5-2500 ng mL ⁻¹	BPA, BPB,BPS,	[4]
				BPF, BPAF	
SPE-HPLC-DAD	1.2-2.0 ng mL ⁻¹	-	20-2000 ng mL ⁻¹	BPA, BPB, BPS,	[5]
				BPF	
GC-MS	0.9-2.5 ng L ⁻¹	3.2-8.4 ng L ⁻¹	-	BPA, BPF	[6]
GC-MS	8.0-8.7 ng g ⁻¹	26.7-29.2 ng g ⁻¹	-	BPA, BPF	[7]
MALDI-MS	0.93-14.6 pmol	3.07-48.18 pmol	50-500 μM	BPA, BPB, BPS,	This
				BPF, BPAF	work

Table S2. Comparison of the quantitative determination of the bisphenols with the traditional methods.

Table S3.	Determination	of BPS i	n the sewage an	d the recover	ries test (n=3).
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Compound	Added (µM)	Found (µM)	Recovery (%)	RSD (%)
BPS	20	15.3	76.3	7.9
BPS	50	47.3	94.6	6.2
BPS	100	95.5	95.5	5.2

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