Supplementary Information

Electrochemically fabricated ZIF-67/[HOEMIM]BF$_4$ coating for the solid-phase microextraction and detection of polycyclic aromatic hydrocarbons

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Instruments and reagents

The ZIF-67/[HOEMIM]BF$_4$ composite coatings were prepared by CHI 660B electrochemical workstation (Shanghai Chenhua Instrument Co., China) equipped with a three-electrode system: stainless steel wire (SSW) (1.5 cm × 250 μm O.D.) as the working electrode, Pt wire (2.5 cm × 0.1 cm O.D.) as the counter electrode, and Ag/AgCl as the reference electrode. A SP-7890 Plus gas chromatograph (Shandong Lunan Ruihong Chemical Instrument Co., China) equipped with a flame ionization detector (GC-FID) was employed for this work. An SE-54 capillary column (30 m × 0.25 mm × 0.25 μm O.D., Lanzhou Zhongke Antai Analysis Technology Co., China) was used for the chromatographic separation. Gas chromatography was programmed as follows: the temperatures of injection port and detector were both 280 °C, and the oven temperature program was set as follows: maintained at 30 °C for 4 min, then rose to 200 °C with a rate of 19 °C min^{-1} and further to 240 °C with a rate of 4.5 °C min^{-1} and kept it for 2 min. N$_2$ was used as the carrier gas at a column flow rate of 1 mL min^{-1}, and no-splitting mode was adopted. The air and hydrogen flow rates were set at 400 mL min^{-1} and 40 mL min^{-1}, respectively. Commercial extraction fiber with polydimethylsiloxane/divinylbenzene (PDMS/DVB, film thickness: 100 μm) coating was purchased from Supelco, USA. A laboratory-made solid phase microextraction handle was used for the fixing of MOF-IL coated SSW. The surface morphology characterization of the coating was performed with a Sigma FESEM (Zeiss, Germany). In addition, a SETSYS-16 thermogravimetric analyzer (TGA Setaram，France) and a Nicolet iS10 Fourier transform infrared (FT-IR) spectrometer (Thermo Fisher, USA) were applied to study the composition of the ZIF-67/[HOEMIM]BF$_4$ and the thermal stability, respectively. A S10-3 constant temperature magnetic stirrer (Shanghai Sile Instrument Co., Shanghai, China) was used for HS-SPME.

Naphthalene (NAP), 1-methylnaphthalene (1-MN), biphenyl (BP), acenaphthene (ACE) and fluorene (FLR) were purchased from Aladdin Chemical Co., Ltd. (Shanghai, China). Biphenyl, cobalt acetate tetrahydrate (Co(Ac)$_2$·4H$_2$O), sodium chloride (NaCl), sodium hydroxide (NaOH), nitric acid (HNO$_3$) and methanol were

purchased from Sinophasic Chemical Reagent Co., Ltd (Shanghai, China). 2-Methylimidazole (2-MI) was purchased from Sigma-Aldrich Trading Co., Ltd. (Shanghai, China). All ILs including 1-(2'-hydroxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([HOEMIM]NTf$_2$), 1-(2'-hydroxylethyl)-3-methylimidazolium hexafluorophosphate([HOEMIM]PF$_6$), 1-(2'-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([HOEMIM]BF$_4$), 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]BF$_4$), 1-aminopropyl-3-methylimidazolium tetrafluoroborate ([APMIM]BF$_4$) were obtained from Lanzhou Institute of Chemical Physics (China). The structures and properties of PAHs and biphenyl were shown in Table S1. A standard solution of 1 mg mL^{-1} for each PAH was prepared and stored in a refrigerator. The working standard solutions were obtained by diluting the standard stock solution with methanol. Water samples came from nature, East lake and factory. Ultrapure water (18.25 MΩ cm) was used throughout the experiments. All water samples were filtered through a 0.22 μm filter before detection.
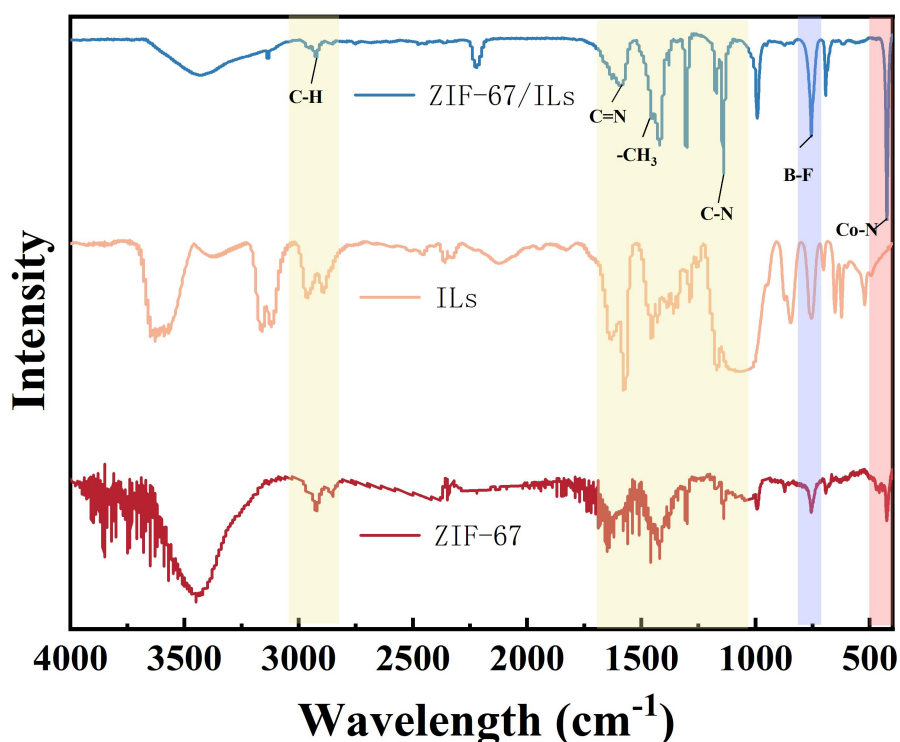

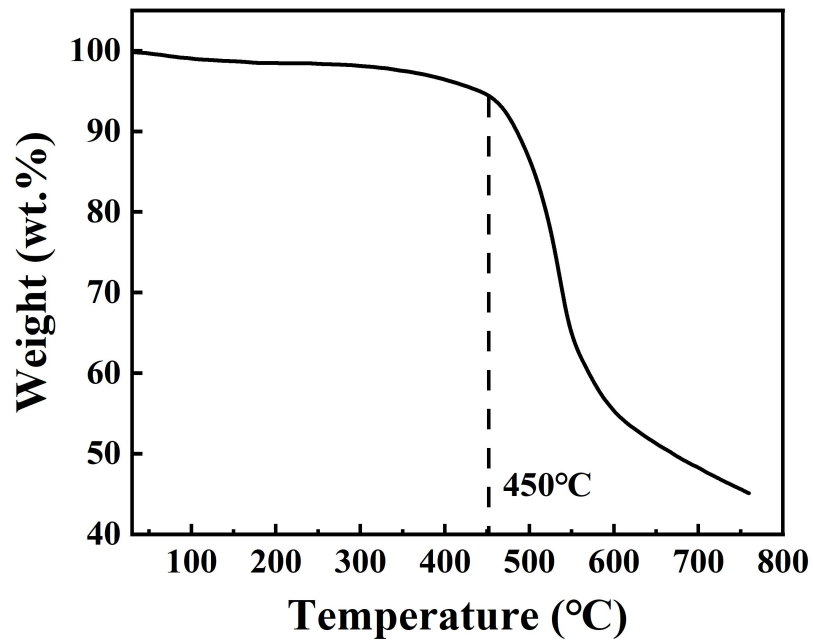**Fig. S1.** FT-IR spectra of different materials.

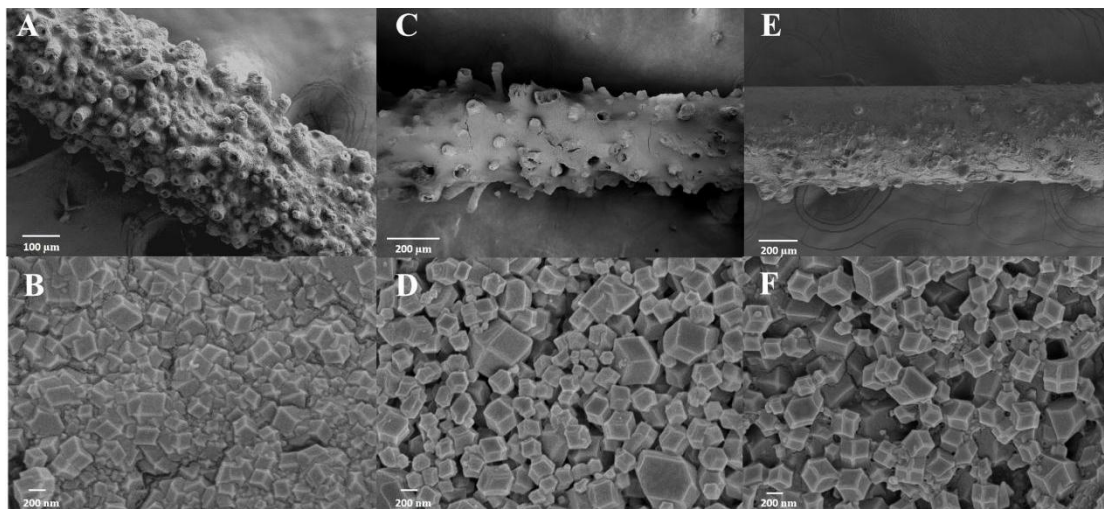**Fig. S2.** Thermogravimetric curve of ZIF-67/[HOEMIM]BF$_4$.

Fig. S3. SEM images of (A, B) ZIF-67/[HOEMIM]BF$_4$, (C, D) ZIF-67/[HOEMIM]PF$_6$ and (E, F) ZIF-67/[HOEMIM]NTf$_2$.
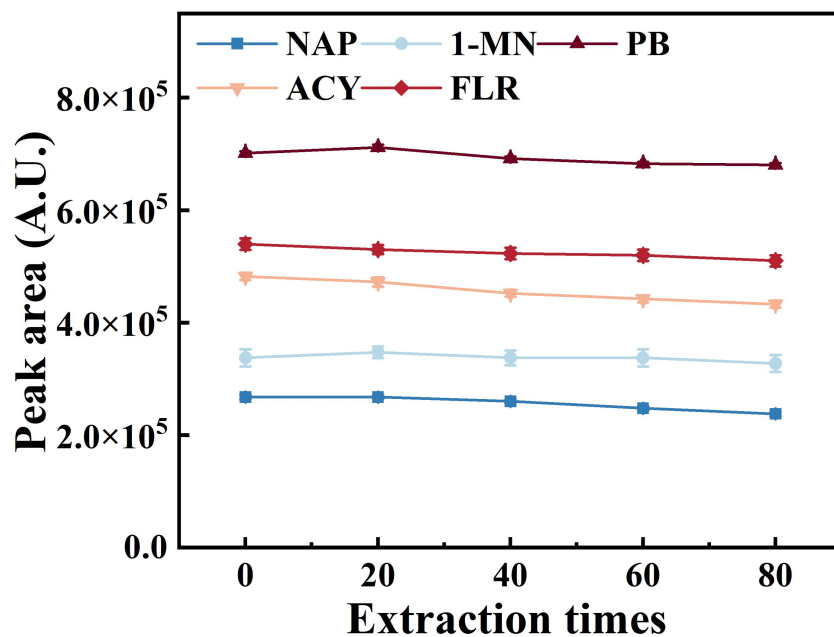
Fig. S4. Coating life span of ZIF-67/[HOEMIM]BF$_4$. Common experimental conditions: extraction temperature: 70 °C; extraction time: 50 min; salt concentration: saturated NaCl solution; stirring speed: 800 rpm; desorption temperature: 260 °C; desorption time: 4 min; sample volume: 10 mL; concentration of PAHs: 100 μg·L^{-1}. Electrodeposition conditions: constant potential: -5 V; electrodeposition time: 50 min. (n = 3)
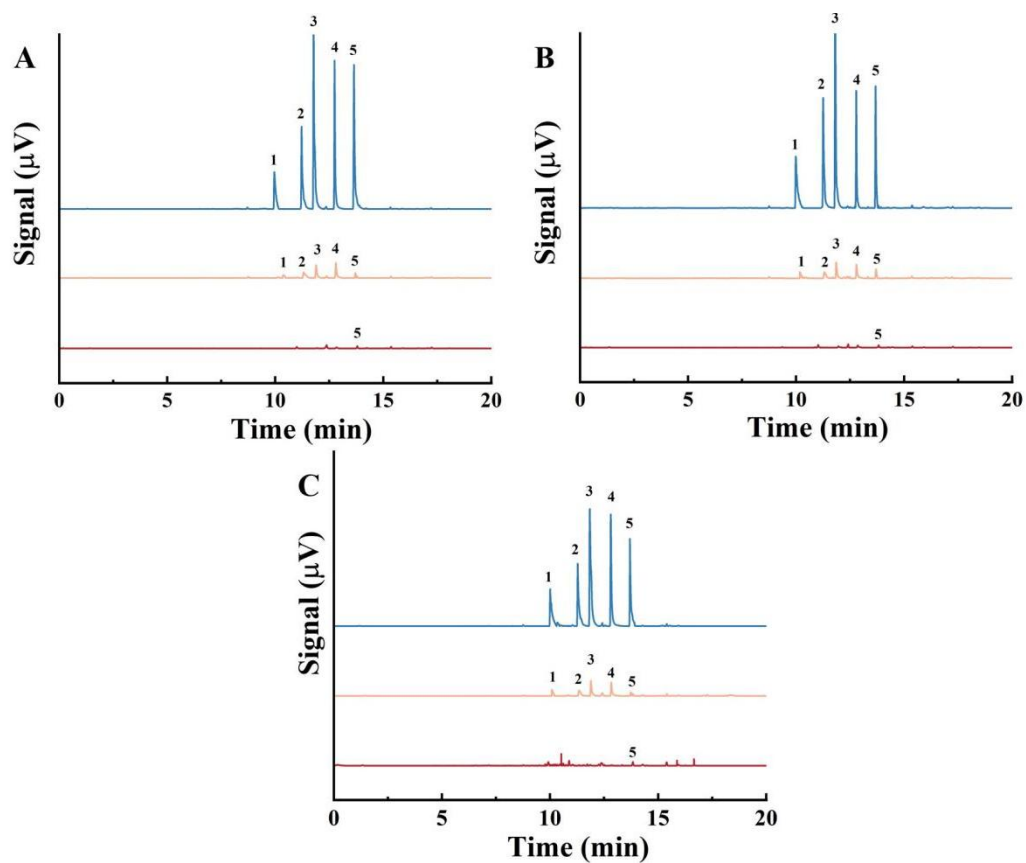
Fig. S5. Chromatograms of PAHs in three samples after HS-SPME. A. rain water; B. river water; C. factory water. red line: sample; yellow line: added 5 μg L^{-1} standard solution; blue line: added 5 μg·L^{-1} standard solution. Peaks: 1: NAP; 2: 1-MN; 3: PB; 4: ACY; 5: FLR

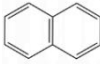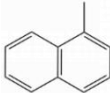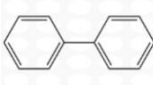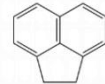**Table S1.** Chemical structure and physical-chemical properties of PAHs.
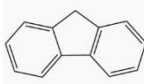
PAHs	Structure	Boiling point (℃)	Kow
NAP		218℃	3.30
1-MN		240-243℃	3.87
BP		255℃	4.05
ACY		277.5℃	3.92
FLR		295℃	4.18

Table S2. Parameters of analytical performance

PAHs	Regression equation	Linear range ($\mu g \ L^{-1}$)	LODs ($ng \ L^{-1}$)	R^2	One fiber (RSD, n=5) (%)	Fiber to fiber (RSD, n=5) (%)
NAP	Y = 2084.1X + 17954	0.1-500	3.8-5.2	0.9962	6.0	5.7
1-MN	Y = 3266.6X + 2678.4	0.1-100	3.8-5.2	0.9934	3.4	7.1
PB	Y = 7028.1X + 3828.0	0.01-100	0.27-0.28	0.9995	7.4	7.7
ACY	Y = 4649.8X + 9547.6	0.01-100	0.28-0.51	0.9975	6.0	4.7
FLR	Y = 5289.3X - 2488.1	0.5-100	0.26-0.27	0.9958	8.0	10.7

Table S3. Comparison with other reported methods for the determination of PAHs.

material	Pretreatment method	Thermal stability	Analytical method	LOD (ng L^{-1})	Linear range (μg L^{-1})	Ref
MWCNTs	SPE	/	GC-MS	2.0-8.5	0.02-5	[1]
SiO$_2$	IT-SPME	/	GC-FID	220-470	1-4000	[2]
PTMS-SBA-15	HS-SPME	300 °C	GC-FID	5.1-37.2	0.01-100	[3]
ZIF-8	HS-SPME	460 °C	GC-FID	10-54	0.05-50	[4]
MOF/COF	HS-SPME	/	GC-FID	20-70	0.2-50	[5]
ZIF-67/ILs	HS-SPME	450 °C	GC-FID	0.27-5.17	0.01-500	This work

References

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