Electronic Supplementary Material (ESI) for Analyst.

Electronic Supplementary Information for

Isoreticular bio-MOFs 100-102 coated solid-phase microextraction fibers for fast and sensitive determination of organic pollutants by pore structure dominated mechanism

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Reagents and Materials. Stainless-steel wires were purchased from Component Supply Co., (Fort Meade, MD, USA). Hexachlorobenzene (HCB, 99.5%), trans-chlordane (98.0%), o,p-DDT (98.0%), p,p-DDT (98.5%), mirex (99.0%), Phenanthrene (Ph, 99.5%), Fluoranthene (Flt, 98.5%), Benzo(a)pyrene (BaP, 99.9%), Benzo(b)fluoranthene (BbF, 98.1%) and Benzo(g,h,i)perylene (BghiP, 99.3%) were purchased from Dr. Ehrenstorfer GmbH (Germany). $Zn(OAc)_2 \cdot 2H_2O$ and adenine were purchased from Sigma-aldrich Co., (St. Louis, MO, USA). 2,6-naphthalene dicarboxylic acid (NDC) and 4,4'-biphenyldicarboxylic acid (BPDC) were purchased from TCI (Tokyo, Japan). The 4,4'-azobenzenedicarboxylic acid (ABDC) was purchased from Shanghai Ge Lan Medicine Science Co., (Shanghai, China). N,N-dimethylformamide (DMF) and N-methylpyrolidinone (NMP) were bought from Aladdin (Shanghai, China). Neutral silicone sealant was bought from Sikasil Ltd., (Guangzhou, China). The commercial PDMS/DVB fiber was purchased from Supelco (Bellefonte, PA).

Instruments. The Synthesis was carried on a heating oven from Binder (Tuttlingen, Germany). Scanning electron microscopy (SEM) images were conducted by a Quanta 400 Thermal FE Environment Scanning Electron Microscope instrument (FEI, Netherlands). The surface images of the bio-MOFs coatings were obtained at 20 kV. The powder X-ray diffraction (PXRD) peaks were obtained from a Bruker D8 ADVANCE X-ray powder diffractometer (Cu kα) and the 2θ was ranged from 2 to 10°. Thermal stability was evaluated by a thermogravimetric (TG) analyzer (Netzsch-209, Bavaria, Germany) from room temperature to 800 °C at the rate of 10 °C min^{-1} under nitrogenous atmosphere.

The optimization and evaluation procedures of the self-made fibers were conducted with an Agilent 7890 GC-FID (Palo Alto, CA, USA). The GC-MS (6890-5975 B) equipped with a HP-5 MS capillary column (30 m × 0.32 mm i.d. × 0.25 μm film thickness) from Agilent (Palo Alto, CA, USA) was employed to evaluate the analytical performance of the self-made fibers and analyze the environmental water samples. PDMS/DVB (65 μm) SPME fiber was obtained from Supelco (Bellefonte, PA, USA).

Solvothermal synthesis of bio-MOF-101. Stock solution of $Zn(OAc)_2·2H_2O$ (0.05M), adenine (0.05M), and 2,6-naphthalene dicarboxylic acid (NDC) (0.1M) in DMF were prepared first. Then 9 m Solvothermal synthesis of bio-MOF-101. Stock solution of Zn(OAc)2·2H2O (0.05M), adenine (0.05M), and 2,6-naphthalene dicarboxylic acid (NDC) (0.1M) in DMF were prepared first. Then 9 mL of the Zn(OAc)2 2H2O, 3 mL of the adenine and 3 mL of the NDC stock solution along with 1.5 mL ultrapure water were added into a 20 mL glass vail. The reaction mixture was heated in an 85 °C oven for 24 hours to yield bio-MOF-101. The product was washed with DMF for 3 times and dried under 100 °C.

Ligand exchange from bio-MOF-101 to bio-MOF-100. About 200 mg of bio-MOF-101 was added to BPDC/DMF/NMP (DMF:NMP=1:1) solution (0.05M, 4mL) in a 10 mL glass vail. The vail was heated at 75 °C oven for 24 hours. Then the solution was removed, replaced with 4 mL fresh BPDC solution and the vail was again heated at 75 °C oven for 24 hours. The obtained bio-MOF-100 was thoroughly washed with DMF and dried under 100 °C.

Ligand exchange from bio-MOF-100 to bio-MOF-102. About 200mg of bio-MOF-100 was added to ABDC/DMF solution (0.05M, 4mL) in a 10 mL glass vail. The mixture was heated at 75 °C oven for 24 hours. Then the solution was removed, replaced with 4 mL fresh ABDC solution and the vail was again heated at 75 °C oven for 24 hours. The obtained bio-MOF-100 was thoroughly washed with DMF until the solution was colorless and dried under 100 °C.

Fabrication of bio-MOFs Coatings. The one-component neutral cure silicone sealant with very low modulus and high elongation has been widely studied for sealing concrete structure and adhering different materials together. When the silicone sealant whose main component was PDMS was contacted by the moisture from the air, the solidification reaction occurred. With the help of the solidification, different materials could bind together without changing their properties. Therefore, the self-made fibers were fabricated by sequentially coating the stainless steel fiber with silicone sealant thin film and bio-MOFs powder layer by layer, which could effectively avoid the pore blocking phenomenon that might be caused by the sol-gel technique. Figure 1 showed the fabrication scheme of the self-made coatings.

Before fabricating the SPME coatings, the stainless steel wires were firstly cut into 3 cm, and then ultrasonically cleaned in water, methanol and acetone for 30 min, respectively. The cleaned wires were dried at room temperature for 12 h. About 0.5 g neutral silicone sealant was dispersed in a sample tube by using 1.0 mL o-xylene as dispersing agent. Then the cleaned steel wire was dipped into the mixture and taken out immediately. After being wiped by a piece of filter paper, an extremely thin film of silicone sealant was left on the surface of the steel wire, and the wire was subsequently rotated in the powder of the synthesized bio-MOF-101 to get the single-layer coating. Then the single-layer fiber was cured at 150 °C for 30 min to evaporate the solvent and realize the solidification reaction before the next coating procedure. Repeat the above procedures for twice and a three-layer bio-MOF-101 fiber was obtained. Finally, the coated wire was dipped into the diluted silicone sealant again to form a thin film of polymer to avoid the flaking of the crystal and create a hydrophobic surface of the coating. The bio-MOF-100 and bio-MOF-102 coatings were fabricated by the same procedures. In order to confirm the effect of the neutral silicone sealant, a fiber coated with the pure silicone sealant was prepared as well. Before use, the prepared fibers were conditioned at 250 °C for 60 min in the GC injection port under nitrogenous atmosphere to avoid any contamination or carryover.

SPME Procedure and GC Analysis. Standard aqueous solutions of PAHs and OCPs were prepared daily by diluting the stock solution (0.10/0.12 mg mL^{-1} for PAHs/OCPs) with pure water. The extractions were conducted by a MPS multipurpose sampler with the use of 10 mL glass vials. Direct immersing (DI) SPME parameters such as agitation speed, extraction temperature, extraction time and desorption temperature were optimized by the MPS sampler. After a certain extraction time, the fiber was directly transferred into the GC injector for desorption and analysis.

In GC-FID analysis, injector temperature was set at 260 °C under splitless mode. Nitrogen was used as the carrier gas at a constant flow rate of 1.2 mL min^{-1}. The initial oven temperature was 40 °C (held for 1 min), and then increased to 80 °C at a rate of 50 °C min^{-1}, held for 0.2 min, then increased to 250 °C at a rate of 20 °C min^{-1}, held for 2 min, and finally increased to 300 °C at a rate of 15 °C min^{-1}, held for 10 min. The total run time was 25.8 min. In GC-MS analysis, injector temperature was set at 260 °C under splitless mode. Helium was used as the carrier gas at a constant flow rate of 0.9 mL min^{-1}. The initial oven temperature was 50 °C (held for 1 min), and increased to 80 °C at a rate of 50 °C min^{-1}, held for 0.2 min, then increased to 220 °C at a rate of 20 °C min^{-1}, subsequently increased to 235 °C at a rate of 2 °C min^{-1}, held for 2 min and finally increased to 300 °C at a rate of 15 °C min^{-1}, held for 6 min. The total run time was 30.8 min.

Theoretical Analysis. The calculations of adsorption energy and quantity were performed with Materials Studio. Simulated annealing carried out by Adsorption Locator Module was used to calculate the adsorption energies of three bio-MOFs for ten target analytes. Each simulation was composed of 5 cycles and each cycle consisted of 5×10^4 steps. In each cycle, the system was heated up to 10^5 K and then slowly cooled down to 100 K. DREIDING force field and QEq charge were used in the simulation. The other parameters were set to default. The adsorption quantities of the bio-MOFs for the ten target analytes were simulated at 298 K and 101.325 kPa using Metropolis Monte Carlo method, and carried out by Sorption module. For each simulation, the pressure of each analyte was in direct proportion to the analyte’s concentration in working solution used for SPME process. DREIDING force field and QEq charge were used in the simulation. The other parameters were also set to default.

Real Sample Preparation. The environmental water samples included the pond water and the river water. The pond water was collected from our campus while the river water was collected from the Pearl River (Guangzhou, China). Before analysis, all of the water samples were filtered with the 0.45 μm filter membranes.

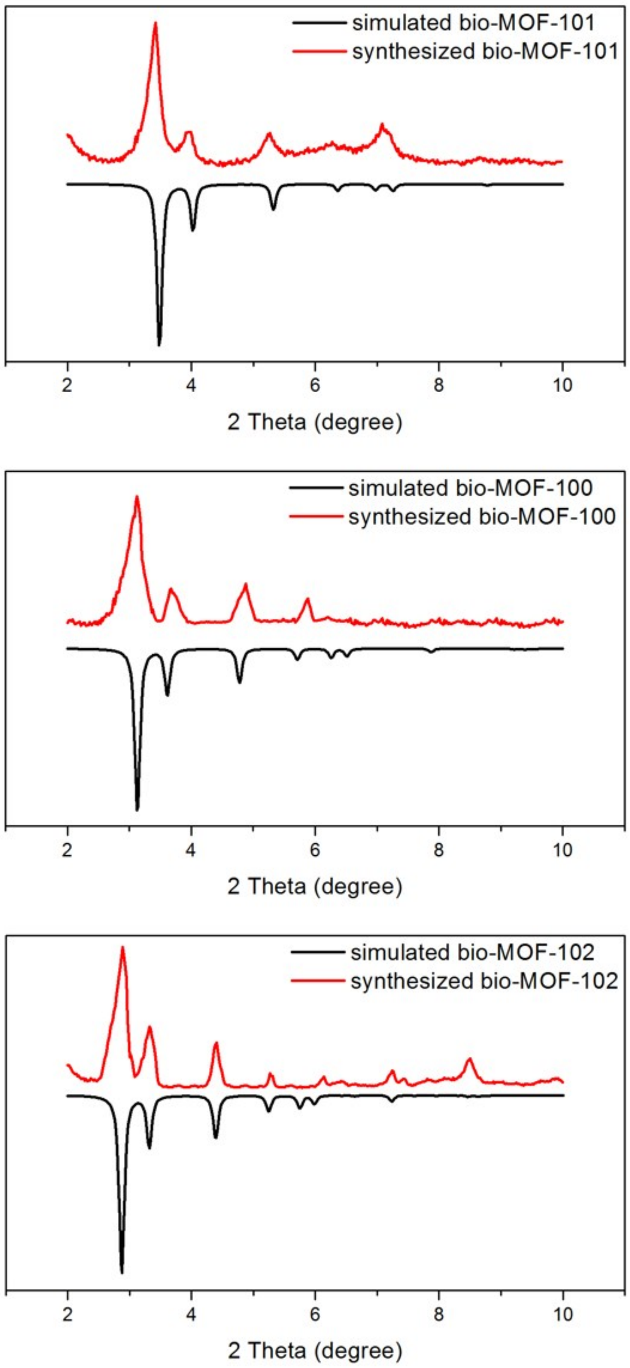

Fig. S1. PXRD patterns of the as-synthesized bio-MOFs 100-102 (red curve, upward) and simulated bio-MOFs 100-102 (black curve, downward).

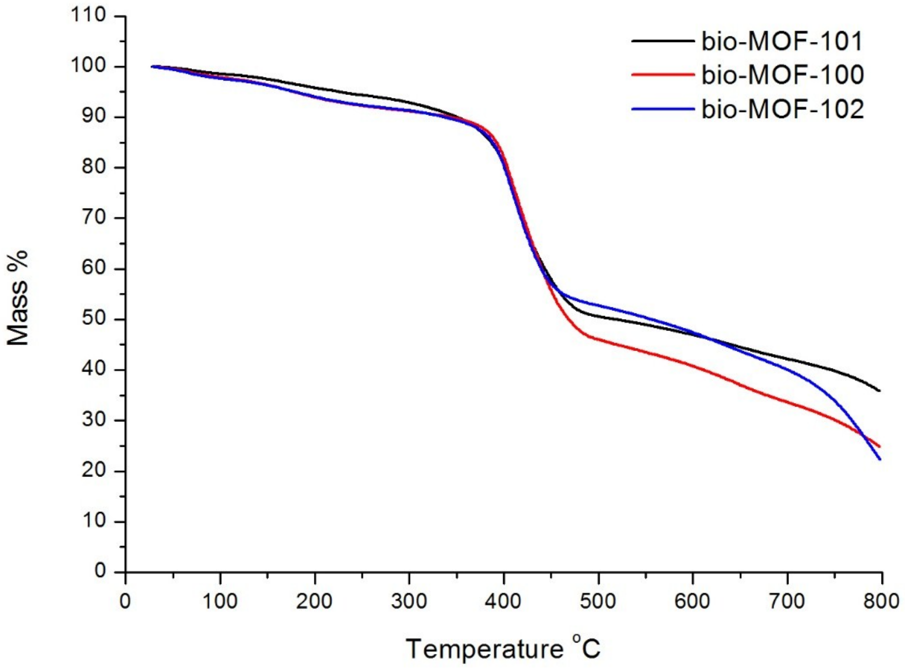

Fig. S2. TG curves of the as-synthesized bio-MOFs 100-102

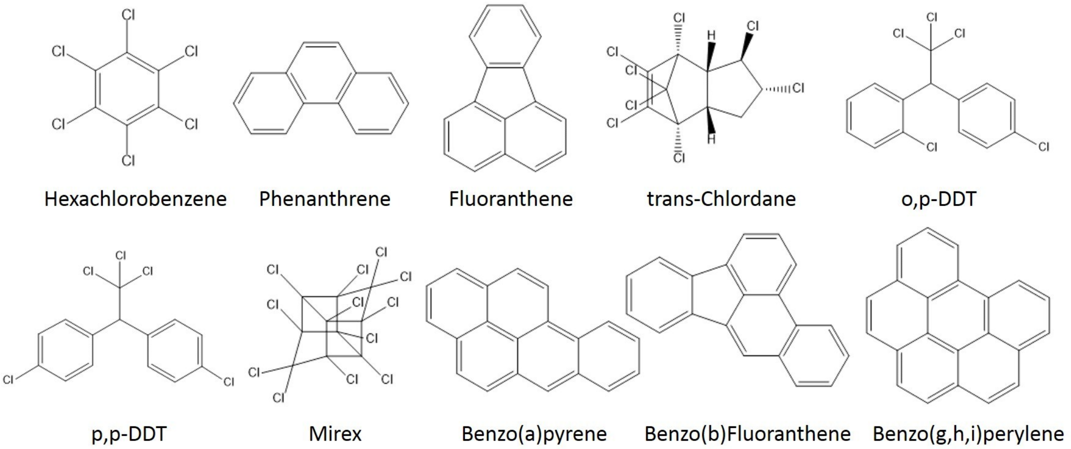

Fig. S3. The ten PAHs and OCPs chosen as the target analytes for the evaluation of the bio-MOFs 100-102 SPME coatings

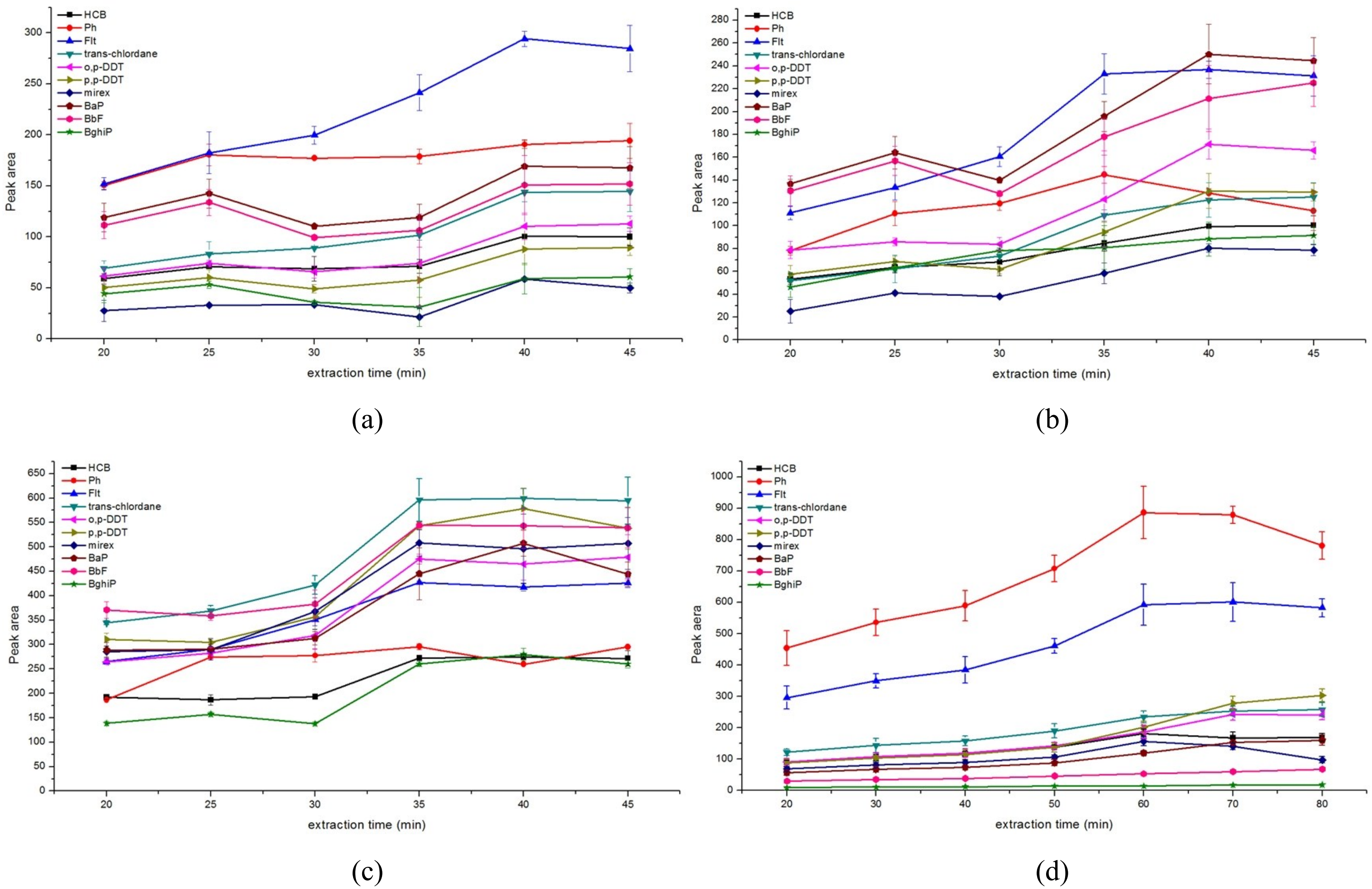

Fig. S4. The extraction time profiles of (a) bio-MOF-101, (b) bio-MOF-100, (c) bio-MOF-102 and (d) PDMS/DVB fibers.

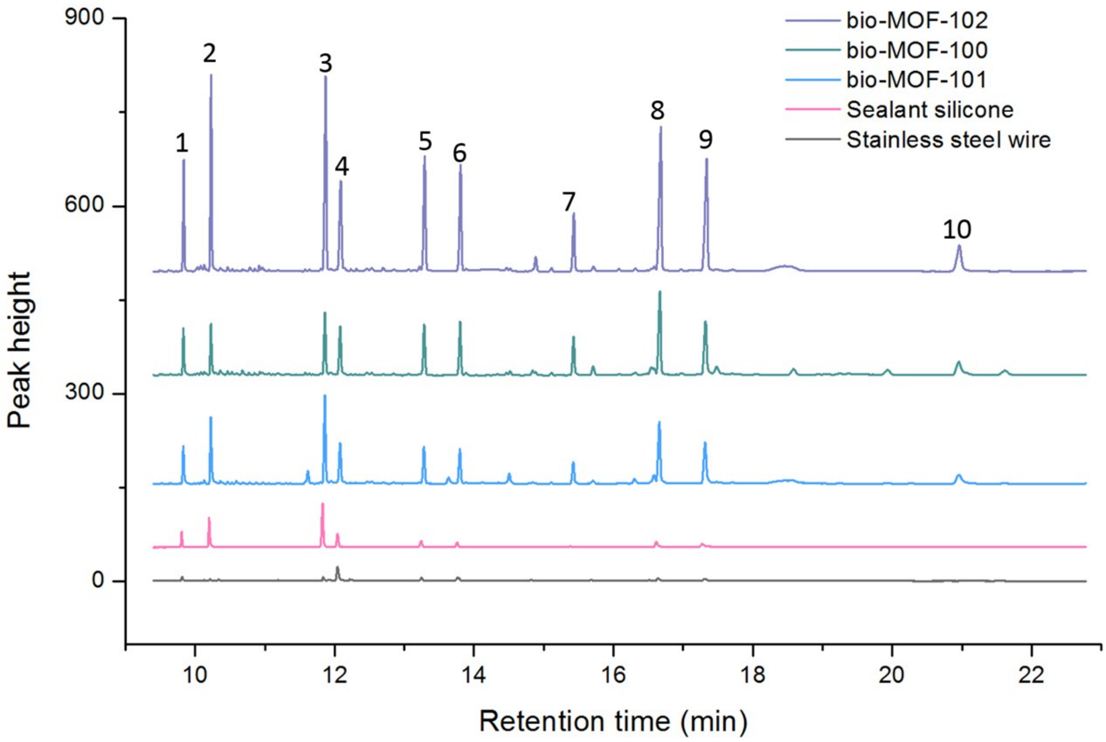

Fig. S5. Comparison of the extraction efficiencies of the bio-MOFs coated fibers, the silicon sealant fiber and the stainless steel wire. (1, HCB; 2, Ph; 3, Flt; 4, trans-Chlordane; 5, o,p-DDT; 6, p,p-DDT; 7, Mirex; 8, Bap; 9, BbF; 10, BghiP.)

Table S1. Physical properties of the target analytes

Analytes	Log K_{ow} [a]	Dipole moment [b]	Molar volume [c] (cm^3 mol^{-1})	Maximum diameter [d] (Å)
HCB	5.73	0.0009	145.6	9.8
Phenanthrene	4.46	0.0178	138.7	11.7
Fluoranthene	5.16	0.1595	148.8	11.6
trans-Chlordane	6.22	2.7616	195.5	11.3
o,p-DDT	6.79	3.9840	221.9	12.3
p,p-DDT	6.91	1.0813	241.1	13.4
Mirex	6.89	1.0281	248.8	11.6
Benzo(a)pyrene	6.13	0.0225	195.2	13.9
Benzo(b)fluoranthene	5.78	0.2019	184.3	13.8
Benzo(g,h,i)perylene	6.63	0.0439	207.2	12.0

[a] K_{ow}: the octanol-water partition coefficient represented the water solubility or the hydrophobicity of the analyte, which was calculated by EPI SuiteTM v4.11.

[b] Dipole moment and molar volume were calculated by Guassian 09 software after operating the structure optimization procedure.

[c] Maximum diameter of the analyte molecule was calculated as the distance between the two farthest-apart atoms plus the van der Waals radii of the two atoms (van der Waals radii of hydrogen, 1.2 Å; chlorine, 1.8Å) by ChemBio 3D Ultra 12.0.

Table S2. Analytical performance of the bio-MOF-102 coated fiber

Analytes	Linear range (ng L^{-1})	R^2	LOD (ng L^{-1})	LOQ (ng L^{-1})	RSD, %	
					Single fiber (n = 5)	Fiber-to-fiber (n = 3)
HCB	6-6,000	0.9958	0.90	3.0	3.9	10
Phenanthrene	5-5,000	0.9901	0.60	2.0	2.8	9.0
Fluoranthene	5-5,000	0.9910	0.23	0.77	4.0	8.5
trans-Chlordane	6-6,000	0.9959	0.64	2.1	10	13
o,p-DDT	12-6,000	0.9981	2.2	7.2	7.1	9.8
p,p-DDT	12-6,000	0.9937	2.3	7.8	9.9	11
Mirex	6-6,000	0.9982	0.59	2.0	4.3	14
Benzo(a)pyrene	5-5,000	0.9923	0.80	2.7	9.0	10
Benzo(b)fluoranthene	5-5,000	0.9908	0.78	2.6	3.1	7.3
Benzo(g,h,i)perylene	10-1,000	0.9968	2.2	7.5	6.4	6.7

Table S3. Analytical results for the determination of PAHs and OCPs in water samples using the proposed SPME-GC-MS method

Analytes	Pond water		River water	
	Detected concentration (ng L^{-1})	Recovery[b] (%)	Detected concentration (ng L^{-1})	Recovery[b] (%)
HCB	20.7±1.0	84.8	16.2±0.8	87.1
Phenanthrene	nd[a]	92.8	nd[a]	113.2
Fluoranthene	14.8±0.9	110.2	nd[a]	97.2
trans-Chlordane	16.5±1.5	89.2	nd[a]	81.6
o,p-DDT	nd[a]	83.6	nd[a]	92.8
p,p-DDT	nd[a]	107.5	nd[a]	84.4
Mirex	33.8±1.5	89.5	20.3±1.3	108.2
Benzo(a)pyrene	nd[a]	110.8	nd[a]	95.1
Benzo(b)fluoranthene	nd[a]	98.5	nd[a]	88.7
Benzo(g,h,i)perylene	nd[a]	79.8	nd[a]	81.0

[a] nd: not detected.

[b] Recovery of spiked 20/24 ng L^{-1} of PAHs/OCPs.