

**Supporting Information for**  
**Simultaneous and Direct Analysis of Multiple Types of Organic Contaminants in**  
**Water Based on Suitable Amount of Au Nanoparticles Decorated MOF Using**  
**SALDI-TOF MS**

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## Chemicals and Materials

Potassium borohydride ( $\text{KBH}_4$ ), N,N-dimethylformamide (DMF, 99.5%), chloroauric acid ( $\text{HAuCl}_4$ ), and ethanol were purchased from Sinopharm Chemistry Reagent Co., Ltd. (Beijing, China). Zirconium (IV) chloride ( $\text{ZrCl}_4$ ) was from Strem Chemicals, Inc. (Newburyport, MA, USA). The  $\alpha$ -cyano-4-hydroxycinnamic acid (CHCA), 2,5-dihydroxybenzoic acid (2, 5-DHB), potassium salts of perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluorooctanesulfonate (PFOS) tetrabromobisphenol A (TBBPA) and pentabromophenol (PBP) were purchased from Sigma-Aldrich (Oakville, ON, Canada). Pentachlorophenol (PCP), tetrachlorobisphenol A (TCBPA), L-thyronine (T3), L-thyroxine (T4), 17- $\alpha$ -ethynylestradiol (EE2), and 2-amino-1,4-benzenedicarboxylic acid ( $\text{NH}_2\text{-H}_2\text{BDC}$ ) were from TCI Development Co. LTD (Shanghai, China). Bisphenol A (BPA) and 1,4-benzenedicarboxylic acid (99%,  $\text{H}_2\text{BDC}$ ) were supplied by Acros Organics (Morris Plains, NJ, USA). Benzo(a)pyrene (BaP) was obtained from AccuStandard (New Haven, USA). All the target chemicals were dissolved in ethanol for use. HPLC-grade acetonitrile was from Fisher Scientific (NJ, USA). All chemicals were of analytical reagent grade and used without further purification. Ultrapure water was prepared in the lab by using a Milli-Q SP reagent water system (Millipore, Bedford, MA, USA).

### Preparation of UiO-66 and UiO-66-NH<sub>2</sub>

To prepare UiO-66, 0.932g  $\text{ZrCl}_4$  and 0.792g  $\text{H}_2\text{BDC}$  were mixed with 40 mL DMF in a Teflon-lined autoclave and heated to 130 °C for 24 h. After cooling down to room temperature, the white precipitates were obtained by centrifugation and washed with DMF and ethanol, and then dried in vacuum at 120°C for 4 h.

The UiO-66-NH<sub>2</sub> was prepared according to the method reported in literature.<sup>37</sup> Briefly,  $\text{ZrCl}_4$  (1.50) and  $\text{NH}_2\text{-H}_2\text{BDC}$  (1.56g) were dissolved in 160 mL of DMF at room temperature. The resulting mixture was transferred into a Teflon-lined stainless-steel autoclave and sealed to heat at 80 °C for 12 h and then held at 100 °C for 24h. When the autoclave was cooled to room temperature, the obtained products were washed with DMF three times and repeatedly washed with absolute ethanol for 3 days while heated at 60 °C. Finally the yellow powder was dried and activated at 120°C under vacuum for 4 h.

### Preparation of UiO-66-NH<sub>2</sub>@Au composites

UiO-66 and UiO-66-NH<sub>2</sub> were synthesized according to the methods reported in literature.<sup>43</sup> UiO-66-NH<sub>2</sub>@Au composites were prepared via an aqueous impregnation method. In a typical procedure, 200 mg of UiO-66-NH<sub>2</sub> were dispersed in 150 mL deionized water. Then 5 ml HAuCl<sub>4</sub> solution (1.0 mM) was added into the UiO-66-NH<sub>2</sub> suspension under the mechanical agitation and stirred overnight. After that, 5 mL of fresh NaBH<sub>4</sub> (0.1 M) was added into the mixture and the reaction was allowed to proceed for another 2 h under stirring. The brown products were washed with ethanol and deionized water three times, followed by drying at 60 °C under vacuum. The characterization of the obtained materials was present in Supporting Information.

### **Sample Preparation**

CHCA (10 mg mL<sup>-1</sup>) and DHB (10 mg mL<sup>-1</sup>) were dissolved in the mixture of ACN and 0.1% aqueous TFA (2:1, V/V), respectively. The UiO-66-NH<sub>2</sub>@Au matrix were dispersed in deionized water and sonicated for 1 min to form homogeneous suspension solution (1 mg mL<sup>-1</sup>). In a typical LDI-TOF MS analysis, 10 μL of the matrix solution and 10 μL of analyte solution were mixed by vortex in a centrifuge tube, followed by directly dotting 1 μL of the matrix–analyte mixture onto the MALDI target plate (AnchorChip TM target plate, Bruker Daltonics, Germany), and air-dried for LDI-TOF MS analysis.

### **Enrichment and Analysis of Halogenated Flame Retardants and PFCs from Water**

Suitable amount of UiO-66-NH<sub>2</sub>@Au was dispersed into 40 mL of water solution containing target pollutants, the mixture was vibrated for 30 min for enrichment. After that, the mixture was centrifugated for 10 min to collect the UiO-66-NH<sub>2</sub>@Au. The UiO-66-NH<sub>2</sub>@Au with the sorbed analytes were redispersed in 1 mL of acetonitrile/water solution (1:1, V:V) and sonicated for 30 s. Finally, 1 μL of the above mixture was spotted onto the stainless steel plate for LDI-TOF MS analysis. Two river water samples and tap water were filtered through 0.45 μm nylon filter to remove the suspended materials before use.

### **MALDI-TOF MS Instrumentation**

MALDI-TOF MS experiments were performed on a Bruker Autoflex II mass spectrometer (Bruker Daltonics, Germany) equipped with a nitrogen laser operated at 337 nm and laser attenuator offset of ~30 % in positive and negative reflection mode. An accelerating voltage from -20 kV to 20 kV was employed. The spectra were recorded by summing 200 laser shots with a LeCroy 9314 digital oscilloscope. All mass spectra were analyzed by Flex Analysis software provided by Bruker Daltonics

Corp.

### **Characterization of the Material**

The size and morphology of the synthesized materials were surveyed using a Hitachi S-5500 field-emission scanning electron microscope (FE-SEM, Tokyo, Japan) and a JEOL JEM-2010 high-resolution transmission electron microscope (HRTEM, Kyoto, Japan). X-Ray powder diffraction (XRD, Almelo, Netherlands) which using a Cu K $\alpha$  radiation ranging from 5° to 90° with a resolution of 0.02° was utilized to analysis the crystalline. Fourier Transform infrared spectroscopy (FTIR) spectra were obtained from 4000 to 400 cm<sup>-1</sup> by a NEXUS 670 Infrared Fourier Transform Spectrometer (Nicolet Thermo, Waltham, MA). The sample powder was prepared by mixing with KBr and then pressing the mixture into transparent disks. Surface area, pore size and volume were measured by Brunauer-Emmett-Teller (BET) methods (ASAP2000 V3.01A; Micromeritics, Norcross, GA). X-Ray photoelectron spectroscopy (XPS) was measured with an ESCA-Lab-200i-XL spectrometer (Thermo Scientific, Waltham, MA) with monochromatic Al K $\alpha$  radiation (1486.6 eV).

### **Pretreatment of water samples with UiO-66-NH<sub>2</sub>@Au as adsorbents via the traditional SPE method**

After adsorption for 30 min, the water samples were centrifugated for 10 min to collect the UiO-66-NH<sub>2</sub>@Au. Phenols were eluted with acetonitrile and PFCs were desorbed with methanol three times respectively. The eluents were concentrated to 0.5 mL with a stream of N<sub>2</sub> at 50 °C. Phenols were detected with HPLC system (Dionex, USA). The HPLC equipment includes a Dionex P680 HPLC pump, an on-line connected degasser solvent rack (SOR-100), a thermostated column compartment TCC-100, a PDA-100 photodiode array detector. The separations were conducted on a Diamonsil® C18 column (250×4.6 mm; particle size, 5 μm). Samples were injected into a 20 μL loop, and the mobile phase for phenols was acetonitrile: 0.5% HAC (80:20, v/v) at a flow rate of 1.0 mL min<sup>-1</sup>. The wavelength was set at 220 nm.

For PFCs, mass spectrometry was performed with a tandem mass spectrometer system (API 3200; Applied Biosystems/MDS SCIEX, Foster City, CA) with an electrospray ionization source (ESI-MS/MS) operated in electrospray negative ionization mode and Analyst 1.4.2 software. A 10 min dualistic gradient of 100% methanol (A) and 50 mmol L<sup>-1</sup> NH<sub>4</sub>OAc (B) was employed. Generally, it began with 28% NH<sub>4</sub>OAc, and NH<sub>4</sub>OAc was reduced to 5% at 4 min before being returned to the original condition at 7 min. The flow rate was operated at 1.0 mL min<sup>-1</sup>. The analysis and quantification were conducted using the ESI-MS/MS system. MS/MS parameters were optimized in multiselected reaction monitoring (MRM). The parent/daughter ions (Q1/Q3) and retention time for PFOS, PFHxS and PFBS are 498.9/79.9, 4.35 min, 398.8/79.9, 3.30 min, and 298.9/79.9, 2.31 min, respectively. Correlation between peak areas and analyte concentrations (0.5-50 ng L<sup>-1</sup>) was determined by linear regression with a correlation coefficient in the range of 0.995-0.999.

**Table S1** Content of each element on UiO-66-NH<sub>2</sub> and UiO-66-NH<sub>2</sub>@Au according to the XPS analysis

Element	UiO-66-NH <sub>2</sub> @Au Atomic%	UiO-66-NH <sub>2</sub> Atomic%
Au	0.3	
Zr	4.39	4.7
C	56.18	55.73
N	6.95	7.47
O	32.19	32.11

**Table S2** Analytical parameters of the targets detected in a single run using SALDI-TOF MS

Analytes	Calibration equation	Linear Range (pg)	Correlation Coefficients	LOD (pg) (S/N=3)	RSD (%)
<b>BPA</b>	y = 1.8703x + 19.366	50-1000	0.998	30.6	10.2-18.9
<b>PCP</b>	y = 19.527x + 268.81	50-1000	0.993	5.17	8.91-16.3
<b>EE2</b>	y = 2.2497x - 19.044	50-1000	0.999	38.2	9.53-16.5
<b>TCBPA</b>	y = 10.576x + 205.83	50-1000	0.998	18.8	8.55-14.3
<b>PBP</b>	y = 9.6725x + 689.21	50-1000	0.989	3.06	7.52-18.1
<b>TBBPA</b>	y = 6.5434x + 135.69	50-1000	0.997	25.2	9.19-19.0
<b>T3</b>	y = 0.4294x + 62.667	100-10000	0.994	44.2	5.45-14.2
<b>T4</b>	y = 0.5191x + 145.33	100-10000	0.997	36.1	5.22-11.3
<b>PFBS</b>	y = 41.183x + 232.22	1-100	0.997	0.65	11.9-18.4
<b>PFHxS</b>	y = 84.132x + 180.78	1-100	0.999	0.25	8.79-16.7
<b>PFOS</b>	y = 178.16x - 223.56	1-100	0.995	0.19	9.11-12.9

**Table S3** Analytical parameters of the targets detected individually using SALDI-

TOF MS

Analytes	Calibration equation	Linear Range (pg)	R <sup>2</sup>	LOD (pg) (S/N=3)	RSD (%)
PBP	$y=109.333x-0.37$	50-1000	0.992	2.55	8.2-17.8
TCBPA	$y=4.507x-0.131$	50-1000	0.991	16.9	10.1-15.9
TBBPA	$y=3.882x+0.115$	50-1000	0.994	21.9	6.3-12.2
PCP	$y=3.756x+1.815$	50-1000	0.985	4.31	8.8-14.7
BPA	$y=2.504x-0.074$	50-1000	0.987	28.9	12.0-18.9
EE2	$y=2.251x+0.0346$	50-1000	0.986	33.5	12.1-19.3
T3	$y=0.412x+0.111$	100-10000	0.991	40.2	5.3-14.8
T4	$y=0.551x-0.005$	100-10000	0.995	35.4	5.9-11.3
PFBS	$y=77.75x-5.968$	1-100	0.995	0.54	11.1-18.2
PFHxS	$y=106.47x-2.617$	1-100	0.997	0.22	8.4-16.7
PFOS	$y=158.29x-1.92$	1-100	0.996	0.16	9.2-12.5

**Table S4** Analytical parameters of the targets detected simultaneously using SPE-

Analytes	Calibration Equation	R <sup>2</sup>	Linear	Detection	RSD (%)
			Range (ng mL <sup>-1</sup> )	Limits (ng mL <sup>-1</sup> )	
PFBS	y=394.17x-197.27	0.987	0.05-10	0.12	9.8-15.5
PFHxS	y=617.52x+58.529	0.991	0.05-10	0.044	11.2-17.6
PFOS	y=1275.8x+201.79	0.988	0.05-10	0.020	10.5-17.5
TCBPA	y=114.08x+16.552	0.994	0.5-50	0.80	7.8-14
PBP	y=206.83x+254.48	0.993	0.5-50	0.21	11.2-17.9
TBBPA	y=95.103x+161.79	0.994	0.5-50	0.73	9.7-15.7

SALDI-TOF MS technique

**Table S5** LODs and recoveries of halogenated phenols and PFCs obtained by the traditional SPE and SALDI-TOF MS methods

	Technique	Analytes					
		PBP	TCBPA	TBBPA	PFBS	PFHxS	PFOS
LOD (ng/mL) <sup>a</sup>	SPE-HPLV-UV or SPE-HPLC/MS	1.41	0.51	0.195	0.008	0.006	0.003
	SPE-SALDI-TOF MS	0.80	0.73	0.21	0.12	0.044	0.020
Recovery (%) <sup>b</sup>	SPE-HPLV-UV or SPE-HPLC/MS	25.3	57.5	72.5	12.8	16.0	21.8
	SPE-SALDI-TOF MS	30.4	52.8	75.8	11.2	12.5	21.0

<sup>a</sup> The concentration range for halogenated phenols is 5-500 ng/mL; and for PFCs is 0.5-50 ng/mL

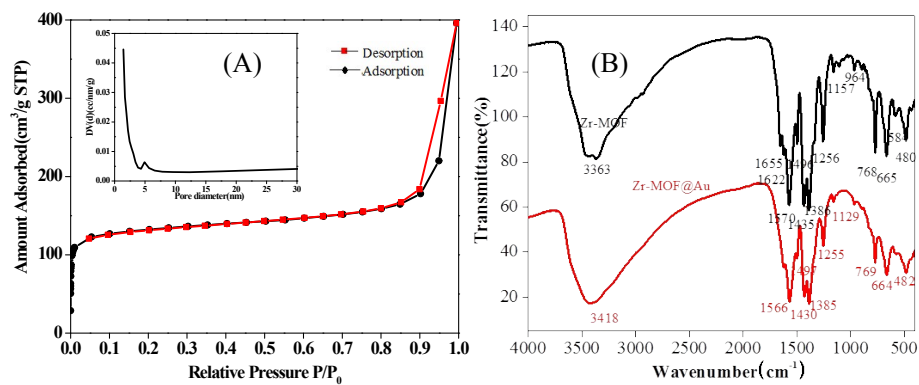
<sup>b</sup> The spiked concentration of halogenated phenols is 10 ng/mL, PFCs 1 ng/mL

**Table S6** Recoveries and RSD of analytes spiked in tap water and river water samples

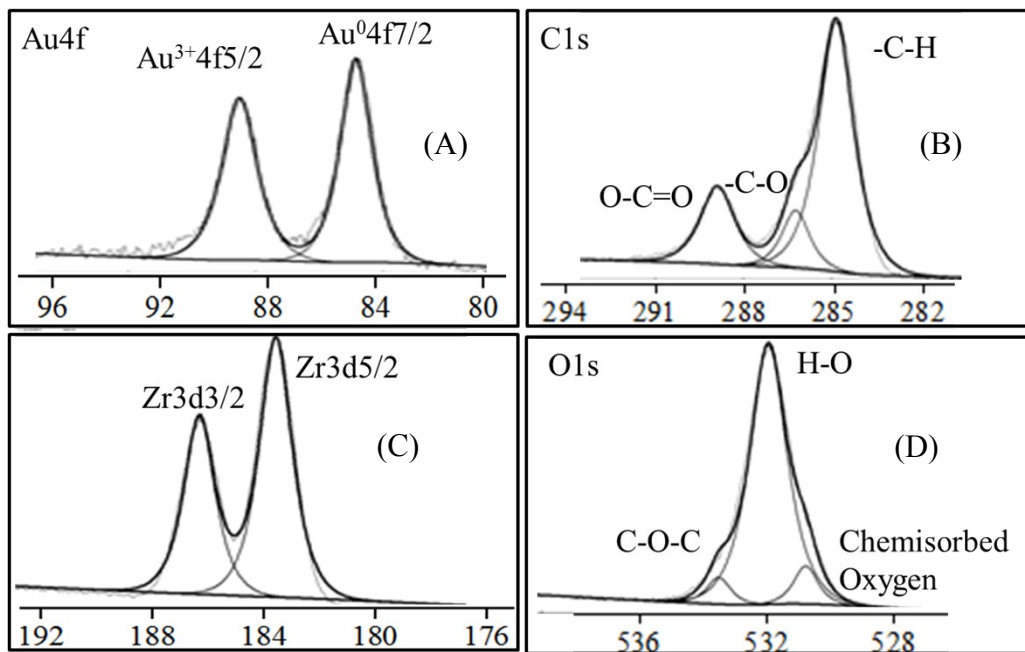
Analytes	Direct detection			SPE-SALDI-TOF MS		
		50 ng mL <sup>-1</sup>			10 ng mL <sup>-1</sup>	
<b>PBP</b>	93.0 (13.2%)	84.2 (12.7%)	81.2 (14.5%)			
<b>TCBPA</b>	93.0 (11.4%)	91.0 (9.5%)	86.8 (12.4%)			
<b>TBBPA</b>	89.1 (7.8%)	84.4 (6.9%)	80.3 (8.9%)			
	5 ng mL <sup>-1</sup>			10 ng mL <sup>-1</sup>		
<b>PFBS</b>	91.7 (11.4%)	85.0 (12.9%)	83.3 (14.5%)			
<b>PFHxS</b>	92.4 (10.7%)	86.1 (9.6%)	83.8 (12.5%)			
<b>PFOS</b>	93.3 (6.3%)	90.7 (8.4%)	86.7 (7.5%)			
	10 ng mL <sup>-1</sup>			1 ng mL <sup>-1</sup>		
<b>PBP</b>	87.9 (12.2%)	81.6 (13.9%)	71.8 (10.7%)	93.2 (6.5%)	89.5 (5.8%)	85.6 (7.1%)
<b>TCBPA</b>	-	-	-	92.0 (9.8%)	87.8 (11.5%)	82.0 (14.2%)
<b>TBBPA</b>	-	-	-	95.9 (7.4%)	88.9 (8.3%)	83.7 (10.7%)
	1 ng mL <sup>-1</sup>			1 ng mL <sup>-1</sup>		
<b>PFBS</b>	85.6 (16.7%)	75.8 (17.6%)	72.0 (17.9%)	91.7 (11.3%)	82.5 (12.5%)	79.2 (14.5%)
<b>PFHxS</b>	87.9 (13.4%)	79.9 (12.7%)	77.9 (15.1%)	91.9 (10.5%)	87.4 (9.8%)	78.1 (12.5%)
<b>PFOS</b>	89.7 (11.7%)	87.6 (9.3%)	81.1 (8.9%)	89.9 (7.7%)	82.6 (8.4%)	72.1 (6.7%)

- Not detected

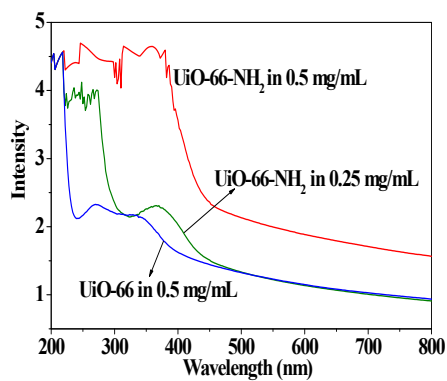




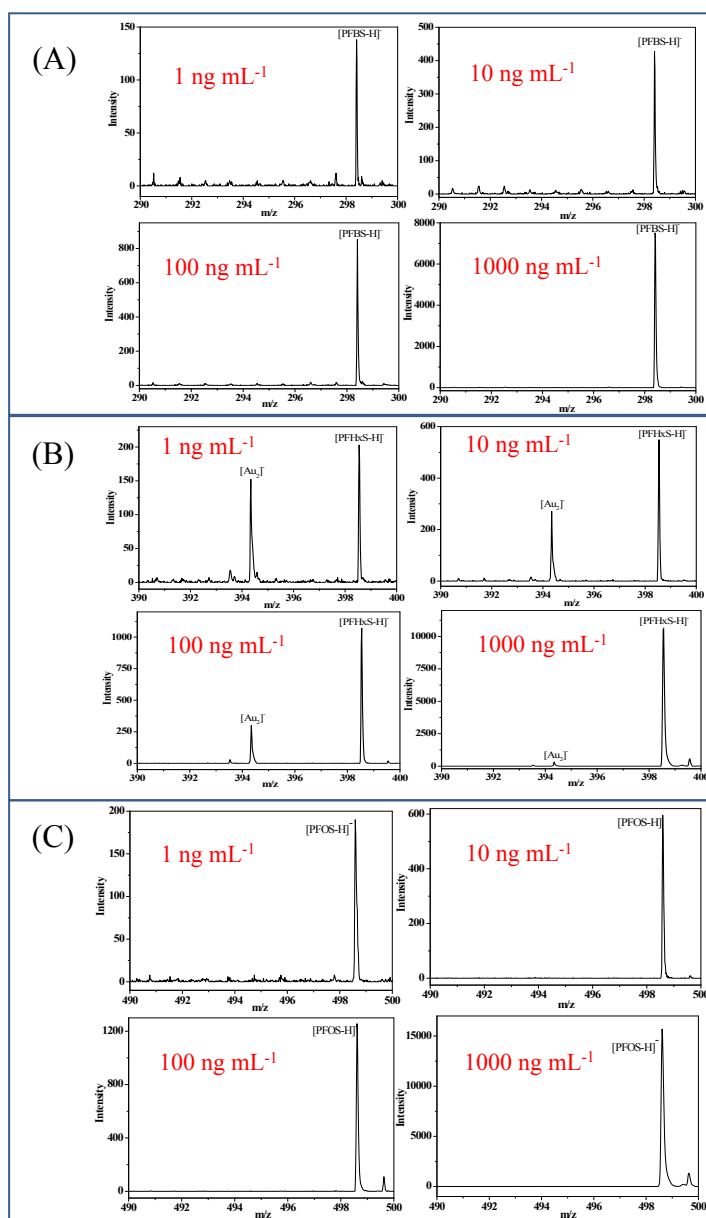
**Fig. S1.** Nitrogen adsorption-desorption isotherm of UiO-66-NH<sub>2</sub>@Au (inset is the pore size distribution of UiO-66-NH<sub>2</sub>@Au) (A) and FTIR spectra of UiO-66-NH<sub>2</sub> and UiO-66-NH<sub>2</sub>@Au (B)



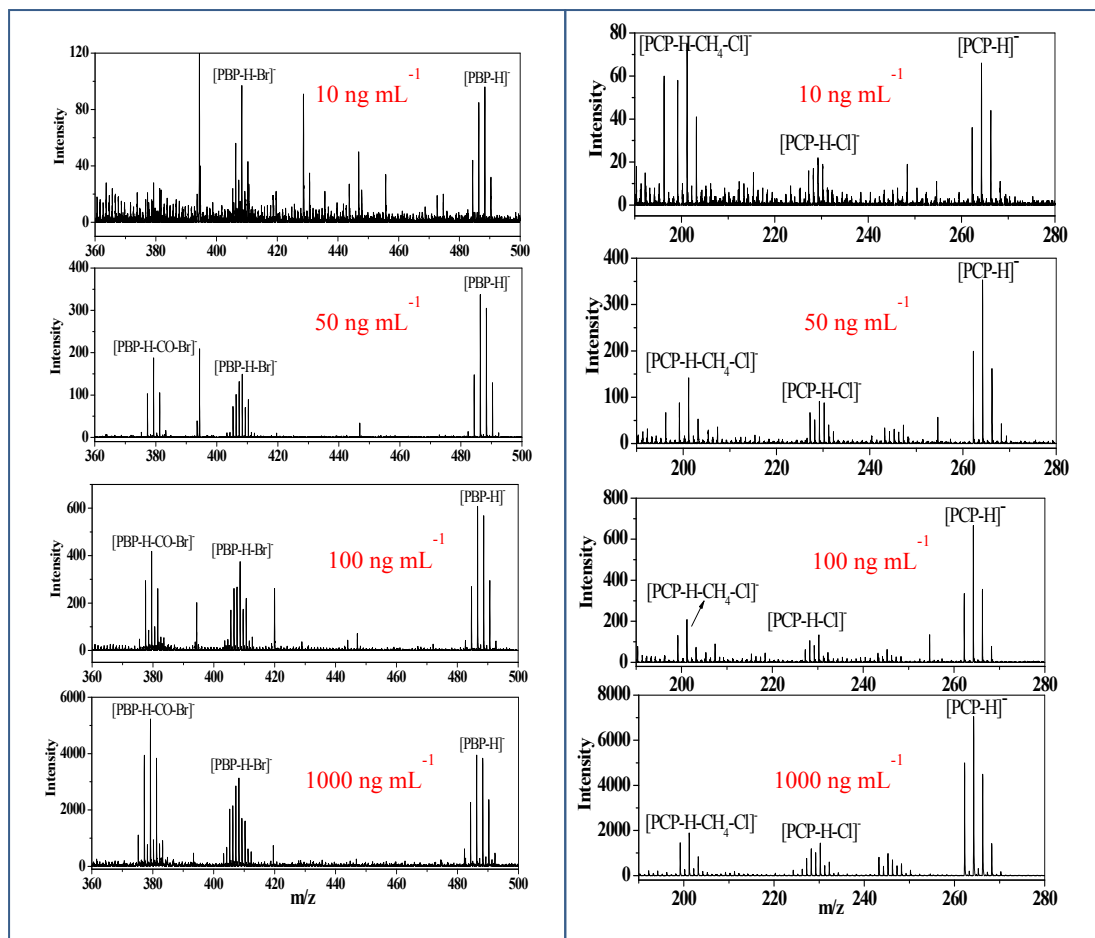
**Fig.S2.** Peak fitting of the XPS Au4f (A), C1s (B), Zr3d (C), and O1s (D) core-level lines of UiO-66-NH<sub>2</sub>@Au.



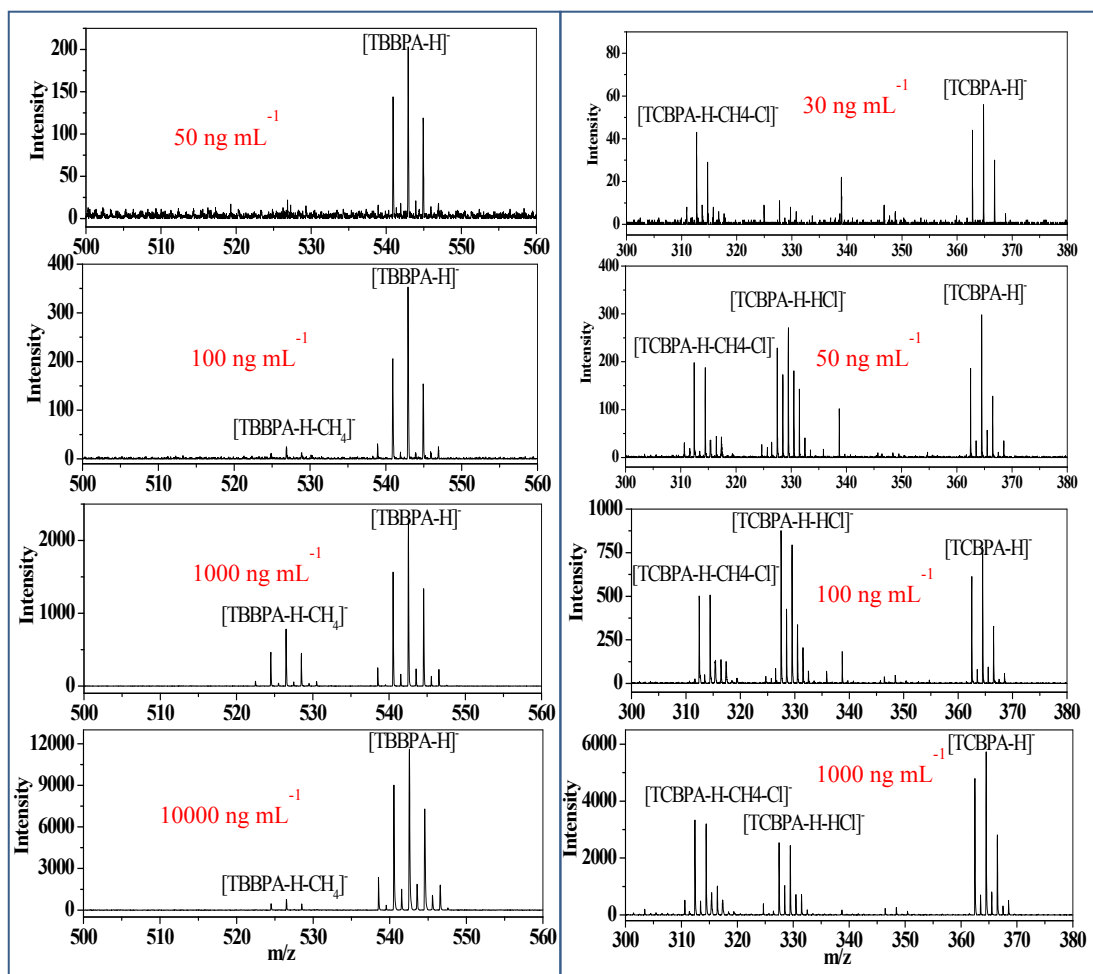
**Fig. S3.** UV-Vis spectra of UiO-66 and UiO-66-NH<sub>2</sub>, the adsorbance of UiO-66-NH<sub>2</sub> increases twice at 337 nm than that of UiO-66, the obvious peak in the spectrum of UiO-66-NH<sub>2</sub> at 365 nm is probably attributed to the -NH<sub>2</sub> group.



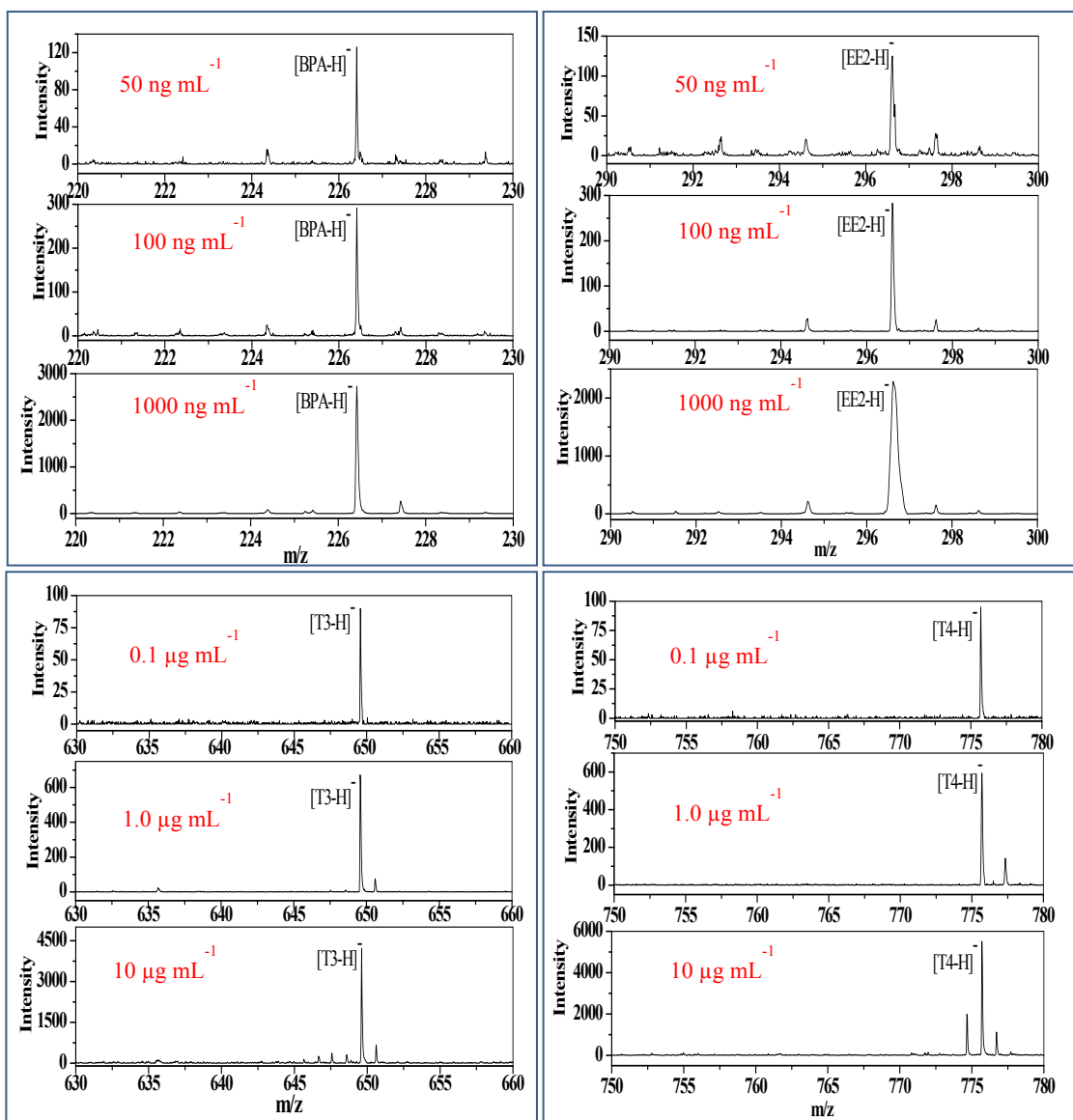
**Fig. S4.** MS spectra of BaP and PFCs in different concentration detected by SALDI-TOF MS assisted by UiO-66-NH<sub>2</sub>@Au matrix: PFBS (A), PFHxS (B) and PFOS (C) in negative reflection mode.



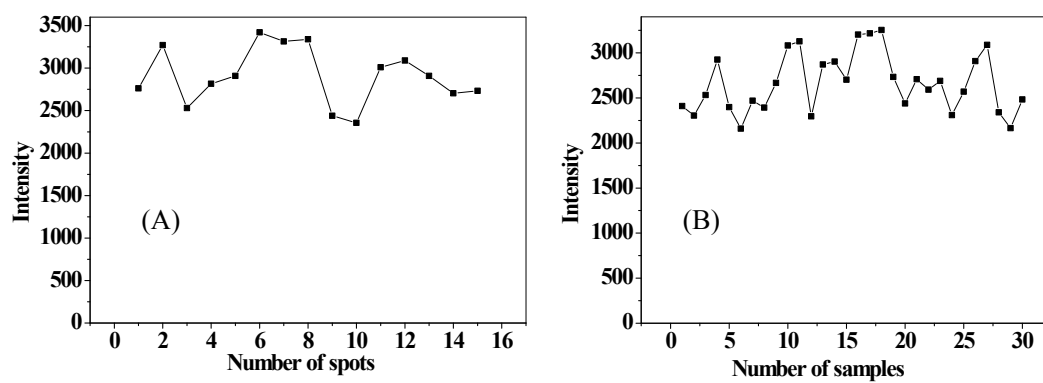
**Fig. S5.** MS spectra of PBP and PCP in various concentrations detected by SALDI-TOF MS assisted by UiO-66-NH<sub>2</sub>@Au matrix in negative reflection mode.



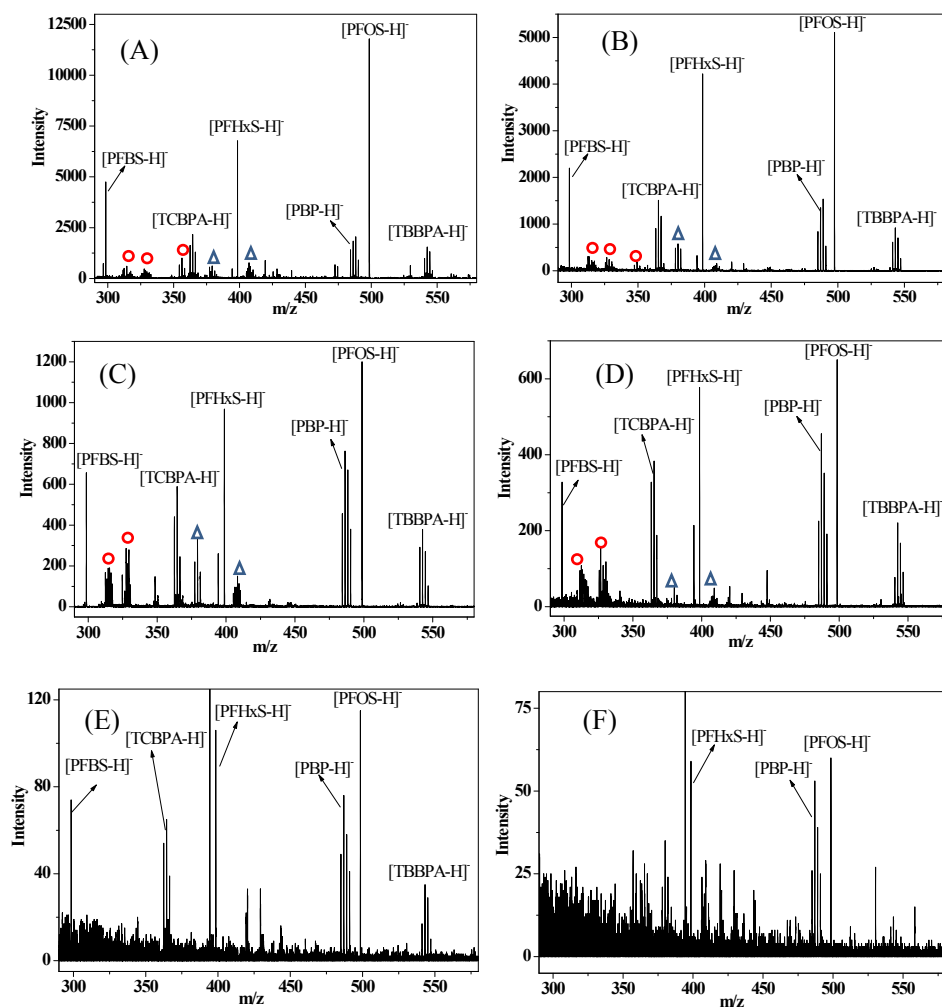
**Fig. S6.** MS spectra of TBBPA and TCBPA in various concentrations detected by SALDI-TOF MS assisted by UiO-66-NH<sub>2</sub>@Au matrix in negative reflection mode.



**Fig. S7.** MS spectra of BPA, EE2, T3 and T4 in various concentrations detected by SALDI-TOF MS assisted by UiO-66-NH<sub>2</sub>@Au matrix in negative reflection mode.

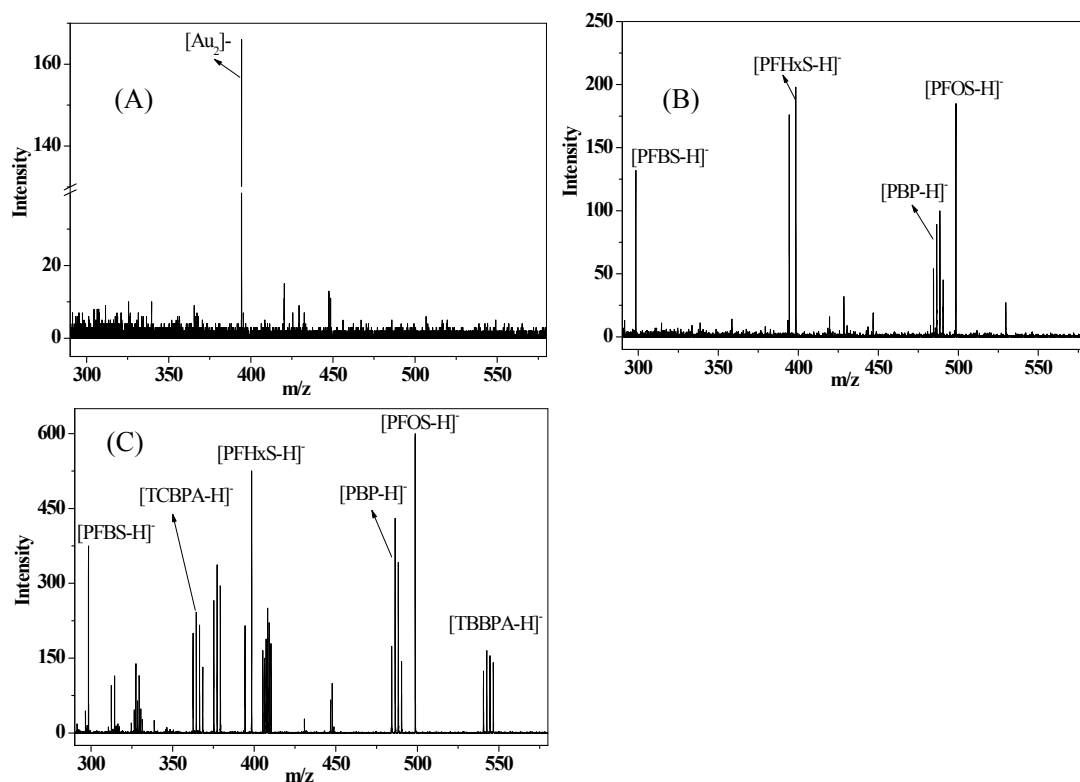


**Fig. S8.** MS signal intensity of 100 ng mL<sup>-1</sup> PBP reproducibility gained from the same sample spot (A) and from 30 different sample spots (B) with UiO-66-NH<sub>2</sub>@Au as matrix.

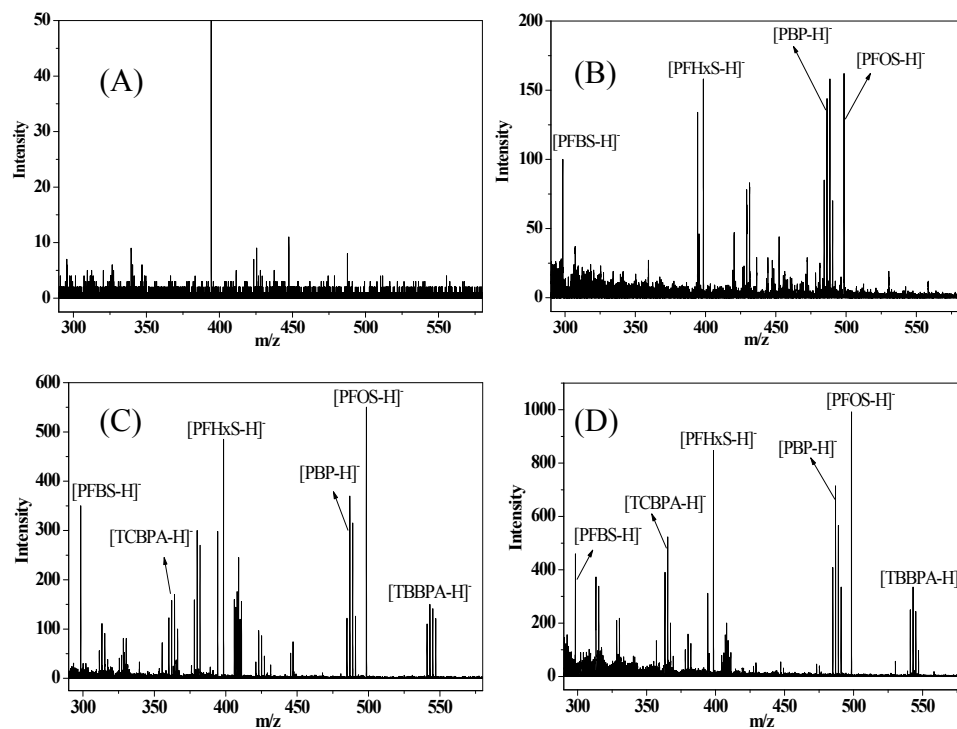


**Fig. S9.** Simultaneous analysis of PFCs and halogenated fire retardants from 40 mL of deionized water samples after SPE with  $\text{UiO-66-NH}_2@Au$  and measured directly using SALDI-TOF MS, the concentration of halogenated fire retardants and PFCs were 50 and 10  $\text{ng mL}^{-1}$  (A), 30 and 5  $\text{ng mL}^{-1}$  (B), 10 and 1  $\text{ng mL}^{-1}$  (C), 5 and 0.5  $\text{ng mL}^{-1}$  (D), 1 and 0.1  $\text{ng mL}^{-1}$  (E), and 0.5 and 0.05  $\text{ng mL}^{-1}$  (F), respectively. Circle, and triangle represent the fragment ions of TCBPA and PBP.

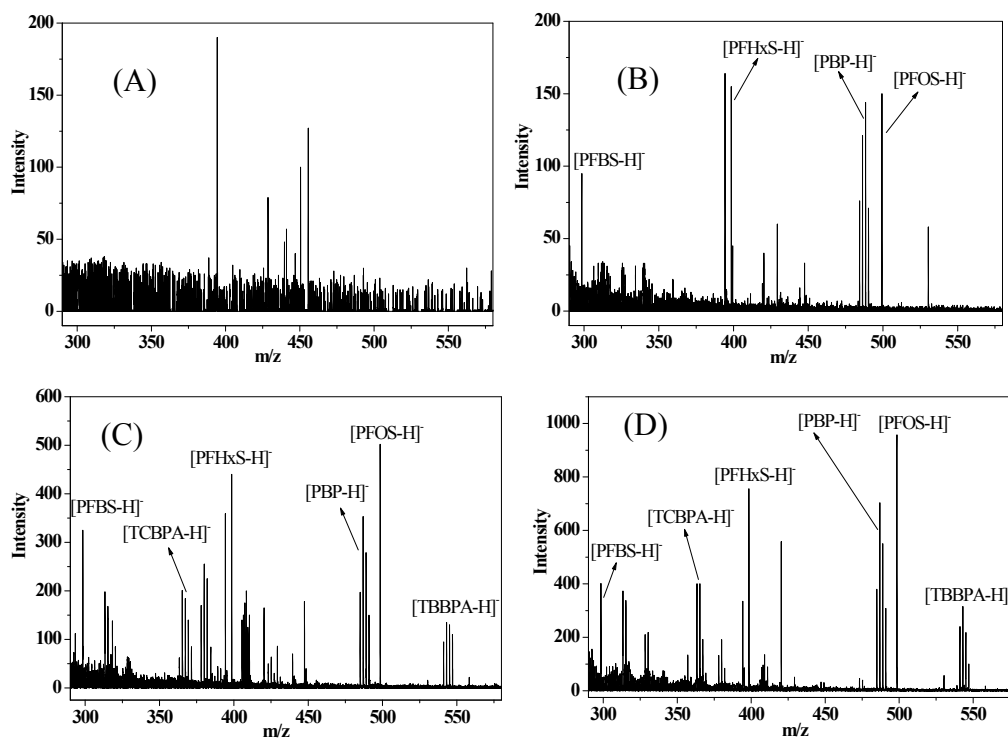




**Fig. S10.** MS spectra of blank tap water sample (A), 10 ng mL<sup>-1</sup> of halogenated fire retardants and 1 ng mL<sup>-1</sup> of PFCs spiked in DI water (B), and 50 ng mL<sup>-1</sup> of halogenated fire retardants and 5 ng mL<sup>-1</sup> of PFCs spiked in DI water (C).



**Fig. S11.** Simultaneous analysis of PFCs and halogenated fire retardants in Xiaoqing River water samples using the established SPE-SALDI-TOF MS technique: MS spectra of blank river water (A), 10 ng mL<sup>-1</sup> of halogenated fire retardants and 1 ng mL<sup>-1</sup> of PFCs spiked in river water (B), 50 ng mL<sup>-1</sup> of halogenated fire retardants and 5 ng mL<sup>-1</sup> of PFCs spiked in river water (C), and MS spectra of 10 ng mL<sup>-1</sup> of halogenated fire retardants and 1 ng mL<sup>-1</sup> of PFCs in river water (D) after preconcentrated with UiO-66-NH<sub>2</sub>@Au and direct detected using SALDI-TOF MS.



**Fig. S12.** Simultaneous analysis of PFCs and halogenated fire retardants in Tonghui River water samples using the established SPE-SALDI-TOF MS technique: MS spectra of blank river water (A), 10 ng mL<sup>-1</sup> of halogenated fire retardants and 1 ng mL<sup>-1</sup> of PFCs spiked in river water (B), 50 ng mL<sup>-1</sup> of halogenated fire retardants and 5 ng mL<sup>-1</sup> of PFCs spiked in river water (C), and MS spectra of 10 ng mL<sup>-1</sup> of halogenated fire retardants and 1 ng mL<sup>-1</sup> of PFCs in water sample (D) after preconcentrated with UiO-66-NH<sub>2</sub>@Au and direct detected using SALDI-TOF MS.