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Electronic Supplementary Material

Metal organic framework/chitosan foams functionalized with polyethylene oxide as sorbent for enrichment and analysis of bisphenols in beverages and water

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Content list

1. Information of reagents and materials

Polyethylene oxide was obtained from Macklin Chemistry Co. (Shanghai, China). Chitosan was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium chloride (NaCl), and acetic acid glacial were gained from Damao Chemical Reagent Factory (Tianjin, China). Ethyl acetate, dichloromethane, and cyclohexane were acquired from Yuwang Group (Shandong, China). Glutaraldehyde was obtained from Fuchen Chemical Reagent Factory (Tianjin, China). Gelatin was obtained from Hengxing Chemical Reagent Factory (Tianjin, China). All of the above reagents were of analytical grade. HPLC-grade methanol, acetonitrile, acetone, and ethanol were bought from Yuwang Group (Shandong, China). Ultrapure water was obtained using a Milli-Q Reagent water system.

2. Screening experiments of MOF/CS/PEO foams

Different types of MOF/CS/PEO foams were placed into 10 mL of the sample solution (pH 7.0) spiked with 10 ng/L standard solutions of the five targets in a 10 mL centrifuge tube (Eppendorf tube) under vortex for 30 min. The foam was then taken out and placed into a 4 mL centrifuge tube (Eppendorf tube) with a pair of tweezers followed by drying with filter paper. Subsequently, 1 mL of acetone was added to desorb the analytes by vortexing for 30 min. The desorption solvent was dried with a gentle stream of nitrogen at 30°C and 200 μL of initial mobile phase was used for the re-dissolution of the residues. Finally, the resulting solution was referred as an analytical solution for HPLC-FLD analysis after filtration through a 0.22 μm organic membrane.

3. Chemical structures of the five analytes

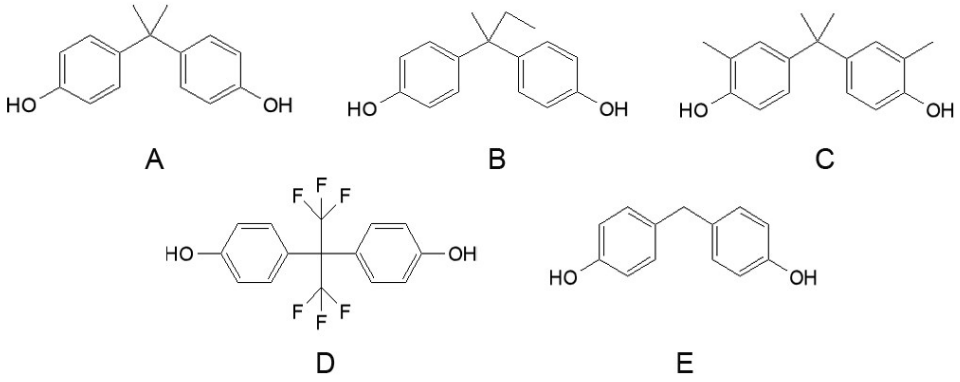

Fig. S1 Chemical structures of the five analytes. (A) Bisphenol A (BPA), (B) Bisphenol B (BPB), (C) Bisphenol C (BPC), (D) Bisphenol AF (BPAF) and (E) Bisphenol F (BPF).

4. Interaction mode between MIL-53 and bisphenols

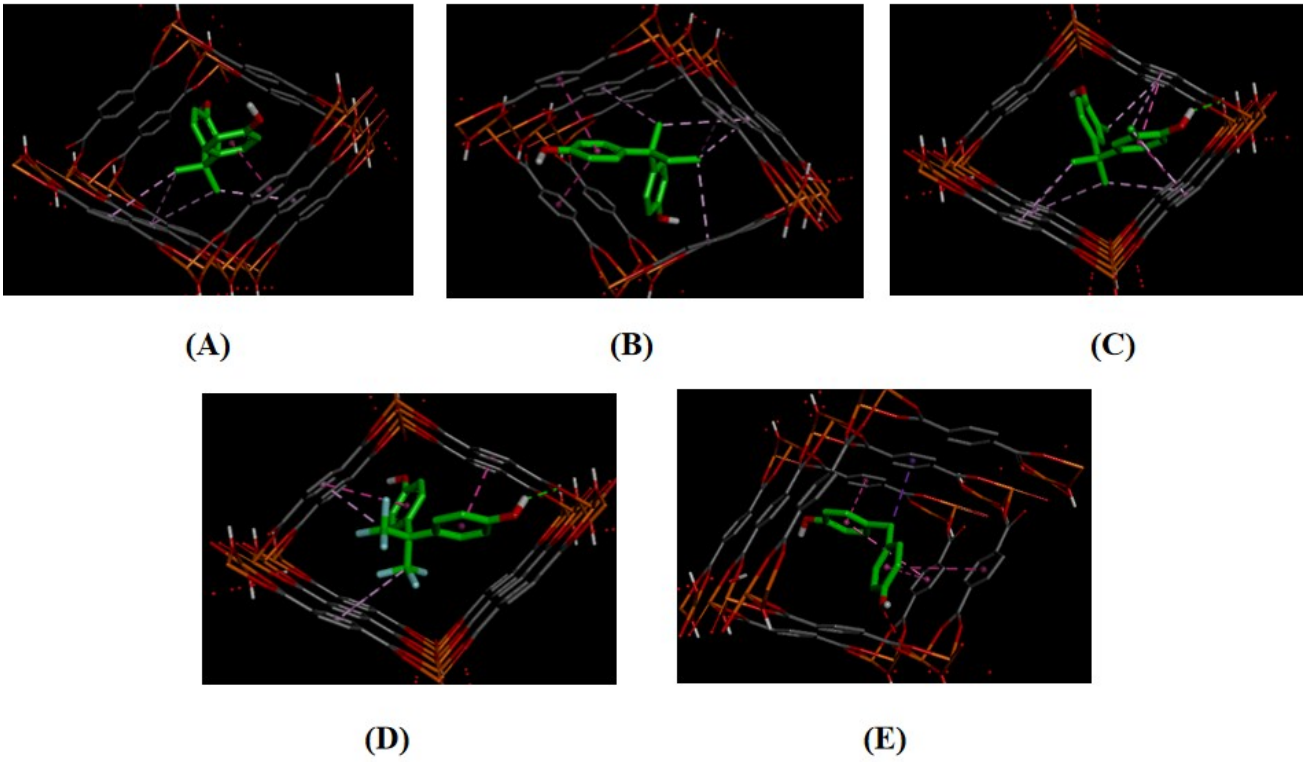

Fig.S2. Combination modes between MIL-53 and (A) BPA, (B) BPB, (C) BPC, (D) BPAF, (E) BPF. The ligands were displayed in ball-and-stick style by marking carbon atoms in green and oxygen atoms in red. The receptor was displayed in thin stick style by marking oxygen atoms in red and metal ions in orange.

5. Interaction mode between UiO-66 and bisphenols

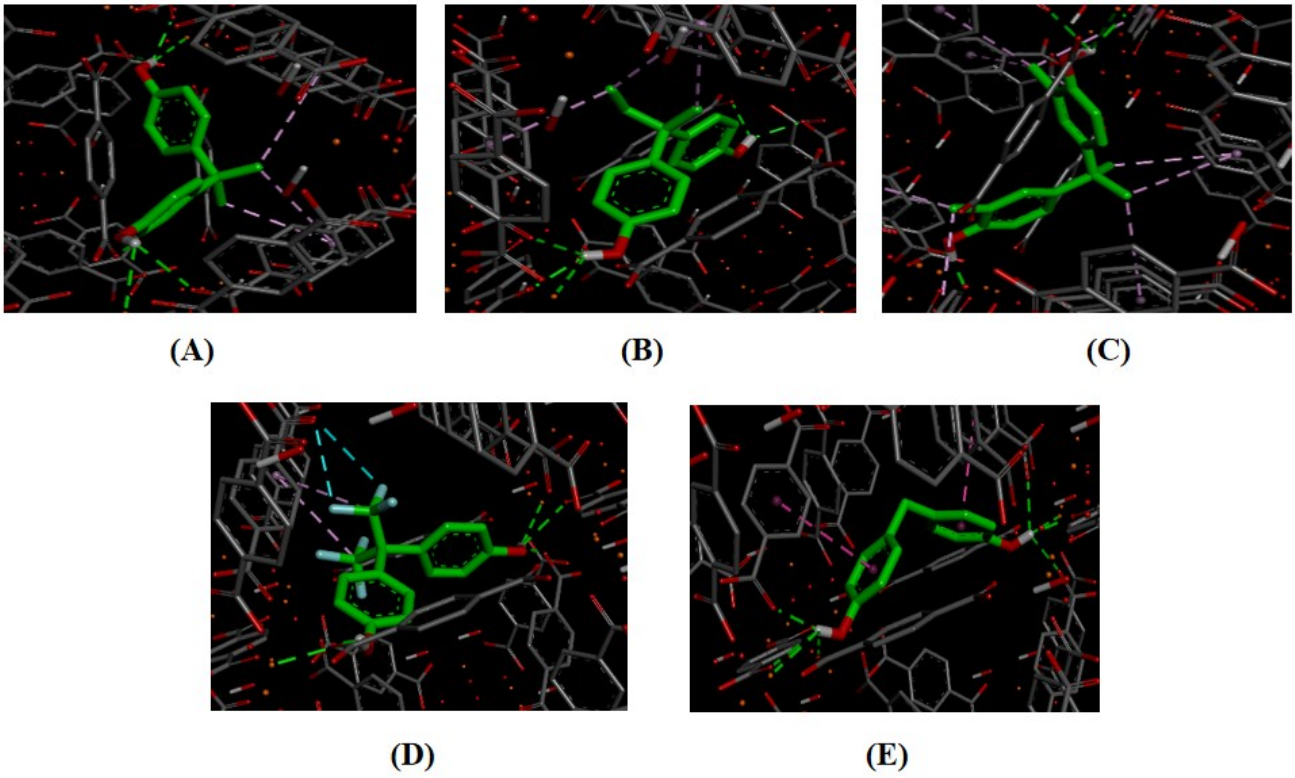

Fig.S3. Combination modes between UiO-66 and (A) BPA, (B) BPB, (C) BPC, (D) BPAF, (E) BPF. The ligands were displayed in ball-and-stick style by marking carbon atoms in green and oxygen atoms in red. The receptor was displayed in thin stick style by marking oxygen atoms in red and metal ions in blue.

6. Interaction mode between MIL-100 and bisphenols

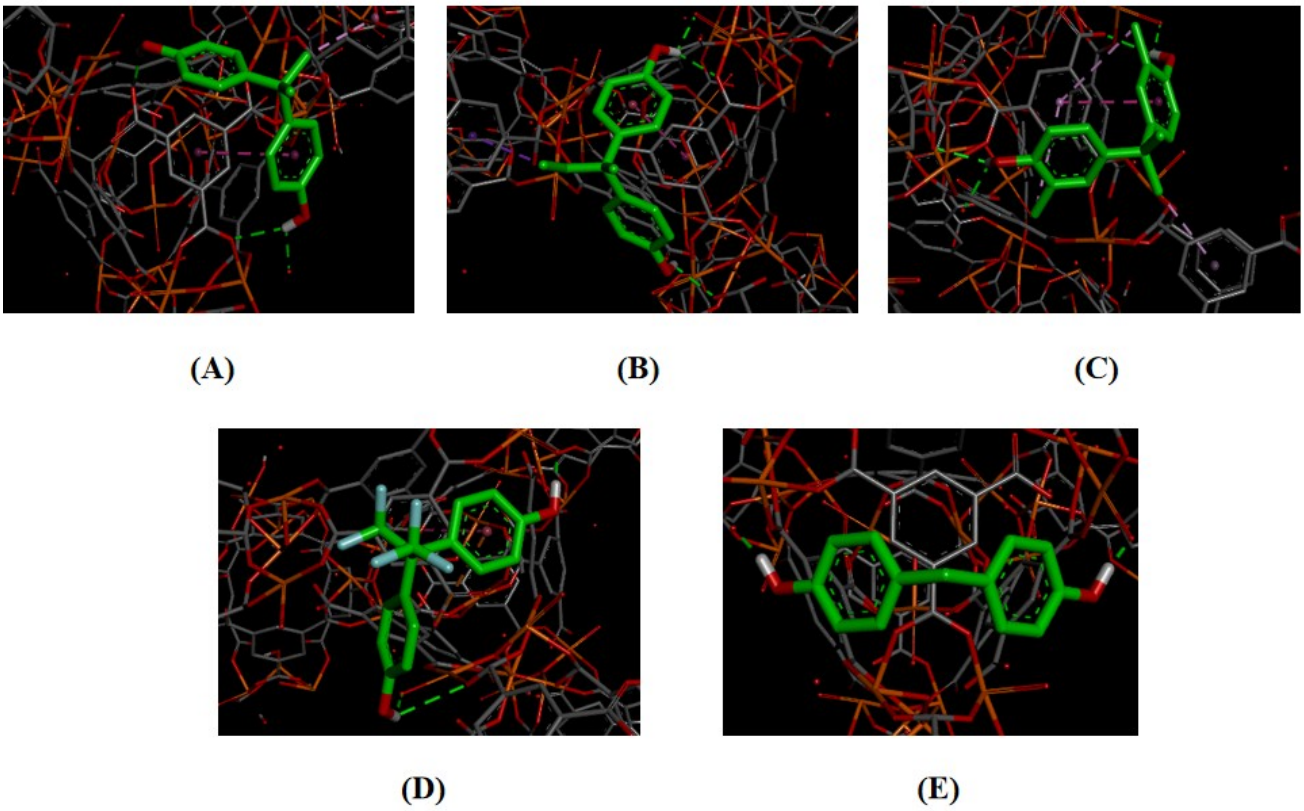

Fig.S4. Combination modes between MIL-100 and (A) BPA, (B) BPB, (C) BPC, (D) BPAF, (E) BPF. The ligands were displayed in ball-and-stick style by marking carbon atoms in green and oxygen atoms in red. The receptor was displayed in thin stick style by marking oxygen atoms in red and metal ions in orange.

7. Interaction mode between MIL-101 and bisphenols

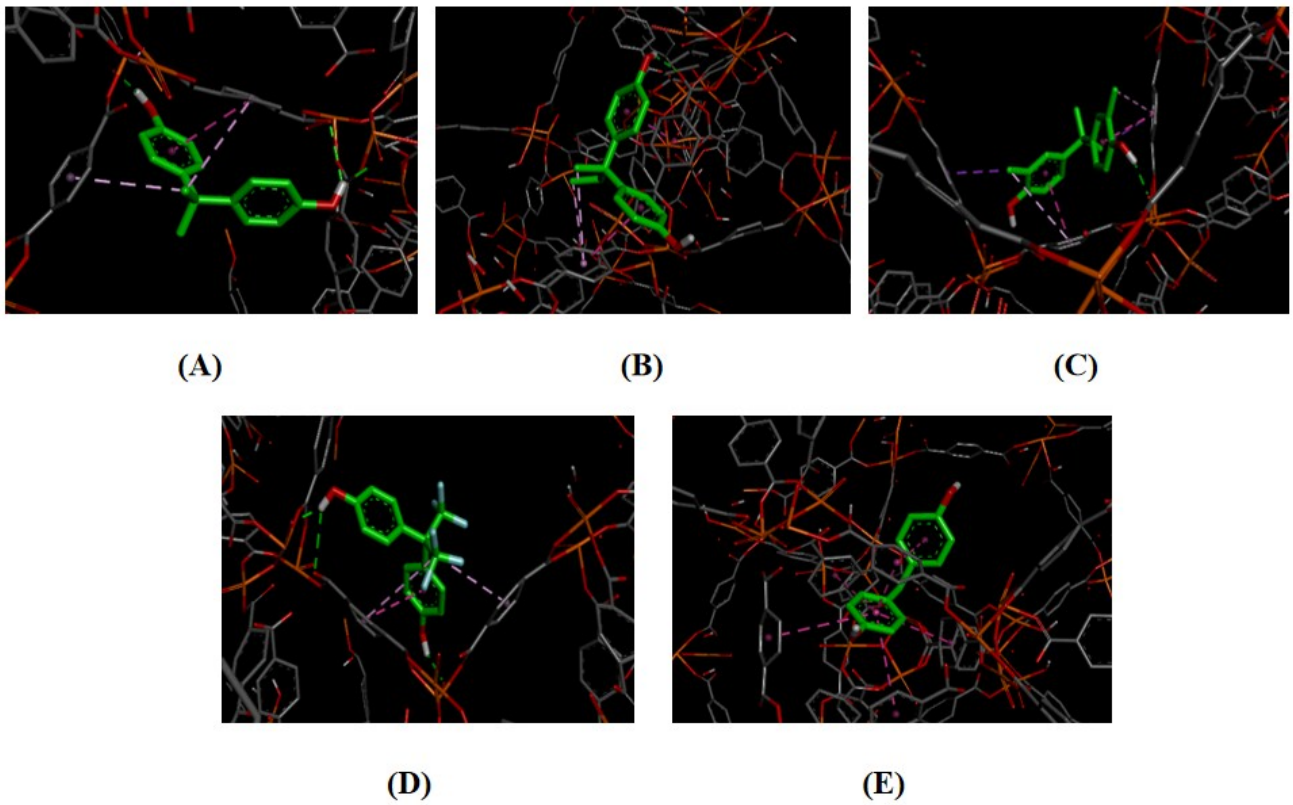

Fig.S5. Combination modes between MIL-101 and (A) BPA, (B) BPB, (C) BPC, (D) BPAF, (E) BPF. The ligands were displayed in ball-and-stick style by marking carbon atoms in green and oxygen atoms in red. The receptor was displayed in thin stick style by marking oxygen atoms in red and metal ions in orange.

8. Reusability of MIL-53(Al)/CS/PEO foam

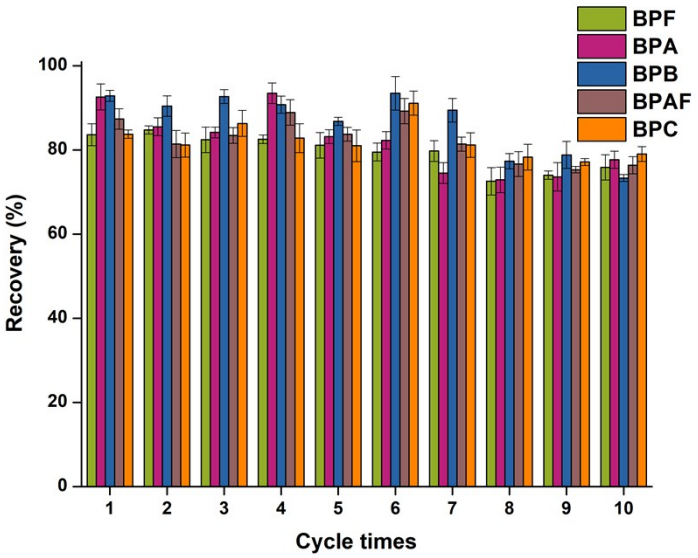

Fig. S6. Reusability of MIL-53(Al)/CS/PEO foam in VA-SPE for the target analytes under the optimal conditions.

9. HPLC-FLD chromatograms of standard solution, spiked water sample and drink sample

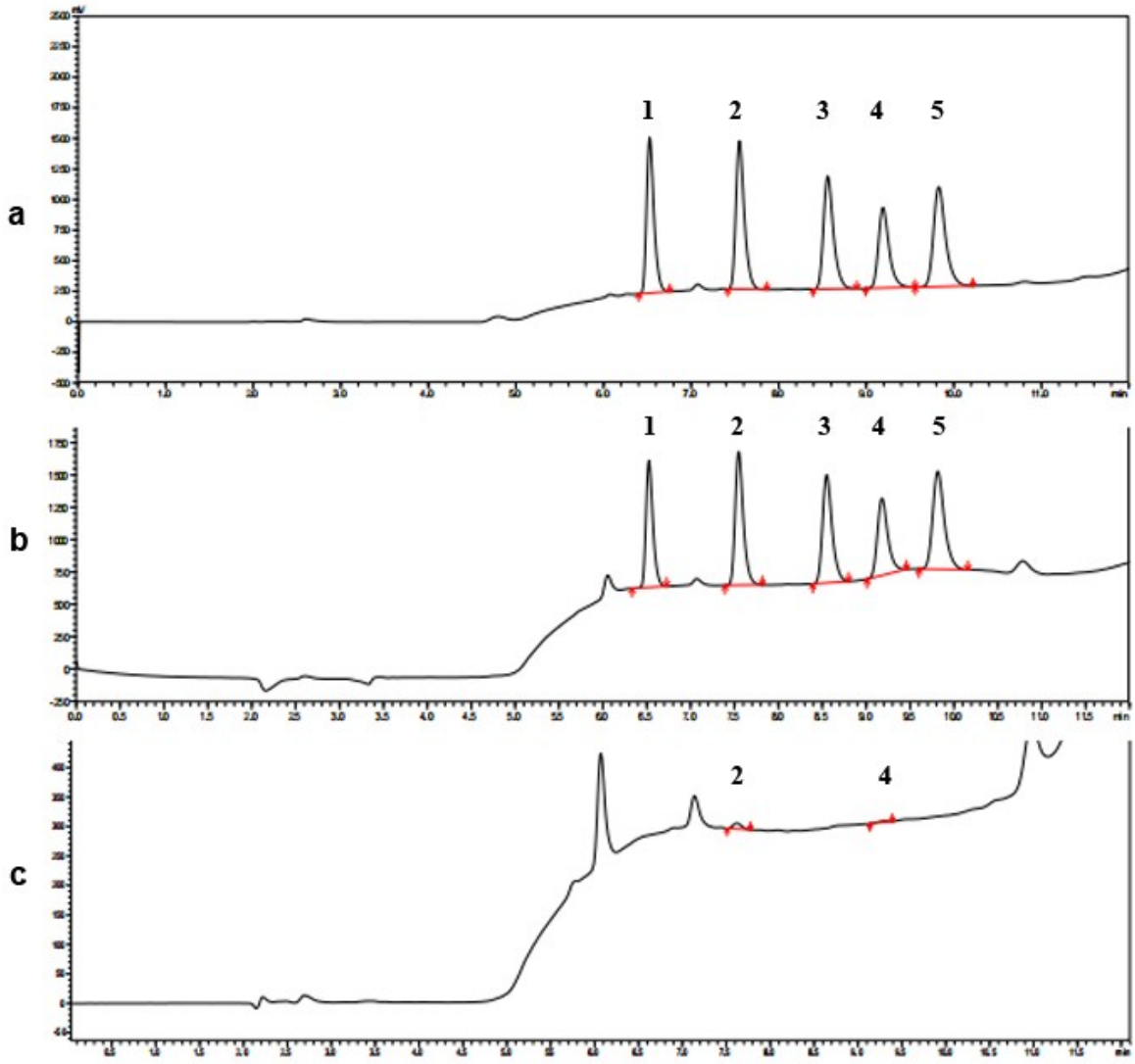

Fig. S7. HPLC-FLD chromatograms of standard solution (a), spiked water sample (10 ng/mL)(b), beverage sample of no. 4 (c). Peak identification: (1) BPF, (2) BPA, (3) BPB, (4) BPAF, (5) BPC.

10. Table S1 Binding energy (BE) and binding constants of MOFs towards bisphenols

Analyte	UiO-66		MIL-100		MIL-101		MIL-53	
	BE (kcal mol^{-1})	lnK_0	BE (kcal mol^{-1})	lnK_0	BE (kcal mol^{-1})	lnK_0	BE (kcal mol^{-1})	lnK_0
BPA	−6.89	11.64	−5.0	8.44	−5.77	9.75	−7.38	12.47
BPB	−7.13	12.05	−5.04	8.51	−5.78	9.768	−7.55	12.76
BPC	−7.79	13.17	−5.0	8.44	−6.50	10.98	−7.97	13.47
BPAF	−6.39	10.80	−3.31	5.59	−5.38	9.09	−6.94	11.73
BPF	−6.46	10.92	−3.54	5.98	−6.52	11.02	−6.95	11.75

11. **Table S2 Factors and levels of the orthogonal experiments**

Levels	Factors *			
	A	B	C	D
1	10	150	4:1	80
2	12	200	3:1	120
3	14	250	2:1	160

*A, the amount of MOFs (mg); B, glutaraldehyde dosage (μL); C, the proportions of CS/PEO (w/w); D, acetic acid glacial dosage (μL)

12. **Table S3 Result analysis of the orthogonal experiments**

No.	Factors*				Recovery (%)
	A	B	C	D	
1	1	1	1	1	70.06
2	1	2	2	2	76.52
3	1	3	3	3	75.64
4	2	1	2	3	85.98
5	2	2	3	1	86.64
6	2	3	1	2	85.03
7	3	1	3	2	84.24
8	3	2	1	3	86.63
9	3	3	2	1	85.76
K1	222.22	240.28	241.72	242.46	
K2	257.65	249.79	248.26	245.79	
K3	256.63	246.43	246.52	248.25	
k1	74.073	80.093	80.573	80.820	
k2	85.883	83.263	82.753	81.930	
k3	85.543	82.143	82.173	82.750	
R	11.810	3.170	1.600	1.930	

*A, the amount of MOFs (mg); B, glutaraldehyde dosage (μL); C, the proportions of CS/PEO (w/w); D, acetic acid glacial dosage (μL)

13. Table S4 Limits of detection, limits of quantification, precision and repeatability of analytical method

Analyte	MDL (μg/L)	MQL (μg/L)	Interday precision (RSD%, n = 18)			Intraday precision (RSD%, n = 9)			Repeatability (RSD%, n = 6)
			Low[a]	Middle[b]	High[c]	Low[a]	Middle[b]	High[c]	
Sample 1									
BPA	0.024	0.072	5.8	3.7	3.1	4.6	3.6	3.7	6.5
BPB	0.058	0.174	4.5	4.2	2.7	4.9	5.2	4.2	4.6
BPC	0.052	0.156	5.8	3.2	4.3	6.2	6.4	5.1	4.6
BPAF	0.047	0.141	6.3	4.1	3.6	7.0	3.8	2.9	5.2
BPF	0.029	0.087	7.2	5.3	4.1	5.8	4.5	4.6	3.8
Sample 2									
BPA	0.022	0.066	4.9	4.1	5.8	5.4	5.8	3.3	5.8
BPB	0.061	0.183	5.7	5.5	4.3	4.6	6.1	4.5	6.4
BPC	0.058	0.174	5.2	3.6	2.8	4.9	3.2	3.7	5.1
BPAF	0.049	0.147	6.8	5.4	3.4	6.3	4.7	2.3	3.7
BPF	0.031	0.093	7.1	6.9	4.6	3.9	4.4	3.1	4.6
Sample 3									
BPA	0.021	0.063	5.7	4.7	5.3	4.7	4.3	3.6	4.2
BPB	0.066	0.198	5.9	4.2	2.4	6.3	5.4	2.7	5.8
BPC	0.059	0.177	6.1	3.5	7.6	3.2	3.2	4.8	3.5
BPAF	0.050	0.150	7.2	3.7	4.3	4.6	2.8	5.1	7.4
BPF	0.027	0.081	4.3	2.9	2.3	6.9	4.1	3.6	5.3
Sample 4									
BPA	0.026	0.078	4.6	4.4	2.6	5.4	4.7	4.8	3.8
BPB	0.062	0.186	5.8	3.2	3.8	6.6	6.7	3.6	4.3
BPC	0.056	0.168	6.3	5.1	4.1	3.7	5.6	2.9	3.2

BPAF	0.055	0.165	3.8	5.4	3.5	4.8	3.1	3.5	3.9
BPF	0.026	0.078	4.7	5.7	2.7	3.6	5.2	4.6	5.6
Sample 5									
BPA	0.023	0.069	6.7	5.3	3.4	6.4	3.6	2.4	5.3
BPB	0.052	0.156	7.4	4.1	4.0	3.4	4.2	3.1	4.2
BPC	0.054	0.162	3.9	6.3	5.5	3.7	4.1	4.2	7.3
BPAF	0.044	0.132	6.2	3.6	3.7	3.2	3.9	3.4	2.8
BPF	0.032	0.096	4.1	4.2	4.6	5.1	4.4	2.6	5.6
Sample 6									
BPA	0.019	0.057	6.9	3.5	2.8	5.2	4.3	2.4	7.4
BPB	0.060	0.18	5.7	7.1	3.0	3.9	5.2	3.6	5.2
BPC	0.062	0.186	4.8	4.8	4.1	5.9	3.3	2.7	4.2
BPAF	0.059	0.177	5.8	3.9	2.9	6.4	4.6	3.1	3.8
BPF	0.033	0.099	4.0	4.6	3.5	5.7	4.1	2.9	6.0
Sample 7									
BPA	0.025	0.075	5.1	5.3	4.1	5.1	3.1	2.4	7.4
BPB	0.065	0.195	6.8	4.8	3.2	6.2	4.2	4.7	4.8
BPC	0.057	0.171	7.0	5.5	2.4	3.9	5.6	2.9	7.2
BPAF	0.063	0.189	3.8	4.2	4.2	5.8	3.2	3.3	4.4
BPF	0.024	0.072	6.4	2.5	2.0	5.6	4.7	3.2	3.5

a : 0.2 μg/L for BPA and BPF, 0.4 μg/L for BPB, BPF and BPAF

b : 1 μg/L for BPA and BPF, 2 μg/L for BPB, BPF and BPAF

c : 7.5 μg/L for BPA and BPF, 15 μg/L for BPB, BPF and BPAF

14. Table S5 Comparison of the current method with previously reported methods for the determination of bisphenols

Analyte	Method	Adsorbent material	Matrix	Mass of adsorbents	Desorption solvent and its volume	MDL (μg/L)	References
BPA, BPB, BPAP, BPAF	DSPE-HPLC	Ni@N-GrTs[a]	Milk	5 mg	2 mL Acetone	0.1-0.2	[33]
BPA, BPB, BPF, BPAP, BPAF	SPE-HPLC	MagG@PDA@Zr-MOF[b]	Water	30 mg	1 mL Methanol	0.1-1	[34]
BPA, BPB, BPS, BPF, BPZ, BPAP, BPAF	SPE-HPLC-MS/MS	DMIP[c]	Sewage, sludge	200 mg	12 mL Methanol	0.0007-16.3 ng/L	[35]
BPA, BPB, BPC,BPAF, BPF	VA-SPE-HPLC	MIL-53(Al)/chitosan/PEO foam	Water, Beverage	12 mg	1 mL Acetone	0.019-0.065	Present work

a: nickel-based N-doped graphene tubes

b: magnetic graphene @polydopamine @Zr-MOF

c: dummy molecularly imprinted