

Electronic Supplementary Material

Polymer monolith containing embedded covalent organic framework for effective enrichment of benzophenones

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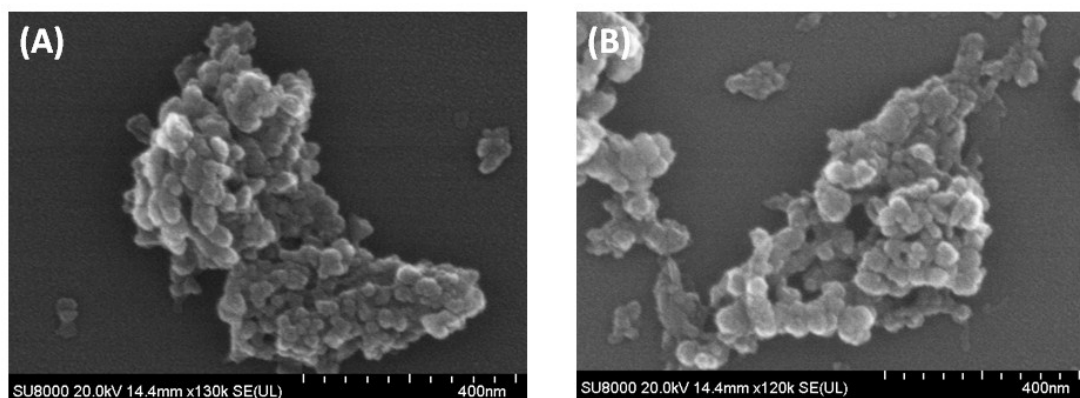


Figure S1 SEM images of (A) COF-COOH and (B) COF-SH

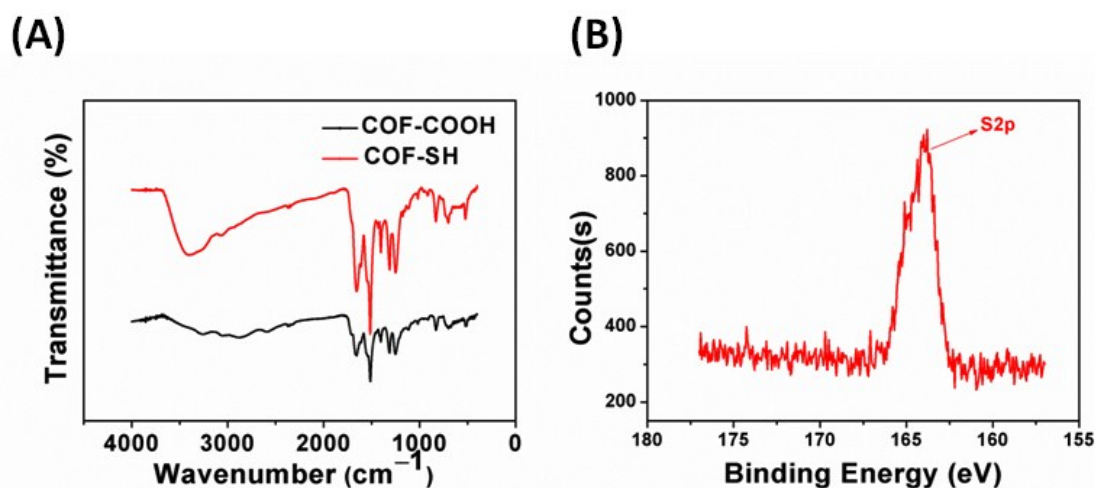


Figure S2 (A) IR spectra of COF-COOH and COF-SH. (B) XPS spectrum for S element of COF-SH

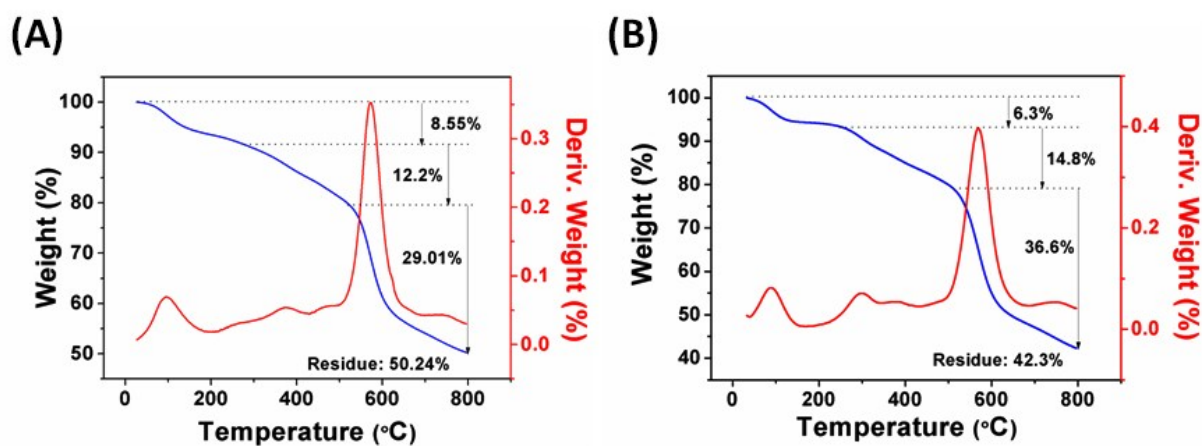


Figure S3 Thermal analyses of (A) COF-COOH and (B) COF-SH

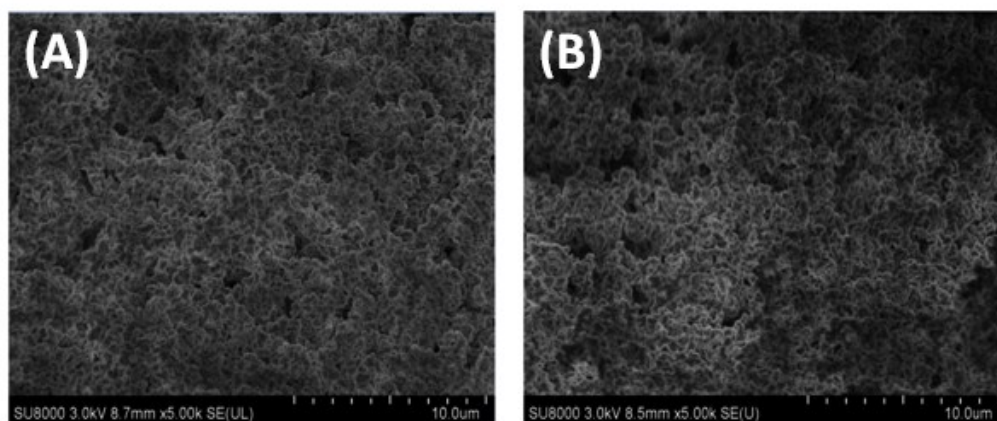


Figure S4 SEM images of COF@poly(GMA-EDMA) monolith (A) before and (B) after extraction

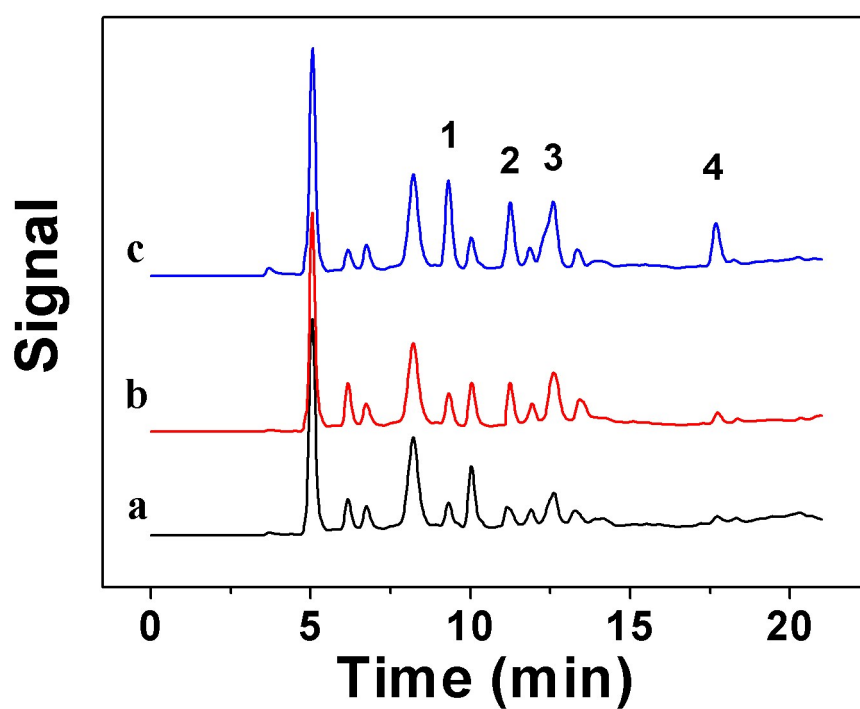


Figure S5 Chromatograms of BPs in serum samples obtained by PMME procedures: (a) unspiked sample; (b) sample spiked with Level 1; (c) sample spiked with Level 2; peaks: (1) DHBP, (2) HBP, (3) DHMBP, and (4) HMBP

Table S1 Permeability and SP values of different monoliths

Column	Monomers (% w/w)		Porogen (% w/w)		Permeability ($\times 10^{-9} \text{ cm}^2$) ^a	SP
	GMA	EDMA	Cyclohexanol	Dodecanol		
C-1	24	16	54	6	5.13	0.44
C-2	21	14	58.5	6.5	5.69	0.42
C-3	18	12	63	7	6.42	0.39

^a The permeability of the monolithic columns was determined with MeOH as the mobile phase at 0.3 mL min^{-1}

Table S2 Comparison of various methods for the determination of the BPs.

Analysts			Samples	Pretreatment methods	Analytical techniques	LOD (ng mL ⁻¹)	EF	Ref.
HBP,	DHBP,	HMBP,	Human serum samples	DLLME	UPLC-MS/MS	0.1-0.2	–	1
DHMBP								
HBP, DHBP, HMBP			Sunscreen samples	DLLME	CE	3.9-6.7	32.0-40.5 ^a	5
HBP, DHBP, HMBP			Water samples	DLLME	HPLC	2.4-6.4	18.9-21.7	7
HBP, DHBP, HMBP			Water samples	Magnetic PMME	HPLC	0.4-0.8	–	8
HBP,	DHBP,	HMBP,	Human menstrual blood samples	DLLME	UHPLC-MS/MS	0.1-0.3	–	9
DHMBP								
HBP,	DHBP,	HMBP,	Water samples	Dispersive SPME	HPLC-MS/MS	0.16-1.21	17.3-49.2	12
DHMBP								
DHBP, HMBP, DHMBP			Human serum samples	DLLME	HPLC-MS/MS	7-8	3.1-7.4 ^b	48
DHBP, HMBP			Toner samples	DSPE	HPLC	0.9-1.2	–	50
HBP,	DHBP,	HMBP,	Human urine and serum samples	PMME	HPLC	0.4–0.7	17.5-40.3	This work
DHMBP								

^a EF was defined as the ratio between the analyte concentration in the final diluted phase (C_f) and the initial concentration of analyte (C_0) within the sample.

^b EF was defined as the ratio between the analyte concentration in the organic sedimented phase (C_{sed}) and the initial concentration of this compound in the aqueous phase (C_0).

Table S3 Recoveries (%) of the four BPs in real samples ($n = 3$)

Sample			DHBP	HBP	DHMBP	HMBP
Urine sample 1	Measured (ng mL ⁻¹)		< LOD	< LOD	23.9	< LOD
	Recovery ± RSD (%)	Level 1	81.2 ± 5.4	79.5 ± 2.0	86.5 ± 2.3	100.8 ± 5.1
		Level 2	82.7 ± 6.0	94.5 ± 4.9	104.5 ± 5.6	93.3 ± 6.7
Urine sample 2	Measured (ng mL ⁻¹)		14.5	< LOD	23.3	< LOD
	Recovery ± RSD (%)	Level 1	101.6 ± 3.2	82.7 ± 3.1	95.5 ± 2.0	88.1 ± 6.9
		Level 2	98.0 ± 5.7	93.9 ± 5.5	82.7 ± 2.6	95.6 ± 0.7
Urine sample 3	Measured (ng mL ⁻¹)		6.4	< LOD	36.6	< LOD
	Recovery ± RSD (%)	Level 1	91.4 ± 6.7	93.5 ± 1.5	83.5 ± 5.4	85.5 ± 5.1
		Level 2	87.4 ± 5.6	92.2 ± 4.1	91.9 ± 5.2	103.7 ± 3.6
Serum sample 1	Measured (ng mL ⁻¹)		22.6	15.6	16.4	6.2
	Recovery ± RSD (%)	Level 1	97.4 ± 5.6	89.1 ± 3.1	88.2 ± 4.4	99.4 ± 5.1
		Level 2	102.0 ± 7.4	99.0 ± 0.9	97.7 ± 5.4	89.0 ± 6.7
Serum sample 2	Measured (ng mL ⁻¹)		< LOD	34.9	105.1	< LOD
	Recovery ± RSD (%)	Level 1	87.9 ± 6.5	96.4 ± 7.5	97.4 ± 2.3	85.4 ± 6.1

Serum sample 3	Measured (ng mL ⁻¹)	Level 2	99.4 ± 5.2	96.8 ± 7.7	97.2 ± 7.0	105.0 ± 8.2
			< LOD	22.3	25.6	14.3
	Recovery ± RSD (%)	Level 1	97.9 ± 3.5	98.4 ± 3.5	107.7 ± 1.3	95.4 ± 2.5
		Level 2	79.8 ± 5.9	86.8 ± 0.7	92.0 ± 7.2	105.7 ± 5.0