

## **Supporting information**

### **Conjugated Microporous Polymers with Built-in Magnetic Nanoparticles for Excellent Enrichment of Trace Hydroxylated Polycyclic Aromatic Hydrocarbons in Human Urine**

Langjun Zhou, Yuling Hu<sup>\*</sup>, Gongke Li<sup>\*</sup>

School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou, 510275, China

\* Corresponding author: Yuling Hu, Gongke Li

Tel. : +86-20-84110922

Fax : +86-20-84115107

E-mail : ceshyl@mail.sysu.edu.cn

cesgkl@mail.sysu.edu.cn

Section 1. Synthetic Method of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> Nanoparticles

Section 2. HPLC Conditions

Section 3. FTIR Spectrum

Section 4. Fluorescence Spectra

Section 5. TGA Measurement

Section 6. Pore Size Distribution

Section 7. Adsorption Amount Curves

Section 8. Adsorption Mechanism of OH-PAHs on Magnetic PP-CMP

Section 9. Optimization of the Extraction Conditions

Section 10. Chemical Stability of Magnetic PP-CMP

## Section 1. Synthetic Method of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> Nanoparticles

*Synthesis of Fe<sub>3</sub>O<sub>4</sub> Nanoparticles with 10 nm Size.* 10 nm Fe<sub>3</sub>O<sub>4</sub> nanoparticles were prepared via the modified coprecipitation method.<sup>1</sup> In a typical run, FeCl<sub>2</sub>·4H<sub>2</sub>O (2.4 g) and FeCl<sub>3</sub>·6H<sub>2</sub>O (4.6 g) were first dissolved in oxygen-free ultrapure water (pH 2, 20 mL) and subsequently were filtered into ultrapure water (80 mL). After purging with nitrogen gas for 30 min, NH<sub>3</sub>·H<sub>2</sub>O (28 wt%, 10 mL) was dropwise added into the above mixed solution under vigorous stirring at room temperature with nitrogen protection. The black colloidal solution was stirred at 40°C for 0.5 h and 85°C for 2 h, respectively. Finally, the Fe<sub>3</sub>O<sub>4</sub> nanoparticles were separated and purified by magnetic separation and washed with deionized water and ethanol 3 times, respectively, and then dried in vacuum oven at 60°C for future use.

*Synthesis of Fe<sub>3</sub>O<sub>4</sub> Nanoparticles with 150 nm Size.* 150 nm Fe<sub>3</sub>O<sub>4</sub> nanoparticles were prepared via the modified solvothermal reduction method.<sup>2</sup> Briefly, ferric chloride (1.35 g) and sodium acetate (3.6 g) were dissolved in ethylene glycol (35 mL) and dissolved by an ultrasonic method. The mixture was transferred to a reaction still for 8 h solvothermal reaction at 200°C. After that, the Fe<sub>3</sub>O<sub>4</sub> nanoparticles were washed with deionized water and then washed with ethanol 3 times, dried in vacuum oven at 60°C for future use.

10 nm Fe<sub>3</sub>O<sub>4</sub> nanoparticles or 150 nm Fe<sub>3</sub>O<sub>4</sub> nanoparticles (4.0 g) were dispersed in mixed solution of deionized water (40 mL) and ethanol (160 mL) and then NH<sub>3</sub>·H<sub>2</sub>O (28 wt%, 3 mL) and TEOS (2 mL) were added under mechanical mixing. After the mixture was stirred at 40°C for 24 h, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles were obtained and washed with ethanol 5 times, dried in vacuum oven at 150°C for future use.

### Supporting Reference

S1. Guan, G.; Yang, L.; Mei, Q.; Zhang, K.; Zhang, Z.; Han, M. *Anal. Chem.* **2012**, *84*, 9492-9497.

S2. Deng, H.; Li, X.; Peng, Q.; Wang, X.; Chen, J.; Li, Y. *Angew. Chem. Int. Ed.* **2005**, *44*, 2782-2785.

## Section 2. HPLC Conditions

All HPLC measurements were performed using a Waters 1525 (Waters, USA), which equipped with a fluorescence detector (Waters 2475). Separation was carried out on a reversed-phase column of C<sub>18</sub> (250 mm × 4.6 mm i.d., 5 μm) (Dimark, China). The mobile phase consisted of methanol and acetic acid-water (0.1%, v/v). The mobile phases were eluted at 1.0 mL·min<sup>-1</sup> at 40°C following the gradient as follows: 50% methanol and maintained for 5 min, gradually change to 65% of methanol in 9 min and maintained for 12 min, increased to 85% within 5 min and then increased to 100% within 9 min and held for 5 min. Fluorescence was monitored following the procedure as follows: 0-18.0 min, λ<sub>ex</sub> = 227 nm, λ<sub>em</sub> = 355 nm; 18.0-21.5 min, λ<sub>ex</sub> = 272 nm, λ<sub>em</sub> = 336 nm; 21.5-29.0 min, λ<sub>ex</sub> = 254 nm, λ<sub>em</sub> = 369 nm; 29.0-33.0 min, λ<sub>ex</sub> = 239 nm, λ<sub>em</sub> = 392 nm; 33.0-45.0 min, λ<sub>ex</sub> = 269 nm, λ<sub>em</sub> = 392 nm. The injection volume was 20 μL.

### Section 3. FTIR Spectrum

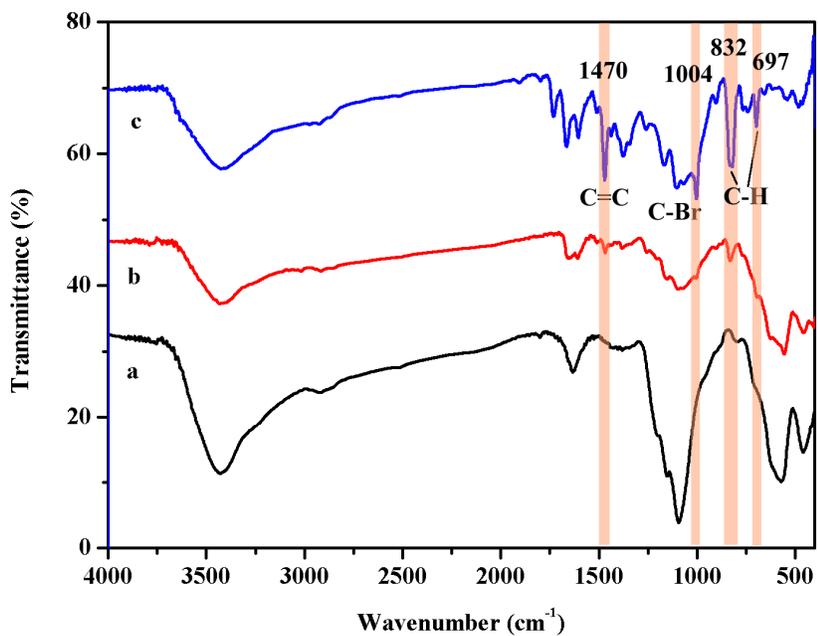


Figure S1. FTIR spectrum of (a) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-APB-10, (b) magnetic PP-CMP-10 composites and (c) bare PP-CMP.

## Section 4. Fluorescence Spectra

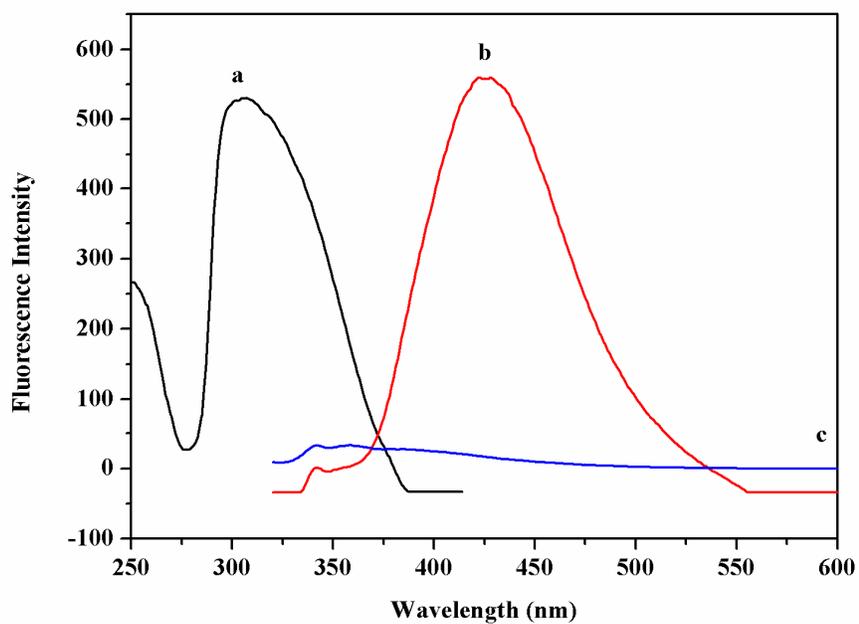


Figure S2. Fluorescence spectra: (a) fluorescence excitation spectra of magnetic PP-CMP composites, (b) fluorescence emission spectra of magnetic PP-CMP composites and (c) fluorescence emission spectra of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APB}$ .

## Section 5. TGA Measurement

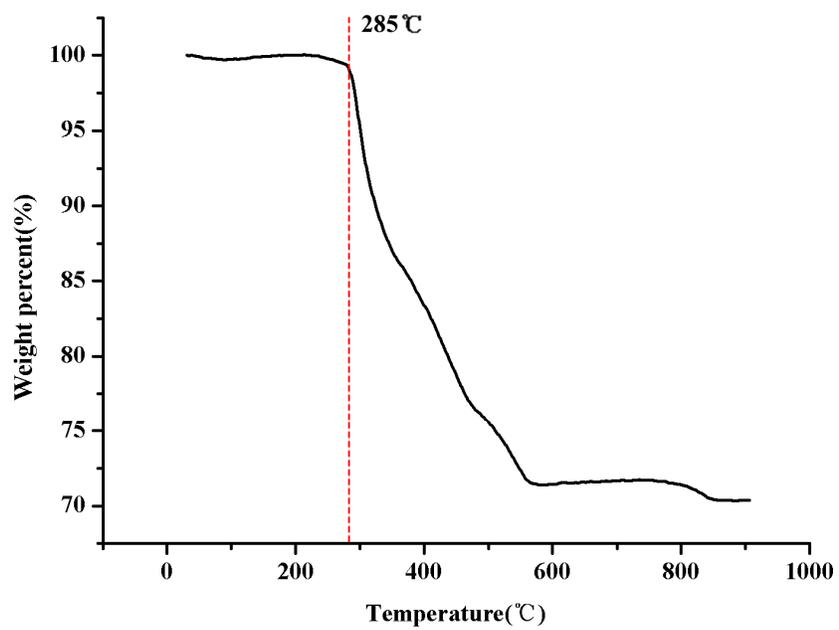


Figure S3. TGA measurement of magnetic PP-CMP-10.

## Section 6. Pore Size Distribution

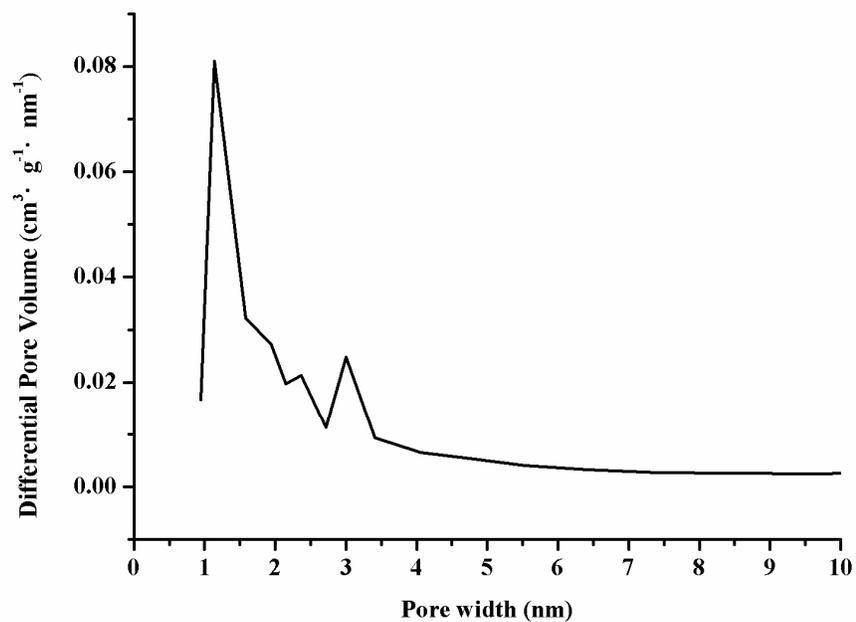


Figure S4. Pore size distributions of magnetic PP-CMP-10 by using  $\text{N}_2$  adsorption isotherms at 77 K with the nonlocal density functional theory (NLDFT) method.

## Section 7. Adsorption Amount Curves

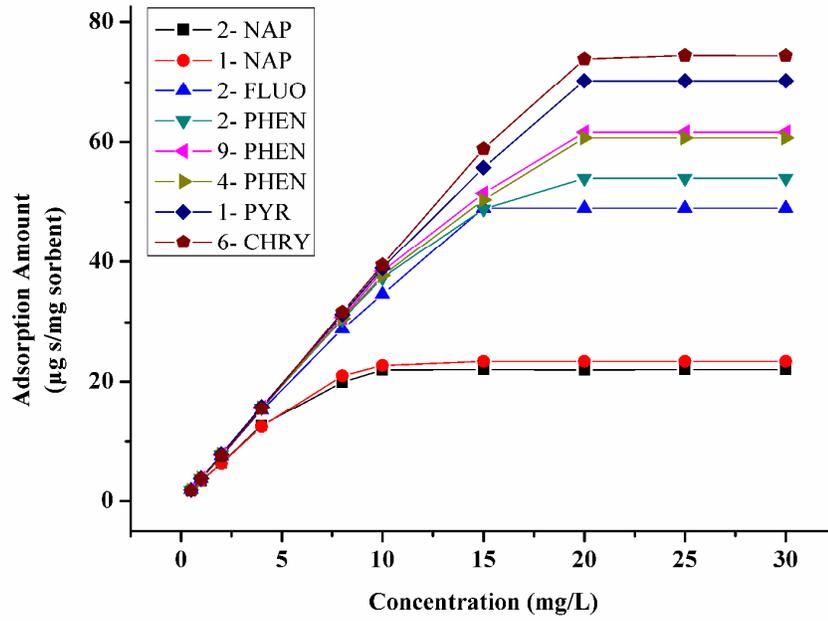


Figure S5. Adsorption amount curves of OH-PAHs on magnetic PP-CMP-10.

## Section 8. Adsorption Mechanism of OH-PAHs on Magnetic PP-CMP

Table S1. Adsorption Isotherm Parameters of OH-PAHs on the Magnetic PP-CMP

Compounds	Henry equation		Langmuir equation			Freundlich equation		
	$K_d$ (L·g <sup>-1</sup> )	R <sup>2</sup>	$q_{max}$ (μg·mg <sup>-1</sup> )	$K_L$ (L·mg <sup>-1</sup> )	R <sup>2</sup>	$K_F$ (μg·mg <sup>-1</sup> )(mg·L <sup>-1</sup> ) <sup>-n</sup>	$n$	R <sup>2</sup>
2-NAP	13.16	0.9943	10.61	5.539	0.9586	12.74	0.5977	0.9832
1-NAP	11.97	0.9952	9.007	9.145	0.9260	11.78	0.5304	0.9762
2-FLUO	69.98	0.9911	46.00	2.432	0.9631	54.45	0.8133	0.9733
2-PHEN	167.2	0.9846	-15.00	-5.773	0.7492	302.0	1.277	0.9129
4-PHEN	166.2	0.9813	-14.32	-5.939	0.7018	312.6	1.289	0.8920
1-PYR	466.2	0.9484	-3.201	-19.39	0.7200	20654	2.350	0.8468

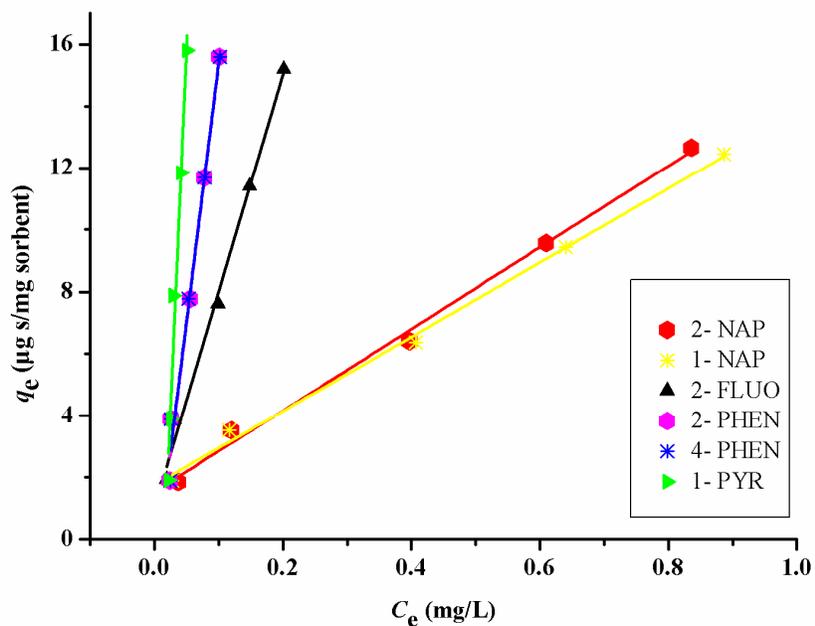


Figure S6. Adsorption isotherms of 6 OH-PAHs with typical structure.

## Section 9. Optimization of the Extraction Conditions

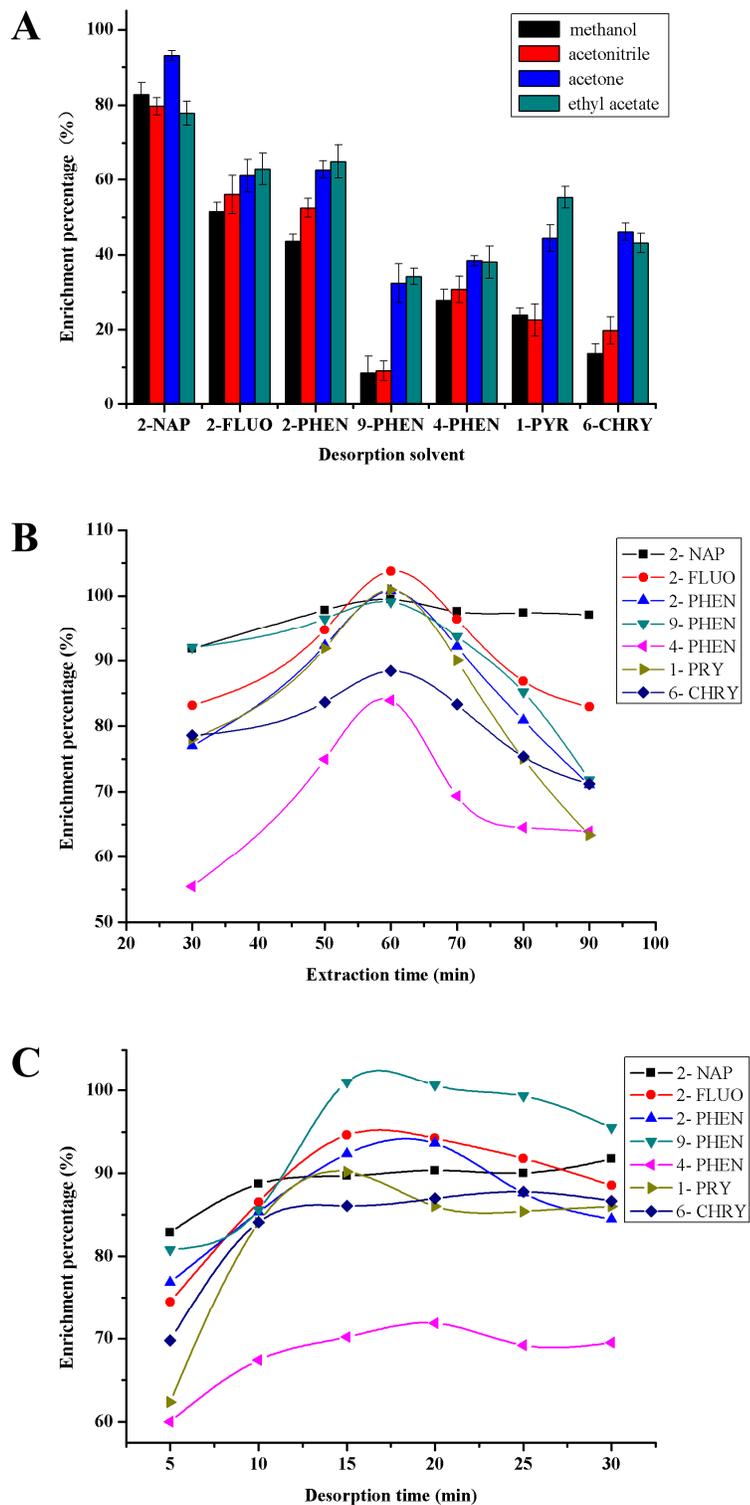


Figure S7. Effect of the experimental conditions, including desorption solvent (A), extraction time (B) and desorption time (C) on the extraction efficiency of the magnetic PP-CMP.

## Section 10. Chemical Stability of Magnetic PP-CMP

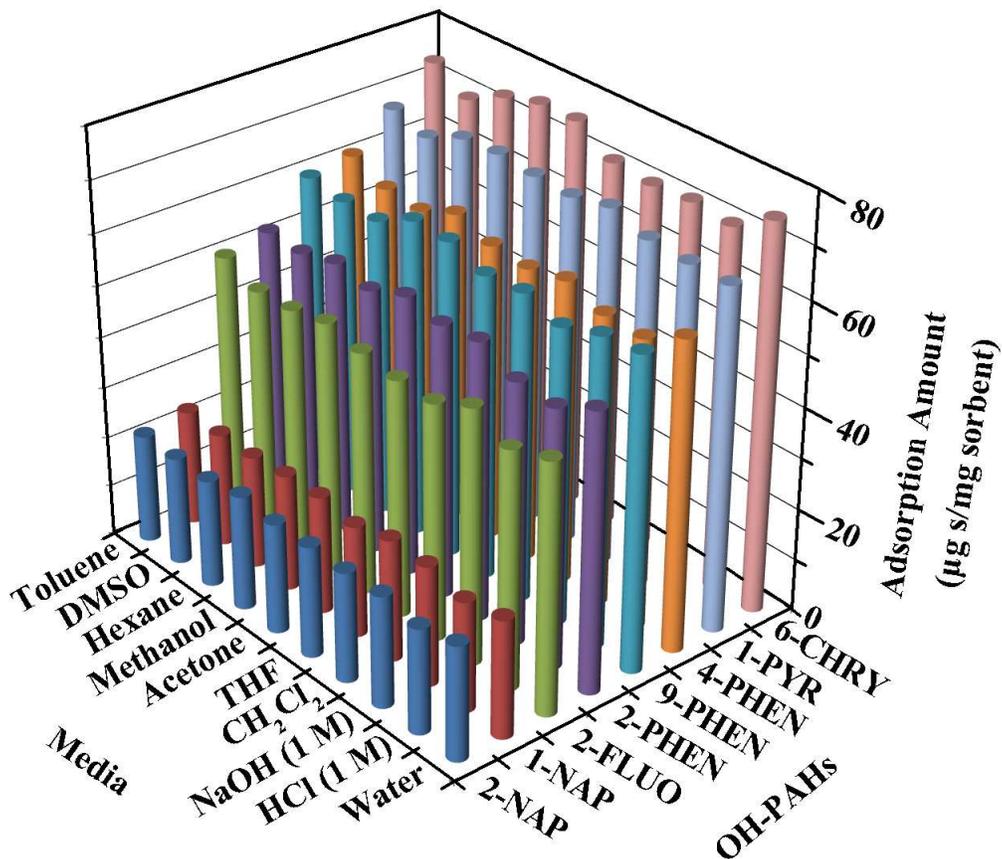


Figure S8. Adsorption amounts of OH-PAHs on magnetic PP-CMP-10 treated with different solvents. The magnetic PP-CMP-10 was soaked in each solvent for 7 days before adsorption experience.