

**Electronic Supplementary Information (ESI) for**  
**Facile synthesis and immobilization of boroxine polymers containing carbon**  
**chains and its application as adsorbents**

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## **A. Supplementary Method**

### **1. Materials**

(3-aminopropyl)triethoxysilane (APTES) and 9,9-dioctylfluorene-2,7-diboronic acid (DOFDB) were purchased from Sigma-Aldrich (MO, USA). 1,3,5-trimethylbenzene was bought from Macklin (Shanghai, China). 1,4-dioxane, sodium hydroxide (NaOH), sodium carbonate anhydrous ( $\text{Na}_2\text{CO}_3$ ), ethyl acetate, formic acid, acetone, ethanol (HPLC grade) and phosphoric acid ( $\text{H}_3\text{PO}_4$ , HPLC grade) were commercially available from Kermel (Tianjin, China). Hydrochloric acid (HCl) was obtained from KL (Sichuan, China). Rhein and emodin were provided by yuanye (Shanghai, China). Acetonitrile and methanol were HPLC grade and supplied by Tedia (OH, USA). Deionized water was purified with UPL-20UV system from Fly Science (18.2 M $\Omega$ , Beijing, China).

### **2. Measurements**

The morphology and chemical elements of B-COPs coated microcap were investigated by Quanta FEG 250 SEM (USA) equipped with Inca X-Max 50 energy spectrum analyzer. X-ray diffractogram was recorded on Shimadzu LabX XRD-6100 (Japan). Fourier transform infrared spectroscopy (FT-IR) spectra was performed by a Nicolet Nexus 410 system (USA) from 4000 to 500  $\text{cm}^{-1}$ . Thermal gravimetric (TG) analysis was carried out by NETZSCH STA 409 PC/PG (Germany). Solid-state  $^{11}\text{B}$  magic angle spinning ( $^{11}\text{B}$  MAS),  $^{13}\text{C}$  cross polarization magic angle spinning ( $^{13}\text{C}$  CPMAS) nuclear magnetic resonance (NMR) spectra was obtained on a Bruker Avance III 400 NMR spectrometer (Germany). The surface area and pore size distribution were performed on Micromeritics ASAP 2460 (USA) by nitrogen adsorption and desorption experiment at 77 K.

### **3. Preparation of B-COPs@microcap**

#### **3.1 Fabrication of B-COPs@microcap**

Firstly, microcaps (o.d.  $\times$  i.d. = 1.1  $\times$  0.9 mm and length 3.4 cm) were cut out and sealed

by liquefied petroleum gas (LPG) flame at both ends. The bare microcaps were sequentially immersed in 0.1 mol/L NaOH and 0.1 mol/L HCl to sonicate for 2 h and 10 min. Then microcaps were washed for three times with deionized water and dried at 95°C for the following experiments. Secondly, 15 mg of APTES, 15 mg of DOFDB, 5 mL of 1,4-dioxane, and 5 mL of 1,3,5-trimethylbenzene were added into a pressure-resistant glass vial (15 mL). The mixture was sonicated for obtaining a homogenous dispersion. Thirdly, 50 of activated microcaps were dipped into pressure-resistant glass vial, and the vial was stoppered and heated at 95°C for 24 h. After ultrasonic washing for 10 min with acetonitrile and drying at 95°C, B-COPs coated microcaps (B-COPs@microcap) were obtained. The immobilization process of COPs was repeated four times to attain homogenous and stable coating.

### 3.2 Optimization of preparation procedure

In order to enhance the extraction capacity of coating, the effect of reaction temperature, APTES to DOFDB ratio, concentration of APTES and DOFDB were investigated. Emodin and physcion were selected as analytes to evaluate extraction performance of coating. The extraction process was performed in 50 mL Teflon baker containing 18 ng/mL of emodin and 44 ng/mL of physcion. The volume of sampling solution was 20 mL. After stirring 75 min, the stir bar was transferred into pipette tip with one side sealed, and 200  $\mu$ L of acetonitrile was added to elute analytes by standing for 15 min. Then 10  $\mu$ L of desorption solvent was injected in UPLC system. Analysis of targets was performed on Shimadzu 2040C 3D UPLC system (Tokyo, Japan) with binary pump, a six-port valve, a DAD detector and a sample loop of 40  $\mu$ L. The separation of analytes depended on Sepax BR-C<sub>18</sub> column (2.1 $\times$ 50 mm, 3  $\mu$ m). Data collection was performed on Shimadzu Labsolutions software. Mobile phase consisted of acetonitrile and 0.1% phosphate solution (50/50, v/v). The wavelength of detector, flow rate, column temperature and injection volume were set at 285 nm, 0.6 mL/min, 30°C and 10  $\mu$ L.

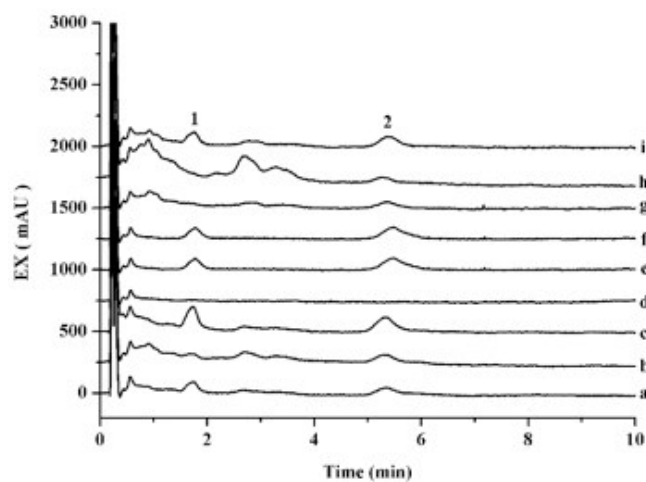
### 4. Stir bar sorptive extraction procedure

The B-COPs@microcap was used to extract rhein and emodin in rat serum. Extraction procedure was carried out in 50 mL Teflon beaker containing 20 mL sample solution. The coated microcap was locked by the grooves made on the inner surface of Teflon beaker, and 1 cm of stainless steel rod ( $d=1$  mm) as magneton was added. After stirring for 75 min with 1100 rpm, the B-COPs@microcap dried with filter paper was immersed in pipette tip with one end sealed containing 200  $\mu\text{L}$  of sodium carbonate aqueous solution. Then 10  $\mu\text{L}$  of eluent was collected for analysis on UPLC system (Shimadzu LC-2040C 3D, Tokyo, Japan), which consisted of binary pump, a six-port valve, a DAD detector and a sample loop of 40  $\mu\text{L}$ . Chromatography separation was realized by a  $\text{C}_{18}$  column (75 mm  $\times$  2.0 mm i.d., Tokyo, Japan) with 2.2  $\mu\text{m}$  particle size from Shimadzu. Data collection was performed on Shimadzu Labsolutions software. Mobile phase consisted of 0.1% phosphoric acid aqueous solution and methanol (23:77, v/v). The wavelength of DAD detector, flow rate, column temperature and injection volume were set at 254 nm, 0.4 mL/min, 30°C and 10  $\mu\text{L}$ .

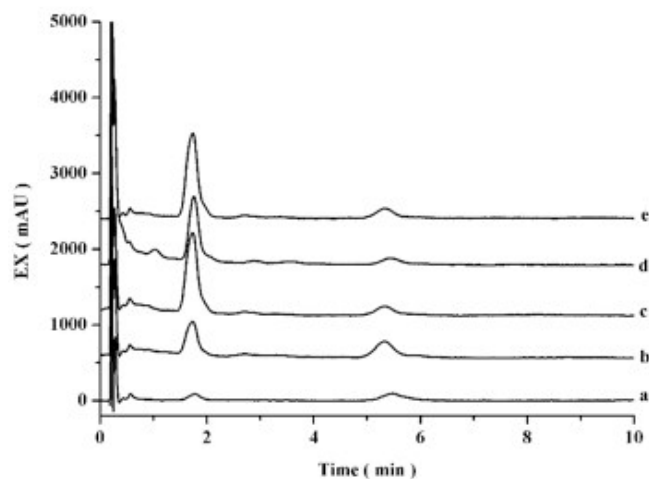
## **5. Sample preparation**

Blank plasma sample was collected from healthy rat. After centrifuging for 15 min at 3000 rpm, serum was obtained. 500  $\mu\text{L}$  standards solution (10  $\mu\text{g}/\text{mL}$  rhein and emodin), 2 mL methanol and 100  $\mu\text{L}$  0.1% (v/v) formic acid aqueous solution were mixed with 500  $\mu\text{L}$  serum. The mixture was vortexed for 1 min and centrifuged at 12000 rpm for 10 min. The supernatant was evaporated at 30°C with vacuum concentrator. Then, residue was reconstituted with 500  $\mu\text{L}$  methanol and sonicated for 1 min before centrifugation at 12000 rpm for 10 min again. 5  $\mu\text{L}$  supernatant was diluted to 20 mL with deionized water as loading solution for further extraction.

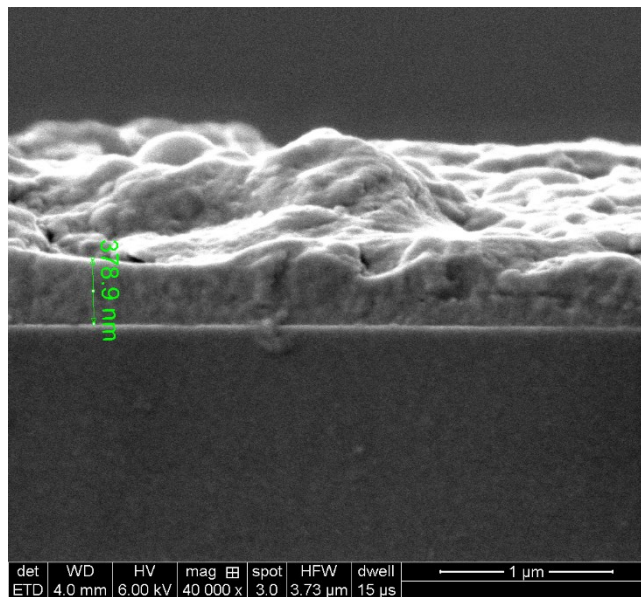
## B. Supplementary Figures



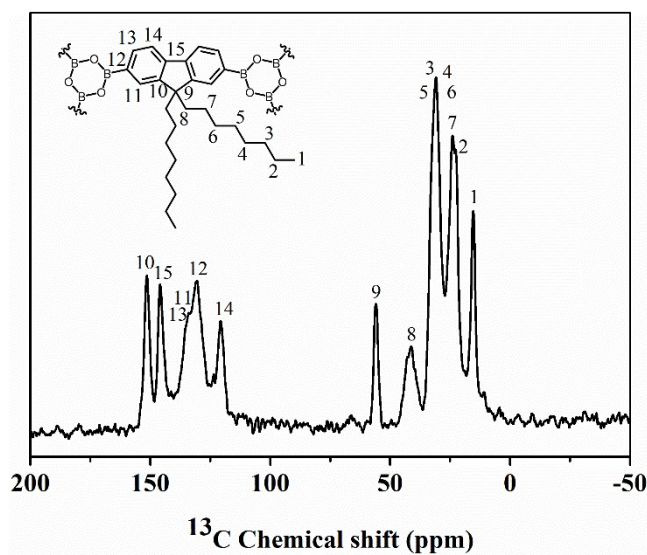
**Fig. S1.** Chromatogram results about the effect of reaction temperature and APTES to DOFDB ratio on extraction performance. 1: emodin, 2: physcion. DOFDB: 0.15 mg/mL; 75°C, 1:5, 1:1, 10:1 (a-c); 95°C, 1:5, 1:1, 10:1 (d-f); 115°C, 1:5, 1:1, 10:1 (g-i).



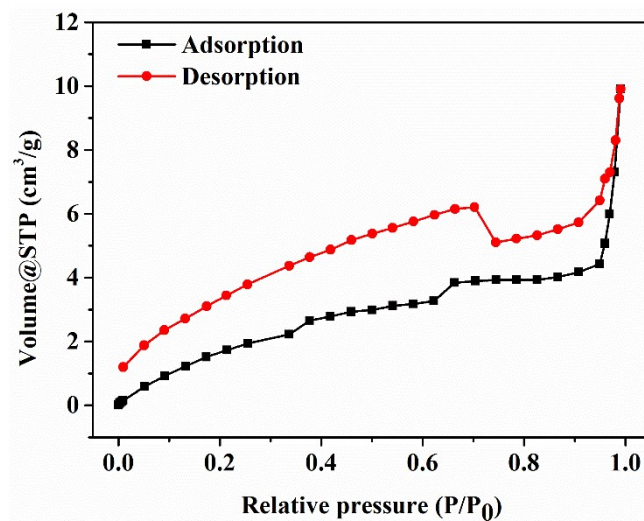
**Fig. S2.** Chromatogram results about the effect of the concentration of APTES and DOFDB on extraction performance. The concentration of APTES and DOFDB was 0.15, 0.75, 1.5, 2.3, 3.0 mg/mL (a-e).



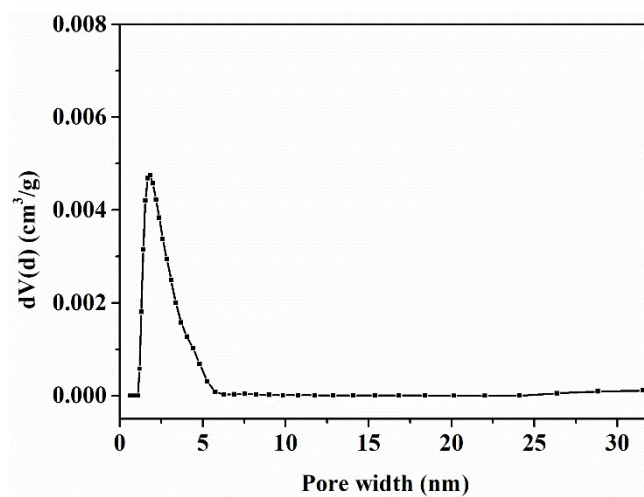
**Fig. S3.** FESME of B-COPs@microcap at 40000×.



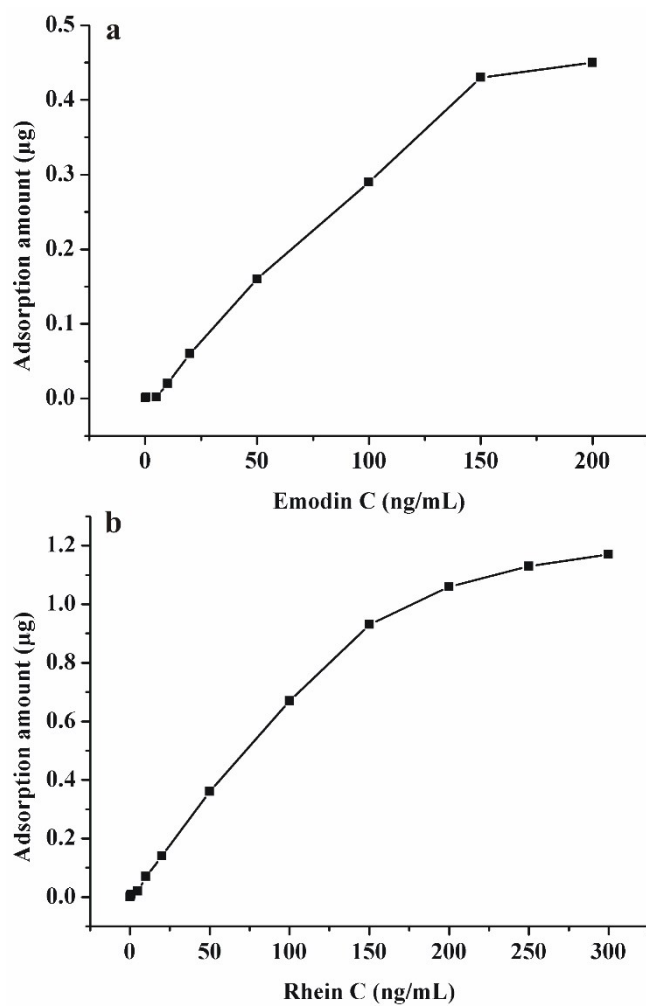
**Fig. S4.** <sup>13</sup>C CPMAS spectrum of B-COPs.



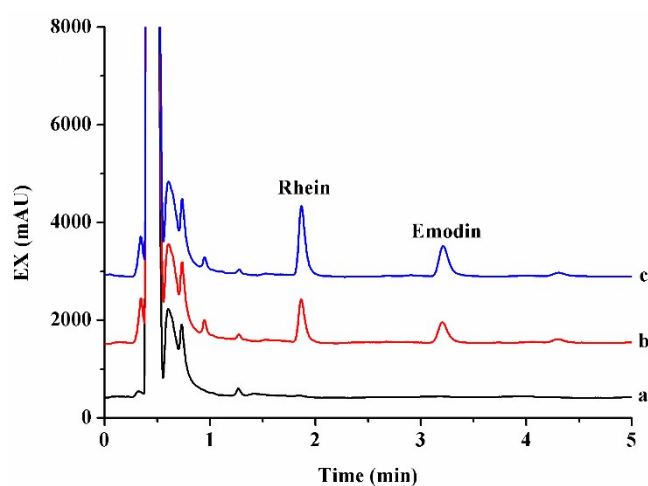
**Fig. S5.** Nitrogen adsorption/desorption isotherms of B-COPs at 77 K.



**Fig. S6.** Pore size distribution of B-COPs obtained by the QSDFT model.



**Fig. S7.** Adsorption curve of emodin (a) and rhein (b), emodin was 0.1, 0.5, 1, 5, 10, 20, 50, 100, 150, 200 ng/mL, besides that rhein was 250, 300 ng/mL.



**Fig. S8.** UPLC-DAD chromatogram of rhein and emodin in rat serum sample obtained by direct injection (a), with B-COPs@microcap BSE (b), spiked at 0.5 ng/mL with B-COPs@microcap BSE (c).



### C. Supplementary Tables

**Table S1** The recyclability (RSD, %) of B-COPs@microcap

Using time	1	2	3	4	5	6	7	8	9	10	RSD (%)	
Peak	Rhein	68727	57948	60003	61054	60690	71022	57309	61054	67776	62573	6.8%
area	Emodin	23867	24583	23175	23388	25603	24036	24414	23388	23175	28624	7.5%

**Table S2** Analytical performance of B-COPs@microcap-BSE-UPLC for rhein and emodin

Analytes	LOD (ng/mL)	LOQ (ng/mL)	Linear equation (ng/mL)	R <sup>2</sup>	Linear range (ng/mL)	EE(%)	RSD (% , n = 7, c = 10 ng/mL)
Rhein	0.015	0.045	Y=3918.6x+30.809	0.9996	0.1-50	54.4%	4.5%
Emodin	0.006	0.018	Y=1709.5x+563.83	0.9995	0.1-50	39.5%	5.9%

The concentration levels were 0.1, 0.5, 1, 5, 10, 20, 50 ng/mL for rhein and emodin in linear equation investigating.

**Table S3** Recoveries for determination of rhein and emodin in rat serum sample with B-COPs@microcap-BSE-UPLC

Analytes	Initial Amount	Added ( ng/mL )	Founded ( ng/mL )	Relative recovery %
Rhein	0.93	0.5	1.38±0.09	88.7
		5	6.22±0.56	105.8
		20	17.99±0.55	85.0
Emodin	1.16	0.5	1.68±0.15	104.2
		5	5.48±0.81	86.4
		20	19.22±0.30	90.3

**Table S4** Comparison of the proposed method with other reported methods for the determination of rhein and emodin

Method	Adsorbent	Extraction time (min)	Adsorbent mass	LOD (ng/mL)	Linear range (ng/mL)	Ref.
UAE-HPLC/UV	NADES	90	30 mL	-	-	1
SPE- UHPLC/FLD	BTO-SPE	<2	100 mg	5.1-5.7	0.015-1.800	2
ASE-SPE- UHPLC/DAD	DMIMS	>25	11 mL, 100 mg	40-67	120-40000	3
SPE-HPLC/FLD	CTAB-coated Fe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> NPs	5	0.04-0.28 mL, 0.1-0.8 mg	0.2-0.5	0.5-5000	4
MSPE- UHPLC/TOF/MS	rGO/Fe <sub>3</sub> O <sub>4</sub>	5	10 mg	0.023- 0.00028	0.13-27.77	5
BSE- UHPLC/DAD	B-COPs	75	378.9 nm of thickness	0.006- 0.015	0.1-50	This work

UAE: ultrasound-assisted extraction; HPLC/UV: high performance liquid chromatography/ultraviolet detector; NADES: natural deep eutectic solvents; SPE: solid phase extraction; UHPLC/FLD: ultra high performance liquid chromatography/fluorescence detector; BTO-SPE: bis(tetraoxacalix[2]arene[2]triazine); ASE: accelerated solvent extraction; DAD: diode array detector; DMIMS: dummy molecularly imprinted microspheres; CTAB-coated Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> NPs: cetyltrimethyl ammonium bromide coated Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> core/shell nanoparticles; MSPE: magnetic solid phase extraction; TOF/MS: time of flight /mass spectrometry; rGO/Fe<sub>3</sub>O<sub>4</sub>: reduced graphene oxide with iron oxide; Ref.: reference.

Reference:

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