## **Supporting Information**

## One-pot synthesis of UiO-66@SiO<sub>2</sub> shell-core microspheres as stationary phase for high

## performance liquid chromatography

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**Fig. S9:** Chromatograms of PAHs on UiO-66@SiO<sub>2</sub>-0.16 packed column with 20% ACN as mobile phase at a flow rate of 1.0 mL min<sup>-1</sup>. The signals were monitored with a UV detector at 254 nm.

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Sample name	ZrCl <sub>4</sub>	H <sub>2</sub> BDC	Acetic acid	Temperature	Time
	(g)	(g)	(mL)	(°C)	(h)
UiO-66@SiO <sub>2</sub> -0.08	0.08	0.057	0.5	120	24
UiO-66@SiO <sub>2</sub> -0.16	0.16	0.114	1.0	120	24
UiO-66@SiO <sub>2</sub> -0.32	0.32	0.228	2.0	120	24
UiO-66@SiO <sub>2</sub> -0.64	0.64	0.456	4.0	120	24
UiO-66@SiO <sub>2</sub> -1.28	1.28	0.912	8.0	120	24
UiO-66@SiO <sub>2</sub> -2.56	2.56	1.824	16.0	120	24
85 °C	0.64	0.456	4.0	85	24
100 °C	0.64	0.456	4.0	100	24
110 °C	0.64	0.456	4.0	110	24
3 h	0.64	0.456	4.0	120	3
6 h	0.64	0.456	4.0	120	6
12 h	0.64	0.456	4.0	120	12

Table S1 The synthesis conditions for different UiO-66@SiO<sub>2</sub> composites.<sup>a</sup>

<sup>a</sup>The synthesis of the UiO-66@SiO<sub>2</sub> composites was identical to what was described in experimental section.

**Table S2** The retention time  $(t_r)$  and retention factors (k) of aniline compounds on the UiO-66@SiO2 packedcolumns with different loading amount of UiO-66 shell.<sup>a</sup>

	p-phenylenediamine		aniline		N,N-dimethylaniline		p-chloroaniline	
Column	t <sub>r</sub> (min)	k						
UiO-66@SiO <sub>2</sub> -0.16	2.071	0.126	2.657	0.319	3.225	0.439	4.397	0.588
UiO-66@SiO <sub>2</sub> -0.32	1.331	0.047	1.635	0.224	2.151	0.410	5.366	0.764
UiO-66@SiO <sub>2</sub> -0.64	1.624	0.158	2.647	0.484	3.846	0.645	6.526	0.791

<sup>a</sup>Experimental conditions were identical to Fig. 8.



Fig. S1. SEM images of (A) UiO-66@SiO<sub>2</sub>-0.08; (B) UiO-66@SiO<sub>2</sub>-1.28; (C) UiO-66@SiO<sub>2</sub>-2.56.



Fig. S2. SEM image of UiO-66.



Fig. S3. XRD patterns of UiO-66@SiO<sub>2</sub> composites prepared at 85°C, 100°C, 110°C and 120°C for 24 h. It can be seen that the signal intensity of the characteristic peaks of UiO-66 increases with the reaction temperature.



Fig. S4. XRD patterns of UiO-66@SiO<sub>2</sub> composites prepared at 120°C for 3 h, 6 h, 12 h and 24 h. It can be seen that the signal intensity of the characteristic peaks of UiO-66 increases with the reaction time.



**Fig. S5.** SEM images of (A) UiO-66@SiO<sub>2</sub>-0.16; (B) UiO-66@SiO<sub>2</sub>-0.32; (C) UiO-66@SiO<sub>2</sub>-0.64 after ultrasonic for 10 min in a dichloromethane solution.



**Fig. S6.** Effect of the flow rate on the column backpressure on UiO-66@SiO<sub>2</sub>-0.16 packed column. 100% ACN was used as mobile phase.



**Fig. S7.** Chromatograms of the separation of (A) xylenes and ethylbenzene, (B) alkyl benzenes, (C) anilines and (D) substituted benzenes on UiO-66@SiO<sub>2</sub>-0.16 packed column with different ratio of ACN/H<sub>2</sub>O as mobile phase. Other separation conditions are identical to Fig. 6.



**Fig. S8.** Chromatograms on commercial C18 column for the separation of four groups of analytes: (A) xylenes and ethylbenzene; mobile phase, 50% ACN; (B) alkyl benzenes; mobile phase, 70% ACN; (C) anilines; mobile phase, 50% ACN; (D) substituted benzenes; mobile phase, 50% ACN. Other separation conditions are identical to Fig. 6.



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Fig. S10. Chromatograms of phenolic compounds on (A) UiO-66@SiO<sub>2</sub>-0.16 packed column and (B) aminosilica packed column with different ratio of ACN/H<sub>2</sub>O as mobile phase at a flow rate of 1.0 mL min<sup>-1</sup>. The signals were monitored with a UV detector at 270 nm.