

Supporting Information

PVBA-UiO-66 using the flexible PVBA with multi-coordination groups as mixed ligands and their super adsorption towards methylene blue

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Characterization. ¹H NMR spectra of 4-VBA and PVBA were recorded on a Varian 300 spectrometer. Fourier transform infrared absorption spectra (FTIR) were recorded on a Bio-Rad FTS 6000 system using diffuse reflectance sampling accessories. The thermal properties of UiO-66 and the PVBA-UiO-66 were measured by thermo gravimetric analysis (TGA). The samples were heated to 800 °C at a heating rate of 10 K/min under pure nitrogen (100 mL/min) gas stream on a SDT Q600. Powder X-ray diffraction (XRD) patterns were characterized using X-ray diffraction (XRD, D/max-2500 with Cu K radiation ($\lambda=1.5406 \text{ \AA}$)). Brunauer-Emmett-Teller (BET) surface area of the samples was determined using specific surface and pore properties analyzer (ASAP2020) by the Barrett–Joyner–Halenda (BJH) method. The morphology of UiO-66 and the PVBA-UiO-66 were observed by scanning electronic micrograph (SEM, JEOL JSM-5600). Size exclusion chromatography (SEC) measurements were performed on a system equipped with a Hitachi L-2130 HPLC pump, a Hitachi L-2350 column oven operated at 40 °C, three Varian PL columns with 1000 K-100 K (100,000 Å), 100 K-10 K (10,000 Å), and 100-10 K (1000 Å)

molecular ranges, and a Hitachi L-2490 refractive index detector. THF was used as eluant at a flow rate of 1.0 mL/min. The apparent molecular weight was calculated based on PS standards.

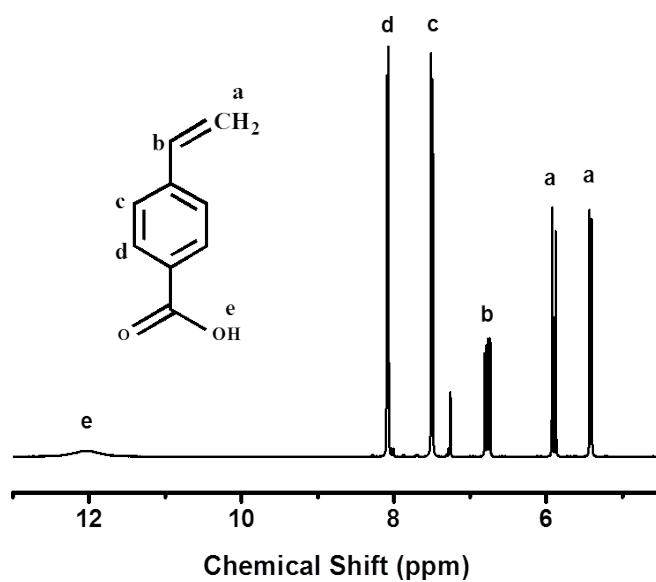


Figure S1. ¹H NMR spectrum of 4-VBA.

¹H NMR spectrum of 4-VBA in CDCl₃ is shown in Fig. S1. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 12.88 (s, 1H, -COOH), 8.07 (d, 2H, ph-H), 7.52 (d, 2H, ph-H), 6.77 (q, 1H, ph-CHd), 5.91 (d, 1H, dCH), 5.44 (d, 1H, dCH).

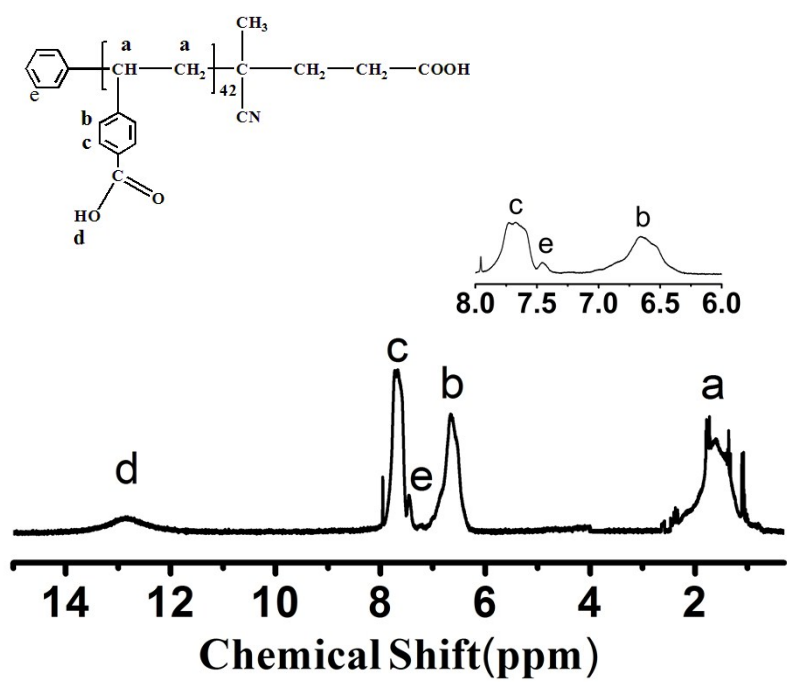


Figure S2. ¹H NMR spectrum of PVBA.

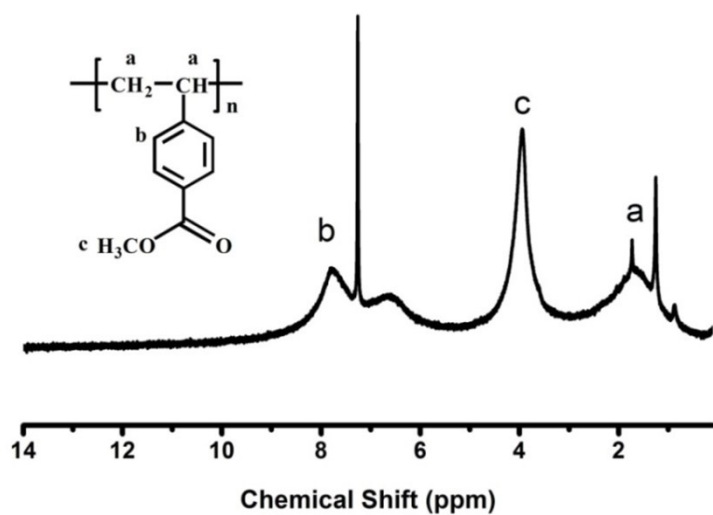


Figure S3. ¹H NMR spectrum of poly(p-vinylbenzoate).

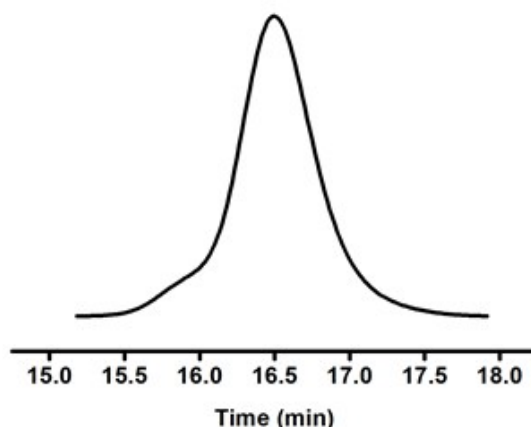


Figure S4. GPC spectrum of poly(p-vinylbenzoate).

Poly(p-vinylbenzoate) were synthesized by esterifying PVBA with methanol to determine the molecular weight and the molecular weight distribution of PVBA. The structure of poly(p-vinylbenzoate) was characterized by ^1H NMR and GPC (Fig. S3 and Fig. S4). No chemical shift at 12.8 ppm which attribute to the hydroxyl protons on the carboxylic acid groups was observed, indicating a complete esterification of PVBA. The molecular weight and the polymer dispersity index of poly(p-vinylbenzoate) homopolymer determined by GPC are about 7.1 K and 1.2, which indicates the molecular weight of PVBA is 6.2 K. This value is consistent with the result obtained from ^1H NMR.

Table S1 The carboxyl percentage in PVBA-UiO-66 determined via acid-base titration and TGA results

	PVBA(10%)- UiO-66	PVBA(26%)- UiO-66	PVBA(43%)- UiO-66	PVBA(69%)- UiO-66	PVBA(100%)- UiO-66
Acid-base titration (%)	3.9	6.8	19.8	15.5	16.0
TGA (%)	4.3	7.0	12.5	9.42	9.95

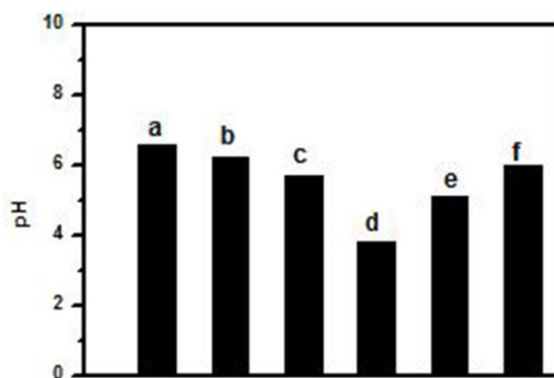


Figure S5. The zero-charge point for (a) UiO-66, (b) PVBA(10%)-UiO-66, (c) PVBA(26%)-UiO-66, (d) PVBA(43%)-UiO-66, (e) PVBA(69%)-UiO-66 and (f) PVBA(100%)-UiO-66.

Table S2 Zr content and Zeta potential of a series of PVBA-UiO-66

Materials	Zr content (%)	Zeta potential (mv)
UiO-66	14.6	31.2
PVBA(10%)-UiO-66	19.22	9.4
PVBA(26%)-UiO-66	25.85	3.2
PVBA(43%)-UiO-66	37.89	-21.8
PVBA(69%)-UiO-66	23.9	-3.4
PVBA(100%)-UiO-66	20.1	4.2

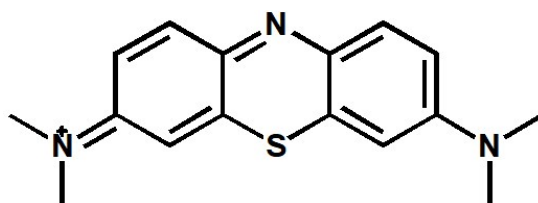


Figure S6. The structure of MB.

Table S3 Adsorption data for MB onto UiO-66 and PVBA(43%)-UiO-66 at various initial concentration of MB (pH = 5.4, $t_c=180$ min, T=293 K, $M_{MPCL}=2$ mg)

UiO-66	C_e	26	56	96.4	136	182
	q_e	120	220	268	340	320
PVBA(43%)- UiO-66	C_e	8	26	49	73	106
	q_e	210	370	505	635	720

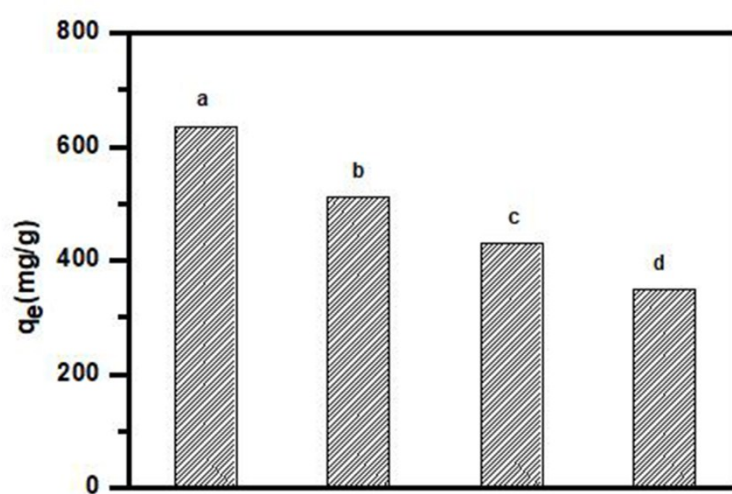


Figure S7. Adsorption toward (a) MB, (b) RhB, (c) Sudan III and (d) MO with initial concentration 200 mg/L for PVBA(43%)-UiO-66.

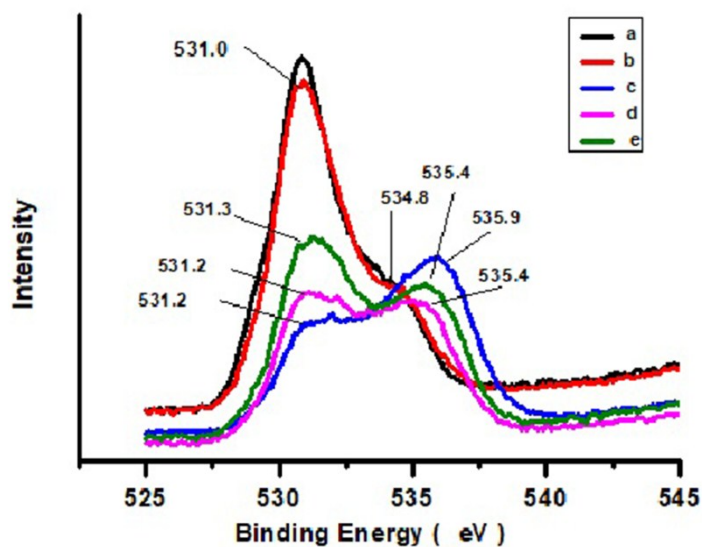


Figure S8. XPS spectra for O 1s in (a) PVBA(43%)-UiO-66, (b) PVBA(43%)-UiO-66-MO, (c) PVBA(43%)-UiO-66-sudan III, (d) PVBA(43%)-UiO-66-MB and (e) PVBA(43%)-UiO-66-RhB.

Table S4 Separation factor for the adsorption of MB onto UiO-66 and PVBA(43%)-UiO-66 in terms of initial concentration of MB (pH = 5.4, $t_c=180$ min, $T=293$ K, $M_{MPCL}=2$ mg)

UiO-66	C_e	26	56	96.4	136	182
	R_L	0.678	0.49	0.37	0.28	0.23
PVBA(43%)- UiO-66	C_e	8	26	49	73	106
	R_L	0.81	0.57	0.41	0.31	0.24

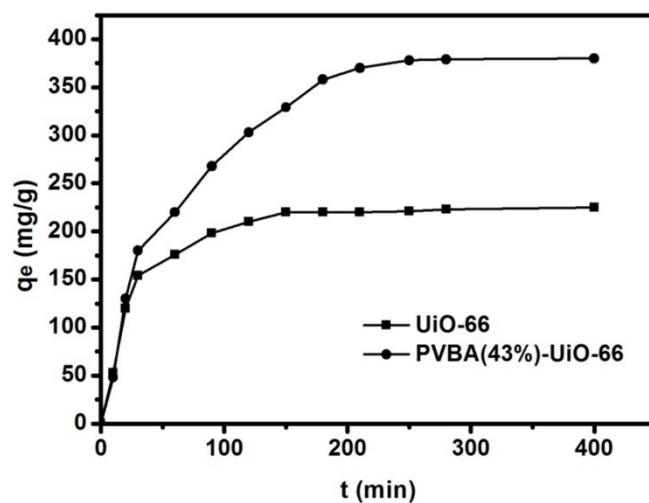


Figure S9. Kinetic adsorption data plots of MB onto UiO-66 and PVBA(43%)-UiO-66 (initial concentration of MB: 100 mg/L; adsorbent dose: 0.02 g/L, T=293 K).

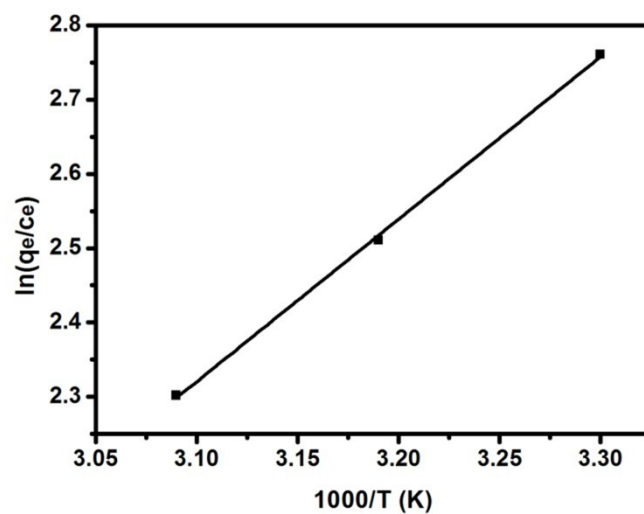


Figure S10. Van't Hoff plots for the adsorption of MB onto PVBA(43%)-UiO-66.

($X_0=30$ mg/L, pH=5.4, $M_{MPCl}=2$ mg, $t_c=180$ min).