Supporting Information for

A Generalizable Method for the Construction of MOF@Polymer Functional Composites

through Surface-Initiated Atom Transfer Radical Polymerization

Sanfeng He, Hongliang Wang, Cuizheng Zhang, Songwei Zhang, Yi Yu, Yongjin Lee and Tao Li*

School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China.

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Section 1. Materials and Characterization Methods

Azobisisobutyronitrile (AIBN) was recrystallized from ethyl alcohol. Anisole was distilled over calcium hydride. All monomers and crosslinkers were passed through basic alumina columns to remove inhibitors before polymerization. Cuprous bromide (CuBr) was washed with acetic acid and ethyl alcohol repeatedly, and then dried under vacuum before use. Other chemical reagents were obtained from commercial sources and used without further purification.

¹H NMR spectra were obtained on Bruker AVANCE III HD (400 MHz or 500 MHz) at room temperature (RT). Gel permeation chromatography (GPC) experiment was carried out on Malvern GPC TDA305 with D6000M general mixed org columns and calibrated using PMMA standards. Powder X-ray diffraction (PXRD) patterns were collected on a X-ray diffractometers (Bruker D2 PHASER or D8 ADVANCE). X-ray photoelectron spectroscopy (XPS) data were determined by Thermo Fisher ESCALAB 250 Xi. Thermogravimetric analyses (TGA) were performed on PerkinElmer TGA 8000. Firstly, samples were heated to 150 °C at the rate of 20 °C/min and the temperature kept at 150 °C for 30 min at N_2 atmosphere to remove the solvent. Then temperature rose to 600 °C at the rate of 20 °C/min at O₂ atmosphere. Dynamic light scattering (DLS) experiments were performed on Malvern Zetasizer Nano ZS. Ultramicrotomy was conducted on Leica EM UC7 ultramicrotome and the slice thickness is 100 nm. Transmission electron microscope (TEM) images were taken on a Tecnai G2 Spirit (120kV) and JEM 2100 plus (200 kV). STEM and EDS mapping images were taken on JEM 2100 plus (200 kV). Scanning electron microscope (SEM) images were taken on JSM 7800F Prime. Infrared spectroscopy was collected on PerkinElmer Frontier FT-IR. N₂ adsorption-desorption analysis was performed on QUADRASORB SI; CO₂ adsorption-desorption analysis was performed on BELSORP-max and Quantachrome iQ; water vapor uptake measurements were conducted on BELSORP-aqua3. Gas Before gas adsorption-desorption measurement, all samples were soaked in volatile solvates to exchange the nonvolatile solvates and were activated for 10 h at 120 °C. Water contact angle measurements were performed on a contact angle meter (Kino SL200K series). Before water contact angle measurements, the sample dispersed in solvent (with a relatively high concentration) was dropped onto a glass slide to form a completely covered and flat surface after the solvent was evaporated.

Section 2. Experimental Details

Synthesis of P(BIEM-r-MMA)

Synthesis of RAFT agent 2-cyano-2-propanyl dodecyl trithiocarbonate (CPDTC). CPDTC was synthesized according to a previously reported method with slight modification.¹ Firstly, n-dodecylthiol (2.54 g, 12.5 mmol) and 5 mL of 30 wt% sodium methylate (15 mmol) methanol solution were mixed with 10 mL of ethanol slowly. Next, carbon disulfide (1.14 g, 15 mmoL) was added to the mixture solution and the reaction was allowed to stir 2 h at RT. After iodine (1.9 g, 7.5 mmol) and 20 mL of ethyl acetate were added to the mixture solution and the reaction was allowed to stir for another 2 h. Then the mixture solution was washed by sodium thiosulfate aqueous solution (3 times) and brine (1 time) and dried over Na₂SO₄. After filtration to remove the Na₂SO₄, the solvents were removed by rotary evaporation and the product was dissolved in 20 mL ethyl acetate. Then AIBN (2.46 g, 15 mmol) was added to solution and the mixture was heated to reflux overnight. The crude product was purified by running through a silica gel column using petroleum ether/ethyl acetate (20/1) as eluent. ¹H NMR (500 MHz, CDCl₃) δ = 3.34 (t, 2H, -CH₂CH₂-S-), 1.87 (s, 6H, (CH₃)₂C(CN)–), 1.70 (m, 2H, -CH₂CH₂-S-), 1.40 (m, 2H, CH₃CH₂-L, 1.26 (br s, 16H, -CH₂(CH₂)₆CH₂-), and 0.88 (t, 3H, CH₃CH₂-).

Synthesis of 2-(2-bromoisobutyryloxy) ethyl methacrylate (BIEM). The synthetic procedure was based on a previously reported literature² with slight modification. Firstly, 2-hydroxyethyl methacrylate (1 g, 7.68 mmol) and triethylamine (1.01 g, 10 mmol) were dissolved in 50 mL of dichloromethane (DCM). After the mixture was cooled down in an ice bath, a solution of 2-bromoisobutyryl bromide (2.3 g, 10 mmol) in 10 mL DCM was slowly added. The mixture was allowed to warm up to RT and stirred for 6 h. Then the DCM was removed by rotary evaporation and 50 mL ethyl acetate was added. The mixture was purified by washing with deionized water (1 time), saturated sodium bicarbonate solution (3 times) and brine (1 time) and dried over Na₂SO₄. Then the product was further purified by passing through basic alumina. ¹H NMR (500 MHz, CDCl₃) δ = 6.14 (s, 1H, CH₂=C(CH₃)-), 5.60 (s, 1H, CH₂=C(CH₃)-), 4.42 (m, 4H, -COOCH₂CH₂OCO-), 1.96 (s, 3H, CH₂=C(CH₃)-), and 1.94 (s, 6H, -C(CH₃)₂Br).

Synthesis of P1. Typically, BIEM (1 g, 3.58 mmol), tert-butyl methacrylate (tBuMA) (56.6 mg, 0.398 mmol), AIBN (4.3 mg, 0.0265 mmol), and CPDTC (36 mg, 0.106 mmol) were dissolved in 1 mL of dimethyl formamide (DMF) in an ampoule. After three cycles of freeze-pump-thaw, the reaction mixture was sealed and then heated at 60 °C for 20 h. P(BIEM-co-tBuMA) were obtained by multiple cycles of solvent precipitation in methanol and then dried under vacuum overnight. GPC (PMMA calibration): Dispersity (Đ) = 1.48, $M_n = 10,305$ g/mol, $M_w = 15,286$ g/mol. P(BIEM-co-tBuMA) were then treated with trifluoroacetic acid (TFA) for 2 h to remove t-butyl groups and **P1** were obtained by multiple cycles of solvent precipitation in methanol.

Synthesis of P2. BIEM (1.50 g, 5.37 mmol), tert-butyl methacrylate (tBuMA) (84.9 mg, 0.597 mmol), and AIBN (7.5 mg, 0.0457 mmol) were dissolved in 1.5 mL of dimethyl formamide (DMF) in an ampoule. After three cycles of freeze-pump-thaw, the reaction mixture was sealed and then heated at 70 °C for 1 h. P(BIEM-co-tBuMA) were obtained by multiple cycles of solvent precipitation in methanol and then dried under vacuum. GPC (PMMA calibration): Dispersity (D) = 6.89, M_n = 80,975 g/mol, M_w = 557,522 g/mol. P(BIEM-co-tBuMA) were then treated with trifluoroacetic acid (TFA) for 2 h to remove t-butyl groups and **P2** were obtained by multiple cycles of solvent precipitation in methanol and dried under vacuum overnight.

Synthesis of MOFs

Synthesis of UiO-66. ZrCl₄ (0.349 g, 1.5 mmol) and 1-4-benzendicarboxylic acid (H₂BDC; 0.249 g, 1.5 mmol) were dissolved in 100 ml of 1.6 M acetic acid DMF solution in a glass vial. The vial was capped and placed at 120 °C for 12 hours. The crystals were collected by centrifugation, washed with DMF (2 times) and methanol (3 times) and soaked in methanol.

Synthesis of micron-sized UiO-66. $ZrCl_4$ (0.558 g, 2.4 mmol) and H_2BDC (0.398 g, 2.4 mmol) were dissolved in 100 ml of 2.4 M acetic acid DMF solution in a glass vial. The vial was capped and placed at 120 °C for 12 hours. The crystals were collected by centrifugation, washed with DMF (2 times) and methanol (3 times) and soaked in methanol.

Synthesis of ZIF-8. $Zn(NO_3)_2 \cdot 6H_2O(0.744 \text{ g}, 2.5 \text{ mmol})$ was dissolved in 50 mL of methanol, and 2-methylimidazole (0.821 g, 10 mmol) was dissolved in another 50 mL of methanol. Then two solutions were mixed quickly and allowed to sit at RT for 12 h without stirring. The crystals were collected by centrifugation, washed with methanol (3 times) and soaked in methanol.

Synthesis of ZIF-67. $Co(NO_3)_2 \cdot 6H_2O$ (0.435 g, 1.5 mmol) was dissolved in 50 mL of methanol, and 2-methylimidazole (0.985 g, 12 mmol) was dissolved in another 50 mL of methanol. Then two solutions were mixed quickly and allowed to sit for 12 h without stirring. The crystals were collected by centrifugation, washed with methanol (3 times) and soaked in methanol.

Synthesis of MIL-96(AI). Al(NO₃)₃·9H₂O (0.375 g, 1 mmol) was dissolved in 6 mL deionized water and benzene-1,3,5-tricarboxylic acid (H₃BTC; 0.21 g, 1 mmol) was dissolved in 6 mL DMF. Then two solutions was mixed in a teflon-lined autoclave and 0.5 mL of 40 mM acetic acid solution was added. After the reaction was kept at 150 °C for 2 h, the crystals were collected by centrifugation, washed with DMF (2 times) and methanol (3 times) and soaked in methanol.

Synthesis of MIL-101(Cr). Cr(NO₃)₃·9H₂O (1.0 g, 2.5 mmol), H₂BDC (0.415 g, 2.5 mmol), and deionized water (10 mL) were mixed in a teflon-lined autoclave and kept in an oven at 200 °C for 16 h. The crystals was collected by centrifugation, washed with DMF (2 times) and soaked in DMF overnight at 50 °C to remove the excess H₂BDC. Then the large-grained impurities were removed by centrifugation at 1000 rpm for 30 s and MIL-101(Cr) in the supernatant was recovered by centrifugation. The crystals were washed with DMF (2 times) and methanol (3 times) and soaked in methanol.

Synthesis of MOF@xPoly

Typically, MOF (20 mg) preserved in methanol was collected by centrifugation, and re-dispersed in 1 mL of DCM containing 10 mg **P1** by ultrasonic. After incubation for about 1 min, the mixture was washed with DCM (2 times) and **solvent1** (1 time) to remove free **P1** in the solution and re-dispersed in 0.4 mL of **solvent1** in an ampoule. Then monomer (0.2 g), crosslinker (1,4-butanediol diacrylate (BDDA) or 1,4-butanediol dimethacrylate (BDDMA); $n = 0.1n_{monomer}$) and CuBr (2 mg) were added. After three cycles of freeze-pump-thaw, PMDETA (5.8 µL) was added in nitrogen condition and another cycle of freeze-pump-thaw was performed. Then the ampoule was sealed and placed in oil bath at 80 °C and stirred for several hours. The reaction was quenched by cooling and the catalyst and excess monomers were removed by washing with DMF (2 times) and **solvent2** (3 times). The solvents, crosslinkers and reaction time in each case are described in Table S1. The synthesis procedure of UiO-66@xPS' are similar to the UiO-66@xPS, and **P2** was used as macroinitiator instead and the polymerization temperature was 70 °C. The average polymer thickness values were determined by TEM images based on no less than 50 measures for each sample.

Synthesis of UiO@xPSyz with different coating thickness (yz denoted the thickness of PS)

The synthesis procedures are similar to the synthesis of **MOF@xPoly** and different coating thicknesses were achieved by controlling the concentration of monomer and the reaction time (described in Table S2). In all cases, the mass of UiO-66 is 20 mg; the solvent is anisole (0.4 mL) and the crosslinker is BDDA ($n = 0.1n_{monomer}$).

Synthesis of UiO@xPS@Poly

Typically, UiO-66@xPS or UiO-66@xPS₅₉ (20 mg) was dispersed in solvent (0.4 mL) and then monomer (m = $10m_{MOF}$) and CuBr (2 mg) were added to the suspension. After three cycles of freeze-pump-thaw, PMDETA (5.8 μ L) was added in nitrogen atmosphere and another cycle of freeze-pump-thaw was performed. The polymerization was allowed to stir in oil bath at 80 °C for different

time. The reaction was quenched by cooling and the catalyst and excess monomers were removed by washing with DMF (2 times) and then DCM or methanol (3 times). Solvents and monomers in each case are described in the Table S3.

Synthesis of UiO-66@xPS"

Micron-sized UiO-66 (1 g) preserved in methanol was collected by centrifugation, and re-dispersed in 20 mL of DCM containing 100 mg **P1** by ultrasonic. After incubation for about 1 min, the mixture was washed with DCM (2 times) and DCM (1 time) to remove free **P1** in the solution and dispersed in 13.2 mL of anisole in an ampoule. Then styrene (2 g), divinylbenzene (0.74 g, n = $0.25n_{styrene}$) and CuBr (20 mg) were added. After three cycles of freeze-pump-thaw, PMDETA (58 µL) was added in nitrogen condition and another cycle of freeze-pump-thaw was performed. Then the ampoule was sealed and placed in oil bath at 70 °C and stirred for 12 hours. The reaction was quenched by cooling and the catalyst and excess monomers were removed by washing with DMF (2 times) and DCM (3 times).

Chemical stability test for UiO-66 and UiO-66@xPS"

Two portions micron-sized UiO-66 (about 100 mg of each portion) were dispersed in 10 mL of 1 M NaOH aqueous solution and 1 M H₂SO₄ aqueous solution respectively and stirred at 50 °C for 10 min. After being washed with deionized water (5times) and methanol (2 times), these samples were dried under vacuum at 60 °C. Two portions UiO-66@xPS'' (100 mg of each portion) were dispersed in 10 mL of 1 M NaOH aqueous solution and 1 M H₂SO₄ aqueous solution respectively and stirred at 50 °C for 24 h. After washing with deionized water (5 times) and methanol (2 times), these samples were dried under vacuum at 60 °C. Then PXRD experiments were performed to determine the crystallinity and CO₂ uptake measurements were conducted at 195 K to determine the porosity after being activated for 10 h at 120 °C.

Section 3. Calculation Details

The Composition of P1

In Figure S1, integrations of the peaks of the hydrogen protons on the methylene of BIEM (at about δ = 4.30, n = 4) and tertbutyl of the tBuMA (at about δ = 1.41 ppm, n = 9) were used to calculate the chemical composition of P(BIEM-co-tBuMA). The M_n of P(BIEM-co-tBuMA) is 10,305 g/mol from GPC data. The average number of BIEM (denoted as N(BIEM)) and the average number of tBuMA (denoted as N(tBuMA)) in each P(BIEM-co-tBuMA) chain can be calculated by the following equations:

$$\frac{N(BIEM)}{N(tBuMA)} = \frac{\frac{I(\delta = 4.30)}{4}}{\frac{I(\delta = 1.41)}{9}} = 8.52$$

 $N(BIEM) \times M(BIEM) + N(tBuMA) \times M(tBuMA) = 10305$

 $I(\delta = X)$ means the integration of the peak at δ = X and these data were shown in Figure S1. M(BIEM) and M(tBuMA) mean the formula weight of BIEM and tBuMA respectively. By calculation, N(BIEM) is approximately equal to 35 and N(tBuMA) is approximately equal to 4.

After hydrolysis, **P1** should, in principle, maintain monomer mole fractions as in P(BIEM-co-tBuMA). So each **P1** chain comprises about 35 bromoisobutyrate (BiB) groups and 4 carboxylic acid groups on the back-bone.

Estimating the average surface density of the BiB group

Considering UiO-66 particles as ideal octahedrons with an average edge length of 451 ± 15 nm and the density of UiO-66 is 1.409 g/cm³ (1.409E-21 g/nm³) based on the ideal crystal structure, we can calculate that the external surface area of 1 g of UiO-66 is equal to 1.16E19 nm². As about 30 mg of **P1** (M_n = 10,305 g/mol; each polymer chain comprises 35 BiB groups) was loaded onto 1 g of UiO-66, there are about 6.13E19 BiB groups were loaded on the surface of 1 g UiO-66. So we can estimate the average surface density of the BiB group on UiO-66 to be 5.3/nm².

Quantifying the polymer mass fraction of MOF@polymer by TGA

M(MOF)

The data used for quantifying polymer mass fraction are shown in Table S4 and S5. The value of M(oxide) can be obtained m(MOF)

from the TGA data of MOF and this value is the intrinsic property of MOF. So for MOF@polymer, the value of m(oxide) is equal to M(MOF)

the value of M(oxide). Although the mass of MOF in the sample MOF@polymer cannot be obtained by directly from the TGA data $\frac{m(MOF)}{m(MOF)} = \frac{M(MOF)}{m(MOF)}$

of MOF@polymer, it can be calculated from the equation $\overline{m(oxide)} - \overline{M(oxide)}$. So the polymer mass fraction of MOF@polymer can be calculated by the following equation:

Polymer mass fraction

$$=\frac{m(polymer)}{m(MOF@polymer)} = \frac{m(MOF@polymer) - m(MOF)}{m(MOF@polymer)} = 1 - \frac{m(oxide) \times \frac{M(MOF)}{M(oxide)}}{m(MOF@polymer)} = 1$$

×100%

 $\frac{M(MOF)}{M(oxide)} and \frac{m(MOF@polymer)}{m(oxide)}$ for MOF@polymer and the calculated polymer mass fraction results were described in Table S5.

Section 4. Molecular Dynamics Simulation

To construct simulation cells, firstly, we prepared a slab model of UiO-66 by expanding unit cell³ and cutting the supercell with two [100] surfaces (top and bottom) in the z direction. After cleaving, the unsaturated metal ions were terminated by hydroxyl groups or waters. Then, we added a vacuum gap for the slab model in the z axis to avoid any interactions between the slab and its periodic images in this direction, and further expanded it 3 times in both x and y directions. The final dimension of a slab model was 6.293 nm×6.293 nm×19 nm. Next, with two constitutional units which are MAA and BIEM, random copolymers (RCP) were generated using the Materials Studio 7.0.⁴ Each RCP chain has 4 MAA and 35 BIEM with random distribution. We prepared two cubic boxes of 15 nm×15 nm×15 nm containing 10 RCPs in each box. Then, with a closed boundary condition in z direction while applying periodic boundary conditions in x and y orientations, RCPs were relaxed by performing molecular dynamics runs (MD) using the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator)³ with a canonical ensemble (NVT) at a fixed temperature of 298.15 K. During relaxation, box sizes were adjusted so that the final dimensions of each box became 6.293 nm×6.293 nm×5 nm. Then, boxes were combined with the slab model to construct composite systems which have polymers on UiO-66 surfaces. Finally, vacuum spaces were filled with toluene molecules at a density of 0.87 g/cm³.⁵

Forcefield parameters for polymers and toluene were employed from the consistent-valence forcefield.⁶ UiO-66 was treated as a rigid framework and the Lennard-Jones parameters were adopted using the universal force field.⁷ Atomic charges were obtained using the Rappe-Goddard charge equilibration method (QEq).⁸ In our calculations, the van der Waals and Coulombic interactions were subject to a 14 Å cut-off.

To obtain equilibrated configuration of the composite system, we performed relaxation procedures consisted of 10 steps with five cycles of two MD simulations at different temperature; 1) NVT at 500 K and 2) NVT at 300 K. Each MD runs over 1 ns with a timestep of 1fs. Next, the MD production runs were performed during 300 ps in the NVT ensemble at 298.15 K. Figure S17 and S18 show an equilibrated configuration obtained from the MD production runs and the density plot of polymer and UiO-66 atoms as a function of the z axis, respectively.

In Figure S19, trajectories of the numbers of hydrogen bonds are shown during the MD production runs. The cutoff identifying a hydrogen bond was set as 2.5 Å. It is observed that the numbers of hydrogen bonds in all types (inter, intra, and interfacial) maintains well with an oscillating behavior, which demonstrates that dynamics in our composite system reached at steady-state through our relaxation procedures. Figure S20 and S21 show average numbers of inter polymer, intra polymer, and interfacial hydrogen bonds per chain. While there is negligible number of hydrogen bond between polymers and UiO-66 surface, our calculations showed that each polymer chain has about two intra and two inter hydrogen bonds, respectively.

Section 5. Supplementary Tables

Samples	Solvent1	Monomers	Crosslinkers	Reaction time/h	Solvent2
UiO-66@xPS ⁺	anisole	styrene	styrene DBBA 12 styrene DBBA 10 (at 70 °C)		DCM
UiO-66@xPS'	anisole	styrene			DCM
ZIF-8@xPS	anisole	styrene	DBBA	12	DCM
ZIF-67@xPS	anisole	styrene	DBBA	12	DCM
MIL-101(Cr)@xPS	anisole	styrene	DBBA	4.5	DCM
MIL-96(Al)@xPS	anisole	styrene	DBBA DBBA	12	DCM
UiO-66@xPCS [‡]	anisole	4-chlorostyrene		18	DCM
UiO-66@xPHEA ⁺	DMSO	2-hydroxyethyl acrylate	DBBA	7	methanol
UiO-66@xPBA⁺	anisole	n-butyl acrylate	DBBA	4	DCM
ΠίΩ-66@xP(BzMΔ-co-	anisole &	benzyl methacrylate &			henzotri-
DEMA)‡	benzotri-fluoride	1H,1H,2H,2H-perfluorodecyl	DBBMA	16	fluoride
FFINAJ	(1/1, v/v)	methacrylate (1/1)			nuonue
	benzotri-fluoride	1H,1H,2H,2H-perfluorodecyl		4	benzotri-
		methacrylate	UDDIVIA	4	fluoride

Table S1. The solvents and reaction time in each case for MOF@xPoly.

⁺ The dosage in these cases was 10 times that of in the typical process;

[‡] The dosage in these cases was doubled.

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Table S2. The mass of monomer (styrene) and reaction time for PS coated UiO-66 with three different thicknesses

Sample	Mass of styrene/g	Reaction time/h		
UiO-66@xPS ₁₃	0.2	6		
UiO-66@xPS ₂₃	0.4	6		
UiO-66@xPS ₃₂ [†]	0.2	12		
UiO-66@xPS ₅₉	0.4	12		

† This sample is UiO-66@xPS described above.

 Table S3. The solvents, monomers and reaction time for UiO-66@xPS@Poly.

Samples	Solvents	Monomers	Time/h
UiO-66@xPS ₅₉ @P4VP	N-methyl pyrrolidone	4-vinylpyridine	22
UiO-66@xPS@PtBuMA	anisole	tert-butyl methacrylate	12
UiO-66@xPS@PHEMA	DMF	2-hydroxyethyl methacrylate	12
UiO-66@xPS@PDMAEMA	DMF	2-(dimethylamino)ethyl methacrylate	12

Samples		Mass at 150 °C			Mass at 600 °C
MOF		M(MOF)			M(oxide)
MOF@polyme	r n	m(MOF@polymer) = m(polymer) + m(MOF)) m(oxide)
Table S5. The po	he polymer mass fraction of MOF@polymer calculated based on the TGA data.				
Complex	Ma	cc at 600 °C / N	Polymer loading		
Samples	IVId		(wt%)		
	Test 1	Test 2	Test 3	Average	_
010-66	2.135	2.126	2.133	2.131	
UiO-66@P1		2.197	7		3.097
UiO-66@xPS ₁₃		2.735			22.08
UiO-66@xPS ₂₃		2.971			28.27
UiO-66@xPS ₅₉		4.752	2		55.16
UiO-66@xPS		3.042	2		29.95
UiO-66@xPBA		2.736	5		22.13
UiO-66 micro		2.307	7		
UiO-66@xPS''		2.447	7		5.721

 Table S4. The data needed for quantifying polymer mass fraction in MOF@polymer composite.

Section 6. Supplementary Figures



Figure S1. ¹H NMR (500 MHz, CDCl₃) spectrum of P(BIEM-co-tBuMA) synthesized by RAFT polymerization. Peaks in the range of 0.7-1.3 ppm correspond to poly methacrylate backbone hydrogen atoms.



Figure S2. ¹H NMR spectrum (500 MHz, CDCl₃) of P1. The peak at δ = 1.41 ppm disappeared means the complete removal of tertbutyl groups. Peaks in the range of 0.7-1.3 ppm correspond to poly methacrylate backbone hydrogen atoms.



Figure S3. ¹H NMR (500 MHz, CDCl₃) spectrum of P(BIEM-co-tBuMA) synthesized by AIBN initiated non-controlled free radical polymerization. Peaks in the range of 0.7-1.3 ppm correspond to poly methacrylate backbone hydrogen atoms.



Figure S4. ¹H NMR spectrum (400 MHz, CDCl₃) of **P2**. The peak at δ = 1.41 ppm disappeared means the complete removal of tertbutyl groups. Peaks in the range of 0.7-1.3 ppm correspond to poly methacrylate backbone hydrogen atoms.



Figure S5. SEM images of UiO-66 (A), ZIF-8 (B), ZIF-67 (C), MIL-96(AI) (D), and MIL-101(Cr) (E).



Figure S6. TEM images of UiO-66 (A), ZIF-8 (B), ZIF-67 (C), MIL-96(AI) (D), and MIL-101(Cr) (E).



Figure S7. PXRD patterns of UiO-66 simulated from crystal structure (black), synthesized UiO-66 (navy) and UiO-66@xPS (red).



Figure S8. PXRD patterns of ZIF-8 simulated from crystal structure (black), synthesized ZIF-8 (navy) and ZIF-8@xPS (red).



Figure S9. PXRD patterns of ZIF-67 simulated from crystal structure (black), synthesized ZIF-67 (navy) and ZIF-67@xPS (red).



Figure S10. PXRD patterns of MIL-101(Cr) simulated from crystal structure (black), synthesized MIL-101(Cr) (navy) and MIL-101(Cr)@xPS (red).



Figure S11. PXRD patterns of MIL-96(AI) simulated from crystal structure (black), synthesized MIL-96(AI) (navy) and MIL-96(AI)@xPS (red).



Figure S12. Picture of UiO-66 and UiO-66@P1 dispersed in DCM.



Figure S13. XPS measurements of UiO-66 (navy) and UiO-66@P1 (red). (A) XPS wide scan spectrum and (B) high-resolution XPS Br 3d spectrum.



Figure S14. TEM images of UiO-66@xPS (A), ZIF-8@xPS (B), ZIF-67@xPS (C), MIL-101(Cr)@xPS (D), MIL-96(AI)@xPS (E), and xPS capsule (F).



Figure S15. TEM images of UiO-66@xPS'



Figure S16. TEM images of UiO-66@xPCS (A, B) and ultrathin slice of UiO-66@xPCS composite in PS matrix (C).



Figure S17. Schematics of UiO-66/polymer composite systems in toluene (upper picture). In the bottom picture, only polymers and UiO-66 are shown for clarity.



Figure S18. Density of polymer (red line) and UiO-66 atoms (blue line) as a function of the z coordinate for the equilibrated configuration of a composite system.



Figure S19. Trajectories of number of inter polymer (black line), intra polymer (red line), and interfacial (green bar) hydrogen bonds per chain during the molecular dynamics production runs.



Figure S20. Average numbers of inter polymer (black bar), intra polymer (red bar), and interfacial (green bar) hydrogen bonds per chain.



Figure S21. Inter and intra hydrogen bonds among three selected polymers. Polymers are represented as lines and each polymer chain is colored as different color (orange, light green, and light blue). UiO-66 is depicted as grey lines. "Ball and stick" representation is applied to hydrogen and oxygen atoms making inter hydrogen bond and atoms connected with them. For the intra hydrogen bond case, "stick" model is used.



Figure S22. TEM images of UiO-66@xPS@P4VP.



Figure S23. TEM images of UiO-66@xPS@PHEMA.



Figure S24. TEM images of UiO-66@xPS@PDMAEMA.



Figure S25. TEM images of UiO-66@xPS@PtBuMA.



Figure S26. TEM images of UiO-66@xPHEA.



Figure S27. TEM images of UiO-66@xPBA.



Figure S28. TEM images of UiO-66@xP(BzMA-co-PFMA).



Figure S29. TEM images of UiO-66@xPPFMA.



Figure S30. TEM images of UiO-66@xPS".



Figure S31. SEM images of UiO-66@xPS" (A) after treating with 1 M NaOH and UiO-66 (B) after treating with 1 M NaOH.



Figure S32. N₂ adsorption-desorption isotherms (77 K) of UiO-66 (navy), UiO-66@xPS (red) and UiO-66@xPBA (green).



Figure S33. CO₂ adsorption-desorption isotherms (195 K) of UiO-66 (navy), UiO-66@xPS (red) and UiO-66@xPBA (green).



Figure S34. CO₂ adsorption-desorption isotherms (273 K) of UiO-66 (navy), UiO-66@xPS (red) and UiO-66@xPBA (green).



Figure S35. Water vapor adsorption-desorption isotherms (298 K) of UiO-66 (navy), UiO-66@xPS (red) and UiO-66@xPBA (green).



Figure S36. CO₂ adsorption-desorption isotherms (195 K) of UiO-66@xPS'' (navy), UiO-66@xPS'' after treating with 1 M H₂SO₄ (red) and UiO-66@xPS'' after treating with 1 M NaOH (green).



Figure S37. CO₂ adsorption-desorption isotherms (195 K) of UiO-66 (navy), UiO-66 after treating with 1 M H₂SO₄ (red) and UiO-66 after treating with 1 M NaOH (green).



Figure S38. N₂ adsorption-desorption isotherms (77 K) of UiO-66 (navy), UiO-66 after treating with 1 M NaOH (red).



Figure S39. CO_2 fraction uptake at 273 K for UiO-66 and UiO-66@xPBA.

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