Electronic supplementary information (ESI) for:

Polymer Brushes on Metal–Organic Frameworks by UV-Induced Photopolymerization

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Synthesis and characterization

Preparation of MOFs

UiO-66 was prepared according to the literature.[1] Zirconium (IV) chloride ($ZrCl_4$, 0.40 g, 1.71 mmol) was dissolved in 100 mL of N,N'-dimethylformamide (DMF) at room temperature by sonication. Terephthalic acid (0.28 g, 1.71 mmol) and a small amount of water (0.13 mL, 6.84 mmol) were added to the solution, respectively. The tightly capped jars were placed in a preheated oven at 120 °C. After 24 h, the solutions were cooled to room temperature, and the precipitates were isolated by centrifugation. The MOF nanoparticles were thoroughly rinsed with 40 mL of DMF three times, followed by washing with 40 mL of methanol three times. During each washing step, the MOF suspension was kept at room temperature for at least 12 h to allow a complete solvent exchange. The solvent was decanted, and the MOF nanoparticles were dried at 150 °C under vacuum prior to use and characterization.

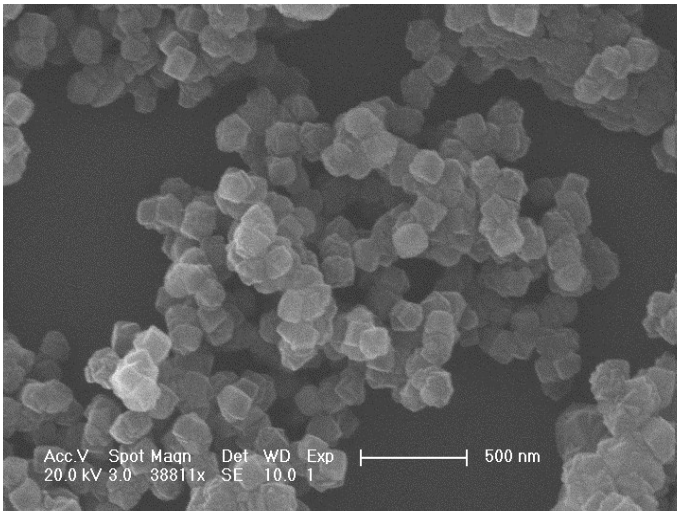

Figure S1. SEM image of the as-synthesized UiO-66.

UiO-66-NH_2 was prepared according to the literature.[2] Briefly, $ZrCl_4$ (1.50 g, 6.4 mmol) and 2-amino-1,4-benzenedicarboxylic acid (NH_2-BDC) (1.56 g, 6.4 mmol) were dissolved in DMF (180 mL) at room temperature in a volumetric flask. The resulting mixture was placed in a preheated oven at 80 °C for 12 h and then held at 100 °C for 24 h. After the solution was cooled to room temperature in air, the resulting solid was filtered and repeatedly washed with absolute ethanol for 3 days while heated at 60 °C in a water bath. The resulting yellow powder was filtered, transferred to a Schlenk flask, and dried under vacuum at room temperature.

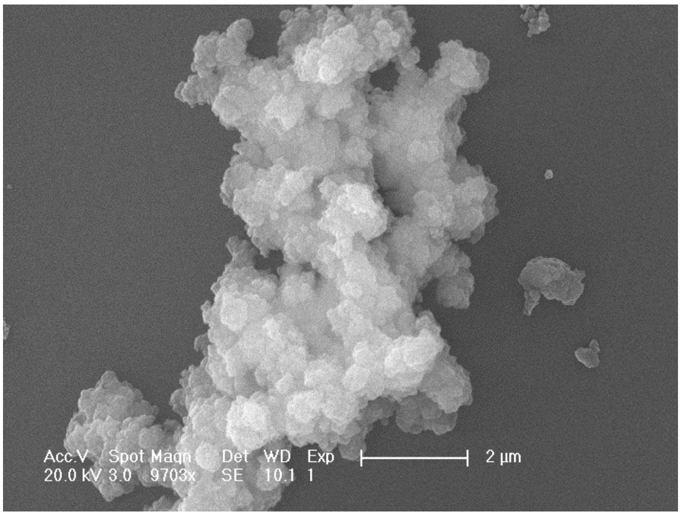

Figure S2. SEM image of the as-synthesized UiO-66-NH_2.

MIL-125(Ti) was prepared according to the literature.[3] Briefly, NH_2-BDC (0.56 g, 3.1 mmol) was dissolved in DMF and methanol mixed solvent ($V_{DMF}/V_{methanol}$ =9:1) with total solvent volumes of 40 mL. Then titanium isopropoxide (0.6 mL, 2.0 mmol) was added to the NH_2-BDC solution. After stirring by ultrasonic concussion for 5 minutes, the mixture was transferred to a 100 mL Teflon-lined steel autoclave and placed in an oven at 150 °C for 24 h under static conditions. After cooling, the yellow solid product was washed three times with DMF and twice with methanol, and then isolated by centrifugation. These samples were then activated in boiling DMF for 5 h in order to remove the remaining unreacted reactant trapped in the pores. After drying overnight in a vacuum oven at 50 °C, the samples were calcined at 200 °C for 6 h to remove the free solvents.

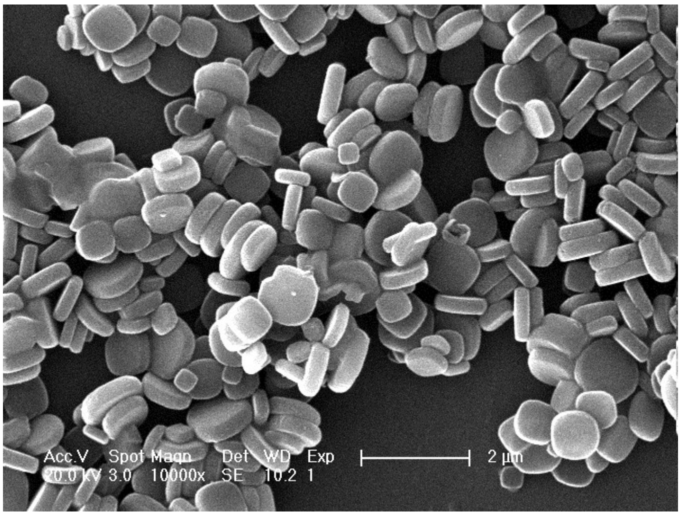

Figure S3. SEM image of the as-synthesized MIL-125(Ti).

MOF-5 was synthesized according to the literature.[4] Two solutions prepared separately by dissolving terephthalic acid (66 mg, 0.4 mmol) in 7.5 mL of DMF and $Zn(CH_3COO)_2{\cdot}2H_2O$ (88−220 mg, 0.4−1 mmol) in 7.5 mL of DMF were mixed and stirred at room temperature for 4−24 h. The resulting suspension was isolated by repeated centrifugation and washing with DMF.

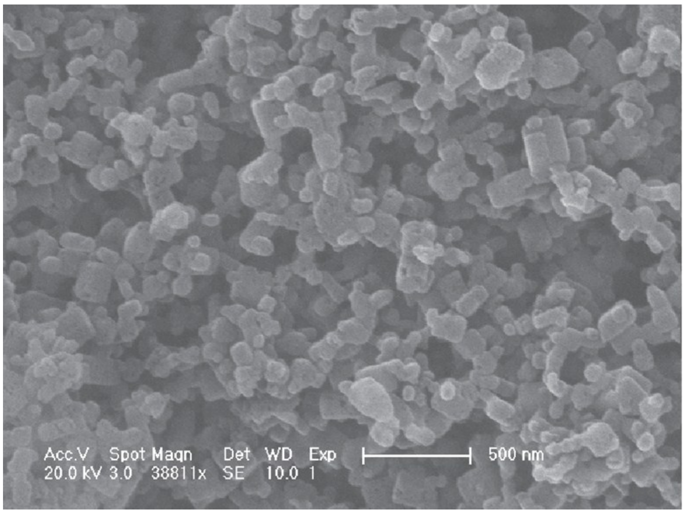

Figure S4. SEM image of the as-synthesized MOF-5.

IRMOF-3 was synthesized according to the literature.[5] Briefly, a 10 mL of DMF solution of $Zn(CH_3COO)_2{\cdot}2H_2O$ (80 mM) was rapidly pouring into a 15 mL of DMF solution of NH_2-BDC (20 mM) at room temperature. The mixture turned to turbid immediately, the nanocrystals were isolated by centrifugation (12000 rpm) and washed with DMF and CH_2Cl_2 after 1 min of the reaction.

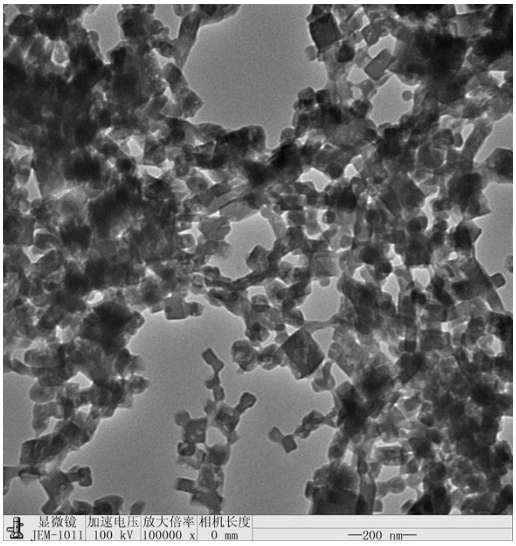

Figure S5. TEM image of the as-synthesized IRMOF-3.

ZIF-8 was synthesized according to the literature.[6] Briefly, $Zn(NO_3)_2$ (258 mg) was dissolved in methanol (20 mL) to obtain a solution. 2-Methylimidazole (263 mg) was dissolved in methanol (20 mL) to generate another clear solution. Then, both of them were mixed together, and stirred for 5 min. The solution was aged at room temperature for 24 h, yielding white precipitates. The powders were washed very carefully with methanol and dried prior to use and characterization.

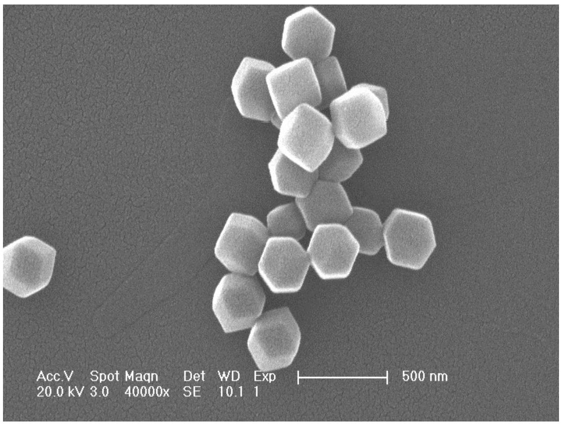

Figure S6. SEM image of the as-synthesized ZIF-8.

$[Cu(BTCA)_{0.5}(H_2O)_3]\cdot 2H_2O$ was synthesized according to the literature.[7] Briefly, a mixture of $CuCl_2\cdot 2H_2O$ (0.086 g, 0.5 mmol) and NaOH (0.04 g, 1 mmol) in water was stirred for 10 min at room temperature, then the $Cu(OH)_2$ solid was filtered. 1,2,3,4-Butanetetracarboxylic acid (H_4BTCA) (0.058 g, 0.25 mmol) was added to the $Cu(OH)_2$ suspension in water with constant stirring for 1 h and the blue precipitate was obtained, which was filtered, washed with water and dissolved in a minimum amount of aqueous ammonia (14 M). Blue crystals were obtained by slow evaporation of the ammoniacal solution at room temperature.

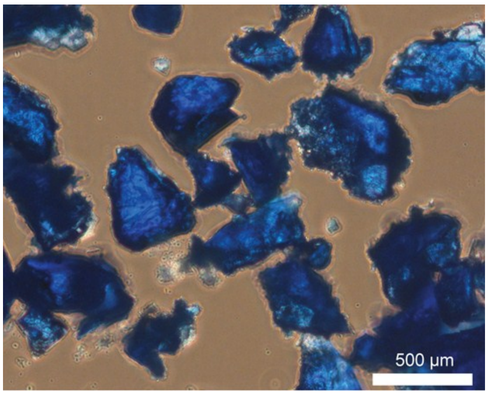

Figure S7. Photodiagram of the crushed $[Cu(BTCA)_{0.5}(H_2O)_3]\cdot 2H_2O$.

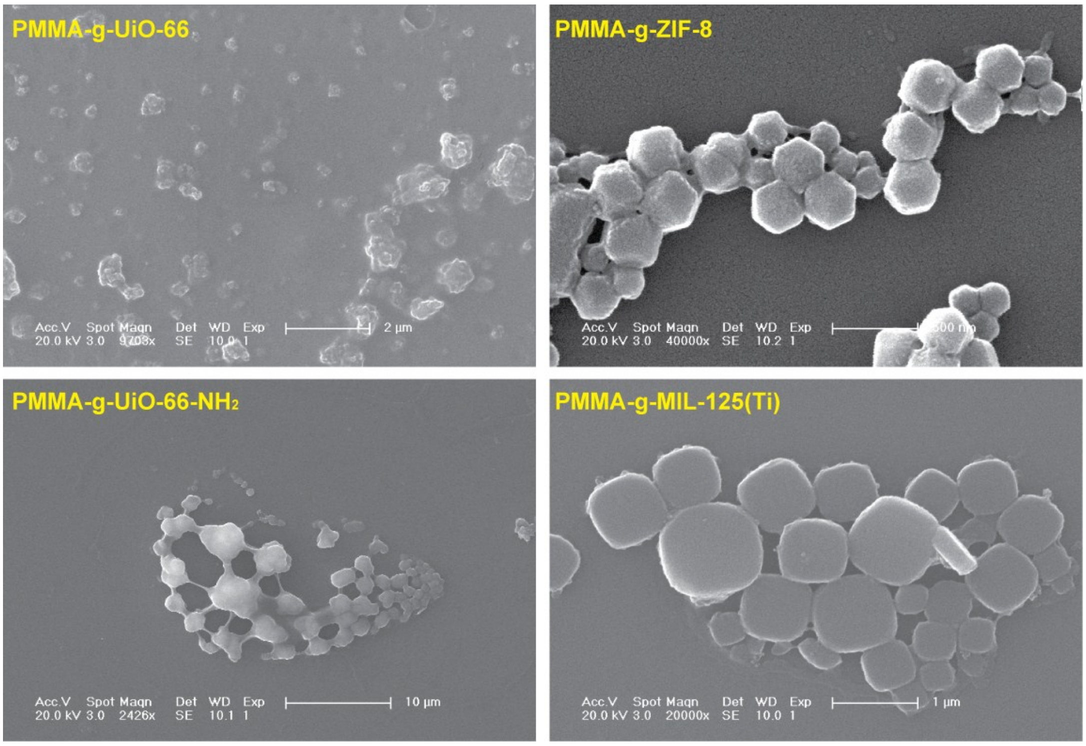

Figure S8. SEM images of PMMA-g-UiO-66, PMMA-g-ZIF-8, PMMA-g-UiO-66-NH_2 and PMMA-g-MIL-125(Ti).

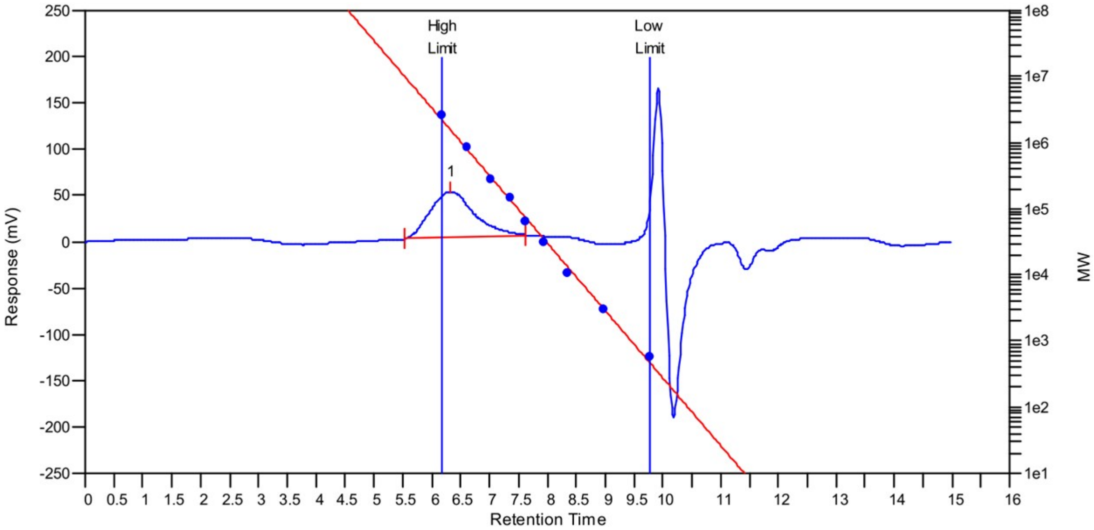

Figure S9. GPC trace for surface-grafted PMMA from digestion of PMMA-UiO-66-NH_2 after a UV-induced photopolymerization of MMA for 5 h.

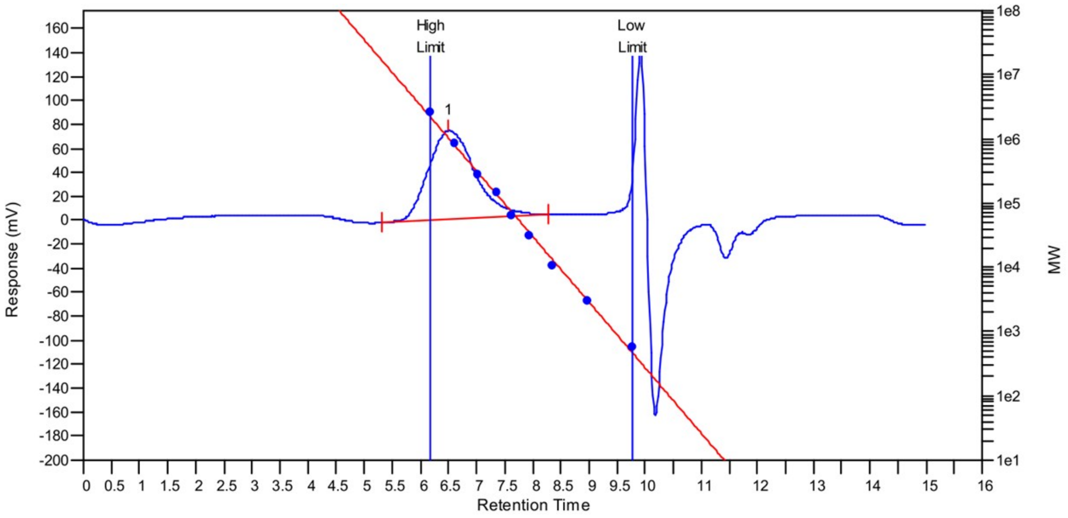

Figure S10. GPC trace for PMMA obtained in bulk solution using UiO-66-NH_2 after a UV-induced photopolymerization of MMA for 5 h.

XPS measurements

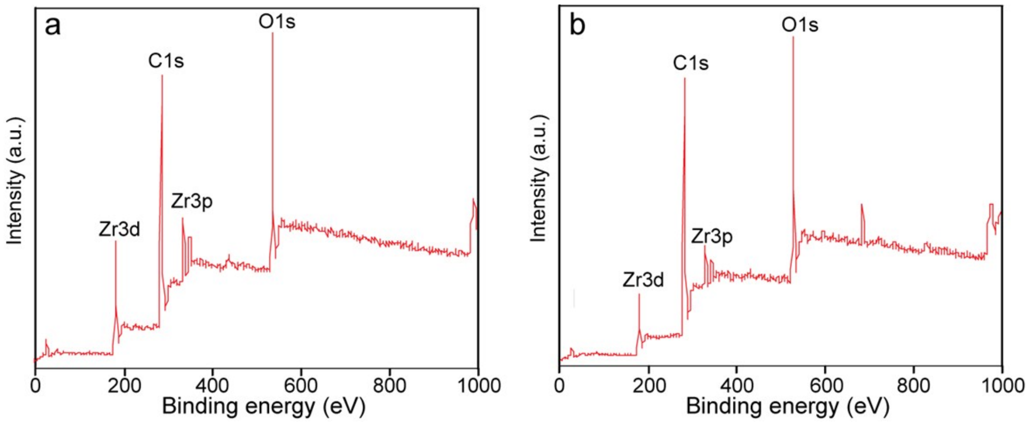

Figure S11. XPS survey scans of UiO-66 (a) and PMMA-g-UiO-66 after UV-induced photopolymerization of MMA for 2h (b).

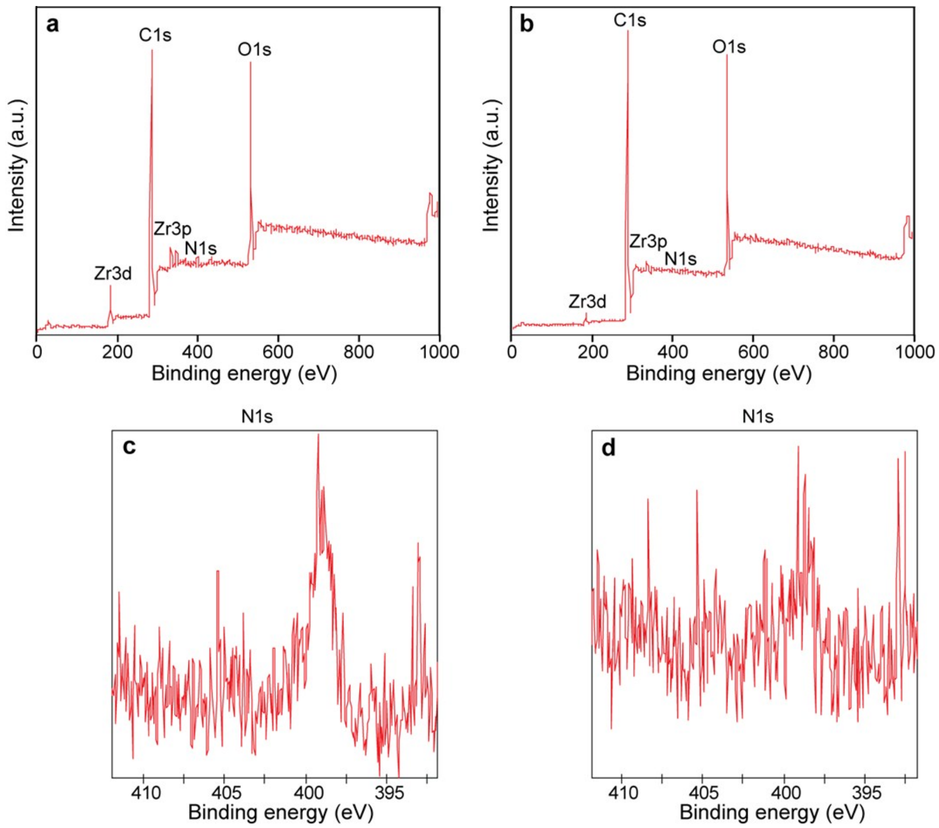

Figure S12. XPS survey scans of UiO-66-NH_2 (a), PMMA-g-UiO-66-NH_2 obtained after photopolymerization of MMA for 2h (b), high-resolution N1s XPS spectra of UiO-66-NH_2 (c), PMMA-g-UiO-66-NH_2 obtained after photopolymerization of MMA for 2h (d). Signal at 399 eV is assigned to the primary amine from UiO-66-NH_2. After photografting polymerization of MMA for 2 hour, the signal from the primary amine decreases significantly and a weak and new signal arises at 401 eV assignable to the secondary amine obtained after the abstraction reaction from the amine group of UiO-66.

TGA measurements

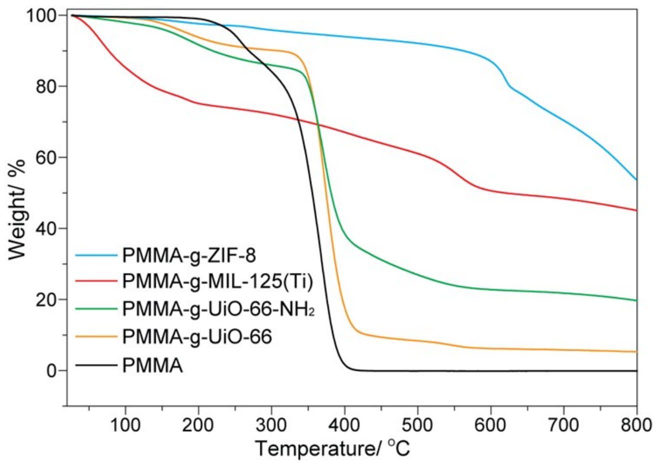

Figure S13. TGA analysis of PMMA, PMMA-g-UiO-66, PMMA-g-UiO-66-NH_2, PMMA-g-MIL-125(Ti) and PMMA-g-ZIF-8 in air at a heating rate of 10 °C min^{-1}.

Polymer brushes on UiO-66-NH_2 films via UV-induced photopolymerization. UiO-66-NH_2 films coated substrates were submerged in approximately 1mL of freshly distilled MMA in a glass vial. The monomer solution was degassed thoroughly and placed in the photochemical reactor at room temperature. After the photopolymerization, the substrate was cleaned by ultrasonication in toluene, ethyl acetate and ethanol to remove unreacted monomers and physisorbed polymers.

References

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