Supporting Information for

Seaming the Interfaces between Topologically Distinct Metal-Organic Frameworks Using Random Copolymer Glues

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Materials and Characterization Methods

Chemicals and Materials

All reagents were obtained through commercial sources without further purification unless specified. All monomers were passed through basic alumina columns to remove inhibitors before polymerization. Azobisisobutyronitrile (AIBN) was recrystallized from ethyl alcohol. Deionized water was used for all solution preparations. Hydrogen (Airgas, 99.999%) was used for heterogeneous catalysis.

Instrumentation

^{1}H NMR spectra were obtained on a Bruker AVANCE III HD (400 MHz or 500 MHz) at room temperature. Gel permeation chromatography (GPC) experiment was carried out on a Malvern GPC TDA305 with D6000M general mixed org columns and calibrated using PS standards. Powder X-ray diffraction (PXRD) patterns were collected on an X-ray diffractometer (Bruker D2 PHASER or D8 ADVANCE). Thermogravimetric analysis (TGA) was performed on a PerkinElmer TGA 8000. Infrared spectroscopy was collected on a PerkinElmer Frontier FT-IR. High-resolution scanning electron microscope (HRSEM) images were obtained using a JSM-7800F Prime Scanning Electron Microscopy. Samples were coated with Au for 10 seconds using an SBC-12 sputter coater. Transmission electron microscope (TEM) images were taken on a JEM 2100 plus (200 kV) or JEM 1400 plus (120KV). Samples were first diluted 10 times using methanol. Then, a 2.0 µl solution droplet was added onto a carbon-coated copper grid. Gas chromatography (GC) was performed on an Agilent Technologies 7890B GC system.

Experimental Details

■ Synthesis of Polymers

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 2h 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 Na_2SO_4. After filtration to remove the Na_2SO_4, 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, $CDCl_3$) δ = 3.34 (t, 2H, $-CH_2CH_2-S-$), 1.87 (s, 6H, $(CH_3)_2C(CN)-$), 1.70 (m, 2H, $-CH_2CH_2-S-$), 1.40 (m, 2H, $CH_3CH_2CH_2-$), 1.26 (br s, 16H, $-CH_2(CH_2)6CH_2-$) and 0.88 (t, 3H, CH_3CH_2-).

Synthesis of P1 (PAA). P1 was synthesized through RAFT polymerization. Typically, tert-butyl acrylate (tBA, 7 mmol), AIBN (3.7mg, 0.022mmol) and CPDTC (31 mg, 0.090mmol) were dissolved in 800uL of dimethyl formamide (DMF) in an ampoule. After three cycles of freeze-pump-thaw, the reaction mixture was sealed and then heated at 65 °C for 12 h. PtBA was obtained by multiple cycles of solvent precipitation in acetone/H_2O and then dried under vacuum overnight. GPC (PS calibration): PDI = 1.10, PtBA were then treated with trifluoroacetic acid (TFA) for 2 h to remove t-butyl groups and PAA were obtained by multiple cycles of solvent precipitation in methanol and dried under vacuum overnight.

Synthesis of P2 (P(MMA-co-MAA)). Methyl methacrylate (MMA, 3mmol), tert-butyl methacrylate (tBMA, 3mmol), AIBN (3.0mg, 0.018mmol) and CPDTC (25 mg, 0.073mmol) were dissolved in 750uL of dimethyl formamide (DMF) in an ampoule. After three cycles of freeze-pump-thaw, the reaction mixture was sealed and then heated at 65 °C for 12 h. P(MMA-co-tBMA) was obtained by multiple cycles of solvent precipitation in acetone/H_2O and then dried under vacuum overnight. GPC (PS calibration): PDI = 1.06, P(MMA-co-tBMA) were then treated with trifluoroacetic acid (TFA) for 2 h to remove *t*-butyl groups and P(MMA-co-MAA) were obtained by multiple cycles of solvent precipitation in methanol and dried under vacuum overnight.

Synthesis of P3 (P(MMA-co-4VP)). Methyl methacrylate (MMA, 2mmol), 4-vinyl pyridine (4VP, 4mmol), AIBN (2.5mg, 0.015mmol) and CPDTC (21.4 mg, 0.062mmol) were dissolved in 600uL of dimethyl formamide (DMF) in an ampoule. After three cycles of freeze-pump-thaw, the reaction mixture was sealed and then heated at 65 °C for 12 h. P(MMA-co-4VP) was obtained by multiple cycles of solvent precipitation in acetone/H_2O and then dried under vacuum overnight. GPC (PS calibration): PDI = 1.04.

Synthesis of P4 (P(MAA-co-4VP)). Tert-butyl methacrylate (tBMA, 1.5mmol), 4-vinyl pyridine (4VP, 4.5mmol), AIBN (2.8mg, 0.017mmol) and CPDTC (23.8 mg, 0.069mmol) were dissolved in 750uL of dimethyl formamide (DMF) in an ampoule. After three cycles of freeze-pump-thaw, the reaction mixture was sealed and then heated at 65 °C for 12 h. P(tBMA-co-4VP) was obtained by multiple cycles of solvent precipitation in acetone/H_2O and then dried under vacuum overnight. GPC (PS calibration): PDI = 1.05. P(tBMA-co-4VP) were then treated with trifluoroacetic acid (TFA) for 2 h to remove t-butyl groups and P(MAA-co-4VP) were obtained by multiple cycles of solvent precipitation in methanol and dried under vacuum overnight.

Synthesis of P5 (P(MMA-co-MAA-co-4VP)). Methyl methacrylate (MMA, 1mmol), tert-butyl methacrylate (tBMA, 2mmol), 4-vinyl pyridine (4VP, 6mmol), AIBN (3.3mg, 0.020mmol) and CPDTC (27.5 mg, 0.080mmol) were dissolved in 800uL of dimethyl formamide (DMF) in an ampoule. After three cycles of freeze-pump-thaw, the reaction mixture was sealed and then heated at 65 °C for 12 h. P(MMA-co-tBMA-co-4VP) was obtained by multiple cycles of solvent precipitation in acetone/H_2O and then dried under vacuum overnight. GPC (PS calibration): PDI = 1.06, P(MMA-co-tBMA-co-4VP) were then treated with trifluoroacetic acid (TFA) for 2 h to remove t-butyl groups and P(MMA-co-MAA-co-4VP) were obtained by multiple cycles of solvent precipitation in methanol and dried under vacuum overnight.

Synthesis of P6 (P4VP). Typically, 4-vinyl pyridine (4VP, 8mmol), AIBN (3.5mg, 0.021mmol) and CPDTC (29.0 mg, 0.084mmol) were dissolved in 800uL of dimethyl formamide (DMF) in an ampoule. After three cycles of freeze-pump-thaw, the reaction mixture was sealed and then heated at 65 °C for 12 h. P4VP was obtained by multiple cycles of solvent precipitation in acetone/H_2O and then dried under vacuum overnight. GPC (PS calibration): PDI = 1.23.

■ Synthesis of MOFs and MOF@ZIF-8

Synthesis of UiO-66. $ZrCl_4$ (58.26 mg, 25mM) and 1-4-benzendicarboxylic acid (H_2BDC 41.53mg, 25mM) were dissolved in 10 ml DMF followed by addition of 1.37mL acetic acid. Then the vial was capped and placed in a 120 °C oven for 12 hours. After cooling, the solid was collected by centrifugation, washed with DMF (2 times) and methanol (3 times) and kept in methanol.

Synthesis of MIL-101(Cr). $Cr(NO_3)_3 \cdot 9H_2O$ (1.0 g, 2.5mmol), H_2BDC (0.415 g, 2.5mmol) and deionized water (10 mL) were mixed in a Teflon-lined autoclave and kept in a 200 °C oven for 16 h. The solid was collected by centrifugation, washed with DMF (2 times) and soaked in DMF overnight at 50 °C to remove excess H_2BDC. The large-grained impurities were removed by centrifugation at 1000 rpm for 30 s and suspended MIL-101(Cr) particles was collected by centrifugation. The solid was washed with DMF (2 times) and methanol (3 times) and kept in methanol.[2]

Synthesis of MIL-53(Cr). $Cr(NO_3)_3 \cdot 9H_2O$ (0.8 g, 2mmol), H_2BDC (0.332 g, 2mmol), HF (34.8uL, 2mmol) and deionized water (10 mL, 280mmol) were mixed in a Teflon-lined autoclave and kept in a 220 °C oven for 3 days. The solid was collected by centrifugation, washed with DMF (2 times) and methanol (3 times) and kept in methanol.

Synthesis of MIL-96(Al). $Al(NO_3)_3 \cdot 9H_2O$ (0.375 g, 1mmol) was dissolved in 6 mL deionized water and benzene-1,3,5-tricarboxylic acid (H_3BTC; 0.21 g, 1mmol) was dissolved in 6 mL DMF, respectively. Then two solutions were mixed in a Teflon-lined autoclave. Then 0.5 mL of acetic acid was added and the autoclave was kept in a 150 °C oven for 2 h. The solid was collected by centrifugation, washed with DMF (2 times) and methanol (3 times) and kept in methanol.[3]

Synthesis of MOF-801(Zr). $ZrCl_4$ (18mmol) and fumaric acid (18mmol) were dissolved in 600 ml DMF containing 41.4 mL acetic acid. Then 1.8 mL triethylamine was added. The vial was capped and placed in a 85 °C oven for 18 hours. After cooling, The solid was collected by centrifugation, washed with DMF (2 times) and methanol (3 times) and kept in methanol.[4]

Synthesis of MOF@ZIF-8. 5mg MOF (UiO-66, MOF-801, MIL-96(Al), MIL-101(Cr), MIL-53(Cr)) was mixed and incubated with 1mL polymer (P1 to P6, 10mg/ mL) solution in methanol for 1 h. The solid was collected by centrifugation, washed with methanol (2 times) and soaked in 100uL methanol. 914 uL 2-methylimidazole (MIM) (576 mM) methanol solution was mixed with above solution and sonicated for 5 minutes. After sonication, 914 uL $Zn(NO_3)_2 \cdot 6H_2O$ (24 mM) methanol solution was added. The solution was then sonicated for another 5 minutes and then stirred for 12 hours at room temperature. The solid was then collected, washed with methanol 3 times, and re-dispersed in methanol.

■ Synthesis of Pt-UiO-66@ZIF-8 and Catalytic study

Synthesis of Pt-UiO-66. A 10 ml DMF solution containing $ZrCl_4$ (25mM), 1-4-benzendicarboxylic acid (H_2BDC, 25mM), and 1.37mL acetic acid was prepared. Then 2 mg Pt-nanoparticles (1mg/mL in DMF) was added into the solution. The vial was capped and placed in a 120 °C oven for 12 hours. After cooling down, Pt-UiO-66 particles were collected by centrifugation, washed with DMF (2 times) and methanol (3 times) and stored in methanol.

Synthesis of Pt-UiO-66@ZIF-8. 5mg Pt-UiO-66 was mixed and incubated with 1mL P4 (10mg/ mL) solution in methanol for 1 h. The solid was collected by centrifugation, washed with methanol (2 times) and soaked in 100uL methanol.Toward a MIM methanol solution (576mM, 914uL) was added 5mg Pt-UiO-66 followed by 5 min sonication. Then, $Zn(NO_3)_2 \cdot 6H_2O$ methanol solution (24mM, 914uL) was added. The reaction was stirred for 12 hours at room temperature, collected, washed by methanol 3 times, and re-dispersed in methanol.

Catalytic study. Pt-UiO-66 and Pt-UiO-66@ZIF-8 (containing 2mg Pt-nanoparticles) were re-dispersed in 400uL methanol and toward which added 20uL octene or cyclooctene. The samples were reacted at room temperature under H_2 atmosphere (15 bar). For all reactions, the products were analyzed with GC.

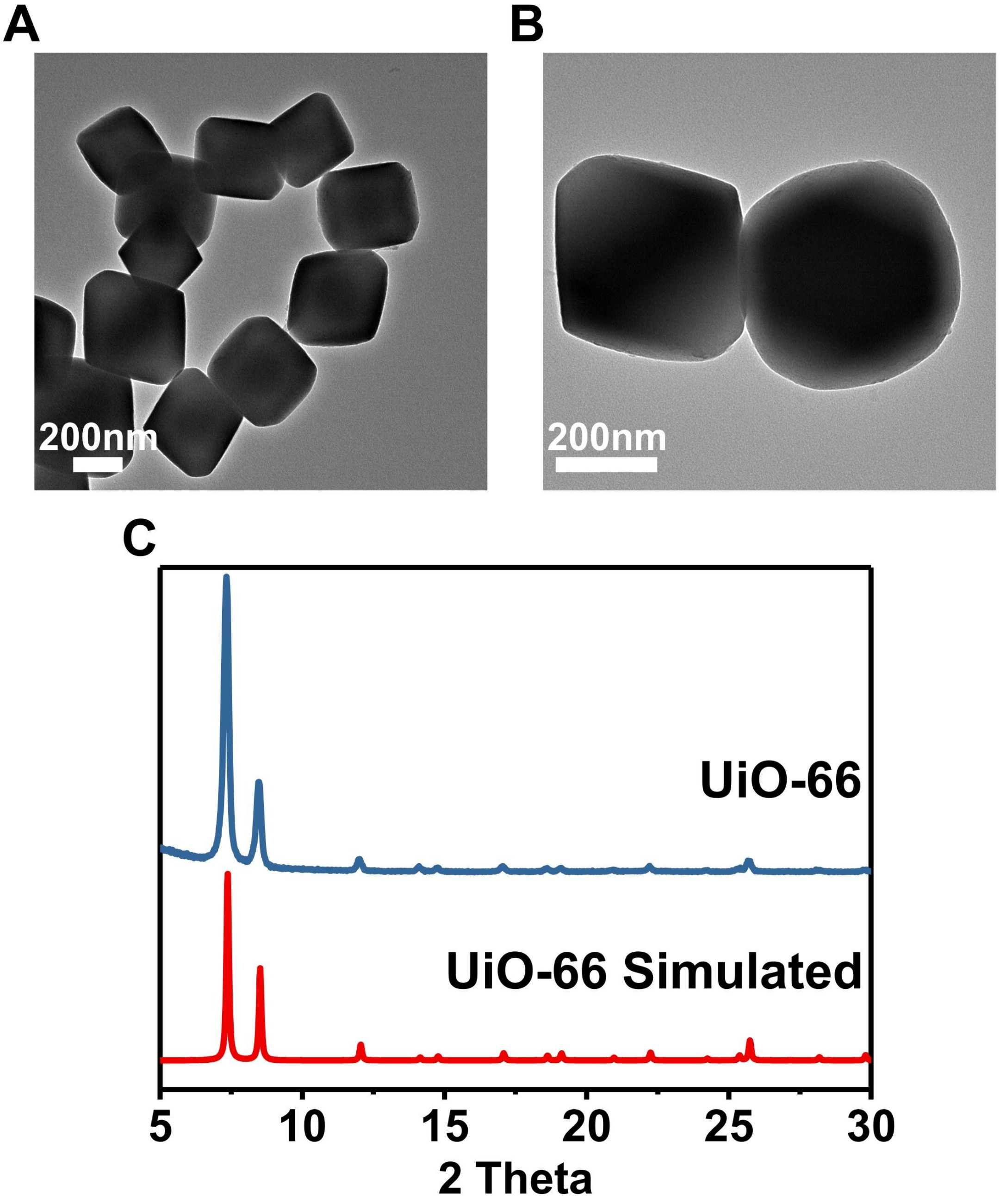

Figure S1. (A-B) TEM images of UiO-66; (C) PXRD of UiO-66.

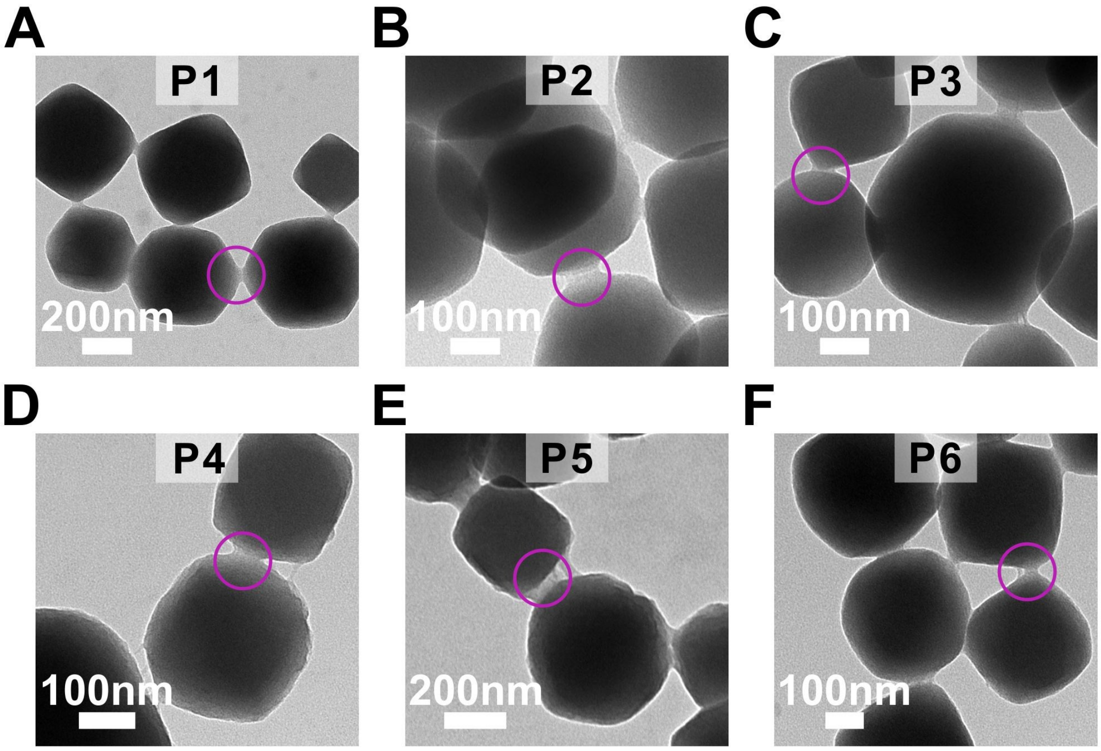

Figure S2. TEM images of UiO-66@Pn. (A) UiO-66@P1; (B) UiO-66@P2; (C) UiO-66@P3; (D) UiO-66@P4; (E) UiO-66@P5; (F) UiO-66@P6.

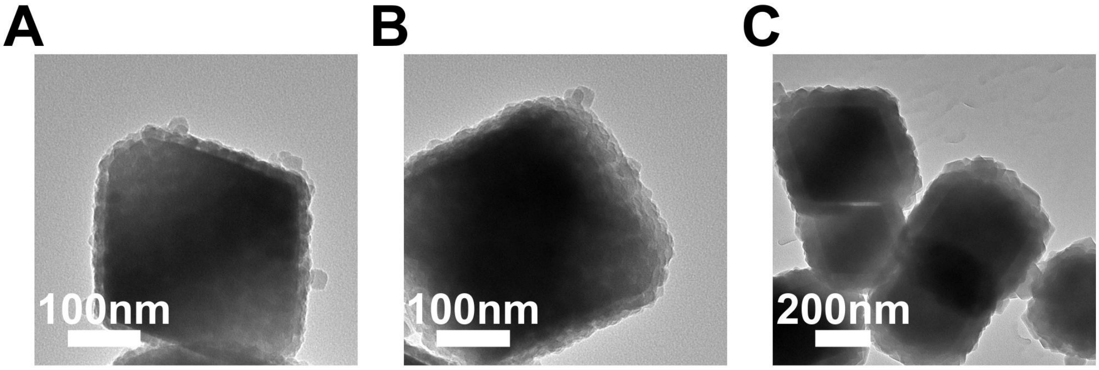

Figure S3. TEM images of UiO-66@ZIF-8 grown with the addition of (A) 1 time; (B) 3 times; and (C) 5 times $Zn(NO_3)_2 \cdot 6H_2O$ and MIM to UiO-66@Pn solution.

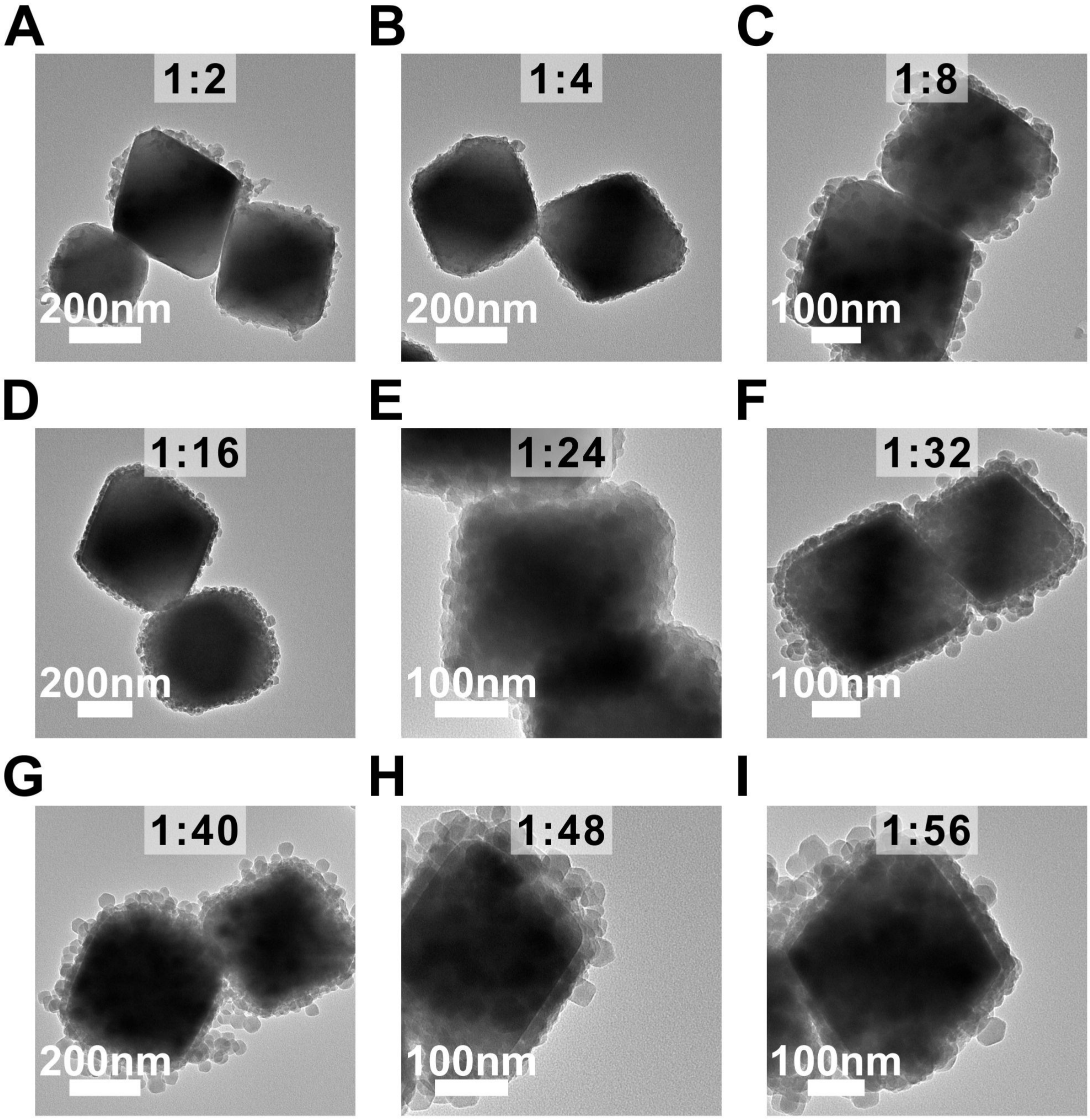

Figure S4. TEM images of UiO-66@ZIF-8 grown with various $Zn(NO_3)_2 \cdot 6H_2O$ and MIM molar ratios.

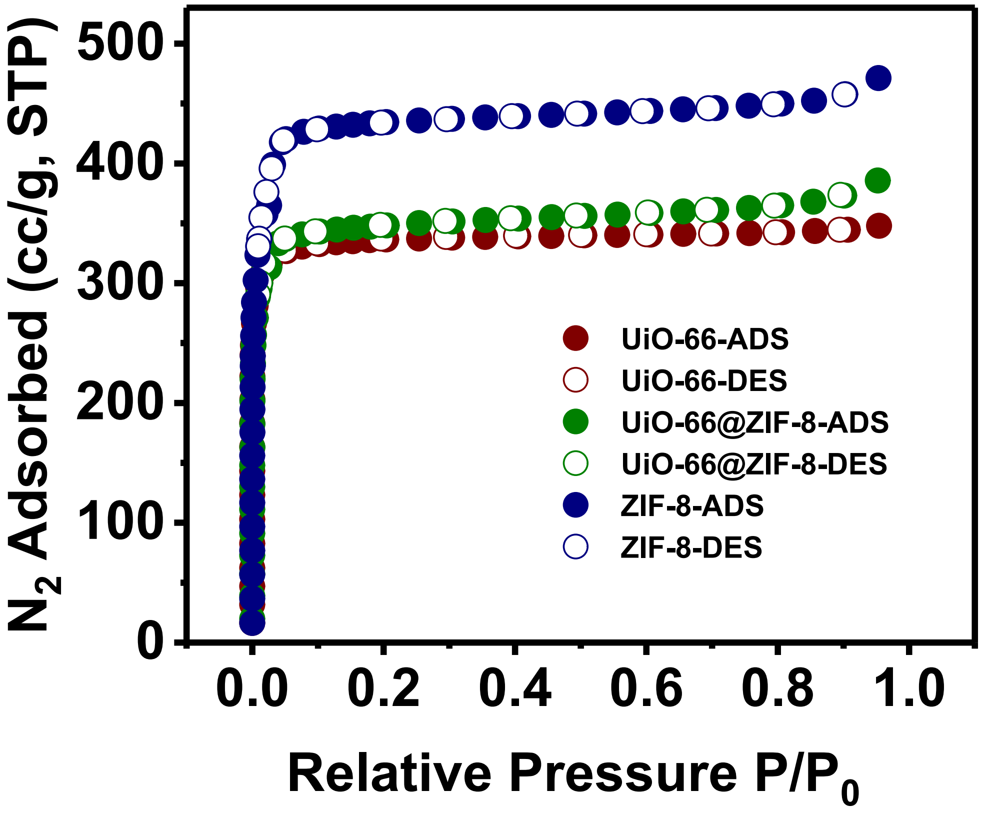

Figure S5. N_2 adsorption-desorption isotherms at 77 K of UiO-66, UiO-66@ZIF-8, ZIF-8.

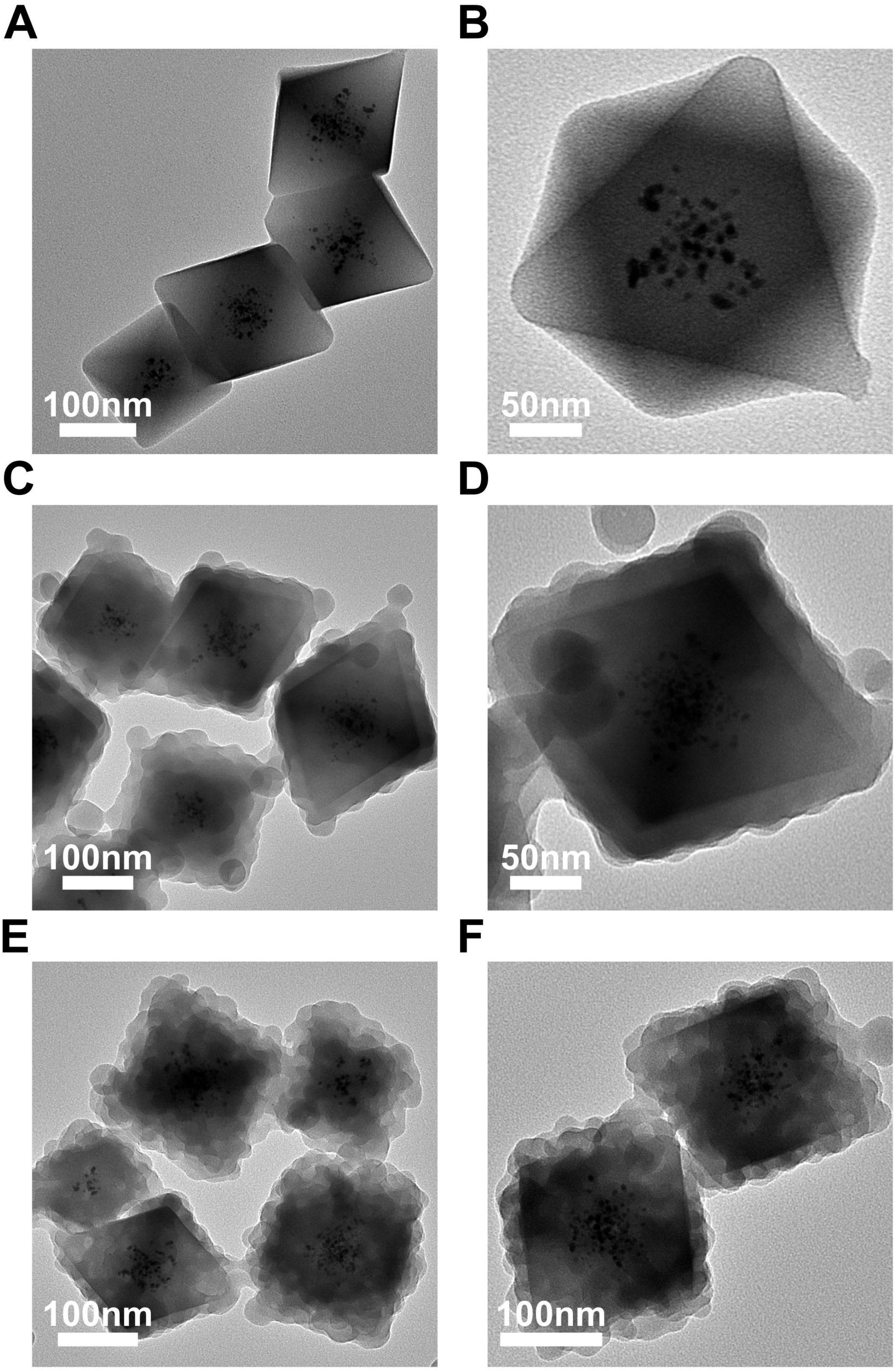

Figure S6. TEM images of (A-B) Pt-UiO-66; (C-D) Pt-UiO-66@ZIF-8; and (E-F) Pt-UiO-66@ZIF-8 after catalyst.

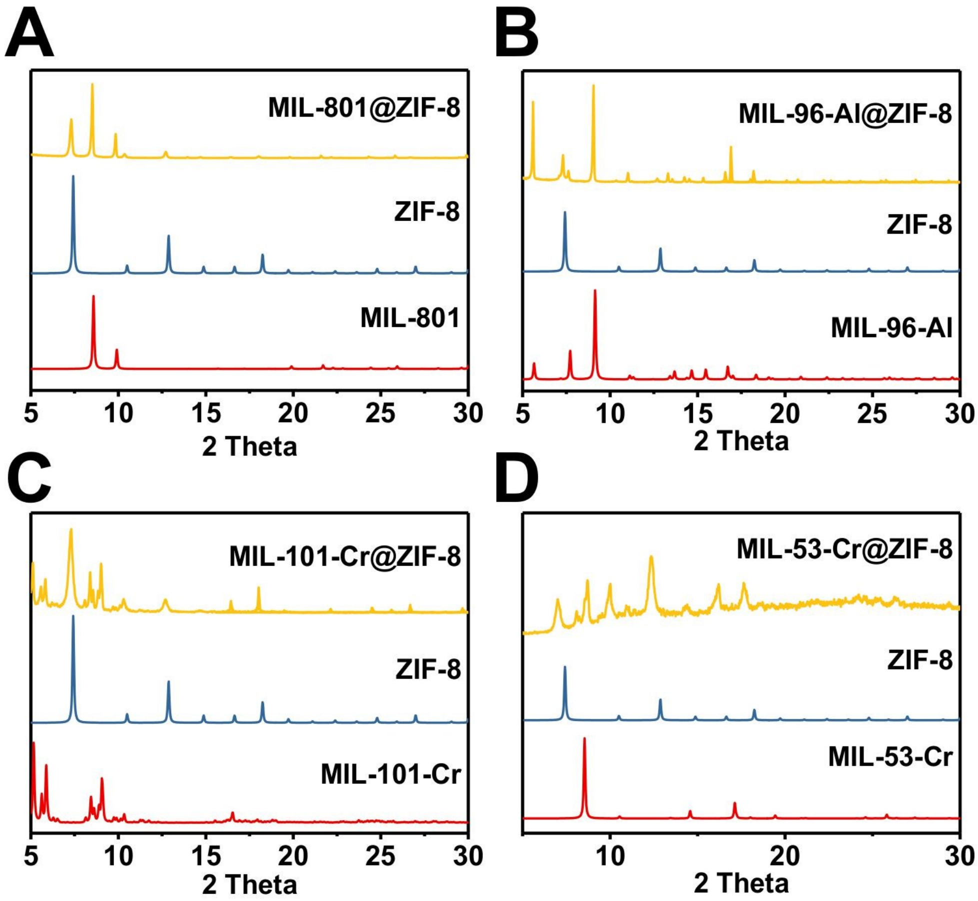

Figure S7. PXRD patterns of (A) MOF-801@ZIF-8; (B) MIL-96(Al)@ZIF-8; (C) MIL-101(Cr)@ZIF-8; (D) MIL-53(Cr)@ZIF-8.

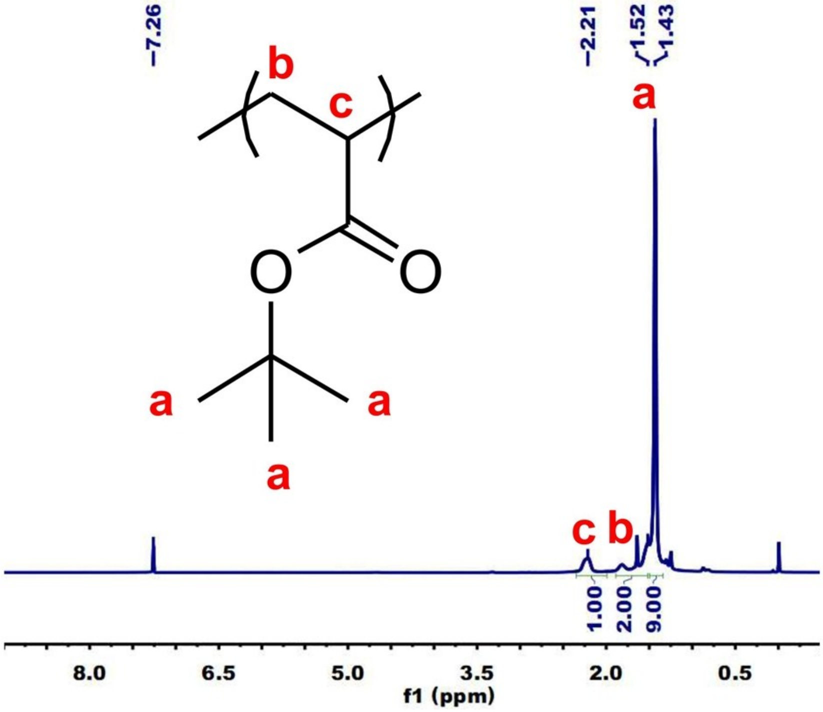

Figure S8. ^{1}H NMR spectrum of **PtBA**.

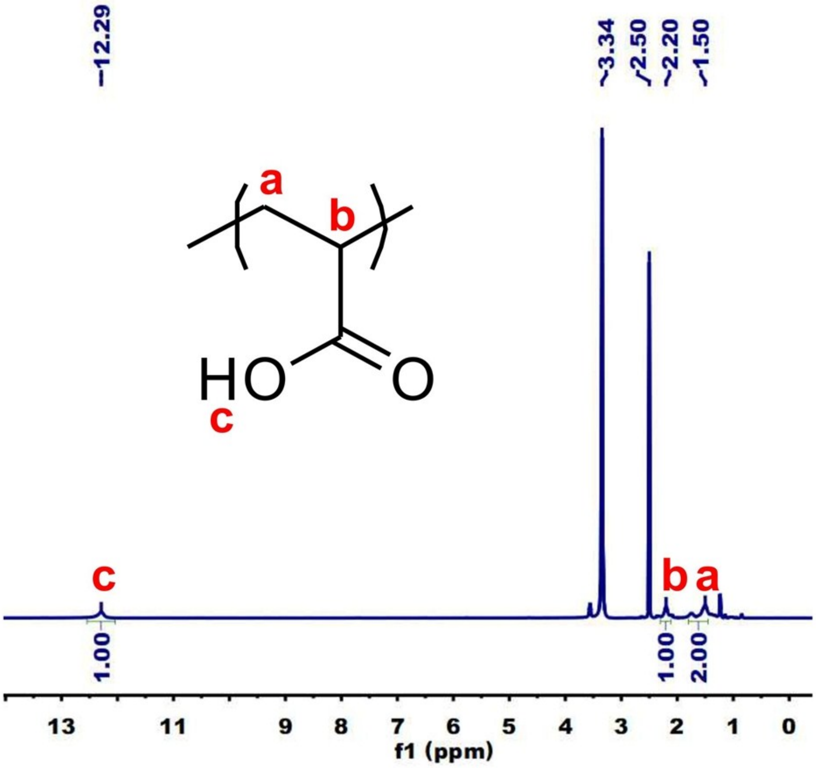

Figure S9. ^{1}H NMR spectrum of **P1**.

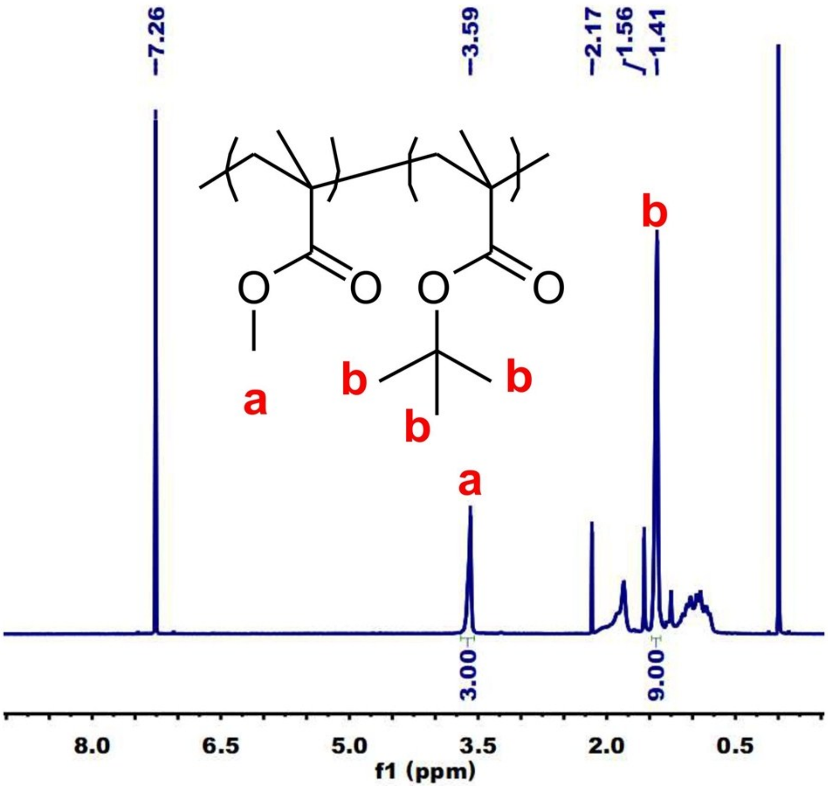

Figure S10. ^{1}H NMR spectrum of **P(MMA-co-tBMA)**.

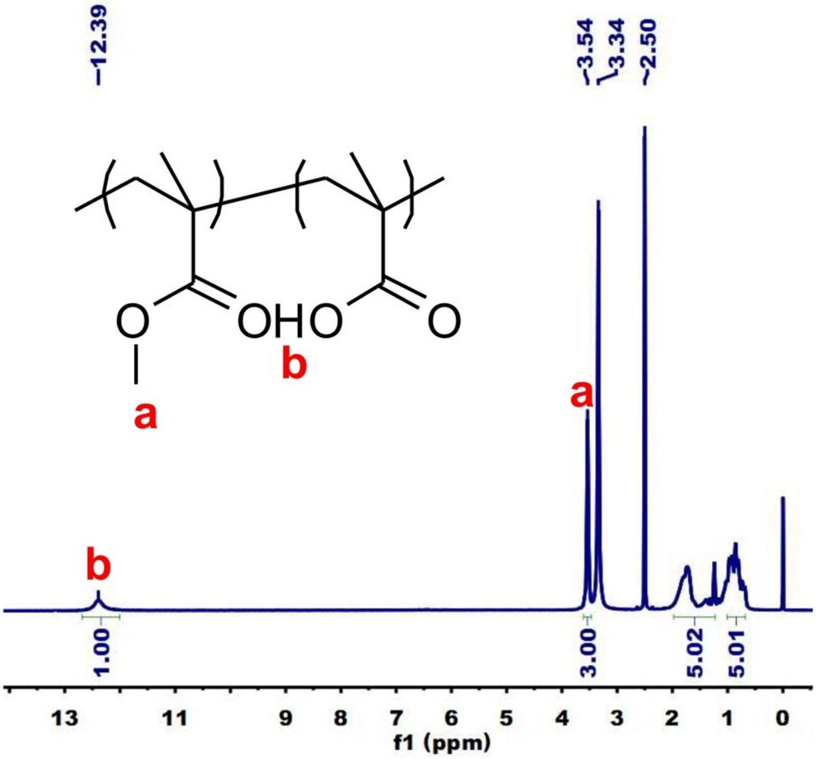

Figure S11. ^{1}H NMR spectrum of **P2**.

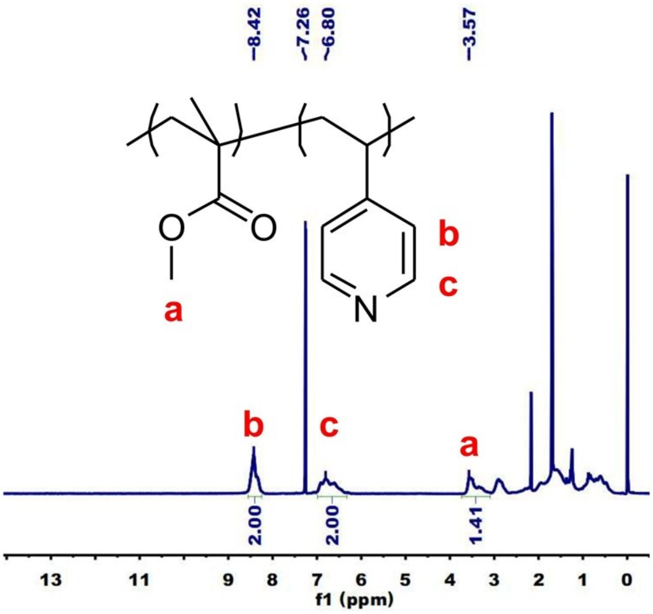

Figure S12. ^{1}H NMR spectrum of **P3**.

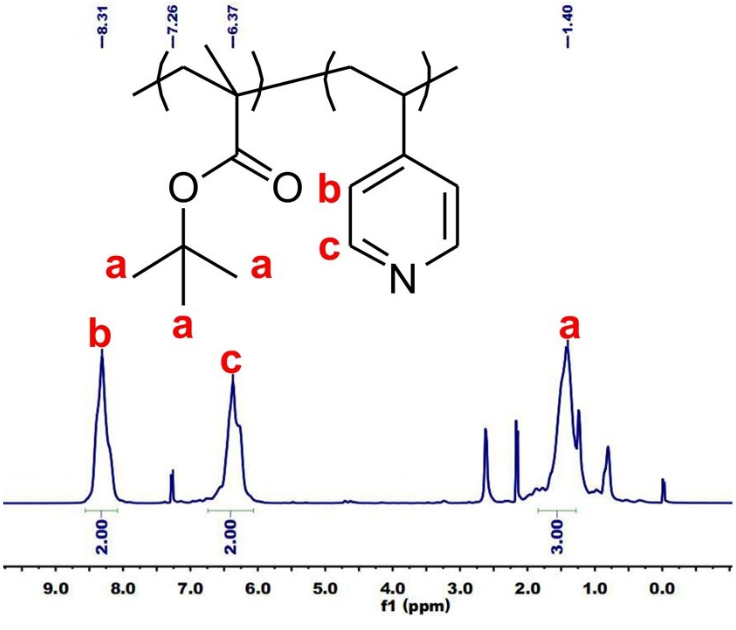

Figure S13. ^{1}H NMR spectrum of **P(tBMA-co-4VP)**.

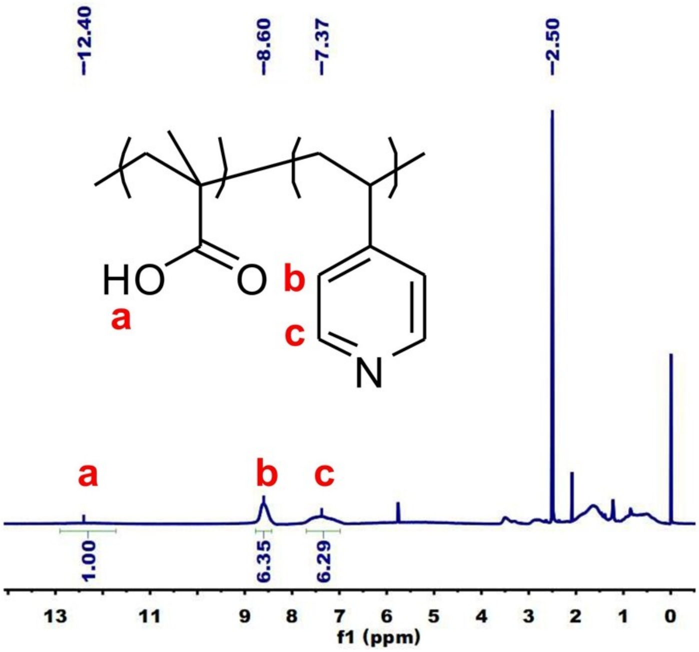

Figure S14. ^{1}H NMR spectrum of **P4**.

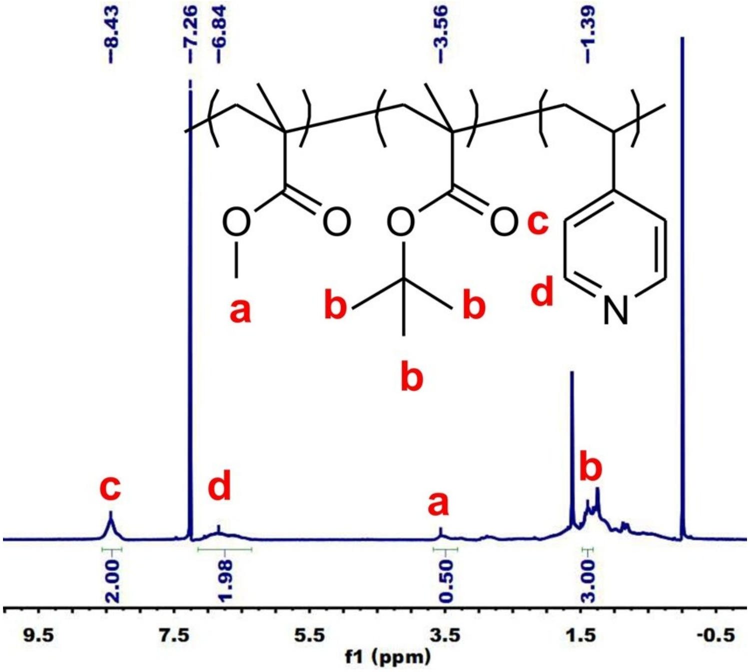

Figure S15. ^{1}H NMR spectrum of **P(MMA-co-tBMA-4VP)**.

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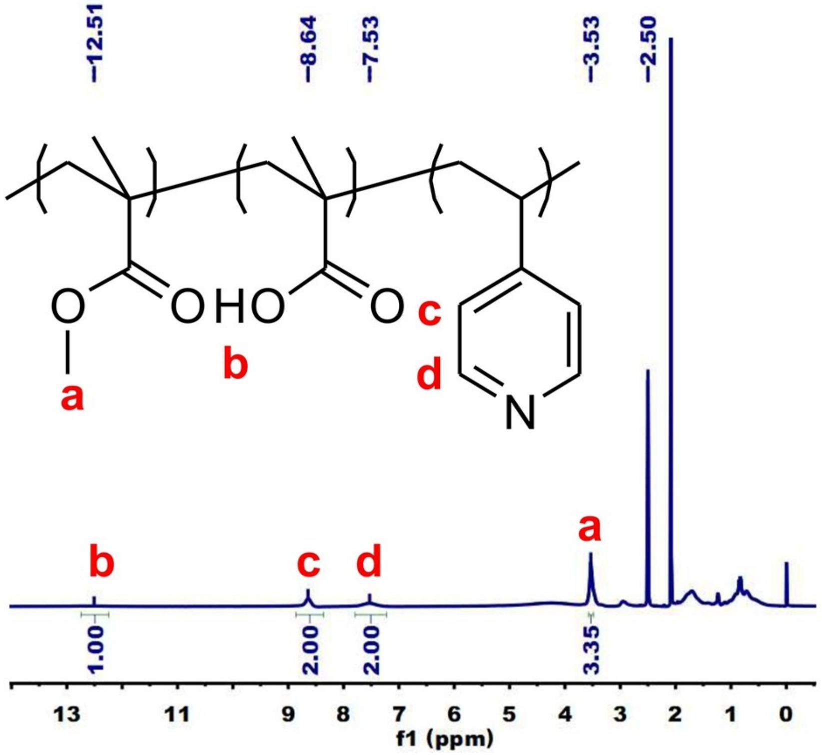

Figure S16. ^{1}H NMR spectrum of **P5**

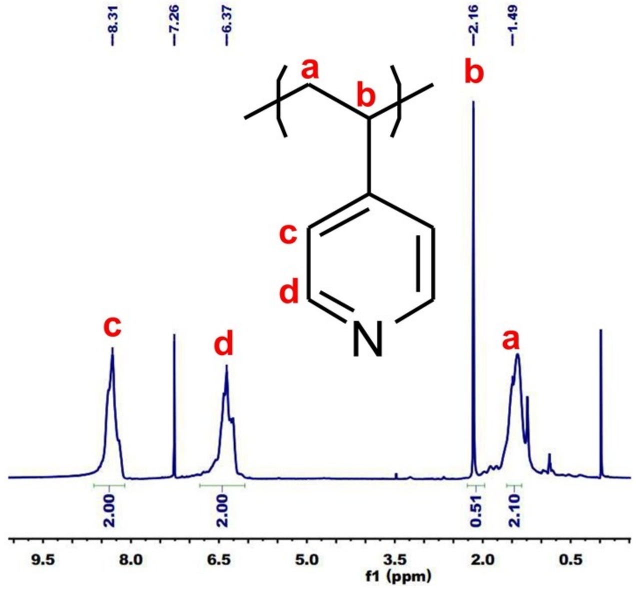

Figure S17. ^{1}H NMR spectrum of **P6**.

Table S1. The dispersity (*Đ*) and number average molecular weight of polymers

Samples	**Monomer ratio**	***Đ***	**M_n (kDa)**	**# of tBA**	**# of MMA**	**# of tBMA**	**# of 4VP**
PtBA	/	1.10	36.8	288			
P(MMA-co-tBMA)	1:1	1.06	30.3		125	125	
P(MMA- 4VP)	1:2	1.04	30.4		97		194
P(tBMA-co-4VP)	1:3	1.05	23.3			50	150
P(MMA-co-tBMA-co-4VP)	1:2:6	1.06	28.6		28	56	168
P4VP	/	1.23	33.2				316
				# of AA	**# of MMA**	**# of MAA**	**# of 4VP**
P1	/		20.7	288			
P2	1:1		23.3		125	125	
P3	1:2		30.4		97		194
P4	1:3		20.4			50	150
P5	1:2:6		25.6		28	56	168

*The molecular weight values for P1-P6 were calculated based on the M_n values before TFA hydrolysis and ^{1}H-NMR data.

Supplementary References

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