Supplementary Information

Polymer@MOF@MOF: "Grafting From" Atom Transfer Radical Polymerization for the Synthesis of Hybrid Porous Solids

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I. Experimental Procedures

Starting reagents. Zinc nitrate hexahydrate (Fisher Scientific, ACS reagent), 1,4-benzenedicarboxylic acid (H_2BDC, Fisher Scientific, 98%), 2-amino-1,4-benzenedicarboxylic acid (H_2ABDC, Sigma Aldrich, 99%), dichloromethane (DCM, Fisher Scientific, >99.9%), xylenes (Sigma-Aldrich, >98.5%, ACS reagent), tetrahydrofuran (Fisher Scientific, HPLC grade), dimethylformamide (DMF, Fisher Scientific, >99.5%), 2-bromoisobutyric anhydride (Sigma Aldrich, 95%), copper bromide (Sigma Aldrich, 98%), 1,4,8,11-tetraaza-1,4,8,11-tetramethylcyclotetradecane (Me_4Cyclam, Sigma Aldrich, >97%), and sodium hydroxide (NaOH, Fisher Scientific, ACS grade) were used as-received without further purification. Diethylformamide (DEF, TCI, >99.0%) was purified by storing over activated carbon for ~1 month and subsequently passed through a column containing silica gel. Methyl methacrylate (MMA, Fisher Scientific, 99%) was purified by passing through a hydroquinone and monomethyl ether hydroquinone removal column (Scientific Polymer Products Inc.).

Zinc nitrate tetrahydrate, $Zn(NO_3)_2$•$4H_2O$. Zinc nitrate tetrahydrate was prepared as previously described.[1]

IRMOF-3@MOF-5. IRMOF-3@MOF-5 was prepared by a method slightly modified from the literature procedure.[2] H_2ABDC (48.0 mg, 0.265 mmol) and H_2BDC (0.100 g, 0.602 mmol) were added to separate 20 mL vials. $Zn(NO_3)_2$•$4H_2O$ (0.500 g, 1.91 mmol) dissolved in 15 mL of DEF was added to the vial containing H_2BDC and $Zn(NO_3)_2$•$4H_2O$ (0.208 g, 0.795 mmol) dissolved in 10 mL of DEF was added to the vial containing H_2ABDC. The two mixtures were sonicated for 15 minutes and heated to 100 °C for 12 hours. Both solutions were decanted and the supernatants were exchanged. The mixtures were heated at 100 °C for another 4 hours. The products were then washed with DEF (4×15 mL over 24 hours) and washed/soaked in CH_2Cl_2 (4×15 mL over 24 hours).

Post-synthetic modification to form initiator carrying linker@MOF-5 (ICL@IRMOF-3@MOF-5). ICL@IRMOF-3@MOF-5 was prepared by a method slightly modified from the literature procedure by Cohen and coworkers[3] 2-Bromoisobutyric anhydride (2-BIBA) (71.2 mg, 0.225 mmol) was added to a 20 mL septum-capped vial in a glovebox. The 2-BIBA was taken out of the glovebox and dissolved in 15 mL of degassed DCM. IRMOF-3@MOF-5 crystals, in CH_2Cl_2, were transferred to a separate 20 mL septum capped vial, the CH_2Cl_2 solution was decanted from the crystals and the vial was capped and purged with nitrogen. The solution of DCM and 2-BIBA was then injected into the vial containing IRMOF-3@MOF-5 using a 25 mL degassed syringe. The mixture was allowed to shake at room temperature for 72 h and subsequently washed thoroughly with DCM 4×15 mL over 24 hours. The sample was then activated and the product was weighed yielding ~40.3 mg of ICL@IRMOF-3@MOF-5.

Atom transfer radical polymerization to generate PMMA@IRMOF-3@MOF-5. ATRP of methyl methacrylate (MMA) at ICL@IRMOF-3@MOF-5 was carried out under air-free conditions. In an N_2 filled glovebox, ICL@IRMOF-3@MOF-5 (20.0 mg) was weighed into a 20 mL septum-capped vial (vial 1). 1,4,8,11-Tetraaza-1,4,8,11-tetramethylcyclotetradecane (Me_4Cyclam) (15.0 mg, 0.0585 mmol) and CuBr (1.20 mg, 0.00836 mmol) were weighed out into another 20 mL septum-capped vial (vial 2). Xylenes (4 mL) were added to vial 2 and the solution was sonicated and heated gently for 20 minutes. The catalyst solution (vial 2) was added to vial 1 using a cannula. After the reaction mixture was stirred for 10 minutes, methyl methacrylate (2 mL) was introduced via a degassed syringe and the reaction mixture was heated slowly to 65 °C, then shaken for one hour. The reaction mixture was cooled and the crystals were washed thoroughly with xylenes (4×15 mL over 24 hours), THF (4×15 mL over 24 hours), and then washed in DCM (4×15 mL over 24 hours) prior to activation. The product was weighed and yielded ~30.8 mg of PMMA@IRMOF-3@MOF-5.

Activation. Samples were activated by exposure to a dynamic vacuum (10^{-2} Torr) for 24 hours.

Powder X-ray diffraction. Powder X-ray diffraction (PXRD) patterns were collected using a Rigaku R-axis Spider diffractometer with an image plate detector and graphite monochromated Cu-Kα radiation (1.5406 Å). The patterns were collected with the tube operating at 40 kV and 44 mA. Images were collected in transmission mode with χ set at 45°, ϕ rotating at 10°/min, and ω oscillating between 5° and 50° to minimize the effects of preferred orientation. Integration of the resulting images was performed in the AreaMax (2.0) software package with a step size of 0.1 in 2θ.

Gas sorption measurements. Sorption experiments were carried out using a NOVA *e*-series 4200 surface area analyser (Quantachrome Instruments, Boynton Beach, Florida, USA). N_2 (99.999%) was purchased from Cryogenic Gases and used as received. For N_2 measurements, a glass sample cell was charged with ~20 mg sample and analysed at 77 K. Sorption isotherms were collected in the NOVAwin software.

Thermogravimetric Analysis. A TA Instruments Q50 TGA was used to obtain thermogravimetric data in which the analyte was heated from 25 °C to 600 °C at a rate of 10 °C/min and analysed in a platinum pan under flowing nitrogen.

Gel Permeation Chromatography. GPC of PMMA@IRMOF-3@MOF-5 was performed after a basic digestion using 1M NaOH and isolation of the polymer by a CH_2Cl_2 extraction. The isolated polymer samples were dissolved in THF. The GPC analysis was performed on a Shimadzu GPC containing three columns in series with a refractive index detector and a diode array UV-Vis detector. The GPC was calibrated with narrow polydispersity polystyrene standards and the molecular weights are reported as polystyrene equivalents based on UV-Vis detection.

Raman Spectroscopy. For Raman mapping of PMMA@IRMOF-3@MOF-5, a single crystal was cleaved mechanically to expose the internal cross-section; the same procedure was followed for the Raman mapping of IRMOF-3@MOF-5. Raman spectra were obtained using a Renishaw inVia Raman microscope equipped with a RenCan CCD detector, 532 nm laser, 1800 lines/mm grating, and 50 μm slit was used for collecting data. Spectra were collected using the mapping setting in which a region of the cross-section (interior to exterior) was selected for analysis. The spectra were collected using a static scan mode in the range of 950-1475 cm^{-1} for IRMOF-3@MOF-5 and 700-1200 cm^{-1} for PMMA@IRMOF-3@MOF-5 and then analysed using the Wire 3.4 software package. Calibration of the instrument was performed using a silicon standard for all experiments.

II. Powder X-ray Diffraction (PXRD) of MOF-5, IRMOF-3@MOF-5, ICL@IRMOF-3@MOF-5 and PMMA@IRMOF-3@MOF-5

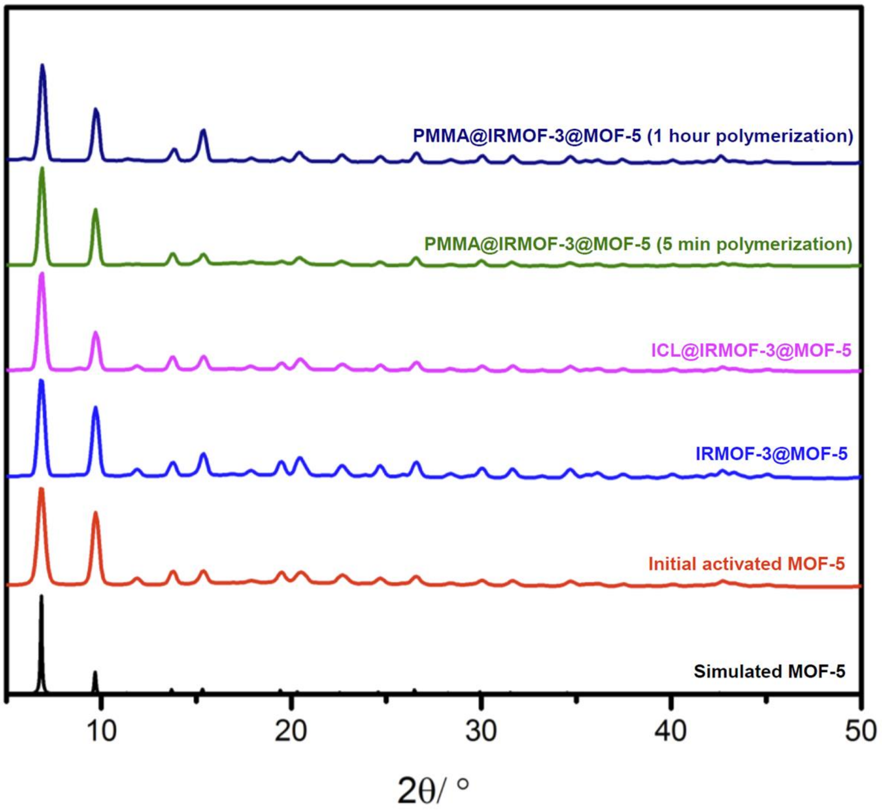

Figure S1: Powder X-ray diffraction (PXRD) patterns comparing the simulated MOF-5 pattern (black) to the diffractograms of as-synthesized MOF-5 (red), IRMOF-3@MOF-5 (light blue), ICL@IRMOF-3@MOF-5 (pink), PMMA@IRMOF-3@MOF-5 after 5 minutes of polymerization at 65 °C (green), and PMMA@IRMOF-3@MOF-5 after 1 hour of polymerization at 65 °C (dark blue).

III. Consistency criteria for applying the BET method to the N_2 sorption isotherms[4] of MOF-5, ICL@IRMOF-3@MOF-5, and PMMA@IRMOF-3@MOF-5 (5 minutes and 1 hour)

Initial activated MOF-5

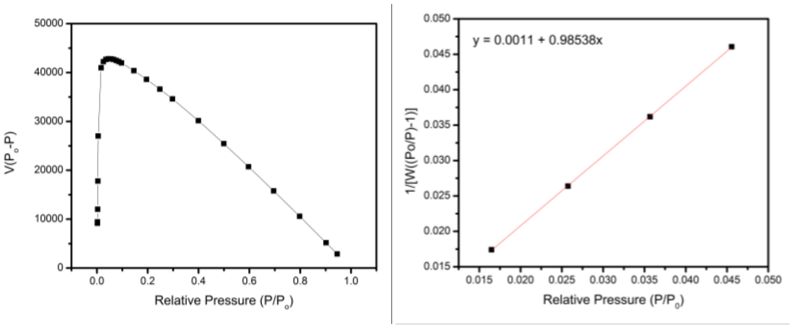

Figure S2: (left) Consistency criterion plot for determining the P/P_o range for BET analysis and (right) BET plot used to calculate the surface area of MOF-5 (3530 m^2g^{-1})

ICL@IRMOF-3@MOF-5

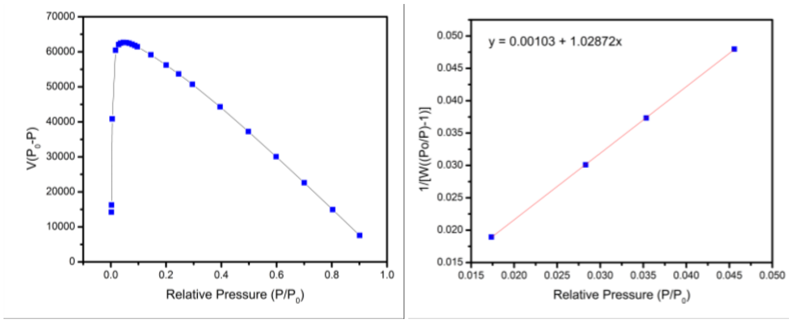

Figure S3: (left) Consistency criterion plot for determining the P/P_o range for BET analysis and (right) BET plot used to calculate the surface area of ICL@IRMOF-3@MOF-5 (3381 m^2g^{-1})

PMMA@IRMOF-3@MOF-5 (5 minutes)

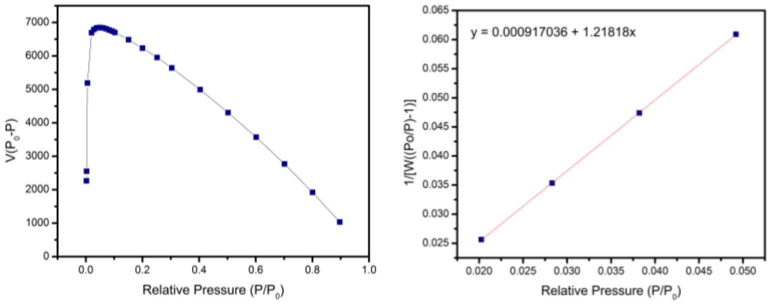

Figure S4: (left) Consistency criterion plot for determining the P/P$_o$ range for BET analysis and (right) BET plot used to calculate the surface area of PMMA@IRMOF-3@MOF-5 (5 minutes polymerization) (2857 m^{2}g^{-1})

PMMA@IRMOF-3@MOF-5 (1 hour)

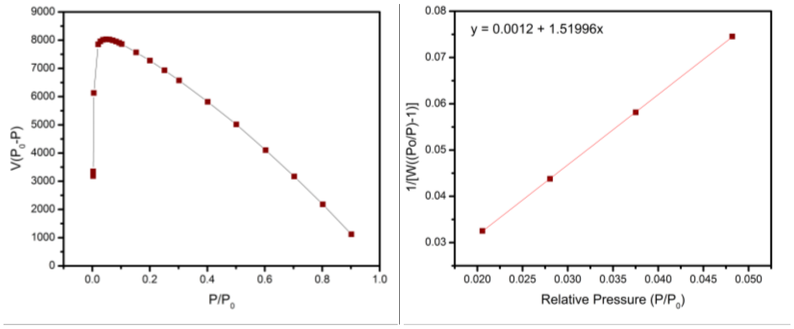

Figure S5: (left) Consistency criterion plot for determining the P/P$_o$ range for BET analysis and (right) BET plot used to calculate the surface area of PMMA@IRMOF-3@MOF-5 (1 hour polymerization) (2289 m^{2}g^{-1})

IV. TGA of ICL@IRMOF-3@MOF-5 and PMMA@IRMOF-3@MOF-5

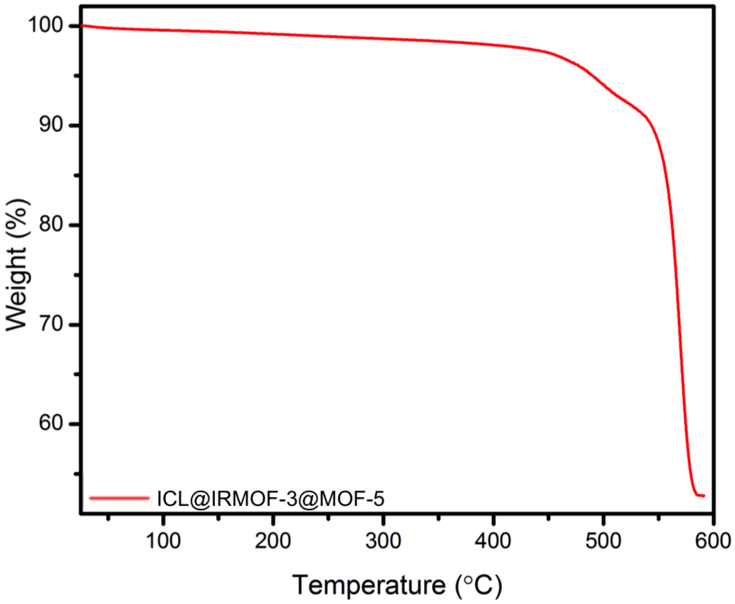

Figure S6: Thermogravimetric Analysis (TGA) of ICL@IRMOF-3@MOF-5 using a ramp rate of 10 °C/min.

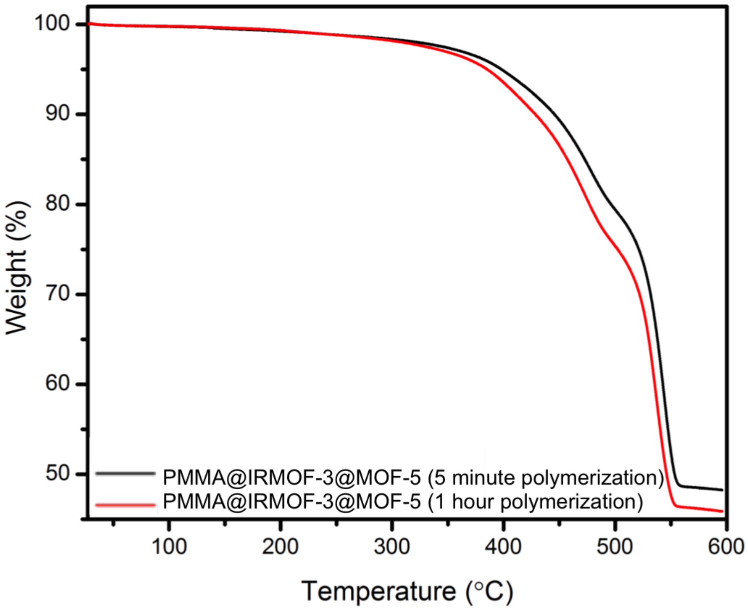

Figure S7: TGA of PMMA@IRMOF-3@MOF-5 after 5 minutes (black) and 1 hour (red) polymerization using a ramp rate of 10 °C/min.

V. Gel Permeation Chromatography (GPC) of Extracted PMMA from PMMA@IRMOF-3@MOF-5

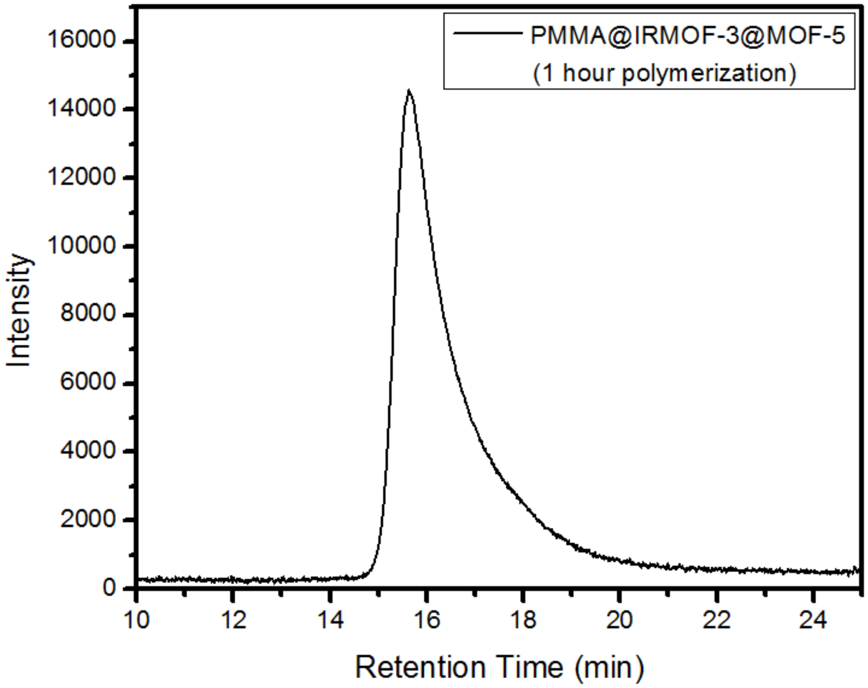

Figure S8: Example GPC of PMMA extracted from digested PMMA@IRMOF-3@MOF-5 after a 1 hour polymerization. The molecular weight of the resulting polymer was determined to have an Mn of 615 kDa with a polydispersity of 1.44. The molecular weight was determined at 218 nm from the UV-Vis detector with integration limits from 14.549 to 19.851 minutes.

VI. Raman Mapping of IRMOF-3@MOF-5

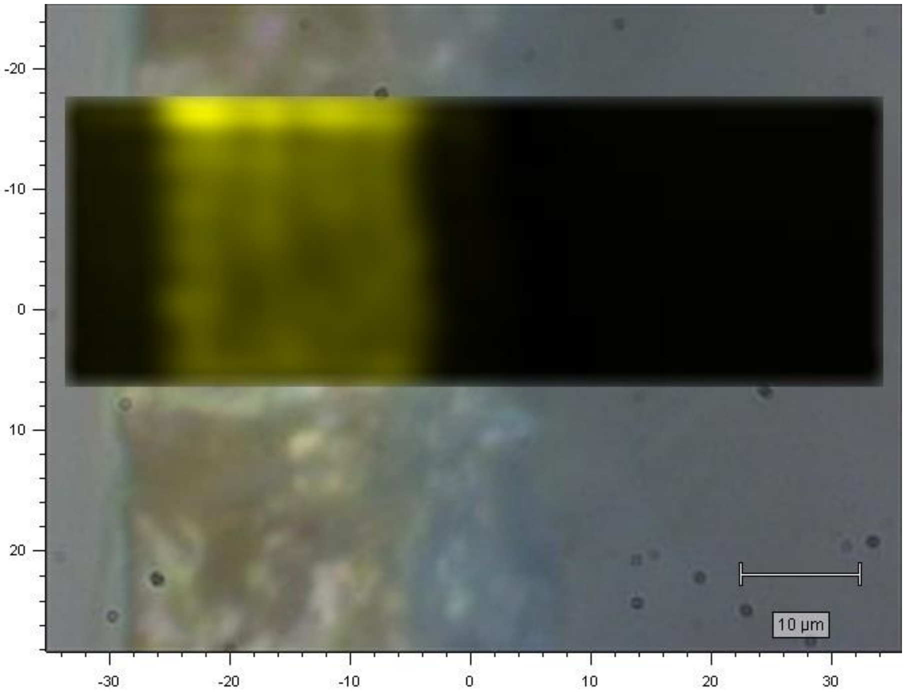

Figure S9: Raman mapping of IRMOF-3@MOF-5 showing the intensity at 1494 cm^{-1} representative of the fluorescence intensity of the IRMOF-3 shell.

VII. Disclaimer

This work was prepared as an account of work sponsored by the Department of Energy (DOE), an agency of the United States Government, under grant number DE-SC0004888. Neither the United States or any agency thereof, nor any of their employees, makes any warranty, express or implied, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

VIII. References

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