Polymer-MOF Hybrid Composites with High Porosity and Stability through Surface-Selective Ligand Exchange

Vincent J. Pastore, Timothy R. Cook\*, Javid Rzayev\*

University at Buffalo, the State University of New York, Buffalo, NY 14260-3000, United States

## Supporting Information Contents

Figure S1. PXRD diffractograms of MOF-5, PAA, MOF-5/PAA, and MOF-5/PI	Page 2
Figure S2. PXRD diffractograms of ZIF-8 and <b>ZIF-8/MOF-5</b> composites	Page 2
Figure S3. PXRD diffractograms of UiO-66	Page 2
Figure S4. <sup>1</sup> H NMR spectrum of <b>PAA</b>	Page 3
Figure S5. <sup>1</sup> H NMR spectrum of <b>MEPA</b>	Page 3
Figure S6. <sup>1</sup> H NMR spectrum of <b>PVBA</b>	Page 4
Figure S7. GPC traces of PAA-high, PAA-low, and MEPA	Page 4
Table S1. Polymer molecular weight data	Page 4
Figure S8. SEM images of free polymer-coated MOF-5	Page 5
Figure S9. FT-IR spectra of PAA and PI	Page 5
Figure S10. FT-IR spectra of MOF-5/PAA and MOF-5/PI	Page 5
Figure S11. TGA curves of microcrystalline MOF-5, PAA, and microcrystalline MOF-5/PAA	Page 6
Figure S12. TGA curves of nanocrystalline MOF-5, PAA, and nanocrystalline MOF-5/PAA	Page 6
Figure S13. TGA curves of ZIF-8, PAA, and ZIF-8/PAA	Page 7
Figure S14. DSC curves of PAA, microcrystalline MOF-5/PAA, nanocrystalline MOF-5/PAA,	Ū.
and ZIF-8/PAA	Page 7
Figure S15. N <sub>2</sub> adsorption-desorption isotherms of ZIF-8 and <b>ZIF-8/PAA</b>	Page 8
Figure S16. N <sub>2</sub> adsorption-desorption isotherms of nanocrystalline MOF-5 and nanocrystalline	-
MOF-5/PAA	Page 8



Figure S1. PXRD diffractograms of PAA (a), MOF-5 simulated (b, CCDC no. 256965<sup>1</sup>), microcrystalline MOF-5 experimental (c), nanocrystalline MOF-5 experimental (d) MOF-5/PAA (e) and MOF-5/PI (f)



Figure S2. PXRD diffractograms of ZIF-8 simulated (bottom, CCDC no. 602542<sup>2</sup>) and experimental (top)



Figure S3. PXRD diffractograms of UiO-66 simulated (bottom, CCDC no. 733458<sup>3</sup>) and experimental (top)







Figure S7. GPC traces of PAA high (a), PAA low (b), and MEPA (c)

Polymer	M <sub>n</sub> / Da	M <sub>w</sub> / Da	$M_w/M_n$
PAA high	239,500	500,500	2.09
PAA low	4,600	7,500	1.63
MEPA	5,500	15,000	2.73

Table S1. Polymer molecular weight information<sup>a</sup>

<sup>a</sup>Molecular weights and distributions were obtained from GPC relative to linear PEO calibration.



Figure S8. SEM images of polymer-coated MOF-5 isolated prior to crosslinking



Figure S9. FT-IR spectra of PAA (top) and PI (bottom)



Figure S10. FT-IR spectra of MOF-5/PAA (top) and MOF-5/PI (bottom)



Figure S11. TGA curves of microcrystalline MOF-5 (black), PAA (red, dashed), and microcrystalline 77% MOF-5/PAA (blue, dotted).



Figure S12. TGA curves of nanocrystalline MOF-5 (black), PAA (red, dashed), and nanocrystalline 50% MOF-5/PAA (blue, dotted).



Figure S13. TGA curves of ZIF-8 (black), PAA (red, dashed), and 50% ZIF-8/PAA (blue, dotted).



Figure S14. DSC cooling curves of (a) PAA ( $T_g$  = 399°C), (b) microcrystalline 77% MOF-5/PAA ( $T_g$  = 396°C), (c) nanocrystalline 50% MOF-5/PAA ( $T_g$  = 399°C), and (d) 50% ZIF-8/PAA ( $T_g$  = 399°C).



Figure S15. N<sub>2</sub> adsorption-desorption isotherms of ZIF-8 (top) and 69% ZIF-8/PAA (bottom).



Figure S16. N<sub>2</sub> adsorption-desorption isotherms of nanocrystalline MOF-5 (top) and nanocrystalline 50% MOF-5/PAA (bottom).