Supplementary Information For

Improving Mixed-Matrix Membrane Performance Via PMMA Grafting From Functionalized NH_2-UiO-66

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Synthesis of MOFs

UiO-66 was prepared according to the procedure reported in previous study [1,2]. Briefly, UiO-66 was synthesized by dissolving 2.27 mmol (0.53 g) of zirconium (IV) chloride ($ZrCl_4$) and 2.27 mmol (0.38 g) of terephthalic acid in 30 ml DMF. Afterwards, the solution was transferred to a 50 mL Teflon-lined autoclave in an oven at 120°C for 24 h. The as-synthesized UiO-66 was separated by centrifugation after the reaction solution was cooled

down to room temperature. The product washed out three times with DMF and then further three times with chloroform under sonication for 10 min to remove unreacted reactants. Washed samples were solvent exchanged by soaking for 5 days in 2 × 15 mL of chloroform followed by sonicating for 10 min. Finally the white product was collected by filtrating and heated at 100°C under dynamic vacuum for 24 h. The same procedure was used to synthesis NH_2-UiO-66 [2,3], where terephthalic acid was replaced by 2-ATA (0.41 g).

Synthesis of GMA-UiO-66

GMA-UiO-66 was synthesized according to the procedure described in previous study [3]. Measured amount of NH_2-UiO-66 nanoparticles and GMA were suspended in THF through sonicating for 20 min. the functionalization was completed at 55°C for 36 h. The prepared powder washed out three times with THF and then further three times with chloroform under sonication for 10 min to remove unreacted GMA, and solvent exchange was accomplished with chloroform for three days. Finally the yellow GMA-UiO-66 nanoparticles were dried at 50°C for 24 h under vacuum. Fig. S1 illustrates the schematics of functionalization reactions to obtain GMA-UiO-66 and PMMA grafted UiO-66 (PMMA-g-GMA-UiO-66).

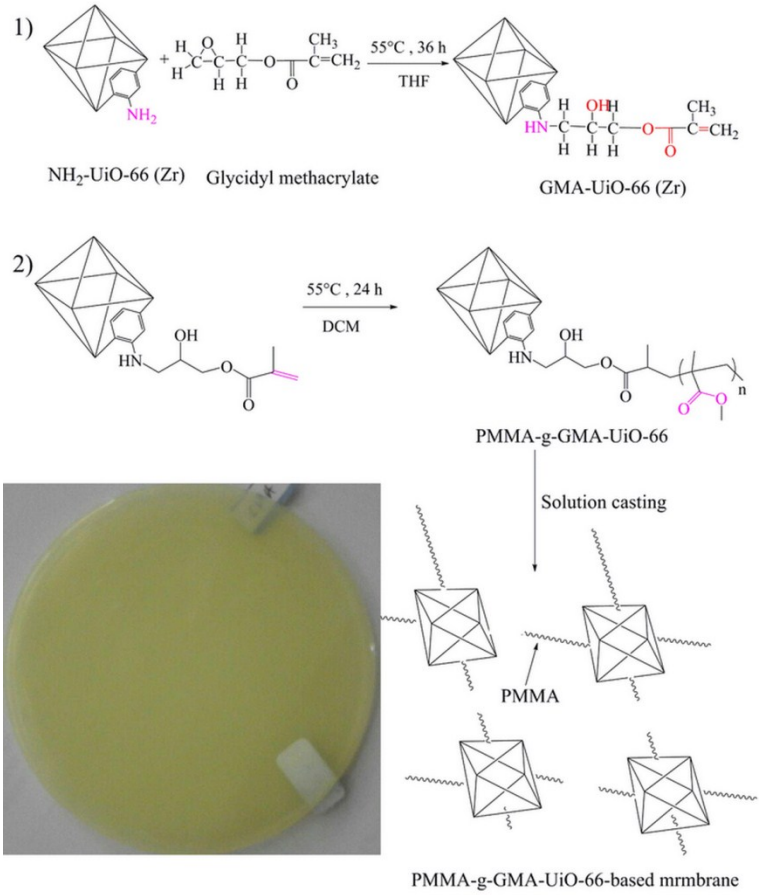


Fig. S1. Post-synthetic modification of NH_2-UiO-66 to produce PMMA-g-GMA-UiO-66. (1) Preparation of GMA-UiO-66 by the reaction between NH_2-UiO-66 and GMA and (2) synthesis of PMMA-g-GMA-UiO-66 by in-situ polymerization of methyl methacrylate (MMA) in presence of GMA-UiO-66.

Gas permeation apparatus

The set-up was prepared according to the gas permeation apparatus reported in Ref. [4].

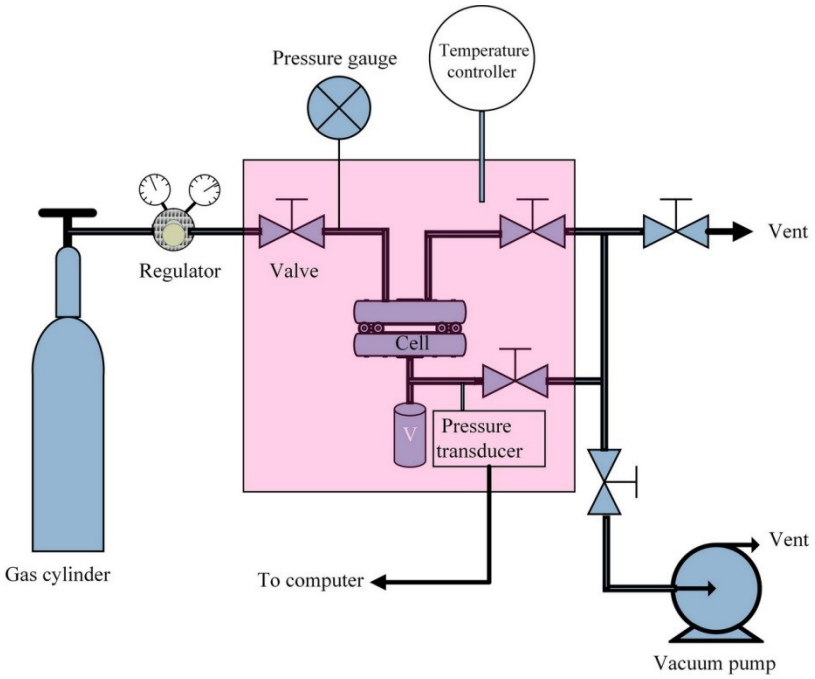


Fig. S2. Experimental setup used for the gas permeation tests.

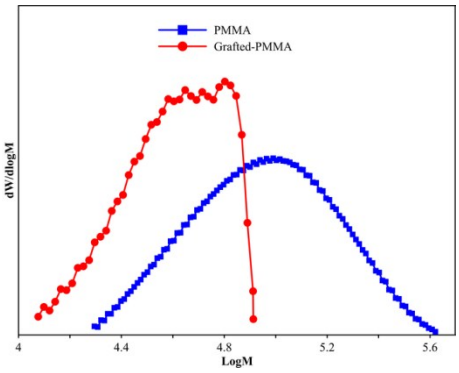


Fig. S3. GPC traces of PMMAs.

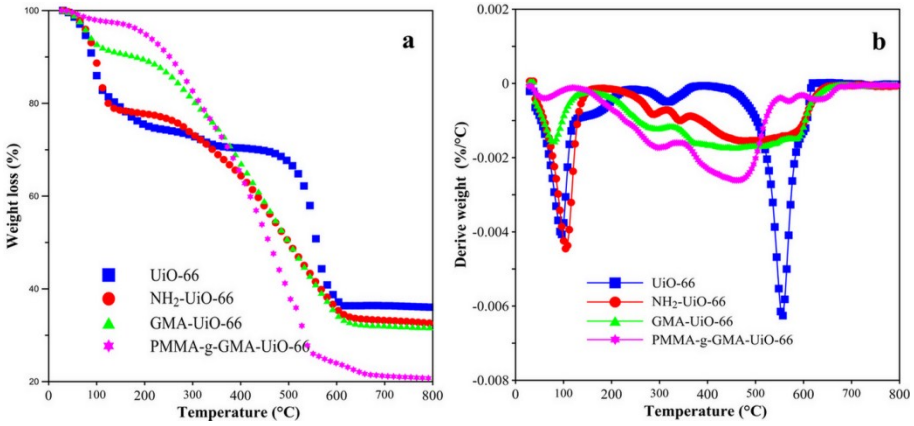


Fig. S4. TGA (a) and derivative TG (DTG) (b) curves for all MOFs.

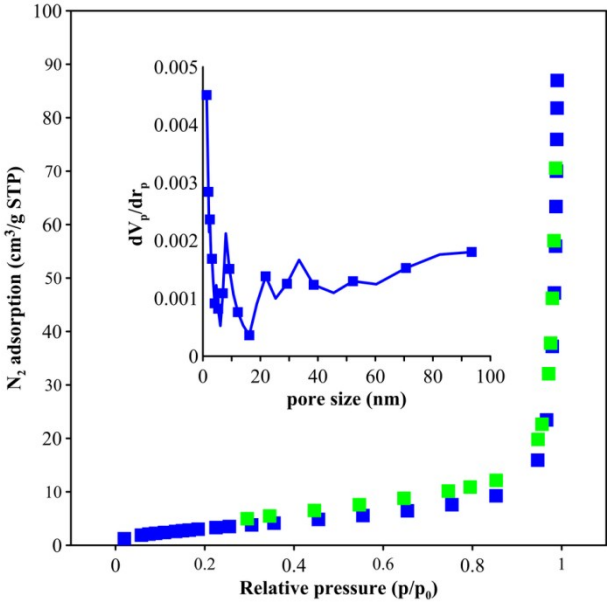


Fig. S5. N_2 adsorption/desorption and pore size distribution of PMMA-g-GMA-UiO-66.

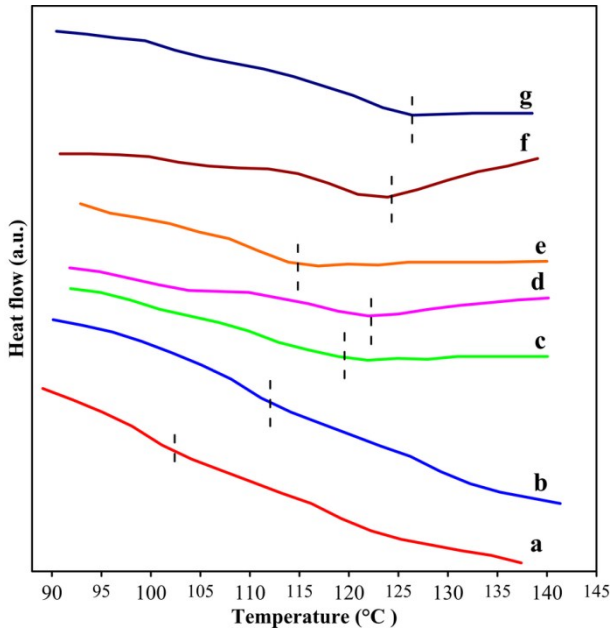


Fig. S6. DSC curves of neat PMMA (a), MMM-1 (b), MMM-2 (c), MMM-3 (d), MMM-4 (e), m-MMM (f), and g-MMM (g).

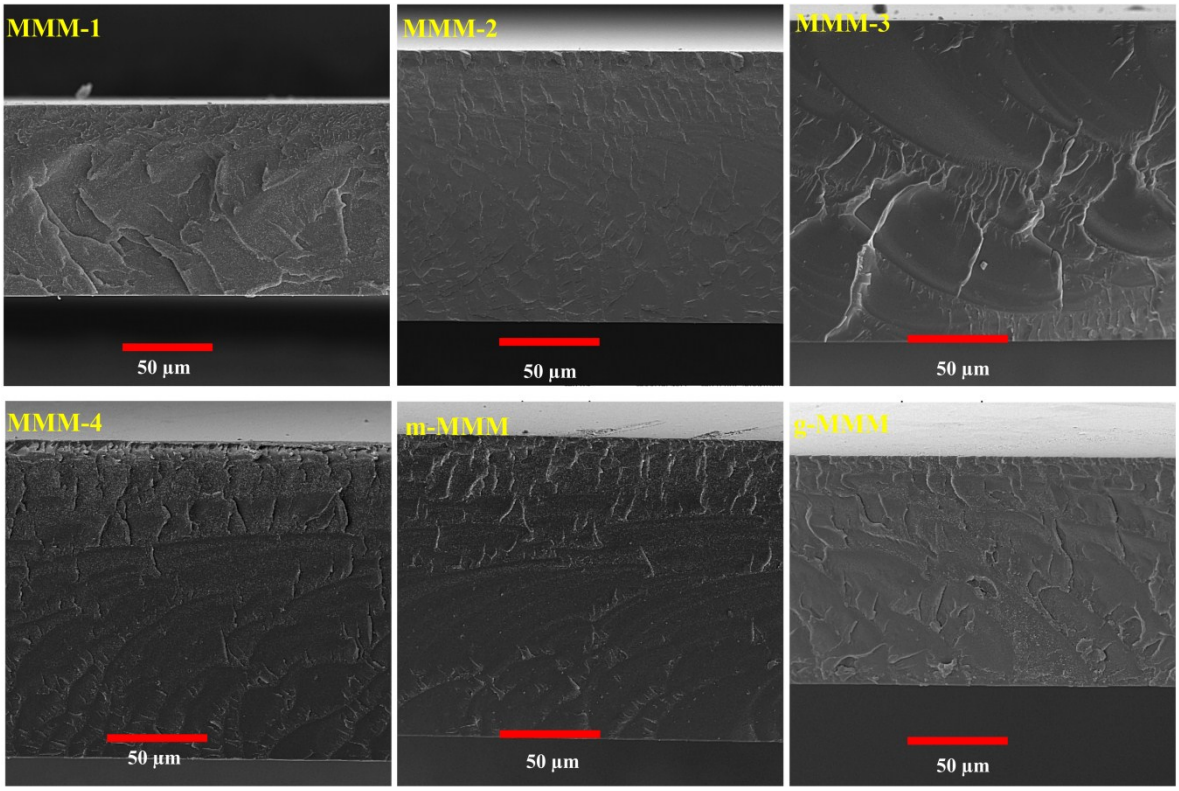


Fig. S7. The low magnification FESEM images of the whole cross-section of MMMs.

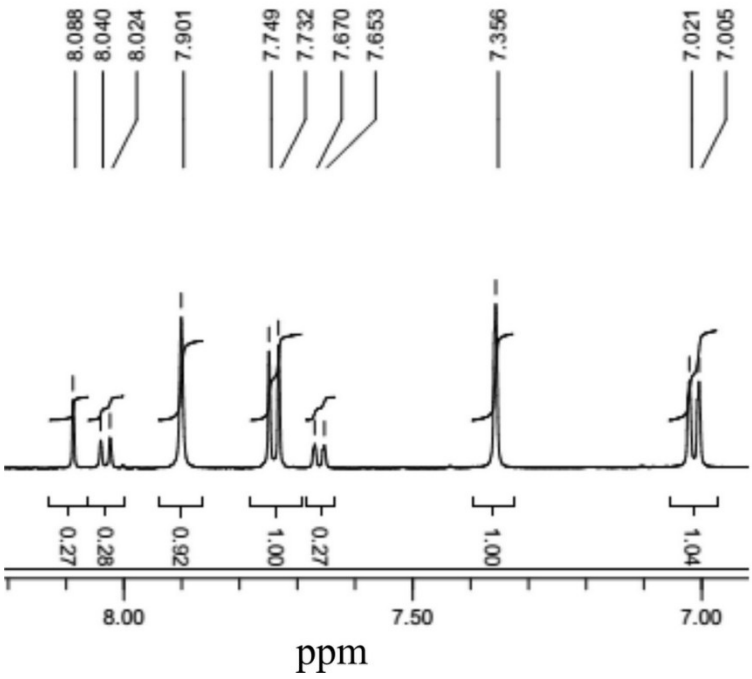
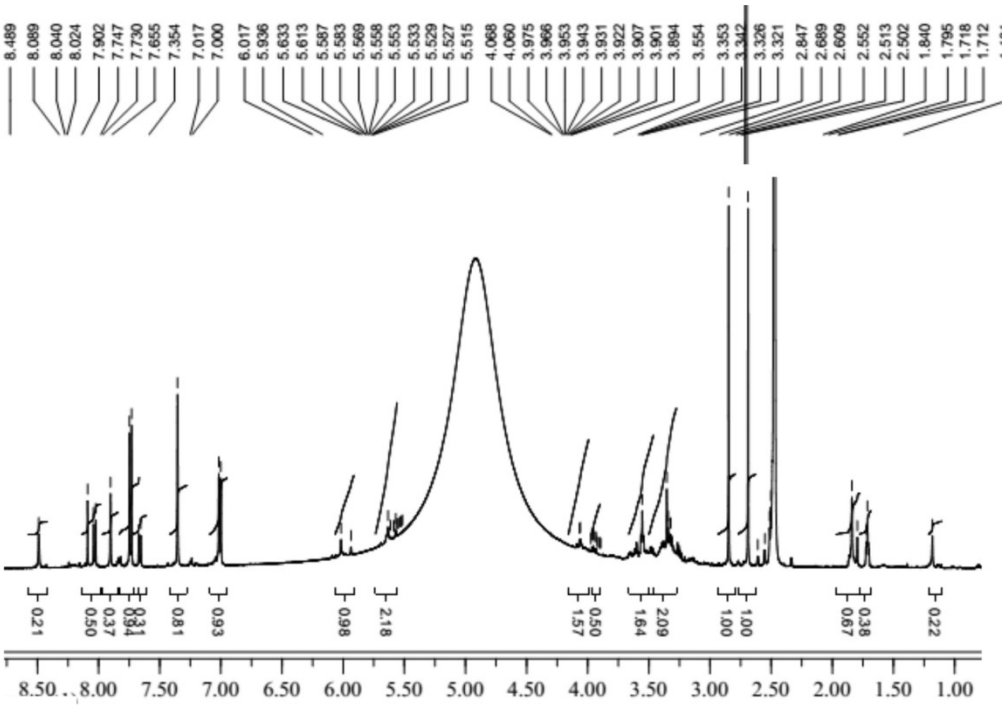


Fig. S8. ^{1}H NMR spectrum of NH_2-UiO-66.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5.633
5.613
5.587
5.583
5.569
5.558
5.553
5.533
5.529
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5.515
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4.060
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3.953
3.943
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3.922
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3.342
3.326
3.321
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2.552
2.513
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0.37
0.31
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0.81
0.93
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0.50
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6.50
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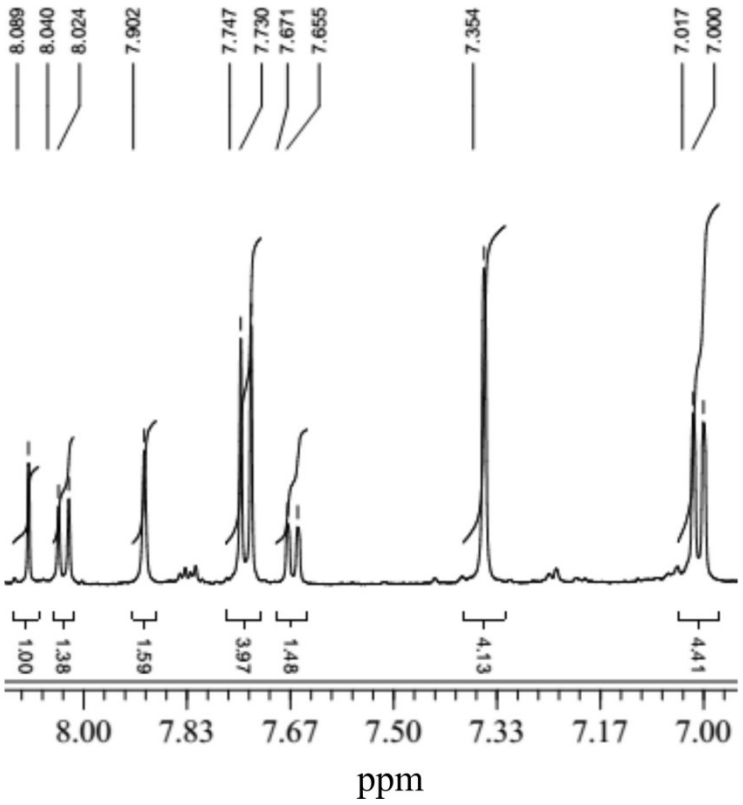
66



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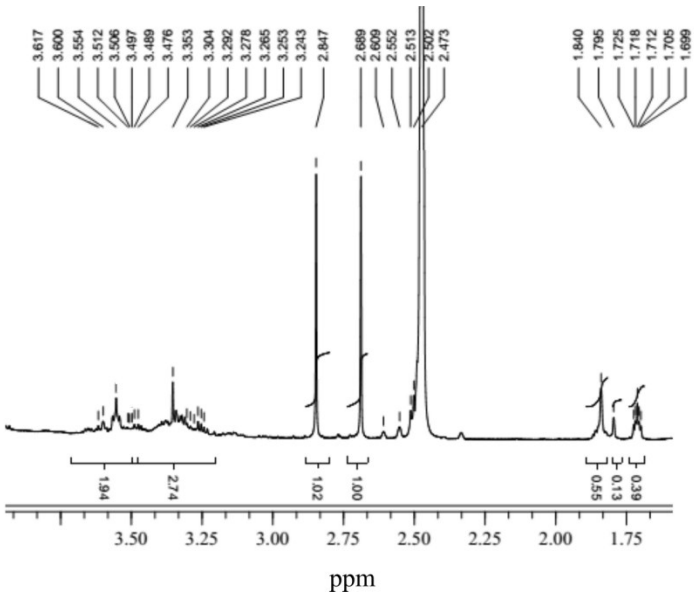

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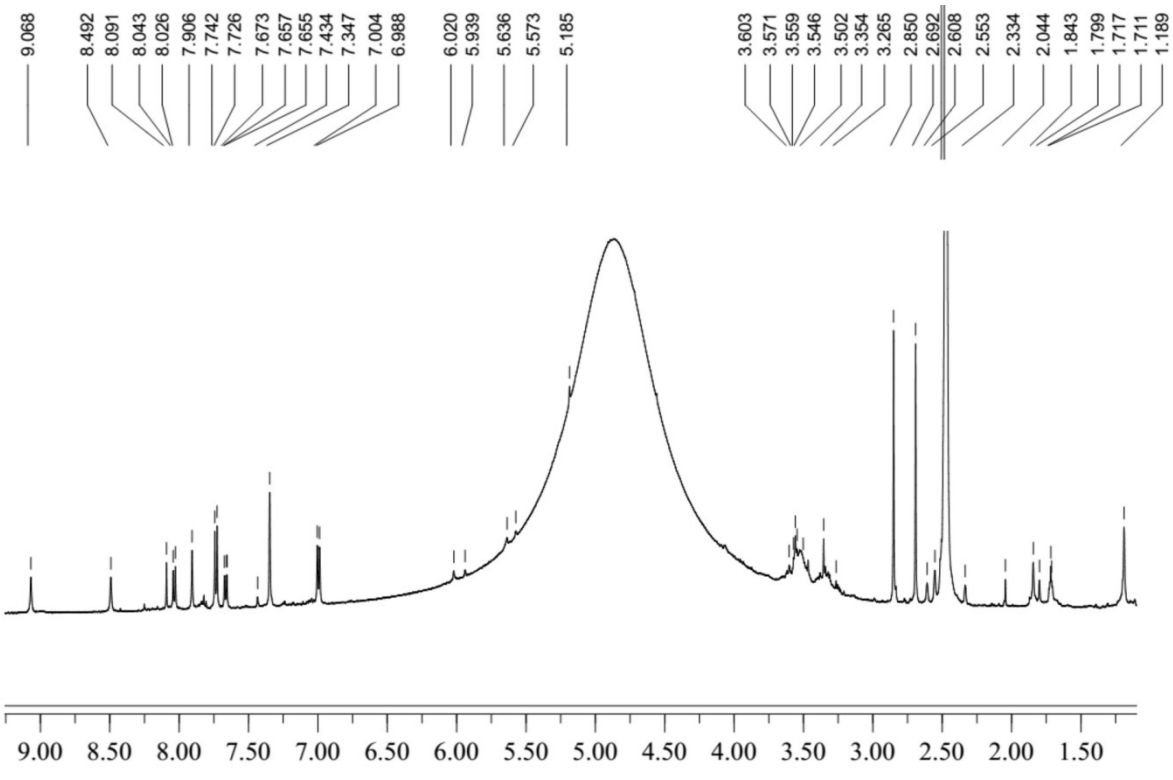
69 Fig. S9. ^{1}H NMR spectrum of GMA-UiO-66.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7.004
6.988
6.020
5.939
5.636
5.573
5.185
3.603
3.571
3.559
3.546
3.502
3.354
3.265
2.850
2.692
2.608
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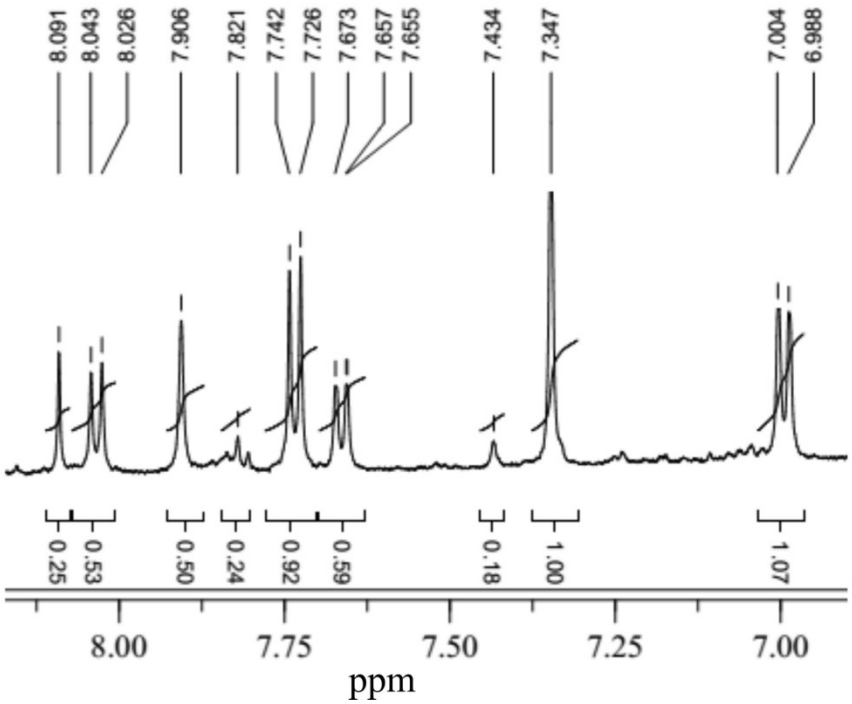
ppm

70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71

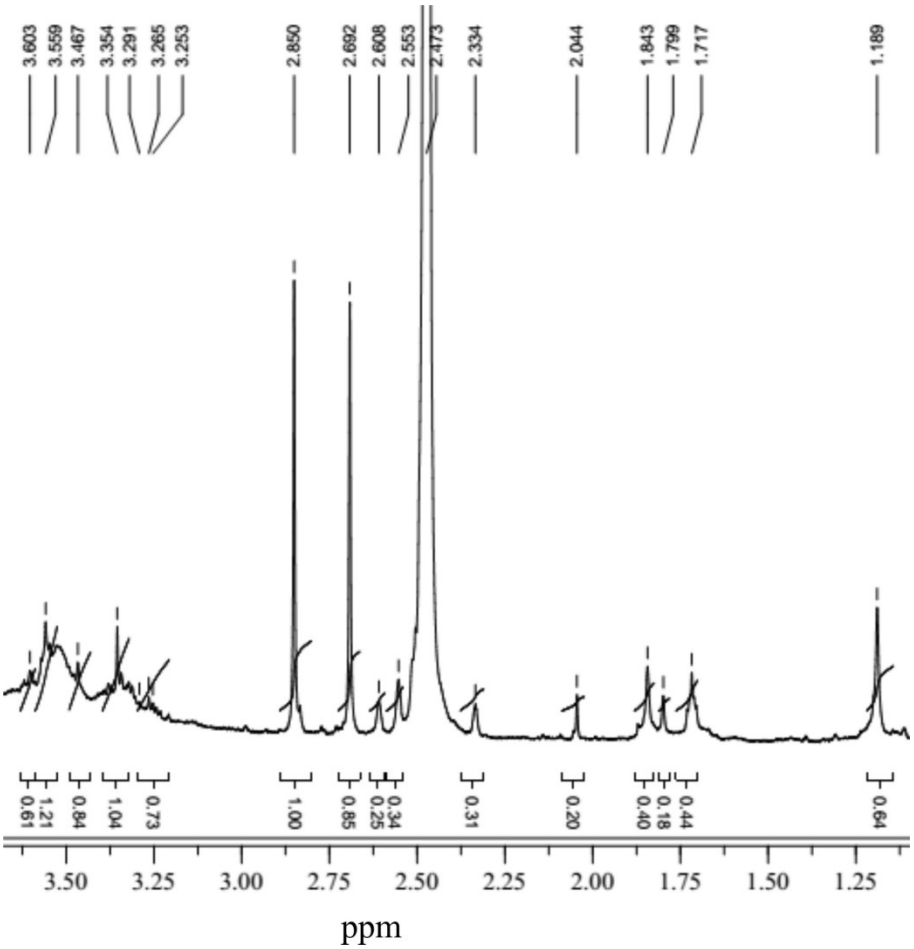

Fig. S10. ^{1}H NMR spectrum of PMMA-g-GMA-UiO-66.

79 Table S1. Physical properties and Zr content of all MOFs.

MOFs	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	Zr contents (wt%)[a]
UiO-66	1276	0.54	27.63
NH_2-UiO-66	1258	0.51	55.68
GMA-UiO-66	965	0.43	46.33
PMMA-g-GMA-UiO-66	13	0.14	12.34

[a] Zr contents analyzed by ICP-OES.

80

81 Table S2. Physical parameters of the gases considered in this investigation [5].

Gas	Kinetics diameter (Å)	Critical temperature (K)	Polarizability × $10^{25}/cm^3$	Dipole moment × 10^{18}/esu cm	Quadruple moment × 10^{26}/esu cm^2
He	2.551	5.19	2.0496	0	0.0
CO_2	3.3	304.12	29.11	0	4.30
N_2	3.64	126.20	17.403	0	1.52
CH_4	3.8	190.56	25.93	0	0

82

References

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[4] Q. Song, S.K. Nataraj, M. V. Roussenova, J.C. Tan, D.J. Hughes, W. Li, P. Bourgoin, M.A. Alam, A.K. Cheetham, S. a. Al-Muhtaseb, E. Sivaniah, Energy Environ. Sci. 2012, **5**, 8359-8369.

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