Removal of Confined Ionic Liquid From A Metal Organic Framework By Extraction With Molecular Solvents.

Manish P. Singh¹ Nilesh R. Dhumal,² Hyung J. Kim,^{2,3} Johannes Kiefer,^{1,4} James A. Anderson,^{1*}

¹Chemical and Materials Engineering Group, School of Engineering, University of Aberdeen,

Aberdeen, UK, AB24 3UE.

²Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, USA.

³School of Computational Sciences, Korea Institute for Advanced Study, Seoul 02455, Korea.

⁴Technische Thermodynamik and MAPEX Center for Materials and Processes, Universität

Bremen, Bremen 28359, Germany.

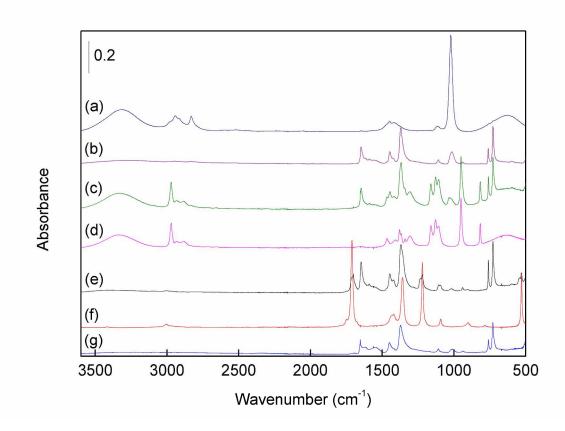


Fig. S1 FTIR spectra of confined solvent in CuBTC MOF: (a) Methanol, (b) CuBTC with methanol, (c) CuBTC with isopropanol, (d) isopropanol, (e) CuBTC with acetone, (f) acetone, and (g) pristine CuBTC.

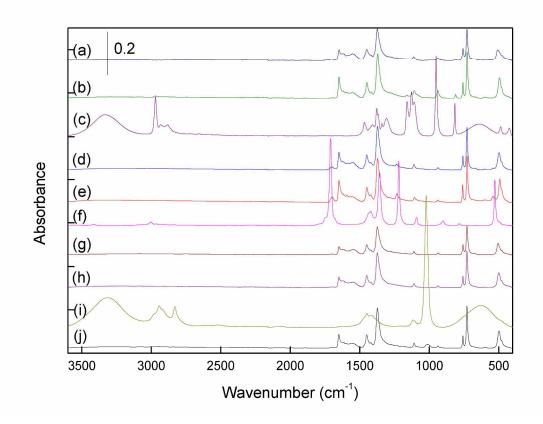


Fig. S2. FTIR spectra of pristine and CuBTC washed with solvents and dried for 24 h (a) CuBTC washed with isopropanol and dried at 150 °C, (b) CuBTC washed with isopropanol and dried at 70°C, (c) pure isopropanol, (d) washed with acetone and dried CuBTC at 150°C, (e) washed with acetone and dried CuBTC at 70°C, (f) pure acetone, (g) washed CuBTC with methanol and dried at 150°C, (h) washed CuBTC with methanol and dried at 70°C, (i) methanol, and (j) pristine CuBTC

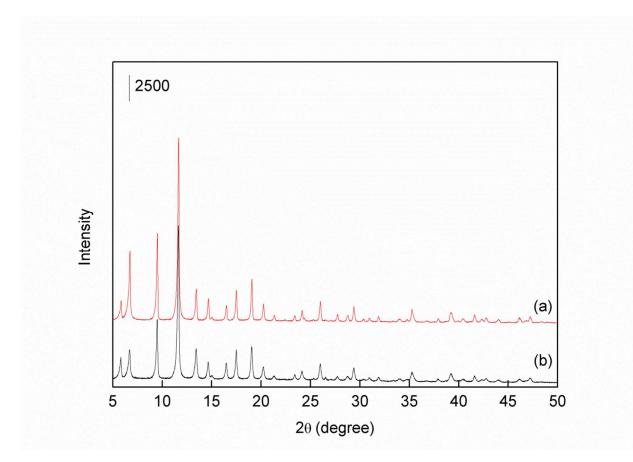


Fig. S3 PXRD pattern of IL extracted CuBTC with methanol (a) pristine CuBTC, (b) CuBTC after washing with methanol and dried at 70°C for 24 h.

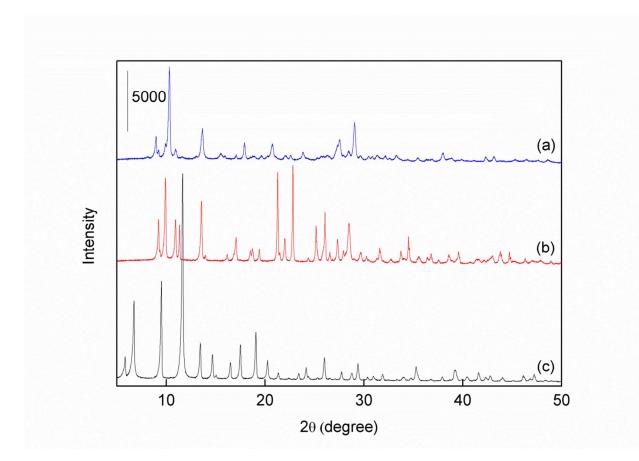


Fig. S4 PXRD patterns of CuBTC after holding 5h in water filtered and dried (a) at 150°C for 24 h, (b) at 70°C for 24 h, and (c) pristine CuBTC

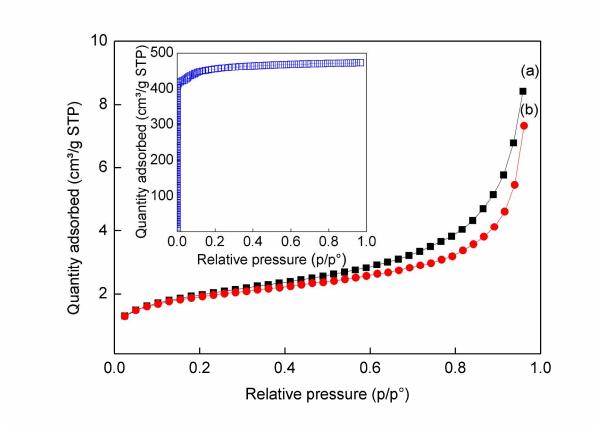


Fig. S5 Nitrogen adsorption isotherms of CuBTC and IL removed CuBTC. (a) pre-treated at 70°C for 24 h (b) pre-treated at 150°C for 24 h. Inset shows N_2 adsorption isotherms of pristine CuBTC pre-treated at 150°C for 24 h.

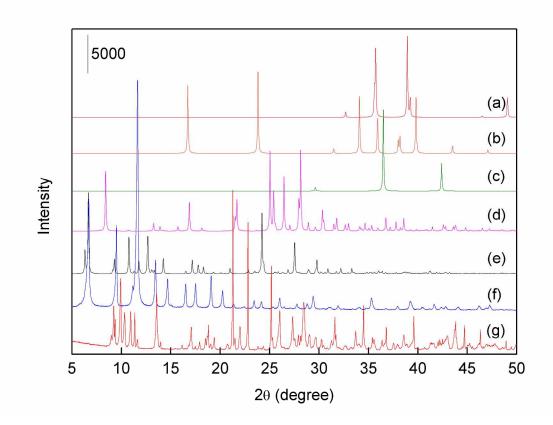


Fig. S6A Comparison of XRD pattern (a) CuO^1 , (b) $Cu(OH)_2^1$, (c) Cu_2O^1 , (d) 1,3,5-benzene try carboxylic acid with two water molecules^{2,} (C₆H₃(CO₂H)₃.2H₂O), (e) 1,3,5-benzene try carboxylic acid³, (C₆H₃(CO₂H)₃, (f) activated CuBTC, and (g) IL impregnated CuBTC after washing with water.

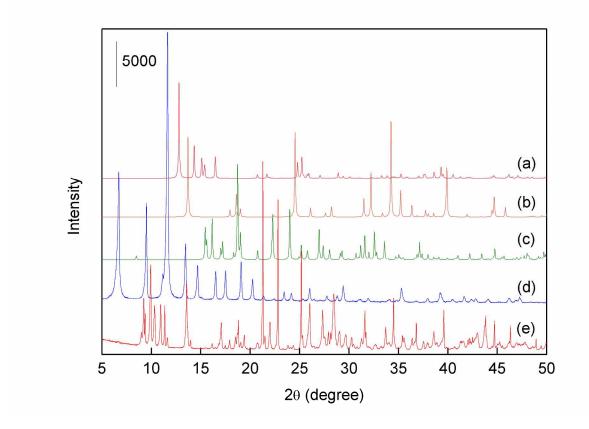


Fig. S6B Comparison of XRD pattern (a) $Cu_2(CH_3CO_2)_4.2H_2O_{,}^4$ (b) $Cu_2SO_4^{,1}$ (c) $CuSO_4.5H_2O_{,}^1$ (d) activated CuBTC, and (e) IL impregnated CuBTC after washing with water.

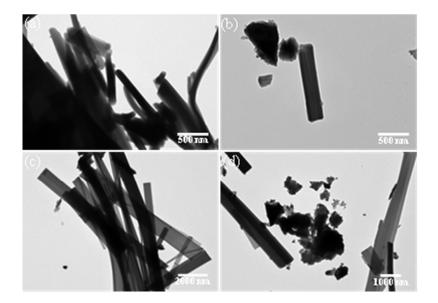


Fig. S7 TEM images of pristine CuBTC after washing with water at one place (a), and at another place of same sample (b), IL impregnated CuBTC after washing with water (c), and at another place of same sample (d).

References

- http://www.crystallography.net/. The CIF file of Cu₂SO₄ (COD ID:9009694),
 CuSO₄.5H₂O (COD ID:1010527), CuO (COD ID: 9008961), Cu(OH)₂ (COD ID: 9007849), and Cu₂O (COD ID:1010941) were taken from Crystallography Open Database (COD).
- 2 Fan, Z.-Z.; Lib, X.-H.; Wang, G.-P. Trimesic Acid Dihydrate. *Acta Crystallogr. Sect. E.-Struct Rep. Online*, **2005**, E61, o1607-o1608.
- 3 Duchampt, D. J.; Marsh, R. E. <u>The Crystal Structure of Trimesic Acid (Benzene-1,3,5-Tri</u> <u>Carboxylic Acid</u>). *Acta Crystallogr. Sect. B-Struct. Sci.*, **1969**, B25, 5-19.
- 4 The CIF file of Cu₂(CH₃CO₂)₄.2H₂O was taken from <u>http://physical-</u> chemistry.scb.uwa.edu.au/tonto/wiki/index.php/Metal_hydrates.cif.