Electronic Supplementary Information (ESI)

A Microporous Cu^{2+} MOF based on a Pyridyl – Isophthalic Acid Schiff Base Ligand with High CO_2 Uptake

Andreas Kourtellaris,[a] Eleni E. Moushi,[a] Ioannis Spanopoulos,[b] Christos Tampaxis,[b,c] Georgia Charalambopoulou,[c] Theodore A. Steriotis,[c] Giannis S. Papaefstathiou,[d] Pantelis N. Trikalitis[b] and Anastasios J. Tasiopoulos[*,a]

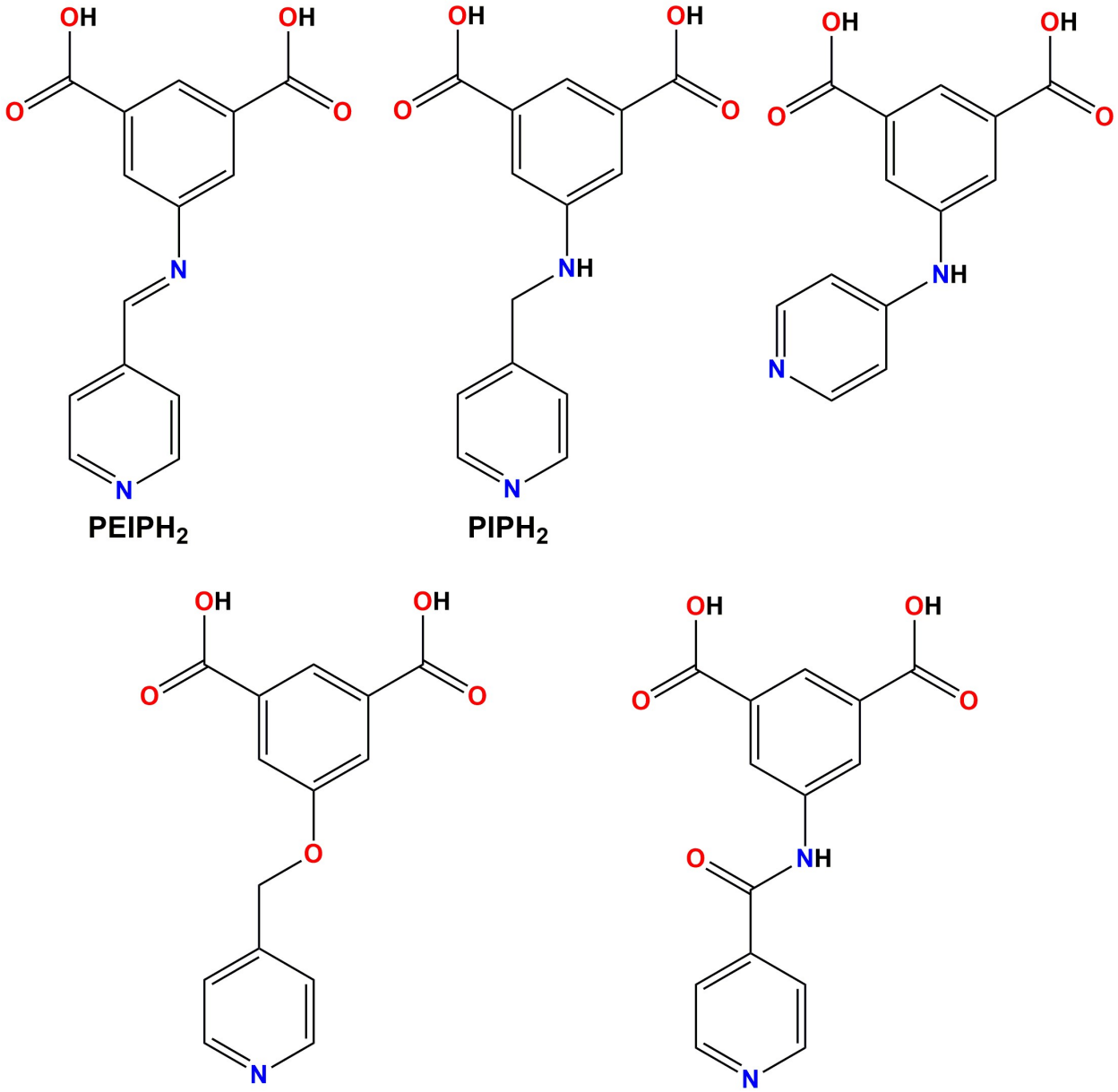
[a] Department of Chemistry, University of Cyprus, 1678 Nicosia, Cyprus. Fax: ++357 22895451; Tel: ++357 22892765; E-mail: atasio@ucy.ac.cy

[b] Department of Chemistry, University of Crete, Voutes 71003, Heraklion, Greece.

[c] National Center for Scientific Research "Demokritos", 15341 Agia Paraskevi Attikis, Greece.

[d] Laboratory of Inorganic Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis Zografou 157 71, Greece.

Table of Contents



Scheme S1. The ligands $PEIPH_2$ and $PIPH_2$ employed in this study and some representative examples of tritopic ligands consisting of a pyridyl and an isophthalic acid moieties.

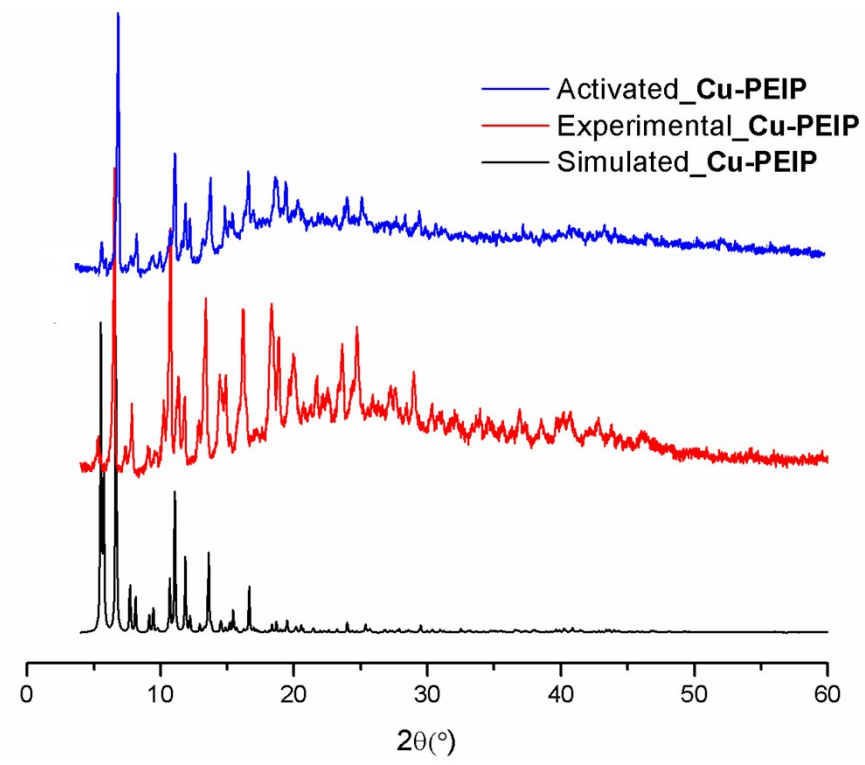


Figure S1. Power X-ray diffraction patterns for **Cu-PEIP**.

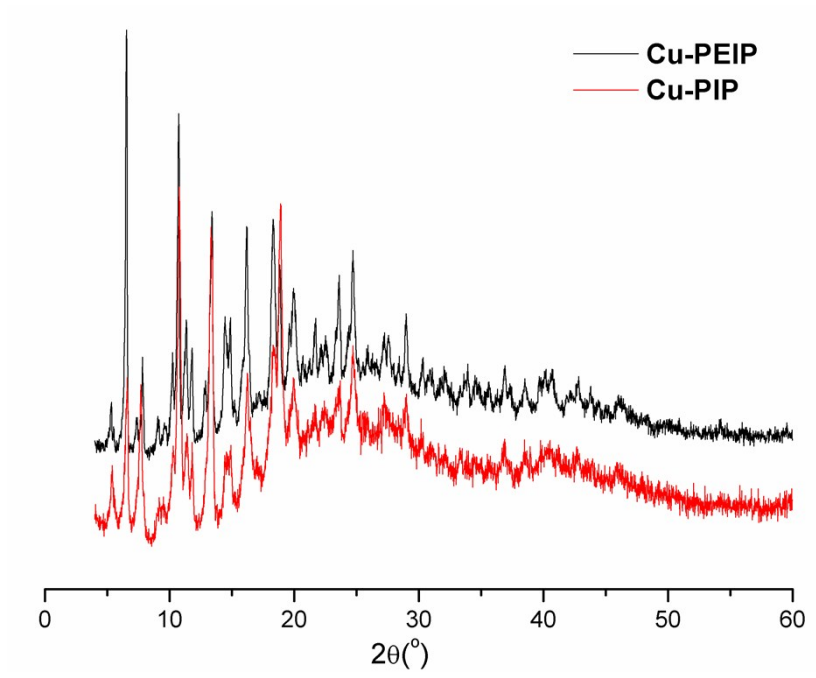


Figure S2. Power X-ray diffraction patterns (experimental) for **Cu-PEIP** and **Cu-PIP**.

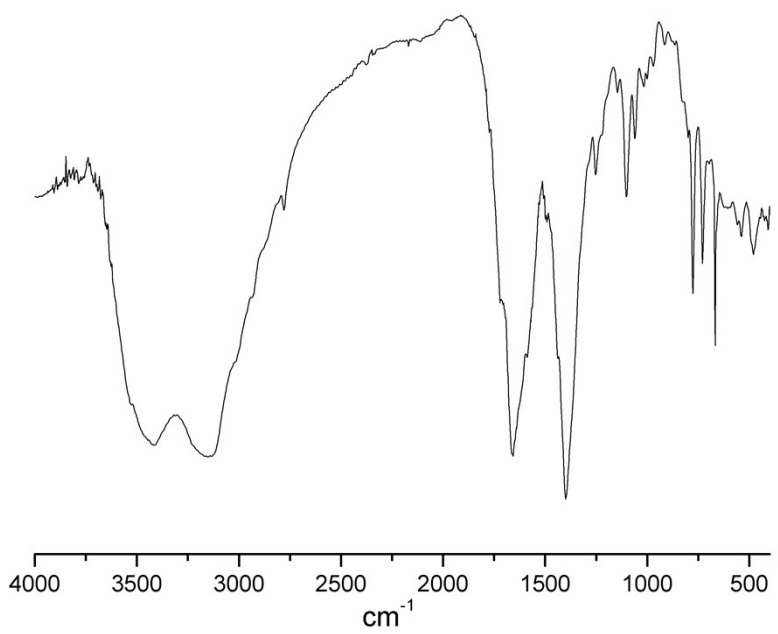


Figure S3. FTIR spectra for **Cu-PEIP**.

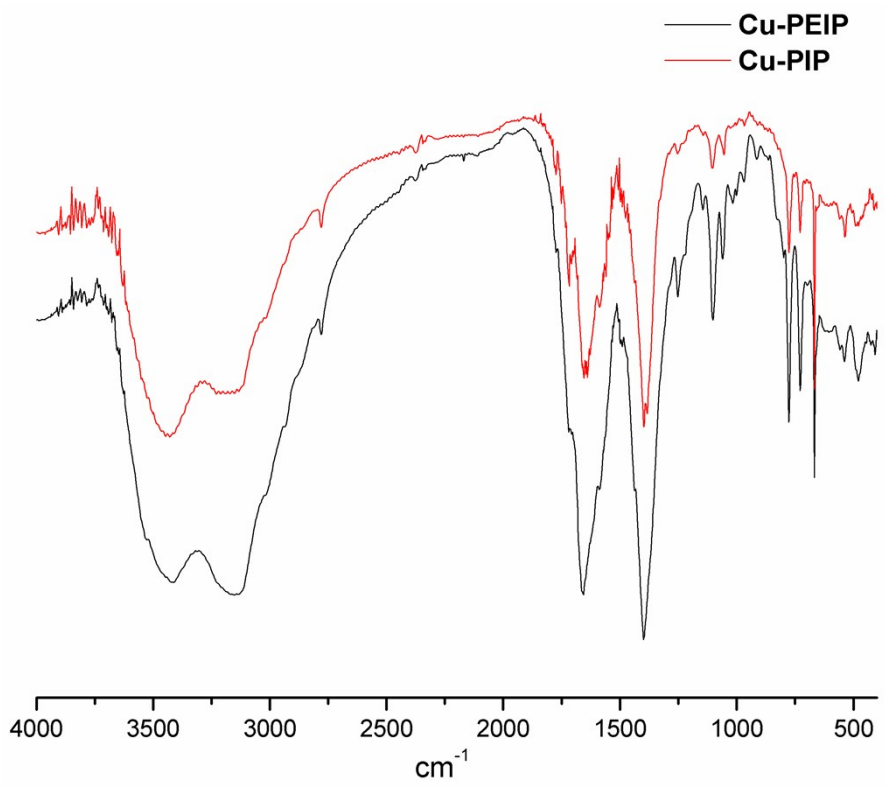


Figure S4. FTIR spectra for **Cu-PEIP** and **Cu-PIP**.

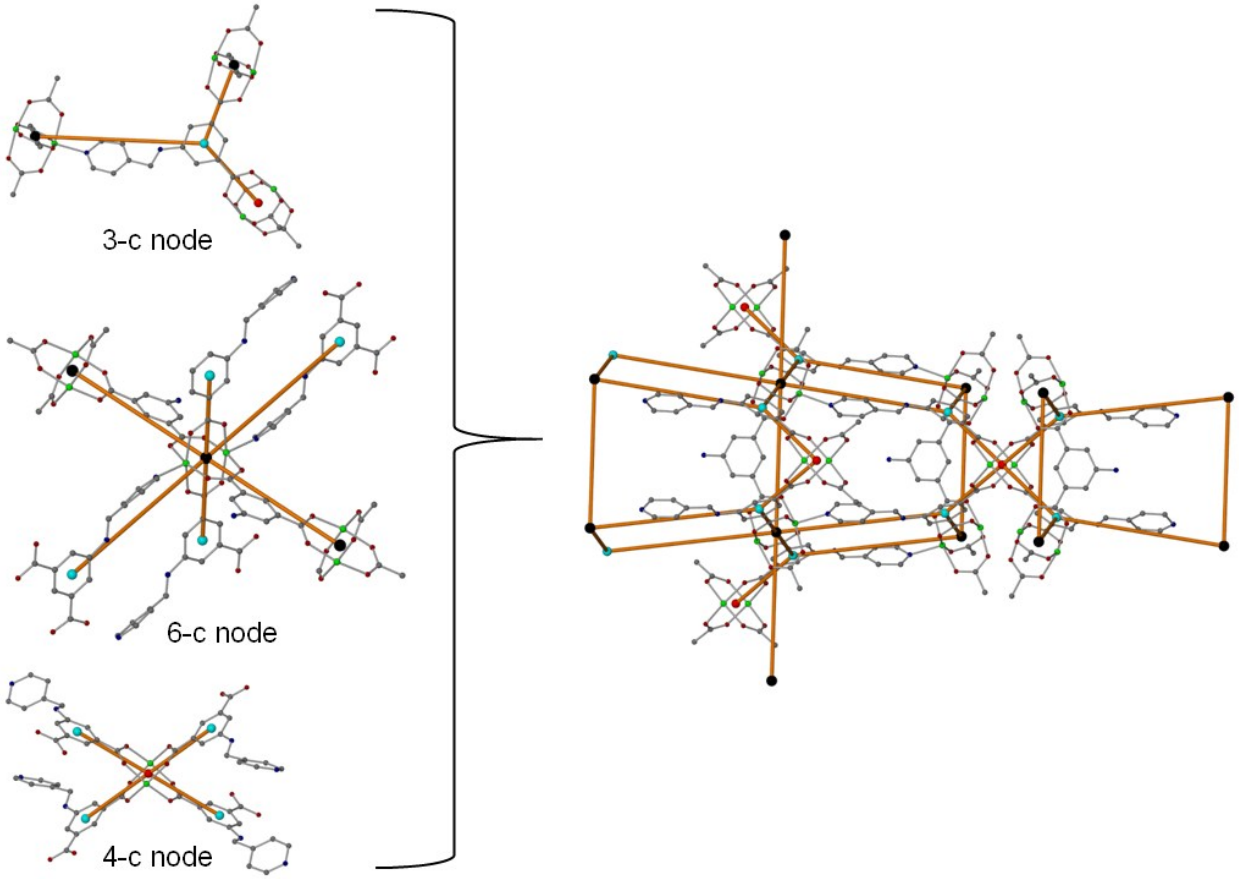


Figure S5: The deconstruction of the underline network of **Cu-PEIP**.

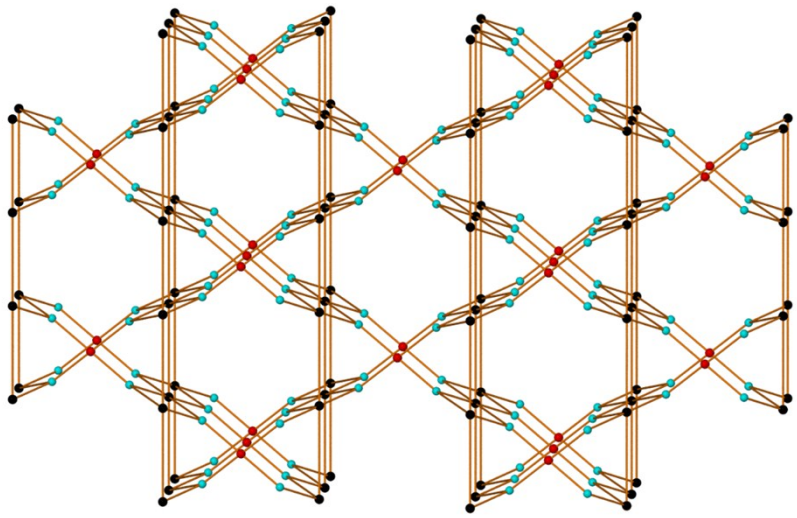


Figure S6. The trinodal net of **Cu-PEIP** down to a axis.

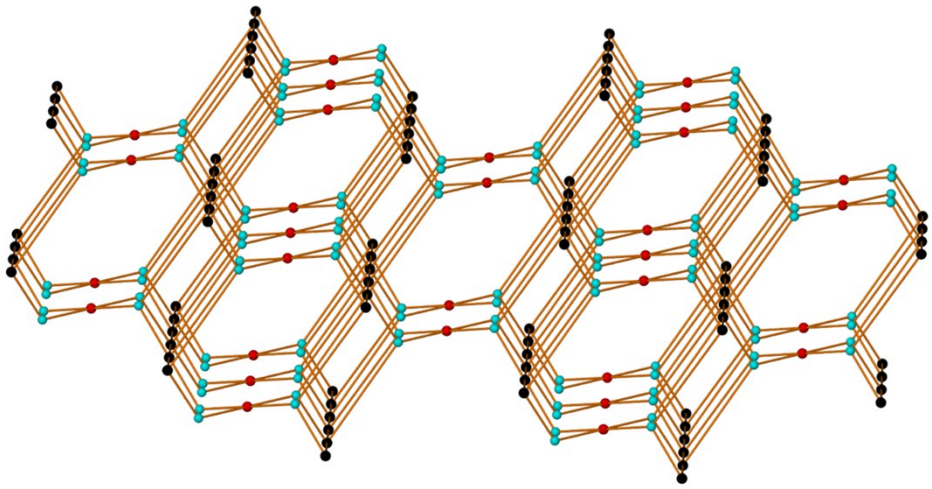


Figure S7. The trinodal net of **Cu-PEIP** down to b axis.

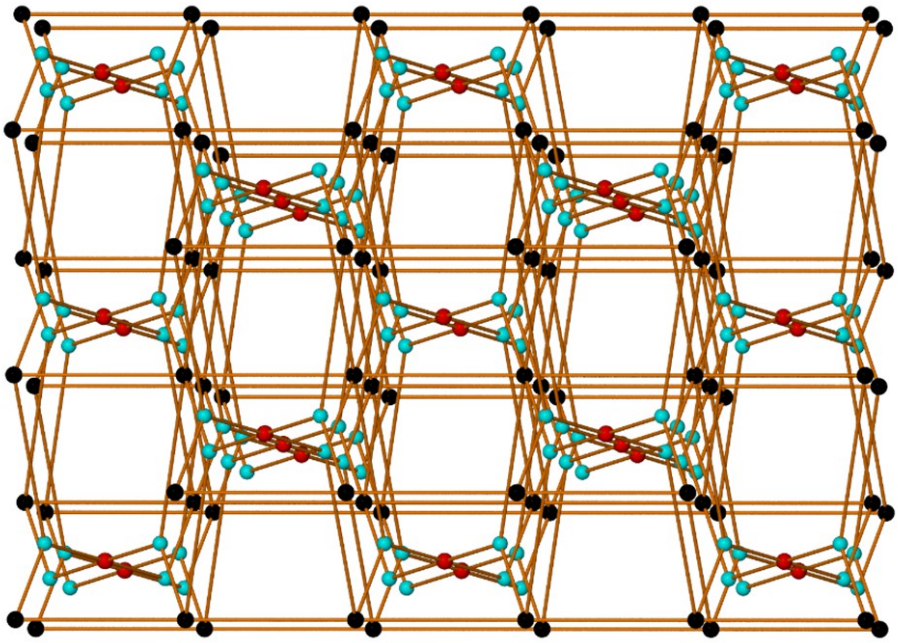


Figure S8. The trinodal net of **Cu-PEIP** down to c axis.

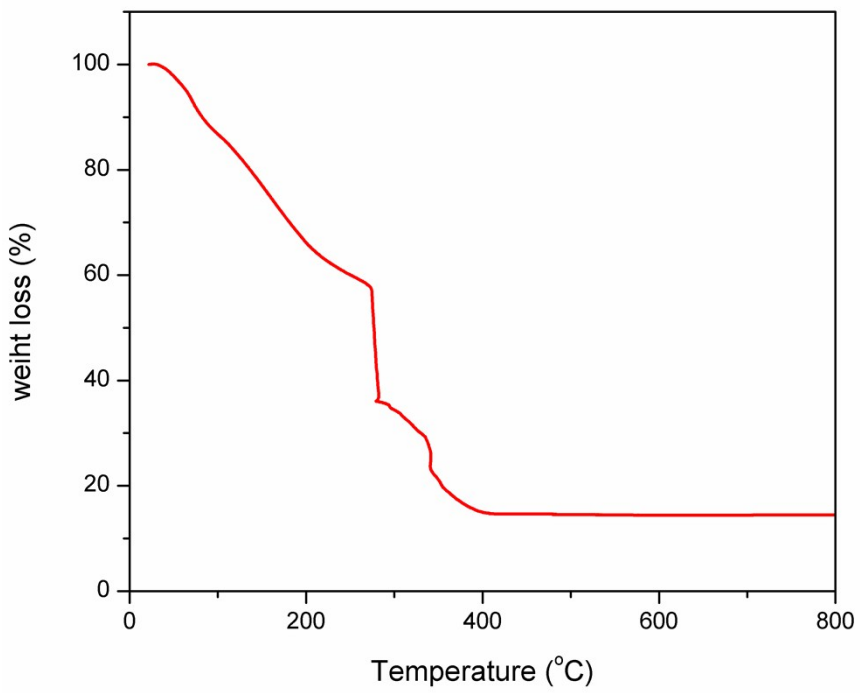


Figure S9. TGA curve of **Cu-PEIP**.

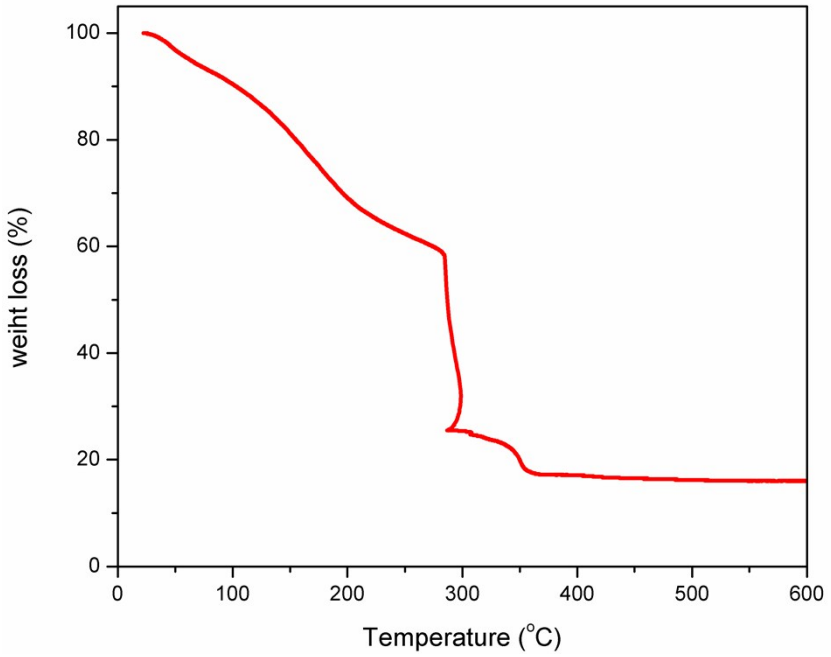


Figure S10. TGA curve of **Cu-PIP**.

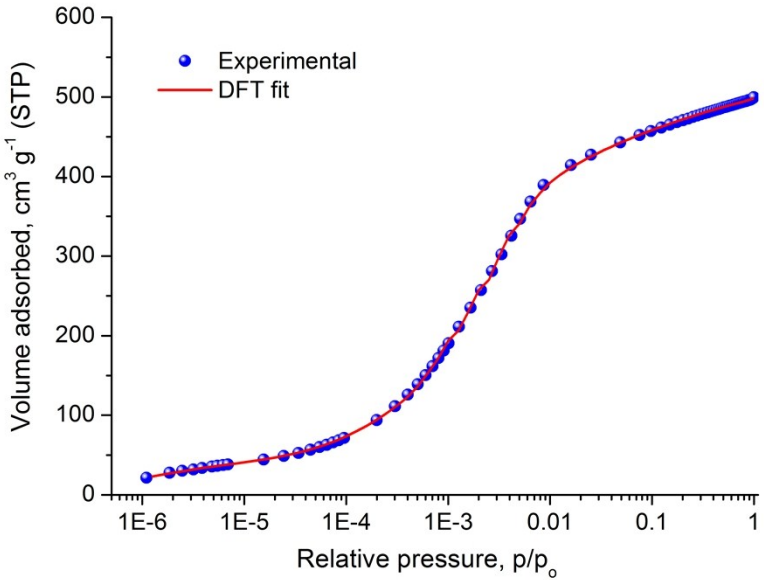


Figure S11. Argon adsorption isotherm of **Cu-PEIP** recorded at 87 K and the corresponding NLDFT fitting.

Low pressure CO_2, N_2 and CH_4 sorption isotherms, determination of heat of adsorption and selectivity (CO_2/N_2, CO_2/CH_4) calculations using IAST.

Heat of adsorption. To calculate heats of adsorptions, the corresponding adsorption isotherms at different temperatures were simultaneously fitted using the virial type[1] Equation 1:

$$\ln P = \ln N + \frac{1}{T}\sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad (1)$$

The heat of adsorption at zero coverage was calculated from Equation 2, where as a function of surface coverage, from Equation 3:

$$Q_{st} = -Ra_o \qquad (2)$$

$$Q_{st}(N) = -R\sum_{i=0}^{m} a_i N^i \qquad (3)$$

For the determination of the isosteric heat of adsorption using the Clausious Clapeyron equation a commercially available software, ASiQwin (version 3.01) purchased from Quantachrome, was used.

Gas selectivity using IAST. The corresponding calculations were performed according to an established procedure.[2] Specifically, the single-component adsorption isotherms were described by fitting the data with the following virial-type equation:

$$p = \frac{n}{K} exp(c_1 1n + c_2 n^2 + c_3 n^3 + c_4 n^4) \qquad (4)$$

where p is the pressure in Torr, n is the adsorbed amount in mmol g^{-1}, K is the Henry constant in mmol g^{-1} $Torr^{-1}$ and c_i are the constants of the virial equation.

The free energy of desorption at a given temperature and pressure of the gas is obtained from the analytical integration of eq. (4):

$$G(T,p) = RT\int_0^p \frac{n}{p}dp = RT(n + \frac{1}{2}c_1n^2 + \frac{2}{3}c_2n^3 + \frac{3}{4}c_3n^4 + \frac{4}{5}c_4n^5) \qquad (5)$$

The free energy of desorption is a function of temperature and pressure *G(T,p)* and describes the minimum work (Gibbs free energy) that required to completely degas the adsorbent surface.

For a binary mixture of component *i* and *j* eq. (5) yields the individual pure loadings $n_i^0$and n_j^0 at the same free energy of desorption:

$$G_i^0(n_i^0) = G_j^0(n_j^0) \qquad (6)$$

The partial pressure of component *i* and *j* in an ideal adsorption mixture is given by the following equations:

$$py_i = p_i^0(n_i^0)x_i \qquad (7)$$

$$py_j = p_j^0(n_j^0)x_j \qquad (8)$$

where y_i *(=1-*y_j*)* and x_i *(=1-*x_j*)* is the molar fraction of component *i* in the gas phase and the adsorbed phase respectively and p_i^0, $p_j^0$is the pure component pressure of *i* and *j* respectively. From eq. (6)-(8) and (3), the selectivity for the adsorbates *i* and *j* ($S_{i,j}$) and the total pressure (p) of the gas mixture were calculated from eq. (9) and eq. (10), respectively.

$$S_{ij} = \frac{x_i/y_i}{x_j/y_j} = \frac{p_j^0}{p_i^o} \qquad (9)$$

$$p = \sum_{i}^{j} (p_i^o x_i) \qquad (10)$$

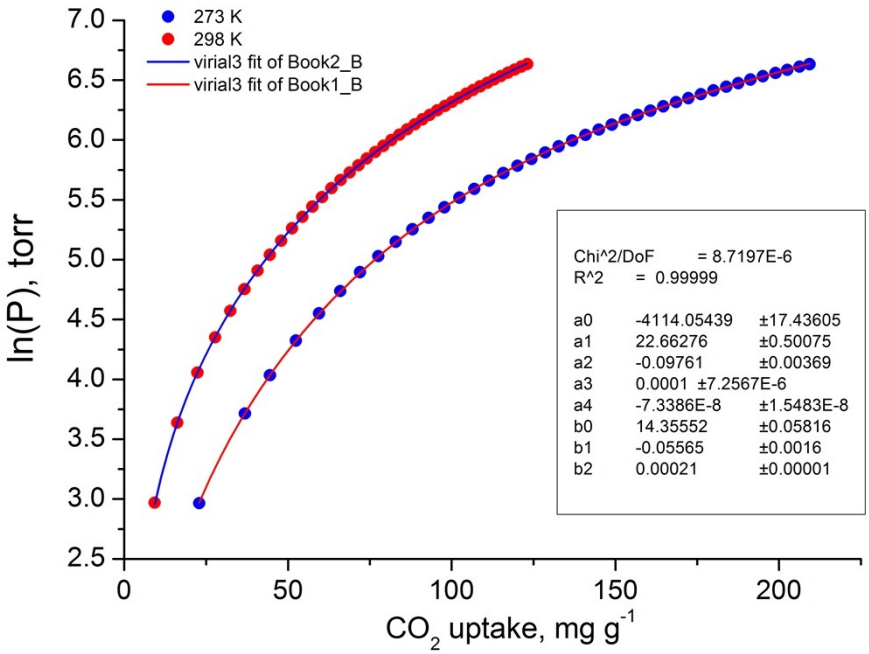


Figure S12. Virial type fitting of CO_2 adsorption isotherms of **Cu-PEIP** at 273 K and 298 K according to equation 1.

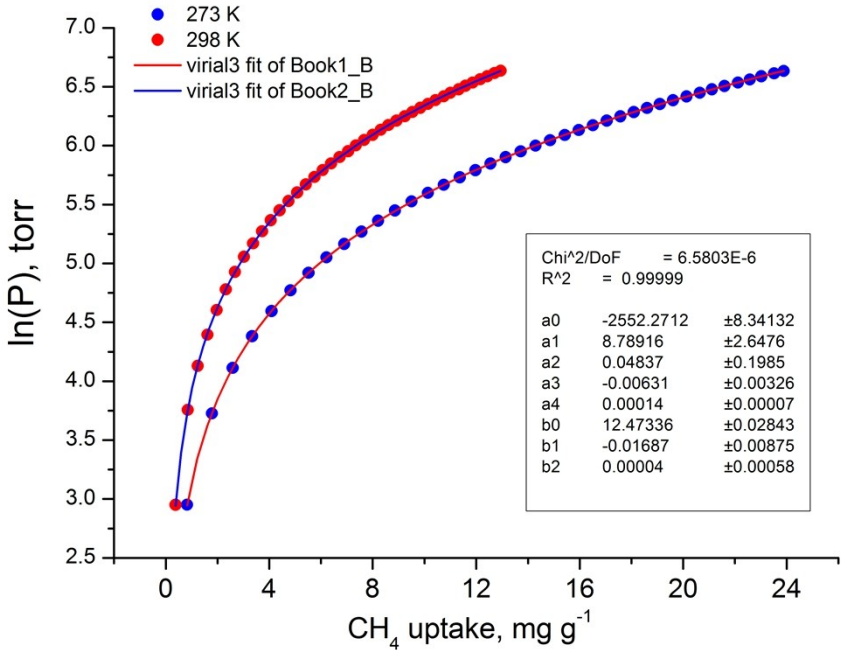


Figure S13. Virial type fitting of CH_4 adsorption isotherms of **Cu-PEIP** at 273 K and 298 K according to equation 1.

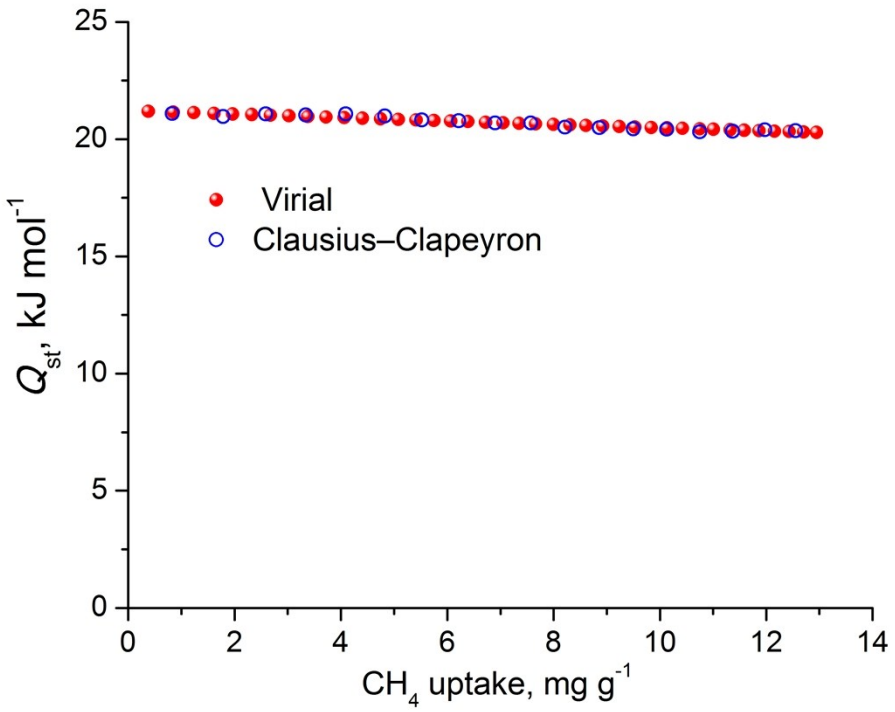


Figure S14. CH_4 isosteric heat of adsorption (Q_{st}) of **Cu-PEIP** as a function of surface coverage, calculated from a virial-type analysis. The corresponding Clausius-Clapeyron calculation is shown with the solid line.

Table S1. Comparison of **Cu-PEIP** with selected MOFs in terms of BET surface area, crystallographic density and total CH_4 uptake at 65 bar, working capacity (5-65 bar) at 298 K and isosteric heat of adsorption.

Material	**BET area** $m^2\ g^{-1}$	**Crystal density** $g\ cm^{-3}$	**Total gravimetric uptake** $g\ g^{-1}$	**Total volumetric uptake** $cm^3\ cm^{-3}$	**Gravimetric working capacity** $g\ g^{-1}$	**Volumetric working capacity** $cm^3\ cm^{-3}$	Q_{st0} kJ mol^{-1}
Cu-PEIP	1785	0.645	0.166	176	0.119	125	21.2
MAF-38	2022	0.761	0.247	263	0.176	187	21.6
Ni-MOF-74[3]	1350	1.195	0.148	251	0.077	129	21.4

UTSA-76[4]	2820	0.699	0.263	257	0.201	197	15.4
NU-111[5]	4930	0.409	0.360	205	0.313	177	14.2
HKUST-1[6]	1850	0.881	0.216	267	0.154	190	17
PCN-14[6]	2000	0.819	0.197	230	0.136	157	18.7
NU-1100[6]	4020	0.467	0.270	180	0.24	160	13.7

Table S2. Comparison of **Cu-PEIP** with selected MOFs in terms of total CH_4 uptake, and working capacity between 5-35 bar and 5-80 bar at 298 K.[7]

Material	**Surface area,** $m^2\ g^{-1}$		**Density,** $g\ cm^{-3}$	**Total uptake at 35 bar,** $cm^3\ cm^{-3}$	**Total uptake at 80 bar,** $cm^3\ cm^{-3}$	**Total uptake at 80 bar,** $g\ g^{-1}$	**Working capacity at 35 bar,** $cm^3\ cm^{-3}$	**Working capacity at 80 bar,** $cm^3\ cm^{-3}$	**Working capacity at 80 bar,** $g\ g^{-1}$
	BET	Langmuir							
Cu-PEIP	1785	1814	0.762	150	187	0.176	99	136	0.129
MAF-38	2022	2229	0.761	226	273	0.256	150	197	0.185
MOF-520	3290	3930	0.586	162	231	0.282	125	194	0.237
Ni-MOF-74	1350	1438	1.195	230	267	0.160	115	152	0.091
HKUST-1	-	1977	0.881	225	272	0.221	153	200	0.162
PCN-14	-	2360	0.819	200	250	0.218	128	178	0.155

AX-21	-	4880	0.487	153	222	0.326	103	172	0.252

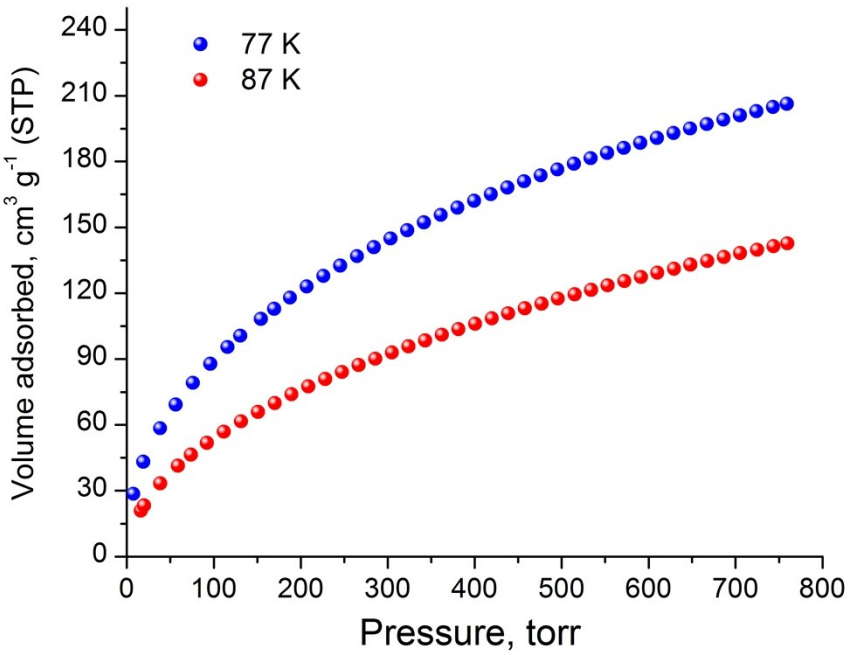


Figure S15. Hydrogen sorption isotherms of **Cu-PEIP** recorded at 77 K and 87 K.

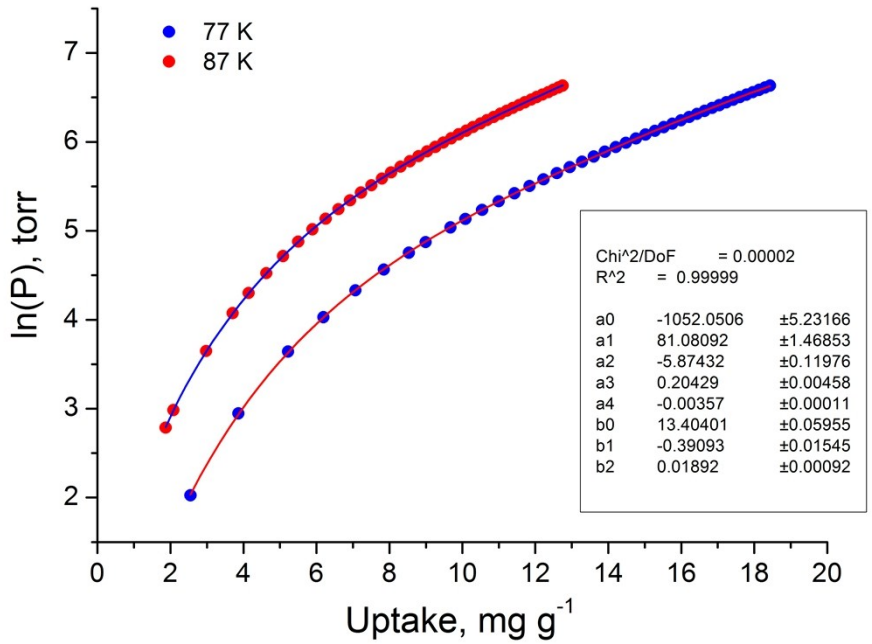


Figure S16. Virial type fitting of H_2 adsorption isotherms of **Cu-PEIP** at 77 K and 87 K according to equation 1.

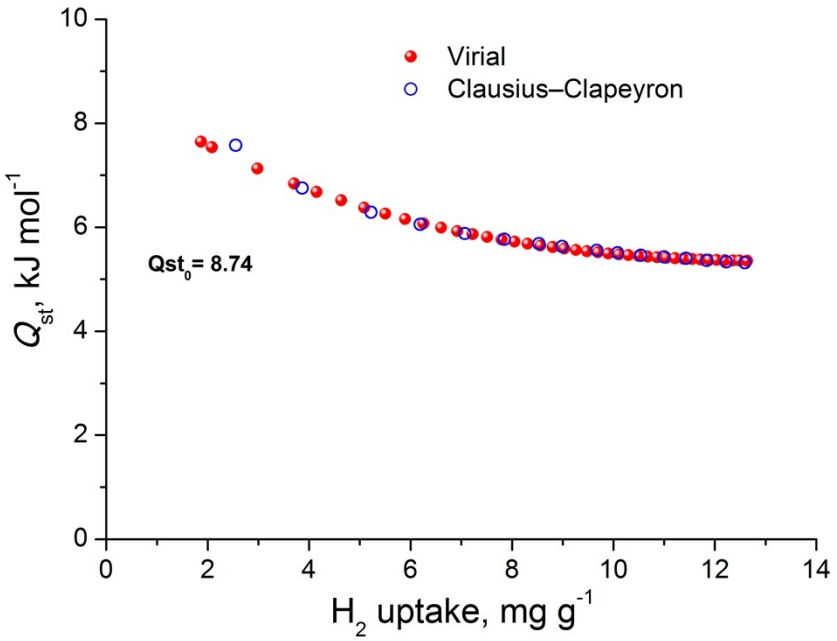


Figure S17. Hydrogen isosteric heat of adsorption (Q_{st}) of **Cu-PEIP** as a function of surface coverage, calculated from a virial-type analysis. The corresponding Clausius-Clapeyron calculation is show with the solid line.

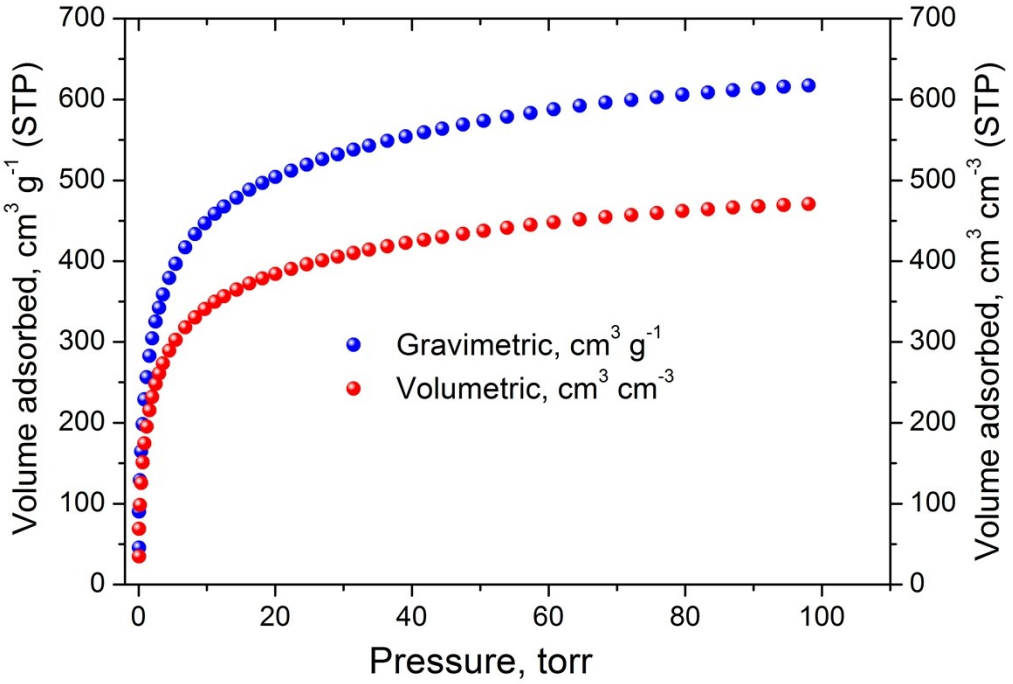


Figure S18. High pressure H_2 adsorption isotherm (up to 100 bar) of **Cu-PEIP** recorded at 77 K.

References

1 (a) L. Czepirski, J. Jagiello , *Chem. Eng. Sci*., 1989, **44**, 797-801, (b) K. Sumida , D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae, J. R. Long, *Chem. Rev.,* 2012, **112**, 724-781.

2 (a) A. L. Myers, J. M. Prausnitz, *AIChE J*., 1965, **11**, 121-127. (b) Y. Bae, K. L. Mulfort, H. Frost, P. Ryan, S. Punnathanam, L. J. Broadbelt, J. T. Hupp, R. Q. Snurr, *Langmuir*, 2008, **24**, 8592-8598. (c) G.S. Armatas, M.G. Kanatzidis, *Nat. Mater*, 2009, **8**, 217-222.

3 Y. Peng, V. Krungleviciute, I. Eryazici, J. T. Hupp, O. K. Farha, T. Yildirim, *J. Am. Chem. Soc*., 2013, **135**, 11887-11894.

4 B. Li, H. Wen, H. Wang, H. Wu, M. Tyagi, T. Yildirim, W. Zhou, Chen B., *J. Am. Chem. Soc*., 2014, **136**, 6207-6210.

5 Y. Peng, G. Srinivas, C. E. Wilmer, I. Eryazici, R.Q. Snurr, J. T. Hupp, T. Yildirim, O. K. Farha, *Chem. Commun*., 2013, **49**, 2992-2994.

6 O. V. Gutov, W. Bury, D. A. Gomez-Gualdron, V. Krungleviciute, D. Fairen-Jimenez, J. E. Mondloch, A. A. Sarjeant, S. S. Al-Juaid, R. Q. Snurr, J. T. Hupp, T. Yildirim, O. K. Farha, *Chem. Eur. J.,* 2014, **20**, 12389-12393.

7 F.Gándara, H. Furukawa, S. Lee, O. M. Yaghi, *J. Am. Chem. Soc.,* 2014, **136**, 5271-5274.