Online Supplementary Material for:

Influence of sterically non-hindering methyl groups on adsorption properties of two classical zinc and copper MOF types

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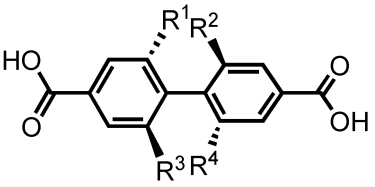
Table S1 MOFs with known structure based on 4,4′-biphenyldicarboxylates with at least one non-H *meta*-substituent, with a condition that the substituent should not be a carboxylate group and that no bonds between the substituents are allowed.[a]

H_2L = 

R^1, R^2, R^3, R^4	Comment	Reported properties or transformations	Ref. Doi (dx.doi.org/...)
NO_2, NO_2, H, H	3D mixed ligand (with 1,3-dipyrid-4-yl-propane) coordination polymers of Mn, Co, Ni, Cd	Magnetism	B. Li, G. Li, D. Liu, Y. Peng, X. Zhou, J. Hua, Z. Shi, S. Feng, CrystEngComm 13 (2011) 1291-1298. 10.1039/c0ce00252f
	[ML(phen)], M = Co, Ni, Zn, 3D mixed ligand MOFs	Magnetism	J.-Y. Zhang, Y. Ma, A.-L. Cheng, Q. Yue, Q. Sun, E.-Q. Gao, Dalton Trans. 40 (2011) 7219–7227. 10.1039/c1dt10158g
	3D mixed ligand (with 1,3-diimidazol-4-ylalkanes) coordination polymers of Mn, Co, Cu, Zn, Cd	Magnetism	B. Li, X. Zhou, Q. Zhou, G. Li, J. Hua, Y. Bi, Y. Li, Z. Shi, S. Feng, CrystEngComm 13 (2011) 4592-4598. 10.1039/c1ce05061c
2-NHR, H, H, H R = H, COOtBu	Non-interpenetrated $[Zn_4OL_3]$ IRMOF	Postsynthetic modification by thermally induced cleavage of Boc protecting group	R. K. Deshpande, J. L. Minnaar, S. G. Telfer, Angew. Chem. Int. Ed. 49 (2010) 4598-4602. 10.1002/anie.200905960
Me, Me, OH, OH	Non-interpenetrated $[Cu_2L_2]$ · Guest, **nbo** network	Catalytic enantioselective carbonyl-ene and Diels-Alder reactions (removal of guest without framework collapse molecules was not achieved)	K. S. Jeong, Y. B. Go, S. M. Shin, S. J. Lee, J. Kim, O. M. Yaghi, N. Jeong, Chem. Sci. 2 (2011) 877-882. 10.1039/c0sc00582g
R, H, H, H R = CHO, C=N-NH-2,4-$C_6H_4(NO_2)_2$, OMe	Doubly-interpenetrated $[Zn_4OL_3]$ IRMOF	Postsynthetic modification (hydrazone formation) and mixed ligand IRMOFs. Interpenetration control	A. D. Burrows, C. G. Frost, M. F. Mahon and C. Richardson, Angew. Chem. Int. Ed. 47 (2008) 8482-8486. 10.1002/anie.200802908
Me, Me, Me, Me	Non- and doubly interpenetrated $[Zn_4OL_{3-x}L^2_x]$ IRMOF	Mixed ligand IRMOFs, interpenetration control	T.-H. Park, K. Koh, A. G. Wong-Foy, A. J. Matzger, Cryst. Growth Des. 11 (2011) 2059-2063. 10.1021/cg200271e

CN, CN, H, H Me, Me, H, H I, I, H, H	$[Cu_2L_2]$ · Guest, NbO network	Demonstration of network design possibilities, Selective adsorption studies	H. Furukawa, J. Kim, N. W. Ockwig, M. O'Keeffe, O. M. Yaghi, J. Am. Chem. Soc. 130 (2008) 11650-11661. 10.1021/ja803783c
CH_2SMe, H, H, H CH2SO2Me, H, H, H	Doubly-interpenetrated $[Zn_4OL_3]$ IRMOF	Postsynthetic modification of (sulfide to sulfone).	A. D. Burrows, C. G. Frost, M. F. Mahon and C. Richardson, Chem. Commun. (2009) 4218-4220. 10.1039/b906170c

[a] Cambridge Structure Database search, version 5.33, November 2011. Not shown in the Table are the cases, when R= COOH, or an R-R linkage is present.

Synthesis

2,2',6,6'-tetramethyl-4,4'-biphenyldicarboxylic acid, H_2Me_4BPDC, **1**:

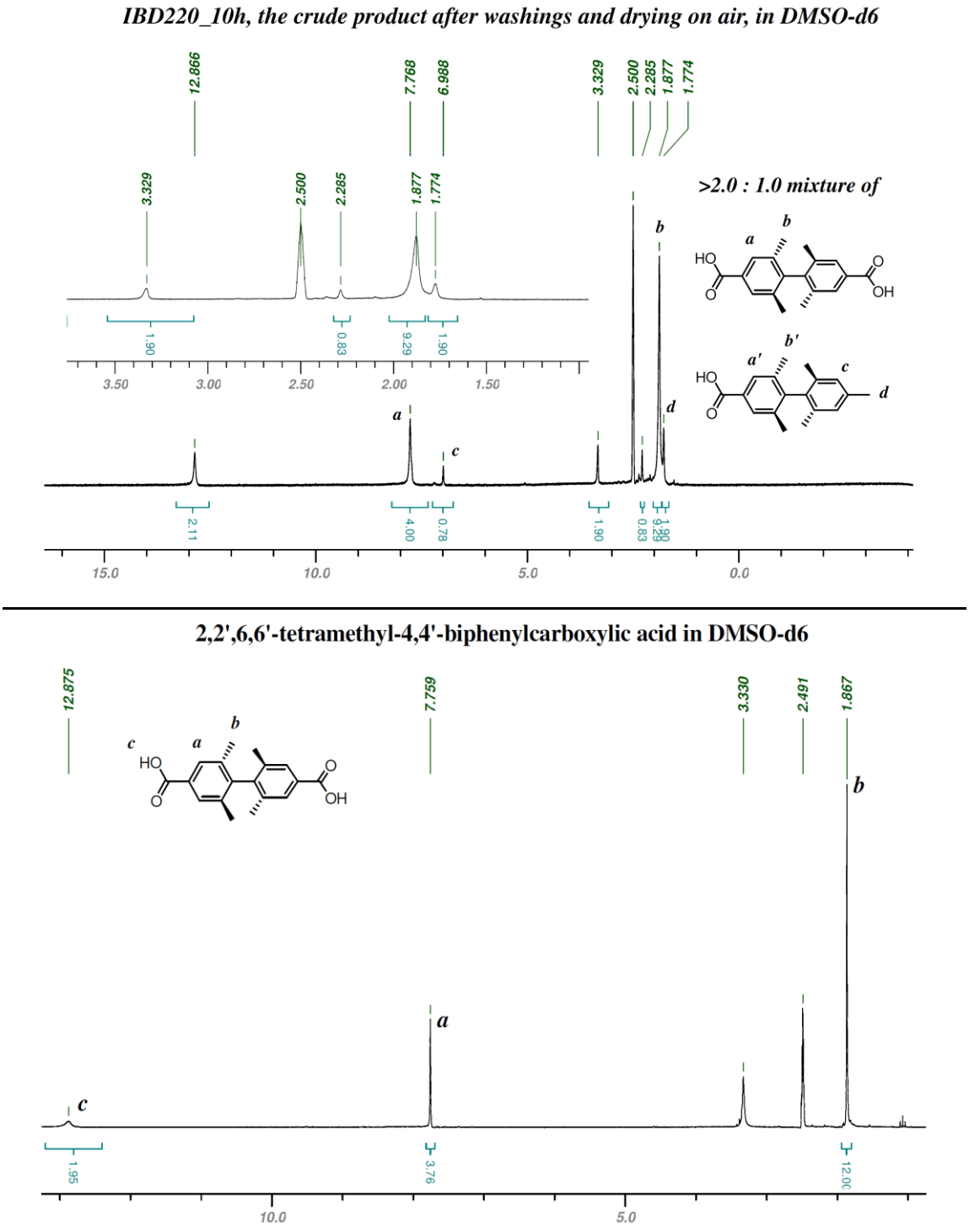


Fig. S1 1H NMR spectra of the crude reaction mixture of H_2Me_4BPDC and 4-(2,4,6-trimethylphenyl)-3,5-dimethylphenylcarboxylic acid with a molar ratio of about 2.1:1.0 (above) and the pure H_2Me_4BPDC (below, crop from the first extraction).

Thermogravimetric - differential thermal analysis (TG-DTA)

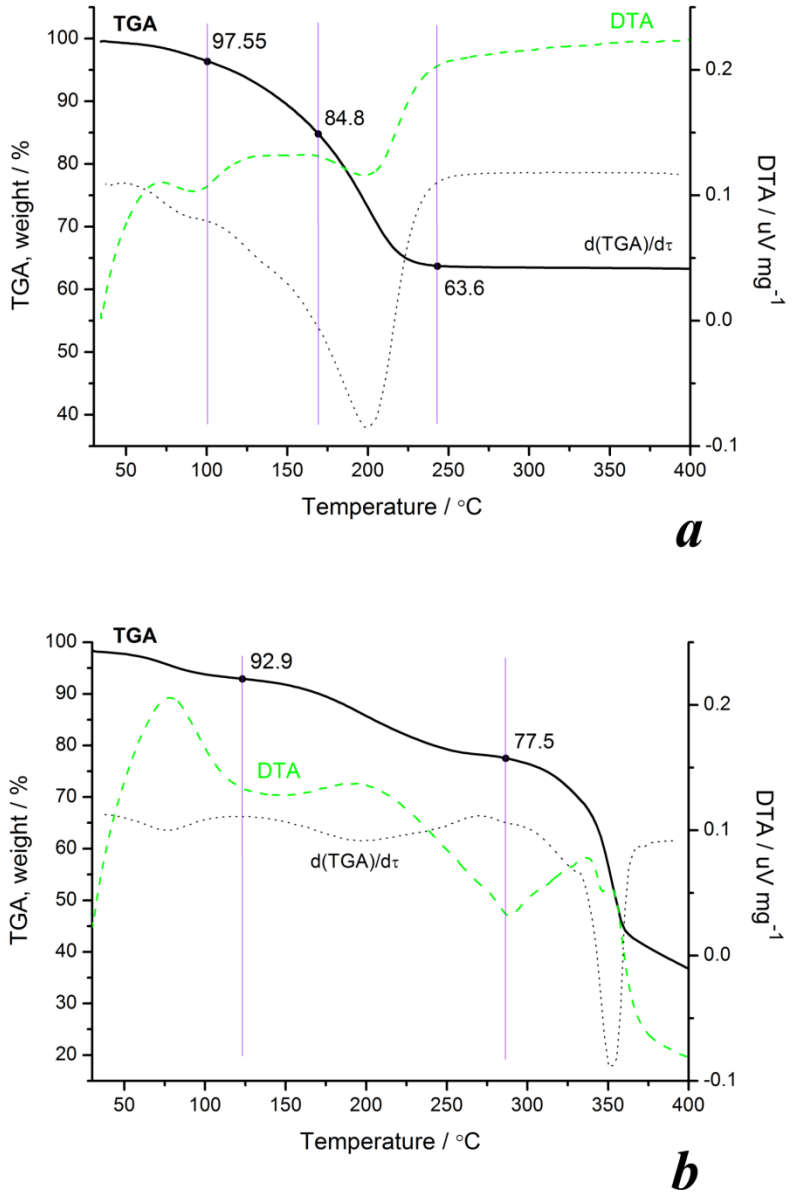


Fig. S2 TG-DTA for **2** · 9 DMF (as synthesized) and **3** (after degassing of the partially solvent-exchanged **3** · 9 DMF)

Infrared (IR) spectra

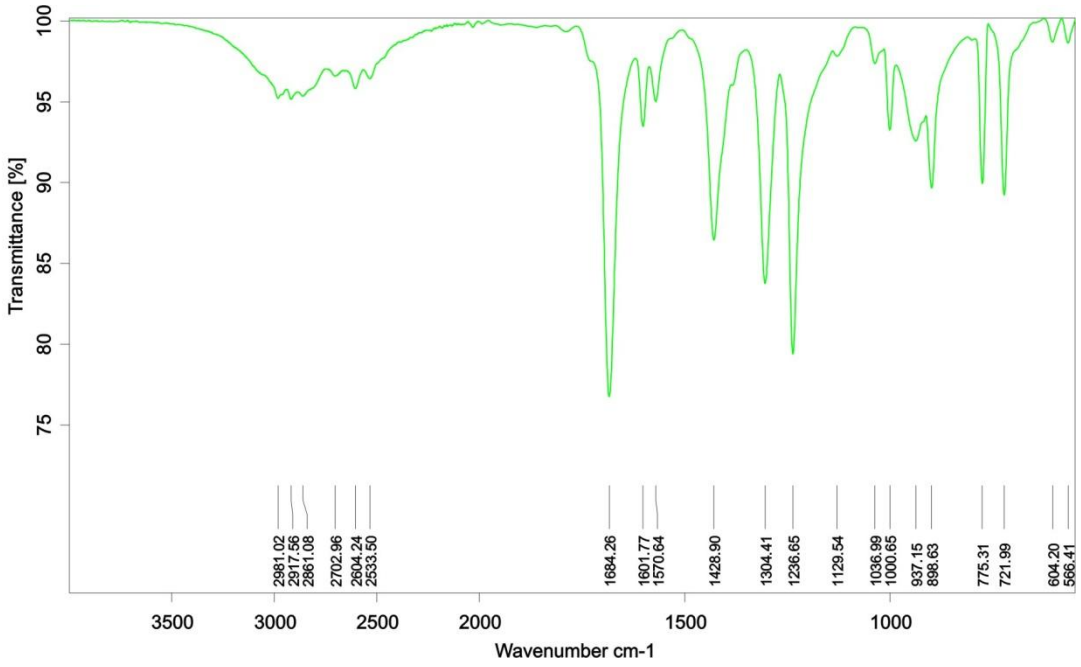


Fig. S3 IR spectrum of H_2Me_4BPDC

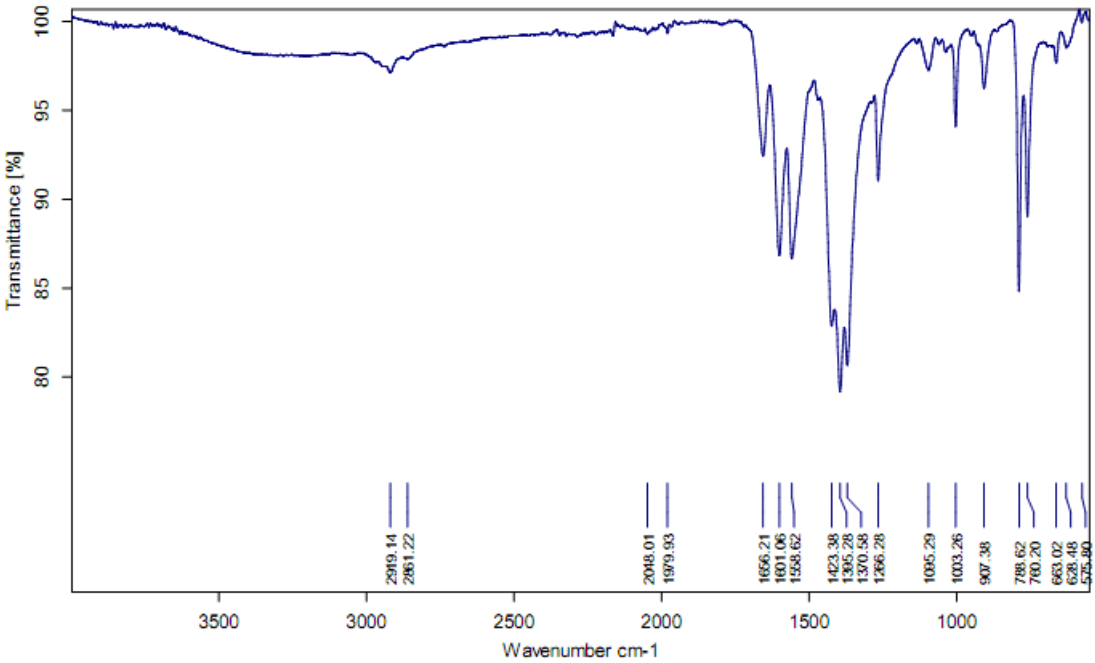


Fig. S4 IR spectrum of $[Zn_4O(Me_4BPDC)_3] \cdot 9$ DMF, **2** · 9 DMF, (as synthesized).

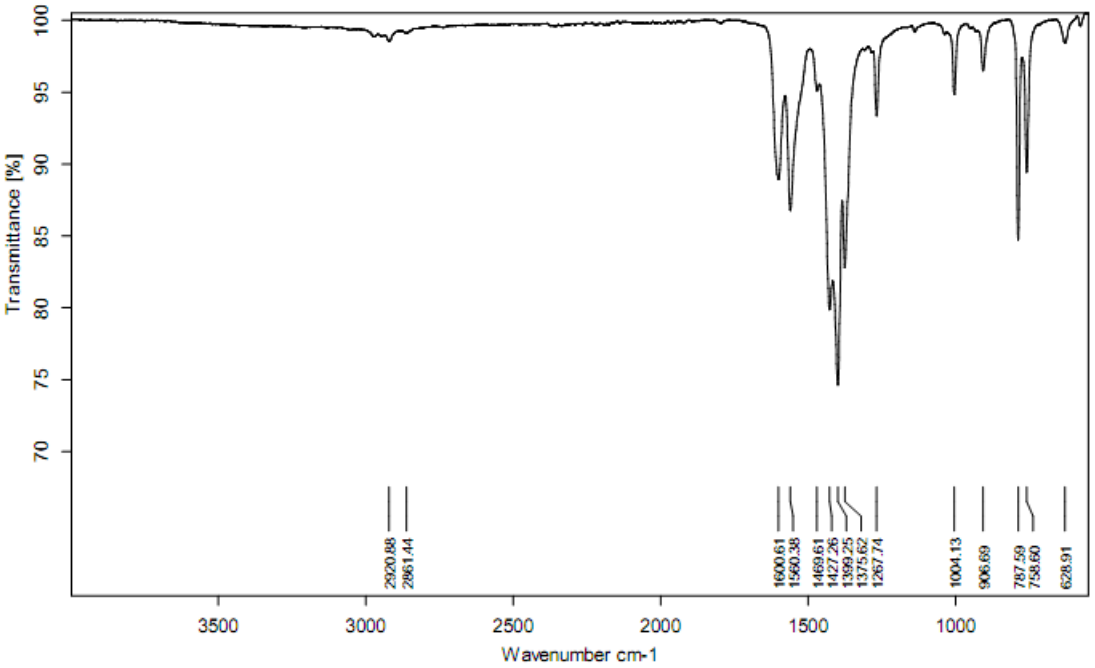


Fig. S5 IR spectrum of $[Zn_4O(Me_4BPDC)_3]$, **2** (degassed).

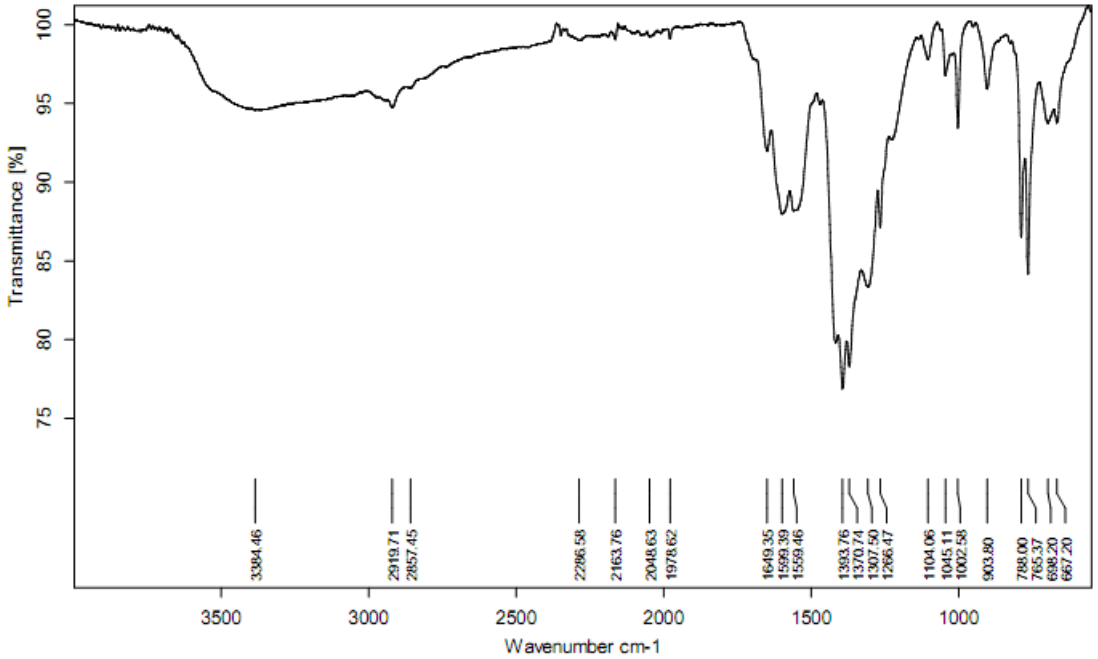


Fig. S6 IR spectrum of $[Cu_2(Me_4BPDC)_2] \cdot 9$ DMF, **3** · 9 DMF (as synthesized).

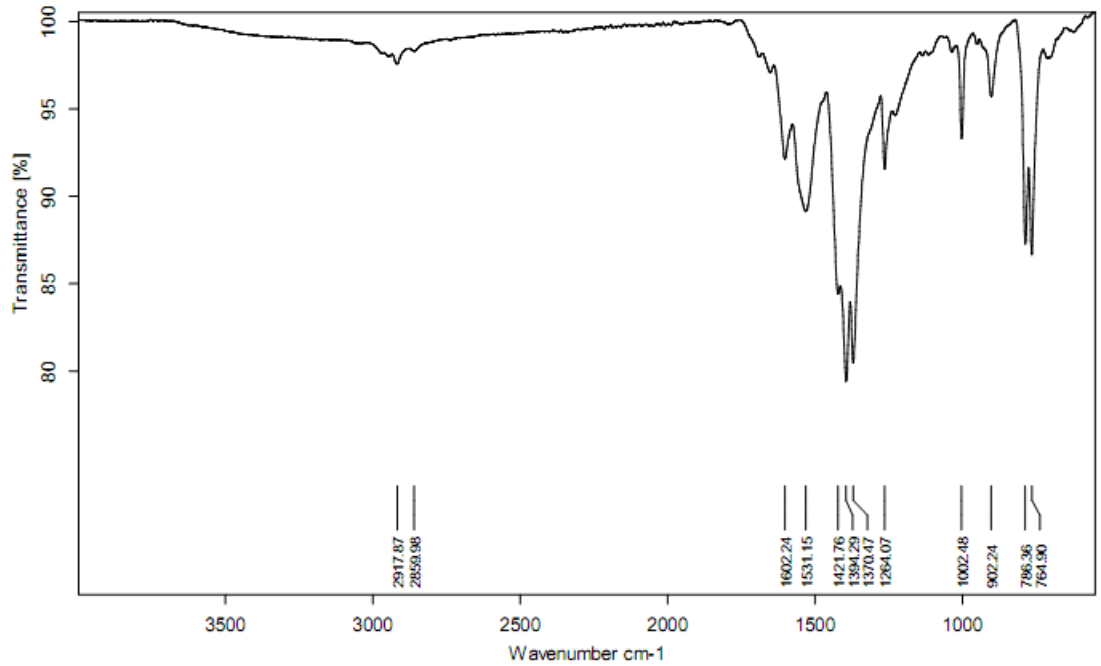


Fig. S7 IR spectrum of $[Cu_2(Me_4BPDC)_2]$, **3** (degassed).

Table S2 Assignments of IR data for the as synthesized and activated samples **2** and **3**.

2 · 9 DMF	**2**	**3** · 9 DMF	**3**	**Assignments**
~3300 (w, vbr)		3384 (w, vbr)		υ N_{amide}H DMF
2919 (vw)	2921 (vw)	2920 (vw)	2918 (vvw)	w; υ C_{Ar}H
				w; υ C_{aliph}H
2861 (vw)	2861 (vw)	2857 (vw)	2860 (vvw)	
1666 (m)		1649 (m)		υ_{as} C=O [DMF]
1601 (s)	1602 (s)	1599 (m)	1602 (m)	υ_{as} CO_2^-
1559 (s)	1560 (s)	1559(m)	1531(m)	υ_{as} CO_2^-
1423 (s)	1427 (s)	1422 (s)	1421 (s)	υ Ph
1395 (s)	1399 (s)	1394 (vs)	1391 (s)	υ_s CO_2^-
1371 (s)	1376 (s)	1371 (vs)	1370 (s)	υ_s CO_2^-, υ CH [(**CH**$_3$)NCHO]
		1308 (s)		
1266 (m)	1268 (m)	1266 (m)	1266 (m)	υ Ph(?)
1095 (w)	-	1104 (w)		DMF (?)
		1045 (m)		
1003 (w)	1004 (w)	1002 (m)	1002 (m)	γ C_{Ar}H, DMF
907 (w)	907 (w)	904 (w)	902 (w)	
789 (s;	788 (s)	788(s)	786(s)	γ C_{Ar}H
760 (s;	759 (s)	765 (s)	762 (s)	δ CO_2^-
663(vw)	629 (vw)	698 (m)		
628 (vw)		667 (m)		

υ - stretching; δ - in-plane deformation; γ - out-of-plane deformation;

v - very; s - strong; m - medium; w - weak; sh - shoulder; br - broad;

subscripts: as - asymmetric; s - symetric

The assignment was done according to [1].

[1] H.T.Varghese, C.Y. Panicker, D. Philip, K. Sreevalsan, V. Anithakumary, Spectrochim. Acta Part A: Molec. Biomolec. Spectr. 68 (2007) 817-822.

Pore size distribution according to DFT calculations (N_2 sorption data)

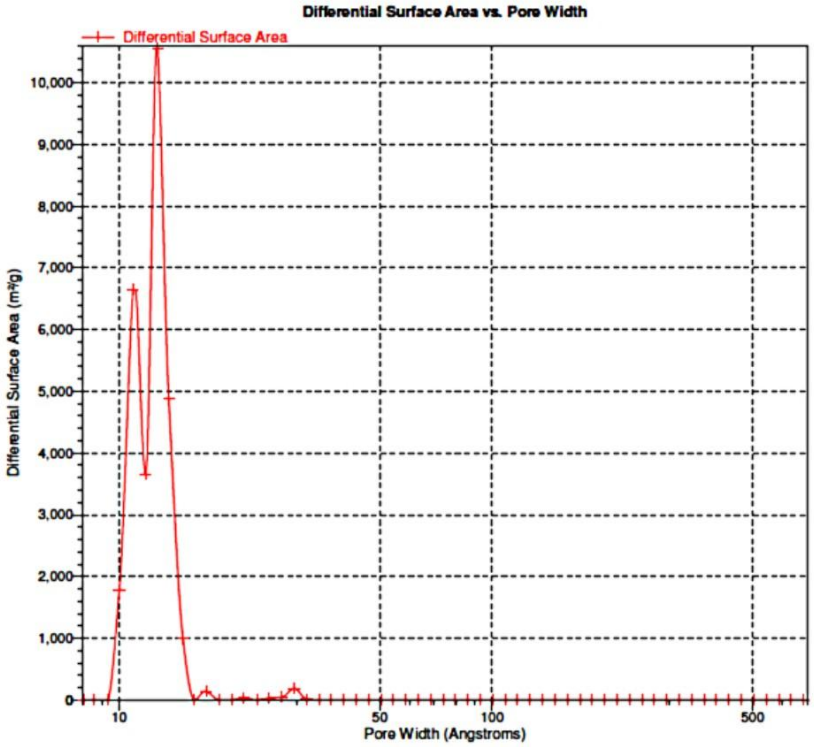


Fig. S8 DFT calculations for **2** (differential surface area (m^2 / g) versus pore width (Å))

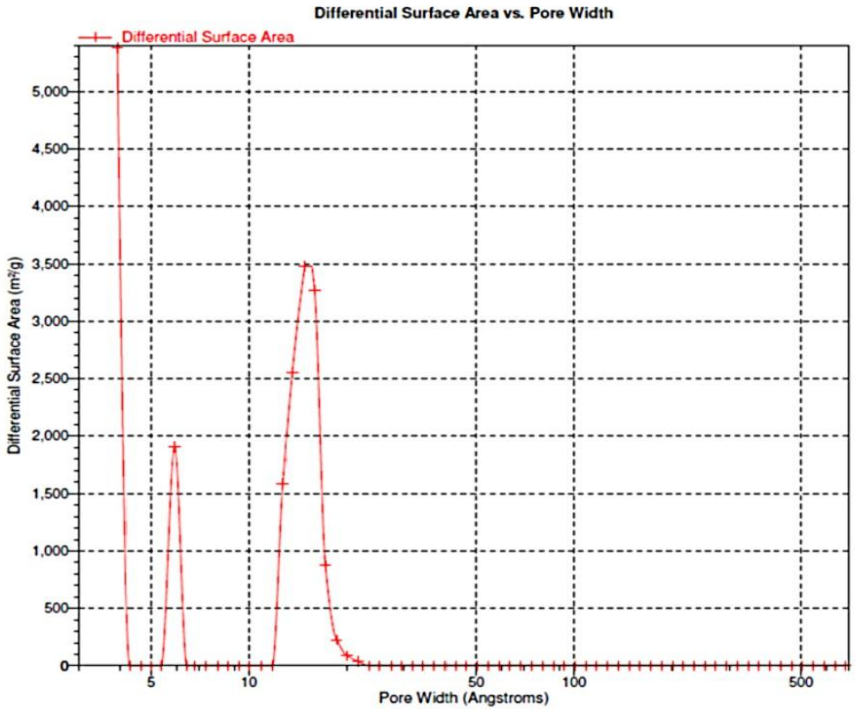


Fig. S9 DFT calculations for **3** (differential surface area (m^2 / g) versus pore width (Å))

Powder X-ray diffraction patterns

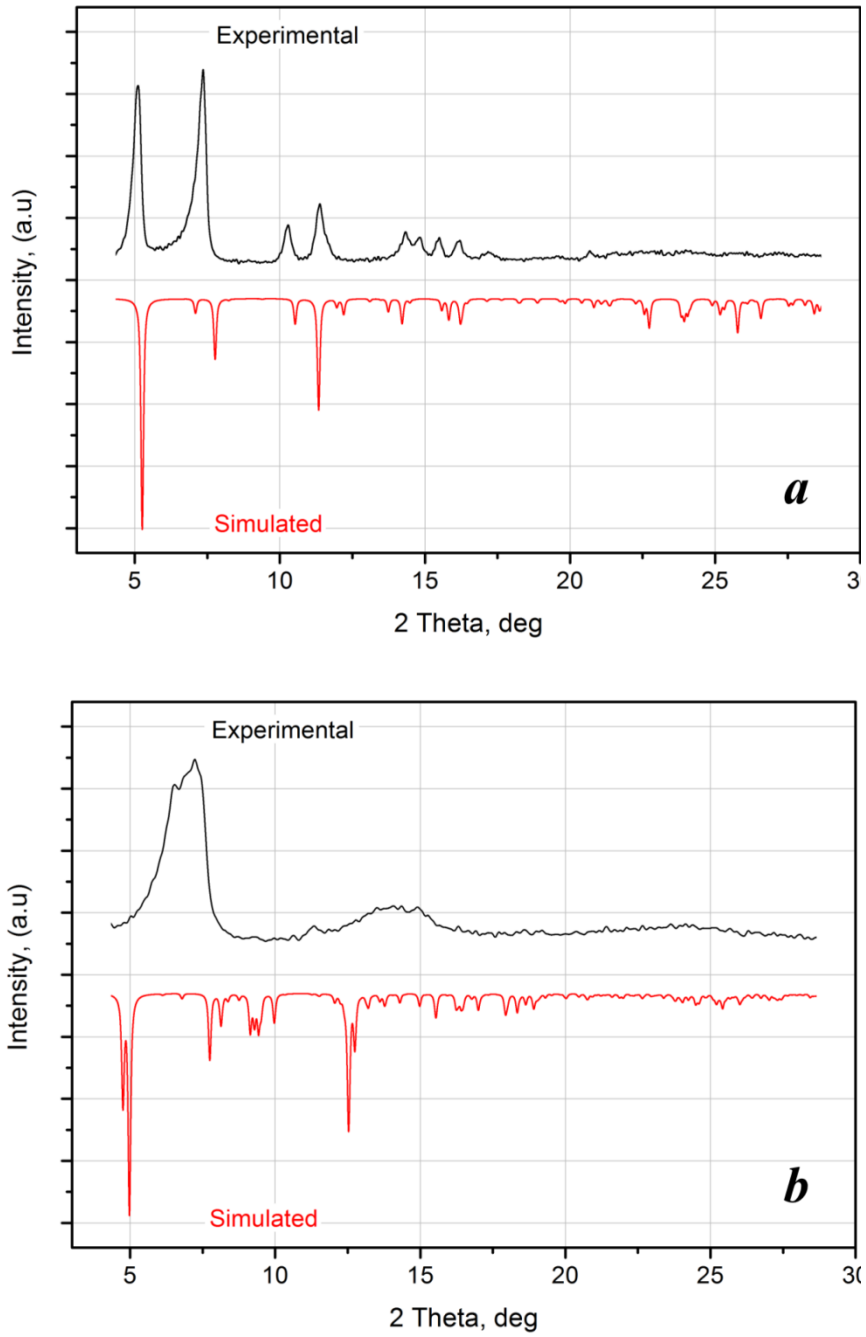


Fig. S10 Powder X-ray diffraction patterns of **2** (a) and **3** (b) after degassing, compared with the simulated diffractogram based on the data of the single crystal XRD structural experiment (all the solvent atoms were removed prior to simulation).

Approximate heat of adsorption (HoA) dependence on adsorbed quantities of CO_2 and CH_4 for 2 and 3^I

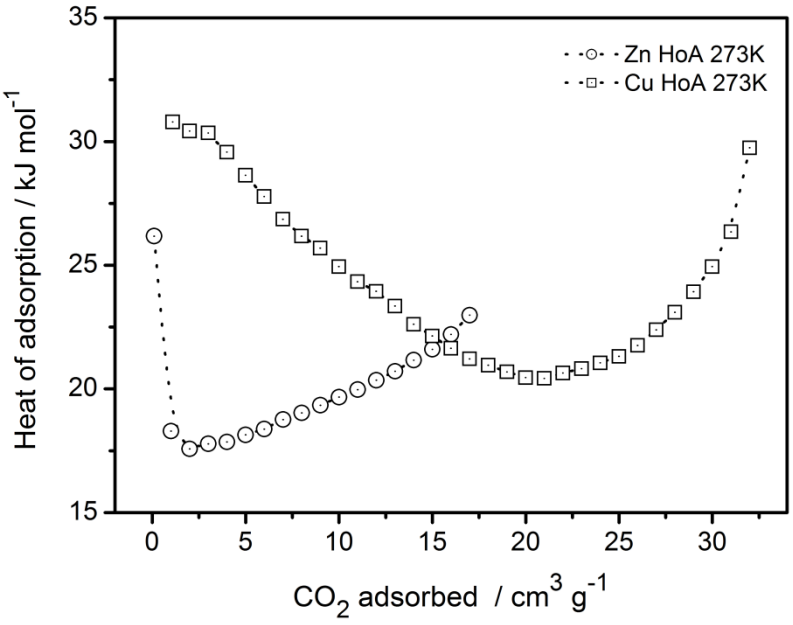


Fig. S10 HoA of CO_2 for the samples **2** (Zn) and $\mathbf{3^I}$ (Cu), 273-293K.

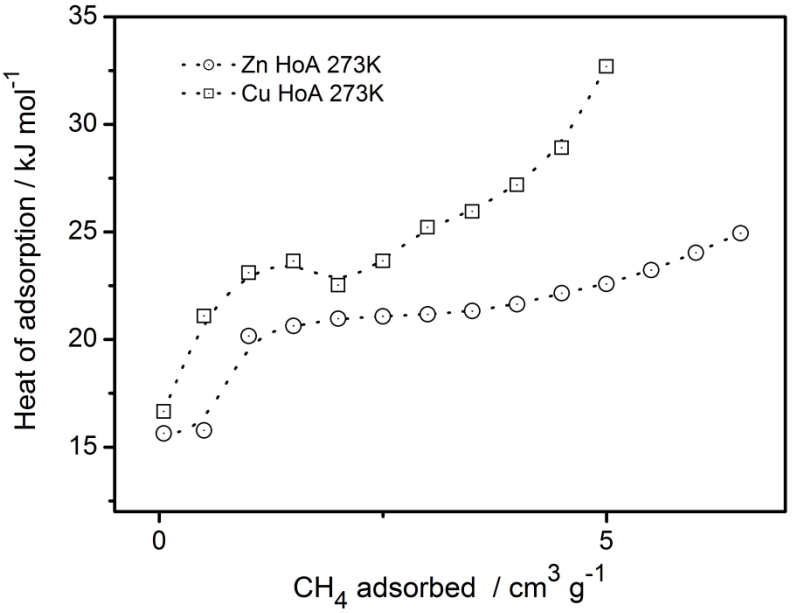


Fig. S11 HoA of CH_4 for the samples **2** (Zn) and $\mathbf{3^I}$ (Cu), 273-293K.