Electronic Supplementary Information (ESI)

Metal-organic framework structures of fused hexagonal motifs with cuprophilic interactions of a triangular Cu(I)₃(pyrazolate-benzoate) metallo-linker

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1. Synthesis

Reagents and solvents were obtained from commercial sources and used as received without further purification. $Cu(NO_3)_2 \cdot 2.5H_2O$ (98%) was purchased from Alfa Aeser, $Zn(NO_3)_2 \cdot 4H_2O$ (98%) from ALFA Chemistry and $Zn(CH_3COO)_2 \cdot 2H_2O$ (98%) from VWR. *N*,*N*-dimethylformamide (DMF) p.a. were obtained from Riedel-de Haën, tetrafluoroboric acid (HBF₄) (48 wt% in H₂O) from Sigma-Aldrich and conc. nitric acid from Chemsolute. The synthesis of 4-(3,5-dimethyl-1*H*-pyrazol-4-yl)benzoic acid (H₂mpba), was carried out according to the literature procedure.¹

The results of synthetic screening and synthesis of the final phase pure compounds are summarized in Table S1 and Scheme S1, S2.

Table S1 Summary of the synthetic conditions for the mixture, containing the phases **1-3** in single crystal form, and the phase pure compounds **1**, **2** (powder) and **3**.

, ,		, , ,					
	Metal salt	Metal salt	Molar ratio	Solvent	HBF ₄	Temp.	Time
	1	2	M1:M2:L		[µL]	[°C]	[d]
1-3 mixed ^a	Cu(NO ₃) ₂ ·2.5H ₂ O	Zn(NO ₃) ₂ ·4H ₂ O	1:0.66:1	DMF	/	80,90	4,7
1	Cu(NO ₃) ₂ ·2.5H ₂ O	Zn(NO ₃) ₂ ·4H ₂ O	1:0.66:1	DMF	0	90	6
2 ^b	Cu(NO ₃) ₂ ·2.5H ₂ O	Zn(CH ₃ COO) ₂ ·2H ₂ O	1:0.75:1	DMF	30	90	9
3	Cu(NO ₃) ₂ ·2.5H ₂ O	Zn(CH ₃ COO) ₂ ·2H ₂ O	1:0.75:1	DMF	10	90	6

^a The conditions correspond to concomitant formation of phases **1-3**, containing single-crystals, suitable for SCXRD determination. Phase **2** is a minor component and could be observed in single-crystal form only under the given conditions.

^b The phase is represented by a powder.



Scheme S1 Synthesis scheme of the compounds 1-3.

Preparation of the **1-3** mixture, containing **2** in single crystal form, suitable for SCXRD analysis:

20.0 mg (0.092 mmol) of H₂mpba, 21.5 mg (0.092 mmol) of Cu(NO₃)₂·2.5H₂O and 16.9 mg (0.065 mmol) of Zn(NO₃)₂·4H₂O were separately dissolved in 1 mL of *N*,*N*-dimethylformamide (DMF). The solutions were then combined in a glass vial equipped with a screw cap, sealed and transferred in a preheated oven and heated 80 °C for four days and up to 90 °C for seven days. A mixture of clear yellow block-shaped crystals and a considerable amount of green amorphous admixture was obtained. The share of **2** varied strongly and in many cases, it was rather small compared to the content of phases **1** and **3**, so that it was not possible to separate a macroscopic amount for analysis.

Synthesis optimization studies for compounds 1-3:



Scheme S2 Results of the optimization studies towards phase-pure compounds (L = H₂mpba).

The optimization studies included the variation of temperature (both maximum temperature and temperature-time profiles), concentration, type and ratio of the precursors, the use of HNO₃ or HBF₄ as an additive . First, the temperature was varied from 40 °C upwards to 110 °C. Temperatures below 80 °C led to amorphous products. Temperatures above 100 °C led to brown/reddish precipitates. At 90 °C, phase-pure 1 was formed. All other temperatures resulted in a mixture of 1 and 3 according to the powder diffractogram and optical examination under the microscope. Next, the molar ratios of Cu:Zn:L (L = H₂mpba) were systematically varied in small steps from 2:1:2 via 1:1:1 to 1:0.75:1 and the various solutions were placed in a preheated oven at 90°C for crystallization. As a result of varying the molar ratios, both amorphous products and mixed phases were obtained. Subsequently, the different molar ratios were also tested at different temperature profiles (T_{max} , time at T_{max} and cooling rates were varied), which led to no improvement regarding phase purity. The use of conc. HNO₃ as a modulator always resulted in a white precipitate at temperatures between 80/90 °C and a reddish/brown precipitation at temperatures above 100 °C. Last but not least, an attempt was made to obtain **2** by changing the starting material $Zn(NO_3)_2 \cdot 4H_2O$ to zinc acetate. Here, the same systematic experiments were carried out as described above. By the use of Cu:Zn:L in a molar ratio of 1:0.75:1 and by adding 10 µL of a 48% min w/w aqueous solution of tetrafluoroboric acid (HBF₄). Phase pure **3** could be obtained at a crystallization temperature of 90 °C for six days. By adding 30 µL HBF₄ and longer synthesis time, 2 could be obtained as an off-white powder (PXRD pattern given in Fig. S3).

2. Single crystal micrographs



Fig. S1 Micrograph images of crystals of **1**: (a) overview; (b) selected crystals for single crystal X-ray structure determination.



Fig. S2 Micrograph images of crystals of **3**: (a) overview; (b) selected crystals for single crystal X-ray structure determination; (c) crystals after drying.

3. Powder X-ray diffractograms



Fig. S3a PXRD patterns of the as-synthesized **1**, **2**, **3** and their simulated PXRD patterns based on the crystal structure. The activated compound **3**-act. and **3**-act. after gas sorption measurements. Furthermore, the PXRD shows an example of the activation attempt of **1** (**1**-act.).

In order to access the purity of the samples a Le Bail fitting was performed (the Le Bail fitting tests the correctness of the cell dimensions and symmetry). As the primitive cell dimensions are principally different – see the next chapter – the Le Bail fitting was more practical compared to Rietveld refinement (the latter is quite cumbersome for such a large cells: the reflections are strongly overlapping after $2\theta = 15^{\circ}$, and while selected regions could be fit with minimal adjustments, it is problematic to cover a significant angular range, assuming the only realistic possibility when most of the atom coordinates and thermal displacement parameters are fixed).

The Le Bail fittings (Fig. 3b,c,d) were performed using the Jana 2006 software. The short conclusion, also based on the change of the refined cell parameters, is that **1** is pure, **2** is quite non-pure, and **3** contains some amount of impurities.







Fig. S3d Le Bail fit for **3**, Rp = 4.24% (2θ = 2-50°). A significant amount of impurities is assumed to be present.

4. Crystallographic data and structure refinement details

The structures were solved by ShelXS and refined by ShelXL using Olex2 [2] (Table S2).

General refinement principles. Multiple fragments of the structures of **1-3** feature disorder, which was explicitly modelled in the case of the Zn atoms (**1**, **3**) or the Me₂NH₂⁺ counter ion (**1**), as well as in the case of the particularly well resolved disorder of the mpba ligand (**1-3**). When the disorder contributions in the latter were small, the ligand molecules were refined using the averaged positions of the constituent atoms, with the interatomic distances restrained using DFIX/SAME/SADI/FLAT restraints (see cif files) and the thermal displacement factors using RIGU/SIMU restraints (see cif files). Several restraints were used to establish chemical and crystallographic satisfying structures. At some points minor disorders were ignored to simplify the overall structure and to emphasize the topological significance. The coordinated solvent molecules were interpreted as belonging to DMF or water molecules (the occupancies were not refined, but fixed at rounded approximate value, typically at 0.5). The non-coordinated solvent molecules, occupying the pores were modelled by the SQUEEZE (Platon) procedure (structures **1** and **3**) or by solvent masking as implemented in OLEX 2 (structure **2**). The hydrogen atoms in all structures were positioned geometrically and refined using riding models with U_{iso}(H) values set equal to $1.2 \cdot U_{eq}(CH_{arom.})/U_{eq}(NH)$ or $1.5 \cdot U_{eq}(CH_3)$.

Compound	1	2	3
CCCD no.	2105164	2105165	2105166
Empirical formula	$C_{118}H_{119}Cu_9N_{22}O_{20}Zn_4$	$C_{159}H_{155}Cu_{12}N_{29}O_{29}Zn_6$	C153H136Cu12N27O32.67Zn7
	C ₁₀₈ H ₉₀ Cu ₉ N ₁₈ O ₁₈ Zn ₄ , C ₂ H ₇ N, C ₂ H ₈ N, 2(C ₃ H ₇ NO)	C144H120Cu12N24O24Zn6, 5(C3H7NO)	C144H105Cu12N24O23.67Zn7, O, 5(H2O), 3(C3H7NO)
M/g·mol ^{−1}	2998.68	4090.81	4095.71
Crystal dimensions/mm	0.09×0.08×0.04	0.25×0.11×0.04	0.20×0.11×0.07

Table S2 Cr	ystal data	and structure	refinement for	1, 2 and 3.
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т/к	100	100	100
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	Сс
<i>a /</i> Å	20.2449(16)	14.5957(2)	41.6099(5)
b/Ă	21.975(2)	21.9429(2)	13.3781(1)
<i>c /</i> Å	22.074(2)	37.0299(3)	44.2601(5)
α /°	119.388(3)	88.0398(3)	90.0522(6)
β /°	93.018(3)	82.7812(8)	117.8069(15)
γ /°	104.938(3)	82.6290(7)	89.9655(7)
V/Å ³	8078.2(12)	11666.43(18)	21792.8(5)
Z	2	2	4
µ/ mm ^{−1}	1.80	2.25	2.54
F(000)	3044	4144	8250
Max./min. transmission	0.911/0.834	1.000/0.578	0.840/0.595
Meas., indep., obs. reflections	34651, 34651, 19641	169664/41507/36374	152524/35511/30944
Rint	0.0515	0.031	0.028
Data/restraints/parameters	34651/376/1556	41507/426/2418	35511/1210/2170
Max./min. $\Delta \rho^{[a]}$ /e Å ⁻³	0.95, -0.82	1.45, -1.91	0.84, -0.81
R, wR(F ²), S [I> 2σ (I)] ^[b]	0.075, 0.208, 1.050	0.064/0.2105/1.156	0.079/0.234/1.07
R, wR(F ²), S [all data] ^[b]	0.144, 0.179, 1.054	0.069/0.2160/1.020	0.083/0.244/8.230
Squeeze void count electrons ^[C]	604	1131	1894

^[a] Largest difference peak and hole. ^[b] $R_1 = [\sum(||F_o| - |F_c||)/\sum|F_o|]; wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}.$ Goodness-of-fit = $[\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}.$ ^[c] Per unit cell.

5. Additional crystallographic images and figures



Compound 1:

Fig. S4 Details of the Zn/Me₂NH, Me₂NH₂⁺ disorder in **1** showing both major and minor components. For the Zn atoms these components are denoted with A (81%) and B (19%) suffixes. The ZnA,B atoms are alternating between two positions corresponding to pseudo-chelating carboxylate groups. The Me₂NH and Me₂NH₂⁺ species are site sharing with the additional hydrogen of the latter shown half-transparent. When the Zn atom is located in the vicinity of the N atom, the latter represents the amine, while in the alternative case, it represents the charge-compensating dimethylammonium cation forming H-bonds with the non-coordinated O-atoms of the carboxylates, Symmetry codes: (i) x, y+1, z+1; (iii) x, y, z+1; (iv) x, y-1, z.



Fig. S5 Space-filling representation of (a) side-view and (b) on-top view (along *b* and *a* axis, respectively) of a section of a single 3-layer slab in **1**. Only the major component of the disordered Zn atoms was used for the drawing. Hydrogen atoms are not shown for clarity, except for the $Me_2NH_2^+$ cation, which is site-sharing with the Me_2NH ligand.



Fig. S6 Space-filling representation of (a) side-view and (b) on-top view (along *b* and *a* axis, respectively) of a section of three polycatenated 3-layer slabs in **1**. The three slabs are differentiated by their green, red and cyan color. Hydrogen atoms are not shown for clarity. Only the major contribution to the disorder of Zn3 and Zn4 was used in the drawing.



Fig. S7 Cu¹...Cu¹ distances (grey dashed lines, in Å) within the $\{Cu_3^{\dagger}(pz)_3\}$ moieties of the metallo-linkers in **1**.



Fig. S8 Representation of the N-H···O hydrogen bonds in **1** (violet-dashed lines). Symmetry codes: (iii) =x, y, 1+z (iv) = x, -1+y, z. The dimethylammonium cation forms three N-H···O hydrogen bonds with the carboxylate groups in the major A component of the disorder; the B component features a similar set of H-bonds). Table S3 summarizes the N-H···O hydrogen bonding.³

D-H··A	D-H/Å	H∙∙A /Å	D∙∙A /Å	D-H··A /°				
N3-H3A ··O1_7 ⁱ ^v	0.91	2.56	3.19	127				
N3-H3A ··O2_9	0.91	1.90	2.70	145				
N3-H3B ··O1_8 ⁱⁱⁱ	0.91	2.34	2.82	113				

 Table S3
 N-H···O hydrogen bonding interactions.

Symmetry codes: (iii) =x, y, 1+z; (iv) = x, -1+y, z.

Compound 2:



Fig. S9 Details of the (a) Zn2 and (b) carboxylate and DMF disorder around Zn5/Zn6 and Zn4, respectively, in **2**. The contributions are Zn2A - 66(4)%, Zn2B - 34(4)%, carboxylate A_5 - 56.6(9)%, carboxylate B_5 - 34.4(9)%, DMF_15 - 85.9(8)%, DMF_16 - 14.1(8)%. Symmetry codes: (i) x-1, y-1, z+1; (ii) x-1, y, z+1.



Fig. S10 Space-filling representation of (a) side-view and (b) on-top view (along *b* and *a* axis, respectively) of two adjacent 2-layer slabs in **2**. The two stacks are differentiated by their green and red color. Only the major components of the disorder was used in the drawing.

Compound **3**:



Fig. S11 The disorder model for the $\{Zn_4(\mu_4-O)(O_2C-)_6\}$ cluster in **3**. All Zn atoms in this SBU are refined with an occupation factor of 80%; the Zn8A and Zn8B components of the Zn8 atom have refined occupation factors of 32.8(7)%, and 47.2(7)%, respectively. (a) Ball and stick representation with atom numbering scheme; Symmetry codes: (iv) x+1/2, y+1/2, z; (v) x+1/2, -y-3/2, z+1/2; (vi) x+1/2, -y-1/2, z+1/2. (b) thermal ellipsoid plot. (c) Simplified interpretation of the disorder as consisting of three overlapping $\{Zn_4(\mu_4-O)(O_2C-)_6\}$ clusters.

6. Topological analysis

	Dimensionality		Point symbol ^b	Vertex symbol	Topolo-	TD10
	[interpenetration];				gical type	
	node stoichiometry/					
	correspondence ^a					
1	2D [2D+2D, parallel, 2-	(C1),(C2):	{4.6^2}2	[4.6.6][4.6(2).6(2)]	-	365
	fold{2D}∩{2D}∩	(Z2):	{4^2.6^6.8^2}	[4.4.6.6.6.6.6.6(2).8.8]		
	→ 3D via infinite	(C3):	{6^3}	[6.6.6(2)]		
	polycatenation];	(Z1):	{6^5.8}	[6.6.6.6.6.8(6)]		
	(3-c)(3-c)(3-c)(4-c)(5-c)					
	/					
	(C1) (C2) (C3) (Z1) (Z2)					
2 ^c	2D;	(C1-4):	{4^3}2	[4.4.4];	3,6L66 ^d	251
	(3-c) ₂ (6-c)	(Z1,2):	{4^3.6^12}	[4(2).4(2).4(2).6(2).6(2).		
	(C1-4)(Z1,2)			6(2).6(2).6(2).6(2).6(2).		
				6(2).6(2).6(2).6(2).6(2)]		
3	3D	(C1-4):	{4.6.8}	[4.6(2).8(6)]	sqc -3,6-	1641
	[3D+3D, 2-fold]	(Z1,2):	{4^2.6^5.8^5.	[4.4.6.6.6.6.6(2).8(2).8(Fdd2-2	
			10^3}	2).8(3).8(3).8(8).10(4).1	(sqc	
	(3-c)2(6-c)			0(10).10(10)]	subnet) ^e	
	(C1,2)(Z1) =					
	(C3,4)(Z2)					

Table S4 Topological overview of structures 1-3.

^a C# - Cu based node, Z# - Zn-based node (Z# corresponds to the numeration in Fig. 9 in the main text).

^b The nodes are listed in the order of appearance in the point symbol, given in ascending order of the ring sizes.

^c Alternative interpretation: 'dual-strand' hexagonal network, which is formed from two stacked hexagonal networks with ½ of the alternating 3-c vertices merged in 6- c vertices.

^d 32 representatives of the 3,6L66 net are listed by the <u>topcryst.com</u> resource (CSD codes are): APEBAZ[†], BETXUW[†], BOXVIV02[†], BOXVOB[†], BOXVUH[†], CAXTOM[†], CIKQEU[†], COFCAD, COFCEH, DUMZAP[†], EPEGUD[†], GICNIR[†], GICNOX, GOYCOP[†], IRUYEB02 (erroneous assignment), ITOKAF, JUNLAI, JUNLAI, LAGKUA[†], LEZMAG[†], NALKIX[†], PELVIO (erroneous assignment), POQSEW[†], QELDIX[†], SEQRUD[†], TAFWOP[†], TAFWUV[†], UGONEL, VUCHIN[†], ZESQIZ[†], ZESQIZ01[†], ZUMKUQ[†] (the entries marked by [†] are coordination polymers based on a tritopic near-triangular carboxylate ligand and approximately following the two stacked **hcb** network morphology, similar to the one found in **2**).

^e 4,8-c **sqc** derived net; **sqc**/I 41/a m d->F d d 2 (a-b,a+b,c; 0,3/4,1/4), bond sets: 2,3,4 (regarding net relations, see ref. ⁴).

5 representatives of the **sqc**-3,6-Fdd2-2 net are listed by the <u>topcryst.com</u> resource: DOLDUE, BUVQIT, QUXZIV, OCOTUX, GOFNEV.



Fig. S12 (a) The dominant hexagonal motif in the structures of **1-3** shown on the example of a fragment in the structure of **1**. (b) The common SBU is the 3-c $\{Cu_3(Me_2pz)_3\}$ motif, while the "extended" Zn-based SBUs are variable. The higher connectedness of the latter ensures additional connectivity between the hexagonal motifs.



Fig. S13 Comparison of the stacking of the {Cu₃(pz)₃} units which is an immanent feature of the structures of **1** (a), **2** (b) and **3** (c). The stacked columns are infinite (*i.e.* there are no gaps) and similar regarding the 'staggered' orientation of the neighboring units. Hence, the columns could be regarded as approximately ABAB type for all the structures, even if the crystallographically independent part of the columns contains 6, 4, and 4 units for **1**, **2** and **3**, respectively.



Fig. S14 The topological representation of a separated hexagonal ring (a), and the mode of their combination, or 'fusing', (b) in the structure of **1**.



Fig. S15 Interlocked local fragments of the structures of 1 (a) and 3 (b) illustrating the interpenetration.



Fig. S16 Highlighting (encircling) of the 4-rings in the fused **hcb** nets of (a) **1**, (b) **2** and (c) **3**. In **2** only 4- and 6-rings are observed as smallest cycles. In **1** and **3** also larger rings appear upon the 'fusing' of the **hcb** layers.

7. Atomic absorption spectroscopy

For atomic absorption spectroscopy measurements (AAS), the samples were dissolved by aqua regia or conc. HCl. For this purpose, a carefully weighted amount of 2.10 mg of sample **1** was mixed with 5 mL of aqua regia and heated to reflux. Heating was continued until only a white residue remained, which could be taken up in 1 mL of conc. HNO₃. The solution was transferred to a 20 mL graduated flask and filled up with Millipore water to the calibration mark. 1 mL of this stock solution was then taken and diluted again in a 20 mL volumetric flask. For the measurement of sample **3**, 2.10 mg of the sample was dissolved in 6 mL conc. HCl with constant heating and stirring. The solution was transferred to a 20 mL graduated flask and filled up with Millipore water to the calibration mark. 1 mL of this stock solution was then diluted again in a 20 mL volumetric flask.

Com-	weighted mass	c(Cu) measured	c(Zn) measured	m(Cu)	m(Zn)	Cu	Zn	Molar ratio found	Molar ratio calculated ^a
pound	[mg] [mg/L] [mg/L]	[mg]	[mg]	found [wt%]	found [Cu:Zn] [wt%]		[Cu:Zn]		
1	2.10	0.72	0.33	0.29	0.13	13.8	6.19	1:0.44	9:4 = 1:0.44
3	2.10	0.83	0.44	0.33	0.18	15.7	8.57	1:0.53	12:7 = 1:0.58

Table S5 Atomic absorption spectroscopy measurement and calculations.

^a based on SCXRD structure

8. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopic (EDX) elemental mapping



Fig. S17 SEM image and corresponding elemental mapping images of copper (cyan) and zinc (orange) in 1.



Fig. S18 SEM image and corresponding elemental mapping images of copper (cyan) and zinc (orange) in 3.



Fig. S19 EDX analysis of 1.

Table S6 Overview of the EDX results of 1 and the calculated Cu/Zn ratio.

Sample	Cu	Zn	Molar ratio Cu/Zn
1 a	10.98	4.60	1: 0.42
1 a	6.89	2.87	1: 0.42
1 b	9.03	4.05	1: 0.45
1 b	11.67	5.28	1: 0.45
		average	1:0.44



Fig. S20 EDX analysis of 3.

Table S7 Overview of the EDX results of 3 and the calculated Cu/Zn ratio.

Sample	Cu	Zn	Molar ratio Cu/Zn
3 a	15.84	8.64	1: 0.55
3 a	5.18	2.72	1: 0.53
3 b	9.94	5.21	1: 0.52
3 b	9.03	4.67	1: 0.52
		average:	1: 0.53

9. Thermogravimetric analysis (TGA) and IR-spectra



Fig. S21 (a) TGA curve of **1** and **2** in the temperature range 20-600 °C with a heating rate of 5 K min⁻¹ under nitrogen atmosphere. The loss of 17.9% corresponds to 9 DMF molecules calc. 17.8% for 9 DMF and the loss of 25.9% corresponds to 18 DMF molecules calc. 26.1% for 18 DMF. Deviations in the found and calculated mass percent for the solvent loss based on the single-crystal X-ray structure results are due to the already occurring solvent loss during sample preparation (drying and weighing) before the TGA measurement. (b) TGA curve of **3** and for **3**-act. in the temperature range 20-600 °C with a heating rate of 5 K min⁻¹ under nitrogen atmosphere. The loss of 20.0% corresponds to 13.6 DMF molecules calc. 20.0% for 13.6 DMF. The small mass increase by **3**-act. is due to balance fluctuation.



Fig. S22 IR-spectra (KBr) of 1, 2, 3 and DMF (NIST, black).^[5]

10. X-ray photoelectron spectroscopy (XPS)



Fig. S23 Survey XP spectrum for 1 (a), 2 (b) and 3 (c).







Fig. S25 High resolution Cu 2p (a) and Zn 2p (b) XP spectrum for 2.



Fig. S26 High resolution Cu 2p (a) and Zn 2p (b) XP spectrum for 3.



Fig. S27 Cu LMM Auger lines for 1 (a), 2 (b) and 3 (c).



Table S8 Atom composition from XPS.

Compound	С	0	N	Cu	Zn	Cu/Zn	Cu/Zn
Compound	[at.%]	[at.%]	[at.%]	[at.%]	[at.%]	exp.	theor.
1	25 17	17 76	0.20	26.02	11.05	9:4 =	9:4 =
L	I 35.17 17.76 8.29 20.83	11.95	1: 0.44	1:0.44			
2	20.20	17.00	7.85 22.93	7 05	22.00	1.1	12:6 =
Z	29.29	29.29 17.06		7.85 22.93	22.80	1.1	1:0.5
2	24.10	10.75		1.54	12:7 =		
3	34.19 19.75	0.204	22.94	14.80	1:54	1:0.58	

Table S9 Quantification of copper and zinc by XPS analysis from the high resolution XP spectra.

Compound		Area	ASF ^a	Cu/Zn	Cu/Zn
				exp.	theor.
1	Copper	3437.72	969.19 ^{b,c}	1:0.72	9:4 =
	Zinc	2614.90	701.80 ^{d,e}		1:0.44
2	Copper	2006.32	565.64 ^{b,c}	1:0.91	12:6 =
	Zinc	1931.07	518.27 ^{d,e}		1:0.5
3	Cooper	1161.41	327.43 ^{b,c}	1:0.73	12:7 =
	Zinc	892.35	239.49 ^{d,e}		1:0.58

^a The <u>a</u>tomic <u>s</u>ensitivity <u>f</u>actor (F_{ASF}) is element specific.; ASF = Area/ F_{ASF} . ^b The Cu 2p3/2 orbital was used for calculations. ^c F_{ASF} = 3.547. ^d The Zn 2p3/2 orbital were used for calculations. ^e F_{ASF} = 3.726.



Fig. S29 High resolution spectra of carbon 1s, nitrogen 1s and oxygen 1s for 1 (a), 2 (b) and 3 (c).

11. Gas sorption measurements



Fig. S30 N₂ sorption isotherm at 77 K for 3-act.



Fig. S31 (a) NLDFT pore size distribution curve for **3**-act. from Ar adsorption isotherm (at 87 K, Fig. 6). The pore size distribution was estimated using non-localized density functional theory (NLDFT) with a "slit-pore model". (b) BET plot for **3**-act. from Ar adsorption isotherm (at 87 K, Fig. 6).



Fig. S32 Henry plots for CO₂ and CH₄ from the adsorption isotherms at 273 K and 293 K for **3**-act. The regression lines are given as red dashed lines.

Table S10 Overview of the results from the Henry-Plots.

Compound	Temp. [K]	Gradient CO ₂ [cm ³ /g]	Gradient CH₄ [cm³/g]	Selectivity CO ₂ : CH ₄
3 -act.	273	0.097	0.020	4.8:1
3 -act.	293	0.052	0.015	3.5:1

Isosteric enthalpy of adsorption calculation

For the virial fit the isotherm measured at two different temperatures are brought into an $\ln p$ vs. *n* form (Fig. S33). The following equation is then used to fit all three isotherms simultaneously, that is with the same fitting parameters a_i and b_i .

$$\ln p = \ln n + \frac{1}{T} \sum_{i=0}^{m} a_i n^i + \sum_{i=0}^{m} b_i n^i$$

In the equation, p is the pressure in kPa, n is the of total amount adsorbed in mmol/g, T is the temperature in K (e.g 273 K, 293 K), a_i and b_i are the virial coefficients and m represents the number of coefficients required to adequately fit the isotherms.



Fig. S33 Virial analysis of the adsorption isotherms for CO_2 (a) and CH_4 (b) adsorption isotherms of **3**-act. at 273 K and 293 K with the fitting parameters (virial coefficients) a_i and b_i .



Fig. S34 Isosteric enthalpy of adsorption, ΔH_{ads} , of CO₂ (a) and CH₄ (b) for **3**-act. from the respective isotherms at 273 K and 293 K (cf. Figure 10).

Theoretical surface area, pore volume and experimental gas uptake

The theoretical surface area and pore volume of **1-3** was calculated using the program CrystalExplorer⁶ following the methodology outlined in ref.⁷, by a 'Void' calculation with Mercury^{8,9} and by a 'Calc Void/Solv' calculation with Platon.³

The coordinated DMF solvent molecules were included in the calculations. Only the minor disordered parts in the asymmetric unit were removed. The calculated values are listed in Table S11.

Table 0121. Sallace aleas and pole tolalles io	leempear	100 =) = 01			1		
	1 (no disorder)		2		3		
Z, M _{asym unit} (g mol ⁻¹),	2, 2998.68,		2, 4090.81,		4, 4095.71,		
V from X-ray structures;	8078.2	8078.2		43	21792.8	3	
cf. Table S2 in Supp. Info.							
CrystalExplorer calculation (crystal voids)			ise	ovalue			
surface area (no disorder) ^b	0.002	0.0003	0.002	0.0003	0.002	0.0003	
- S _{unit cell} (Å ²)	2575	1665	3378	2317	6911	4562	
- specific (m ² g ⁻¹) ^a	2585	1672	2486	1705	2540	1677	
					(low resolution) ^d		
pore volume <i>(no disorder)</i> ^b							
- V _{unit cell} (Å ³)	2910	1687	4670	3078	8046	4735	
- specific (cm ³ g ⁻¹) ^a	0.292	0.169	0.344	0.227	0.296	0.174	
					(low res	solution) ^d	
Mercury 'Void' calculation							
(probe radius 1.2 Å, grid spacing 0.7 Å)	calc. usi	calc. using solvent accessible surface					
void volume, V _{unit cell} (Å ³) (no disorder) ^b	931		2002		2629		
(% of unit cell volume V)	(11.5)		(17)		(12)		
- specific (cm ³ g ⁻¹) ^a	0.093		0.147		0.097		
	calc. usi	ing contac	t surface	!			
void volume, V _{unit cell} (Å ³) <i>(no disorder)</i> ^b	2671		4436		7243		
(% of unit cell volume)	(33)		(38)		(33)		
- specific (cm ³ g ⁻¹) ^a	0.268		0.326		0.266		
Platon 'Calc Void/Solv' calculation							
tot. pot. solv. area volume (SAV) (Å ³)	2749		4537		7602		
(% of unit cell vol. V) (<i>no disorder</i>)	(34)		(39)		(35)		
- specific pore volume (cm ³ g ⁻¹) from SAV ^a	0.276		0.334		0.279		
experimental gas uptake							
CO ₂ (cm ³ g ⁻¹) (273 K, 760 Torr)					78		
CO ₂ (mmol·g ⁻¹) (273 K, 760 Torr) ^e						3.43	
- x 44 g/mol = CO ₂ (g/g)	-		-		0.15		
/ ρ_{CO2} ^c = CO ₂ (cm ³ liq. CO ₂ /gMOF)	-		-		0.15		
pore filling CO ₂ (cm ³ liq. CO ₂ /gMOF) /							
specific pore volume (cm ³ g ⁻¹) from SAV x	-		-		54		
100%							

Table S11.	Surface areas	and pore	volumes fo	or compound	ls 1 . 2	and 3
	surrace areas					

^a Specific surface area calculated according to $(S_{unit cell} \times N_A)/(Z \times M_{asym unit})$; specific pore volume calculated according to $(V_{unit cell} \times N_A)/(Z \times M_{asym unit})$ or $(SAV \times N_A)/(Z \times M_{asym unit})$; N_A = Avogadro's constant, 6.022 \cdot 10²³ mol⁻¹, Z = number of asymmetric formula units, $M_{asym unit}$ = molecular weight of asymmetric formula unit (in g mol⁻¹). As a help to reproduce the specific number the values for Z and $M_{asym unit}$ from the X-ray structures are included.

^b Disorder in **1**, **2** and **3** removed, leaving only the major contributions.

 c Density of 1.032 g cm $^{-3}$ of liquid CO $_2$ at 253 K to approximate the volume of CO $_2$ adsorbed in the MOFs at 760 Torr (1.0 bar) and 273 K

^d Due to the large unit cell, the calculation had to be carried out with CrystalExplorer17.5 Version 3.1, Revision 1448, and using "Resolution: Low" upon surface generation. Attempted calculations with CrystalExplorer21.5, Version 21.5 failed.

^e Value in cm³ g⁻¹ divided by 22.711 L/mol (= cm³/mmol) (22.711 L is the molar volume of an ideal gas at 1 bar and 273 K).

Comment on the results from CrystalExplorer:

Fig. S35-S37 illustrate the iso-surface areas at 0.002 and 0.0003 au around the pore/channel windows.

The 0.0003 au calculated surface area is seen as a better choice for estimating the internal surface area in porous materials than the 0.002 isosurface.⁷ The value of 0.002 au corresponds approximately to a smoothed van der Waals surface and 0.0003 au seems to be more appropriate for mapping "empty" space in molecular crystals.⁷ From the above comparison in Table S11 it is, however, apparent that the isovalue of 0.002 gives a better match in the pore volumes which are also derived from Mercury and Platon.

The calculated surface area presents an upper bound which can be approached but it will be physically unrealistic to expect that the experimental measurements will surpass the calculated value.



(b)

Fig. S35 Void surfaces (a) 0.002 au and (b) 0.0003 au around pore windows in **1** superimposed on spacefilling representations of the unit cell content, view along *a*. From the vertical and horizontal axis lengths of of *c* = 22.07 and *b* = 21.98 Å, respectively, the open channel cross-sections are measured to about 3.3 x 6.6 Å (0.002 au) and 2.2 x 5.5 Å (0.0003 au).



(b)

Fig. S36 Void surfaces (a) 0.002 au and (b) 0.0003 au around pore windows in **2** superimposed on spacefilling representations of the unit cell content, view along *a*. From the vertical and horizontal axis lengths of b = 21.94 and c = 37.03 Å, respectively, the open channel cross-sections are measured to about 4.5 x 7.0 Å (0.002 au) and 3.2 x 5.7 Å (0.0003 au).



view along *b* (*a* to bottom, *c* to right)



view along c (a to right, b to top)



Fig. S37 Void surfaces (a) 0.002 au and (b) 0.0003 au around pore windows in **3** superimposed on spacefilling representations of the unit cell content. From the axis lengths of a = 41.61, b = 13.38 and c = 44.26 Å the open channel cross-sections are measured to about 4.6 x 4.6 Å (0.002 au) and 3.3 x 3.3 Å (0.0003 au).

Images from Mercury void calculations

In Mercury⁸ voids can be calculated using two different methods (probe radius 1.2 Å, grid spacing 0.7 Å): - Calculate voids using Solvent Accessible Surface gives the volume which can be occupied by the center of a probe of a given radius.

- Calculate voids using Contact Surface maps the volume that can be occupied by the full probe (including its radius) and thus gives a better estimate of the volume that could be filled by solvent or guest molecules.
- A full description of these two different surfaces and the ways in which they can be used is given in: L. J. Barbour, *Chem. Commun.* 2006, 1163–1168.

The dimensions of the crystallograpic axes are given to facilitate the estimate of the cross-sections of the pore apertures:

	1	2	3
a/Å	20.2449(16)	14.5957(2)	41.6099(5)
b/Å	21.975(2)	21.9429(2)	13.3781(1)
c/Å	22.074(2)	37.0299(3)	44.2601(5)

Mercury-calculated void with *solvent accessible surface*:



Fig. S38 Images from Mercury void calculations for compound **1** (no disorder), top: view along *a* (*b* to right, *c* to bottom); bottom: view along *c* (*a* to right, *b* to bottom).



Fig. S39 Images from Mercury void calculations for compound **2** (no disorder), top: view along a (c to right, b to bottom); bottom: view along b (c to right, a to bottom).



Fig. S40 Images from Mercury void calculations for compound **3** (no disorder), top: view along *c* (*a* to right, *b* to bottom); middle: view along *a* (*c* to right, *b* to top); bottom: view along *b* (*c* to right, *a* to bottom).

Mercury-calculated void with *contact surface*:



Fig. S41 Images from Mercury void calculations for compound **1** (no disord), top: view along *a* (*b* to right, *c* to bottom); bottom: view along *c* (*a* to right, *b* to bottom).



Fig. S42 Images from Mercury void calculations for compound **2** (no disorder), top: view along a (c to right, b to bottom); bottom: view along b (c to right, a to bottom).



Fig. S43 Images from Mercury void calculations for compound **3** (no disorder), top: view along *c* (*a* to right, *b* to bottom); middle: view along *a* (*c* to right, *b* to top); bottom: view along *b* (*c* to right, *a* to bottom).

12. Linker flexibility



(a) bbc-linker in DUT-40(Zn) (CCDC 850713);¹⁰ the symmetry-equivalent biphenyl-carboxylate groups at left bend up and down of the central ring plane by 3.1(5)°.



(b) bbc-linker in DUT-44(Co) (CCDC 850717);¹⁰ the biphenyl-carboxylate group at left bends down of the central ring plane by $5.0(1)^\circ$, the one at front by $6.3(1)^\circ$, the one at rear-right by $5.2(1)^\circ$.



(c) bbc-linker in MOF-1005(Zr) (from deposited file MOF-1005_290K1_DMF.cif);¹¹ the three symmetryequivalent biphenyl-carboxylate groups bend out of the central ring plane by 5.1(5)°.



(d) bte-linker in MOF-1004(Zr) (from deposited file MOF-1004_100K_DMF.cif);¹¹ the two symmetry-equivalent ethinyl-benzoate groups at left and to the rear bend out of the central ring plane by 4(1)°, the one at right by 10(1)°. At the same time the two symmetry-equivalent ethinyl-benzoate groups (pink lines) deviate from a near 120° orientation (blue lines) by 14.5(1.5)° so that the angle between the pink lines is 94°.

Fig. S44 Examples of distortions in the trigonal linkers (a)-(c) 4,4',4''-(benzene-1,3,5-triyl-tris(benzene-4,1-diyl))tribenzoate (bbc³⁻) = 1,3,5-tris(4'-carboxy[1,1'-biphenyl]-4-yl-)benzene (tcbpb³⁻)

and (d) 4,4',4''-(benzene-1,3,5-triyl-tris(ethyne-2,1-diyl))tribenzoate (bte³⁻). The plane through the central benzene ring is shown in blue. The lines from the carboxylate C-atoms to the central benzene centroid are given in pink.



Linker plane through	Cu11-12-13		Cu21-22-23		Cu31-32-33		Cu41-42-43
line to Cu₃ centroid from	angle line-plane (°)	line to Cu₃ centroid from	angle line-plane (°)	line to Cu₃ centroid from	angle line-plane (°)	line to Cu₃ centroid from	angle line-plane (°)
C12_1	14.5(1)	C12-4	8.6(1)	C12_7	7.9(1)	C12_10	0.7(1)
C12_2	3.8(1)	C12_5	7.8(1)	C12_8	6.0(1)	C12_11	11.0(1)
C12_3	1.9(1)	C12_6	7.6(1)	C12A_9	1.1(1)	C12_12	6.8(1)

Fig. S45 Distortions in the $Cu_3^{1}(mpba)_3$ ³⁻ metallo-linkers in the example of the structure of **2**, $[Zn_6\{Cu_3^{1}(mpba)_3\}_4(DMF)_5]$, with its four crystallographically different $Cu_3^{1}(mpba)_3$ ³⁻ metallo-linkers. The plane through the three Cu atoms is shown in blue. The lines from the carboxylate C-atoms to the Cu₃ centroid (white atom) are given in pink.

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