Electronic Supplementary Information (ESI)

Flexible bifunctional monoethylphosphonate/carboxylates of Zn(II) and Co(II) reinforced with DABCO co-ligand: paradigmatic structural organization with pcu topology

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1 ¹H, ¹³C, and ³¹P NMR spectra

1.1 Methyl 4-iodobenzoate



Fig. S1 ¹H NMR spectrum (300 MHz, CDCl₃) of methyl 4-iodobenzoate.



Fig. S2 ¹³C NMR spectrum (75 MHz, CDCl₃) of methyl 4-iodobenzoate.

1.2 Methyl-4-(diethoxyphosphoryl)benzoate



Fig. S4 ¹³C NMR spectrum (75 MHz, DMSO-d₆) of methyl-4-(diethoxyphosphoryl)benzoate.



Fig. S5 ³¹P NMR spectrum (121 MHz, CDCl₃) of methyl-4-(diethoxyphosphoryl)benzoate.



1.3 O-ethyl-P-(4-carboxyphenyl)phosphonic acid, H₂EtBCP

Fig. S6 ¹H NMR spectrum (300 MHz, DMSO-d₆) of H₂EtBCP.



Fig. S7 ¹³C NMR spectrum (75 MHz, DMSO-d₆) of H₂EtBCP.



Fig. S8 ³¹P NMR spectrum (242 MHz, DMSO-d₆) of H₂EtBCP.

2 Overview of surface area and CO₂ adsorption data for (monoalkyl)phosphonate MOFs based on selected ligands.



Fig. S9 Overview of high symmetry trigonal and tetragonal ligands used for the synthesis of MOFs.^{1,9,10,11,12}



Fig. S10 Overview of monoalkyl-phosphonate ligands used for the synthesis of MOFs.^{2,3,4,5,6,7,8}

Table S1. Surface area and CO_2 adsorption data for selected monoalkyl-phosphonate and phosphonate-based MOFs.

Lineud	MOE		Surface Area	CO ₂ uptake [mmol g ⁻¹]			Ref.
Ligand	INIOF	wetai	[m ² g ⁻¹]	293 K	273 K	195 K	
Monoalkyl-phosphonate-carboxylate MOFs							
HaFtBCP	[M ₂ (EtBCP) ₂ - (DABCO) _{0.5}] · 2DMA	Со	327 ^{a,c} ; 310 ^{b,c}	1.0	1.5	5.7	This
		Zn	330 ^{a,c} ; 310 ^{b,c}	0.9	1.4	5.1	work
Monoalkyl-p	hosphonate MOFs						
H_2Et_2L	CALS-4	Со	140ª; 139 ^b	/	/	1.9	2
H _a Ft _a BDP	[M(Ft ₂ BDP)]	Cu	/	/	0.1	/	3
		Zn	312 ^{a,c} ; 264 ^{b,c}	/	1.1	2.8	4
H ₂ Me ₂ BDP	[Cu(Me ₂ BDP)]	Cu	153 ^{a,c} ; 150 ^{b,c}	/	1.4	/	3
H _a Ft _a BPDP	[M(Et ₂ BPDP)(TIB)	Cd	16 ^{a,c}	/	/	1.3	5
	$(H_2O)_2] \cdot 6H_2O$	Cu	70 ^{a,c}	/	/	1.8	
H ₄ Et ₄ L	CALF-25	Ва	385 ^b	/	0.9	4.0	6
H ₃ ⁱ Pr ₃ BTP	CALF-30		312 ^{a,c} ; 244 ^{b,c}	/	/	1.0	7
H ₃ Et ₃ BTB	CALF-33Et ₃	Cu	1030ª; 842 ^b	~0.6	0.9	/	8
H_4Et_2BTB	CALF-33Et ₂ H		950ª; 810 ^b	~1.2	1.8 ^d	/	
Phosphonate	e-MOFs						
H ₆ L	PCMOF20		180 ^b	/	1.9	/	9
H ₈ TPPM	SZ-1		17ª; 10 ^b	/	/	0.8	
H ₈ TPPA	SZ-2	Zr	357ª; 225 ^b	/	/	5.8	10
	SZ-3		695ª; 572 ^b	/	/	5.3	
H ₆ PPT	CAU-14	Cu	647 ^b	1.1 ^e	/	/	11
H ₆ BTBP	[Sr ₂ (H ₂ BTBP)- (CH ₃ OH)(H ₂ O) ₄]	Sr	146 ^{b,d}	/	/	/	12

^a Langmuir surface area; ^b BET surface area; ^c calculated from CO_2 adsorption isotherm at 195 or 273 K.^d 278 K measurement temperature; ^e 298 K measurement temperature.

3 Synthesis, verification of the role of formic acid, and PXRD patterns for [Zn₂(EtBCP)₂(Solv)] · Solv', 1

3.1 Synthesis and the PXRD patterns

Synthesis of 1: a mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (51.7 mg, 0.17 mmol), H_2EtBCP (20 mg 0.09 mmol), DMF (2 mL) and 0.1 mL conc. HNO₃ was transferred in a Pyrex tube. The tube was transferred to a programmable oven and heated up to 120 °C in 2 h. During the second step, the temperature was raised linearly to 130 °C within three days and then cooled down in 24 h to room temperature. A reasonably crystalline probe of $[Zn_2(EtBCP)_2(Solv)] \cdot Solv'$ consisting of single crystals suitable for SCXRD analysis was obtained in a yield of 26 mg (52%).

Unlike the reliable syntheses of **2** and **3**, the synthesis of **1** is very sensitive to admixtures and/or the regime of recrystallization. The crystallization outcome was not well-reproducible. Only once it was possible to obtain single crystals suitable for XRD structure determination, however the phase was not pure. A reasonably phase-pure sample was obtained in a few repeated experiments according to the reasonably good PXRD pattern matching with the simulated one (Fig. S11 demonstrates the comparison between the activated and the as-synthesized sample for the case when the best match was reached). The material lost its crystallinity to a significant extent after activation (Fig. S11), but it is the low reproducibility, which put an end to further investigations.



Fig. S11 The PXRD patterns of: [Zn₂(EtBCP)₂(Solv)] · (Solv'), 2 simulated from X-ray single crystal diffraction data (red);
2 bulk sample, as synthesized (black);

2' activated sample (grey).

3.2 The potential role of *in-situ* formed formic acid

The single crystal XRD structure (see Chapt. 4) features a molecular moiety, which could be a bridging ligand, with a role, similar to the role of DABCO in **2**. The fragment could be potentially interpreted as a formate bridge, as formic acid is indeed present in the reaction medium due to the hydrolysis of DMF under elevated temperatures by the residual water impurities, including the water introduced

by the metal salt hydrates. An indirect supporting argument is that the formation of **1** is DMF specific and could not be observed in DMA, which should kinetically be more stable towards hydrolysis.

The structural motif of **1** was reasonably well established, and the structure organization principle is similar to **2**, which imposes the presence of a non-charged bridge. Hence, formate could not be the dominant representative of the potentially site-sharing ligands instead of DABCO, but it might play an important role as a modulator, guiding the assembly of **1**.

In order to verify a possible role of the formic acid, we performed three comparative experiments. They were carried out under strictly the same conditions except the varied amount of formic acid (0, 10 and 65 molar equivalents compared to the amount of the ligand; in the latter case no HNO_3 was added). The amounts of other reactants were the same as in the standard synthesis, described above. After 3 days of linear temperature increase form 120 °C to 130 °C the sample with 65 equivalents of formic acid did not demonstrate the formation of a precipitate, so the reaction time for all samples was extended further for 3 days at 130 °C. The prolonged heating increased the yield of **1** in the experiment with 0 eq. and 10 eq. of formic acid and caused the formation of a crystalline precipitate in the experiment with 65 eq. of formic acid.

The micrographs (Fig. S12) and the comparative PXRD patterns (Fig. S13) demonstrate, that in the presence of formic acid a new phase forms. The new phase has a morphology of spherical "concretions" composed of very thin needles; the size of the crystallites is way below the necessary size for the single crystal XRD structure determination. The PXRD confirms that the new phase is significantly different from **1**, though it might bear some local similarities. No further investigation of the new phase was attempted.





(c)

Fig. S12 Micrographs of the products in the comparative syntheses with (a) 0 equivalents of formic acid compared to H_2L ; (b) 10 eq. of formic acid; (c) 65 eq. of formic acid.



Fig. S13 Comparison of the PXRD patterns for: the simulated **1**, (red), derived from experimental SCXRD; the as-synthesized **1** (black); the as-synthesized comparative sample with 10 eq. of formic acid (blue); the as-synthesized comparative sample with 65 eq. of formic acid (purple); the as-synthesised $[Zn_2(EtBCP)_2(DABCO)_{0.5}] \cdot 2DMA$, **2**.

4 Crystallographic data and structure refinement for [Zn₂(EtBCP)₂(Solv)] · Solv[′], 1

The *O*-ethoxyphosphonate group of the ligand is disordered over two mirror plane related positions. Its ethoxy fragment (OEt) was refined using distance and thermal displacement parameter restraints using DFIX and SIMU instructions. The latter was also applied for the C atoms of the phenyl group.

The aromatic hydrogen atoms of the ligand were positioned geometrically (C-H = 0.95 Å) and refined using a riding model (AFIX 43) with $U_{iso}(H) = 1.2U_{eq}(C)$. The ethylene and methylene hydrogen atoms of the phosphonate group of the ligand, H_2 EtBCP, were positioned geometrically (d(C-H) are 0.96 Å for CH₂ and 0.97 Å for CH₃) and refined using a riding model (AFIX 23 for ethylene -CH₂-, AFIX 33 for CH₃), with $U_{iso}(H) = 1.2^*U_{eq}$.

Unfortunately, it was not possible to establish the nature of the molecule coordinated to the apical position of the paddle-wheel unit in **1** (the hypothesis regarding the possible role of the formate anion, similar in size, was tested with a negative result; see Chapt. 3.2). The electron densities of the respective part of the structure were modeled by an "O(0.5)-P(0.25)"-fragment (the numbers in the brackets are the respective occupation factors). The atoms belonging to the fragment are marked with X and Y atoms on the picture of the extended asymmetric unit (Fig. S14).



Fig. S14 The extended asymmetric unit of $[Zn_2(EtBCP)_2(Solv)] \cdot Solv'$, **1**, thermal ellipsoid plot representation (50%). Symmetry transformations: (i) y, -x+1, z; (ii) -y+1, x, z; (iii) -x+1, -y+1, z; (iv) -x+1, -y+1, -z+1; (v) y-1/2, -x+3/2, -z+1/2; (vi) -x+1, -y+2, z; (vii). -y+3/2, x+1/2, -z+1/2; (viii) -x+1, y, -z+1; (ix) x, y, -z+1; (x) y, -x+1, -z; (xi) -x+1, -y+1, -z.



Fig. S15 The disposition of two adjacent paddle-wheel SBUs in $[Zn_2(EtBCP)_2(Solv)] \cdot Solv'$, **1**, d(Zn2-Zn2) = 6.3 Å (the ethyl groups are not shown for clarity). The structure contains a bridge of still unknown origin (equivalent to DABCO regarding the connectivity). This unclear bridge might be a minor impurity, possibly formed in-situ from the used reactants or solvent molecule.

$C_9H_9O_{5.50}P_{1.25}Zn$				
309.24				
0.25 x 0.08 x 0.02				
260				
Tetragonal				
/4/mmm				
21.4445 (11), 21.4445 (11), 9.3118 (5)				
4282.2 (5)				
8				
0.962				
1.24				
1254				
0.887, 0.975				
1.72, -0.61				
47819, 2112, 1636				
0.044				
0.059, 0.187, 1.10				
$w = 1/[\sigma^2(F_o^2) + (0.1387P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. Goodness-of-fit $S = [\Sigma]$				
$[w(F_o^2-F_c^2)^2]/(n-p)]^{1/2}.$				

Table S2 Crystal data and refinement details for [Zn₂(EtBCP)₂(Solv)] · Solv', 1

5 Crystallographic details for [Zn₂(EtBCP)₂(DABCO)_{0.5}] · 2DMA, 2



Fig. S16 The extended asymmetric unit of $[Zn_2(EtBCP)_2(DABCO)_{0.5}] \cdot 2DMA$, **2** thermal ellipsoid (50%) plot representation, with the exception of the disordered ethoxide group, which is plotted in ball-and-stick model for clarity. DABCO is given without hydrogen atoms for better visibility of the disordered components. Symmetry transformations: (i) -x+1, -y, z; (ii) -y+1/2, x-1/2, -z+3/2; (iii) y+1/2, -x+1/2, -z+3/2; (iv) y, -x+1, z; (v) -y+1, x, z; (vi) -x+1, -y+1, z; (vii) -x+1, -y+1, z; (vii) -x+1, -y+1, z; (vii) -x+1, -y+1, z; (viii) x, y, -z+1; (ix) x, y, -z+2.

Table S3. Selected bond lengths [Å	Å] and angles [°] for $[Zn_2(EtBCP)_2(DABCO)_{0.5}] \cdot 2$	2DMA, 2 .
------------------------------------	--------------------------------------------------------------	------------------

Bond	Length, [Å]	Bond	Length, [Å]
Zn1—01	1.913(4)	C5—O3 ^{vii}	1.231(6)
Zn1—O1 ⁱ	1.913(4)	N1—C6C	1.451(13)
Zn1—O1 ⁱⁱ	1.913(4)	N1—C6A	1.466(13)
Zn1—O1 ⁱⁱⁱ	1.913(4)	N1—C6B	1.502(13)
Zn2—03	2.021(5)	C6A—C6A ^{viii}	1.53(4)
Zn2—O3 ^{iv}	2.021(5)	C6B—C6B ^{viii}	1.63(4)
Zn2—O3 ^v	2.021(5)	C6C—C6C ^{viii}	1.47(4)
Zn2—03 ^{vi}	2.021(5)	01S—C2S	1.293(10)
Zn2—N1	2.039(7)	C2S—N1S	1.342(10)
P-O1 ^{vii}	1.484(4)	C2S-C1S	1.508(9)
P-01	1.484(4)	N1S—C3S	1.460(9)
P02	1.536(9)	N1S—C4S	1.460(9)
P-C1	1.786(8)	C7—C8	1.498(10)
O2—C7	1.392(10)	C1—C2 ^{vii}	1.357(8)
C1—C2	1.357(8)	C4—C5	1.527(13)
C2—C3	1.364(10)	C5—O3	1.231(6)

	N/ 1 F03		N/ 1 F03
Angle	Value, [°]	Angle	Value, [°]
01—Zn1—01 ⁱ	109.6(3)	O3 ^{vii} —C5—C4	117.1(4)
01—Zn1—01"	109.40(15)	C5—O3—Zn2	127.0(5)
01 ⁱ —Zn1—01 ⁱⁱ	109.40(15)	C6C—N1—C6A	111.2(8)
01—Zn1—01 ⁱⁱⁱ	109.40(15)	C6C—N1—C6B	108.0(8)
01 ⁱ —Zn1—O1 ⁱⁱⁱ	109.40(15)	C6A—N1—C6B	105.8(8)
01"—Zn1—01"	109.6(3)	C6C—N1—Zn2	112.3(8)
03—Zn2—O3 ^{iv}	88.33(4)	C6A—N1—Zn2	110.9(9)
03—Zn2—O3 ^v	88.33(4)	C6B—N1—Zn2	108.4(8)
03 ^{iv} —Zn2—O3 ^v	160.3(2)	N1—C6A—C6A ^{viii}	110.9(9)
03—Zn2—O3 ^{vi}	160.3(2)	N1—C6B—C6B ^{viii}	108.4(8)
03 ^{iv} —Zn2—O3 ^{vi}	88.33(4)	N1-C6C-C6C ^{viii}	112.3(8)
03 ^v —Zn2—O3 ^{vi}	88.33(4)	O1S—C2S—N1S	115.1(18)
O3—Zn2—N1	99.83(12)	O1S-C2S-C1S	125.6(17)
O3 ^{iv} —Zn2—N1	99.83(12)	N1S-C2S-C1S	115.8(14)
O3 ^v —Zn2—N1	99.83(12)	C2S—N1S—C3S	118.3(15)
O3 ^{vi} —Zn2—N1	99.83(12)	C2S—N1S—C4S	119.3(14)
01 ^{vii} —P—01	119.4(4)	C3S—N1S—C4S	121.5(14)
01 ^{vii} —P—02	113.3(6)	C2 ^{vii} —C1—P	121.1(4)
01—P—02	97.9(6)	C2—C1—P	121.1(4)
O1 ^{vii} —P—C1	109.5(2)	C1-C2-C3	121.7(6)
01—P—C1	109.5(2)	C2-C3-C4	119.9(6)
02—P—C1	106.1(4)	C3 ^{vii} —C4—C3	118.9(8)
P—O1—Zn1	153.6(4)	C3 ^{vii} —C4—C5	120.5(4)
С7—О2—Р	118.8(15)	C3-C4-C5	120.5(4)
02-07-08	114(2)	03—C5—O3 ^{vii}	125.7(9)
C2 ^{vii} —C1—C2	117.6(8)	O3-C5-C4	117.1(4)

Symmetry transformations: (i) -x+1, -y, z; (ii) -y+1/2, x-1/2, -z+3/2; (iii) y+1/2, -x+1/2, -z+3/2; (iv) y, -x+1, z; (v) -y+1, x, z; (vi) -x+1, -y+1, z; (vii) -x+1, -y+1, -z+1; (viii) x, y, -z+1; (ix) x, y, -z+2.

6 Topological analysis of **2**







Fig. S17 The extended topological scheme for the structure of 2.

(a) The view on the framework along the *c*-axis (no H-atoms are given for clarity) with an underlayimage of the ball-and-stick model image (with H-atoms). (b) The wireframe model of a representative part of the structure (the disorder is given explicitly). (c) As previous, but with the underlying net shown. (d) The $\{Zn_2(PO_2(OEt))_2\}_n$ phosphonate-monoester chain-SBU (note, that the attached phenyl groups are also shown for better assessment); the 4-c $\{Zn_2(PO_2(OEt))_2\}$ and the 6-c $\{[Zn_2(PO_2(OEt))_2]_2\}$ topological node interpretations are explained (e) The $\{Zn_2(COO)_4(DABCO)\}_n$ extended paddle-wheel chain-SBU sustained by standard paddle-wheel units, joined axially by bridging DABCO molecules (note, that the attached phenyl groups are also shown for better assessment). (f,g,h,i) Different levels of topological interpretations (see the legends).



Fig. S18 Alternative, more conventional presentation on the structural organization of **2** (isostructural to **3**): (a) the $\{Zn_2(O_2C-)_4\}$ standard paddle-wheel arrangement with four equatorial carboxylates (square-planar geometry) and two axial DABCO molecules; (b) the $Zn_2(PO_2(OEt))_2\}$ chain arrangement of the infinite phosphonate-monoester chain-SBU. (c) the 1D phosphonate-monoester chain-SBU in ball-and-stick and polyhedral representations; (d) a topological representation of the framework, based on 1D chains of axially connected 6-c units (e, f) the ball-and-stick and the space-filling representation of the framework respectively.

The topological assessment using the Topos software¹³ was performed on structural input files with manually created dummy atoms, corresponding to the respective nodes. An important peculiarity is that the interpretation on the level of the 6-c $\{[Zn_2(PO_2(OEt))_2]_2\}$ node (marked green on Fig. S15) demanded a decrease of the symmetry of the structure from /4/m to *P*4. It was necessary, as in /4/m every neighboring pair of $\{Zn_2(PO_2(OEt))_2\}$ nodes (marked blue on Fig. S15) has a corresponding $\{[Zn_2(PO_2(OEt))_2]_2\}$ node between them. However, the joining of two 4-c $\{Zn_2(PO_2(OEt))_2\}$ nodes in one 6-c $\{[Zn_2(PO_2(OEt))_2]_2\}$ node essentially halves the amount of the latter, which is only compatible with the lowered symmetry.

All the topological interpretations were checked by Topos. The outputs for the **pcu** and **nbo** nets are trivial, while the output for the seemingly new 4,6-c net is the next chapter.

The crystallographic file in res-format (SHELX) for the nodes of the nets of different levels of interpretation in *P*4 symmetry is given in the penultimate subchapter of this section (note the comment sections after the "!" sign).

6.1 Topos-output for the topology of **2** on the level of 4,6-c net

The TOPOS output for the topology of **2** on the level of $4-c \{[Zn_2(PO_2(OEt))_2]\}$ and the 6-c augmented $\{Zn_2(COO)_4(DABCO)\}$ paddle-wheel units:

"{Zn₂(RCOO)₄} paddle-wheel" Point symbol:{5^8.6^4.8^3}

Extended point symbol: [5.5.5.5.5.5.5.6(2).6(2).6(2).6(2).8(6).8(6).8(8)]

"{Zn₂(PO₂(OEt))₂}" Point symbol:{5^5.6} Extended point symbol:[5.5.5.5.5(2).6(2)]

Point symbol for net: {5^5.6}2{5^8.6^4.8^3} 4,6-c net with stoichiometry (4-c)2(6-c); 2-nodal net

6.2 Res-file input in *P*4 symmetry for different levels of topological interpretation

```
TITL 2 topol symplified in P4
CELL 1.5478 19.9120 19.9120 9.5338 90.0000 90.0000 90.0000
ZERR 0.0000 0.0040 0.0040 0.0017 0.0000 0.0000 0.0000
LATT -1
SYMM -y, x, z
SYMM -x, -y, z
SYMM y, -x, z
SFAC Au Ag Al Br Bi Be
cn1a 1 0.50000 0.50000 0.50000 0.2500 0.05000
                                                      ! Paddle wheel, 4c
cn1b 1 0.00000 0.00000 0.00000 0.2500 0.05000
                                                      ! Paddle wheel, 4-c
ct2a 2 0.50000 0.50000 1.00000 0.2500 0.05000
                                                      ! DABCO ligand (connector)
ct2b 2 0.00000 0.00000 0.50000 0.2500 0.05000
                                                      ! DABCO ligand (connector)
ct1a 3 0.50000 0.25000 0.37500 1.0000 0.05000
                                                      ! \{Zn_2(PO_2(OEt))_2\} node, 4c in 6,6-c net
! ot1a 6 0.50000 0.25000 0.50000 1.0000 0.05000
                                                      ! alternatively to ct1a in 4,6-c net
```



6.3 Illustration of the possible isoreticular expansion of **2**

Fig. S19 Projections of the structure of **2** and its isoreticularly expanded analogue, based on a ligand with a biphenyl core, on the *ab* plane. Note that the monoethylphosphonate ligands are oriented parallel to the ab plane (though not coplanarly), and the connectivity along the *c*-axis is sustained by the 1D SBUs, also by means of the DABCO co-ligands. Hence, the isoreticular expansion *via* the elongation of the monoethylphosphonate ligand affects only two dimensions out of three.

7 Geometrical surface area and pore volume based on structural data

The geometrical ('theoretical', Connoly) surface area and the void volume (*i.e.* solvent/probe accessible pore volume) for $[Zn_2(EtBCP)_2(DABCO)_{0.5}]$ **2**' were calculated using the program Surface Area Program (by Düren/Snurr)¹⁴ [] and the Zeo++ program¹⁵, both of which based on Monte-Carlo approach of volume-filling of the structure by probe-spheres. For comparison, the pore volume was also calculated with Platon,¹⁶ using a simpler and less precise grid-point calculation based approach (fixed "equivalent probe" diameter of 2.4 Å). The calculation results by Platon proved to be strongly overestimated, and rather approximate an asymptotic value to the integral void volume (*i.e.* equivalent for a void volume found for a probe, which size tends to zero). It is known situation for the Platon software, and thence the respective data is not reliable for very narrow pore structures.

The input files for all the programs were prepared as follows: the DMA solvent molecules were removed, the symmetry was lowered to P1 (i.e. all the symmetry equivalent atoms were generated) the disorder was collapsed to one component for both the DABCO and OEt moieties. If the disorder were not collapsed, which would be a mistake as the given programs do not account the occupation factors, the error is relatively modest (e.g. for Platon is relatively small, ~10%) as the rotational disorder of DABCO does not take away a lot of volume, while the disorder of OEt is relatively well localized. The calculated values are listed in Table S4.

Table S4. The geometrical surface areas and pore volumes calculated using different software for $[M_2(EtBCP)_2(DABCO)_{0.5}]$ (M = Zn, 2') and the relevant experimental data (M = Zn, 2'; M = Co, 3')

Surface Area Program ^a					
Total surface area, m ² g ⁻¹	904				
Zeo++ ^a					
Total accessible surface area, m ² g ⁻¹	1057				
Total non-accessible surface area, m ² g ⁻¹	0				
Maximum included sphere diameter	5.91				
Maximum free sphere diameter (i.e. passable through the pore system), Å	4.62				
Void volume (3.68 Å probe diam., equiv. to N_2), % {cm ³ g ⁻¹ }	4.7 {0.041}				
Void volume (3.30 Å probe diam., equiv. to CO_2), % {cm ³ g ⁻¹ }	7.3 {0.065}				
Void volume (2.40 Å probe diam., equiv. to H_2O), % {cm ³ g ⁻¹ }	15.7 {0.139}				
Void volume (1 Å probe diam., approximation of total free vol.), % {cm ³ g ⁻¹ }	36.7 {0.325}				

Platon 'Calc Void/Solv'

Void volume (2.4 Å probe diam., equiv. to 44.6 {0.394}

H₂O), % {cm³ g⁻¹} ^a

Experimental CO₂ uptake

V _{pore} (cm ³ g ⁻¹) (195 K) ^b			
First step (end)	M = Zn: 0.11 (P/P ₀ = 0.08)		
	$M = Co: 0.12 (P/P_0 = 0.11)$		
Second step (end)	M = Zn: 0.21 (P/P ₀ = 1.0)		
	$M = Co: 0.23 (P/P_0 = 1.0)$		
	V _{pore} (cm ³ g ⁻¹) (298 K) ^b		
First step	M = Zn: 0.11 (P/P ₀ = 0.19)		
	$M = Co: 0.15 (P/P_0 = 0.19)$		

^a Probe diameter is 3.681 Å, equals to the kinetic diameter of N_2 molecule (if not given otherwise explicitly), framework density is 1.13 g cm⁻³ (solvent molecules removed)

^b Experimental pore volumes are calculated under the assumption of the validity of the Gurvich rule¹⁷ according to (specific amount adsorbed)/(density of liquid CO₂) with $\rho_{CO2, 195 \text{ K}} = 1.10 \text{ g cm}^{-3}$ and $\rho_{CO2, 298 \text{ K}} = 0.71 \text{ g cm}^{-3}$.



Fig. S20 PXRD patterns of:

 $[Zn_2(EtBCP)_2(DABCO)_{0.5}] \cdot 2DMA$, **2**, simulated from X-ray crystal diffraction data (red);

the measured PXRD pattern for the as-synthesized sample of ${\bf 2}$ (green);

the sample activated by 160°C, 2' (teal);

the activated sample after sorption measurement, $\mathbf{2'}_{abs}$ (orange);

the activated sample after re-solvation by DMA, $\mathbf{2}_{resolv}$.



Fig. S21 Comparison of the low and high-pressure sorption isotherms for CO_2 at 195 K and 298 K respectively for $[Zn_2(EtBCP)_2(DABCO)_{0.5}]$, **2**' (green) and $[Co_2(EtBCP)_2(DABCO)_{0.5}]$, **3**' (blue). The red point symbolizes the first step which was used to calculate the maximal micropore volume for the particular isotherm before the assumed structural transformation.



Fig. S22 Isosteric heat of adsorption of CO_2 for **2**' (left) and **3**'(right), derived from CO_2 adsorption isotherms at 273 and 293 K.



Fig. S23 Adsorption and desorption isotherms of Ar, N_2 and H_2 for $[Zn_2(EtBCP)_2(DABCO)_{0.5}]$, **2**' (left) and $[Co_2(EtBCP)_2(DABCO)_{0.5}]$, **3**' (right).

Notes: a) The Ar adsorption/desorption isotherm for **3**' at 87 K shows an effect of a very short equilibrium time. Argon is adsorbed to a small extent, but it is not desorbed fast enough. As in other cases, the measurement error is large due to the small amount adsorbed.

b) The H_2 adsorption/desorption isotherm for **3**['] at 77 K demonstrates an artefact regarding the desorption branch. The appearance of such artefacts is quite possible for low amount adsorbed. The measurement is marked by poor-quality, but was not repeated due to the low amount adsorbed.

8 BET and Langmuir surface areas and the respective experimental adsorption raw data

The use of CO₂ gas adsorption data for the calculation of the BET area is controversial. CO₂ at low temperatures does not correspond well to the demands of the phenomenological BET model. Despite the low precision, the method is occasionally used in practice.^{18,19,20,21} The discussion of the correctness of the approach is outside of the scope of this publication. We use the method as a crude estimate along with the Langmuir model. The latter is, in principle, suits better for the treatment of the experimental data, however also has precision issues due to the low acting relative pressures and hence the low adsorbed amounts.

Nevertheless, the results obtained *via* the use of the BET and Langmuir model are quite close and indicates consistency, even if the precision remains unclear.

8.1 Langmuir report for [Zn₂(EtBCP)₂(DABCO)_{0.5}], **2**'

Langmuir surface area: Slope: Y-intercept: b: Qm:	330.2708 ± 0.01 0.15 0.08 72.3	9,2532 m ² g ⁻¹ .3830 ± 0,000387 g cm ⁻³ STP 67 ± 0.014 mmHg g cm ⁻³ STP 88088 1 mmHg ⁻¹ 6086 cm ³ g ⁻¹ STP
Correlation coefficient:	0.998434	
Molecular cross-section	al area: 0.17	'00 nm²
Pressure,	Quantity adsorbed	I P/Q (STP),
mmHg	(STP),	mmHg cm ^{−3}
	2 1	
	cm³ g⁻¹	
5.707641	cm³ g ⁻¹ 24.2983	0.235
5.707641 9.573032	cm³ g ⁻¹ 24.2983 30.5375	0.235 0.313
5.707641 9.573032 21.194822	cm ³ g ⁻¹ 24.2983 30.5375 49.6882	0.235 0.313 0.427
5.707641 9.573032 21.194822 33.597107	24.2983 30.5375 49.6882 54.9401	0.235 0.313 0.427 0.612
5.707641 9.573032 21.194822 33.597107 45.386738	cm ³ g ⁻¹ 24.2983 30.5375 49.6882 54.9401 57.7457	0.235 0.313 0.427 0.612 0.786



Fig. S24 Langmuir surface area plot for 2'.

8.2 BET report for [Zn₂(EtBCP)₂(DABCO)_{0.5}], **2**'

BET surface area:	310.5327 ± 9	.4466 m² g ^{−1}
Slope:	0.014602 ± 0	0.000447 g cm ⁻³ STP
Y-intercept:	0.000107 ± 0	0.000011 g cm ⁻³ STP
C:	138.080668	
Qm:	67.9872 cm ³	g ^{−1} STP
Correlation coefficient:	0.9981285	
Molecular cross-sectional are	a: 0.1700 nm ²	
Relative pressure, P/P _o	Quantity adsorbed	$1/[Q(P_0/P - 1)]$
	(CTD)	
	(312),	
	(STP), cm ³ g ⁻¹	
0.004047972	(STP), cm ³ g ⁻¹ 24.2983	0.000167
0.004047972 0.006789385	(STP), cm ³ g ⁻¹ 24.2983 30.5375	0.000167 0.000224
0.004047972 0.006789385 0.015031789	(STP), cm ³ g ⁻¹ 24.2983 30.5375 49.6882	0.000167 0.000224 0.000307
0.004047972 0.006789385 0.015031789 0.023827735	(STP), cm ³ g ⁻¹ 24.2983 30.5375 49.6882 54.9401	0.000167 0.000224 0.000307 0.000444
0.004047972 0.006789385 0.015031789 0.023827735 0.032189176	(STP), cm ³ g ⁻¹ 24.2983 30.5375 49.6882 54.9401 57.7457	0.000167 0.000224 0.000307 0.000444 0.000576



Fig. S25 BET surface area plot for 2'.

8.3	Langmuir report for	[Co ₂ (EtBCP) ₂ (DABCO) _{0.5}	;] , 3 ′
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326,8281 ± 1,2338 m ² g ⁻¹
0.013975 ± 0,000053 g cm ⁻³ STP
0.080 ± 0,002 mmHgKg cm ⁻³ STP
0.174252 1/mmHg
71.5548 cm ³ g ⁻¹ STP
0.999971
0.1700 nm ²

Pressure,	Quantityadsorbed (STP),	P/Q (STP),
mmHg	cm³ g ⁻¹	mmHg cm ⁻³
5.984107	35.8666	0.167
9.519302	44.9481	0.212
19.044296	55.4762	0.343
31.617212	60.5244	0.522
44.528290	63.2270	0.704
59.221222	65.2755	0.907



Fig. S26 Langmuir surface area plot for 3'.

8.4 BET report for [Co₂(EtBCP)₂(DABCO)_{0.5}], **3**'

BET surface area:	$309.7723 \pm 2.1570 \text{ m}^2 \text{ g}^{-1}$
Slope:	0.014693 ± 0.000103 g cm ⁻³ STP
Y-intercept:	$0.000052 \pm 0.000002 \text{ g cm}^{-3}\text{STP}$
C:	282.925279
Qm:	67.8207 cm ³ g ⁻¹ STP
Correlation coefficient:	0.9999024
Molecular cross-sectional area:	0.1700 nm ²

Relative pressure, P/P _o	Quantity adsorbed (STP), cm ³ g ⁻¹	1/[Q(P ₀ /P - 1)]
0.004244048	35.8666	0.000119
0.006751278	44.9481	0.000151
0.013506593	55.4762	0.000247
0.022423555	60.5244	0.000379
0.031580347	63.2270	0.000516
0.042000867	65.2755	0.000672



Fig. S27 BET surface area plot for 3'.

9 Comparison of low pressure CO₂ adsorption isotherms collected using different equilibration times for **3'** (assessing kinetic effects)

In order to verify the influence of kinetic factors, we measured the CO_2 adsorption isotherms for **3'** using three different instrumental equilibration-time settings, 20 s, 40 s, and 100 s. Note that those numbers do not have very direct physical sense: they are only the time intervals after, which the instrument (Micromeritics ASAP 2020, in this case) checks the change of the pressure with time, and concludes, whether the acquisition of the data point is finished or a next equilibration-period should be applied. Hence, the real equilibration time consists of multiple time intervals. The precise acquisition times for the collected data points are given in Table S5.



Fig. S28 Comparison of the CO_2 physisorption isotherms (195 K) of **3'** measured using different instrumental equilibration-time parameters (20 s, 40 s, 100 s). (a) Overlay of the three physisorption isotherms (b) overlay of the desorption branches only (c,d,e) complete individual physisorption isotherms.

The measurements clearly indicate that the presence of hysteresis is at least partially, but most probably entirely, kinetically conditioned for the analog materials 2' and 3'. For the longest equilibration-time parameter (100 s) the hysteresis width is roughly half of the one observed in the

shortest time (20 s). The adsorption and the desorption branches of the physisorption isotherm become practically indistinguishable for the first adsorption step at the longest equilibration time, indicating that complete return to the initial framework geometry occurs.

	20 s 40 s				100 s *			
Pressure, mbar	Quantity adsorbed, cm ³ g ⁻¹ STP	Elapsed time, h:min	Pressure, mbar	Quantity adsorbed, cm ³ g ⁻¹ STP	Elapsed time, h:min	Pressure , mbar	Quantity adsorbed, cm ³ g ⁻¹ STP	Elapsed time, h:min
0.0127	0.0671	1:55	0.0150	0.114	2:00	0.0187	0.1101	2:12
0.0808	0.704	2:06	0.0752	0.809	2:17	0.0842	0.8091	2:38
0.672	5.09	2:20	0.679	5.72	2:34	0.731	5.59	3:05
0.962	7.01	2:30	0.962	7.53	2:50	0.971	6.93	3:31
1.29	9.22	2:39	1.30	9.57	3:18	1.29	8.68	3:55
3.28	20.65	2:49	3.30	20.44	3:03	3.30	19.42	4:22
7.98	35.87	2:56	8.02	35.13	3:30	8.03	34.32	4:42
12.69	44.95	3:04	12.81	43.66	3:41	13.20	42.65	5:02
25.39	55.48	3:12	27.77	55.04	3:52	20.01	49.30	5:23
42.15	60.52	3:17	42.03	59.33	4:02	25.70	52.61	5:43
59.37	63.23	3:21	58.61	62.29	4:11	38.48	57.02	6:04
78.96	65.28	3:25	79.14	64.80	4:19	52.25	59.82	6:23
106.39	67.33	3:28	103.62	69.79	4:42	78.53	63.13	6:41
147.51	87.07	3:50	168.43	109.27	5:00	105.64	65.55	7:02
203.05	112.99	4:02	235.32	116.23	5:13	121.15	72.31	7:47
281.83	123.00	4:08	283.40	119.27	5:25	132.70	86.64	8:39
351.09	126.17	4:12	332.05	121.27	5:34	152.64	101.41	9:18
418.79	127.66	4:15	399.83	123.17	5:43	202.54	109.74	9:48
486.10	128.47	4:01	466.84	124.33	5:51	248.65	114.16	10:15
553.60	128.91	4:20	533.61	125.16	5:58	283.79	116.59	10:41
619.70	129.13	4:22	600.32	125.73	6:06	333.46	119.05	11:04
686.63	129.16	4:24	666.93	126.09	6:14	400.80	121.16	11:25
753.44	129.07	4:26	733.67	126.35	6:22	466.57	122.48	11:44
819.96	128.90	4:28	800.24	126.49	6:29	534.46	123.42	12:03
886.72	128.65	4:31	866.91	126.58	6:37	600.39	124.06	12:22
960.07	128.30	4:33	940.17	126.60	6:45	666.94	124.49	12:41
1019.90	128.05	4:35	1020.03	126.49	6:53	733.71	124.76	13:00
886.70	129.14	4:37	887.77	126.88	7:01	800.28	124.96	13:18
779.78	129.88	4:40	780.36	127.06	7:09	867.16	125.08	13:37
647.25	130.46	4:42	647.78	127.05	7:17	940.57	125.08	13:56
514.75	130.75	4:44	535.46	126.78	7:25	1020.33	125.01	14:15
381.19	130.50	4:47	401.50	126.01	7:33	887.21	125.71	14:34
267.88	129.31	4:50	267.97	124.13	7:42	780.23	126.06	14:53
136.83	123.97	4:57	137.00	118.04	8:02	647.59	126.22	15:11
74.91	102.38	5:22	74.57	97.64	9:42	514.58	125.96	15:30
39.44	59.31	5:34	39.02	56.54	10:06	401.06	125.29	15:49
13.59	44.77	5:46	13.53	40.76	11:00	268.26	123.34	16:12
6.55	30.74	5:58	6.21	24.62	11:57	200.83	121.01	16:43
						135.56	115.83	17:49
						105.10	108.96	19:38
						91.60	97.67	23:19
						73.29	63.12	23:52
						36.92	53.02	25:54:00
						27.24	48.37	27:17:00
						13.56	38.71	27:40:00
						6.56	22.22	31:08:00

Table S5. Data-points for the CO_2 physisorption isotherms measured with various equilibration-time parameters (20 s, 40 s and 100 s) for **3'** with acquisition times given.

^{*} There were some additional data points measured for the desorption branch of the adsorption isotherm

10 Stability tests in air and the water vapor adsorption by 3'

The stability tests regarding moisture in air were performed *via* exposure of the samples to ambient air at ~ 295 K (~50% relative humidity, typical for indoors conditions. As the test is qualitative, no indepth control of humidity was pursued). No significant changes were observed in all cases.

The starting sample for **2**, denoted as "**2**, a.s." in Fig. S29 was a different sample then the one used for the PXRD in Fig. 3 (MS). Hence, the slight changes in the peak intensities compared to Fig. 3. The starting sample for **3**, denoted as "**3**, re-solvated" was a sample which had been used for CO_2 and water vapor sorption studies. After the water vapor sorption measurement, the sample was re-solvated with DMA. Hence, again the slight changes in the peak intensities compared to Fig. 3 (MS).



Fig. S29 PXRD stability tests for 2, 2' (a) and 3, 3' (b) in air for 2 days.



Fig. S30 (a) H_2O adsorption and desorption isotherm at 298 K for **3**' measured on the Quantachrome VSTAR vapor sorption analyser; (b) PXRD monitoring of the changes after activation (160°C, vacuum) and after the performed water vapor adsorption.

11 Solvent stability tests performed on 2

In order to assess the solvent stability of **2**, a long-term soaking (~3 days) of the as-synthesized material in chloroform, ethanol, acetone and in water (~1 day) was carried out. The exchanged materials were subjected to additional "reverse exchange" *via* soaking in DMA (~3 days). While the treatment of the degassed samples would give a faster and to some extent more reliable result, the long-term soaking of the as-synthesized sample is also satisfactory, while the result is not affected by the crystallinity deterioration due to the degassing:



Fig. S31 PXRD patterns of **2** after soaking in different solvents, followed by "reverse-exchange" with *N*,*N*-dimethylacetamide (DMA).

Soaking in chloroform resulted only in a minor change of crystallinity according to the PXRD pattern, while ethanol caused a significant change. However, in both cases a complete return to the initial state took place after soaking the exchanged material in pure DMA. Interestingly, acetone caused a strong change, but the reversal was also complete. Finally, water caused a transformation to a different phase with an appreciable crystallinity, which did not return to the initial state after soaking in DMA.

The experimental observation suggests significant stability against the action of chloroform, ethanol and acetone. The exchange causes rather reversible deformation of the flexible framework without loss of crystallinity and with full recovery of the initial state after subsequent soaking in DMA. The situation with water is more complex: while the crystallinity is not lost completely, the transformation is irreversible. Hence, the conclusion is that **2** is not truly stable in contact with liquid water and in the best case transforms to another unknown crystalline phase with somewhat compromised crystallinity.

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