SUPPORTING INFORMATION

Supramolecular open-framework architectures based on dicarboxylate H-bond acceptors and polytopic cations with three/four N-H^+ donor units.

Georges Mouchaham,[a,b] Marion Gualino,[a,b] Nans Roques,[a,b] Carine Duhayon, [a,b] Stéphane Brandès[c] and Jean-Pascal Sutter [a,b]

[a] *CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, F-31077 Toulouse, France. E-mail: nans.roques@lcc-toulouse.fr, sutter@lcc-toulouse.fr*

[b] *Université de Toulouse, UPS, INPT, LCC, F-31077, Toulouse, France.*

[c] *ICMUB (Institut de Chimie Moléculaire de l'Université de Bourgogne), UMR 6302 CNRS, Université de Bourgogne, F-21078, Dijon, France.*

CONTENT

Fig. S1. Asymmetric unit of [{(H_3TrIB)$(CA)_{1.5}$}·2DMF·2.5H_2O]**, 1** (with solvent molecules in bottom view, Symmetry operation: (*) -1-x, 1-y, 1-z). Plot with thermal ellipsoids drawn at the 50% probability level. Solvent molecules are omitted for the sake of clarity. Label for H-atoms which are not involved in strong H-bonds are omitted for the same reason.

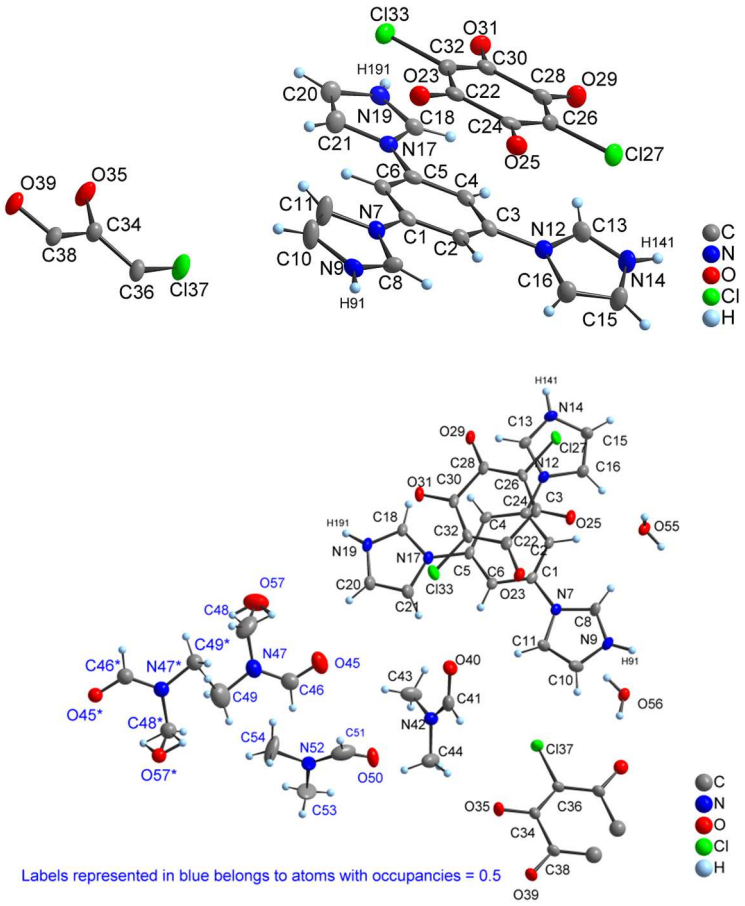

Fig. S2. H-bonded assemblage patterns in **1**. Symmetry operations: (a) 1+x, 0.5-y, 0.5+z; (b) 1-x, -0.5+y, 1.5-z; (c) -1+x, y, z.

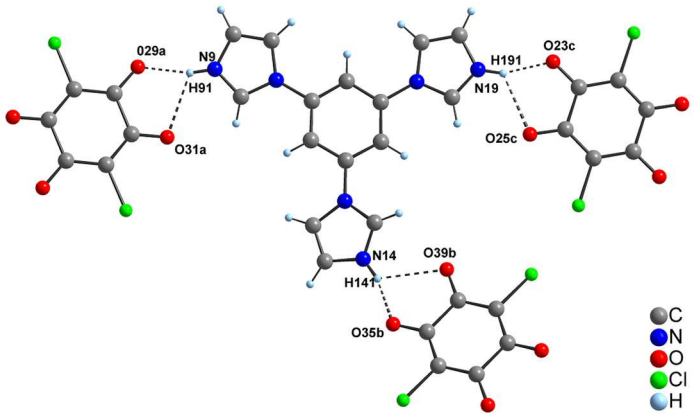

Fig. S3. 2D H-bonded grids packing in **1** along the *a* direction showing π···π interactions between CA^{2-} units and TrIB benzene rings of different layers. For the sake of clarity, space-filling representation is used for those molecules involved in π···π interactions in the view. Solvent molecules are omitted.

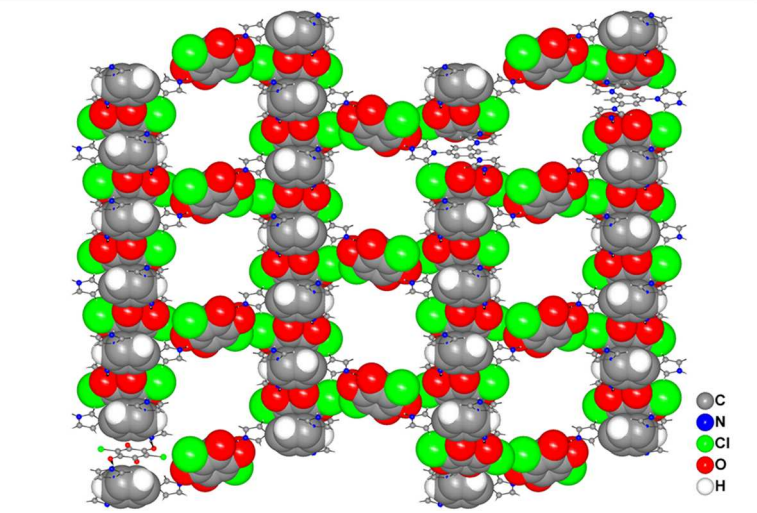

Fig. S4. Side view for the packing of three different layers in **1**.

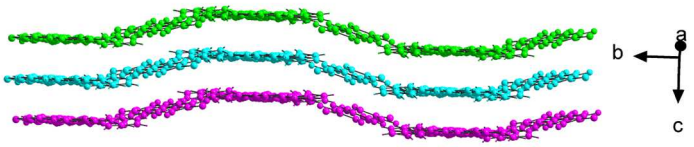

Fig. S5. View of the smaller pores along the *a+c* crystallographic direction in **1**. Colour codes: C, grey; H, white; N, blue; O, red and Cl, green.

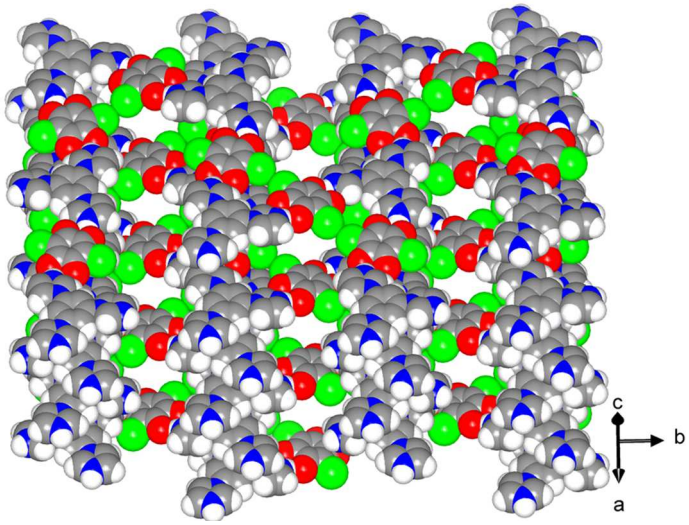

Fig. S6. Asymmetric unit of [{(H_4Tetrapy)$(CA)_2$}·3DMF], **2**. Plot with thermal ellipsoids drawn at the 50% probability level. Solvent molecules are omitted for the sake of clarity. Label for H-atoms which are not involved in strong H-bonds are omitted for the same reason.

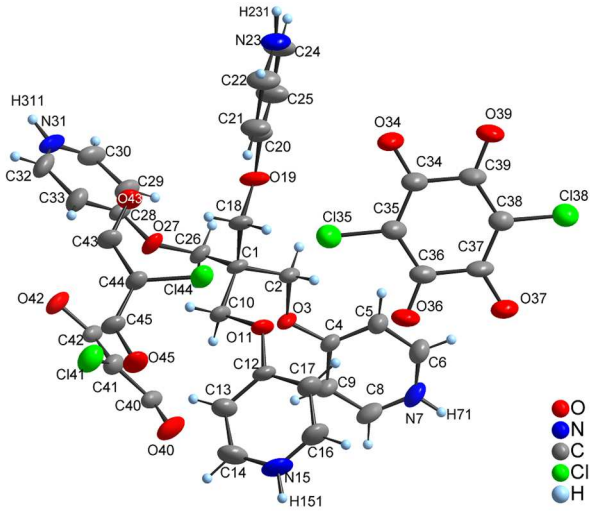

Fig. S7. H-bonded assemblage patterns in **2**. Symmetry operations:(a) -1+x, 0.5-y, -0.5+z ; (b) -1+x, y, z ; (c) 1-x, 1-y, 1-z ; (d) 1+x, y, z ; (e) 2-x, 1-y, -z .

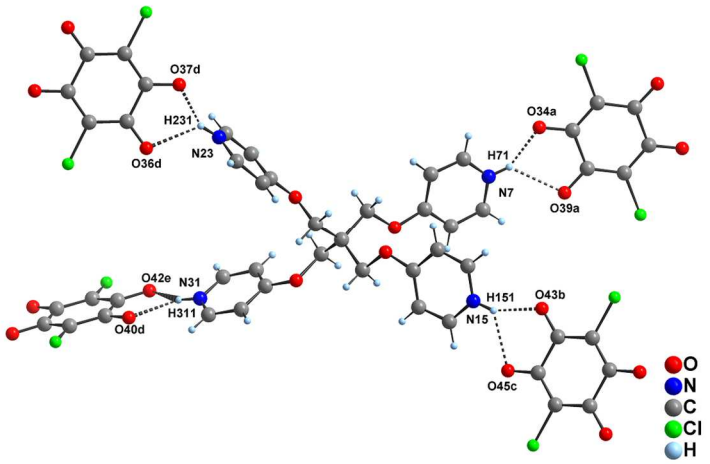

Fig. S8. Asymmetric unit of [{(H_3TrIB)(H-Ox)(Ox)}·5H_2O], **3**. Plot with thermal ellipsoids drawn at the 50% probability level. Solvent molecules are omitted for the sake of clarity. Label for H-atoms which are not involved in strong H-bonds are omitted for the same reason.

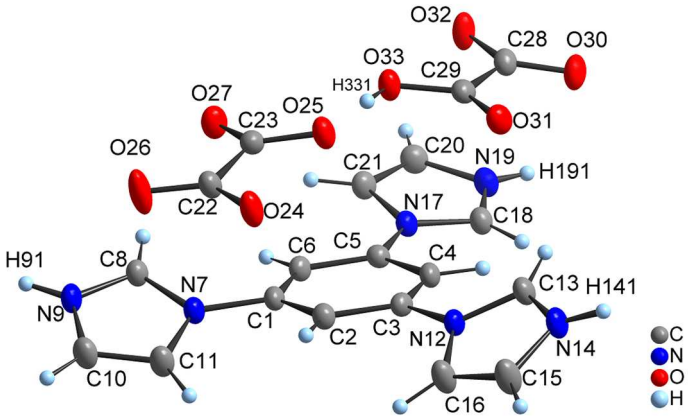

Fig. S9. Molecular packing in **3**. (a) View of four chains packing along *a*. (b) View of two walls along the *b* crystallographic direction. (c) Walls are isolated one from each other by H-bonded water molecules. Colour codes: C, grey; H, white; N, blue; O, red.

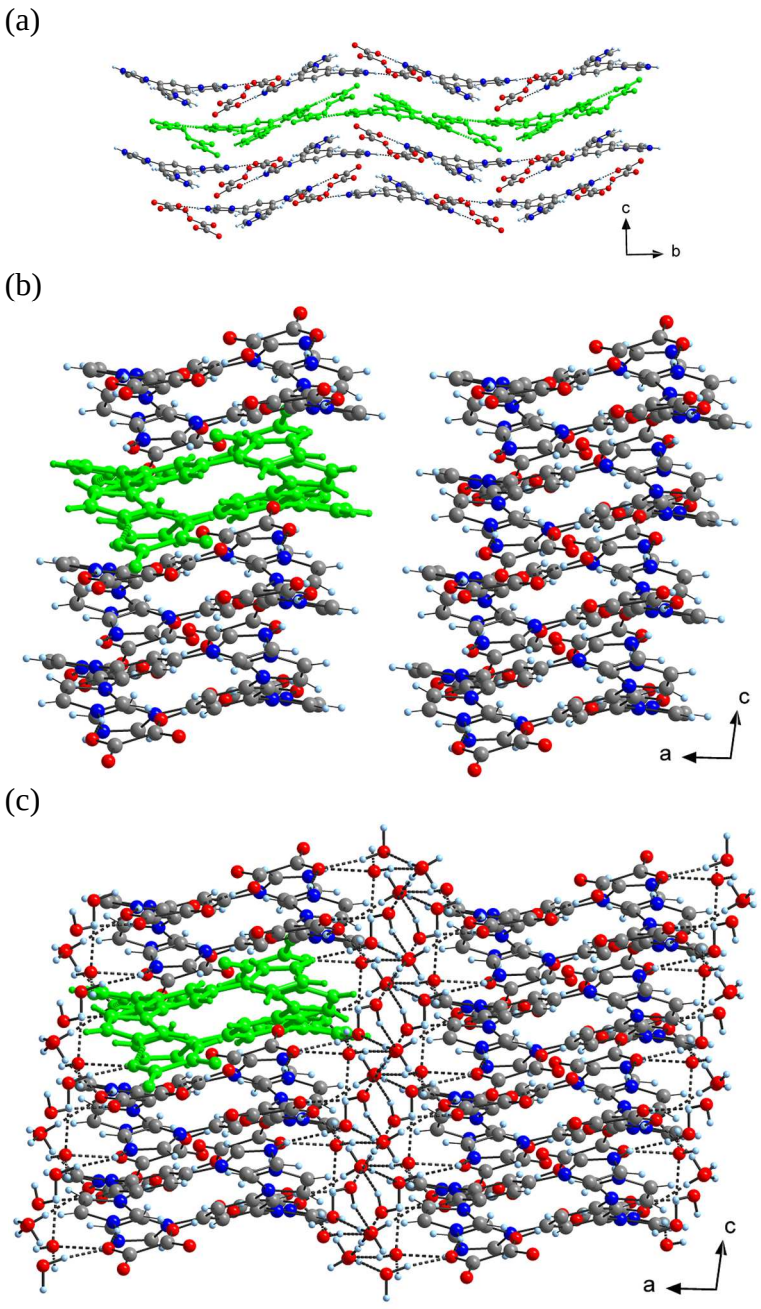

Fig. S10. Asymmetric unit of [{(H_4Tetrapy)(Ox)$_2$}·5H_2O], **4**. Plot with thermal ellipsoids drawn at the 50% probability level. Label for H-atoms which are not involved in strong H-bonds are omitted for the sake of clarity. For the same reason, molecules observed in the asymmetric unit are represented in two different pictures.

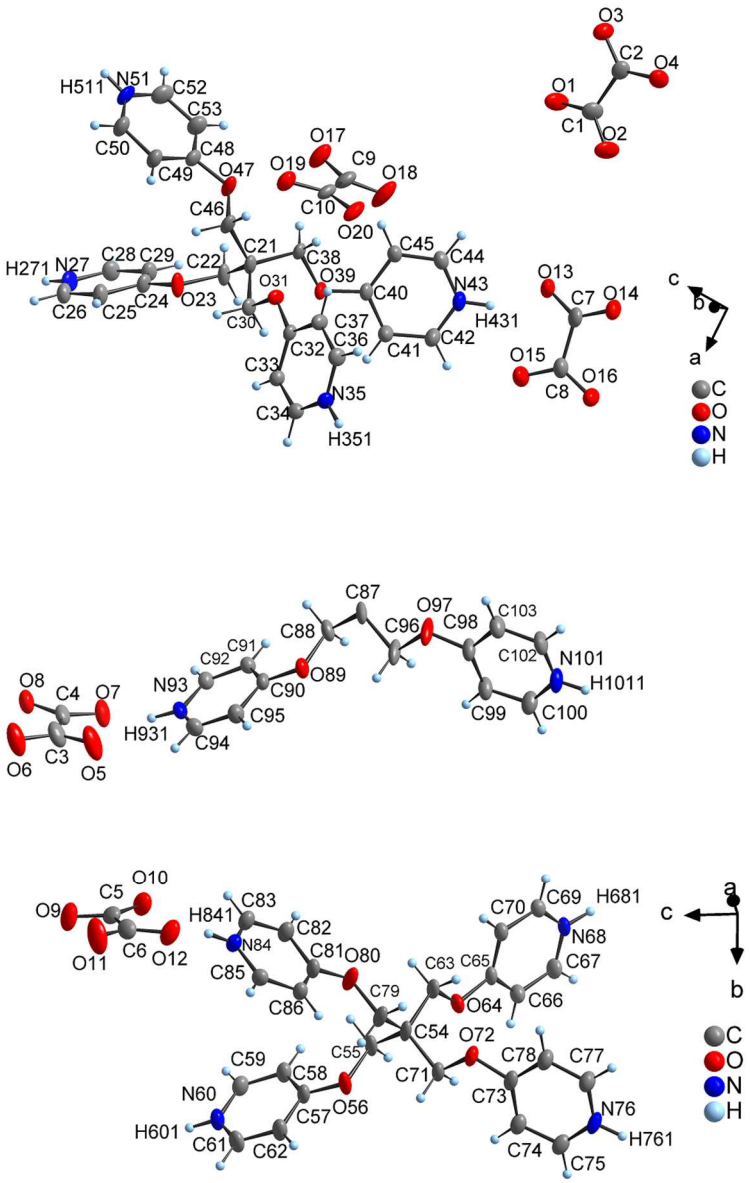

Fig. S11. H-bonded assemblage patterns in **4**. S11_Symmetry operations:(a) : 0.25+y, 0.75-x, 1.75-z ; (b) : 1-x, 1-y, 1-z ; (c) : 1-x, 1-y, 2-z ; (d) 0.75-y, 0.25+x, -0.75+z ; (e) : 0.75-y, -0.25+x, 0.75-z.

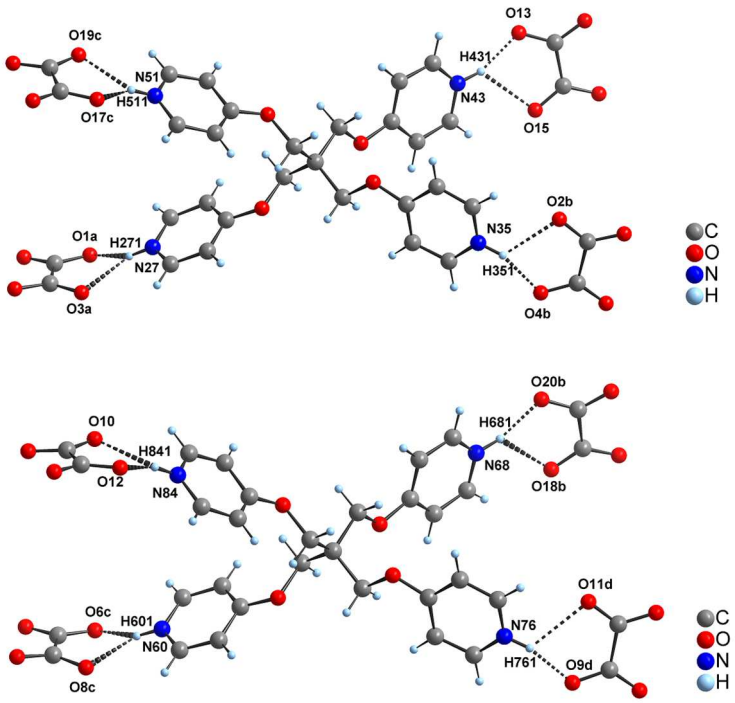

Fig. S12. Asymmetric unit of [{(H_4Tetrapy)(BDC)$_2$(H_2O)}·1DMF·3H_2O], **5**. Plot with thermal ellipsoids drawn at the 50% probability level. Guest solvent molecules are omitted for the sake of clarity. Label for H-atoms which are not involved in strong H-bonds are omitted for the same reason.

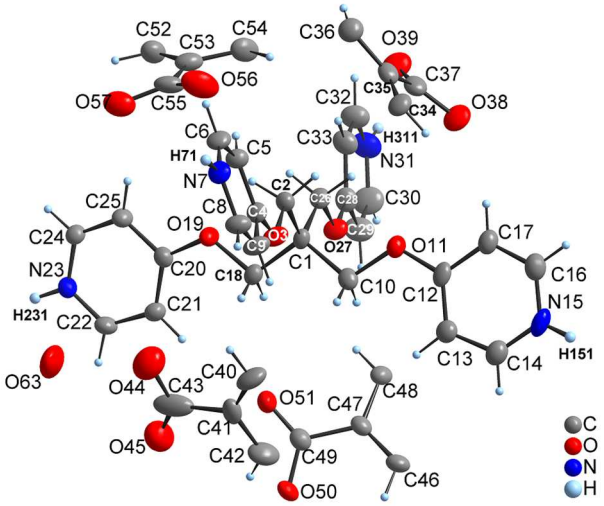

Fig. S13. H-bonded assemblage patterns in shorter edges of the adamantanoid cage in **5**. Symmetry operations: (a) : -1+x, y, z ; (b) : -x, 1-y, 1-z ; (c) : -1-x, 1-y, 1-z; (d) : 1+x, y, z; (e) : 2-x, -y, 1-z; (f) : 3-x, -y, 1-z; (g) : 1-x, -y, 2-z; (h) : -1+x, -1+y, z; (i) : -x, -1-y, 2-z.

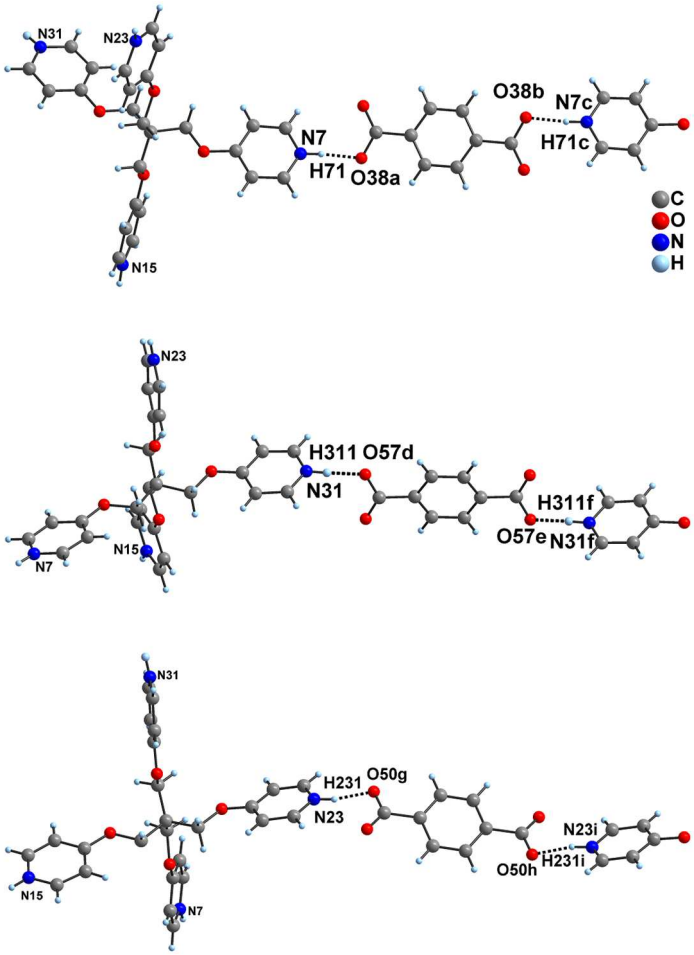

Fig. S14. H-bonded assemblage patterns in longer edges of the adamantanoid cage in **5**. Symmetry operations: (j) : 1+x, 1+y, z; (k) : 2-x, 2-y, 2-z; (l) : 3-x, 3-y, 2-z.

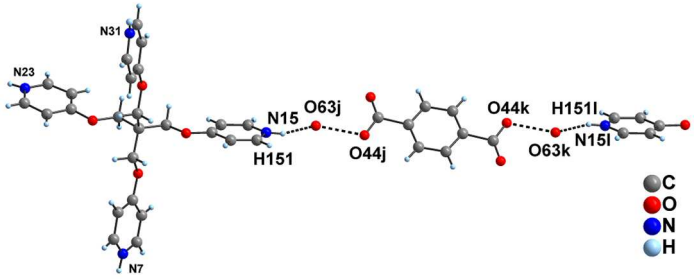

Fig. S15. Molecular packing showing narrow 1D channels in **5**. Guest solvent molecules are omitted for the sake of clarity. Colour codes: C, grey; H, white; N, blue; O, red.

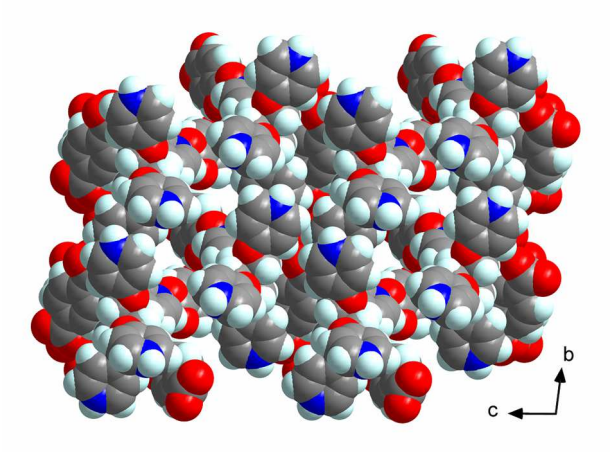

Fig. S16. TGA and DTA traces for as-synthesized **1** (a), **2** (b), **4** (c) and **5** (d).

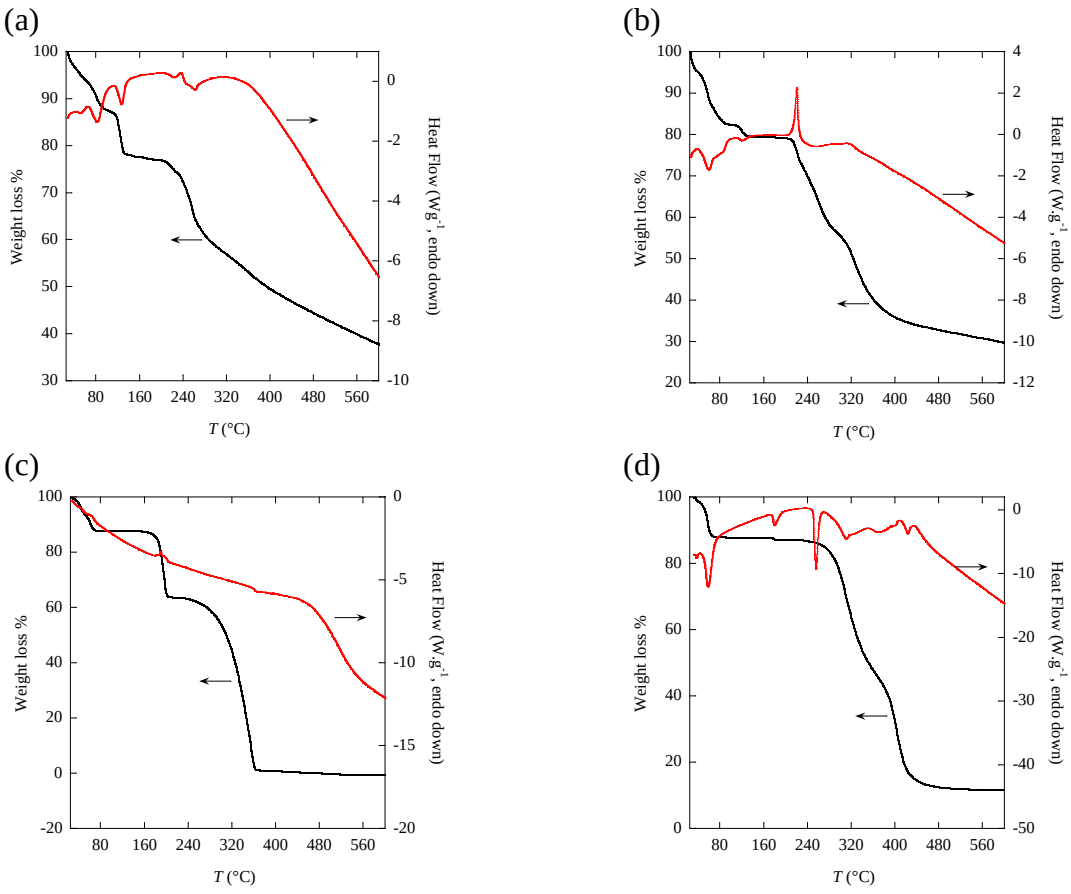

Fig. S17. XRPD patterns for **1**. (a) Calculated from SCXRD data; (b) pristine sample (c), activated sample (vacuum for 6h at RT), (d) after re-immersion in DMF. The cell parameters for the pristine sample of **1** have been obtained by analysis with Le Bail Algorithm implemented in the Highscore+ package.

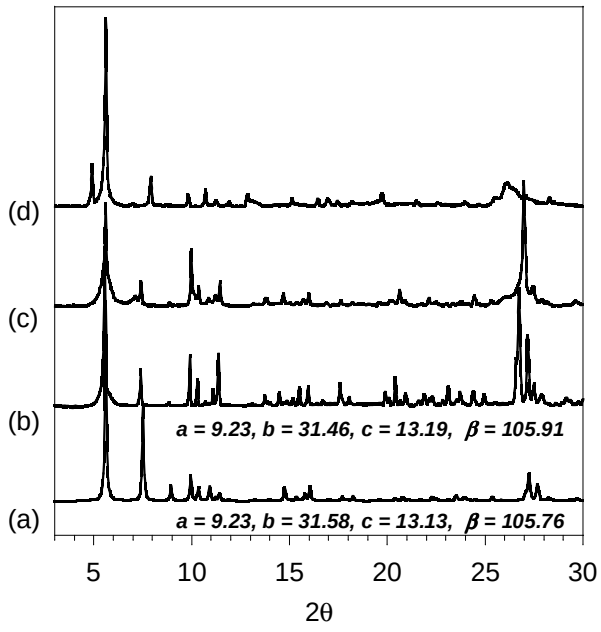

Table S1. Crystallographic data and structural refinement parameters for **1-5**.

	1	**2**	**3**	**4**	**5**
Formula	$C_{60}H_{68}Cl_6N_{16}O_{21}$	$C_{46}H_{49}Cl_4N_7O_{15}$	$C_{19}H_{26}N_6O_{13}$	$C_{29}H_{38}N_4O_{17}$	$C_{44}H_{51}N_5O_{17}$
M ($g.mol^{-1}$)	1562.01	1081.74	546.45	714.64	921.91
Crystal system	Monoclinic	Monoclinic	Monoclinic	Trigonal	Triclinic
Space group	P $2_1/c$	P $2_1/c$	P $2_1/c$	I $4_1/a$	P -1
a (Å)	9.2264(7)	10.7229(1)	13.3011(4)	38.2977(5)	10.3014(6)
b (Å)	31.583(3)	34.3062(4)	24.6348(6)	38.2977(5)	12.5123(8)
c (Å)	13.126(1)	15.2099(2)	7.1285(2)	22.9827(4)	17.750(1)
α (°)	90	90	90	90	94.575(5)
β (°)	105.764(3)	114.800(1)	96.565(3)	90	97.802(5)
γ (°)	90	90	90	90	104.605(5)
V ($Å^3$)	3680.9(5)	5079.15(11)	2320.50(12)	33709.0(8)	2177.9(2)
Z	2	4	4	40	2
T (K)	100	180	180	110	125
ρ_{calcd} ($g.cm^{-1}$)	1.407	1.415	1.564	1.408	1.406
μ (mm^{-1})	0.315 (Mo-Kα)	2.748 (Cu-Kα)	1.158 (Cu-Kα)	1.008 (Cu-Kα)	0.920 (Cu-Kα)
F(000)	1616	2248	1144	15040	960
Theta range for data coll. (°)	1.3-25.0	3.5-62.0	3.3-71.8	3.2-71.7	3.7-60.8
Reflections measured	95094	41877	23350	171562	25169
Unique reflections	6447	7995	4532	16442	6554
R_{int}	0.044	0.026	0.022	0.052	0.047
Reflns used for refinement	5627	7130	4185	13902	4866
Nb parameters	514	649	343	1014	595
Final R/wR indices ($I>n\sigma(I)$)	0.075/0.072 (n=3)	0.070/0.086 (n=3)	0.035/0.041 (n=3)	0.071/0.080 (n=3)	0.077/0.091 (n=2.5)
largest diff peak and hole ($e.Å^{-3}$)	1.73/-0.60	1.48/-0.87	0.35/-0.28	0.43/-0.44	1.09/-0.50

Table S2. Selected Hydrogen bonds in **1-5**.

Atoms D−H···A	Dist. D−A (Å)	Angle D−H−A (°)
	Compound 1[#]	
N9−H91···O29a	2.667(4)	165
N9−H91···O31a	2.879(4)	117
N14−H141···O35b	2.607(4)	165
N14−H141···O39b	2.942(4)	118
N19−H191···O23c	2.613(4)	158
N19−H191···O25c	2.908(4)	120
	Compound 2[#]	
N7−H71···O34a	2.643(4)	149
N7−H71···O39a	2.905(4)	130
N15−H151···O43b	2.674(5)	153
N15−H151···O45c	2.900(5)	127
N23−H231···O36d	2.889(4)	129
N23−H231···O37d	2.584(4)	149
N31−H311···O40d	2.769(4)	138
N45−H451···O42e	2.757(6)	141
	Compound 3[#]	
N9−H91···O32a	2.582(1)	160
N9−H91···O33a	2.975(1)	123
N14−H141···O24b	2.606(1)	159
N14−H141···O25b	2.963(1)	122
O33−H331···O25	2.482(1)	176

Atoms D−H···A	Dist. D−A (Å)	Angle D−H−A (°)
	Compound 4[#]	
N27−H271···O1a	2.631(2)	147
N27−H271···O3a	2.918(2)	132
N35−H351···O2b	2.870(2)	121
N35−H351···O4b	2.704(2)	153
N43−H431···O13	2.661(2)	154
N43−H431···O15	2.889(2)	121
N51−H511···O17c	2.625(2)	145
N51−H511···O19c	2.913(2)	134
N60−H601···O6c	2.617(2)	150
N60−H601···O8c	2.863(2)	127
N68−H681···O18b	2.816(2)	123
N68−H681···O20b	2.699(2)	150
N76−H761···O9d	2.658(2)	161
N76−H761···O11d	2.915(2)	117
N84−H841···O10	2.951(2)	123
N84−H841···O12	2.589(2)	155
N93−H931···O5	2.968(2)	120
N93−H931···O7	2.626(2)	139
N101−H1011···O14e	2.901(2)	131
N101−H1011···O16e	2.614(2)	147
	Compound 5[#]	
N7−H71···O38a	2.579(5)	171
N15−H151···O63b	2.725(5)	159
N23−H231···O50c	2.559(4)	168
N31−H311···O57d	2.563(6)	168

[#]Symmetry operations:

For **1**: (a) 1+x, 0.5-y, 0.5+z; (b) 1-x, -0.5+y, 1.5-z; (c) -1+x, y, z. For **2** : (a) -1+x, 0.5-y, -0.5+z ; (b) -1+x, y, z ; (c) 1-x, 1-y, 1-z ; (d) 1+x, y, z ; (e) 2-x, 1-y, -z ; For **3** : (a) 2-x, 1-y, 1-z ; (b) x, 0.5-y, -0.5+z ; For **4** : (a) : 0.25+y, 0.75-x, 1.75-z ; (b) : 1-x, 1-y, 1-z ; (c) : 1-x, 1-y, 2-z ; (d) 0.75-y, 0.25+x, -0.75+z ; (e) : 0.75-y, -0.25+x, 0.75-z ; For **5** : (a) : -1+x, y, z ; (b) : 1+x, 1+y, z ; (c) : 1-x, -y, 2-z ; (d) : 1+x, y, z.

Table S3. Elemental Analyses and TGA results for materials **1-5**.

Compound	SCXRD formula	Elemental analysis formula	Elemental Analysis (%)[a]	TGA Weight Loss (%)[b]
1	[{(H_3TrIB)($CA)_{1.5}$}·2DMF·2.5H_2O]	[{(H_3TrIB)($CA)_{1.5}$}·2.3DMF·3H_2O]	found: C: 45.48; H: 4.75; N: 14.22 calc.: C: 45.71; H: 4.61; N: 14.32	found: 23.0 (at 190°C) calc.: 27.3
2	[{(H_4Tetrapy)($CA)_2$}·3DMF]	[{(H_4Tetrapy)($CA)_2$}·2.9DMF·1.5H_2O]	found: C: 50.01; H: 4.59; N: 8.63 calc.: C: 49.83; H: 4.69; N: 8.77	found: 20.8 (at 190°C) calc.: 21.7
3	[{(H_3TrIB)(H-Ox)(Ox)}·5H_2O]	[{(H_3TrIB)(H-Ox)(Ox)}·4.9H_2O]	found: C: 41.72; H: 4.36; N: 15.36 calc.: C: 41.90; H: 4.77; N: 15.43	–
4	[{(H_4Tetrapy)($Ox)_2$}·5H_2O]	[{(H_4Tetrapy)($Ox)_2$}·4.75H_2O]	found: C: 49.10; H: 5.41; N: 7.73 calc.: C: 49.05; H: 5.32; N: 7.89	found: 12.2 (at 130°C) calc.: 12.0
5	[{(H_4Tetrapy)($BDC)_2$(H_2O)}·1DMF·3H_2O]	[{(H_4Tetrapy)($BDC)_2$(H_2O)}·1DMF·2H_2O]	found: C: 59.85; H: 5.90; N: 8.04 calc.: C: 59.66; H: 5.35; N: 7.91	found: 13.0 calc.: 12.3

[a] Elemental analysis formula is used to access calc. values.

[b] Calculated weight loss is determined considering the departure of all the guests identified in Elemental analysis formula.