Two-step crystal engineering of porous nets from [$Cr_3(\mu_3\text{-}O)(RCO_2)_6$] and [$Cu_3(\mu_3\text{-}Cl)(RNH_2)_6Cl_6$] molecular building blocks.

Sameh K. Elsaidi, Mona H. Mohamed, Lukasz Wojtas, Amy J. Cairns, Mohamed Eddaoudi, and Michael J. Zaworotko

Supplementary materials

Materials and Methods

All starting materials were purchased in high purity grade and used as purchased without further purification. Solvents were purified according to standard methods and stored in the presence of molecular sieves. Thermogravimetric analysis (TGA) was performed under nitrogen on a TA Instrument TGA 2950 Hi-Res. X-ray powder diffraction (XPD) data were recorded on a Bruker D8 Advance X-ray diffractometer at 20 kV, 5 mA for CukR (λ = 1.5418 Å), with a scan speed of 0.5 s/step (6°/min) and a step size of 0.05° in 2θ at room temperature. The simulated XPD patterns were produced using Powder Cell for Windows Version 2.4 (programmed by W. Kraus and G. Nolze, BAM Berlin, 2000). The variable temperature X-ray powder diffraction (XPD) data were recorded on PANalytical X`PERT powder diffractometer (45 kV/ 40 mA, CuK $_\alpha$, λ = 1.5406Å) equipped. Gas adsorption was measured on the Micrometrics ASAP 2020 Surface Area and Porosity Analyzer**.**

Preparation of tp-PMBB-5:

In a typical procedure, $Cr(NO_3)_3 \cdot 9\,H_2O$ (0.400 g, 1.00 mmol) was dissolved in MeOH (15 mL) and refluxed for 10 minutes. Then m-aminobenzoic acid (0.274 g, 2.00 mmol) was added and reflux was continued for 3 hours. After cooling to room temperature, the solvent was removed *in vacuo* (yield: 0.674 g, 100%). The as-isolated crude product was used to conduct synthesis of network structures based upon tp-PMBB-5.

Preparation of tp-PMBB-6:

$Cr(NO_3)_3 \cdot 9\,H_2O$ (0.400 g, 1.00 mmol) was dissolved in MeOH (15 mL) and refluxed for 10 minutes. Then p-aminobenzoic acid (0.274 g, 2.00 mmol) was added and reflux was continued for 3 hours. After cooling to room temperature, the solvent was removed *in vacuo* (yield: 0.674 g, 100%). (yield: 0.674 g, 100%) . A single crystal has been harvested by a diffusion of chloroform to a methanolic solution of tp-PMBB-6.

Preparation of tp-PMBB-5-acs-1:

2ml DMF solution of **tp-PMBB-5** (0.06 mmol, 0.0690 g) onto which was carefully layered 2ml of 2:1 MeCN/DMF solution containing $CuCl_2 \cdot 2\,H_2O$ (0.06 mmol, 0.011 g) green rode-like crystals had formed after 2 weeks (yield 53% based on $CuCl_2$).

Preparation of tp-PMBB-6-stp-1

$CuCl_2 \cdot 2\,H_2O$ (0.0400 mmol, 0.00700 g) were dissolved in 2ml of a 2:1 THF/MeOH mixture onto which was carefully layered 2ml of a methanol solution containing **tp-PMBB-6** (0.0600 mmol, 0.0690g), dark green black rode-like crystals had formed after 1day. (yield 75% 0.156g based on $CuCl_2$).

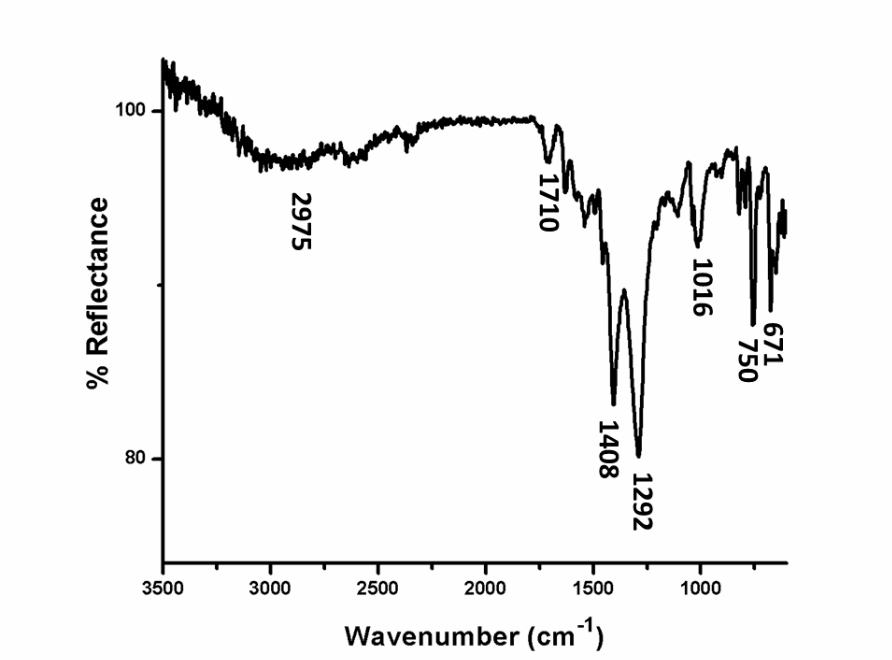


Figure S1. IR spectrum of **tp-PMBB-5.**

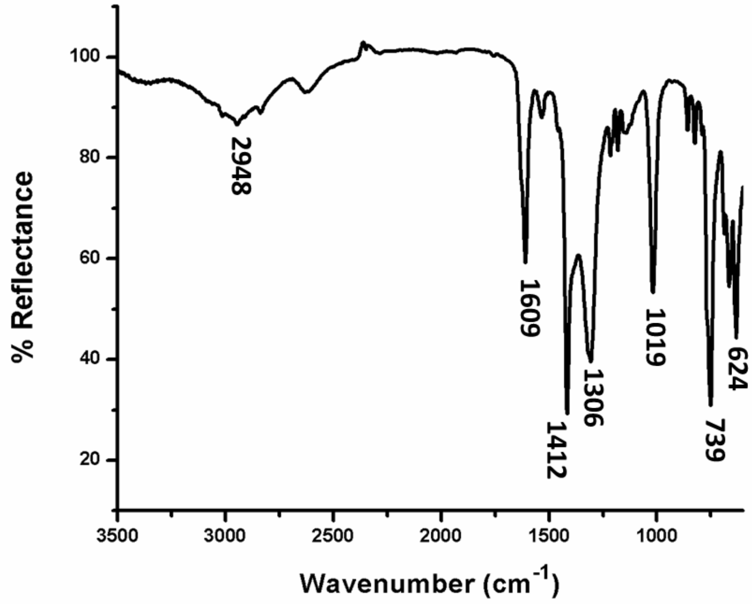


Figure S2. IR spectrum of **tp-PMBB-6.**

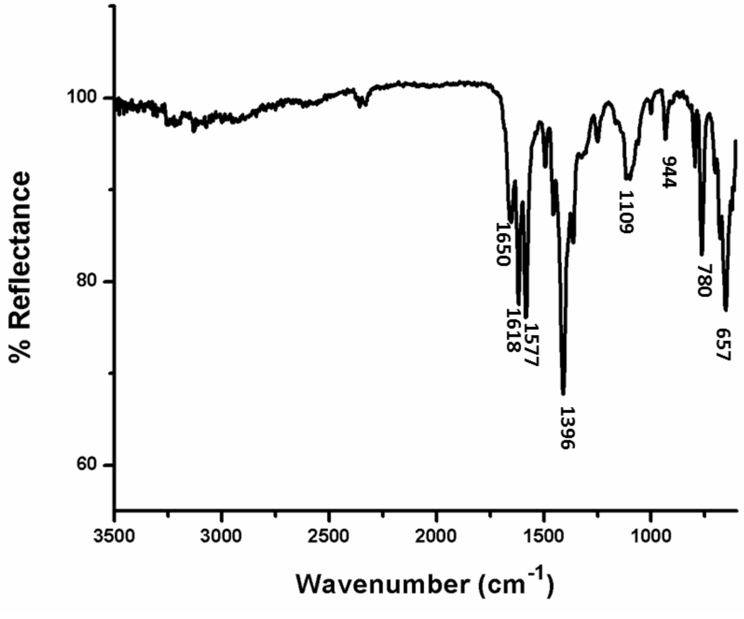


Figure S3. IR spectrum of **tp-PMBB-5-acs-1**.

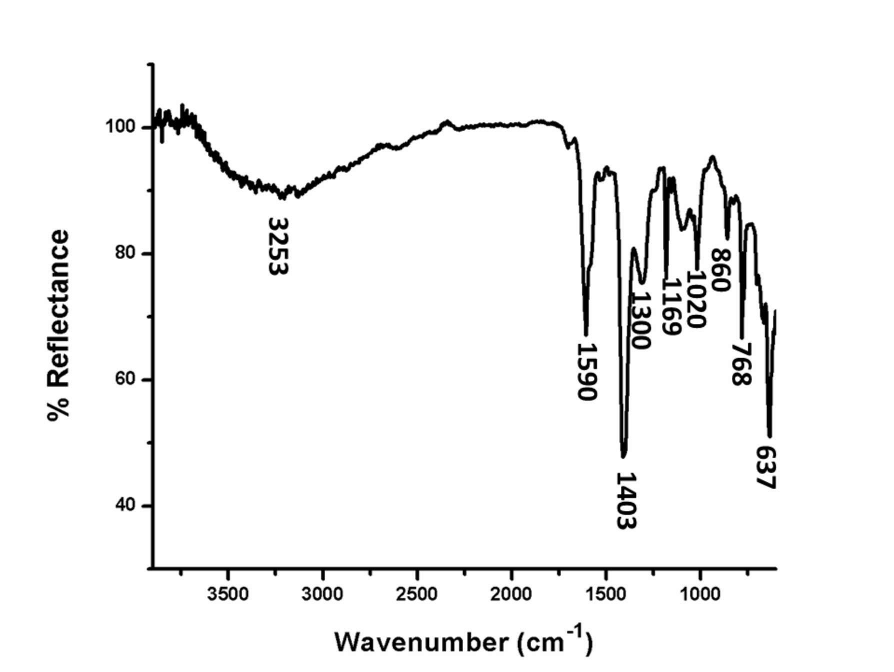


Figure S4. IR spectrum of **tp-PMBB-6-stp-1.**

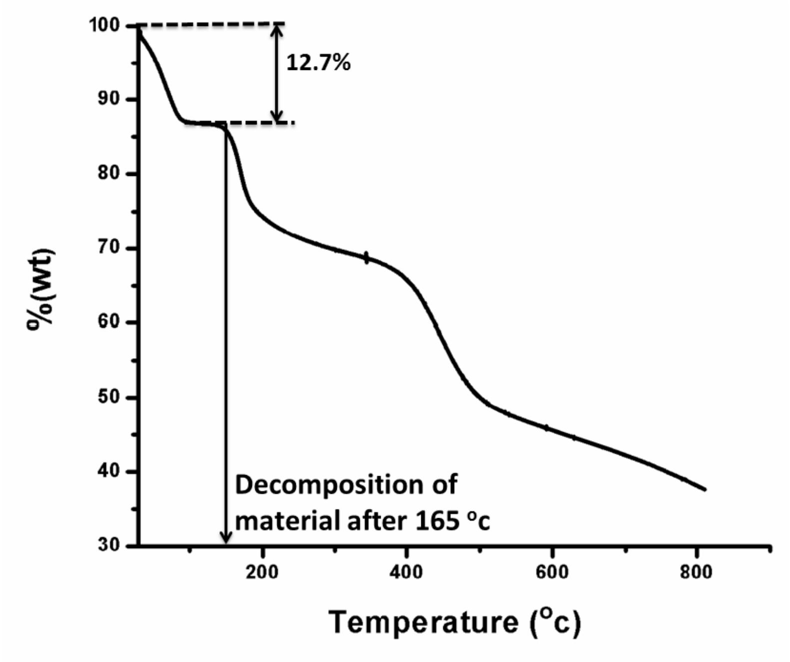


Figure S5. The TGA plot of **tp-PMBB-5-acs-1** reveals a 12.7% weight loss up to 100°C corresponding to loss of solvent. The material is stable up to 165°C as validated by variable temperature PXRD. The estimated weight loss of 18% was presumably not observed because solvent had already left the structure at room temperature and/or because solvent remained in the channels through bonding to open metal sites.

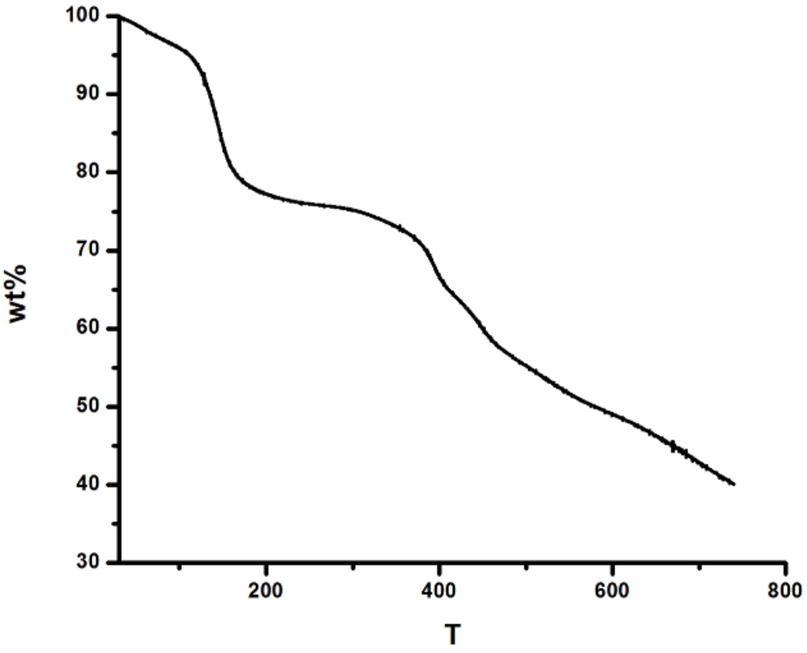


Figure S6. The TGA plot of **tp-PMBB-6-stp-1** indicates that the material is stable only to 108 ^{o}C.

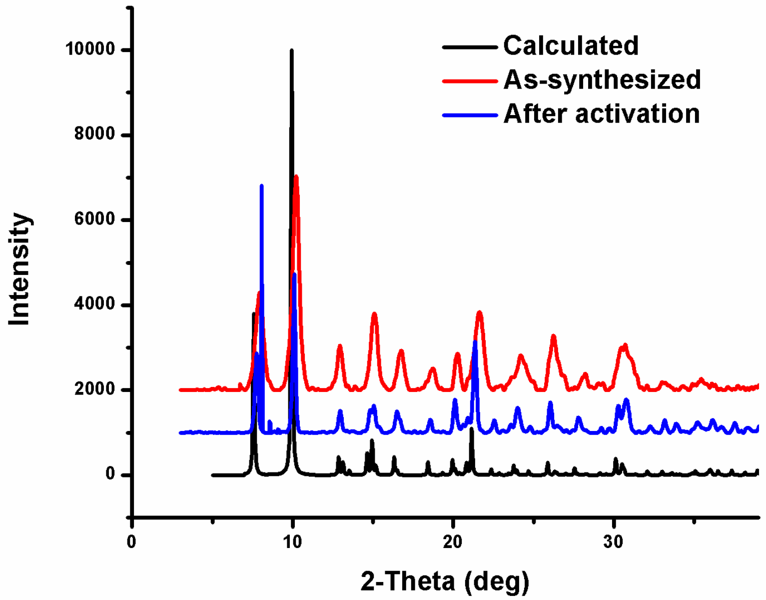


Figure S7. PXRD patterns of **tp-PMBB-5-acs-1**.

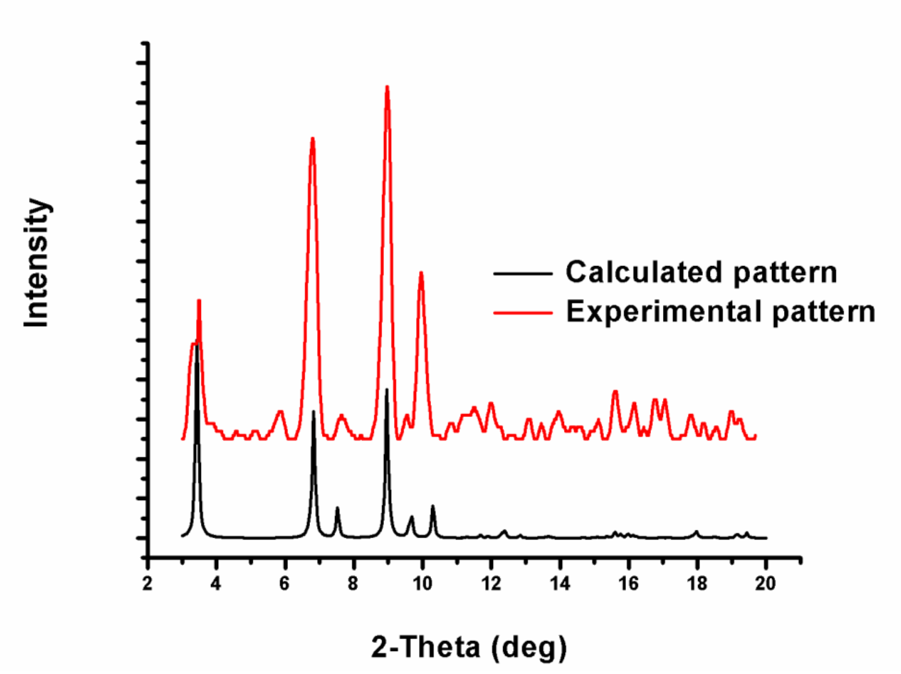


Figure S8. Experimental and calculated PXRD patterns for **tp-PMBB-6-stp-1**.

Gas sorption properties

The calculated surface areas for **tp-PMBB-6-stp-1** and **tp-PMBB-5-acs-1** are 2930 and 849 m^2/g, respectively while the experimental BET surface areas are 323 and 710 m^2/g, respectively. The low observed surface area of **tp-PMBB-6-stp-1** might be linked to its relatively low thermal stability (stable only up to 108°C). Activation of the crystals was conducted using supercritical CO_2 drying.

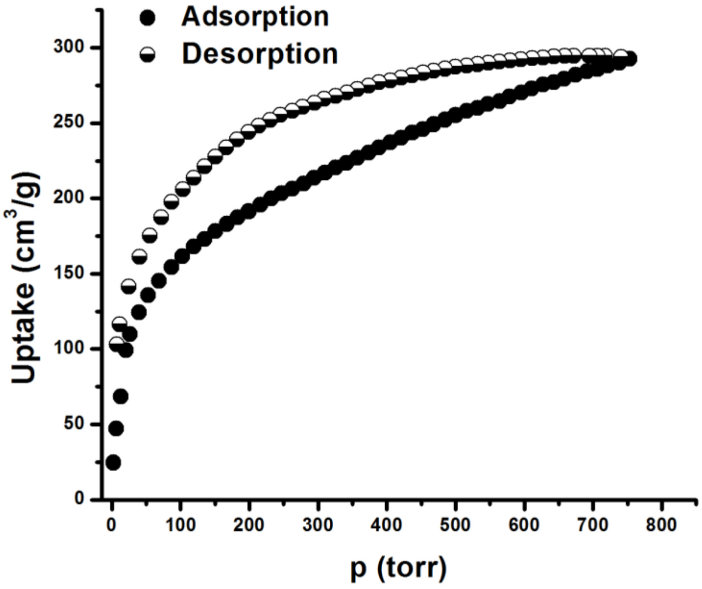


Figure S9. CO_2 isotherm at 195 K for **tp-PMBB-5-acs-1**.

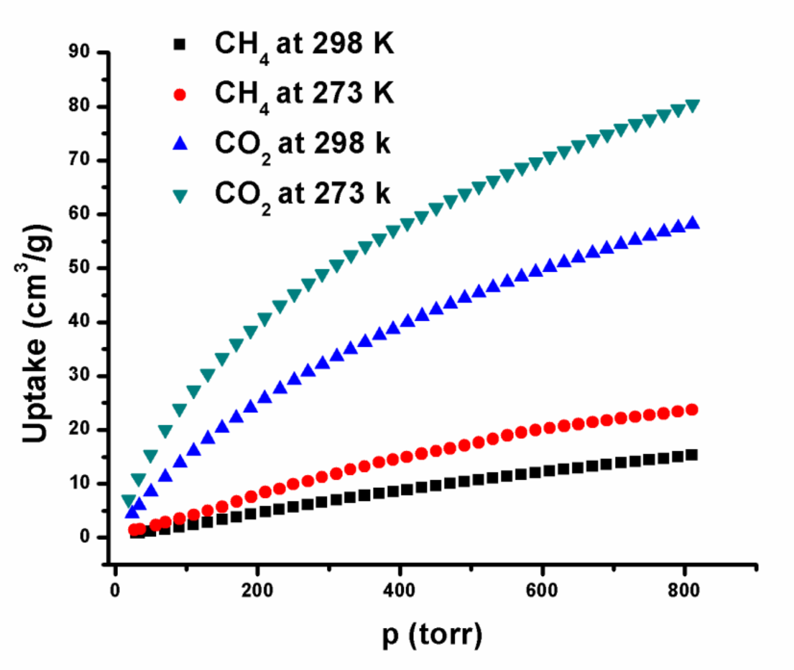
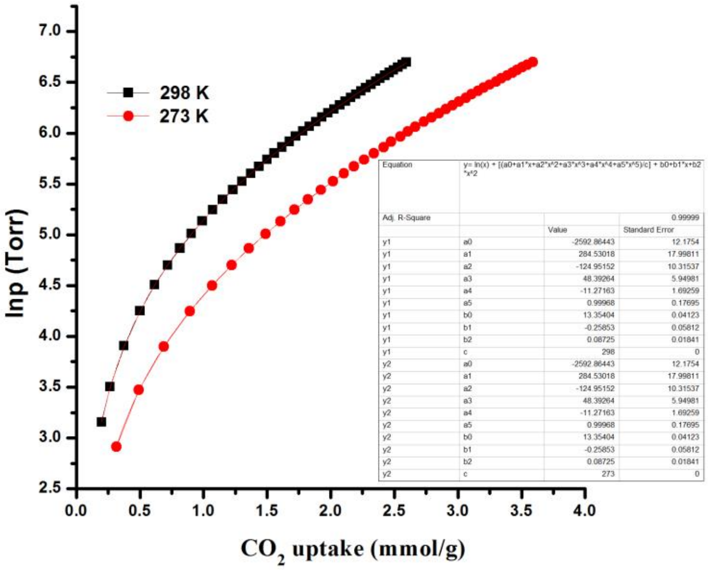


Figure S10. CO_2 and CH_4 adsorption isotherms for **tp-PMBB-5-acs-1** at 273 K and 298 K.



Equation	y= ln(x) + [(a0+a1*x+a2*x^2+a3*x^3+a4*x^4+a5*x^5)/c] + b0+b1*x+b2*x^2		
Adj. R-Square			0.99999
		Value	Standard Error
y1	a0	-2592.86443	12.1754
y1	a1	284.53018	17.99811
y1	a2	-124.95152	10.31537
y1	a3	48.39264	5.94981
y1	a4	-11.27163	1.69259
y1	a5	0.99968	0.17695
y1	b0	13.35404	0.04123
y1	b1	-0.25853	0.05812
y1	b2	0.08725	0.01841
y1	c	298	0
y2	a0	-2592.86443	12.1754
y2	a1	284.53018	17.99811
y2	a2	-124.95152	10.31537
y2	a3	48.39264	5.94981
y2	a4	-11.27163	1.69259
y2	a5	0.99968	0.17695
y2	b0	13.35404	0.04123
y2	b1	-0.25853	0.05812
y2	b2	0.08725	0.01841
y2	c	273	0

Figure S11. Fitted CO_2 adsorption isotherms of **tp-PMBB-5-acs-1.**

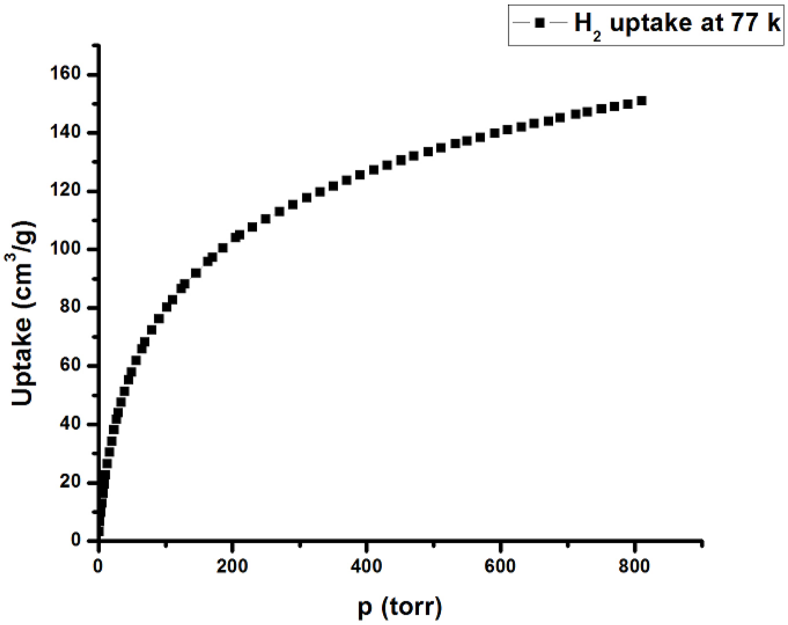


Figure S12. Hydrogen adsorption isotherm of **tp-PMBB-5-acs-1** at 77K.

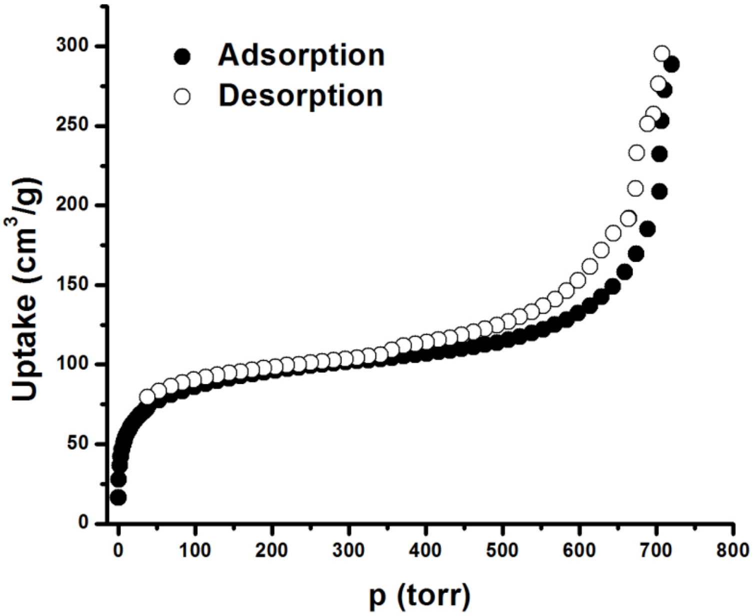


Figure S13 : N_2 isotherm at 77 K for **tp-PMBB-6-stp-1**.

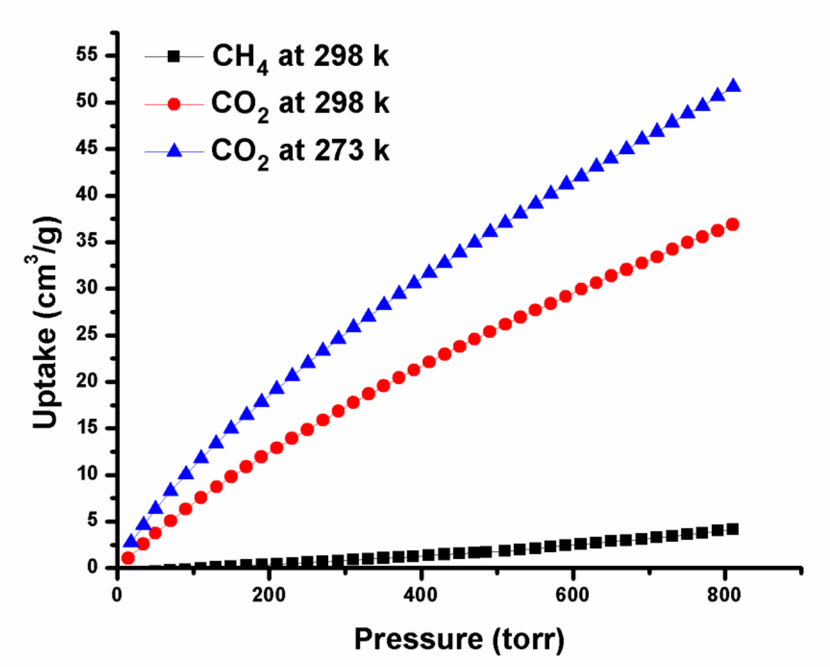
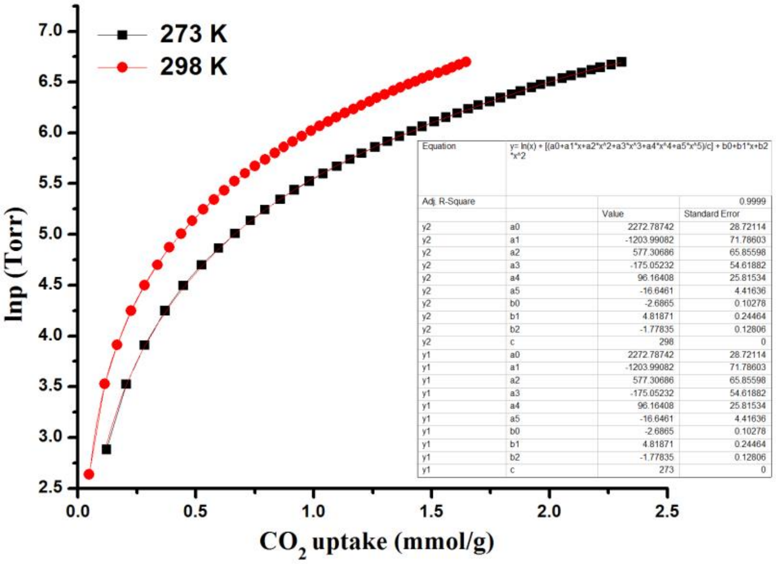


Figure S14. CO_2 adsorption isotherms at 273 K and 298 K and CH_4 adsorption isotherm at 298 K for **tp-PMBB-6-stp-1**.



Equation	y= ln(x) + [(a0+a1*x+a2*x^2+a3*x^3+a4*x^4+a5*x^5)/c] + b0+b1*x+b2 *x^2		
Adj. R-Square			0.9999
		Value	Standard Error
y2	a0	2272.78742	28.72114
y2	a1	-1203.99082	71.78603
y2	a2	577.30686	65.85598
y2	a3	-175.05232	54.61882
y2	a4	96.16408	25.81534
y2	a5	-16.6461	4.41636
y2	b0	-2.6865	0.10278
y2	b1	4.81871	0.24464
y2	b2	-1.77835	0.12806
y2	c	298	0
y1	a0	2272.78742	28.72114
y1	a1	-1203.99082	71.78603
y1	a2	577.30686	65.85598
y1	a3	-175.05232	54.61882
y1	a4	96.16408	25.81534
y1	a5	-16.6461	4.41636
y1	b0	-2.6865	0.10278
y1	b1	4.81871	0.24464
y1	b2	-1.77835	0.12806
y1	c	273	0

Figure S15. Fitted CO_2 adsorption isotherms for **tp-PMBB-6-stp-1**.

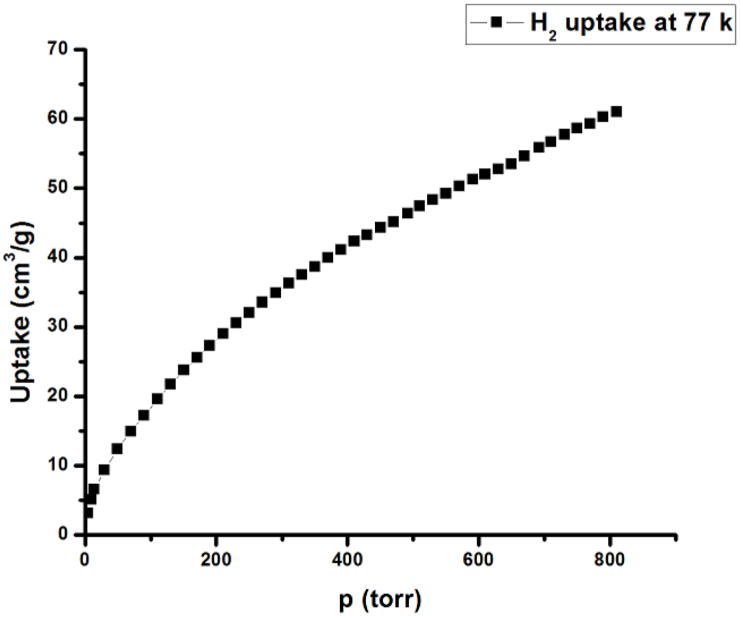


Figure S16. Hydrogen adsorption isotherm for **tp-PMBB-6-stp-1** at 77K.

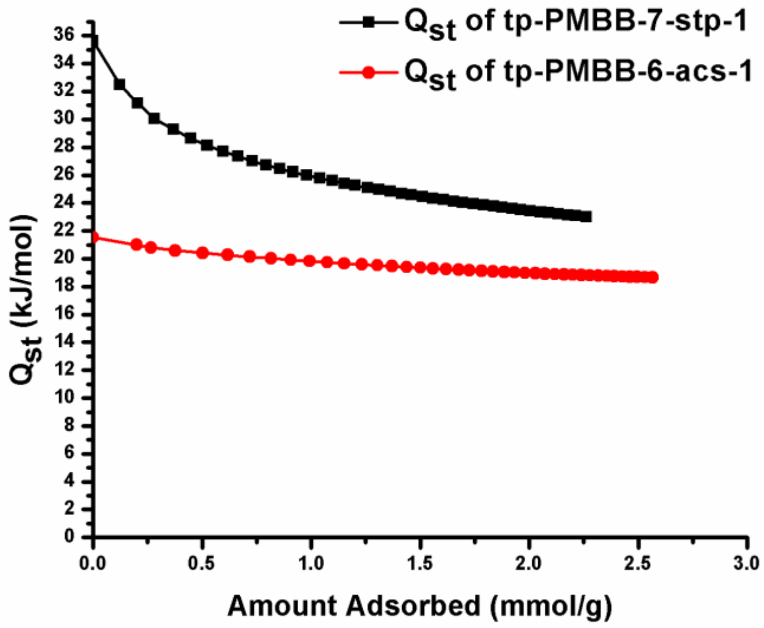


Figure S17. Isosteric heat of adsorption (Q_{st}) for carbon dioxide exhibited by tp-PMBB-6-**stp**-1 and tp-PMBB-5-**acs**-1 as calculated from the adsorption isotherms collected at 298 K and 273 K.

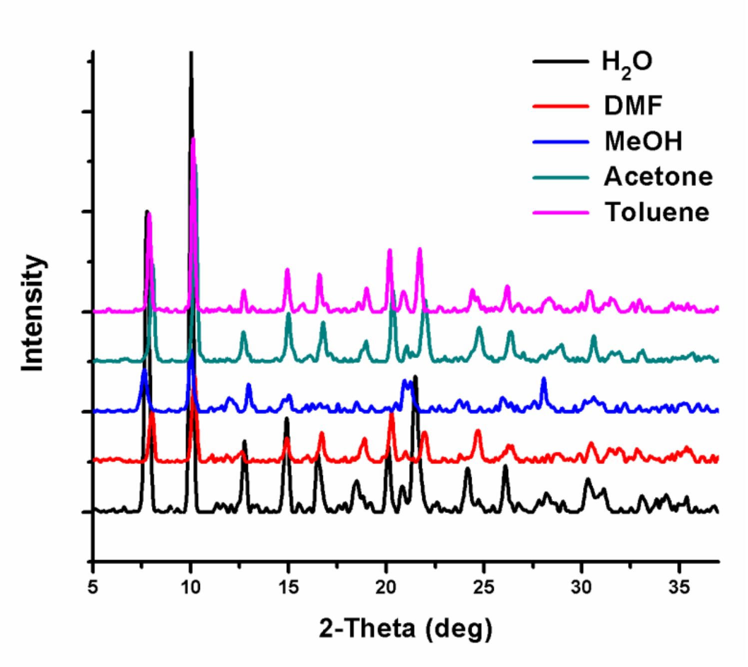


Figure S18. PXRD patterns of **tp-PMBB-5-acs-1** exposed to different solvents.

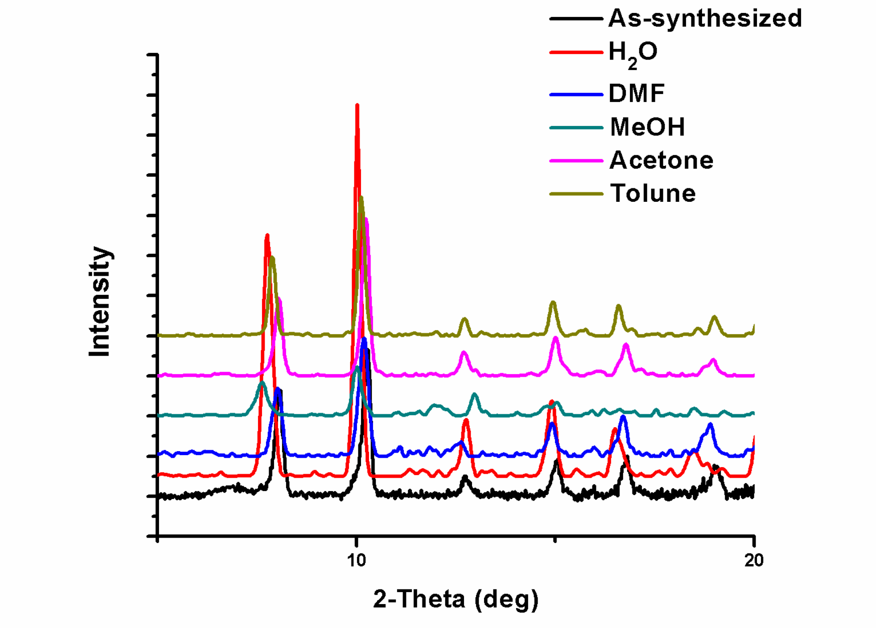


Figure S19. Low angle PXRD patterns of tp-PMBB-5-acs-1 upon exposure to different solvents.

Table 1: Cell parameters of tp-PMBB-acs-1 following exposure to different solvent.

Type of post treatment	a(Å)	c(Å)
As-synthesized (Wet sample)	13.47	27.51
After activation (Dried sample)	13.17	27.51
Adsorption of H_2O	13.99	27.51
Adsorption of DMF	13.47	27.51
Adsorption of MeOH	14.14	26.99
Adsorption of acetone	13.47	27.51
Adsorption of toluene	13.47	27.51

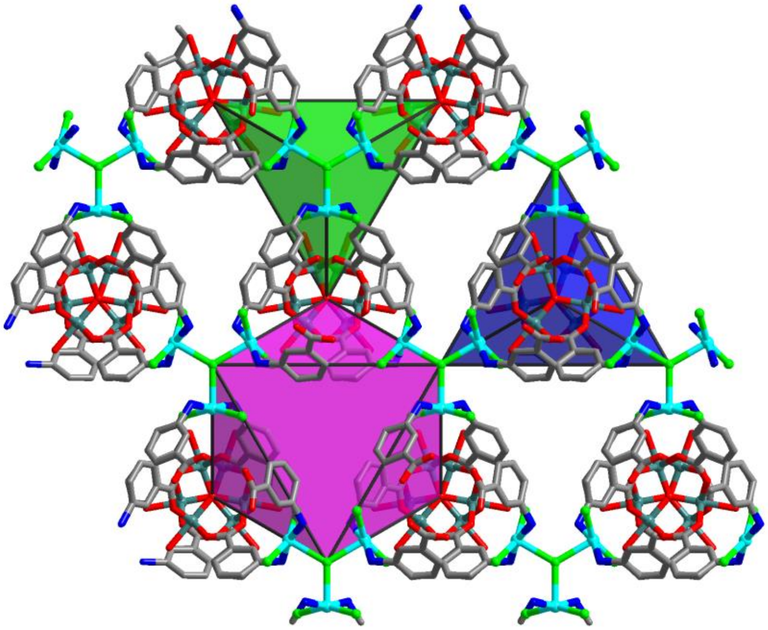


Figure S20. The three different cages in **tp-PMBB-5-acs-1** viewed along 001.

X-ray Crystallography

Single-Crystal X-Ray Diffraction for tp-PMBB-6

X-ray diffraction data were collected using a Bruker-AXS SMART-APEXII CCD diffractometer Indexing was performed using *APEX2* [1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01 [2]. Absorption correction was performed by multi-scan method implemented in SADABS [3]. Space groups were determined using XPREP implemented in APEX2 [1]. The structure was solved using SHELXS-97 (direct methods) or using Apex2's Intrinsic Phasing and refined using WinGX v1.70.01[4,5,6,7] and SHELXL-97 (full-matrix least-squares on F^2) contained in OLEX2 [8] programs.

tp-PMBB-6: The tp-PMBB-6 crystallizes in the polar space group R3m. The following atoms lie on symmetry elements: Site symmetry (.m) - Cr1, Cl1, O4, C6, C10, O9, C7, N4, C1, Cl4, N2, O6, N1, C5, C2, C13, O7,C14, C11, Cl3, O2; Site symmetry (3m) - Cl2, O15, O5, N3, C16, C12, C17, N5, O14. All non-hydrogen atoms of the Cr-trimer were refined anisotropically. Heavily disordered nitrate / solvent was refined isotropically and, in some cases, with restraints. Hydrogen atoms of –CH, -CH3 groups were placed in geometrically calculated positions and included in the refinement process using a riding model with isotropic thermal parameters: Uiso (H) = 1.2(1.5) Ueq [-CH(-CH3)]. The structure contains solvent accessible voids of 120 A^3 possibly containing disordered nitrate anions. The crystal was found to be a twin and was refined using an HKL5 type file generated using {-1 0 0 1 1 0 0 0 -1 matrix = 180 rotation about [120] direct lattice direction, BASF = 0.353(3)}. Crystal data and details of structure refinement are shown in Table 2.

Table 2 Crystal data and structure refinement for compound tp-PMBB-6.

Identification code	**tp-PMBB-6**
Empirical formula	$C_{53.25}H_{98.33}Cl_9Cr_3N_{13}O_{52.4}$
Moiety formula	$(C_{54}H_{42}N_6O_{16}\ Cr_3)^{7+}$,7($NO_3^-$), 3($CHCl_3$), 8.25($CH_3OH$), 10.16($H_2O$)
Formula weight	2234.23
Temperature/K	100(2)
Crystal system	trigonal
Space group	R3m
a/Å	15.2032(6)
b/Å	15.2032(6)
c/Å	46.090(2)
α/°	90.00
β/°	90.00
γ/°	120.00
Volume/Å^3	9225.8(7)
Z	3
ρ_{calc}mg/mm^3	1.206
m/mm^{-1}	4.653
F(000)	3459.0
Crystal size/mm^3	0.31 × 0.28 × 0.26
2Θ range for data collection	7.74 to 131.76°
Index ranges	$-18 \leq h \leq 18$, $-17 \leq k \leq 18$, $-53 \leq l \leq 51$
Reflections collected	14040
Independent reflections	14040 [R(int) = 0.0000]
Data/restraints/parameters	14040/21/258
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.1109, wR_2 = 0.2833
Final R indexes [all data]	R_1 = 0.1374, wR_2 = 0.3143
Largest diff. peak/hole / e Å^{-3}	0.99/-0.72
Flack parameter	0.073(12)

Single-Crystal X-Ray Diffraction for tp-PMBB-5-acs-1

X-ray diffraction data were collected using a Bruker-AXS SMART-APEXII CCD diffractometer using CuKα (λ = 1.54178 Å). Indexing was performed using *APEX2* [1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01 [2]. Absorption correction was performed by multi-scan method implemented in SADABS [3]. Space groups were determined using XPREP implemented in APEX2 [1]. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (full-matrix least-squares on F^2) contained in APEX2 [1] and WinGX. All non-H atoms were found in the difference Fourier map and refined anisotropically. The lack of high angle diffraction data can be attributed to the presence of disordered solvent in structural cavities. C, N and O atoms were refined using geometry restraints / constraints (DFIX, AFIX 66). Restraints were also used to refine the anisotropic displacement parameters (SIMU). Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using a riding model with isotropic thermal parameters: Uiso(H) = 1.2 U_{eq}(-CH, -NH_2). The contribution of disordered solvent molecules was treated as diffuse using the Squeeze procedure implemented in the Platon program[9,10]. tp-PMBB-5-acs-1 crystallizes in the polar space group P-6c2. The following atoms lie on symmetry elements: site symmetry (..2) Cu1; site symmetry (m..) Cr1, O3; site symmetry (3.2) Cl2; site symmetry (-6..) O4. It was not possible to establish the formula using Squeeze because a mixture of DMF and MeCN was used and water molecules could also be present. Squeeze resulted in 248 el per formula unit of $C_{42}H_{36}Cl_7Cr_3Cu_3N_6O_{16}$ contained in a volume of 994 A^3. This would correspond to 6 DMF molecules (444A^3) or 11 MeCN molecules (484A^3) or 25 H_2O (475A^3) molecules and additional weight of 438 or 451 g/mole per formula unit. A reasonable estimate of the formula would be $[Cr_3O(H_2O)_3(C_7H_6NO_2)_6Cu_3Cl_7]$. *x*DMF,*y*MECN,*z*H2O with the total number of electrons from solvent not exceeding 248. Crystal data and refinement conditions are shown in Table 3.

Table 3. Crystal data and structure refinement for compound tp-PMBB-5-acs-1

Identification code	**tp-PMBB-5-acs-1**
Empirical formula	$C_{42} H_{36} Cl_7 Cr_3 Cu_3 N_6 O_{16}$
Formula weight	1475.54
Temperature	228(2) K
Wavelength	1.54178 A
Crystal system, space group	Hexagonal, P-6c2
Unit cell dimensions	a = 13.469(12) A alpha = 90 deg. b = 13.469(12) A beta = 90 deg. c = 27.51(2) A gamma = 120 deg.
Volume	4323(6) A^3
Z, Calculated density	2, 1.134 Mg/m^3
Absorption coefficient	6.185 mm^-1
F(000)	1472
Crystal size	0.10 x 0.08 x 0.07 mm
Theta range for data collection	3.79 to 38.97 deg.
Limiting indices	-8<=h<=10, -8<=k<=4, -22<=l<=8
Reflections collected / unique	2324 / 794 [R(int) = 0.0759]
Completeness to theta = 38.97	97.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6713 and 0.5767
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	794 / 63 / 109
Goodness-of-fit on F^2	0.946
Final R indices [I>2sigma(I)]	R1 = 0.0449, wR2 = 0.0887
R indices (all data)	R1 = 0.0599, wR2 = 0.0936
Absolute structure parameter	0.10(2)
Largest diff. peak and hole	0.168 and -0.196 e.A^-3

Single-Crystal X-Ray Diffraction for tp-PMBB-6-stp-1

X-ray diffraction data were collected using synchrotron radiation, $\lambda = 0.40663$ Å, at the Advanced Photon Source, Chicago Il. Indexing was performed using *APEX2* [1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01 [2]. Absorption correction was performed by multi-scan method implemented in SADABS [3]. Space groups were determined using XPREP implemented in APEX2 [1]. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (full-matrix least-squares on F^2) contained in APEX2 [1] and WinGX v1.70.01 [4,5,6,7] programs packages. Despite using synchrotron source and trying several crystals from different batches, diffraction spots were observed only up to 1.45 Å resolution. This can be attributed ligand and solvent disorder. All non-H atoms were found in the difference Fourier map but due to the low resolution they were refined using geometry restraints. Restraints were also used to refine the anisotropic displacement parameters of the C,N and O atoms. Atoms C12, C13, C14 and N15 of the 4-aminobenzoate moiety were refined isotropically and were found to exhibit much lrger thermal ellipsoids than other atoms due to disorder. Occupancies of atoms O31, O32 and O33 were refined and converged to approximately 1 for O31, 0.5 for O32 and 0.75 for O33. The formula has been updated. The reason for including oxygen atoms O31, O32 and O33 in the model is that O31 bridges two -NH2 groups through hydrogen bonding. This explains why it was still possible to locate the non-coordinated part of the ligand in the channel. This also suggests that the occupancy of this oxygen atom could be 100% assuming that NH2 groups are bridged by two water molecules. The disorder and lower resolution cause inaccuracies in distances of intermolecular contacts but no distance restraints were used to refine this part of the structure and the thermal parameters of these oxygen atoms was freely refined. The low resolution of data did not allow for more precise modeling of disorder. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using a riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH,-NH,-NH2). The contribution of heavily disordered solvent molecules was treated as diffuse using the Squeeze procedure implemented in the Platon program [9,10]. The tp-PMBB-6-stp-1 crystallizes in P63/mcm. The following atoms lie on symmetry elements: site symmetry (..m) Cr3, O3; site symmetry (m..) C1, C2, C14, N15; site symmetry (3.2) Cl2; site symmetry (3..) O6; site symmetry (..m) O31, O32, O33; site symmetry (m2m) Cr2, O1, O4; site symmetry (..2) Cu1.

It was not possible to establish the formula using Squeeze because a mixture of MeOH and CH2Cl2 had been used and water molecules could also be present. Squeeze resulted in 1317 el per formula unit of $C_{126}H_{161}Cl_{14}Cr_9Cu_6N_{18}O_{65.5}$ contained in the cell volume of 6677A^3. This would correspond to 32 CH_2Cl_2 molecules (1744A^3) or 74 MeOH molecules (2553A^3) or 133 H_2O (2487A^3) molecules and additional weight of 2717 or 2368 or 2394 g/mole per formula unit. Most reasonably there is a mixture of solvent present in the pores so a formula of $[(Cr_3O)_3(H_2O)_3(C_7H_6NO_2)_{18}(Cu3ClCl6)_2].23.5H_2O$. ($x$$CH_2Cl_2$,$y$MeOH,$z$$H_2O$ with the total number of electrons not exceeding 1332 has been assigned. Crystal data and refinement conditions are shown in Table 4.

Table 4 Crystal data and structure refinement for compound tp-PMBB-6-stp-1	
Identification code	**tp-PMBB-6-stp-1**
Empirical formula	$C_{126}H_{161}Cl_{14}Cr_9Cu_6N_{18}O_{65.5}$
Formula weight	4321.27
Temperature/K	100(2)
Crystal system	hexagonal
Space group	$P6_3/mcm$
a/Å	29.72(2)
b/Å	29.72(2)
c/Å	26.388(18)
α/°	90.00
β/°	90.00
γ/°	120.00
Volume/$Å^3$	20192(24)
Z	2
$\rho_{calc}mg/mm^3$	0.711
m/mm^{-1}	0.128
F(000)	4390.0
Crystal size/mm^3	0.1 × 0.1 × 0.02
2Θ range for data collection	1.82 to 16.12°
Index ranges	$-19 \leq h \leq 20$, $-20 \leq k \leq 20$, $-17 \leq l \leq 17$
Reflections collected	7178
Independent reflections	1228[R(int) = 0.1506]
Data/restraints/parameters	1228/136/177
Goodness-of-fit on F^2	1.120
Final R indexes [I>=2σ (I)]	$R_1 = 0.0931$, $wR_2 = 0.2290$
Final R indexes [all data]	$R_1 = 0.1336$, $wR_2 = 0.2452$
Largest diff. peak/hole / e $Å^{-3}$	0.32/-0.32

Table 5. CCDC numbers of the three deposited cif files

Compound Name	tp-PMBB-6-stp-1	tp-PMBB-6	tp-PMBB-5-acs-1
CCDC Number	943023	943024	943025

Additional references:

[1] Bruker (2010). *APEX2*). Bruker AXS Inc., Madison, Wisconsin, USA.

[2] Bruker (2009). SAINT. Data Reduction Software. Bruker AXS Inc., Madison, Wisconsin, USA.

[3] Sheldrick, G. M. (2008). *SADABS. Program for Empirical Absorption Correction.* University of Gottingen, Germany.

[4] Farrugia L.J. Appl. Cryst. (1999). 32, 837±838

[5] Sheldrick, G.M. (1997) SHELXL-97. Program for the Refinement of Crystal

[6] Sheldrick, G.M. (1990) Acta Cryst. A46, 467-473

[7] Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.

[8] Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H., OLEX2: A complete structure solution, refinement and analysis program (2009). J. Appl. Cryst., 42, 339-341.

[9] Spek, T.L., Acta Cryst. (1990). A46, 194-201.

[10] Spek, T.L., Acta Cryst. (1990). A46, c34.