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Journal Name

COMMUNICATION

Network Diversity Through Two-Step Crystal Engineering of a Decorated 6-Connected Primary Molecular Building Block

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Supporting Information

1. Physical Methods

Powder X-ray diffraction analyses were performed with a Philips X'Pert PRO MPD, equipped with a Cu-K_α source. Thermogravimetric analyses were carried out on a TA Instruments Q50 system under flow of N_2 using a heating rate of 10 °C min^{-1}. Gas sorption isotherms were measured using Micromeritics Tristar II 3030 and 3Flex 3500 surface characterization analysers.

Single-crystal reflection data were collected on a Bruker Quest diffractometer equipped with a CMOS detector and IμS microfocus X-ray source (Cu K_α, λ = 1.5418 Å) or using synchrotron radiation at APS, ChemMatCARS Sector 15, Argonne National Laboratory (**tp-PMBB-2-rtl-1 and tp-PMBB-2-stp-1**). Indexing was performed using *APEX2*[Bruker, 2012] (Difference Vectors method). Data integration and reduction were performed using SaintPlus[Bruker, 2012]. Absorption correction was performed by multi-scan method implemented in SADABS. Space group was determined using XPREP implemented in APEX2[Bruker, 2012]. Structural solution and refinement against F^2 were carried out using the SHELXL programs[1] through Olex2 interface[2]. All non-hydrogen framework atoms were refined with anisotropic parameters, while H atoms were placed in calculated positions and refined using a riding model. Some of disordered atoms have been refined isotropically. The contribution of heavily disordered mixture of solvent molecules, for all but **tp-PMBB-2-pcu-1** structure, was treated as diffuse using Squeeze procedure implemented in Platon program[3]. Crystallographic data and structural refinement information are listed in **Tables S1-S5**. **tp-PMBB-2-acs-1:** The structure has been refined as two component twin (180° rotation about [100] direct lattice direction, twin law: 100/-1-10/00-1) in $P6_3/m$ space group. Several atoms therefore have

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† Electronic Supplementary Information (ESI) available: Experimental details, Single-crystal XRD data (CCDC number: 1482197-1482201), PXRD patterns, TGA curves. See DOI: 10.1039/x0xx00000x

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crystallographically imposed symmetry: Cu1 (-1), Cr1 (m), O1 (-6), O2 (m). Distance restraints have been used during refinement. **tp-PMBB-2-rtl-1**: Restraints have been used to refine disordered solvent molecules and counterions. Some of disordered solvent have been modeled as O atoms. The structure was solved and refined in P-42_1c space group. Several atoms therefore have crystallographically imposed symmetry: Cr1 (2), O31 (2), O61 (2). The disordered solvent molecules were refined using restraints. **tp-PMBB-2-stp-1:** The structure was solved and refined in $P6_3$/mcm space group. Several atoms therefore have crystallographically imposed symmetry: Mn1 (2/m), Cr1 (m), Cl1 (m), O1 (-6), O21 (m). The disordered methanol molecule has been refined using restraint. **tp-PMBB-2-fsc-1**: Disordered framework atoms have been refined using restraints and constraints (AFIX 66). The structure was solved and refined in Ccca space group. Several atoms therefore have crystallographically imposed symmetry: Cd1 (2), Cd2 (-1), Cr2 (2), O1 (2), O8(2). **tp-PMBB-2-pcu-1**: Disordered DMF molecules have refined using restraints. The structure was solved and refined in R-3c space group. Several atoms therefore have crystallographically imposed symmetry: O3 (3).

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1482197-1482201.

1. G. M. Sheldrick, *Acta Cryst*. **2015**, C71, 3-8.
2. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H., OLEX2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst*., **2009**, 42, 339-341.
3. Spek, A.L. *Acta Cryst.* **2015**, C71, 9-18.

2. Syntheses and Characterization

Commercially available reagents were purchased in high purity grade and used as received.

2.1 Synthesis of building block PMBB

Preparation of tp-PMBB-2: The preparation and structure of tp-PMBB-2 from stoichiometric amounts of $Cr(NO_3)_3{\cdot}9H_2O$ and nicotinic acid has been previously reported in the literature. In this contribution we followed a slightly different procedure to obtain PMBB-2: 3-pyridinecarboxylic acid (2.46 g, 20.0 mmol) and $Cr(NO_3)_3{\cdot}9H_2O$ (4.00 g, 10.0 mmol) were ground by hand with 3 drops of deionized H_2O in an agate mortar for 15 minutes. The resulting purple solid was placed in an open container at 85°C and allowed to react for 24 h or until it reached dryness.

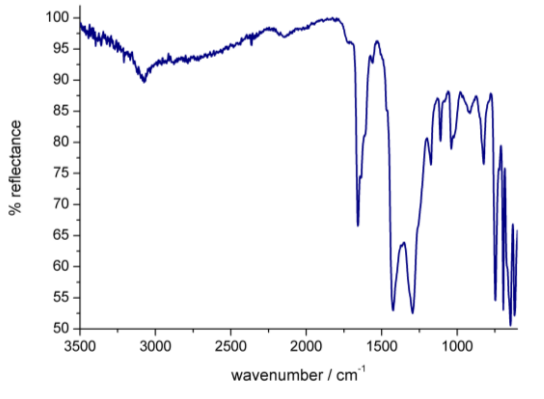

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Figure S1. FT-IR of tp-PMBB-2.

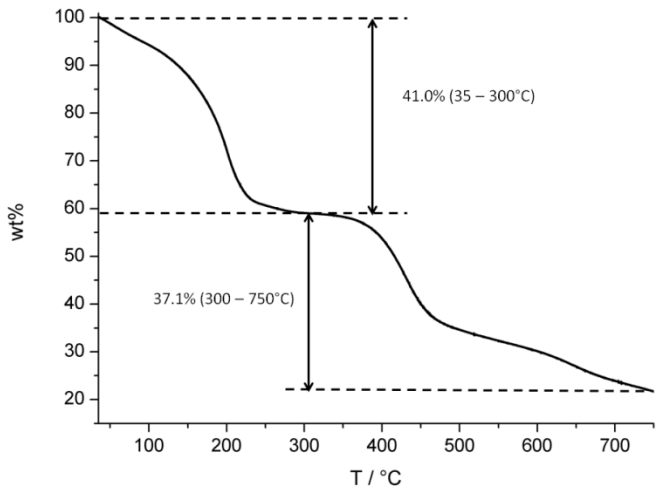

Figure S2. TGA of tp-PMBB-2.

2.2 Synthesis of coordination networks by using PMBB (Two-Step Crystal Engineering)

tp-PMBB-2-acs-1: tp-PMBB-2 (0.01125 mmol, 15.8 mg) was dissolved in 1.5 mL of a 2:1 mixture of DMF and CH_3CN. The resulting solution was placed in a test tube and layered first with 0.5 mL of 1:1 mixture of DMF/CH_3CN and then with a solution of $Cu(NO_3)_2{\cdot}3H_2O$ (0.0375 mmol, 9 mg) in 1.5 mL of a 1:2 mixture of DMF/CH_3CN. After 4 days, green hexagonal-shaped crystals suitable for single-crystal X-ray were harvested. Yield: 33%. IR: ν_{max} (cm^{-1}) = 3120, 1637, 1415, 1293, 1175, 1134, 1108, 1063, 1012, 828, 768, 707, 645.

tp-PMBB-2-stp-1: tp-PMBB-2 (0.2524 g) was suspended in 8.0 mL of tetrahydrofuran and 1.3 mL of a saturated aqueous sodium bicarbonate solution was added. After stirring for 15 minutes, the solution was filtered and the THF layer was decanted. 2 mL of the THF solution were placed into a test tube and layered with a solution of $MnCl_2{\cdot}4H_2O$ (0.15 mmol, 0.0297 g) in 2 mL MeOH. After 3 days at room temperature, a light-green hexagonal-shaped single crystal suitable for single crystal X-ray was harvested. The rest of the crystalline product was collected by filtration, washed with small amounts of THF and dried briefly in air. Yield: 9%. IR: ν_{max} (cm^{-1}) = 1625, 1495, 1463, 1405, 1194, 1118, 1023, 1012, 769, 717, 647.

tp-PMBB-2-rtl-1: tp-PMBB-2 (0.125 g) was dissolved in 4.0 mL of methanol together with 0.042 mL of triethylamine. Then 2 mL of this solution was layered onto a solution of $Cd(NO_3)_2{\cdot}4\ H_2O$ (0.15 mmol, 0.0463 g) in 2 mL of ethanol. After 4 days at room temperature, a long green prismatic single crystal suitable for single crystal X-ray was harvested. The rest of the crystalline product was collected by filtration, washed with small amounts of

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MeOH and dried briefly in air. Yield: 18 %. IR: ν_{max} (cm^{-1}) = 2907, 2811, 1633, 1402, 1315, 1204, 1138, 1024, 848, 772, 645.

tp-PMBB-2-fsc-1: tp-PMBB-2 (0.01125 mmol, 15.8 mg) was dissolved in 1.5 mL of a 2:1 mixture of DMF and CH_3CN. The resulting solution was placed in a test tube and layered first with 0.5 mL of 1:1 mixture of DMF/CH_3CN and then with a solution of $CdCl_2$ (0.0375 mmol, 6.8 mg) in 1.5 mL of a 1:2 mixture of DMF/CH_3CN. After 7 days, green square prism crystals suitable for single-crystal X-ray were harvested. Yield: 18%. IR: ν_{max} (cm^{-1}) = 3066, 1622, 1571, 1480, 1432, 1407, 1248, 1197, 1168, 1118, 1095, 1045, 1030, 852, 696.

tp-PMBB-2-pcu-1: A mixture of tp-PMBB-2 (0.01125 mmol, 15.8 mg), $CuCl_2$ (0.0375 mmol, 5 mg), DMF (2 mL) was added to a glass vial with 7 ml volume. The vial was capped tightly and placed in an oven at 75 °C for 24 h, after which the vial was cooled to room temperature. After rinsing several times with fresh DMF, green hexagonal crystals were obtained. Yield, 65% based on Cu. IR: ν_{max} (cm^{-1}) = 3081, 1623, 1586, 1576, 1483, 1439, 1395, 1290, 1251, 1196, 1171, 1119, 1098, 1055, 1033, 945, 862, 761, 712, 693.

Table S1. Crystal data and structure refinement for PMBB-2-acs-1.

Identification code	PMBB-2-acs-1
Empirical formula	$C_{36}H_{54}Cr_3Cu_3N_{13}O_{49}$
Formula weight	1799.54
Temperature/K	100(2)
Crystal system	hexagonal
Space group	$P6_3/m$
a/Å	20.772(9)
b/Å	20.772(9)
c/Å	21.0530(10)
α/°	90
β/°	90
γ/°	120
Volume/$Å^3$	7867(7)
Z	2
$\rho_{calc}g/cm^3$	0.760
μ/mm^{-1}	2.468
F(000)	1824.0
Crystal size/mm^3	0.060 × 0.040 × 0.040
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.196 to 85.03
Index ranges	$-18 \le h \le 18$, $-18 \le k \le 16$, $-18 \le l \le 18$
Reflections collected	19289

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Independent reflections	1933 [R_{int} = 0.0604, R_{sigma} = 0.0256]
Data/restraints/parameters	1933/9/121
Goodness-of-fit on F^2	1.089
Final R indexes [I>=2σ (I)]	R_1 = 0.0726, wR_2 = 0.2137
Final R indexes [all data]	R_1 = 0.0887, wR_2 = 0.2411
Largest diff. peak/hole / e $Å^{-3}$	0.34/-0.34

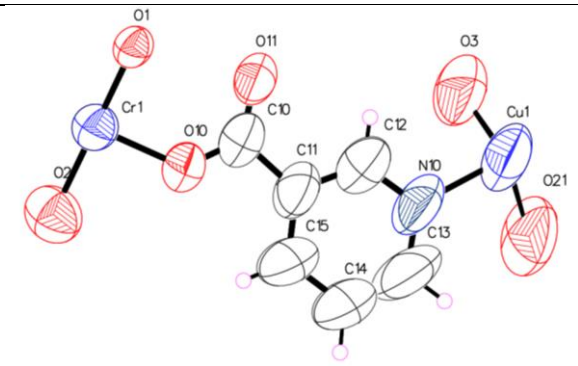

Figure S3. Asymmetric unit of **tp-PMBB-2-acs-1**. Atomic displacement parameters have been drawn at 50% probability.

Table S2. Crystal data and structure refinement for tp-PMBB-2-stp-1.	
Identification code	PMBB-2-stp-1
Empirical formula	$C_{78}H_{84}Cl_6Cr_6Mn_3N_{14}O_{44}$
Formula weight	2611.11
Temperature/K	100.15
Crystal system	hexagonal
Space group	$P6_3/mcm$
a/Å	22.045(2)
b/Å	22.045(2)
c/Å	21.768(2)
α/°	90
β/°	90
γ/°	120
Volume/$Å^3$	9161.6(19)
Z	2
ρ_{calc}g/cm^3	0.947
μ/mm^{-1}	0.132
F(000)	2646.0
Crystal size/mm^3	0.05 × 0.02 × 0.02
Radiation	synchrotron (λ = 0.41328)
2Θ range for data collection/°	2.408 to 28.192
Index ranges	-24 ≤ h ≤ 17, -25 ≤ k ≤ 24, -23 ≤ l ≤ 25
Reflections collected	31739
Independent reflections	2824 [R_{int} = 0.0835, R_{sigma} = 0.0390]
Data/restraints/parameters	2824/2/117

Goodness-of-fit on F^2	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0601, wR_2 = 0.1945
Final R indexes [all data]	R_1 = 0.0961, wR_2 = 0.2415
Largest diff. peak/hole / e $Å^{-3}$	0.49/-0.30

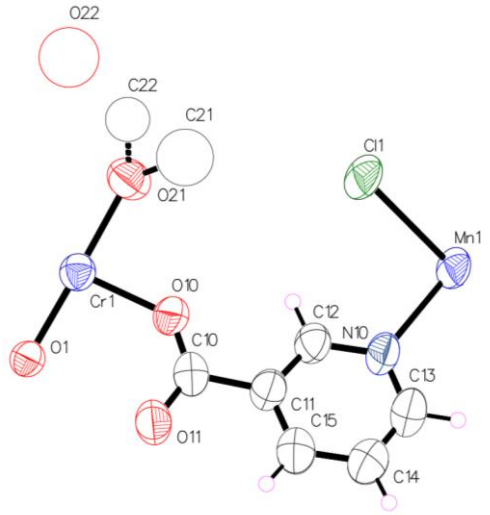

Figure S4. Asymmetric unit of **tp-PMBB-2-stp-1**. Atomic displacement parameters have been drawn at 50% probability.

Table S3. Crystal data and structure refinement for tp-PMBB-2-rtl-1.	
Identification code	PMBB-2-rtl-1
Empirical formula	$C_{46}H_{70}Cd_2Cr_3N_{11}O_{41}$
Formula weight	1813.93
Temperature/K	100(2)
Crystal system	tetragonal
Space group	$P\text{-}42_1c$
a/Å	20.608(2)
b/Å	20.608(2)
c/Å	22.350(2)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	9491.7(16)
Z	4
$\rho_{calc}g/cm^3$	1.269
μ/mm^{-1}	0.660
F(000)	3676.0
Crystal size/mm^3	0.100 × 0.020 × 0.020
Radiation	synchrotron (λ = 0.41328)
2Θ range for data collection/°	2.53 to 29.968
Index ranges	-25 ≤ h ≤ 24, -25 ≤ k ≤ 25, -26 ≤ l ≤ 27
Reflections collected	73700

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Independent reflections	9447 [R_{int} = 0.0670, R_{sigma} = 0.0469]
Data/restraints/parameters	9447/107/542
Goodness-of-fit on F^2	1.113
Final R indexes [I>=2σ (I)]	R_1 = 0.0562, wR_2 = 0.1565
Final R indexes [all data]	R_1 = 0.0737, wR_2 = 0.1711
Largest diff. peak/hole / e Å^{-3}	0.73/-0.46
Flack parameter	0.025(4)

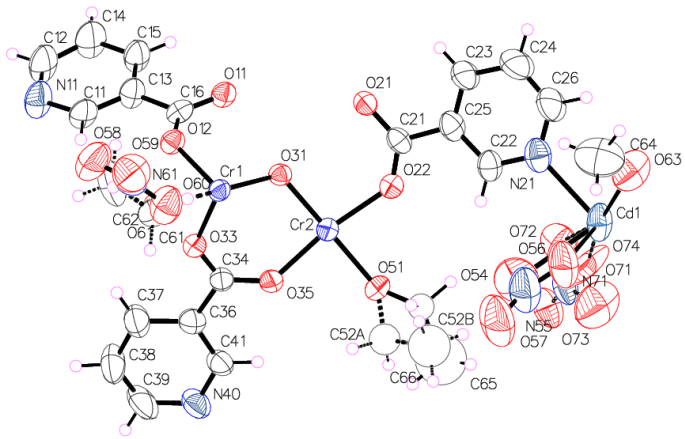

Figure S5. Asymmetric unit of **tp-PMBB-2-rtl-1**. Solvent atoms in the cavity have been omitted for clarity. Atomic displacement parameters have been drawn at 50% probability.

Table S4. Crystal data and structure refinement for tp-PMBB-2-fsc-1.	
Identification code	PMBB-2-fsc-1
Empirical formula	$C_{39}H_{35}Cd_2Cl_5Cr_3N_7O_{16}$
Formula weight	1415.80
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	Ccca
a/Å	23.751(3)
b/Å	30.607(4)
c/Å	23.764(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	17275(4)
Z	8
ρ_{calc}g/cm^3	1.086
μ/mm^{-1}	1.047
F(000)	5560.0
Crystal size/mm^3	0.020 × 0.020 × 0.020
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.324 to 41.626
Index ranges	-23 ≤ h ≤ 23, -30 ≤ k ≤ 30, -23 ≤ l ≤ 23
Reflections collected	107969

Independent reflections	4531 [R_{int} = 0.1450, R_{sigma} = 0.0505]
Data/restraints/parameters	4531/282/348
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0939, wR_2 = 0.2555
Final R indexes [all data]	R_1 = 0.1758, wR_2 = 0.3387
Largest diff. peak/hole / e $Å^{-3}$	1.12/-0.74

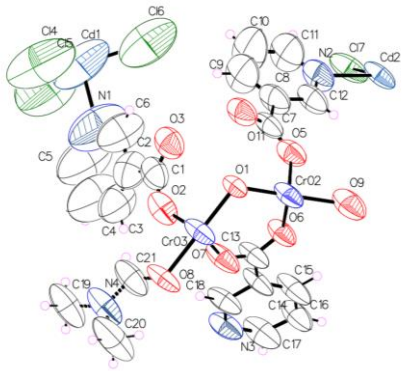

Figure S6. Asymmetric unit of **tp-PMBB-2-fsc-1**. Atomic displacement parameters have been drawn at 50% probability.

Table S5. Crystal data and structure refinement for tp-PMBB-2-pcu-1.	
Identification code	PMBB-2-pcu-1
Empirical formula	$C_{117}H_{155}Cl_{14}Cr_6Cu_6N_{27}O_{42}$
Formula weight	3801.21
Temperature/K	100.11
Crystal system	trigonal
Space group	R-3c
a/Å	21.6177(6)
b/Å	21.6177(6)
c/Å	61.464(4)
α/°	90
β/°	90
γ/°	120
Volume/$Å^3$	24875(2)
Z	6
ρ_{calc}g/cm^3	1.522
μ/mm^{-1}	6.658
F(000)	11628.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.528 to 125.018
Index ranges	-24 ≤ h ≤ 24, -21 ≤ k ≤ 24, -65 ≤ l ≤ 70
Reflections collected	29562

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Independent reflections	4375 [R_{int} = 0.0689, R_{sigma} = 0.0427]
Data/restraints/parameters	4375/119/393
Goodness-of-fit on F^2	1.105
Final R indexes [I>=2σ (I)]	R_1 = 0.0634, wR_2 = 0.1631
Final R indexes [all data]	R_1 = 0.0742, wR_2 = 0.1695
Largest diff. peak/hole / e $Å^{-3}$	0.89/-0.76

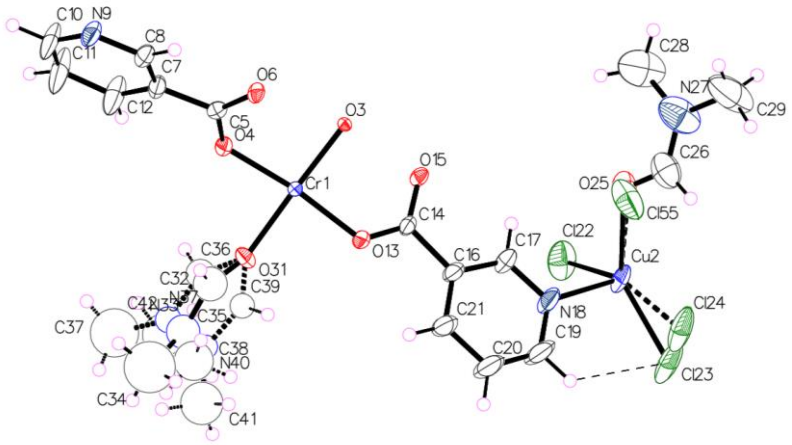

Figure S7. Asymmetric unit of **tp-PMBB-2-pcu-1**. Solvent molecules in the cavity have been omitted for clarity. Atomic displacement parameters have been drawn at 50% probability.

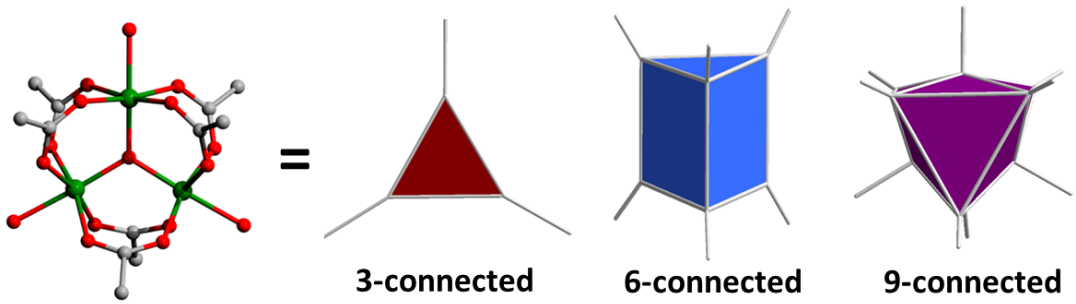

Figure S8. Trigonal prismatic MBBs can implement 3-, 6- or 9-connected nodes.

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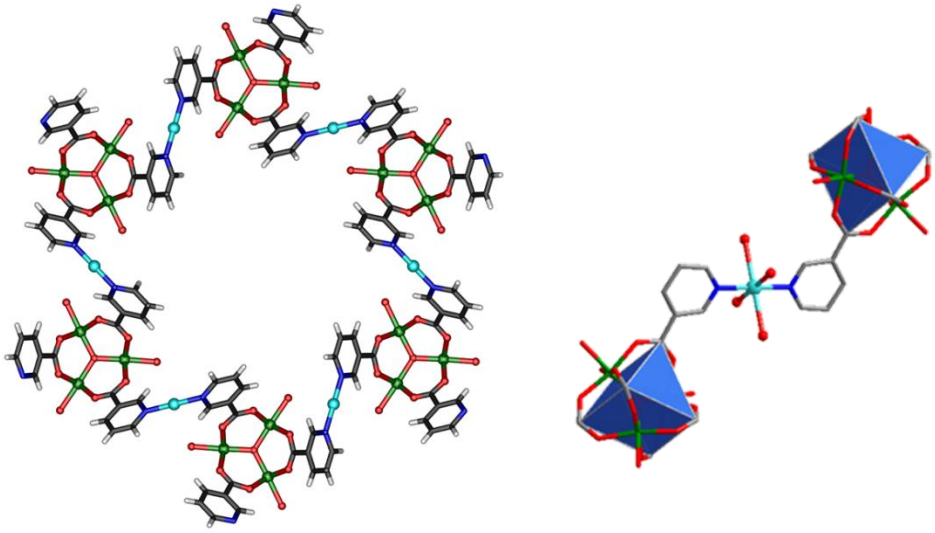

Figure S9. Single crystal X-ray structures of tp-PMBB-2-**acs**-1, tp-PMBB-2 act as 6-connected trigonal-prismatic nodes.

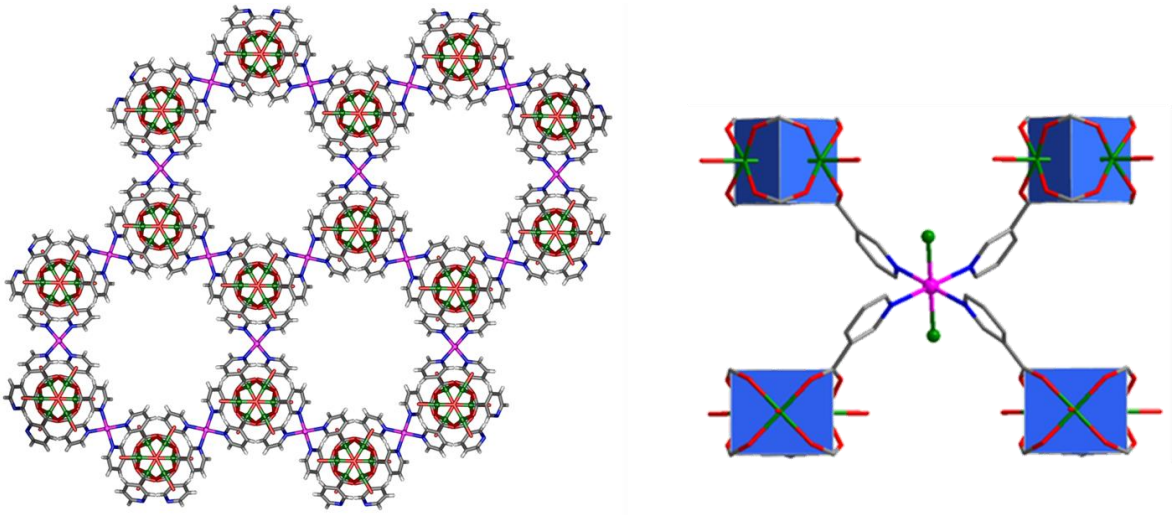

Figure S10. Single crystal X-ray structures of tp-PMBB-2-**stp**-1, tp-PMBB-2 act as 6-connected trigonal-prismatic nodes and Mn^{2+} act as 4-connected square nodes.

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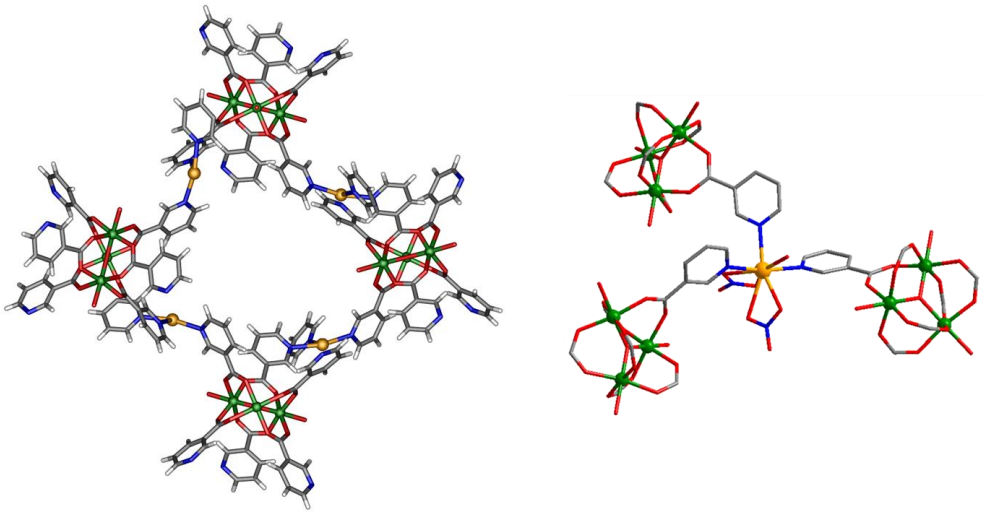

Figure S11. Single crystal X-ray structures of tp-PMBB-2-**rtl**-1, tp-PMBB-2 act as 6-connected octahedral nodes and Cd^{2+} act as 3-connected T-shape nodes.

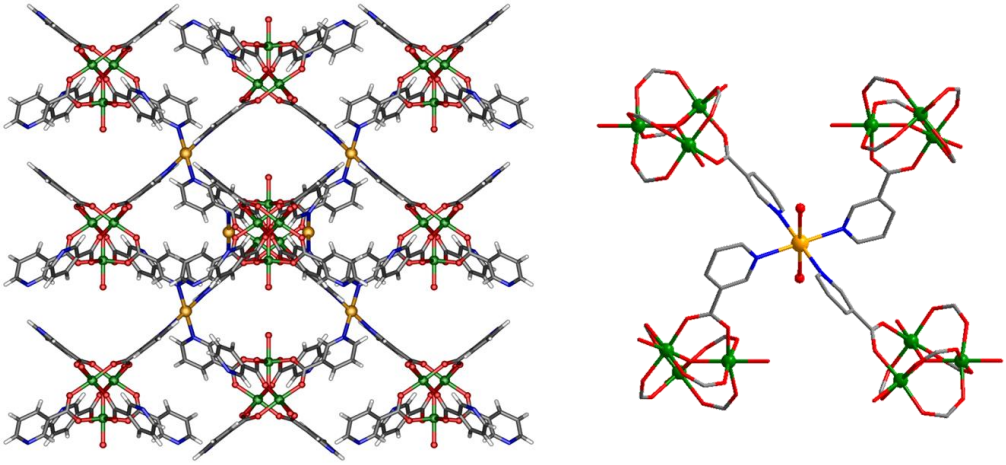

Figure S12. Single crystal X-ray structures of tp-PMBB-2-**fsc**-1, tp-PMBB-2 act as 6-connected octahedral nodes and Cd^{2+} act as 4-connected square nodes.

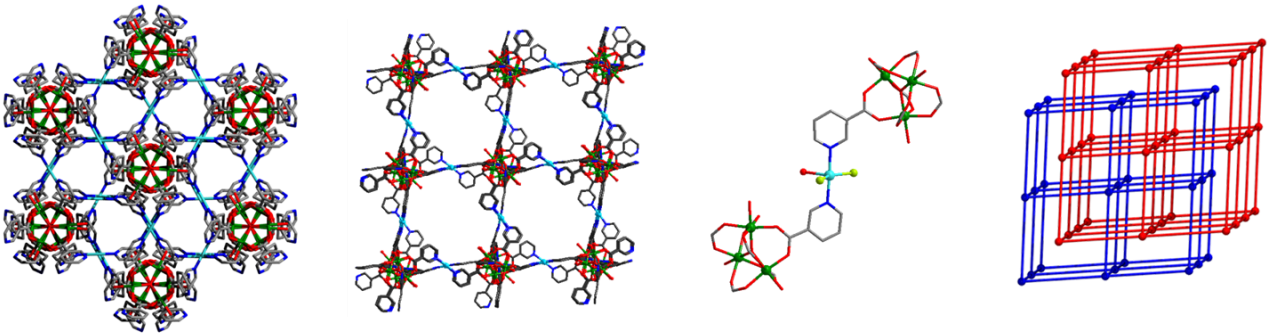

Figure S13. Single crystal X-ray structures of 2-fold interpenetrated tp-PMBB-2-**pcu**-1, tp-PMBB-2 act as 6-connected octahedral nodes.

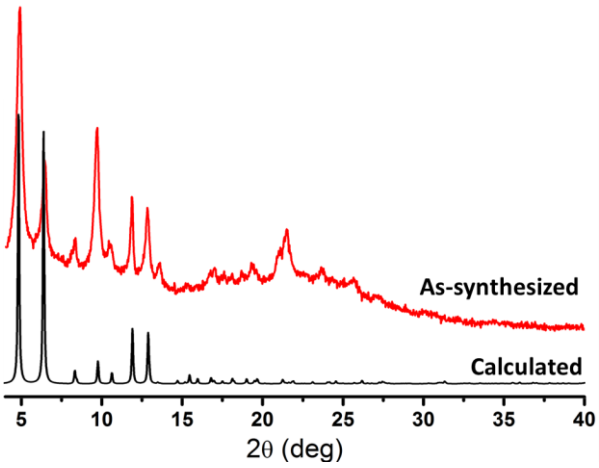

Figure S14. Comparison of experimental and calculated powder X-ray diffraction patterns of tp-PMBB-2-**acs**-1.

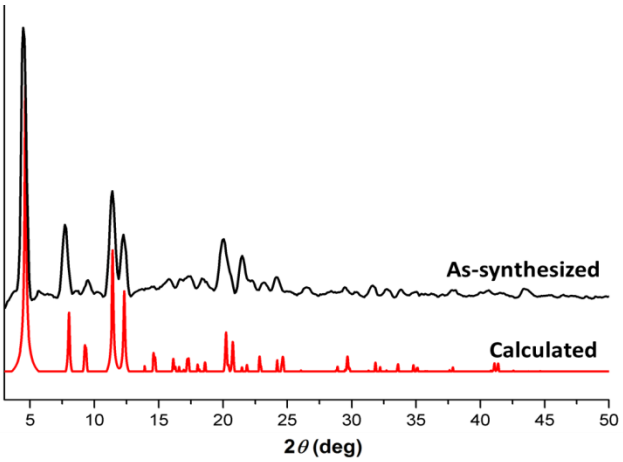

Figure S15. Comparison of experimental (background corrected) and calculated powder X-ray diffraction patterns of tp-PMBB-2-**stp**-1.

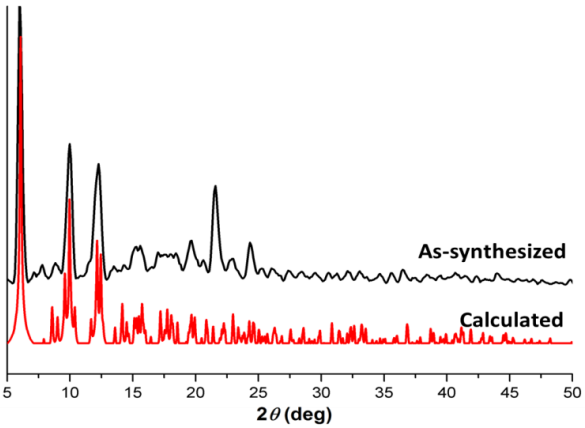

Figure S16. Comparison of experimental (background corrected) and calculated powder X-ray diffraction patterns of tp-PMBB-2-**rtl**-1.

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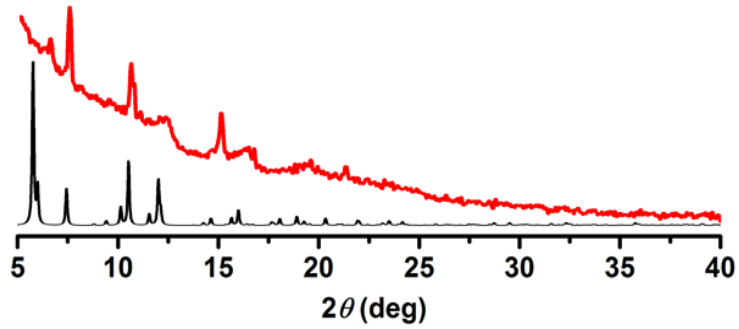

Figure S17. Comparison of experimental (red curve) and calculated (black curve) powder X-ray diffraction patterns of tp-PMBB-2-**fsc**-1.

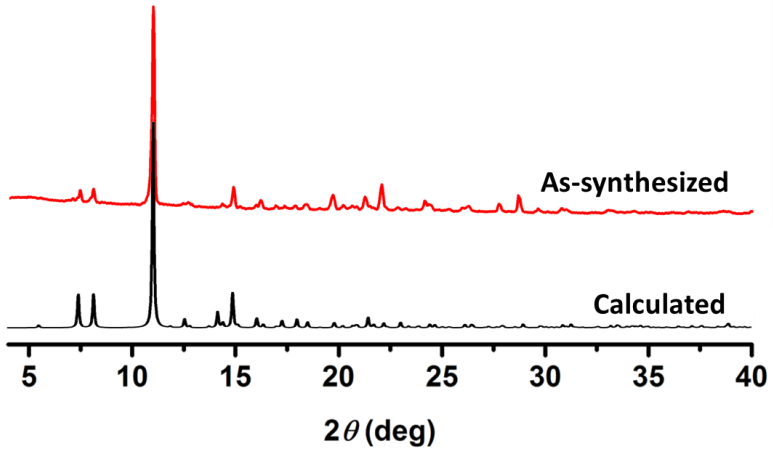

Figure S18. Comparison of experimental and calculated powder X-ray diffraction patterns of tp-PMBB-2-**pcu**-1.

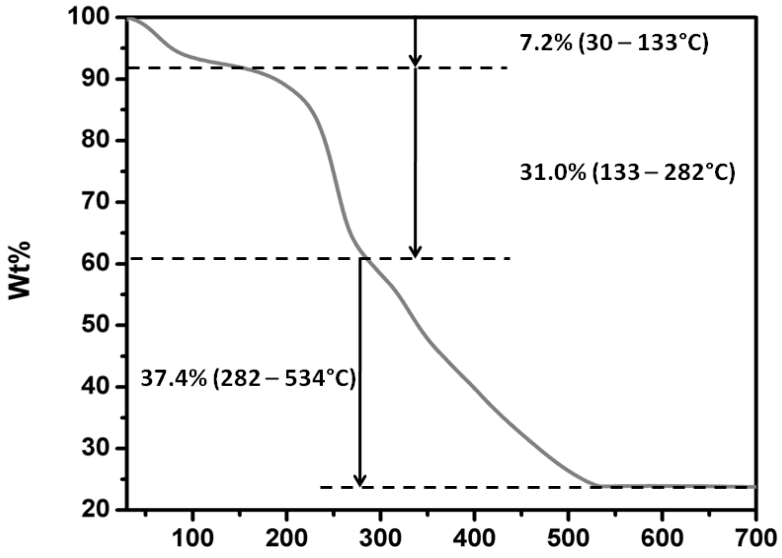

Figure S19. TGA of tp-PMBB-2-**acs**-1.

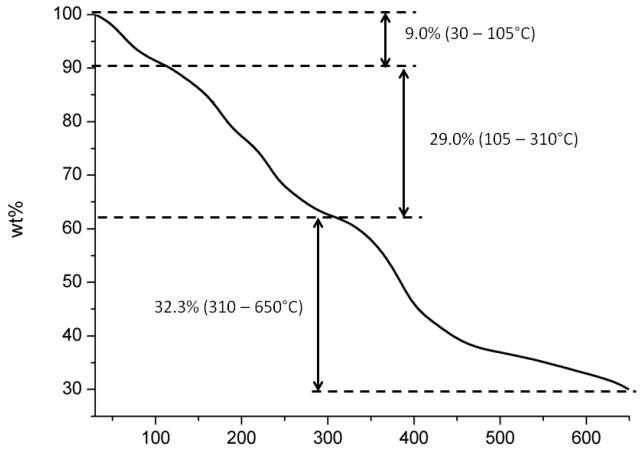

Figure S20. TGA of tp-PMBB-2-**stp**-1.

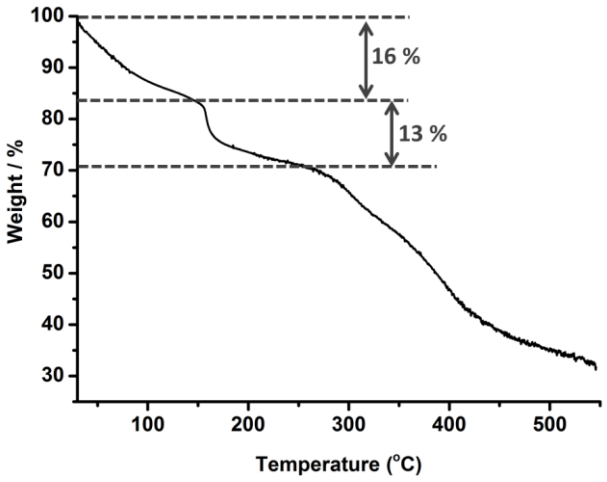

Figure S21. TGA of tp-PMBB-2-**rtl**-1.

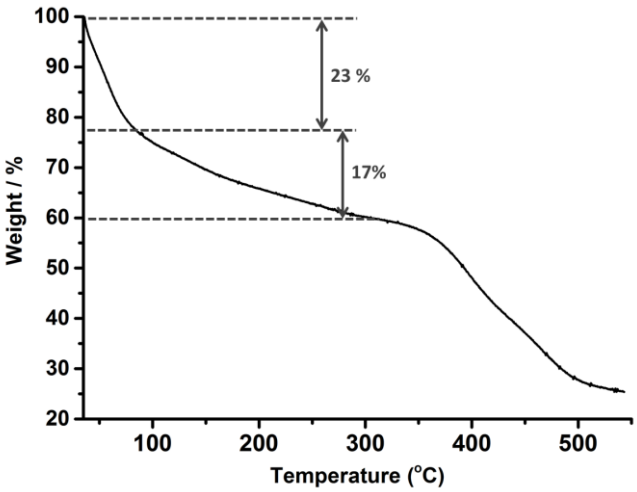

Figure S22. TGA of tp-PMBB-2-**fsc**-1.

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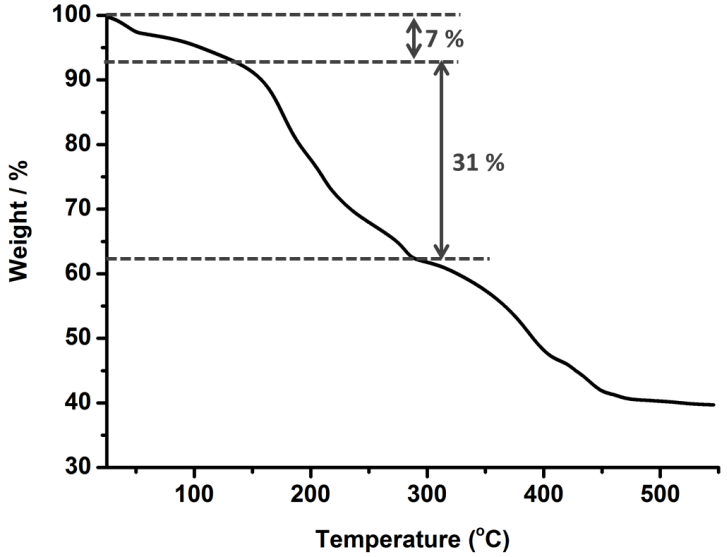

Figure S23. TGA of tp-PMBB-2-**pcu**-1.

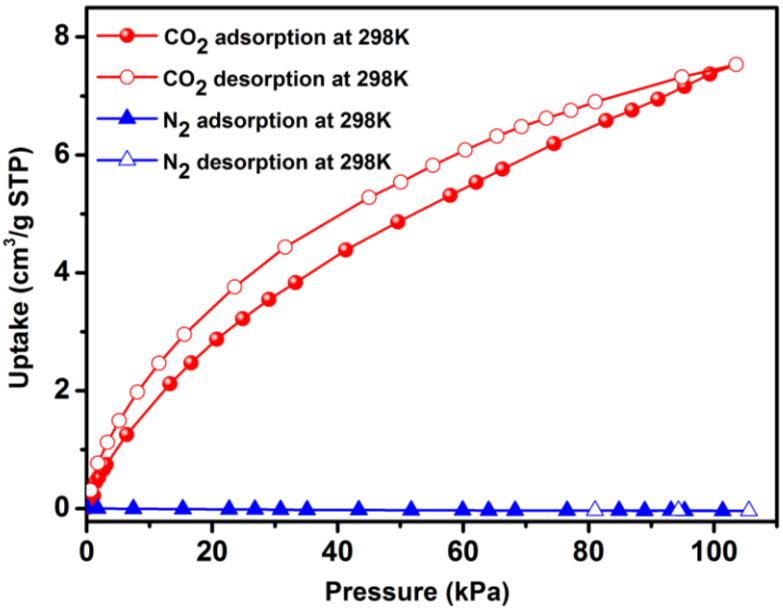

Figure S24. CO_2 (circle) and N_2 (triangle) sorption data at 298 K for tp-PMBB-2-**pcu**-1.