Electronic Supplementary Information

Vertex-Directed Self-Assembly of a High Symmetry Supermolecular Building Block Using a Custom-Designed Porphyrin

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General methods

Commercially available reagents were purchased as high purity from Fisher Scientific or Frontier Scientific and used without further purification. Tetrakis(3,5-dicarboxyphenyl)porphine (H_{10}tdcpp) was synthesized by the literature.[1,2] Solvents were purified according to standard methods and stored in the presence of molecular sieve. 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).

<u>Synthesis of MMPF-4</u>:

Typically, a mixture of tetrakis(3,5-dicarboxyphenyl)porphine (0.001 g), $Zn(NO_3)_2\cdot 6H_2O$ (0.003 g), and 1.0 mL DMSO was sealed in a Pyrex tube under vacuum and heated to 135 °C for 24 hours. The resulting dark red block crystals were washed with DMSO to give pure MMPF-4, $[Zn_{19}(tdcpp)_3][(NO_3)_8]\cdot(DMSO)_{61}\cdot(H_2O)_{25}$ (yield: 55% based on tdcpp). Anal. Calc. for MMPF-4: C, 33.96; H, 4.94; N, 2.85; Found: C, 35.99; H, 5.12; N, 2.78. MMPF-4 can be easily scaled to hundreds of milligrams by dispensing a larger amount of reactants mixture into multiple glass tubes.

<u>Synthesis of MMPF-5</u>:

A mixture of tetrakis(3,5-dicarboxyphenyl)porphine (0.001 g), $Cd(NO_3)_2\cdot 6H_2O$ (0.003 g), and 1.0 mL DMSO was sealed in a Pyrex tube under vacuum and heated to 135 °C for 24 hours. The resulting dark red block crystals were washed with DMSO to give pure MMPF-5 $[Cd_{11}(tdcpp)_3][(H_3O)_8]\cdot(DMSO)_{36}\cdot(H_2O)_{11}$ (yield: 62% based on tdcpp). Anal. Calc. for MMPF-5: C, 37.58; H, 4.69; N, 2.31; Found: C, 39.45; H, 4.52; N, 2.46. MMPF-5 can be easily scaled to hundreds of milligrams by dispensing a larger amount of reactants mixture into multiple glass tubes.

Single-Crystal X-Ray Diffraction Studies:

For MMPF-4: The X-ray diffraction data were collected using synchrotron radiation, λ = 0.41328 Å, at Advanced Photon Source, Chicago IL. Indexing was performed using *APEX2*[3] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01[4]. Absorption correction was performed by multi-scan method implemented in SADABS[5]. Space groups were determined using XPREP implemented in APEX2[3]. 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[6-9] programs packages. Despite of using synchrotron source and trying several crystals from different batches, the diffraction spots were observed only up to 1.1 Å resolution. This can be attributed to the presence of the ligand/solvent disorder. All non-H atoms were found in the difference Fourier map and were refined using the distance restraints. Restraints were also used to refine the anisotropic displacement parameters of C,N,O atoms. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH). The structure can be solved in *Pm*-3*m* space group using smaller unit cell parameters but refinement results in much higher values of anisotropic thermal parameters. The observed pseudosymmetry is most likely due to the merohedral twinning with [0 1 0 1 0 0 0 0 -1] twin low. The contribution of heavily disordered solvent molecules was treated as diffuse using Squeeze procedure implemented in Platon program.[10,11] Crystal data and refinement conditions are shown in Table S1.

For MMPF-5: The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer using CuKα (λ = 1.54178 Å). Indexing was performed using *APEX2*[3] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01[4]. Absorption correction was performed by multi-scan method implemented in SADABS[5]. Space groups were determined using XPREP implemented in APEX2[3]. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (full-matrix least-squares on F^2) contained in APEX2[3] and WinGX v1.70.01[6-9] programs packages. Despite of using synchrotron source and trying several crystals from different batches, the diffraction spots were observed only up to 1.4 Å resolution. This can be attributed to the presence of the ligand/solvent disorder. All non-H atoms were found in the difference Fourier map and were refined using the distance restraints. Restraints were also used to refine the anisotropic displacement parameters of C,N,O atoms. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH). The contribution of heavily disordered solvent molecules was treated as diffuse using Squeeze procedure implemented in Platon program[10,11]. Crystal data and refinement conditions are shown in Table S2.

Gas Adsorption Experiments.

Gas adsorption isotherms of MMPF-4/5 were collected using the surface area analyzer ASAP-2020. Before the measurements, Before the measurements, MMPF-4/5 were evacuated with supercritical CO_2 in a Tousimis™ Samdri® PVT-30 critical point dryer.[12] Prior to drying, the DMSO solvated MMPF-4/5 samples were soaked in absolute methanol (MeOH), replacing the soaking solution every 24 hrs for 72 hrs, to exchange the occluded solvent for MeOH. After the 72 hr exchange process was complete the methanol-containing samples were placed inside the dryer and the ethanol was exchanged with CO_2(L) over a period of 6 hrs. During this time the liquid CO_2 was vented under positive pressure for five minutes each hour. The rate of venting of CO_2(L) was always kept below the rate of filling so as to maintain a full drying chamber. After 6 hrs of venting and soaking with CO_2(L) the chamber was sealed and the temperature was raised to 40ºC. This brought the chamber pressure to around 1300 psi above the critical point of CO_2. The chamber was held above the critical point for 1 hour at which point the chamber was slowly vented over the course of 15-18 hrs. After activation, the sample and tube were re-weighed to obtain the precise mass of the evacuated sample. N_2, Ar, and O_2 gas adsorption isotherms were measured at 77 K or 87K using a liquid N_2 or Ar bath, respectively; Low-pressure CO_2 adsorption isotherms were measured at 273K and 298K, the temperature was held constant using an ice water bath or 298K water bath.

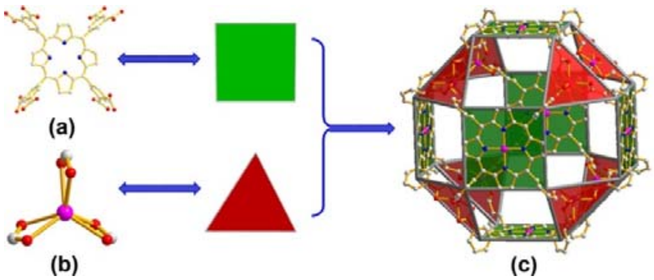


Fig. S1 (a) tdcpp ligand serving as the square MBB; (b) $Cd(CO_2)_3$ paddlewheel moiety serving as the triangular MBB; (c) the SBB of *small cubicuboctahedron* formed by 6 square Cd-tdcpp MBBs and 8 triangular $Cd(CO_2)_3$ MBBs with the cage internal diameter of 22.521 Å and window dimensions of 8.004 Å × 8.195 Å (atom to atom distance) in MMPF-5.

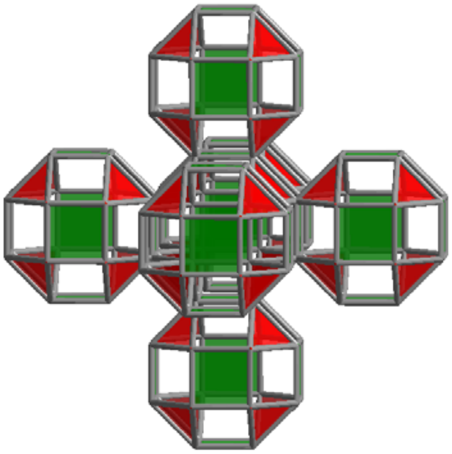


Fig. S2 A small cubicuboctahedral cage serving as the six-connected node linking with six adjacent small cubicuboctahedral cages through the faces of tdcpp moieties to support an augumented ***pcu*** network.

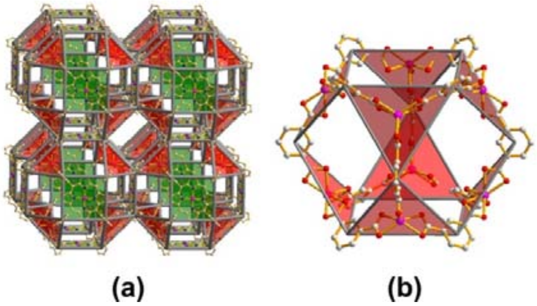


Fig. S3 (a) The ability of Cd-tdcpp ligands to fuse the square faces of *small cubicuboctahedron* results in an augmented ***pcu*** network with two types of cavity in MMPF-5; (b) The cage formed between the SBBs can be described as octahemioctahedron and has an internal diameter of 11.589 Å and window dimensions of 8.195 Å × 8.195 Å.

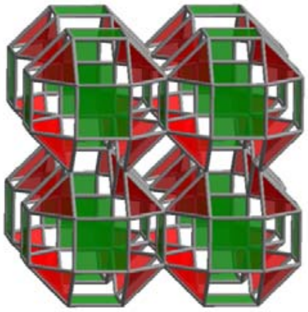


Fig. S4 One octahemioctahedron connecting with 8 adjacent *small cubicuboctahedrons* through 8 triangular MBBs to support an 8-connected network.

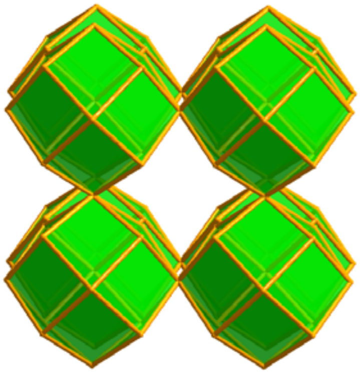
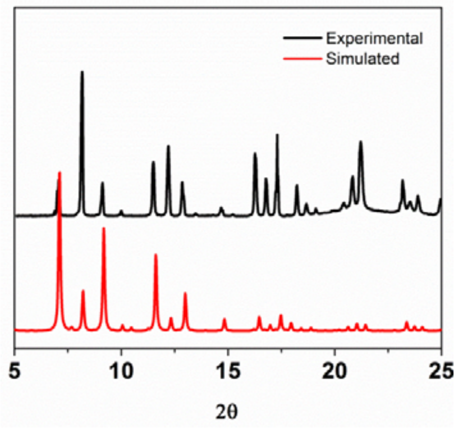
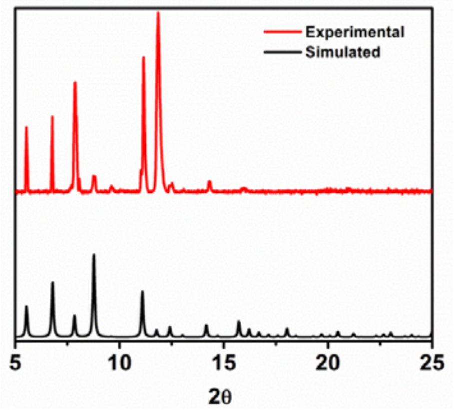


Fig. S5 (3,8)-connected ***the*** topology of MMPF-4/5



(a)



(b)

Fig. S6 Powder X-ray patterns of (a) **MMPF-4**; (b) **MMPF-5**.

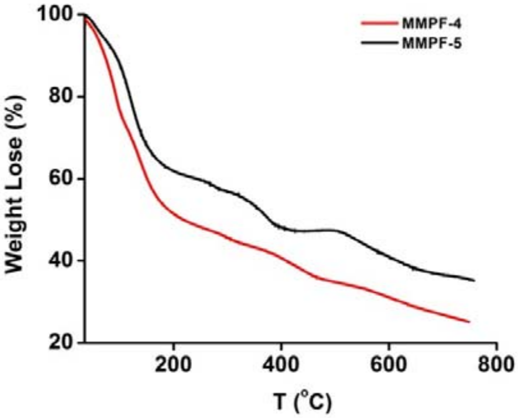


Fig. S7 TGA plots of MMPF-4 and MMPF-5.

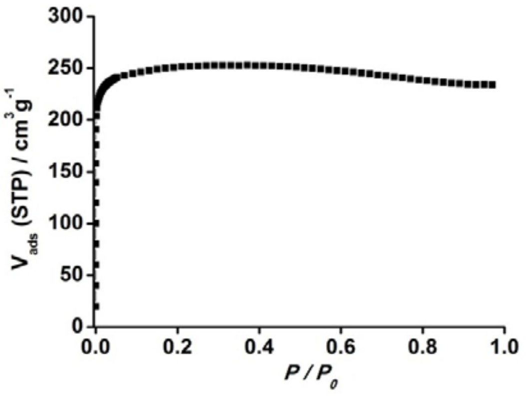


Fig. S8 N_2 adsorption isotherm of MMPF-4 at 77K (Langmuir surface area (P/P_0 = 0.9): 1100 m^2/g; BET surface area (P/P_0 = 0.01~0.15): 967 m^2/g).

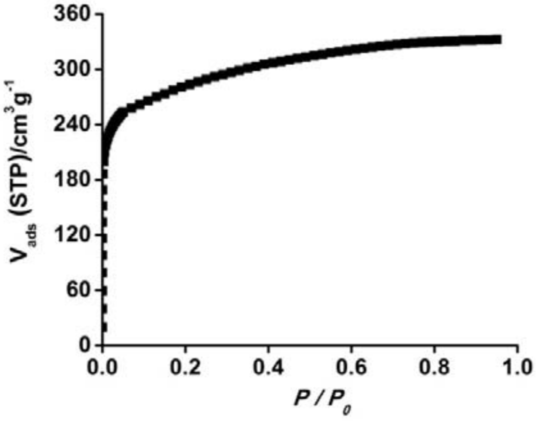


Fig. S9 O_2 adsorption isotherm of MMPF-4 at 87K (Langmuir surface area (P/P_0 = 0.9): 1255 m^2/g; BET surface area (P/P_0 = 0.01~0.15): 873 m^2/g).

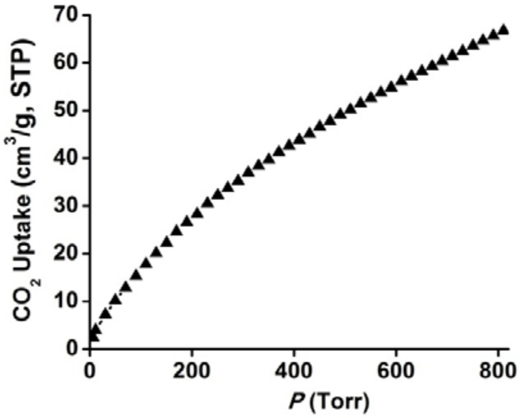


Fig. S10 CO_2 adsorption isotherm of MMPF-5 at 273 K.

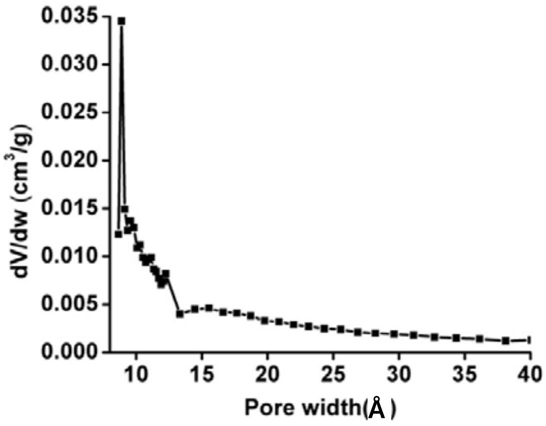


Fig. S11 Pore size distribution of MMPF-4 derived from Ar adsorption data at 87 K (HK model).

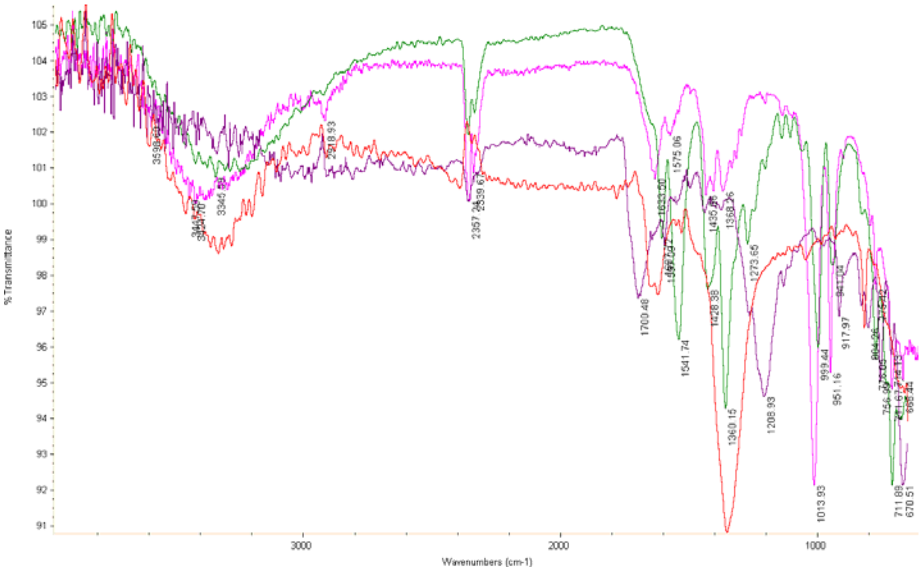
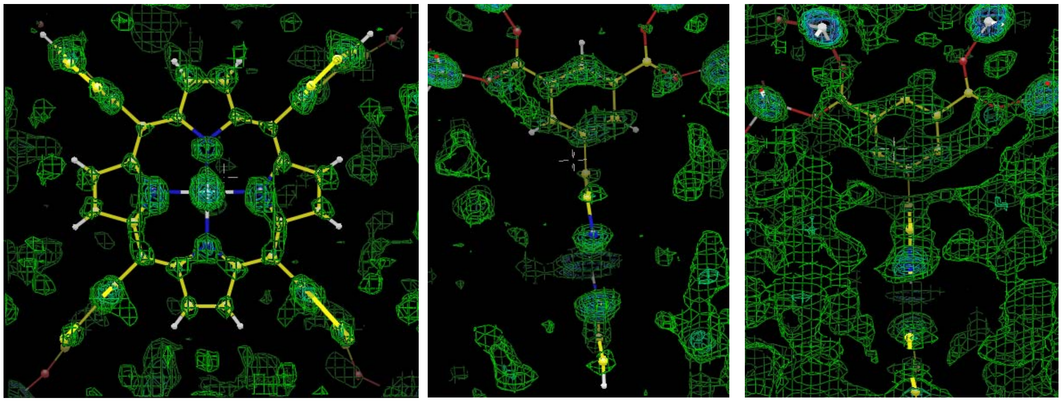


Fig. S12 IR spectra of MMPF-4(pink), MMPF-5 (green), H_{10}tdcpp ligand (purple) and $Zn(NO_3)_2$ (red).



(a) (b) (c)

Fig. S13 2F$_O$ - Fc electron density map indicating the position and conformation of the ligand in MMPF-4. The map was plotted at 1 sigma level (a) and 1 sigma level (b) and 0.3 sigma level using MIFit 2010.10.[13]

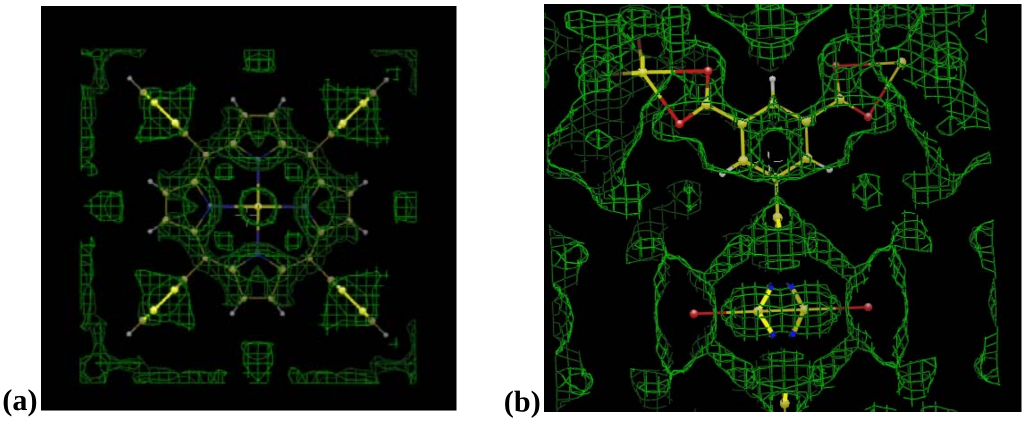
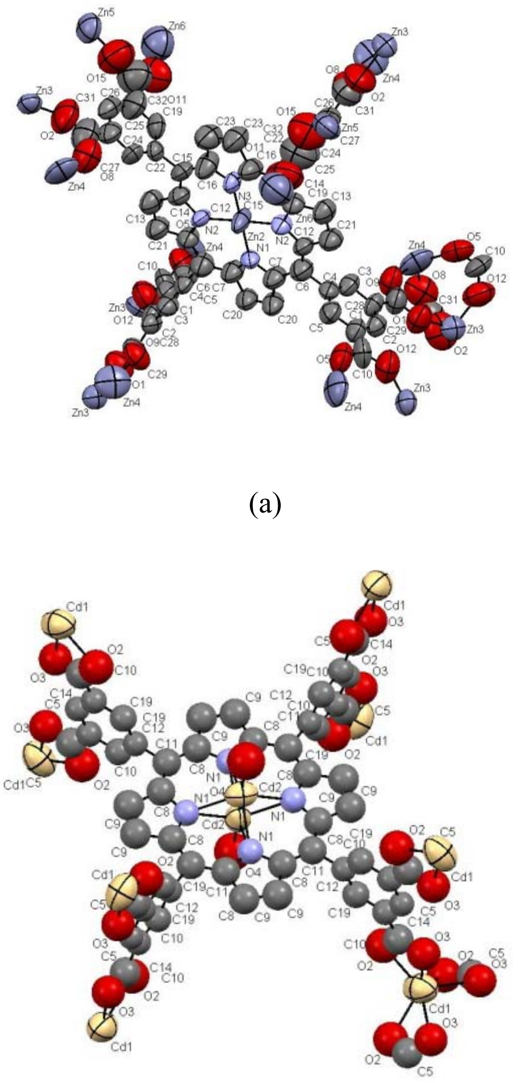


Fig. S14 2F$_O$ - Fc electron density map indicating the position and conformation of the ligand in MMPF-5. The map was plotted at 0.5 sigma level (a) and 0.25 sigma level (b) using MIFit 2010.10.[13]



(a)

(b)

Fig. S15 Coordination and atom numbering scheme for (a) MMPF-4 and (b) MMPF-5 (Atomic displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity).

Table S1 Crystal data and structure refinement for MMPF-4

Identification code	MMPF-4
Empirical formula	$C_{156}\ H_{60}\ N_{12}\ O_{50}\ Zn_{19}$
Empirical formula (including solvent)	$[Zn_{19}(C_{52}H2_{0}N_{4}O_{16})_{3}][(NO_{3})_{8}]\cdot(C_{2}H_{6}SO)_{61}\cdot(H_{2}O)_{25})$ = $C_{278}\ H_{476}\ N_{20}\ O_{156}\ S_{61}\ Zn_{19}$
Formula weight	4144.19 (9824.9 including solvent)
Temperature	100(2) K
Wavelength	0.41328 A
Crystal system, space group	Cubic, *Ia*-3
Unit cell dimensions	*a* = 43.030(2) A *alpha* = 90 deg.
	b = 43.030(2) A *beta* = 90 deg.
	c = 43.030(2) A *gamma* = 90 deg.
Volume	79671(6) A^3
Z, Calculated density	8, 0.691 Mg/m^3 (1.63Mg/m^3 including solvent)
Absorption coefficient	0.243 mm^-1 (0.41 mm-1 including solvent)
F(000)	16400 (40624 including solvent)
Crystal size	0.05 x 0.05 x 0.05 mm
Theta range for data collection	0.78 to 10.83 deg.
Limiting indices	-39<=h<=34, -33<=k<=38, -35<=l<=39
Reflections collected / unique	61875 / 5235 [R(int) = 0.1131]
Completeness to theta = 10.83	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9880 and 0.9880
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5235 / 270 / 359
Goodness-of-fit on F^2	1.088
Final R indices [I>2sigma(I)]	*R*1 = 0.1163, *wR*2 = 0.2742
R indices (all data)	*R*1 = 0.1429, *wR*2 = 0.2905
Largest diff. peak and hole	0.962 and -0.510 e.A^-3

Table S2 Crystal data and structure refinement for MMPF-5

Identification code	MMPF-5
Empirical formula	$C_{156}H_{60}Cd_{11}N_{12}O_{51}$
Empirical formula (including solvent)	$[Cd_{11}(C_{52}H_{20}N_4O_{16})_3][(H_3O)_8]\cdot(C_2H_6SO)_{36}\cdot(H_2O)_{11})$ $C_{228}H_{322}Cd_{11}N_{12}O_{103}S_{36}$
Formula weight	4154.56 (7269.88 including solvent)
Temperature	293(2) K
Wavelength	1.54178 A
Crystal system, space group	Cubic, *Pm*-3*m*
Unit cell dimensions	*a* = 22.521(15) A *alpha* = 90 deg.
	b = 22.521(15) A *beta* = 90 deg.
	c = 22.521(15) A *gamma* = 90 deg.
Volume	11423(13) A^3
Z, Calculated density	1, 0.604 Mg/m^3 (1.06 Mg/m^3 including solvent)
Absorption coefficient	4.273 mm^-1 (6.04 mm^-1 including solvent)
F(000)	2016 (3702 including solvent)
Crystal size	0.10 x 0.10 x 0.10 mm
Theta range for data collection	1.96 to 33.35 deg.
Limiting indices	-8<=h<=15, -16<=k<=15, -5<=l<=15
Reflections collected / unique	5323 / 483 [R(int) = 0.0856]
Completeness to theta = 33.35	97.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6746 and 0.6746
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	483 / 19 / 38
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	*R*1 = 0.0816, *wR*2 = 0.2268
R indices (all data)	*R*1 = 0.1067, *wR*2 = 0.2483
Largest diff. peak and hole	0.388 and -0.324 e.A^-3

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