Electronic Supplementary Information (ESI) for

An unusual uninodal 10-connected self-penetrating network built from sixteen-nuclear hybrid cadmium clusters

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Materials and Methods:

All reagents of A. R. grade employed were commercially available and used without further purification. C, H, and N elemental analyses were determined on an Elementar Vario EL III elemental analyzer. The FT-IR spectra (KBr pellets) were recorded on a Nicolet Avatar 360 FT-IR Spectrometer in the range of 4000–400 cm^{-1}. Thermal stability studies were carried out on a NETSCHZ STA–449 C thermoanalyzer under nitrogen atmosphere (40–1000 ^{o}C range) at a heating rate of 10 ^{o}C min^{-1}. Powder X-ray diffraction (PXRD) pattern was measured on a Rigaku DMAX 2500 powder diffractmeter at 40 kV and 100 mA using Cu-Kα (λ = 1.54056 Å), with a scan speed of 0.2 s/step and a step size of 0.02°. The simulated powder pattern was calculated using single-crystal X-ray diffraction data and processed by the free Mercury 2.3 program provided by the Cambridge Crystallographic Data Centre. The solid-state fluorescence spectra were measured at room temperature using a Cary Eclipse fluorescence spectrophotometer. The excitation slit and emission slit both were 2.5 nm.

Table S1. Crystal data and structure refinements for **1**.

Empirical formula	$Cd_8F_3S_2C_{24}N_{35}H_{22}$
Formula weight	1821.09
Temperature (K)	293(2)
Crystal system, Space group	Tetragonal, *P*4(2)/*mnm*
Unit cell dimensions	*a* = 17.8722(8) Å *b* = 17.8722(8) Å *c* = 14.3521(13) Å *V* = 4584.3(5) $Å^3$
Z, Density(cal.)	4, 2.639 g/cm^3
Absorption coefficient	3.807 mm^{-1}
F(000)	3416
Crystal Size (mm)	0.20 × 0.18 × 0.12
Theta range for data collection	3.22 to 24.99
Limiting indices	-21<=h<=21, -21<=k<=21, -17<=l<=11
Reflections collected / unique	27955 / 2208 [R(int) = 0.0406]
Observed Reflection	1625 ($I>2\sigma(I)$)
Data Completeness measured	0.996
Refinement Method	Full-matrix least-squares on F^2
Parameter/Restraints/Data(obs.)	2208 / 66 / 187
Goodness-of-fit	1.068
Final R indices ($I>2\sigma(I)$)	R1 = 0.0415, wR2 = 0.0881
R indices (all)	R1 = 0.0628, wR2 = 0.0986
Largest difference peak	2.514 and -1.512 $e·A^{-3}$

[a] $R1 = \sum(|F_o| - |F_c|) / \sum|F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{0.5}$.

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1**.

atom	*x*	*y*	*z*	*U*(eq)
Cd(1)	0	0	1301(1)	20(1)
Cd(2)	3291(1)	1552(1)	1323(1)	22(1)
Cd(3)	4610(1)	2883(1)	0	25(1)
Cd(4)	1722(14)	-1722(14)	0	27(1)
Cd(4')	1446(1)	-1446(1)	0	27(1)
S(1)	3703(2)	432(2)	0	47(1)
F(1)	611(3)	-611(3)	0	25(2)
F(2)	3472(4)	2260(4)	0	34(2)
C(1)	-1165(5)	359(6)	3059(7)	47(3)
C(2)	1634(4)	813(4)	1181(6)	26(2)
C(3)	5649(5)	2143(5)	1719(6)	35(2)
C(4)	2996(8)	-187(9)	0	44(4)
C(5)	2379(6)	-1554(5)	-1893(7)	47(3)
C(6)	4936(5)	1441(5)	2448(6)	30(2)
C(7)	6037(6)	3963(6)	0	47(4)
C(8)	6539(6)	2963(6)	0	80(3)
N(1)	-624(4)	624(4)	2516(7)	32(3)
N(2)	-1249(4)	717(4)	3852(5)	37(2)
N(3)	886(3)	886(3)	1203(7)	24(2)
N(4)	2491(7)	-587(6)	0	42(3)
N(5)	1998(4)	1458(4)	1167(5)	26(2)
N(6)	4563(4)	1638(4)	1692(5)	31(2)
N(7)	5036(4)	2105(4)	1215(5)	34(2)
N(8)	5628(4)	1752(4)	2500(5)	34(2)
N(9)	5871(6)	3323(6)	0	75(3)
N(10)	6539(6)	2963(6)	0	80(3)
N(11)	1809(5)	-1809(5)	-1368(7)	38(3)
N(12)	2478(4)	-1934(4)	-2661(5)	37(2)

Table S3. Selected bond lengths (Å) and bond angles (°) for **1**.

Cd(1)-N(1)	2.353(10)	Cd(2)-F(2)	2.304(4)	Cd(4)-N(11)	1.976(11)
Cd(1)-N(3)	2.245(9)	Cd(2)-S(1)	2.855(3)	Cd(4')-N(4)	2.417(10)
Cd(1)-F(1)	2.423(6)	Cd(3)-N(2)#5	2.337(7)	Cd(4')-N(11)	2.168(10)
Cd(2)-N(5)	2.328(6)	Cd(3)-N(7)	2.357(7)	Cd(4')-F(1)	2.109(9)
Cd(2)-N(6)	2.339(7)	Cd(3)-F(2)	2.318(7)	S(1)-C(4)	1.678(16)
Cd(2)-N(8)#4	2.364(7)	Cd(3)-N9	2.388(9)	C(4)-N(4)	1.152(16)
Cd(2)-N(12)#3	2.301(7)	Cd(4)-N(4)	2.450(12)		
N(3)#1-Cd(1)-N(3)	172.9(5)	N(5)-Cd(2)-N(8)#4	89.2(2)	N(7)-Cd(3)-N(9)	83.6(3)
N(3)#1-Cd(1)-N(1)	92.65(19)	N(6)-Cd(2)-N(8)#4	85.2(2)	N(11)-Cd(4)-N(11)#7	167(2)
N(1)-Cd(1)-N(1)#1	84.3(5)	N(12)#3-Cd(2)-S(1)	174.1(2)	N(11)-Cd(4)-N(4)	91.20(13)
N(3)-Cd(1)-F(1)	87.25(19)	F(2)-Cd(2)-S(1)	78.49(16)	N(4)#8-Cd(4)-N(4)	158.2(17)
N(1)-Cd(1)-F(1)	177.5(3)	N(5)-Cd(2)-S(1)	98.11(18)	F(1)-Cd(4')-N(11)	115.0(3)
N(1)#1-Cd(1)-F(1)	98.3(3)	N(6)-Cd(2)-S(1)	86.9(2)	N(11)-Cd(4')-N(11)#7	129.9(6)
F(1)-Cd(1)-F(1)#2	79.2(3)	N(8)#4-Cd(2)-S(1)	89.6(2)	F(1)-Cd(4')-N(4)	95.6(3)
N(12)#3-Cd(2)-F(2)	97.7(2)	F(2)-Cd(3)-N(2)#5	95.8(2)	N(11)-Cd(4')-N(4)	87.63(13)
N(12)#3-Cd(2)-N(5)	86.7(2)	N(2)#5-Cd(3)-N(2)#6	89.6(4)	N(4)#8-Cd(4')-N(4)	168.8(6)
F(2)-Cd(2)-N(5)	95.7(2)	F(2)-Cd(3)-N(7)	90.0(2)	Cd(2)-S(1)-Cd(2)#7	105.5(4)
N(12)#3-Cd(2)-N(6)	88.7(3)	N(2)#5-Cd(3)-N(7)	87.2(3)	Cd(4')-F(1)-Cd(1)	129.62(16)
F(2)-Cd(2)-N(6)	90.8(2)	N(2)#6-Cd(3)-N(7)	173.6(3)	Cd(1)#2-F(1)-Cd(1)	100.8(3)
N(5)-Cd(2)-N(6)	172.5(2)	N(7)-Cd(3)-N(7)#7	95.5(4)	Cd(3)-F(2)-Cd(2)	112.75(19)
N(12)#3-Cd(2)-N(8)#4	93.9(3)	F(2)-Cd(3)-N(9)	170.5(3)	Cd(2)#7-F(2)-Cd(2)	111.0(3)
F(2)-Cd(2)-N(8)#4	167.7(2)	N(2)#6-Cd(3)-N(9)	90.9(3)		

Symmetry transformations used to generate equivalent atoms: #1 – x, – y, z; #2 – x, – y, – z; #3 y + 1/2, – x + 1/2, z + 1/2; #4 – y + 1/2, x – 1/2, – z + 1/2; #5 – y + 1/2, x + 1/2, – z + 1/2; #6 – y +1/2, x + 1/2, z – 1/2; #7 x, y, – z; #8 – y, – x, z.

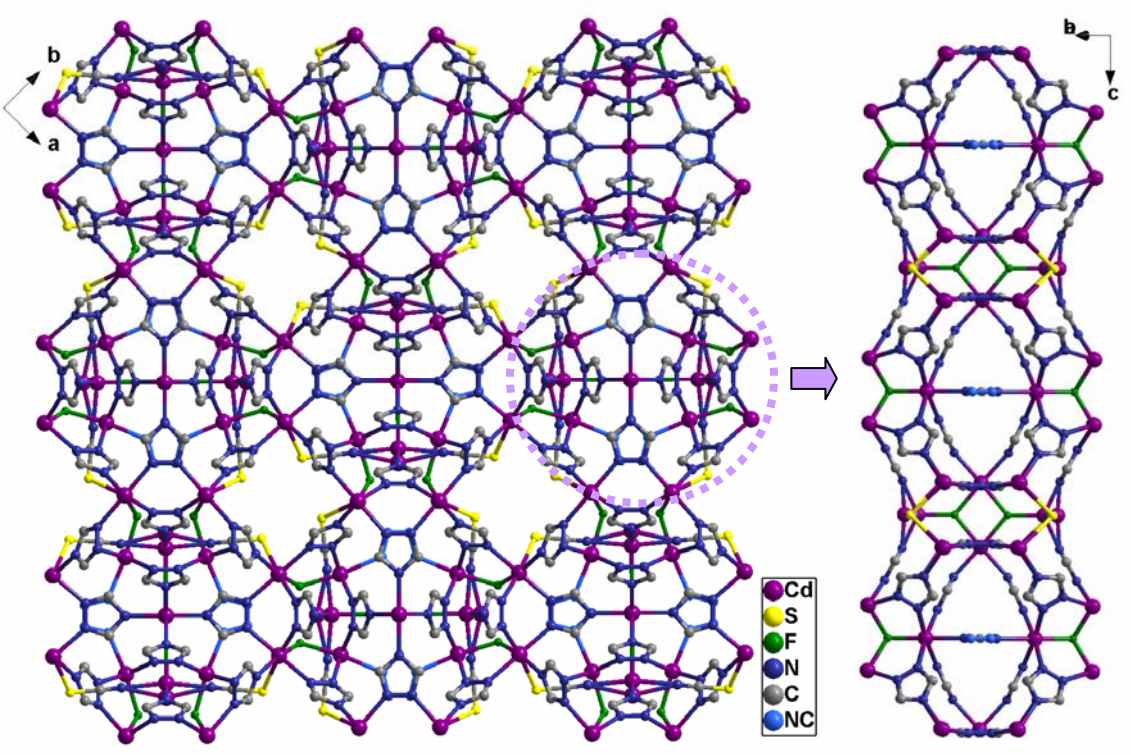

Fig. S1 The complicated 3D framework of **1** viewed from the *c*-axis direction.

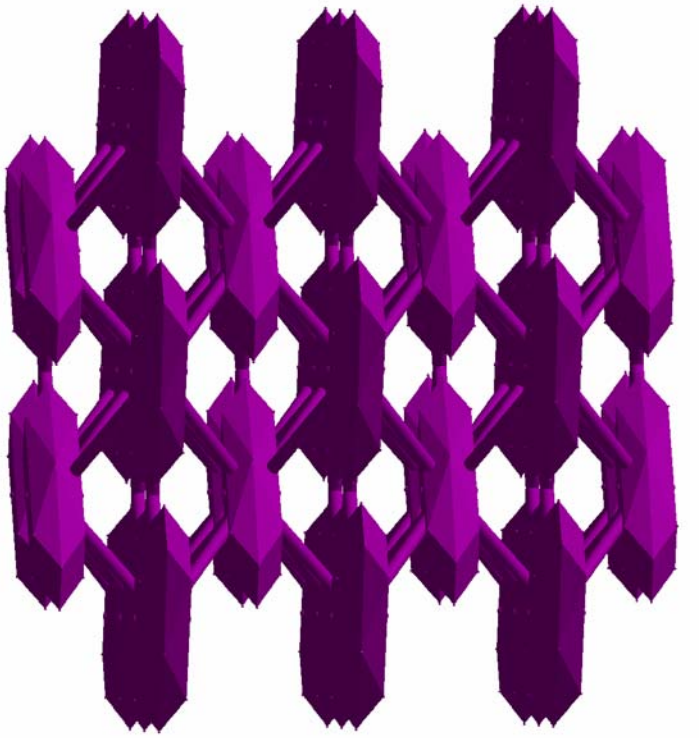

Fig. S2 The polyhedral demonstration of the 10-conneted topological net of **1**.

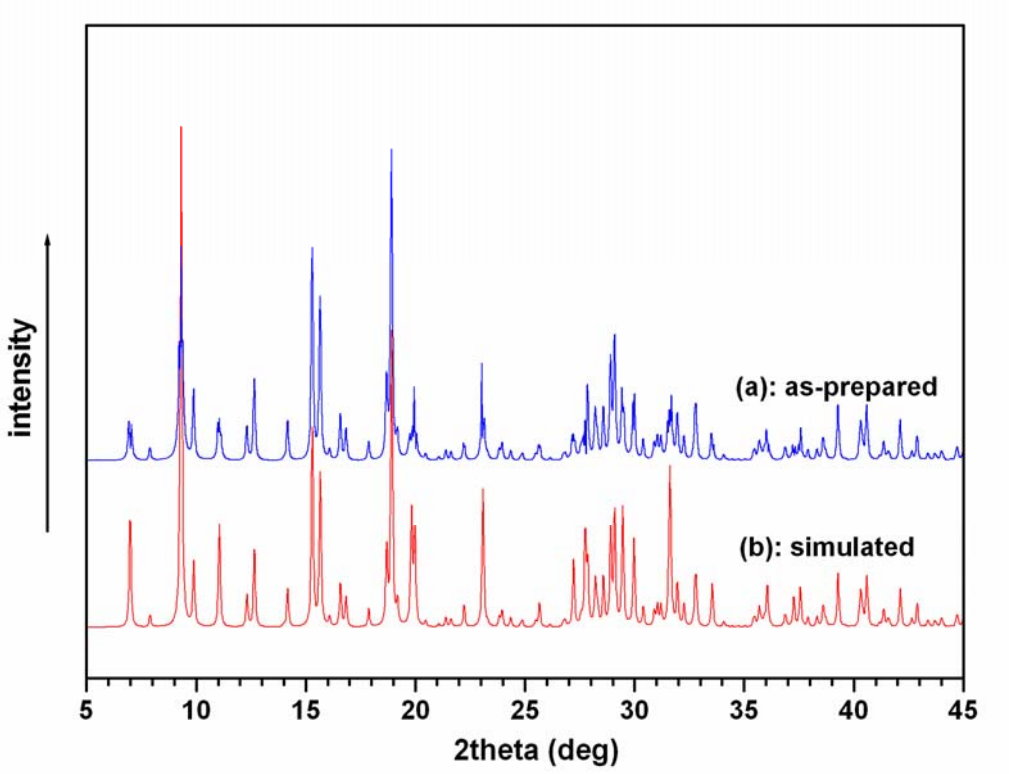

Fig. S3 PXRD patterns for compound **1**.

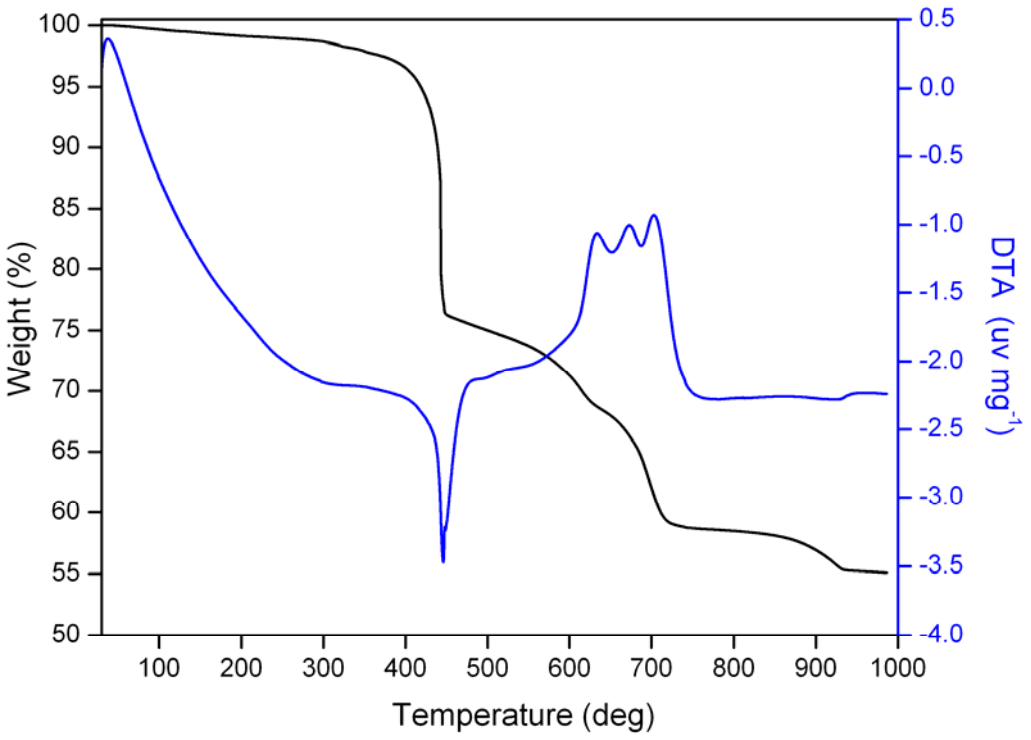

Fig. S4 TG/DTA curves of compound **1**.

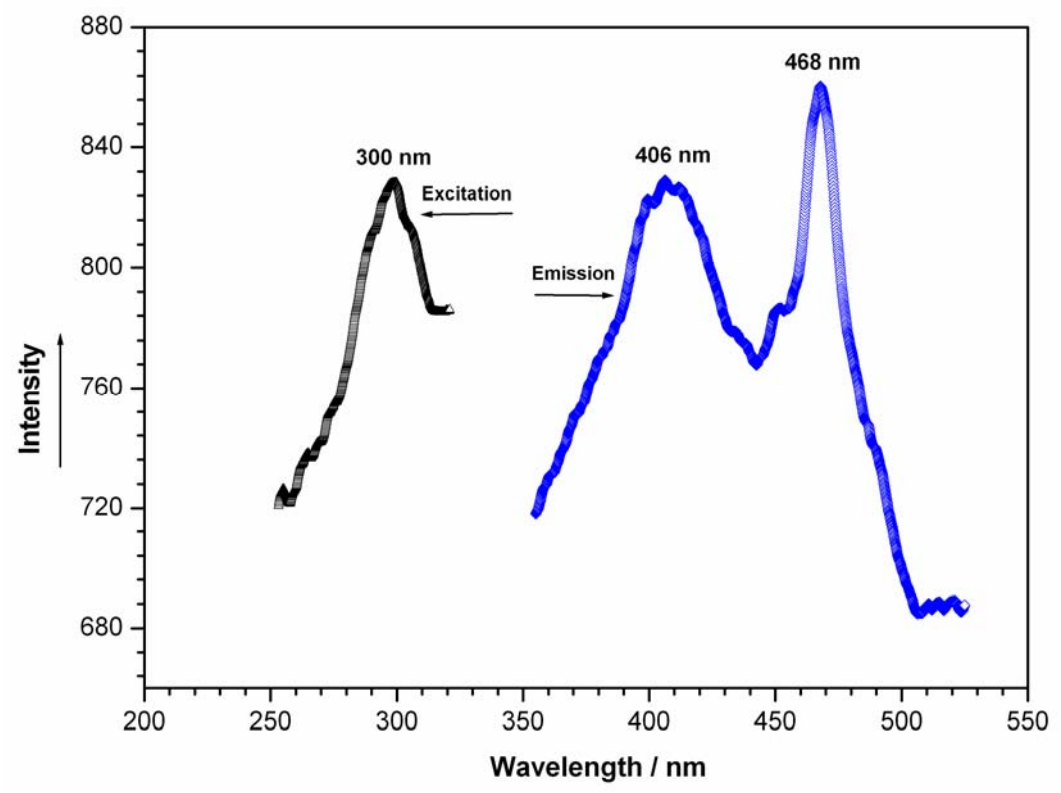

Fig. S5 Solid state excitation and emission spectra of **1** at room temperature.

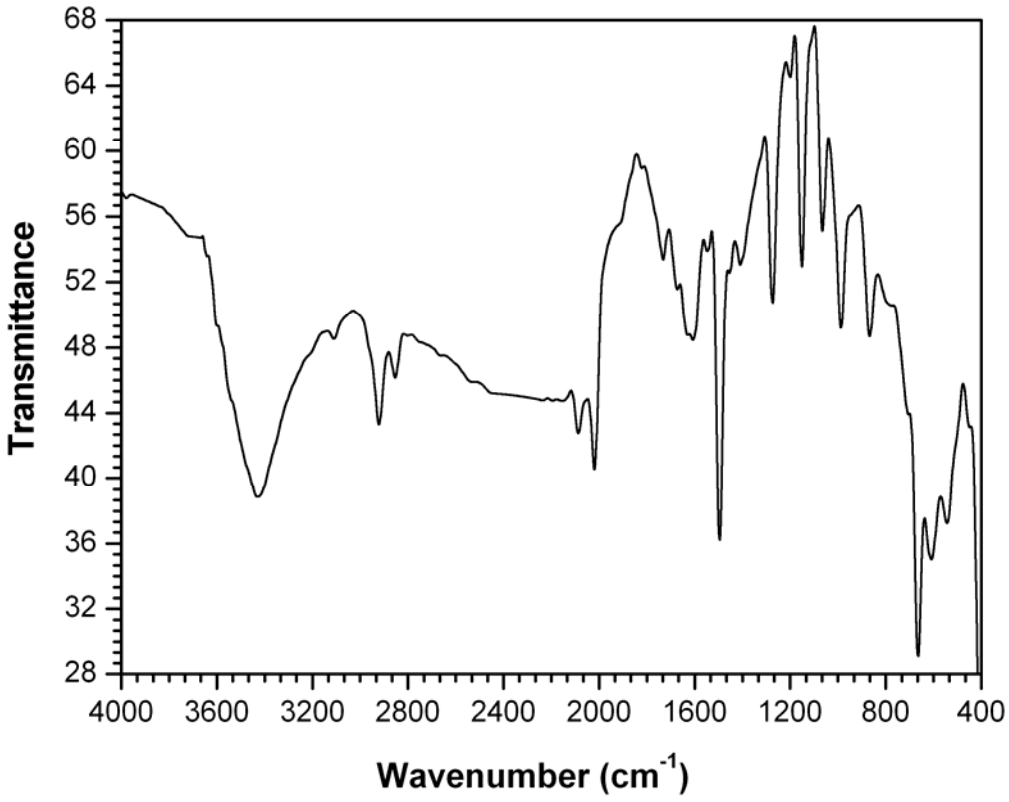

Fig. S6 FT-IR spectrum for **1**.