Supporting information for

A highly-connected acentric organic-inorganic hybrid material with unique 3D inorganic and 3D organic connectivity

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Experimental Section

General Remarks. All of the chemicals are commercially available and used without further purification. Elemental analyses were determined using Elementar Vario EL elemental analyser. The IR spectra were recorded in the 4000 to 400 cm^{-1} region using KBr pellets and a Bruker EQUINOX 55 spectrometer. The thermogravimetric analyses (TGA) was carried out on Netzsch TG-209 Thermogravimetry Analyzer in air atmosphere. The Powder X-ray diffraction patterns were recorded on D8 ADVANCE X-Ray Diffractometer. The single crystal data were collected on a Bruker Smart 1000 CCD diffractometer.

Preparation. $Cd(OAc)_2 \cdot 2H_2O$ (1.0 mmol, 0.266 g), ethyl tetrazolate-5-carboxylate (0.5 mmol, 0.071 g) and methanol (4.5 mL) were mixed and stirred for ten minutes, then KOH aqueous solution (0.5 mL, 1 mol/L) was added. After further stirred for 5 minutes, the resulting solution was transferred to Teflon-lined autoclave and heated at 160°C for 72 h. The autoclave was cooled over a period of 26 h with a rate of 5°C·h^{-1}.

Block-shaped colorless crystals of **1** were collected by filtration, washed with water, and dried in air. Yield: 62%. Anal. Calcd for $C_8H_6N_{16}O_{14}Cd_7$: C, 7.19; H, 0.45; N, 16.76. Found: C, 7.08; H, 0.51; N, 16.83. IR (KBr, cm^{-1}): 3482(s), 1610(vs), 1509(m), 1426(m), 1407(w), 1338(s), 1209(w), 1160(w), 1094(w), 1053(w), 892(w), 826(w), 815(m), 679(m).

X-ray Crystallography. Single-crystal data for **1** was collected on a Bruker Smart 1000 CCD diffractometer, with Mo-Kα radiation (λ = 0.71073 Å). All empirical absorption corrections were applied using the SADABS program.[1] The structure was solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. The position disorder of O4 was treated by performing half occupancies. The hydrogen atom attached O3 was assigned in the difference Fourier maps, while the hydrogen atom attached O4 was placed in calculated position, with fixed isotropic thermal parameters and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL system of computer programs.[2]

Nonlinear Optical Measurement. Second-order nonlinear optical effect for the powder samples of **1** was investigated by optical second-harmonic generation (SHG) at room temperature. SHG intensity data were obtained by placing the powder sample in an intense fundamental beam from a Q-switched Nd: YAG laser with a wavelength 1064 nm. The output (λ = 532 nm) was filtered firstly to remove the multiplier and then displayed on an oscilloscope. This procedure was repeated using a standard NLO material (microcrystalline KDP), and the ratio of the second-harmonic intensity outputs was calculated. The observed SHG efficiency of **1** is as twice as that of KDP.

Topological Analysis by TOPOS 4.0. Atom coordinates (V1 = 4-conntected [Tzc] anion, V2 = 8-conntected [Cd(OH)$_2$] unit, V3 = 16-connected [Cd$_6$(OH)$_4$]$^{8+}$ cluster)

Name	x	y	z
V1	0.8905	0.7372	0.5997
V2	0.5000	0.5000	0.5000
V3	1.0000	0.5000	0.2500

Topology for V1

The links to Atom V1

V2	0.0000	1.0000	1.0000	(0 1 1)	4.533 Å
V3	0.5000	1.0000	0.7500	(0 1 0)	4.905 Å
V3	0.0000	0.5000	1.2500	(0 1 2)	5.379 Å
V3	0.5000	0.0000	0.7500	(0 0 0)	6.608 Å

Topology for V2

The links to Atom V2

V1	-0.3905	-0.2372	0.0997	(-1 0 1)	4.533 Å
V1	0.2372	-0.3905	-0.0997	(0 -1 -1)	4.533 Å
V1	-0.2372	0.3905	-0.0997	(0 1 -1)	4.533 Å
V1	0.3905	0.2372	0.0997	(1 0 1)	4.533 Å
V3	0.0000	-0.5000	0.2500	(0 0 1)	5.836 Å
V3	0.0000	0.5000	0.2500	(0 1 1)	5.836 Å
V3	0.5000	0.0000	-0.2500	(0 0 -1)	5.836 Å
V3	-0.5000	0.0000	-0.2500	(-1 0 -1)	5.836 Å

Topology for V3

The links to Atom V3

V1	0.7628	0.3905	0.9003	(1 1 0)	4.905 Å
V1	0.1095	0.2628	0.5997	(-1 0 1)	4.905 Å
V1	0.2372	-0.3905	0.9003	(0-1 0)	4.905 Å
V1	0.8905	-0.2628	0.5997	(1-1 1)	4.905 Å
V1	0.6095	-0.2372	1.0997	(0 0 2)	5.379 Å
V1	0.3905	0.2372	1.0997	(1 0 2)	5.379 Å

V1	0.7372	0.1095	0.4003	(0-1-1)	5.379 Å
V1	0.2628	-0.1095	0.4003	(0 0-1)	5.379 Å
V1	0.7628	-0.6095	0.9003	(1 0 0)	6.608 Å
V1	1.1095	0.2628	0.5997	(0 0 1)	6.608 Å
V1	0.2372	0.6095	0.9003	(0 0 0)	6.608 Å
V1	-0.1095	-0.2628	0.5997	(0-1 1)	6.608 Å
V2	0.5000	-0.5000	0.5000	(0-1 0)	5.836 Å
V2	0.5000	0.5000	0.5000	(0 0 0)	5.836 Å
V2	1.0000	0.0000	1.0000	(1 0 1)	5.836 Å
V2	0.0000	0.0000	1.0000	(0 0 1)	5.836 Å

Coordination sequences

V1	1	2	3	4	5	6	7	8	9	10
Num	4	41	59	182	238	373	468	715	748	1122
Cum	5	46	105	287	525	898	1366	2081	2829	3951

V2	1	2	3	4	5	6	7	8	9	10
Num	8	48	80	178	240	408	460	726	772	1136
Cum	9	57	137	315	555	963	1423	2149	2921	4057

V2	1	2	3	4	5	6	7	8	9	10
Num	16	24	116	150	276	344	564	598	928	948
Cum	17	41	157	307	583	927	1491	2089	3017	3965

Vertex symbols for selected sublattice

V1 Point (Schläfli) symbol: $\{3^2.4^3.5\}$

Extended point symbol: $[3.4_2.3.4_2.4_2.5_4]$

V2 Point (Schläfli) symbol: $\{3^8.4^{10}.5^8.6^2\}$

Extended point symbol: $[3.3.3.3.3.3.3.3.4.4.4.4.4_2.4_2.4_2.4_2.4_2.4_2.5_4.5_4.5_4.5_4.5_4.5_4.5_4.5_4.6_8.6_8]$

V3 Point (Schläfli) symbol: $\{3^8.4^{32}.5^{36}.6^{30}.7^{14}\}$

Extended point symbol: [3.3.3.3.3.3.3.3.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.

$4.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5_2.5_2.5_2.5_2.6.6.6.6.6.6.6.6.6_2.6_2.6_3.6_3.$

$6_3.6_3.6_3.6_3.6_3.6_3.6_3.6_3.6_3.6_3.6_4.6_4.6_4.6_4.6_7.6_7.6_7.6_7.7_3.7_3.7_3.7_3.7_4.7_4.7_5.7_5.7_5.7_5.7_7.7_7.7_7.7_7]$

Point (Schläfli) symbol for net: $\{3^2.4^3.5\}_4\{3^8.4^{10}.5^8.6^2\}\{3^8.4^{32}.5^{36}.6^{30}.7^{14}\}$

4,8,16-*c* net with stoichiometry (4-*c*)(8-*c*)(16-*c*); 3-nodal net

New topology, please contact the authors (78739 types in 10 databases)

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References

1 G. M. Sheldrick, *SADABS, Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Göttingen, 1996.

2 G. M. Sheldrick, *SHELXS 97*, *Program for Crystal Structure Refinement*; University of Göttingen, Göttingen, 1997.

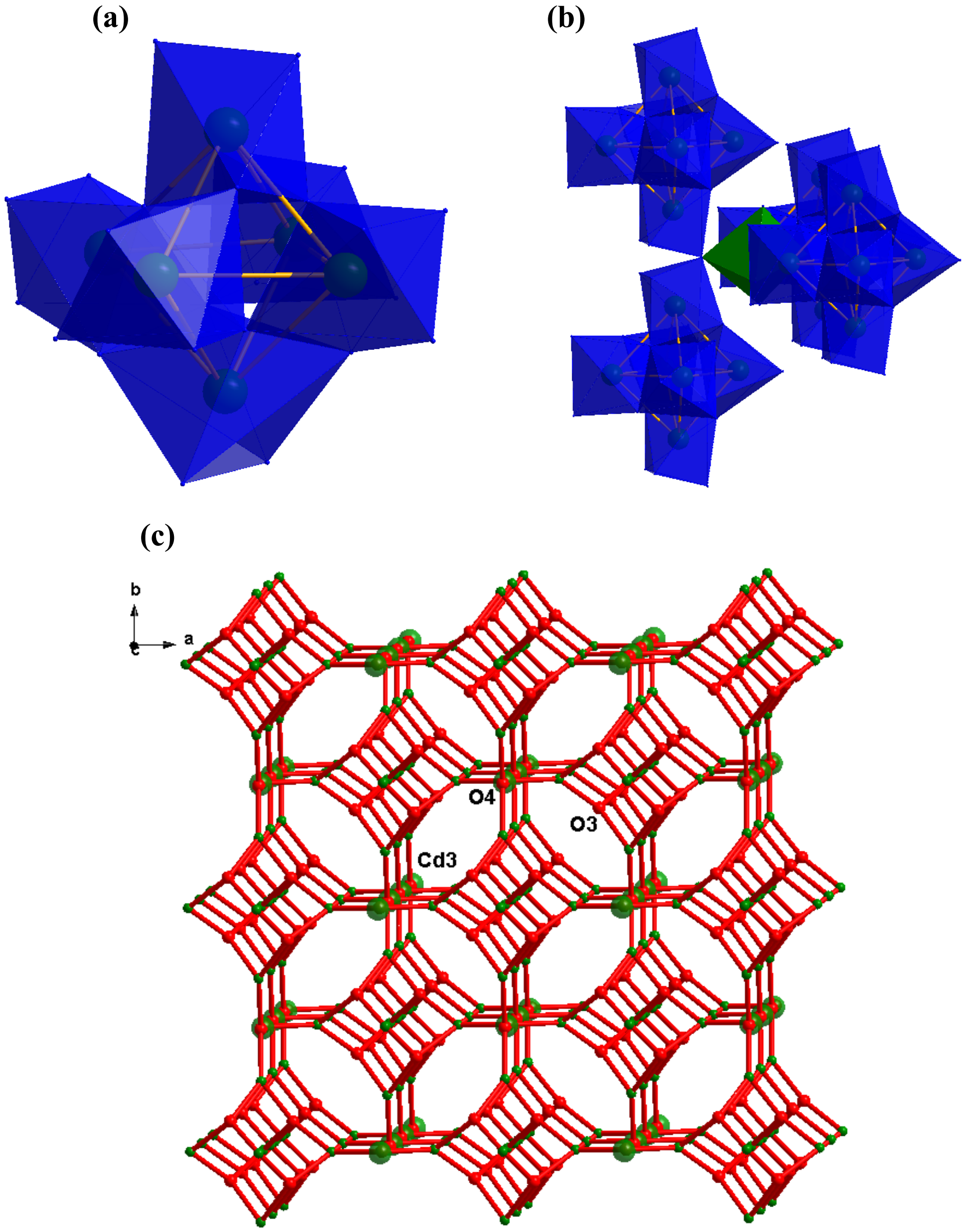

Fig. S1 The polyhedron drawings of (a) Cd1 and Cd2 in distorted octahedral geometries, four Cd1 and two Cd2 forming an octahedral hexanuclear cadmium(II) cluster. (b) Hexanuclear Cd_6 clusters (blue) and Cd3 atom (green) are connected through sharing the vertexes. (c) The 3D inorganic connectivity skeleton in **1**.

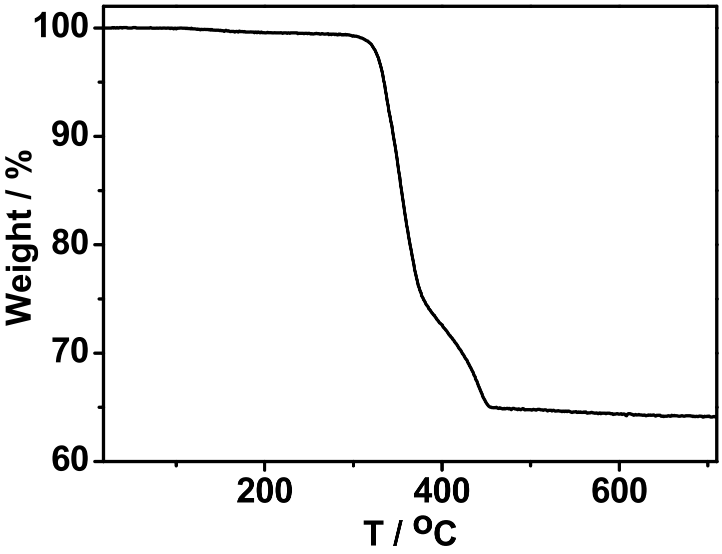

Fig. S2 The TGA curve for **1**.

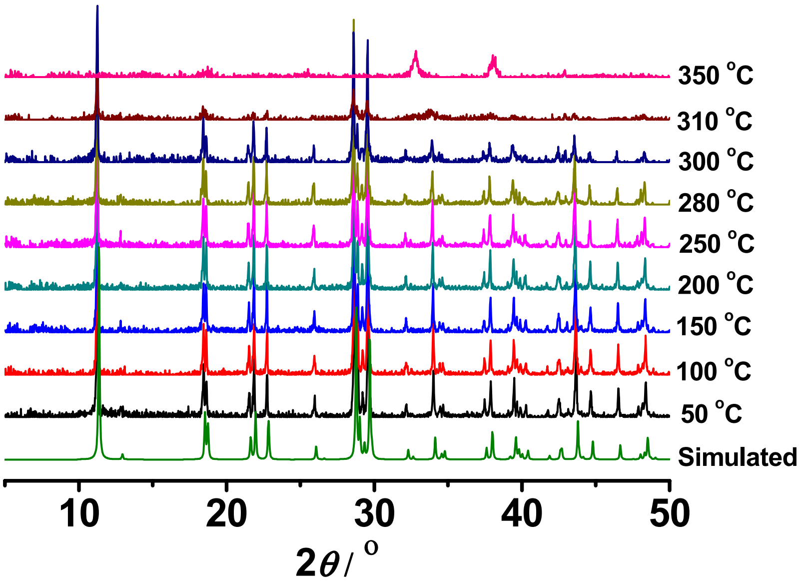

Fig. S3 The variable temperature XPRD patterns for **1.**