

Supporting Information

A rare I^2O^3 hybrid organic-inorganic material with high-connection and quadruple-stranded helices

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S1. Materials and Measurements

All chemical reagents except H₄TCBA ligand were obtained from commercial sources and used as received. Elemental analyses were performed with an Elementar Vario EL analyzer and IR spectra were measured as KBr discs on a Nicolet Avatar 5700 FT-IR spectrometer in the 4000–400 cm⁻¹ region. ¹H-NMR spectra were recorded at 400 MHz on a Bruker WH400 DS spectrometer. Mass spectra were taken on an Agilent Liquid chromatography-mass analyzer spectrometry (LC-MS) 1100 series instrument in the electrospray ionization [negative electrospray ionization (ESI)] mode. Fluorescence measurements were made on a Hitachi F-7000 fluorophotometer at room temperature. Thermogravimetric curves were recorded with a Perkin-Elmer Diamond TG/DTA Thermal Analyzer, a platinum container was used for heating the sample with a heating rate of 10 °C/min under a N₂ atmosphere. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8-DVANCE X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$).

S2. Synthesis

The ligand 3,4,5-tris(carboxymethoxy)benzoic acid (H₄TCBA) was prepared according to the literature methods.¹

Preparation of 3,4,5-tris(carboxymethoxy)benzoic acid (H₄TCBA). To 50 mL of water suspension of 3,4,5-trihydroxybenzoic acid (0.1 mol) was added NaOH (0.6 mol) at ambient temperature. After the reaction mixture became clear, a 50 mL solution of ClCH₂COOH (0.3 mol) was added dropwisely at ca. 90 °C with vigorous stirring. After continuing the reaction for 5h, the resulting mixture was acidified with HCl to pH 2–3 and a gray product precipitated, then was filtered off, washed with 3 \times 10 mL of deionized H₂O, and air-dried. Yield 89%. MS (ESI⁻) m/z (M-H) 343.04. Anal. Calcd: C, 45.36; H, 3.51. Found: C, 45.72; H, 3.79. Mp: 296-297 °C. Main IR frequencies: 3483, 1708, 1500, 1419, 1331, 1139, 1030, 871, 771 cm⁻¹. ¹H NMR (DMSO-d₆, 400MHz) δ : 4.60 (s, 6H, CH₂), 7.15 (s, 2H, ArH).

Synthesis of [Cd₃(OH)₂(TCBA)(H₂O)] (1). A mixture of CdCl₂·2.5H₂O (0.023 g, 0.1 mmol), H₄TCBA (0.034 g, 0.1 mmol), NaOH (0.1 mmol) and distilled water (10 mL) was sealed in a Teflon-lined stainless reactor (23 mL) and heated 110 °C for 72 h

under autogenous pressure. Colorless block crystals were obtained. Yield: 32.5% (based on Cd). Anal. Calcd. for $C_{13}H_{12}Cd_3O_{14}$ (%): C 21.40; H 1.66. Found: C 21.56; H 1.86. IR data (KBr pellet, ν/cm^{-1}): 3433 s, 1609 vs, 1403 vs, 1331 m, 1220 w, 1141 m, 1027 w, 789 w, 598 w.

S3. X-ray crystallography

The single-crystal X-ray data of **1** was collected on a Bruker APEX II area detector diffractometer with a graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Semi-empirical absorption corrections were applied to the title complexes using the SADABS program.² The structures were solved by direct methods,³ and refined by full-matrix least squares on F^2 using SHELXL-97.⁴ All non-hydrogen atoms were refined anisotropically. The hydroxyl H and water H atoms were located from difference Fourier maps, the other hydrogen atoms were placed in geometrically calculated positions. CCDC reference number is 999327. This data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Experimental details for X-ray data collection of **1** are presented in Table S1, and selected bond lengths are listed in Table S2, and the selected hydrogen bonding lengths and angles are listed in Table S3.

Table S1. Crystal data for complex **1**

Complex	1
Empirical formula	$C_{13}H_{12}O_{14}Cd_3$
Formula weight	729.43
T/K	291(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
$a/\text{\AA}$	11.8373(10)
$b/\text{\AA}$	11.5492(9)
$c/\text{\AA}$	12.7035(10)
$\alpha/^\circ$	90
$\beta/^\circ$	95.0680(10)
$\gamma/^\circ$	90
$V/\text{\AA}^3$	1729.9(2)
Z	4
$F(000)$	1384
$D_C/g\cdot\text{cm}^{-3}$	2.801
θ range/ $^\circ$	2.39-25.50

μ /mm ⁻¹	3.735
<i>GOF</i>	1.089
Reflections collected	12544
Independent reflections	3207
R_{int}	0.0167
$R_1, wR_2[I > 2\sigma(I)]$	0.0288, 0.0811
$R_1, wR_2(\text{all data})$	0.0312, 0.0826

Table S2. Selected bond lengths (Å) for **1**

1			
Cd(1)–O(1) ^{#1}	2.414(4)	Cd(1)–O(2) ^{#1}	2.409(4)
Cd(1)–O(10)	2.330(4)	Cd(1)–O(12) ^{#2}	2.277(3)
Cd(1)–O(13)	2.251(3)	Cd(1)–O(14)	2.366(3)
Cd(2)–O(4) ^{#3}	2.466(5)	Cd(2)–O(5) ^{#3}	2.430(5)
Cd(2)–O(6)	2.503(3)	Cd(2)–O(8)	2.277(4)
Cd(2)–O(9)	2.538(4)	Cd(2)–O(10) ^{#4}	2.317(4)
Cd(2)–O(11)	2.326(4)	Cd(2)–O(12)	2.369(4)
Cd(3)–O(5) ^{#3}	2.407(5)	Cd(3)–O(7) ^{#5}	2.342(4)
Cd(3)–O(12)	2.188(3)	Cd(3)–O(13)	2.355(3)
Cd(3)–O(13) ^{#6}	2.216(3)		

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

Table S3. Hydrogen bonding geometry (Å and °) for **1**

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
O(14)–H(1W)···O(8) ^{#1}	0.83	1.89	2.705(5)	170.1
O(14)–H(2W)···O(2) ^{#2}	0.84	1.86	2.692(5)	173.3

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 1, -z + 2$; #2 $-x + 2, -y + 1, -z + 2$.

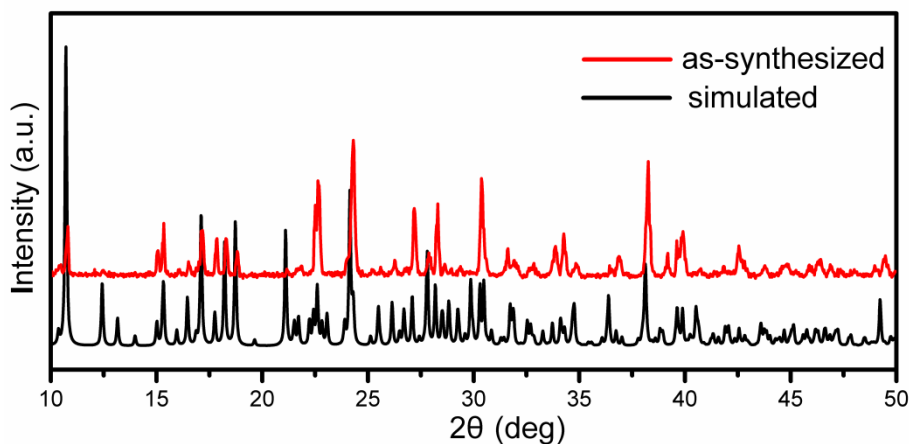


Fig. S1 Simulated and as-synthesized PXRD patterns of **1**.

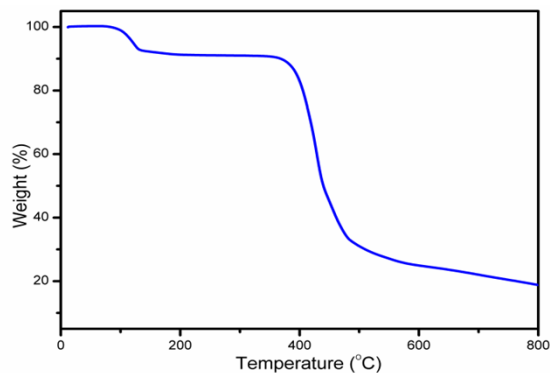


Fig. S2 Thermal gravimetric curve of **1**.

References

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