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A Second-order Nonlinear Optical Material with Hydrated Homochiral Helix via Spontaneous Symmetric Breaking Crystallization from an Achiral Ligand

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EXPERIMENTAL SECTION

Materials and Methods. The reagents and solvents employed were commercially available and used as received. IR absorption spectra of the compounds were recorded in the range of 400–4000 cm^{-1} on a Nicolet (Impact 410) spectrometer with KBr pellets (5 mg of sample in 500 mg of KBr). C, H, and N analyses were carried out with a Perkin–Elmer 240C elemental analyzer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu–Kα radiation (λ = 1.5418 Å), in which the X-ray tube was operated at 40 kV and 40 mA. The as-synthesized samples were characterized by thermogravimetric analysis (TGA) on a Perkin Elmer thermogravimetric analyzer Pyris 1 TGA up to 1023 K using a heating rate of 10 K min^{-1} under N_2 atmosphere. Luminescent spectra were recorded with a SHIMAZU VF-320 X-ray fluorescence spectrophotometer at room temperature. The powder samples (50mg) were ground and sieved into particle size ranges (< 40, 40-75, 75-105, 105-145, 145-205, 205-260, and 260-335 μm). The sieved urea powders were used as reference materials to assume the effect. A pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate a SHG signal. The backscattered SHG light was collected by a spherical concave mirror and passed through a filter that transmits only 532 nm radiation.

Syntheses of Compound 1. A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (30.1 mg, 0.1 mmol), imidazole (6.8 mg, 0.1 mmol) and H_2L (25.7 mg, 0.1 mmol) was dissolved in 4.5 mL of DMF/H_2O(1:8, v/v). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at 85 °C for 3 d. after cooled to room temperature, the solid was filtered and the solution was static evaporated at room temperature for three days, then pale yellow crystals were

obtained, which were washed with mother liquid, and dried under ambient conditions (Yield: 40% based on H_2L). Anal. Calcd for $C_{37}H_{55}O_{19}N_5Cd_2$: C, 40.41, H, 5.01, N, 6.37; found C, 40.34, H, 5.03, N, 6.35.

Crystal Structure Determination. X-ray crystallographic data of **1** was collected at room temperature using epoxy-coated crystals mounted on glass fiber. All measurements were made on a Bruker Apex Smart CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures of compounds **1** was olved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedures based on F^2 values.[21] The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. The relevant crystallographic data are presented in Table S1, while the selected bond lengths and angles are given in Supporting Information, Table S2.

Table S1. Crystallographic Data for Compound **1**

Formula	$C_{37}H_{55}Cd_2N_5O_{19}$
Formula Weight	1098.66
Crystal System	monoclinic
Space group	$P2_1$
a (Å)	9.6120(10)
b (Å)	16.4062(17)
c (Å)	14.7042(15)
α (deg)	90
β (deg)	104.0780(10)
γ (deg)	90
V (Å^3)	2249.2(4)
Z	2
D_c (g cm^{-3})	1.662
μ(Mo) Ka)(mm^{-1})	1.026
F(000)	1120
R(int)	0.0286
Observed data [$I > 2\sigma(I)$]	6532
R1, wR2 [I> 2σ(I)]	0.0345, 0.0986
S	1.026
Min. and Max. Resdens (e·Å^{-3})	-1.209, 2.292
Absolute structure parameter	0.00(3)

Table S2. Selected Bond Lengths (Å) and Angles (deg) for Compound **1**

Compound **1**			
Cd1-O1	2.417(4)	Cd1-O2	2.409(4)
Cd1-O3#1	2.345(4)	Cd1-O4#1	2.427(4)
Cd1-O9	2.296(5)	Cd1-O10	2.272(4)
Cd1-O13	2.333(5)	Cd2-O5	2.414(5)
Cd2-O6	2.374(4)	Cd2-O7#1	2.390(4)
Cd2-O8#1	2.393(4)	Cd2-O11	2.264(4)
Cd2-O12	2.297(4)	Cd2-O14	2.269(4)
O10-Cd1-O9	89.13(16)	O10-Cd1-O13	81.98(15)
O9-Cd1-O13	170.48(14)	O10-Cd1-O3#1	139.33(14)
O9-Cd1-O3#1	94.92(18)	O10-Cd1-O3#1	94.06(17)
O10-Cd1-O2	138.30(14)	O9-Cd1-O2	97.58(18)
O13-Cd1-O2	86.91(17)	O3#1-Cd1-O2	81.27(12)
O10-Cd1-O1	86.07(15)	O9-Cd1-O1	84.97(15)
O13-Cd1-O1	90.99(16)	O3#1-Cd1-O1	134.59(14)
O1-Cd1-O2	53.95(14)	O10-Cd1-O4#1	85.46(14)
O9-Cd1-O4#1	89.36(18)	O13-Cd1-O4#1	93.32(19)
O3#1-Cd1-O4#1	54.22(12)	O2-Cd1-O4#1	135.43(12)
O1-Cd1-O4#1	169.87(14)	O11-Cd2-O14	173.22(17)
O11-Cd2-O12	89.87(18)	O14-Cd2-O12	86.76(18)
O11-Cd2-O6	92.32(16)	O14-Cd2-O6	93.19(16)
O12-Cd2-O6	84.23(17)	O11-Cd2-O7#1	98.20(16)
O14-Cd2-O7#1	80.82(16)	O12-Cd2-O7#1	140.64(14)
O6-Cd2-O7#1	133.37(17)	O11-Cd2-O8#1	86.01(15)
O14-Cd2-O8#1	87.97(16)	O12-Cd2-O8#1	87.57(16)
O6-Cd2-O8#1	171.6(2)	O7#1-Cd2-O8#1	54.99(16)

O11-Cd2-O5	90.97(19)	O14-Cd2-O5	95.5(2)
O12-Cd2-O5	138.69(15)	O6-Cd2-O5	54.48(17)
O7#1-Cd2-O5	79.93(14)	O8#1-Cd2-O5	133.68(16)

#1 = *x*-1, *y*, *z*-1

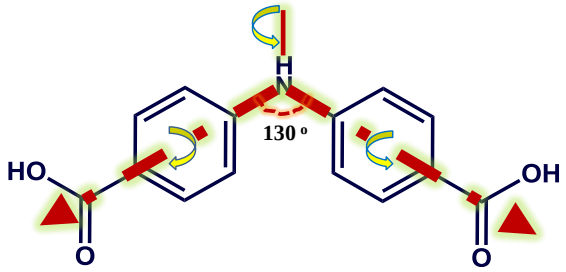
Table S3. Specified Hydrogen Bonds of Compound **1**

D–H–A	d(D···H)(Å)	d(H···A)(Å)	d(D···A)(Å)	(DHA)(deg)
N3-H3A-O17 #1	0.86	2.09	2.948(7)	172
N4-H4A-O16 #2	0.86	2.33	3.156(4)	160
O9-H9A-O5 #3	0.85	2.19	2.733(4)	122
O9-H9B-O7 #2	0.85	2.05	2.769(5)	143
O10-H10A-O6 #4	0.96	2.09	2.740(4)	123
O10-H10B-O18 #5	0.96	1.88	2.785(4)	156
O11-H11A-O3 #6	0.85	2.06	2.739(3)	136
O11-H11C-O2 #7	0.85	2.11	2.754(5)	132
O12-H12B-O19 #7	0.85	1.95	2.796(4)	177
O12-H12C-O4 #8	0.85	1.90	2.744(7)	173
O16-H16C-O15 #5	0.85	2.37	2.798(4)	111
O16-H16C-O1 #9	0.85	2.42	2.957(4)	122
O17-H17A-O15 #10	0.85	2.36	2.901(5)	122
O17-H17B-O8 #4	0.85	2.27	2.850(5)	126
O18-H18B-O7 #11	0.85	1.99	2.775(7)	152
O18-H18B-O14 #12	0.85	2.66	3.140(4)	117

O19-H19D-O2	0.85	2.06	2.909(5)	179
O19-H19A-O18#2	0.85	2.19	2.873(6)	138

(#1) -*x*+1, *y*+1/2, -*z*+1 ; (#2) -*x*+1, *y*-1/2, -*z*+1; (#3) -*x*, *y*-1/2, -*z*; (#4) *x*-1, *y*-1, *z*; (#5) -*x*, *y*-1/2, -*z*+1; (#6) *x*-1, *y*+1, *z*-1; (#7) *x*, *y*+1, *z*; (#8) *x*, *y*+1, *z*-1; (#9) -*x*, *y*+1/2, -*z*+1; (#10) *x*, *y*-1, *z*; (#11) *x*-1, *y*, *z*; (#12) *x*, *y*, *z*+1.

Scheme S1. The Rigid and Flexible V-shaped Polycarboxylate Ligands



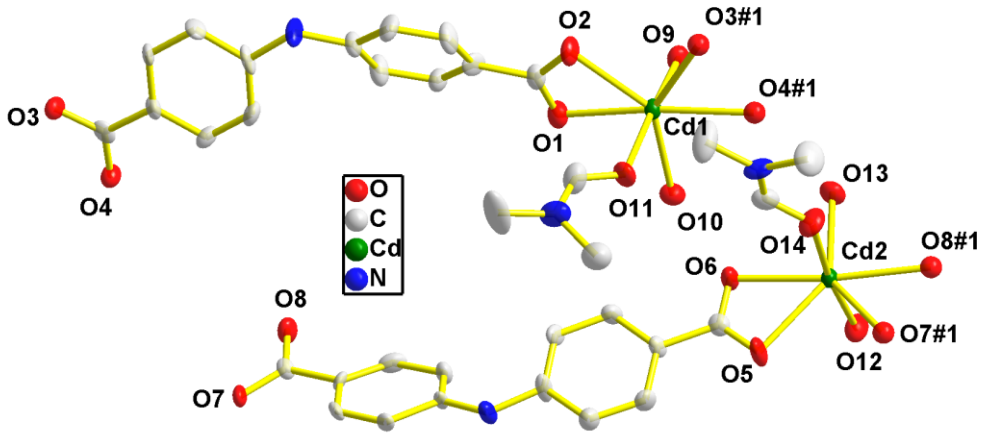


Figure S1. Coordination environment of Cd(II) ions in **1.** The hydrogen atoms are omitted for clarity (30% ellipsoid probability). Symmetry codes: (#1) -1+*x*, *y*, -1+*z*.

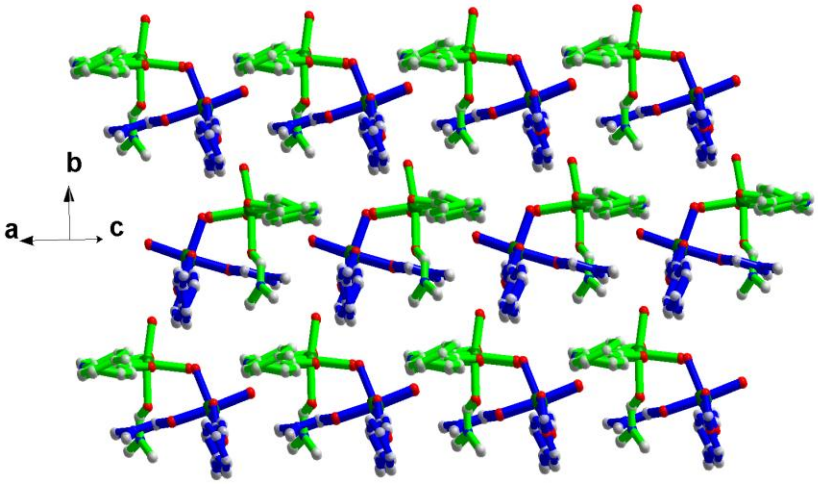


Figure S2. The arrangement of linear chains in **1**.

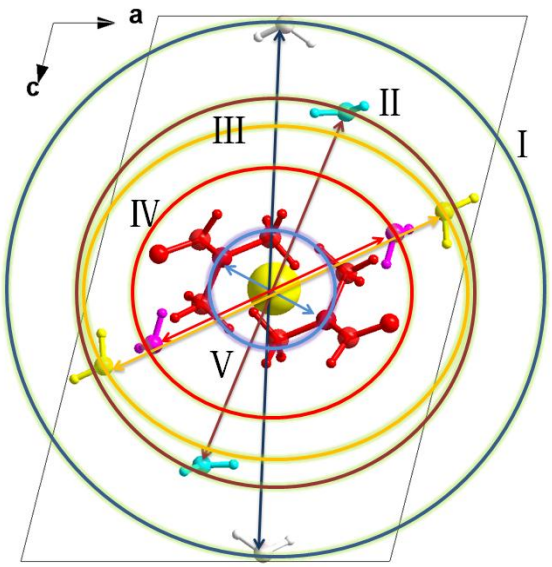


Figure S3. The helical arrangement of water and DMF molecules see from the b axis direction.

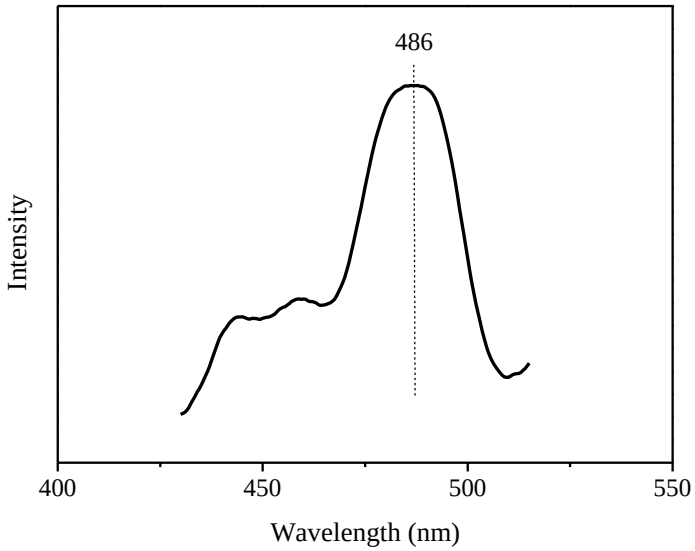


Figure S4. Solid-state photoluminescent spectra of **1**.

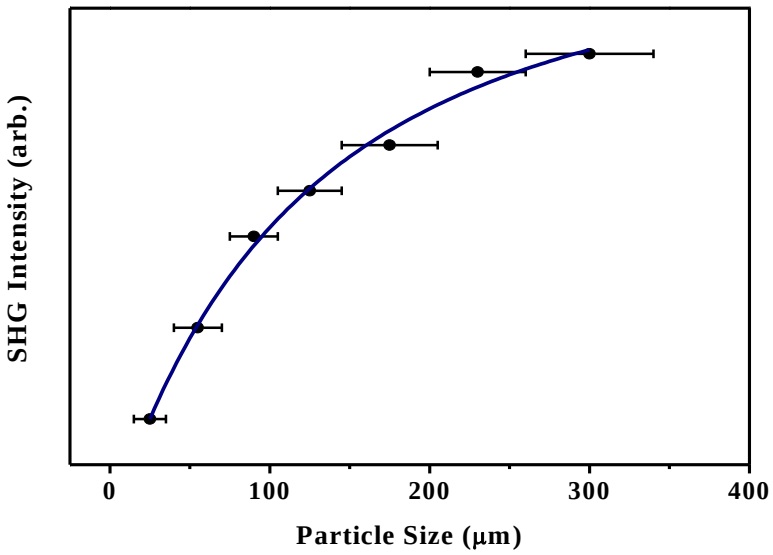


Figure S5. Phase-matching curve for **1**. The curve drawn is to guide the eye and not a fit to the data.

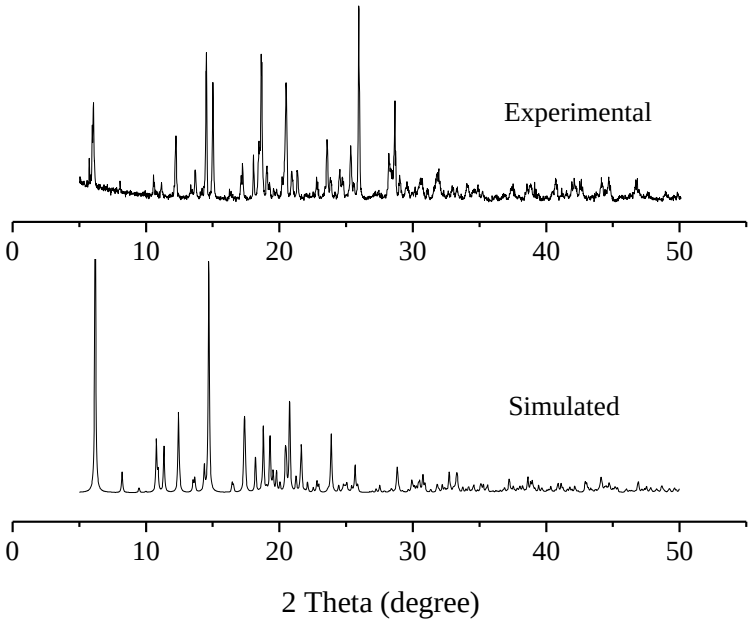


Figure S6. Powder X-ray diffraction patterns of **1**.

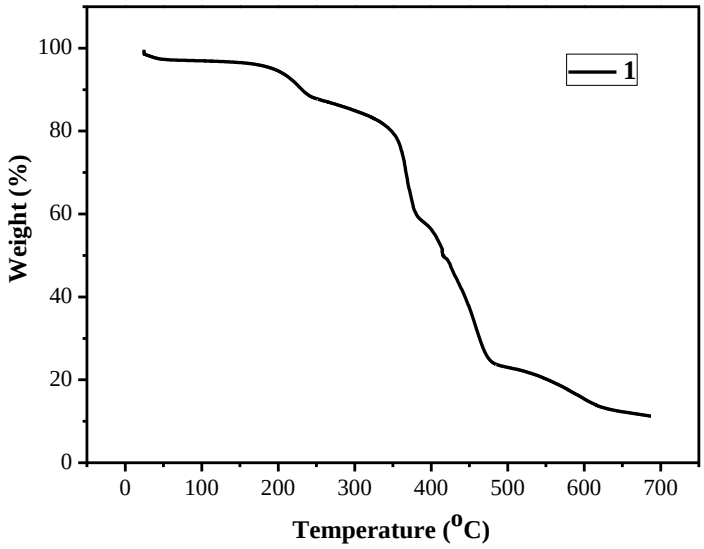


Figure S7. TG plots of **1**.

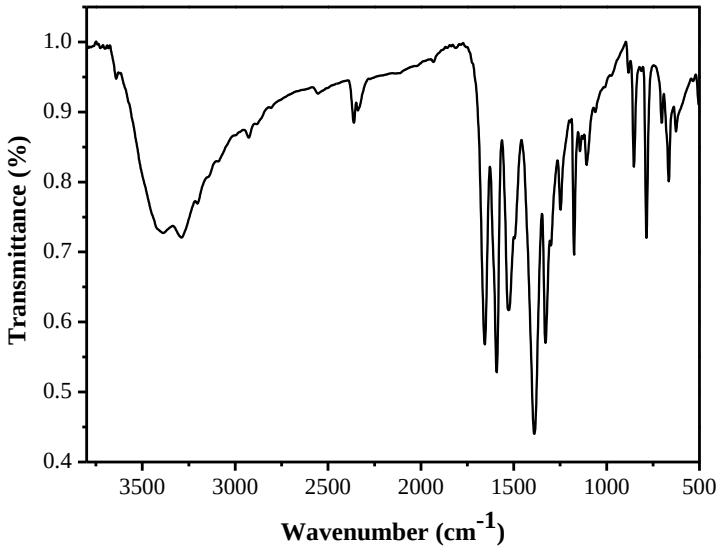


Figure S8. IR spectra of **1** at room temperature.