Electronic Supplementary Information

$C_{10}H_6NO_2Cd(NO_3)\cdot 2H_2O$: A Birefringent Crystal with Enlarged Band-Gap Derived from the Covalent Edge-Sharing Connection

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Contents

Reagents

$Cd(NO_3)_2·4H_2O$ (99%) and $C_{10}H_7NO_2$ (98%) were purchased from Aladdin and used as received.

Synthesis of $C_{10}H_6NO_2Cd(NO_3)·2H_2O$ (1)

Polycrystalline samples of **1** were synthesized by a simple evaporation technique of aqueous solution. The raw reactants of $Cd(NO_3)_2·4H_2O$ (2.500 g, 10 mmol) and $C_{10}H_7NO_2$ (0.030 g, 0.2 mmol) were mixed together with deionized water (10 mL) in a plastic beaker. The solution is heated and stirred with a magnetic stirrer for 30 minutes to get a clear liquid. The beaker was sealed with perforated plastic wrap and left to stand at 25 °C for about days. Colorless lamellar crystals were obtained at the bottom of beaker. The purity of the obtained product is confirmed by the powder X-ray diffraction (XRD) patterns, which were taken on a Rigaku MiniFlex II diffractometer (Cu *Kα* radiation) in the range of $2\theta = 5°-70°$ with a step width of 0.01° and a sampling rate of 1° min^{-1}. The results agree well with the calculated XRD patterns from single-crystal XRD analyses (Fig. 2a).

Single-Crystal Structure Determination

A colorless **1** crystal (0.06 × 0.03 × 0.03 mm^3) was selected using an optical microscope for single-crystal XRD analysis. The diffraction data were collected by using graphite-monochromatized Mo *Kα* radiation (λ = 0.71073 Å) at 293 (2) K on on an XtaLAB Pro II AFC12 equipped with a Hybrid Pixel Array Detector. The collection of the intensity data, cell refinement, and data reduction were carried out with the program CrysAlisPro.[1] Using Olex2,[2-3] the structure was solved with SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL[4] refinement package using Least Squares minimisation. Details of crystal parameters, data collection, and structure refinement are summarized in Table S1. The atomic coordinates and equivalent isotropic displacement parameters are listed in Table S2, and the anisotropic displacement parameters are listed in Table S3. The selected bond distances and angles are presented in Tables S4−S5. Hydrogen Bonds are listed in Table S6.

Thermal Stability Analysis

The thermogravimetric (TG) and differential scanning calorimetric (DSC) of **1** was carried out on a NETZSCH STA 449F3 simultaneous analyzer. About 9.4 mg of **1** was placed in Al_2O_3 crucibles, heated at a rate of 20 °C min^{-1} from room temperature to 600 °C under flowing nitrogen.

UV-Vis-NIR Diffuse Reflectance Spectroscopy

The UV/Vis/NIR diffuse reflection data were collected on a PerkinElmer Lamda-1050 UV/vis/NIR spectrophotometer. A whiteboard provided by the merchant was used as a reference (100% reflectance) in the range from 200 nm to 800 nm.

Infrared Spectroscopy

Infrared spectrum was measured on a Nicolet iS50FT-IR spectrometer with KBr pellets as a standard in the range of 4000~400 cm^{-1}. The mixture of **1** and dried KBr (mass ratio = 1:100) was ground thoroughly in an agate mortar, and then pressed into a thin slice for measurement.

Birefringence Measurements

The Birefringence of **1** was obtained through a polarizing microscope (Nikon LV1000) equipped with a Berek compensator at a wavelength of 550 nm. Small crystal was chosen for the measurement. The following formula was listed to calculate birefringence: $R = |N_e - N_o| = \Delta n \times T$, where R denotes the optical path difference, Δn represents birefringence, and T denotes the thickness of the crystal.

Computational Methods

The first-principles calculations for **1** were performed by CASTEP[5] on a plane-wave pseudopotential total energy package based density functional theory (DFT).[6] The functional developed by Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA)[7–8] form was adopted to describe the exchange-correlation energy. The ultrasoft pseudopotentials were used to model the effective interaction between atom cores and valence electrons. The electrons H $1s^1$, C $2s^22p^2$, N $2s^22p^3$, O $2s^22p^4$ and Cd $4d^{10}5s^2$ are regarded as valence electrons of **1**, and the electrons H $1s^1$, C $2s^22p^2$, N $2s^22p^3$ and O $2s^22p^4$ are regarded as valence electrons of isoquinoline-1-carboxylic acid. The kinetic energy cut-off point of 380 eV was selected in the Brillouin zones, the dense 1 × 2 × 1 and 2 × 1 × 1 Monkhorst-Pack[9] k-point meshes was selected in the Brillouin zones respectively. 3 × 2 × 2 and 2 × 3 × 2 k-point meshes was selected for the calculations of density of states and optical properties respectively.The linear optical properties were examined based on the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The imaginary part of dielectric function ε_2 can be calculated based on the electronic structures and the real part is obtained by the Kramers-Kronig transformation, accordingly the refractive indices and the birefringence (Δn) can be calculated. The frequency-dependent refractive index of **1** is calculated to demonstrate the validity of the birefringence measurement.

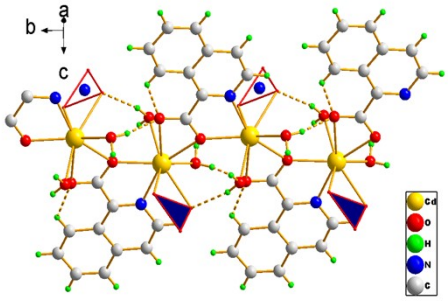

Fig. S1 Crystal structure and hydrogen bond connection of **1**.

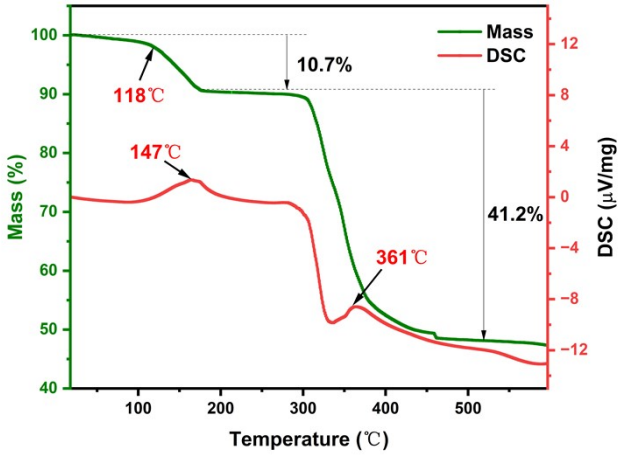

Fig. S2 Thermal stability analysis for **1**.

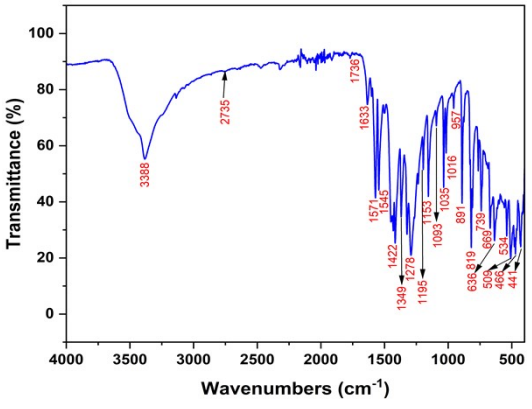

Fig. S3 Infrared spectrum of **1.**

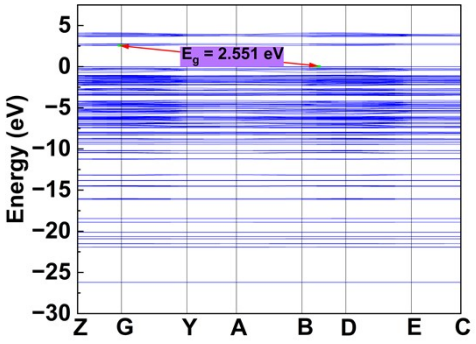

Fig. S4 Electronic band structure for **1**.

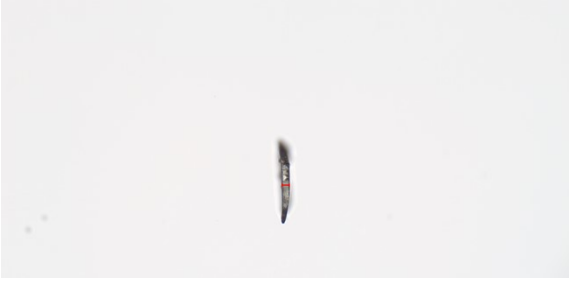

Fig. S5 The crystal thickness of **1**.

Table S1. Crystal Data and Structural Refinement for $C_{10}H_6NO_2Cd(NO_3)\cdot 2H_2O$.

Empirical formula	$C_{10}H_{10}CdN_2O_7$
Formula weight	382.60
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.9513(6)
b/Å	8.1881(3)
c/Å	13.4580(8)
α/°	90
β/°	114.729(7)
γ/°	90
Volume/Å^3	1196.21(12)
Z	4
ρ_{calc}g/cm^3	2.124
μ/mm^{-1}	1.862
F(000)	752.0
Crystal size/mm^3	0.06 × 0.03 × 0.03
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.836 to 54.28
Index ranges	$-14 \le h \le 15$, $-10 \le k \le 6$, $-16 \le l \le 16$
Reflections collected	9890
Independent reflections	2491 [R_{int} = 0.0533, R_{sigma} = 0.0524]
Data/restraints/parameters	2491/14/193
Goodness-of-fit on F^2	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0344, wR_2 = 0.0637
Final R indexes [all data]	R_1 = 0.0465, wR_2 = 0.0675

Table S2. The Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for $C_{10}H_6NO_2Cd(NO_3)\cdot 2H_2O$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)	BVS
Cd1	6860.5(2)	1063.7(3)	2603.4(2)	24.47(11)	2.058
O1	7514(2)	-557(3)	4396(2)	37.9(7)	
O2	9013(3)	165(5)	5896(3)	87.4(12)	
O3	8549(2)	1613(3)	4448(2)	43.0(7)	
O4	6395(2)	6246(3)	2982(2)	30.7(6)	
O5	6963(2)	3889(3)	2589(2)	30.9(6)	
O6	5870(2)	1716(3)	604(2)	36.1(6)	
O7	5328(2)	-925(3)	1838(2)	32.4(6)	
N1	8375(3)	403(4)	4935(3)	36.5(8)	
N2	5513(2)	2219(3)	3246(2)	22.9(7)	
C1	5376(3)	3832(4)	3228(3)	19.4(7)	
C2	4473(3)	4596(4)	3505(3)	20.8(7)	
C3	4243(3)	6289(4)	3458(3)	31.7(9)	
C4	3341(3)	6907(5)	3723(3)	36.3(9)	
C5	2630(4)	5870(5)	4045(3)	39.7(11)	
C6	2816(3)	4244(5)	4108(3)	35.1(10)	
C7	3742(3)	3559(4)	3840(3)	25.3(8)	
C8	3952(3)	1869(5)	3885(3)	32.1(9)	
C9	4806(3)	1257(4)	3582(3)	31.1(9)	
C10	6287(3)	4731(4)	2908(3)	21.7(8)	

Table S3. Anisotropic Displacement Parameters ($Å^2×10^3$) for $C_{10}H_6NO_2Cd(NO_3)·2H_2O$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cd1	26.14(17)	20.66(16)	31.75(18)	-2.04(11)	17.16(13)	1.29(11)
O1	40.6(16)	32.9(15)	40.4(16)	-3.7(13)	17.3(14)	-5.8(13)
O2	98(3)	94(3)	31.6(19)	5(2)	-10.8(19)	3(2)
O3	40.8(16)	41.6(17)	42.8(13)	-1.9(14)	13.7(10)	-8.4(15)
O4	36.0(15)	18.5(13)	43.3(16)	1.8(11)	22.2(13)	-5.2(12)
O5	31.8(15)	26.4(15)	46.3(17)	0.1(12)	28.1(14)	-1.7(11)
O6	37.2(16)	31.5(16)	44.2(16)	3.7(14)	21.6(13)	-1.8(14)
O7	33.9(15)	23.3(14)	39.9(16)	-0.2(12)	15.4(13)	-0.8(12)
N1	40(2)	36(2)	31(2)	-5.0(17)	13.4(17)	6.7(18)
N2	26.2(16)	18.1(15)	29.6(17)	-3.6(13)	16.8(14)	-3.8(13)
C1	24.5(18)	15.8(17)	20.3(18)	-0.7(14)	11.6(15)	-3.7(15)
C2	22.6(18)	20.9(18)	18.8(18)	-0.9(15)	8.6(15)	2.5(16)
C3	35(2)	26(2)	40(2)	0.9(17)	21.4(19)	-2.6(18)
C4	36(2)	30(2)	43(2)	-2(2)	16(2)	12(2)
C5	31(2)	50(3)	45(3)	-10(2)	22(2)	7(2)
C6	30(2)	47(3)	37(2)	-3.9(19)	22.3(19)	-1.7(19)
C7	24.6(19)	28(2)	26(2)	-1.8(16)	13.0(16)	1.0(16)
C8	37(2)	26(2)	43(2)	-1.2(19)	26(2)	-8.4(19)
C9	40(2)	20.7(19)	41(2)	-3.8(16)	25(2)	-7.4(17)
C10	20.5(18)	21.8(19)	21.5(19)	4.6(15)	7.4(15)	-1.7(16)

Table S4. Bond Lengths for $C_{10}H_6NO_2Cd(NO_3)\cdot 2H_2O$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cd1	O1	2.572(3)	N2	C1	1.329(4)
Cd1	O3	2.499(3)	N2	C9	1.364(4)
Cd1	O4[1]	2.523(2)	C1	C2	1.425(4)
Cd1	O5[1]	2.349(2)	C1	C10	1.518(4)
Cd1	O5	2.317(2)	C2	C3	1.409(4)
Cd1	O6	2.502(3)	C2	C7	1.419(4)
Cd1	O7	2.343(2)	C3	C4	1.365(5)
Cd1	N2	2.324(3)	C4	C5	1.393(5)
O1	N1	1.256(4)	C5	C6	1.346(5)
O2	N1	1.212(4)	C6	C7	1.416(4)
O3	N1	1.252(4)	C7	C8	1.403(5)
O4	C10	1.247(4)	C8	C9	1.344(5)
O5	C10	1.267(4)			

[(1)]3/2-X,-1/2+Y,1/2-Z

Table S5. Bond Angles for $C_{10}H_6NO_2Cd(NO_3)\cdot 2H_2O$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O3	Cd1	O1	50.13(8)	N1	O3	Cd1	97.8(2)
O3	Cd1	O4[1]	82.55(8)	C10	O4	Cd1[2]	89.3(2)
O3	Cd1	O6	148.43(9)	Cd1	O5	Cd1[2]	142.54(10)
O4[1]	Cd1	O1	110.95(8)	C10	O5	Cd1	119.8(2)
O5	Cd1	O1	121.78(8)	C10	O5	Cd1[2]	96.98(19)
O5[1]	Cd1	O1	75.61(8)	O2	N1	O1	120.9(4)
O5[1]	Cd1	O3	88.51(9)	O2	N1	O3	121.2(4)
O5	Cd1	O3	78.76(9)	O3	N1	O1	118.0(3)
O5[1]	Cd1	O4[1]	53.10(7)	C1	N2	Cd1	119.8(2)
O5	Cd1	O4[1]	83.38(7)	C1	N2	C9	119.4(3)
O5	Cd1	O5[1]	136.02(4)	C9	N2	Cd1	120.7(2)
O5[1]	Cd1	O6	94.54(8)	N2	C1	C2	122.2(3)
O5	Cd1	O6	77.34(9)	N2	C1	C10	112.9(3)
O5	Cd1	O7	136.43(8)	C2	C1	C10	124.9(3)
O5	Cd1	N2	69.14(8)	C3	C2	C1	125.1(3)
O6	Cd1	O1	160.07(8)	C3	C2	C7	117.9(3)
O6	Cd1	O4[1]	74.49(8)	C7	C2	C1	117.0(3)
O7	Cd1	O1	85.90(9)	C4	C3	C2	120.9(3)
O7	Cd1	O3	136.03(9)	C3	C4	C5	120.4(4)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O7	Cd1	O4[1]	120.00(8)	C6	C5	C4	121.1(4)
O7	Cd1	O5[1]	79.55(8)	C5	C6	C7	120.1(4)
O7	Cd1	O6	75.18(9)	C6	C7	C2	119.6(3)
N2	Cd1	O1	81.19(9)	C8	C7	C2	118.8(3)
N2	Cd1	O3	87.40(9)	C8	C7	C6	121.6(3)
N2	Cd1	O4[1]	152.12(8)	C9	C8	C7	119.9(3)
N2	Cd1	O5[1]	152.80(9)	C8	C9	N2	122.7(3)
N2	Cd1	O6	102.88(9)	O4	C10	O5	120.6(3)
N2	Cd1	O7	84.86(9)	O4	C10	C1	121.5(3)
N1	O1	Cd1	94.1(2)	O5	C10	C1	117.9(3)

[(1)]3/2-X,-1/2+Y,1/2-Z; [(2)]3/2-X,1/2+Y,1/2-Z

Table S6. Hydrogen Bonds for $C_{10}H_6NO_2Cd(NO_3)\cdot 2H_2O$.

D	H	A	d(D−H)/Å	d(H−A)/Å	d(D−A)/Å	D−H−A/
O6	H6A	O3	0.820(18)	2.17(2)	2.894(4)	147(3)
O7	H7A	O4	0.888(9)	1.918(13)	2.778(3)	163(3)
C3	H3	O4	0.93	2.27	2.900(4)	124.7

[(1)]-1/2+X,1/2-Y,-1/2+Z; [(2)]+X,-1+Y,+Z

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