

Electronic Supporting Information

Dual-tuning birefringence in hybrid crystals via Cd/Zn metal centers and organic ligand isomerism

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Reagents

C₉H₆BrN (95%), C₉H₆BrN (97%), ZnF₂ (99%), CdCO₃ (97%) and HCl (36%~38%) were purchased from Aladdin and used as received.

Synthesis of (C₉H₇NBr)CdCl₃·H₂O (named **4CdCl**), (C₉H₇NBr)₂ZnCl₄ (named **4ZnCl**) and (C₉H₇NBr)₂CdCl₄ (named **8CdCl**).

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 K α radiation) in the range of $2\theta = 7^\circ - 70^\circ$ with a step width of 0.01° and a sampling rate of 5° min^{-1} . The results agree well with the calculated XRD patterns from single-crystal XRD analyses (Figure S6).

Single-Crystal Structure Determination

Transparent crystal **4CdCl** ($0.05 \times 0.04 \times 0.04 \text{ mm}^3$), transparent crystal **4ZnCl** ($0.09 \times 0.07 \times 0.04 \text{ mm}^3$), transparent crystal **8CdCl** ($0.04 \times 0.02 \times 0.03 \text{ mm}^3$) and was selected using an optical microscope for single-crystal XRD analysis. The diffraction data were collected by using graphite-monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 297 (10) K on an Agilent SuperNova Dual diffractometer with an Atlas detector. The collection of the intensity data, cell refinement, and data reduction were carried out with the program CrysAlisPro.¹ Using Olex2,² the structure was solved with the olex2.solve³ structure solution program using Charge Flipping and refined with the SHELXL⁴ 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 Table S4–S5. Torsion Angles in Table S7. The hydrogen atom and isotropic displacement parameters in Table S8. Birefringent crystal statistical chart crystal size in Table S8.

Thermal Stability Analysis

The thermogravimetric (TG) was carried out on a NETZSCH TG 209 F3 simultaneous analyzer. Approximately 10.8173 mg of **4CdCl**, 5.9299 mg of **4ZnCl** and 9.3524 mg of **8CdCl** were loaded into Al₂O₃ crucibles and heated from room temperature to 300 °C at a rate of 10 °C min⁻¹ under a flowing nitrogen atmosphere.

UV-Vis-NIR Diffuse Reflectance Spectroscopy

UV Vis NIR diffuse reflectance spectra were recorded on a PerkinElmer Lambda-1050 UV-Vis-NIR spectrophotometer. Measurements were performed from 220 to 800 nm using a certified white standard as the 100% reflectance reference. The reflectance data were converted to the absorption coefficient via the Kubelka–Munk function: $F(R) = (1 - R)^2/2R$,⁵ where R represents the measured reflectance.

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. At a mass ratio of 1:100 with dried KBr, samples of **4CdCl**, **4ZnCl** and **8CdCl** were separately processed. Each was ground thoroughly in an agate mortar and pressed into a thin pellet for subsequent measurement.

Computational Methods

The first-principles calculations for **4CdCl**, **4ZnCl** and **8CdCl** were performed by CASTEP⁶ on a plane-wave pseudopotential total energy package based density functional theory (DFT).⁷ The functional developed by Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA)⁸⁻⁹ 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. H 1s¹, C 2s²2p², N 2s²2p³, O 2s²2p⁴, Cl 3s²3p⁵, Zn 4s²3d¹⁰, Cd 5s²5p²4d¹⁰, and Br 4s²4p⁵ electrons were treated as valence electrons. Substance **4CdCl** selected a kinetic energy cutoff of 571.40 eV and a dense grid of 2 × 1 × 2 Monkhorst-Pack¹⁰ k-point meshes in the Brillouin zones were chosen. **4ZnCl** selected a kinetic energy cutoff of 517 eV and a dense grid of 1 × 2 × 2 Monkhorst-Pack¹⁰ k-point meshes in the Brillouin zones were chosen. Substance **8CdCl** selected a kinetic energy cutoff of 435.40 eV and a dense grid of 1 × 2 × 1 Monkhorst-Pack¹⁰ k-point meshes in the Brillouin zones were chosen. The linear optical properties were examined based on the dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$. 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 indices were calculated to demonstrate the validity of birefringence measurements.

The polarizability anisotropy was defined using the static polarizability. To explore the polarizability anisotropy and electronic structure of the [C₉H₇NBr]⁺ (4-bromoquinoline) and [C₉H₇NBr]⁺ (8-bromoquinoline) groups, the Gaussian 09 package¹⁰ was used for conducting systematic calculations, employing the hybrid B3LYP functional at the 6-31G (d, p) level. The computational results were analyzed using the Multiwfn 3.8 software.¹¹ The polarizability anisotropy was defined using the static polarizability according to the equation $\delta = \frac{\alpha_{max} - \alpha_{min}}{\alpha_{max} + \alpha_{min}}$, where α represents the static polarizability, and δ is the polarizability anisotropy.¹²⁻¹³

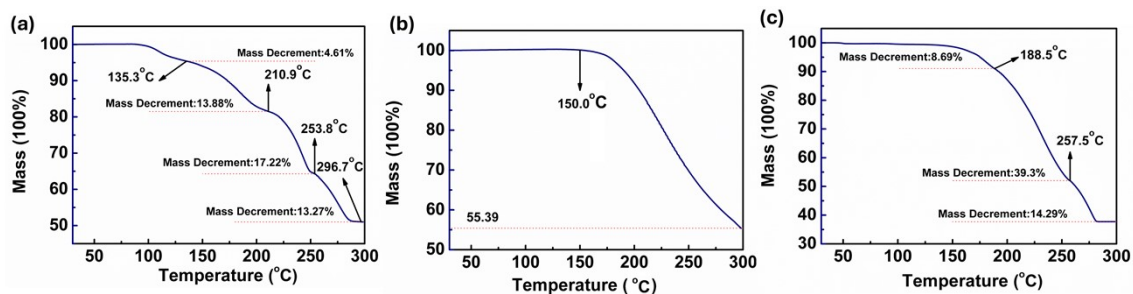


Fig. S1. Thermal stability analysis of (a) 4CdCl, (b) 4ZnCl and (c) 8CdCl.

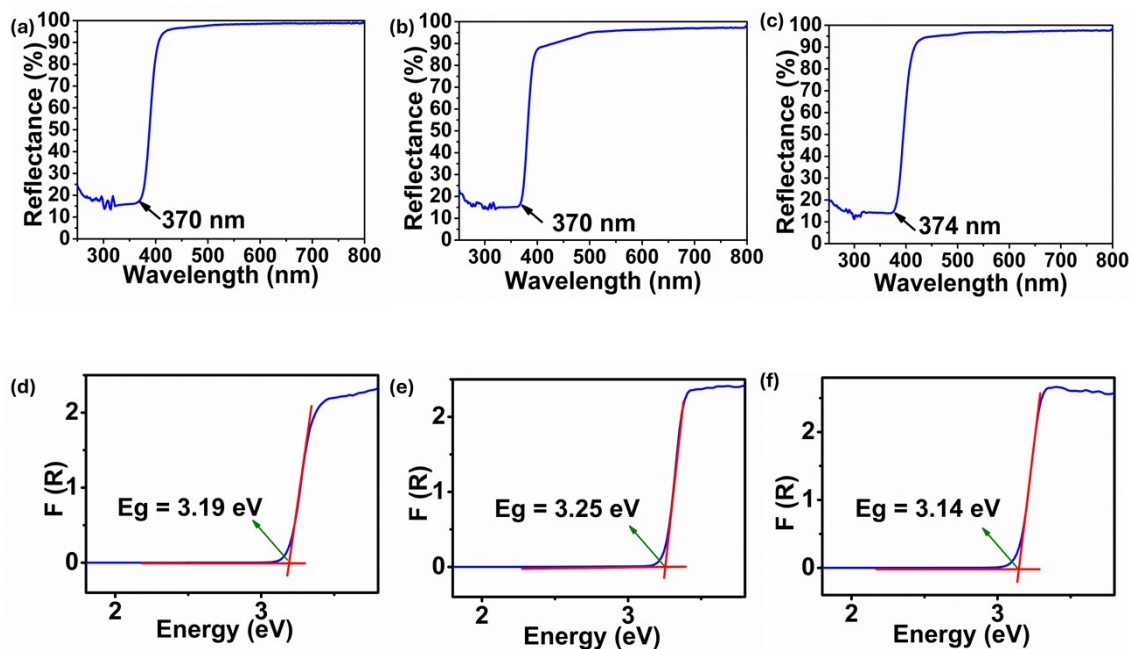


Fig. S2. The UV-vis-NIR diffuse reflectance spectrum of (a) (d) 4CdCl, (b) (e) 4ZnCl, and (c) (f) 8CdCl.

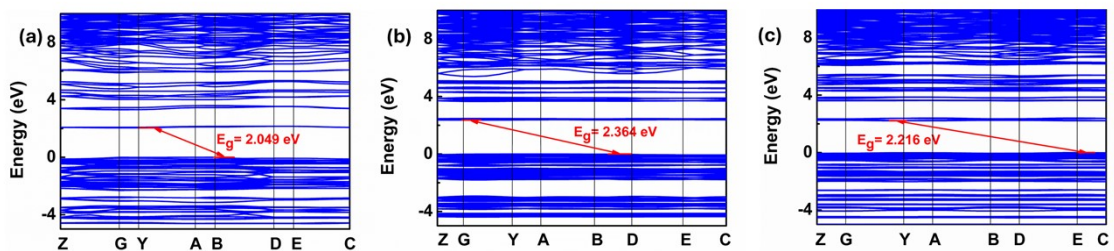


Fig. S3. Electronic band structure of (a) 4CdCl, (b) 4ZnCl, and (c) 8CdCl.

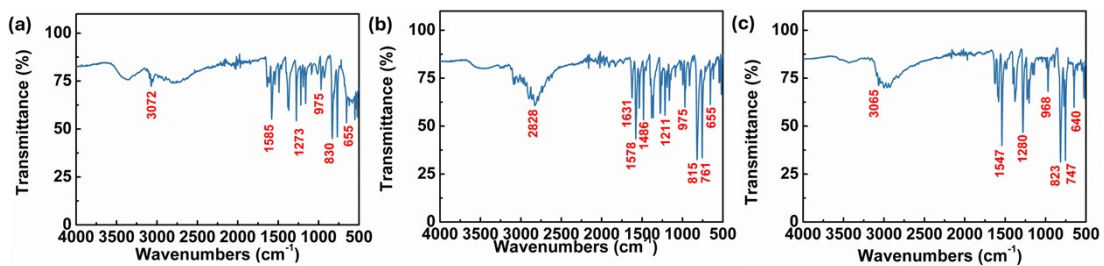


Fig. S4. Infrared spectrum of (a) 4CdCl, (b) 4ZnCl, and (c) 8CdCl.

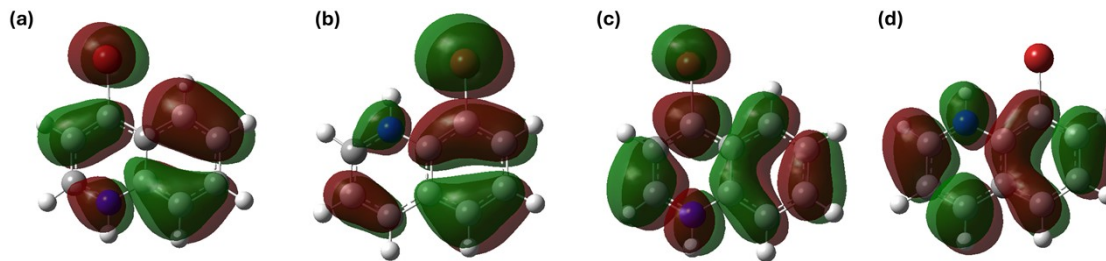


Fig. S5. The HOMO diagram of protonated (a) 4-bromoquinoline, (b) 8-bromoquinoline. The LUMO diagram of protonated (c) 4-Bromoquinoline, (d) 8-Bromoquinoline.

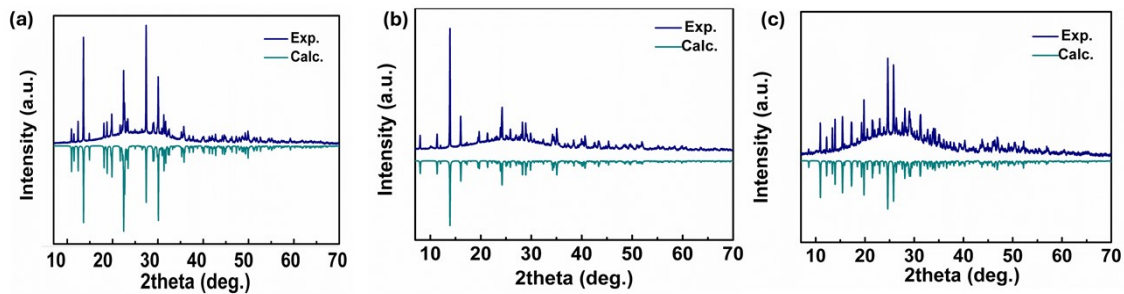


Fig. S6. Experimental XRD patterns of (a) 4CdCl, (b) 4ZnCl and (c) 8CdCl.

Table S1. Crystal Data and Structural Refinement for 4CdCl, 4ZnCl and 8CdCl.

4CdCl	
Empirical formula	(C ₉ H ₇ NBr)CdCl ₃ ·H ₂ O
Formula weight	445.83
Temperature/K	293(2)
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	7.8674(4)
<i>b</i> /Å	22.0685(12)
<i>c</i> /Å	7.5146(4)
α /°	90
β /°	98.071(5)
γ /°	90
Volume/Å ³	1291.77(12)
<i>Z</i>	4
ρ_{calc} g/cm ³	2.292
μ /mm ⁻¹	5.380
F(000)	848.0
Crystal size/mm ³	0.05 × 0.04 × 0.04
Radiation	Mo K α (λ = 0.71073)
2 Θ range for data collection/°	3.692 to 54.272
Index ranges	-9 ≤ <i>h</i> ≤ 9, -19 ≤ <i>k</i> ≤ 27, -9 ≤ <i>l</i> ≤ 8
Reflections collected	9944
Independent reflections	2665 [<i>R</i> _{int} = 0.0556, <i>R</i> _{sigma} = 0.0580]
Data/restraints/parameters	2665/1/148
Goodness-of-fit on F ²	1.065
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0411, <i>wR</i> ₂ = 0.0941
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0555, <i>wR</i> ₂ = 0.1021
4ZnCl	
Empirical formula	(C ₉ H ₇ NBr) ₂ ZnCl ₄
Formula weight	625.338
Temperature/K	298
Crystal system	monoclinic
Space group	<i>I</i> 2/ <i>a</i>
<i>a</i> /Å	17.8207(14)
<i>b</i> /Å	9.5169(5)
<i>c</i> /Å	15.2828(13)
α /°	90

$\beta/^\circ$	121.725(12)
$\gamma/^\circ$	90
Volume/ \AA^3	2204.6(4)
Z	4
$\rho_{\text{calc}} \text{ g/cm}^3$	1.884
μ/mm^{-1}	5.230
F(000)	1218.6
Crystal size/ mm^3	$0.09 \times 0.07 \times 0.04$
Radiation	Mo K α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	5.06 to 54.16
Index ranges	$-22 \leq h \leq 22, -9 \leq k \leq 12, -19 \leq l \leq 18$
Reflections collected	10764
Independent reflections	2312 [$R_{\text{int}} = 0.0273, R_{\text{sigma}} = 0.0285$]
Data/restraints/parameters	2312/0/123
Goodness-of-fit on F^2	1.006
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0324, wR_2 = 0.0755$
Final R indexes [all data]	$R_1 = 0.0453, wR_2 = 0.0800$

8CdCl

Empirical formula	$(\text{C}_9\text{H}_7\text{NBr})_2\text{CdCl}_4$
Formula weight	672.33
Temperature/K	303
Crystal system	monoclinic
Space group	$P2_1/n$
a/ \AA	16.6604(6)
b/ \AA	8.0767(3)
c/ \AA	16.8133(7)
$\alpha/^\circ$	90
$\beta/^\circ$	104.304(4)
$\gamma/^\circ$	90
Volume/ \AA^3	2192.28(15)
Z	4
$\rho_{\text{calc}} \text{ g/cm}^3$	2.037
μ/mm^{-1}	5.136
F(000)	1288.0
Crystal size/ mm^3	$0.04 \times 0.02 \times 0.03$
Radiation	Mo K α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	3.966 to 53.934
Index ranges	$-21 \leq h \leq 20, -7 \leq k \leq 10, -14 \leq l \leq 21$

Reflections collected	11328
Independent reflections	4483 [$R_{\text{int}} = 0.0210$, $R_{\text{sigma}} = 0.0387$]
Data/restraints/parameters	4483/0/244
Goodness-of-fit on F^2	1.050
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0318$, $wR_2 = 0.0542$
Final R indexes [all data]	$R_1 = 0.0501$, $wR_2 = 0.0577$

Table S2. The Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 4CdCl, 4ZnCl and 8CdCl. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

4CdCl				
Atom	x	y	z	U(eq)
Cd1	4558.4(5)	5054.1(2)	2447.8(4)	26.92(15)
Cl1	1427.4(17)	5356.4(6)	2314.4(19)	44.3(4)
Cl2	5664.4(17)	5773.7(5)	5116.7(15)	30.3(3)
Cl3	5600.4(19)	5761.9(6)	86.3(15)	35.4(3)
Br1	12022.5(7)	1891.6(2)	1002.2(7)	37.71(18)
N1	9092(6)	3633.3(18)	1918(5)	36.0(11)
C1	8305(6)	3096(2)	2270(6)	28.5(12)
C2	6702(7)	3097(3)	2880(6)	36.2(13)
C3	6008(6)	2557(2)	3163(7)	33.0(13)
C4	6761(7)	2014(3)	2900(7)	39.7(14)
C5	8320(6)	2004(2)	2296(6)	29.9(12)
C6	9166(6)	2554(2)	1948(6)	24.7(11)
C7	10782(6)	2603(2)	1361(6)	25.5(11)
C8	11480(7)	3150(2)	1049(7)	33.0(12)
C9	10586(7)	3664(2)	1349(6)	34.2(13)
O1	7833(5)	4726.9(16)	3135(5)	38.3(9)

4ZnCl				
Atom	x	y	z	U(eq)
Br1	6135.5(2)	-123.3(3)	3971.1(3)	54.54(14)
N1	4639.1(15)	2978(3)	4821.3(18)	47.9(6)
C1	5387.8(19)	2361(3)	5620(2)	43.6(7)
C2	5651(2)	2674(4)	6636(2)	56.9(8)
C3	6366(2)	1997(4)	7404(2)	65.7(10)
C4	6836(2)	1036(4)	7203(3)	62.5(9)
C5	6601(2)	732(3)	6219(2)	51.3(8)
C6	5855.0(17)	1396(3)	5385(2)	38.8(6)
C7	5531.8(18)	1144(3)	4332(2)	41.5(7)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
C8	4782.2(18)	1773(3)	3573(2)	44.2(7)
C9	4341(2)	2700(4)	3846(2)	51.1(8)
Zn1	7500	6098.9(4)	5000	35.15(14)
Cl1	6289.5(6)	4757.8(9)	4545.3(8)	68.3(3)
Cl2	7707.4(5)	7409.1(7)	6337.5(5)	45.0(2)

8CdCl

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
Cd1	4996.8(2)	6607.3(3)	2877.2(2)	35.26(8)
Cl1	5324.7(5)	7166.9(10)	4370.9(5)	46.0(2)
Cl2	3956.3(5)	4333.9(9)	2685.6(5)	42.1(2)
Cl3	4370.4(5)	8917.4(10)	2009.2(5)	48.8(2)
Cl4	6274.6(5)	5778.3(11)	2509.2(5)	52.1(2)
Br1	-9.3(2)	8527.0(4)	4007.0(2)	45.52(11)
N1	1676.2(13)	7012(3)	3873.6(14)	30.4(6)
C1	2348.4(19)	6441(4)	3678(2)	40.6(8)
C2	2912.1(19)	5500(4)	4217(2)	44.0(9)
C3	2769.6(18)	5136(4)	4965(2)	43.3(9)
C4	2046.5(17)	5699(3)	5176.2(19)	32.6(7)
C5	1862.5(19)	5321(4)	5926(2)	44.1(9)
C6	1153(2)	5874(4)	6092(2)	49.9(9)
C7	593.9(19)	6834(4)	5513(2)	45.1(9)
C8	751.3(17)	7238(4)	4786.2(18)	33.7(7)
C9	1483.6(16)	6660(3)	4599.1(17)	26.4(7)
Br2	3507.7(2)	10042.6(4)	3522.5(2)	46.95(11)
N2	4054.2(13)	8679(3)	5293.5(15)	33.9(6)
C10	4414(2)	8001(4)	6016(2)	43.9(9)
C11	4062(2)	8170(4)	6667(2)	56.6(10)
C12	3326(2)	9007(4)	6562(2)	54.2(9)
C13	2947.9(19)	9739(4)	5805(2)	37.9(8)
C14	2193(2)	10616(4)	5673(2)	51.2(9)
C15	1866(2)	11298(4)	4925(3)	52.6(10)
C16	2255.4(18)	11149(4)	4275(2)	41.9(8)
C17	2983.1(17)	10292(3)	4394.0(18)	32.6(7)
C18	3335.8(17)	9571(3)	5154.9(19)	30.0(7)

Table S3. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 4CdCl, 4ZnCl and 8CdCl. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

4CdCl						
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cd1	36.2(3)	24.0(3)	22.3(2)	-0.08(14)	9.92(16)	-1.29(16)
Cl1	32.2(8)	39.6(9)	60.4(9)	4.0(7)	4.6(6)	0.4(6)
Cl2	43.5(8)	20.6(7)	28.2(6)	-0.4(5)	9.7(5)	-5.4(6)
Cl3	56.3(9)	23.0(7)	30.0(7)	-2.9(5)	16.5(6)	-9.0(6)
Br1	33.9(3)	35.3(4)	43.9(3)	-5.4(2)	5.1(2)	10.9(2)
N1	43(3)	23(2)	41(3)	0(2)	2(2)	10(2)
C1	30(3)	27(3)	29(3)	-1(2)	4(2)	4(2)
C2	33(3)	47(4)	30(3)	-6(2)	6(2)	9(3)
C3	19(3)	51(4)	28(3)	-2(3)	2(2)	-4(3)
C4	43(3)	49(4)	27(3)	7(3)	6(2)	-18(3)
C5	33(3)	24(3)	32(3)	0(2)	0(2)	-6(2)
C6	29(3)	23(3)	21(2)	-0.2(19)	1(2)	1(2)
C7	27(3)	28(3)	22(3)	-4(2)	3(2)	2(2)
C8	30(3)	29(3)	41(3)	-3(2)	8(2)	-4(2)
C9	39(3)	26(3)	39(3)	3(2)	9(3)	-7(2)
O1	38(2)	34(2)	45(2)	-2.7(18)	13.1(18)	-4.2(18)

4ZnCl						
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	54.1(2)	53.6(2)	63.6(2)	5.40(14)	36.20(19)	-1.60(15)
N1	34.3(13)	65.8(17)	50.6(15)	3.2(12)	27.2(12)	-3.0(13)
C1	37.3(16)	52.4(18)	45.1(16)	-7.8(13)	24.3(14)	1.7(14)
C2	56(2)	69(2)	52.9(19)	-8.8(17)	33.7(17)	-3.3(17)
C3	71(2)	83(3)	40.7(18)	-17(2)	27.3(18)	1.5(18)
C4	62(2)	60(2)	49(2)	-5.6(18)	17.4(17)	13.9(16)
C5	47.4(18)	44.4(18)	55.2(19)	-0.5(15)	22.3(16)	6.4(14)
C6	35.3(15)	37.5(15)	44.9(16)	-8.8(12)	22.0(13)	2.4(12)
C7	37.8(16)	44.0(16)	52.0(17)	-5.6(13)	30.0(14)	-1.3(13)
C8	34.3(15)	57.7(18)	39.7(15)	1.1(14)	18.9(13)	1.5(14)
C9	32.8(16)	71(2)	46.4(17)	4.6(15)	19.1(13)	4.4(16)
Zn1	31.6(2)	37.4(3)	41.3(3)	-0	22.4(2)	0
Cl1	62.0(6)	61.8(5)	107.9(8)	-28.8(4)	63.2(6)	-36.1(5)
Cl2	49.8(4)	50.6(4)	32.1(3)	-0.6(3)	19.8(3)	-1.2(3)

8CdCl						
Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Cd1	31.90(13)	37.40(15)	36.06(15)	3.48(11)	7.58(10)	3.16(10)
Cl1	38.7(4)	58.5(5)	38.2(5)	-6.4(4)	4.7(4)	10.1(4)
Cl2	43.2(5)	45.9(5)	38.4(5)	-4.2(4)	12.3(4)	-8.7(4)
Cl3	52.2(5)	47.8(5)	48.7(6)	16.6(4)	16.7(4)	15.3(4)
Cl4	34.9(4)	70.1(6)	53.3(6)	3.9(5)	14.7(4)	9.9(4)
Br1	34.73(18)	60.6(2)	41.6(2)	8.48(17)	10.05(15)	14.48(15)
N1	28.5(13)	31.0(14)	32.1(15)	-5.0(12)	8.1(11)	-2.5(11)
C1	40.6(19)	42(2)	44(2)	-14.2(17)	20.6(17)	-9.4(16)
C2	34.7(18)	40(2)	65(3)	-11.8(19)	26.1(18)	4.0(15)
C3	34.2(18)	36(2)	56(2)	-5.3(17)	2.8(17)	2.6(15)
C4	29.1(16)	31.7(18)	36(2)	-4.2(15)	5.8(15)	3.2(14)
C5	43(2)	46(2)	40(2)	9.0(17)	2.6(17)	8.6(16)
C6	60(2)	60(2)	33(2)	11.3(18)	17.3(18)	13.8(19)
C7	42.8(19)	57(2)	40(2)	2.7(18)	18.2(17)	10.8(16)
C8	30.6(16)	39.0(18)	30.6(19)	-0.6(15)	5.6(14)	3.7(14)
C9	28.0(15)	25.8(16)	26.2(17)	-4.7(14)	8.4(13)	-4.2(13)
Br2	41.48(19)	59.5(2)	40.0(2)	13.43(17)	10.38(16)	0.56(16)
N2	31.7(14)	39.0(16)	31.1(16)	0.9(12)	8.0(12)	-1.2(12)
C10	38.3(19)	40(2)	48(2)	8.0(17)	0.0(18)	-2.8(15)
C11	72(3)	61(3)	31(2)	13.1(18)	2(2)	-3(2)
C12	63(2)	63(2)	42(2)	-2(2)	23.2(19)	-6(2)
C13	37.4(18)	38.9(19)	39(2)	-5.8(16)	12.2(16)	-3.9(15)
C14	45(2)	55(2)	61(3)	-12(2)	26.1(19)	1.8(18)
C15	33.5(19)	47(2)	77(3)	-11(2)	12(2)	8.1(16)
C16	33.4(18)	36.7(19)	47(2)	-1.1(16)	-5.3(16)	1.9(15)
C17	26.9(16)	31.4(17)	38(2)	-0.8(15)	4.7(14)	-4.6(13)
C18	24.4(15)	27.1(17)	37(2)	-0.3(15)	4.6(14)	-5.2(13)

Table S4. Bond Lengths for 4CdCl, 4ZnCl and 8CdCl.

4CdCl					
Atom Atom Length/Å			Atom Atom Length/Å		
Cd1	Cl1	2.5403(14)	C1	C6	1.411(6)
Cd1	Cl2	2.6098(12)	C2	C3	1.338(7)
Cd1	Cl2 ¹	2.6091(12)	C3	C4	1.365(7)
Cd1	Cl3	2.5826(13)	C4	C5	1.366(7)
Cd1	Cl3 ²	2.6112(12)	C5	C6	1.427(6)
Br1	C7	1.888(5)	C6	C7	1.407(7)

Atom Atom Length/Å			Atom Atom Length/Å		
N1	C1	1.380(6)	C7	C8	1.360(6)
N1	C9	1.308(6)	C8	C9	1.370(7)
C1	C2	1.401(7)			

¹1-X,1-Y,1-Z; ²1-X,1-Y,-Z

4ZnCl

Atom Atom Length/Å			Atom Atom Length/Å		
Br1	C7	1.882(3)	C5	C6	1.417(4)
N1	C1	1.379(4)	C6	C7	1.416(4)
N1	C9	1.319(4)	C7	C8	1.363(4)
C1	C2	1.398(4)	C8	C9	1.386(4)
C1	C6	1.407(4)	Zn1	Cl1 ¹	2.2779(8)
C2	C3	1.358(5)	Zn1	Cl1	2.2779(8)
C3	C4	1.380(5)	Zn1	Cl2 ¹	2.2528(7)
C4	C5	1.362(5)	Zn1	Cl2	2.2528(7)

¹3/2-X,+Y,1-Z

8CdCl

Atom Atom Length/Å			Atom Atom Length/Å		
Cd1	Cl1	2.4763(8)	C7	C8	1.352(4)
Cd1	Cl2	2.4908(8)	C8	C9	1.412(4)
Cd1	Cl3	2.4388(8)	Br2	C17	1.893(3)
Cd1	Cl4	2.4524(8)	N2	C10	1.332(4)
Br1	C8	1.894(3)	N2	C18	1.367(3)
N1	C1	1.326(3)	C10	C11	1.370(5)
N1	C9	1.366(3)	C11	C12	1.373(5)
C1	C2	1.364(4)	C12	C13	1.403(4)
C2	C3	1.368(4)	C13	C14	1.412(4)
C3	C4	1.413(4)	C13	C18	1.408(4)
C4	C5	1.402(4)	C14	C15	1.358(4)
C4	C9	1.405(4)	C15	C16	1.405(5)
C5	C6	1.356(4)	C16	C17	1.367(4)
C6	C7	1.402(4)	C17	C18	1.396(4)

Table S5. Bond Angles for 4CdCl, 4ZnCl and 8CdCl.

4CdCl						
Atom Atom Atom Angle/°			Atom Atom Atom Angle/°			
Cl1	Cd1	Cl2 ¹	92.94(4)	N1	C1 C6	117.1(5)

Atom Atom Atom Angle/°				Atom Atom Atom Angle/°			
C11	Cd1	Cl2	95.01(5)	C2	C1	C6	122.2(5)
C11	Cd1	Cl3 ²	101.86(5)	C3	C2	C1	117.2(5)
C11	Cd1	Cl3	102.34(5)	C2	C3	C4	124.3(5)
Cl2 ¹	Cd1	Cl2	86.27(4)	C3	C4	C5	119.3(5)
Cl2 ¹	Cd1	Cl3 ²	91.58(4)	C4	C5	C6	120.7(5)
Cl2	Cd1	Cl3 ²	163.08(5)	C1	C6	C5	116.2(5)
Cl3	Cd1	Cl2	93.22(4)	C7	C6	C1	117.7(4)
Cl3	Cd1	Cl2 ¹	164.70(5)	C7	C6	C5	126.0(4)
Cl3	Cd1	Cl3 ²	84.46(4)	C6	C7	Br1	119.3(4)
Cd1 ¹	Cl2	Cd1	93.73(4)	C8	C7	Br1	119.0(4)
Cd1	Cl3	Cd1 ²	95.55(4)	C8	C7	C6	121.8(5)
C9	N1	C1	123.7(4)	C7	C8	C9	118.5(5)
N1	C1	C2	120.7(5)	N1	C9	C8	121.1(5)

¹1-X,1-Y,1-Z; ²1-X,1-Y,-Z

4ZnCl

Atom Atom Atom Angle/°				Atom Atom Atom Angle/°			
C9	N1	C1	122.8(3)	C6	C7	Br1	119.2(2)
C2	C1	N1	119.7(3)	C8	C7	Br1	119.1(2)
C6	C1	N1	118.7(2)	C8	C7	C6	121.6(3)
C6	C1	C2	121.6(3)	C9	C8	C7	118.7(3)
C3	C2	C1	118.3(3)	C8	C9	N1	120.8(3)
C4	C3	C2	121.7(3)	Cl1 ¹	Zn1	Cl1	111.85(5)
C5	C4	C3	121.1(3)	Cl2	Zn1	Cl1 ¹	110.86(3)
C6	C5	C4	119.8(3)	Cl2 ¹	Zn1	Cl1	110.86(3)
C5	C6	C1	117.6(3)	Cl2	Zn1	Cl1	105.32(3)
C7	C6	C1	117.3(3)	Cl2 ¹	Zn1	Cl1 ¹	105.32(3)
C7	C6	C5	125.1(3)	Cl2	Zn1	Cl2 ¹	112.78(4)

³2-X,+Y,1-Z

8CdCl

Atom Atom Atom Angle/°				Atom Atom Atom Angle/°			
Cl1	Cd1	Cl2	103.76(3)	N1	C9	C4	117.9(3)
Cl3	Cd1	Cl1	114.95(3)	N1	C9	C8	122.4(3)
Cl3	Cd1	Cl2	107.78(3)	C4	C9	C8	119.7(3)
Cl3	Cd1	Cl4	109.13(3)	C10	N2	C18	123.3(3)
Cl4	Cd1	Cl1	108.54(3)	N2	C10	C11	120.2(3)
Cl4	Cd1	Cl2	112.70(3)	C10	C11	C12	119.4(3)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	C9	123.3(3)	C11	C12	C13	120.8(3)
N1	C1	C2	120.9(3)	C12	C13	C14	122.5(3)
C1	C2	C3	118.9(3)	C12	C13	C18	118.3(3)
C2	C3	C4	121.0(3)	C18	C13	C14	119.2(3)
C5	C4	C3	123.0(3)	C15	C14	C13	119.1(3)
C5	C4	C9	119.0(3)	C14	C15	C16	121.9(3)
C9	C4	C3	118.0(3)	C17	C16	C15	119.5(3)
C6	C5	C4	120.5(3)	C16	C17	Br2	120.2(2)
C5	C6	C7	120.2(3)	C16	C17	C18	120.1(3)
C8	C7	C6	121.1(3)	C18	C17	Br2	119.6(2)
C7	C8	Br1	120.8(2)	N2	C18	C13	118.0(3)
C7	C8	C9	119.5(3)	N2	C18	C17	121.9(3)
C9	C8	Br1	119.7(2)	C17	C18	C13	120.1(3)

Table S6. Torsion Angles for 4CdCl, 4ZnCl and 8CdCl.

4CdCl									
A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C7	C8	C9	-178.7(4)	C3	C4	C5	C6	0.3(7)
N1	C1	C2	C3	179.0(4)	C4	C5	C6	C1	0.3(7)
N1	C1	C6	C5	-179.2(4)	C4	C5	C6	C7	178.6(5)
N1	C1	C6	C7	2.3(6)	C5	C6	C7	Br1	-0.8(6)
C1	N1	C9	C8	0.4(7)	C5	C6	C7	C8	179.4(4)
C1	C2	C3	C4	0.1(8)	C6	C1	C2	C3	0.5(7)
C1	C6	C7	Br1	177.6(3)	C6	C7	C8	C9	1.1(7)
C1	C6	C7	C8	-2.2(7)	C7	C8	C9	N1	-0.1(7)
C2	C1	C6	C5	-0.6(7)	C9	N1	C1	C2	180.0(5)
C2	C1	C6	C7	-179.1(4)	C9	N1	C1	C6	-1.5(7)
C2	C3	C4	C5	-0.5(8)					

4ZnCl									
A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C7	C6	C1	179.4(2)	C1	C6	C5	C4	0.4(3)
Br1	C7	C6	C5	-1.8(3)	C1	C6	C7	C8	-2.2(3)
Br1	C7	C8	C9	179.8(2)	C2	C3	C4	C5	0.2(4)
N1	C1	C2	C3	176.8(3)	C3	C4	C5	C6	-0.9(4)
N1	C1	C6	C5	-177.4(3)	C4	C5	C6	C7	-178.4(3)
N1	C1	C6	C7	1.4(3)	C5	C6	C7	C8	176.6(3)
N1	C9	C8	C7	0.3(4)	C6	C7	C8	C9	1.3(3)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	0.9(4)					

8CdCl

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C8	C9	N1	0.9(4)	Br2	C17	C18	N2	-0.1(4)
Br1	C8	C9	C4	-179.8(2)	Br2	C17	C18	C13	-179.6(2)
N1	C1	C2	C3	0.6(5)	N2	C10	C11	C12	1.6(5)
C1	N1	C9	C4	2.7(4)	C10	N2	C18	C13	-1.8(4)
C1	N1	C9	C8	-178.0(3)	C10	N2	C18	C17	178.8(3)
C1	C2	C3	C4	0.9(5)	C10	C11	C12	C13	-2.3(5)
C2	C3	C4	C5	178.2(3)	C11	C12	C13	C14	-179.7(3)
C2	C3	C4	C9	-0.7(4)	C11	C12	C13	C18	1.0(5)
C3	C4	C5	C6	-179.0(3)	C12	C13	C14	C15	179.7(3)
C3	C4	C9	N1	-1.0(4)	C12	C13	C18	N2	1.0(4)
C3	C4	C9	C8	179.6(3)	C12	C13	C18	C17	-179.5(3)
C4	C5	C6	C7	0.0(5)	C13	C14	C15	C16	0.4(5)
C5	C4	C9	N1	-180.0(3)	C14	C13	C18	N2	-178.3(3)
C5	C4	C9	C8	0.7(4)	C14	C13	C18	C17	1.2(4)
C5	C6	C7	C8	-0.5(5)	C14	C15	C16	C17	0.1(5)
C6	C7	C8	Br1	179.7(2)	C15	C16	C17	Br2	178.9(2)
C6	C7	C8	C9	1.1(5)	C15	C16	C17	C18	0.0(4)
C7	C8	C9	N1	179.5(3)	C16	C17	C18	N2	178.8(3)
C7	C8	C9	C4	-1.2(4)	C16	C17	C18	C13	-0.7(4)
C9	N1	C1	C2	-2.5(4)	C18	N2	C10	C11	0.4(4)
C9	C4	C5	C6	-0.1(5)	C18	C13	C14	C15	-1.0(5)

Table S7. Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 4CdCl, 4ZnCl and 8CdCl.

4CdCl

Atom	x	y	z	U(eq)
H1	8570.21	3966.74	2083.19	43
H2	6142.63	3456.39	3078.33	43
H3	4943.59	2552.98	3566.49	40
H4	6218.78	1653.35	3129.94	48
H5	8835.91	1634.43	2110.21	36
H8	12541.08	3174.76	642.07	40
H9	11049.15	4041.55	1143.63	41
H1A	8556.06	4971.9	2794.73	57

Atom	x	y	z	U(eq)
H1B	8048.98	4730.24	4275.63	57

4ZnCl

Atom	x	y	z	U(eq)
H1	4354.6(15)	3569(3)	4965.4(18)	57.4(7)
H2	5345(2)	3330(4)	6782(2)	68.2(10)
H3	6544(2)	2186(4)	8084(2)	78.9(12)
H4	7321(2)	588(4)	7747(3)	75.0(11)
H5	6929(2)	92(3)	6095(2)	61.5(9)
H8	4571.3(18)	1582(3)	2885(2)	53.0(8)
H9	3827(2)	3133(4)	3336(2)	61.3(9)

8CdCl

Atom	x	y	z	U(eq)
H1	1344.79	7635.1	3526.39	37
H1A	2436.91	6685.88	3165.72	49
H2	3385.35	5111.78	4078.18	53
H3	3154.32	4509.2	5339.42	52
H5	2230.22	4684.6	6312.34	53
H6	1036.31	5616.98	6590.62	60
H7	106.91	7199.59	5631.56	54
H2A	4285.81	8548.29	4893.86	41
H10	4904.98	7412.13	6078.35	53
H11	4319.8	7721.71	7175.48	68
H12	3075.2	9089.55	6996.61	65
H14	1923.26	10725.22	6092.63	61
H15	1371.02	11880.76	4839.15	63
H16	2019.63	11629.61	3768.89	50

Table S8. Birefringence Comparisons of Organic-Inorganic Hybrid Materials

Number	substance	Birefringence	Reference
1	(CHNO)(CHNO)ZnCl	0.048	14
2	Na(C ₂ H ₁₀ N ₂) ₂ [Zn ₃ (PO ₄) ₂ (H _{0.5} PO ₄) ₂]	0.060@546 nm	15
3	KPb ₃ (3-C ₅ H ₄ NCOO) ₂ Cl ₃ Br ₂	0.13@1064 nm	16
4	(CHNO)ZnCl (II)	0.063	14
5	(C ₂ H ₁₀ N ₂)[Zn ₂ (HPO ₄) ₂ Cl ₂]	0.066@546 nm	17
6	(CHNO)ZnBr (III)]	0.071	16
7	(C ₃ N ₆ H ₇) ₃ HgCl ₅	0.093@1064 nm	18

8	$\text{Ba}_3(\text{C}_4\text{H}_4\text{O}_5)_2(\text{OH})_2$	0.1@546 nm	19
9	$(\text{C}_8\text{H}_7\text{N}_2\text{O}_2)_2[\text{Bi}_2\text{Br}_8] \cdot 2\text{H}_2\text{O}$	0.1@550 nm	20
10	$\text{KPb}_3(3\text{-C}_5\text{H}_4\text{NCOO})_2\text{Br}_5$	0.109@546 nm	16
11	$(3\text{-C}_6\text{H}_{10}\text{N}_2)\text{ZnCl}_4$	0.129@546 nm	21
12	$\text{C}_{10}\text{H}_6\text{NO}_2\text{Cd}(\text{NO}_3) \cdot 2\text{H}_2\text{O}$	0.137@550 nm	22
13	$(3\text{-C}_6\text{H}_{10}\text{N}_2)\text{ZnBr}_4$	0.144 @ 546 nm	21
14	$(\text{C}_6\text{H}_{10}\text{N}_2)\text{CdBr}_4 \cdot \text{H}_2\text{O}$	0.158@546 nm	23
15	$\text{Mg}(\text{C}_3\text{O}_4\text{H}_2)(\text{H}_2\text{O})_2$	0.164@546.1 nm	24
16	$(\text{C}_7\text{H}_8\text{N}_2\text{S})_4\text{CdCl}_2$	0.17@546 nm	25
17	$(\text{C}_{12}\text{H}_9\text{N}_2)_2\text{TeBr}_6 \cdot 2\text{H}_2\text{O}$	0.17@546 nm	26
18	$(\text{C}_{10}\text{N}_2\text{H}_{10})(\text{HI}_2\text{O}_6)(\text{HIO}_3)(\text{IO}_3)$	0.171@550 nm	27
19	$(\text{H}_7\text{C}_5\text{N}_2)_6(\text{V}_{10}\text{O}_{28}) \cdot 2\text{H}_2\text{O}$	0.219	28
20	$\text{Cs}_3(\text{H}_2\text{C}_3\text{N}_3\text{O}_3)_3(\text{H}_3\text{C}_3\text{N}_3\text{O}_3) \cdot 3\text{H}_2\text{O}$	0.23@1064 nm	29
21	$\text{Cd}(\text{C}_6\text{H}_4\text{NO}_2)\text{I} \cdot \text{H}_2\text{O}$	0.243@550 nm	30
22	$(\text{C}_3\text{N}_6\text{H}_7)(\text{C}_3\text{N}_6\text{H}_6)\text{HgCl}_3$	0.246@1064 nm	18
23	$(\text{H}_7\text{C}_3\text{N}_6) \cdot (\text{H}_6\text{C}_3\text{N}_6)\text{ZnCl}_3$	0.255@1064 nm	31
24	$\text{CdF}(\text{C}_6\text{H}_4\text{NO}_2)$	0.26@546 nm	32
25	$\text{Sr}_2\text{Zn}(\text{C}_3\text{N}_3\text{O}_3)_2$	0.31@1064 nm	33
26	$(\text{C}_{12}\text{H}_9\text{N}_2)_2\text{TeBr}_6$	0.31@546nm	26
27	$(\text{C}_9\text{H}_7\text{NBr})_2(\text{ZnCl}_4)$	0.310 @ 550 nm	This work
28	$\text{KLa}_2(\text{C}_3\text{N}_3\text{O}_3)_2\text{Cl}$	0.316@1064	34
29	$(\text{C}_3\text{H}_8\text{N}_6)\text{PbBr}_4$	0.322 @ 546nm	35
30	$(\text{C}_{14}\text{H}_{14}\text{N}_2)\text{ZnCl}_4$	0.325 @ 1064 nm	36
31	$[\text{Mg}(\text{H}_2\text{O})_6][(\text{C}_7\text{H}_4\text{NO}_4)\text{H}_2\text{O}]_2$	0.34 @ 546 nm	37
32	$(\text{C}_{14}\text{H}_{14}\text{N}_2)\text{CdCl}_4$	0.341 @ 1064 nm	36
33	$(\text{C}_9\text{H}_7\text{NBr})_2(\text{CdCl}_4)$	0.378@550 nm	This work
34	$(\text{C}_7\text{H}_{10}\text{N})_3\text{Bi}_2\text{I}_9\text{I}_2$	0.39 @ 589 nm	38
35	$(\text{C}_9\text{H}_7\text{NBr})(\text{CdCl}_3) \cdot \text{H}_2\text{O}$	0.405 @ 550 nm	This work

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