Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

The halogen substitution strategy of inorganic skeletons triggers dielectric and band gap regulation of hybrid perovskites

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Physical Measurements

Single-Crystal X-ray Crystallography

Single-crystal X-ray diffraction data of compound **1** were collected using Mo Kα radiation (λ=0.71073 Å) at 213 and 298 K, on a Rigaku Saturn 924 diffractometer in ω scan mode. The data of compound **2** at 298 and 233 K were also collected. The room and low-temperature structures of the crystal data were shown in supporting (Table S1 and S2).

Cambridge Crystallographic Data Center (CCDC) (deposition numbers: 2272301-2272304) and can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/getstructures.

IR Studies

The dried samples and dried KBr were fully mixed in an agate mortar at a ratio of 1:100, and ground into powder. The powder was pressed into translucent, uniform, and non-cracked round slices, which were placed in the sample test rack of the infrared spectrometer for testing and data collection (Figure S4).

Thermal analysis

To study the effect of halogen substitution on the phase transition behavior, differential scanning calorimetry (DSC) was performed to facilitate the detection of phase transitions. Take approximately 10 mg of the sample and place it in an aluminum crucible, flattening the crucible. Place it in the instrument, and the measurement was performed under the atmosphere of nitrogen. The heating and cooling rate was 20 K/min. Finally, the data were collected and processed.

Dielectric properties

The crystal was ground into powder, pressed into a sheet, and fixed on the electrode with silver glue and 0.02 mm copper wire to measure the dielectric. The temperature of the measured dielectric would not exceed its melting point. The complex dielectric constant ε is measured by the TH2828A instrument.

Ultraviolet-visible diffuse reflectance spectra

The UV absorption spectra of powder samples **1** and **2** were measured at room temperature using a Shimadzu UV-2600 Spectrophotometer. First, prepare a standard whiteboard. An appropriate amount of anhydrous $BaSO_4$ powder was added to the sample tank, and then the powder was compacted with a glass column so that the anhydrous $BaSO_4$ powder was pressed into a flat surface and filled the entire sample tank completely. (In order to facilitate the cleaning of the glass cylinder, the surface of anhydrous $BaSO_4$ powder was generally covered with a piece of weighing paper and then pressed with the glass cylinder, so that the glass cylinder does not come into direct contact with the sample.) For the standard UV measurements, $BaSO_4$ as a blank reference is required. It should be that anhydrous $BaSO_4$ standard whiteboard to test the background baseline. Anhydrous $BaSO_4$ is a chemical commonly used in solid UV testing. Anhydrous $BaSO_4$ has good UV reflective properties, especially in the 200-400 m wavelength range. This is because anhydrous $BaSO_4$ has good optical properties to reflect or transmit UV light. Therefore, anhydrous $BaSO_4$ coatings are widely used in UV testing. Then, a standard whiteboard was used to test the background baseline: the pressed standard whiteboard was put into the sample slot position, and it was used as the background test baseline. After the baseline was measured, a small amount of powder of compound **1** was added to the substrate of a standard white plate and the sample was again flattened with a glass cylinder to obtain a sample plate. Finally, the sample plate was placed into the sample slot for testing. After testing a sample, the standard white plate was re-prepared and then the sample plate was pressed on top of the standard white plate to continue the test.

Hirshfeld surfaces and two-dimensional fingerprint plots analysis

Hirshfeld surfaces and 2D fingerprint plots are calculated by entering CIF structure files into the CrystalExplorer software. Hirshfeld surfaces of two compounds were obtained using a standard (high) surface resolution, which can provide information about intermolecular interactions in the crystal. The 2D fingerprint plot is a combination of d_e and d_i that summarizes intermolecular contacts in the crystal and complements the Hirshfeld surfaces. The normalized contact distance d_{norm} is calculated according to:

$$d_{norm} = \frac{d_i - r^{vdW}}{r_i^{vdW}} + \frac{d_e - r}{r_e^{vdW}}$$

d_{norm} surface is used for the identification of close intermolecular interactions. The normalized contact distance d_{norm} is based on d_e, d_i, and the van der Waals (vdW) radii of the two atoms external (r_e^{vdW}) and internal (r_i^{vdW}) to the surface. The value of d_{norm} is negative or positive when intermolecular contacts are shorter or longer than, respectively. Hirshfeld surface with d_{norm} values display a red-blue-white color scheme: where red regions correspond to closer contacts and negative d_{norm} value; the blue regions correspond to longer contacts and positive d_{norm} value; and the white regions correspond to the distance of contacts are exactly the van der Waals separation and with a d_{norm} value of zero.

Table S1 Crystallographic data and structural refinement details of compound **1**.

Compound	**LTP$_1$**	**RTP$_1$**
Empirical formula	$[C_7H_{16}N]PbI_3$	$[C_7H_{16}N]PbI_3$
Formula weight	702.10	702.10
Temperature/K	213 K	298 K
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	11.9805(9)	11.554(3)
b/Å	16.4269(12)	17.566(4)
c/Å	7.8664(4)	7.9189(16)
β/°	102.060(3)	101.329(5)
Volume/Å^3	1513.96(18)	1575.9(6)

μ/mm^{-1}	21.206	16.547
Z	4	4
GOF	1.062	1.042
R_1[I>=2σ (I)]	0.0529	0.0482
wR_2[I>=2σ (I)]	0.1082	0.1003

Table S2 Crystallographic data and structural refinement details of compound **2**.

Compound	**LTP$_2$**	**RTP$_2$**
Empirical formula	$[C_7H_{16}N]PbBr_3$	$[C_7H_{16}N]PbBr_3$
Formula weight	561.13	561.13
Temperature/K	233 K	298 K
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*
a/Å	15.8846(8)	17.0361(8)
b/Å	7.6949(3)	7.6699(3)
c/Å	22.2250(10)	21.3038(12)
β/°	90	90
Volume/Å^3	2716.6(2)	2783.7(2)
μ/mm^{-1}	21.206	20.692
Z	8	8
GOF	1.076	1.068
R_1[I>=2σ (I)]	0.0498	0.0805
wR_2[I>=2σ (I)]	0.1021	0.1858

Table S3. Bond lengths (Å) for **1** at 213 K

Bond lengths (Å) for **1** at 213 K			
Pb1—I1	3.1885 (8)	N1—C1	1.495 (15)
Pb1—I1^{i}	3.2037 (8)	N1—C2	1.528 (15)
Pb1—I2^{i}	3.2603 (8)	N1—C3	1.491 (16)
Pb1—I2	3.2539 (8)	C4—C5	1.496 (17)
Pb1—I3	3.1887 (8)	C5—C7	1.52 (2)
Pb1—I3^{ii}	3.2637 (8)	C5—C6	1.526 (17)
N1—C4	1.528 (13)	C7—C6	1.51 (3)

Table S4. Bond angles (°) for **1** at 213 K

Bond angles (°) for **1** at 213 K			
I1—Pb1—I1^{i}	90.96 (2)	Pb1—I1—Pb1^{ii}	75.949 (17)
I1^{i}—Pb1—I2	177.30 (2)	Pb1—I2—Pb1^{ii}	74.283 (17)
I1—Pb1—I2^{i}	177.96 (2)	Pb1—I3—Pb1^{i}	75.107 (17)
I1—Pb1—I2	88.43 (2)	C1—N1—C4	106.9 (10)
I1^{i}—Pb1—I2^{i}	88.06 (2)	C1—N1—C2	107.8 (9)
I1—Pb1—I3	94.16 (2)	C1—N1—C3	110.5 (11)
I1^{i}—Pb1—I3^{ii}	96.17 (2)	C2—N1—C4	110.7 (9)

I1—Pb1—I3^{ii}	84.41 (2)	C3—N1—C4	110.4 (9)
I2—Pb1—I2^{i}	92.64 (2)	C3—N1—C2	110.4 (11)
I2—Pb1—I3^{ii}	86.40 (2)	C5—C4—N1	113.5 (9)
I2^{i}—Pb1—I3^{ii}	93.93 (2)	C4—C5—C7	119.3 (11)
I3—Pb1—I1^{i}	85.39 (2)	C4—C5—C6	114.0 (11)
I3—Pb1—I2^{i}	87.54 (2)	C7—C5—C6	59.4 (11)
I3—Pb1—I2	92.03 (2)	C6—C7—C5	60.7 (10)
I3—Pb1—I3^{ii}	177.89 (2)	C7—C6—C5	60.0 (10)

Symmetry codes: (i) *x*, −*y*+3/2, *z*+1/2; (ii) *x*, −*y*+3/2, *z*−1/2.

Table S5. Bond lengths (Å) for **1** at 298 K

Bond lengths (Å) for **1** at 298 K			
Pb3—I9	3.2540 (10)	N1—C7	1.479 (9)
Pb3—I9^{i}	3.2761 (10)	N1—C4	1.509 (19)
Pb3—I8	3.2006 (10)	N1—C2	1.510 (19)
Pb3—I8^{i}	3.2284 (10)	N1—C5	1.515 (19)
Pb3—I7^{ii}	3.2366 (10)	C8—C9	1.503 (10)
Pb3—I7	3.2276 (10)	C11—C10	1.495 (10)
N1—C8	1.473 (10)	C11—C9	1.497 (9)
N1—C3	1.512 (16)	C10—C9	1.498 (10)
N1—C1	1.516 (16)	C9—C7	1.490 (10)
N1—C6	1.506 (17)		

Table S6. Bond angles (°) for **1** at 298 K

Bond angles (°) for **1** at 298 K			
I3—Pb1—I3^{i}	93.66 (3)	C4B—N1—C3A	71 (3)
I2^{i}—Pb1—I3^{i}	85.63 (3)	C2A—N1—C1A	101.1 (16)
I2—Pb1—I3	86.45 (3)	C3A—N1—C2A	116.8 (18)
I2^{i}—Pb1—I3	178.81 (2)	C3A—N1—C1A	106.9 (18)
I2—Pb1—I3^{i}	179.59 (3)	C4A—N1—C2B	152 (4)
I2—Pb1—I2^{i}	94.28 (3)	C4A—N1—C1B	85 (3)
I2—Pb1—I1	92.82 (3)	C4A—N1—C3B	117 (4)
I2^{i}—Pb1—I1^{ii}	93.20 (3)	C2B—N1—C1B	121 (5)
I2—Pb1—I1^{ii}	85.93 (3)	C2B—N1—C3B	37 (4)
I1^{ii}—Pb1—I3	87.79 (3)	C1B—N1—C3B	137 (5)
I1—Pb1—I3^{i}	87.57 (3)	N1—C4B—C5	113.0 (14)
I1—Pb1—I3	93.40 (3)	C6—C7—C5	60.1 (5)
I1^{ii}—Pb1—I3^{i}	93.68 (3)	C7—C6—C5	60.0 (5)
I1—Pb1—I2^{i}	85.62 (3)	C7—C5—C4B	94.5 (18)
I1—Pb1—I1^{ii}	178.22 (4)	C7—C5—C6	59.9 (5)
Pb1—I3—Pb1^{ii}	74.65 (2)	C6—C5—C4B	125 (3)
Pb1—I2—Pb1^{ii}	76.03 (2)	C4A—C5—C7	129.7 (19)
Pb1—I1—Pb1^{i}	75.54 (2)	C4A—C5—C6	115.6 (15)

C4B—N1—C2A	131.7 (18)	N1—C4A—C5	113.4 (13)
C4B—N1—C1A	123 (3)		

Symmetry codes: (i) *x*, −*y*+3/2, *z*+1/2; (ii) *x*, −*y*+3/2, *z*−1/2.

Table S7. Bond lengths (Å) for **2** at 233 K

Bond lengths (Å) for **2** at 233 K			
Pb1—Br1	2.9673 (9)	N1—C4	1.524 (13)
Pb1—Br1^{i}	3.0627 (10)	N1—C1	1.461 (14)
Pb1—Br2^{ii}	3.1830 (11)	N1—C2	1.518 (14)
Pb1—Br2	2.9173 (11)	C5—C4	1.519 (14)
Pb1—Br3	3.0277 (10)	C5—C6	1.518 (15)
Pb1—Br3^{i}	3.0949 (10)	C5—C7	1.525 (14)
N1—C3	1.513 (13)	C6—C7	1.529 (18)

Table S8. Bond angles (°) for **2** at 233 K

Bond angles (°) for **2** at 233 K			
Br1—Pb1—Br1^{i}	92.83 (3)	Pb1—Br1—Pb1^{ii}	79.28 (2)
Br1^{i}—Pb1—Br2^{ii}	101.16 (3)	Pb1—Br2—Pb1^{i}	78.07 (2)
Br1—Pb1—Br2^{ii}	80.99 (3)	Pb1—Br3—Pb1^{ii}	77.86 (2)
Br1^{i}—Pb1—Br3^{i}	85.29 (3)	C3—N1—C4	110.0 (8)
Br1—Pb1—Br3^{i}	178.10 (3)	C1—N1—C3	109.2 (10)
Br1—Pb1—Br3	88.18 (3)	C1—N1—C4	112.2 (8)
Br2—Pb1—Br1	94.72 (3)	C1—N1—C2	110.7 (10)
Br2—Pb1—Br1^{i}	83.85 (3)	C2—N1—C3	107.4 (8)
Br2—Pb1—Br2^{ii}	173.50 (3)	C2—N1—C4	107.3 (9)
Br2—Pb1—Br3	92.99 (3)	C4—C5—C7	114.4 (9)
Br2—Pb1—Br3^{i}	85.36 (3)	C6—C5—C4	118.9 (9)
Br3—Pb1—Br1^{i}	176.75 (3)	C6—C5—C7	60.3 (8)
Br3—Pb1—Br2^{ii}	82.04 (3)	C5—C4—N1	112.8 (8)
Br3^{i}—Pb1—Br2^{ii}	99.10 (3)	C5—C6—C7	60.1 (8)
Br3—Pb1—Br3^{i}	93.71 (3)	C6—C7—C5	59.6 (7)

Symmetry codes: (i) −*x*+1/2, *y*−1/2, *z*; (ii) −*x*+1/2, *y*+1/2, *z*.

Table S9. Bond lengths (Å) for **2** at 298 K

Bond lengths (Å) for **2** at 298 K			
Pb1—Br1	3.002 (2)	N1—C3A	1.537 (17)
Pb1—Br1i	3.019 (2)	N1—C2A	1.530 (17)
Pb1—Br2i	3.062 (2)	N1—C4A	1.535 (16)
Pb1—Br2	3.051 (2)	C5B—C6B	1.536 (19)
Pb1—Br3	3.015 (2)	C5B—C7B	1.535 (19)
Pb1—Br3ii	3.045 (2)	C5B—C4B	1.533 (19)
N1—C2B	1.537 (18)	C6B—C7B	1.538 (18)
N1—C3B	1.536 (18)	C4A—C5A	1.530 (18)

N1—C4B	1.536 (18)	C5A—C6A	1.536 (19)
N1—C1B	1.535 (18)	C5A—C7A	1.534 (19)
N1—C1A	1.537 (16)	C6A—C7A	1.535 (19)

Table S10. Bond angles (°) for **2** at 298 K

Bond angles (°) for **2** at 298 K			
Br1—Pb1—Br1^{i}	98.35 (8)	C1B—N1—C2B	100 (4)
Br1^{i}—Pb1—Br2	177.64 (7)	C1B—N1—C3B	128 (5)
Br1^{i}—Pb1—Br2^{i}	83.40 (7)	C1B—N1—C4B	124 (5)
Br1—Pb1—Br2	83.88 (7)	C3A—N1—C1A	105 (4)
Br1—Pb1—Br2^{i}	177.76 (7)	C2A—N1—C1A	109.5 (16)
Br1^{i}—Pb1—Br3^{ii}	94.90 (7)	C2A—N1—C3A	97 (3)
Br1—Pb1—Br3^{ii}	84.34 (7)	C2A—N1—C4A	125 (3)
Br1—Pb1—Br3	93.90 (7)	C4A—N1—C1A	108.0 (16)
Br2—Pb1—Br2^{i}	94.38 (8)	C4A—N1—C3A	111.5 (18)
Br3—Pb1—Br1^{i}	84.55 (6)	C7B—C5B—C6B	60.1 (8)
Br3—Pb1—Br2^{i}	84.87 (6)	C4B—C5B—C6B	119 (6)
Br3^{ii}—Pb1—Br2	84.56 (6)	C4B—C5B—C7B	107 (5)
Br3—Pb1—Br2	96.07 (7)	C5B—C6B—C7B	59.9 (8)
Br3^{ii}—Pb1—Br2^{i}	96.91 (7)	C5B—C7B—C6B	60.0 (8)
Br3—Pb1—Br3^{ii}	178.06 (10)	C5B—C4B—N1	125 (6)
Pb1—Br1—Pb1^{ii}	79.12 (5)	C5A—C4A—N1	103 (3)
Pb1—Br2—Pb1^{ii}	77.71 (6)	C4A—C5A—C6A	145 (5)
Pb1—Br3—Pb1^{i}	78.52 (5)	C4A—C5A—C7A	87 (5)
C3B—N1—C2B	104 (4)	C7A—C5A—C6A	60.0 (8)
C4B—N1—C2B	72 (5)	C7A—C6A—C5A	59.9 (8)
C4B—N1—C3B	108 (5)	C5A—C7A—C6A	60.1 (8)

Symmetry codes: (i) x, $-y+3/2$, $z+1/2$; (ii) x, $-y+3/2$, $z-1/2$.

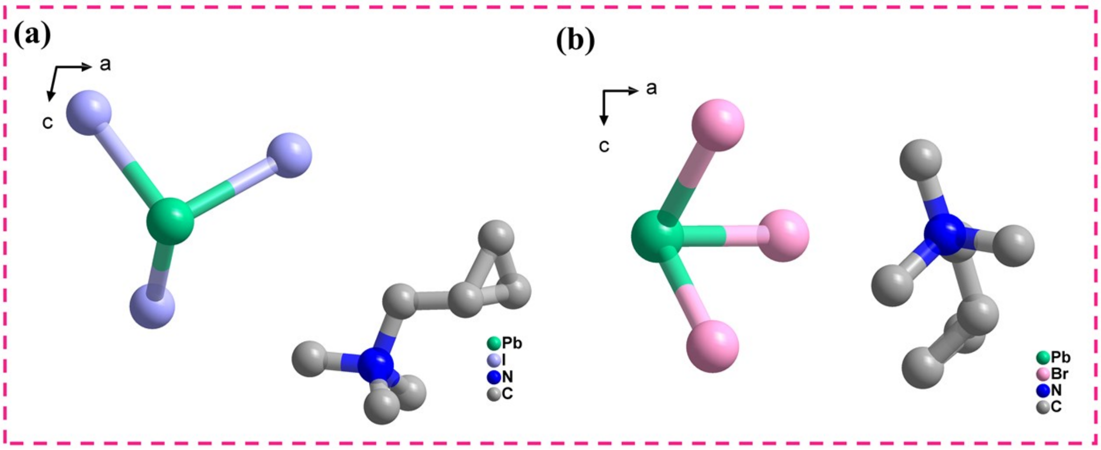

Fig. S1 Schematic diagram of the least asymmetric unit of compounds **1** and **2** along the b-axis.

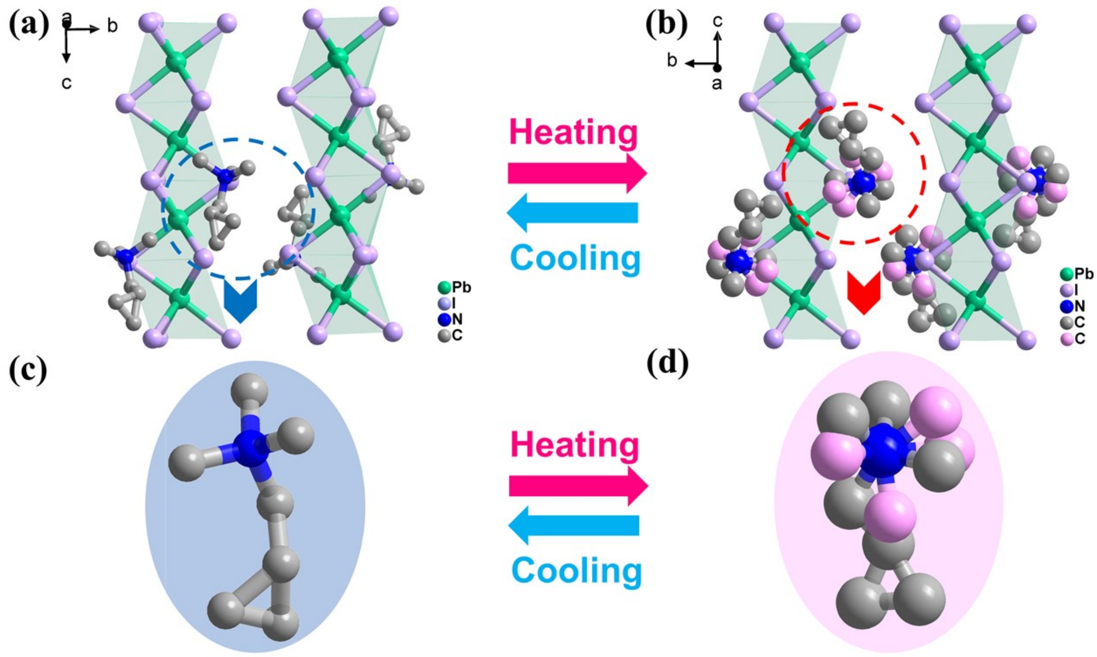

Fig. S2 Crystal packing diagram of **1-LTP** (a) and **1-RTP** (b). Ordered state (c) and disordered state (f) of $[C_7H_{16}N]+$.

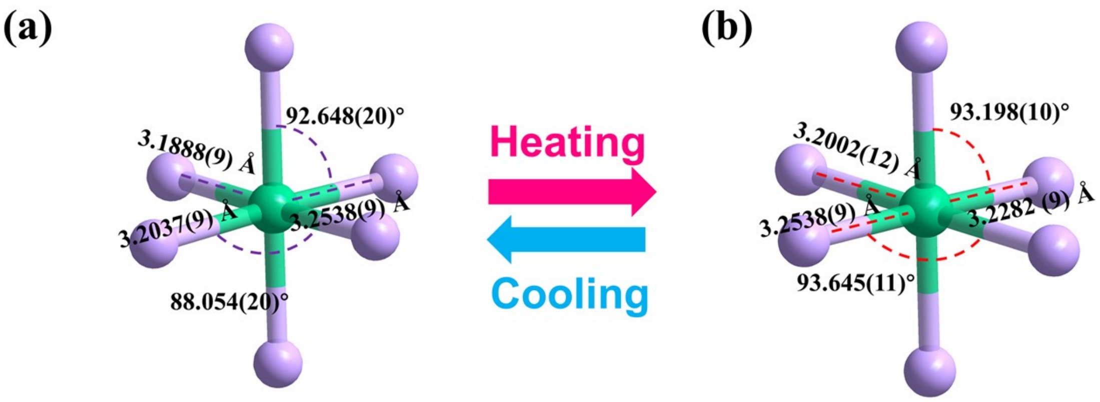

Fig. S3 Enlarged diagram of the inorganic skeleton in the ordered state (a) and disordered state (b).

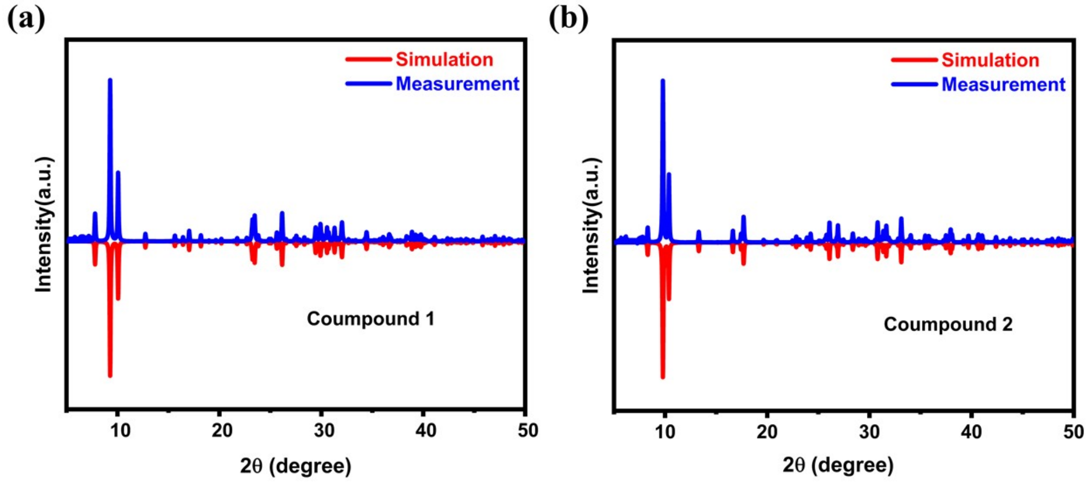

Fig. S4 Powder X-ray diffraction patterns at 298 K (a) **1** and (b) **2**.

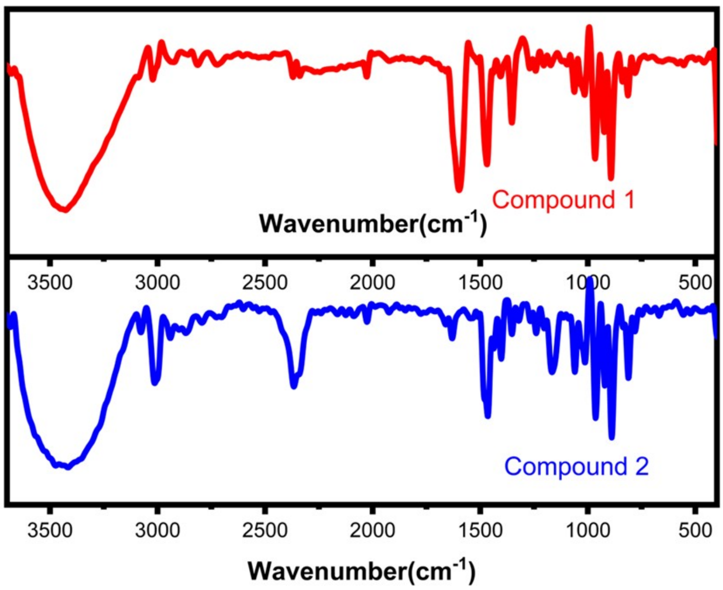

Fig. S5 The IR spectrum for compound **1** and compound **2** displays the characteristics peaks for stretching and bending vibrations.