Supplementary Information

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Experimental Measurement Methods

Hirshfeld Surfaces and Intermolecular Interaction Analysis.

For compounds **1**, the CrystalExplorer program was used to input the structure file in CIF format at 273 K, respectively, to calculate the Hirshfeld surface and 2D fingerprint[1]. The intensity of molecular interaction is expressed by mapping to the Hirshfeld surface using the corresponding red-blue-white scheme: where red, white, and blue represent contacts shorter than, equal to, and longer than the van der Waals distance, respectively. In the 2D fingerprint map, each point represents a pair (d_i, d_e), reflecting the distance between the inner (d_i) and outer (d_e) nearest atoms of the Hirshfeld d_{norm} surface. 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:

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

d_{norm} surface represents close intermolecular interactions.

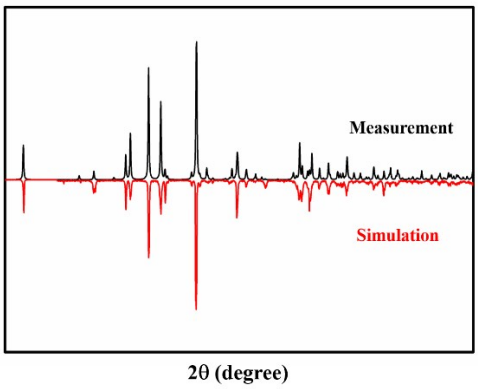

Figure S1 Measured and simulated powder X-ray diffraction patterns of compound **1**.

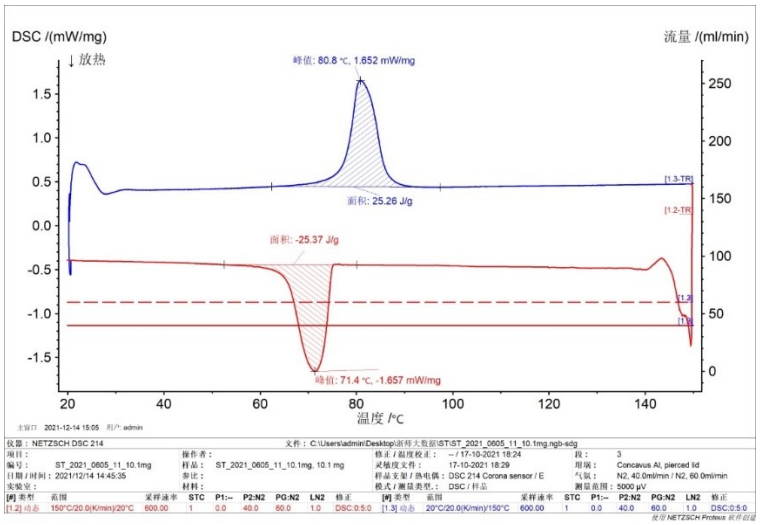

Figure S2 The original integration diagram of DSC curves.

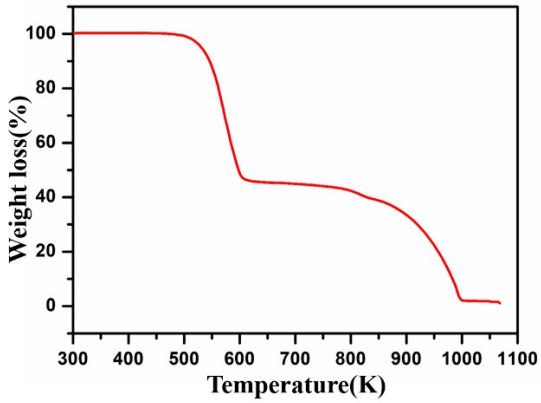

Figure S3 TGA curve of compounds **1** in the temperature range of 300 K-1050 K.

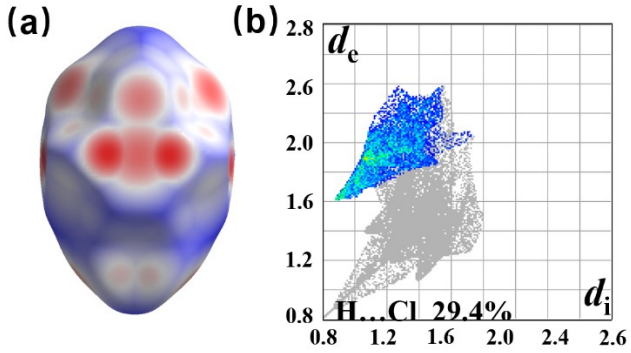

Figure S4 (a) Hirshfeld surface of compound **1** at 373 K. (b) 2D fingerprint plot of compound **1** at 373 K.

Table S1. Crystal data and structure refinements for compound at 273 K and 373 K.

	LTP (273 K)	**HTP (373 K)**
Empirical formula	$C_8H_{16}CdCl_4F_4N_2$	$C_8H_{16}CdCl_4F_4N_2$
Formula weight	470.43	470.43
Space group	$C_2/_C$	$P4_2/ncm$
Crystal system	Monoclinic	Tetragonal
a/ Å	26.252	7.747
b/ Å	7.5959	7.747
c/ Å	7.6397	26.484
β/°	95.399	90
Volume/ Å^3	1516.6	1589.4
Z	4	4
F(000)	920	920
GOF	1.177	1.030
$R_1[I>2\sigma(I)]$	0.1220	0.0723
$wR_2[I>2\sigma(I)]$	0.3419	0.2869

Table S2. Selected bond lengths [Å] and bond angles at 273 K.

bond lengths [Å]		bond angles [°]	
Cd1—Cl1^{i}	2.482 (2)	Cl1^{i}—Cd1—Cl1	180.0
Cd1—Cl1	2.482 (2)	Cl1^{i}—Cd1—Cl2	88.79 (7)
Cd1—Cl2	2.722 (2)	Cl1—Cd1—Cl2	91.21 (7)
Cd1—Cl2^{i}	2.722 (2)	Cl1^{i}—Cd1—Cl2^{i}	91.21 (7)
Cd1—Cl2^{ii}	2.748 (2)	Cl1—Cd1—Cl2^{i}	88.79 (7)
Cd1—Cl2^{iii}	2.748 (2)	Cl2—Cd1—Cl2^{i}	180.0
Cl2—Cd1^{iv}	2.748 (2)	Cl1^{i}—Cd1—Cl2^{ii}	87.21 (7)
		Cl1—Cd1—Cl2^{ii}	92.79 (7)
		Cl2—Cd1—Cl2^{ii}	90.816 (18)
		Cl2^{i}—Cd1—Cl2^{ii}	89.184 (18)
		Cl1^{i}—Cd1—Cl2^{iii}	92.79 (7)
		Cl1—Cd1—Cl2^{iii}	87.21 (7)
		Cl2—Cd1—Cl2^{iii}	89.184 (18)
		Cl2^{i}—Cd1—Cl2^{iii}	90.816 (18)
		Cl2^{ii}—Cd1—Cl2^{iii}	180.0
		Cd1—Cl2—Cd1^{iv}	159.97 (9)

Table S3. Selected bond lengths [Å] and bond angles at 373 K.

bond lengths [Å]		bond angles [°]	
Cd1—Cl3	2.462 (3)	Cl3^{i}—Cd1—Cl3	180.0
Cd1—Cl3^{i}	2.462 (3)	Cl3^{i}—Cd1—Cl2^{i}	90.0
Cd1—Cl2^{i}	2.7389	Cl3—Cd1—Cl2^{i}	90.0
Cd1—Cl2	2.7389	Cl3^{i}—Cd1—Cl2	90.0
Cd1—Cl1	2.7784 (8)	Cl3—Cd1—Cl2	90.0
Cd1—Cl1^{i}	2.7784(9)	Cl2^{i}—Cd1—Cl2	180.0
Cl1—Cd1^{ii}	2.7784 (8)	Cl3^{i}—Cd1—Cl1	89.53 (14)
Cl2—Cd1^{iii}	2.7389	Cl3—Cd1—Cl1	90.47 (14)
		Cl2^{i}—Cd1—Cl1	90.0
		Cl2—Cd1—Cl1	90.0
		Cl3^{i}—Cd1—Cl1^{i}	90.47 (14)
		Cl3—Cd1—Cl1^{i}	89.53 (14)
		Cl2^{i}—Cd1—Cl1^{i}	90.0
		Cl2—Cd1—Cl1^{i}	90.0
		Cl1—Cd1—Cl1^{i}	180.0
		Cd1^{ii}—Cl1—Cd1	160.67 (19)
		Cd1^{iii}—Cl2—Cd1	180.0

Table S4. H_{inside}-$Cl_{outside}$ surface area, mean d_i and mean d_e in compound **1**.

Compound	**Temperature**	**H_{inside}-$Cl_{outside}$ surface area**	**Mean d_i**	**Mean d_e**
1	273 K	30.5%	1.5085	1.7491
	373 K	29.4%	1.3185	1.6284

Table S5. Hydrogen-bond geometry (Å, °) for compound **1** at 273 K.

D—H	**D(D—H)**	**D(H···A)**	**<DHA**	**D(D···A)**	**A**
N1-H1A	0.89	2.617	161.5	3.472	Cl2
N1-H1B	0.89	2.816	113.7	3.277	Cl2
N1-H1C	0.89	2.842	121.62	3.394	Cl2
N1-H1C	0.89	2.696	117.69	3.208	Cl1
N1-H1C	0.89	2.901	121.05	3.445	Cl1
C4-H4A	0.97	2.587	110.24	3.061	F2
C4-H4A	0.97	2.406	177.68	3.376	F1

Symmetry codes: x, y+1, z; x, -y+1, z+1/2; -x+1/2, y+1/2, -z+1/2; x, -y+1, z-1/2; -x+1, -y+2, -z+1; x, -y+2, z+1/2.

Table S6. Hydrogen-bond geometry (Å, °) for compound **1** at 373 K.

D—H	D(D—H)	D(H···A)	<DHA	D(D···A)	A
N1-H1B_a	0.89	2.95	112.68	3.394	Cl3
N1-H1B_a	0.89	2.651	157.03	3.488	Cl2
N1-H1C_a	0.89	2.599	149.09	3.394	Cl3
N1-H1D_a	0.89	2.807	129.24	3.44	Cl1
N1-H1D_a	0.89	2.759	139.99	3.488	Cl2
C6_a-H6B_a	0.96	2.542	131.08	3.254	F1_a

Symmetry codes: x-1, y, z; -x, -y+1, -z+1; -x+1/2, -y+3/2, z; -y+1, x+1/2, -z+3/2.

Reference

1.Turner, M. J.; McKinnon, J. J.; Wolff, S. K.; Grimwood, D. J.; Spackman, P. R.; Jayatilaka, D.; Spackman, M. A. CrystalExplorer17; University of Western Australia, 2017, http://hirshfeldsurface.net