Supporting Information

Organic-Inorganic hybrid materials with high phase transition temperatures regulated by halogen substitution

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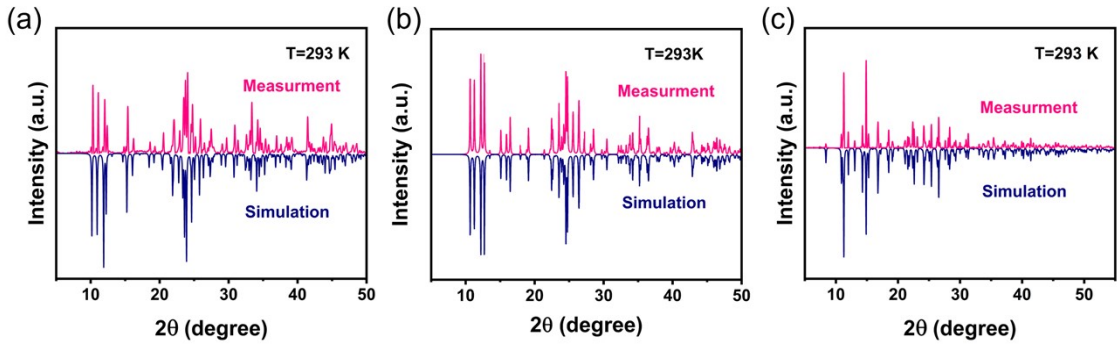

Fig. S1 Powder X-ray diffraction (PXRD) of crystal **1** (a), **2** (b) and **3** (c)

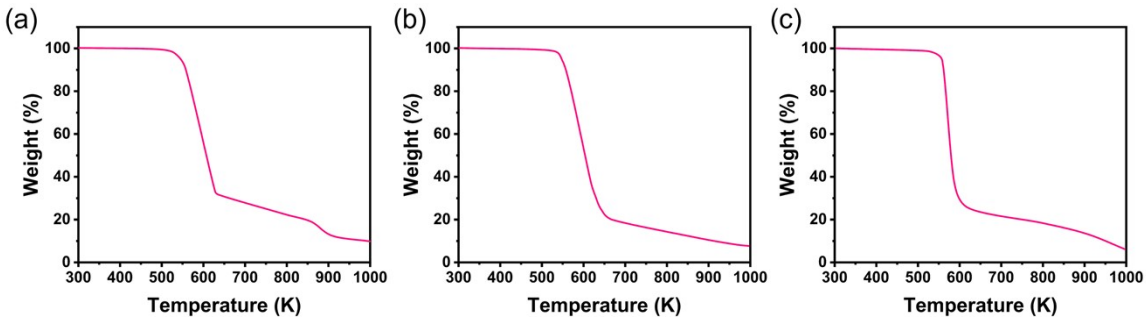

Fig. S2 The TG curves for **1-3** (a-d), indicating that the three crystals are stable at least up to 600 K

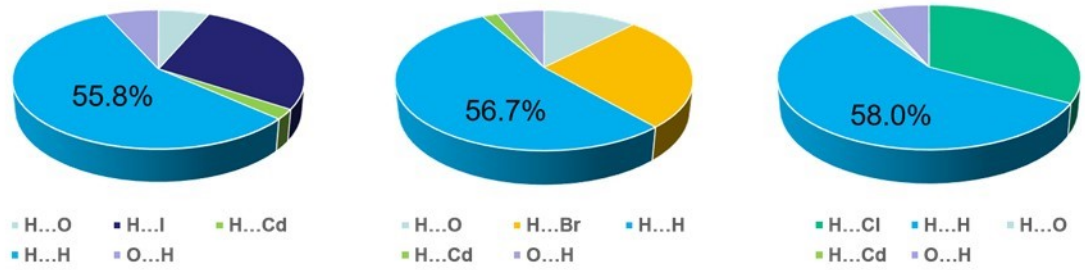

Fig. S3 Distribution of intermolecular interactions in crystals **1-3** and their percentages

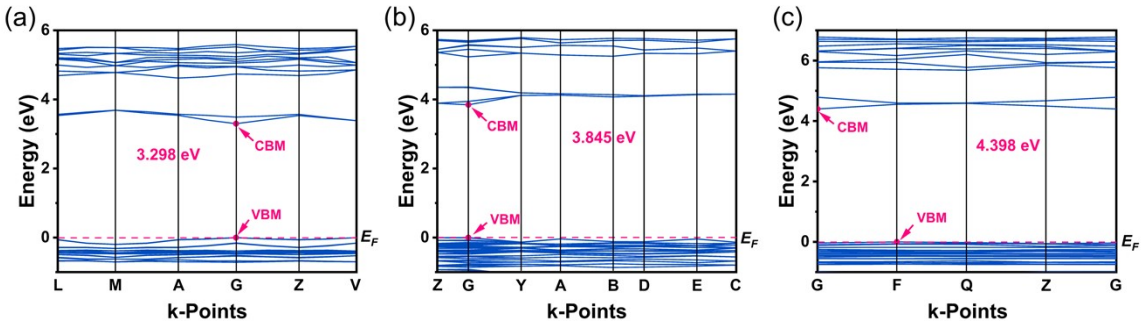

Fig. S4 The calculated band structure of crystal **1** (a), **2** (b) and **3** (c)

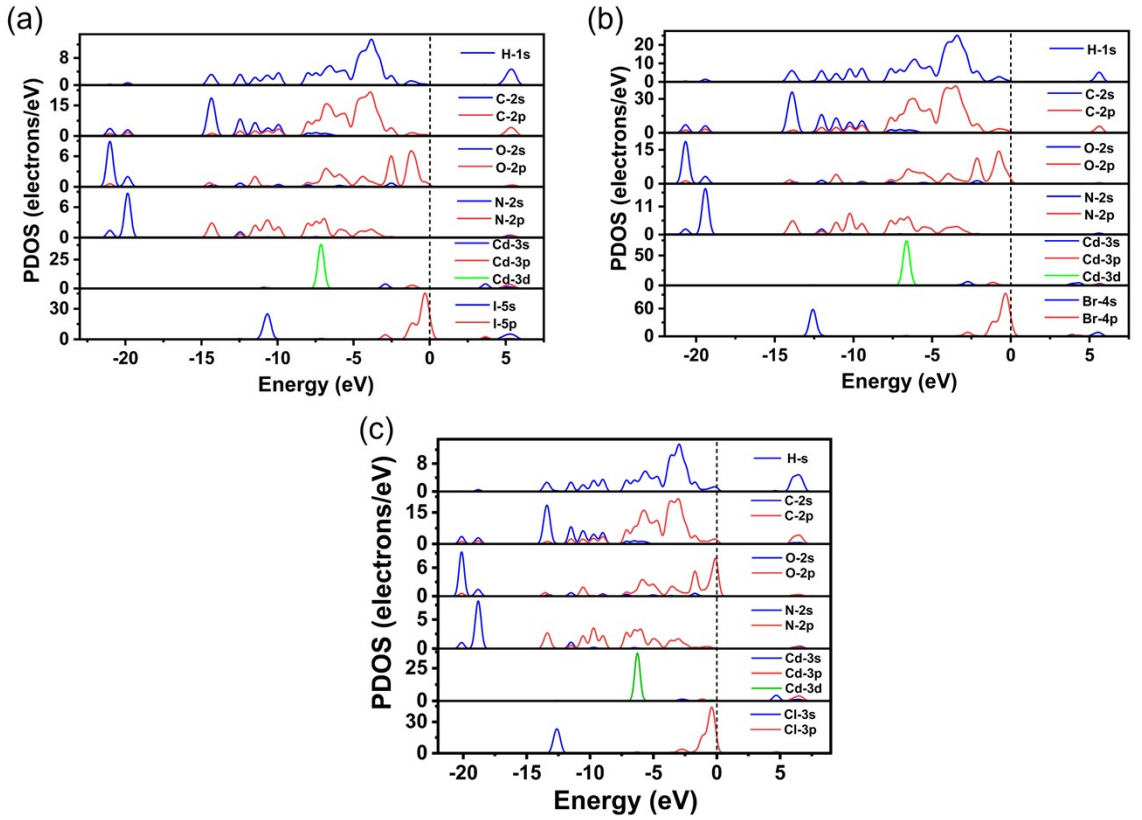

Fig. S5 Partial density of states (PDOS) of crystal **1** (a), **2** (b) and **3** (c)

The optical bandgap (Eg) of the crystals was determined using the Tauc equation.

$(\alpha h\upsilon)^n = A(h\upsilon - E_g)$

Where:

- α is the absorption coefficient, derived from the Kubelka-Munk function F(R) = $(1\text{-}R)^2/2R$ (where R is the reflectance);
- h is Planck's constant;
- υ is the photon frequency;

- A is a constant of proportionality;
- n is an index that characterizes the type of electronic transition. For the direct allowed transitions typically observed in these $[C_6H_{14}NO]_2CdX_4$ hybrid materials, n = 2.

Table S1. Crystal data and structure refinements for crystals **1-3** at 296.15 K.

Moiety formula	**$[C_6H_{14}NO]_2CdI_4$**	**$[C_6H_{14}NO]_2CdBr_4$**	**$[C_6H_{14}NO]_2CdCl_4$**
T（K）	296.15	296.15	296.15
Formula weight	852.36	664.40	486.56
Crystal system	monoclinic	monoclinic	triclinic
Space group	*C*2/*c*	*C*2/*c*	*P*-1
a/Å	13.548(3)	13.1657(11)	8.3016(3)
b/Å	10.083(3)	9.811(9)	10.5798(4)
c/Å	17.418(4)	16.6682 (12)	12.1096(4)
α/deg	90.00	90	89.598(2)
β/deg	93.764(13)	95.053(5)	79.447(2)
γ/deg	90.00	90	83.943(2)
Volume ($Å^3$)	2374.3(10)	2144.7(3)	1039.67(6)
Z	4	4	2
D_c (g/cm^{-3}）	2.385	2.058	1.554
M (mm^{-1})	6.126	8.475	1.568
F (000)	1560.0	1272.0	492.0
2θ range [°]	4.68 to 54.2	4.9 to 54.88	3.44 to 55.02
Reflections collected	11303	4832	12761
R_1, wR_2 [I>=2σ (I)]	0.0261, 0.0605	0.0320, 0.0623	0.0285, 0.0716
R_1, wR_2 [all data]	0.0297, 0.0624	0.0568, 0.0685	0.0308, 0.0746
GOF	1.157	1.018	0.967
Largest peak and hole ($e/Å^3$)	0.75 and -1.36	0.56 and -0.59	0.69 and -0.61

Table S2. Cd-I Bond Lengths [Å] and I-Cd-I Bond Angles [°] of Crystal **1**

Atom-Atom	Length/ Å	Atom-Atom-Atom	Angle/°
I^1- Cd^2	2.7726(6)	I^1- Cd^2- I^{11}	107.72(3)
Cd^2- I^{11}	2.7726(6)	I^{31}- Cd^2- I^{11}	108.002(17)
Cd^2- I^{31}	2.7659(6)	I^{31}- Cd^2- I^1	107.756(4)
Cd^2- I^3	2.7659(6)	I^3- Cd^2- I^{11}	107.756(4)
		I^3- Cd^2- I^1	108.002(17)
		I^3- Cd^2- I^{31}	117.26(3)

Table S3. Cd-Br Bond Lengths [Å] and Br-Cd-Br Bond Angles [°] of Crystal **2**

Atom-Atom	Length/ Å	Atom-Atom-Atom	Angle/°
Cd^{1}- Br^{21}	2.5896(5)	Br^{2}- Cd^{1}- Br^{21}	107.55(2)
Cd^{1}- Br^{2}	2.5896(5)	Br^{31}- Cd^{1}- Br^{2}	105.257(16)
Cd^{1}- Br^{31}	2.5640(4)	Br^{31}- Cd^{1}- Br^{21}	109.657(15)
Cd^{1}- Br^{3}	2.5640(4)	Br^{3}- Cd^{1}- Br^{21}	105.257(16)
		Br^{3}- Cd^{1}- Br^{2}	109.657(15)
		Br^{31}- Cd^{1}- Br^{3}	119.03(3)

Table S4. Cd-Cl Bond Lengths [Å] and Cl-Cd-Cl Bond Angles [°] of Crystal **3**

Atom-Atom	Length/ Å	Atom-Atom-Atom	Angle/°
Cd^{1}- Cl^{1}	2.4593(7)	Cl^{2}- Cd^{1}- Cl^{1}	108.94(3)
Cd^{1}- Cl^{2}	2.4474(7)	Cl^{2}- Cd^{1}- Cl^{3}	105.94(3)
Cd^{1}- Cl^{3}	2.4551 (7)	Cl^{3}- Cd^{1}- Cl^{1}	108.222)
Cd^{1}- Cl^{4}	2.4270(7)	Cl^{4}- Cd^{1}- Cl^{1}	107.19(3)
		Cl^{4}- Cd^{1}- Cl^{2}	108.18(3)
		Cl^{4}- Cd^{1}- Cl^{3}	118.13(3)