Halogen Substitution Effects on Optical and Electrical Properties in 3D Molecular Perovskites

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EXPERIMENTAL SECTION

Synthesis

Synthesis of triethyl-(2-fluoro-ethyl)-phosphonium bromide. All reagents and solvents in the syntheses were used as purchased without further purification. Anhydrous acetonitrile (100 mL) was added into a dry three-diameter flask under nitrogen at room temperature. Then 2-fluoro-1-bromoethane (5 mL, 67.1 mmol) and triethylphosphine (7.5 mL, 55.88 mmol) were added to this solusion by syringe, respectively. Reaction mixture was left to stand at room temperature and stirred for 7 hours. The solvent was then removed under vacuum, and the residue was dried to obtain triethyl-(2-fluoro-ethyl)-phosphonium bromide as a white solid, in *ca.* 41.3% yield based on triethylphosphine that could be recrystallized from ethyl acetate and deionized water.

Synthesis of triethyl-(2-chloro-ethyl)-phosphonium chlorine. Anhydrous tetrahydrofuran (100 mL) was added into a dry three-diameter flask under nitrogen at room temperature. Then 2-chloroethanol (35.3 mmol) and triethylphosphine (37.3 mmol) were added to this solution by syringe, respectively. Reaction mixture was left to stand at 50℃ for 24 hours. The solvent was then removed by filter, and the residue was dried to obtain triethyl-(2-hydroxy-ethyl)-phosphonium as a white solid, in *ca.* 90% yield based on triethylphosphine. Triethyl-(2-hydroxy-ethyl)-phosphonium (8.3 g, 34.3 mmol) was added into a dry three-diameter flask at room temperature. Then thionyl chloride (100 mL) was added by syringe. Reaction mixture was left to stand at room temperature for 2 hours. The solvent was then removed under vacuum, and the residue was dried to obtain triethyl-(2-chloro-ethyl)-phosphonium chlorine as a white solid, in *ca.* 80% yield based on triethyl-(2-hydroxy-ethyl)-phosphonium.

Synthesis of 1 and 2

The **1** and **2** were obtained by evaporation of deionized water solution containing Na(dca) (0.5342 g, 6.0 mmol), $Cd(NO_3)_2 \cdot 4H_2O$ (0.6169 g, 2.0 mmol) and triethyl-(2-chloro-ethyl)-phosphonium chlorine (0.4339 g, 2.0mmol, for **1**), triethyl-(2-fluoro-ethyl)-phosphonium bromide (0.4900g, 2.0mmol, for **2**), respectively. Cubic colourless crystals of two compounds were collected by filtration and purified by recrystallization from deionized water. The formation of compound **1** and **2** was certified by the IR spectroscopy recorded on a Shimadzu model IR-60 spectrometer.

X-ray Crystallography

The room temperature single-crystal X-ray diffraction data sets of **1** and **2** were collected equipped with a Rigaku Saturn 924 diffractometer and using Mo Kα radiation (λ = 0.71073 Å). Data processing including empirical absorption correction was performed by using the Crystal-clear software package (Rigaku, 2005). The crystal structures of compounds were solved by direct methods and then refined by the full-matrix method refinements on F^2 by means of the SHELXLTL software package. All non-H atoms were refined anisotropically and the position of all H atoms were generated geometrically. Crystallographic data and structure refinement details for compounds **1** and **2** are summarized in Table S1.

CCDC 1835650, 1835651, 1845895 and 1845896 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Ceter via www.ccdc.cam.ac.uk/data.request/cif.

Powder X-ray Diffraction

A PANalytical X'Pert PRO X-ray diffractometer was used to measured **1** and **2** by X-ray powder diffraction (PXRD) at 293 K-453 K. Diffraction patterns were collected in the 2θ range of 5-50° with a step size of 0.02°.

Differential Scanning Calorimetry

DSC measurements were carried out on a NETZSCH DSC 200F3 instrument by heating and cooling the crystalline samples of **1** and **2** with a rate of 10 K/min under a nitrogen atmosphere. The samples (each one is around 5 mg) were placed in aluminum crucible at atmosphere.

Dielectric Constant Measurement

Crystalline powdered samples of **1** and **2** deposited with carbon conducting glue were used in dielectric measurements. The temperature-dependent dielectric constant was performed on a TongHui 2828 impedance analyzer at frequencies of 1 MHz, 100 kHz, 10 kHz, 5 kHz, 1 kHz, 0.5 kHz with an applied electric field of 1 V.

SHG Switching Measurements

SHG switching experiment was measured on powder samples with pulsed Nd: YAG (1064 nm, Vibrant 355 II, OPOTEK) and an input pulse of 350 mV on an FLS 920.
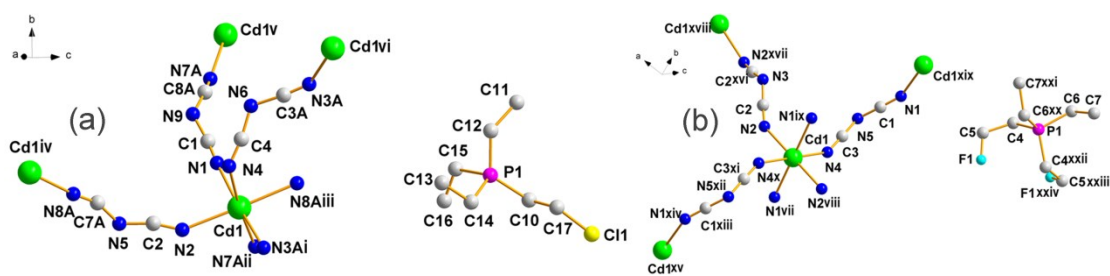
Figure S1. The asymmetric units of **1** (a) and **2** (b) at 293 K. Symmetry codes: (i) -x, -0.5+y, 0.5-z; (ii) 1-x, -0.5+y, 0.5-z; (iii) 0.5-x, 2-y, 0.5+z; (iv) 0.5-x, 2-y, -0.5+z; (v) 1-x, 0.5+y, 0.5-z; (vi) -x, 0.5+y, 0.5-z; (vii) 0.5-x, -0.5+y, 0.5-z; (viii) 0.5-x, 0.5-y, -z; (ix) x, 1-y, -0.5+z, (x) 0.5-x, 0.5-y, -z; (xi) 0.5-x, 0.5-y, -z; (xii) 0.5-x, 0.5-y, -z; (xiii) 0.5-x, 0.5-y, -z; (xiv) 0.5-x, 0.5-y, -z; (xv) 0.5-x, -0.5+y, -0.5-z; (xvi) -x, y, 1.5-z; (xvii) 1-x, y, 0.5-z; (xviii) 1-x, y, 0.5-z; (xix) 0.5-x, 0.5+y, 0.5-z; (xx) -x, y, 1.5-z; (xxi) -x, y, 1.5-z; (xxii) -x, y, 1.5-z; (xxiii) -x, y, 1.5-z; (xxiv) -x, y, 1.5-z.
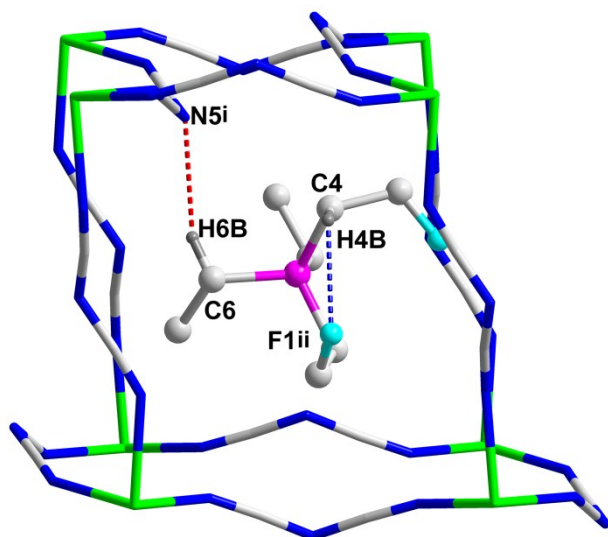

Figure S2. The weak C-H···N and C-H···F hydrogen bonds in **2** presented with dashed lines at room temperature.
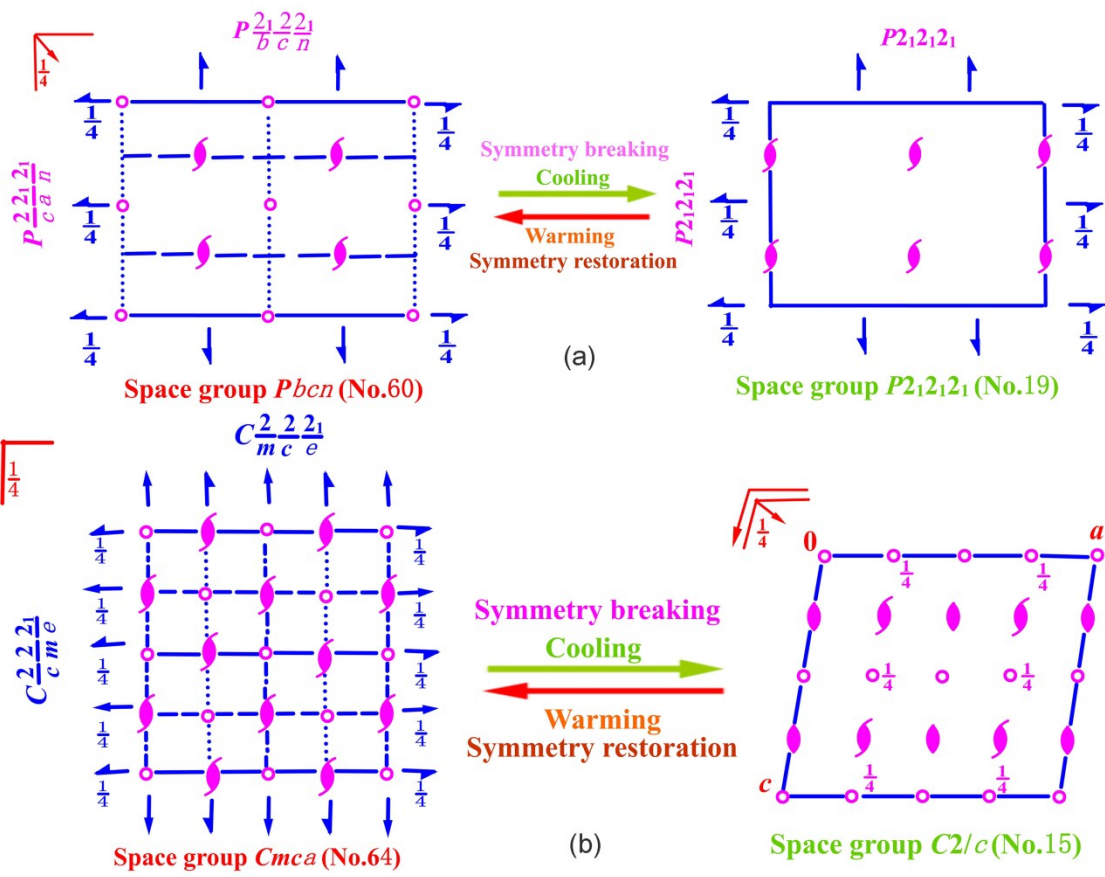
Figure S3. Symmetry transformations of space group of **1**(a) from α_1 to β_1 and **2**(b) from α_2 to β_2.
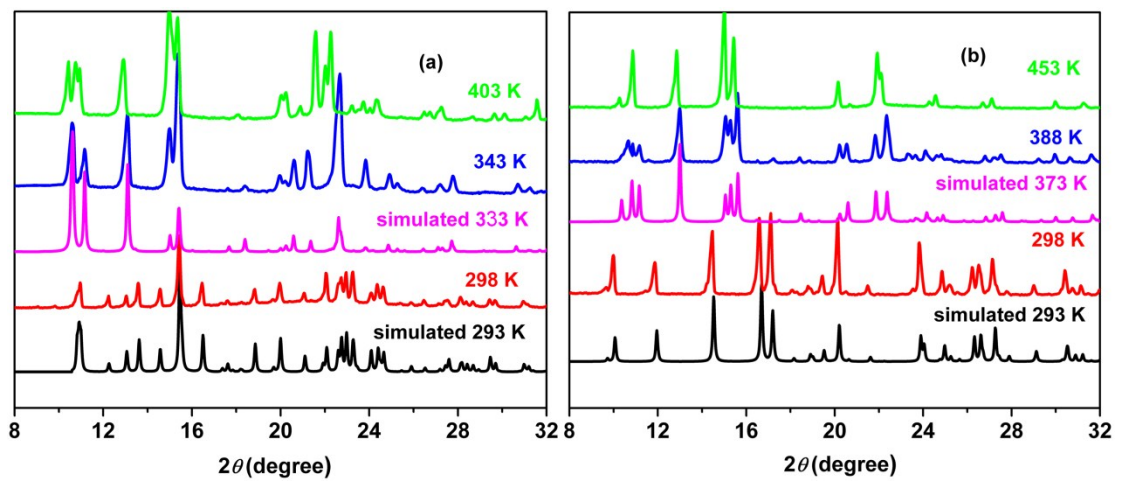

Figure S4. Variable-temperature PXRD patterns of **1** (a) and **2** (b).
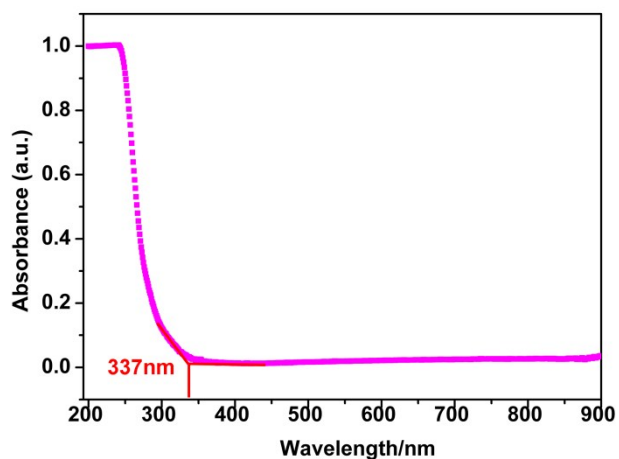
Figure S5. UV-vis diffuse reflection spectrum of **1.**
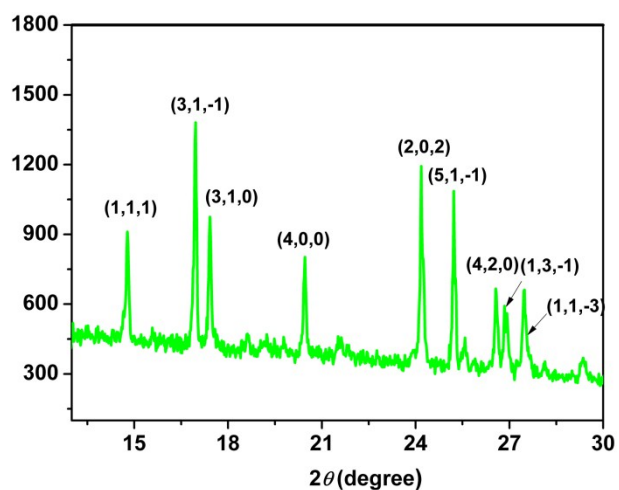
Figure S6. X-ray diffraction pattern for the thin film on ITO-glass of **2** at 293 K.

Figure S7. Evolution of the domain structures of **2** in the heating and cooling process.

Table S1. Crystal data, data collection and reduction parameter of crystals of **1** and **2** at 293 K.

Compound	**1**	**2**
Chemical Formula	$C_{14}H_{19}CdClN_9P$	$C_{14}H_{18}CdFN_9P$
Formula weight	492.20	474.75
Temperature	293 K	293 K
Crystal system	Orthorhombic	Monoclinic

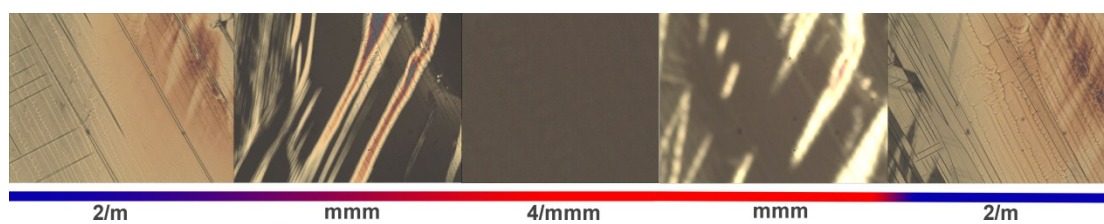|	$P2_12_12_1$	$C2/_C$
Space group	$P2_12_12_1$	$C2/_C$
a, Å	10.7129(4)	18.909(4)
b, Å	12.1860(5)	10.618(2)
c, Å	16.3333(5)	10.507(2)
α, deg	90.00	90.00
β, deg	90.00	111.75(3)
γ, deg	90.00	90.00
V, Å^3	2132.27(14)	1959.4(8)
Z	4	4
Index ranges	$-13 \leq h \leq 14$	$-24 \leq h \leq 24$
	$-22 \leq l \leq 21$	$-13 \leq l \leq 13$
	$-16 \leq k \leq 13$	$-11 \leq k \leq 13$
μ, mm^{-1}	1.241	1.223
reflns measured	14198	6580
independent reflns	5690	2248
reflns used	3874	1981
Goodness-of-fit on F^2	1.342	1.064
Flack parameter	0.27(7)	
Final R indices	$R_1 =0.1210$	$R_1 =0.0242$,
[$I > 2\text{sigma}(I)$]	$wR_2 = 0.3370$	$wR_2 = 0.0574$

Table S2. Crystal data of crystals of **1** and **2**.

Compound	**1**	**2**
Chemical Formula	$C_{14}H_{19}CdClN_9P$	$C_{14}H_{18}CdFN_9P$
Formula weight	492.20	474.75
Temperature	333 K	373 K
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbcn*	*Cmca*
a, Å	16.650(5)	16.172(2)
b, Å	16.667(5)	15.6943(17)
c, Å	15.809(5)	16.8867(18)
α, deg	90.00	90.00
β, deg	90.00	90.00
γ, deg	90.00	90.00
V, Å^3	4387(2)	4286.0(8)
Z	8	8
Index ranges	$-17 \leq h \leq 19$	$-22 \leq h \leq 18$
	$-18 \leq l \leq 18$	$-24 \leq l \leq 24$
	$-19 \leq k \leq 19$	$-22 \leq k \leq 21$
μ, mm^{-1}	1.207	1.118
reflns measured	17662	20435
independent reflns	3815	3329
reflns used	2104	1379

Goodness-of-fit on F^2	0.719	0.884
Final R indices [$I > 2\text{sigma}(I)$]	$R_1 = 0.1289$ $wR_2 = 0.3511$	$R_1 = 0.1470,$ $wR_2 = 0.3692$

Table S3. Parameters of the weak hydrogen bonds for the C2/c form of **2** at 293 K.

Compound	D-H···A	H···A (Å)	D···A (Å)	D-H···A (°)
2	C(6)-H(6B)···N(5)i	2.57	3.432(3)	148
	C(4)-H(4B)···F(1)ii	2.50	3.148(3)	124

Symmetry codes: (i) 0.5-x, 0.5+y, 1.5-z; (ii) -x, y, 1.5-z.

Spontaneous Strain Calculation

The phase transition from β_2 to α_2 phase belongs to the 94 species of ferroelastic phase transitions with an *Aizu* notation of *mmm*F2/*m* in **2**, suggesting it may have potential ferroelastic properties. The total symmetric elements of the crystallographic point group decrease from 8 (E, C_2, C'_2, C''_2, i, σ_h, σ_V, σ'_V) to 4 (E, C_2, i, and σ_h). Hence the possible domain number is $q = 8/4$, *i.e.* two. That is, the spatial orientations of two ferroelastic domains are regarded as a result of symmetry reduction. The spontaneous strain Xs for the two orientational states S_{1a} and S_{1b} is given as

$$x_{s1}(S_{1a}) = \begin{bmatrix} 0 & \epsilon & 0 \\ \epsilon & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix},$$

$$X_{s1}(S_{1b}) = \begin{bmatrix} 0 & -\epsilon & 0 \\ -\epsilon & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{1}$$

The spontaneous strain tensor ϵ obtained from the given lattice parameters is

$$\epsilon = \frac{e_{11} - e_{22}}{2} = (\beta_1 - \pi/2)/2 = 0.190 \tag{2}$$

where e_{11} and e_{22} are the strains and β_1 is the lattice parameter in the monoclinic phase in **2**. The spontaneous strain is equal in all the orientation states of ferroelastic phase, and becomes zero over the whole temperature range in the paraelastic phase. We can calculate the spontaneous strain $x_{s1}(S_l)$ (l = 1, 2) by

$$x_{s1} = \sqrt{2}\,\epsilon = 0.269 \tag{3}$$

These spontaneous strains are write as

$$x_{s1}(S_{1a}) = x_{s1}(S_{1b}) = 0.269 \tag{4}$$

Accompanying with the second phase transition from γ_2 to β_2 phase, symmetry breaking occurred with an *Aizu* notation 4/*mmm*F*mmm* in **2**, which also belongs to the 94 species of ferroelastic phase transitions. Sixteen symmetry elements in the paraelastic phase (tetragonal; 4/*mmm*) decrease to eight in the ferroelastic phase

(orthorhombic; *mmm*). Hence this predicts two (16/8 = 2) possible orientation states. The spontaneous strain Xs for the two orientational states S_{2a} and S_{2b} is given as

$$x_{s2}(S_{2a}) = \begin{bmatrix} \epsilon & 0 & 0 \\ 0 & -\epsilon & 0 \\ 0 & 0 & 0 \end{bmatrix},$$

$$X_{s2}(S_{2b}) = \begin{bmatrix} -\epsilon & 0 & 0 \\ 0 & \epsilon & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{5}$$

The spontaneous strain tensor ϵ obtained from the given lattice parameters is

$$\epsilon = \frac{e_{11} - e_{22}}{2} = \left| \frac{a_2 - c_2}{a_2 + c_2} \right| = 0.02 \tag{6}$$

where e_{11} and e_{22} are the strains and a_2 and c_2 are the lattice parameters in the orthorhombic phase in **2**. We can calculate the spontaneous strain Xs(S_z) (z = 1, 2) by

$$x_{s2} = \sqrt{2}\,\epsilon = 0.03 \tag{7}$$

These spontaneous strains are write as

$$X_{s2}(S_{2a}) = x_{s2}(S_{2b}) = 0.03 \tag{8}$$