Supporting Information

Photoluminescence of Sn^{2+}-I^{-}-mixed molecular perovskites

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Experimental section

Synthesis of starting materials. MDABCO (MDABCO = N-methyl-N'-diazabicyclo(2,2,2)octonium) slats. MDABCO slats were prepared by evaporation of a solution containing stoichiometric MDABCO iodide and the HBF_4 or $HReO_4$ in air. The materials were heating at around 333 K for one day to remove yellow I_2 impurities. The Mdabco iodide was prepared by reaction of dabco and CH_3I in toluene.

Crystal growth. $MDABCO(NH_4)(BF_4)_3$ (**I**) or $MDABCO(NH_4)(ReO_4)_3$ (**II**) was obtained as crystal by evaporation of a solution containing stoichiometric $MDABCO(BF_4)_2$ or $MDABCO(ReO_4)_2$ and NH_4BF_4 or NH_4ReO_4 at around 333 K. The purity of the bulk phases was verified by PXRD (Fig. S1).

Mixing of Sn^{2+}. The crystals of Sn^{2+}-mixed compound were grown as the same method as that for non-mixed compound, except that $SnCl_2$ and H_3PO_2 were used. The used volume amounts of H_3PO_2 solution (50%) is about one sixth of the whole. The use of H_3PO_2 is to avoid of the oxidation of Sn^{2+}. To avoid contamination of the impurities, the crystals were separated before the drying of the solution in the evaporation.

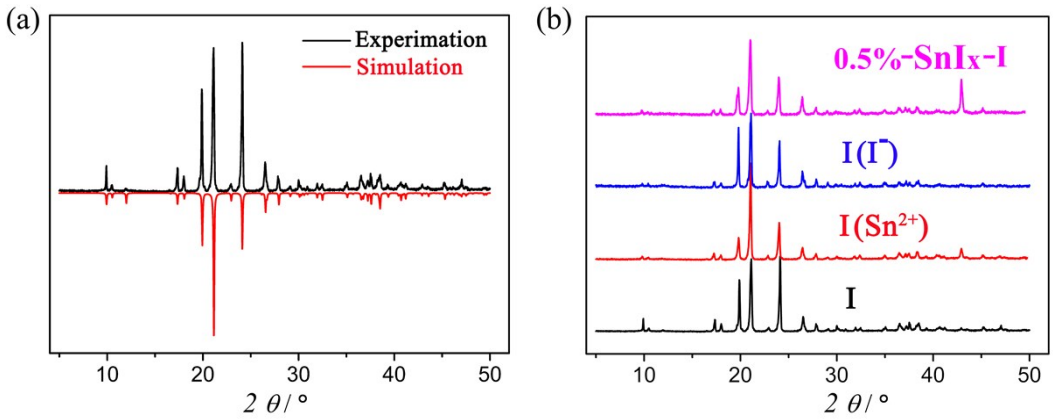

Figure S1. Powder X-ray diffraction pattern of (a) **I** and (b) mixing of SnI_x^{y-} measured at room temperature, verifying the purity of the bulk.

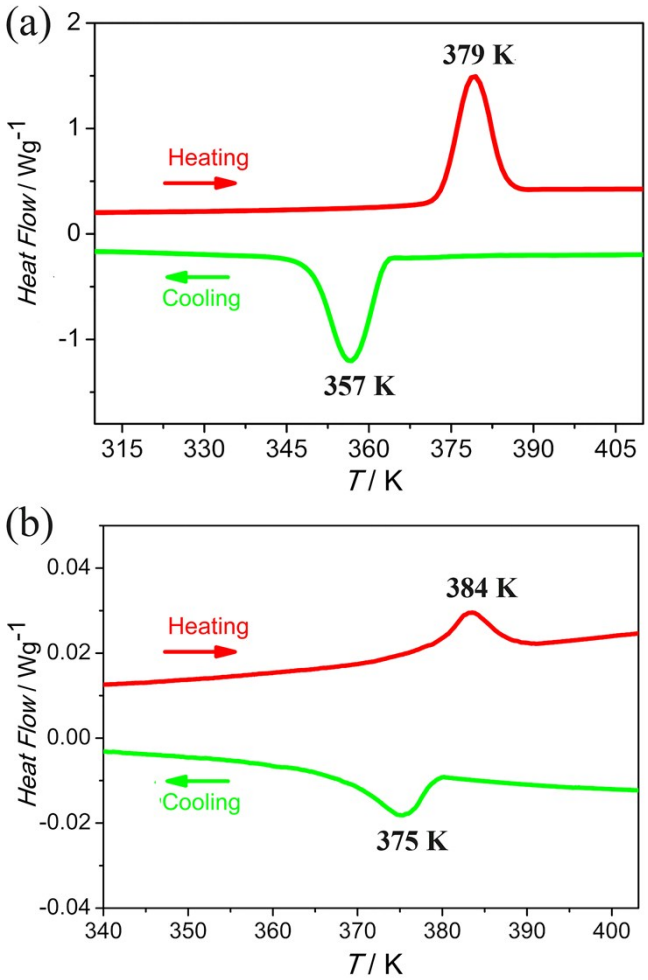

Figure S2. DSC curves of (a) **I** and (b) **II** measured in the heating-cooling cycle.

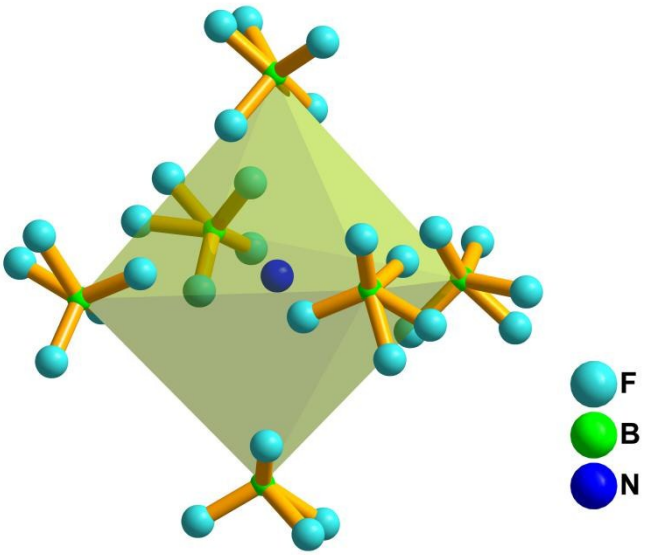

Figure S3. The structure of the $NH_4(BF_4)_6$ octahedron in $(MDABCO)(NH_4)(BF_4)_3$ (**I**), showing the tilting geometry from that of the regular one.

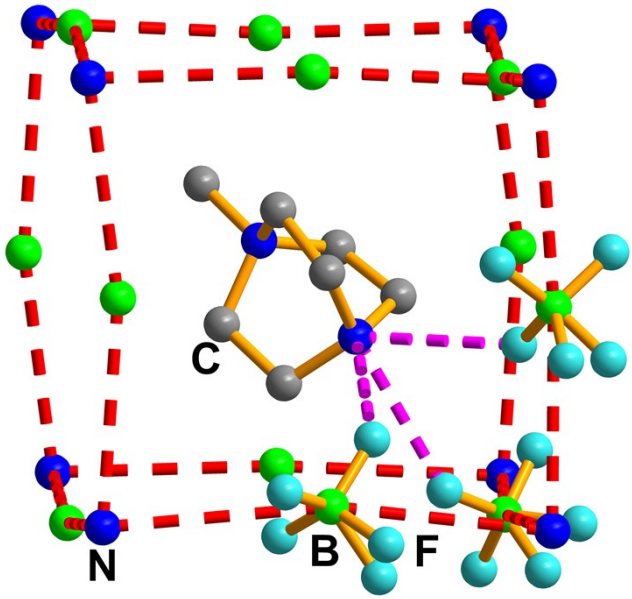

Figure S4. The cage-like structure of $(MDABCO)(NH_4)(BF_4)_3$ (**I**), showing the hydrogen bond interactions between the A-site organic cation the X-site BF_4^- anion. The pink dashed lines indicate the hydrogen bonds. Hydrogen atoms and partial fluorine atoms are omitted for clarity.

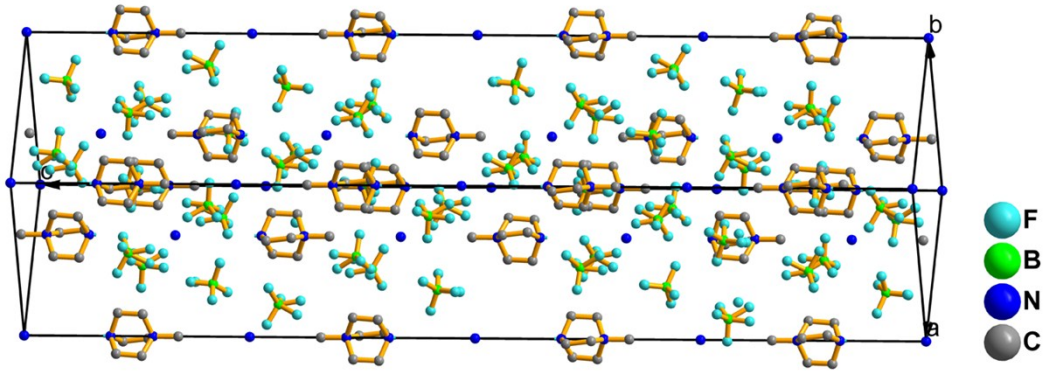

Figure S5. The packing view of $(MDABCO)(NH_4)(BF_4)_3$ (**I**), showing centrosymmetric structure with the head-to-head and tail-to-tail arrangement of the organic cation.

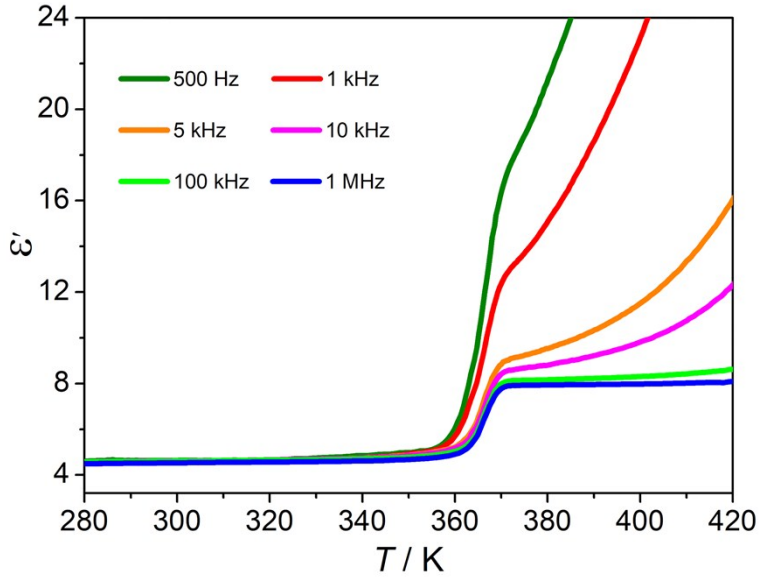

Figure S6. The real part of complex dielectric permittivity (ε') of **I** as a function of temperature at the frequency range from 500 Hz to 1 MHz.

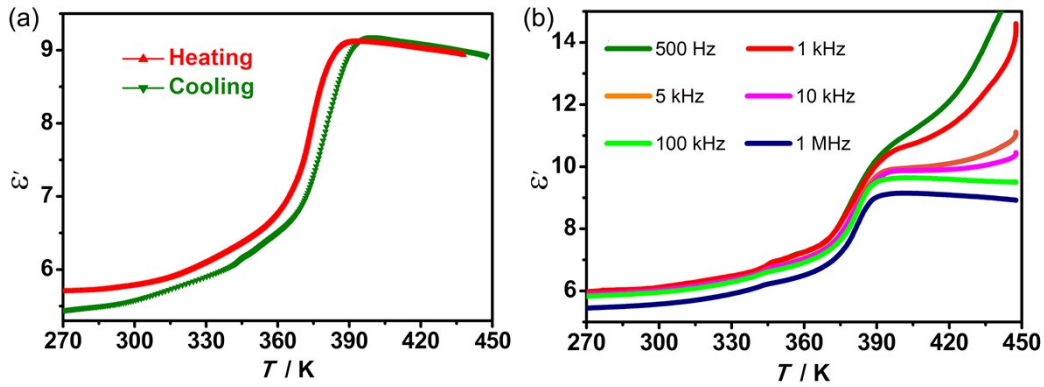

Figure S7. The real part of complex dielectric permittivity (ε') of **II** as a function of temperature at (a) 1 MHz and (b) at the frequency range from 500 Hz to 1 MHz.

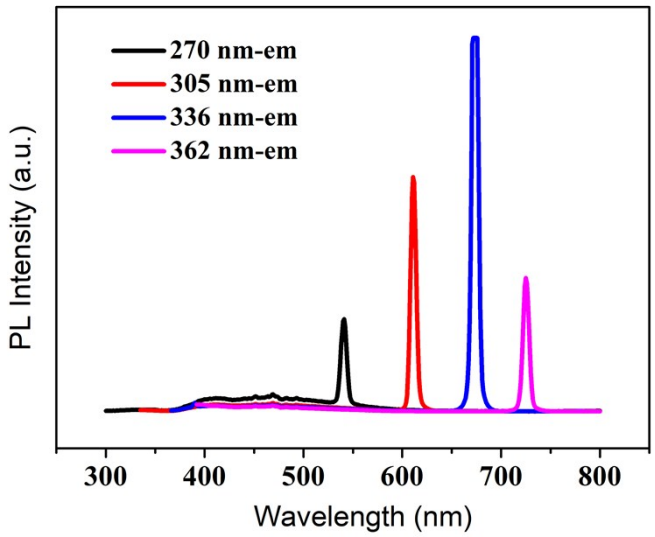

Figure S8. Emission spectra of **I**, confirming that **I** do not emit light under UV excitation.

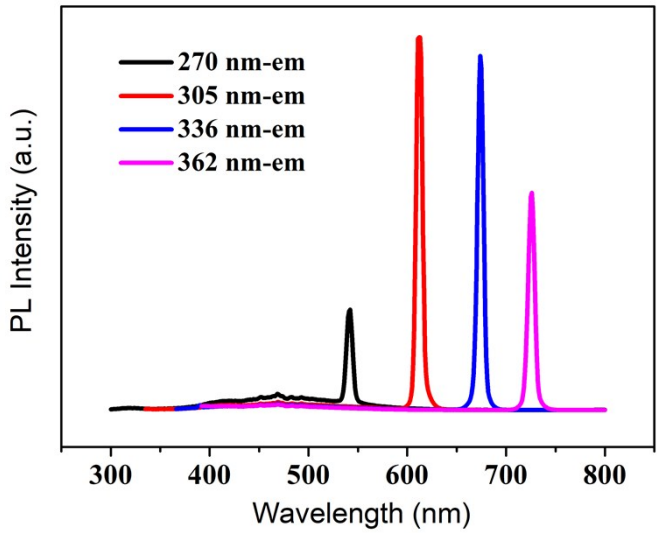

Figure S9. Emission spectra of **I**(I^-), confirming that **I**(I^-)do not emit light under UV excitation.

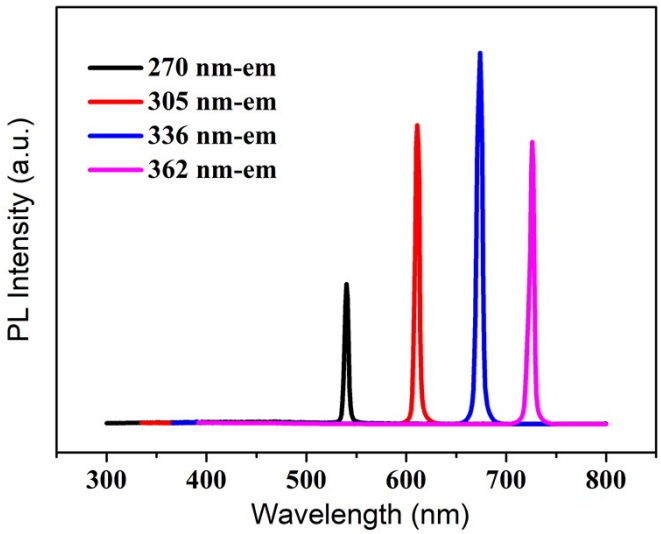

Figure S10. Emission spectra of **I**(Sn^{2+}), confirming that **I**(Sn^{2+}) do not emit light under UV excitation.

Table S1. Crystal data and structure refinements for **I**.

	293 K	408 K
Formula	$C_7H_{20}B_3F_{12}N_3$	$C_7H_{20}B_3F_{12}N_3$
M_w	406.69	406.69
Crystal system	Trigonal	cubic
Space group	*R*−3*c*	*Pm*−3*m*

a [Å]	10.213(2)	7.4699(6)
b [Å]	10.213(2)	7.4699(6)
c [Å]	53.387(9)	7.4699(6)
α [°]	90	90
β [°]	90	90
γ [°]	120	90
V [Å^3]	4823(2)	416.82(10)
Z	12	1
D_{calc} / g·cm^{-3}	1.680	1.620
μ [mm^{-1}]	0.196	0.189
Reflections collected unique	6151 / 1216	666 / 144
R_{int}	0.0572	0.0453
R_1[a], wR_2[b] ($I > 2\sigma(I)$)	0.1254, 0.3255	0.2214, 0.6111
R_1[a], wR_2[b] (all data)	0.1470, 0.3425	0.2710, 0.6333
GOF	1.129	2.454
$\Delta\rho$[c] [e·Å^{-3}]	0.514 / −0.480	0.107 / −0.097

[a] $R_1 = \Sigma||F_o|-|F_c||/|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$. [c] Maximum and minimum residual electron density.

Table S2. Crystal data and structure refinements for **II**.

	293 K	403 K
Formula	$C_7H_{16}N_3O_{12}Re_3$	$C_7H_{16}N_3O_{12}Re_3$
M_w	892.86	892.86
Crystal system	monoclinic	cubic
Space group	$P2_1/c$	$Pm\bar{3}m$
a [Å]	10.3825(8)	7.699(4)
b [Å]	11.2230(5)	7.699(4)
c [Å]	15.1415(9)	7.699(4)
α [°]	90	90
β [°]	90.205(6)	90
γ [°]	90	90
V [Å^3]	1764.32(19)	456.4(7)
Z	4	1
D_{calc} / g·cm^{-3}	3.361	3.088
μ [mm^{-1}]	20.595	19.893

Reflections collected unique	12840 / 4043	1677 / 139
R_{int}	0.0634	0.0500
R_1[a], wR_2[b] ($I > 2\sigma(I)$)	0.0506, 0.1161	0.0512, 0.1350
R_1[a], wR_2[b] (all data)	0.0581, 0.1212	0.0531, 0.1362
GOF	1.155	1.342
$\Delta\rho$[c] [e·Å^{-3}]	2.003 / −2.617	0.987 / −0.800

[a] $R_1 = \Sigma||F_o|-|F_c||/|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$. [c] Maximum and minimum residual electron density.