Electronic Supplementary Information

Crystal-glass phase transition enabling reversible fluorescence switching in zero-dimensional antimony halides

Meijuan Yin,[a] Bohan Li,[a,b] Zishuo Yi,[a] Yuchi Zhang,[a] Zhiguo Xia*[b] and Yan Xu*[a]

[a]Department of Chemistry, College of Sciences, Northeastern University, Shenyang, Liaoning 110819, China

[b]State Key Laboratory of Luminescent Materials and Devices, School of Physics and Optoelectronics, South China University of Technology, Guangzhou, 510641, China.

***Corresponding Author:**

xiazg@scut.edu.cn (Zhiguo Xia)

xuyan@mail.neu.edu.cn (Yan Xu)

Experimental Section:

Materials The raw materials used in the research include Antimony (III) chloride ($SbCl_3$, 98%, Aladdin, Shanghai, China), Methyltriphenylphosphonium chloride (MEPCl, 98%, Aladdin, Shanghai, China), Ethyltriphenylphosphonium chloride (ETPCl, 98%, Aladdin, Shanghai, China), Butyltriphenylphosphonium chloride (BUPCl, 98%, Aladdin, Shanghai, China), Benzyltriphenylphosphonium chloride (BTPCl, 98%, Aladdin, Shanghai, China), N, N-dimethylacetamide (DMF, 99%, Damao, Tianjin, China), Ethyl ether (Et_2O, 99.7%, Sinopharm, shanghai, China), and acetone (99.7%, Sinopharm, shanghai, China). All chemicals were analytically graded and used without further purification.

Synthesis of 0D Sb-based OIMH crystals. 0.1 mmol $SbCl_3$ (0.0228 g) and 0.2 mmol of different organic cations, such as MEPCl (0.0625 g), ETPCl (0.0652 g), BUPCl (0.0710 g) or BTPCl (0.0778 g) were mixed at a molar ratio of 1: 2, which were then dissolved in 2 mL DMF to form a clear precursor solution. After diffusing 2 mL Et_2O into 1 mL DMF, the bulk crystals were obtained by placing the solution overnight at room temperature.

Reversible crystal-glass phase transition of 0D Sb-based OIMH crystals. The glassy state of $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$, and $(BTP)_2SbCl_5$ were obtained by heating the crystals or mixing $SbCl_3$ with the corresponding organic cations of MEPCl, ETPCl, BUPCl, or BTPCl in a molar of 1: 2 to a molten state at 220 ℃ under air condition, and then cooling the melt liquid to room temperature. A reversible glass-crystal phase transition was feasibly accomplished by placing the glass powder in an acetone atmosphere or by heating the glass powder at 90 °C for an hour.

Characterizations. The single crystal data of $(BUP)_2SbCl_5$ OIMHs was collected at 293 K and $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$ and $(BUP)_2SbCl_5$ were collected at 100 K, using the XtaLAB AFC12 X-ray four-circle single crystal diffractometer (Rigaku) equipped with a CCD-detector using a graphite monochromator and the Cu Kα radiation source. Powder X-ray diffraction (PXRD) patterns were taken on an Aeris PXRD diffractometer (PANalytical Corporation, the Netherlands) operating at 40 kV and 15 mA with a monochromatized Cu Kα radiation (λ = 1.5406 Å). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. The CCDC numbers of the $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$, and $(BTP)_2SbCl_5$ crystals are 2285973, 2285974, 2285975, 2285976. The temperature-dependent PXRD patterns of samples after heating were performed by holding the glasses at each temperature (30, 60, 90, 120, 150, 180, 210, and 240 °C) for 30 min prior to the measurement. The photoluminescence excitation (PLE), photoluminescence (PL), PL decay spectra and PLQY measurements were performed on a FLS1000 fluorescence spectrophotometer (Edinburgh Instruments Ltd., UK). The PLQYs were calculated based on the equation: $\eta QE = I_S/(E_R - E_S)$, in which I_S denotes the luminescence emission integrated intensities of the sample, E_R is the integrated intensities of the excitation light of the empty integrated sphere, and E_S is the excitation integrated intensities of the excited sample.[1] Differential Scanning Calorimetry (DSC) measurement was performed on a TA DSC Q2000 instrument to investigate the thermodynamic behaviors of different samples at a heating rate of 5 °C min^{-1}. Thermal gravimetric analysis (TGA) of the samples was conducted on a TG 209F3 from 30 to 500 °C in argon atmosphere with an annealing ramping rate of 10 °C min^{-1}. The light transmittance spectra of the melted $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$, and $(BTP)_2SbCl_5$ glasses were recorded using a Lambda 750 spectrophotometer (PerkinElmer, USA)

in the range from 500 to 2000 nm. The UV-vis absorption spectra of the samples were recorded using a Lambda 750 spectrophotometer (PerkinElmer, USA) in the range from 300 to 800 nm. Raman data was collected on XploRA PLUS (λ = 785 nm). Fourier-transform infrared (FTIR) was performed on a Bruker VERTEX 70 with a KBr pelleting method.

Figure Captions:

Table S1. The crystal structure parameters of $(MEP)_2SbCl_5$.

Table S2. The crystal structure parameters of $(ETP)_2SbCl_5$.

Table S3. The crystal structure parameters of $(BUP)_2SbCl_5$.

Table S4. The crystal structure parameters of $(BTP)_2SbCl_5$.

Figure S1. (a-d) The simulated and experiment PXRD patterns of $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$ and $(BTP)_2SbCl_5$ crystals.

Figure S2. The light transmittance of $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$ and $(BTP)_2SbCl_5$ glasses.

Figure S3. (a-d) The UV-vis absorption spectra of $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$ and $(BTP)_2SbCl_5$ crystals and glasses.

Figure S4. (a-d) Photoluminescence excitation, and photoluminescence emission spectra of $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$ and $(BTP)_2SbCl_5$ crystals.

Figure S5. (a-d) The PLQY spectra of $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$ and $(BTP)_2SbCl_5$ crystals.

Figure S6. (a-d) Photoluminescence excitation, and photoluminescence emission spectra of $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$ and $(BTP)_2SbCl_5$ glasses.

Figure S7. (a-d) The PLQY spectra of $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$ and $(BTP)_2SbCl_5$ glasses

Figure S8. (a-d) The simulated and experiment PXRD patterns of $(MEP)_2SbCl_5$,

$(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$ and $(BTP)_2SbCl_5$ crystals by the acetone vapor-induced recrystallization.

Figure S9. (a-d) PXRD of $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$ and $(BTP)_2SbCl_5$ glasses after heating.

Figure S10. (a-d) Photoluminescence excitation, and photoluminescence emission spectra of $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$ and $(BTP)_2SbCl_5$ crystals by the acetone vapor-induced recrystallization (Re-crystals).

Table S1. The crystal structure parameters of $(MEP)_2SbCl_5$.

Formula moiety	$C_{38}H_{36}Cl_5P_2Sb$
Dimension (mm)	0.2×0.15×0.1
Molecular weight	853.61
Temperature (K)	150
Crystal system	Monoclinic
Space group	$P2_1/n$
Z	2
a (Å)	9.1192(3)
b (Å)	15.8880(7)
c (Å)	13.1739(5)
β(°)	102.6770 (10) °
V (Å^3)	1862.90(12)
ρ_{calc} (g/cm^3)	1.522
μ (mm^{-1})	1.212
Reflections measured	33175
Reflections independent	3289
2θ max (θ)	50.054
h, k, l -limits	-10≤h≤10 -18≤k≤18 -15≤l≤15
R_{int}	0.0292
R_1 [I > 2sigma(I)][a]	0.0818
$wR(F_2)$·[I > 2sigma(I)][b]	0.1749
Goof	1.059
$\Delta\rho_{max}$ (e/Å^3)	0.82
$\Delta\rho_{min}$ (e/Å^3)	-1.65

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$, [b] $wR_2 = [w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table S2. The crystal structure parameters of $(ETP)_2SbCl_5$.

Formula moiety	$C_{40}H_{40}Cl_5P_2Sb$
Dimension (mm)	0.2×0.18×0.16
Molecular weight	881.66
Temperature (K)	100(2)
Crystal system	Triclinic
Space group	*P*1
Z	3
a (Å)	10.23120(10)
b (Å)	10.29850(10)
c (Å)	28.7642(4)
β(°)	97.0070(10)
V (Å^3)	2957.62(6)
ρ_{calc} (g/cm^3)	1.485
μ (mm^{-1})	1.148
Reflections measured	53935
Reflections independent	17391
2*θ* max (*θ*)	50.484
h, *k*, *l* -limits	-15≤*h*≤14 -14≤*k*≤13 -42≤*l*≤41
R_{int}	0.0250
R_1 [$I > 2\text{sigma}(I)$][a]	0.0274
$wR(F_2)\cdot[I > 2\text{sigma}(I)]$[b]	0.0594
Goof	1.060
$\Delta\rho_{max}$ (e/Å^3)	1.175
$\Delta\rho_{min}$ (e/Å^3)	-1.760

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$, [b] $wR_2 = [w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table S3. The crystal structure parameters of $(BUP)_2SbCl_5$.

Formula moiety	$C_{44}H_{48}Cl_5P_2Sb$
Dimension (mm)	0.3×0.2×0.1
Molecular weight	937.76
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
Z	2
a (Å)	10.0525(12)
b (Å)	16.9015(17)
c (Å)	13.739(2)
β(°)	109.287(16) °
V (Å^3)	2203.2(6)
ρ_{calc} (g/cm^3)	1.414
μ (mm^{-1})	1.032
Reflections measured	10469
Reflections independent	5152
2θ max (θ)	58.558
h, k, l -limits	-10≤h≤13 -23≤k≤21 -18≤l≤21
R_{int}	0.0227
R_1 [I > 2sigma(I)][a]	0.0452
$wR(F_2)$·[I > 2sigma(I)][b]	0.0851
Goof	0.998
$\Delta\rho_{max}$ (e/Å^3)	0.540
$\Delta\rho_{min}$ (e/Å^3)	-1.263

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$, [b] $wR_2 = [w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table S4. The crystal structure parameters of $(BTP)_2SbCl_5$.

Formula moiety	$C_{50}H_{44}Cl_5P_2Sb$
Dimension (mm)	0.2×0.18×0.16
Molecular weight	1005.79
Temperature (K)	150
Crystal system	Monoclinic
Space group	$P2_1/n$
Z	2
a (Å)	10.4844(4)
b (Å)	14.5953(4)
c (Å)	15.1518(6)
β(°)	103.5520(10) °
V (Å^3)	2254.02(14)
ρ_{calc} (g/cm^3)	1.482
μ (mm^{-1})	1.014
Reflections measured	9846
Reflections independent	4622
2θ max (θ)	50.484
h, k, l -limits	-13≤h≤13 -18≤k≤18 -18≤l≤18
R_{int}	0.0440
R_1 [I > 2sigma(I)][a]	0.0339
$wR(F_2)$·[I > 2sigma(I)][b]	0.0640
Goof	1.057
$\Delta\rho_{max}$ (e/Å^3)	0.557
$\Delta\rho_{min}$ (e/Å^3)	-1.554

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$, [b] $wR_2 = [w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

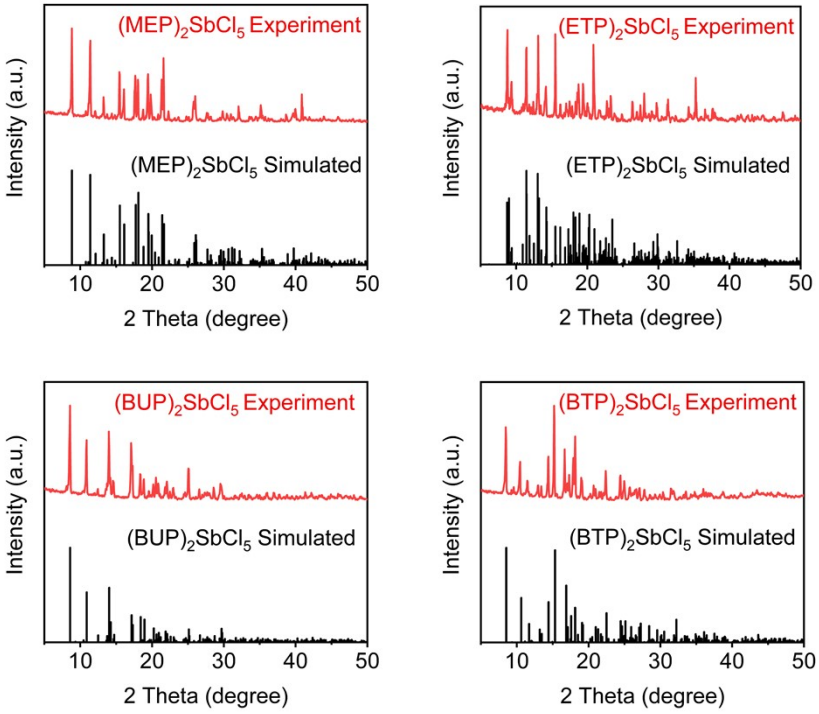

Figure S1. (a-d) The simulated and experiment PXRD patterns of $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$ and $(BTP)_2SbCl_5$ crystals.

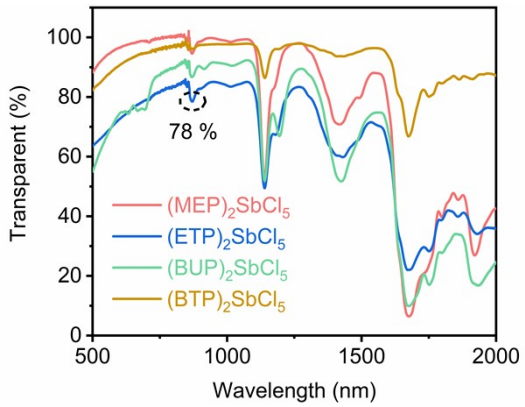

Figure S2. The light transmittance of $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$ and $(BTP)_2SbCl_5$ glasses.

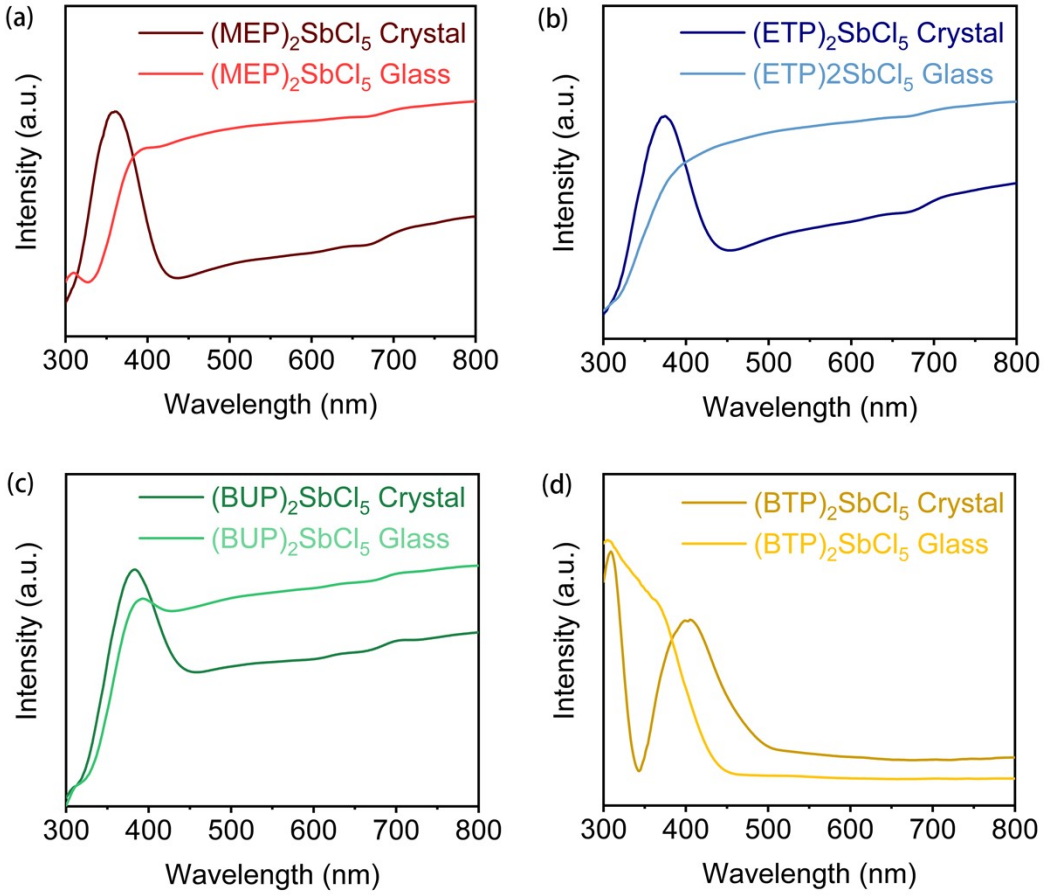

Figure S3. (a-d) The UV-vis absorption spectra of $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$ and $(BTP)_2SbCl_5$ crystals and glasses.

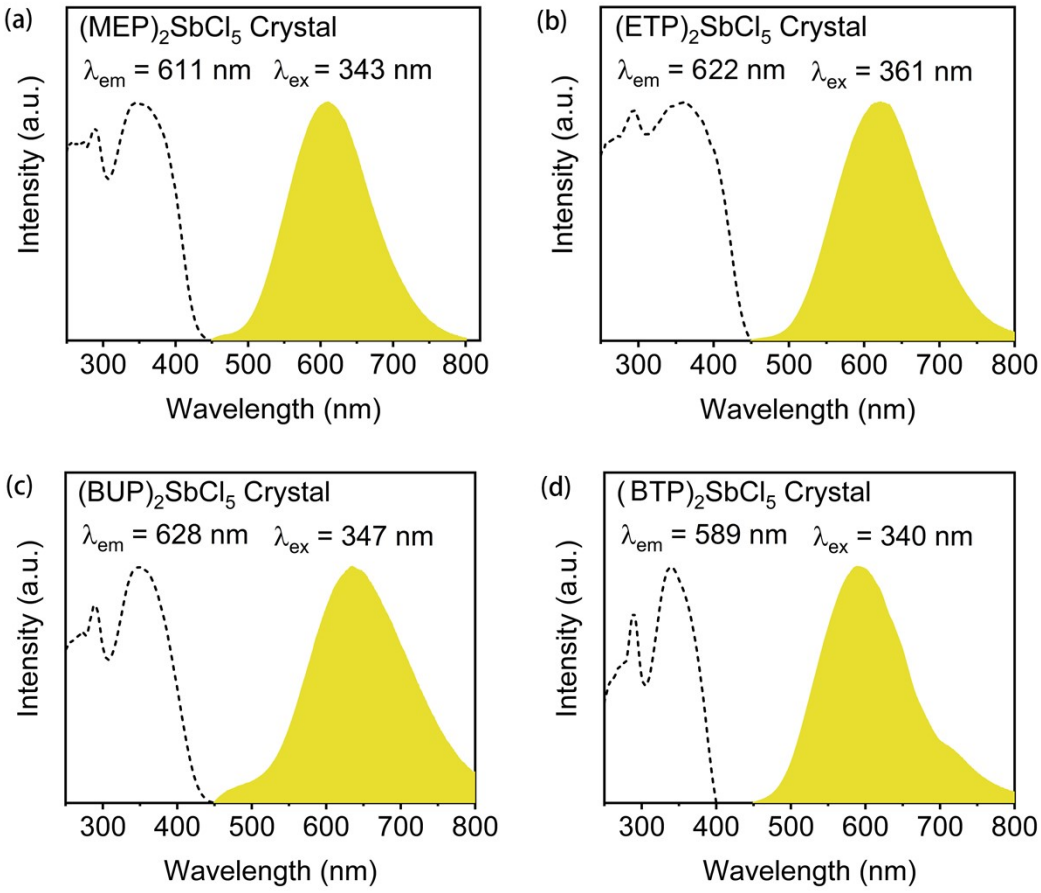

Figure S4. (a-d) Photoluminescence excitation, and photoluminescence emission spectra of $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$ and $(BTP)_2SbCl_5$ crystals.

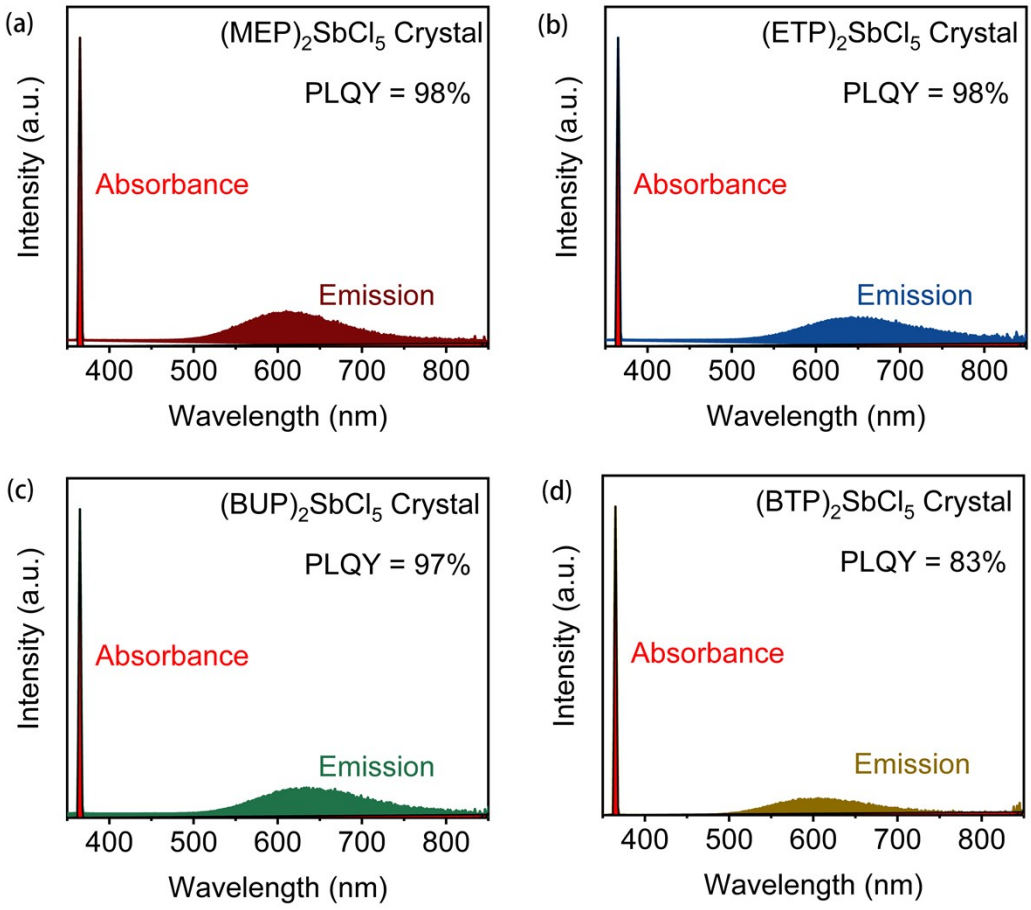

Figure S5. (a-d) The PLQY spectra of $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$ and $(BTP)_2SbCl_5$ crystals.

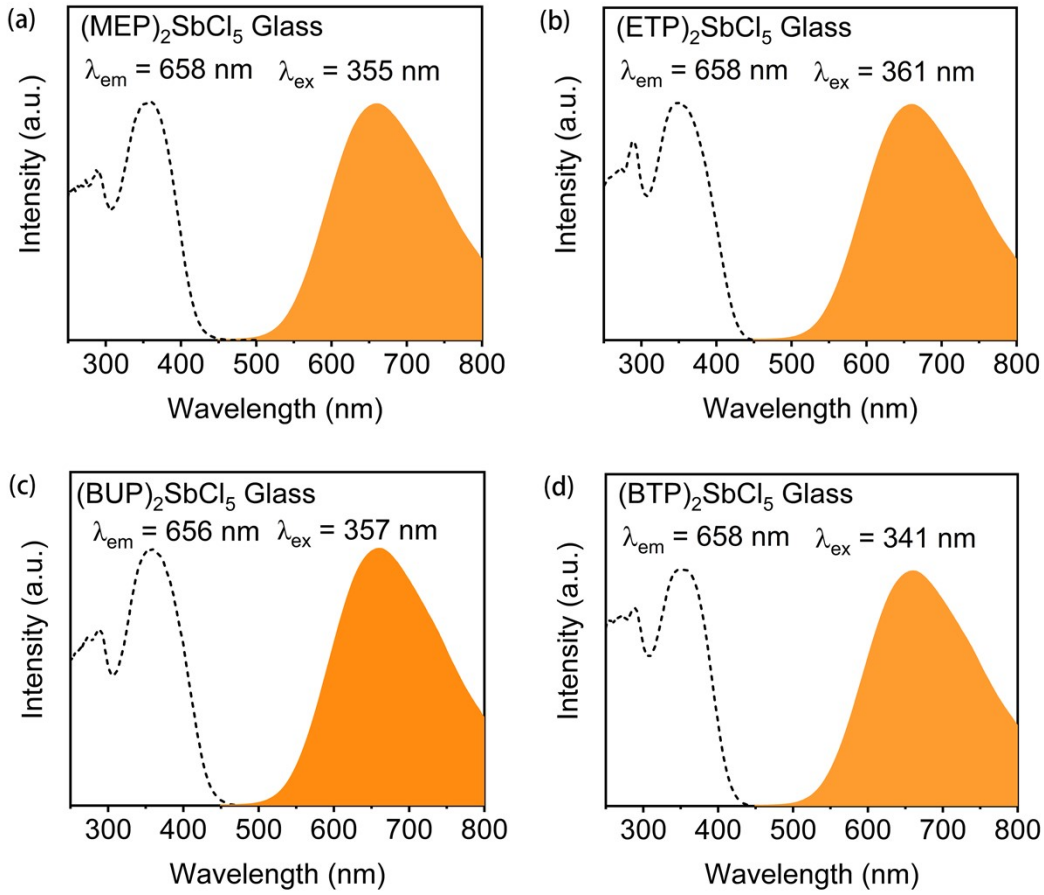

Figure S6. (a-d) Photoluminescence excitation, and photoluminescence emission spectra of $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$ and $(BTP)_2SbCl_5$ glasses.

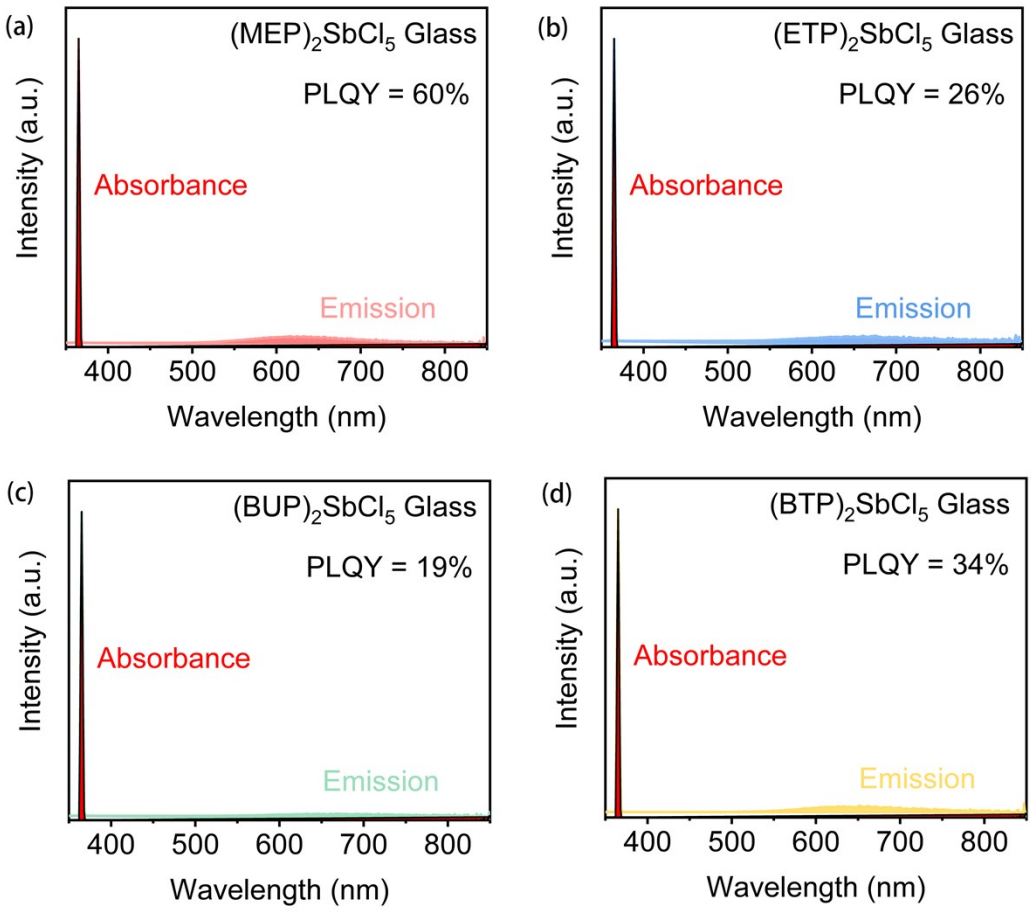

Figure S7. (a-d) The PLQY spectra of $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$ and $(BTP)_2SbCl_5$ glasses.

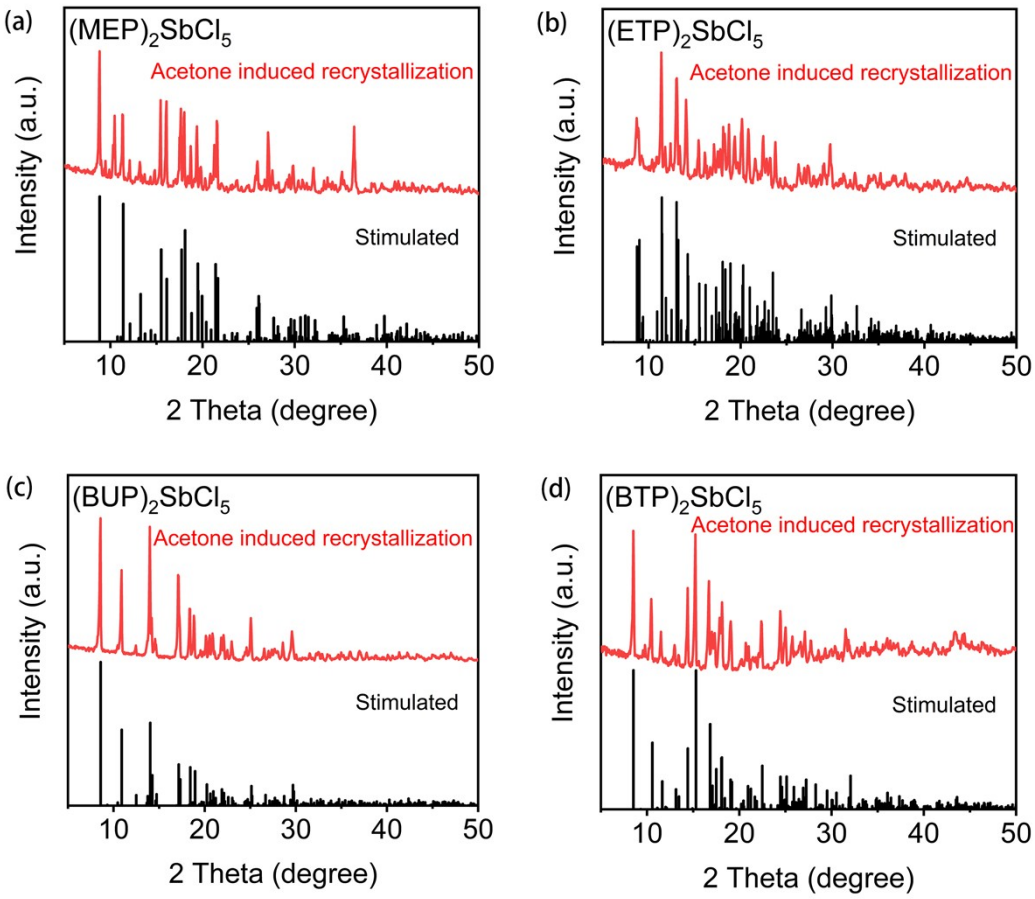

Figure S8. (a-d) The simulated and experiment PXRD patterns of $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$ and $(BTP)_2SbCl_5$ crystals by the acetone vapor-induced recrystallization.

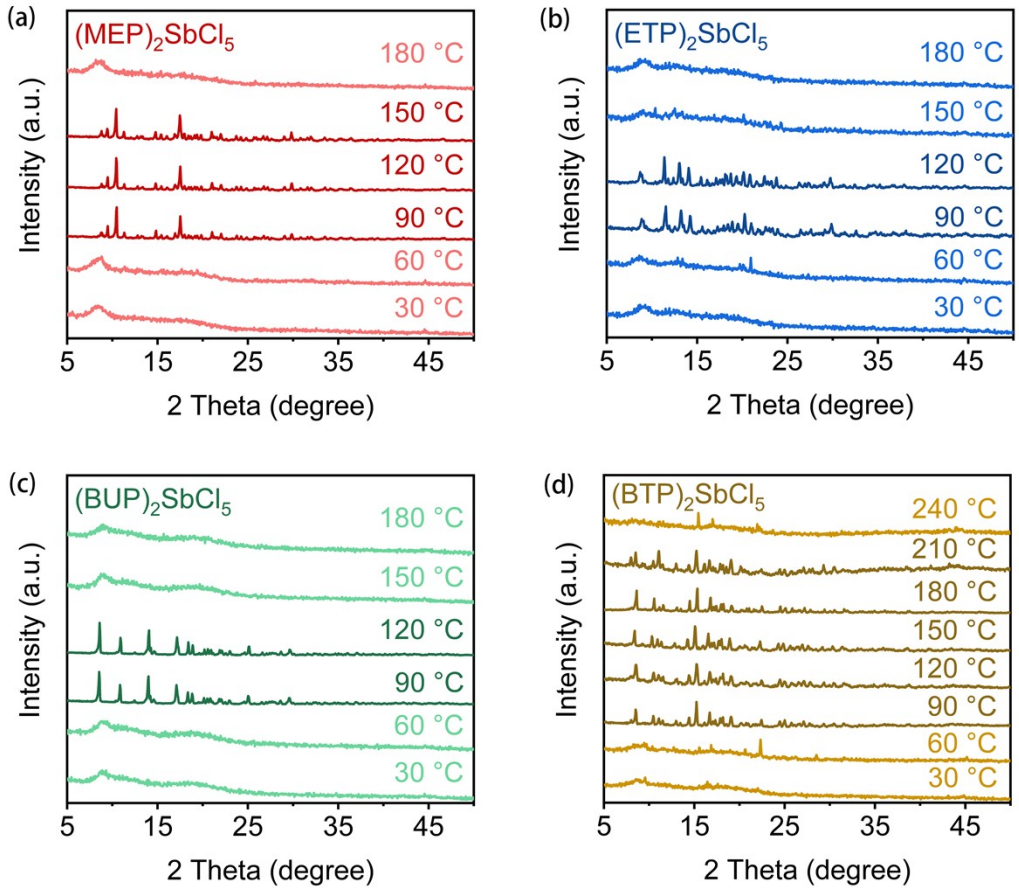

Figure S9. (a-d) PXRD of $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$ and $(BTP)_2SbCl_5$ glasses after heating.

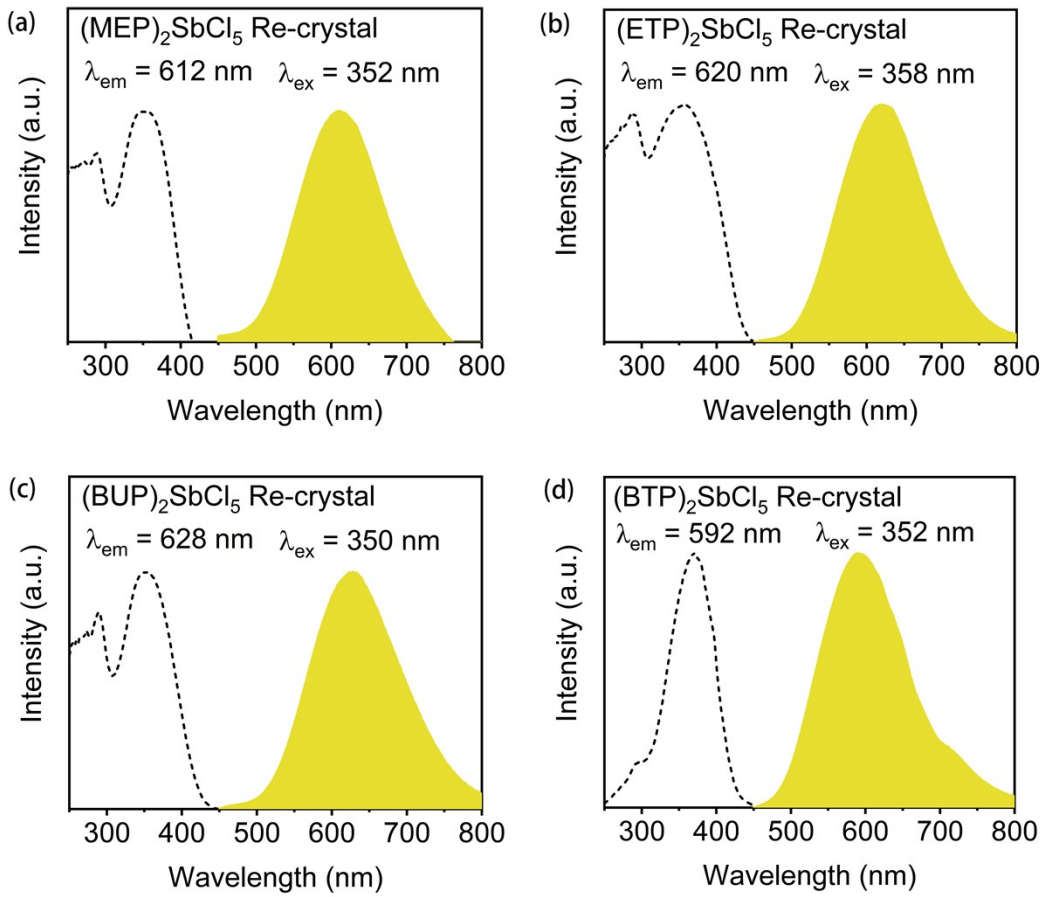

Figure S10. (a-d) Photoluminescence excitation, and photoluminescence emission spectra of $(MEP)_2SbCl_5$, $(ETP)_2SbCl_5$, $(BUP)_2SbCl_5$ and $(BTP)_2SbCl_5$ crystals by the acetone vapor-induced recrystallization (Re-crystals).

Reference

1 X. Bai, G. Caputo, Z. Hao, V. T. Freitas, J. Zhang, R. L. Longo, O. L. Malta, R. A. S. Ferreira and N. Pinna, *Nat. Commun.*, 2014, **5**, 5702.