Supplementary data

Stepwise structural transformation in Hybrid Antimony Chloride for Time-resolved and Multi-Stages Informational Encryption and Anti-counterfeiting

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Experimental

1. Materials and Methods

All the reagents and chemicals including $SbCl_3$ (99%, Aladdin), [Bzmim]Cl (>99%, Lanzhou Greenchem ILs), N, N'-dimethylformamide (DMF, 97%), and ethanol (99.7%, CHRON CHEMICALS) were commercially available and used as supplied without further purification.

Powder X-ray diffraction (PXRD) patterns were obtained from a Miniflex II diffractometer. The theoretical PXRD patterns were simulated from the Mercury program. Emission and excitation spectra at RT and 200 K were measured on FLS1000 produced by Edinburgh instrument. Element analysis was measured on Elementar Analysensysteme GmbH Unicube instrument. The Single-crystal X-ray diffraction data were collected on a SuperNova CCD diffractometer with graphite-monochromated MoK_α (0.71073 Å) at 295(2) K.

Element analysis of C, H and N was performed on a German Elementary Vario EL III instrument. $C_{44}H_{52}N_8Sb_4Cl_{16}$ (**1**) Calculated: C, 30.29%, H, 3%, N, 6.41%; found: C, 30.53%, H, 2.87%, N, 6.59%.); $C_{22}N_4H_{26}SbCl_5$ (**2**) Calculated: C, 40.94%; H, 4.06%;

N, 8.68%; Found: C, 40.68; H, 3.59%; N, 8.73%; $C_{33}N_6H_{39}SbCl_6$ (**3**) Calculated: C, 46.40%; H, 4.60%; N, 9.84%; Found: C, 45.58%; H, 4.79%; N, 9.62%.

2. Crystallography

Structures of **1** was determined by single-crystal X-ray diffraction, and were solved by direct methods and refined by full-matrix least-squares on F^2 by using the programs SHELX.[1]

Crystal data for compound **1**: $C_{44}H_{52}N_8Sb_4Cl_{16}$, M = 1747.13, monoclinic, $P2_1/n$, a = 10.1143(3), b = 20.4472(6), c = 16.4932(6) Å, β = 105.624(4)°, V = 3284.91(19) Å^3, T = 295(2) K, Z = 2, μ(Mo-K_α) = 2.315 mm^{-1}, F(000) = 1696, crystal size 0.4 × 0.28 × 0.27 mm, 7505 independent reflections (R_{int} = 0.0620). Final R_1 = 0.0398 for 5515 reflections with $I > 2\sigma(I)$ and wR_2 = 0.914 for all data.

3. Synthesis of 1, 2 and 3.

1 was formed phase-pure from reaction of $SbCl_3$ and [Bzmim]Cl with a molecular ratio of 1:1. The mixture was dissolved in methanol, and then crystals of **1** would generate after evaporation of methanal with a yield of about 79%.

2 was formed phase-pure from reaction of $SbCl_3$ and [Bzmim]Cl with a molecular ratio of 1:2. The mixture was dissolved in DMF. After adding diethyl ether into the mixture, crystals of **2** would be formed immediately. The yield of the reaction is about 90%.

3 was formed phase-pure from reaction of $SbCl_3$ and [Bzmim]Cl with a molecular ratio of 1:3. The mixture was dissolved in DMF. After adding diethyl ether into the mixture, crystals of **3** would be formed immediately. The yield of the reaction is about 95%.

4. Concentration-controlled reaction rate

A series of [Bzmim]Cl ethanol solutions with concentrations of 1 mol/L, 1.5 mol/L, 2 mol/L, 2.5 mol/L, 3 mol/L, and 4 mol/L, and $SbCl_3$ ethanol solution with concentrations of 1 mol/L were prepared firstly. 100 μL $SbCl_3$ solution was respectively added to the plastic vials. Then 100 μL [Bzmim]Cl solutions with concentrations of 1, 1.5, 2, 2.5, 3, and 4 mol/L were dripped in the vials,

respectively. The PL switching from red to green-yellow light shown in Figure 2 was performed by heated the vails at 343 K for 1 hour.

5. Time-resolved Information decryption processes

On filter paper: [Bzmim]Cl ethanol solution with concentrations of 4.5 mol/L, and a series of $SbCl_3$ ethanol solutions with concentrations of 0.5 mol/L, 1 mol/L, and 1.5 mol/L were prepared firstly. $SbCl_3$ solutions were dripped on the filter papers (0.5 cm × 0.5 cm) according to the order shown in Figure 4b. Then [Bzmim]Cl solutions with concentrations of 4.5 mol/L were dripped on the papers, note that the papers must be fully soaked with [Bzmim]Cl solution.

Letter on paper: $SbCl_3$ solutions with concentrations of 1.5, 0.8, and 0.5 mol/L were used as inks to write 'L', '¯' and 'I' respectively on filter paper (Figure 4b). Then the paper was fully immersed in [Bzmim]Cl solution with a concentration of 4.5 mol/L for 1 second.

6. Information multi-stage encryption processes

$SbCl_3$ solutions with concentrations of 0.5 and 1 mol/L were used as ink to written 'dis' and 'agree' respectively on filter paper (Figure 5b, 2 cm*4 cm). Then the paper was fully immersed in [Bzmim]Cl solution with a concentration of 4.5 mol/L for 1 second. 1 hour later, the word 'disagree' emerged with red colour emission under a UV lamp (390 nm). After transferring the paper into a pre-heated oven (353 K) and kept there for half an hour, the PL colour of 'agree' would change from red to yellow-green.

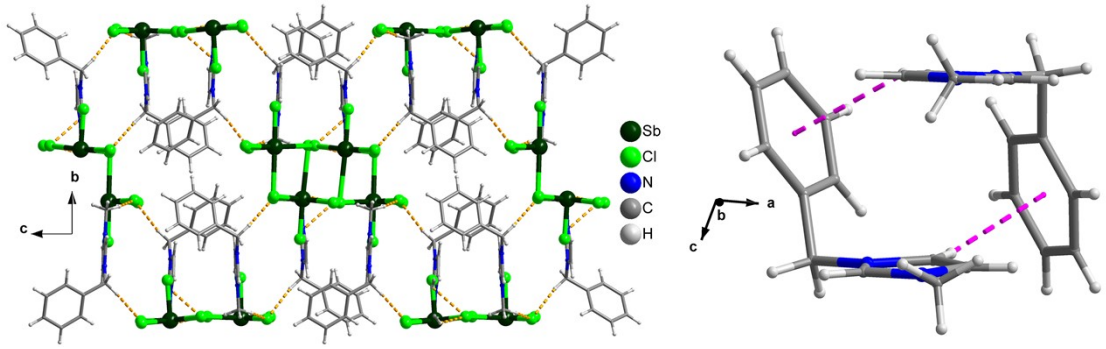

Figure S1. C-H···Cl hydrogen bonds (left) and C-H···π interactions (right) in **1**.

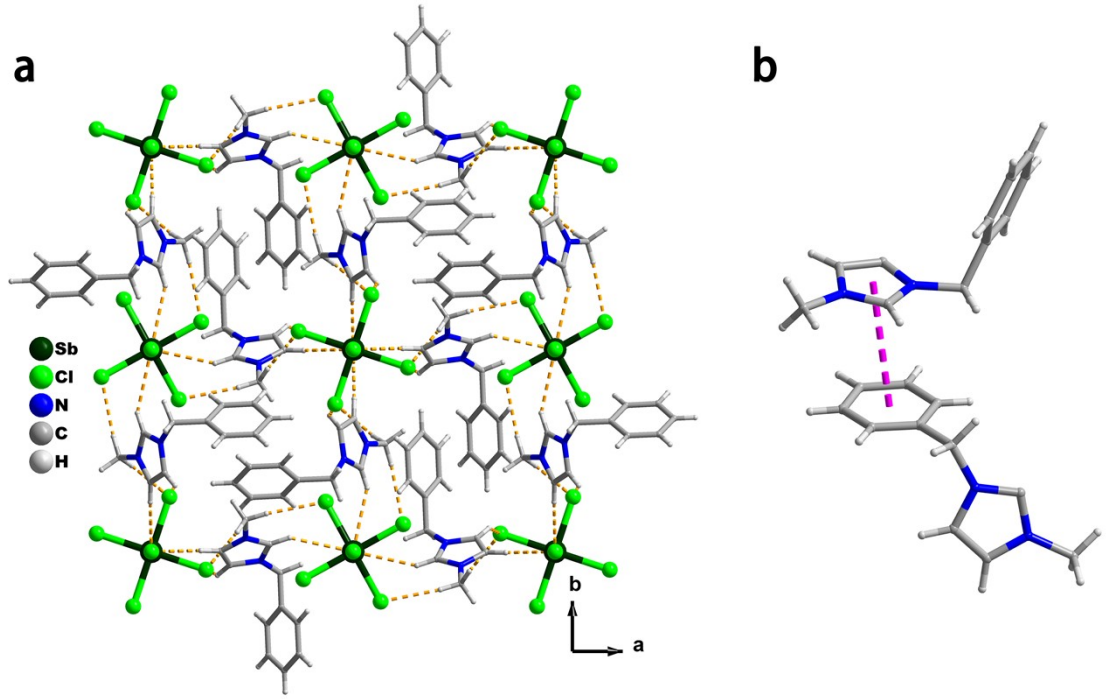

Figure S2. C-H···Cl hydrogen bonds (left) and π···π interactions (right) in **2**.

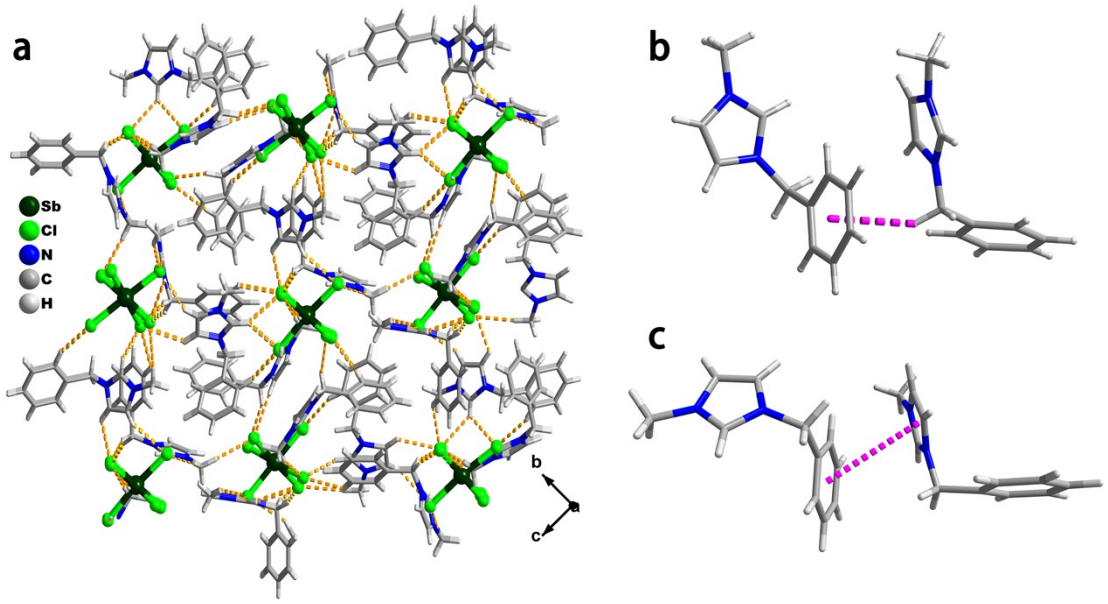

Figure S3. (a) C-H···Cl hydrogen bonds in **3**. (b) C-H···π interactions in **3**. (c) π···π interactions in **3**.

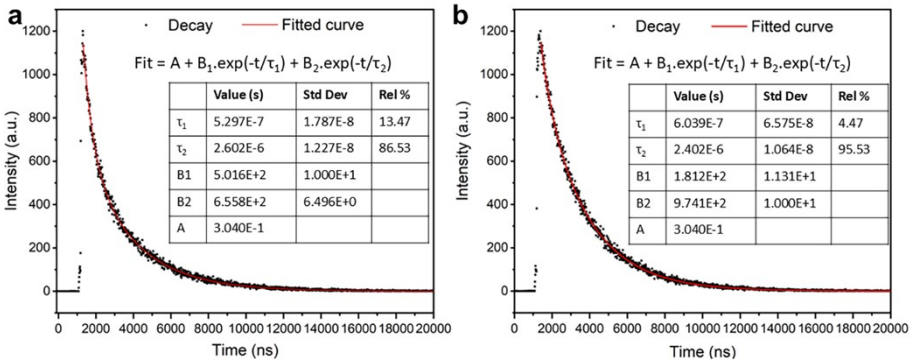

Figure S4. The decay and fitted curves of **2** (a) and **3** (b).

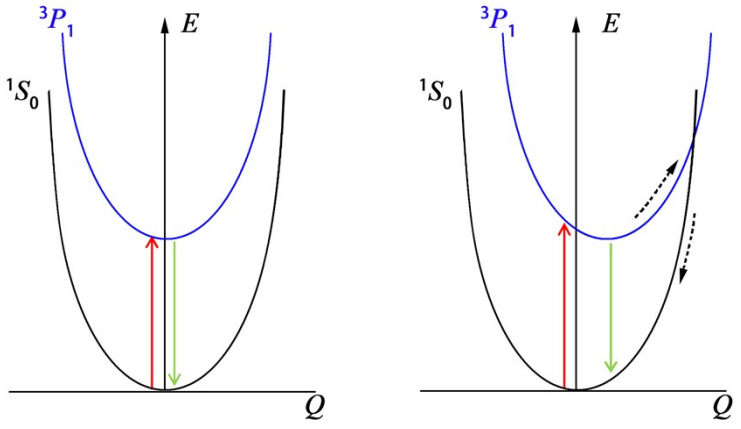

Figure S5. The possible configurational coordinate diagram of isolated $[SbCl_6]^{3-}$ (left) and $[Sb_4Cl_{16}]^{4-}$ (right). The energy E is plotted vs the coordinate Q. $^1S_0$ and $^3P_1$ refer to the ground state and excited state, respectively. The absorption transition is indicated by red line, the emission transition is indicated by green line. Dotted line indicates the thermally induced luminescent quenching process.

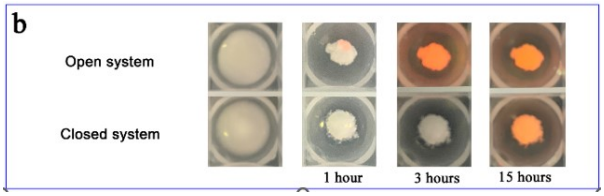

Figure S6. The transformation time in open and closed systems.

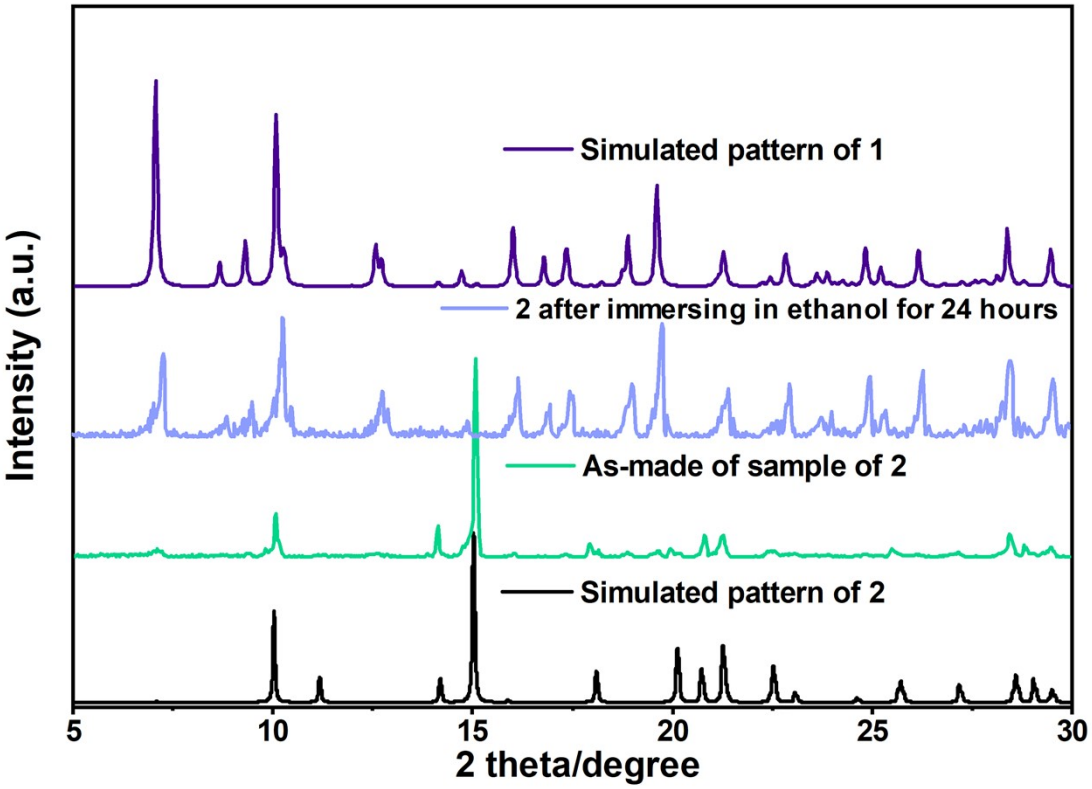

Figure S7. PXRD patterns of the powder of **2** before (green line) and after (purple line) immersed in ethanol.

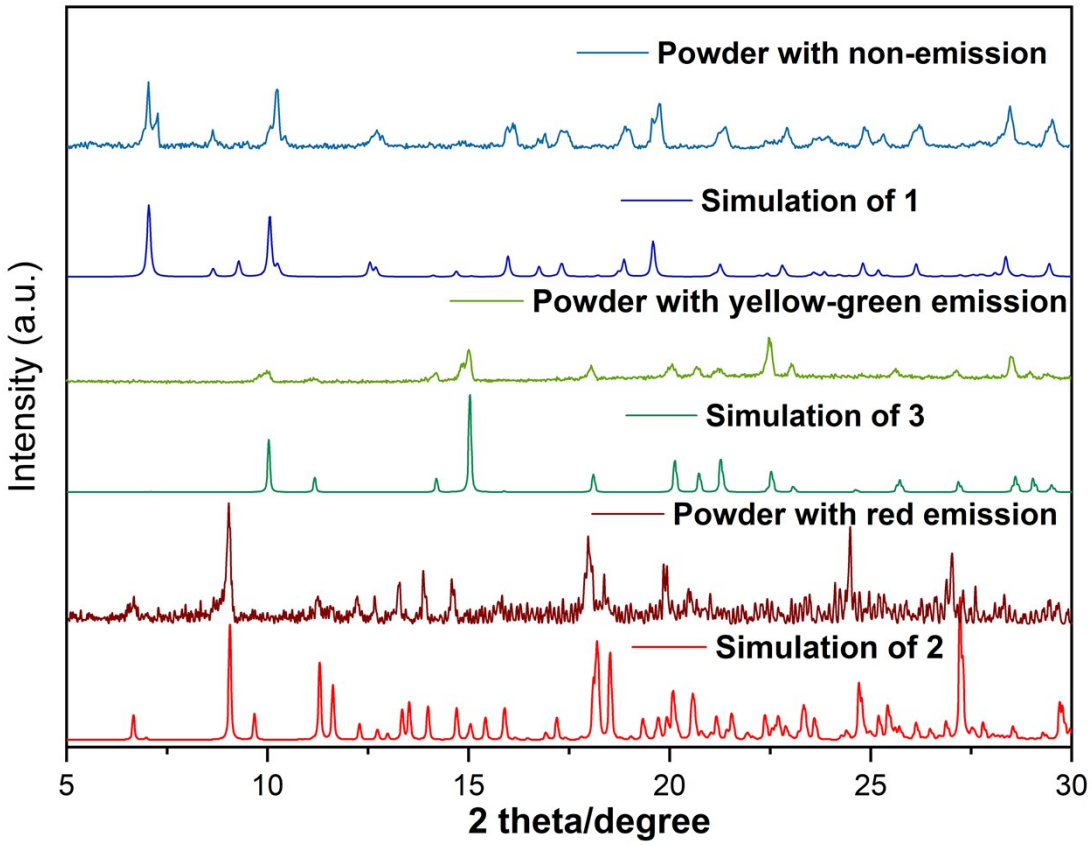

Figure S8. Comparation of the PXRD patterns of the powder with non-emission, yellow-green (green line) and red (blue line) emission with the simulated PXRD patterns of **1**, **2**, and **3** from the corresponding single-crystal X-ray data.

Reference:

1. Sheldrick, G.M. SHELXT–Integrated space-group and crystal-structure determination, Acta Crystallogr. Sect. C. 71 (2015) 3-8.