Supporting Information

# Ultrabroad NIR Emission from Paired $[SbCl_4]^-$ Clusters in Hybrid Antimony Chlorides

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## MATERIAL AND METHOD

### Materials Preparation.

Antimony (III) chloride ($SbCl_3$, 99%), Benzyltriethylammonium chloride (TEBAC, 98%), Benzyltriphenylphosphonium chlorid (BPPC), Benzyltrimethylammonium Chloride (TMBAC, 98%), Methyltriphenyl phosphonium chloride (MTPC, 98%),Tetrapropylammonium Chloride (TPAC, 98%), Phenyltributylammonium chloride (TBBAC, 98%) were all purchased from Aladdin, and they were used directly without any purification and other treatments.

### Synthesis of $XSbCl_4$ single crystals

$X_2SbCl_4$ SCs were synthesized by a Slow cooling crystallization method. Firstly, 1 mmol Organic salt and 1 mmol $SbCl_3$ were dissolved in 5~15 mL HCl at 120 °C to form a clear precursor solution. The solution is then slowly cooled to room temperature. Colorless transparent crystals are precipitated, cleaned with ethanol and dried overnight in an oven at 65°C.

### Synthesis of $XSbCl_4$ powder.

$X_2SbCl_4$ were obtained by a room-temperature solution co-precipitation method in hydrochloric acid. Firstly, 2mmol of organic salt and 2mmol of $SbCl_3$ were dissolved in 10 mL of HCl and ultrasounded at room temperature for 1 minute. Then we get a white powder precipitated and

cleaned with ethanol. All samples are finally dried in vacuum drying oven for 8 hours before grinding into powder for later use.

**Characterization.**

Single crystal X-ray diffraction measurements were performed on a Rigaku AFC10 diffractometer equipped with graphite-monochromated Kα (λ = 0.71073 Å) radiation. A Rigaku D/MAX 2500V 18KW X-ray diffractometer with Cu Kα radiation (λ= 1.54059 Å) was used to collect the powder X-ray diffraction (XRD) data in the 2θ range of 5°-60°. Scanning electron microscopy (SEM, Zeiss Sigma 500) was used to observe the morphology. The element composition and distribution were observed by energy-dispersive spectrometry (EDS, Oxford X-max20). The Raman spectrum was characterized by a WITec alpha300R Raman fluorescence spectrometer with a 633 nm laser as an excitation source. The photoluminescence (PL), PL excitation (PLE) spectrum, and the time-resolved photoluminescence (TRPL), temperature-dependent PL spectra, and photoluminescence quantum yields (PLQYs) were measured by using the FLS-1000 spectrometer (Edinburgh) with a PLQY accessory. The Shimadzu UV-3600PLUS spectrophotometer was used to measure the absorption spectrum.

**Calculation details**

All calculations at density functional theory are carried out using the Vienna Ab initio simulation package (VASP).[1] The generalized gradient approximation of the Perdew–Burke–Ernzerhof (PBE) parameterization with projector-augmented wave method is performed for the exchange and correlation functional.[2] For all elements, ultra-soft pseudopotentials are used. The kinetic-energy cutoff of 520 eV and a 2×2×4 Monkhorst–Pack k-mesh for the wavefunction basis set is employed. The energy convergence criterion is set as 1.0×10-5 eV for structural relaxations.

The bond valence was calculated using the standard expression:

$$s = exp\left(\frac{R_0 - d}{B}\right)$$

The bond valence parameters were taken from the IUCr bond-valence parameter database (bvparm2020.cif, released on 2020-12-09), with $R_0 = 2.35$Å and $B = 0.37$Å for $Sb^{3+}$–$Cl^-$ pairs.

The bond length distortion (Δd) and angular distortion ($\sigma^2$) of $Sb_2Cl_8$ units defined as:

$$\Delta d = 1/5 \sum_{n=1}^{5} \left[\frac{d_n - d}{d}\right]^2$$

$$\sigma^2 = 1/10 \sum_{n=1}^{10} (\theta_i - 90)^2$$

**Table S1.** Crystal data and structure refinement for $XSbCl_4$ at 293 K.

| Identification code | Compound 1 | Compound 2 | Compound 3 |
|---|---|---|---|
| Empirical formula | $C_{13}H_{22}Cl_4NSb$ | $C_{25}H_{22}Cl_4PSb$ | $C_{10}H_{16}Cl_4NSb$ |
| Formula weight | 455.86 | 616.94 | 413.79 |
| Crystal system | monoclinic | triclinic | monoclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ | $P2_1/c$ |
| $a$/Å | 22.4251(12) | 9.8525(2) | 9.7655(6) |
| $b$/Å | 11.3044(6) | 12.1196(3) | 14.7378(10) |
| $c$/Å | 14.6335(9) | 12.8409(3) | 11.2162(7) |
| $\alpha$/° | 90 | 66.573(2) | 90 |
| $\beta$/° | 90.4329(16) | 71.049(2) | 99.9930(19) |
| $\gamma$/° | 90 | 66.204(2) | 90 |
| Volume/Å$^3$ | 3709.5(4) | 1262.41(6) | 1589.77(18) |
| Z | 8 | 2 | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.663 | 1.623 | 1.729 |
| μ/mm$^{-1}$ | 1.745 | 1.832 | 2.455 |
| F(000) | 1808 | 612 | 808 |
| Radiation | Mo Kα (λ = 0.71073) | Mo Kα (λ = 0.71073) | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.124 to 528.622 | 2.238 to 52.124 | 1.924 to 57.620 |
| h,k,lmax | 28,15,20 | 13,17,15 | 13,21,16 |

**Table S2.** Crystal data and structure refinement for $XSbCl_4$ at 293 K.

| Identification code | Compound 4 | Compound 5 | Compound 6 |
|---|---|---|---|
| Empirical formula | $C_{19}H_{18}Cl_4PSb$ | $C_{12}H_{28}Cl_4NSb$ | $C_{19}H_{34}Cl_4NSb$ |
| Formula weight | 540.85 | 449.9 | 540.02 |
| Crystal system | monoclinic | monoclinic | monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ |
| a/Å | 10.8726(3) | 18.19840(10) | 10.3132(3) |
| b/Å | 17.8886(4) | 15.74030(10) | 14.4255(4) |
| c/Å | 12.0972(3) | 13.67940(10) | 16.6030(4) |
| α/° | 90 | 90 | 90 |
| β/° | 115.0220(10) | 91.5970(10) | 93.5680(11) |
| γ/° | 90 | 90 | 90 |
| Volume/Å$^3$ | 2132.03(9) | 3916.92 (4) | 2465.29(12) |
| Z | 4 | 8 | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.685 | 1.526 | 1.455 |
| μ/mm$^{-1}$ | 1.871 | 1.687 | 1.556 |
| F(000) | 1064.66 | 1808 | 1096.0 |
| Radiation | Mo Kα (λ = 0.71073) | Mo Kα (λ = 0.71073) | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | 1.982 to 56.614 | 5.09 to 55.088 | 1.968 to 56.610 |
| h,k,lmax | 14,23,16 | 22,19,17 | 13,19,22 |

**Table S3.** Bond lengths of six compounds.

| Compound | Sb-Cl1 (Å) | Sb-Cl2 (Å) | Sb-Cl3 (Å) | Sb-Cl4 (Å) |
|---|---|---|---|---|
| 1 | 2.5404 | 2.4328 | 2.7275 | 2.3719 |
| 2 | 2.4617 | 2.4607 | 2.8975 | 2.3626 |
| 3 | 2.4733 | 2.3656 | 2.7521 | 2.4385 |
| 4 | 2.4127 | 2.4891 | 2.8021 | 2.3615 |
| 5 | 2.4698 | 2.3557 | 2.8286 | 2.4448 |
| 6 | 2.3442 | 2.4476 | 2.8397 | 2.4120 |

**Table S4.** Bond angles of six compounds.

| Compound | Cl-Sb-Cl1 | Cl-Sb-Cl2 | Cl-Sb-Cl3 | Cl-Sb-Cl4 | Cl-Sb-Cl5 | Cl-Sb-Cl6 |
|---|---|---|---|---|---|---|
| 1 | 172.76° | 92.22° | 94.70° | 88.20° | 89.44° | 92.02° |
| 2 | 176.735° | 92.239° | 91.224° | 91.276° | 90.939° | 89.40° |
| 3 | 175.87° | 89.43° | 91.85° | 91.35° | 93.64° | 90.26° |
| 4 | 178.55° | 89.956° | 90.89° | 90.007° | 94.03° | 88.749° |
| 5 | 178.38° | 91.95° | 86.52° | 92.50° | 89.24° | 90.31° |
| 6 | 173.65° | 84.41° | 90.35° | 93.30° | 90.70° | 93.23° |

**Table S5.** Bond valence of the secondary bonding in the six compounds

| Compound | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Distance (Å) | 2.900 | 2.904 | 2.941 | 3.068 | 3.125 | 2.986 |
| Bond valence (v.u.) | 0.226 | 0.223 | 0.202 | 0.143 | 0.123 | 0.179 |

**Table S6.** Distortion indices of the $Sb_2Cl_8$ dimers in the six compounds

| **Compound** | **1** | **2** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|---|
| ***Δd*** | **0.028** | **0.040** | **0.035** | **0.052** | **0.060** | **0.048** |
| **σ2($10^3$)** | **14.11** | **14.98** | **14.91** | **14.63** | **15.45** | **14.88** |

**Table S7.** Optical property of recently reported some compounds with NIR emission.

| Chemical formula | Coverage area | Emission (nm) | FWHM (nm) | Synthesis temperature | Ref |
|---|---|---|---|---|---|
| $(C_{20}H_{20}P)_2ZnCl_{3.6}Br_{0.4}$:20%Sb | 550-1050 | 730 | 196 | RM | 3 |
| $K_2NaInF_6:Cr^{3+}$ | 700-950 | 116 | 116 | 220°C | 4 |
| $CaSc_{1-x}Al_{1+x}SiO_6$ | 700-1300 | 950 | 205 | 1450°C | 5 |
| Cs2AgBiCl6: $Cr^{3+}$ | 500-1000 | 700 | 270 | 180°C | 6 |
| $Cs_2ZrCl_6$: $Te^{4+}/Ln^{3+}$ | 1520-1580 | 1540 | / | 80°C | 7 |
| $Cs_2ZnCl_4:Sb^{3+}$ | 500~1000 | 745 | 175 | 120°C | 8 |
| $CsPbI_3$-PbS | 800-1200 | 1000 | 150 | 150°C | 9 |
| $Cs_2Zr_{1-x}Mo_xCl$ | 850-1350 | 940 | 200 | | 10 |
| $ZnGa_2O_4$: $Cr^{3+}$ | 650-800 | 700 | 101 | 1300°C | 11 |
| $Na_3GaF_6:Cr^{3+}$, $Li^+$ | 650-950 | 758 | 107 | 300°C | 12 |
| $Cr^{3+}:Mg_3Ga_2GeO_8$ | 600-1100 | 770 | 160 | 1400°C | 13 |
| $Ni^{2+}:Mg_3Ga_2GeO_8$ | 1100-1650 | 1425 | 200 | 1400°C | 13 |
| $K_3LuSi_2O_7:Eu^{2+}$ | 550-1000 | 740 | 160 | 1350°C | 14 |
| $Ca_3MgHfGe_3O_{12}:Cr^{3+}$ | 700-1200 | 800 | ~100 | 1350 | 15 |
| $TEA_2HfCl:Cr^{3+}$ | 700-1300 | 920 | 164 | 180 | 16 |
| $Cs_2NaScCl_6:Cr^{3+}$ | 800-1200 | 950 | ~120 | 180 | 17 |
| $(BTP)_2ZnBr_4$: $Sb^{3+}$ | 550-1050 | 725 | 179 | RM | 18 |
| $Ga_2O_3$: $Ni^{i2+}$ | 1200-1700 | 1420 | 304 | 1450 | 19 |
| $(Ga/Sc)_2O_3:0.02Cr^{3+}$ | 600-1100 | 820 | 147 | 1200°C | 20 |
| $MgO:Cr^{3+}$ | 620-1100 | 810 | ~130 | 1750 | 21 |
| **Compound 1** | 600-1250 | 855 | 277 | RM | This work |
| **Compound 2** | 600-1300 | 910 | 285 | RM | This work |
| **Compound 3** | 600-1400 | 962 | 319 | RM | This work |
| **Compound 4** | 600-1450 | 1000 | 333 | RM | This work |
| **Compound 5** | 600-1510 | 1055 | 375 | RM | This work |
| **Compound 6** | 600-1600 | 1114 | 415 | RM | This work |

**Table S8.** The PLQY under 334 nm excitation for six compounds and took the average value.

| Compound | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| **1** | **14.01** | **12.19** | **7.36** | **14.98** | **9.57** | **9.31** |
| **2** | **12.24** | **13.84** | **8.48** | **15.24** | **13.98** | **10.26** |
| **3** | **12.01** | **12.98** | **6.87** | **14.05** | **12.45** | **8.99** |
| **4** | **11.11** | **14.11** | **9.26** | **15.67** | **13.04** | **11.08** |
| **5** | **13.22** | **14.08** | **7.51** | **13.85** | **13.51** | **9.79** |
| **Average** | **12.52** | **13.44** | **7.90** | **14.76** | **12.51** | **9.87** |

**Table S9.** Raman bands and assignment of six compounds.

| Compound | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Bending modes | 108<br>139 | 106<br>138 | 120<br>160 | 107<br>134 | 121<br>143 | 109<br>146 |
| ν Sb-Cl bridge | | 224 | | | | |
| ν Sb-Cl terminal | 230<br>280<br>324 | 245<br>278<br>330 | 258<br>282<br>322 | 252<br>289<br>332 | 243<br>289<br>337 | 260<br>291<br>342 |


Figure S1. Compound **6** was synthesized from 2 mmol of $SbCl_3$ and 2 mmol of benzyltributylammonium chloride, affording 1.0338 g of product.

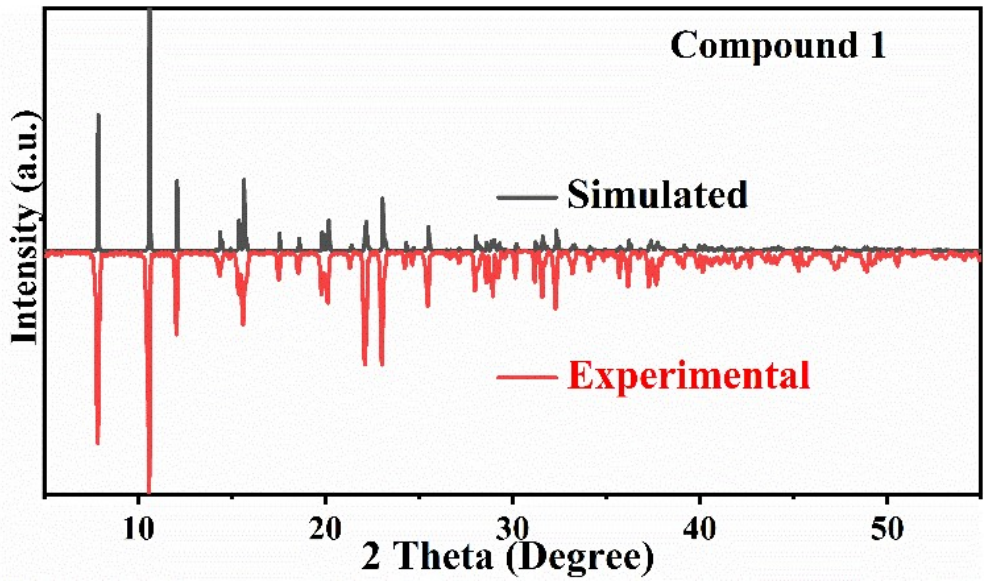

Figure S2. PXRD patterns of **Compound 1** and the simulated from crystal structure.

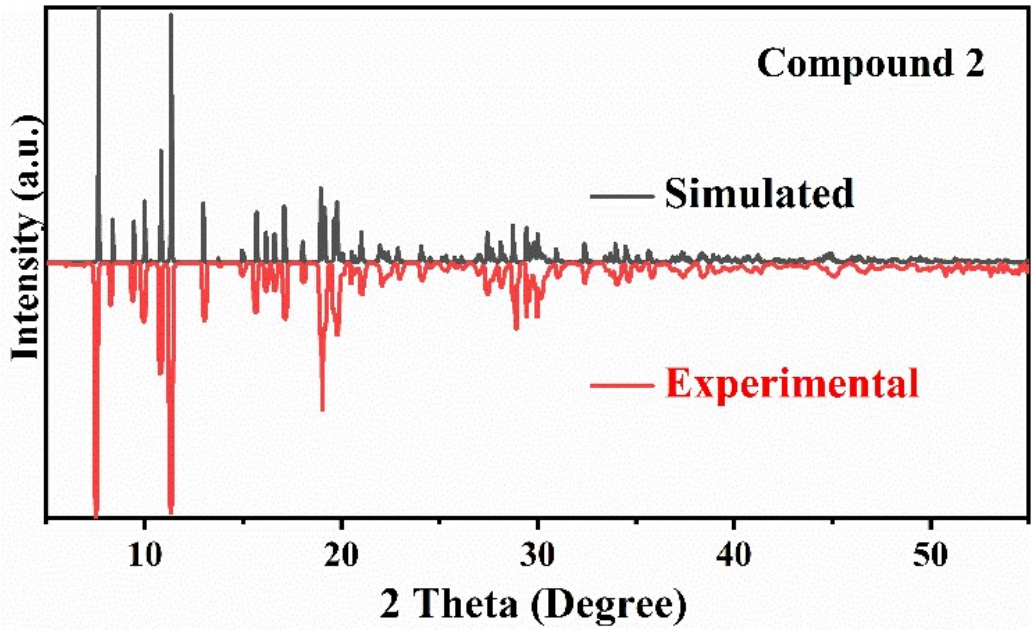

Figure S3. PXRD patterns of **Compound 2** and the simulated from crystal structure.

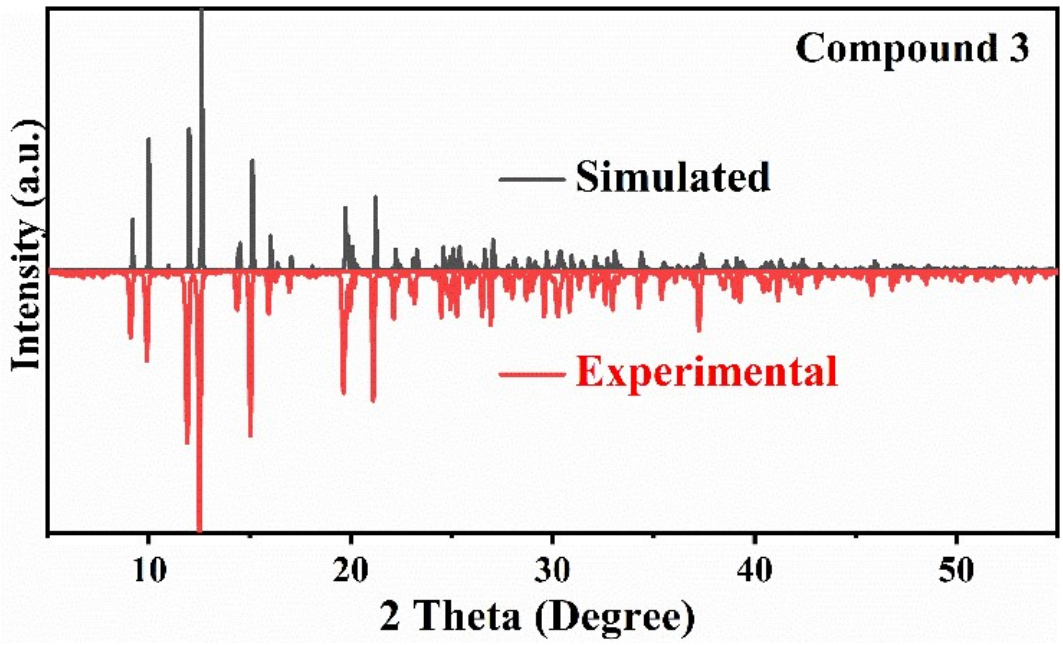

Figure S4. PXRD patterns of **Compound 3** and the simulated from crystal structure.

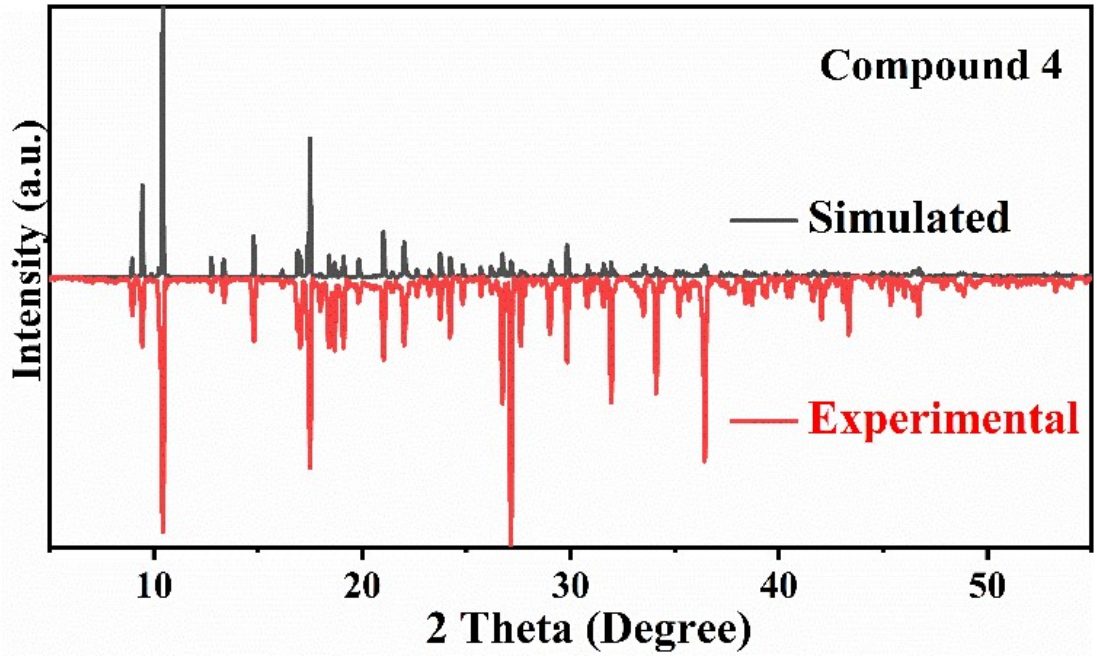

Figure S5. PXRD patterns of **Compound 4** and the simulated from crystal structure.

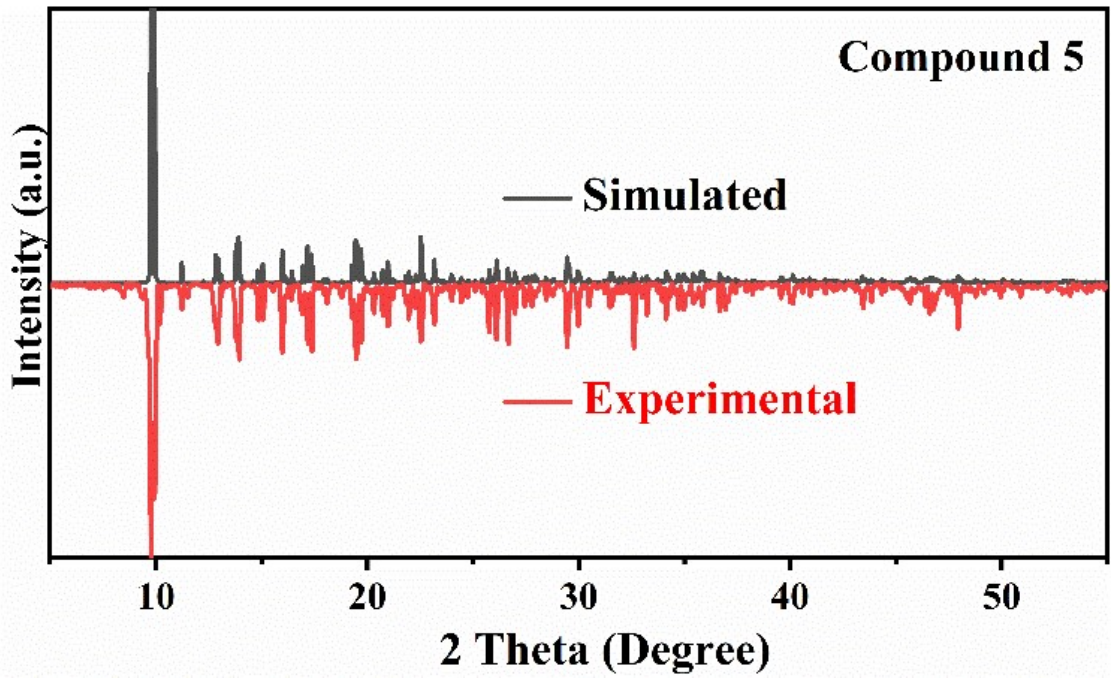


Figure S6. PXRD patterns of **Compound 5** and the simulated from crystal structure.

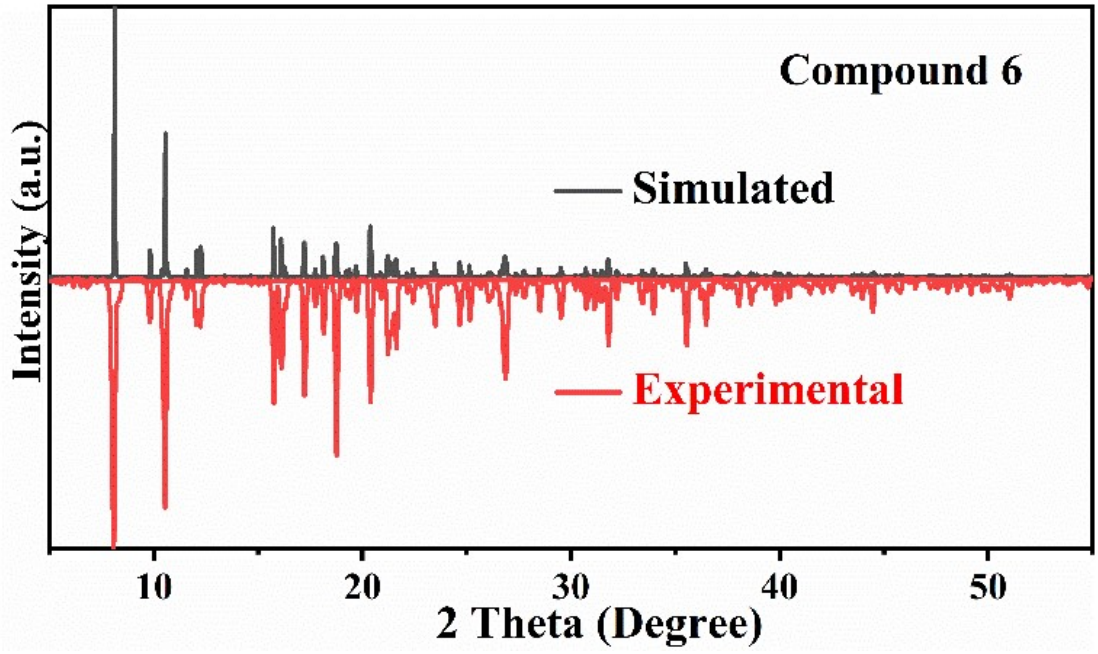


Figure S7. PXRD patterns of **Compound 6** and the simulated from crystal structure.

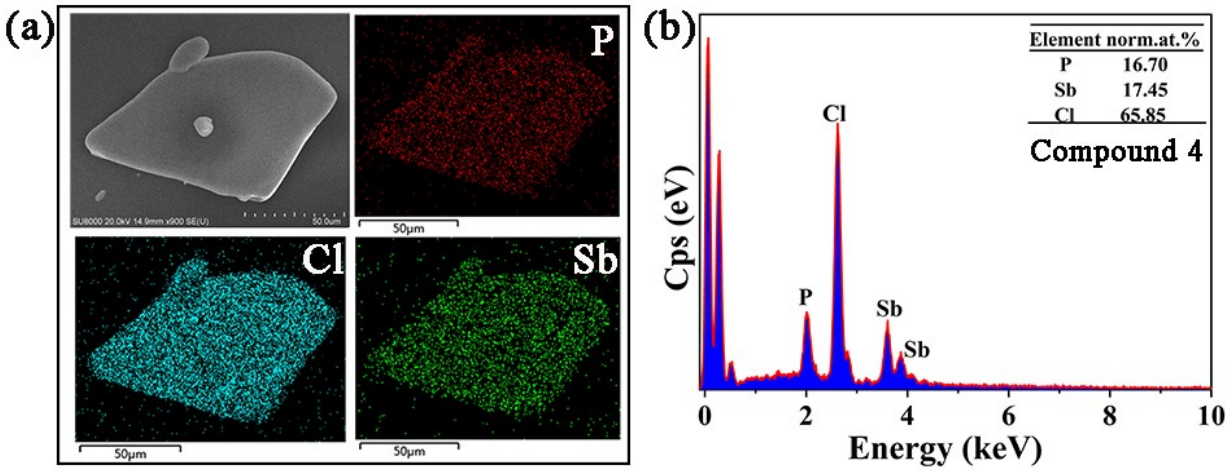


Figure S8. (a) SEM image and EDS-mapping of P, Cl and Sb and (b) energy disperse spectrum of **Compound 4**.

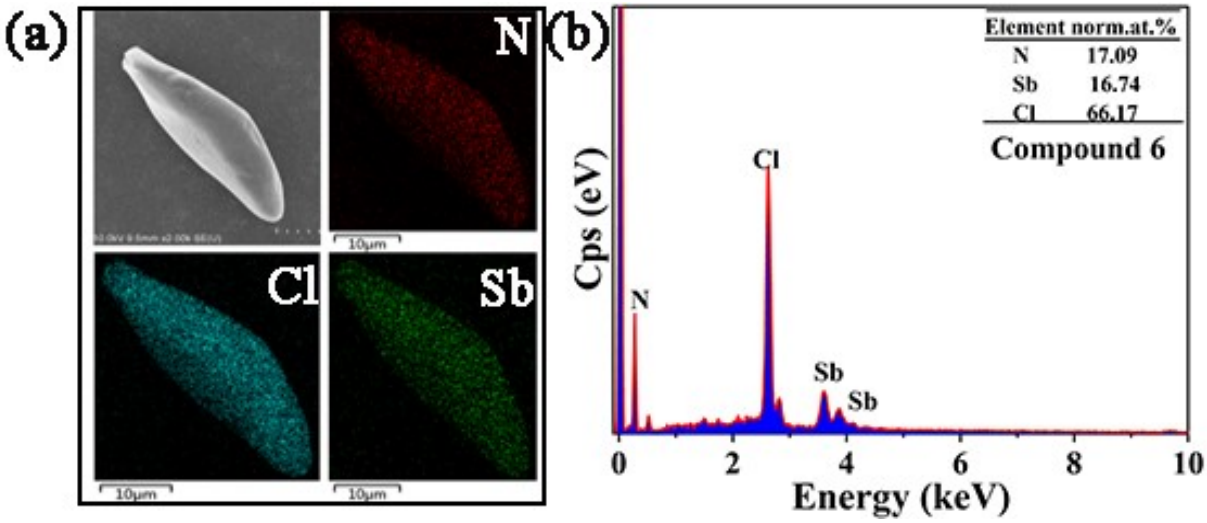


Figure S9. (a) SEM image and EDS-mapping of P, Cl and Sb and (b) energy disperse spectrum of **Compound 6**.

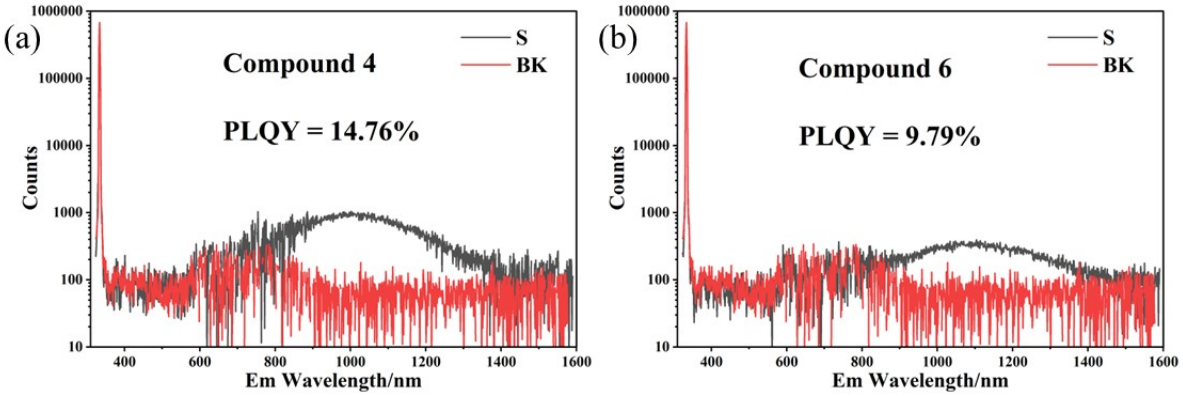


Figure S10. (a) PLQY data of Compound **4**. (b) PLQY data of Compound **6**.

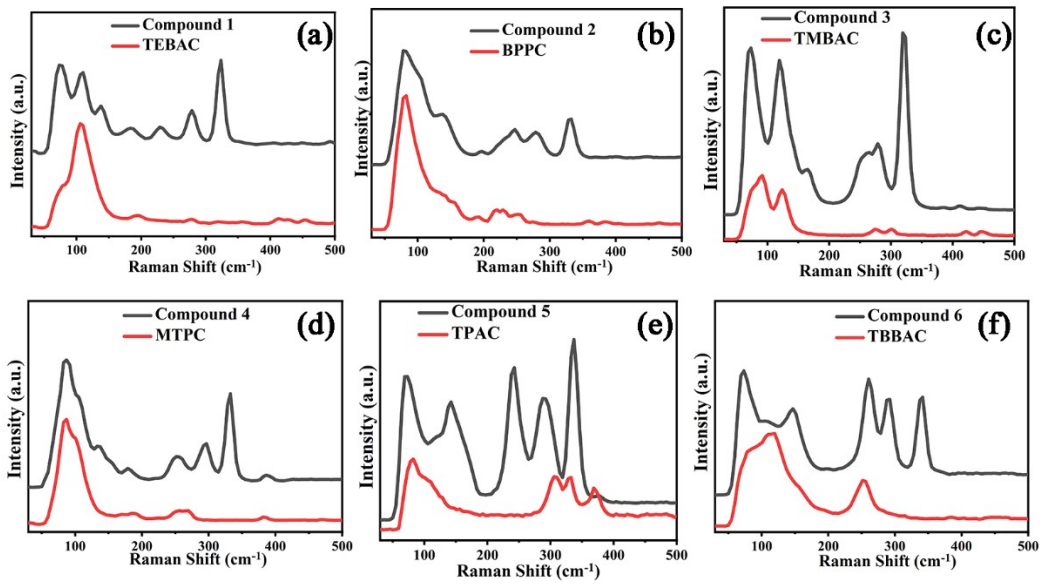


Figure S11. Raman spectra of all compounds. (a) **Compound 1**, (b) **Compound 2**, (c) **Compound 3**, (d) **Compound 4**, (e) **Compound 5**, (f) **Compound 6**.

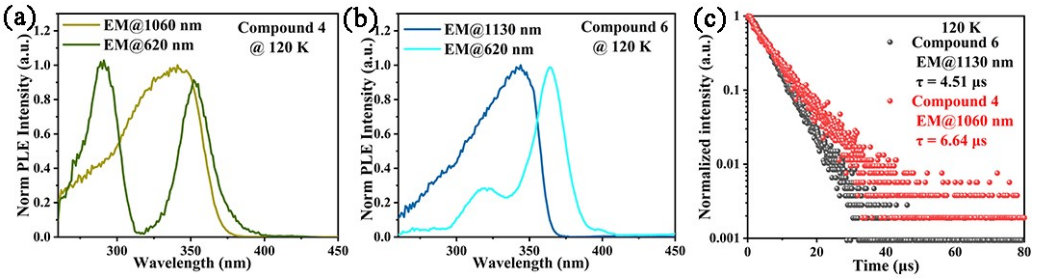


Figure S12. (a) PLE spectrum of compound 4 at 120 K. (b) PLE spectrum of compound 6 at 120 K. (c) Lifetime of compounds 4 and 6 monitored at 1060 nm and 1130 nm, respectively, at 120K.

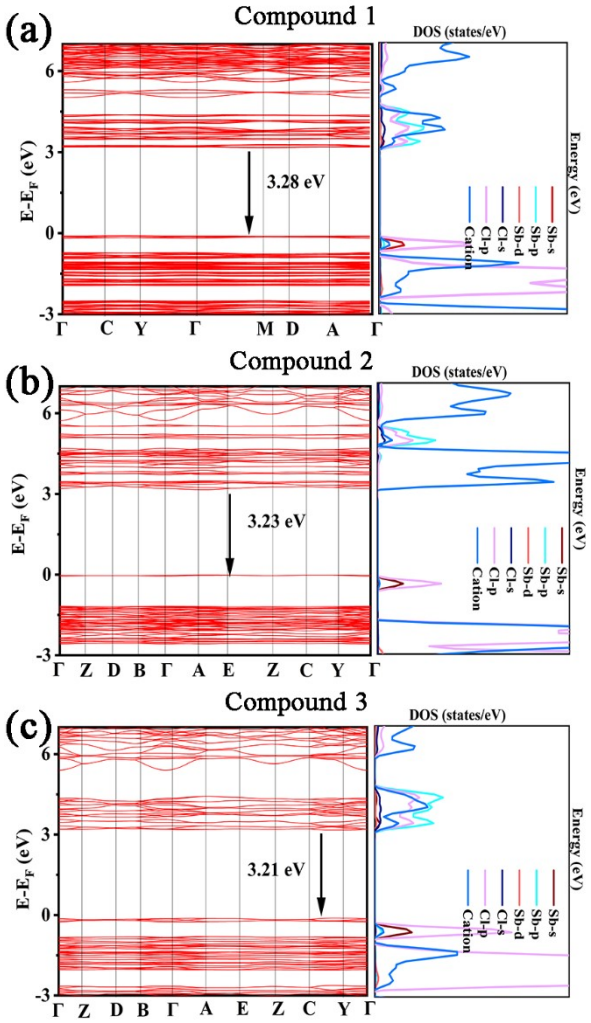


Figure S13. (a) Band structures and PDOS for **Compound 1**. (b) Band structures and PDOS for **Compound 2**. (c) Band structures and PDOS for **Compound 3**.

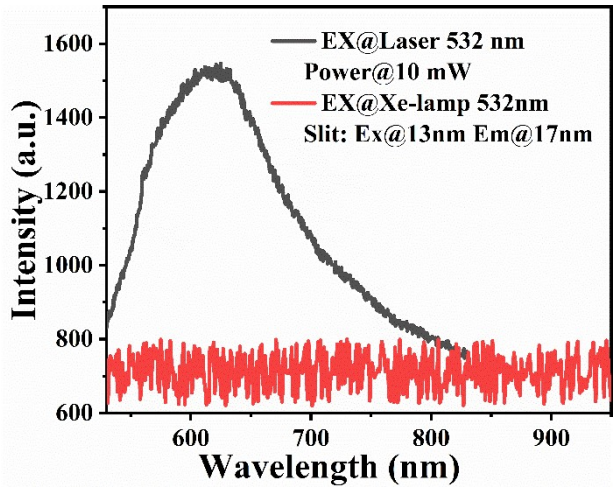


Figure S14. PL spectra of Compound **6** under laser and Xe-lamp excitation at 532 nm.

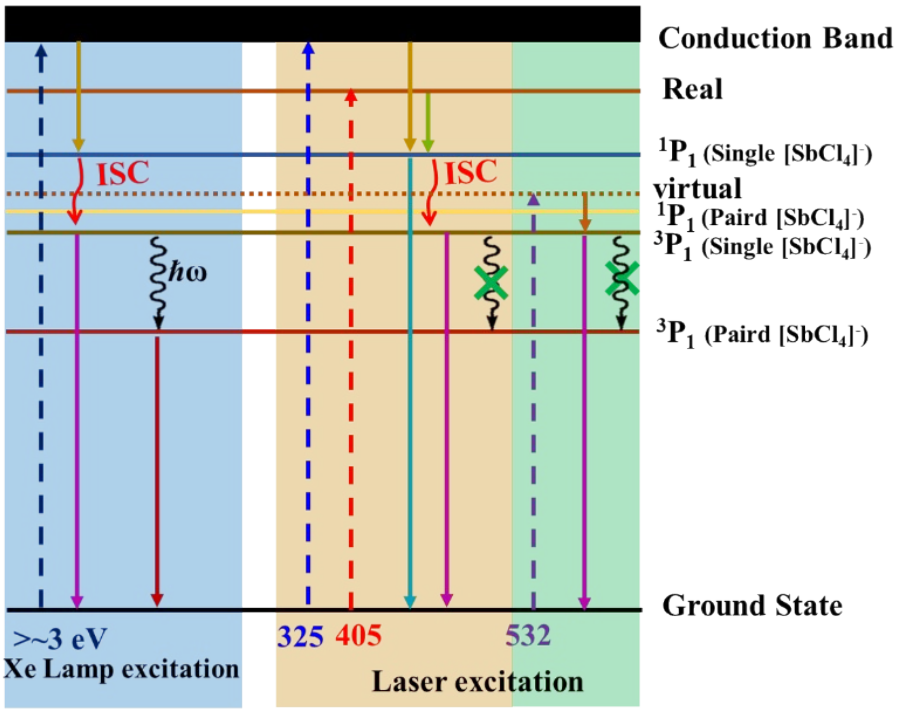


Figure S15. Photophysical processes of Compound **6** under laser and xenon lamp excitation.

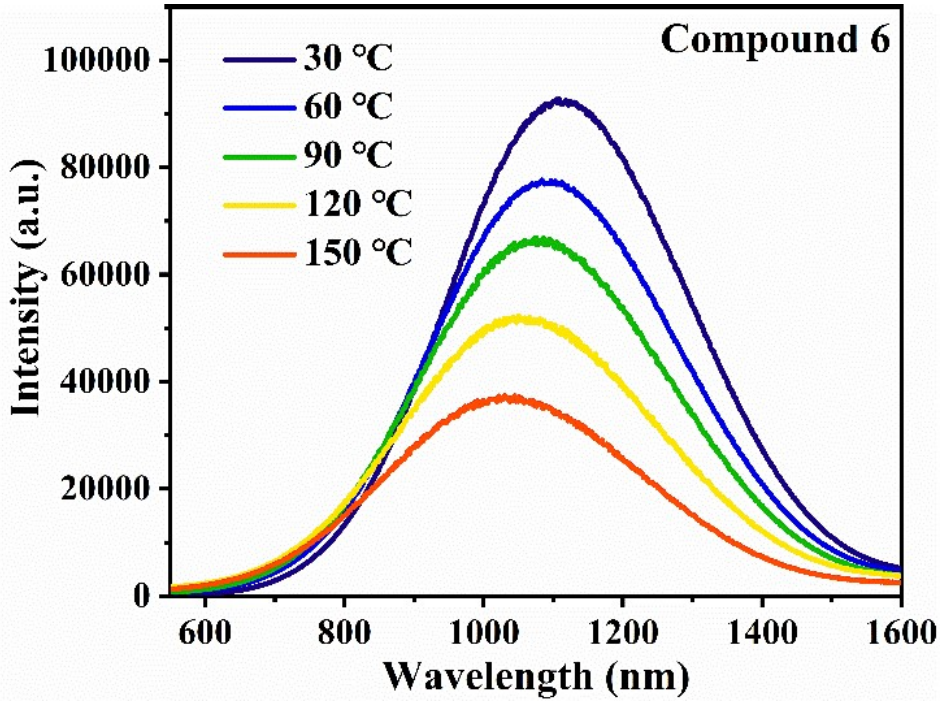


Figure S16. PL spectra of Compound **6** from 30°C to 150°C.

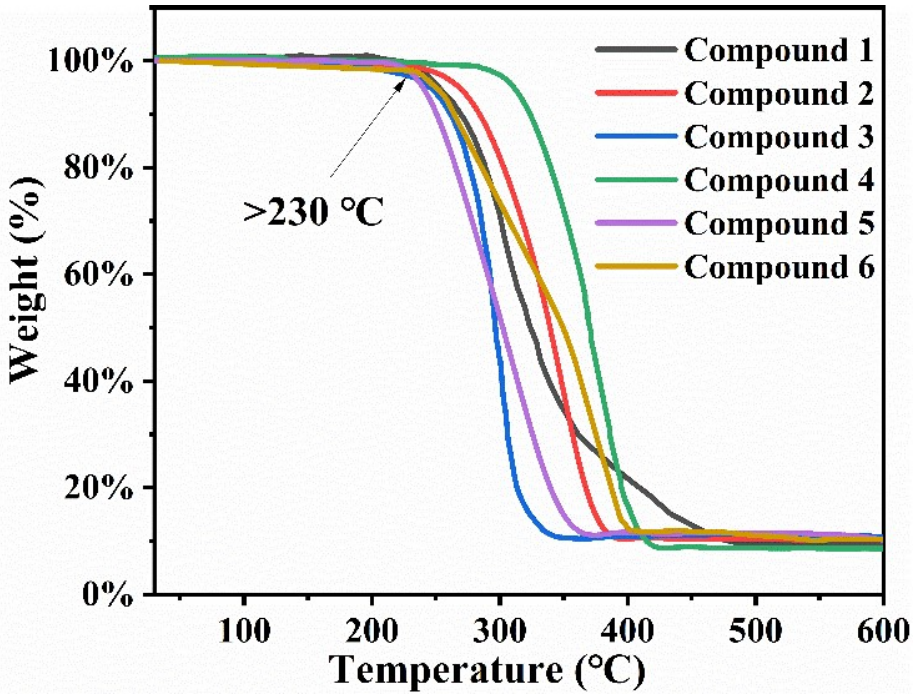


Figure S17. TGA curves of six compounds.

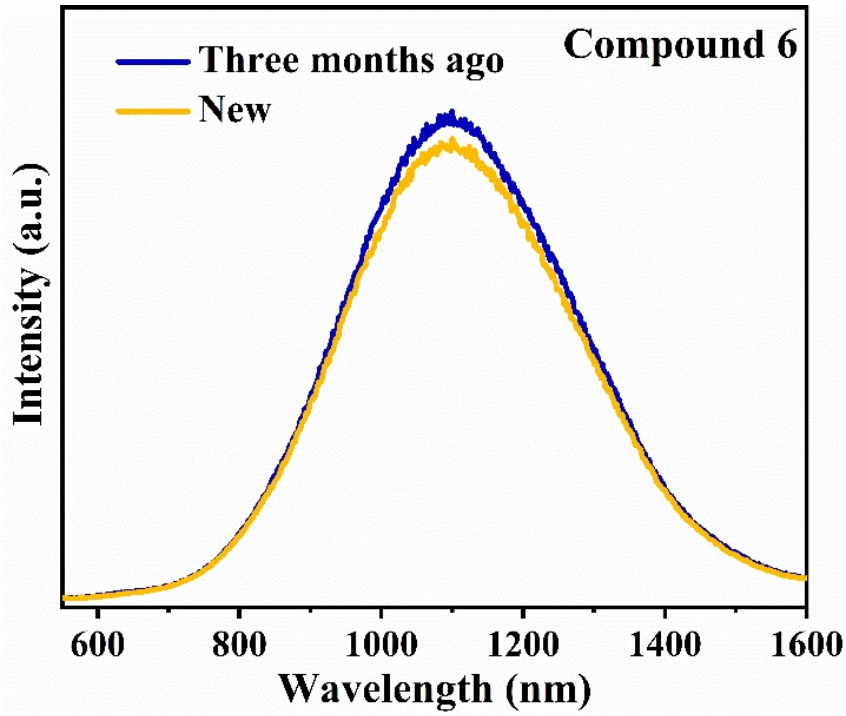


Figure S18. PL spectra of the Compound **6** stored in air for three months (~60 % relative humidity).

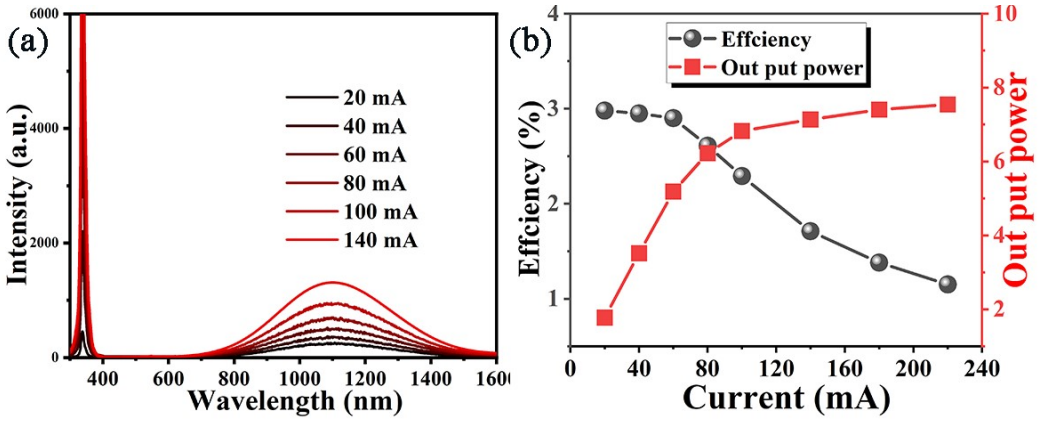


Figure S19. (a) PL spectra of the pc-LED upon various driving currents. (b) Dependence of NIR output power, and conversion photoelectric efficiency on currents.

## References


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