Supporting Information for

Halogen-Driven Emission Switching in Zero-Dimensional Indium Halides: From Efficient Blue to Yellow Emission

Liao-Kuo Gong[a,b]*, Jing-Yue Zhang[a], Jia-Xin Cui[a], Xin-Ping Guo[b], Hao-Wei Lin[b], Yuan Niu[a]

[a]School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu, Shandong, 273165, P. R. China. E-mail: liaokuogong@163.com

[b]State Key Laboratory of Structure Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China.

Experimental section

Materials

All chemical reagents and solvents were used as received without further purification: Anhydrous ethanol (EtOH, > 99.7 %, FuYu chemical), 1-Ethylpyridinium chloride ([Epy]Cl, 99 %, Lanzhou Institute of chemical physics ILs, Lanzhou, China), 1-Ethypyridinium bromide ([Epy]Br, 99 %, Lanzhou Institute of chemical physics ILs, Lanzhou, China), Indium bromide ($InBr_3$, > 99.9 %) was supplied by Macklin, indium chloride ($InCl_3$, > 99.99 %) was supplied by Adamas-beta.

Synthesis

Synthesis of $[Epy]_2[InCl_5(py)]$ (1) : $InCl_3$ (0.5 mmol, 0.11059 g) and [Epy]Cl (1 mmol, 0.14159 g) were weighed and dissolved in the 5 mL anhydrous ethanol solution. The above reaction solution was placed into a 28 mL Teflon-lined steel autoclave. Then, the Teflon-lined steel autoclave was put into the oven for heating. Then, the reactor was heated at 160 °C for 3 day. After slowing it to naturally cool to room temperature (RT), colorless plate crystals were obtained.

Synthesis of $[Epy]_2[InBr_5(py)]$ (2) : $InBr_3$ (0.5mmol, 0.1773 g) and [Epy]Br (1mmol, 0.18807 g) were weighed and dissolved in the 5 mL anhydrous ethanol solution. The above reaction solution was placed placed into a 28 mL Teflon-lined steel autoclave. Then, the Teflon-lined steel autoclave was put into the oven for heating. Then, the reactor was heated at 160 °C for 3 day. After slowing it to naturally cool to room temperature (RT), and then placed in the top layer of the refrigerator at 4 °C to obtain brown flake crystal.

Characterization

Single Crystal X-ray diffraction (SCXRD): The single crystal data of compounds **1** and **2** were collected on a Bruker X-ray diffractometer (SMART APEX CCD, Mo-Kα) at 298K. The single crystal data of 1 was directly solved and refined by using OLEX 1.3.0 software, and **2** was solved by direct methods and refined by fullmatrix least-squares on F^2 using the SHELX-2018 program package. All the C, N, In and Cl atoms were refined with anisotropic thermal vibration factors except the H atoms, which were theoretically defined according to geometrical configurations of organic groups and refined with isotropic thermal vibration factors.

Powder X-ray diffraction (PXRD): Data were measured on a PANalytical X-ray Diffractometer Model X pert3 powder X-ray diffractometer (Mo K_α) in the 2θ range of 5-50°. The simulated PXRD pattern was calculated by using the single crystal X-ray structural data at RT via Mecury software.

UV-visible absorption spectroscopy (UV-vis): The UV-vis absorption was measured directly on ground single crystals with $BaSO_4$ as substrate in the wavelength range of 200-800nm on UV-2600i UV-vis spectrophotometer (Shimadzu). The absorption data was then obtained from the reflectance spectra by using the Kubelka-Munk function $\alpha/S = (1\text{-}R)^2/2R$, where α refers to the absorption coefficient, S refers to the scattering coefficient, and R refers to the reflectance.

Photoluminescence Characterization: The Photoluminescence excitation (PLE) and photoluminescence emission (PL) spectra were measured on an FL4600 fluorescence spectrometer at room temperature. PL decay spectra and photoluminescent quantum yields (PLQY) were measured in FLS1000 UV/V/NIR fluorescence spectrometer. Temperature-dependent PL spectra were measured on FLS980 UV/V/NIR fluorescence spectrometer with temperatures ranging from 80 K to 298K. The CIE calculator software was used for calculation of CIE chromaticity coordinates based on the emission spectra.

Theoretical calculation method: The crystal band structure and density of state (DOS) are calculated from the crystal structure data obtained from the single-crystal X-ray diffraction experiment. Throughout the theoretical calculation process, the theoretical calculation of electronic band structure (DOS) is calculated with using the CASTEP software package based on density functional theory (DFT). The Perdew-

Burke-Ernzerhof (PBE) function and the generalized gradient approximation (GGA) were used to calculate the exchange correlation energy of Hamilton.

Table S1. Crystallographic data of Compounds **1** and **2**

Compound	**1**	**2**
CCDC number	2519494	2519654
Empirical formula	$C_{19}H_{25}Cl_5InN_3$	$C_{19}H_{25}Br_5InN_3$
Formula weight	587.49	809.59
Crystal system	Orthorhombic	Orthorhombic
Space group	$Pca2_1$	$Pca2_1$
a/Å	15.0964(4)	15.6529(19)
b/Å	11.3661(3)	11.6904(13)
c/Å	14.5292(4)	14.6839(14)
α/°	90	90
β/°	90	90
γ/°	90	90
V/Å^3	2493.02(12)	2687.0(5)
Z	4	4
Temperature/K	298.0	298.0
Density (mg·m^3)	1.565	2.001
Absorption coefficient (mm^{-1})	1.494	8.325
F(000)	1176	1536
Theta range for data collection (°)	2.243-28.323	2.579-28.495
Data / restraints / parameters	5833/1/255	6659/1/257
GOF on F^2	1.018	0.966
R_1,wR$_2$[I>2$\sigma(I)$]	0.0241,0.0390	0.0450,0.0917
R,wR[all data]	0.0411,0.0434	0.0837,0.1065
Largest diff. peak and hole (e Å^3)	0.264,-0.353	1.031,-1.336

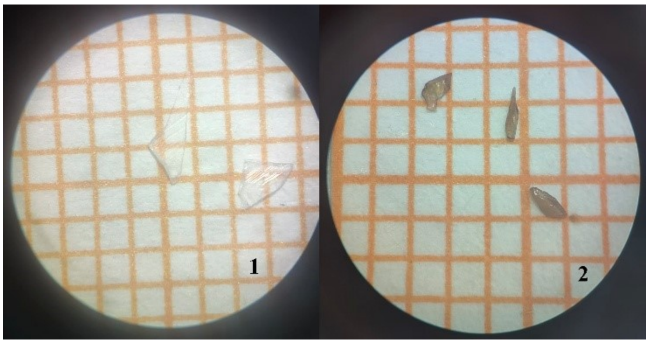


Figure S1. Digital photographs of **1** and **2**.

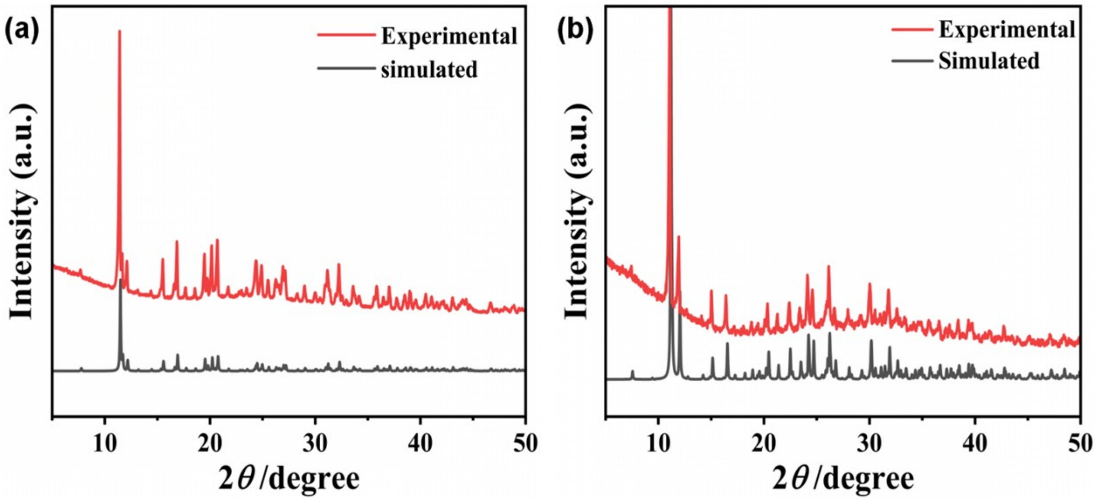


Figure S2. The PXRD of simulated and experimental data of compounds **1** (a) and **2** (b).

Table S2. Selected π-π interactions data for **1**.

	Cg-Cg (Å)	α(°)	β(°)	γ(°)	CgI_Perp	CgJ_Perp
Cg1→Cg2	4.006(3)	18.6(3)	16.0	34.3	3.312(2)	3.850(2)
Cg1→Cg3	3.849(3)	17.4(3)	10.0	25.5	3.476(2)	3.792(2)
Cg2→Cg1	4.006(3)	18.6(3)	34.3	16.0	3.851(2)	3.311(2)
Cg3→Cg1	3.850(3)	17.4(3)	25.5	10.0	3.792(2)	3.476(2)

Cg(1): N1→C8→C9→C10→C11→C12

Cg(2): N2→C16→C15→C14→C13→C17

Cg(3): N3→C3→C4→C5→C6→C7

Table S3. Selected π-π interactions data for 2.

	Cg-Cg (Å)	α(°)	β(°)	γ(°)	CgI_Perp	CgJ_Perp
Cg1→Cg2	4.118(9))	23.8(8)	12.4	36.2	3.323(7)	4.022(6)
Cg1→Cg3	4.024(9)	22.7(8)	10.5	27.7	3.564(7)	3.957(6)
Cg2→Cg1	4.117(9)	23.8(8)	36.2	12.4	4.022(6)	3.323(7)
Cg3→Cg1	4.025(9)	22.7(8)	27.7	10.5	3.957(6)	3.564(7)

Cg(1): N2→C8→C9→C10→C11→C12

Cg(2): N1→C3→C2A→C1→C4→C5

Cg(3): N3→C13→C14→C15→C16→C17

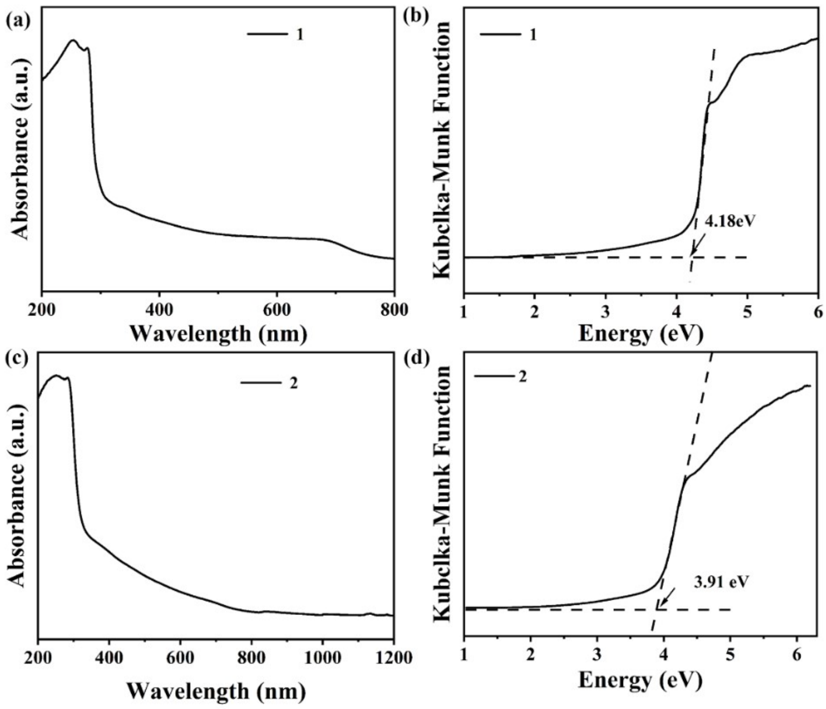


Figure S3. Solid-state optical absorption spectra of **1** (a) and **2** (c); Tauc plots of absorption spectra of **1** (c) and **2** (d).

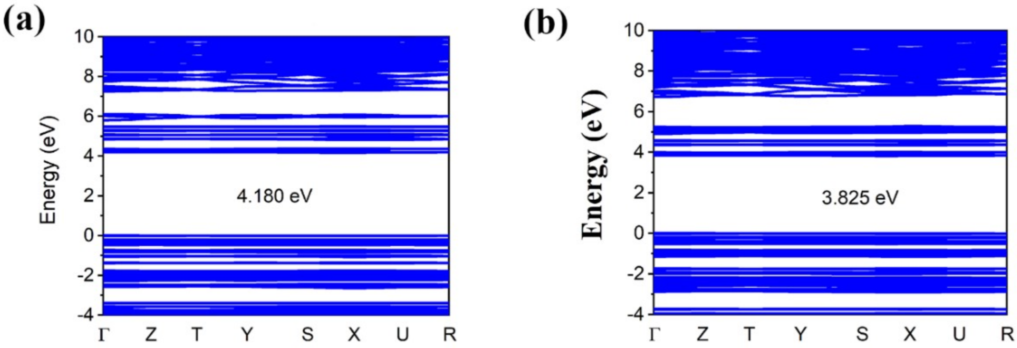
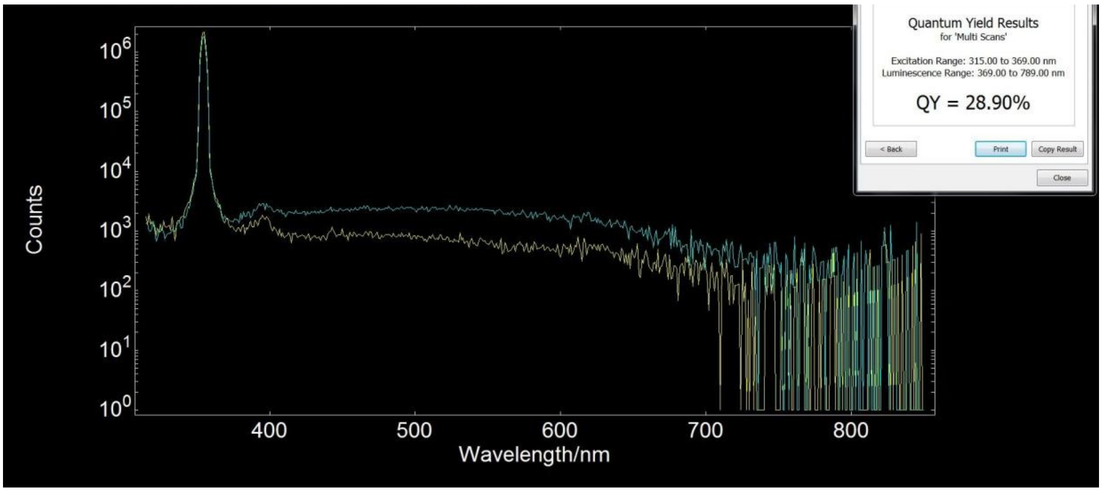


Figure S4. Calculated bandgap of **1** (a) and **2** (b).



Quantum Yield Results
for 'Multi Scans'

Excitation Range: 315.00 to 369.00 nm
Luminescence Range: 369.00 to 789.00 nm

QY = 28.90%

Figure S5. PLQY of compound **1.**

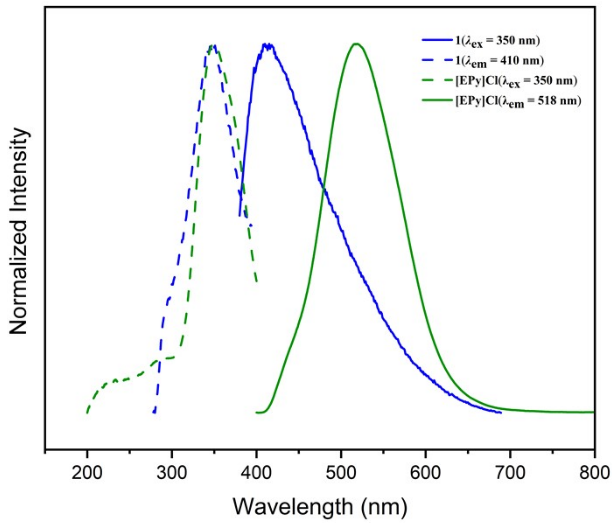


Figure S6. Compare with PLE and PL spectra of **1** and **[EPy]Cl**.

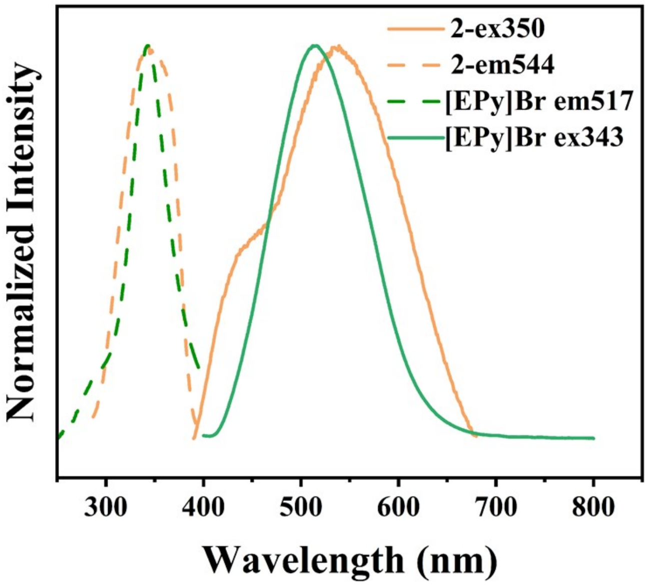


Figure S7. Compare with PLE and PL spectra of **2** and **[EPy]Br**.

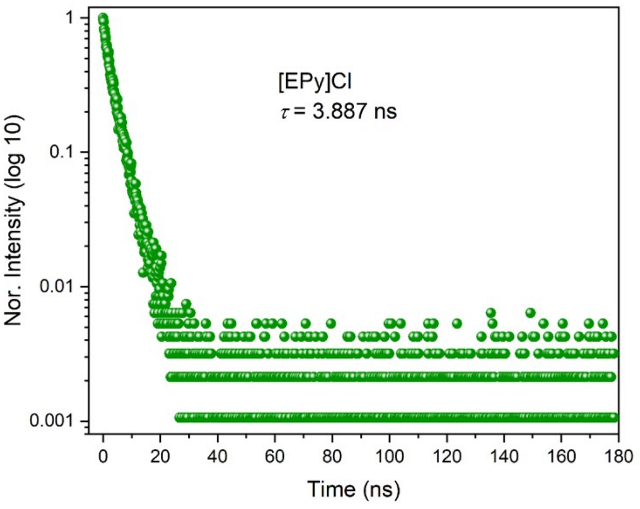


Figure S8. Time-resolved PL decay dynamics of **[EPy]Cl**.

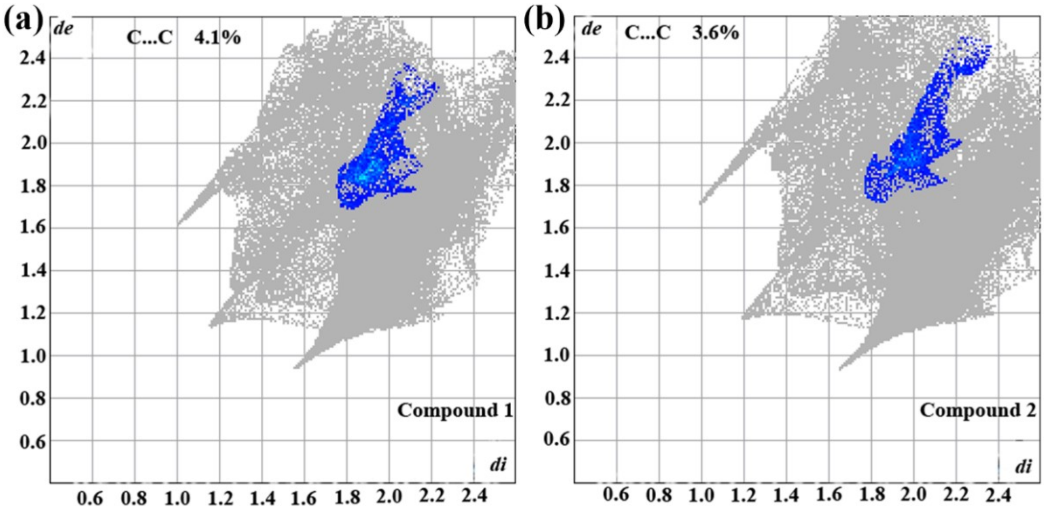


Figure S9. The 2D fingerprint plots. d_i is the distance between the Hirshfeld surface and the nearest atom inside the Hirshfeld surface, while d_e is the distance between the Hirshfeld surface and the nearest atom outside the Hirshfeld surface. The intense of the color in the fingerprint plots represents the contribution of a pair (d_i, d_e) on the Hirshfeld surface.