## Defect-Assisted Emission from Hybrid Indium Bromide Single Crystals

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Organic-inorganic hybrid metal halides (OIHMH) are non-toxic alternatives to lead halide perovskites. In this regard, indium-based OIHMHs have been studied by many research groups. Although several types of indium-based OIHMHs have been reported, a correlation between their structure, defects, and optical properties is still needed. In this study, we investigate the delayed photoluminescence (PL) from 4-piperidinopiperidine indium bromide  $(C_{10}H_{22}N_2)_4In_4Br_{20}$  single crystals prepared by a facile solution processing.

The (C<sub>10</sub>H<sub>22</sub>N<sub>2</sub>)<sub>4</sub>In<sub>4</sub>Br<sub>20</sub> single crystals excited by a 405 nm constant wave laser show green [530 nm, Fig. 1a,b(i)] or yellow [590 nm, Fig. 1a,b(ii)] emission. The PL decays (Fig. 1c) of the crystals are recorded using a time-correlated single-photon counting (TCSPC) system. The PL lifetime of the green- and yellow-emitting crystals are 3.2 and 10.7 ns, respectively. We investigate the role of halogen vacancies on the PL properties of the crystals by breaking the green-emitting crystals following by adding a Br<sup>-</sup> solution. The emission color of the broken yellow-emitting crystal changes to green immediately after adding a Br<sup>-</sup> solution. Also, the PL lifetime of the crystal decreases by Br vacancy filling, indicating halide vacancy-assisted delayed yellow emission. The PL emission color, intensity, and lifetime of the crystals are correlated with the halide vacancy density.

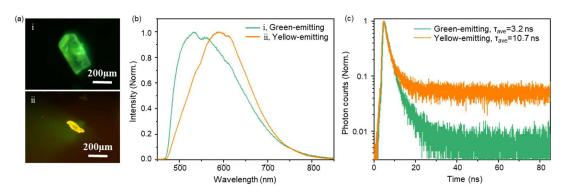


Fig 1. (a) PL images, (b) PL spectra, and (c) PL decays of i) green- and ii) yellow-emitting crystals.

1) Z. Wang, X. Huang, *Chem. Euro. J.* **2022**, *28*, e202200609. 2) N. Sun, J. Lin, S. He, J. Cao, Z. Guo, J. Zhao, Q. Liu, W. Yuan, *Inorg. Chem.* **2023**, *62*, 3018–3025.