Electronic Supplementary Material (ESI) for Materials Advances.

Electronic Supplementary Information for:

Air-Grown Hybrid Copper (I) Halide Single Crystals: Structural Transformations and Ultraviolet-Pumped Photoluminescence Applications

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Fig. S1. Photos of $Gua_6Cu_4I_{10}$ single crystal at sunlight (**A**), and UV-254 nm (**B**) condition. (**C**) Powder and single-crystal X-ray diffraction (PXRD) patterns of $Gua_6Cu_4I_{10}$. PLE and PL spectra of $Gua_6Cu_4I_{10}$ single crystal (**D**).

Fig. S2. Core level XPS spectra for (**A**) wide scan of $Gua_3Cu_2I_5$ single crystals, (**B**) C 1s, (**C**) N 1s, (D) I 3d, and (**E**) Cu 2p, fitted with peaks having an 80% Gaussian and 20% Lorentzian peak shape after applying background subtraction with Shirley function. Core level XPS spectra for (**F**) wide scan of $Gua_4Cu_4Br_8$ single crystals, (**G**) C 1s, (**H**) N 1s, (**I**) Cu 2p, and (**J**) Br 3d, fitted with peaks having an 80% Gaussian and 20% Lorentzian peak shape after applying background subtraction with Shirley function.

Fig. S3. Spatial distributions of VBM (**A**) and CBM (**B**) of $Gua_3Cu_2I_5$ at Γ point calculated by DFT.

Fig. S4. TGA/DSC diagrams of $Gua_4Cu_4Br_8$ and $Gua_3Cu_2I_5$.

Fig. S5. Photos of $Gua_3Cu_2I_5$ at room temperature and 100 ^oC under the irradiation of UV-254nm

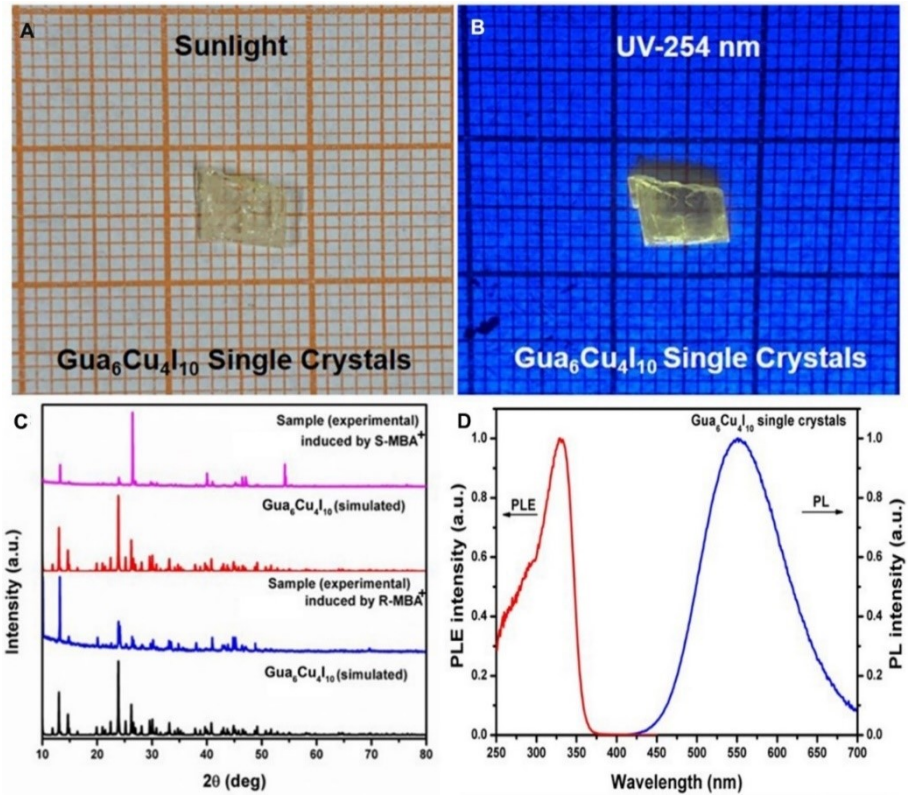
Fig. S6. Absolute PLQY of $Gua_3Cu_2I_5$ powders based on $BaSO_4$ as standard material

Fig. S7. PL decay lifetime of $Gua_6Cu_4I_{10}$ powders.

Fig. S8. Absolute PLQY of $Gua_6Cu_4I_{10}$ powders based on $BaSO_4$ standard material

Table S1. Crystal structure data for $Gua_4Cu_4Br_8$, $Gua_3Cu_2I_5$ and $Gua_6Cu_4I_{10}$.

Movie S1. Video of UV-pumped LEDs based on $Gua_3Cu_2I_5$ single crystals.



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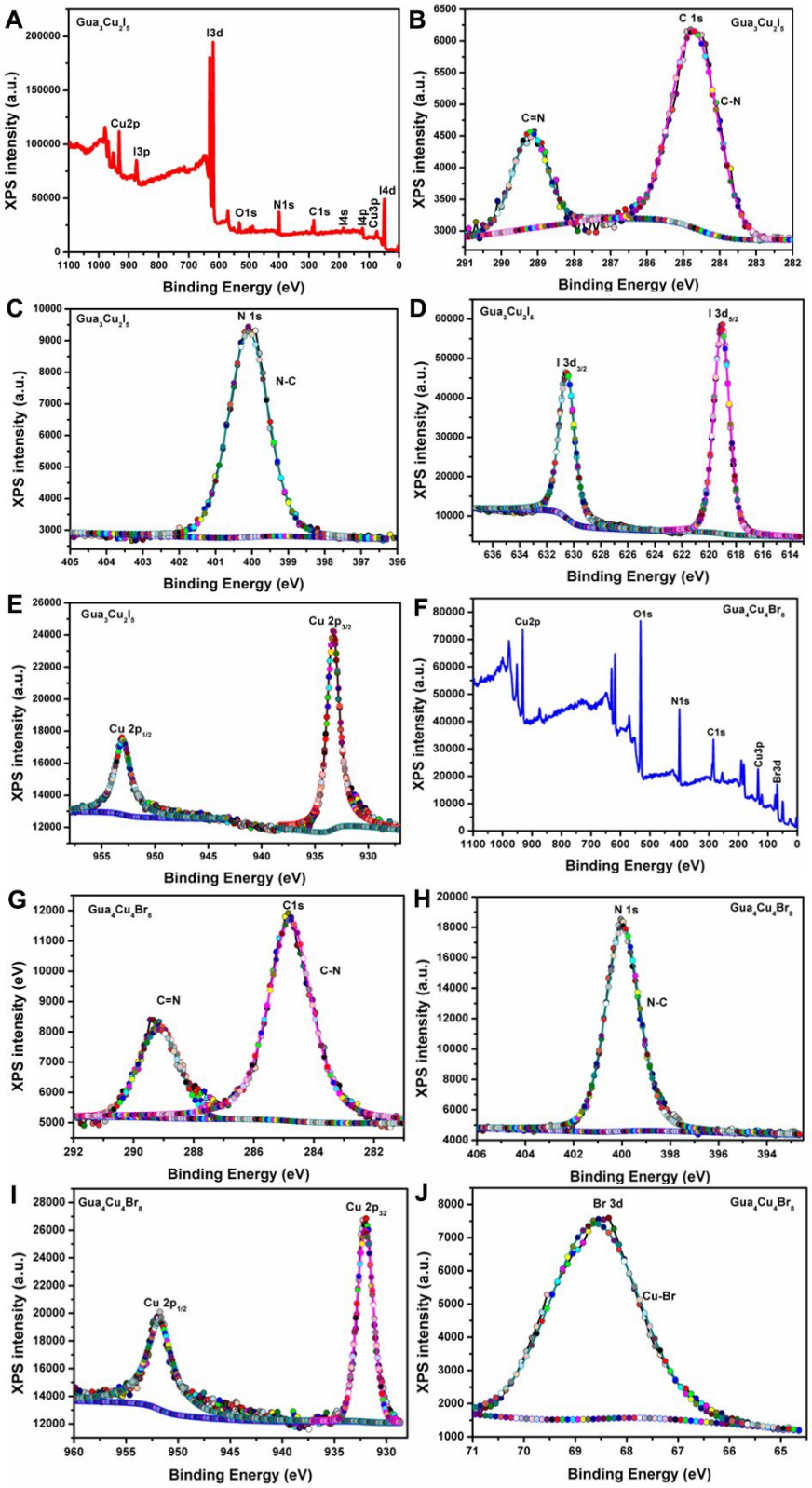

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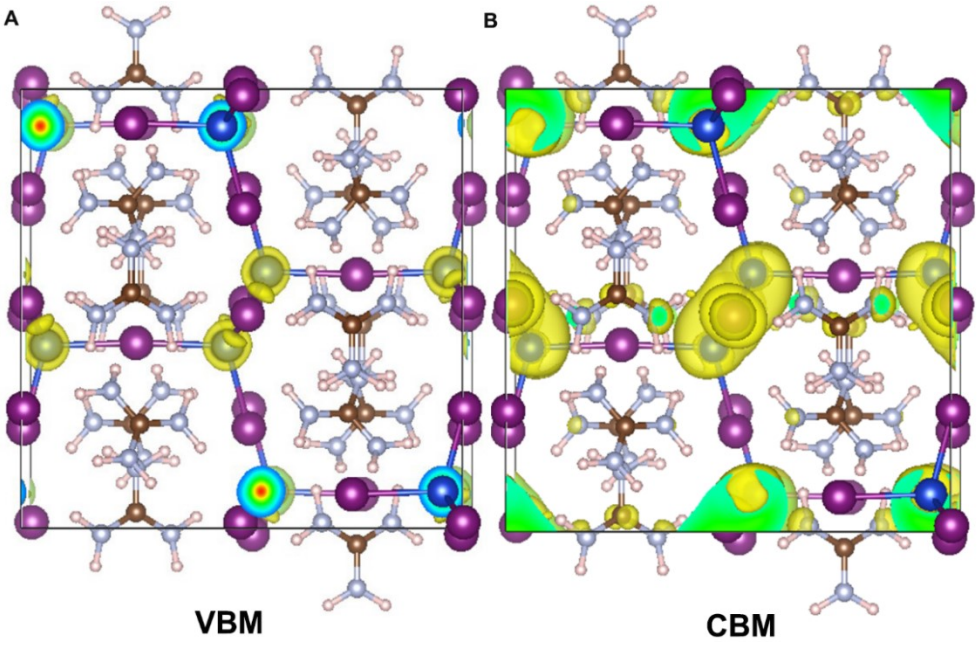

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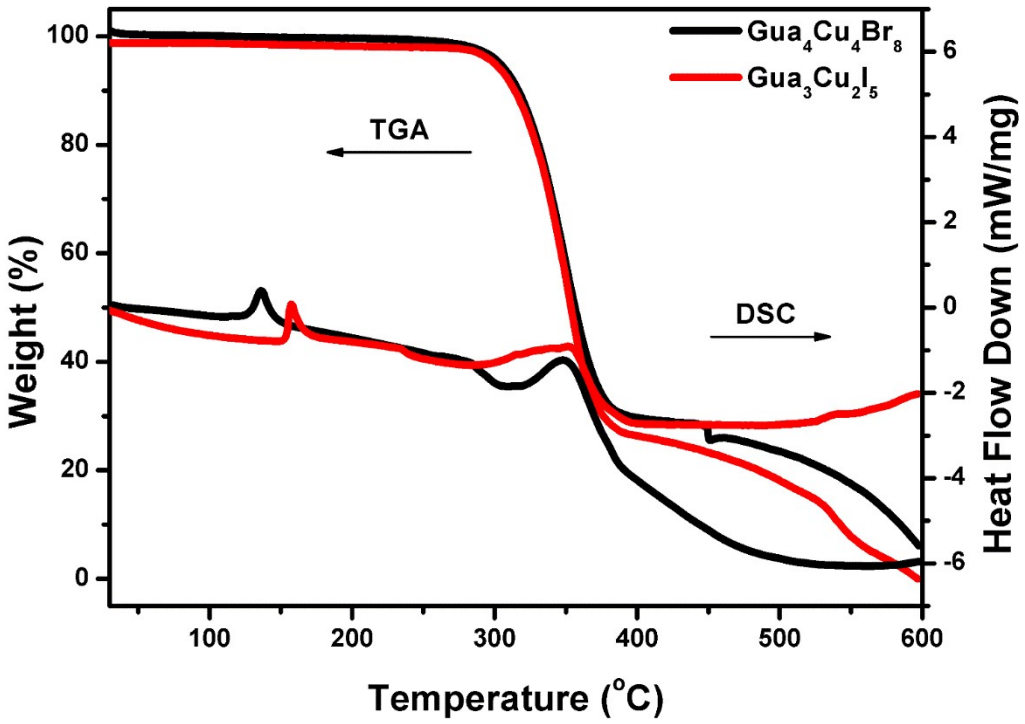

Fig. S4. TGA/DSC diagrams of $Gua_4Cu_4Br_8$ and $Gua_3Cu_2I_5$.

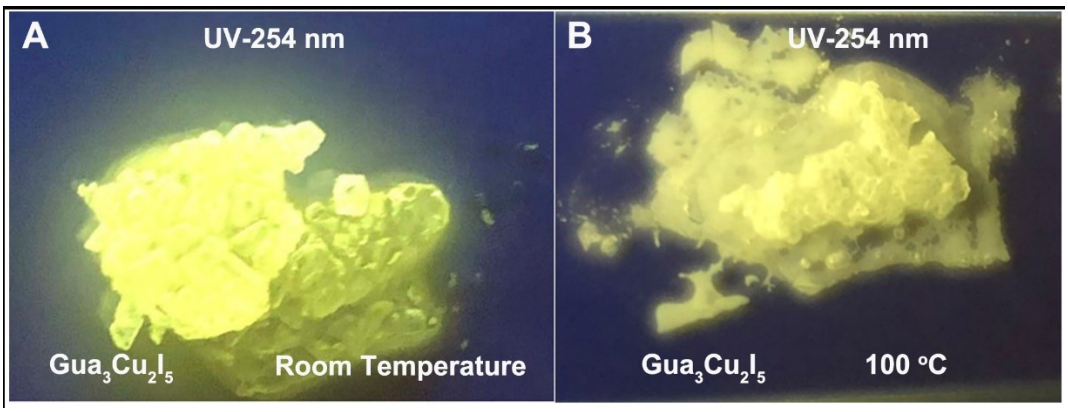

Fig. S5. Photos of $Gua_3Cu_2I_5$ at room temperature and 100 °C under the irradiation of UV-254nm

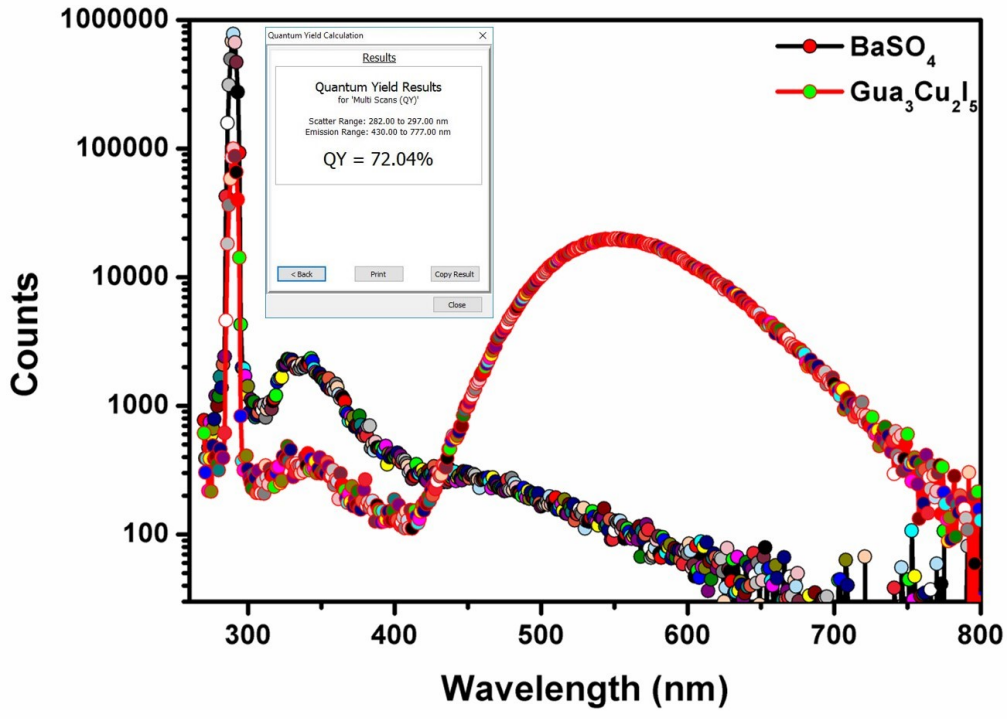

Fig. S6. Absolute PLQY of $Gua_3Cu_2I_5$ powders based on $BaSO_4$ standard material

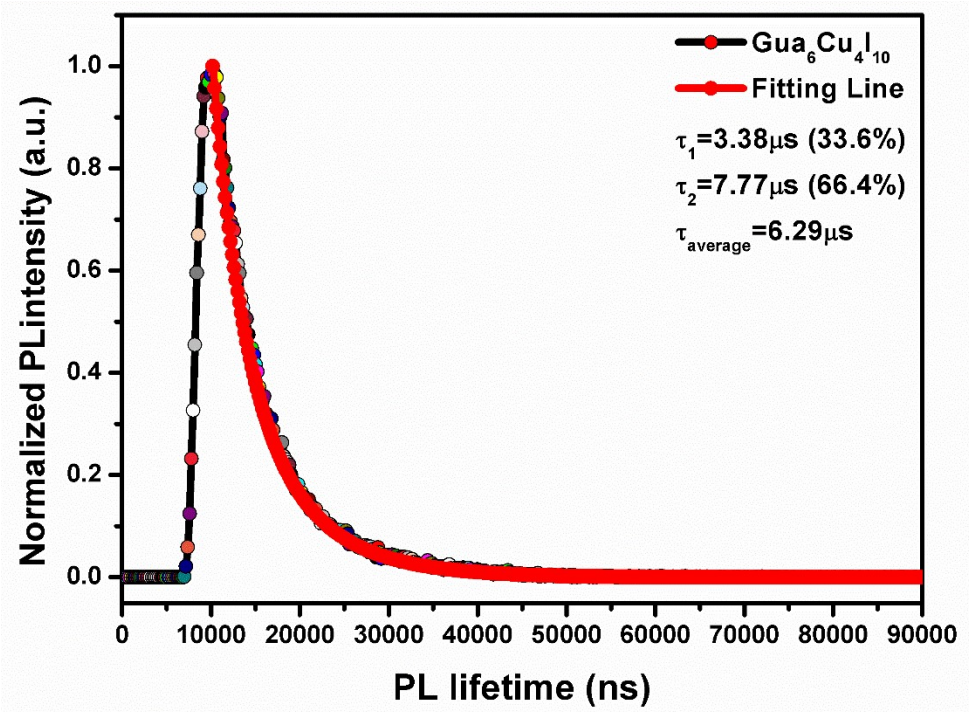

Fig. S7. PL decay lifetime of $Gua_6Cu_4I_{10}$ powders.

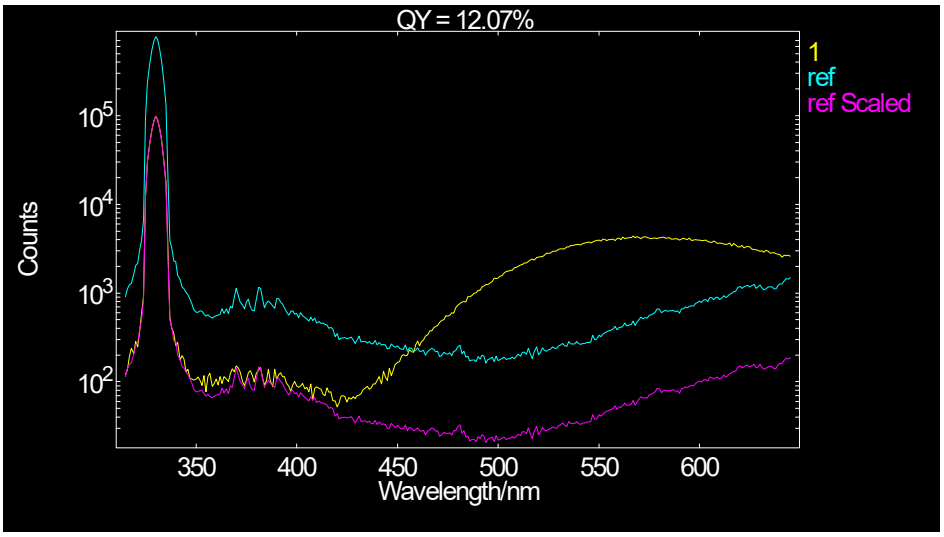

Fig. S8. Absolute PLQY of $Gua_6Cu_4I_{10}$ powders based on $BaSO_4$ standard material.

Table S1. Crystal structure data for $Gua_4Cu_4Br_8$, $Gua_3Cu_2I_5$ and $Gua_6Cu_4I_{10}$.

Identification code	**$Gua_4Cu_4Br_8$**	**$Gua_3Cu_2I_5$**	**$Gua_6Cu_4I_{10}$**
Empirical formula	$C_4H_{24}Br_8Cu_4N_{12}$	$C_3H_{18}Cu_2I_5N_9$	$C_6Cu_4I_{10}N_{18}$
Formula weight/g·mol^{-1}	1133.79	941.84	1847.40
Temperature/K	293(2)K	293(2)K	293(2)K
Wavelength/Å		0.71073	
Crystal color	Colorless	Colorless	Colorless
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$ (no.14)	$C2/c$ (no.15)	$Cmc2_1$ (no.36)
a/Å	8.0772(2)	12.0317(9)	12.072(3)
b/Å	11.5386(4)	13.2491(10)	13.215(3)
c/Å	29.4561(11)	13.5695(10)	13.581(3)
α/°	90.00	90.00	90.00
β/°	96.1640(10)	90.985(7)	90.00
γ/°	90.00	90.00	90.00
Volume/Å^3	2729.42(15)	2162.8(3)	2166.6(9)
Crystal size (mm^3)	0.15 × 0.12 × 0.1	0.15 × 0.12 × 0.1	0.12×0.1×0.1
Z	4	4	2
Density/g·cm^{-3}	2.759	2.893	2.832
μ(mm^{-1})	14.804	9.105	9.087
F (000)	2112.0	1688.0	1616.0
GOF on F^2	1.079	1.111	1.087
Absolute Flack Factor	---	---	0.3(3)

Absorption correction	Semi-empirical from equivalents		
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	6789/0/255	2204/0/91	2789/64/105
R_1, wR_2 [$I > 2\sigma(I)$]	0.0397, 0.0855	0.0638, 0.1954	0.0593, 0.1295
R_2, wR_2 (all data)	0.0670, 0.0970	0.0716, 0.1997	0.0797, 0.1416
Min/Max $\Delta\rho$ /eÅ^{-3}	-1.35/0.78	-2.48/3.17	-2.84/2.74
CCDC	**2113135**	**2113134**	**2113136**