Strongly emissive white-light-emitting silver iodide based inorganic-organic hybrid structures with comparable quantum efficiency to commercial phosphors

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Supporting information

Materials. Materials. AgI (99.99% metals basis, Aladdin), CuI (AR,≥99.5%, Aladdin), N,N-Dimethylformamide (DMF, AR,99.5%,Macklin),Dichloromethane (DMC, ACS,≥99.5%, Aladdin),4,4'-bipyridine, (4,4'-bpy, 98%, Aladdin), triphenylphosphine (tpp, GC,>99.0%, Aladdin).

Synthesis of 1D-$Ag_2I_2(tpp)_2$(4,4'-bpy) (1). The synthesis of **1** was carried out by a modified version of the reported method.[1, 2] AgI (0.05 g, 0.2 mmol), tpp (0.13 g, 0.5 mmol), 4,4'-bpy (0.08 g, 0.5 mmol) was added into 8 ml DMF/DCM（v:v=1:1). The reaction mixture has been stirred under magnetic stirring at room temperature. Pure phase of powder sample was collected by filtration after 8 h of continuous stirring. Upon completion of reactions, powder samples were collected by filtration from the reaction solution and washed with a small amount of methanol three times. These samples were then dried in a vacuum oven overnight before other measurements were made. The yield is 68% based on Ag.

Synthesis of 1D-$Ag_{2-x}Cu_xI_2(tpp)_2$(4,4'-bpy) (2-5). The syntheses of substituted compounds 1D-$Ag_{2-x}Cu_xI_2(tpp)_2$(4,4'-bpy) (x<2) are similar as that of their parent structure **1**. A stock solution of 10^{-4} M CuI in DMF/DCM（v:v=1:1) was pre-made. The substituted structures obtained are 1D-$Ag_{2-x}Cu_xI_2(tpp)_2$(4,4'-bpy) (x = 0.001, **2**; x = 0.005, **3**; x = 0.01, **4**; x = 0.02, **5**). All products were collected by filtration and dried in vacuum oven for further characterization. The yield is ~70% based on Ag for **2**-**5**.

Synthesis of 1D-$Cu_2I_2(tpp)_2$(4,4'-bpy) (6).[3] The synthesis of **6** is similar as that of **1** except using CuI instead of AgI.[3] Pure phase of powder sample was collected by filtration after 8 h of continuous stirring and was dried in vacuum overnight. The yield is 83% based on Cu.

Powder X-ray diffraction (PXRD). PXRD analyses were carried out on a Bruker D8 Advance automated diffraction system using Cu Kα radiation (λ = 1.5406 Å). The data were collected at room temperature in a 2θ range of 3–50° with a scan speed of 1°/min. The operating power was 40 kV/40 mA.

Optical diffuse reflectance measurements. Optical diffuse reflectance spectra were measured at room temperature on a Shimadzu UV-3600 spectrophotometer. Data were collected in the wavelength range of 300-1200 nm. $BaSO_4$ powder was used as a standard (100% reflectance). A similar procedure as previously described was used to collect and convert the data using the Kubelka-Munk function. The scattering coefficient (S) was treated as a constant since the average particle size of the samples used in the measurements was significantly larger than 5 μm.

Thermogravimetric (TG) analysis. TG analyses of the title compounds were performed on a computer-controlled TG 550 (TA Instrument). Pure powder samples were loaded into platinum pans and heated with a ramp rate of 10 °C/min from room temperature to 700 °C.

Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) measurements. The percentages of Cu present in the final samples were estimated by ICP-MS using an Agilent 7700 instrument.

Photoluminescence measurements. Excitation spectra were measured at room temperature on a FLS1000 spectrofluorometer (Edinburgh Instruments) monitored at

maximum of emission spectra. Steady-state photoluminescence spectra were obtained at room temperature on a FLS1000 spectrofluorometer.

Internal quantum yield measurements. Internal quantum yields of samples in powder form were measured on a C9920-03 absolute quantum yield measurement system (Hamamatsu Photonics) with a 150 W xenon monochromatic light source and 3.3 inch integrating sphere.

Time-resolved photoluminescence. Time-resolved emission data were collected at room temperature using the FLS100 spectrofluorometer. The dynamics of emission decay were monitored by using the FLS1000's time-correlated single-photon counting capability (1024 channels; 10 μs window) with data collection for 10,000 counts. Excitation was provided by an Edinburgh EPL-360 picosecond pulsed diode laser.

DFT Calculations. First-principle calculations of the band structure (BS) and density of states (DOS) of compounds **1** were carried out using the CASTEP code implemented in the Material studio 5.0 package. Generalized gradient approximations (GGA) with Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional (xc) were used in all calculations. The plane-wave basis set energy cutoff was set at 10.0 eV, ultrasoft pseudopotentials were used for all chemical elements and the total energy tolerance was set to be 1×10^{-5} eV/atom.

Fabrication of LED bulbs. Selected phosphors **2-4** (0.5 g) was added into 2 mL binder solution and well dispersed by stirring. The solution mixture was then applied onto the surface of a 1 cm 360 nm LED chip and allowed to dry in open air. This process was then repeated three times to ensure uniform coating.

Table S1. Theoretical Cu-Ag ratio and experimental ratio determined by ICP-MS

Compound	Theoretical	Experimental
2	0.05%	0.07%
3	0.25%	0.33%
4	0.5%	0.68%
5	1.0%	1.48%

Table S2. Elemental analysis results for compounds **1-6**.

Compound		C %	H %	N %
1	Calculated	48.0	3.3	2.4
	Experimental	47.6	3.2	2.5
2	Calculated	48.0	3.3	2.4
	Experimental	48.1	3.2	2.4
3	Calculated	48.0	3.3	2.4
	Experimental	47.9	3.2	2.3
4	Calculated	48.0	3.3	2.4
	Experimental	47.8	3.4	2.3
5	Calculated	48.0	3.3	2.4
	Experimental	47.6	3.2	2.4
6	Calculated	52.0	3.6	2.6
	Experimental	51.6	3.5	2.5

Table S3. The cost of the raw materials compared with commercial phosphor YAG. The price of the chemical species has been estimated from Alibaba.com.

Chemical Species	Price ($/Kg)
AgI	~400
CuI	~30
triphenylphosphine	~10
4,4’-bipyridine	~200
YAG: Ce	~1000

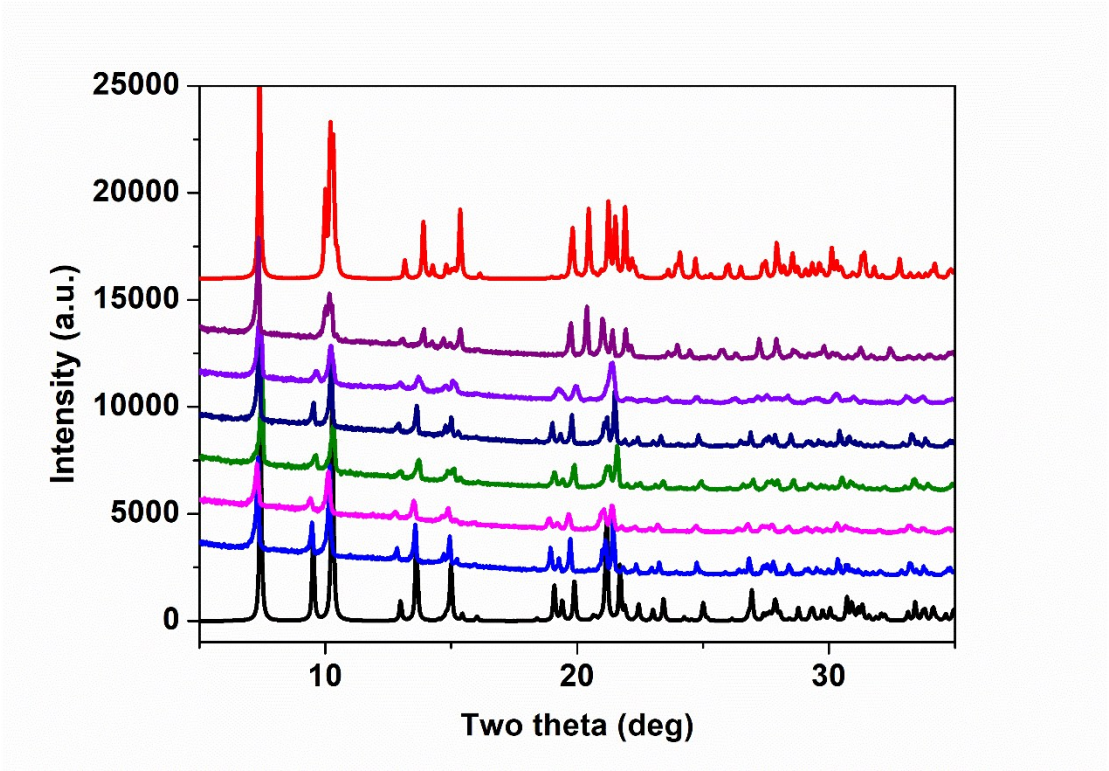

Figure S1. PXRD patterns of compounds **1**-**6** compared to simulated patterns. From bottom to top: simulated **1**, as made **1**, as made **2**, as made **3**, as made **4**, as made **5**, as made **6**, simulated **6**.

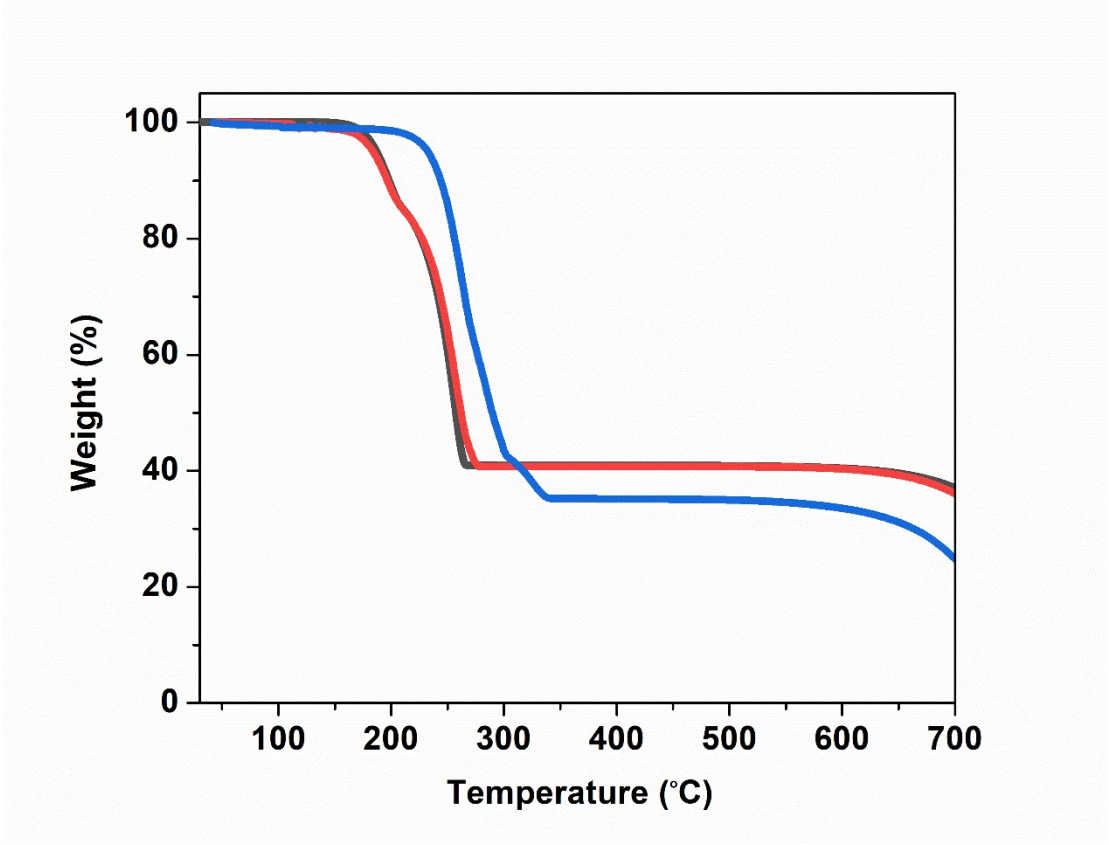

Figure S2. TGA plots of **1** (black), **4** (red) and **6** (blue).

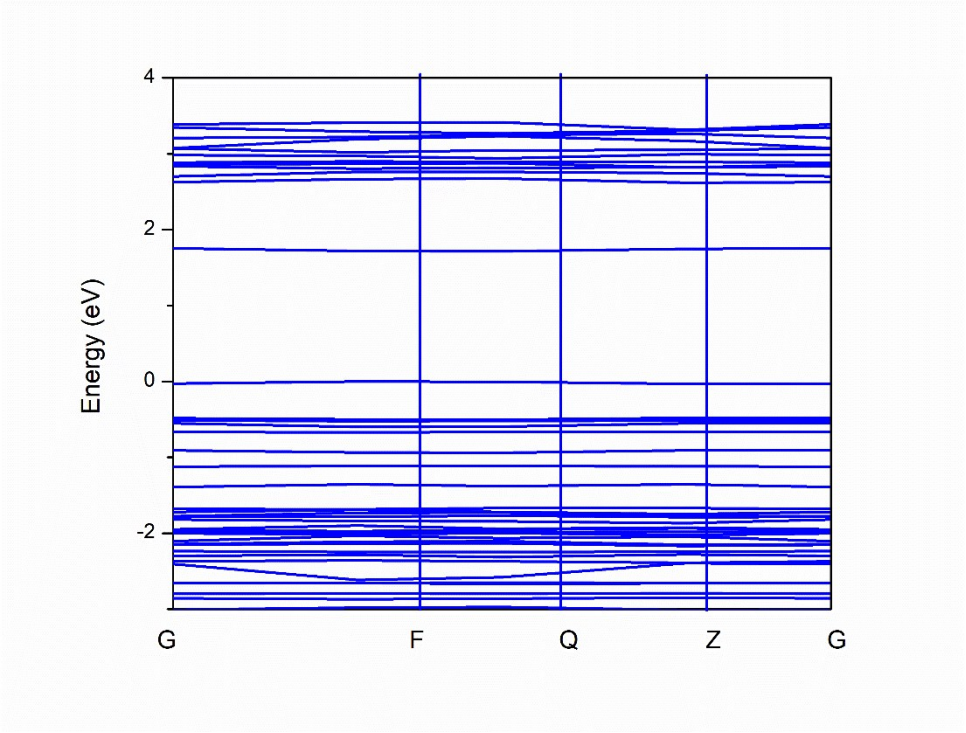

Figure S3. Calculated band structure for **1**.

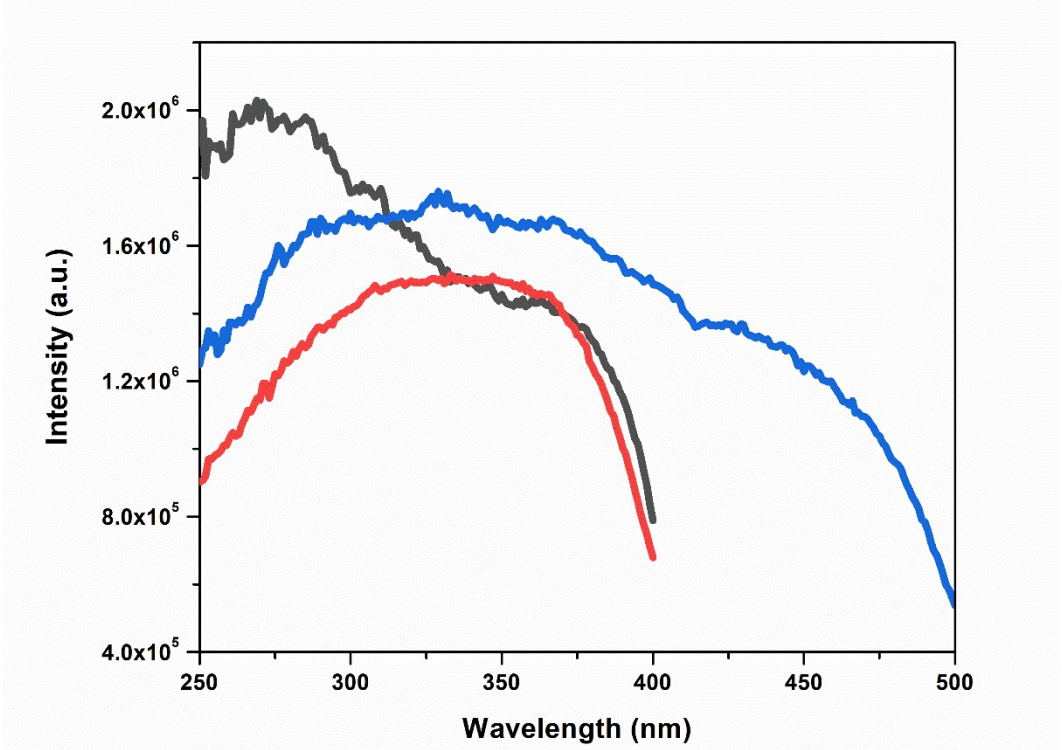

Figure S4. Excitation spectra of **1** (black, λ_{em} = 460nm), **4** (red, λ_{em} = 460nm) and **6** (blue, λ_{em} = 550nm).

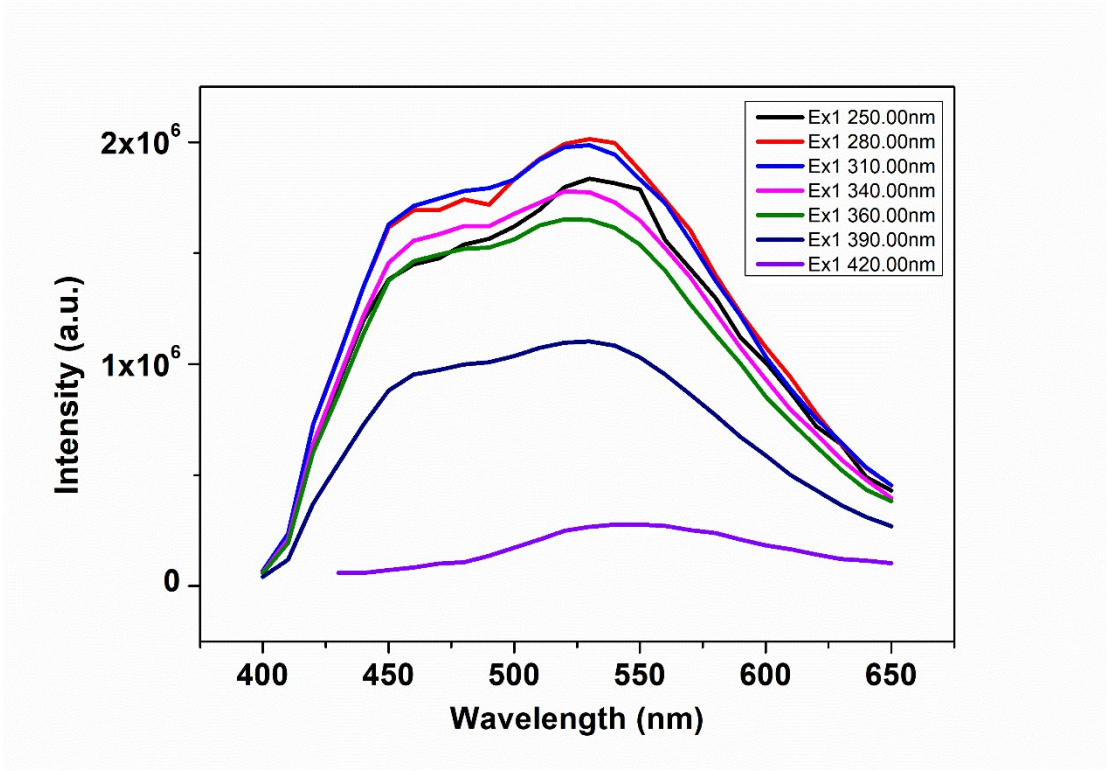

Figure S5. Emission spectra of **2** under various excitation energies.

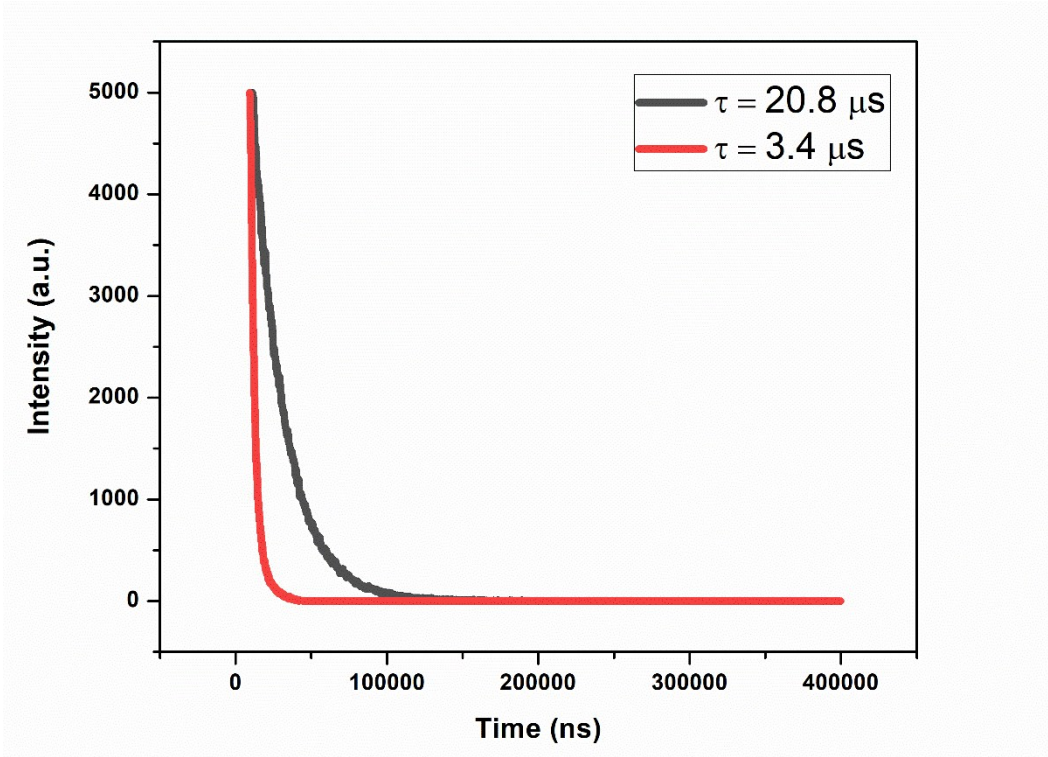

Figure S6. Luminescence decay spectra of **4** at 460 nm (black) and 550 nm (red). λ_{ex} = 360nm.

References

1. W. Liu, Y. Fang, G. Z. Wei, S. J. Teat, K. Xiong, Z. Hu, W. P. Lustig and J. Li, *Journal of the American Chemical Society*, 2015, **137**, 9400-9408.
2. J. T. Sampanthar and J. J. Vittal, *Cryst. Eng.*, 2000, **3**, 117-133.
3. R.-Z. Li, D. Li, X.-C. Huang, Z.-Y. Qi and X.-M. Chen, *Inorg. Chem. Commun.*, 2003, **6**, 1017-1019.