

Supporting information

A highly luminescent and stable copper halide ionic hybrid structure with anionic $\text{CuBr}_2(\text{tpp})_2$ module

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Materials and Characterization

Materials. Copper (I) bromide, triphenylphosphine, 1,4-diazabicyclo[2.2.2]octane (*ted*), benzyl bromide, acetone, toluene, dichloromethane, ethanol were purchased from Aladdin. All reagents and solvents were used without further purification unless otherwise stated.

Synthesis of *bz-ted*. *Ted* (1.12 g, 10 mmol) was dissolved in acetone (50 mL) upon sonication and benzyl bromide (1.71 g, 10 mmol) was added to it under magnetic stirring. A white precipitate formed in a few hours. The precipitate was collected by filtration, washed with ethyl acetate, and dried under vacuum. The yield is 79%.

Synthesis of **1.** CuBr (0.29 g, 0.2 mmol), *tpp* (0.5 g) and *bz-ted* (0.2 mmol) were added to a CH_2Cl_2 /toluene mixture (1 : 1/v : v) and were heated at 80 °C overnight. Colorless plate-shaped crystals were filtered via vacuum filtration for further characterization. The weight of the product is 0.15 g. The reaction yield is 75 % based on Cu.

Sample Washing and Drying. Upon completion of reactions, a powder sample of **1** was collected by filtration from the reaction solution and washed with a small amount of acetonitrile three times. The sample was then dried in a vacuum oven overnight before other measurements were made.

Single crystal X-ray diffraction (SXRD). Single crystal X-ray diffraction data were collected at 203K on a Bruker APEX-II CCD with graphite-monochromated Ga K α radiation ($\lambda = 1.34139 \text{ \AA}$) The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the Bruker SHELXTL package.¹ These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_re-quest/cif. The structures were deposited in Cambridge Structural Database (CSD) and the number is 2013295.

Powder X-ray diffraction (PXRD). PXRD analyses were carried out on a Bruker D8 Advance automated diffraction system using Cu K α 1 radiation ($\lambda=1.54056 \text{ \AA}$). 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. BaSO₄ 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 800 °C.

Excitation spectrum measurements. Excitation spectra were measured at room temperature on an FLS1000 spectrofluorometer (Edinburgh Instruments) monitored at a maximum of emission spectra.

Photoluminescence measurements. Steady-state photoluminescence spectra were obtained at room temperature and 77 K (liquid nitrogen was used to cool the samples) on an FLS1000 spectrofluorometer.

Internal quantum yield measurements. Internal quantum yield (QY) of samples in powder form was 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. Sodium salicylate (99%, Merck) was used as the standard with an IQY value of 60 % when excited at 360 nm. The IQY value of the standard was measured to be 62%, indicating an experimental error of less than 5 %.

Time-resolved photoluminescence. Time-Resolved Emission data were collected at room temperature using the FLS1000 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. Long lifetime measurements at 77K (1024 channels; 800 μs window) were collected using Xe flash lamp as the excitation source. The lifetime was obtained by mono-exponential fitting.

Density-Functional Theory (DFT) calculations. Compound **1** is a coordination compound consisting of a complex cation and a complex anion. DFT calculations have been carried out on the cation and anion, respectively, using two different functions (M06 and B3LYP-D3). The HOMO-LUMO gap of the anion is 3.86 eV (M06) and 3.45

eV (B3LYP-D3), which are generally consistent with each other and agree with the experimental observation.

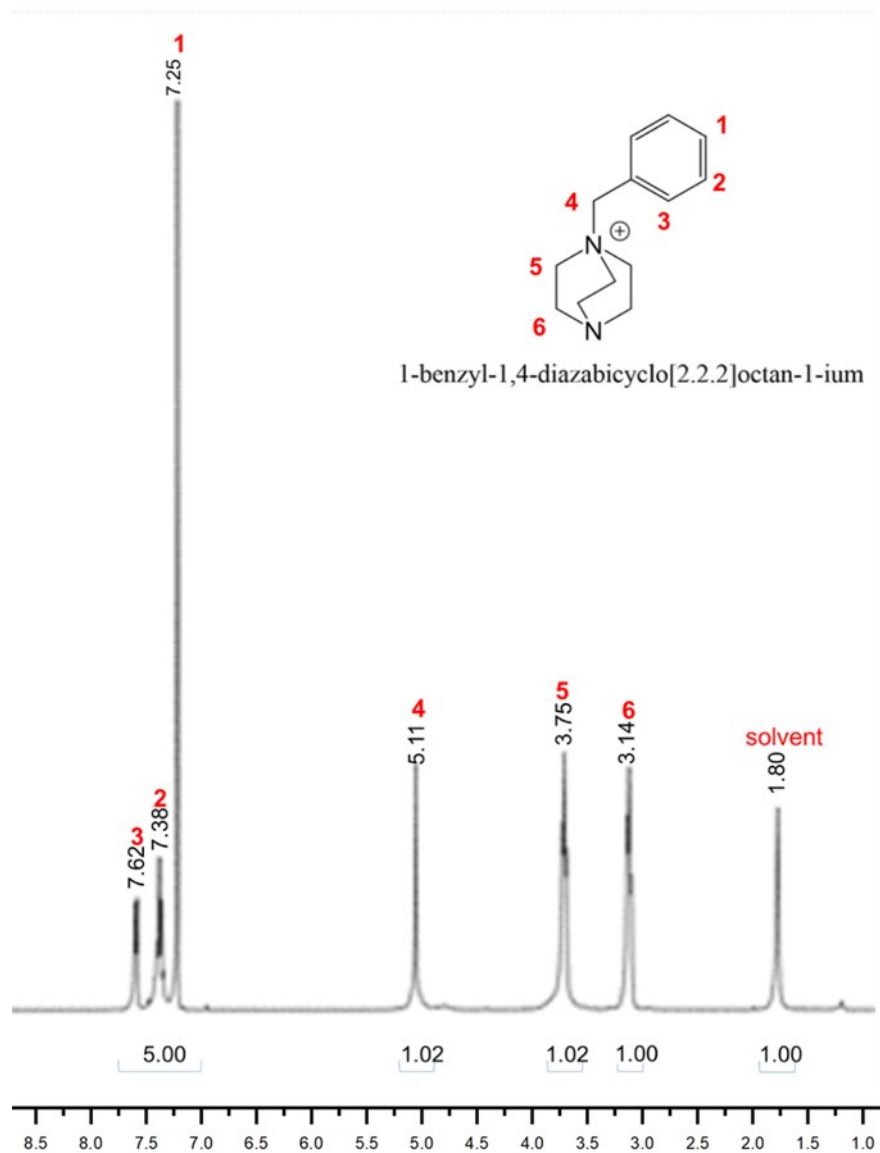


Figure S1. ¹H NMR spectrum of the organic ligand *bz-td*.

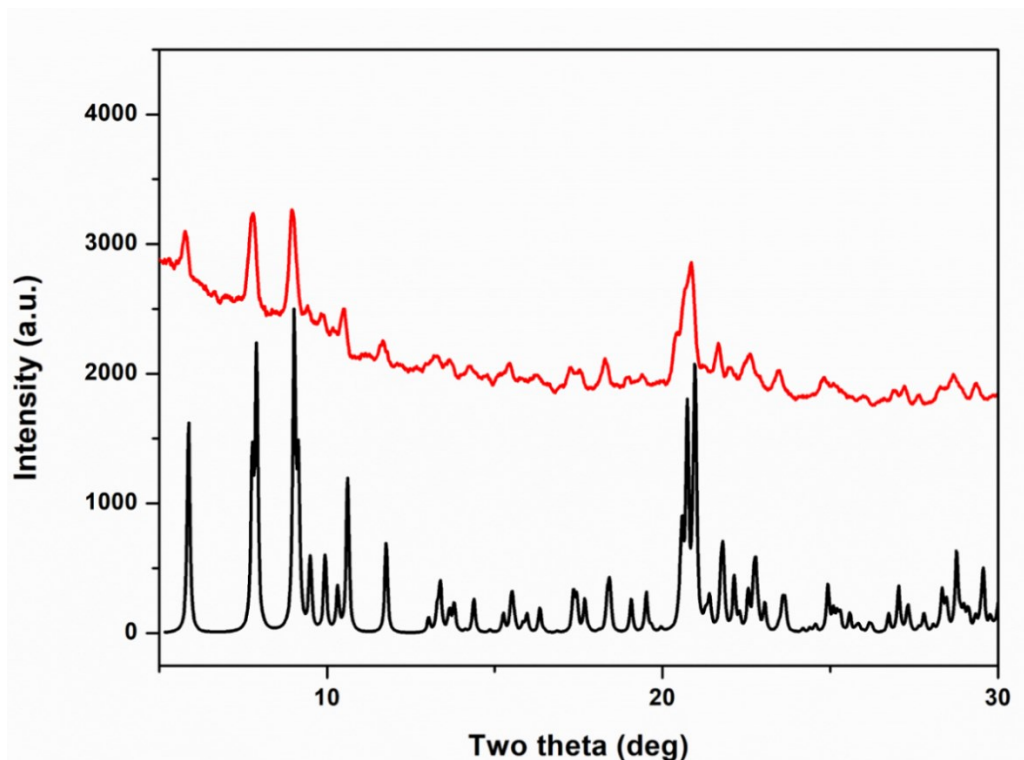


Figure S2. PXRD patterns of as-made (top) and simulated pattern of compound **1** (bottom).

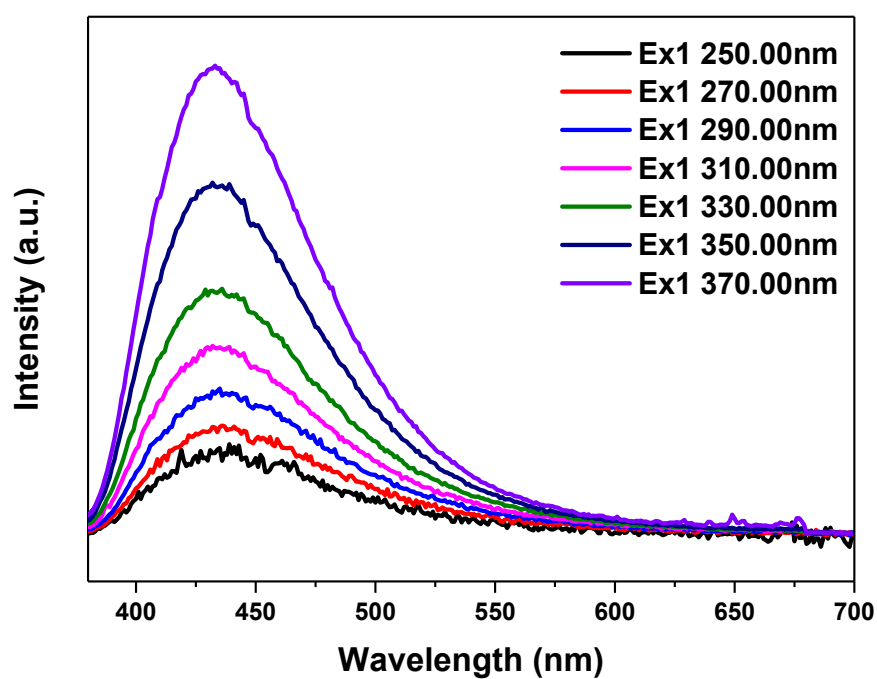


Figure S3. Emission spectra of **1** under various excitation energies.

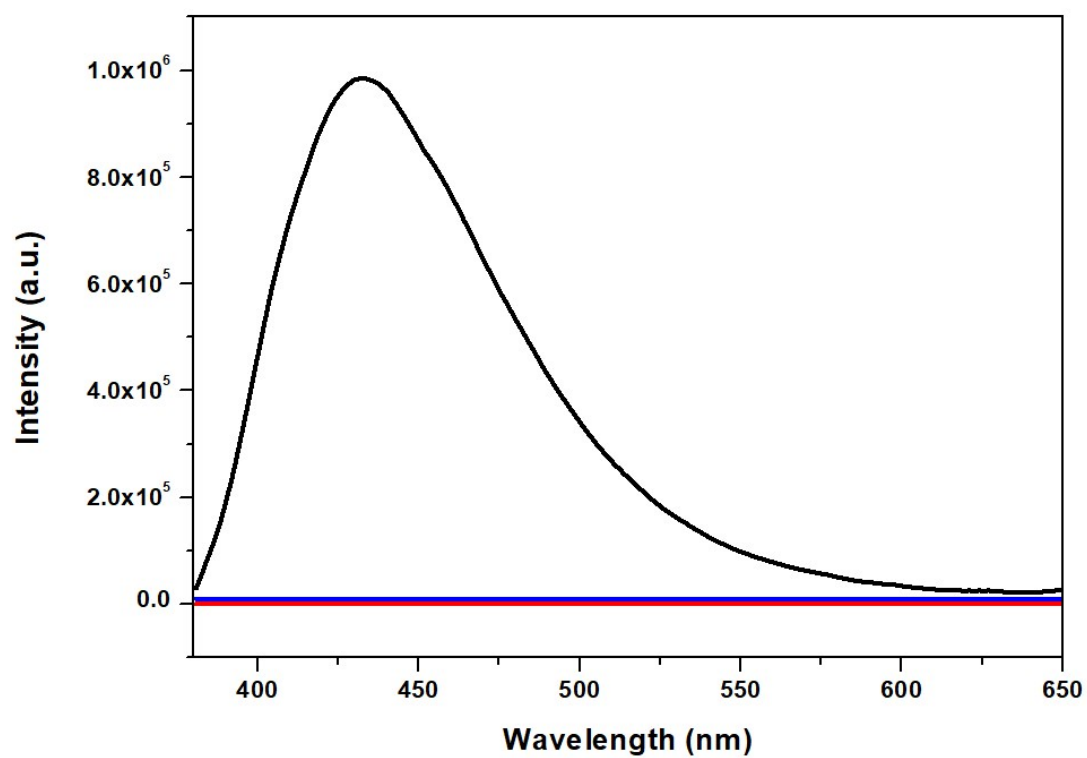


Figure S4. Emission spectra of **1** (black), *tpp* (blue) and *bz-ted* (red). $\lambda_{\text{ex}} = 360$ nm.

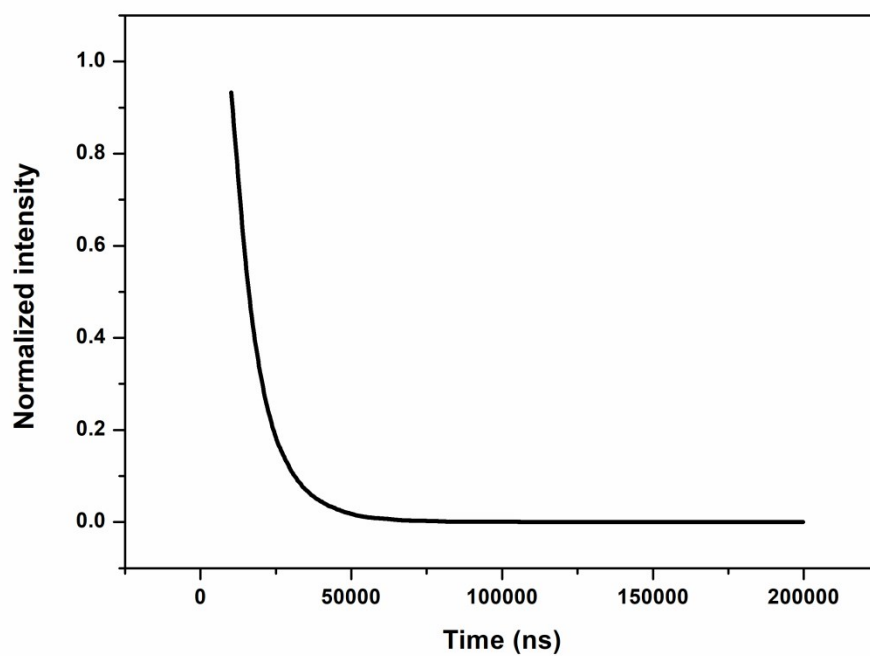


Figure S5. Luminescence decay curve at room temperature of compound **1**.

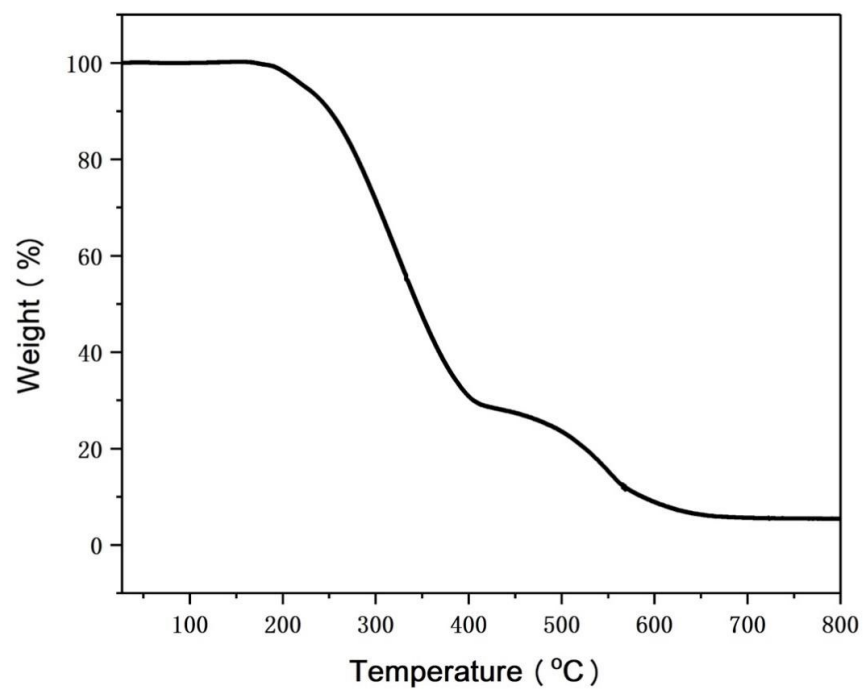


Figure S6. TGA plot of compound **1**.

Table S1. Crystal data and structure refinement details of compounds 1

Compound	1
Formula	C ₄₉ H ₅₁ Br ₂ CuN ₂ OP ₂
Fw	969.21
Space Group	<i>P</i> -1
<i>a</i> (Å)	13.1166(10)
<i>b</i> (Å)	13.1497(10)
<i>c</i> (Å)	15.2644(12)
α (°)	80.358(3)
β (°)	82.951(3)
γ (°)	60.542(3)
<i>V</i> (Å ³)	2257.5(3)
<i>Z</i>	2
<i>T</i> (K)	203(2)
λ (Å)	1.34139
ρ (g·cm ⁻³)	1.426
R_1^a [$I > 2\sigma(I)$]	0.0397
wR_2^a [$I > 2\sigma(I)$]	0.0964
R_1^a (all data)	0.0334
wR_2^a (all data)	0.0923
CCDC #	2013295

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}. \quad wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}.$$

Table S2. Elemental analysis of compound 1.

Compound		C %	H %	N %
	Calculated	60.7	5.3	2.9
	Experimental	60.0	5.2	2.9

Table S3. Density-Functional Theory (DFT) calculation results of compound **1**.

Species	Method	B3LYP-D3	M06
	HOMO/LUMO (eV)		
$\text{CuBr}_2(\text{tpp})^-$		3.45	3.86
bz-ted^+		5.90	6.43

Table S4. A summary of recent reported blue-emitting organic-inorganic hybrid structures

Compounds	λ_{ex} (nm)	λ_{em} (nm)	Emission color	IQY (%)
0D-Cu ₂ I ₂ (tpp) ₂ (4-pc) ₂ ¹	360	450	blue	86.7
0D-Cu ₂ I ₂ (tpp) ₂ (3-pc) ₂ ¹	360	455	blue	90.3
0D-Cu ₂ I ₂ (tpp) ₂ (4,6-dm-pm) ₂ ¹	360	465	blue	72.3
0D-Cu ₂ I ₂ (tpp) ₂ (1-me-bzim) ₂ ¹	360	465	blue	74.3
1D-CuI(3-pc) ²	360	469	blue	37.2
1D-Cu ₂ I ₂ (tpp) ₂ (bpp) ₃ ³	360	458	blue	91.7
[BAPrEDA]PbCl ₆ ·(H ₂ O) ₂ ⁴	254	392	blue-violet	21.3
(C ₁₃ H ₁₉ N ₄) ₂ PbBr ₄ ⁵	360	460	blue	40
Bmpip ₂ PbBr ₄ ⁵	360	470	blue	24
(C ₉ NH ₂₀) ₇ (PbCl ₄)Pb ₃ Cl ₁₁ ⁶	360	470	blue	83
K ₂ CuCl ₃ ⁷	291	392	blue	96.58
K ₂ CuBr ₃ ⁷	296	388	blue	55
Rb ₈ CuSc ₃ Cl ₁₈ ⁸	--	473	blue	--

Reference

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