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A highly luminescent and stable copper halide ionic hybrid structure with an anionic CuBr₂(tpp)₂ module⁺

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Here, we report a novel copper bromide ionic compound (bz-ted) $CuBr_2(tpp)_2 \cdot H_2O$ (1, tpp = triphenylphosphine, and bz-ted = 1-benzyl-1,4-diazabicyclo[2.2.2]octan-1-ium) by a facile wet chemistry method. The inorganic module of the compound is $CuBr_2^-$ coordinated to two tpp molecules, generating strong blue photoluminescence originating from the metal-to-ligand-charge-transfer (MLCT) process. The combination of both ionic bonds and covalent bonds in the hybrid cluster makes compound 1 strongly emissive, robust and solution-processable. Such a coordinated anionic inorganic module presents a new approach for the development of highly luminescent and stable copper halide ionic hybrid structures.

Crystalline organic–inorganic hybrid materials are composed of inorganic and organic moieties that are combined at the molecular scale.^{1–7} This type of hybrid compound is both fundamentally and technologically important because of the structural versatility and interesting properties that result from the incorporation of both inorganic and organic components in a single crystal lattice.^{8–13} Such inorganic motifs are further connected by different kinds of organic ligands, either aliphatic or aromatic, forming zero-dimensional (0D) molecular clusters to one-dimensional (1D) chains, and from two-dimensional (2D) sheets to three-dimensional (3D) frameworks.^{6,14,15} These materials are a very important class of functional materials with structural variety and interesting properties, showing potential applications in a variety of areas, including light-emitting diodes (LEDs), chemical sensors, functional coatings, *etc.*^{16,17}

Among them, hybrid structures based on copper halides are a representative luminescent hybrid structure family that has been studied intensively recently due to their unique photophysical and photochemical properties originating from the d¹⁰ electronic configuration of the Cu atoms.¹⁸⁻²⁰ A variety of inorganic modules have been reported, from discrete inorganic units to extended infinite chains or layers.²¹ These inorganic motifs are combined with different types of organic ligand, mostly N-containing ligands (N-ligands), either aliphatic or aromatic, to form molecular clusters, chains, layers, and extended networks.18,21 The bondings between the two components are coordinate bonds, ionic bonds or both. Their luminescence mechanisms include metal-to-ligand-charge-transfer (MLCT), halide-to-ligand-charge-transfer (XLCT), metal-centered change transfer (CC), or a combination of them.^{22,23} The remarkable structural diversity of the copper halide hybrid structure family is a result of a vast variety of available inorganic modules and organic ligands, as well as many possible coordination modes between them.¹⁸ It has been found that the ionic bonding in the hybrid structures could enhance their stability, while the coordinative bonding is important for their luminescence.^{24,25} Thermochromic, vapochromic, and mechanochromic luminescence has been observed and well studied for this family of materials.²⁶⁻²⁸

The remarkable structural diversity of the copper halide hybrid structure family is a result of a vast variety of available inorganic modules and organic ligands, and many possible coordination modes between them.¹⁸ They have been grouped based on the nature of chemical bonding: the neutral structures are those built on coordinative Cu-ligand bonds, and therefore both the inorganic module (CuI) and organic ligands are charge-neutral; the ionic structures are those that are made of cationic ligands and anionic inorganic modules without direct coordinative bonds between the two; all-in-one (AIO) type structures are those with both coordinate and ionic bonds between the inorganic module and organic ligand.¹⁸ It has been found out that the ionic bonding in the hybrid structure could enhance their stability, while the coordinative bonding is important for their luminescence.^{24,25} The copper halide ionic organic-inorganic hybrid structures are much more stable compared to the neutral structures with similar structure and

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composition. However, they generally display weak or no luminescence due to the absence of metal-to-ligand charge transfer (MLCT) luminescence mechanism since there are no coordination bonds between the inorganic species and the organic species. The studies on AIO compounds reveal that the coordination bonds between the ligand molecules and copper atoms are the key factors for the strong luminescence of these hybrid compounds.^{24,25}

Here, a new design strategy has been developed for the development of hybrid structures with both ionic bonds and coordinative bonds. A coordinated anionic inorganic cluster $\text{CuBr}_2(\text{tpp})_2^-$ has been constructed with CuBr_2^- anion coordinated with two neutral triphenylphosphine (tpp) molecules. Such $\text{CuBr}_2(\text{tpp})_2^-$ clusters are surrounded by cationic bz-ted (bz-ted = 1-benzyl-1, 4-diazabicyclo[2.2.2]octan-1-ium), forming an ionic organic–inorganic hybrid structure (bz-ted)CuBr_2(tpp)_2·H_2O (1). In this structure, the cationic cluster $\text{CuBr}_2(\text{tpp})_2^-$ contains the Cu–ligand coordination bonds, generating strong blue luminescence due to the charge transfer among the ligand molecules and the metal. The ionic bonds between cationic and anionic species improve the stability and solubility of the hybrid structures.

The preparation of bz-ted bromide is conducted by a modified method and its ¹H NMR spectrum is shown in Fig. S1 (ESI[†]).²⁹ 1,4-Diazabicyclo[2.2.2]octane (ted) was first dissolved in acetone (50 mL) and benzyl bromide was added dropwise into it under magnetic stirring. The reaction mixture was stirred for 12 h and a white precipitate formed that was collected by filtration. Colorless plate-shaped single crystals of 1 were obtained by heating the mixture of CuBr, tpp, and bzted bromide in a mixed CH2Cl2/toluene (1:1/v:v) solvent system at 80 °C. Crystals formed overnight and were typically suitable for X-ray single-crystal diffraction analysis. The reaction yield is 75% based on Cu. The single crystal X-ray diffraction analysis shows that 1 crystallizes in the triclinic space group $P\bar{1}$ with 2 formula units in the unit cell and all atoms are in general positions. There are also water molecules in the structure. Detailed cryptographic data are summarized in Table S1 (ESI⁺). Each Cu atom is coordinated by two Br atoms and two tpp molecules in a tetrahedral geometry, forming a negatively charged $CuBr_2(tpp)_2^-$ species (Fig. 1a). The ligand is positively charged and is surrounded by the $CuBr_2(tpp)_2^-$ species (Fig. 1b). There is no coordination bond between the N atoms and the Cu atoms, though there is an uncoordinated N atom in the ligand. $CuBr_2(tpp)_2^-$ and the ligand are connected by hydrogen bonds. The distance between O(1) and N(2) is 3.052(1) Å and the angle of $\angle O(H(1C) \cdots N(2))$ is 161.1(2)°, while the distance between O(1) and Br(2) is 3.550(4) Å and the angle of $\angle O(H(1B) \cdots Br_2^{i})$ (symmetry code: i, x, y - 1, z) is 169.5(5)°. The phase purity of compound 1 was confirmed by powder X-ray diffraction analysis (PXRD, Fig. S2, ESI†). The peak positions observed in the PXRD patterns are in good agreement with those simulated from single-crystal X-ray data, indicating that a pure phase is obtained. The compositions of the crystals were further verified by elemental analysis (Table S2, ESI⁺). Details of synthesis and characterization can be found in the ESI.†

The optical absorption spectrum for compound **1** was collected at room temperature and converted to the Kubelka–Munk



Fig. 1 (a) Structural plot of the compound 1 (cyan balls: Cu; dark yellow balls: Br; pink balls: P atoms; grey balls: C atoms; blue balls: N atoms; dark grey balls: H atoms; red ball: O atom). (b) Structural plot of coordinated copper halide modules and the surrounding ligands (blue balls). Some atoms are hidden for clarity.

function, as shown in Fig. 2a. The absorption edge for compound 1 was found to be 3.0 eV. This value is also under the densityfunctional theory (DFT) calculation results of compound 1 (Table S3, ESI[†]). Single crystals of 1 are colorless and transparent under natural light, suggesting almost no absorption in the visible region with a wide band gap, while under photoexcitation at the excitation energy (360 nm), the single crystal of 1 emits intense blue light (Fig. 2b inset). Upon excitation, the electrons are excited from the valence bands to the conduction bands, and the radiative recombination of electrons and holes leads to the strong blue luminescence of the compound. Fig. 2b is the photoluminescence of compound 1 under 360 nm excitation at room temperature. As shown in this figure, it exhibits strong blue emission with a full width at half-maximum (fwhm) of \sim 75 nm. The emission peaks at 430 nm, and such a highenergy and deep blue emission is very rare among copper halide-based hybrid structures.16,18,20 The excitation spectrum of 1 covers most of the UV light region with the strongest peak of 360 nm. Photoluminescence under various excitation energies has been investigated and the spectra are plotted in Fig. S3 (ESI⁺). The spectra show that though the emission intensities change, the emission range remains the same, indicating that the emission is from a single excitation state.

Temperature-dependent photoluminescence emission was studied under the excitation of 360 nm and the spectra are plotted in Fig. 3a. At various temperatures from 77 K to 277 K,



Fig. 2 (a) UV-vis absorption spectrum of **1**. (b) Excitation (black) and emission spectra (blue) of **1**. $\lambda_{ex} = 360$ nm, and $\lambda_{em} = 430$ nm. Inset: Crystalline sample of **1** under UV light.

this compound emits stable blue emission without any change in the emission energy and range, indicating that there is no thermochromic behaviour found for 1. As the temperature decreases, the photoluminescence intensity increases for this compound. An AIO type of copper iodide-based cluster with bzted as the organic ligand, 0D-Cu₃I₅(bz-ted)₂, has been reported as a yellow emitter with an emission maximum at 560 nm.²⁵ It has been studied that for 0D-Cu₃I₅(bz-ted)₂, the luminescence is majorly contributed from Cu-Cu interaction, and the ligands have little influence on its luminescence. Thermochromic behaviour has also been found for this compound, which is the major characteristic of metal-centered change transfer.³⁰ Similar luminescence behaviour has been observed for Cu₄I₄ cubane-based structures and other ionic structures without Culigand bonds.^{27,31} There is only one Cu atom in the inorganic module of 1, eliminating the possibility of Cu-Cu interaction. Also, the organic ligands are not fluorescent, as shown in Fig. S4 (ESI[†]). The strong high-energy emission of 1 suggests the MLCT mechanism as observed for other neutral copper halide molecular complexes.^{19,20} The intense blue emission of the compound is originated from the charge transfer between the tpp molecules and the Cu atoms. Compared to the luminescence of 0D-Cu₃I₅(bz-ted)₂, though the inorganic modules of the two clusters are different, the blue shift in emission energy of 1 is highly related to the introduction of tpp, confirming that the organic ligands play a vital role in the luminescence and this type of compound is optically tunable.



Fig. 3 (a) Emission spectra at various temperatures, λ_{ex} = 360 nm. (b) CIE coordinates of 1, inset: luminescent coating made by 1.

The Commission Internationale de l'Eclairage (CIE) chromaticity coordinates for the compound are calculated to be (0.15, 0.11), as shown in Fig. 3b. The room temperature internal quantum yields (IQYs) were measured on a C9920-03 absolute quantum yield measurement system (Hamamatsu Photonics). The IQY of compound 1 is 81% when excited at the energy of 360 nm. Such a high IQY is rare among the blue-emitting hybrid compounds and Cu-based all inorganic materials (Table S4, ESI⁺).^{12,13,32-34} The luminescence decay curve of the compound at room temperature is shown in Fig. S5 (ESI[†]), giving a long lifetime of approximately 8.89 µs by monoexponential fitting, which indicates the phosphorescence nature. Copper halide ionic organic-inorganic hybrid structures are relatively stable but typically display weak luminescence due to the absence of the metal-to-ligand charge transfer (MLCT) process, which limits their practical applications. Most of the copper halide ionic structures have very low IOY, since the MLCT luminescence is absent in these structures as there are no covalent bonds between the Cu atoms and the organic ligands. Though compound 1 has an ionic structure, there are Cu-tpp covalent bonds that lead to the strong electron transfer between the metal and the ligands, which results in the high quantum efficiency of compound 1.

Most of the previously reported copper halide hybrid structures with strong blue emission are neutral molecular clusters.¹⁸ Though their IQYs are high, poor stability is the major obstacle for their practical applications. The thermal stability of these clusters is typically below 60 °C. The stability of copper halide hybrid structures could be enhanced by the incorporation of the emissive core into multi-dimensional frameworks.³⁰ However, hybrid structures prepared by such an approach are generally extended structures that show poor solubility in common organic solvents. As shown from the TGA plot (Fig. S6, ESI⁺), the decomposition temperature of compound 1 is as high as 200 °C. The decomposition of this compound starts from the loss of the organic molecules and water molecules. The improved stability of compound 1 is achieved by combining both the inorganic and organic bonds in the hybrid structures. In addition, the Cu-P bonds show higher bond energy compared to that of Cu-N bonds, which would form hybrid clusters with higher stability.^{18,19}

Compound 1 is soluble in common organic solvents, such as methanol, DMSO, etc., at room temperature. About 100 mg of 1 can be completely dissolved in 1 mL of DMSO within 5 min at room temperature under ultrasonication. No luminescence has been observed for the dissolved sample. The good solubility of compound 1 in DMSO can be attributed to the formation of CuI-L-DMSO complexes and the 1@DMSO solution is nonluminescent due to the dissociation of Cu-N bonds, which eliminates the MLCT and XLCT charge transfer in 1.24 The luminescent sample of 1 could be recovered by mild heating of the solution until it dried out and the sample could be recrystallized. As shown in the inset of Fig. 3b, a thin film of compound 1 has been prepared by drop-casting 1@DMSO solution on a glass substrate, showing a strong blue signal under UV light. This one-pot synthetic approach by using both neutral and ionic ligands to combine both ionic and coordination bonds is an effective and facile strategy for the design and synthesis of organic-inorganic hybrid structures with strong luminescence, high stability and solution processability. Further expansion of high-performance copper halide hybrid structures with the coordinated anionic inorganic cluster is currently underway by using such a synthetic strategy with different kinds of organic ligands.

Conclusions

In summary, we have synthesized and characterized a novel copper bromide ionic organic-inorganic hybrid structure with efficient blue emission. The structure contains anionic inorganic clusters that are coordinated with neutral organic ligands. The internal quantum yield of the compound is as high as 81%, which is the result of the covalent bonds between the metal and the ligands in the anionic species. The stability of the hybrid compound is improved by the ionic bonds in the structure. This compound is solution-processable and facile to synthesize, serving as a good example of environment-friendly, cost-effective and rare-earth element-free light-emitting materials.

Such structure design strategy represents a new method for the synthesis of highly luminescent and stable copper halide hybrid compounds.

Author contributions

H. T. and C. X. carried out the experiment. H. T. carried out the DFT calculations. W. L. wrote the manuscript and supervised the findings of this work. All the authors discussed the results and contributed to the final manuscript.

Conflicts of interest

There are no conflicts to declare.

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