Stable Lead-Free Blue-Emitting Cs$_3$Cu$_2$Br$_5$ Single Crystal with Self-Trap Exciton Emission for Optoelectronics

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Owing to their excellent photoelectric properties, perovskite materials have broad application prospects; however, the toxicity of Pb limits the application of Pb-based perovskite materials. To overcome this problem, Pb-free perovskite materials are prepared by replacing Pb with nontoxic elements including Ge and Sn; nevertheless, the stabilities of these materials are low. Herein, single crystals of nontoxic Cu(I)-based ternary metal halide (Cs$_3$Cu$_2$Br$_5$) with outstanding stabilities and self-trapped exciton (STE) emission are constructed by an antisolvent method for the first time; these crystals exhibit central blue emission at 458 nm and large Stokes shifts. Photoluminescence (PL) intensities of the single crystals remain above 96.9% of their initial intensities when these crystals are exposed to an atmospheric environment for 90 days. Moreover, the stabilities of the Cs$_3$Cu$_2$Br$_5$ single crystals are investigated by temperature-dependent PL spectroscopy, which suggests a considerable exciton binding energy of 503 meV, and derivative thermogravimetric analysis, which indicate that the temperature of complete decomposition of Cs$_3$Cu$_2$Br$_5$ is above 930 °C. Furthermore, a new class of white light-emitting diodes with an ultrahigh color rendering index of 97.8 and satisfactory performance is produced using the Cs$_3$Cu$_2$Br$_5$ single crystals. The study demonstrates significant potentials of Cu(I)-based single crystals in the field of optoelectronics.

1. Introduction

Lead halide perovskite materials are widely used in optoelectronic devices due to their excellent performances;[1–10] nevertheless, organic metal halide perovskites easily decompose under humid and high-temperature conditions.[11–14] However, the toxicity of Pb substantially limits the commercialization of all-inorganic metal halide perovskites such as CsPbX$_3$, which is still a significant challenge for the practical application of metal halide perovskite materials.[15–19] Thus, the investigation of less-toxic, stable, and environmentally friendly metal halide materials can be considered as a cutting-edge approach in this regard.[20–22]

CsSnX$_3$ nanocrystals have been synthesized by Jellicoe et al. by introducing Sn$_2^{2+}$ into perovskites.[23] Ge-based perovskite materials including MAGeX$_3$, FAGeX$_4$, and CsGeX$_3$ have been mainly reported by Mathews.[24] Nevertheless, Sn$^{2+}$ and Ge$^{2+}$ easily oxidize, and the devices based on these materials have very low stabilities.[25–27] Han and co-workers prepared low-toxicity Cs$_3$Bi$_2$X$_9$ materials, which could be stored in the atmosphere at room temperature for 30 days, and demonstrated appropriate stabilities when Bi$^{3+}$ was substituted for Pb$^{2+}$.[28] The ionic radius of Cu$^+$ (77 pm) is smaller than that of Pb$^{2+}$ (119 pm); therefore, the Cu—X bond has a shorter length and higher binding energy than those of the Pb—X bond, which will theoretically facilitate the formation of a more stable crystal lattice.[29] Cu-based halide materials have been extensively studied as powerful alternatives to Pb-based metal halides.[30–35] A Cs$_3$CuI$_5$ single crystal with a blue self-trapped excitation (STE) emission was fabricated by Hosono, which was further applied to the preparation of light-emitting diodes (LEDs).[36] Then, He and co-workers compared multiphoton absorption (MPA) properties of Cs$_3$CuI$_5$ and Cs$_2$Cu$_2$I$_3$ single crystals for the first time. This study broadened the applications of Cs Cu halides in nonlinear optoelectronics and light polarization-related devices.[37] Furthermore, CsCu$_2$I$_3$ and Cs$_2$Cu$_2$X$_5$ powders were synthesized using a dry ball-milling method; however, they were unstable in air.[38] In the same year, Saparov and co-workers reported that the stabilities of Cs$_2$Cu$_2$X$_5$ materials were significantly higher than those of traditional Pb-based perovskite materials.[39]
Subsequently, Zhang and co-workers constructed a series of all-inorganic Cu(I)-based ternary metal halide (Cs$_3$Cu$_2$X$_5$ (X = Cl, Br, or I)) micrometer-scale crystals with high quantum yields; these crystals exhibited STE emissions originating from structural deformation that enhanced the symmetry of the local structure. In recent years, a series of Cs$_3$Cu$_2$X$_5$ nanocrystals with STE emissions have been prepared. Nevertheless, these Cs$_3$Cu$_2$X$_5$ nanocrystals or powders have relatively low environmental stabilities. Therefore, developing the synthesis methods for Cs$_3$Cu$_2$X$_5$ single crystals is highly necessary to solve these issues, which will be beneficial for improving the commercialization of white LEDs (WLEDs).

In this study, Cu(I)-based ternary metal halide Cs$_3$Cu$_2$Br$_5$ single crystals with 0D electronic dimensions and STE emissions were fabricated via an antisolvent method for the first time; these crystals exhibited blue emissions with wide spectra at the center peaks of 458 nm and large Stokes shifts (160 nm). The crystals still maintained strong photoluminescence (PL) intensities after being exposed to an atmospheric environment for 90 days, and derivative thermogravimetric (DTG) analysis implied that the complete decomposition temperature of Cs$_3$Cu$_2$Br$_5$ was higher than 930 °C, and the stabilities of the Cs$_3$Cu$_2$Br$_5$ crystals were excellent. Remarkably, the Cs$_3$Cu$_2$Br$_5$ single crystals fabricated herein were applied to construct WLEDs, which demonstrated superhigh Ra values of over 95. The WLED exhibited outstanding stabilities at high temperatures. Thus, this study demonstrates considerable potentials of Cu(I)-based single crystals in the field of lighting.

### 2. Results and Discussion

A schematic of the preparation of Cs$_3$Cu$_2$Br$_5$ single crystals is shown in Figure S1, Supporting Information. Figure 1a,b depicts the images of the obtained crystals under fluorescent light and 254 nm ultraviolet (UV) light; the single crystals emitted blue fluorescent emissions, and the sizes of the crystal were $\approx 3 \times 2 \times 1$ mm$^3$. Temperature is an important factor affecting the growth of crystals. For the antisolvent method, it is extremely crucial to determine the temperature at which the solute has the lowest solubility in the solution such that the crystallization of the solute can be maximized. Cs$_3$Cu$_2$Br$_5$ is highly unstable in N, N-dimethylformamide (DMF) and eventually decomposes into CsBr and CsCuBr$_2$ after being stirred and heated in the solution. Consequently, traditional methods cannot be used to acquire the solubility curves of Cs$_3$Cu$_2$Br$_5$. Therefore, to explore the suitable temperature for crystal growth to obtain crystals with larger sizes and high quality (below the boiling point of the methanol), four sets of experiments at different temperatures ranging from 38 to 53 °C at intervals of 5 °C were conducted for the growth of Cs$_3$Cu$_2$Br$_5$ crystals, and crystal growth at room temperature (25 °C) was also analyzed. The weights of the crystals acquired at each temperature were recorded, and the difference between the mass ratios of Br in the product and the raw material at each temperature was calculated via molecular weight (Figure 1c). The conversion rate of Br reached $\approx 30\%$ near 48 °C, and it significantly decreased at higher or lower temperatures. The conversion rate of Br was $\approx 10\%$ at 53 °C and only $\approx 3\%$ at 25 or 38 °C; nevertheless, the single crystals grown at 25 and 38 °C were in fine powder forms had low qualities, and could not meet the requirements for the analysis. Thus, it was reasonable to choose stirring and heating at 60 °C during the preparation of these crystals. Although the solubility of Cs$_3$Cu$_2$Br$_5$ was higher at high temperature, higher temperatures promoted the reduction of Cu(II) cations in the raw materials. The solubility of Cs$_3$Cu$_2$Br$_5$ in solution was the lowest at $\approx 48\%$, and crystals with larger sizes and high qualities were easily achieved at this temperature (Figure S2, Supporting Information). Powder X-ray diffraction (XRD) patterns of the Cs$_3$Cu$_2$Br$_5$ single crystals grown at different temperatures are shown in Figure S3, Supporting Information. The crystal phase or structure of Cs$_3$Cu$_2$Br$_5$ was not affected by changes in the crystal growth temperature.

The single-crystal XRD structure of the crystal is depicted in Figure 1. a,b) Images of the obtained crystals under fluorescent light and 254 nm UV light and c) conversion rate of Br based on the difference between the mass ratios of Br in the product and the raw material.

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**Figure 1.** a,b) Images of the obtained crystals under fluorescent light and 254 nm UV light and c) conversion rate of Br based on the difference between the mass ratios of Br in the product and the raw material.
that form a common edge, creating the \([\text{Cu}_2\text{Br}_5]^{3-}\) structural unit. Each \([\text{Cu}_2\text{Br}_5]^{3-}\) unit is completely separated by Cs atoms, forming a relatively stable \(\text{Cs}_3\text{Cu}_2\text{Br}_5\) structure. Compared with the case of the traditional perovskite structure, the \([\text{Cu}_2\text{Br}_5]^{3-}\) units are not connected to each other in the single-crystal structure of \(\text{Cs}_3\text{Cu}_2\text{Br}_5\), which may affect the transmission of electrons, in \(\text{Cs}_3\text{Cu}_2\text{Br}_5\), and lead to different electronic dimensions of \(\text{Cs}_3\text{Cu}_2\text{Br}_5\), as compared with those of traditional perovskite materials; this may be a structural reason for the 0D electronic dimension of \(\text{Cs}_3\text{Cu}_2\text{Br}_5\). Single-crystal XRD shows that the \(\text{Cs}_3\text{Cu}_2\text{Br}_5\) crystal belongs to the \(Pnma\) space group, and the lattice parameters are presented in Table S1, Supporting Information.

XRD patterns of \(\text{Cs}_3\text{Cu}_2\text{Br}_5\) are shown in Figure 2c; the main diffraction peaks of the powder XRD pattern of \(\text{Cs}_3\text{Cu}_2\text{Br}_5\) are in appropriate agreement with PDF#04-014-2735, indicating that \(\text{Cs}_3\text{Cu}_2\text{Br}_5\) is relatively pure and has no impurities or other phases.

**Figure 3** depicts the scanning electron microscopy (SEM) image and elemental distribution of the \(\text{Cs}_3\text{Cu}_2\text{Br}_5\) crystal powder. Elements were uniformly distributed without considerable aggregation or loss. Energy-dispersive X-ray spectrum of the sample is shown in Figure S4, Supporting Information; the peak position of each element was relatively clear, and interference was not noticed between the peaks. Therefore, this spectrum can be basically used to qualitatively determine the proportion of each element in the sample. The proportions of all elements are provided in Table S2, Supporting Information. The results of the qualitative analysis of element proportions were mainly consistent with the structure solved by single-crystal XRD, and the ratio of Cs:Cu:Br ratio was close to 3:2:5. This implied that the ions of the crystals, prepared by the antisolvent method, that entered the crystal lattice were relatively uniform, and the acquired material had a single elemental composition and was relatively pure without miscellaneous phases or impurities.

The generation of STE emission in semiconductors is highly dependent on the deformability of the lattice because a deformable lattice can produce strong electron–phonon coupling interactions. To reveal the electronic structure properties of \(\text{Cs}_3\text{Cu}_2\text{Br}_5\), density functional theory (DFT) calculations were performed. The structures of the ground and excited states of the \([\text{Cu}_2\text{Br}_5]^{3-}\) unit are shown in **Figure 4a,b**, respectively. The structure of the \([\text{Cu}_2\text{Br}_5]^{3-}\) unit underwent significant deformation after the ground state transformed to the excited state; variations in the specific bond length and bond angle are presented in Table S3 and S4, Supporting Information, and the label of each atom is defined in Figure 4a. The lengths of \(\text{Cu}_1–\text{Br}_3\)
and Cu₁—Br₄ bonds (with Br₃ and Br₄) represent the two Br atoms in the tetrahedron far from the triangle and Cu₁ is the Cu atom at the center of the tetrahedron extended from 2.28436 and 2.28433 Å to 2.37293 and 2.36363 Å, respectively, and the bond angle between these three atoms reduced from 159.399° to 127.017°. Compared with those in the case of the ground state, the bond length and angle of the tetrahedra with Cu₁ as the center in the excited state considerably changed, whereas the bond length and angle of the triangle with Cu₂ as the center in the excited state demonstrated relatively insignificant changes as compared with those in the case of the ground state; this indicated that the photophysical properties of the crystal might be more influenced by the tetrahedron and Cu₁, Br₃, and Br₄ played major roles.

Energy band structure diagram and density of states (DOS) of the Cs₃Cu₂Br₅ crystal are depicted in Figure 4c,d, respectively. Theoretical calculations revealed that the Cs₃Cu₂Br₅ single crystal had a direct bandgap at the Γ point, and the band gap was 2.2532 eV. Valence band maximum (VBM) of the Cs₃Cu₂Br₅ single crystal was composed of a completely flat band, which reflected the high limitation of electrons due to carriers. DOS disclosed that the VBM mainly comprised Cu 3d orbitals, whereas the conduction band maximum (CBM) stemmed from the mixture of Cu 4s and Br 5p orbitals, and Cs cations did not contribute to the CBM or the VBM. Therefore, it can be considered that Cs₃Cu₂Br₅ consists of two parts: 0D photoactive sites composed of [Cu₂Br₅]³⁻ and Cs ion as a separator.

Powder PL intensity of Cs₃Cu₂Br₅ had a certain correlation with the crystal growth temperature, which might be due to the influence of crystal growth temperature on the activities of ions in the solution during crystallization. The PL intensity of the sample grown at 48 °C was the strongest under the same test conditions (Figure S5, Supporting Information); therefore, we used this sample as an example to analyze the PL performance of Cs₃Cu₂Br₅. The excitation and PL spectra of the Cs₃Cu₂Br₅ crystals grown at 48 °C are shown in Figure 5a. The emission peak of Cs₃Cu₂Br₅ was obtained at 458 nm, which had a wide full-width at half-maximum (FWHM) of ∼80 nm and a large Stokes shift of ∼160 nm. The excitation spectrum reached a peak near 298 nm and then demonstrated an abrupt cutoff and rapidly decreased to 0; these all are the characteristics of STE emission in the PL spectrum. The excitation spectrum was acquired in the range of 420–510 nm with an interval of 10 nm, and the results are depicted in Figure 5b. Peak shapes and trends of the ten excitation spectra were basically consistent, which suggested that the wide FWHM was completely caused by the relaxation of the same excited state of Cs₃Cu₂Br₅.

Figure 5c shows the contrast diagram of the PL intensity of Cs₃Cu₂Br₅ obtained by adjusting the power density of the excitation light, which reflects the relationship between the PL intensity generated by the stimulated emission of Cs₃Cu₂Br₅ and the magnitude of the excitation light power density. The PL intensity of Cs₃Cu₂Br₅ and the magnitude of the excitation light power density were linearly correlated, the $R^2$ of the fitting curve was 0.996, and the data fitting was quite consistent.
The PL intensity of Cs$_3$Cu$_2$Br$_5$ exhibited a positive linear relationship with excitation power density, and it showed no sign of saturation with an increase in the excitation power density, implying that the wide FWHM luminescence of Cs$_3$Cu$_2$Br$_5$ was induced by the intrinsic emitting states of the material instead of the defect states of the material. Based on the aforementioned analysis, Cs$_3$Cu$_2$Br$_5$ demonstrates an STE emission effect. Because of these features, Cs$_3$Cu$_2$Br$_5$ has substantial advantages in the field of light-emitting materials and considerable potential for application in LEDs.

To examine the stability of the PL intensity of a single crystal, PL spectra of the freshly prepared crystal powder and the same batch of crystal powder after 90 days of storage were measured under the same test conditions. The PL intensity of the crystal powder placed in an atmospheric environment for 90 days was only slightly lower than that of the fresh crystal powder; the PL intensity of the crystal powder placed in an atmospheric environment for 90 days was 96.91% than that of the fresh crystal powder, and the reduction was less than 3.1%. The PL intensity of the same types of quantum dots decreased by half after these quantum dots were exposed to N$_2$ atmosphere for 16 days, and the stability of the PL intensity of crystals was relatively excellent.

Time-resolved PL (TRPL) decay spectrum of Cs$_3$Cu$_2$Br$_5$ is shown in Figure 6b, where the PL lifetime was fit by Equation (1), and the parameter $\tau$ obtained was the PL lifetime of the material.

$$I = Ae^{-t/\tau}$$

$\tau$ reached 15.77 $\mu$s, which was an order of magnitude higher as compared with those of traditional perovskite materials and was better when compared with those of the same types of quantum dots; this implied that Cs$_3$Cu$_2$Br$_5$ had a lower ability to absorb the photons generated by its own stimulated emission and was more suitable for application in luminescent materials and devices.

PL intensity of Cs$_3$Cu$_2$Br$_5$ varied with temperature (Figure 6c), and the PL intensity of Cs$_3$Cu$_2$Br$_5$ was evaluated from room temperature (298 K) to 90 K. With a decrease in temperature, the PL intensity of Cs$_3$Cu$_2$Br$_5$ gradually increased; however, when the temperature was decreased to 170 K, the trend of enhancement slowed down, and basically, the highest PL intensity was achieved. No considerable shift was noticed in the emission wavelength; nevertheless, the FWHM became narrower, no higher emission peak related to free excitons was acquired at all temperatures, and only one broadband emission was observed. The PL integral intensity and the reciprocal of different

Figure 5. a) Excitation and PL spectra, b) excitation spectrum at different PL wavelengths, c) PL intensity at different power densities of excitation light, and d) integrated PL intensity versus excitation power density for the Cs$_3$Cu$_2$Br$_5$ powder.
temperatures were fit using Equation (2) (Figure 6d), where $I_0$ is the fluorescence integral intensity at low temperatures, $I_{PL}$ is the PL integral intensity varying with temperature, $A$ is the ratio between the radiative and nonradiative decay rates, $k_B$ is the Boltzmann constant, and the $E_b$ is exciton binding energy. $E_b$ of Cs$_3$Cu$_2$Br$_5$ is $\approx$503 meV, which is one order of magnitude higher than that of traditional Pb-based perovskite quantum dots (18 meV), and would reduce the occurrence of nonradiative recombination and significantly improve the stability of the PL intensity.

$$I_{PL} = \frac{I_0}{1 + Ae^{E_b/k_B T}}$$

(2)

TG–DTG curves of Cs$_3$Cu$_2$Br$_5$ are depicted in Figure 7, and DTG was performed by calculating the first derivative of the TG curve, which more clearly showed the changes in the quality of the material with respect to temperature. The quality of the material slowly declined after 500 °C, indicating that the material began to decompose; subsequently, the quality rapidly deteriorated after 700 °C. When the temperature reached 929 °C, the speed of mass change was the highest (0.9 %°C$^{-1}$). At this temperature, 96% quality of the material was lost, and Cs$_3$Cu$_2$Br$_5$ completely decomposed. The temperature of complete decomposition of Cs$_3$Cu$_2$Br$_5$ was $\approx$300 °C higher than those of traditional perovskite materials and 100 °C higher than those of the same type of quantum dots, indicating relatively better thermal stability of Cs$_3$Cu$_2$Br$_5$. 

Figure 6. a) Stability of the PL intensity of a Cs$_3$Cu$_2$Br$_5$ single crystal and b) TRPL decay spectra, c) temperature-dependent PL spectra, and d) temperature-dependent PL integrated intensity of the Cs$_3$Cu$_2$Br$_5$ powder.

Figure 7. TG–DTG curves of Cs$_3$Cu$_2$Br$_5$ powder.
The Cs₃Cu₂Br₅ crystals powder and phosphor powder were mixed and coated on a near-UV LED chip (λ = 310 nm) to prepare a WLED prototype lamp. At a constant temperature of 25°C, when the operating forward current was increased from 200 to 300 mA, the current decreased to less than 275 mA, and the PL excited by UV light spectra intensity increases. Thereafter, the intensity of the PL spectra decreased. The related PL spectra acquired under UV light (at different forward currents) for the device are shown in Figure S7, Supporting Information. At a forward current of 275 mA and in the temperature range from 10 to 110°C, the device exhibited excellent white emission with an outstanding color rendering index (Ra) of over 95 (Figure S8, Supporting Information). The Ra increased up to 97.8 at 20°C. No substantial change was noticed in the Ra of the device, with a further increase in the temperature. The crystal powder was fabricated into a WLED revealing better thermal stability. At 25°C, the CIE color coordinates of the WLED were x = 0.3037, y = 0.3005 (Figure 8a), and the inset of Figure 8a depicts the images of the WLED. The Ra was 97.5. The packaged WLED lamp mainly demonstrated a full-spectrum emission in the 400–700 nm range (Figure 8b).

3. Conclusion

In this study, Cs₃Cu₂Br₅ single crystal with 0D electronic dimensions based on STE emission were successfully prepared by the antisolvent method; these crystals exhibited blue emissions with wide FWHM (80 nm) at the center peak of 458 nm and large Stokes shifts (160 nm). DFT calculations indicated that the photophysical properties of the crystals were affected by the Cs₂Br₃⁻ unit. Furthermore, suitable conditions for crystal growth were explored by adjusting the crystal growth temperature. The Cs₃Cu₂Br₅ crystal showed excellent PL and thermal stabilities. The PL intensity of the single crystal exposed to an atmospheric environment for 90 days remained above 96.9% of the initial intensity, and the exciton binding energy of Cs₃Cu₂Br₅ was ≈503 meV, which reduced the occurrence of nonradiative recombination and significantly improved the stability of the PL intensity. The temperature of the complete decomposition of Cs₃Cu₂Br₅ was above 930°C. Because single crystals have lower trap-state densities and longer carrier diffusion lengths, we used Cs₃Cu₂Br₅ single crystals to construct a WLED with a superhigh Ra of over 95. At the optimal operation current, the WLED exhibited high thermal stability at high temperatures. Owing to these good characteristics, we believe that Cs₃Cu₂Br₅ single crystals will be potential application materials for optoelectronic devices.

4. Experimental Section

Materials: Cesium bromide (CsBr, 99.9%), copper(II) bromide (CuBr₂, 99.9%), and N,N-Dimethylformamide (DMF, >99.9%) were purchased from Aladdin. Methanol (MeOH) was purchased from Tianjin Huilhang Chemical Technology Co., Ltd. All reagents and raw materials were directly used without further processing.

Single-Crystal Growth: Cs₃Cu₂Br₅ single crystals were synthesized by the antisolvent diffusion method, CsBr and CuBr₂ with a molar ratio of 1:0.9 were weighed in a quartz bottle, and DMF was injected into the bottle to form a solution of 1 m concentration. The solution was heated and stirred in an oil bath at 60°C for 24 h. Because the aldehyde group of DMF and the halide anions had certain reducibilities, and the Cu(II) cations were relatively easy to reduce, the Cu(II) cations in CuBr₂ were reduced to Cu(I) cations. Moreover, a black solution was obtained after filtering the abovementioned solution via the 0.22 μm polytetrafluoroethylene (PTFE) membrane filter. The solution was put in a new quartz bottle and covered using a sealing film with several small holes; then, this quartz bottle was placed in a sealed beaker containing MeOH. The volume of MeOH should be slightly higher than the volume of the quartz bottle to ensure that bottle can be filled with an antisolvent. The Cs₃Cu₂Br₅ single crystals were obtained after a week in a constant temperature drying box at 48°C. To detect whether DMF reacted with Cu(II) cations, Fourier-transform infrared (FTIR) spectra of the solution before and after the reaction were acquired (Figure S6, Supporting Information).

Characterization Methods: Single-crystal XRD data were collected using a single-crystal diffractometer (Agilent Super Nova CCD). Powder XRD patterns of the materials were collected by Rigaku (SmartLab-3 kW) X-ray diffractometer with Cu Kα X-ray at 40 kV and 30 mA. The scan range was 15°–50°. The PL spectra, TRPL decay spectra, and

Figure 8. a) CIE coordinates of the WLED (inset shows the images of the WLED) and b) emission spectra of the WLED fabricated using a mixture of Cs₃Cu₂Br₅ crystal powder and phosphor powder.
temperature-dependent PL spectra of the crystal powders were obtained using a 55 spectrophotometer with a 298 nm excitation source for powders of the crystal at room temperature in air. Energy-dispersive X-ray spectroscopy (EDS) was obtained using a low-vacuum scanning electron microscope model (JSM-6390LV). Thermogravimetric analysis (TGA) of the materials was performed using NETZSCH STA 449F5. The sample was placed in an Al2O3 crucible, followed by heating from 25 to 1000 °C at a ramp of 20 °C min\(^{-1}\) under N2 atmosphere at a flow rate of 40 mL min\(^{-1}\). 10 mg of sample was used for measurement. The FTIR spectra were obtained using Nicolet iS50, in the range of 4000–400 cm\(^{-1}\).

**DFT Calculation:** The spin-polarized DFT calculations were conducted using the Vienna Ab-initio Simulation Package (VASP) via the projected augmented wave (PAW) method. For all geometry optimizations and band structures, 500 eV was chosen as the cutoff energy of the plane-wave basis to ensure the precision of the calculations. Herein, \(3 \times 3 \times 2\) Monkhorst–Pack grids were used to perform surface calculations on all the models. The convergence thresholds for structural optimization were set at 0.01 eV Å\(^{-1}\) in force. The convergence criterion for energy was 10\(^{-4}\) eV. In this study, static calculations were performed using the Gaussian 09 program. The geometric optimizations for the S0 and S1 states were calculated using DFT and time-dependent density functional theory (TDDFT) methods, respectively. Becke’s three-parameter hybrid-exchange functional with the Lee–Yang–Parr gradient-corrected correlation functional (B3LYP) was used. Frequency calculations were performed to confirm that each optimized ground- and excited-state geometry corresponded to the local minima on the S0 and S1 energy surfaces, respectively. All geometry optimizations were calculated in the gas-phase environment.

**Fabrication and Characterization of Prototype WLED Devices:** Prototype WLED lamps were packaged by integrating the Cs\(_3\)Cu\(_2\)Br\(_5\) crystal powder and fluorescent powders on a UV LED chip (\(\lambda = 310 \text{ nm}\)). The approximate weight ratio of the Cs\(_3\)Cu\(_2\)Br\(_5\) crystal powder and fluorescent powders was \(\approx 1:1\). The temperature-dependent PL excited by UV light spectra, \(R\alpha\), and CIE color coordinates of the packaged WLEDs were characterized using a spectrophotocolorimeter system (HAAS-2000, Hangzhou Everfine Ltd.). The measurements of all samples were conducted under the same conditions.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Research data are not shared.

**Keywords**

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