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New Copper Bromide Organic-Inorganic Hybrid Molecular Compounds with Anionic Inorganic Core and Cationic Organic Ligands

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Abstract: Here, organic-inorganic hybrid molecular compounds based on copper(I) bromide have been synthesized by slow-diffusion method. The inorganic modules of these two structures are $Cu_2Br_4^{2-}$ anion, and the inorganic modules are coordinated to cationic organic ligands via Cu-N coordinative bonds. Both of these compounds are luminescent, emitting green emissions under UV excitation.

Keywords: organic-inorganic hybrid; luminescence; copper bromide

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Citation: Luo, D.; Zhang, J.; Liang, Y.; Ni, J.; Wang, F.; Liu, W. New Copper Bromide Organic-Inorganic Hybrid Molecular Compounds with Anionic Inorganic Core and Cationic Organic Ligands. *Crystals* **2022**, *12*, 19. https://doi.org/10.3390/cryst12010019

Academic Editors: Wei Liu, Xin Wu, Haoran Lin, Kil Sik Min and Alessandro Chiasera

Received: 8 November 2021
Accepted: 14 December 2021
Published: 23 December 2021

1. Introduction

Organic-inorganic hybrid materials are a significant type of material with distinctive properties [1–6]. There are both inorganic components and organic ligands in their structures, and the interesting properties (optical, electrical, magnetic, etc.) of inorganic species, as well as the flexibility and tunability of organic ligands are shown by hybrid compounds [7–10]. The combination of the two species would also lead to new properties. Several hybrid material groups have been identified, and among them, organic-inorganic hybrid structures of copper halides show significant potential as rare-earth element-free (REEs) light-emitting materials with the benefits of low cost, optical tunability, high quantum efficiency and solution processability [11–14]. The luminescence of the parent copper halides is weak. The luminescence of the total hybrids could be substantially improved when copper halides coordinate with the organic ligands [15–17]. This is similar to luminescent hybrid materials based on other semiconductors, while the luminescence originates from the combination of both inorganic and organic components [11,18,19]. Due to the strong luminescence of these hybrid structures, they exhibit potential application as REE-free solid-state lighting materials [10,18,20–24].

Copper halide hybrid structures are generally constructed by the interaction of copper halide inorganic motifs with organic ligands, and the chemical bonds between them are either covalent bonds or ionic bonds [25]. Various inorganic modules have been reported, including discrete units (monomers, dimers, etc.), as well as extended modules (chains, layers, etc.). The organic ligands for these structures can be either aliphatic or aromatic, and can be considered as bridges, linking the inorganic units into hybrid structures with different dimensions (0D, 1D, 2D and 3D) [12,26]. In order to meet the requirements as new lighting materials, light-emitting materials should have a number of characteristics, such as high internal quantum yields (IQYs), high thermal stability, optical tunability and so on [27,28]. The recently reported zwitterionic type of copper-iodide-based structures shows improved quantum efficiency and thermal stability compared to traditional neutral and ionic structures, and is considered to be promising as a rare-earth-metal-free alternative to commercial lighting phosphors [15,25,29]. In this unique type of structure, the anionic inorganic modules and the cationic organic ligands are linked by coordination bonds. In particular, the organic cations used for synthesis are designed to have free coordination atoms in organic ligands that could be coordinated with copper atoms. Both aliphatic and aromatic ligands could be used for synthesis, and inorganic components tempered by synthetic conditions have a number of modules, not only discrete inorganic modules but also extended inorganic chains. In these structures, there are both ionic bonds and coordinative bonds, and therefore both the luminescence efficiency and stability could be enhanced in these structures. They also demonstrate good solubility in a number of organic solvents, making film processing much easier [30]. Earlier works focused on the copper-iodide-based zwitterionic type of structures, while the zwitterionic type of copper bromide hybrid structures was much less studied [31–33].

Here, two zwitterionic types of copper bromide organic-inorganic molecular compounds are presented. They are 0D-$Cu_2Br_4(L_1)_2$ (1, L_1 = 1-(2-chloroethyl)-1,4-diazabicyclo [2.2.2]-octan-1-ium) and 0D-$Cu_2Br_4(L_2)_2$ (2, L_2 = 1-(2-bromoethyl)-1,4-diazabicyclo [2.2.2]-octan-1-ium). Single crystal X-ray diffraction reveals that the two structures are molecular species. The inorganic module of the two compounds is Cu_2Br_4 anion, which is similar to the Cu_2Br_2 rhomboid dimer with the two copper atoms coordinated to three bromine atoms. The coordination atoms are the unalkylated N atoms in the cationic ligands. Since the molecular structures contain both ionic and coordinating bonds, they can be referred to as the zwitterionic form of hybrid structures.

2. Materials and Methods

CuBr, KBr, acetonitrile, 1,4-diazabicyclo [2.2.2]-octane (DABCO), methanol, ethyl acetate, acetone, methyl sulfoxide, N, N-dimethylformamide, ethanol, dibromoethane and 1-bromo-2-chloroethane have been purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China) and have been used as received without any purification. The detailed test and synthesis methods are shown in the Supplementary Materials.

3. Results and Discussion

To construct hybrid structures of such kind, organic ligands with special structures have been designed [34]. The ligands should be cationic while having free coordination atoms as binding sites. The cationic ligands in the reaction will allow the formation of ionic compounds with anionic inorganic modules. On the other hand, the free binding sites in the organic ligands would allow the coordination to Cu atoms forming coordination bonds. A common strategy for designing the organic ligands for the construction of the zwitterionic type of hybrid structures is by using the controlled alkylating approach of bidentate N-ligands. In this approach, a bidentate N-ligand is selected and the alkylation is controlled at the stage where only one of the tertiary N atoms would be alkylated and the other N site remains unreacted. 1,4-Diazabicyclo [2.2.2] octane (DABCO) was selected as the bidentate N-ligand and two cationic ligands were prepared. These types of ligands have been selected since they have good coordination ability with copper atoms. They are 1-(2-chloroethyl)-1,4-diazabicyclo [2.2.2]-octan-1-ium) (L_1) and 1-(2-bromoethyl)-1,4-diazabicyclo [2.2.2]-octan-1-ium) (L_2) (Figure 1). The reaction scheme is shown in Figure 2. ^{1}H NMR spectroscopy of the synthesized ligands L_1 and L_2 is shown in Figure S1.

By slow-diffusion reaction, single crystals of two copper halide hybrid materials have been grown using L_1 and L_2, and the structures are 0D-$Cu_2Br_4(L_1)_2$ (**1**) and 0D-$Cu_2Br_2(L_2)_2$ (**2**) as shown in Figure S1. Their crystal structures and unit cell packing diagrams are shown in Figure 3, Figures S2 and S3.

1-(2-chloroethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium 1-(2-bromoethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium

Figure 1. Structural plots of organic ligands.

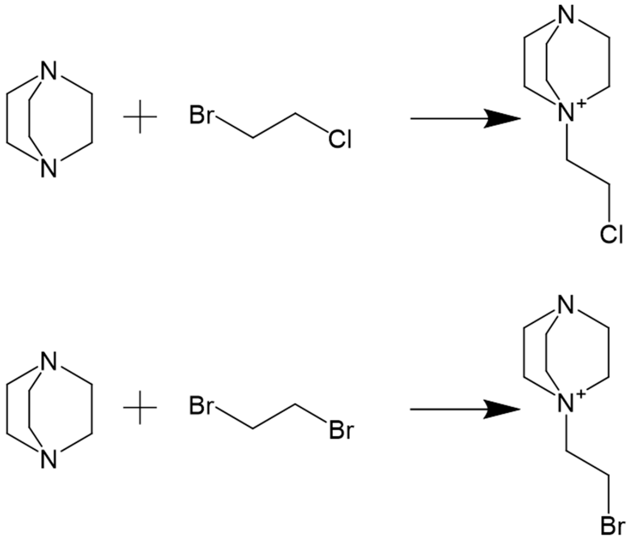

Figure 2. Synthetic routes of L_1 and L_2.

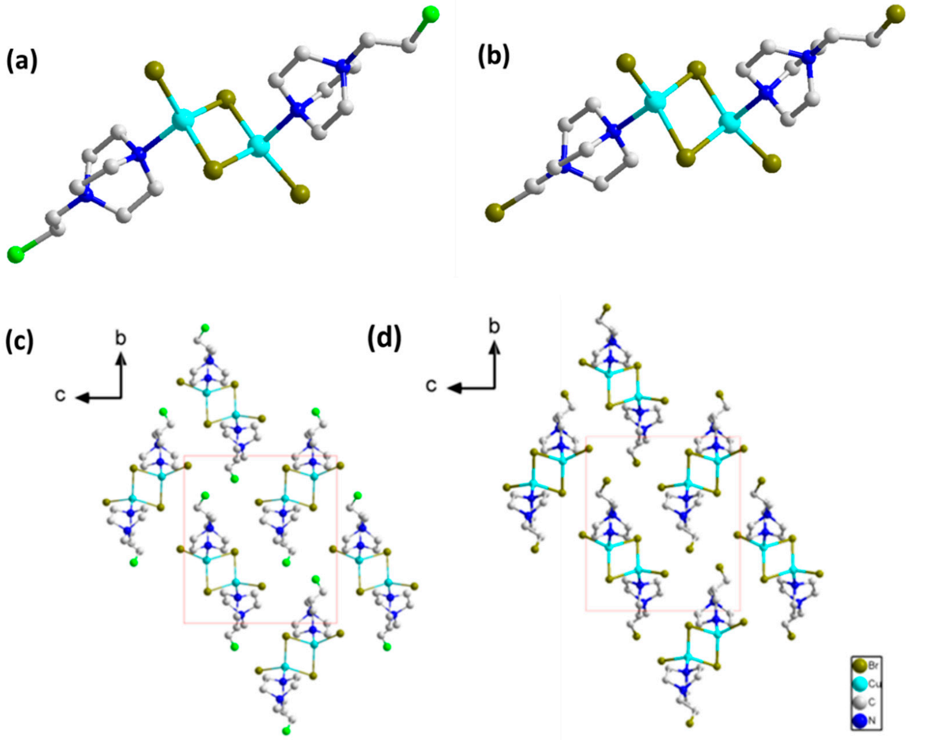

Figure 3. Structural plot of compound **1** (**a**) and **2** (**b**). Unit cell packing diagrams of **1** (**c**) and **2** (**d**).

In a typical synthesis, CuBr/KBr-saturated solution and the ligand/ethanol were placed as bottom layer and upper layer, respectively, while acetonitrile has been introduced as an interlayer. Single crystals of **1** and **2** were obtained within a few days. Single crystal X-ray diffraction results show that the monoclinic space group of both **1** and **2** is $P2_1$. There are 2 formula units in the unit cell and all atoms are in general positions. The crystallographic data are provided in Table 1. In these anionic inorganic modules, all copper atoms are tetrahedrally coordinated to three bromine atoms and one ligand molecule. In these structures, the inorganic cores are anionic and the ligands are cationic and there are coordinative bonds connecting them. The Cu-N bond lengths are approximately 2.4 Å, similar to other CuBr-based hybrid structures containing coordination bonds. The possibility of halogen bonding in these types of compounds should also be considered [35,36]. The inorganic core of both compounds is identical, and after the halogen on the alkyl chain is changed from Cl to Br, the bond length increases from 1.795~1.841 Å to 1.926~1.949 Å, and the distance between the halogen and the copper increases from 8.7809~8.7828 Å to 8.8906~8.8974 Å. Therefore, with the replacement of halogen atoms, the distance between atoms increases, and the intermolecular forces weaken. Pure phase of powder samples of **1** and **2** have been obtained and their phase purity is confirmed by powder X-ray diffraction analysis (PXRD, Figure 4).

Table 1. Single crystal X-ray diffraction data of compounds **1** and **2**.

Compound	1	2
Formula	$C_{16}H_{32}Br_4Cl_2Cu_2N_4$	$C_{16}H_{32}Br_6Cu_2N_4$
Fw	798.07	886.99
Space Group	$P2_1$	$P2_1$
a (Å)	8.5917(14)	8.7020(5)
b (Å)	12.765(2)	12.8893(8)
c (Å)	11.7691(18)	11.6700(6)
α (°)	90	90
β (°)	99.485(2)	99.235(4)
γ (°)	90	90
V (Å^3)	1273.1(4)	1291.97(13)
Z	2	2
T (K)	296(2)	296(2)
λ (Å)	0.71073	0.71073
CCDC #	2033422	2033420

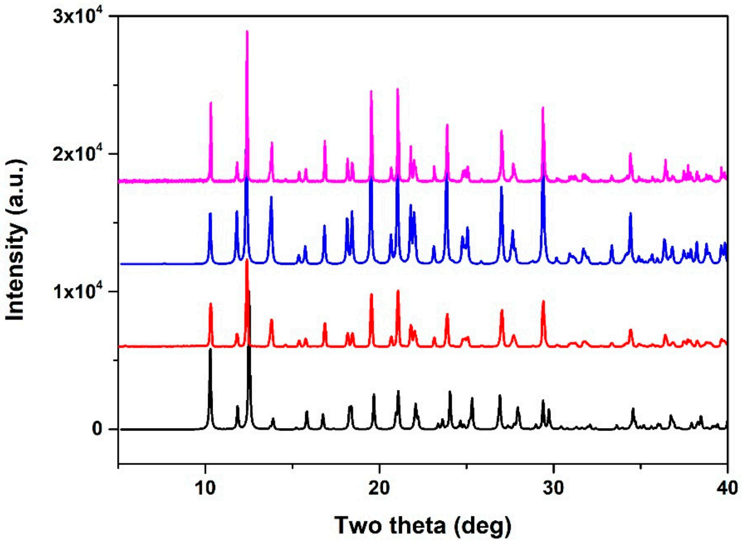

Figure 4. PXRD patterns **1**–**2**. From bottom to top: simulated **1**, as made **1**, simulated **2**, as made **2**.

The optical absorption spectra were collected for compounds **1** and **2** at room temperature and converted by the use of the Kubelka-Munk function, as shown in Figure 5. The absorption edges of compounds **1** and **2** were measured to be 3.0 eV and 2.9 eV, respectively. Since the inorganic core of both compounds is identical, the slight difference in band gaps for these compounds may be the result of the substituted group on the alkyl chain in the DABCO. Chlorine is more electron donating compared to bromine as it will cause the hybrid compounds to have higher band gaps.

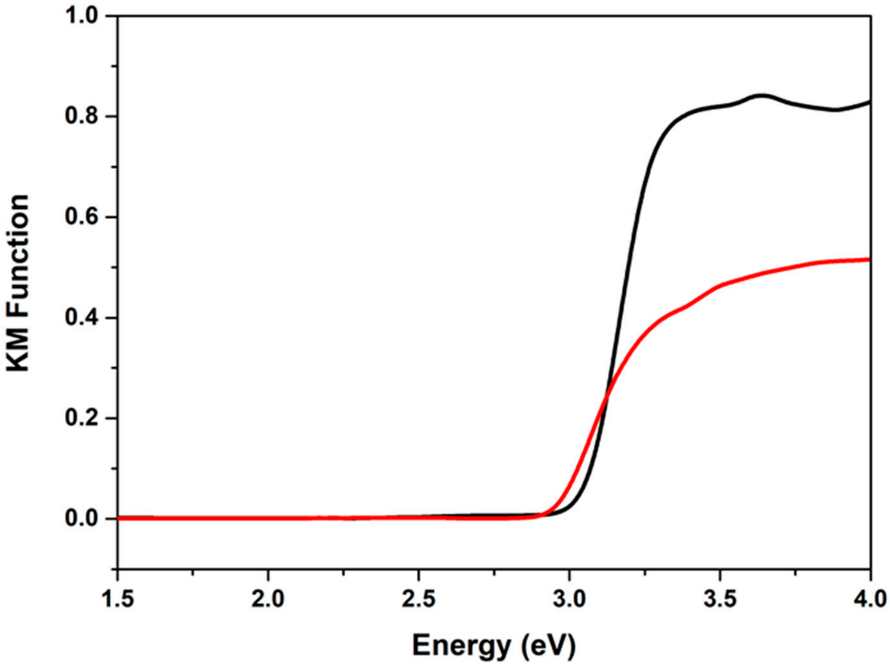

Figure 5. UV-vis absorption plots of **1** (black) and **2** (red).

Density functional theory (DFT) calculations were conducted on **1** and **2** using the Cambridge Serial Total Energy Package (CASTEP) in Materials Studio 8.0, as shown in Figure 6a,b, respectively. For both compounds, the conduction band minimum (CBM) is majorly contributed from the C 2p orbitals from the organic ligands while the valence band maximum (VBM) is mainly contributed from Cu 3d and Br 4p orbitals. Since there are halide atoms in the organic ligands, the contribution of halides should also be counted (Cl 3p and Br 4p). Such band structures resemble what has been observed for neutral copper halide hybrid structures with dimer or staircase chain modules [37,38].

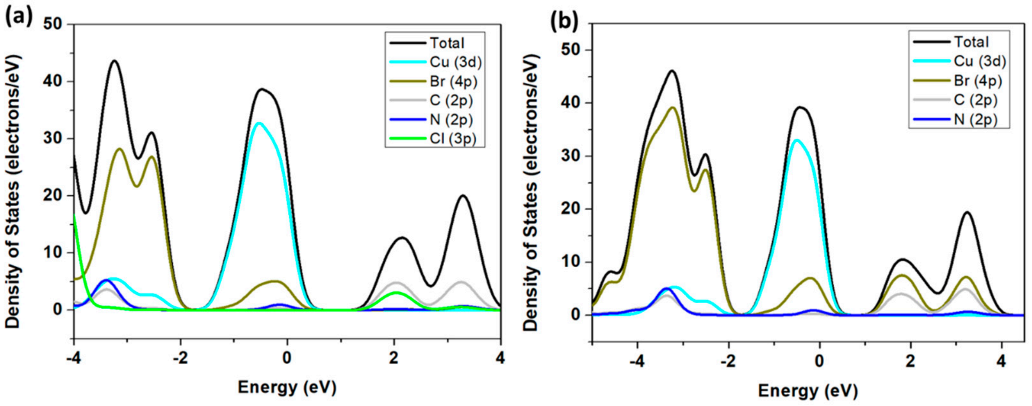

Figure 6. Density of states plots for **1** (**a**) and **2** (**b**).

Single crystals of **1** and **2** are colorless and transparent under natural light, indicating that they have little absorption of the visible light. Green light is emitted for both compounds under UV excitation, which is a result of the radiative recombination of electron and holes (inset of Figure 7a,b). Figure 7a,b are the emission and excitation spectra of compound **1** and **2**, respectively. The green emission bands have full width at half-maximum (FWHM) of around 100 nm and the emission peaks for both bands are at 525 nm. Based on their excitation spectra, 320 nm is an optimized excitation wavelength. The CIE coordinates calculated for the emissions are (0.28, 0.48).

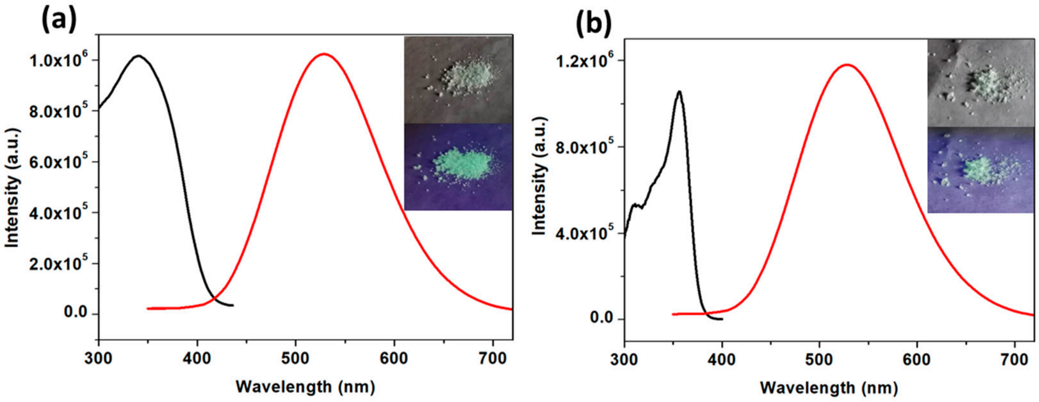

Figure 7. Emission spectra plots (red) and excitation spectra plots of **1** (**a**) and **2** (**b**). λex = 320 nm, λem = 525 nm. Inset: sample under natural light and UV light.

The internal quantum yields (IQYs) were measured on a C9920-03 absolute quantum yield measurement system (Hamamatsu Photonics) at room temperature, and the values are given in Table 2. The IQYs of compound **1** and **2** are 11.5% and 10.6%, respectively, at excitation energy of 320 nm. The weak emission and lower IQYs of these compounds can be explained by the absence of metal-to-ligand charge transfer (MLCT) or halide-to-ligand charge transfer (XLCT) due to the aliphatic ligands in these structures. Their luminescence mechanism can be attributed to a triplet cluster-centered excited state from the strong Cu to Cu interaction. The photoluminescence property of the compounds and the mechanism is similar to that of Cu_4I_4 cubane tetramer-based hybrid compounds [39]. The luminescent decay curves of these two green emitters at room temperature are shown in Figure 8, and their lifetime values are approximately 10.66 µs and 10.34 µs by monoexponential fitting. The microsecond lifetime values of these two compounds at room temperature suggest that their luminescence is phosphorescent emissions. Table 2 summarizes the major photophysical properties of **1** and **2**.

Table 2. Summary of photophysical properties of **1** and **2**.

Compound	1	2
Band Gap (eV)	3.0	2.9
λ_{ex} (nm)	320	320
λ_{em} (nm)	525	525
Emission color	Green	Green
IQY (320 nm)	11.5 %	10.6 %
τ (µs)	10.66	10.34
CIE	0.28, 0.48	0.28, 0.48
T_D (°C)	190	200

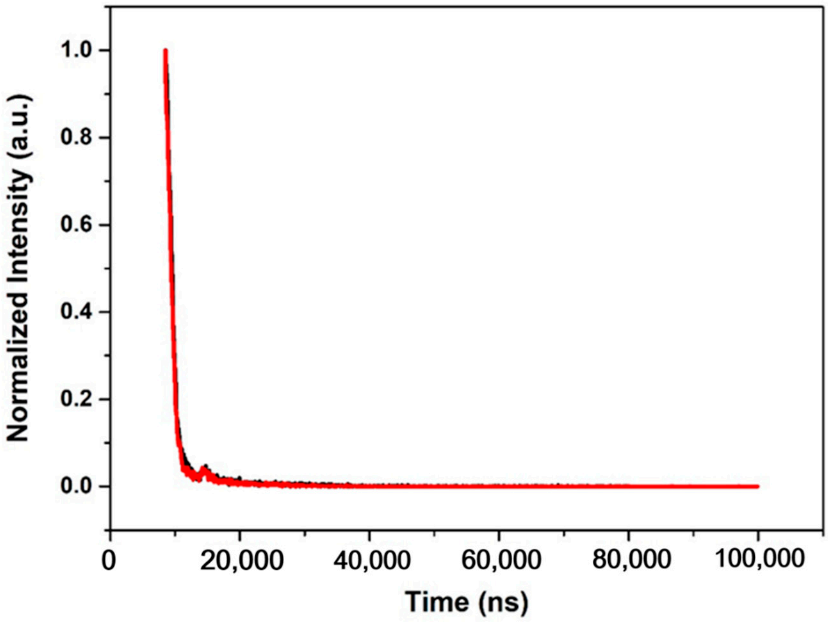

Figure 8. Luminescent decay curves of **1** (red) and **2** (blue).

Thermal stability of the compounds was assessed by TG analysis (Figure 9). Decomposition of structures begins with loss of the organic ligands. The decomposition temperature (TD) was analyzed as 190 °C and 200 °C for compounds **1** and **2**, respectively. The exposure of the sample to the atmosphere for weeks also shows no noticeable change in its emission intensity. Most of the previously reported copper bromide molecular compounds decompose below 60 °C. The significantly enhanced thermal stability is the result of ionic bonding in the structures. Due to its ionic structure, both the compounds are soluble in a number of organic solvents, including dimethyl sulfoxide (DMSO), N, N-dimethylformamide (DMF), etc. Thin film of the organic-inorganic hybrid materials can be prepared by spin coating, dip coating, etc. [40,41]. The solubility in common organic solvents makes it easier to process high-quality films for optoelectronic devices.

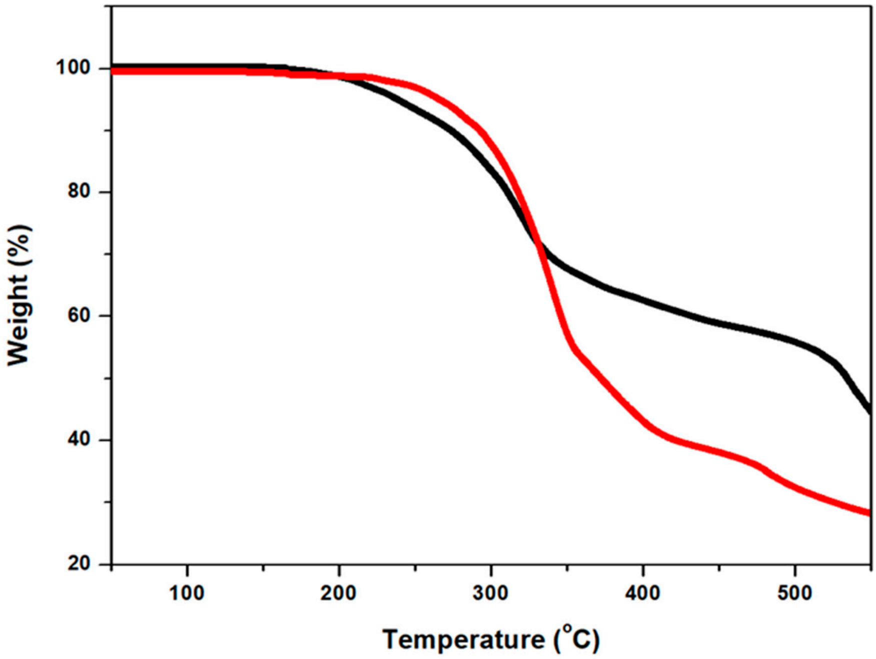

Figure 9. TGA curves of **1** (black) and **2** (red).

4. Conclusions

(1) Two zwitterionic copper-bromide-based organic-inorganic hybrid compounds have been synthesized using the slow-diffusion method.

(2) The two structures are molecular compounds with anionic inorganic core and cationic organic ligands. The inorganic modules of these two structures are $Cu_2Br_4{}^{2-}$ anion, which are coordinated to the cationic organic ligands via Cu-N coordinative bonds.

(3) Both of these compounds are luminescent, emitting UV-excited green emissions. The IQYs of the two compounds are 11.5% and 10.6% for **1** and **2**, respectively. They are highly stable and are new members of the zwitterionic type of structure family.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/cryst12010019/s1, Figure S1. H NMR spectroscopy of the synthesized ligands L_1 (a) and L_2 (b). L_1: ^{1}H NMR (400 MHz, Methanol-d_4) δ: 4.06 (t, J = 6.0 Hz, 2H), 3.71 (t, J = 6.0 Hz, 2H), 3.49 (t, J = 8.0 Hz, 6H), 3.20 (t, J = 8.0 Hz, 6H). L_2: ^{1}H NMR (400 MHz, Methanol-d_4) δ: 4.06 (t, J = 6.0 Hz, 2H), 3.71 (t, J = 6.0 Hz, 2H), 3.49 (t, J = 8.0 Hz, 6H), 3.20 (t, J = 8.0 Hz, 6H); Figure S2. (a) Supramolecular network viewed along the a-axis of **1**. (b) Supramolecular network viewed along the b-axis of **1**. (c) The accumulation of copper bromide modules in compound **1**. Figure S3. (a) Supramolecular network viewed along the *a*-axis of **2**. (b) Supramolecular network viewed along the b-axis of **2**. (c) The accumulation of copper bromide modules in compound **2**. The terminal Br atoms have been marked red.

Author Contributions: Investigation, D.L., J.Z. and Y.L. all contributed equally; methodology, J.N.; resources, F.W. and W.L.; supervision, F.W. and W.L. conceptualization, F.W. and W.L. All authors have read and agreed to the published version of the manuscript.

Funding: Financial support from the Shenzhen Sci. and Tech. Research grant (JCYJ20180307102051326) and the Innovation Project of Guangdong Education Department (2021KTSCX278) is gratefully acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

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