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ARTICLE TYPE

White phosphorescent coordination polymer with Cu_2I_2 alternating units linked by benzo-18-crown-6

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A new approach has been illustrated for the development of stable, efficient, and environmentally “friendly” white phosphorescent materials. Under mild conditions, a new one-dimensional coordination polymer has been prepared from benzo-18-crown-6 with CuI in the presence of KI , which is capable of emitting direct white light in solid state.

Solid-state light-emitting-diode (LED) materials have been extensively investigated in the recent years because of their potential applications in lighting and displays.^{1, 2} With a vision towards solving the environmental problems, tremendous efforts have been dedicated to search for environmentally more friendly, safer and more energy efficient white phosphor materials for use in the white LEDs (WLEDs) instead of mercury used in fluorescent lamps,³⁻⁷ these include hybrid inorganic materials, rare-earth metal doped zeolites, organic compounds, nanomaterials and metal complexes. To generate white emission, two types of white phosphor materials are commonly used, including (i) dichromatic emitters that blend blue and yellow light and (ii) trichromatic emitters that combine red, green and blue lights, while monochromatic emitters have not been well developed till now.^{8, 9} On the other hand, cuprous complexes have become an important class of luminescent materials because of their relative abundance, low cost and rich structural and photophysical properties.¹⁰⁻¹² Among them, the cuprous halide (CuX , $X = \text{Cl}$, Br , I) clusters display a wide variety of structural formats that are characterized by strikingly different emissive behaviors,¹³⁻²¹ in which the combination of the higher energy (HE) and lower energy (LE) emission bands may result in a white luminescence suitable for WLED application.

In this communication, we report a new white phosphorescent Cu_2I_2 chain-like polymer bridged by a sandwich of benzo-18-crown-6, which can be quickly assembled from common, commercially available reagents CuI and benzo-18-crown-6 in the presence of KI . Different KX/CuX ($X = \text{I}$, Br , Cl) have been employed to investigate how the resulting products are influenced by the use of the different halides in the presence of benzo-18-crown-6 or 18-crown-6.

By treating a suspension of CuX/KX in toluene with quantitative benzo-18-crown-6 at 120 °C for 24 h afforded the corresponding compounds **C1** ($X = \text{I}$), **C2** ($X = \text{Br}$) and **C3** ($X = \text{Cl}$). Similarly, **C4** ($X = \text{I}$), **C5** ($X = \text{Br}$) and **C6** ($X = \text{Cl}$) were prepared using 18-crown-6 instead of benzo-18-crown-6. These

analytically pure compounds were obtained in high yields (90%) followed by filtration to remove excessive potassium halides and cuprous halides and then recrystallization from a mixture of hexane and dichloromethane. Impressively, these compounds are very soluble in most common solvents, such as dichloromethane and methanol. The white powders of these compounds are very stable in the atmosphere, while in aerated solution they are relatively sensitive to adventitious oxygen and water. The crystals of **C1**, **C2**, **C5** and **C6** suitable for X-ray diffraction analysis were obtained by diffusion of hexane into the dichloromethane solution of the complexes and each of them was characterized by crystallographic analyses.

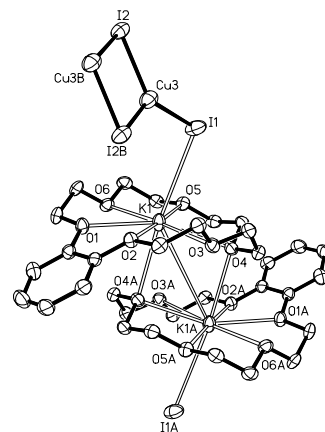


Fig. 1 A perspective view of **C1** (hydrogen atoms are omitted for clarity).

As shown in **Fig. 1**, two potassium complexes of benzo-18-crown-6 units are first assembled into a sandwich through two arms between one peripheral O and the centered K atoms, and further bridged by a rhombus Cu_2I_2 and two Γ to afford a 1-D linear coordination polymer **C1** $\{[\text{K}(\text{benzo-18-crown-6})]_2(\text{Cu}_2\text{I}_4)\}_n$. The length of the arm is 3.089(2) Å (K1–O4). The Cu_2I_2 rhombus formed displays a much closer Cu3-Cu3 distance (2.792 Å), much separated I2–I2 distance (4.329 Å), Cu3-I2 2.572(14) Å, I2– Cu3-I2 114.26(5)°, and Cu3-I2-Cu3 65.74(4)°. Another Γ connects the Cu_2I_2 rhombus with the K^+ center of the sandwich with K1–I1 of 3.682(3) Å and Cu3-I1 of 2.509 (11) Å. The zigzag angle in **C4** is 101.59(3)° (K1–I1– Cu3). It should be noted that the relatively short Cu3-Cu3 distance in **C1** is less than twice the van der Waals radius (1.4 Å) of Cu(I) , implying the

strong Cu–Cu interaction. The phenomenon of Cu–Cu interaction has been extensively observed for Cu_4I_4 clusters and other multinuclear copper(I) complexes.^{12, 29, 30} In contrast, **C2** was confirmed to be a dimeric structure $\{[\text{K}(\text{benzo-18-crown-6})]_2(\text{CuBr}_2)_2\}$ upon replacing the Γ^- with Br^- under the same reaction condition (Fig. S1 in Supporting Information). Similarly two molecules of the potassium complex of benzo-18-crown-6 in **C2** were linked by two arms of K–O firstly, and then further coordinated with cuprous bromide outside the sandwich. The length of the arm is 2.934(3) Å (K1–O3), which is slightly shorter than that of **C1** (3.089(2) Å). The Cu centers feature a linear coordination geometry with Br–Cu–Br angle of 176.34(3)° and the Cu–Br distances falling in the range of 2.218(7)–2.223(7) Å. A different coordination mode was expected using 18-crown-6 instead of benzo-18-crown-6 under the same experimental condition. As shown in Fig. S1, 1-D linear coordination polymers **C5** and **C6** have a very similar crystal structure as $\{[\text{K}(\text{18-crown-6})](\text{CuX}_2)]_n$ (X = Br, Cl), in which the crown ether acts as a wheel connected by a zigzag axis of K–X–Cu–X. The zigzag axis displays a K1–Br1 distance of 3.3722(8) Å and regular Cu1–Br1 distance of 2.2012(7) Å in **C5**, in comparison to the shorter K1–Cl1 length of 3.2699(7) Å and Cu1–Cl1 distance of 2.0948(7) Å in **C6** induced by the small radius of Cl^- ion. The zig-zag angles are close to a perpendicular type with K1–Br1–Cu1 angle of 94.63(2)° and K1–Cl1–Cu1 angle of 96.52(2)° in **C5** and **C6**, respectively. Unfortunately, single crystals of **C3** and **C4** for X-ray diffraction were not obtained.

As expected, the cuprous halide clusters containing benzo-18-crown-6 show higher thermal stability than that of 18-crown-6 when the same CuX (**C1** > **C4**, **C2** > **C5**, **C3** > **C6**) was used. With the same crown ether, the sequence of thermal stability of halogen coordinated complexes (**C1** > **C2** > **C3**, **C4** > **C5** > **C6**) corresponds to the order of electron-donating ability of the halides ($\Gamma^- > \text{Br}^- > \text{Cl}^-$) (Fig. S2).

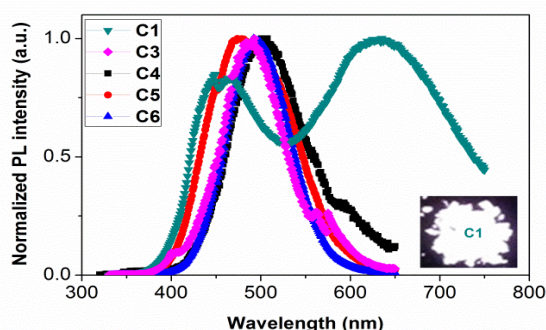


Fig. 2 PL spectra of cuprous halide clusters **C1** and **C3**–**C6** and **C6** in the solid state at room temperature (inset: the **C1** powder under UV irradiation at 254 nm at room temperature).

The photoluminescence (PL) behaviors of the cuprous halide clusters are often very dependent on their structures.³¹ Upon exposure to the UV radiation at room temperature, **C1** exhibits a very strong white luminescence, and a very broad emission spectrum in the range of 360–800 nm was observed with two maximum peaks centered at 465 and 632 nm ($\lambda_{\text{ex}} = 282$ nm) (Fig. 2 and Table 1). On the contrary, **C4**, **C5** and **C6** emit an intense blue or green light while **C2** and **C3** display a very weak blue emission under UV irradiation (Fig. S3). Obviously, the emission

spectra of **C4**, **C5** and **C6** in the solid state are similar due to their analogous structures with the maximum peaks at 476, 495 and 502 nm ($\lambda_{\text{ex}} = 256$ nm), respectively. The subtle change of their emission maximum was probably attributed to the different ligand field strengths and electronegativity of the halides. As for **C4**, the high energy and low energy bands at 298 K exhibit the same lifetime of 4.8 μs , while **C4**, **C5**, **C6** and **C3** show the lifetime values of 4.4, 275.6, 26.8 and 2.2 μs , respectively. The microsecond lifetime scale implies that these transitions arise from the triplet excited states. At room temperature, **C1** displays the highest luminescence quantum yield (Φ_{PL}) of 0.22 in the microcrystalline powder.

Table 1 Photophysical properties at 298 and 77 K and decomposition temperatures of **C1**–**C6**.

Complex	Ex/nm ^a	Em/nm ^a		Φ	τ (μs) ^a	Em/nm ^b		T_{dec} (°C) ^c
		298 K	77 K			77 K	77 K	
C1	282	465, 632	0.22	4.8, 4.8	670	290		
C2	–	– ^d	–	–	–	267		
C3	276	489	–	2.2	–	263		
C4	256	502	0.04	4.4	443	283		
C5	256	476	0.05	275.6	420	250		
C6	256	495	0.08	26.8	411	235		

^a Values obtained in powder at room temperature; ^b Values obtained in powder upon excitation at 337 nm at 77 K; ^c Defined as the temperature of 10% weight loss; ^d very weak luminescence.

The observed photoluminescence could be attributed to any one of the transitions, viz. ligand-centered, metal-centered, or charge transfer.^{32, 33} The systems described here display no possibility of metal-ligand charge-transfer transitions because of the absence of ligands coordinated to copper atoms. Although it was reported that the presence of a crown ether in the unit cell can change the wavelength of the fluorescent emission of a CuX complex,³⁴ clearly the potassium complex of benzo-18-crown-6 and 18-crown-6 moieties in the present case cannot be responsible for the emission observed as no fluorescence is detected for them.^{35, 36} And CuI in the solid state has been shown to display the 420 nm emission when excited with a nitrogen laser.³⁷ Without doubt, the Cu–X bond should be the only possibility acting as a source of emission in the cuprous halide clusters. Since **C1** also shows Cu–Cu distances of less than 3.0 Å, the emission data suggest that a metal-centered process involving more than one metal center is reasonable for the broad emission extending to 800 nm, and is consistent with the assignment reported in the literature.³⁸ As for **C4**–**C6**, the halide to copper charge transfer (XMCT) unambiguously contributes to the blue or green luminescence, while the change of coordination environment for **C2** and **C3** leads to a very weak blue luminescence.

Upon lowering the temperature, the low-energy emission band of **C1** is red-shifted while the high-energy emission band disappears at 77 K, as shown in Fig. S4. We can presume that because of the rather shorter Cu–Cu distances by lowering the temperature, an increase of the electronic interactions between adjacent copper ions in the excited state is the reason for the shift of the emission band. Indeed, from the DFT calculations in literatures, the Cu–Cu interactions in the excited state (T_1) are of the bonding character.^{10, 22, 39} As the temperature decreases, the

Cu–Cu distances become shorter, the bonding character increases, the energy level is lowered, and thus the low-energy emission band shifts to the longer wavelength. The crystal structures of other complexes imply no Cu-Cu interactions, and decreasing the temperature is not enough to induce significant metallic interaction. As for **C4**, **C5** and **C6**, only a slight blue shift of the fluorescence bands takes place upon lowering the temperature to 77 K.

Conclusions

A new class of stable, efficient, and environmentally “friendly” white and blue phosphorescent Cu(I) based materials have been prepared from different CuX/KX (X = I, Br and Cl) and various crown ethers under mild conditions. Single crystal X-ray analyses show that **C1** showed a 1D polymeric structure of {[K(benzo-18-crown-6)]₂(Cu₂L₄)_n}_n with Cu₂I₂ rhombus alternately connected by sandwich-like [K(benzo-18-crown-6)]₂, while **C5** and **C6** were constructed in a one-dimensional zig-zag coordination polymer {[K(18-crown-6)](CuX₂)_n}_n (X = Br, Cl), with the CuBr₂ or CuCl₂ cluster units alternately connected by the cationic [K(18-crown-6)]⁺ bridge. In addition, a dimeric structure of {[K(benzo-18-crown-6)]₂(CuBr₂)₂} was confirmed for **C2**. Impressively, **C1** displays a strong white phosphorescence at room temperature which can be attributed to halide-to-metal charge transfer (XMCT) and emission from the Cu₂I₂ cluster-centered (³CC) excited state, whereas the solids of **C4**, **C5** and **C6** exhibit very strong blue emissions at room temperature. Benefiting from the cheap and nontoxic copper meal, ease of structural variation, and the synthetic simplicity, the new approach opens a new perspective for the development of highly white and blue phosphorescent materials.

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Notes and references

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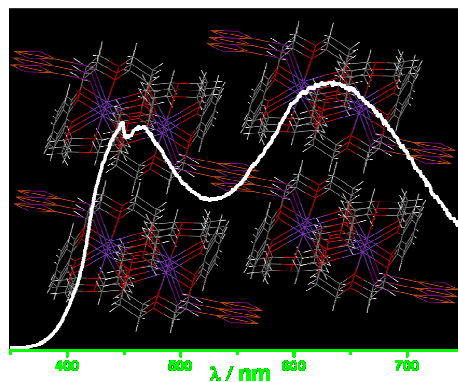
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† Electronic Supplementary Information (ESI) available: General experimental, synthetic procedure and characterization data for the complexes, and crystallographic data in CIF for CCDC 989694–989697. See DOI: 10.1039/b000000x/

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Table of contents



A 1D polymer of $\{[K(\text{benzo-18-crown-6})]_2(\text{Cu}_2\text{I}_4)]\}_n$ with Cu_2I_2 rhombus alternately connected by sandwich-like $[K(\text{benzo-18-crown-6})]_2$ displays direct white light in solid state.