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Copper iodide organic-inorganic hybrid chelating clusters as luminescent coating materials

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ABSTRACT

Here, three copper iodide hybrid chelating clusters have been synthesized and all these compounds emit lowenergy emission ranging from orange to red. The stability of these molecular compounds have been enhanced by the formation of a five-member ring among the inorganic motif and the coordinating atoms from the organic ligands. The solution processability of these hybrid clusters make them suitable as functional coating materials.

1. Introduction

Organic-inorganic hybrid materials are a kind of composite structures formed by chemical bonding between inorganic species and organic ligands [1,2]. Its inorganic unit can be zero dimensional clusters, multi-dimensional inorganic chains or layers [3–5]. These inorganic modules are combined with organic ligands through covalent or ionic bonds to form a variety of organic-inorganic hybrid structures [6]. The hybrid materials not only exhibit the optical, electrical and magnetic properties of the original inorganic material, but also has the flexibility and tunability of the organic species [7–9]. Also, new excellent properties will be derived by the integration of inorganic and organic components at molecular level. In the past few decades, numerous hybrid material systems have been developed, and their interesting properties were explored intensively.

Luminescent materials with excellent solution processability are of great importance due to their capability of making fine coatings or films for high-performance optoelectronic devices [10–13]. They can also be used as sensors for a variety of applications, including corrosion monitoring, detection of chemical explosives and volatile organic compounds (VOCs), etc [14–16]. The typical procedure for the fabrication of luminescent coatings is to add light-emitting materials into regular coatings. Nearly all of the commercial light-emitting materials contain rare earth elements (REEs). Mining, refining, and recycling of REEs have serious environmental consequences and has already caused major environmental damages around the globe [17]. Therefore, developing non-REE

light-emitting industrial products has long-term significance.

Copper iodide based inorganic–organic hybrid semiconductors represent an important class of crystalline materials with unique properties, including structural variety, optical tunability, strong luminescence, solution processability, etc [18–21]. Much attention has been paid on these materials in the past decade due to their potential applications in green and energy-saving solid-state lighting technology, as they could be developed as rare-earth (RE) free alternative lighting materials [22–25]. The inorganic motifs of these hybrid structures are either discrete clusters or infinite chains/layers constructed by Cu_mI_n tetrahedral. The connection between inorganic and organic components is coordination bond, ionic bond or both. Up to now, inorganic modules of zero-dimensional (0D) cluster, one-dimensional (1D) chain and twodimensional (2D) layers have been found, and they are further connected by organic ligands to form structures from 0D molecules to 3D frameworks [22].

The optical properties and stability of this structural family are highly related to both the inorganic modules and the organic ligands. The luminescence mechanism of these hybrids has been studied to be metal-to-ligand charge transfer (MLCT), halide-to-ligand charge transfer (XLCT), cluster centered (CC), or combinations of them [26]. Among all these diverse structures, 0D molecular clusters have attracted the most interests because of their structural simplicity, strong luminescence and solution processability. For neutral hybrid clusters, their inorganic modules are CuI monomer, Cu₂I₂ rhomboid dimer, Cu₃I₃ trimer, Cu₄I₄ tetramer, etc. We reason that the hybrid clusters with CuI monomer

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Research paper



should have better luminescent property and solubility. For CuI monomer based compounds, each Cu atom coordinate to one I atom and three coordination atoms from ligand molecules. The rich Cu-ligand bonds lead to active MCLT process, resulting in the strong luminescence. However, they have been much less investigated compared to hybrid structures with other CuI motifs.

Here, 1,10-phenanthroline and its derivatives have been selected as organic ligands for the construction of three copper iodide organic-inorganic hybrid chelating clusters (Fig. S1). They are 0D-CuI(tpp) (2,9-dimethyl-1,10-phenanthroline) (1, tpp = triphenylphosphine), 0D-CuI(tpp)(2,9-dichloro-1,10-phenanthroline) (2) and 0D-CuI(tpp)(5chloro-6-methyl-1,10-phenanthroline) (3). We describe the crystal growth and structure determination of the three compounds, as well as their thermal stability, optical absorption and emission properties. The inorganic modules of these hybrids are all CuI monomers, which is the simplest CuI inorganic module. All of the three compounds show lowenergy photoluminescence ranging from orange to red under UV excitation. Due to their molecular nature, these hybrids show excellent solubility in common organic solvents, showing potential as functional coating materials. The stability of these molecular compounds have been enhanced by the formation of a five-member ring among the inorganic motif and the coordinating atoms from the organic ligands.

2. Experimental

2.1. Materials

CuI, acetone, methyl sulfoxide, ethanol, dichloromethane, toluene, triphenylphosphine, polyethylene oxide, 2,9-dimethyl-1,10-phenanthroline, 2,9-dichloro-1,10-phenanthroline, 5-chloro-6-methyl-1,10-phenanthroline have been purchased from Aladdin and have been used as received without any purification.

2.2. Synthesis

For compound 1, CuI (0.10 g, 0.1 mmol), tpp (0.13 g, 0.5 mmol) and 2,9-dimethyl-1,10-phenanthroline (0.10 g, 0.5 mmol) have been placed in 5 mL CH₂Cl₂/toluene (1:1/v:v) solution and has been sonicating for 10 min. After that, the reaction mixture has been placed in the reaction vial and heated at 80 °C overnight. Crystals and crystalline powder were formed. Yield is 67% based on Cu. The preparation of **2** and **3** is similar as that of **1** except the ligands used are different. Yields are 70% and 67% based on Cu for **2** and **3**. The products were collected by filtration from the reaction solution and washed with a small amount of acetone three times. These samples were then dried in a vacuum oven overnight before other measurements were made.

2.3. Single crystal X-ray diffraction (SXRD)

Single crystal X-ray diffraction data were collected on a Bruker D8 Venture diffractometer with graphite-monochromated Ga Kalpha radiation ($\lambda = 1.34139$ Å) The structures were solved by direct methods and refined by full-matrix least-squares on F² using the Bruker SHELXTL package. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The structures were deposited in Cambridge Structural Database (CSD) and the number is 2,039,972 (1), 2,039,970 (2) and 2,039,971 (3).

2.4. Powder X-ray diffraction (PXRD)

PXRD analyses were carried out on a Bruker D8 Advance automated diffraction system using Cu K α radiation ($\lambda = 1.5418$ Å). The data were collected at room temperature in a 2 θ range of 3-50° with a scan speed of 1°/min. The operating power was 40 kV/40 mA.

2.5. 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 μ m.

2.6. Thermogravimetric (TG) analysis

TG analyses of the title compounds were performed on a computercontrolled 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 600 °C.

2.7. Excitation spectrum measurements

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

2.8. Photoluminescence measurements

Steady-state photoluminescence spectra were obtained at room temperature on a FLS1000 spectrofluorometer.

2.9. Internal quantum yield measurements

Internal quantum yield (IQY) 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 in. integrating sphere.

2.10. 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 μ s window) with data collection for 10,000 counts. Excitation was provided by an Edinburgh EPL-360 picosecond pulsed diode laser. The lifetime was obtained by mono-exponential fitting.

3. Results and discussion

The classical coordination chemistry principle shows that the stability of the chelates formed by metal ions and polydentate ligands is much higher compared with that of the regular molecular complexes generated by monodentate ligands. Previous studies have shown that the luminescent efficiency of the zero dimensional molecular clusters show much higher quantum efficiency compared to that of the hybrid structures with multi-dimensional inorganic chains or layers [27]. In addition, the bonding mode and bonding type between inorganic moieties and organic ligands have a significant impact on the luminescent properties and stability of the whole hybrid structures [13]. Under these considerations, we plan to design and synthesize chelating copper iodide hybrid molecular clusters, in order to obtain high luminescent efficiency and high stability. In such a hybrid material, copper atoms and organic ligand molecules are fully connected and chelated to form a ring through coordination bonds, which provides an effective channel for electron transfer and ensures its high-efficiency luminescence performance. At the same time, the organic ligands are firmly chelated around the copper atoms, which is not easy to leave, so as to enhance the stability of the

hybrid molecular clusters.

Phenanthroline based organic molecules are ideal organic ligand candidates for the construction of copper halide chelating clusters since there are two adjacent N atoms in the aromatic ring [28-32]. The structure of the ligands have been plotted in Fig. S1. Both the two N atoms in one ligand molecule could coordinate to Cu to form hybrid structures. The *tpp* is commonly used for the synthesis of copper halide organic-inorganic hybrid clusters with discrete inorganic modules due to the steric hindrance of the tpp. Therefore, they have been selected as organic ligands for the synthesis of copper iodide chelating clusters. Crystals suitable for single crystal X-ray diffraction were obtained by heating a mixture of the CuI, tpp and the N-ligands in a mixed CH₂Cl₂ toluene (1:1/v:v) solvent system at 80 °C. Crystals typically form within 24 h. The structures of these bulk crystals were determined using SCXRD and their crystallographic data are summarized in Table S1. The phase correctness and purity of powder samples were confirmed by comparing the PXRD patterns with simulated ones (Fig. S2). In these structures, the Cu atoms tetrahedrally coordinate to one iodide atom, one tpp molecule and one 1,10-phenanthroline derivative molecule as shown Fig. 1. Compound 1, 2, and 3 are crystalized in space group C2/c, P-1 and $P2_1/c$ *n*, respectively. The structures have been deposited in the Cambridge Structural Database (CSD), with CCDC number 2,039,972 (1), 2,039,970 (2) and 2,039,971 (3). Details of the crystal data are summarized in Table S1. The figures of the asymmetric unit as a thermal ellipsoid plot is shown in Figs. 2-4. Selected bond lengths and angles have been summarized in Table S2–S4. Typically, the coordination atoms in bidentate ligands coordinate to different Cu atoms, which results in the formation of extended structures. However, here the two N atoms in one ligand molecule coordinate to one Cu atom, forming a five member ring between the inorganic and organic component in the molecular structure (Fig. 1d). Since these three molecular clusters share the same chelating structural characteristics, the structural formation of such chelating clusters is a result of ligand choice, which is largely determined by the chemical structure of the coordinating aromatic ring, while the chemical structure of the substitute groups of the organic ligands play little effect on the final structures.

The photophysical properties of these hybrids were characterized using UV–vis absorption spectroscopy, as well as photoluminescence



Fig. 2. Emission spectra and excitation spectra of **1** (a), **2** (b) and **3** (c). Black: excitation spectra; red: emission spectra. $\lambda_{ex} = 360$ nm, $\lambda_{em} =$ emission maximum. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 1. Structural plots of 1 (a), 2 (b) and 3 (c) and the chelating ring formed in the structure (d). Cyan: Cu; green: I; grey: C; blue: N; green: Cl. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 3. (a) TGA plots of 1, 2 and 3. (b) CIE coordinates of 1 (triangle), 2 (square) and 3 (circle). Inset: 1 (top) and 2 (bottom) coated onto glass substrates.

emission spectroscopy. The major photophysical properties of these hybrid structures are summarized in Table 1. All of these structures display a sharp optical absorption edge as illustrated in Fig. S3. The high absorption coefficients suggest that they are strong energy absorbers, which are ideal for the conversion of UV light to visible light. Their bandgaps were estimated from optical absorption spectra and the values are listed in Table 1.

The energy bandgaps were determined using optical absorption spectroscopy using the Tauc equation of $(\alpha h\nu)^2 = A(h\nu - E_g)$, where A is a

Table	1

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Compound	1	2	3
Band gap (eV)	2.2	2.1	2.0
λ_{ex} (nm)	360	360	360
λ _{em} (nm)	605	620	650
Emission color	Orange	Orange-red	Red
IQY (360 nm)	25.8%	19.3%	3.8%
IQY (450 nm)	20.8%	19.8%	3.1%
τ (μs)	12.83	6.53	4.10
CIE	0.52, 0.46	0.55, 0.43	0.62, 0.35
TD (°C)	190	180	180

constant, $h\nu$ is photon energy, and α is the absorption coefficient. Their bandgaps values are 2.2 eV, 2.1 eV and 2.0 eV for compound **1**, **2** and **3**, respectively. Such values indicate that these compounds are suitable for both UV light and blue light excitation. Solid state photoluminescence spectra were collected at room temperature in the solid state. Their emission spectra confirm that all compounds emit in the visible light region (mostly in the red light region) and their emission profile is a single band type with full widths at half maximum (FWHM) of around 110 nm (Fig. 2). Their emission peaks are 605 nm, 620 nm and 650 nm for compound **1**, **2** and **3**, respectively. All of these compounds could be excited by either UV light or blue light.

A common copper iodide hybrid molecular cluster 0D-CuI(3-pico-line)₃ has been selected as a reference. This compound decomposes at 50 °C and is not air or moisture stable. The decomposition temperatures (T_D) of compound **1–3** are summarized in Table 1. The T_D for these structures are as high as 180 °C (Fig. 3a). These compounds are also air and moisture stable. The increase stability of these molecular clusters could be explained by the annulation of the chelating ring. Such annulation approach could be applied for the design of more stable organic–inorganic hybrid structures.

The Commission Internationale de l'Eclairage (CIE) chromaticity coordinates for these compounds are calculated to be (0.52, 0.46), (0.55, 0.46)0.43) and (0.62, 0.35) for 1, 2 and 3, respectively, as show in Fig. 3b. The room temperature internal quantum yields (IQYs) were measured on a C9920-03 absolute quantum yield measurement system (Hamamatsu Photonics). The IQYs of compound 1-3 have been collected. The IQY values for 1-3 are 25.8%, 19.3% and 3.8% when excited at 360 nm, and are 20.8%, 19.8% and 3.1% when excited at 450 nm. The luminescent decay curves of these compounds at room temperature are shown in Fig. S4. The lifetimes of these compounds are approximately 12.83 µs, 6.53 µs and 4.10 µs by monoexponential fitting for 1-3, respectively. The decay lifetimes in microseconds at room temperature suggest that they are phosphorescent emissions. The IQYs these compounds are relatively higher compared to most of other copper halide based hybrid structures with orange to red emission (their IQYs are generally lower than 10%) [33]. However, the IQYs need to be further increased for practical applications since the IQYs for commercial red phosphors are typically higher than 70% [34].

All these three hybrid complexes are soluble in common organic solvents, including methyl sulfoxide (DMSO), CH_2Cl_2 etc., at room temperature. The excellent solubility of them is due to their molecular nature and structural simplicity. About 100 mg of **1–2** can be completely dissolved in 1 mL DMSO and has been mixed with polyethylene oxide in ethanol solution at room temperature under ultrasonication. Subsequently solidified of the resin upon evaporation of the ethanol produced thin layers of uniformly dispersed clusters (Inset of Fig. 3b). The strong light signal from the coatings show the potential application of these luminescent hybrid compounds as luminescent coating materials.

The substituted group on the organic ligands play an important role in determining the band gaps and emission energies of these structures. The compounds with ligands having electron donating group (methyl group) show higher band gap and emission energies as compound 1, while compounds with ligands having electron withdrawing groups show red shift in band gap and emission energies as compound 2. The position of the substituted group also play certain effect. Such optical tunability resembles what have been observed for neutral Cu₂I₂ dimer and 1D-CuI(*L*) staircase chain based structures and such resemblance suggests a combination of MLCT and XLCT luminescence mechanisms [33]. Both the band gaps and emission ranges of these compounds are tunable. Since there two ligands for each hybrid complex, both the *tpp* and the *N*-ligands are involved in the MTCL luminescence [22].

4. Conclusions

In summary, a series of copper iodide organic-inorganic hybrid chelating clusters have been prepared and they exhibit luminescence from orange to red. The inorganic module of these compounds is CuI monomer, which is the simplest copper halide building unit. The stability of these molecular compounds have been enhanced by the formation of a five-member ring among the inorganic motif and the coordinating atoms from the organic ligands. These light-emitting hybrid molecular clusters can be used as functional coating materials, showing the capability of making fine coatings or films for practical applications.

5. Author statement

Le Lv: Writing the draft characterization and measurements; Siqi Wang: sample preparation and data analysis; Wei Liu: writing the draft and project supervision. All authors read and contributed to the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2020.120241.

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