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Long-lived photoluminescence and high quantum yield of copper(II) complexes with novel nanostructures

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Abstract

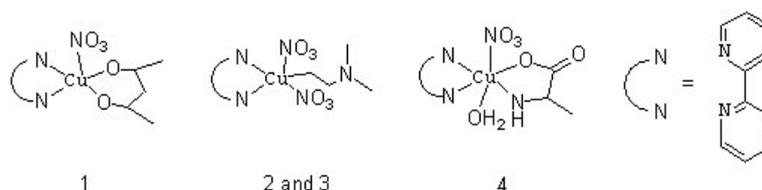
We report four crystalline mixed-ligand complexes with high luminescence intensity, long-lived photoluminescence and quantum yield, which are rarely research in the field of bivalent copper ion. Three kinds of novel nanostructures were prepared from the Cu^{II}-based bulk crystals, and they are the first mixed-ligand copper (II) complexes to be studied in the direction of nanostructures. The research shows that crystal stacking, π system and rigid flat structure are important for the photophysics of copper complexes.

Introduction

The design and synthesis of highly fluorescent compounds with tunable emission properties is one of the major challenges for the development of chemosensors and molecular-scale photonic devices.^{1, 2} A common feature of the majority of systems reported to date is that their structure is based on the covalent linking of a fluorophore moiety to a chelating unit, which allows one to monitor the interplay between fluorescence emission and metal cation complexation.³ 2, 2'-Bipyridyne (bipy), as a polydentate ligand, can be coordinated with lots of transition metal which has been discussed fully by Brandt in early 1954.⁴ With the further research on metal compounds,⁵⁻⁷ a new field about the luminescence of bipy metal compounds has been studied.⁸ Then, the rational design and assembly of coordination compound based on 2,2'-Bipyridyne and metal-organic frameworks have aroused significant interest due to their intriguing structural and interesting functional properties, such as luminescence, catalysis, porosity and electrochemiluminescence.⁹⁻²²

Copper(II) with d^9 electronic configuration does not have any interests for luminescence-related applications, because of the interaction of the electron in the $d_{x^2-y^2}$ orbital of the copper center with the unpaired electrons of the intra-ligand $\pi-\pi^*$ excited state.^{23, 24} And most of the reports about the fluorescent of copper (II) compounds showed Copper(II) ion deactivation via ultrafast non-radioactive pathways and its coordination could cause a quenching of the fluorescence emission.²⁵⁻²⁹ Copper(I) was studied widely in the field of spectroscopy, such as luminescence, lifetime and quantum yield.^{30, 31} However, with the influence of quenching, the luminescence of copper(II) compounds were rarely studied, let alone the quantum yield or lifetime. Recently, we have synthesized two kinds of mononuclear copper(II) complexes with bipy and Phen respectively, which have shown that the rigid structural plane can affect the photoluminescence of aromatic ligands.³² Then we considered that the coordination architecture can affect the luminescent emission of its coordinated aromatic ligands tremendously, such as the rings of bipy can rotate around the linking C-C single bond to relieve repulsive interactions between nitrogen lone pairs (LPs) but its coordinated has been fixed.³³⁻³⁵ Other reports considered that the coordination of metal with 2, 2'-Bipyridyne might improve the structural rigidity which can reduce distortion excited state.^{36, 37} Hence, the functions of Cu^{II} -coordinated geometries and $\pi-\pi$ stacking interactions in crystal lattice for the solid-state luminescence of coordinated ligands are still needed to be studied. Adjusting coordination geometry and $\pi-\pi$ stacking distance is possibly useful for the enhancement of luminescence intensity.³⁸ To further study the functions of

crystal stacking, π system and rigid flat structure for the photophysics of copper complexes, we have designed four bipy-based copper complexes (Scheme 1), and then studied its nano-structure and spectroscopy.



Scheme 1 Synthesis of copper(II) complexes

Experimental

Materials and measurements

All reagents were directly obtained from commercial supplies and were of analytical grade. All manipulations were carried out in a laboratory atmosphere. IR spectra were obtained from a Bruker EQUINOX55 spectrometer with KBr disks. UV-vis spectra were determined using a SHIMADZU UV-2550 spectrometer in an aqueous solution. Redox potential $E_{\text{Cu(II)/Cu(I)}}$ were measured using CHI-832 electrochemical workstation in 0.1 M KCl was used as a supporting electrolyte; 1.25×10^{-3} M aqueous solutions of these complexes. The potential was scanned from -0.65 to 0.5 V with a scan rate of 50 mVs^{-1} , glassy carbon, Pt foil, and Ag wire as working, auxiliary, and reference electrodes, respectively. Solid state fluorescence spectra were recorded on an FL4500 fluorescence spectrophotometer (Japan Hitachi Company) at room temperature in identical operating conditions. The lifetimes were measured at room temperature on FLS920 Steady State & Time-resolved Fluorescence Spectrometer (Edinburgh Instrument) for complexes 1-4. The emission quantum yields were measured at room

temperature using a Quantum Yield Measurement System Fluorolog®-3 (HORIBA company) with a 450W Xe lamp coupled to a monochromator for wavelength discrimination, an integrating sphere as sample chamber, and an analyzer R928P for signal detection.

Synthesis of complex 1-4

Synthesis of [Cu(bipy)(acac)(NO₃)] (1). Cu(NO₃)₂·3H₂O (0.2416g, 1 mmol) and bipy (0.1562g, 1 mmol) were dissolved in acetylacetone (40 ml) by stirring 12 h. The final solution was filtrated and the filtrate was transferred into six tubes (18*180 cm) layered with Et₂O. Then dark blue rectangular block crystals were obtained 2 weeks later. Elemental analysis (%), calc (exp) for C₁₅H₁₅CuN₃O₅: C 47.3 (47.26), H 3.94 (3.93), N 11.03 (11.02), O 21.02 (21.00). IR (cm⁻¹, KBr): 3426 s, 1600 w, 1581 w, 1523 m, 1447 w, 1384 vs, 1032 w, 783 w, 450 w.

Synthesis of [Cu(bipy)(DMF)(NO₃)₂] (2). Complex 2 was synthesized in the same procedure as complex 1, except that acetylacetone was replaced by N,N-dimethylformamide (DMF). Then blue rectangular block crystals were obtained 2 weeks later. Elemental analysis (%) calc (exp) for C₁₃H₁₅CuN₅O₇: C 37.45 (37.42), H 3.60 (3.59), N 16.80 (16.79), O 26.88 (26.86). IR (cm⁻¹, KBr): 3455 s, 3035 w, 1601 m, 1573 w, 1446 m, 1385 vs, 1334 m, 1031 w, 775 m, 732 w.

Synthesis of [Cu(bipy)(DMF)(NO₃)₂] (3). Complex 3 was synthesized in the same procedure as complex 1, except that acetylacetone was replaced by mixed solution (DMF/acetonitrile 1:1). Then green rectangular block crystals were obtained 2 weeks later. Elemental analysis (%), calc (exp) for C₁₃H₁₅CuN₅O₇: C 37.45 (37.42), H 3.60

(3.59), N 16.80 (16.79), O 26.88 (26.86). IR (cm^{-1} , KBr): 3442 m, 3108 w, 1647 s, 1601 m, 1473 m, 1384 vs, 1292 m, 1024 w, 776 s, 730 w.

Synthesis of [Cu(bipy)(Ala)(NO₃)] (4). Complex 4 was synthesized in the same procedure as complex 1, except that acetylacetonone was replaced by mixed solution (CH₃CH₂OH/H₂O 5:1), and used the secondly ligand of Ala (alanine) Then blue needle like crystals were obtained 2 weeks later. Elemental analysis (%), calc (exp) for C₁₃H₁₄CuN₄O₆: C 40.46 (40.43), H 3.63 (3.62), N 14.52 (14.51), O 24.90 (24.88). IR (cm^{-1} , KBr): 3450 vs, 1614 vs, 1588 s, 1447 s, 1521 w, 1401s, 1378 m, 1148 w, 848 m, 733 m, 645 w.

X-ray crystallography

Single crystal X-ray analyses were performed on a Bruker APEXII area detector device with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) by the Φ - ω scan method. Bruker SMART CCD diffract meter equipped with a Mo anode and graphite monochromator ($\lambda=0.70713 \text{ \AA}$). Crystals were mounted on a glass fiber at 293(2) K. The initial unit cell was determined using a least squares analysis of a set of random reflections obtained from three short (20 data frame) series of 0.3°-wide ω -scans which were well distributed in space. The intensities were collected using ω -scans with a crystal-to-detector distance of 5 cm to yield the complete sphere of data to a resolution of 0.75 \AA . The final unit cell was calculated using a least squares refinement of reflections culled from the entire data set. Empirical absorption corrections were made from ψ -scan data using the program SHELXTL 97 at the data reduction stage along with the correction for Lorentz and polarization effects. The

structure was solved using direct methods and refined against $|F_2|$ using the routines included in the APEX-2 software suite. Hydrogen positions were not readily discernible from electron density maps. The crystallographic data, CCDC number and experimental details for the structural analyses of complex 1-4 in this paper are summarized in Table 1.

Table 1 Crystallographic data for complexes 1-4

	1	2	3	4
Formula	C ₁₅ H ₁₅ CuN ₃ O ₅	C ₁₃ H ₁₅ CuN ₅ O ₇	C ₁₃ H ₁₅ CuN ₅ O ₇	C ₁₃ H ₁₄ CuN ₄ O ₆
Fw	380.84	416.84	416.84	385.82
Crystal system	Monoclinic	Orthorhombic	Triclinic	Orthorhombic
Space group	P2(1)/c	pnma	P -1	Pbca
a (Å)	8.8890(2)	8.0946(6)	8.3639(5)	19.4754(18)
b (Å)	11.9445(3)	16.0439(12)	9.9381(5)	7.2595(5)
c (Å)	15.1962(4)	14.1781(11)	11.0317(6)	22.789(2)
α (°)	90.00	90.00	75.219(3)	90
β (°)	99.838(2)	90.00	76.986(3)	90
γ (°)	90.00	90.00	86.001(2)	90
V (Å ³)	1589.73(7)	1841.3(2)	863.78(8)	3222.0(5)
Z	4	4	2	8
Dcalc (mg cm ⁻³)	1.591	1.504	1.603	1.591
T (K)	298(2)	298(2)	298(2)	298(2)
collected reflns	17798	8631	11947	14980
unique reflns	2811	1690	4035	2797
R ₁ [I > 2σ(I)] ^a	0.0265	0.0552	0.0429	0.1431
wR ₂ [I > 2σ(I)] ^b	0.0714	0.1714	0.1111	0.2969
R ₁ [all data]	0.0303	0.0820	0.0678	0.2053
wR ₂ [all data]	0.0744	0.2092	0.1260	0.3247
S	1.058	1.117	1.039	1.062
CCDC	996769	996767	996768	996766

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

Computational ΔE

The calculations for the energy gap (ΔE) between π* and π of free and coordinated phen are calculated under B3LYP/6-31+G* method using Gaussian 03 program.

Results and discussion

Description of the structures

The molecular structure of complex 1 is shown in Fig. S5A, and selected crystallographic data are listed in Table 1. Each copper(II) ion coordinated with one bipy, one acetylacetonone and one nitrate anion formed a tetragonal pyramidal geometry by N1, N2, O4, O5 and O3 (Fig. S8). The bond lengths of Cu1-N1, Cu1-N2, Cu1-O4, Cu1-O5 and Cu1-O3 are 1.9940(17), 2.0005(17), 1.9180(14), 1.9068(14) and 2.3538(16) Å respectively. More details on the coordination bond lengths and angles are listed in Table S1. In complex 1, Each [Cu(bipy)(acac)(NO₃)] molecule stacks with its adjacent molecule head to head along the b axis by π interaction (Fig. 1d). To gain further insight into the effect of π interaction, TEM analyses were conducted to characterize its structure. As shown in Fig. 1(a-c), a large amount of novel nanosheets with the length and width of a few tens of nanometers have been prepared and photographed, which have certified further the π interaction of two adjacent molecules in Fig. 1d.

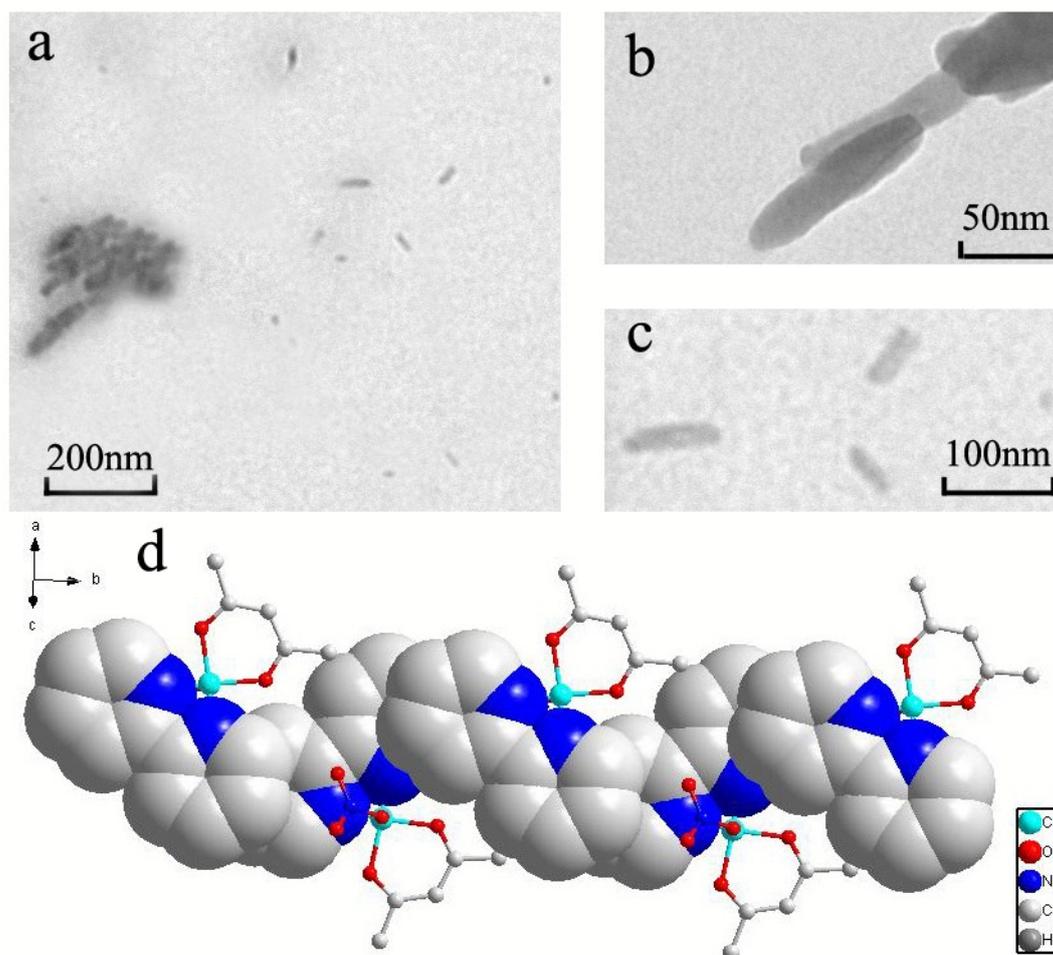


Fig. 1 TEM images of complex 1 prepared by grind (2 h), ultra-sonication (24 h), and centrifuging (8000 r/s, 10 s), and photographed under different magnification (a, b and c). The π - π stacking interaction of complex 1 is shown by space-filling mode (d).

Complex 2 crystallized in orthorhombic system with space group Pnma. The central Copper(II) atom has a five-coordinate tetragonal pyramidal geometry with two N-donor atoms of one chelating bipy ligand, one O-atom of one DMF (Dimethyl Formamide) ligand and the other two O-atoms of the coordinated nitrate group (Fig. S5B). In CuN₂O₃ coordination sphere, Cu-N (Cu1-N1 and Cu1-N1#1) and Cu-O (Cu1-O1 and Cu1-O1#1) bond lengths are 1.991(4) Å and 1.996(4) Å respectively, and the Cu1-O4 bond length of 2.201(5) Å is within the normal range. Under the influence of loosened stacking mode, complex 2 exhibited a sharp nano particle size

distribution (8.9 ± 0.5 nm, Fig. 2a, b).

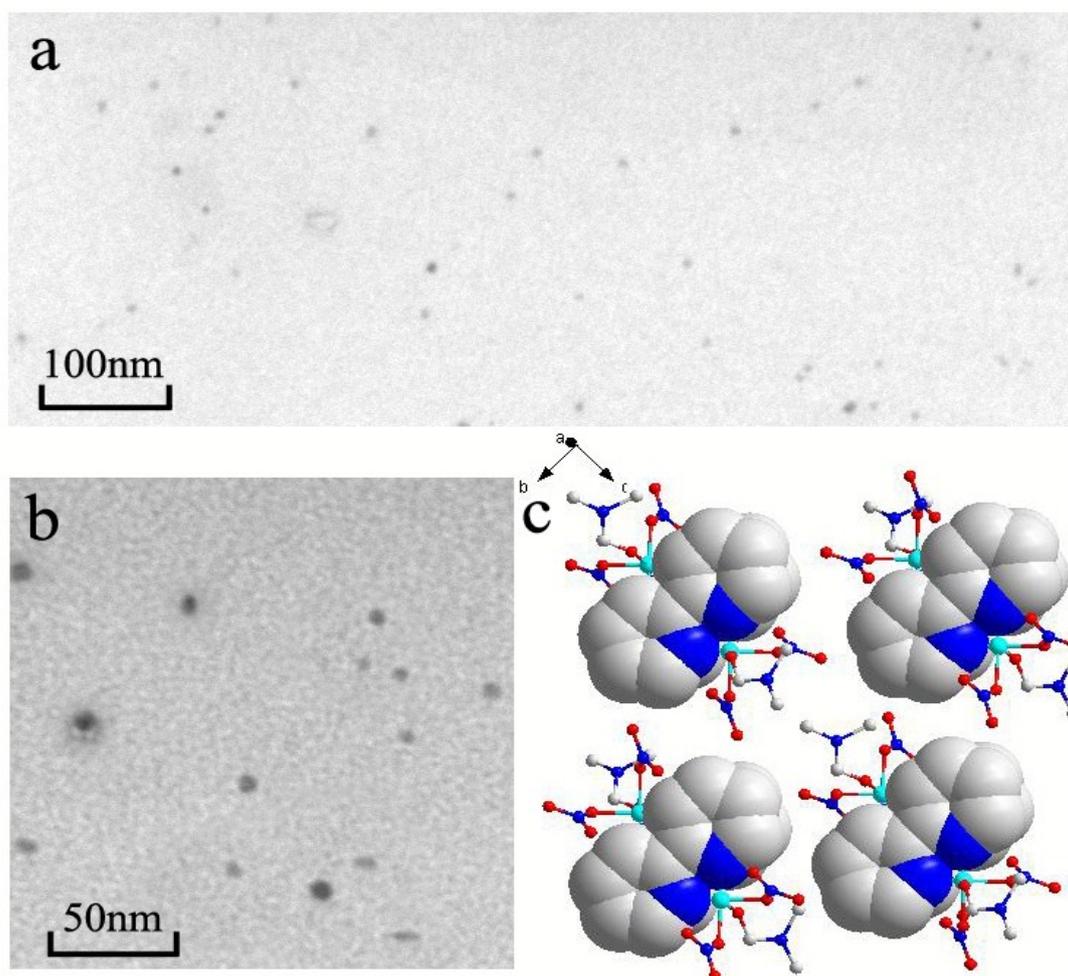


Fig. 2 TEM images of complex 2 prepared by grind (2 h), ultra-sonication (24 h), and centrifuging (8000 r/s, 10 s), and photographed under different magnification (a, b). The π - π stacking interaction of complex 2 is viewed in space-filling mode (c).

Crystallographic analysis revealed that complex 3 crystallizes in the triclinic space group P-1. Complex 3 and 2 have the same molecular formula, while the central Cu^{II} atom linking with one bipy ligand, one DMF ligand and two coordinated nitrate group formed a trigonal-bipyramidal geometry (CuN_2O_3) by N1, N2, and O1, and O2, O10. Bond lengths and angles are compared in Table S1. Unlike complex 2, complex 3 packed closely and showed a sharp nano particle with diameter dozens of nanometers

(Fig. 3a, b)

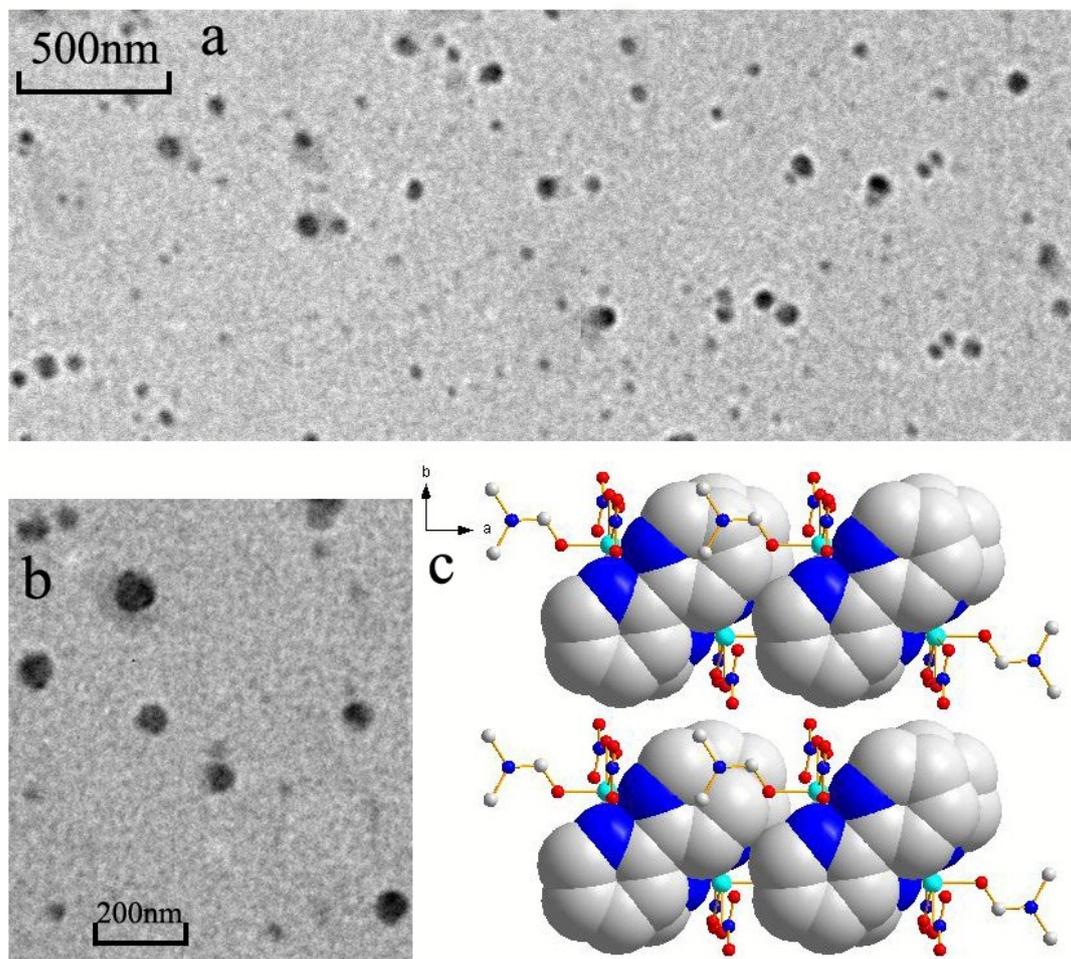


Fig.3 TEM images of complex 3 prepared by grind (2 h), ultra-sonication (24 h), and centrifuging (8000 r/s, 10 s), and photographed under different magnification (a, b). The π - π stacking interaction of complex 3 is viewed in space-filling mode (c).

The asymmetric unit for complex 4 consists of one Cu^{II} ion, one bipy ligand, one Ala ligand, one nitrate anion and one water molecules. The central copper(II) atom has a distorted six-coordinate octahedral geometry (Fig. S5D, Fig. S8D). Equatorial bond lengths [Cu1-N1 = 2.008(11), Cu1-N2 = 2.014(11), Cu1-N3 = 1.982(11), Cu1-O1 = 1.915(9)] and weakly bound axial bond lengths [Cu1-O3 = 2.464(11), Cu1-O4 = 2.708(12)] were listed in Table S1. In addition, each unit couples with its enantiomer head to tail by hydrogen bond and stacks with the other molecule head to

head by π - π interaction, which formed a semi-circular structure. And the nanostructure of complex 4 exhibited rare rupturing nanoparticles which might be related with the semi-circular structure (Fig. 4c).

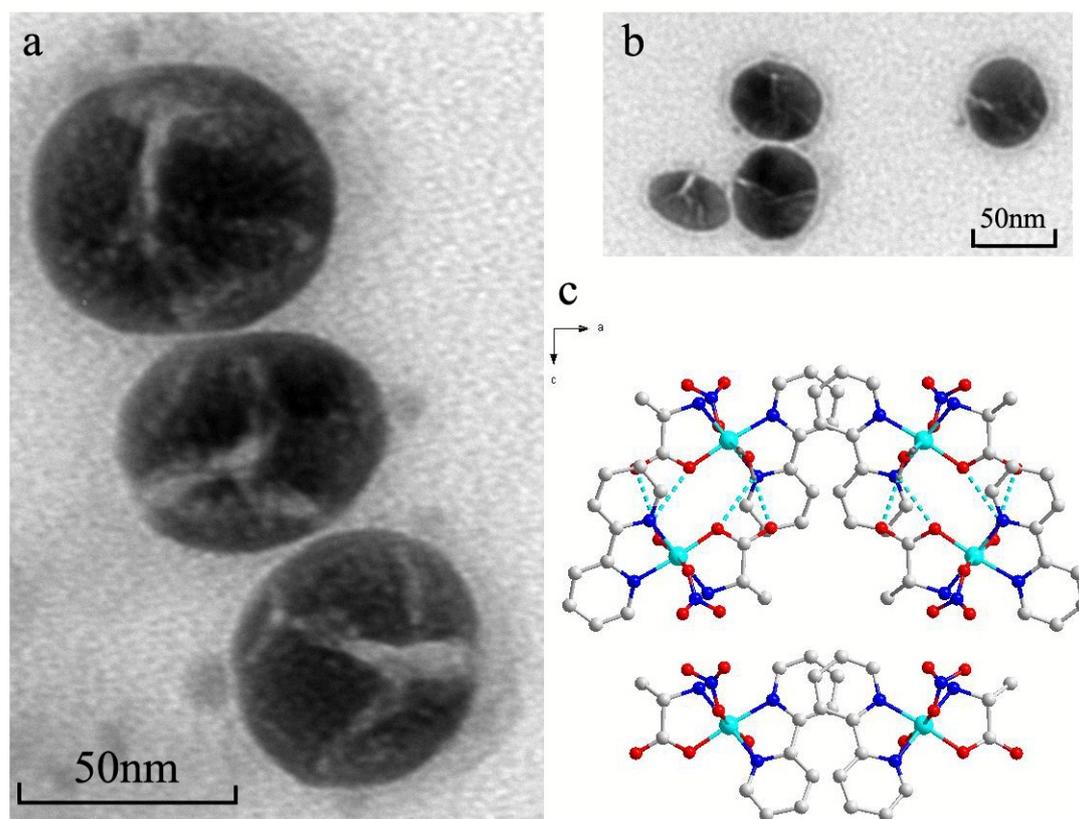


Fig.4 TEM images of complex 4 prepared by grind (2 h), ultra-sonication (24 h), and centrifuging (8000 r/s, 10 s), and photographed under different magnification (a, b). The π - π stacking interaction of complex 4 is viewed in space-filling mode (c).

Photoluminescence Spectra

Solid-state photoluminescence properties of complexes 1–4 and free ligand were investigated at room temperature. As shown in Fig. 5, the free bipy ligand displayed very weak intensities in the emission spectra with four main peaks, which presented a main peak at 412 nm (1500 a.u.) with one left shoulder at 375 nm and two smaller bands at 433 nm and 462 nm. However, their associated complexes 1-4 exhibited

similar emission spectra with an enhancement in the intensities, which are about 40nm red-shifted. Notably, a new stronger peak at 468 nm should relate with the 5-membered condensed rings coordinated between copper (II) and bipy. In addition, the intensities of four complexes have been enhanced (the minimum 2 approximate 5-folds and maximum 3 approximate 20-folds), which are not common in copper complexes. The Cu^{II} ion exhibits no ability for luminescence emission and its complexes exhibit the fluorescence quenching phenomenon.³⁹ Hence, the significantly enhanced luminescent efficiency can be attributed to the fact that free bipy ligand coordinates with copper ion to form a condensed ring, which would impose rigidity and the $\pi^*-\pi$ transition of the coordinated aromatic ligands.^{40, 41}

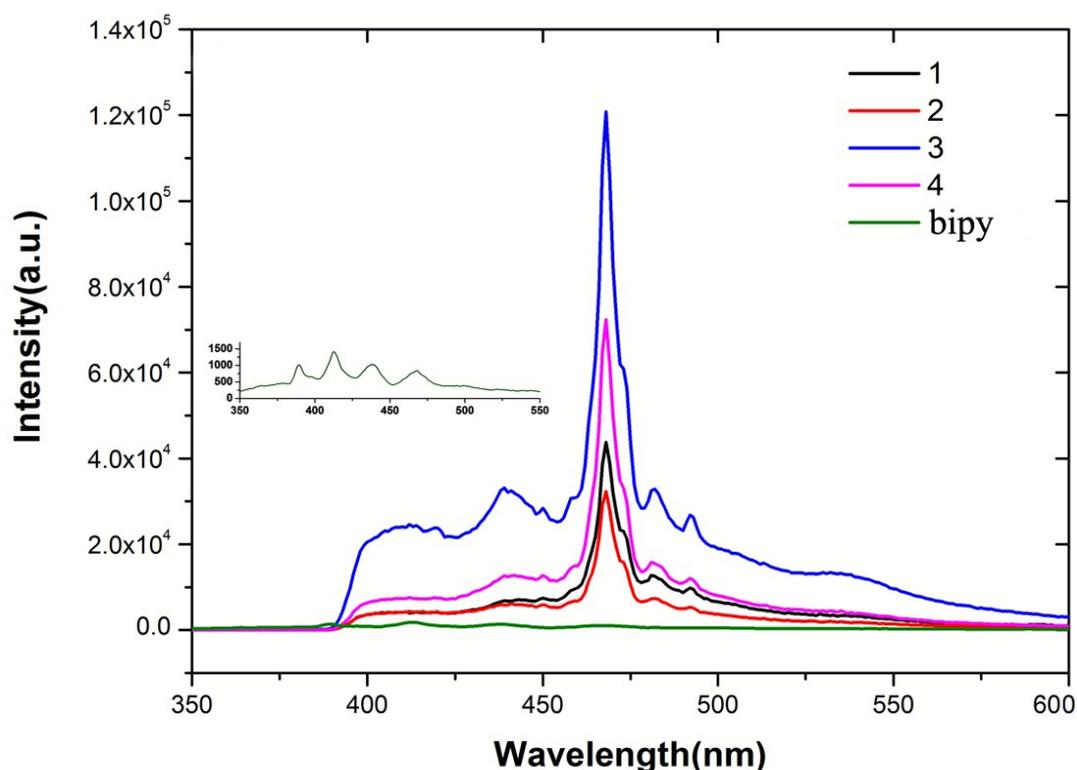


Fig. 5 Solid-state emission spectra of four complexes and the free bipy ligand, with maximum absorptions at 468 nm, were investigated at room temperature,

To gain further insight into the mechanism of luminescence, we considered that the

packing mode and the molecular structure can influence the property of luminescence. Complex 2 and 3 have the same molecular formula but different space group (table 1), which shows the co-ligand with few effect for compounds. Furthermore, the centroid-centroid distances of four compounds are 3.617, 4.089, 3.887 and 3.633 Å respectively (Fig. S6). It is easy to find that the distance of complex 2 is higher than the π - π interaction distances within the range of 3 to 4 Å,^{42,43} and it leads 2 in a lower intensity. The interactional area of other three complexes further illustrates the fiction of π system for luminescence (S3 > S4 > S1, Fig. S7).

Emissive transition metal copper complexes dispersed in support materials have been widely utilized as molecular oxygen sensors and most researches on the copper (I)^{44,45}. To the best of our knowledge, they are the first copper(II) compounds having been studied the lifetime and quantum yield. The lifetime and quantum yield of the photoluminescence in the solid state under air at room temperature are tabulated in Table 2. The decay curves of the emission of the present complexes in the solid state can be fitted with a double exponential function.⁴⁶ The lifetime and quantum yield of copper (II) complexes are even higher than the recent research on bipy copper (I) compounds under air.⁴⁷ The model first proposed for the photophysics of phen-derivative copper(I) complexes suggested that increases in the lifetime and quantum yield^{48,49} result when substantial steric hindrance at the metal or solid state interactions enforce the pseudotetrahedral ground state geometry. The nanoscale of four compounds perfectly illustrates the regular of lifetime. In addition, we consider

that quantum yield might relate to the intensity of luminescent which have concluded from the data of quantum yield and luminescent intensity (Fig. 5, Table 2).

Table 2 the lifetime and quantum yield of compounds under air. The samples were excited at $\lambda_{ex}=322$ nm.

Formula	Lifetime ^c (τ / us)	Quantum yield (ϕ / %)
[Cu(bipy)(acac)(NO ₃)]	9.55	3.09
[Cu(bipy)(DMF)(NO ₃) ₂]	5.22	2.17
[Cu(bipy)(DMF)(NO ₃) ₂]	7.75	7.86
[Cu(bipy)(Ala)(NO ₃)]	11.2	3.14

^c The decay curves of the emission of the complexes can be fitted with a exponential curve, and a double exponential curve (fit= $B_1 \cdot \exp(-t/\tau_1) + B_2 \cdot \exp(-t/\tau_2)$).

The changes of the energy gap from the free to coordinated ligands

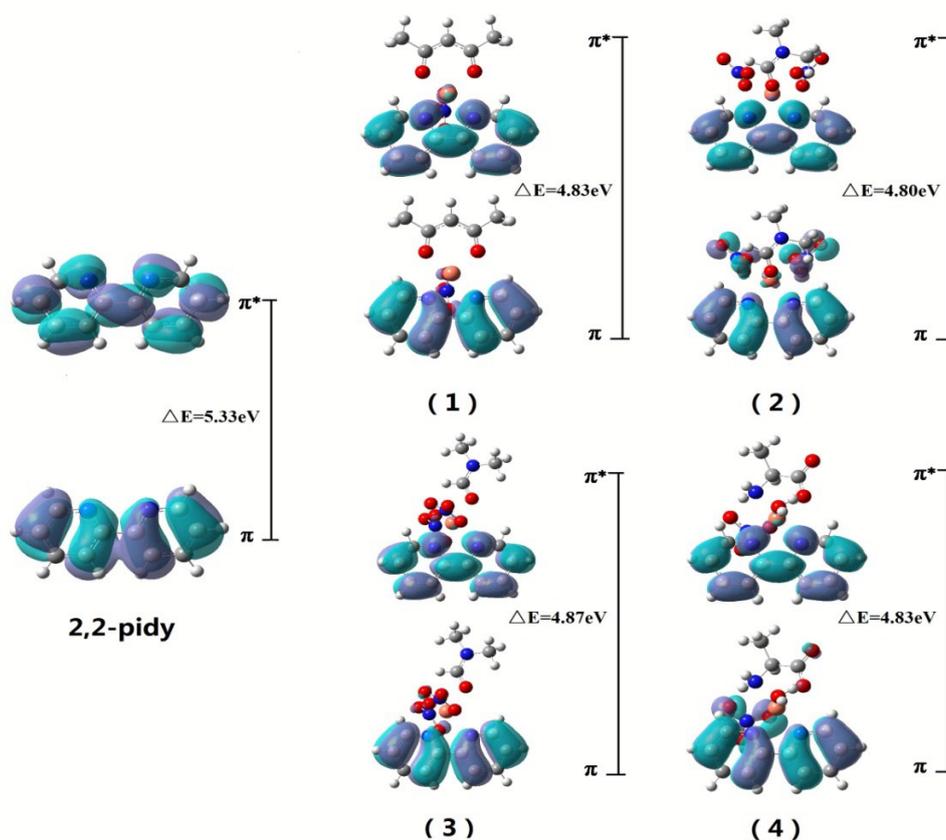


Fig. 6 The ΔE ($\Delta E = E_{\pi^*} - E_{\pi}$) of the free and coordinated bipy in complexes.

To further illustrate the function of π system for luminescence, the energy gaps

($\Delta = E_{\text{HOMO}} - E_{\text{LUMO}}$) of phen in free and coordinated states are calculated.⁵⁰ A molecule with a small frontier orbital gap is more polarizable and is generally associated with high chemical reactivity and low kinetic stability.^{51,52} In other words, a complex with a lower value of frontier orbital gap is more active. As shown in Fig. 6, all compounds and ligands were calculated in the same condition by fixing the distance of O and Cu atom, except that the O-atom of complex 4 always moves which leads the ΔE_4 lower than actual value. The data ($\Delta E_3 > \Delta E_1 > \Delta E_2$) showed that the complex 3 is stable, of which has proved that the relation among π system, luminescence and quantum yield.

Cyclic voltammetry and UV-vis

The cyclic voltammogram of complex 1-4 are shown in Figure 7. Four complexes are redox active and show quasireversible cyclic voltammetric response, which can be assigned to the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ couple at 0.266 and 0.145 V vs Ag/AgCl. The redox potential [$\mathbf{3}(-0.07\text{V}) < \mathbf{4}(0.01) < \mathbf{1}(0.02) < \mathbf{2}(0.05)$] attributed to the extension of the corresponding π framework around the metal center. UV-vis was tested in deionized water. Main peaks of Complexes 1-4 present at 602, 624, 704 and 606 nm respectively. The low-energy bands are assigned as the d-d orbital of Cu^{II} to the ligand (π^*) transitions typical of copper (II) complexes and the stable π system. Both CV and UV-vis showed the π fiction of molecule structure which would benefit for luminescence.

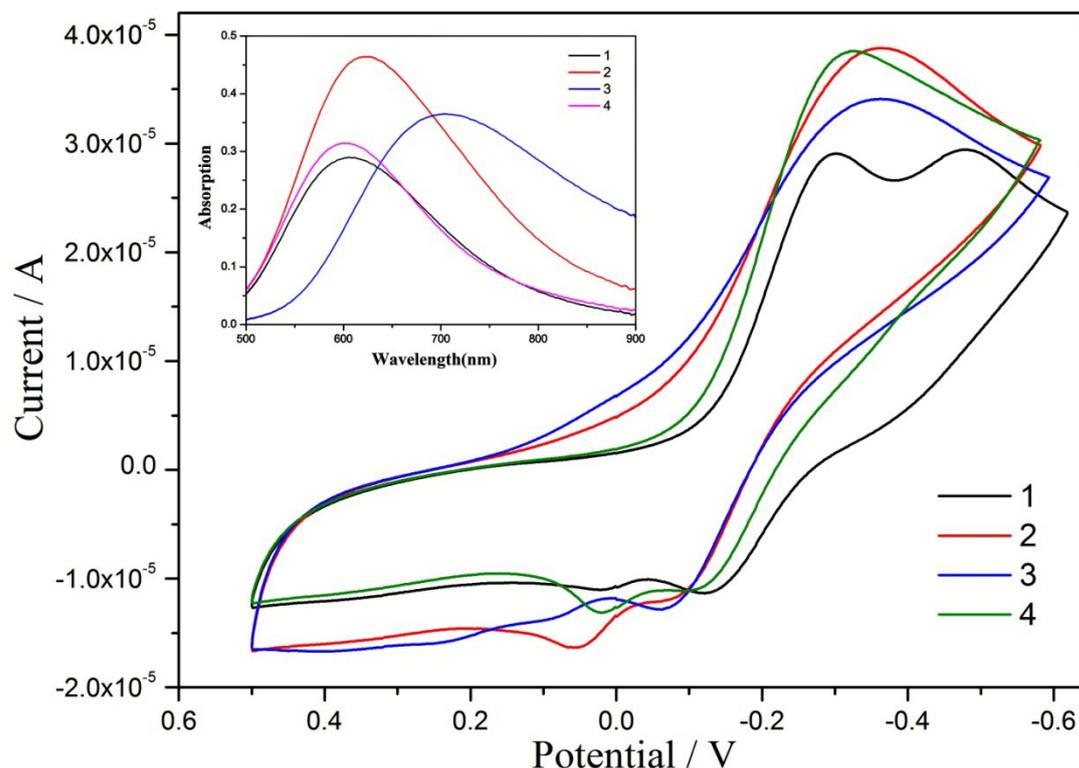


Fig. 7 The cyclic voltammety (CV) curves of the two complexes (0.1M KCl was used as a supporting electrolyte; 1.25×10^{-3} M aqueous solutions of these complexes. The potential was scanned from -0.65 to 0.5 V with a scan rate of 50 mV s^{-1} .), and the UV-vis spectra of complexes 1-4 tested in aqua (upper-left).

Conclusions

We have synthesized four novel bipy-based copper(II) compounds [Cu(bipy)(acac)(NO₃)] (1), [Cu(bipy)(DMF)(NO₃)₂] (2), [Cu(bipy)(DMF)(NO₃)₂] (3) and [Cu(bipy)(Ala)(NO₃)] (4), and characterized by X-ray diffraction, elemental analysis, UV-vis, Photoluminescence Spectra, TEM, the energy gap and cyclic voltammety. Four compounds have three types of novel nano-structure containing with nanosheets, nano -particles and fractured nano-particles. The intensity of luminescence increased significantly when Cu^{II} is coordinated with bipy and is much higher than the free bipy molecule. Importantly, four compounds have long-lived photoluminescence and high quantum yield under air which have rarely been

researched on bivalent copper complexes. We consider that crystal stacking, π system and rigid flat structure are important for the photophysics of copper complexes. TEM, energy gap and cyclic voltammetry were introduced to prove the conclusions.

Associated content

Supporting Information for crystallographic data

The authors declare no competing financial interest.

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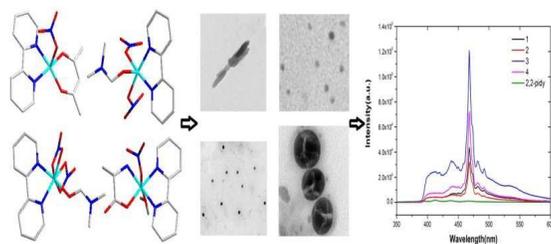
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