



Diamine ligands with multiple coplanar conjugation rings and their phosphorescent copper complexes: Synthesis, characterization, crystal structures, and photophysical property

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ABSTRACT

In this paper, we report a series of diamine ligands with multiple coplanar conjugation rings and their corresponding phosphorescent Cu(I) complexes, including their synthesis, crystal structures, photophysical properties, and electronic nature. Geometric parameters suggest that the Cu(I) center localizes at a distorted tetrahedral geometry within the Cu(I) complexes. Theoretical calculation reveals that all emissions originate from triplet metal-to-ligand-charge-transfer excited state. It is found that the free rotation of conjugation rings may compromise the coplanar plane and thus has little effect on the photophysical property of their corresponding Cu(I) complexes. But excess coplanar conjugation moiety is harmful for emissive state. The detailed quenching mechanism is investigated.

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1. Introduction

Recently, phosphorescent Cu(I) complexes, as a new class of optoelectrical material, have shown numerous applications for chemical sensors, display devices, biological probes, phototherapy, and solar-energy conversion, and thus drawn much attention due to their advantages of less toxic, low cost, redundant resource, and environmental friendliness [1,2]. In general, emission signals from charge-transfer (CT) excited states of copper(I) complexes are typically weak and short lived because the lowest energy CT state of a d^{10} system involves excitation from a metal–ligand $d\sigma^*$ orbital [3,4]. An important consequence is that the excited state typically prefers a tetragonally flattened geometry whereas the ground state usually adopts a tetrahedral-like coordination geometry appropriate for a closed-shell ion. Aside from reducing energy content, the geometric relaxation that occurs in excited states facilitates relaxation back to ground state [5,6].

Mixed-ligand systems involving triphenylphosphane seem to be promising because they exhibit long excited state lifetimes in solid state and frozen solutions [7,8]. A series of new mixed-ligand copper(I) complexes such as $[\text{Cu}(\text{N}-\text{N})(\text{POP})]^+$ [POP = bis(2-(diphenylphosphanyl)phenyl) ether] which are superior emitters have been synthesized. It is found that the exciplex quenching is relatively inefficient for the CT excited state in this POP system. In addition, introduction of sterically blocking ligands can impede geometric relaxation as well as solvent attack [9]. Here, steric effect cooperates to effectively block the excited state close to the ground-state geometry, which has been proved by the theoretical studies finished by Feng and coworkers on $[\text{Cu}(\text{N}-\text{N})(\text{P}-\text{P})]^+$ system [10]. For a typical phosphorescent $[\text{Cu}(\text{N}-\text{N})(\text{POP})]^+$ complex, the highest occupied molecular orbital (HOMO) has predominant metal Cu d character, while, the lowest unoccupied orbital (LUMO) is essentially π^* orbital localized on the diamine ligand. The photoluminescence (PL) corresponds to the lowest triplet T_1 and is thus assigned as a character of metal-to-ligand-charge-transfer $^3\text{MLCT}$ [$d(\text{Cu}) \rightarrow \pi^*(\text{diamine ligand})$]. Zhang et al. report that the photophysical properties of $[\text{Cu}(\text{N}-\text{N})(\text{POP})]\text{BF}_4$ complexes are usually sensitive towards both ligand structures and environment surroundings [11].

In this paper, we report six diamine ligands with multiple coplanar conjugation rings and their corresponding phosphorescent Cu(I) complexes, including their synthesis, crystal structures, photophysical properties, and their electronic nature. The correlation between conjugation system in diamine ligands and the photophysical characters of their corresponding Cu(I) complexes is investigated in detail.

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2. Experimental

A synthetic procedure for the six diamine ligands with multiple coplanar conjugation rings and their corresponding Cu(I) complexes is shown in Scheme 1. 1,10-Phenanthroline (Phen), Cu(BF₄)₂, bis(2-(diphenylphosphanyl)phenyl) ether (referred as POP), bromoethane (EtBr), benzaldehyde, 1-naphthaldehyde, and anthracene-9-carbaldehyde were purchased from Aldrich Chemical Co. and used without further purifications. The starting material of 1,10-phenanthroline-5,6-dione (referred as Phen-O) was synthesized according to the literature procedure [12]. All organic solvents were purified using standard procedures.

2.1. Synthesis of diamine ligands

A typical synthetic procedure for 2-phenyl-1H-imidazo[4,5-f][1,10]phenanthroline (referred as Phen-Ph), 2-(naphthalen-1-yl)-1H-imidazo[4,5-f][1,10]phenanthroline (referred as Phen-Np), and 2-(anthracen-9-yl)-1H-imidazo[4,5-f][1,10]phenanthroline (referred as Phen-An) is described as follows. The mixture of 20 mmol of Phen-O, 22 mmol of aromatic aldehyde, 15.40 g of NH₄Ac, and 30 mL of HAc was stirred at 90 °C for 4 h. Then the mixture was poured into cold water and extracted with CH₂Cl₂. After the evaporation of solvent, the crude product was further purified by recrystallization from EtOH.

Phen-Ph. ¹H NMR (CDCl₃, 300 MHz) δ [ppm]: 11.59 (s, 1H), 9.16 (m, 2H), 9.08 (m, 1H), 8.61 (m, 1H), 7.74 (m, 4H), 7.59 (m, 3H).

Phen-Np. ¹H NMR (CDCl₃, 300 MHz) δ [ppm]: 11.62 (s, 1H), 9.13 (m, 2H), 8.79 (m, 1H), 8.54 (m, 1H), 7.94 (m, 3H), 7.72 (m, 1H), 7.63 (m, 1H), 7.56 (m, 4H).

Phen-An. ¹H NMR (CDCl₃, 300 MHz) δ [ppm]: 11.65 (s, 1H), 9.26 (m, 2H), 9.16 (m, 1H), 8.72 (m, 2H), 8.15 (m, 2H), 7.78 (m, 2H), 7.57 (m, 4H), 7.47 (m, 2H).

A typical synthetic procedure for 1-ethyl-2-phenyl-1H-imidazo[4,5-f][1,10]phenanthroline (referred as Phen-Ph-Et), 1-ethyl-2-(naphthalen-1-yl)-1H-imidazo[4,5-f][1,10]phenanthroline (referred as Phen-Np-Et), and 2-(anthracen-9-yl)-1-ethyl-1H-imidazo[4,5-f][1,10]phenanthroline (referred as Phen-An-Et) is described as follows. The mixture of 20 mmol of NaH and 100 mL of anhydrous *N,N*-dimethylformamide was stirred for 1 h, then 10 mmol of Phen-Ph/Phen-Np/Phen-An and 50 mmol of EtBr were added into above solution. The mixture was heated to reflux for 24 h. After cooling, the mixture was poured into cold water and extracted with CH₂Cl₂. After the evaporation of solvent, the residue was further purified by recrystallization from hot methanol to give the desired product.

Phen-Ph-Et. ¹H NMR (CDCl₃, 300 MHz) δ [ppm]: 9.17 (m, 2H), 9.07 (m, 1H), 8.61 (m, 1H), 7.73 (m, 4H), 7.58 (m, 3H), 4.64 (q, 2H), 1.59 (t, 3H).

Phen-Np-Et. ¹H NMR (CDCl₃, 300 MHz) δ [ppm]: 9.17 (m, 2H), 9.09 (d, *J* = 4.5 Hz, 1H), 8.65 (m, 1H), 8.09 (m, 1H), 7.99 (m, 1H), 7.72 (m, 3H), 7.67 (m, 1H), 7.54 (m, 2H), 7.49 (m, 1H), 4.42 (q, 2H), 1.435 (t, 3H).

Phen-An-Et. ¹H NMR (CDCl₃, 300 MHz) δ [ppm]: 9.26 (m, 2H), 9.16 (m, 1H), 8.72 (m, 2H), 8.15 (m, 2H), 7.78 (m, 2H), 7.57 (m, 4H), 7.47 (m, 2H), 4.33 (q, 2H), 1.32 (t, 3H).

2.2. Synthesis of Cu(I) complexes

All the Cu(I) complexes were synthesized according to the classic literature procedure [7]. Their identity was confirmed by ¹H NMR, ³¹P NMR [13], elemental analysis, IR spectra, and single crystal XRD.

[Cu(Phen-Ph)(POP)]BF₄. ¹H NMR (CDCl₃, 300 MHz) δ [ppm]: 9.25 (d, *J* = 5.4 Hz, 2H), 8.55 (d, *J* = 5.5 Hz, 2H), 8.44 (d, *J* = 5.7 Hz, 2H), 7.63 (m, 2H), 7.58 (m, 2H), 7.47 (t, 1H), 7.29 (m, 2H), 7.24 (m,

4H), 7.10 (t, 12H), 6.98 (m, 8H), 6.81 (m, 2H). ³¹P NMR δ: ±1.31 (s, P(C₆H₅)₂C₆H₄). Anal. Calcd. for C₅₅H₄₀BCuF₄N₄OP₂: C, 67.05; H, 4.09; N, 5.69. Found: C, 67.13; H, 4.18; N, 5.56. IR (KBr pellet): ν 3495, 3042, 1626, 1439, 1249, 1081, 793, 731, 684, 502 cm⁻¹.

[Cu(Phen-Ph-Et)(POP)]BF₄. ¹H NMR (CDCl₃, 300 MHz) δ [ppm]: 9.11 (m, 2H), 8.71 (d, *J* = 6.0 Hz, 1H), 8.66 (d, *J* = 5.5 Hz, 1H), 7.98 (m, 1H), 7.77 (m, 2H), 7.62 (m, 4H), 7.31 (t, 2H), 7.24 (m, 4H), 7.11 (m, 10H), 6.99 (t, 10H), 6.78 (m, 2H), 4.83 (q, 2H), 1.62 (t, 3H). ³¹P NMR δ: ±1.35 (s, P(C₆H₅)₂C₆H₄). Anal. Calcd. for C₅₇H₄₄BCuF₄N₄OP₂: C, 67.56; H, 4.38; N, 5.53. Found: C, 67.42; H, 4.47; N, 5.39. IR (KBr pellet): ν 3478, 3039, 2921, 2864, 1632, 1558, 1445, 1258, 1043, 801, 734, 686, 501 cm⁻¹.

[Cu(Phen-Np)(POP)]BF₄. ¹H NMR (CDCl₃, 300 MHz) δ [ppm]: 12.67 (s, 1H), 9.28 (m, 3H), 8.57 (m, 2H), 8.34 (m, 1H), 7.90 (m, 2H), 7.65 (m, 4H), 7.52 (m, 1H), 7.30 (m, 2H), 7.23 (m, 4H), 7.11 (m, 8H), 7.07 (m, 4H), 7.02 (t, 8H), 6.81 (m, 2H). ³¹P NMR δ: ±1.33 (s, P(C₆H₅)₂C₆H₄). Anal. Calcd. for C₅₉H₄₂BCuF₄N₄OP₂: C, 68.45; H, 4.09; N, 5.41. Found: C, 68.53; H, 4.13; N, 5.63. IR (KBr pellet): ν 3514, 3059, 1558, 1422, 1251, 1074, 776, 745, 691, 514 cm⁻¹.

[Cu(Phen-Np-Et)(POP)]BF₄. ¹H NMR (CDCl₃, 300 MHz) δ [ppm]: 9.13 (m, 2H), 8.74 (d, *J* = 5.4 Hz, 2H), 8.11 (d, *J* = 6.0 Hz, 1H), 7.98 (d, *J* = 6.0 Hz, 1H), 7.62 (m, 7H), 7.15 (m, 8H), 6.99 (m, 12H), 6.29 (m, 2H), 4.59 (q, 2H), 1.45 (t, 3H). ³¹P NMR δ: ±1.35 (s, P(C₆H₅)₂C₆H₄). Anal. Calcd. for C₆₁H₄₆BCuF₄N₄OP₂: C, 68.90; H, 4.36; N, 5.27. Found: C, 68.81; H, 4.24; N, 5.35. IR (KBr pellet): ν 3041, 2985, 1587, 1554, 1425, 1248, 1048, 864, 801, 771, 721 cm⁻¹.

[Cu(Phen-An-Et)(POP)]BF₄. ¹H NMR (CDCl₃, 300 MHz) δ [ppm]: 9.27 (m, 1H), 9.19 (d, *J* = 6.3 Hz, 1H), 8.81 (d, *J* = 5.5 Hz, 1H), 8.76 (s, 1H), 8.68 (d, *J* = 5.5 Hz, 1H), 8.17 (d, *J* = 6.3 Hz, 2H), 8.11 (m, 1H), 7.65 (m, 1H), 7.55 (m, 2H), 7.48 (m, 4H), 7.32 (m, 6H), 7.17 (m, 8H), 7.09 (d, *J* = 6.3 Hz, 2H), 7.02 (t, 10H), 6.82 (m, 2H), 4.47 (q, 2H), 1.35 (t, 3H). ³¹P NMR δ: ±1.36 (s, P(C₆H₅)₂C₆H₄). Anal. Calcd. for C₆₅H₄₈BCuF₄N₄OP₂: C, 70.12; H, 4.35; N, 5.03. Found: C, 70.24; H, 4.43; N, 5.14. IR (KBr pellet): ν 3047, 2942, 2867, 1616, 1554, 1436, 1251, 1059, 813, 729, 694, 514 cm⁻¹.

2.3. Methods and measurements

Density functional theory (DFT) and singlet excitation calculations using time-dependent density functional theory (TD-DFT) were performed on the Cu(I) complexes at RB3PW91/SBKJC level. The initial geometries were obtained from their single crystal structures or simulated by MOPAC 2009 using PM6 semiempirical calculation. All computations were finished by GAMESS and MOPAC 2009 software package.

The IR spectra were recorded using a Magna560 FT-IR spectrophotometer. Excited state lifetimes were obtained with a 355 nm light generated from the third-harmonic-generator pump, using pulsed Nd:YAG laser as the excitation source. The Nd:YAG laser possesses a line width of 1.0 cm⁻¹, pulse duration of 10 ns, and repetition frequency of 10 Hz. A Rhodamine 6G dye pumped by the same Nd:YAG laser was used as the frequency-selective excitation source. All PL spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. The emission quantum yields were measured according to the literature procedure [11]. UV-vis absorption spectra were recorded using a Shimadzu UV-3101PC spectrophotometer. ¹H and ³¹P NMR spectra were obtained with the use of a Varian INOVA 300 spectrometer. Elemental analysis was performed on a Carlo Erba 1106 elemental analyzer. Single crystals data were collected on a Siemens P4 single-crystal X-ray diffractometer with a Smart CCD-1000 detector and graphite-monochromated Mo Kα radiation, operating at 50 kV and 30 A at 298 K. All hydrogen atoms were calculated. All data were recorded using single crystal samples in the air at room temperature without being specified.

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