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# Synthesis, crystal structure, and conjugation properties of phenanthroline copper phosphine complexes

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#### 1. Introduction

The mixed-ligand metal complexes with diimines were of current interest for a wide variety of potential chemical and material applications, including electroluminescence for organic light emitting diode (OLED) [1], water splitting catalyst [2], luminescence quenching material [3], strong solid luminescence material [4], functional metal complexes [5], catalyst for organic synthesis [6], magnetic materials [7], electron transfer regent [8], and light induced hydrogen production [9].

Among these complexes, copper-based complexes are draw attention due to the low cost advantage [4]. However the emission signals from charge-transfer (CT) excited states of copper(I) complexes are typically weak and short-lived due to the lowest energy CT state of a d<sup>10</sup> system involves excitation from a metal–ligand d orbital [3]. The mixed-ligand copper systems including phosphine, however, looks promising because they exhibit strong luminescence with long lifetimes in the solid or frozen solution state [4]. This stimulated us to prepare phen ligands with unique substitution patterns. The literatures revealed mostly the 2,9-position substituted phen, but the 4 or 7 position substituted phen were scarcely reported.

#### ABSTRACT

Facial synthetic method of 4,7-position conjugation extended phenanthrolines and X-ray structure of copper phosphine phenanthroline complexe were reported. The crystal structures showed  $\pi$ -stacking and hydrogen bonding, and a small torsional angle between phen and phenylacetylene. These complexes exhibited strong conjugation dependant MLCT luminescence. The electronic and fluorescence spectra displayed a gradual red shift of the MLCT band as the conjugation increased. The presence of the phenyl groups reduced the energy of the  $\pi^*$  state in the d- $\pi^*$  MLCT transition, allowing for the red shift. The electron-donating tri-isopropylsilyl (TIPS) groups on the ethynyl moiety increased the energy of the MLCT charge vector, allowing for the blue shift at the luminescence.

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Previously, one group made 4,4'-diethynylbipyridine, but the analogous substituted phen using the same reaction conditions could not give any desired products [10]. Another group success-fully made 4,7-diphenylethynyl-3,8-dihexylphen [11]. The hexyl groups were added to the phen to enhance the solubility, but this method could not make the simple 4,7-diacetylide phen. Very recently, one group synthesized 4,7-diethynyl phen using 4,7-dicarbaldehydehyde phen [12]. But this precursor 4,7-dicarbaldehydehyde phen is too expensive to become a largely applicable materials.

We devised the facial synthetic method of conjugated 4.7 position for phen ligands by simple modified Sonogashira reaction, and we prepared copper phosphine phenanthroline complexes to study the conjugation varible luminescnece properties followed by structural confirmation with exact X-ray crystallography.

### 2. Experimental and results

Trial with 10 mol% of copper iodide co-catalyst and check the Pd coupling reaction resulted in less than 30% yield. We found that the reaction yield dramatically enhanced when we used a copper complexed phen as a reactant. We envisaged that the copper (I) iodide was first chelated to the nitrogen atoms on the phen, resulting in a bis Cu(I) structure with changing the color immediately dark red. The synthetic procedure was shown in Scheme 1. The chemicals 4,7-dichloro phen [13], triisopropylsilyl acetylene, palladium



Note



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Scheme 1. Synthesis of conjugation extended phen and copper phosphine complexes.

catalyst (5 mol%), copper iodide (60 mol%), and triethylamine (2 eq.) were suspended in benzene. This suspension was refluxed 72 h in an argon environment. After the reaction, the copper ion was removed by potassium cyanide solution.

The copper phosphine complexes were synthesized by simple stirring with copper phosphine tetrafluoroborate in ether solution. The quality X-ray crystal were obtained via slow evaporation of methanol solution. The X-ray structures of Cu(I) triphenylphosphine complex containing 4,7-disubstituted phenylethynyl substituent was shown in Fig. 1. The phenanthroline molecule was planar due to the extended  $\pi$ -conjugation, but the large torsional angle (75°) between the phenylethynyl group and the phenanthroline was due to the packing force in the crystal lattice. It should be noted that the triphenylphosphine ligand does not participate in the  $\pi$  stacking in the unit cell packing.

The coordination environment around the copper atom was pseudo-tetrahedral (Fig. 2), which was the expected geometry for the copper(I) oxidation state. The nitrogen-copper bond length was 2.1 Å and the phosphorus-copper bond length was 2.3 Å. The bond angle for N–Cu–N was 80° and the bond angle for P–Cu–P was 122°. The BF<sub>4</sub>-centered hydrogen bonding was complex. Bonding between fifteen different hydrogen centers occured. The BF<sub>4</sub> was connected via hydrogen bonding to 3 phenylacetylenes, 3 triphenylphosphines, 1 phenanthroline, and 1 methanol. It was notable that the hydrogen bond length between the methanol and the BF<sub>4</sub> was very short (2.0 and 2.2 Å), indicating that the BF<sub>4</sub> hydrogen bonding was very strong.

Fig. 3 showed the UV–Vis and photoluminescence spectra for all the 2,9-dimethylsubstituted Cu(I) complexes. The spectra showed

visible absorption bands at 360–410 nm due to a metal-to-ligand charge transfer (MLCT) transition. This displayed a gradual red shift as the conjugation increases. The presence of the electron-withdrawing (in a  $\pi$  sense) phenyl groups reduced the energy of the  $\pi^*$  state in the d– $\pi^*$  MLCT transition. On the other hand, the presence of the electron-donating triisopropylsilyl (TIPS) groups on the ethynyl moiety increased the energy of the MLCT charge vector.

The phenylethynyl-substituted phenanthroline showed two MLCT bands. This might be due to the presence of additional  $\pi$ -conjugation. Alternatively, it was described by previous study that the two energy states stem from a staggered or eclipsed conformation between the phenyl ethynyl and the phenanthroline ring [12].

Fig. 3b showed the uncorrected solution-based emission for all the 2,9 dimethyl substituted phen Cu(I) complexes. Substitution at the 2 and 9 positions protected the Cu(I) metal center from Lewis base solvents, which leaded vibration deactivation of the excited state [14,15].

Table 1 indicated photophysical data for copper complexes. The quantum yields and life times were increased compared to dmp compound. This means extended conjugation enhance the lumines-cence properties. A gradual red shift occured in the emission maximum as the ligand conjugation was increased. The 4,7-diethynyl-substituted Cu(I) complex was red-shifted by about 45 nm relative to the dmp complex. The TIPS ethynylphen complex was slightly blue-shifted (by about 3 nm) from the 4,7-diethynyl substituted complex. This might be due to the electron-donating properties of TIPS. The phenylethynyl-substituted complex was again red-shifted (by about 12 nm, based on the lower energy transition) than the



Fig. 1. X-ray structures of compound 9, (a) asymmetric unit, (b) unit cell contents.

4,7-diethynyl substituted compound. The conjugation in this case was extended by the phenyl group. The blue-shifted peak at 580 nm was perhaps due to an eclipsed form between the phenyl-ethynyl and the phenanthroline ring caused by excitation into the  $\pi^*$  manifold of the phenanthroline system, leading to possible rotation about the ethynyl group (i.e., a TICT state) [16].

#### 3. Conclusion

In summary, we developed efficient coupling of 4,7-position of phenanthrolines by modifying the amount of copper iodide used in the coupling reaction. The copper phosphine phenanthroline complexes were prepared and these showed strong luminescence. The crystal structures indicated the presence of  $\pi$ -stacking and hydrogen bonding as a means to facilitate crystal growth, and a small torsional angle for the phenyl groups when they were attached. The conjugation-extended phenanthrolines were planar in shape for an extended  $\pi$ -conjugation and this planarity allowed for the  $\pi$ -stacked network. The small torsional angles of the phenanthrolines were due to both hydrogen bonding and crystal packing forces. The Cu(I) complexes exhibited a distinctive MLCT (metalto-ligand charge transfer) absorption band. The UV–VIS spectra





**Fig. 2.** X-ray structures of compound 9, (a) copper centered coordination environment, (b)  $BF_4$  centered hydrogen bonding.

displayed a gradual red shift of the MLCT band as the conjugation increased. The presence of the phenyl groups reduced the energy of the  $\pi^*$  state in the d- $\pi^*$  MLCT transition, allowing for the red shift. On the other hand, the presence of the electron-donating triisopropylsilyl (TIPS) groups on the ethynyl moiety increased the energy of the MLCT charge vector.

#### 4. Experimental section

Experimental Details. 0.30 g (1.2 mmol) of 4,7-dichloro-1,10phenanthroline, 0.27 g (2.2 eq.) of phenylacetylene, 0.05 g(0.05 eq.) of (dppf)PdCl<sub>2n</sub>·CH<sub>2</sub>Cl<sub>2</sub>, 0.24 g (2 eq.) of triethylamine, and 0.14 g (0.6 eq.) of copper iodide were suspended in 10 mL of benzene. This suspension was refluxed for 72 h under argon. 10 mL of a 10% aqueous KCN solution and 10 mL dichloromethane were then added and the resulting mixture was stirred for 30 min at room temperature. The organic layer was extracted with 50 mL of dichloromethane twice and washed with water three times. The solvent was then evaporated and the solid was purified by alumina column chromatography (dichloromethane and gradient with methanol; the middle of the three bands is the desired product)



**Fig. 3.** (a) UV spectra of copper phen phosphine complexed compounds  $(10^{-5}M \text{ in dichloromethane})$ ; (b) PL spectra of copper phen phosphine complexed compounds (excited at 400 nm,  $10^{-5}$  M in dichloromethane).

Table 1Photophysical data for copper complexes

$\lambda_{\max}$ (ADS), nm	$\lambda_{\max}$ (Em) (nm)	$\Phi^{a}$	$\tau^{\mathbf{b}}(\mu s)$
365	540	0.0014	0.33
395	588	0.0025	0.48
398	560	0.0019	0.43
390	585	0.0029	0.52
	365 395 398 390	365         540           395         588           398         560           390         585	365         540         0.0014           395         588         0.0025           398         560         0.0019           390         585         0.0029

<sup>a</sup> Error ±10%.

<sup>b</sup> Fitted by single exponential, measured in argon bubbled dichloromethane at room temperature. Emission maxima and yields were measured by excitation at 400 nm. Lifetimes were determined by pulsed excitation at 400 nm.

to obtain an ivory solid (compound 1, 0.36 g, 78%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 9.18(d, *J* = 4.5 Hz, 2H), 8.48(s, 2H), 7.80(d, *J* = 4.5 Hz, 2H), 7.70(m, 4H), 7.45(m, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 149.83, 146.27, 131.98, 129.96, 129.51, 128.64, 128.37, 125.47, 125.02, 122.10, 99.21, 85.04. MS: 380.6(M, 100%).

Ten milligram (0.018 mmol) of compound 1 and 27 mg (1.2 eq.) of Cu(PPh<sub>3</sub>)<sub>4</sub>BF<sub>4</sub> (previously prepared by refluxing 4:1 M equivalents of triphenylphosphine and one mole equivalent of CuBF4 in ethanol for eight hours, followed by filtration and washing with cold ethanol and ether) 16 were suspended in 20 mL of an ether/ ethanol (4:1 v/v) solution. The suspension was stirred overnight at room temperature. The filtrate solution was evaporated and purified by alumina column chromatography (dichloromethane with a methanol gradient; the third of the four bands is the desired product) to obtain a viscous liquid (compound 9, 15 mg, 67%). Ele-

mental Analysis:  $C_{70}H_{78}BCuF_4N_2P_2Si_2$ , calc. C 69.15; H 6.47; obs. C 69.66; H 6.02. High resolutions MS(ESI): M-BF<sub>4</sub> ( $C_{64}H_{46}CuN_2P_2$ , calc. 967.2532, obs 967.2412)

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.09.028.

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