

## New luminescent copper(I) complexes with extended $\pi$ -conjugation

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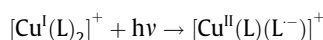
### ABSTRACT

While copper(I)-bis(diimine) complexes  $[\text{Cu}^{\text{I}}(\text{L})_2]^+$  are considered as potent substitutes for  $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ , they exhibit low molar extinction coefficients with respect to ruthenium parent analogues. One interesting possibility to improve the light collection ability of  $[\text{Cu}^{\text{I}}(\text{L})_2]^+$  consists in increasing the length of the Cu-L dipole. In order to achieve this goal, we propose in this contribution to fuse aromatic rings onto the 2,9-di-*n*-butyl-1,10-phenanthroline core and examine how the properties of the corresponding copper(I) complexes are impacted. Electrochemical, absorption and emission properties are assessed; rewardingly, the envisioned approach was successful since extinction coefficients above  $10,000 \text{ M}^{-1} \cdot \text{cm}^{-1}$  were measured. All copper(I) complexes remain photoluminescent, with emission maxima greatly varying from 725 to 815 nm, strongly affected by the molecular structures. A rationale to explain the variations of the emission quantum yields is proposed.

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### 1. Introduction

Copper(I) complexes  $[\text{Cu}^{\text{I}}(\text{L})_2]^+$  where L is a chelating diimine ligand such as 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) have attracted considerable attention since McMillins' breakthrough in 1980 [1], revealing that those molecular species can feature near IR (NIR) photoluminescence if the ligands L are sterically challenged in  $\alpha$  of the chelating nitrogen atoms. There has been since an extensive work on the impact of bulky substituents around the copper(I) coordination sphere, leading to an overall understanding of the photo-induced processes within such copper complexes [2–17]. Briefly,  $[\text{Cu}^{\text{I}}(\text{L})_2]^+$  complexes undergo an internal charge transfer upon MLCT excitation following the equation below:



When the complex is excited, the copper(I) ion is transiently oxidized into copper(II) while an electron from the  $3d_{\text{Cu}}$  orbitals is transferred onto a ligand centred  $\pi^*$  orbital. Given that copper (I) and copper(II) ions display different preferred geometries (tetrahedral and square planar respectively), the excitation of those complexes in their metal-to-ligand-charge-transfer (MLCT) states entails a dramatic flattening of the structure which is responsible

for quick, radiationless deactivation of the excited state [5,11,18]. This deactivation is due to the strong stabilization of the lowest excited states during flattening favouring non radiative decay by virtue of the gap law. Additionally, the distortion of the complex frees space above the copper(II) ion allowing the latter to be attacked by any kind of nucleophile to reach the stable five-coordinate square planar pyramidal geometry; solvent molecules play an important role in this process [6,19,20].

A collection of copper(I)-bis(diimine) luminescent complexes, both homoleptic ( $[\text{Cu}(\text{L})_2]^+$ ) and heteroleptic ( $[\text{Cu}(\text{L})(\text{L}')^+]$ ) [21,22] exhibiting interesting properties in their excited states have thus been isolated and studied in various domains (dye sensitized solar cells [23–31], photo-induced water splitting [32], organic photochemistry [32–37], supramolecular photo-induced electron transfer) [38–46]. Those complexes are particularly well-suited for photo-reductive mechanisms since their photo-reductive power is higher than the champion photosensitizer  $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$  [47].

However, bearing in mind that the ultimate aim is to replace the latter by copper(I)-bis(diimine) complexes, there remain a few issues to address. In particular,  $[\text{Cu}^{\text{I}}(\text{L})_2]^+$  complexes are weak emitters, kinetically labile and endowed with small extinction coefficients. Great progresses have been made with copper complexes  $[\text{Cu}^{\text{I}}(\text{L})_2]^+$  where L is *tert*-butyl [7,13], *sec*-butyl [4,9] or *iso*-propyl [10] 2,9-substituted phen. These complexes, however, remain weak absorbers with extinction coefficients ranging between 3100 and  $7500 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$  [7]. Incidentally, grafting

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methyl groups in positions 3, 4, 7 and 8 on the already 2,9-disubstituted phen core was very beneficial from all points of view, since the emission lifetime was greatly improved and the extinction coefficient too (ca.  $10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ) [9,10]. The inductive effects of the methyl groups tend to increase the dipole length and this materializes into a more intense MLCT band [6,48].

A similar approach consists in using chromogenic diimine ligands [29,49]: by increasing the extent of  $\pi$  conjugation over the phen core and tethering electron donating groups, the dipole length is increased and additional ligand centred transitions can overlay with the MLCT band. Very high extinction coefficients have been obtained using this approach, but loss of the MLCT excited state properties were experienced in a few cases because the absorption features of the ligand override those of the copper-diimine chromophore.

To sum up, increasing the extent of  $\pi$  delocalization is a good strategy to improve the extinction coefficients of the MLCT and we propose in this contribution to apply the latter by fusing aromatic rings to the phenanthroline ligand. Several examples can be found in the literature where concatenation of extra aromatic rings lead to improved  $\epsilon$ , the epitome of all being famous dipyrrodo [3,2-a:2',3'-c]phenazine ligand, best known as dppz [50,51]. The latter ligand results from the fusion of the phenazine electron acceptor with a bipyridine cavity. This ligand and complexes thereof have been abundantly studied owing to their intriguing electronic properties [52–55] and tested in many different fields such as cytotoxic agents design [56–58], photo-induced electron transfer platforms [59,60], catalysis [61–64] and of course DNA probes [65]. Although the phenazine spacer is known to be electronically decoupled from the dipyrrodo coordination sphere [52,66], the extinction coefficient of e.g.  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{dppz})]^{2+}$  is significantly higher than parent  $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$  [60], probably thanks to the increased dipole length. Fusion of one additional benzene onto dppz yielded yet again improved extinction coefficients, to a lesser extent though [67]. Importantly, the ligand centred absorption features of  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{dppz})]^{2+}$  stand below the  $\text{Ru} \rightarrow \text{L}$  MLCT and do not interfere with the MLCT transition. Thus, dppz seems a good candidate to improve copper(I) complexes light harvesting capacity, since  $[\text{Cu}^{\text{I}}(\text{L})_2]^+$  complexes exhibit absorption profiles which are surprisingly similar to those of  $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ . The latter was incidentally employed in the field of diphosphine-diimine [64] and diimine<sup>A</sup>-diimine<sup>B</sup> [68], heteroleptic copper(I) complexes and afforded indeed better absorbing complexes than their associated references. Besides, a little studied ligand, yet closely related to dppz and showing increased  $\pi$  conjugation too is ligand np (Fig. 1), consisting of an anthracene spacer fused to a bipyridine cavity [69–71]. Although np and dppz are very look-alike, their electronic properties are quite different. In particular, the anthracene moiety is a far less potent electron acceptor than phenazine, and this translates into very different electrochemical behaviors. Importantly,  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{np})]^{2+}$  features an improved MLCT extinction coefficient compared to  $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$  [69].

Dppz and np ligands are thus our primary targets for this contribution. They however cannot be used as such and it is mandatory to tether bulky substituents in  $\alpha$  of the chelating nitrogen atoms of dppz and np to design room temperature, solution phase luminescent copper(I) complexes. Interestingly, Guo et al. have published a theoretical article where heteroleptic copper(I) complexes bearing methyl-substituted dppz and np have been reported for future use in dye sensitized solar cells [70]. Critically, the complexes were praised for their enhanced MLCT oscillator strengths, justifying the interest in preparing these species. We thus embarked in the synthesis of ligands **L1** and **L3** (Fig. 1), consisting respectively of dppz and np molecules encumbered with two *n*butyl chains on both sides of the diimine chelate. On our way, we isolated ligand **L2**, displaying a potentially high dipole

length too, and decided to explore the ground and excited states properties of the corresponding copper(I) complex.

In this article, we evidence the fusing of aromatic rings onto phenanthroline as a good approach to increase the extinction coefficients of related copper(I) complexes without sacrificing to too large an extent the luminescence quantum yields.

## 2. Experimental section

Chemicals were purchased from Sigma–Aldrich or Alfa Aesar and used as received. Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with Merck 5735 Kieselgel 60F<sub>254</sub>. Column chromatography was carried out either with Merck 5735 Kieselgel 60F (0.040–0.063 mm mesh). <sup>1</sup>H spectra were recorded on an AVANCE 300 UltraShield BRUKER. Chemical shifts for <sup>1</sup>H NMR spectra are referenced relative to residual protium in the deuterated solvent (CDCl<sub>3</sub>  $\delta = 7.26$  ppm). NMR spectra were recorded at room temperature, chemical shifts are written in ppm and coupling constants in Hz. High-resolution mass (HR-MS) spectra were obtained either by electrospray ionization coupled with high resolution ion trap orbitrap (LTQ-Orbitrap, Thermo-Fisher Scientific,) or by MALDI-TOF-TOF (Autoflex III, Bruker), working in ion-positive or ion-negative mode. Electrochemical measurements were made under an argon atmosphere in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>. Cyclic voltammetry experiments were performed by using an Autolab PGSTAT 302 N potentiostat/galvanostat. A standard three-electrode electrochemical cell was used. Potentials were referenced to a saturated calomel electrode (SCE) as internal reference. All potentials are quoted relative to SCE. The working electrode was a glassy carbon disk and the auxiliary electrode was a Pt wire. In all the experiments the scan rate was 100 mV·s<sup>-1</sup>. UV–Vis absorption spectra were recorded on a UV-2401PC Shimadzu, using 1 cm path length cells. Emission spectra were recorded on a Fluoromax-4 Horiba Jobin Yvon spectrofluorimeter (1 cm quartz cells). Luminescence decays were recorded with a DELTAFLUX time correlated single photon counting system (HORIBA) on degassed dichloromethane solutions.

All calculations were performed with ADF 2013 package [72] at the DFT level of theory with B3LYP functional [73]. The atoms were described by the all electrons Slater-type TZP basis set [74]. Scalar relativistic corrections were included through the ZORA Hamiltonian [75]. Solvent corrections for dichloromethane were introduced using PCM model [76]. The structures were fully optimized and the absorption spectra were computed by means of TD-DFT [77] on these structures. For the spectra, only the non-equilibrium response of the solvent were included and Tamm–Dancoff [78] corrections introduced. In all the calculations, the butyl chains were replaced by methyl.

2,9-di-*n*butyl-1,10-phenanthroline [2], 2,9-di-*n*butyl-1,10-phenanthroline-5,6-dione [79] (**1**) and complex **C4** [80] were synthesized according to previously published literature procedures.

### 2.1. Ligand 3,6-di-*n*butyl-dipyrido[3,2-a:2',3'-c]phenazine **L1**

0.12 mmol of **1** (40 mg) and 0.12 mmol of 1,2-diaminobenzene **2** (13.4 mg) were dissolved in ethanol (20 mL) and heated to reflux for 8 h. The solvent was then evaporated and dissolved in dichloromethane (10 mL). The latter solution was washed three times with aqueous 1 M HCl (100 mL  $\times$  2), then pure water. The organic phase was subsequently dried on sodium sulphate, filtered and evaporated to dryness, affording a pale yellow powder.

Yield: 38 mg (80%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 9.56$  (2H, d,  $J = 8.1$  Hz), 8.34 (2H, dd,  $J = 3.3$  Hz,  $J = 6.6$  Hz), 7.90, (2H, dd,  $J = 3.3$  Hz,  $J = 6.6$  Hz), 7.68 (2H, d,  $J = 8.4$  Hz), 3.28 (4H, m), 1.96 (4H, m), 1.55 (4H, m), 1.03 (6H, t,  $J = 7.5$  Hz) ppm. HRMS

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