New luminescent copper(I) complexes with extended π-conjugation

Kévin Soulis a, Christophe Gourlaouen b, Chantal Daniel b, Alessia Quatela c, Fabrice Odobel a, Errol Blart a, Yann Pellegrin a,*

aUniversité UNAM, CNRS, Chimie Et Interdisciplinarité: Synthèse, Analyse, Modélisation (CEISAM), UMR 6230, 2, rue de la Houssinière – BP 92208, 44322 Nantes Cedex 3, France
bLaboratoire de Chimie Quantique Institut de Chimie UMR 7177 CNRS-Université de Strasbourg, 4, Rue Blaise Pascal CS 90032, F-67081 Strasbourg Cedex, France
*cHORIBA France SAS, Avenue de la Vauve – Passage Jobin Yvon CS 45002, 91120 Palaiseau, France

1. Introduction

Copper(I) complexes \([\text{Cu}^\text{I}(\text{L})_2]^+\) where \(\text{L}\) 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 \(\text{L}\) are sterically oxidized into copper(II) while an electron from the 3d \(\text{Cu}\) orbitals is transferred onto a ligand centred 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 homoepotic ([Cu(L) 2] +) and heteroleptic ([Cu(L)(L′)]) 2+ 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, [Cu(L) 2] + complexes are weak emitters, kinetically labile and endowed with small extinction coefficients. Great progresses have been made with copper complexes [Cu(L) 2] + where \(\text{L}\) 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 L.mol⁻¹.cm⁻¹ [7]. Incidentally, grafting...
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 L mol⁻¹ 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 π 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 π 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 σ, the epimere of all being famous dipyrido[3,2-a:2,3-c]phenazine, best known as dpzp [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 dipyrido coordination sphere [52,66], the extinction coefficient of e.g. [Ru(bpy)₂(dpzp)]²⁺ is significantly higher than parent [Ru(bpy)₂]²⁺ [60], probably thanks to the increased dipole length. Fusion of one additional benzene onto dpzp yielded yet again improved extinction coefficients, to a lesser extent though [67]. Importantly, the ligand centred absorption features of [Ru(bpy)₂(dpzp)]²⁺ stand below the Ru → MLCT and do not interfere with the MLCT transition. Thus, dpzp seems a good candidate to improve copper(I) complexes light harvesting capacity, since [Cu(L)₂]⁺ complexes exhibit absorption profiles which are surprisingly similar to those of [Ru(bpy)₂]²⁺. The latter was incidentally employed in the field of diphosphine-diimine [64] and diimine-D-diimine [68], heteroleptic copper(I) complexes and afforded indeed better absorbing complexes than their associated references. Besides, a little studied ligand, yet closely related to dpzp and showing increased π conjugation too is ligand np (Fig. 1), consisting of an anthracene spacer fused to a bipyridine cavity [69–71]. Although np and dpzp 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. Inorganic chemical measurements were made under an argon atmosphere in CH₂Cl₂ with 0.1 M Bu₄NPF₆. 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⁻¹. 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 DELTAFLEX 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. 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 60F₂₅₄. Column chromatography was carried out either with Merck 5735 Kieselgel 60F (0.040–0.063 mm mesh).¹H spectra were recorded on an AVANCE 300 UltraShield Bruker. Chemical shifts for ¹H NMR spectra are referenced relative to residual protium in the deuterated solvent (CDCl₃ δ = 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 CH₂Cl₂ with 0.1 M Bu₄NPF₆. Cyclic voltammetry experiments were performed 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⁻¹. 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 DELTAFLEX time correlated single photon counting system (HORIBA) on degassed dichloromethane solutions.

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2.1. Ligand 3,6-di-n-butyldipyrido[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 × 2), then pure water. The organic phase was subsequently dried on sodium sulphate, filtered and evaporated to dryness, affording a pale yellow powder.

Yield: 38mg (80%).¹H NMR (300 MHz, CDCl₃, 25°C): δ = 9.56 (2H, dd, 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