Research paper

Heteroleptic Cu(I) complexes containing polypyridyl ligands and triphenylphosphine: Synthesis, structure, photophysical properties, DFT studies and applications in co-sensitized solar cells

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A B S T R A C T

The synthesis and characterization by IR and 1H NMR spectroscopy, ESI-TOF mass spectrometry, cyclic voltammetry, single-crystal X-ray diffraction and thermal analysis of two novel heteroleptic Cu(I) complexes of general composition [Cu(I)(L1)(PPh3)2]PF6•C10.75CHCl3(1) and [Cu(I)(L2)(PPh3)2]PF6•C12.5CHCl3(2) is reported. Both complexes show interesting photophysical properties, which were studied experimentally in solution and in the solid state by UV–Vis and fluorescence spectroscopy, and theoretically by using TD-DFT calculations. Additionally, their performance as co-sensitizer in DSSC was evaluated.

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1. Introduction

The supply of secure, clean, sustainable energy is arguably the most important scientific and technical challenge facing humanity in the 21st century. As solar energy is the only renewable source with the capacity to supply the world’s increasing energy needs, low-cost and efficient conversion of solar energy has emerged as a crucial goal [1]. The enormous power that the Sun continuously delivers to Earth, 1.2 × 1017 terawatts, dwarfs every other energy source, renewable or non-renewable [2]. In this field, the dye-sensitized electrochemical photovoltaic system has become a validated and credible competitor to solid-state junction devices for the conversion of solar energy into electricity [3]. The synthesis of novel transition metal complexes to be used as sensitizers in dye-sensitized solar cell (DSSC) is of great interest [4–8]. In this context, ruthenium(II), osmium(II), and rhenium(II) complexes have received special attention because of their fascinating properties and potential applications. At the same time, the strong appealing possibility of using costless and nontoxic metals such as copper or zinc, as substitutes of the above-mentioned more expensive heavy metal ions, has stimulated further research in this field [9,10].

To develop easily accessible and sustainable materials for organic light emitting diodes (OLEDs) [11,12] and DSSCs [13–15], the photophysical and electrochemical properties of Cu(I) complexes have received increasing attention in recent years due to their high relative abundance, low cost, and environmentally friendly features [16].

Copper(I)-based complexes of the type [Cu(N^N)(P^P)]+ or [Cu(P^P)2]+ (N^N and P^P = diimine and diphosphine chelating ligands) are promising contenders for applications in OLEDs due to their excellent emissive properties. Some of these complexes, particularly those with bulky PPh3 and diimine ligands, are found to be excellent emitters as their charge-transfer (CT) excited states are not quenched by solvent-induced exciplex [16,17]. Also, the sterically demanding ligands can impede geometric relaxation from tetrahedral to square planar in the excited state [18].

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Since the discovery by Sauvage and coworkers [19] of Cu(I) polypyrrolid complexes of the type [Cu(N^N)Cl] as dyes with large band-gap semiconductors (TiO₂ and ZnO) for DSSCs, significant progress has been made in the development of homoleptic [Cu(N^N)]⁺ and heteroleptic [Cu(N^N)Cl(N^N)]⁺ or [Cu(N^N)(P^P)]⁺ sensitizers (N^N = dimine chelating ligand; P^P = diphosphines chelating ligand) in dye sensitized solar cells [20–21].

We are interested in exploring the coordination chemistry of Cu(I) complexes with phosphines and polypyrridine ligands because of their promising photoluminescence properties and intriguing coordination architectures.

In previous studies regarding the coordination behavior of polypyrrolid ligands, we analyzed the influence of non-covalent interactions on the supramolecular structure of metal complexes [22–26]. In this contribution, we report on two new Cu(I) complexes of general composition [Cu(L1)][PPh₃]₂PF₆ (1) and [Cu(L2)]PF₆ (2) with triphenylphosphine (PPh₃) and either cis-(±)-2,4,5-tris(2-pyridyl)imidazoline (L1) or 2,4,6-tris(2-pyridyl)triazine (L2) as ligands, for which we explored their photophysical properties, both experimentally and theoretically, and electrochemical properties. In addition, their performance as co-sensitizer in DSSC has been evaluated.

2. Experimental

2.1. Materials and methods

All chemicals including ligand L2 and dye N719 ([Di-tetrabutyllammonium cis-bis (isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II)]) were purchased from Aldrich and used as received without further purification. The synthesis and spectroscopic data for L1 have been reported elsewhere [27]. The metal complexes were prepared under normal environment conditions. Infrared spectra (KBr) were measured on a Bruker Alpha Tensor 27 spectrophotometer using KBr pellets in the 4000–500 cm⁻¹ region. Thermogravimetric analyses were performed under nitrogen (50 mL min⁻¹) in the temperature range of 50–800 °C (10 °C min⁻¹) using a TA SDT Q600 apparatus. ¹H NMR spectra were recorded at 400 MHz with a BrukerAvance III spectrometer at 30 °C unless otherwise specified. Chemical shifts are reported in ppm and were referenced based on residual solvent resonances. High-resolution mass spectrometry (HRMS) data were obtained with a microTOF-Q III mass spectrometer using electrospray ionization in the positive mode and sodium formate as calibrant. UV–Vis absorption spectra were recorded on a Shimadzu UV-1800 UV spectrophotometer. Emission spectra in solution and in the solid state were obtained on a Perkin Elmer LS-55 fluorescence spectrophotometer. Electrochemistry was carried out using gold working and counter electrodes, and the ferrocene/ferrocenium component, the SIMU and DELU instructions implemented in the SHEXL program were used. Hydrogen-bonding interactions in the crystal lattice were calculated with the MERCURY program [31]. Figures were created with Diamond [32].

2.2. Complexes

2.2.1. [Cu(L1)][PPh₃]₂PF₆ (1)

Cu(MeCN)₄PF₆ (50 mg, 0.134 mmol) was added to a cold (ice bath) stirring solution of cis-(±)-2-(di-pyridin-2-yl)-4,5-dihydro-1H-imidazol-4-yl)pyridine (L1) (40.3 mg, 0.134 mmol) and triphenylphosphine (PPh₃) (70.2 mg, 0.268 mmol) in chloroform (3 mL) to obtain a yellow solution (see Scheme 1). The solution was stirred for 3 h at 5 °C and filtered. Yellow single-crystals were obtained by vapor diffusion of n-pentane into a solution of 1 in CHCl₃. Yield (129 mg, 85%). IR (KBr): 3638, 3429, 3054, 3014, 2960, 2872, 1585, 1519, 1435, 1335, 1303, 1259, 1220, 1183, 1154, 1095, 999, 843, 747, 696, 557 and 513 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ ppm: 7.28 (1H, d, J = 4.16), 8.23 (1H, d, J = 4.40), 8.16 (1H, d, J = 4.40), 7.20 (8H, t, J = 7.82), 7.64 (8H, t, J = 7.34), 7.24–7.10 (6H, m), 7.10 (12H, m), 6.84 (8H, m, J = 7.82), 6.84–6.77 (2H, m), 6.63 (1H, t, J = 7.34), 7.38 (5H, m, J = 7.82, 5.50 (2H, bs). HRMS (ESI-TOF) m/z: calculated for: C₄₂H₃₅CuN₅P [M–PPh₃]⁺: 626.1539, found: 626.1550.

2.2.2. [Cu(L2)]PF₆ (2)

To a stirring solution of 2,4,6-tris(2-pyridyl)triazine (L2) (41.8 mg, 0.134 mmol) and triphenylphosphine (PPh₃) (70.2 mg, 0.268 mmol) in chloroform (3 mL) over an ice bath, Cu(MeCN)₄PF₆ (50 mg, 0.134 mmol) was added to obtain a dark red solution (see Scheme 1). The mixture was stirred over a period of 3 h at 5 °C and then filtered. Red single-crystals were obtained by vapor diffusion of n-pentane into the solution of 2 in CHCl₃. Yield (85 mg, 47%). IR (KBr): 3057, 1539, 1513, 1477, 1434, 1373, 1255, 1095, 841, 764, 747, 698, 670. ¹H NMR (400 MHz, CDCl₃): δ ppm: 8.97 (3H, d, J = 8.07 Hz), 8.23–7.97 (3H, m), 7.74–7.53 (3H, m), 7.35 (9H, m, J = 7.82), 7.18 (12H, m, J = 7.34 Hz), 7.12 (12H, m, J = 7.34 Hz), 7.05–6.93 (8H, m), 7.05–6.93 (8H, m), 6.84 (8H, m, J = 7.82), 6.84–6.77 (2H, m), 6.84 (8H, m, J = 7.82), 6.84 (8H, m, J = 7.82), 6.84–6.77 (2H, m), 6.84 (8H, m, J = 7.82). HRMS (ESI-TOF) m/z: calculated for: C₃₅H₂₇CuN₅P [M–PPh₃]⁺: 637.1331, found: 637.1354.

2.3. Cell construction

Fluorine-doped tin oxide (FTO) glass plates (Solaronix TC030-8, 3 mm thickness) were cleaned in a detergent solution, deionized water and ethanol, using an ultrasonic bath for 10 min, and finishing with a bath in a UV chamber for 10 min in a peroxide solution (1%). Then, the plates were immersed in 40 mM TiCl₄ (aqueous) at 70 °C for 30 min and washed with water and ethanol. A layer was prepared on the FTO glass plates by using a doctor blade painting TiO₂ paste [33]. The electrodes were gradually heated (10 °C/min) to 370 °C for 30 min, 450 °C for 30 min and then cooled to RT. The electrodes were treated again with TiCl₄ and heated following the same procedure. After cooling, a 1 cm² surface was delimited with a blade and immersed in the dye solution for 24 h protected from light. Finally, the electrode was dried under environment conditions. FTO plates for the counter electrodes were drilled (two holes) and cleaned by the same procedure. After that, a platinum paste (Platisol T, Solaronix) was deposited by a doctor blade ethnic and heated according to the above procedure. Then, DSSCs were assembled into a sealed sandwich-type cell using a 60 μm sealing.
spacer (Meltonix 1170–60, Solaronix) and the $I^-/I_3^-$ redox couple electrolyte [34].

### 2.4. Computational details

DFT structure calculations were performed with the Gaussian09 package [35]. Minimum energy structures were calculated and confirmed through a frequency calculation (no imaginary frequencies) [36,37]. The transitions between the different orbitals were evaluated with time-dependent (TD) DFT [38,39] using the M06 hybrid-meta-GGA functional [40] combined with the 6-31G(d) basis set for atoms C, H, N and P, and the DZVP [42] basis set for the Cu atom. The effects of a solvated environment were evaluated with the integral equation formalism for the polarizable continuum model (IEF-PCM) and the implementation of the non-equilibrium solvation model [43]. The solvent considered for this analysis was ethanol.

### 3. Results and discussion

Combination of Cu(MeCN)$_4$PF$_6$ with triphenylphosphine and cis-(±)-2-(2,5-di(pyridin-2-yl)-4,5-dihydro-1H-imidazol-4-yl)pyridine (L1) or 2,4,6-tris(2-pyridyl)triazine (L2) provided Cu(I) complexes of compositions [CuI(L1)(PPh$_3$)$_2$]PF$_6$ ($\mathbf{1}$) and [CuI(L2)(PPh$_3$)$_2$]PF$_6$ 2.5CHCl$_3$ ($\mathbf{2}$). In both cases, the phosphine ligands play a crucial role in the stabilization of the molecular structures [44]. The complexes have been characterized by IR and $^1$H NMR spectroscopy, high resolution ESI-TOF mass spectrometry and single-crystal X-ray diffraction analysis. Experimental and theoretical IR spectral data of complexes $\mathbf{1}$ and $\mathbf{2}$ are listed in Tables S1 and S2, respectively, in Supplementary material.

### Table 1

Crystallographic data and collection parameters for $\mathbf{1}$ and $\mathbf{2}$. 

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[a] $\lambda_{MoK_a} = 0.71073$ Å.

[b] $I > 2\sigma(I)$.

c) $R = \sum |F_{o,l}|-|F_{c,l}|/\sum |F_{o,l}|$.

[d] All data.

[e] $R_{w} = [\sum w(F_{o}^2- F_{c}^2)^2/\sum w(F_{o}^2)]^{1/2}$.

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**Scheme 1.** Synthetic routes for complexes $\mathbf{1}$ and $\mathbf{2}$. 

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3.1. IR and NMR spectroscopic analysis

The IR spectra for compounds 1 and 2 are in good agreement with the results of the X-ray structural analyses. They show characteristic absorption bands from the skeletal vibrations of the aromatic rings in 3054–3057 cm\(^{-1}\), the C=N and C=C stretching vibrations of the pyridyl substituents appear in the range of 1580–1477 cm\(^{-1}\). In complex 1 an intense band at 3429 cm\(^{-1}\), is assigned to the stretching vibration of the N\(_A\)H group, while the absorption band in 2960 cm\(^{-1}\) is characteristic of the aliphatic C\(_A\)H stretching vibrations. The typical band for the C=N vibration of the central imidazoline ring is located at 1585 cm\(^{-1}\), confirming the presence of ligand L1 in 1 [23,26].

Fig. 1. Perspective view of the molecular structure of [Cu(L1)(PPh\(_3\))\(_2\)]\(^{+}\) in the crystal structure of compound 1. Hydrogen atoms, the counterion and the chloroform solvate molecule have been omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

Complexes 1 and 2 exhibit the P–C\(_\text{Ar}\) [45] vibration of the phosphine ligand around 1435 cm\(^{-1}\) and other band in the range of 841–843 cm\(^{-1}\) for the P–F stretching vibrations of the hexafluorophosphate counter ion.

In the \(^1\)H NMR spectrum of 1 (Fig. S1, Supplementary material), the resonances in the region 8.29–6.26 ppm are assigned to 42 aromatic hydrogens and the N\(_A\)H group of L1, implying that the ligand coordinates to the Cu(I) centre as a neutral ligand without deprotonation of the N–H bond, as revealed by X-ray crystallography (vide infra); the two aliphatic hydrogens in the imidazoline ring appear at 5.50 ppm as broad singlet(2H). The \(^1\)H NMR spectrum of 2 (Fig. S2) displays six sets of peaks in the region

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Table 2

Selected bond lengths [Å] and bond angles [°] for the description of the coordination geometries of the copper(I) atoms in compounds 1 and 2.

![Fig. 2. Perspective view of the molecular structure of [Cu(L2)(PPh\(_3\))\(_2\)]\(^{+}\) in the crystal structure of compound 2. Hydrogen atoms, the counterion and the chloroform solvate molecules have been omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.](image-url)
9.0–7.1 ppm that integrate for the 42 aromatic hydrogens in the compound (12 hydrogens in L2 and 30 hydrogens in the phosphine ligands). As revealed by the line broadening observed in $^1$H NMR spectra, both complexes undergo fluxional processes in solution.

3.2. X-ray crystallographic

Complexes 1 and 2 were also characterized by single-crystal X-ray diffraction analysis. The most relevant crystallographic data are summarized in Table 1. The molecular structures of 1 and 2 are given in Figs. 1 and 2, respectively. Selected bond lengths and bond angles are given in Table 2; the theoretical values are listed in Table S3. Hydrogen bonding geometries are listed in Tables S4 and S5 (see Supplementary material).

The crystallographic study revealed that [Cu(I)(L1)(PPh3)2]PF6·0.75CHCl3 (1) and [Cu(I)(L2)(PPh3)2]PF6·2.5CHCl3 (2) crystallized in triclinic crystal systems with space group P-1. The asymmetric unit of the complexes are composed of one copper(I) atom as metal centre, one polypyridine ligand, two triphenylphosphine molecules, one hexafluorophosphate counterion and a varying number of uncoordinated chloroform molecules (see Table 1).

The copper atoms in 1 are embedded in N$_2$P$_2$ environments, resulting from the coordination by the triphenylphosphine co-ligands and two N atoms from the neutral form of the tris-pyridine ligand, which adopted a bidentate coordination mode by bonding with one of the pyridyl substituents (N5) and one of the imidazoline nitrogen (N1). Thus, five-membered Cu—N—C—C—N chelate rings with Cu—N bond lengths in the range of 2.054(2)–2.1112(2) Å are observed. The Cu—P bond lengths are in the range of 2.2465(7) and 2.2605(7) Å and the bond angles at Cu(1) range from 79.69(8) to 117.95(6), of which the smallest value corresponds to the five-membered chelate ring formed with L1 and the largest to the angle formed with the sterically demanding triphenylphosphines. The coordination geometry is best described as distorted tetrahedral, as indicated by the $\tau_4$-value of 0.88 [46]. The geometry of complex 1 is similar to that reported previously for [Cu(pbb)(DPPMB)][BF$_4$]; pbb = 2-(2-0-pyr-dyl) benzimidazolyl benzene, DPPMB = bis-(diphenylphosphinomethyl) diphenyl borate [47].

In contrast to 1, the Cu atom in 2 is embedded in a five-coordinate Cu$_2$N$_3$ coordination polyhedron with a distorted square pyramidal coordination geometry ($\tau_5 = 0.15$) [48]. Two of the three Cu—N bonds and the Cu—P bonds have distances similar to those found for 1 (see Table 2); however, the Cu(1)—N(4) bond with a distance of 3.050(2) Å is close to the sum of the van der Waals radii (2.95 Å).

![Fig. 3. Hydrogen-bonded dimeric units in the crystal structure of 1, formed through N—H · · · F, C—H · · · F and C—H · · · N interactions. Hydrogen atoms not involved in hydrogen bonding interactions have been omitted for clarity. Symmetry operators: (i) $-x + 2, -y + 2, -z + 1$; (ii) $-x + 2, -y + 2, -z + 2$; (iii) $x, y, z + 1$; (iv) $-x + 2, -y + 1, -z + 1$.](image-url)
The existence of the interaction is clearly established by significant changes of the bond angles when compared to 1 (see Table 2). In 2, the bond angles of the CuP₂N₂ core (i.e. without considering the Cu1—N4 bond) vary from 98.13(5) to 127.59(2)°, giving a $\tau_{4}$-value of 0.75 [46], which is significantly smaller than in 1.

A close inspection of the crystal structure of 1 reveals a 3D hydrogen bonded network, in which two different dimeric units formed through N—H···F, C—H···F and C—H···N hydrogen bonding interactions between two [Cu(L1)(PPh₃)₂]⁺ cations and two PF₆⁻ counterions can be distinguished (Fig. 3a and b). The crystal structure is further stabilized by a series of additional C—H···F, C—H···N and C—H···Cl contacts between the components of the complex (Table S4).

The crystal structure of complex 2 also exhibits a 3D hydrogen bonded network based on two dimeric assemblies, which are formed by two [Cu(L2)(PPh₃)₂]⁺ cations and two PF₆⁻ counterions through a series of C—H···F interactions (Fig. 4a-b).

These units are interconnected and exhibit further contacts of the C—H···Cl, C—H···N, C—H···π, Cl···π and Cl···Cl type with the chloroform solvate molecules (Fig. 4b). The details of the supramolecular interactions are summarized in Table S5. All intermolecular distances and angles in 1 and 2 are within the range found in previously reported structures [49–52].

### 3.3. Theoretical investigations

The origin of the charge transfer between molecular orbitals is an important aspect in the study of molecular systems. In the frontier molecular orbital theory, the HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital) and related orbitals are most important for the electronic properties of chemical compounds. HOMO orbitals usually act as electron donors and LUMO orbitals as electron acceptors. The energy gap between the HOMO and the LUMO has been used to prove some properties resulting from intramolecular charge transfer (ICT) and also reflects the chemical activity of the molecule [53]. To better understand the nature of the electronic transitions, DFT calculations were performed at the M06/6-31G(d)+DZVP level of calculation [40].

The results of the TD-DFT calculations indicate six major transitions for complex 1 (Table S6 and Fig. S3), five in the UV region and one in the visible region, and five main transitions for 2 (Table S7 and Fig. S4), two in the UV region and three in the visible region.

The absorption band at $\lambda_{max}$ corresponds to the transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). In both complexes, the HOMO electron density distribution is located at the copper metal...
centre and at the phosphorus atoms, while the LUMO electron density is distributed over the ligands (Fig. 5). For 1, the energy of the highest occupied molecular orbital \( (E_{\text{HOMO}}) \) is \(-5.948 \text{ eV}\), and the energy of the lowest unoccupied molecular orbital \( (E_{\text{LUMO}}) \) is \(-1.935 \text{ eV}\). Thus, the \( \Delta E_{\text{LUMO-HOMO}} \) gap in the compound is 4.013 eV. For 2, \( E_{\text{HOMO}} \) is \(-6.268 \text{ eV}\) and \( E_{\text{LUMO}} \) is \(-2.549 \text{ eV}\) with a \( \Delta E_{\text{LUMO-HOMO}} \) gap of 3.719 eV.

### 3.4. Photophysical properties

The absorption and emission spectra of the free ligands and their respective Cu(I) complexes were measured in EtOH at room temperature. The free ligands display multiple absorption bands in the UV region (<330 nm), due to ligand-centered \( \pi-\pi^* \) transitions. \( \lambda_{\text{max}} \) for L1 is located at 246 nm \( (\varepsilon = 14,900) \) and \( \lambda_{\text{max}} \) for L2 at 282 nm \( (\varepsilon = 24,300) \), see Fig. 6.

Cu(I) complexes 1 and 2 show one broad absorption band in the UV region due to ligand-centered \( \pi-\pi^* \) transitions (for 1, at 265 nm, \( \varepsilon = 26,000; \) for 2 at 287 nm, \( \varepsilon = 45,000 \)), which are slightly red-shifted due to the more extended \( \pi \)-conjugation, relative to the free ligands. A broad band in the visible region characteristic of metal-to-ligand charge transfer transitions (MLCT) [44,54] at 371 and 448 nm for 1 and 2, respectively, is also observed with a notable quenching in the absorption of 1 (Fig. 7), which is consistent with the molecular distortion of the complexes from \( D_{2d} \) symmetry [55]. The intensity of the low-energy shoulder is a rough measure of the distortion away from \( D_{2d} \) symmetry [54].

As suggested by TD-DFT studies (vide infra), the lowest energy electronic transitions of 1 and 2 can be assigned to the Cu(3d) →
N^N and phosphine → N^N charge transfer (1MLCT/1LLCT) transitions.

The luminescence properties in the solid state of compounds 1 and 2 were studied at room temperature, using an excitation wavelength of 350 nm for both compounds (Figs. S5 and S6). As illustrated in Fig. 8, complexes 1 and 2 show a broad band in the green region (~530 nm), which is common for copper compounds [56], which can be assigned to the dσ(Cu) → π(diimine) and σ-MLCT excited states [57–59] and are probably mixed with some contributions from the phosphine ligands.

The intense solid emissions of 1 is attributed to the decrease in the excited state distortion of Cu(I) complex and non-radiative decay in solid state. Compound 2 exhibits a marked quenching in the photoluminescence properties in comparison with 1, which can be attributed to the formation of the fifth bond (Cu1-N4) between the metal centre and an additional pyridyl substituent of L2, resulting in the formation of a five-coordinate exciplex [60]. By measuring the photoluminescence in solution (Fig. 9), a similar behavior is observed in the emission spectrum, probably because the exciplex structure in solution is retained. It has been reported that an increase of the P–Cu–P angle can reduce the d–σ* interactions and increase the energy required for the MLCT [61–62]. Thus, it is likely that the P–Cu–P angle plays a particular role for the emission variations of 1 and 2. Thus, it is possible that a larger P–Cu–P angle of 2 (127.59°) relative to that of 1 (117.32°), follows the same order as the MLCT, which is consistent with the observations of McMillin et al. [62].

The emission maxima of 1 and 2 in the solid state, to some degree, are red-shifted by 100 and 96 nm, respectively, compared to those of their corresponding solutions, as a consequence of the crystal packing effects, which have a significant influence on the relaxation pathways of the excitation energy. The solid-state emission maxima of 1 is greater than 2, which is in agreement with that in solution (emission maxima of 1 > 2). This further suggests that the P–Cu–P bond angle relative to the electronic nature of phosphine, plays a more significant role in the luminescence properties of Cu(I) complexes.

The relative intensities of the fluorescence bands of 1 and 2 reflect the same color for each compound. As depicted in Fig. 8, the emissions of 1 and 2 in the CIE diagram (CIE = Commission internationale de l’éclairage) correspond to green color region with coordinates x = 0.329, y = 0.522 for compound 1 and x = 0.339, y = 0.426 for compound 2 [63].

In EtOH solution at room temperature, complexes 1 and 2 show a broad single emission band in the blue region centered at 430 (Fig. 9), using an excitation wavelength of 350 nm for both compounds (Fig. S5 and S6 in Supplementary material). As shown in Fig. 8, the emissions of 1 and 2 in the CIE diagram correspond to deep blue color region with coordinates x = 0.1540, y = 0.0860 and x = 0.1479, y = 0.0817, respectively [63].

3.5. Electrochemistry

The redox potentials, Ered and Eox, for heteroleptic complexes 1 and 2 were measured by cyclic voltammetry using the ferrocene redox couple as a reference. The redox potentials for compounds 1 and 2 are listed in Table 3, and the cyclic voltammograms are shown in Fig. S7. The first oxidation potential occurs within the range 0.9–0.21 V and can be assigned to the Cu(I)/Cu(II) oxidation process. A curve crossing is observed in the range 0.48–1.13 V, indicating that the oxidation process is irreversible. The corresponding Cu(I)/Cu(II) oxidation for complex 2 occurs at a more positive potential, around +1.21 V (Table 3). This increase in the Cu(I) oxidation potential is due to the dπ–dσ interaction with the electron withdrawing phosphine ligand [64].

The Eonset,ox values were used to calculate the energy of the HOMO levels using the empirical Bredas equation and including the value of −4.4 eV for ferrocene [65].

\[ E(\text{HOMO}) = -e(E_{\text{onset,ox}} + 4.4) \]

The values obtained from the electrochemical studies (−5.182 and −5.486 eV, respectively) were very close to the values obtained by DFT computations.

Due to the irreversibility of the redox process, it was not possible to obtain a good approach for the LUMO values.

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Fig. 8. Solid state emission spectra of 1 and 2 recorded at room temperature upon excitation at λ = 350 nm. Inset: CIE color space chromaticity diagram of the complexes emissions and amplified emission spectrum of 2.
3.6. Application in DSSCs

To further explore the feasibility of using the two compounds as co-sensitizers in photovoltaic devices for DSSCs, the absorption spectra of the mixtures were first investigated.

The UV–visible absorption spectra of 1, 2 and dye N719 in ethanol solution combined with TiO₂ are displayed in Fig. 10. Strikingly, compounds 1 and 2 display a metal to ligand charge transfer (MLCT) absorption band between 330 and 450 nm. Compared with the absorption spectrum of dye N719, the absorption spectra of compounds 1 and 2 could compensate for that of dye N719 in the low wavelength region of ultraviolet and blue-violet, especially in the region of 330–450 nm. Indeed, when dye N719 is combined with 1 or 2, the absorption in the region of 350–500 nm is enhanced, as expected. To apply this improvement in the absorption, three solar devices were assembled; one of them was sensitized with N719 exclusively as control, and two were co-sensitized with a 1:1 mixture of 1, 2 and N719. It is important to mention that the amount of N719 of the co-sensitized devices is half than that employed in the control device. The results are summarized in Table 4.

The performances of cells co-sensitized with 1 or 2 and N719 are in the order of N719 > 1/N719 > 2/N719 (Fig. S8). As shown in Table 4, the electrode yield of the co-sensitized solar cell based on 1/N719/TiO₂ decreases less than 27% with a 50% reduction of N719 under standard global AM1 solar irradiation conditions, without an expense of lower open circuit voltage (Voc). This result suggests that co-sensitization of the TiO₂ photoelectrode with 1 is an effective way to reduce the amount of N719 and save costs without a drastic impact in the efficiency of the DSSCs.

3.7. Thermal analysis

To examine the thermal stability of 1 and 2, thermal gravimetric analyses (TGA) were performed under N₂ for crystalline samples with a heating rate of 10 °C min⁻¹ from ambient temperature up to 1000 °C (see Fig. S9).

The TGA curve of compound 1 reveals two main regions of weight loss. The first initiates at 100 °C with completeness at 150 °C, which corresponds to the release of the lattice CHCl₃ molecule. This phenomenon can be understood because of the presence of hydrogen-bonding interactions between the lattice CHCl₃ and phenyl rings. The observed weight loss of 10.79% is close to the calculated value of 10.36%. In the second region, in the temperature
range of 150–500 °C, two steps are observed which are attributed to the loss of L1 and the phosphine ligands, since the observed weight loss of 70.65% is in good agreement with the calculated value of 71.53%. Above 500 °C, the decomposition of the remaining CuP(C6H4F) occurs. According to the TGA curve, the decomposition of compound 2 occurs in four steps. The first, which reaches completeness at 80 °C, corresponds to the release of approximately 0.5 equivalents of CHCl3 from the crystal lattice, indicating that part of the chloroform solvate molecules had already evaporated during the sample preparation. The following three steps in the temperature range of 200–450 °C correspond to the loss of L2 and the phosphine ligands in good agreement with the observed value of 75.45% and calculated weight loss of 75.70%. Finally, as observed for compound 1, the CuP(C6H4F) residue decomposes.

4. Conclusions

Two new copper(I) complexes with polypyridine chelating ligands and phosphine groups were synthesized and characterized by single-crystal X-ray crystallography, mass spectrometry and NMR, FT-IR, UV–Vis and fluorescence spectroscopy. Electrochemical, spectroscopic and computational methods were used to understand the electronic characteristics of these compounds. Complexes 1 and 2 display low-intensity bands at 371 and 448 nm, respectively, corresponding to MLCT transitions, in accordance with the theoretical calculations. The fluorescence intensity in 2 is quenched due to the formation of a five-coordinate exocyclic. This was confirmed by the single-crystal X-ray diffraction analysis, revealing a distorted tetrahedral coordination environment for 1 and a distorted square pyramidal geometry for 2. A series of supramolecular interactions such as C–H···F, N–H···F, C–H···N, C–H···Cl, and C–H···π contacts play a significant role in stabilizing the crystal structures of compound 1 and 2.

According to electrochemical data, complexes 1 and 2 show irreversible oxidation processes, which constitute a drawback for the dye regeneration within DSSC devices. Significantly, devices display low-intensity bands at 371 and 448 nm, respectively, corresponding to MLCT transitions, in accordance with the theoretical calculations. The fluorescence intensity in 2 is quenched due to the formation of a five-coordinate exocyclic.

Acknowledgments

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Table 4

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References


