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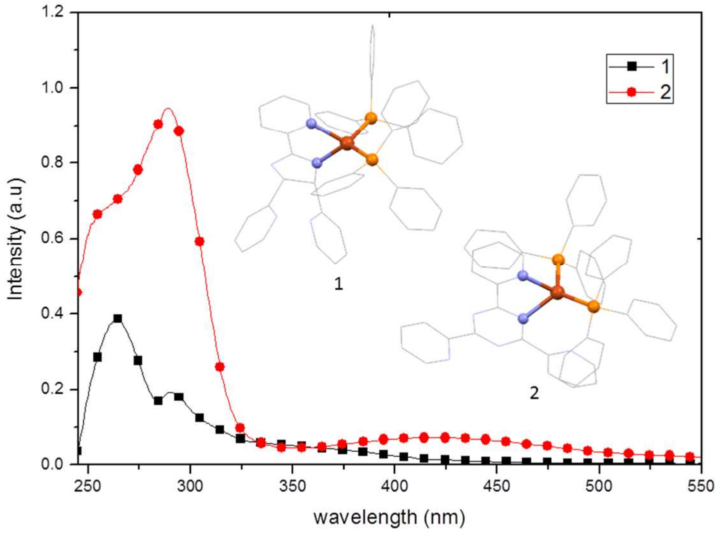
Abstract

Two novel photoluminescent copper(I) complexes having the compositions $[Cu^I(\mathbf{L1})(PPh_3)_2]NO_3\cdot 3CHCl_3$(**1**) and $[Cu^I(\mathbf{L2})(PPh_3)_2]NO_3\cdot H_2O$(**2**) withPPh$_3$=triphenylphosphine, **L1**=*cis*-(±)-2-(2,5-di(pyridin-2-yl)-4,5-dihydro-1H-imidazol-4-yl)pyridine and **L2**=2,4,6-tris(2-pyridyl)triazine have been successfully synthesized and characterized by, IR and ^{1}H-NMR spectroscopy, FAB$^+$ mass spectrometry and single-crystal X-ray diffraction analysis. Both complexes showed 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.



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Two novel photoluminescent copper(I) complexes having the compositions $[Cu^I(\mathbf{L1})(PPh_3)_2]NO_3\cdot 3CHCl_3(\mathbf{1})$ and $[Cu^I(\mathbf{L2})(PPh_3)_2]NO_3\cdot H_2O(\mathbf{2})$ withPPh_3=triphenylphosphine, **L1**=*cis*-(±)-2-(2,5-di(pyridin-2-yl)-4,5-dihydro-1H-imidazol-4-yl)pyridine and **L2**=2,4,6-tris(2-pyridyl)triazine have been successfully synthesized and characterized by, IR and ^{1}H-NMR spectroscopy, FAB$^+$mass spectrometry and single-crystal X-ray diffraction analysis. Both complexes showed 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.

Introduction

In the past decades, inorganic photochemistry has focused on molecular systems that possess low-lying metal-to-ligand charge transfer excited states capable of electron and energy transfer. In this context, ruthenium(II), osmium(II), and rhenium(II) complexes have received specialattentionbecause of their fascinating properties and potential applicationsfor chemical sensing, display devices, probes of biological processes, phototherapy, and solar energy conversion schemes.[1,2]

At the same time, the strong appealing possibility of using costless and nontoxic metals such as copper or zinc,as substitutesof the above-mentioned more expensive heavy metal ions, has stimulated further research in this field.[3]Copper(I) forms pseudotetrahedral complexes with polypyridine ligands. A few coordination polymers of Cu(I) and mixed-valence Cu(I)-Cu(II) complexes of 2,4,6-tris(2-pyridyl)triazine (L2) with a four coordinated metal center have been reported.[4]There is a number of complexes which are susceptible offluorescent light emission. Cu(I) complexes prepared from phosphines and polypyridine ligands were first studied more than three decades ago,whichresulted potentially useful as sensorsdue totheir long lifetimes upon light excitation.

We are interested in exploring the coordination chemistry of Cu(I) complexes with phosphines and polypyridine ligands because of their promising photoluminescence properties and intriguing coordination architectures.[3,5]

In previous studies regarding the coordination behaviour of polypyridylligands, we analysed the influence ofnon-covalent interactions on the supramolecular structure of metal complexes.[6]In this contribution, we report on two new Cu(I) complexes withtriphenylphosphine and *cis*-(±)-2,4,5-tris(2-pyridyl)imidazoline(**L1**) and 2,4,6-tris(2-pyridyl)triazine(**L2**)ligands for which we explored their photophysical properties, bothexperimentally and theoretically.

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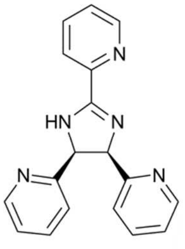
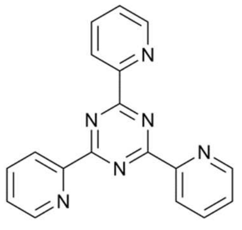


L1



L2

Experimental

Materials and methods

All chemicals including ligand **L2** were purchased from Aldrich and used as received without further purification. Complex **1**wassynthetized under argon atmosphere with solvents purified according to reported methodologies,[7] stored and manipulated underinert atmosphere by Schlenk techniques. Complex **2** was prepared under normal environment conditions. In both cases, phosphine ligands play a crucial role in the stabilization of the complexes.[8]The startingcomplex[Cu(PPh$_3$)$_2$(NO$_3$)]was synthesized by a previously reported methodology.[9]The synthesis and spectroscopic data for**L1** have been reported elsewhere.[10] Infrared spectra (KBr) were measured on a Bruker Alpha Tensor 27 spectrophotometerusingKBr pellets in the 4000–500 cm^{-1}region.Thermogravimetrtic 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. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded with a Varian400 and 500 NMR instrument. Chemical shifts are reported in ppm and were referenced toresidual solvent resonances. HR-FAB$^+$ mass-spectrometric studies were carried out on a JMS-700 MSTATION JEOL equipment. UV-Vis absorption spectra were recorded on a Shimadzu UV-1800 UV spectrophotometer. Emission spectra in solution and in the solid state were obtainedon a Perkin Elmer LS-55 fluorescence spectrophotometer. Single-crystal X-ray structures were determined on a Bruker-APEX diffractometer equipped with a CCD area detector ($\lambda_{Mo\text{-}K\alpha}$=0.71073Å, monochromator: graphite). Frames were collected via ω/ϕ-rotation at 10 s per frame (SMART).[11] The measured intensities were reduced to F^2 and corrected for absorption with SADABS (SAINT-NT).[12] Corrections were made for Lorentz and polarization effects. Structure solution, refinement and data output were carried out with the SHELXTL-NT program package.[13] Non hydrogen atoms were placed in geometrically calculated positions using a riding model. The asymmetric compound **1** contains three CHCl$_3$ molecules, one of which is disordered over two positions. The N-H hydrogen atom has been localized by difference Fourier maps, whereupon the N-H distance has been fixed to 0.860 Å, but the coordinates have been freely refined. The N(H) atom has approximatesp^3 hybridization. Figures were created with ORTEP[14]and MERCURY.[15] Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications, CCDC 969083-969084.

Preparation of [Cu^I(L1)(PPh$_3$)$_2$]NO$_3$·3CHCl$_3$ (1)

[Cu(PPh$_3$)$_2$(NO$_3$)] (0.210 g, 0.33mmol) and *cis*-(±)2-(2,5-di(pyridin-2-yl)-4,5-dihydro-1H-imidazol-4-yl)pyridine (**L1**) (0.100 g, 0.33 mmol)were dissolved in dry dichloromethane (3 mL) under argon atmosphere to obtain a yellow solution.The solution was stirred for 3 h at room temperature, and then concentrated to 1 mL under reduced pressure whereupon diethyl ether (3 mL) was added to obtain an orange microcrystalline solid.The product was filtered, washed with diethyl ether (2x3 mL) and dried under vacuum(0.28 g, 89%). The crude solid product was recrystallized by vapor diffusion of pentane into aconcentrated solution of **1**in chloroform. IR (KBr): 3168, 3047, 3012, 2857, 1583, 1522, 1475, 1433, 1381, 1325, 1093, 746, 696 cm^{-1}. ^{1}H NMR (CDCl3, 399.7 MHz): resonancesof**L1** are slightlybroadwhiletwoofthreephosphineresonances are sharp; δ9.60 (br s, NH, 1H), 8.85 (slbr s, 1H), 8.16 (slbr m, 1H), 8.12 (slbr s, 2H), 7.98 (slbr m, 1H), 7.33 (t, J = 7.2 Hz, 8H, thereis a smallpeakhiddenbythisresonance), 7.28 (slbr s, 1H), 7.18 (t, 7.6 Hz, 12H), 7.02 (br m, 12H), 6.82 (slbr m, 1H), 6.66 (slbr s, 2H), 6.56 (slbr s, 1H), 5.66 (slbr s, 2H). ^{31}P {^{1}H} NMR (CDCl$_3$, 161.8 MHz): δ0.49 (broad s, PPh$_3$).MS [FAB$^+$,*m/z*]: 951[M+H]$^+$, 689 [(M+H)-PPh$_3$]$^+$, 626 [M-PPh$_3$-NO$_3$]$^+$, 549 [M-PPh$_3$-Ph-NO$_3$]$^+$ 364 [M-2PPh$_3$-NO$_3$]$^+$, 286[M-2PPh$_3$-Py-NO$_3$]$^+$.Exactmass-FAB(HR-FAB$^+$)calcd. for C$_{54}$H$_{46}$O$_3$N$_6$P$_2$Cu [M+H]$^+$, 951.2403, found: 951.2316.

Preparation of [Cu^I(L2)(PPh$_3$)$_2$]NO$_3$·H$_2$O (2)

To a stirring solution of [Cu(PPh$_3$)$_2$(NO$_3$)] (0.208 g, 0.32 mmol) in chloroform (4 mL) under argon was added 2,4,6-tris(2-pyridyl)triazine (0.100 g, 0.32 mmol) to give a dark red solution. The resulting mixture was stirred over a period of 3 h and then filtered. The filtrate was concentrated (3 mL) and red single crystals were obtained by vapour diffusion of diethyl ether into the solution(0.12g, 39%). IR (KBr): 3057, 1584, 1476, 1435, 1375 cm^{-1}. ^{1}H NMR (CDCl$_3$, 499.9 MHz): resonances of **L2** are slightly broad; δ 8.91 (br d, J = 6.1 Hz, 3 H), 8.04 (br m, 3H), 7.62-7.78 (m, 3H), 7.39-7.51 (br m, 3H), 7.32 (t, J = 7.2 Hz, 6H), 7.15 (t, J = 7.4 Hz, 12H), 7.09 (slbr m, 12 H). ^{31}P {^{1}H} NMR (CDCl$_3$, 202.3 MHz), selected resonance for the main species: δ 1.91 (broad s, PPh$_3$), other minor unidentified species are present. MS [FAB$^+$,*m/z*]: 899 [M-NO$_3$]$^+$, 637[M-PPh$_3$-NO$_3$]$^+$, 485 [M-2Ph-PPh$_3$-NO$_3$]$^+$. Exactmass-FAB$^+$(HR-FAB$^+$)calcd. forC$_{36}$H$_{27}$CuN$_6$P [M-NO$_3$-PPh$_3$]$^+$, 637.1331, found: 637.1918.

Computational details

DFT structure calculations were performed with the Gaussian09 package.[16]Minimum energy structureswere calculatedand confirmed through a frequency calculation (no imaginary frequencies).[17] The transitions between the different orbitals were evaluated with time-dependent (TD) DFT,[18]using the M06 hybrid-meta-GGA functional[19] combined with the 6-31G(d)[20]basis set for atoms C, H, N and P, and the DZVP[21]basis set for the Cu atom. The effects of a solvated environment were evaluated with the integral equation formalism for thepolarizable continuum model (IEF-PCM) and the implementation of the non-equilibrium solvation model.[22]The solvents considered for this analysiswere dichloromethaneand chloroform.

Results and discussion

Combination of bis(triphenylphosphine)copper(I) nitrate with *cis*-(±)2-(2,5-di(pyridin-2-yl)-4,5-dihydro-1H-imidazol-4-yl)pyridine (**L1**) or2,4,6-tris(2-pyridyl)triazine (**L2**) both under argon atmosphere, provided Cu(I) complexes of compositions $[Cu^I(L1)(PPh_3)_2]NO_3\cdot 3CHCl_3$ (**1**) and $[Cu^I(L2)(PPh_3)_2]NO_3\cdot H_2O$ (**2**). Both complexes have been characterized by IRand^{1}H-NMR spectroscopy, FAB$^+$mass spectrometry and single-crystal X-ray diffraction analysis.

Table 1. Crystallographic data for compounds **1**and **2**.

Crystal data[a]	**$1\cdot NO_3\cdot 3CHCl_3$**	**$2\cdot NO_3\cdot H_2O$**
Formula	$C_{57}H_{48}Cl_9CuN_6O_3P_2$	$C_{54}H_{44}CuN_7O_4P_2$
M_w (g/mol^{-1})	1309.55	980.44
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
Temp(K)	100(2)	100(2)
Crystal size (mm^3)	0.39x0.43x0.45	0.42x0.45x0.48
a/Å	16.0948(11)	10.7485(16)
b/Å	21.1398(15)	14.948(2)
c/Å	17.9889(12)	16.371(3)
α/°	90	86.290(2)
β/°	100.028(1)	73.060(2)
γ/°	90	70.947(2)
V/Å^3	6027.1(7)	2377.0(6=
Z	4	2
$\rho_{calcd.}$/ g cm^{-3}	1.443	1.370
μ/mm^{-1}	0.863	0.582
F(000)	2680	1016
θ range for data collection/°	1.50 to 25.00	1.90 to 25.00
Reflections collected	35918	22415
Independent reflections	10597	8341
Observed reflections (I> 2σ (I)	9201	7641
R(int)	0.032	0.0361
$R_1[I > 2\sigma(I)]$[b,c]	0.0631	0.0529
wR$_2$ [I>2σ(I)]	0.1588	0.1285
R_1(all data)$_w$[d,e]	0.0716	0.0583
wR_2 [all data]	0.1650	0.1316
Goof (F^2)	1.027	1.135

[a] $\lambda_{MoK\alpha}$ = 0.71073 Å. [b] $F_o > 4\sigma(F_o)$. [c] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [d] All data. [e] $R_w = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{½}$.

In the IR spectrumof complex **1**, the intense band at 3168 cm^{-1} is assigned to the stretching vibration of the N-H group.Theabsorptionsat 3047 and 3012 cm^{-1}are characteristic of the C-H aromatic and aliphatic stretching vibrations, respectively, while the bands in the region of 1522-1475cm^{-1}can be assigned to the C=N and C=C stretching vibrations of the pyridyl substituents. The typical band for the C=N vibration of the central imidazoline ring is located at 1583 cm^{-1}, confirming the presence of ligand **L1** in **1**. Complex formation is additionally supported by bands at 1433and 1381cm^{-1}, which are characteristic for the P-C$_{Ar}$[23]and N-O stretching vibrations in the phosphine and nitrate ligands, respectively.

The IR spectrum of complex **2**,showsa band at 3057 cm^{-1}, characteristic ofthe C-H aromatic stretching vibrations. The absorptionsin the region of 1584-1476 cm^{-1} can be assignedto the C=N and C=C vibrationsof the pyridylsubstituentsin **L2**.As for **1**, the absorption at 1435 cm^{-1}is characteristic for the P-C$_{Ar}$[23]vibration of the phosphine ligand and the band at 1375 cm^{-1}is typical ofthe nitrate counter ion.

The experimental values of the main vibrations in the IR spectra were confirmedby the theoretical results (Table S1 and S2).†

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.

1	
Cu(1) - N(1)	2.023(3)
Cu(1) - N(3)	2.135(3)
Cu(1) - P(1)	2.2482(10)
Cu(1) - P(2)	2.2264(11)
N(1) - Cu(1) - N(3)	80.05(12)
N(1) - Cu(1) - P(2)	128.24(10)
N(3) - Cu(1) - P(2)	108.30(9)
N(1) - Cu(1) - P(1)	106.32(9)
N(3) - Cu(1) - P(1)	113.87(9)
P(2) - Cu(1) - P(1)	115.02(4)

2	
Cu(1) - N(1)	2.106(2)
Cu(1) - N(4)	2.137(2)
Cu(1) - P(1)	2.3032(8)
Cu(1) - P(2)	2.2597(8)
N(4) - Cu(1) - N(1)	78.22(9)
N(4) - Cu(1) - P(2)	113.55(7)
N(1) - Cu(1) - P(2)	125.95(6)
N(4) - Cu(1) - P(1)	97.87(7)
N(1) - Cu(1) - P(1)	99.93(6)
P(2) - Cu(1) - P(1)	127.66(3)

The ^{1}H NMR spectrum of **1**(Figure S1 and S2)† showed slightly broad resonances for all hydrogens of **L1**, while two of three phosphine resonances are sharp. For example, resonances in the region 6.50-8.90 ppm are assigned to 42 aromatic hydrogens; the two aliphatic hydrogens in the imidazoline ring appear at 5.66 ppm, whereas the characteristic NH of **L1** is observed as a broad singlet at 9.60 ppm and is taken as evidence that the ligand coordinates to the Cu(I) centre as a neutral ligand without deprotonation of the NH group, as revealed by X-ray crystallography (*vide infra*). Two triplets, assigned to phosphine hydrogens, are observed at 7.18 (J = 7.6 Hz) and 7.33 ppm (J = 7.2 Hz). The ^{1}H NMR spectrum of **2**(Figure S4)† displays four sets of slightly broad peaks in the region 7.39-9.0 ppm for the 12 aromatic hydrogens in **L2** and three sets in the region 7.02-7.36 ppm for the 30 hydrogens in the phosphine ligands.

In summary, both complexes are fluxional molecules in solution, as revealed by the line broadening observed in ^{1}H NMR. Additional evidence of this behavior was obtained by ^{31}P

NMR analysis of **1** and **2**(Figure S3 and S5)†, which showed very broad singlets at 0.49 and 1.91 ppm, respectively.

The FAB$^+$ mass spectrum of complex **1**showsa peak at m/z = 951 for the expected molecular ion $[M+H]^+$; however, for **2**onlypeaksfor fragments are observed, which support the molecular composition of the complex. The mass spectrum of compound **1**shows five additional peaks at m/z=689, 626, 549, 364 and 286,corresponding to fragments of composition $[(M+H)\text{-}PPh_3]^+$, $[M\text{-}PPh_3\text{-}NO_3]^+$, $[M\text{-}PPh_3\text{-}Ph\text{-}NO_3]^+$, $[M\text{-}2PPh_3\text{-}NO_3]^+$ and $[M\text{-}2PPh_3\text{-}Py\text{-}NO_3]^+$,respectively. For compound **2**, peaks areobserved at m/z=899, 637 and 485, corresponding to fragments of the composition $[M\text{-}NO_3]^+$, $[M\text{-}PPh_3\text{-}NO_3]^+$ and $[M\text{-}2Ph\text{-}PPh_3\text{-}NO_3]^+$, respectively. The correct assignment of the peaks at m/z=951 for **1** and m/z=637 for **2**has been confirmed by high-resolution FAB$^+$mass spectrometry.

X-Ray Crystallographic Study

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 Table S4 and S5.†

The X-ray crystallographic studiesrevealed that both the complexes are composed of onecopper(I) atom as metal centre, onepolypyridine ligand, two triphenylphosphine molecules, onenitratecounterion and a varying number of uncoordinated solvent molecules (three $CHCl_3$ for **1** and one H_2O for **2**).

In both samples, the Cu(I) atoms are embedded in N_2P_2environments, resulting from coordination by the triphenylphosphine co-ligands and twoNatomsfrom the neutral form of the tris-pyridine ligands, which adopted a bidentate coordination mode by bonding with one of the pyridyl substituents and one of the imidazoline or triazinenitrogens, respectively. Thus, five-membered Cu-N-C-C-N chelate rings are observed in the molecular structure of both complexes. The Cu-N bond lengths arein the range of 2.023-2.137 Å, similar to the distances reported previously for $[Cu(pbb)(DPPMB)][BF_4]$; pbb= 2-(2′-pyridyl)benzimidazolyl benzene, DPPMB= bis-(diphenylphosphinomethyl)diphenyl borate.[3a]

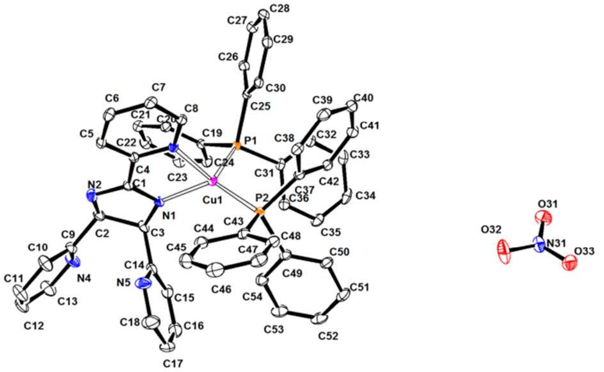


Fig. 1 Perspective view of the molecularstructure of compound **1**. Hydrogen atoms and chloroform molecules have been omitted for clarity. The displacement ellipsoids are shown at 30% probability level.

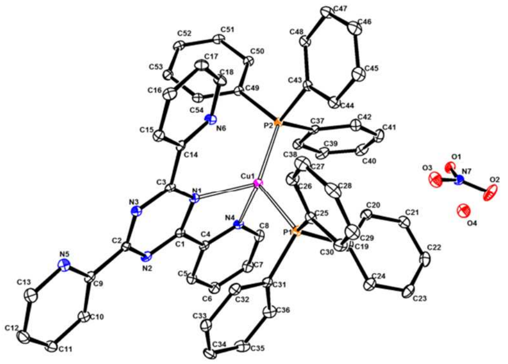


Fig. 2 Perspective view of the molecularstructure of compound **2**. Hydrogen atoms have been omitted for clarity. The displacement ellipsoids are shown at 30% probability level.

The crystallographic study revealed that**1**crystallized in a monoclinic crystal system with the space group $P2_1/n$. The asymmetric unit contains the $[Cu(\mathbf{L1})(PPh_3)_2]^+$cation, one NO_3^- anion and three chloroform molecules. The copper atom in **1** has a distorted tetrahedralcoordination environment (τ_4=0.83),[24] with Cu-N and Cu-P bond lengths in the range of 2.023(3) to 2.2482(10) Å. The bond angles range from 80.05(12) to 128.24(10)°, of which the smallest value corresponds to the five-membered chelate ring formed with the polypyridine ligand and the largest to the P-Cu-P bond angle formed with the sterically hindered PPh_3ligand.Compound**2**crystallized in a triclinic crystal system with space group $P\overline{1}$. The asymmetric unit contains the $[Cu(\mathbf{L2})(PPh_3)_2]^+$cation, one NO_3^- anion and one water molecule. In contrast with**1**, the Cu atom in **2** is embedded in a four-coordinate coordination polyhedron with a distorted trigonalpyramidal coordination geometry (τ_4=0.7545).[24] The Cu-N and Cu-P bond lengths are in the range of 2.137(2)-2.3032(8) Å. The bond angles vary from 78.22(9) to 127.66(3)°.

A close inspection of the crystal structure of **1** reveals the presence ofdimeric units of composition $\{[Cu(\mathbf{L1})(PPh_3)_2][NO_3]\}_2$, in which the Cu(I) cations are linkedthrough intermolecular π-π interactions between the metal-coordinated 2-(2-pyridyl)of ligand **L1** (centroid···centroid = 3.744 Å),[25] anda series of fourC-H···O and two N-H···O hydrogen bonding interactions formed with intermediate uncoordinated nitrate ions (Fig. 3).

These dimeric units are further arranged into one-dimensional (1D) chainsalong*c*through intermolecular C–H···N contacts formed by interactions between two H atoms of the pendant pyridyl rings and the nitrogen atoms of the two uncoordinated pyridyl groups (Fig. 4).The geometric details of these supramolecular interactions are summarized in Table S4.†All intermolecular distances and angles are within the expected range.[26,27]

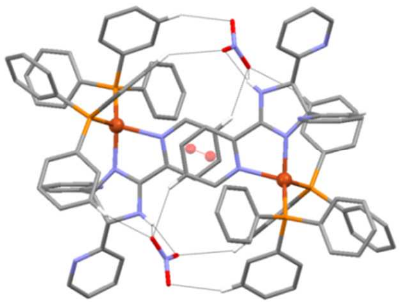


Fig. 3 Fragment of the crystal structure of **1**, showing the dimeric entities formed through a series of π-π, N-H···O and C-H···O interactions. Hydrogen atoms not involved in hydrogen bonding interactions have been omitted for clarity.

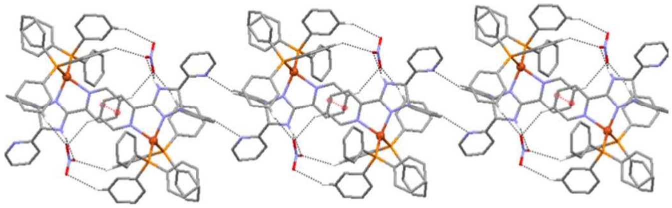


Fig. 4 1D hydrogen-bonded chains in the crystal structure of**1**, formed throughC-H···N interactions.Hydrogen atoms not involved in hydrogen bonding interactions have been omitted for clarity.

As shown in Fig. 5, in the crystal structure of complex **2** a 2D supramolecular network is formed through a total of one O-H···O, twoO-H···N, fourC-H···O and one C-H···Nhydrogen bonds, in which the NO_3^-anions and solvate H_2O molecules interconnect the [Cu^I(**L2**)(PPh_3)$_2$]$^+$cations. Of these, the O-H···O interactions are formed between water molecules and nitrate ions; the O-H···N interactions are the result of interactions between water molecules and nitrogen atoms of the central triazineandpyridyl rings. As for complex **1,** the C-H···O interactions are formed between the H atoms of the pyridylrings and the nitrate oxygen atoms. Finally, between neighbouring phenyl and uncoordinated pyridyl rings C-H···N intermolecular interactions are observed. The details of these supramolecular interactions are summarized in Table S5.† All intermolecular distances and angles are within the range found inpreviously reported structures.[26,27]

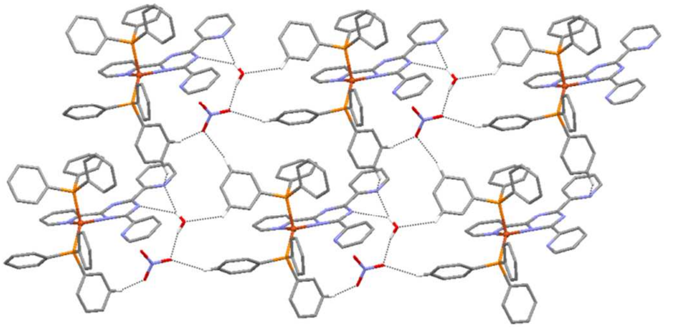


Fig. 5 Perspective view of the 2D hydrogen-bonded network in the crystal structure of**2**, formed through O-H···O, O-H···N and C-H···O interactions.Hydrogen atoms not involved in hydrogen bonding interactions have been omitted for clarity.

Photophysical Properties

The absorption and emission spectra of the free ligands and their respective Cu(I) complexes were measured in CH_2Cl_2 at room temperature. The free ligands display multiple absorption bands in the UV region (<330 nm), due to ligand-centered π–π* transitions. λ_{max} for **L1** is located at 265 nm (ε=13,900) and $\lambda_{max}$for**L2** at 282 nm (ε=33,700), see Fig. 6.

Both complexes showtwo bands in the UV region due to ligand-centered π–π* transitions (for **1**, at 265 nm, ε=19,250 and for **2** at 290 nm, ε=47,250) atwavelengths close to those observed for the uncoordinated ligand.A broad band in the visible region characteristic of metal-to-ligandcharge transfer-transitions (MLCT)[8,28] is also observedwith a notable quenching in the absorption of **1**(Fig. 7), which is consistent with the molecular distortion of the complex from *D2d* symmetry (τ_4=0.8279).[29] This low-symmetry conformation likely occurs to maximize intramolecular *π*-stacking interactions between opposing ligands **L1**. These interactions are clearly seen in the solid-state structure (*vide supra*). Thus, the intensity of the low-energy shoulder is a rough measure of the distortion away from *D2d* symmetry. Conversely, as themore sterically demanding ligands impart more rigidity to the complex and enforce *D2d* symmetry, the low-energy shoulder should decrease.[29]As suggested by TD-DFT studies (*vide infra*), the lowest-lying transition of **1** and **2** are ascribed as Cu(3d)→N^N and phosphine→N^N charge transfer (1MLCT/1LLCT) transitions.

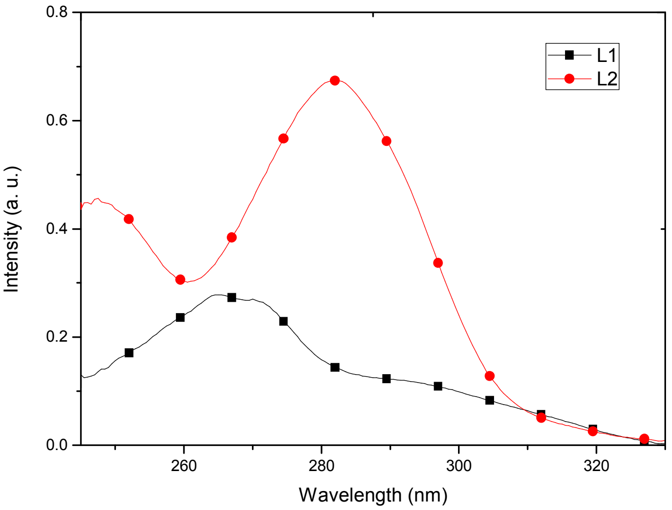


Fig. 6. Absorption spectra of **L1** y **L2** recorded in a 2.0 x10^{-5}mol/LsolutioninCH$_2$Cl$_2$.

The solid state emission spectra of complexes**1** and **2** are shown in Fig.8. Both complexes showa broad band in the green region (535 nm),which is common for copper compounds,[30] and can be assigned tod$_\pi$(Cu)→π*(diimine) and ^{3}MLCT excited states,[31]mixed with some contributions from the phosphine ligands.

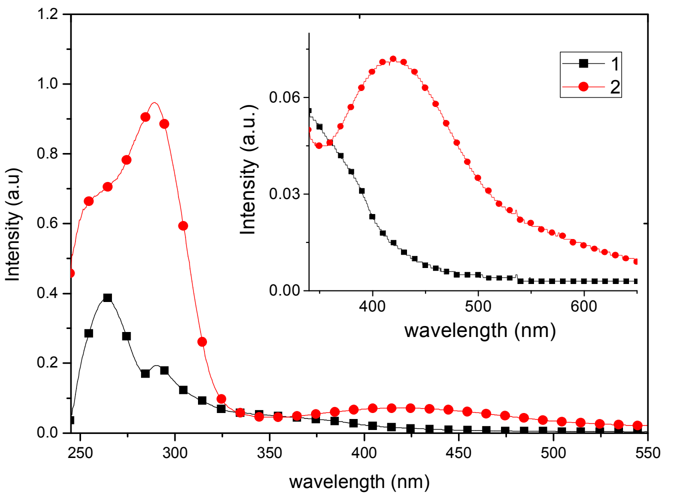


Fig. 7. Absorption spectra of **1** and **2** recorded in a 2.0 x10^{-5}mol/Lsolution inCH_2Cl_2. Inset: amplified visible region of the absorption spectra.

Compound **1**exhibits a marked enhancement in the photoluminescence properties in comparison with **2**, which can be attributed to the dimericsupramolecular structure (*vide supra*), which showsthe presence of intermolecular π-π stacking interactions that can efficiently suppress the relaxation processfrom the excited state, decreasing the non-radiative rate constant.[23]By measuring thephotoluminescenceinsolution (Fig. 9), a similar behaviour is observed inthe emission spectrum,probably becausedimericsupramolecularstructurein solutionis retained.

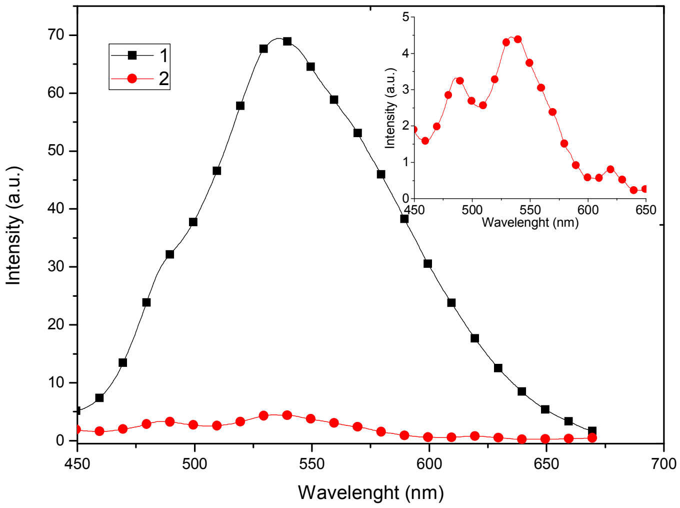


Fig. 8.Solid state emission spectra of **1** and **2** recorded at room temperature upon excitation at λ=320 nm. Inset: amplified emission spectrum of **2**.

In CH_2Cl_2 solution at roomtemperature, complexes **1** and **2**show a broad single emission band (Fig. 9) centered at 454 and 465 nm, respectively. 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.[32]Thus, it is likely that the P-Cu-P angle plays a partial role on the emission variation of **1** and **2,** and virtually the P-Cu-P angle of **1** (115.02°) and **2** (127.66°)follow the same order as the MLCT (454 and 465 nm, respectively), consistent with the observations of MacMillin*et al*.[32a,33]Therefore, the emissions of **1** and **2**are markedly affected by both the electronic properties of the phosphines and the P−Cu−P angles.

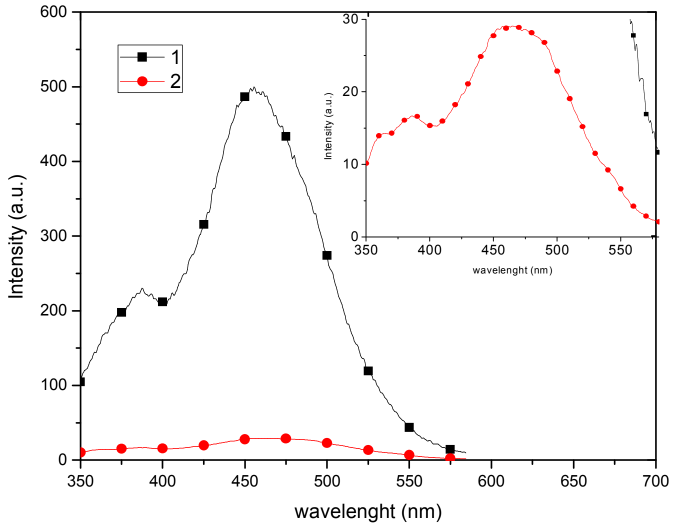


Fig. 9. Emission spectra of **1** and **2** recorded in 1x10^{-4}mol/L CH_2Cl_2 solution at room temperature upon excitation at λ=320 nm. Inset: amplified emission spectrum of **2**.

Theoretical Investigations

The origin of the charge transfer between molecular orbitals is an important aspect in the study of molecular systems. Fig. 10 shows the isodensity plots of some of the molecular orbitals at the M06/6-31G(d)+DZVP level of calculation.[19]The absorption band at λ_{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 center and at the phosphorus atoms, while the LUMO electron density is distributed over the ligands.

The results of the TD-DFT calculations indicate five major transitions for complex **1**. In the UV region, a ligand-to-ligand transition (**L1-L1**) between the HOMO-4→LUMO orbitals andthree metal/phosphorus→ligand transitions: HOMO→LUMO+6, HOMO→LUMO+2 and HOMO→LUMO+7. In the visible region there is one metal/phosphor→ligand HOMO→LUMO transition. Four main transitions can be observed for **2**, a HOMO-4→LUMO charge transfer (**L2-L2**) in the UV region and threemetal/phosphor→ligand transitions in the visible region: HOMO-1→LUMO, HOMO→LUMO+1 and HOMO→LUMO. This analysis shows that there is indeed a mixture of charge transfer interactions between the components of the complex.A detail of the assignments of TD-DFT in terms of FMO areincluded in the supplementary material (Table S6 and Figure S6).†

Thermal analyses

To examine the thermal stability of **1** and **2**, thermal gravimetric analyses (TGA) were performed under N_2 atmosphere for crystalline samples with a heating rate of 10 °Cmin^{-1} from ambient temperature up to 1000 °C. The TGA curve of compound **1** reveals four main regions of weight loss (see Fig. S7, ESI†).The first initiates at 30 °C with completeness at 150 °C, whichcorresponds to the release of three lattice $CHCl_3$ molecules. This phenomenon can be understood because of the presence of hydrogen-bonding interactions between the lattice $CHCl_3$, NO_3^- and phenyl rings. The observed weight loss of 25.6% is close to the calculated value (27.3%). The second step in the temperature range of 150 to 330 °C corresponds to the loss of twoPPh_3 ligands. The observed weight loss of 40.3% is in good agreement with the calculated value (40.0%). The third step (found 11.3%; theoretical,11.9%), in the range of 330−500 °C, is attributed to the loss of two Py molecules. Finally, a fourth step in the temperature range of 600 to 1000°C correspondsto the loss one Py and one imidazoline molecule (found 10.0%, theoretical, 11.0%).As shown in Fig. S7†, the TGA curve of compound **2** reveals also four main steps of weight loss. The first, starting at 90 °C with completeness at 150°C, corresponds to the release of the crystal lattice water molecules. The observed weight loss of 2.6% is slightly larger than the calculated value (1.8%). The second step, from 150 to290 °C, corresponds to the loss of two PPh_3 ligands. The observed weight loss of 52.5% is in good agreement with the calculated value (53.4%).The third step (found 20.0%; theoretical, 20.6%), in the range of 290−400 °C, is attributed to the loss of twoPy molecules and one NO_2^- ion. Finally, the fourth step in thetemperature range of 400 to 1000°C correspondsto the loss one Py and one triazine molecule (found 15.0%, theoretical, 15.9%).

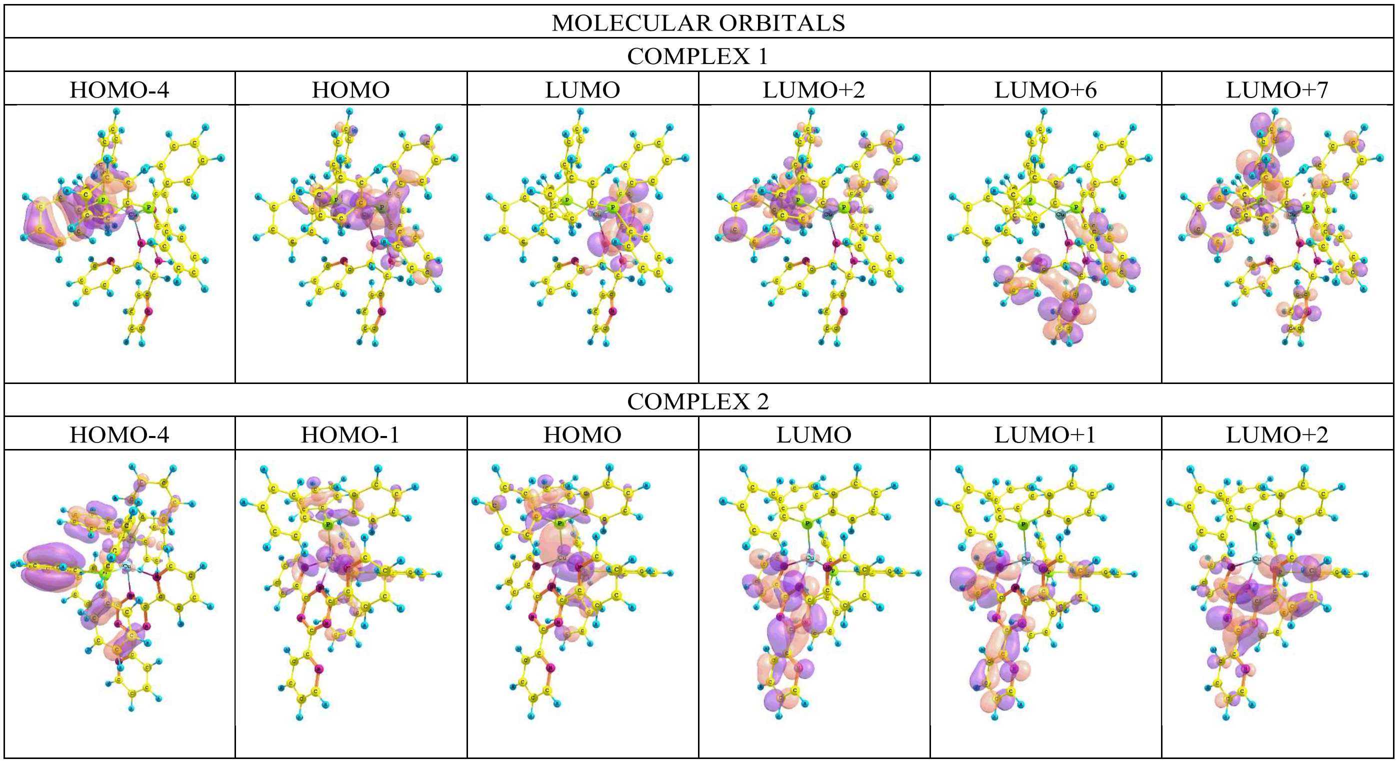


Fig. 10. Plots of the frontier orbitals involved in the lowest-lying electronic absorption transitions of the complexes.

Conclusions

Two new copper(I) complexes with polypyridine chelating ligands and phosphine groups were synthetized and characterized by single-crystal X-ray crystallography as well as NMR, FT-IR, MS, UV-Vis and fluorescence spectroscopy. Their photophysical properties are reported. It isfound that the fluorescence intensity in **1** is enhanced due to its rigid structure caused by π-stacking which generates a pseudo sandwich structure. A series of additional interactions such as O-H···N, O-H···O, C-H···N and π-π contacts also play a significant role in stabilizing the supramolecular network. The application of mononuclear Cu(I) complexes in the field of solar cell sensitizers needs further research.

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Notes and references

†Electronic Supplementary Information (ESI) available: Experimental and theoretical IR spectral data of complexes **1** and **2**;Table of hydrogen bonding geometries of compounds **1** and **2**;TD-DFT assessment data, ^{1}H-NMR and

^{31}P {^{1}H} NMR spectrums and thermograms of compounds **1** and **2**. CCDC reference numbers 969083-969084. For ESI and crystallographic data in CIF or other electronic format seeDOI: 10.1039/b000000x/

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