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Luminescent Cu(I) complex with bis(indazol-1-yl)phenylmethane as chelating ligand

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Keywords: copper(I), luminescence, N-donor ligands, indazole

Abstract

The cationic Cu(I) complex $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]^+$, where $\text{N}^{\wedge}\text{N}$ is bis(indazol-1-yl)phenylmethane, was synthesized as chloride or tetrafluoroborate salt by reacting CuCl or $[\text{Cu}(\text{NCCH}_3)_4][\text{BF}_4]$ with bis(indazol-1-yl)phenylmethane under mild conditions. The structure of $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]\text{Cl}$ was ascertained by single-crystal X-ray diffraction. The complex exhibited bright yellow emission upon excitation with near UV and violet light, attributed to triplet LLCT/MLCT transitions on the basis of experimental data and computational outcomes.

Communication

Photoactive complexes based on earth-abundant transition metals are of huge interest for their application in advanced technology [1]. In this context, a role of paramount importance is played by Cu(I)-based coordination compounds, that can be successfully applied in the field of electrical/light energy conversion. Depending upon the molecular structure, both singlet and triplet excited states are potentially involved in the emission from Cu(I) compounds [2-10].

The copper(I) metal centre has high affinity towards N-donor ligands. Since the pioneering work of McMillin *et al.* [11-15], species based on the 1,10-phenanthroline skeleton (phen^{R}) have been

widely used as chelating ligands for the preparation of luminescent Cu(I) coordination compounds, such as homoleptic species having general formula $[\text{Cu}(\text{phen}^R)_2]^+$ [16-18]. The chemical nature, the size and the position of the substituents on the phenanthroline rings influence the ground and excited state geometries, thus modulating the MLCT absorption and emission properties of the corresponding complexes.

Despite the fact that most of the studies actually reported in the literature are focused on Cu(II) derivatives [19-28], N-donor ligands containing the indazole heterocycle recently showed to be viable alternatives to polypyridines for the preparation of luminescent Cu(I) complexes. In particular, homo- and heteroleptic compounds with indazolyl-imine ligands were reported by Cabrera and co-workers [29-30]. It was highlighted that the introduction of electro-withdrawing or unsaturated functional groups at different positions in the indazole fragment allowed the fine-tuning of the photoluminescence properties.

The coordination chemistry of bis(indazol-1-yl)methane and bis(indazol-2-yl)methane towards Cu(I) was deeply investigated by Pettinari, Álvarez and co-workers, but the complexes were not studied from a photophysical point of view [31]. Comparable ligands were less investigated, for instance bis(indazol-1-yl)phenylmethane was used only for the preparation of a Rh(I) derivative [32].

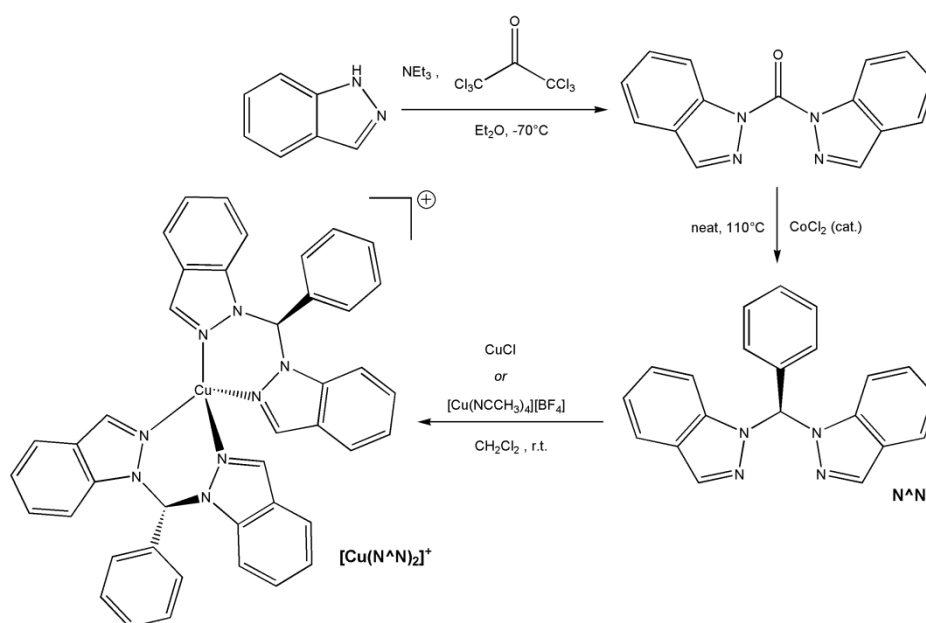
We developed an improved synthetic method for the preparation of bis(benzotriazol-1-yl)arylmethane ligands [33], and recently we extended it to the synthesis of bis(indazol-1-yl)phenylmethane. Because of the interest of our research group towards the preparation of inexpensive luminescent coordination compounds based on first row transition elements [34-38], we investigated the reaction between copper(I) precursors and the ligand bis(indazol-1-yl)phenylmethane ($N^{\wedge}N$), obtaining the photoluminescent homoleptic complex $[\text{Cu}(N^{\wedge}N)_2]^+$.

Bis(indazol-1-yl)phenylmethane was synthesized in a two-steps procedure, first reacting 1*H*-indazole with triphosgene under mild conditions, to obtain 1*H*,1'*H*-1,1'-carbonyl-di-indazole. The preparation of the same compound using phosgene as reactant was reported in 1924 [39], but the new synthetic procedure and the spectroscopic characterization data are provided in ESI for completeness. 1*H*,1'*H*-1,1'-carbonyl-di-indazole was then reacted with benzaldehyde under neat conditions in the presence of CoCl_2 to afford the final bis(indazol-1-yl)phenylmethane ligand (see ESI for experimental details). It is worth noting that the same compound was previously obtained

from the reaction of 1*H*-indazole with benzaldehyde in the presence of ZnCl₂, or with benzaldehyde dimethyl acetal in the presence of toluene-4-sulfonic acid, or with benzylidene dichloride in the presence of NaOH [40].

Electrochemical measurements on bis(indazol-1-yl)phenylmethane showed an irreversible reduction peak around -2.6 V vs. Fc/Fc⁺ using acetone as solvent and glassy carbon as working electrode. From the onset of the peak, the energy of the LUMO was estimated around -2.6 eV [41]. On the basis of DFT calculations, the LUMO and LUMO+1 are π* molecular orbitals localized on the indazole fragments.

Bis(indazol-1-yl)phenylmethane (N[^]N) was reacted with the copper precursors CuCl or [Cu(NCCH₃)₄][BF₄] under mild conditions, and in both the cases the homoleptic complex [Cu(N[^]N)₂]⁺ (X = Cl, BF₄) was isolated. The reactions affording the ligand and the corresponding complex are summarized in Scheme 1 for clarity.



Scheme 1. Synthesis of N[^]N and of [Cu(N[^]N)₂]⁺.

Experimental details and characterization data are reported in ESI. Elemental analyses are in agreement with the proposed formula and conductivity measurements indicate that the complexes behave as 1:1 electrolytes. DSC-TGA measurements on [Cu(N[^]N)₂]Cl showed that, after

the melting at 155 °C, the compound start decomposing, as evidenced by the progressive weight loss (see Figure S1).

The IR spectrum shows bands comparable to those of the free ligand, with the addition of the ν_{BF_4} stretching between 1180 and 1050 cm^{-1} in the case of $X = \text{BF}_4$ [42]. The most diagnostic signals fall between 1620 and 1450 cm^{-1} and are related to $\nu_{\text{C}=\text{N}}$ and $\nu_{\text{C}=\text{C}}$ stretchings. The ^1H NMR spectra do not show any signal attributable to coordinated acetonitrile, and the resonances of the coordinated $\text{N}^{\wedge}\text{N}$ ligands in DMSO-d_6 solution are broad at 298 K, becoming sharp on heating the sample above 330 K and revealing that the two coordinated ligands are equivalent on the NMR timescale (Figure 1). Diagnostic signals are the singlets related to the methine fragment at 9.23 ppm and to the indazole-CH at 8.18 ppm at 338 K. It is worth noting that broad resonances were detected for $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]\text{Cl}$ also in CDCl_3 solution in the temperature range 213 – 318 K (Figure S2). NMR data therefore suggest fluxional behaviour of the complex in solution.

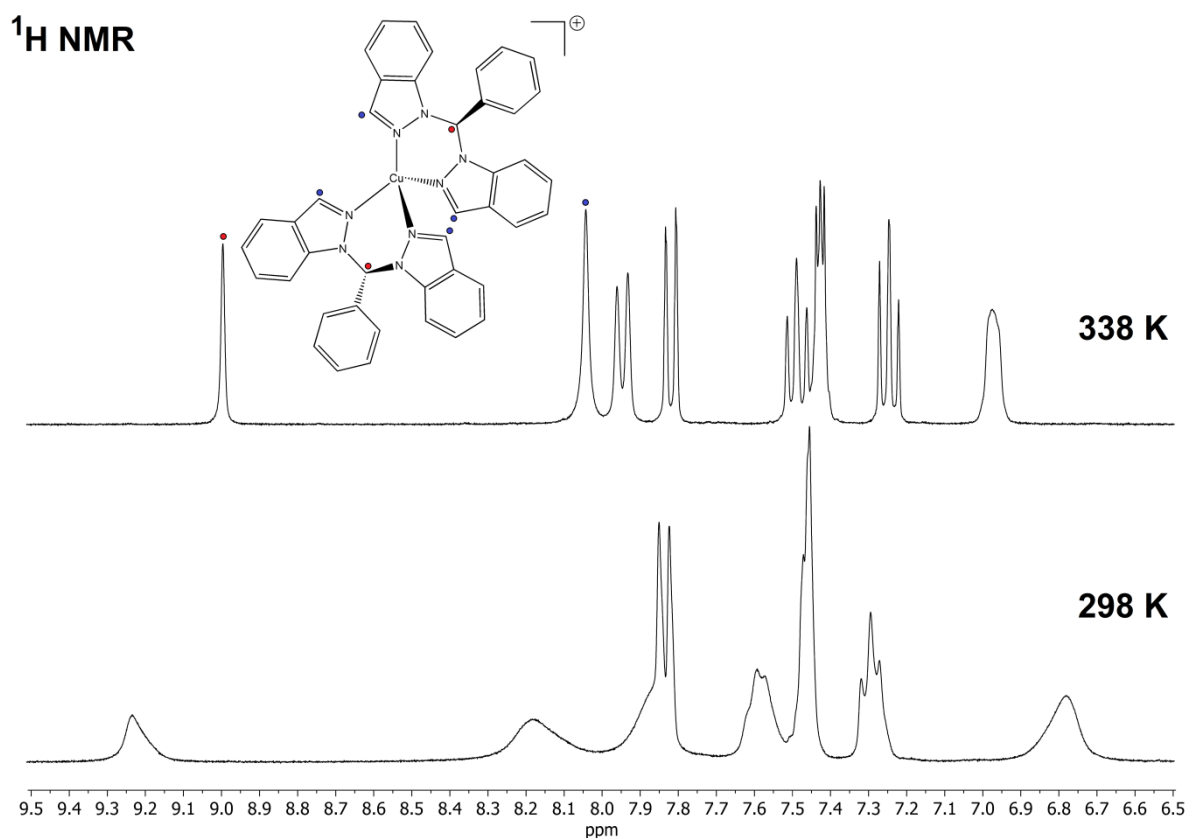


Fig. 1. ^1H NMR spectra of $[\text{Cu}(\text{N}^{\wedge}\text{N})_2][\text{BF}_4]$ in DMSO-d_6 at 298 and 338 K.

The unambiguous characterization of the complex was obtained from single crystal X-ray structure determination of $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]\text{Cl}$. Figure 2 shows an ORTEP [43] view of the cation found in the compound. Selected distances and angles are set out in Table 1. The cation complex consists of two bidentate neutral 1,1'-(phenylmethylene)bis(1*H*-indazole) ligands coordinating a copper(I) atom in a distorted tetrahedral fashion (see below). Cu-N bond distances are between 2.026(2) and 2.033(2) Å, a narrow range consistent with the oxidation state for the copper atom and similar to those found in other four coordinated compounds with bis(pyrazol-1-yl) [44-48] or tris(pyrazol-1-yl) [49-50] ligands. Bond-valence calculation [51] performed with PLATON [52-53] gives for the Cu atom a value of 1.007, in agreement with the oxidation state 1+ for it. The angle between chelating CuN12N22 and CuN42N52 planes (expected 90° for perfect tetrahedron) is 81.75(84)°, somewhat far from the value of 74.5° found in the related $[\text{Cu}^{\text{I}}(\text{H}_2\text{CPz}_2)_2][\text{ClO}_4]$ ($\text{H}_2\text{CPz}_2 = \text{bis}(\text{pyrazol-1-yl})\text{methane}$) [44] compound. In other words, $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]^+$ is less planar and closer to tetrahedron regularity than the bis(pyrazol-yl)methane compound. Accordingly, the τ_4 -descriptor for 4-coordination [54] is 0.70 (extreme forms: 0.00 for square planar, 1.00 for tetrahedron and 0.85 for trigonal pyramid), so the polyhedron around copper atom is best described as a distorted seesaw with a N(22)-Cu-N(42) angle of 130.87(8)° and, almost perpendicular, a N(12)-Cu-N(52) angle of 116.99(8)°. Dihedral angle between these planes, CuN22N42 and CuN12N52 ones, is 76.96(9)°. Figure S3 shows the seesaw geometry. On the other hand, the chelate angles are 92.19(8) and 92.62(8)°, only slightly lower than those found in the related bis(pyrazol-1-yl)methane compound, 94.1° [44]. The chelate rings adopt a boat conformation with the methylene [0.437(2) and 0.431(3) Å] and the copper atom [0.4161(10) and 0.3966(10) Å] above the best plane. The phenyl rings are in axial position with respect to the plane, angles of 11.37(13) and 10.98(16)° with the normal of each plane. Figure S4 shows these features.

As stated in the ESI, the chloride anion could not be modelled, so the interactions between cation and anion could not be studied. However, the cations are connected by means of π,π -stacking interactions between the indazol-1-yl moieties. Figure S5 shows one of them, causing the growth of the crystal along the *a* axis. This π,π -interaction (symm. op. $x-0.5, y, 0.5-z$ and $x+0.5, y, 0.5-z$) leaves a distance between centroids of the benzene rings of 3.772(2) Å and a slippage of 1.021 Å. The dihedral angle between planes is 13.70(14)°. Other interesting interactions between planes (See Figure S6) are those formed between one indazol-1-yl ring and its symmetrical equivalent

(symm. op. 0.5-x, 0.5-y, 0.5-z), which generates dimeric entities. The distance between centroids is 4.139(2) Å and the ring slippage is 1.181 Å. The dihedral angle between planes is 1.7 (2)°.

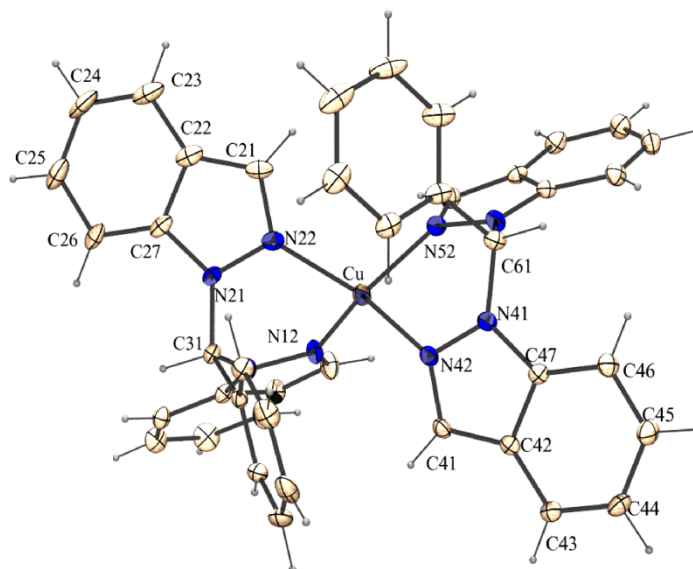


Fig. 2. ORTEP view of the cation found in $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]\text{Cl}$. Atoms are drawn at 30% probability level.

Table 1. Selected bond lengths [Å] and angles [°] for $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]\text{Cl}$.

Cu-N(12)	2.032(2)	Cu-N(22)	2.030(2)
Cu-N(42)	2.026(2)	Cu-N(52)	2.033(2)
N(12)-Cu-N(22)	92.19(8)	N(12)-Cu-N(42)	113.93(9)
N(12)-Cu-N(52)	116.99(8)	N(22)-Cu-N(42)	130.87(8)
N(22)-Cu-N(52)	112.28(9)	N(42)-Cu-N(52)	92.62(8)

$[\text{Cu}(\text{N}^{\wedge}\text{N})_2]^+$ absorbs light in CH_2Cl_2 and DMSO solution for wavelengths below 410 nm. As observable in Figure 3, the use of a coordinating solvent such as DMSO changes the absorption features, being markedly less pronounced the band centred around 329 nm. This outcome suggests that the lowest energy absorption could be related to charge transfer between metal centre and coordinated ligands. TD-DFT calculations clearly indicated that the lowest energy singlet transition has MLCT character, involving metal-centred occupied molecular orbitals (HOMO, HOMO-1) and unoccupied π^* orbitals localized on the indazol-1-yl fragments (LUMO, LUMO+1, LUMO+12 and LUMO+13), depicted for clarity in Figure S7. Figure 3 shows as example the superposition of the HOMO-1 (green) and of the LUMO (yellow).

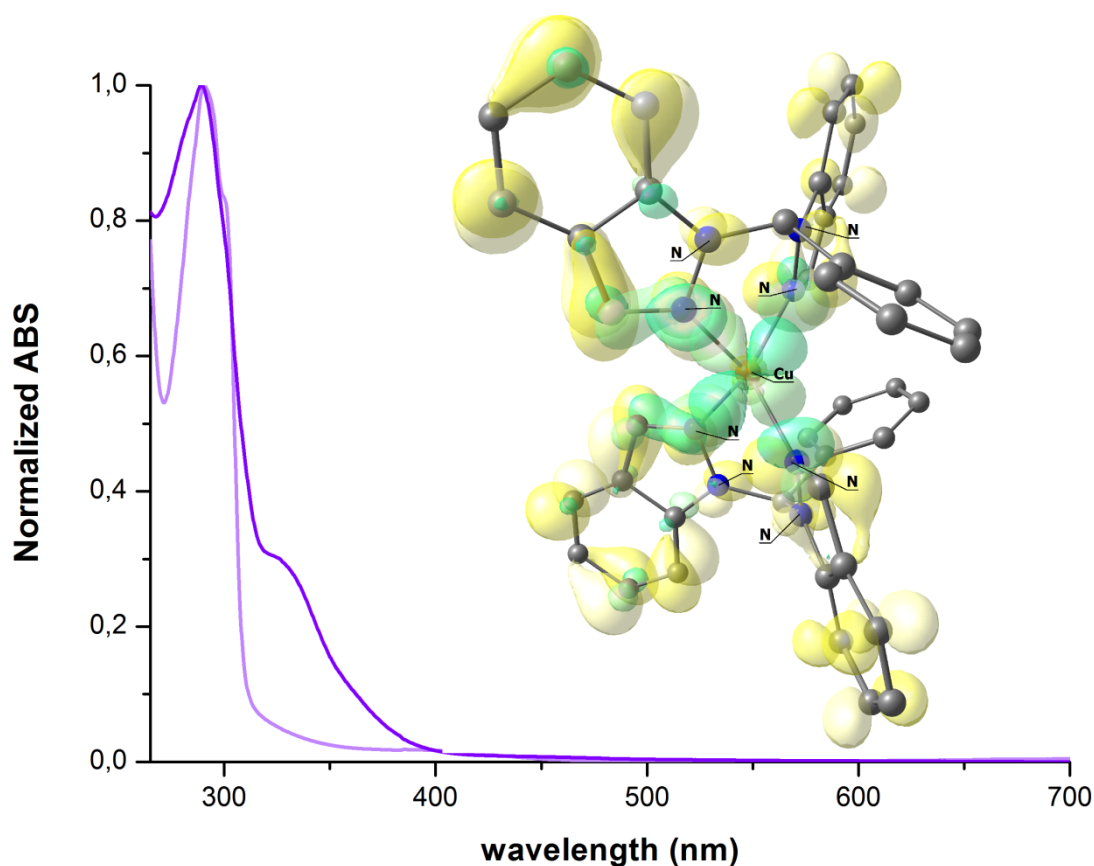


Fig. 3. Normalized absorption spectra of $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]^+$ in DMSO (light violet line) and CH_2Cl_2 (violet line). DFT-optimized structure of $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]^+$ ($\omega\text{B97X}/\text{def2-SVP}$ calculation) with superimposed HOMO-1 (green) and LUMO (yellow). Surface isovalue = 0.03 a.u. Hydrogen atoms are omitted for clarity.

Solid $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]\text{X}$ complexes exhibit bright yellow emission upon excitation with near-UV and violet light. The maximum of the emission band (PL, Figure 4) lies at 565 nm and the FWHM is 4600 cm^{-1} . The emission from $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]\text{X}$ can be obtained for excitation wavelengths below 450 nm, as observable in the excitation (PLE) spectrum reported in Figure 4, with PLE maximum at 386 nm. The emission spectrum remains constant on varying the excitation wavelength in the PLE range and, as observable in Figure 4, it is independent upon the nature of the counterion. Powder and crystals of the compound show the same photoluminescence features. The CIE 1931 chromaticity coordinates are $x = 0.437$, $y = 0.477$, falling between the yellow and the yellowish orange regions of the diagram in Figure 4.

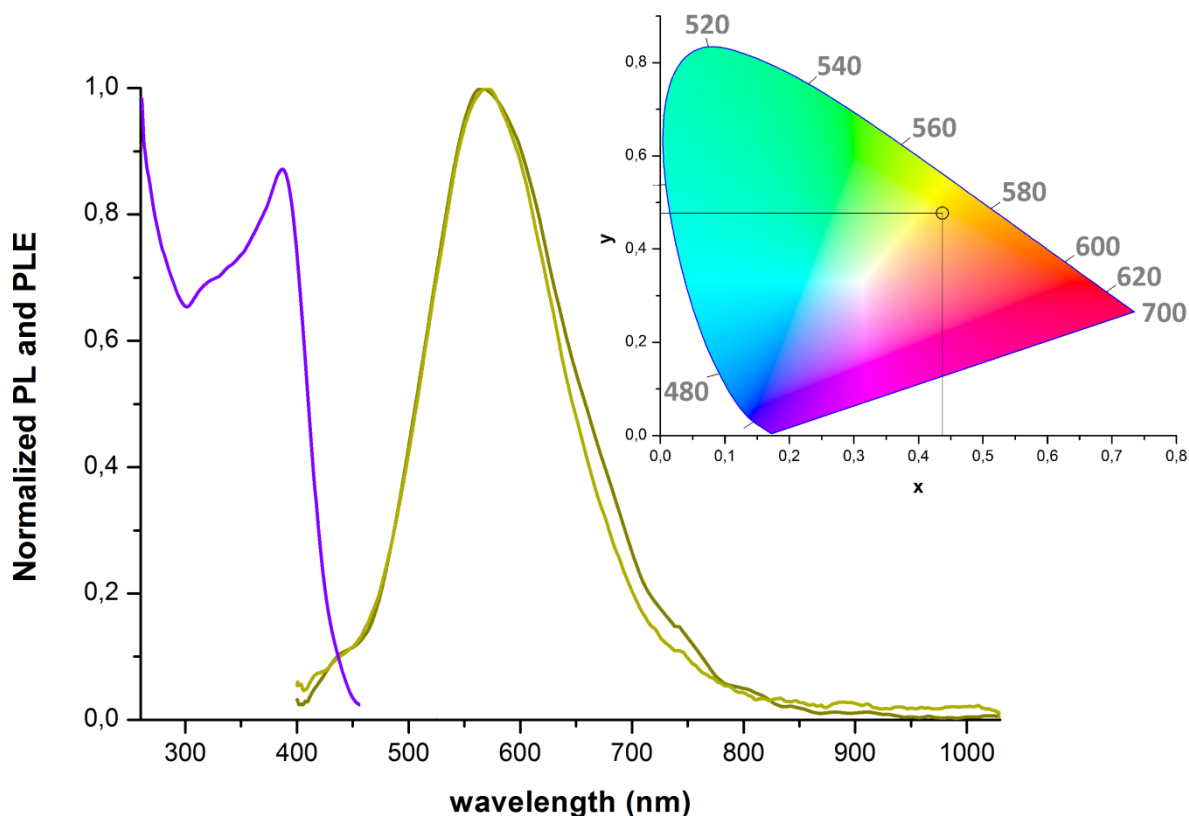


Fig. 4. Normalized PLE (violet line, $\lambda_{\text{emission}} = 600$ nm) and PL spectra ($\lambda_{\text{excitation}} = 375$ nm) of $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]\text{X}$ (X = Cl, yellow line; X = BF_4 , dark yellow line) and CIE 1931 chromaticity diagram.

The time-resolved photoluminescence spectrum reported in Figure 5 clearly shows the presence of two decay components, characterized by τ values of 12 (63%) and 73 μs (37%), respectively. The average lifetime is 35 μs . The tenths of microseconds range indicate that triplet excited states are involved. Biexponential decay is quite common for luminescent Cu(I) complexes, recent examples being oligophosphine-thiocyanate derivatives [55] and PNP coordination compounds [56]. In the case of $[\text{Cu}(\text{TP})(\text{PPh}_3)_2]^+$, where TP = 2-(1H-tetrazol-5-yl)pyridine, the two lifetimes were assigned as the triplet decays of MLCT and LLCT excited states [57]. For what concerns $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]^+$, the TD-DFT optimized geometries of the first (T1) and second (T2) triplet states agree with $^3\text{LLCT}/^3\text{MLCT}$ transitions, being the electronic structures described by the electron transfer from Cu- and indazole-centred molecular orbitals (mainly HOMO, HOMO-1 and HOMO-2) to indazole-localized unoccupied orbitals (mainly LUMO). The orbitals most involved are depicted in see Figure 5. T1 and T2 states have quite similar geometry, as depicted in Figure S8, and the poor rigidity of the molecule was indicated by NMR studies. The energy difference between the two excited states at

T2 geometry is only 470 cm^{-1} , therefore both T1 and T2 appear reasonably involved in the emission from the complex.

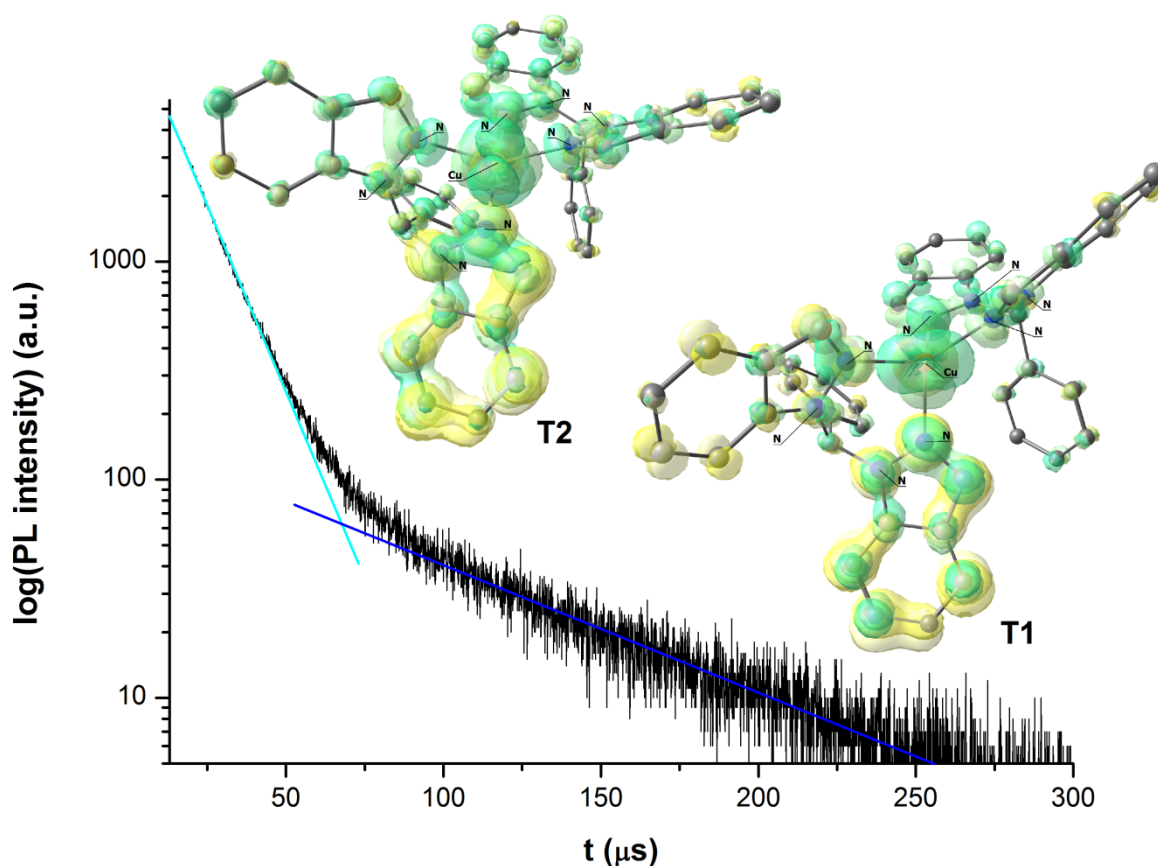


Fig. 5. Semi-log plot of the time-resolved luminescence decay of $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]\text{Cl}$. TD-DFT-optimized structures of T1 and T2 states of $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]^+$ ($\omega\text{B97X}/\text{def2-SVP}$ calculation). Superimposed orbitals for T1: HOMO-2 and HOMO (green), LUMO (yellow). Superimposed orbitals for T2: HOMO-1 and HOMO (green), LUMO (yellow). Surface isovalue = 0.03 a.u. Hydrogen atoms are omitted for clarity.

The photoluminescence quantum yield (PLQY) measured at room temperature for powder samples is 1.3%. The radiative (k^r) and non-radiative (k^{nr}) rate constants are estimated on the basis of the equation $\text{PLQY} = k^r/(k^r+k^{nr}) = \tau^m k^r$ [5] to be $k^r = 3.7 \cdot 10^2 \text{ s}^{-1}$ and $k^{nr} = 2.8 \cdot 10^4 \text{ s}^{-1}$. The low quantum yield can be explained on considering the scarce rigidity of the molecule and its distortion towards square planar geometry [9], evident for the T2 excited state, with τ_4 parameter of 0.44 [54]. Both these factors favour non-radiative decay routes.

In conclusion, in this communication we described the straightforward preparation and characterization of a new copper(I) homoleptic complex, representing the first example of luminescent species with a ligand based on the bis(indazol-1-yl)methane skeleton. Lifetime measurements indicate that the photophysical features are based on the population of triplet states. The non-radiative decay appears related to the distortion of the first coordination sphere, and it is therefore likely to suppose that proper modifications of the bulk of the donor moieties could improve the photoluminescence quantum yield.

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Appendix A. Supplementary data

Experimental and computational details. Analytical and spectroscopic data. Crystal data (Table S1). Thermogravimetric analysis (Fig. S1). Variable-temperature NMR spectra (Fig. S2). Views of the X-ray structure and of the solid-state intermolecular interactions (Fig. S3-S6). Selected molecular orbitals of $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]^+$ (Fig. S7). Comparison of T1 and T2 geometries (Fig. S8). Cartesian coordinates of the DFT and TD-DFT optimized structures.

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