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

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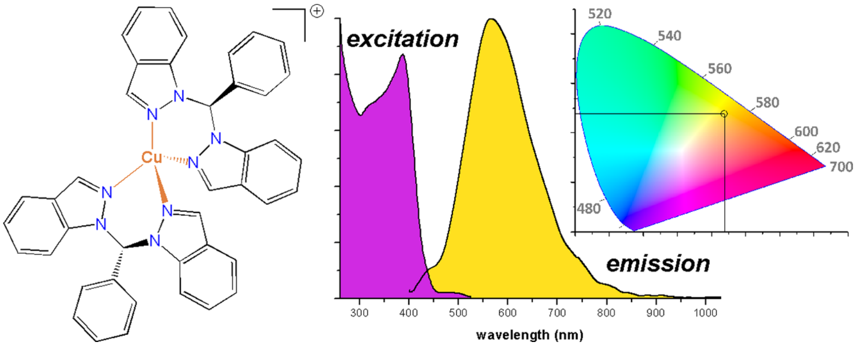
GRAPHICAL ABSTRACT



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ABSTRACT

The cationic Cu(I) complex $[Cu(N\hat{}N)_2]^+$, where N^N is bis(indazol-1-yl)phenylmethane, was synthesized as chloride or tetrafluoroborate salt by reacting CuCl or $[Cu(NCCH_3)_4][BF_4]$ with bis(indazol-1-yl)phenylmethane under mild conditions. The structure of $[Cu(N\hat{}N)_2]Cl$ 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.

1. 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 Cu(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-phenathroline 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 $[Cu(phen^R)_2]^+$ [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.

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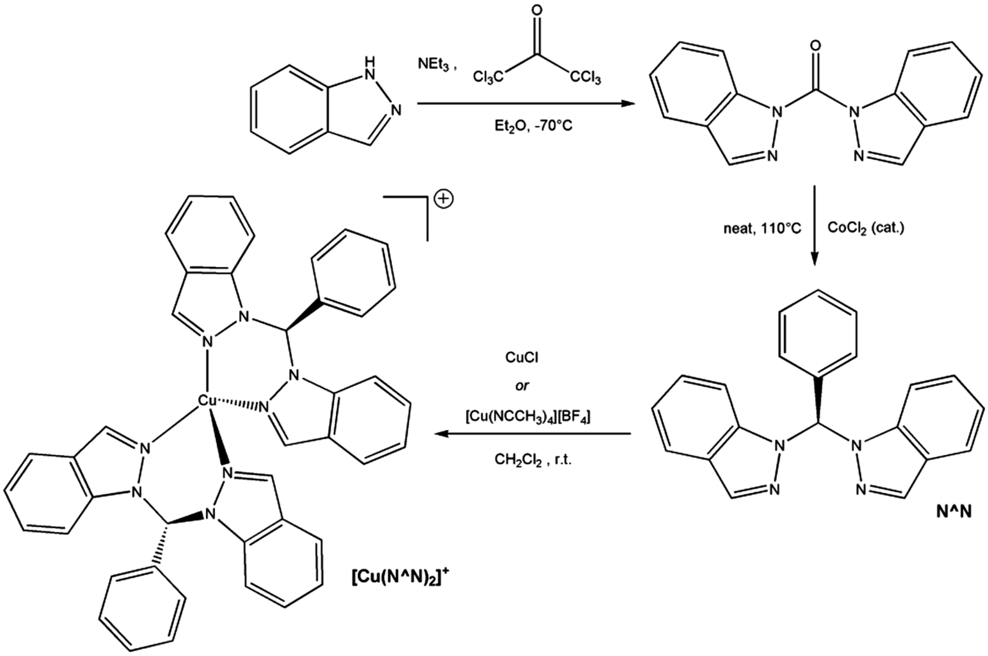

Scheme 1. Synthesis of NˆN and of [Cu(NˆN)$_2$]$^+$.

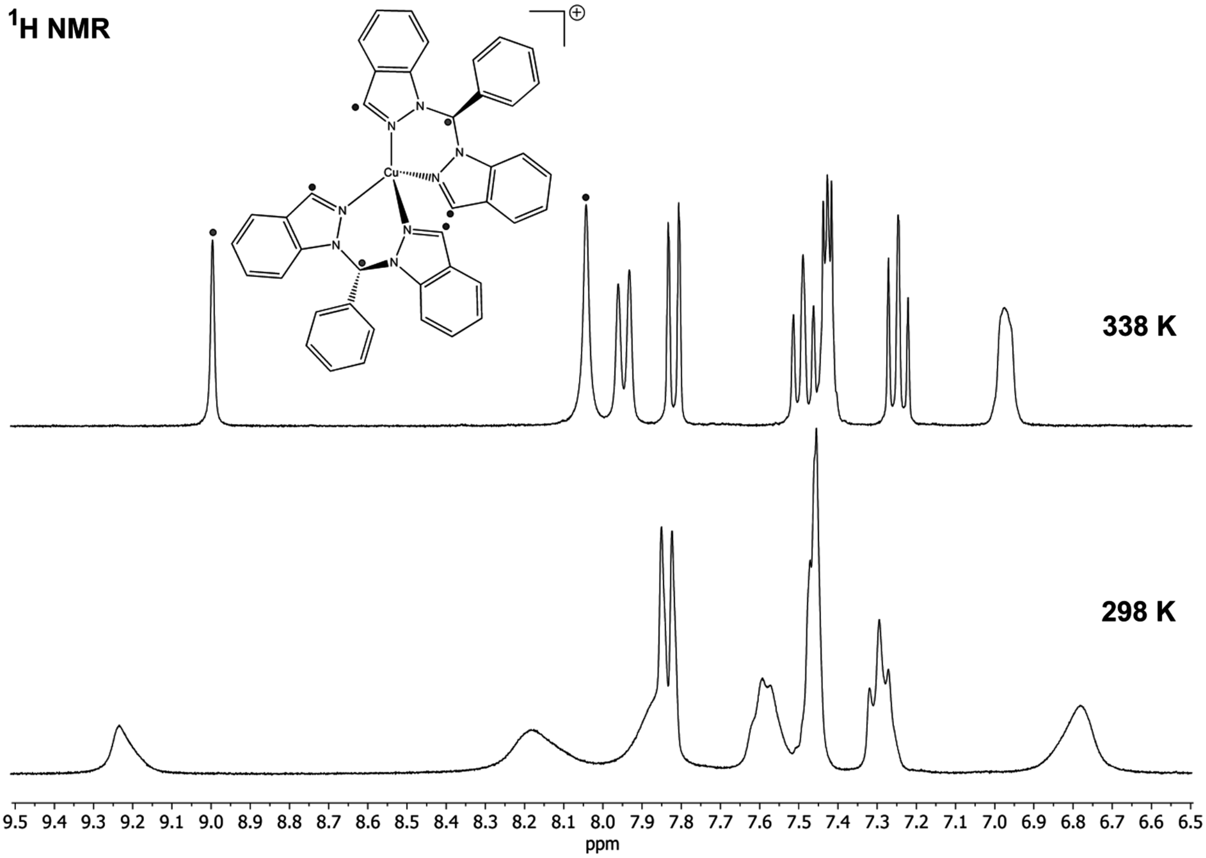

Fig. 1. ^{1}H NMR spectra of [Cu(NˆN)$_2$][BF$_4$] in DMSO-d_6 at 298 and 338 K.

Focusing the attention on azoles, pyrazole-based ligands showed interesting features, allowing for instance the isolation of luminescent mono- and polynuclear Cu(I) halide complexes with coordination numbers three and four [19–21]. N-donor ligands containing the comparable indazole heterocycle recently showed to be viable alternatives to polypyridines for the preparation of luminescent Cu(I) complexes, despite the fact that most of the studies actually reported in literature are focused on Cu(II) derivatives [22–31]. In particular, homo- and heteroleptic compounds with indazolyl-imine ligands were reported by Cabrera and co-workers [32,33]. 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

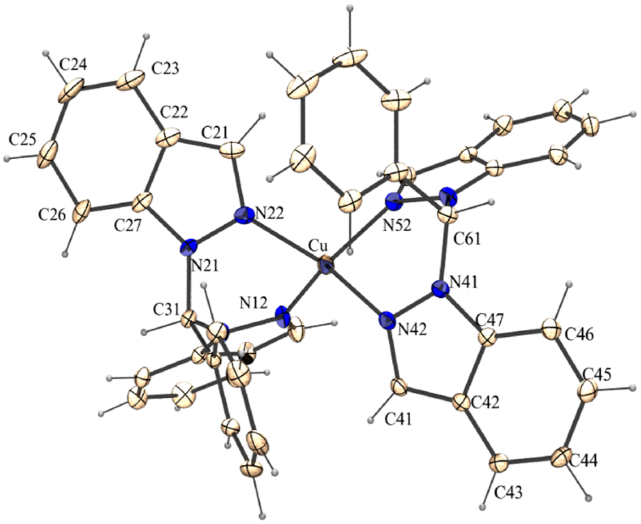

Fig. 2. ORTEP view of the cation found in [Cu(N^N)$_2$]Cl. Atoms are drawn at 30% probability level.

Table 1
Selected bond lengths [Å] and angles [°] for [Cu(N^N)$_2$]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)

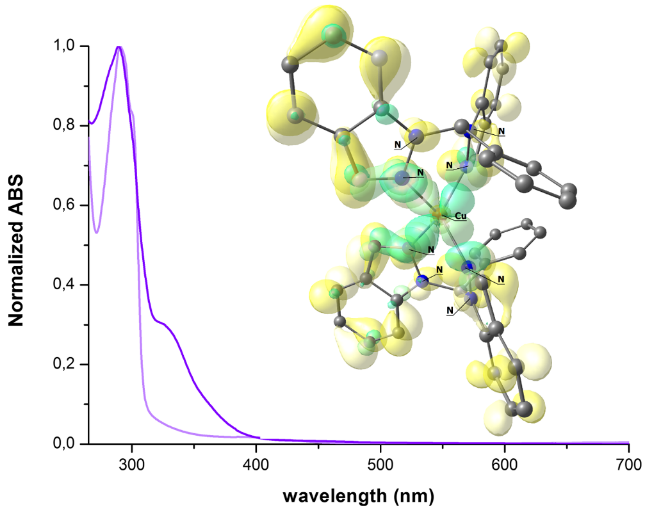

Fig. 3. Normalized absorption spectra of [Cu(N^N)$_2$]$^+$ in DMSO (light violet line) and CH$_2$Cl$_2$ (violet line). DFT-optimized structure of [Cu(N^N)$_2$]$^+$ (ωB97X/def2-SVP calculation) with superimposed HOMO-1 (green) and LUMO (yellow). Surface isovalue = 0.03 a.u. Hydrogen atoms are omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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 [34]. Comparable ligands were less investigated, for instance bis(indazol-1-yl)phenylmethane was used only for the preparation of a Rh(I) derivative [35].

We developed an improved synthetic method for the preparation of bis(benzotriazol-1-yl)arylmethane ligands [36], 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 [37–41], we investigated the reaction between Cu (I) precursors and the ligand bis(indazol-1-yl)phenylmethane (N^N), obtaining the photoluminescent homoleptic complex [Cu(N^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 [42], 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 ZnCl$_2$, or with benzaldehyde dimethyl acetal in the presence of toluene-4-sulfonic acid, or with benzylidene dichloride in the presence of NaOH [43]. Characterization data are summarized in ESI (see Fig. S1 for the HSQC NMR spectrum).

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 [44]. 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 precursors CuCl or [Cu(NCCH$_3$)$_4$][BF$_4$] under mild conditions, and in both the cases the homoleptic complex [Cu(N^N)$_2$]X (X = Cl, BF$_4$) was isolated. The reactions affording the ligand and the corresponding complex are summarized in Scheme 1 for clarity.

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 melting at 155 °C, the compound starts decomposing, as evidenced by the progressive weight loss (see Fig. S2).

The IR spectrum shows bands comparable to those of the free ligand, with the addition of the υ_{BF4} stretching between 1180 and 1050 cm^{-1} in the case of X = BF$_4$ [45]. The most diagnostic signals fall between 1620 and 1450 cm^{-1} and are related to $\upsilon_{C=N}$ and $\upsilon_{C=C}$ stretching vibrations. The ^{1}H NMR spectra do not show any signal attributable to coordinated acetonitrile, and the resonances of the coordinated N^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 (Fig. 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 [Cu(N^N)$_2$]Cl also in CDCl$_3$ solution in the temperature range 213–318 K (Fig. S3). NMR data therefore suggest fluxional behaviour of the complex in solution.

The unambiguous characterization of the complex was obtained from single crystal X-ray structure determination of [Cu(N^N)$_2$]Cl. Fig. 2 shows an ORTEP [46] 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 Cu(I) 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) [47–51] or tris(pyrazol-1-yl) [52,53] ligands. Bond-valence calculation [54] performed with PLATON [55,56] 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

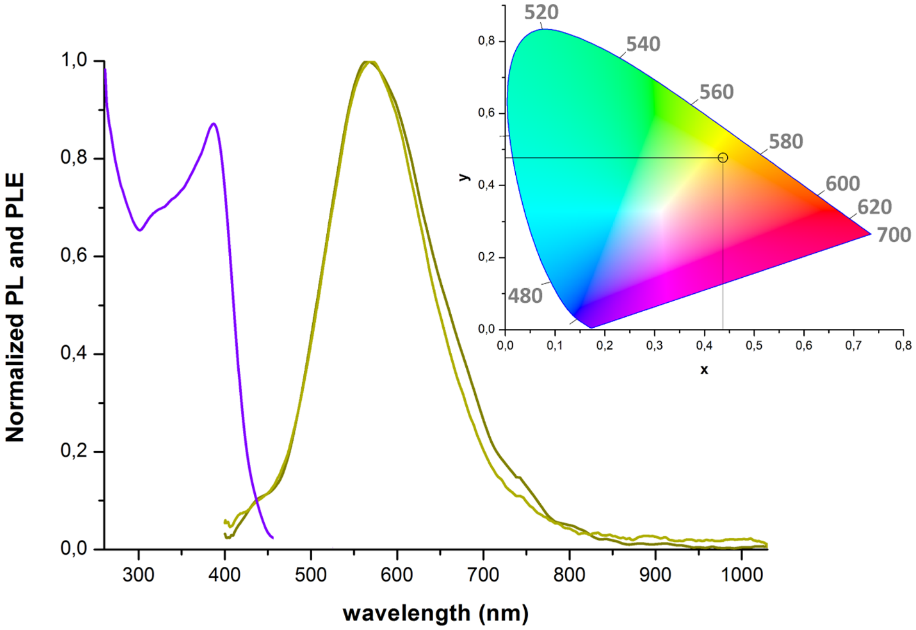

Fig. 4. Normalized PLE (violet line, $\lambda_{emission}$ = 600 nm) and PL spectra ($\lambda_{excitation}$ = 375 nm) of [Cu(NˆN)$_2$]X (X = Cl, yellow line; X = BF$_4$, dark yellow line) and CIE 1931 chromaticity diagram. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the value of 74.5° found in the related [Cu^I(H$_2$CPz$_2$)$_2$][ClO$_4$] (H$_2$CPz$_2$ = bis(pyrazol-1-yl)methane) [47] compound. In other words, [Cu(NˆN)$_2$]$^+$ is less planar and closer to tetrahedron regularity than the bis(pyrazol-yl)methane compound. Accordingly, the τ_4-descriptor for 4-coordination [57] 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)°. Fig. S4 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° [47]. 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. Fig. S5 shows these features.

As stated in the ESI, the position of the chloride anion resulted to be disordered and therefore it 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. Fig. S6 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 Fig. S7) 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)°.

[Cu(NˆN)$_2$]$^+$ absorbs light in CH$_2$Cl$_2$ and DMSO solution for wavelengths below 410 nm. As observable in Fig. 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 Fig. S8. Fig. 3 shows as example the superposition of the HOMO-1 (green) and of the LUMO (yellow).

Solid [Cu(NˆN)$_2$]X complexes exhibit bright yellow emission upon excitation with near-UV and violet light. The maximum of the emission band (PL, Fig. 4) lies at 565 nm and the FWHM is 4600 cm^{-1}. The emission from [Cu(NˆN)$_2$]X can be obtained for excitation wavelengths below 450 nm, as observable in the excitation (PLE) spectrum reported in Fig. 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 Fig. 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 Fig. 4.

The time-resolved photoluminescence spectrum reported in Fig. 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 [58] and PNP coordination compounds [59]. In the case of [Cu(TP)(PPh$_3$)$_2$]$^+$, where TP = 2-(1*H*-tetrazol-5-yl)pyridine, the two lifetimes were assigned as the triplet decays of MLCT and LLCT excited states [60]. For what concerns [Cu(NˆN)$_2$]$^+$, the TD-DFT optimized geometries of the first (T1) and second (T2) triplet states agree with ^{3}LLCT/^{3}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 Fig. 5. T1 and T2 states have quite similar geometry, as depicted in Fig. S9, 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.

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 PLQY = $k^r/(k^r + k^{nr}) = \tau^m k^r$ [5] to be $k^r = 3.7 \cdot 10^2$ s^{-1} and

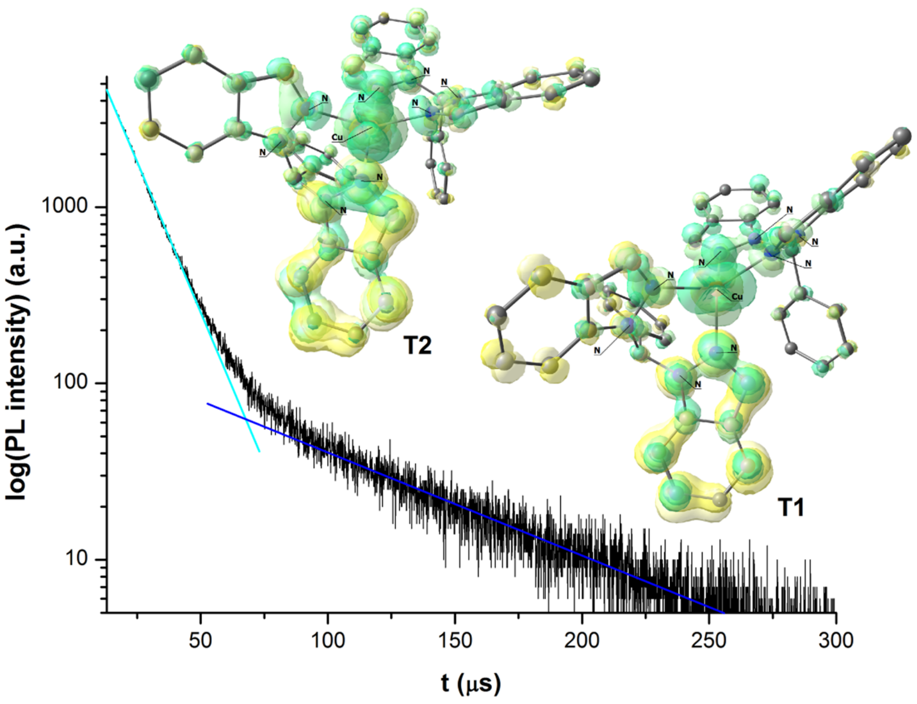

Fig. 5. Semi-log plot of the time-resolved luminescence decay of $[Cu(N^\wedge N)_2]Cl$. TD-DFT-optimized structures of T1 and T2 states of $[Cu(N^\wedge N)_2]^+$ (ωB97X/def2-SVP calculation). Superimposed orbitals for T1: HOMO-2 and HOMO (green), LUMO (yellow). Superimposed orbitals for T2: HOMO-1 and HOMO (green), LUMO (yellow). Surface isovalue = 0.03 a.u. Hydrogen atoms are omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Absorption and photoluminescence data of $[Cu(N^\wedge N)_2]X$.

X = Cl	X = BF_4
UV–VIS (CH_2Cl_2, 298 K, nm) < 410, 288 (max), 329 (sh). **PL** (solid, r.t., $\lambda_{excitation}$ = 375 nm, nm) 565 (FWHM = 4600 cm^{-1}). **CIE 1931**: x = 0.437, y = 0.477. **PLE** (solid, $\lambda_{emission}$ = 600 nm, nm) < 450, 389 (max). τ (solid, r.t., $\lambda_{excitation}$ = 317 nm, $\lambda_{emission}$ = 635 nm, μs): 12 (63%), 73 (37%). **PLQY**: 1.3%. **k^r** = $3.7{\cdot}10^2$ s^{-1}. **k^{nr}** = $2.8{\cdot}10^4$ s^{-1}.	**UV–VIS** (DMSO, 298 K, nm) < 410, 291 (max), 298 (sh), 311 (sh) **PL** (solid, r.t., $\lambda_{excitation}$ = 375 nm, nm) 565 (FWHM = 4600 cm^{-1}). **CIE 1931**: x = 0.437, y = 0.477. **PLE** (solid, $\lambda_{emission}$ = 600 nm, nm) < 450, 389 (max).

k^{nr} = $2.8{\cdot}10^4$ 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 [57]. Both these factors favour non-radiative decay routes. The photoluminescence data are summarized in Table 2.

In conclusion, in this communication we described the straightforward preparation and characterization of a new Cu(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.

CRediT authorship contribution statement

Valentina Ferraro: Conceptualization, Investigation, Supervision. **Marco Bortoluzzi:** Conceptualization, Investigation, Funding acquisition, Formal analysis. **Jesús Castro:** Investigation, Formal analysis. **Alberto Vomiero:** Investigation. **Shujie You:** Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.inoche.2020.107894.

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