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Outstanding luminescence from neutral copper(I) complexes with pyridyl-tetrazolate and phosphine ligands†

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Strongly luminescent, neutral copper(I) complexes bearing 5-(2-pyridyl)-tetrazolate and various phosphine ligands were synthesized. While the cationic copper(I) precursors 1b–4b do not exceed photoluminescence quantum yields (PLQY) of 4–46%, the neutral complexes 1a–4a show PLQYs of up to 89%.

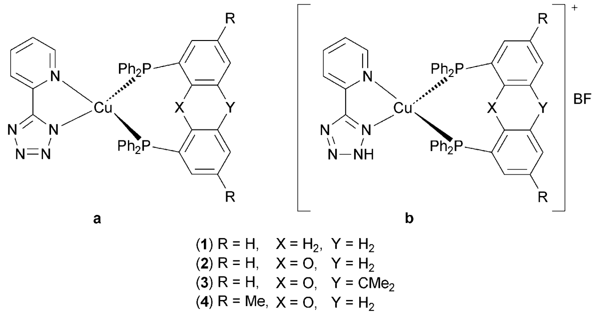

Fig. 1 Molecular structures of **1a–4a** and **1b–4b**. For **2b** the molecular formula $[(DPEPhos)_2Cu_2(PyrTet)_2H]BF_4$ was determined using elemental and X-ray analysis.

Luminescent Cu(I) complexes have gained increasing interest for their application in organic light emitting devices (OLEDs), as they offer a new path to efficient emitters that can make use of both singlet and triplet excitons.[1] Their structural diversity and easy accessibility allow for designing emitters with desired properties like emission colour or additional functionalities while maintaining high efficiencies.[1b,2] In contrast to their charged counterparts, mononuclear, neutral Cu(I) complexes are favourable emitters for OLED applications due to their superior emission characteristics[3] and the lack of mobile counterions, which can have a negative influence on the device performance.[4] So far, only a few examples of neutral Cu(I) complexes have proven their suitability for OLEDs,[5] but they still suffer from disadvantages. On the one hand, their high sensitivity towards oxygen complicates synthesis,[3c,d,6] while on the other hand their susceptibility to structural changes in the excited state and a subsequent non-radiative decay result in low quantum yields.[7]

Herein, we present four neutral, mononuclear Cu(I) complexes **1a–4a** with high PLQYs (ϕ_{em}) and good stability towards oxygen, and compare them to their cationic precursors **1b–4b**, which show only moderate luminescence properties (Fig. 1). All neutral Cu(I) complexes contain 5-(2-pyridyl)tetrazolate (PyrTet) as a chromophoric N^N ligand, which has been chosen as a model ligand since its soft base character favours strong binding to the soft Cu(I) centre (HSAB concept),[8] leading to reduced sensitivity towards oxygen, while offering protonation sites at the same time. Tetrazole-containing ligands have been used for the preparation of cationic Cu(I) complexes lately,[2a,9] but not yet for neutral ones. In addition to aforementioned advantages, tetrazoles show high acidity due to their mesomeric structure, which simplifies the synthesis of the complexes, due to the need for only mild bases for deprotonation. While PyrTet was used as the chromophoric ligand, several neutral and bulky phosphine ligands were tested, which are also soft Lewis bases. They provide mostly steric advantages,[3b] inhibiting flattening of the complex in the excited state. Either commercially available or easily accessible phosphines with different steric demands and rigidity were used to synthesize the presented Cu(I) complexes: triphenylphosphine (PPh_3), bis[2-(diphenylphosphino)phenyl]ether (DPEPhos), 9,9-dimethyl-4,6-bis(diphenylphosphino)xanthene (Xantphos) and bis[2-(diphenylphosphino)-*p*-tolyl]ether (PTEPhos).

Cationic complexes $[(PPh_3)_2Cu(PyrTetH)]BF_4$ **1b**, $[(DPEPhos)_2Cu_2(PyrTet)_2H]BF_4$ **2b**, [(Xantphos)Cu(PyrTetH)] BF_4 **3b**, and [(PTEPhos)Cu(PyrTetH)]BF_4 **4b** were synthesized from the appropriate ligands and $[Cu(CH_3CN)_4]BF_4$ as a copper source in a 2 : 1 : 1 or 1 : 1 : 1 ratio, respectively. The neutral complexes $[(PPh_3)_2Cu(PyrTet)]$ **1a**, [(DPEPhos)Cu(PyrTet)] **2a**, [(Xantphos)Cu(PyrTet)] **3a**, and [(PTEPhos)Cu(PyrTet)] **4a** were obtained by deprotonation of the tetrazole moieties of the cationic precursors with potassium hydroxide in dry methanol solutions. All complexes are stable under

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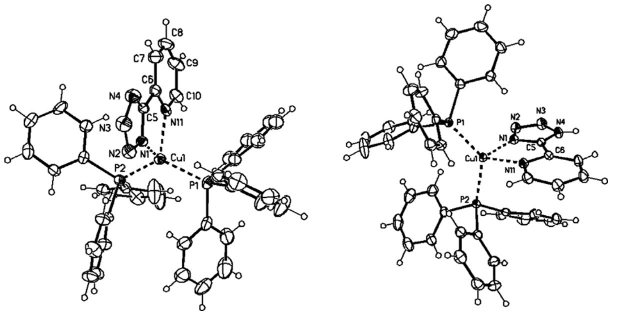

Fig. 2 Molecular structures of **1a** (left) and **1b** (right) (displacement parameters are drawn at 50% probability level). The counterion is omitted for clarity.

ambient conditions in the solid state, and even for days in aerated solution, which is a major improvement for neutral Cu(I) emitters.[3c,d,6] The complexes were characterized using elemental analysis, ^{1}H and ^{31}P NMR and X-ray diffraction if suitable crystals were obtained.

The crystal structures of **1a** and **1b** are shown in Fig. 2, demonstrating the tetrahedral geometry of the complexes, typical for mononuclear Cu(I) complexes.[7d] The comparison of the neutral and cationic species reveals several differences, which arise due to the loss of a proton and the counterion: the Cu–N distances in the neutral complexes are shorter than those in the cationic ones, which can be explained by a stronger coordination of the deprotonated N^N ligand to the metal centre (**1a**: Cu–N1 2.043, Cu–N11 2.118, **1b**: Cu–N1 2.079, Cu–N11 2.140 Å). Associated with this shortening of Cu–N bonds is a decrease in the P1–Cu1–P2 angle along with an increased torsion of the tetrazole ring *versus* the pyridine ring. The Cu–N, Cu–P bond lengths and N1–Cu1–N11 angles of **2a–4a** are similar to the values of **1a**, but the P1–Cu1–P2 angles are slightly smaller due to lower steric hindrance of the bis(phosphines) compared to that of two PPh_3 ligands.[7c] Two isomers with different proton positions are possible for each of the cationic complexes **1b–4b**. The proton of **1b** is located on N4 probably due to steric reasons. In the case of **2b**, the proton is bound to N2 and bridges one cationic and one neutral complex *via* hydrogen bonding in each unit cell (Fig. S1 and Table S1, ESI†).

All complexes exhibit broad and intense absorption bands between 260–281 nm ($\varepsilon = 1.7–2.5 \times 10^4$ M^{-1} cm^{-1}) in dichloromethane solution, which can be attributed to ligand-centred (LC) transitions of the phosphine and PyrTet ligands (Fig. S2, ESI†). A small redshift of these latter bands in neutral complexes (**1a**, **3a**, **4a**) relative to the charged compounds can be explained with the stronger coordination of the PyrTet ligand to Cu(I) after deprotonation, leading to an energetic stabilization of the molecular orbitals involved in the LC transitions. Additional shoulders around 339–341 nm for neutral complexes **1a–4a**, which are not observed for the free ligands, are assigned to metal-to-ligand charge transfer (MLCT) transitions ($\varepsilon = 2.6–5.0 \times 10^3$ M^{-1} cm^{-1}). The corresponding MLCT bands of the cationic complexes **1b–4b** are red-shifted to 347–362 nm ($\varepsilon = 1.7–3.0 \times 10^3$ M^{-1} cm^{-1}).

To explain these experimental results, compounds **1a** and **1b** were chosen as model complexes and studied by means of density functional theory (DFT) calculations using the BP86 functional.[10] As observed in similar complexes,[9] the highest occupied molecular orbital (HOMO) of cationic **1b** is mainly located on the metal centre and the phosphorous atoms, while the lowest unoccupied molecular orbital (LUMO) is located on the PyrTetH ligand. Consequently, the absorption band at 348 nm is assigned to a MLCT transition. The neutral complex **1a** shows a different localization of the frontier orbitals, with the HOMO mainly confined to Cu(I) and the tetrazole moiety with small contributions from the pyridine-N atom, and the LUMO located primarily on the pyridine ring and to a smaller extent on the tetrazole ring (Fig. S3, ESI†). The strong intraligand charge transfer (ILCT) character of these transitions is further confirmed by the hardly detectable MLCT maximum in the absorption spectra of the neutral complex **1a**. Interestingly the phosphines do not contribute to the frontier orbitals, *i.e.* they should not influence the emission wavelength directly.

All of the neutral complexes **1a–4a** show strong luminescence in the green spectral region from 502–545 nm with PLQYs of 76–89% and lifetimes of 17.8–26.6 μs in the solid state (powder) when excited at 350 nm (Table 1); a representative emission spectrum of **2a** is shown in Fig. 3 (Fig. S4, ESI†). The cationic complexes **1b–4b** exhibit red-shifted emission bands from 518–569 nm, in accordance with the DFT calculations (Table S2, ESI†), and significantly decreased PLQYs of 4–46%. A shortening of lifetimes in cationic complexes as seen for **1b–4b** (5.2–15.3 μs) is also observed in a similar study with 2-(2′-quinolyl)benzimidazole as an N^N ligand.[5b] Especially the complexes **3b** and **4b** show strongly red-shifted emission bands accompanied by a strong drop in the PLQY. In addition, the very broad PL emission bands of **3b** and **4b** (full width at half maximum in nm, **1b**: 122; **2b**: 130; **3b**: 145; **4b**: 169) and emission decays with non-resolvable short-lived components indicate two emissive states. When comparing absorption spectra and calculated excitation energies (Fig. S2 and Table S2, ESI†), the experimentally found MLCT bands of **1b** and **2b** fit very well to the calculated values of **1b(N4)** and **2b(N2)**, for which the position of the proton was determined by X-ray analysis. The excitation of the other possible isomers **1b(N2)** and

Table 1 Photophysical properties of **1a–4a** and **1b–4b**

Complex	Absorbance[a] λ_{max} [nm] (ε [10^4 M^{-1} cm^{-1}])	Emission[b] λ_{max} [nm]	$\phi_{em} \pm 0.05$	τ_{ave}[c] [μs]	k_r [s^{-1}]	k_{nr} [s^{-1}]
1a	260 (2.49), 273 (sh, 2.27), 339 (sh, 0.26)	512	0.85	20.6	4.1×10^4	7.3×10^3
2a	265 (2.16), 280 (sh, 2.15), 341 (sh, 0.56)	510	0.78	19.9	3.9×10^4	1.1×10^4
3a	278 (2.39), 341 (0.44)	545	0.76	26.6	2.9×10^4	9.0×10^3
4a	276 (1.92), 340 (sh, 0.50)	502	0.89	17.8	5.0×10^4	6.2×10^3
1b	260 (2.47), 348 (0.17)	522	0.46	13.5	3.4×10^4	4.0×10^4
2b	265 (1.78), 281 (1.69), 347 (sh, 0.30)	518	0.21	15.3	1.4×10^4	5.2×10^4
3b	274 (2.48), 353 (0.23)	559	0.06	5.9[d]	1.0×10^4	1.6×10^5
4b	265 (2.22), 274 (sh, 2.12), 362 (0.25)	569	0.04	5.2[d]	7.7×10^3	1.9×10^5

[a] In CH_2Cl_2, 10^{-5} mol L^{-1}. [b] In the solid state. [c] PL lifetime is composed of two components. For simplicity, a weighted-average lifetime was used (τ_{ave}) and calculated by the equation $\tau_{ave} = \sum A_i\tau_i / \sum A_i$ with A_i as the pre-exponential factor for the lifetime. [d] With short-lived components.

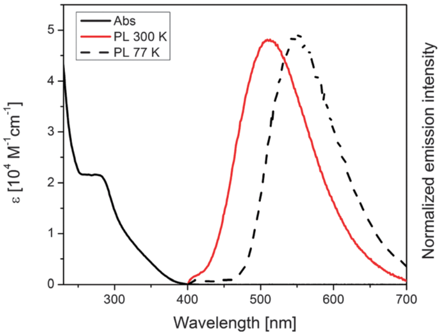

Fig. 3 Absorption spectrum in CH$_2$Cl$_2$ at room temperature and emission spectra in the solid state at different temperatures of **2a**.

2b(**N4**) is predicted to be red-shifted by more than 50 nm, but has not been observed in the experiments. In contrast, the absorption spectrum of **4b** is extended to much longer wavelengths, thus indicating a mixture of isomers. Furthermore, the trend of longer emission wavelengths of **3b** and **4b** compared to those of **1b** and **2b** is confirmed by calculated phosphorescence energies. All these observations lead to the assumption that **3b** and **4b** are present as mixed forms **3b**(**N2**) and **3b**(**N4**), or **4b**(**N2**) and **4b**(**N4**), respectively.

Based on these findings, one can assume that the proton in the cationic complexes not only leads to different emissive states (MLCT *vs.* (ML + IL)CT) but also to less efficient luminescence due to vibrational quenching of the N–H bond on the tetrazole ring,[11] which has already been observed for similar complexes with 2-(2′-quinolyl)benzimidazole ligands.[5b] The fact that two energetically similar complex isomers are possible with the PyrTetH ligand might even lead to lower PLQY. Additionally, counterions in cationic complexes can have a negative influence on the emission properties, when they are in close proximity to the chromophoric moieties.[12]

In general, the neutral Cu(I) complexes **1a–4a** show superior PLQYs due to a strong binding of the anionic PyrTet ligand with soft base character, leading to a rigid complex structure. Similar emission wavelengths for **1a–4a** indicate that the various phosphines hardly have any influence on the emissive states, as predicted by DFT. Their influence is confined to steric aspects, which are mostly reflected in the non-radiative rate constants k_{nr}. While complexes **1a**, with a high mutual steric hindrance of two PPh$_3$ molecules, and **4a**, where the phosphines are linked *via* an ether bridge for rigidity, exhibit low k_{nr} values, complex **3a** shows k_{nr} values almost 50% larger. The most important distortion of tetrahedral Cu(I) complexes in the excited state is considered to be a flattening of the tetrahedral coordination geometry. This flattening is often represented by the change in the dihedral angle between the Cu–N–N and the Cu–P–P planes in the excited state *versus* the ground state. The largest flattening value has been calculated for the least efficient neutral complex **3a** (S$_0$ 90.0°, T$_1$ 55.7°), but it has to be kept in mind that the torsion of the N^N ligand out of plane is not taken into account in this method, which is especially pronounced for **2a** and **4a** (Table S1, ESI†). In any case, there seems to be a correlation between the PLQY and the ligand movement, like in other Cu(I) emitters.

Low temperature measurements were conducted with complex **2a** in the solid state in order to gain a deeper understanding of the emissive states of the neutral species. Upon cooling from 293 K to 77 K, a strong redshift from 510 to 549 nm is observed, and lifetimes increase significantly to 111.5 μs (Fig. 3 and Fig. S5, ESI†), which indicates the effect of thermally activated delayed fluorescence (TADF), which has already been described as Singlet Harvesting for Cu(I) complexes.[1,3a,13] Emission at 293 K occurs from a higher lying singlet state S$_1$, which is in thermal equilibrium with a lower lying triplet state T$_1$, and is repopulated by means of thermal energy $k_{\mathrm{B}}T$.

Electrochemical data obtained from cyclic voltammetry are in good agreement with the experimentally observed high stabilities towards oxygen for neutral complexes **1a–4a**. For **2a** the irreversible oxidation potential is 1.07 eV, which is assumed to be the oxidation of the phosphine ligand. An irreversible reduction peak was found at −0.91 eV (Fig. S6, ESI†).

In conclusion, four mononuclear, neutral Cu(I) complexes with 5-(2-pyridyl)tetrazolate and various phosphine ligands were studied and their photophysical properties were compared to those of their cationic precursor complexes. The neutral compounds show efficient emission from mixed (ML + IL)CT states, with virtually no electronic contribution from the phosphine ligands, which only influence the rigidity of the molecules. Singlet harvesting was shown for **2a** illustratively.

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