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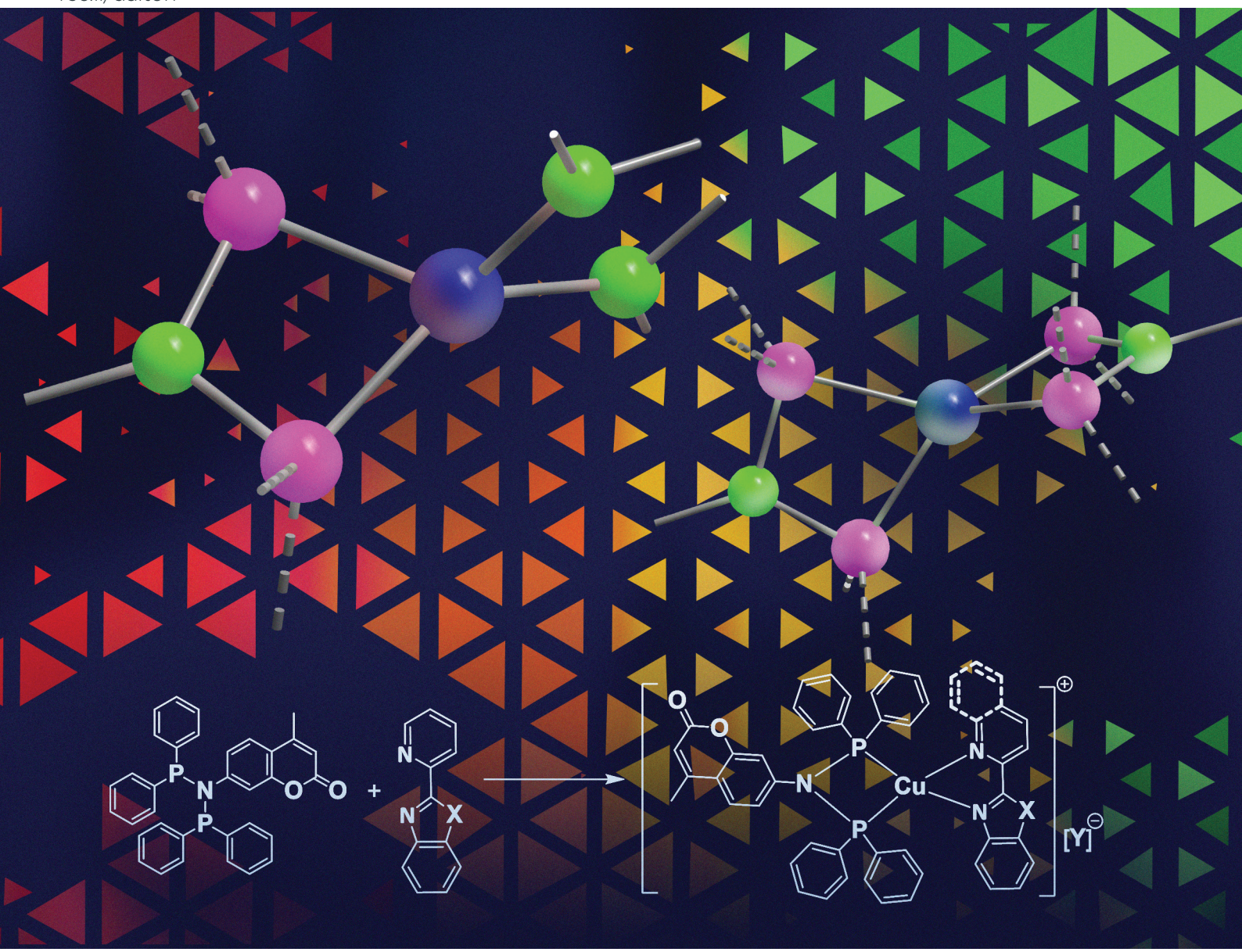

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Heteroleptic copper(I) complexes with coumarin-substituted aminodiphosphine and diimine ligands: synthesis and photophysical studies†

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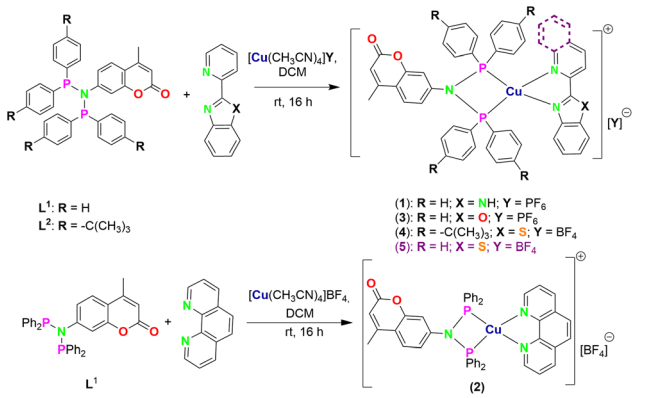
The synthesis of heteroleptic Cu(I) complexes with coumarin-functionalized aminodiphosphine and diimine ligands is described. The complexes show yellow to deep-red phosphorescence in the solid state at ambient temperature with quantum yields up to 21%. The emission color of the complexes can be tuned by systematic modifications in the ligand system.

Introduction

Copper complexes represent a large class of coordination compounds with rich photoluminescence (PL) and electroluminescence properties and high potential for various applications, for instance, as luminescent materials in organic light emitting diodes (OLEDs).[1–4] The iconic group of emissive Cu(I) complexes is undoubtedly that of homoleptic Cu(I)-bisphenanthrolines, which are especially numerous and well studied to date.[5,6] In the last few years, however, heteroleptic Cu(I) complexes, in particular those comprising phosphine and diimine ligands, have gained increased attention.[7,8] It has been well established in the literature that in comparison with related homoleptic structures, a combination of phosphine and diimine ligands may lead to stabilization of the excited state geometry (decreasing flattening distortion due to the oxidation of Cu(I) to Cu(II)) and thereby to enhanced PL properties.[9–12]

After the isolation of the first heteroleptic copper complex by Buckner and McMillin in 1978, a wide variety of substituted diimine and diphosphine ligands have been investigated in order to tune the characteristics of the excited states and the resulting PL, which can proceed as fluorescence, phosphorescence or thermally activated delayed fluorescence.[13–15] It has been shown that these characteristics can be significantly modulated by a relatively moderate change in the substitution patterns of the coordinating ligands.[7,16–19] In this respect, the introduction of a new type of ligand has good prospects for obtaining Cu(I) complexes with distinct PL properties. For instance, aminodiphosphines, which otherwise have prominent applications in coordination chemistry, have been relatively scarcely employed in the synthesis of heteroleptic copper complexes.[20,21] The introduction of efficient chromophores as ligand substituents may further impact the optical properties.[22,23] Recently, we introduced a coumarin functionalized aminodiphosphine (Scheme 1) as a bidentate ligand for the synthesis of homoleptic mono-, di- and trimetallic copper and silver complexes. These compounds feature rich photophysical properties, including coumarin-based blue fluorescence, and green phosphorescence, which is efficient at low temperatures. In frozen solutions, this green phosphorescence



Scheme 1 Synthesis of the heteroleptic copper(I) complexes **1–5** with coumarin–aminodiphosphine and *N^N* ligands.

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shows unusually long decay on the time scale of seconds in high quantum yields.[24]

In this work, we present a series of heteroleptic Cu(I) complexes synthesized using $\mathbf{L^1}$ and a more soluble derivative $\mathbf{L^2}$ as well as different diimines as co-ligands. In general, diimine- and phosphine-based heteroleptic copper complexes exhibit green and yellow luminescence.[11,16] In this respect, Steffen *et al.* reported Cu(I) complexes emitting in the near-infrared region, in which a sulfur atom was introduced into the backbone of a diimine ligand.[25] Very recently, Müller, Grachova and co-workers have demonstrated that the emission color can be affected by replacement of a nitrogen atom in a diimine ligand with phosphorus.[26] The compounds described below exhibit yellow to deep-red phosphorescence, primarily depending on the heteroatom (nitrogen, oxygen or sulfur) in the diimine scaffold.

Results and discussion

For our studies, we employed two aminodiphosphine ligands $\mathbf{L^1}$ and $\mathbf{L^2}$ with a coumarin group in the backbone. $\mathbf{L^1}$ was prepared as described in a previous study[24] from coumarin and $ClPPh_2$, while $\mathbf{L^2}$ was synthesized in a similar way from bis(4-(*tert*-butyl)phenyl)chlorophosphine. The heteroleptic copper complexes **1–3** and **5** were synthesized by reacting an equimolar amount of $\mathbf{L^1}$ and $[Cu(CH_3CN)_4]BF_4$ or $[Cu(CH_3CN)_4]PF_6$ with one equivalent of an appropriate *N*^*N* precursor (*N*^*N* = 2-(2-pyridyl)benzimidazole, 1,10-phenanthroline, 2-(2-pyridyl) benzoxazole, and 2-(2′-quinoline)benzothiazole) in dichloromethane (DCM). Complex **4** was synthesized following a similar procedure except that aminodiphosphine ligand $\mathbf{L^2}$ was used instead of $\mathbf{L^1}$ for better solubility, in combination with *N*^*N* = 2-(2′-pyridine)benzothiazole. The synthetic route is described in Scheme 1 and the molecular structures of the crystallized complexes obtained by single crystal X-ray diffraction (XRD) are displayed in Fig. 1. All crucial structural parameters are provided in the ESI (Fig. S40–S44†).

The spectroscopic characteristics of the complexes were determined using ^1H and $^{31}P\{^1H\}$ NMR, elemental analysis, IR and high-resolution electrospray ionization mass spectrometry (HRESI-MS). A downfield-shift of the $^{31}P\{^1H\}$ NMR signal compared to that of aminodiphosphine confirms the complexation of the ligand to the metal center. NMR studies of complexes **1–5** dissolved in DCM revealed that there exist ligand exchange and a dynamic equilibrium between the heteroleptic and related homoleptic structures (see the ESI†). Such dissociative and non-dissociative structural equilibria have already been reported for several heteroleptic mono- and dinuclear Cu(I) complexes.[27–30] The dynamic equilibrium in solution could be followed for **1–5** by variable temperature $^{31}P\{^1H\}$ NMR at temperatures down to 193 K. For instance, the $^{31}P\{^1H\}$ NMR of **2** displays two distinct signals which are in agreement with the presence of heteroleptic **2** and a homoleptic phosphine complex (Fig. S9†). Both homoleptic and heteroleptic species are observed for **1–5** within the whole temperature range

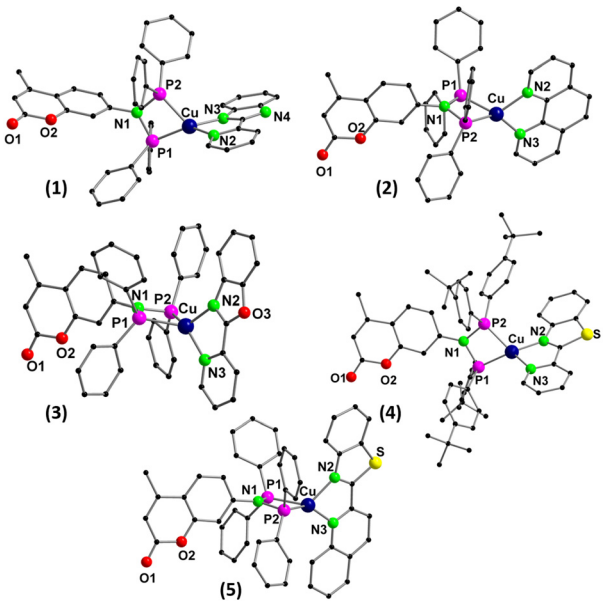

Fig. 1 Molecular structure of the cationic part of the copper complexes **1–5** in the solid state. Hydrogen atoms, counter anions and the non-coordinating solvent molecules are omitted for clarity. Structural parameters are provided in the ESI.†

probed (193–285 K), with the dominance of the former for **5** and the latter for **1–4**. Similar to other observations,[29] low temperatures favor formation of the heteroleptic structures. HRESI-MS measurements additionally confirm the existence of an equilibrium between the complexes (Fig. S30–S39†). These results and NMR experiments suggest that the latter is already achieved on the time scale of minutes. Similar to the reaction solutions (Scheme 1), analytically pure heteroleptic complexes can be isolated from the dissolved samples by recrystallization as confirmed by single crystal X-ray diffraction. Moreover, the recrystallized samples show PL bands characteristic of the heteroleptic complexes, further proving their purity.

One important issue regarding metal complexes demonstrating dissociative equilibria is the stability of the respective solutions. For instance, a complete decomposition of solutions of dinuclear Cu(I) complexes with bis(diphenylphosphanyl) acetylene and phenanthroline-based ligands has been observed within a few hours.[29] In comparison, the stability of DCM solutions of **1–5** appears outstanding: after nearly 3 months of storage (at ambient temperature in the dark under exclusion of air), the NMR signals of **3** and **4** remained nearly unchanged and those of **1**, **2** and **5** diminished to about 20–50% of the initial values (Fig. S22†). The stability of these complexes is similar to other mononuclear heteroleptic copper complexes reported in the literature.[28] In contrast, the $CDCl_3$ solutions of complexes **1–4** tend to decompose rapidly when heated at 50 °C for 5 h. Practically, no decomposition was observed for complex **5**. The order of stability of the copper complexes is as follows: complex **5** > **4** > **3** > **2** ~ **1** (Fig. S23†).

All the complexes exhibit a similar coordination environment in the solid state wherein the copper atom exists in the

+1 oxidation state and adopts a distorted tetrahedral geometry, being coordinated to the phosphine and *N^N* ligands with similar structural metrics (bond lengths and angles). Exemplarily, in complex **1**, Cu–P1 2.2503(9) Å and Cu–P2 2.3011(9) Å bond distances are nearly equal, as well as Cu–N bond distances, *i.e.* Cu–N2 2.057(3) Å and Cu–N3 2.015(3) Å. There is no significant variation in the P–N bond lengths of the aminodiphosphine ligand upon coordination to the metal. The bite angles were found to be N2–Cu–N3 82.21(11)° and P1–Cu–P2 74.24(3)°. These are much smaller than those of other reported chelating phosphines (*e.g.* DPEPhos: ~116° and carborane diphosphine: ~98°).[16,27,31] Some deviations from the structural similarity of **1–5** can be found in complex **5**, where the N2–Cu–N3 angle is narrowed by *ca.* 2° compared to that of other complexes.

Copper complexes **1–5** do not exhibit any significant photoluminescence (PL) in DCM solution (free of oxygen), both at ambient and liquid nitrogen temperatures. This apparently correlates with their dissociation in solution and a dynamic equilibrium between the hetero- and homoleptic species. The dissociation may also suggest that the solvent molecules can readily enter the coordinating sphere in **1–5** and effectively quench electronic excitation in the complexes, even in frozen DCM at 77 K. Hence, the PL properties of **1–5** were investigated in the solid (polycrystalline) state only.

Fig. 2 shows the comparison of the PL emission and excitation (PLE) spectra of solids **1–5** at ambient temperature (295 K) and at 77 K. The onset of absorption in the PLE spectra red-shifts from *ca.* 460 to 580 nm (77 K) in the series of **1–5**, correlating with the visual appearance of the samples as yellow (**1–3**), orange (**4**) and orange-red (**5**) polycrystalline powders. All the complexes feature efficient PL at 77 K with a broad emission band whose maximum, λ_{max}, increases from *ca.* 570 nm in **1** to 690 nm in **5**, *i.e.* following the same trend as that of the PLE spectra. The PL is phosphorescence as indicated by the decay times of several microseconds at 295 K and up to hundreds of microseconds at 77 K (Fig. S50†). The emission spectra remain unchanged on varying the excitation wavelength. They moderately blue-shift upon increasing the temperature to 295 K. Compounds **3–5** retain a PL intensity comparable to that at 77 K, whereas the emission of **2** is much weaker and **1** is practically non-luminescent. The PL efficiency, Φ_{PL}, of the complexes at 295 K was determined in an integrating sphere at λ_{exc} = 450 nm to be 2.8, 21.0, 4.3 and 7.4% for **2–5**, respectively. For **1**, Φ_{PL} was estimated to be less than 0.05%. At 77 K, however, the PL of **1** is comparable in intensity to that of other complexes (measured at the same instrumental parameters). The reason for such peculiar temperature dependence of the PL of **1** in comparison with, *e.g.*, that of **3** (Φ_{PL} = 21.0% at 295 K) is not clear at the moment, especially given the similar PL behavior observed for homologous Cu(I) complexes with 2-(2-pyridyl)benzimidazole *versus* 2-(2-pyridyl)benzoxazole ligands.[32]

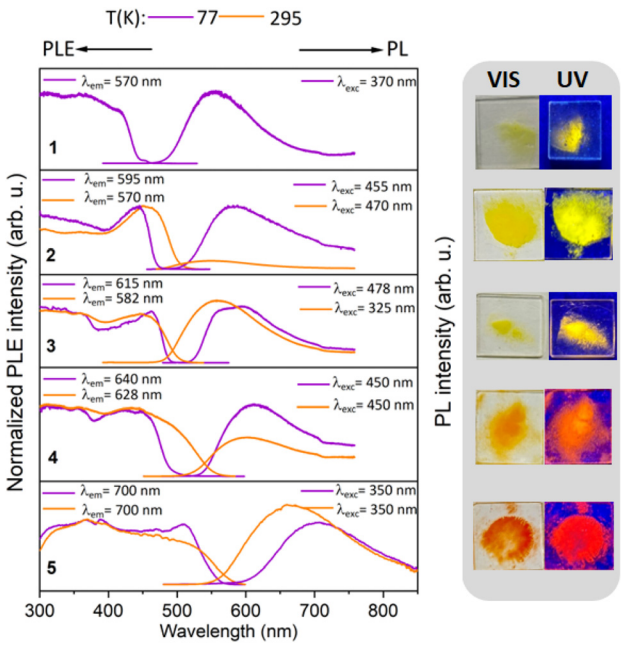

Fig. 2 Photoluminescence excitation (PLE) and emission (PL) spectra of solid (polycrystalline) heteroleptic copper(I) complexes **1–5** at ambient temperature and 77 K. PLE and PL spectra were recorded at the indicated emission and excitation wavelengths (λ_{em} and λ_{exc}). Photographs of the samples: left: in daylight; right: under a UV lamp (λ_{exc} = 365 nm). The photograph of sample **1** was captured at low temperature.

The red shift in emission going from **1** to **5** apparently relates to the variation of the diimine ligand. Replacing the NH group in **1** with an oxygen atom in **3** leads to a bathochromic shift in the PL spectra by *ca.* 45 nm (at 77 K). Upon introducing sulfur instead of oxygen in the ligand backbone in **4**, the phosphorescence red shifts by *ca.* 25 nm to *ca.* 640 nm. A further bathochromic shift by 45 nm is observed when an aromatic ring is attached to the pyridine moiety of the diimine ligand in complex **5**. These results show that the emission wavelength of heteroleptic diimine–phosphine Cu(I) complexes can be finely tuned by a systematic change in the electronic properties of the diimine ligand.

It is worthwhile to compare the optical properties of the heteroleptic Cu(I) complexes with those of the related homoleptic aminodiphosphine complex Cu($\mathbf{L}^1$)$_2$, which is formed by ligand exchange in solutions of **1–3** and **5**. It was prepared and characterized in our previous work.[24] The homoleptic complex shows a weak blue fluorescence in DCM solution at ambient temperature and moderately intense and vibronically structured green phosphorescence which dominates in the solid state and (frozen) DCM solution at low temperatures (<150 K). Both emissions are primarily attributed to the coumarin groups. In **1–5**, these chromophores can apparently contribute to the higher energy excitations in the PLE/absorption spectra, which then have to relax fast to the lowest singlet state mostly confined on the diimine ligands (see the calculation results below). Remarkably, a very weak signature of the coumarin phosphorescence within the ~460–560 nm spectral range could still be observed in the PL spectra of **1–3** and particularly in those of **5**, however, only at temperatures below ~50 K (Fig. S51†). Increasing the temperature likely further acceler-

ates internal conversion so that the coumarin phosphorescence (very minor electronic relaxation channel) is not observable anymore.

For complexes **1–5** as well as for homoleptic Cu($\mathbf{L^1}$)$_2$, we have carried out a series of comparative theoretical calculations. In the homoleptic complex Cu($\mathbf{L^1}$)$_2$, the HOMO and HOMO−1 are mainly located on the copper atom with a significant contribution from the coordinating phosphines, while the LUMO and LUMO+1 are distributed over the coumarin moieties. The calculated HOMO–LUMO energy gap, ΔE, is 6.78 eV. When one of the coumarin-linked aminodiphosphine ligands is replaced with a diimine in **1–5**, the HOMOs roughly retain the above configuration, whereas the LUMOs become almost completely confined on the diimines and energetically stabilized in comparison with those of the homoleptic complex with ΔE = 3.26, 3.32, 3.14, 2.96 and 2.99 eV in **1–5**, respectively (Fig. S53–S54†).

One can note that a reduced energy gap between the frontier molecular orbitals of phosphine–diimine complexes makes them good candidates for electron transfer (photo)reactions in comparison with homoleptic phosphine complexes. A similar trend to that for ΔE (decreasing from **1** to **5**) was found for the excited singlet (S_1) and triplet (T_1) energies in **1–5** (Table S3†). Hence, the T_1 states were found at 0.85–1.22 eV below the S_1 states. Accordingly, the calculations reasonably reproduce the order of the PL emission maxima, especially for the structurally closely related complexes **1** and **3–5** with the diimine ligands (λ_{em}: **1** < **3** < **4** < **5**). The rather distinct HOMOs and LUMOs suggest a charge transfer character of the excited states in **1–5**. Hence, the calculated S_1 and T_1 dipole moments in **1** and **3–5** correlate with the onset of absorption and emission maximum as depicted in Table S4.† For instance, complex **5** shows the lowest dipole moment in S_1 and T_1 states and the most red-shifted absorption onset and emission band, while complex **1**, with the highest dipole moment, exhibits the onset of absorption and emission maximum at higher energies.

Conclusions

In conclusion, we have accomplished the synthesis of heteroleptic Cu(I) complexes **1–5** with coumarin-derived aminodiphosphine and several diimine ligands. The complexes feature a dynamic equilibrium resulting from ligand exchange in the solution. It is noteworthy that the solutions remain relatively stable over weeks and **1–5** can be readily obtained by crystallization. In the solid state, these complexes are stable and show phosphorescence with a decay time of a few microseconds and quantum yields up to 21.0% at ambient temperature. The complexes show different emissive behavior compared to the homoleptic aminodiphosphine copper complex Cu($\mathbf{L^1}$)$_2$. The emission maxima of the complexes vary between 570 and 690 nm, which is dependent on the heteroatom present in the diimine ligand scaffold. These results show that the emission properties of the compounds can be tuned by systematic modifications in the ligand system. Quantum chemical calculations reveal that the energy gap between the frontier molecular orbitals for the heteroleptic complexes is significantly reduced compared to that of the homoleptic structure, which make them promising photoactive materials.

Conflicts of interest

There are no conflicts to declare.

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