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Cuprophilic interactions in highly luminescent dicopper(I)–NHC–picolyl complexes – fast phosphorescence or TADF?[†]

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This case study on a series of monomeric, dimeric and polymeric Cu^I chlorido NHC–picolyl complexes shows that cuprophilic interactions can ensure strong spin–orbit coupling for fast (reverse)inter-system-crossing $T_1 \leftrightarrow S_1$ and $T_1 \rightarrow S_0$, and therefore can serve as a design motif for the construction of highly efficient Cu^I-based TADF or T_1 emitters.

Luminescent molecules showing thermally activated delayed fluorescence (TADF), *i.e.* thermally induced reverse intersystem-crossing (RISC) $T_1 \rightarrow S_1$ with subsequent emission from the singlet excited state $S_1 \rightarrow S_0$, have proven to be particularly suitable materials for OLEDs and other photonic applications, as they are able to bypass the spin-forbidden phosphorescence $T_1 \rightarrow S_0$.^{1–3} In this regard, Cu^I complexes with a d^{10} configuration have gained a lot of attention in the last 5 years, as the absence of metal centred d–d* transitions, leading to non-radiative decay, in combination with TADF makes them competitive to Ir^{III}- and Pt^{II}-based emitters.^{4–16} Although some structure–property relationships have been formulated,^{17–19} TADF in copper complexes is still difficult to predict *a priori*, let alone to design TADF materials, as it is an excited state property. In contrast, cuprophilic interactions can be pre-arranged in the ground state by careful choice of the ligand environment, and they have been shown to allow, albeit inefficiently, phosphorescence in simple dinuclear Cu^I complexes with bridging diphosphines and other systems,^{20–23} and also in clusters.^{24–26} A few dicopper(I) complexes with short Cu–Cu contacts (<2.8 Å) have been reported to emit efficiently *via*

TADF, but the influence of cuprophilic interactions in those has yet not been addressed.^{4,8,19,27–29}

In this case study on a family of new bidentate copper(I) NHC–picolyl complexes we show that cuprophilic interactions can greatly enhance the radiative rate constants of the T_1 state by increasing spin–orbit coupling (SOC), giving emission lifetimes comparable to TADF, and can even be involved in the luminescence mechanisms when TADF is present. Thus, cuprophilic interactions provide a design methodology for highly efficient Cu^I emitters.

For this study, we have prepared a series of Cu^I NHC–picolyl complexes (**1–7**, Fig. 1) by a facile one-step silver-free procedure from azolium chlorides in aqueous ammonia as basic and copper complexing medium (see ESI[†]).³⁰ The azolium salts include new picolyl linkers, functionalized in the *para* position

Fig. 1 Chemical structures of complexes **1–7**, for dimers representative molecular structure of **1** obtained from X-ray diffraction and intermolecular Cu–Cu distances of **1–4**.

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with Cl, Me, OMe and NO₂. The complexes obtained are related to previously reported analogs, of which no photophysical properties have been described,^{31–35} and also form monomeric, dimeric and polymeric structures depending on the picolyl donor strength and/or the crystallization method.

The molecular structures of **1–4**, obtained by single-crystal X-ray diffraction (Fig. 1 and ESI†), exhibit two bidentate IMesPic^R ligands attached to two CuCl fragments such that each of them bridges the two copper centers, resulting in Cu1...Cu1A distances ranging from 2.5226(8) Å (**1**) to 2.5744(9) Å (**4**), indicative for cuprophilic interactions. Indeed, our DFT calculations give a Mayer bond order for the Cu–Cu bond in **1–4** of *ca.* 0.3. NBO analysis suggests a weak orbital interaction between the d orbitals of the two copper atoms, which we even find in HOMO–6 and HOMO–7 of compound **4** with the longest Cu–Cu distance (Fig. S10, ESI†). The NHC moieties interact with both metal centers leading to C1–Cu1 bond lengths between 1.940(2) Å (**4**) and 1.9462(19) Å (**1**), and longer C1A...Cu1 distances between 2.5483(19) Å (**1**) and 2.621(3) Å (**4**). The mesityl and pyridyl rings of the two ligands are oriented in a nearly coplanar fashion.

The pyridyl substituents R = Cl (**1**), Me (**3**) and OMe (**4**) have no significant effect on the general packing pattern of the molecules in the solid state, but a linear monomeric structure is obtained for R = NO₂ (**7**), and we also found **6** (R = H) as a polymorph of **2** (see ESI†). In these cases, the NHC–picolyl moiety coordinates exclusively with its carbene moiety (Cu1–C1 = 1.8960(14)/1.891(2) Å (**6/7**)). A third structural motif can be realized when the mesityl substituent of the NHC is replaced by a 2,6-diisopropylphenyl group (Fig. 1 and Fig. S14, ESI†). As in **1–4**, the NHC–picolyl moiety acts as a bidentate ligand which bridges two copper centres. However, this does not result in the formation of a dimeric structure, but in a coordination polymer instead. A comparison of the bond lengths in **2** and **5** reveals a significant elongation of the Cu1–Cl1 bond (+0.122 Å), a less pronounced increase of the Cu1–N3A bond length (+0.015 Å) and a shortening of the Cu1–C1 bond (–0.041 Å). The sum of the bond angles around the tricoordinate copper atom equals to 359.9° (N3A–Cu1–Cl1 = 101.46(4)°; C1–Cu1–Cl1 = 134.78(6)°; C1–Cu1–N3A = 123.67(7)°) testifying to a planar, but distorted trigonal coordination geometry.

While the monomers **6** and **7** are not luminescent due to missing coordination of the picolyl moiety, crystalline **1–5** show bright greenish emission under near-UV excitation (Fig. 2 and Table 1). The broad excitation and emission spectra indicate a charge transfer (CT) nature of the involved excited states. Interestingly, the radiative rate constants of the dimers **1–4** ($k_r = 4.4\text{--}7.4 \times 10^4 \text{ s}^{-1}$), which all exhibit cuprophilic interactions (Fig. 1), are greatly enhanced by a factor of 2–3 compared to polymeric [CuCl(IDippPic)]_∞ (**5**) ($k_r = 2.2 \times 10^4 \text{ s}^{-1}$) with no Cu–Cu contacts, leading to much higher quantum yields.

There are two reasons for the enhanced radiative rate constants of the dimers [Cu₂Cl₂(IMesPic^R)₂]: (i) TADF is operative in **1** (R = Cl), **2** (R = H) and **3** (R = Me) (Fig. 3 and Fig. S5 (ESI†), Table 2), (ii) exceptional strong SOC leads to fast phosphorescence from T₁ in **4** (R = OMe) and, again, in **3**. The temperature dependent emission lifetime measurements

Fig. 2 Solid state excitation and emission spectra of crystalline dimers **1–4** and polymeric **5**; inset: crystalline **2** under UV irradiation.

Table 1 Luminescence data of compounds **1–5** recorded in the solid state under argon

Cpd	298 K				77 K	
	λ_{max} (nm)	Φ	τ (μs)	k_r (10^4 s^{-1})	λ_{max} (nm)	τ^a (μs)
1	550	0.49	11.0	4.5	559	90 (0.83); 155 (0.17)
2	520	0.59	11.0	5.4	530	97.6
3	523	0.68	9.2	7.4	536	23 (0.90); 113 (0.10)
4	538	0.67	15.3	4.4	544	18.7
5	538	0.31	14.6	2.2	525	19.5

^a For bi-exponential decays, pre-exponential factors given in brackets (see ESI).

Fig. 3 Temperature dependence of the emission lifetime and decay profiles at 298 K and 77 K (insets). Left: [Cu₂Cl₂(IMesPic)₂] (**2**); the red line represents the fit of the experimental data according to eqn (1). Right: [Cu₂Cl₂(IMesPic^{OMe})₂] (**4**, green), [CuCl(IDippPic)]_∞ (**5**, black).

of **1** and **2** give largely monoexponential decays and suggest thermally equilibrated states being involved. The experimental data have been fitted to eqn (1)

$$\tau = \frac{[3 + \exp(-\Delta E(S_1 - T_1)/k_B T)]}{[3/\tau(T_1) + 1/\tau(S_1) * \exp(\Delta E(S_1 - T_1)/k_B T)]} \quad (1)$$

with the Boltzmann constant k_B , $\tau(S_1)$ and $\tau(T_1)$ being the intrinsic lifetimes of the singlet and triplet excited states, respectively, and the activation energy $\Delta E(S_1 - T_1)$. The resulting energy gap $\Delta E(S_1 - T_1)$ of only *ca.* 710–740 cm^{–1} is in agreement with our TD-DFT calculations, which suggest $\Delta E(S_1 - T_1)$ of

Table 2 Singlet (S_1) and triplet (T_1) excited state properties of **1–3** exhibiting TADF

Cpd	1 ^c	2	3 (τ_1)	3 (τ_2)
$\Delta E(S_1-T_1)^a$ (cm ⁻¹)	740	710	620	670
$\tau(T_1)$ (μ s)	101	93	23	110
$\tau(S_1)$ (ns)	93	151	170	170
$\Delta E(S_1-T_1)^b$ (cm ⁻¹)	960	630	670	

^a Obtained from the fit according to eqn (1). ^b Experimental values obtained from emission spectra at 297 and 77 K. ^c The amplitude-weighted lifetime was used for the fit (see ESI).

583 and 700 cm⁻¹ for **1** and **2**, respectively (see ESI†). These gaps are small enough to allow efficient thermal RISC from the long-lived triplet state T_1 (τ = 101 μ s (**1**), 93 μ s (**2**) at 77 K) to the energetically higher lying, short-lived singlet state S_1 , and thus account for the decrease of the lifetime (or increase in k_r) by a factor of 8–9 upon warming from 77 K to room temperature.¹ Polymeric **5** behaves differently as a pure triplet emitter with a much lower k_r at 298 K, as indicated by the linear increase of its emission lifetime with decreasing temperature (Fig. 3).

In contrast, strong SOC mediated by the two copper(i) atoms leads to unusually fast radiative decay (τ $\approx$ 19 μ s at 77 K) from the T_1 state in **4** (R = OMe) with no TADF (Fig. 3), which suggests $\Delta E(S_1-T_1) > 1800$ cm⁻¹ as supported by our TD-DFT calculations (see ESI†). Interestingly, compound **3** (R = Me) displays both TADF and very fast phosphorescence from a triplet state, and thus appears to be a photophysical Janus compound. At 77 K, the emission is dominated by a triplet state with strong SOC and a short lifetime of only 23 μ s. However, a minor component (10%) with a much longer lifetime of 113 μ s is also present. The pre-exponential factors of the biexponential decays change in favor of this long-lived emission with increasing temperature (Fig. 4).

The two distinctly different lifetimes at 77 K are indicative for two thermally non-equilibrated triplet states, which are of different nature. Both seem to be involved in TADF processes, as the respective lifetime fits according to eqn (1) give the same S_1 lifetime of 170 ns (Fig. 4 and Table 2). Above 247 K, all three states, *i.e.* the two triplets and the singlet, are thermalized leading to a single lifetime.

According to our DFT calculations (PBE0-D3BJ/def2-TZVP/ZORA), the T_1 states of the TADF emitters **1** (R = Cl) and **2** (R = H) can be characterized as MLCT with only one copper(i) atom mainly being involved (Fig. 5 and Fig. S6, ESI†). This assignment is in agreement with other Cuⁱ TADF emitters, of which the ³MLCT states exhibit similar lifetimes as found for **1** and **2**.^{4–19,28,29} However, the T_1 state of the highly efficient pure triplet emitter **4** (R = OMe) contains a significant Cu₂ $\rightarrow$ NHC/py contribution, allowing for very efficient SOC, coupling T_1 with the ground state S_0 . Consequently, we conclude that TADF and phosphorescence in the Janus compound **3** originate from two distinctly different triplet states, which are a ³MLCT with a long lifetime (τ_{77K} = 113 μ s) similar to **1** and **2**, and a ³(Cu₂)LCT state with a short lifetime (τ_{77K} = 23 μ s) similar to **4**.

Apparently the degree of cuprophilic interactions involved in the triplet state T_1 , which increases the effective SOC and

Fig. 4 Temperature dependence of the emission processes and decay profiles of dimer **3** (R = Me). The amplitude-weighted lifetime τ_{av} illustrates the relative influence of the biexponential decay components (top left). Red lines represent the fit of the experimental data according to eqn (1).

Fig. 5 Electron (red) and hole (grey) of the DFT-(PBE0-D3BJ/def2-TZVP)-optimized T_1 states of **2** (left) and **4** (right).

decreases the T_1 lifetime, can be controlled as it scales for **1–4** with the donor strength of the *para*-substituents of the picolyl ligands ($\tau(T_1)$ [μ s] = 90/155 (R = Cl, **1**), 93 (R = H, **2**), 23/110 (R = Me, **3**), 19 (R = OMe, **4**)). Despite the varying nature of the triplet states in **1–4**, additional TD-DFT calculations show that the S_1 state of all investigated dimers is of Cu₂ $\rightarrow$ py nature (see ESI†). This should help to facilitate reverse-ISC $T_1 \rightarrow S_1$, necessary for TADF, due to strong SOC.

Our combined photophysical and DFT study indicates that the previously found TADF efficiency of dicopper(i) complexes is influenced by cuprophilic interactions. This is exemplified by comparison of the polymeric compound [CuCl(IDippPic)]_∞ (**5**) with no Cu–Cu contacts and inefficient pure phosphorescence, and the TADF exhibiting dimers [Cu₂Cl₂(IMesPic^R)₂] (**1**: R = Cl, **2**: R = H), which show formation of ¹(Cu₂ $\rightarrow$ py)CT and ³(Cu $\rightarrow$ py)CT states. The frontier orbitals, which are involved in the transitions $S_0 \rightarrow S_1$ of many of the previously reported efficient dicopper(i) TADF emitters, are located at the respective Cu₂ core,^{4,8,19,27–29} which corroborates our findings. The photophysical behaviour and the nature of the states involved for **1** and **2** are summarized in Fig. 6 (left).

The strong SOC mediated by the cuprophilic interactions is also responsible for the exceptionally fast pure phosphorescence ($\tau(T_1)_{77K}$ = 19 μ s) from a ³(Cu₂ $\rightarrow$ NHC/py)CT state in dimer **4** (R = OMe), as depicted in Fig. 6 (right). In terms of design criteria, this finding shows how important it is to keep

Fig. 6 Energy level diagrams and emission processes for dimers **1** (R = Cl) and **2** (R = H) showing TADF (left), and the pure triplet emitter **4** (R = OMe) (right). Both mechanisms apply for complex **3** (R = Me). The phosphorescence decay times are the T₁ lifetimes at 77 K, and the TADF lifetime is determined at room temperature. ΔE(S₁-T₁) is obtained from fitting the experimental data to eqn (1).

the electron density of the triplet state close to the Cu₂ core. The highly exciting Janus behaviour of dimer **3** (R = Me) combines the two mechanisms, allowing the longer-lived ³MLCT and the short-lived ³(Cu₂)LCT to participate in the TADF mechanism. Thus, cuprophilic interactions can ensure strong SOC for fast ISC T₁ ↔ S₁ and T₁ → S₀, and therefore can serve as a design motif for the construction of highly efficient Cu^I-based emitters with high radiative rate constants *k_r*, either by TADF or by fast phosphorescence.

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