

Highly efficient thermally activated fluorescence of a new rigid Cu(I) complex [Cu(dmp)(phanephos)]^{††}Rafał Czerwieniec,^{*a} Konrad Kowalski^{*b} and Hartmut Yersin^{*a}Cite this: *Dalton Trans.*, 2013, **42**, 9826

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The rigid [Cu(dmp)(phanephos)][†] complex displays a high luminescence quantum yield of 80% at ambient temperature. In contrast to the long-lived phosphorescence of 240 μs at $T < 120$ K with a radiative rate of $k_r = 3 \times 10^3 \text{ s}^{-1}$, the ambient-temperature emission represents a thermally activated delayed fluorescence (DF) with a decay time of only 14 μs and a radiative rate of $k_r(\text{DF}) = 6 \times 10^4 \text{ s}^{-1}$. Evidence for the involvement of the excited singlet state in the emission process is presented. This material has high potential to be applied in efficient OLEDs taking advantage of the singlet harvesting mechanism.

In the past decade, substantial investigations were carried out to develop novel materials for organic light emitting diodes (OLEDs),¹ in particular, to increase the device efficiency. In this respect, luminescent materials and excitation mechanisms play a crucial role. A breakthrough was reached by applying organometallic complexes based on the 3rd-row transition metals iridium and platinum.^{2–6} These substances frequently display high phosphorescence quantum yields approaching even 100% and short emission decay times of a few μs.⁷ Of special importance is the fact that by an electroluminescent excitation all triplet and singlet excitons formed in the emissive layer of an OLED can be utilized for light generation, whereby the emission stems from the lowest triplet state. This mechanism, representing the triplet harvesting effect,^{8,9} is based on the properties of the organometallic

compounds. It allows one to achieve much higher OLED efficiencies than obtainable with typical organic fluorescent (singlet) emitters by which only 25% of the total number of excitons can be exploited. However, the triplet emitters are based on high-cost platinum group metals. Therefore, alternative materials, such as Cu(I) complexes,^{5,6,10–14} came into the focus of research.

At first sight, Cu(I) complexes seem to exhibit substantial problems with regard to OLED applications: (1) compared to Ir or Pt, Cu as a 1st row transition metal induces much weaker spin–orbit coupling.¹⁵ As a consequence, transitions between the excited triplet state and the singlet ground state are largely forbidden. Thus, long phosphorescence decay times of several 100 μs are found.^{5,6} Therefore, in an OLED, strong saturation effects would result. (2) Cu(I) complexes with reducible ligands, *i.e.* with energetically low-lying π^* orbitals, such as aromatic diimines, often display distinct low-energy metal-to-ligand charge-transfer (MLCT) transitions in the visible part of the spectrum. With this type of electronic excitation, a flattening distortion of the molecular structure takes place.^{13a,16–18} Such structural rearrangements are usually connected with an increase of non-radiative deactivation or even quenching of the emission due to an increase of the Franck–Condon factors that couple the excited state and the ground state.^{19,20} This is especially distinct in non-rigid environments.²¹

This contribution presents a new, adequately designed Cu(I) complex that may be used to overcome both problems.

The very long emission decay time of the lowest excited triplet state T_1 does not become effective if the energy separation between this state and the higher lying singlet state S_1 , $\Delta E(S_1-T_1)$, is sufficiently small to thermally populate the S_1 state from the lower lying triplet state by fast up-intersystem crossing at ambient temperature. Accordingly, a thermally activated delayed $S_1 \rightarrow S_0$ fluorescence²² (TADF; compare also ref. 5, 6, 13, 21–25) occurs and the overall emission decay time becomes much shorter than that of the $T_1 \rightarrow S_0$ phosphorescence. With respect to electroluminescent applications, this mechanism can thus also be used to harvest all triplet and singlet excitons for light generation, though in the excited

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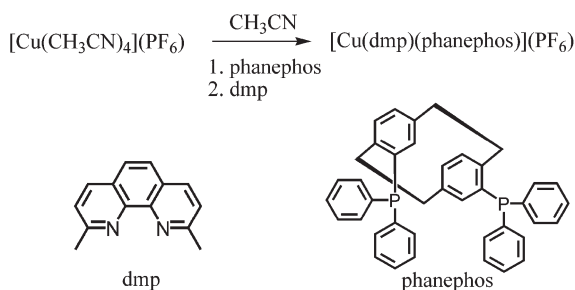
†Electronic supplementary information (ESI) available: X-ray crystallographic data files (CIF), instrumentation, experimental procedures, synthesis details, crystal structures of [Cu(dmp)(*R*_p-phanephos)](PF₆) and [Cu(dmp)(*S*_p-phanephos)](PF₆), lowest electronic transitions according to TD-DFT calculations, and estimation of the radiative decay rate of the $S_1 \rightarrow S_0$ electronic transition (prompt fluorescence) from an analysis of the absorption spectrum. CCDC 921267 and 921268. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt51006a

singlet state. Therefore, this mechanism is termed “singlet harvesting”.^{5,6,24,25} The problem of the molecular flattening upon electronic excitation is addressed by the use of ligands with high steric demands. For instance, sterically demanding groups on the 2 and 9 positions of 1,10-phenanthroline can effectively hamper the flattening tendency in homo- and heteroleptic diimine Cu(I) complexes.^{18,21} Applying this ligand in combination with a chelating ligand that exhibits a wide bite angle,²⁶ the molecular structure of the complex can be distinctly further rigidified. It will be shown that the title compound overcomes the problems discussed above.

The studied complex was synthesized by reacting $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{PF}_6)$ with equimolar amounts of two chelating ligands: dmp = 2,9-dimethyl-1,10-phenanthroline and phanephos = 4,12-bis(diphenylphosphino)-[2.2]paracyclophane (Scheme 1). The molecular structures of both enantiomers²⁷ of $[\text{Cu}(\text{dmp})(\text{phanephos})]^+$ are displayed in Fig. S2 (ESI[†]) and bond lengths and angles are listed in Table S1.† The X-ray investigations reveal a strongly distorted tetrahedral coordination of the four-coordinated metal center due to distinctly different steric requirements of the dmp and phanephos ligands. In particular, the phanephos ligand with the bulky paracyclophane backbone and the two diphenylphosphino functions separated by a P...P distance of about 3.9 Å and the relatively wide P–Cu–P bite angle of 116° form a rigid “semi-cage” for the metal ion and the dmp ligand. Apparently, both ligands provide a firm framework around the metal ion, suppressing strong molecular geometry changes and shielding the metal center from the environment.

Fig. 1 shows electronic absorption and emission spectra of the studied complex recorded at ambient temperature. $[\text{Cu}(\text{dmp})(\text{phanephos})]^+$ dissolved in dichloromethane²⁸ displays intense high energy absorption bands with maxima at ≈ 230 nm ($\epsilon \approx 74\,000\text{ M}^{-1}\text{ cm}^{-1}$) and ≈ 270 nm ($\epsilon \approx 36\,000\text{ M}^{-1}\text{ cm}^{-1}$), which are assigned to $\pi\text{-}\pi^*$ ligand centered (LC) transitions of dmp and phanephos. Between ≈ 320 and ≈ 440 nm distinctly weaker absorptions ($\epsilon(380\text{ nm}) \approx 3900\text{ M}^{-1}\text{ cm}^{-1}$) occur. These are attributed to metal-to-ligand charge-transfer (MLCT) excited singlet states involving mainly the metal and the dmp ligand.¹⁸ The MLCT character of the lowest electronic transitions is also supported by the results of TD-DFT calculations (ESI[†]).

The studied Cu(I) complex displays intense green-yellow luminescence at ambient temperature even in solution. The



Scheme 1 Synthesis of $[\text{Cu}(\text{dmp})(\text{phanephos})](\text{PF}_6)$.

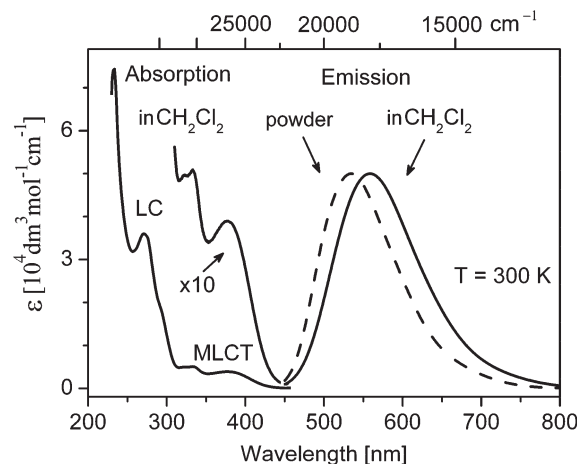


Fig. 1 Ambient temperature absorption and luminescence spectra of $[\text{Cu}(\text{dmp})(\text{phanephos})]^+$ recorded for a diluted ($c \approx 3 \times 10^{-5}\text{ M}^{-1}$) dichloromethane solution²⁸ (solid lines) and a powder sample (dashed line) of $[\text{Cu}(\text{dmp})(\text{phanephos})](\text{PF}_6)$. LC and MLCT describe ligand centered ($\pi\text{-}\pi^*$) and metal-to-ligand charge-transfer ($d\text{-}\pi^*$) transitions, respectively.

emission properties were studied in degassed dichloromethane, in PMMA, and in the solid phase (as powder) (Fig. 1). Emission data are summarized in Table 1. Independent of the matrix, the emission spectra are broad and unstructured even down to 20 K. This is in accordance with the MLCT nature of the emitting state. At ambient temperature, the emission bands measured as powder, in PMMA, and in CH_2Cl_2 are centered at 530, 535, and 558 nm, respectively. This red shift is associated with a lowering of the matrix rigidity and an increasing freedom for changes of the molecular geometry upon MLCT excitation. In addition to this bathochromic shift, the geometry change results in an increase of radiationless deactivation according to a better overlap of the vibrational wave functions of the ground and the excited state^{19,20} and thus to a decrease of the emission quantum yield from $\phi_{\text{PL}} = 80\%$ (powder) to 65% (PMMA) and to 40% (dissolved in CH_2Cl_2). Interestingly, the change of the luminescence properties of $[\text{Cu}(\text{dmp})(\text{phanephos})]^+$ with a variation of the matrix rigidity is much less distinct than is found for other Cu(I) complexes. For example, for the complexes $[\text{Cu}(\text{dmp})(\text{pop})]^+$ ^{26a-c} and

Table 1 Luminescence properties of $[\text{Cu}(\text{dmp})(\text{phanephos})](\text{PF}_6)$ in dichloromethane, in PMMA (poly(methyl methacrylate)), and as powder

	$T = 300\text{ K}$			$T = 77\text{ K}$		
	λ_{max}^c [nm]	τ^d [μs]	ϕ_{PL}^e [%]	λ_{max}^c [nm]	τ^d [μs]	ϕ_{PL}^e [%]
CH_2Cl_2^a	558	10	40	548	130	60
PMMA ^b	535	20	65	567	170	60
Powder ^b	530	14	80	562	240	70

^a The CH_2Cl_2 solution was degassed by repeated freeze–thaw cycles.

^b Measured in a nitrogen gas atmosphere. ^c Emission maximum.

^d Emission decay time (error $\pm 5\%$) measured after pulsed diode laser excitation ($\lambda_{\text{exc}} = 372\text{ nm}$, pulse width 100 ps). ^e Photoluminescence quantum yield (relative error $\pm 10\%$ at 300 K; $\pm 20\%$ at 77 K).

[Cu(pop)(pz₂Bph₂)],^{5,24} with pop = bis[2-(diphenylphosphino)phenyl]ether and pz₂Bph₂ = diphenyl-bis(pyrazol-1-yl)borate, showing ϕ_{PL} values in rigid powders up to 90%, the emission quantum yields measured in CH₂Cl₂ amount to only 15 and 8%, respectively. Thus, the title compound belongs to the strongest emitting Cu(I) complexes (even in solution) reported so far.^{5,10,13c,24,26a-c,29} Obviously, due to the relatively stiff “semi-cage” provided by the combined steric effects of the two ligands, phanephos and dmp, the excited state geometry rearrangements are less distinct than found for other Cu(I) complexes. This result may be of high significance with respect to optoelectronic applications.

The emission decay time is strongly dependent on temperature (Fig. 2). Between 20 K and about 120 K, the decay time of the powder sample is almost constant and as long as $\tau \approx 240 \mu\text{s}$. Therefore, we assign this emission to a T₁ → S₀ phosphorescence. Obviously, no other decay mechanism is activated in this temperature range of ≈ 100 K corresponding to a thermal energy range of $\approx 70 \text{ cm}^{-1}$. However, with further temperature increase, a steep decrease of the decay time is observed (Fig. 2). This is connected with a drastic increase of the radiative decay rate k_r . According to the data given in Table 1 and the relation $k_r = \phi_{\text{PL}}/\tau$, the rates are determined to be $k_r = 3 \times 10^3 \text{ s}^{-1}$ at 77 K and $k_r = 6 \times 10^4 \text{ s}^{-1}$ at ambient temperature, respectively. This corresponds to an increase of the radiative rate by a factor of twenty. These drastic changes with temperature increase are assigned to be related to a growing involvement of the higher lying S₁ singlet state with its much higher decay rate. The S₁ state is thermally activated from the lower lying T₁ state. Hence, the ambient temperature emission represents a thermally activated delayed fluorescence (DF) that exhibits a decay time of $\tau(\text{DF}) = 14 \mu\text{s}$ at 300 K.

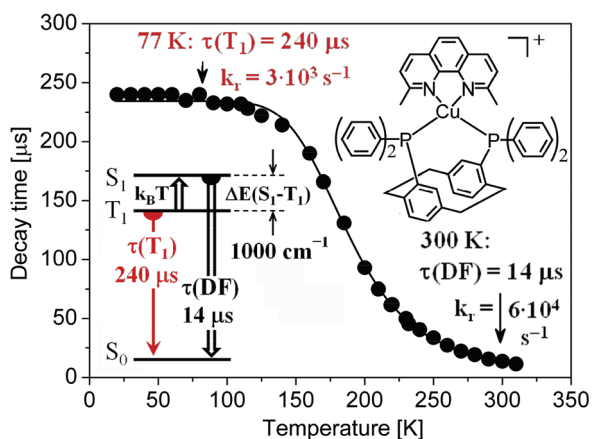


Fig. 2 Emission decay time of [Cu(dmp)(phanephos)](PF₆) powder versus temperature. The sample was excited with a pulsed UV laser at $\lambda_{\text{exc}} = 355 \text{ nm}$ (pulse width 7 ns). The emission was detected at $\lambda_{\text{det}} = 550 \text{ nm}$. The solid line represents a fit of eqn (1) to the experimental data with the phosphorescence decay time $\tau(T_1) = 240 \mu\text{s}$ measured at 77 K. The resulting fit parameters are $\Delta E(S_1-T_1) = 1000 \text{ cm}^{-1}$ and $\tau(S_1) = 40 \text{ ns}$, representing the magnitude of the singlet–triplet splitting and the decay time of the spontaneous S₁ → S₀ fluorescence, respectively. The spontaneous fluorescence is not observed directly due to much faster intersystem crossing. $\tau(\text{DF}) = 14 \mu\text{s}$ is the decay time of the delayed fluorescence at ambient temperature.

The temperature dependence of $\tau = \tau(T)$, as displayed in Fig. 2, can be interpreted in terms of a three state kinetic model involving the electronic ground state S₀, the lowest triplet state T₁, and the singlet state S₁. Under the assumption of a fast thermalization between the T₁ and S₁ states (assuming temperature-independent decay rates), the decay time at a given temperature can be expressed by^{5,6,24,25}

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

Herein k_B is the Boltzmann constant, $\tau(T_1)$ and $\tau(S_1)$ are the individual decay times of the triplet (phosphorescence) and the singlet (spontaneous fluorescence) excited states, and $\Delta E(S_1-T_1)$ is the energy separation (activation energy) between the two emitting states. By fitting the above equation to the measured decay times and inserting the measured decay time $\tau(T_1) = 240 \mu\text{s}$ (plateau at $20 \text{ K} < T < 120 \text{ K}$), values of $\tau(S_1) = 40 \text{ ns}$ and $\Delta E(S_1-T_1) = 1000 \text{ cm}^{-1}$ are obtained (see the inset of Fig. 2). It is remarked that $\Delta E(S_1-T_1)$ of 1000 cm^{-1} found for the powder material corresponds well to the spectral blue shift observed for the emission maximum with temperature increase from $T = 77 \text{ K}$ ($\lambda_{\text{max}} = 562 \text{ nm}$) to 300 K ($\lambda_{\text{max}} = 530 \text{ nm}$) (Table 1). This correspondence between the activation energy and the spectral shift upon temperature increase represents further support for the model presented.

The same trend holds also for the compound doped into PMMA. On the other hand, in fluid solution, temperature reduction leads to a blue shift of the emission, which does not seem to agree with the discussed model. However, in this situation the usual rigidochromic blue shift, related to the phase transition of CH₂Cl₂ at 176 K, obviously prevails.

The time constant $\tau(S_1) = 40 \text{ ns}$ of the S₁ → S₀ process (corresponding to a spontaneous fluorescence under the assumption of vanishing intersystem crossing) resulting from the fit procedure gives a radiative decay rate of $k_r(S_1 \rightarrow S_0, \text{fit}) = 2 \times 10^7 \text{ s}^{-1}$ (50 ns; if it is taken into account that the emission quantum yield amounts to $\phi_{\text{PL}} = 80\%$, Table 1). Related information can be independently determined from an analysis of the absorption spectrum.³⁰ According to Fig. 1, the absorption peak of the lowest energy centered at 380 nm and showing a slight spectral overlap with the emission is assigned to represent this S₀ → S₁ transition. Thus, a (radiative) transition rate for the related emission can be directly estimated to be $k_r(S_1 \rightarrow S_0, \text{abs}) = 1.2 \times 10^7 \text{ s}^{-1}$ (corresponding to $\approx 80 \text{ ns}$) (for details see the ESI†). This value corresponds to a moderately allowed transition, as is expected for a S₀ → ¹MLCT type transition. With respect to the errors of the two different and independent methods of determination/estimates, both values for the transition rate are in good agreement. This is an important result since it strongly supports the model presented above with respect to the involvement of the singlet S₁ state in the emission process at ambient temperature, being the basis for the thermally activated short-lived emission. Moreover, it is concluded that the still slightly occurring geometry change in the excited state relative to the electronic ground state does not

significantly alter the $S_0 \rightarrow S_1$ transition rate, determined from the absorption (unrelaxed geometry), as compared to the $S_1 \rightarrow S_0$ rate, determined for the relaxed emitting states.

Conclusions

The phanephos ligand can be successfully applied to engineer highly luminescent Cu(I) complexes. According to the large P–Cu–P bite angle, the robustness of the paracyclophane core, and the overall bulkiness of the phanephos ligand in combination with the steric demands of the dmp ligand, photo-induced flattening of the molecular structure is not strongly important. As a consequence, non-radiative relaxations to the ground state are reduced and intense emission even in solution is observed. At ambient temperature, the luminescence of [Cu(dmp)(phanephos)](PF₆) is dominated by a thermally activated delayed fluorescence. The emission stems from the singlet state S_1 (¹MLCT) being thermally populated from the lowest triplet state T_1 (³MLCT), which serves as a reservoir of excited molecules. As a consequence, the decay time τ is reduced by a factor of nearly twenty from 240 μ s at 77 K to 14 μ s at ambient temperature. Since both emissions, the phosphorescence at lower temperatures and the delayed fluorescence at higher temperatures, display high quantum yields, this shortening of the decay time is related to a drastic increase of the radiative rate. These properties suggest high potential of [Cu(dmp)(phanephos)]⁺ and related compounds as emitter materials in opto-electronic applications, such as OLEDs, taking advantage of the singlet harvesting mechanism. Accordingly, high electroluminescence efficiencies will be potentially obtained even with low-cost emitter materials.

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- 27 The photophysical characterizations reported in this work were carried out for [Cu(dmp)(*Rp*-phanephos)](PF₆). Since the spectroscopic properties studied are identical for both enantiomers, the prefix *Rp* is omitted.
- 28 (a) [Cu(dmp)(phanephos)]⁺ remains stable in a CH₂Cl₂ solution as checked by NMR spectroscopy at least for the time necessary for sample preparation and photophysical measurements. All measurements were done with freshly prepared samples. Coordinating solvents have been avoided in order to prevent ligand exchange reactions.^{26a,28b} As powder material or doped into PMMA: the emitter is stable over many months; (b) C. Femoni, S. Muzzioli, A. Palazzi, S. Stagni, S. Zacchini, F. Monti, G. Accorsi, M. Bolognesi, N. Armaroli, M. Massi, G. Valenti and M. Marcaccio, *Dalton Trans.*, 2013, **42**, 997.
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