Novel luminescent iminephosphine complex of copper(I) with high photochemical and electrochemical stability†

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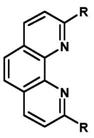
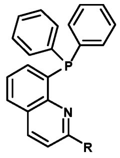
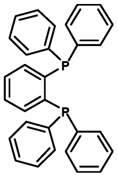
Luminescent heteroleptic Cu^I complexes based on asymmetrical iminephosphine ligands exhibit improved electrochemical and photochemical stability as compared to the analogous complexes based on traditional diimine or diphosphine ligands.

Photoluminescent complexes including bi- or tridentate aromatic *N*-heterocyclic ligands and low-valent metal ions like Ru^{II}, Os^{II}, Ir^{III}, Re^I or Cu^I have been exploited for practical applications in solar energy conversion, chemical sensing, biological probing and displays due to possessing an available low-lying metal-to-ligand charge-transfer (MLCT) excited state.[1,2] Though the economical and environmental considerations make Cu^I-diimines ([Cu(NN)$_2$]$^+$) far more attractive than the well-known MLCT complex Ru^{II}-polypyridine, the tendency to display weak emission and short-lived excited states has limited their practical applications.[2] The replacement of *N*-coordinating ligands with *P*-coordinating ligands is often found to improve the emission properties of the MLCT complexes because the strong π-acidity group of phosphine can enhance the energy level of the excited states and therefore decrease non-radiative deactivations.[3] In 2002, by using mixed-ligands, McMillin's group reported the first example of a highly emissive mononuclear copper complex [Cu(dmp)(DPEphos)]$^+$ (where dmp = 2,9-dimethyl-1,10-phenanthroline and DPEphos = bis[2-(diphenylphosphino)phenyl]ether).[4] Subsequently, a great number of similar complexes ([Cu(NN)(PP)]$^+$) were prepared and have been used as efficient electrophosphorescent materials successfully in multilayer organic light-emitting diodes (OLEDs) and simpler light emitting electrochemical cells (LECs).[5] More recently, room temperature phosphorescence was even observed from a series of [Cu(PP)$_2$]$^+$ complexes.[6,7] Based on the 1,2-bis(diphenylphosphino)benzene (dppb) ligand, both homoleptic [Cu(dppb)$_2$]$^+$ and heteroleptic [Cu(dppb)(DPEphos)]$^+$ complexes exhibit bright luminescence in the solid state as well as in OLEDs, which was also suspected to have originated from their MLCT excited state.

In this communication, we report the synthesis and characterization of two novel mixed-ligand Cu^I complexes [Cu(NP)(DPEphos)]$^+$, where NP = 8-diphenylphosphanyl-quinoline (dppq) (**1**) or 2-methyl-8-diphenylphosphanyl-quinoline (mdppq) (**2**). The chelating iminephosphine ligands of dppq and mdppq bear both imine and phosphine donor groups that can be looked as the structural units of phen (1,10-phenanthroline) and dppb, respectively. An unexpected finding is that the Cu^I complex based on the asymmetrical mdppq ligand processes a considerably higher reduced state and exited state stability than the analogous complexes based on symmetrical diimine or diphosphine ligand.


phen (R = H)
dmp (R = CH$_3$)


dppq (R = H)
mdppq (R = CH$_3$)


dppb

The iminephosphine ligands used herein have been used to fabricate Ni^I, Ru^{II} and Pd^{II} complexes previously,[8] and can be readily prepared by the literature method.[9] Complexes **1** and **2** can be obtained from the reaction of [Cu(NCCH$_3$)$_4$](BF$_4$) with one equivalent of DPEphos and iminephosphine ligand in CH$_2$Cl$_2$. Slow diffusion of diethyl ether into the ethanol or CH$_2$Cl$_2$ solutions of complexes gave yellow and air-stable crystals in good yields. As revealed by single-crystal X-ray diffraction analysis, the Cu^I center in both complexes has a distorted tetrahedral geometry (Fig. 1a).‡§ Since diphenylphosphanyl affords a significantly larger steric hindrance than the quinoline group in the asymmetrical dppq ligand, the angle between the P1–Cu1 bond and the P2–Cu1–P3 plane (155.0°) is much larger than that between the N1–Cu1 bond and the P2–Cu1–P3 plane (121.8°) in complex **1**. The introduction of sterically active substituents (methyl groups) on the quinoline ring, by contrast, makes these two angles more similar (140.4° *vs.* 135.6°) in complex **2**. Additionally, the methyl groups increase the Cu–N and Cu–P (DPEphos) distances in complex **2** about 0.04 Å and 0.02 Å, respectively, consistent with the precedent found in the phen and dmp analogues.[4] Whereas, by comparison with the [Cu(NN)(DPEphos)]$^+$ systems (**1** *vs.* phen complex, **2** *vs.* dmp complex), the average Cu–N and Cu–P (DPEphos) distances of the iminephosphine analogues elongate

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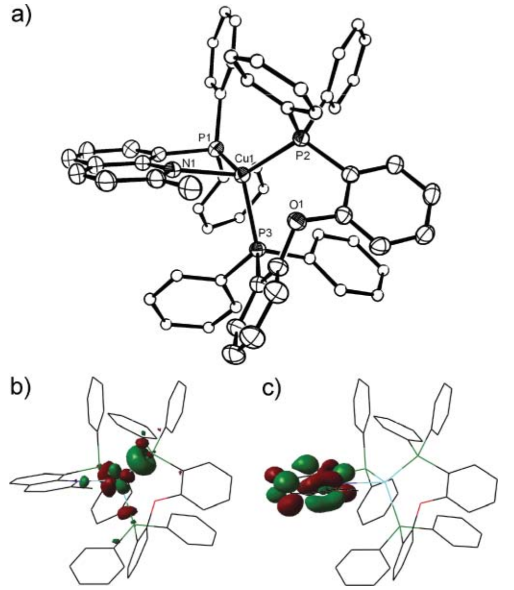

Fig. 1 (a) ORTEP diagram of the complex cation in **2**. Selected bond distances (Å) and angles (°): Cu1–N1 2.193(4), Cu1–P1 2.2798(14), Cu1–P2 2.2998(12), Cu1–P3 2.3170(12); N1–Cu1–P1 84.33(11), P2–Cu1–P3 108.90(4). Bond distances (Å) and bond angles (°) in the structure of **1**: Cu1–N1 2.153(2), Cu1–P1 2.2990(8), Cu1–P2 2.2909(7), Cu1–P3 2.2913(8); N1–Cu1–P1 83.25(6), P2–Cu1–P3 109.59(2). (b) The HOMO of **2**. (c) The LUMO of **2**.

about 0.08 Å and 0.04 Å, respectively,[4] indicating a more sterically crowded coordination sphere of central copper atom in both complexes.

The photophysical data of **1** and **2** in degassed CH_2Cl_2 solution and poly(methyl methacrylate) (PMMA) film are listed in Table 1. With reference to our previous work, the intense absorption at *ca.* 280 nm is assigned to the π–π* transition of the NP ligand, while the week shoulders ($\varepsilon \approx 1700\ M^{-1}cm^{-1}$) at 350–360 nm can be attributed to the MLCT transition involving the NP ligand and the Cu^I cation. To better understand the nature of the frontier orbitals, DFT calculations using the B3LYP method were carried out for **2**. As shown in Fig. 1b and Fig. 1c, the electron density in the highest occupied molecular orbital (HOMO) is mainly associated with the Cu^I center and Cu–P σ-bonding orbital, while that in the lowest unoccupied molecular orbital (LUMO) is localized on the π*-antibonding orbital of the quinoline ring. Thus, the lowest excited state of **2** is attributed to metal-to-ligand charge-transfer (MLCT) transition that mixed with a ligand-to-ligand charge-transfer (LLCT) state.

Table 1 Photophysical data for **1** and **2** at room temperature

Complex	$\lambda_{max,abs}$/nm	$\lambda_{max,em}$/nm	ϕ^a	τ/μs
Solution (in degassed CH_2Cl_2)				
1	274, 360 (sh)	642	0.0013	0.13^b
2	282, 350 (sh)	608	0.012	0.70^b
Film (20 wt% in PMMA)				
1	275, 356 (sh)	560	0.09	131^c
2	282, 350 (sh)	555	0.29	108^c

[a] Error ± 10%. [b] Fitted by single-exponential. [c] Since the decay is best-fit by three-exponentials, a weighted-average lifetime (τ_{av}) was used and calculated by the equation $\tau_{av} = \sum A_i\tau_i^2/\sum A_i\tau_i$, where A_i is the pre-exponential for the lifetime τ_i.

In CH_2Cl_2, complexes **1** and **2** emit with maximum at 642 nm and 608 nm, respectively. Similar to those suggested for $[Cu(NN)(DPEphos)]^+$ complexes,[4] the introduction of methyl group on the quinoline group blue-shifted the absorption and emission band as well as significantly increase the quantum yield (ϕ) and lifetime (τ) from 0.0013 and 0.13 μs for **1** to 0.012 and 0.70 μs for **2**, respectively. The reason for this can be explained as that the sterically active substituent prevents the excited state conformation change from a tetrahedral to a flattened structure, which has a lower MLCT energy and a larger non-radiative rate constant.[7] In the rigid medium of PMMA, relaxation caused by bond vibrations and rotations was restrained, leading to decrease in Stokes shift and increase in quantum yield and lifetime relative to those in solution. Though the quantum yield of 0.29 for **2** is still smaller than that of 0.49 for $[Cu(dmp)(DPEphos)]^+$,[7] it is comparable to the value ($\phi = 0.28$) found in a thin film of tris-(8-hydroxyquinoline) aluminum (Alq_3), a classical OLED material. Considered the energy harvesting by phosphorescent heavy-metal complexes is fourfold than that by fluorescent compounds in OLEDs, **2** can be anticipated to be a useful triplet emitter for electroluminescent applications.

The electrochemical properties of **1** and **2** were investigated by cyclic voltammetry (CV) at room temperature in dried and argon purged CH_3CN solutions, along with the comparative complexes $[Cu(dmp)(DPEphos)]^+$ and $[Cu(dppb)(DPEphos)]^+$. Similar to their dmp and dppb analogues, both **1** and **2** display irreversible and multiple oxidation peaks that might be attributed to multiple electron-transfer originating from the Cu^I center and the *P*-coordinating groups (ESI, Fig. S1).† The first oxidation peaks of 0.89 V (*vs.* Fc/Fc^+) for **1** and **2** are close to that for the dppb analogue but 0.10 V more positive than that for the dmp analogue, in accordance with the greater π-acid nature of the *P*-coordinating group. In CH_3CN solution, **1** shows an irreversible one-electron reduction as a consequence of the rapid decomposition of the $[Cu^+(dppq)^-(DPEphos)]$ species (ESI, Fig. S2).† The poor electrochemical stability of **1** should be related with the remarkable asymmetry of the steric hindrance for dppq ligand. However, **2** displays a reversible reduction couple with the $E_{1/2}$ value of −2.13 V (*vs.* Fc/Fc^+). Furthermore, the more interesting is that the electrochemical stability of **2** in its reduction process is even higher than that of $[Cu(dmp)(DPEphos)]^+$, in defiance of the relatively weaker metal–ligand bonds of **2**. As shown in Fig. 2a, the reduction wave of **2** presents good repeatability even after 10 scans with a variance less than 4%, while that of the dmp analogue changed significantly from reversible to irreversible in the first 10 cycles. We assume that the instability of $[Cu^+(dmp)^-(DPEphos)]$ species arise from the prolongation of Cu–N bond, which inevitably promotes ligand dechelation and substitution. In the case of $[Cu^+(mdppq)^-(DPEphos)]$ species, the negative charge is localized on the quinoline ring and mainly destabilized the Cu–N bond, but the less affected Cu–P bond from one coordinate unit will assist ligand rebinding, and hence prevent the ligand exchange reactions. Alternatively, the large steric hindrance of mdppq might also help reduction products against substitution

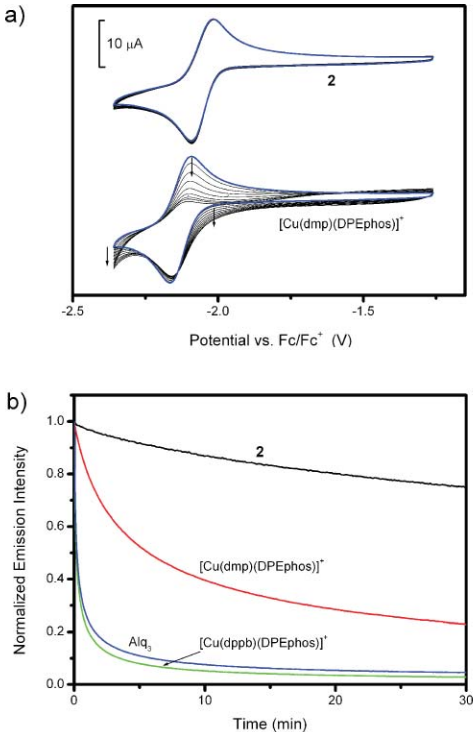

Fig. 2 (a) Multiple scan CVs for the reduction of **2** and $[Cu(dmp)(DPEphos)]^+$ in acetonitrile solution at room temperature. Scan rate 100 mV s^{-1} in 0.1 M TBAP. (b) Photodegradation of **2**, $[Cu(dmp)(DPEphos)]^+$, $[Cu(dppb)(DPEphos)]^+$ and Alq_3 on the surface of nanometer Al_2O_3 particles. (0.025 mmol complex mixed with 1.0 g Al_2O_3).

reactions by inhibiting the coordinating solvent from attacking the metal center. However, since the comparative complex with more bulky ligand, dppb, shows no electrochemical activity in the reduction process, the second explanation can not be examined further.

It's known that the photo-exited or electro-exited emitters can react with atmospheric moisture or oxygen resulting in degradation. If either explanation mentioned above established, it can be deduced that **2** will be more resistant to moisture or oxygen in its excited state, leading to an improved photo- or electroluminescent stability. To assess the photoluminescent stability of the new complex **2** in amorphous state and ambient condition, we loaded the selected complexes (**2**, $[Cu(dmp)(DPEphos)]^+$, $[Cu(dppb)(DPEphos)]^+$ and Alq_3) on the surface of nanometer Al_2O_3 particles with a concentration of 0.025 mmol g^{-1}, and then studied the emission intensity change of the compacted powder samples under UV irradiation. Since all complexes exhibit a similar extinction coefficient at 330 nm in CH_2Cl_2 (ESI, Fig. S3),† they were all irradiated at this wavelength using a 150 W Xe-lamp. As expected, **2** is the most photostable that maintained more than 75% of its initial intensity after 30 min (Fig. 2b). In contrast, the time to achieve the similar decay is only 1.5 min for $[Cu(dmp)(DPEphos)]^+$ and as short as 5 s for $[Cu(dppb)(DPEphos)]^+$ and Alq_3. Very similar result was also observed in the samples loaded on silica-gel plates (ESI, Fig. S4).† In view of the fact that the structure character of mdppq is intermediate between dmp and dppb, the best photochemical stability of mdppq complex can not be explained in the terms of improved hydrophobicity as some Ru^{II} or Ir^{III} systems,[10] but should be associated with the asymmetrical electronic character of mdppq ligand.

In short, the observation of high electrochemical and photochemical stability for iminephosphine complex **2** gives us a new way to improve the stability of MLCT complexes, which is identified as a critical fact to achieve long life devices for display or lighting applications. The application of complex **2** in electroluminescence devices is under way.

Acknowledgements

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Notes and references

‡ Crystal data for **1** $C_{59}H_{50}BCuF_4NO_2P_3$: M_r = 1048.27, triclinic, space group $P\bar{1}$, $a = 11.023(3)$, $b = 14.753(4)$, $c = 16.362(4)$ Å, $\alpha = 92.285(4)$, $\beta = 91.635(5)$, $\gamma = 96.309(3)°$, $V = 2641.2(12)$ Å^3, $T = 293$ K, $Z = 2$, $D_{calcd} = 1.318$ g cm^{-3}, $\mu(MoK\alpha) = 0.562$ mm^{-1}, 20 583 reflections measured, 11 808 unique ($R_{int} = 0.0208$) which were used in all calculations. The final $R(F^2)$ was 0.0545 [$I > 2\sigma(I)$].

§ Crystal data for **2** $C_{59}H_{48}BCl_2CuF_4NOP_3$: M_r = 1101.15, monoclinic, space group $P2_1/c$, $a = 18.361(5)$, $b = 12.831(4)$, $c = 24.921(7)$ Å, $\beta = 103.232(5)°$, $V = 5715(3)$ Å^3, $T = 293$ K, $Z = 4$, $D_{calcd} = 1.280$ g cm^{-3}, $\mu(MoK\alpha) = 0.612$ mm^{-1}, 34 854 reflections measured, 10 007 unique ($R_{int} = 0.0426$) which were used in all calculations. The final $R(F^2)$ was 0.0710 [$I > 2\sigma(I)$].

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