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COMMUNICATION

Efficient luminescence from a copper(I) complex doped in organic light-emitting diodes by suppressing C–H vibrational quenching†

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Efficient luminescence was realized by suppressing not only excited-state distortion but also C–H vibrational quenching in a Cu complex. Organic light-emitting diodes containing the Cu complex as an emitting dopant exhibited a maximum external quantum efficiency of 7.4%.

Organic light-emitting diodes (OLEDs) containing phosphorescent Ir complexes have achieved highly efficient electroluminescence (EL) with an external quantum efficiency (EQE) of greater than 20%.[1] Since a report by Zhang *et al.* in 2004, Cu complexes have attracted increasing attention because those exhibiting phosphorescence and thermally activated delayed fluorescence are potential candidates for realizing efficient OLEDs without using noble metals.[2] Recently, some OLEDs containing Cu complexes realized efficiencies comparable to those containing Ir complexes.[3] However, examples of Cu complex-based OLEDs demonstrating EQE ≥ 5% are still limited because most Cu complexes show low photoluminescence (PL) quantum efficiency.[3,4]

In this communication, we report a Cu complex with an improved PL quantum efficiency, [Cu(QuTz)(DPEphos)]BF_4 (**3**) (QuTz = 2-(5-tetrazolyl)quinoline), DPEphos = bis[2-(diphenylphosphino)phenyl]ether (Fig. 1), which was realized based on an effective strategy of suppressing both excited-state distortion and C–H vibrational quenching. OLEDs containing **3** displayed efficient luminescence with EQE = 7.4%.

Until now, the strategy used to improve the PL quantum efficiency of Cu complexes has involved suppressing nonradiative decay caused by distortion of the excited states of Cu complexes.[5] However, the PL quantum efficiencies of these Cu complexes are not sufficiently high compared with those of Ir complexes. To obtain high PL quantum efficiency, the rate of nonradiative decay of Cu complexes needs to be suppressed more strongly than that of Ir complexes due to the smaller spin–orbit coupling of Cu (ζ_{Ir} = 3909 cm^{-1}, ζ_{Cu} = 857 cm^{-1}).[6] In this study, we focused on another approach to suppress nonradiative decay through vibrational quenching in addition to suppression of distortion. According to the energy gap law, high-frequency vibrational modes such as C–H bond vibration effectively quench luminescence.[7] By replacing these modes with those of lower frequency, the PL quantum efficiency should be improved.

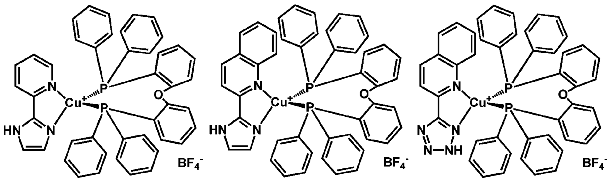

Fig. 1 Molecular structures of **1**, **2** and **3**.

The molecular structures of [Cu(PyIm)(DPEphos)]BF_4 (**1**) (PyIm = 2-(2′-pyridyl)imidazole), [Cu(QuIm)(DPEphos)]BF_4 (**2**) (QuIm = 2-(2′-quinolyl)imidazole) and **3** were designed by considering the following points (Fig. 1). A bulky DPEphos ligand is commonly introduced into Cu complexes to inhibit excited-state distortion, leading to an enhanced PL quantum efficiency. The aromatic *N*-heterocyclic ligand PyIm was introduced into **1** to promote luminescence from metal-to-ligand charge transfer (MLCT).[8] **2** contains a quinoline unit that can suppress excited-state distortion by increasing the steric hindrance between QuIm and DPEphos, resulting in an improved PL quantum efficiency. Complex **3** contains a tetrazole unit, which exhibits lower frequency modes from N–N and N–H bonds compared with those from C–H bonds. This can suppress nonradiative decay caused by C–H vibrational quenching, so a higher PL quantum efficiency is expected. The effects of suppressing excited-state distortion and C–H vibrational quenching on PL quantum efficiency were studied by comparing the properties of **1–3** with systematically changed ligands.

PyIm, QuIm and QuTz were synthesized according to literature procedures.[9,10] **1**, **2** and **3** were synthesized in moderate yield (79–90%) by reacting [$Cu(CH_3CN)_4$]BF_4 with DPEphos and PyIm, QuIm or QuTz in $CHCl_3$, respectively. Single crystals suitable for X-ray analysis were obtained by layering *n*-hexane on the surface of a solution of **3** in $CHCl_3$.

The molecular structure of **3** was determined by X-ray structural analysis; an ORTEP drawing of **3** is shown in Fig. 2. **3** is a

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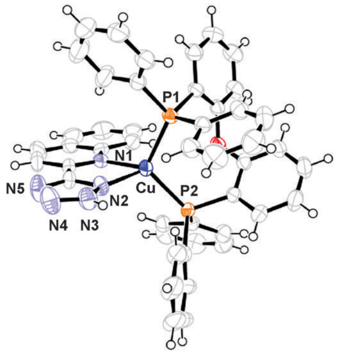

Fig. 2 ORTEP drawing of **3**. Thermal ellipsoids are drawn at the 50% probability level. Counterion and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cu–N1 2.069(5), Cu–N2 2.251(5), Cu–P1 2.2668(18), Cu–P2 2.2482(17); N1–Cu–N2 78.8(2), P1–Cu–P2 112.12(7).

mononuclear complex with a distorted tetrahedral structure. The Cu–N1, Cu–P1 and Cu–P2 bond lengths and N1–Cu–N2 and P1–Cu–P2 angles for **3** are similar to values for previously reported [Cu(N^N)(DPEphos)] complexes, but the Cu–N2 bond length is slightly longer.[4,5b,11] Interestingly, the H atom in the tetrazole unit was connected not to N5 but N3. The H atom increases the steric hindrance with a DPEphos ligand, which may increase the Cu–N2 bond length. Because of this steric hindrance, more effective suppression of distortion in the excited state is expected.

Absorption spectra for **1–3** in $CHCl_3$ are shown in Fig. 3(a). A shoulder at 300 nm and weaker absorption band at 352 nm were observed for **1** (Table 1). Based on a previous report,[11] the absorption shoulder at 300 nm is assigned to the π–π^* transition of PyIm and the absorption band at 352 nm is assigned to the MLCT transition from the Cu^I ion to PyIm. Similar absorptions at longer wavelengths were observed for **2** and **3**. This red shift is because QuIm and QuTz possess increased conjugation compared with PyIm. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for **1**, **2** and **3** were confirmed by DFT calculation (Fig. S1, ESI†). The electron density in the HOMOs was mainly localized at the Cu^I ion and Cu–P σ-bonding orbital, while that in the LUMOs was localized over PyIm, QuIm or QuTz. The calculations confirmed that the absorptions at 352 nm for **1**, 393 nm for **2**, and 387 nm for **3** were the result of MLCT transitions.

Films of **1**, **2** and **3** in 2,6-dicarbazolo–1,5-pyridine (PYD2) displayed green or yellow luminescence when irradiated with light of 365 nm, respectively (Fig. 3(a), inset). The PL spectra for films containing 10 wt% **1**, **2** and **3** in PYD2 are shown in Fig. 3(a), and the PL properties of these films are summarized in Table 1. PYD2, which is a 1,3-bis(carbazol-9-yl)benzene derivative with a higher lowest triplet excited-state (T_1) level (T_1 = 2.93 eV), was selected as a host material to confine triplet excitons of Cu complexes effectively.[12] The PL quantum yield (Φ_{PL}) was 0.25 for **1**, 0.27 for **2** and 0.36 for **3**. To clarify the reasons why **3** showed the highest Φ_{PL}, the radiative decay rate (k_r) and the nonradiative decay rate (k_{nr}) were calculated from Φ_{PL} and τ_{ave}. The k_r for **2** is smaller than that for **1** by about 1/10. However, the k_{nr} for **2** is smaller than that for **1** by about 1/11, which caused the slight improvement of PL quantum efficiency. Furthermore, k_{nr} for **3** is smaller than that for **2** by about 2/3 despite their identical k_r, which caused **3** to exhibit a PL quantum efficiency 1.3 times higher than that of **2**. From these results, it can be ascertained that the suppression of nonradiative decay probably leads to higher Φ_{PL}. To confirm this, Φ_{PL} and τ_{ave} were measured at various temperatures between 50 and 300 K, and then k_r and k_{nr} were calculated (Fig. 3(b),(c) and Fig. S2, ESI†). For **1**, Φ_{PL} decreased significantly with increasing temperature, while for **2**, Φ_{PL} decreased slightly. On the other hand, Φ_{PL} of **3** exhibited rather weak temperature dependence. As for k_{nr}, that of **1** increased

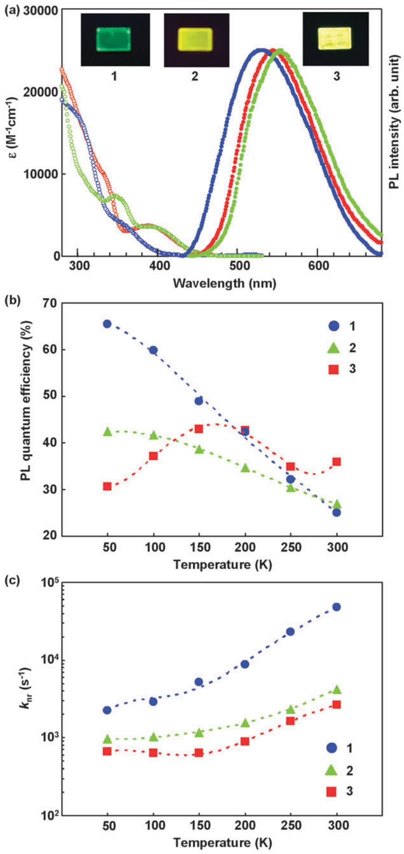

Fig. 3 (a) Absorption spectra in $CHCl_3$ and PL spectra in PYD2 films of **1** (blue), **2** (green) and **3** (red). Inset: photographs of **1**, **2** and **3** in PYD2 films under UV light at 365 nm. (b) Temperature dependence of Φ_{PL} for **1** (blue), **2** (green) and **3** (red) in PYD2 films. (c) Temperature dependence of k_{nr} for **1** (blue), **2** (green) and **3** (red) in PYD2 films.

Table 1 Photophysical properties of **1**,**2** and **3**

	Absorption[a]	Emission[b]				
complex	λ_{max}/nm (ε/M^{-1} cm^{-1})	λ_{max}/nm	ϕ	τ_{ave}[c]/μs	k_r/s^{-1}	k_{nr}/s^{-1}
1	300 (17 000), 352 (4200)	530	0.25	15.5	1.6×10^4	4.8×10^4
2	347 (7300), 393 (3600)	549	0.27	174.7	1.5×10^3	4.2×10^3
3	332 (10 000), 387 (3700)	544	0.36	243.0	1.5×10^3	2.6×10^3

[a] In $CHCl_3$. [b] In PYD2 film. [c] PL liftime is composed of two components. For simplicity, a weighted-average lifetime (τ_{ave}) was used and calculated by the equation $\tau_{ave} = \sum A_i\tau_i/\sum A_i$, where A_i is the pre-exponential factor for the lifetime. Two components (τ_f, τ_s) and their pre-exponential factors (A_f, A_s) are shown in Table S1–S3.

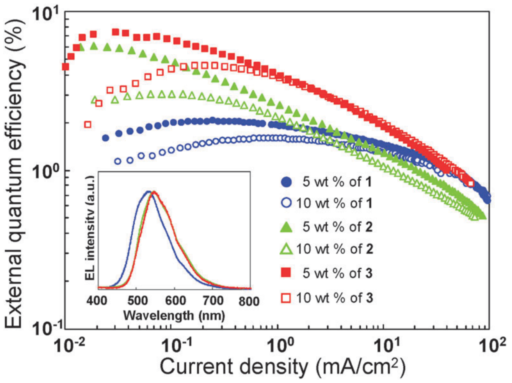

Fig. 4 Dependence of EQE on current density for OLEDs with the structure ITO/PEDOT:PSS (40 nm)/X wt% of Cu complex:PYD2 (30 nm)/DPEPO (50 nm)/LiF (0.7 nm)/Al (100 nm). Inset: EL spectra of OLEDs containing **1**, **2** and **3**.

more significantly with increasing temperature than those of **2** and **3**, which means that thermally dependent nonradiative decay is suppressed more effectively in **2** and **3** than in **1**. k_{nr} increased similarly for **2** and **3**; however, k_{nr} of **3** was lower than that of **2** at all temperatures, so thermally independent nonradiative decay is suppressed more effectively in **3** than in **2**. These results confirm that suppression of nonradiative decay leads to **3** possessing higher Φ_{PL} at room temperature than **1** and **2**.

Next, the reasons why nonradiative decay is effectively suppressed in **3** are discussed. Reduced excited-state distortion and C–H vibrational quenching both probably play a role in this suppression. Riesgo *et al.* stated that the distortion of Cu complexes is directly related to their "Stokes-like" shift, that is, the difference in wavelength between absorption and emission spectra.[13,14] Therefore, the Stokes-like shifts for **1**, **2** and **3** were estimated. The Stokes-like shifts were 178, 156 and 157 nm for **1**, **2** and **3**, respectively. The smaller Stokes-like shifts for **2** and **3** compared with that of **1** indicate that excited-state distortion is suppressed more effectively in **2** and **3**. In addition, the number of C–H bonds in the ligands is different for **2** and **3**: 8 for QuIm and 6 for QuTz. Because the Stokes-like shifts of **2** and **3** are almost identical, it would be possible to infer that Φ_{PL} of **3** is further improved by suppression of C–H vibrational quenching.

OLEDs containing **1**, **2** and **3** were fabricated to evaluate the EL properties of the Cu complexes. Devices with the structure ITO/PEDOT:PSS (40 nm)/10 wt% of **1**, **2** or **3**: PYD2 (30 nm)/DPEPO (50 nm)/LiF (0.7 nm)/Al (100 nm) (ITO is indium tin oxide, PEDOT:PSS is poly (3, 4-ethylenedioxythiophene)–poly-(styrenesulfonic acid), and DPEPO is bis{2-[di(phenyl)phosphino]-phenyl}ether oxide) were produced. DPEPO was selected as a hole blocking and electron transport layer to confine triplet excitons effectively because of its high T_1 level (T_1 = 3.0 eV).[15] The emitting layer consisting of a Cu complex and PYD2 was formed by spin-coating, and DPEPO was deposited by thermal evaporation. EL spectra of the OLEDs showed green or yellow luminescence at 535 nm for **1**, 549 nm for **2** and 548 nm for **3**, which are similar to the PL spectra of the Cu complexes doped in PYD2 films (Fig. 4, inset). The maximum EQE was 1.6% for **1**, 3.0% for **2** and 4.5% for **3**, respectively, and the order coincides with that of the PL quantum efficiency described above (Fig. 4). To further improve the EQE by suppressing concentration quenching, OLEDs with an emitting layer of 5 wt% Cu complex doped in PYD2 were fabricated. As a result, the maximum EQE was improved to 2.0% for **1**, 6.1% for **2** and 7.4% for **3**.

In conclusion, we developed a luminescent Cu complex with improved PL quantum efficiency based on the effective strategy of suppressing not only the excited-state distortion but also C–H vibrational quenching. An OLED containing the Cu complex demonstrated efficient luminescence with EQE = 7.4%.

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Notes and references

1 (*a*) C. Adachi, M. A. Baldo, M. E. Thompson and S. R. Forrest, *J. Appl. Phys.*, 2001, **90**, 5048; (*b*) M. E. Kondakova, T. D. Pawlik, R. H. Young, D. J. Giesen, D. Y. Kondakov, C. T. Brown, J. C. Deaton, J. R. Lenhard and K. P. Klubek, *J. Appl. Phys.*, 2008, **104**, 094501; (*c*) N. Chopra, J. Lee, Y. Zheng, S.-H. Eom, J. Xue and F. So, *Appl. Phys. Lett.*, 2008, **93**, 143307; (*d*) D. Tanaka, H. Sasabe, Y.-J. Li, S.-J. Su, T. Takeda and J. Kido, *Jpn. J. Appl. Phys.*, 2007, **46**, L10; (*e*) D. Tanaka, Y. Agata, T. Takeda, S. Watanabe and J. Kido, *Jpn. J. Appl. Phys.*, 2007, **46**, L117.

2 Q. Zhang, Q. Zhou, Y. Cheng, L. Wang, D. Ma, X. Jing and F. Wang, *Adv. Mater.*, 2004, **16**, 432.

3 (*a*) J. C. Deaton, S. C. Switalski, D. Y. Kondakov, R. H. Young, T. D. Pawlik, D. J. Giesen, S. B. Harkins, A. J. M. Miller, S. F. Mickenberg and J. C. Peters, *J. Am. Chem. Soc.*, 2010, **132**, 9499; (*b*) M. Hashimoto, S. Igawa, M. Yashima, I. Kawata, M. Hoshino and M. Osawa, *J. Am. Chem. Soc.*, 2011, **133**, 10348.

4 C.-W. Hsu, C.-C. Lin, M.-W. Chung, Y. Chi, G.-H. Lee, P.-T. Chou, C.-H. Chang and P.-Y. Chen, *J. Am. Chem. Soc.*, 2011, **133**, 12085.

5 (*a*) D. R. McMillin and K. M. McNett, *Chem. Rev.*, 1998, **98**, 1201; (*b*) D. G. Cuttell, S.-M. Kuang, P. E. Fanwick, D. R. McMillin and R. A. Walton, *J. Am. Chem. Soc.*, 2002, **124**, 6; (*c*) S. B. Harkins and J. C. Peters, *J. Am. Chem. Soc.*, 2005, **127**, 2030; (*d*) K. Saito, T. Arai, N. Takahashi, T. Tsukuda and T. Tsubomura, *Dalton Trans.*, 2006, 4444; (*e*) Q. Zhang, J. Ding, Y. Cheng, L. Wang, Z. Xie, X. Jing and F. Wang, *Adv. Funct. Mater.*, 2007, **17**, 2983; (*f*) A. Tsuboyama, K. Kuge, M. Furugori, S. Okada, M. Hoshino and K. Ueno, *Inorg. Chem.*, 2007, **46**, 1992; (*g*) O. Moudam, A. Kaeser, B. Delavaux-Nicot, C. Duhayon, M. Holler, G. Accorsi, N. Armaroli, I. Séguy, J. Navarro, P. Destruel and J.-F. Nierengarten, *Chem. Commun.*, 2007, 3077; (*h*) L. Qin, Q. Zhang, W. Sun, J. Wang, C. Lu, Y. Cheng and L. Wang, *Dalton Trans.*, 2009, 9388.

6 M. Montalti, A. Credi, L. Prodi and M. T. Gandolfi, *Handbook of Photochemistry*, Taylor and Francis, Boca Raton, 2006.

7 (*a*) N. J. Turro, *Modern Molecular Photochemistry*, University Science Books, 1991; (*b*) C. Rondo, *Luminescence*, Willey, Weinheim, 2008; (*c*) G. Stein and E. Würzberg, *J. Chem. Phys.*, 1975, **62**, 208; (*d*) Y. Haas, G. Stein and E. Würzberg, *J. Chem. Phys.*, 1974, **60**, 258.

8 (*a*) A. Barbieri, G. Accorsi and N. Armaroli, *Chem. Commun.*, 2008, 2185; (*b*) L. Zhang, B. Li and Z. Su, *J. Phys. Chem. C*, 2009, **113**, 13968; (*c*) W. Sun, Q. Zhang, L. Qin, Y. Cheng, Z. Xie, C. Lu and L. Wang, *Eur. J. Inorg. Chem.*, 2010, 4009.

9 (*a*) Z. P. Demko and K. B. Sharpless, *J. Org. Chem.*, 2001, **66**, 7945; (*b*) N. M. Lân, R. Burgard and C. Wentrup, *J. Org. Chem.*, 2004, **69**, 2033.

10 G. Stupka, L. Gremaud and A. F. Williams, *Helv. Chim. Acta*, 2005, **88**, 487.

11 J. Min, Q. Zhang, W. Sun, Y. Cheng and L. Wang, *Dalton Trans.*, 2011, **40**, 686.

12 K. S. Son, M. Yahiro, T. Imai, H. Yoshizaki and C. Adachi, *Chem. Mater.*, 2008, **20**, 4439.

13 E. C. Riesgo, Y.-Z. Hu, F. Bouvier, R. P. Thummel, D. V. Scaltrito and G. J. Meyer, *Inorg. Chem.*, 2001, **40**, 3413.

14 The Stoke shift is the energetic difference between absorption and emission from the same state. Since the states of the absorption and emission of these Cu complexes have not been identified completely, we use the term "Stokes-like" shift.

15 C. Han, Y. Zhao, H. Xu, J. Chen, Z. Deng, D. Ma, Q. Li and P. Yan, *Chem.–Eur. J.*, 2011, **17**, 5800.