Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Efficient Luminescence from a Copper(I) Complex Doped in Organic Light-Emitting Diodes by Suppressing C-H Vibrational Quenching

Atsushi Wada, Qisheng Zhang, Takuma Yasuda, Isao Takasu, Shintaro Enomoto and Chihaya Adachi

Experimental section

General. ^{1}H and ^{13}C NMR spectra were recorded on an Avance III 500 spectrometer (Bruker Biospin, Germany). MALDI-TOF mass spectra were obtained on an Autoflex III spectrometer (Bruker Daltonics, Germany) in reflection/positive mode with dithranol as a matrix. Elemental analysis was performed on a MT-5 CHN analyzer (Yanaco, Japan) at the Service Center of Elemental Analysis of Organic Compounds at Kyushu University. Solvents and starting materials were purchased from Sigma-Aldrich (USA), Tokyo Chemical Industry (Japan), or Wako Chemicals (Japan), and used without further purification. 2-(2'-Pyridyl)imidazole (PyIm),[S1] 2-(2'-Quinolyl)imidazole (QuIm),[S1] and 2-(5-tetrazolyl)quinoline) (QuTz) [S2] were synthesized according to the literature.

Synthesis. 2-(2'-Quinolyl)imidazole (QuIm). 2-Quinoline carboxaldehyde (1.45 g, 9.23 mmol) in EtOH (20 mL) was added to a solution of glyoxal (1.3 mL, 40% aq. solution) in EtOH (10 mL) at 0 °C. Ice-cold ammonia (3.7 mL, 28% aq. solution) was added rapidly. The mixture was stirred at 0 °C for 1 h and then allowed to warm to r.t. The mixture was extracted with Et_2O (50 mL×3), dried over Na_2SO_4, and the solvent was evaporated. The residue was heated under reflux in EtOH (30 mL) in the presence of charcoal for 2 h. After filtration, the solvent was evaporated under reduced pressure and dried *in vacuo*. Recrystallization from $CHCl_3$/*n*-hexane gave QuIm as a yellow powder: yield 0.90 g (50%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.59 (s, 1H), 8.31 (d, J = 8.6 Hz, 1H), 8.23 (d, J = 8.6 Hz, 1H), 8.03 (d, J = 8.5 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.72 (t, J = 5.6 Hz, 1H), 7.53 (t, J = 5.9 Hz, 1H), 7.30 (s, 1H), 7.22 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 148.4, 147.5, 146.6, 137.5, 137.2, 130.0, 128.7, 128.0, 127.9, 126.5, 118.8, 118.1. MALDI-TOF-MS: *m/z* 195.81 (M^+).

[Cu(PyIm)(DPEphos)]BF_4 (1). A mixture of $[Cu(CH_3CN)_4]BF_4$ (0.43 g, 1.37 mmol) and bis[2-(diphenylphosphino)phenyl]ether (0.80 g, 1.37 mmol) in $CHCl_3$ (10 mL) was stirred at room temperature for 1 h and then added to a solution of PyIm (0.20 g, 1.38 mmol) in $CHCl_3$ (5 mL). The reaction mixture was stirred for an additional 1 h and then filtered. The yellow filtrate was concentrated to ~2 mL. *n*-Hexane was added to the surface of the solution, resulting in yellow crystals of **1**; yield 1.03 g (90%). Anal. Calcd for $C_{44.4}H_{35.4}BC_{l1.2}CuF_4N_3OP_2$ (*i.e.*, [Cu(PyIm)(DPEphos)]BF_4·0.4$CHCl_3$): C, 60.47; H, 4.05; N, 4.77%. Found: C, 60.32; H, 4.02; N, 4.71%.

[Cu(QuIm)(DPEphos)]BF_4 (2). A mixture of $[Cu(CH_3CN)_4]BF_4$ (0.19 g, 0.59 mmol)

and bis[2-(diphenylphosphino)phenyl]ether (0.35 g, 0.59 mmol) in $CHCl_3$ (5 mL) was stirred at room temperature for 1 h and then added to a solution of QuIm (0.12 g, 0.59 mmol) in $CHCl_3$ (5 mL). The reaction mixture was stirred for an additional 1 h and then filtered. The yellow filtrate was concentrated to ~2 mL. *n*-Hexane was added to the surface of the solution, resulting in a yellow powder of **2**; yield 0.42 g (80%). Anal. Calcd for $C_{48.9}H_{37.9}BCl_{2.7}CuF_4N_3OP_2$ (*i.e.*, $[Cu(QuIm)(DPEphos)]BF_4 \cdot 0.9CHCl_3$): C, 59.23; H, 3.85; N, 4.24%. Found: C, 59.16; H, 3.84; N, 4.04%.

[Cu(QuTz)(DPEphos)]BF_4 (3). A mixture of $[Cu(CH_3CN)_4]BF_4$ (0.20 g, 0.64 mmol) and bis[2-(diphenylphosphino)phenyl]ether (0.38 g, 0.64 mmol) in $CHCl_3$ (5 mL) was stirred at room temperature for 1 h and then added to a solution of QuTz (0.13 g, 0.64 mmol) in $CHCl_3$ (5 mL). The reaction mixture was stirred for an additional 1 h and then filtered. The yellow filtrate was concentrated to ~2 mL. *n*-Hexane was added to the surface of the solution, resulting in yellow crystals of **3**; yield 0.45 g (79%). Anal. Calcd for $C_{46.5}H_{35.5}BC_{l1.5}CuF_4N_5OP_2$ (*i.e.*. $[Cu(QuTz)(DPEphos)]BF_4 \cdot 0.5CHCl_3$): C, 59.05; H, 3.78; N, 7.41%. Found: C, 59.22; H, 3.91; N, 7.56%.

X-ray Crystallography. X-ray structural analysis was performed at the Center of Advanced Instrumental Analysis, Kyushu University. A single crystal suitable for X-ray analysis was protected by araldite, attached to a glass fiber, and mounted on a goniometer head. The measurements were carried out at 268 K using a Bruker SMART APEX CCD detector with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and a 2 kW rotating anode generator. The data frames were integrated using SAINT (Version 6.45) and merged to give a unique data set for the structure determination. Empirical absorption corrections were carried out using SADABS.[S3] The structure was solved by direct methods and refined by a full-matrix least-squares technique on all $F2$ data using the SHELX suite of programs.[S4] Non-hydrogen atoms were refined with anisotropic displacement factors. Hydrogen atoms were placed at calculated positions and included in the structure factor calculation but not refined.

DFT calculation. DFT calculations were performed using Gaussian 03 at the B3LYP level.[S5] For **1** and **2**, the ground state geometry was optimized and molecular orbitals were calculated using 6-31+G* as a basis set for C, H, N, O and P atoms and LANL2DZ for Cu. For **3**, the ground state geometry was inferred from the crystal structure, and only molecular orbitals were calculated using the same method described

for **1** and **2**.

Photophysical measurements. Absorption spectra were measured with an ultraviolet-visible-near infrared (UV-vis-NIR) absorption spectrometer (PerkinElmer, Lambda 950-PKA, USA). Photoluminescence spectra were measured with a photoluminescence spectrometer (Horiba Jovan Yvon, FluoroMax-4). PL quantum efficiency was measured with an absolute photoluminescence quantum yield measurement system (Hamamatsu, C9920-02, Japan). PL quantum efficiency and lifetime at a range of temperatures were measured with a streak camera system (Hamamatsu, C4334, Japan).

OLED fabrication and measurement. PEDOT:PSS (Clevious P VP. AI4083, H. C. Starck, Germany) was deposited as a hole injection layer onto a pre-cleaned indium tin oxide (ITO) substrate by spin-coating, yielding a layer with a thickness of ~40 nm. The PEDOT:PSS layer was baked at 200 °C for 10 minutes to remove any residual solvent. A solution of Cu complex and PYD2 in CH_2Cl_2 was spin-coated on top of the PEDOT:PSS layer, yielding a film that was ~30 nm thick. DPEPO with a thickness of ~50 nm was deposited by thermal evaporation as an electron transport layer. LiF with a thickness of ~0.7 nm and Al with a thickness of ~100 nm were deposited by thermal evaporation as an electron injection layer and cathode, respectively. Current density–voltage-luminance characteristics of the OLEDs were measured at ambient temperature using a semiconductor parameter analyzer (Agilent, E5273A, USA) and an optical power meter (Newport, 1930C, USA). EL spectra of the OLEDs were obtained on a multichannel spectrometer (Ocean Optics, USB2000, USA).

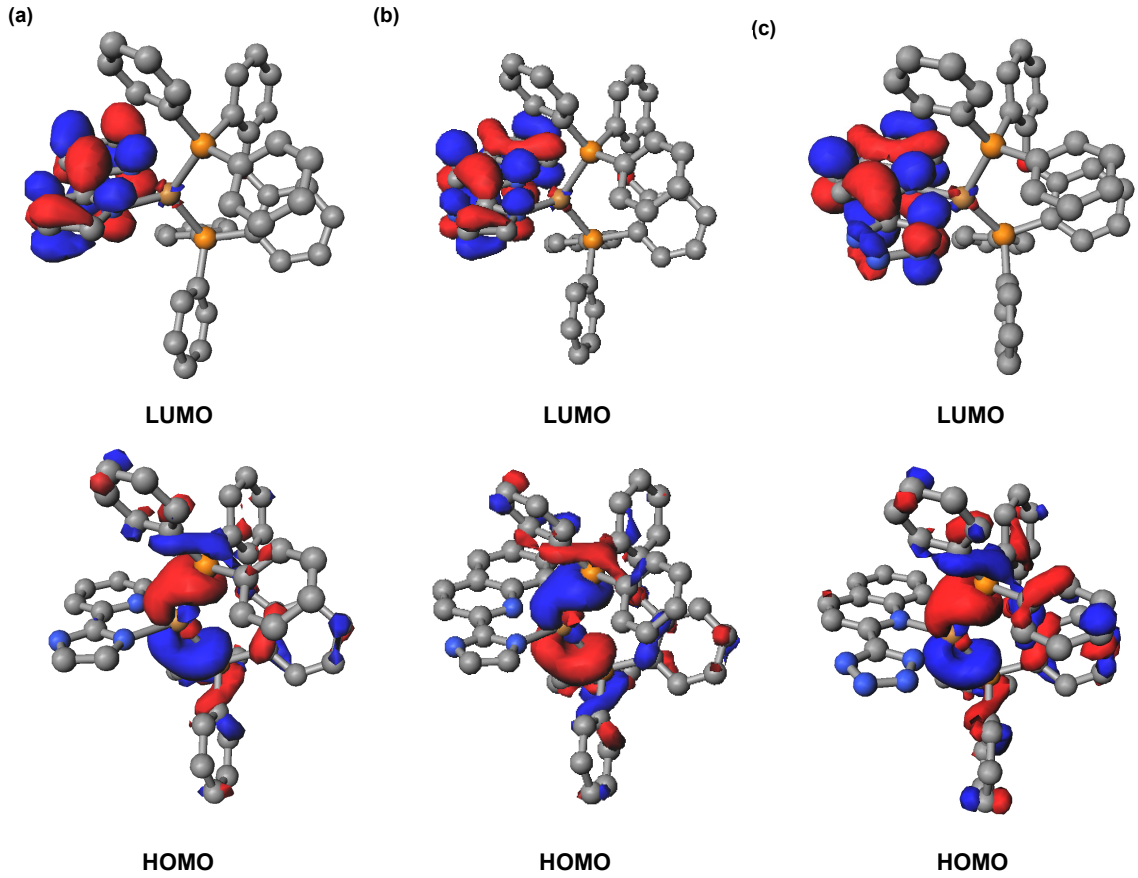

Fig. S1 HOMO and LUMO distributions of (a) **1**, (b) **2** and (c) **3**.

Table S1 Lifetime data of 10 wt% **1** in PYD2. They are obtained using two-exponential decay function $I = A_f\exp(-t/\tau_f) + A_s\exp(-t/\tau_s)$.

T / K	τ_f / μs	τ_s / μs	A_f	A_s	τ_{ave} / μs
300	14	25	1.15	0.18	15.5
250	24	45	0.88	0.27	28.9
200	45	98	0.74	0.35	62.0
150	74	164	1.42	0.49	97.1
100	110	280	0.65	0.16	143.6
50	122	393	1.29	0.25	166.0

Table S2 Lifetime data of 10 wt% **2** in PYD2. They are obtained using two-exponential decay function $I = A_f\exp(-t/\tau_f) + A_s\exp(-t/\tau_s)$.

T / K	τ_f / μs	τ_s / μs	A_f	A_s	τ_{ave} / μs
300	145	549	1.26	0.10	174.7
250	198	794	0.90	0.20	306.4
200	278	885	0.80	0.26	426.9
150	369	975	0.80	0.29	530.2
100	411	1026	0.77	0.29	579.3
50	447	1111	0.78	0.24	603.2

Table S3 Lifetime data of 10 wt% **3** in PYD2. They are obtained using two-exponential decay function $I = A_f\exp(-t/\tau_f) + A_s\exp(-t/\tau_s)$.

T / K	τ_f / μs	τ_s / μs	A_f	A_s	τ_{ave} / μs
300	181	869	1.11	0.11	243.0
250	237	950	0.85	0.23	388.8
200	375	1392	0.77	0.29	653.2
150	649	1651	0.74	0.26	909.5
100	804	2090	0.85	0.15	996.9
50	847	2184	0.87	0.15	1043.6

Table S4 Φ_f, Φ_s and Φ_{tatal} of 10 wt% **1** in PYD2.

T / K	ϕ_f	ϕ_s	ϕ_{total}
300	0.20	0.05	0.25
250	0.21	0.12	0.33
200	0.22	0.20	0.42
150	0.27	0.21	0.48
100	0.39	0.21	0.60
50	0.43	0.23	0.66

Table S5 Φ_f, Φ_s and Φ_{tatal} of 10 wt% **2** in PYD2.

T / K	ϕ_f	ϕ_s	ϕ_{total}
300	0.21	0.06	0.27
250	0.17	0.14	0.31
200	0.17	0.17	0.34
150	0.20	0.19	0.39
100	0.21	0.20	0.41
50	0.24	0.18	0.42

Table S6 Φ_f, Φ_s and Φ_{tatal} of 10 wt% **3** in PYD2.

T / K	ϕ_f	ϕ_s	ϕ_{total}
300	0.24	0.12	0.36
250	0.17	0.18	0.35
200	0.18	0.25	0.43
150	0.22	0.20	0.42
100	0.26	0.11	0.37
50	0.22	0.09	0.31

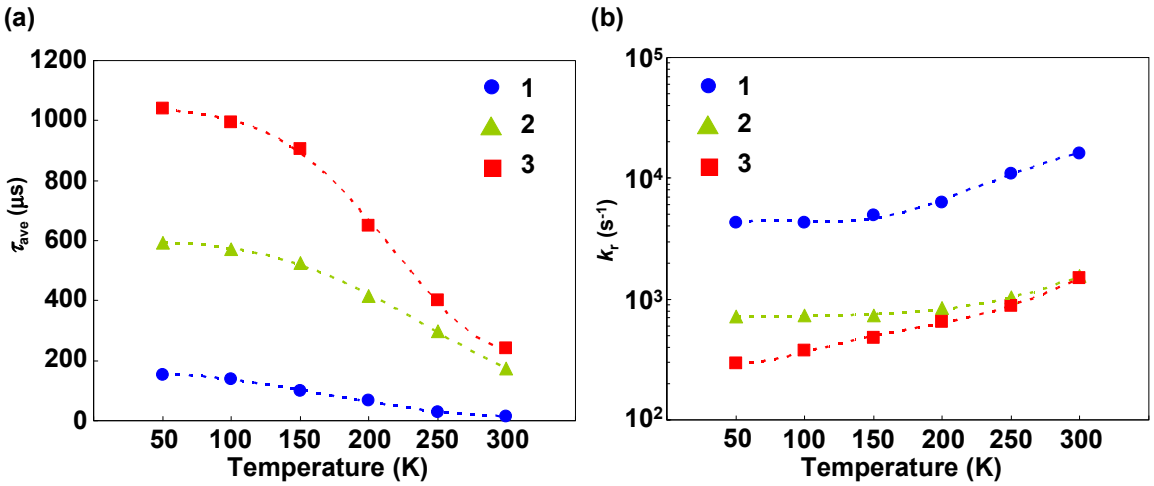

Fig. S2 (a) Temperature dependence of the lifetime (τ_{ave}) of **1** (blue), **2** (green) and **3** (red) in PYD2 films. (b) Temperature dependence of the rate of radiative decay (k_r) for **1** (blue), **2** (green) and **3** (red) in PYD2 films.

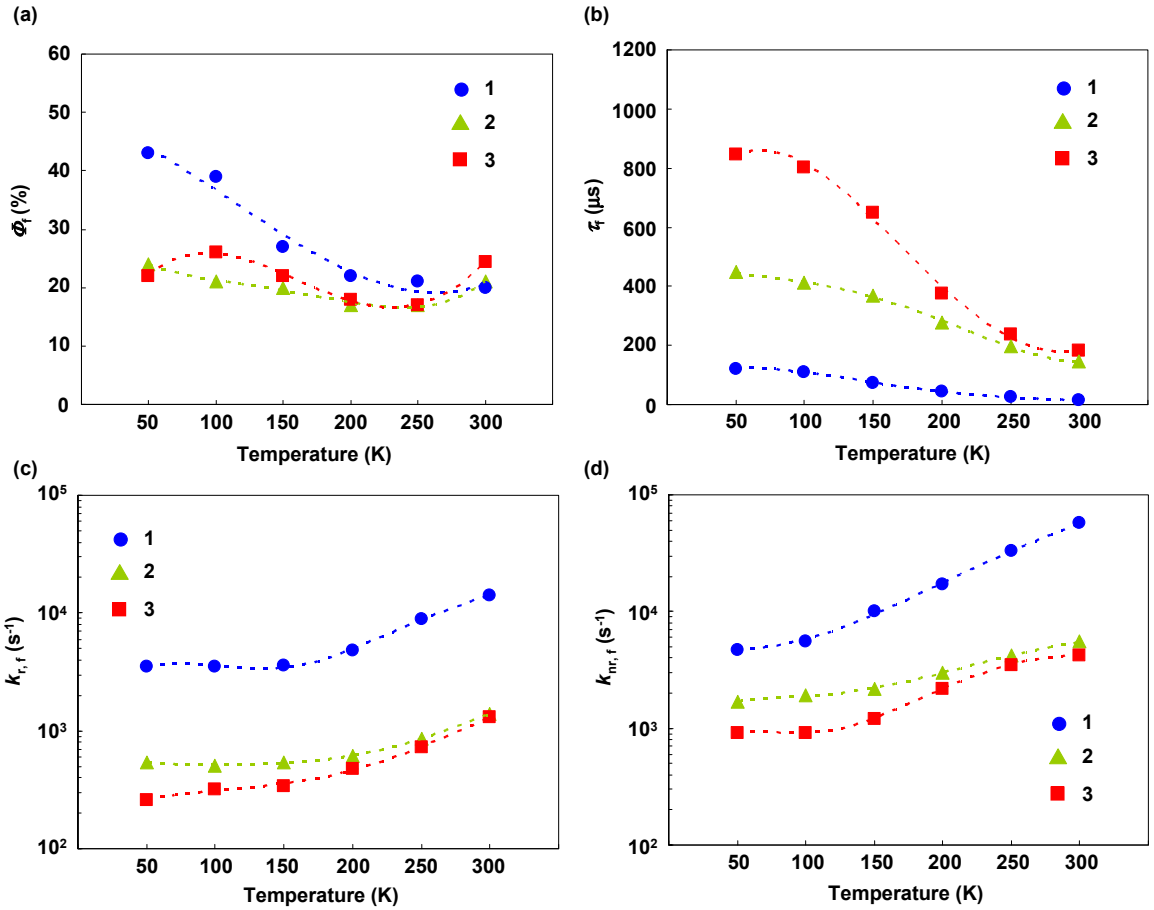

Fig. S3 (a) Temperature dependence of Φ_f for **1** (blue), **2** (green) and **3** (red) in PYD2 films. (b) Temperature dependence of the lifetime (τ_f) of **1** (blue), **2** (green) and **3** (red) in PYD2 films. (c) Temperature dependence of the rate of radiative decay ($k_{r,f}$) for **1** (blue), **2** (green) and **3** (red) in PYD2 films. (d) Temperature dependence of $k_{nr,f}$ for **1** (blue), **2** (green) and **3** (red) in PYD2 films.

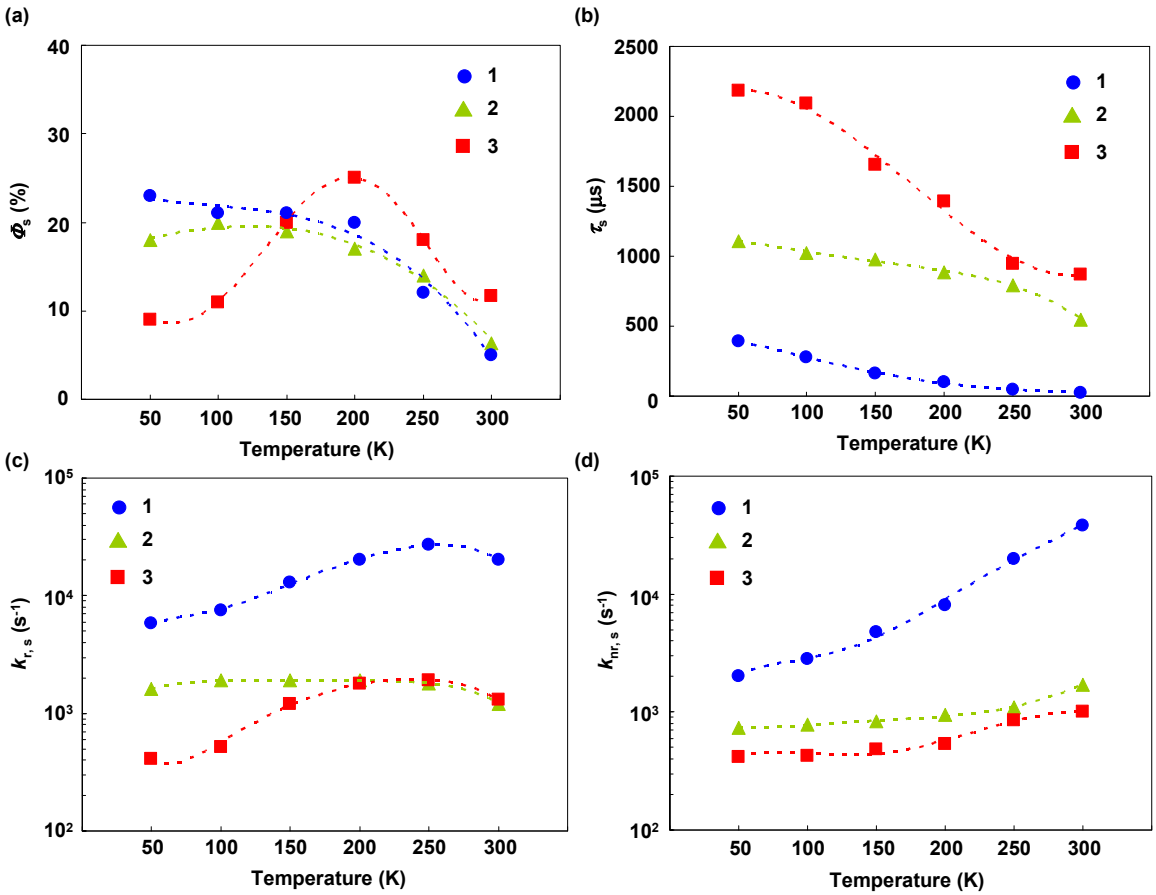

Fig. S4 (a) Temperature dependence of Φ_s for **1** (blue), **2** (green) and **3** (red) in PYD2 films. (b) Temperature dependence of the lifetime (τ_s) of **1** (blue), **2** (green) and **3** (red) in PYD2 films. (c) Temperature dependence of the rate of radiative decay ($k_{r,s}$) for **1** (blue), **2** (green) and **3** (red) in PYD2 films. (d) Temperature dependence of $k_{nr,s}$ for **1** (blue), **2** (green) and **3** (red) in PYD2 films.

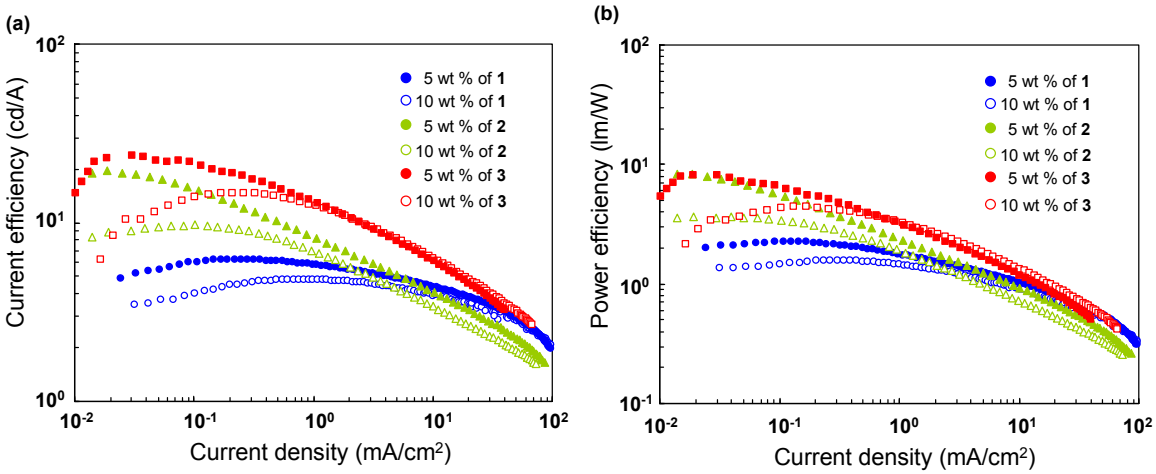

Fig. S5 (a) Dependence of current efficiency on current density for OLEDs with the structure ITO/PEDOT:PSS (40 nm)/X wt% of Cu complex:PYD2 (30 nm)/DPEPO (50 nm)/LiF (0.7 nm)/Al (100 nm). (b) Dependence of power efficiency on current density for OLEDs with the structure ITO/PEDOT:PSS (40 nm)/X wt% of Cu complex:PYD2 (30 nm)/DPEPO (50 nm)/LiF (0.7 nm)/Al (100 nm).

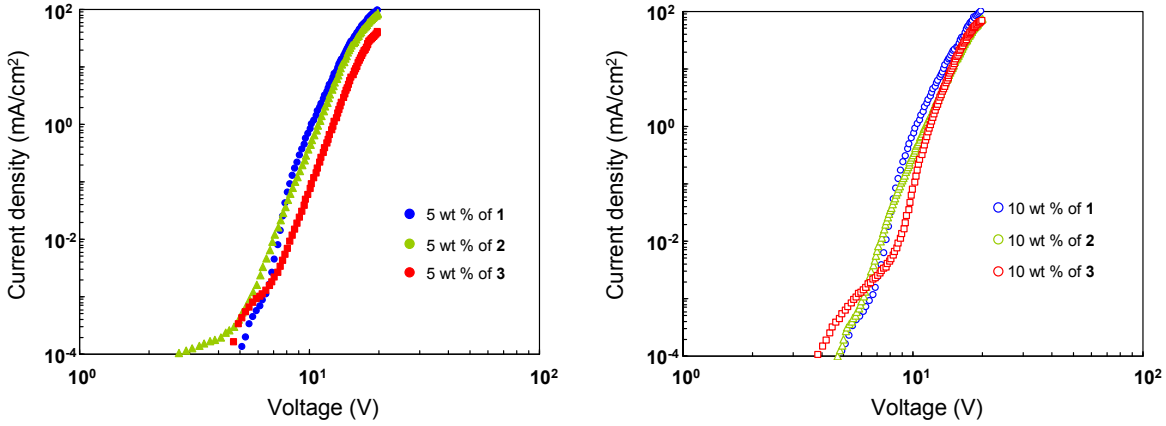

Fig. S6 *J-V* characteristics for OLEDs with the structure ITO/PEDOT:PSS (40 nm)/X wt% of Cu complex:PYD2 (30 nm)/DPEPO (50 nm)/LiF (0.7 nm)/Al (100 nm).

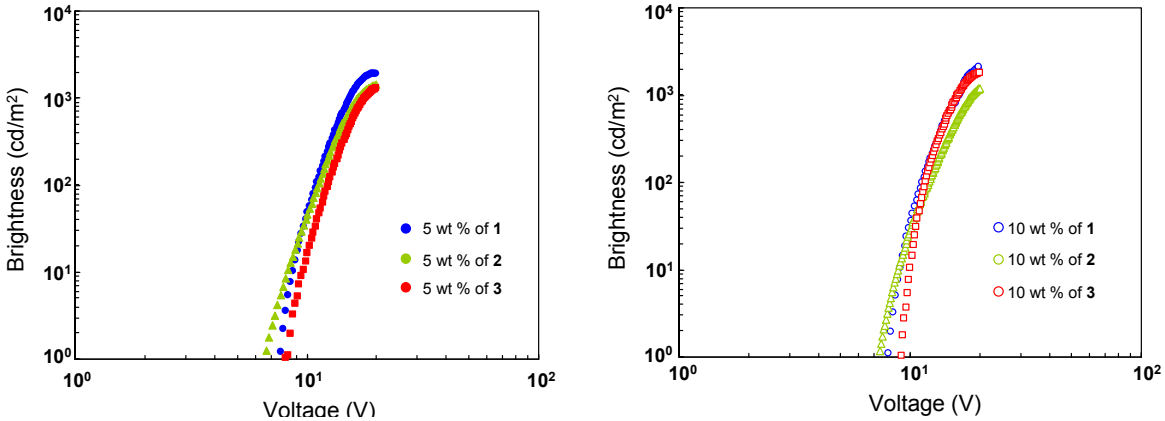

Fig. S7 *L-V* characteristics for OLEDs with the structure ITO/PEDOT:PSS (40 nm)/X wt% of Cu complex:PYD2 (30 nm)/DPEPO (50 nm)/LiF (0.7 nm)/Al (100 nm).

Reference

S1 G. Stupka, L. Gremaud and A. F. Williams, *Helv. Chim. Acta*, 2005, **88**, 487.

S2 (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.

S3 G. M. Sheldrick, *SADABS*, University of Goettingen, Germany, 1996.

S4 G. M. Sheldrick, SHELXL97 and SHELXS97, University of Goettingen, Germany, 1997.

S5 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitano, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. Pople, *Gaussian 03*, revision E.01, Gaussian, Inc., Wallingford, CT, 2004.