Supplementary Material

for

Luminescent Ir(III) complexes containing benzothiazole-based tridentate ligands: synthesis, characterization, and application to organic light-emitting diodes

Junpei Kuwabara,[a] Tomomi Namekawa,[a] Masa-aki Haga,[b] Takaki Kanbara*[a]

[a]Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1, Tennodai, Tsukuba, Japan; E-mail: kanbara@ims.tsukuba.ac.jp
[b]Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, 1-13-27, Kasuga, Bunkyo-ku, Tokyo, Japan.

E-mail: kanbara@ims.tsukuba.ac.jp

Experimental

General, measurement, and materials.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a JEOL ESC-400, a JEOL EX-270, and a Bruker AVANCE 400 NMR spectrometer. IR spectra were recorded on a JASCO IR-810 spectrophotometer. ESI Mass spectra were recorded on a Applied Biosystems Qstar Pulsar I. MALDI-MS spectra were recorded on a Kratos-Shimadzu AXIMA-CFR plus MALDI-TOF MS. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN Elemental Analyzer. UV/Vis absorption spectra were recorded on a JASCO V-630iRM spectrophotometer. Photoluminescent spectra were recorded on a JASCO FP-6200 spectrophotometer. Luminescence quantum yields were obtained by a Hamamatsu photonics C9920-02. The reactions applying microwave irradiation were carried out with CEM Discover LabMate. $IrCl_3•4H_2O$, terpyridine, benzothiazole, and other chemicals were used as received from commercial suppliers. Anhydrous DMF was purchased from Kanto Chemical and used as a dry solvent.

1,3-Diiodo-4,6-dimethylbenzene[1] and Ir(tpy)Cl_3[2] were prepared according to the literature methods.

Crystal structure determination.

Intensity data were collected on a Rigaku R-AXIS Rapid diffractometer with Mo *K*α radiation. Crystals were mounted on glass capillary tubes. A full matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters method by SHELXL-97 program. Hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. CCDC 834013 and 834012 contains the supplementary crystallographic data for compounds **[Ir(bbtx)(tpy)]2PF_6** and **Ir(bbtx)(ppy)Cl**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Synthetic Methods

Synthesis of 1,3-bis(2-benzothiazolyl)-4,6-dimethylbenzene (bbtxH)

A mixture of 1,3-diiodo-4,6-dimethylbenzene (845 mg, 2.5 mmol), benzothiazole (678 μL, 6.3 mmol), Cs_2CO_3 (2.04 g, 6.3 mmol), CuBr (143 mg, 1.0 mmol), $Pd(OAc)_2$ (56.1 mg, 0.25 mmol), and P(*t*-Bu)$_3$·HBF_4 (145 mg, 0.5 mmol) was stirred in anhydrous DMF (25 mL) for 12 h at 150 °C under nitrogen atmosphere. After cooling to room temperature, the resulting mixture was extracted with CH_2Cl_2 and washed with water and brine. After drying over Na_2SO_4, the solution was filtered and evaporated in vacuo. The product was isolated by column chromatography on silica gel using $CHCl_3$ as an eluent (645 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* =7.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 2H) 7.34 (s, 1H), 2.72 (s, 6H). $^{13}C\{^1H\}$ (67.8 MHz, $CDCl_3$): δ 166.7, 153.6, 139.0, 135.3, 134.8, 132.4, 131.0, 126.1, 125.0, 123.3, 121.2, 21.3. Anal. calcd for $C_{22}H_{16}N_2S_2$: C, 70.88; H, 4.45; N, 7.69; found C, 70.93; H, 4.33; N, 7.52.

Synthesis of [Ir(bbtx)Cl_2]$_2$

A mixture of **bbtxH** (419 mg, 1.1 mmol) and $IrCl_3$•$4H_2O$ (208 mg, 0.56 mmol) was stirred in a 1:1 mixture of 2-methoxyethanol and 1,2-dichloroethane (15 mL) for 24 h at 100 °C under nitrogen atmosphere. After cooling to room temperature, the resulting precipitate was washed with methanol and $CHCl_3$ (316 mg, 89%). MALDI-MS Calcd for $C_{44}H_{30}Cl_3Ir_2N_4S_4$ $[M-Cl]^+$ 1232.5, Found 1232.9. Anal. Calcd for $C_{22}H_{15}Cl_2IrN_2S_2 \cdot H_2O$: C, 40.49; H, 2.63; N, 4.29, Found: C, 40.19; H, 2.83; N 4.09.

Synthesis of [Ir(bbtx)(tpy)]2PF_6

A mixture of Ir(tpy)Cl_3 (29.8 mg, 0.055 mmol) and **bbtxH** (29.3 mg, 0.080 mmol) was stirred in ethylene glycol (8 mL) for 24 h at 210 °C under nitrogen atmosphere. After cooling to room temperature, aqueous solution of NH_4PF_6 (10 mL) was added to the mixture. The resulting precipitate was filtered and washed with toluene to remove excess **bbtxH** and extracted with CH_3CN. Evaporation of CH_3CN in vacuo gave orange solid of **Ir(bbtx)(tpy)]2PF$_6$** (40.8 mg, 66%). Analytically pure sample was obtained by crystallization from DMF/*i*-Pr_2O. ^1H NMR (400 MHz, CD_3CN): δ 8.99 (d, *J* = 7.6 Hz, 1H), 8.98 (d, *J* = 9.6 Hz, 1H), 8.90 (dd, *J* = 9.6 and 7.6 Hz , 1H), 8.44 (d, *J* = 8.0 Hz, 2H), 7.97 (d, *J* =8.4 Hz, 2H), 7.93 (dt, *J* = 8.4 and 1.2 Hz, 2H) 7.55 (s, 1 H), 7.42 (dd, *J* = 6.0 and 1.2 Hz, 2H), 7.36 (ddd, *J* = 8.0, 7.2, and 1.2 Hz, 2H), 7.26 (ddd, *J* = 8.0, 6.0, and 1.2 Hz, 2H), 7.19 (ddd, *J* = 8.4, 7.2, and 1.2 Hz, 2H), 5.91 (d, *J* = 8.4 Hz, 2H), 3.04 (s, 6H). ESI-MS Calcd for $C_{37}H_{26}IrN_5S_2$ $[M]^{2+}$ 398.5, Found 398.6. Anal. Calcd for $C_{37}H_{26}F_{12}IrN_5P_2S_2$: C, 40.89, H, 2.41; N, 6.44; Found: C, 40.92; H, 2.41; N, 6.66.

[Ir(bbtx)(tpy)]2PF$_6$ was also obtained by a reaction of **[Ir(bbtx)Cl$_2$]$_2$** (25.0 mg, 0.020 mmol) and terpyridine (45.9 mg, 0.20 mmol) in ethylene glycol (8 mL) for 24 h at 210 °C under nitrogen atmosphere (29.0 mg, 64%).

Synthesis of Ir(bbtx)(ppy)Cl by using microwave radiation

A mixture of **[Ir(bbtx)Cl$_2$]$_2$** (25.0 mg, 0.020 mmol) and 2-phenylpyridine (47.0 μL mg, 0.33 mmol) in ethylene glycol (8 mL) was irradiated with microwave (300 W) for 4 min. After cooling to room temperature, water was added to the mixture for precipitation of the product. The resulting precipitate was filtered and washed with diethyl ether and hexane. Recrystalization from CHCl$_3$/hexane gave **Ir(bbtx)(ppy)Cl** (22.4 mg, 76%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 10.7 (d, *J* = 5.4 Hz, 1H, ppy), 8.15 (overlapped, 2H, ppy), 7.73 (td, *J* = 5.4 and 3.3 Hz, 1H, ppy), 7.70 (d, *J* = 7.8 Hz 2H, bbtx), 7.52 (d, *J* = 7.7 Hz 1H, ppy), 7.19 (t, *J* = 7.2 Hz, 2H, bbtx), 7.04 (s, 1H, bbtx), 7.02 (t, *J* = 7.2 Hz, 2H, bbtx), 6.63 (t, *J* = 7.5 Hz, 1H, ppy), 6.54 (d, *J* =8.2 Hz, 2H, bbtx), 6.53 (overlapped, 1H, ppy), 5.90 (d, *J* = 7.6 Hz, 1H, ppy), 2.93 (s, 6H). ESI-Ms Calcd for $C_{33}H_{23}IrN_3S_2$ [M-Cl]$^+$ 718.1, Found 718.1. Anal. Calcd for $C_{33}H_{23}ClIrN_3S_2 \cdot 0.5CHCl_3$: C, 49.49, H, 2.91; N, 5.17; Found: C, 49.09; H, 3.02; N, 4.88.

Synthesis of Ir(bbtx)(ppy)Cl by using conventional heating method

A mixture of **[Ir(NCN)Cl$_2$]$_2$** (213 mg, 0.17 mmol) and 2-phenylpyridine (400 μL, 2.8 mmol) in ethylene glycol (60 mL) was heated for 20 h at 235 °C. **Ir(bbtx)(ppy)Cl** was isolated by the same procedure using microwave radiation. (79.9 mg, 32%).

Thermogravimetric analysis (TGA) of Ir(bbtx)(ppy)Cl.

TGA was carried out with Seiko EXTRA TG-DTA-6300. The sample was dried in a vacuum for 3 h at 250 °C prior to analysis. The rate of temperature rise was 10 °C/min.

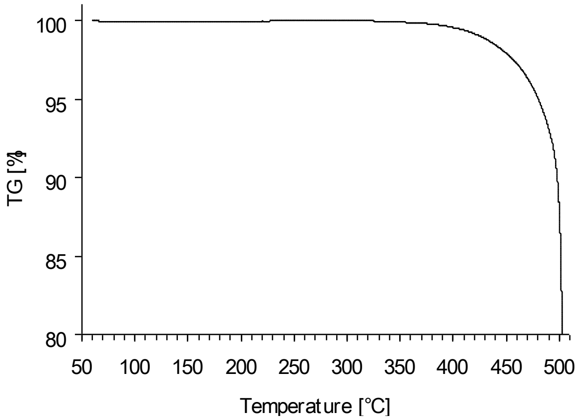

Fig. S-1. TGA degradation of **Ir(bbtx)(ppy)Cl**.

Evaluation of OLED with Ir(bbtx)(ppy)Cl

Luminance measurements were carried out with Topcon SR-UL2. External quantum yields were obtained by the integral of spectral radiance. Following materials were used for fabricating organic light-emitting diodes.

Anode: Al (200 nm)

Electron injection layer: LiF (0.5 nm)

Electron transfer layer: 4,7-diphenyl-1,10-phenanthroline (4 nm) and arylanthracene (35 nm)

Host material in the emitting layer: 4,4´-bis(9-dicarbazolyl)-2,2´-biphenyl (30 nm) or bis(2-methyl-8-quinolinolato)phenolatealuminium(III) (30 nm)

Dopant: **Ir(bbtx)(ppy)Cl** or bis(1-phenylisoquinoline)(acetylacetonate)iridium(III) (7% in host materials)

Hole transfer layer: *N*,*N*´-bis(naphthalen-1-yl)-*N*,*N*´-bis(phenyl)-benzidine (30 nm)

Hole injection layer: triarylamine (30 nm)

Cathode: ITO (100 nm)

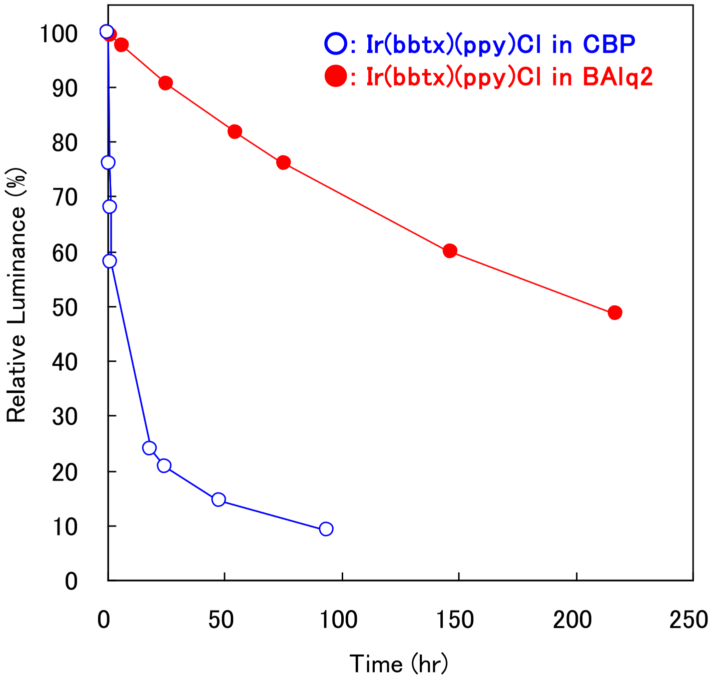

Fig. S-2. Time course of relative luminance of device I (open circle) and II (filled circle).

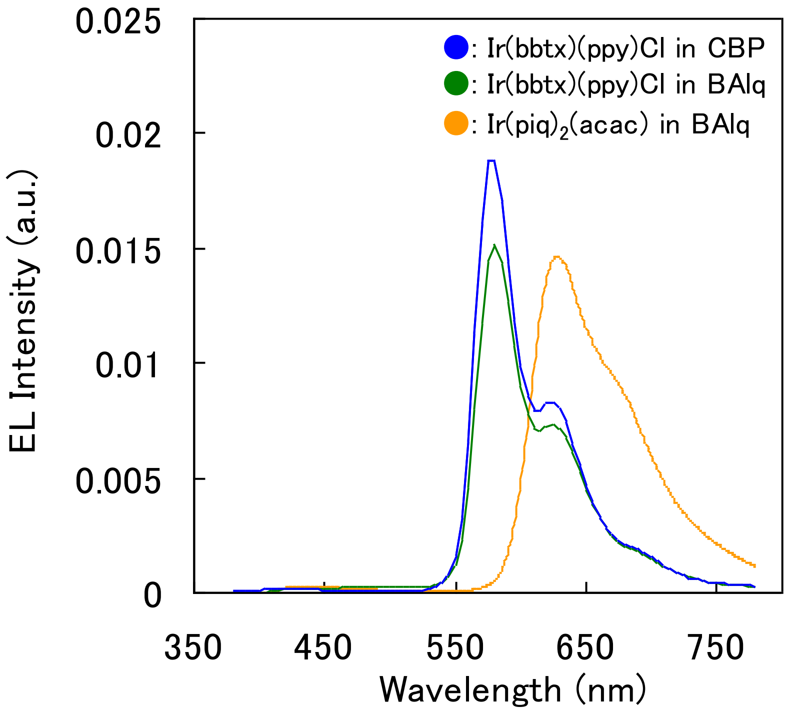

Fig. S-3. EL spectra of device I (blue), II (green), and III (orange).

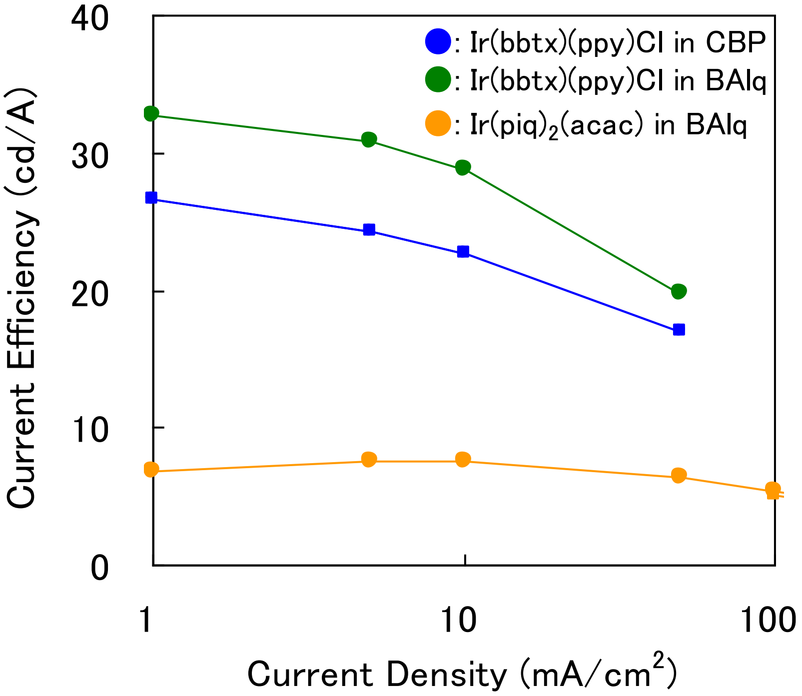

Fig. S-4. Current efficiency of device I (blue), II (green), and III (orange).

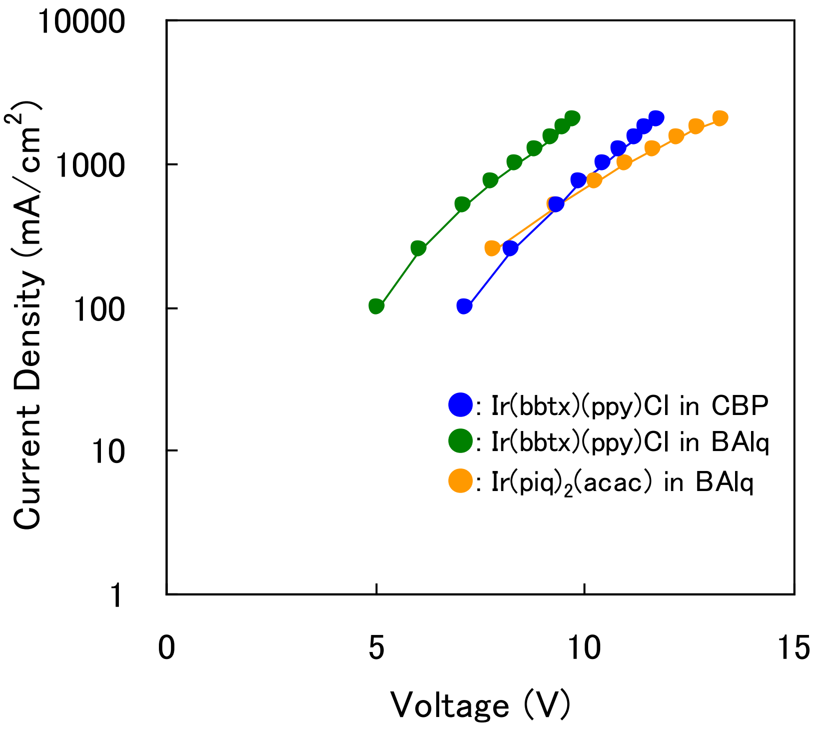

Fig. S-5. Current density vs voltage of device I (blue), II (green), and III (orange).

References

1 E. B. Merkushev, N. D. Simakhina and G. M. Koveshnikova, *Synthesis*, 1980, **6**, 486.

2 J.-P. Collin, I. M. Dixon, J.-P. Sauvage, J. A. G. Williams, F. Barigelletti and L. Flamigni, *J. Am. Chem. Soc.*, 1999, **121**, 5009.