Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Synthesis, structure and efficient electroluminescence of heteroleptic dipyridylamido/bis(pyridylphenyl) iridium(III) complex

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General methods

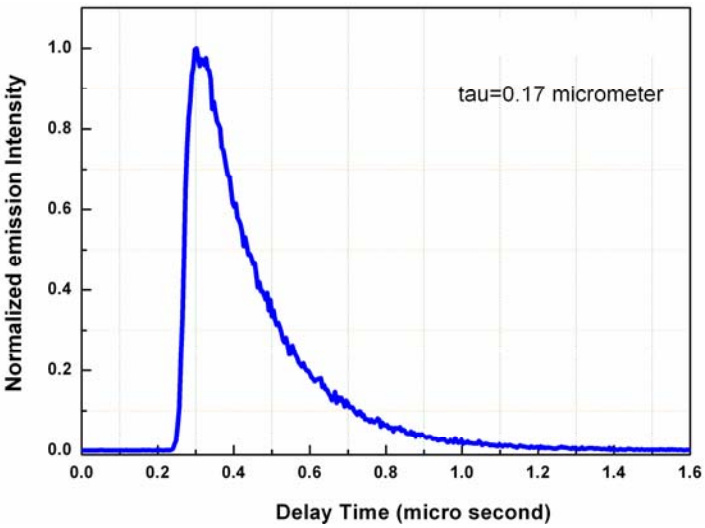
All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an MBRAUN Labmaster 130 glovebox. The nitrogen was purified by being passed through a dry clean column (4A molecular sieves, Nikka Seiko Co.) and a Gas clean GC-XR column (Nikka Seiko Co.). The nitrogen in the glovebox was constantly circulating through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer (MBRAUN) to ensure both were always below 0.1 ppm. Materials obtained from commercial supplier were used without further purification unless otherwise mentioned. THF, toluene and diethyl-ether (dehydrated, stabilizer-free) were obtained Kanto Kagaku Co. and purified by use of a MBRAUN SPS-800 solvent purification system. Samples for NMR spectroscopic measurements were prepared in the glovebox by use of J. Young valve NMR tubes. NMR (^{1}H, ^{13}C) spectra were recorded on a JNM-AL 300 spectrometer. Elemental analyses (C, H, N) were performed on a MICRO CORDER JM10 apparatus (J-SCIENCE LAB. Co.). The TGA were measured by Shimadzu TGA-50/5H Thermal Analysis Instruments. [{Ir(ppy)$_2$(μ-Cl)}$_2$] was prepared according to the literature.[1]

[Ir(ppy)$_2$(dpa)] (1) In a 50 mL flask, N-litho-dipyridylamido which was prepared from the reaction of 2,2`-dipyridylamine (68.5 mg, 0.4 mmol) with 2.6 M n-BuLi in hexane (0.15 mL), was added dropwise to the [{(ppy)$_2$Ir(μ-Cl)}$_2$] (220 mg, 0.2 mmol) in THF (15 ml). After being stirred at 80 °C for 16 hours under nitrogen, the reaction mixture was cooled down to room temperature, and the solvent was evaporated under vacuum. In order to remove THF completely, the residue was dissolved in toluene and evaporated under reduced pressure. The product was dissolved again in toluene and filtered to remove lithium chloride. The crude product was washed with Et_2O to give **1**

(mg, 70% yield). Single crystals suitable for X-ray analysis were obtained by recrystallization in benzene.

^{1}H NMR (300 MHz, C_4D_8O, rt): δ (ppm) 8.36 (d, *J* = 5.5 Hz, 2 H), 7.94 (d, *J* = 8.1 Hz, 2 H), 7.73 (t, *J* = 7.3 Hz, 2 H), 7.58 (d, *J* = 7.7 Hz, 2 H), 7.15 (d, *J* = 5.1 Hz, 2 H), 7.05–6.97 (m, 4 H), 6.75 (t, *J* = 7.3 Hz, 2 H), 6.61 (d, *J* = 6.6 Hz, 4 H), 6.12 (d, *J* = 7.3 Hz, 2 H), 5.75 (t, *J* = 6.0 Hz, 2 H). ^{13}C NMR (75 MHz, C_4D_8O, rt): δ (ppm) 168.6, 155.6, 155.6, 149.6, 144.2, 149.1, 136.9, 134.0, 131.8, 129.4, 124.2, 123.4, 122.0, 120.7, 118.9, 110.9. Anal. calcd. for $C_{32}H_{24}IrN_5$: C, 57.30; H, 3.61; N, 10.44. Found: C, 56.99; H, 3.89; N, 10.53.

Absorption and PL Measurements: The absorption and photoluminescence (PL) spectra of complex **1** in degassed dichloromethane have been measured on a Shimadzu UV-2550 UV-VIS spectrometer and on a fluorescence spectrometer Shimadzu RF-5301PC with a Xe arc lamp excitation source, respectively. The quantum yields were measured relative to quinine sulfate in 1 N H_2SO_4 assuming a quantum yield of 0.546 when excited at 350 nm. The solutions for the lifetime measurement were freshly prepared by dissolving the complex **1** into spectroscopic grade $CHCl_3$. Measurements were carried out by using a streak-camera based system (Hamamatsu, C4780) combined with a femto second Ti:sapphire laser system (Spectra-Physics, Spitfire). The excitation and detection wavelengths were 397 nm and 450–700 nm, respectively. The time resolution was 30–40 ns. The lifetimes and the quantum yields have errors bars of ±10%.



SFigure 1. Phosphorescent life time of [Ir(ppy)$_2$(dpa)].

Electrochemical measurement:

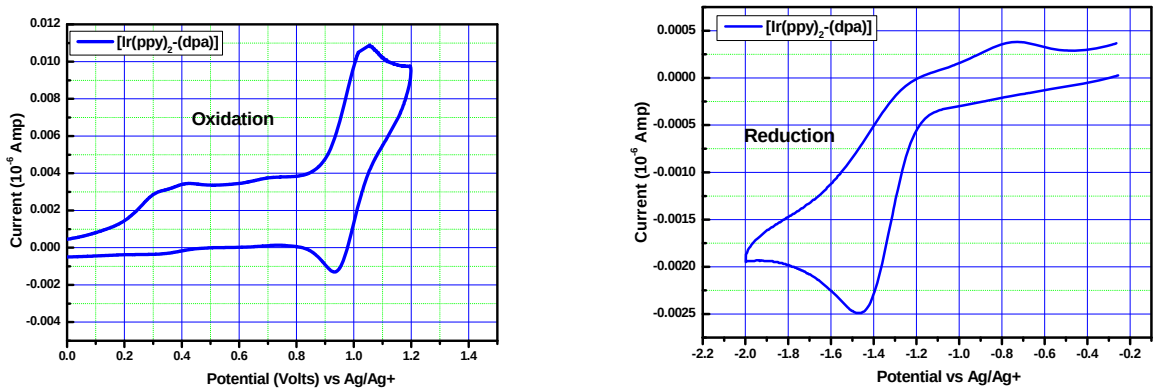
The oxidation potential of complex **1** in acetonitrile was measured at scan rate 100mV/s on a cyclic voltammeter (HSV-100-Hokuto Denko Corporation) with an electrochemical work station, using Pt

working electrode, platinum wire as auxiliary electrode, and $Ag/AgNO_3$ as reference electrode under nitrogen atmosphere. Each measurement was calibrated with an internal standard, ferrocene/ferrocenium (Fc) redox system. The HOMO energy values were calculated based on the value of –4.8 eV for Fc with respect to zero vacuum level[2]. The results are listed in STable 1.

STable 1 Electrochemical data for the $[Ir(ppy)_2(dpa)]$ and some materials used in this work**.**

Materials	HOMO[eV]	LUMO[eV]	Eg[eV]	E^{ox}[V][a]
NPB	–5.4	–2.4	3	-
CBP	–6.1	–3.0	3.1	-
$[Ir(ppy)_2(dpa)]$	–5.62	–3.04	2.58	1.04
BCP	–6.7	–3.2	3.5	-
Alq3	–6.0	–3.3	2.7	-

[a] 0.1 M [TBAP] in Acetonitrile, scan rate 100 mV s^{-1}, versus Ag/Ag^+ couple. HOMO= (E_{ox} – $E_{Fc/Fc+}$)+ 4.8eV and LUMO = HOMO + E_g. E_g were estimated from the onset wavelength of the optical absorption. The values for NPB, CBP, BCP and AlQ were taken from literature [3].



SFigure 2. CV graphs of $[Ir(ppy)_2(dpa)]$ in acetonitrile.

Fabrication of the OLEDs and EL measurements:

Indium-tin oxide (ITO) coated glass substrate with a sheet resistance 20Ω/Ω were patterned and cleaned using deionized water, acetone, and isopropyl alcohol sequentially for 20 minutes using an ultrasonic bath and dried in flowing nitrogen. Prior to organic film deposition, the ITO surface was treated with oxygen plasma for 15 minutes. All organics were purified by train sublimation method and thermally evaporated at a rate of 1.0 Å/s at a base pressure of 8×10^{-4} Pa. Thickness of the deposited layers was measured in situ by a quartz crystal monitor. A 1 nm thick LiF layer was deposited at a rate of 0.2 Å/s. The Al electrode (cathode) was deposited at a rate of 10 Å/s. The

active area of the diode segments was 5×5 mm^2. The electroluminescence (EL) spectra have been measured using a high resolution spectrometer (Stellar net Blue wave UV-VIS-NIR). The current density-voltage-luminescence (*I-V-L*) characteristics were measured with a luminance meter Chroma-Meter CS-200 (Konika Minolta, Japan) and a Keithley 2400 programmable voltage-current digital source meter. All measurements were carried out at room temperature under ambient conditions. 4,4`-bis(N-(1-naphthyl)-N-phenylamino)biphenyl (NPB) act as an hole transport layer (HTL). 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) and tris(8-hydroxyquinoline) aluminum (Alq_3) were used as hole blocking layer (HBL) and electron-transporting layer (ETL), respectively. LiF and aluminium was deposited as an electron injection layer and metal cathode respectively.

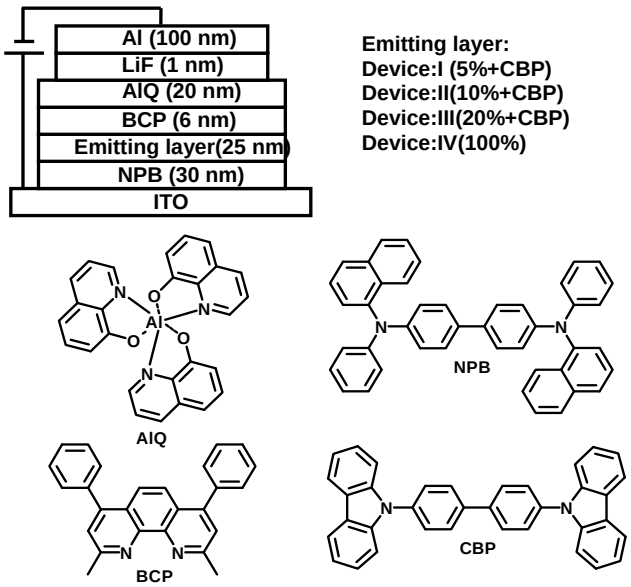
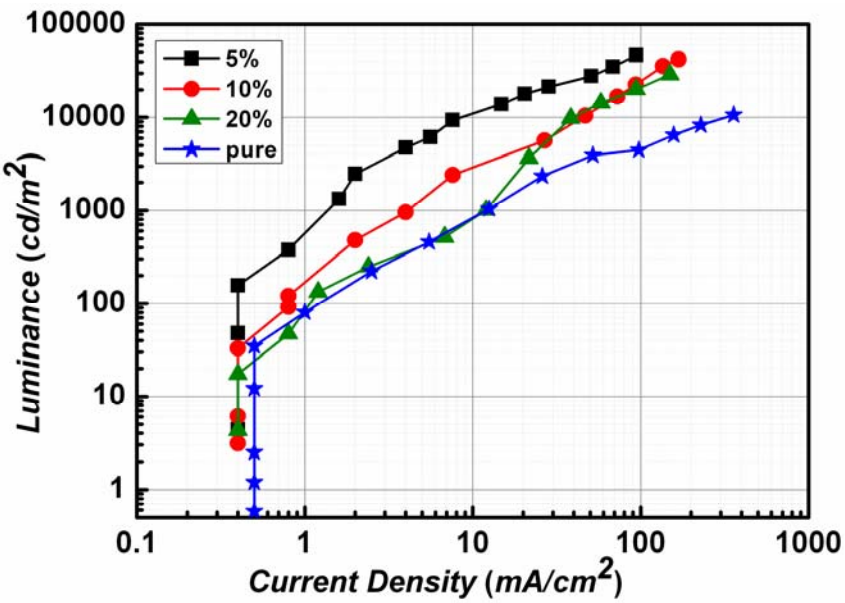


Figure 3. Device configuration and structures of the materials used in this work.



SFigure 4. Current density (*J*) vs Luminance (*L*) characteristics of devices at 5%, 10%, 20% and 100% concentrations.

X-ray crystallographic studies.

The crystal was manipulated in the glovebox and was sealed in thin walled glass capillaries. Data collection was performed at –100 °C on a Bruker CCD APEX diffractometer with a CCD area detector, by using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed by using SAINT and SADABS to yield the reflection data file. The structures were solved by the use of the SHELXTL program. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 807864. Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References:

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3. Adachi, C.; Thompson, M. E.; Forrest, S. R. *IEEE J. Select. Top. Quantum Electron.* **2002**, 8, 372