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Syntheses and Photophyscial Properties of Optical-active Blue-phosphorescent Iridium Complexes Bearing Asymmetric Tridentate Ligand

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Supporting information

Materials. $IrCl_3 \cdot nH_2O$ (Heraeus), n-butyl-lithium (Kanto), $Pd(PPh_3)_2Cl_2$ (TCI), 1,1'-bis(diphenylphosphino)ferrocene-palladium(II)dichloride dichloromethane (Aldrich), ethylenediamine-tetraacetic-acid disodium-salt dehydrate (Kanto), 2-(tributylstannyl)pyridine (Wako), and N-metheylimidazole (TCI) were used as received. 2,4-Difluoro-1,5-dibromobenzene was synthesized according to the previously reported procedure.1) The other synthetic reagents were purchased from Kanto Kagaku and used as received. For the photophysical measurements, spectroscopic-grade 1,2-dichloromethane and toluene were purchased from Nacalai Tesque Inc, Kyoto, Japan. For the electrochemical measurements, *N*,*N*-dimethylformamide (DMF) for non-aqueous titrimetry (Nacalai) was used as supplied, and tetra-*n*-butylammonium tetrafluoroborate (Nacalai) was purified by recrystallization from EtOH and dried before use.

1) Electrochemical measurements

The electrochemical measurements were carried out in a standard one-compartment cell under nitrogen gas flow equipped with a BAS glass-carbon (φ = 3 mm) working electrode, platinum-wire counter electrode, and Ag/Ag^+ reference electrode along with an ALS/CH model 660A electrochemical analyzer. The reference electrode was composed of $Ag/AgNO_3$ (0.01 M in 0.1 M $TBABF_4$ CH_3CN), which is abbreviated as Ag/Ag^+. The ferrocene/ferrocenium (Fc^0/Fc^+) redox potential was used as the internal reference standard, and The redox potentials were reported against Fc^0/Fc^+.

2) Syntheses of ligand and iridium complexes

Synthesis of 1-(2-pyridyl)-3-(N-methylimidazol-2-yl)-4,6-difluorobenzene2), 3)

n-butyl-lithium (41.2 ml of a 1.6 M solution in hexane, 66 mmol) was added to a solution of N-metheylimidazole (4.5 g, 55 mmol) in dry-THF (60 ml) at –70℃ under an argon atmosphere and stirred for two hours. A solution of anhydrous zinc dichloride (9.0 g, 66 mmol) in dry-THF (70 ml) was added to that mixture, resulting in the formation of a white precipitate. After being warmed to room temperature, 1,1'-bis(diphenylphosphino)ferrocene-palladium(II)dichloride•dichloromethane (898 mg, 1.1 mmol), and then 1,5-dibromo-2,4-diflorobenzene (15.0 g, 55 mmol) in dry-THF (20 ml) were added to the solution. The mixture was heated under reflux for an hour and a half. Further, another portion of anhydrous zinc chloride (15.6 g, 114 mmol) was added, and refluxed for five days. After being cooled, the reaction mixture was poured into water (1.5 L) containing ethylenediamine tetraacetic acid disodium-salt dehydrate (132 g, 354 mmol), and the solution pH was adjusted to 8 with a sodium carbonate solution (10%). The organic product was then extracted with dichloromethane. The combined organic extracts were dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The resulting brown oil was purified by column chromatography on silica gel with ethyl acetate as an eluent to give 1-bromo3-(N-methylimidazol-2yl)4,6-difluorobenzene as a yellow solid. The solid was further purified by sublimation to give pure 1-bromo3-(N-methylimidazol-2yl)4,6-difluorobenzene as a white solid (0.706 g, 47%).

The mixture of 1-bromo-3-(N-methylimidazol-2yl)4,6-difluorobenzene (6.2 g, 22.6 mmol), 2-(tributylstannyl)pyridine (10.0 g, 27.2 mmol), $Pd(PPh_3)_2Cl_2$ (496 mg, 0.708 mmol), and LiCl (3.84 g, 90.6 mmol) in dry-toluene (80 ml) was heated under reflux for four days. After cooling the mixture to room temperature, a saturated KF aqueous solution (80 ml) was added and stirred for three hours. The resulting solid residue was collected by filtration. To the filtrate CH_2Cl_2 (50 ml) and 5% $NaHCO_3$ aqueous solution (300 ml) were then added. The organic phase was separated, dried over Na_2SO_4, and evaporated *in vacuo.* The crude product was purified by column chromatography on silica gel with ethyl acetate to give 1-(2-pyridyl)-3-(N-methylimidazol-2yl)4,6-difluorobenzene as a white solid (5.51 g , 90%).

Anal.Calcd for $C_{15}H_{11}F_2N_3$: C,66.42: H, 4.09: N, 15.49. Found: C,66.16: H, 3.98: N, 15.02. ^{1}H-NMR(Acetone-*d6*): δ 8.72(d, 1H, J = 4.6 Hz), 8.29 (t, 1H, J = 8.9 Hz), 7.94-7.88(m, 2H), 7.40 (ddd, 1H, J = 7.4, 4.6, 1.1 Hz), 7.34 (dd, 1H, J_{H-F} = 11.5, 10.3 Hz), 7.25(d, 1H, J = 1.1 Hz), 7.06 (d, 1H, J = 1.1 Hz), 3.70 (d, 3H, J = 1.7 Hz)
ESI-MS m/z 272.1229 (272.0999 required for $[C_{15}H_{11}F_2N_3+H^+]$)

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

The mixture of $IrCl_3\cdot 3H_2O$ (2.07 g, 5.9 mmol) and pyifb (2.4 g, 8.8 mmol) was heated at 100℃ in 2-ethoxyethanol (30 ml) for on day. After cooling the mixture to room temperature, the resulting precipitate was collected and washed with hexane followed by ether. (2.91 g, 91%)

[Ir(pyifb)(fppy)Cl]

The mixture of [Ir(pyifb)Cl_2]$_2$ (500 mg, 0.46 mmol) and fppy(400 mg, 2.3 mmol)$^{4)}$ in ethylene glycol (25 ml) was irradiated in a microwave (650 W, multimode) for 3 min.

After the mixture was cooled to room temperature, water was added to give a yellow precipitate. The precipitate was collected by filtration and washed with hexane. The crude product was purified by column chromatography on silica gel with methanol -dichlromethane (1:25 v/v) to give [Ir(pyifb)(fppy)Cl] as a yellow solid. (289 mg, 47%). Anal.Calcd for $C_{26}H_{17}ClF_3IrN_4$: C,46.60: H, 2.56: N, 8.36. Found: C,46.32: H, 2.57: N, 8.01. ^{1}H-NMR($CDCl_3$): δ 10.06(d, 1H, *J* = 5.2 Hz), 8.12 (d, 1H, *J* = 8.6 Hz), 7.95-7.92(m, 2H), 7.62 (dd, 1H, *J* = 5.7, 1.1 Hz) , 7.59 (td, 1H, *J* = 7.9, 1.5 Hz), 7.55(dd, 1H, *J* = 8.6, 5.7 Hz), 7.48-7.47 (m, 1H), 6.85-6.82 (m, 1H), 6.76 (t, 1H, *J* = 11.7 Hz), 6.65 (d, 1H, *J* = 1.7 Hz), 6.45 (td, 1H, *J* = 8.6, 2.9 Hz), 6.21 (d, 1H, *J* = 1.7 Hz), 5.63 (dd, 1H, *J* = 10.0, 2.6 Hz), 4.09 (d, 3H, *J* = 4.6 Hz)
ESI-MS m/z 635.1252 (635.1036 required for $[M-Cl]^+$, M = $C_{26}H_{17}F_3IrN_4Cl$)

[Ir(pyifb)(fppy)CN]

The mixture of [Ir(pyifb)(fppy)Cl](300 mg, 0.045mmol) and KCN(292 mg, 0.45 mmol) in methanol (40 ml) was heated under reflux for one day. After being cooled to room temperature, the solvent was evaporated *in vacuo*. Water was added to the product to give a yellow precipitate. The crude product was purified by chromatography on silica gel with methanol-to-dichlromethane ratio of 1:25 as eluent to give [Ir(pyifb)(fppy)CN] as a yellow solid. (114 mg , 38%).

Anal.Calcd for $C_{27}H_{17}F_3IrN_5$: C,49.08: H, 2.59: N, 10.60. Found: C,49.11: H, 2.77: N, 10.60. ^{1}H-NMR($CDCl_3$): δ 10.00(d, 1H, *J* = 5.2 Hz), 8.14 (d, 1H, *J* = 8.6 Hz), 7.96-7.95(m, 2H), 7.70 (d, 1H, *J* = 5.2 Hz), 7.62-7.59 (m, 2H), 7.42(td, 1H, *J* = 5.7, 2.7 Hz) , 6.84-6.78 (m, 2H), 6.67 (d, 1H, *J* = 1.1 Hz), 6.49 (td, 1H, *J* = 8.6, 2.9 Hz), 6.26 (d, 1H, *J* = 1.7 Hz), 5.64 (dd, 1H, *J* = 9.5, 2.6 Hz), 4.10 (d, 3H, *J* = 5.2 Hz)
ESI-MS m/z 635.1341 (635.1036 required for $[M-CN]^+$; M = $C_{27}H_{17}F_3IrN_5$)
FT-IR(KBr): 2106.92 cm^{-1}[ν(CN)]

References:

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2) Optical resolution of iridium complexes 2a and 2b by HPLC with chiral column

Optical separations were carried out on a HPLC chiral column of CHIRALPAK IA (Daicel Chemical Ind. Column size, 250 x 4.6 mm) with CH_2Cl_2 as an eluent. A CH_2Cl_2 solution of the Ir complex **2a** or **2b** containing 5 mg/0.2 mL was injected and separated into 1.5 mg of each optically pure complex. This HPLC separation procedure was repeated 40 times, which afforded total 30 mg of each optically pure isomer.

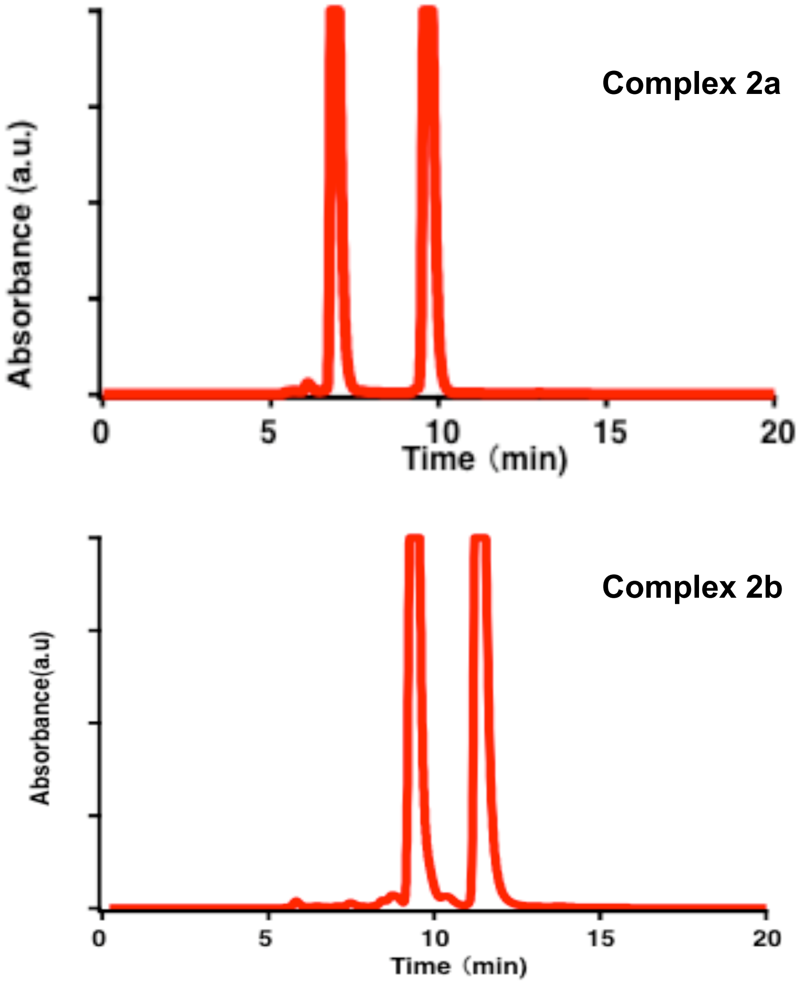

Figure 1S. HPLC chromatograms for complexes **2a** and **2b.** The chiral column of CHIRALPAK IA (Daicel Chemical Ind. Column size, 250 x 4.5 mm) was used: with CH_2Cl_2 as an eluent. A flow rate and a monitored wavelength are 0.5 ml/min and 380 nm, respectively.

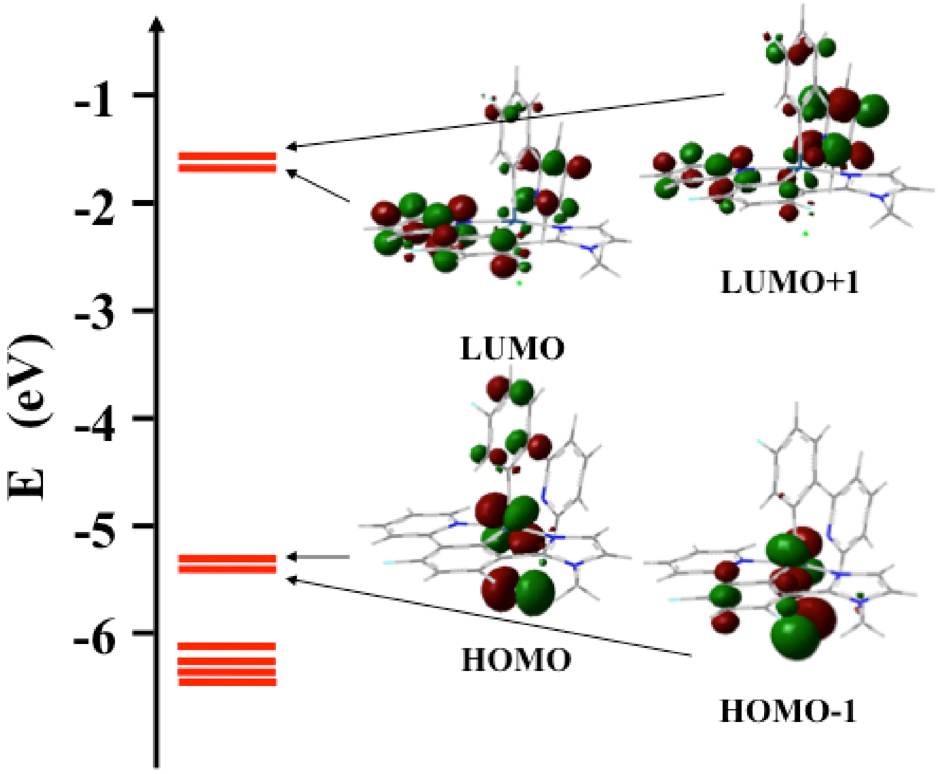

Figure 2S: Frontier MOs of complex 2a calculated by Gaussian 03 suite$^{1)}$ using a hybrid density functional B3PW91/LAN2DZ level.

Reference

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