

Solution-Processible Iridium Complexes for Efficient Orange-Red and White Organic Light-Emitting Diodes

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Supporting Information

General Information: ¹H NMR and ¹³C NMR spectra were recorded on a 400 MHz Varian Unity Inova spectrophotometer. Mass spectra were taken on MALDI micro MX and HP1100LC/MSD MS spectrometers. The photoluminescence and UV-vis absorption spectra measurements were performed on a Perkin-Elmer LS55 spectrometer and a Perkin-Elmer Lambda 35 spectrophotometer, respectively. Phosphorescence spectra and lifetimes were measured on a Horiba Jobin Yvon Fluoro Max-4 (TCSPC) instrument in degassed dichloromethane solutions with excitation wavelength at 400 nm. The quality of the spin-coated film was monitored using atomic force microscope (AFM) technique.

The electrochemical measurements of these iridium complexes were carried out by using a conventional three-electrode configuration and an electrochemical workstation (BAS100B, USA) at a scan rate of 100 mV s⁻¹. A glass carbon working electrode, a Pt-wire counter electrode, and a saturated calomel electrode (SCE) reference electrode were used. All measurements were made at room temperature on samples dissolved in dichloromethane, deoxygenated with argon, and with 0.1 M [Bu₄N]PF₆ as the electrolyte.

Density functional theory (DFT) calculations using B3LYP functional were performed. The basis set used for C, H, N, O and S atoms was 6-31G while the LanL2DZ basis set were employed for Ir atoms. There are no imaginary frequencies for both optimized structures. All these calculations were performed with Gaussian 03.¹

Preparation of 6-(1-naphthalenylphenylamino)-2-phenylbenzothiazole: 6-bromo-2-phenylbenzothiazoles (1 g, 3.45 mmol), 1-naphthylphenylamine (0.91 g, 4.14 mmol), Pd(OAc)₂ (15.5 mg, 0.07 mmol), (t-Bu)₃P (16.7 mg, 0.08 mmol) and sodium *tert*-butoxide (0.58 g, 5.18 mmol) and toluene (40 mL) were charged in a two-necked flask kept under nitrogen. After refluxing for 5 h, the reaction mixture was cooled to room temperature and the solvent was removed under vacuum. The residue was poured into water and extracted with dichloromethane. The product was purified by column chromatograph over silica using petroleum ether and dichloromethane (3:1) as eluent to yield the pure product as pale yellow oil (2.68 g, 90.8 %). ¹H NMR (400 MHz, CDCl₃) δ 8.03-8.00 (m, 2H), 7.96-7.94 (d, *J*=8.0 Hz, 1H), 7.91-7.87 (m, 2H), 7.81-7.79 (d, *J*=8.0 Hz, 1H), 7.51-7.34 (m, 8H), 7.24-7.21 (m, 3H), 7.10-7.08 (d, *J*=8.0 Hz, 2H), 7.00-6.97 (m, 1H). APCI-MS (*m/z*): 429 [M+H]⁺.

Preparation of 1: A solution of 6-(1-naphthalenylphenylamino)-2-phenylbenzothiazole (900 mg, 2.10 mmol) and [Ir(acac)₃] (285 mg, 0.58 mmol) in glycerol (8 mL) was heated to 220 °C under N₂ atmosphere. After 24 h, the reaction mixture was cooled to room temperature and water (50 mL) was added. The resulting mixture was extracted with CH₂Cl₂ and the organic phase was dried over MgSO₄. Upon removal of solvent under vacuum, the residue was purified by column chromatography using a dichloromethane/light petroleum mixture (1:10-1:0) as eluent to afford the title compound as an orange solid (75 mg, 9 %). ¹H NMR (400 MHz,

CDCl₃) δ 7.87-7.85 (d, J =8.0 Hz, 3H), 7.81-7.79 (d, J =8.0 Hz, 3H), 7.76-7.74 (d, J =8.0 Hz, 3H), 7.55-7.53 (d, J =8.0 Hz, 3H), 7.42-7.38 (m, 3H), 7.36-7.32 (m, 3H), 7.22-6.95 (m, 24H), 6.89-6.85 (m, 3H), 6.79-6.75 (m, 3H), 6.69-6.67 (d, J =8.0 Hz, 3H), 6.55-6.53 (d, J =8.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 176.9, 157.5, 148.0, 147.3, 146.1, 143.2, 141.1, 136.2, 135.2, 133.9, 130.8, 130.6, 129.3, 128.4, 127.3, 126.7, 126.6, 126.4, 126.3, 125.5, 124.0, 122.6, 122.4, 121.5, 120.3, 120.1, 114.2. MALDI-TOF-MS (m/z): 1474.0 [M]⁺. Anal. calcd. For C₈₇H₅₇IrN₆S₃: C 70.85, H 3.90, N 5.70; found: C 70.58, H 3.96, N 5.42.

Preparation of 2: IrCl₃•3H₂O (240mg, 0.68 mmol) and the ligand 6-(1-naphthalenylphenylamino)-2-phenylbenzothiazole (700mg, 1.64 mmol) were added in a 16 mL of mixture of 2-ethoxyethanol and water (v/v=3:1). The mixture was refluxed under nitrogen for 24 h and cooled to room temperature. The orange precipitate was collected by filtration and washed with water, ethanol and hexane. The solid was then pumped dry completely to give crude chloro-bridged dimer complex. Without further purification, the dimer was added in a mixture of Na₂CO₃ (362 mg, 3.42 mmol), acetyl acetone (0.11 ml, 1.02 mmol), and 2-ethoxyethanol (10 mL). After refluxing under nitrogen for 24 h, the solution was cooled to room temperature. The orange precipitate was filtered off and washed with water, ethanol and hexane. The crude product was purified by column chromatography on silica gel using petroleum ether/dichloromethane as mobile phase. The target product was obtained as an orange solid (568 mg, 73 %). ¹H NMR (400 MHz, CDCl₃) δ 7.99-7.97 (d, J =8.0 Hz, 2H), 7.93-7.91 (d, J =8.0 Hz, 2H), 7.85-7.82 (m, 4H), 7.55-7.11 (m, 22H), 7.01-6.97 (m, 2H), 6.82-6.78 (m, 2H), 6.65-6.61 (m, 2H), 6.41-6.39 (d, J =8.0 Hz, 2H), 5.16 (s, 1H), 1.71 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 185.5, 177.9, 147.9, 147.5, 146.4, 145.8, 143.1, 142.1, 135.4, 134.7, 132.8, 131.2, 129.5, 129.4, 128.5, 127.6, 127.0, 126.7,

126.5, 126.4, 125.2, 124.1, 122.5, 122.4, 121.7, 121.0, 120.4, 113.5, 101.7, 60.4, 28.5.

MALDI-TOF-MS (m/z): 1146.0 $[M]^+$. Anal. calcd. For $C_{63}H_{45}IrN_4O_2S_2$: C 66.00, H 3.96, N 4.89; found: C 65.57, H 3.94, N 4.62.

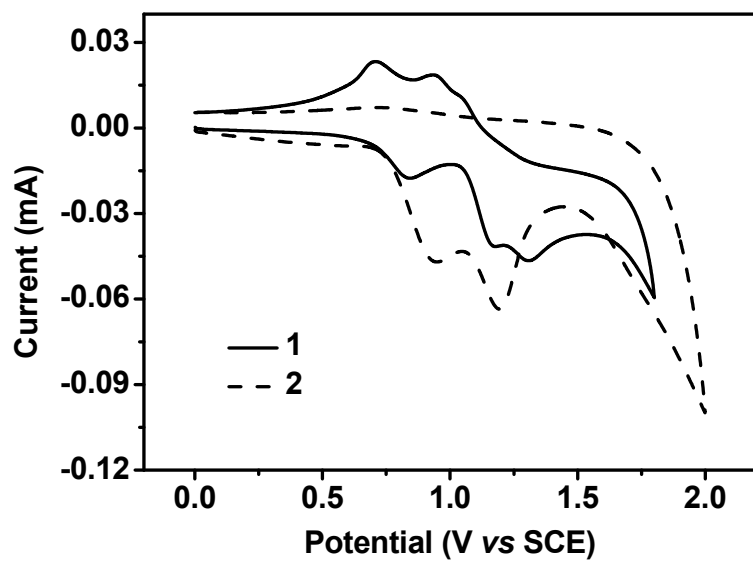


Figure S1. The cyclic voltammograms of complexes **1** and **2**.

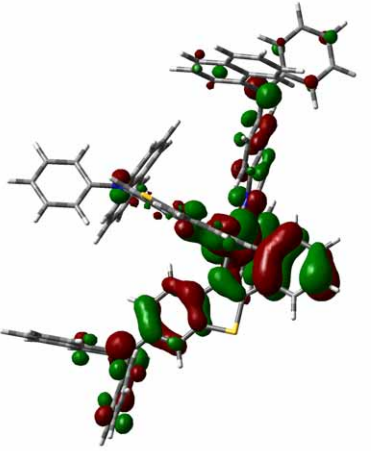
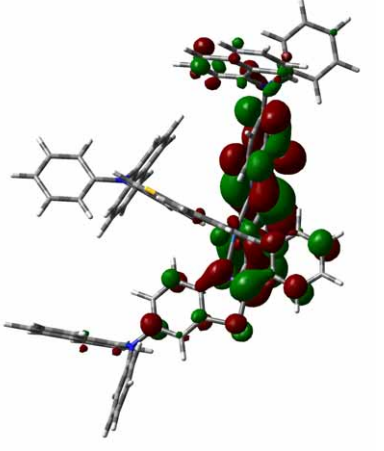
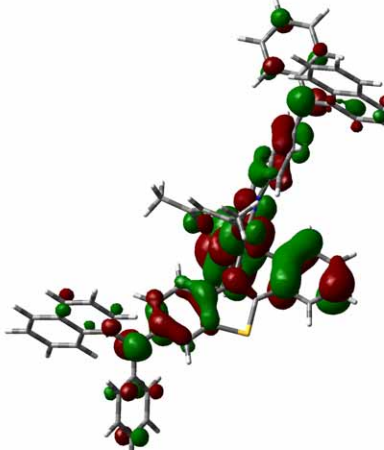
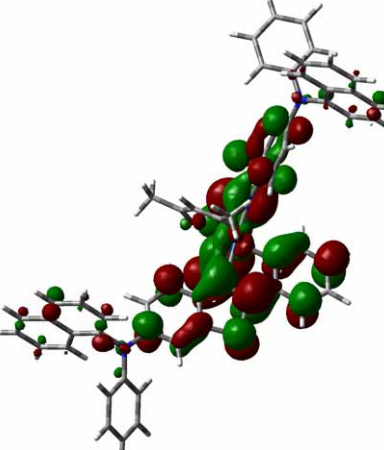
complex	HOMO	LUMO
1		
2		

Figure S2. The distribution of HOMO and LUMO for complexes **1** and **2**.

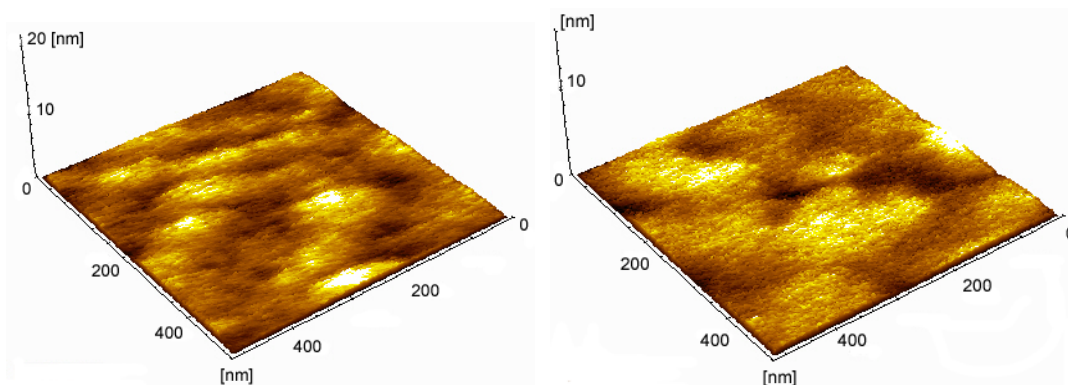


Figure S3. AFM topographic images of the spin-coated CBP films doped with 5 wt% of complex 1 (left) or 2 (right).

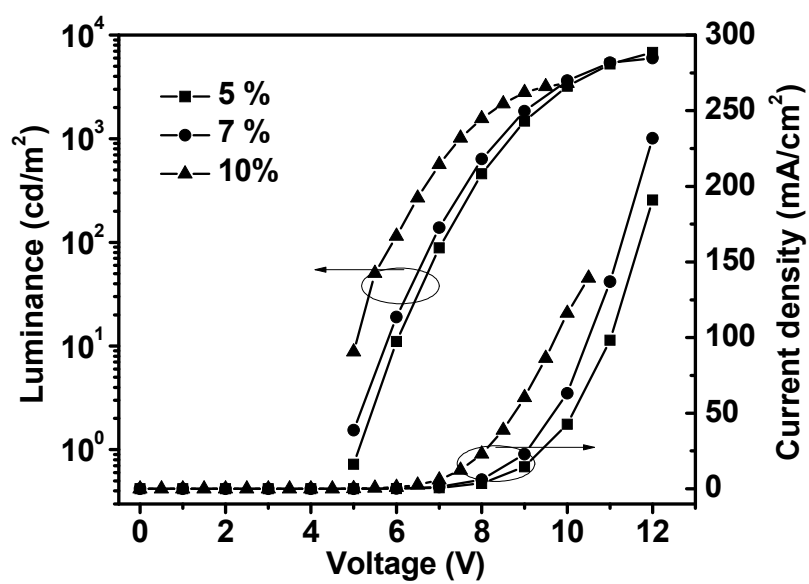


Figure S4. The current density-voltage-luminance (L - V - J) characteristics of 1-doped OLEDs A-C.

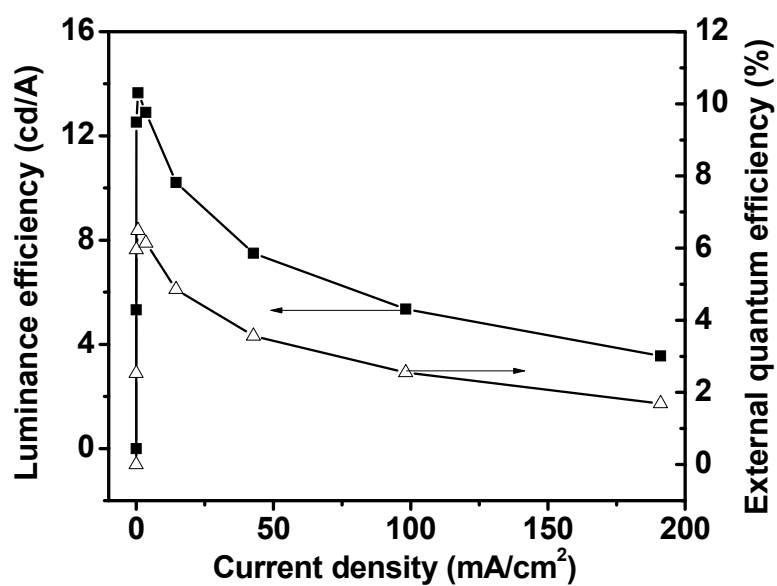


Figure S5. The plots of luminance efficiency and external quantum efficiency versus current density for 1-doped device A.

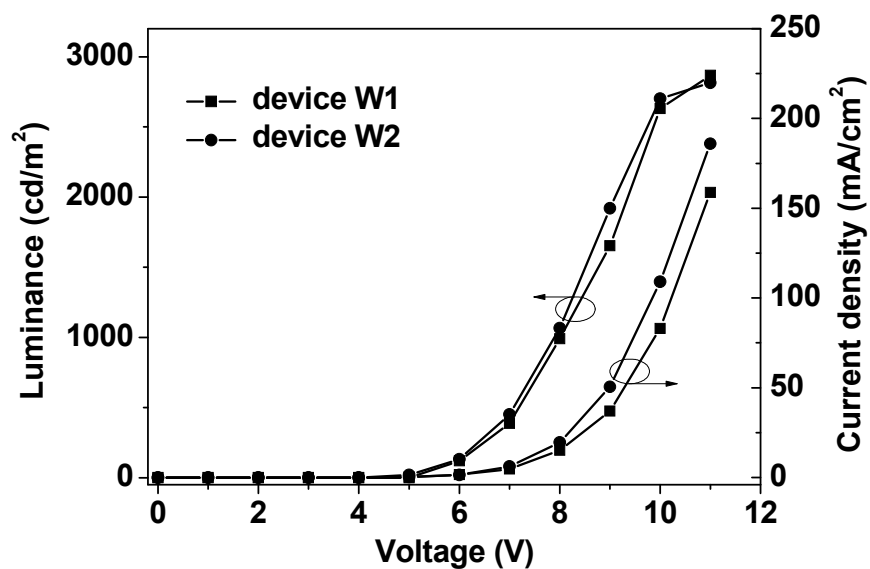


Figure S6. The L - V - J curves for white OLEDs W1 and W2.

Reference

1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., 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. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, 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. A. Pople, *Gaussian 03* (Revision C.02), Gaussian, Inc., Wallingford CT, 2004.