

**A spiro-configured ambipolar host material for impressively efficient *single-layer* green electrophosphorescent devices**

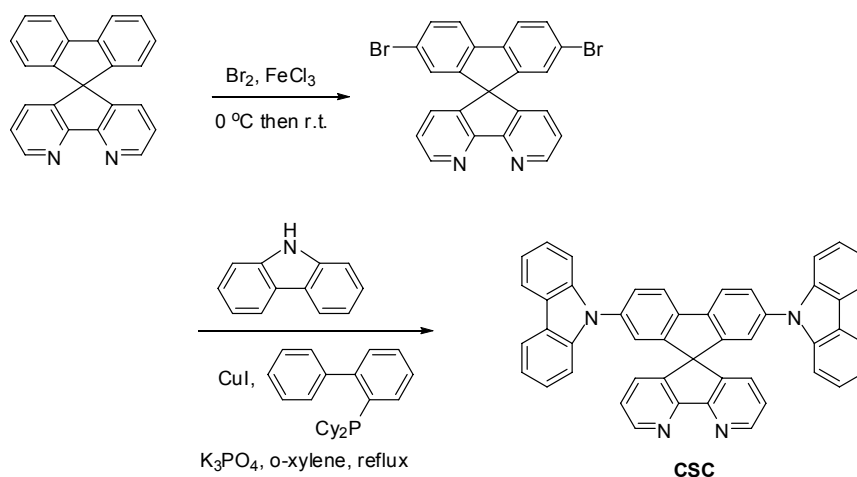
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**Electronic Supplementary Information**

The synthesis of **CSC** depicted in Scheme S-1 was reported previously<sup>1</sup>. In this paper, we report herein an improved bromination method of 4,5-diaza-9,9'-spirobifluorene through stepwise temperature control to afford 4,5-diaza-2',7'-dibromo-9,9'-spirobifluorene<sup>2</sup> in 95% yield without tedious column separation. The final product (**CSC**) was synthesized in 77% yield by Cu-mediated C-N bond formation of 4,5-diaza-2',7'-dibromo-9,9'-spirobifluorene with an excess amount of carbazole in the presence of a catalytic amount of biphenyl-2-ylidicyclohexylphosphane.



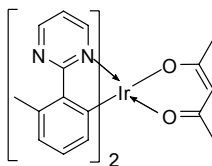
Scheme S-1. The synthetic pathway of **CSC**.

<sup>1</sup> K.-T. Wong, H.-F. Chen and F.-C. Fang, *Org. Lett.* **2006**, 8, 3501.

<sup>2</sup> K.-T. Wong, R.-T. Chen, F.-C. Fang, C.-C. Wu and Y.-T. Lin *Org. Lett.* **2005**, 7, 1979.

Synthesis of 4,5-diaza-2',7'-dibromo-9,9'-spirobifluorene:

A mixture of 4,5-diaza-9,9'-spirobifluorene (2.35 g, 7.39 mmol) and iron chloride (2.51 g, 15.49 mmol) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL). Bromine (0.87 ml, 16.48 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (120 mL) was added slowly to this mixture at 0°C with constant stirring. The mixture was covered with aluminum foil to avoid light and refluxed for 16 hr. The resulting solution was quenched with NaOH<sub>(aq)</sub> and extracted with CHCl<sub>3</sub>. The combined organic extracts were dried over MgSO<sub>4</sub> and concentrated by rotary evaporation. The crude was washed with THF and hexane to afford 4,5-diaza-2',7'-dibromo-9,9'-spirobifluorene (3.33 g, 95 %) as a light yellow solid.



### Synthesis of Ir(TPm)<sub>2</sub>(acac)

Cyclometalated Ir(III) chloro-bridged dimers were synthesized by the method reported by Nonoyama<sup>3</sup>. A mixture of IrCl<sub>3</sub>·nH<sub>2</sub>O (1.0 g, 3.16 mmol) and 2-*o*-tolylpyrimidine (1.18 g, 6.95 mmol) was refluxing in a mixture of 2-ethoxyethanol (90 mL) and water (30 mL) for 18 h. The resulting precipitate was filtered and washed with water. The crude product was then used in the next step without further purification. [Ir(TPm)<sub>2</sub>Cl]<sub>2</sub> (1 g, 0.88 mmol), 2,4-pentanedione (221 mg, 2.21 mmol), and sodium carbonate (4.68 mg, 4.42 mmol) were refluxed in 2-ethoxyethanol (70 mL) for 15 h. After cooling to room temperature, the colored precipitate was filtered off and was washed with water. The crude product as purified by column chromatography on silica gel with dichloromethane as the eluent to afford pure product (720 mg, 74%) as a light yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.77 (dd, *J* = 4.8, 2.4 Hz, 2H), 8.67 (dd, *J* = 5.6, 2.4 Hz, 2H), 7.07 (t, *J* = 5.6 Hz, 2H), 6.66~6.60 (m, 4H), 6.14 (d, *J* = 3.2 Hz, 2H), 5.20 (s, 2H), 2.82 (s, 6H), 1.78 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 185.0, 177.7, 156.0, 154.8, 149.1, 141.1, 138.9, 130.4, 130.0, 125.6, 116.6, 116.1, 100.5, 44.8, 28.6, 22.6, 22.4; MS (*m/z*, FAB<sup>+</sup>) 630.1; HRMS (*m/z*, FAB<sup>+</sup>) Calcd for C<sub>27</sub>H<sub>26</sub>IrN<sub>4</sub>O<sub>2</sub> 630.7379, found (M<sup>+</sup>H<sup>+</sup>) 631.1682. Anal. Calcd. for C<sub>27</sub>H<sub>26</sub>IrN<sub>4</sub>O<sub>2</sub>: N, 8.90; C, 51.50; H, 4.00. Found: N, 9.09; C, 51.81; H, 4.28.

<sup>3</sup> S. Sprouse, K. A. King, P. J. Spellane, R. J. Watts, *J. Am. Chem. Soc.*, 1984, **106**, 6647. (b) O. Lohse, P. Thevenin, E. Waldvogel, *Synlett*, 1999, **1**, 45. (c) M. Nonoyama, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 767.

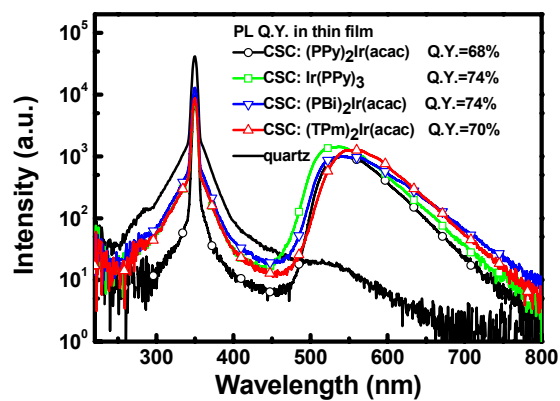


Figure S-1 PL quantum yield of CSC doped with green phosphors in thin film using a calibrated integration sphere (HAMAMATSU C9920).

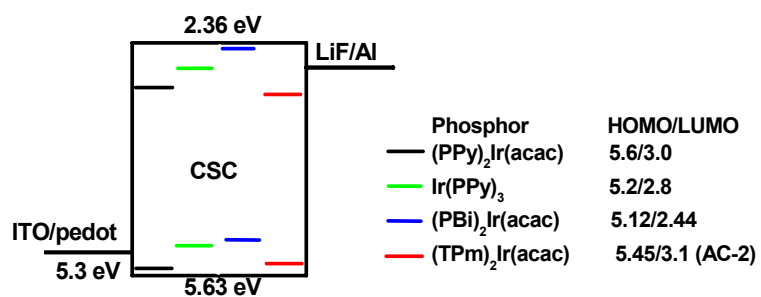


Figure S-2 Energy levels of CSC and the green phosphors used in this study.

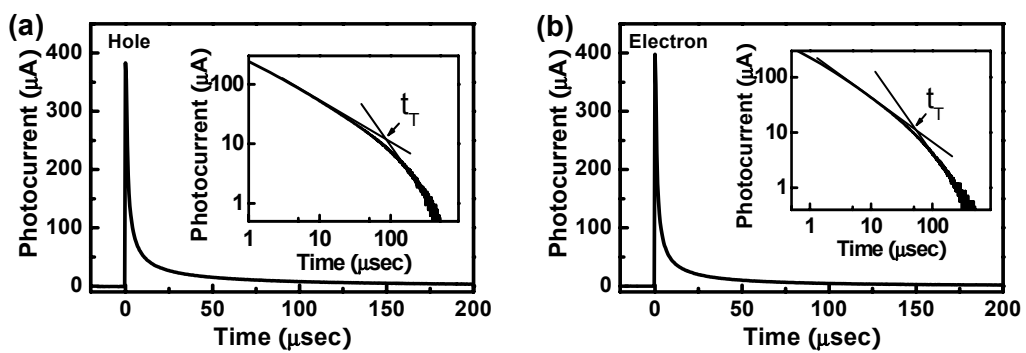


Fig. S-3 Typical transient photocurrent signals for CSC (thickness:  $1.67 \mu\text{m}$ ) at an electric field strength ( $E$ ) of  $6 \times 10^5 \text{ V/cm}$ : (a) holes; (b) electrons. Insets: Double logarithmic plots of (a) and (b).

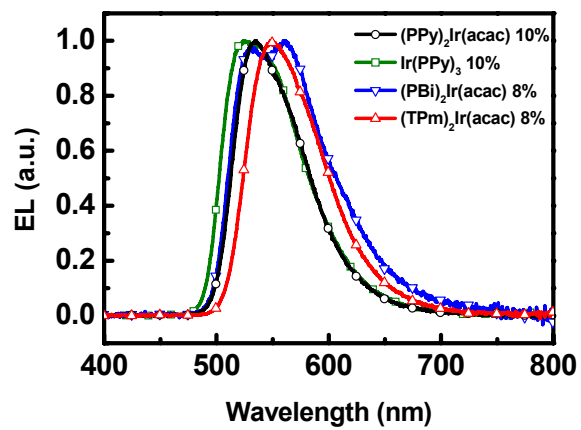


Fig. S-4 EL spectra of the single-layer PhOLEDs