Supporting Information
for the Communication Entitled

Electroluminescence Based on Thermally Activated Delayed Fluorescence Generated by a Spirobifluorene Donor-Acceptor Structure

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1 Synthesis of Spiro-CN

The bipolar compound comprises a cyano-substituted biphenyl branch as the acceptor orthogonally bridged to a donor branch bearing di-p-tolylamino group via a sp³-hybridized carbon. Scheme 1 presents our synthetic routes toward this bipolar molecule. Starting from 2,7-dicyano-9,9´-spirobifluorene (1), which was reacted with I₂ and HIO₃ in AcOH and CHCl₃ to give 2,2´-diiodo-9,9´-spirobifluorene (2) in 80% yield. Subsequent Pd-catalyzed C–N bond formation through the cross-coupling of the diiodospirobifluorene 2 with di(p-tolyl)amine afforded the bipolar Spiro-CN in 60% yield. The detailed synthetic procedures and structural characterizations have been reported in the literature.

Synthesis scheme of Spiro-CN

2 Experimental Details

The Spiro-CN: mCP (100 nm) co-deposited films were fabricated by thermal deposition. The film thickness was monitored in-situ by an oscillating quartz thickness monitor during thermal deposition process. Fluorescence and TADF characteristics were measured under vacuum using a streak camera system (C4334, Hamamatsu Co.). Temperature dependence of PL properties were measured using a streak camera system (C4334, Hamamatsu Co.) equipped with a cryostat (GASESCRT-006-2000, IWATANI Co.) A nitrogen gas laser (MNL200, LASERTECHNIK BERLIN) with an excitation wavelength of 337nm was used. Excitation light was absolutely cut off by putting a 370 nm long band-pass filter (SCF-50S-37L, SIGMA KOKI CO., LTD.) in front of the photo-detector. PL quantum efficiency was measured using integrating sphere system (C9920-02, HAMAMATSU Co.) with a multichannel spectrometer (PMA-11, HAMAMATSU Co.) The current density-voltage-luminance (J-V-L) characteristics were measured using a semiconductor parameter analyzer (Agilent Co., HP4155C) with an optical power meter (Newport, Model 1835-C). AFM measurement was conducted by using JSPM-5400, JEOL.

3 Determination method of $\Phi_{\text{prompt}}$ and $\Phi_{\text{delayed}}$

In this study, $\Phi_{\text{prompt}}$ and $\Phi_{\text{delayed}}$ were determined by using total PL quantum efficiency and the ratio between prompt and delayed components which was calculated from transient PL measurements. The intensity ratio between prompt ($r_1$) and delayed ($r_2$) components were determined using emission life time ($\tau_1$, $\tau_2$) and fitting parameter ($A_1$, $A_2$) as follow.

\[
I(t) = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} \quad (1)
\]

\[
r_1 = \frac{A_1 \tau_1}{A_1 \tau_1 + A_2 \tau_2} \quad (2)
\]

\[
r_2 = \frac{A_2 \tau_2}{A_1 \tau_1 + A_2 \tau_2} \quad (3)
\]

Then, $\Phi_{\text{prompt}}$ and $\Phi_{\text{delayed}}$ were determined using intensity ratio ($r_1$, $r_2$) and total emission quantum yield.

\[
\Phi_{\text{total}} = \Phi_{\text{prompt}} + \Phi_{\text{delayed}} \quad (4)
\]

\[
\Phi_{\text{prompt}} = r_1 \Phi_{\text{total}} \quad (5)
\]

\[
\Phi_{\text{delayed}} = r_2 \Phi_{\text{total}} \quad (6)
\]
4 Experimental Data

4-1 Transient PL spectrum of Spiro-CN in toluene solution

![Image of transient PL spectrum of Spiro-CN in toluene solution](image)

**Fig. S1.** Transient PL spectrum of Spiro-CN toluene solution (1.3 × 10^{-5} M). (a) with nitrogen bubbling (without containing oxygen). (b) without nitrogen bubbling (containing oxygen).

4-2 Transient PL spectrum of 6 wt% Spiro-CN:NPD co-deposited films

![Image of transient PL spectrum of 6 wt% Spiro-CN:NPD co-deposited films](image)

**Fig. S2.** Transient PL spectrum of 6wt % spiro-CN: α-NPD co-deposited film (blue line) and 6wt% Spiro-CN: mCP co-deposited film (black line). Inset: PL spectrum of 6wt % spiro-CN: α-NPD co-deposited film.
4-3 Triplet formation efficiency of Spiro-CN

For the Berberan-Santos plot, the shape of the slope is very sensitive to the function of $\phi_T$. Continuous variation of this parameter in the search for the maximum linearity gives the best value of $\phi_T$ as well as $\Delta E_{ST}$. As shown in Fig. S6, the best linear fitting was obtained when $\phi_T$ is 0.78. Based on this method, the triplet formation efficiency of Spiro-CN was obtained to be $\phi_T = 0.78$.


4-4 Luminance-current density characteristics

For glass/ITO/α-NPD (60 nm)/6wt% Spiro-CN:mCP (20 nm)/Bphen (40 nm)/ MgAg (100 nm)/Ag (20 nm), inset shows luminance-current density characteristics at low current density region.
5 Complete Reference 18