Supporting Information

for the Communication Entitled

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

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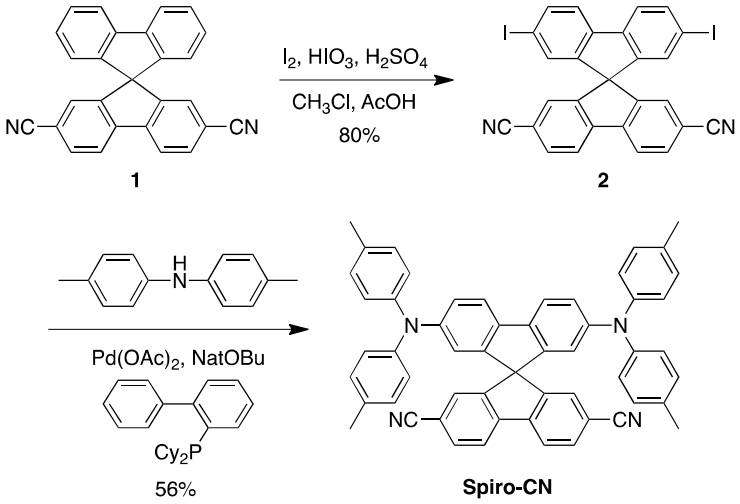
Contents

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 sp^3-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 I_2 and HIO_3 in AcOH and $CHCl_3$ 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 detail synthetic procedures and structural characterizations have been reported in the literature[1].



Synthesis scheme of Spiro-CN

[1] Ku S.-Y., Hung W.-Y., Chen C.-W., Yang S.-W., Mondal E., Chi Y., Wong K.-T. *Chem. Asain J.* **2011**, DOI: 10.1002/asia.201100467.

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 φ_{prompt} and $\varphi_{delayed}$

In this study, φ_{prompt} and $\varphi_{delayed}$ 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 (τ_1, τ_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, φ_{prompt} and $\varphi_{delayed}$ were determined using intensity ratio (r_1, r_2) and total emission quantum yield.

$$\Phi_{total} = \Phi_{prompt} + \Phi_{delayed} \quad (4)$$

$$\Phi_{prompt} = r_1\Phi_{total} \quad (5)$$

$$\Phi_{delayed} = r_2\Phi_{total} \quad (6)$$

4 Experimental Data

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

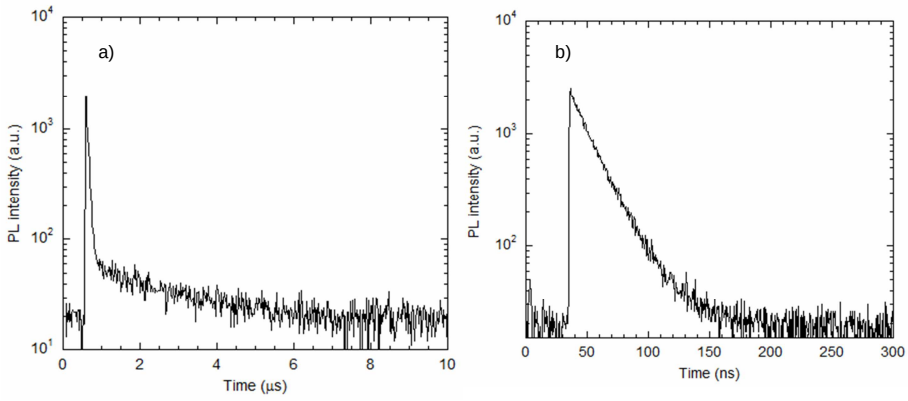


Fig. S1. Transient PL spectrum of Spiro-CN toluene solution (1.3×10^{-5} M). (a) with nitrogen bubbling (without containing oxygen). (b) without nitrogen bubbling (containing oxygen).

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

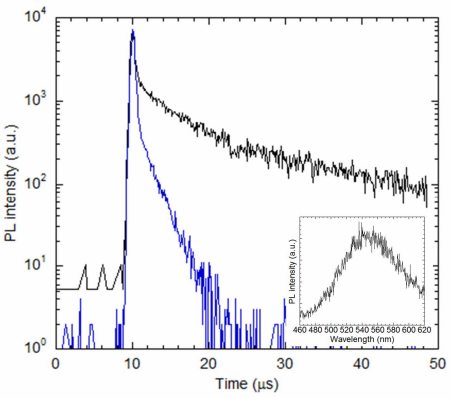


Fig. S2. Transient PL spectrum of 6wt % spiro-CN: α-NPD co-deposited film (blue line) and 6wt% Spiro-CN: mCP co-deposited film (black line). Inset: PL spectrum of 6wt % spiro-CN: α-NPD co-deposited film.

4-3 Triplet formation efficiency of Spiro-CN

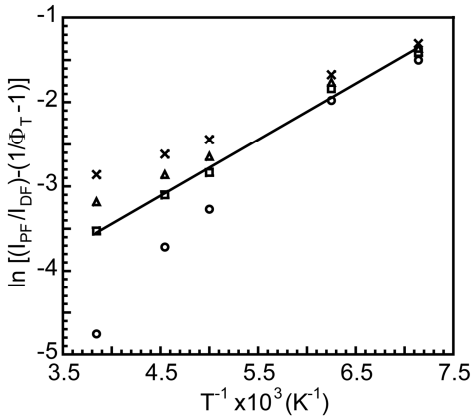


Fig. S3. Fit of I_{PF}/I_{DF} vs $1/T$. Φ_T = 0.80 (×), 0.79 (△), 0.78 (□) and 0.77 (○). The best linier fitting was obtained when Φ_T is 0.78.

For the Berberan-Santos plot, the shape of the slope is very sensitive to the function of φ_T. Continuous variation of this parameter in the search for the maximum linearity gives the best value of φ_T as well as ΔE_{ST}.[2] As shown in Fig. S6, the best linear fitting was obtained when φ_T is 0.78. Based on this method, the triplet formation efficiency of Spiro-CN was obtained to be φ_T = 0.78.

[2] Berberan-Santos, M. N.; Garcia, J. M. M. *J. Am. Chem. Soc.* **1996**, *118*, 9391.

4-4 Luminance-current density characteristics

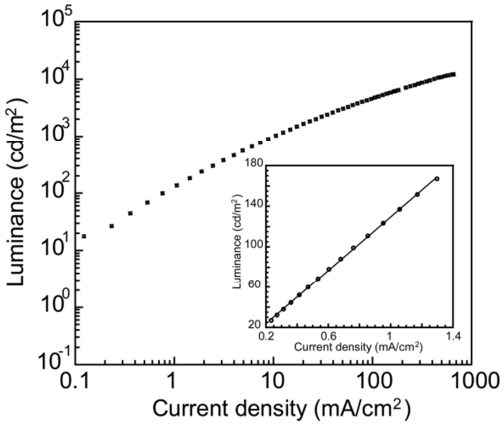


Fig. S4. Luminance-current density characteristics for glass/ITO/α-NPD (60 nm)/6wt% Spiro-CN:mCP (20 nm)/Bphen (40 nm)/ MgAg (100 nm)/Ag (20 nm). Inset shows luminance-current density characteristics at low current density region.

5 Complete Reference 18

(18) Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W. ; Schlegel, H. B. ; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G. ; Barone, V. ; Mennucci, B.; Petersson, G. A. ; Nakatsuji, H. ; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J. ; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M. ; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C. ; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.