

Electronic supplementary information

High efficiency, thermally activated, delayed fluorescence based on 1,3,5-tris (4-(diphenylamino)phenyl)-2,4,6-tricyanobenzene

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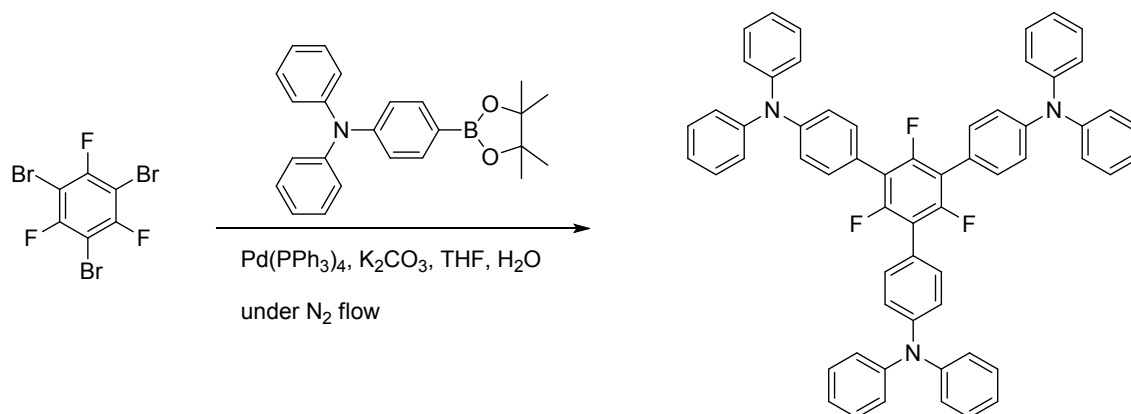
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S.I. 1. General comments

^1H NMR spectra were determined using a Bruker Avance III 500 spectrometer with CDCl_3 as the solvent and TMS as an internal standard ($\delta = 0$). MALDI-TOF mass spectra were obtained using a Bruker Autoflex II and sinapic acid was used as a matrix. Elemental analysis was performed by the Service Center of the Elementary Analysis of Organic Compounds affiliated with the Faculty of Sciences at Kyushu University. The absorption spectra were measured using a LAMBDA 950 UV/Vis/NIR spectrophotometer (PerkinElmer) at room temperature. The emission spectra were measured using a FluoroMax-4 (HORIBA) at room temperature. The phosphorescence quantum yield (Φ_{PL}) was measured using a Hamamatsu Photonics Quantaaurus-QY (C11347) using an excitation wavelength of 337 nm.

S.I. 2. Synthesis and characterization

S.I. 2.1 Synthesis of 1,3,5-tris(4-(diphenylamino)phenyl)-2,4,6-trifluorobenzene

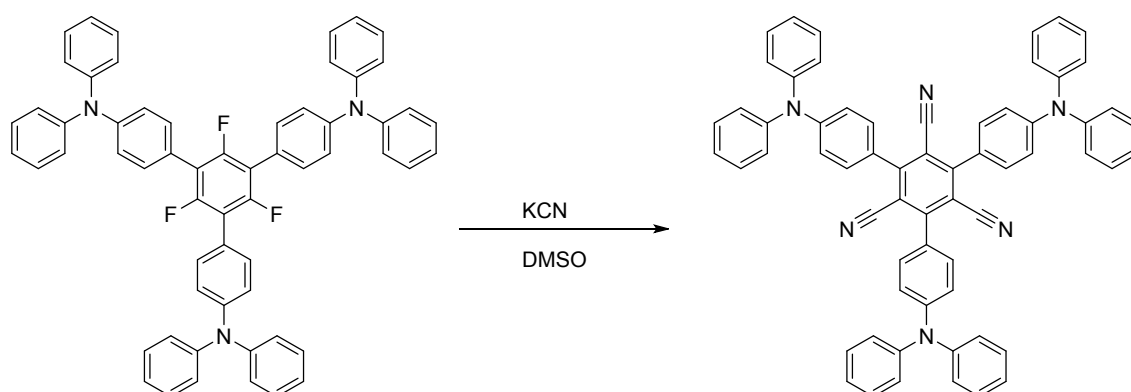


1,3,5-Tribromo-2,4,6-trifluorobenzene (0.74 g, 2 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.30 g, 0.26 mmol), 2-(4-(diphenylamino)phenyl-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.25 g, 0.7 mmol), degassed THF (55 mL) and degassed K_2CO_3 aq. (15 mL) were added to a 200-mL three-neck round-bottom flask with stir bar and condenser. The mixture was heated to 66 °C under the flow of nitrogen and then 20 mL of 2-(4-(diphenylamino)phenyl-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.0 g, 5.4 mmol) in toluene was added dropwise over 12 h. The mixture was heated for 4 days. After the solution was cooled to room temperature, THF was evaporated in vacuo and the obtained residue was filtrated and washed with water. Recrystallization of the obtained solid from dichloromethane/n-hexane produced 1,3,5-tris(4-(diphenylamino) phenyl)-2,4,6-trifluorobenzene as a white powder (0.58 g, 0.67 mmol, 34%).

^1H NMR (500 MHz, CDCl_3): $\delta = 7.05$ (t, $J = 7.3$ Hz, 6H; ArH), 7.13 (dd, $J_{\text{ortho}} = 8.8$ Hz,

$J_{\text{meta}} = 2.0$ Hz, 6H; ArH), 7.15 (td, $J_{\text{ortho}} = 7.5$ Hz, $J_{\text{meta}} = 1.1$ Hz, 12H; ArH), 7.28 (dt, $J_{\text{ortho}} = 7.0$ Hz, $J_{\text{meta}} = 1.5$ Hz, 12H; ArH), 7.34 (d, $J = 8.5$ Hz, 6H; ArH). ^{19}F NMR (500 MHz, CDCl_3): $\delta = -117.09$. Anal. Calcd for $\text{C}_{60}\text{H}_{42}\text{F}_3\text{N}_3$: C, 83.60; H, 4.91; 4.87%. Found: C, 85.36; H, 4.90; 4.91%.

S.I. 2.2 Synthesis of 1,3,5-tris(4-(diphenylamino)phenyl)-2,4,6-tricyanobenzene (3DPA3CN)



1,3,5-Tris(4-(diphenylamino)phenyl)-2,4,6-trifluorobenzene (0.86 g, 1.0 mmol) and KCN (1.02 g, 16 mmol) were added into a 200-mL three-neck round-bottom flask with a stir bar and condenser under the flow of nitrogen. Sixty microliters of DMSO was then added. The mixture was heated to 160 °C for 80 min. After the solution was cooled to room temperature, dichloromethane (450) was added and the solution was washed with water. The obtained organic layer was washed with saturated aqueous NaCl solution and dried over MgSO_4 . The solvent was evaporated in vacuo and the obtained residue was recrystallized from dichloromethane/*n*-hexane. An orange solid identified as 1,3,5-tris(4-(diphenylamino)phenyl)-2,4,6-tricyano-benzene was obtained (0.88 g, 0.99 mmol, 99%).

^1H NMR (500 MHz, CDCl_3): $\delta = 7.11$ -7.14 (m, 12H; ArH), 7.21 (d, $J = 7.6$ Hz, 12H; ArH), 7.32 (t, $J = 7.9$ Hz, 12H; ArH), 7.41 (d, $J = 8.7$ Hz, 6H; ArH); ^{13}C NMR (125 MHz, CDCl_3): $\delta = 113.49$, 115.55, 120.39, 124.42, 125.96, 125.98, 129.61, 130.32, 146.67, 150.12, 153.70. MALDI-TOF-MS: Calcd for $[\text{C}_{63}\text{H}_{42}\text{N}_6]^+$, $m/z = 882.35$; found 882.28. Anal. Calcd. for $\text{C}_{63}\text{H}_{42}\text{N}_6$: C, 85.69; H, 4.79; N, 9.52%. Found: C, 85.44; H, 4.74; N, 9.42%.

S.I. 3. Fabrication of Films

All deposited organic materials were purified by sublimation. The organic layers

were deposited at a vacuum of $< 2 \times 10^{-4}$ Pa with an evaporation rate of 0.1 nm/s. The substrates were rotated at equivalent positions from the axis during deposition. The thickness of the films was approximately 50 nm. Quartz substrates were used for measurement of the absorption and emission spectra and for photoluminescence quantum yield measurements. Si substrates were used for ellipsometry.

S.I. 4. Variable Angle Spectroscopic Ellipsometry (VASE)

VASE was performed using a fast spectroscopic ellipsometer (M-2000U, J. A. Woollam). Measurements were taken at seven different angles of the incident light from 45° to 75° in steps of 5° . At each angle, the experimental ellipsometric parameters ψ and Δ were simultaneously obtained in steps of 1.6 nm throughout the spectral region from 245 to 1000 nm. The analysis of the data was performed using the software “WVASE32” (J. A. Woollam).

S.I. 5. Fabrication of OLEDs

All organic layers were deposited at a vacuum of $< 2 \times 10^{-4}$ Pa with an evaporation rate of 0.1 nm/s except for the emitter, which was deposited at a rate of 0.06–0.1 nm/s. The substrates were rotated at equivalent positions from the axis during deposition. The active area was circularly shaped with a diameter of 1 mm.

S.I. 6. Measurement of the OLED device characteristics

Current density (I)–voltage (V)–luminance (L) characteristics were measured using a semiconductor parameter analyzer (4155C; Agilent Technologies Inc.) connected to a silicon photodiode (1835-C; Newport Co.).

S.I. 7. Absorption and emission spectra of 6wt% 3DPA3CN-doped DPEPO film

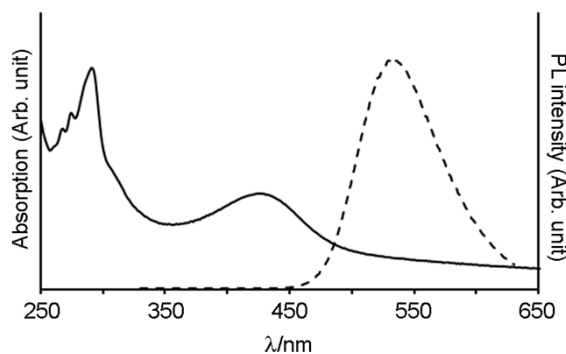


Figure S.I. 1. The absorption (solid line) and emission (broken line) spectra of 6wt% 3DPA3CN-doped DPEPO film.

S.I. 8. Transient decay characteristics of 6wt% 3DPA3CN-doped DPEPO film

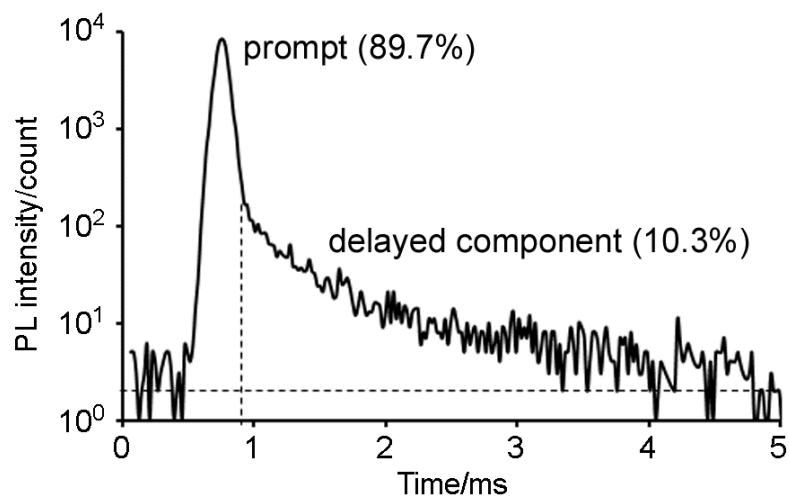


Figure SI 2a. The relative contribution of fluorescence and TADF at 300 K.

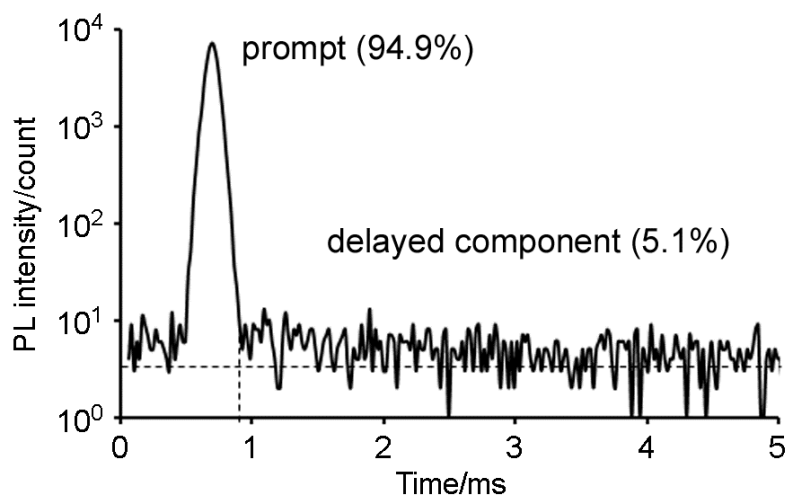


Figure SI 2b. The relative contribution of fluorescence and TADF at 100 K.