

An electron-transporting host material compatible with diverse triplet emitters used for highly efficient red- and green-electrophosphorescent devices

Tsyr-Yuan Hwu,^a Tsung-Cheng Tsai,^b Wen-Yi Hung,^{*b} Sheng-Yuan Chang,^c Yun Chi,^{*c} Mei-Hsin Chen,^d Chih-I Wu,^d
Ken-Tsung Wong,^{*a} and Liang-Chen Chi^a

^a Department of Chemistry, National Taiwan University, Taipei, Taiwan 106. Fax: 886 2 33661667; Tel: 886 2 33661665;
E-mail: kenwong@ntu.edu.tw

^b Institute of Optoelectronic Sciences, National Taiwan Ocean University, Keelung, Taiwan 202. E-mail:
wenhung@mail.ntou.edu.tw

^c Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300

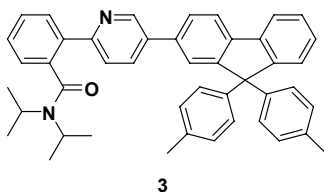
^d Department of Electrical Engineering and Graduate Institute of Electro-optical Engineering, National Taiwan University,
Taipei, Taiwan 106.

Electronic Supplementary Information

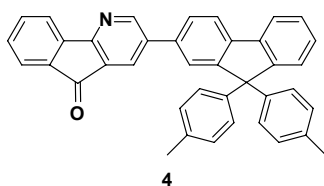
SynthesisS2–S3

Figure S-1. Ultraviolet photoelectron spectroscopy (UPS) measurements of T2 and T2N.....S4

Synthesis



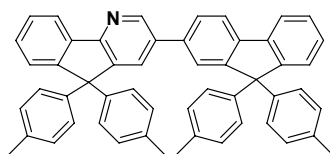
2-(5-(9,9-Di-*p*-tolyl-9*H*-fluoren-2-yl)pyridin-2-yl)-*N,N*-diisopropylbenzamide (3). A mixture of 2-(5-bromo-2-pyridinyl)-*N,N*-diisopropylbenzamide ¹ (**1**, 0.36 g, 1.0 mmol), 2-[9,9-ditolyl-9*H*-fluoren-2-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane² (**2**, 0.52 g, 1.1 mmol), Pd(PPh₃)₄ (0.05 g, 0.044 mmol), Na₂CO₃(aq) (2.0 M, 25 mL), and P^tBu₃ (0.05 M in toluene, 1.75 mL, 0.09 mmol) in toluene (50 mL) was heated under reflux under argon for 48 h. The reaction mixture was cooled to room temperature and extracted with EtOAc. The organic extracts were dried (MgSO₄) and concentrated under reduced pressure. The crude product was purified through column chromatography (SiO₂; 30% EtOAc/hexane) to afford **3** as a white solid (425 mg, 68%). M.p.: 129 °C (DSC); IR (KBr) ν 2963, 2864, 1624, 1448, 1337, 1032 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 8.85 (d, *J* = 1.8 Hz, 1H), 7.85–7.72 (m, 5H), 7.65–7.57 (m, 2H), 7.50–7.34 (m, 4H), 7.32–7.28 (m, 2H), 7.14 (d, *J* = 8.2 Hz, 4H), 7.05 (d, *J* = 8.2 Hz, 4H), 3.70–3.60 (m, 1H), 3.38–3.30 (m, 1H), 2.30 (s, 6H), 1.54 (d, *J* = 6.8 Hz, 3H), 1.40 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.62 (d, *J* = 6.7 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 152.9, 151.3, 142.2, 138.8, 137.5, 135.9, 129.0, 128.3, 127.7, 127.6, 127.1, 126.1, 126.0, 125.8, 124.2, 123.6, 120.4, 120.1, 65.1, 51.1, 45.9, 21.4, 21.1, 21.0, 20.2, 20.1; MS (FAB): *m/z* (%) 627.4 (5), 526 (60); HRMS (M⁺, FAB) Calcd. for C₄₅H₄₂N₂O: *m/z* 626.3297; found: 626.3270.; Anal. Calcd. for C₄₅H₄₂N₂O; C, 86.22; H, 6.75; N, 4.47; Found. C, 85.90; H, 6.80; N, 4.27.



3-(9,9-Di-*p*-tolyl-9*H*-fluoren-2-yl)-5*H*-indeno[1,2-*b*]pyridin-5-one (4). LDA (0.5 M, 12 mL, 6.0 mmol) was added dropwise to a solution of **3** (1.88 g, 3.0 mmol) in THF (90 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and then it was warmed to room temperature and stirred for an additional 16 h. NH₄Cl_(aq) was added and the mixture extracted with EtOAc. The organic phase was washed with water and brine, dried (MgSO₄), and concentrated under rotary evaporation. The crude product was purified through column chromatography (SiO₂; 25% EtOAc/hexane) to give **4** (1.26 g, 80%) as a pale-yellow powder. IR (KBr) ν 2922, 1720, 1445, 746 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 8.80 (d, *J* = 2.2 Hz, 1H), 8.05 (d, *J* = 2.2 Hz, 1H), 7.86 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.63–7.58 (m, 3H), 7.46–7.35 (m, 3H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 4H), 7.06 (d, *J* = 8.2 Hz, 4H), 2.30 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 191.5, 152.7, 152.1, 151.7, 143.1, 142.4, 140.6, 139.0, 136.7, 136.2, 136.0, 135.3, 135.0, 130.7, 129.6, 129.0, 128.1, 127.8, 127.4, 126.1, 126.0, 124.1, 120.9, 120.7, 120.3, 65.0, 21.1; MS (FAB): *m/z* (%) 526 (68), 434 (20); HRMS (M+H⁺, FAB) Calcd. for C₃₉H₂₇NO: *m/z* 525.2093; found: 525.2118. Anal. Calcd. for C₃₉H₂₇NO; C, 89.11; H, 5.18; N, 2.66. Found: C, 88.77; H, 5.21; N, 2.57.

(1) K.-T. Wong, T.-Y. Hwu, A. Balaiah, T.-C. Chao, F.-C. Fang, C.-T. Lee, Y.-C. Peng, *Org. Lett.*, 2006, **8**, 1415.

(2) K.-T. Wong, Y.-Y. Chien, R.-T. Chen, C.-F. Wang, Y.-T. Lin, H.-H. Chiang, P.-Y. Hsieh, C.-C. Wu, C. H. Chou, Y. O. Su, G.-H. Lee, S.-M. Peng, *J. Am. Chem. Soc.*, 2002, **124**, 11576.



T2N

3-(9,9-Di-*p*-tolyl-9*H*-fluoren-2-yl)-5,5-di-*p*-tolyl-5*H*-indeno[1,2-*b*]pyridine (T2N). *p*-Tolylmagnesium bromide (1.0 M in THF, 4 mL, 4 mmol) was added to a solution of **4** (1.05 g, 2.0 mmol) in THF (50 mL). The reaction mixture was stirred at room temperature for 6 h before being poured into water and extracted with EtOAc. The organic phase was washed with brine and then dried (MgSO₄). After evaporating the solvent, the crude product was dissolved in toluene (50 mL) and added to a warm mixture of toluene (50 mL) and H₂SO₄ (2 mL). The mixture was heated under reflux for 16 h and then cooled to room temperature. 2 M K₂CO_{3(aq)} was added and then the organic phase was separated, dried (MgSO₄), filtered, and evaporated to dryness. The residue was purified through column chromatography (SiO₂; 10% EtOAc/hexane) to afford **T2N** as a yellowish solid (496 mg, 42%). M.p.: 297 °C (DSC); IR (KBr) ν 3025, 2920, 2858, 1740, 1508, 1441, 1235 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 8.75 (s, 1H), 8.24 (d, *J* = 7.4 Hz, 1H), 7.90 (s, 1H), 7.82–7.76 (m, 2H), 7.59 (s, 1H), 7.55–7.26 (m, 7H), 7.14–7.03 (m, 16H), 2.31 (s, 12H); ¹³C NMR (CDCl₃, 100 MHz) δ 151.9, 151.6, 151.2, 145.0, 142.3, 141.4, 139.5, 138.9, 137.2, 136.2, 135.9, 135.0, 131.2, 129.2, 128.7, 128.6, 127.6, 127.5, 126.3, 125.8, 125.7, 124.3, 120.8, 120.2, 120.0, 65.0, 63.0, 21.4; MS (FAB): *m/z* (%) 692 (25), 600 (5); HRMS ([M + H]⁺, FAB) Calcd. for C₅₄H₄₂N: *m/z* 692.3317; found: 692.3328. Anal. Calcd. for C₅₃H₄₁N: C, 92.00; H, 5.97; N, 2.02; Found. C, 92.13; H, 6.02; N, 2.03.

Ultraviolet Photoemission Spectroscopy Measurement

The valence-band ultraviolet photoemission spectra (UPS) were carried out with He I (21.2 eV) and He II (40.8 eV) as excitation sources. The Fermi level of the system was measured on the gold substrate before the organic deposition. The energy levels of the HOMOs of organic samples were determined by extrapolating the edges of the HOMO peak down to the background of the UPS spectra. The vacuum levels of the films were deduced from the onset of lowest binding energy in the spectra and photon energy.

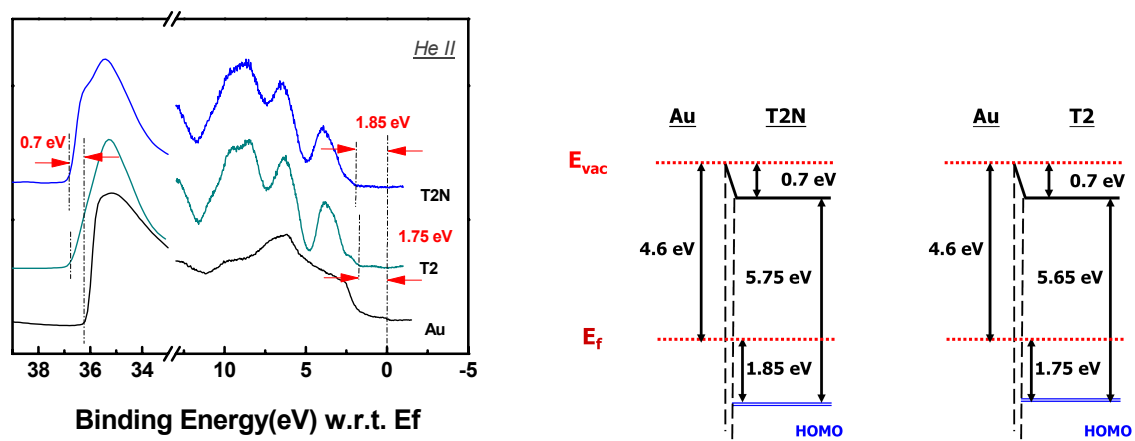


Figure S-1. Ultraviolet photoelectron spectroscopy (UPS) measurements of the bifluorene derivatives **T2** and **T2N**. The energy band diagrams of **T2** and **T2N** can be obtained from the UPS data and illustrated at the right hand side.