Supplementary Information

Three-Carbazole-Armed Host Materials with Various Cores for RGB Phosphorescent Organic Light-Emitting Diodes

Shi-Jian Su,*¹ Chao Cai,² and Junji Kido*²

¹State Key Laboratory of Luminescent Materials and Devices (South China University of Technology) and Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology, Guangzhou 510640, China

²Department of Organic Device Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan,

Yonezawa, Yamagata 992-8510, Japan

E-mail: mssjsu@scut.edu.cn; kid@yz.yamagata-u.ac.jp

Materials

All the reagents were purchased from Sigma-Aldrich and were used without further purification. 1,3,5-Tri(*m*-bromophenyl) benzene (1),¹ 9-(3-bromophenyl)-carbazole (3),² 9-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-carbazole (4)² were synthesized according to the literature procedures.

Synthesis of 2,4,6-tris(3-bromophenyl)pyridine (2). A mixture of 3-bromobenzaldehyde (1.85 g, 10 mmol), 3-bromoacetophenone (3.98 g, 20 mmol), and KOH (0.561 g, 10 mmol) in ethanol (150 mL) and concentrated NH₄OH (60 mL) was stirred under reflux for four days. A white precipitate was found during this procedure. After cooling to room temperature, the precipitate was collected by a glass filter and then washed with deionized water and methanol successively. The subjection of the crude product to silica gel chromatography (eluent: chloroform) afforded **2** (1.79 g, 33%) as white powders. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.318 (t, *J*=1.5 Hz, 2H), 8.118-8.101 (m, 2H), 7.871 (t, *J*=1.5 Hz, 1H),7.823 (s, 2H), 7.669-7.652 (m, 1H), 7.639-7.617 (m, 1H), 7.607-7.585 (m, 2H), 7.435-7.386 (m, 3H). ¹³C NMR (500 MHz, CDCl₃): δ (ppm) 156.351, 149.210, 141.092, 140.631, 132.284, 132.227, 130.747, 130.343, 130.228, 130.163, 125.860, 125.742, 123.354, 123.095, 117.056. EIMS: m/z 544 [M⁺] (calcd m/z 544.08).

Synthesis of 2,4,6-tris(3-(carbazol-9-yl)phenyl)-pyridine (TCPY). A mixture of 2 (0.979 g, 1.8 mmol), carbazole (1.05 g, 6.3 mmol), PdCl₂ (28.7 mg, 0.162 mmol), tris(*tert*-butyl)phosphine (131 mg, 0.648 mmol), and sodium *tert*-butoxide (0.778 g, 8.1 mmol) in anhydrous *o*-xylene (100 mL) was stirred at 120 °C for 17 hr under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into water and then extracted with toluene. The combined organic phase was washed with brine and dried over MgSO₄. The subjection of the crude mixture to silica gel chromatography (chloroform/n-hexane = 2/1) afforded TCPY (1.32 g, 91%) as white powders. 1,3,5-Tris(3-(carbazol-9-yl)phenyl)-benzene (TCPB) was synthesized in a similar manner to that of TCPY.

TCPY. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.385 (t, *J*=2.0 Hz, 2H), 8.287-8.266 (m, 2H), 8.156-8.141 (m, 6H), 7.988 (s, 2H), 7.942 (t, *J*=2.0 Hz, 1H), 7.837-7.816 (m, 1H), 7.750 (t, *J*=7.5 Hz, 1H), 7.723 (t, *J*=7.5 Hz, 2H), 7.688-7.666 (m, 1H), 7.647-7.625 (m, 2H), 7.460-7.424 (m, 6H), 7.398-7.364 (m, 2H), 7.348-7.251 (m, 10H). ¹³C NMR (500 MHz, CDCl₃): δ (ppm) 157.264, 149.967, 141.407, 141.159, 141.037, 140.831, 139.000, 138.553, 131.058, 130.588, 128.189, 128.120, 126.472, 126.343, 126.232, 126.125, 123.741, 123.638, 120.670, 120.541,

120.422, 120.216, 117.897, 110.020, 109.833. EIMS: m/z 804 [M⁺H⁺] (calcd m/z 802.96). Anal. Calc. for C₅₉H₃₈N₄ (%): C, 88.25; H, 4.77; N, 6.98. Found: C, 88.14; H, 4.89; N, 6.85.

TCPB. 1.28 g, 89%. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.139 (d, *J*=7.5 Hz, 6H), 7.891 (s, 6H), 7.782 (d, *J*=8.0 Hz, 3H), 7.692 (t, *J*=8.0 Hz, 3H), 7.582 (d, *J*=8.0 Hz, 3H), 7.443 (d, *J*=8.0 Hz, 6H), 7.376 (t, *J*=7.5 Hz, 6H), 7.275 (t, *J*=7.5 Hz, 6H). ¹³C NMR (500 MHz, CDCl₃): δ (ppm) 142.636, 141.805, 140.874, 138.376, 130.468, 126.474, 126.432, 126.047, 125.993, 125.692, 123.384, 120.348, 119.985, 109.729. EIMS: m/z 803 [M⁺H⁺] (calcd m/z 801.97). Anal. Calc. for C₆₀H₃₉N₃ (%): C, 89.86; H, 4.90; N, 5.24. Found: C, 89.70; H, 4.99; N, 5.10.

Synthesis of 2,4,6-tris(3-(carbazol-9-yl)phenyl)-pyrimidine (TCPM). A mixture of **4** (1.94 g, 5.25 mmol), 2,4,6-trichloropyrimidine (0.275 g, 1.5 mmol), bis(triphenylphosphine)palladium (II) chloride (PdCl₂(PPh₃)₂) (70 mg, 0.1 mmol), and 2M K₂CO₃ (30 mL) in 1,4-dioxane (120 mL) was stirred at 90°C for 24 hr under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into water and then extracted with chloroform. The combined organic phase was washed with brine and dried over MgSO₄. The subjection of the crude mixture to silica gel chromatography (chloroform/n-hexane = 3/2) afforded TCPM (1.07 g, 89%) as white powders. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.902 (t, *J*=1.5 Hz, 1H), 8.777-8.755 (m, 1H), 8.476 (t, *J*=2.0 Hz, 2H), 8.348-8.327 (m, 2H), 8.175-8.141 (m, 6H), 8.092 (s, 1H), 7.782-7.678 (m, 6H), 7.464-7.436 (m, 6H), 7.346-7.258 (m, 12H). ¹³C NMR (500 MHz, CDCl₃): δ (ppm) 164.407, 164.155, 140.947, 140.779, 139.764, 139.161, 138.616, 138.105, 130.620, 130.117, 129.590, 127.630, 127.305, 126.314, 126.096, 126.035, 125.993, 123.487, 123.376, 120.378, 120.264, 120.176, 119.955, 110.948, 109.796, 109.632. EIMS: m/z 805 [M⁺H⁺] (calcd m/z 803.95). Anal. Calc. for C₅₈H₃₇N₅ (%): C, 86.65; H, 4.64; N, 8.71. Found: C, 86.57; H, 4.82; N, 8.57.

References

1. S.-J. Su, T. Chiba, T. Takeda and J. Kido, Adv. Mater., 2008, 20, 2125.

2. S.-J. Su, H. Sasabe, T. Takeda and J. Kido, Chem. Mater., 2008, 20, 1691.



Scheme S1. Molecular structures and acronyms of the host materials with an arylene core and two phenyl carbazole arms.



Figure S1. Photoluminescence spectra for the RGB triplet emitters ((a). FIrpic; (b). Ir(PPy)₃; (c). Ir(piq)₃) co-deposited with TCPB, TCPY, and TCPM.

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Scheme S2. Molecular structures and acronyms of the materials used for device fabrication.



Figure S2. Current density (*J*) (open) and luminance (*L*) (closed) *vs* driving voltage (*V*) characteristics of the RGB phosphorescent OLEDs in structures: (a) ITO / TPDPES:TBPAH (20 nm) / 3DTAPBP (30 nm) / host:11 wt% FIrpic (10 nm) / BP4mPy (40 nm) / LiF (0.5 nm) / Al (100 nm); (b) ITO / TPDPES:TBPAH (20 nm) / TAPC (30 nm) / host:8 wt% Ir(PPy)₃ (10 nm) / TmPyBPZ (50 nm) / LiF (0.5 nm) / Al (100 nm); (c) ITO / TPDPES:TBPAH (20 nm) / TAPC (35 nm) / host:4 wt% Ir(piq)₃ (10 nm) / TmPyBPZ (65 nm) / LiF (0.5 nm) / Al (100 nm). Host: TCPB (\bigcirc ●), TCPY (\square ■), and TCPM (\diamondsuit ●).



Figure S3. Electroluminecent (EL) spectra of the RGB phosphorescent OLEDs in structures: (a) ITO / TPDPES:TBPAH (20 nm) / 3DTAPBP (30 nm) / host:11 wt% FIrpic (10 nm) / BP4mPy (40 nm) / LiF (0.5 nm) / Al (100 nm); (b) ITO / TPDPES:TBPAH (20 nm) / TAPC (30 nm) / host:8 wt% Ir(PPy)₃ (10 nm) / TmPyBPZ (50 nm) / LiF (0.5 nm) / Al (100 nm); (c) ITO / TPDPES:TBPAH (20 nm) / TAPC (35 nm) / host:4 wt% Ir(piq)₃ (10 nm) / TmPyBPZ (65 nm) / LiF (0.5 nm) / Al (100 nm). Host: TCPB (\bigcirc), TCPY (\Box), and TCPM (\diamondsuit).



Figure S4. External quantum efficiency (η_{ext}) (closed) and power efficiency (η_P) (open) *vs* luminance (*L*) characteristics of the red phosphorescent OLEDs in structure: ITO / TPDPES:TBPAH (20 nm) / TAPC (35 nm) / host:4 wt% Ir(piq)₃ (10 nm) / TmPyBPZ (65 nm) / LiF (0.5 nm) / Al (100 nm). Host: (a) TCPY ($\bigcirc \bullet$), 26DCzPPy ($\bigcirc \bullet$); (b) TCPM ($\bigcirc \bullet$), 24DCzPPm ($\square \blacksquare$), 46DCzPPm ($\diamondsuit \bullet$).