Supporting Information

Electronic Supplementary Information

Effective Blocking the Molecular Aggregation of Novel Truxene-Based Emitters with *spiro*Bifluorene and Electron-Donating Moieties for Furnishing Highly Efficient Non-Doped Blue-Emitting OLEDs

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Synthetic details

Truxene (1): Under nitrogen atmosphere, 3-phenylpropanoic acid (5.0 g, 33.3 mmol) was mixed with polyphosphoric acid (100 g) and reacted at ca. 70 °C for 45 minutes, then heated up to ca. 160 °C and kept stirring for another 3 hours. After cooling to room temperature, the reaction mixture was poured into ice water and brown precipitate formed. The suspension was collected under suction and washed with water. The residue was recrystallized from toluene and gave the title compound as light-yellow solid (1.64 g, 43%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.95 (d, J = 7.2 Hz, 3H), 7.69 (d, J = 7.2 Hz, 3H), 7.50 (t, J = 7.2 Hz, 3H), 7.39 (t, J = 7.2 Hz, 3H); FAB-MS (m/z): 342 [M]⁺; Anal. calcd. for C₂₇H₁₈: C, 94.70; H, 5.30; found: C, 94.51; H, 4.98.

Tr-C: To a suspend solution of **1** (1.37 g, 4.00 mmol) in 40 mL THF under nitrogen atmosphere, n-BuLi (2.5 M in hexane, 6.4 mL, 16.0 mmol) was slowly added via a syringe in 15 minutes at room temperature. The solution was stirred for another 45 minutes and then 1-bromohexane (2.65 g, 16.0 mmol) was added to the solution. After stirring for 2 hours, the second portion of n-BuLi (2.5 M in hexane, 6.4 mL, 16.0 mmol) was added and after 45 minutes, the second portion of 1-bromohexane (2.65 g, 16.0 mmol) was added. The reaction mixture was stirred overnight and quenched with diluted hydrochloric acid. The solution was extracted with dichloromethane and the combined organic phase was dried over anhydrous Na₂SO₄. The solvent was removed to get crude product, which was purified by column chromatography on silica gel, eluting with petroleum ether (b.p. 60-90 °C) and giving the title compound as a yellow solid (2.92 g, 86%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.37 (d, *J* = 7.6 Hz, 3H), 7.46 (d, *J* = 7.2 Hz, 3H), 7.41-7.34 (m, 6H), 3.00-2.92 (m, 6H), 2.10-2.03 (m, 6H), 0.93-0.82 (m, 36H), 0.59 (t, *J* = 7.2 Hz, 18H), 0.51-0.45 (m, 12H); ¹³C NMR (100

MHz, CDCl₃): δ [ppm] 153.60, 144.77, 140.30, 138.30, 126.27, 125.91, 124.59, 122.13, 55.55, 36.90, 31.47, 29.48, 23.85, 22.26, 13.88; FAB-MS (*m/z*): 847 [M]⁺; Anal. calcd. for C₆₃H₉₀: C, 89.29; H, 10.71; found: C, 88.89; H, 10.65.

Tr-CBr: Bromine (0.54 mL, 10.5 mmol) was added to a stirring solution of **2** (2.54 g, 3.0 mmol) dichloromethane (40 mL) free from light in 5 minutes at room temperature. After 18 hours, the reaction mixture was washed with saturated sodium thiosulfate solution and extracted with dichloromethane and the combined organic phase was dried over anhydrous Na₂SO₄. The solvent was removed and the crude product was purified by column chromatography on silica gel, eluting with petroleum ether (b.p. 60-90 °C) and giving the title compound as a yellow crystal (3.56 g, 93.0%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.17 (d, *J* = 8.4 Hz, 3H), 7.56 (s, 3H), 7.51 (d, *J* = 8.4 Hz, 3H), 2.87-2.80 (m, 6H), 2.04-1.97 (m, 6H), 0.94-0.79 (m, 36H), 0.59 (t, *J* = 7.2 Hz, 18H), 0.50-0.46 (m, 12H); FAB-MS (*m/z*): 1082, 1084 [M]⁺; Anal. calcd. for C₆₃H₈₇Br₃: C, 69.80; H, 8.09; found: C, 69.63; H, 7.86.

Tr-Ar1: Under a nitrogen atmosphere, **Tr-CBr** (0.54 g, 0.50 mmol) and 2-thienylboronic acid (0.23 g, 1.80 mmol) and Pd(PPh₃)₄ (5 mol- % per C-Br bond) were added to a mixture solution of THF (20 mL) and 2M Na₂CO₃ (5mL). The resulting mixture was stirred at 100 °C for 24 h. Then, the reaction mixture was cooled to room temperature and extracted with dichloromethane. The combined organic phase was dried with anhydrous Na₂SO₄. The solvent was then removed and the residue was purified by column chromatography with petroleum ether (PE) (b.p. 60-90 °C) to give the title compound as a light yellow power (0.46 g, 84 %). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.37 (d, *J* = 8.8 Hz, 3H), 7.70-7.69 (m, 6H), 7.48 (d, *J* = 3.6 Hz, 3H), 7.34 (d, *J* = 5.2 Hz, 3H), 7.16 (dd, *J* = 4.0 Hz, 4.8 Hz, 3H), 3.00-2.96 (m, 6H), 2.18-2.12 (m, 6H), 0.99-0.83 (m, 36H), 0.63-0.55 (m, 30H); ¹³C

NMR (100 MHz, CDCl₃): δ (ppm) 154.40, 145.09, 144.93, 139.77, 137.99, 132.48, 128.08, 124.94, 124.55, 124.14, 122.90, 119.31, 55.77, 37.08, 31.47, 29.48, 23.96, 22.26, 13.86; FAB-MS (*m/z*): 1092 [M]⁺; Anal. calcd. for C₇₅H₉₆S₃: C, 82.36; H, 8.85; found: C, 82.11; H, 8.63.

Tr-Ar2: Under a nitrogen atmosphere, **Tr-CBr** (0.54 g, 0.50 mmol) and (9-ethyl-9H-carbazol-3yl) boronic acid (0.42 g, 1.76 mmol) and Pd(PPh₃)₄ (5 mol- % per C-Br bond) were added to a mixture solution of THF (20 mL) and 2M Na₂CO₃ (5mL). The resulting mixture was stirred at 100 °C for 24 h. Then, the reaction mixture was cooled to room temperature and extracted with dichloromethane. The combined organic phase was dried with anhydrous Na₂SO₄. The solvent was then removed and the residue was purified by column chromatography with a mixture solution of petroleum ether (PE) (b.p. 60-90 °C) and dichloromethane ($V_{PE}/V_{DCM} = 5:1$) to give the title compound as a white power (0.53 g, 74 %). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.52-8.49 (m, 6H), 8.27 (d, J = 7.6 Hz, 3H), 7.94 (d, J = 8.4 Hz, 3H), 7.85-7.82 (m, 6H), 7.58-7.47 (m, 9H), 7.31 (t, J =7.2 Hz, 3H), 4.49-4.44 (m, 6H), 3.15-3.08 (m, 6H), 2.31-2.24 (m, 6H), 1.52 (t, J = 7.2 Hz, 9H), 1.03-0.95 (m, 36H), 0.71-0.64 (m, 30H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 154.41, 140.42, 139.94, 139.42, 138.97, 132.57, 125.80, 125.25, 123.53, 123.17, 120.70, 118.92, 118.87, 108.68, 108.61, 55.78, 37.68, 37.19, 31.57, 29.62, 24.04, 22.34, 13.96, 13.88; FAB-MS (*m/z*): 1427 [M]⁺; Anal. calcd. for C₁₀₅H₁₂₃N₃: C, 88.37; H, 8.69; N, 2.94; found: C, 88.10; H, 8.31; N, 2.79.

Tr-Ar3: Under a nitrogen atmosphere, **Tr-CBr** (0.54 g, 0.50 mmol) and (4-(diphenylamino)phenyl) boronic acid (0.50 g, 1.73 mmol) and Pd(PPh₃)₄ (5 mol- % per C-Br bond) were added to a mixture solution of THF (20 mL) and 2M Na₂CO₃ (5mL). The resulting mixture was stirred at 100 °C for 24 h. Then, the reaction mixture was cooled to room temperature and extracted with dichloromethane. The combined organic phase was dried with anhydrous Na₂SO₄. The solvent

was then removed and the residue was purified by column chromatography with a mixture solution of petroleum ether (PE) (b.p. 60-90 °C) and dichloromethane ($V_{PE}/V_{DCM} = 5:1$) to give the title compound as a white power (0.62 g, 78 %). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.40 (d, J = 8.0 Hz, 3H), 7.67-7.62 (m, 12H), 7.30 (t, J = 7.6 Hz, 12H), 7.22 (d, J = 8.4 Hz, 6H), 7.18 (d, J = 7.6 Hz, 12H), 7.05 (t, J = 7.2 Hz, 6H), 3.04-2.97 (m, 6H), 2.17-2.10 (m, 6H), 0.93-0.85 (m, 36H), 0.61-0.55 (m, 30H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 154.27, 147.68, 147.03, 144.90, 139.26, 138.32, 138.01, 135.26, 129.27, 127.65, 124.85, 124.55, 124.33, 124.10, 122.87, 119.92, 55.69, 37.06, 31.49, 29.51, 23.92, 22.27, 13.91; FAB-MS (m/z): 1577 [M]⁺; Anal. calcd. for C₁₁₇H₁₂₉N₃: C, 89.09; H, 8.24; N, 2.66; found: C, 88.79; H, 8.11; N, 2.38.

Tr-ArBr1: To a stirring solution of **Tr-Ar1** (0.33 g, 0.30 mmol) in dichloromethane (25 mL) at room temperature, *N*-bromosuccinimide (0.18 g, 1.00 mmol) was added and continued stirred for overnight. The solution was washed with water and extracted with dichloromethane. The crude product was purified by column chromatography with the mixture of PE and DCM ($V_{PE}/V_{DCM} = 8:1$) to get corresponding title compound as light yellow power (0.39 g, 97 %). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.34 (d, *J* = 8.8 Hz, 3H), 7.59-7.58 (m, 6H), 7.20 (d, *J* = 4.0 Hz, 3H), 7.10 (d, *J* = 4.0 Hz, 3H), 2.97-2.90 (m, 6H), 2.13-2.06 (m, 6H), 0.98-79 (m, 36H), 0.59 (t, *J* = 7.2 Hz, 18H), 0.52-0.50 (m, 12H); FAB-MS (*m/z*): 1328, 1330 [M]⁺; Anal. calcd. for C₇₅H₉₃Br₃S₃: C, 67.71; H, 7.07; found: C, 67.59; H, 6.83.

Tr-ArBr2: To a stirring solution of **Tr-Ar2** (0.43 g, 0.30 mmol) in dichloromethane (25 mL) at room temperature, *N*-bromosuccinimide (0.18 g, 1.00 mmol) was added and continued stirred for overnight. The solution was washed with water and extracted with dichloromethane. The crude product was purified by column chromatography with the mixture of PE and DCM ($V_{PE}/V_{DCM} = 5:1$)

to get corresponding title compound as white power (0.48 g, 96 %). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.50 (d, J = 8.4 Hz, 3H), 8.44 (s, 3H), 8.35 (s, 3H), 7.94 (dd, J = 1.2 Hz, 8.4 Hz, 3H), 7.80-7.78 (m, 6H), 7.59 (dd, J = 1.6 Hz, 8.4 Hz, 3H), 7.55 (d, J = 8.4 Hz, 3H), 7.34 (d, J = 8.4 Hz, 3H), 4.46-4.40 (m, 6H), 3.11-3.07 (m, 6H), 2.28-2.23 (m, 6H), 1.49 (t, J = 7.2 Hz, 9H), 1.03-0.91 (m, 36H), 0.68-0.61 (m, 30H); FAB-MS (*m/z*): 1663, 1665 [M]⁺; Anal. calcd. for C₁₀₅H₁₂₀Br₃N₃: C, 75.80; H, 7.27; N, 2.53; found: C, 75.59; H, 7.03; N, 2.18.

Tr-ArBr3: To a stirring solution of **Tr-Ar3** (0.47 g, 0.30 mmol) in dichloromethane (25 mL) at room temperature, *N*-bromosuccinimide (0.36 g, 2.00 mmol) was added and continued stirred for overnight. The solution was washed with water and extracted with dichloromethane. The crude product was purified by column chromatography with the mixture of PE and DCM ($V_{PE}/V_{DCM} = 5:1$) to get corresponding title compound as white power (0.57 g, 93 %). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.41 (d, J = 8.0 Hz, 3H), 7.68-7.62 (m, 12H), 7.39 (d, J = 8.4 Hz, 12H), 7.19 (d, J = 8.4 Hz, 6H), 7.03 (d, J = 8.8 Hz, 12H), 3.04-2.97 (m, 6H), 2.18-2.10 (m, 6H), 0.93-0.84 (m, 36H), 0.61-0.54 (m, 30H); FAB-MS (m/z): 2050 [M]⁺; Anal. calcd. for C₁₁₇H₁₂₃Br₆N₃: C, 68.53; H, 6.05; N, 2.05; found: C, 68.15; H, 5.89; N, 1.83.

Tr1: Under a nitrogen atmosphere, **Tr-CBr** (0.54 g, 0.50 mmol) and 9,9'-*spiro* bifluoren-7-yl boronic acid (0.63 g, 1.75 mmol) and Pd(PPh₃)₄ (5 mol- % per C-Br bond) were added to a mixture solution of THF (20 mL) and 2M Na₂CO₃ (5mL). The resulting mixture was stirred at 100 °C for 24 h. Then, the reaction mixture was cooled to room temperature and extracted with dichloromethane. The combined organic phase was dried with anhydrous Na₂SO₄. The solvent was then removed and the residue was purified by column chromatography with a mixture solution of petroleum ether (PE) (b.p. 60-90 °C) and dichloromethane ($V_{PE}/V_{DCM} = 8:1$) to give the title compound as a white power

(0.65 g, 73 %). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.22 (d, J = 8.4 Hz, 3H), 7.96 (d, J = 7.6 Hz, 3H), 7.90 (d, J = 7.6 Hz, 9H), 7.76 (dd, J = 1.6 Hz, 8.0 Hz, 3H), 7.55 (s, 3H), 7.43-7.38 (m, 12H), 7.17-7.11 (m, 12H), 6.83 (d, J = 7.2 Hz, 6H), 6.74 (d, J = 7.6 Hz, 3H), 2.85-2.78 (m, 6H), 2.05-1.97 (m, 6H), 0.88-0.70 (m, 36H), 0.52 (t, J = 7.2 Hz, 18H), 0.43-0.39 (m, 12H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 154.16, 149.41, 149.26, 148.82, 145.02, 141.85, 141.43, 141.01, 139.54, 138.63, 137.87, 127.91, 127.79, 126.94, 125.18, 124.62, 124.21, 124.01, 122.39, 120.29, 120.17, 120.08, 120.05, 66.10, 55.69, 36.97, 31.46, 29.47, 23.92, 22.24, 13.85; FAB-MS (m/z): 1813 [M+Na]⁺; Anal. calcd. for C₁₃₈H₁₃₂: C, 92.57; H, 7.43; found: C, 92.39; H, 7.29.

Tr2: Under a nitrogen atmosphere, **Tr-ArBr1** (0.27 g, 0.20 mmol) and 9,9'-*spiro*bifluoren-7-yl boronic acid (0.25 g, 0.69 mmol) and Pd(PPh₃)₄ (5 mol- % per C-Br bond) were added to a mixture solution of THF (20 mL) and 2M Na₂CO₃ (5mL). The resulting mixture was stirred at 100 °C for 24 h. Then, the reaction mixture was cooled to room temperature and extracted with dichloromethane. The combined organic phase was dried with anhydrous Na₂SO₄. The solvent was then removed and the residue was purified by column chromatography with a mixture solution of petroleum ether (PE) (b.p. 60-90 °C) and dichloromethane ($V_{PE}/V_{DCM} = 7.2$) to give the title compound as a light yellow power (0.29 g, 71 %). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.29 (d, *J* = 8.4 Hz, 3H), 7.92-7.86 (m, 12H), 7.72 (dd, *J* = 1.6 Hz, 8.0 Hz, 3H), 7.61 (d, *J* = 7.6 Hz, 3H), 7.59 (s, 3H), 7.44-7.37 (m, 12H), 7.31 (d, *J* = 3.6 Hz, 3H), 7.19-7.10 (m, 16H), 7.02 (s, 3H), 6.81 (d, *J* = 7.6 Hz, 6H), 6.73 (d, *J* = 7.2 Hz, 3H), 2.93-2.86 (m, 6H), 2.10-2.03 (m, 6H), 0.92-0.77 (m, 36H), 0.57-0.48 (m, 30H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 154.36, 149.53, 149.15, 148.54, 145.04, 143.89, 143.17, 141.79, 141.29, 141.18, 139.71, 137.90, 134.03, 132.23, 127.93, 127.81, 125.48, 124.83, 124.18, 123.98, 123.66, 120.99, 120.45, 120.05, 119.99, 118.90, 65.97, 55.71, 37.00, 31.42, 29.42, 23.89, 22.22, 13.85; FAB-

MS (*m*/*z*): 2035 [M]⁺; Anal. calcd. for C₁₅₀H₁₃₈S₃: C, 88.45; H, 6.38; found: C, 88.28; H, 6.07.

Tr3: Under a nitrogen atmosphere, Tr-ArBr2 (0.33 g, 0.20 mmol) and 9,9'-spirobifluoren-7-yl boronic acid (0.25 g, 0.69 mmol) and Pd(PPh₃)₄ (5 mol- % per C-Br bond) were added to a mixture solution of THF (20 mL) and 2M Na₂CO₃ (5mL). The resulting mixture was stirred at 100 °C for 24 h. Then, the reaction mixture was cooled to room temperature and extracted with dichloromethane. The combined organic phase was dried with anhydrous Na₂SO₄. The solvent was then removed and the residue was purified by column chromatography with a mixture solution of petroleum ether (PE) (b.p. 60-90 °C) and dichloromethane ($V_{PE}/V_{DCM} = 3:2$) to give the title compound as a white power (0.35 g, 74 %). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.51-8.48 (m, 6H), 8.30 (s, 3H), 7.98 (d, J = 8.0 Hz, 3H), 7.90 (d, J = 7.6 Hz, 12H), 7.82-7.80 (m, 9H), 7.61 (d, J = 8.8 Hz, 3H), 7.53 (d, J = 8.4 Hz, 3H), 7.42-7.38 (m, 12H), 7.18-7.10 (m, 12H), 6.86 (d, J = 7.6 Hz, 6H), 6.75 (d, J = 7.6 Hz, 3H), 4.43-4.41 (m, 6H), 3.11-3.06 (m, 6H), 2.28-2.21 (m, 6H), 1.48 (t, J = 7.2 Hz, 9H), 1.01-0.92 (m, 36H), 0.66-0.63 (m, 30H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 154.38, 149.42, 149.16, 148.94, 144.78, 141.90, 141.84, 141.58, 140.30, 139.88, 139.84, 138.99, 138.19, 132.78, 132.24, 127.88, 127.70, 127.59, 127.01, 125.42, 125.30, 124.90, 124.26, 123.97, 123.65, 123.59, 122.84, 120.71, 120.29, 120.01, 119.93, 119.05, 108.79, 108.64, 66.11, 55.80, 37.79, 37.19, 31.57, 29.60, 24.02, 22.36, 14.00, 13.86; FAB-MS (*m/z*): 2369 [M]⁺; Anal. calcd. for C₁₈₀H₁₆₅N₃: C, 91.21; H, 7.02; N, 1.77; found: C, 91.07; H, 7.06; N, 1.49.

Tr4: Under a nitrogen atmosphere, **Tr-ArBr3** (0.41 g, 0.20 mmol) and (4-(diphenylamino)phenyl) boronic acid (0.40 g, 1.38 mmol) and Pd(PPh₃)₄ (5 mol- % per C-Br bond) were added to a mixture solution of THF (25 mL) and 2M Na₂CO₃ (5mL). The resulting mixture was stirred at 100 °C for 24 h. Then, the reaction mixture was cooled to room temperature and extracted with dichloromethane.

The combined organic phase was dried with anhydrous Na₂SO₄. The solvent was then removed and the residue was purified by column chromatography with a mixture solution of petroleum ether (PE) (b.p. 60-90 °C) and dichloromethane ($V_{PE}/V_{DCM} = 3:1$) to give the title compound as a white power (0.44 g, 73 %). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.41 (d, J = 8.0 Hz, 3H), 7.71-7.65 (m, 12H), 7.53-7.48 (m, 24H), 7.30-7.26 (m, 42H), 7.15 (d, J = 7.6 Hz, 36H), 7.04 (t, J = 7.2 Hz, 12H), 3.02-3.00 (m, 6H), 2.17-2.15 (m, 6H), 0.95-0.86 (m, 36H), 0.62-0.58 (m, 30H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 154.31, 147.69, 146.80, 146.44, 144.96, 139.33, 138.31, 138.04, 135.57, 135.11, 134.63, 129.25, 127.76, 127.41, 127.33, 124.89, 124.41, 124.32, 124.20, 124.04, 122.84, 119.98, 55.73, 37.10, 31.50, 29.52, 23.95, 22.28, 13.92; FAB-MS (m/z): 3036 [M]⁺; Anal. calcd. for C₂₂₅H₂₀₇N₉: C, 88.89; H, 6.87; N, 4.15; found: C, 88.65; H, 6.58; N, 3.98.



(b) ¹³C NMR for Tr1



(c) ¹H NMR for Tr2



(d) ¹³C NMR for Tr2



(f) ¹³C NMR for Tr3



(h) ¹³C NMR for Tr4



Figure S1 The NMR spectra of the truxene-based compounds

(b) Tr2



Figure S2 The MS spectra of the truxene-based compounds



Figure S3 The TGA and DSC traces of the truxene-based compounds.



Figure S4 The PL spectra for Tr4 in different solvents together with that in thin film.



Figure S5 The possible rotamers for Tr1 in "real" configuration and the possible molecular aggregation behavior of Tr1.

For **Tr1**, two possible rotamers maybe exist in "real" configuration, namely, rotamer **A** with all three *spiro*-bifluorenes locate on one side of the truxene molecular plane and rotamer **B** bearing one *spiro*-bifluorene on the opposite site of the truxene molecular plane. The theoretical results reveal that the energy of these two rotamers are quite similar ($E_A = -2607716.948$ kcal/mol and $E_B = -$ 2607716.907 kcal/mol). Therefore, both of these two rotamers maybe exist in "real" configuration of **Tr1**. If rotamer **B** mainly exists in "real" configuration, the aggregation among the molecules of **Tr1** should be effectively blocked. However, the PL spectra of films and EL spectra reveals that serious aggregation exists in **Tr1**. So, **Tr1** is prone to adopt the configuration of rotamer **A**. According to theoretical calculation, six hexyl groups are perpendicular to truxene plane. Thus, two molecules of **Tr1** might form aggregation with the way of dislocation overlap shown in Figure S3.



Figure S6 The CV curves of the truxene-based compounds in the positive potential range.





Figure S7 The EL efficiency-current density curves for device A and B.