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Covalent Functionalized Conjugated Dendrimers for Organic Light Emitting Diode: Synthesis, Characterization, and the Deep Blue Electroluminescence

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Fig. S1. The absorption and photoluminance spectrums of the dropcasting films(Left), and the cyclovoltamitry spectrums of the dropcasting films(right). The spot line and the solid line corresponded to the compound **11** and **12**, respectively.





2-bromo-9-H-fluorene (2.44 g, 10 mmol) was dissolved into 100 mL DMSO with stirring. 3 mL of 50% NaOH(aq) were added to the solution dropwisely and the mixture were stirred for 1 h under room temperature. 1-bromohexane (6.09 g, 21 mmol) were added and the mixtures were stirred overnight under room temperature. The reaction was quenched by water and extracted by dichloromethane. The organic layer was washed with brine, HCl (2 M) and water, dried over Na₂SO₄. The solvent was removed under vacuum and the residue was purified by chromatograph (silica gel, petroleum: dichloromethane = 6:1) to give 14.1 g white powder, yield 95 %. ¹H-NMR (CDCl₃, 300 MHz, ppm): δ 8.08-8.05 (4H, m, Ar-H), 7.60-7.63 (1H, m, Ar-H), 7.50-7.53 (1H, d, *J* = 8.1 Hz, Ar-H), 7.38-7.44 (6H, m, Ar-H), 7.17-7.38 (11H, m, Ar-H), 4.12-4.17 (4H, t, *J* = 7.5 Hz, CH₂), 1.80-1.86 (4H, m, CH₂), 1.64-1.68 (4H, m, CH₂), 1.14-1.05 (8H, m, CH₂), 0.56-0.50 (4H, m, CH₂). ¹³C-NMR (CDCl₃, 75 MHz, ppm): δ 152.8, 150.1, 140.6, 126.1, 125.9, 125.6, 123.0, 121.3, 120.6, 120.4, 119.0, 118.8, 108.9, 108.7, 55.4, 43.1, 40.3, 29.8, 29.0, 27.0, 23.7. MALDI-TOF MS, *m/z*:

742 (M⁺).



Compound 1(1.44 g, 2 mmol), dioxanborolane (0.533 g, 2.1 mmol), potassium acetate (0.400 g, 4 mmol), Pd₂(dba)₃ (10 mg), tricyclohexylphosphine (10 mg), were added to a two-neck round flask with stirrer. 100 mL of dioxane were added to the flask via syringe under N₂. The mixtures were stirred for 1 h at room temperature and heated to 100° C overnight. The reaction was quenched by water and extracted with dichloromethane. The organic layer was washed with brine, HCl (2 M) and water, dried over Na₂SO₄. The solvent was removed under vacuum and the residue was purified by chromatograph (silica gel, petroleum: dichloromethane = 3:1) to give 1.34 g white powder, yield 85 %. ¹H-NMR (CDCl₃, 300 MHz, ppm): δ 8.04-8.07 (4H, m, Ar-H), 7.80-7.83 (1H, m, Ar-H), 7.67-7.72 (3H, m, Ar-H), 7.39-7.44 (4H, m, Ar-H), 7.15-7.33 (11H, m, Ar-H), 4.11-4.16 (4H, t, *J* = 7.2 Hz, CH₂), 1.83-1.95 (4H, m, CH₂), 1.62-1.66 (4H, m, CH₂), 1.35 (12H, s, CH₃), 1.02-1.18 (8H, m, CH₂), 0.45-0.60 (4H, m, CH₂). ¹³C-NMR (CDCl₃, 75 MHz, ppm): δ 151.1, 149.8, 144.4, 141.1, 140.6, 129.0, 125.8, 125.7, 123.0, 120.6, 120.5, 119.3, 118.9, 118.8, 109.0, 108.7, 84.0, 55.1, 43.1,



Compound 2(0.347 g, 0.44 mmol), compound 3(0.220 g, 0.2 mmol), potassium carbonate (0.138 g, 1 mmol), Pd(PPh₃)₄ (10 mg) were added to a two-neck round flask with stirrer. 50 mL of THF and 0.5 mL deionized water were added to the flask via syringe under N₂. The reaction was heated to reflux overnight. The mixtures were extracted with dichloromethane. The organic layer was washed with brine, and water, dried over Na₂SO₄. The solvent was removed under vacuum and the residue was purified by chromatograph (silica gel, petroleum: dichloromethane = 2:1) to give 0.164 g white powder, yield 72 %. ¹H-NMR (CDCl₃, 300 MHz, ppm): δ 10.11 (1H, s, CHO), 8.48-8.51 (3H, d, J= 8.1 Hz, Ar-H), 8.06-8.09 (12H, m, Ar-H), 7.93-7.96 (2H, d, J = 8.4 Hz, Ar-H), 7.70-7.84 (17H, m, Ar-H), 7.18-7.42 (28H, m, Ar-H), 4.15-4.30 (8H, t, J = 7.2 Hz, CH₂), 3.02-3.06 (6H, m, CH₂), 2.18-2.22(6H, m, CH₂), 1.99-2.04 (8H, m, CH₂), 1.68-1.73 (8H, m, CH₂), 1.17-1.15 (16H, m, CH₂), 0.90-0.95 (38H, s, CH₃), 0.50-0.70 (36 H, m, CH₂), ¹³C-NMR (CDCl₃, 75 MHz, ppm): δ192.2, 154.8, 154.6, 151.5, 150.8, 145.9, 145.7, 145.4, 141.2, 141.1, 140.7, 140.6, 140.4, 139.8, 138.6, 138.5, 138.1, 137.8, 135.4, 130.7, 127.9, 127.4, 125.9, 125.7, 125.3, 123.0, 121.3, 121.2, 121.0, 120.6, 120.5, 120.2, 120.0, 119.0, 118.9, 118.6, 109.0, 108.8, 56.2, 55.4, 43.1, 40.7, 37.5, 37.2, 31.8, 30.1, 29.9, 29.0, 28.7, 27.2, 24.3, 24.0, 22.6, 22.3, 14.3, 14.2. MALDI-TOF MS, *m/z*: 2192 (M⁺-85).



Compound 7 (1.108 g, 1 mmol), and compound 9 (2.04 g, 2.1 mmol) were added to the 200 mL round flask with stirred. 100 mL of THF, 100 mg of tertrabutylamounium bromide and 20 mL of 50% KOH (aq) were added to the mixture. The reaction were stirred overnight at room temperature. The mixtures were extracted with dichloromethane. The organic layer was washed with brine, and water, dried over Na₂SO₄. The solvent was removed under vacuum and the residue was purified by chromatograph (silica gel, petroleum: dichloromethane: ethyl acetate = 2:1:0.01) to give 2.65 g white powder, yield 92 %. ¹H-NMR (CDCl₃, 300 MHz, ppm): δ 8.33-8.39(2H, m, Ar-H), 8.21-8.24(1H, d, *J* = 8.7 Hz, Ar-H), 7.50-7.70 (15H, m, Ar-H), 7.31-7.48 (26H, m, Ar-H), 7.10-7.24 (20H, m, Ar-H), 6.63 (4H, s, Ar-H), 5.00 (4H, s, CH₂), 4.16-4.26 (12H, m, CH₂), 3.88-3.95 (12H, m, CH₂), 2.70-3.10 (6H, m, CH₂), 2.00-2.20 (6H, m, CH₂), 1.60-1.90 (24H, m, CH₂), 1.30-1.50 (28H, m, CH₂), 0.80-1.00 (30H, m, CH₂), 0.40-0.55 (24H, m, CH₂, CH₃). ¹³C-NMR (CDCl₃, 75 MHz, ppm): δ 153.4, 140.6, 138.9, 125.9, 125.7, 123.0, 120.6, 120.5, 119.5, 118.9, 109.0, 10*.7, 69.0, 43.1, 31.7, 29.7, 29.5, 29.1, 27.4, 27.2, 26.0, 24.1, 22.5. MALDI-TOF MS, *m/z*: 2906 (M⁺+23).



Compound 4 (220 mg, 0.1 mmol) and compound 13 (45 mg, 0.03 mmol) were added to a dried 100 mL two-neck round flask with stirred. 50 mL of THF were added to the flask via syringe under nitrogen. The solution were kept stirring under -78 °C for 30 mins. The THF solution of the potassium t-butyloxide were added to the cooled solution under -78 $^{\circ}$ C via syringe in 2 h. The mixture were kept stirring under the low temperature for additional 4 hours. The reaction was quanched by pulling the solution into ice cooled HCl (6 M). The organic layer was extracted by dichloromathane and washed by brine, dried over Na₂SO₄. The solvent was removed under vacuum. The residue was purified by the chromatograph (silica gel, pertolium: dichloromethane: ethyl acetate = 1:1:0.01) to give 168 mg light yellow powder as product, yield 72 %. ¹H-NMR (CDCl₃, 400 MHz, ppm): δ 8.45-8.55 (12H, m, Ar-H), 8.08-8.06 (24H, d, J = 7.8 Hz, Ar-H), 7.84-7.69 (72H, m, Ar-H), 7.44-7.40 (26H, m, Ar-H), 7.32-7.28 (47H, m, Ar-H), 7.22-7.18 (22H, m, Ar-H), 4.19-4.16 (24H, t, J = 7.8 Hz, CH₂), 3.00-3.10 (24H, m, CH₂), 2.18-2.30(24H, m, CH₂), 1.99-2.04 (24H, m, CH₂), 1.68-1.73 (24H, m, CH₂), 1.17-1.15 (54H, m, CH₂), 0.90-0.99 (156H, m, CH₂), 0.50-0.70 (150 H, m, CH₂, CH₃), ¹³C-NMR (CDCl₃, 100 MHz, ppm): δ 154.4, 154.3 , 151.4, 150.5, 145.2, 145.16, 140.8, 140.5, 140.4, 140.3, 140.1, 139.8, 139.6, 139.4, 138.5, 138.1, 136.4, 132.4, 128.2, 127.3, 127.1, 126.9, 126.1, 125.6, 125.5, 125.4, 125.2, 125.0, 122.7, 121.0, 120.4, 120.3, 120.0, 119.8, 118.3, 108.6, 55.8, 55.0, 42.9, 40.4, 37.2, 31.54, 31.52, 31.49, 29.8, 29.7, 29.62,





Compound 10 (0.29g, 0.1 mmol) and compound 13(45 mg, 0.03 mmol) were added to a dried 100 mL two-neck round flask with stirred. 50 mL of THF were added to the flask via syringe under nitrogen. The solution were kept stirring under -78 °C for 30 mins. The THF solution of the potassium t-butyloxide were added to the cooled solution under -78 $^{\circ}$ C via syringe in 2 h. The mixture were kept stirring under the low temperature for additional 4 hours. The reaction was quanched by pulling the solution into ice cooled HCl (6 M). The organic layer was extracted by dichloromathane and washed by brine, dried over Na₂SO₄. The solvent was removed under vacuum. The residue was purified by the chromatograph (silica gel, pertolium: dichloromethane: ethyl acetate = 1:1:0.01) to give 220 mg light yellow powder as product, yield 75 %. ¹H-NMR $(CDCI_3, 400 \text{ MHz}, ppm)$: δ 8.39-8.45 (12H, m, Ar-H), 8.07-8.10 (36H, m, Ar-H), 7.63, 7.83 (60H, m, Ar-H), 7.30-7.46 (78H, m, Ar-H), 7.18-7.23 (36H, m, Ar-H), 7.11-7.13 (12H, d, J = 8.8 Hz, Ar-H), 6.64 (12H, s, Ar-H), 5.01 (12H, s, Ar-H), 4.23-4.27 (24H, t, J = 7.2 Hz, CH₂), 4.17-4.20 (12H, t, J = 7.2 Hz, CH₂), 3.88-3.95 (36H, m, CH₂), 2.94-3.08(24H, m, CH₂), 2.10-2.20 (24H, m, CH₂), 1.64-1.89 (75H, m, CH₂), 1.37-1.54 (78H, m, CH₂), 0.80-0.99 (145H, m, CH₂), 0.50-0.70 (114 H, m, CH₂, CH₃), ¹³C-NMR (CDCl₃, 100 MHz, ppm): δ 158.3, 154.3 , 153.2, 145.0, 140.4, 139.2, 138.6, 138.1, 137.8, 134.2, 132.0, 128.3, 128.1, 127.3, 127.1, 125.60, 125.58, 125.0, 124.9, 122.8, 120.4, 118.75, 118.72, 118.6, 115.2,108.6,108.5, 106.7, 73.1, 70.8, 68.8, 55.8, 42.90, 42.85, 37.2, 37.1, 31.5, 30.1, 29.6,

29.2, 28.9, 27.1, 27.0, 24.0, 22.3, 13.9. MALDI-TOF MS, *m*/*z*: 9780 (M⁺). All other compounds were synthesised in our previous publications.