Syntheses and Structures of Novel Heteroarene-Fused Coplanar π -Conjugated Chromophores

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2a

To a solution of ethyl 2-iodobenzoate (1.46 g, 5.28 mmol), Pd(PPh₃)₄ (277 mg, 0.24 mmol) and 2-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)-8,8-diphenyl-8*H*-3-thia-cyclopenta[*a*]indene^[1] (**1a**, 2.16 g, 4.8 mmol) in dioxane (50 ml), were added tri-*tert*-butylphosphine (0.05 M in toluene, 4.8 ml, 0.24 mmol) and K₃PO₄ aqueous solution (2 M, 5.0 ml, 10 mmol). The reaction mixture was refluxed for 48 h. Upon completion, the mixture was extracted with dichloromethane, and then dried over MgSO₄. The product was purified by silica gel column chromatography (ethyl acetate/hexanes = 1/9) to afford yellow solid (2.01 g, 88%). mp 144~145 °C; IR (KBr) ν 2946, 1706, 1600, 1481, 1441, 1355, 1341, 1288, 1255, 1129, 1096 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.66 (d, *J* = 4.4 Hz, 1H), 7.52 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.46~7.49 (m, 2H), 7.39 (dd, *J* = 7.2, 1.2 Hz, 2H), 7.31 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.18~7.26 (m, 11H), 6.94 (s, 1H), 3.88 (q, *J* = 3.2 Hz, 2H), 0.83 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 169.0, 155.3, 152.4, 144.9, 144.6, 141.1, 137.1, 133.9, 132.1, 130.7, 130.5, 129.2, 128.1, 127.7, 127.6, 127.5, 126.6, 126.1, 125.7, 122.2, 119.3, 63.8, 61.4, 13.8; MS (*m/z*, FAB⁺) 472.2 (70); HRMS (M⁺, FAB⁺) Calcd. for C₃₂H₂₄O₂S 472.1497. Found 472.1474.

2b

To a solution of ethyl 2-iodobenzoate (0.98 g, 3.5 mmol), Pd(PPh₃)₄ (186 mg, 0.16 mmol) and 2-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)-8,8-ditolyl-8*H*-3-thia-cyclopenta[*a*]indene^[1] (**1b**, 1.54 g, 3.2 mmol) in dioxane (30 ml), were added tri-*tert*-butylphosphine (0.05 M in toluene, 3.2 ml, 0.16 mmol) and K₃PO₄ aqueous solution (2 M, 3.4 ml, 6.8 mmol). The reaction mixture was refluxed for 48 h. Upon completion, the mixture was extracted with dichloromethane. The combined organic solution was dried over MgSO₄. The product was purified by silica gel column chromatography (ethyl acetate/hexanes = 1/9) to afford yellow solid (0.97 g, 60%). mp 143~146 °C; IR (KBr) ν 2906, 1714, 1598, 1513, 1445, 1360, 1293, 1244, 1164, 1122, 1079 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.73 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.38~7.52 (m, 4H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.19~7.25 (m, 5H), 7.09 (d, *J* = 8.0 Hz, 4H), 7.00 (s, 1H), 3.99 (q, *J* = 6.8 Hz, 2H), 2.34 (s, 6H), 0.93 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 169.0, 155.7, 152.8, 144.7, 141.6, 140.9, 137.0, 136.1, 133.8, 132.0, 130.6, 130.4, 129.1, 128.8, 127.6, 127.3, 125.9, 125.6, 122.1, 119.2, 63.2, 61.3, 21.0, 13.7; MS (*m/z*, FAB⁺) 500.2 (80); HRMS (M⁺, FAB⁺) Calcd. for C₃₂H₂₈O₂S 500.1810. Found 500.1803.

To a solution of compound **2a** (1.3 g, 2.75 mmol) in THF (30 ml), was added with phenyl magnesium bromide which was prepared in advance from bromobenzene (1.2 ml, 11.0 mmol) and magnesium turnings (268 mg, 11.0 mmol). After refluxing for overnight, the reaction mixture was quenched with water, extracted with ethyl acetate and dried over MgSO_4 . After the removal of solvent, the crude product was dissolved in acetic acid (80 ml) and added one drop of H_2SO_4 . The mixture was refluxed for 4 hours and cooled. The reaction mixture was extracted with ethyl acetate and dried over MgSO_4 , then concentrated by rotary evaporation. The product was purified by silica gel chromatography (chloroform/hexanes = 1/4) to afford **3a** as a yellow solid (1.1 g, 71%). mp 401 °C (DSC); IR (KBr) ν 3052, 1600, 1593, 1487, 1448, 1322, 1282, 1156, 1083, 1030 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.41 (d, J = 7.6 Hz, 2H), 7.20 (dt, J = 6.8, 1.6 Hz, 2H), 7.01~7.06 (m, 4H), 6.87~6.92 (m, 12H), 6.76~6.80 (m, 8H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 156.3, 150.0, 144.6, 140.4, 135.9, 127.5, 127.4, 127.1, 126.7, 126.2, 126.0, 125.9, 124.8, 117.7, 64.5; MS (m/z , FAB^+) 564.2 (80); Anal. Calcd. for $\text{C}_{42}\text{H}_{28}\text{S}$: C, 89.32; H, 5.00; S, 5.68. Found: C, 89.34; H, 4.89; S, 5.66.

To a solution of compound **2a** (2.0 g, 4.2 mmol) in THF (50 ml), was added with *p*-tolyl magnesium bromide which was prepared in advance from 4-bromotoluene (2.2 ml, 17.8 mmol) and magnesium turnings (432 mg, 17.8 mmol). After refluxing for overnight, the reaction mixture was quenched with water, extracted with ethyl acetate and dried over MgSO_4 . After the removal of solvent, the crude product was dissolved in acetic acid (100 ml) and added one drop of H_2SO_4 . The mixture was refluxed for 4 hours and cooled. The reaction mixture was extracted with ethyl acetate and dried over MgSO_4 , then concentrated by rotary evaporation. The product was purified by silica gel chromatography (chloroform/hexanes = 1/4) to afford **3b** as a yellow solid (1.25 g, 50%). mp 288 °C (DSC); IR (KBr) ν 3059, 2906, 2840, 1600, 1501, 1441, 1328, 1282, 1182, 1162, 1023 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.43 (d, J = 3.2 Hz, 1H), 7.41 (d, J = 3.6 Hz, 1H), 7.18~7.23 (m, 2H), 7.00~7.09 (m, 4H), 6.95 (t, J = 7.6 Hz, 2H), 6.89 (d, J = 7.2 Hz, 4H), 6.77~6.81 (m, 8H), 6.58 (d, J = 7.6 Hz, 4H), 2.18 (s, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 156.6, 156.3, 150.6, 150.0, 144.4, 144.3, 140.5, 137.4, 135.9, 135.8, 135.0, 127.9, 127.6, 127.3, 127.1, 126.7, 126.6, 125.9, 125.8, 125.2, 124.8, 124.6, 117.7, 64.4, 63.8, 21.2; MS (m/z , FAB^+) 592.2 (100); Anal. Calcd. for $\text{C}_{44}\text{H}_{32}\text{S}$: C, 89.15; H, 5.44; S, 5.41. Found: C, 89.13; H, 5.55; S, 5.00.

To a solution of compound **2b** (1.8 g, 3.6 mmol) in THF (50 ml), was added with *p*-tolyl magnesium bromide which was prepared in advance from 4-bromotoluene (1.8 ml, 14.4 mmol) and magnesium turnings (350 mg, 14.4 mmol). After refluxing for overnight, the reaction mixture was quenched with water, extracted with ethyl acetate and dried over MgSO₄. After the removal of solvent, the crude product was dissolved in acetic acid (100 ml) and added one drop of H₂SO₄. The mixture was refluxed for 4 hours and cooled. The reaction mixture was extracted with ethyl acetate and dried over MgSO₄, then concentrated by rotary evaporation. The product was purified by silica gel chromatography (chloroform/hexanes = 1/4) to afford **3c** as a yellow solid (1.23 g, 55%). mp 302 °C (DSC); IR (KBr) ν 3019, 2906, 2840, 1706, 1600, 1507, 1467, 1328, 1282, 1176, 1103, 1023 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.18 (dt, *J* = 7.6, 1.2 Hz, 2H), 6.98~7.06 (m, 4H), 6.75 (d, *J* = 8 Hz, 8H), 6.59 (d, *J* = 7.6 Hz, 8H), 2.19 (s, 12H); ¹³C NMR (CDCl₃, 100 MHz) δ 156.6, 150.4, 144.2, 137.6, 135.9, 135.0, 127.7, 127.4, 126.6, 125.8, 124.6, 117.6, 63.9, 21.3; MS (*m/z*, FAB⁺) 620.2 (100); Anal. Calcd. for C₄₆H₃₆S: C, 88.99; H, 5.84; S, 5.16. Found: C, 88.86; H, 5.95; S, 4.80.

To a solution of 2-thienyl magnesium bromide which was prepared in advance from 2-bromothiophene (2.8 ml, 28.8 mmol) and magnesium turnings (702 mg, 28.8 mmol) in THF (30 ml) at 0 °C, was added zinc chloride solution (3.91 g in 30 mL THF) in one portion and then stirred for 30 minutes at 0 °C. After removal of the ice-bath, diethyl 2,5-dibromoterephthalate (4.38 g, 11.5 mmol) and Pd(PPh₃)₄ (266 mg, 2 mol%) were added directly. The reaction mixture was refluxed overnight. Upon completion, the reaction mixture was filtered over celite, extracted with ethyl acetate, and then dried over MgSO₄. The product was purified by silica gel chromatography (ethyl acetate/hexanes = 1/9) to afford light yellow liquid (3.3 g, 73%). mp 103~104 °C; IR (KBr) ν 3112, 2986, 2983, 1806, 1726, 1534, 1487, 1368, 1328, 1282, 1136, 1003 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.81 (s, 2H), 7.39 (dd, *J* = 4.8, 1.2 Hz, 2H), 7.08 (m, 4H), 4.22 (q, *J* = 7.2 Hz, 4H), 1.16 (t, *J* = 7.2 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 166.9, 139.8, 133.5, 132.9, 131.3, 126.9, 126.5, 126.0, 61.6, 14.2; MS (*m/z*, FAB⁺) 386.0 (100); HRMS (M⁺, FAB⁺) Calcd. for C₂₀H₁₈O₄S₂ 386.0647. Found 386.0642.

To a solution of **4** (1.0 g, 2.6 mmol) in THF (20 ml), was added with *p*-tolyl magnesium bromide which was prepared in advance from 4-bromotoluene (1.9 ml, 15.3 mmol) and magnesium turnings (378 mg, 15.5 mmol). The reaction mixture was refluxed overnight. The reaction was quenched with water, extracted with ethyl acetate, and then dried over MgSO₄. After the removal of solvent, the crude product was dissolved in acetic acid (100 ml) and added one drop of H₂SO₄. The mixture was refluxed for 4 hours and cooled. The reaction mixture was extracted with ethyl acetate, dried over MgSO₄, then purified by silica gel chromatography (chloroform/hexanes = 1/4) to afford white solid (1.05 g, 65%). mp 424 °C (DSC); IR (KBr) ν 3092, 3012, 2919, 1514, 1448, 1388, 1315, 1255, 1176, 1103, 1076 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.41 (s, 2H), 7.24 (d, *J* = 5.2 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 8H), 7.05 (d, *J* = 8.4 Hz, 8H), 6.97 (d, *J* = 5.2 Hz, 2H), 2.31 (s, 12H); ¹³C NMR (CDCl₃, 100 MHz) δ 155.1, 152.8, 141.4, 140.7, 135.9, 134.7, 128.6, 127.5, 127.2, 122.6, 117.1, 117.0, 62.6, 21.4; MS (*m/z*, FAB⁺) 626.2 (100); Anal. Calcd. for C₄₄H₃₄S₂: C, 84.30; H, 5.47; S, 10.23. Found: C, 84.29; H, 5.43; S, 10.28.

A mixture of diethyl 2,5-dibromoterephthalate (3.80 g, 10 mmol) and benzo[*b*]thiophen-2-boronic acid (5.34 g, 30 mmol)[ref], Pd(PPh₃)₄ (580 mg, 0.5 mmol), Na₂CO₃ (30 ml, 2 M), tri-*tert*-butylphosphine (15 ml, 0.05 M in toluene, 0.75 mmol) in 1,4-dioxane (65 ml) was refluxed for 2 days. After cooling to room temp., the mixture was extracted twice with CHCl₃. The combined organic solution was washed with brine and dried over MgSO₄, the product was isolated as white crystals by recrystallization from CH₂Cl₂/hexanes (3.99 g, 82 %). mp 168~169 °C ; IR (KBr) ν 3054, 2987, 1729, 1422, 1265, 896, 744, 705 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.96 (s, 2H), 7.86 (dd, *J* = 1.6, 6.8, 2H), 7.80 (dd, *J* = 1.6, 6.8 Hz, 2H), 7.41-7.36 (m, 4H), 7.34 (s, 2H), 4.24 (q, *J* = 7.2 Hz, 8H), 1.10 (t, *J* = 7.2 Hz, 8H) ; ¹³C NMR (CDCl₃, 100 MHz) δ 167.1, 140.4, 140.2, 139.7, 134.1, 133.9, 132.0, 124.5, 124.5, 123.7, 123.6, 122.0, 61.8, 13.9; MS (*m/z*, FAB⁺) 486 (35); HRMS (*m/z*, FAB⁺) Calcd. for C₂₈H₂₂O₄S₂ 486.0960. Found 486.0971.

4-Bromotoluene (14.3 g, 83.6 mmol) in THF (120 ml) were treated with n-BuLi (51 ml, 1.6 M in hexane, 83.6 mmol) at -78 °C and quenched with a solution of diester **6** (2.52 g, 5.16 mmol) dissolved in THF (50 ml). The reaction was kept at -78 °C for 1 hour and slowly warmed to room temp for stirring another 12 hours. The solution was quenched with water (100 ml). The organic solvent was removed by rotary evaporation. The resulting white solids were collected by filtration and washed with hexanes, and then extracted into CH₂Cl₂. The combined organic solution was dried (MgSO₄) and concentrated by rotary evaporation. The crude product was dissolved in boiling acetic acid (100 ml) and dropwisely added with concentrated HCl (10 ml). The reaction was allowed to reflux for 3 hours then quenched with water (100 ml). The precipitate was collected and washed twice with methanol, affording product **7** as a white solid (3.2 g, 85 %). mp 461 °C (DSC) ; IR (KBr) ν 3054, 2987, 1422, 1265, 896, 739, 705; ¹H NMR (CDCl₃, 400 MHz) δ 7.83-7.81 (m, 2H), 7.57 (s, 2H) 7.24-7.19 (m, 12H), 7.07 (d, *J* = 7.6 Hz, 8H), 2.30 (s, 12H) ; ¹³C NMR (C₂D₂Cl₄, 100 MHz) δ 156.2, 148.5, 144.0, 142.0, 139.8, 136.7, 136.3, 134.2, 129.3, 128.6, 124.8, 124.2, 123.9, 122.5, 117.1, 64.1, 22.0; MS(*m/z*, FAB⁺) 726 (0.3); HRMS (*m/z*, FAB⁺) Calcd. for C₅₂H₃₈S₂ 726.2415, found 726.2440; Anal. Calcd C, 85.91; H, 5.27; S, 8.82. Found C, 85.95; H, 5.17; S, 8.94.

4,6-Dibromoisophthalic acid (16.6 g, 51.2 mmol) was dissolved in ethanol (250 ml) and added conc. H₂SO₄ (15 ml). The mixture was heated to reflux for 48 hours. The reaction mixture was concentrated in vacuum vacuo, and then extracted with CH₂Cl₂. The combined organic layers were washed with brine, dried over MgSO₄ and concentrated under reduced pressure. Diethyl 4,6-dibromoisophthalate was isolated by column chromatography on silica gel (ethyl acetate/hexanes = 1/4) to give white solids.(13.23 g, 68 %). mp 60-62 °C; IR (KBr) ν 3019, 1729, 1216, 1052, 762, 669 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 8.23 (s, 1H), 8.01 (s, 1H), 4.42 (q, *J* = 7.2 Hz, 4H), 1.43 (t, *J* = 7.2 Hz, 6H) ; ¹³C NMR (CDCl₃, 100 MHz) δ 163.8, 139.0, 133.2, 130.7, 125.0, 62.1, 14.5; MS (*m/z*, FAB⁺) 380.9 (10); HRMS (*m/z*, FAB⁺) Calcd. for C₁₂H₁₃⁷⁹Br₂O₄ 377.9102 found 378.9198; for C₁₂H₁₃⁷⁹Br⁸¹BrO₄ 379.9082 found 380.9161 , Calcd. for C₁₂H₁₃⁸¹Br₂O₄ 381.9061. Found 382.9135.

A solution of *p*-tolyl magnesium bromide (15.0 mmol) which was prepared in advance from 2-bromothiophene (2.45 g, 15.0 mmol) and magnesium turnings (364.5 mg, 15.0 mmol) was cooled to 0 °C, and then ZnCl₂ (2.04 g, 15.0 mmole) was added. After 1 hour at 0 °C, Pd(PPh₃)₄ (231 mg, 0.2 mmol) and diethyl 4,6-dibromoisophthalate (1.52 g, 4.0 mmol) were added. After refluxing for 12 hours, the reaction mixture was quenched with water, extracted with dichloromethane and dried over MgSO₄. The crude product was purified by column chromatography on silica gel (ethyl acetate/hexanes = 1/5) to afford compound **8** (1.42 g, 92 %). mp 55-56 °C ; IR (KBr) ν 3443, 3019, 1721, 1216, 773, 669 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 8.14 (s, 1H), 7.61 (s, 1H), 7.39 (d, *J* = 4.4 Hz, 2H), 7.11-7.07 (m, 4H), 4.24 (q, *J* = 7.2 Hz, 4H), 1.19 (t, *J* = 7.0 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 166.5, 139.8, 136.0, 133.1, 130.5, 130.3, 126.8, 126.6, 126.1, 61.4, 14.1; MS (*m/z*, FAB⁺) 385.2 (10); HRMS (*m/z*, FAB⁺) Calcd. for C₂₀H₁₈O₄S₂ 386.0647. Found 386.0641.

To a solution of compound **8** in THF (30 ml) was added with *p*-tolyl magnesium bromide (60 mmol) which was prepared in advance from 4-bromotoluene (10.3 g, 60 mmol) and magnesium turnings (1.46 g, 60 mmol). After refluxing for 12 hours, the reaction mixture was quenched with water, extracted with dichloromethane and dried over MgSO₄. After the removal of solvent, the crude product was dissolved in acetic acid (150 ml) and added H₂SO₄ (3 ml). The mixture was refluxed for 12 hours and cooled. The reaction mixture was concentrated, and then extracted with CH₂Cl₂. The combined organic layers were washed with brine, dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (ethyl acetate / hexanes = 1/8) to afford product **9** (3.66 g, 58 %). mp 326 °C (DSC); IR (KBr) ν 3019, 1510, 1215, 758, 669 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.52 (s, 1H), 7.38 (s, 1H), 7.28 (d, *J* = 4.4 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 8H), 7.00 (d, *J* = 4.4 Hz, 8H), 6.97 (d, *J* = 8.4 Hz, 8H), 2.29 (s, 12H); ¹³C NMR (CDCl₃, 100 MHz) δ 155.4, 150.9, 141.3, 140.3, 136.2, 135.7, 128.4, 127.5, 127.3, 124.3, 122.7, 109.9, 62.7, 21.3; MS (*m/z*, FAB⁺) 626.3 (50); HRMS (*m/z*, FAB⁺) Calcd. for C₄₄H₃₄S₂ 626.2102. Found 626.2090. Anal. Calcd C, 84.22; H, 5.30; S, 10.14. Found C, 84.30; H, 5.47; S, 10.23.

12

A mixture of 3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-phenyl-9H-carbazole (4.95 g, 10 mmol)^[2] and ethyl 2-iodobenzoate (7.17 g, 26 mmol), Pd(PPh₃)₄ (580 mg, 0.5 mmol), K₃PO₄ (30 ml, 2 M), tri-*tert*-butylphosphine (10 ml, 0.05 M in toluene, 0.1 mmol) in toluene (50 ml) was refluxed for 2 days. After cooling to room temp., the mixture was extracted twice with CHCl₃. The combined organic solution was washed with brine and dried over MgSO₄, the product was isolated as white crystals by recrystallization from CH₂Cl₂/hexanes (4.96 g, 92 %). mp 147~148 °C ; IR (KBr) ν 3054, 2987, 1720, 1422, 1265, 896, 735, 705 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 8.09 (s, 2H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.64-7.36 (m, 15H), 4.10 (q, *J* = 7.2 Hz, 4H), 1.0 (t, *J* = 7.2 Hz, 6H) ; ¹³C NMR (CDCl₃, 100 MHz) δ 168.9, 142.6, 140.3, 137.4, 133.3, 131.4, 131.0, 130.9, 129.8, 129.5, 127.4, 126.8, 126.6, 123.2, 119.9, 109.2, 60.9, 14.0; MS (m/z, FAB⁺) 539 (100) HRMS (m/z, FAB⁺) Calcd. for C₃₆H₂₉NO₄ 539.2097. Found 539.2098.

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4-Bromotoluene (5.47 g, 32 mmol) in THF (45 ml) were treated with n-BuLi (20 ml, 1.6 M in hexane, 32 mmol) at -78 °C and quenched with a solution of diester **12** (1.08 g, 2.0 mmol) dissolved in THF (30 ml). The reaction was kept at -78 °C for 1 hour and slowly warmed to room temp for stirring another 12 hours. The solution was quenched with water (50 ml). The organic solvent was removed by rotary evaporation. The resulting white solids were collected by filtration and washed with hexanes, and then extracted into CH₂Cl₂. The combined organic solution was dried (MgSO₄) and concentrated by rotary evaporation. The crude product was dissolved in boiling acetic acid (80 ml) and dropwisely added with concentrated HCl (10 ml). The reaction was allowed to reflux for 3 hours then quenched with water (100 ml). The precipitate was collected and washed twice with methanol, affording product **15** as a white solid (1.38 g, 89 %). mp 346 °C (DSC) ; IR (KBr) ν 3054, 2987, 1422, 1265, 896, 731, 705 cm⁻¹ ; ¹H NMR (CDCl₃, 400 MHz) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.58-7.54 (m, 3H), 7.49-7.27 (m, 14H), 7.20-7.13 (m, 2H), 7.05 (dd, *J* = 3.6, 8.0 Hz, 8H), 6.97 (d, *J* = 8.0 Hz, 2H) ; ¹³C NMR (CDCl₃, 100 MHz) δ 153.2, 150.2, 149.5, 146.9, 143.3, 141.8, 141.5, 140.5, 140.0, 138.7, 137.0, 135.8, 135.5, 133.1, 132.1, 128.4, 127.7, 127.3, 126.9, 126.8, 125.8, 125.6, 125.2, 121.8, 120.4, 118.8, 118.6, 117.7, 116.5, 109.4, 106.5, 65.6, 64.7, 21.4, 21.3; MS (m/z, FAB⁺) 779 (20);

HRMS (m/z, FAB⁺) Calcd. for C₆₀H₄₅N 779.3552. Found 779.3562; Anal. Calcd C, 92.39; H, 5.81; N, 1.80. Found C, 92.69; H, 5.75; N, 1.80.

Reference

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Figure S-1. (a) Top and (b) side views of the solid state structure of **5**.

Table S-1: The crystal data of **3c**, **5**, **7**, **9** and **15**

Compounds	3c	5	7	9	15
Empirical formula	C ₄₆ H ₃₆ S • C ₄ H ₈ O	C ₄₄ H ₃₄ S ₂ •2CH ₂ Cl ₂	C ₅₂ H ₃₈ S ₂	C ₄₄ H ₃₄ S ₂	C ₆₀ H ₄₅ N
formula weight	692.91	796.68	726.94	626.83	779.97
crystal dimensions	0.25×0.15×0.10	0.25×0.20×0.15	0.25×0.20×0.15	0.30×0.20×0.15	0.25×0.20×0.15
crystal system	monoclinic	triclinic	triclinic	triclinic	triclinic
space group	P2 ₁ /n	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	15.8840(5)	10.3765(2)	9.8963(3)	9.0731(6)	10.53280(10)
<i>b</i> (Å)	10.9150(3)	10.4444(2)	10.7278(5)	14.1751(7)	14.2613(2)
<i>c</i> (Å)	23.3469(7)	10.7639(2)	10.7354(4)	14.4817(9)	17.2050(3)
α (deg)	90	107.4040(10)	110.407(2)	73.659(3)	67.3510(7)
β (deg)	109.8740(15)	109.7960(10)	104.026(2)	81.407(3)	72.1960(8)
γ (deg)	90	99.0340(10)	107.311(2)	77.206(4)	70.4790(8)
cell volume (Å) ³	3806.7(2)	1003.08(3)	940.43(6)	1735.34(18)	2200.91(5)
<i>Z</i>	4	1	1	2	2
density (calc) g/ cm ³	1.209	1.319	1.284	1.200	1.177
<i>F</i> (000)	1472	414	382	660	824
Temperature (°K)	295(2)	295(2)	295(2)	295 (2)	295(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
no. of reflns collected	18477	8709	7074	12137	16694
no. of indep reflns (<i>R</i> _{int})	8157(0.0507)	4549(0.0204)	4128(0.0472)	7617(0.0596)	10010(0.0327)
<i>R</i> (<i>F</i>), <i>wR</i> 2 [<i>I</i> >2 σ (<i>I</i>)]	0.0791, 0.1891	0.0555, 0.1530	0.0612, 0.1490	0.0637, 0.1365	0.0596, 0.1452
<i>R</i> (<i>F</i>), <i>wR</i> 2 (all data)	0.1725, 0.2344	0.0706, 0.1789	0.1106, 0.1822	0.1551, 0.1821	0.1110, 0.1780

Figure S-2. Crystal packing diagram of **3c** (a) along the *ac*-plane, the co-crystallized solvent (THF) was omitted for clarity, and (b) the packing pattern of π -conjugated backbone, the *p*-tolyl substitutions are omitted for clarity. The partial overlap of terminal phenylene rings of two neighboring **3c** molecules which are arranged in an anti parallel manner reveals the existence of a very weak π - π interaction. The plane-to-plane distance was estimated to be 3.52 Å.

Figure S-3. Crystal packing diagram of **5** (a) along the *bc*-plane, the co-crystallized solvent (CH_2Cl_2) was omitted for clarity, and (b) the packing features of π -conjugated backbones, the *p*-tolyl substitutions are omitted for clarity. The backbones of **5** are packing into a slipped-stairs feature along the *b*-axis. The aryl substitutions occupying the top and bottom faces block the face-to-face overlaps of conjugated backbone efficiently. An edge-to-edge overlap of the terminal thiophene rings with a plane-to-plane distance estimated to be 3.50 Å indicates a very weak intermolecular interaction.

Figure S-4. Crystal packing diagram of **7** (a) along the *bc*-plane, and (b) the packing features of π -conjugated backbones, the *p*-tolyl substitutions are omitted for clarity. The π -conjugation can be efficiently extended by introducing benzothiophene as the subunit of the conjugated backbone. However, the phenylene ring of the benzothiophene in **7** was slightly away from the *p*-tolyl groups that occupy the top and bottom faces of the molecular plane. The lack of steric protection leads the terminal phenylene rings to have a face-to-face overlap with a closest plane-to-plane distance of 3.50 Å, indicating weak intermolecular interaction exist.

Figure S-5. Crystal packing diagram of **9** (a) along the *bc*-plane, and (b) the packing features of π -conjugated backbones, the *p*-tolyl substitutions are omitted for clarity. These packing diagrams clearly indicate the role of *p*-tolyl substitutions on efficiently suppressing the intermolecular interactions and the lack of effective π - π interactions of conjugated backbones. There is no indication of any overlap between terminal thiophene rings, the closest S-S distance of two neighboring molecules which are arranged in an anti-parallel manner was calculated to be 3.47 Å.

Figure S-6. Crystal packing diagram of **15** (a) along the *bc*-plane, and (b) the packing features of π -conjugated backbones, the *p*-tolyl substitutions are omitted for clarity. The closest plane-to-plane distance of two neighboring molecules that are arranged in an anti-parallel manner was estimated to be 3.74 Å. This result indicates that the unsymmetrical molecular backbone and the *p*-tolyl substitutions that occupy the top and bottom faces of the molecular plane can block the face-to-face π - π interactions efficiently.

Pulse Sequence: s2pu1

13C OBSERVE KTW(2004)

Pulse Sequence: s2pu1

STANDARD 1H OBSERVE

Pulse Sequence: s2pu1

2b

Pulse Sequence: s2pu1

PP1
Pulse Sequence: s2pu1

3a

STANDARD 1H OBSERVE

Pulse Sequence: s2pu1

3b

PS-1

Pulse Sequence: s2pu1

3b

TS-1

Pulse Sequence: s2pu1

3c

TS-1
Pulse Sequence: s2pu1

STANDARD 1H OBSERVE

Pulse Sequence: s2pu1

4

¹³C OBSERVE

Pulse Sequence: s2pu1

4

STANDARD 1H OBSERVE

Pulse Sequence: s2pu1

5

IT
Pulse Sequence: s2pu1

5

Pulse Sequence: s2pu1

¹³C OBSERVE

Pulse Sequence: s2pu1

STANDARD 1H OBSERVE

Pulse Sequence: s2pu1

15