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Three-dimensional quater- and quinquethiophenesilanes as promising electron-donor materials for bulk heterojunction photovoltaic cells and photodetectors

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Details of the synthesis of all final and precursor compounds.

***Tetrakis*(5'-trimethylsilyl-2,2'-bithiophen-5-yl)silane (6).** 7.91 mL (12.24 mmol) of 1.6M n-BuLi in hexane was added slowly to the solution of 2,2'-bitien-5-yl(trimethyl)silane (3.01 g, 12.61 mmol) in 150 mL of THF at -78 °C. Then tetrachlorosilane (0.52 mL, 3.06 mmol) was added in one portion and stirred during 1.5 hours at -78 °C. According to the GPC results, the reaction mixture contained 59% of the target product. The reaction mixture was worked up by adding 250 mL of freshly distilled diethyl ether and 400 mL of ice water. The organic phase was separated, washed several times with water until pH=7, dried over anhydrous Na_2SO_4 with the following solvent evaporation stage on the rotary evaporator. The raw product was purified by column chromatography on silica gel (toluene being the eluent) followed by recrystallization to yield 1.52 g (47%) as a white solid sunstance. Anal.Calcd. for $C_{44}H_{52}S_8Si_5$ (%): C, 54.05; H, 5.36; S, 26.23; Si, 14.36. Found: C, 54.22; H, 5.42; S, 25.98; Si, 14.38. ^{1}H NMR (δ in $CDCl_3$): 0.31 (s, 36H), 7.12 (d, 4H, J = 3,7 Hz), 7.31 (8H, dd, J_1 = 3.1 Hz, J_2 = 6.7 Hz), 7.39 (d, 4H, J = 3.7 Hz) ppm. ^{13}C NMR (δ in $CDCl_3$): 0.32, 125.23, 125.74, 131.72, 134.78, 139.34, 140.62, 141.76, 145.47 ppm. ^{29}Si NMR (δ in $CDCl_3$): -35.81, -6.43 ppm. MALDI-MS: *m/z* 978 (M^+, requires 977.85).

***Tetrakis*(5'-bromo-2,2'-bithien-5-yl)silane (7).** 2.24 g (12.60 mmol) of NBS in 70 mL of DMF was added slowly to the solution of 1.40 g (1.43 mmol) of compound **6** in 160 mL of DMF and 210 mL of chloroform at 0…+10 °C. Then the reaction mixture was stirred at room temperature during 6 hrs. The crude reaction mixture contained 76% of the target product

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according to the results of GPC. The reaction mixture was worked up by adding 250 mL of freshly distilled diethyl ether and 400 mL of ice water. The organic phase was separated, washed several times with water until pH=7, dried over anhydrous Na_2SO_4, and concentrated in vacuum. The raw product was purified by repeatable precipitation from a toluene solution by the addition of hexane to yield 0.96 g (58%) as a white solid substance. Anal. Calcd. for $C_{32}H_{16}Br_4S_8Si$ (%): C, 38.26; H, 1.61; Br, 31.81; S, 25.53; Si, 2.80. Found: C, 39.91; H, 1.84; Br, 30.88; S, 24.54; Si, 2.89. ^1H NMR (δ in $CDCl_3$): 6.97 (d, 8H, J = 3.7 Hz), 7.24(4H, d, J = 3.7 Hz), 7.38 (4H, d, J = 3.7 Hz) ppm. ^{13}C NMR (δ in $CDCl_3$): 144.69, 139.42, 138.26, 131.98, 130.79, 125.54, 124.76, 112.05 ppm. ^{29}Si NMR (δ in $CDCl_3$): -35.76 ppm. MALDI-MS: *m/z* 1005 (M^+, requires 1004.70).

***Tetrakis*(5'''-hexyl-2,2':5',2'':5'',2'''-quaterthien-5-yl)silane (2).** 0.39 g (1.04 mmol) of 2-(5'-hexyl-2,2'-bithien-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**9**) and 0.20 g (0.02 mmol) of compound **7** were dissolved in 16 mL of toluene and added to 60 mg of $Pd(PPh_3)_4$ contained in the reaction vessel. Afterwards, 1.6 mL of the 2M sodium carbonate solution was added. The reaction mixture was stirred at reflux for 30 hours. According to the GPC analysis, the reaction mixture contained 37% of the target product. Dry toluene (50 mL) was added to the reaction mixture and water was removed by azeotropic distillation. The raw product was purified by column chromatography on silica gel (toluene being the eluent, T=85 °C) followed by recrystallization and preparative GPC chromatography to yield 0.087 g (26%) of **2** as an orange solid substance. T_m = 195 °C, ΔH_m = 48.3 J/g. Anal. Calcd. for $C_{88}H_{84}S_{16}Si$ (%): C, 62.99; H, 5.15; S, 30.16; Si, 1.76. Found: C, 62.81; H, 5.03; S, 30.49; Si, 1.67. ^1H NMR (δ in $CDCl_3$): 0.88 (t, 12H, *J* = 6.7 Hz), 1.23-1.45 (24H, overlapping peaks with a maximum at 1.32 ppm), 1.67 (m, 8H, *J*= 7.3 Hz), 2.78 (t, 8H, *J* = 7.3 Hz), 6.67 (d, 4H, *J* = 3.7 Hz), 6.97 (t, 8H, *J* = 3.7 Hz), 7.05 (d, 8H, *J* = 3.7 Hz), 7.14 (d, 4H, *J* = 3.7 Hz), 7,31 (d, 4H, *J* = 3.7 Hz), 7.43 (d, 4H, *J* = 3.7 Hz) ppm. MALDI-MS: *m/z* 1683 (M^+, requires 1682.76).

5-(2-ethylhexyl)-2,2':5',2''-terthiophene (11). A Grignard reagent, freshly prepared from 4.43 g (27.2 mmol) of 2-bromothiophene and 0.72 g (28.5 mmol) of magnesium in 90 mL of THF, was added dropwise to the reaction vessel, containing 9.71 g (27.2 mmol) of 5-bromo-5'-(2-ethylhexyl)-2,2'-bithiophene (**10**), 110 mg (0.1 mmol) of $Pd(dppf)Cl_2$ and 60 mL of THF kept at temperature in the range from 0 to +5 ^oC. The reaction mixture was stirred for 2 hours and after that, the temperature was allowed to rise to 20 ^oC, which was followed by stirring for an additional 16 hours. According to the results of GPC, the reaction mixture contained 99% of the target product. The reaction mixture was worked up by adding 250 mL of freshly distilled diethyl ether and 400 mL of ice water. The organic phase was separated, washed several times with water until pH=7, dried over anhydrous Na_2SO_4, with following solvent evaporation on the rotary evaporator. The raw product was purified by column chromatography on silica gel (hexane being the eluent), to yield 8.50g (86.7%) of compound **11** as a yellow solid substance. Anal. Calcd. for $C_{20}H_{24}S_3$ (%): C, 66.62; H, 6.71; S, 26.68; Found: C, 66.89; H, 6.58; S, 26.47. ^{1}H NMR (δ in $CDCl_3$): 0.91 (t, 6H, J = 7.3 Hz), 1.31 -1.40 (overlapping peaks with a maximum at 1.32 ppm, 8H), 1.60 (m, 1H, J= 6.1 Hz), 2.75 (d, 2H, J= 6.7 Hz), 6.68 (d, 1H, J = 3.7 Hz), 6.98 (d, 1H, J = 3.7 Hz), 7.00 (d, 1H, J = 3.7 Hz), 7.03 (dd, 1H, J_1 = 4.9 Hz, J_2 = 1.2 Hz,), 7.07 (d, 1H, J = 3.7 Hz,), 7.17 (dd, 1H, J_1 = 3.7 Hz, J_2 = 1.2 Hz,), 7.22 (dd, 1H, J_1 = 4.9 Hz, J_2 = 1.2 Hz) ppm. ^{13}C NMR (δ in $CDCl_3$): 144.15, 137.29, 136.82, 135.42, 134.65, 127.81, 125.87, 124.22, 124.21, 123.45, 123.42, 123.24, 41.37, 34.11, 32.33, 28.85, 25.47, 22.98, 14.13, 10.82 ppm. MALDI-MS: *m/z* 361 (M^+, requires 360.61).

2-[5''-(2-ethylhexyl)-2,2':5',2''-terthien-5-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12). 1.50 g (4.2 mmol) of compound **11** in 60 mL of THF was added dropwise to 2.60 mL (4.2 mmol) the 1.6 M solution of BuLi in hexane at -78 °C. The cooling bath was removed and the temperature was allowed to rise to 0 °C. Then the reaction mixture was cooled to -78 °C again and 0.774 g (4.2 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added in one portion. The reaction mixture was stirred for 2 hours at -78°C, after which the cooling bath was removed, and stirring continued for 1 hour at 0 ºC and then for 1 hour at 20 ºC. The reaction mixture was worked up by adding 150 mL of ice water degassed by means of argon, mixed with 3.68 mL of 1 N HCl, and 250 mL of distilled diethyl ether. The organic phase was separated, washed several times with water until pH=7, dried over anhydrous Na_2SO_4, after which the solvent was removed by rotary evaporator. The procedure yielded 2.042 g (93%) of the compound of interest as a blue solid substance. Anal. Calcd. for $C_{26}H_{35}BO_2S_3$ (%): C, 64.18; H, 7.25; B, 2.22; S, 19.77. Found: C, 64.16; H, 7.30; B, 2.16; S, 20.01. ^{1}H NMR (δ in $CDCl_3$): 0.91 (t, 6H, J = 7.3 Hz), 1.31-1.40 (overlapping peaks with a maximum at 1.36 ppm, 20H), 1.60 (m, 1H, J= 6.1 Hz), 2.75 (d, 2H, J= 6.7 Hz), 6.68 (d, 1H, J = 3.7 Hz), 7.00 (2H, dd, J_1 = 1.8 Hz, J_2 = 3.7 Hz), 7.12 (d, 1H, J = 3.7 Hz), 7.23 (d, 1H, J = 3.7 Hz), 7.52 (1H, d, J = 3.7 Hz) ppm. ^{13}C NMR (δ in $CDCl_3$): 144.36, 143.97, 137.95, 137.51, 135.25, 134.55, 125.90, 124.94, 124.62, 124.23, 123.57, 123.43, 84.16, 41.38, 34.13, 32.34, 28.85, 25.51, 25.48, 24.74, 22.98, 14.12, 10.81 ppm. MALDI-MS: *m/z* 487 (M^+, requires 486.57).

***Tetrakis*[5''''-(2-ethylhexyl)-2,2':5',2'':5'',2''':5''',2''''-quinquethien-5-yl]silane (3).** The solution of 1.01 g (2.07 mmol) of compound **12** and 0.40 g (0.40 mmol) of compound **7** in 30 mL of toluene was added to 120 mg (0.10 mmol) of $Pd(PPh_3)_4$ contained in a reaction vessel. Then 1.6 mL of 2M degassed sodium carbonate solution was added. The reaction mixture was refluxed for 10 hours, after which according to the GPC results, it contained 59% of the target product. Dry toluene (50 mL) was added to the reaction mixture followed by azeotropic distillation to remove the water. The raw product was purified by column chromatography on silica gel (toluene being the eluent , T=85 °C) followed by recrystallization from toluene and preparative GPC chromatography to yield 0.388 g (46%) as an orange solid substabce. T_m = 180 °C, ΔH_m = 30.3 J/g. Anal. Calcd. for $C_{112}H_{108}S_{20}Si$ (%): C, 63.35; H, 5.13; S, 30.20; Si, 1.32. Found: C, 63.83; H, 5.32; S, 29.95; Si, 1.48. ^{1}H NMR (δ in $CDCl_3$): 0.89 (t, 24H, J = 6.7 Hz), 1.29 (m, 32H, J= 6.7 Hz), 1.60 (m, 4H, *J*= 6.1 Hz), 2.73 (d, 8H, *J*= 6.7 Hz), 6.66 (d, 4H, *J* = 3.7 Hz), 6,98 (8H, dd, J_1 = 2.4 Hz, J_2 = 3.7 Hz), 7.07-7.03 (overlapping peaks with a maximum at 7.05 ppm, 16H), 7.15 (d, 4H, *J* = 4.3 Hz), 7.31 (d, 4H, *J* = 3,7 Hz), 7.43 (d, 4H, *J* = 3.1 Hz) ppm. MALDI-MS: *m/z* 2123 (M^+, requires 2123.48).