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Synthesis and properties of a new luminescent oligoarylsilane dendrimer

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Experimental

[5'-(4-Bromophenyl)-2,2'-bithien-5-yl]bis(5'-hexyl-2,2'-thien-5-yl)methylsilane **2**. A solution of 0.88 ml (10 mmol) of dibromoethane in 15 ml of diethyl ether was added dropwise to 0.265 g (11 mmol) of magnesium and 3 ml of diethyl ether. Afterwards, the mixture was stirred under reflux for 2 h. In another flask, 6.0 g (8 mmol) of compound **1** was dissolved in 160 ml of THF, after which the reaction container was cooled down to –78 °C. Then, 3.4 ml (8 mmol) of a 2.5 M solution of BuLi in hexane was added dropwise at a temperature below –70 °C. After that, the temperature was increased to 0 °C and then the reaction mixture was cooled to –50 °C. Further, the previously prepared diethyl ether solution of the $MgBr_2 \cdot Et_2O$ complex was poured in from the first flask. The reaction mixture was stirred for 1.5 h, during which the temperature rose to approximately 20 °C. Then, the reaction mixture was added dropwise at 0 °C to 6.004 g (25 mmol) of 1,4-dibromobenzene and 0.12 g (0.17 mmol) of $Pd(dppf)Cl_2$ dissolved in 40 ml of THF. At the following step, the cooling was stopped and the contents of the flask were stirred for 20 h. When the reaction was complete, the mixture was poured into 300 ml of ice water and 500 ml of diethyl ether. The organic layer was separated, rinsed with distilled water and dried over anhydrous sodium sulfate, after which the organic solvent was boiled out in a rotary vacuum evaporator. After purification by column chromatography [silica gel; eluent, hexane–toluene (5:1)], 4.16 g of the pure product was obtained (57% on a theoretical basis). MALDI-MS, *m*/*z*: 861 (M^+, calc. 861). ^{1}H NMR ($CDCl_3$) δ: 0.88 (t, 6H, *J* 6.7 Hz), 0.93 (s, 3H), 1.31 (m, 12H), 1.66 (m, 4H), 2.77 (t, 4H, *J* 7.3 Hz), 6.66 (d, 2H, *J* 3.7 Hz), 7.02 (d, 2H, *J* 3.1 Hz), 7.15–7.21 (overlap, 4H), 7.26–7.32 (overlap, 4H), 7.46 (dd, 4H, *J* 13.4 Hz). ^{29}Si NMR ($CDCl_3$) δ: –25.41. ^{13}C NMR ($CDCl_3$) δ: –0.1, 14.17, 22.65, 28.81, 30.25, 31.61, 31.64, 76.67, 77.10, 77.52, 121.48, 124.09, 124.30, 124.46, 124.93, 125.25, 125.30, 127.09, 132.10, 132.92, 133.04, 134.36, 134.60, 136.86, 137.95, 142.19, 144.22, 145.32, 146.09. Found (%): C, 59.76; H, 5.30; S, 22.17; Si, 3.44; Br, 9.37. Calc. for $C_{43}H_{45}BrS_6Si$ (%): C, 59.90; H, 5.26; S, 22.31; Si, 3.26; Br, 9.27.

Bis(5'-hexyl-2,2'-bithien-5-yl)(methyl){5'-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-phenyl]-2,2'-bithien-5-yl}silane **3**. 1.57 ml of a 1.6 M solution of BuLi (2.5 mmol) in hexane was added dropwise to a solution of 2.16 g (2.5 mmol) of compound **2** in 75 ml of pure THF at –70 to –75 °C. The reaction mixture was stirred for 60 min at –75 °C, then 0.51 ml (2.5 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added. After stirring the mixture for 60 min at –78 °C, the cooling was stopped and the stirring continued for 3 h. After the completion of the reaction, 200 ml of diethyl ether and 100 ml of icy water containing 2.5 ml of 1 N HCl were added to the reaction mixture. The organic phase was separated, rinsed several times with water until pH 7, and dried over anhydrous Na_2SO_4, after which the solvent was removed. According to the results of GPC analysis, the mixture contained 77% of the product of interest. The purification was conducted by gradient chromatography using a 1:3 mixture of toluene–hexane (100 ml), 1:1 mixture of toluene–hexane (120 ml), then toluene (250 ml), and finally THF (150 ml) as the eluents. As a result, 1.57 g (70%) of the target product was recovered. ^{1}H NMR ($CDCl_3$) δ: 0.85–0.99 (overlap, 9H), 1.24–1.43 (overlap, 24H), 1.66 (m, 4H), 2.77 (t, 4H, *J* 7.3 Hz), 6.66 (d, 2H, *J* 3.1 Hz), 7.01 (d, 2H, *J* 3.7 Hz), 7.19 (d, 3H, *J* 3.1 Hz), 7.27–7.31 (overlap, 5H), 7.58 (d, 2H, *J* 7.9 Hz), 7.80 (d, 2H, *J* 7.9 Hz). ^{29}Si NMR ($CDCl_3$) δ: –25.42. ^{13}C NMR ($CDCl_3$) δ: –0.09, 14.14, 22.63, 24.83, 24.94, 28.80, 30.24, 31.60, 31.63, 76.66, 77.09, 77.51, 83.92, 124.08, 124.46, 124.76, 124.92, 125.16, 125.27, 133.01, 134.40, 134.42, 135.48, 136.56, 136.89, 137.93, 143.49, 144.46, 145.30, 146.06. Found (%): C, 64.79; H, 6.34; S, 21.08; Si, 3.23; B, 1.27. Calc. for $C_{49}H_{57}BO_2S_6Si$ (%): C, 64.73; H, 6.32; S, 21.16; Si, 3.09; B, 1.19.

(Methylsilanetriyl)tris[5'-(4-{5'-[bis(5'-hexyl-2,2'-bithien-5-yl)(methyl)silyl]-2,2'-bithien-5-yl}phenyl)-2,2'-bithiophene] **D3**. 72 mg (0.0627 mmol) of $Pd(PPh_3)_4$ was placed in a reaction flask under an inert atmosphere, then, degassed solutions of 1.122 g (0.125 mmol) of compound **3** and 270 mg (0.0627 mmol) of compound **4** in 25 ml of toluene, 1.8 ml of a 2 M solution of Na_2CO_3, and 1.8 ml of ethanol were added; the contents were heated to boiling. After 27 h of stirring under reflux, the reaction mixture was cooled down to room temperature and poured into 150 ml of water and 150 ml of toluene. The organic layer was rinsed with water until pH 7 and dried over anhydrous Na_2SO_4; the solvent was removed *in vacuo*. As a result, 1.5 g of the target product with 58.5% purity (GPC) was obtained. The purification by column chromatography (toluene as the eluent) and preparative GPC (THF as the eluent) yielded 465 mg (39%) of pure dendrimer **D3**, mp 128 °C. MALDI-MS, *m*/*z*: 2883 (M^+, calc. 2882.79). ^{29}Si NMR ($CDCl_3$) δ: –25.42; –25.27. ^{1}H NMR ($CDCl_3$) δ: 0.87 (t, 18H, *J* 6.1 Hz), 0.93 (s, 9H), 0.98 (s, 4H), 1.31 (m, 39H), 1.66 (m, 13H), 2.77 (t, 12H, *J* 7.3 Hz), 6.66 (d, 6H, *J* 3.7 Hz), 7.01 (d, 6H, *J* 3.1 Hz), 7.15–7.36 (overlap,

31H), 7.59 (s, 12H). ^{13}C NMR ($CDCl_3$) δ: –0.1, 13.99, 22.55, 28.74, 30.20, 31.52, 76.58, 77.42, 123.96, 124.08, 124.84, 126.04, 133.16, 134.44, 134.53, 137.85, 138.01, 143.10, 143.23, 144.67, 145.33, 146.04. Found (%): C, 65.45; H, 5.39; S, 25.95; Si, 4.15. Calc. for $C_{154}H_{150}S_{24}Si_4$ (%): C, 64.16; H, 5.24; S, 26.69; Si, 3.90.