

Synthesis of silene spaced divinyl naphthalene copolymers

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Dedicated to Prof. T. R. Govindachari on the occasion of his 85th birthday
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Abstract

A convenient procedure for the preparation of 2,6-bis[(2-dimethylsilyl)vinyl]naphthalene **1** and 2,6-(bis-ethynyl)naphthalene **2** are reported. Reactions of **1** and **2** in the presence of RhCl(PPh₃)₃ give the corresponding copolymer **3** at different Mn depending on the reaction conditions.

Keywords: Silylene spaced copolymers, divinyl naphthalene copolymers

Introduction

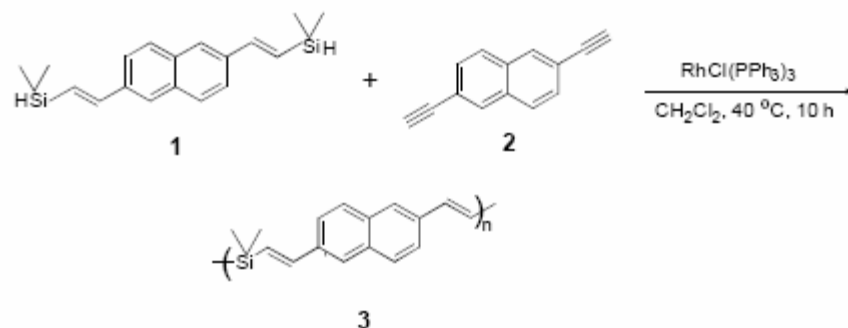
Conjugated polymers are known to exhibit diverse optoelectronic properties.¹⁻³ A polyphenylene-vinylene based device has been shown to serve as a light emitting diode.⁴ Introduction of spacers between well-defined chromophores in the polymeric backbone can occasionally increase the processibility and in the mean time, the emission wavelength can be predicted.^{5,6} Silylene moiety appears to be an attractive spacer for this purpose.⁶

As part of our continuing interest on the structure activity investigation on the photophysics of silylene-spaced divinylarene copolymers,⁷⁻¹¹ we report here the synthesis of the precursors **1** and **2** and the corresponding silylene-spaced divinyl naphthalene copolymers **3**.

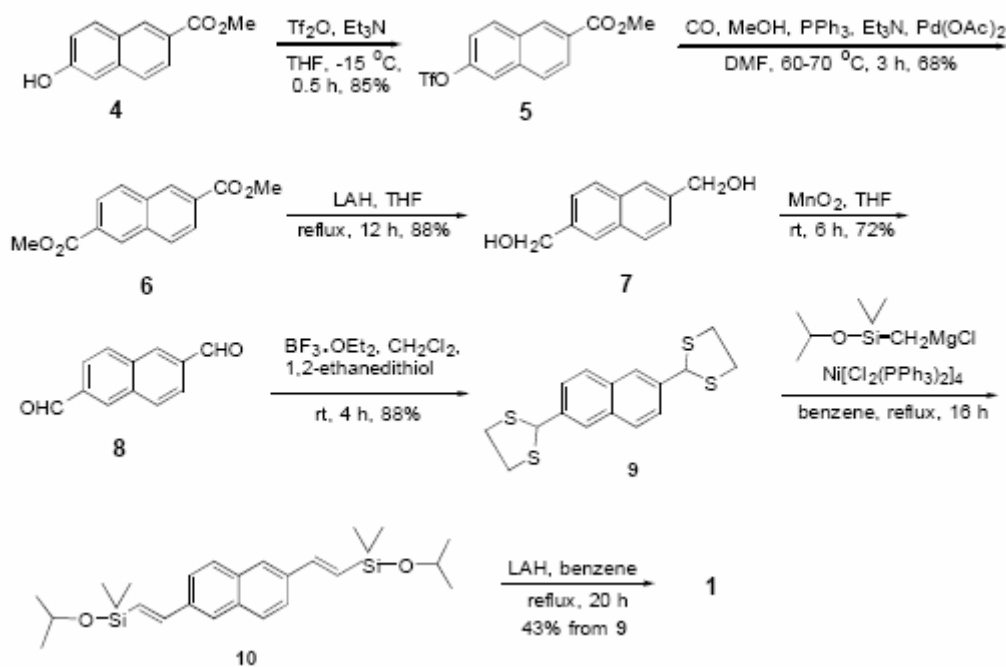
Results and Discussion

The methyl ester of 6-hydroxy-2-naphthoic acid **4** was converted into triflate **5** upon treatment with triethylamine and triflic anhydride in THF.¹² Palladium catalyzed carbonylation in methanol¹³ afforded **6** in 68% yield. The aldehyde **8** was prepared by refluxing a THF solution of **6** with an excess LAH to furnish the alcohol **7**, which after treatment with manganese dioxide yielded 72% of the corresponding 2,6-diformylnaphthalene **8**. Reaction of **8** with 1,2-ethanedithiol in the presence of boron trifluoride diethyl etherate gave the naphthalene-2,6-bis-dithioacetal **9** with a yield of 88%. The vinyl dimethylsilane **10** was synthesized from the bis-

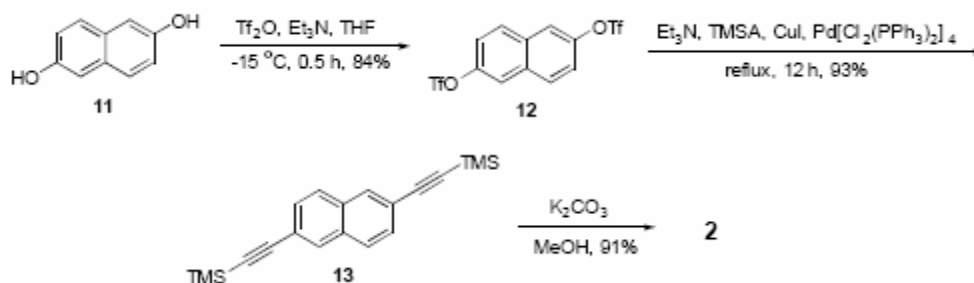
dithioacetal **9** and $\text{Me}_2(\text{PrO})\text{CH}_2\text{MgCl}$ in the presence of 5 mol% $\text{NiCl}_2(\text{PPh}_3)_2$.¹⁴ The crude product of **10** was directly used for the next step. Reduction of the Si-O bond was achieved by treatment of **10** with an excess of LAH to yield 43% (from **9**) of the monomer **1** (Scheme 1).



2,6-Dialkynynaphthalene **2**, was conveniently synthesized in three steps from naphthalene-2,6-diol (**11**) (Scheme 2). A THF solution of compound **11** was treated with triflic anhydride in the presence of triethylamine to yield the corresponding ditriflate **12**. Sonogashira reaction¹⁵ of **12** led to the 2,6-bis[(trimethylsilyl)ethynyl] naphthalene (**13**) with a yield of 93%, which after treatment with potassium carbonate gave 91% of 2,6-(bis-ethynyl)naphthalene (**2**).



Scheme 1



Scheme 2

The reaction of 2,6-bis[2-(dimethylsilyl)vinyl]naphthalene **1** and the 2,6-diethynynaphthalene (**2**) in the presence of a catalytic amount of $\text{RhCl}(\text{PPh}_3)_3$ led to the copolymer **3** ($M_n = 2600$; PDI 2.5) with a yield of 61%. An increase of the concentration of the catalyst gave the copolymer **3** in 53% yield ($M_n = 4500$; PDI 3.3).

Experimental Section

Methyl 6-hydroxy-2-naphthoate (4). Concentrated sulfuric acid (2 mL) was added to a methanolic solution of 6-hydroxy-2-naphthoic acid (50.0 g, 266 mmol). The solution was refluxed for 12 h. Then the solution was cooled to rt and the crude **4** was precipitated from the solution. After filtration the crude product was added to a 5% NaHCO_3 solution and stirred for 0.5 h. The solid was filtered, washed several times with water and dried in vacuum to give **4** (47.0 g, 88%); mp 157–158 °C (EtOAc-hexane); (Lit.¹⁶ mp 158–159 °C).

6-Methoxycarbonyl-2-naphthyl triflate (5). Triflic anhydride (12.5 mL, 74.3 mmol) was added to a cooled solution (–15 °C) of **4** (10.0 g, 49.5 mmol) and Et_3N (20.5 mL, 148 mmol) in THF (100 mL). After stirring for 0.5 h at the same temperature, water was added and the mixture was extracted with Et_2O . The organic phase was separated, washed with an ice-cold 1% aqueous NaOH solution, water and brine and evaporated to yield **5** (14.0 g, 85%) as a white solid; mp 70–71 °C (CHCl_3 -hexane). IR (KBr): ν 3010, 2920, 1719, 1442, 1429, 1298, 1252, 1208, 1150, 962, 924, 874, 817, 610 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 3.97 (s, 3 H), 7.41 (dd, $J = 9.2, 2.2$ Hz, 1 H), 7.76 (d, $J = 2.2$ Hz, 1 H), 7.89 (d, $J = 8.8$ Hz, 1 H), 8.01 (d, $J = 9.2$ Hz, 1 H), 8.13 (dd, $J = 8.8, 1.4$ Hz, 1 H), 8.61 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 52.4, 118.7 ($J_{\text{C-F}} = 319$ Hz), 119.2, 120.5, 126.9, 128.3, 128.8, 130.8, 131.4, 132.1, 135.5, 148.6, 166.6; MS m/z (%) 334 (66) [M^+], 201 (76), 173 (100), 142 (36), 114 (33); HRMS Calcd for $\text{C}_{13}\text{H}_9\text{F}_3\text{O}_5\text{S}$: 334.0123; Found: 334.0125; Anal. Calcd for $\text{C}_{13}\text{H}_9\text{F}_3\text{O}_5\text{S}$: C, 46.71; H, 2.71. Found: C, 46.83; H, 2.50.

Dimethylnaphthalene-2,6-dicarboxylate (6). A mixture of **5** (11.0 g, 32.9 mmol), Et_3N (9.1 mL, 65.8 mmol), $\text{Pd}(\text{OAc})_2$ (0.74 g, 3.28 mmol), PPh_3 (0.55 g, 2.09 mmol) and MeOH (26 mL, 650 mmol) in DMF (100 mL) was purged with CO for 5 min and stirred under a CO atmosphere (1 atm) for 3 h at 60 °C. Then the reaction mixture was cooled to rt, treated with brine and

extracted with Et₂O. The organic layer was washed with water, ice-cold 1N HCl and brine, dried with Na₂SO₄ and evaporated to dryness to yield **6** (5.5 g, 68%) as a colorless solid. mp 185–186 °C (MeOH); (Lit.¹⁷ mp 186–187 °C).

2,6-Bis-hydroxymethylnaphthalene (7). A mixture of **6** (4.4 g, 18.0 mmol) and LAH (3.0 g, 78.9 mmol) in THF (100 mL) was refluxed for 12 h. The reaction mixture was cooled to rt and the excess LAH was quenched by a slow addition of water. The precipitate was filtered and the filtrate was extracted with Et₂O. The organic layer was washed with water and brine and dried with Na₂SO₄. After evaporation, the crude product was crystallized from EtOH to yield **7** (3.0 g, 88%) as colorless crystals; mp 168–169 °C; (Lit.¹⁸ mp 169–170 °C).

2,6-Diformylnaphthalene (8). A THF (75 mL) solution of **7** (3.0 g, 16.0 mmol) was treated with MnO₂ (8.30 g, 95.43 mmol) at rt for 6 h. Then the reaction mixture was filtered through a celite pad. After evaporation, the crude product was crystallized from CHCl₃-MeOH to yield **8** (2.1 g, 72%) as colorless crystals; mp 173–175 °C; (Lit.¹⁹ mp 174–176 °C).

2,6-Bis(1,3-dithiolan-2-yl)naphthalene (9). Into a stirred solution of **8** (2.0 g, 10.87 mmol) and boron trifluoride diethyl etherate (0.5 mL, 3.87 mmol) in CH₂Cl₂ (30 mL) was added 1,2-ethanedithiol (2.1 mL, 24.5 mmol) and stirring was continued at rt for 4 h. Then the reaction mixture was poured into an aqueous 10% NaOH solution. The organic phase was separated and the aqueous layer was extracted with CH₂Cl₂. The combined organic layers were washed with a 10% NaOH solution (4 × 30 mL) and brine, dried with Na₂SO₄ and evaporated to yield **9** (3.2 g, 88%) as a colorless solid; mp 150–152 °C (CHCl₃-hexane); IR (KBr): ν 2922, 1719, 1507, 1432, 1425, 1350, 1278, 1244, 1211, 1144, 899, 821, 756, 484 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 3.36–3.42 (m, 4 H), 3.49–3.55 (m, 4 H), 5.78 (s, 1 H), 7.65 (d, *J* = 8.4 Hz, 2 H), 7.75 (d, *J* = 8.4 Hz, 2 H), 7.83 (s, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ 40.4, 56.4, 126.3, 126.4, 128.5, 132.6, 138.1; MS *m/z* (%) 334 (100) [M⁺], 308 (28), 304 (24), 275 (22), 247 (36), 216 (32), 203 (46), 185 (26), 171 (34), 84 (18); HRMS Calcd for C₁₆H₁₆S₄: 336.0135; Found: 336.0134; Calcd for C₁₆H₁₆S₄: C, 57.10; H, 4.79. Found: C, 57.03; H, 4.80.

2,6-Bis{2-[dimethyl(isopropoxy)silyl]vinyl}naphthalene (10). A catalytic amount of 1,2-dibromoethane was added to flame dried magnesium (2.0 g, 83.3 mmol) in THF (5 mL). To this mixture, a solution of Me₂(^{*i*}PrO)SiCH₂Cl (15.1 mL, 83.3 mmol) in THF (15 mL) was added dropwise and stirred until all magnesium had been reacted. Then the THF was evacuated as much as possible to give Me₂(^{*i*}PrO)SiCH₂MgCl which was dissolved in benzene (50 mL) and transferred through a canula into a solution of **9** (2.8 g, 8.33 mmol) and NiCl₂(PPh₃)₂ (0.27 g, 0.41 mmol) in benzene (100 mL). The mixture was refluxed for 20 h, cooled to rt and an aqueous Na₂CO₃ solution was added. The organic layer was separated and the aqueous layer was extracted twice with Et₂O (50 mL). The combined organic layers were washed with an aqueous solution of 10% NaOH (2 × 30 mL) and brine and dried with Na₂SO₄. After evaporation the residue was distilled under reduced pressure to give **10** (7.0 g) as a viscous liquid, which was directly used for the next step without further purification.

2,6-Bis[(2-dimethylsilyl)vinyl]naphthalene (1) A benzene (100 mL) solution of crude **10** (7.0 g, 17.0 mmol) and LAH (2.6 g, 68.4 mmol) was heated for 20 h at refluxing temperature. Then

the reaction mixture was cooled with an ice-bath and the excess LAH was quenched by a slow addition of water. The precipitate was filtered; the organic layer was washed with brine and dried with MgSO_4 . After evaporation the residue was purified by column chromatography (silica gel, hexane) to yield **1** as colorless needles (1.1 g, 43% two steps) mp 102–104 °C (hexane); IR (KBr): ν 3070, 2962, 2929, 2118, 1696, 1250, 1050, 988, 893, 830, 814 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 0.25 (d, $J = 3.7$ Hz, 12 H), 4.22–4.24 (m, 2 H), 6.56 (dd, $J = 19.1, 2.3$ Hz, 2 H), 7.1 (d, $J = 19.1$ Hz, 2 H), 7.63 (dd, $J = 8.2, 1.1$ Hz, 2 H), 7.73 (s, 2 H), 7.76 (d, $J = 8.2$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3): δ -4.0, 123.9, 126.5, 126.9, 128.5, 133.6, 136.0, 145.4; MS m/z (%) 296 (34) [M^+], 237 (62), 221 (38), 211 (100), 147 (20), 131 (20), 73 (8); HRMS Calcd for $\text{C}_{18}\text{H}_{24}\text{Si}_2$: 296.1417; Found: 296.1426; Calcd for $\text{C}_{18}\text{H}_{24}\text{Si}_2$: C, 72.90; H, 8.16. Found: C, 72.64; H, 8.32.

Naphthalene-2,6-diyl-bis(trifluoromethane sulfonate) (12). Into a cooled (–15 °C) solution of **11** (5.0 g, 31.3 mmol) and Et_3N (26.0 mL, 188 mmol) in THF (50 mL) was added triflic anhydride (16.5 mL, 97.7 mmol) and the solution was stirred for 0.5 h at the same temperature. Then the reaction mixture was diluted with H_2O and extracted with Et_2O . The organic phase was washed with an ice cold aqueous 1% NaOH solution and brine and dried with Na_2SO_4 . After evaporation, the crude product was crystallized from CHCl_3 -MeOH to yield **12** (11.1 g, 83%) as a pale brown solid; mp 84–85 °C.

2,6-Bis[(trimethylsilyl)ethynyl]naphthalene (13). To a solution of **12** (10.7 g, 25.2 mmol), CuI (0.238 g, 1.25 mmol) and $\text{PdCl}_2(\text{PPh}_3)_2$ (0.877 g, 1.25 mmol) in Et_3N (75 mL) was added (trimethylsilyl)acetylene (7.8 mL, 55.7 mmol). The reaction mixture was heated under reflux to give for 12 h and then cooled to rt. The mixture was filtered and the filtrate was evaporated to dryness to give the crude product which was crystallized from CHCl_3 -hexane to yield **13** (7.5 g, 93%) as a pale brown solid. mp 120–121 °C; IR (KBr): ν 2962, 2869, 2156, 1498, 1260, 1250, 940, 899, 847, 759 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 0.27 (s, 18 H), 7.48 (dd, $J = 8.4, 1.2$ Hz, 2 H), 7.67 (d, $J = 8.4$ Hz, 2 H), 7.92 (s, 2 H); ^{13}C NMR (100 MHz, CDCl_3): δ -0.1, 95.4, 105.1, 121.3, 127.7, 129.2, 131.7, 132.3; MS m/z (%) 320 (92) [M^+], 305 (100), 145 (30); HRMS Calcd for $\text{C}_{20}\text{H}_{24}\text{Si}_2$: 320.1417; Found: 320.1407.

2,6-(Bis-ethynyl)naphthalene (2). To a stirred suspension of **13** (8.0 g, 25.0 mmol) in MeOH (50 mL) was added K_2CO_3 (0.62 g, 4.50 mmol) and stirring was continued for 6 h at rt. Then the reaction mixture was filtered, and the filtrate was evaporated to yield the crude product which was crystallized from CHCl_3 -hexane to yield **2** (4.0 g, 91%) as a pale brown solid; m.p. 138–139 °C (hexane); IR (KBr): ν 3272, 2990, 2920, 2106, 1596, 1363, 1272, 1253, 886, 820, 705, 676, 627 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 3.17 (s, 2 H), 7.52 (dd, $J = 8.4, 1.2$ Hz, 2 H), 7.71 (d, $J = 8.4$ Hz, 2 H), 7.96 (s, 2 H); ^{13}C NMR (100 MHz, CDCl_3): δ 78.2, 83.7, 120.4, 127.8, 129.3, 132.0, 132.4; MS m/z (%) 176 (100) [M^+], 150 (20), 75 (8); HRMS Calcd for C_{14}H_8 : 176.0626; Found: 176.0623.

Poly(2,6-divinylnaphthyl)dimethylsilylene (3). A mixture of **1** (296 mg, 1.0 mmol), **2** (176 mg, 1.0 mmol) and $\text{RhCl}(\text{PPh}_3)_3$ (4.6 mg, 0.005 mmol) in CH_2Cl_2 (5 mL) was heated under reflux for 10 h. After cooling to rt MeOH was added to precipitate the crude polymer, which was dissolved

in CHCl_3 , and re-precipitated upon treatment with MeOH. After filtration the solid was washed twice with MeOH and dried to yield **3** (230 mg, 61%) as a yellow solid; $M_n = 2600$ (PDI: 2.5) ^1H NMR (400 MHz, CDCl_3): δ 0.36 (bs, 6 H), 6.65 (bd, $J \sim 19.0$ Hz, 2 H), 7.11 (bd, $J \sim 19.0$ Hz, 2 H) 7.66–7.75 (m, 6 H).

The other copolymer of $M_n = 4500$ (PDI: 3.3) was prepared as described above, by treatment of **1** (296 mg, 1.0 mmol), **2** (176 mg, 1.0 mmol) and $\text{RhCl}(\text{PPh}_3)_3$ (9.2 mg, 0.01 mmol) in CH_2Cl_2 (5 mL). After work up it was yielded (250 mg, 53%) as a yellow solid.

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