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Effect of Conjugation Length on Intrachain Chromophore–Chromophore Interaction in Silylene-Spaced Divinyloligoarene Copolymers

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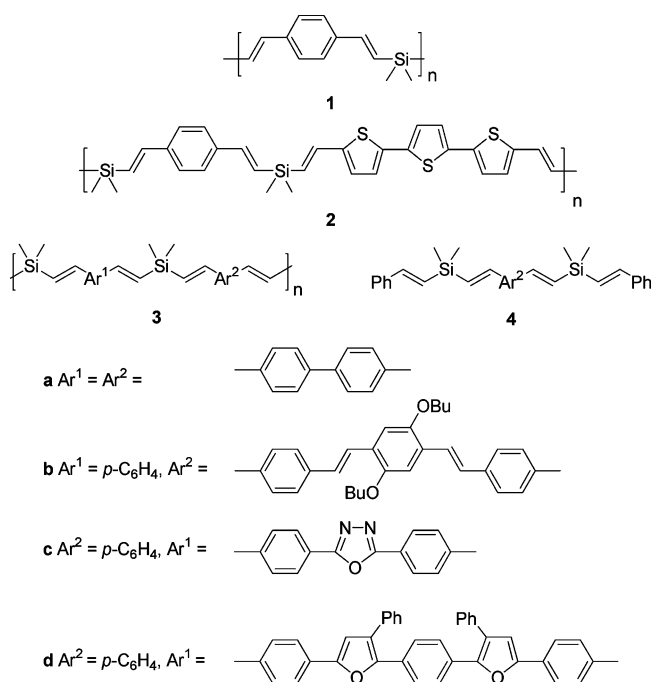
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ABSTRACT: A range of silylene-spaced divinyloligoarene alternating copolymer **3** has been synthesized regioregularly by rhodium-catalyzed hydrosilylation of bis(alkynes) **5** with bis(silanes) **6**. Monomeric reference compounds **4** having similar chromophore components were also prepared for comparison. The silylene moieties serve as insulating spacers between chromophores. Intrachain interaction appears to be negligible due to the localization of exciton in these conjugated chromophores, resulting in the emission that closely resembles that of the parent chromophore.

Introduction

Well designed interruption of π -conjugation along the polymer backbone by insulating spacers allows tuning of the photophysical properties of the polymers and furnishes processable materials.^{1–5} There has been an increasing study of using silylene moiety as the spacer.^{2–5} In general, when the silylene spacer contains only one silicon atom, no conjugative interactions between the π systems and the silicon moiety is observed. We recently reported a series of silylene-spaced divinylarene copolymers that exhibit versatile photophysical properties such as intrachain energy transfer,⁶ through space chromophore–chromophore interactions,⁷ and the transmission of chiroptical properties.⁸ Theoretical^{9–11} and experimental¹² studies on inter- or intrachain interactions between chromophores have been extensive. Model compounds such as paracyclophanes and polystyrene derivatives provide useful insight for understanding interchromophore delocalization through space.¹² The extent of such through-space interactions in the excited state has been suggested to be dependent on the conjugation length of chromophores. The shorter the conjugation length, the more is prone to delocalization over interacting chromophores leading to excimer formation. On the contrary, as the conjugation length increases, the interactions between chromophores may be significantly reduced because the geometry relaxation in the excited state of longer conjugated moieties may stabilize the localization of exciton in a single chromophore. Indeed, the aforementioned silylene-spaced divinylbenzene copolymers **1** have been shown to exhibit molecular-weight dependent aggregate emission profiles which suggest that significant intrachain chromophore–chromophore interactions may occur.^{7,13} In our preliminary communication, we found that the emission spectrum of copolymer **2** is very similar to that of the corresponding monomer.⁷ The divinylterthiophene moiety has longer conjugation length than divinylbenzene chromophore so that exciton may be able to localize in this chromophore. In this paper, we report a systematic

investigation on the effect of conjugation length of chromophore in a series of silylene-spaced regioregular divinyloligoarene copolymers **3**.



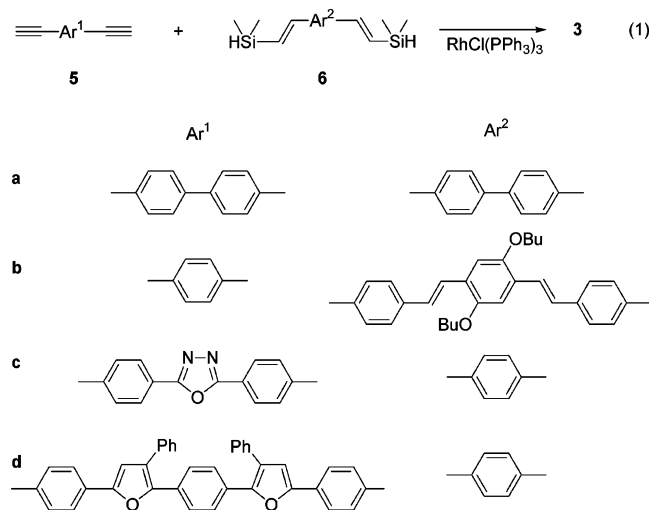
Results and Discussion

Synthesis. The divinyloligoarene chromophores of different conjugation lengths and structural variety were incorporated into the corresponding copolymers **3a–d**. Copolymers **3a–d** were synthesized by the hydrosilylation of bis(alkynes) **5** with the corresponding bis(silane) **6** in a manner similar to those described previously (eq 1).⁵ The corresponding monomeric model compounds **4a–d** were prepared similarly by either hydrosilylation of bis(silanes) **6** with phenylacetylene (**7**) or bis(alkynes) **5** with 2-(phenyl)vinyltrimethylsilane (**8**) (eqs 2 and 3).⁷ The preparation of furan-containing pentaaryls **4d** was based on the one-pot furan synthesis recently developed in our laboratory.¹⁴ Thus, treatment of propargylic dithioacetal **9** with *n*-BuLi followed by terephthalaldehyde to give the intermediate

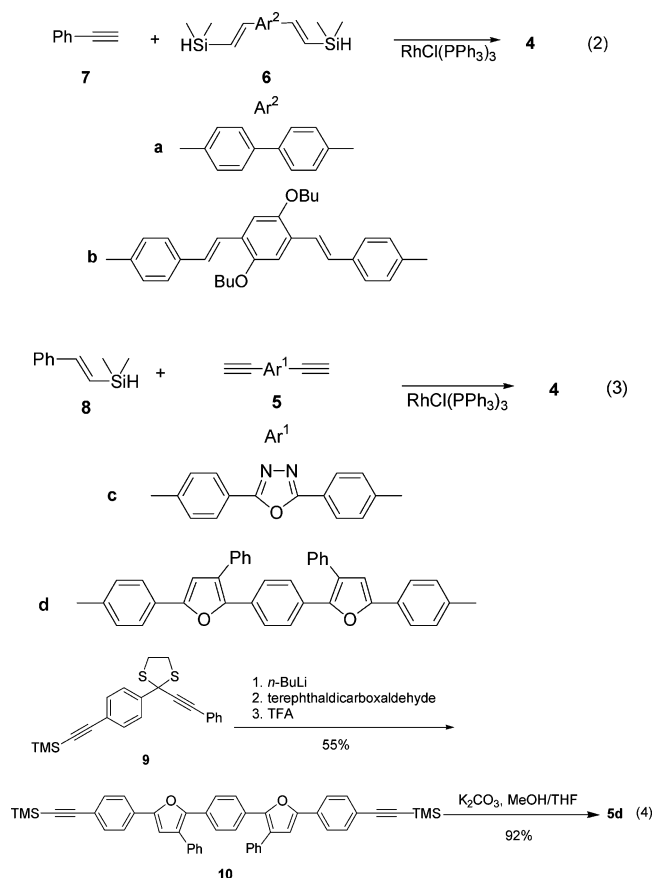
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which underwent cyclization under acidic condition to yield furan-containing pentaaryl **10** in 55% yield. Deprotection of the TMS group in **10** afforded **5d** in 92% yield (eq 4). The details are summarized in the Experimental Section.



Photophysical Properties

The absorption, emission and excitation spectra of copolymers **3a–d** are shown in Figures 1–4, and those of the corresponding monomeric compounds **4a–d** are compared in the respective figures. The λ_{max} of the chromophores were chosen as the corresponding excitation wavelengths in emission spectra for each of these copolymers. It is noteworthy that the aromatic moieties in polymers **3b–d** have relatively long conjugation length in comparison with that in **1**. Figures

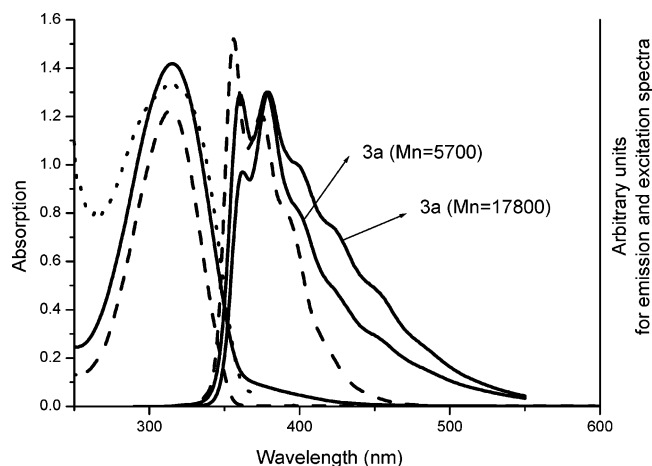


Figure 1. Absorption spectra of **3a** (solid line) and **4a** (dashed line), excitation spectrum of **3a** (dotted line, $\lambda_{\text{em}} = 370$ nm) in CHCl_3 , and emission spectra of **3a** ($M_n = 5700$ and 17800, solid line) and **4a** (dashed line, $\lambda_{\text{ex}} = 310$ nm) in CHCl_3 .

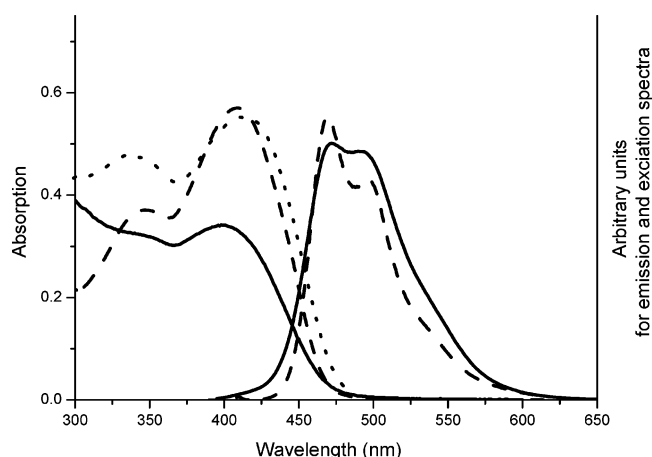


Figure 2. Absorption spectra of **3b** (solid line) and **4b** (dashed line) and excitation spectrum of **3b** (dotted line, $\lambda_{\text{em}} = 490$ nm) in CHCl_3 and emission spectra of **3b** (solid line) and **4b** (dashed line, $\lambda_{\text{ex}} = 410$ nm) in CHCl_3 .

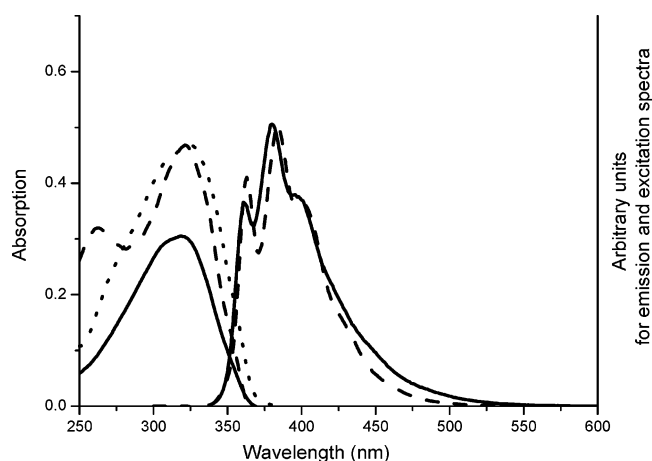


Figure 3. Absorption spectra of **3c** (solid line) and **4c** (dashed line) and excitation spectrum of **3c** (dotted line, $\lambda_{\text{em}} = 390$ nm) in CHCl_3 and emission spectra of **3c** (solid line) and **4c** (dashed line, $\lambda_{\text{ex}} = 324$ nm) in CHCl_3 .

2–4 show the spectroscopic properties of three representative examples, polymer **3b** having terphenylene-tetravinylene chromophore, polymer **3c** containing divinylphenylloxazole chromophore, and polymer **3d** containing divinylpentaaryl chromophore. The excita-

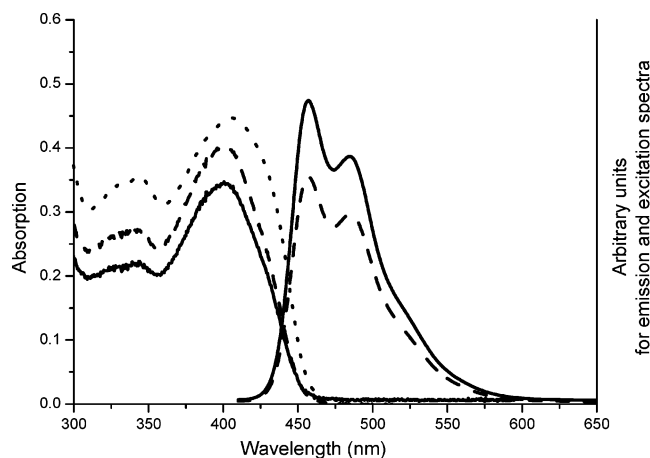


Figure 4. Absorption spectra of **3d** (solid line) and **4d** (dashed line) and excitation spectrum of **3d** (dotted line, $\lambda_{\text{em}} = 485$ nm) in CHCl_3 and emission spectrum of **3d** (solid line) and **4d** (dashed line, $\lambda_{\text{ex}} = 400$ nm) in CHCl_3 .

tion and absorption spectra of polymers **3b–d** are very similar to those of corresponding monomers **4b–d**, respectively. In addition, the emission profiles for polymers **3b–d** are essentially the same as those for the corresponding monomers **4b–d** having the same divinyloligoarene chromophores. The silicon moiety in these polymers may serve as an insulating spacer.

These results suggested that the photophysical properties of **3b–d** are very different from those of **1** or related silylene-spaced mononuclear divinylarene copolymers.^{7a} It is thus believed that intrachain through-space interaction between chromophores in these polymers due to folding of the polymeric chain may not take place leading to the excimer formation.

As shown in Figure 1, besides the absorption at the corresponding λ_{max} , there was a tailing absorption extended to the longer wavelength for copolymers **3a** having divinylbiphenyl chromophores. Similar to those of divinylbenzene copolymers **1**,⁷ the emission at longer wavelengths may arise from the through-space intrachain interaction between chromophores owing to the folding aggregate.¹³ The relative intensity for the longer wavelength emission in **3a**, however, is slightly affected by increasing the degree of polymerization. Vibronic fine splittings were vaguely found in these fluorescence spectra. The intrachain π – π interaction between divinylbiphenyl moieties in **3a** might, therefore, be less favorable than those of divinylbenzene analogues **1** because of its longer conjugation length. These results are consistent with the models on the interactions of conjugated systems.¹²

Conclusions

In summary, we have systematically investigated the influence of conjugation length of chromophores on the photophysical behavior of silylene-spaced divinylarene copolymers **3**. When the chromophores in silylene-spaced copolymer are mononuclear divinylarenes, through-space delocalized interchromophoric contact prevails, leading to emission at longer wavelengths due to intrachain aggregation.^{7a} When the conjugation length of chromophore increases, the intrachain interaction appears to be negligible due to the localization of exciton in these longer conjugated chromophores, resulting in the emission that closely resembles that of the parent chromophore. Our results suggest that the

silylene moieties simply serve as insulating spacer, no conjugation with the π -system being observed.^{3f}

Experimental Section

Compounds **4c**,^{6a} **5c**,^{6a} **6b**,⁸ **6c**,^{7a} and **8^{7a}** were prepared according to literature procedures. The absorption spectra were recorded on a Hitachi U-3310 spectrometer. The photoluminescence and excitation spectra were recorded on a Hitachi F-4500 fluorescence spectrometer. Gel permeation chromatography (GPC) was performed on a Waters GPC machine using an isocratic HPLC pump (1515) and a refractive index detector (2414). THF was used as the eluent (flow rate = 1 mLmin^{−1}). Waters Styragel HR2, HR3 and HR3 and HR4 (7.8 × 300 mm) were employed for molecular weight determination. Polystyrene were used as standard (M_n values range from 375 to 3.5×10^6).

Bis(2-dimethylsilyl)vinylbiphenyl (6a). A THF solution of $\text{Me}_2(\text{PrO})\text{SiCH}_2\text{MgCl}$ (10 equiv) was evacuated as much as possible and benzene (30 mL) was introduced. Under N_2 , to this mixture was introduced a solution of 4,4'-bis(1,3-dithiolan-2-yl)biphenyl (1.45 g, 4.0 mmol) and $\text{NiCl}_2(\text{PPh}_3)_2$ (0.28 g, 0.4 mmol) in benzene (50 mL). The mixture was refluxed under N_2 for 16 h and then poured into saturated NH_4Cl . The organic layer was separated and the aqueous layer was extracted twice (2×20 mL) with ether. The combined organic portions were washed twice with 10% NaOH (2×20 mL) and brine (20 mL) and dried (MgSO_4). The solvent was removed in vacuo and the residue was triturated with MeOH to give the solid residue which was mixed with LiAlH_4 (304 mg, 8.0 mmol) in benzene (50 mL). The mixture was refluxed under N_2 for 18 h and then cooled to room temperature, quenched with water, and filtered. The organic layer was separated, dried (MgSO_4) and the solvent was removed in vacuo to give the residue which was chromatographed on silica gel (hexane) to afford **6a** (0.75 g, 58%); mp 151–153 °C (pentane). ^1H NMR (200 MHz, CDCl_3): δ = 0.24 (d, J = 3.6 Hz, 12 H), 4.2 (m, 2 H) 6.47 (dd, J_1 = 19.2 Hz, J_2 = 2.5 Hz, 2 H), 6.98 (d, J = 19.2 Hz, 2 H), 7.48 (d, J = 8.0 Hz, 4 H), 7.56 (d, J = 8.0 Hz, 4 H). ^{13}C NMR (50 MHz, CDCl_3): δ = −4.0, 126.3, 126.9, 127.0, 137.3, 140.3, 140.8. IR (KBr): ν = 2966, 2906, 2117, 1660, 1501, 1400, 1249, 1202, 1123, 990, 888, 794, 744, 639. MS: m/z (70 ev) 322. Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{Si}_2$: C, 74.46; H, 8.12. Found: C, 74.24; H, 8.27.

4,4'-Bis[2-(dimethylstyrylsilyl)vinyl]biphenyl (4a). A mixture of **6a** (0.16 g, 0.5 mmol), phenylacetylene **7** (0.102 g, 1 mmol), and $\text{RhCl}_3(\text{PPh}_3)_3$ (2.3 mg, 0.5 mol %) in THF (5 mL) was refluxed for 8 h. Removal of the solvent in vacuo and chromatographic purification on silica gel (pentane) afforded **4a** (0.16 g, 61%); mp 185–187 °C (pentane). ^1H NMR (200 MHz, CDCl_3): δ = 0.35 (s, 12 H), 6.53 (d, J = 19 Hz, 2 H), 6.55 (d, J = 19 Hz, 2 H), 6.95 (d, J = 19 Hz, 2 H), 6.97 (d, J = 19 Hz, 2 H), 7.23–7.60 (m, 18 H). ^{13}C NMR (75 MHz, CDCl_3): δ = −2.5, 126.5, 126.9, 127.0, 127.4, 127.6, 128.1, 128.5, 137.4, 138.3, 140.3, 144.3, 145.0. IR (KBr): ν = 3030, 2989, 2985, 2899, 1912, 1604, 1574, 1448, 1401, 1335, 1250, 1198, 989, 837, 793, 733. MS m/z 526. Anal. Calcd for $\text{C}_{36}\text{H}_{38}\text{Si}_2$: C, 82.07; H, 7.27. Found: C, 82.35; H, 7.40.

2,5-Bis[2,4-(2-dimethyl(2-styryl)silylvinyl)phenylvinyl]-1,4-dibutoxybenzene (4b). Under N_2 , a mixture of phenylacetylene (**7**) (0.102 g, 1.0 mmol), **6b** (0.30 g, 0.5 mmol), and $\text{RhCl}(\text{PPh}_3)_3$ (2.3 mg, 0.5 mol %) in THF (5 mL) was refluxed for 4 h. Removal of the solvent and chromatographic separation on silica gel (hexane) afforded **4b** (0.34 g, 85%); mp 167–168 °C. ^1H NMR (300 MHz, CDCl_3): δ = 0.31 (s, 12 H), 1.01 (t, J = 7.4 Hz, 6 H), 1.53–1.61 (m, 4 H), 1.80–1.90 (m, 4 H), 4.05 (t, J = 6.3 Hz, 4 H), 6.52 (d, J = 19.1 Hz, 4 H), 6.94 (d, J = 19.1 Hz, 4 H), 7.00–7.60 (m, 24 H). ^{13}C NMR (75 MHz, CDCl_3): δ = −2.5, 13.9, 19.5, 31.6, 69.2, 110.5, 114.2, 123.5, 126.5, 126.7, 126.8, 127.1, 127.4, 128.1, 128.4, 128.5, 137.4, 137.8, 138.3, 144.5, 144.9, 151.1. HRMS: calcd for $\text{C}_{54}\text{H}_{62}\text{Si}_2\text{O}_2$, 798.4288; found, 798.4285. Anal. Calcd for $\text{C}_{54}\text{H}_{62}\text{Si}_2\text{O}_2$: C, 81.15; H, 7.82. Found: C, 80.96; H, 7.87.

1,4-Bis[1,3-phenyl-5-(4-trimethylsilylphenyl)-furyl]-2-yl]benzene (10). Under argon atmosphere, a 2.5 M

n-BuLi in hexane solution (4.1 mL, 10.2 mmol) was introduced dropwisely to a THF (20 mL) solution of propargylic dithioacetal **9** (3.22 g, 8.5 mmol) at -78°C , and the mixture was stirred for 50 min. To this mixture was added slowly a THF (10 mL) solution of terephthalaldicarboxaldehyde (0.52 g, 3.9 mmol) at -78°C . The reaction mixture was stirred for 1 h at -78°C , and gradually warmed to room temperature. After further stirring for 1 h at room temperature, TFA (1.59 mL, 14.8 mmol) was added and the mixture was stirred at room temperature overnight. The reaction mixture was quenched with saturated NH_4Cl (30 mL), and the organic layer was separated. The aqueous layer was extracted with Et_2O (40 mL \times 2). The combined organic layer was washed with saturated NaHCO_3 (40 mL \times 2), dried (MgSO_4), filtered, and evaporated in vacuo. The resulting residue was purified by flash column chromatography (silica gel, CH_2Cl_2 /hexane 1:4) to afford the desired **10** as a pale yellow solid (1.52 g, 55%): mp $184\text{--}185^{\circ}\text{C}$. ^1H NMR (500 MHz, CDCl_3): δ = 0.27 (s, 18 H), 6.83 (s, 2 H), 7.3–7.5 (m, 10 H), 7.53 (d, J = 8.3 Hz, 4 H), 7.54 (s, 4 H), 7.68 (d, J = 8.3 Hz, 4 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 0.0, 95.3, 105.1, 110.8, 122.0, 123.4, 125.3, 125.9, 127.5, 128.8, 129.8, 130.2, 132.4, 134.0, 148.0, 151.9. IR (KBr): ν = 2966, 2157, 1673, 1606, 1493, 1251, 929, 865, 842, 764, 698. HRMS: calcd for $\text{C}_{48}\text{H}_{42}\text{O}_2\text{Si}_2$, 706.2723; found, 707.2736. Anal. Calcd: C, 81.54; H, 5.99. Found: C, 81.18; H, 5.74.

1,4-Bis{[3-phenyl-5-(4-ethynylphenyl)furyl]-2-yl}benzene (5d). To a solution of **10** (0.42 g, 0.6 mmol) in methanol (100 mL) and THF (125 mL) was added potassium hydroxide (0.38 g, 6 mmol). The mixture was stirred at room temperature for 1 h. After removal of the solvent, the product was extracted with chloroform then purified by flash chromatography to give **5d** (0.31 g, 92%): mp 342°C (dec). ^1H NMR (500 MHz, CDCl_3): δ = 3.14 (s, 2 H), 6.84 (s, 2 H), 7.3–7.5 (m, 10 H), 7.53 (d, J = 8.3 Hz, 4 H), 7.55 (s, 4 H), 7.70 (d, J = 8.3 Hz, 4 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 78.1, 83.7, 110.9, 120.9, 123.5, 125.3, 125.9, 127.6, 128.7, 128.8, 129.8, 130.6, 132.6, 134.0, 148.0, 151.8. IR (KBr): ν = 3293, 3059, 2926, 2110, 1625, 1493, 1392, 1246, 1018, 840, 765, 697. HRMS: calcd for $\text{C}_{42}\text{H}_{26}\text{O}_2$, 562.1933; found, 562.1932. Anal. Calcd: C, 89.66; H, 4.66. Found: C, 89.39; H, 4.48.

1,4-Bis{[3-phenyl-5-(4-[2-(dimethylstyrylsilanyl)-vinyl]-phenyl)furyl]-2-yl}benzene (4d). Under N_2 , a mixture of **8** (0.107 g, 0.66 mmol), **5d** (0.187 g, 0.33 mmol), and $\text{RhCl}(\text{PPh}_3)_3$ (1.5 mg, 0.5 mol %) in CHCl_3 (3 mL) was refluxed for 6 h. Removal of the solvent and chromatographic separation on silica gel (CH_2Cl_2) to afford a yellow solid, **4d** (0.17 g, 58%): mp $201\text{--}203^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ = 0.34 (s, 12 H), 6.54 (d, J = 19.1 Hz, 2 H), 6.57 (d, J = 19.1 Hz, 2 H), 6.82 (s, 2 H), 6.98 (d, J = 19.1 Hz, 4 H), 7.3–7.55 (m, 24 H), 7.56 (s, 4 H), 7.73 (d, J = 8.4 Hz, 4 H). ^{13}C NMR (100 MHz, CDCl_3): δ = -2.5 , 109.3, 110.1, 123.9, 125.2, 125.8, 126.5, 126.9, 127.3, 127.5, 127.6, 128.1, 128.6, 128.8, 130.0, 134.2, 137.4, 138.2, 138.3, 144.3, 145.0, 147.7, 152.5. IR (KBr): ν = 2960, 1680, 1604, 1507, 1408, 1254, 1051, 989, 843, 798, 765, 699. HRMS: calcd for $\text{C}_{62}\text{H}_{54}\text{O}_2\text{Si}_2$, 886.3662; found, 886.3661. Anal. Calcd: C, 83.93; H, 6.13. Found: C, 83.55; H, 6.44.

Polymer 3a. A mixture of **6a** (48 mg, 0.15 mmol), **5a** (30 mg, 0.15 mmol), and $\text{RhCl}(\text{PPh}_3)_3$ (4.6 mg, 0.005 mmol) in THF (2.5 mL) was refluxed under N_2 for 4 h. Methanol was added. The precipitate was collected and redissolved in THF and then precipitated again with methanol. The product was collected by filtration and washed with methanol to give **3a** (67 mg, 86%). ^1H NMR (200 MHz, CDCl_3): δ = 0.33 (br s, 6 H), 6.56 (d, J = 19 Hz, 2 H), 6.98 (d, J = 19 Hz, 2 H), 7.3–7.6 (m, 8 H). IR (KBr): ν = 3032, 2959, 1646, 1604, 1496, 1402, 1252, 1050, 988, 837, 796, 645. Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{Si}$: C, 82.38; H, 6.91. Found: C, 81.51; H, 6.03.

$\text{RhCl}(\text{PPh}_3)_3$ ($\text{M} \times 10^{-3}$)	time (h)	temp ($^{\circ}\text{C}$)	% yield	M_n	DPI
2.0	6	40	75	5700	2.8
2.0	4	refluxing THF	86	17800	3.2

Polymer 3b. To a solution of **6b** (0.30 g, 0.5 mmol) and **5b** (0.063 g, 0.5 mmol) in THF (2.5 mL) was added $\text{Rh}(\text{PPh}_3)_3\text{Cl}$

(2.3 mg, 0.5 mol %) under N_2 . The mixture was refluxed for 4 h. Using the same purification procedure as described above, **3b** was obtained (0.29 g, 81%); M_n = 6600, PDI = 2.32. IR (KBr): ν = 3043, 2955, 2869, 1597, 1507, 1418, 1247, 1197, 1063, 1025, 839, 732 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 0.31 (s, 12 H), 0.98–1.03 (m, 6 H), 1.54 (m, 4 H), 1.85 (m, 4 H), 4.04 (m, 4 H), 6.51 (d, J = 19.2 Hz, 2 H), 6.93 (d, J = 19.4 Hz, 2 H), 7.07–7.13 (m, 4 H), 7.41–7.46 (m, 18 H). Anal. Calcd for $\text{C}_{48}\text{H}_{56}\text{O}_2\text{Si}_2$: C, 79.95; H, 7.83. Found: C, 79.38; H, 7.52.

Polymer 3c. To a solution of **6c** (123 mg, 0.5 mmol) and **5c** (135 mg, 0.5 mmol) in THF (2.5 mL) was added $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (2.3 mg, 0.5 mol %) under N_2 . Using the same purification procedure as described above, **3c** was obtained (210 mg, 82%); M_n = 15600, PDI = 2.97. IR (KBr): ν = 2949, 1608, 1541, 1489, 1247, 1180, 1014, 984, 836, 727, 668. ^1H NMR (400 MHz, CDCl_3): δ = 0.36 (br s, 12 H), 6.55 (d, 4 H), 6.70 (d, 4 H), 6.8–7.1 (m, 4 H), 7.45 (s, 4 H), 7.61 (s, 4 H), 8.11 (s, 4 H). Anal. Calcd: C, 74.37; H, 6.24. Found: C, 75.45; H, 7.22.

Polymer 3d. To a solution of **6c** (0.1 g, 0.4 mmol) and **5d** (0.26 g, 0.4 mmol) in THF (2.5 mL) was added $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (1.9 mg, 0.5 mol %) under N_2 . The mixture was refluxed for 4 h. Using the same purification procedure as described above, **3d** was obtained (0.25 g, 71%); M_n = 13200, PDI = 2.75. ^1H NMR (400 MHz, CDCl_3): δ = 0.33 (br s, 12 H), 6.4–6.6 (m, 4 H), 6.8 (s, 2 H), 6.9–7.1 (m, 4 H), 7.3–7.6 (m, 22 H), 7.6–7.8 (m, 4 H). IR (KBr): ν = 2961, 1673, 1604, 1447, 1408, 1255, 1048, 990, 843. Anal. Calcd: C, 83.12; H, 5.98. Found: C, 84.21; H, 6.67.

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