Intrachain Chromophore Interactions in Silanylene-Spaced Divinylbenzene Copolymers

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ABSTRACT: A range of silanylene-spaced divinylbenzene copolymers (1) and the corresponding monomers (2) have been synthesized by the rhodium-catalyzed hydrosilylation of the corresponding bisalkynes with bissilyl hydrides, and the photophysical properties of 1 and 2 have been investigated. The silicon moiety in 1 serves as an insulating tetrahedral spacer that makes 1 highly folded. The two chromophores may be in close proximity such that a ground-state intrachain interaction between two conjugated moieties through space might occur. © 2003 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 41: 2218–2231, 2003

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INTRODUCTION

There has been a burgeoning interest in the synthesis and photophysics of silanylene-spaced conjugated copolymers.¹⁻²³ The tetrahedral silanylene linkers may serve as insulators such that the electron-hole excitation may be localized in the isolated conjugated segments in these polymers. Alternatively, energy transfer between the neighboring donor-acceptor chromophores separated by the silanylene moiety may also occur.²² In addition, the presence of these tetrahedral silanylene groups could also lead the polymers to more flexible conformations so that the polymers may be highly folded. Consequently, the two π -conjugated moieties may be in close proximity so that intrachain $\pi - \pi$ interactions between chromophores may occur.²⁴⁻³³ In our preliminary communication, we found that silanylene-spaced *p*-divinylbenzene copolymer exhibited dual fluorescence spectra.²³ Significant intrachain interactions between lumophores in 1a both at the ground state and at the excited state could occur, and such interactions were more important as the polymer became larger. We report here a systematic structure-activity investigation of the photophysics of a range of silanylene-spaced divinylbenzene copolymers (1):

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RESULTS

Syntheses

A series of silanylene-spaced divinylbenzene copolymers (1) have been synthesized by the rhodium-catalyzed hydrosilylation³⁴ of bisalkynes (4) with bissilylhydrides (3): The number-average molecular weights $(M_n$'s) of **1** depend on the reaction conditions. A higher concentration, a higher temperature, or a longer reaction time leads to the formation of **1** with a higher degree of polymerization. Representative examples are described in the Experimental sec-

tion. The monomeric model compounds (2) have been prepared similarly:



The synthetic strategy of **3** is mainly based on the silylolefination of the corresponding dithioacetals followed by the reduction of the corresponding Si—O bond,^{35–38} whereas the Sonogashira reaction³⁹ has been employed for the synthesis of **4**. The details are summarized in the Experimental section.

Absorption Spectra

The ultraviolet–visible (UV–vis) spectra of the copolymers (1) and their corresponding monomeric model compounds (2) are shown in Figure 1(a–e), and the maximum wavelength (λ_{max}) for each of these molecules is summarized in Table 1. Some interesting features can be observed for the absorption of copolymers **1a–1d**. As shown in Figure 1(a–d), besides the absorption at the corresponding λ_{max} 's, there is a tailing absorption extended to the longer wavelength for **1a–1d**.

Polymer **1e** has bulky alkoxy substituents. The UV–vis spectrum for **1e** appears to be not very different from that of **2d** [Fig. 1(e)], and there is no longer a wavelength tailing absorption for **1e**.

Emission Spectra

The emission spectra of copolymers **1a–1d** are shown in Figure 2. With the exception of **1e**, all the **1** polymers exhibit dual fluorescence spectra (Fig. 2). In addition to the higher energy emission, which is comparable to those for the corresponding monomers (**2**), there exists an emission in the longer wavelength region. The emission pattern in this longer wavelength region depends on the nature of the chromophore and on the degree of polymerization of **1**. The profile for each of these spectra remains unchanged with the concentration (10^{-2} to 10^{-4} g/L). Some of these spectra exhibit distinct vibronic fine structures at the longer wavelength emission. The fluorescence lifetimes at different wavelengths and the quantum yields for both **2** and **1** are also summarized in Table 1.

The excitation spectra for each of the **1** polymers are compared with the absorption spectra of the same chromophore shown in Figure 1. The relative intensity at longer wavelengths in these excitation spectra appears to be much higher than that in the absorption profile for copolymers **1a-1e**.

DISCUSSION

Role of the Silanylene Moiety in 1

On the basis of the spectroscopic properties of the 1 copolymers and the corresponding 2 monomers shown in Figures 1 and 2, it is apparent that the silicon moiety in 1 plays two interesting roles dictating the photophysical properties of **1**. First, it can serve as an insulating spacer. As such, both the absorption and emission spectra for 1 and 2 having the same conjugated moiety will be alike. Copolymer 1e is a representative example. Second, the silicon moiety has a tetrahedral structure, and 1 can be expected to be highly folded. Accordingly, the two chromophores may be in close proximity such that intrachain interactions between two conjugated moieties through space might occur. The fluorescence spectra shown in Figure 2 are typical examples illustrating this phenomenon. The emission profile remains essentially unchanged when the concentration of polymer 1b ranges from 10^{-2} to 10^{-4} g/L. This observation suggests that the interactions between chromophores, if any, should occur intramolecularly at these concentrations.

Mononuclear Divinylbenzene-Silanylene Copolymers

Three different kinds of divinylbenzene-silanylene copolymers (1a-1c) are compared. Polymer 1a has *p*-divinylbenzene chromophores, and polymer 1b contains *m*-divinylbenzene moieties, whereas polymer 1c consists of alternating *p*- and *m*-divinylbenzene groups separated by the silicon atom. No significant shifts in the absorption spectra between polymers 1a-1c and the corresponding monomers 2a and 2b have been observed. However, there appears to be a tailing weak absorption in the region of 340-400 nm for 1a-1c, and the intensity in this region slightly increases with the degree of polymerization.²³

Polymer 1a exhibits dual fluorescence spectra (Fig. 2). The higher energy emissions around 340 and 360 nm for 1a are compatible with those for **2a**. The relative intensity of the emission in the blue light region increases with the degree of polymerization of 1a, and vibronic fine structures have been observed in this region. The emission profiles remain essentially unchanged with the concentration (5–100-fold) and solvents (<8 nm in MeCy, benzene, or CHCl₃). Time-resolved fluorescence spectra of $1a (M_n = 10,700)$ and 2a in CHCl₃ have been monitored at 341 and 414 nm. The fluorescence of 1a at 414 nm shows a slow decay with a lifetime (τ) of 1.1 ns. However, both **1a** and **2a** exhibit a fast fluorescent decay ($\tau = 0.1$ ns) at 341 nm. When the fluorescence spectrum of **1a** is monitored at a 1-ns delay time after laser excitation, only a low-energy emission can be observed (Fig. 3). These data suggest that the emission of **1a** at these two wavelengths might arise from different species.

In the excitation spectrum for 1a [Fig. 1(a)], the intensity at 375 nm is substantially enhanced in comparison with that in the absorption spectrum. This observation indicates that significant intrachain interactions between chromophores⁴⁰ in 1a both at the ground state and at the excited state might occur, and such interactions seem to be more important as the polymer becomes larger. In other words, the opportunity for one chromophore unit in 1a located proximal to the other in space would increase with the molecular weight. Intrachain aggregation of chromophores has also been observed in block copolymers obtained by the ring-opening metathesis polymerization of 2,2-paracyclophanene and norbornene.41-44

The photophysical behaviors of polymers 1b and 1c are similar to those of 1a. Again, dual fluorescence emissions have been observed for each of these polymers, vibronic fine structures being found at longer wavelengths (Fig. 2). The higher energy emissions around 340 and 360 nm for 1b and 1c are comparable to those for 2a and 2b. A peak at about 370 nm in the excitation spectra for 1b and 1c [Fig. 1(b,c)], in comparison with the respective absorption spectra, indicates that intrachain interactions between chromophores may also occur at both the ground state and the excited state. This result is similar to that observed for 1a, as previously described.

The *m*-divinylbenzene chromophore has a shorter conjugation length. Therefore, both the absorption maximum and emission wavelength

for monomer 2b and polymer 1b appear expectedly at shorter wavelengths, as shown in Table 1 and Figures 1(b,c) and 2. The longer wavelength emission for 1b occurs at 393 nm with a fluorescence lifetime of $\tau = 0.9$ ns. The fluorescence lifetime at 414 nm for 1c ($\tau = 1.1$ ns) is comparable to that for **1a** at the same wavelength ($\tau = 1.1$ ns). However, there is an additional emission at 393 nm for **1c**, and the lifetime of 0.8 ns is similar to that for the all-meta isomer $\mathbf{1b}$ ($\tau = 0.9$ ns). The difference in the lifetimes for the emission at 414 and 393 nm for 1c indicates that they arise from different species. As mentioned earlier, the emission in this region is ascribed to the strong intrachain interaction between two chromophores at both the ground and excited states. The similarities in the lifetimes for 1c and for 1a and 1b at respective wavelengths suggest that the interaction pattern might be alike. Presumably, chromophores in 1b having comparable energy would interact preferentially.

Substituted Divinylbenzene-Silyene Copolymers

The introduction of a substituent into the aromatic ring of the divinylbenzene chromophores may cause changes in the electronic states of these moieties so that the photophysical properties may be modified. Therefore, the 2,5-difluoro-1,4-divinylbenzene/silanylene copolymer (1d) and the corresponding monomer (2c) have been subjected to spectroscopic analysis. As shown in Figure 1(d), the absorption spectra for 1d and 2c are compared with the excitation spectrum for 1d. Although the λ_{\max} values for **1d** and **2c** are similar, the tailing in the longer wavelength regions appears to be characteristic. The relative intensity at this longer wavelength region in the absorption spectrum for 1d is less than that in the excitation spectrum for 1d. These results again suggest that interactions of the fluoro-substituted chromophores in **1d** may take place even at the ground state. The interactions of polyfluoro-substituted benzene moieties with other aromatic rings in the solid state are well documented.⁴⁵ The fluorescence spectra shown in Figure 2 also exhibit longer wavelength emissions because of interactions of lumiphores similar to those of unsubstituted divinylbenzene chromophores described in the previous paragraphs. The presence of the fluorine substituent does not change the spectroscopic profiles in 1d.

A fluorine atom is small, and the presence of a fluoro substituent does not alter the steric hin-



(b)

Figure 1. Absorption spectra for 1 (dashed line) and 2 (solid line) and an excitation spectrum for 1 (dotted line) in CHCl_3 : (a) **1a** $(M_n = 10,700)$, **2a**, and an excitation spectrum monitored at 414 nm; (b) **1b** $(M_n = 3000)$, **2b**, and an excitation spectrum monitored at 392 nm; (c) **1c** $(M_n = 3500)$, **2b**, and an excitation spectrum monitored at 415 nm; (d) **1d** $(M_n = 4800)$, **2c**, and an excitation spectrum monitored at 417 nm; and (e) **1e** $(M_n = 15,900)$, **2d**, and an excitation spectrum monitored at 418 nm.



Figure 1. (Continued from the previous page)



Figure 1. (Continued from the previous page)

Table 1.	Photophysical Properties of Polymers $1a-1e$ and Monomers $2a-2d$ Measured in $CHCI_3$	

	$M_{\rm n}~({ m PDI})$	$\lambda_{\max} (nm)$	$\lambda_{\rm em}~(nm)^{\rm a}$	$ au ({ m ns})^{ m b}$	$\Phi_{\mathbf{f}}^{\mathbf{c}}$	$\lambda_{\mathrm{excitation}} \ (\mathrm{nm})$
1a	10,700 (3.5)	300	341	0.1	0.03	300
	-,,	360^{d}	354			367
			414	1.1		
			441			
1b	3,000 (2.7)	$258^{ m d}$	354		0.15	258
	·		392	0.9		370
1c	3,500 (3.6)	$260^{ m d}$	356	0.1	0.14	258
			393	0.8		
			415	1.1		372
			441			372
1d	4,800 (2.7)	286	350	0.3	0.08	287
		$313^{ m e}$	417	1.2		
			441	1.4		368
1e	15,900 (2.2)	286	418	2.6	0.32	286
2a		264	335	0.1	0.05	
		300	354			
2b		260	354	0.3	0.15	
2c		258	348	0.3	0.09	
		295	360			
2d		262	418	2.5	0.36	
		360				

^a The absorption λ_{\max} was used to excite the substrate. ^b τ was obtained from the time-resolved spectra with $y = y_0 + A_1 \exp(x_0 - x)t + A_2 \exp(x_0 - x)t$ for simulation. ^c Quantum yield. ^d Tailing extended to about 400 nm. ^e Tailing extended to about 460 nm.



Figure 2. Emission spectra for **1a** ($M_n = 10,700$; solid line), **1b** ($M_n = 3000$; dotted line), **1c** ($M_n = 6200$; dashed line), and **1d** ($M_n = 4800$; dashed-dotted) in CHCl₃.

drance significantly. Despite the electron-withdrawing character for the fluorine substituent, polymer **1d** is expected to fold in a manner similar to that of simple divinylbenzene copolymer **1a**. The introduction of a bulky substituent may, however, alter the situation. Therefore, the emission profiles for polymer **1e** appear similar to that for the corresponding monomer **2d**, no excimer-like



Figure 3. Time-resolved spectra of $1a (M_n = 10,700)$ in CHCl₃ monitored at different decay times: 0 (solid line), 0.3 (dashed line), and 1 ns (dotted line).

emission being observed in the fluorescence spectrum. In addition, no tailing in the longer wavelength has been observed in the UV-vis spectrum for **1e** [Fig. 1(e)]. Apparently, the bulky alkoxy substituent prohibits the interactions between chromophores.

CONCLUSIONS

We have demonstrated the mode of intrachain interaction between chromophores in silanylenespaced divinylbenzene copolymers (1). When the benzene moiety contains no bulky substituents, interchromophoric contact prevails, leading to ground-state interactions. When the chromophores are substituted with bulky substituents, the intrachain interactions appear to be negligible for steric reasons. These results may provide useful insights into how chromophores in conjugated polymers (particularly those with structural defects) interact intramolecularly.

EXPERIMENTAL

¹H NMR spectra were recorded in a CDCl_3 solution on Bruker AC-200, AC-300, and AC-400 spectrometers. Mass spectrometry (MS) and high-resolution mass spectrometry (HRMS) were measured on a Finnigan-TSQ-46C spectrometer and a JEOL SX-102A spectrometer, respectively. UV-vis absorption spectra were determined with a Shimadzu UV 1601-PC spectrometer. The fluorescence emission was detected with an Aminco-Bowman series 2 luminescence spectrometer with a slit width of 2.5 nm (SLM-Aminco, Urbana, IL). The synthesis of polymer **1a** and its relative monomer **2a** has been published elsewhere.^{5,6}

1,3-Bis(2-dithiolanyl)benzene (6a)

A CHCl₃ solution (100 mL) of **5a** (8.04 g, 60.0 mmol), $BF_3 \cdot Et_2O$ (1.5 mL, 6.0 mmol), and 1,2-ethanedithiol (14.8 mL, 160 mmol) was stirred at room temperature for 4 h. The mixture was poured into 10% NaOH, and the organic layer was washed with 10% NaOH (50 mL × 3) and brine (50 mL) and dried (MgSO₄). The solvent was removed *in vacuo* to give **6a** (14.7 g, 86%).

mp: 102–103 °C (hexane). ¹H NMR (300 MHz, CDCl₃, δ): 3.20–3.60 (m, 8 H), 5.60 (s, 2 H), 7.25 (t, J = 6.9 Hz, 1 H), 7.42 (d, J = 6.9 Hz, 2 H), 7.61 (s, 1 H). ¹³C NMR (75 MHz, CDCl₃, δ): 40.2, 56.0,

127.5, 127.7, 128.7, 140.6. HRMS Calcd. for $C_{12}H_{14}S_4$: 285.9978. Found: 285.9983. ELEM. ANAL. Calcd.: C, 50.31%; H, 4.93%. Found: C, 50.07%; H, 4.82%.

1,3-Bis(2-dimethylsilanyl)vinylbenzene (3b)

The solvent of a tetrahydrofuran (THF) solution of Me₂(ⁱPrO)SiCH₂MgCl (100 mmol), prepared from Me₂(ⁱPrO)SiCH₂Cl (18.6 mL, 100 mmol) and Mg turning (2.43 g, 100 mmol), was removed under reduced pressure, and the residue was evacuated. Under N_2 , a solution of **6a** (2.86 g, 10 mmol) and NiCl₂(PPh₃)₂ (0.33 g, 0.5 mmol) in benzene (100 mL) was introduced, and the mixture was refluxed for 16 h and then poured into 5% Na_2CO_3 . The organic layer was separated, and the aqueous layer was extracted with ether (2 \times 50 mL). The combined organic portions were washed with 10% NaOH (2 \times 50 mL) and brine (50 mL) and dried (MgSO₄). The solvent was removed in vacuo to afford a gummy mass, which was taken in benzene (100 mL). LiAlH₄ (1.6 g, 40 mmol) was then added, and the mixture was refluxed for 18 h, cooled to room temperature, and quenched carefully with water. After filtration, the organic layer was dried $(MgSO_4)$, and the solvent was removed *in vacuo* to give the residue, which was chromatographed on silica gel (hexane) to afford **3b** (1.36 g, 55%, two steps).

bp: 125 °C (0.2 mmHg). ¹H NMR (300 MHz, CDCl₃, δ): 0.22 (d, J = 3.6 Hz, 12 H), 4.10–4.25 (m, 2 H), 6.47 (dd, J = 19.1 Hz, J = 2.3 Hz, 2 H), 6.95 (d, J = 19.1 Hz, 2 H), 7.24–7.36 (m, 3 H), 7.50 (s, 1 H). ¹³C NMR (75 MHz, CDCl₃, δ): –4.0, 124.5, 126.2, 126.4, 128.7, 138.4, 145.1. IR (ν , KBr): 2119 cm⁻¹. HRMS Calcd. for C₁₄H₂₂Si₂: 246.1260. Found: 246.1253. ELEM. ANAL. Calcd. for C₁₄H₂₂Si₂: C, 68.22%; H, 9.00%. Found: C, 67.73%; H, 8.66%.

1,4-Diethynyl-2,5-difluorobenzene (4c)

A solution of **7c** (X = Br, 544 mg, 2.0 mmol) in triethylamine (Et₃N) (20 mL) was mixed with trimethylsilylacetylene (588 mg, 6.0 mmol), CuI (8 mg, 0.04 mmol), and PdCl₂(PPh₃)₂ (56 mg, 0.08 mmol). The mixture was refluxed under N₂ for 12 h. Et₃N was removed under reduced pressure, and the residue was taken in Et₂O and filtered. The filtrate was washed with water, dried (MgSO₄), and evaporated *in vacuo* to give **8c** (495 mg, 81%).

mp: 81–82 °C [methanol (MeOH)]. ¹H NMR (300 MHz, CDCl₃, δ): 0.24 (s, 18 H), 7.06–7.11 (t, $J = 7.2 \text{ Hz}, 2 \text{ H}). {}^{13}\text{C} \text{ NMR} (75 \text{ MHz}, \text{CDCl}_3, \delta): \\ -0.3, 96.3, 103.3, 113.0 (dd, J = 16, 28 \text{ Hz}), 119.8 \\ (m), 158.3 (dd, J = 4.4, 250 \text{ Hz}). \text{ IR} (\nu, \text{KBr}): 2961, \\ 2902, 2162, 1493, 1411, 1260, 872, 838 \text{ cm}^{-1}. m/z: \\ 306. \text{ ELEM. ANAL. Calcd. for } \text{C}_{16}\text{H}_{20}\text{F}_2\text{Si}_2: \text{ C}, \\ 62.70\%; \text{ H}, 6.57\%. \text{ Found: C}, 62.31; \text{ H} 6.66\%. \\ \end{cases}$

To a suspension of **8c** (612 mg, 2.0 mmol) in MeOH (10 mL) was added K_2CO_3 (56 mg, 0.4 mmol), and the mixture was stirred at room temperature for 2 h. The solvent was removed *in vacuo*, and the residue was chromatographed on silica gel [ethyl acetate (EtOAc)/hexane = 5:95] to afford **4c** (279 mg, 86%) as a solid.

mp: 132–134 °C (CH₂Cl₂/hexane). ¹H NMR (200 MHz, CDCl₃, δ): 3.39 (s, 2 H), 7.11–7.23 (t, J = 7.4 Hz, 2 H). ¹³C NMR(75 MHz, CDCl₃, δ): 75.5, 85.0, 112.2 (dd, J = 16, 27 Hz), 120.0 (m), 158.7 (dd, J = 4.4, 250 Hz). IR (ν , KBr): 3289, 3070, 2119, 1753, 1501, 1410, 1206, 884, 717 cm⁻¹. m/z: 162. ELEM. ANAL. Calcd. for C₁₀H₄F₂: C, 74.07%; H, 2.47%. Found: C, 73.68%; H, 2.83%.

1,4-Dicyano-2,5-difluorobenzene (9)

To a solution of **7c** (X = Br, 272 mg, 1 mmol) in dry dimethylacetamide (4 mL) was added CuCN (270 mg, 3.0 mmol), and the mixture was heated at 160 °C for 4.5 h. The solvent was removed *in vacuo*, and the residue was taken up in CHCl₃. The organic extract was filtered over celite, and the residue was washed several times with CHCl₃. The filtrate was evaporated *in vacuo* to give the residue, which was chromatographed on silica gel (EtOAc/hexane = 2:98) to afford **9** (88 mg, 54%).

mp: 175–177 °C (Et₂O/hexane), ¹H NMR (200 MHz, CDCl₃, δ): 7.52 (t, J = 7.2 Hz, 2 H). ¹³C NMR (50 MHz, CDCl₃, δ): 107.5 (d, J = 2.8 Hz), 111.1 (s), 121.2 (m), 158.3 (dd, J = 4.4, 250 Hz). IR (ν , KBr): 2100 cm⁻¹. m/z: 164 (M+, 100%), 137, 120.1, 105, 91, 77. ELEM. ANAL. Calcd. for C₈H₂F₂N₂: C, 58.54%; H, 1.22%. Found: C, 58.11; H 1.10%.

2,5-Difluroterepthaldehyde (5b)

To a solution of **9** (332 mg, 2.0 mmol) in benzene (20 mL) was slowly added diisobutylaluminum hydride (DIBAH) (1 M in hexane, 4.5 mL) at the ambient temperature, and the mixture was stirred for a further period of 6 h. To this mixture was added a mixture of MeOH and benzene (1:1, 2 mL) followed by MeOH and water (1:1, 2 mL) and then 20% H_2SO_4 (3 mL), and the mixture was stirred for a further period of 20 min. After being cooled to 0 °C, the mixture was neutralized by the

careful addition of a saturated NaHCO₃ solution and extracted with EtOAc, and the organic layer was thoroughly washed with water and brine and dried (MgSO₄). The removal of the solvent *in vacuo* afforded a gummy material, which was chromatographed on silica gel (EtOAc/hexane = 5:95) to afford **5b** as a colorless solid (302 mg, 89%).

mp: 155–157 °C. ¹H NMR (200 MHz, CDCl₃, δ): 7.67 (t, J = 7.2 Hz, 2 H), 10.35 (s, 2 H). ¹³C NMR (75 MHz, CDCl₃, δ): 116.2 (m), 128.9 (dd, J = 8, 17 Hz), 160.1 (dd, J = 4.4, 256 Hz), 185.1. IR (ν , KBr): 1692 cm⁻¹. ELEM. ANAL. Calcd. for C₈H₄F₂O₂: C, 56.48%; H, 2.37%. Found: C, 56.49%; H, 2.59%.

2,5-Difluoro-1,4-bis(2-dithiolanyl)benzene (6b)

To a solution of **5b** (375 mg, 2.2 mmol) in CHCl₃ (25 mL) were added 1,2-ethanedithiol (620 mg, 6.6 mmol) and a catalytic amount of $BF_3 \cdot Et_2O$. The mixture was stirred at room temperature overnight, quenched with a 10% aqueous NaOH solution, and extracted with CHCl₃. The organic extract was thoroughly washed with brine and dried (MgSO₄). The removal of the solvent *in vacuo*, followed by column chromatography on silica gel (EtOAc/hexane = 5:95), afforded **6b** (584 mg, 82%) as a solid.

mp: 135–137 °C (hexane). ¹H NMR (200 MHz, CDCl₃, δ): 3.25–3.45 (m, 8 H), 5.79 (s, 2 H), 7.36 (t, J = 8.4 Hz, 2 H). ¹³C NMR (75 MHz, CDCl₃, δ): 39.7 (s), 47.3 (s), 115.7 (dd, J = 17, 29 Hz), 130.0 (dd, J = 10, 23 Hz), 154.1 (dd, J = 4, 243 Hz). m/z: 294. ELEM. ANAL. Calcd. for C₂₂H₁₂F₂S₄: C, 44.69%; H, 3.75%. Found: C, 44.79%; H, 3.56%.

2,5-Difluoro-1,4-bis(2-dimethylsilanyl)vinylbenzene (3c)

To a solution of Me₂(ⁱPrO)SiCH₂MgCl prepared from Me₂(ⁱPrO)SiCH₂Cl (2.7 g, 16.3 mmol) and Mg (360 mg, 15 mmol) was added bisdithioacetal **6b** (480 mg, 1.50 mmol) in toluene (30 mL) and $NiCl_2(PPh_3)_2$ (400 mg, 0.6 mmol). The mixture was refluxed for 32 h and then quenched with a saturated aqueous NH₄Cl solution. The organic layer was extracted with Et₂O and washed with a 10% aqueous NaOH solution and brine. The solvent was removed in vacuo to afford a gummy mass, which was taken in benzene. $LiAlH_4$ (480) mg, 14.1 mmol) was added, and the mixture was refluxed for 12 h. After being cooled to room temperature, the mixture was slowly added to cold Et_2O , and $LiAlH_4$ was quenched with the careful addition of water followed by a 10% NaOH solution. The organic layer was filtered through celite and dried (MgSO₄), and the solvent was removed *in vacuo* to afford a viscous liquid, which was chromatographed on silica gel (hexane) to afford **3c** as an oil (95 mg, 23%, two steps).

¹H NMR (200 MHz, CDCl₃, δ): 0.21 (d, J = 2.3Hz, 2 H), 4.19 (m, 1 H), 6.49 (dd, J = 2.6, 19.2 Hz), 7.06 (d, J = 19.2 Hz, 2 H), 7.17 (t, J = 8.6 Hz, 2 H). ¹³C NMR (75 MHz, CDCl₃, δ): -4.1, 112.9, 126.7, 130.6, 135.7, 155 (dd, J = 2.7, 241 Hz). HRMS Calcd. for C₁₄H₂₀F₂Si₂: 282.1071. Found: 282.1077.

1,4-Diiodo-2,5-dimyrtoxybenzene (7d)

To a solution of **10** (9.20 g, 25.4 mmol) and 11^{22} (16.5 g, 53.5 mmol) in DMSO (175 mL) was added KOH (4.5 g, 80.2 mmol). After being stirred at room temperature for 36 h, the mixture was

poured into water and extracted twice with ether. The combined organic layers were washed with a 10% NaOH solution, water, and brine successively, dried (MgSO₄), and then filtered. The solvent was removed *in vacuo* to give **7d** (0.5 g, 59%).

mp: 109–110 °C (CHCl₃/CH₃OH). α_D^{25} : -4.0 (*c* 0.1 g/mL, CHCl₃). ¹H NMR (300 MHz, CDCl₃, δ): 0.87 (s, 6 H), 1.22 (s, 6 H), 1.30–1.50 (m, 4 H), 1.70–1.95 (m, 8 H), 1.96–2.10 (m, 4 H), 2.40–2.65 (m, 2 H), 3.64–3.74 (m, 4 H), 7.13 (s, 2 H). ¹³C NMR (75 MHz, CDCl₃, δ): 18.6, 20.2, 23.8, 24.1, 26.7, 35.0, 39.4, 40.9, 42.7, 74.5, 86.2, 122.8, 153.0. IR (ν , KBr): 2952, 2913, 2870, 1486, 1354, 1210, 1057, 1016 cm⁻¹. MS *m/z* (relative intensity): 634 (M⁺, 80), 498 (21), 362 (81), 236 (9), 137 (47), 121 (9), 95 (36), 81 (100), 69 (65), 55(16). ELEM. ANAL. Calcd. for C₂₆H₃₆I₂O₂: C, 49.23%; H, 5.72%. Found: C, 49.09: H, 5.61%.



1,4-Diethynyl-2,5-dimyrtoxy-benzene (4d)

To a stirred mixture of **7d** (5.02 g, 7.9 mmol), CuI (0.12 g, 0.64 mmol), Pd(PPh₃)₂Cl₂ (0.28 g, 0.40 mmol), and Et₃N (3.5 mL, 24.4 mmol) in THF (15 mL) was added dropwise a solution of trimethyl-silyacetylene (2.61 mL, 17.4 mmol) in THF (5 mL). The mixture was stirred at room temperature for 4 h, and the solid was filtered through silica gel. The filtrate was evaporated *in vacuo* to give **8d** (4.2 g, 92%).

mp: 181–182 °C (CHCl₃/CH₃OH). α_D^{25} : -13.0 (*c* 0.05 g/mL, CHCl₃). ¹H NMR (300 MHz, CDCl₃, δ): 0.23 (s, 18 H), 0.86 (s, 6 H), 1.22 (s, 6 H), 1.30–1.45(m, 4 H), 1.55–1.80 (m, 8 H), 1.81–1.95 (m, 2 H), 1.96–2.15 (m, 2 H), 2.40–2.60 (m, 2 H), 3.67–3.72 (m, 4 H), 6.85 (s, 2 H). ¹³C NMR (75 MHz, CDCl₃, δ): 0.0, 18.1, 20.2, 23.6, 24.1, 26.7, 35.1, 39.3, 40.9, 42.6, 72.9, 100.0, 101.1, 113.7, 116.8, 154.1. IR (ν , KBr): 2159 cm⁻¹. MS *m/z* (relative intensity): 574. ELEM. ANAL. Calcd. for C₃₆H₅₄O₂Si₂: C, 75.20%; H, 9.47%. Found: C, 75.56%; H, 9.32%.

To a stirred solution of **8d** (3.38 g, 5.9 mmol) in THF (100 mL) were added MeOH (50 mL) and a 20% aqueous KOH solution (3.5 mL) at room temperature. After being stirred for 2 h, the mixture was filtered. The filtrate was extracted with CH_2Cl_2 , and the organic layer was washed with water and brine and dried (MgSO₄). The solvent was removed *in vacuo* to give the residue, which was chromatographed on silica gel (EtOAc/hexane = 5:95) to yield **4d** (2.0 g, 79%).

mp: 103–105 °C (CHCl₃–CH₃OH). α_D^{25} : -8.0 (*c* 0.17 g/mL, CHCl₃). ¹H NMR (300 MHz, CDCl₃, δ): 0.85 (s, 6 H), 1.21 (s, 6 H), 1.35–1.48 (m, 4 H), 1.65–1,90 (m, 8 H), 1.90–2.02 (m, 2 H), 2.02–2.15 (m, 2 H), 2.40–2.55 (m, 2 H), 3.30 (s, 2 H), 3.66–3.80 (m, 4 H), 6.91 (s, 2 H). ¹³C NMR (75 MHz, CDCl₃, δ): 18.3, 20.1, 23.6, 24.0, 26.6, 34.8, 39.2, 40.8, 42.5, 73.6, 79.7, 82.4, 113.3, 117.8, 154.2. IR (ν , KBr): 3293, 2110 cm⁻¹. MS *m/z*: 430. ELEM. ANAL. Calcd. for C₃₀H₃₈O₂: C, 83.68%; H, 8.89%. Found: C, 83.68%; H, 8.77%.

1,3-Bis-2-(dimethylstyrylsilanyl)vinylbenzene (2b)

Under N_2 , a mixture of phenylacetylene (112 mg, 1.1 mmol), **3b** (123 mg, 0.5 mmol), and RhCl(PPh₃)₃ (1.0 mg, 0.001 mmol) in CH₂Cl₂ (1 mL) was stirred at room temperature for 12 h; the mixture was chromatographed on silica gel (hexane) to afford **2b** as a colorless oil (202 mg, 86%).

¹H NMR (400 MHz, CDCl_3 , δ): 0.32 (s, 12 H), 6.51 (d, J = 19.1 Hz, 2 H), 6.54 (d, J = 19.1 Hz, 2 H), 6.95 (d, J = 19.1 Hz, 4 H), 7.10–7.50 (m, 13 H), 7.55 (s, 1H). ¹³C NMR (75 MHz, CDCl₃, δ): -2.6, 124.5, 126.2, 126.4, 127.3, 127.7, 128.1, 128.5, 128.7, 138.2, 138.4, 144.7, 144.9. HRMS Calcd. for C₃₀H₃₄Si₂: 450.2199. Found: 450.2191. ELEM. ANAL. Calcd. for C₃₀H₃₄Si₂: C, 79.94%; H, 7.60%. Found: C, 79.97%; H, 7.37%.

2,5-Difluoro-1,4-bis-2-

(dimethylstyrylsilanyl)vinylbenzene (2c)

To a solution of $(\beta$ -styryl)dimethylsilane (162 mg, 1.0 mmol) and **4c** (81 mg, 0.5 mmol) in THF (2 mL) was added RhCl(PPh₃)₃ (2.3 mg), and the mixture was heated at 55–60 °C for 4.5 h. The solvent was removed *in vacuo* to give the residue, which was chromatographed on silica gel (hexane) to afford **2c** (102 mg, 42%) as a colorless solid.

¹H NMR (200 MHz, CDCl_3 , δ): 0.30 (s, 12 H), 6.46 (d, J = 19.2 Hz, 2 H), 6.56 (d, J = 19.2 Hz, 2 H), 6.93 (d, J = 18.9 Hz, 2 H), 7.06 (d, J = 18.9 Hz, 2 H), 7.19 (t, J = 8.7 Hz, 2 H), 7.27–7.50 (m, 12 H). ¹³C NMR (75 MHz, CDCl_3 , δ): -2.7, 113.0 (dd, J = 17.27 Hz), 126.7 (m), 127.2, 128.2 (m), 131.9, 135.2 (m), 138.1 (m), 144.3, 145.2, 156.3 (dd, J = 4.4, 246 Hz). HRMS Calcd. for $C_{30}H_{32}F_2Si_2$: 486.2010. Found 486.2018.

2,5-Bis(dimethylstyrylsilanyl)vinyl-1,4dimyrtoxybenzene (2d)

A mixture of (β -styryl)dimethylsilane (320 mg, 2.3 mmol), **4d** (446 mg, 1.0 mmol), and RhCl(PPh₃)₃ (1.5 mg, 0.0016 mmol) in CH₂Cl₂ (1.5 mL) was stirred under N₂ at room temperature for 12 h. After the removal of the solvent, the residue was chromatographed on silica gel (EtOAc/hexane = 3:97) to afford **2d** (380 mg, 50%).

mp: 103–104 °C. $\alpha_{\rm D}^{25}$: -11 (c 0.1 g/mL, CHCl₃). ¹H NMR (CDCl₃, 200 MHz, δ): 0.31 (s, 12 H), 0.83 (s, 6 H), 1.19 (s, 6 H), 1.30–1.48 (m. 2 H), 1.60– 1.80 (m, 8 H), 1.80–1.93 (m, 2 H), 1.95–2.12 (m, 2 H), 2.40–2.60 (m, 2 H), 3.74 (m, 4 H), 6.44 (d, J = 19.2 Hz, 2 H), 6.51 (d, J = 19.1 Hz, 2 H), 6.94 (d, J = 19.1 Hz, 2 H), 7.01 (s, 2 H), 7.18–7.48 (m, 12 H). ¹³C NMR (CDCl₃, 75 MHz, δ): 18.5, 20.2, 23.7, 14.1, 16.7, 35.3, 39.3, 40.9, 42.9, 73.4, 110.3, 126.4, 127.4, 128.0, 128.1, 128.5, 138.3, 139.1, 144.8, 151.0. MS *m/z*: 754. ELEM. ANAL. Calcd. for C₅₀H₆₆O₂Si₂: C, 79.52%; H, 8.81%. Found: C, 79.52%; H, 8.24%.

Polymer 1b

A mixture of **4b** (65.6 mg, 0.52 mmol), **3b** (128 mg, 0.52 mmol), and RhCl(PPh₃)₃ (1.1 mg, 0.0012 mmol) in CH₂Cl₂ (0.5 mL) was refluxed under N₂ for 4 h. After the mixture cooled, MeOH was added to precipitate crude **1b**, which was dissolved in CH₂Cl₂ and reprecipitated with MeOH. After filtration, the solid was washed with MeOH and dried to give **1b** (121 mg, 63%).

¹H NMR (300 MHz, CDCl_3 , δ): 0.32 (br s, 12 H), 6.55 (br d, J = 18.9 Hz, 4 H), 6.95 (br d, J = 18.9 Hz, 4 H), 7.20–7.60 (br m, 8 H). M_n : 3000 [polydispersity index (PDI) = 2.65]. ELEM. ANAL. Calcd. for $C_{24}H_{28}Si_2$: C, 77.35, H, 7.57%. Found: C, 78.24, H, 7.44%.

Polymer 1c

A mixture of **4a** (63 mg, 0.52 mmol), **3b** (123 mg, 0.50 mmol), and RhCl(PPh₃)₃ (1.0 mg, 0.001 mmol) in CH₂Cl₂ (1.0 mL) was refluxed under N₂ for 8 h. After a workup in a manner similar to that described previously, **1c** was obtained (155 mg, 83%).

¹H NMR (300 MHz, CDCl_3 , δ): 0.32 (br s, 12 H), 6.53 (br d, J = 18.7 Hz, 4 H), 6.93 (br d, J = 18.7Hz, 4 H), 7.10–7.60 (br m, 8 H). ELEM. ANAL. Calcd. for $C_{24}H_{28}Si_2$: C, 77.35, H, 7.57%. Found: C, 78.90, H, 6.43%.

For 0.05 M RhCl(PPh₃)₃, the time was 24 h, the temperature was 25 °C, the yield was 85%, M_n was 2200, and DPI was 2.8. For 0.1 M RhCl(PPh₃)₃, the time was 8 h, the temperature was 50 °C, the yield was 83%, M_n was 3500, and DPI was 3.6. For 1.0 M RhCl(PPh₃)₃, the time was 8 h, the temperature was 50 °C, the yield was 80%, M_n was 6200, and DPI was 4.7.

RhCI(PPh ₃) ₃ (M)	Time (H)	Temp (°(C)	%Yield	M _n	DPI
0.05	24	25	84	2,200	2.8
0.1	8	50	83	3,500	3.6
1.0	8	50	80	6,200	4.7

Polymer 1d

In a manner similar to that described previously, a mixture of **4c** (16 mg, 0.1 mmol), **3c** (28 mg, 0.1 mmol), and RhCl(PPh₃)₃ (1.5 mg, 0.0015 mmol) in THF (0.7 mL) was heated under N₂ to 55–60 °C for 6 h. After the workup, **1d** was obtained (9.3 mg, 21%).

¹H NMR (200 MHz, CDCl₃, δ): 0.30 (br s, 6H), 6.51 (d, J = 19 Hz, 2 H), 7.05 (d, J = 18 Hz, 2 H), 7.15 (t, J = 8 Hz, 2 H). ELEM. ANAL. Calcd. for C₁₂H₁₂Si C, 64.82%; H, 5.44%. Found C, 64.00%; H, 6.13%.

For 0.2 M RhCl(PPh₃)₃, there were two sets of conditions: (1) the time was 3 h, the temperature was 50 °C, the yield was 49%, $M_{\rm n}$ was 1800, and DPI was 1.6, and (2) the time was 6 h, the temperature was 57–60 °C, the yield was 21%, $M_{\rm n}$ was 4800, and DPI was 2.7.

RhCI(PPh ₃) ₃ (M)	Time (H)	Temp (°(C)	%Yield	M _n	DPI
0.2	3	50	49	1,800	$\begin{array}{c} 1.6\\ 2.7\end{array}$
0.2	6	55–60	21	4,800	

Polymer 1f

To a solution of **4e** (0.45 g, 1.0 mmol) and **3a** (0.25 g 1.0 mmol) in THF (5 mL) was added $Rh(PPh_3)_3Cl$ (4.6 mg, 0.005 mmol) under N₂. The mixture was refluxed for 10 h. After cooling to room temperature, the mixture was poured into CH_3OH to precipitate the crude **1f**. The precipitate was collected and redissolved in THF and then precipitated again with CH_3OH . Polymer **1f** was collected by filtration and washed with CH_3OH (0.49 g, 70%).

 $M_{\rm n}$: 15,900 (PDI = 2.2). ¹H NMR (300 MHz, CDCl₃, δ): 0.3 (br s, 12 H), 0.84 (br s, 6 H), 1.19 (br s, 6 H), 1.3–2.75 (m, 16 H), 3.25–4.1 (m, 4 H), 6.2–6.7 (m, 4 H), 6.7–7.2 (m, 6 H), 7.25–7.6 (m, 4 H). ELEM. ANAL. Calcd. for C₄₄H₆₀O₂Si₂: C, 78.05%; H, 8.93%. Found: C, 77.76%; H, 8.55%.

Time-Resolved Fluorescence and Quantum Yield Measurements

Compound 2 (10^{-5} to 10^{-6} M) or polymer 1 (10^{-3} to 10^{-4} g/L) was dissolved in CHCl₃ (spectroscopic grade), and the solution was subjected to photophysical measurements. The quantum yield was calculated with reference to standard quinine sulfate dihydrate in 0.1 N H₂SO₄ ($\Phi = 0.546$) or coumarin 1 in EtOAc ($\Phi = 0.99$). The excitation spectra of polymer 1 were monitored at the wavelengths specified. The fluorescence decay curves and time-resolved fluorescence were measured with a picosecond-correlated single-photon-counting apparatus equipped with a second harmonic of a mode-locked Nd³⁺:/YAG laser (I-400, coher-

ent). The excitation wavelength was based on the absorption λ_{max} . The exponential fittings were simulated by the equation $y = y_0 + A_1 \exp(x_0 - x)t_1 + A_2 \exp(x_0 - x)t_2$ from time-resolved fluorescence spectra.

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