Thorpe−Ingold Effect on Photoinduced Electron Transfer of Dialkylsilylene-Spaced Divinylarene Copolymers Having Alternating Donor and Acceptor Chromophores

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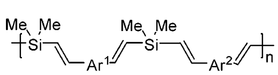
ABSTRACT: Dialkylsilylene-spaced divinylarene copolymers having alternating donor and acceptor chromophores are designed and synthesized. The rates of photoinduced electron transfer (PET) depend on the nature of the substituent on silicon. A replacement of the methyl substituent by the bulky isopropyl group has been shown to enhance the rate of PET. The results are rationalized in terms of the Thorpe−Ingold effect, which would bring the neighboring donor and acceptor chromophores in closer proximity. The STM images of the isopropyl-substituted copolymers are more folded than those of the methyl-substituted analogues, and these results are consistent with the outcome of photophysical studies of these copolymers.

Introduction

Replacement of two geminal hydrogen atoms on a carbon tethering chain connecting two reacting centers by two alkyl substituents has been known to lead to conformational equilibrium changes which would bring the two reacting centers in close proximity and the reactivity is thus enhanced.[1] Such geminal disubstitution effect, known as Thorpe−Ingold effect, has been widely applied in organic syntheses.[1] This concept has been briefly explored for the conformational investigations of peptides[2] and polymers.[3] Alternating silylene-conjugated chromophore copolymers **1**[4] have been shown to exhibit a range of interesting photophysical properties, such as intrachain chromophore−chromophore aggregation,[5] light harvesting and fluorescence resonance energy transfer (FRET),[6] photoinduced electron transfer,[7] and transfer of chiroptical properties.[8] The folding nature of **1** may be indispensable to dictate these photophysical properties. The origin of this folding character may arise from the conformational equilibrium of divinylsilane moiety in **1** (eq 1).



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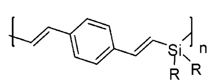
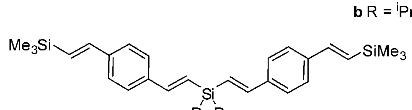
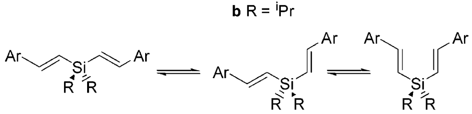


2a R = Me
b R = ^{i}Pr



3a R = Me
b R = ^{i}Pr



A **B** **C** (1)

It seems likely that conformations **B** and **C** might contribute significantly to the folding of **1**. The relative populations of these conformers would depend on the nature of the substituent R. Copolymer **1** would be more folded when R is a bulkier isopropyl group than when R is a methyl. Indeed, we recently found that emissions at longer wavelengths for **2b** is significantly enhanced than those for **2a**.[5b] Two kinds of chromophore−chromophore interactions have been proposed. Through space interaction between non-neighboring chromophores would be responsible for the emission of **2** in the blue light region. Alternatively, the contribution from conformer **C** would bring two neighboring chromophores in close proximity so that interactions between these chromophores would lead to emission around 390 nm. The emission in this region was also found in dimers **3**.

It is well documented that the efficacies of photoinduced electron transfer (PET) processes depend on the distance between donor and acceptor chromophores.[9] We have recently shown that PET occurred efficiently in dimethylsilylene-spaced divinylarene copolymers **1** having alternating donor and acceptor chromophores.[7] Through-space interaction between neighboring chromophores has been suggested.[7,10] It is envisaged that a replacement of the methyl substituent by the bulky isopropyl group would bring the neighboring donor and acceptor chromophores in closer proximity. In this paper, we report the first example on Thorpe−Ingold effect on the rates of electron-transfer process in silylene-spaced divinylarene copolymers **4** and **5** having alternating donor and acceptor chromophores.

Results and Discussion

Synthesis. Polymers **4** and **5** contain divinylene−terphenylene and terphenylene−tetravinylene, respectively, as the fluorophores and aminostyrene as the quencher were designed and synthesized. Silylene-spaced copolymers **4a** and **4b** were obtained by the rhodium-catalyzed hydrosilylation[5−8] of bis(alkyne) **6** with bis(silanes) **7** (eq 2). Copolymers **5** were prepared similarly from **8** with **9** (eq 3). The details for the preparation of starting alkynes **6**[7] and **8**[7] and silanes **7** and **9** are described in the Experimental Section.

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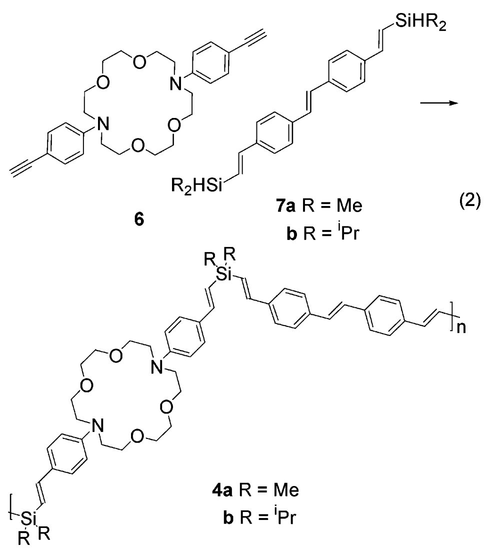
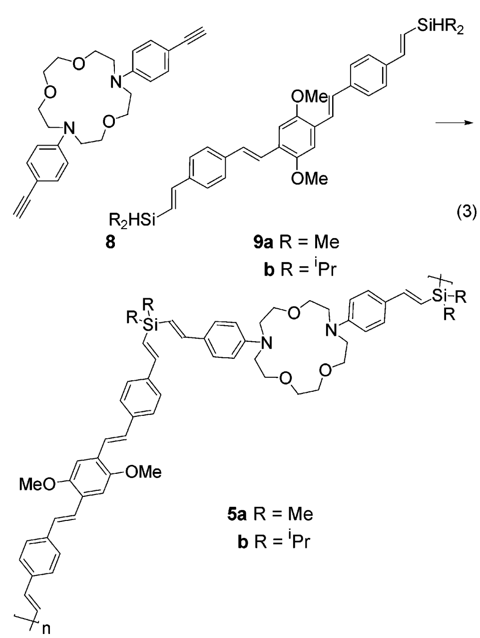


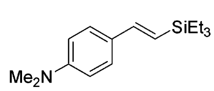
6 **7a** R = Me **b** R = ^{i}Pr (2)

4a R = Me **b** R = ^{i}Pr



8 **9a** R = Me **b** R = ^{i}Pr (3)

5a R = Me **b** R = ^{i}Pr



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Photophysical Properties. The absorption spectra of **4** and **5** and the corresponding monomers (or model compound) **7**, **9**, and **10** are shown in Figure 1. As expected, there is no difference in the absorption spectra between the methyl-substituted and the isopropyl-substituted monomers and polymers. The emission spectra of these compounds are shown in Figure 2. These photophysical properties together with the oxidation potentials of these compounds are summarized in Table 1 and the frontier orbital energies were thus estimated.

Upon excitation at 355 nm, both **7a** and **7b** in CH_2Cl_2 showed emission maxima at 390 and 410 with quantum yields 0.91. The fluorescence of **4a** and **4b** in CH_2Cl_2 at 390 and 410 nm were very weak, and the corresponding quantum yields were 0.06 and 0.05, respectively. When the measurements were carried in cyclohexane, the quantum yields for **4a** and **4b** were 0.49 and 0.14, respectively. The emission of **9a** and **9b** in CH_2Cl_2 appeared at 469 and 495 nm upon excitation at 410 nm and the quantum yields were 0.71 and 0.70, respectively. Again, the luminescence of **5a** and **5b** in CH_2Cl_2 appeared at the same wavelengths with quantum yields 0.51 and 0.12, respectively. The quantum yields for the emission of **5a** and **5b** in cyclohexane were 0.68 and 0.55, respectively.

Table 1. Photophysical Properties of Polymers 4 and 5 and the Corresponding Monomers 7, 9, and 10 and the Frontier Orbital Energies of the Corresponding Chromophores

	λ_{max} (nm)[a]	λ_{em} (nm)[a]	$\Phi^{a,b}$	E_{ox}[c] (V)	HOMO[d] (eV)	LUMO[e] (eV)
4a	338	390, 410	0.06 (0.49)			
4b	338	390, 410	0.05 (0.14)			
5a	334, 411	469, 495	0.51 (0.68)			
5b	335, 409	469, 495	0.12 (0.55)			
7a	342, 355	390, 410	0.91	0.82	−5.62	−2.44
7b	342, 355	390, 410	0.91	0.82	−5.62	−2.44
9a	337, 411	469, 495	0.71	0.46	−5.26	−2.56
9b	338, 409	469, 495	0.70	0.46	−5.26	−2.59
10	308	378	0.03	0.18	−4.98	−1.57

[a] Measured in CH_2Cl_2 unless otherwise specified. [b] Using coumarin 1 in EtOAc ($\Phi = 0.99$) as the standard. The numbers in the bracket are the quantum yield measured in cyclohexane. [c] Oxidation potentials determined by cyclicvoltammetry using 0.1 M Bu_4NPF_6 as electrolyte in CH_2Cl_2 with Pt working electrode, Pt wire counter electrode, and $Ag/AgNO_3$ reference electrode. [d] Estimated by E_{ox} vs Fc/Fc^+. [e] Estimated by HOMO and optical band gap from the absorption spectra.

Table 2. Fluorescence Lifetime (τ) and the Reciprocal of the Fluorescence Lifetime (k_s) of 7a,b and 9a,b in CH_2Cl_2 and Cyclohexane at Ambient Temperature

substrate[a]	solvent	fluorescence lifetime[b] τ (ps)	reciprocal of the fluorescence lifetime k_s (ns^{-1})
7a (**7b**)	CH_2Cl_2	941	1.1
	cyclohexane	880	1.1
9a (**9b**)	CH_2Cl_2	1400	0.7
	cyclohexane	1200	0.8

[a] The concentrations (~10^{-5} M) for **7** and **9**. [b] Time-resolved fluorescence lifetimes are estimated by exponential fitting of decay curve ($R^2 = 0.996-0.999$).

As expected, the quantum yields of the polymers were much smaller than those of the monomeric compounds when CH_2Cl_2 was used as the solvent. Photoinduced electron-transfer between the aminostyrene and oligophenylene−vinylene chromophores may readily take place in this polar solvent. It is particularly noteworthy that the decrease in quantum yields were more prominent for polymers **4b** and **5b** having isopropyl substituent on silicon than those for **4a** and **5a** with methyl substituent. Apparently, Thorpe−Ingold effect may dictate the conformation of **4b** and **5b** to bring the two neighboring chromophores in conformation C (eq 1). As such, polymers **4b** and **5b** might be more folded and the chances for the two chromophores to meet each other in space might be larger and the electron-transfer process might be facilitated.

As can be seen from Table 1, the quantum yields in **4** were more significantly reduced than those in **5** in comparison with the quantum yields of the corresponding monomeric model compounds **7** and **9**, respectively.

The emissions of polymers **4** and **5** were very much solvent dependent. Presumably, the conformation of polymers **4** and **5** would also depend on the nature of the solvent. It is particularly interesting to note that the lifetime of **5a** was comparable to that of **9a** in cyclohexane. This result suggested that there might be no electron transfer in **5a** in this nonpolar solvent. On the other hand, the emission was somewhat quenched in **5b** even in cyclohexane when isopropyl substituent on silicon was incorporated. It seems likely that the bulky isopropyl substituent may bring the neighboring chromophores in closer proximity so that electron transfer might facilely take place.

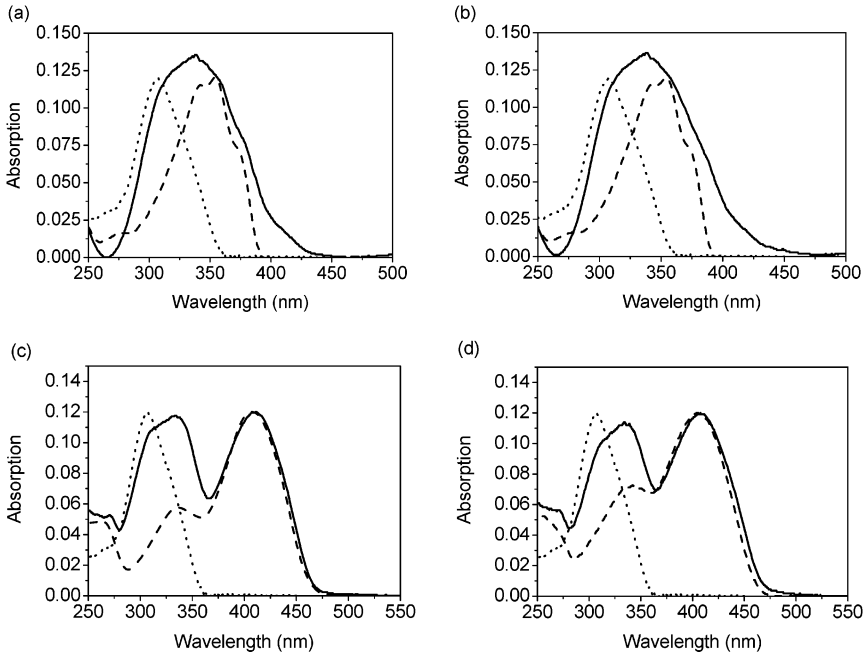


Figure 1. Absorption spectra of polymers **4** or **5** (solid line) and the corresponding monomeric model compounds **7** or **9** (dashed line) and **10** (dotted line) in CH_2Cl_2. Key: (a) **4a**, **7a**, and **10**; (b) **4b**, **7b**, and **10**; (c) **5a**, **9a**, and **10**; (d) **5b**, **9b**, and **10** (concentration: 1×10^{-5} M).

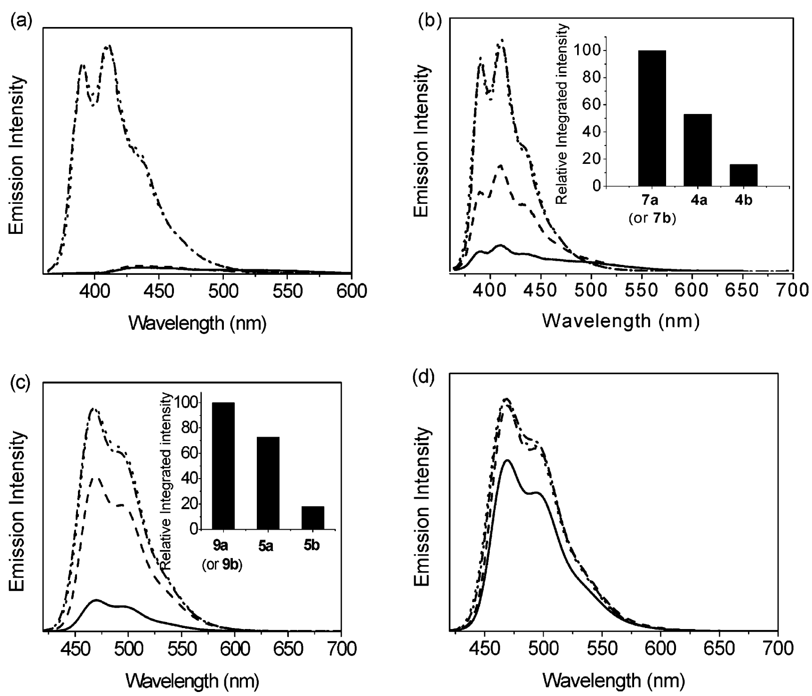


Figure 2. Emission spectra of **4a** (dashed line), **4b** (solid line), **7a** (dashed-dotted line), and **7b** (dotted line) in (a) CH_2Cl_2 and (b) cyclohexane. Inset: the relative ratios of the integrated emission intensities of **4** and **7**. ($\lambda_{ex} = 355$ nm). Emission spectra of **5a** (dashed line), **5b** (solid line), **9a** (dashed−dotted line), and **9b** (dotted line) in (c) CH_2Cl_2. Inset: the relative ratios of the integrated emission intensities of **5** and **9**; (d) cyclohexane ($\lambda_{ex} = 410$ nm) (concentration: 1×10^{-5} M).

Time-Resolved Fluorescence Spectroscopy. Femtosecond laser equipped with streak camera was employed to measure the time-resolved spectra of fluorescence decay in polymers **4**, **5** and the corresponding monomers **7** and **9** in CH_2Cl_2 and in cyclohexane. The fluorescence decay profiles of **4a**, **4b** and **5a**, **5b** in CH_2Cl_2 and in cyclohexane are shown in Figure 3. The fluorescence decay lifetimes (τ) were estimated by one-exponential curve-fittings for monomers **7** and **9** and two-exponential curve-fittings for polymers **4** and **5**, unless otherwise specified. The results are summarized in Tables 2 and 3.

The fluorescence lifetimes, τ, in general, were shorter for **4** than those for **5**; hence the charge separation rates k_{CS} for **4** were larger than those for **5**. In addition, shorter τ's and larger k_{CS}'s were observed for isopropyl-substituted polymers **4b** and **5b** than those for methyl-substituted analogues **4a** and **5a**. As expected, the τ's were shorter and k_{CS}'s were faster in CH_2Cl_2 than those in cyclohexane.

As can be seen from Table 3, two parameters were used to fit the fluorescence decay curves. This observation suggested that there might be two different modes of electron-transfer processes in polymers **4** and **5**. The shorter lifetimes τ_1's, the faster k_{CS1}'s, and the higher charge separation yields Φ_{CS1} may arise from the interaction of two neighboring chromophores separated by a silylene moiety. We have shown that silylene-

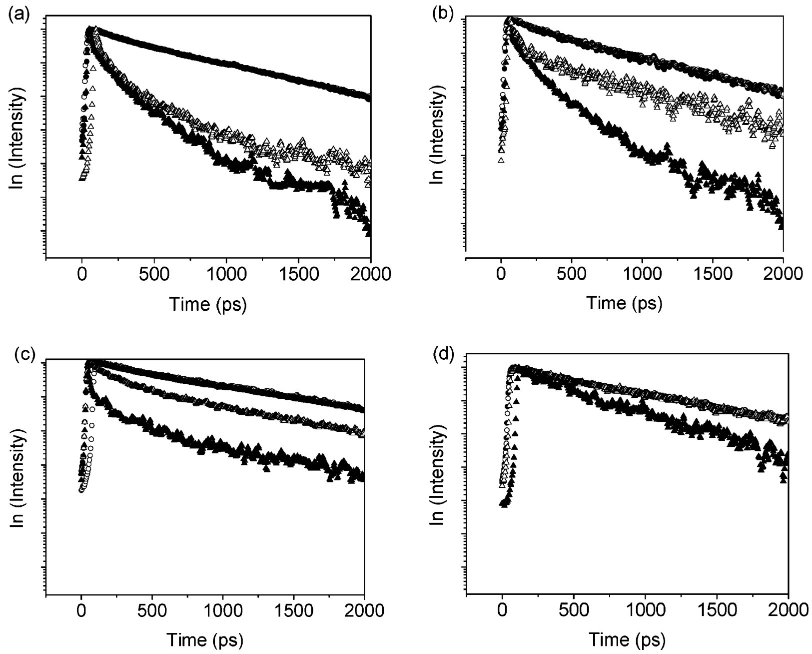


Figure 3. Time-resolved fluorescence decays of **4a** (open up triangle), **4b** (solid up triangle), **7a** (open circle), and **7b** (solid circle) in (a) CH_2Cl_2; (b) cyclohexane (λ_{ex} = 375 nm and monitored at 400 nm). Time-resolved fluorescence decays of **5a** (open up triangle), **5b** (solid up triangle), **9a** (open circle), and **9b** (solid circle) in (c) CH_2Cl_2; (d) cyclohexane (λ_{ex} = 410 nm and monitored at 475 nm) (concentration: 1×10^{-5} M).

Table 3. Fluorescence Lifetime (τ), Charge-Transfer Rate Constant (k_{cs}) and Charge-separation Yield (Φ_{cs}) of 4a,b and 5a,b in CH_2Cl_2 and Cyclohexane at Ambient Temperature[11]

		fluorescence lifetime[b] τ (ps)		charge-transfer rate k_{cs} (ns^{-1})[d]		charge-separation yield Φ_{cs}	
substrate[a]	solvent	τ_1	τ_2	k_{cs1}	k_{cs2}	Φ_{cs1}	Φ_{cs2}
4a	CH_2Cl_2	49 (0.80)	463 (0.20)	19.0	1.1	0.95	0.51
	cyclohexane	91 (0.56)	857 (0.44)	9.9	0.03	0.89	0.03
4b	CH_2Cl_2	29 (0.83)	263 (0.17)	33.0	2.7	0.97	0.72
	cyclohexane	54 (0.71)	303 (0.29)	17.0	2.2	0.94	0.66
5a	CH_2Cl_2	192 (0.50)	1300 (0.50)	4.5	0.03	0.86	0.04
	cyclohexane		1198[c] (1.00)				
5b	CH_2Cl_2	48 (0.80)	854 (0.20)	20.0	0.45	0.97	0.40
	cyclohexane	358 (0.37)	878 (0.63)	2.0	0.3	0.70	0.27

[a] The concentrations (~10^{-5} M) for **4** and **5**. [b] Time-resolved fluorescence lifetimes are estimated by exponential fitting of decay curve (R^2 = 0.97−0.99). The numbers in the bracket are the relative weight of different time constants. [c] One exponential fitting. [d] $k_{cs} = \tau^{-1} - k_s$ where τ is corresponding fluorescence lifetime and k_s is the reciprocal of the fluorescence lifetime of the corresponding monomer (ref 11).

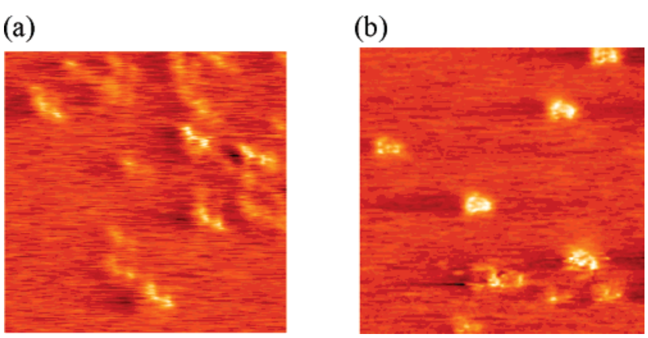


Figure 4. STM image of (a) **4a** and (b) **4b**. Conditions: (a) image size, 27 × 27 nm, E_{bias} 0.80 V, $i_{tunneling}$ 20 pA; (b) image size, 27 × 27 nm, E_{bias} 0.50 V, $i_{tunneling}$ 20 pA.

spaced divinylarene copolymers are highly folded. Accordingly, there is possibility that two non-neighboring chromophores may meet each other through space. Such folding may lead to a second type of interaction between chromophores and, therefore, a second set of longer τ_2's, slower k_{CS2}'s, and the smaller Φ_{CS2}-was observed as depicted in Table 3.

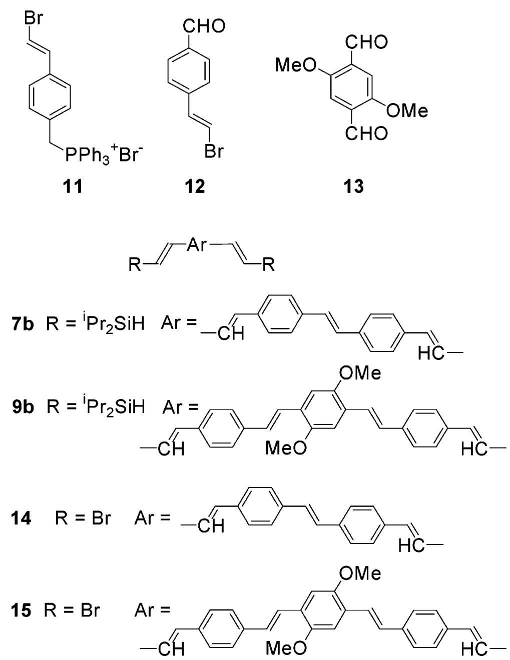
Scanning Tunneling Microscopy. Scanning tunneling microscopy was employed to examine the morphology of polymer **4** on highly ordered pyrolyzed graphite (HOPG) surface and the results are shown in Figure 4. The images of **4a** are fuzzier than those of **4b**, presumably due to the more fluxional conformation of **4a** than that of **4b**. The methyl-substituted **4a** exhibited a relatively loose and elongated feature with a length roughly about 4.3 nm. On the other hand, the morphology of **4b** appeared to be very different and the average diameter was 3.4 nm. Apparently, the isopropyl group may provide a bulky environment to provoke the divinylsilane moieties in **4b** to adopt conformation **C** (eq 1). As a result, the conformation for **4b** would be expected to be in highly coiled structure. Such kind of coiled structure may lead strong interactions between chromophores in **4b** and is seredipiously consistent with the photophysical results described above.

Conclusions

In summary, we have demonstrated the use of the concept of Thorpe−Ingold effect to direct the conformation of silylene-spaced divinylarene copolymers. Since distance is known to play an important role in PET processes, the present investigation suggested that bulky substituent on silicon would bring the chromophores in closer proximity. Copolymers with bulky isopropyl substituent are more folded so that intrachain PET between these chromophores will become more prominent leading to more efficient fluorescence quenching. The results from the STM images appear to be consistent with the outcome of photophysical studies of these polymers. Further investigations on integration of light harvesting and electron transfer in a single polymer are in progress.

Experimental Section

General Data. 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 = 1.0 mLmin^{-1}). Waters Styragel HR2, HR3, HR4 (7.8 × 300 mm) were employed using polystyrene as standard (M_n values range from 375 to 3.5 × 10^6). Absorption spectra and emission spectra were measured with Hitachi U-3310 and Hitachi F-4500 fluorescence spectrophotometers, respectively. Quantum yield was obtained using coumarin **1** in EtOAc as reference (Φ = 0.99).



1,4′-Bis(2-bromovinyl)stilbene (14). To a mixture of **11**[12] (2.80 g, 5.2 mmol) and **12**[13] (1.08 g, 5.1 mmol) in EtOH (90 mL) was added NaOEt [prepared from sodium (0.18 g, 7.8 mmol) in ethanol (30 mL)]. The mixture was refluxed for 15 h and cooled to room temperature. Methanol was added, and the precipitate was collected. The solid was dissolved in toluene to which a trace amount of iodine was added. The mixture was refluxed for 24 h. Solvent was removed in vacuo, and the residue was washed with hexane until washings were almost colorless. The residue was recrystallized from toluene to give **14** as a white solid (1.69 g, 85%): mp 89−90 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 (d, *J* = 14.0 Hz, 2 H), 7.08 (s, 2 H), 7.10 (d, *J* = 14.0 Hz, 2 H), 7.29 (d, *J* = 8.2 Hz, 4 H), 7.47 (d, *J* = 8.2 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 106.5, 126.3, 126.8, 128.2, 135.1, 136.6, 137.0. IR (KBr): ν 3068, 3007, 2921, 1704, 1646, 1503, 1491, 1405, 984, 956, 935, 884, 785 cm^{-1}. HRMS (FAB): calcd for $C_{18}H_{14}{}^{79}Br_2$, 387.9462; found, 387.9454. Anal. Calcd for $C_{18}H_{14}Br_2$: C, 55.42; H, 3.62. Found: C, 55.39; H, 3.32.

1,4-Bis(4-(2-bromovinyl)styryl)-2,5-dimethoxybenzene (15). To a mixture of **11**[12] (5.5 g, 10.3 mmol) and **13** (1.0 g, 5.1 mmol) in EtOH (90 mL) was added NaOEt [prepared from sodium (0.35 g, 15.5 mmol) in ethanol (60 mL)]. The mixture was refluxed for 15 h and cooled to room temperature. Methanol (150 mL) was added, and the resulting precipitate was collected. The solid was dissolved in toluene (100 mL), and the mixture was refluxed in the presence of a trace amount of iodine for 1 day. Solvent was removed in vacuo, and the residue was washed with hexane (300 mL) until washings were almost colorless; the residue was then recrystallized from toluene to give compound **15** as a yellow solid (2.25 g, 80%): mp 189−190 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.94 (s, 6 H), 6.79 (d, *J* = 14.0 Hz, 2 H), 7.09 (d, *J* = 16.4 Hz, 2 H), 7.10 (d, *J* = 14.0 Hz, 2 H), 7.13 (s, 2 H), 7.29 (d, *J* = 8.0 Hz, 4 H), 7.49 (d, *J* = 8.0 Hz, 4 H), 7.50 (d, *J* = 16.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.4, 106.1, 108.7, 123.2, 126.0, 126.2, 126.6, 127.9, 134.5, 136.4, 137.3, 150.9. IR (KBr): ν 3048, 2983, 2917, 2856, 2811, 1597, 1561, 1509 1459, 1410, 1340, 1263, 1212, 1037, 955, 845, 776, 669 cm^{-1}. HRMS (FAB): calcd $C_{28}H_{24}O_2{}^{79}Br_2$, 550.0143; found, 550.0146. Anal. Calcd for $C_{28}H_{24}O_2Br_2$: C, 60.89; H, 4.38. Found: C, 60.57; H, 4.40.

1,4′-Bis[(2-diisopropylsilyl)vinyl]stilbene (7b). Under N_2, to a solution of **14** (0.39 g, 1.0 mmol) in THF (30 mL) cooled at −78 °C was added slowly ^{t}BuLi (2.7 mL of 1.55 M in pentane, 4.2 mmol). After this mixture was stirred for 30 min at −78 °C, chlorodiisopropylsilane (0.4 mL, 2.1 mmol) was added, and the mixture was gradually warmed to room temperature, stirring was continued for 3 h, and the reaction was quenched with H_2O (3.0 mL). The aqueous layer was extracted with Et_2O (3 × 10 mL), and the organic layer was washed with brine (20 mL), dried ($MgSO_4$), filtered, and evaporated in vacuo. The residue was chromatographed on Et_3N-treated silica gel (CH_2Cl_2/hexane 1:4) to afford **7b** as an oil (0.37 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05−1.16 (m, 28 H), 3.76−3.78 (m, 2 H), 6.43 (dd, *J* = 19.0, 4.7 Hz, 2 H), 7.05 (d, *J* = 19.0 Hz, 2 H), 7.11 (s, 2 H), 7.45 (d, *J* = 8.3 Hz, 4 H), 7.50 (d, *J* = 8.3 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.9, 18.7, 126.4, 126.6, 126.7, 128.1, 137.0, 137.4, 146.9. IR (KBr): ν 2962, 2917, 2852, 2325, 1593, 1462, 1381 cm^{-1}. HRMS (FAB): calcd for $C_{30}H_{44}Si_2$, 460.2982; found, 460.2977.

1,4-Bis(4-(2-diisopropylsilylvinyl)styryl)-2,5-dimethoxybenzene (9b). Under N_2, to a solution of **15** (0.55 g, 1.0 mmol) in THF (30 mL) cooled at −78 °C was added slowly ^{t}BuLi (2.7 mL of 1.55 M in pentane, 4.2 mmol). After the reaction was stirred for 30 min at −78 °C, chlorodiisopropylsilane (0.4 mL, 2.1 mmol) was added, and the mixture was gradually warmed to room temperature, stirring was continued for 3 h, and the reaction was quenched with H_2O (3.0 mL). The aqueous layer was extracted with Et_2O (3 × 20 mL), and the organic layer was washed with brine (20 mL), dried ($MgSO_4$), filtered, and evaporated in vacuo. The residue was chromatographed on Et_3N-treated silica gel (CH_2Cl_2/*n*-hexane 1:4) and the solid was recrystallized from pentane to afford **9b** as a yellow solid (0.50 g, 81%): mp 183−184 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00−1.20 (m, 28 H), 3.75−3.77 (m, 2 H), 3.95 (s, 6 H), 6.40 (dd, *J* = 19.1, 4.7 Hz, 2 H), 7.04 (d, *J* = 19.1 Hz, 2 H), 7.12 (d, *J* = 16.7 Hz, 2 H), 7.12 (s, 2 H), 7.44 (d, *J* = 8.3 Hz, 4 H), 7.50 (d, *J* = 16.7 Hz, 2 H), 7.53 (d, *J* = 8.3 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 19.0, 56.5, 108.7, 121.2, 122.8, 126.2, 126.4, 128.1, 132.0, 136.9, 137.2, 146.7, 151.0. IR (KBr): ν 2950, 2933, 2885, 2852, 2831, 2104, 1556, 1516, 1487, 1462, 1348, 1205, 1176, 964, 882, 870, 788, 764, 637 cm^{-1}. HRMS (FAB): calcd for $C_{40}H_{54}O_2Si_2$, 622.3662; found, 622.3657.

Polymer 4a. A mixture of **6**[7] (93 mg, 0.2 mmol), **7a** (70 mg, 0.2 mmol), NaI (64 mg), and $RhCl(PPh_3)_3$ (4.6 mg, 0.001 mmol) in THF (5 mL) was refluxed under N_2 for 10 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 polymer (122 mg, 75%): M_n = 9300; PDI = 2.45. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.30 (s, 12 H), 3.61−3.69 (m, 24 H), 6.19−6.24 (d, 2 H), 6.45−6.61 (m, 6 H), 6.82−6.90 (m, 4 H), 7.08 (s, 2 H), 7.26−7.30 (d, 4 H), 7.33−7.44 (m, 8 H). IR (KBr): ν 3391, 2951, 2866, 1605, 1515, 1390, 1349, 1247, 1185, 1113, 986, 838, 736 cm^{-1}. Anal. Calcd for $C_{50}H_{62}N_2O_4Si_2$: C, 74.03; H, 7.70; N, 3.45. Found: C, 73.09; H, 7.32; N, 3.39.

Polymer 4b. In a manner similar to that described above, a mixture of **6** (93 mg, 0.2 mmol), **7b** (92 mg, 0.2 mmol), NaI (64 mg), and $Rh(PPh_3)_3Cl$ (4.6 mg, 0.001 mmol) was converted to **4b** (115 mg, 62%): M_n = 8600; PDI = 2.27. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07−1.12 (m, 28 H), 3.63−3.71 (m, 24 H), 6.16−6.20 (d, 2 H), 6.60−6.64 (d, 2 H), 6.66−6.90 (d, 4 H), 6.90−6.99 (m, 4 H), 7.11 (d, 2 H), 7.35−7.37 (d, 4 H), 7.48−7.50 (m, 8 H).

IR (KBr): ν 3446, 2948, 2861, 1652, 1604, 1539, 1520, 1457, 1424, 1387, 1350, 1275, 1229, 1184, 989, 881, 789 cm^{-1}.

Polymer 5a. In a manner similar to that described above, a mixture of **8**[7] (84 mg, 0.2 mmol), **9a** (102 mg, 0.2 mmol), NaI (64 mg), and $Rh(PPh_3)_3Cl$ (4.6 mg, 0.001 mmol) was converted to **5a** (140 mg, 75%): M_n = 8700; PDI = 2.05. ^1H NMR (400 MHz, $CDCl_3$): δ 0.28 (s, 12 H), 3.50−3.65 (16 H), 3.65−3.80 (m, 4 H), 3.93 (s, 6 H), 6.20−6.30 (d, 2 H), 6.45−6.55 (d, 2 H), 6.55−6.75 (d, 4 H), 6.80−7.00 (m, 4 H), 7.05−7.15 (m, 4 H), 7.30−7.35 (d, 4 H), 7.40−7.55 (m, 10 H). IR (KBr): ν 3620, 3187, 2921, 2840, 1659, 1589, 1516, 1250, 1209, 1176, 1107, 1033, 821, 674 cm^{-1}.

Polymer 5b. In a manner similar to that described above, a mixture of **8** (84 mg, 0.2 mmol), **9b** (125 mg, 0.2 mmol), NaI (64 mg), and $Rh(PPh_3)_3Cl$ (4.6 mg, 0.001 mmol) was converted to **5b** (125 mg, 60%): M_n = 7500; PDI = 2.17. ^1H NMR (400 MHz, $CDCl_3$): δ 1.05−1.20 (m, 28 H), 3.55−3.70 (m, 16 H), 3.70−3.80 (m, 4 H), 3.95 (s, 6 H), 6.15−6.25 (d, 2 H), 6.45−6.55 (d, 2 H), 6.60−6.70 (d, 4 H), 6.85−7.05 (m, 4 H), 7.05−7.15 (m, 4 H), 7.30−7.40 (d, 4 H), 7.45−7.60 (m, 10 H). IR (KBr) ν 3436, 2950, 2885, 2856, 1650, 1614, 1520, 1458, 1405, 1368, 1221, 1185, 1119, 972, 788, 633 cm^{-1}.

Time-Resolved Fluorescence Measurements. A mode-locked Ti:sapphire laser (wavelength, 750 nm for **4**, 820 nm for **5**; repetition rate, 76 MHz; pulse width, <200 fs) passed through an optical parametric amplifier. The fluorescence of sample was reflected by a grating (150 g/mm; BLZ: 500 nm) and detected by an optically triggered streak camera (Hamamatsu C5680) with a time resolution of about 3 ps.

STM Characterization. STM imaging of polymers **4a** and **4b** was carried out with a NanoScope IIIa controller equipped with a low-current converter for experiments requiring high tunneling impedance (Veeco Metrology Group/Digital Instruments, USA). The STM probes were commercially available Pt/Ir tips (PT, Nanotips, Veeco Metrology Group/Digital Instruments, USA). To observe individual polymers, a relatively diluted solution was prepared by dissolving 1 μg/mL **4a**or **4b** in hexane (ca. 0.25 μM). The polymers were drop-cast onto freshly cleaved HOPG (highly orientated pyrolytic graphite, grade ZYD, Advanced Ceramics Corp.), subjected to vacuum-dry (∼30 min, 120 mTorr) to remove trace amount of solvent, and rapidly transferred to a chamber where dry N_2 was purging throughout the experiments and the humidity was lower than 2%. Typical imaging conditions were 0.5−1.2 V in bias voltage and 10∼50 pA in tunneling current. The dimensions of images were calibrated by the unit cell vectors of the underlying HOPG.

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Supporting Information Available: Figures showing ^1H NMR spectra of all new compounds and electrochemical properties of **7** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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