Articles

Coupling of FRET and Photoinduced Electron Transfer in Regioregular Silylene-Spaced Energy Donor–Acceptor−Electron Donor Copolymers

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ABSTRACT: Two new silylene-spaced copolymers containing three kinds of different chromophores in regioregular manner were synthesized by rhodium-catalyzed hydrosilylation of a bisalkyne with a bis-silyl hydride. The photophysical and electrochemical properties of these polymers and the corresponding monomeric models were investigated. Time-resolved fluorescence spectroscopy has been employed for detailed kinetic analyses. The chromophores in these polymers have been shown to exhibit light harvesting to collect light energy, energy transfer, and efficient charge separation. The overall efficiencies involving both FRET and PET in these silylene-spaced vinylarene copolymers can be up to 96%.

Introduction

Natural photosynthetic process occurs in a nanometric assembly of chromophores that serve as antenna to induce energy transfer and launch a series of electron transfer processes that ultimately reach the reaction center which drives the reduction of various substrates.[1,2] Research on artificial light harvesting and photoinduced electron transfer systems by assembling chromophores in dendrimers,[3] functionalized polymers,[4,5] Langmuir–Blodgett films,[6] microspheres,[7] monolayers,[8] hydrogen-bonded organic gels,[9] and organic–inorganic hybrid materials[10] have been extensive. However, integrations of light harvesting and electron transfer components into one system have been sporadically explored.[11] To illustrate, supramolecular systems involving covalently bonded metal prophyrins, metal-free porphyrins and fullerene, and related approaches have been designed as models for photosynthetic processes.[11] We recently reported a series of silylene-spaced divinylarene copolymers having alternating donor–acceptor chromophores that exhibit versatile photophysical properties including highly efficient intrachain energy or electron transfer.[5] For example, effective photoinduced electron transfer from amino styrene moiety to anthracene chromophore has been found in copolymer **1**.[5f] The silylene moiety in **1** can be considered as an insulating spacer, and no conjugative interactions between the π systems and the silicon moiety may occur.[5,12] The advantage of using silylene-spaced divinylarene copolymers relies on the easy accessibility by regioselective hydrosilylation of a bisalkyne with a bis-silyl hydride. To illustrate, three different kinds of chromophores can be selectively assembled into the polymeric backbone where sequential energy transfer has been observed.[5d] It is envisaged that regioselective incorporation of a donor chromophore as an antenna for absorbing light into **1** or the like could lead to an integrated polymeric archetype for light harvesting and electron transfer. We now wish to report the design, synthesis, and photophysical investigations of the integrated three-component systems in regioselective manner for investigating sequential energy and electron transfer.

Results and Discussion

Strategy. The general strategy is to design a polymer having an energy donor ($\mathbf{D_E}$), an electron donor ($\mathbf{E_d}$), and an acceptor (**A**) to collect fluorescence resonance energy from $\mathbf{D_E}$ forming an excited state of **A**, which will then accept an electron from $\mathbf{E_d}$. The most important criterion is to have these chromophores $\mathbf{D_E}$, **A**, and $\mathbf{E_d}$ in close proximity so that fluorescence resonance energy transfer (FRET) and electron transfer can take place efficiently because they are distance dependent. Hydrosilylation reaction of a bisalkyne with a bis-silyl hydride has been shown to be extremely efficient for the synthesis of silylene spaced divinylarene copolymers like **1** having different chromophores arranged in alternating manner.[5] Thus, two different kinds of polymers **2** were designed in this investigation. Polymer **2a** involved an energy transfer pair consisted of 4,4′-divinylbiphenyl ($\mathbf{D_E}$) and 4,4′-divinylstilbene (**A**).[5c] It is known that amines may quench the fluorescence of a fluorophore by means of the photoinduced electron transfer (PET).[13] Accordingly, bis-aniline moiety was employed as an $\mathbf{E_d}$ locating next to an **A**.

In a similar manner, the second system **2b** was comprised of 4,4′-divinylbiphenyl and 9-vinylanthracene as the FRET pair which was coupled with an aza-crown ether moiety as an electron donor for the PET. As shown in Figure 1, the emission maximum of **5** matched well with the absorption maximum of

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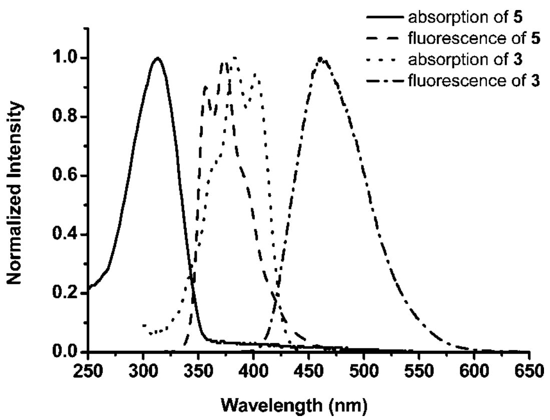


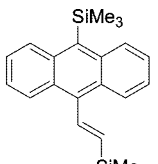
Figure 1. Normalized absorption spectrum of **5** (solid line) and **3** (dashed line) and emission spectra of **5** (dotted line, excitation wavelength: 310 nm) and **3** (dash-dotted line, excitation wavelength: 382 nm) in CH_2Cl_2.

Table 1. Photophysical Properties and Frontier Orbital Energies of 3, 4, 5, 6, and 7 in CH_2Cl_2

	$\lambda_{\max\ abs}$ (nm)	$\lambda_{\max\ em}$ (nm)	Φ^a	$E_{ox}{}^b$ (eV)	HOMO^c (eV)	LUMO^d (eV)
3	382	461	0.64	0.53	−5.33	−2.45
4	307	378	0.03	0.18	−4.98	−1.57
5	310	360, 375	0.86	1.05	−5.85	−2.31
6	270	335	0.07	0.29	−5.09	−1.25
7	355	390, 410	0.91	0.78	−5.58	−2.40

[a] Using coumarin 1 as a reference. [b] Oxidation potentials determined by cyclic voltammetry using 0.1 M Bu_4NPF_6 as electrolyte with Pt working electrode, Pt wire counter electrode, and $Ag/AgNO_3$ reference electrode. [c] Estimated by E_{ox} vs Fc/Fc^+. [d] Estimated by HOMO and optical band gap from absorption spectra.

3. The photophysical properties and frontier orbital energies of the model compounds **3–7** containing these chromophores are outlined in Table 1.



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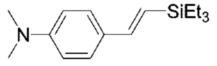

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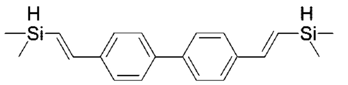

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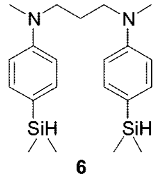

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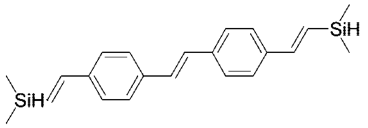

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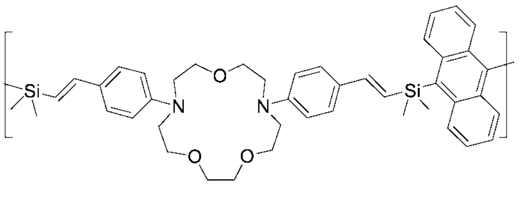
Synthesis. Monomer **3** was prepared by Heck reaction of **8**[14] with trimethylvinylsilane (eq 1). Diamine **6** was prepared according to eq 1. Bromination of **9**[15] afforded the corresponding dibromide **10**, which was treated with BuLi followed with chlorodimethylsilane to give **6** in 68% overall yield. Polymer **2a** was synthesized regioselectively according to Scheme 1. Wittig–Horner reaction of **11** with **12** afforded 84% yield of **13**. Sequential Sonogashira reaction of **13** upon treatment with 1 equiv of triisopropylsilylacetylene yielded **14**, which was then allowed to react with trimethylsilylacetylene to afford **15** in 74% overall yield. Selective removal of the trimethylsilyl group in **15** with base led to 81% yield of **16**. Rhodium-catalyzed hydrosilylation of **5**[5e] with 2 equiv of **16** resulted in the formation of **17** in 66% yield. Desilylation of the TIPS group in **17** with TBAF furnished **18** in 90% yield. Hydrosilylation of **18** with **6** afforded the silylene-spaced polymer **2a** consisting of three chromophores in a regioregular arrangement. The molar fraction of each chromophore in polymer **2a** was 1 to 2 to 2, corresponding to $\mathbf{D_E}$, **A**, and $\mathbf{E_d}$, respectively.



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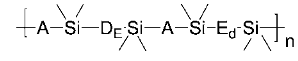

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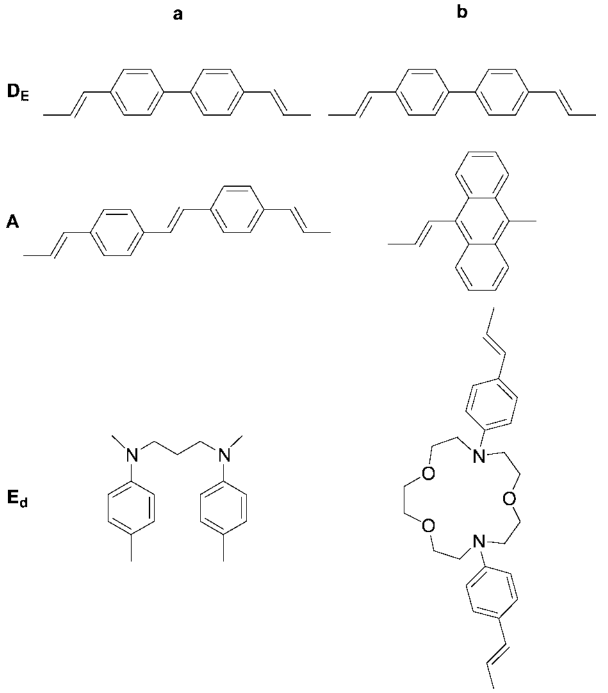
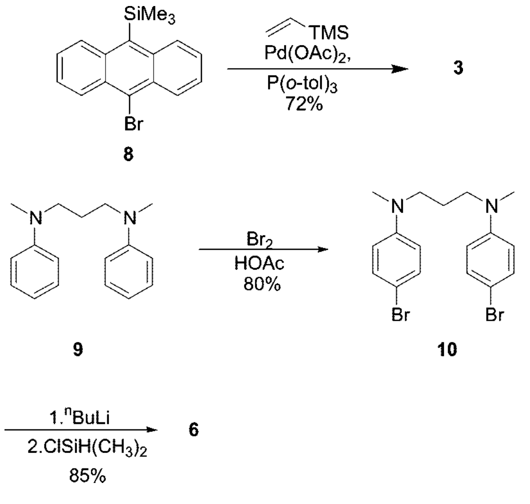
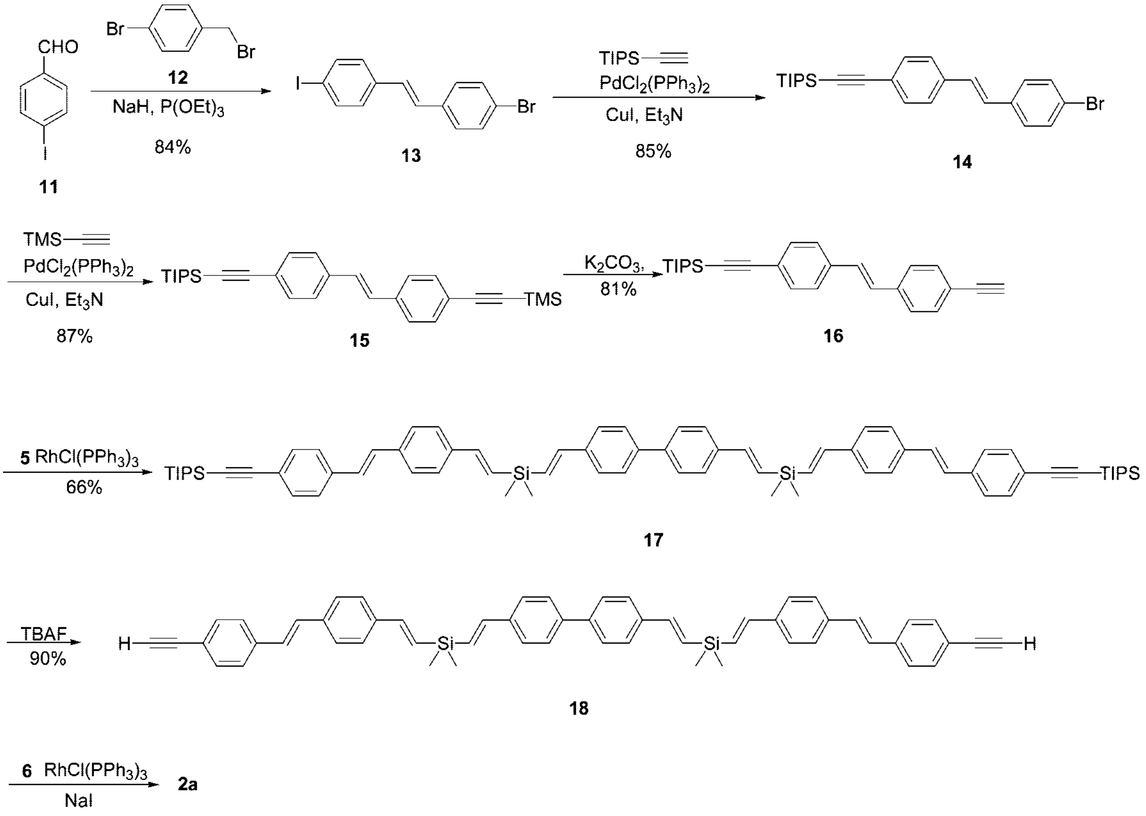
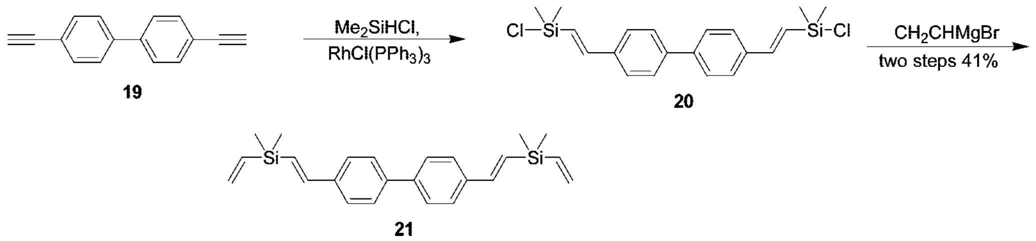




Scheme 1



Scheme 2



Treatment of bisalkyne **19** with chlorodimethylsilane in the presence of $RhCl(PPh_3)_3$ gave **20**, followed by substitution with vinyl Grignard reagent to obtain **21** (Scheme 2).

Dibromoanthracene was treated with BuLi followed by chlorodimethylsilane to give **22** in 51% yield. Rhodium-catalyzed hydrosilylation of bis-alkynyl-substituted aza-crown ether **23** with **22** gave **24** which underwent palladium-catalyzed Heck reaction with **21** furnished **2b** with a regioregular combination of three different chromophores separated by dimethylsilylene moieties.

Photophysical Properties of Polymers. The absorption spectrum of polymer **2a** in CH_2Cl_2 is shown in Figure 2a. In comparison with the λ_{max} of the corresponding monomers **5–7**, the absorption profile for **2a** can be considered as the summation of the absorption of each of these monomeric chromophores. Thus, the absorption around 350 nm was attributed to divinylstilbene chromophore in **2a**, around 310 nm to the absorption of the divinylbiphenyl moiety, and around 270 nm as the absorption of the aminostyrene group. The emission spectra of **2a** in different solvents are shown in Figure 2b. The quantum yields of the emission of **2a** around 400 nm were solvent dependent (Table 2), and no emission due to divinylbiphenyl chromophore was observed. It is interesting to note that charge transfer band around 500 nm was observed when the measurements were taken in CH_2Cl_2 or THF.[16] These results suggested that energy transfer was very efficient, and photoinduced electron transfer between the aminobenzene group (**E$_d$**) and the divinylstilbene moiety (**A**) might readily take place in **2a**.

The UV absorption and emission spectra for **2a** were further examined by titration with $Zn(ClO_4)_2$ in CH_2Cl_2 (Figure 3). The intensities at 270 nm in the absorption spectra were decreased with the added zinc ion concentration. On the other hand, the emission intensities around 411 nm were increased with Zn^{2+} concentration. Diamine moiety in **2a** is known to form chelation complex with metal ions. Chelation-enhanced fluorescence (CHEF) was indeed observed for **2a** upon addition of Zn^{2+}. These results further support the electron transfer process between the aminobenzene group (**E$_d$**) and the divinylstilbene moiety (**A**) in **2a**.

The absorption and emission spectra (excitation at 310 nm) of **2b** are shown in Figure 4. The quantum yields were also solvent dependent, and the results are shown in Table 2 and Figure 4c. Similar to those observed for **2a**, the addition of Pb^{2+} also perturbed the absorption and emission profiles (Figure 4), presumably due to complexation with the crown ether moiety in **2b**. It is interesting to note that there was very weak emission arising from **D$_E$** chromophore (4,4′-divinylbiphenyl).

Time-Resolved Spectroscopy. Femtosecond laser equipped with a streak camera was employed to measure the time-resolved

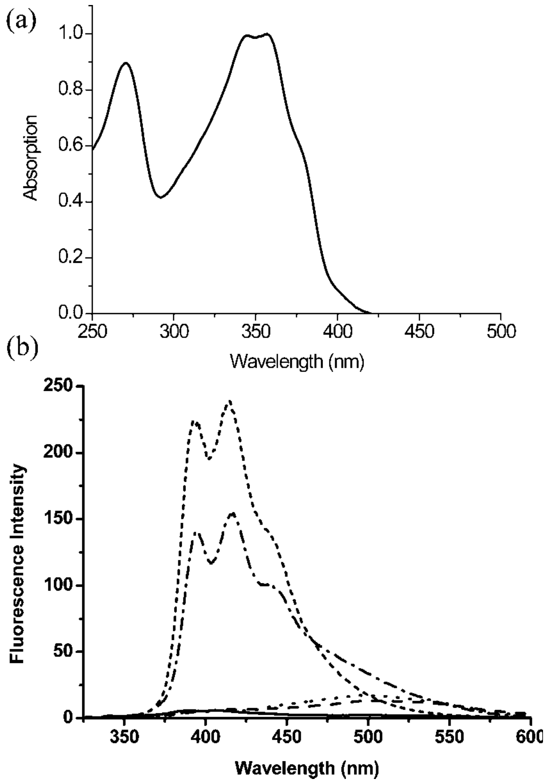


Figure 2. (a) Absorption spectrum of **2a** (10^{-5} M) in CH_2Cl_2. (b) Fluorescence spectra of **2a** (10^{-5} M, $\lambda_{ex} = 310$ nm) in CH_3CN (solid line), CH_2Cl_2 (dashed line), THF (dotted line), toluene (dash-dotted line), and cyclohexane (short-dashed line).

Table 2. Quantum Yields[a] of 2a and 2b in Different Solvents

polymer	cyclohexane	toluene	THF	CH_2Cl_2	CH_3CN
2a	0.643	0.438	0.065	0.064	0.026
2b	0.417	0.167	0.066	0.065	

[a] Quantum yield was obtained using coumarin-I in EtOAc as reference ($\Phi = 0.99$).

spectra of fluorescence quenching in copolymers **2a** and **2b**. As discussed previously, both FRET between $\mathbf{D_E}$ and **A** chromophores and PET between $\mathbf{E_d}$ and **A** would take place. The two processes can be monitored by the fluorescence decay of chromophores in copolymers, and the rate constant and efficiency can be estimated comparing with the corresponding reference monomers.

As shown in Figure 4, there is residual emission from the donor chromophore divinylbiphenyl moiety. The fluorescence decay profiles of divinylbiphenyl moiety ($\mathbf{D_E}$) in copolymer **2b** and the corresponding reference monomer **5** are shown in Figure 5. The fluorescence decay lifetimes (τ_E) were estimated by exponential curve fittings to give lifetimes 54 ps for $\mathbf{D_E}$ in **2b** and 900 ps for **5**, and the energy transfer rate and efficiency were calculated by eqs 1 and 2.

$$k_E = {\tau_E}^{-1} - k \tag{1}$$

$$\Phi_E = k_E/{\tau_E}^{-1} \tag{2}$$

where τ_E is the fluorescence decay lifetimes of $\mathbf{D_E}$ and k is the reciprocal of the fluorescence lifetime of corresponding reference monomers (e.g., **5**).[17] Φ_E and k_E denote energy transfer efficiency and rate, respectively. The k_E and Φ_E between $\mathbf{D_E}$ and **A** moieties in copolymer **2b** were thus calculated to be 1.7 × 10^{10} s^{-1} and 0.93.

Unlike **2b**, FRET between $\mathbf{D_E}$ and **A** in **2a** was much more efficient than that in **2b** (Figure 2b). The energy transfer from biphenyldivinyl moiety ($\mathbf{D_E}$) to divinylstilbene chromophore (**A**) in **2a** was too fast to be measured by a streak camera with instrument limitation about 3 ps. As a result, the fluorescence decay lifetime of $\mathbf{D_E}$ in **2a** was assumed to be 3 ps. The rate constant k_E and quantum efficiency Φ_E between $\mathbf{D_E}$ and **A** moieties in **2a** were estimated to be 3.3 × 10^{11} s^{-1} and 0.99, respectively. These results are outlined in Table 3.

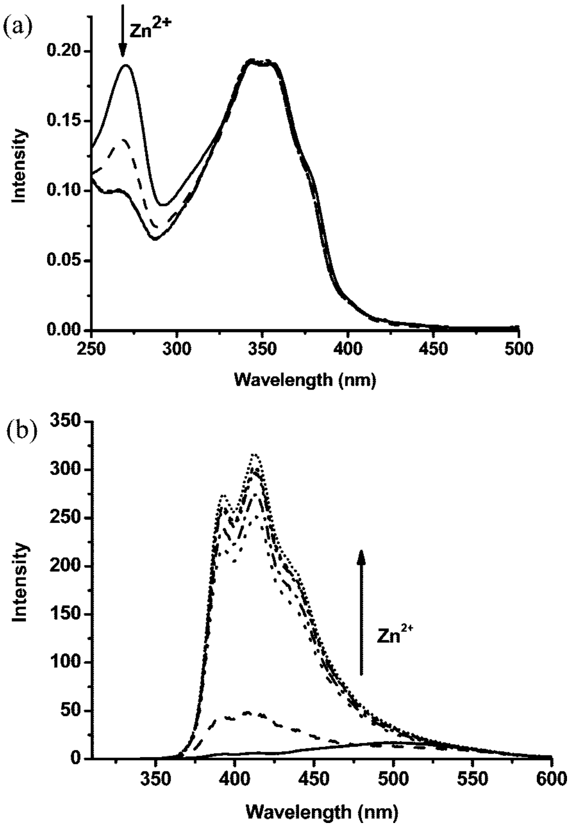


Figure 3. (a) Absorption and (b) emission spectra ($\lambda_{ex} = 310$ nm) of **2a** (1 × 10^{-5} M) in CH_2Cl_2 titrated with $Zn(ClO_4)_2$.

The PET in copolymers **2** was investigated by time-resolved spectra of fluorescence quenching monitoring at the emission of **A**. The charge transfer rate constant k_{CS} and charge-separation yield Φ_{CS} were calculated according to eqs 3 and 4,[18] in which the k_s is the reciprocal of the fluorescence lifetime of corresponding reference monomers[17] and τ_{CS} is the fluorescence decay lifetime of **A** in copolymers.

$$k_{CS} = {\tau_{CS}}^{-1} - k_s \tag{3}$$

$$\Phi_{CS} = k_{CS}/{\tau_{CS}}^{-1} \tag{4}$$

Figure 6 shows the fluorescence decay profiles of divinylstilbene chromophore (**A**) in **2a** and corresponding reference monomer **7**. Biexponential fitting was employed to obtain lifetimes of divinylstilbene chromophore (**A**) to be 28 ps (67%) and 412 ps (33%), and the fluorescence lifetime of **7** is 1050 ps. According to eqs 3 and 4, the k_{CS} and Φ_{CS} were calculated, and the results are summarized in Table 3. The fluorescence decay profiles of the 10-vinylanthracene chromophore (**A**) in **2b** is shown in Figure 7. The fluorescence decay lifetimes (τ_E) were estimated by exponential fittings as 22 ps (65%) and 194 ps (28%) for 10-vinylanthracene chromophore (**A**) in **2b**, and the fluorescence lifetime of **3** is 12 ns measured by single photon counting. The charge-transfer rate constant k_{CS} and the corresponding charge-separation yield Φ_{CS}'s were calculated according to eqs 3 and 4, and the results are listed in Table 3.

As can be seen from Table 3, two different fluorescence

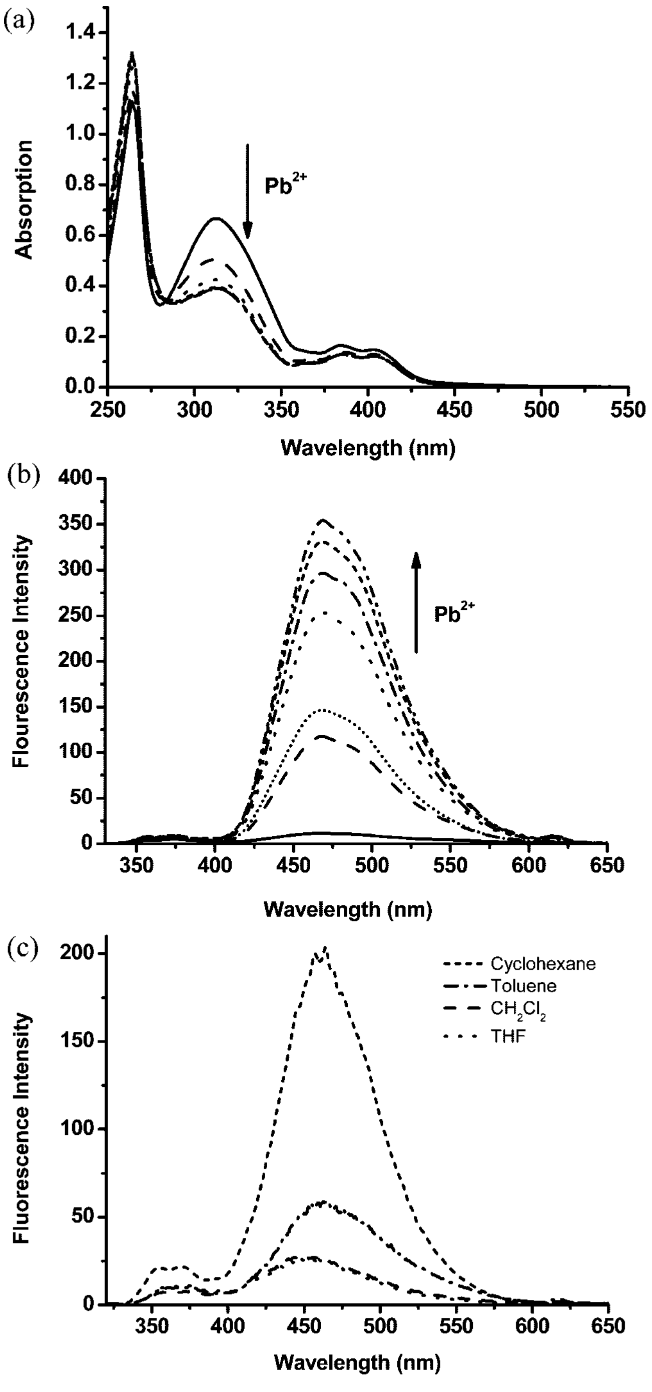


Figure 4. (a) Absorption and (b) emission spectra ($\lambda_{ex} = 311$ nm) of **2b** in CH_2Cl_2 (10^{-5} M) titrated with Pb^{2+}. (c) Emission spectra of **2b** (10^{-5} M) in different solvents.

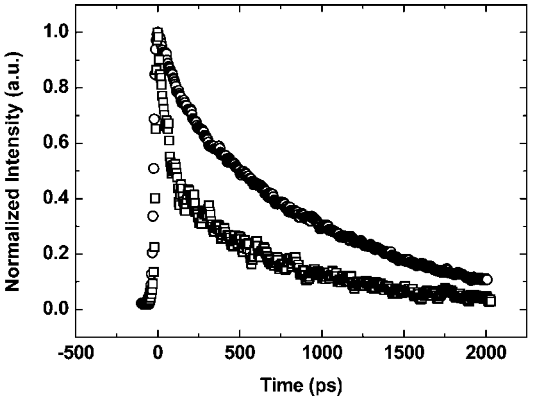


Figure 5. Time-resolved fluorescence decay of divinylbiphenyl chromophore (**D**$_E$) in **2b** (open square) and the corresponding monomeric reference **5** (open square) in CH_2Cl_2 monitoring at 360–380 nm ($\lambda_{ex} = 300$ nm).

Table 3. Fluorescence Lifetime (τ), Rate Constant (k_{CS}), and Yield (Φ_{CS}) of 2a and 2b in CH_2Cl_2 at Ambient Temperature

	energy transfer			electron transfer			
	τ_E (ps)	k_E (s^{-1})	Φ_E	τ_E (ps)	k_{CS} (s^{-1})	Φ_{CS}	Φ_{total}[a]
2a	3[b]	3.3×10^{11}	0.99	28 (67%)	3.5×10^{10}	0.97	0.96
				412 (33%)	0.37×10^{9}	0.57	0.56
2b	54	1.7×10^{10}	0.93	22 (67%)	4.54×10^{10}	0.99	0.92
				194 (33%)	5.07×10^{9}	0.98	0.91

[a] Φ_{total} is the total efficiency from energy transfer to electron transfer. It can be obtained by multiplying Φ_E and Φ_{CS}. [b] The lifetime was obtained by the limitation of instrument.

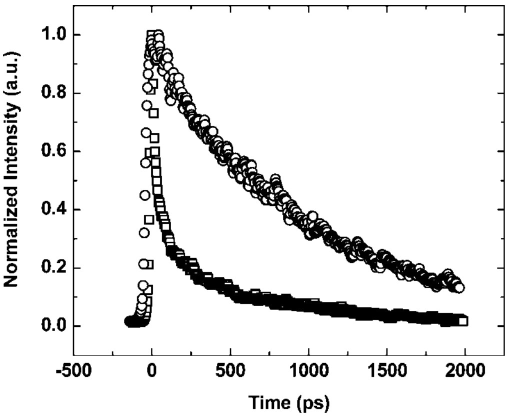


Figure 6. Time-resolved fluorescence decay of **A** in copolymer **2a** (open square) and corresponding monomer **7** (open circle) in CH_2Cl_2 monitoring at 410–420 nm ($\lambda_{ex} = 300$ nm).

lifetimes were obtained for each of **2a** and **2b**. Similar behavior was observed in related systems.[5f,h] This observation suggested that there might be two different modes of electron transfer processes in these polymers. The shorter lifetimes τ_1's, the faster k_{CS}'s, and the higher charge separation yields Φ_{CS} may arise from the interaction of two neighboring chromophores separated by a silylene moiety. It is interesting to note that the presence of the geminal dimethyl group on silicon might dictate the relative conformation of the remaining substituents on this silicon atom. Indeed, it has recently been shown that the Thorpe−Ingold effect might play an important role on the photophysics of silylene-spaced divinylarene copolymers.[5g,h] Accordingly, the silylene-spaced divinylarene copolymers are highly folded.[5] As such, the two non-neighboring chromophores might meet each other through space. Slower rates might be expected from the through-space electron transfer between non-neighboring donor aminostyrene chromophore and the acceptor moiety in **2a** or **2b**.

Conclusions

It is now well documented that the silylene-spaced copolymers exhibit a variety of fascinating photophysical properties.[5] These copolymers are conveniently synthesized by rhodium-catalyzed hydrosilylation of a bisalkyne with a bis-silyl hydride. The silylene moiety has provided an insulating tetrahedral spacer between two conjugated moieties. The emission wavelength can thus be well-adjusted, and the photophysical properties of polymers can be readily tuned. In addition, because of the presence of alkyl substituents on silicon which may increase the chain flexibility, the polymers may be more soluble in

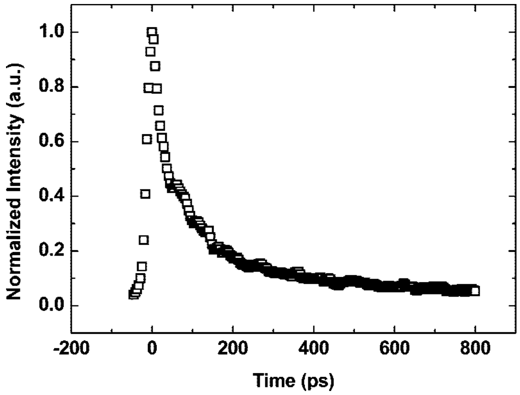


Figure 7. Time-resolved fluorescence decay of **A** in copolymer **2b** (open square) monitoring at 460–480 nm (λ_{ex} = 300 nm).

organic solvent and therefore more processable. Since the silylene moiety has tetrahedral structure, the silylene−chromophore copolymer may be highly folded. The distance between two neighboring chromophores separated by a silylene moiety (e.g., **2**) xptk;1would be relatively short so that the chromophores in these polymers can exhibit light harvesting to collect light energy, energy transfer, and efficient charge separation. The overall efficiencies involving both FRET and PET in these silylene-spaced vinylarene copolymers can be up to 96%.

Experimental Section

General. High-resolution mass spectrometric measurements were obtained from Jeol-JMS-700 mass spectrometry using FAB method in 3-nitrobenzyl alcohol matrix. 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 mL/min). Waters Styragel HR2, HR3, HR3, and HR4 (7.8 × 300 mm) columns were employed for molecular weight determination, and polystyrenes were used as standard (M_n values ranging from 375 to 3.5 × 10^6). Absorption spectra were measured with a Hitachi U-3310 spectrophotometer and emission spectra with a Hitachi F-4500 fluorescence spectrophotometer. The quantum yield was obtained using coumarin-I in EtOAc as reference (Φ = 0.99). In time-resolved fluorescence experiments, a mode-locked Ti:sapphire laser (wavelength: 900 nm; repetition rate: 76 MHz; pulse width: <200 fs) passed through an optical parametric amplifier. The fluorescence of sample was reflected by a grating (150 grooves/mm; BLZ: 500 nm) and detected by an optically triggered streak camera (Hamamatsu C5680) with a time resolution of about 0.3 ps. Oxidation potentials were determined by cyclic voltammetry using 0.1 M Bu_4NPF_6 as electrolyte with Pt working electrode, Pt wire as counter electrode, and Ag/$AgNO_3$ as reference electrode. Samples of 1 mM solution were prepared in dry CH_2Cl_2. HOMO was estimated by E_{ox} vs Fc/Fc^+, and LUMO was estimated by HOMO and optical band gap from the absorption spectra. Monomers **4**,[5f] **5**,[5e] and **7**[5a] were prepared according to literature procedures.

(10-Bromoanthracen-9-yl)trimethylsilane (8). A solution of *n*-BuLi in hexane (6.0 mL of 2.5 M solution, 14.9 mmol) was added dropwise to a suspension of 9,10-dibromoanthracene (5.00 g, 14.9 mmol) in THF (400 mL) at −78 °C. The mixture was stirred at −78 °C for 15 min. Chlorotrimethylsilane (2.77 g, 25.5 mmol) was added dropwise at −78 °C, and the mixture was allowed to warm gradually to room temperature (rt) and stirred for 8 h. $NaHCO_3$ solution was added, and the organic layer was separated. The aqueous layer was extracted with ether, the combined organic solution was dried ($MgSO_4$) and evaporated in vacuo, and the residue was passed through a short column of silica gel (hexane) to give **8** (3.20 g, 65%); mp 74–75 °C. IR (KBr): ν 3079, 3028, 2952, 2895, 2867, 1440, 1419, 1384, 1306, 1268, 1253, 1230, 920, 875, 837, 770, 743, 654 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.72 (s, 9 H), 7.48–7.60 (m, 4 H), 8.44 (d, J = 8.8 Hz, 2 H), 8.64 (d, J = 8.9, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.6, 124.8, 126.3, 126.6, 128.8, 129.0, 130.2, 137.1, 137.6. HRMS (FAB) (M^+, $C_{17}H_{17}{}^{79}BrSi$): calcd: 328.0283; found: 328.0279.

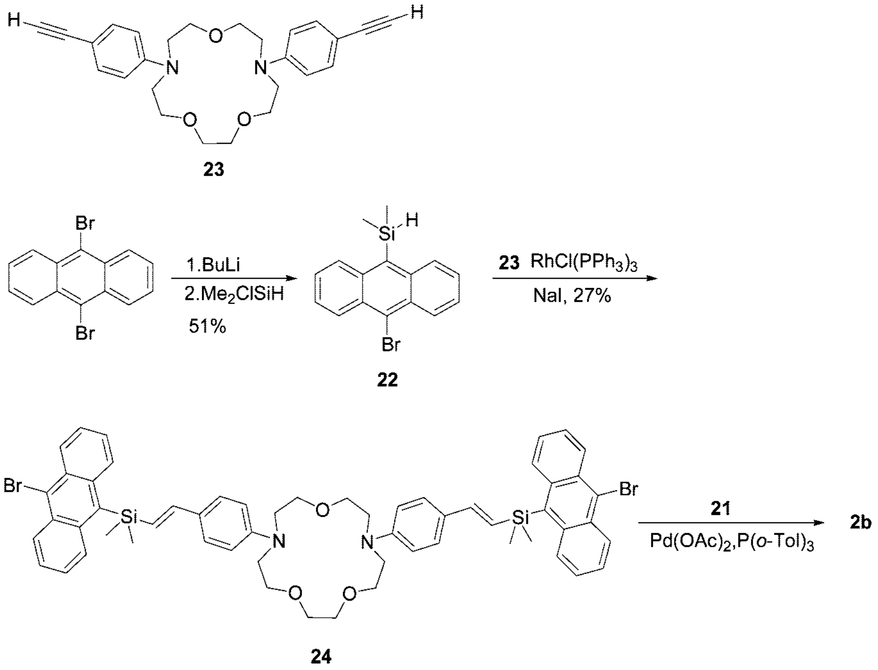
10-(Trimethylsilyl)-9-(*E*-2-(trimethylsilyl)vinyl)anthracene (3). Under nitrogen, a mixture of **8** (1.65 g, 5.0 mmol), trimethylvinylsilane (1.0 mg, 10.0 mmol), and dried DMF (15.0 mL) in a Schlenk flask was added $Pd(OAc)_2$ (90 mg, 0.4 mmol), P(*o*-Tol)$_3$ (60 mg, 0.2 mmol), and dried NEt_3 (6.0 mL). The mixture was stirred at 70 °C for 36 h. After cooling to rt, the mixture was poured into H_2O, extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$) and evaporated in vacuo to give the residue which was passed through a short column of silica gel (hexane) (1.25 g, 72%). IR (KBr): ν 3076, 2953, 2895, 1511, 1439, 1401, 1249, 993, 935, 867, 839, 779, 769, 725, 692, 665 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.33 (s, 9 H), 0.70 (s, 9 H), 6.32 (d, J = 19.6 Hz, 1 H), 7.43–7.46 (m, 4 H), 7.69 (d, J = 19.6 Hz, 1 H), 8.28–8.31 (m, 2 H), 8.42–8.44 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –1.1, 4.6, 124.2, 124.4, 126.9, 128.3, 129.1, 135.3, 136.8, 138.3, 141.0, 141.1. HRMS (FAB) (M^+, $C_{22}H_{28}Si_2$): calcd: 348.1730; found: 348.1734.

2,6-Bis(4-dibromophenyl)-2,6-diazaheptane (10). A solution of Br_2 (6.4 g, 40 mol) in HOAc (120 mL) was added into a mixture of **9**[15] (5.09 g, 20 mmol), HOAc (80 mL), and I_2 (trace) cooled in an ice bath. The mixture was then refluxed for 2 h. After cooling to rt, the mixture was poured into water and separated. The aqueous layer was extracted with ether (3 × 150 mL), and the combined organic layer was washed with brine, water, and dried ($MgSO_4$). The solvent was removed in vacuo to give the residue which was purified by flash chromatography using hexane as an eluent to afford **10** (6.59 g, 80%); mp 70–71 °C. IR (KBr): ν 2938, 2868, 2815, 1634, 1593, 1499, 1373, 1311, 1291, 1192, 1140, 1111, 1078, 988, 806 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.84 (quint, J = 7.1 Hz, 2 H), 2.89 (s, 6 H), 3.32 (t, J = 7.1 Hz, 4 H), 6.54 (d, J = 8.6 Hz, 4 H), 7.27 (d, J = 8.6 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.2, 38.7, 50.4, 107.9, 113.6, 131.3, 147.5. HRMS (EI) ($C_{17}H_{20}{}^{79}Br_1{}^{81}Br_1N_2$): calcd: 411.9967; found: 411.9965.

2,6-Bis[4-(dimethylsilyl)phenyl]-2,6-diazaheptane (6). Under N_2, to a solution of **10** (0.21 g, 0.5 mmol) in THF (30 mL) cooled at −78 °C was added slowly ^{n}BuLi (1.2 mL of 2.5 M in pentane, 3.0 mmol). After stirred for 1 h at −78 °C, chlorodimethylsilane (1.0 mL, 3.0 mmol) was added, and the mixture was gradually warmed to rt, continued stirring for 3 h, and quenched with H_2O (5.0 mL). The aqueous layer was extracted with Et_2O (3 × 30 mL), and the organic layer was washed with brine (30 mL), dried ($MgSO_4$), filtered, and evaporated in vacuo. The residue was chromatographed on silica gel (hexane) to give **6** (0.16 g, 85%). IR (KBr): ν 3443, 2942, 2104, 1634, 1598, 1507, 1377, 1246, 1205, 1107, 1009, 878, 829, 800, 760 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.36 (d, J = 3.6 Hz, 12 H), 1.93 (quint, J = 7.2 Hz, 2 H), 2.98 (s, 6 H), 3.42 (t, J = 7.2 Hz, 4 H), 4.43–4.45 (m, 2 H), 6.74 (d, J = 8.4 Hz, 4 H), 7.43 (d, J = 8.4 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –2.8, 24.7, 38.5, 50.3, 111.5, 121.8, 134.7, 149.3. HRMS (FAB^+) ($C_{21}H_{34}N_2Si_2$): calcd: 370.2261; found: 370.2260.

4-Bromo-4′-iodo-*trans*-stilbene (13). A mixture of **12** (4.5 g, 18.1 mmol) and $P(OEt)_3$ (3.7 mL, 21.7 mmol) was refluxed under N_2 for 3 h and then cooled to rt. DMF (50 mL) was added and then cooled to 0 °C. After stirred for 0.5 h at 0 °C, NaH (1.1 g, 27.2 mmol) was added, and the mixture was continued stirring for 0.5 h. Compound **11** (4.2 g, 18.1 mmol) in DMF (10 mL) was added, and the mixture was gradually warmed to rt, continued stirring for 5 h, and the mixture was poured into H_2O. The precipitate was collected and washed with MeOH to give **13** as a white solid (5.14 g, 84%); mp 237–238 °C. IR (KBr): ν 3077, 3040, 3007, 2917, 1961, 1908, 1483, 1405, 972, 821, 715 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.02 (AB quartet, J = 16.6 Hz, 16.6 Hz, 2 H), 7.24 (d, J = 8.4 Hz, 2 H), 7.36 (d, J = 8.6 Hz, 2 H), 7.48 (d, J = 8.6 Hz, 2 H), 7.68 (d, J = 8.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 93.0, 121.4, 126.7, 127.5, 127.7, 127.8, 131.5, 135.4, 136.1, 137.4. HRMS (FAB^+) (M^+, $C_{14}H_{10}{}^{79}BrI$) calcd: 383.9011;

Scheme 3



found: 383.9002. Anal. Calcd for $C_{14}H_{10}BrI$: C, 43.67; H, 2.62; found: C, 43.14; H, 2.81.

4-Bromo-4′-[2-(triisopropylsilyl)ethynyl]-*trans*-stilbene (14). A mixture of **13** (3.85 g, 10.0 mmol), (triisopropylsilyl)acetylene (2.5 mL, 11.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.35 g, 0.5 mmol), and CuI (95 mg, 0.5 mmol) in NEt_3 (40 mL) was refluxed under N_2 for 18 h and then cooled to rt. The mixture was filtered, and NEt_3 was evaporated. The crude product was chromatographed on silica gel (CH_2Cl_2/hexane = 1/ 5) to give **14** as a white solid (3.74 g, 85%); mp 68–69 °C. IR (KBr): ν 2942, 2889, 2864, 2153, 1601, 1458, 1074, 968, 882, 833, 670 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.15 (s, 21 H), 7.05 (AB quartet, J = 16.6 Hz, 16.6 Hz, 2 H), 7.36–7.49 (m, 8 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.8, 19.1, 91.6, 106.8, 121.3, 122.5, 125.9, 127.6, 127.8, 128.3, 131.4, 132.0, 135.6, 136.4. HRMS (FAB$^+$) (M$^+$, $C_{25}H_{31}{}^{79}BrSi$) calcd: 438.1378; found: 438.1374. Anal. Calcd for $C_{25}H_{31}BrSi$: C, 68.32; H, 7.11; found: C, 68.90; H, 6.89.

4-[2-(Triisopropylsilyl)ethynyl]-4′-[2-(trimethylsilyl)ethynyl]-*trans*-stilbene (15). To a mixture of trimethylsilylacetylene (1.5 mL, 7.2 mmol) and **14** (2.11 g, 4.8 mmol) in piperidine (40 mL) was added $Pd(PPh_3)_2Cl_2$ (0.1 g, 0.14 mmol) and CuI (30 mg, 0.15 mmol). The mixture was refluxed for 12 h under N_2 and then cooled to rt. After filtration, the solvent was evaporated in vacuo, and the residue was chromatographed on silica gel (CH_2Cl_2/hexane = 1/8) to afford **15** as a white solid (1.91 g, 87%); mp 58–59 °C. IR (KBr): ν 3085, 3029, 2943, 2865, 2893, 2154, 1510, 1463, 1412, 1250, 1233, 1016, 996, 760, 863, 838 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.29 (s, 9 H), 1.16 (s, 21 H), 7.07 (s, 2 H), 7.43–7.48 (m, 8 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.6, 11.8, 19.1, 91.6, 95.1, 104.9, 106.8, 122.0, 122.5, 126.0, 127.9, 128.3, 128.5, 131.91, 131.98, 136.5, 136.7. HRMS (FAB$^+$) (M$^+$, $C_{30}H_{40}Si_2$) calcd: 456.2669; found: 456.2665. Anal. Calcd for $C_{30}H_{40}Si_2$: C, 78.88; H, 8.83; found: C, 78.75; H, 8.60.

4-(2-Ethynyl)-4′-[2-(triisopropylsilyl)ethynyl]-*trans*-stilbene (16). A mixture of **15** (1.60 g, 3.5 mmol) and NaOH (0.14 g, 3.5 mmol) in MeOH (10 mL), and THF (10 mL) was stirred at rt for 1 h. After filtration, the solvent was evaporated in vacuo, and the residue was chromatographed on silica gel (hexane) to give **16** as a white solid (1.09 g, 81%); mp 88–89 °C. IR (KBr): ν 3301, 2946, 2864, 2149, 1458, 972, 882, 841 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.15 (s, 21 H), 3.15 (s, 1 H), 7.09 (s, 2 H), 7.45–7.48 (m, 8 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.8, 19.1, 78.0, 83.6, 91.7, 106.8, 120.9, 122.5, 125.97, 126.03, 128.1, 128.7, 131.96, 132.05, 136.4, 137.0. HRMS (FAB$^+$) (M$^+$, $C_{27}H_{33}Si$) calcd: 385.2352; found: 385.2348. Anal. Calcd for $C_{27}H_{33}Si$: C, 84.31; H, 8.39; found: C, 84.52; H, 8.08.

4,4′ -Bis(*E*- 2- (dimethyl(*E*-4-(*E*-4-((triisopropylsilyl)ethynyl) styryl)styryl)silyl)vinyl)biphenyl (17). Under argon, a mixture of **16** (0.72 g, 1.86 mmol), **5** (0.30 g, 0.93 mmol), and $Rh(PPh_3)_3Cl$ (8 mg) in THF (5 mL) was refluxed for 2 h. After cooled to rt, the mixture was poured into MeOH (20 mL). The precipitate was collected and recrystallized from hexane to give **17** (0.67 g, 66%); mp 145–147 °C. IR (KBr): ν 3077, 3027, 2958, 2938, 2889, 2864, 2717, 2153, 1908, 1610, 1511, 1462, 1250, 988, 841, 800 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.35(s, 12 H), 1.15 (s, 42 H), 6.56 (d, J = 19.2 Hz, 2 H), 6.57 (d, J = 19.2 Hz, 2 H), 6.96 (d, J = 19.2 Hz, 2 H), 6.99 (d, J = 19.2 Hz, 2 H), 7.10 (s, 4 H), 7.43–7.50 (m, 16 H), 7.53 (d, J = 8.4 Hz, 4 H), 7.60 (d, J = 8.4 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –2.5, 11.3, 18.7, 91.6, 107.2, 122.6, 126.2, 126.8, 126.89, 126.95, 127.0, 127.6, 128.0, 129.1, 132.4, 136.9, 137.26, 137.34, 137.8, 140.2, 144.4. HRMS (FAB$^+$) ($C_{74}H_{90}Si_4$) calcd 1090.6120; found 1090.6141.

4,4′-Bis(*E*-2-((*E*-4-(*E*-4-ethynylstyryl)styryl)dimethylsilyl)vinyl)biphenyl (18). To a solution of **17** (0.22 g, 0.2 mmol) in THF (5 mL) was added dropwise a 1 M solution of TBAF (0.5 mL, 0.5 mmol). The mixture was stirred at rt for 2.5 h, diluted with water, and extracted with CH_2Cl_2 (2 × 20 mL). The organic layer was washed with brine (10 mL) and dried ($MgSO_4$). Solvent was removed in vacuo to give a brown solid which was recrystallized from $CHCl_3$ to give **18** (0.14 g, 90%); mp 119–120 °C. IR (KBr) ν 3285, 3077, 3023, 2987, 2954, 2917, 2848, 1961, 1675, 1605, 1381, 1250, 1095, 1046, 984, 837 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.35 (s, 12 H), 3.14 (s, 2 H), 6.56 (d, J = 19.2 Hz, 2 H), 6.57 (d, J = 19.2 Hz, 2 H), 6.96 (d, J = 19.2 Hz, 2 H), 6.99 (d, J = 19.2 Hz, 2 H), 7.10 (s, 4 H), 7.44–7.50 (m, 16 H), 7.53 (d, J = 8.6 Hz, 4 H), 7.60 (d, J = 8.6 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –2.5, 78.0, 83.6, 120.6, 126.2, 126.8, 126.88, 126.94, 127.0, 127.6, 128.0, 129.1, 132.4, 136.9, 137.27, 137.33, 137.8, 140.2, 144.3. HRMS (FAB$^+$) ($C_{56}H_{51}Si_2$) calcd 779.3529; found 779.3545.

Polymer 2a. A mixture of **6** (111 mg, 0.3 mmol), **18** (234 mg, 0.3 mmol), and $Rh(PPh_3)_3Cl$ (6.9 mg, 0.0015 mmol) in THF (5 mL) was refluxed under N_2 for 4 h. After cooling to rt, the mixture was poured into MeOH. The precipitate was collected and redissolved in THF and then reprecipitated with MeOH. The product was collected by filtration and washed with MeOH (0.276 g, 80%).

$M_n = 7667$; PDI = 2.53. IR (KBr): ν 3414, 2950, 2900, 2889, 1700, 1663, 1595, 1491, 1405, 1378, 1350, 1227, 1175, 1111, 1046, 850 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.25 (s, 12 H), 0.39 (s, 12 H), 1.85–1.95 (m, 2 H), 2.96 (s, 6 H), 3.35–3.42 (m, 4 H), 6.53–6.62 (m, 4 H), 6.62–6.82 (d, 4 H), 6.89–6.97 (m, 4 H), 7.06 (s, 4 H), 7.44–7.59 (m, 28 H).

4,4′-Bis{*E*-2-[dimethyl(vinyl)silyl]vinyl}biphenyl (21). Under nitrogen, a mixture of **19** (2.5 g, 12.4 mmol), chlorodimethylsilane (4.1 mL, 37.1 mmol), and $Rh(PPh_3)_3Cl$ (400 mg, 0.43 mmol) in THF (25 mL) was refluxed for 8 h. A solution of vinyl Grignard reagent in THF (1 M, 31 mL) was then added dropwise, and the reaction was refluxed for 8 h. After the mixture was cooled to rt, the solvent was evaporated in vacuo. The residue was chromatographed on silica gel (hexane treated with a trace amount of NEt_3) (1.9 mg, 41%); mp 103–104 °C. IR (KBr): ν 3049, 2987, 2953, 1905, 1603, 1492, 1402, 1247, 1005, 988, 944, 838, 785, 756, 685 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.28 (s, 12 H), 5.80 (dd, J = 20.2 Hz, 3.7 Hz, 2 H), 6.06 (dd, J = 14.5 Hz, 3.7 Hz,2 H), 6.26 (dd, J = 20.2, 14.5, 2 H), 6.52 (d, J = 19.1 Hz, 2 H), 6.96 (d, J = 19.1 Hz, 2 H), 7.56 (dd, J = 8.1 Hz, 30.0 Hz, 8 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –2.9, 126.9, 127.0, 127.4. 132.4, 137.3, 138.2, 140.2, 144.3. MS m/z (rel intensity): 374 (M^+, 100), 347 (53), 321 (75), 275 (29), 245 (32), 233 (27), 221 (18), 159 (42), 133 (25), 131 (11). HRMS (FAB) (M^+, $C_{24}H_{30}Si_2$) calcd: 374.1886; found: 374.1880.

(10-Bromoanthracen-9-yl)dimethylsilane (22). A solution of ^{n}BuLi in hexane (6.0 mL of 2.5 M solution, 14.9 mmol) was added dropwise to a suspension of 9,10-dibromoanthracene (5.00 g, 14.9 mmol) in THF (400 mL) at −78 °C, and the mixture was stirred at −78 °C for 15 min. Chlorodimethylsilane (2.41 g, 25.5 mmol) was then added dropwise at −78 °C. The mixture was allowed to warm gradually to rt and stirred for 8 h. $NaHCO_3$ solution was then added, and the organic layer was separated. The aqueous layer was extracted with ether, and the combined organic solution was dried ($MgSO_4$) and evaporated in vacuo to give the residue which was passed through a short column of silica gel (hexane) to furnish **22** (2.38 g, 51%); mp 53–55 °C. IR (KBr): ν 3078, 3052, 2952, 2144, 1607, 1434, 1258, 918, 883, 837 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.71 (d, J = 4.0 Hz, 6 H), 5.49 (m, 1 H), 7.52–7.64 (m, 4 H), 8.55–8.68 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –1.4, 125.5, 126.5, 127.0, 128.6, 128.9, 130.1, 134.3, 137.4. MS m/z (rel intensity): 314 (M^+, 58), 316 (58), 256 (100), 178 (37). HRMS (FAB) (M^+, $C_{16}H_{15}{}^{79}BrSi$): calcd: 314.0126; found: 314.0128.

7,13-Bis(4-{2-[(10-bromoanthracen-9-yl)dimethylsilyl]vinyl}-phenyl)-1,4,10-trioxa-7,13-diazacyclopentadecane (24). Under nitrogen, a mixture of **23** (1.25 g, 3.0 mmol), **22** (1.89 g, 6.0 mmol), $Rh(PPh_3)_3Cl$ (138 mg), and NaI (480 mg) in THF (45 mL) was refluxed for 8 h. After cooled it to room temperature, the mixture was poured into MeOH. The precipitate was collected and was chromatographed on silica gel ($CHCl_3$:hexane = 2:3 and some NEt_3) (0.85 g, 27%); mp 125–127 °C. IR (KBr): ν 3020, 2952, 2867, 1602, 1515, 1434, 1385, 1350, 1552, 1184, 1124, 869, 814, 750 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.80 (s, 12 H), 3.55–3.70 (m, 16 H), 3.75–3.77 (m, 4 H), 6.65–6.66 (m, 6 H), 6.96 (d, J = 18.9 Hz, 2 H), 7.31 (d, J = 8.6 Hz, 4 H), 7.43–7.48 (m, 4 H), 7.52–7.59 (m, 4 H), 8.56–8.72 (m, 8 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 3.3, 51.7, 51.9, 68.8, 70.2, 70.8, 112.0, 124.0, 124.8, 126.4, 126.77, 126.83, 127.8, 128.6, 129.5, 130.2, 135.9, 137.8, 143.8, 148.3. MS m/z (rel intensity): 1047 ($M^+ + H$, 54), 1003 (48), 1002 (46), 969 (18), 931 (23), 929 (20), 885 (50), 883(22), 859 (8), 739 (80), 737 (100), 709 (12), 690 (20), 664 (13), 628(20), 626 (19), 613 (18), 590 (10), 554 (42), 552 (42), 532 (19), 502 (18). HRMS (FAB) ($M^+ + H$, $C_{58}H_{61}N_2O_3{}^{79}Br_2Si_2$): calcd: 1047.2587; found: 1047.2594.

Polymer 2b. Under nitrogen, a mixture of **24** (300 mg, 0.29 mmol), **21** (107 mg, 0.29 mmol), and dried DMF (2.5 mL) in Schlenk flask was added $Pd(OAc)_2$ (3.0 mg, 0.04 mmol), P(*o*-Tol)$_3$ (20.0 mg, 0.2 mmol), and dried NEt_3 (1.0 mL). The mixture was stirred at 70 °C for 36 h. After cooled it to room temperature, the mixture was poured into H_2O. The precipitate was collected and reprecipitated with THF and MeOH for 3 times. Finally, the solid was washed with Hexane. $M_n = 3600$; PDI = 1.09. IR (KBr): ν 3078, 3025, 2939, 2860, 1602, 1515, 1349, 1249, 1182, 1116, 986, 838, 815, 790 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.50 (s, 12 H), 0.77 (s, 12 H), 3.57–3.76 (br, 20 H), 6.61–6.74 (br, 6 H), 6.91–6.97 (m, 2 H), 7.15 (d, J = 19.1 Hz, 2 H), 7.30 (d, J = 8.0 Hz, 4 H), 7.41–7.52 (br, 8 H), 8.00 (d, J = 19.1 Hz, 2 H),7.30–7.35 (br, 4 H), 7.53–7.56 (br, 4 H).

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Supporting Information Available: ^{1}H NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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