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 materials10 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 phyrins, 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.3 For example, effective photoinduced electron transfer from amino styrene moiety to anthracene chromophore has been found in copolymer 1.5 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.5 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 (DE), an electron donor (E4), and an acceptor (A) to collect fluorescence resonance energy from DE forming an excited state of A, which will then accept an electron from E4. The most important criterion is to have these chromophores DE, A, and E4 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 (DE) and 4,4′-divinylstilbene (A).5 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 E4 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 anaza-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
The photophysical properties and frontier orbital energies of the model compounds 3–7 containing these chromophores are outlined in Table 1.

**Synthesis.** Monomer 3 was prepared by Heck reaction of 8 with trimethylvinylsilane (eq 1). Diamine 6 was prepared according to eq 1. Bromination of 9 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 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 D_E, A, and E_d, respectively.

![Diagram](image_url)

**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**

<table>
<thead>
<tr>
<th></th>
<th>(\lambda_{\text{max , abs}}) (nm)</th>
<th>(\lambda_{\text{max , em}}) (nm)</th>
<th>(\phi^a)</th>
<th>(E_{\text{ox}}^b) (eV)</th>
<th>HOMO(^c) (eV)</th>
<th>LUMO(^d) (eV)</th>
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<tbody>
<tr>
<td>3</td>
<td>382</td>
<td>461</td>
<td>0.64</td>
<td>0.53</td>
<td>-5.33</td>
<td>-2.45</td>
</tr>
<tr>
<td>4</td>
<td>307</td>
<td>378</td>
<td>0.03</td>
<td>0.18</td>
<td>-4.98</td>
<td>-1.57</td>
</tr>
<tr>
<td>5</td>
<td>310</td>
<td>360, 375</td>
<td>0.86</td>
<td>1.05</td>
<td>-5.85</td>
<td>-2.31</td>
</tr>
<tr>
<td>6</td>
<td>270</td>
<td>335</td>
<td>0.07</td>
<td>0.29</td>
<td>-5.09</td>
<td>-1.25</td>
</tr>
<tr>
<td>7</td>
<td>355</td>
<td>390, 410</td>
<td>0.91</td>
<td>0.78</td>
<td>-5.58</td>
<td>-2.40</td>
</tr>
</tbody>
</table>

\(^a\) 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 \(E_{\text{ox}}^b\) vs Fc/Fc^+. \(^d\) Estimated by HOMO and optical band gap from absorption spectra.
Treatment of bisalkyne 19 with chlorodimethylsilane in the presence of RhCl(PPh3)3 gave 22, followed by substitution with vinyl Grignard reagent to obtain 23 (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 CH2Cl2 is shown in Figure 2a. In comparison with the λmax 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 350 nm was observed when the measurements were taken in CH2Cl2 or THF. These results suggested that energy transfer was very efficient, and photoinduced electron transfer between the aminobenzene group (Ed) 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(ClO4)2 in CH2Cl2 (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 Zn2+ 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 Zn2+. These results further support the electron transfer process between the aminobenzene group (Ed) 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 Pb2+ 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 D6 chromophore (4,4′-divinylbiphenyl).

Time-Resolved Spectroscopy. Femtosecond laser equipped with a streak camera was employed to measure the time-resolved
spectra of fluorescence quenching in copolymers 2a and 2b. As discussed previously, both FRET between D_E and A chromophores and PET between 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 (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 D_E in 2b and 900 ps for 5, and the energy transfer rate and efficiency were calculated by eqs 1 and 2.

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

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

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

Unlike 2b, FRET between D_E and A in 2a was much more efficient than that in 2b (Figure 2b). The energy transfer from biphenyldivinyl moiety (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 D_E in 2a was assumed to be 3 ps. The rate constant \(k_E\) and quantum efficiency \(\Phi_E\) between D_E and A moieties in 2a were estimated to be 3.3 × 10^{11} \text{ s}^{-1} and 0.99, respectively. These results are outlined in Table 3.

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 \(\Phi_{CS}\) were calculated according to eqs 3 and 4, in which the \(k_s\) is the reciprocal of the fluorescence lifetime of corresponding reference monomers and \(\tau_{CS}\) is the fluorescence decay lifetime of A in copolymers.

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

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

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 \(\Phi_{CS}\) 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 \(\Phi_{CS}\)’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
lifetimes were obtained for each of 2a and 2b. Similar behavior was observed in related systems. This observation suggested that there might be two different modes of electron transfer processes in these polymers. The shorter lifetimes τ’s, the faster kCS’s, and the higher charge separation yields ΦCS 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. Accordingly, the silylene-spaced divinylarene copolymers are highly folded. 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. 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 4](image-url)

![Figure 5](image-url)

![Figure 6](image-url)

<table>
<thead>
<tr>
<th>Energy Transfer</th>
<th>Electron Transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>τE (ps)</td>
<td>kE (s⁻¹)</td>
</tr>
<tr>
<td>2a</td>
<td>28 (67%)</td>
</tr>
<tr>
<td>2b</td>
<td>414 (33%)</td>
</tr>
</tbody>
</table>

a Φtotal is the total efficiency from energy transfer to electron transfer. It can be obtained by multiplying ΦE and ΦCS. b The lifetime was obtained by the limitation of instrument.
organic solvent and therefore more processable. Since the silylene moiety is 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;1 would 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 vinylidene 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 solvent and therefore more processable. Since the silylene moiety is 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;1 would 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 vinylidene copolymers can be up to 96%.

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10-(Trimethylsilyl)-9-(E-2-(trimethylsilylvinyl)anthracene (3). Under nitrogen, a mixture of 8 (1.65 g, 5.0 mmol), trimethylvinylsilane (1.0 g, 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), (60 mg, 0.2 mmol), and dried NEt3 (6.0 mL). The mixture was stirred at 70 °C for 36 h. After cooling to rt, the mixture was poured into H2O, extracted with CH2Cl2. The organic layer was dried (MgSO4) and evaporated in vacuo to give the residue which was passed through a short column of silica gel (hexane) (1.25 g, 72%). 1H NMR (400 MHz, CDCl3): 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). 13C NMR (100 MHz, CDCl3): δ 46.0, 124.8, 126.3, 126.6, 128.8, 129.0, 130.2, 137.1, 137.6. HRMS (FAB) (M+): C14H1079Br12Si: calcd: 328.0283; found: 328.0279.

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found: 383.9002. Anal. Calcd for C_{14}H_{10}BrI: C, 43.67; H, 2.62; found: C, 43.52; H, 2.80.

4,4′-Bis[(E)-4-(2-ethyl)-4-(dimethyl(vinyl)styryl)styryl]vinyl]biphenyl (18). To a solution of 17 (0.22 g, 0.4 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, filtered, and washed with CHCl_{3} (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, 2932, 2987, 2954, 2917, 2848, 2861, 1675, 1605, 1381, 1250, 1095, 1046, 984, 837 cm^{-1}. 1H NMR (400 MHz, CDCl_{3}): δ 0.35 (s, 12 H), 1.15 (s, 21 H), 1.16 (s, 2 H), 6.47–7.48 (m, 8 H). 13C 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, 140.2, 144.3. HRMS (FAB^+) (M^+, C_{26}H_{34}Si) calcd: 579.2432; found: 579.2448.

**Polymer 2a.** A mixture of 6 (111 mg, 0.3 mmol), 18 (234 mg, 0.3 mmol), and Rh(PPh_{3})Cl (6.9 mg, 0.0015 mmol) in THF (5 mL) was refluxed for 4 h. After cooling to rt, the mixture was poured into MeOH. The precipitate was collected and redisolved in THF and then reprecipitated with MeOH. The product was collected by filtration and washed with MeOH (0.276 g, 80%).
was washed with hexane. $M_n = 3600; PDI = 1.09$. IR (KBr): $\nu = 3078, 2973, 2860, 1306, 1512, 1349, 1248, 1116, 986, 838, 815, 790 \text{ cm}^{-1}$. 1H NMR (400 MHz, CDCl3): $\delta$ 0.50 (s, 12 H), 0.77 (s, 12 H), 1.25–3.76 (br, 20 H), 3.42–6.75 (br, 6 H), 6.91–6.97 (m, 2 H), 7.18 (d, $J = 19.1$ Hz, 2 H), 7.30 (d, $J = 8$ Hz, 4 H), 7.42–7.52 (br, 8 H), 8.00 (d, $J = 19.1$ Hz, 2 H), 7.35–7.56 (br, 4 H).

Acknowledgment. We thank the National Science Council, National Taiwan University, and Shanghai Institute of Organic Chemistry for support.

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

References and Notes


(17) The fluorescence lifetime of the corresponding monomer was employed as the standard (ref 18) to estimate the rate constant of the fluorescence decay of chromophores in copolymers 2. The environment of the chromophore in 2 may be different from the corresponding monomer in solution. There is possibility that self-quenching may occur in 2 because of folding. However, it is known that intrachain chromophore–chromophore interactions are important only if the persistent length of the conjugated system is relatively short (e.g., divinylbenzene, refs 5a and 5d). In other words, when the persistent length is long, the emission profiles of the silylene-spaced divinylarene copolymers are very similar to those of the corresponding monomeric chromophores (ref 5d). In this regard, self-quenching might not be important.