Photoinduced Electron Transfer in Silylene-Spaced Copolymers Having Alternating Donor–Acceptor Chromophores

Hsian-Wen Wang,† Yen-Ju Cheng,† Chih-Hsien Chen,†,‡ Tsong-Shin Lim,§ Wunshain Fann,§ Cheng-Lan Lin,†,‡ Yuan-Pin Chang,† Kin-Chuan Lin,† and Tien-Yau Luh*†

Department of Chemistry, National Taiwan University, Taipei, Taiwan 106; Institute of Chemistry, Academia Sinica, Taipei, Taiwan 115; and Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan 106

ABSTRACT: Silylene-spaced copolymers with alternating azacrown and anthracene moieties were synthesized for photoinduced electron transfer investigations. These polymers exhibited efficient intrachain photoinduced electron transfer with charge separation yield about 0.96–0.99 and corresponding charge-transfer rates around 10.8–32.2 ns⁻¹ in different solvents. Metal cations have been shown to enhance the fluorescence intensity due to complexation. These results are comparable to those of small molecules having similar chromophores. The geminal dimethyl substituents on silicon in these copolymers may direct the relative conformation (or distance) of the remaining substituents on silicon. Intrachain interactions between these chromophores may readily take place leading to highly efficient electron transfer processes.

Introduction

There have been ever burgeoning interests in model systems to simulate photoinduced electron transfer (PET) in photosynthetic systems. Donors and acceptors can be covalently bonded in small molecules, in self-assembled systems, in dendrimers, or in polymers. We recently reported that silylene-spaced divinyl silane copolymers constituting of alternating donor and acceptor chromophores have demonstrated versatile photophysical properties such as intrachain fluorescence resonance energy transfer (FRET), through-space chromophore–chromophore interactions, and the transmission of chiroptical properties. The monosilylene moiety is considered as an insulating spacer, and no conjugative interactions between the π systems and the silicon moiety may occur. The enhancement of emission from the acceptor chromophore indicates that light harvesting may take place in these regioregular silicon-containing copolymers. The donor and acceptor chromophores would therefore be in close proximity. The use of the silylene spacer to link donor and acceptor chromophores for electron transfer has been briefly explored. It is envisaged that the photoinduced electron transfer might also occur in such silylene-spaced copolymers when the donor and acceptor chromophores are regioregularly arranged. In particular, copolymer 1 can easily be accessible by hydrosilylation of the corresponding bis-alkyne and bis-vinylsilanes in an alternating manner.

It is known that amines may quench the fluorescence of a fluorophore by means of PET. Our design involves the synthesis of silicon-containing polymers similar to 1 by incorporation of fluorophores and amine receptors in alternating manners separated by insulating silylene spacers. Anthracene moiety was chosen as the fluorescent probe because its photophysical properties have been well-studied, and it has been widely used for fluorescent sensing studies. Crown ethers are well-known for their excellent affinity toward different metal cations. Various fluorescent PET sensors have been made through the combination of a guest binding site and a fluorophore. Azacrown ethers occasionally act as the receptor for metal ions, and the nitrogen moiety acts as the donor for electron transfer. We now wish to report the design and synthesis of silylene-spaced alternating donor–acceptor copolymers for PETs.

Results and Discussion

Synthesis. 9,10-Bis(dimethylsilyl)anthracene (2) was prepared according to literature procedure (eq 1).

The azacrown moiety was synthesized in a manner similar to that described in the literature (Scheme 1). Reaction of triglycolyl chloride with 4-iodoaniline afforded bisamide in 82% yield. Reduction of 4 with BH₃·SMe₂ gave 85% yield of diamine 5 which was allowed to react with diglycolyl chloride under high dilution conditions to furnish macrocyclic bislactam 6 in 74% yield. Similarly, bislactam 7 was obtained in 68% yield when 3 was employed. Reduction of 6 and 7 with BH₃·SMe₂ gave 8 and 9 in 71 and 82% yield, respectively. Palladium-catalyzed Sonogashira reactions of 8 and 9 with trimethylsilylacetylene afforded 73 and 70% yield of 10 and 11, respectively. Desilylated bisalkynes 12 and 13 were obtained from the reactions of 10 and 11 in methanolic sodium hydroxide in 90% yield each.
hydrosilylation reactions. Presumably, the basic amine moiety may coordinate to the rhodium resulting in deactivation of the catalyst. Sodium ion may compete with the coordination site(s) of the azacrown ether moiety so that the rhodium catalyst may be released for the catalytic process. The ratios of the aminostyrene donor to anthracene chromophore in copolymers 14 and 15 were 2 to 1. The parent amine 16 was synthesized similarly by the rhodium-catalyzed hydrosilylation of 17 with Et₃SiH.

*Key Reagents: (a) 4-I-C₆H₄NH₂, py, THF, rt, 2 h, 82%; (b) BH₃.SMe₂, THF, reflux, 16 h, 71%; (c) 3 or 3-oxyglutaric dichloride, py, PhMe, rt, 12 h, 71% (n = 1), 68% (n = 2); (d) BH₃.SMe₂, THF, reflux, 16 h, 71% (n = 1); 82% (n = 2); (e) TMSC=CH, PdCl₂(PPh₃)₂, CuL, THF/Et₃N (1:2), reflux, 8 h, 73% (n = 1); 70% (n = 2); (f) NaOH, CH₂OH/THF (1:1), rt, 1 h, 90% (n = 1); 90% (n = 2).

**Table 1. Photophysical Properties and Frontier Orbital Energies of 2 and 16**

<table>
<thead>
<tr>
<th></th>
<th>λ&lt;sub&gt;max,abs&lt;/sub&gt; (nm)</th>
<th>λ&lt;sub&gt;max,em&lt;/sub&gt; (nm)</th>
<th>φ&lt;sup&gt;a&lt;/sup&gt;</th>
<th>E&lt;sub&gt;ox&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt; (V)</th>
<th>HOMO&lt;sup&gt;c&lt;/sup&gt; (eV)</th>
<th>LUMO&lt;sup&gt;d&lt;/sup&gt; (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>378</td>
<td>412, 433</td>
<td>0.65</td>
<td>0.18</td>
<td>-5.55</td>
<td>-2.54</td>
</tr>
<tr>
<td>16</td>
<td>308</td>
<td>378</td>
<td>0.03</td>
<td>0.75</td>
<td>-4.98</td>
<td>-1.57</td>
</tr>
</tbody>
</table>

<sup>a</sup> Using coumarin-1 as a reference.  <sup>b</sup> Oxidation potentials determined by cyclic voltammetry using 0.1 M Bu₄NPF₆ as electrolyte with Pt working electrode, Pt wire as counter electrode, and Ag/AgNO₃ as reference electrode.  <sup>c</sup> Estimated by E<sub>ox</sub> vs Fc/Fc<sup>+</sup>.  <sup>d</sup> Estimated by HOMO and optical band gap from absorption spectra.

**Photophysical Properties.** Polymers 14 and 15 contain anthracene as the fluorophore and aminostyrene as the quencher. Using 2 and 16 as the model compounds, the photophysical and electrochemical properties (see Supporting Information) of these chromophores were examined, and the frontier orbital energies were thus estimated (Table 1).

The absorption and emission spectra of 2 and copolymers 14 and 15 in CH₂Cl₂ are shown in Figure 1. The absorption from 350 to 430 nm with vibronic fine structures was attributed to anthracene chromophore in 14 and 15, and the broad peak around 310 nm was assigned to the absorption of the aminostyrene moiety. It is striking to note that the relative absorbance at 310 nm for 14 and 15 are different. Presumably, the incorporation of different azacrown ether moieties in these copolymers might cause conformational change, resulting in discrepancy in extinction coefficients of the aminostyrene chromophores. Compound 2 showed emission maximum at 412 and 433 nm with the quantum yield 0.65. The emissions of 14 and 15 around 410 nm were very weak, and the corresponding quantum yields were 0.011 and 0.006 (Figure 2). These results suggested that photoinduced electron transfer between the aminostyrene group and the anthracene moiety might take place. Indeed, addition of metal cations such as Ca<sup>2+</sup> or other cations (e.g., Sr<sup>2+</sup> or Ba<sup>2+</sup>; see Supporting Information) showed significant enhancement of fluorescence intensity (Figure 3). This result supports the PET mechanism in these silylene-spaced copolymers 14 and 15.

**Time-Resolved Fluorescence Spectroscopy.** The fluorescence lifetime for the reference 2 was determined to be 14 ns by the time-correlated photon counting system (see Supporting Information). A femtosecond laser equipped with a streak camera was employed to measure the time-resolved spectra of fluorescence quenching in polymers 14 and 15 due to PET. The fluorescence decay profiles of 14 and 15 in CHCl₃ and CH₂Cl₂ are shown in Figure 4. The fluorescence decay lifetimes (τ) were estimated by biexponential curve-fittings, and the results are

---

**Figure 1.** Absorption spectra of 2 (solid line, 1 × 10⁻⁵ M), 14 (dash-dotted line, 7.4 mg/L), and 15 (dotted line, 7.9 mg/L) in CH₂Cl₂.

Copolymers 14 and 15 were synthesized by hydrosilylation of 12 and 13 with 2 in a similar manner as those described previously. ⁵⁻⁹ It is noteworthy that the presence of a stoichiometric amount of sodium iodide was necessary in these
the charge-transfer rate constant \( k_{CS} \) and the corresponding charge-separation yield \( \Phi_{CS} \) were calculated according to eqs 1 and 2,
\[
\begin{align*}
    k_{CS} &= \tau^{-1} - k_s \\
    \Phi_{CS} &= \frac{k_{CS}}{\tau^{-1}}
\end{align*}
\]

The presence of the geminal dimethyl group on silicon might dictate the relative conformation of the remaining substituents on this silicon atom. In other words, the Thorpe–Ingold effect

due to the presence of such geminal dimethyl group would enable the aminostyrene group and the anthracene moiety in close proximity. Consequently, electron transfer between neighboring donor aminostyrene chromophore and acceptor anthracene moiety might be facile, leading to fast charge transfer rate (\( k_{CS} \sim 10.8 \text{--} 32.2 \text{ ns}^{-1} \)).

It is known that conformational change may influence the rate of the intramolecular electron transfer. Because of different arrangements of the chromophores, dual electron transfer rates are occasionally obtained. The silylene-divinylarene copolymers are highly folded. Through-space interaction between two chromophore would therefore be feasible in these copolymers. Slower rates (\( k_{CS} \sim 1.7 \text{--} 4.4 \text{ ns}^{-1} \)) might be expected from the through-space electron transfer between nonneighboring donor aminostyrene chromophore and the acceptor anthracene moiety in 14 or 15.

Our results indicated that the charge separation of 14 and 15 are highly efficient in these silylene-spaced alternating donor–

---

**Table 2. Fluorescence Lifetime (\( \tau \), Rate Constant (\( k_{CS} \)), and Yield (\( \Phi_{CS} \)) of 14 and 15 in CHCl\(_3\) and CH\(_2\)Cl\(_2\) at Ambient Temperature**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Fluorescence Lifetime (( \tau ), ps)</th>
<th>Charge-Transfer Rate (( k_{CS} ), ns(^{-1} ))</th>
<th>Charge-Separation Yield (( \Phi_{CS} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>CH(_2)Cl(_2)</td>
<td>31 (0.69) 225 (0.31)</td>
<td>13.1 2.3</td>
<td>0.99 0.97</td>
</tr>
<tr>
<td>15</td>
<td>CH(_2)Cl(_2)</td>
<td>47 (0.88) 404 (0.12)</td>
<td>21.2 2.4</td>
<td>0.99 0.97</td>
</tr>
<tr>
<td>18</td>
<td>Hexanol</td>
<td>333</td>
<td>2.9 0.97</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>H(_2)O</td>
<td>320</td>
<td>3.0 0.97</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>CH(_3)CN</td>
<td>39</td>
<td>25.2 0.98</td>
<td></td>
</tr>
</tbody>
</table>

---

The concentrations (\( \sim 10^{-5} \) M) of 14 and 15 are determined by extinction coefficient, and 9,10-disilyl anthracene is used to be reference. Time-resolved fluorescence lifetimes are estimated by exponential fitting of decay curve (\( R^2 = 0.98\text{--}0.99 \)). The relative weights of different time constants are included in parentheses. From ref 19. From ref 20. From ref 21. Calculated values based on the corresponding literature data in refs 19–21.
acceptor copolymers. In comparison with the charge separation efficiencies of other small molecules containing similar donor and acceptor moieties (e.g., 18–20 Table 2), similar efficiencies were obtained from copolymers 14 and 15.

**Conclusions**

The silylene-spaced copolymers have been shown to exhibit a variety of fascinating photophysical properties because of conformational flexibility. The silylene moiety has provided an insulating spacer between two linking conjugated moieties. In this study, we have demonstrated a new type of silylene-spaced copolymer with alternating aminostyrene and anthracene moieties for efficient photoinduced electron transfer. These spaced copolymer with alternating aminostyrene and anthracene interaction between these substituents may readily take place. Preliminary examinations suggested that these aza-crown ether-containing copolymers may serve as sensors comparable to those in small molecules having similar chromophores. Preliminary examinations suggested that these azacrown ether-containing copolymers may serve as sensors selective for large divalent cations such as Cd²⁺, Sr²⁺, or Ba²⁺ cations. Further investigations are in progress in our laboratory.

**Experimental Section**

**General.** High-resolution mass was 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 (Mₚ values ranging from 375 to 3.5 × 10⁶). Absorption spectra were measured with Hitachi U-3310 spectrophotometer and emission spectra with Hitachi F-4500 fluorescence spectrophotometer. Quantum yield was measured with Hitachi U-3310 spectrophotometer and emission spectra with Hitachi F-4500 fluorescence spectrophotometer. Conclusions

The silylene-spaced copolymers have been shown to exhibit a variety of fascinating photophysical properties because of conformational flexibility. The silylene moiety has provided an insulating spacer between two linking conjugated moieties. In this study, we have demonstrated a new type of silylene-spaced copolymer with alternating aminostyrene and anthracene moieties for efficient photoinduced electron transfer. These spaced copolymer with alternating aminostyrene and anthracene interaction between these substituents may readily take place. Preliminary examinations suggested that these aza-crown ether-containing copolymers may serve as sensors comparable to those in small molecules having similar chromophores. Preliminary examinations suggested that these azacrown ether-containing copolymers may serve as sensors selective for large divalent cations such as Cd²⁺, Sr²⁺, or Ba²⁺ cations. Further investigations are in progress in our laboratory.
stirring at room temperature, the mixture was filtered and the filtrate was evaporated. The residue was purified by column chromatography (silica gel with CHCl₃) (1.54 g, 74%); mp 177–178 °C. IR (KBr): ν 3044, 2872, 1608, 1734, 1631, 1513, 1428, 1268, 1151, 1078, 985, 833, 753 cm⁻¹. 1H NMR (400 MHz, CDCl₃); δ 3.40–3.70 (m, 12 H), 3.85–4.00 (m, 8 H), 7.13 (d, J = 7.5 Hz, 4 H), 7.78 (d, J = 7.5 Hz, 4 H). 13C NMR (CDCl₃, 100 MHz): δ 47.7, 67.2, 70.1, 70.4, 71.1, 93.9, 130.8, 138.9, 139.9, 169.9. MS m/z (rel intensity): 695 (M⁺ + H), 667 (5), 562 (5), 207 (4), 420 (2), 340 (7). HRMS (FAB) (M⁺ + H, C₂₄H₂₃I₂N₂O₄): calcéd 695.0915; found 695.0910. Anal. Calcéd for C₂₄H₂₃I₂N₂O₄: C, 42.46; H, 3.54. Found: C, 42.45; H, 4.54.

7.13-Bis(4-iodophenyl)-1,4,10,13-tetraoxa-7,13-diazacyclopentadecane (12). A mixture of 10 (1.38 g, 2.45 mmol) and NaOH (0.20 g, 4.9 mmol) in MeOH (50 mL) and THF (50 mL) was stirred at room temperature for 1 h. After filtration, the solvent was evaporated in vacuo. The residue was purified by column chromatography (silica gel with CHCl₃) (0.92 g, 90%); mp 94–96 °C. IR (KBr): ν 3287, 3045, 2876, 2097, 1606, 1493, 1393, 1351, 1286, 1180, 1127, 817 cm⁻¹. 1H NMR (400 MHz, CDCl₃); δ 2.98 (s, 2H), 3.55–3.64 (m, 16 H), 7.31–7.37 (m, 4 H). 13C NMR (CDCl₃, 100 MHz): δ 51.9, 52.1, 68.8, 70.0, 70.8, 74.8, 84.6, 108.5, 111.4, 132.8, 147.8. MS m/z (rel intensity): 418 (M⁺, 100), 414 (27), 387 (10), 370 (5), 289 (4), 242 (47), 200 (6), 174 (20), 144 (28), 119 (15), HRMS (FAB) (M⁺, C₁₃H₁₂NO₄S): calcéd 418.2256; found 418.2247.

7.13-Bis(4-ethylphenyl)-1,4,10,13-tetraoxa-7,13-diazacyclopentadecane (13). A mixture of 11 (0.60 mg, 0.11 mmol) and NaN₃ (8 mg, 0.22 mmol) in MeOH (10 mL) and THF (10 mL) was stirred at room temperature for 1 h. After filtration, the solvent was evaporated in vacuo. The residue was purified by column chromatography (silica gel with CHCl₃) (42 mg, 90%); mp 110–112 °C. IR (KBr): ν 3291, 3098, 3048, 2873, 2100, 1896, 1608, 1517, 1456, 1394, 1281, 1255, 1234, 1185, 1160, 1008, 818 cm⁻¹. 1H NMR (400 MHz, CDCl₃); δ 0.29 (s, 2H), 3.60–3.64 (m, 24 H), 6.57 (d, J = 8.7 Hz, 4 H). 3J (d, J = 8.7 Hz, 4 H). 13C NMR (CDCl₃, 100 MHz): δ 51.1, 68.9, 71.0, 74.8, 84.7, 108.5, 111.1, 133.4, 148.0. MS m/z (rel intensity): 462 (M⁺, 100), 439 (10), 387 (6), 340 (7), 326 (6), 280 (6), 244 (14), 212 (26), 170 (26), 144 (47), 130 (37), HRMS (FAB) (M⁺, C₁₃H₁₂NO₄S): calcéd 462.2519; found 462.2530.

Polymers 14 and 15. Under nitrogen, a mixture of 12 (0.125 g, 0.3 mmol), 2 (0.087 g, 0.3 mmol), Na(96 mg), and Rh(Ph₃)Cl₂ (15 mg) in THF (5 mL) was refluxed for 8 h. After cooling to rt, the mixture was poured into MeOH. The precipitate was collected and dissolved in THF and then precipitated with MeOH. The product 1a was collected by filtration and washed with MeOH: Mw = 6654, PDI = 1.42. IR (KBr): ν 3960, 2867, 1603, 1516, 1384, 1350, 1252, 1184, 1120, 814 cm⁻¹. 1H NMR (400 MHz, CDCl₃); δ 0.7–0.8 (m, 12 H), 3.4–3.8 (m, 20 H), 6.6–6.7 (m, 6 H), 6.9–7.0 (m, 2 H), 7.2–7.4 (m, 8 H), 8.5–8.6 (m, 4 H).

Polymer 15. Under nitrogen, a mixture of 13 (1387 mg, 0.3 mmol), 2 (87.6 mg, 0.3 mmol), Na(96 mg), and Rh(Ph₃)Cl₂ (15 mg) in THF (5 mL) was refluxed for 8 h. After cooling to rt, the mixture was poured into MeOH. The precipitate was collected and dissolved in THF and then precipitated with MeOH. The product 1b was collected by filtration and washed with MeOH: Mw = 7942, PDI = 2.74. IR (KBr): ν 3085, 3045, 2946, 2868, 1604, 1515, 1385, 1350, 1264, 1186, 1114, 812.73 cm⁻¹. 1H NMR (400 MHz, CDCl₃); δ 0.7–0.8 (m, 12 H), 3.4–3.9 (m, 24 H), 6.6–6.7 (m, 6 H), 6.9–7.0 (m, 2 H), 7.2–7.4 (m, 8 H), 8.5–8.6 (m, 4 H).

(E)-N,N-Dimethyl-4-[2-(triethylsilyl)vinyl]aniline (16). Under a nitrogen atmosphere, a THF solution (15 mL) of 17 (174 mg, 1.22 mmol), Et₃SiH (140 mg, 1.2 mmol), Na(92 mg, 1.2 mmol), and RhCl(Ph₃)₂ (55 mg, 0.06 mmol) was refluxed for 4 h. After cooled to rt, the solvent was removed in vacuo, and the residue was chromatographed on silica gel (hexane) to give 16 as oil.
(106 mg, 34%). IR (KBr): v 3014, 2951, 2908, 2873, 1602, 1519, 1343, 1150, 1126, 1095, 1005, 995, 885, 851, 764, 722, 695, 665, 634 cm⁻¹. 1H NMR (400 MHz, CDC13): δ 0.69 (q, J = 7.9 Hz, 6 H), 1.03 (t, J = 7.9 Hz, 9 H), 2.99 (s, 6 H), 6.20 (d, J = 19.3 Hz, 1 H), 6.72 (d, J = 8.6 Hz, 2 H), 6.86 (d, J = 19.3 Hz, 1 H), 7.38 (d, J = 8.6 Hz, 2 H). 13C NMR (CDCl3, 100 MHz): δ 3.6, 7.4, 40.5, 112.2, 120.0, 127.28, 127.32, 144.7, 150.3. MS m/z (rel intensity): 261 (100), 260 (36), 232 (21), 204 (3), 134 (4), 115 (7). HRMS (FAB) (M+, C20H27-N2Si): calc'd 516.1913; found 516.1920.

Acknowledgment. This work was supported by the National Science Council, Academia Sinica, and National Taiwan University of the Republic of China.

Supporting Information Available: 1H NMR spectra of all new compounds, influences of cations on the photophysical properties of 15, and electrochemical properties of 2 and 16. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


(16) Attempts to obtain copolymers 14 or 15 with higher molecular weights under various conditions (amount of the Wilkinson catalyst, solvent, temperature, etc.) were unsuccessful.

MMA070119T