Controlling Conformations in Alternating Dialkylsilylene-Spaced Donor–Acceptor Copolymers by a Cooperative Thorpe–Ingold Effect and Polymer Folding

Chih-Hsien Chen, Yen-Chin Huang, Wei-Chih Liao, Tsong-Shin Lim, Kuan-Lin Liu, I-Chia Chen, and Tien-Yau Luh*

Dedicated to Professor Leon M. Stock on the occasion of his 80th birthday

Abstract: A series of dialkylsilylene-spaced copolymers 6 and 7, which contain Me₂Si and iPr₂Si spacer groups, respectively, and have alternating donor and acceptor chromophores, have been designed and regioselectively synthesized by hydrosilylation. The ratio of the donor and acceptor chromophores for each repeat unit is 2:1, and the two donor chromophores are linked by a trimethylene bridge. A 4-aminostyrene moiety is used as the donor and a series of acceptor chromophores with different reduction potentials are employed. Both steady-state and kinetic measurements reveal that the photoinduced electron transfer (PET) in 6 obeyed the Marcus theory in which normal and inverted regions are observed. On the other hand, the iPr₂Si-spaced copolymers 7 exhibit absorption and emission from the charge-transfer complexes exclusively due to ground-state interactions between the donor and acceptor chromophores. The discrepancy in photophysical behavior may have arisen from the difference in distance between the adjacent donor and acceptor chromophores. The bulkiness of the substituents on the silicon atom (i.e., Me versus iPr) may exert the Thorpe–Ingold effect on the local conformation around the silicon atom. The differences in the small energetic barriers for each of the conformational states may be amplified by extending the distance of the folding structure, which results in perturbing the conformation around the silicon atom. These results suggest that the electronic interactions between adjacent donor–acceptor pairs in these copolymers are controlled by the synchronization of the substitution effect and corresponding polymeric structures.

Introduction

Polymer folding represents, among other things, an ensemble of rotation about the sigma bonds along the polymeric backbones, through-space electrostatic and steric interactions between non-neighboring sites, and solvophobic effects. The differences in the small energetic barriers for each of the conformational states may be amplified by extending the distance of the folding structure, which results in a more stable conformation. Numerous secondary structures of polymers and proteins are known to be stabilized by hydrogen bonding. Also, π–π stacking interactions play an important role in the folding and intermolecular aggregation/assembly of a polymer. Circular dichroism, fluorescence quenching, and excimer formation have frequently been used as probes for the folding of macromolecules. Nevertheless, knowledge of the precise conformational arrangement of artificial polymers remains a challenging problem, especially for subnanometric variations in folded structures. Photoinduced electron transfer (PET) has been known to be sensitive to subtle changes in distance on the angstrom scale. In other words, electronic coupling between the donor and acceptor is strongly perturbed by a slight variation in the distance between the chromophores. The use of this strategy for investigation of protein conformation has been carried out. It is envisaged that the use of PET as a probe might also provide information about the fine structures of folded polymers.

Keywords: Marcus theory · photoinduced electron transfer · polymer folding · silicon · substituted silylene · Thorpe–Ingold effect

Monosilylene-spaced copolymers are known to exhibit extraordinary photophysical properties; furthermore, different aryl groups (i.e., Ar¹ and Ar²) can be regioselectively incorporated in the polymer chain by using a simple hydrosilylation protocol. The silicon moiety in 1, in general,
is considered to be an insulating tetrahedral spacer.\textsuperscript{[14–19]} Thus, the electronic interactions between chromophores can be simplified in comparison with conjugated polymers. Moreover, the steric nature of the substituents on the silicon atom can have a bearing on the morphological changes.\textsuperscript{[20]} Such a small variation might fine-tune the features of the ensembled polymers that originate from the conformational equilibrium of divinylsilane moiety in 1 due to the Thorpe–Ingold effect [Eq. (1)]. Accordingly, we chose monosilylene-spaced copolymer 1 as a skeleton to study the conformational change of the polymeric structure by utilizing the features of the PET process in polymers.

Results and Discussion

\textbf{Strategy}: To decrease the complexity of conformational changes in 1, one of the two vinyl moieties in 1 was replaced by an aryl group so that the equilibrium shown in Equation (1) could be simplified to Equation (2), in which only syn and anti equilibrium will be considered.

\begin{equation}
\text{Ar}^-\text{Ar}^-\text{Si}^-\text{Ar}^-\text{Ar}^+
\end{equation}

Aromatic amines are widely used as electron donors in PET reactions.\textsuperscript{[21]} Because of synthetic convenience, we decided to use two donors symmetrically located at both ends of the acceptor chromophore. First, model compounds 2 and 3 were synthesized,\textsuperscript{[22]} in which the aminostyrene group was employed as the donor and the stilbene moiety as the acceptor. The absorption spectra for 2 and 3 were almost identical (Figure 1). Both 2 and 3 exhibit dual emission bands at $\lambda = 380$ nm due to intrinsic local excited (LE) emission of the stilbene chromophore and at $\lambda = 500$ nm which are likely to belong to the emission from the charge-separation state (CT emission; Figure 1). It is interesting to note that the relative intensity of the LE appeared to be much lower in 3 with two donor chromophores than in 2, which has only one donor chromophore. In addition, the relative intensity of the CT emission was much higher in 3 than in 2. Accordingly, PET would be more efficient in 3 than in 2.

Oligomethylene bridges were designed to link two amino-styrene chromophores. To test the effect of the chain length on the photophysical properties of the PET processes, 4 and 5 with ethylene and propylene bridges, respectively, were prepared. There was essentially no difference in their emission spectra (Figure 2). Based on these preliminary studies,
polymers 6 and 7 were designed and synthesized for the conformational investigations.

**Synthesis:** A rhodium(I)-catalyzed hydroisilylation protocol was used for the syntheses of 6 and 7 from the corresponding bis-alkyne 8 and bis-silyl hydride 9 or 10 shown in Equation (3).\[^{[14,22]}\] The presence of one equivalent of NaI was essential to facilitate the rhodium-catalyzed hydroisilylation reactions.\[^{[18]}\] Bis-alkyne 8 was obtained from the Sonogashira reaction of 11 and trimethylsilylacetylene followed by desilylation. Bis-silyl hydrides 9 and 10 containing acceptor chromophores were prepared from the metal/halogen exchange between bis-bromide 12 and nBuLi followed by reaction with RSiHCl, where R was a methyl or isopropyl group. The acceptor chromophores in 9 and 10 were chosen so that the relative free-energy differences in the PET process for 6 could be tuned. In addition, the lengths of these acceptor chromophores were kept as close as possible to maintain similar center-to-center distances between the donor and acceptor chromophores in 6 and 7.

![Chemical structures](image)

**Photophysical and electrochemical properties of monomers 9 and 13:** The photophysical properties, the redox potentials \(E_{\text{ox}}\) and \(E_{\text{red}}\), and the relevant properties of monomers 9a–f are compiled in Table 1. The frontier orbital energies for each of these chromophores were thus calculated. Accordingly, the PET would be expected from the HOMO of the aminostyrene moiety to the HOMO of the excited state of the chromophore in 9.

**Dissimilarity between SiMe2- and SiPr2-spaced copolymers based on steady-state spectroscopic analysis:** As shown in Equation (3), a series of polymers 6 was designed so that the differences in the free energy \(\Delta G_o\) for the charge separation processes were systematically tuned. By using the Weller equation,\[^{[23]}\] the \(\Delta G_o\) values in the electron-transfer process for 6 were estimated based on the data for the corresponding monomers 9 and 13 (Table 2).\[^{[22]}\]

The absorption and emission spectra of 6, 7, and the corresponding acceptor monomers 9 in cyclohexane and THF are compared in Figures 3–9. Interestingly, the absorption spectra for 6 were essentially solvent independent. However, the absorption spectra for 7 exhibited noticeable additional absorption bands at longer wavelengths in cyclohexane and THF, which are attributed to the absorption for the charge-transfer complex.\[^{[24]}\] Indeed, these lower-energy absorption bands shifted to further longer wavelengths with relatively higher intensities in the more-polar THF solvent than in cyclohexane. These results clearly indicate that interactions between the donor and acceptor chromophores at the ground state might be more significant in 7, and thus the excitation pathways for 6 and 7 might be different.

The emission spectra of 6 and 7 exhibited completely different trends. The emission profile of 6a in cyclohexane was almost identical to that of the corresponding monomer 9a and the full-width half maxima (FWHM) of the emission band was only slightly broader in THF (Figure 3b). The emission intensities of 6a in 2-methyltetrahydrofuran (MTHF) remained similar at different temperatures in the range 298–180 K (Figure 3d). In the emission spectrum of 7a, besides the LE emission of the acceptor chromophore at \(\lambda = 424\) and 446 nm, a longer wavelength emission at approximately \(\lambda = 450–500\) nm started to emerge (Figure 3c). Interestingly, the emission intensities of 7a were enhanced with

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**Table 1.** The photophysical and electrochemical properties of monomers 9 and 13.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\lambda_{\text{max}}[^{[a]}]) [nm]</th>
<th>(\lambda_{\text{em}}[^{[b]}]) [nm]</th>
<th>(E_{\text{ox}}[^{[d]}]) [eV]</th>
<th>(\Phi[^{[c]}])</th>
<th>(\tau_\text{f}[^{[e]}]) [ns]</th>
<th>(E_{\text{red}}[^{[f]}]) [eV]</th>
<th>(E_{\text{red}}[^{[f]}]) [eV]</th>
<th>HOMO[^{[g]}] [eV]</th>
<th>LUMO[^{[g]}] [eV]</th>
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<tr>
<td>9a</td>
<td>365</td>
<td>424, 446</td>
<td>3.02</td>
<td>0.12</td>
<td>0.20</td>
<td>0.69</td>
<td>-2.48</td>
<td>-5.30</td>
<td>-2.67</td>
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<tr>
<td>9b</td>
<td>324, 273</td>
<td>396</td>
<td>3.41</td>
<td>0.80</td>
<td>1.00</td>
<td>0.89</td>
<td>-2.71</td>
<td>-5.50</td>
<td>-2.90</td>
</tr>
<tr>
<td>9c</td>
<td>320, 308</td>
<td>350, 366</td>
<td>3.62</td>
<td>0.26</td>
<td>0.18</td>
<td>1.24</td>
<td>-2.48</td>
<td>-5.85</td>
<td>-2.67</td>
</tr>
<tr>
<td>9d</td>
<td>292</td>
<td>345, 360</td>
<td>3.78</td>
<td>0.79</td>
<td>0.95</td>
<td>-</td>
<td>-2.37</td>
<td>-2.56</td>
<td>-2.58</td>
</tr>
<tr>
<td>9e</td>
<td>265</td>
<td>344</td>
<td>4.05</td>
<td>0.28</td>
<td>1.95</td>
<td>-</td>
<td>-2.39</td>
<td>-2.58</td>
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<tr>
<td>9f</td>
<td>243</td>
<td>343</td>
<td>4.11</td>
<td>0.10</td>
<td>0.74</td>
<td>-</td>
<td>-2.18</td>
<td>-</td>
<td>-2.37</td>
</tr>
<tr>
<td>13</td>
<td>305</td>
<td>-</td>
<td>3.54</td>
<td>-</td>
<td>3.54</td>
<td>-</td>
<td>0.33</td>
<td>-4.94</td>
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</table>

[^{[a]}]: The \(\lambda_{\text{max}}\) and \(\lambda_{\text{em}}\) values were measured in THF.\[^{[b]}\]: The \(\Phi\) value was determined using coumarin-1 (\(\Phi = 0.99\) in ethyl acetate) and 2,5-diphenyl-1,3,4-oxadiazole (\(\Phi = 1.0\) in ethanol) as a standard.\[^{[c]}\]: Fluorescence lifetime \(\tau_\text{f}\) was estimated by single-exponential fitting of the fluorescence decay profile.\[^{[d]}\]: HOMOs were estimated by oxidation potentials \(E_{\text{ox}}\) of 9a–c and 13. The \(E_{\text{ox}}\) values of 9d–f were not measured because they were beyond the instrument limitation (1.3 V versus Ag/Ag*).\[^{[e]}\]: LUMOs were estimated by reduction potential \(E_{\text{red}}\) of 9 and that of 13 was obtained by HOMO + \(E_{\text{ox}}\).
The intensities of the CT emission in 7a became more prominent than those for the LE and CT emissions for 6b (Figure 3e). The formation of the charge-transfer complex in 7a might be plausible.

The dissimilarities in the emission properties between 6 and 7 were more prominent when $-\Delta G_o$ became larger. The emission spectrum of 6b in cyclohexane at ambient temperature was the same as that of the corresponding monomeric acceptor chromophore 9b (Figure 4b). It is worth noting that a shoulder appeared at approximately $\lambda =$ 480 nm in THF. These dual fluorescence bands were assigned as the LE of the acceptor moiety and no emission at longer wavelengths arising from the CT emission being observed. On the other hand, the emission properties of 7e in THF at ambient temperature and in MTHF at variable temperatures appeared to be similar to those of 7b and 7c (Figure 6c,e). The presence of the geminal diisopropyl groups on the silicon atoms in 7 would exert the Thorpe–Ingold effect,[20] which may lead to modification of the average spacing and orientation between the donor and acceptor chromophores in 7 relative to those in 6. Accordingly, the mode of the interactions between these donor and acceptor chromophores might lead to the discrepancy in photophysical behavior between these two series of copolymer. The absorption spectra of 6 were essentially the sum of all the contributing chromophores (in Figures 3–6), whereas those spectra of 7 consisted of an additional solvent-dependent absorption band at the longer wavelength because of the interactions between the donor and acceptor chromophores at the ground state; furthermore, the fluororescence observed for 7 might be attributed to the emission that arises from this charge-transfer complex.[25]

**Steady-state observation of the Marcus-inverted region in 6:**

The $-\Delta G_o$ values for the charge-separation processes in the copolymers 6d and 6f were estimated to be 1.27 and 1.79 eV, respectively. The emission behaviors of 6d (Figure 7a) and 6c were comparable. However, the relative intensity of the LE versus CT emission for 6d appeared to be more prominent than those for 6c in both cyclohexane and THF solvents. It is worth mentioning that the $-\Delta G_o$ value was lowered (Figure 5d). Presumably, the solvent polarity may be enhanced as the temperature decreases,[26] and thus the charge-separation state might be stabilized to a lower energy level. It seems likely that the interaction between this excited state and the higher vibrational level of the ground state might result in a thermal-relaxation process to decrease the opportunity of radiative relaxation.[27,28] In contrast, the temperature-dependent behavior of emission profiles of 7c was similar to that observed for 7b, as described above (Figure 5e).

When the $-\Delta G_o$ value for the donor–acceptor couple was raised to 1.52 eV for 6e, the emission profiles in cyclohexane and THF again became a single LE emission at $\lambda =$ 350 nm (Figure 6b) and were essentially temperature independent (Figure 6d). These properties were similar to those of 6a, as described above. In other words, the emission spectra of 6a and 6e may have arisen mainly from the LE emission of the acceptor moiety and no emission at longer wavelengths arising from the CT emission being observed. On the other hand, the emission properties of 7e in THF at ambient temperature and in MTHF at variable temperatures appeared to be similar to those of 7b and 7c (Figure 6c,e).

Table 2. Number-average molecular weight $M_n$, polydispersity index (PDI), and kinetic parameters of 6 and 7.

<table>
<thead>
<tr>
<th>$M_n$ (PDI)</th>
<th>$-\Delta G_o^{[a]}$ [eV]</th>
<th>$\tau_{CS}$ [ps]</th>
<th>$k_{CS} \times 10^{-10}$ [s$^{-1}$]</th>
<th>$M_n$ (PDI)</th>
<th>$\tau_d$ [ps]</th>
<th>$k_d \times 10^{-9}$ [s$^{-1}$]</th>
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<tr>
<td>a</td>
<td>17000</td>
<td>0.40</td>
<td>45</td>
<td>1.7</td>
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<tr>
<td>(1.6)</td>
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<td></td>
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<td>(2.4)</td>
<td>176</td>
</tr>
<tr>
<td>b</td>
<td>15000</td>
<td>0.56</td>
<td>34</td>
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<tr>
<td>c</td>
<td>20000</td>
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<td>9</td>
<td>10.6</td>
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<td>150</td>
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<td>(2.4)</td>
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<tr>
<td>d</td>
<td>17800</td>
<td>1.27</td>
<td>14</td>
<td>7.0</td>
<td>5200</td>
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<td>(1.8)</td>
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<tr>
<td>e</td>
<td>10600</td>
<td>1.52</td>
<td>19</td>
<td>5.2</td>
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<tr>
<td>f</td>
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<td>1.79</td>
<td>35</td>
<td>2.7</td>
<td>5200</td>
<td>160</td>
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<td>(1.8)</td>
<td></td>
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<td></td>
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<td>(1.7)</td>
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</table>

[a] Weller equation: $-\Delta G_o = -E_{ox(D)} - E_{red(A)} + C/R_{CS}$ where $C = e^2A_0\pi r_0^2 = 3.04 \times 10^{-20}$ J m$^{-3}$ and $R_{CS} =$ center-to-center distance between the donor (D) and acceptor (A) chromophores in 6 estimated by the DFT calculations of model compounds Ma–F.

[b] Two-exponential fitting was utilized to give two lifetimes (see Figures S4–S6 in the Supporting Information). The shorter component $\tau_{CS}$ was the major route for the fluorescence decay (~99%).
more negative for 6d than for 6c. As expected, the emission properties of 6f (Figure 8a) were similar to those of 6e because they represented relatively large $-\Delta G_0$ values. The temperature-dependent emission spectra of 6d displayed a classic behavior of CT emission, as observed for 6c (Figure 7b). Furthermore, 6f behaved in a similar manner to 6e when the temperature was changed (Figure 8b).

A plot of the integrated intensity ratios of CT ($F_{CT}$) and LE ($F_{LE}$) emissions for 6 against the $-\Delta G_0$ value is shown in Figure 9. It is interesting to note that the $F_{CT}/F_{LE}$ ratios increased with increasing $-\Delta G_0$ value, reached a maximum, and then decreased again. These observations, based on the steady-state spectra, suggest that there was no CT emission when the $-\Delta G_0$ value was smaller than 0.5 eV or larger than 1.5 eV. The charge-transfer process became predominant when the $-\Delta G_0$ value was around 1 eV. These steady-state results matched nicely with the Marcus theory. On the contrary, no similar behavior was found with copolymer 7.

**Time-resolved fluorescence spectroscopy:** Time-resolved fluorescence spectroscopy with a femtosecond Ti:sapphire laser and a streak camera was employed to obtain the emission decays of 6 and 7 (see Figures S1–S3 in the Supporting Information). The LE emission wavelengths of the corresponding acceptor chromophores in 6 were monitored, and the decay lifetimes attributed to charge-separation process
were obtained (Table 2). The rate constants of charge separation processes \( k_{CS} \) were thus calculated.\(^{[30]} \) When the \( \Delta G_c \) values became more negative, the \( k_{CS} \) values increased initially, reached a maximum, and then decreased. A plot of \( k_{CS} \) against \( \Delta G_c \) is shown in Figure 10. Notably, the Marcus-inverted region was observed for the first time based on forward PET processes in a polymeric system.

Polymers 6c and 6d exhibited dual emissions, from which the CT emissions at longer wavelengths were prominent (in Figure 5b and 7a). The fluorescence decay at these wavelengths as a result of the CT emission were monitored, and these lifetimes were 4.5 and 2.6 ns for 6c and 6d, respectively. The corresponding rate constant of the charge-recombination process was calculated to be \( k_{CR} = 2.2 \) and \( 3.8 \times 10^8 \) s\(^{-1}\). The free-energy changes of these relaxation processes of 6c and 6d (determined by \( -\Delta G_{CR} = E_0 + \Delta G_c \) ) were \( -\Delta G_{CR} = -2.63 \) and \( 2.52 \) eV, respectively. It is worth mentioning that these \( k_{CR} \) values fitted nicely into the inverted region. The emission lifetimes \( t_d \) for 7 and the rate of the deactivation processes \( k_d \) are also listed in Table 2. It is interesting to note that the emission-decay profile of 7a was treated by a two-exponential fitting to give two lifetimes \( \tau_d = 38 \) and 176 ps. The magnitude of the longer lifetime was similar to other \( \tau_d \) values of 7b, 7c, and 7e, and the magnitude of the shorter lifetime was close to \( \tau_{CS} \) values of 6a. These results were consistent with the steady-emission spec-

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Figure 4. a) Absorption spectra of 6b (black) and 7b (gray) in cyclohexane (-----) and THF (----); concentration = 1.0 \times 10^{-5} \text{m}. b) Emission spectra of 6b in cyclohexane (-----) and THF (----) and 9b (——) in THF. c) Emission spectra of 7b in cyclohexane (-----) and THF (----) and 10b (——) in THF. Variable-temperature emission spectra of d) 6b and e) 7b in MTHF (-----: 298 K, ----: 270 K, -----: 240 K, ----: 210 K, ----: 180 K; concentration = 1.0 \times 10^{-5} \text{m}; excitation wavelength = 370 nm).
tra of 7a, in which the emission spectra showed a broad band that possibly involved two different radiative-relaxation processes from the LE emission of the acceptor and the emission of the charge-transfer complex. The $k_d$ values for 7 were similar, whereas the $k_{CS}$ and $k_{CR}$ values for 6 followed a bell-shape distribution (Table 2).

It seems likely that the electronic coupling between the LE and CT states in 6 and 7 would be different, thus leading to different radiative-relaxation pathways. These results reiterate the discrepancy of the alkyl substituents on the silicon atom on the conformations of 6 and 7 due to the Thorpe–Ingold effect, which would dictate the photophysical behavior of the donor–acceptor pair in these copolymers. Indeed, a broad transient maximum at $\lambda = 530$ nm was characterized in 6c, but there was no transient feature at $\lambda = 530$ nm in 7c (Figure 11). These results further confirmed that the transient species of the excited state were different for 6c and 7c.

Thorpe–Ingold effect and polymer folding: It is known that silylene-spaced divinylarene and related copolymers are highly folded.[13,14] Through-space interactions between non-adjacent divinylbenzene chromophores readily take place to result in the appearance of emission bands at longer wavelengths with vibronic fine structures.[15] To rule out such a possibility, copolymers 14a and 14b were synthesized by replacing the N-methyl amino groups in 6 and 7 with ethyl-
dene moieties. No PET process between the stilbene chromophore and para-alkyl-substituted styrene moieties would be expected as a result of the mismatch of the frontier orbital energies. The absorption and emission spectra of 14a and 14b are shown in Figure 12. Similar fluorescence spectra of 14a and 14b as a result of the intrinsic emission of the stilbene chromophore suggest that no intrachain through-space interactions that lead to the longer-wavelength emissions in these polymers would take place, no matter whether the substituent on the silicon atom is a methyl or isopropyl group. These results indicate the absorption and emission features observed in 7 would arise from the charge-transfer complex.

The experimental evidence discussed above suggests the importance of the Thorpe–Ingold effect on the conformation of the dialkysilylene-spaced copolymers 6 and 7, which would bring the adjacent donor–acceptor chromophores in proximity. As such, the mode of interaction between these
chromophores would be different depending on the steric bulkiness of the substituents on the silicon atom. For the purpose of establishing the importance of the interactions between adjacent donor–acceptor chromophores modulated by silylene moieties in 6 and 7, the monomeric model donor–acceptor pairs 2 and 15 were synthesized. The absorption spectra were essentially independent of the solvent polarity (see Figure S7 in the Supporting Information), and there is no characteristic charge-transfer absorption for 2 and 15. The emission spectra of 2 and 15 are compared with those of 6c and 7c in Figure 13a, b, respectively. The emission spectrum of 2 in cyclohexane showed LE emission of the acceptor moiety at $\lambda = 370$ nm and a tailing signal toward $\lambda = 450$ nm. When THF was used as the solvent, dual emissions were observed at $\lambda = 370$ and 510 nm, and these two emissions were assigned to LE and CT emissions, respectively, which is similar to those of 6c. The emission spectrum of 15 also displayed the LE and CT emissions at $\lambda = 370$ and 450 nm, respectively, in cyclohexane; furthermore, the CT emission shifted to $\lambda = 510$ nm in THF. Interestingly, the emission profiles of 15 were similar to those of 2 or 6c, but completely different from those of 7c under the same conditions. Unlike the emissions of 7c, no emission as a result of the charge-transfer complex was observed at all for 15, although both 7c and 15 contain the iPr2Si linker between the donor and acceptor chromophores. As discussed above, the bulky isopropyl substituents would exert the Thorpe–Ingold effect to bring the adjacent chromophores into proximity. Compound 15 is a small molecule. Rotation about the sigma bonds might occur relatively freely, thus
leading to an ensemble of different conformers. The distance between the donor and acceptor chromophores might not be fixed in 15. Accordingly, the mode of interaction between the donor and acceptor chromophores for 2 and 15 would be similar. It is worth noting that the relative intensity of the CT emission of 15 was much stronger than that of 2. Presumably, the Thorpe–Ingold effect remained to play an important role. On the other hand, silylene-spaced copolymers would be highly folded and the Thorpe–Ingold effect may generate a variation in the local conformation. Such a change in the local conformation may lead to a different folding nature of a polymer. It seems likely that the folding of polymer 7c might further perturb the relative distance between the adjacent donor and acceptor chromophores, thus resulting in different photophysical behavior.

Random copolymers 16 with different ratios of Me2Si and iPr2Si linkers (Me2Si/iPr2Si = 9:1, 4:1, and 1:1) were synthesized. The absorbance of the charge-transfer absorption at approximately λ = 400 nm increases with increasing molar fractions of the iPr2Si moieties (Figure 14a). The relative intensity of the emission at λ = 510 nm (Figure 14b), as a result of the CT emission from the donor–acceptor pair linked by the Me2Si spacer, decreases with decreasing molar...
fraction of the Me2Si linkers in 16. In the meantime, the emission at $\lambda = 450$ nm, which arises from the emission from the iPr2Si-spaced donor–acceptor pair, became stronger when the molar fraction of the iPr2Si spacer increases. As expected, the intensity of the emission band at approximately $\lambda = 450$ nm increases with decreasing temperature, whereas that of the emission band at around $\lambda = 500$–550 nm decreases with concomitant bathchromic shift at the same time. These behaviors are same as the temperature-dependent emissions of 6c and 7c discussed previously. In other words, when the donor and acceptor chromophores were spaced by the iPr2Si group, a charge-transfer complex would be formed between these chromophores in the polymers and the emission of the Me2Si-spaced donor–acceptor pair in 16 exhibits typical CT emissions as those observed for 6c. These results suggest that concomitance of the Thorpe–Ingold effect and polymer folding is indispensable to control the electronic interactions between adjacent donor–acceptor chromophores.

Conclusion

In summary, we have demonstrated the fundamental differences between the photophysical properties of 6 and 7 owing to a difference in the alkyl substituents on the silylene spacer. The variation of the steric environment around the silicon atom may generate different conformations and folding so that the spatial arrangement and orientation of the donor and acceptor chromophores could be adjusted. The free-energy differences between the LE and CT states for 6 could readily be tuned and dual emissions were observed in those polymers with appropriate the $\Delta G_o$ values for the charge-separation processes. In particular, the Marcus-inverted region was observed in both steady-state and fast kinetic measurements for 6. In contrast, the photophysical behavior is completely different when the substituents on the silicon atom are changed from dimethyl to disopropyl groups. Because of the synchronized Thorpe–Ingold effect exerted by the bulky isopropyl substituents and the perturbation of the conformation of the polymer, the adjacent donor and acceptor chromophores in 7 may be brought closer. A charge-transfer complex may thus be formed from a strong interaction between these neighboring chromophores at the ground state. Evidence to support the importance of folding on the photophysical behavior of 6 and 7 can be illustrated by a systematic investigation on the oligomers with the same structural features of 6 and 7.[31]

Experimental Section

**General:** Gel-permeation chromatography (GPC) was performed on a Waters GPC machine with an isocratic HPLC pump (1515) and a refractive-index detector (2414). THF was used as the eluent (flow rate = 1.0 mL min$^{-1}$). Waters Styragel HR2, HR3, and HR4 columns (7.8 x 300 mm) were employed for determination of the relative molecular weight with polystyrene as a standard ($M_n$ values ranged from 375 to 3000 plg.

**Figure 14.** a) Absorption and b) emission spectra of 6c, 7c, and 16 with different ratios of Me2Si and iPr2Si spacers (--- 6c, ----- 16 Me2Si/iPr2Si = 9:1, ------ 16 Me2Si/iPr2Si = 4:1, -------- 16 Me2Si/iPr2Si = 1:1, ---- 7c; concentration = 4.5 x 10$^{-5}$ M). c) Variable-temperature emission spectra of 16 (SiMe2/SiPr2 = 9:1) in MTHF (--- 298 K, ---- 270 K, ------ 240 K, ----- 210 K, ---- 180 K; concentration = 1.0 x 10$^{-5}$ M; excitation wavelength = 330 nm).
Absorption spectra were measured on a Hitachi U-3310 spectrophotometer and emission spectra on a Hitachi F-4500 fluorescence spectrophotometer. An ECO Chemie μA-tolub III potentiostat/galvanostat was used for the electrochemical experiments in which Pt electrodes were used as the working and counter electrodes and a Ag/AgNO₃ electrode was used as the reference electrode.

**Time-resolved fluorescence experiments:** A mode-locked Ti:sapphire laser (repetition rate: 76 MHz; pulse width: <200 fs) passed through an optical parametric amplifier to produce the desired wavelength of the pulse laser. The fluorescence of the 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 0.3 ps. The sample was prepared in a concentration of 1.0 × 10⁻⁶ M, and using an ultramicro cuvette with a pathlength of 1 mm to maintain the excitation at the same time. The signal was collected ten times to decrease the signal-to-noise ratio.

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**References**


[30] The rate constant $k_{CS}$ was obtained based on $k_{CS} = 1/t_{CS} - 1/t_o$, where $t_{CS}$ denotes the observed decay lifetime of LE bands in 6 and $t_o$ denotes the intrinsic fluorescence decay lifetime of the corresponding monomers 9.

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