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Folding of Alternating Dialkylsilylene-Spaced Donor–Acceptor Copolymers: The Oligomer Approach

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Dedicated to Prof. Tak-Hang Chan for his outstanding contributions to organosilicon chemistry

Abstract: A series of oligmers with donor–acceptor pairs separated by diisopropylsilylene ($i\mathrm{Pr}_2\mathrm{Si}$) spacers, composed of monomer **4b**, dimer **5**, trimer **6**, and tetramer **7**, were synthesized to scrutinize the folding behavior. Monomer **4a** with a dimethylsilylene ($\mathrm{Me}_2\mathrm{Si}$) spacer was also prepared for comparison. The 4-aminostyrene moiety was used as the donor and the stilbene moiety as the acceptor. Both steady-state and time-resolved fluorescence spectroscopic measurement were made. Regardless of the substituents on the silicon atom, the emission spectra of **4a** and **4b** exhibit both local excited (LE) emission of the acceptor chromophore and emission from the charge-separated state (CT emission), which are similar to that of the corresponding $\mathrm{Me}_2\mathrm{Si}$-spaced copolymer **2a** with the same donor and acceptor chromophores, but different from that of the copolymer with the $i\mathrm{Pr}_2\mathrm{Si}$ spacer **2b**. Dimer **5** behaves like **4** and **2a**. As the chain length of the oligomers increases, the emission properties of the higher homologues become prone to that of **2b**. Thus, tetramer **7** exhibits emission from the charge-transfer complex, which is essentially same as that of **2b**. Moreover, charge-transfer absorptions emerge in **6** and **7**. These results suggest that the folding nature of oligomers approaches that of the corresponding polymer, as the degree of oligomerization increases, and the electronic interactions between adjacent donor–acceptor pairs are controlled by the steric effect of the substituents on the silicon atoms and concomitant amplification of the stabilizing energy by extending the distance of the folding structure.

Keywords: oligomers • photoinduced electron transfer • polymer folding • substituted silylene • silicon • Thorpe–Ingold effect

Introduction

The macroscopic functional properties of polymeric materials should be closely related to the intrachain folding and intermolecular interactions of polymeric molecules. The folding nature in general is governed by numerous through-space noncovalent interactions along the polymeric backbone.[1–9] A polymeric molecule is folded so that the loss of entropy due to conformational change can be compensated by the enthalpic gain through such intrachain interactions.[10] The differences in small energetic barriers for each of the conformational states may be amplified by extending the distance of the folding structure, thus resulting in a more stable conformation.[11] It is, therefore, envisaged that an increase of repetitive units in oligomers can achieve a structural feature with similar folding behavior of a polymer. The use of oligomers to mimic the optoelectronic properties of conjugated polymers has been extensive.[12] Moreover, foldamers provide another useful model for the folding of biomacromolecules.[2]

We recently found that the size of the substituents on the silicon atom in dialkylsilylene-spaced divinyl arene copolymers (e.g., **1**) may exert the Thorpe–Ingold effect, thus resulting in a discrepancy in the photophysical and morphological behavior of the polymers.[13–15] The silylene moiety in **1** is, in general, considered to be an insulating tetrahedral spacer.[13–19] Fluorescence resonance energy transfer (FRET),[17] chiroptical property transfer,[18] and photoinduced electron transfer (PET)[15,19] can readily take place between chromophores separated by the silylene moieties. To illustrate this approach, both the local emission (LE) of acceptor chromophores and emission from the charge-separated state (CT emission) are observed for **2a**, whereas emission from the charge-transfer complex is found for **2b**.[15] The difference in the photophysical properties might be attributed to the change in the distance between the donor and acceptor chromophores in **2a** and **2b**. Such a morphological discrepancy may have arisen from the change in the

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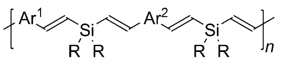
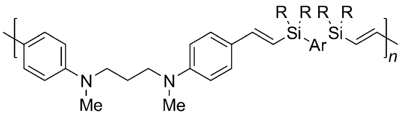
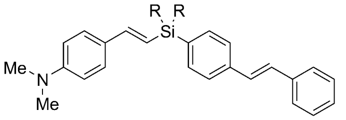
local conformation that surrounds the silicon atom due to the steric effect of the substituents. Interestingly, both the LE and CT emission are observed in the model monomeric compounds **3a** and **3b**, which contain the same pair of donor and acceptor chromophores; albeit, the relative intensities of these two emissions are somewhat different. Unlike **2b**, no charge-transfer absorption and the corresponding emission were observed for **3b** with isopropyl substituents on the silicon atom. It is envisaged that, in addition to the Thorpe–Ingold effect, other factors such as polymer folding may also play a pivotal role on the photophysical discrepancies in **2**. To mimic the folding nature of **2**, we have designed and synthesized monomers **4** and oligomers **5**–**7** of different chain lengths with the same structural features of the repetitive units in **2**.



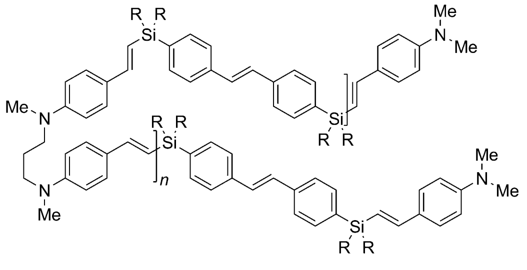
1a R = Me **1b** R = ^{i}Pr



2a R = Me **2b** R = *i*Pr



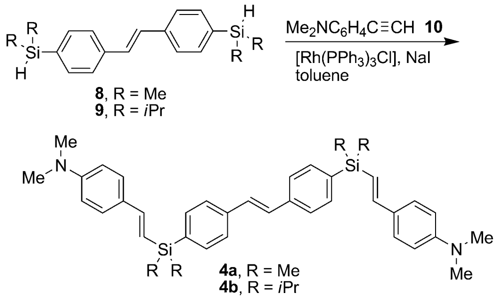
3a R = Me **3b** R = *i*Pr



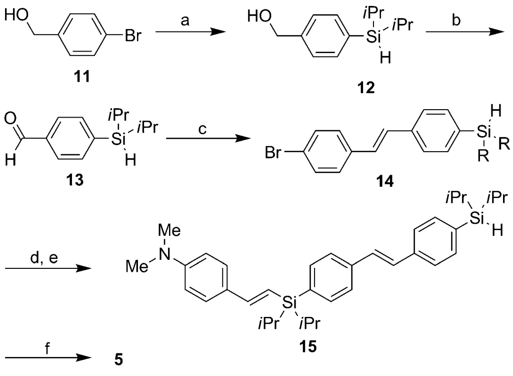
4 *n* = 0 **a** R = Me **b** R = *i*Pr
5 *n* = 1 **6** *n* = 2 **7** *n* = 3 R = *i*Pr

Results

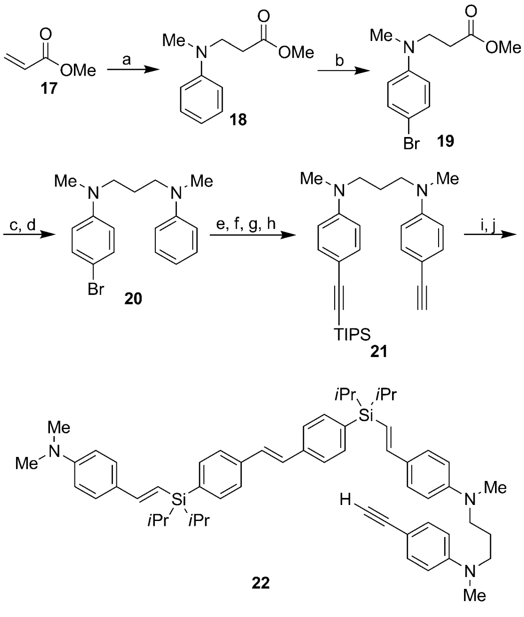
Synthesis: Similar to the synthesis of **2**,[15] the rhodium(I)-catalyzed hydrosilylation protocol was used to construct **4**–**7**, with silylene spacers between the donor and acceptor chromophores. It is interesting to note that the presence of a stoichiometric amount of NaI (relative to the equivalents of the amino moiety in the reactants) was essential to facilitate the hydrosilylation reactions.[15,19] Thus, monomers **4a** and **4b** were synthesized from the hydrosilylation of **10** with **8** and **9**, respectively [Eq. (1)]. The synthesis of dimer **5** is summarized in Scheme 1. Scheme 2 outlines the synthesis of key intermediate **22** for trimer **6** and tetramer **7**, which are shown in Scheme 3.[20]



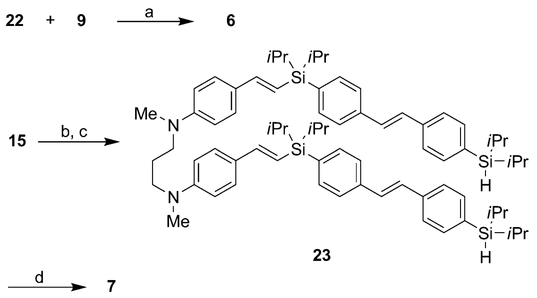
(1)



Scheme 1. a) *n*BuLi, *i*Pr$_2$SiHCl (73 %); b) MnO$_2$ (90 %); c) 4-BrC$_6$H$_4$PO(OEt)$_2$, KO*t*Bu (66 %); d) **10**, [Rh(PPh$_3$)$_3$Cl], NaI (76 %); e) *n*BuLi, *i*Pr$_2$SiHCl (79 %); f) $\mathrm{HC{\equiv}CC_6H_4NMe(CH_2)_3NMeC_6H_4C{\equiv}CH}$ (**16**), [Rh(PPh$_3$)$_3$Cl], NaI (36 %).



Scheme 2. a) *N*-methylaniline (33 %); b) NBS (99 %); c) AlMe$_3$ (66 %); d) LAH (97 %); e) I$_2$ (70 %); f) TMSC≡CH, [Pd(PPh$_2$)$_2$Cl$_2$], CuI, TEA (72 %); g) TIPSC≡CH, [Pd(PPh$_2$)$_2$Cl$_2$], CuI, PPh$_3$ (69 %); h) K$_2$CO$_3$ (99 %); i) **15**, [Rh(PPh$_3$)$_3$Cl], NaI (56 %); j) TBAF, 50 %. LAH = lithium aluminum hydride, NBS = *N*-bromosuccinimide, TBAF = tetrabutylammonium fluoride, TEA = *N*,*N*,*N*-triethylamine, TIPS = triisopropylsilyl, TMS = trimethylsilyl.



Scheme 3. a) $[Rh(PPh_3)_3Cl]$, NaI (41 %); b) **16**, $[Rh(PPh_3)_3Cl]$, NaI (56 %); c) *n*BuLi, iPr_2SiHCl (79 %); d) **22**, $[Rh(PPh_3)_3Cl]$, NaI (36 %).

Crystal structures of 4:[20] The ORTEP structures of **4a** and **4b** are shown in Figure 1. Both crystals belong to the $P2_1/n$ space group with a center of symmetry. It is noteworthy that **4a** with dimethylsilylene spacers exclusively shows an *anti* conformation for both the vinylsilane and stilbene moieties. The center-to-center distance between the aniline donor and stilbene acceptor chromophores for the single crystal **4a** is 10.47 Å. On the other hand, **4b** with diisopropyl linkers exhibits 50 % of the crystal structure similar to that of **4a** and the center-to-center distances between the aniline and stilbene chromophores of this structure is 11.07 Å. In addition, another 50 % constitutes disorder structures of equal amounts of *syn* and *anti* conformations for the vinylsilane groups, whereas the center-to-center distances between the aniline and stilbene chromophores of this structure is 9.79 Å. Interestingly, the orientation of the stilbene moiety in these disordered structures of **4b** (Figure 1 c) is different from that in the *anti* conformation in both **4a** and **4b** (Figure 1 a,b). The X-ray data for **4a** and **4b** offer direct evidence to show that the size of the substituents on the silicon atom should exert the Thorpe–Ingold effect on the orientation of the remaining groups attached to this silicon atom, and thus the conformation of the molecules.

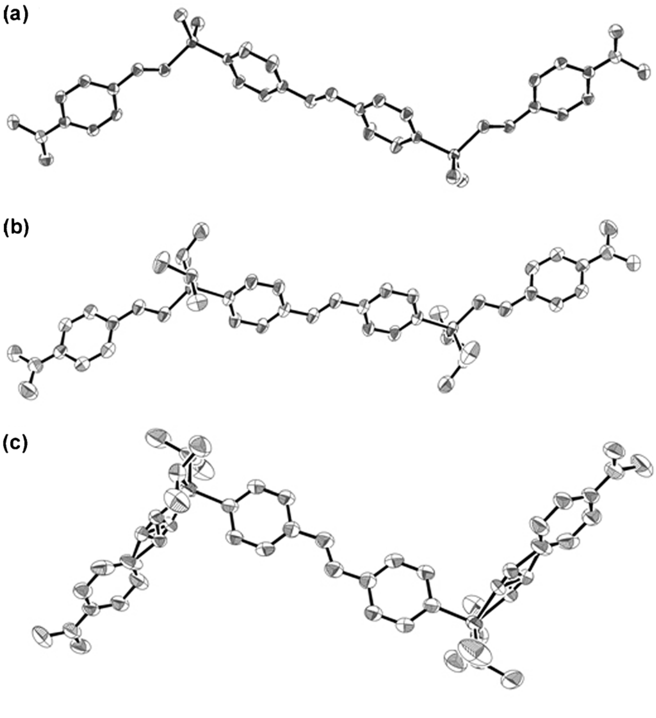


Figure 1. ORTEP (30 % probability level) drawing of a) **4a**, b) **4b** without disorder, and c) **4b** with disorder of the vinylsilane groups.

Photophysical properties of 4: As mentioned previously,[15] the simple donor–acceptor monomeric pairs **3a** and **3b** exhibit similar photophysical properties. This observation indicates that the substituents on the silicon atom might have little effect on the adjacent chromophore–chromophore interaction separated by the silylene spacers in these monomers. It is noteworthy that polymers **2a** and **2b** consist of two donors and one acceptor species in each of the repetitive units. Monomers **4a**[15] and **4b** and oligomers **5**–**7** with the same ratio of donor and acceptor chromophores as those in **2** were thus synthesized in the hope that they could serve as a better model for the photophysical properties of polymers **2**. The absorption and emission spectra of **4a** and **4b** are shown in Figure 2. Interestingly, the absorption profiles of both **4a** and **4b** were the sum of the absorptions of the donor and acceptor chromophores with no characteristic band at relatively longer wavelengths for the charge-transfer complex,[21] which was observed in **2b**.[15] Moreover, the absorption spectra of **4a** and **4b** were independent of the solvent polarity. The emission profiles exhibited dual emissions at $\lambda = 360$ and 450 nm in cyclohexane, and the latter emission shifted to $\lambda = 510$ nm in THF. The emission band at the shorter wavelength was assigned as the LE of the acceptor chromophore and the emission band at the longer wavelength could have arisen from the CT emission. In nonpolar cyclohexane, the relative intensity of the LE was stronger than that of the CT emission, whereas the relative intensities were reversed in THF. The behavior of monomers **4a** and **4b**, in general, are similar to copolymer **2a**, and the size of the substituents (Me versus *i*Pr) on the silicon atom appeared to be irrelevant.

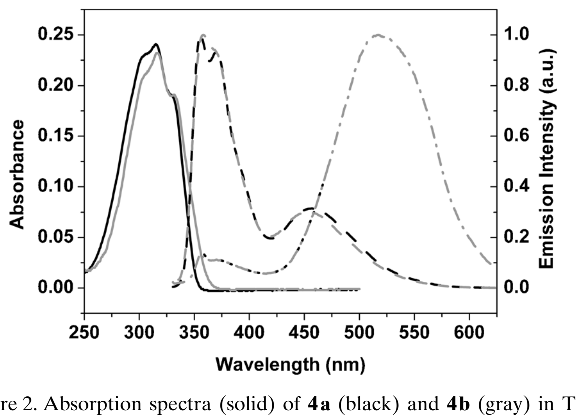


Figure 2. Absorption spectra (solid) of **4a** (black) and **4b** (gray) in THF and emission spectra of **4a** (black) and **4b** (gray) in cyclohexane (-----) and THF (–•–•). Concentration = 5×10^{-6} M; excitation wavelength = 330 nm.

Photophysical properties of oligomers 5–7: The absorption and emission spectra of dimer **5**, trimer **6**, and tetramer **7** with the diisopropylsilylene spacer in THF are shown in Figure 3. The photophysical properties of **5** are almost identical to those of **4a** and **4b**. Interestingly, the absorbance at approximately $\lambda=350$–400 nm increased with increasing oligomeric chain length. This absorption band could be attributed to the charge-transfer absorption for the formation of the charge-transfer complex as observed in **2b**. The emission spectrum of dimer **5** was similar to those spectra of copolymer **2a** and the corresponding monomers **4a** and **4b** (Figure 3b), in which both LE and CT emission at $\lambda=375$ and 510 nm were observed. Interestingly, trimer **6** exhibited an emission band at $\lambda=430$ nm with a vibronic structure in THF. The emission band further shifted to $\lambda=450$ nm in tetramer **7**, which was similar to the emission of copolymer **2b** with the diisopropylsilylene spacer. The discrepancy in the emission profiles among these diisopropylsilylene-spaced oligomers **5**–**7**, monomers **4b**, and copolymer **2b** may arise from the difference in the number of repetitive units in the oligomeric and polymeric chains. In other words, when the degree of oligomerization was four (as in **7**) or above, the ground-state interaction between adjacent donor–acceptor pairs should become similar, thus resulting in the formation of charge-transfer complexes. Presumably, the folding nature of copolymer **2b** should be similar to that of oligomer **7**.

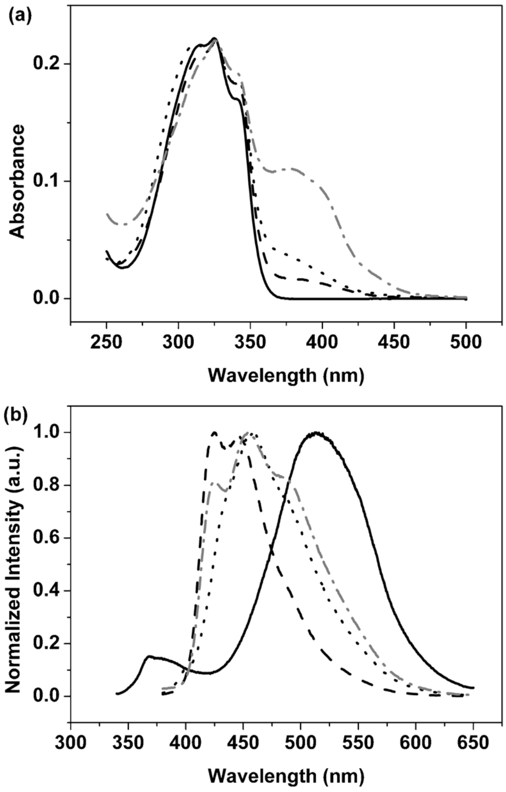


Figure 3. a) Absorption and b) emission spectra of **5** (——, $\lambda_{ex}=330$ nm), **6** (-----, $\lambda_{ex}=380$ nm), **7** (•••••, $\lambda_{ex}=380$ nm), and **2b** (–•–•, $\lambda_{ex}=330$ nm) in THF. Concentration $=1\times10^{-6}$ M.

As mentioned above (Figure 3a), the absorption of the acceptor stilbene chromophore in these oligomers **5**–**7** is at approximately $\lambda=300$–350 nm and that of the charge-transfer complex is at approximately $\lambda=350$–400 nm. Because **5** does not exhibit any absorption beyond $\lambda=350$ nm, no change in emission spectra was observed at different excitation wavelengths. On the other hand, the emission profiles for **6** and **7** are excitation-wavelength dependent (Figure 4). When the shorter excitation wavelength was employed, the emission maxima at approximately $\lambda=500$ nm were observed for both **6** and **7**. Presumably, local excitation of the acceptor stilbene chromophore might take place followed by charge transfer, thus leading to CT emission at this wavelength. The relative intensities of the emission band at approximately $\lambda=500$ nm for both **6** and **7**, however, decreased when the excitation wavelength increased from $\lambda=330$ to 380 nm. In addition, the emission of the charge-transfer complex at $\lambda=430$–470 nm was also observed. Alternatively, excitation at the longer wavelength ($\lambda>360$ nm) due to the absorption of the charge-transfer complexes in **6** and **7** gave an emission band only at approximately $\lambda=430$–470 nm, which is attributed to the emission of the charge-

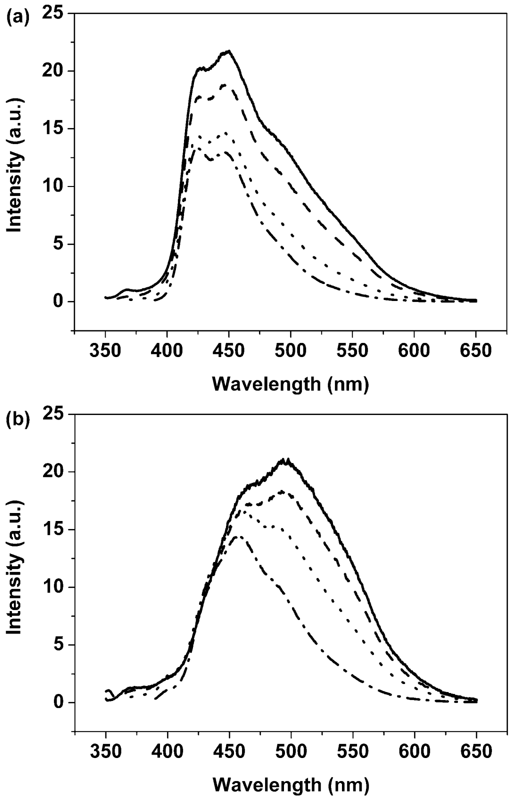


Figure 4. Emission spectra of a) **6** and b) **7** in THF at different excitation wavelengths (——: $\lambda_{ex}=330$ nm, -----: $\lambda_{ex}=350$ nm, •••••: $\lambda_{ex}=360$ nm, –•–•: $\lambda_{ex}=380$ nm).

transfer complexes between the donor and acceptor chromophores of these oligomers.

The normalized excitation spectra of **6** and **7** are shown in Figure 5. The relative intensities at approximately $\lambda = 360$–400 nm increased when the monitoring wavelengths gradually changed from $\lambda = 570$ to 480 nm. It is noteworthy that the relative enhancement at approximately $\lambda = 360$–400 nm was more prominent in **7** that in **6**. The band at approximately $\lambda = 360$–400 nm in these excitation spectra would be contributed to by the charge-transfer absorption, and the emission band at $\lambda = 330$ nm in the excitation spectra should be assigned as the absorption of the stilbene chromophore. As mentioned above, the characteristic CT emission of **6** and **7** appeared at a longer wavelength (at approximately $\lambda =$ 500 nm) and that of the radiative relaxation from the charge-transfer complex occurred at a shorter wavelength ($\lambda = 430$–470 nm). Consequently, when the shorter monitoring wavelengths were chosen, the band at approximately $\lambda =$ 360–400 nm in the excitation spectra was enhanced.

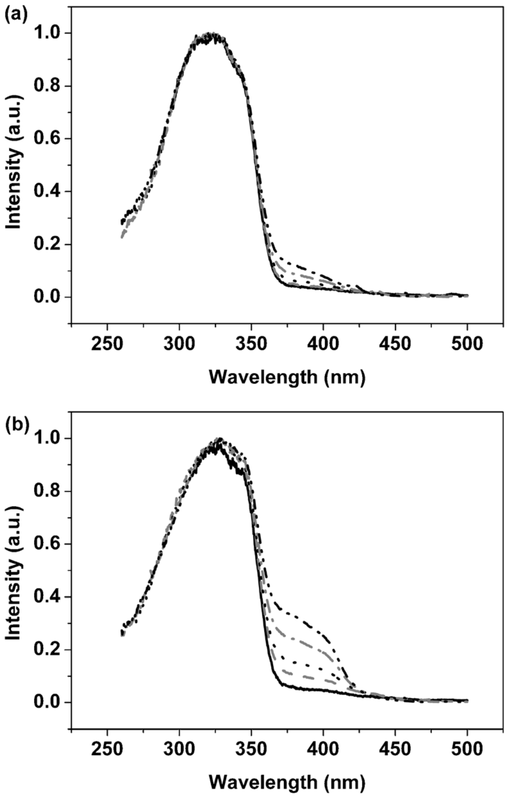


Figure 5. Excitation spectra of a) **6** and b) **7** in THF with different monitored wavelengths (——: $\lambda_{ex} = 570$ nm, -----: $\lambda_{ex} = 550$ nm, •••••: $\lambda_{ex} =$ 525 nm, –•–•: $\lambda_{ex} = 500$ nm, –••–••: $\lambda_{ex} = 480$ nm).

Temperature-dependent emission spectra of 4–7: Compounds **4a**, **4b**, and **5** exhibit dual emission (Figures 2 and 3), which should consist of the LE of the acceptor stilbene chromophore at $\lambda = 370$ nm and the CT emission at approximately $\lambda = 510$ nm. We have previously demonstrated that the CT emission in polymer **2a** at approximately $\lambda = 510$ nm gradually shifted to a long wavelength with lowering intensities as the temperature decreased.[15] Similar behavior was observed for **4** and **5** in methyltetrahydrofuran (MTHF; Figure 6a–c). This observation appears to be the characteristic property of CT emissions in these systems. When the temperature is lowered, the polarity of the solvent should be enhanced.[22] The energy level of CT state should thus be lowered, thereby resulting in a decrease in the energy gap between the CT and ground states.[23] Moreover, the LE for **4** and **5** at approximately $\lambda = 370$ nm is somewhat enhanced at lower temperatures (Figure 6a–c). The thermal relaxation of

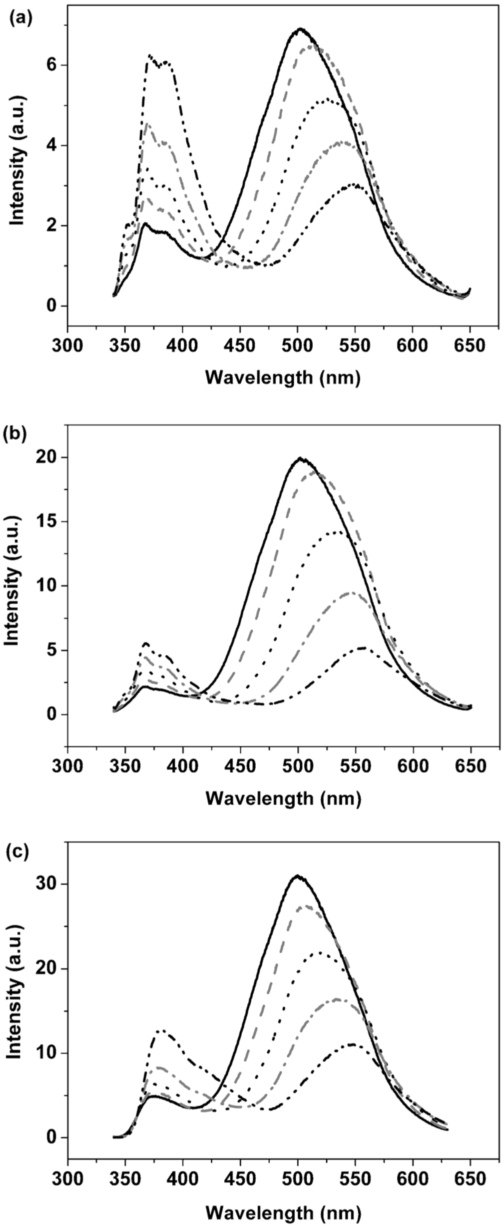


Figure 6. Temperature-dependent emission spectra of a) **4a**, b) **4b**, and c) **5** in THF at different temperatures (——: 295 K, -----: 270 K, •••••: 240 K, –•–•: 210 K, –••–••: 180 K). Excitation wavelength = 330 nm.

the corresponding excited state might be restricted at lower temperatures.[24]

The temperature-dependent emission spectra of **6** and **7** represented completely different behavior from **4** and **5** (Figure 7a, b), that is, the intensity increased with decreasing temperature no matter whether the excitation wavelengths were $\lambda = 350$ or 370 nm. The excitation wavelength at $\lambda = 350$ nm for **6** and **7** might trigger the occurrence of the CT emission (Figure 4). However, the increase in the emission intensity during lowing of the temperature should dominate so that the variation of the CT emission, if any, could not be detected. The similar emission behavior between **6**, **7**, and polymer **2b** further suggests that the folding nature of **6** and **7** should take place in the same manner of that of **2b**.

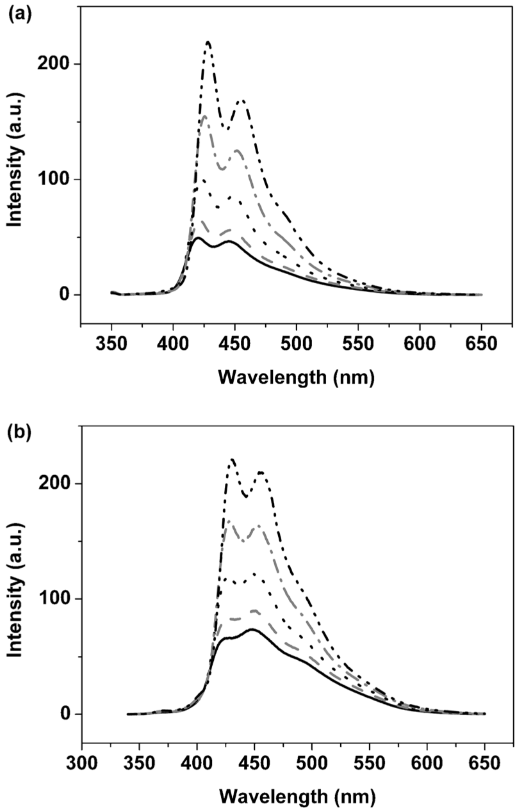


Figure 7. Temperature-dependent emission spectra of a) **6** and b) **7** in THF at different temperatures (——: 295 K, -----: 270 K, •••••: 240 K, –•–•: 210 K, –••–: 180 K). Excitation wavelength = 330 nm.

Time-resolved fluorescence spectroscopy: Time-resolved fluorescence spectroscopy with a femto-second Ti/sapphire laser equipped with a streak camera was employed to obtain the fluorescence decay lifetimes τ of **4**–**7** in THF. The results are compared with the lifetimes of **2a** and **2b** in Table 1. The decay of the LE emissions for **4** and **5** were monitored at $\lambda = 360$–380 nm, and the fluorescence decays of the charge-transfer complexes for **6** and **7** were monitored at $\lambda = 440$–460 nm. The τ values of monomers **4a**,**b** and dimer **5** are close to the fluorescence decay lifetime of the LE emission for **2a** (i.e., $\tau = 9$ ps). On the other hand, the τ values of the charge-transfer complexes observed in **6** and **7** are also similar to that observed in **2b**. It is worth mentioning that the kinetic results are consistent with the observed photophysical properties of the steady state in these oligomers and polymers.

Table 1. The fluorescence decay lifetimes τ of **2**–**7**.

	τ [ps]	
	Measured at $\lambda = 360$–380 nm	Measured at $\lambda = 440$–460 nm
4a	12	–
4b	10	–
5	10	–
6	–	175
7	–	160
2a	9[a]	
2b		150[a]

[a] Ref. [15].

Discussion

We examined the detailed photophysical properties of monomers **4a** and **4b**, dimer **5**, trimer **6**, and tetramer **7**, which have similar repetitive units as that of polymers **2a** and **2b** (described in the accompanying report).[15] Two distinct categories were found in the photophysical behavior of these molecules. Small molecules **4** and **5** and polymer **2a** exhibit similar emission profiles with typical LE and CT emission, no matter whether the substituents on the silicon atom are methyl or isopropyl. On the other hand, both the CT emission and emission from the charge-transfer complexes for oligomers **6** and **7** were observed upon excitation at $\lambda = 330$ nm (Figure 4). This CT emission disappeared when the excitation wavelength was $\lambda = 370$ nm. In this regard, oligomers **6** and **7** gave similar photophysical properties from the charge-transfer complex between the adjacent aminostyrene donor and stilbene acceptor chromophores as that of polymer **2b**.

Notably, only monomer **4a** and polymer **2a** have the dimethylsilylene spacer, whereas the rest have the bulky diisopropylsilylene spacers. The crystal structures of **4a** and **4b** clearly demonstrated that the bulkiness of the substituents on the silicon atom may exert the Thorpe–Ingold effect, thus leading to different conformations around the silicon atom. The change from the CT emission to the charge-transfer complex emission in **4**–**7** indicates that there is a discrepancy in the electronic coupling between the donor and acceptor chromophores. It seems likely that such electronic coupling might be relatively weak in **4** and **5** and strong in **6** and **7**. In other words, the electron-transfer processes might be altered from non-adiabatic to adiabatic regimes.[21] As mentioned in the accompanying report,[15] the electronic coupling for PET in **2a** was estimated to be around 25 cm^{-1} and those for **6** and **7** were calculated on the basis of the model developed by Mulliken and Hush[21,25] to be 600 and 1000 cm^{-1} per repeating unit, respectively.[20]

Intriguingly, the substituents on the silicon atom for **4b** and **5**–**7** were isopropyl groups, which should exert a similar Thorpe–Ingold effect on the local conformation around the silicon atom. The discrepancy in the photophysical behavior could only have arisen from the number of the repetitive units in these oligomers. The similarity in photophysical properties between polymer **2b** and larger oligomers **6** and **7** suggests that the folding nature might be similar. In other words, as the chain length of the oligomer becomes longer, they should be more folded. Through-space intrachain van der Waal interactions might restrict the degree of freedom of the oligomeric chain to bring the adjacent donor–acceptor chromophores closer. As such, this geometrical perturbation may change the nature of the electronic coupling from weak to strong by increasing the degree of polymerization. It is believed that synchronization of the Thorpe–Ingold effect and the conformational changes of the oligomers may occur in these larger oligomers **6** and **7** and polymer **2b**. A similar enhancement was not observed either in small molecules **4b** and **5** with the diisopropylsilylene linkers or in polymer **2a** with the dimethylsilylene spacers. Our results suggest that the folding nature of trimer **6** and tetramer **7** should emerge to be similar to that of the corresponding polymer **2b** in these silylene-spaced copolymers.

Conclusion

In summary, we have demonstrated that an increase in the oligomer chain length in **4**–**7** should gradually shift the photophysical properties due to a different folding nature. The presence of bulky isopropyl substituents together with conformational changes should play a pivotal role on the folding of these oligomers, and thus the corresponding polymers **2**. This approach appears to be consistent with the suggestion that the differences in the small energetic barriers for each of the conformational states may be amplified by extending the distance of the folding structure, thus resulting in a more stable conformation.[11] Like foldamers,[2] oligomers **4**–**7** have provided a useful model toward understanding the folding behavior of the corresponding polymers **2**.

Experimental Section

General: The absorption spectra were measured on a Hitachi U-3310 spectrophotometer and the emission spectra on a Hitachi F-4500 fluorescence spectrophotometer. High-resolution mass-spectrometric measurements were obtained on a Jeol-JMS-700 mass spectrometer by using the fast-atom bombardment (FAB) method in a 3-nitrobenzyl alcohol matrix. Electron impact (EI) measurements were collected with a resolution of 8000 (3000; 5% valley definition) and MALDI-TOF spectra were taken by using an Applied-Biosystem-DE-PRO mass spectrometer.

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 $g\,mm^{-1}$; 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^{-5} M and an ultramicro cuvette with a path length of 1 mm was used 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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[1] a) V. N. Uversky, E. A. Permyakov, *Method in Protein Structure and Stability Analysis*, Nova Biomedical, New York, **2007**; b) A. Tramontano, *Protein Structure Prediction: Concepts and Applications*, Wiley-VCH, Weinheim, **2006**.

[2] S. Hecht, I. Huc, *Foldamers*, Wiley-VCH, Weinheim, **2007**.

[3] For reviews, see: a) L. Brunsveld, B. J. B. Folmer, E. W. Meijer, R. P. Sijbesma, *Chem. Rev.* **2001**, *101*, 4071–4097; b) D. J. Hill, M. J. Mio, R. B. Prince, T. S. Hughes, J. S. Moore, *Chem. Rev.* **2001**, *101*, 3893–4011.

[4] For reviews, see: a) R. P. Cheng, S. H. Gellman, W. F. Degrado, *Chem. Rev.* **2001**, *101*, 3219–3232; b) G. D. Rose, P. J. Fleming, J. R. Banavar, A. Maritan, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 16623–16633; c) A. Patgiri, A. L. Jochin, P. S. Arora, *Acc. Chem. Res.* **2008**, *41*, 1289–1300.

[5] For reviews, see: a) E. A. Meyer, R. K. Castellano, F. Diederich, *Angew. Chem.* **2003**, *115*, 1244–1287; *Angew. Chem. Int. Ed.* **2003**, *42*, 1210–1250; b) M. Fathalla, C. M. Lawrence, N. Zhang, J. L. Sessler, J. Jayawickramarajah, *Chem. Soc. Rev.* **2009**, *38*, 1608–1620; c) J. L. Sessler, J. Jayawickramarajah, *Chem. Commun.* **2005**, 1939–1949; d) D. Pijper, B. L. Feringa, *Soft Matter* **2008**, *4*, 1349–1372; e) A. Berresheim, M. Müller, K. Müllen, *Chem. Rev.* **1999**, *99*, 1747–1785; f) P. Leclère, E. Hennebicq, A. Calderone, P. Brocorens, A. C. Grimsdale, K. Müllen, J. L. Brédas, R. Lazzaroni, *Pros. Polym. Sci.* **2003**, *28*, 55–81; g) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schennung, *Chem. Rev.* **2005**, *105*, 1491–1546; h) J. R. Rudick, V. Percec, *Acc. Chem. Res.* **2008**, *41*, 1641–1652; i) E. Yashima, K. Maeda, H. Lida, Y. Furusho, K. Nagai, *Chem. Rev.* **2009**, *109*, 6102–6211.

[6] a) J. C. Nelson, J. G. Saven, J. S. Moore, P. G. Wolynes, *Science* **1997**, *277*, 1793–1796; b) R. B. Prince, J. G. Saven, P. G. Wolynes, J. S. Moore, *J. Am. Chem. Soc.* **1999**, *121*, 3114–3121; c) R. B. Prince, L. Brunsveld, E. W. Meijer, J. S. Moore, *Angew. Chem.* **2000**, *112*, 234–236; *Angew. Chem. Int. Ed.* **2000**, *39*, 228–230; d) J. Kim, T. M. Swager, *Nature* **2001**, *411*, 1030–1034; e) J. Kim, I. A. Levitsky, D. T. McQuade, T. M. Swager, *J. Am. Chem. Soc.* **2002**, *124*, 7710–7718.

[7] a) J. H. K. K. Hirschberg, L. Brunsveld, A. Ramzi, J. A. J. M. Vekemans, R. P. Sijbesma, E. W. Meijer, *Nature* **2000**, *407*, 167–170; b) E. J. Foster, E. B. Berda, E. W. Meijer, *J. Am. Chem. Soc.* **2009**, *131*, 6964–6966.

[8] a) B. W. Greenland, S. Burattini, W. Hayes, H. M. Colquhoun, *Tetrahedron* **2008**, *64*, 8346–8354; b) S. Burattini, B. W. Greenland, D. H. Merino, W. Weng, J. Seppala, H. M. Colquhoun, W. Hayes, M. E. Mackay, I. W. Hamley, S. J. Rowan, *J. Am. Chem. Soc.* **2010**, *132*, 12051–12058; c) S. Burattini, B. W. Greenland, W. Hayes, M. E. Mackay, S. J. Rowan, H. M. Colquhoun, *Mater. Chem.* **2011**, *23*, 6–8.

[9] a) M. Hagihara, N. J. Anthony, T. J. Stout, J. Clardy, S. L. Schreiber, *J. Am. Chem. Soc.* **1992**, *114*, 6568–6570; b) E. Yashima, T. Matsushima, Y. Okamoto, *J. Am. Chem. Soc.* **1997**, *119*, 6345–6359; c) K. Kirshenbaum, A. E. Barron, R. A. Goldsmith, P. Armand, E. K. Bradley, K. T. V. Truong, K. A. Dill, F. E. Cohen, R. N. Zuck-

ermann, *Proc. Natl. Acad. Sci. USA* **1998**, *95*, 4303–4308; d) R. Nonokawa, E. Yashima, *J. Am. Chem. Soc.* **2003**, *125*, 1278–1283; e) P. Cordier, F. Tournilhac, C. Soulié-Ziakovic, L. Leibler, *Nature* **2008**, *451*, 977–980.

[10] For a review, see: O. Jardetzky, *Prog. Biophys. Mol. Biol.* **1996**, *65*, 171–219.

[11] For a review, see: J. W. Lockman, N. M. Paul, J. R. Parquette, *Prog. Polym. Sci.* **2005**, *30*, 423–452.

[12] For a review, see: a) R. E. Martin, F. Diederich, *Angew. Chem.* **1999**, *111*, 1440–1469; *Angew. Chem. Int. Ed.* **1999**, *38*, 1350–1377; b) K. Müllen, G. Wegner, *Electronic Materials: The Oligomer Approach*, Wiley-VCH, Weinheim, **1998**.

[13] a) T.-Y. Luh, Z. Hu, *Dalton Trans.* **2010**, *39*, 9185–9192; b) T.-Y. Luh, *Pure Appl. Chem.* **2010**, *82*, 613–624.

[14] a) M.-Y. Yeh, H.-C. Lin, S.-L Lee, C.-h. Chen, T.-S. Lim, W. Fann, T.-Y. Luh, *Chem. Commun.* **2007**, 3459–3461; b) M.-Y. Yeh, H-C. Lin, S.-L. Lee, C.-h. Chen, T.-S. Lim, W. Fann, T.-Y. Luh, *Macromolecules* **2007**, *40*, 9238–9243; c) M.-Y. Yeh, T.-Y. Luh, *Chem. Asian J.* **2008**, *3*, 1620–1624.

[15] See accompanying paper: C.-H. Chen, Y.-C. Huang, W.-C. Liao, T.-S. Lim, K.-L. Liu, I.-C. Chen, T.-Y. Luh, *Chem. Eur. J.* **2011**; DOI: 10.1002/chem.201102032.

[16] a) J. Ohshita, D. Kanaya, M. Ishikawa, T. Koike, T. Yamanaka, *Macromolecules* **1991**, *24*, 2106–2107; b) A. Kunai, E. Toyoda, I. Nagamoto, T. Horio, M. Ishikawa, *Organometallics* **1996**, *15*, 75–83; c) M.-C. Fang, A. Watanabe, M. Matsuda, *Macromolecules* **1996**, *29*, 6807–6813; d) R. Gleiter, W. Schäfer, H. Sakurai, *J. Am. Chem. Soc.* **1985**, *107*, 3046–3050; e) W.-Y. Wong, C.-K. Wong, G.-L. Lu, A. W.-M. Lee, K.-W. Cheah, J. X. Shi, *Macromolecules* **2003**, *36*, 983–990.

[17] For a review, see: T.-Y. Luh, Y.-J. Cheng, *Chem. Commun.* **2006**, 4669–4678.

[18] Y.-J. Cheng, H. Liang, T.-Y. Luh, *Macromolecules* **2003**, *36*, 5912–5914.

[19] a) H.-W. Wang, Y.-J. Cheng, C.-H. Chen, T.-S. Lim, W. Fann, C.-L. Lin, Y.-P. Chang, K.-C. Lin, T.-Y. Luh, *Macromolecules* **2007**, *40*, 2666–2671; b) H.-W. Wang, M.-Y. Yeh, C.-H. Chen, T.-S. Lim, W. Fann, T.-Y. Luh, *Macromolecules* **2008**, *41*, 2762–2770.

[20] The details are given in the Supporting Information.

[21] R. S. Mulliken, W. B. Person, *Molecular Complexes*, Wiley, New York, **1969**.

[22] J. A. Riddick, W. B. Bunger, T. K. Sakano, *Organic Solvent, Physical Properties and Methods of Purification*, Wiley, New York, **1986**.

[23] a) J. Kurzawa, S. Scheider, J. Büber, R. Gleiter, T. Clark, *Phys. Chem. Chem. Phys.* **2004**, *6*, 3811–3823; b) M. Tachiya, K. Seki, *J. Phys. Chem. A* **2007**, *111*, 9553–9559; c) N. Mataga, H. Chrosrowjan, S. Taniguchi, *J. Photochem. Photobiol. C* **2005**, *6*, 37–79.

[24] M. Klessinger, J. Michl, *Excited States and Photochemistry of Organic Molecules*, VCH, Weinheim, **1994**.

[25] a) N. S. Hush, *Trans. Faraday Soc.* **1961**, *57*, 557–580; b) N. S. Hush, *Electrochim. Acta* **1968**, *13*, 1005–1023; c) C. Creutz, M. D. Newton, N. Sutin, *J. Photochem. Photobiol. A* **1994**, *82*, 47–59; d) S. V. Rosokha, J. K. Kochi, *New J. Chem.* **2002**, *26*, 851–860.

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