Macromolecules

Article

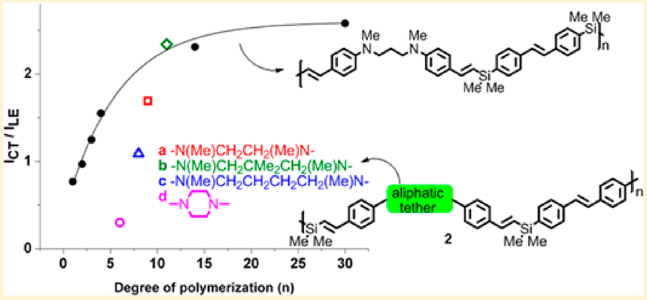
pubs.acs.org/Macromolecules

Photoinduced Electron Transfer as a Probe for the Folding Behavior of Dimethylsilylene-Spaced Alternating Donor–Acceptor Oligomers and Polymers

Wei-Chih Liao,[†,§] Wen-Hao Chen,[†,§] Chih-Hsien Chen,*[,†] Tsong-Shin Lim,[‡] and Tien-Yau Luh*[,†]

[†]Department of Chemistry, National Taiwan University, Taipei, Taiwan 106
[‡]Department of Physics, Tunghai University, Taichung, Taiwan 407

Supporting Information



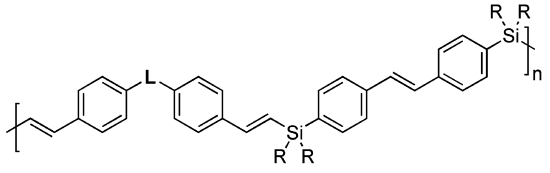
ABSTRACT: A series of oligomers and polymers having dimethylsilylene-spaced alternating 4-aminostyrene donor and stilbene acceptor chromophores (two to one) are regioselectively synthesized, and the two donor chromophores are separated by different bridges between two donors. Photophysical tools have been used to examine the folding behavior of these copolymers. Both steady-state and time-resolved fluorescence spectroscopic measurements were examined. The relative intensities (I_{CT}/I_{LE}) between emission from charge-separated state (CT emission) and local excited emission of acceptor chromophore (LE emission) increase with increasing number of repeating units, and reach a plateau, when the linkers between the two aminostyrene chromophores are trimethylene bridges. Replacements of these by dimethylene or tetramethylene linker reduce the relative intensities of CT emission of the polymers, owing to the different folding behavior of these polymers. The CT emission intensity of the polymer with rigid piperazine linkers is much lower than that with trimethylene-bridged copolymer of the same degree of polymerization. Slight conformational change of these polymers would lead to slight variation of the distance between donor and acceptor chromophores so that the nonadiabatic interactions in the excited state between donor–acceptor pairs in these oligomers and polymers would be perturbed by such change of conformations.

■ INTRODUCTION

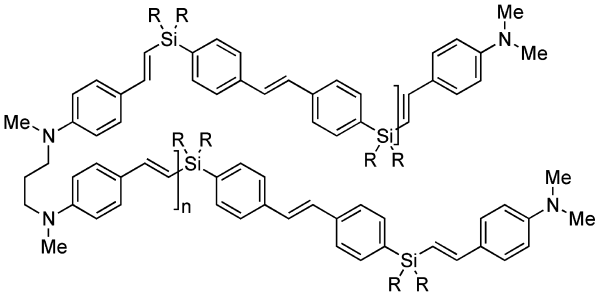
The macroscopic properties of a polymeric material are determined by, inter alia, an ensemble of different conformations of folded polymers. The folding behavior may be rendered from numerous through-space noncovalent interactions along the polymeric backbone.[1−10] The differences of small energetic barriers for each of the conformational states in a polymer may be added up with the increase of chain length of a polymer, leading to a more stable conformation.[8] Our knowledge on polymer foldings, however, remains to be limited. Several probes have been used to examine the folding of macromolecules by means of circular dichroism, fluorescence quenching, and excimer formation.[11] Photoinduced electron transfer (PET) has been extensively used for the investigation of protein conformations.[12] The rate of PET is governed by electronic coupling between reactant and product state, free energy of reaction, and reorganization energy. These parameters are particularly sensitive to the distance between donor and acceptor chromophores. It is envisaged that the use of PET as a probe might provide information about the nature of folded polymers. Indeed, we recently found that the size of the substituents R on silicon affect the mode of PET between adjacent aminostyrene donor group and stilbene acceptor moiety separated by dialkylsilylene in **1** and **2**.[13] The distance between adjacent donor chromophore and acceptor chromophore would be closer in **2** than that in **1** due to, inter alia, the Thorpe–Ingold effect.[14,15] Accordingly, nonadiabatic PET is observed in **1** (R = Me), whereas adiabatic PET prevails in **2** (R = ^{i}Pr). The photophysical properties of a series of small molecules **3a**–**3d** having similar repeating units to that of **2** have been examined. Interestingly, the emission profiles of monomer **3a** and dimer **3b** are similar to that of **1**, whereas those of trimer **3c** and tetramer **3d** behave closer to that of **2**.[13b] It is worth mentioning that the substituents on silicon in these oligomers are bulky isopropyl groups. Thus, the Thorpe–Ingold effect might exert similarly in all these small oligomers. The discrepancy on the photophysical properties in these small molecules may be arisen not only from the Thorpe–Ingold effect but also from the different folding nature of the oligomers and thus the polymers. It is, therefore, envisaged that a series of oligomers and polymers with different degree of polymerization might offer a platform to realize the folding ensemble of polymers. We now wish to report a systematic comparison of a series of oligomers **4** and the corresponding polymers **1** with

Received: November 19, 2012
Revised: January 11, 2013
Published: February 6, 2013

different degree of polymerization in the hope of understanding the change of folding behavior of these oligomers/polymers with the chain lengths. Dimethylsilylene bridges were chosen in **1** and **4** to eliminate the influence of the Thorpe–Ingold effect on the photophysical properties of these substrates.



1 R = Me, **2** R = ^{i}Pr, L = -N(Me)CH$_2$CH$_2$CH$_2$(Me)N-



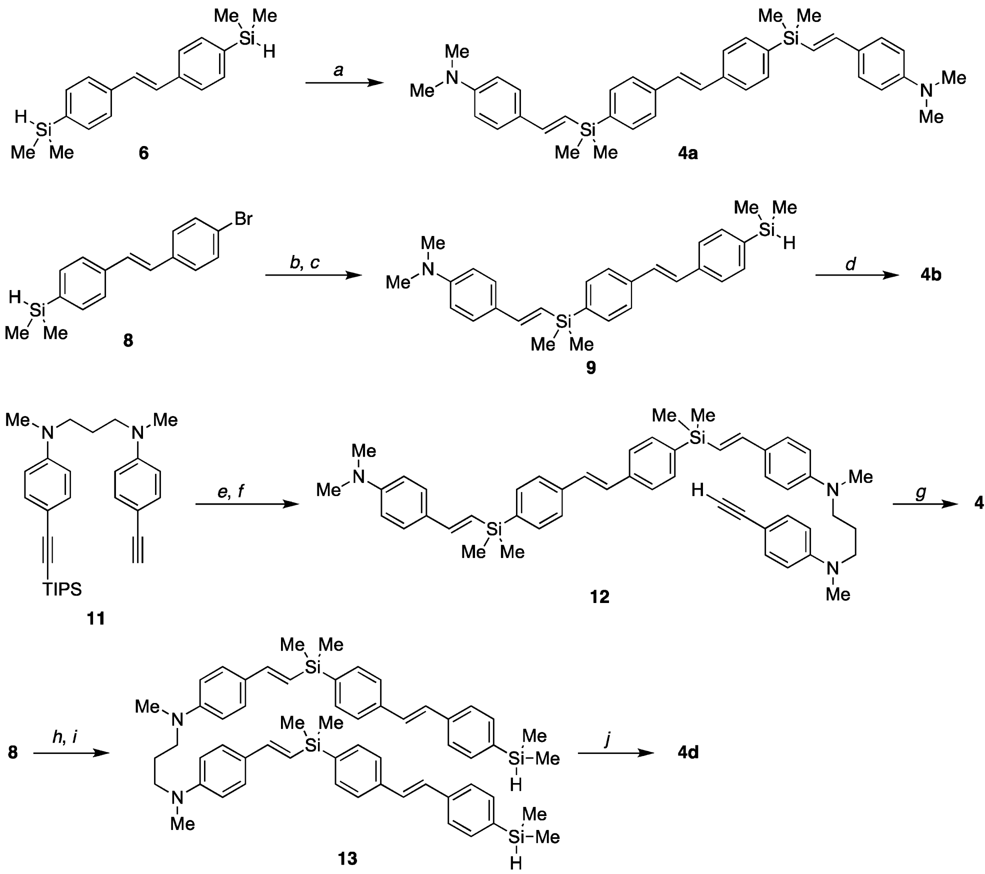
3 R = ^{i}Pr **a** n = 0 **b** n = 1 **c** n = 2 **d** n = 3
4 R = Me **a** n = 0 **b** n = 1 **c** n = 2 **d** n = 3

RESULTS AND DISCUSSION

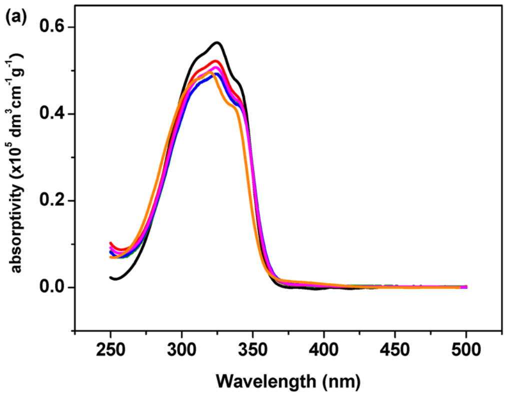
Synthesis of 4. Similar to the synthesis of **3**,[13b] Rh(I)-catalyzed hydrosilylation protocol was used to construct **4** having a dimethylsilylene spacer between donor and acceptor chromophores. It is interesting to note that the presence of a stoichiometric amount of NaI (relative to the equivalents of the amino moiety in the reactants) was essential to facilitate the hydrosilylation reactions.[13,16] The syntheses of **4a–4d** are summarized in Scheme 1. Polymers $\mathbf{1}_{14}$ (n = 14) and $\mathbf{1}_{30}$ (n = 30) were also synthesized by hydrosilylation of **10** with **6**. The details are described in the Supporting Information.

Steady-State Spectroscopies of $\mathbf{1}_{14}$, $\mathbf{1}_{30}$, and 4. The absorption and emission spectra of **4a–4d**, $\mathbf{1}_{14}$, and $\mathbf{1}_{30}$ in cyclohexane are shown in Figure 1. The absorption profiles of **4a–4d**, $\mathbf{1}_{14}$, and $\mathbf{1}_{30}$ were essentially the sum of the absorptions of the donor and acceptor chromophores. There is no additional absorption band due to ground-state interactions between donor and acceptor moieties. The same modes of PET for **4a–4d**, $\mathbf{1}_{14}$, and $\mathbf{1}_{30}$ were observed and could be attributed to the nonadiabatic electron transfer despite of the difference in the degree of polymerization. The luminescence spectra of **4a–4d**, $\mathbf{1}_{14}$, and $\mathbf{1}_{30}$ show dual emissions around 360 nm due to the local excited emission of the acceptor stilbene chromophore (LE emission) and at 450 nm which may be arisen from the emission of the charge-separated state of donor–acceptor pair (CT emission).[13,17] The same CT emission wavelengths for **4**

Scheme 1. Syntheses of 4a–4d[a]



[a]Reagents and conditions: (a) Me$_2$NC$_6$H$_4$C≡CH (**7**), Rh(PPh$_3$)$_3$Cl, NaI, 39%; (b) **7**, Rh(PPh$_3$)$_3$Cl, NaI, 56%; (c) ^{n}BuLi, Me$_2$SiHCl, 99%; (d) HC≡CC$_6$H$_4$NMe(CH$_2$)$_3$NMeC$_6$H$_4$C≡CH (**10**), Rh(PPh$_3$)$_3$Cl, NaI, 41%; (e) **9**, Rh(PPh$_3$)$_3$Cl, NaI, 35%; (f) TBAF, 97%; (g) **6**, Rh(PPh$_3$)$_3$Cl, NaI, 35%; (h) **10**, Rh(PPh$_3$)$_3$Cl, NaI, 63%; (i) ^{n}BuLi, Me$_2$SiHCl, 40%; (j) **12**, Rh(PPh$_3$)$_3$Cl, NaI, 39%.



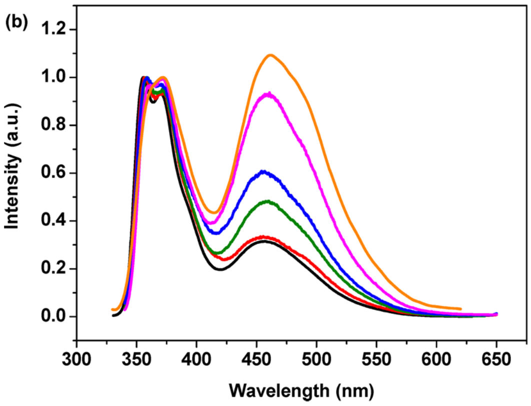


Figure 1. (a) Absorption and (b) emission spectra of **4a** (black), **4b** (red), **4c** (green), **4d** (blue), $\mathbf{1}_{14}$ (magenta), and $\mathbf{1}_{30}$ (orange) in cyclohexane (λ_{ex} = 320 nm).

and **1** suggest that the mode of interactions between donor and acceptor chromophores would be the same. Since **4a** contains only one acceptor chromophore and two adjacent donor chromophores, it seem likely that interaction between adjacent chromophores in these oligomers **4** and polymers **1** would be responsible for the CT emission. Interestingly, the relative intensity of CT emission (I_{CT}) to LE emission (I_{LE}) is increased when the degree of polymerization increases and reaches a plateau. A plot of I_{CT}/I_{LE} for these substrates against the degree of polymerization is shown in Figure 2. It is noteworthy that the CT emission is more populated when the polymer is more folded.

Temperature-dependent emission spectra were performed to investigate the effect of polar solvent such as methyltetrahydrofuran (MTHF) on the PET. For example, the spectra of **4b** and $\mathbf{1}_{30}$ at different temperatures are shown in Figure 3. In comparison with fluorescence spectra measured in cyclohexane, the emission in MTHF at longer wavelength further red-shifted and became more prominent because of increasing solvent polarity. On the other hand, the intensities of the CT emissions in **4b** and $\mathbf{1}_{30}$ decreased significantly together with bathochromic shifts as temperature was lowered. The polar solvents would be more polar as the temperature decreases,[21] and thus, the charge separation state of donor−acceptor pairs might be stabilized to lower energy level. The interaction between this excited state and the higher vibrational level of the ground state might result in thermal relaxation process to reduce the opportunity of radiative relaxation.[22,23] These results are consistent with the characteristic property of CT emission in these oligomers and polymers.[24]

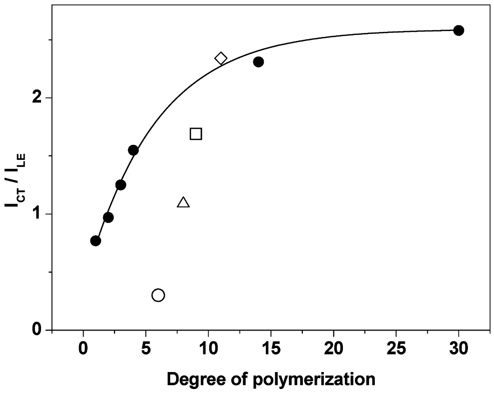
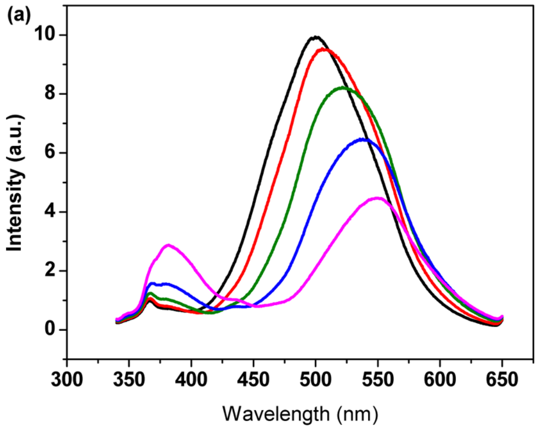


Figure 2. Ratios of intensities of the CT emissions to the LE emissions of oligomers **4** (solid circle) and polymers **1** (solid circle), **5a** (open triangle), **5b** (open diamond), **5c** (open square), and **5d** (open circle) in cyclohexane.



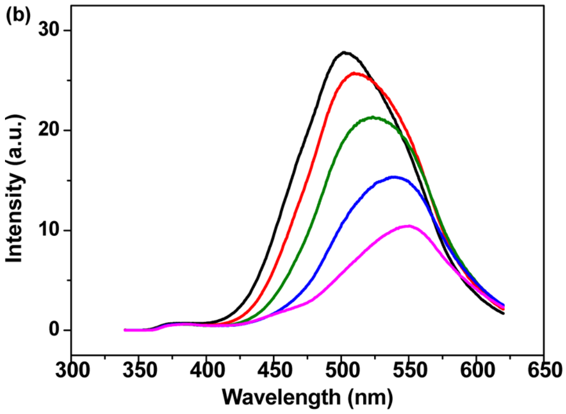


Figure 3. Temperature-dependent emission spectra of (a) **4b** and (b) $\mathbf{1}_{30}$ measured in MTHF: 298 K, black; 270 K, red; 240 K, green; 210 K, blue; 180 K, magenta (λ_{ex} = 320 nm).

The relative ratios of I_{CT}/I_{LE} for **4a−4d,** $\mathbf{1}_{14}$, and $\mathbf{1}_{30}$ are compared with the degree of polymerization at different temperatures. As shown in Figure 4a, the I_{CT}/I_{LE} ratios increase with increasing degree of polymerization and reach a plateau. Interestingly, the ratios of $I_{CT}(T\text{ K})/I_{CT}(300\text{ K})$ for **4a−4d,** $\mathbf{1}_{14}$, and $\mathbf{1}_{30}$ decrease with lowing temperature (Figure 4b). It is worthy to note that $I_{CT}(T\text{ K})/I_{CT}(300\text{ K})$ ratios for **4a** were more sensitive to the change in temperatures, whereas the variations of $I_{CT}(T\text{ K})/I_{CT}(300\text{ K})$ ratios for polymers $\mathbf{1}_{14}$ and $\mathbf{1}_{30}$ are less prominent than those for small oligomers. It seems

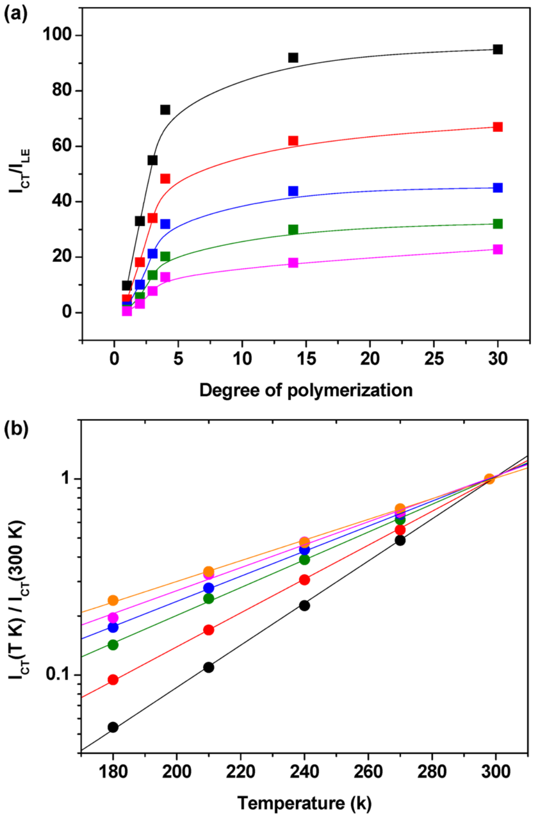


Figure 4. (a) Plot of I_{CT}/I_{LE} versus degree of polymerization for **4a**–**4d**, **1_{14}**, and **1_{30}** in MTHF at different temperatures: 298 K, black; 270 K, red; 240 K, green; 210 K, blue; 180 K, magenta. (b) Ratio of $I_{CT}(T\ K)/I_{CT}(300\ K)$ at different temperatures for **4a** (black), **4b** (red), **4c** (green), **4d** (blue), **1_{14}** (magenta), and **1_{30}** (orange) in MTHF.

likely that the radiative transition from the charge separation state to ground state in charge recombination process might be enhanced due to folding of polymer, resulting in more constrained structure. Presumably, the geometrical reorganization of electronic structure in PET process might play an important role. It is worthy to note that the degree of bathochromic shift of CT emission for **4a**–**4d**, **1_{14}**, and **1_{30}** are almost the same at different temperatures. These results indicate that the energy gap between charge separation state and ground state would be same in these oligomers and polymers. Accordingly, the dissimilarity of relative I_{CT} values between oligomers and polymers may only be influenced by the folding nature of the oligomers and polymers.

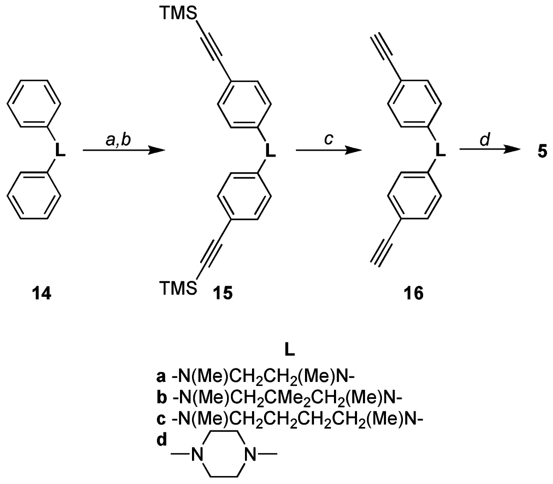
Kinetic Measurement of Oligomers. Time-resolved fluorescence spectroscopy with a femtosecond Ti:sapphire laser was employed to obtain the emission decay profiles of oligomers **4a**–**4d** and copolymers **1_{14}** and **1_{30}**. The fluorescence decay of LE emission was monitored for **4a**–**4d**, **1_{14}**, and **1_{30}** in THF. Single-exponential fittings were utilized to give the decay lifetimes, τ_{cs}, which were attributed to the charge separation process (Table 1). The τ_{cs}'s of copolymers **1** and oligomers **4** are around 9–13 ps. These results further suggest that the same mode of charge separation process proceed in **4a**–**4d**, **1_{14}**, and **1_{30}**. The lifetimes of charge recombination processes, τ_{cr}, were also measured in THF. As can be seen from Table 1, τ_{cr}'s decrease with increasing degree of oligomerization/polymerization and reached a constant lifetime at 4.5 ns. As the polymer becomes more folded, τ_{cr} turns out to be shorter and τ_{cr} of tetramer **4d** was similar to those of **1_{14}** and **1_{30}**. These kinetic results are consistent with those of steady-state measurements as described in the previous sections.

Table 1. Fluorescence Lifetimes of 4a–4d, 1_{14}, and 1_{30} in THF

	lifetimes	
	τ_{cs} (ps)	τ_{cr} (ns)
4a	12	7.9
4b	13	7.1
4c	11	5.1
4d	11	4.6
1_{14}	9	4.5
1_{30}	9	4.5

Replacement of Aliphatic Bridges between Aminostyrenes. Polymers **1** contain trimethylene bridges to connect each pair of aminostyrene donor chromophores. It seems likely that the nature of the tethering chain may also influence the conformation of such polymers. Accordingly, the trimethylene linkages in **1** were replaced by four kinds of linkers, and polymers **5** (**5a**: ethylene; **5b**: 2,2-dimethylpropylene; **5c**: tetramethylene; **5d**: piperazine) were thus synthesized (Scheme 2). The properties of **5** are summarized in Table 2. It is interesting to note that the glass transition temperature (T_g) for **5d** having a piperazine bridge is much higher than those for **1** and **5a**–**5c** with simple aliphatic tethers.

Scheme 2. Syntheses of Polymers 5a–5d[a]



[a] Reagents and conditions: (a) NBS, $CHCl_3$; (b) $PdCl_2(PPh_3)_2$, CuI, trimethylsilylacetylene (**15a**, 65%; **15b**, 56%; **15c**, 59%; **15d**, 42%). (c) K_2CO_3 (**16a**, 80%; **16b**, 82%; **16c**, 85%; **16d**, 86%. (d) **6**, $Rh(PPh_3)_3Cl$ (5 mol %), NaI (2 equiv) (**5a**, 75%; **5b**, 78%; **5c**, 75%; **5d**, 75%).

Effect of Tether between Two Aminostyrenes on the Photophysical Properties of 5. The absorption and emission spectra of **5a**–**5d** in cyclohexane are shown in Figure 5. In a manner similar to those of **4a**–**4d**, **1_{14}**, and **1_{30}**, **5a**–**5d** exhibit LE emissions at 360 nm and CT emission at 450 nm in cyclohexane. Polymer **5b** contains a geminal dimethyl group on trimethylene bridge. Considering the M_n of **5b**, the I_{CT}/I_{LE} ratio falls onto the curve shown in Figure 2. This may imply that the conformation of **5b** may be similar to that of trimethylene-bridge polymers **1** with the same degree of polymerization. Polymer **5c** has tetramethylene bridge between two aminostyrene donor chromophores. The I_{CT}/I_{LE} ratio for **5c** is lower

Table 2. Number-Average Molecular Weight (M_n), Repeated Unit (n), Polydispersity Index (PDI), Glass Transition Temperature (T_g), and Lifetimes (τ_{cs}, τ_0, and τ_{cr}) of $\mathbf{1}_{14}$, $\mathbf{1}_{30}$, and 5a−5d

					lifetimes		
	M_n[a]	PDI[a]	n[b]	T_g (°C)	τ_{cs}[c] (ps)	τ_0[c] (ps)	τ_{cr}[d] (ns)
$\mathbf{1}_{14}$	8200	1.4	14	103	9 (100%)		4.5
$\mathbf{1}_{30}$	17800	1.8	30	101	9 (100%)		4.5
5a	4600	1.7	8	82	28 (77%)	180 (23%)	8.3
5b	6800	2.1	11	99	11 (98%)	180 (2%)	4.7
5c	5500	1.8	9	87	15 (95%)	180 (5%)	7.8
5d	3400	1.4	6	173	17 (61%)	180 (39%)	8.5

[a] Measured in THF by gel permeation chromatography. [b] Degree of polymerization. [c] The emission decay profiles were measured in THF from LE emissions, and two-exponential fitting was utilized to give two lifetimes with relative weight percent. [d] The emission decay profiles were measured in THF from CT emissions, and single-exponential fitting was used to give lifetimes.

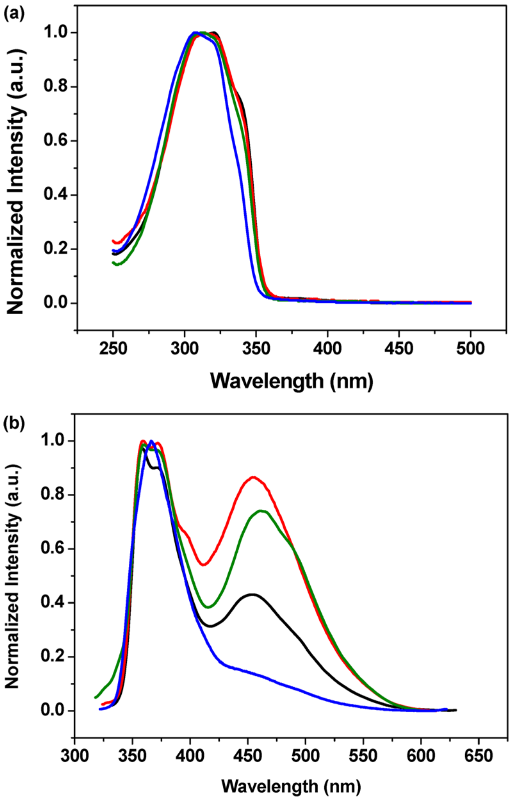


Figure 5. (a) Absorption and (b) emission spectra of **5a** (black), **5b** (red), **5c** (green), and **5d** (blue) in cyclohexane.

than that expected for trimethylene-bridge polymers **1** with same number of repeating units (Figure 2). These results suggest that the CT emission would be less efficient in **5c** containing tetramethylene linkers than that in **1** having trimethylene connectors. It is noteworthy that the ethylene-bridged copolymer **5a** exhibits even much smaller I_{CT}/I_{LE} ratio in comparison with that for **1**. Apparently, the chain lengths of these oligomethylene linkages determine the folding nature of these polymers and thus the process of PET in the overall photophysical processes in these copolymers.

The photophysical properties of 1,ω-diphenylalkanes have been investigated in detail.[25] It is interesting to note that intramolecular excimer formation is observed only in 1,3-diphenylpropane, but not in 1,2-diphenylethane and 1,4-diphenylbutane. DFT calculations on these diphenylalkanes indicate that both tetramethylene- and ethylene-bridged substrates would prefer all-anti conformations, whereas the syn-conformation may contribute significantly in diphenylpropane.[26] These results certainly offer a useful clue on the change of local conformation of two aminostyrene chromophores linked by these oligomethylene linkage in **5a**−**5c**. Such variation of local conformation may couple with the polymer folding behavior to dictate the discrepancy of photophysical properties of polymers **5a**−**5c** from those of **1**.

When piperazine bridge was used, the I_{CT}/I_{LE} ratio of **5d** shows the largest deviation from the curve (Figure 2). The piperazine ring is rigid, and the energy barrier between boat and chair conformers of piperazine is around 5−6 kcal/mol.[27] Incorporation of piperazine moiety into a polyamide, for example, would result in a rodlike structure.[28] It seems likely that little contribution of folding would be expected from piperazine linkers in the polymeric backbone. The small I_{CT}/I_{LE} ratio of **5d** can thus be understood within such framework.

Kinetic Measurements of 5a−5d. Two-exponential fittings were utilized to give the decay lifetimes, τ_{cs} and τ_0, in which τ_0 was attributed to the intrinsic radiative transition. The kinetic parameters of **5** are shown in Table 2. The τ_{cs}'s and their relative weight percent for **5b** are similar to those for **1** and **4**, but τ_{cs}'s of **5a**, **5c**, and **5d** are somewhat longer than that for **5b** with smaller weight percent. Longer lifetime of charge separation with relatively smaller weight percent might indicate less efficient of PET in the system. It seems apparent that different aliphatic tethers might construct different folding behavior to alter PET processes in these systems. On the other hand, the τ_{cr}'s of **5** are also affected by the tethers. The τ_{cr} of **5b** with 2,2-dimethylpropylene bridge is 4.7 ns, and that of **5d** with a piperazine bridge is 8.5 ns. These kinetic results of **5** are consistent with those of **4a**−**4d**, $\mathbf{1}_{14}$, and $\mathbf{1}_{30}$.

■ CONCLUSIONS

In summary, we have demonstrated that the photophysical properties of polymers **1** and **5** and the related oligomers **4a**−**4d** having alternating donor and acceptor chromophores separated by dimethylsilylene moieties. CT emissions were observed for all of these substrates, but the relative intensities were significantly affected by the degree of polymerization and by the nature of tethering groups between two aminostyrene donors. A slight conformational change of these polymers would lead to slight variation of the distance between donor and acceptor chromophores Since the PET process is very sensitive to distance between chromophores, the nonadiabatic interactions in the excited state between donor−acceptor pairs in these oligomers and polymers would be significantly perturbed with the variation of conformations. Our results have offered a useful platform to elucidate the folding nature of these silicon-containing polymers. Extension to other polymeric systems is in progress in our laboratory.

■ 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). Waters Styragel HR2, HR3, and HR4 columns (7.8 × 300 mm) were employed for determination of relative molecular weight using polystyrene as standard (M_n values ranged from 375 to 3.5 × 10^6). Absorption spectra were measured on a Hitachi U-3310 spectrophotometer and emission spectra on a Hitachi F-4500 fluorescence spectrophotometer.

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 desired wavelength of pulse laser. The fluorescence of sample was reflected by a grating (150 grooves/mm; BLZ: 500 nm) and detected by an optically triggered streak camera (Hamamatsu C5680) with a time resolution of about 1.0 ps. The sample was prepared with 1.0×10^{-5} M concentration and using ultra-microcuvette with 0.5 mm path length to maintain the excitation at the same time. The signal was collected for 10 times to decrease the signal-to-noise ratio.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis details and ^{1}H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: tyluh@ntu.edu.tw (T.-Y.L.); chhschen@ntu.edu.tw (C.-H.C.).

Author Contributions

§These authors contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Science Council and the National Taiwan University of the Republic of China for support. We are grateful to Professor Huan-Cheng Chang for allowing us to use the femtosecond laser facilities for the kinetic measurements.

■ REFERENCES

(1) Hecht, S., Huc, I., Eds.; *Foldamers*; Wiley-VCH: Weinheim, 2007.

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

(3) (a) Fathalla, M.; Lawrence, C. M.; Zhang, N.; Sessler, J. L.; Jayawickramarajah, J. *Chem. Soc. Rev.* **2009**, *38*, 1608−1620. (b) Sessler, J. L.; Jayawickramarajah, J. *Chem. Commun.* **2005**, 1939−1949. (c) Yagai, S. *J. Photochem. Photobiol., C* **2006**, *7*, 164−182. (d) Rudick, J. R.; Percec, V. *Acc. Chem. Res.* **2008**, *41*, 1641−1652. (e) Yashima, E.; Maeda, K.; Lida, H.; Furusho, Y.; Nagai, K. *Chem. Rev.* **2009**, *109*, 6102−6211.

(4) (a) Hagihara, M.; Anthony, N. J.; Stout, T. J.; Clardy, J.; Schreiber, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 6568. (b) Hirschberg, J. H. K. K.; Brunsveld, L.; Ramzi, A.; Vekemans, J. A. J. M.; Sijbesma, R. P.; Meijer, E. W. *Nature* **2000**, *147*, 167. (c) Cordier, P.; Tournilhac, F.; Soulié-Ziakovic, C.; Leibler, L. *Nature* **2008**, *451*, 977. (d) Foster, E. J.; Berda, E. B.; Meijer, E. W. *J. Am. Chem. Soc.* **2009**, *131*, 6992.

(5) (a) Uversky, V. N., Permyakov, E. A., Eds.; *Method in Protein Structure and Stability Analysis*; Nova Biomedical Books: New York, 2007. (b) Tramontano, A., Ed.; *Protein Structure Prediction: Concepts and Applications*; Wiley-VCH: Weinheim, 2006. (c) Buchner, J., Kiefhaber, Y., Eds.; *Protein Folding Handbook*; Wiley-VCH: Weinheim, 2005.

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

(7) For reviews, see: (a) Meyer, E. A.; Castellano, R. K.; Diederich, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1210−1250. (b) Pijper, D.; Feringa, B. L. *Soft Matter* **2008**, *4*, 1349−1372. (c) Berresheim, A.; Müller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747−1785. (d) Leclère, P.; Hennebicq, E.; Calderone, A.; Brocorens, P.; Grimsdale, A. C.; Müllen, K.; Brédas, J. L.; Lazzaroni, R. *Prog. Polym. Sci.* **2003**, *28*, 55−81. (e) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schennung, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491−1546.

(8) For a review, see: Lockman, J. W.; Paul, N. M.; Parquette, J. R. *Prog. Polym. Sci.* **2005**, *30*, 423−452.

(9) (a) Kirshenbaum, K.; Barron, A. E.; Goldsmith, R. A.; Armand, P.; Bradley, E. K.; Truong, K. T. V.; Dill, K. A.; Cohen, F. E.; Zuckermann, R. N. *Proc. Natl. Acad. Sci. U. S. A.* **1998**, *95*, 4303−4308. (b) Yashima, E.; Matsushima, T.; Okamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 6345−6359. (c) Nonokawa, R.; Yashima, E. *J. Am. Chem. Soc.* **2003**, *125*, 1278−1283. (d) Prince, R. B.; Brunsveld, L.; Meijer, E. W.; Moore, J. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 228−230.

(10) Chiellini, E.; Laus, M. In *Handbook of Liquid Crystals: High Molecular Weight Liquid Crystals*; Demus, D., Goodby, J., Gray, G. W., Speiss, H.-W., Vill, V., Eds.; Wiley-VCH: Weinheim, 1998, Vol. *3*, pp 26−51.

(11) (a) Price, R. B.; Saven, J. G.; Wolynes, P. G.; Moore, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 3114−3121. (b) Kim, J.; Swager, T. M. *Nature* **2001**, *411*, 1030−1034. (c) Kim, J.; Levitsky, I. A.; McQuade, D. T.; Swager, T. M. *J. Am. Chem. Soc.* **2002**, *124*, 7710−7718. (d) Kirshenbaum, K.; Barron, A. E.; Goldsmith, R. A.; Armand, P.; Bradley, E. K.; Truong, K. T. V.; Dill, K. A.; Cohen, F. E.; Zuckermann, R. N. *Proc. Natl. Acad. Sci. U. S. A.* **1998**, *95*, 4303−4308. (e) Yashima, E.; Matsushima, T.; Y. Okamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 6345−6359. (f) Nonokawa, R.; Yashima, E. *J. Am. Chem. Soc.* **2003**, *125*, 1278−1283. (g) Prince, R. B.; Brunsveld, L.; Meijer, E. W.; Moore, J. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 228−230.

(12) For reviews see: (a) Winkler, J. R.; Gray, H. B. *Chem. Rev.* **1992**, *92*, 369−379. (b) Mataga, N.; Chosrowjan, H.; Taniguchi, S. *J. Photochem. Photobiol., C* **2004**, *5*, 155−168. (c) Michalet, X.; Weiss, S.; Jäger, M. *Chem. Rev.* **2006**, *106*, 1785−1813. (d) Berezin, M. Y.; Achilefu, S. *Chem. Rev.* **2010**, *110*, 2641−2684.

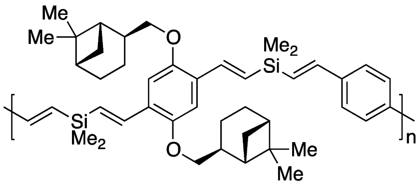
(13) (a) Chen, C.-H.; Huang, Y.-C.; Liao, W.-C.; Lim, T.-S.; Liu, K.-L.; Chen, I.-C.; Luh, T.-Y. *Chem.—Eur. J.* **2012**, *18*, 334−346. (b) Chen, C.-H.; Chen, W.-H.; Liu, Y.-H.; Lim, T.-S.; Luh, T.-Y. *Chem.—Eur. J.* **2012**, *18*, 347−354.

(14) For a reveiw, see: Luh, T.-Y.; Hu, Z. *Dalton Trans.* **2010**, *39*, 9185−9192.

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

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

(17) The photophyscial processes in these silylene-spaced divinylarene copolymers have been established to occur via intrachain interactions [ground-state interactions (refs 15, 18), fluorescence resonance energy transfer (ref 19), and PET (refs 13, 16) between chromophores]. For example, polymer **A** (ref 20) containing chiral auxiliaries does not exhibit circular dichroic response at low concentration (1 mg/L), but strong CD profile together with bathochromic shift of fluorescence maximum at high concentration (1 g/L). At the concentration used in this study (10^{-5} M), no interachain interaction might take place. For a reveiw, see: Luh, T.-Y.; Cheng, Y.-J. *Chem. Commun.* **2006**, 4669−4678.



A

(18) Chen, R.-M.; Chien, K.-M.; Wong, K.-T.; Jin, B.-Y.; Luh, T.-Y.; Hsu, J.-H.; Fann, W. *J. Am. Chem. Soc.* **1997**, *119*, 11321−11322.

(19) (a) Cheng, Y.-J.; Hwu, T.-Y.; Hsu, J.-H.; Luh, T.-Y. *Chem. Commun.* **2002**, 1978−1979. (b) Cheng, Y.-J.; Luh, T.-Y. *Chem.—Eur. J.* **2004**, *10*, 5361−5368. (c) Cheng, Y.-J.; Luh, T.-Y. *Macromolecules* **2005**, *38*, 4563−4568.

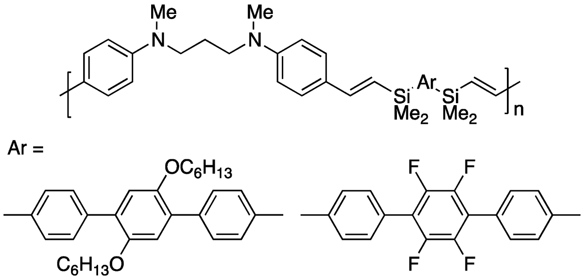
(20) Cheng, Y.-J.; Liang, H.; Luh, T.-Y. *Macromolecules* **2003**, *36*, 5912−5914.

(21) Riddick, J. A., Bunger, W. B., Sakano, T. K., Eds.; *Organic Solvent, Physical Properties and Methods of Purification*; Wiley: New York, 1986.

(22) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952−957. (b) Kurzawa, J.; Scheider, S.; Büber, J.; Gleiter, R.; Clark, T. *Phys. Chem. Chem. Phys.* **2004**, *6*, 3811−3823. (c) Tachiya, M.; Seki, K. *J. Phys. Chem A* **2007**, *111*, 9553−9559.

(23) For a review, see: Mataga, N.; Chrosrowjan, H.; Taniguchi, S. *J. Photochem. Photobiol., C* **2005**, *6*, 37−79.

(24) One reviewer questioned that the solubility problem at low temperatures may cause discrepancy of the emission spectra of **1** and **4**. It is worthy to note that such temperature-dependent emission properties occur only when the free energy difference between the LE and CT states is around −1 eV in dimethylsilylene-spaced copolymers having alternating donor and acceptor chromophores such as **1**. When the free energy difference is around −0.5 or more negative than −1.5 eV for other related copolymers with different acceptor chromophores **B** and **C**, the emission profiles are not temperature dependent (ref 13a). It seems unlikely that different solubilities of the similar polymers at different temperatures would make such variations in temperature-related emission profiles.



B **C**

(25) Vala, M. T. J.; Haebic, J.; Rice, S. A. *J. Chem. Phys.* **1965**, *43*, 886−895.

(26) Zamora, M. A.; Santagata, L. N.; Masman, M. F.; Bombasaro, J. A.; Freile, M. L.; Enriz, R. D. *Can. J. Chem.* **2005**, *83*, 122−137.

(27) Montaudo, G.; Finocchiaro, P.; Overberger, C. G. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 2727−2737.

(28) (a) Murray, J. S.; Redfern, P. C.; Lane, P.; Politzer, Willer, R. L. *J. Mol. Struct.* **1990**, *207*, 177−191. (b) Boiocchi, M.; Bonizzoni, M.; Fabbrizzi, L.; Foti, F.; Licchelli, M.; Taglietti, A.; Zema, M. *Dalton Trans.* **2004**, *33*, 653−658.