

Figure 1. Absorption spectra of polymers **4** or **5** (solid line) and the corresponding monomeric model compounds **7** or **9** (dashed line) and **10** (dotted line) in CH_2Cl_2 . Key: (a) **4a**, **7a**, and **10**; (b) **4b**, **7b**, and **10**; (c) **5a**, **9a**, and **10**; (d) **5b**, **9b**, and **10** (concentration: 1×10^{-5} M).

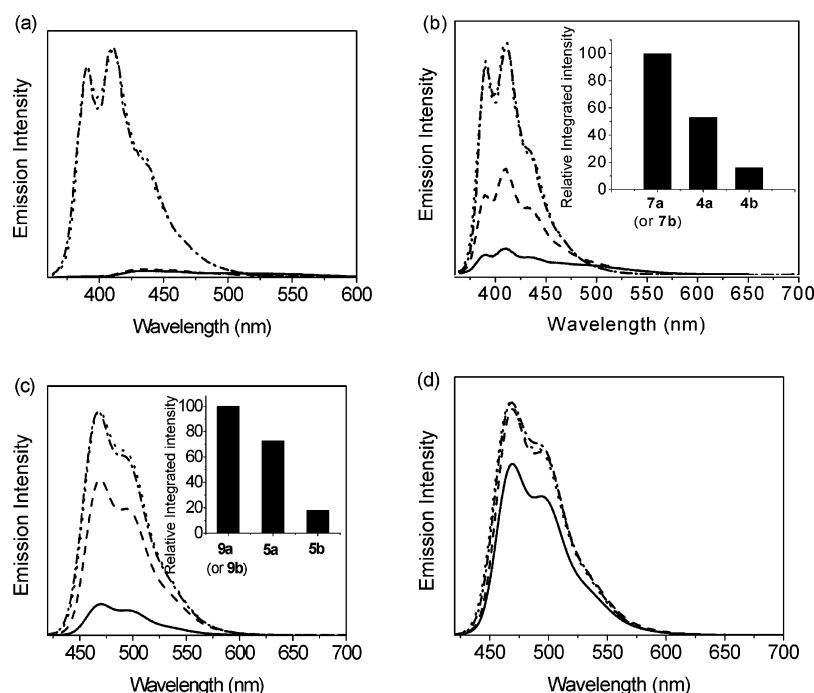


Figure 2. Emission spectra of **4a** (dashed line), **4b** (solid line), **7a** (dashed-dotted line), and **7b** (dotted line) in (a) CH_2Cl_2 and (b) cyclohexane. Inset: the relative ratios of the integrated emission intensities of **4** and **7** ($\lambda_{\text{ex}} = 355$ nm). Emission spectra of **5a** (dashed line), **5b** (solid line), **9a** (dashed-dotted line), and **9b** (dotted line) in (c) CH_2Cl_2 . Inset: the relative ratios of the integrated emission intensities of **5** and **9**; (d) cyclohexane ($\lambda_{\text{ex}} = 410$ nm) (concentration: 1×10^{-5} M).

Time-Resolved Fluorescence Spectroscopy. Femtosecond laser equipped with streak camera was employed to measure the time-resolved spectra of fluorescence decay in polymers **4**, **5** and the corresponding monomers **7** and **9** in CH_2Cl_2 and in cyclohexane. The fluorescence decay profiles of **4a**, **4b** and **5a**, **5b** in CH_2Cl_2 and in cyclohexane are shown in Figure 3. The fluorescence decay lifetimes (τ) were estimated by one-exponential curve-fittings for monomers **7** and **9** and two-exponential curve-fittings for polymers **4** and **5**, unless otherwise specified. The results are summarized in Tables 2 and 3.

The fluorescence lifetimes, τ , in general, were shorter for **4** than those for **5**; hence the charge separation rates k_{CS} for **4**

were larger than those for **5**. In addition, shorter τ 's and larger k_{CS} 's were observed for isopropyl-substituted polymers **4b** and **5b** than those for methyl-substituted analogues **4a** and **5a**. As expected, the τ 's were shorter and k_{CS} 's were faster in CH_2Cl_2 than those in cyclohexane.

As can be seen from Table 3, two parameters were used to fit the fluorescence decay curves. This observation suggested that there might be two different modes of electron-transfer processes in polymers **4** and **5**. The shorter lifetimes τ_1 's, the faster k_{CS1} 's, and the higher charge separation yields Φ_{CS1} may arise from the interaction of two neighboring chromophores separated by a silylene moiety. We have shown that silylene-

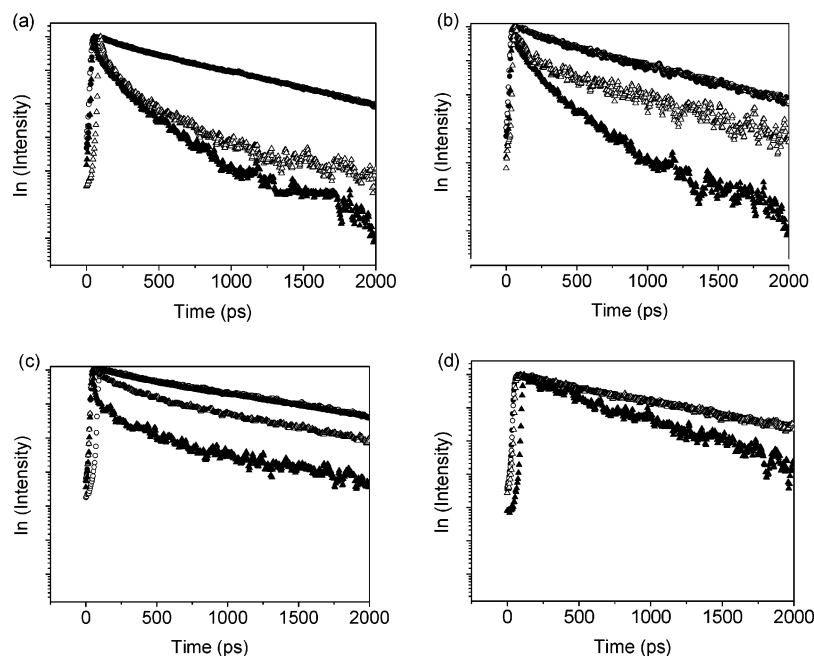


Figure 3. Time-resolved fluorescence decays of **4a** (open up triangle), **4b** (solid up triangle), **7a** (open circle), and **7b** (solid circle) in (a) CH_2Cl_2 ; (b) cyclohexane ($\lambda_{\text{ex}} = 375$ nm and monitored at 400 nm). Time-resolved fluorescence decays of **5a** (open up triangle), **5b** (solid up triangle), **9a** (open circle), and **9b** (solid circle) in (c) CH_2Cl_2 ; (d) cyclohexane ($\lambda_{\text{ex}} = 410$ nm and monitored at 475 nm) (concentration: 1×10^{-5} M).

Table 3. Fluorescence Lifetime (τ), Charge-Transfer Rate Constant (k_{cs}) and Charge-separation Yield (Φ_{cs}) of **4a,b** and **5a,b** in CH_2Cl_2 and Cyclohexane at Ambient Temperature¹¹

substrate ^a	solvent	fluorescence lifetime ^b τ (ps)		charge-transfer rate k_{cs} (ns^{-1}) ^d		charge-separation yield Φ_{cs}	
		τ_1	τ_2	k_{cs1}	k_{cs2}	Φ_{cs1}	Φ_{cs2}
4a	CH_2Cl_2	49 (0.80)	463 (0.20)	19.0	1.1	0.95	0.51
	cyclohexane	91 (0.56)	857 (0.44)	9.9	0.03	0.89	0.03
4b	CH_2Cl_2	29 (0.83)	263 (0.17)	33.0	2.7	0.97	0.72
	cyclohexane	54 (0.71)	303 (0.29)	17.0	2.2	0.94	0.66
5a	CH_2Cl_2	192 (0.50)	1300 (0.50)	4.5	0.03	0.86	0.04
	cyclohexane		1198 ^c (1.00)				
5b	CH_2Cl_2	48 (0.80)	854 (0.20)	20.0	0.45	0.97	0.40
	cyclohexane	358 (0.37)	878 (0.63)	2.0	0.3	0.70	0.27

^a The concentrations ($\sim 10^{-5}$ M) for **4** and **5**. ^b Time-resolved fluorescence lifetimes are estimated by exponential fitting of decay curve ($R^2 = 0.97$ – 0.99). The numbers in the bracket are the relative weight of different time constants. ^c One exponential fitting. ^d $k_{\text{cs}} = \tau^{-1} - k_{\text{s}}$ where τ is corresponding fluorescence lifetime and k_{s} is the reciprocal of the fluorescence lifetime of the corresponding monomer (ref 11).

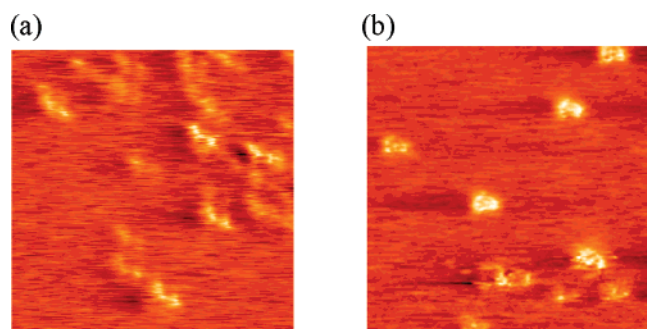


Figure 4. STM image of (a) **4a** and (b) **4b**. Conditions: (a) image size, 27×27 nm, $E_{\text{bias}} 0.80$ V, $i_{\text{tunneling}} 20$ pA; (b) image size, 27×27 nm, $E_{\text{bias}} 0.50$ V, $i_{\text{tunneling}} 20$ pA.

spaced divinylarene copolymers are highly folded. Accordingly, there is possibility that two non-neighboring chromophores may meet each other through space. Such folding may lead to a second type of interaction between chromophores and, therefore, a second set of longer τ_2 's, slower k_{CS2} 's, and the smaller Φ_{CS2} -was observed as depicted in Table 3.

Scanning Tunneling Microscopy. Scanning tunneling microscopy was employed to examine the morphology of polymer **4** on highly ordered pyrolyzed graphite (HOPG) surface and the results are shown in Figure 4. The images of **4a** are fuzzier

than those of **4b**, presumably due to the more fluxional conformation of **4a** than that of **4b**. The methyl-substituted **4a** exhibited a relatively loose and elongated feature with a length roughly about 4.3 nm. On the other hand, the morphology of **4b** appeared to be very different and the average diameter was 3.4 nm. Apparently, the isopropyl group may provide a bulky environment to provoke the divinylsilane moieties in **4b** to adopt conformation **C** (eq 1). As a result, the conformation for **4b** would be expected to be in highly coiled structure. Such kind of coiled structure may lead strong interactions between chromophores in **4b** and is serendipitously consistent with the photophysical results described above.

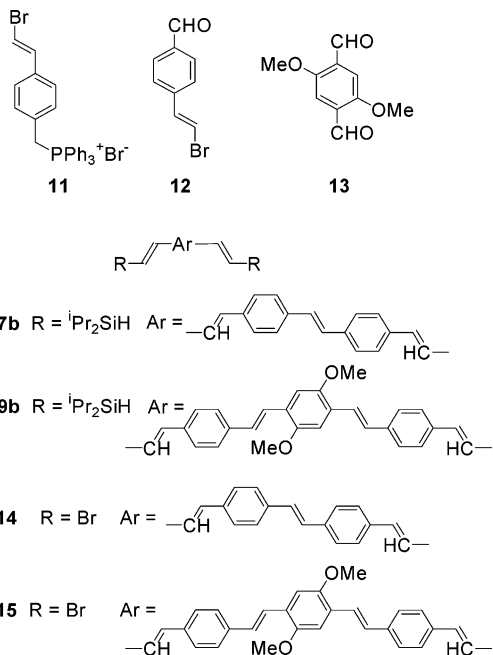
Conclusions

In summary, we have demonstrated the use of the concept of Thorpe–Ingold effect to direct the conformation of silylene-spaced divinylarene copolymers. Since distance is known to play an important role in PET processes, the present investigation suggested that bulky substituent on silicon would bring the chromophores in closer proximity. Copolymers with bulky isopropyl substituent are more folded so that intrachain PET between these chromophores will become more prominent leading to more efficient fluorescence quenching. The results from the STM images appear to be consistent with the outcome

of photophysical studies of these polymers. Further investigations on integration of light harvesting and electron transfer in a single polymer are in progress.

Experimental Section

General Data. Gel permeation chromatography (GPC) was performed on a Waters GPC machine using an isocratic HPLC pump (1515) and a refractive index detector (2414). THF was used as the eluent (flow rate = 1.0 mLmin⁻¹). Waters Styragel HR2, HR3, HR4 (7.8 × 300 mm) were employed using polystyrene as standard (M_n values range from 375 to 3.5 × 10⁶). Absorption spectra and emission spectra were measured with Hitachi U-3310 and Hitachi F-4500 fluorescence spectrophotometers, respectively. Quantum yield was obtained using coumarin **1** in EtOAc as reference ($\Phi = 0.99$).



1,4'-Bis(2-bromovinyl)stilbene (14). To a mixture of **11**¹² (2.80 g, 5.2 mmol) and **12**¹³ (1.08 g, 5.1 mmol) in EtOH (90 mL) was added NaOEt [prepared from sodium (0.18 g, 7.8 mmol) in ethanol (30 mL)]. The mixture was refluxed for 15 h and cooled to room temperature. Methanol was added, and the precipitate was collected. The solid was dissolved in toluene to which a trace amount of iodine was added. The mixture was refluxed for 24 h. Solvent was removed in vacuo, and the residue was washed with hexane until washings were almost colorless. The residue was recrystallized from toluene to give **14** as a white solid (1.69 g, 85%): mp 89–90 °C; ¹H NMR (400 MHz, CDCl₃): δ 6.80 (d, $J = 14.0$ Hz, 2 H), 7.08 (s, 2 H), 7.10 (d, $J = 14.0$ Hz, 2 H), 7.29 (d, $J = 8.2$ Hz, 4 H), 7.47 (d, $J = 8.2$ Hz, 4 H). ¹³C NMR (100 MHz, CDCl₃): δ 106.5, 126.3, 126.8, 128.2, 135.1, 136.6, 137.0. IR (KBr): ν 3068, 3007, 2921, 1704, 1646, 1503, 1491, 1405, 984, 956, 935, 884, 785 cm⁻¹. HRMS (FAB): calcd for C₁₈H₁₄⁷⁹Br₂, 387.9462; found, 387.9454. Anal. Calcd for C₁₈H₁₄Br₂: C, 55.42; H, 3.62. Found: C, 55.39; H, 3.32.

1,4-Bis(4-(2-bromovinyl)styryl)-2,5-dimethoxybenzene (15). To a mixture of **11**¹² (5.5 g, 10.3 mmol) and **13** (1.0 g, 5.1 mmol) in EtOH (90 mL) was added NaOEt [prepared from sodium (0.35 g, 15.5 mmol) in ethanol (60 mL)]. The mixture was refluxed for 15 h and cooled to room temperature. Methanol (150 mL) was added, and the resulting precipitate was collected. The solid was dissolved in toluene (100 mL), and the mixture was refluxed in the presence of a trace amount of iodine for 1 day. Solvent was removed in vacuo, and the residue was washed with hexane (300 mL) until washings were almost colorless; the residue was then recrystallized from toluene to give compound **15** as a yellow solid

(2.25 g, 80%): mp 189–190 °C. ¹H NMR (400 MHz, CDCl₃): δ 3.94 (s, 6 H), 6.79 (d, $J = 14.0$ Hz, 2 H), 7.09 (d, $J = 16.4$ Hz, 2 H), 7.10 (d, $J = 14.0$ Hz, 2 H), 7.13 (s, 2 H), 7.29 (d, $J = 8.0$ Hz, 4 H), 7.49 (d, $J = 8.0$ Hz, 4 H), 7.50 (d, $J = 16.4$ Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃): δ 56.4, 106.1, 108.7, 123.2, 126.0, 126.2, 126.6, 127.9, 134.5, 136.4, 137.3, 150.9. IR (KBr): ν 3048, 2983, 2917, 2856, 2811, 1597, 1561, 1509, 1459, 1410, 1340, 1263, 1212, 1037, 955, 845, 776, 669 cm⁻¹. HRMS (FAB): calcd C₂₈H₂₄O₂⁷⁹-Br₂, 550.0143; found, 550.0146. Anal. Calcd for C₂₈H₂₄O₂Br₂: C, 60.89; H, 4.38. Found: C, 60.57; H, 4.40.

1,4'-Bis[(2-diisopropylsilyl)vinyl]stilbene (7b). Under N₂, to a solution of **14** (0.39 g, 1.0 mmol) in THF (30 mL) cooled at -78 °C was added slowly ^tBuLi (2.7 mL of 1.55 M in pentane, 4.2 mmol). After this mixture was stirred for 30 min at -78 °C, chlorodiisopropylsilane (0.4 mL, 2.1 mmol) was added, and the mixture was gradually warmed to room temperature, stirring was continued for 3 h, and the reaction was quenched with H₂O (3.0 mL). The aqueous layer was extracted with Et₂O (3 × 10 mL), and the organic layer was washed with brine (20 mL), dried (MgSO₄), filtered, and evaporated in vacuo. The residue was chromatographed on Et₃N-treated silica gel (CH₂Cl₂/hexane 1:4) to afford **7b** as an oil (0.37 g, 80%). ¹H NMR (400 MHz, CDCl₃): δ 1.05–1.16 (m, 28 H), 3.76–3.78 (m, 2 H), 6.43 (dd, $J = 19.0$, 4.7 Hz, 2 H), 7.05 (d, $J = 19.0$ Hz, 2 H), 7.11 (s, 2 H), 7.45 (d, $J = 8.3$ Hz, 4 H), 7.50 (d, $J = 8.3$ Hz, 4 H). ¹³C NMR (100 MHz, CDCl₃): δ 10.9, 18.7, 126.4, 126.6, 126.7, 128.1, 137.0, 137.4, 146.9. IR (KBr): ν 2962, 2917, 2852, 2325, 1593, 1462, 1381 cm⁻¹. HRMS (FAB): calcd for C₃₀H₄₄Si₂, 460.2982; found, 460.2977.

1,4-Bis(4-(2-diisopropylsilyl)vinyl)styryl)-2,5-dimethoxybenzene (9b). Under N₂, to a solution of **15** (0.55 g, 1.0 mmol) in THF (30 mL) cooled at -78 °C was added slowly ^tBuLi (2.7 mL of 1.55 M in pentane, 4.2 mmol). After the reaction was stirred for 30 min at -78 °C, chlorodiisopropylsilane (0.4 mL, 2.1 mmol) was added, and the mixture was gradually warmed to room temperature, stirring was continued for 3 h, and the reaction was quenched with H₂O (3.0 mL). The aqueous layer was extracted with Et₂O (3 × 20 mL), and the organic layer was washed with brine (20 mL), dried (MgSO₄), filtered, and evaporated in vacuo. The residue was chromatographed on Et₃N-treated silica gel (CH₂-Cl₂/*n*-hexane 1:4) and the solid was recrystallized from pentane to afford **9b** as a yellow solid (0.50 g, 81%): mp 183–184 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.00–1.20 (m, 28 H), 3.75–3.77 (m, 2 H), 3.95 (s, 6 H), 6.40 (dd, $J = 19.1$, 4.7 Hz, 2 H), 7.04 (d, $J = 19.1$ Hz, 2 H), 7.12 (d, $J = 16.7$ Hz, 2 H), 7.12 (s, 2 H), 7.44 (d, $J = 8.3$ Hz, 4 H), 7.50 (d, $J = 16.7$ Hz, 2 H), 7.53 (d, $J = 8.3$ Hz, 4 H). ¹³C NMR (100 MHz, CDCl₃): δ 11.3, 19.0, 56.5, 108.7, 121.2, 122.8, 126.2, 126.4, 128.1, 132.0, 136.9, 137.2, 146.7, 151.0. IR (KBr): ν 2950, 2933, 2885, 2852, 2831, 2104, 1556, 1516, 1487, 1462, 1348, 1205, 1176, 964, 882, 870, 788, 764, 637 cm⁻¹. HRMS (FAB): calcd for C₄₀H₅₄O₂Si₂, 622.3662; found, 622.3657.

Polymer 4a. A mixture of **6**⁷ (93 mg, 0.2 mmol), **7a** (70 mg, 0.2 mmol), NaI (64 mg), and RhCl(PPh₃)₃ (4.6 mg, 0.001 mmol) in THF (5 mL) was refluxed under N₂ for 10 h. Methanol was added. The precipitate was collected and redissolved in THF and then precipitated again with methanol. The product was collected by filtration and washed with methanol to give polymer (**122** mg, 75%): $M_n = 9300$; PDI = 2.45. ¹H NMR (400 MHz, CDCl₃): δ 0.30 (s, 12 H), 3.61–3.69 (m, 24 H), 6.19–6.24 (d, 2 H), 6.45–6.61 (m, 6 H), 6.82–6.90 (m, 4 H), 7.08 (s, 2 H), 7.26–7.30 (d, 4 H), 7.33–7.44 (m, 8 H). IR (KBr): ν 3391, 2951, 2866, 1605, 1515, 1390, 1349, 1247, 1185, 1113, 986, 838, 736 cm⁻¹. Anal. Calcd for C₅₀H₆₂N₂O₄Si₂: C, 74.03; H, 7.70; N, 3.45. Found: C, 73.09; H, 7.32; N, 3.39.

Polymer 4b. In a manner similar to that described above, a mixture of **6** (93 mg, 0.2 mmol), **7b** (92 mg, 0.2 mmol), NaI (64 mg), and Rh(PPh₃)₃Cl (4.6 mg, 0.001 mmol) was converted to **4b** (115 mg, 62%): $M_n = 8600$; PDI = 2.27. ¹H NMR (400 MHz, CDCl₃): δ 1.07–1.12 (m, 28 H), 3.63–3.71 (m, 24 H), 6.16–6.20 (d, 2 H), 6.60–6.64 (d, 2 H), 6.66–6.90 (d, 4 H), 6.90–6.99 (m, 4 H), 7.11 (d, 2 H), 7.35–7.37 (d, 4 H), 7.48–7.50 (m, 8 H).

IR (KBr): ν 3446, 2948, 2861, 1652, 1604, 1539, 1520, 1457, 1424, 1387, 1350, 1275, 1229, 1184, 989, 881, 789 cm^{-1} .

Polymer 5a. In a manner similar to that described above, a mixture of **8** (84 mg, 0.2 mmol), **9a** (102 mg, 0.2 mmol), NaI (64 mg), and $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (4.6 mg, 0.001 mmol) was converted to **5a** (140 mg, 75%): $M_n = 8700$; PDI = 2.05. ^1H NMR (400 MHz, CDCl_3): δ 0.28 (s, 12 H), 3.50–3.65 (16 H), 3.65–3.80 (m, 4 H), 3.93 (s, 6 H), 6.20–6.30 (d, 2 H), 6.45–6.55 (d, 2 H), 6.55–6.75 (d, 4 H), 6.80–7.00 (m, 4 H), 7.05–7.15 (m, 4 H), 7.30–7.35 (d, 4 H), 7.40–7.55 (m, 10 H). IR (KBr): ν 3620, 3187, 2921, 2840, 1659, 1589, 1516, 1250, 1209, 1176, 1107, 1033, 821, 674 cm^{-1} .

Polymer 5b. In a manner similar to that described above, a mixture of **8** (84 mg, 0.2 mmol), **9b** (125 mg, 0.2 mmol), NaI (64 mg), and $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (4.6 mg, 0.001 mmol) was converted to **5b** (125 mg, 60%): $M_n = 7500$; PDI = 2.17. ^1H NMR (400 MHz, CDCl_3): δ 1.05–1.20 (m, 28 H), 3.55–3.70 (m, 16 H), 3.70–3.80 (m, 4 H), 3.95 (s, 6 H), 6.15–6.25 (d, 2 H), 6.45–6.55 (d, 2 H), 6.60–6.70 (d, 4 H), 6.85–7.05 (m, 4 H), 7.05–7.15 (m, 4 H), 7.30–7.40 (d, 4 H), 7.45–7.60 (m, 10 H). IR (KBr) ν 3436, 2950, 2885, 2856, 1650, 1614, 1520, 1458, 1405, 1368, 1221, 1185, 1119, 972, 788, 633 cm^{-1} .

Time-Resolved Fluorescence Measurements. A mode-locked Ti:sapphire laser (wavelength, 750 nm for **4**, 820 nm for **5**; repetition rate, 76 MHz; pulse width, <200 fs) passed through an optical parametric amplifier. The fluorescence of 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 3 ps.

STM Characterization. STM imaging of polymers **4a** and **4b** was carried out with a NanoScope IIIa controller equipped with a low-current converter for experiments requiring high tunneling impedance (Veeco Metrology Group/Digital Instruments, USA). The STM probes were commercially available Pt/Ir tips (PT, Nanotips, Veeco Metrology Group/Digital Instruments, USA). To observe individual polymers, a relatively diluted solution was prepared by dissolving 1 $\mu\text{g/mL}$ **4a** or **4b** in hexane (ca. 0.25 μM). The polymers were drop-cast onto freshly cleaved HOPG (highly orientated pyrolytic graphite, grade ZYD, Advanced Ceramics Corp.), subjected to vacuum-dry (~30 min, 120 mTorr) to remove trace amount of solvent, and rapidly transferred to a chamber where dry N_2 was purging throughout the experiments and the humidity was lower than 2%. Typical imaging conditions were 0.5–1.2 V in bias voltage and 10–50 pA in tunneling current. The dimensions of images were calibrated by the unit cell vectors of the underlying HOPG.

Acknowledgment. This work is supported by the National Science Council and the National Taiwan University of the Republic of China.

Supporting Information Available: Figures showing ^1H NMR spectra of all new compounds and electrochemical properties of **7** and **9**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) For reviews, see: (a) Jung, M. E.; Piizzi, G. *Chem. Rev.* **2005**, *105*, 1735. (b) Sammes, P. G.; Weller, D. J. *Synthesis* **1995**, 1205. (c) Galli, C.; Mandolini, L. *Eur. J. Org. Chem.* **2000**, 3117.
- (2) For a recent review, see: (a) Toniolo, C.; Crisma, M.; Formaggio, F.; Peggion, C. *Biopolymers* **2001**, *60*, 396. (b) Bunz, U. H. F. *Top. Curr. Chem.* **1999**, *210*, 131.
- (3) (a) Alder, R. W.; Maunder, C. M.; Orpen, A. G. *Tetrahedron Lett.* **1990**, *31*, 6717. (b) Alder, R. W.; Allen, P. R.; Khosravi, E. *J. Chem. Soc. Chem. Commun.* **1994**, 1235. (c) Alder, R. W.; Anderson, K. R.; Benjes, P. A.; Butts, C. P.; Koutentis, P. A.; Orpen, A. G. *Chem. Commun.* **1998**, 309. (d) Alder, R. W.; Allen, P. R.; Hnyk, D.; Rankin, D. W. H.; Robertson, H. E.; Smart, B. A.; Gillespie, R. J.; Bytheway, I. J. *J. Org. Chem.* **1999**, *64*, 4226. (e) Alder, R. W.; Allen, P. R.; Anderson, K. R.; Butts, C. P.; Khosravi, E.; Martín, A.; Maunder, C. M.; Orpen, A. G.; Pourçain, C. B. *St. J. Chem. Soc., Perkin Trans. 2* **1998**, 2083.
- (4) (a) Luh, T.-Y.; Cheng, Y.-J. *Chem. Commun.* **2006**, *45*, 4669. (b) Hu, S. S.; Webber, W. P. *Polym. Bull. (Berlin)* **1989**, *21*, 133. (c) Ijadi-Maghsoodi, S.; Barton, T. J. *Macromolecules* **1990**, *23*, 4485. (d) Corriu, R. J. P.; Guerin, C.; Henner, B.; Jean, A.; Garnier, F.; Yassar, A.; Kuhlmann, T. *Chem. Mater.* **1990**, *2*, 351. (e) Ohshita, J.; Kanaya, D.; Ishikawa, M.; Koike, T.; Yamanaka, T. *Macromolecules* **1991**, *24*, 2106. (f) Wu, H. J.; Interrante, L. V. *Macromolecules* **1992**, *25*, 1840. (g) Miao, Y.-J.; Bazan, G. C. *Macromolecules* **1997**, *30*, 7414. (h) Mori, A.; Takahisa, E.; Kajiro, H.; Nishihara, Y.; Hiyama, T. *Macromolecules* **2000**, *33*, 1115. (i) Jung, S.-H.; Kim, H. K.; Kim, S.-H.; Kim, Y. H.; Jeoung, S. C.; Kim, D. *Macromolecules* **2000**, *33*, 9277. (j) Ishikawa, M.; Hatano, T.; Hasegawa, Y.; Horio, T.; Kunai, A.; Miyai, A.; Ishida, T.; Tsukihara, T.; Yamanaka, T.; Koike, T.; Shioya, J. *Organometallics* **1992**, *11*, 1604. (k) You, Y.; An, C.-G.; Lee, D.-S.; Kim, J.-J.; Park, S. Y. *J. Mater. Chem.* **2006**, *16*, 4706. (l) West, R. J. *Organomet. Chem.* **1986**, *300*, 327. (m) Birot, M.; Pillot, J.-P.; Dunoguè, J. *Chem. Rev.* **1995**, *95*, 1443. (n) Brouwer, H. J.; Krasnikov, V. V.; Hilberer, A.; Hadziioannou, G. *Adv. Mater.* **1996**, *8*, 935. (o) Ryu, M.-K.; Kim, K. D.; Lee, S. M.; Cho, S. W.; Park, J. W. *Macromolecules* **1998**, *31*, 1114. (p) Malliaras, G. G.; Herrema, J. K.; Wildeman, J.; Wieringa, R. H.; Gill, R. E.; Lampoura, S. S.; Hadziioannou, G. *Adv. Mater.* **1993**, *5*, 721. (q) Ohshita, J.; Kangai, S.; Yoshida, H.; Kunai, A.; Kajiura, S.; Ooyama, Y.; Harima, Y. *J. Organomet. Chem.* **2007**, *692*, 801.
- (5) (a) 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. (b) Yeh, M.-Y.; Lin, H.-C.; Lee, S.-L.; Chen, C.-h.; Lim, T.-S.; Fann, W.; Luh, T.-Y. *Chem. Commun.* **2007**, 3459. (c) Hwu, T.-Y.; Basu, S.; Chen, R.-M.; Cheng, Y.-J.; Hsu, J.-H.; Fann, W.; Luh, T.-Y. *J. Polym. Sci. Part A: Polym. Chem.* **2003**, *40*, 2218.
- (6) (a) Cheng, Y.-J.; Luh, T.-Y. *Chem.—Eur. J.* **2004**, *10*, 5361. (b) Luh, T.-Y. *Pure Appl. Chem.* **2005**, *77*, 2083. (c) Cheng, Y.-J.; Hwu, T.-Y.; Hsu, J.-H.; Luh, T.-Y. *Chem. Commun.* **2002**, 1978.
- (7) Wang, H.-W.; Cheng, Y.-J.; Chen, C.-H.; Lim, T.-S.; Fann, W.; Lin, C.-L.; Luh, T.-Y. *Macromolecules* **2007**, *40*, 2666.
- (8) Cheng, Y.-J.; Liang, H.; Luh, T.-Y. *Macromolecules* **2003**, *36*, 5912.
- (9) Pourtois, G.; Beljonne, D.; Cornil, J.; Ratner, M. A.; Brédas, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 4436.
- (10) van Walree, C. A.; Roest, M. R. P.; Schuddeboom, W.; Jenneskens, L. W.; Verhoeven, J. W.; Warman, J. M.; Kooijman, H.; Spek, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 8395.
- (11) The charge-transfer rate constant k_{cs} and the corresponding charge-separation yield Φ_{cs} were calculated according to literature methods: (a) Sandanayaka, A. S. D.; Taguri, Y.; Araki, Y.; Ishi-i, T.; Mataka, S.; Ito, O. *J. Phys. Chem. B* **2005**, *109*, 22502. (b) Hattori, S.; Ohkubo, K.; Urano, Y.; Sunahara, H.; Nagano, T.; Wada, Y.; Tkachenko, N. V.; Lemmetyinen, H.; Fukuzumi, S. *J. Phys. Chem. B* **2005**, *109*, 15368.
- (12) Martín-Villamil, R.; Lafuente, A.; Rodríguez, J. G. *Tetrahedron* **2003**, *59*, 1021.
- (13) Thomas, K.; Christel, N.; Gabriele, N. *Chem. Ber.* **1994**, *127*, 659.

MA702197K