6980 *Macromolecules* **2010**, *43*, 6980–6985
DOI: 10.1021/ma101326u

Macromolecules
ARTICLE

Stereocontrolled Synthesis and Photoisomerization Behavior of All-Cis and All-Trans Poly(*m*-phenylenevinylene)s

Masayuki Wakioka,[†] **Masashi Ikegami,**[‡] **and Fumiyuki Ozawa***[,†]

[†]*International Research Center for Elements Science (IRCELS), Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan, and* [‡]*Graduate School of Engineering, Toin University of Yokohama, 1614 Kurogane-cho, Aoba, Yokohama, Kanagawa 225-8502, Japan*

Received June 15, 2010; Revised Manuscript Received July 31, 2010

ABSTRACT: All-cis and all-trans isomers of poly[(arylenevinylene)-*alt*-(5-octyloxy-1,3-phenylenevinylene)]s having three kinds of arylene groups (PmPVs: arylene = *m*-phenylene (**1a**), *p*-phenylene (**1b**), 4,4′-biphenylene (**1c**)) have been synthesized in almost perfect stereoregularity by two types of palladium-catalyzed polycondensation reactions, respectively. Suzuki−Miyaura-type polycondensation of (*Z*,*Z*)-bis(2-bromoethenyl)arenes with 5-octyloxy-1,3-benzenediboronic acid pinacolate affords all-cis **1a**−**c**, whereas Hiyama-type polycondensation of (*E*,*E*)-bis(2-silylethenyl)arenes with 5-octyloxy-1,3-diiodobenzene forms all-trans **1a**−**c**. The resulting polymers with relatively short effective π-conjugation lengths interrupted by *m*-phenylene units undergo two-way photoisomerization to give PmPVs containing *cis*- and *trans*-vinylene groups in nearly 1:1 ratios irrespective of the arylene groups of staring polymers.

Introduction

Poly(phenylenevinylene)s and their homologues are π-conjugated polymers that have wide application in optoelectronic devices.[1] It has been recognized that π-conjugated polymers are advantageous over small organic molecules as well as inorganic compounds in terms of accessibility of thin films, which enables easy and low-cost fabrication of large-area devices. We recently found that poly(*p*-phenylenevinylene)s (PpPVs) gain a unique film-forming property when the vinylene linkages in the polymer chain are entirely stereoregulated to cis geometry.[2] All-cis PpPVs are readily soluble in common organic solvents and form highly amorphous films by spin-coating. Interestingly, the resulting films are insolubilized under UV light, along with cis-to-trans isomerization of vinylene linkages to give all-trans PpPVs. This phenomenon (i.e., photoinduced insolubilization) has been successfully applied to direct microscale patterning of PpPVs on a quartz substrate in an extremely simple procedure.[2a,e]

The photoinduced insolubilization involves one-way photoisomerization from all-cis isomers to all-trans isomers of PpPVs. The one-way photoisomerization has been documented in several instances of alkene molecules.[3] While stilbene undergoes two-way photoisomerization between cis and trans isomers to give a cis-rich mixture in the photostationary state, aromatic alkenes with an extended π-conjugated system tend to be isomerized solely from the cis isomer to the trans isomer. Recent studies on oligo(*p*-phenylenevinylene)s (OpPVs) have revealed that OpPVs having more than two phenylenevinylene units undergo one-way photoisomerization via either the singlet or the triplet excited state.[4]

This paper deals with the synthesis and photoisomerization of all-cis and all-trans poly[(arylenevinylene)-*alt*-(5-octyloxy-1,3-phenylenevinylene)]s with three different arylene groups (PmPVs; **1a**−**c** in Chart 1). We have been interested in the effect of π-conjugation length on photoisomerization of polymeric alkenes, in connection with the one-way photoisomerization of PpPVs. Although photoisomerization has been extensively studied for small alkenes, related studies on polymeric compounds have been limited.[5] In this study, we compared photoisomerization behaviors of **1a**−**c** with those of the model compounds of their constitution units (**2**−**5** in Chart 1). Unlike PpPVs with extended π-conjugated systems, PmPVs possess a relatively short π-conjugation length interrupted by *m*-phenylene units.[6] It has been found that PmPVs undergo two-way photoisomerization both in solution and in thin films. The cis/trans ratios in the photostationary state are clearly different from those of the constitution units, and fall into nearly 1:1 irrespective of the π-conjugation lengths.

Results and Discussion

Synthesis and Characterization of PmPVs. All-cis and all-trans PmPVs were synthesized by Suzuki−Miyaura-type[2,7] and Hiyama-type polycondensations,[8,9] respectively (Scheme 1). The choice of catalytic cross-coupling reactions dependent on desirable stereochemistry is based on our previous findings on PpPVs synthesis.[2,8] The inverse use of the reactions often causes structural defects in resulting polymers. Suzuki−Miyaura-type polycondensation of (*E*,*E*)-isomers of bis(2-bromoethenyl)arenes tends to involve homocoupling reactions providing butadiene and biaryl units,[2d,10] and Hiyama-type polycondensation of (*Z*,*Z*)-bis(2-silylethenyl)arenes commonly affords (*E*)-vinylene linkages in the polymer chain.[2b,8]

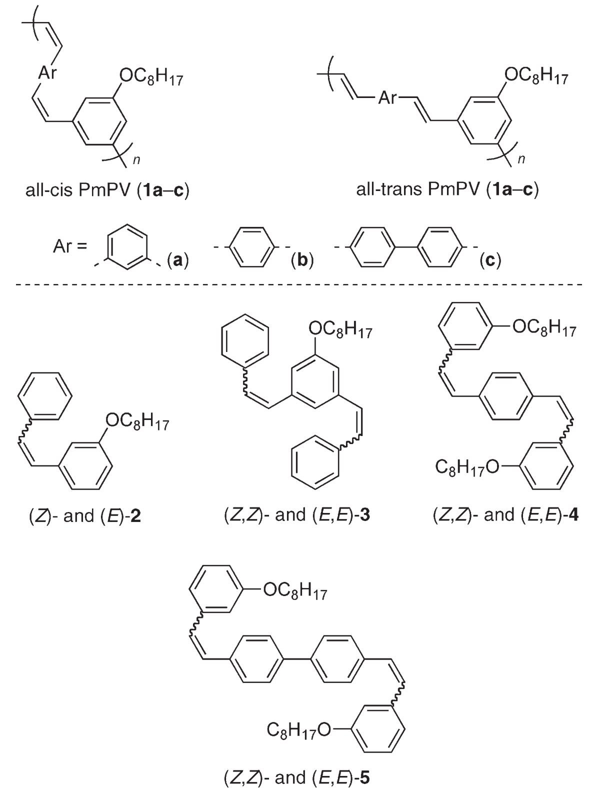
Table 1 summarizes the results of synthetic reactions. Treatment of (*Z*,*Z*)-bis(2-bromoethenyl)arenes (**6a**−**c**) with 5-octyloxy-1,3-benzenediboronic acid ester (**7**) in toluene at 80 °C in the presence of $[Pd(PPh_3)_4]$ (1.0 mol %), aqueous KOH (3 M, 3 equiv), and Bu_4NBr (1 equiv) for 24 h afforded all-cis **1a**−**c** in 84−97% yields (entries 1−3). On the other hand, the reactions of (*E*,*E*)-bis(2-silylethenyl)arenes (**8a**−**c**) with 5-octyloxy-1,3-diiodobenzene (**9**) in THF at room temperature in the presence of $[Pd(\mu\text{-Cl})(\eta^3\text{-allyl})]_2$ (5 mol %) and Bu_4NF (2 equiv) for 100 h formed all-trans **1a**−**c** in quantitative yields (entries 4−6).

The polymers were isolated as gummy pastes (all-cis PmPVs) or powdery solids (all-trans PmPVs), respectively.

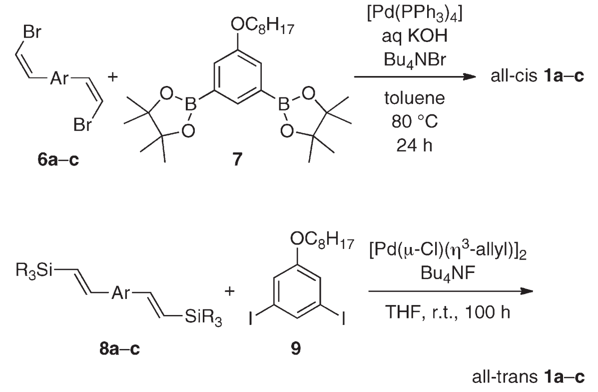
---

*Corresponding author. E-mail: ozawa@scl.kyoto-u.ac.jp.

Chart 1. List of PmPVs and Their Model Compounds Prepared in This Study



Scheme 1. Synthesis of All-Cis and All-Trans 1 (SiR_3 = 3.5-$(CF_3)_2C_6H_3SiMe_2$)



The geometry and stereoregularity of vinylene linkages were unequivocally confirmed by NMR spectroscopy. Table 2 compares the NMR data of **1a**–**c** with those of **2**–**5**. The vinylic carbons of cis and trans isomers have different chemical shifts at around δ 130 and 129, respectively. The OCH_2 proton signals of octyloxy groups are observed separately. As seen from the ^1H NMR spectra in Figure 1, the signals of *cis*- and *trans*-**1a** appear at δ 3.59 and 4.03, respectively.[11,12] The cis/trans ratios listed in Table 1 are evaluated from the peak intensities of those signals.

Table 1. Synthesis of All-Cis and All-Trans PmPVs (1a–c)

entry	product	yield (%)[a]	M_n[b]	M_w/M_n[b]	cis/trans[c]
1	all-cis **1a**	97	3800	3.43	> 99/1
2	all-cis **1b**	84	4300	4.23	> 99/1
3	all-cis **1c**	95	4700	5.27	> 99/1
4	all-trans **1a**	> 99	5200	1.75	< 1/99
5	all-trans **1b**	> 99	4200	1.47	< 1/99
6	all-trans **1c**	> 99	8300	2.35	< 1/99

[a] Isolated yield of MeOH-insoluble polymer. [b] Determined by GPC calibration based on polystyrene standards. [c] Determined by ^1H NMR analysis.

Table 2. Selected NMR Data for PmPVs (1a–c) and Model Compounds (2–5)[a]

compound	^{13}C NMR ($\delta_{C=C}$)	^1H NMR (δ_{OCH_2})
all-cis **1a**	130.1, 130.1	3.59
all-cis **1b**	130.0, 130.0	3.62
all-cis **1c**	130.4, 130.2	3.63
(*Z*)-**2**	130.3, 130.3	3.77
(*Z*,*Z*)-**3**	130.4, 130.0	3.59
(*Z*,*Z*)-**4**	130.2, 130.0	3.81
(*Z*,*Z*)-**5**	130.4, 129.8	3.80
all-trans **1a**	129.0, 128.8	4.03
all-trans **1b**	128.7, 128.5	4.05
all-trans **1c**	128.6, 128.6	4.07
(*E*)-**2**	128.9, 128.7	4.00
(*E*,*E*)-**3**	129.2, 128.5	4.05
(*E*,*E*)-**4**	128.6, 128.5	4.00
(*E*,*E*)-**5**	128.8, 128.4	4.01

[a] Measured in $CDCl_3$ at room temperature.

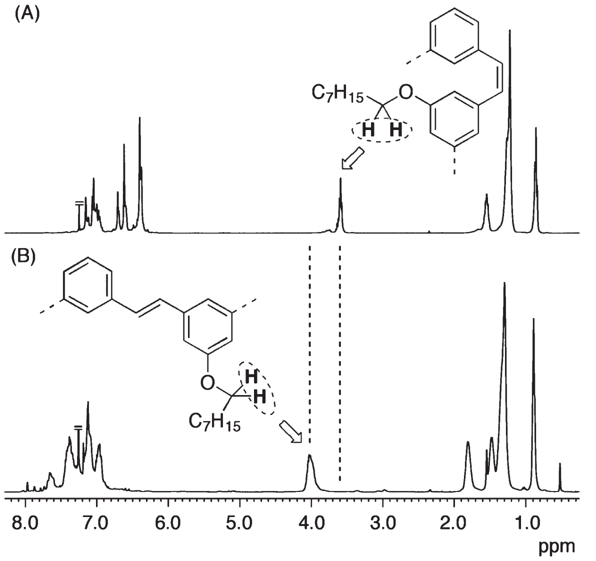


Figure 1. ^1H NMR spectra of all-cis **1a** (A) and all-trans **1a** (B) in $CDCl_3$ at room temperature.

Photoisomerization of PmPVs in Solution. All-cis and all-trans PmPVs were dissolved in benzene (4.0 mg L^{-1}) and irradiated with a Xe lamp (λ_{max} = 365 nm, 0.87 mW cm^{-2}) in a quartz cell under a nitrogen atmosphere at room temperature. The sample solution was observed at intervals by UV–vis spectroscopy. Figure 2 shows the change of absorption spectra of all-cis **1c** (A) and all-trans **1c** (B). Upon UV-irradiation, the absorption of all-cis isomer (λ_{max} = 328 nm) increases whereas that of all-trans isomer (λ_{max} = 366 nm) decreases to achieve the photostationary state within a few minutes.[13] The cis content in the equilibrium mixture is estimated to be 53% according to the following equation: cis (%) = $(A_{trans} - A_{pss})/(A_{trans} - A_{cis}) \times 100$, where A_{trans} and A_{cis} stand for the absorbance of all-trans and all-cis isomers at 366 nm before UV-irradiation, respectively, and A_{pss} for the absorbance at the same wavelength in the photostationary state.

Table 3 summarizes the results of photoisomerization. Unlike PpPVs that undergo one-way photoisomerization, **1a**–**c** undergo two-way photoisomerization to give PmPVs containing *cis*- and *trans*-vinylene groups. It is seen that the

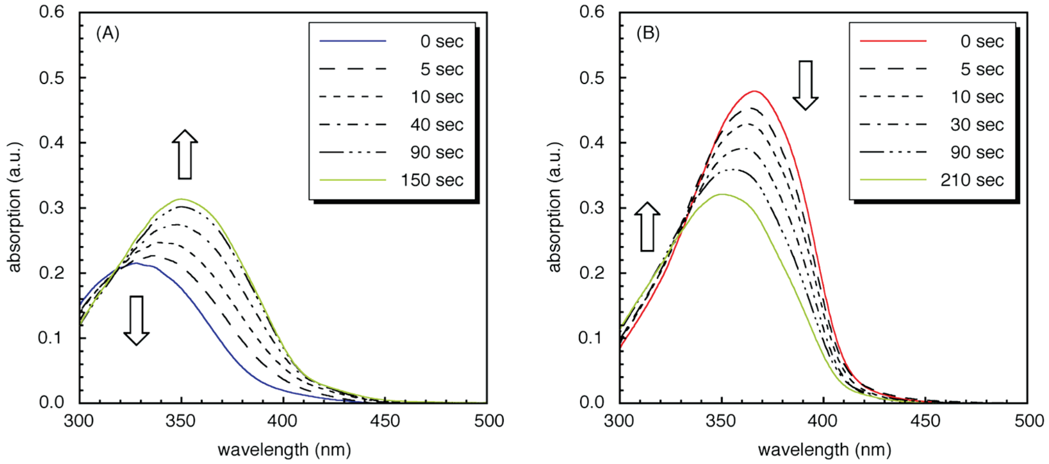


Figure 2. Changes of UV−vis absorption spectra of all-cis **1c** (A) and all-trans **1c** (B) under UV-irradiation in benzene (4.0 mg L^{-1}).

Table 3. Photoisomerization of 1a−c and 2−5 in Benzene[a]

	λ_{max} (nm)				
compound	all-cis	all-trans	pss[b]	time (s)[c]	cis/trans[d]
1a	273[e]	311	307	90	54/46
1b	319	372	368	330	46/54
1c	328	366	350	150	53/47
2	280[e]	310	f	30	86/14
3	269[e]	313	f	30	31/69
4	318	362	362	150	4/96
5	328	356	356	150	< 1/99

[a] A benzene solution of the compound (4.0 mg L^{-1}) was irradiated with a Xe lamp (λ_{max} = 365 nm, 0.87 mW cm^{-2}) in a quartz cell under nitrogen atmosphere at room temperature, and examined by UV−vis spectroscopy. [b] pss = photostationary state. [c] The time to achieve the photostationary state starting from cis isomer. [d] The cis/trans ratio in the photostationary state. The value for **1a−c** denotes the cis/trans ratio of vinylene groups in the polymer chain. [e] Measured in CH_2Cl_2. [f] The value was unidentified due to the overlap with the absorption of solvent benzene.

Table 4. Fluorescence Data for All-Trans PmPVs and Model Compounds

compound	λ_{max} (nm)[a]	Φ[a,b]
all-trans **1a**	378, 397	0.21
all-trans **1b**	406, 431	0.32
all-trans **1c**	408, 433	0.47
(*E*)-**2**	363	0.27
(*E*,*E*)-**4**	397, 418	0.76
(*E*,*E*)-**5**	401, 425	0.83

[a] Emission peaks and quantum yields were obtained with the excitation at 330 nm in benzene. [b] Quantum yields were determined relative to anthracene in EtOH (Φ = 0.27).

cis/trans ratios in the photostationary state ([cis/trans]$_{pss}$) are quite different from those of **2−5**. Meeting the general expectations,[3] the trans contents of **2−5** in the photostationary state increase with elongation of the effective π-conjugation lengths in the order **2** < **3** < **4** < **5**. In contrast, the cis/trans ratios of **1a−c** converge at nearly 1:1 irrespective of the arylene groups. Since the λ_{max} values of **1a−c** are in good agreement with those of **3−5**, respectively, it is convincing that each polymer has almost the same π-conjugation length as the corresponding constituent. Nevertheless, the vinylene groups reach equilibrium in a nearly 1:1 ratio.

It is known that two-way photoisomerization of stilbene proceeds via a singlet excited state with the 90°-twisted form as the potential minimum, which affords a cis/trans mixture of stilbene upon deactivation. However, the 90°-twisted form is no longer the potential minimum for an alkene integrated into an extended π-conjugated system, because the trans conformer gains the stability due to π-conjugation to a great extent. In this case, when the triplet state with a trans configuration is the potential minimum, the alkene molecule changes its geometry solely from the cis form to the trans form, along the triplet state potential surface. This phenomenon is referred to as one-way photoisomerization.[3] The variation in cis/trans ratios observed for **2−5** clearly follows this tendency. On the other hand, as for the polymeric alkenes **1a−c**, there is a possibility that the 90°-twisted form remains as the energy minimum in the excited state to avoid steric congestion within the molecule. In this case, the excited state should be deactivated from the twisted form to give PmPVs containing both *cis*- and *trans*-vinylene units. Thus, we carried out emission experiments to gain more direct information on the geometrical structure in the excited state. When the potential minimum adopts a twisted structure, the excited molecule undergoes two-way photoisomerization and thereby the fluorescence quantum yield decreases. On the other hand, when the trans configuration constitutes the potential minimum, the alkene molecule very probably exhibits strong emission.

Table 4 lists the fluorescence data measured in benzene under 330 nm irradiation. The fluorescence quantum yields of all-trans PmPVs (Φ = 0.2−0.5) are comparable to that of the stilbene derivative (*E*)-**2** (Φ = 0.27), but significantly smaller than those of (*E*,*E*)-**4** and **-5** with extended π-conjugated systems ($\Phi \sim 0.8$). These data are consistent with the twisted form of vinylene unit of PmPVs in the excited state, which is converted to a cis/trans mixture without notable fluorescence.

Photoisomerization of PmPVs in Thin Films. All-cis and all-trans PmPVs underwent two-way photoisomerization in thin films as well. Figure 3 shows the change of UV−vis absorption spectra of **1a** in thin films, which were prepared from a $CHCl_3$ solution (0.2 wt %) by spin-coating on a quartz substrate, and irradiated with a Xe lamp (λ_{max} = 365 nm, 21.0 mW cm^{-2}) under vacuum at room temperature. It was noted that the absorption maxima of all-cis and all-trans **1a** are red-shifted by 2 and 11 nm, respectively, as compared with those in solution. Although the photoisomerization could not be evaluated quantitatively, because of variation in the thickness of films depending on the experimental runs, the spectroscopic change in this figure indicates a very similar cis/trans ratio to the solution system. Interestingly, the photoirradiated films remained on the substrate in high

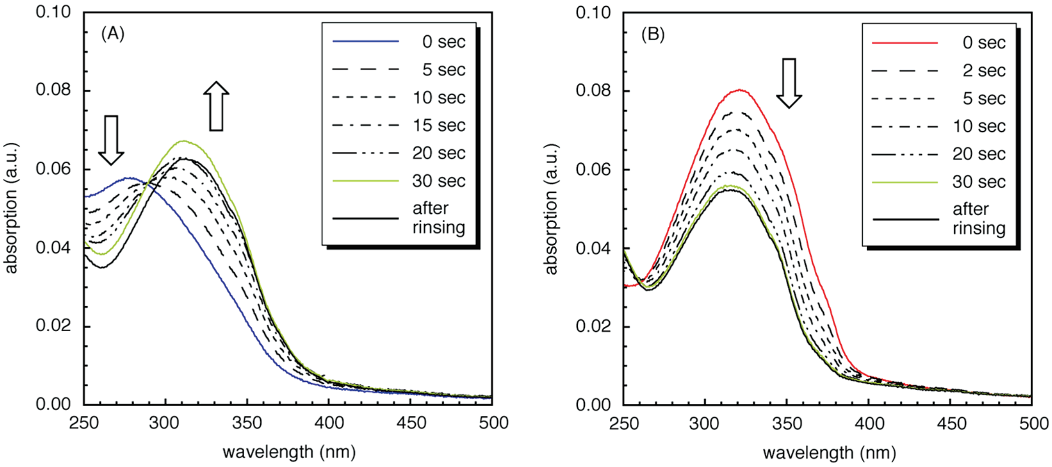


Figure 3. Changes of UV−vis absorption spectra of all-cis **1a** (A) and all-trans **1a** (B) under UV-irradiation in thin films.

percentages after rising twice with $CHCl_3$, as seen from relative intensities of green and black lines. Thus, it was found that PmPVs undergo photoinduced insolubilization in thin films. The insolubilization was completed within a few minutes. This change was much faster than that of PpPVs, which are gradually insolubilized over 1 h along with one-way photoisomerization from all-trans isomers to all-cis isomers.[2e]

Conclusion

Suzuki−Miyaura-type and Hiyama-type polycondensation reactions provide all-cis and all-trans PmPVs in perfect stereoregularity, respectively. The resulting polymers (**1a**−**c**) undergo two-way photoisomerization of vinylene units in solution as well as in thin films, giving PmPVs containing *cis*- and *trans*-vinylene groups in nearly 1:1 ratios, irrespective of the effective π-conjugation lengths of constitution units. This behavior is clearly different from that of model compounds **2**−**5**, for which the trans content in the photostationary state increases with elongation of the effective π-conjugation length. The photoisomerization behavior observed for **1a**−**c** is consistent with the 90°-twisted form of the energy minimum in the excited sate, which is provided by steric congestion within the polymeric alkenes. This assumption has been supported by emission experiments showing moderate fluorescence quantum yields of **1a**−**c**.

Experimental Section

General Considerations. All manipulations using organometallic compounds were carried out under a nitrogen or argon atmosphere using conventional Schlenk techniques. Nitrogen and argon gas were dried by passing through P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on a Bruker Avance 400 spectrometer (^{1}H NMR 400.13 MHz and ^{13}C NMR 100.62 MHz). Chemical shifts are reported in δ (ppm), referenced to the ^{1}H (residual protons) and ^{13}C signals of deuterated solvents. Analytical GPC was carried out on a JASCO GPC assembly consisting of a model PU-980 precision pump, a model RI-1530 refractive index detector, and three polystyrene gel columns (Shodex KF-801, KF-803 L, KF-805 L). THF was used as the mobile phase with a flow rate of 1.0 mL min^{-1} at 40 °C. The columns were calibrated against nine standard polystyrene samples (Shodex; M_n = 980−1920000). Spin-coating of PmPV was performed with a Mikasa spin coater 1H-DX2. Photoirradiation was carried out at room temperature using an Asahi Spectra LAX-101 Xe lamp. The wavelength (λ_{max} = 365 nm) that corresponds to the I-line of Hg lamp was selected for covering the absorptions of all samples employed. UV−vis absorption and fluorescence spectra were recorded on a JASCO V-560 spectrometer and a FP-6600 fluorescence spectrometer, respectively.

Toluene was dried over sodium benzophenone ketyl, distilled, and stored over activated molecular sieves (MS4A). THF (Wako, dehydrated) was used as received. The following compounds were synthesized according to the literature: $[Pd(PPh_3)_4]$,[14] $[Pd(\mu\text{-Cl})(\eta^3\text{-allyl})]_2$,[15] (*Z*,*Z*)-bis(2-bromoethenyl)arenes (**6a**−**c**),[16] and (*E*,*E*)-1,4-bis(2-silylethenyl)benzene (**8b**).[8] Synthetic procedures for **2**−**5**, 1,3-diboryl-5-octyloxybenzene (**7**), (*E*,*E*)-bis(2-silylethenyl)arenes (**8a**,**c**), and 1,3-diiodo-5-octyloxybenzene (**9**) are reported as Supporting Information. All other chemicals were obtained from commercial suppliers and used without further purification.

Synthesis of All-Cis PmPVs (1). A typical procedure is reported for all-cis **1a**. To a solution of **6a** (28.8 mg, 0.100 mmol), **7** (45.8 mg, 0.100 mmol), and Bu_4NBr (32.2 mg, 0.100 mmol) in toluene (0.5 mL) were added $[Pd(PPh_3)_4]$ (1.2 mg, 1.0 μmol) and 3.0 M aqueous KOH (0.10 mL, 0.30 mmol). The mixture was stirred at 80 °C for 24 h in the dark. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 (1 mL), washed with water (3 × 3 mL), and then poured into vigorously stirred MeOH (50 mL). A pale yellow, sticky precipitate of all-cis **1a** was collected by decantation, washed with MeOH, and dried under vacuum at room temperature overnight (32.3 mg, 97% yield).

All-Cis 1a. Pale yellow gummy paste. ^{1}H NMR ($CDCl_3$): δ 7.20−6.90 (m, C_6H_4), 6.73−6.67 (m, H^2 of C_6H_3OR), 6.64−6.57 (m, H^{4,6} of C_6H_3OR), 6.44−6.32 (m, CH=CH), 3.84−3.70 (m, OCH_2 of terminal C_6H_4OR), 3.59 (t, J = 6.5 Hz, OCH_2), 1.80−1.49 and 1.43−1.14 (m, CH_2), 0.92−0.80 (m, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 158.7 (s, C^5 of C_6H_3OR), 138.3 (s, C^{1,3} of C_6H_3OR), 137.1 (s, C^{1,3} of C_6H_4), 130.1, 130.1 (each s, CH=CH), 129.7 (s, C^5 of C_6H_4), 127.8 (s, C^2 of C_6H_4), 127.6 (s, C^{4,6} of C_6H_4), 122.2 (s, C^2 of C_6H_3OR), 113.8 (s, C^{4,6} of C_6H_3OR), 67.8 (s, OCH_2), 31.9, 29.3, 29.3, 29.1, 26.1, 22.7 (each s, CH_2), 14.1 (s, CH_3).

All-Cis 1b. Yellow gummy paste. ^{1}H NMR ($CDCl_3$): δ 7.06 (br, C_6H_4), 6.74 (br, H^2 of C_6H_3OR), 6.62 (br, H^{4,6} of C_6H_3OR), 6.43 (br, CH=CH), 3.62 (t, J = 6.3 Hz, OCH_2), 1.73−1.53 and 1.43−1.16 (m, CH_2), 0.92−0.80 (m, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 158.8 (s, C^5 of C_6H_3OR), 138.5 (s, C^{1,3} of C_6H_3OR), 135.9 (s, C^{1,4} of C_6H_4), 130.0, 130.0 (each s, CH=CH), 128.9 (s, C^{2,3,5,6} of C_6H_4), 121.8 (s, C^2 of C_6H_3OR), 113.7 (s, C^{4,6} of C_6H_3OR), 83.8 (s, $C(CH_3)_2$ of terminal $BOC(CH_3)_2$), 67.8 (s, OCH_2), 31.8, 29.3, 29.3, 29.1, 25.9 (each s, CH_2), 24.8 (s, $C(CH_3)_2$ of terminal $BOC(CH_3)_2$), 22.7, 14.1 (s, CH_3).

All-cis 1c. Yellow solid. ^{1}H NMR ($CDCl_3$): δ 7.52−7.15 (m, H$^{2,6,2',6'}$ and H$^{3,5,3',5'}$ of $C_{12}H_8$), 6.83 (br, H^6 of C_6H_3OR), 6.68 (br, H^{2,4} of C_6H_3OR), 6.53−6.42 (m, CH=CH), 3.63 (br, 2H, OCH_2), 1.74−1.47 (br, 2H, CH_2), 1.45−1.07 (br, 10H, CH_2), 1.31 (s, $C(CH_3)_2$ of terminal $BOC(CH_3)_2$), 0.92−0.74 (br, 3H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 158.9 (s, C^3 of C_6H_3), 139.1, 138.6, 136.1 (each s, $C^{1,1'}$ and $C^{4,4'}$ of $C_{12}H_8$ and $C^{1,5}$ of C_6H_3), 130.4, 130.2 (each s, CH=CH), 129.4, 126.4 (each s, $C^{2,6,2',6'}$ and $C^{3,5,3',5'}$ of C_8H_{12}), 121.7 (s, C^6 of C_6H_3), 113.8 (s, $C^{2,4}$ of C_6H_3), 83.8 (s, $\mathit{C}(CH_3)_2$ of terminal $BOC(CH_3)_2$), 67.8 (s, OCH_2), 31.8, 29.3, 29.2, 29.1, 25.9, 22.7 (each s, CH_2), 24.8 (s, $C(\mathit{C}H_3)_2$ of terminal $BOC(CH_3)_2$), 14.1 (s, CH_3).

Synthesis of All-Trans PmPVs (1). A typical procedure is reported for of all-trans **1a**. To a solution of **8a** (67.7 mg, 0.100 mmol) and **9** (45.4 mg, 0.100 mmol) in THF (1.0 mL) were added $[Pd(\mu\text{-}Cl)(\eta^3\text{-allyl})]_2$ (1.8 mg, 5.0 μmol) and a 1.0 M solution of $Bu_4NF\cdot 3H_2O$ in THF (0.20 mL, 0.20 mmol). The mixture was stirred at room temperature for 100 h. The resulting suspension was poured into vigorously stirred MeOH (50 mL). A white precipitate of all-trans **1a** was collected by a membrane filter (0.5 μm), washed with MeOH, and dried under vacuum at room temperature overnight (36.0 mg, >99% yield).

All-Trans 1a. White solid. ^1H NMR ($CDCl_3$): δ 8.03 (br s, $H^{2,6}$ of C_6H_3-3,5-$(CF_3)_2$ of terminal $CH{=}CHSi(CH_3)_2Ar$), 7.87 (br s, H^4 of C_6H_3-3,5-$(CF_3)_2$ of terminal $CH{=}CHSi(CH_3)_2Ar$), 7.71−7.57 (m, H^3 of C_6H_4), 7.50−7.25 (m, $H^{4,6}$ and H^5 of C_6H_4), 7.25−7.04 (m, H^2 of C_6H_3OR and CH=CH), 7.04−6.86 (m, $H^{2,6}$ of C_6H_3OR), 4.11−3.88 (m, OCH_2), 1.90−1.73 and 1.57−1.20 (m, CH_2), 0.93−0.83 (m, CH_3), 0.52 (s, CH_3 of terminal $CH{=}CHSi(CH_3)_2Ar$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.8 (s, C^5 of C_6H_3OR), 138.8 (s, $C^{1,3}$ of C_6H_3OR), 137.6 (s, $C^{1,3}$ of C_6H_4), 129.0, 128.8 (each s, CH=CH), 128.8 (s, C^2 of C_6H_4), 125.9 (s, $C^{4,6}$ of C_6H_4), 124.8 (s, C^5 of C_6H_4), 118.0 (s, C^2 of C_6H_3OR), 111.8 (s, $C^{4,6}$ of C_6H_3OR), 68.1 (s, OCH_2), 31.9, 29.4, 29.3, 26.1, 22.7 (each s, CH_2), 14.1 (s, CH_3), −2.8 (s, CH_3 of terminal $CH{=}CHSi(CH_3)_2Ar$).

All-Trans 1b. Yellow solid. ^1H NMR ($CDCl_3$): δ 7.97 (br s, $H^{2,6}$ of C_6H_3-3,5-$(CF_3)_2$ of terminal $CH{=}CHSi(CH_3)_2Ar$), 7.87 (br s, H^4 of C_6H_3-3,5-$(CF_3)_2$ of terminal $CH{=}CHSi(CH_3)_2Ar$), 7.54 (s, C_6H_4), 7.20−7.03 (m, H^2 of C_6H_3 and CH=CH), 6.99 (s, $H^{2,6}$ of C_6H_3), 4.05 (t, J = 6.4 Hz, OCH_2), 3.95 (t, J = 6.4 Hz, OCH_2 of therminal $C_6H_3IOC_8H_{17}$), 1.90−1.73 (m, CH_2), 1.57−1.22 (m, CH_2), 0.93−0.83 (m, CH_3), 0.52 (s, CH_3 of terminal $CH{=}CHSi(CH_3)_2Ar$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.8 (s, C^5 of C_6H_3), 138.9 (s, $C^{1,3}$ of C_6H_3), 136.7 ($C^{1,4}$ of C_6H_4), 128.7, 128.5 (each s, CH=CH), 127.0 (s, $C^{2,3,5,6}$ of C_6H_4), 118.0 (s, C^2 of C_6H_3), 111.7 (s, $C^{4,6}$ of C_6H_3), 94.7 (s, C^1 of C_6H_3 of terminal $C_6H_3IOC_8H_{17}$), 68.1 (s, OCH_2), 31.8, 29.4, 29.3, 29.3, 26.1, 22.7 (each s, CH_2), 14.1 (s, CH_3), −2.7 (s, CH_3 of terminal $CH{=}CHSi(CH_3)_2Ar$).

All-Trans 1c. Yellowish green solid. ^1H NMR ($CDCl_3$): δ 7.98 (br s, $H^{2,6}$ of C_6H_3-3,5-$(CF_3)_2$ of terminal $CH{=}CHSi(CH_3)_2Ar$), 7.88 (br s, H^4 of C_6H_3-3,5-$(CF_3)_2$ of terminal $CH{=}CHSi(CH_3)_2Ar$), 7.70−7.50 (m, 8H, $H^{2,6,2',6'}$ and $H^{3,5,3',5'}$ of $C_{12}H_8$), 7.23−7.00 (m, 5H, $H^{2,4}$ and H^6 of C_6H_3 and 2 × CH=CH), 6.57 (d, J = 18.8 Hz, CH=CH of terminal $CH{=}CHSi(CH_3)_2Ar$), 4.07 (t, J = 6.4 Hz, OCH_2), 3.97 (t, J = 6.4 Hz, OCH_2 of terminal $C_6H_3IOC_8H_{17}$), 1.89−1.75 (br, 2H, CH_2), 1.56−1.25 (br, 10H, CH_2), 0.94−0.87 (br, 3H, CH_3), 0.53 (s, CH_3 of terminal $CH{=}CHSi(CH_3)_2Ar$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.9, 159.8 (each s, C^5 of C_6H_3 and C^3 of C_6H_3 of terminal $C_6H_3IOC_8H_{17}$), 139.7, 138.9, 136.3 (each s, $C^{1,1'}$ and $C^{4,4'}$ of $C_{12}H_8$ and $C^{1,5}$ of C_6H_3), 128.6 (br s, CH=CH), 127.0 (br s, $C^{2,6,2',6'}$ and $C^{3,5,3',5'}$ of C_8H_{12}), 118.1 (s, C^2 of C_6H_3), 111.7 (s, $C^{4,6}$ of C_6H_3), 94.7 (s, C^1 of C_6H_3 of terminal $C_6H_3IOC_8H_{17}$), 68.1 (s, OCH_2), 31.9, 29.4, 29.3, 26.2, 22.7 (each s, CH_2), 14.2 (s, CH_3), −2.7 (s, CH_3 of terminal $CH{=}CHSi(CH_3)_2Ar$).

Photoisomerization in Solution. A sample solution in benzene (4 mg L^{-1}) was prepared in a quartz cell. Nitrogen gas was bubbled through the solution at room temperature for 5 min. The sample was irradiated with a Xe lamp (λ_{max} = 365 nm, 0.87 mW cm^{-2}), and examined at intervals by UV−vis absorption spectroscopy.

Fluorescence and Quantum Yield Measurement. All emission studies were performed at room temperature in optically dilute benzene solutions with absorption maxima less than 0.1 to avoid the inner filter effect. The quantum yields were measured relative to anthracene in EtOH assuming a quantum yield of 0.27. A correction for refractive indices was applied.

Photoisomerization of PmPVs in Thin Films. A solution of PmPV in $CHCl_3$ (0.2 wt %) was passed through a syringe filter (DISMIC-13 JP, PTFE 0.50 μm, Hydrophobic; ADVANTEC). A thin film of PmPV was prepared by spin-coating on a quartz plate (1 cm^2); the filtrate (50 μL) was added dropwise on a plate, and the plate was accelerated to 1200 rpm for 2 s, kept at this rate for 10 s, and then rotated at 2000 rpm for 60 s. The film was dried under vacuum at room temperature for 30 min and analyzed by UV−vis absorption spectroscopy under a nitrogen atmosphere. The film was placed in a stainless-steel holder with a quartz window, and the system was evacuated by pumping. The sample was irradiated with a Xe lamp (λ_{max} = 365 nm, 21.0 mW cm^{-2}), and examined at intervals by UV−vis absorption spectroscopy. Finally, the film was rinsed twice in $CHCl_3$ (each 3 mL) with light shaking, dried under vacuum, and examined again by UV−vis absorption spectroscopy.

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. We are grateful to Prof. Norihiro Tokitoh, Institute for Chemical Research, Kyoto University, for the support of fluorescence measurements.

Supporting Information Available: Text giving experimental procedures and schemes showing the preparation of **2**−**5** and **7**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For reviews, see: (a) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 403–428. (b) Scherf, U. *Top. Curr. Chem.* **1999**, *201*, 163–222. (c) Akcelrud, L. *Prog. Polym. Sci.* **2003**, *28*, 875–962. (d) Segura, J. L.; Martin, N.; Guldi, D. M. *Chem. Soc. Rev.* **2005**, *34*, 31–47. (e) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491–1546. (f) Coropceanu, V.; Cornil, J.; Da Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Bredas, J.-L. *Chem. Rev.* **2007**, *107*, 926–952. (g) Samuel, I. D. W.; Turnbull, G. A. *Chem. Rev.* **2007**, *107*, 1272–1295. (h) Günes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324–1338. (i) Thomas, S. W., III; Joly, G. D.; Swager, T. M. *Chem. Rev.* **2007**, *107*, 1339–1386. (j) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897–1091.

(2) (a) Katayama, H.; Nagao, M.; Nishimura, T.; Matsui, Y.; Umeda, K.; Akamatsu, K.; Tsuruoka, T.; Nawafune, H.; Ozawa, F. *J. Am. Chem. Soc.* **2005**, *127*, 4350–4353. (b) Katayama, H.; Nagao, M.; Nishimura, T.; Matsui, Y.; Fukuse, Y.; Wakioka, M.; Ozawa, F. *Macromolecules* **2006**, *39*, 2039–2048. (c) Katayama, H.; Ozawa, F.; Matsumiya, Y.; Watanabe, H. *Polym. J.* **2006**, *38*, 184–189. (d) Wakioka, M.; Mutoh, Y.; Takita, R.; Ozawa, F. *Bull. Chem. Soc. Jpn.* **2009**, *82*, 1292–1298. (e) Mutoh, Y.; Yamamoto, Y.; Wakioka, M.; Takita, R.; Nakamura, J.; Iida, T.; Ozawa, F. *Bull. Chem. Soc. Jpn.* **2009**, *82*, 1533–1537.

(3) (a) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415–436. (b) Meier, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1399–1420. (c) Arai, T.; Tokumaru, K. *Chem. Rev.* **1993**, *93*, 23–39.

(4) (a) Katayama, H.; Nagao, M.; Ozawa, F.; Ikegami, M.; Arai, T. *J. Org. Chem.* **2006**, *71*, 2699–2705. (b) Ikegami, M.; Nagao, M.; Katayama, H.; Ozawa, F.; Arai, T. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1833–1835.

(5) (a) Wang, F.; He, F.; Xie, X. Q.; Li, Y. P.; Hanif, M.; Li, M.; Ma, Y. *Macromol. Chem. Phys.* **2008**, *209*, 1381–1388. (b) Moslin, R. M.; Espino, C. G.; Swager, T. M. *Macromolecules* **2009**, *42*, 452–454.

(6) (a) Doi, S.; Osada, T.; Tsuchida, Y.; Noguchi, T.; Ohnishi, T. *Synth. Met.* **1997**, *85*, 1281–1282. (b) Davey, A. P.; Drury, A.; Maier, S.; Byrne, H. J.; Blau, W. J. *Synth. Met.* **1999**, *103*, 2478–2479. (c) Ahn, T.; Jang, M. S.; Shim, H.-K.; Hwang, D.-H.; Zyung, T. *Macromolecules* **1999**, *32*, 3279–3285. (d) Pang, Y.; Li, J.; Hu, B.; Karasz, F. E. *Macromolecules* **1999**, *32*, 3946–3950. (e) Schlick, H.; Stelzer, F.; Tasch, S.; Leising, G. *J. Mol. Catal. A: Chem.* **2000**, *160*, 71–84.

(f) Schlick, H.; Stelzer, F.; Meghdadi, F.; Leising, G. *Synth. Met.* **2001**, *119*, 529–530. (g) Liao, L.; Pang, Y.; Ding, L.; Karasz, F. E. *Macromolecules* **2001**, *34*, 6756–6760. (h) Liao, L.; Pang, Y.; Ding, L.; Karasz, F. E. *Macromolecules* **2001**, *34*, 7300–7305. (i) Drury, A.; Maier, S.; Ruether, M.; Blau, W. J. *J. Mater. Chem.* **2003**, *13*, 485–490.

(7) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483. (b) Miyaura, N. In *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Chapter 2.

(8) Katayama, H.; Nagao, M.; Moriguchi, R.; Ozawa, F. *J. Organomet. Chem.* **2003**, *676*, 49–54.

(9) (a) Hatanaka, Y.; Hiyama, T. *Synlett* **1991**, 845–853. (b) Hiyama, T.; Hatanaka, Y. *Pure Appl. Chem.* **1994**, *66*, 1471–1478. (c) Hiyama, T. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Chapter 10. (d) Denmark, S. E.; Sweis, R. F. In *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Chapter 4.

(10) (a) Wakioka, M.; Nagao, M.; Ozawa, F. *Organometallics* **2008**, *27*, 602–608. (b) Wakioka, M.; Nakajima, Y.; Ozawa, F. *Organometallics* **2009**, *28*, 2527–2534.

(11) The upfield shifts observed for cis isomers are due to the shielding effects of arylene rings as previously reported.[2a,b]

(12) The small signal observed at 3.84−3.70 for all-cis **1a** ((a) in Figure 1A) was assigned to the OCH_2 protons of terminal $C_6H_4OC_8H_{17}$ group, formed by hydrolysis of benzeneboronic acid ester; the chemical shift was in accordance with that of (*Z*)-**2** (δ 3.77).

(13) The absorption intensity gradually decreased upon prolonged irradiation, probably due to the occurrence of side reactions such as [2 + 2] cycloaddition of vinylene groups: Meier, H.; Kretzschmann, H.; Lang, M.; Frass, W.; Albrecht, C.; Maerz, K. *J. Prakt. Chem.* **1994**, *336*, 297–302.

(14) Coulson, D. R. *Inorg. Synth.* **1971**, *13*, 121–124.

(15) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 220–221.

(16) Nagao, M.; Asano, K.; Umeda, K.; Katayama, H.; Ozawa, F. *J. Org. Chem.* **2005**, *70*, 10511–10514.