Articles

Stereocontrolled Synthesis and Characterization of *cis*-Poly(arylenevinylene)s

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ABSTRACT: A highly stereocontrolled synthesis of five kinds of *cis*-poly[(arylenevinylene)-*alt*-(2,5-dioctyloxy-1,4-phenylenevinylene)]s has been accomplished by Suzuki−Miyaura-type polycondensation [arylene = *p*-phenylene (**3af**), *m*-phenylene (**3bf**), 4,4′-biphenylene (**3cf**), 2,7-fluorenylene (**3df**), 9,9-dihexyl-2,7-fluorenylene (**3ef**)]. Reactions of (*Z*,*Z*)-bis(2-bromoethenyl)arenes (**1a**−**e**) with 2,5-dioctyloxybenzene-1,4-diboronic acid (**2fx**) in toluene in the presence of $Pd(PPh_3)_4$ catalyst, aqueous KOH base, and Bu_4NBr as a phase-transfer catalyst at 80 °C for 24 h form **3af**−**ef** with number-average molecular weight (M_n) of 5700−9500 in 77−99% yields. The stereoregularity of vinylene linkages in the polymer backbone has been found at least 95%. The starting monomers (**1a**−**e**) were prepared in almost geometrically pure forms (≥99% cis), either by ruthenium-catalyzed hydrosilylation of diethynylarenes followed by bromodesilylation of the resulting bis(2-bromoethenyl)arenes or by addition of bromine to arenediacrylic acids followed by debrominative decarboxylation promoted by Et_3N. MALDI-TOF-MS analysis of *cis*-**3af** has revealed the presence of two types of polymers having different end groups. Type I polymer bears (*Z*)-4-(2-bromoethenyl)phenyl and 2,5-dioctyloxyphenyl group at each end, whereas type II polymer has 2,5-dioctyloxyphenyl groups at both ends. Type I polymer is successfully converted to type II polymer by palladium-catalyzed reaction with 2,5-dioctyloxybenzeneboronic acid to obtain *cis*-poly[(*p*-phenylenevinylene)-*alt*-(2,5-dioctyloxy-1,4-phenylenevinylene)] in a single form.

Introduction

Organic molecules with extended π-electron systems have found wide application in optoelectronic devices including light-emitting diodes, photovoltaic cells, plastic lasers, and field-effect transistors.[1] In this context, synthetic design of π-conjugated polymers has attracted a great deal of recent interest.[2] It has been recognized that π-conjugated polymers are advantageous over small organic molecules as well as inorganic compounds in terms of accessibility and flexibility of thin films. This property is useful for fabricating large-area devices. We have recently found that poly(phenylenevinylene)s (PPVs) have a unique film-forming property when the vinylene units are highly regulated to cis geometry (>99%).[3] Thus, *cis*-PPVs form highly amorphous films by spin-coating, owing to their zigzag structures. Furthermore, the resulting PPV films are insolubilized under UV irradiation, along with cis−trans isomerization of vinylene units. On the basis of these findings, an extremely simple procedure for generating microscale patterns of PPVs on a quartz substrate has been developed. This paper reports full details of the preparation and characterization of *cis*-PPVs and related polymers (i.e., *cis*-poly(arylenevinylene)s: PAVs).[4−6]

It has been documented that physical properties of PAVs are strongly dependent on stereoregularity of vinylene units.[7−11] Son and Galvin et al. demonstrated that poly(*p*-phenylenevinylene) having *cis*- and *trans*-vinylenes in a moderate ratio exhibits higher electroluminescence efficiency than the conventional trans homologue.[7] It has been considered that the folded structures of *cis*-vinylene linkages interfere with the packing of the polymer chains to reduce the interchain fluorescence−quenching interactions. Similar phenomena have been observed for poly(*m*-phenylenevinylene)[8c] and poly(terphenylenevinylene)[9a] by Pang et al. and Cassano et al., respectively. The latter group also reported strong dependence of third-order nonlinear optics upon cis/trans ratio of poly(terphenylenevinylene)s.[9b]

PAVs have been prepared by several methods, e.g., thermolysis of sulfonium polymer precursors (Wessling route), dehydrohalogenative polycondensation of xylylene dihalides (Gilch route), Wittig−Horner-type polycondensation of xylylene diphosphonates with phthaldehydes, and palladium-catalyzed Heck-type polycondensation of divinylarenes with dihaloarenes. In all cases, trans isomers of PAVs are preferentially formed due to thermodynamic reasons. On the other hand, cis-selective routes to PAVs have remained almost unexplored. While Wittig-type polycondensation has been employed, the stereoregularity of resulting PAVs has been up to 70%.[8,10] In pursuit of a more stereocontrolled route, we examined transition-metal-catalyzed cross-coupling reactions of alkenyl halides because such reactions usually proceed with retention of the geometry around C=C bonds.[12] We herein describe that almost perfectly stereoregulated *cis*-PAVs (**3**) are synthesized by Suzuki−Miyaura-type polycondensation of (*Z*,*Z*)-bis(2-bromoethenyl)arenes (**1**) and arenediboronic acids (**2**) (Scheme 1).

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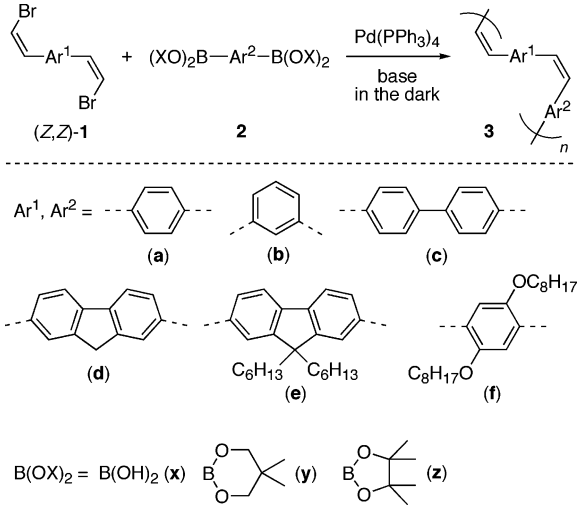
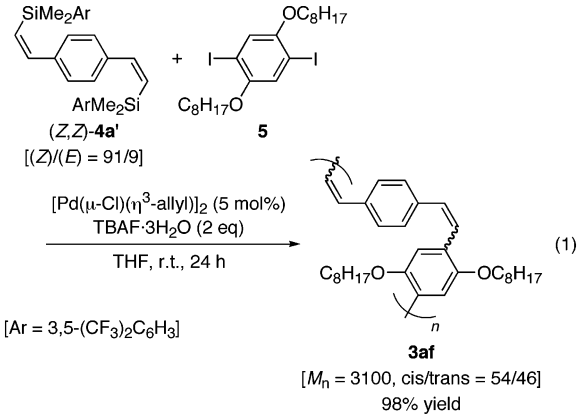
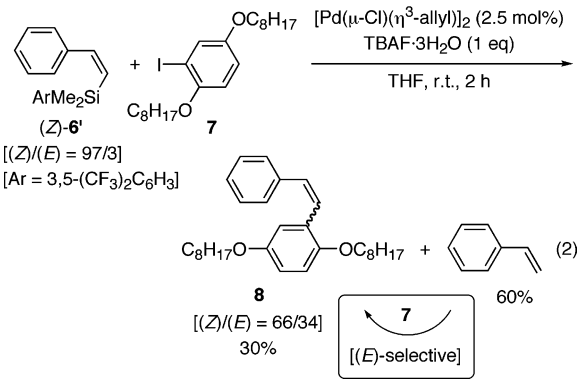
Scheme 1. Synthesis of *cis*-PAVs (3) by Suzuki−Miyaura-Type Polycondensation



Results and Discussion

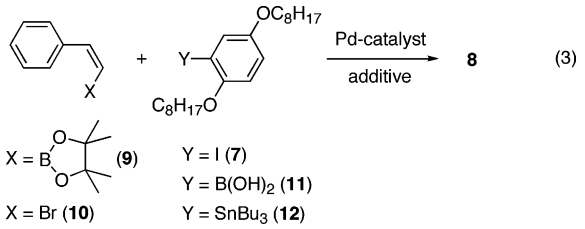
Examination of Cross-Coupling Systems. We previously examined the synthesis of *cis*-poly[(*p*-phenylenevinylene)-*alt*-(2,5-dioctyloxy-1,4-phenylenevinylene)] (**3af**) by Hiyama-type polycondensation of (*Z*,*Z*)-1,4-bis(2-silylethenyl)benzene (**4a′**) and 1,4-diiodo-2,5-dioctyloxybenzene (**5**) in THF in the presence of [Pd(μ-Cl)(η^3-allyl)]$_2$ as a catalyst and TBAF·3H$_2$O (TBAF = Bu$_4$NF) as an activator (eq 1).[13] However, cis−trans isomerization of C=C double bonds took place to a considerable extent, leading to **3af** with a low cis content (cis/trans = 54/46). We first examined the reason for this drop in stereoregularity using model reactions. It has been found that the trans isomer is formed by TBAF-induced desilylation of alkenylsilane followed by Mizoroki−Heck arylation of the resulting alkene (eq 2).





Reaction of (*Z*)-1-styrylsilane (**6′**) [(*Z*)/(*E*) = 97/3] with 2-iodo-1,4-dioctyloxybenzene (**7**) in THF in the presence of [Pd(μ-Cl)(η^3-allyl)]$_2$ (2.5 mol %) and TBAF·3H$_2$O (1 equiv) for 2 h at room temperature gave styrene in a 60% yield together with a mixture of (*Z*)- and (*E*)-2,5-dioctyloxystilbenes (**8**, total 30%). Treatment of styrene with **7** in the same catalytic system formed (*E*)-**8** selectively. This result is in marked contrast to the Hiyama-type cross-coupling of simple phenyl iodide with (*Z*)-**6′** to yield (*Z*)-stilbene exclusively.[14] Probably, the bulky octyloxy groups on **7** retard the transmetalation of (*Z*)-**6′** with an arylpalladium complex formed by oxidative addition of **7** to a palladium(0) species in the catalytic system. As a result, the TBAF-induced desilylation of (*Z*)-**6′** to give styrene preferentially takes place, although such substituents are necessary to perform polycondensation in a homogeneous system.

To find a more efficient catalytic system for stereoselective synthesis of (*Z*)-**8**, several combinations of cross-coupling reagents were examined (eq 3). Table 1 summarizes the results. (*Z*)-Styrylboronic acid ester **9** [(*Z*)/(*E*) = 90/10], prepared by rhodium-catalyzed hydroboration of phenylacetylene,[15] reacted with **7** under the standard Suzuki−Miyaura conditions to give **8** in a 87% yield. In this case, the (*Z*)-content of **9** was completely preserved in **8** (run 1). The product yield was further improved by switching the reaction mode from "alkenyl metal + aryl halide" to "alkenyl halide + aryl metal" (run 2). Thus, the treatment of (*Z*)-*β*-bromostyrene (**10**) with 2,5-dioctyloxybenzeneboronic acid (**11**) in toluene at 80 °C for 7 h in the presence of Pd(PPh$_3$)$_4$ (1.5 mol %) and aqueous KOH (3 equiv) afforded a quantitative yield of (*Z*)-**8** (run 2). The complex Pd(dba)$_2$ (dba = 1,5-diphenyl-3-pentadienone) also exhibited the catalytic activity in combination with phosphine or arsine ligands, while the product yield and selectivity were lowered (runs 3−8). In these runs, the formation of small amounts of 1,4-dioctyloxybenzene and 2,2′,5,5′-tetraoctyloxybiphenyl were observed. On the other hand, arylstannane **12** proved to be much less reactive than **11** (runs 9 and 10).



Synthesis of *cis*-PAVs. Taking the above information into consideration, *cis*-PAVs (**3**) were synthesized by Suzuki−Miyaura-type polycondensation using (*Z*,*Z*)-bis(2-bromoethenyl)arenes (**1**) and arenediboronic acids (**2**) as monomers (Scheme 1). Since the stereoregularity of PAVs is mainly dictated by geometrical purity of (*Z*,*Z*)-**1**, they were prepared in high selectivities by two synthetic routes shown in Scheme 2. Route (a) utilizes highly (*Z*)-selective hydrosilylation of terminal alkynes catalyzed by a diphosphinidenecyclobutene-coordinated ruthenium catalyst.[3] Treatment of the hydrosilylation products (*Z*,*Z*)-**4a**−**d** with NBS results in bromodesilylation in a stereospecific manner to give desired compounds (*Z*,*Z*)-**1a**−**d** in over 99% purities.[16] These products are fairly stable toward air, heat, and light. They can be stored without notable change under ambient conditions.

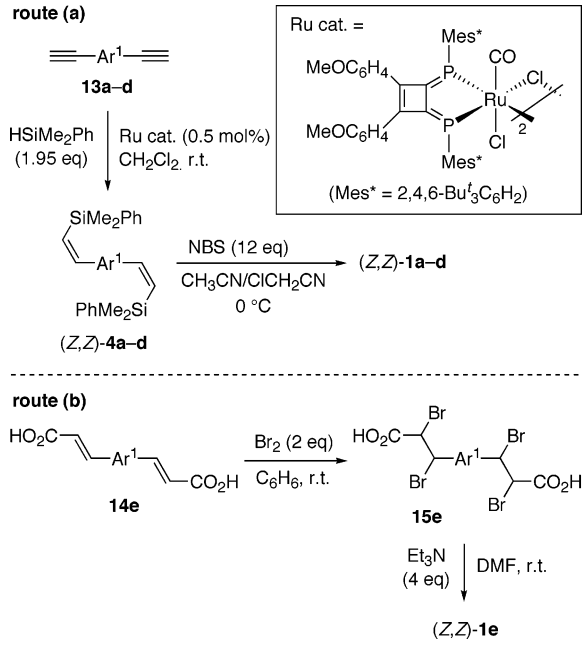
On the other hand, since the hydrosilylation in route (a) did not proceed well with a bulky substrate, (*Z*,*Z*)-**1e** was prepared by the other route (b).[17] Reaction of 9,9-dihexylfluorene-2,7-diacrylic acid (**14e**) with bromine in benzene gave bromine

Table 1. Cross-Coupling Reactions To Give Stilbene Derivative 8[a]

run	PhCH=CHX [(*Z*)/(*E*)]	ArY	catalyst	additive	time (h)	yield[b] (%)	(*Z*)/(*E*)[c]
1	**9** [90/10]	**7**	$Pd(PPh_3)_4$	aq K_3PO_4	6	87	90/10
2	**10** [>99/1]	**11**	$Pd(PPh_3)_4$	aq KOH	7	>99	>99/1
3	**10** [>99/1]	**11**	$Pd(dba)_2/4PPh_3$	aq KOH	4	96	96/4
4	**10** [>99/1]	**11**	$Pd(dba)_2/4P(o\text{-tol})_3$	aq KOH	6	68	89/11
5	**10** [>99/1]	**11**	$Pd(dba)_2/4P(2\text{-furyl})_3$	aq KOH	5	74	95/5
6	**10** [>99/1]	**11**	$Pd(dba)_2/4AsPh_3$	aq KOH	9	57	94/6
7	**10** [>99/1]	**11**	$Pd(dba)_2/PBu^t_3$	aq KOH	10	80	92/8
8	**10** [>99/1]	**11**	$Pd(dba)_2/P(\text{biphenyl})Cy_2$	aq KOH	7	59	93/7
9[d]	**10** [>99/1]	**12**	$Pd(PPh_3)_4$	none	48	0	
10[d]	**10** [>99/1]	**12**	$Pd_2(dba)_3/PBu^t_3$	none	48	45	*e*

[a] All reactions were run at 80 °C using PhCH=CHX (0.21 mmol), ArY (0.20 mmol), additive (0.60 mmol), and catalyst (1.5 mol %) in toluene (1.0 mL), unless otherwise noted. [b] Determined by GLC using 4,4′-dimethylbiphenyl as an internal standard. [c] Determined by ^{1}H NMR. [d] 1-Methyl-2-pyrrolidinone was used as a solvent. [e] Not determined.

Scheme 2. Synthetic Routes to (*Z*,*Z*)-Bis(2-bromoethenyl)arenes (1)



adduct **15e** in a quantitative yield, which was subsequently treated with Et_3N in DMF to give (*Z*,*Z*)-**1e** in 42% yield after purification with recycle GPC. Unlike (*Z*,*Z*)-**1a**−**d**, (*Z*,*Z*)-**1e** is very prone to undergo cis−trans isomerization even in the dark.

Next, polycondensation of (*Z*,*Z*)-**1a** with 2,5-dioctyloxybenzene-1,4-diboronic acid derivatives (**2fx**−**fz**) was examined under various reaction conditions (Table 2). A 1:1 mixture of (*Z*,*Z*)-**1a** and **2fx** was heated in toluene at 80 °C in the presence of $Pd(PPh_3)_4$ (1 mol %) and aqueous KOH (3 equiv) for 24 h. The orange fluorescent solution thus formed was washed with water and poured into a large quantity of MeOH to give a yellowish-orange solid of *cis*-**3af** in 95% yield [M_n = 2700, M_w/M_n = 1.79] (run 1).[18] ^{1}H and ^{13}C{^{1}H} NMR analysis revealed an all-cis arrangement (>99%) of vinylene units (vide infra). The polymer is readily soluble in THF, $CHCl_3$, CH_2Cl_2, and toluene, and the observed solubility is much higher than that of *trans*-**3af** with similar molecular weight.[13] All procedures were conducted in the dark to avoid cis−trans isomerization of the polymer.

Aqueous KOH or K_3PO_4 has been proven the bases of choice. Toluene and THF served as suitable solvents (runs 1, 2, and 6). On the other hand, the polymers prepared using other bases and solvents involved structural defects consisting of phenylene−phenylene linkages in the polymer backbone (runs 3, 4, 7, and 8). The polymerization proceeded under anhydrous conditions, while the molecular weight of polymer was somewhat lowered (run 9). The use of boronic acid esters (**2fy** and **2fz**) instead of boronic acid (**2fx**) gave comparable results (runs 10 and 11). The molecular weight was significantly increased by addition of Bu_4NBr as a phase-transfer agent to the system (run 12).

The polycondensation of the other (*Z*,*Z*)-dibromides (**1b**−**e**) with **2fx** were carried out under the optimized conditions using 1 mol % of $Pd(PPh_3)_4$, 3 equiv of aqueous KOH, and 1 equiv of Bu_4NBr in toluene at 80 °C for 24 h. Table 3 summarizes the results. Four kinds of *cis*-PAVs were prepared in over 95% stereoregularity as confirmed by NMR analysis (vide infra). Although no notable peaks assignable to *trans*-vinylene units were observed in all cases, the cis/trans values are shown at confidence levels based on S/N ratios of the NMR spectra.

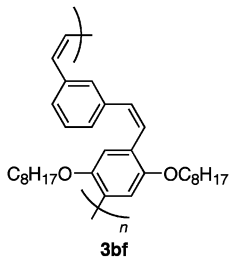
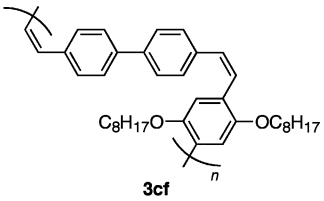
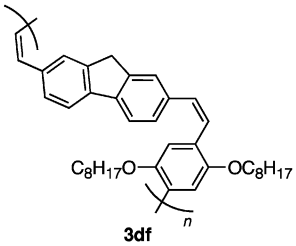
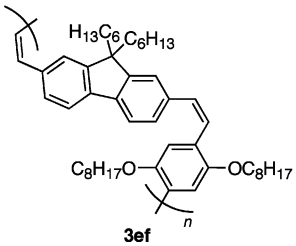
Preparation of **3af** was also examined with the other combination of monomers, (*Z*,*Z*)-**1f** and **2ax** (eq 4). Thus, the two octyloxy groups were introduced to dibromide instead of

Table 2. Palladium-Catalyzed Polycondensation of (*Z*,*Z*)-1a with 2f[a]

run	**2f**	base	solvent	additive	yield (%)[b]	M_n[c]	M_w/M_n[c]	cis/trans[d]
1	**2fx**	aq KOH	toluene	none	95	2700	1.79	>99/1
2	**2fx**	aq K_3PO_4	toluene	none	98	3800	2.48	>99/1
3	**2fx**	aq $NaHCO_3$	toluene	none	58[e]	2000	1.38	>99/1
4	**2fx**	aq Ag_2O	toluene	none	60[e]	1800	1.39	>99/1
5	**2fx**	aq $Ba(OH)_2$	toluene	none	0			
6	**2fx**	aq KOH	THF	none	99	2300	1.65	>99/1
7	**2fx**	aq KOH	DMF	none	71[e]	2600	2.48	>99/1
8	**2fx**	aq KOH	dioxane	none	94[e]	2600	1.61	>99/1
9	**2fx**	KOH	THF	none	97	1800	1.34	>99/1
10	**2fy**	aq KOH	toluene	none	99	2400	1.90	>99/1
11	**2fz**	aq KOH	toluene	none	97	2600	1.87	>99/1
12	**2fx**	aq KOH	toluene	Bu_4NBr	90	9100	3.72	99/1

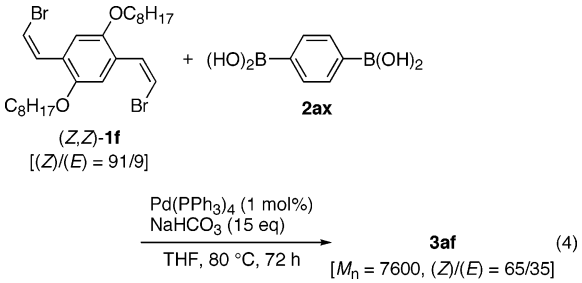
[a] All reactions were run at 80 °C for 24 h using (*Z*,*Z*)-**1a** [(*Z*)/(*E*) > 99/1] (0.20 mmol), **2f** (0.20 mmol), base (0.60 mmol), additive (0.20 mmol), $Pd(PPh_3)_4$ (1.0 mol %) in toluene (1.0 mL), unless otherwise noted. [b] Isolated yield of MeOH-insoluble polymer. [c] Determined by GPC calibration based on polystyrene standards. [d] Determined by ^{1}H NMR. [e] Polymer **3af** with structural defects was obtained.

Table 3. Synthesis of *cis*-PAVs[a]

run	**1** [(*Z*)/(*E*)]	product	yield (%)[b]	M_n[c]	M_w/M_n[c]	cis/trans[d]
1	(*Z*,*Z*)-**1b** [>99/1]	 **3bf**	84	6500	2.76	>99/1
2	(*Z*,*Z*)-**1c** [99/1]	 **3cf**	77	5700	1.92	>98/1
3	(*Z*,*Z*)-**1d** [>99/1]	 **3df**	78	7400	2.42	>97/3
4	(*Z*,*Z*)-**1e** [>99/1]	 **3ef**	>99	9500	2.28	>95/5

[a] All reactions were run at 80 °C for 24 h with (*Z*,*Z*)-**1** (0.20 mmol), **2fx** (0.20 mmol), KOH (0.60 mmol), Bu_4NBr (0.20 mmol), and $Pd(PPh_3)_4$ (1.0 mol %) in toluene (1.0 mL). [b] Yield of MeOH-insoluble polymer. [c] Determined by GPC calibration based on polystyrene standards. [d] Determined by ^1H NMR.

diboronic acid. However, the starting (*Z*,*Z*)-**1f** could be obtained in 91% (*Z*)-purity by route (b) in Scheme 2, and polycondensation of (*Z*,*Z*)-**1f** with **2ax** resulted in further drop in geometrical purity (65%).



Characterization of *cis*-PAVs. Stereoregularities of polymers were determined by NMR spectroscopy. Table 4 shows NMR data for *cis*- and *trans*-PAVs. Also listed are the data for model compounds, 1,4-dioctyloxy-2,5-distyrylbenzene (**16**) and 2,7-bis(2′,5′-dioctyloxystyryl)fluorene (**17**). It is seen that vinylic carbon signals appear at clearly different regions depending on the geometry of vinylene units. The *cis*-vinylene exhibits the carbon signals at around δ 130 and 125, whereas *trans*-vinylene carbons appear at δ 129 and 123. This tendency is irrespective of the sorts of arylene units. The other useful index of estimating the cis/trans ratio is provided by ^1H NMR spectroscopy. Thus, as already pointed out by Pang et al. for poly[(*m*-phenylenevinylene)-*alt*-(2,5-dialkoxy-1,4-phenylenevinylene)]s,[8c] the OCH_2 proton signals of the octyloxy groups appear at δ 3.62−3.47 and 4.10−3.99 for cis and trans isomers, respectively. The

Table 4. Selected NMR Data for *cis*- and *trans*-PAVs (3) and Model Compounds (16, 17)

	^{13}C NMR[a]		^1H NMR[a]	
compound	$\delta_{cis-C=C}$	$\delta_{trans-C=C}$	$\delta_{OCH_2(cis)}$	$\delta_{OCH_2(trans)}$
cis-**3af**	129.4, 125.2		3.54	
trans-**3af**		128.6, 123.5		4.08
(*Z*,*Z*)-**16**	129.9, 125.4		3.49	
(*Z*,*E*)-**16**	130.0, 125.4	128.7, 123.6	3.56	4.02
(*E*,*E*)-**16**		128.7, 123.5		4.01
cis-**3bf**	129.5, 125.2		3.51	
trans-**3bf**		128.8, 123.8		4.09
cis-**3cf**	129.5, 125.7		3.54	
cis-**3df**	130.1, 125.1		3.50	
trans-**3df**		*b*		4.10
cis-**3ef**	130.4, 125.3		3.47	
(*Z*,*Z*)-**17**	130.3, 125.3		3.62	
(*E*,*E*)-**17**		129.4, 123.0		3.99

[a] Measured in $CDCl_3$ at room temperature. [b] NMR analysis was infeasible due to low solubility.

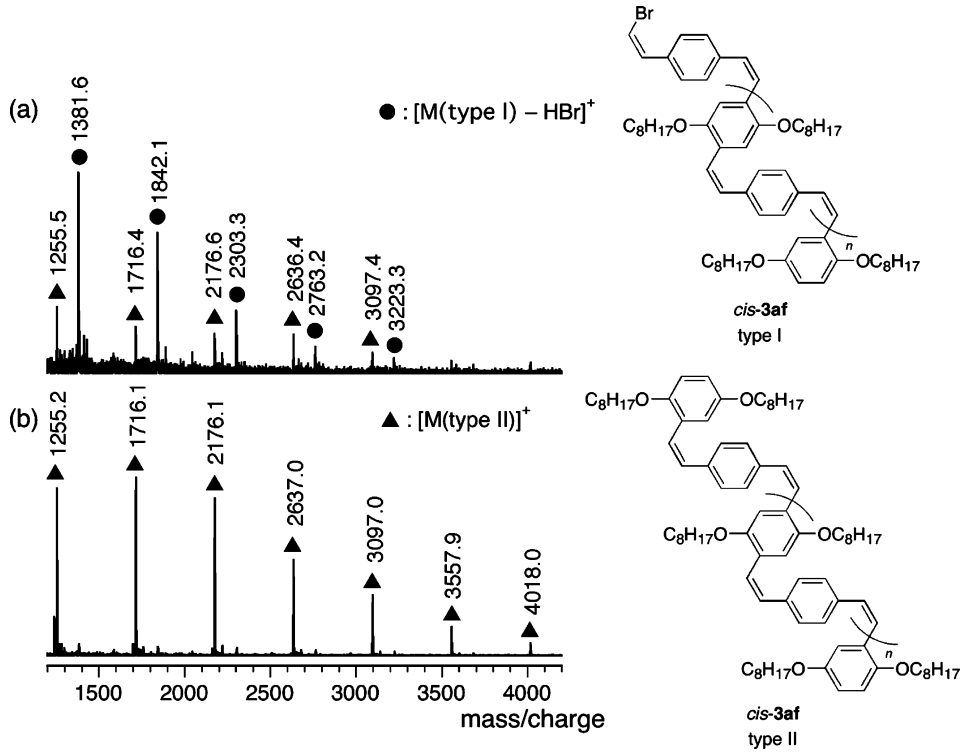
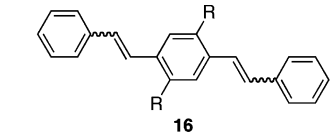


Figure 1. MALDI-TOF-MS spectra (linear mode) of *cis*-**3af** prepared by run 1 in Table 2. (a) After precipitation from MeOH. (b) After end-capping with **11**.

upfield shifts observed for cis isomers are due to magnetic shielding by ring current of arylene rings, which are located upon vinylic protons in the zigzag structures of *cis*-PAVs.



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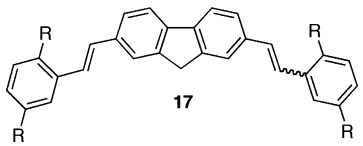


17

R = OC_8H_{17}

In the previous NMR investigations,[3] we found two types of terminal groups in *cis*-**3af**, i.e., (*Z*)-4-(2-bromoethenyl)phenyl and 2,5-dioctyloxyphenyl. The former group is derived from (*Z*,*Z*)-**1a**, whereas the latter group is formed by hydrolysis of a benzeneboronic acid moiety at the polymer end. In the present study, further details of the polymer structures have been examined by MALDI-TOF-MS spectrometry. Figure 1a shows the spectrum of *cis*-**3af**, which was isolated from the polycondensation system of run 1 in Table 2, simply by precipitation from MeOH. There are two series of peaks at regular intervals, as marked with filled circles and triangles, respectively. Judging from mass numbers of the peaks, the former series is assignable to the polymer bearing (*Z*)-4-(2-bromoethenyl)phenyl and 2,5-dioctyloxyphenyl group at each end (type I)[19] and the latter to the polymer having 2,5-dioctyloxyphenyl groups at both ends (type II). The peak interval is ca. 460 for both series, and this value is in agreement with the mass number of the repeating unit, $C_6H_2(OC_8H_{17})_2CH{=}CHC_6H_4CH{=}CH$.

The type I polymer has been found to be converted to type II polymer by the treatment with 2,5-dioctyloxybenzeneboronic acid (**11**) in the presence of a palladium catalyst. Thus, the polycondensation of (*Z*,*Z*)-**1a** and **2fx** was initially carried out under the reaction conditions of run 1 in Table 2. Then, **11** (2 equiv/**1a**) was added to the system, and the mixture was heated at 80 °C for additional 48 h. Figure 1b shows the MALDI-TOF-MS spectrum of the resulting polymer ($M_{n,GPC}$ = 2400, M_w/M_n = 1.24), isolated by precipitation from a large quantity of MeOH. The peaks of type I polymer almost disappeared and converged on the peaks of type II polymer.

Conclusions

We have described that *cis*-poly(arylenevinylene)s with five kinds of arylene units (**3af**−**ef**) are synthesized in over 95% stereoregularity by Suzuki−Miyaura-type polycondensation of (*Z*,*Z*)-bis(2-bromoethenyl)arenes (**1a**−**e**) with 2,5-dioctyloxybenzene-1,4-diboronic acid (**2fx**) in toluene in the presence of $Pd(PPh_3)_4$ as a catalyst and aqueous KOH as a base. The monomer combination, i.e., **1a**−**e** and **2fx**, is of particular importance to perform highly stereocontrolled synthesis of *cis*-PAVs. The number-average molecular weights reach 5700−9500 in the presence of Bu_4NBr as a phase-transfer catalyst. Since the trans isomers of PAVs are prepared by Hiyama-type polycondensation of (*E*,*E*)-bis(2-silylethenyl)arenes with 2,5-dioctyloxy-1,4-diiodobenzene,[13] it becomes feasible to synthesize both isomers of PAVs in almost geometrically pure forms using palladium-catalyzed polycondensations. Optical and electrical properties of those polymers will be reported in due course.

Experimental Section

General Considerations. All manipulations using organometallic compounds were carried out under a nitrogen atmosphere using conventional Schlenk techniques. Nitrogen gas was dried by passing through P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on a Varian Mercury 300 spectrometer. Chemical shifts are reported in δ (ppm), referenced to ^1H of residual protons and ^{13}C signals of the deuterated solvents. Analytical GPC was carried out on a

JASCO GPC assembly consisting of a model PU-980 pump, a model RI-1530 refractive index detector, and three GPC gel columns (Shodex KF-801, KF-803L, KF-805L). Polystyrene standards were used for calibration, and THF was used as the mobile phase with a flow rate of 1.0 mL/min. Recycling preparative GPC was carried out on a JAI LC918U equipped with two preparative GPC columns (JAIGEL-1H-A and -2H-A). Chloroform was used as the mobile phase with a flow rate of 3.8 mL/min. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on an Applied Biosystems Voyager-DE STR, operating at an accelerating potential of 20 kV in linear mode. Angiotensin I (human; MW = 1296.5) and insulin (bovine pancreas 28.3; MW = 5733.50) were used as internal standards to calibrate the mass scale. Samples for MALDI-TOF-MS analysis were prepared by mixing a polymer solution in THF (1 mg/mL) and a solution of the matrix [1,8-dihydroxy-9(10*H*)-anthracenone; dithranol] in THF (3 mg/mL). Then 1 μL portions of the mixture were deposited onto wells of the gold-coated sample plate and dried in air at room temperature.

Toluene and THF were dried over sodium benzophenone ketyl. Acetonitrile was dried over CaH_2. These solvents were distilled and stored over activated molecular sieves (MS4A or MS5A). The following compounds were synthesized according to the literature: (*Z*,*Z*)-bis(2-bromoethenyl)arenes **1a**−**d**,[16] 2,5-dioctyloxybenzene-1,4-diboronic acid (**2fx**),[20] 1,4-dioctyloxybenzene,[21] 2-bromo-1,4-dioctyloxybenzene,[22] 1,4-diiodo-2,5-dioctyloxybenzene (**5**),[23] (*Z*)- and (*E*)-2-[{dimethyl(3,5-bis(trifluoromethyl)phenyl)silyl}-ethenyl]benzene (**6′**),[14] 2-[(*Z*)-2-phenylethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**9**),[15] (*Z*)-β-bromostyrene (**10**),[17] 2,5-dioctyloxybenzeneboronic acid (**11**),[22] 2,7-diformyl-9,9-dihexylfluorene,[24] 2,7-diethynylfluorene,[25] tetrabutylammonium peroxydisulfate $[(Bu_4N)_2S_2O_8]$,[26] $[Pd(\mu\text{-Cl})(\eta^3\text{-allyl})]_2$,[27] $Pd(PPh_3)_4$,[28] $Pd(dba)_2$,[29] $Pd_2(dba)_3{\cdot}CHCl_3$,[29] and $RuHCl(CO)(PPh_3)_3$.[30] All other chemicals were obtained from commercial suppliers and used without further purification.

Synthesis of 2-Iodo-1,4-dioctyloxybenzene (7).[30] A solution of 1,4-dioctyloxybenzene (1.67 g, 4.99 mmol), iodine (2.53 g, 10.0 mmol), and $(Bu_4N)_2S_2O_8$ (6.77 g, 10.0 mmol) in acetonitrile (150 mL) was stirred at 50 °C for 8 h. The reaction mixture was poured into a 1.0 M aqueous Na_2SO_3 (150 mL) and extracted with ether. The organic layer was dried over $MgSO_4$. The drying agent was filtered off, and the filtrate was evaporated under reduced pressure to give a reddish-brown oil, which was subjected to flash column chromatography on silica gel eluted with hexane and then with hexane/CH_2Cl_2 (9/1). The colorless eluate thus obtained was evaporated to afford **7** as a colorless oil (1.08 g, 47% yield). The NMR data were identical with those reported.[22]

Hiyama-Type Cross-Coupling Reaction of (*Z*)-6′ with 7 (Eq 2). To a solution of (*Z*)-**6′** [(*Z*)/(*E*) = 97/3] (92.0 mg, 0.246 mmol) and **7** (111 mg, 0.241 mmol) in THF (2.2 mL) were successively added $[Pd(\mu\text{-Cl})(\eta^3\text{-allyl})]_2$ (2.3 mg, 6.3 μmol) and a 1.0 M solution of TBAF·3H$_2$O in THF (0.25 mL, 0.25 mmol). The mixture was stirred at room temperature for 24 h. GLC analysis of the resulting dark brown solution revealed the formation of a (*Z*)/(*E*)-mixture of **8** and styrene in 30% and 60% yields, respectively. The solution was evaporated by pumping, and the residue was purified by flash column chromatography on silica gel eluted with hexane/ethyl acetate (50/1). Evaporation of the eluate afforded **8** with (*Z*)/(*E*) content of 66/34 as a yellow oil (31.4 mg, 30% yield). The ^{1}H NMR data for the (*E*)-isomer in $CDCl_3$ are as follows: δ 7.53−7.51, 7.38−7.33, 7.26−7.22 (m, 5H, Ph), 7.46 (d, J = 16.5 Hz, 1H, ArC*H*═CHPh), 7.15 (d, J = 2.9 Hz, 1H, H^6 of C_6H_3), 7.11 (d, J = 16.5 Hz, 1H, ArCH═C*H*Ph), 6.83 (d, J = 9.0 Hz, 1H, H^3 of C_6H_3), 6.76 (dd, J = 9.0, 2.9 Hz, 1H, H^4 of C_6H_3), 3.96 (t, J = 6.4 Hz, 2H, OCH_2), 3.95 (d, J = 6.6 Hz, 2H, OCH_2), 1.87−1.73 (m, 4H, CH_2), 1.54−1.21 (m, 20H, CH_2), 0.88 (t, J = 6.4 Hz, 6H, CH_3).

Suzuki−Miyaura-Type Cross-Coupling Reaction of (*Z*)-10 with 11 (Run 2 in Table 1). To a solution of (*Z*)-**10** [(*Z*)/(*E*) > 99/1] (38.4 mg, 0.210 mmol) and **11** (75.7 mg, 0.200 mmol) in toluene (1.0 mL) were successively added $Pd(PPh_3)_4$ (3.5 mg, 3.0 μmol) and a 3.0 M aqueous KOH (0.20 mL, 0.60 mmol). The mixture was stirred at 80 °C for 7 h in the dark. The resulting pale yellow solution was concentrated to dryness to give a yellow oil, which was purified by flash column chromatography on silica gel eluted with hexane/CH_2Cl_2 (7/1). Evaporation of the eluate afforded (*Z*)-2,5-dioctyloxystilbene (**8**) with >99% geometrical purity as a yellow oil (86.9 mg, >99% yield). ^{1}H NMR ($CDCl_3$): δ 7.28−7.11 (m, 5H, Ph), 6.79 (dd, J = 7.1, 2.2 Hz, 1H, H^4 of C_6H_3), 6.73 (d, J = 2.2 Hz, 1H, H^6 of C_6H_3), 6.72 (d, J = 7.1 Hz, 1H, H^3 of C_6H_3), 6.69, 6.60 (each d, J = 12.4 Hz, 1H, CH═CH), 3.90 (t, J = 6.6 Hz, 2H, OCH_2), 3.60 (t, J = 6.6 Hz, 2H, OCH_2), 1.75−1.66 (m, 2H, CH_2), 1.63−1.54 (m, 2H, CH_2), 1.44−1.22 (m, 20H, CH_2), 0.88 (t, J = 6.4 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 152.4, 151.0 (each s, C^{2,5} of C_6H_3), 137.4 (s, *ipso*-C of Ph), 130.0 (s, CH═CH), 128.8, 128.0 (each s, *o*,*m*-C of Ph), 127.0 (s, C^1 of C_6H_3), 126.9 (s, *p*-C of Ph), 125.7 (s, CH═CH), 115.5, 115.3, 113.6 (each s, C^{3,4,6} of C_6H_3), 69.3, 68.4 (each s, OCH_2), 31.8, 29.4, 29.3, 29.2, 29.1, 26.1, 26.0, 22.7 (each s, CH_2), 14.1 (s, CH_3). Anal. Calcd for $C_{30}H_{44}O_2$: C, 82.52; H, 10.16. Found: C, 82.51; H, 10.16.

Synthesis of 2-Tributylstannyl-1,4-dioctyloxybenzene (12). To a solution of 2-bromo-1,4-dioctyloxybenzene (821 mg, 1.99 mmol) in THF (10 mL) was added dropwise a 2.6 M solution of *n*-BuLi in hexane (0.93 mL, 2.4 mmol) at −78 °C. The mixture was stirred at this temperature for 2 h. Tributyltin chloride (0.81 mL, 3.0 mmol) was added, and the solution was stirred at −78 °C for 1 h and then at room temperature for 17 h. The reaction mixture was diluted with ether and washed with water repeatedly. The organic layer was dried over $MgSO_4$ and filtered through a short column of alumina. Evaporation of the filtrate gave a colorless oil of **12**, which was further purified by recycle GPC (760 mg, 61% yield). ^{1}H NMR ($CDCl_3$): δ 6.92 (d, J = 2.9 Hz, $^3J_{SnH}$ = 46.5 Hz, 1H, H^3 of C_6H_3), 6.77 (dd, J = 8.8, 2.9 Hz, 1H, H^6 of C_6H_3), 6.69 (d, J = 8.8 Hz, 1H, H^5 of C_6H_3), 3.90 (t, J = 6.6 Hz, 2H, OCH_2), 3.84 (t, J = 6.4 Hz, 2H, OCH_2), 1.80−1.68 (m, 4H, CH_2), 1.58−1.22 (m, 32H, CH_2), 1.14−0.93 (m, 6H, $SnCH_2$), 0.93−0.84 (m, 15H, CH_3). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 157.5, 153.1 (each s, C^{1,4} of C_6H_3), 131.4 (s, C^2 of C_6H_3), 123.8 (s, $^2J_{SnC}$ = 25 Hz, C^3 of C_6H_3), 114.4 (s, C^5 of C_6H_3), 109.6 (s, $^3J_{SnC}$ = 25 Hz, C^6 of C_6H_3), 68.7, 68.1 (each s, OCH_2), 31.8, 31.8, 29.6, 29.5, 29.5, 29.4, 29.3, 29.3, 29.2, 29.0 (each s, CH_2), 27.4 (s, $^2J_{SnC}$ = 60 Hz, $SnCH_2CH_2$), 26.2, 26.1, 22.7 (each s, CH_2), 14.1, 13.7 (each s, CH_3), 9.9 (s, $^1J_{119_{SnC}}$ = 349 Hz, $^1J_{117_{SnC}}$ = 341 Hz, $SnCH_2$). Anal. Calcd for $C_{34}H_{64}O_2Sn$: C, 65.49; H, 10.34. Found: C, 65.47; H, 10.38.

Synthesis of (*Z*,*Z*)-2,7-Bis(2-bromoethenyl)-9,9-dihexylfluorene (1e). This compound was prepared by the following two-step procedure. A solution of 2,7-diformyl-9,9-dihexylfluorene (1.13 g, 2.89 mmol), malonic acid (697 mg, 6.70 mmol), and piperidine (541 mg, 6.36 mmol) in pyridine (10 mL) was stirred at 50 °C for 2 h and then at 120 °C for 3 h. The reaction mixture was cooled and acidified with a 5% aqueous HCl. A yellow solid of 9,9-dihexylfluorene-2,7-diacrylic acid (**14e**) thus precipitated was collected by filtration, washed with CH_2Cl_2, and dried under vacuum (891 mg, 65% yield); mp 248 °C. ^{1}H NMR (DMSO-d_6): δ 7.86 (d, J = 7.9 Hz, 2H, H^{4,5} of Fl^{Hex}), 7.84 (s, 2H, H^{1,8} of Fl^{Hex}), 7.65 (d, J = 7.9 Hz, 2H, H^{3,6} of Fl^{Hex}), 7.65 (d, J = 15.9 Hz, 2H, Fl^{Hex}C*H*═CHCO$_2$H), 6.62 (d, J = 15.9 Hz, 2H, Fl^{Hex}CH═C*H*CO$_2$H), 2.08−1.95 (br, 4H, CH_2), 1.08−0.86 (br, 12H, CH_2), 0.69 (t, J = 6.7 Hz, 6H, CH_3), 0.53−0.36 (br, 4H, CH_2). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 167.7 (s, CO_2H), 151.5 (s, Fl^{Hex}*C*H═CHCO$_2$H), 144.3, 142.0, 133.8, 128.0, 122.5, 120.7 (each s, Fl^{Hex}), 118.7 (s, Fl^{Hex}CH═*C*HCO$_2$H), 54.8 (s, C^9 of Fl^{Hex}), 40.1, 30.8, 28.9, 23.3, 21.9 (each s, CH_2), 13.8 (s, CH_3).

Bromine (0.24 mL, 4.7 mmol) was added dropwise to a solution of **14e** (701 mg, 1.48 mmol) in benzene (12 mL) at 0 °C. The reaction solution was stirred at room temperature for 8 h. Volatile materials were removed under reduced pressure to give the bromine adduct **15e** as a brown solid. To this solid were successively added DMF (5.6 mL) and triethylamine (0.86 mL, 6.2 mmol). The mixture was stirred at room temperature for 15 h and then extracted with ethyl acetate and water. The combined organic extract was dried over $MgSO_4$, filtered, and concentrated to dryness to give a brown oil, which was subjected to flash column chromatography on silica

gel eluted with hexane. The colorless eluate thus obtained was evaporated, giving **1e** with (*Z*)/(*E*) content of 95/5 as a pale yellow oil (593 mg, 74% yield). Further purification by recycle GPC afforded geometrically pure [(*Z*)/(*E*) > 99/1] (*Z*,*Z*)-**1e** as a colorless oil (338 mg, 42% yield). ^{1}H NMR ($CDCl_3$): δ 7.73 (s, 2H, $H^{1,8}$ of Fl^{Hex}), 7.69, 7.63 (each d, J = 7.9 Hz, H^{3-6} of Fl^{Hex}), 7.16 (d, J = 8.1 Hz, 2H, $Fl^{Hex}CH$═CHBr), 6.45 (d, J = 8.1 Hz, 2H, $Fl^{Hex}CH$═CHBr), 2.06−1.86 (br, 4H, CH_2), 1.20−0.90 (br, 12H, CH_2), 0.76 (t, J = 6.8 Hz, 6H, CH_3), 0.68 (br, 4H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 151.1, 140.8, 133.8 (each s, Fl^{Hex}), 132.8 (s, $Fl^{Hex}CH$═CHBr), 128.0, 123.5, 119.6 (each s, Fl^{Hex}), 105.7 (s, $Fl^{Hex}CH$═CHBr), 55.1 (s, C^9 of Fl^{Hex}), 40.2, 31.5, 29.7, 23.7, 22.6 (each s, CH_2), 14.0 (s, CH_3). Anal. Calcd for $C_{29}H_{36}Br_2$: C, 63.98; H, 6.67. Found: C, 63.90; H, 6.63.

Synthesis of 1,4-Bis(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-2,5-dioctyloxybenzene (2fy). A solution of **2fx** (425 mg, 1.01 mmol) and neopentyl glycol (422 mg, 4.05 mmol) in toluene (10 mL) was refluxed for 12 h with stirring. The solvent was removed under reduced pressure, and the residue was repeatedly recrystallized from hot hexane to give **2fy** as white crystals (339 mg, 60% yield); mp 34−36 °C. ^{1}H NMR ($CDCl_3$): δ 7.08 (s, 2H, C_6H_2), 3.93 (t, J = 6.4 Hz, 4H, OCH_2), 3.76 (s, 8H, $BOCH_2$), 1.79−1.69 (m, 4H, CH_2), 1.51−1.24 (m, 20H, CH_2), 1.04 (s, 12H, $C(CH_3)_2$), 0.88 (t, J = 7.0 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 157.2 (s, $C^{2,5}$ of C_6H_2), 119.4 (s, $C^{3,6}$ of C_6H_2), 72.4 (s, $BOCH_2$), 69.7 (s, OCH_2), 31.8, 31.7, 29.7, 29.5, 29.4, 26.1, 22.7 (each s, CH_2 and $C(CH_3)_2$), 21.9 (s, $C(CH_3)_2$), 14.1 (s, CH_3). Anal. Calcd for $C_{32}H_{56}B_2O_6$: C, 68.83; H, 10.11. Found: C, 68.80; H, 10.19.

Synthesis of 1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5-dioctyloxybenzene (2fz). This compound was synthesized similarly to **2fy**, starting from **2fx** (844 mg, 2.00 mmol) and pinacol (520 mg, 4.40 mmol). Recrystallization from hot hexane afforded white crystals of **2fz** (954 mg, 90% yield); mp 65 °C. ^{1}H NMR ($CDCl_3$): δ 7.08 (s, 2H, C_6H_2), 3.93 (t, J = 6.4 Hz, 4H, OCH_2), 1.79−1.7), 0 (m, 4H, CH_2), 1.56−1.24 (m, 20H, CH_2), 1.34 (s, 12H, $OC(CH_3)_2$), 0.88 (t, J = 6.8 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 157.6 (s, $C^{2,5}$ of C_6H_2), 119.8 (s, $C^{3,6}$ of C_6H_2), 83.4 (s, $OC(CH_3)_2$), 69.7 (s, OCH_2), 31.9, 29.7, 29.5, 29.4, 26.1 (each s, CH_2), 24.9 (s, $OC(CH_3)_2$), 22.7 (s, CH_2), 14.1 (s, CH_3). Anal. Calcd for $C_{34}H_{60}B_2O_6$: C, 69.63; H, 10.31. Found: C, 69.76; H, 10.38.

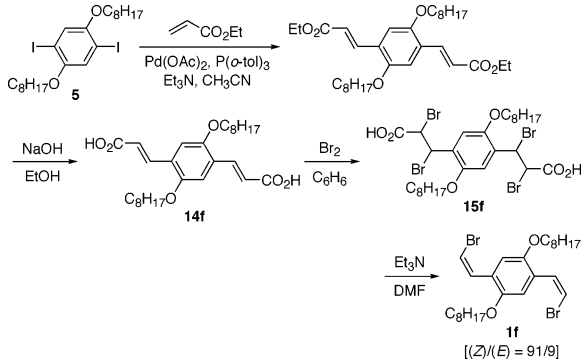
Polycondensation of (*Z*,*Z*)-1 and 2f. The experimental procedure and identification data for *cis*-**3af** and -**3bf** were already reported.[3] The data for the new arylenevinylene polymers are as follows.

***cis*-3cf.** ^{1}H NMR ($CDCl_3$): δ 7.75 (d, J = 8.2 Hz, C_6H_4 of terminal BrCH═CHC_6H_4), 7.57 (d, J = 8.2 Hz, C_6H_4 of terminal BrCH═CHC_6H_4), 7.45 (d, J = 8.2 Hz, C_6H_4), 7.36 (d, J = 8.2 Hz, C_6H_4), 7.08 (d, J = 8.1 Hz, BrCH═C*H* of terminal BrCH═CHC_6H_4), 6.79 (s, C_6H_2), 6.71 (d, J = 12.3 Hz, CH═CH), 6.61 (d, J = 12.3 Hz, CH═CH), 6.45 (d, J = 8.1 Hz, BrC*H*═CH of terminal BrCH═CHC_6H_4), 3.99 (t, J = 6.8 Hz, OCH_2 of terminal C_6H_3-$\{B(OH)_2\}(OC_8H_{17})_2$), 3.91 (t, J = 6.8 Hz, OCH_2 of terminal C_6H_4-$(OC_8H_{17})_2$), 3.65 (t, J = 6.8 Hz, OCH_2 of terminal $C_6H_3\{B(OH)_2\}$-$(OC_8H_{17})_2$), 3.59 (t, J = 6.8 Hz, OCH_2 of terminal $C_6H_4(OC_8H_{17})_2$), 3.54 (t, J = 6.6 Hz, OCH_2), 1.84−1.46 (m, CH_2), 1.26−1.12 (br, CH_2), 0.84 (t, J = 6.8 Hz, CH_3). $^{13}C\{^1H\}$ NMR: δ 150.2 (s, $C^{2,5}$ of C_6H_2), 139.1, 136.7 (each s, $C^{1,4}$ of C_6H_4), 131.8 (s, BrCH═*C*H of terminal BrCH═CHC_6H_4) 129.5, 129.4 (each s, C_6H_4 and CH═CH), 126.5, 126.5, 126.3, 126.2, 125.9, 125.7 (each s, $C^{1,4}$ of C_6H_2, C_6H_4, and CH═CH), 114.1 (s, $C^{3,6}$ of C_6H_2), 106.3 (s, Br*C*H═CH of terminal BrCH═CHC_6H_4), 68.9 (s, OCH_2), 31.8, 29.3, 29.2, 29.2, 26.0, 22.7 (each s, CH_2), 14.1 (s, CH_3).

***cis*-3df.** ^{1}H NMR ($CDCl_3$): δ 7.89, 7.70 (each s, Fl of terminal BrCH═CHFl), 7.65 (d, J = 7.9 Hz, Fl of terminal BrCH═CHFl), 7.58 (d, J = 8.1 Hz, $H^{4,5}$ of Fl), 7.48 (s, $H^{1,8}$ of Fl), 7.36 (d, J = 8.1 Hz, $H^{3,6}$ of Fl), 7.12 (d, J = 8.2 Hz, BrCH═C*H* of terminal BrCH═CHFl), 6.85−6.63 (m, CH═CH and C_6H_2), 6.42 (d, J = 8.2 Hz, BrC*H*═CH of terminal BrCH═CHFl), 3.95 (br, OCH_2 of terminal $C_6H_3\{B(OH)_2\}(OC_8H_{17})_2$), 3.84 (s, CH_2 of terminal Fl), 3.75 (s, CH_2 of Fl), 3.50 (t, J = 6.6 Hz, OCH_2), 1.83−1.36 (m, CH_2), 1.10 (br, CH_2), 0.85 (t, J = 6.8 Hz, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 150.2 (s, $C^{2,5}$ of C_6H_2), 143.5, 143.2, 141.7, 140.4, 140.1, 136.7, 136.2, 133.3, 132.5 (each s, Fl), 130.1 (s, CH═CH), 128.1, 127.8 (each s, Fl), 126.4 (s, $C^{1,4}$ of C_6H_2), 125.5, 125.4 (each s, Fl), 125.1 (s, CH═CH), 119.7, 119.5, 119.4 (each s, Fl), 114.1 (s, $C^{3,6}$ of C_6H_2), 105.6 (s, BrCH═CH of terminal BrCH═CHFl), 69.0 (s, OCH_2), 36.8 (s, CH_2 of Fl), 31.8, 29.2, 29.1, 25.9, 22.6 (each s, CH_2), 14.1 (s, CH_3).

***cis*-3ef.** ^{1}H NMR ($CDCl_3$): δ 7.70, 7.61 (each s, Fl^{Hex} of terminal BrCH═$CHFl^{Hex}$), 7.48 (d, J = 8.0 Hz, $H^{4,5}$ of Fl^{Hex}), 7.29 (d, J = 8.0 Hz, $H^{3,6}$ of Fl^{Hex}), 7.17 (s, $H^{1,8}$ of Fl^{Hex}), 6.79−6.61 (m, CH═CH and C_6H_2), 6.42 (d, J = 8.2 Hz, BrC*H*═CH of terminal BrCH═$CHFl^{Hex}$), 5.68 (s, $B(OH)_2$ of terminal $C_6H_3\{B(OH)_2\}(OC_8H_{17})_2$), 4.01, 3.53 (each t, J = 7.0 Hz, OCH_2 of terminal $C_6H_3\{B(OH)_2\}$-$(OC_8H_{17})_2$), 3.47 (t, J = 6.4 Hz, OCH_2), 2.00−0.95 (br m, CH_2), 0.84 (t, J = 6.6 Hz, CH_3 of OC_8H_{17}), 0.78 (t, J = 7.0 Hz, CH_3 of Hex), 0.61 (br, CH_2 of Hex). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 151.0, 150.7 (each s, $C^{2,5}$ of C_6H_2), 139.6, 136.4 (each s, Fl^{Hex}), 130.4 (s, CH═C), 127.6 (s, Fl^{Hex}), 126.2 (s, $C^{1,4}$ of C_6H_2), 125.3 (s, CH═CH), 123.5 (s, Fl^{Hex}), 119.1 (s, Fl^{Hex}), 114.0 (s, $C^{3,6}$ of C_6H_2), 68.6 (s, OCH_2), 54.7 (s, CH_2 of Hex), 40.2 (s, Fl^{Hex}), 31.8, 31.5, 29.8, 29.3, 29.2, 29.2, 25.9, 23.8, 22.8, 22.7 (each s, CH_2), 14.1, 14.1 (each s, CH_3).

Synthesis of (*Z*,*Z*)-1,4-Bis(2-bromoethenyl)-2,5-dioctyloxybenzene (1f). To a solution of **5** (10.1 g, 17.2 mmol), $Pd(OAc)_2$ (194 mg, 0.864 mmol), and tri(*o*-tolyl)phosphine (210 mg, 0.690 mmol) in acetonitrile (53 mL) were added ethyl acrylate (8.64 g, 86.3 mmol) and triethylamine (24 mL, 17 mmol). The mixture was stirred at 100 °C for 46 h. The resulting black suspension was cooled and extracted with CH_2Cl_2 and water. The combined organic extract was dried over $MgSO_4$, filtered, and evaporated. The residue was purified by flash column chromatography on silica gel eluted with hexane/CH_2Cl_2 (2/1) to give 2,5-dioctyloxybenzene-1,4-diacrylic acid diethyl ester as a yellow solid (8.26 g, 90% yield). ^{1}H NMR ($CDCl_3$): δ 7.95 (d, J = 16.1 Hz, 2H, ArC*H*═CHCO$_2$Et), 7.02 (s, 2H, C_6H_2), 6.53 (d, J = 16.1 Hz, 2H, ArCH═C*H*CO$_2$Et), 4.26 (q, J = 7.1 Hz, 4H, CH_2 of CO_2Et), 3.99 (t, J = 6.6 Hz, 4H, OCH_2), 1.88−1.79 (m, 4H, CH_2), 1.53−1.24 (m, 24H, CH_2), 1.34 (t, J = 7.1 Hz, 6H, CH_3 of CO_2Et), 0.89 (t, J = 6.6 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 167.2 (s, *C*O$_2$Et), 151.9 (s, $C^{2,5}$ of C_6H_2), 139.2 (s, Ar*C*H═CHCO$_2$Et), 126.1 (s, $C^{1,4}$ of C_6H_2), 119.6 (s, ArCH═*C*HCO$_2$Et), 112.1 (s, $C^{3,6}$ of C_6H_2), 69.2 (s, OCH_2), 60.4 (s, CH_2 of CO_2Et), 31.8, 29.3, 29.2, 29.2, 26.1, 22.6 (each s, CH_2), 14.3, 14.1 (each s, CH_3). Anal. Calcd for $C_{32}H_{50}O_6$: C, 72.42; H, 9.50. Found: C, 72.47; H, 9.46.

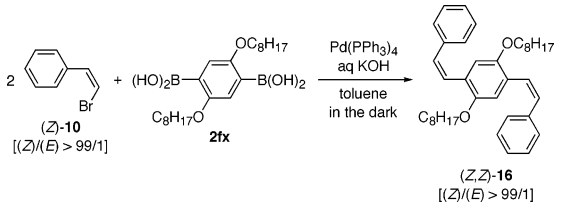


A mixture of 2,5-dioctyloxybenzene-1,4-diacrylic acid diethyl ester (8.26 g, 15.6 mmol), EtOH (156 mL), and a 1.3 M aqueous NaOH (48 mL, 62 mmol) was stirred at 100 °C for 1 h. The resulting yellow solution was cooled and extracted with THF/CH_2Cl_2 (1/1) and water. The combined organic extract was dried over $MgSO_4$, filtered, and evaporated. A yellow solid of 2,5-dioctyloxybenzene-1,4-diacrylic acid (**14f**) thus obtained was dried at 100 °C under vacuum overnight (7.33 g, 99% yield). ^{1}H NMR (DMSO-d_6): δ 7.79 (d, J = 16.1 Hz, 2H, ArC*H*═CHCO$_2$H), 7.35 (s, 2H, C_6H_2), 6.67 (d, J = 16.1 Hz, 2H, ArCH═C*H*CO$_2$H), 4.05 (t, J = 6.4 Hz, 4H, OCH_2), 1.77−1.68 (m, 4H, CH_2), 1.47−1.16 (m, 24H, CH_2), 0.84 (t, J = 7.0 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ

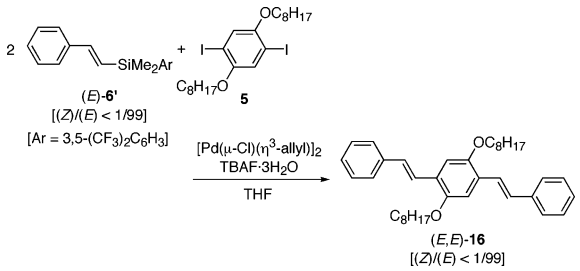
167.9 (s, CO_2H), 151.3 (s, $C^{2,5}$ of C_6H_2), 138.0 (s, Ar*C*H=CHCO$_2$H), 125.5 (s, $C^{1,4}$ of C_6H_2), 120.6 (s, ArCH = *C*HCO$_2$Et), 112.3 (s, $C^{3,6}$ of C_6H_2), 68.7 (s, OCH_2), 31.2, 28.7, 28.7, 25.6, 22.1 (each s, CH_2), 14.0 (s, CH_3). Anal. Calcd for $C_{28}H_{42}O_6$: C, 70.86; H, 8.92. Found: C, 70.60; H, 8.92.

Bromine (5.2 mL, 0.10 mol) was added dropwise to a solution of **14f** (7.27 g, 15.3 mmol) in benzene (76 mL) at 0 °C. The reaction solution was stirred at 50 °C for 18 h. The mixture was further treated with additional bromine (2.7 mL, 53 mmol) at 60 °C for 5 h. Volatile materials were removed under reduced pressure to give the bromine adduct **15f** as a brown solid. This solid was dissolved in DMF (50 mL), and triethylamine (3.7 mL, 27 mmol) was added. The mixture was stirred at room temperature for 2.5 h and then extracted with ether and water. The combined organic extract was dried over $MgSO_4$, filtered, and concentrated to dryness. The residue was purified by flash column chromatography on silica gel eluted with hexane, followed by recrystallization from hot hexane. Compound **1f** with (*Z*,*Z*)-content of 91% was obtained as yellow crystals (6.10 g, 73% yield); mp 50 °C. ^{1}H NMR ($CDCl_3$): δ 7.60 (s, 2H, C_6H_2), 7.33 (d, J = 8.1 Hz, 2H, (*Z*)-ArC*H*=CHBr), 6.99 (d, J = 13.9 Hz, 0.09H, (*E*)-ArCH=C*H*Br), (s, 0.09H, C_6H_2 of (*Z*,*E*)-isomer), 6.45 (d, J = 8.1 Hz, 2H, (*Z*)-ArCH=C*H*Br), 3.97 (t, J = 6.6 Hz, 4H, OCH_2), 3.92 (t, J = 7.0 Hz, 0.18H, OCH_2 of (*Z*,*E*)-isomer), 1.83−1.74 (m, 4H, CH_2), 1.50−1.20 (m, 24H, CH_2), 0.89 (t, J = 7.0 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 149.8 (s, $C^{2,5}$ of C_6H_2), 127.3 (s, Ar*C*H=CHBr), 124.5 (s, $C^{1,4}$ of C_6H_2), 112.8 (s, $C^{3,6}$ of C_6H_2), 106.8 (s, ArCH=*C*HBr), 69.2 (s, OCH_2), 31.8, 29.3, 29.2, 26.1, 22.7 (each s, CH_2), 14.1 (s, CH_3). Anal. Calcd for $C_{26}H_{40}Br_2O_2$: C, 57.36; H, 7.41. Found: C, 57.28; H, 7.34.

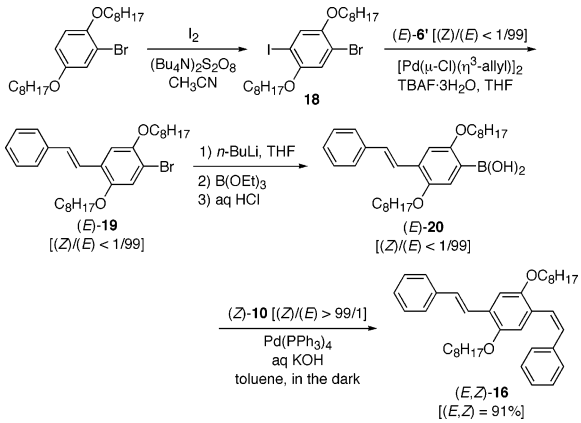
Synthesis of (*Z*,*Z*)-1,4-Dioctyloxy-2,5-distyrylbenzene (16). To a suspension of (*Z*)-**10** (276 mg, 1.51 mmol) and **2fx** (309 mg, 0.711 mmol) in toluene (3.6 mL) were successively added a 3.0 M aqueous KOH (0.71 mL, 2.1 mmol) and $Pd(PPh_3)_4$ (8.2 mg, 7.0 μmol). The mixture was stirred at 80 °C for 45 h in the dark. The resulting pale yellow solution was cooled and extracted with ether and water. The combined organic extract was dried over $MgSO_4$, filtered, and evaporated. The residual solid was purified by flash column chromatography on silica gel eluted with hexane/CH_2Cl_2 (4/1) to give (*Z*,*Z*)-**16** [(*Z*)/(*E*) > 99/1] as a yellow solid (167 mg, 90% yield); mp 52 °C. ^{1}H NMR ($CDCl_3$): δ 7.36−7.13 (m, 10H, Ph), 6.70 (s, 2H, C_6H_2), 6.69, 6.60 (each d, J = 12.1 Hz, 2H, CH=CH), 3.49 (t, J = 6.6 Hz, 4H, OCH_2), 1.58−1.48 (m, 4H, CH_2), 1.35−1.15 (br m, 20H, CH_2), 0.89 (t, J = 6.4 Hz, 6H, CH_3). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 150.1 (s, $C^{1,4}$ of C_6H_2), 137.7 (s, *ipso*-C of Ph), 129.9 (s, CH=CH), 128.9, 128.1 (each s, *o*,*m*-C of Ph), 126.9 (s, *p*-C of Ph), 126.0 (s, $C^{2,5}$ of C_6H_2), 125.4 (s, CH=CH), 114.0 (s, $C^{3,6}$ of C_6H_2), 68.8 (s, OCH_2), 31.8, 29.2, 29.1, 25.9, 22.7 (each s, CH_2), 14.1 (s, CH_3). Anal. Calcd for $C_{38}H_{50}O_2$: C, 84.71; H, 9.35. Found: C, 84.74; H, 9.29.



Synthesis of (*E*,*E*)-16. To a solution of (*E*)-**6′** [(*Z*)/(*E*) < 1/99] (123 mg, 0.328 mmol) and **5** (87 mg, 0.15 mmol) in THF (1.2 mL) were successively added [Pd(μ-Cl)(η^3-allyl)]$_2$ (2.8 mg, 7.6 μmol) and a 1.0 M solution of TBAF·3H$_2$O in THF (0.33 mL, 0.33 mmol). The mixture was stirred at room temperature for 24 h and then evaporated by pumping. The oily residue was subjected to flash column chromatography on silica gel eluted with hexane/CH_2Cl_2 (7/1) to give (*E*,*E*)-**16** [(*Z*)/(*E*) < 1/99] as a colorless oil (66 mg, 82% yield). ^{1}H NMR ($CDCl_3$): δ 7.55 (d, J = 7.3 Hz, 4H, *o*-H of Ph), 7.50 (d, J = 16.5 Hz, 2H, CH=CH), 7.37 (t, J = 7.3 Hz, 4H, *m*-H of Ph), 7.28−7.24 (m, 2H, *p*-H of Ph), 7.15 (d, J = 16.5 Hz, 2H, CH=CH), 7.14 (s, 2H, C_6H_2), 4.07 (t, J = 6.6 Hz, 4H, OCH_2), 1.93−1.84 (m, 4H, CH_2), 1.61−1.25 (m, 20H, CH_2), 0.90 (t, J = 6.8 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.1 (s, $C^{1,4}$ of C_6H_2), 137.9 (s, *ipso*-C of Ph), 128.7 (s, CH=CH), 128.6 (s, *m*-C of Ph), 127.4 (s, *p*-C of Ph), 126.9 (s, $C^{2,5}$ of C_6H_2), 126.5 (s, *o*-C of Ph), 123.5 (s, CH=CH), 110.7 (s, $C^{3,6}$ of C_6H_2), 69.6 (s, OCH_2), 31.8, 29.5, 29.4, 29.3, 26.3, 22.7 (each s, CH_2), 14.1 (s, CH_3). Anal. Calcd for $C_{38}H_{50}O_2$: C, 84.71; H, 9.35. Found: C, 84.72; H, 9.30.



Synthesis of (*E*,*Z*)-16. A solution of 2-bromo-1,4-dioctyloxybenzene (207 mg, 0.501 mmol), iodine (254 mg, 1.00 mmol), and $(Bu_4N)_2S_2O_8$ (678 mg, 1.00 mmol) in acetonitrile (5 mL) was stirred at 50 °C for 12 h. The reaction mixture was poured into a 1.0 M aqueous Na_2SO_3 (10 mL) and extracted with ether. The organic layer was dried over $MgSO_4$. The drying agent was filtered off, and the filtrate was evaporated under reduced pressure to give a yellow oil, which was subjected to flash column chromatography on silica gel eluted with hexane and then with hexane/CH_2Cl_2 (50/1). The colorless eluate thus obtained was evaporated to afford 1-bromo-4-iodo-2,5-dioctyloxybenzene (**18**) as a pale yellow solid (200 mg, 74% yield). The NMR data were identical with those reported.[20]



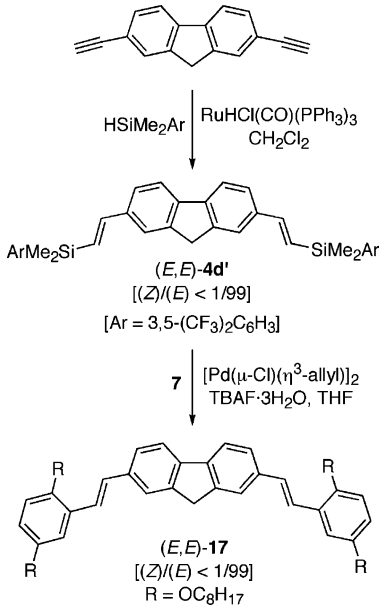
To a solution of **18** (591 mg, 1.10 mmol) and (*E*)-**6′** [(*Z*)/(*E*) < 1/99] (432 mg, 1.16 mmol) in THF (4.3 mL) were successively added [Pd(μ-Cl)(η^3-allyl)]$_2$ (20.1 mg, 54.9 μmol) and a 1.0 M solution of TBAF·3H$_2$O in THF (1.2 mL, 1.2 mmol). The mixture was stirred at room temperature for 24 h and then evaporated by pumping. The residue was purified by flash column chromatography on silica gel eluted with hexane/CH_2Cl_2 (8/1) to give (*E*)-1-bromo-4-styryl-2,5-dioctyloxybenzene (**19**) [(*Z*)/(*E*) < 1/99] as a colorless oil (422 mg, 74% yield). ^{1}H NMR ($CDCl_3$): δ 7.56−7.50 (m, 2H, Ph), 7.39 (d, J = 16.7 Hz, 1H, ArC*H*=CHPh), 7.38−7.33 (m, 2H, Ph), 7.29−7.24 (m, 1H, Ph), 7.13 (s, 1H, C_6H_2), 7.10 (d, J = 16.7 Hz, 1H, ArCH=C*H*Ph), 7.08 (s, 1H, C_6H_2), 4.03 (t, J = 6.5 Hz, 2H, OCH_2), 3.96 (t, J = 6.4 Hz, 2H, OCH_2), 1.89−1.78 (m, 4H, CH_2), 1.59−1.25 (m, 20H, CH_2), 0.91−0.83 (m, 6H, CH_3). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 151.0 (s, C^2 of C_6H_2), 149.7 (s, C^5 of C_6H_2), 137.6 (s, *ipso*-C of Ph), 129.3 (s, CH=CH), 128.6 (s, *m*-C of Ph), 127.5 (s, *p*-C of Ph), 126.5 (s, *o*-C of Ph), 123.0 (s, CH=CH), 117.7 (s, C^6 of C_6H_2), 111.8 (s, C^1 of C_6H_2), 111.6 (s, C^3 of C_6H_2), 70.2, 69.5 (each s, OCH_2), 31.8, 31.8, 29.3, 29.3, 26.2, 26.0, 22.7 (each s, CH_2), 14.1, 14.1 (each s, CH_3). Anal. Calcd for $C_{30}H_{43}BrO_2$: C, 69.89; H, 8.41. Found: C, 69.85; H, 8.42.

To a solution of (*E*)-**19** (108 mg, 0.209 mmol) in THF (1.2 mL) was added dropwise a 1.6 M solution of *n*-BuLi in hexane (0.15 mL, 0.24 mmol) at −78 °C. After the mixture was stirred at this temperature for 30 min, triethyl borate (0.11 mL, 0.65 mmol) was slowly added. The reaction solution was stirred at −78 °C for 2 h and then at room temperature for 17 h. A 1.0 M aqueous HCl (ca. 2 mL) was added, and the resulting mixture was extracted with ether, dried over $MgSO_4$, and filtered. Evaporation of the filtrate gave a yellow oil, which was subjected to flash column chromatography on silica gel eluted with CH_2Cl_2 and then CH_2Cl_2/ethyl acetate (6/1). The colorless eluate thus obtained was evaporated to give (*E*)-4-styryl-2,5-dioctyloxybenzene-1-boronic acid (**20**) [(*Z*)/(*E*) < 1/99] as a white solid (70.1 mg, 70% yield). ^{1}H NMR ($CDCl_3$): δ 7.56−7.52 (m, 2H, Ph), 7.49 (d, J = 16.5 Hz, 1H, ArC*H*=CHPh), 7.39−7.34 (m, 2H, Ph), 7.35 (s, 1H, C_6H_2), 7.30−7.24 (m, 1H, Ph), 7.17 (d, J = 16.5 Hz, 1H, ArCH=C*H*Ph), 7.11 (s, 1H, C_6H_2), 5.79 (br s, 2H, $B(OH)_2$), 4.11, 4.04 (each t, J = 6.6 Hz, 2H, OCH_2), 1.91−1.79 (m, 4H, CH_2), 1.60−1.24 (m, 20H, CH_2), 0.91−0.85 (m, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 158.3 (s, C^2 of C_6H_2), 150.9 (s, C^5 of C_6H_2), 137.6 (s, *ipso*-C of Ph), 130.4 (s, C^4 of C_6H_2), 130.1 (s, CH=CH), 128.7 (s, *m*-C of Ph), 127.7 (s, *p*-C of Ph), 126.6 (s, *o*-C of Ph), 123.5 (s, CH=CH), 120.1 (s, C^6 of C_6H_2), 108.7 (s, C^3 of C_6H_2), 70.2, 69.5 (each s, OCH_2), 31.8, 31.8, 29.3, 29.3, 26.2, 26.0, 22.7 (each s, CH_2), 14.1, 14.1 (each s, CH_3). The ^{13}C signal of C^1 of the C_6H_2 group was obscure due to coupling with quadrupolar ^{11}B nucleus. Anal. Calcd for $C_{30}H_{43}BrO_2$: C, 74.99; H, 9.44. Found: C, 75.06; H, 9.57.

To a solution of (*E*)-**20** (32.0 mg, 66.6 μmol) and (*Z*)-**10** [(*Z*)/(*E*) > 99/1] (12.8 mg, 70.0 mmol) in toluene were successively added $Pd(PPh_3)_4$ (0.80 mg, 0.69 μmol) and a 3.0 M aqueous KOH (67 μL, 0.20 mmol). The mixture was stirred at 80 °C for 9 h in the dark. Volatile materials were thoroughly removed by pumping. ^{1}H and ^{13}C{^{1}H} NMR analysis of the residue revealed the formation of (*E*,*Z*)-**16** [(*E*,*Z*) = 91%] in 91% yield, while its isolation by silica gel column chromatography was unsuccessful due to rapid *Z*−*E* isomerization. The NMR data for (*E*,*Z*)-**16** are as follows. ^{1}H NMR ($CDCl_3$): δ 7.55−7.50 (m, 2H, Ph of (*E*)-PhCH=CH), 7.50 (d, J = 15.9 Hz, 1H, (*E*)-CH=CH), 7.45−7.18 (m, 9H, Ph and C_6H_2), 7.13 (d, J = 15.9 Hz, 1H, (*E*)-CH=CH), 6.77 (d, J = 12.3 Hz, 1H, (*Z*)-CH=CH), 6.75 (s, 1H, C_6H_2), 6.65 (d, J = 12.3 Hz, 1H, (*Z*)-CH=CH), 4.02 (t, J = 6.4 Hz, 2H, OCH_2), 3.56 (t, J = 6.6 Hz, 2H, OCH_2), 1.84−1.75 (m, 2H, CH_2), 1.69−1.60 (m, 2H, CH_2), 1.54−1.20 (m, 20H, CH_2), 0.93−0.88 (m, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.1, 150.1 (each s, $C^{1,4}$ of C_6H_2), 138.0, 137.6 (each s, *ipso*-C of Ph), 130.0 (s, (*Z*)−CH=CH), 128.9 (s, Ph of (*Z*)-PhCH=CH), 128.7 (s, (*E*)-CH=CH), 128.6 (s, Ph of (*E*)-PhCH=CH), 128.1 (s, Ph of (*Z*)-PhCH=CH), 127.3 (s, Ph of (*E*)-PhCH=CH), 126.9 (s, $C^{2,5}$ of C_6H_2), 126.5 (s, Ph of (*E*)-PhCH=CH), 126.4 (s, $C^{2,5}$ of C_6H_2), 125.4 (s, (*Z*)-CH=CH), 123.6 (s, (*E*)−CH=CH), 114.6, 110.2 (each s, $C^{3,6}$ of C_6H_2), 69.3, 68.9 (each s, OCH_2), 31.8, 31.8, 29.5, 29.4, 29.3, 29.2, 26.1, 26.1, 22.7 (each s, CH_2), 14.1 (s, CH_3).

Synthesis of (*Z*,*Z*)-2,7-Bis(2′,5′-dioctyloxystyryl)fluorene (17). This compound was synthesized like (*Z*,*Z*)-**16**, starting from (*Z*,*Z*)-**1d** [(*Z*)/(*E*) > 99/1] (66.6 mg, 0.177 mmol), **11** (167 mg, 0.443 mmol), $Pd(PPh_3)_4$ (10.2 mg, 8.85 μmol), aqueous KOH (3.0 M, 0.44 mL, 1.3 mmol), and toluene (1.8 mL). The crude product was purified by column chromatography on silica gel eluted with hexane/CH_2Cl_2 (3/1) to give (*Z*,*Z*)-**17** [(*Z*)/(*E*) = 99/1] as a pale yellow solid (136 mg, 87%); mp 45 °C. ^{1}H NMR ($CDCl_3$): δ 7.55 (d, J = 8.0 Hz, 2H, $H^{4,5}$ of Fl), 7.42 (s, 2H, $H^{1,8}$ of Fl), 7.29 (d, J = 8.0 Hz, 2H, $H^{3,6}$ of Fl), 6.82 (d, J = 11.9 Hz, 2H, CH=CH), 6.82 (d, J = 9.0 Hz, 2H, $H^{3'}$ of C_6H_3), 6.74 (dd, J = 9.0, 2.9 Hz, 2H, $H^{4'}$ of C_6H_3), 6.67 (d, J = 2.9 Hz, 2H, $H^{6'}$ of C_6H_3), 6.64 (d, J = 11.9 Hz, 2H, CH=CH), 3.92 (d, J = 6.4 Hz, 4H, OCH_2), 3.70 (s, 2H, CH_2 of Fl), 3.62 (t, J = 6.4 Hz, 4H, OCH_2), 1.76−1.66 (m, 4H, CH_2), 1.58−1.50 (m, 4H, CH_2), 1.45−1.12 (m, 40H, CH_2), 0.88 (t, J = 6.0 Hz, 6H, CH_3), 0.86 (t, J = 7.0 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 152.6, 151.0 (each s, $C^{2',5'}$ of C_6H_3), 143.2, 140.4, 135.9 (each s, Fl), 130.3 (s, CH=CH), 127.8 (s, Fl), 127.4 (s, $C^{1'}$ of C_6H_3), 125.4 (each s, Fl), 125.3 (s, CH=CH), 119.3 (s, Fl), 115.6, 115.3, 113.6 (each s, $C^{3',4',6'}$ of C_6H_3), 69.3, 68.6 (each s, OCH_2), 36.7 (s, CH_2 of Fl), 31.8, 31.8, 29.4, 29.4, 29.2, 29.2, 29.1, 26.1, 25.9, 22.6 (each s, CH_2), 14.1 (s, CH_3). Anal. Calcd for $C_{61}H_{86}O_4$: C, 82.94; H, 9.81. Found: C, 82.85; H, 10.00.

Synthesis of (*E*,*E*)-17. 2,7-Diethynylfluorene (107 mg, 0.499 mmol) and $RuHCl(CO)(PPh_3)_3$ (47 mg, 49 μmol) were dissolved in CH_2Cl_2 (1.8 mL). Dimethyl{3,5-bis(trifluoromethyl)phenyl}silane (900 mg, 3.31 mmol) was added, and the mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel eluted with hexane/CH_2Cl_2 (4/1) to give (*E*,*E*)-2,7-bis[2-{dimethyl(3,5-bis(trifluoromethyl)phenyl)silyl}ethenyl]-fluorene (**4d′**) [(*Z*)/(*E*) < 1/99] as a pale yellow solid (305 mg, 80%). ^{1}H NMR ($CDCl_3$): δ 7.97 (s, 4H, $H^{2,6}$ of $C_6H_3(CF_3)_2$), 7.87 (s, 2H, H^4 of $C_6H_3(CF_3)_2$), 7.75 (d, J = 8.1 Hz, 2H, $H^{4,5}$ of Fl), 7.67 (s, 2H, $H^{1,8}$ of Fl), 7.48 (d, J = 8.1 Hz, 2H, $H^{3,6}$ of Fl), 7.06 (d, J = 19.1 Hz, 2H, FlC*H*=CHSi), 6.56 (d, J = 19.1 Hz, 2H, FlCH=C*H*Si), 3.92 (s, 2H, CH_2 of Fl), 0.53 (s, 12H, $SiMe_2$). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 147.0 (s, Fl*C*H=CHSi), 144.1 (s, Fl), 142.4 (s, $C_6H_3(CF_3)_2$), 141.9, 136.5 (each s, Fl), 133.6 (s, $C_6H_3(CF_3)_2$), 130.7 (q, $^2J_{FC}$ = 32 Hz, $C_6H_3(CF_3)_2$), 126.1 (s, FlCH=C*H*Si), 123.9 (s, Fl), 123.0 (s, Fl and $C_6H_3(CF_3)_2$), 122.0 (q, $^1J_{FC}$ = 278 Hz, CF_3), 120.2 (s, Fl), 36.7 (s, CH2 of Fl), −2.7 (s, $SiMe_2$). Anal. Calcd for $C_{37}H_{30}F_{12}Si_2$: C, 58.57; H, 3.99. Found: C, 58.68; H, 3.97.



To a solution of (*E*,*E*)-**4d′** [(*Z*)/(*E*) < 1/99] (136 mg, 0.180 mmol) and **7** (174 mg, 0.378 mmol) in THF (1.8 mL) were successively added $[Pd(\mu\text{-Cl})(\eta^3\text{-allyl})]_2$ (3.3 mg, 9.1 μmol) and a 1.0 M solution of TBAF·$3H_2O$ in THF (0.36 mL, 0.36 mmol). The mixture was stirred at room temperature for 65 h and then evaporated by pumping. The oily residue was subjected to flash column chromatography on silica gel eluted with hexane/CH_2Cl_2 (1/3) to give (*E*,*E*)-**17** [(*Z*)/(*E*) < 1/99] as a yellow solid (109 mg, 73% yield); mp 72 °C. ^{1}H NMR ($CDCl_3$): δ 7.74 (d, J = 8.1 Hz, 2H, $H^{4,5}$ of Fl), 7.71 (s, 2H, $H^{1,8}$ of Fl), 7.53 (d, J = 8.1 Hz, 2H, $H^{3,6}$ of Fl), 7.52, 7.20 (each d, J = 16.7 Hz, 2H, CH=CH), 7.17 (d, J = 2.7 Hz, 2H, $H^{6'}$ of C_6H_3), 6.84 (d, J = 9.0 Hz, 2H, $H^{3'}$ of C_6H_3), 6.77 (dd, J = 9.0, 2.7 Hz, 2H, $H^{4'}$ of C_6H_3), 3.99, 3.97 (each d, J = 6.4 Hz, 4H, OCH_2), 3.95 (s, 2H, CH_2 of Fl), 1.90−1.75 (m, 8H, CH_2), 1.58−1.25 (m, 40H, CH_2), 0.92−0.86 (m, 12H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 153.3, 150.9 (each s, $C^{2',5'}$ of C_6H_3), 144.0, 141.0, 136.7 (each s, Fl), 129.4 (s, CH=CH), 127.7 (s, $C^{1'}$ of C_6H_3), 125.8 (s, Fl), 123.0 (s, CH=CH), 122.8 (s, Fl), 119.9 (s, Fl), 114.4, 114.0, 112.3 (each s, $C^{3',4',6'}$ of C_6H_3), 69.6, 68.7 (each s, OCH2), 36.8 (s, CH_2 of Fl), 31.8, 29.5, 29.5, 29.4, 29.4, 29.3, 29.3, 26.3, 26.1, 22.7 (each s, CH_2), 14.1 (s, CH_3). Anal. Calcd for $C_{61}H_{86}O_4$: C, 82.94; H, 9.81. Found: C, 82.75; H, 9.86.

Synthesis of *trans*-Poly[(2,7-fluorenylenevinylene)-*alt*-(2,5-dioctyloxy-1,4-phenylenevinylene)] (3df). (*E*,*E*)-**21** (152 mg, 0.200 mmol), **5** (117 mg, 0.200 mmol), and $[Pd(\mu\text{-Cl})(\eta^3\text{-allyl})]_2$ (3.7 mg, 0.10 mmol) were dissolved in THF (1.6 mL). A 1.0 M solution of TBAF·$3H_2O$ in THF (0.40 mL, 0.40 mmol) was added, and the mixture was stirred at room temperature for 24 h. TLC analysis of the solution revealed the complete consumption of both monomers. The mixture was poured into a vigorously stirred MeOH (30 mL). A yellow solid of *trans*-**3df** thus precipitated was collected by filtration over a 1.0 mm membrane filter, washed with MeOH, and dried under vacuum at room temperature overnight (119 mg, >99% yield). GPC analysis revealed the molecular weight (M_n) and molecular weight distribution (M_w/M_n) of 4300 and 1.49, respectively. ^{1}H NMR ($CDCl_3$): δ 7.75−7.64 (m, Fl), 7.62−7.45 (m, Fl and CH═CH), 7.28−7.19 (m, CH═CH), 7.17 (br s, C_6H_2), 4.10 (t, J = 6.0 Hz, OCH_2), 3.96 (s, CH_2 of Fl), 1.96−1.64 (m, CH_2), 1.60−1.09 (m, CH_2), 0.90 (br, CH_3). $^{13}C\{^1H\}$ NMR analysis was infeasible due to low solubility.

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Supporting Information Available: NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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