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Stereoselective Synthesis of *cis*- and *trans*-Oligo(phenylenevinylene)s via Palladium-Catalyzed Cross-Coupling Reactions

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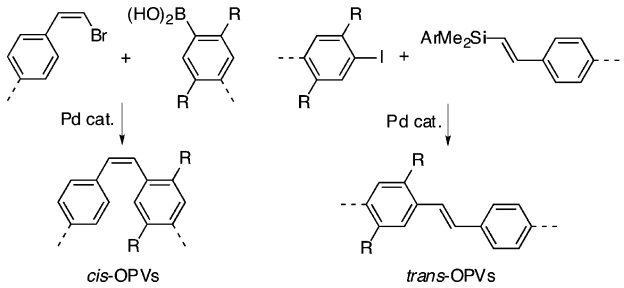

cis-Oligo(phenylenevinylene)s (OPVs) are synthesized by Suzuki−Miyaura coupling of arylboronic acids with (*Z*)-bromoalkenes in over 96% geometrical purity. On the other hand, *trans*-oligo(phenylenevinylene)s can be synthesized by Hiyama coupling of aryl iodide with (*E*)-alkenylsilanes in almost perfect purities. Effect of π-conjugation chain length on photoisomerization behavior of OPVs is described.

Introduction

Oligo(phenylenevinylene)s (OPVs) have attracted considerable recent interest because of their potential applications in optoelectronic devices such as light-emitting diodes and photovoltaic cells.[1,2] OPVs have also been investigated as well-defined models of poly(phenylenevinylene)s (PPVs) with precise conjugation lengths and structures. Such studies are useful for understanding the relations between bulk material properties and molecular structures of PPVs.

Recently, we succeeded for the first time in the synthesis of all-cis PPVs, in which vinylene linkages in the polymer backbone are entirely stereoregulated to cis geometry.[3] The all-cis PPVs readily underwent photoisomerization to the corresponding all-trans PPVs in solution. The cis-to-trans isomerization also took place when thin films of all-cis PPVs were exposed to UV light. Interestingly, the PPV films were insolubilized during the photoisomerization. On the basis of these findings, an extremely simple method of generating microscale patterns of PPVs onto quartz substrates was developed.

The cis-to-trans isomerization of PPVs involves a rather simple change of absorption spectrum. Thus, while the all-cis PPVs that we have prepared have 12−42 vinylene units in the polymer chain, the UV−vis spectrum changes clearly with isosbestic points. Furthermore, no notable shift of the absorption maximum of trans isomer has been observed during the isomerization. These observations are consistent with the isomerization process that converts *cis*-vinylene units in the polymer chain all at once to the trans groups, rather than stepwise.

The one-way photoisomerization of conjugated olefins has been documented in several instances.[4] Thus, while stilbene undergoes two-way isomerization to give a cis/trans mixture in the photostationary state, the olefins with extended π-conjugation systems such as alkenylanthracene and styrylstilbene are isomerized solely from the cis to trans isomer.

To examine the effect of π-conjugation length on photoisomerization behavior of PPVs, we tried to synthesize all-cis and all-trans OPVs in a stereoselective manner. Although all-trans isomers have been prepared by Horner−Wadsworth−Emmons olefination of aldehydes or by Heck-type arylation of

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(1) For reviews, see: (a) (a) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350. (b) Scherf, U. *Top. Curr. Chem.* **1999**, *201*, 163. (c) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537. (d) Segura, J. L.; Martín, N.; Guldi, D. M. *Chem. Soc. Rev.* **2005**, *34*, 31. (e) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491.

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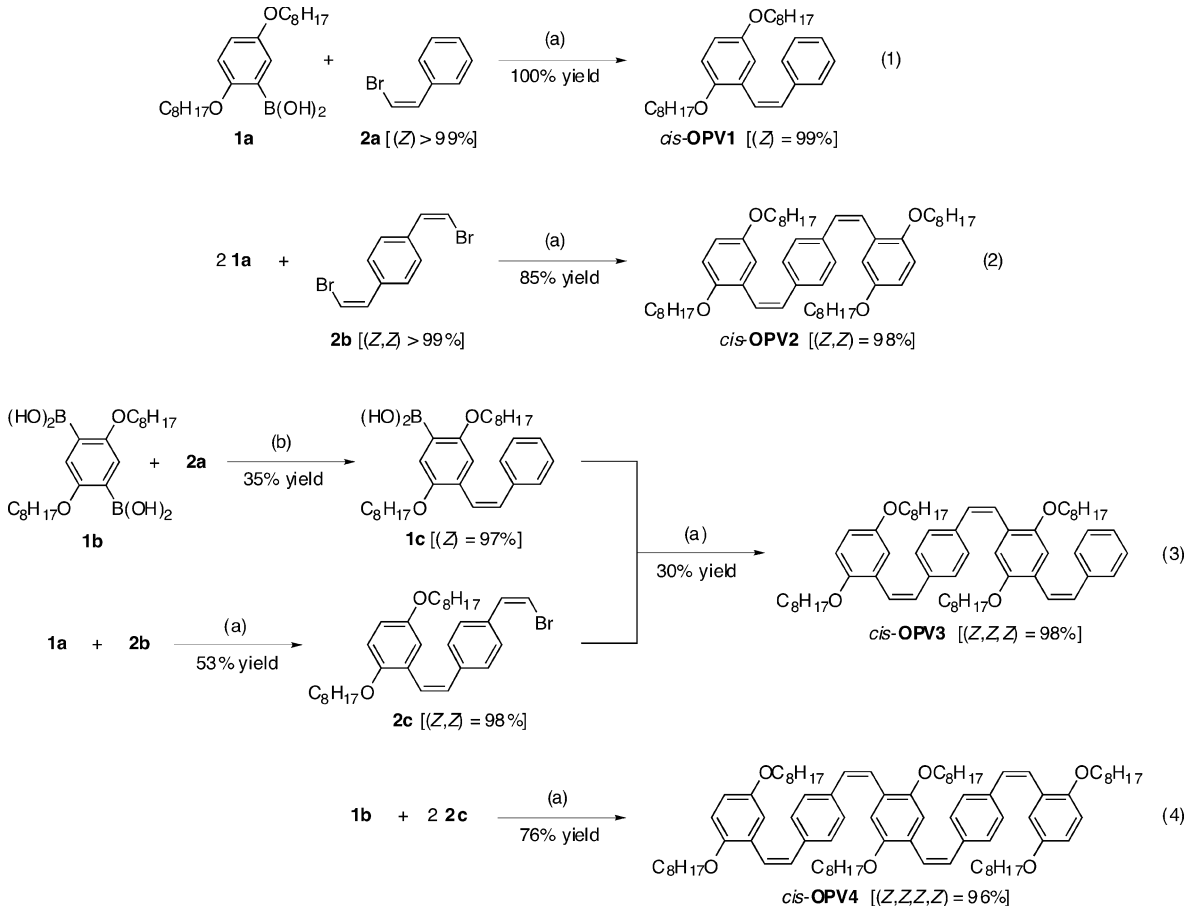
SCHEME 1. Synthesis of *cis*-OPV1−4[a]



[a] Reagents and conditions: (a) $Pd(PPh_3)_4$ (1.5 mol %), aq KOH, toluene, 80 °C; (b) $Pd(PPh_3)_4$ (1.5 mol %), aq KOH, THF, 60 °C.

olefins,[1,2] the synthesis of all-cis analogues has not been reported. Herein, we describe that both isomers of OPVs having 1−4 vinylene units are successfully prepared by palladium-catalyzed cross-coupling reactions.

Results and Discussion

Synthesis of *cis*-Oligo(phenylenevinylene)s. ***cis*-OPV1−4** were synthesized by Suzuki−Miyaura coupling using four kinds of starting materials, **1a**, **1b**, **2a**, and **2b** (Scheme 1). 2,5-Dioctyloxybenzeneboronic acid (**1a**) reacted cleanly with (*Z*)-styryl bromide (**2a**) in toluene at 80 °C in the presence of $Pd(PPh_3)_4$ and aqueous KOH to afford ***cis*-OPV1** in quantitative yield (eq 1). Similarly, 2 equiv of **1a** reacted with (*Z*,*Z*)-1,4-bis(2-bromoethenyl)benzene (**2b**) to give ***cis*-OPV2** with 98% geometrical purity in 85% yield (eq 2). In this case, (*Z*,*Z*)-**2b** as a substrate was prepared by bromodesilylation of (*Z*,*Z*)-1,4-bis[2-(dimethylphenylsilyl)ethenyl]benzene (**4b**) with NBS.[5] Therefore, the synthesis of ***cis*-OPV2** was attempted by Hiyama coupling of (*Z*,*Z*)-**4b** with 2 equiv of 2,5-dioctyloxyiodobenzene (**3a**) in THF in the presence of a palladium catalyst and TBAF·$3H_2O$. However, hydrodesilylation of (*Z*,*Z*)-**4b** induced by fluoride ion took place to a considerable extent, giving 1,4-divinylbenzene. This compound subsequently underwent the Heck-type arylation with **3a** to lead to *trans*-**OPV2** (ca. 40%) as a byproduct.

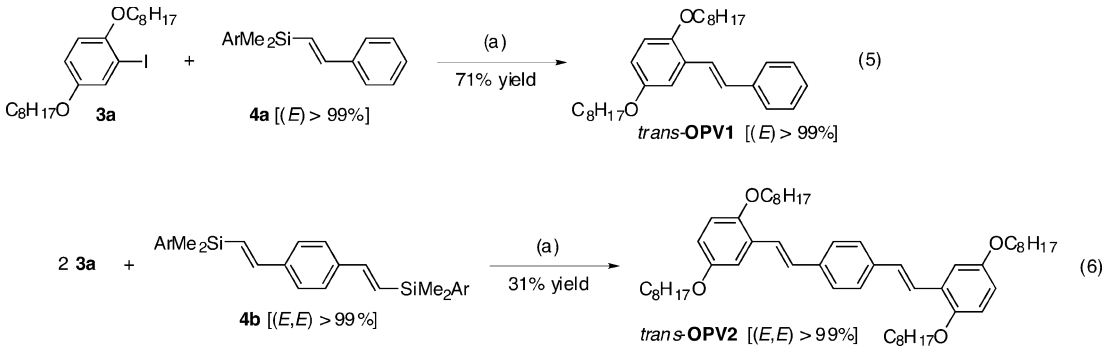
Next, boronic acid **1c** and alkenyl bromide **2c** were assembled into *cis*-**OPV3** (eq 3). (*Z*)-4-Styrylbenzeneboronic acid **1c** was synthesized from **1b** and **2a**, whereas (*Z*,*Z*)-(2-bromoethenyl)-stilbene **2c** was prepared by 1:1 coupling of **1a** and **2b** in 53% yield. In the former case, because diboronic acid **1b** was poorly soluble in toluene, 1:2 coupling of **1b** and **2a** to give *cis*-**OPV2** predominated under the conditions (a). Therefore, the cross-coupling reaction was performed in THF (condition (b)) using a 2-fold excess of **1b** against **2a**, where (*Z*)-**1c** was formed in 35% yield. Finally, the resulting (*Z*)-**1c** and (*Z*,*Z*)-**2c** were treated under the conditions (a), and *cis*-**OPV3** with 98% geometrical purity was isolated in 30% yield. *cis*-**OPV4** was similarly prepared by 1:2 coupling of **1b** and **2c** in 76% yield (eq 4).

Synthesis of *trans*-Oligo(phenylenevinylene)s. We previously reported that hydrosilylation of phenylacetylene with $HSiMe_2Ar$ [Ar = 3,5-$(CF_3)_2C_6H_3$] catalyzed by $RuHCl(CO)(PPh_3)_3$, followed by Hiyama coupling of the resulting styrylsilane with phenyl iodide, causes highly stereoselective synthesis of (*E*)-stilbene.[6] A series of *trans*-OPVs was prepared by this method (Schemes 2 and 3).

2,5-Dioctyloxyiodobenzene (**3a**) was treated with (*E*)-2-silylethenylbenzene **4a** in THF at room temperature in the presence of TBAF·$3H_2O$ and a catalytic amount of [Pd(η^3-allyl)-(μ-Cl)]$_2$ for 24 h (eq 5). Column chromatographic purification of the reaction product afforded *trans*-**OPV1** in 71% yield. Similarly, *trans*-**OPV2** was prepared in 31% yield by the reaction of 2 equiv of **3a** with (*E*,*E*)-1,4-bis(2-silylethenyl)-benzene **4b** (eq 6).

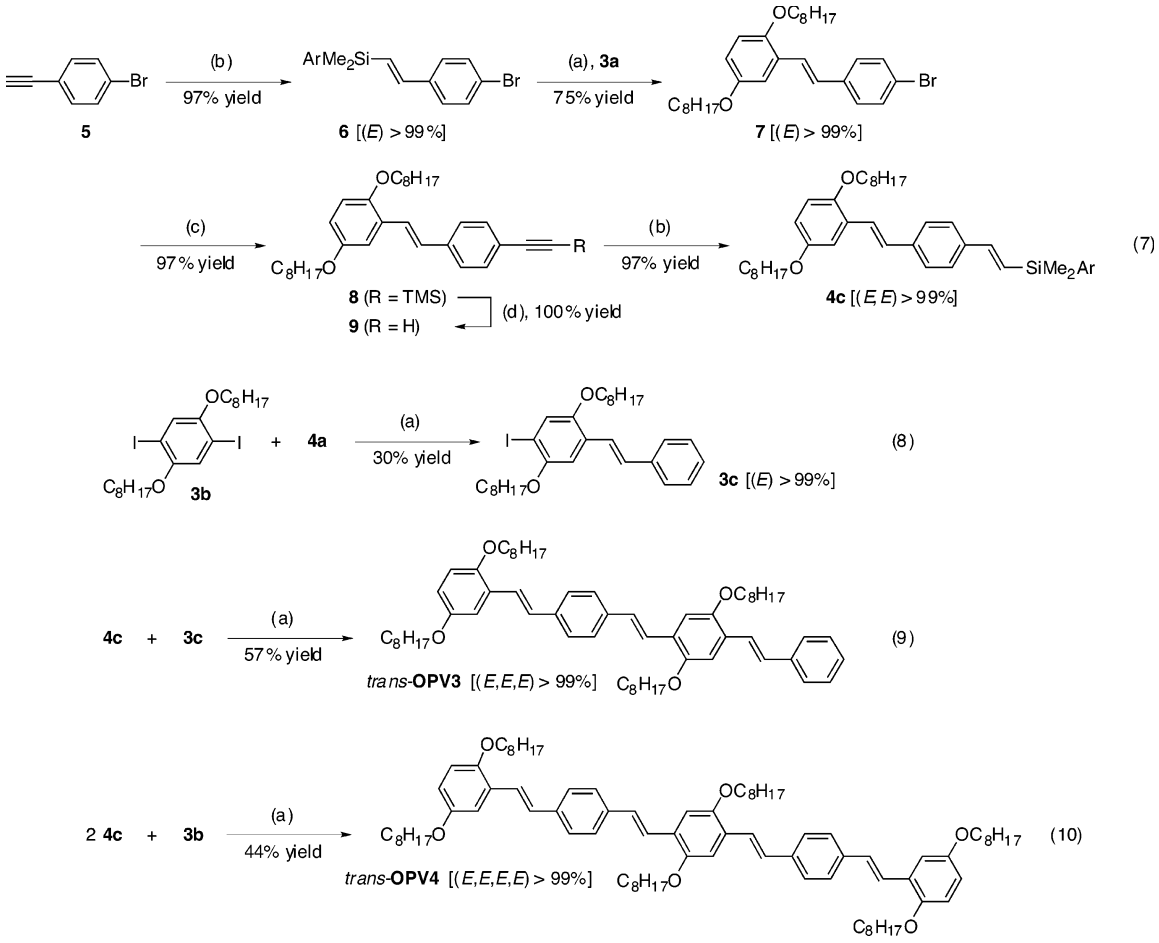
trans-**OPV3** and **OPV4** were prepared by using (*E*,*E*)-4-(2-silylethenyl)stilbene **4c** as a common starting material (Scheme

SCHEME 2. Synthesis of *trans*-OPV1 and 2[a]



[a] $SiMe_2Ar$ = $SiMe_2[C_6H_3(CF_3)_2$-3,5]. Reagents and conditions: (a) $[Pd(\eta^3$-allyl$)(\mu$-Cl$)]_2$ (5 mol %), TBAF·$3H_2O$ (1 equiv), THF, rt.

SCHEME 3. Synthesis of *trans*-OPV3 and 4[a]



[a] $SiMe_2Ar$ = $SiMe_2[C_6H_3(CF_3)_2$-3,5]. Reagents and conditions: (a) $[Pd(\eta^3$-allyl$)(\mu$-Cl$)]_2$ (5 mol %), TBAF·$3H_2O$ (1 equiv), THF, rt; (b) $HSiMe_2Ar$, $RuHCl(CO)(PPh_3)_3$ (5 mol %), CH_2Cl_2, rt; (c) HC≡$CSiMe_3$, $PdCl_2(PPh_3)_2$, CuI, NEt_3, 60 °C; (d) aq KOH, MeOH, THF, rt.

3). This compound was obtained by the sequence of reactions outlined in eq 7. Hydrosilylation of 4-bromophenylacetylene (**5**) with $HSiMe_2Ar$ catalyzed by $RuHCl(CO)(PPh_3)_3$ in CH_2Cl_2 was completed in 1.5 h at room temperature to give (*E*)-**6** in almost quantitative yield. The product was then coupled with 2,5-dioxyloxyiodobenzene (**3a**) under Hiyama coupling conditions (a), giving (*E*)-4-bromostilbene **7** in 75% yield. Compound **7** was then converted to terminal acetylene **9** by Sonogashira coupling with (trimethylsilyl)acetylene, followed by desilylation. Finally, **9** was subjected to (*E*)-selective hydrosilylation catalyzed by $RuHCl(CO)(PPh_3)_3$, and the desired compound **4c** was obtained in 68% overall yield starting from **5**.

Treatment of (*E*,*E*)-**4c** with (*E*)-iodostilbene **3c**, prepared by 1:1 coupling of **3b** and **4a** (eq 8), in THF in the presence TBAF·$3H_2O$ and $[Pd(\eta^3$-allyl$)(\mu$-Cl$)]_2$ catalyst at room temperature for 15 h afforded *trans*-**OPV3** in 57% yield (eq 9). On the other hand, 2:1 coupling of **4c** with 2,5-dioctyloxy-1,4-diiodobenzene (**3b**) under almost the same reaction conditions formed *trans*-**OPV4** in 44% isolated yield (eq 10).

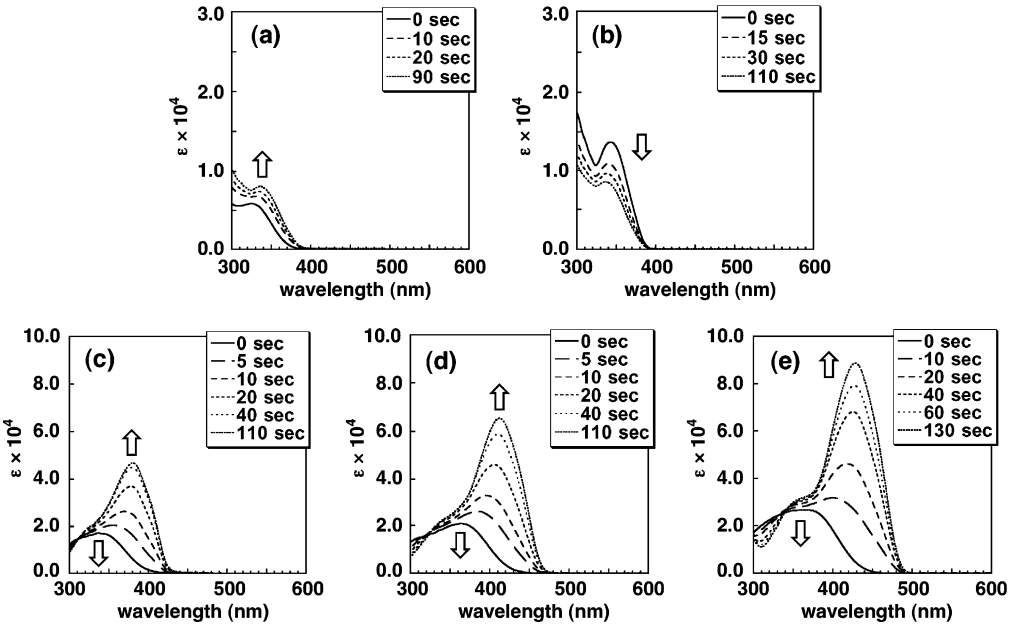


FIGURE 1. Changes of UV−vis absorption spectra of OPVs under photoirradiation in benzene: (a) **OPV1** (from cis isomer), (b) **OPV1** (from trans isomer), (c) **OPV2** (cis to trans), (d) **OPV3** (cis to trans), (e) **OPV4** (cis to trans).

Photoisomerization of OPV1−4. The *cis*- and *trans*-OPVs thus prepared were dissolved in benzene (0.01 mM) in a quartz cell and irradiated by a Xe lamp (λ_{max} = 365 nm, 0.87 mW cm^{-2}) under a nitrogen atmosphere at room temperature. The sample solutions were monitored at intervals by UV−vis spectroscopy as illustrated in Figure 1a−e. **OPV1** underwent two-way isomerization to give a mixture of the cis and trans isomers in a 52:48 ratio [(a), (b)]. On the other hand, **OPV2−4** underwent one-way isomerization from cis to trans isomer [(c), (d), (e)]. ^{1}H NMR analysis of the products revealed quantitative (>99%) conversion of *cis*-**OPV2−4** to the corresponding trans isomers (see the Supporting Information). These observations are consistent with the previous ones,[4] particularly the report for 4-styrylstilbene by Sandros et al.[7] Further study of photoisomerization of OPVs, particularly focused on the mechanisms, will be reported in due course.

Experimental Section

(*Z*)-2,5-Dioctyloxystilbene (*cis*-OPV1). To a solution of **1a** (75.7 mg, 0.200 mmol) and **2a** [(*Z*) > 99%] (38.4 mg, 0.210 mmol) in toluene (1.0 mL) were successively added $Pd(PPh_3)_4$ (3.5 mmol, 3.0 μmol) and 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 *cis*-**OPV1** with 99% geometrical purity as a pale yellow oil (86.9 mg, 100% yield). ^{1}H NMR ($CDCl_3$): δ 7.28−7.11 (m, 5H), 6.79 (dd, J = 7.1, 2.2 Hz, 1H), 6.73 (d, J = 2.2 Hz, 1H), 6.72 (d, J = 7.1 Hz, 1H), 6.69 (d, J = 12.4 Hz, 1H), 6.60 (d, J = 12.4 Hz, 1H), 3.90 (t, J = 6.6 Hz, 2H), 3.60 (t, J = 6.6 Hz, 2H), 1.75−1.66 (m, 2H), 1.63−1.54 (m, 2H), 1.44−1.22 (m, 20 H), 0.88 (t, J = 6.4 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 152.4, 151.0, 137.4, 130.0, 128.8, 128.0, 127.0, 126.9, 125.7, 115.5, 115.3, 113.6, 69.3, 68.4, 31.8, 29.4, 29.3, 29.2, 29.1, 26.1, 26.0, 22.7, 14.1. Anal. Calcd for $C_{30}H_{44}O_2$: C, 82.52; H, 10.16. Found: C, 82.51; H, 10.16.

1,4-Bis[(*Z*)-2,5-dioctyloxystyryl]benzene (*cis*-OPV2). This compound was synthesized similarly to *cis*-**OPV1**, starting from **1a** (279

(2) For recent studies on OPVs as emissive materials, see: (a) Lin, H.-C.; Tsai, C.-M.; Huang, G.-H.; Lin, J.-M. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 783. (b) Summers, M. A.; Bazan, G. C.; Buratto, S. K. *J. Am. Chem. Soc*. **2005**, *127*, 16202. (c) Hoeben, F. J. M.; Schenning, A. P. H. J.; Meijer, E. W. *ChemPhysChem* **2005**, *6*, 2337. (d) Varghese, R.; George, S. J.; Ajayaghosh, A. *Chem. Commun.* **2005**, 593. (e) Mahler, A. K.; Schlick, H.; Saf, R.; Stelzer, F.; Meghdadi, F.; Pogantsch, A.; Leising, G.; Möller, K.-C.; Besenhard, J. O. *Macromol. Chem. Phys.* **2004**, *205*, 1840. OPVs in photovoltaic cells, see: (f) Jorgensen, M.; Krebs, F. C. *J. Org. Chem.* **2004**, *69*, 6688. (g) Ramos, A. M.; Beckers, E. H. A.; Offermans, T.; Meskers, S. C. J.; Janssen, R. A. J. *J. Phys. Chem. A* **2004**, *108*, 8201. (h) Wurthner, F.; Chen, Z. J.; Hoeben, F. J. M.; Osswald, P.; You, C. C.; Jonkheijm, P.; van Herrikhuyzen, J.; Schenning, A. P. H. J.; van der Schoot, P. P. A. M.; Meijer, E. W.; Beckers, E. H. A.; Meskers, S. C. J.; Janssen, R. A. J. *J. Am. Chem. Soc.* **2004**, *126*, 10611. (i) Melzer, C.; Krasnikov, V. V.; Hadziioannou, G. *J. Polym. Sci. Part B: Polym. Phys.* **2003**, *41*, 2665. (j) Neuteboom, E. E.; Meskers, S. C. J.; van Hal, P. A.; van Duren, J. K. J.; Meijer, E. W.; Janssen, R. A. J.; Dupin, H.; Pourtois, G.; Cornil, J.; Lazzaroni, R.; Bredas, J. L.; Beljonne, D. *J. Am. Chem. Soc.* **2003**, *125*, 8625. For OPVs in functional supramolecular systems, see: (k) George, S. J.; Ajayaghosh, A. *Chem. Eur. J.* **2005**, *11*, 3217. (l) Hulvat, J. F.; Sofos, M.; Tajima, K.; Stupp, S. I. *J. Am. Chem. Soc.* **2005**, *127*, 366. (m) Messmore, B. W.; Hulvat, J. F.; Sone, E. D.; Stupp, S. I. *J. Am. Chem. Soc.* **2004**, *126*, 14452. (n) van Herrikhuyzen, J.; Syamakumari, A.; Schenning, A. P. H. J.; Meijer, E. W. *J. Am. Chem. Soc.* **2004**, *126*, 10021. (o) Ajayaghosh, A.; George, S. J.; Praveen, V. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 332. (p) Ajayaghosh, A.; George, S. J. *J. Am. Chem. Soc.* **2001**, *123*, 5148. For other examples of synthesis and properties of OPVs, see: (q) Jian, H.; Tour, J. M. *J. Org. Chem.* **2005**, *70*, 3396. (r) Xue, C.; Luo, F.-T. *J. Org. Chem.* **2003**, *68*, 4417. (s) Stuhr-Hansen, N.; Christensen, J. B.; Harrit, N.; Bjørnholm, T. *J. Org. Chem.* **2003**, *68*, 1275. (t) Gu, T.; Ceroni, P.; Marconi, G.; Armaroli, N.; Nierengarten, J.-F. *J. Org. Chem.* **2001**, *66*, 6432. (u) Hilberer, A.; van Hutten, P. F.; Wildeman, J.; Hadziioannou, G. *Macromol. Chem. Phys.* **1997**, *198*, 2211. (v) Koch, F.; Heitz, W. *Macromol. Chem. Phys.* **1997**, *198*, 1531.

(3) 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.

(4) Arai, T.; Tokumaru, K. *Chem. Rev.* **1993**, *93*, 23.

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

(6) (a) Katayama, H.; Taniguchi, K.; Kobayashi, M.; Sagawa, T.; Minami, T.; Ozawa, F. *J. Organomet. Chem.* **2002**, *645*, 192. (b) Katayama, H.; Nagao, M.; Moriguchi, R.; Ozawa, F. *J. Organomet. Chem.* **2003**, *676*, 49.

(7) Sandros, K.; Sundahl, M.; Wennerström, O.; Norinder, U. *J. Am. Chem. Soc.* **1990**, *112*, 3082.

mg, 0.736 mmol), **2b** [(*Z*,*Z*) > 99%] (79.5 mg, 0.276 mmol), toluene (2.7 mL), $Pd(PPh_3)_4$ (4.7 mg, 4.1 μmol), and 3.0 M aqueous KOH (0.60 mL, 1.8 mmol). The reaction was completed after 40 h. After chromatographic purification using hexane/CH_2Cl_2 (2/1) as an eluent, a yellow solid of *cis*-**OPV2** [(*Z*,*Z*) = 98%] was obtained (188 mg, 85%). Mp: 72 °C. ^{1}H NMR ($CDCl_3$): δ 7.12 (s, 4H), 6.78 (d, J = 8.7 Hz, 2H), 6.77 (d, J = 3.0 Hz, 2H), 6.70 (dd, J = 8.7, 3.0 Hz, 2H), 6.63 (d, J = 12.3 Hz, 2H), 6.51 (d, J = 12.3 Hz, 2H), 3.88 (t, J = 6.6 Hz, 4H), 3.65 (t, J = 6.6 Hz, 4H), 1.74−1.54 (m, 4H), 1.45−1.26 (m, 20H), 0.88 (t, J = 7.1 Hz, 6H), 0.87 (t, J = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 152.5, 150.9, 136.0, 129.8, 128.6, 127.2, 125.6, 115.6, 115.1, 113.5, 69.2, 68.5, 31.8, 29.4, 29.3, 29.2, 26.1, 26.0, 22.7, 14.1. Anal. Calcd for $C_{54}H_{82}O_4$: C, 81.56; H, 10.39. Found: C, 81.38; H, 10.52.

(*Z*)-2,5-Dioctyloxystilbene-4-boronic Acid (1c). This compound was synthesized similarly to *cis*-**OPV1**, starting from **1b** (3.38 g, 8.01 mmol), **2a** [(*Z*) > 99%] (738 mg, 4.03 mmol), THF (80 mL), $Pd(PPh_3)_4$ (34.7 mg, 30.0 μmol), and 3.0 M aqueous KOH (4.00 mL, 12.0 mmol). The reaction was completed after 2 h. After chromatographic purification using hexane/AcOEt (10/1) as an eluent, and then recrystallization from hexane, a white solid of **1c** [(*Z*) = 97%] was obtained (666 mg, 35%). Mp: 69 °C. ^{1}H NMR ($CDCl_3$): δ 7.42−7.11 (m, 5H), 7.31 (s, 1H), 6.75 (d, J = 12.3 Hz, 1H), 6.70 (s, 1H), 6.68 (d, J = 12.3 Hz, 1H), 5.81 (s, 2H), 3.99 (d, J = 6.6 Hz, 2H), 3.56 (d, J = 6.6 Hz, 2H), 1.79−1.70 (m, 4H), 1.62−1.54 (m, 4H), 1.45−1.26 (m, 20H), 0.89 (t, J = 6.6 Hz, 3H), 0.88 (t, J = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 157.3, 151.1, 137.4, 130.9, 130.2, 128.9, 128.2, 127.0, 125.6, 119.5, 113.0, 69.1, 68.6, 31.8, 31.8, 29.4, 29.2, 29.1, 29.0, 26.1, 25.8, 22.7, 22.6, 14.1. Anal. Calcd for $C_{30}H_{45}BO_4$: C, 74.99; H, 9.44. Found: C, 74.89; H, 9.55.

(*Z*)-4′-[(*Z*)-2-Bromoethenyl]-2,5-dioctyloxystilbene (2c). This compound was synthesized similarly to *cis*-**OPV1**, starting from **1a** (945 mg, 2.50 mmol), **2b** [(*Z*,*Z*) > 99%] (864 mg, 3.00 mmol), toluene (13 mL), $Pd(PPh_3)_4$ (43.3 mg, 37.5 μmol), and 3.0 M aqueous KOH (2.50 mL, 7.50 mmol). The reaction was completed after 24 h. After chromatographic purification using hexane/AcOEt (50/1) as an eluent, a fluorescent yellow solid of **1c** [(*Z*,*Z*) = 98%] was obtained (710 mg, 53%). Mp: 40 °C. ^{1}H NMR ($CDCl_3$): δ 7.55 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 8.1 Hz, 1H), 6.82−6.72 (m, 3H), 6.71 (d, J = 12.3 Hz, 1H), 6.57 (d, J = 12.3 Hz, 1H), 6.38 (d, J = 8.1 Hz, 1H), 3.90 (t, J = 6.6 Hz, 2H), 3.64 (t, J = 6.6 Hz, 2H), 1.71−1.56 (m, 4H), 1.34−1.26 (m, 20H), 0.88 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 152.5, 150.9, 137.6, 133.4, 132.0, 129.5, 128.7, 126.9, 126.5, 115.5, 113.6, 105.9, 69.3, 68.5, 31.8, 31.8, 29.4, 29.3, 29.2, 29.2, 26.1, 25.9, 22.7, 14.1. Anal. Calcd for $C_{32}H_{45}BrO_2$: C, 70.96; H, 8.37. Found: C, 71.10; H, 8.42.

(*Z*)-2,5-Dioctyloxy-4′-[(*Z*)-2,5-dioctyloxy-4-[(*Z*)-styryl]styryl]-stilbene (*cis*-OPV3). This compound was synthesized similarly to *cis*-**OPV1**, starting from **1c** [(*Z*) = 97%] (217 mg, 0.401 mmol), **2c** [(*Z*,*Z*) = 98%] (193 mg, 0.402 mmol), toluene (2.0 mL), $Pd(PPh_3)_4$ (3.5 mg, 3.0 μmol), and 3.0 M aqueous KOH (0.20 mL, 0.60 mmol). The reaction was completed after 24 h. After chromatographic purification using hexane/AcOEt (10/1) as an eluent, and then recycle GPC, a yellow solid of *cis*-**OPV3** [(*Z*) = 98%] was obtained (109 mg, 30%). Mp: 66 °C. ^{1}H NMR ($CDCl_3$): δ 7.31−7.13 (m, 5H), 7.16 (s, 4H), 6.79 (d, J = 8.7 Hz, 1H), 6.77 (d, J = 3.3 Hz, 1H), 6.75 (s, 1H), 6.71 (dd, J = 8.7, 3.3 Hz, 1H), 6.69 (d, J = 12.5 Hz, 1H), 6.68 (s, 1H), 6.64 (d, J = 12.5 Hz, 1H), 6.62 (d, J = 12.3 Hz, 1H), 6.59 (d, J = 12.5 Hz, 1H), 6.52 (d, J = 12.5 Hz, 1H), 6.50 (d, J = 12.3 Hz, 1H), 3.89 (t, J = 6.5 Hz, 2H), 3.65 (t, J = 6.6 Hz, 2H), 3.55 (t, J = 6.5 Hz, 2H), 3.47 (t, J = 6.6 Hz, 2H), 1.75−1.38 (m, 8H) 1.25 (br, 40H), 0.89−0.86 (m, 12H). ^{13}C NMR ($CDCl_3$): δ 152.4, 150.9, 150.1, 150.0, 137.7, 136.2, 136.0, 129.8, 129.7, 129.6, 128.9, 128.6, 128.6, 128.1, 127.2, 126.9, 126.1, 126.1, 125.7, 125.4, 125.3, 115.7, 115.0, 114.0, 114.0, 113.5, 69.3, 68.9, 68.7, 68.5, 31.8, 29.4, 29.3, 29.3, 29.2, 29.2, 29.2, 29.1, 26.1, 26.0, 25.9, 22.7, 14.1. Anal. Calcd for $C_{62}H_{88}O_4$: C, 82.98; H, 9.88. Found: C, 83.06; H, 9.89.

1,4-Bis[(*Z*)-4-[(*Z*)-2,5-dioctyloxystyryl]styryl]-2,5-dioctyloxybenzene (*cis*-OPV4). This compound was synthesized similarly to *cis*-**OPV1**, starting from **1b** (90.1 g, 0.213 mmol), **2c** [(*Z*,*Z*) = 98%] (232 mg, 0.428 mmol), toluene (2.1 mL), $Pd(PPh_3)_4$ (3.7 mg, 3.2 μmol), and 3.0 M aqueous KOH (0.21 mL, 0.63 mmol). The reaction was completed after 41 h. After chromatographic purification using hexane/CH_2Cl_2 (1/1) as an eluent, and then recycle GPC, a yellow solid of *cis*-**OPV4** [(*Z*,*Z*,*Z*,*Z*) = 96%] was obtained (204 mg, 76%). Mp: 96 °C. ^{1}H NMR ($CDCl_3$): δ 7.17 (d, J = 9.5 Hz, 4H), 7.14 (d, J = 9.5 Hz, 4H), 6.78 (d, J = 8.9 Hz, 2H), 6.76 (d, J = 3.3 Hz, 2H), 6.75 (s, 2H), 6.71 (dd, J = 8.9, 3.3 Hz, 2H), 6.64 (d, J = 12.5 Hz, 2H), 6.63 (d, J = 12.3 Hz, 2H), 6.51 (d, J = 12.5 Hz, 2H), 6.49 (d, J = 12.3 Hz, 2H), 3.89 (t, J = 6.5 Hz, 4H), 3.65 (t, J = 6.7 Hz, 4H), 3.53 (t, J = 6.5 Hz, 4H), 1.75−1.38 (m, 12H) 1.24 (br, 60H), 0.89−0.85 (m, 18H). ^{13}C NMR ($CDCl_3$): δ 152.5, 150.9, 150.1, 136.2, 136.0, 129.7, 129.5, 128.6, 127.2, 126.2, 125.7, 125.3, 115.7, 115.0, 113.9, 113.5, 69.2, 68.8, 68.5, 31.8, 29.4, 29.3, 29.3, 29.2, 26.1, 26.0, 22.7, 14.1. Anal. Calcd for $C_{86}H_{126}O_6$: C, 82.24; H, 10.11. Found: C, 82.00; H, 10.16.

(*E*)-2,5-Dioctyloxystilbene (*trans*-OPV1). To a solution of **3a** (206 mg, 0.447 mmol) and **4a** [(*E*) > 99%] (205 mg, 0.548 mmol) in THF (1.7 mL) were successively added $[Pd(\eta^3\text{-allyl})(\mu\text{-Cl})]_2$ (8.4 mg, 23 μmol) and 1.0 M solution of TBAF·$3H_2O$ in THF (0.55 mL, 0.55 mmol). The mixture was stirred at rt for 24 h and then evaporated by pumping. The oily residue was subjected to flash column chromatography on silica gel eluted with hexane/AcOEt (50/1) to give *trans*-**OPV1** [(*E*) > 99%] as pale yellow oil containing small amounts of contaminant arise from silicon compounds. Further purification was performed by recycle GPC to give *trans*-**OPV1** [(*E*) > 99%] as a colorless oil (138 mg, 71%). Identification data was consistent with the literature.[2u] ^{1}H NMR ($CDCl_3$): δ 7.53−7.51 (m, 5H), 7.46 (d, J = 16.5 Hz, 1H), 7.38−7.33 (m, 5H), 7.26−7.22 (m, 5H), 7.15 (d, J = 2.9 Hz, 1H), 7.11 (d, J = 16.5 Hz, 1H), 6.83 (d, J = 9.0 Hz, 1H), 6.76 (dd, J = 9.0, 2.9 Hz, 1H), 3.96 (t, J = 6.4 Hz, 2H), 3.95 (t, J = 6.6 Hz, 2H), 1.87−1.73 (m, 4H), 1.54−1.21 (m, 20H), 0.91−0.86 (m, 6H). Anal. Calcd for $C_{30}H_{44}O_2$: C, 82.52; H, 10.16. Found: C, 82.43; H, 10.18.

1,4-Bis[(*E*)-2,5-dioctyloxystyryl]benzene (*trans*-OPV2). This compound was synthesized similarly to *trans*-**OPV1**, starting from **3a** (193 mg, 0.420 mmol), **4b** [(*E*,*E*) > 99%] (134 mg, 0.200 mmol), THF (1.6 mL), $[Pd(\eta^3\text{-allyl})(\mu\text{-Cl})]_2$ (3.7 mg, 10 μmol), and 1.0 M solution of TBAF·$3H_2O$ in THF (0.40 mL, 0.40 mmol). The reaction was completed after 24 h. After chromatographic purification using hexane/AcOEt (50/1) as an eluent, and then recycle GPC, a yellow solid of *trans*-**OPV2** [(*E*,*E*) > 99%] was obtained (50 mg, 32%). Identification data was consistent with the literature.[2u] ^{1}H NMR ($CDCl_3$): δ 7.50 (s, 4H), 7.48 (d, J = 16.5 Hz, 1H), 7.15 (d, J = 2.9 Hz, 1H), 7.11 (d, J = 16.5 Hz, 1H), 6.83 (d, J = 8.8 Hz, 1H), 6.76 (dd, J = 8.8, 2.9 Hz, 1H), 3.97 (t, J = 6.4 Hz, 2H), 3.96 (t, J = 6.5 Hz, 2H), 1.88−1.74 (m, 4H), 1.55−1.25 (m, 20H), 0.91−0.87 (m, 6H). Anal. Calcd for $C_{54}H_{82}O_4$: C, 81.56; H, 10.39. Found: C, 81.35; H, 10.52.

Dimethyl[3,5-bis(trifluoromethyl)phenyl][(*E*)-4-bromostyryl]-silane (6). To a solution of (4-bromophenyl)acetylene (1.58 g, 8.73 mmol) and dimethyl[3,5-bis(trifluoromethyl)phenyl]silane (4.75 g, 17.5 mmol) in CH_2Cl_2 (44 mL) was added $RuHCl(CO)(PPh_3)_3$ (416 mg, 0.437 mmol). The mixture was stirred at room temperature for 1.5 h and then evaporated by pumping. The oily residue was subjected to flash column chromatography on silica gel eluted with hexane to give **6** [(*E*) > 99%] as a colorless oil (3.83 g, 97%). ^{1}H NMR ($CDCl_3$): δ 7.94 (br, 2H), 7.87 (br, 1H), 7.50−7.46 (m, 4H), 7.34−7.30 (m, 4H), 6.90 (d, J = 19.2 Hz, 1H), 6.51 (d, J = 19.2 Hz, 1H), 0.50 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 145.5, 142.0, 136.4, 133.5, 131.8, 130.8, 128.1, 125.6, 123.5, 123.0, 121.7, −3.0. MS, *m*/*z* (rel intensity): 454, 452 (M^+, 5, 5), 439 (7), 436 (6), 358 (18), 356 (18), 277 (27), 257 (25), 225 (15), 223 (14), 145 (9), 143 (10), 102 (11), 81 (15), 77 (100), 75 (14), 59 (14), 51 (12), 44 (23), 43

(19), 40 (53). Anal. Calcd for $C_8H_{15}O_6BrFSi$: C, 47.69; H, 3.34. Found: C, 47.93; H, 3.29.

(*E*)-4′-Bromo-2,5-dioctyloxystilbene (7). This compound was synthesized similarly to *trans*-**OPV1**, starting from **6** [(*E*) > 99%] (2.33 g, 5.14 mmol), **3a** (2.40 g, 5.21 mmol), THF (26 mL), [Pd(η^3-allyl)(μ-Cl)]$_2$ (94.0 mg, 257 μmol), and 1.0 M solution of TBAF·3H$_2$O in THF (5.2 mL, 5.2 mmol). The reaction was completed after 10 h. After chromatographic purification using hexane/CH_2Cl_2 (10/1) as an eluent, a yellow oil of **7** [(*E*) > 99%] was obtained (2.00 g, 75%). ^{1}H NMR ($CDCl_3$): δ 7.49−7.46 (m, 4H), 7.39−7.36 (m, 4H), 7.43 (d, J = 16.6 Hz, 1H), 7.12 (d, J = 2.7 Hz, 1H), 7.04 (d, J = 16.6 Hz, 1H), 6.82 (d, J = 9.0 Hz, 1H), 6.78 (dd, J = 9.0, 2.7 Hz, 1H), 3.96 (t, J = 6.4 Hz, 2H), 3.94 (t, J = 6.6 Hz, 2H), 1.86−1.71 (m, 4H), 1.51−1.22 (br, 20H), 0.90−0.86 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 153.2, 150.9, 136.8, 131.6, 128.0, 127.2, 127.0, 124.3, 121.0, 114.7, 113.8, 112.4, 69.4, 68.6, 31.8, 31.8, 29.4, 29.4, 29.3, 29.3, 26.2, 26.1, 22.7, 14.1. Anal. Calcd for $C_{30}H_{43}BrO_2$: C, 69.89; H, 8.41. Found: C, 69.92; H, 8.39.

(*E*)-2,5-Dioctyloxy-4′-[(trimethylsilyl)ethynyl]stilbene (8). To a solution of **7** (1.99 g, 3.86 mmol) in NEt_3 (19 mL) were successively added $PdCl_2(PPh_3)_2$ (108 mg, 0.154 mmol), CuI (29.4 mg, 154 mmol), and (trimethylsilyl)acetylene (818 μL, 5.79 mmol). The mixture was stirred at 60 °C for 17 h. The resulting dark green suspension was filtered, and volatile materials were removed by pumping. The oily residue was poured into water and then extracted with ether (100 mL × 3). The combined organic extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off, and the resulting filtrate was evaporated to give a brown solid, which was subjected to flash column chromatography on silica gel eluted with hexane/benzene (5/1) to give **8** (2.00 g, 97%) as a yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.47 (d, J = 16.5 Hz, 1H), 7.44 (s, 4H), 7.13 (d, J = 2.6 Hz, 1H), 7.08 (d, J = 16.5 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 6.77 (dd, J = 8.4, 2.6 Hz, 1H), 3.97 (d, J = 6.4 Hz, 2H), 3.95 (d, J = 6.4 Hz, 2H), 1.87−1.73 (m, 4H), 1.56−1.25 (br, 20H), 0.91−0.86 (m, 6H), 0.26 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 153.2, 151.0, 138.1, 132.2, 128.3, 127.1, 126.2, 124.5, 121.7, 114.8, 113.8, 112.3, 105.3, 94.8, 69.5, 68.6, 31.8, 31.8, 29.4, 29.4, 29.3, 29.4, 26.2, 26.1, 14.1, 0.0. Anal. Calcd for $C_{35}H_{52}O_2Si$: C, 78.89; H, 9.84. Found: C, 78.95; H, 9.98.

(*E*)-2,5-Dioctylocy-4′-ethynylstilbene (9). To a solution of **8** (2.00 g, 3.75 mmol) in MeOH/THF (2/1, 62 mL) was added 0.8 M aqueous KOH (5.6 mL, 4.5 mmol). The mixture was stirred at room temperature for 2 h. The resulting yellow solution was evaporated under reduced pressure. The oily residue was added H_2O (100 mL) and extracted with ether (100 mL × 3). The combined organic extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off, and the filtrate was evaporated to give an orange oil, which was subjected to flash column chromatography on silica gel eluted with hexane/CH_2Cl_2 (1/1) to give **9** (1.73 g, 100%) as a yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.48 (d, J = 16.6 Hz, 1H), 7.46 (s, 4H), 7.13 (d, J = 2.7 Hz, 1H), 7.08 (d, J = 16.6 Hz, 1H), 6.83 (d, J = 8.8 Hz, 1H), 6.78 (dd, J = 8.8, 2.7 Hz, 1H), 3.96 (t, J = 6.5 Hz, 2H), 3.95 (t, J = 6.5 Hz, 2H), 3.12 (s, 1H), 1.87−1.72 (m, 4H), 1.55−1.26 (br, 20H), 0.90−0.86 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 153.2, 151.0, 138.4, 132.4, 128.1, 127.0, 126.3, 124.8, 120.7, 114.9, 113.8, 112.4, 83.8, 77.7, 69.5, 68.6, 31.8, 29.4, 29.4, 29.3, 29.3, 26.2, 26.1, 22.7, 14.1. Anal. Calcd for $C_{32}H_{44}O_2$: C, 83.43; H, 9.63. Found: C, 83.20; H, 9.72.

(*E*)-2,5-Dioctyloxy-4′-[(*E*)-2-[dimethyl(3,5-bis(trifluoromethyl)phenyl)silyl]ethenyl]stilbene (4c). This compound was synthesized similarly to **6**, starting from **9** (408 mg, 0.886 mmol), dimethyl[3,5-bis(trifluoromethyl)phenyl]silane (548 mg, 2.01 mmol), CH_2Cl_2 (5.0 mL), and RuHCl(CO)$(PPh_3)_3$ (47.6 mg, 50.0 μmol). The reaction was completed after 1 h. After chromatographic purification using hexane as eluent, a yellow solid of **4c** [(*E*,*E*) > 99%] was obtained (628 mg, 98%). Mp: 39 °C. ^{1}H NMR ($CDCl_3$): δ 7.96 (br, 2H), 7.86 (br, 1H), 7.50 (d, J = 8.2 Hz, 2H), 7.48 (d, J = 16.5 Hz, 1H), 7.44 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 2.7 Hz, 1H), 7.10 (d, J = 16.5 Hz, 1H), 6.98 (d, J = 19.1 Hz, 1H) 6.83 (d, J = 9.0 Hz, 1H), 6.77 (dd, J = 9.0, 2.7 Hz, 1H), 6.51 (d, J = 19.1 Hz, 1H), 3.97 (t, J = 6.4 Hz, 2H), 3.95 (t, J = 6.5 Hz, 2H), 1.87−1.73 (m, 4H), 1.52−1.24 (br, 20H), 0.91−0.85 (m, 6H), 0.51 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 153.2, 151.0, 146.4, 142.4, 138.4, 136.6, 133.6, 130.7, 128.4, 127.3, 127.0, 126.8, 124.0, 124.0, 122.9, 123.6, 114.7, 113.8, 112.2, 69.5, 68.6, 31.8, 29.4, 29.4, 29.3, 29.3, 26.3, 26.1, 22.7, 14.1, 14.1, −2.7. Anal. Calcd for $C_{42}H_{54}F_6O_2Si$: C, 68.82; H, 7.43. Found: C, 68.82; H, 7.47.

(*E*)-2,5-Dioctyloxy-4-iodostilbene (3c). This compound was synthesized similarly to *trans*-**OPV1**, starting from **3b** (1.13 g, 1.92 mmol), **4a** [(*E*) > 99%] (606 mg, 1.62 mmol), THF (6.4 mL), [Pd(η^3-allyl)(μ-Cl)]$_2$ (14.6 mg, 400 μmol), and 1.0 M solution of TBAF·3H2O in THF (1.6 mL, 1.6 mmol). The reaction was completed after 14 h. After chromatographic purification using hexane/AcOEt (50/1) as an eluent, and then recycle GPC, an orange oil of **3c** [(*E*) > 99%] was obtained (270 mg, 30%). ^{1}H NMR ($CDCl_3$): δ 7.53−7.51, 7.38−7.33 (m, 5H), 7.39 (d, J = 16.7 Hz, 1H), 7.28 (s, 1H), 7.12 (d, J = 16.7 Hz, 1H), 7.03 (s, 1H), 4.02 (t, J = 6.4 Hz, 2H), 3.95 (t, J = 6.5 Hz, 2H), 1.89−1.78 (m, 4H), 1.55−1.26 (br, 20H), 0.91−0.86 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 152.2, 151.3, 137.6, 129.4, 128.6, 127.6, 127.5, 126.5, 123.6, 123.1, 109.1, 85.8, 70.2, 69.6, 31.8, 31.8, 29.3, 29.3, 29.3, 26.2, 26.1, 22.7, 14.1, 14.1. Anal. Calcd for $C_{30}H_{43}IO_2$: C, 64.05; H, 7.70. Found: C, 64.01; H, 7.61.

(*E*)-2,5-Dioctyloxy-4′-[(*E*)-2,5-dioctyloxy-4-[(*E*)-styryl]styryl]-stilbene (*trans*-OPV3). This compound was synthesized similarly to *trans*-**OPV1**, starting from **3c** [(*E*) > 99%] (246 mg, 0.437 mmol), **4c** [(*E*,*E*) > 99%] (338 mg, 0.461 mmol), THF (1.8 mL), [Pd(η^3-allyl)(μ-Cl)]$_2$ (9.0 mg, 24 μmol), and 1.0 M solution of TBAF·3H$_2$O in THF (0.46 mL, 0.46 mmol). The reaction was completed after 15 h. After chromatographic purification using hexane/AcOEt (50/1) as an eluent, and then recycle GPC, a yellow solid of *trans*-**OPV3** [(*E*,*E*,*E*) > 99%] was obtained (222 mg, 57%). Mp: 56 °C. ^{1}H NMR ($CDCl_3$): δ 7.55−7.52 (m, 2H), 7.52 (s, 8H), 7.50 (d, J = 16.3 Hz, 2H), 7.49 (d, J = 16.1 Hz, 2H), 7.48 (d, J = 16.1 Hz, 1H), 7.39−7.43 (m, 2H), 7.28−7.23 (m, 1H), 7.16 (d, J = 3.0 Hz, 1H), 7.14 (d, J = 16.1 Hz, 2H), 7.14 (s, 2H), 7.12 (d, J = 16.3 Hz, 1H), 6.83 (d, J = 8.9 Hz, 2H), 6.77 (dd, J = 8.9, 2.9 Hz, 2H), 4.07 (t, J = 6.5 Hz, 4H), 3.98 (t, J = 6.5 Hz, 2H), 3.96 (t, J = 6.5 Hz, 2H), 1.93−1.74 (m, 12H), 1.61−1.24 (br, 60H), 0.91−0.87 (m, 18H). ^{13}C NMR ($CDCl_3$): δ 153.2, 151.1, 150.9, 137.9, 137.1, 128.7, 128.6, 128.4, 127.5, 127.4, 126.9, 126.8, 126.8, 126.5, 123.5, 123.4, 123,1, 114.4, 113.8, 112.2, 110.6, 110.5, 69.6, 69.5, 68.6, 31.8, 29.5, 29.4, 29.4, 29.3, 29.3, 29.3, 26.3, 26.3, 26.1, 22.7, 14.1. Anal. Calcd for $C_{62}H_{88}O_4$: C, 82.98; H, 9.88. Found: C, 82.60; H, 9.91.

1,4-Bis[(*E*)-4-[(*E*)-2,5-dioctyloxystyryl]styryl]-2,5-dioctyloxybenzene (*trans*-OPV4). This compound was synthesized similarly to *trans*-**OPV1**, starting from **3b** (157 mg, 0.265 mmol), **4c** [(*E*,*E*) > 99%] (427 mg, 0.582 mmol), THF (2.1 mL), [Pd(η^3-allyl)(μ-Cl)]$_2$ (4.9 mg, 13 μmol), and 1.0 M solution of TBAF·3H$_2$O in THF (0.58 mL, 0.58 mmol). The reaction was completed after 15 h. After chromatographic purification using hexane/CH_2Cl_2 (2/1) as an eluent, and then recycle GPC, a yellow solid of *trans*-**OPV4** [(*E*,*E*,*E*,*E*) > 99%] was obtained (143 mg, 44%). Mp: 90 °C. ^{1}H NMR ($CDCl_3$): δ 7.52 (s, 8H), 7.50 (d, J = 16.3 Hz, 2H), 7.48 (d, J = 16.3 Hz, 2H), 7.16 (d, J = 2.9 Hz, 2H), 7.14 (d, J = 16.3 Hz, 2H), 7.14 (s, 2H), 7.12 (d, J = 16.3 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H), 6.77 (dd, J = 8.9, 2.9 Hz, 2H), 4.07 (t, J = 6.5 Hz, 4H), 3.98 (t, J = 6.5 Hz, 2H), 3.96 (t, J = 6.5 Hz, 2H), 1.93−1.74 (m, 12H), 1.61−1.24 (br, 60H), 0.92−0.87 (m, 18H). ^{13}C NMR ($CDCl_3$): δ 153.3, 151.1, 150.9, 137.1, 137.1, 128.7, 128.4, 127.5, 126.9, 126.8, 126.8, 123.3, 123.2, 114.5, 113.8, 112.2, 110.5, 69.6, 69.5, 68.6, 31.8, 29.5, 29.4, 29.4, 29.3, 29.3, 29.3, 26.3, 26.3, 26.1, 22.7, 14.1. Anal. Calcd for $C_{86}H_{126}O_6$: C, 82.24; H, 10.11. Found: C, 82.14; H, 10.23.

Photoirradiation. A benzene solution of OPV (0.01 mM) was prepared in a quartz cell. Nitrogen gas was bubbled through the

solution at room temperature for 5 min. A Xe lamp ($\lambda = 365$ nm, 0.87 mW cm^{-2}) was used to irradiate the sample, and the photoisomerization was monitored by UV−vis absorption spectroscopy. The photoirradiation experiment was also performed with a more concentrated solution of OPV (0.10 mM) and a stronger UV light (21 mW cm^{-2}). After irradiation for 60 min under a nitrogen atmosphere, the solution was evaporated by pumping, and the residue was analyzed by ^1H NMR spectroscopy (see the Supporting Information).

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Supporting Information Available: General experimental method. Copies of ^1H and $^{13}C\{^1H\}$ NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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