A Synthetic Strategy Leading to Monodisperse PPV Oligomers by Coupling Reactions of Vinyltrimethylsilanes

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A novel strategy for the synthesis of well-defined oligo(phenylenevinylene)s was developed. The procedure is entirely based upon two coupling processes, both involving vinyltrimethylsilanes. Bis(styryl)benzenes **2a**−**g** bearing two octyloxy groups in the central aromatic ring and various substituents on the external aromatic rings were prepared in good yield by a regio- and stereoselective coupling reaction of **1** with different arenediazonium tetrafluoroborates. Oligomers with a more extended conjugated system, **4a**−**c**, and with *m*-phenylene subunits **13a**,**b**, were also readily obtained by conversion of the unsaturated trimethylsilyl derivatives **3a**,**c**,**d** to the corresponding boron derivatives and a subsequent coupling reaction with compounds **2a** and **2c**.

Introduction

Organic polymers possessing a long conjugated system are attracting a widespread interest due to their electrical and optical properties.[1] Despite these special features, in many cases the structural aspects of these materials are poorly defined and this uncertainty makes it difficult to establish firm structure−property relationships. For this purpose, conjugated monodisperse oligomers play a key role since a detailed knowledge of their molecular structure is more easily accessible with respect to their polymeric counterparts.[2] Moreover, conjugated oligomers may present the same electrical and optical features as those of the related polydisperse high molecular weight polymers.[3]

Recent reports have shown that poly(1,4-phenylenevinylene) (PPV) and its derivatives are among the most promising materials in organic electroluminescent devices technology,[3d,4,5] and therefore oligomeric models for these polymers have been studied, mainly in order to obtain structural information on the solid-state properties.[6] Furthermore, oligophenylenevinylenes, either pure[6b,7] or blended with polymers such as polystyrene[8] or PMMA,[9] have been successfully used in preparing emissive layers for organic light emitting diodes (OLED). Nonlinear optical properties[10] and amplified stimulated emission under pulsed optical excitations[3d,5c,11] have also been highlighted in some PPV oligomers.

These important features have stimulated the develop-

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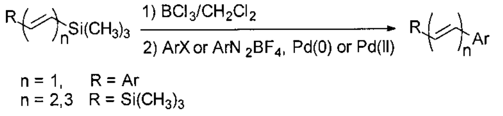
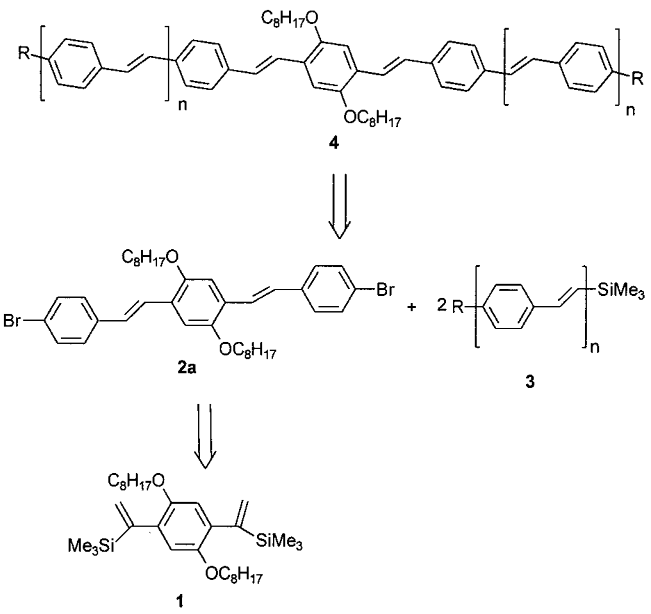
ment of various synthetic methods for PPV oligomers, mainly based upon the classical procedures used in organic chemistry to synthesize carbon–carbon double bonds of stilbene derivatives.[12] Thus, Wittig,[13] Horner–Wittig,[6c,14] McMurry,[15] and Heck[6c,16] synthetic strategies, as well as stepwise approaches requiring different reaction types for each step,[17] have been largely employed for the preparation of PPV oligomers, with various outcomes with regard to the regio- and stereoselectivity. Indeed, in some cases, variable amount of *cis* isomers are formed,[15,17b] which can be either converted to an *all-trans* isomer by iodine or a thermal isomerization reaction or separated by chromatography. Moreover, the Heck reaction generates small amounts of regioisomers.[16] Stereoselective approaches, such as cross-coupling reactions of unsaturated tin[5a,18] and boron[19] organometallic reagents, have mainly been employed, by us and by other workers, for preparing polydisperse materials rather than well-defined oligomers. On the contrary, although some regio- and stereoselective useful coupling reactions of vinylsilanes with various compounds have been reported, the potential use of silicon unsaturated derivatives for the synthesis of PPV oligomers and polymers so far has not been exploited. These reactions involve alkenylfluoro compounds,[20] alkoxysilanes,[21] or alkenylsilacyclobutanes[22] as starting materials since the simple trimethylsilyl unsaturated compounds are considered to be of poor synthetic interest as reagents for transition metal-catalyzed cross-coupling reactions.[23] To overcome this drawback, recently we developed a simple strategy by converting, in a stereoselective way, unsaturated silanes into boron derivatives, which are then coupled with organic halides[24] or arenediazonium tetrafluoroborates[25] in the presence of a Pd catalyst. It is worth noting that the whole procedure represents a formal Suzuki–Miyaura type cross-coupling reaction of vinyltrimethylsilanes (Scheme 1).

Scheme 1



In connection with our work on the synthesis of conjugated oligomers and polymers of potential interest in the field of materials for optical and electronic devices,[3d,5,26] in the present paper we report an unprecedented strategy for the stereoselective synthesis of monodisperse PPV oligomers **4** (Scheme 2), starting with unsaturated trimethylsilyl derivatives.

Scheme 2



Results and Discussion

Our synthetic approach to PPV oligomers is reported in the retrosynthetic Scheme 2.

A crucial role in Scheme 2 is represented by the bisstyryl derivative **2a**. In fact, beside contributing with two double bonds and three phenyl rings to the final structure, this compound bears two alkoxy substituents which are needed to increase the solubility of the final product.

The straightforward route leading to derivative **2a** is reported in Scheme 3. The diiodoarene **5** was converted into the corresponding organomagnesium derivative **6** and cross-coupled with commercially available 1-bromo-1-(trimethylsilyl)ethene **7** to give α,α′-bis(trimethylsilyl)-1,4-divinylbenzene **1**. This compound was subjected to reaction with *p*-bromobenzenediazonium tetrafluoroborate **8a** by adopting a procedure reported by Kikukawa and co-workers for the corresponding monosubstituted system, i.e., α-silylated styrenes.[27] As expected from the work previously reported,[27] the reaction was both regio- and stereoselective. Furthermore, in our case the reaction appeared to be also chemoselective since only the diazonium functional group was involved in the production of **2a**.

The procedure outlined in Scheme 3 represents a general methodology for the stereoselective synthesis of distyryl benzenes with various substituents on the external aromatic rings. For this reason, along the way leading to compounds of type **4**, it was considered of interest to investigate further examples of compounds of type **2** (Scheme 4).

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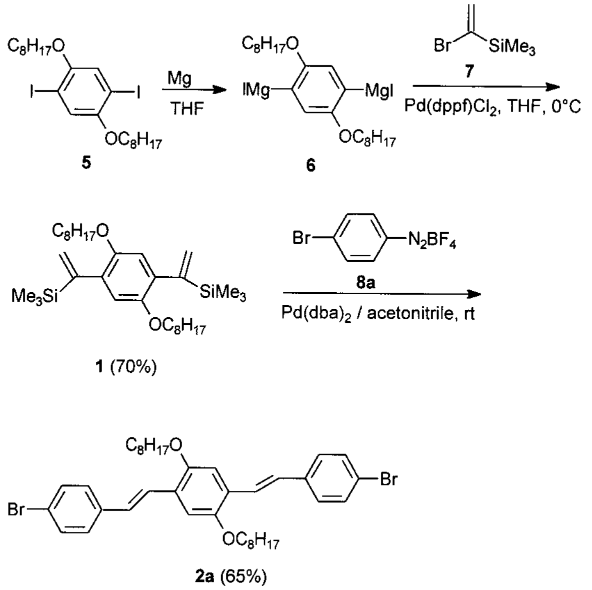
Scheme 3

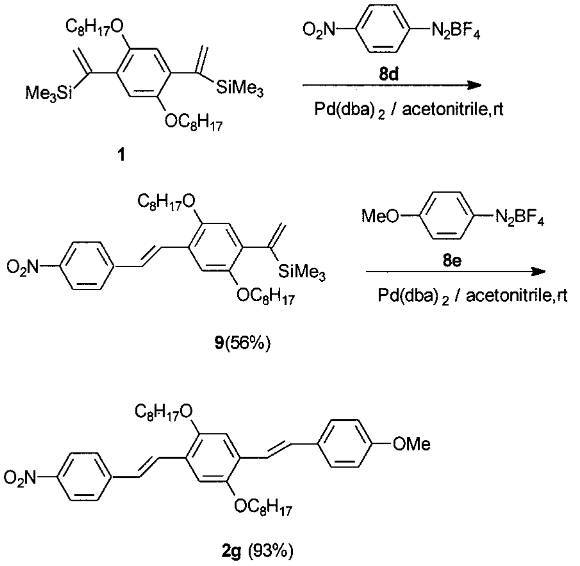


The results reported in Table 1 show that compounds **2b**–**f**, bearing either electron-donating or electron-withdrawing groups in the *meta* or *para* position were easily obtained in fair to good yields, according to a simple experimental protocol (see Experimental Section). Similar bis(styryl)benzenes with donor–π-donor or acceptor–donor–acceptor structural motifs have recently been demonstrated to be important NLO chromophores exhibiting exceptionally large values of two-photon absorption cross sections.[10b] As reported in Scheme 5, we have also proved that the reaction of **1** with *p*-nitrobenzenediazonium tetrafluoroborate **8d** is chemoselective, thus leading to compound **9**, which can then react with the diazonium salt **8e** to give the push–pull derivative **2g**.

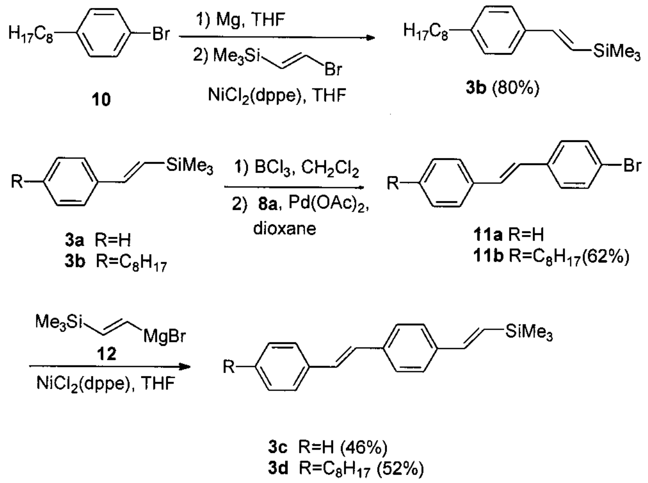
The extension of the conjugated system present in compound **2a**, according to the retrosynthetic Scheme 2, was carried out by using a coupling reaction with the silyl derivatives **3a**,**c**,**d** (Scheme 6).

The silane homologues **3c** and **3d** were easily prepared starting from **3a**[24a] and the octyl styrene **3b**, respectively (Scheme 6). The latter was obtained, as described in Scheme 6, by following the procedure previously reported by us for **3a**.[24a] The homologation process required, according to our protocol,[25] the conversion of the vinylsilanes **3a** and **3b** into the corresponding boron derivatives, by treatment with BCl_3 in dichloromethane at 0 °C, followed by a cross-coupling reaction with an arenediazonium salt (i.e., *p*-bromobenzenediazonium tetrafluoroborate **8a**). Both steps occurred stereoselectively.

Scheme 5



Scheme 6



In the final step, conversion of the 2-trimethylsilylstyrene[24a] **3a**, or its homologues **3c** and **3d**, into the corresponding boron counterparts followed by the cross-coupling reaction with the aromatic dihalide **2a** yielded the oligomers **4a**, **4b**, and **4c** with five or seven aromatic rings (Scheme 7). The low solubility of the derivative **4b**, in organic solvents, despite the presence of the two alkoxy chains, prevented its NMR characterization. On the contrary, the oligomer **4c**, with two additional alkyl chains on the external aromatic rings, showed a higher solubility, and ^1H and ^{13}C NMR spectra could be recorded for this compound.

It is worth noting that the transformation of **3a** or **3b** into **3c** or **3d**, respectively (Scheme 6), involved elongation of the chain with the styryl unit. In principle, the process could be further iterated. Since in the final cross-

Scheme 4

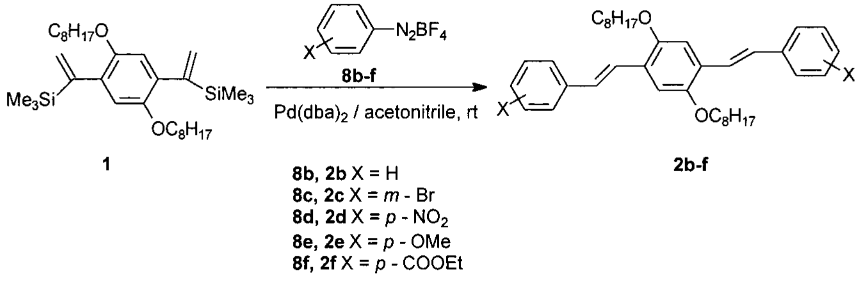
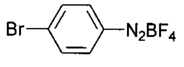
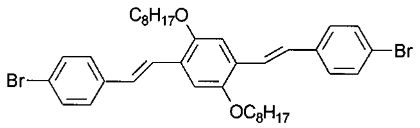
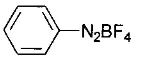
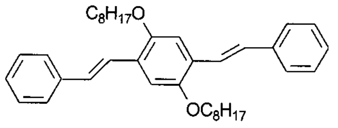
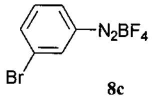
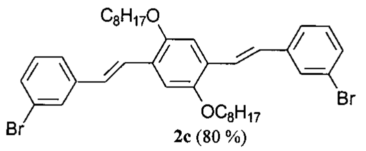
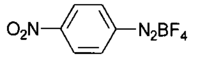
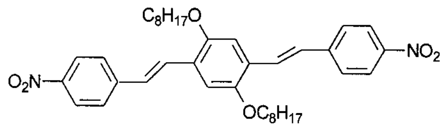
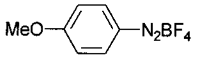
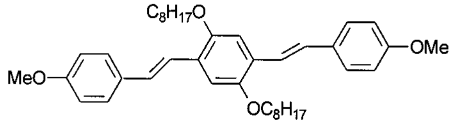
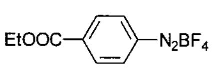
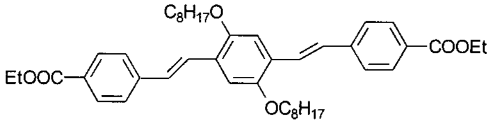
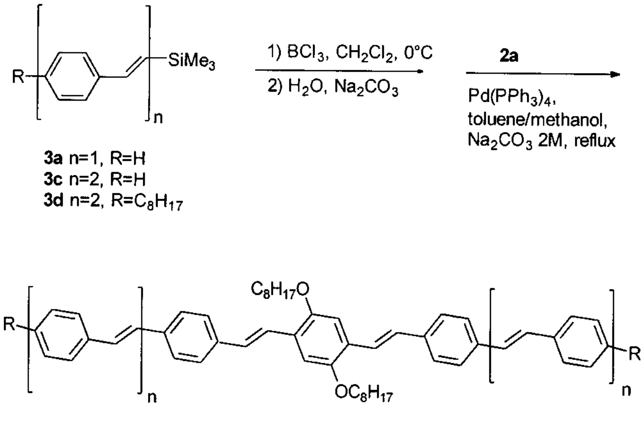


Table 1. Cross-Coupling Reactions of 1 with Arenediazonium Tetrafluoroborates

Diazonium tetrafluoroborate	Coupling products (yield%)
 **8a**	 **2a** (65 %)
 **8b**	 **2b** (56 %)
 **8c**	 **2c** (80 %)
 **8d**	 **2d** (45 %)
 **8e**	 **2e** (66 %)
 **8f**	 **2f** (83 %)

coupling (Scheme 7) two molecules of unsaturated silane **3** are required for one molecule of dibromo compound **2a**, each iteration would lead to an increase of two repeating units in the final chain. However, due to the risk of low solubility of the final product **4**, no efforts were made to reach *n* values higher than two.

Scheme 7

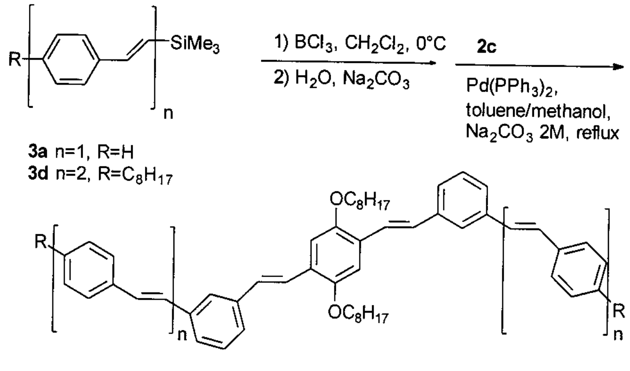


3a n=1, R=H
3c n=2, R=H
3d n=2, R=C_8H_{17}

4a n=1, R=H (66%)
4b n=2, R=H (83%)
4c n=2, R=C_8H_{17} (60%)

Finally, the reaction reported in Scheme 8 highlights an additional feature of our strategy. Indeed, by replacing **2a** with **2c** in the synthetic Scheme 2 the oligomers **13a** and **13b** were obtained. These compounds present the interesting structural variation of combining the *para*-with the *meta*-bridging substitution pattern on the same structure. In fact, the *meta*-bridging provides higher solubility and, acting as π-conjugation interrupter, has been demonstrated to induce charge localization both in

Scheme 8



3a n=1, R=H
3d n=2, R=C_8H_{17}

13a n=1 R=H (94%)
13b n=2 R= C_8H_{17} (58%)

neutral and in ionic (doped) compounds.[13c] Furthermore, this special situation of the conjugated system has been suggested to generate some particular interesting properties, such as ferromagnetism, on doped oligomers and polymers with *m*-phenylene subunits,[28] and a blue shift of the electroluminescence light emission in alkoxy-substituted poly(*p*-phenylenevinylene) containing some *meta*-linkages.[29]

Conclusions

PPV monodisperse oligomers **4** with up to seven aromatic rings have been obtained by following a synthetic strategy involving vinyltrimethylsilanes as building blocks. The aryldesilylation reaction of α,α'-bis(trimethylsilyl)-1,4-divinylbenzene **1** with arenediazonium tetrafluoroborates and the formal Suzuki–Miyaura cross-coupling process of β-styrylsilanes with aromatic halides and diazonium salts, following the protocol previously developed in our laboratories, represent two key reactions which are both based upon the use of vinylsilanes. Our methodology compares favorably with other synthetic approaches to this class of policonjugated compounds for the simplicity of the experimental procedure, the use of mild reaction conditions, and the regio- and stereoselectivity of the processes involved. Besides the final products **4**, functionalized distyrylbenzenes **2a**–**f** with electron-donating or electron-withdrawing substituents and push–pull oligomers such as **2g**, which are of potential interest in the field of materials having NLO properties,[10] are important compounds which become easily accessible by our procedure. Moreover, besides the oligomers **4a**–**c** containing only *para*-linkages, also compounds **13a**,**b**, with *m*-phenylene subunits in the π-chain, are now readily available through our methodology. Finally, our procedure, at least in principle, should be suitable for the preparation of longer chains.

Experimental Section

Silica gel 60 (particle size 0.040–0.063) for flash column chromatography and aluminum sheets with silica gel 60 F_{254} for TLC were used. GC analyses were performed on a gas chromatograph equipped with a SE-30 (methylsilicone, 30 m × 0.25 mm i.d.) capillary column. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ at 500 MHz and at 125 MHz, respectively, using the residual $CHCl_3$ as the standard at 7.24 ppm for ^1H spectra and the $CDCl_3$ signal at 77 ppm for ^{13}C spectra. To obtain reproducible results, it is recommended that commercial 1 M solutions of BCl_3 in methylene chloride be stored in a freezer under nitrogen over anhydrous Na_2CO_3. 1,4-Dioxane, tetrahydrofuran, and benzene were distilled from benzophenone ketyl immediately prior to use. Dichlorometane was distilled over phosphorus pentoxide and acetonitrile from 4 Å molecular sieves immediately prior to use. All reactions were performed under a nitrogen atmosphere. Arenediazonium tetrafluoroborates were prepared from commercial aromatic amines according to published methods.[30] If necessary, the salts were purified by several recrystallizations from acetone/diethyl ether and could be stored for several weeks at −4 °C. Bis(dibenzylideneacetone)palladium(0),[31] dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium(II),[32] 2-trimethysilylstyrene (**3a**),[24a] 1,4-bis(octyloxy)-2,5diiodobenzene (**5**),[33] 4-*n*-octylbromobenzene (**10**),[34] and 4-bromostilbene (**11a**)[25] were prepared as reported in the literature. (1-Bromovinyl)trimethylsilane (**7**), (2-bromovinyl)trimethylsilane, and tetrakis(triphenylphosphino)palladium(0) were commercial products.

1,4-Bis(octyloxy)-2,5-bis(1-trimethylsilylethenyl)benzene (1). In a flame-dried flask was suspended magnesium (0.450 g, 18.51 mmol) in anhydrous THF (15 mL) in a nitrogen atmosphere. A solution of 1,4-bis(octyloxy)-2,5diiodobenzene (**5**) (3.501 g, 5.97 mmol) in THF (45 mL) was added dropwise under gentle reflux. After addition completion, the mixture was further refluxed for 1 h. The resulting solution of the diorganomagnesium reagent **6** was added dropwise to a vigorously stirred suspension of (1-bromovinyl)trimethylsilane (**7**) (2.670 g, 14.91 mmol) and $PdCl_2(dppf)$ (0.270 g, 0.37 mmol) in THF (20 mL) at 0 °C. The resulting mixture was warmed to room temperature and stirred for 4 h. After this time the reaction was quenched with water (100 mL), and the organic phase was extracted with ethyl acetate (3 × 40 mL) and dried over anhydrous sodium sulfate. The solvent was removed at reduced pressure and the residue crystallized from methanol. A total of 2.21 g (70% yield) of **1** was recovered (mp 69–70 °C). GC/MS (70 eV) *m*/*e* 530 (M^+, 100), 73 (75), 43 (48). IR (KBr): ν 1495, 1471, 1394, 1247, 1005, 889, 837 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 0.09 (s, 18H), 0.87 (t, $J = 6.8$ Hz, 6H), 1.18–1.44 (m, 20H), 1.71 (quintet, $J = 6.4$ Hz, 4H), 3.84 (t, $J = 6.9$ Hz, 4H), 5.60 (d, $J = 3.2$ Hz, 2H), 5.75 (d, $J = 3.2$ Hz, 2H), 6.44 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ −0.68, 14.09, 22.65, 26.10, 29.25, 29.39, 29.47, 31.61, 69.00, 112.83, 127.18, 133.13, 149.02, 152.52 ppm. Anal. Calcd for $C_{32}H_{58}O_2Si_2$: C, 72.38; H, 11.01. Found: C, 72.15; H, 10.94.

(*E*,*E*)-1,4-Bis(octyloxy)-2,5-bis[2-(4-bromophenyl)ethenyl]benzene (2a). Silane **1** (0.250 g, 0.47 mmol), 4-bromophenyldiazonium tetrafluoroborate **8a** (0.318 g, 1.17 mmol), and $Pd(dba)_2$ (0.067 g, 0.12 mmol) were dissolved in dry acetonitrile (10 mL), at room temperature, under a nitrogen atmosphere. After 30 min, a yellow-green solid precipitated from the reaction mixture. This solid was filtered, washed with acetonitrile (10 mL), and purified by flash chromatography (petroleum ether/dichloromethane 9/1 as eluent). A yellow solid was obtained (0.212 g, 65% yield; mp 123–125 °C from methanol). IR (KBr): ν 1627, 1425, 1205, 1072, 807 cm^{-1}. λ_{max} ($CHCl_3$): 391, 327 nm. ^1H NMR ($CDCl_3$, 500 MHz): δ 0.95–1.9 (m, 30H), 4.05 (t, $J = 6.5$ Hz, 4H), 7.05 (d, $J = 16.5$, Hz, 2H), 7.07 (s, 2H), 7.37 (d, $J = 8.4$ Hz, 4H), 7.43 (d, $J = 16.5$ Hz, 2H), 7.46 (d, $J = 8.4$ Hz, 4H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.17, 22.75, 26.36, 29.39, 29.48, 29.54, 31.89, 69.62, 110.74, 121.16, 124.28, 126.81, 127.74, 128.03, 131.81, 136.97, 151.20 ppm. Anal. Calcd for $C_{38}H_{48}O_2Br_2$: C, 65.52; H, 6.95. Found: C, 65.36; H, 6.83.

(*E*,*E*)-1,4-Bis(octyloxy)-2,5-bis(2-phenylethenyl)benzene (2b). The compound was prepared starting from **1** (0.237 g, 0.45 mmol), phenyldiazonium tetrafluoroborate **8b** (0.224 g, 1.17 mmol), and $Pd(dba)_2$ (0.069 g, 0.12 mmol) in dry acetonitrile (15 mL) at room temperature (30 min reaction time). The crude product was purified by flash chromatography (ethyl acetate/petroleum ether 9/1). A pale yellow solid was obtained (0.136 g, 56% yield; mp 120–122 °C from methanol). IR (KBr): ν 1592, 1182, 1057, 962, 759 cm^{-1}. λ_{max} ($CHCl_3$): 391, 322 nm. ^1H NMR ($CDCl_3$, 500 MHz): δ 0.90 (t, $J = 6.9$ Hz, 6H), 1.24–1.42 (m, 16H), 1.53–1.62 (m, 4H), 1.90 (quintet, $J = 6.5$ Hz, 4H), 4.06 (t, $J = 6.5$ Hz, 4H), 7.15 (d, $J = 16.4$ Hz, 2H), 7.13 (s, 2H), 7.26 (t, $J = 7.5$ Hz, 2H), 7.37 (t, $J = 7.5$ Hz, 4H), 7.5 (d, $J = 16.4$ Hz, 2H), 7.54 (d, $J = 7.5$ Hz, 4H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 151.05, 137.92, 128.61, 127.33, 126.72, 126.43, 123.44, 110.51, 69.58, 31.82, 29.50, 29.46, 29.29, 26.34, 22.71, 14.15 ppm. Anal. Calcd for $C_{38}H_{50}O_2$: C, 84.71; H, 9.35. Found: C, 84.49; H, 9.17.

(*E*,*E*)-1,4-Bis(octyloxy)-2,5-bis[2-(3-bromophenyl)ethenyl)]benzene (2c). The compound was prepared starting from

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1 (0.350 g, 0.66 mmol), 3-bromophenyldiazonium tetrafluoroborate **8c** (0.458 g, 1.69 mmol), and Pd(dba)$_2$ (0.097 g, 0.16 mmol) in dry acetonitrile (12 mL) at room temperature (30 min reaction time). The crude product was purified by flash chromatography (dichloromethane/petroleum ether 1/8). A yellow solid was obtained (0.370 g, 80% yield; mp 98−100 °C from ethanol). IR (KBr): ν 1588, 1474, 1426, 1205, 1156, 966, 880 cm^{-1}. λ_{max} (CHCl$_3$): 391, 328 nm. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 0.86 (t, J = 6.8 Hz, 6H), 1.19−1.46 (m, 16H), 1.49−1.59 (m, 4H), 1.86 (quintet, J = 6.5 Hz, 4H), 4.03 (t, J = 6.5 Hz, 4H), 7.05 (d, J = 16.4 Hz, 2H), 7.07 (s, 2H), 7.20 (m, 2H), 7.33−7.37 (m, 2H), 7.41−7.44 (m, 2H), 7.42 (d, J = 16.4 Hz, 2H), 7.62−7.67 (m, 2H) ppm. ^{13}C NMR (CDCl$_3$, 125 MHz): δ 14.10, 22.67, 26.30, 29.32, 29.42, 29.44, 31.81, 69.48, 110.74, 122.85, 124.92, 125.01, 126.62, 127.44, 129.33, 130.07, 130.15, 140.11, 151.13 ppm. Anal. Calcd for $C_{38}H_{48}O_2Br_2$: C, 65.52; H, 6.95. Found: C, 65.34; H, 6.73.

(*E,E*)-1,4-Bis(octyloxy)-2,5-bis[2-(4-nitrophenyl)ethenyl]benzene (2d). The compound was prepared starting from **1** (0.300 g, 0.56 mmol), 4-nitrophenyldiazonium tetrafluoroborate **8d** (0.337 g, 1.42 mmol), and Pd(dba)$_2$ (0.082 g, 0.14 mmol) in dry acetonitrile (20 mL) at room temperature (45 min reaction time). The crude product was purified by flash chromatography (ethyl acetate/petroleum ether 9/1). A red solid was obtained (0.160 g, 45% yield; mp 185−186 °C from ethyl acetate/petroleum ether). IR (KBr): ν 1625, 1591, 1510, 1426, 1336, 1261, 1215, 1108, 970 cm^{-1}. λ_{max} (CHCl$_3$): 438, 350 nm. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 0.87 (t, J = 6.8 Hz, 6H), 1.21−1.61 (m, 20H), 1.88 (quintet, J = 6.5 Hz, 4H), 4.07 (t, J = 6.5 Hz, 4H), 7.12 (s, 2H), 7.20 (d, J = 16.4 Hz, 2H), 7.61 (d, J = 16.4 Hz, 2H), 7.62 (d, J = 8.8 Hz, 4H), 8.21 (d, J = 8.8 Hz, 4H) ppm. ^{13}C NMR (CDCl$_3$, 125 MHz): δ 14.09, 22.66, 26.27, 29.30, 29.37, 31.80, 69.45, 110.79, 124.15, 126.79, 126.82, 127.02, 127.96, 144.34, 146.63, 151.45 ppm. Anal. Calcd for $C_{38}H_{48}N_2O_6$: C, 72.58; H, 7.69; N, 4.46. Found: C, 72.35; H, 7.39; N, 4.23.

(*E,E*)-1,4-Bis(octyloxy)-2,5-bis[2-(4-methoxyphenyl)ethenyl]benzene (2e). The compound was prepared starting from **1** (0.430 g, 0.81 mmol), 4-methoxyphenyldiazonium tetrafluoroborate **8e** (0.450 g, 2.03 mmol), and Pd(dba)$_2$ (0.117 g, 0.20 mmol) in dry acetonitrile (15 mL) at room temperature (15 min reaction time). The crude product was purified by flash chromatography (ethyl acetate/petroleum ether 2/8). A yellow solid was obtained (0.320 g, 66% yield; mp 112−113 °C from methanol). IR (KBr): ν 1604, 1511,1424, 1259, 1176, 1032, 821, 805 cm^{-1}. λ_{max} (CHCl$_3$): 357, 310 nm. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 0.86 (t, J = 6.8 Hz, 6H), 1.22−1.61 (m, 20H), 1.84 (quintet, J = 6.5 Hz, 4H), 3.82 (s, 6H), 4.02 (t, J = 6.5 Hz, 4H), 6.88 (d, J = 8.7 Hz, 4H), 7.06 (d, J = 16.4 Hz, 2H), 7.08 (s, 2H), 7.32 (d, J = 16.4 Hz, 2H), 7.45 (d, J = 8.7 Hz, 4H) ppm. ^{13}C NMR (CDCl$_3$, 125 MHz): δ 14.11, 22.68, 26.29, 29.31, 29.42, 29.53, 31.81, 55.29, 69.61, 110.47, 114.07, 121.43, 126.62, 127.67, 128.08, 130.86, 150.93, 159.10 ppm. Anal. Calcd for $C_{40}H_{54}O_4$: C, 80.22; H, 9.09. Found: C, 79.97; H, 8.98.

(*E,E*)-1,4-Bis(octyloxy)-2,5-bis[2-(4-carboethoxyphenyl)ethenyl]benzene (2f). The compound was prepared starting from **1** (0.700 g, 1.32 mmol), 4-carboethoxyphenyldiazonium tetrafluoroborate **8f** (0.871 g, 3.30 mmol), and Pd(dba)$_2$ (0.190 g, 0.33 mmol) in dry acetonitrile (30 mL) at room temperature (30 min reaction time). The crude product was purified by flash chromatography (ethyl acetate/petroleum ether 9/1). A yellow solid was obtained (0.750 g, 83% yield; mp 126−128 °C from methanol). IR (KBr): ν 1707, 1601, 1275, 1104, 1019, 803, 769 cm^{-1}. λ_{max} (CHCl$_3$): 406, 336 nm. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 0.86 (t, J = 6.9 Hz, 6H), 1.20−1.43 (m, 16H), 1.38 (t, J = 7.1 Hz, 6H), 1.49−1.56 (m, 4H), 1.86 (quintet, J = 6.4 Hz, 4H), 4.05 (t, J = 6.5 Hz, 4H), 4.36 (q, J = 7.1 Hz, 4H), 7.11 (s, 2H), 7.15 (d, J = 16.4 Hz, 2H), 7.55 (d, J = 8.7 Hz, 4H), 7.56 (d, J = 16.4 Hz, 2H), 8.01 (d, J = 8.7 Hz, 4H) ppm. ^{13}C NMR (CDCl$_3$, 125 MHz): δ 14.09, 14.34, 22.66, 26.28, 29.31, 29.39, 29.44, 31.80, 60.87, 69.51, 110.69, 125.87, 126.24, 126.84, 127.98, 129.03, 129.95, 142.28, 151.27, 166.43 ppm. Anal. Calcd for $C_{44}H_{58}O_6$: C, 77.38; H, 8.56. Found: C, 77.53; H, 8.74.

1,4-Bis(octyloxy)-2-(1-trimethylsilyl-ethenyl)-5-[(1*E*)-2-(4-nitrophenyl)ethenyl]benzene (9). The compound was prepared starting from **1** (0.900 g, 1.70 mmol), 4-nitrophenyldiazonium tetrafluoroborate **8d** (0.300 g, 1.27 mmol), and Pd(dba)$_2$ (0.098 g, 0.17 mmol) in dry acetonitrile (25 mL) at room temperature (20 min reaction time). The crude product was purified by flash chromatography (ethyl acetate/petroleum ether 1/9). A yellow solid was obtained (0.412 g, 56% yield; mp 112−113 °C from methanol). IR (KBr): ν 1617, 1508, 1407, 1261, 1158 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 0.08 (s, 9H), 0.82−0.99 (m, 6H), 1.18−1.59 (m, 20H), 1.76 (quintet, J = 7.0 Hz, 2H), 1.82 (quintet, J = 6.5 Hz, 2H), 3.92 (t, J = 6.8 Hz, 2H), 3.98 (t, J = 6.5 Hz, 2H), 5.63 (d, J = 3.1 Hz, 1H), 5.75 (d, J = 3.1 Hz, 1H), 6.55 (s, 1H), 6.99 (s, 1H), 7.13 (d, J = 16.5 Hz, 1H), 7.60 (d, J = 7.0 Hz, 2H), 7.61 (d, J = 16.5 Hz, 1H), 8.19 (d, J = 7.0 Hz, 2H) ppm. ^{13}C NMR (CDCl$_3$, 125 MHz): δ −0.75, 14.10, 22.66, 26.10, 26.27, 29.26, 29.30, 29.38, 29.45, 29.90, 31.80, 69.03, 69.37, 109.54, 113.92, 123.52, 124.13, 125.50, 126.60, 127.71, 128.68, 137.29, 144.89, 146.37, 149.60, 151.23, 152.31 ppm. Anal. Calcd for $C_{35}H_{53}NO_4Si$: C, 72.49; H, 9.21; N, 2.42. Found: C, 72.36; H, 9.02; N, 2.18.

(*E,E*)-1,4-Bis(octyloxy)-2-[2-(4-methoxyphenyl)ethenyl]-5-[2-(4-nitrophenyl)ethenyl]benzene (2g). The compound was prepared starting from **9** (0.100 g, 0.17 mmol), 4-methoxyphenyldiazonium tetrafluoroborate **8e** (0.150 g, 0.68 mmol), and Pd(dba)$_2$ (0.005 g, 0.01 mmol) in dry acetonitrile (15 mL) at room temperature (20 min reaction time). The crude product was purified by flash chromatography (ethyl acetate/petroleum ether 2/8). A red solid was obtained (0.097 g, 93% yield; mp103−104 °C from ethanol). IR (KBr): ν 1586, 1513, 1377, 1205, 1110, 959 cm^{-1}. λ_{max} (CHCl$_3$): 431, 335 nm. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 0.78−0.89 (m, 6H), 1.23−1.42 (m, 20H), 1.44−1.58 (m, 2H), 1.82−1.92 (m, 2H), 3.82 (s, 3H), 4.03 (t, J = 6.5 Hz, 2H), 4.06 (t, J = 6.5 Hz, 2H), 6.88−6.91 (m, 2H), 7.07 (s, 1H), 7.09 (s, 1H), 7.10 (d, J = 16.9 Hz, 1H), 7.15 (d, J = 16.5 Hz, 1H), 7.32 (d, J = 16.5 Hz, 1H), 7.44−7.47 (m, 2H), 7.59−7.62 (m, 2H), 7.61 (d, J = 16,9 Hz, 1H), 8.18−8.21 (m, 2H) ppm. ^{13}C NMR (CDCl$_3$, 125 MHz): δ 14.10, 22.67, 26.29, 29.31, 29.40, 29.69, 32.73, 55.32, 69.43, 69.65, 110.21, 111.03, 114.15, 121.11, 124.14, 124.94, 125.97, 126.67, 127.84, 128.84, 129.21, 130.57, 131.51, 144.73, 146.44, 150.83, 151.67, 159.38 ppm. Anal. Calcd for $C_{39}H_{51}NO_5$: C, 76.31; H, 8.37; N, 2.28. Found: C, 76.54; H, 8.57; N, 2.34.

(*E*)-2-(4-*n*-Octylphenyl)-1-trimethylsilylethene (3b). This product was prepared following the procedure reported for compound **3a**.[24a] A yellow oil was obtained, which was purified by distillation in a Kughelroh apparatus (oven temp 150 °C, 10^{-3} mbar; 80% yield). IR (neat): ν 1608, 986, 868, 836 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 0.18 (s, 9H), 0.91 (t, J = 7.2 Hz, 3H), 1.22−1.39 (m, 10H), 1.57−1.66 (m, 2H), 2.61 (t, J = 7.6 Hz, 2H), 6.45 (d, J = 19.1 Hz, 1H), 6.98 (d, J = 19.1 Hz, 1H), 7.16 (d, J = 7.9 Hz, 2H), 7.38 (d, J = 7.9 Hz, 2H) ppm. Anal. Calcd for $C_{19}H_{32}Si$: C, 79.09; H, 11.18. Found: C, 78.98; H, 11.05.

(*E*)-4-[2-(*E*)-Trimethylsilylethenyl]stilbene (3c). A solution of (*E*)-2-trimethylsilylvinylmagnesium bromide **12** (11 mL, 0.655 M, 7.20 mmol) in THF was added dropwise to a stirred solution of (*E*)-4-bromostilbene **11a** (0.900 g, 3.47 mmol) and NiCl$_2$(dppe) (0.218 g, 0.41 mmol) in anhydrous THF (17 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 12 h. After reaction completion (revealed by GC analysis), water (30 mL) was added to the reaction mixture and the organic phase was extracted with ethyl acetate (3 × 20 mL). The combined extracts were dried over anhydrous sodium sulfate and the solvent was removed at reduced pressure. The product was purified by flash chromatography (petroleum ether). A white solid was obtained (0.444 g, 46% yield; mp 147−150 °C from ethanol). IR (KBr): ν 1626, 1251, 1242, 992, 969, 831, 797 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 0.15 (s, 9H), 6.48 (d, J = 19.1 Hz, 1H), 6.85 (d, J = 19.10 Hz, 1H), 7.07 (d, J = 16.4 Hz, 1H), 7.11 (d, J = 16.4 Hz, 1H), 7.21−7.27 (m, 1H), 7.32−7.37 (m, 2H), 7.41 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.3 Hz, 2H), 7.48−7.52 (m, 2H) ppm. ^{13}C NMR (CDCl$_3$, 125 MHz): δ −1.23, 126.48, 126.68, 127.61, 128.30, 128.58, 128.68, 129.55, 136.95, 137.31, 137.67, 143.09 ppm. Anal. Calcd for $C_{19}H_{22}Si$: C, 81.95; H, 7.96. Found: C, 81.87; H, 7.79.

(*E*)-4-Bromo-4′-*n*-octylstilbene (11b). BCl_3 (8.50 mL of a 1 M solution in CH_2Cl_2, 8.50 mmol) was added dropwise to a stirred solution of **3b** (2.000 g, 6.93 mmol) in anhydrous CH_2Cl_2 (60 mL) at 0 °C under a nitrogen atmosphere. After 30 min, a saturated aqueous solution of Na_2CO_3 (20 mL) and then water (10 mL) were added. The organic phase was extracted with CH_2Cl_2 (3×30 mL) and dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The resulting crude boron derivative, 4-bromobenzenediazonium tetrafluoroborate **8a** (1.200 g, 4.45 mmol), and palladium acetate (0.065 g, 0.29 mmol) were dissolved under a nitrogen atmosphere in dry dioxane (15 mL) at room temperature. The resulting mixture was stirred for 24 h. After reaction completion (revealed by GC analysis), water (30 mL) was added to the reaction mixture and the organic phase was extracted with ethyl acetate (3×30 mL). The combined extracts were dried over anhydrous sodium sulfate, and the solvent was removed at reduced pressure. The product was purified by flash chromatography (petroleum ether). A white solid was obtained (1.019 g, 62% yield; mp 147−150 °C from ethanol). IR (KBr): ν 1510, 1487, 1467, 970, 827 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 0.86 (t, $J = 6.9$ Hz, 3H), 1.22−1.38 (m, 10H), 1.56−1.64 (m, 2H), 2.59 (t, $J = 7.7$ Hz, 2H), 6.97 (d, $J = 16.3$ Hz, 1H), 7.06 (d, $J = 16.3$ Hz, 1H), 7.15 (d, $J = 8.1$ Hz, 2H), 7.32−7.37 (m, 2H), 7.40 (d, $J = 8.1$ Hz, 2H), 7.42−7.47 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.10, 22.66, 29.25, 29.30, 29.47, 31.39, 31.87, 35.74, 121.10, 126.41, 126.47, 127.85, 128.80, 129.39, 131.72, 134.36, 136.49, 143.00 ppm. Anal. Calcd for $C_{22}H_{27}Br$: C, 71.15; H, 7.33. Found: C, 71.33; H, 7.55.

(*E*)-4-[(*E*)-2-(Trimethylsilyl)ethenyl]-4′-*n*-octylstilbene (3d). This compound was prepared by following the procedure reported for **3c**, starting from **11b** (0.497 g, 1.34 mmol), $NiCl_2$(dppe) (0.050 g, 0.10 mmol) in anhydrous THF (9 mL), and a THF solution of (*E*)-2-trimethylsilylvinylmagnesium bromide **12** (6 mL, 0.54 M, 3.24 mmol). A white solid was obtained (0.272 g, 52% yield; mp 87−90 °C from ethanol). IR (KBr): ν 1598, 1514, 1248, 989, 968, 868, 837 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 0.16 (s, 9H), 0.88 (t, $J = 6.7$ Hz, 3H), 1.22−1.38 (m, 10H), 1.48−1.67 (m, 2H), 2.60 (t, $J = 7.7$ Hz, 2H), 6.49 (d, $J = 19.1$ Hz, 1H), 6.87 (d, $J = 19.1$ Hz, 1H), 7.04 (d, $J = 16.3$ Hz, 1H), 7.10 (d, $J = 16.3$ Hz, 1H), 7.14−7.21 (m, 2H), 7.38−7.48 (m, 6H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ −1.20, 14.13, 22.69, 29.29, 29.35, 29.51, 31.44, 31.90, 35.76, 126.43, 126.57, 126.69, 127.35, 128.60, 128.77, 129.33, 134.74, 137.21, 137.46, 142.70, 143.17 ppm. Anal. Calcd for $C_{27}H_{38}Si$: C, 83.01; H, 9.80. Found: C, 82.81; H, 9.68.

1,4-Bis(octyloxy)-2,5-bis[(1*E*)-2-[4-(1*E*)-2-phenylethenyl]phenylethenyl]benzene (4a). BCl_3 (0.33 mL of a 1 M solution in CH_2Cl_2, 0.33 mmol) was added dropwise at 0 °C under a nitrogen atmosphere to a stirred solution of (*E*)-1-trimethylsilyl-2-phenylethene **3a** (0.39 g, 0.22 mmol) in anhydrous CH_2Cl_2 (3 mL). After 4 h, a saturated aqueous solution of Na_2CO_3 (3 mL) was added, followed by water (10 mL). The organic phase was extracted with CH_2Cl_2 (3×10 mL) and dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The resulting crude boron derivative, compound **2a** (0.071 g, 0.102 mmol), and $Pd(PPh_3)_4$ (0.024 g, 0.021 mmol) were suspended under a nitrogen atmosphere in a mixture of toluene (3.3 mL) and methanol (3.3 mL), and an aqueous solution of Na_2CO_3 (2M 1.8 mL) was added dropwise at room temperature. The resulting mixture was refluxed for 5 h; then water (50 mL) was added. The organic phase was extracted with ethyl acetate (3×10 mL) and dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (petroleum ether/dichloromethane 7/3). A bright yellow solid was obtained (0.050 g, 66% yield; mp 168−170 °C from ethanol). The spectroscopic data are consistent with those reported in the literature.[13d]

IR (KBr): ν 1592, 1511, 1425, 1343, 1203, 963 cm^{-1}. λ_{max} ($CHCl_3$): 419, 391 nm. ^1H NMR ($CDCl_3$, 500 MHz): δ 0.89 (t, $J = 6.8$ Hz, 6H), 1.22−1.47 (m, 16H), 1.52−1.62 (m, 4H), 1.88 (quintet, $J = 6.4$ Hz, 4H), 4.06 (t, $J = 6.4$ Hz, 4H), 7.07−7.19 (m, 8H), 7.23−7.28 (m, 2H), 7.33−7.28 (m, 4H), 7.47−7.54 (m, 14H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.12, 22.69, 26.31, 29.33, 29.44, 29.52, 31.83, 69.57, 110.56, 123.39, 126.48, 126.82, 126.92, 127.57, 128.33, 128,37, 128.67, 136.43, 137.36, 137.39, 151.13 ppm. Anal. Calcd for $C_{54}H_{62}O_2$: C, 87.28; H, 8.41. Found: C, 87.37; H, 8.73.

1,4-Bis(octyloxy)-2,5-bis[(1*E*)-2-[4-(1*E*)-2-[4-(1*E*)-2-phenylethenyl]phenylethenyl]phenylethenyl]benzene (4b). BCl_3 (0.67 mL of a 1 M solution in CH_2Cl_2, 0.67 mmol) was added dropwise at 0 °C to a stirred solution of (*E*)-4-[2-(*E*)-trimethylsilylethenyl]stilbene **3c** (0.156 g, 0.56 mmol) in anhydrous CH_2Cl_2 (5 mL). After 30 min a saturated aqueous solution of Na_2CO_3 (1.5 mL) was added, followed by water (10 mL). The organic phase was extracted with CH_2Cl_2 (3×10 mL) and dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The resulting crude boron derivative, compound **2a** (0.056 g, 0.08 mmol), and $Pd(PPh_3)_4$ (0.023 g, 0.02 mmol) were suspended under a nitrogen atmosphere in a mixture of toluene (5 mL) and methanol (5 mL), and an aqueous solution of Na_2CO_3 (2 M, 1.5 mL) was added dropwise at room temperature. The resulting mixture was refluxed for 2 h and then water was added. A deep yellow solid, insoluble in organic solvents, was filtered and purified by extraction with chloroform in a Soxhlet apparatus (0.063 g, 83% yield; mp 270 °C dec). IR (KBr): ν 1590, 1515, 1201, 964, 821, 803 cm^{-1} Anal. Calcd for $C_{70}H_{74}O_2$: C, 88.75; H, 7.87. Found: C, 88.93; H, 7.92.

1,4-Bis(octyloxy)-2,5-bis[(1*E*)-2-[4-(1*E*)-2-[4-(1*E*)-2-(4-*n*-octyl)phenylethenyl]phenylethenyl]phenylethenyl]benzene (4c). This product was prepared by following the procedure reported for **4a**. The boron derivative was prepared from **3d** (0.082 g, 0.21 mmol), BCl_3 (0.27 mL of a 1 M solution in CH_2Cl_2, 0.27 mmol), and aqueous Na_2CO_3 (0.7 mL, 2 M). The subsequent coupling reaction was performed with **2a** (0.049 g, 0.07 mmol), $Pd(PPh_3)_4$ (0.012 g, 0.01 mmol), and aqueous Na_2CO_3 (0.7 mL, 2 M) in toluene/methanol (1/1 mixture 10 mL). The crude product was purified by flash chromatography (petroleum ether/dichloromethane 7/3), followed by extraction with chloroform in a Soxhlet apparatus. A deep yellow solid was obtained (0.049 g, 60% yield; mp 218−220 °C from dichloromethane/diethyl ether). IR (KBr): ν 1580, 1516, 1194, 966, 827 cm^{-1}. λ_{max} ($CHCl_3$): 432 nm. ^1H NMR ($CDCl_3$, 500 MHz): δ 0.88 (t, $J = 7.1$ Hz, 6H), 0.89 (t, $J = 7.0$ Hz, 6H), 1.22−1.68 (m, 44H), 1.88 (quintet, $J = 7.0$ Hz, 4H), 2.60 (t, $J = 7.6$ Hz, 4H), 4.06 (t, $J = 6.3$ Hz, 4H), 7.02−7.19 (m, 16H), 7.38−7.55 (m, 22H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.04, 22.66, 26.38, 29.26, 29.34, 29.48, 29.63, 31.37, 31.90, 35.79, 69.85, 111.04, 123.67, 126.50, 126.60, 126.67, 127.26, 127.47, 128.21, 128.27, 128.56, 128.80, 134.94, 136.69, 137.11, 137.58, 142.77, 151.39 ppm. Anal. Calcd for $C_{86}H_{106}O_2$: C, 88.15; H, 9.12. Found: C, 88.36; H, 9.27.

1,4-Bis(octyloxy)-2,5-bis[(1*E*)-2-[3-(1*E*)-2-phenylethenyl]phenylethenyl]benzene (13a). The product was prepared by following the procedure reported for the oligomer **4a**, using the *m*-bromo derivative **2c** instead of **2a**. A green-yellow solid was obtained (0.071 g, 94% yield; mp 149−150 °C from ethanol). IR (KBr): ν 1631, 1587, 1498, 1474, 1426, 1334, 1205, 966 cm^{-1}. λ_{max} ($CHCl_3$): 391, 349 nm. ^1H NMR ($CDCl_3$, 500 MHz): δ 0.79−0.92 (m, 6H), 1.27−1.62 (m, 20H), 1.87 (quintet, $J = 6.5$ Hz, 4H), 4.07 (t, $J = 6.5$ Hz, 4H), 7.09−7.20 (m, 8H), 7.24−7.27 (m, 2H), 7.32−7.46 (m, 10H), 7.49−7.54 (m, 6H), 7.62−7.65 (m, 2H) ppm. Anal. Calcd for $C_{54}H_{62}O_2$: C, 87.28; H, 8.41. Found: C, 87.07; H, 8.33.

1,4-Bis(octyloxy)-2,5-bis[(*E*)-2-[4-(1*E*)-2-[3-(1*E*)-2-(4-*n*-octyl)phenylethenyl]phenylethenyl]phenylethenyl]benzene (13b). This product was prepared by following the procedure reported for **4c**, using the *m*-bromo derivative **2c** instead of **2a**. The crude product was purified by flash chromatography (petroleum ether/dichloromethane 7/3). A green-yellow solid was obtained (0.048 g, 58% yield; mp 224−226 °C from dichloromethane/diethyl ether). IR (KBr): ν 1580, 1515, 1205, 966, 823 cm^{-1}. λ_{max} ($CHCl_3$): 364 nm. ^1H NMR

($CDCl_3$, 500 MHz): δ 0.61−0.92 (m, 12H), 1.20−1.65 (m, 44H), 1.84−1.94 (m, 4H), 2.60 (t, $J = 7.7$ Hz, 4H), 4.08 (t, $J = 6.5$ Hz, 4H), 7.03−7.19 (m, 16H), 7.32−7.54 (m, 20 H), 7.64 (br s, 2H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 13.92, 22.54, 26.27, 29.14, 29.23, 29.37, 29.52, 29.58, 31.25, 31.57, 31.78, 35.67, 69.75, 111.12, 124.02, 124.87, 125.44, 125.58, 126.38, 126.67, 126.79, 127.10, 127.34, 128.41, 128.60, 128.68, 128.77, 128.87, 134.80, 136.50, 137.06, 137.76, 138.44, 142.66, 151.40 ppm. Anal. Calcd for $C_{86}H_{106}O_2$ C: 88.15; H 9.12. Found: C 88.22; H 9.17.

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