JOC Article

Efficient and Rapid Synthesis of Oligo(*p*-phenylenevinylene) via Iterative Coherent Approach

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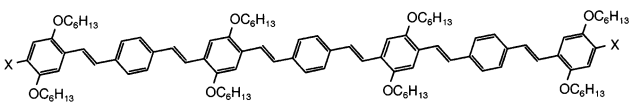
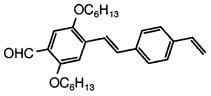
A general and controlled bidirectional growth strategy enables a very rapid and efficient construction of OPV compounds possessing functional groups such as aldehyde and mercapto groups at both ends. The strategy employs only one reaction type with high yields and stereoselectivities to grow the conjugated chains, eliminating the need for protecting groups in the overall intermediates.

Recently, poly-*para*-phenylenevinylene (PPV) and oligo-*para*-phenylene-vinylene (OPV) derivatives that possess long conjugated systems have drawn much attention in materials science due to their electrooptic properties.[1] Thus, various applications in light-emitting diodes, in semiconductive or photoconductive devices, in nonlinear optics, conversion of sunlight, etc., have been reported.[2] In particular, PPV has been used as an emissive material for use in electroluminescent devices. In addition, OPV molecules possessing well-defined conjugation lengths and structures may also serve as model systems for understanding the relationships between bulk material properties and molecular structures in conducting polymers. Though it is well-documented that bulk conjugated organic materials can be semiconducting or even conducting when doped, the synthesis of mercapto-ended linear conjugated molecules that orient themselves on gold surfaces is still limited. Herein, we describe a rapid synthetic route for the formation of soluble oligo(2,5-dihexyloxy-1,4-phenylenevinylene)s, potential molecular nanoscale wires, by a rapid iterative coherent approach. These mercapto-ends can serve as molecular-scale alligator clips for adhesion of the molecular scale wires to the gold probes. Recently, there has been considerable effort to prepare large conjugated molecules of precise length and constitution.[1h,3,4] Our approach to these compounds maintains several key features that make it well-suited for the requisite large molecular architectures for molecular-scale electronics studies. Specifically, the route involves (1) a rapid construction method that permits large prolongation of molecular length at each coupling stage to afford an unbranched oligomer, (2) using only one key molecular building block to make the desired linear molecular wires, (3) very simple and efficient separation and purification by recrystallization at each step, (4) an iterative coherent approach so that the same high-yielding reaction can be used throughout the sequence, (5) products that are stable to light and air so that subsequent engineering manipulations will not be impeded, (6) products that could easily permit independent functionalization of the ends to mercapto groups to serve as molecular alligator clips that are required for surface contacts to metal probes, and (7) products that serve as useful models for the understanding of bulk polymeric materials.



1 (X = I or Br)



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Our initial synthetic results showed that the stepwise synthesis of oligo(*p*-phenylenevinylene) larger than decamers via Heck-type reaction of aryl bromide or iodide with a styryl vinyl group (e.g., **1** and **2**) could provide only low yields and other unidentified byproducts by using various palladium catalysts. We then turned our attention to the iterative coherent approach as shown in Scheme 1.

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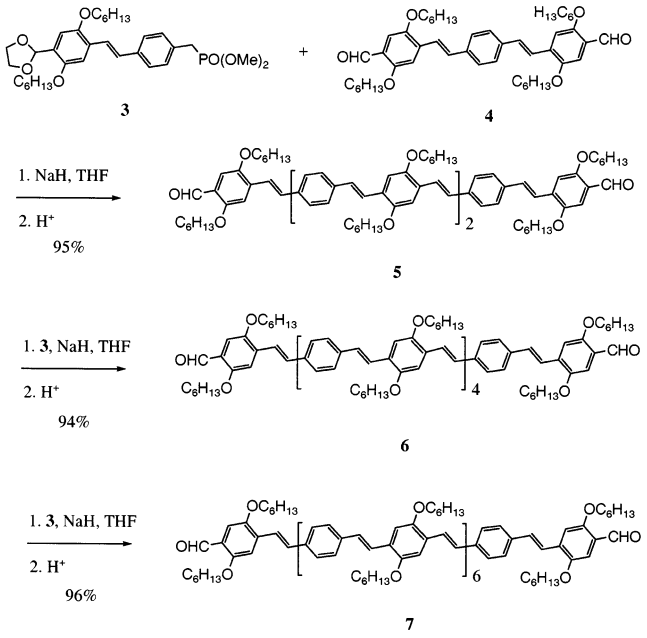
SCHEME 1



The key to the overall strategy is the synthesis of the building block molecule, monomer **3**, which possesses a dimethylphosphonate ester group at one end and a cyclic acetal functional group at the other end. Monomer **4** possesses a dialdehyde group at both ends. The phosphonate terminus of 2 equiv of monomer **3** can couple with both aldehyde termini of monomer **4** under the Horner−Wadsworth−Emmons reaction conditions and give oligomer **5** in 95% yield after hydrolysis of the cyclic acetal group under acidic conditions. Similar condensation of oligomer **5** with monomer **3** under the Horner−Wadsworth−Emmons reaction conditions and followed by the sequential hydrolysis under acidic conditions could afford oligomer **6** in 94% yield. Iterative condensation of oligomer **6** with monomer **3** and followed by acidic hydrolysis could successfully afford oligomer **7** in 96% yield. Therefore, the growth of the OPV chain commences with compound **4** and thereafter monomer **3** is added in a repetitive stepwise fashion. The process could be repeated to quickly build up longer OPV molecules possessing aldehyde groups as the functionalized termini. Oligomers **5**−**7** with two aldehyde groups at the termini can further undergo Horner−Wadsworth−Emmons reaction with **8**, the molecule with methyl sulfide at the one end and the dimethylphosphonate ester group at the other end, to form **9**−**11** in 96, 94, and 93% yields, respectively (Scheme 2). The transformation of the terminal methyl sulfide groups on **9** to the two terminal mercapto groups in good yield (>90% yield) can be done by treating **9** with 5 equiv of sodium 2-methyl-2-propanethiolate in very dry DMF.[5]

Both monomers **3** and **4** are conveniently prepared in a highly stereoselective manner from **12**[6−8] and **13**, which

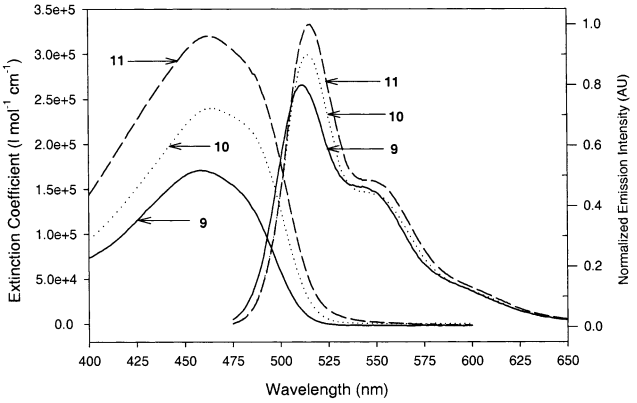


FIGURE 1. Absorption and emission spectra of compounds **9**−**11** in a dilute solution of dichloromethane.

is itself derived from monoprotection as cyclic ethylene acetal in 70% yield of 2,5-dihexyloxybenzene-1,4-dicarbaldehyde[9] in one simple step. Thus, under the Horner−Wadsworth−Emmons reaction conditions, **12** and **13** could afford **3** and **14** in a ratio of 2:3 in 98% total yield. Compounds **3** and **14** can be separated and purified by column chromatography (silica gel, hexane/EtOAc = 25:1 and CH_2Cl_2:EtOAc = 10:1). Acidic hydrolysis of **14** could afford **4** in quantitative yield (Scheme 3). The trans stereochemistry of the styryl double bonds in **3** and **4** was confirmed by their ^{1}H NMR spectral analysis.

Interestingly, under the Horner−Wadsworth−Emmons reaction conditions, no cis isomers of **3** and **4** were detected. The solubility of **5**−**7** and **9**−**11** in $CHCl_3$ and CH_2Cl_2 is noteworthy. When we attempted to prepare the analogues of these oligomers with 2,5-dimethyoxyl or 2,5-dihexyloxyl groups at alternative positions of the benzene rings without attaching the 2,5-dihexyloxyl groups, only the analogue of **6** with 2,5-dimethyoxyl groups and the analogue of **5** with 2,5-dihexyloxyl groups at the alternative positions of the benzene rings were obtained in good yields but with very low solubilities in various organic solvents. In contrast, oligomers **5**−**7** and **9**−**11** without the 2,5-alkoxyl groups at the alternative positions of the benzene rings can easily dissolve in chloroform. Yields for each of the Horner−Wadsworth−Emmons reaction steps to prepare oligomers **5**−**7** and **9**−**11** were good without the influence from the longer length of the oligomers. Thus, oligomers **9**−**11** can be obtained in 91, 88, and 89% isolated yields, respectively, starting from monomers **3** and **4**. Presently, we have succeeded in the synthesis and purification of compound **11**, which possesses 17 aryl rings and 16 styryl double bonds in its conjugation pathway, and a molecular weight of 3404. Synthesis of longer oligomers is still in progress. All of the spectroscopic studies and high-resolution mass spectral results are consistent with the proposed molecular structures. The synthesis of other smaller building blocks in good to moderate yields via the conventional pathway is shown in Schemes 4 and 5.

The absorption and emission spectra for the series of OPVs **9**−**11** that possess two methyl sulfide end groups are shown in Figure 1. All of the oligomers show strong

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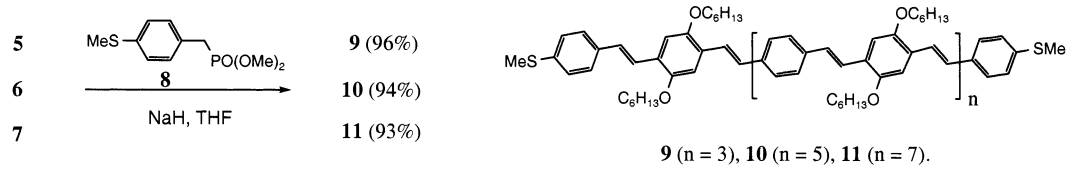
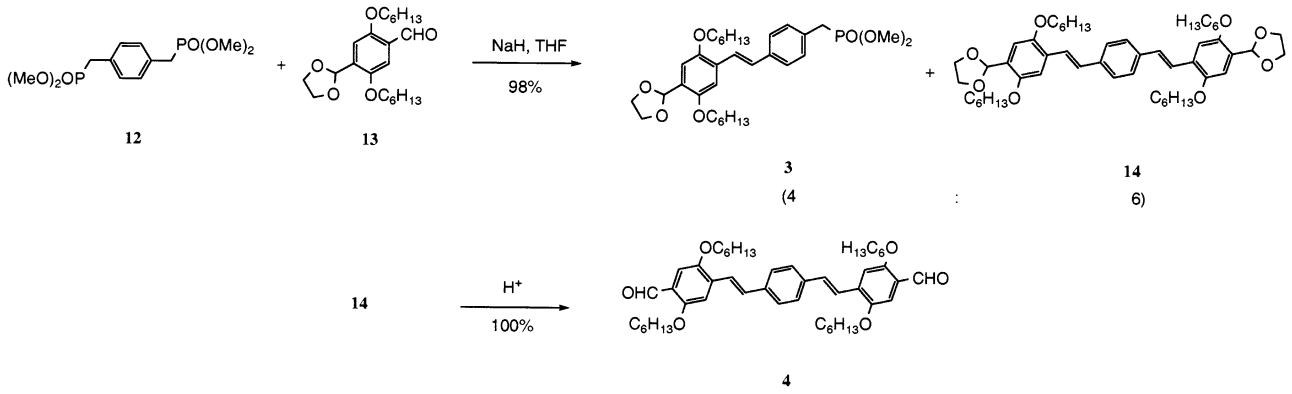
SCHEME 2

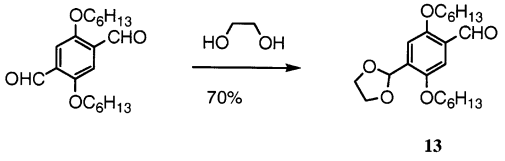


9 (n = 3), **10** (n = 5), **11** (n = 7).

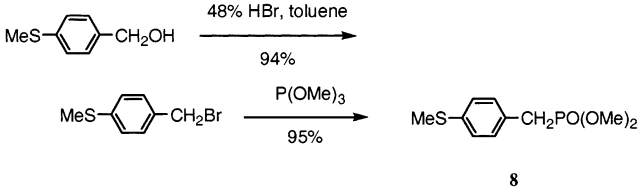
SCHEME 3



SCHEME 4



SCHEME 5



and broad absorption in the visible region. Elongation of the conjugation length from **9** to **11** results in a red shift of 4 nm in the emission spectra but a red shift of 6 nm from **9** to **10** and the same λ_{max} for **10** and **11** in the absorption spectra. The small red shift and blue shift in the absorption spectra of oligomers **9** to **11** are noteworthy. They indicate that the limitations to electron delocalization in the longer oligomers have been reached.[10] Thus, the effective conjugation length in this series of oligomers is reached at oligomer **10**. The absorption wavelength maximum in the oligomers converges to that of PPV over relatively short conjugation lengths, which suggests the validity of using OPV to better understand the electronic properties of electroactive PPV materials. The extinction coefficients for compounds **9**−**11** are 1.71 × 10^5, 2.40 × 10^5, and 3.20 × 10^5, respectively. This indicates that increasing the conjugation length of OPV may also increase the transition probability of electrons from their ground states to the excited states. Solutions of these oligomers **9**−**11** give a brilliant green fluorescence. There is a major band with a shoulder to the red of moderate intensity in the emission spectrum of oligomers **9**−**11**. The fluorescence quantum yields of the oligomers **9** to **11** in dichloromethane are 36, 37, and 33%, respectively.

It should be pointed out that various syntheses of different OPVs have been reported in the past.[3,4,11−12] Schenk et al. have investigated the charging capacity of OPV molecules and the charge distribution within the OPV chain.[11] Katz et al. have studied the fluorescence dynamics of OPVs both in solution and the solid state and observed little difference between them.[12] Yu et al. has presented an orthogonal approach to stepwise synthesis of long oligomers with 12 rings and 11 double bonds.[3] Meier et al. has reported the synthesis of OPV oligomers with 16 rings and 15 double bonds in low yield via a multistep synthesis on the basis of hydroquinone.[4] In this paper, we use an iterative coherent approach to effectively and rapidly synthesize longer oligomers with 17 rings and 16 double bonds. Due to the fact that the Horner−Wadsworth−Emmons reaction can tolerate a wide variety of functional groups, it should be possible to synthesize many different OPV molecules of various lengths and structures. This is useful for fine-tuning the band gap in emissive organic materials that will more closely resemble organic polymeric conducting materials. Also noteworthy is the use of only one reaction type to construct the requisite functionality; this eliminates the need of repetitive protection steps in the overall intermediates. The use of a stilbene analogue as the building block allows for efficient and fast construction of the OPV chain. After each step, two aldehyde functional groups are left for further chemical manipulation, which may include either continued elongation or reaction with an

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end-functionalized polymer to form novel diblock copolymers or with an end-capped monomer to form longer oligomers.

In summary, our general and controlled bidirectional growth strategy enables a very rapid and efficient construction of OPV compounds possessing functional groups at both ends. The strategy employs only one reaction type to grow the conjugated chains, eliminating the need for a protecting group in the overall intermediates. We intend to use these molecules in the production of novel molecular wires.

Experimental Section

Solvents were dried by appropriate methods wherever needed. All organic extracts were dried over anhydrous magnesium sulfate. TLC was done on aluminum sheets with precoated silica gel 60 F_{254} (40 × 80 mm). Purification by column chromatography was carried out with neutral silica gel 60 (70−230 mesh ASTM). The purity of each compound was judged to be >95% by ^{1}H NMR or ^{13}C NMR spectral analyses. Melting points were taken on a capillary tube apparatus and are uncorrected. IR spectra were recorded as either Nujol mulls or in the solution form as denoted. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on either a 300 or 400 MHz instrument using TMS (0 ppm) and $CDCl_3$ (77.0 ppm) as internal standards. HRMS spectra were collected on an orthogonal acceleration−time-of-flight mass spectrometer with a resolution of 6000 (5% valley definition) and fitted with a magnet bypass flight tube. MALDI-MS spectra were collected on a spectrometer equipped with a nitrogen laser (337 nm) and operated in the delayed extraction reflector mode. MS spectra were determined on a quadrupole spectrometer or a GC/MS spectrometer. UV and fluorescent spectra were recorded in CH_2Cl_2 solution.

4-(1,3-Dioxolan-2-yl)-2,5-dihexyloxybenzaldehyde 13. 2,5-Bis-hexyloxy-1,4-dibenzaldehyde (7.4 g, 22 mmol), 1.3 equiv of ethylene glycol, and a catalytic amount of *p*-toluenesulfonic acid in 100 mL of toluene were stirred under reflux for 12 h. After cooling to room temperature, the solution was washed with water (3 × 50 mL) and dried over $MgSO_4$, and the solvent was removed in a vacuum. The crude product was then purified by column chromatography (silica gel, hexene:EtOAc = 25:1) to yield the desired acetal **13** as a yellow solid (5.9 g, 70% yield). Mp: 36−37 °C. ^{1}H NMR ($CDCl_3$, TMS): δ 0.88−0.92 (m, 6 H), 1.23−1.28 (m, 8 H), 1.32−1.35 (m, 4 H), 1.74−1.85 (m, 4 H), 3.98−4.18 (m, 8 H), 6.11 (s, 1 H), 7.19 (s, 1 H), 7.32 (s, 1 H), 10.47 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 13.98, 22.56, 25.63, 25.72, 29.07, 29.15, 31.49, 65.38, 69.21, 98.71, 110.14, 111.91, 125.50, 133.95, 151.24, 156.06, 189.52 ppm. IR (CH_2Cl_2) υ_{max}: 2876, 2854, 1679, 1617, 1468, 1206, 1024 cm^{-1}. MS *m*/*z*: 378 (M^+). HRMS: calcd for $C_{22}H_{34}O_5$, 378.2406; found, 378.2410.

Preparation of Monomers ({4-[(1*E*)-2-(4-(1,3-Dioxolan-2-yl)-2,5-dihexyloxy-phenyl)vinyl]phenyl}methyl)-dimethoxyphosphino-1-one 3 and 4-((1*E*)-2-{4-[(1*E*)-2-(4-Formyl-2,5-dihexyloxyphenyl)vinyl]phenyl}vinyl)-2,5-dihexyloxybenzaldehyde 4. Compound **13** (1.0 g, 2.6 mmol) and NaH (0.3 g, 12.5 mmol) were sequentially added to the solution of compound **12**[5−7] (2.0 g, 6.2 mmol) in 50 mL of dry THF. The mixture was stirred at 40 °C for 4 h. After cooling to room temperature, the mixture was diluted with EtOAc (50 mL), washed with brine (3 × 50 mL), and dried over $MgSO_4$. The solvent was evaporated, and the residue was purified by column chromatography (silica gel), first employing hexene:EtOAc = 25:1 as the eluent to give intermediate compound **14** and then using CH_2Cl_2:EtOAc = 10:1 to obtain compound **3** as a yellow oil (0.59 g, 39% yield).

HCl (2 M, 15 mL) was gradually added to the solution of compound **14** in 20 mL of $CHCl_3$. The mixture was stirred at room temperature for 5 h. The organic layer was separated, washed with 15% $NaHCO_3$ (3 × 30 mL) and brine (3 × 30 mL), and dried over $MgSO_4$. The solvent was evaporated, and the residue was recrystallized from hexane/EtOAc to provide pure compound **4** as a yellow solid (0.56 g, 57% yield).

Compound 3. ^{1}H NMR ($CDCl_3$, TMS): δ 0.92 (t, J = 7 Hz, 6 H), 1.34−1.37 (m, 8 H), 1.45−1.50 (m, 4 H), 1.79−1.85 (m, 4 H), 3.18 (d, J = 20 Hz, 2 H), 3.68 (d, J = 10 Hz, 6 H), 3.98−4.16 (m, 8 H), 6.13 (s, 1 H), 7.08 (d, J = 16 Hz, 1 H), 7.09 (s, 1 H), 7.10 (s, 1 H), 7.28 (dd, J = 2.4, 8.1 Hz, 2 H), 7.45 (d, J = 16 Hz, 1 H), 7.46 (s, 1 H), 7.49 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 14.11, 22.72, 25.84, 26.01, 29.45, 29.52, 31.69, 32.15, 33.52, 52.99, 53.06, 65.35, 65.38, 69.57, 69.64, 99.27, 110.65, 111.65, 123.77, 123.79, 126.38, 126.89, 126.92, 128.10, 128.84, 128.87, 130.04, 130.11, 130.40, 130.50, 136.80, 150.95, 151.65 ppm. IR (CH_2Cl_2) υ_{max}: 2848, 1604, 1512, 1450, 1036 cm^{-1}. MS *m*/*z*: 574 (M^+). HRMS: calcd for $C_{32}H_{47}O_7P$, 574.3059; found, 574.3054.

Compound 4. Mp: 130−131 °C. ^{1}H NMR ($CDCl_3$, TMS): δ 0.92 (t, J = 6.8 Hz, 12 H), 1.38 (m, 16 H), 1.52−1.57 (m, 8 H), 1.83−1.88 (m, 8 H), 4.04 (t, J = 6.4 Hz, 4 H), 4.12 (t, J = 6.4 Hz, 4 H), 7.18 (s, 2 H), 7.22 (d, J = 16 Hz, 2 H), 7.33 (s, 2 H), 7.48 (d, J = 16 Hz, 2.H), 7.56 (s, 4 H), 10.45 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 14.01, 22.61, 25.79, 25.86, 29.24, 31.57, 69.20, 69.32, 110.25, 110.62, 123.20, 124.40, 127.31, 131.71, 134.19, 137.22, 150.84, 156.24, 189.14 ppm. IR (CH_2Cl_2) υ_{max}: 2869, 2850, 1673, 1209, 1023 cm^{-1}. MS *m*/*z*: 738 (M^+). HRMS: calcd for $C_{48}H_{66}O_6$, 738.4859; found, 738.4841.

General Procedure for the Preparation of Oligomers 5−7. NaH (0.2 g, 8.33 mmol) was added to a solution of dialdehyde **4** (0.26 g, 0.35 mmol) and **3** (0.43 g, 0.75 mmol) in dry THF (25 mL). The mixture was stirred at 50 °C for 5−12 h. After cooling to room temperature, the reaction mixture was diluted with $CHCl_3$ (50 mL) and washed with water (3 × 30 mL). The organic layer was separated and concentrated to give the condensation product. This product was redissolved in $CHCl_3$ (30 mL), and 2 M HCl (20 mL) was gradually added; the mixture was stirred at room temperature for 5−10 h. The organic layer was separated, washed with 15% $NaHCO_3$ solution (3 × 30 mL) and brine (3 × 30 mL), and dried over $MgSO_4$. The solvent was removed to give crude product, which was washed with EtOAc and hexane to yield the pure product **5** in 95% yield.

Compound 5. Mp: 140−142 °C. ^{1}H NMR ($CDCl_3$, TMS): δ 0.93−0.97 (m, 24 H), 1.36−1.44 (m, 32 H), 1.53−1.57 (m, 16 H), 1.87−1.89 (m, 16 H), 4.03−4.11 (m, 16 H), 7.14−7.32 (m, 12 H), 7.47−7.54 (m, 20 H), 10.45 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 14.35, 22.93, 22.97, 26.09, 26.17, 26.29, 29.54, 29.81, 31.88, 31.97, 69.47, 69.58, 69.94, 110.48, 110.79, 110.86, 110.94, 122.89, 123.54, 124.13, 124.53, 127.18, 127.54, 128.50, 128.84, 132.23, 134.70, 136.66, 137.50, 138.36, 151.07, 151.47, 151.54, 156.55, 189.43 ppm. IR (CH_2Cl_2) υ_{max}: 2870, 2848, 1674, 1210, 1025 cm^{-1}. MS *m*/*z*: 1547 (M^+). HRMS: calcd for $C_{104}H_{138}O_{10}$, 1547.0290; found, 1547.0293.

Compound 6. Yield: 94%. Mp: 195−197 °C. ^{1}H NMR ($CDCl_3$, TMS): δ 0.92−0.97 (m, 36 H), 1.36−1.42 (m, 48 H), 1.56−1.59 (m, 24 H), 1.85−1.91 (m, 24 H), 4.04−4.12 (m, 24 H), 7.13−7.33 (m, 20 H), 7.48−7.54 (m, 32 H), 10.45 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 14.04, 22.57, 22.60, 22.65, 25.76, 25.84, 25.96, 29.20, 29.48, 31.53, 31.55, 31.64, 69.13, 69.22, 69.59, 110.12, 110.42, 110.53, 122.54, 123.21, 123.79, 124.17, 126.82, 127.22, 128.15, 128.39, 128.52, 131.90, 134.36, 137.16, 150.73, 151.14, 156.22, 189.13 ppm. IR (CH_2Cl_2) υ_{max}: 2867, 2846, 1667, 1208, 1023 cm^{-1}. MS *m*/*z*: 2356 (M^+). HRMS: calcd for $C_{160}H_{210}O_{14}$, 2355.5721; found, 2355.5652.

Compound 7. Yield: 96% yield. Mp: 206−208 °C. ^{1}H NMR ($CDCl_3$, TMS): δ 0.94−0.98 (m, 48 H), 1.38−1.43 (m, 64 H), 1.58−1.61 (m, 32 H), 1.88−1.93 (m, 32 H), 4.04−4.15 (m, 32 H), 7.14−7.56 (m, 72 H), 10.46 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 14.03, 22.64, 25.75, 25.82, 25.94, 29.18, 29.45, 31.53, 31.62, 69.10, 69.19, 69.56, 110.08, 110.37, 110.48, 122.50, 123.17, 123.75, 124.12, 126.80, 127.21, 128.12, 128.37, 131.89, 137.14, 150.69, 151.11, 156.20, 189.16 ppm. IR (CH_2Cl_2) υ_{max}:

2865, 2844, 1667, 1206, 1024 cm^{-1}. MS *m*/*z*: 3164 (M^+). HRMS: calcd for $C_{216}H_{282}O_{18}$, 3164.1151; found, 3164.1139.

Dimethyl (4-Methylthiobenzyl)phosphonate 8. 4-(Methylthio)benzyl alcohol (2.0 g, 13 mmol) and 48% hydrobromic acid (4 mL, 36 mmol) were stirred in 20 mL of toluene at 90 °C for 1 h. The organic layer was separated, washed with water (3 × 30 mL), and dried over $MgSO_4$, and the solvent was removed under reduced pressure to provide 4-methylthiobenzyl bromide as a white solid, which was then stirred with $P(OCH_3)_3$ (8 mL, 69 mmol) at 120 °C for 10 h. Excess trimethyl phosphite was distilled under vacuum to yield a faint brown oil, which was purified by column chromatography (silica gel, CH_2Cl_2:EtOAc = 10:1) to give compound **8** as a colorless oil (95% yield). ^{1}H NMR ($CDCl_3$, TMS): δ 2.47 (s, 3 H), 3.12 (d, J = 20 Hz, 2 H), 3.67 (d, J = 11 Hz, 6 H), 7.21 (s, 4 H) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 15.81, 31.31, 33.15, 52.79, 52.88, 126.86, 127.83, 127.96, 130.01, 130.10, 137.16 ppm. IR (CH_2Cl_2) υ_{max}: 2851, 1603, 1184, 1096, 969 cm^{-1}. MS *m*/*z*: 246 (M^+). HRMS: calcd for $C_{10}H_{15}O_3PS$, 246.0480; found, 246.0476.

Representative Procedure for the Preparation of Oligomers 9−11. Oligomer **5** was reacted with 3 equiv of compound **8** in the presence of 10 equiv of NaH in dry THF, similar to the procedure for the preparation of **5**. Oligomers **9**−**11** were obtained in 96, 94, and 93% yields, respectively.

Compound 9. Mp: 215−217 °C. ^{1}H NMR ($CDCl_3$, TMS): δ 0.93−0.97 (m, 24 H), 1.38−1.41 (m, 32 H), 1.56−1.58 (m, 16 H), 1.88−1.93 (m, 16 H), 2.51 (s, 6 H), 4.04−4.09 (m, 16 H), 7.07−7.23 (m, 20 H), 7.42−7.53 (m, 24 H) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 14.17, 16.01, 22.79, 26.10, 29.62, 31.78, 69.74, 110.70, 123.05, 123.36, 126.95, 127.01, 127.11, 128.22, 128.54, 135.16, 137.31, 137.63, 151.29 ppm. IR (CH_2Cl_2) υ_{max}: 2863, 2842, 1601, 1215, 975 cm^{-1}. MS *m*/*z*: 1787 (M^+). HRMS: calcd for $C_{120}H_{154}O_8S_2$, 1787.1085; found, 1787.1021.

Compound 10. Mp: 226−228 °C. ^{1}H NMR ($CDCl_3$, TMS): δ 0.90−0.96 (m, 36 H), 1.33−1.50 (m, 48 H), 1.57−1.59 (m, 24 H), 1.89−1.95 (m, 24 H), 2.52 (s, 6 H), 4.06−4.11 (m, 24 H), 7.08−7.54 (m, 64 H) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 13.97, 15.98, 22.61, 25.94, 29.48, 31.62, 69.68, 110.72, 123.30, 126.79, 128.45, 137.21, 151.21 ppm. IR (CH_2Cl_2) υ_{max}: 2860, 2841, 1601, 1213, 970 cm^{-1}. MS *m*/*z*: 2596 (M^+). HRMS: calcd for $C_{176}H_{226}O_{12}S_2$, 2595.6516; found, 2595.6430.

Compound 11. Mp: 255−257 °C. ^{1}H NMR ($CDCl_3$, TMS): δ 0.93−0.95 (m, 48 H), 1.40−1.42 (m, 64 H), 1.58−1.60 (m, 32 H), 1.88−1.92 (m, 32 H), 2.51 (s, 6 H), 4.07−4.10 (m, 32 H), 7.07−7.54 (m, 84 H) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 14.13, 15.98, 22.74, 26.06, 29.58, 31.73, 69.72, 110.69, 123.33, 126.91, 128.19, 128.52, 137.28, 151.26 ppm. IR (CH_2Cl_2) υ_{max}: 2864, 2840, 1601, 973 cm^{-1}. MS *m*/*z*: 3404 (M^+). HRMS: calcd for $C_{232}H_{298}O_{16}S_2$, 3404.1943; found, 3404.1916.

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Supporting Information Available: Copies of ^{1}H NMR and ^{13}C NMR spectra of oligomers **5**−**11**, monomers **3** and **4**, and small molecules **8** and **13** are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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