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Simple Synthesis of Monomers for Regioregular Poly(dialkylbiphenylenevinylene) Conducting Polymers through Directional Polymerization

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Introduction

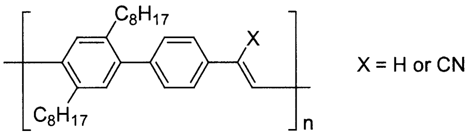
The number of studies concerning conducting polymers and their use for making light-emitting diodes,[1] all polymer displays,[2] all polymer electronic circuits,[3] and all plastic solar cells[4] has increased significantly in recent years. While the literature covering physical characterization and device fabrication is vast all studies are based on a narrow set of conducting polymer families, namely, the polyhetroaromatic systems such as polypyrrole and polythiophenes, the poly(arylenealkenylene)s and poly(arylalkynylene)s, and the less diverse families such as the polyacetylenes and polyanilines.

In this paper we present the efficient synthesis of two boronic acids that are very suited for the synthesis of monomers for conducting polymers; we further apply these to the synthesis of two conducting polymers of the poly(dialkylbiphenylenevinylene) type (as shown in Scheme 1). Ultraviolet photoelectron spectroscopy was used to establish the position of the energy levels on a polycrystalline gold substrate, which is a very important physical property pertaining to conducting polymer research with emphasis on carrier transport across the metal electrode-conducting polymer interface.

Results and Discussion

Some of the literature reports on synthesis of poly(phenylenevinylene)s (PPV) make use of the Horner−Wadsworth−Emmons reaction between an arylmethyldialkylphosphonyl derivative and an arylaldehyde to give a PPV type polymer[5] or a Knoevenagel type condensation between an arylmethylcyanide and an aromatic aldehyde to give a PPCNV type polymer.[6] While the syntheses of poly(biphenylenevinylene)s have been reported[7] the synthetic strategy was not explored. We found it desirable to have precursor molecules for this type of synthetic work and prepared the boronic acids **4** and **5** as shown in Scheme 2 to suit this need. First, 4-methylphenyl-1,3,2-borolane was brominated using *N*-bromosuccinimide in CCl_4 to give the common intermediate **1** that could be reacted with either triethyl phosphite to give **2** or potassium cyanide in DMF to give **3**. Both compounds **2** and **3** could be distilled to high purity as established by GCMS and NMR. Both compounds are however hygroscopic and easily hydrolyzed. This is an advantage in terms of preparation of the boronic acids **4** and **5** but also problematic in terms of elemental analysis. While compound **5** has been reported[8] we found our synthetic procedure to have the major advantage that the intermediate 1,3,2-borolane can be distilled to high purity.

Scheme 1



The synthetic strategy for obtaining the biphenylene system was using a standard Suzuki reaction coupling the boronic acids **4** and **5** with the common protected aldehyde **8**. This was synthesized from the known 1,4-dibromo-2,5-dioctylbenzene[14] by monolithiation and reaction with DMF to give **6**. Protection with neopentylglycol gave **7**, which was converted into the more reactive iodide **8** by lithium−halogen exchange and subsequent reaction with elemental iodine. While this reaction was found to be efficient and simple the direct halogen lithium exchange on 1,4-diiodo-2,5-dioctylbenzene should be possible thus saving one synthetic step. The advantage of using the 1,4-dibromo-2,5-dioctylbenzene is that it can be made in large quantities (1 kg) and stored for long periods of time without degradation. Compound **8** could be reacted with either **4** or **5** under standard Suzuki reaction conditions using $(PPh_3)_2PdCl_2$ as a catalyst and Na_2CO_3 as base in a toluene/water solvent system. This gave the protected monomers **9** and **10** which could be deprotected using trifluoroacetic acid to give the monomers **11** and **12** as shown in Scheme 3.

The idea of having a protected monomer was that it could be possible to make the polymerization stepwise and in principle obtain oligomers of any length by performing a condensation of the first protected monomer onto a suitable terminus followed by a number of condensation−deprotection cycles to obtain the desired oligomer. In a practical sense the number of condensation−deprotection cycles would be limited to a small value. It was also possible to arrive at **11** and **12** by standard Suzuki reactions with **4** or **5** and **6**, respectively. The demonstration of the polymerization of **11** and **12** to the polymers **13** and **14** is shown in Scheme 4 where the polymerization/condensation of **11** employs anhydrous conditions and sodium hydride as base and the polymerization of **12** employs an aqueous THF/*t*BuOH solvent system with $n\mathrm{Bu_4NOH(aq)}$ as base. The intention of having the monomers with an aldehyde on one end of the monomer and the condensing group (phosphonylmethyl or cyanomethyl) on the other end of the monomer was that the polymer obtained should be regioregular and proceed in one direction.

The molecular weights of the polymers obtained in this manner were determined using size exclusion chromatography (SEC) and found to of low molecular weight ($M_w = 4600$ and $14\,600$ g mol^{-1} respectively for **13** and **14**). Because of the rigid nature of the backbone which is comparable to poly(phenylenevinylene) that is known to be a rigid rod, we assume that these polymers are also linear.

The differences in electronic properties between polymers **13** and **14** is expected to be solely due to the cyano substituent in compound **14**. While it is expected that **13** is a conductor of holes the introduction of the cyano

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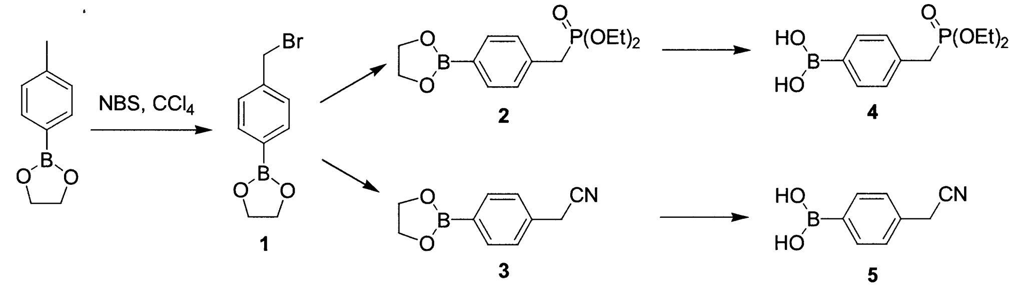
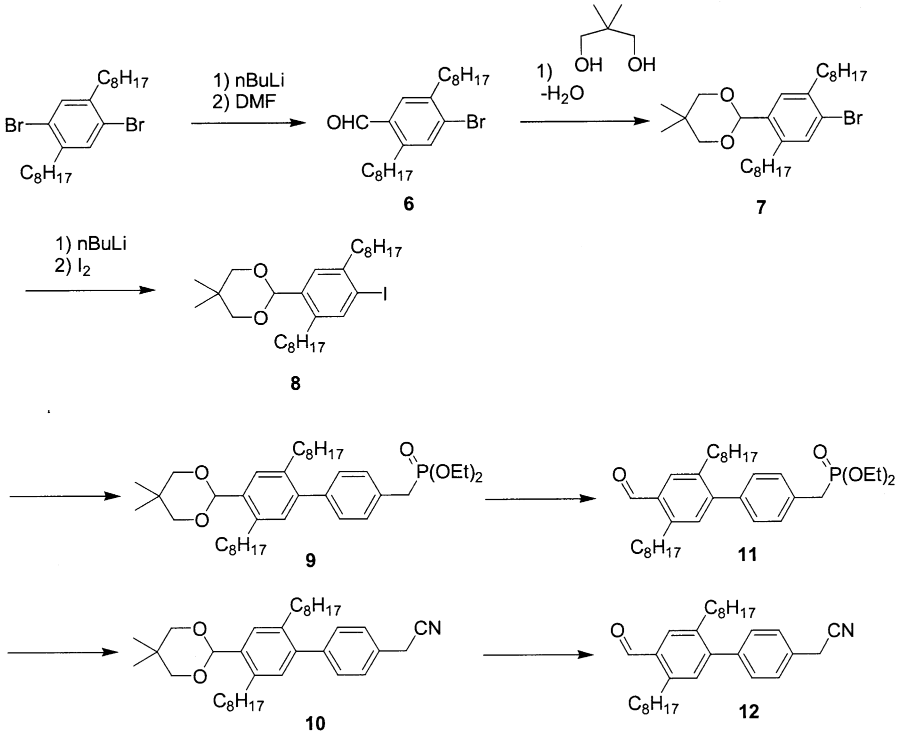
Scheme 2



Scheme 3



Scheme 4

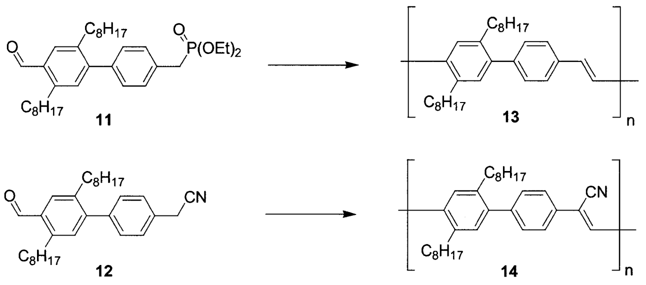


Table 1. Data from the Photoelectron Spectra for the Au Substrate and the Polymers 13 and 14

compd	E_F^{VB}	E_F^{VAC}	cutoff	Δ	IP
13	1.60	3.15	45.25	−1.75	4.75
14	2.40	2.35	45.25	−2.55	4.75

substituent to give **14** serves the purpose of lowering the energy levels and makes the polymer acquire some electron acceptor properties that should lead to the possibility of increased electronic conduction. Of the two polymers presented here, **13** is termed the hole conductor (p-type) and **14** is termed the electron conductor (n-type). Aside from the slightly smaller optical band gap in **14** than **13**, the absolute positions of the electronic energy levels were quantified using photoelectron spectroscopy on thin films of **13** and **14** on a polycrystalline gold substrate. This showed a significant difference in the valence band edge, E_{VB}, due to the cyano substituent which leads to a lowering by 0.8 eV as shown in Table 1. The position of the electronic energy levels can be controlled by chemical substitution via two different mechanisms where either a purely inductive effect or a resonance effect is used.[9] The desire is to be able to shift the energy levels up and down the energy scale without altering any other physical properties, which in reality is very difficult to achieve. The inductive effect most easily allows for this, and an example is the substitution of hydrogen with a strongly electron-withdrawing substituent like a fluorine atom[10] or a cyano group. The resonance effect is most often accompanied by structural or conformational changes such as replacement of alkyl to alkoxy or amino as documented by Bredas et al. that treated how the positions of both filled and empty energy levels change with substitution pattern.[11] The effects of broken substitution and cyano substitution have also been studied by Holmes et al.[12,13]

The position of the energy levels and the shifts observed here are typical for poly(arenylenevinylene) conducting polymers with a large band gap. The injection barrier for holes is smaller for **13** than **14** as expected. The optical absorption properties for the two polymers is remarkably similar where the absorption maximum, $\lambda_{\max}$, for polymer **14** is slightly red-shifted by 8 nm when compared to $\lambda_{\max}$ for polymer **13**. The polymers are transparent to most of the visible part of the spectrum and could be suited for applications where transparency is an issue while maintaining the possibility for carrier transport.

Conclusions

We have presented the synthesis of a range of new compounds and versatile intermediates pertaining to conducting polymers. We have prepared two new conducting polymers therefrom by a new route enabling the directional growth of the polymer chain. We have further characterized the conducting polymers with respect to their electronic energy levels using UPS and their UV−vis properties.

Experimental Section

Commercially available compounds were purchased from Aldrich. 1,4-Dibromo-2,5-dioctylbenzene was prepared as described in ref 14; 4-methylphenyl-1,3,2-dioxaborolane was prepared from tolylboronic acid and ethylene glycol by reflux in toluene with a water separator for 1 h. The product was distilled (bp 120−121 °C/17 mmHg) and obtained in 81% yield. The analytical data were as in ref 15. For compounds **1**−**5** there was one signal missing in the ^{13}C NMR spectra; this is ascribed to the carbon atom bonded to boron due to the fast relaxation pathway that the boron atom provides. In compounds **6**−**8** and **10**−**12** one or more signals were missing in the ^{13}C NMR spectra, and this is ascribed to accidental isochrony. In some cases they were clearly visible as some signals were broad (indicated by a "b" in the list of signals for each compound when applicable).

4-Bromomethylphenyl-1,3,2-dioxaborolane (1). 4-Methyl-1,3,2-dioxaborolane (79.15 g, 0.49 mol) was refluxed vigorously in CCl_4 (0.6 L) containing fresh *N*-bromosuccinimide (90 g, excess). A little benzoyl peroxide was added. The reaction was followed using GCMS but was generally complete in less than 1 h depending on the purity of the *N*-bromosuccinimide. The mixture was then cooled, the solids were filtered, and the filtrate was concentrated to give an oil that was distilled in a vacuum. The fraction boiling in the interval 120−135 °C/0.5 mmHg was collected. The material crystallized in the condenser, which was kept at 100 °C. This gave **1** as a colorless solid in 92% yield (108 g); mp 84−85 °C. ^{1}H NMR (250 MHz, $CDCl_3$, 300 K, TMS): $\delta = 4.4$ (s, 4H, CH_2), 4.5 (s, 2H, CH_2), 7.4 (d, ^3J(H,H) = 8 Hz, 2H, ArH), 7.8 (d, ^3J(H,H) = 8 Hz, 2H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$, 300 K, TMS): $\delta = 33.8$, 66.6, 129.0, 135.8, 141.5. Anal. Calcd for $C_9H_{10}BBrO_2$: C, 44.87; H, 4.18. Found: C, 44.62; H, 3.95.

4-Diethylphosphonylmethylphenyl-1,3,2-dioxaborolane (2). Compound **1** (43 g, 0.18 mmol) was refluxed in triethyl phosphite (50 mL, excess) with an air condenser. The reaction was complete in 15 min after an initial vigorous evolution of ethyl bromide. The excess triethyl phosphite was distilled off, and the residual oil was distilled with in a vacuum. The fraction boiling at 190−195 °C/1 mmHg was collected. The product solidified upon standing. This gave **2** as a hygroscopic colorless solid in 85% yield (45 g); mp 67−68 °C. ^{1}H NMR (250 MHz, $CDCl_3$, 300 K, TMS): $\delta = 1.1$ (t, 6H, CH_3), 3.1 (d, 2H, CH_2), 3.9 (m, 4H, CH_2), 4.2 (s, 4H, CH_2), 7.2 (d, 2H, ArH), 7.6 (d, 2H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$, 300 K, TMS): $\delta =$ 16.6 (d, $J = 6$ Hz), 34.4 (d, $J = 137$ Hz), 62.4 (d, $J = 7$ Hz), 66.3, 129.6 (d, $J = 7$ Hz), 135.3 (d, $J = 3$ Hz), 135.5 (d, $J = 9$ Hz). Anal. Calcd for $C_{52}H_{80}B_4P_4O_{20}\cdot H_2O$: C, 51.60; H, 6.83. Found: C, 51.85; H, 6.63.

4-Cyanomethylphenyl-1,3,2-dioxaborolane (3). Compound **1** (10 g, 41.6 mmol) was dissolved in dry DMF (25 mL). Potassium cyanide (2.75 g, 41.6 mmol) (*caution! strong poison*) and potassium iodide (6.9 g, 41.6 mmol) were added. The mixture was heated to reflux where the color changed from yellow to light brown. The reaction was followed using GCMS and was generally complete in 10 min. The mixture was cooled and poured into chloroform (200 mL), and the salts were removed by filtration. Evaporation gave a red oil that was distilled. The fraction boiling at 140−150 °C/0.5 mmHg was collected. This gave **3** as a hygroscopic colorless solid in 50% yield (3.9 g); mp 86−88 °C. ^{1}H NMR (250 MHz, $CDCl_3$, 330 K, TMS): $\delta = 3.8$ (s, 2H, CH_2), 4.4 (s, 4H, CH_2), 7.3 (d, 2H, ArH), 7.8 (d, 2H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$, 300 K, TMS): δ = 24.4, 66.7, 118.2, 128.0, 133.7, 136.2. Anal. Calcd for $C_{20}H_{20}B_2N_2O_4\cdot H_2O$: C, 61.28; H, 5.66; N, 7.15. Found: C, 61.22; H, 5.35; N, 6.92.

4-Diethylphosphonylmethylphenylboronic Acid (4). Compound **2** (10.32 g, 35 mmol) was dissolved in MeOH (100 mL), and HCl(aq) (50 mL, 37%) was added. The mixture was stirred for 1 min when water (100 mL) was added, and the mixture was stirred in an ice/acetone bath. After 5 min of stirring a white precipitate formed. The product was filtered and dried at 50 °C in a vacuum oven. This gave **4** as a colorless solid in 90% yield (8.5 g); mp 150−152 °C. ^{1}H NMR (250 MHz, DMSO-d_6, 300 K, TMS): $\delta = 1.2$ (t, 6H, CH_3), 3.2 (d, 2H, CH_2), 3.9 (m, 4H, CH_2), 7.2 (d, 2H, ArH), 7.7 (d, 2H, ArH), 8.0 (s, 2H, OH). ^{13}C NMR (63 MHz, DMSO-d_6, 300 K, TMS): $\delta =$ 17.0 (d, $J = 5$ Hz), 33.3 (d, $J = 135$ Hz), 62.2 (d, $J = 7$ Hz), 129.7 (d, $J = 7$ Hz), 134.8 (d, $J = 3$ Hz), 134.9 (d, $J = 6$ Hz). Anal. Calcd for $C_{11}H_{18}BPO_5$: C, 48.57; H, 6.67. Found: C, 48.52; H, 6.52.

4-Cyanomethylphenylboronic Acid (5). Compound **3** (4.6 g, 25.7 mmol) was dissolved in dry THF (200 mL). HCl(aq) (50 mL, 6 M) was added, and after 5 min of stirring water (100 mL) was added. The mixture was stirred for 1 h. The THF was then removed in a vacuum whereby the product precipitated as a light yellow solid that was filterer and dried in a vacuum at room temperature. This gave **5** as a light yellow solid in 68% yield (2.8 g); mp 144−146 °C. ^{1}H NMR (250 MHz, DMSO-d_6, 300 K, TMS): $\delta = 4.0$ (s, 2H, CH_2), 7.3 (d, 2H, ArH), 7.8 (d, 2H, ArH). ^{13}C NMR (63 MHz, DMSO-d_6, 300 K, TMS): δ = 23.3, 120.0, 127.9, 133.8, 135.6. Anal. Calcd for $C_8H_8BNO_2$: C, 59.69; H, 5.01; N, 8.70. Found: C, 59.48; H, 4.89; N, 8.81.

1-Bromo-4-formyl-2,5-dioctylbenzene (6). 1,4-Dibromo-2,5-dioctylbenzene (75 g, 0.163 mol) was dissolved in dry THF (200 mL) and added to a solution of *n*BuLi (110 mL, 1.6 M, excess) in dry THF (300 mL), keeping the temperature during the addition below −60 °C. The mixture was then left to stir for 10 min. Dry DMF (50 mL, excess) was then added, and the mixture was allowed to reach room temperature. After 1 h HCl(aq) (100 mL, 37%) was added, and the mixture evaporated until the THF was removed. The aqueous phase was extracted with ether (2 × 300 mL), and the light yellow ether phase was washed with water (2 × 300 mL). The organic phase was dried ($MgSO_4$) and evaporated to give an oil that was dissolved in boiling ethanol (600 mL) and left in the freezer to crystallize. This gave **6** as a colorless solid in 89% yield (60 g); mp 37−38 °C. ^{1}H NMR (250 MHz, $CDCl_3$, 300 K, TMS): $\delta = 0.9$ (t, 6H, CH_3), 1.1−1.4 (m, 20H, CH_2), 1.5−1.7 (m, 4H, CH_2), 2.7 (t, 2H, CH_2), 2.9 (t, 2H, CH_2), 7.4 (s, 1H, ArH), 7.6 (s, 1H, ArH), 10.2 (s, 1H, CHO). ^{13}C NMR (63 MHz, $CDCl_3$, 300 K, TMS): $\delta = 14.7$, 23.3, 29.9 (b), 30.0 (b), 30.1, 30.4, 32.2, 32.52, 32.53, 32.9, 32.9, 36.2, 131.7, 133.0, 133.4, 135.7, 141.2, 145.2, 192.0. Anal. Calcd for $C_{23}H_{37}BrO$: C, 67.47; H, 9.11. Found: C, 67.33; H, 9.25.

1-Bromo-4-(5,5-dimethyl-1,3-dioxan-2-yl)-2,5-dioctylbenzene (7). Compound **6** (60 g, 0.146 mol) was refluxed in benzene (500 mL) containing neopentylglycol (16 g, 0.154 mol) and *p*-toluenesulfonic acid (100 mg, catalyst). The mixture was refluxed with a water separator. After 5 h the mixture was cooled and washed with Na_2CO_3(aq) (1 M, 200 mL) and water (200 mL), dried ($MgSO_4$), and evaporated. This gave **7** as a colorless oil in 84% yield (61 g). ^{1}H NMR (250 MHz, $CDCl_3$, 300 K, TMS): $\delta = 0.8$ (s, 3H, CH_3), 0.9−1.0 (m, 6H, CH_3), 1.2−1.4 (m, 23H, CH_2, CH_3), 1.6−1.7 (m, 4H, CH_2), 2.6 (t, 2H, CH_2), 2.7 (t, 2H, CH_2), 3.7 (d, 2H, CH_2), 3.8 (d, 2H, CH_2), 5.5 (s, 1H, CH), 7.4 (s, 1H, ArH), 7.5 (s, 1H, ArH). ^{13}C NMR (63 MHz,

$CDCl_3$, 300 K, TMS): δ = 14.7, 22.5, 23.3, 23.8, 29.8, 29.9, 30.0, 30.1, 30.2, 30.3, 30.7, 30.8, 31.9, 32.2, 32.5, 36.5, 78.5, 100.1, 125.4, 128.6, 133.9, 135.8, 140.2, 140.5. Anal. Calcd for $C_{28}H_{47}BrO_2$: C, 67.86; H, 9.56. Found: C, 68.09; H, 9.64.

1-Iodo-4-(5,5-dimethyl-1,3-dioxan-2-yl)-2,5-dioctylbenzene (8). Compound **7** (125.9 g, 0.254 mol) was dissolved in dry THF (1 L) and cooled to −78 °C. *n*BuLi (1.6 M, 160 mL, 0.256 mol) was added. The mixture was stirred for 15 min when iodine (70 g, excess) was added, and the mixture was allowed to reach room temperature. NaOH(aq) (0.1 M, 500 mL) was added followed by solid $Na_2S_2O_6$ with vigorous stirring until the color of iodine disappeared. The organic phase was separated and passed through silica (4 cm × 10 cm diameter) with an overlayer (1 cm) of $MgSO_4$. The silica was washed with ether (1.5 L), and the combined organic phases were evaporated. This gave **8** as a colorless oil in 92% yield (126 g). ^1H NMR (250 MHz, $CDCl_3$, 300 K, TMS): δ = 0.8 (s, 3H, CH_3), 0.9−1.0 (m, 6H, CH_3), 1.3−1.4 (m, 23H, CH_2, CH_3), 1.5−1.6 (m, 4H, CH_2), 2.6 (t, 2H, CH_2), 2.7 (t, 2H, CH_2), 3.6 (d, 2H, CH_2), 3.8 (d, 2H, CH_2), 5.4 (s, 1H, CH), 7.4 (s, 1H, ArH), 7.6 (s, 1H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$, 300 K, TMS): δ = 14.8, 22.5, 23.3, 23.9, 29.90, 29.96, 30.1, 30.2, 30.3, 30.9, 31.1, 32.0, 32.1, 32.6, 41.1, 78.6, 100.2, 101.9, 127.5, 136.8, 140.6, 140.7, 143.7. Anal. Calcd for $C_{28}H_{47}IO_2$: C, 61.98; H, 8.73. Found: C, 62.20; H, 8.77.

4-(5,5-Dimethyl-1,3-dioxan-2-yl)-4′-diethylphosphonylmethyl-2,5-dioctylbiphenyl (9). Compound **8** (3.5 g, 6.4 mmol), diethylphosphonylmethylphenylboronic acid (1.76 g, 6.5 mmol), Na_2CO_3(aq) (2 M, 50 mL), and toluene (100 mL) were mixed and degassed with argon. $(PPh_3)_2PdCl_2$ (200 mg, catalyst) was added, and the mixture was refluxed under argon for 4 h where reaction mixture became black in color with a fine black precipitate. The toluene phase was separated and passed trough silica and washed with ether that was evaporated in a vacuum. This gave **9** as a light yellow oil in 85% yield (3.5 g). ^1H NMR (250 MHz, $CDCl_3$, 300 K, TMS): δ = 0.8−0.9 (m, 9H, CH_3), 1.2−1.6 (m, 33H), 2.5 (t, 2H, CH_2), 2.6 (t, 2H, CH_2), 3.2 (d, 2H, CH_2), 3.6 (d, 2H, CH_2), 3.7 (d, 2H, CH_2), 4.0 (q, 4H, CH_2), 5.5 (s, 1H, CH), 6.9 (s, 1H, ArH), 7.2 (d, 2H, ArH), 7.3 (d, 2H, ArH), 7.5 (s, 1H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$, 300 K, TMS): δ = 14.4, 14.5, 16.8 (d, J = 5 Hz), 22.3, 23.0, 23.1, 23.7, 29.60, 29.64, 29.7, 29.8, 30.0, 30.2, 30.6, 31.8, 31.9, 32.2, 32.3, 32.4, 33.2, 33.3 (d, J = 135 Hz), 62.5 (d, J = 7 Hz), 78.3, 100.3, 127.2, 129.7 (d, J = 3 Hz), 129.8, 130.3 (d, J = 7 Hz), 131.6, 135.2, 137.9, 138.3, 141.1 (d, J = 6 Hz), 142.1. Anal. Calcd for $C_{39}H_{63}PO_5$: C, 72.86; H, 9.88. Found: C, 72.45; H, 9.91.

4-(5,5-Dimethyl-1,3-dioxan-2-yl)-4′-cyanomethyl-2,5-dioctylbiphenyl (10). Compound **8** (3.5 g, 6.4 mmol), diethylphosphonylmethylphenylboronic acid (1.05 g, 6.5 mmol), Na_2CO_3(aq) (2 M, 50 mL), and toluene (100 mL) were mixed and degassed with argon. $(PPh_3)_2PdCl_2$ (200 mg, catalyst) was added, and the mixture was refluxed under argon for 2 h where GCMS showed that compound **8** had been consumed. The toluene phase was separated and passed trough silica and washed with toluene that was evaporated in a vacuum. This gave **10** as a colorless oil in 91% (3.1 g). ^1H NMR (250 MHz, $CDCl_3$, 300 K, TMS): δ = 0.8−0.9 (m, 9H, CH_3), 1.1−1.6 (m, 27H), 2.5 (t, 2H, CH_2), 2.7 (t, 2H, CH_2), 3.6 (d, 2H, CH_2), 3.7 (s, 2H, CH_2), 3.8 (d, 2H, CH_2), 5.5 (s, 1H, CH), 6.9 (s, 1H, ArH), 7.2 (d, 2H, ArH), 7.3 (d, 2H, ArH), 7.5 (s, 1H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$, 300 K, TMS): δ = 14.5, 22.3, 23.0, 23.1, 23.7, 23.8, 29.5, 29.6, 29.8, 29.9, 30.1, 30.6, 31.8, 31.9, 32.2, 32.3, 32.4, 33.1, 78.4, 100.2, 118.3, 127.4, 127.9, 128.6, 130.3, 131.4, 135.5, 138.0, 138.3, 141.5, 142.5. Anal. Calcd for $C_{36}H_{53}NO_2$: C, 81.30; H, 10.05; N, 2.63. Found: C, 81.22; H, 10.16; N, 2.67.

4-Formyl-4′-diethylphosphonylmethyl-2,5-dioctylbiphenyl (11). Compound **9** (1.5 g, 2.3 mmol) was dissolved in (*caution! corrosive*) trifluoroacetic acid (150 mL) and heated to reflux. Water (150 mL) was added, and the mixture was left to cool while stirring. After 1 h the mixture was poured into water (500 mL), and the mixture was extracted with CH_2Cl_2 (2 × 300 mL). The organic phase was washed with water (200 mL) and $NaHCO_3$(aq) (1 M, 200 mL), dried over $MgSO_4$, and evaporated. This gave **11** as a colorless oil in 81% yield (1 g). ^1H NMR (250 MHz, $CDCl_3$, 300 K, TMS): δ = 0.9 (s, 6H, CH_3), 1.1−1.6 (m, 30H), 2.6 (t, 2H, CH_2), 3.0 (t, 2H, CH_2), 3.1 (d, 2H, CH_2), 4.1 (m, 4H, CH_2), 7.0 (s, 1H, ArH), 7.2 (d, 2H, ArH), 7.4 (d, 2H, ArH), 7.8 (s, 1H, ArH), 10.3 (s, 1H, CHO). ^{13}C NMR (63 MHz, $CDCl_3$, 300 K, TMS): δ = 14.0, 16.3 (d, J = 6 Hz), 22.6, 29.10, 29.18, 29.24, 29.3, 29.4, 29.5, 29.8, 31.1, 31.7, 31.8, 31.9, 32.4, 33.5 (d, J = 138 Hz), 62.1 (d, J = 7 Hz), 128.9 (d, J = 6 Hz), 129.6 (d, J = 9 Hz), 130.8, 130.9, 132.0, 132.6, 138.6, 139.5 (d J = 3 Hz), 142.9, 146.9, 192.0. Anal. Calcd for $C_{34}H_{53}O_4P\cdot{}^1/_2H_2O$: C, 72.18; H, 9.62. Found: C, 72.52; H, 9.79.

4-Formyl-4′-cyanomethyl-2,5-dioctylbiphenyl (12). Compound **10** (2.5 g, 4.7 mmol) was dissolved in (*caution! corrosive*) trifluoroacetic acid (150 mL) and heated to reflux. Water (150 mL) was added, and the mixture was left to cool while stirring. After 1 h the mixture was poured into water (500 mL), and the mixture was extracted with CH_2Cl_2 (2 × 300 mL). The organic phase was washed with water (200 mL) and $NaHCO_3$(aq) (1 M, 200 mL), dried over $MgSO_4$, and evaporated. The crude oil could be crystallized from light petroleum (25 mL). This gave **11** as a colorless solid in 89% yield (1.9 g); mp 28−31 °C. ^1H NMR (250 MHz, $CDCl_3$, 300 K, TMS): δ = 0.9 (s, 6H, CH_3), 1.1−1.6 (m, 24H), 2.6 (t, 2H, CH_2), 3.0 (t, 2H, CH_2), 3.8 (s, 2H, CH_2), 7.0 (s, 1H, ArH), 7.2 (d, 2H, ArH), 7.3 (d, 2H, ArH), 7.8 (s, 1H, ArH), 10.3 (s, 1H, CHO). ^{13}C NMR (63 MHz, $CDCl_3$, 300 K, TMS): δ = 14.5, 23.0, 23.8, 29.5, 29.6, 29.7, 29.8, 29.9, 30.0, 31.5, 32.2, 32.3, 32.4, 32.8, 32.9, 118.1, 128.2, 129.5, 130.0, 132.6, 133.0, 133.3, 139.0, 141.2, 143.4, 146.7, 192.4. Anal. Calcd for $C_{31}H_{43}NO$: C, 83.54; H, 9.72; N, 3.14. Found: C, 83.42; H, 9.72; N, 3.16.

Poly(4,4′-(2,5-dioctyl)biphenylenevinylene) (13). Compound **11** (3 g, 5.4 mmol) was dissolved in dry THF (150 mL) under argon. *t*BuOK (1 g, excess) was added, and the mixture was refluxed overnight. The mixture was cooled, and methanol (200 mL) containing HCl(aq) (25 mL, 37%) was added; the mixture was stirred for 5 min and then filtered. The fluffy product was washed with acetone and dried. This gave **13** as a colorless solid in 96% yield (2.1 g). ^1H NMR (250 MHz, $CDCl_3$, 330 K, TMS): δ = 0.89 (broad s, 6H, CH_3), 1.2−1.8 (m, 24H, CH_2) 2.65 (m, 2H, CH_2Ar), 2.9 (m, 2H, CH_2Ar), 6.9−7.7 (m, 8H, ArH); M_p = 3210, M_n = 3120, M_w/M_n = 1.49.

Poly(4,4′-(2,5-dioctyl)biphenylenecyanovinylene) (14). Compound **12** (5 g, 11.2 mmol), dry THF (50 mL), and *t*BuOH (100 mL) were stirred at 50 °C under argon. *t*BuOK (100 mg) was added, and the mixture became dark red in 10 s. nBu_4NOH(aq) (40%, 2 mL) was added. The mixture becomes dark gray and forms a gel almost immediately. After 5 min of stirring the mixture became a thick pale yellow paste. After stirring for 10 min further the mixture was poured into a beaker containing MeOH (200 mL) and HCl(aq) (5 mL, 37%). The bright yellow product was filtered, washed with methanol, and dried in a vacuum oven at 40 °C. This gave **14** as a light yellow solid in 86% yield (4.14 g). ^1H NMR (250 MHz, $CDCl_3$, 330 K, TMS): δ = 0.89 (broad s, 6H, CH_3), 1.2−1.8 (m, 24H, CH_2), 2.73 (broad t, 4H, J = 7 Hz, CH_2Ar), 7.16 (s, 1H, ArH), 7.48 (d, 2H, J = 8 Hz, ArH), 7.79 (d, 2H, J = 7 Hz, ArH), 7.95 (d, 2H, J = 7 Hz, ArH); M_p = 6690, M_n = 7500, M_w/M_n = 1.94.

Photophysical Methods. The UV−vis spectra were recorded in dry THF. The absorption maxima, extinction coefficients, and minimum-energy cutoff were respectively 350 nm, 19 000 M^{-1} cm^{-1}, and 3.1 eV for **13** and 358 nm, 21 000 M^{-1} cm^{-1}, and 3.0 eV for **14**. The minimum-energy cutoff was the position at the low-energy side where the absorbance was 5% of the maximum absorbance. This value was used as the optical band gap energy, E_g. The samples for ultraviolet photoelectron spectroscopy measurements (UPS) were prepared by spin-coating a 1 mg mL^{-1} solution of **13** and **14** in THF onto a freshly prepared (by sputtering) polycrystalline gold substrate. The samples were then dried in a vacuum oven at 50 °C for 24 h. The photoelectron spectra were recorded at the ASTRID storage ring at Aarhus University, Denmark. The beamline consists of an SX-700 monochromator and a hemispherical electron energy analyzer. An ESCA (electron spectroscopy for chemical analysis) of the samples was recorded first to check the cleanliness of the area where the incident photons illuminated the sample and to confirm the presence of the elements (C for **13**, C and N for **14**). The photoelectrons were measured at an angle normal to the sample surface. The ESCA scans were performed with 800 eV photons and a resolution of 0.4 eV. The photoelectron spectra were recorded using 50 eV incident photons and a resolution of 0.2 eV. The sample holder was electrically isolated from the chamber, and the sample was kept at a potential of −9.5 V relative to the surrounding instrument. This serves to eliminate the contribution from the instrument work function at the low-energy cutoff. A clean gold substrate was first entered and sputtered with ionized argon using an emission current of 22 mA and a potential of 3 kV. The sputtering was stopped after 1 h. Subsequent measurements of the gold work function gave the reference value. The samples of **13** and **14** were introduced, and the photoelectron spectra were recorded. The onset and cutoff of the intensity normalized photoelectron spectra were used to compute the work function in the case of the pure gold substrate and the ionization potential and valence band edge in the case of the gold substrates containing the samples. The data are presented in Table 1. The gold work function, Φ_{Au}, was determined to be 4.9 eV. The position of the valence band edge for **13** and **14**, E_F^{VB}, was lower than the Fermi level of gold. The Fermi level in compounds **13** and **14** are thus situated in the forbidden band gap of the materials, and the distance from the Fermi level of the samples to the vacuum level is given by the difference between the ionization potential, IP, and E_F^{VB} giving E_F^{VAC}. The vacuum level shift, Δ, is thus obtained as $\Delta = E_F^{VAC} - \Phi_{Au}$. The vacuum level shift reflects how the molecules orient at the surface giving a dipole layer. The procedure employed in the analysis of the data has been reported.[10,16]

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