Controlling the Energy Levels of Conducting Polymers. Hydrogen versus Fluorine in Poly(dialkylterphenylenevinylene)s

Frederik C. Krebs* and Mikkel Jørgensen

The Danish Polymer Centre, RISØ National Laboratory, P.O. Box 49, DK-4000 Roskilde, Denmark

Received May 3, 2002; Revised Manuscript Received June 27, 2002

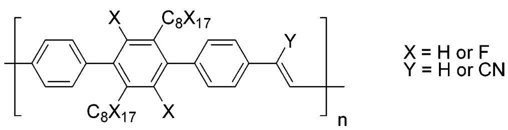
ABSTRACT: The control of the position of the energy levels in conducting polymers through fluorine substitution is demonstrated. The synthesis of four different monomers and polymers of the poly(terphenylenevinylene) type is presented. The synthetic procedure started with 4-bromo-2,5-dioctylphenylboronic acid (**1**) coupled by the Suzuki method with 4-bromobenzaldehyde to give 4′-bromo-2′,5′-dioctyl-4-formylbiphenyl (**2**) that was again coupled by the Suzuki method with 4-diethylphosphonylmethylphenylboronic acid and 4-cyanomethylphenylboronic acid to give the monomers 4″-diethylphosphonylmethyl-2′,5′-dioctyl-4-formylterphenyl (**3**) and 4″-cyanomethyl-2′,5′-dioctyl-4-formylterphenyl (**4**). The partially fluorinated analogous monomers were prepared similarly employing 2,5-difluoro-3,6-diperfluorooctyl-1,4-dibromobenzene. This gave 4-bromo-2,5-difluoro-3,6-diperfluorooctyl-4′-diethylphosphonylmethylbiphenyl (**5**) and 4-bromo-2,5-difluoro-3,6-diperfluorooctyl-4′-cyanomethylbiphenyl (**6**). Compounds **5** and **6** were both subjected to Suzuki couplings with 4-formylphenylboronic acid to give respectively 4-formyl-2′,5′-difluoro-3′,6′-diperfluorooctyl-4″-diethylphosphonylmethylterphenyl (**7**) and 4-formyl-2′,5′-difluoro-3′,6′-diperfluorooctyl-4″-cyanomethylterphenyl (**8**). The monomers **3**, **4**, **7,** and **8** were polymerized to give the polymers poly(2′,5′-dioctyl-4,4″-terphenylenevinylene) (**9**), poly(2′,5′-dioctyl-4,4″-terphenylenecyanovinylene) (**10**), poly(2′,5′-difluoro-3′,6′-diperfluorooctyl-4,4″-terphenylenevinylene) (**11**), and poly(2′,5′-difluoro-3′,6′-diperfluorooctyl-4,4″-terphenylenecyanovinylene) (**12**). Thin films of the polymers on polycrystalline gold substrates were subjected to ultraviolet photoelectron spectroscopy, and the ionization potentials were determined to be 4.85, 4.60, 4.75, and 5.95 eV for **9**, **10**, **11**, and **12** respectively. The positions of the highest occupied energy levels were determined to be 1.45, 2.65, 2.25, and 3.05 eV lower than that of gold for **9**, **10**, **11**, and **12**, respectively. Fluorine and cyano substitution thus allows for an energy level tuning by as much as 1.6 eV.

Introduction

The field of conducting polymers has received an enormous amount of attention in recent years due to their potential widespread usage in many aspects of science and technology. Light-emitting diodes,[1] polymer-based electronic circuitry,[2] and all polymer photovoltaic cells[3] are just a few of the very promising areas of application. The performance of the devices made from these polymer materials is very dependent on the physical properties of the materials. Of central importance is the carrier mobility, the positions of the energy levels, and the organization/structure of the materials. Most effort is currently being placed in one of these three general areas. Our particular interest is the control of each of these parameters by synthetic design of the monomers and the resultant polymers.

The systematic study of the properties and carrier mobilities of conducting polymers belonging to the class of poly(arylenealkenylene)s has been reported.[4] It was noteworthy that the poly(terphenylenevinylene) system was the polymer material that gave the highest intrinsic carrier mobility of 2.38×10^{-7} m^2 V^{-1} s^{-1}. In terms of applicability of the conducting polymer materials, one aims for the largest possible carrier mobility and the longest carrier lifetime. The carrier mobility in these polymer materials is low compared to organic single crystals where 1−3 orders of magnitude larger mobilities have been reported and even superconductivity has been proposed.[5] Despite this, polymer materials have been subject to intense study for the purpose of molecular electronics and polymer-based electronics. This is mostly due to the promises held by these materials in terms of processability, ease of application, potentially low production cost, possibility of self-organization through formation of aggregates directly onto a device structure, etc. The positions of the electronic energy levels of the polymer materials determine the performance of a given device based on that material. Often the variability of the device structure is limited, and an understanding of how the electronic energy levels can be tuned to match the device structure (without altering any other physical properties of the polymer material) is of crucial importance. In the world of molecular materials and polymers it is rarely possible to alter a physical property (for instance, the positions of the electronic energy levels) without altering many other physical properties (i.e., solubility, glass transition temperature, conductivity, optical absorption maxima, polarity, etc.). The main reason for this is that the only means of changing the properties is by changing the molecular composition, and the aim of the game is thus to choose a molecular alteration or chemical substitution that will not alter the other properties of interest in any detrimental way.

Scheme 1



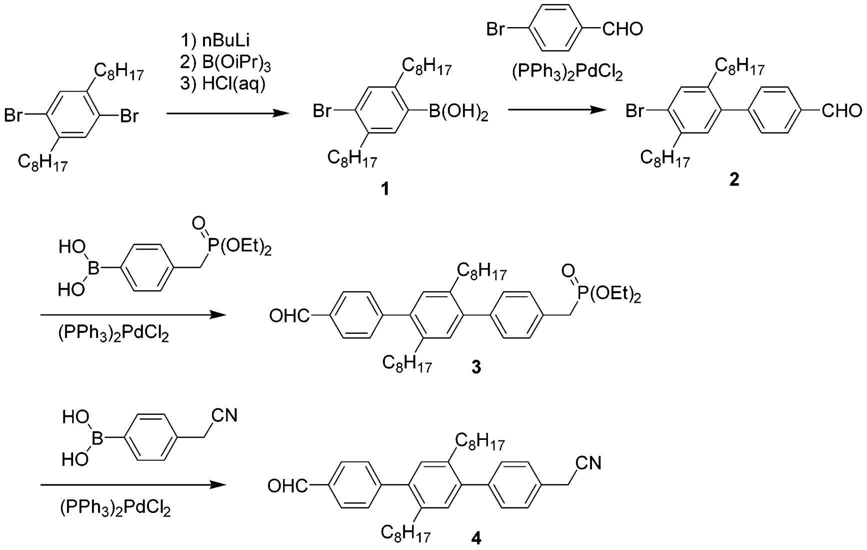
In this paper we focus on the available energy level span for a given conducting polymer of the poly(terphenylenevinylene) type as shown in Scheme 1. Molecular substitution of hydrogen atoms with cyano

---

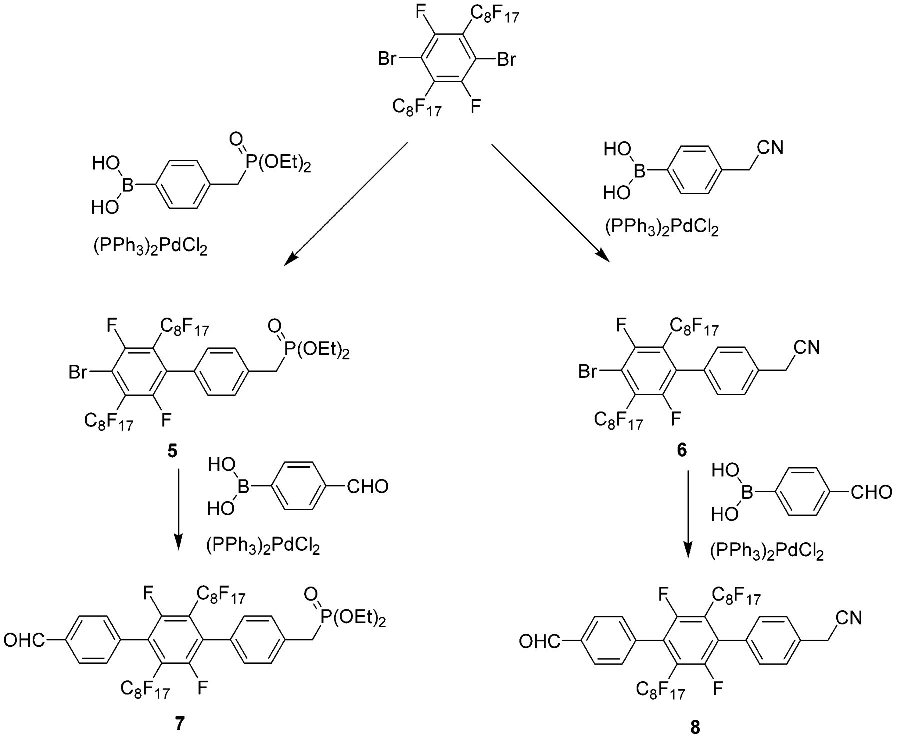
* Corresponding author: e-mail Frederik.krebs@risoe.dk.

10.1021/ma020678u CCC: $22.00

Scheme 2



Scheme 3



groups and fluorine atoms in the same terphenylene-vinylene polymer backbone followed by ultraviolet photoelectron spectroscopy studies allowed us to show how much the positions of the energy levels for this system could be tuned as the molecular substitution pattern was altered.

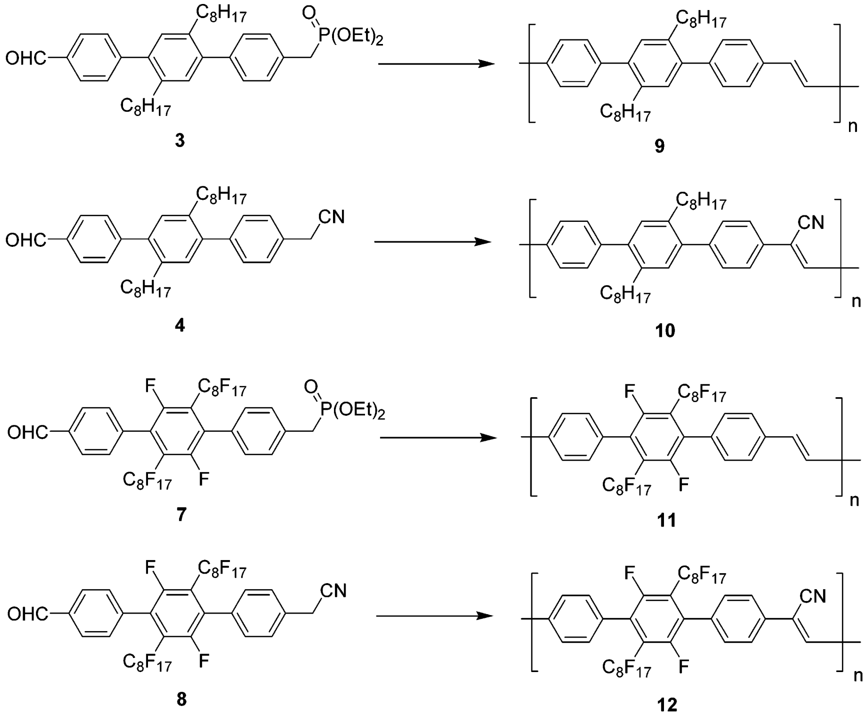
Results and Discussion

Synthesis. The hydrogen monomers were prepared as shown in Scheme 2 starting from 1,4-dibromodioctylbenzene[6] by metal−halogen exchange with *n*BuLi in THF and reaction with triisopropylborate followed by hydrolysis to give the boronic acid **1**. Subsequent aryl−aryl coupling using a standard Suzuki reaction of **1** with 4-bromobenzaldehyde gave the biphenyl system **2** that served as the common starting material for each of the monomers **3** and **4** that were also obtained by aryl−aryl standard Suzuki coupling reactions.

The fluorinated analogous monomers were also prepared by aryl−aryl Suzuki coupling reactions as shown in Scheme 3, but unlike the hydrogen monomers metal−halogen exchange was in our hands not possible. The coupling of only one 4-formylphenylboronic acid onto 1,4-dibromo-2,5-difluoro-3,6-diperfluorooctylbenzene[7a] was very difficult, and it was found necessary to make two separate synthetic pathways using separately 4-diethylphosphonylmethylphenylboronic acid[7b] to give **5** and 4-cyanomethylphenylboronic acid[7b] to give **6**. **5** and **6** could then both be reacted with 4-formylphenylboronic acid to give the fluorinated monomers **7** and **8**.

Both of the polymerization reaction types employed here are of the condensation type. In the case of **3** and **7** the polymerization proceeded under anhydrous condi-

Scheme 4



tions using sodium hydride as the base to give the terphenylenevinylene polymers **9** and **11**. The polymerization of the monomers **4** and **8** were carried out using *t*BuOK in aqueous THF/*t*BuOH/*n*Bu_4NOH, giving the terphenylenecyanovinylene polymers **10** and **12** as shown in Scheme 4.[8]

The characterization of the polymers under the same conditions proved difficult due to the very different solubility properties of the all-hydrogen vs the partially fluorinated polymers. The molecular weights for the polymers **9** and **10** were thus determined by SEC (solvent exclusion chromatography) with reference to a polystyrene standard, indicating molecular weights (M_w) of respectively 30 000 and 140 000 g mol^{-1}. It was in our hands not possible to obtain MALDI–TOF spectra for **9** and **10**. The determination of the molecular weights of the fluorinated polymers **11** and **12** on the other hand could not be obtained by SEC due to a very poor solubility in common solvents at room temperature. For these polymers, however, it was possible to obtain MALDI–TOF spectra, and molecular weights up to 12 000 and 22 000 g mol^{-1} could be observed respectively for **11** and **12**. This corresponds to oligomers with a degree of polymerization of 10 and 20, respectively. It was not possible to obtain an indication of (M_w) due to the very high laser powers that were used to obtain the spectrum. This gave rise to a large nonlinear background due to degradation products. An added difficulty with MALDI–TOF is the unknown and different ionization cross sections for the different oligomers.

UV–vis Spectra. The solution UV–vis spectra were recorded on the polymers dissolved in 1,2-dichlorobenzene and on thin films spin-coated onto glass slides from boiling 1,2-dichlorobenzene. The results are presented in Table 1. The absorption maxima and shift were determined on thin films of the polymers spin-coated onto glass slides. The extinction coefficient could not be determined reliably in this fashion so only the position of the maxima is reported. The general trend was a slight red shift of the absorption maxima in the films as compared to the absorption maximum obtained for the polymers in 1,2-dichlorobenzene solution. The magnitude of the extinction coefficients for the fluorinated polymers was largest for **9**. We believe that the lower extinction coefficient for **10** is due to the steric effect of the cyano group, which also shifts the absorption maximum by about 10 nm to longer wavelengths.

Table 1. UV–vis Data E_g (eV), λ_{max} (nm) (for Thin Films and in Solution), and ϵ (M^{-1} cm^{-1}) Based on the Solution Data

compd	E_g (eV)[a]	$\lambda_{max,film}$ (nm)	$\lambda_{max,soln}$ (nm)	ϵ (M^{-1} cm^{-1})
9	3.2	348	345	61 000
10	2.9	360	355	31 000
11	3.4	338	337	4 300
12	3.3 (1.5)[b]	325	315[c]	12 500[c]

[a] The optical band gap is based on the low-energy onset in the UV–vis spectra. [b] There is a weak shoulder that extends far into the visible range which gives the material a yellow color; the estimated cutoff for this shoulder is given in parentheses (see also the Supporting Information). [c] Because of the solvent cutoff at the short wavelengths, it was not possible to determine whether there was a maximum at a lower wavelength than 300 nm which the shape of the absorption curve seemed to indicate.

The extinction coefficients for the fluorinated polymers are much lower, and we ascribe this to, first, a steric effect due to an increased torsion angle between the phenyl rings of the terphenylene system (the steric effect of the difluorodiperfluorooctylphenylene ring) and, second, due to a smaller degree of polymerization. The optical band gap values were based on the value obtained for the low-energy onset in the UV–vis spectra obtained in solution. As expected, the band gap for the cyanovinylene derivatives (**10** and **12**) was smaller than for the vinylene derivatives (**9** and **11**). It is noticeable when comparing the fluorinated and nonfluorinated derivatives that the band gaps are significantly larger for the fluorinated derivatives. We also ascribe this to the steric effect of the 2,5-difluoro-3,6-diperfluoro-

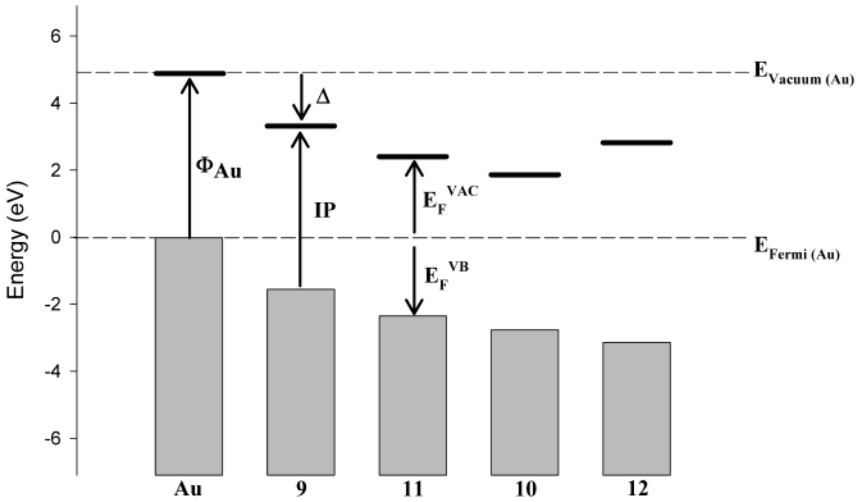


Figure 1. Energy levels as observed on thin films of the polymers on a polycrystalline gold substrate using ultraviolet photoelectron spectroscopy with an incident photon energy of 50 eV. The filled boxes indicate the filled levels, and the solid lines indicate the vacuum level of the polymer material. The data are given in Table 2. To illustrate graphically the parameters involved in the measurements, the gold work function, Φ_{Au}, is shown for gold. The ionization potential, IP, and the vacuum level shift, Δ, are shown for **9**. Finally, the distances from the position of the Fermi level of gold to the valence band edge of the polymer, E_F^{VB}, and to the vacuum level, E_F^{VAC}, are shown for **11**.

octylphenylene moieties which essentially result in a smaller degree of conjugation. The polymer **12** however has a yellow color, and this is in direct contrast to the observed band gap based on the low-energy cutoff of 3.3 eV. UV−vis spectra of concentrated solutions showed that there is a weak shoulder that extends well into the visible region and that thus explains this yellow coloration (see Supporting Information). The corresponding band gap, based on an estimated cutoff for this broad feature, is 1.5 eV as given in parentheses in Table 1. The shoulder did not seem to arise due to an impurity since the same UV−vis spectra were obtained upon repeated reprecipitation from 1,2-dichlorobenzene.

Energy Levels. It is well-known that for a given molecular system the electronic structure[9] is altered by chemical substitution and that this effect can be separated into two contributions: an inductive effect (where the electron donating or withdrawing effect of the substituents shift both the HOMO and LUMO) and a nonresonance or steric effect (where the steric effect of the substituents causes the conjugation in the conducting polymer backbone to increase or decrease). The inductive effect causes the absolute position of the entire band structure to shift up and down on the energy scale whereas the resonance/steric effect can (but not necessarily) lead to a shift in the relative positions of the energy levels and does always lead to a change in the electronic structure. The change in the electronic structure is most often seen as a change in the optical absorption properties. The alterations possible range from changes in the bandwidth of the valence and conduction bands and a shift in their position that are not necessarily correlated as for instance a change in the geometry can lead to an increase in the band gap without altering the position of the valence band as documented by Bredas et al.[10] It is desirable to be able to shift the position of the energy levels without changing the optical absorption properties too much. For this purpose we have synthesized derivatives of the poly(terphenylenevinylene) system where we use perfluorination to shift the energy levels without changing the optical absorption. The use of a cyano group leads to a change in the position of the energy levels as well as a change in the optical absorption properties.

In Figure 1 it is clear how a combination of fluorine and cyano substitution can be used to tune the position of the topmost filled electronic energy level within an 1.6 eV range to suit the need of matching the energy levels to external circuitry.

These results were obtained from the photoelectron spectroscopy data and involve firstly the measurement of the work function for a clean gold substrate, Φ_{Au}. The onset where photoelectrons become detectable in the spectrometer at low binding energies defines the position of the Fermi level of the substrate (gold). Once determined, it serves as the zero binding energy reference level. The work function of the substrate is determined directly as the ionization potential, which is the difference between the secondary electron cutoff at high binding energies (BE_{max}) and the incoming photon energy, $h\nu$, as given by eq 1.

$$\Phi_{Au} = h\nu - BE_{max} \tag{1}$$

$$E_F^{VB} = BE_{min} \tag{2}$$

$$E_F^{VAC} = h\nu - (BE_{max} + BE_{min}) \tag{3}$$

$$IP = E_F^{VAC} + E_F^{VB} \tag{4}$$

$$\Delta = E_F^{VAC} - \Phi_{Au} \tag{5}$$

A gold substrate containing a thin polymer film is then introduced, and the onset of photoelectrons toward low binding energies, BE_{min}, defines the position of the valence band edge for the polymer material, E_F^{VB}, with respect to the Fermi level of gold. E_F^{VB} is given in eq 2. In Figure 2 it is shown how BE_{max} and BE_{min} are obtained. For the polymer samples studied here the onset was lower than the Fermi level of gold (in absolute energy terms). E_F^{VB} can be considered as the barrier to hole injection from the metal substrate into the polymer material. The distance from the position of the Fermi level of the metal substrate to the vacuum level of the polymer layer, E_F^{VAC}, is given by eq 3. Together, E_F^{VAC} and E_F^{VB} define the ionization potential, IP, of the polymer which is a material constant as given in eq 4.

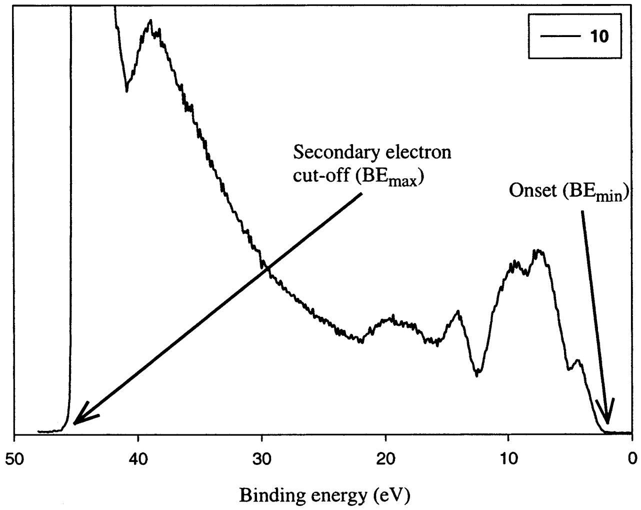


Figure 2. Photoelectron spectrum of the polymer **10** showing the binding energies of the detected photoelectrons. The incident UV photons had a wavelength of 50 eV, and the binding energy scale is referenced to the Fermi level of gold. An indication of where the values for the secondary electron cutoff (BE_{max}) and the photoelectron onset (BE_{min}) are found is given by the arrows.

The Fermi level is thus situated in the forbidden band gap of the materials. Often the position of the vacuum level for the polymer layer is shifted relative to the vacuum level observed for the reference metal substrate. The vacuum level shift, Δ, is given by eq 5. The vacuum level shift reflects how the molecules orient at the surface, often giving rise to a dipole layer that depending on the direction of the dipoles with respect to the normal of the surface can make the escape of electrons easier or more difficult.

Conclusions

We have presented the synthesis of four new polymers sharing the same terphenylenevinylene repeat unit. Different chemical substitution patterns of the four polymers allowed us to control the position of the electronic energy levels by 1.6 eV. Two types of substitution were used a cyano group and fluorine for hydrogen substitution, and it was found that both fluorine and cyano substitution lead to a lowering of the position of the electronic energy levels with a small influence on the band gap.

Experimental Section

Commercially available compounds were purchased from Aldrich. 1,4-Dibromo-2,5-dioctylbenzene was prepared as described in ref 6, and 4-formylphenylboronic acid was prepared as described in ref 11. In compounds **1** and **2** some signals were missing in the ^{13}C NMR spectrum; this is ascribed to accidental isochrony and further evidenced by some signals that were broad. In the fluorinated compounds **5**, **6**, **7**, and **8** the ^{13}C NMR signals from the carbon atoms in the central ring with the fluorine and diperfluorooctyl substituents were not discernible from the background noise. Traditional ^{13}C NMR without special broadband C−F decoupling schemes gives rise to a myriad of signals due to the large magnitude of the various carbon−fluorine coupling constants. The recording of ^{13}C NMR spectra of the neat compounds in the molten state when possible (with a capillary containing DMSO-d_6) for extended periods of time of 1−2 days gave only limited information. The ^{19}F NMR spectra were run with a sealed capillary containing hexafluorobenzene (C_6F_6) as standard. Elemental analysis was possible with addition of V_2O_5 to avoid combustion problems.

4-Bromo-2,5-dioctylphenylboronic Acid (1). 1,4-Dibromo-2,5-dioctylbenzene (56 g, 0.122) was placed in a 1 L roundbottom flask under argon with dry THF (500 mL) giving a clear solution. The mixture was cooled on a CO_2(s)/acetone bath to −30 °C where it began to precipitate. At this point *n*BuLi (76 mL, 1.6 M in hexanes) was added whereby the solids dissolved, and cooling was continued until a temperature of −70 °C was reached. Triisopropylborate (30 mL, excess) was added, the cooling bath removed, and the mixture allowed to reach room temperature overnight. HCl(aq) (100 mL, 6 M) was added, and the mixture was stirred for 1 h. The mixture was then evaporated on the rotary evaporator, giving a colorless solid toward the end of the evaporation that was filtered, washed with water, and dried. This gave **1** as a colorless material in 96% yield (50 g); mp 82−84 °C. ^1H NMR (250 MHz, $CDCl_3$/DMSO-d_6, 300 K, TMS): $\delta = 0.9$ (t, 6H, CH_3), 1.3−1.6, (m, 24H, CH_2), 2.6 (t, 2H, CH_2), 2.8 (t, 2H, CH_2), 7.3 (s, 1H, ArH), 7.5 (s, 1H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$/DMSO-d_6, 300 K, TMS): $\delta = 13.9$, 22.3, 28.9, 29.1, 29.3, 29.3, 29.8, 30.0, 31.6, 32.4, 34.8, 35.3, 125.1, 132.3, 135.9, 137.5, 147.1. Anal. Calcd for $C_{22}H_{38}BBrO_2$: C, 62.14; H, 9.01. Found: C, 62.28; H, 8.98.

4′-Bromo-2′,5′-dioctyl-4-formylbiphenyl (2). Compound **1** (50 g, 0.117 mol), toluene (250 mL), 4-bromobenzaldehyde (22 g, excess), and Na_2CO_3(aq) (2 M, 100 mL) were mixed in a 1 L conical flask and degassed with argon while stirring. After 10 min $(PPh_3)_2PdCl_2$ (0.5 g, catalyst) was added, and the mixture heated to reflux with vigorous stirring under argon overnight. The mixture was then cooled, and the toluene phase separated and filtered through silica (2 cm × 5 cm). The silica was washed with toluene (100 mL), and the combined filtrate was subjected to steam distillation to remove the toluene and the excess 4-bromobenzaldehyde. The contents of the steam distillation flask were cooled and extracted with ether (3 × 300 mL). The combined extracts were dried ($MgSO_4$) and evaporated to give a light yellow oil that was chromatographed on silica with light petroleum:ethyl acetate/10:1 ($R_f = 0.5$). This gave **2** as a colorless oil in 74% yield (42 g). ^1H NMR (250 MHz, $CDCl_3$, 300 K, TMS): $\delta = 0.9$ (t, 6H, CH_3), 1.1−1.6, (m, 24H, CH_2), 2.5 (t, 2H, CH_2), 2.7 (t, 2H, CH_2), 7.0 (s, 1H, ArH), 7.4 (d, 2H, ArH), 7.5 (s, 1H, ArH), 7.9 (d, 2H, ArH), 10.1 (s, 1H, CHO). ^{13}C NMR (63 MHz, $CDCl_3$, 300 K, TMS): $\delta = 14.7$, 14.8, 23.3, 23.4, 29.7, 29.8, 29.9, 30.0, 30.1, 30.2, 30.7, 31.8, 32.4, 32.5, 33.1, 36.4, 124.8, 130.2, 130.6, 131.9, 134.1, 135.8, 140.2, 140.3, 148.3, 192.6. Anal. Calcd for $C_{29}H_{41}BrO$: C, 71.74; H, 8.51. Found: C, 71.80; H, 8.58.

4″-Diethylphosphonylmethyl-2′,5′-dioctyl-4-formylterphenyl (3). Compound **2** (8.93 g, 18.4 mmol), 4-(diethylphosphonylmethyl)phenylboronic acid (5 g, 18.4 mmol), toluene (200 mL), and Na_2CO_3(aq) (50 mL, 2 M) were mixed in a 500 mL conical flask and degassed with argon. After 10 min $(PPh_3)_2PdCl_2$ (0.5 g, catalyst) was added, and the mixture refluxed for 24 h. The mixture was cooled to room temperature, and the organic phase was separated and filtered through silica (2 cm × 5 cm) and the silca washed with toluene (200 mL). The combined organic filtrate was concentrated to give a yellow oil that was chromatographed on silica using heptane: ethyl acetate/2:1 ($R_f = 0.4$). This gave **3** as a colorless oil in 70% yield (8.1 g). ^1H NMR (250 MHz, $CDCl_3$, 300 K, TMS): $\delta = 0.8$ (t, 6H, CH_3), 1.1−1.6, (m, 30H), 2.5 (t, 4H, CH_2), 3.2 (d, 2H, CH_2), 4.1 (m, 4H, CH_2), 7.1 (d, 2H, ArH), 7.3 (s, 1H, ArH), 7.4 (s, 1H, ArH), 7.4 (d, 2H, ArH), 7.6 (d, 2H, ArH), 8.0 (d, 2H, ArH), 10.1 (s, 1H, CHO). ^{13}C NMR (63 MHz, $CDCl_3$, 300 K, TMS): $\delta = 14.4$, 14.5, 16.7(d, $J = 6$ Hz), 22.8, 22.9, 23.0, 29.5, 29.6, 29.7, 29.8, 29.9, 31.7, 31.8, 31.9, 32.2, 33.0, 33.1, 34.1 (d, $J = 138$ Hz), 62.8 (d, $J = 7$ Hz), 129.7 (d, $J = 6$ Hz), 129.8, 129.9, 130.0, 130.4, 130.5 (d, $J = 9$ Hz), 130.9, 131.5, 135.3, 137.7, 138.2, 139.8, 140.7 (d, $J = 3$ Hz), 141.6, 192.4. Anal. Calcd for $C_{40}H_{57}O_4P$: C, 75.91; H, 9.08. Found: C, 75.88; H, 9.10.

4″-Cyanomethyl-2′,5′-dioctyl-4-formylterphenyl (4). Compound **2** (7.9 g, 16.2 mmol), 4-cyanomethylphenylboronic acid (2.6 g, 16.2 mmol), toluene (200 mL), and Na_2CO_3(aq) (50 mL, 2 M) were mixed in a 500 mL conical flask and degassed with argon. After 10 min $(PPh_3)_2PdCl_2$ (0.5 g, catalyst) was added, and the mixture was refluxed for 24 h. The mixture was cooled to room temperature, and the organic phased was separated and filtered through silica (2 cm × 5 cm o.d.) and the silca washed with toluene (200 mL). The combined organic filtrate was evaporated to give an oil that was taken up in boiling heptane. Upon cooling, crystals formed that were filtered, washed with heptane, and dried. This gave **4** as a colorless solid in 36% yield (3.1 g); mp 63−64 °C. ^{1}H NMR (250 MHz, $CDCl_3$, 300 K, TMS): $\delta = 0.8$ (t, 6H, CH_3), 1.1−1.3 (m, 20H, CH_2), 1.4−1.5 (m, 4H, CH_2), 2.6 (t, 4H, CH_2), 3.9 (s, 2H, CH_2), 7.1 (s, 2H ArH), 7.4 (s, 4H, ArH), 7.5 (d, 2H, ArH), 8.0 (d, 2H, ArH), 10.1 (s, 1H, CHO). ^{13}C NMR (63 MHz, $CDCl_3$, 300 K, TMS): $\delta = 14.7$, 14.8, 23.1, 23.3, 24.1, 29.7, 29.8, 29.9, 30.1, 30.2, 31.9, 32.0, 32.1, 32.2, 32.4, 32.5, 33.2, 118.5, 128.4, 129.1, 130.2, 130.6, 130.7, 131.2, 131.7, 135.6, 138.1, 138.4, 140.4, 141.3, 142.3, 149.1, 192.6. Anal. Calcd for $C_{37}H_{47}NO$: C, 85.17; H, 9.08; N, 2.68. Found: C, 84.81; H, 9.44; N, 2.52.

4-Bromo-2,5-difluoro-3,6-diperfluorooctyl-4′-diethylphosphonylmethylbiphenyl (5). 1,4-Dibromo-2,5-difluoro-3,6-diperfluorooctylbenzene (13 g, 11.7 mol), 4-(diethylphosphonylmethyl)phenylboronic acid (3.2 g, 11.8 mmol), Na_2CO_3 (14 g), water (150 mL), and toluene (400 mL) were mixed and degassed with argon. $(PPh_3)_2PdCl_2$ (500 mg, catalyst) was added, and the mixture was refluxed for 72 h. The upper light yellow toluene phase was separated and filtered through silica (5 cm × 10 cm o.d.). After washing with toluene the toluene filtrate was discarded, and the column washed with THF (1 L) to liberate the product. The filtrate was evaporated to give a solid that was recrystallized from toluene (100 mL). This gave **5** as a colorless material in 38% yield (5.6 g); mp 120−121 °C. ^{1}H NMR (250 MHz, $CDCl_3$, 300 K, TMS): $\delta = 1.2$ (t, 6H, CH_3), 3.2 (d, 2H, CH_2), 3.9−4.1 (m, 4H, CH_2), 7.1 (d, 2H, ArH), 7.4 (d, 2H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$, 300 K, TMS): $\delta = 16.8$(d, $J = 6$ Hz), 34.4 (d, $J = 138$ Hz), 62.9 (d, $J = 7$ Hz), 129.1 (b), 129.8 (b), 130.2 (d, $J = 7$ Hz), 133.7 (d, $J = 9$ Hz). ^{19}F NMR (235 MHz, $CDCl_3$, 330K, C_6F_6): $\delta = -122.5$ (m, 4F, CF_2), −119.1 (m, 4F, CF_2), −118.1 (m, 12F, CF_2), −116.6 (m, 2F, CF_2), −115.8 (m, 2F, CF_2), −106.1 (m, 1F, ArF), −100.5 (m, 2F, CF_2), −99.4 (m, 2F, CF_2), −93.1 (m, 1F, ArF), −77.5 (m, 6F, CF_3). Anal. Calcd for $C_{33}H_{16}BrF_{36}O_3P$: C, 31.57; H, 1.28. Found: C, 31.16; H, 0.90.

4-Bromo-2,5-difluoro-3,6-diperfluorooctyl-4′-cyanomethylbiphenyl (6). 1,4-Dibromo-2,5-difluoro-3,6-diperfluorooctylbenzene (13 g, 11.7 mol), 4-cyanomethylphenylboronic acid (2 g, 12.4 mmol), Na_2CO_3 (14 g), water (150 mL), and toluene (400 mL) were mixed and degassed with argon. $(PPh_3)_2PdCl_2$ (500 mg, catalyst) was added, and the mixture was refluxed for 72 h. The mixture was filtered to remove a little black material. The organic phase was then separated and filtered through a little silica (1 cm × 10 cm o.d.) that was washed with boiling toluene (300 mL). The combined filtrate was evaporated and dissolved in toluene (750 mL) and left to stand at room temperature. The precipitated material was filtered and discarded. The filtrate was concentrated to a volume of 50 mL and left to crystallize. The product was filtered, washed with heptane, and dried. This gave **6** as a colorless material in 41% yield (5.5 g); mp 124−126 °C. ^{1}H NMR (250 MHz, $CDCl_3$, 330 K, TMS): $\delta = 3.8$ (s, 2H, CH_2), 7.2 (d, 2H, ArH), 7.4 (d, 2H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$, 330 K, TMS): $\delta = 24.2$, 117.7, 128.4, 130.6, 130.8, 132.0. ^{19}F NMR (235 MHz, $CDCl_3$, 330 K, C_6F_6): $\delta = -122.5$ (m, 4F, CF_2), −119.1 (m, 4F, CF_2), −118.1 (m, 12F, CF_2), −116.7 (m, 2F, CF_2), −115.8 (m, 2F, CF_2), −106.3 (m, 1F, ArF), −100.7 (m, 2F, CF_2), −98.4 (m, 2F, CF_2), −92.8 (m, 1F, ArF), −77.5 (m, 6F, CF_3). Anal. Calcd for $C_{30}H_6BrF_{36}N$: C, 31.49; H, 0.53; N, 1.21. Found: C, 31.68; H, 0.66; N, 1.24.

4-Formyl-2′,5′-difluoro-3′,6′-diperfluorooctyl-4′′-diethylphosphonylmethylterphenyl (7). Compound **5** (3 g, 2.4 mmol), 4-formylphenylboronic acid (1 g, excess), Na_2CO_3 (4 g), water (50 mL), and toluene (100 mL) were mixed and degassed with argon. After 10 min $(PPh_3)_2PdCl_2$ (500 mg, catalyst) was added, and the mixture was refluxed overnight. After cooling, the organic phase was separated and passed through silica (2 cm × 5 cm o.d.), and the silica was washed with toluene (200 mL). The filtrate was evaporated to give a solid that was recrystallized from toluene:heptane/1:1. This gave **7** as a colorless material in 68% yield (2.1 g); mp 139−140 °C. ^{1}H NMR (250 MHz, $CDCl_3$, 300 K, TMS): $\delta = 1.2$ (t, 6H, CH_3), 3.2 (d, 2H, CH_2), 3.9−4.1 (m, 4H, CH_2), 7.2 (d, 2H, ArH), 7.4 (d, 2H, ArH), 7.5 (d, 2H, ArH), 8.0 (d, 2H, ArH), 10.1 (s, 1H, CHO). ^{13}C NMR (63 MHz, $CDCl_3$, 300 K, TMS): $\delta = 16.5$ (d, $J = 6$ Hz), 34.1 (d, $J = 138$ Hz), 62.7 (d, $J = 7$ Hz), 129.1, 129.6 (b), 129.8, 129.9, 130.4, 133.3 (d, $J = 9$ Hz), 136.9, 137.0 (d, $J = 6$ Hz), 191.9. ^{19}F NMR (235 MHz, $CDCl_3$, 330 K, C_6F_6): $\delta = -122.5$ (m, 4F, CF_2), −119.1 (m, 4F, CF_2), −118.1 (m, 12F, CF_2), −115.8 (m, 4F, CF_2), −103.6 (m, 1F, ArF), −102.8 (m, 1F, ArF), −98.2 (m, 4F, CF_2), −77.5 (m, 6F, CF_3). Anal. Calcd for $C_{40}H_{21}F_{36}O_4P$: C, 37.52; H, 1.65. Found: C, 37.35; H, 1.38.

4-Formyl-2′,5′-difluoro-3′,6′-diperfluorooctyl-4′′-cyanomethylterphenyl (8). Compound **6** (2 g, 1.75 mmol), 4-formylphenylboronic acid (1 g, excess), Na_2CO_3 (7 g), water (125 mL), and toluene (250 mL) were mixed and degassed with argon. $(PPh_3)_2PdCl_2$ (500 mg, catalyst) was added, and the mixture was refluxed under Ar for 24 h. The mixture was filtered through silica (2 cm × 5 cm). The silica was washed with boiling toluene (100 mL), and the combined filtrate was evaporated and dissolved in boiling toluene (150 mL) and left to stand. Hairlike colorless crystals formed that were filtered, washed with toluene and light petroleum, and finally dried. This gave **8** as a colorless material in 90% yield (1.85 g); mp 162−163 °C. ^{1}H NMR (250 MHz, $CDCl_3$, 330 K, TMS): $\delta = 3.8$ (s, 2H, CH_2), 7.3 (d, 2H, ArH), 7.5 (d, 2H, ArH), 7.5 (d, 2H, ArH), 8.0 (d, 2H, ArH), 10.1, (s, 1H, CHO). ^{13}C NMR (63 MHz, $CDCl_3$, 330 K, TMS): $\delta = 24.2$, 128.4, 129.8, 130.7 (b), 130.9, 131.9, 137.2 (b), 137.6, 137.7(d, $J = 6$ Hz), 191.9. ^{19}F NMR (235 MHz, $CDCl_3$, 330 K, C_6F_6): $\delta = -122.6$ (m, 4F, CF_2), −119.1 (m, 4F, CF_2), −118.1 (m, 12F, CF_2), −115.9 (m, 4F, CF_2), −103.1 (m, 2F, ArF), −98.3 (m, 4F, CF_2), −77.6 (m, 6F, CF_3). Anal. Calcd for $C_{37}H_{11}F_{36}NO$: C, 38.00; H, 0.95; N, 1.20. Found: C, 37.78; H, 0.79; N, 0.91.

Poly(2′,5′-dioctyl-4,4′′-terphenylenevinylene) (9). Compound **3** (1.6 g, 2.5 mmol), diphenyl ether (100 mL), and 1,2-dichlorobenzene (100 mL) were placed in a 500 mL conical flask under argon. NaH (1 g, 60% in paraffin, excess) was added, and the mixture was stirred under argon at 150 °C for 16 h. The mixture became a light brown suspension. The mixture was cooled, methanol (200 mL) containing HCl(aq) (25 mL, 37%) was added, and the mixture was stirred for 30 min and then filtered. The light brown product was dissolved in chloroform (200 mL), filtered, and precipitated with hexane. The product was filtered and dried. This gave **9** as a colorless solid in 84% yield (0.95 g). ^{1}H NMR (250 MHz, $C_6D_4Cl_2$, 400 K, TMS): $\delta = 0.88$ (broad singlet, 6H), 1.27 (broad singlet, 20H), 1.66 (broad singlet, 4H), 2.79 (broad singlet, 4H), 7.25−7.65 (m, 12H). ^{13}C NMR (62.9 MHz, $C_6D_4Cl_2$, 400 K, TMS): $\delta = 14.0$, 22.8, 29.5, 31.7, 32.0, 32.2, 33.4, 129.2, 131.4, 136.8, 138.1, 141.3, 142.2. $M_w/M_n = 1.99$ (SEC).

Poly(2′,5′-dioctyl-4,4′′-terphenylenecyanovinylene) (10). Compound **4** (2 g, 3.83 mmol) was placed in a 100 mL round-bottomed flask containing THF (8 mL) and *t*BuOH (25 mL) under argon. The mixture was heated to a temperature of 50 °C. *t*BuOK (42 mg, 0.385 mmol) was added followed by nBu$_4$NOH(aq) (1.5 mL, 40%). A light brown precipitate formed immediately, and the mixture was left stirring for 15 min and then poured into a beaker containing MeOH (200 mL) and HCl(aq) (5 mL, 37%). The mixture was stirred for 10 min, and the light yellow product was then filtered and dried. This gave **10** as a light yellow solid in 98% yield (1.79 g). ^{1}H NMR (250 MHz, $CDCl_3$, 330 K, TMS): $\delta = 0.78$ (broad singlet,6H), 1.13 (broad singlet, 20H), 1.48 (broad singlet, 4H), 2.52 (broad singlet, 4H), 7.0−7.9 (m, 11H). ^{13}C NMR (62.9 MHz,, $C_6D_4Cl_2$, 400 K, TMS): $\delta = 14.5$, 23.1, 29.6, 29.7, 29.9, 31.9, 32.2, 33.1, 126.1, 129.5, 129.9, 130.4, 131.3, 138.1, 140.6. $M_w/M_n = 4.45$ (SEC).

Poly(2′,5′-difluoro-3′,6′-diperfluorooctyl-4,4′′-terphenylenevinylene) (11). Compound **7** (0.1 g, 0.08 mmol) was boiled in a mixture of 1,2-dichlorobenzene (50 mL) and diphenyl ether (25 mL) under argon when NaH (10 mg, 60% in paraffin, excess) was added. The mixture was boiled overnight and became peach colored. The mixture was then cooled and poured into methanol (250 mL) containing HCl-

(aq) (37%, 10 mL) and stirred. The precipitate was filtered and washed with methanol and hexane and finally dried. This gave **11** as a colorless material in 55% yield (50 mg). ^{1}H NMR (250 MHz, $C_6D_4Cl_2$, 420 K, TMS): $\delta = 7.16$ (m, 4H), 7.21 (d, 4H, $J = 7$ Hz), 7.3−7.4 (m, 2H), 7.5−7.6 (m, 2H). ^{19}F NMR (235 MHz, $C_6D_4Cl_2$, 420 K, C_6F_6): $\delta = -125.7, -122.4, -121.2, -119.2, -118.9, -109.2, -107.2, -101.0, -81.5$.

Poly(2′,5′-difluoro-3′,6′-diperfluorooctyl-4,4″-terphenylenecyanovinylene) (12). Compound **8** (0.21 g, 0.18 mmol), dry THF (100 mL), and *t*BuOH (40 mL) were placed in 500 mL conical flask under argon and heated to boiling. *t*BuOK (5 mg, catalyst) was added, and the mixture acquired a peachlike color. After 2 min it became opaque, and *n*Bu_4NOH(aq) (0.5 mL, 40%) was added whereby the color abruptly changed to green. The mixture was left at 50 °C for 1 h while the color became red and finally brown/red. The mixture was poured into a beaker containing MeOH (100 mL) and HCl(aq) (1 mL, 37%). The precipitated product was filtered and dried. This gave **12** as a yellow solid in 72% yield (0.15 g). ^{19}F NMR (235 MHz, $C_6D_4Cl_2$, 420 K, C_6F_6): $\delta = -125.8, -122.4, -121.5, -121.2, -119.0, -117.9, -106.7, -101.2, -99.7, -81.6$.

Differential Scanning Calorimetry (DSC). The polymers **9**, **10**, **11**, and **12** showed no phase transitions in the temperture range 20−300 °C.

Solvent Exclusion Chromatography (SEC) and MALDI-TOF. SEC on **9** and **10** was performed in THF using a polystyrene standard. MALDI−TOF on **11** and **12** was performed using a 337 nm laser wavelength and HABA matrix.

Photoelectron Spectroscopy. The samples for ultraviolet photoelectron spectroscopy measurements (UPS) were prepared by spin-coating a 1 mg L^{-1} solution of **9**, **10**, **11**, and **12** in boiling 1,2-dichlorobenzene onto a freshly prepared 5000 Å thick polycrystalline gold surface (evaporated onto the sample holder). 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 comprises 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 **9**, C and N for **10**, C and F for **11**, and C, N, and F for **12**). In the same manner the samples were checked for the absence of any chlorine which would have indicated the inclusion of solvent in the polymer films. The photoelectron detector was placed 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 experimental chamber was equipped with an ion gun, a mass spectrometer, and a gas dosing system. 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 served 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. Polymer film samples of **9**, **10**, **11**, and **12** 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 2.

Table 2. Data from the Photoelectron Spectra for the Au Substrate and the Polymers 9, 10, 11, and 12

compd	E_F^{VB}	E_F^{VAC}	cutoff	Δ	IP
9	1.45	3.40	45.15	−1.50	4.85
10	2.65	1.95	45.40	−2.95	4.60
11	2.25	2.50	45.25	−2.40	4.75
12	3.05	2.90	44.05	−2.00	5.95

The gold work function, Φ_{Au}, was determined to be 4.9 eV. The position of the valence band edge for **9**−**12**, E_F^{VB}, was lower than the Fermi level of gold. The procedure employed in the analysis of the data has been reported.[12]

Acknowledgment. This work was supported by the Danish Technical Science Foundation of Denmark (STVF). We also express sincere gratitude to Ole Hagemann for assistance with the synthetic organic chemistry, Jan Alstrup for the DSC measurements, Sokol Ndoni for technical assistance with SEC measurements, and Zheshen Li, Søren V. Hoffmann, and Philip Hofmann for technical support at the ASTRID storage ring and at the beamline.

Supporting Information Available: UV−vis spectra and NMR spectra for the polymers **9**, **10**, **11**, and **12**. This material is available free of charge via the Internet at http//:pubs.acs.org.

References and Notes

(1) Ho, P. K. H.; Kim, J.-S.; Burroughes, H.; Becker, S. F. Y.; Brown, T. M.; Caclalli, F.; Friend, R. H. *Nature (London)* **2000**, *404*, 408. Yang, Y. *Mater. Res. Soc. Bull.* **1997**, *22*, 16−24.

(2) Katz, H. E.; Lovinger, A. J.; Johnson, J.; Kloc, C.; Siegrist, T.; Li, W.; Lin, Y.-Y.; Dodabalapur, A. *Nature (London)* **2000**, *404*, 478−480. Drury, C. J.; Mutsaers, C. M. J.; Hart, C. M.; Matters, M.; de Leeuw, D. M. *Appl. Phys. Lett.* **1998**, *73*, 108−110. Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *393*, 619−620.

(3) Schön, J. H.; Kloc, C.; Bucher, E.; Batlogg, B. *Nature (London)* **2000**, *403*, 408−410.

(4) Remmers, M.; Neher, D.; Grüner, J.; Friend, R. H.; Gelinck, G. H.; Warman, J. M.; Quattrocchi, C.; dos Santos, D. A.; Brédas, J.-L. *Macromoecules* **1996**, *29*, 7432−7445.

(5) Schön, J. H.; Kloc, C.; Batlogg, B. *Nature (London)* **2000**, *406*, 702−704.

(6) Rehahn, M.; Schlueter, A.-D.; Feast, J. W. *Synthesis* **1988**, *5*, 386−388.

(7) (a) Krebs, F. C.; Spanggaard, H. *J. Org. Chem.*, in press. (b) Krebs, F. C.; Jørgensen, M. *Macromolecules*, submitted.

(8) Gill, R. E.; van Hutten, P. F.; Meetsma, A.; Hadziioannou, G. *Chem. Mater.* **1996**, *8*, 1341−1346.

(9) Seki, K.; Furuyama, T.; Kawasumi, T.-O.; Sakurai, Y.; Ishii, H.; Kajikawa, K.; Ouchi, Y.; Masuda, T. *J. Phys. Chem. B* **1997**, *101*, 9165−9169.

(10) Brédas, J. L.; Heeger, A. J. *Chem. Phys. Lett.* **1994**, *217*, 506−512.

(11) Park, P. C.; Yoshino, K.; Tomiyasu, H. *Synthesis* **1999**, *12*, 2041−2044.

(12) Salaneck, W. R.; Lögdlund, M.; Fahlman, M.; Greczynski, G.; Kugler, Th. *Mater. Sci. Eng.* **2001**, *R34*, 121−146.

MA020678U