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A Precursor Route to 2,7-Poly(9-fluorenone)

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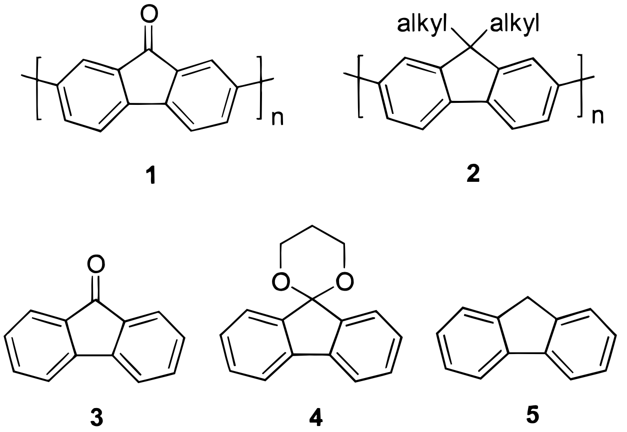
ABSTRACT: 2,7-Poly(9-fluorenone) (PF) (**1**), a unique electron-deficient conjugated polymer, was prepared via a precursor route, using 2,7-poly(spiro[4′,4′-dioctyl-2′,6′-dioxocyclohexane-1′,9-fluorene]) (**10b**) (POFK) as precursor polymer. Ketalization of 2,7-dibromo-9-fluorenone (**6**) with the diol 2,2-dioctyl-1,3-propanediol (**8b**) afforded a dibrominated ketal derivative of fluorenone (**9b**) which after Ni(0)-induced coupling provided the well-processable, structurally defined precursor polymer **10b** with a polyphenylene backbone. Conversion to PF (**1**) proceeded smoothly by treating a POFK (**10b**) film with dichloroacetic acid. The cyclic voltammogram of PF (**1**) exhibits a reversible reduction with a $E_{1/2}{}^0$ of −1.48 V vs Fc/Fc$^+$ which qualifies **1**, together with its facile accessibility, e.g., as electron transport material in multilayer LED.

Introduction

The synthesis of conjugated polymers has developed from a purely structural motivation to providing materials for electrical and optical applications.[1−5] Many such applications are related to the formation and migration of charge. However, there are only few reports on electron-deficient conjugated polymers. Characteristic features of these structures are their low-lying conduction bands and their high electron affinity, which would qualify them as candidates for n-type electrical conductors. Typical applications would be conceivable in photovoltaic cells or in multilayer light-emitting diodes (LED). When serving as electron transport materials, electron-deficient conjugated polymers can improve the properties of LED's in two ways. On one hand, the injection of electrons from the cathode metal into the device is promoted, and on the other hand, holes, migrating from the ITO anode toward the cathode, are blocked in the emitter layer. Consequently, the balance of holes and electrons is restored and the probability of charge carrier recombination is enhanced. This leads to a dramatically increased efficiency and a decreased driving voltage of the LED.

Our idea is to introduce 2,7-poly(9-fluorenone) (PF) (**1**) as a new electron-deficient polymer. PF (**1**) seems to be an easily accessible poly(*p*-phenylene) (PPP) derivative, in which the withdrawing effect of the carbonyl groups can lower the reduction potential and render the material n-conducting. Hitherto, there is only one report on PF (**1**). Zecchin et al.[6] described a method using a "cathodic coupling" of Ni(PPh$_3$)$_2$(2-bromo-7-fluorenyl)Br in acetonitrile. However, there is no analytical data available for the unprocessable film deposited on a glassy carbon electrode. Thus, it remains a considerable challenge preparing a well-defined and processable polyfluorenone. An additional motivation for this design comes from the fact that a closely related polymer, namely 2,7-poly(9,9-dialkylfluorene) (**2**), has recently attracted interest as emitter component in LED's.[7−11] The structural relation between fluorenone (**3**), its ketal (**4**), and fluorene (**5**) (Scheme 1) is, indeed, key to our concept.

Scheme 1. Structures of 2,7-Poly(9-fluorenone) (1), 2,7-Poly(9,9-dialkylfluorenone) (2), Fluorenone (3), Its Ketal (4), and Fluorene (5)



Results and Discussion

The insolubility of even low-molecular-weight oligomers of fluorenone, which we will present below, makes it necessary to develop a new synthetic approach to PF (**1**). Thus, it is essential to introduce solubilizing groups to obtain a structurally defined and processable polymer. On the other hand, it is well-known that alkyl groups, next to "diluting" the electronic behavior and complicating the synthesis, lead to a marked mutual twisting of the aromatic subunits when attached directly at the PPP backbone. This manifests itself in a drastic inhibition of the conjugative interaction which would negatively compromise the electronic and electrooptic properties. For this reason, we decided to elaborate a precursor route. Considering the fluorenone building block, the carbonyl group provides an apparent target for a possible modification of the structure. Since it is important to guarantee an easy conversion of the polymer precursor to PF (**1**), our idea was to use the ketal reaction for introducing solubilizing substituents. Hitherto, there are only few reports on ketalizing fluorenone.[12,13] Additionally, the yields obtained, e.g., for the simple derivatives spiro[1,3-dioxolane-2,9′-fluorene] and spiro[1,3-dioxane-2,9′-fluorene] were only poor. Consequently, a specific selection of the alcohol component, which also should provide solubility, is mandatory. Using the dialcohol 2,2-dimethyl-1,3-propanediol (**8a**), one can combine three advantages. First, the steric demand of the two methyl groups and intramolecular hydrogen bonding promote the syn-peripla-

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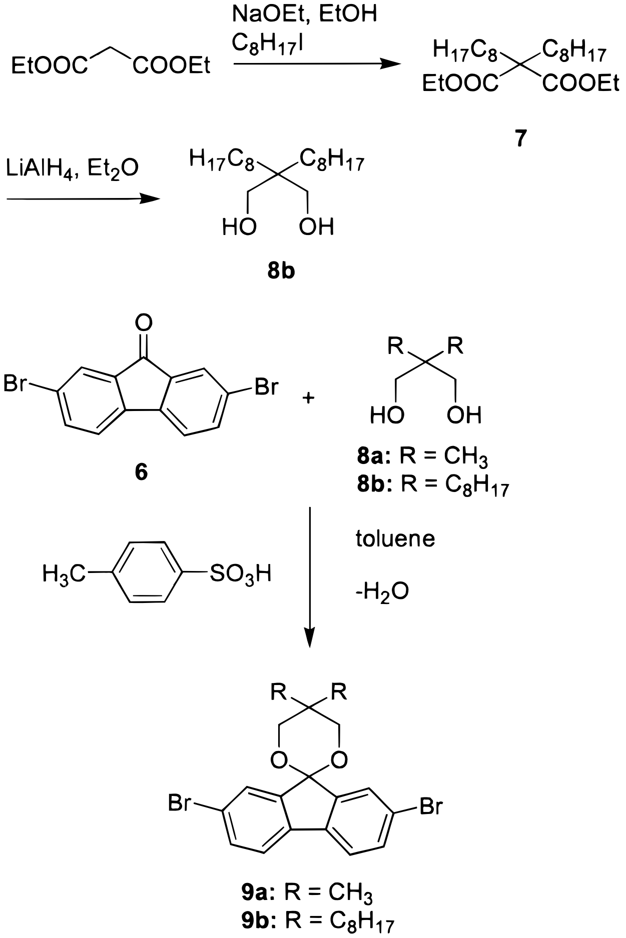
nar conformation of the hydroxy groups, which facilitates ring formation; second, ketones are expected to be more readily converted into 1,3-dioxanes than into 1,3-dioxolanes;[14,15] and third, the perpendicular arrangement of the fluorene and the dioxane plane in combination with the spikelike order of the two methyl groups should ensure a sufficient solubility.

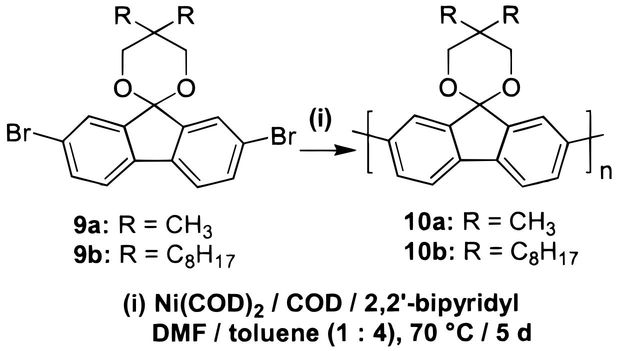
A “polyfluorene ketal” can function not only as a precursor for PF (**1**) but also as blue-light emitter. This is due to its PPP structure with bridged biphenyl subunits. We have recently demonstrated this concept with the synthesis of 2,7-poly(4,9-dioctyl-4,5,9,10-tetrahydropyrene).[16]

The preparation of the precursor polymer started with the synthesis of the monomer 2,7-dibromo-spiro[4′,4′-dimethyl-2′,6′-dioxocyclohexane-1′,9-fluorene] (**9a**). 2,7-Dibromo-9-fluorenone (**6**) and 2,2-dimethyl-1,3-propanediol (**8a**) were dissolved in benzene and refluxed in the presence of *p*-toluenesulfonic acid under dehydrating conditions. In contrast to described procedures,[14] it is necessary to use approximately equivalent amounts of ketone and *p*-toluenesulfonic acid. For the polymerization of the monomer we choose the Ni(0)-induced dehalogenation polycondensation (Yamamoto coupling), using modified reaction conditions that we described before.[16] Unfortunately, the obtained product, 2,7-poly(spiro[4′,4′-dimethyl-2′,6′-dioxocyclohexane-1′,9-fluorene]) (**10a**), was a poorly soluble material indicating that the solubilizing effect of the spiro element and the methyl groups are insufficient. The soluble part contained oligomers of up to six subunits as detected by MALDI-TOF mass spectrometry. For this reason, we prepared 2,7-dibromo-spiro[4′,4′-dioctyl-2′,6′-dioxocyclohexane-1′,9-fluorene] (**9b**) in which both methyl groups are replaced by octyl groups. The synthesis included a Knoevenagel reaction starting from malonic acid diethyl ester and *n*-octyl iodide (64% yield) (Scheme 2). Then, reduction of the dialkylated diester (**7**) with lithium aluminum hydride provided the diol (**8b**) in 99% yield which was reacted with 2,7-dibromo-9-fluorenone (**6**) as described for the dimethyl derivative **9a**. In this way, after successive purification with column chromatography (basic alumina, petrol ether/acetic acid diethyl ester 10:1 by volume), recrystallization from 2-propanol, and column chromatography (basic alumina, petrol ether/acetic acid diethyl ester 20:1 by volume), the dibromoketal **9b** was obtained in 21% yield. This low value reflects the above-mentioned difficulty in ketalizing fluorenone which requires the separation of product **9b** from larger amounts of unreacted 2,7-dibromo-9-fluorenone (**5**). The ^{1}H NMR spectrum of **9b** shows two doublets at $\delta = 7.46$ and 7.55 ($^3J = 8.3$ Hz) characterizing the aromatic fluorene protons 3-H, 6-H and 4-H, 5-H, respectively. A singlet at $\delta = 7.46$ identifies the protons 1-H, 8-H. The methylene protons of the ketal ring (3′-H and 5′-H) are observed at δ 4.00. Finally, a multiplet between δ 0.91 and 1.63 can be ascribed to the methylene and methyl protons of the octyl chains. Once more, polymerization of **9b** took place by Yamamoto coupling (Scheme 3). The removal of residues of nickel in the raw polymer 2,7-poly(spiro[4′,4′-dioctyl-2′,6′-dioxocyclohexane-1′,9-fluorene]) (**10b**) (POFK) presents a major challenge. Since treatment with acid would cleave the ketal group, it is impossible to use hydrochloric acid as washing reagent, which usually presents a reliable method for removing nickel rests. We have found that repeated extraction of a chloroform solution of the polymer with an aqueous sodium sulfide solution provides a material suitable for electrooptical applications. Using this method, POFK (**10b**) was obtained as a light yellow solid in 85% yield after precipitation from methanol. POFK (**10b**) is a polymer with an excellent processability. Thus, its good solubility in common solvents such as chloroform or toluene allows formation of homogeneous and transparent films.

Scheme 2



Scheme 3



Characterization of the Precursor Polymer 10b. The ^{1}H NMR spectrum of POFK (**10b**) (Figure 1) proves its structural regularity. Two broad signals at δ 7.70 and δ 8.00 can be assigned to the aromatic protons 1, 3, 4, 5, 6, 8 of the polymer main chain. The methylene protons of the ketal ring (3′-H and 5′-H) are observed at δ 4.17. A multiplet between δ 1.27 and 1.67 can be ascribed to the methylene protons of the octyl chains. Finally, the signal at δ 0.86 characterizes the methyl

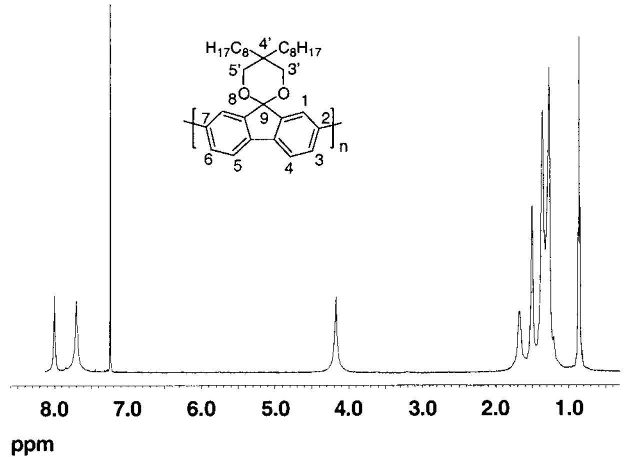


Figure 1. ^{1}H NMR spectrum of POFK (**10b**) in $CDCl_3$ at 298 K.

protons of the octyl groups. The absence of end group signals suggests that POFK (**10b**) possesses a high molecular weight.

The gel permeation chromatography (GPC) of POFK (**10b**) shows a monomodal distribution with a number-average molecular weight (M_n) of 76 000 and a weight-average molecular weight (M_w) of 200 000 (polystyrene calibration). This corresponds to a number-average degree of polymerization of about 165, which is equal to a polymer chain with 330 linearly coupled benzene rings. Of course, when evaluating these values, one has to consider that GPC analysis of rigid-rod polymers using polystyrene standards as calibration overestimate the molecular weight.[17]

The TGA of POFK (**10b**) is characterized by a 5% weight loss at 314 °C. Major decomposition can then be observed at 366 °C (61% degradation), which is due to the extrusion of the octyl groups.

The DSC analysis indicates that POFK (**10b**) possesses a completely amorphous structure, and no phase transition was observed between −100 and 200 °C. This is in contrast to 2,7-poly(9,9-dioctylfluorene), which, according to the findings of Bradley,[8] shows a thermotropic liquid crystalline behavior. The reason for the different behavior of both polymers can be attributed to the spiro unit of POFK (**10b**) which prevents a packing with a supramolecular order.

The absorption spectrum of POFK (**10b**) shows a maximum at 384 nm. The fluorescence emission maximum of **10b** (excitation wavelength 380 nm) is located in the blue (chloroform, 414 nm; film, 456 nm). These optical properties together with the good film-forming properties qualify POFK (**10b**) not only as a precursor polymer for PF (**1**) but also as a useful blue emitter in LED.

Conversion of POFK (10b) to PF (1). The conversion of POFK (**10b**) to PF (**1**) proceeds very easily by treating a POFK (**10b**) film with dichloroacetic acid, which we preferred to mineral acids because it can be used along with sensitive substrates (Scheme 4). For the cleavage of the ketal group a POFK (**10b**) film was heated to approximately 50 °C and exposed to a dichloroacetic acid atmosphere. The conversion proceeded almost spontaneously accompanied by a color change from light yellow to red. After washing with acetone, an insoluble, homogeneous, and transparent PF (**1**) film was received.

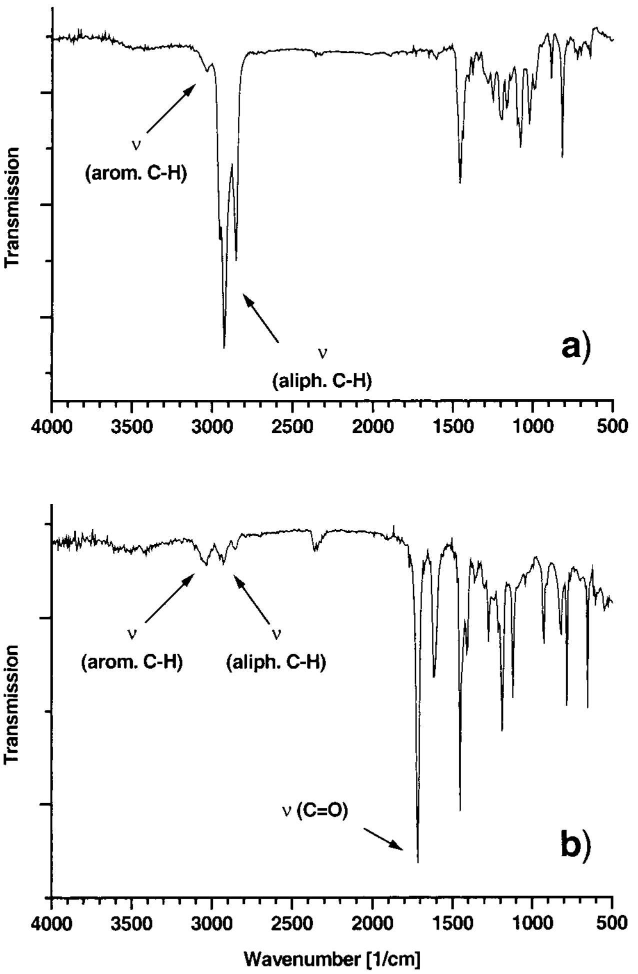


Figure 2. IR spectra (silicon) of (a) POFK (**10b**) and (b) PF (**1**).

Clear evidence for an almost quantitative conversion to PF (**1**) could be obtained by IR spectroscopy. The aliphatic C−H vibrations at 2853, 2928, and 2955 cm^{-1} in the IR spectrum of POFK (**10b**) (Figure 2a) almost disappear in the spectrum of PF (**1**) (Figure 2b). Thus, the transmission of the band at 2928 cm^{-1} of POFK (**10b**) increases from 50% to 97% after the ketal cleavage. As expected, the IR spectrum of PF (**1**) shows a strong carbonyl band (1716 cm^{-1}).

The absorption spectra of POFK (**10b**) and PF (**1**) (Figure 3) differ significantly. The precursor polymer **10b** shows the characteristic $\pi \rightarrow \pi^*$ transition (λ_{max} = 385 nm), whereas for PF (**1**) three absorption bands at 306, 374, and 480 nm are observed. The absorption at 480 nm can be assigned to the symmetry-forbidden $n \rightarrow \pi^*$ transition of the carbonyl groups. The low energy of this band is a consequence of the interaction with the delocalized π-system. This can be clearly demonstrated when comparing the absorption maxima of PF (**1**) (480 nm, film), 9-fluorenone (**3**) (386 nm,[18] ethanol), and the "dimeric" compound 2,2-bi(9-fluorenone) (**12**) (412 nm, $CHCl_3$) which we readily synthesized via Yamamoto coupling of 2-bromo-9-fluorenone (**11**) (Scheme 5) and an ensuing purification with column chromatography (silica, CH_2Cl_2) in 75% yield. A second absorption of **1** assigned to the $\pi \rightarrow \pi^*$ transition of the PPP backbone is observed at 374 nm.

Cyclic Voltammetry. First indications of the qualification of PF (**1**) as electron-deficient polymer were

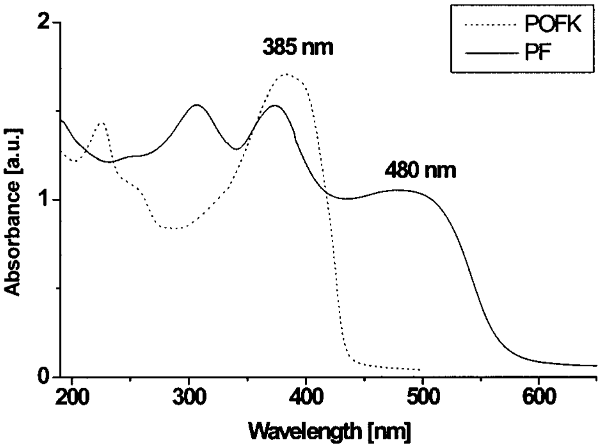
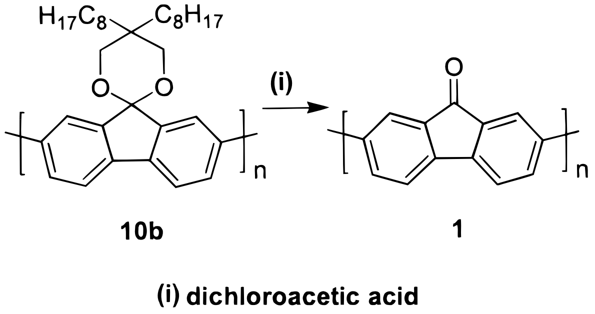
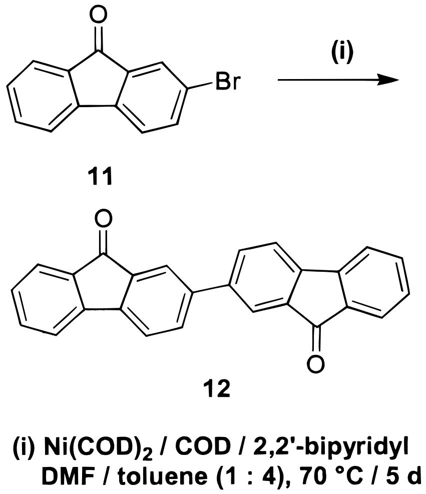


Figure 3. Absorption spectra (film on quartz) of PF (**1**) and POFK (**10b**).

Scheme 4



Scheme 5



derived from the cyclic voltammetric investigation. The cyclic voltammogram (CV) of a PF (**1**) film on indium/tin oxide (ITO) in acetonitrile (Figure 4) shows a reversible reduction at a low potential of −1.48 V vs ferrocene/ferrocenium. Therefore, **1** is more readily reduced than its monomeric counterpart unit 9-fluorenone (**3**) (reversible reduction at −1.70 V in acetonitrile). The CV of the "dimer" **12** (Figure 5) exhibits two reversible reductions at −1.63 and −1.73 V (acetonitrile) with the first potential located between the corresponding value of PF (**1**) and 9-fluorenone (**3**). Thus, it is obvious that the reduction potential is shifted to more positive values with increasing degree of polymerization, e.g., with extended π-delocalization of the PPP backbone of PF (**1**).

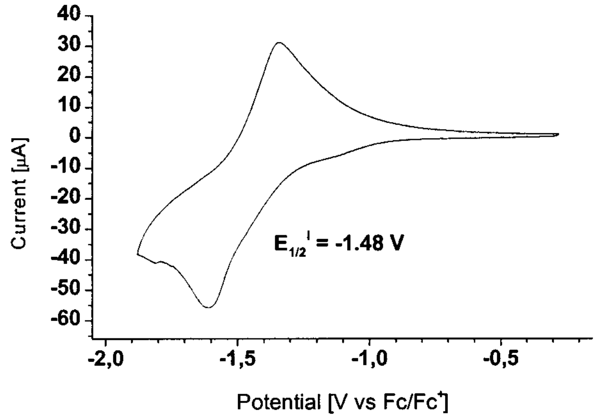


Figure 4. Cyclic voltammogram (reduction) of PF (**1**) (film on ITO, 0.1 M TBAHFP/acetonitrile, 293 K, scan 10 mV/s).

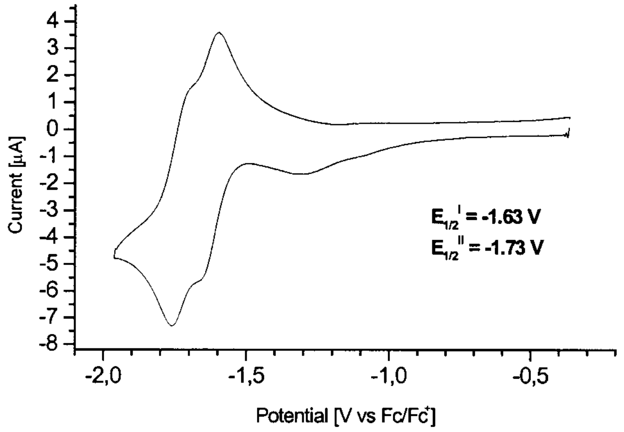


Figure 5. Cyclic voltammogram (reduction) of dimer **12** (0.1 M TBAHFP/acetonitrile, 293 K, scan 100 mV/s).

These results contradict the values that Zecchin et al.[6] received for the electrochemically prepared 2,7-poly-(9-fluorenone). Thus, this group reported on a reversible reduction step of the material at −1.65 V vs Ag/AgClO$_4$ (corresponding to −1.62 V vs ferrocene) in acetonitrile. Besides, they found an equal potential for 9-fluorenone. Consequently, incorporation of this monomer unit into a polymer would not affect the electrochemical properties. For this reason and since no analytical data were available for the insoluble material, we assume that the synthesis of Zecchin et al.[6] did not provide PF (**10**).

If the reduction potential of a material is known, an estimation of the LUMO energy is possible by correlation with the vacuum energy level of the ferrocene/ferrocenium standard (−4.8 eV).[19−21] For PF (**1**), this calculation results in a value of −3.3 eV for the LUMO level. This is a promising result since the LUMO level is on the order of the work function of a magnesium electrode (−3.7 eV). Consequently, formation of an Ohmic contact between magnesium and PF (**1**) is possible, which permits facile, only space charge limited injection of electrons[22] into the electron transport material during LED operation. A comparison with other electron-deficient materials allows an evaluation of the suitability of PF (**1**) as electron transport layer in LEDs. 2-(4-Biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) is often used in multilayer LEDs because of its good electron mobility. However, with a LUMO energy level of −2.4 eV,[19] electrons have to overcome an energy barrier of approximately 1.3 eV when they are injected from a magnesium cathode into PBD.

Friend and Holmes determined the onset potential of the reduction of a film of CN−PPV, a dialkoxy-substituted poly(*p*-phenylenevinylene) (PPV) derivative with cyano groups on the vinylene units,[2] from which they derived the LUMO level of −3.02 eV. Thus, a high-energy barrier impedes injection of electrons from the low work function electrode into the material. Additionally, the reduction turned out to be irreversible.

Conclusion

In summary, we present PF (**1**), a new conjugated polymer with a high electron affinity. **1** is readily accessible via a precursor route. Thus, ketal reaction of 2,7-dibromo-9-fluorenone (**6**) with the diol 2,2-dioctyl-1,3-propanediol (**8b**) affords monomer **9b**, which after polymerization gives a well-processable, structurally defined precursor polymer **9b** with a PPP backbone. The conversion to PF (**1**) occurs easily by treating a film of the precursor polymer **10b** with dichloroacetic acid.

The withdrawing effect of the carbonyl groups in PF (**1**) lowers the LUMO level and makes the polymer readily reducible. This was clearly proven by cyclic voltammetry. In addition, it could be shown that the reduction potential of PF (**1**) is located almost on the same level as the work function of magnesium. Since this allows a facile injection of electrons from the cathode in the material, PF (**1**) is a promising candidate for use as an electron transport layer in multilayer LED. Consequently, LED investigations of PF (**1**) now have to confirm the validity of the results of the CV analysis. We will report on the outcome of these examinations elsewhere.

Experimental Section

Materials and General Procedures. The solvents used were of commercial p.a. quality; toluene was distilled from sodium, and *N*,*N*-dimethylformamide (DMF) was distilled from calcium hydride.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX 500 (500 and 125 MHz, respectively). UV−vis data were obtained on a Perkin-Elmer Lambda 9. Gel permeation chromatography (GPC) analysis was performed with PL gel columns (10^3 and 10^4 Å pore widths) connected to a UV−vis detector. The calibration was based on polystyrene standards with narrow weight distribution. TGA analysis was performed on a Mettler 500 thermogravimetric analyzer (heating rate 10 °C/min, N_2 atmosphere). DSC data were obtained on a Mettler TC 10 A (heating rate 20 °C/min, N_2 atmosphere). The infrared (IR) spectra were recorded on a Nicolet FT-IR 320 (silicon).

The cyclic voltammetry experiments were performed on a model 273 potentiostat. The experiments were carried out at room temperature under a purified argon atmosphere. Argon gas was also used to purge all solutions prior to experimentation. The concentration of the electroactive species was 5×10^{-4} mol/L. Tetrabutylammonium−PF_6 (0.1 M) was added as a supporting electrolyte. A platinum electrode was used as a working electrode. Ferrocene was used as an internal standard. The obtained data were processed with the research electrochemistry software M270.

2,2-Dioctylmalonic Acid Diethyl Ester (7). Malonic acid diethyl ester (25.0 g, 0.16 mol) and sodium ethylate (130 g, 0.54 mol) were dissolved in 500 mL of dry ethanol and heated under reflux. Then 1-iodoctane (50.0 g, 0.74 mol) in 150 mL of dry ethanol was added. After heating the reaction mixture under reflux for 3 days, the solvent was evaporated in vacuo and ice was added carefully to the residue. The ensuing mixture was extracted with 100 mL of diethyl ether (three times). The combined organic layers were washed with water (three times) and dried over magnesium sulfate. After evaporation of the solvent, low-boiling fractions were removed by vacuum distillation (200 °C, 0.1 hPa). Final purification by column chromatography [silica, hexane] afforded 39.2 g (64%) of **7** as a colorless oil. Anal. Calcd: C, 71.83; H, 11.53. Found: C, 72.37; H, 11.51. ^{1}H NMR ($CDCl_3$): δ (ppm) 4.13 (q, 4H), 1.82 (m, 4H), 1.02−1.32 (m, 30H), 0.84 (t, 6H). ^{13}C NMR ($CDCl_3$): δ (ppm) 172.4, 61.2, 58.0, 32.6, 32.2, 30.2, 29.6, 29.5, 28.9, 24.3, 23.0, 14.5, 14.4.

2,2-Dioctyl-1,3-propanediol (8b). A solution of 2,2-dioctylmalonic acid diethyl ester (**7**) (36.0 g, 0.094 mol) in 150 mL of dry diethyl ether was added to a suspension of lithium aluminum hydride (5.00 g, 0.132 mol) in 150 mL of dry diethyl ether. The mixture was then heated for 4 h under reflux. After cooling, ice water was added carefully to the reaction mixture. The resulting precipitate was dissolved by addition of sulfuric acid (10%). The organic layer was separated and the aqueous portion extracted with diethyl ether (three times). The combined organic layers were washed with water (three times) and dried over magnesium sulfate. Evaporation of the solvent afforded 27.9 g (99%) of **8b** as a colorless solid. Anal. Calcd: C, 75.94; H, 13.42. Found: C, 75.87; H, 13.48; mp 28 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 3.53 (s, 4H), 2.65 (s, 2H), 1.11−1.38 (m, 28H), 0.85 (t, 6H). ^{13}C NMR ($CDCl_3$): δ (ppm) 69.7, 41.4, 32.3, 31.2, 31.0, 29.9, 29.7, 23.2, 23.0, 23.0, 14.5.

2,7-Dibromospiro[4′,4′-dioctyl-2′,6′-dioxocyclohexane-1′,9-fluorene] (9b). 2,7-Dibromo-9-fluorenone (**6**) (5.00 g, 14.8 mmol), 2,2-dioctyl-1,3-propanediol (**8b**) (10.0 g, 33.3 mmol), and *p*-toluenesulfonic acid (1.50 g, 7.89 mmol) were dissolved in 500 mL of dry toluene. The mixture was then heated for 3 days at 115 °C under dehydrating conditions. After cooling, the solvent was removed in vacuo. The residue was purified by column chromatography on basic alumina with petrol ether/acetic acid diethyl ester (10:1 by volume), recrystallization from 2-propanol, and column chromatography on basic alumina with petrol ether/acetic acid diethyl ester (20:1 by volume) to yield 1.9 g (21%) of **9b** (colorless crystals). Anal. Calcd: C, 61.94; H, 7.15. Found: C, 62.06; H, 7.23; mp 74 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.83 (s, 2H, 1.9 Hz), 7.55 (d, 2H, 8.3 and 1.9 Hz), 7.46 (d, 2H, 8.3 Hz), 4.00 (s, 4H), 1.33−1.63 (28H), 0.91 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 146.3, 137.7, 122.2, 133.4, 128.5, 121.9, 103.5, 70.3, 40.0, 32.8, 32.4, 30.9, 30.0, 29.7, 23.2, 23.1, 14.3.

2,7-Poly(spiro[4′,4′-dioctyl-2′,6′-dioxocyclohexane-1′,9-fluorene]) (10b). DMF (6 mL) was added to a 100 mL Schlenk flask equipped with a stirring bar and containing bis(1,5-cyclooctadiene)nickel(0) (460 mg, 1.67 mmol), 2,2′-bipyridyl (262 mg, 1.68 mmol), and 1,5-cyclooctadiene (185 mg, 1.71 mmol) under an argon atmosphere via a syringe. The ensuing deep blue/lilac solution was stirred at 60 °C for 30 min, and then a solution of **9b** (500 mg, 0.81 mmol) in toluene (18 mL) was added. The reaction mixture was then stirred at 70 °C under exclusion of light for 5 days. The mixture was cooled to room temperature and added to a solution of 200 mL of methanol, 200 mL of acetone, and 20 mL of aqueous ammonia. After stirring for 2 h, the mixture was filtered. The residue was then dissolved in chloroform and washed successively with an aqueous solution of sodium sulfide (three times) and water (three times). The organic layer was dried over magnesium sulfate and the solvent evaporated. After a final purification by column chromatography [basic alumina, chloroform], **9b** was precipitated by adding a chloroform solution of **10b** to methanol. Filtration and removal of the solvent under reduced pressure afforded 315 mg (85%) of **10b** as a light yellow solid. Anal. Calcd: C, 83.43; H, 9.63. Found: C, 80.50; H, 9.76. IR (KBr): ν (cm^{-1}) 3029, 2955, 2928, 2853, 1601, 1455, 1440, 1285, 1250, 1195, 1163, 1097, 1078, 1024, 989, 886, 816. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.00 (bs, 2H), 7.70 (bs, 4H), 4.17 (s, 4H), 1.27−1.67 (m, 28H), 0.86 (t, 6H). ^{13}C NMR ($CDCl_3$): δ (ppm) 145.0, 141.2, 138.3, 129.0, 123.8, 120.5, 103.8, 69.9, 35.4, 33.0, 32.0, 30.7, 29.7, 29.4, 23.0, 22.7, 14.1. $M_n = 76\,000$, $M_w = 200\,000$, DP = 165 GPC, PS calbration). UV−vis ($CHCl_3$): λ_{max} (nm) 384.

2,7-Poly(9-fluorenone) (1). A POFK (**10b**) film was heated to 50 °C and exposed to a dichloroacetic acid atmosphere. The conversion proceeded almost spontaneously accompanied by a color change from light yellow to red. After washing with acetone and drying in vacuo, a red, homogeneous and transparent PF (**1**) film was received. Anal. Calcd: C, 87.63; H, 3.39. Found: C, 85.58; H, 3.68. IR (KBr): ν (cm^{-1}) 3033, 2928 (w), 2852 (w), 1716, 1617, 1454, 1408, 1275, 1189, 1123, 930, 823, 782, 654. UV−vis (quartz): λ = 306, 374, 480 nm.

2,2-Bi(9-fluorenone) (12). DMF (6 mL) was added to a 100 mL Schlenk flask equipped with a stirring bar and containing bis(1,5-cyclooctadiene)nickel(0) (212 mg, 0.77 mmol), 2,2′-bipyridyl (120 mg, 0.77 mmol), and 1,5-cyclooctadiene (83 mg, 0.77 mmol) under an argon atmosphere via a syringe. The resulting deep blue/lilac solution was stirred at 60 °C for 30 min, and then a solution of 2-bromo-9-fluorenone (**11**) (100 mg, 0.39 mmol) in toluene (18 mL) was added. The reaction mixture was then stirred at 70 °C under exclusion of light for 5 days. After cooling to room temperature 100 mL of chloroform was added, and the resulting solution was washed with 50 mL of 2 N hydrochloric acid (three times) and water (three times).Final purification by column chromatography [silica, CH_2Cl_2] afforded 52 mg (75%) of **12** as a yellow/orange solid. Anal. Calcd: C, 87.13; H, 3.94. Found: C, 87.17; H, 3.99; mp 292 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.90 (s, 2H, 1.26), 7.75 (d, 2H, 7.9 Hz), 7.67 (d, 2H, 7.2 Hz), 7.59 (d, 2H, 7.8), 7.52 (m, 4H), 7.30 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 193.4, 144.2, 143.9, 141.1, 135.2, 134.8, 134.7, 132.8, 129.2, 124.5, 122.6, 120.8, 120.5.

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