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A Novel Ferrocene-DOPPV Conjugated Copolymer

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Summary: The synthesis of a conjugated copolymer, poly[(1,1′-ferrocenylenevinylene)-co-(2,5-di-*n*-octyloxy)-*p*-phenylenevinylene] (**PFV-DOPPV**) *via* McMurry coupling of 1,1′-ferrocenedialdehyde and 2,5-di-*n*-octyloxybenzene-1,4-dialdehyde is reported. **PFV-DOPPV** was fully characterized by ^{1}H NMR, FTIR, FT-Raman, UV-VIS, cyclic voltammetry, size exclusion chromatography (SEC), inductively coupled plasma - optical emission spectrometry (ICP-OES), thermogravimetry (TG) and differential scanning calorimetry (DSC). The ionization potential, band-gap energy, electron affinity, HOMO and LUMO levels could be estimated. Electrical measurements in a sandwich device exposed to magnetic fields revealed magnetoresistance.

Keywords: conducting polymers; copolymerization; ferrocene; magnetoresistance; McMurry coupling

Introduction

The incorporation of organometallic units to a conjugated polymer may greatly affect its properties.[1] In the last decade, the interest in organometallic polymers has increased owing their application in light emitting diodes,[2] molecular magnets,[3] gas sensors,[4] photovoltaic devices,[5] besides in many others. With 18 electrons in the valence shell, ferrocene is the most stable member of the metallocenes,[6,7] being not sensitive to air and humidity. However, it may be easily oxidized electrochemically or by weak oxidants. Ferrocene is an electron-rich arene and reacts up to 100 times faster than benzene in Friedel-Crafts reactions.[7]

Among many kinds of conjugated polymers, poly(*p*-phenylenevinylene) (PPV) and its derivatives,[8] formed essentially by aromatic moieties attached to vinylenic units, are highly attractive because of their successful application in electroluminescent devices[9] and, more recently, in solar cells,[10] magnetic transistors[11,12] and electronic noses.[13–15]

In this communication, we report the synthesis and characterization of a novel copolymer of the poly(*p*-phenylenevinylene) (PPV) family, formed by 1,1′- ferrocenylenevinylene units alternated with 2,5-di-*n*- octyloxy-*p*-phenylenevinylene units, *i.e.*, poly[(1,1′-ferrocenylenevinylene)-co-(2,5-di-*n*-octyloxy)-*p*-phenylenevinylene] (**PFV-DOPPV**).

Experimental Part

General Methods

For the cyclic voltammetry (CV) experiment, commercial acetonitrile (MeCN) was purified and dried as described elsewhere.[16] All other commercially available materials were used as received. ^{1}H NMR FT spectra (200 MHz) were recorded on a Bruker AC-200 spectrometer using deuteriated chloroform/TMS (Aldrich) as solvent/reference. FTIR spectra were recorded as a KBr disc, on a Perkin-Elmer 1750 series grating. Only major or important absorptions are given. FT-Raman spectrum was recorded in a Bruker spectrometer, model FTS100/S, equipped with a Nd-YAG continuous laser (1064 nm and

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power of 100 mW) and a liquid nitrogen cooled Ge diode detector; the recording resolution was 4 cm^{-1} with laser power of ~150 mW and 256 co-additions. Differential scanning calorimetry (DSC) was carried out on a Shimadzu DSC50 calorimeter, and thermogravimetry (TG) on a Shimadzu TGA50 thermogravimeter. The heating rate was $10\,^{\circ}C \cdot min^{-1}$ and synthetic air was the purge gas in both cases. Molecular weight determination was made by size exclusion chromatography (SEC) at a flow rate of $1\ mL \cdot min^{-1}$ in tetrahydrofurane (THF) on a Shimadzu Class - LC10 HPLC equipped with three Supelco Progel columns (G5000 + G4000 + G3000). The molecular weight is reported relative to narrow dispersivity polystyrene standards (5120, 8300, 16700, 29300, 47500, 111000 and 216000. A Spectro CirosCCD Inductively Coupled Plasma - Optical Emission Spectrometer – ICP OES (Spectro Analytical Instruments, Kleve, Germany) with axial plasma viewing was used, the ICP operating conditions are generator free-running at 27.12 MHz, power 1400 W, nebulizer cross-flow (Spectro), spray chamber double pass (Scott-type), outer gas: $12\ L \cdot min^{-1}$, intermediate gas: $1.0\ L \cdot min^{-1}$, nebulizer gas: $1.0\ L \cdot min^{-1}$, sample uptake rate: $1.5\ ml \cdot min^{-1}$, analytical wavelength for Fe: 259.941 nm. Cyclic voltammetry (CV) experiment was run on a **PFV-DOPPV** film deposited on a gold-coated glass electrode and measured *vs.* an Ag/Ag^{+} reference electrode using a graphite electrode as counter electrode. A Microquimica MQPG-01 potentiostat was employed with scan rate of $50\ mV \cdot s^{-1}$.

Au/**PFV-DOPPV/**Al sandwich devices were prepared for electrical measurements. Metallic contacts were evaporated at a pressure of 5×10^{-5} Torr, using resistive tungsten crucibles. The electric measurements were made using a computer controlled Keithley 196 multimeter and Keithley 230 voltage source.

Preparation of Precursors

1,1′-Ferrocenedialdehyde (**2**) was obtained from commercial ferrocene by generation of the dilithium derivative and its further reaction with *N,N*-dimethylformamide (DMF).[17] 2,5-(*n*-octyloxy)-benzene-1,4-dialdehyde (**3**) was prepared according to a procedure described in the literature.[18]

Synthesis of the Polymer

In a dry three-necked round-bottomed flask a suspension of zinc powder (1.21 g, 16.1 mmol) in 20 mL of dry THF was stirred at $-10\,^{\circ}C$ under nitrogen atmosphere, while titanium tetrachloride (1.20 mL, 12.0 mmol) was slowly added. After 10 minutes, a solution of 1,1′-ferrocenedialdehyde (**1**, 0.149 g, 0.596 mmol) and 2,5-(*n*-octyloxy)-benzene-1,4-dialdehyde (**2**, 0.233 g, 0.595 mmol) in 14 mL THF was added to the flask. The mixture was allowed to reflux for 9 hours, then cooled and poured into 40 mL of 10% aqueous potassium carbonate. This mixture was stirred for 30 minutes then the solid material formed was filtered off and dried in a vacuum desiccator. The solid was then extracted for 24 hours in a Soxhlet apparatus to chloroform. The solvent was removed resulting in **PFV-DOPPV** (0.243 g, 0.420 mmol, 70 %) as a reddish brown viscous material. ^{1}H NMR: 0.88 (m, 6H), 1.29 (m, 20H), 1.72 (m, 4H), 3.27–4.81 (s, 12H), 7.52–6.71 (m, 6H), 9.75 (s, CHO terminal). FTIR: 3045 (CH, aromatic and vinylic), 2915, 2848 (CH, aliphatic), 1726 (C=O, terminal aldehyde), 1622 (C=C, aliphatic), 1504, 1468 (CH aromatic), 1443, 1379 (CH aliphatic), 1201, (COC), 954 (HC=CH *trans*), 856 (HC=CH *cis*), 827, 815 (CH aromatic).[19] FT-Raman: 1242 cm^{-1} (HC=CH *cis*), 1313 cm^{-1} (HC=CH *trans*).[19] TG/DSC: $214\,^{\circ}C$ (exo, $\Delta m = -5\%$); $373\,^{\circ}C$ (exo, $\Delta m = -11\%$); $683\,^{\circ}C$ (exo, $\Delta m = -79\%$). SEC: $\overline{M}_w = 3000\ g \cdot mol^{-1}$, $\overline{M}_w/\overline{M}_n = 1.6$; degree of polymerization ≈10. ICP-OES % Fe = 6.3%.

Sandwich Device Preparation

The Au/**PFV-DOPPV**/Al device was made over a silanized glass substrate. The silanization was made immersing the glass sample in a solution of isopropanol:H_2O:3-trimethoxysilyl)-1-propanethiol and rinsing it in isopropanol (1:25:25 by volume). The procedure was repeated three times. Gold was in the sequence deposited over half the surface, followed by a polymer layer deposition by spin-coating 50 μL of a solution of 5 mg **PFV-DOPPV** in 1 mL of chloroform, leaving part of the gold uncoated (first contact), for further electrical wires connection. Then, aluminum was deposited onto the polymer layer forming the second electrical contact of the device.

Magnetoresistance Test

Current *vs.* potential curves of the Au/**PFV-DOPPV**/Al device were recorded in the absence, immediately after the presence of a constant magnetic field (200 mT), as well as after 3 minutes of exposure to that field.

Results and Discussion

PFV-DOPPV was synthesized in 70 % yield *via* McMurry coupling reaction of 1,1′-ferrocenedialdehyde (**1**) and 2,5-(*n*-octyloxy)-benzene-1,4-dialdehyde (**2**), as shown in Figure 1.

The chemical structure of **PFV-DOPPV** was confirmed by ^{1}H NMR, FTIR and Raman analyses. The presence of CHO (aldehyde) as terminal groups was confirmed both by ^{1}H NMR (singlet at 9.75 ppm) and FTIR (1726 cm^{-1}) spectra, besides other characteristic absorption bands, *e.g.* C(sp^2)–H stretching at 3045 cm^{-1}, C=C stretching at 1622 cm^{-1}, asymmetric C–O–C stretching at 1201 cm^{-1} and both *cis* (856 cm^{-1}) and *trans* (954 cm^{-1}) H–C=C–H absorptions,[19] which could be confirmed by two bands, one at 1242 cm^{-1} (*cis*) and the other at 1313 cm^{-1} (*trans*)[20] in the Raman spectrum.

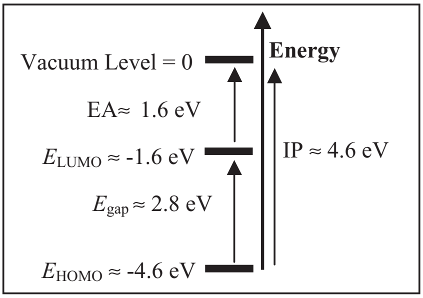


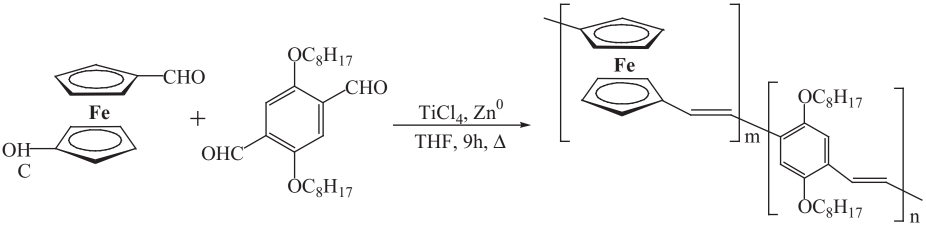
Figure 2.
Energy diagram of **PFV-DOPPV**.

SEC analysis of **PFV-DOPPV** showed an average molecular weight of 3000 g mol^{-1}, polydispersity index of 1.6 and an average degree of polymerization of 10. These data show that the obtained product was oligomeric in nature.

ICP-OES experiment revealed 6.3% of iron in **PFV-DOPPV**, which means that the ratio between the units of 1,1′-ferrocenylenevinylene (FV) and 2,5-dioctyloxy-*p*-phenylenevinylene (DOPPV) is 2:3, respectively.

Thermal analyses (TG and DSC) showed that the polymer is stable up to 214 °C (5% weight loss). A residual weight was observed at 800 °C, which is compatible with the formation of non-volatile Fe_2O_3.

Cyclic voltammetry (CV) and UV-VIS spectroscopy experiments allowed drawing the energy diagram of **PFV-DOPPV** (Figure 2). From the oxidation onset of the voltammetric wave it was possible to estimate the ionization potential (IP ≈ 4.6 eV),[21] and the absorption onset in



1 **2** **PFV-DOPPV**

Figure 1.
Synthesis of **PFV-DOPPV** *via* McMurry coupling reaction.

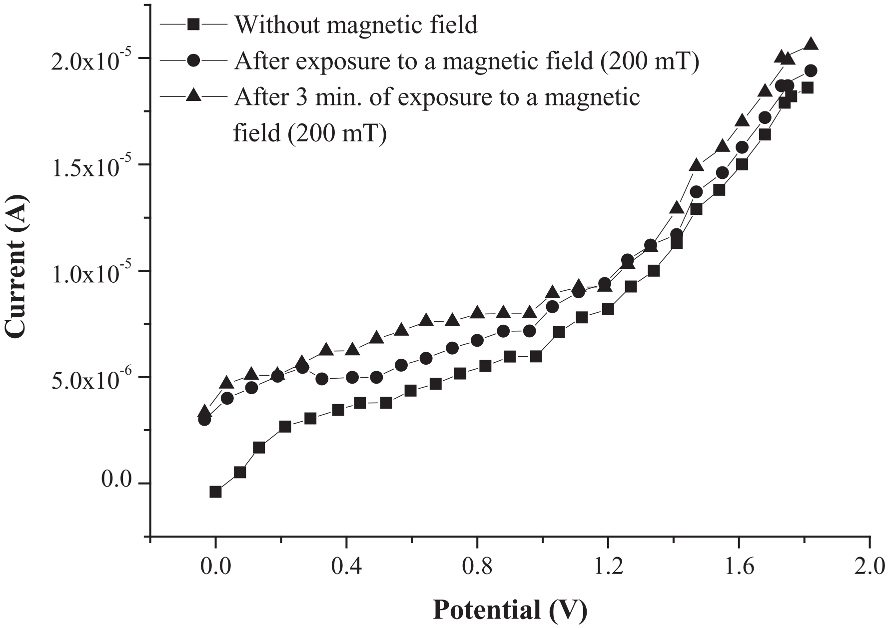


Figure 3.
Current *vs.* potential curves of an Au/**PFV-DOPPV**/Al device before and after exposure to a magnetic field.

the UV-VIS spectrum gave the band-gap energy ($E_{gap} \approx 2.8$ eV).[22] The optical band-gap subtracted from the ionization potential led to an estimated electroaffinity (EA ≈ 1.8 eV). Thus, LUMO ($E_{LUMO} \approx -1.8$ eV) and HOMO ($E_{HOMO} \approx -4.6$ eV) could also be estimated.

Preliminary results obtained from current *vs.* potential curves of **PFV-DOPPV** sandwiched between two metallic contacts (Au and Al) recorded in the absence and in the presence of a magnetic field (Figure 3) suggested magnetoresistance, a property recently also observed in other organic semiconducting polymers.[11,12,23] Further investigations are currently being carried out.

Conclusions

PFV-DOPPV was synthesized in good yield (70%) by McMurry coupling reaction of dialdehydes. It was characterized by several techniques. SEC showed average molar mass of 3000 $g \cdot mol^{-1}$ and a degree of polymerization of 10. Thermal analyses showed the polymer to be stable up to 214 °C. Cyclic voltammetry and UV-VIS spectroscopy experiments allowed to estimate parameters such as ionization potential (IP ≈ 4.6 eV), band-gap ($E_{gap} \approx$ 2.8 eV), HOMO ($E_{HOMO} \approx -4.6$ eV), electronic affinity (EA ≈ 1.8 eV) and LUMO ($E_{LUMO} \approx -1.8$ eV).

Current *vs.* potential curves obtained for gold/**PFV-DOPPV**/aluminum sandwich devices in the presence and absence of a magnetic field suggested magnetoresistance.

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