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Synthesis, characterization, optical and electrical properties of bis(phenylvinyl)anthracene-based polymers

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ABSTRACT

A series of bis(phenylvinyl)anthracene-based polymers containing different lengths of polar ethylene glycol groups in the main chain (**P1**–**3**) were efficiently synthesized by Wittig polycondensation. These polymers are fully soluble in volatile solvents, which helped a lot to obtain high quality films. Moreover, these semi-conducting materials exhibited semi-crystalline morphology with relatively high glass transition temperature. In this article, the UV–visible absorption and fluorescence properties of **P1**–**3** were studied consequently both in solution and as thin solid film: tan absorption-onset at 433 nm was observed and all these bis(phenylvinyl)anthracene-based polymers (**P1**–**3**) show a blue emission in solution, fluorescence quantum efficiencies being respectively 52% for **P1**, 75% for **P2** and 67% for **P3**. In addition, the HOMO/LUMO energy levels were evaluated by cyclic voltammetry measurements and indicate a *p*-type semi-conducting materials. Finally, the electrical properties of **P1**–**3** were investigated by recording current-tension characteristics and these experimental results were modeled by the current space-charge-limited (SCLC) mechanism.

1. Introduction

Conjugated polymers attracted an increasing amount of attention in recent years for various organic electronic devices because of their potential advantages over inorganic and small-molecule organic semiconductors [1]. The goal with organics-based devices is not necessarily to attain or exceed the level of performance of inorganic semiconductor technologies but to benefit from a unique set of characteristics combining the electrical properties of semiconductors with the typical plastics properties, i.e. low cost, chemical synthesis versatility, easy processing and flexibility [2]. Organic semiconductors are designed and investigated in many research fields today, particularly in organic electronics, including light-emitting diodes (PLEDs) [3,4], thin-film transistors [5], solar cells [6] and chemical sensors [7], these latter being currently expanding.

In this context, anthracene was one of the first organic molecule employed in organic light emitting diodes OLED). Indeed, the Electroluminescence from an anthracene single crystal was reported by M. Pope et *al*. in 1963 [8] but it is only twenty years later (in the middle of the 1980s) that such an organic light-emitting material was incorporated in light-emitting diode (LEDs) as the active component. At this stage, the device performance was rather poor due to the organic layer thickness and the high voltage over 100 V. But later on, an important improvement was achieved after obtaining anthracene layers by using the vacuum evaporating deposit technique, the operating voltage being then lowered up to 30 V [9]. Since, anthracene derivatives have received considerable interest in the field of OLEDs and are also tested in organic field-effect transistors OFET [10] as well as photovoltaic devices. More precisely, lots of anthracene-based electroluminescent materials were developed [11,12] due to anthracene's unique chemical and electron-rich structure, low electronic band gap and strong blue fluorescence. More recently, anthracene derivatives have been extensively tested as fluorescent chromophores in the building of chemosensors [13–15].

Based on these interesting properties observed with

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anthracene molecular derivatives, many researchers investigated finally a polymer approach, anthracene and its 9,10-substituted derivatives being incorporated either into polymer main-chains [16–19] or being linked as pendent groups: the main objectives was always to contribute to solve the problem of preparing good optical quality films, in order to suppress excimer formation. As examples, numerous 9, 10-substituted anthracenes based polymers have been already developed and studied as blue light-emitting materials for OLED devices [20–27]. Furthermore, PPV derivatives containing non-conjugated blocks as spacer have been also studied [28,29]: in this case, the interruption of π-conjugated systems results usually in a blue-shift of their PL and EL spectra compared to the corresponding fully conjugated materials, but simultaneously the non-conjugated spacer increases the solubility of the materials.

These is the reason why n this contribution we follow a similar strategy, as we report the synthesis and characterization of a series of new soluble bis(phenylvinyl)anthracene-based polymers containing ethylene glycol types polar spacer groups, looking for potential organic thin-layer electronic applications. To conclude, the optical, electrochemical and electrical behaviors of these organic semi-conducting materials are fully investigated.

2. Experimental

Dimethylforamide was and distilled over Calcium hydrur (CaH_2) under argon. Anthracene (Fluka, 97%), 4-hydroxy-3-methoxybenzaldehyde (Vanillin) (Acros, 97%), paraformaldehyde (Acros, 96%), 1,10-Dibromododecane (Acros, 97%) triphenylphosphine (Acros, 99%), potassium carbonate (Acros, 99%). Sodium hydrid(Aldrich 60% dispersion in mineral oil), tetraethylene glycol(Across 99%) triethylene glycol (Across 99%) decaethylene glycol (Aldrich). p-toluene sulfonyl chloride(Aldrich), were directly purchased from chemical companies. ^{1}H-NMR and ^{13}C-NMR spectral data were obtained on a Bruker AV 300 spectrometer. Fourier transform infrared (FT-IR) spectra were acquired on a Perkin-Elmer BX (0.5 cm^{-1} resolution). FT-IR system spectrometer by dispersing samples in KBr disks. Steric exclusion chromatography (SEC) was performed on an Agilent Technologies 1200 HPLC: experiment was done at room temperature using THF as eluent with standard polystyrene calibration. DSC was performed on a Mettler Toledo DSC 1 with a heating rate of 10 °C min^{-1}. Thermogravimetric analysis (TGA) was carried out on TA Instruments Q50 (TA Instruments, USA) under nitrogen at a heating rate of 10 °C min^{-1}. The UV–visible absorption spectra were recorded on a Cary 5000 UV–vis–NIR spectrophotometer. Fluorescence spectra were obtained from a Jobin-Yvon spectrometer HR460 coupled to a nitrogen-cooled Si charged-coupled device (CCD) detector (2000 pixels), samples being excited at 365 nm with a 450 W Xenon lamp. The spectral sensitivity of the measurement system was calibrated using tungsten standard lamp. For solid state measurements, the films were spin-coated onto a quartz substrate from a chloroform solution (2.10^{-2} M) and using 2000 tr.min^{-1} speed: note that prealably the film thicknesses were measured by a Dektak profilometer (Sloan, USA) and were about 100 nm. For solid state measurements, the films were deposited onto a quartz substrate from a chloroform solution. All measurements were performed at room temperature. Cyclic Voltammetry (CV) was performed with a CHI 660B electrochemical station, based on a three-electrode cell and using material films that were drop-casted onto an indium tin oxide (ITO) as the working electrode. The measurement were carried out at 25 °C, after cell deoxygenation with argon, at a scanning rate of 50 $mV.s^{-1}$ against a saturated calomel reference electrode (SCE) and using 0.1 M tetrabutylammonium perchlorate ($(n\text{-}Bu)_4ClO_4$) in acetonitrile as supporting electrolyte and solvent:the electrochemical cell was externally calibrated with ferrocene, before each reductive scan.

2.1. Monomers synthesis

2.1.1. Synthesis of 9,10-dichlormethylanthracene (AnCl)

A mixture of anthracene (1.83 g, 10 mmol), paraformaldehyde (1.56 g, 50 mmol of CH_2O) and 37% aqueous HCl (5 mL, 60 mmol) in acetic acid (30 mL) was heated at 50 °C for 24 h. The resulting mixture was then cooled to room temperature, poured into distilled water and extracted with chloroform. The organic layer was washed several times with distilled water before the organic phase was dried over anhydrous magnesium sulfate. The resulting solution was then concentrated before an ultimate precipitation in diethyl ether.

AnCl: Yield 75%, yellow powder. ^{1}HNMR (300 MHz, $CDCl_3$, δ): 8.3(dd, J = 6.9 Hz, J = 3 Hz, 4H, Ar–H), 7.6 (dd, J = 6.9 Hz, J = 3 Hz, 4H, Ar–H), 5.6 (s, 4H, CH_2Cl). ^{13}C-NMR (75.5 MHz, $CDCl_3$, δ): 129.8, 129.8, 126.7, 124.4, 38.8. FT-IR (cm^{-1}):3086(w, aromatic C–H stretching), 1517 (s, C=C stretching), 796 (s, aromatic C–H out of plane bending), 625 (s, C–Cl stretching).

2.1.2. 9,10-bis(triphenylphosphoniomethyl)anthracene dichloride (AnP)

A solution of $AnCl_2$ (2.75 g, 10 mmol) and triphenylphosphine (5.82 g, 22 mmol) in anhydrous toluene (50 mL) was stirred and heated at reflux for 24 h under argon atmosphere. After cooling the reaction mixture, the toluene was removed and the final yellow solid was filtered off, washed several times with diethyl ether and dried under vacuum.

AnP: Yield: 75%, yellow powder .^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.02–8.00 (dd, 3J = 6.3 Hz, 4J = 2.7 Hz, 4H, anthracene), 6.98–6.94 (dd, 3J = 6.3 Hz, 4J = 2.7 Hz, 4H, anthracene), 7.81–7.49 (m, 30 H, $P(Ph)_3$), 6.22 (d, $^2J_{H\text{-}P}$ = 13.8 Hz, 4H, $CH_{2\text{-}P}$. ^{13}C-NMR (75.5 MHz, $CDCl_3$, δ): 135.4, 134.8, 134.7, 134.6, 130.7, 130.2, 130.1, 130.0, 125.7, 125.5, 122.2, 118.2, 117.1, 31.6, 30.6. FT-IR (cm^{-1}): ν(*P*–C) 1112, $\nu(P^+Cl^-)$ 512.

2.1.3. Synthesis of the tosylated monomers

60 mL of 5 M aqueous NaOH was added to 50 mL of THF and 0.2 mmol oligo(ethylene glycol). The mixture was then cooled at5 °C before a solution of 4-toluenesulfonylchloride (36.22 g, 190 mmol) in 50 mL of THF was added dropwise. After 2 h, the mixture was placed in a separating funnel and the aqueous phase was extracted with diethyl ether (3 × 50 ml). The organic phases were combined and washed with water, dried over $MgSO_4$ and the solvent was eventually evaporated under vaccuum. The crude product was at the end purified by several washings in ethanol.

A1: Yield 75%, viscous yellow liquid. ^{1}H-NMR (300 MHz, CDCl3, δ): 7.72 (d, J = 8.4 Hz, 4H, Ar–H), 7.25 (d, J = 8.1 Hz, 4H, Ar–H), 4,05 (t, J = 4.8 Hz, 4H, $SOCH_2$), 3.56 (t, J = 4.8 Hz, 4H,OCH_2), 3.44 (t,4H, OCH_2–CH_2O), 2.36 (s, 6H, Ar-CH3). ^{13}C-NMR (75.5 MHz, $CDCl_3$, δ): 144.0, 132.0, 130.8, 129.7, 71.2, 70.7, 69.4, 20.5.

A2: Yield 68%, viscous white liquid. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 7.76 (d, J = 8.1 Hz, 4H, Ar–H), 7.32 (d, J = 7.8 Hz, 4H, Ar–H), 4.13 (t, J = 4.8 Hz, 4H, $SOCH_2$), 3.49–3.69 (m, 12 H, OCH_2–CH_2O), 2.41 (s, 6H, Ar-CH_3). ^{13}C-NMR (75.5 MHz, $CDCl_3$, δ):143.0, 130.8, 127.9, 126.0, 68.75, 68.5, 67.4, 19.7.

A3: Yield 65%, viscous yellow liquid. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 7.78 (d, J = 8.1 Hz, 4H, Ar–H), 7.32 (d, J = 8.1 Hz, 4H, Ar–H),4.14 (t, J = 4.5 Hz, 4H, $SOCH_2$), 3.48–3.73 (m, 20 H, OCH_2–CH_2O), 2.42 (s, 6H, Ar-CH_3). ^{13}C-NMR (75.5 MHz, $CDCl_3$, δ):142.3, 133.7, 130.5, 128.7, 71.4, 70.4, 69.6, 68.6, 68.0, 21.4.