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Thiophene pyrenyl derivatives for the supramolecular processability of single-walled carbon nanotubes in thin film heterojunction

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ABSTRACT

A major problem for the use of single-wall carbon nanotubes (SWCNTs) in electronic devices relates to their poor processability. Chemical modification inevitably introduces defects in the nanotube lattice, resulting in a loss of electronic properties. In this contest, we report on a supramolecular approach with the aim of increasing the dispersion of SWCNTs in solution and in organic semiconductor matrices by ensuring the optoelectronic properties. In particular, new pyrenyl derivatives of thiophene have been synthesized and used to improve the solubility of SWCNTs for electron transfer in thin film heterojunction with poly(3-hexylthiophene) (P3HT) as donor system. Photoinduced electron transfer to SWCNTs has been demonstrated and the effect of different alkyl spacers, between the pyrene unit and the thiophene moiety, has revealed to play a key role. Electron transfer has been maximized by the compound with a spacer coplanar with the pyrene moiety due to the reduced separation between P3HT and SWCNTs.

1. Introduction

Single-wall carbon nanotubes (SWCNTs) are scarcely soluble in common organic and aqueous media and this limits their processability by standard solution-based methodologies. The solubility of SWCNTs can be improved by functionalization processes [1–7] aimed at debundling the pristine material and at modifying the surface of individual nanostructures. In this context, our work aims to explore the possibility to obtain photoactive thin films based on a dispersion of SWCNTs in a poly-3-hexylthiophene (P3HT) matrix. [8–14] To this aim, it is mandatory to hamper the aggregation of SWCNTs enabling the exploitation of the properties of individual nanostructures.

We have previously demonstrated that the covalent functionalization obtained by addition of diazonium salts is a powerful tool to tune the solubility of CNTs in different solvents (from DMF to ethanol) [15]. While this novel process allows for a tight control on the covalent functionalization process, it inevitably introduces defects within the sp^2 lattice and thus partially limits the electronic properties of CNTs [16–18]. Alternatively, non-covalent strategies, mainly based on π-π interactions [19], have been explored to improve the solubility of SWCNTs without affecting their electronic properties [20–24]. In this context, by preparing gold nanoparticles covered with a monolayer of pyrene derivatives acting as interfacial agent, we were able to improve their interaction with CNTs [25].

Moreover, Nogueira et al. have successfully exploited thiophene chemistry to improve the interfacial compatibility and the physical contact between SWCNTs and polymer matrix as well as P3HT and silicon in photovoltaic (PV) applications [26,27].

Inspired by these works, we herein present a study about the use of 3-alkythiophene derivatives with pyrene side groups as a suitable interfacial system in SWCNT:P3HT systems for application in thin films heterojunction [9,28–32].

2. Experimental

2.1. Materials and methods

All the reagents and solvents were purchased from Sigma-Aldrich and were used as received if not otherwise specified. SWCNTs were purchased from CNI (lot # P2150) and were used as received. ^{1}H and

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^{13}C NMR spectra were collected using an Avance 300 MHz NMR spectrometer (Bruker) and $CDCl_3$ as a solvent. Multiplicity is given as follows: s = singlet, d = doublet, dd = doublet of doublets, m = multiplet, br = broad peak. Centrifugations were performed on a MR23i Jouan ultracentrifuge equipped with a SWM 180.5 swinging bucket rotor (Thermo electron corporation) at 3000 rpm for 10 min. Absorption spectra in air-equilibrated solvents were registered with a Varian Cary 5000 spectrophotometer, at room temperature, between 280 and 1400 nm, data interval = 0.5 nm, scan rate = 300 nm/min, SBW = 2 nm. Emission spectra in solution were recorded on a Perkin-Elmer LS55 fluorometer using quartz cuvettes with 1 cm length path. Infrared spectra were recorded between 4000 and 400 cm^{-1} on a FT-IR Nicolet 5700. Dispersions of SWCNTs were achieved using the Sonicator 3000 (Misonix) with the following pulse parameters: time on = 3 s, time off = 3 s, power level = 2 (4–6 W) for 30 min. 2-bromo-3-thiopheneethanol (3) was obtained according to reported procedures.

2.2. Synthesis

2.2.1. Synthesis of 2-(thiophen-3-yl)ethyl pyren-1-yl carboxylate (1a) [33]

The reaction was carried out at 0 °C. A solution of 1-pyrencarboxylic acid (250.8 mg, 1.018 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) (212.9 mg, 1.111 mmol) and 4-dimethylaminopyridine (DMAP) (14.0 mg, 0.114 mmol) in dichloromethane (7.5 mL) was added to a solution of thiopheneethanol (137.7 mg, 1.074 mmol), in dichloromethane (7.5 mL) under magnetic stirring. The reaction was monitored by TLC (silica gel, eluent: ETP/diethylether 2:1, R_F = 0.52). After 6 h, a solution of DMAP (27.7 mg, 0.227 mmol) in dichloromethane (10 mL) was added. After 48 h, the reaction mixture was quenched in MilliQ water (10 mL) and was washed with dichloromethane (3 × 50 mL). The organic phase was washed with a 10% w/w aqueous solution of NH_4Cl, dried over magnesium sulfate and then the solvent was removed at reduced pressure. The dark oil obtained was purified by column chromatography on silica gel (eluent: ETP/diethylether 2:1) obtaining the desired product as yellow oil (243 mg, 0.682 mmol, 67.0% yield).

Anal. Calcd. for $C_{23}H_{16}O_2S$: C, 77.50; H, 4.52; S, 9.00. Found: C, 76.96; H, 4.64; S, 9.46.

^{1}H NMR (200 MHz, $CDCl_3$) δ 9.21 (d, J = 9.4 Hz, 1H), 8.62 (d, J = 8.1 Hz, 1H), 8.49–7.84 (m, 9H), 7.38 (dd, J = 4.9, 3.0 Hz, 1H), 7.26–7.20 (m, 1H), 7.17 (d, J = 4.9 Hz, 1H), 4.78 (t, J = 6.8 Hz, 3H), 3.30 (t, J = 6.8 Hz, 3H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 168.21, 138.51, 134.53, 131.22, 130.59, 129.84, 129.63, 128.59, 127.37, 126.51, 126.38, 126.03, 125.12, 124.35, 123.85, 122.06, 65.34, 30.07.

IR (KBr) 3104 (w), 3043 (w), 2954(w), 1706 (s), 1595 (m), 1507(w), 1384 (w), 1324 (w), 1251 (s), 1229 (s), 1196 (m), 1145 (s), 1134 (s), 1089 (s), 1044 (m), 851 (s), 840 (s), 774 (m), 710 (s).

UV–vis (DMF) λ(ϵ): 352.5(24159); 384.5(7634).

2.2.2. Synthesis of 2-(thiophen-3-yl)ethyl pyren-1-yl acetate (1b)

The reaction was carried out at 0 °C. A solution of 1-pyrenacetic acid (499 mg, 1.92 mmol), EDC (397 mg, 2.07 mmol) and DMAP (27.4 mg, 0.224 mmol) in dichloromethane (15 mL) was added to a solution of thiopheneethanol (138 mg, 1.074 mmol), in dichloromethane (15 mL) under magnetic stirring. The reaction was monitored by TLC (silica gel, eluent: ETP/diethylether 2:1, R_F = 0.51). After 48 h, the reaction mixture was quenched in MilliQ water (100 mL) and was washed with dichloromethane (3 × 50 mL). The organic phase was washed with deionized water (150 mL), dried over magnesium sulfate and then the solvent was removed at reduced pressure. The dark oil obtained was purified by column chromatography on silica gel (eluent: ETP/diethylether 2:1) obtaining the desired product as yellow oil (456 mg, 1.23 mmol, 64.3% yield).

Anal. Calcd for $C_{23}H_{16}O_2S$: C, 77.81; H, 4.90; S, 8.66. Found: C, 77.67; H, 4.95; S, 9.03.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (dd, J = 8.5, 6.7 Hz, 3H), 8.15 (dd, J = 8.5, 6.1 Hz, 2H), 8.08 (d, J = 0.6 Hz, 2H), 8.05 (dd, J = 8.0, 7.17 Hz, 2H), 7.94 (d, J = 7.8 Hz, 1H), 7.12 (dd, J = 4.9, 3.0 Hz, 1H), 6.84 (m, 1H), 6.79 (dd, J = 4.9, 1.3 Hz, 1H), 4.39 (t, J = 6.7, 2H), 4.36 (s, 2H), 2.93 (t, J = 6.7 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.89, 138.22, 131.72, 131.21, 129.83, 128.77, 128.57, 128.48, 128.34, 127.81, 127.70, 126.39, 125.82, 125.80, 125.69, 125.55, 125.43, 125.26, 125.15, 123.63, 121.97, 65.26, 39.98, 29.88.

FT-IR (NaCl) 3106 (w), 3045 (w), 2956 (w), 2922 (w), 1735 (s), 1313 (m), 1254 (s), 1164 (s), 1010 (m), 842(s), 774 (m), 713 (m).

UV–vis (DMF) λ(ϵ): 314(11869); 327.5(28688); 344(42705).

2.2.3. Synthesis of 2-(thiophen-3-yl)ethyl pyren-1-yl butyrate (1c) [34,35]

The reaction was carried out at 0 °C. A solution of 1-pyrenbutyric acid (136 mg, 0.472 mmol), EDC (101 mg, 0.526 mmol) and DMAP (6.4 mg, 0.052 mmol) in dichloromethane (5 mL) was added to a solution of thiopheneethanol (71.1 mg, 0.555 mmol), in dichloromethane (5 mL) under magnetic stirring. After 3 h, a solution of DMAP (13.1 mg, 0.107 mmol) in dichloromethane (5 mL) was added. After 66 h, the reaction mixture was quenched in MilliQ water (100 mL) and was washed with dichloromethane (3 × 50 mL). The organic phase was washed with 10% w/w aqueous solution of NH_4Cl (100 mL), dried over magnesium sulfate and then the solvent was removed at reduced pressure. The dark oil obtained was purified by column chromatography on silica gel (eluent: ETP/diethylether 2:1, R_F = 0.50) obtaining the desired product as yellow oil (116 mg, 0.290 mmol, 61.5% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (dd, J = 9.2, 2.2 Hz, 1H), 8.24–8.10 (m, 4H), 8.07–7.97 (m, 3H), 7.86 (dd, J = 8.0, 2.2 Hz, 1H), 7.27 (m, 1H), 7.08–6.93 (m, 2H), 4.33 (t, J = 6.9 Hz, 2H), 3.48–3.29 (m, 2H), 2.99 (t, J = 6.9 Hz, 2H), 2.48 (t, J = 7.2 Hz, 2H), 2.21 (qn, J = 6.9 Hz, 2H).

UV–vis (DMF) λ(ϵ): 314.5(10563); 328(25616); 344.5(37897).

2.2.4. Synthesis of 2-([2-2′-dithiophen]-3-yl)ethyl pyren-1-ylacetate (2)

The reaction was carried out at 0 °C. A solution of pyren-1-acetic acid (499 mg, 1.92 mmol), EDC (397 mg, 2.07 mmol) and DMAP (27.4 mg, 0.224 mmol) in dichloromethane (15 mL) was added to a cold solution of 2-([2-2′-dithiophen]-3-yl)ethanol [36] (409 mg, 1.9 mmol) in dichloromethane (15 mL). The solution darkened. The reaction was monitored by TLC (silica gel, eluent: ETP/diethylether 2:1, R_F = 0.50). After 16 h, fresh DMAP (50.3 mg) was added to the solution. After 48 h, the reaction mixture was quenched in MilliQ water (100 mL) and was washed with dichloromethane (3 × 50 mL). The organic phase was washed with deionized water (150 mL), dried over magnesium sulfate and then the solvent was removed at reduced pressure. The dark oil obtained was purified by column chromatography on silica gel (eluent: ETP/diethylether 2:1) obtaining the desired product as yellow oil (160 mg, 1.23 mmol, 19.7% yield).

^{1}H NMR (200 MHz, $CDCl_3$) δ 8.41–7.82 (m, 9H), 7.31 (dd, J = 5.1, 1.2 Hz, 1H), 7.13 (dd, J = 3.6, 1.2 Hz, 1H), 7.05 (dd, J = 5.1, 3.6 Hz, 1H), 6.98 (d, J = 5.2 Hz, 1H), 6.70 (d, J = 5.2 Hz, 1H), 4.43 (t, J = 6.6 Hz, 2H), 4.35 (s, 2H), 3.10 (t, J = 6.8 Hz, 2H).

UV–vis (DMF): 314; 328; 344.

2.3. Electrochemical characterization

Pyrene derivatives have been characterized by means of electrochemical methods in a common three electrodes cell connected to a Potentiostat/Galvanostat (Metrohm Autolab PGSTAT 128N). Glassy carbon rods (GC, diameter = 3 mm, Bio-Logic SAS) have been used as working electrodes. Graphite rod and Ag/AgCl (3.5 M) have been used as counter and reference electrodes respectively. The electrolytic solutions have been prepared with pyrene derivatives in concentration of 2E–03 M and 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6, purum ≥98%, Sigma Aldrich) in acetonitrile (CH_3CN,