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Organic Electronics

Thionation of naphthalene diimide molecules: Thin-film microstructure and transistor performance

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ABSTRACT

The replacement of the imide oxygen atoms with sulfur atoms in the naphthalene diimide (NDI) framework is an attractive strategy for tuning of the electronic properties of such molecules. Here we report the synthesis and characterization of the full series of six thionated NDI molecules with branched side chains. In order to provide a direct comparison with the unthionated parent molecule, a top-gate, bottom contact geometry is adopted, with work function-modified gold electrodes facilitating electron injection. The highest electron mobility was observed for the S2-*cis* molecule, with a mobility of 0.20 cm²/Vs compared to 0.068 cm²/Vs for the parent molecule. Mobilities slightly lower than that achieved for the S2-*cis* molecule were also achieved for the S2-*trans* and S3 derivatives, with the S1, S4 and S2-*cis imide* derivatives showing mobilities lower than the parent molecule. The thin film microstructure of these molecules has also been explored using a combination of grazing-incidence wide-angle X-ray scattering and near-edge X-ray absorption fine-structure spectroscopy. The performance and microstructure of thin films deposited either by spin-coating or blade coating are also compared.

1. Introduction

The development of organic semiconductors is facilitating the realization of new technologies based on flexible devices with novel form factors produced through low-temperature processing [1]. The ability to prepare organic field-effect transistors (OFETs) on a variety of flexible, transparent substrates at high throughput and low cost will potentially enable organic semiconductors to succeed in a variety of niche applications that traditional silicon-based electronics are unsuitable for, such as radio frequency identification (RFID) tags, flexible displays, and sensors [1,2]. Early progress in OFET research was dominated by the development of hole transporting (or "p-type") organic semiconductors [3] but in order to fully develop electronic applications, electron transporting (or "n-type") organic semiconductors must make strides to keep pace. Progress in n-type organic semiconductor development has been partially hampered by the difficulty of creating air stable electron transporting materials that retain the necessary solution processability. To achieve air stability, the lowest unoccupied molecular orbital (LUMO) level must be suitably low (LUMO < − 4.0 eV) to allow air

stable charge transport within the conjugated core of the organic semiconductor [4]. Having materials with deep LUMO levels also facilitates electron injection from electrodes, another problem that has hampered the development of n-type organic semiconductors [4]. The addition of strong electron withdrawing groups to the conjugated framework has been an effective strategy to lower the LUMO levels of organic semiconductors to realize n-type function [5]. Rylene diimide-based organic semiconductors in particular have been an important class of n-type organic semiconductor exhibiting relatively high electron affinities, high electron mobilities, and excellent chemical, thermal, and photochemical stabilities [6,7]. Rylene diimides such as naphthalene diimide (NDI) and perylene diimide (PDI) possess relatively deep LUMO levels due to the electron withdrawing nature of the imide groups at either end of the molecule. Solubilising side chains can be attached to the nitrogen atoms enabling solution processability. As well as being applied as so-called small molecules, NDI and PDI molecules have also been widely used as acceptor units in donor-acceptor co-polymers [3]. Both small molecule and polymeric organic semiconductors based on NDI and PDI units have proven to be excellent

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materials for n-type OFETs with mobilities of 1–5 cm^2/Vs [8–10].

Recently, the replacement of the imide oxygen atoms with sulfur atoms in NDI and PDI molecules has been shown to be an attractive strategy for tuning of LUMO values and electron mobility [11–13]. Sulfur substitution is achieved by treating with Lawesson's reagent and controlling the reaction time to tune the extent of thionation at the imide carbonyl positions. It was reported that all the thionated PDI regioisomers could be successfully isolated in reasonable yields except for the S2 *cis-imide*-PDI (which could be isolated in trace amounts only) presumably due to unfavourable double thionation of adjacent carbonyl positions. For PDI molecules with branched side-chains, increasing the number of sulphur substitutions from 0 to 4 was found to increase the electron affinity from −3.67 eV to −4.12 eV, while the electron mobility was found to systematically increase with the degree of thionation from 6.9×10^{-4} cm^2/Vs for the unsubstituted parent molecule to 0.16 cm^2/Vs for the S4 molecule with all four oxygen atoms replaced with sulfur atoms [11]. For NDI-based molecules similar variation in electron affinity has been reported, both for molecules based on branched [12] and linear [13] side-chains. Chen et al. – who reported four thionated derivatives of NDI (S1, S2-*trans*, S2-*cis* and S3) – found that the best electron mobility was attained for the S2-*trans* molecule with a value of 1.0×10^{-2} cm^2/Vs reported [12]. The authors however were not able to measure an electron mobility of the parent molecule likely due to difficulties achieving electron injection. Shortly after, Kozyvz et al. reported the properties of S1, S2-*trans*, S2-*cis*, S3 and S4 derivatives of NDI with linear side chains. While they were not able to observe transistor action in the S4 derivative, the authors reported similar mobilities of 3.9×10^{-2} cm^2/Vs to 7.4×10^{-2} cm^2/Vs for the other thionated derivatives compared to a much lower mobility of 3.0×10^{-5} cm^2/Vs for the parent molecule.

Here we report the synthesis and properties of the full set of 6 thionated derivatives including the S2-*cis imide* derivative not previous reported. Furthermore, through the adoption of a top-gate bottom contact geometry with work-function modified electrodes we are able to achieve significantly higher mobilities than previously reported for the unthionated parent molecule. Overcoming problems associated with electron injection for the parent molecule is important in order to provide a true comparison of the charge transporting properties of thionated *vs.* unthionated molecules. We also report overall higher mobilities for the thionated NDI derivatives, with a mobility of up to 0.20 cm^2/Vs achieved for the S2-*cis* derivative and 0.068 cm^2/Vs for the parent molecule. Finally, we also present microstructural characterization of films of these NDI molecules using a combination of grazing incidence wide angle X-ray scattering (GIWAXS) and near edge X-ray absorption fine structure (NEXAFS) spectroscopy, and compare the microstructure of spin-coated and blade-coated samples.

2. Materials and methods

2.1. Synthesis

The parent compound (P) was synthesised following Xiong et al. [14], though we note that the microwave synthesis of thionated NDI materials has also been recently reported [15]. Analytical thin layer chromatography was performed on aluminium plates coated with silica gel (Silica 60 F$_{254}$). Column chromatography was conducted using Merck silica gel 60, with a pore size between 0.063 and 0.200 mm. The eluent conditions are expressed as volume-to-volume *(v/v)* ratios. High-resolution electron impact mass spectrometry (HR-ESI) was performed on an Agilent Technologies 6220 Accurate-Mass Time-of-Flight LC/MS as the solutions specified. For mass spectrometry [M]$^+$ denotes the molecular ion. Analyses were performed in positive ion mode (ESI$^+$) unless otherwise stated. Melting points were recorded on a MP50 Mettler Toledo digital melting point apparatus at 5 °C/min. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded using a Bruker DRX 400 MHz NMR spectrometer (400 MHz for ^{1}H NMR,

100 MHz for ^{13}C NMR), using deuterated chloroform (CDCl$_3$). Chemical shifts are reported relative to the resonances of residual CHCl$_3$ at δ = 7.26 (H) and δ = 77.2 (C). For ^{1}H NMR spectra each resonance was assigned according to the following convention: chemical shift (δ) measured in parts per million (ppm), multiplicity, coupling constant, (*J* Hz), number of protons and assignment. Multiplicities are denoted as (s) singlet, (d) doublet, (t) triplet, (q) quartet, (p) pentet, or (m) multiplet and prefixed (br) broad where appropriate. The ^{13}C NMR spectra were recorded using proton decoupled pulse sequence unless stated otherwise. For ^{13}C NMR each resonance was assigned according to the following convention: chemical shift (δ) measured in parts per million (ppm).

A solution of Lawesson's reagent (3.70 g, 9.15 mmol) and NDI (P) in anhydrous toluene (40 mL) was heated at reflux for 50 h under nitrogen. The resulting brown solution was cooled to room temperature and concentrated under vacuum to give the crude mixture which was subjected to column chromatography (40% hexane in dichloromethane) to give the following compounds. Each fraction was recrystallised from (50% methanol in dichloromethane).

2.1.1. 2,7-bis(2-ethylhexyl)-8-thioxo-7,8-dihydrobenzo[lmn][3,8] phenanthroline-1,3,6(2H)-trione, S1

Green yellow solid (193 mg, 20%). M.p. 175–176 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.06 (d, *J* = 8.0, 1H, NDI), 8.77–8.72 (m, 2H, NDI), 8.65 (d, *J* = 8.0, 1H, NDI), 4.79–4.69 (m, 2H, CH$_2$), 4.19–4.09 (m, 2H, CH$_2$), 2.21–2.14 (m, 1H, CH), 1.97–1.91 (m, 1H, CH), 1.43–1.24 (m, 16H, CH$_2$), 0.96–0.85 (m, 12H, CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ 193.7, 163.7, 163.6, 161.0, 136.2, 131.7, 131.1, 130.7, 130.3, 127.0, 126.8, 126.4, 125.4, 125.2, 51.0, 44.7, 38.1, 37.1, 30.9, 30.8, 28.8, 28.7, 24.2, 23.22, 23.18, 14.2, 10.9, 10.8. HRMS (TQ-MS-ESI) *m/z* obsd [M + H]$^+$ 507.2670, calcd C$_{30}$H$_{39}$N$_2$O$_3$S [M + H]$^+$ 507.2676.

2.1.2. 2,7-bis(2-ethylhexyl)-3,6-dithioxo-2,3,6,7-tetrahydrobenzo[lmn] [3,8]phenanthroline-1,8-dione, S2-cis

Brown red solid (152 mg, 16%). M.p. 182–183 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.89 (s, 2H, NDI), 8.70 (s, 2H, NDI), 4.76–4.65 (m, 4H, CH$_2$), 2.19–2.11 (m, 2H, CH), 1.43–1.27 (m, 16H, CH$_2$), 0.93–0.85 (m, 12H, CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ 193.7, 161.2, 135.7, 131.4, 128.9, 126.4, 125.2, 50.9, 37.1, 30.8, 28.7, 24.2, 23.2, 14.2, 10.9. HRMS (TQ-MS-ESI) *m/z* obsd [M + H]$^+$ 523.2440, calcd C$_{30}$H$_{39}$N$_2$O$_2$S$_2$ [M + H]$^+$ 523.2447.

2.1.3. 2,7-bis(2-ethylhexyl)-3,8-dithioxo-2,3,7,8-tetrahydrobenzo[lmn] [3,8]phenanthroline-1,6-dione, S2-trans

Red solid (168 mg, 18%). M.p. 181–182 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.98 (d, *J* = 8.0, 2H, NDI), 8.57 (d, *J* = 8.0, 2H, NDI), 4.74–4.64 (m, 4H, CH$_2$), 2.20–2.10 (m, 2H, CH), 1.43–1.25 (m, 16H, CH$_2$), 0.93–0.85 (m, 12H, CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ 193.7, 161.2, 136.1, 131.1, 129.7, 125.4, 125.2, 51.0, 37.1, 30.8, 28.7, 24.2, 23.2, 14.2, 10.9. HRMS (TQ-MS-ESI) *m/z* obsd [M + H]$^+$ 523.2441, calcd C$_{30}$H$_{39}$N$_2$O$_2$S$_2$ [M + H]$^+$ 523.2447.

2.1.4. 2,7-bis(2-ethylhexyl)-6,8-dithioxo-7,8-dihydrobenzo[lmn][3,8] phenanthroline-1,3(2H,6H)-dione, S2-cis imide

Orange red solid (17 mg, 2%). M.p. 181–182 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.90 (d, *J* = 8.0, 2H, NDI), 8.58 (d, *J* = 8.0, 2H, NDI), 5.56–5.43 (m, 2H, CH$_2$), 4.17–4.07 (m, 2H, CH$_2$), 2.34–2.26 (m, 1H, CH), 1.96–1.90 (m, 1H, CH), 1.43–1.24 (m, 16H, CH$_2$), 0.95–0.83 (m, 12H, CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ 190.8, 164.0, 137.3, 131.8, 130.6, 127.1, 124.8, 121.9, 57.63, 44.7, 38.1, 37.6, 31.7, 30.9, 30.7, 28.84, 28.81, 24.2, 24.1, 23.21, 23.19, 22.8, 14.6, 14.2, 11.2, 10.8. HRMS (TQ-MS-ESI) *m/z* obsd [M + H]$^+$ 523.2441, calcd C$_{30}$H$_{39}$N$_2$O$_2$S$_2$ [M + H]$^+$ 523.2447.