

Proceeding Paper

Side Chain Engineering of a Solution-Processed Non-Acidic Hole Transport Material for Organic Electronics [†]

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Abstract

Organic semiconductors have the potential to contribute to sustainable electronics manufacture due to their ability to be processed from low-energy solution-processing methods. However, improvements must be made in the lifetime of such devices. PEDOT:PSS, a popular hole transport material, is acidic, which causes degradation in devices over time. Therefore, a replacement is needed to allow for longer lasting organic semiconductor devices. We have previously reported BEDOTPy, a non-acidic, molecular material that could be used to improve the device lifetime of OLEDs. In this work we explore how molecular engineering of BEDOTPy, by modifying the molecule's side chain, affects the physical properties that are important to device performance and lifetime.

Keywords: organic electronics; device lifetime; non-acidic; PEDOT:PSS; organic semiconductors

1. Introduction

PEDOT:PSS is one of the most widely used materials in organic electronics as it can be formulated to be highly conductive, or transparent with the moderate conductivity needed to act as a hole transport layer (HTL). It is water-based, meaning it is processed from a benign solvent, and it allows for orthogonal processing to manufacture multi-layer solution-processed devices. This can contribute to a significant reduction in energy requirements for semiconductor device fabrication by avoiding energy-intensive processes such as thermal evaporation. However, it has been established that the acidity of PEDOT:PSS can cause device degradation, with etching of the transparent ITO electrode a common observation [1,2]. This limits the lifetime of solution-processed semiconductor devices. Therefore, alternative materials should be developed to improve longevity. Using non-acidic alternatives to PEDOT:PSS can be an effective strategy to improve the lifetime [3–5]. One example reported by Hussien et al. [6] involved the use of a molecular system, BEDOTPy, which is oxidatively dimerised to form a conductive material. This was shown to improve the lifetime of a Super Yellow-based OLED compared to an analogous PEDOT:PSS-containing device [6]. However, further improvements in device performance and reliability should be sought for such materials to be used in devices that can compete with conventional electronics.

Another advantage of the BEDOTPy structure compared to PEDOT:PSS is the ease in which the structure can be modified to exhibit different physical properties. In this work we explore the modification of the side chain of the quaternised pyridine unit (Scheme 1) and the effect on important parameters for hole transport materials.



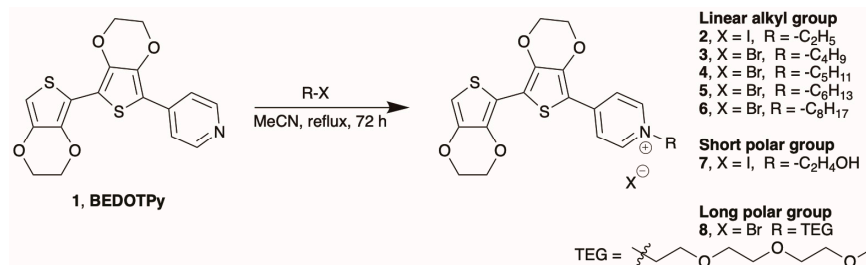
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Scheme 1. Side chain engineering of BEDOTPy structure.

2. Experimental

All chemicals were bought from commercial sources and used as received. BEDOTPy was prepared using a previously reported procedure [6]. The quaternisation reactions were carried out using an analogous procedure to that used for the synthesis BEDOTPy-EtOH-I [6], where BEDOTPy and a halide-containing side chain precursor were reacted at reflux in acetonitrile for 72 h. Detailed experimental procedures will be published elsewhere. The molecules were doped by mixing with 2.5 molar equivalents of nitrosonium salt (NOPF₆ or NOSbF₆) in acetonitrile or acetonitrile/chloroform mixture.

Conductivity measurements were carried out using a two-probe method. Thin films of the BEDOTPy-based material were deposited by spin-coating at 2000 rpm for 60 s (compounds 4–8) or, where solubility was poor (compounds 1–3), drop-casting onto a glass substrate (15 × 15 mm). The films were annealed at 100 °C for 20 min. Aluminium electrodes were deposited onto the film by thermal evaporation. Current-voltage characteristics were measured between aluminium electrodes with a width of 0.15 cm and a separation distance of 0.1 cm. A Keithley 4200-SCS source meter (Keithley Instruments, Cleveland, OH, USA) was used for the measurements. Film thicknesses were measured by scratching the film using a blade and scanning the profile using atomic force microscopy (Dimension 3100, Veeco, Plainview, NY, USA). AFM images were analysed using WSxM 5.0 software [7].

3. Results and Discussion

The structure of BEDOTPy lends itself to facile modification as quaternisation reactions can be carried out using a primary haloalkane-derived reagent in high yield with simple purification required. In this study we used linear alkyl, short polar and long polar halide-containing groups as a means to determine the influence of the side chain properties on hole transport layer performance. The general synthesis scheme is shown above in Scheme 1.

3.1. Electrical Characterisation

In order to become conductive, the BEDOTPy derivatives must be doped. This is achieved by oxidation using nitrosonium salts as the oxidant. This also causes a dimerisation reaction. The doped dimer molecule will have counter ions associated for charge balance. However, for simplicity, we will herein refer to such species as ‘doped compound’, where the compound is labelled according to its assigned name or number. The conductivity of the deposited, doped thin films was compared to understand the optimum type of side chain for the BEDOTPy structures to be used as hole transport layers. The measured conductivity values are shown in Table 1.

The most conductive film formed is doped BEDOTPy, which does not have any side chain. Doped compounds with alkyl side chains give similar conductivity values, with only a slight decrease as the chain length increases. However, this is approximately two orders of magnitude lower on average than for doped BEDOTPy. The use of a short polar chain improves the conductivity compared to the use of non-polar groups, but lengthening this results in a significant increase in resistivity, caused by the disruption of π - π aggregation.

Table 1. Summary of conductivities measured for BEDOTPy derivatives.

Compound	Side Chain	Average Conductivity (S cm ⁻¹) ¹
1, BEDOTPy ²	No chain	1.06 ± 0.87
	Linear alkyl	
2 ³	Ethyl	0.04 ± 0.025
3 ³	Butyl	0.019 ± 0.003
4 ³	Pentyl	0.018 ± 0.012
5 ³	Hexyl	0.014 ± 0.003
6 ³	Octyl	2.8 × 10 ⁻⁷ ± 1.8 × 10 ⁻⁷
	Short polar	
7 BEDOPy-EtOH-I ³	Ethanol	0.28 ± 0.15
	Long polar	
8 ³	Triethyleneglycol	2.4 × 10 ⁻⁴ ± 4.2 × 10 ⁻⁴

¹ Standard deviation reported as error; ² doped using NOSbF₆ (2.5 molar equivalents); and ³ doped using NOPF₆ (2.5 molar equivalents).

3.2. Surface Topography

To further understand differences influenced by the choice of side chain, atomic force microscopy was used to study the surface topography of prepared thin films (Figure 1). The film of compound 2, which has a short alkyl chain (ethyl, Figure 1a), shows the formation of x-shaped aggregates. Where a short polar chain is used (ethanol, compound 7, Figure 1b) there are fibre-like structures in the film, which can be considered to be effective for improved charge transport. The use of a longer alkyl chain (compound 5, hexyl, Figure 1c) leads to smaller aggregates compared to short alkyl chains. This can be explained by the improved solubility of the longer chain-containing molecule reducing the propensity to form large aggregates. While the morphology resulting from a short polar chain shows high roughness, the fibre-like morphology could be a result of favorable intermolecular interactions due to the presence of the hydroxyl group. When the BEDOTPy material is doped, the ionic nature is more compatible with polar side groups compared to non-polar groups, which can be expected to phase separate.

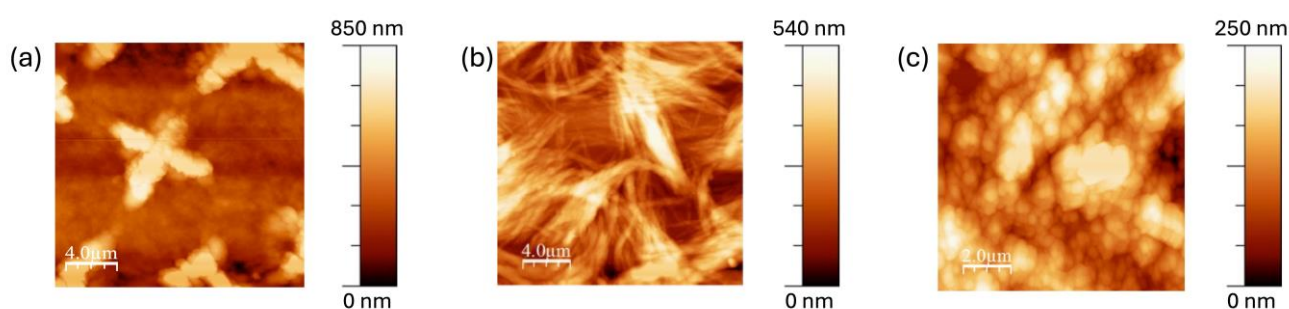


Figure 1. Atomic force microscopy topography images of BEDOTPy analogue: (a) 2 (scan area 20 × 20 μm², scale bar = 4 μm); (b) 7 (scan area 20 × 20 μm², scale bar = 4 μm); and (c) 5 (scan area 10 × 10 μm², scale bar = 2 μm).

4. Conclusions

In this paper we demonstrate the influence of side chain length and type in doped, quaternised BEDOTPy-based materials. It is clear that there is a difficult balance to be struck in improving the solubility of the material, while ensuring effective charge transport. Each of these molecules is non-acidic; therefore, it can be expected that the problem of etching ITO electrodes will be avoided or reduced. However, other properties such as

conductivity [8] and how the interface influences active layer morphology [9] can influence device lifetime. In this respect, we believe that for BEDOTPy-based systems, short-to-medium polar side chains are optimum for allowing solution-processing while maintaining high conductivity. However, further improvements could be made by forming a composite film with a carrier polymer such as polystyrene [10] or a bio-derived equivalent.

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