An N-annulated perylene butyl tetraester for alcohol processed semiconducting organic thin films

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Abstract

Herein, we report on the design and synthesis of an N-annulated perylene butyl tetraester (PTEN-H) for use in alcohol processed semiconducting films. PTEN-H was contrasted with the known N-annulated perylene diimide (PDIN-H) where the former has ring-opened imide positions which in turn lowers the electron affinity (i.e. rendering hole transporting) and improves polar green solvent solubility. PTEN-H can be solubilized in 1-butanol up to 10 mg ml\(^{-1}\) with gentle heating and can be spin-cast or slot-die coated to form uniform thin films on glass and/or plastic substrates. Organic field-effect transistors (OFETs) were fabricated using PTEN-H in the active material layer which was deposited from solution using 1-butanol as the solvent. While hole mobilities were achieved (0.39 \(\times\) \(10^{-4}\) cm\(^2\) Vs\(^{-1}\)), blending the molecular material with a previously reported green solvent processable semiconducting polymer, IIG20-OH, was done to boost performance. This led to increased mobilities for not only the native molecular PTEN-H material, but for the native IIG20-OH polymer as well. Furthermore, a blend of PTEN-H and IIG20-OH were slot-die coated onto a polyethylene terephthalate (PET) substrate giving uniform thin films suitable for large area device fabrication.

1. Introduction

In the past several decades, organic π-conjugated molecules and/or polymers have emerged as viable materials to prepare semiconducting films for operation in organic thin-film transistors (OTFTs) [1–6], photovoltaics (OPVs) [7–9], and light emitting diodes (OLEDs) [10–12]. Molecular organic semiconductors (OSC) are of particular interest owing to well-defined structures, atom-economical synthesis, linear structure–property relationships, and an ability to be rendered soluble in organic solvents for the printing/coating of active films [13, 14]. However, a challenge remains to form high performance semiconducting films from green solvents. Green organic solvents for printed electronics are considered as having a low toxicity (in reference to human interaction with solvent vapours during device manufacturing and environmental impact during solvent disposal) relative to carcinogenic halogenated solvents most commonly used to process organic conjugated materials into films [15]. Some low-cost greener solvents used for solution processing of OSCs are water, alcohols, naturally occurring compounds such as 3-methylcyclohexanone, and food additives such as anisole or 2-methyl anisole [15]. Of these, short-chain alcohols (C2-C4) are target solvents for printing due to their ideal vapor pressure for uniform/smooth film formation.

Among the top molecular semiconducting materials in terms of stability, performance, and solubility in greener organic solvents are perylene diimides (PDIs; figure 1) [16–18]. One class of PDIs is the N-annulated PDI (PDIN-H; figure 1) where bay N-annulation decreases the electron affinity of the compound via addition of an electron rich pyrrole ring and can be rendered polar solvent soluble (water and alcohols) via deprotonation of the pyrrolic N-H
Figure 1. Structural evolution of perylene-based semiconductors. (Left) structure of the classic perylene diimide electron transporting material. (Middle) structure of the bay N-annulated perylene diimide, an electron transporting material. (Right) structure of the target compound in this study, the bay N-annulated perylene butyl tetraester, a hole transporting material.

moiety [18]. Contrary to the extensively reported PDI materials, perylene tetraesters (PTEs) are relatively underexplored counterparts that differ by ring opening at the imide positions to provide four ester substituents. PTEs are soluble in a variety of polar organic solvents, making them a good candidate for green solvent processing. To date, PTEs have been explored as an alternating unit in a polymeric acceptor material for OPVs [19], as a supramolecular nanostructure in water by use of ethylene glycol units on the ester positions [20], as a fluorescent probe [21], and for the development of fundamental structure-property relationships [22, 23]. Bay N-annulated PTEs have been explored for their liquid crystallinity, however, this only includes alkyl chains of C6, C8, C10, and C12 on the ester positions [24, 25]. To the best of our knowledge, PTEN-H (figure 1) has not been reported as a semiconducting material nor for its alcohol processability.

Herein, PTEN-H is reported, and structural, electrochemical, optical, and electronic properties determined. Furthermore, the intermolecular interactions of PTEN-H in solution were probed via variable concentration/temperature $^1$H-NMR spectroscopy, while the solid-state morphology was elucidated via polarized optical microscopy (POM), atomic force microscopy (AFM), and powder x-ray diffraction (PXRD). The hole-only charge carrier mobilities of PTEN-H as a thin-film were obtained by solution casting the material as the active layer in a bottom-gate top-contact OFET device from 1-butanol. The hole mobilities for the PTEN-H material alone reached a maximum of $3.9 \times 10^{-4}$ cm$^2$ Vs$^{-1}$. In order to boost the mobilities of the OFET devices, PTEN-H was then blended with a 1-butanol/anisole soluble semiconducting polymer, IIG20-OH [26], which lead to an increase in the hole mobilities for not only the native PTEN-H molecule, but as well the native IIG20-OH polymer for a maximum hole mobility of $5.8 \times 10^{-4}$ cm Vs$^{-1}$.

2. PDIN-H vs. PTEN-H

Imides, being strong electron withdrawing groups, stabilize the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of PDIN-H, making it a suitable n-type semiconductor. However, OFET devices that use n-type OSCs suffer from poor stability and low charge carrier mobilities in comparison to those that use p-type OSCs. By altering the electron withdrawing group on the perylene core from imides to esters (weakly electron withdrawing), the PTEN-H material is then rendered as a suitable p-type semiconductor via destabilization of the HOMO and LUMO. Furthermore, the butyl ester groups on PTEN-H drastically changes the physical properties of the material when compared to PDIN-H, now rendering the material soluble in the green solvent 1-butanol without the need for additives. This section demonstrates the importance of molecular design to tune the electrochemical, optical, and physical properties of perylene based materials.

2.1. Synthesis

Previously, PDIN-H has been synthesized, characterized, and reported [18, 27–29]. The synthesis of PDIN-H has been optimized to afford PDIN-H on a multi-gram scale without the need for purification by column chromatography [30]. PTEN-H derivatives (esters with alkyl chains C6, C8, C10, and C12) have been previously synthesized [24, 25], however, a modified synthetic scheme was employed for this work (Scheme 1). First, the ring opening of perylene dianhydride (PDA) to make PTE was carried out according to the procedure by Sengupta et al [31]. Then, PTE was reacted with fuming nitric acid in dichloromethane (DCM) at room temperature to give NO$_2$-PTE. Finally, a Cadogan cyclization using triethylphosphite was performed to afford PTEN-H. The final PTEN-H product was purified via column
chromatography and recrystallization from ethanol; the structure and purity determined by $^1$H-NMR and $^{13}$C-NMR spectroscopy, mass spectrometry, and elemental analysis. See the Supporting Information for full synthetic and characterization details.

2.2. Electrochemical properties
PDIN-H and PTEN-H were probed for their electrochemical properties using solution cyclic voltammetry (CV; figure 2(b)) and differential pulse voltammetry (DPV; figure S10). The HOMO and LUMO were determined using the $E_{1/2}$ values with Fc/Fc$^+$ as the reference. PDIN-H exhibits two reversible reduction waves, while PTEN-H exhibits one reversible oxidation wave and two reversible reduction waves with a potential third present. For PDIN-H, as reported previously, the HOMO and LUMO energy levels were found to be $-5.8$ eV and $-3.6$ eV, respectively [27]. For PTEN-H, the HOMO and LUMO energy levels were found to be $-5.6$ eV and $-3.0$ eV, respectively. The destabilization of the HOMO and LUMO energy levels in PTEN-H relative to PDIN-H can be attributed to the replacement of the strong electron withdrawing imide groups with the weakly electron withdrawing alkyl ester groups.

2.3. Optical properties
The optical properties for PDIN-H and PTEN-H were obtained via UV-Visible spectroscopy (figure 3). PDIN-H exhibits an onset at 540 nm, which corresponds to 2.3 eV, while PTEN-H exhibits an onset at 486 nm, which corresponds to 2.6 eV. The difference between the band gaps of PDIN-H and PTEN-H thus being 0.3 eV with a visible hypsochromic shift when going from PDIN-H to PTEN-H (figure 3). The shape of the spectra is mostly retained when comparing PDIN-H to PTEN-H, which illustrates that the $0 \rightarrow 0$, $0 \rightarrow 1$, and $0 \rightarrow 2$ transitions are relatively unchanged due to their occurrence on the perylene core [17]. The molar extinction coefficient was calculated for PTEN-H to be 39 000 M$^{-1}$ cm$^{-1}$ at 460 nm (figures S11 and S12).

2.4. Green solvent processing
PDIN-H exhibits good solubility in greener solvents such as alcohols or water, however, a base is required as an additive to ionize the molecule (figure 4) [18]. PTEN-H exhibits solubility in common organic solvents such as tetrahydrofuran, chloroform, toluene, and o-xylene in concentrations >50 mg ml$^{-1}$, where ink formulations of 1–50 mg ml$^{-1}$ are suitable for thin film formation with a thickness of 10–500 nm.

Figure 2. (a) PDIN-H vs. PTEN-H; chemical structures and respective HOMO/LUMO energies determined from CV $E_{1/2}$ values and (b) corresponding CVs for PDIN-H and PTEN-H with $E_{1/2}$ values.
Figure 3. Normalized UV-visible spectra for PDIN-H and PTEN-H in a 1-butanol solution (concentrations are less than 1 mg ml$^{-1}$).

Figure 4. (a) PDIN-H solution processing schematic; deprotonation of PDIN-H via butylamine in 1-butanol (1:1 v/v) results in an ionic species that is soluble at 10 mg ml$^{-1}$. Pictured film (1.3 cm $\times$ 1.3 cm) was slot-die coated from a 10 mg ml$^{-1}$ solution in 1-butanol & butylamine (1:1 v/v). (b) UV–Visible absorption spectra of PDIN-H films made use slot-die and spin coating methods. (c) PTEN-H solution processing schematic; PTEN-H is soluble in 1-butanol at 10 mg ml$^{-1}$ with heating at 60 °C for 1 h. Pictured film is slot-die coated from a 10 mg ml$^{-1}$ solution in 1-butanol (1.3 cm $\times$ 1.3 cm). (d) UV–visible absorption spectra of PTEN-H films made use slot-die and spin coating methods.

which is required for most organic thin film technologies. PTEN-H can be solubilized in the greener solvent 1-butanol up to 10 mg ml$^{-1}$ upon heating at 60 °C for 1 h without the need of a basic additive (figure 4). Upon solubilizing a 10 mg ml$^{-1}$ PTEN-H solution in 1-butanol with heating, PTEN-H remains soluble at room temperature for one hour before the compound precipitates out. At 5 mg ml$^{-1}$ this 1-butanol/PTEN-H mixture remains soluble for several hours (~12 h) after heating. This allows PTEN-H to be coated from green ink formulations to form highly uniform thin films at room temperature. Film optical absorption spectra are shown in figures 4(b) and (d). Compared to solution the onset of optical absorption is red shifted, as expected due to aggregation in the film, while spin-coated films see the largest changes. AFM images (vide infra) reveal the spin-coated films of PTEN-H have a surface comprised of larger aggregates than those seen in the slot-die coated films.

3. PTEN-H characterization

3.1. Solution dynamics

Variable concentration $^1$H-NMR spectroscopic experiments were performed to probe the dominant intermolecular interactions for PTEN-H as with increased concentration the $^1$H-NMR proton resonances are expected to shift either upfield or downfield with increasing or decreasing electron density, respectively, and thus for $\pi$-conjugated molecules can help elucidate if strong $\pi$–$\pi$ interactions are present in solution [32–35]. Indeed, all aromatic resonances exhibit considerable shifts upfield with increased
concentration, with the most prominent shift being for the green-labelled proton environment (headland position opposing the pyrrole) for a shift of 0.15 ppm (figure 5). This can be attributed to increased \( \pi-\pi \) stacking and a subsequent increase in the ring-current effect [32–35]. This type of upfield shift in variable concentration \(^1\)H-NMR spectra is due to increased \( \pi-\pi \) stacking has also been observed in PDI-based materials [36]. Furthermore, strong aggregation is evident as the pyrrolic N-H resonance was expected to shift the peak downfield due to decreased electron density as a result from aggregation induced hydrogen bonding [37–39], however, the slight shift upfield for the N-H peak suggests the increased proximal ring-current from \( \pi-\pi \) stacking overcomes the deshielding effect of hydrogen bonding (figure 5).

To further elucidate the dominant intermolecular forces between PTEN-H molecules, variable temperature \(^1\)H-NMR spectroscopy was also performed with incremental heating from 20 °C to 120 °C (figure 6). Generally, variable temperature \(^1\)H-NMR spectroscopic experiments are either used to help resolve broadened peaks due to strong aggregation/low solubility or to probe temperature-dependent folding conformations or aggregations in proteins [40, 41]. In this case, incremental heating serves to reduce aggregates in solution which results in reduced intermolecular interactions. The variable temperature \(^1\)H-NMR spectroscopic experiment for PTEN-H shows a distinct upfield shift for the pyrrolic proton resonance (N-H), while all other aromatic resonances exhibit a shift downfield (figure 6). Furthermore, the aliphatic protons also exhibit a slight shift downfield (figure 6). The upfield shift for the N-H resonance can be attributed to increased electron density resulting from less hydrogen bonding [37–39], while all other aromatic resonances see a shift downfield as a result of decreased electron density, which can be attributed to a decrease in \( \pi-\pi \) stacking and subsequent ring current effects [32–35]. The shifting of the aliphatic proton peaks can be attributed inductive effects that pull electron density away from these environments due to the decrease in electron density at the core. These results suggest that the strong interactions between PTEN-H molecules in the form of \( \pi-\pi \) stacking is prevalent. In comparison to the variable concentration \(^1\)H-NMR spectroscopic experiment performed, the resonance shifts observed in the variable temperature \(^1\)H-NMR spectroscopic experiment are of greater magnitude for a maximum shift of 0.26 ppm, suggesting that an increase in temperature is effective at breaking up aggregates of PTEN-H in solution.

3.2. Film crystallization and surface topology
Since PTEN-H is soluble in 1-butanol up to 10 mg mL\(^{-1}\), it can be solution processed to make thin films via drop-casting, spin-coating, and slot-die coating methods. To determine the crystallinity of the drop-cast and spin-coated films, optical
microscopy (OM) and POM were used to image the films on a micron scale (figure 7). As seen in figure 7, both the drop-cast and spin-coated films exhibit crystallinity when observed with POM, in which crystals are illuminated blue, green, and yellow against the darkfield. When observing the drop-cast film, PTEN-H crystallizes into long needle-like strands resulting in areas of voids and a lack of uniformity. However, the spin-coated films are uniform and result in small crystalline domains that are illuminated green and blue under POM (figure 7). Furthermore, PXRD was performed for each of these films which resulted in amorphous scattering although with some definable diffraction peaks. The presence of these peaks simply provides evidence of crystallinity, a favourable characteristic for charge transport in OSCs [42]. Drop-cast films resulted in three distinct peaks: 5.8°2θ, which corresponds 15.1 Å, 8.1°2θ, which corresponds to 10.9 Å, and 16.1°2θ, which corresponds to 5.5 Å. However, in the spin-cast films only the 5.8°2θ and 8.1°2θ peaks were maintained.

To further probe the film uniformity and smoothness, OM and AFM were performed on slot-die coated and spin-cast films (figure 8). The slot-die coated films and spin-cast films were analysed for film uniformity and smoothness both visually and via the root-mean-square (RMS) values obtained by AFM (figure 8). The slot-die coated films exhibit uniformity while analysis with AFM reveals an RMS of 5.2 nm. For the spin-cast films OM reveals uniformity and AFM reveals that the crystalline domains present result in a rougher surface with an RMS value of 10.5 nm.
Figure 9. Structure of IIG20-OH and the bottom-gate top-contact OFET device data for PTEN-H, IIG20-OH, and the 1:1, 2:1, 4:1, and 6:1 blends of IIG20-OH to PTEN-H. Top right graph demonstrates the change in mobilities for the blends in relation to the IIG20-OH (1:0) and PTEN-H reference (0:1).

Table 1. OFET device data for IIG20-OH (reference), PTEN-H, and blends of IIG20-OH to PTEN-H in 1:1, 2:1, 4:1, and 6:1 ratios.

| Blend (IIG20-OH:PTEN-H) | annealing | Mobility $\mu_{av}$ $\mu_{max}$ ($10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$) | $V^H_{TH}$ | $I_{ON/OFF}$ |
|-------------------------|-----------|-------------------------------------------------|--------------|-------------|
| IIG20-OH (Ref.)         | 150 °C    | 1.08/1.22 ± 0.09                                 | −21.1        | $10^3$      |
| PTEN-H                  | 70 °C     | 0.39/0.45 ± 0.04                                 | −38.4        | $10^3$      |
| 1:1                     | 150 °C    | 0.52/0.64 ± 0.08                                 | −31.0        | $10^2$      |
| 2:1                     | 150 °C    | 1.49/2.44 ± 0.87                                 | −23.5        | $10^3$      |
| 4:1                     | 150 °C    | 4.15/5.58 ± 1.25                                 | −24.8        | $10^3$      |
| 6:1                     | 150 °C    | 1.41/1.69 ± 0.21                                 | −30.3        | $10^2$      |

*All devices were fabricated on OTS treated Si$^{++}$/SiO$_2$ wafers. The active material layer was solution processed and cast using spin-coating and ink solutions of the active material and 1-butanol 30% anisole, except for PTEN-H which was processed from 1-butanol. Gold electrodes deposited using physical vapour deposition.

4. Applications

4.1. OFET devices

Although analogues of PTEN-H have been probed for liquid crystalline properties [24, 25] we report, to the best of our knowledge, the first OFET devices that use molecular PTEN-H in the active material layer. Bottom-gate top-contact devices were fabricated using the solvent 1-butanol and tested in inert atmosphere [43]. A detailed experimental procedure can be found in the Supporting Information. Briefly, PTEN-H was solubilized in 1-butanol (10 mg ml$^{-1}$), and stirred for 1 h at 60 °C. The solution was then spin-cast onto a Si$^{++}$/SiO$_2$ wafer functionalized with an $n$-octadecyltrimethoxysilane (OTS) monolayer. The coated substrate was then annealed at 70°C for 30 min and gold electrodes were deposited using physical vapour deposition. These devices resulted in hole mobilities with a maximum of $0.39 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ and a threshold voltage of $-38.4$ V. Thus, PTEN-H was then blended with an alcohol-soluble semiconducting polymer to improve the mobility and reduce the threshold voltage. Previously, the blending of semiconducting molecular and polymer materials has been reported to demonstrate an increase of n-type, p-type, and ambipolar charge carrier mobilities compared to native molecular and polymer active materials in organic transistors due to migration of the materials and a subsequent increase in crystalline domains [44–48]. An isoindigo-based polymer with 20% incorporation of galactose pendant side chains (IIG20-OH; figure 9) was chosen due to previous reports of processability of the polymer in a blend of 1-butanol and o-anisole [26], a solvent system compatible with PTEN-H.

The small molecule and polymer were blended in ratios from 1:1 to 6:1 IIG20-OH:PTEN-H, keeping the mass of IIG20-OH consistent while varying the mass of PTEN-H. The resulting OFET performance of these blends is summarized in table 1. Device transfer and output curves can be found in Supporting Information (figures S14 and S15). In order to disrupt the $\pi-\pi$ aggregation of the conjugated polymer and favour the formation of good quality films, o-anisole was used as an additive (30% v/v) with 1-butanol to solubilize the blends for device fabrication. The solution was then stirred at 60 °C for 1 h and deposited onto OTS-treated Si$^{++}$/SiO$_2$ wafers using the same procedure as the PTEN-H devices. To optimize device performance, the blended films were tested after annealing at 70 °C, 100 °C and 150 °C, with the latter resulting in the best performance for all blends.

A 4:1 ratio of IIG20-OH to PTEN-H resulted in the highest hole mobility, while both greater and lesser ratios showed significantly decreased values. The 4:1 ratio demonstrated a maximum hole mobility...
of $5.58 \times 10^{-4}$ cm$^2$ V$^{-1}$, a four-fold increase compared to IIG20-OH and a nearly 13 times improvement compared to PTEN-H. The incorporation of IIG20-OH significantly decreased the threshold voltage of the devices, with the 2:1 and 4:1 blends both demonstrating comparable values to the previously reported IIG20-OH [26].

4.2. Towards large area film formation

To further demonstrate the versatility of these blends, PTEN-H & IIG20-OH in a 1:1 ratio was slot-die coated using a FOM Technologies Roll Coater from a 10 mg ml$^{-1}$ solution in 1-butanol with 30% anisole onto a PET substrate (figure 10). The coating of this blend on PET resulted in uniform thin films as observed by the eye and under optical microscopy, while AFM resulted in an RMS of 7.1 nm. The ability to slot-die coat these ink formulations onto plastic substrates, such as PET, is promising for the further development of flexible electronics using these materials. This proof-of-concept is important for the ultimate commercialization of these materials and devices, as it provides a viable means for large scale production methods.

5. Conclusion

In summary, the organic π-conjugated molecule PTEN-H was reported as a semiconducting material for the first time. PTEN-H bears four butyl ester substituents on the long axis of an N-annulated perylene core. In comparison to the known PDIN-H compound, the HOMO/LUMO energy levels are destabilized, and the compound is soluble in 1-butanol upon heating without the need for basic additives. Based on these properties and the ability to cast PTEN-H into thin films from 1-butanol, the compound was found to be a suitable hole transport material for green printed electronic OFET devices. The change from imide to ester groups did not prevent π–π interactions in solution as per the variable concentration/temperature $^1$H-NMR spectroscopy experiments, which showcases an ability for PTEN-H to retain aggregation behaviour similar to PDIs. Upon blending PTEN-H with an organic π-conjugated polymer, hole mobilities increased to greater than their neat film counterparts. This work opens a pathway for developing green solvent processable OSCs. As the field moves towards commercialization, it is critical that devices are made in a green manner. Owing to the p-type behaviour of the OFET devices there lies a great opportunity to use new p-type dopants to boost the transistors device performance.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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