Short communication

Facile synthesis of an indacenodithiophene-based conjugated polymer for acid vapor sensing

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A R T I C L E   I N F O
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Paper sensor

A B S T R A C T
The use of organic conjugated polymers in sensors has attracted greater attention due to their application in materials technology. In the present communication, we utilized Schiff’s condensation polymerization reaction for the synthesis of a novel conjugated polymer poly(tetrahexadecyl-dihydroidencindodithiophene)-alt-(p-phenylenedilimine) (PIDTPD) consisting of indacenodithiophene (IDT) and p-phenylene diamine (PDA) units for use in acid vapor sensing. Conventionally, the characteristics and applications of conjugated polymers are affected by their counterparts that form the main framework and backbone of the polymers [4,5]. In addition, the functionalities, linkages, and bonds found within these macromolecules are considered very important because they form key receptor sites when they are employed as actuators and chemical and biochemical sensors [6].

Conjugated polymers with imine linkage chemistry have recently been employed in a diverse range of applications in numerous fields [7], including in solar cells and organic electronic devices [8–10]. This class of materials has also been observed to demonstrate acid sensory properties. The weak non-covalent van der Waals interactions between the hydrogen in the imine functionality and analytes offer a unique acid–base chemistry, which enables these moieties to be used as a pH sensor [2,7,11,12]. Thus, the lone pair of electrons on the nitrogen atom of imine bonds in these moieties acts as a functional determining site. Acid-vapor and polymer interaction results in the protonation of the above-mentioned linkage sites. This generally renders a red shifting of material absorption band, thereby administering a change in color, hence enabling analyte determination. However, most of the conjugated polymers used in these applications have complicated structures and functionalities, and simple conjugated polymers have rarely been exploited for such applications.

In the present study, we present a research on the preparation, optoelectronic analysis, and acid vapor sensing properties of the π-conjugated polymer poly(tetrahexadecyl-dihydroidencindodithiophene)-alt-(p-phenylenedilimine) (PIDTPD), which consists of indaceno[1,2-b:5,6-b’]dithiophene and p-phenylene diamine units combined using Schiff’s condensation polymerization. The polymer was characterized using absorption spectra, cyclic voltammetry (CV), X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), and electrochemical impedance spectroscopy (EIS) analysis. We

1. Introduction

Conjugated polymers with an π-electron system composed primarily of networks of single or double C–C bonds have attracted immense interest in several research areas due to intrinsic properties that make them particularly suitable for use in a variety of applications [1–3]. A number of their characteristics, including their transition and electrical conductive properties, which are highly tunable and mainly dependent on the counterparts that form the main framework and backbone of the polymers [4,5]. In addition, the functionalities, linkages, and bonds found within these macromolecules are considered very important because they form key receptor sites when they are employed as actuators and chemical and biochemical sensors [6].

Conjugated polymers with imine linkage chemistry have recently been employed in a diverse range of applications in numerous fields [7], including in solar cells and organic electronic devices [8–10]. This class of materials has also been observed to demonstrate acid sensory properties. The weak non-covalent van der Waals interactions between the hydrogen in the imine functionality and analytes offer a unique acid–base chemistry, which enables these moieties to be used as a pH sensor [2,7,11,12]. Thus, the lone pair of electrons on the nitrogen atom of imine bonds in these moieties acts as a functional determining site. Acid-vapor and polymer interaction results in the protonation of the above-mentioned linkage sites. This generally renders a red shifting of material absorption band, thereby administering a change in color, hence enabling analyte determination. However, most of the conjugated polymers used in these applications have complicated structures and functionalities, and simple conjugated polymers have rarely been exploited for such applications.

In the present study, we present a research on the preparation, optoelectronic analysis, and acid vapor sensing properties of the π-conjugated polymer poly(tetrahexadecyl-dihydroidencindodithiophene)-alt-(p-phenylenedilimine) (PIDTPD), which consists of indaceno[1,2-b:5,6-b’]dithiophene and p-phenylene diamine units combined using Schiff’s condensation polymerization. The polymer was characterized using absorption spectra, cyclic voltammetry (CV), X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), and electrochemical impedance spectroscopy (EIS) analysis. We
demonstrated that protonation via acidochromism occurs by reducing the bandgap from 2.22 to 1.72 eV. We also employed the polymer-based material in a paper sensor, leading to a significant detection of change.

2. Experimental

2.1. Materials and methods

Indacenodithiophene, bromohexadecane, toluene, sodium hydroxide, tetrabutyl ammonium bromide (TBAB), diethyl ether, n-ButLi (2.5 M), dry dimethylformamide (DMF), p-phenylenediamine, p-toluenesulfonic acid (PTSA), anhydrous CaCl₂, dry K₂CO₃, and high purity solvents were purchased from Sigma Aldrich and used without further purification.

2.2. Characterization

Thin layer chromatography (TLC) was performed on silica gel plates precoated with a fluorescent indicator. Standardized silica gel was used for column chromatography purifications. Mixtures of eluent are given in v/v ratio. The synthesized compounds were characterized with ¹H NMR and ¹³C NMR spectroscopy using a Bruker 300 MHz nuclear magnetic resonance (NMR) spectrometer. Commercial NMR solvents obtained from Aldrich with TMS as internal standard were used, and chemical shifts were measured in δ ppm scale. The number and weight average molecular weights of the polymers were determined by gel permeation chromatography (GPC; Viscotek) equipped with a TDA-302 detector and a PL-gel (Varian) column, using chloroform as the eluent (Table 1). The PIDTPD obtained after purification was characterized and found: C, 80.72; H, 11.34; O, 2.58; S, 5.21.

2.3. Synthesis of tetrahexadecyl-dihydroindacenodithiophene dicarbaldheyde (3)

In a Schlenk tube (100 mL), Compound 3 (200 mg, 0.16 mmol), p-phenylenediamine (19 mg, 0.16 mmol), p-toluenesulfonic acid (PTSA) (3.4 mg, 0.008 mmol, 5 mol%), anhydrous CaCl₂ (200 mg), and anhydrous toluene (50 mL) were mixed in a nitrogen atmosphere. The tube was then sealed in a nitrogen atmosphere. The mixture was allowed to warm up to room temperature and was then stirred for 48 h. The mixture was then filtered through a nylon filter and washed with toluene to remove the drying agent and any insoluble salts. After removing the solvent in a vacuum, the polymer was collected as a red solid (150 mg, yield 71%).

3. Result and discussion

3.1. Synthesis of PIDTPD

The synthesis of the monomer and polymer is illustrated in Fig. 1. In the first step, 4,9-dihydro-s-indacen [1,2-b:5,6-b']dithiophene (1) was functionalized with a hexadecane alkyl chain with a biphatic reaction using sodium hydroxide base, TBAB as a catalyst, and 1-bromohexadecane as an alkylation agent to obtain 4,4,9,9-tetrahexadecyl-4,9-dihydro-s-indacen [1,2-b:5,6-b']dithiophene (2). In the second step, Compound 2 was formylated using n-ButLi/DMF at -78 °C to obtain tetrahexadecyl-dihydroindacenodithiophenedicarbaldheyde (3). Finally, polymerization was carried out in a Schlenk tube using Compound 3 and p-phenylene diamine. P-toluene sulfonic acid was used as a catalyst and CaCl₂ as an internal dehydrating agent, while the mixture was refluxed at 110 °C for 48 h. The reaction mass was then filtered through a nylon filter. The solvent from the filtrate was removed in vacuum to obtain the red solid. After isolating the product, the material was subjected to gel permeation chromatography (GPC) analysis and Mn, Mw, and PDI were determined (Table 1). The PIDTPD obtained after purification was characterized and employed in acid vapor sensing. All of the intermediates and final products were characterized using spectral techniques.

2.3.2. Synthesis of tetrahexadecyl-dihydroindacenodithiophene dicarbaldheyde (3)

Compound 2 (500 mg, 0.75 mmol) and ethyl ether (10 mL) were added to a 50-mL round-bottomed flask in an argon atmosphere. n-BuLi (2.5 M, 0.8 mL, 1.9 mmol) was added at -78 °C. After stirring at -78 °C for 30 min, dry DMF (1.1 mL, 2.6 mmol) was added dropwise at -78 °C. The mixture was allowed to warm up to room temperature and was then stirred for 1 h. The mixture was then quenched with HCl (20 mL, 1 M aqueous solution). The aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined extracts were washed with distilled water and dried over anhydrous Na₂SO₄. After removal of the solvents under reduced pressure, the residue was purified via chromatography with silica (eluent: hexane/dichloromethane = 4/1 to 1/1) to afford an off-white solid product. The yield was 390 mg (75%). ¹H NMR (CDCl₃, 300 MHz, δ (ppm)): 9.84 (s, 2H), 7.84 (s, 2H), 7.48 (d, 2H), 1.87 (t, 8H), 1.26–1.31 (m, 112 H), 0.87–0.90 (t, 12H); ¹³C NMR (CDCl₃, 100 MHz, δ (ppm)): 182.5, 141.6, 136.2, 133.8, 133.4, 129.7, 126.2, 125.5, 53.8, 44.7, 31.8, 30.4, 29.8, 29.5, 24.6, 22.8, and 14.1. Elemental analysis calculated: C, 80.70; H, 11.34; O, 2.58; S, 5.21.

2.3.3. Synthesis of poly(tetrahexadecyl-dihydroindacenodithiophene)-alt-(p-phenyleneedimine) (PIDTPD)

The synthesis of the monomer and polymer is illustrated in Fig. 1. In the first step, 4,9-dihydro-s-indacen [1,2-b:5,6-b']dithiophene (2) was functionalized with a hexadecane alkyl chain with a biphatic reaction using sodium hydroxide base, TBAB as a catalyst, and 1-bromohexadecane as an alkylation agent to obtain 4,4,9,9-tetrahexadecyl-4,9-dihydro-s-indacen [1,2-b:5,6-b']dithiophene (2). In the second step, Compound 2 was formylated using n-ButLi/DMF at -78 °C to obtain tetrahexadecyl-dihydroindacenodithiophenedicarbaldheyde (3). Finally, polymerization was carried out in a Schlenk tube using Compound 3 and p-phenylene diamine. P-toluene sulfonic acid was used as a catalyst and CaCl₂ as an internal dehydrating agent, while the mixture was refluxed at 110 °C for 48 h. The reaction mass was then filtered through a nylon filter. The solvent from the filtrate was removed in vacuum to obtain the red solid. After isolating the product, the material was subjected to gel permeation chromatography (GPC) analysis and Mn, Mw, and PDI were determined (Table 1). The PIDTPD obtained after purification was characterized and employed in acid vapor sensing. All of the intermediates and final products were characterized using spectral techniques.
3.2. Optical properties

The UV–Vis spectra of the copolymer in chloroform solution and thin film is presented in Fig. 2a. The absorption spectra of polymer in solution and on treating with HCl is illustrated in Fig. 2b and the corresponding absorption properties are summarized in Table 2. The absorption maximum ($\lambda_{\text{max}}$) of the PIDTPD solution before exposing to acid vapor was observed at ~500 nm, while $\lambda_{\text{onset}}$ was at ~560 nm. After exposing the solution to the acid vapor, $\lambda_{\text{max}}$ shifted to ~650 nm and $\lambda_{\text{onset}}$ was observed at ~720 nm. The absorption maximum ($\lambda_{\text{max}}$) of the polymer on filter paper (Fig. 2c), was 550 nm, while $\lambda_{\text{onset}}$ was at 590 nm. After exposure to the acid vapor, the $\lambda_{\text{max}}$ of the polymer shifted to ~552 nm, and $\lambda_{\text{onset}}$ was at 700 nm. The absorption spectra displayed an absorption band that is characteristic of the push-pull units along the polymer backbone introduced by the polymer via intramolecular charge transfer (ICT) [13]. The optical bandgap for the polymer in solution and on treating with HCl was estimated from the absorption edge to be 2.22 eV and 1.72 eV, respectively. Tough plot was employed to calculate the bandgap of the polymer (Fig. 2d). The PIDTPD polymer solution in CHCl₃ changed color from red to dark blue with the addition of HCl. The energy levels for the PIDTPD were also determined via DFT using DMol3 software (Fig. 3). PIDTPD exhibited a dipole moment of 3.1 D (Table 3) and highest occupied molecular orbital (HOMO) energy levels at ~4.9 eV. The lone pairs on the nitrogen atoms in imine bond (C–N) can be transferred to dihydroindacenodithiophene (IDT) which is commonly known as ICT (Fig. S2). This phenomenon increases the bandgap (2.22 eV) of the pristine polymer. We have also tried to verify the bandgap by DFT calculation using one unit. As we have determined the parameters for one repeating unit, there is a small difference between the experimental and theoretical bandgap (3.01 eV). In acidic condition, these lone pair of electrons are blocked by H⁺ ions. Eventually ICT phenomenon is turned off in protonated PIDTPD polymer, inducing the lower bandgap (1.72 eV). There is a strong correlation between the energy levels of the PIDTPD determined by experimental and theoretical analysis [14].

3.3. Surface analysis

The size, shape, and surface morphology of the prepared PIDTPD was investigated using field emission SEM (FE-SEM). Fig. 4a and b shows representative FE-SEM images of the PIDTPD, which exhibited variously sized spherical nanoparticles. In particular, the small spherical nanoparticles (30–35 nm) formed agglomerates on top of the larger nanoparticles (c.a. 147 nm) with a porous morphology. The porous structure of the PIDTPD can enhance the charge accumulation at the interface of the material, which can lead to an increase in its chemical capacitance, enhancing its usefulness in the gas-sensing process [15]. When the surface topology of the polymer film was probed using atomic force microscopy (AFM), a similar trend was observed, with irregularly packed crystallites producing a large surface area for enhanced interaction (RMS 4.476 nm) as observed in Fig. 4c and d, when XRD was employed to examine the crystallinity of the polymer, no discerning peaks were identified, indicating the presence of an amorphous microstructure (Fig. S1). This is in agreement with the crystal orientation of IDT-based polymers [16,17].

3.4. Electrochemical properties of the polymer

3.4.1. Cyclic voltammetry (CV)

The oxidation reduction potential of the prepared PIDTPD was characterized using CV in a three-electrode system at a scan rate of 50 mV/s. PIDTPD-coated glassy carbon was used as the working electrode, Ag/AgCl as the reference electrode, and platinum wire as the counter electrode in an acetonitrile solution containing 10 mM of LiI, 1 mM of I₂, and 0.01 M of LiClO₄ as the supporting electrolyte. Fig. 5a shows a pair of oxidation and reduction peaks with an oxidation onset potential of 0.288 V and the corresponding reduction peak at 0.221 V. The peak-to-peak separation and peak current density indicate the better reversibility of the redox reaction. The HOMO level ($E_{\text{HOMO}}$) of the prepared PIDTPD was estimated from the oxidation onset potential ($E_{\text{ox}}$) using the following equation:

$$E_{\text{HOMO}} = E_{\text{ox}} - 4.4 $$

Table 1

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_0$ [kg/mol]</th>
<th>$M_w$ [kg/mol]</th>
<th>PDI</th>
<th>Yield [%]</th>
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<tbody>
<tr>
<td>PIDTPD</td>
<td>17.1</td>
<td>29.2</td>
<td>1.7</td>
<td>71</td>
</tr>
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</table>

* Molecular weights were determined using gel permeation chromatography (GPC) against polystyrene standards in chloroform as an eluent.

**Fig. 1.** Scheme for the synthesis of monomer and polymer.
HOMO = (E_{ox} − E_{fc} + 4.8) (eV)

where E_{fc} is the potential of the reference redox reaction (E_{fc}/E_{fc}^{+} = 0.25 eV). The HOMO level of PIDTPD was estimated to be −4.84 eV, with the lowest unoccupied molecular orbital (LUMO) level calculated to be −2.62 eV using E_{LUMO} = E_{LUMO} - E_{HOMO}.

3.4.2. Conductivity plot (I–V curve)

Fig. 5b presents the I–V curve for the PIDTPD measured in the dark. The analysis was conducted using a two-electrode device with a Keithley voltage source meter (2400 pico ammeter) by sandwiching the PIDTPD between the FTO substrate. The linear I–V response to the applied voltage affirmed the ohmic behavior of the sample. The conductivity of the PIDTPD was calculated from the linear fit using the formula (σ = l/RA). Here, σ is the conductivity of the sample, R represents the resistance based on the slope of the linear fit, A is the area of coated material on the FTO (0.16 cm²), and l is the thickness of the PIDTPD thin film (9.62 μm). From the linear fit of the I–V curve, the conductivity of the PIDTPD was calculated to be 0.49987 mS/cm.

3.4.3. EIS-Nyquist and bode phase plots

Fig. 5c presents the EIS-Nyquist plot for the PIDTPD material, showing two semicircles for an applied open circuit potential of 50 mV at room temperature. Measurements were taken using a three-electrode system by varying the frequency of the applied potential from 1 MHz to 0.1 Hz. Two charge transport resistances were identified in the system, with the high-frequency semicircle arising from charge transport resistance (R_{ct1}) at the electrolyte/PIDTPD material interface and the mid-frequency semicircle attributed to electron transport resistance (R_{ct2}) at the interface of the PIDTPD grain interior. The presence of two semicircles was also indicated by the two-phase angle shift in the Bode phase plot (Fig. 5d) [18]. The inset of Fig. 5c shows an enlarged view of the high-frequency semicircle and the corresponding equivalent circuit model used for fitting. The high-frequency intercept on the real axis of impedance provides the series resistance, which was found to be R_{s} =

Table 2
Optical and electrochemical properties of PIDTPD.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>λ_{max}^a (Sol) (nm)</th>
<th>λ_{max}^b (Paper)(nm)</th>
<th>E_{g}^{opt,c} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIDTPD</td>
<td>500</td>
<td>550</td>
<td>2.22</td>
</tr>
<tr>
<td>PIDTPD + HCl</td>
<td>650</td>
<td>552</td>
<td>1.72</td>
</tr>
</tbody>
</table>

^a Measured in CHCl₃ solution.

^b Coated on filter paper.

^c Determined from the equation 1240/λ_{onset}.

Fig. 2. UV–Vis spectra of (a) PIDTPD in CHCl₃ solution and in thin film state (b) PIDTPD in CHCl₃ solution and with HCl (c) PIDTPD on filter paper and with HCl (d) Bandgap plot for PIDTPD and for PIDTPD with HCl (Inset: Images of PIDTPD in CHCl₃ and with the addition of HCl.).
It was eminent from Table 4 that the charge transport resistance ($R_{ct1} = 0.599 \Omega$) between the electrolyte/PIDTPD interface was very low owing to the high planarity of the $\pi$-$\pi$ conjugation in the PIDTPD structure. In the grain interior, the charge transportation was quite low due to the increased grain growth originating from the agglomeration of small particles on top of the large spherical particles. This increases the charge transport distance and the electron transport resistance in the grains. The high planarity of the $\pi$-$\pi$ conjugation in the PIDTPD structure was also used to enhance the chemical capacitance, which facilitates its use in sensor devices [19].

3.5. Mechanisms of acid sensing

The absorption band for the PIDTPD solution in CHCl$_3$ was observed at 250–550 nm. The color of the solution changed from red to dark blue.

**Table 3**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>HOMO$^a$ (eV)</th>
<th>LUMO$^b$ (eV)</th>
<th>$E_{opt}^{\text{HOMO}}$ (eV)</th>
<th>Dipole Moment (D)$^d$</th>
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<tbody>
<tr>
<td>PIDTPD</td>
<td>−4.84</td>
<td>−2.62</td>
<td>2.22</td>
<td>3.10</td>
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</tbody>
</table>

$^a$ The HOMO level of the polymer was determined from the onset voltage of the first oxidation potential with reference to ferrocene at $−4.8$ eV.

$^b$ The LUMO level of the polymer was estimated from the optical bandgap and the HOMO energy level.

$^c$ The optical bandgap was calculated from the UV–Vis absorption onset in the film.

$^d$ Calculated using DFT.
due to the appearance of the protonation-driven band at 450–720 nm. Pristine PIDTPD is red and its color changes after the addition of a small quantity of acid [20]. Based on our preliminary interpretation, we explored PIDTPD for use in a paper acid vapor sensor. Filter paper coated with the PIDTPD/CHCl₃ solution was placed in a chamber containing HCl vapor. The reversibility of the PIDTPD-coated sensor was confirmed by treating it with triethylamine vapor [21]. The change in the spectra from a lower to higher wavelength was mainly due to the protonation of one proton (light blue color) followed by two protons (dark blue) in the PIDTPD [6,22,23]. This stepwise protonation and the mechanisms of acid sensing are illustrated in Fig. 6. This study clearly supports the use of the polymer as an acid sensor, with the PIDTPD film changing from red to blue following exposure to acid vapor. The film turned red again following exposure to triethylamine vapor (Supporting Information). Thus, the PIDTPD exhibited sensing properties in solution, on paper, and as a thin film, illustrating its wide applicability on different substrates. The sensing of acid vapor based on deprotonation, mono-protonation, and bis-protonation is summarized in Table 5.

4. Conclusion

In summary, we successfully synthesized and characterized the novel conjugated polymer poly(indacenodithiophene)-alt-(p-phenylenediamine) (PIDTPD) by combining indacenodithiophene and p-phenylene diamine building units using Schiff’s condensation polymerization and employed it in an acid vapor sensor. The polymer exhibited photophysical properties that identified it as a promising candidate for use in sensor applications. As a proof of the concept, we utilized the polymer in acid vapor sensing application. The material exhibited the protonation induced color shift towards the longer wavelength region via acido-chromism. Color change is mainly attributed to the reduction of band gap from 2.22 eV to 1.72 eV, during protonation of nitrogen atom in the imine bond of the polymer. Further experimental research is currently underway in our laboratory to explore the acid vapor sensor concept to other classes of imine-based conjugated polymers.

Author statement

Chinna Bathula: Conceptualization, methodology, Writing - Original Draft; Opoku Henry: Formal analysis; Ashok Kumar K: Experimental; Subhalakshmi K: Data Curation; Atanu Jana: Formal analysis; Iqra
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2020.108847.

Table 5

<table>
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<th>Sl No</th>
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<th>Structure</th>
<th>Color</th>
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<td>2</td>
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References


