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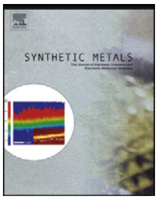

Physical, optical, electronic properties and mobility measurements of a new donor–acceptor–donor oligomer

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ABSTRACT

A new organic compound (tertmethoxy di-triphenylamine di-thiophene-benzothiadiazole; DTBT-DTPA-TMeO) recently synthesized displays two strong absorption peaks in the visible range of the solar spectrum. Thermal behavior of this new donor–acceptor–donor (D–A–D) oligomer is investigated by differential scanning calorimetry and thermogravimetric analysis. The decomposition temperature is found to be at about 400 °C and a smectic mesophase transition at about 115 °C (crystal liquid–crystal transition). Solution and solution processed films onto ITO and ITO/MoO_3 are characterized by UV–Vis, AFM and XPS-UPS measurements. An optical band gap of 1.85 eV is reported from the UV–Vis data and agrees well with the theoretical value of 1.99 eV. AFM analysis of spin coated films shows smooth uniform coverage free of pin holes. Work functions and HOMO energy values are determined from UPS measurements and allow the construction of an energy band diagram. The hole mobility for a un-annealed single diode device is measured at about 10^{-5} cm^2/Vs.

1. Introduction

New kinds of semiconducting organic materials have been synthesized in response to the need for improved optical and electronic properties in the field of organic electronic devices. The demand for broadband absorption, lower band gap (~1.5 eV), thermal stability and ease of fabrication drives researchers to continuously synthesize new organic materials. The use of new π-conjugated compounds with new properties can be utilized to improve performance in organic light emitting diodes (OLED), field effect transistors (OFET) and photovoltaics (OPV). An archetypal organic bulk heterojunction (BHJ) is a P3HT:PCBM blend with reported efficiency as high as 5% [1–3]. New emerging copolymers referred to donor–acceptor–donor (D–A–D) or acceptor–donor–acceptor (A–D–A) oligomers are of interest because donor and acceptor moieties can be manipulated by simply controlling the numbers of donor and acceptor moieties within the repeat unit. As a result, the electronic structure and crystallinity as well as the optical properties are highly tunable. For instance, Haake et al. [4] studied a newly synthesized D–A–D copolymer made of an extended siloxane chains by ultrafast laser spectroscopy. They found that charge transfer occurred between HOMO donor and HOMO acceptor at a time scale of a few ps. Inganas et al. [5] synthesized and investigated the opto-electronic device performance of a new conjugated PF copolymer (poly[2,7-(9,9-dioctylfluoren)-*alt*-5,5-(5′,8′-di-2-thienyl-(2′,3′-bis-(3′′-octyloxyphenyl)-quinoxaline))], APFO-15) with efficiency of 3.7% when blended with PCBM as active layer. Chen and coworkers [6] synthesized new D–A molecules composed of carbazole moieties (donor group) and a benzothiadiazole or anthracene moiety (acceptor group). They investigated D–A interaction by optical absorption, emission spectroscopy and electrochemistry. They show that HOMO–LUMO gaps of the molecules can be tuned in a controlled way by manipulating each moiety of the D–A molecules. Reynolds and co-workers [7] studied the effect of increasing donor strength starting with pure acceptor (PCA) through pure donor (PEDOT) for a series of six D–A–D monomers. Their findings indicate values of band gaps ranging from 1.6 to 1.1 eV as the donor strength is increased and that the HOMO energy level can be altered on doping while the LUMO energy level remained relatively constant. Recently, Wong and coworkers [8] investigated a new donor–acceptor molecule with a central π-bridge (TPDCDTS) that contained a π-conjugated spacer (diphenyl-substituted dithienosilole) between triphenylamine (donor) and dicyanovinylene (acceptor). They found that the bridge facilitated electronic coupling between the donor and the acceptor moieties and extended the spectral response of the molecule to the red portion of the solar spectrum. As of today only a limited number of studies on D–A–D and A–D–A compounds have

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been reported. The focus of most of these early studies is on the synthesis and spectral characterizations and less on their electrical and physical properties in the solid state.

In this paper, we report for the first time thermal, physical, electrical properties, charge carrier mobility measurements of a newly synthesized oligomer [9] composed of three moieties; a benzothiadiazole core (electron accepting-group), and two (dimethoxy) thiophene-triphenylamine groups (electron donating-group) moieties referred to at DTBT-DTPA-TMeO ((dithiophene)benzothiadiazole-di(triphenylamine)-tertmethoxy) in a solid state configuration (powder and film). Thermal analysis (DSC and TGA) are used to investigate the thermal stability of this oligomer (DTBT-DTPA-TMeO). Atomic force microscopy (AFM) provides information on morphology and quality of thin films solution processed onto ITO. Spectroscopic information given by X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) allow the construction of an energy band diagram that positions the HOMO and LUMO energy levels with respect to vacuum level of ITO and ITO/MoO_3. Finally, a single carrier type diodes were constructed to estimate an initial hole mobility (μ_0) of a un-annealed solution processed film.

2. Experimental

The synthesis of this new oligomer is described in details elsewhere [9]. The powder sample was used as received for all measurements shown in this study. Polished float glass 25 mm × 25 mm × 1.1 mm ITO was purchased from Delta Technologies, Limited with $Rs = 15–25\,\Omega$ and cut to 10 mm × 10 mm pieces to be coated with DTBT-DTPA-TMeO films and MoO_3. ITO substrates were cleaned by ultrasonication in detergent, deionized water and acetone, boiled in isopropyl alcohol followed by blow drying with nitrogen gas. The ITO was not ultraviolet-ozone treated.

The diode devices were prepared using the oligomer dissolved in chloroform and spin cast on a thin layer of MoO_3 (~5 nm) vapor deposited (~10^{-6} Torr) on ITO. The thickness of the polymeric film was about 200 nm and the negative Au top electrode (~0.96 mm in diameter) was about 80 nm thick.

Perkin-Elmer DSC 7 and TGA 7 were used to perform thermal analyses. The typical mass of DTBT-DTPA-TMeO used for DSC runs was ~3–3.5 mg. The scans were performed from 50 to 320 °C at rate of 5 °C/min. The thermal stability of DTBT-DTPA-TMeO was studied by TGA under ambient conditions and heating rate of 10 °C/min. The typical mass used was 3 mg.

The absorption spectra of the material were measured in chloroform solution (~10^{-5} M) and for films spin coated on ITO with a Perkin-Elmer UV–Vis 320 spectrometer ran at room temperature.

The surface of bare ITO, un-annealed and annealed DTBT-DTPA-TMeO films was imaged by AFM to study the morphology, microstructure and quality of the deposited films. The chloroform solution (5 mg/mL) was spin coated onto ITO at 2000 RPMs for 120 s. The AFM images were obtained with a Digital Instruments Nanoscope IIIa microscope and analyzed using commercial software from ImageMetrology A/S (SPIP) scanning probe imaging processor. The images were acquired in tapping mode and only processed with a plane correction (quality optimized) and 5 × 1 median filter with horizontal directional noise (high and low values).

XPS and UPS measurements were performed on a Kratos AXIS-165 multi-technique electron spectrometer system with a base pressure of 8×10^{-10} Torr. Monochromatic X-ray radiation of 1487.6 eV (AlKα) was utilized as the XPS excitation source for acquiring the XPS photoelectron spectra. The binding energies were calibrated against the $Au4f_{7/2}$ peak taken to be located at 84 eV and Ag $3d_{5/2}$ peak at 368.3 eV. Powder DTBT-DTPA-TMeO samples were pressed against 99.99% pure indium flattened shots (Alfa Aesar) prior to placing the samples in the vacuum chamber. The same films used for optical measurements were analyzed by XPS and UPS. The samples were grounded with metal clips to minimize any possible charging effect which was tested by switching the neutralizer on and off. No sample charging was detected.

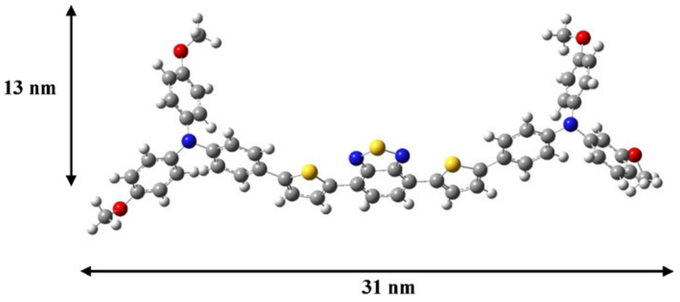

Fig. 1. Ball and bond model of DTBT-DTPA-TMeO.

UPS data on the films were collected with a homemade He lamp source which produces a resonance line He I (21.21 eV) by cold cathode capillary discharge. The spectra were acquired using a hybrid lens that focused the ejected electrons into the Kratos spectrometer. A bias of −20 V was applied to the sample to shift the spectra out of the nonlinear region of the analyzer (0–10 eV kinetic energy). The calibration and energy resolution was determined at the Fermi edge of a clean Ag foil to be better than 150 meV at BE = 0 eV.

3. Results and discussions

Fig. 1 displays a ball & bond type model of the synthesized new compound. The dimensions of DTBT-DTPA-TMeO are approximately 31 nm × 13 nm across. The thermal stability of this molecule was investigated by DSC and TGA and reveals a crystalline to smectic A transition at $T \sim 115\,^{\circ}C$ and a melting temperature at about 235 °C as shown in Fig. 2. The corresponding enthalpies for the transition and melting states are −17 J/g and 15 J/g, respectively. In their study of α,α′-didecyloligothiophenes, Kirchmeyer et al. [10] showed that similar compounds to DTBT-DTPA-TMeO not only have crystal phases but also possess high temperature ordered smectic mesophases (crystal to liquid–crystal transitions). The high transition, melting and decomposition (~400 °C) temperatures

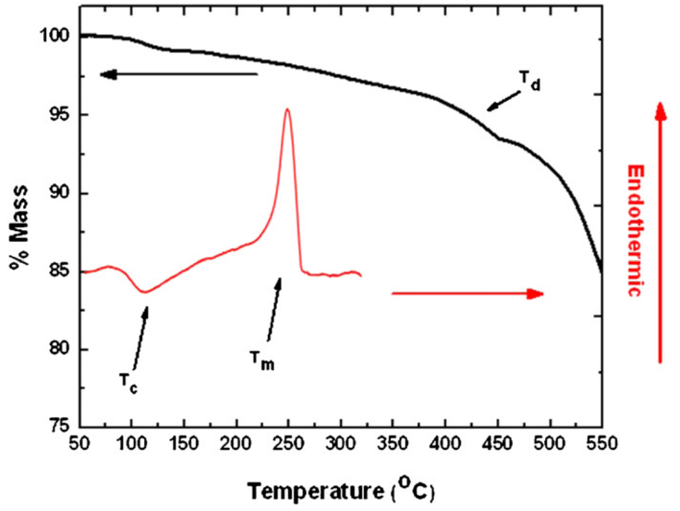

Fig. 2. DSC (red curve) shows the transition (115 °C) and melting (235 °C) temperatures and TGA (black curve) displays the decomposition temperature (400 °C). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

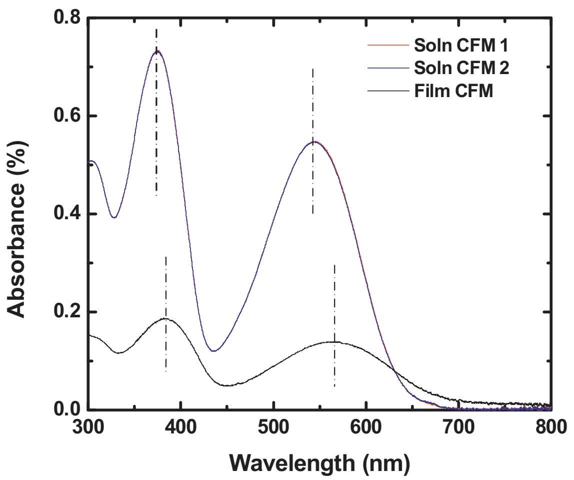

Fig. 3. Absorbance spectra measured in chloroform solution and film solution processes onto clean ITO substrate. Two strong absorbance peaks at 375 and 544 nm were measured in solution. The corresponding peaks were red shifted in the film to 384 and 566 nm, respectively.

which was estimated at the 5% mass loss by TGA for DTBT-DTPA-TMeO indicate a good thermal stability of this compound. A property that is highly desirable for electronic applications such as in organic photovoltaic devices and device fabrication by thermal vacuum deposition.

The absorption spectra for chloroform solution and pure DTBT-DTPA-TMeO solution processed film onto ITO are shown in Fig. 3. Both solution and film spectra display strong absorption at wavelength of 375 and 544 nm (solution) and at 384 and 566 nm (film). A red shift of 9 nm and 22 nm was measured for these two absorption bands between film and solution. The shift can be explained by (1) a higher electron accepting strength of the oligomer (central unit, the benzothiadiazole moiety) in the solid state than in liquid phase resulting in higher partial charge transfer in the film than in solution, and (2) molecules interaction in the film due to the stacking arrangement that does not exist in solution. We tentatively attribute the band at 384 nm (blue) to a delocalized excitonic π–π^* transition and the band at 566 nm (red) to a localized transition between the D–A–D charge transfer states. This was previously reported by Jespersen et al. [11] and more recently by Gadisa et al. [5]. Both groups investigated similar but different polyfluorene copolymers with D–A–D moieties.

The optical band gap of DTBT-DTPA-TMeO determined at the low energy absorption band is 1.85 eV which is in good agreement with the theoretical value of 1.99 eV [9]. The low optical band gap and the strong absorbance of this compound in the visible region of the solar spectrum in addition of its thermal stability make it a promising light harvesting material for solar cell applications.

Fig. 4 displays 50 μm × 50 μm 3-D AFM micrographs of (a) bare ITO, (b) a 40 nm thick film solution processed of pure DTBT-DTPA-TMeO onto ITO in ambient conditions and (c) after annealing at 75 °C for 1 h. This annealing temperature was chosen to be lower than the smectic A transition temperature of 115 °C in order to avoid in this initial work the liquid–crystal phase and a change in the physical state of the film. The AFM images reveal a good quality film with a uniform coverage free of pin holes and features much larger than the thickness of the film. The average roughness, R_a, for the bare ITO surface is 0.3 nm. The relatively smooth surface imaged for the un-annealed film displays a roughness, $R_a = 6.9$ nm. Upon annealing for one hour a small change in morphology was seen with a slightly lower value of the average roughness, $R_a = 4.1$ nm. No other significant changes were observed upon annealing of this material at 75 °C for 1 h (see Fig. 4b and c). The good quality of the produced films ensures an optimized charge carrier mobility which is one of the limiting factors for high efficiency in conjugated polymer-based PV devices.

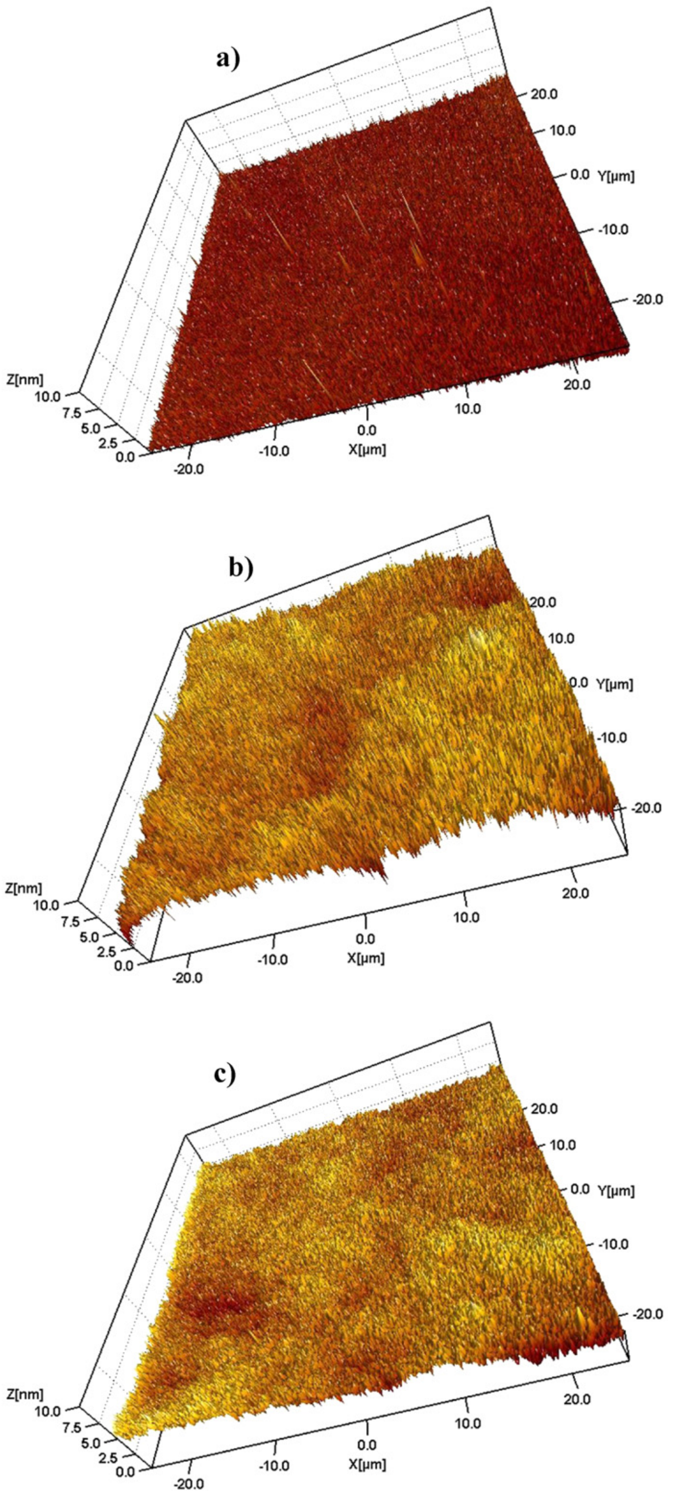

Fig. 4. 3-D AFM micrographs of (a) bare clean ITO, (b) an un-annealed 40 nm DTBT-DTPA-TMeO film solution processed on ITO and (c) annealed to 75 °C for 1 h.

XPS analysis performed on both powder and film displays only peaks associated with the characteristic elements of the compound, mainly S 2p, C 1s, N 1s and O 1s as displayed in Fig. 5. A relative quantification of these elements shows a very good agreement with theoretical values (see Table 1).

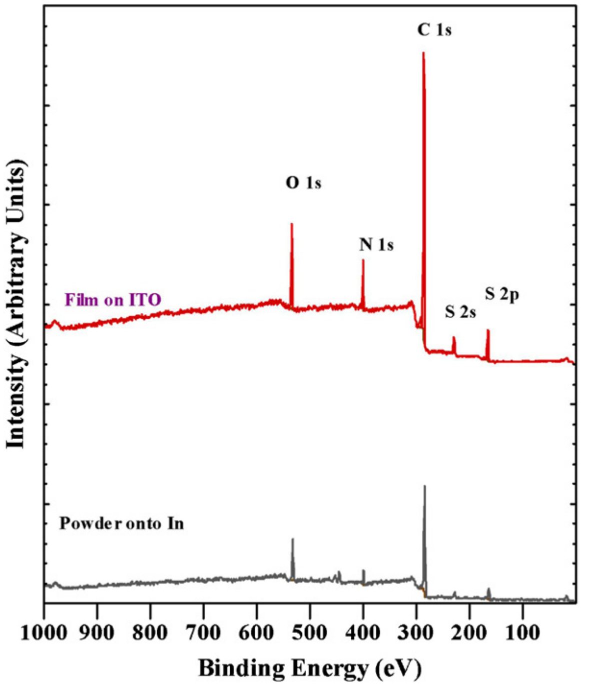

Fig. 5. XPS survey scan of powder DTBT-DTPA-TMeO pressed against 99.99% In and film solution processed onto clean ITO. The same elements were detected on both scans with In 3d doublet appearing on the powder sample.

Table 1
Atomic % concentration of O, N, C and S normalized to C 1s.

	O 1s	N 1s	C 1s	S 2p
Powder	0.11	0.071	1	0.051
Films	0.077	0.072	1	0.054
Theoretical	0.074	0.074	1	0.055

The high resolution XPS spectra of C 1s and S 2p are shown in Fig. 6a and b, respectively. The C 1s peak can be curve fitted with three distinct peaks attributed to C–C or C–H, C–N and C–S at BE = 284.7, 285.9 and 286.8 eV, respectively. The S 2p data is deconvoluted with two peaks corresponding to two sulfur species, thiophene at 164.1 eV and sulfur bonded to the two nitrogen atoms in the benzothiadiazole moiety. The N 1s and O 1s spectra (data not shown) exhibit single peaks.

Fig. 7a displays secondary electron cutoff normalized UPS spectra of bare clean ITO, ITO/MoO_3 and DTBT-DTPA-TMeO solution processed film onto ITO/MoO_3, using HeI with photon energy of 21.21 eV. A shift (Δ) in work functions between the supporting materials, ITO, ITO/MoO_3 and the overlayer film is due to the formation of a dipole moment at the interface substrate–DTBT-DTPA-TMeO. This interfacial dipole moment results in a vacuum energy shift of Δ = + 0.96 eV (oligomer-ITO/MoO_3). The measured work function for ITO, $\Phi_{ITO} = 4.47$ eV is in good agreement with literature values for non-modified ITO [12,13]. The work function for the DTBT-DTPA-TMeO film on ITO/MoO_3 is measured at 4.05 eV. The HOMO energy level for the film is determined directly from Fig. 7b to be 0.86 eV below the Fermi edge of ITO (BE = 0 eV). The knowledge of Φ_{ITO}, $\Phi_{ITO/MoO3}$, and $\Phi_{org/ITO/MoO3}$, HOMO energy levels of ITO/MoO3 and DTBT-DTPA-TMeO (5.57 and 4.91 eV, respectively) and optical band gap, E_g, allows the approximate positioning of the LUMO energy level of the oligomer at 3.06 eV and the construction of an energy band diagram as the one shown in Fig. 8. The insertion of the MoO_3 layer decreases the charge injection barrier from 0.86 eV (ITO) to +0.56 eV (ITO/MoO_3). The vacuum shift and HOMO values measured here are consistent with values for the commonly used donor material, P3HT measured on substrates such as Ag [14], Si/SiO_2 [15], PEDOT [16], Au [17] and covered with Au [18] (with vacuum level shifts ranging from 0.56 to 1.3 eV, and HOMO energy levels from 0.45 to 1.05 eV). Since the measured values of Δ and HOMO for DTBT-DTPA-TMeO spin cast on ITO and ITO/MoO_3 fall in the same range of values as P3HT this oligomer can be categorized as a donor material. To characterize further this new compound we have measured the charge mobility (μ_0) and compared our value to the measured value for P3HT. Therefore single carrier type diodes were constructed to characterize the charge transport of the oligomer. ITO/MoO_3 and gold were chosen as charge injecting and collecting electrodes, respectively. Sufficiently thick films for which the current is bulk limited have been observed to display current densities following the space

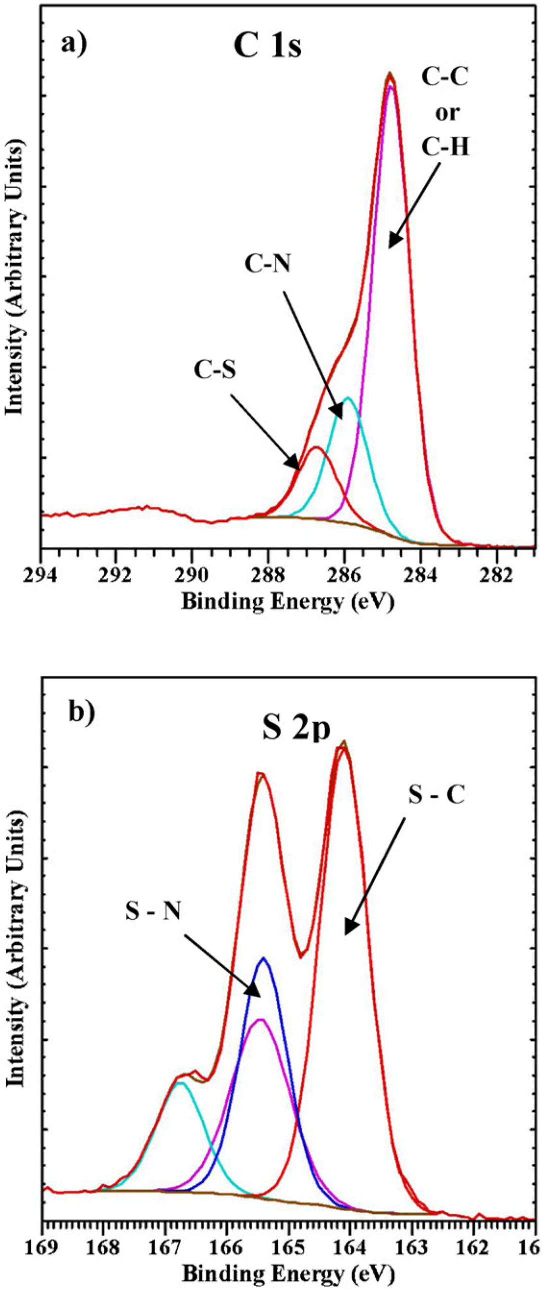

Fig. 6. High resolution XPS spectra of C 1s and S 2p. The curve fitting of the spectra reveals several chemical bonding that are discussed in the text.

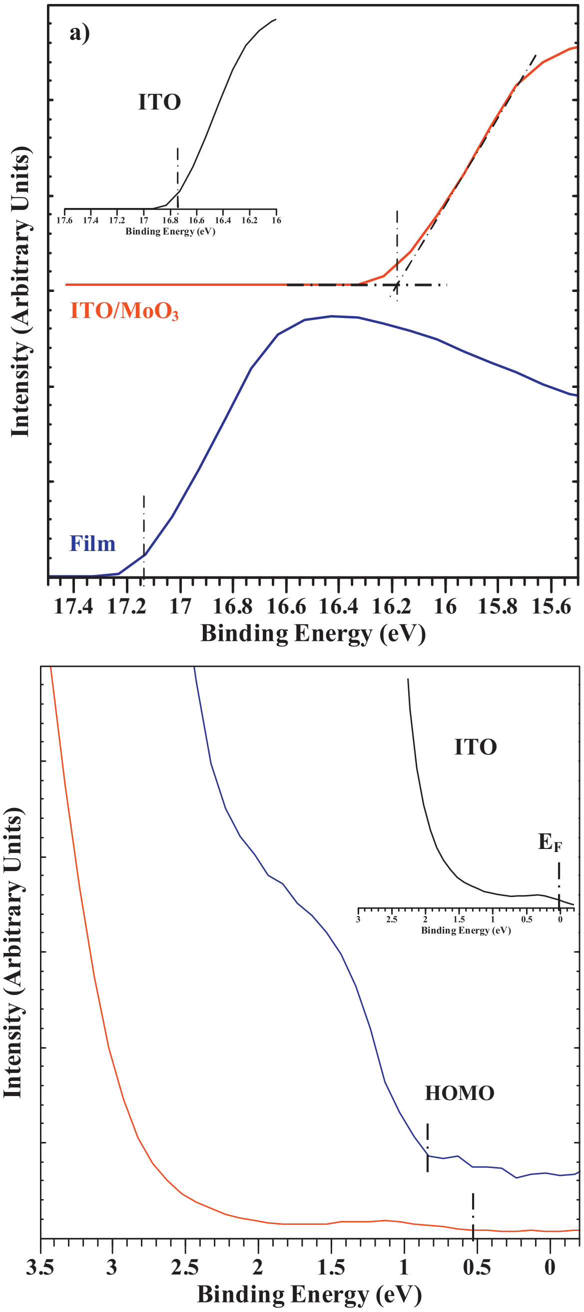

Fig. 7. Normalized UPS spectra of solution processed film of clean bare ITO, ITO/MoO$_3$ and DTBT–DTPA–TMeO onto ITO/MoO$_3$. (a) Secondary electron cut-off and (b) HOMO energy regions.

charge limited current (SCLC) model of Lampert and Mark [19] where the current density is given by

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu(E)\frac{V^2}{d^3}$$

and the mobility by

$$\mu(E) = \mu_0 \exp(\gamma\sqrt{E})$$

where ε_0 and ε_r are the permittivity of free space and the relative permittivity, respectively, μ is the carrier mobility under applied electric field E, V the applied voltage (0–5 V), and d the film thickness (~200 nm). The parameter γ represents the field activation and μ_0 is the zero field mobility.

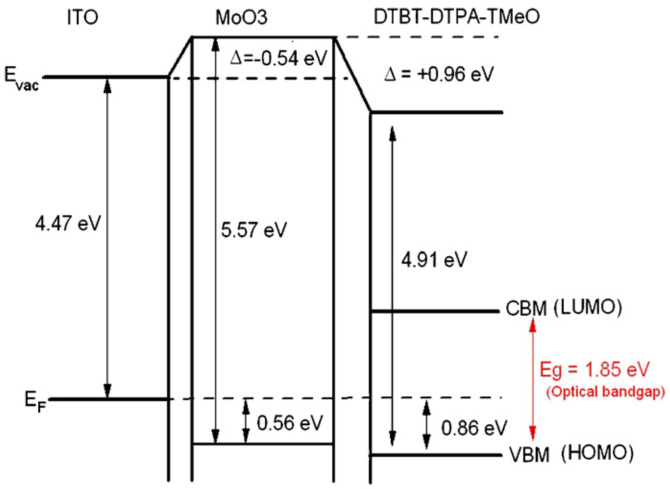

Fig. 8. Energy band diagram constructed from UV–Vis and UPS data for DTBT-DTPA-TMeO film spin coated onto ITO/MoO$_3$.

Charge transport in organic semiconductors has been shown to have a Poole–Frenkel dependence on electric field [20,21] due to the energetic barriers that must be overcome for charge hopping type transport. Current–voltage measurements and their fit to the field-dependent SCLC model are shown in Fig. 9. A typical value of $\varepsilon_r = 3$ was used to extract the zero field mobility ($\mu_0 = 4.15 \pm 0.01) \times 10^{-7}$ cm^2/Vs). This value of the mobility is relatively large for solution processed films which usually display low molecular order. The insertion of a ~5 nm thick MoO$_3$ layer between the organic and the hole injecting ITO electrode to reduce the hole injection barrier from ITO to organic semiconductors [22,23] shows a two order of magnitude increase in the zero field charge carrier mobility $(1.03 \pm 0.01) \times 10^{-5}$ cm^2/Vs with a gamma value of 8×10^{-5}. This value of the charge mobility is smaller than the $(1–2 \times 10^{-4}$ cm^2/Vs) measured by TOF for P3HT on ITO/TiO$_2$ by Ballantyne et al. [24] but is in good agreement with the values of 5×10^{-5} and 3×10^{-5} cm^2/Vs measured for systems such as ITO/PPV/Au [21] and ITO/m-MTDATA/Au [25]. The drastic increase in mobility of the oligomer when deposited on ITO/MoO$_3$ suggests that the current is limited by the injection from ITO to DTBT-DTPA-TMeO as opposed to limited by bulk resistance. Inserting a MoO$_3$ layer reduced the limitation of injection on current and allows for a

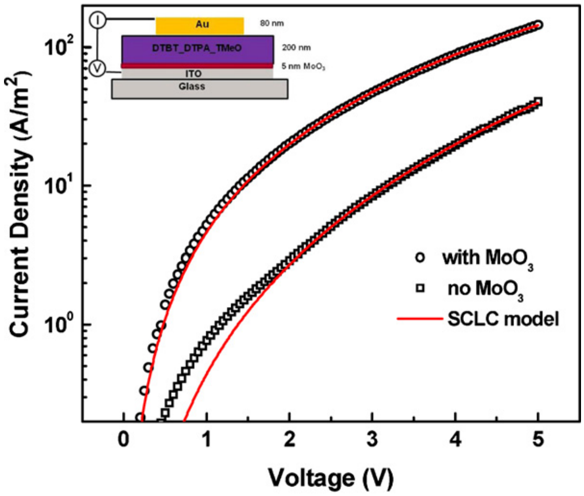

Fig. 9. *J–V* characteristics of a single carrier hole diode without (□) and with (○) a MoO$_3$ interlayer between the hole injecting electrode and the organic layer plotted against the respective field-dependent SCLC.

more accurate hole mobility calculation. A higher value is expected for an annealed film and with the insertion of an electron transporting layer.

Based on the findings in this work DTBT-DTPA-TMeO could be a promising donor material for use in organic solar cell devices

4. Conclusion

In this study we have demonstrated that a newly synthesized oligomer; di-thiophene-benzothiadiazole di-triphenylamine tert-methoxy (DTBT-DTPA-TMeO) is thermally stable, can be solution processed onto ITO and ITO/MoO_3 to produce a good quality film with uniform coverage and free of defects. This new D–A–D compound has interesting optical properties with band gap less than 2 eV and strong absorbance peaks at 384 and 566 nm which encompasses most of the visible range of the solar radiation. The HOMO and LUMO energy levels and vacuum shift are consistent with the commonly used donor material, P3HT which makes this compound a donor material. A hole mobility of $\sim 10^{-5}\,\text{cm}^2/\text{Vs}$ is consistent with other organic donor materials and could be used as active layer in organic BHJ photovoltaic devices when blend with a good acceptor material such as PCBM.

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