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Influence of the molecular orientation of oligothiophene derivatives in vacuum-evaporated thin films on photovoltaic properties

Jianhua Hu [a, b], Lusheng Liang [a], Tuhua Chen [a], Ping Liu [a, *], Wenji Deng [c]

[a] State Key Laboratory of Luminescent Materials and Devices, Research Institute of Materials Science, South China University of Technology, Guangzhou 510640, China
[b] Guangdong TGPM Automotive Industry Group Co., Ltd., Foshan 528222, China
[c] Department of Applied Physics, South China University of Technology, Guangzhou 510640, China

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ABSTRACT

To understand the relationship between molecular orientation in organic thin films and organic photovoltaic properties the donor–acceptor type oligothiophene derivatives 5,5″-dicyano-2,2′:5′,2″-terthiophene and 5,5‴-dicyano-2,2′:5′,2″:5″,2‴-quaterthiophene were synthesized. Polarizing optical microscopy showed that the oligothiophene derivatives had liquid crystalline properties. The crystalline phases of the oligothiophene derivatives showed molecular orientation. Atomic force microscopy also showed that the vacuum-evaporated oligothiophene derivative thin films had molecular orientation. Using the oligothiophene derivative thin films as donor materials and a 3,4,9,10-perylenetetracarboxylic dianhydride thin film as the acceptor material organic photovoltaic devices were fabricated. The structure of these devices is glass-indium tin oxide/donor materials/acceptor material/aluminum. The molecular orientation of the vacuum-evaporated oligothiophene derivative thin films was found to improve the organic photovoltaic performance of these devices.

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1. Introduction

Organic photovoltaic devices have attracted a great deal of attention because of their light weight, processability and the ease of material design on the molecular level. The main focus of recent research in the field of organic photovoltaic devices has been to increase their power conversion efficiency (PCE). The PCE of organic photovoltaic devices composed of polymer-fullerene heterojunctions has improved greatly by variations in processing techniques [1–3]. However, the PCE of current organic photovoltaic devices is still lower than the target PCE of 10–15% for commercialization.

The PCE of organic photovoltaic devices is mainly dependent on the short circuit current density (I_{sc}) and the open circuit voltage (V_{oc}). The I_{sc} and V_{oc} are, in turn, mainly dependent on the organic molecular structure and morphology of the donor (or acceptor) materials. Therefore, an understanding of the relationship between the morphology of the donor (or acceptor) materials and the organic photovoltaic property is important to establish guidelines for the molecular design of the donor (or acceptor) materials. In our previous work we found that intermolecular hydrogen bonding between the donor and acceptor contributed to an increase in the V_{oc} and PCE [4]. We also found that donor materials with a mesogenic property or crystalline morphology could promote forward interfacial electron transfer and transport, and improve organic photovoltaic performance. On the contrary, donor materials with amorphous morphology did not improve organic photovoltaic performance [5,6].

In this paper, we discuss the relationship between the molecular orientation of a vacuum-evaporated oligothiophene derivative thin film and its organic photovoltaic properties. We report the synthesis of the donor–acceptor type oligothiophene derivatives 5,5″-dicyano-2,2′:5′,2″-terthiophene (3T-2CN) and 5,5‴-dicyano-2,2′:5′,2″:5″,2‴-quaterthiophene (4T-2CN) (Scheme 1). Using the 3T-2CN and 4T-2CN thin films as donor materials and a 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) thin film as an acceptor material organic photovoltaic devices were fabricated. The relationship between the molecular orientation of the vacuum-evaporated 3T-2CN and 4T-2CN thin films and organic photovoltaic performance was investigated.

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* Corresponding author. Tel./fax: +86 20 87111686.
E-mail address: mcpliu@scut.edu.cn (P. Liu).

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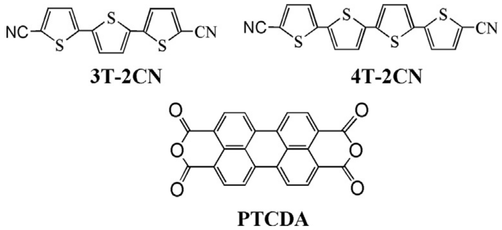

Scheme 1. Molecular structures of 3T-2CN, 4T-2CN and PTCDA.

2. Experimental

2.1. Materials

All solvents were purified and dried by standard methods. 2,2′:5′,2″-Terthiophene (3T) was prepared by a Grignard coupling reaction between 2,5-dibromothiophene and 2-bromomagnesiothiophene in THF. The 2,2′:5′,2″:5″,2‴-quaterthiophene (4T) was also prepared by a Grignard coupling reaction between 2,5′-dibromo-2,2′-dithiophene and 2-bromomagnesiothiophene in THF. *N*-chlorosulfonylisocyanate (CSI), *N*,*N*-dimethylformamide (DMF) and 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) are commercially available.

2.2. Characterization

^{1}H NMR spectra were recorded on a Bruker Avance 400 spectrometer in $CDCl_3$. Mass spectra (MS) were recorded on a Shimadzu GCMS-QP-2010. FT-IR spectra were recorded on a Bruker Tensor 27. Elementary analyses were performed by using Vario ELIII Analyzer. Polarising optical microscopy (POM) was carried out with an OPTIPHOT X2 (Nikon) microscope, fitted with a TH-600PM hot stage (Linkam) and crossed polarizers. Atomic force microscopy (AFM) was carried out with Veeco MultiMode 8. The electronic absorption spectra were recorded on a Thermo spectronic (model HeλOs γ). Cyclic voltammetry was carried out on a CHI-750A voltammetric analyzer (Zhenhua Apparatus Co., Ltd, Shanghai, China). The *I*–*V* characteristic curve of the device was measured with a Keithley electrometer (model 2400) SourceMeter.

2.3. Synthesis

2.3.1. Synthesis of 3T-2CN

3T-2CN was prepared by the reaction between 3T (0.5 g, 2.0 mmol) and CSI (1.5 g, 10.6 mmol) in CH_2Cl_2 at room temperature under a N_2 atmosphere for 5 h and then DMF (50 mL) was added. The solution was stirred for 16 h and then hydrolysed with water. The aqueous solution was extracted with CH_2Cl_2 and washed with brine and water. The solvent was removed under reduced pressure to give 3T-2CN. The product was purified by silica gel column chromatography using toluene as the eluent, to give a pale yellow solid (0.24 g, yield 40%). mp 219–220 °C; IR (KBr, cm^{-1}): 2213 (ν_{CN}); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.57 (d, 2H, ArH), 7.24 (s, 2H, ArH), 7.18 (d, 2H, ArH); ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) = 148, 145, 139, 128, 127, 113, 110; MS (EI): *m*/*z* 298.3, Found: 297.9; Anal. Calcd. for $C_{14}H_6N_2S_3$: C, 56.34; H, 2.03; N, 9.39; S, 32.24; found: C, 56.61; H, 2.33; N, 9.12; S, 31.98.

2.3.2. Synthesis of 4T-2CN

4T-2CN was prepared by the reaction between 4T (0.5 g, 1.5 mmol) and CSI (2.0 g, 14.1 mmol) in CH_2Cl_2 at room temperature under a N_2 atmosphere for 5 h and then DMF (50 mL) was added. The solution was stirred for 16 h and then hydrolyzed with water. The aqueous solution was extracted with CH_2Cl_2 and washed with brine and water. The solvent was removed under reduced pressure to give 3T-2CN. The product was purified by silica gel column chromatography using toluene as the eluent, to give a yellow solid (0.20 g, yield 35%). mp 264–265 °C; IR (KBr, cm^{-1}): 2216 (ν_{CN}); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.55 (d, 2H, ArH), 7.22 (d, 1H, ArH), 7.16 (d, 2H, ArH), 7.14 (d, 2H, ArH); ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) = 147, 143, 140, 138, 130, 128, 127, 113, 110; MS (EI): *m*/*z* 380.5, Found: 379.3 $[M - H]^+$; Anal. Calcd. for $C_{18}H_8N_2S_4$: C, 56.81; H, 2.12; N, 7.36; S, 33.71; found: C, 56.93; H, 2.41; N, 8.97; S, 31.89.

3. Results and discussion

Unsubstituted oligothiophenes are crystalline in nature because of their planar molecular structures. Vacuum-evaporated thin films of unsubstituted oligothiophenes have been reported to be in the crystalline state [7,8]. We have previously synthesized a series of

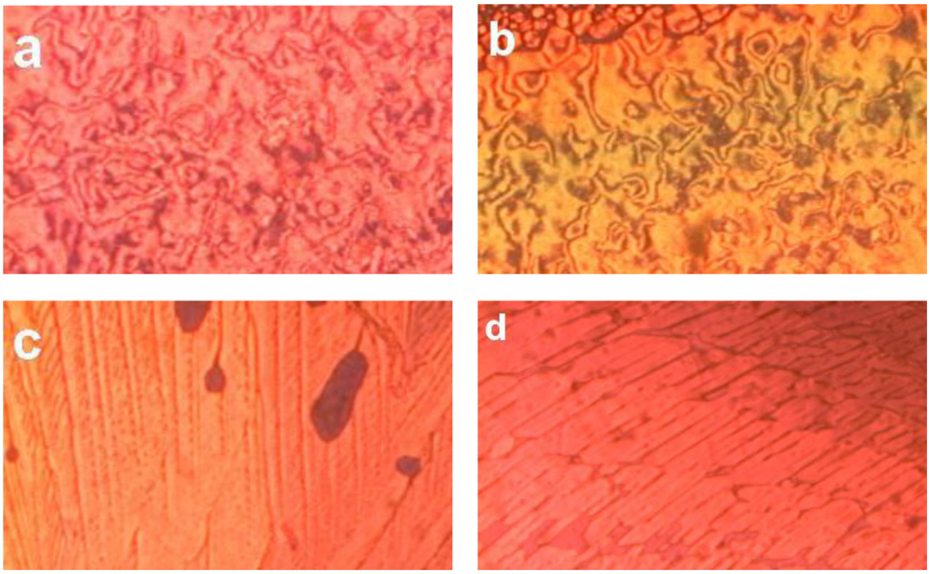

Fig. 1. POM images of the liquid crystalline phase and the crystalline phase of 3T-2CN and 4T-2CN obtained upon cooling the melt. (a): Liquid crystalline phase of 3T-2CN; (b): liquid crystalline phase of 4T-2CN; (c): crystalline phase of 3T-2CN; (d): crystalline phase of 4T-2CN (magnification× 200).

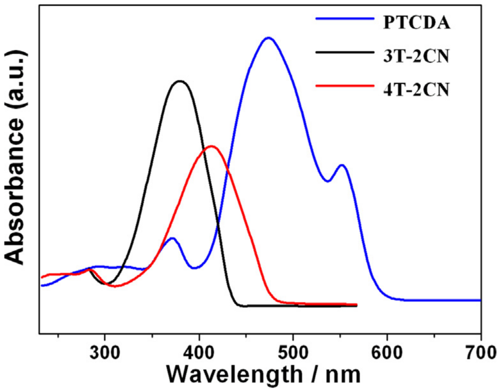

Fig. 2. Electronic absorption spectra of the vacuum-deposited 3T-2CN, 4T-2CN and PTCDA films.

substituted oligothiophene derivatives [9] and found that these substituted oligothiophene derivatives could form a smectic A phase. The –CN group is an electron-withdrawing group and whether the –CN group affects the morphologies of 3T-2CN and 4T-2CN is of interest. We observed the morphologies of the vacuum-evaporated 3T-2CN and 4T-2CN thin films by POM using a hot stage. When the isotropic liquids of 3T-2CN and 4T-2CN were cooled, a smectic A phase was observed at approximately 218 °C and 262 °C, respectively. Upon further cooling the crystalline phases were observed at approximately 206 °C and 248 °C, respectively. Of interest is that the crystalline phases of the 3T-2CN and 4T-2CN thin films have molecular orientation. Fig. 1 shows POM images of the liquid crystalline phase and the crystalline phase for 3T-2CN and 4T-2CN upon cooling the melt.

For most applications of conjugated compounds such as in photovoltaic devices and in photodetectors the conjugated compound thin film absorbance is an important parameter particularly in the visible region. Fig. 2 shows the electronic absorption spectra of the vacuum-deposited 3T-2CN, 4T-2CN and PTCDA thin films. The 3T-2CN thin film absorbed light in a wavelength range from 280 to 450 nm, the 4T-2CN thin film absorbed light in a wavelength range from 250 to 500 nm and the PTCDA thin film absorbed light in a wavelength range from 280 to 620 nm. Therefore, it is expected that devices consisting of 3T-2CN, 4T-2CN and PTCDA might respond to ultraviolet–visible light over a wide wavelength region.

Electrochemical cyclic voltammetry was carried out to determine the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the conjugated compounds. Cyclic voltammograms of 3T-2CN and 4T-2CN were obtained in a solution of tetra-*n*-butylammonium perchlorate (0.1 mol/L) in CH_2Cl_2 and an Ag/AgCl electrode was used as the reference electrode. Both 3T-2CN and 4T-2CN gave one anodic oxidation and one cathodic reduction wave. The first onset of the oxidation potentials for 3T-2CN and 4T-2CN were 1.08 and 1.06 V *vs.* Ag/AgCl, respectively. The first onset of the reduction potentials for 3T-2CN and 4T-2CN were −1.31 and −0.95 V *vs.* Ag/AgCl, respectively. From the literature [10] PTCDA has one anodic oxidation and one cathodic reduction wave. The first oxidation potential and the first reduction potential of PTCDA were at 2.29 V and −0.05 V *vs.* Ag/AgCl, respectively. HOMO and LUMO energy levels were calculated according to the following equations [11]:

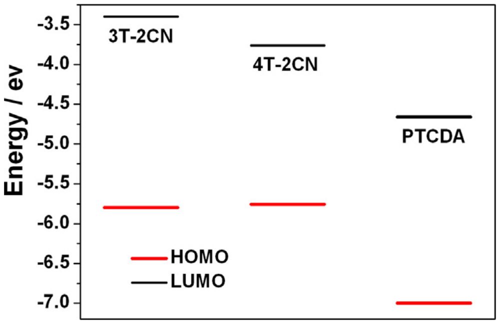

Fig. 3. Energy levels of 3T-2CN, 4T-2CN and PTCDA.

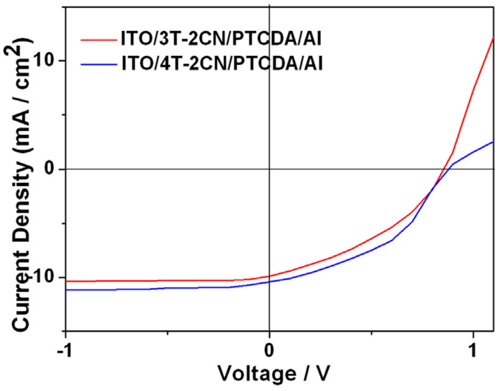

Fig. 4. Current density–voltage characteristics of ITO/3T-2CN/PTCDA/Al (red) and ITO/4T-2CN/PTCDA/Al (blue) under 100 mW/cm^2 simulated sunlight through an ITO electrode. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$$\mathrm{HOMO} = -e\,(E_{\mathrm{ox}} + 4.71)\ (\mathrm{eV}),$$

$$\mathrm{LUMO} = -e\,(E_{\mathrm{red}} + 4.71)\ (\mathrm{eV}),$$

where the unit of potential is V *vs.* Ag/AgCl. The HOMO energy levels of 3T-2CN, 4T-2CN and PTCDA were −5.79, −5.77 and −7.00 eV, respectively. The LUMO energy levels of 3T-2CN, 4T-2CN and PTCDA were −3.40, −3.76 and −4.66 eV, respectively. Fig. 3 clearly shows that the LUMO of PTCDA is less than the LUMO of both 3T-2CN and 4T-2CN. If the 3T-2CN and 4T-2CN were candidates as electron-donor materials and PTCDA was a candidate as an electron-acceptor material they would match well and might have photovoltaic properties.

To understand the relationship between the molecular orientation of the 3T-2CN and 4T-2CN thin films and organic photovoltaic performance, organic photovoltaic devices were fabricated. The structure of the devices was Glass-ITO/3T-2CN (or 4T-2CN)/PTCDA/Al. Organic layers of 3T-2CN, 4T-2CN and PTCDA were deposited by vacuum deposition (vacuum pressure 4×10^{-3} Pa). A solar simulator (CMH-250, Aodite Photoelectronic Technology Ltd., Beijing) with a light intensity of 100 mW/cm^2 was used as the light source.

Fig. 4 shows the *I*–*V* characteristic curves of the devices based on 3T-2CN and 4T-2CN under 100 mW/cm^2 simulated sunlight illumination. The photovoltaic performances are listed in Table 1. The Glass-ITO/3T-2CN/PTCDA/Al and Glass-ITO/4T-2CN/PTCDA/Al

Table 1
Performance characteristics of the devices under 100 mW/cm^2 simulated sunlight through an ITO electrode.

	V_{oc}/V	I_{sc}/mA/cm^2	F.F./%	η/%
Glass-ITO/3T-2CN	0.86	9.9	37.9	3.23
Glass-ITO/4T-2CN	0.88	10.4	43.0	3.94

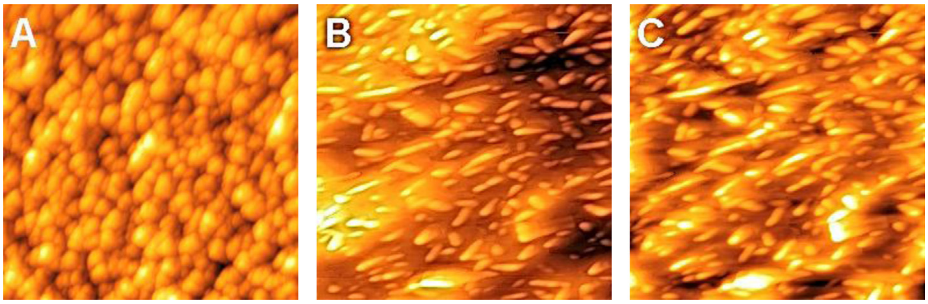

Fig. 5. AFM images of vacuum-evaporated PTCDA (A), 3T-2CN (B) and 4T-2CN (C) thin films.

devices had an I_{sc} of 9.9 mA/cm^2 and 10.4 mA/cm^2, a V_{oc} of 0.86 V and 0.88 V as well as a PCE of 3.23% and 3.94%, respectively.

4T does not contain a substituted group at the α and α' positions, and it is not liquid crystalline. We have previously determined the photovoltaic performance of the Glass-ITO/4T/PTCDA/Al device [12]. The devices based on 4T had an I_{sc} of 0.46 mA/cm^2, a V_{oc} of 0.90 V and a PCE of 0.23%. A comparison of the I_{sc} and PCE parameters of the 4T devices shows that the I_{sc} and PCE of the devices based on 3T-2CN and 4T-2CN were superior. To clarify this result we obtained AFM images of the vacuum-evaporated PTCDA, 3T-2CN and 4T-2CN thin films (Fig. 5). We found that the vacuum-evaporated 3T-2CN and 4T-2CN thin films had molecular orientation and thus the AFM result and the POM result is consistent. Therefore, the molecular orientation of vacuum-evaporated 3T-2CN and 4T-2CN thin films promotes exciton dissociation and charge transport at the donor–acceptor interface and subconducting band trap sites are eliminated. Upon vacuum deposition of the 3T-2CN and 4T-2CN thin films, molecular orientation was apparent because of the liquid crystalline nature of 3T-2CN and 4T-2CN. Under illumination the vacuum-evaporated 3T-2CN and 4T-2CN thin films were excited and the electrons were promoted from the HOMO to the LUMO of the donor. Because the LUMO of the acceptor was significantly lower than the LUMO of the donor the excited electrons relaxed into the acceptor LUMO and thus separated from the hole. Charge separation was far more efficient at the donor–acceptor interface because of the molecular orientation of the vacuum-evaporated 3T-2CN and 4T-2CN thin films that possess liquid crystalline properties.

4. Conclusions

To understand the relationship between the molecular orientation of organic thin films and organic photovoltaic properties the donor–acceptor type oligothiophene derivatives 3T-2CN and 4T-2CN were synthesized. POM observations indicated that 3T-2CN and 4T-2CN had liquid crystalline properties. Atomic force microscopy showed that the vacuum-evaporated 3T-2CN and 4T-2CN thin films had molecular orientation. Using the 3T-2CN and 4T-2CN thin films as donor materials and a PTCDA thin film as an acceptor material organic photovoltaic devices were fabricated. The results show that the molecular orientation of vacuum-evaporated 3T-2CN and 4T-2CN thin films benefits the organic photovoltaic properties of the fabricated devices.

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