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SYNTHESIS AND PHOTOVOLTAIC PROPERTIES OF DONOR-ACCEPTOR OLIGOTHIOPHENE DERIVATIVES POSSESSING MESOGENIC PROPERTIES

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GRAPHICAL ABSTRACT





Abstract For the purpose of developing novel photovoltaic materials and organic photovoltaic devices with good performance characteristics, 5-cyano-2,2':5',2"-terthiophene (3T-CN) and 5-cyano-2,2':5',2":5',2"'-tertathiophene (4T-CN) were synthesized. The 3T-CN and 4T-CN were donor–acceptor oligothiophene derivatives possessing mesogenic properties. The photovoltaic properties of 3T-CN and 4T-CN were studied. The rigid and flexible photovoltaic devices were fabricated using 3T-CN, 4T-CN, and 3,4,9,10-perylenetertracarboxylic dianhydride (PTCDA). The results showed that the -CN group played an important role in increasing short circuit current density (I_{sc}) and power conversion efficiency (PCE). Both rigid device glass-ITO/4T-CN/PTCDA/Al and flexible device PET-ITO (indium tin oxides coated with polyethylene terephthalate)/4T-CN/PTCDA/Al had greater I_{sc} and PCE compared with rigid device glass-ITO/4T/PTCDA/Al. It was possible that the -CN group, with strong electron-withdrawing character, and mesogenic properties of 4T-CN enhanced the efficiency by promoting forward interfacial electron transfer.

Keywords Cyano group; mesogenic property; oligothiophene derivative; photovoltaic property; rigid and flexible photovoltaic devices

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1. INTRODUCTION

Organic photovoltaic devices have attracted a great deal of attention because of their light weight, processability, and ease of material design on the molecular level. When Tang^[1] discovered that bringing a donor and an acceptor together in one cell could dramatically increase power conversion efficiency (PCE), a major break-through came in the field of organic photovoltaics. The concept of heterojunction has since been widely exploited in dye–dye, polymer–dye, polymer–polymer, and polymer–fullerene blend photovoltaic devices. Recently, organic photovoltaic devices employing polymer–fullerene heterojunctions have been shown to have PCE approaching 6–7.4%,^[2] obtained through variations in the processing techniques. However, all these organic photovoltaic devices were processed on rigid glass substrates. Although Maher et al. reported flexible polythiophene organic photovoltaic devices, ^[3] there have been few studies of flexible oligothiophe derivative organic photovoltaic devices require rigid glass substrates, they will offer only limited advantages compared with silicon.

It is well known that the PCE is dependent on the short circuit current density (I_{sc}) and the open circuit voltage (V_{oc}) . Although encouraging progress has been made in recent years with 6–7.4% PCE, the I_{sc} and V_{oc} are still not high. The search for new materials with good performance characteristics to improve the I_{sc} and V_{oc} has been a subject of importance. In our previous works,^[4] we found that intermolecular hydrogen bonding between donor and acceptor contributed to enhancement of the V_{oc} and PCE. Oligothiophenes with well-defined structures have recently received a great deal of attention not only as model compounds for conducting polythiophenes but also as a new class of functional π -electron systems. A variety of oligothiophenes have been synthesized,^[5] and their molecular and crystal structures; self-ordering; and electrochemical, photophysical, optical, and electrical properties have all been studied. In addition, their potential application in field-effect transistors, photovoltaic devices, and organic electroluminescent devices has been investigated.

In this article, we address the aim of developing new organic photovoltaic materials and increasing the I_{sc} based on oligothiophene derivatives. We herein report the synthesis of 5-cyano-2,2':5',2"-terthiophene (3T-CN) and 5-cyano-2,2':5',2":5", 2"'-tertathiophene (4T-CN) (Scheme 1). Because the -CN group has strong



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

electron-withdrawing character, 3T-CN and 4T-CN are conjugated donor–acceptor systems. It is expected that the -CN group plays an important role in increasing short circuit current density (I_{sc}) and PCE. The rigid and flexible photovoltaic devices were fabricated using 3T-CN, 4T-CN, and 3,4,9,10-perylenetertracarboxylic dianhydride (PTCDA). The performance characteristics of devices were investigated.

EXPERIMENTAL

Materials

All solvents were purified and dried by ordinary methods. Glass-ITO (indium tin oxides coated with glass), PET-ITO (indium tin oxides coated with polyethylene terephthalate), and *N*-chlorosulfonyl isocyanate (CSI) are commercially available. 2,2':5',2"-Terthiophene (3T) was prepared by a Grignard coupling reaction of 2,5dibromothiophene with 2-bromomagnesiumthiophene in tetrahydrofuran (THF). Likewise, 2,2':5',2":5",2":5",2"'-teterthiophene (4T) was prepared by Grignard coupling reaction of 2,5'-dibromo-2,2'-dithiophene with 2-bromomagnesiumthiophene in THF.

Characterization

¹H NMR spectra were recorded on a Bruker Avanece 400 spectrometer in CDCl₃. Mass spectra (MS) were recorded on a Shimadzu GCMS-QP-2010. Fourier transform–infrared (FT-IR) spectra were recorded on a Bruker Tensor 27. The electronic absorption spectra of the thin film of materials were recorded with a Thermospectronic (model He λ Os γ). Cyclic voltammetry was carried out on a CHI-750-A voltammetric analyzer (Zhenhua Apparatus Co., Ltd., Shanghai). The *I-V* characteristic of the device was measured with a Keithley electrometer (model 2400) source meter.

Synthesis

3T-CN^[6] was prepared by the reaction of 3T with CSI in methylene chloride at room temperature under a nitrogen atmosphere for 4 h, and then *N*,*N*-dimethylformamide (DMF) was added. The solution was stirred for 15 h and then hydrolyzed with water. The aqueous solution was extracted with methylene chloride and washed with brine and water. The solvent was removed under reduced pressure to give 3T-CN. The product was purified by silica-gel column chromatography using toluene as the eluent. MS (EI): m/z 274 (M⁺); ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.52 (d, 1H, ArH), 7.28 (d, 1H, ArH), 7.22 (d, 1H, ArH), 7.18 (d, 1H, ArH), 7.11 (s, 1H, ArH), 7.10 (s, 1H, ArH), 7.04 (t, 1H, ArH); IR (KBr, cm⁻¹): 2212 (ν_{CN}).

4T-CN was synthesized using analogous procedures with 4T. MS (EI): m/z 355 (M⁺); ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.52 (d, 1H, ArH), 7.24 (d, 1H, ArH), 7.19 (s, 1H, ArH), 7.18 (s, 1H, ArH), 7.15–7.07 (m, 4H, ArH), 7.03 (t, 1H, ArH); IR (KBr, cm⁻¹): 2216 (ν _{CN}).

RESULTS AND DISCUSSION

Electrochemical cyclic voltammetry is performed for determining the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of conjugated compounds. The cyclic voltammograms of 3 T-CN and 4 T-CN were done in the solution of tetra-*n*-butylammonium perchlorate (0.1 mol/L) in dichloromethane, and an Ag/AgCl electrode was used as reference electrode. Both 3 T-CN and 4 T-CN exhibited one anodic oxidation and one cathodic reduction wave. The first onset of oxidation potential and the first onset of reduction potential were 1.51 V and -0.62 V vresus Ag/AgCl for 3 T-CN, and 1.12 V and -0.58 V versus Ag/AgCl for 4 T-CN. According to literature,^[7] PTCDA exhibited one anodic oxidation and one cathodic reduction wave. The first reduction potential were 2.29 V and -0.05 V versus Ag/AgCl for PTCDA. HOMO and LUMO energy levels were calculated according to the following equations:^[8]

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

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

where the unit of potential is V versus Ag/AgCl. The HOMO energy levels of 3 T-CN, 4 T-CN, and PTCDA were -6.22 eV, -5.83 eV, and -7.00 eV, respectively. The LUMO energy levels of 3 T-CN, 4 T-CN, and PTCDA were -4.09 eV, -4.13 eV, and -4.66 eV, respectively. Figure 1 clearly shows that the LUMO of PTCDA was less than the LUMO of 3 T-CN and 4 T-CN. If 3 T-CN and 4 T-CN were candidates as electron-donor materials, and PTCDA was a candidate as the electron-acceptor material, they would match well and might exhibit good photovoltaic properties.

For most of the conjugated compounds, the absorbance in the visible region of the thin film of the compound is an important parameter when they are used as photovoltaic materials. Figure 2 showed the electronic absorption spectra of the vacuum-deposited 3 T-CN, 4 T-CN, and PTCDA films. The 3 T-CN film absorbed light in the wavelength range of 284–570 nm, the 4 T-CN film absorbed light in the wavelength range of 300–630 nm, and the PTCDA film absorbed light in the wavelength range of 400–640 nm. All of the wavelength ranges were useful for photovoltaic



Figure 1. Energy levels of 3 T-CN, 4 T-CN, and PTCDA. (Figure is provided in color online.)



Figure 2. Electronic absorption spectra of the vacuum-deposited 3T-CN, 4T-CN, and PTCDA films. (Figure is provided in color online.)

conversion. Therefore, it is expected that the devices consisting of 3 T-CN, 4 T-CN, and PTCDA might respond to ultraviolet–visible light over a wide wavelength region.

To check the photovoltaic properties of 3 T-CN and 4 T-CN, we have fabricated two rigid photovoltaic devices and two flexible photovoltaic devices, glass-ITO/ 3 T-CN/ PTCDA/Al, glass-ITO/4 T-CN/PTCDA/Al, PET-ITO/3 T-CN/PTCDA/Al, and PET-ITO/4 T-CN/PTCDA/Al. The organic layers of 3 T-CN, 4 T-CN, and PTCDA were deposited by vacuum deposition (vacuum pressure 4×10^{-3} Pa). The thicknesses of 3 T-CN, 4 T-CN, and PTCDA films were about 80–100 nm, 80–100 nm, respectively. A solar simulator (CMH-250, Aodite Photoelectronic Technology Ltd., Beijing) with light intensity of 78.2 mW/cm² was used as light source.

Figure 3 showed the *I-V* curves of the two rigid devices under the illumination of 78.2 mW/cm² simulated sunlight. Figure 4 showed the current density–voltage characteristics for two flexible devices under 78.2 mW/cm² simulated sunlight through the PET-ITO electrode. The photovoltaic properties are listed in Table 1. The glass-ITO/3 T-CN/PTCDA/A1 and glass-ITO/4 T-CN/PTCDA/A1 devices had I_{sc} of 7.60 mA/cm² and 9.68 mA/cm² and PCE of 1.51% and 2.10%, respectively, whereas the PET-ITO/3 T-CN/PTCDA/A1 and PET-ITO/4 T-CN/PTCDA/A1 devices had I_{sc} of 4.17 mA/cm² and 5.42 mA/cm² and PCE of 0.86% and 1.20%, respectively.

Electronic absorption spectra of the vacuum-deposited 3 T-CN and 4 T-CN films showed that the conjugated length of 4 T-CN was longer than that of 3 T-CN. An increase in oligothiophene length provides stronger light absorption and promotes better π - π stacking or aggregation of the oligomers. Therefore, the charge transport properties of 4 T-CN were better than that of 3 T-CN, and the I_{sc} and PCE of the devices glass (or PET)-ITO/4 T-CN/PTCDA/Al were greater than that of the glass (or PET)-ITO/3 T-CN/PTCDA/Al.



Figure 3. I-V curves of the two rigid devices under the illumination of 78.2 mW/cm² simulated sunlight through the glass-ITO electrode. (Figure is provided in color online.)

The 4T does not contain a substituted group at the α position. However, 4T-CN contains a -CN group at the α position. The -CN group can increase the $I_{\rm sc}$ and PCE of the devices. We have determined the photovoltaic properties of the glass-ITO/4T/PTCDA/Al device under the same condition.^[9] It was found that the $I_{\rm sc}$ and PCE of the glass-ITO/4T/PTCDA/Al device were 0.46 mA/cm² and 0.23%. In comparison to $I_{\rm sc}$ and PCE of the glass-ITO/4T/PTCDA/Al device, the $I_{\rm sc}$ of the Glass-ITO/4T-CN/PTCDA/Al was increased from around 0.46 mA/cm² to 9.68 mA/cm², and the PCE was increased from 0.23% to 2.10%. These results confirmed that the -CN group at the α position of oligothiophene affected the photovoltaic device performances. That is to say, the -CN group could increase the $I_{\rm sc}$ and PCE of the devices.



Figure 4. I-V curves of the two flexible devices under the illumination of 78.2 mW/cm² simulated sunlight through the PET-ITO electrode. (Figure is provided in color online.)

	V_{oc} (V)	$I_{sc} (\mathrm{mA \ cm}^{-2)}$	F.F. (%)	η (%)
Glass-ITO/3T-CN	0.65	7.60	23.9	1.51
Glass-ITO/4T-CN	0.83	9.68	20.3	2.10
PET-ITO/3T-CN	0.62	4.17	25.1	0.86
PET-ITO/4T-CN	0.80	5.42	21.7	1.20

Table 1. Photovoltaic properties of the devices under the illumination of 78.2 mW/cm^2 simulated sunlight

Oligothiophenes are crystal in nature because of their planar molecular structures. Vacuum-evaporated and spin-coated films of oligothiophenes have been reported to be crystalline.^[10,11] We observed the morphologies of films of 3 T, 3 T-CN, 4 T, and 4 T-CN by polarizing microscopy with a hot stage. It was found that 3 T and 4 T exhibited crystalline states, whereas 3 T-CN and 4 T-CN films exhibited mesogenic properties. The -CN group played an important role in forming mesogenic properties. It was possible that the molecular orientation of vacuum-evaporated 3 T-CN and 4 T-CN films were better than that of vacuum-evaporated 3 T and 4 T films. The mesogenic properties of 3 T-CN and 4 T-CN enhanced the efficiency by promoting forward interfacial electron transfer.

Under the illumination, the dissociation of excitons diffusing to the heterojunction interface was described in Scheme 2. Because the films of 4 T-CN (or 3 T-CN) possessing mesogenic property have better molecular orientation, the electron was promoted from HOMO to LUMO of the donor, leaving a hole behind when the vacuum-evaporated film of donor 4 T-CN (or 3 T-CN) was excited under the illumination of simulated sunlight. The electron and hole can dissociate. Because the LUMO of the acceptor PTCDA was sufficiently less than the donor LUMO, the excited electron would relax into the acceptor LUMO and in this way separate from the hole. Charge separation was much more efficient at the donor–acceptor interface than at the electrode interface.



Scheme 2. Exciton dissociation and charge transport at the donor-acceptor interface. (Figure is provided in color online.)

It was noteworthy that the *I-V* curves of the two rigid devices glass-ITO/ 3T-CN/ PTCDA/Al and glass-ITO/4T-CN/PTCDA/Al exhibited slope at negative voltage. This effect could result from various factors, such as low shunt resistance, mesogenic properties of 3T-CN and 4T-CN, or photoconductivity. Further work is required to clarify this point.

CONCLUSION

In summary, for the purpose of developing novel photovoltaic materials and organic photovoltaic devices with good performance characteristics, we have fabricated rigid and flexible photovoltaic devices using 3T-CN, 4T-CN, and PTCDA. It was found that 3T-CN and 4T-CN were not only donor-acceptor system but also possessed mesogenic properties. Compared with devices using unsubstituted 4T, the 4T-CN device had greater I_{sc} and PCE. The -CN group at the α position of oligothiophene could increase the I_{sc} and PCE of the device. It was possible that mesogenic properties of 4T-CN enhanced the efficiency by promoting forward interfacial electron transfer.

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