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# *X*-shape oligo(thiophene)s as donor materials for vacuum-deposited organic photovoltaic cells*

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The films of two *x*-shape oligo(thiophene)s, 3, 4-dibithienyl-2, 5-dithienylthiophene (7T) and 2, 5-dibithienyl-3, 4-ditrithienylthiophene (11T), which are prepared by vacuum evaporation, have been investigated as novel electron donor layers in two-layer photovoltaic cells. UV–Vis absorptions show red-shifted and broadened absorptions of the vacuum-evaporated films as compared with those of the corresponding solutions and spin-coating films, which is beneficial for photovoltaic properties. X-ray diffraction (XRD) and differential scanning calorimetry (DSC) measurements show that the vacuum-evaporated films are almost amorphous. Two-layer photovoltaic cells have been realized by the thermal evaporation of 7T and 11T as donors and *N*, *N*′−bis(1-ethylpropyl)-3, 4:9,10-perylene bis(tetracarboxyl diimide) (EP-PTC) as an acceptor. An energy conversion efficiency (ECE) of 0.18% of the cell based on 7T with an irradiation of white light at 100 mw/cm$^2$ has been demonstrated by the measurements of current ($I$)- voltage ($V$) curves of the cells to be higher than the ECE of the reference system based on donor dihexylterthienyl (H3T) that is linear and without $\alpha$, $\beta$ linkage.

**Keywords:** oligo(thiophene)s, vacuum-evaporated film, solar cell
**PACC:** 7855K, 8115N, 8630J

## 1. Introduction

Organic semiconducting materials are promising candidates for applications in photovoltaic devices, because of their outstanding merits, such as low-cost fabrication, easy processing, compatibility with flexible substrates, and low processing temperature.[1−4] During the past two decades, organic small molecular and polymeric semiconducting materials based on conjugated thiophenes have been extensively investigated, with development efforts focusing on applications as donors in a variety of photovoltaic devices,[5−8] because of their high chemical stability and high carrier mobility.[9,10] In comparison with polythiophenes, oligo(thiophene)s have a great many advantages, such as excellence in well-defined conjugation lengths and structures, ease of purification and characterization, owning less deep electron traps in films.[11−13]

Photovoltaic devices based on bulk heterojunctions have reached a high energy conversion efficiency of 5.2%.[14] Meanwhile, significant progress has also been accomplished in multi-layer photovoltaic cells based on vacuum-evaporated films. An efficiency of 5.0% has been reported for solar cells based on copper phthalocyanine (CuPc) and fullerene ($C_{60}$).[15] Because of low dimensionality, organic photovoltaic cells based on linear thiophenes are known to present highly anisotropic charge transport and optical properties that pose specific problems for device fabrication.[16−18] In an attempt to solve these problems, some groups have developed oligothiophene-based two-dimensional (2D) and tri-dimensional (3D) systems.[19−27] The Roncali group has shown that the hybrid systems combining triphenylamine with oligo(thienylenevinylene)s or oligo(thiophene)s branches lead to interesting results

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for the fabrication of solar cells.[20,22,23] They also used 3D conjugated systems of tetrahedral geometry in which four terthiehyl chains are attached to a central silicon node as donors in solar cells.[24] Further, they have described a series of 3D conjugated architectures built by fixing short-chain oligo(thiophene)s to a twisted bithiophene node, leading to encouraging results.[27] Meanwhile, Sun *et al*[28] have shown that *x*-shape all-thiophene (T) oligomers which have special architectures also achieve good results in bulk-heterojunction solar cells. Owing to their highly branched chemical structures, *x*-shape oligothiophenes manifest themselves 3D structure, low aggregation effects and weak intermolecular interaction.[26,28] Although the bulk-heterojunction solar cells based on spin-coating films of *x*-shape oligo(thiophene)s have been realized, the *x*-shape oligo(thiophene)s cannot form uniform spin-coating films because of their potential crystallization tendency. At the same time, thermogravimetric analysis revealed that the *x*-shape oligo(thiophene)s were thermally stable, and started to decompose at temperatures 405.5°C (7T) and 488.2°C (11T) in a nitrogen atmosphere,[26] which provides a possibility to form highly uniform thin films by vacuum evaporation. In addition, films which can be formed by evaporation can eliminate the defects caused by the solvent. Therefore, in order to further investigate the photovoltaic properties of the vacuum-deposited films, the vacuum-evaporated amorphous films of two *x*-shape oligo(thiophene)s 7T and 11T (see scheme 1) have been investigated each as an electron donor, and EP-PTC as an acceptor, since EP-PTC has a wide absorbance, high electron mobility and long exciton diffusion range (up to 2.5 $\mu$m).[29,30] Because 7T, 11T and EP-PTC have proper highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, the exciton dissociation can be expected to occur in the interface between them (as shown in Fig.1).[26] The vacuum-evaporated amorphous films of 7T and 11T have been characterized by UV–Vis absorption, DSC and XRD analyses. And the photovoltaic properties of the solar cells based on 7T, 11T and EP-PTC evaporated films have been investigated by photocurrent and $I-V$ measurements.

**Scheme 1** Structures of *x*-shape oligo(thiophene)s (7T, 11T) and EP-PTC.

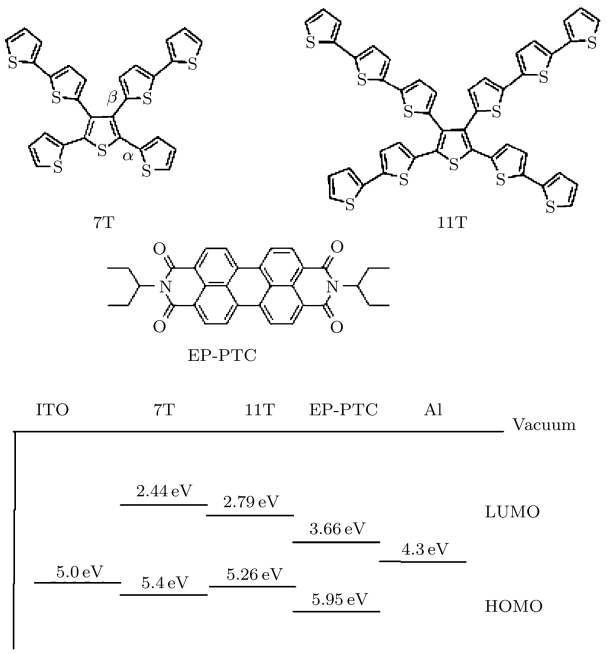



**Fig.1.** Energy levels of compounds 7T, 11T and EP-PTC in devices ITO/PEDOT-PSS/7T or 11T/EP-PTC/Al.

## 2. Experiment

The syntheses of compounds 7T and 11T have been reported elsewhere.[26] EP-PTC was synthesized according to the literature.[31] The UV–Vis absorption spectra were measured with a Shimadzu UV-3100 Spectrometer. The DSC analysis was determined using a NETZSCH (DSC-204) instrument at 10°C min$^{-1}$ in a nitrogen atmosphere. XRD measurements of vacuum-evaporated 7T and 11T films (50 nm) on glass substrates were performed at room temperature with a Rigaku x-ray diffractometer (D/max 2500V) using Cu K$\alpha_1$ radiation of a wavelength of 0.154 nm.

The photovoltaic devices were fabricated in the following sequence. The ITO-coated glass substrates with a sheet resistance of 20 $\Omega/\square$ were cleaned in an ultrasonic bath with toluene, acetone and ethanol, dried in an oven, and treated with boiling $H_2O_2$ for five minutes. Then poly (ethylene dioxythiophene): poly (tyrenesulfonic acid) (PEDOT/PSS, Bayer PVP 4083) was spin-coated on ITO substrates, and dried in a vacuum oven at 95°C for 30 min. Under a pressure of $5\times10^{-4}$ Pa, 40 nm thick 7T and 40 nm thick 11T layers each were deposited onto the PEDOT/PSS films at a rate of 1–2 nm/min. Then 20 nm thick EP-PTC layer was thermally evaporated onto 7T and 11T films at a rate 2 nm/min separately. Finally a 120 nm thick Al layer was deposited through a shadow under

$5 \times 10^{-4}$ Pa.

$I-V$ characteristics of the photovoltaic devices in the dark and under the irradiation of white light with 100 mW/cm$^2$ were measured on a computer-controlled Keithley SourceMeter 2400 source measurement system. The irradiation was provided by white light from a xenon lamp (Jobin Yvon, FL-1039). Photocurrent was measured with monochromatic light from the xenon lamp and detected by a computer-controlled Stanford SR830 lock-in amplifier. All the measurements were performed under ambient atmosphere at room temperature.

# 3. Results and discussion

## 3.1. Optical properties

Figure 2 shows the UV–Vis absorption spectra of compounds 7T and 11T in $CHCl_3$ solution and vacuum-evaporated films sublimed on a quartz substrate under high vacuum. Both 7T and 11T reveal two peaks in the solutions and films. There are $\alpha$, $\alpha$ and $\alpha$, $\beta$ linkages between thiophenes. The $\alpha$, $\alpha$ linkage provides the best $\pi$-electron conjugation, and the conjugation paths along the $\alpha$, $\beta$ linkage exist as additional chromophoric units.[32,33] So, an interesting conjugated effect will occur in these $x$-shape oligo(thiophene)s. The spectrum of the film of 7T shows a red shift of absorption maximum ($\lambda_{max}$) from 331 nm to 353 nm, and that of 11T shows a red shift of $\lambda_{max}$ from 381 nm to 394 nm. These phenomena can be attributed to the intermolecular interactions between the conjugated branches in films, which benefits charge transport.[21,34] Surprisingly, this effect was not observed for spin-coating films obtained at room temperature, of which the $\lambda_{max}$ was almost identical to that of the corresponding solutions.[26] That means that the vacuum-evaporated films will absorb more the longer wavelength light than the spin-coating films. There are also obvious spectrum broadenings of the films of 7T and 11T compared with ones of the solution. The red shift and the appearance of absorption broadening are typical of interacting $\pi$-systems with a preferential parallel orientation,[21,34] and both of them benefit light harvest in the application of solar cells. The longest conjugated lengths of the 7T and 11T by $\alpha$, $\alpha$ linkage oriented parallel to their substrates enhance the absorption cross section for the incident light.[21,25] Furthermore, the arrangements of the molecules increase the efficiency of charge transport through the cell thickness.[21,34] What is more, the absorption from solution to film of 7T is red-shifted by 22 nm, which is 9 nm more than that of 11T. This effect arises from the longer chains of 11T at $\alpha$, $\beta$ linkages which do not allow tight interactions in the solid film compared with 7T. X-ray analysis will clarify this point.

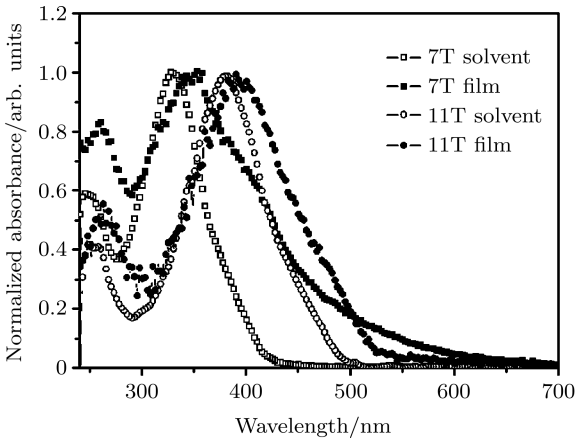



**Fig.2.** Normalized absorption spectra of compounds 7T and 11T in $CHCl_3$ and vacuum-evaporated films.

## 3.2. X-ray diffraction studies

Figure 3 shows the XRD spectra of the two compounds. The powder XRD analyses show a relatively broad peak for 11T and a random scatter for 7T, which demonstrates the gradually decreasing crystalline nature from 7T to 11T. The reason is that 11T has longer chains at the $\beta$ site which are prevented from more closely stacking, thus crystal growing is disturbed. The spectra of 7T and 11T films are almost the same.

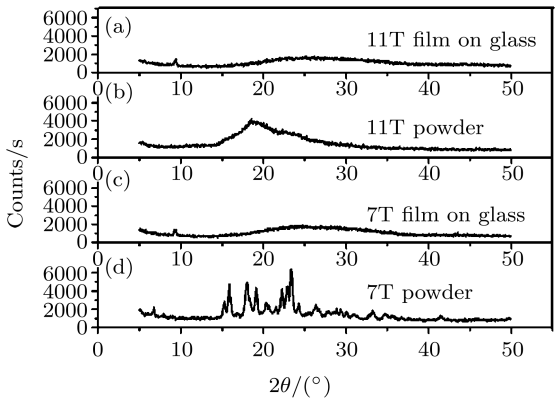



**Fig.3.** Comparison between XRD spectra of vacuum-evaporated films and powder.

The broad bands reveal that the two films are essentially amorphous. Such characteristic features are at-

tributed to the thiophene cycles by $\alpha$, $\beta$ linkage which are not coplanarized to the longest conjugated molecular plane by $\alpha$, $\alpha$ linkages. Hence close contacts among $\pi - \pi$ interacting groups are limited. The amorphous films will absorb more light and so have less reflection than the films with a lot of crystal planes, which is a major drawback of linear oligo(thiophene)s.[34]

## 3.3. Thermal analyses

The forming processes of the vacuum-evaporated films are closely related to the thermodynamic properties of the molecules, thus the two molecules are validated by DSC analysis. The DSC curves of the two oligomers are shown in Fig.4, indicating glass phase transitions ($T_g$) at 47°C and 63°C for 7T and 11T, respectively. There are two endothermic peaks at 205°C and 218°C on heating 7T, of which the later is the melting temperature ($T_m$). But no thermo process on cooling 7T or 11T is observed. That means that 7T and 11T manifest themselves amorphous structures in films, which is consistent with the XRD analysis. The DSC curve of 11T exhibits an endothermic peak at 214°C and an exothermic peak at 125°C on heating, but almost no thermo process occurs on cooling. Such a characteristic feature in the DSC curve indicates that a noncrystalline or semicrystalline morphology has formed on rapidly cooling a melted sample of 11T, but this amorphous state is unstable because of a strong tendency to crystallize on heating it to 125°C. Compared with 11T, 7T is adopted to form a stable amorphous film by evaporation.

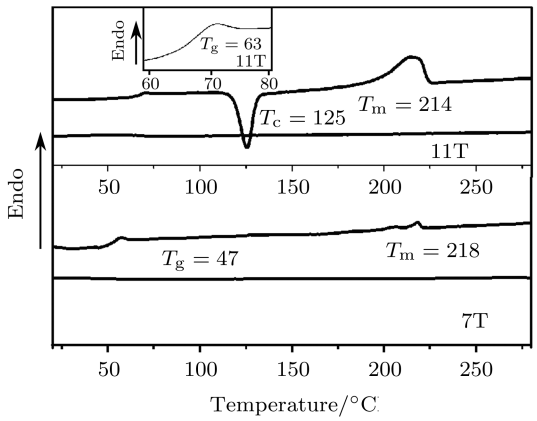



**Fig.4.** The DSC scans of the two oligomers.

## 3.4. Photocurrent spectroscopy

The photocurrent action spectra of the two types of solar cells (ITO/PEDOT-PSS/7T and 11T/EP-PTC/Al) have been measured separately (Fig.5). Both 7T cell and 11T cell have photocurrent actions that are consistent with the absorptions of the double active layers. It is indicated that the absorptions of donors and acceptors contribute to the photocurrent. The photocurrent spectrum of the cell based on 7T shows a main peak at 495 nm that corresponds to an absorption maximum of EP-PTC, and a peak at 338 nm that is attributed to the absorption of 7T. For 11T, the cell shows a photocurrent peak at 409 nm and another one at 495 nm and the former is higher than the later, in which region the absorption of the acceptor is predominant. Because the light passes through the donor layer before it arrives at the acceptor layer, the lower absorbance of 7T allows a direct photoexcitation of the EP-PTC layer. These results clearly show that the sublimed thin films of 7T and 11T make considerably different contributions to the photocurrents.

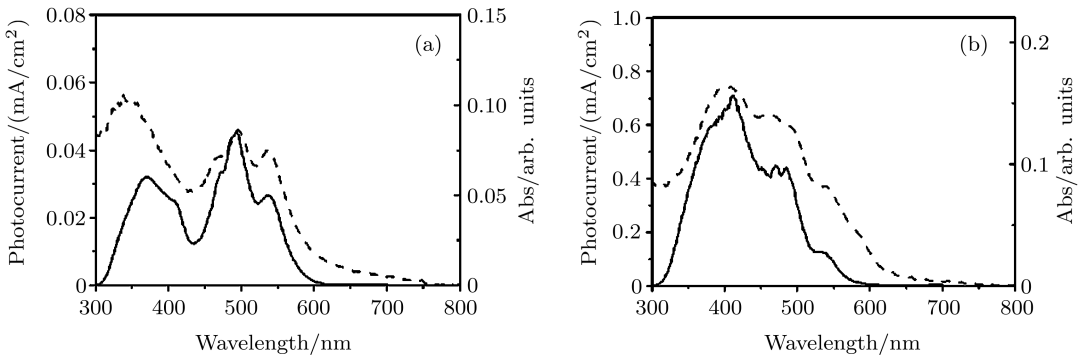



**Fig.5.** Photocurrent action spectra of the solar cells of 7T (a) and 11T (b), where the solid lines represent photocurrents and the dash lines refer to absorption spectra of the double active layers.

### 3.5. Current–voltage characteristics

Figure 6 shows the $I-V$ curves of the two cells under white light irradiation at 100 mW/cm$^2$. For the cell based on 7T, the $I-V$ curve recorded in the dark shows an onset of rectification beyond +0.85 V, while for the cell based on 11T the curve is nearly symmetrical. The cells based on 7T and 11T show $R_s$ and $R_{sh}$ to be 0.20 MΩ and 95.22 KΩ for 7T and 0.018 MΩ and 31.37 kΩ for 11T respectively. So the high series resistance ($R_s$) and low shunt resistance ($R_{sh}$) may cause an almost unchanged slope at negative voltage for the curve of both cells recorded under white light irradiation.

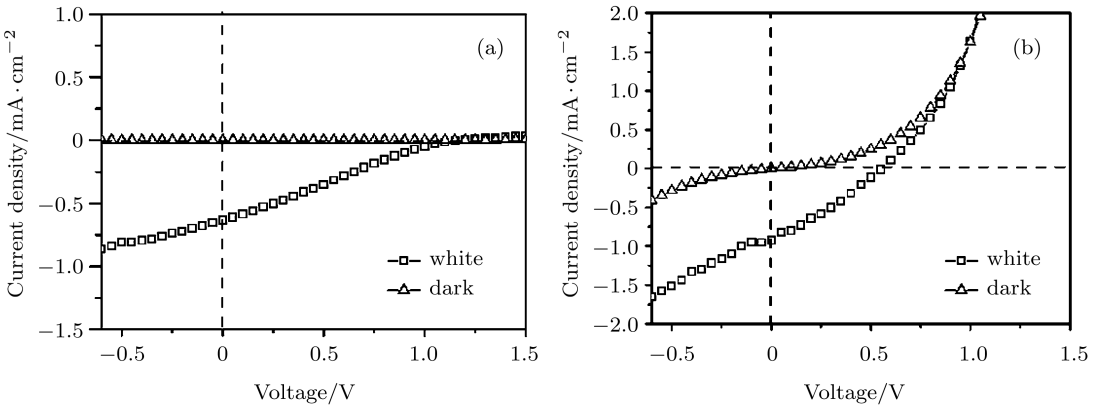



**Fig.6.** Current–voltage curves of bilayer cells of donors 7T (a), 11T (b) and EP-PTC.

The cell based on 7T delivers a short-circuit current ($I_{sc}$) of 0.63 mA · cm$^{-2}$ and an open-circuit voltage ($V_{oc}$) of 1.18 V. Their combining with a filling factor (FF) of 0.24 yields an energy conversion efficiency ($\eta$) of 0.18 %. The $I-V$ curve of the cell based on 11T reveals an increase of $I_{sc}$ to 0.93 mAcm$^{-2}$ but a decrease of $V_{oc}$ to 0.54 V. They together with a slightly better FF of 0.31 lead to an energy conversion efficiency of 0.16% (Table 1). In comparison with the device based on 7T, the device based on 11T has a high absorbance in a long wavelength range, which should be very important for achieving a higher $I_{sc}$, but it is expected to have a lower $V_{oc}$ for the higher HOMO energy levels. On the other hand, the cell of 11T has a low $R_{sh}$ which may cause a lower $V_{oc}$, and perhaps a low efficiency.

Roquet *et al*[24] have reported a reference cell realized by using H3T as a donor and *N*, *N*′-bistridecylperylenedicarboxyimide (DP13), which is similar to perylene, as an acceptor. H3T has a longest conjugated length similar to that of 7T, but no $\alpha$, $\beta$ linkage branches. The cell had the following results: $I_{sc} = 0.14$ mA · cm$^{-2}$, $V_{oc} = 0.76$ V and FF = 0.32 and $\eta = 0.04$%. A comparison between the reference cell based on H3T and the cell of 7T clearly indicates that the cell based on 3D donor 7T has higher values of $I_{sc}$, $V_{oc}$ and $\eta$ than the cell based on molecule without the $\alpha$, $\beta$ linkage branches, because the conjugated chain of the linear thiophene is oriented perpendicular to the substrate, but the longest conjugated length of 7T by $\alpha$, $\alpha$ linkage is oriented parallel to the substrate, which can enhance the absorption cross section for the incident light, and the arrangement of the molecules increases the efficiency of charge transport through the cell thickness.[21,34]

**Table 1.** Photovoltaic characteristics of the two-layer cells based on donors 7T[a)], 11T[a)] and H3T[b)].

| Device | $V_{oc}$/V | $I_{sc}$/mA · cm$^{-2}$ | FF | $\eta$/% |
|---|---|---|---|---|
| H3T/DP13 | 0.76 | 0.14 | 0.32 | 0.04 |
| 7T/EP-PTC | 1.18 | 0.63 | 0.24 | 0.18 |
| 11T/EP-PTC | 0.54 | 0.93 | 0.31 | 0.16 |

[a)] Under the white light irradiation at 100 mW · cm$^{-2}$.
[b)] Under the AM 1.5 simulated solar irradiation with 80 mW · cm$^{-2}$.

## 4. Conclusions

Two oligo(thiophene)s (7T and 11T) are evaporated in vacuum each as a donor and EP-PTC as an acceptor for solar cells. The vacuum-evaporated amorphous films of 7T and 11T are characterized by UV–Vis spectroscopy. Their results reveal the formation of a preferential parallel arrangement of the longest conjugated length by $\alpha$, $\alpha$ linkage to the substrate in films. XRD and DSC data for vacuum-sublimed

films are consistent with amorphous characters of the molecules. The amorphous architectures lead to a significant improvement on the photovoltaic performances. As a result, the device based on 7T achieves an energy conversion efficiency of 0.18%, which is better than that of the device based on linear molecular without $\alpha$, $\beta$ linkage branches.

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