Synthesis of Semiconducting Polymers Based on Oligothiophenes and Electron-Accepting Units for Application to Organic Solar Cells

（オリゴチオフェンと電子アクセプター部位を用いた半導体高分子の合成と有機薄膜太陽電池への応用）

張 羅正

1. Introduction

To achieve higher power conversion efficiency (PCE) in organic solar cells (OSCs), much effort has been devoted to molecular designs on the electron donor materials. As a typical donor polymer used in OSC, regioregular poly(3-hexylthiophene) (P3HT) combined with a fullerene derivative (PCBM) as the electron acceptor have shown relatively high PCEs and especially high fill factor (FF) owning to P3HT's high crystallinity and hole mobility. However, the narrow absorption band only up to 650 nm limits the further improvement of PCE. Use of donor-acceptor (D-A) type structure is the most frequently adopted strategy to achieve a low bandgap (LBG) property in the semiconducting polymers. This design consists of alternating connection of the electron donating and accepting monomer units. It shifts the absorption band of the polymer to a longer wavelength region due to the intramolecular charge transfer transition. However, the absorption in the short wavelength region is often sacrificed. Moreover, D-A alternating structures tend to lead to large torsions in the main chains, resulting in poorly ordered interchain packing in the films. This could cause reduction of the crystallinity and the hole mobility, which are detrimental to the performance of OSCs.

In this research, a new design concept for alternating copolymers is proposed for the application to OSCs: highly crystalline oligomers (D) connected by electron accepting units (A) (Fig. 1). This design should maintain the high crystallinity and hole mobility and at the same time induce the light absorption in the longer wavelength region by the D-A interaction. Original absorption from the oligomer blocks is also expected to be remained to some extent, depending on the block length. In this work, regioregular oligo(3-hexyl)thiophene (O3HT) was used as the crystalline electron-donating part since it can be synthesized by a chain growth polymerization in a precise manner.

Fig. 1. Schematic representation of the polymer design (top) and the two copolymers synthesized (bottom).

2. Synthesis and characterization of the copolymer

O3HT was synthesized by the Ni-catalyzed Grignard metathesis polymerization method (M_n = 4990 and M_w/M_n = 1.09), and its end groups were functionalized with trimethylstannyl groups or Br elements. The resulting O3HT was used as a macromonomer by linking with an electron-accepting unit 2,5-dialkyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DPP) (Fig. 1) through the Stille-coupling reaction. The resulting copolymer is denoted as O3HT-DPP.

GPC charts showed that M_n was increased by 3 times after the Stille-coupling, indicating that the D-A copolymer was successfully synthesized. NMR spectrum also confirmed the formation of O3HT-DPP. As shown in Fig. 2, the copolymer O3HT-DPP has a broader absorption in the visible region than P3HT. Different from traditional D-A
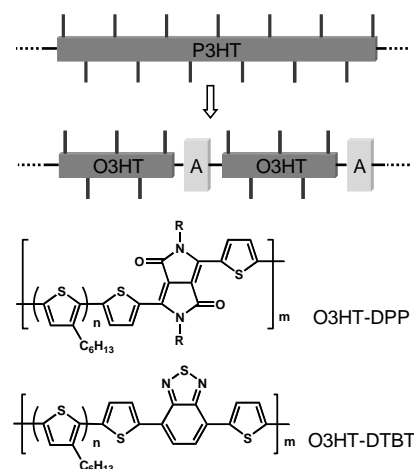
type copolymer, here the absorption band in the short wavelength region is not completely shifted to the long wavelength region, and the copolymer exhibits two absorption bands. This indicates that the excited states of the copolymer are localized in two places, one is in the oligomer part, and the other stays around the acceptor unit region. Therefore, the energy difference between the ground state and the excited state in the oligomer part is different from that in the acceptor unit region, resulting in a two-band light absorption.

In-plane and out-of-plane XRD patterns of the films show that O3HT-DPP films have a similar lamellar structure to that of P3HT, indicating that the introduction of DPP unit into the main chain of P3HT does not change the interlayer packing manner. The π-π stacking distances are 3.84 Å for P3HT and 3.78 Å for O3HT-DPP, indicating that the DPP unit in the backbone could possess a stronger stacking ability compared with P3HT. The enthalpies of fusion of P3HT and O3HT-DPP determined by DSC are about 19 and 14 J g^{-1}, respectively, implying that the doping of DPP unit might produce some structural defects.

Hole mobilities measured in FET devices are 0.04-0.06 and 0.16 $cm^2\,V^{-1}\,s^{-1}$ for O3HT-DPP and P3HT films, respectively. Although O3HT-DPP showed a lower mobility than that of P3HT, it is still one order of magnitude higher than that of regiorandom P3HT (typically 10^{-3}-10^{-4} $cm^2\,V^{-1}\,s^{-1}$) which possesses large structural disorder in the film. These results suggest that the introduction of DPP into the P3HT backbone has a less effect on the mobility, probably because of the strong interactions between the O3HT blocks in the polymer.

3. Solar cell based on the copolymer

OSC devices based on P3HT and O3HT-DPP were fabricated with the configuration of ITO/PEDOT:PSS/polymer:PCBM/Ca/Al. J-V curves under the irradiation of the simulated solar light (AM1.5, 100 mW cm^{-2}) are shown in Fig. 3. The main cause for the different PCEs should be from the change in short-circuit current density (J_{SC}).
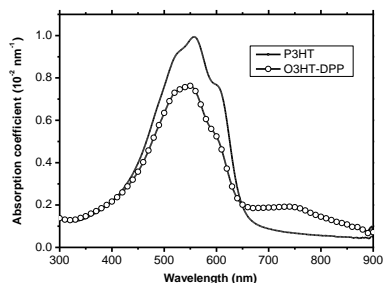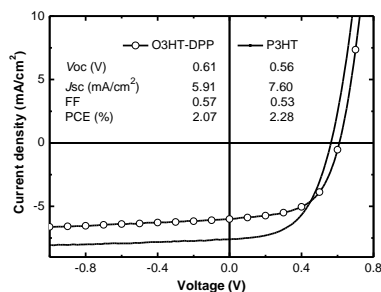
Fig. 2. UV-vis spectra of the polymer films.

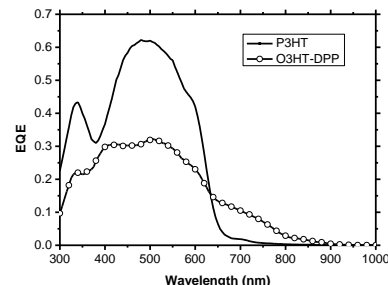Fig. 3. J-V curves of the OSCs based on P3HT and O3HT-DPP.

Fig. 4. EQE spectra of the OSCs based on P3HT and O3HT-DPP.

External quantum efficiency (EQE) spectra are shown in Fig. 4. As expected, the OSC based on O3HT-DPP has an extended light response up to 900 nm. However, the response in the short wavelength region is much lower than that of P3HT, even lower than expected from the reduction of the absorption coefficient. As observed in Fig. 1, O3HT-DPP is of a stepped structure, which may increase the interlayer lamellar distance in the film. XRD patterns showed that this distance was larger by 2% than that of P3HT. This enlarged distance may produce packing defects and thereby trap excitons and slow down the interlayer hopping process, weakening the photoresponse.

4. Effect of oligothiophene length

As can be seen in Fig. 2, the absorption of O3HT-DPP in the longer wavelength region is relatively weak, and this should due to the relatively low concentration of the doped acceptor unit. Since this concentration is related to the length of O3HT block, O3HTs with different lengths were synthesized in this section.

O3HTs with different M_n of 2410, 4040, 6750 were synthesized. O3HT-DPP copolymers synthesized from them (denoted as O3HT(S)-DPP, O3HT(M)-DPP and O3HT(L)-DPP) had M_n of 22200, 18550, 26550, respectively. UV-vis spectra of these copolymers show that the absorption can be enhanced in the longer wavelength region as the M_n of O3HT decreases, and a balanced light absorption can be obtained (Fig. 5).
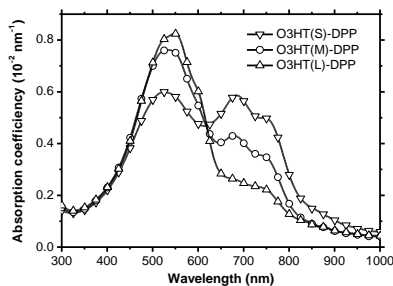

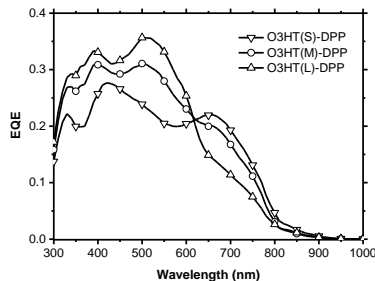Fig. 5. UV-Vis spectra of O3HT-DPP films with different M_n of O3HT.

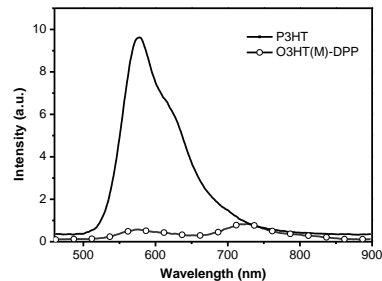Fig. 6. EQE spectra of OSCs with different M_n of O3HT.

Fig. 7. FL spectra of CHCl$_3$ solutions from O3HT(M)-DPP and P3HT.

The photovoltaic performance of these copolymers is listed in Table 1. The PCE variation can be partly reflected by the change of J_{SC} values. EQE spectra, which can generally account for the change of J_{SC}, display a similar trend with UV-vis spectra (Fig. 6). The J_{SC} values calculated from the EQE spectra and AM 1.5 solar spectrum are 5.85, 6.37 and 6.15 mA cm^{-2} for O3HT(S)-DPP, O3HT(M)-DPP and O3HT(L)-DPP, respectively, which are consistent with the changing trend of the experimental results.

Table 1. Photovoltaic performances of the OSCs based on O3HT-DPP with different lengths of O3HT.

	O3HT(S)-DPP	O3HT(M)-DPP	O3HT(L)-DPP	O3HT(M)-DPP[a]	O3HT(M)-DPP[b]	P3HT[a]
V_{OC} (V)	0.60	0.61	0.62	0.60	0.60	0.51
J_{SC} (mA/cm^2)	6.26	6.68	6.58	7.91	8.38	9.13
FF	0.62	0.67	0.66	0.67	0.68	0.68
PCE (%)	2.34	2.72	2.67	3.17	3.38	3.15

[a] Optimized devices using PCBM; [b] Optimized device using PC$_{71}$BM.

The OSCs based on O3HT(M)-DPP and P3HT were further optimized. The PCE of the O3HT(M)-DPP device was improved from 2.72 to 3.17%, which is comparable to that of P3HT device (3.15%); this value increased even higher to 3.38% when PC$_{71}$BM was used as acceptor material. This improvement mainly came from the increase in J_{SC} from 6.58 to 7.91 and 8.38 mA cm^{-2}. However, these J_{SC} values are still lower than that of P3HT device. EQE spectra of the optimized OSCs from O3HT(M)-DPP and P3HT are similar to those shown in Fig. 4. O3HT-DPPs could have somewhat lower hole mobility than P3HT (section 2), which might be a reason for this difference in EQE. This mobility shortage could make the charge transport inefficient, and smaller FFs should be observed as a result. On the contrary, the FFs of OSC based on O3HT-DPP (0.67-0.68) are comparable to this from P3HT, which may rule out the possibility that the lower hole mobility of O3HT-DPP is the main factor to reduce EQE response.

As mentioned before, there could be two excited states with different energy levels coexisting in the copolymer backbone. Thus, an intrachain energy transfer from the O3HT block to the vicinity of DPP unit may occur. As shown in Fig. 7 (λ_{ex}=450 nm), O3HT(M)-DPP solution shows a very weak fluorescence (FL) at 580 nm originating from O3HT excited states, and the appearance of a new band around 725 nm could be assigned to the FL from the excited states in the vicinity of DPP unit. These results suggest that the intrachain energy transfer

could be one of the reasons for the decrease in EQE response below 650 nm. This directional energy transfer process could be advantageous to collect the excitons efficiently in OSCs if more efficient charge transfer to PCBM can be achieved at the vicinity of the electron accepting units.

5. Copolymer with a superior acceptor unit

To reduce the impacts caused by the reasons discussed in section 3 and 4, a collinear copolymer based on O3HT and 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (DTBT) will be investigated. Copolymer O3HT-DTBT shares the same length of O3HT as O3HT-DPP in section 3.

Although the light absorbance in the longer wavelength region is not as obvious as the case for O3HT-DPP, O3HT-DTBT film exhibits an extended absorption in the short wavelength region, thus a broader absorption band relative to P3HT (Fig. 8). In addition, O3HT-DTBT shows a bandgap between the values of P3HT and O3HT-DPP. XRD patterns show that O3HT-DTBT has almost the same lattice parameters as P3HT, suggesting that the introduction of DTBT unit has a much weaker influence on the intermolecular packing than that from DPP. Thermal stability measurement presents that the enthalpies of fusion turns to be 18 J g^{-1}, much closer to that of P3HT, revealing that introducing DTBT into the main chain has little effect on the crystallinity of polythiophene. These results could be attributed to DTBT's collinear shape that has little disturbance to the lamellar structure.
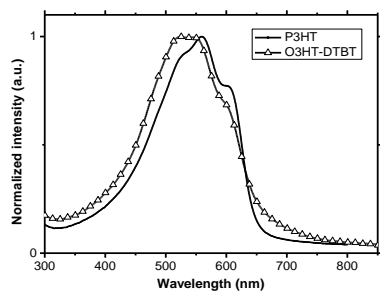

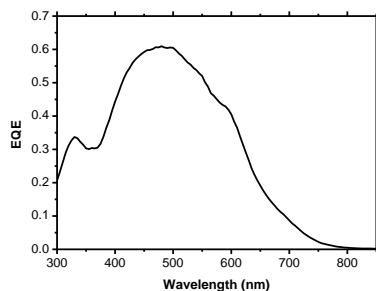Fig. 8. UV-vis spectra of O3HT-DTBT film.
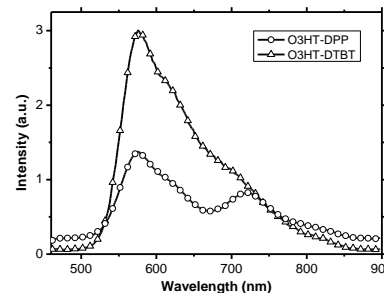

Fig. 9. EQE spectra of O3HT-DTBT based OSC.

Fig. 10. Fluorescence spectra of the polymer solutions in CHCl$_3$.

OSC based on O3HT-DTBT displays an increased PCE of up to 2.5% (relative to 2.07% for O3HT-DPP in section 3. V_{OC} = 0.60 V, J_{SC} = 7.30 mA/cm^2, FF = 0.57). EQE spectrum shows that the maximum response at 500 nm is as high as 60%, indicating that the introduction of DTBT unit lead to the less reduction of EQE than that observed in O3HT-DPP (Fig. 9). Similar to O3HT-DPP, O3HT-DTBT solution also exhibits a fluorescence band in the long wavelength region (Fig. 10, λ_{ex} = 450 nm). It can thus be deduced that intrachain energy transfer may be a common phenomenon for our design concept. Compared with O3HT-DPP, O3HT-DTBT shows a similar V_{OC}, suggesting that the HOMO level of the copolymer doesn't change obviously. However, the bandgap becomes larger and a shallower LUMO level for O3HT-DTBT. This could result in an efficient charge transfer to PCBM, and the energy transferred to the acceptor unit could be more effectively used in O3HT-DTBT device.

As shown in Fig. 9, a linear backbone and an efficient charge transfer to PCBM from the acceptor unit region, the EQE response in the short wavelength region could be enhanced.

6. Summary

In this research, a novel strategy was designed and was demonstrated to be able to provide the copolymer with both broad light absorption and high charge transport ability when regioregular O3HT was used as the oligomer part. It is shown that the choice on the acceptor units significantly influences the photovoltaic properties of the copolymer. Proper acceptor units with little impact on the interchain packing and an efficient charge transferring ability would lead to the rational design of the superior semiconducting polymer for OSC application.