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High performance quinacridone-based polymers in film transistors and photovoltaics: effect of vinylene linkage on crystallinity and morphology

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A novel quinacridone-based polymer containing vinylene linkage, PQTE, was synthesized and exhibited higher performance both in organic thin-film transistor and solar cell than that of the reference polymer PQ2T. Introducing the vinylene linkage, strong interchain interaction is obtained with short π–π stacking distance of 3.49 Å in polymer PQTE, which is responsible for the highest mobility of 0.67 cm² V⁻¹ s⁻¹ reported to date for quinacridone-based semiconductors. More significantly, the incorporation of thienylene-vinylene-thienylene unit contributes to good miscibility between PQTE and PC71BM. Because of the effective intercalation of PC71BM in the PQTE lamellar structure, high power conversion efficiency of 3.9% was achieved without any additives or post-treatments. Our rational molecular design qualifies quinacridone as a promising building block simultaneously in high performance polymer thin-film transistor and solar cell.

Introduction

Recent interests in polymer semiconductors are motivated by their potential application in large-area and roll-to-roll organic electronics like organic thin-film transistors (OTFT) and organic photovoltaics (OPV). Molecular engineering of polymers allows for the adjustment of photo/electrochemical properties, solubility, packing, morphology of thin film and thus achievement of high performance. The common structural feature of these polymer semiconductors is alternating electron-rich (donor) and electron-deficient (acceptor) units linked along polymer chains. Over the years, great efforts have been given to the search of efficient donor or acceptor units and the combination between these units. Impressive power conversion efficiency (PCE) of >8% in OPV and remarkable mobility of >10 cm² V⁻¹ s⁻¹ in OTFT have been achieved by incorporating attractive units, such as benzodithiophene, diketopyrrolopyrrole, benzo diazole, isoindigo and arylene diimides, etc. Among these remarkable works on OPV devices, cosolvents, small-molecule additives, and post-treatments, such as thermal annealing and solvent-vapour annealing, have been proved useful strategies to improve microstructure of blend films. Unfavourably, these additional processes increase fabrication cost and are unable to fulfill commercial requirements. Therefore, the development of new building blocks with excellent properties both in photonics and electronics, as well as a simple fabrication process, is still a major challenge for material chemists.

Recently, we have paid much attention to the quinacridone (QA) units. It is a five-ring planar structure and widely used as the magenta toner with excellent stability. That the nitrogen atoms can be functionalized with alkyl groups make it possible using in photoelectrical devices via solution processibility. However, to the best of our knowledge, only numerable works are reported in the field of OTFT and OPV using in photoelectrical devices via solution processibility. Herein, we firstly introduce vinylene linkage into QA-containing polymer, namely PQTE. In view of its rigid and transconfiguration, thienylene-vinylene-thienylene in polymer PQTE is expected to result in much planar configuration and strong interchain interaction. For
comparison, polymer PQ2T containing QA and bithiophene was also synthesized. As a result, the introduction of vinylene linkage improves not only the crystallinity of thin films but also the miscibility with PC71BM. In OTFTs, PQTE film exhibited a short π-π stacking distance of 3.49 Å and high mobility up to 0.67 cm² V⁻¹ s⁻¹. In solar cell, as donor material, PQTE exhibited PCE up to 3.9% because of the better miscibility with PC71BM than that of PQ2T though PQTE showed stronger intramolecular interaction. It is noteworthy that the PCE of PQTE is among the highest performance for QA-based polymers even though these devices were fabricated without any additives or post-treatments.

Results and discussion

Synthesis and characterization

The synthetic routes of two polymers are shown in Scheme 1. Monomer QA2Br was synthesized according to our previous work. The Stille-coupling reaction between monomer QA2Br and (E)-1,2-bis(5-(trimethylstannyl)thiophene-2-yl)ethene afforded polymer PQTE, while monomer QA2Br reacted with 5,5′-bis(trimethylstannyl)-2,2′-bithiophene via same reaction conditions obtained polymer PQ2T for comparison. Both of polymers are purified by successive Soxhlet extractions. More detailed descriptions of the synthesis are available in the experimental section. Two polymers have almost identical number-average molecular weight \( M_n = 20.60 \text{ kDa for PQTE} \) and \( M_n = 20.11 \text{ kDa for PQ2T} \) with very low polydispersity indexes (PDI) close to 1, as shown in Table 1, Fig. S1† and Fig. S2†. Two polymers showed very good thermal stability which were determined by thermogravimetric analysis (TGA). PQTE showed lower decomposition temperature \( T_d \) of 405.3 °C while PQ2T exhibited a higher \( T_d \) up to 436.3 °C (Fig. S3†). Differential scanning calorimetry (DSC) was employed to investigate the thermal transition of polymers. No obvious thermal transition peak was observed in the range of 25-300 °C for two polymers before decomposition, which is probably attributed to the rigid backbone limiting the chain motion.

Optical and electronic properties

The absorption spectra of two polymers both in dilute chloroform solution and in solid state are show in Fig. 1 and relevant data are summarized in Table 1. Compared with PQ2T, PQTE showed red-shift absorption both in solution and thin film owing to extended π-conjugation induced by integration of vinylene linkage. For PQ2T, the maximum absorption peak was featureless and no obvious spectral shift was observed in solid state compared with that in dilute solution, indicating the polymer might form pre-aggregates in solution. In the case of polymer PQTE, the maximum absorption profile was significantly sharper and there was a prominent shoulder peak at longer wavelength (~499 nm). Moreover, the shoulder peak became much finer and stronger in thin film, which demonstrates that vinylene linkage in PQTE lead to much strongly aggregate in solid state. However, a slightly bathochromic shift (~10 nm) was observed going from solution to thin film for PQTE which was also observed in other polymers. Density-functional theory (DFT, B3LYP/6-31G) was performed to model the electron density distributions of two trimers, as shown in Fig. S4. From their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), we can observe that QA unit exhibited weak electro-deficient character and HOMO is not delocalized over the whole backbone. This is consistent with the fact that the weak shoulder peaks at around 550-630 nm can be attributed to intramolecular charge transfer (ICT). Because of weak electro-deficient character of quinacridone unit, the reduction curves cannot be determined, only oxidation curve are provided in Fig. 1b. The HOMO levels of PQTE and PQ2T calculated from the
onset oxidation potential are almost identical (-5.3 eV) and approximated work function of gold. This indicates that hole injection will be easy from the gold electrode to polymers. Using their optical band gaps, the LUMO levels are calculated to be -3.38 eV and -3.28 eV for PQTE and PQ2T, respectively. Similar HOMO and LUMO energy levels indicate the incorporation of vinylene linkage cannot significantly influence the electrochemical properties of polymers.

OFET properties

To probe how the incorporation of vinylene linkage affects the charge transport of PQTE, bottom-gate/top-contact transistors were fabricated with channel length of 30 µm and channel width of 500 µm. The insulator was 300 nm SiO2 layer passivated with octyltrichlorosilane (OTS). Polymer solution was heated and stirred at 80 °C for 5 hours before spin-coated on the substrate. The film thickness was about 35440 nm. All films were annealed at 150 °C for 30 min. Au was used as source and drain electrodes by vacuum deposition. Fig. 2 shows the typical output and transfer curves of FETs based on two polymers. Carrier transport performances are summarized in Table 1. PQTE based FETs exhibit a maximum hole mobility as high as 0.67 cm2 V-1 s-1 with the average value of 0.54 cm2 V-1 s-1 and high on/off ratio (Ion/Ioff) of 106-107. This value is the highest mobility reported so far for quinacridone-based polymers. For PQ2T-based FETs, the highest mobility is calculated to be 0.30 cm2 V-1 s-1 with the average value of 0.28 cm2 V-1 s-1 and Ion/Ioff of 106-107, which is slightly higher than reported value by Kazuo Takimiya group. We attribute this enhancement to the lower PDI of PQ2T in our work. Smaller threshold voltages (Vth) are also observed for PQTE devices (-9.8 V) than those of PQ2T devices (-12.0 V). The high mobility and low Vth of TFTs based on PQTE are perhaps due to the preferable orientation of PQTE film.

Ordering structure of OFET film

To shed light on the structural effect by introduction of vinylene linkage into PQTE, geometry optimization and molecular ordering were determined by DFT and two-dimensional grazing incidence X-ray diffraction (2D-GIXRD), respectively. The dihedral angle in PQTE trimers is slightly smaller than that of PQ2T trimmers suggesting better coplanar structure in PQTE (Fig. S4). Comparing the XRD pattern of two polymer films, as shown in Fig. 3, both polymer PQTE and PQ2T show (00) diffractions up to the fourth order indicating these polymers are long-range-ordered. However, large arcing diffraction of PQ2T suggested that there is no preferential orientation in the film which is consistent with the reference 19. In contrast, the film of PQTE shows much centralized points along qy axis and distinctly observable (010) diffraction along qx axis. The results indicate that the film of PQTE formed preferentially ordered edge-on orientation on the substrate. The lamellar distances calculated from the out of plane pattern (Fig. 3c and Table S1) are 21.6 Å and 22.7 Å for PQTE and PQ2T, respectively. Shorter lamellar distance of PQTE means that alkyl chains are packed more intensely between adjacent polymer chains than those of PQ2T. From in plane pattern, PQTE shows strong (010) reflection peak corresponding to π-π stacking distance of 3.49 Å which is one of the shortest distances for polymers containing QA unit.

### Table 1 Molecular weights, optical properties, and energy levels of PQTE and PQ2T

<table>
<thead>
<tr>
<th>polymer</th>
<th>Mn (kDa)</th>
<th>PDI</th>
<th>T_d (°C)</th>
<th>λ_{max} (nm)</th>
<th>HOMO* (eV)</th>
<th>LUMO* (eV)</th>
<th>E_g (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PQTE</td>
<td>20.60</td>
<td>1.15</td>
<td>405.3</td>
<td>481,499,576</td>
<td>-5.26</td>
<td>-3.38</td>
<td>1.88</td>
</tr>
<tr>
<td>PQ2T</td>
<td>20.11</td>
<td>1.13</td>
<td>436.3</td>
<td>471,497,574</td>
<td>-5.25</td>
<td>-3.28</td>
<td>1.97</td>
</tr>
</tbody>
</table>

*Calculated from cyclic voltammetry curves. * Determined by LUMO = HOMO + E_g. † Determined from the onset of the thin-film absorption.

### Table 2 Charge transport properties of PQTE and PQ2T

<table>
<thead>
<tr>
<th>polymer</th>
<th>μh (cm2 V-1 s-1)</th>
<th>Ion/Ioff</th>
<th>Vth (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PQTE</td>
<td>0.67 ± 0.09</td>
<td>106-107</td>
<td>-9.8</td>
</tr>
<tr>
<td>PQ2T</td>
<td>0.30 ± 0.02</td>
<td>106-107</td>
<td>-12.0</td>
</tr>
</tbody>
</table>

Maximum and average mobilities are collected from more than 10 devices.

![Graph](image-url)
PQ2T film, weak (010) reflection peak could be observed in the out of plane with the corresponding π-π stacking distance of 3.59 Å. Moreover, the presence of (h00) peaks corresponding to lamellar structure further confirms that both face-on and edge-on orientations exist in this polymer film. Tapping-mode atomic force microscopy (AFM) further demonstrated the difference of morphology between two polymers (Fig. S5). PQTE film exhibit uniform intertwined fibre structures with obviously crystalline zones, which is the result of strong intermolecular interaction. In contrast, PQ2T film shows nodule-like morphology with relatively loose packed grains. According to the result mentioned above, it is confirmed that the insert of vinylene linkage shortens the π-π stacking distance of adjacent polymer chains because of good planarity and extended π-conjugation of vinylene linkage. Strong interchain interaction improves the crystallinity of PQTE film. These observations are in good agreement with the mobility analysis.

Solar cell properties
Bulk heterojunction solar cells were fabricated by employing PQTE or PQ2T as an electron donor and PC71BM as an electron acceptor. The typical device configuration is ITO/PEDOT:PSS/polymer:PC71BM/Ca/Al. J–V curves of the optimized photovoltaic devices are shown in Fig. 4a and the external quantum efficiency (EQE) spectra are displayed in Fig. 4b. The solar cell parameters are collected in Table 3 and Table S2. The optimum polymer:PC71BM ratio was found to be 1:2. The blend solution was spun coated in chlorobenzene at 1000 rpm for 30 s. The thickness of active layer is about 100-115 nm. Note that no processing additives were used at the time of spin coating. Even without any post-treatment, the highest PCE for PQTE was 3.90% with a Jsc of 9.74 mA cm⁻², a Voc of 0.73 V and a modest FF of 55%. For PQ2T, the devices exhibited a moderate PCE of 2.71% with a slightly increase in Voc (0.74 V) and FF (56%) but lower Jsc of 6.95 mA cm⁻² compared with PQTE-based devices. It is noteworthy that PCE of 3.90% is among the highest efficiency reported for quinacridone-based polymers via simple device architecture without any additives or post-treatments, which are unique properties of PQTE. In Fig. 4b, high photo-to-current responses were obtained in the range from 350 to 600 nm for two polymer/PC71BM blend films. For PQTE-based devices, the higher response verified higher Jsc value which supports the results from J–V characteristics. Additively, the results of AFM images (Fig. S6) reveal that the grains in PQTE/PC71BM blend film are fairly homogeneous in

**Table 3 Photovoltaic properties of solar cells based on polymer/PC71BM**

<table>
<thead>
<tr>
<th>polymer</th>
<th>Voc (V)</th>
<th>Jsc (mA cm⁻²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PQTE</td>
<td>0.73</td>
<td>9.74</td>
<td>55</td>
<td>3.90 (3.79±0.09)</td>
</tr>
<tr>
<td>PQ2T</td>
<td>0.74</td>
<td>6.95</td>
<td>56</td>
<td>2.71 (2.62±0.12)</td>
</tr>
</tbody>
</table>

| a) The weight ratio of polymer to PC71BM is 1:2. | b) The value out of brackets represents maximum PCE; The value in brackets represents average values of PCE collected more than 10 devices.

Film morphology and microstructure in solar cell
The morphology of active layers was examined by bright field transmission electron microscopy (TEM) and AFM, respectively. In Fig. 5a, well distributed nano-fibrillar structures are observed in PQTE/PC71BM blend film. This interpenetrating network is beneficial for charge dissociation. For PQTE-based device, macrophase separation limits the probability of exciton dissociation leading to poor Jsc (Fig. 5b). Additively, the results of AFM images (Fig. S6) reveal that the grains in PQTE/PC71BM blend film are fairly homogeneous in
We synthesized a novel quinacridone-based polymer, PQTE, containing thiophene-vinylene-thiophene unit. PQ2T without vinylene linkage was also synthesized for comparison. As a result, the incorporation of vinylene linkage can efficiently shorten π-π stacking distance and improve the crystallinity of thin film. In TFTs, strong intermolecular interaction of PQTE enhances the charge carrier mobility up to 0.67 cm² V⁻¹ s⁻¹. In solar cell, high PCE of 3.9% was obtained by using PQTE as donor and PC₇₀BM as acceptor while PQ2T-based devices showed moderate PCE of 2.70%. It is noteworthy that high PCE were obtained without any additives or post-treatments. Better miscibility was observed in PQTE/PC₇₀BM blend film compared with that of PQ2T/PC₇₀BM blend film although strong interchain interaction existed in polymer PQTE. We suppose that good intercalation of PC₇₀BM into the lamellar structure of PQTE responsible for this high PCE. Our findings indicate that rational molecular modification makes quinacridone to be a promising building block applied in high-performance optoelectronic devices.

Experimental section

Materials and synthesis

5,5’-Bis(trimethylstannyl)-2,2’-bithiophene and (E)-1,2-bis(5-(trimethylstannyl)thiophene-2-yl)ethene were purchased from Suna Tech Inc. and without further purification. All other chemicals were purchased from Aldich and used as received. Number-average and weight-average were determined by gel permeation chromatography (GPC) on a Waters 515 chromatograph connected to a Waters 2410 refractive index detector, using THF as eluent and polystyrene standards as calibrants. Thermogravimetric analysis (TGA) measurements were recorded by Shimadzu thermogravimetric analyzer (model DTG-60) under a nitrogen flow, heating from room temperature to 800 °C, with a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) analyses were performed on a METTLER TOLEDO Instrument with DSC822 calorimeter. UV-vis absorption spectra were measured on a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer. Cyclicvoltammetric experiments were carried out in a conventional three-electrode cell consisting of a platinum working electrode coated with a thin film layer of polymer, a platinum wire auxiliary electrode, and an Ag/AgCl reference electrode with ferrocenium–ferrocene (Fc⁺–Fc) as the internal standard. Tetrabutylammoniumhexafluorophosphate (TBAPF₆) (0.1 M) was used as the supporting electrolyte. Atom force microscopy (AFM) was investigated by Brucker Multimode 8 using tapping mode with a scan speed of 1 Hz. Transmission electron microscopy (TEM) was performed on a JEM-2100 operated at 100 kV. Grazing incidence X-ray diffraction (GIXRD) data were obtained at 1W1A, Beijing Synchrotron Radiation Facility. The films were illuminated at a constant incidence angle of 0.2° (λ = 2dsinθ = 1.5464 Å).

Synthesis of PQTE. Monomer QA2Br (150 mg, 0.131 mmol) and (E)-1,2-bis(5-(trimethylstannyl)thiophene-2-yl)ethene (68...
mg, 0.131 mmol) were added into a Schlenk tube and subsequently dissolved in 6 mL degassed chlorobenzene. The solution degassed before Pd$_2$(dba)$_3$ (2.4 mg, 0.003 mmol) and P(o-tol)$_3$ (6.4 mg, 0.021 mmol) were added. The reaction mixture was further degassed and subsequently sealed. The solution was heated and stirred at 130 °C for 48 h. After cooling to room temperature, the mixture was added to vigorously stirred methanol and filtered. The resulting precipitate was purified by Soxhlet extraction successively with methanol, acetone, hexane, and finally with chloroform, and then precipitated in methanol again. The polymer PQTE was obtained as purple solids (167 mg, 78%).

**Synthesis of PQ2T.** The similar procedure as described above was used to synthesize PQ2T (171 mg, 80%).

**General procedure for devices fabrication**

**OFET devices fabrication and characterization.** Bottom-gate/top-contact FET devices were fabricated on SiO$_2$/Si substrates. First, the substrates were cleaned and treated with octadecyltrichlorosilane (OTS). Polymer solution in chlorobenzene (6 mg mL$^{-1}$) was spin coated at a speed of 2000 rpm for 50 s to obtain film with thickness of ~35 nm. The samples were further placed on a hot plate at 150 °C in N$_2$ for 30 min. Gold source and drain electrodes (60 nm) were deposited by vacuum evaporation on the organic layer through a shadow mask. The channel length ($L$) and width ($W$) were 30 µm and 500 µm, respectively. OFETs were determined at room temperature in air by using a Keithley 4200 SCS (semiconductor characterization system). The mobility of the OTFTs in the saturation region was extracted from the following equation: $I_{DS}=C_i(W/2L)(V_G-V_T)^2$, where $I_{DS}$ is the drain current, $C_i$ is the capacitance of the SiO$_2$ dielectric layer ($C_i=10$ nF cm$^{-2}$), $\mu$ is field-effect hole mobility, $V_G$ and $V_T$ are the gate voltage and threshold voltage, respectively.

**OPV devices fabrication and characterization.** For conventional devices of ITO/PEDOT:PSS/polymer/PC$_7$BM/Ca/Al, the ITO substrates were cleaned and exposed to a 30 min UV/O$_3$ treatment, and then PEDOT:PSS (2000 rpm for 30 min) was spin-coated and followed by a thermal annealing treatment at 150 °C for 15 min. After cooling to room temperature, the chlorobenzene solution of polymer/PC$_7$BM mixture was spin-coated at a speed of 1000 rpm for 30 s. Then Ca/Al cathode was successively deposited on photoactive layer by vacuum evaporation (20 nm/80 nm). The current-voltage ($J-V$) characteristics of the devices were measured by using a Keithley 2400 Source Measure Unit. The measurements were conducted under the irradiation of AM 1.5 G, 100 mW cm$^{-2}$. EQE measurements were carried out on an oriel IQE 200 (Newport).

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**Notes and references**


