



Narrow bandgap semiconducting polymers for solar cells with near-infrared photo response and low energy loss



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ARTICLE INFO

Article history:

Received 26 April 2017

Revised 16 June 2017

Accepted 19 June 2017

Available online 19 June 2017

Keywords:

Polymer solar cell

Energy loss

Diketopyrrolopyrrole

Band gap

ABSTRACT

The alternating diketopyrrolopyrrole (DPP)-Quinoxaline (Qx) based conjugated polymers are synthesized and investigated as electron donors for polymer solar cells (PSCs). Through the substitution of phenyl in Qx unit at para (*p*) and meta (*m*) positions with methoxy group, the resultant DPP-*p*MQx and DPP-*m*MQx polymers possess narrow optical band gap (1.32 and 1.26 eV) with relatively low-lying highest occupied molecular orbitals. The obtained photovoltaic devices indicate that the combination of DPP with weak acceptor Qx is helpful to develop narrow bandgap polymers with near-infrared photo response and low energy loss (0.58 eV for DPP-*m*MQx) in PSC devices.

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Introduction

Polymeric semiconducting materials in thin film bulk-heterojunction (BHJ) polymer solar cells (PSCs) have attracted much attention of researchers over the past decade. It is because that they have great potentials to enable low cost, flexible and light weight photovoltaic devices through massive solution fabrication.^{1–5} Polymeric backbones comprise of the covalently and alternatively flanked electron rich and electron deficient units, which offer the structural design flexibilities in developing polymers with wide range of optoelectronic tunabilities.^{6,7} As results, the joint efforts in polymer development, along with device and interface innovation have drastically raised the power conversion efficiencies (PCEs) of PSCs,^{8–13} now surpassing 12%.^{14,15}

Among these, diketopyrrolopyrrole (DPP)-based polymers revealed ambipolar charge transport characteristics, which allow acting as either electron donors or acceptors.^{16–25} More interestingly, DPP-based polymers yielded PCEs over 9% in PSCs,²⁶ with the assistance of attractive properties of DPP moieties, such as strong absorption, facile synthesis, high mobility and compatibility of blending with fullerene acceptors.^{27–30} It is interesting to note that the previous polymer design is generally to flank DPP moieties with electron rich units, which leads DPP-polymer to have relatively high-lying highest occupied molecular orbitals (HOMOs) and narrow optical bandgap. In the search of new polymeric materials, we paid consideration that Quinoxaline (Qx) is a distinct elec-

tron deficient building block with remarkable optoelectronic properties.^{31–34} In the meanwhile, Qx can be easily engineered to host various side chains, aromatic and functional groups, etc.³⁵

Considering PSCs, one of the influential factors is the energy loss (E_{loss}), which is the open-circuit voltage (V_{oc}) value abstracted from optical band gap ($E_{\text{g opt}}$). Such factor reduces the overall device efficiency of PSC when compared to perovskite solar cells.^{36–40} Literature clarifies that the E_{loss} is typically 0.7–1.0 eV in efficient PSCs while it is less than 0.5 eV for perovskite solar cells. Thus, to enhance the PCE of PSCs, attentions are paid to explore new polymeric materials, which can reduce the E_{loss} of PSC to obtain high V_{oc} , as well as keep a high quantum efficiency for charge generation.^{37,41}

Herein, we design two narrow bandgap polymers based on DPP and Qx moieties, named as DPP-*p*MQx (para methoxy quinoxaline) and DPP-*m*MQx (meta methoxy quinoxaline), wherein the DPP is connected to electron deficient Qx moieties. These two new semiconducting polymers show PCEs of 3.21% (DPP-*p*MQx) and 2.87% (DPP-*m*MQx) in conventional PSC devices with phenyl- C_{71} -butyric acid methyl ester (PC₇₁BM) acceptor. A relative low E_{loss} of 0.58 eV is obtained in this system (DPP-*m*MQx, $E_{\text{g}} = 1.26$ eV) among the DPP-based polymer and fullerene blends.

Experimental sections

Materials and methods

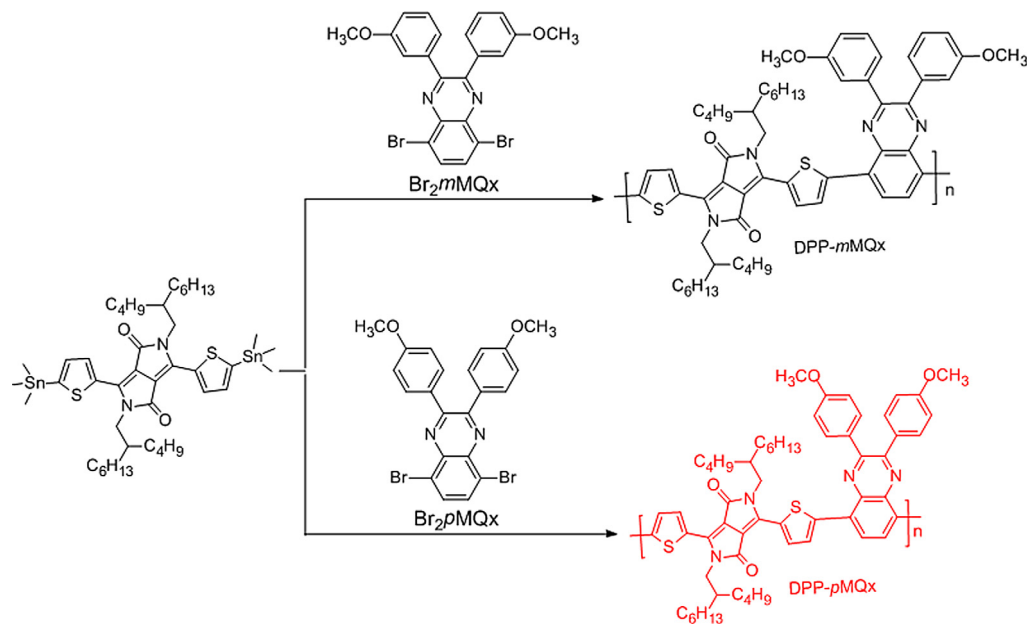
All reactions are carried out under Ar inert atmosphere. Common solvents are dried by standard procedures. 1,8-Diiodooctane

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and *o*-dichlorobenzene are purchased from Sigma-Aldrich. Column chromatography is performed with the use of silica gel 200–300 mesh. 2,5-Bis(2-butyltolyl)-3,6-bis(5-(trimethylstannyl)thiophen-

2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (C4,8-DPP-Sn) is purchased from J&K chemical company. Monomers, 5,8-dibromo-2,3-bis(4-methoxyphenyl)Quinoxaline (Br_2pMQx) and 5,8-



Scheme 1. Synthetic scheme of polymers, DPP-*p*MQx and DPP-*m*MQx. Still cross-coupling polymerization is performed with $\text{Pd}_2(\text{dba})_3$ as a catalyst and $\text{P}(\text{o-tolyl})_3$ ligand in toluene at 110 °C.

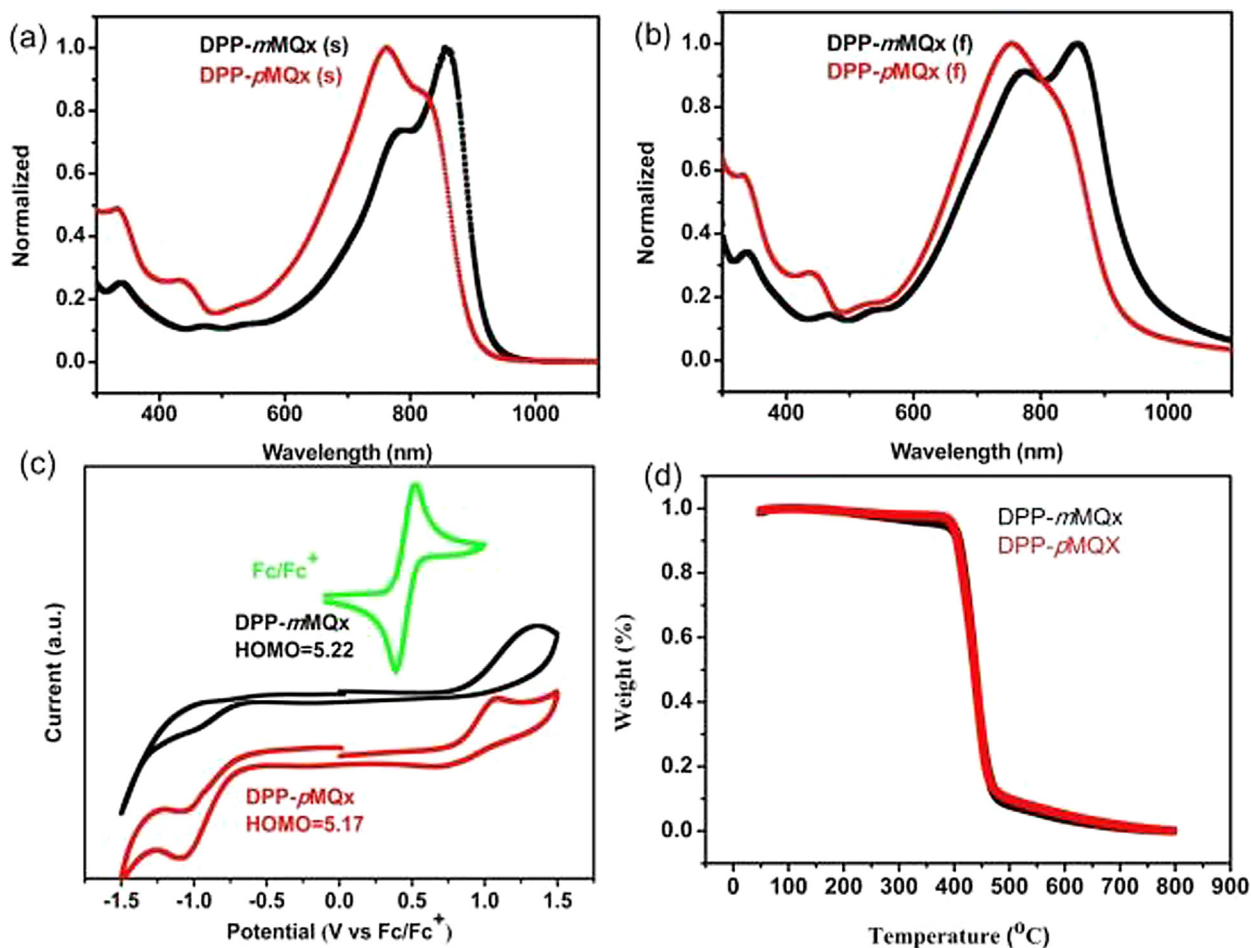


Fig. 1. Normalized UV-vis absorption spectra of the polymers in chloroform solutions and in solid films on quartz: (a) solution, (b) film, (c) CV, and (d) TGA.

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