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Effect of electron-withdrawing side chain modifications on the optical properties of thiophene–quinoxaline acceptor based polymers

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ABSTRACT

Four new thiophene–quinoxaline acceptor based polymers have been synthesized. The parent thiophene–quinoxaline acceptor based copolymer was modified by introducing different electron-withdrawing groups adjacent to the thiophene side group. The effect on the physical, electrochemical and optical properties of the polymer series is discussed with respect to the parent thiophene–quinoxaline acceptor based polymer. The side chain carbonyl from one modified monomer could conveniently be transformed to either a difluoromethylene or an -ylidene malononitrile group via carbonyl transformations. For all polymers incorporating an electron-withdrawing side group both the HOMO and especially the LUMO were significantly shifted away from vacuum while all exhibit enhanced light harvesting ability. Especially the incorporation of an -ylidine malononitrile side group increases both the spectral coverage and absorption coefficient. Incorporation of a difluoromethylene side group resulted in a twofold increase of the molecular weight compared to the parent polymer structure.

1. Introduction

During the past few decades a vast number of conjugated polymers has been developed and various chemical modifications are used to engineer and optimize the physical and optoelectronic properties that suit their specific purpose [1,2]. Common tools that are employed to finetune the bandgap and energy level alignment of conjugated polymers are the donor–acceptor approach and electron donating or accepting side groups, while side chains with different nature regarding length and branching are mostly employed to influence solubility and solid state packing.

One particularly promising conjugated polymer is poly[2,3-bis(3-(octyloxy)phenyl)quinoxaline-alt-thiophene] (TQ-1), which offers good photovoltaic performance (PV) (6% maximum power point) as well as ease of synthesis [3]. The optical bandgap of TQ-1 is 1.7 eV while a bandgap of 1.4 eV was calculated to be most optimal for photovoltaic performance [4]. Therefore, chemical modifications that pursue a combination of redshifting the optical absorption while retaining a deep highest occupied molecular orbital (HOMO) have the potential to improve the PV performance in the future. The established route to achieve these modifications is to alter the chemical structure of the backbone. For instance, in case of TQ1 we have modified acceptor strengths to establish this combination of effects. More particularly, the acceptor strength was enhanced using a pyridopyrazine-based acceptor which led to both a redshift in absorption and a deeper HOMO level [5].

Recently, several groups have shown that an absorption redshift was obtained upon substituting pendent phenyl with thiophene groups. Upon substituting phenyl for thiophene rings in an otherwise identical small molecule or polymer, a redshift in absorption of already 30–50 nm was achieved. Other large differences between phenyl and thiophene substituted materials are observed in properties such as improved on–off voltages, decreased electron/hole mobilities in field-effect transistors (FET) and optical contrast in electrochemical switching devices, and vastly different aggregation behavior [6–9]. We expect that, upon replacing the pendent m-octyloxyphenyl side groups of TQ-1 by 5-octylthiophene rings (**compound 8**, Scheme 1), this modification will result in a redshifted absorption induced by both incorporating a unit that itself has a smaller energy gap and increased polymer planarity.

However, substitutions with stronger electron-donating groups, in this case thiophene, usually lead to a shift of the polymers highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) towards vacuum. We chose to address this problem by introducing electron-withdrawing side groups

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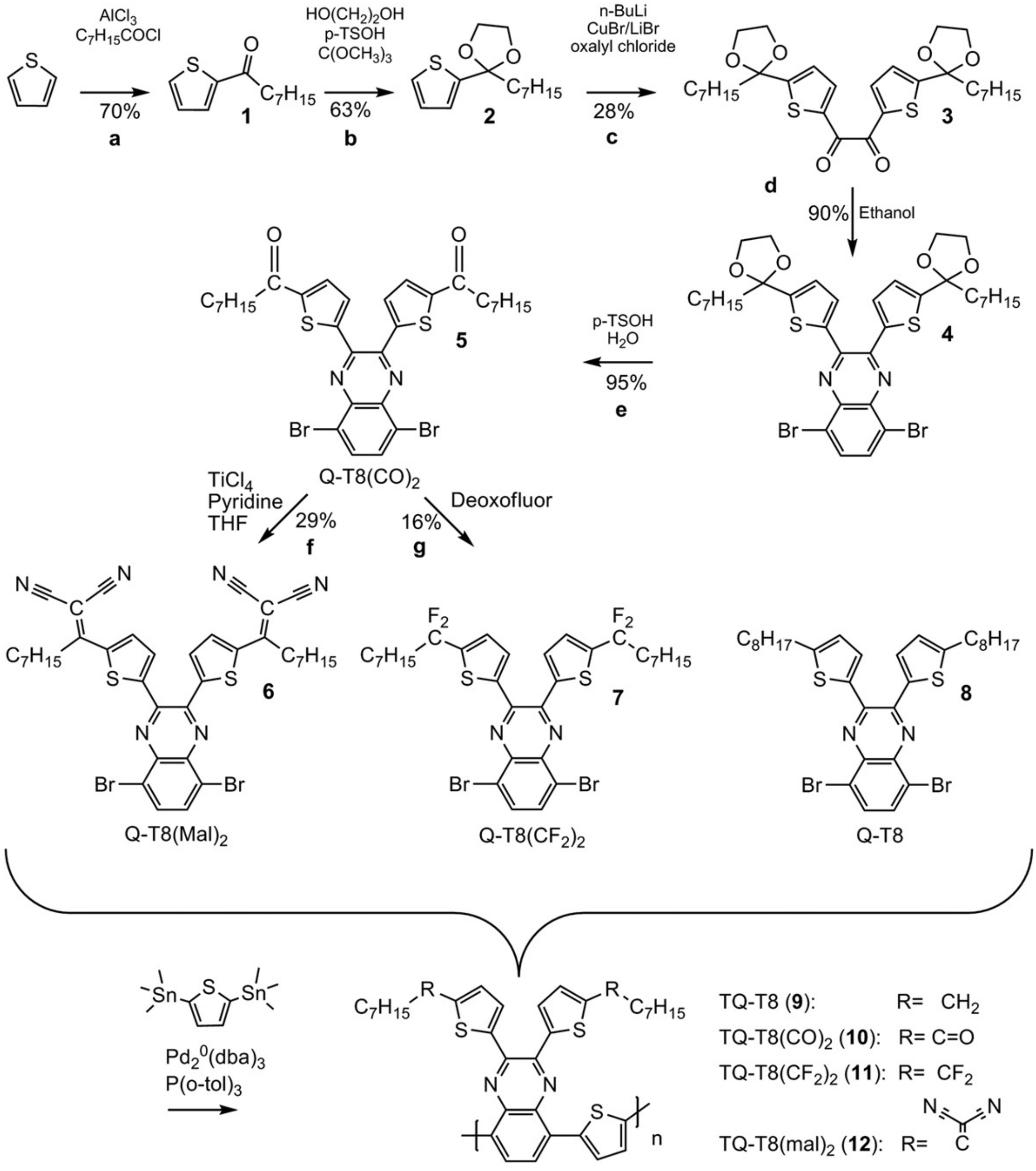

Scheme 1. Synthetic route of monomers and polymers. Experimental details can be found in the SI.

adjacent to the thiophene. In this communication, we demonstrate that this approach permits to mitigate the electron-donating effect of the thiophene which is of benefit for a number of applications such as improving photovoltaic performance by increasing the maximum V_{oc} of a material or to influence the injection barriers in light emitting diodes or FET [10,11].

We chose to substitute the methylene flanking the thiophene with three different functional groups that are known for their strong electron-withdrawing effect; carbonyl, difluoromethylene and -ylidine malononitrile. Choosing the carbonyl as a functional group has the additional advantage of being the precursor for the other two functional groups. These substitutions readjust the energy levels of the polymer away from vacuum and push the absorption edge even further to the near IR. Another advantage from incorporating the malononitrile moiety, and to a lesser extent the carbonyl, is the resulting extended conjugated system perpendicular to the backbone, which has been reported to lead to stronger or broader light absorption compared to their unsubstituted counterparts [12–14].

2. Experimental details and characterization methods

Experimental details and characterization methods are supplied in the Electronic Supplementary material.

3. Results and discussion

The resulting dibromo-2,3-bis(5-octylthiophen-2-yl)quinoxaline monomer was polymerized with bis(2,5-trimethylstannyl) thiophene by Stille polymerization which resulted in the