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Molecular electron-acceptors based on benzodithiophene for organic photovoltaics

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ABSTRACT

Two extended conjugated molecules potentially active as electron-acceptor materials for organic solar cells have been synthesized by grafting the electron-withdrawing dicyanovinyl (**1**) and *p*-cyano pyridyl (**2**) groups on the rigid and planar benzodithiophene (BDT) platform. UV–Vis spectroscopy shows that both compounds absorb in the visible region of the solar spectrum. Cyclic voltammetry indicates that only compound **1** presents a LUMO level comparable to that of fullerene C_{60}. A preliminary evaluation of the potentialities of compound **1** as an electron-acceptor has been carried out on 'all-molecular' solution-processed bulk hetero-junction solar cells using a small triphenylamine-based system as the molecular donor. In spite of a high open-circuit voltage, the devices present a modest efficiency indicating that the light-harvesting properties and charge-mobility of the acceptor-molecules need further structural optimization.

Introduction

Organic photovoltaics (OPV) is the focus of high current interest motivated by the technological opportunities offered by the low-cost, lightness, plasticity and flexibility of organic materials.[1,2] An OPV cell basically involves a heterojunction (HJ) created by interfacing an electron-donor material (D) with an electron acceptor (A).[3] D/A hetero-junctions can be fabricated by contacting layers of D and A materials to form a planar hetero-junction (PHJ), or by creating interpenetrated networks of D and A to produce a bulk hetero-junction (BHJ).[1,2,4] Although soluble conjugated polymers have been for a long time the major class of donor materials for solution-processed BHJ,[1,2,4–6] their inherent polydispersity can pose problems of reproducibility of the composition and properties of the final material. In this context, molecular donors have gained increasing interest as a possible alternative based on the advantages of well-defined chemical structures in terms of synthesis, purification and analysis of structure–property relationships.[7–12] In fact, power conversion efficiencies (PCE) comparable to those obtained with the best polymer cells have recently been reported for BHJs based on molecular donors.[10,11]

Compared to the huge amount of work devoted to the synthesis of donor materials, the design of electron-acceptors has attracted less attention. Although perylene derivatives have been used as electron-acceptors in early work on vacuum-deposited PHJ cells,[3,13–15] the discovery of efficient photo-induced electron transfer from conjugated polymers to fullerene C_{60},[16] has established fullerenes as the standard class of acceptor materials for OPV cells.[1,2,4,12]

However, in spite of their interesting acceptor properties and efficient electron-transport, fullerenes also present some important limitations. On the one hand, due to their wide band gap they absorb only a small part of the solar irradiation spectrum. On the other hand, their energy levels are poorly tunable by molecular engineering. Since the open-circuit voltage (V_{oc}) of OPV cells primarily depends on the difference between the HOMO and LUMO levels of the donor and acceptor materials, respectively,[17] the quasi-fixed LUMO level of fullerenes imposes further constraints to the design of donor materials. In recent years various classes of non-fullerene molecular systems have been synthesized and evaluated as acceptor material in OPV cells[18] such as vinazenes,[19] small bridged systems associated with dicyanovinyl-benzothiadiazole,[20,21] naphtalene-diimides,[22] or perylene-diimides (PDI).[23] Although high conversion efficiencies have been reported for cells involving acceptors based on PDI dimers and highly efficient low band gap polymers, these PDI dimers are rather large and complex molecular systems[23,24] In our continuing interest in the simplification of the structure and synthesis of active OPV materials,[12] we report here our first attempts to develop new molecular acceptors using benzodithiophene (BDT) as the starting platform. BDT was introduced by Liang and Yu some years ago as an important

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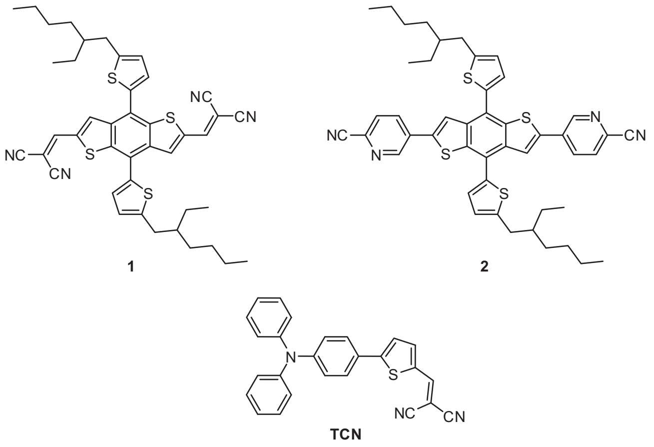
building block for the design of highly efficient low band gap polymers for OPV.[6] This block combines a planar rigid board-like core favorable to pi-stacking with the possibility to design 2D structures, as already exemplified in the case of molecular donors.[9,10]

In this work the dicyanovinyl and the cyanopyridine electron-withdrawing groups have been grafted at the free α-positions of the fused thiophenes of BDT while two thienyl rings 2-substituted by ethylhexyl chains have been introduced on both sides of the molecule in order to ensure the solubility of the final compounds (Scheme 1).

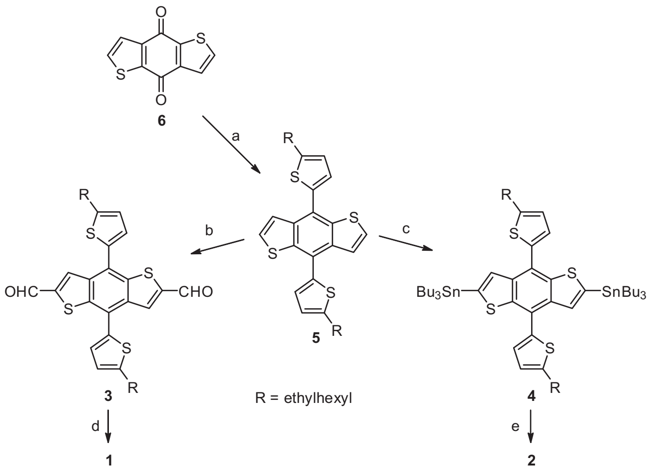
We describe the synthesis of the target molecules, the characterization of their electronic properties by UV–Vis spectroscopy and cyclic voltammetry and a preliminary evaluation of the potential of one of these compounds as electron-acceptor material in an 'all-molecular' BHJ cell using a triphenylamine-based push-pull molecule (TCN) as donor.[25]

Results and discussion

The synthesis of the target compounds **1** and **2** is shown in Scheme 2. 4,8-dihydrobenzo[1,2-b:4,5-b′]dithiophene-4,8-dione (**6**) was synthesized in three steps from 3-thiophene acetic acid according to a known method.[26] The bis-thienyl-substituted benzodithiophene **5** was then prepared by the addition of lithiated 2-(2-ethylhexyl)thiophene on dione **6** in THF [28]. The tributyltin derivative **4** and the dialdehyde **3** were obtained by deprotonation of **5** with *n*-BuLi at −78 °C and subsequent quenching of the lithiated intermediate with tributyltin chloride and dimethylformamide, respectively.



Scheme 1. Structure of the target acceptors (1, 2) and donor compound (TCN).



Scheme 2. Synthesis of the target compounds **1** and **2**. Reagents and conditions: (a) *n*-BuLi, 2-(2-ethylhexyl)thiophene/THF; (b) *n*-BuLi, THF, 0 °C, DMF; (c) *n*-BuLi, Bu$_3$SnCl; (d) malonodinitrile, Bu4NOH/CHCl$_3$; (e) 5-bromo-2-cyanopyridine, Pd(PPh$_3$)$_4$/toluene.

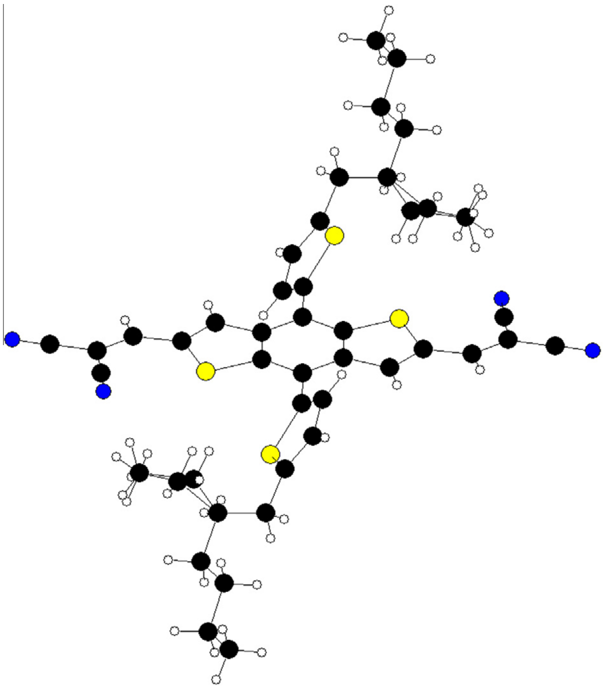


Figure 1. Crystallographic structure of compound **1**.

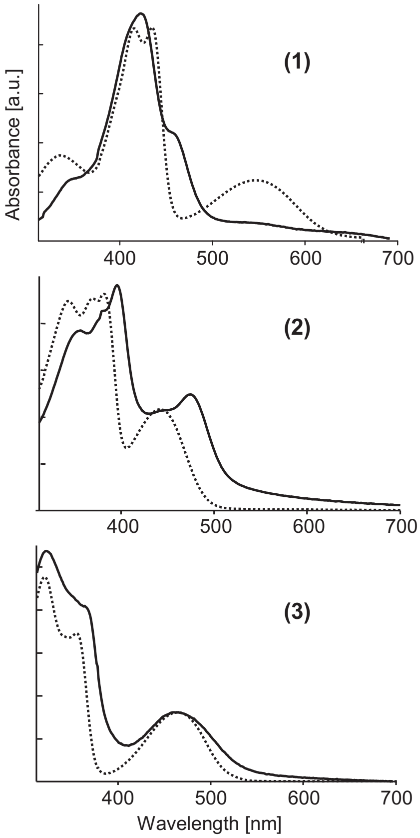


Figure 2. Normalized UV–Vis absorption spectra of compounds **1**–**3**. Dotted lines: in methylene chloride solution, solid lines: as thin films spin-cast on glass from chloroform solutions.