Tetrahedron 65 (2009) 5209–5215

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis and properties of acceptor–donor–acceptor molecules based on oligothiophenes with tunable and low band gap

Yongsheng Liu, Jiaoyan Zhou, Xiangjian Wan, Yongsheng Chen *

Key Laboratory for Functional Polymer Materials and Centre for Nanoscale Science and Technology, Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China

ARTICLE INFO

Article history:
Received 24 February 2009
Received in revised form 24 April 2009
Accepted 28 April 2009
Available online 6 May 2009

Keywords:
Oligothiophene
Donor–acceptor
Low band gap

ABSTRACT

A series of acceptor–donor–acceptor molecules (**DCN3T**, **DCN5T** and **DCN7T**) based on oligothiophenes with low band gap are synthesized. The UV–vis absorption spectra of solution show that the introduction of electron-accepting groups results in a shift of the absorption onset towards longer wavelengths. Moreover, the optical spectra of their films show a large bathochromic shift and broadening of the bands with respect to the spectra in solution. The optical band gaps of film of these A–D–A molecules are 1.90, 1.74 and 1.68 eV, respectively. Cyclic voltammetry shows that all these compounds present a reversible first oxidation process whose potential decreases with the lengthening of oligothiophene cores. Electrochemical band gaps are 2.14, 1.88 and 1.71 eV, respectively.

1. Introduction

Currently, thiophene-based π-conjugated oligomers have been widely used in optoelectronic devices such as field-effect transistors,[1–3] light emitting diodes[4,5] and photovoltaic devices.[6,7] The advantages of oligomers are that finite-size systems can be obtained with high purity and a well-defined chemical structure, thus offers the advantages to investigate the relationship between the chemical structures with device performance by changing the number of thiophene rings and/or chemical modifications or substitutions.[8–11] Oligothiophenes possess extensive π-electron delocalization along the molecular backbone and are well known as high hole-transporting materials. Dipolar push–pull chromophores with a highly polarizable π-electron systems involving a donor group and an acceptor group, have been widely investigated for their nonlinear optical[12–15] and other optoelectronic properties.[16–19] These properties result from the existence of a photoinduced intramolecular charge transfer at relatively low energies, which depends on the efficiency of the π-electron delocalization along the conjugated systems and the electron donating and accepting capability.[20–22]

Dicyanovinyl group has strong electron-accepting properties and its double bond can also participate in the conjugation of the whole backbone π-system and lead to efficient intermolecular interactions. Some dicyanovinyl substituted oligothiophenes have been synthesized and used for solar cells,[23–26] but the relationship of their properties with the number of units (length) of oligothiophenes for this class is rarely studied.[27]

In this paper, we report the synthesis of a series of dicyanovinyl endcapped π-conjugated oligothiophenes (Fig. 1) with low and tunable band gap, and investigate their thermal, optical and electrochemical properties. The characterization of various acceptor–donor–acceptor (A–D–A) molecules based on oligothiophenes has led to a clear understanding, at a molecular level, of the structure–property relationships in this new class of materials.

2. Results and discussion

The synthesis of the target molecules is depicted in Scheme 1. The starting materials, 2-bromo-3-octylthiophene, 2-(3-octylthienyl)magnesium bromide and 3,3″-dioctyl-2,2′:5′,2″-terthiophene **1**, were synthesized according to the literature.[28] Terthiophene **1** and quinquethiophene **3** were brominated with NBS in $CHCl_3$–AcOH at 0 °C to give the corresponding brominated derivative **2** and **4**. For the nickel-catalyzed Kumada cross-coupling reaction,[29] diethyl ether was used as solvent and $Ni(dppp)Cl_2$ was used as the catalyst. For a better yield, an excess of 3.0 equiv of 2-(3-octylthienyl)magnesium bromide was used when reacted with dibromoterthiophene **2** under reflux conditions, which gave a 83% yield of oligothiophene **3** as a golden oil. Using the same method, septithiophene **5** was obtained as a brick red solid in 72% yield. Diformyl oligothiophenes, **6**, **7** and **8**, were prepared similarly by utilizing Vilsmeier–Haack reaction.[23,30,31] Finally, the target molecules **DCN3T**, **DCN5T** and **DCN7T** were obtained by Knoevenagel condensation[23–25,32] of malononitrile with the corresponding aldehydes.

---

* Corresponding author. Tel.: +86 22 23500693; fax: +86 22 23499992.
E-mail address: yschen99@nankai.edu.cn (Y. Chen).

0040-4020/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2009.04.089

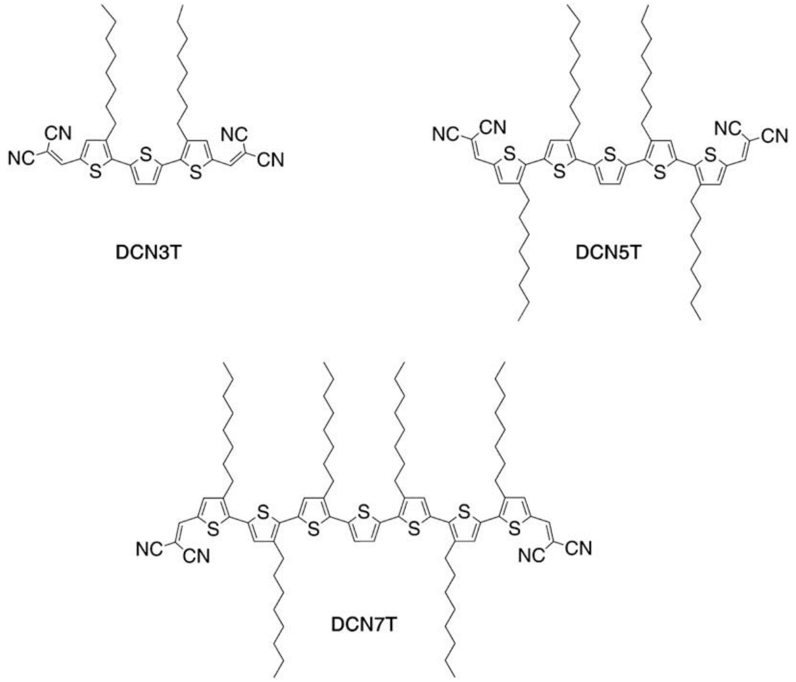

Figure 1. Chemical structures of **DCN3T**, **DCN5T** and **DCN7T**.

The thermal behaviours of A–D–A molecules were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen. TGA analysis revealed that these three A–D–A molecules exhibited an onset degradation temperature above 200 °C under nitrogen. DSC analysis (Fig. 2) revealed that **DCN3T**, **DCN5T** and **DCN7T** had different melting peaks, which were 135, 152 and 168 °C, respectively. It is interesting to point out that only **DCN7T** among these three dicyanovinyl-substituted oliogothiophenes exhibited a glass transition temperatures (T_g) ($\sim$89 °C) during DSC analysis, which is believed due to the increasing length of the oligomers.

The absorption spectra of **DCN3T**, **DCN5T** and **DCN7T** in $CHCl_3$ solution are displayed in Figure 3, and the corresponding data are presented in Table 1. For comparison purposes between dicyanovinyl-substituted and unsubstituted analogues, the absorption spectra of **3T**, **5T** and **7T** are also included in Figure 3, and the corresponding data are also presented in Table 1. The absorption spectra show that the absorption peaks of the oligothiophene cores are gradually red-shifted to longer wavelengths with increasing number of thiophene units. This can be rationalized by better intermolecular π–π interaction with expanding π-conjugation size. Two prominent absorption features were observed in the spectra of all the A–D–A molecules: a lower intensity band in the 488–517 nm range and a higher intensity band in the 304–403 nm range. In all molecules, the lowest-energy peaks have larger extinction coefficients (ε) compared to that of the high-energy peak. The high-energy absorption bands are associated with the π–π^* transitions of the oligothiophene cores. Meanwhile, the lowest-energy absorption band can be assigned to the intramolecular charge transfer (ICT) between the aromatic ring donor part and the acceptor end groups.[18,23,24,33] Compared with unsubstituted oligothiophenes, **DCN3T**, **DCN5T** and **DCN7T** exhibit a rather large bathochromic shift (151, 126 and 107 nm, respectively) of the absorption maximum, which is attributed to the introduction of electron-accepting dicyanovinyl end groups, leading to a conjugated A–D–A system.

Thin films of the **DCN3T**, **DCN5T** and **DCN7T** were obtained by spin-coating of corresponding $CHCl_3$ solutions (c=8 mg mL^{-1}) onto a glass substrate. For a comparison purpose, the absorption spectra data of thin film of oligomer **7T** is also presented in Table 1. Oligomers **3T** and **5T** are oil at room temperature, and their thin films spectra were not measured. Absorption spectra in the solid state (Fig. 4) show the same trends and compared to the solution spectra, and in general, a broadening and bathochromic shift of the bands are visible. The overall spectra show a clear red-shift with increasing the units of the oligomers. As in solution, the lowest-energy absorption band in the solid state is of charge-transfer character. Compared with solution absorption spectra, the absorption maxima of film of **DCN3T**, **DCN5T** and **DCN7T** exhibit a large bathochromic shift, which is 107, 138 and 144 nm, respectively. Optical band gaps (Table 1) in solution and solid state were approximated by extrapolation of the low energy edge of each absorption spectra.[34] The optical band gaps of film of these A–D–A molecules are 1.90, 1.74 and 1.68 eV, respectively. The results show that the optical band gaps decrease with increasing units of oligomers. The wide and strong absorption of the longer members, **DCN5T** and **DCN7T** in the series, covering a broad range of the visible spectra (400–900 nm), has important implications in particular for their applications in photovoltaic devices. Because of the strong intermolecular interaction between π-electrons in the solid state, we ascribe this broadening and bathochromic shift of the bands to the coplanarization of the conjugated systems and a formation of more ordered packing in the film state as observed in many other cases.[25,26] It is important to note that the thin film in the absorption spectra of A–D–A molecules shows a sub/shoulder peak structure at longer wavelength, suggesting a vibronic progression. This is commonly understood in terms of a rigid coplanarization of the conjugated systems enforced by the crystal packing.[26,35]

Fluorescence emission spectra for the whole series of compounds were measured in chloroform (Fig. 5), and the corresponding data are presented in Table 1. The A–D–A molecules exhibit less structured and broader emission bands whose maxima absorptions with respect to the unsubstituted analogues are significantly shifted to the red due to the electron-accepting nature of the end groups. For the A–D–A molecules, the intensity of the emission bands decreased with the enlargement of the conjugated backbone, while the pure unsubstituted oligothiophenes show