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Synthesis and photovoltaic properties of mono-substituted quaterthiophenes bearing strong electron-withdrawing group

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Abstract

We report here on the synthesis and properties of a monosubstituted quaterthiophene derivative asymmetrically functionalized by an electron-withdrawing group using the palladium-catalyzed Stille's coupling reaction. The UV–vis absorption spectrum evidences a strong intramolecular charge transfer transition. Thus oligothiophenes act as electron donors and substituent group as acceptor. The diodes in which monosubstituted quaterthiophenes behave as organic semiconductors, exhibit a rectifying behavior. Photovoltaic measurements show moderate power conversion efficiency.

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1. Introduction

The design and synthesis of complex materials operating highly specialized functions present academic interest and open the way towards molecular electronic

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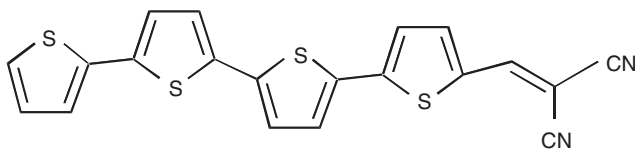


Fig. 1. Hemical structure of dicyanovinyl-quaterthiophene.

devices. Among these materials, conjugated oligomers and polymers have attracted considerable interest over the past ten years because of their low dimensionality and their unique optical and electrical properties [1]. The driving forces behind the design and synthesis of these materials are their applications as active layer in electronic and molecular devices, such as electroluminescence and photovoltaic devices [2]. The photovoltaic effect has been investigated extensively in polythiophenes, oligothiophenes and their derivatives, but these materials have low conversion efficiencies due to poor photoinduced charge separation [3]. Different approaches have been developed to improve the photoinduced charge separation in organic photovoltaic devices. One of the most successful approaches consists in preparing donor–acceptor composite materials. For example, when fullerene C_{60} is blended in conjugated polymers such as poly (*p*-phenylenevinylene) or polythiophene, a net charge transfer occurs between both components under light irradiation [4]. This is because C_{60} acts as an electron-acceptor while the polymer acts as an electron-donor. These composite materials thus meet all requirements for photovoltaic (PV) conversion. Such devices show highly efficient photovoltaic performance. Donor–acceptor conjugated oligomers which exhibit charge dissymmetry and show charge transfer transition in the ground state have been synthesized their optical and electro-optical properties have been investigated [5]. However, no studies have been reported the use of such materials in photovoltaic devices.

In this work, first we report on a new synthetic strategy towards oligothiophenes asymmetrically functionalized by a single electron-withdrawing group, in such structure oligothiophenes act as electron donors and substituent group as acceptor. Secondly, we report on the electrooptical and photovoltaic properties of dicyanovinyl-quaterthiophene $4TV(CN)_2$ as a typical example of this series (see Fig. 1). These molecules possess a permanent dipole moment and show a strong intramolecular charge transfer transition in the UV–visible region.

2. Results and discussions

The general methodology for the synthesis of these quaterthiophenes is shown in Scheme 1. The starting material are 5-trimethyltin 2-2' bithiophene and 5-bromo-5'-formyl-2-2' bithiophene which are monoaldehyde synthesized as follows. 2-2' bithiophene was lithiated with BuLi at -70°C followed by transmetalation with trimethyltin chloride at -70°C , 5-trimethyltin 2-2' bithiophene was isolated in 80% yield by distillation. The formylation of the 2-2' bithiophene leads to 5-formyl-2-2'

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