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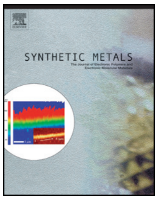

Effect of the ethynylene linker on the properties and carrier mobility of naphthalene derivatives with hexylbithienyl arms

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ABSTRACT

A series of new naphthalene derivatives with (5′-hexyl-2,2′-bithiophene-5-yl)ethynyl side arms attached to the central naphthalene core at positions 1 and 4 (**H2TA14N**), 1 and 5 (**H2TA15N**), and 2 and 6 (**H2TA26N**) were synthesized by a sequencing of alkynylations performed according to a Negishi cross-coupling protocol. This synthetic approach provides higher yields compared to Sonogashira-based alkynylations, particularly when aryl bromides are used as starting materials. Compared to the analogous derivatives with hexylbithienyl arms directly attached to the naphthalene core (**H2T14N**,**H2T15N**, and **H2T26N**), an ethynylene linker ensures the planarity of the molecules, causing a change in the order of derivatives by intramolecular conjugation from **H2T15N** < **H2T14N** < **H2T26N** to **H2TA15N** ≈ **H2TA26N** < **H2TA14N**, as can be seen from the solution, and thin film optical and electrochemical properties as well. However, the order of derivatives by the hole mobility in a field effect transistor remains unaltered by an ethynylene linker (**H2TA14N** < **H2TA15N** < **H2TA26N**). The tendency in charge mobility can be explained by different packing motifs affected by molecular symmetry and was revealed by single crystal X-ray analysis and 2D X-ray GIWAXS and AFM characterization of the thin films.

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1. Introduction

One of the major research areas of organic semiconducting materials is focused on their design, synthesis and application in organic field effect transistors (OFETs) [1–6]. The continuously growing interest in OFETs is the result of an extensive investigation which has revealed the possibility of manufacturing low-cost large area and flexible circuits with a broad range of potential applications [7–14]. Moreover, material properties can be tuned by chemical modification of the molecular structure [15–19]. However, the relationship between the structure and properties of these materials in the field of organic electronics is challenging, as it is still far from trivial.

An important class of semiconductor materials for OFETs are oligothiophene-based compounds [20–26] due to their stability, possibility of well-defined chemical functionalization [27–29] and ability to form tightly stacked structures [30]. One especially common molecular setup of oligothiophene derivatives is represented by those containing thienyl or oligothienyl units directly attached to a central acene core (Fig. 1a) [31–48]. Although oligothienyl units themselves are planar, such derivatives are usually non-planar due to steric repulsion between hydrogen atoms neighboring on the linkage between the acene core and the adjacent thiophene ring. Therefore, the degree of twist between these adjacent aromatic rings primarily depends on the spatial position of the hydrogen atom at the acene core. It has been shown

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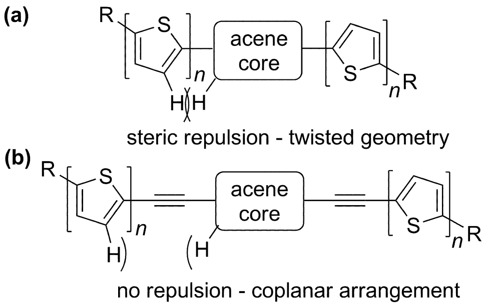

Fig. 1. Molecular setup of oligothiophene derivatives with acene core: (a) those that are interconnected directly, or (b) through an ethynylene linker.

that the planarity of these systems can be achieved by insertion of a linear, sterically non-demanding ethynylene linker (Fig. 1b) [49–57]. Such derivatives containing an ethynylene linker exhibit reasonable charge carrier mobility in OFET (ranging from 8×10^{-4} to 4.5×10^{-1} $cm^2/V\,s$), but the influence of the ethynylene linker on molecular packing and, in particular, on the semiconducting properties is not fully understood, because a direct comparison with analogous linker-void derivatives is often lacking. A direct comparison is available for the series of anthracene derivatives with hexylthienyl arms where insertion of an ethynylene linker caused a 4- to 17-fold enhancement of the hole mobility, up to $0.24\,cm^2/V\,s$ [53]. Insertion of the ethynylene linker to the benzene derivative with hexylbithienyl arms resulted in a 2-fold enhancement of hole mobility, from 0.042 to $0.084\,cm^2/Vs$ [33,49]. However, the report for each compound originates from different groups of authors and the measured mobilities can be affected by differing details in transistor preparation. Although more papers are extant that deal with the structure-properties relationship of the ethynylene-linked and analogous linker-free derivatives of oligothiothienyl-acene type, they provide information only about the optical and electrochemical properties [58,59] or other applications, e.g. in solar cells [60].

In this work we report the synthesis and full characterization, including charge carrier mobility in a transistor device, of a series of new derivatives **H2TAxyN** (Fig. 2, left) where the hexylbithienyl units are attached to a central naphthalene core via an ethynylene linker at positions 1 and 4 (**H2TA14N**), 1 and 5 (**H2TA15N**), and 2 and 6 (**H2TA26N**). Following on our previous work [48] investigating an analogous series of disubstituted naphthalene derivatives **H2TxyN** without an ethynylene linker (Fig. 2, right), our aim is to contribute to a systematic examination of the relationship between the molecular structure, particularly the positions for attachment of bithienyl units at the naphthalene core, and the semiconducting properties. In addition, the closely related series of compounds **H2TxyN** and **H2TAxyN** which are distinguished only by the presence of the ethynylene linkers, should allow evaluating the effect of the ethynylene linker as well.

In the field of materials science, synthesis of diarylacetylene derivatives is almost exclusively accomplished by the Sonogashira coupling reaction due to the simplicity of the coupling protocol [61,62]. In general, this reaction affords target arylacetylenes in high yields when aryl iodides are used as a starting material. The use of aryl bromides results in a slight decrease in product yields. The drop in product yields is more pronounced when a multiple Sonogashira reaction takes place in a single reaction step in the synthesis of oligoalkynylarenes. It has been demonstrated that arylacetylenes can be alternatively synthesized by the Negishi [63–65] or Kumada [66] cross-coupling reactions between an aryl halide or triflate and alkynylzinc or alkynylmagnesium reagent prepared *in situ* from an acetylenic precursor. These reactions could offer comparable or even better results, but strictly anhydrous conditions have to be applied and tolerance of the used organometallic reagent by the present functional groups has to be taken in account. Here, we aim to explore the possibility of using alternative cross-coupling for a more effective synthesis of the target acetylenic derivatives **H2TAxyN**.

2. Results and discussion

2.1. Synthesis

The target compounds **H2TA14N**, **H2TA15N**, **H2TA26N** and their precursor **1** were synthesized by a sequence of Pd-catalyzed alkynylations (Scheme 1). For this purpose two different cross-coupling methods, the Sonogashira and the Negishi reactions, were investigated. First we applied these alkynylation methods for preparation of a bithienylacetylene precursor **1** starting from trimethylsilylacetylene (**2**) and bithienyl bromide **3**. After purification on a short column of silica gel, the crude mixture of silylated intermediate underwent a deprotection using potassium carbonate in a 1:1 mixture of THF/MeOH giving the terminal acetylene derivative **1** in a total 63% yield by the Sonogashira reaction and an

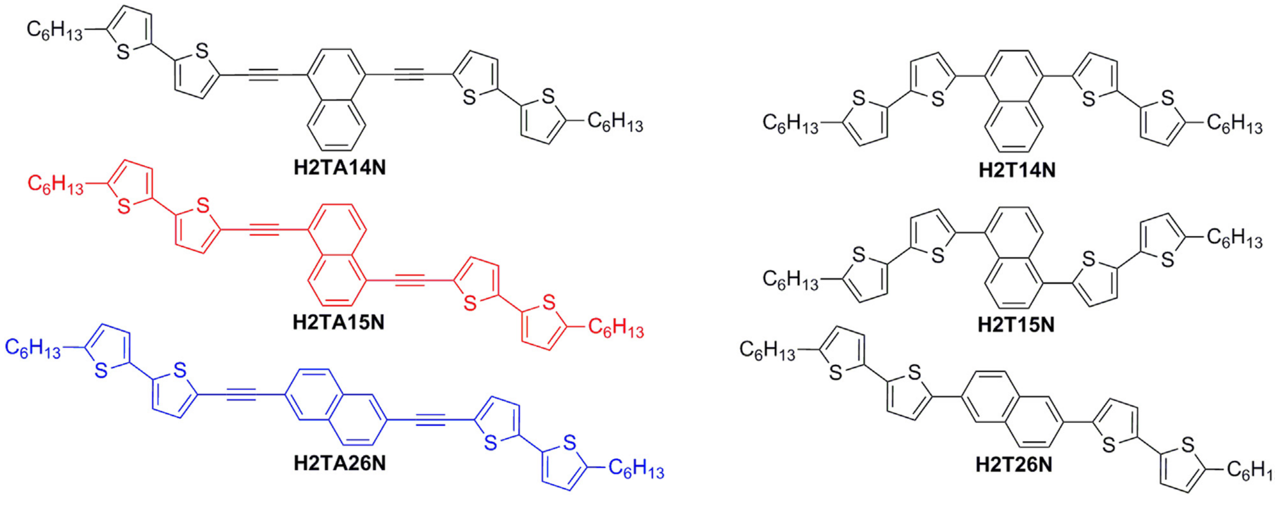

Fig. 2. Structures of the studied derivatives **H2TAxyN** with hexylbithienyl units attached to the central naphthalene core through an ethynylene linker (left) that are compared with the analogous derivatives **H2TxyN** with directly attached hexylbithienyl units (right).

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