



Anthradithiophene-based liquid crystal molecules: High carrier mobilities enhanced by rubbed polyimides for the application in organic field-effect transistors



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ABSTRACT

We synthesize three liquid crystal molecules with angular anthradithiophene (a-ADT) as the core for the application in organic film-effect transistors (OFETs). Thiophene-octyl group and thiophene-dodecyl group are introduced on both sides of the a-ADT core to yield compounds **Bis-C₈T-a-ADT** and **Bis-C₁₂T-a-ADT**. Moreover, thiophene-dodecyl group is attached to the a-ADT core on one side to yield compound **C₁₂T-a-ADT**. The synthesized compounds are measured by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) to determine their mesomorphic properties. Compound **Bis-C₈T-a-ADT** shows nematic and smectic A phases while both compounds **Bis-C₁₂T-a-ADT** and **C₁₂T-a-ADT** reveal smectic A phases. The optical and electrochemical properties of the compounds are characterized by UV–vis spectroscopy and cyclic voltammetry (CV). The HOMO levels for **Bis-C₈T-a-ADT** and **Bis-C₁₂T-a-ADT** are estimated to be -5.27 eV while the HOMO level of **C₁₂T-a-ADT** is estimated to be -5.34 eV. The low-lying HOMO levels of the molecules indicate their great oxidation stability in OFET devices. The carrier mobilities are observed to increase 10–1000 times using rubbed polyimide (PI), resulting from the better arrangements of the liquid crystal molecules, and excellent carrier mobilities of 1.06 and 1.02 cm²/Vs are obtained from compounds **Bis-C₁₂T-a-ADT** and **C₁₂T-a-ADT**, respectively.

1. Introduction

In recent years, organic field-effect transistors (OFETs) have attracted significant attention because of their unique applications in low-cost and flexible displays [1–4]. The research on materials in OFETs has been mainly focused on soluble organic molecules so that devices can be fabricated with solution processes such as spin-coating and ink-jetting techniques [5,6]. Compared with silicon-based field-effect transistors, OFETs have lower carrier mobilities, which are caused by the weakly van der Waals forces rather than the strong covalent bonding [7,8]. To achieve high mobilities in OFETs, an approach is directed towards the exploration of large π -conjugated molecules [9–12]. Pentacene as a semiconductor material affords a high mobility of 1.5 cm²/Vs [13]. The OFETs of pentacene are fabricated by vacuum deposition because of the poor solubility and environmental instability. Recently, thienoacenes have attracted much attention for use as semiconductor

materials in OFETs [14]. In particular, anthradithiophene (ADT) is the most researched material in organic electronic devices. It is difficult, however, to separate the mixture of syn-isomer and anti-isomer in previous synthetic routes [15,16]. On the contrary, there are appropriate synthetic routes to obtain angular-shaped ADT (a-ADT), which has low-lying highest occupied molecular orbital (HOMO) levels and great oxidation stability in OFET devices [17].

To adopt low-cost solution-processed OFETs, there are two deficits for the use of small molecules [18]. First, the surface morphology may be rough and nonuniform during solvent evaporation. Second, the molecular structures are modified with long hydrocarbon chains, which can reduce their melting points. Therefore, the thermal stability of small molecules may be unstable. So far, researchers have focused on designing large π -conjugated molecules with high solubility and great thermal stability. The liquid crystal molecules have the ability to self-assemble into ordered structures, which is beneficial for OFET

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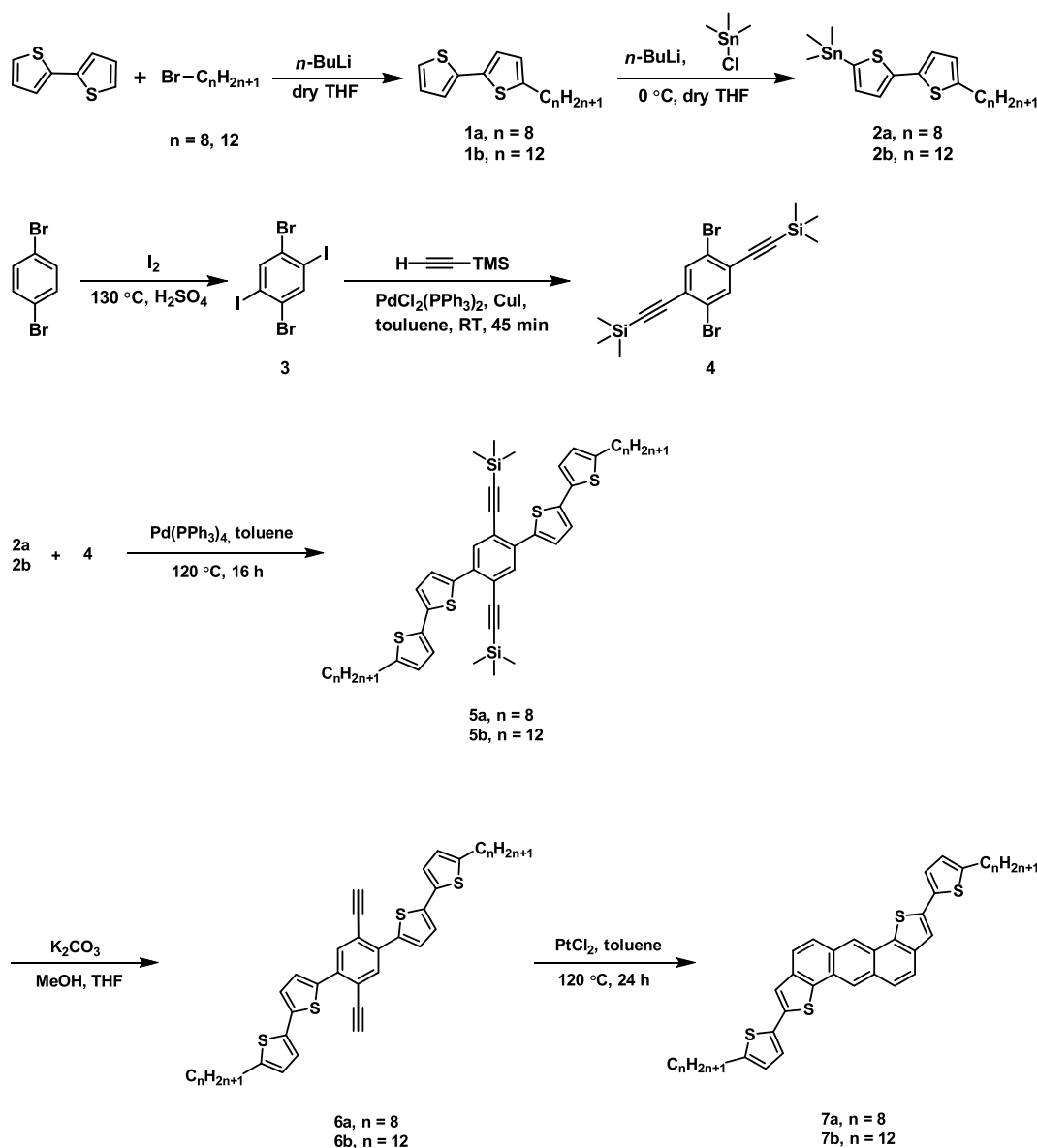
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Scheme 1. Synthetic routes to compounds Bis- $\text{C}_8\text{T-a-ADT}$ and Bis- $\text{C}_{12}\text{T-a-ADT}$ (7a–b).

applications. For example, a mesomorphic semiconductor, 2,6-di(5'-*n*-octyl-2'-thienyl)-naphthalene (8-TNAT-8), has been synthesized and exhibits a high carrier mobility of $0.08 \text{ cm}^2/\text{Vs}$ in OFETs [19]. Another liquid crystal molecule, 2,7-didecylbenzothienobenzothiophene (C_{10} -BTBT), is also synthesized and a high mobility up to $1.0 \text{ cm}^2/\text{Vs}$ can be obtained when the molecule is spin-coated in liquid crystal phase [20]. Moreover, an asymmetric mesomorphic small molecule, 2-octylthienylbenzothienobenzothiophene (8-TP-BTBT), has been reported to possess a high mobility of $1.2 \text{ cm}^2/\text{Vs}$ [21]. According to the previous studies, the liquid crystalline thin films have excellent morphology and uniformity to enhance the carrier mobilities.

In this paper, we choose angular-shaped ADT (a-ADT) as the core with extended thiophene-alkyl groups on both sides. The addition of the thiophene groups makes the molecules more flexible while the long hydrocarbon chains can enhance the solubility. Furthermore, we also design another asymmetric small molecule ($\text{C}_{12}\text{T-a-ADT}$) to reduce the melting points. All compounds are observed to have liquid crystal phases. The optical and electrochemical properties of the compounds are characterized by UV–vis spectroscopy and cyclic voltammetry (CV). The thermal properties and phase transition behaviors of the three compounds are evaluated by thermogravimetric analysis (TGA),

differential scanning calorimetry (DSC), and polarizing optical microscopy (POM). The performances of the OFETs using the liquid crystal molecules are also evaluated using phenyltrichlorosilane (PTS) as the self-assembled monolayers (SAM). In addition, rubbed polyimide (PI) films are introduced, and excellent carrier mobilities of 1.06 and $1.02 \text{ cm}^2/\text{Vs}$ are obtained from compounds Bis- $\text{C}_{12}\text{T-a-ADT}$ and $\text{C}_{12}\text{T-a-ADT}$, respectively. The results suggest that the rubbed PI can assist the arrangements of the liquid crystal molecules in the same direction, as confirmed by X-ray diffractions, resulting in the higher carrier mobilities.

2. Result and discussion

The synthetic routes of three angular anthradithiophene-based liquid crystal molecules are shown in Schemes 1 and 2. In compounds Bis- $\text{C}_8\text{T-a-ADT}$ and Bis- $\text{C}_{12}\text{T-a-ADT}$, there are two thiophene-alkyl groups, which are attached to the fused rings on both sides; the carbon numbers of the alkyl chains are 8 and 12, respectively. In compound $\text{C}_{12}\text{T-a-ADT}$, by comparison, a thiophene-alkyl group is attached to one side of the fused ring and the carbon number is 12. At first, compounds 1a and 1b are synthesized by reacting 2,2'-bithiophene with *n*-

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