



## Solvent boiling point affects the crystalline properties and performances of anthradithiophene-based devices



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### ABSTRACT

We investigated the effects of the solvent boiling point on organic field-effect transistor (OFET) device performances in devices prepared using two newly synthesized anthradithiophene derivatives: 9,10-di(4'-pentylphenylethynyl)-anthra[2,3-b:6,7-b']dithiophene (DPPEADT) and 9,10-bi([9',9'-dimethyl-fluoren-2-ylethynyl])-anthra[2,3-b:6,7-b']dithiophene (DFEADT). DPPEADT exhibited a distinct crystalline morphology whereas DFEADT was amorphous. We characterized the relationship between the molecular structures, film morphologies, and OFET device performances in devices prepared using solvents having one of three different boiling points (chlorobenzene, 1,2-dichlorobenzene, and 1,2,4-trichlorobenzene). 1,2,4-Trichlorobenzene, which provided the highest boiling point among the solvents tested and acted as a good solvent for DPPEADT, significantly improved the field-effect mobilities of DPPEADT devices up to 0.16 cm<sup>2</sup>/V by enhancing the crystallinity of the film. OFETs based on amorphous DFEADT films prepared using the three solvents did not provide enhanced electrical performances. The differences between the transistor performances were attributed to the degree of  $\pi$ -overlap, the molecular structures, and the morphological properties of the films.

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### 1. Introduction

Over the past two decades, organic semiconductors have received significant attention as components in organic field-effect transistors (OFETs) [1,2], organic light emitting diodes (OLEDs) [3,4], organic photovoltaic cells (OPVs) [5,6], and organic photo-detectors (OPDs) [7,8] for potential use in flexible, inexpensive, and large-area electronics applications [9,10]. A variety of organic semiconductor materials have been developed, and their electro-chemical properties have been investigated in an effort to realize more efficient organic electronic device performances. Solution-processable small molecule semiconductors have been most extensively studied because their synthesis, purification, and

structural modifications are relatively easy and they provide low batch-to-batch variability [11,12].

Anthradithiophene (ADT) derivatives are promising candidates for use in organic semiconductors because these derivatives are highly solubility in common organic solvents and they display excellent charge carrier mobilities [13]. ADT derivatives tend to resist oxidation to a greater extent than pentacene, yielding devices with good long-term stability properties [14]. Research efforts geared toward developing high-performance OFETs based on ADT derivatives have focused on novel design strategies that enhance the molecular ordering in a film [15,16]. The electrical properties of ADT derivatives may be enhanced by optimizing the device preparation protocols, including selecting a suitable solvent [17] that yields a high ADT solubility or introducing dielectric surface treatments [18] that induce the formation of favorable crystalline structures.

Previous studies found that high boiling point solvents produced highly crystalline semiconductor thin films because the longer drying times permitted self-organization among the organic

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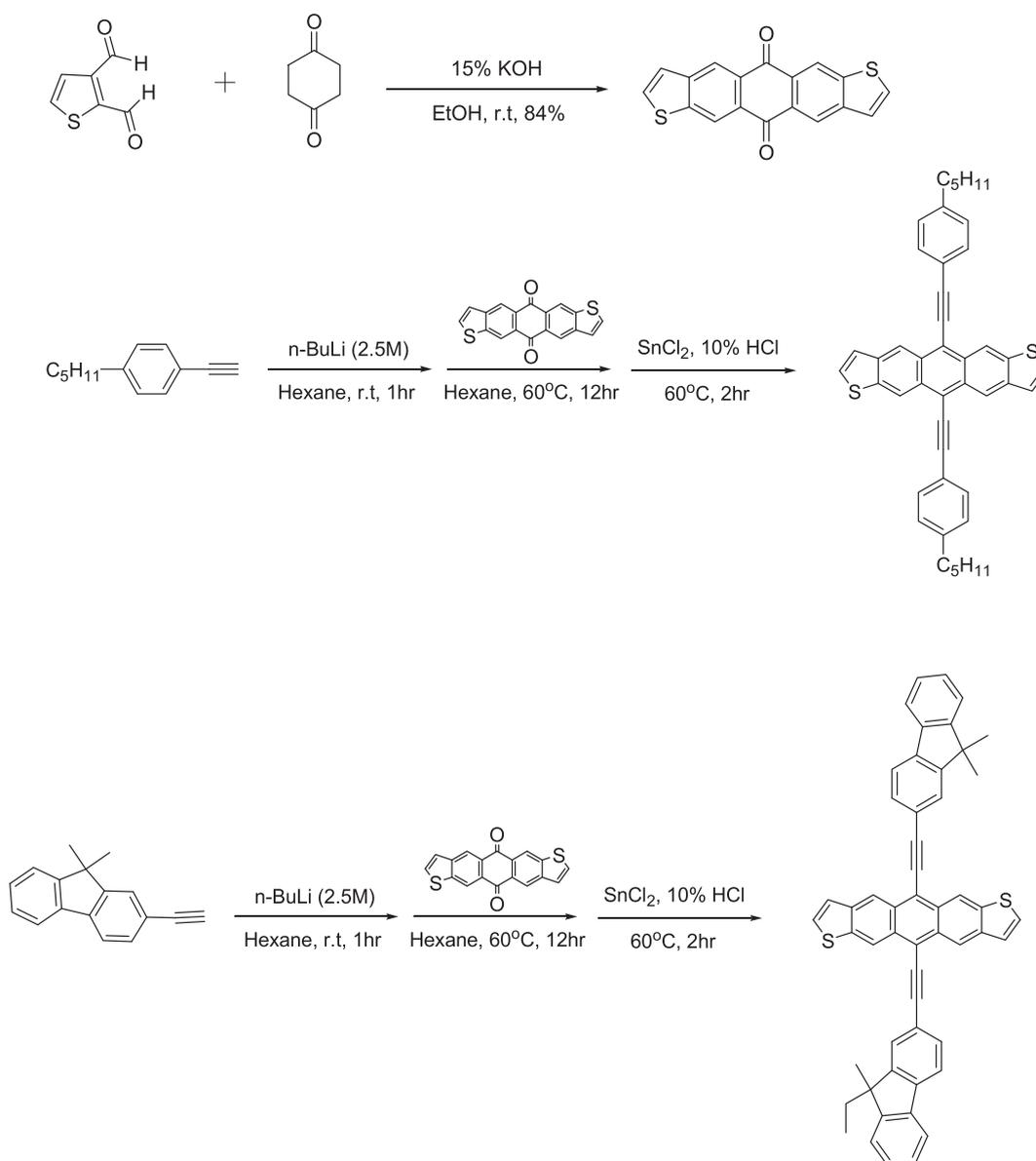
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semiconductor molecules, thereby increasing the field-effect mobility ( $\mu_{\text{FET}}$ ) in the corresponding OFETs [19]. Siringhaus et al. reported enhanced  $\mu_{\text{FET}}$  values for OFETs prepared with poly(3-hexylthiophene) as the semiconductor and 1,2,4-trichlorobenzene as the solvent. Seo et al. improved the performances of a 6,13-bis(triisopropylsilylethynyl) pentacene OFET by introducing solvent additives with high boiling points (b.p.) [20,21]. Unfortunately, the surface tensions of high b.p. solvents tend to be high, whereas the surface energy of the substrate tends to be low. Organic semiconductor films, therefore, tend to dewet during film formation due to the large difference between the surface energies of the solvent and the dielectric surface [22,23].

The gate dielectric surfaces of OFETs are typically modified by introducing hydrophobic oligomeric or polymer materials that minimize the formation of charge carrier traps [24]. A variety of gate dielectric treatment layers has been tested thus far. Hydrophobic self-assembled monolayers (SAMs) are commonly used on polar dielectric layers because they can efficiently cover the underlying polar dielectric functionalities that act as charge carrier

traps, and they can accompany epitaxial growth of organic semiconductor films to improve the values of  $\mu_{\text{FET}}$  [25,26]. Despite the performance improvements obtained through the use of SAMs in OFETs [27,28], the hydrophobicity of the SAM layer promotes dewetting of the solution-processed material from the surface [22,23]. Only solvents with a low b.p. can be used during the solution-processed film formation steps on a hydrophobic SAM-treated substrate [29–31]. The electrical performances of OFETs may be optimized through the use of high b.p. solvent combinations and hydrophobic dielectric surface treatments.

The challenges associated with pairing appropriate solvents and surface treatments were overcome in this research by introducing an ultrathin polymer brush layer. Polymer brushes can produce chemically stable molecular nanolayer films at a dielectric surface. The hydrophobicity of the polymer brushes can be selected so as to overcome the dewetting problems associated with high boiling point solvents. For these reasons, polymer brush-based OFETs provide  $\mu_{\text{FET}}$  values that are comparable to those obtained from SAM-treated dielectric systems [32,33].



**Scheme 1.** Synthetic schemes describing the synthesis of DPPEADT and DFEADT.

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