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High-performance *n*-channel thin-film transistors with acene-based semiconductors

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ABSTRACT

Two acene-based semiconductors were investigated with respect to their performance as n-type materials in organic field-effect transistors. The partially fluorinated ditetracenes (Ditetracen is protected by copywrite through the Patent WO/2007/000268. The patent is property of the Dritte Patentportfolio Beteiligungsgesellschaft mbH & Co. KG.) (**DT**) were synthesized in a high yield with different degrees of fluorination, one with four and another with two fluorine substituents (named as **DT-4F** and **DT-2F**, respectively). Both materials exhibit high thermal stability, with decomposition temperatures above 500 °C. Since both materials are supposed to have a lowered LUMO level compared to the non-fluorinated parent **DT**, n-type operation in thin-film transistors (TFTs) with gold source and drain contacts was expected. TFTs based on **DT-2F,** however, showed weak ambipolar transport only, which demonstrates insufficient fluorination to switch from hole-dominated to electron-dominated transport. On the other hand, high performance n-type TFTs have been achieved from **DT-4F**, with electron mobilities up to 1.0 $cm^2/V\,s$. This result indicates that fluorinated **DT** material can act as excellent n-type semiconductor for applications in complementary circuits. This is demonstrated in a complementary inverter stage using **DT-4F**-based TFTs as n-type transistor and a non-fluorinated **DT** derivative-based TFT as p-type transistor.

1. Introduction

In the past decade much effort has been made to develop electron-transporting organic semiconductors for the application in organic field-effect transistors (FETs) because they enable the achievement of bipolar transistors and complementary circuits. The *n*-channel materials with electron mobility comparable to and even greater than that of amorphous silicon have been achieved in several material classes [1–4], despite that the development of high-performance organic electron-transport materials still lags behind that of hole transport materials to date. Acene-based materials such as tetracene and pentacene and their derivatives rank among the most extensively studied organic semiconductors for (opto)-electronic applications [5,6]. The large delocalized π-electron system characterizing these molecules turns them into excellent charge transporters. For example, rubrene and pentacene keep the record of hole mobility as high as 40 $cm^2/V\,s$ in single crystal FETs as well as 5.5 $cm^2/V\,s$ in organic thin-film transistors (OTFTs) [7,8]. Despite the success as hole transporters, it is found to be more difficult to achieve *n*-channel transport in these acene-based materials [9,10].

An often used strategy to convert a p-type organic semiconductor into an n-type material is to functionalize the π-conjugated core with strong electron-withdrawing

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moieties such as cyano (–CN) and halogen (F– and Cl–) [11–16]. The fluorination or chlorination increases substantially the electron affinity of the molecules, stabilizes electron transport and improves electron injection. n-type and ambipolar semiconductors from acenes via this approach have been demonstrated [17–24]. For example, Suzuki et al. synthesized perfluoropentacene and perfluorotetracene [17–19]. OTFTs from perfluoropentacene showed electron mobility as high as 0.22 cm^2/V s. n-type and ambipolar materials from the soluble acenes [21,22] and the heteracenes [24] with electron mobility of 0.1–0.5 cm^2/V s have also been achieved by the halogenation. However, to produce bipolar transistors and complementary circuits, it would be desirable to have n-type acene-based semiconductors with similar morphological and physical properties as well as electrical transport properties compared to their p-type counterparts (with high hole mobility). In this sense an increase in the electron field-effect mobility is desirable.

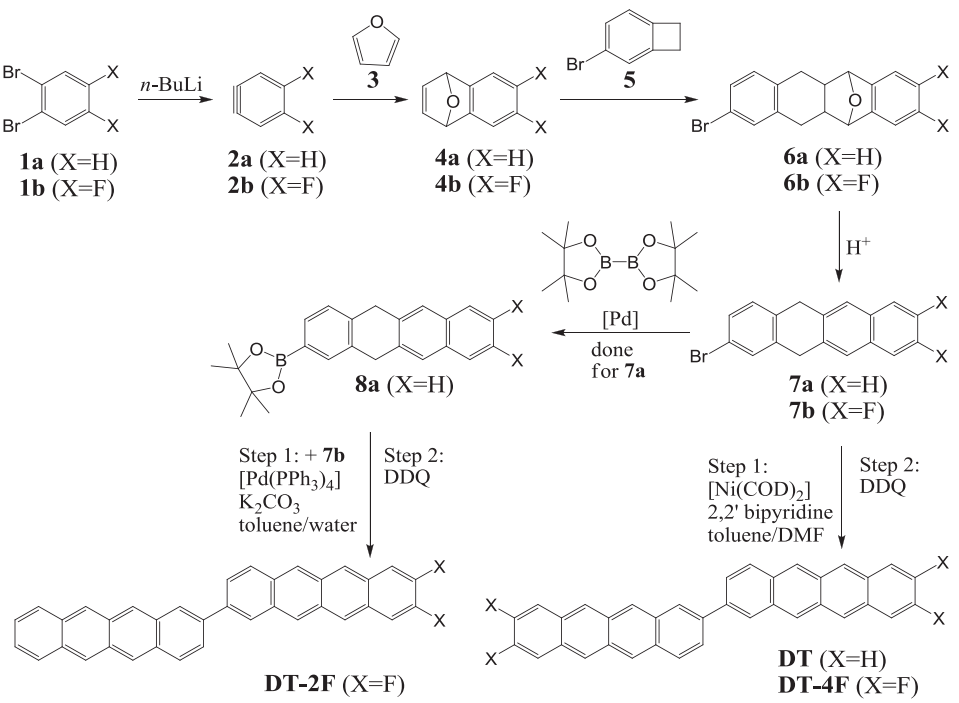
Recently, we have developed ditetracene (DT) as the parent system of a new class of functional oligoacene materials (Scheme 1). It shows good chemical stability as well as hole mobilities as high as 0.7 cm^2/V s in TFTs [25]. The material exhibits an extraordinary thermal stability, with the decomposition temperature higher than 500 °C, which is relevant for the technological applicability. In this article, we report on two *n*-channel acene semiconductors based on partially fluorinated derivatives of the parent **DT** (Scheme 1). One of them exhibits electron mobility as high as 1 cm^2/V s and a current on/off ratio of 10^7 in TFT devices. In addition, it is found that – depending on the degree of fluorination meaning the number of the attached fluorine atoms per ditetracene molecule – both *n*-channel and ambipolar transport can be achieved in TFTs with Au contacts. The applicability of the materials for complementary circuits is demonstrated on the basis of inverter stages realized by employing n- and p-type **DT** derivatives.

2. Results and discussion

2.1. Materials synthesis and characterization

The partially-fluorinated **DT**'s were synthesized with different degree of fluorination, one with four and another with two fluorine substituents (named as **DT-4F** and **DT-2F**, respectively). The synthetic pathway leading to **DT-2F** and **DT-4F** is shown in Scheme 1. The constitution and the high purity of the obtained materials were verified using ^{1}H NMR and ^{13}C NMR spectroscopy and mass spectrometry. The ditetracene compounds **DT-2F** and **DT-4F** were purified by double gradient sublimation. The purification yield was more than 78%.

Both of the materials exhibit melting temperatures higher than 500 °C as well as a decomposition temperature as high as 510 °C as determined by the DTA/TG measurements. This compares well to the parent ditetracene, indicating a good thermal stability independent of the incorporation of fluorine atoms into the **DT** structure. UV–vis spectra of these semiconductors as recorded from deposited thin films (in Fig. 1) show the absorption peak at wavelengths of 450 nm and 470 nm for **DT-4T** and **DT-2F**, respectively. The onset of the absorption in the spectra



Scheme 1. Synthetic pathways leading to the parent ditetracene (**DT**) and to the partially fluorinated ditetracenes **DT-2F** and **DT-4F**.