Journal of Molecular Graphics and Modelling 59 (2015) 50–58

Contents lists available at ScienceDirect

Journal of Molecular Graphics and Modelling

journal homepage: www.elsevier.com/locate/JMGM

Theoretical investigations into the electronic structures and electron transport properties of fluorine and carbonyl end-functionalized quarterthiophenes

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ARTICLE INFO

Article history:
Accepted 3 April 2015
Available online 13 April 2015

Keywords:
Thiophene based transporting material
Fluorination and carbonylation
Electron transport property
Density functional theory

ABSTRACT

In this work, we concentrate on systematic investigation on the fluorination and carbonylation effect on electron transport properties of thiophene-based materials with the aim of seeking and designing electron transport materials. Some relative factors, namely, frontier molecular orbital (FMO), vertical electron affinity (VEA), electron reorganization energy (λ_{ele}), electron transfer integral (t_{ele}), electron drift mobility (μ_{ele}) and band structures have been calculated and discussed based on density functional theory. The results show that the introduction of fluorine atoms and carbonyl group especially for the latter could effectively increase EA and reduce λ_{ele}, which is beneficial to the improvement of electron transport performance. Furthermore, these introductions could also affect the t_{ele} by changing molecular packing manner and distribution of FMO. Finally, according to our calculation, the **3d** system is considered to be a promising electron transport material with small λ_{ele}, high electron transport ability and good ambient stability.

1. Introduction

Organic semiconductor materials have been dramatically developed in the past two decades owing to their potential merits, such as low-cost, large-area coverage, flexibility and ease of processing [1–6]. To achieve more effective and extensive applications, such as organic p-n junctions [7,8], bipolar transistors [9], and organic complementary circuits (CMOS) [10,11], both hole-transporting (p-type) and electron-transporting (n-type) materials are indispensable. However, the development of efficient n-type semiconductors is far behind the p-type's, which is connected to their low electron injection efficiency [12–14] and inferior ambient stability [15–18]. Recently, both experimental and theoretical efforts have proved that introducing strong electron-deficient moieties into traditional p-type materials can change them into n-type ones because of the lower injection barrier and improved molecular stability [19,20].

Thiophene-based transporting materials are a family of preeminent organic semiconductors [21,22] owning to their synthetic availability, widespread possibility and tunable electronic properties [23]. According to the locations of the electron-withdrawing functionalities, such as F, fluorocarbons, CO and CN, the reported n-type thiophene derivatives can be classified into two categories: (i) the ones substituted at the ends of the thiophene chain, that is, bringing in terminal groups; (ii) the ones modified on the side position of the thiophene chain. Thiophene-based materials substituted at the end positions are generally expected to have large π-conjugation by introducing proper aromatic groups, which would provide better intermolecular π···π overlap and thus enhance the transport performance [24–26].

The perfluoroarene and carbonyl terminal modified thiophene-based material **DFCO-4T** is a prominent n-type semiconductor, which exhibits extremely high electron mobility ($\mu_e \approx 0.21\ cm^2\ V^{-1}\ s^{-1}$) [27] in solution-cast film. Fascinated with this, we summarized and analyzed the thiophene-based systems with fluorine or carbonyl group modifications as Fig. 1 shows. It is interesting to note that when a classical p-type thiophene-based transport material is fluorinated by introducing fluoroalkyl, fluorophenyl or fluorine substitutions, the system would always show n-type transport property. While the carbonyl groups do the same. For example, the diperfluorohexyl modified sexithiophene **DFH-6T** exhibits an n-type transport behavior with electron mobility of $0.001\ cm^2\ V^{-1}\ s^{-1}$. [28,29] The **DFH-6T** derivatives with 4 and 5

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http://dx.doi.org/10.1016/j.jmgm.2015.04.001
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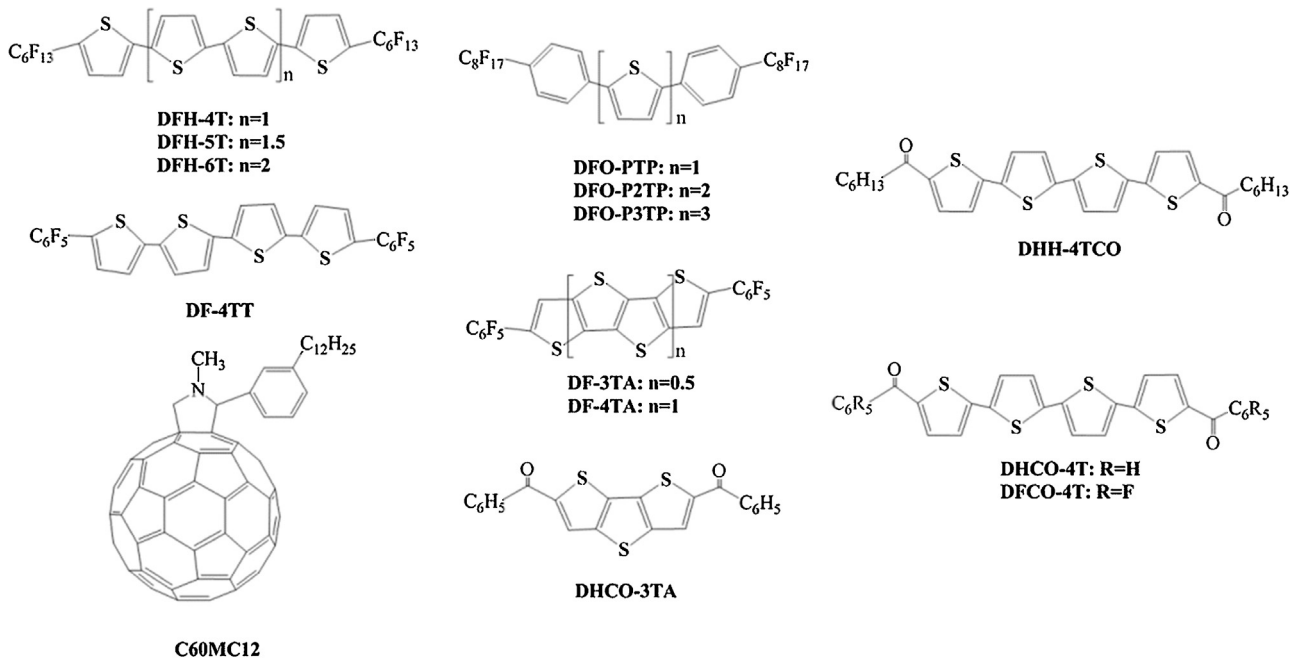

Fig. 1. The reported n-type thiophene-based systems with fluorination and carbonylation along with $\mathbf{C_{60}MC_{12}}$.

thiophene rings [30] and with terminal perfluorooctyl-phenylene modification, such as **DFO-PTP**, **DFO-P2TP** and **DFO-P3TP** [5], also exhibit n-type transport behaviors. Besides, the *F*-substituted systems with other thiophene core conformations also show electron transport behavior, such as iso-quarterthiophene cored **DF-4TT** [21,31], fused-ring thiophene cored **DF-3TA** and **DF-4TA** [32,33]. While, **DHH-4TCO** ($\mu_e \approx 0.1\,cm^2\,V^{-1}\,s^{-1}$) is the only thiophene-based n-type transport material modified by carbonyl groups we can find [34]. Thusly, it is wondered that whether the carbonyl group has any contribution to the electron transport properties in systems like **DFCO-4T** modified with both F atoms and CO group substitutions**,** in what way, and what kind of condition can it happen. It is well-known that the nature of the electron-withdrawing mechanism of the two modifications is different: a $(-I)$ inductive effect is expected for the fluorine substitute, whereas the carbonyl group works as a combination of $(-M)$ π-mediated mesometric and $(-I)$ inductive effects, indicating that the carbonyl group can directly participate in π-conjugation. Does this mean that the CO groups work in a different way with the fluorine substitutes? Here we might say that the mechanism of the carbonyl modification on transport properties is not clear enough, further theoretical study is needed.

What's more, it is reported that comparing to chain linked thiophene cored systems, fused-ring thiophene-cored systems behave flatter molecular structure to ensure better electron delocalization facilitating effective intermolecular overlap, and higher C/H ratio promoting closer π-packing tendency of the system [35]. From this aspect, the conformation of thiophene rings will affect the carrier transport performance. As mentioned above, both fluorine and carbonyl group modifications could convert p-type transport materials into n-type ones. Therefore, we would like to see whether the effects of the substitutions on different conformations of thiophene cores are same. Is the fused-ring thiophene cored systems also exhibit better electron transport behavior after substituted by fluorine or (and) carbonyl group? And which type of thiophene ring conformation is more sensitive to the modifications?

To answer the above questions, we designed the following systems. Three representative thiophene backbones, **1-, 2-** and **3-** series in Fig. 2 were chosen as the investigated subject. In detail: (i) the **1-** series with quarterthiophene (4T) backbone arranging in *trans–trans–trans* conformation; (ii) the **2-** series with quarterthiophene backbone arranging in *cis–trans–cis* conformation; (iii) the **3-** series contain a fused-ring tetrathienoacene. Additionally, the **-a** series are terminal modified with a phenyl group; the **-c** series are the carbonylized systems of **-a** series; and the **-b** and **-d** series are fluorine substituted **-a** and **-c** series, respectively. The electron transport properties of the all 12 systems are systematically investigated with the aim of seeking and designing electron transport materials. Thereby, in this work, some relative factors to transport properties, namely, frontier molecular orbital (FMO), vertical electron affinity (VEA), electron reorganization energy (λ_{ele}), electron transfer integral (t_{ele}), electron drift mobility (μ_{ele}) and band structures have been investigated based on density functional theory calculation. The fluorination and carbonylation effect on electron transport properties was focused on and compared. We hope our study would give a hint for experimental research.

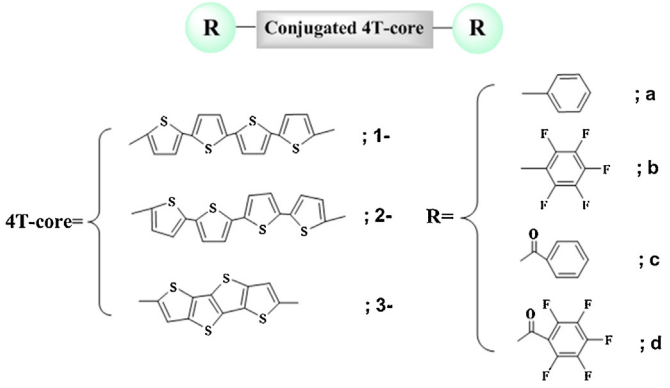

Fig. 2. The molecular model of the systems investigated here with 4T-cores named by numbers (**1**, **2**, **3**) and terminal modifications named by letters (**a**, **b**, **c**).

2. Theoretical and computational methodology

To optimize molecular geometry, both B3LYP [36,37,38] and B3P86 [39,40] functionals with 6-31G(d,p) [41–43] and 6-31+G(d,p) [44,45] basis sets were employed in Gaussian 09