

# An efficient strategy for improving carrier transport performance – Introducing fluorine into aryl substituted tetracene



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## ABSTRACT

Why does the fluorination of just one phenyl in 5,11-diphenyltetracene (**PPT**) bring about so tremendous change of the charge carrier mobility? Herein, we carried out density functional theory (DFT) to provide insight into this remarkable difference by investigating their geometries, electronic structures, reorganization energies, transfer integrals, intermolecular interactions and band structures. The improved charge mobility from **PPT** to **FPPT** (5-(perfluorophenyl)-11-phenyltetracene) can be attributed to favorable molecular packing due to the increase of  $\pi$ – $\pi$  interaction which is confirmed by Hirshfeld surfaces analysis. Furthermore, we calculated charge mobilities of novel compound 4,11-diphenyltetracene (**PPT'**) and its fluorinated derivative 4-(perfluorophenyl)-11-phenyltetracene (**FPPT'**), on the basis of the predicted packing motifs. The largest charge mobility of **FPPT'** (2.49 cm<sup>2</sup>/V s) exhibits one-fold higher than **PPT'** (1.07 cm<sup>2</sup>/V s) due to dense packing structures, which further confirms our finding that fluorination may be an effective means to improve the carrier mobility. This work paves the way towards the development of a computational protocol that could be implemented not only for rationalizing synthetic efforts but also for design of high-performance organic transport materials.

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## 1. Introduction

Recently, the room temperature charge carrier mobilities of several organic semiconductors have achieved a few tens of cm<sup>2</sup>/V s, which are comparable with that of amorphous silicon [1]. With many advantages such as straightforward chemical modification, commercial availability, and low cost, organic carrier transport materials

attract more academic and commercial interests [2]. Generally, the high-performance organic semiconductors have the common feature of an aromatic, delocalized, electronically active core [3], which constitutes some typical systems, such as conjugated acenes [4], oligothiophenes [3b,5], rylene and related diimides [6]. Among these excellent organic semiconductor materials, **rubrene** is set as the benchmark performance for organic single crystal devices so far [7], which is ascribed to its large conjugation of tetracene and favorable solid-state packings (shifted  $\pi$ -stacking), easily forming better intermolecular overlap. While, what will happen if the four outer phenyls reduce by two? Whether the good carrier transport performance is maintained? Since the intermolecular electronic coupling

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only involves the tetracene for **rubrene**. Recently, Okamoto et al. have synthesized two new structurally similar **rubrene** analogues, **PPT** with reduced two outer phenyls and **FPPT** with the fluorination of one phenyl of two outer phenyls (Fig. 1) [8]. Amazingly, the charge mobility of **PPT** is very low. However, when one phenyl is fluorinated, the high charge mobility appears. The fact that the tiny fluorination of one phenyl induces significant difference in carrier mobility arouses our interest. In fact, there are numerous examples showing the influence of fluorine in crystal engineering [9]. Also some theoretical attempts have been made to explain impact of fluorination on the charge-transport parameters of organic field-effect transistors (OFETs) [10]. However, to date, there is still no concise and unambiguous understanding of fluorine interactions, especially for chemical structure, material morphology and macroscopic properties of fluorine compounds.

Theoretical works are certainly favorable to identifying carrier transport behavior, formulating structure-property relationships and proceeding further with rational design of high-performance semiconductors [11]. With the developments of theoretical methodologies, more details on carrier behavior have been investigated [12]. Here, motivated by the interesting phenomenon mentioned above, we investigated the transport properties of **PPT**, **FPPT** and **rubrene** based on density functional theory (DFT) to provide insight into the physical essence. The results show that introducing electron-withdrawing fluorine atoms induces a close face-face stacking motif, which is favorable to enhancing carrier transport ability compared with edge to edge and edge to face ones. Moreover, we also investigated the carrier trans-

port behaviors of **PPT** isomers, 4,11-diphenyltetracene (**PPT'**) [13] and designed 4-(perfluorophenyl)-11-phenyltetracene (**FPPT'**) (Fig. 1) based on crystal structure prediction. The results prove conclusion above-mentioned, and reveal that **FPPT'** exhibits improved carrier transport performance and may be a potential outstanding semiconductors. Thereby, when the origin of enormous difference in mobility induced by fluorination for **FPPT** and **PPT** was explored in this contribution, a new high-performance semiconductor compound, **FPPT'**, was theoretically proved and recommended.

## 2. Theoretical and computational methodology

The charge transport mechanism in organic semiconductors is usually described by mean of two limited cases, the hopping model and the band model, which correspond to the extreme localization and delocalization of the charge carriers, respectively [14]. For the former, the mobility increases with increasing temperature, while for the latter, the carrier mobility decreases with increasing temperature. Under high temperature, charge is generally localized, because the thermal disorder may localize the charge and the phonons are strongly coupled with the carrier motion, thus invalidating the coherent band transport model or its extensions [15]. Here, all the compounds were investigated at 300 K, so the hopping mechanism, widely adopted by precursors and some groups [12a,15–22], was employed just to investigate the structure-property relationship. In the hopping regime, the electron-transfer (ET) rate between two adjacent molecules following the reaction

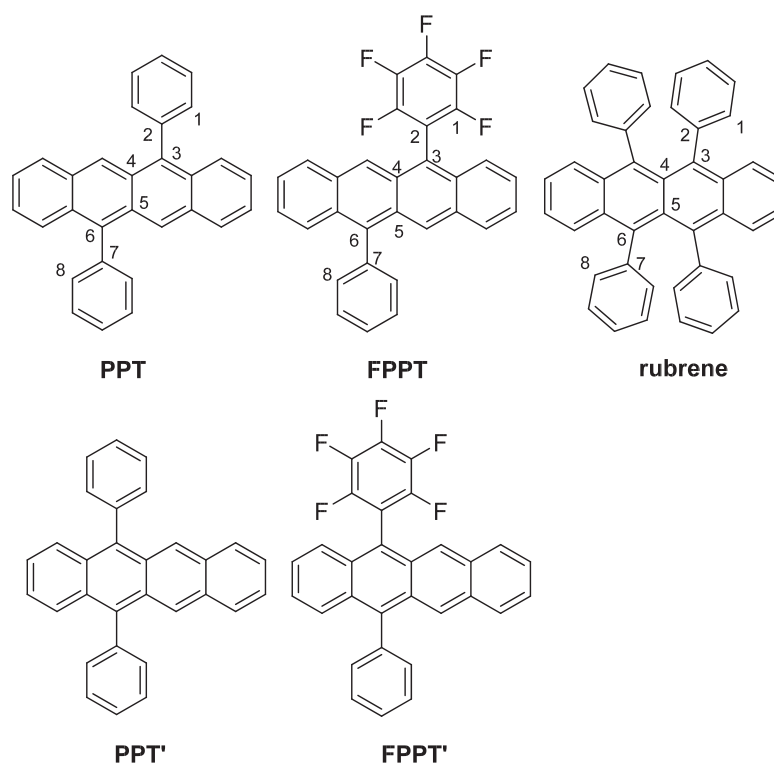


Fig. 1. Molecular models investigated in this work.

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