



Computational investigation of the effects of perfluorination on the charge-transport properties of polyaromatic hydrocarbons



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ABSTRACT

We present a systematic computational study of the effects of perfluorination on the charge-transport properties of three homologous classes of polyaromatic hydrocarbons of interest for molecular electronics: acenes, pyrenes, and circumacenes. By means of Density Functional Theory calculations we first obtained the key molecular properties for transport of both holes and electrons. We then used these parameters in the framework of Marcus theory to compare charge-transfer rates in the high temperatures regime for both unsubstituted and perfluorinated molecules. We additionally estimated the relative charge-mobility of each unsubstituted (perfluorinated) molecule with respect to unsubstituted (perfluorinated) pentacene. We found in all cases that perfluorination reduces the charge-transfer rate in absolute terms. This is largely due to the higher values of the molecular reorganization energies predicted for perfluorinated compounds. Interestingly, however, the charge-transfer rates for both holes and electrons of perfluorinated species are remarkably similar, especially for the larger species. In addition, in the case of the larger circumacenes the charge-mobility values relative to pentacene values are found to increase upon perfluorination.

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1. Introduction

Efficient charge transport in organic materials is of paramount importance for their use as active elements in electronic devices. Carrier mobilities can be finely tailored by chemical modification of the molecular building blocks composing the material. Alteration with strong electronegative substituents, for example, is an effective approach for converting p-type organic semiconductors to n-type [1,2]. To obtain bipolar transistors, in fact, it would be important to have both n-type and p-type organic semiconductors with similar physical and electrical properties [3,4]. Polyaromatic hydrocarbons (PAHs) in their crystalline state are widely used for different applications in molecular electronics. For these compounds, however, it has turned out to be more difficult to achieve n-type transport; e.g., pentacene based organic field-effect transistors exhibit hole mobilities one order of magnitude larger than the electron ones [3]. Typically, n-type materials based on PAHs are produced by attaching to the conjugate core strong electron-withdrawing groups such as CN [5] or by replacing the peripheral hydrogens with halogen atoms (e.g., fluorine and chlorine) [4,6].

Fluorine atoms, in particular, may confer unique qualities: halogen atoms are known to lower both the highest-occupied and lowest-unoccupied molecular orbital energy levels. As a consequence, the electron injection is made easier, the materials display greater resistance against the degradative oxidation processes and organic n-type or ambipolar semiconducting materials may result. Moreover, Carbon–Hydrogen–Fluorine (C–H–F) interactions play a key role in the solid state supramolecular organization, giving rise to a typical π -stack arrangement which enhances charge carrier mobility [7,8].

Theoretical calculations of the building blocks of organic semiconductors can contribute to the knowledge of their properties and provide guidelines for dedicated applicative research [9–12]. A widely adopted framework to compute the charge-transport properties of organic-based semiconductors is the semi-classical Marcus theory [13,14]. This theory describes charge-transfer as a self-exchange hole(electron)-transfer chemical reaction between adjacent molecules. Marcus theory has been applied extensively in conjunction with quantum-chemical calculations to evaluate charge-transport properties of organic semiconductors (see e.g. Ref. [15,9–12]). In this work we followed the same approach adopted in previous investigations [15–18] to quantify the effects of perfluorination (complete substitution of the peripheral hydrogens by fluorine atoms) on the charge-transport properties of three

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homologous classes of PAHs, namely acenes ($C_{4n+2}H_{2n+4}$), pyrenes ($C_{6n-2}H_{2n+4}$), and circumacenes ($C_{8n+8}H_{2n+8}$). The molecules considered, corresponding to $n = 3,4,5$, are sketched in Fig. 1; they cover an ample range of different possible PAHs morphologies from linear to compact, to ultracompact ones. Circumacenes, in particular, characterized by large conjugated cores, have been previously proposed as promising candidates for future technological applications [19].

We first computed the intrinsic molecular properties for charge-transport of both holes and electrons by means of well established Density Functional Theory calculations. In particular, for the calculation of the electron couplings we considered in all cases the simplified approximation of facially stacked structures. It is well known that molecular parameters of charge transport depend on the packing of the monomers in the crystal. Supramolecular issues have been therefore extensively addressed in the literature from both the experimental and theoretical points of views, especially for non-functionalized and functionalized linear acenes [20–24]. In particular, the formation of package structures with a high degree of π -overlap is believed to facilitate charge migration [25]. The face-to-face π -stacking motif is thus more efficient for charge transport than the edge-to-face herringbone-packing structures typical of organic semiconductors such as pentacene, rubrene etc. [25,26]. Several studies have shown that the face-to-face π stacking is more common with molecules possessing a two-dimensional extended aromatic system and is rarely observed for linear molecules such as oligoacenes [27]. For PAHs with large conjugated cores, in particular, self-assembly via strong π - π interactions has been demonstrated to result in the formation of one-dimensional nanostructures [28,29]. Based on the above considerations, since our sample includes molecules expected to pack in very different ways, for comparative purposes we decided to adopt the simplified approximation of treating on the same footing all of the linear, compact, and ultracompact species investigated.

We subsequently used the above parameters in the framework of the semi-classical Marcus theory to compare charge-transfer rates in the high temperatures regime for both unsubstituted and perfluorinated molecules. To ease the comparison between molecules we additionally estimated the relative charge-mobility of each unsubstituted (perfluorinated) molecule with respect to

unsubstituted (perfluorinated) pentacene, which is a benchmark in the field of organic semiconductors (in particular as hole transporter).

2. Computational details

In the framework of Marcus theory [13,14] the charge-transfer rate K_{CT} in the weak-coupling regime is described as a self-exchange hole(electron)-transfer chemical reaction between adjacent molecules. K_{CT} is expressed by the following equation:[30–32]

$$K_{CT} = \frac{\sqrt{\pi}}{h} \frac{t^2}{\sqrt{\lambda k_B T}} \exp\left(-\frac{\lambda}{4k_B T}\right) \quad (1)$$

in which k_B is Boltzmann's constant and T is the absolute temperature. As shown by the above equation, the charge-transfer rate K_{CT} depends critically on two parameters: the intramolecular coupling, or reorganization energy (λ), and the electronic coupling between adjacent molecules, or transfer integral (t). Since λ enters in the argument of an exponential, it has a stronger influence in the hopping rate and, as a consequence, on the mobility of the charge carriers.

We computed both quantities t and λ at the Density Functional Theory level by using the hybrid exchange–correlation functional B3LYP [33] in conjunction with the Gaussian basis-set 6-31G*. The combination B3LYP/6-31G* is widely adopted for the calculation of a vast range of very different compounds, from organic antibiotics [34] to inorganic nanocrystals [35]. All quantum chemical calculations have been performed with the NWChem 6.5 package [36] starting from the geometry available in Ref. [37] for each molecule reported in Fig. 1. The use of the B3LYP functional is rather standard and some limitations are well documented, such as the system-size-dependent errors found for the lowest short-polarized electronic transitions of oligoacenes [38]. In the specific case of PAHs, we have checked in previous works [39,40,18] both the sensitivity of our calculations to different DFT functionals, and their reliability in comparison with available experimental data. Our benchmark investigations included long-range corrected functionals such as CAM-B3LYP [41], which has been devised to handle the wrong asymptotic behavior of B3LYP which decays faster than $1/R$ for large distances R from the nuclei. With only a few

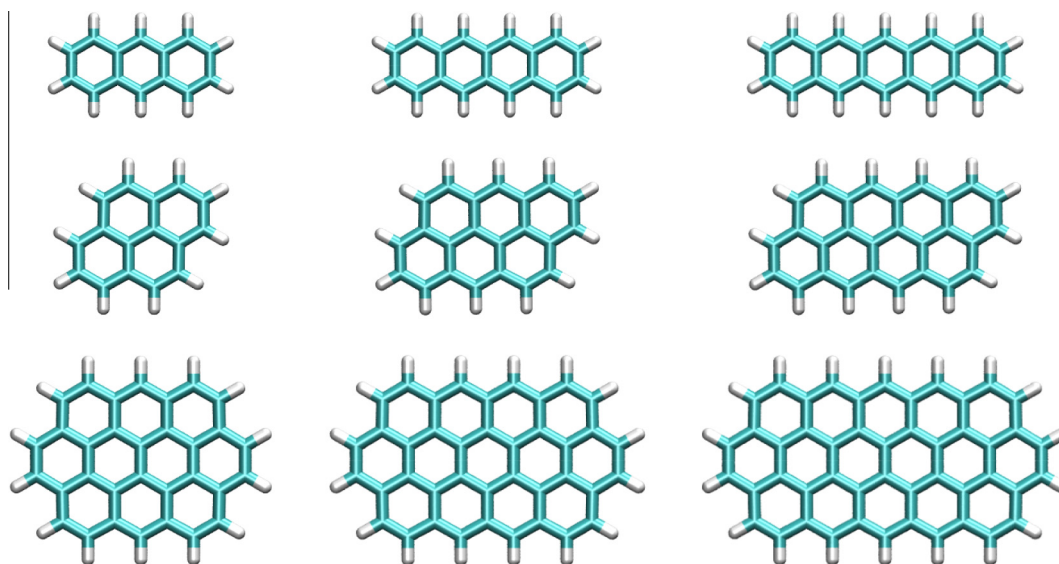


Fig. 1. Schematic depiction of the different families of PAHs investigated. Acenes (top): anthracene, tetracene, pentacene ($C_{4n+2}H_{2n+4}$, $n = 3,4,5$); Pyrenes (middle): pyrene, anthanthrene, peri-naphthacenonaphthacene ($C_{6n-2}H_{2n+4}$, $n = 3,4,5$); Circumacenes (bottom): ovalene, circumanthracene, circumtetracene ($C_{8n+8}H_{2n+8}$, $n = 3,4,5$).

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