



The substituent effect on charge transport property of triisopropylsilylethynyl anthracene derivatives



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ABSTRACT

The charge transport property of two triisopropylsilylethynyl anthracene (TIPSAnt) derivatives TIPSAntBt and TIPSAntNa (bithiophene and naphthalene are introduced at the 2, 6-positions of the TIPSAnt core) were explored through quantum chemical method. To gain a better understanding of the substituent effect on the charge transport property, the results of the parent molecule TIPSAnt was also provided here for comparison. The substituent effect on the molecular geometry, reorganization energy, frontier orbitals, ionization potential (IP) and electronic affinity (EA), crystal property, transfer integrals and charge mobility, band structure and effective mass of the two compounds were investigated to establish the relationship between structures and properties. The introduced bulky TIPS groups made the two compounds adopt two-dimensional, face-to-face, π -stacking structures. The efficient overlaps of π -orbital and smaller π -stacking distance are proved to be the main reason for the high charge mobility of TIPSAntBt and TIPSAntNa. The hole mobilities of TIPSAntBt and TIPSAntNa are 0.88 and 3.60 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively, which is well consistent with experiment values (0.2 and 3.7 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively). For TIPSAntBt, the electron mobility (1.29 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) is a little higher than that of hole due to the more effective transfer integrals of electron. On the contrary, the hole mobility of TIPSAntNa is 20 times larger than that of electron because of the smaller reorganization energy and larger transfer integral of hole, indicating that TIPSAntNa could be used as *p*-type semiconductor. For TIPSAntBt, the transfer integral is smaller than the reorganization energy, so the hopping mechanism plays a key role in the charge transport property. While the bandwidths and effective mass of TIPSAntNa agreed well with the calculated transfer integrals and charge mobility results. The introduced small substituents to TIPSAnt core contributed to the dramatically different charge transport property from an *n*-type semiconductor of TIPSAntBt to *p*-type semiconductor of TIPSAntNa, which shed light on molecular design for an *n*-type semiconductor through simple chemical structural modification.

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1. Introduction

In the past two decades, organic π -conjugated semiconductors have drawn great attention due to their applications as active elements in optoelectronic devices, such as

organic field-effect transistors (OFETs) [1–4], light-emitting diodes (LEDs) [5–7] and photovoltaic cells (PVC) [8–11]. One of the key issues which inhibit the application of organic semiconductors is the low charge mobility. Although great progress has been made and the value of mobility has been achieved more than 10 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ for organic thin film [12] and single crystals [13], there are still great challenges to further improve the charge mobility

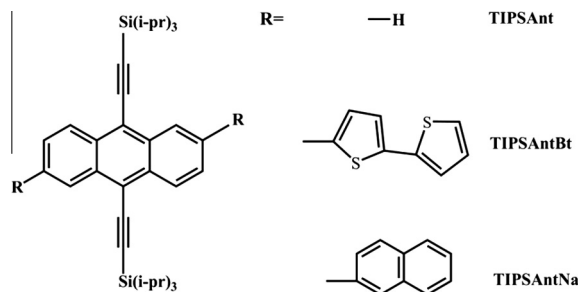
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[14]. One of the most often used methods to obtain high charge mobility is to functionalize organic π -conjugated compounds and receive a larger π -conjugated plane and face-to-face stacking motif. In particular, oligoacenes [15–17] and oligothiophenes [18–22] have been widely explored due to their large π -conjugated plane and high charge mobility.

To date, many modified acenes were reported to exhibit high charge mobility and high stability [14,23–25]. For example, Anthony and co-workers reported that pentacene with triisopropylsilyl ethynyl (TIPS) at the 6 and 13 positions exhibited charge mobility over $1\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ and good solubility [26,27]. They also reported that anthradithiophene, tetracene based OFETs show superior transistor characteristics [28,29]. Tang et al. synthesized two new asymmetric linear acenes, anthran [2,3-b] thiophene and tetraceno [2,3-b] thiophene, which show higher charge mobility and stability [30]. Comparatively, Arulmozhiraja and co-workers designed new semiconductor candidates based on the two compounds mentioned in Tang's work through a theoretical analysis, providing a microscopic view in understanding the relationship between molecular structure and transport properties of materials [31]. Besides, Kjelstrup-Hansen's group investigated the charge transport property in oligo phenylene and phenylene-thiophene nanofibers, and demonstrated charge mobilities as high as $1\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ combining experiment and theoretical techniques [32]. Recently, many anthracene based semiconductors have been explored due to their higher oxidative stability compared with that of pentacene [33–37], both experimentally and theoretically. Meng et al. reported two anthracene derivatives based on thiophene-anthracene oligomers that show the field-effect mobility as high as $0.5\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ [38]. Accordingly, Duan and co-workers investigated the charge transport properties of the same compounds using density functional theory, providing theoretical guidelines for designing novel materials with high charge mobility [39].

Chan Eon and co-workers reported that TIPS anthracene derivatives showed high solubility and moderate OFETs performance from solution processing [40]. Also, they synthesized soluble TIPS-anthracene (TIPSAnt) derivatives containing heteroaromatic derivatives at the 2, 6-positions of the TIPSAnt core. One of them showed the field effect mobility as high as $3.7\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$. Furthermore, they made comparative studies between the molecular-packing parameters and the field-effect mobility in single crystal OFETs experimentally [41]. What still lack is to explore the intrinsic reason of the high charge mobility and the substituent effects for these compounds from microscopic view. Based on the quantum chemical calculations, in this work, we investigated the charge transport property of TIPSAntBt and TIPSAntNa (the chemical structures of TIPSAnt, TIPSAntBt and TIPSAntNa can be seen in Scheme 1) through optimizing the geometry, calculating the reorganization energy, frontier orbitals, IPs, EAs, transfer integrals and charge mobility, band structure and effective mass. Through this work, we are expecting to shed light on designing organic semiconductors with high charge mobility and n -type semiconductors in experiment.



Scheme 1. Chemical structures of TIPSAnt, TIPSAntBt and TIPSAntNa examined in this work.

2. Computational methods

All the calculations are implemented in Gaussian 09 package [42]. The optimized geometries of neutral and charged states are obtained at the DFT level using B3LYP hybrid functional [43,44] and 6-31G** basis set [45–48]. Harmonic vibrational frequencies are also calculated at the same level to ensure the accuracy of the results.

As we all know that there are mainly two theoretical mechanisms in organic semiconductors: the coherent band model and the incoherent hopping model [45]. Generally, the band model is employed for perfectly ordered defect-free organic crystals at low temperature. When the temperature is higher than 150 K, Cheng et al. have demonstrated that the simple band model is not suitable to describe the charge carrier mobility [49]. Although several recent experimental reports indicate that rubrene single crystals etc. show a band-like mechanism for delocalized carrier at room temperature, because its transfer integral is close to its reorganization energy [50–54], Troisi [55–57] and Shuai [58,59] proposed hopping model considering nonlocal electron-phonon coupling and nuclear tunneling effects to give reasonable explanations for the phenomenon of the band-like temperature dependence of the mobility. At high temperature, the thermal disorder may strongly localize the charge and the lattice phonons are strongly coupled with the charge motion, suggesting that the hopping may dominate. Also, Shuai and co-workers [60] demonstrated that when the electronic coupling (V) is much less than the molecular reorganization energy (λ), each molecule acts as a charge trap, it is thus appropriate to choose Marcus theory to calculate the intermolecular charge transfer rates. In order to obtain the charge mobilities of TIPSAntBt and TIPSAntNa at room temperature (298 K), the thermally activated hopping model is adopted to describe the carrier motion process.

In the hopping regime, the charge transfer rate between neighboring molecules i and j can be described by Marcus theory [61],

$$K = \frac{V_{ij}^2}{\hbar} \left(\frac{\pi}{\lambda k_B T} \right)^{1/2} \exp \left(-\frac{\lambda}{4k_B T} \right) \quad (1)$$

Here, k_B is the Boltzmann constant, T is the room temperature (298 K), V is the transfer integral between i and j , and λ is the reorganization energy. It can be noted that

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