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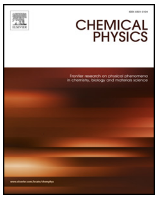

Theoretical studies on 4H-cyclopenta[2,1-b:3,4-b′]dithiophene-based Windmill-shaped nanogrids with low reorganization energies

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ABSTRACT

A new kind of organic charge transport nanomolecule, 4H-cyclopenta[2,1-b:3,4-b′]dithiophene-based windmill-shaped nanogrid called WG-CPDT, and its corresponding derivatives substituted by ethynyl, cyano, fluorine and methyl groups at 1-position of CPDT moiety, was designed and studied theoretically. The density functional theory (DFT) was then employed to investigate the molecular structures and electronic properties such as molecular orbitals, ionization potentials (IPs), electron affinities (EAs), reorganization energies (λ). Furthermore, the noncovalent interaction analysis and the normal mode analysis were utilized to estimate the intramolecular weak interactions and the contributions of each vibrational modes to reorganization energies, respectively. The results indicate that WG-CPDT possesses a small reorganization energy in the electron transfer process, and that WG-CPDT is a kind of potential organic electron transport material. This is especially notable when WG-CPDT is modified with cyano on the 1-position of the CPDT moiety and the electron reorganization energies decrease to 0.099 eV. In addition, the delocalization of LUMO near $C(sp^3)$ position is consistent with the $S\cdots\pi$ and $C{-}H\cdots\pi$ weak interactions, which favors good electron transport properties. This work provides new insights into a type of bulky macrocycle in charge transport materials.

1. Introduction

Organic semiconductors have attracted much attention owing to the obvious advantages of organic devices such as their ultra-thinness, large area, low cost, and flexibility over their inorganic counterparts [1–4]. However, several basic parameters still lag behind in terms of mobility in spite of many efforts made in many other aspects. For example, inorganic semiconductors have an advantage of mobility, as seen in a plasma-grown diamond that has an electron mobility of $4500\ cm^2{\cdot}V^{-1}{\cdot}s^{-1}$ and a hole mobility of $3800\ cm^2{\cdot}V^{-1}{\cdot}s^{-1}$ [5] and as seen in single-crystal silicon with mobilities of 10^2–$10^3\ cm^2{\cdot}V^{-1}{\cdot}s^{-1}$ [6]. Traditionally, organic materials have mobility of around $10^{-5}\ cm^2{\cdot}V^{-1}{\cdot}s^{-1}$ [7], in spite of graphene with a mobility of $15{,}000\ cm^2{\cdot}V^{-1}{\cdot}s^{-1}$ at room temperature. Recently, the mobility of an organic semiconductor for hole reached $36.3\ cm^2{\cdot}V^{-1}{\cdot}s^{-1}$ under a new strategy [8]. Over the past several years, many efforts have been made and great achievements have been accomplished in the application of device technology and molecular design. For instance, the steric hindrance effects [9] such as the bulky end-capped [1]benzothieno[3,2-b]benzothiophene (BTBTs) [10] attempts to modulate the charge transport properties of the resulting materials by changing the molecular packing lattice. However, the measured average hole mobility is still relatively small ($7.1\ cm^2{\cdot}V^{-1}{\cdot}s^{-1}$). Up to now, the mobility improvement is a thorny issue [11]. How to subtly keep the bulky structures with a high mobility still has not been created.

According to Marcus theory, the mobility can be estimated by the two parameters of the reorganization energy and the transfer integral [12]. The internal reorganization energy (λ) has a strong influence on

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organic electronic devices which can be utilized in molecular design strategies to improve the material transport properties. Most organic semiconductors have λ greater than 0.1 eV, while several p-type organic semiconductors have been reported with λ^+ of less than 0.1 eV, including phthalocyanines (0.036–0.098 eV) [13], pentacene (0.093–0.098 eV) [14], and cicum(oligo)acenes (0.057–0.127 eV) [15]. Several *n*-type organic semiconductors with λ^- of less than 0.1 Ev are fullerene C_{60} (0.060 eV) [16], octacyanopentacene (0.095 eV), azadipyrromethene-Based Metal Complexes (0.068–0.210 eV) [17] and polymers of phenylethynyl-1,3,4-thiadiazole (0.07 eV) [18]. The low λ^- of fullerene is explained by its rigidity and large π system that can delocalize electrons over a three-dimensional (3D) framework. The low λ^- for octacyanopentacene is ascribed to the nonbonding character contribution of the cyano groups to the LUMO. The low λ^- of 1,3,7,9-tetraphenylazadipyrromethene and its complexes are due to a strategy of metal complexation. Overall, the common methods to obtain a small λ include rigid structures, extended conjugation, and the nonbonding character of frontier molecular orbitals [19,20]. Substituent effects are of also a primary interest in reducing λ. For example, the cyano group can lead to a nonbonding character of frontier molecular orbitals and thus obtain a smaller λ. Besides, when substitutions reduce the amplitude of the relevant frontier molecular orbital in that segment, the total reorganization energy decreases as seen in chlorine substitutions at appropriate positions in the case of indolo-carbazole [21].

The 4H-cyclopenta[2,1-b:3,4-b]dithiophene (CPDT) moiety is widely used in conjugated polymers [22] due to the intramolecular noncovalent interactions such as the interaction of S···H [23]. CPDT is unstable and is easily oxidized due to the narrow band gap and higher HOMO levels, nevertheless the functionalized CPDT-derivatives have been studied as electron transports materials [24,25]. Here, the 9-phenyl-CPDT is chosen as a good monomer and building block to construct a rigid bulky structure with extended conjugation. Additionally, a CPDT-based windmill-shaped nanogrid termed WG-CPDT is designed and theoretically investigated. This WG-CPDT molecule can be synthesized and accessed via three synthetic routes, namely the Friedel–Craft reaction, C–H activation reaction and Suzuki coupling reaction. The synthetic routes for analogous nanogirds have been reported [26,27] and such kind of windmill-shaped three-member-ring molecules has been reported in organic field effect transistor (OFET) devices [28]. The schematic structures of WG-CPDT are shown in Fig. 1, as well as the derivatives substituted by ethynyl (C1-1-C_2H), cyano (C1-1-CN), fluorine (C1-1-F) and methyl (C1-1-CH_3) groups at 1-position of CPDT. In this study, the geometric structures and electronic properties of WG-CPDT and their derivatives are performed by density functional theory (DFT). The computation results show that WG-CPDT has eight optimized ground-state geometries, and C1-1 with the lowest energy possesses a small strain energy (2.29 kcal/mol). Furthermore, visualization of noncovalent interactions are plotted because they are closely correlated with the delocalization of the LUMO orbitals. Most interestingly, the calculated electron reorganization energy is small (0.105 eV for C1-1), and the substituent effect of a cyano group further reduces the reorganization energy to 0.099 Ev that is suitable for electron transport materials.

2. Theoretical and computation methodology

All the quantum chemical calculations were performed using Gaussian 09 Program package [29]. The density functional theory (DFT) with B3LYP hybrid functional and 6-31G(d) basis set [30] is used to optimize the geometric structures of all of the stationary points (the isomers and transition states of WG-CPDT and their derivatives). Harmonic vibration frequency calculations at the same level are performed to verify all stationary points as local minimum (with no imaginary frequency) or transition state (with one imaginary frequency). The strain energies of WG-CPDTs were calculated using homodesmotic reactions in which reactants and products contain equal numbers of carbon atoms in corresponding states of hybridization [31–34]. Moreover, there is matching of the carbon-hydrogen bonds in terms of the number of hydrogen atoms joined to the individual carbon atoms. The homodesmotic reaction adopted in this work are shown in Scheme 1.

The charge transport processes for hole and electron between two adjacent molecules follow the reactions

$$M + M^+ \rightarrow M^+ + M$$

$$M + M^- \rightarrow M^- + M$$

Here M is the molecule that undergoes the hole and electron transfer processes. The hopping rate can be described by Marcus theory by the following equation:

$$k = \frac{V^2}{\hbar}\left(\frac{\pi}{\lambda k_B T}\right)^{1/2}\exp\left(\frac{\pi}{4k_B T}\right)$$

According to the equation, one important factor that affects the rate of charge transfer is the reorganization energy λ, which is usually evaluated based on the adiabatic potential energy surface (AP) approach [35]. A detailed methodology is represented in Fig. S1. In addition, the normal mode analysis was also conducted using the DUSHIN program [36] for comparison purposes. The λ can be distributed into the normal modes and described as

$$\lambda = \sum \lambda_i = \sum \frac{1}{2}\omega_i^2 \Delta Q_i^2$$

where λ_i is the reorganization energy corresponding to mode *i* with frequency ω_i. ΔQ_i represents the displacement along the *i*-th normal mode coordinate between the equilibrium positions of neutral state and charge state. The total reorganization energy is obtained by summing up the individual reorganization energy corresponding to each vibrational mode.

In order to visualize the weak interaction in the molecules investigated here, the reduced density gradient (RDG) studies were

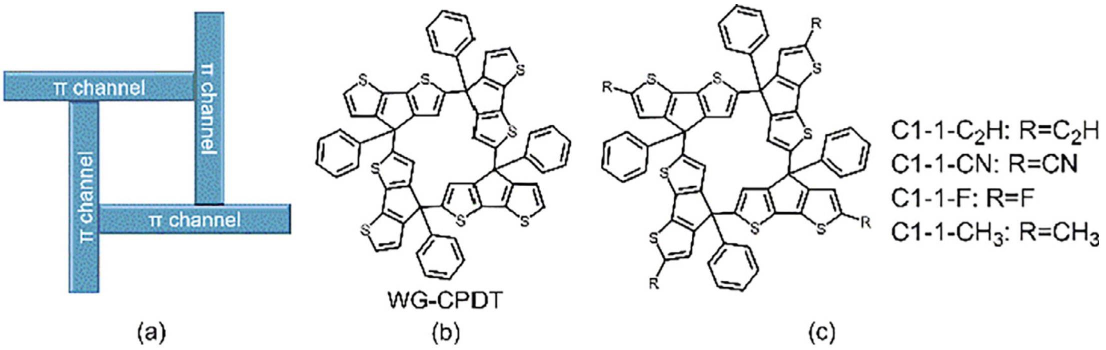

Fig. 1. (a) Schematic diagram of the organic molecules with shapes of the windmill; (b) molecular structures of WG-CPDT; (c) molecular structures of substituent derivatives of WG-CPDT.

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