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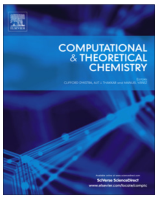

Theoretical investigation on electronic, optical, and charge transport properties of new anthracene derivatives

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ABSTRACT

The electronic structures and charge transport properties of the two new anthracene-core conjugated molecules, 1-(9-anthrylvinyl)-4-benzyloxybenzene (AVB) and 1,4-bis(9-anthrylvinyl)benzene (AV2B) and its derivatives, were investigated by using density functional theory (DFT), which was compared with experimental results. AVB and AV2B derivatives were supposed to be ones of the conductive materials for organic and hybrid applications because of their optoelectronic and electrical properties. The impact of substituents on gap energies and charge mobilities were explored based on TDDFT and Marcus theories, respectively. The calculated results showed that the hole mobility for AVB was high as compared with the AV2B molecule, which was related to the electrical properties. For improving its characteristics, the charge transport properties of AV2B can be significantly tuned via introducing different substituents. Therefore, the hole reorganization energy (λ_+) decreased by increasing the number of PPV units and introducing Ag_3 metal, which was 0.154 for AV2BPPV3TA3 compared with 0.230 for AV2B; so the hole mobility μ_+ which is in inverse ratio to λ_+ will be higher.

1. Introduction

Organic electronics is a field with great potential for future markets. Organic materials with conjugated systems have been extensively employed in the electronics and optoelectronics industries for more than 40 years. Several applications can be observed in the organic semiconductor field [1,2]; among such applications one can find light-emitting diodes, transistors, biosensors, among others [3]. Organic light-emitting diodes (OLEDs) have attracted great interest for decades because of their potential application as new display devices. Charge mobility and solid-state luminescent efficiency are two key factors determining the performance of OLEDs. The high charge mobility usually requires strong intermolecular interaction, so organic π-conjugated molecules with large planarity and long π-system extension are expected. However, on the other side, the strong intermolecular interaction could easily lead to luminescent aggregation quenching. So, a balance between charge mobility and luminescent efficiency is required in order to obtain OLEDs with high performance.

The past few years have seen a large number of theoretical investigations for further developments in the field of organic electronics [4]. We focus here on the application of modern computational techniques to organic materials to accurately describe their hole and electron transport properties. Common features that control the performance of the devices based on organics are charge injection (or collection) at the electrodes [5], charge transport across the active layer [6], charge recombination (or separation) [7], dynamics of exciton formation (or dissociation) [8], energy transfer in the bulk material [9], supramolecular organization of the samples [10], interchain interactions [11], chemical and structural defects, and absorption or emission properties [12].

Anthracene stands out within the group of organic materials due to its natural characteristics of luminescence [13]. Another feature is that its central ring oxidizes and reduces easily, because of the action of the central atoms that keep two phenylic rings and its aromatic system intact; this action enables the incorporation of substituent groups which might increase its capabilities for applications in energy production [14]. Diverse studies both experimental and theoretical have been carried out of anthracene and its derivatives [15]. In regards to theoretical studies, the molecular structure plays an important role because it is directly related to energy parameters such as the ionization potential, electron affinity, and excited states energies.

In this study, two anthracene derivatives, AVB and AV2B, are investigated by experimental technique and theoretical method in order to determine their optoelectronic and electrical properties.

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Furthermore, the effect of the introduction of PPV units and Ag_3 metal [16] is studied in the goal to improve essentially the optical, electronic, and electrical properties of these materials.

2. Computational methods

The ground, the ion, and the excited-states geometries were fully optimized by using density functional theory (DFT) [17] with the B3LYP hybrid functional [18] at the basis set level of 6-31G*. Calculations were performed manly in four steps. Geometry optimization of the molecules in the ground state was performed using DFT/B3LYP/6-31G*. In fact, this basis set has been successfully applied to other anthracene-based systems. The B3LYP functional consists of a Becke's three parameter hybrid exchange functional combined with the Lee–Yang–Parr correlation functional [19]. In this basis set, d-orbitals have been added to non-hydrogen atoms such as carbon and hydrogen atoms. These calculations were followed by a determination of the Hessian to assess whether the stationary points obtained were minima. The second step consisted in a TDDFT/CAM-B3LYP functional at the 6-31G* basis set level calculation [20] of the absorption spectrum of the molecules. The ECP-type basis set (Effective Core Potential) was used to model Ag metal atom. This mixed basis set was created through the use of the GEN keyword in Gaussian 09. Here we were interested to calculate only the first excited singlet state (the highest wavelength). Then, the excitation energies of the low lying excited states were obtained. This method has shown to be ideal in estimating absorption and emission spectra and further details are available in the literature [21]. The third step consisted in the geometry optimization of the chosen excited state, normally obtaining a transition state. Starting from this structure, one seeks along the transition vector to find the minimum that permits the evaluation of the emission wavelength. All calculations were performed using the computational package Gaussian 09 [22] and the graphical interface Gabedit [23].

Generally speaking, two extreme models have been widely used to evaluate the charge (hole and electron) mobility. One is the coherent band model [24]; the other is the incoherent hopping model [25]. In the former, the carrier moves as a highly delocalized plane wave in an energy band with a relatively long mean free path (μm). The interaction between the nearest-neighbor sites (charge transfer integral) is large compared with dynamic disorder, that is the reorganization energy resulting from charge transfer from one molecule to another. This model is usually suitable for inorganic semiconductors where the interaction between different sites is through strong valence bonds and the room temperature mobility is far bigger than 1 $cm^2\,V^{-1}\,s^{-1}$. Accordingly, the hopping model is suitable for most organic materials, and the theoretical prediction of mobility is in good agreement with experimental observations. The carrier is localized and moves by hopping from site to site, carrying a structural deformation with it. The basic characteristic of this model is that the lattice phonons are strongly coupled with the charge carrier, such that the wave momentum (k) that characterizes a band state is not conserved. The room temperature mobility for the hopping model is usually far smaller than 1 $cm^2\,V^{-1}\,s^{-1}$ and is proportional to $\mathrm{Exp}\left(-\frac{E_a}{kT}\right)$, where E_a is the activation energy, that is, the energy barrier that must be overcome to transfer a carrier to an adjacent site. The hole and the electron transport process at the molecular level in the electroluminescent layer can then be portrayed as the electron transfer/hole transfer reactions between the neighboring molecules.

$$A^{+/-\cdot} + A' \rightarrow A' + A^{+/-\cdot}$$

where A' is the neutral molecule interacting with neighboring oxidized or reduced $A^{+/-\cdot}$. In the case of electron transport the interaction can be considered between a molecule in the neutral state interacting with a radical anion and in the case of hole transport the interaction can be considered between a molecule in the neutral state and a cation. The development of quantum chemistry provides an effective means to predict the physical and chemical properties of materials and devices. Our simulation model is based on a combination of first-principles quantum mechanics calculations and Marcus theory [26]. By using the hopping mechanism to describe the charge transfer, the rate (K_{ET}) of intermolecular charge hopping can be described in Eq. (1)

$$K_{ET} = \frac{2\pi t^2}{h}\left(\frac{\pi}{\lambda k_B T}\right)^{1/2} \exp\left(-\frac{\lambda}{4k_B T}\right) \tag{1}$$

Here k_B is the Boltzmann constant, and T is the temperature (298 K). There are two major parameters that the charge-hopping rate and ultimately charge mobility: the intermolecular transfer integral (t) and the intramolecular reorganization energy (λ). The K_{ET} is in direct ratio to t, and is in inverse ratio to λ. An evaluation of t would require the stacking mode between two adjacent molecules [27], and it can be obtained by two approaches: one is to resort to Koopmans' theorem [28]; the other is to directly calculate the coupling matrix element of the frontier orbitals [29]. The reorganization energy is a key parameter to determine the charge-transfer rate K_{ET}, and it can be calculated by using the B3LYP/6-31+G* level (this basis set give reasonable results [30]). As shown in Fig. 1, the reorganization energy for hole transport (λ_+) is the sum of two energy terms: one is the relaxation energy (λ_1) along the cation state potential energy surface when an electron is removed from the neutral geometry; the other is the relaxation energy (λ_2) along the ground-state potential energy surface when an electron is re-accepted from the cation geometry back to the neutral geometry. Similarly, the reorganization energy for electron transport (λ_-) equals the sum of the two relaxation energies λ_3 (neutral to anion) and λ_4 (anion back to neutral). Since the contribution to the reorganization energy from electronic polarization of surrounding molecules is quite small [31], here the environmental factor for reorganization energy is ignored, and only the intra-molecular reorganization energy is evaluated in this work. The internal reorganization energy reflects the geometric changes in the molecule when going from the neutral to the ionized state and vice versa.

The next step is to calculate the transfer integrals. The electronic coupling can be obtained either by Koopmans' theorem, which has been widely employed, or by directly evaluating the coupling element for the frontier orbitals [32]. In the former case, the charge transfer integral t [33] corresponds to half of the splitting of the HOMO and HOMO−1 or LUMO and LUMO+1 levels of the dimers for holes or electrons, respectively. In order to estimate the electronic coupling, all the dimers are optimized by the ωB97XD/6-31G* level with ω = 0.2 (ωB97XD was used because

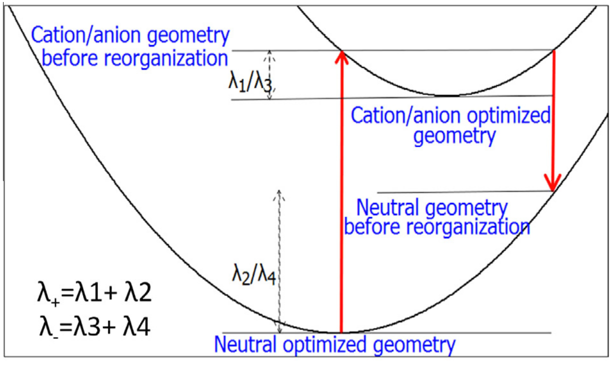

Fig. 1. Calculation of the reorganization energy.