Journal of Physical Chemistry and Functional Materials

Home Page of Journal: https://dergipark.org.tr/jphcfum

A Theoretical Study of Charge-Transfer Properties of a new Material involving Naphthalenyl Unit

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ABSTRACT

In this study, the charge transport properties of 4- [(E)- [(2-hydroxy-1-naphthalenyl) methylene] amino] -3-methyl benzoic acid (HNMB) molecule were determined by using Marcus and DFT methods. In addition to this, reorganization energies (λe and λh), the ionization potentials (IPs) and the electron affinities (EAs) are also reported. It is understood from the results that HNMB has suitable photovoltaic properties in terms of solar cells.

ARTICLE INFO

Keywords:
Marcus method,
charge transport properties,
reorganization energy,
solar cells

Received: 22-04-2021,
Accepted: 12-05-2021
ISSN: 2651-3080

1. INTRODUCTION

In the current scenario, solar energy has received a lot of attention due to its increased energy need and availability worldwide. This energy need is aimed to be met from organic-based solar cells due to the high production costs of silicon-based solar cells [1-3]. In addition, there are results showing that the conjugate molecule used in the solar cell increases the structure-property relationship efficiency [4]. In addition, whether the molecule is suitable for photovoltaic cells is also linked to the relationship between structure and property.

HNMB is a commercial molecule important for mechanochromatic luminescent and OLED materials. In addition, HNMB was synthesized by Zhang et al [5], and its emission properties and reliability in pressure sensor applications were investigated.

The HNMB molecule is a polycyclic aromatic hydrocarbon containing naphthalene. Naphthalene-addition polycyclic aromatic hydrocarbons are available in many experimental [6-9] and theoretical studies [10-13].

In this report, the charge transfer properties for HNMB sample was investigated by Amsterdam density functional (ADF2019) [14].

2. METHOD

ADF is a successful computational chemistry software for calculating molecules in terms of structure, electronics, optics and more. Firstly, the dimer structure of the subject compound has been optimized in the ADF program and is given in Fig. 1. Next, the charge transfer integrals of HNMB molecule optimized at the B3LYP/TZP level was calculated.

Charge transfer rate (W) of HNMB is found by following equation [15-18], known as the Marcus-Hush equation.

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

where λ is the reorganization energy, T is the temperature, V is the effective charge transfer integral and $\hbar$ and k_B are the Planck and Boltzmann constants, respectively.

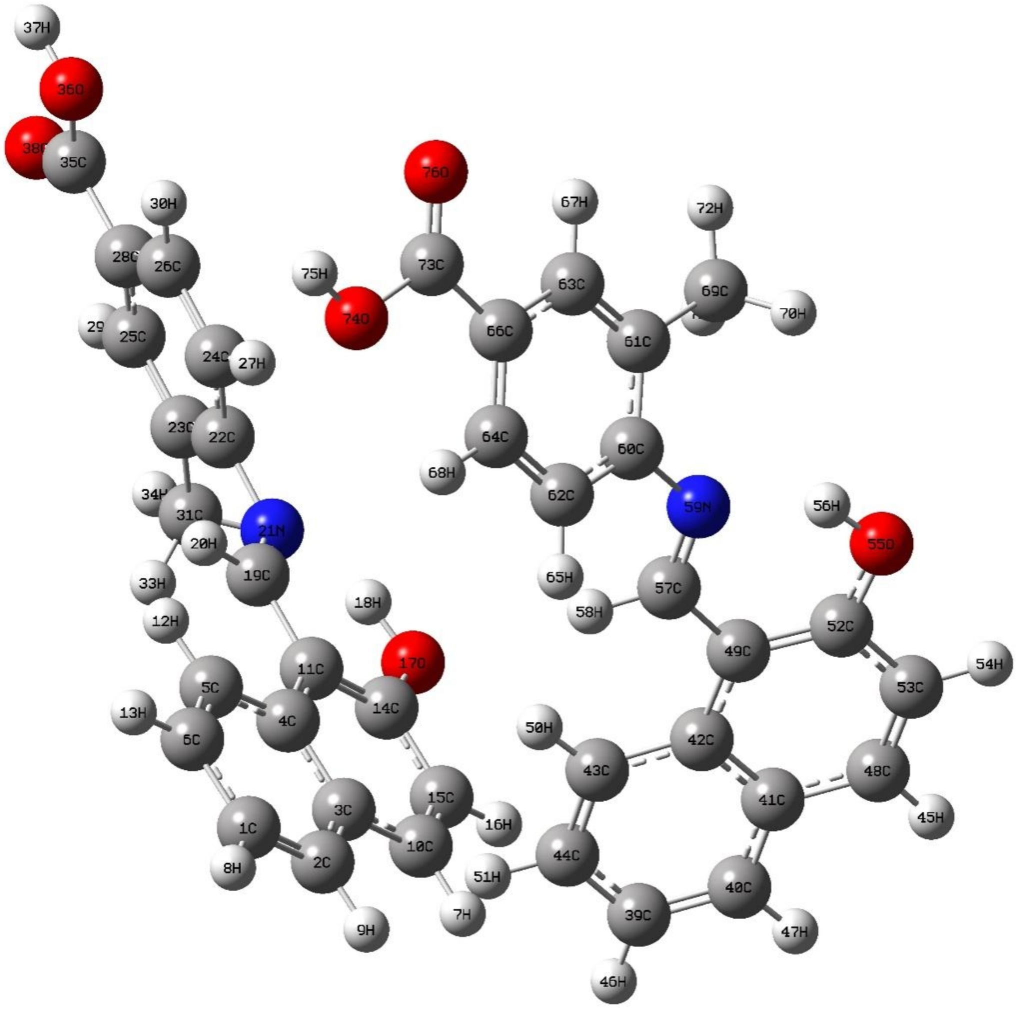

Fig. 1. Optimized structure of HNMB dimer

V_{ij} representing the electronic coupling between intermolecules; depending on the spatial overlap (S_{ij}), charge transfer integrals (J_{ij}) and site energies ($e_i(j)$), respectively,

$$V = \frac{J_{ij} - S_{ij}(e_i + e_j)/2}{1 - S_{ij}^2} \tag{2}$$

Electron (or hole) reorganization energies, λ_e (or λ_h) can be written as follows:

$$\lambda_h = \lambda_1 + \lambda_2 = [E^+(g^0) - E^+(g^+)] + [E^0(g^+) - E^0(g^0)]$$
$$[(E^+(g^0) - E^0(g^0)] - [(E^+(g^+) - E^0(M^+))] \tag{3}$$

and

$$\lambda_e = \lambda_3 + \lambda_4$$
$$[E^0(g^-) - E^0(g^0)] + [E^-(g^0) - E^-(g^-)]$$
$$[E^0(g^-) - E^-(g^-)] - [E^0(g^0) - E^-(g^0)] \tag{4}$$

$E^0(g^0)$ is the energy of the neutral molecule in neutral geometry, $E^{+/-}(g^{+/-})$ is ion energy (cation/anion) in ionic geometry, $E^{+/-}(g^0)$ is ion energy (cation/anion) in neutral geometry, and $E^0(g^{+/-})$ in ionic geometry, the energies of the neutral molecule are shown in equations 3 and 4.

Ionization potentials (IPa/IPv) and electron affinities (EAa/Eav) significantly affect the injection ability of the sample [19-22]. The vertical and adiabatic ionization potentials (IP_v /IP_a), the vertical and adiabatic electron affinities (Ea_v/EA_a) of the HNMB were obtained as follows:

$$IP(v) = E^+(g^0) - E^0(g^0) \tag{5}$$

$$IP(a) = E^+(g^+) - E^0(g^0) \tag{6}$$

$$EA(v) = E^0(g^0) - E^-(g^0) \tag{7}$$

3. RESULTS AND DISCUSSION

The calculated reorganization energies of HNMB molecule are tabulated in Table 1. These calculated values are factors affecting the performance of solar cells. For example, the mobility of electrons and holes is closely related to the reorganizational energy. The reorganization energy of an electron or hole varies inversely with the transport rate. It can be seen from Table 1 that HNMB can be used as electron transport material in solar cells.

The bigger EA and smaller IP means better electron and hole transport [23]. Table 1 shows all adiabatic/vertical EAa/v and IPa/v values of HNMB. The EAa/v and IPa/v values of HNMB 6.416/5.544 and 0.639/0.884 eV. Therefore, the HNMB molecule can form suitable for the electron injection layer.

Table 1. The calculated reorganization energies (in eV).

Molecule	$\lambda_{electron}$	λ_{hole}	IP_a	IP_v	EA_a	EA_v
HNMB	0.682	0.951	0.639	0.884	6.416	5.544

In order to calculate effective transfer integrals, the HNMB dimer structure was created in the anisotropic position of the molecule. Transfer integral results of this geometry are given in Table 2. The larger the transfer integral and the greater the charge transfer will be. The electron transfer integral of HNMB is higher than its hole transfer integral. So, it can be said that HNMB is a good candidate as electron transfer material.

Charge transfer rates ($W_{electron}$ and W_{hole}) are calculated using equation 1 for HNMB in parallel geometry at 298.15 K and are tabulated in Table 2. HNMB molecule has a high electron transfer rate ($260x10^9$ s^{-1}).

Table 2. The charge transfer integrals (in eV) and the charge transfer rates (in s^{-1}).

Molecule	$V_{electron}$	V_{hole}	$W_{electron}$	W_{hole}
HNMB	0.01757	0.00838	$260x10^9$	$140x10^9$

4. CONCLUSION

In the present work, the charge transfer properties of HNMB are obtained by theoretical calculations. Both reorganization energies and Marcus-Hush theory results proved that HNMB is a good electron transfer material. Thus, with these results, HNMB can be used as electron-transporting layers in solar cells and OLED structures.

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