

Anisotropic Charge Transport in 7,10-Diphenyl-8,9-Diazafluoranthene as N-Type Organic Semiconductor: A DFT Study

Rudranarayan Khatua^{1,a)} and Sridhar Sahu^{1, b)}

¹High Performance Computing lab, Department of Applied Physics, Indian Institute of Technology (Indian School of Mines) Dhanbad, India.

^{a)}Corresponding author: khatuarudranarayan@gmail.com
^{b)}sridharsahu@gmail.com

Abstract. We present anisotropic charge transport properties of 7,10-diphenyl-8,9-diazafluoranthene (DDF) organic molecule using quantum chemical density functional theory (DFT). The reorganization energies were found to be 0.56eV (λ_h) and 0.27eV (λ_e) for DDF molecule. The highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and HOMO-LUMO gap for DDF was calculated to be -6.318 eV, -2.735 eV and 3.583eV respectively. The maximum hole and electron mobility of the DDF compound were found to be $1.52 \times 10^{-3} \text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$ and $1.477 \text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$ respectively. The larger electron mobility than hole mobility implies that, the compound can be considered as a promising candidate for n-type organic semiconductor.

INTRODUCTION

Since last few years, organic semiconductors (OSCs) have attracted a considerable attention due to their wide potential applications in various electronic devices such as organic field effect transistors (OFETs), organic photovoltaic devices (OPVs), organic light emitting diodes (OLEDs) and organic solar cells (OSCs) [1, 2, 3]. Unlike their inorganic counterparts, organic semiconducting materials are cost-effective, flexible and light-weight, and also provide the versatility of chemical synthesis [4, 5, 6]. Organic semiconductors are classified into p-type and n-type materials because of their nature of (hole and electron) charge carrier transport. It has been reported that, the n-type materials are significantly lower in number than the p-type materials. Since last few years, researchers continue to focus their attention on organic materials with high electron mobility (electron injection). The sulfur-hetero fluoranthene derivatives were reported by Yan et al. and found that these materials exhibited as good oxidative and thermal stability in the air [7]. The fluoranthene, benzo[k]-fluoranthene and their derivatives has been investigated by Saranya et al. who found that the minimum value of HOMO-LUMO energy gap for thiophene-substituted fluoranthene and methoxyphenyl-substituted benzo[k]-fluoranthene molecules among all studied derivatives [8]. The optoelectronic properties of poly(p-fluoranthenevinylene) (PFV) and its derivatives were experimentally investigated by Palmaerts et al. who reported that the dodecyl-poly(p-fluoranthenevinylene) molecule had significantly high electron mobility ($1.4 \times 10^{-4} \text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$), which is suitable for n-type material [9].

To further understand the charge transport properties of diazafluoranthene derivatives, we report the anisotropic charge transport in 7,10-diphenyl-8,9-diazafluoranthene (DDF) as n-type organic semiconductor using density functional study.

THEORY

The anisotropic charge transport mechanism of organic materials is described by using Marcus-Hush theory at room temperature [10]. The charge hopping rate (K) is calculated by using the hopping mechanism;

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

Where k_B is Boltzmann constant, V is the intermolecular electronic coupling and λ is the reorganization energy.

$$V = \frac{J - S(t_1^{H/L} + t_2^{H/L})/2}{1 - S^2} \quad (2)$$

Where $t_1^{H/L}$ and $t_2^{H/L}$ are the site energies contributed from highest occupied molecular orbitals (HOMOs) or lowest unoccupied molecular orbitals (LUMOs), J and S are charge transfer integral and spatial overlap, respectively. The angular anisotropic charge carrier mobility in the organic crystals can be written as:[11]

$$\mu_\phi = \frac{e}{2k_B T} \sum_i K_i r_i^2 P_i \cos^2 \gamma_i \cos^2(\theta_i - \phi) \quad (3)$$

Where K_i is the hopping rate of charge between the adjacent molecules relative to crystal plane, r_i is the hopping distance, θ_i is the angle between the dimer pathways to the crystallographic reference axis, and ϕ is the orientation angle between the conducting channel to the crystallographic reference axis.

COMPUTATION

The initial geometry of the DDF compound was obtained from the reported crystal structure (CCDC 710133) as provided in the Cambridge Crystallographic Data Center [12]. All the optimization of molecules were performed using B3LYP hybrid exchange-correlation functional and 6-311++G (d, p) basis sets within the framework of density functional theory (DFT). All the optimizations were performed using the computational chemistry software Gaussian 09 [13]. All the calculation of the electronic coupling for the dimers of the DDF compound were calculated at the PW91PW91/6-31G (d) level using AOMIX package.

RESULT AND DISCUSSION

The frontier molecular orbitals (HOMOs and LUMOs) are depicted in Fig. 1 (a). The HOMO/LUMO energy and the HOMO-LUMO gap of DDF molecule are found to be -6.318 eV, -2.735 eV and 3.583 eV respectively. It is found that both HOMO and LUMO, π -orbital contributions are mainly attributed to the core atoms rather than peripheral sites. In addition, the calculated vertical (adiabatic) ionization potential (IP) and electron affinity (EA) are obtained to be 7.43 (7.79) eV and 1.51 (1.37) eV respectively. The electron reorganization energy ($\lambda_e = 0.27$ eV) is found to be lower than hole reorganization energy ($\lambda_h = 0.56$ eV) for DDF molecule. The low electron reorganization energy and large EA value indicate that the DDF molecule can display enhanced n-type characteristics. The molecular packing and charge hopping pathways of DDF crystal is illustrated in Fig. 1 (b). The crystal DDF shows cofacial packing with possible pathways; P, T1, T2, and T3 between the nearest dimers, where T2 is parallel face-to-face dimer, T1 and T3 are the parallel edge-to-edge packing dimer respectively. Φ is an angle of orientation with respect to the reference axis b and the reference plane of the crystal is $b-c$. The spatial overlap (S), electronic coupling (V) and mobility (μ) for all nearest dimers of DDF crystal are listed in Table 1. We observe the largest electronic coupling up to 114.5 meV for electron transport, for the parallel face-to-face T2 dimer, whereas the maximum coupling (12.0 meV) is found for hole transport for the parallel edge-to-edge T3 dimer. The anisotropic electron and hole mobility of DDF crystal is depicted in Fig. 2. The face-to-face parallel dimer (T2) is found to contribute high electron anisotropic mobility ($1.477 \text{ cm}^2 \text{V}^{-1} \text{sec}^{-1}$) as compared with that of the hole ($6.89 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{sec}^{-1}$) at $\Phi = 53^\circ$, and the minimum electron mobility is calculated to be ($6.86 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{sec}^{-1}$) at $\Phi = 143^\circ$. Along P dimer ($\Phi = 0^\circ$) and T3 dimer ($\Phi = 150^\circ$), $\mu_\phi(e)/\mu_\phi(h)$ are found to be $0.54 \text{ cm}^2 \text{V}^{-1} \text{sec}^{-1} / 1.198 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{sec}^{-1}$ and $2.42 \times 10^{-2} \text{ cm}^2 \text{V}^{-1} \text{sec}^{-1} / 1.52 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{sec}^{-1}$ respectively. The maximum hole mobility is found to be $1.52 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{sec}^{-1}$ and minimum hole mobility $2.98 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{sec}^{-1}$ at $\Phi = 152^\circ$ and $\Phi = 62^\circ$ respectively. The larger electron mobility than

hole mobility and lower electron reorganization energy than hole reorganization energy which implies that, the compound is a promising candidate as n-type organic semiconductor.

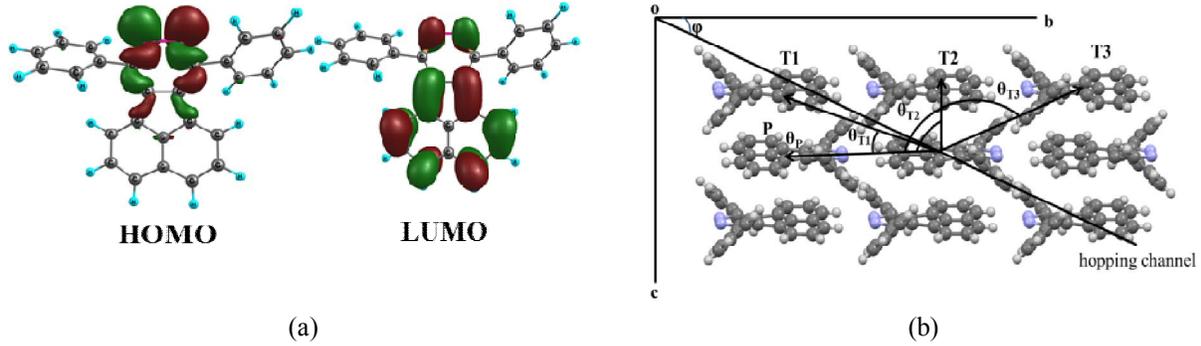


FIGURE 1.(a) The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and (b) molecular packing and charge hopping pathways to a transistor channel in the b-c plane of DDF compound.

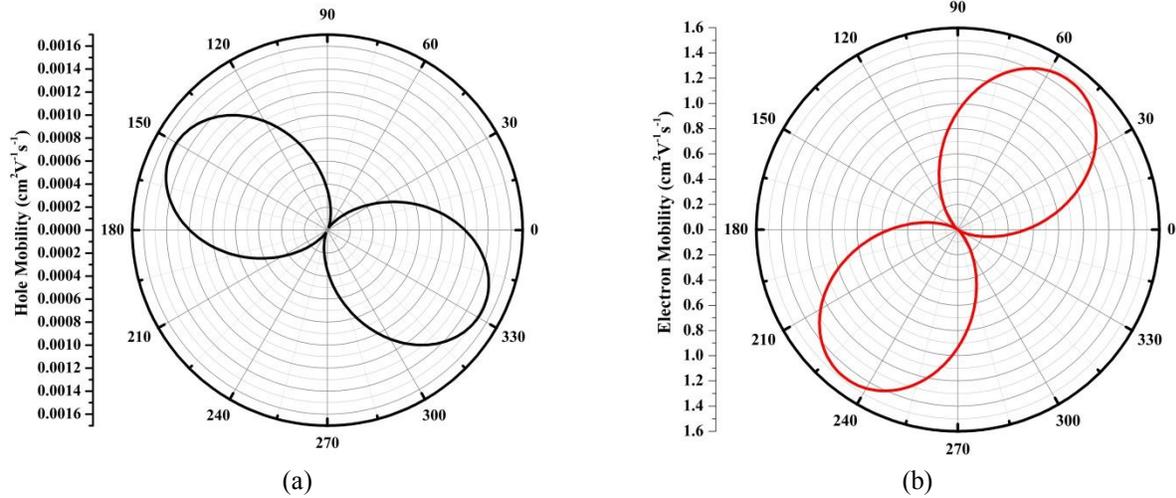


FIGURE 2.The anisotropic hole and electron mobility of DDF compound along a-b reference plane in the crystallographic axis.

TABLE 1. The calculated intermolecular distance (r), angle of orientation (θ), spatial overlap (S), electronic coupling (V), and anisotropic charge mobility (μ_{ϕ}) for DDF compound.

| Channel | r (\AA) | θ ($^{\circ}$) | S_h/S_e (meV) | V_h/V_e (meV) | $\mu_{\phi}(h)/\mu_{\phi}(e)$ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) |
|---------|----------------------|-------------------------|-----------------|-----------------|---|
| P | 9.947 | 0 | 0.8/-1.2 | -5.9/13.2 | $2.98 \times 10^{-5} - 1.52 \times 10^{-3}$ |
| T1 | 13.559 | 17.03 | 0.00/0.00 | 0.00/0.1 | $6.86 \times 10^{-4} - 1.477$ |
| T2 | 4.987 | 52.77 | 0.00/-17.3 | -0.5/114.5 | |
| T3 | 7.987 | 150.19 | 0.7/0.00 | 12.0/2.8 | |

CONCLUSION

In conclusion, we presented the charge transport properties of DDF molecule based on Marcus theory using the density functional theory. The hole reorganization energy was found to be more than twice of the electron reorganization energy. The calculated values of anisotropic hole mobility and electron mobility were found to be $0.00152 \text{ cm}^2\text{V}^{-1}\text{sec}^{-1}$ and $1.477 \text{ cm}^2\text{V}^{-1}\text{sec}^{-1}$, respectively, and the large electron mobility suggests the enhanced n-type characters of DDF molecule.

ACKNOWLEDGMENTS

Dr. S. Sahu gratefully acknowledges to the science and Engineering Research Board, Department of Science and Technology, Government of India, for extra-Mural Research Grant (file number: EMR/2014/000141).

REFERENCES

1. F. Wurthner and R. Schmidt, *Chem. Phys. Chem.* **7**, 793–797 (2006).
2. M. Muccini, *Nat. Mater.* **5**, 605–613 (2006).
3. Y. Shirota and H. Kageyama, *Chem. Rev.* **107**, 953–1010 (2007).
4. Y. Olivier, V. Lemaire, J. L. Bredas and J. Cornil, *J. Phys. Chem. A* **110**, 6356–6364 (2006).
5. Y. Yamashita, *Sci. Technol. Adv. Mater.* **10**, 024313 (2009).
6. M. M. Torrent and C. Rovira, *Chem. Rev.* **111**, 4833–4856 (2011).
7. Q. Yan, Y. Zhou, B. B. Ni, Y. Ma, J. Wang, J. Pei and Y. Cao, *J. Org. Chem.* **73**, 5328–5339 (2008).
8. G. Saranya, P. Kolandaivel, and K. Senthilkumar, *J. Phys. Chem. A* **115**, 14647–14656 (2011).
9. A. Palmaerts, L. Lutsen, T. J. Cleij, D. Vanderzande, A. Pivrikas, H. Neugebauer and N. S. Sariciftci, *Polymer* **50**, 5007–5015 (2009).
10. W. Q. Deng, L. Sun, J. D. Huang, S. Chai, S. H. Wen and K. L. Han, *Nat. Prot.* **10**, 632–642 (2015).
11. J. D. Huang, S. H. Wen, W. Q. Deng and K. L. Han, *J. Phys. Chem. B* **115**, 2140–2147 (2011).
12. N. Rahanyan, A. Linden, K. K. Baldrige and J. S. Siegel, *Org. Biomol. Chem.* **7**, 2082–2092 (2009).
13. M. J. Frisch et al., *Gaussian 09, Revision E.01*, Gaussian, Inc., Wallingford CT, 2013.