Theoretical Investigation of Optoelectronic Properties of Aryl Substituted Pentacene Derivatives

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***Abstract*—Pentacene derivatives have recently emerged as a potential material for organic electronics such as OLEDs, OFETs, and OPVs. In this paper, we report a thorough investigation of a series of pentacene derivatives substituted at the 6,13 position with aryl groups, using density functional theory (DFT) and Marcus formalism. Dispersion corrected Austin-Frisch-Petersson (APFD) functional is used to explore the electronic, optical and charge transport properties. The computed energy gap between the HOMO and LUMO levels of the compounds lie in the visible range between 2.54 eV to 2.80 eV. The viability of these materials as a transport layer in OLED is evaluated by assessing their charge transport characteristics. The large transfer integral and low reorganization energy for electron transport are indicative of a reasonably high electron transfer rate. We find that the 6,13-dithien-2-yl pentacene show higher electron transfer rate and may act as an electron transport material. The substitution with 6,13-bis(5-methoxythien-2-yl) in the pentacene backbone causes a red shift of the optical absorption spectrum. Our results suggest that aryl substitution tunes the charge transport properties along with optical absorption energies of pentacene derivatives.**

Keywords— Density Functional Theory, Marcus Theory, Charge transport, Pentacene derivatives

I. INTRODUCTION

Organic semiconductor materials, particularly π-conjugated molecules, have attracted significant attention in recent years for their use in optoelectronic devices, for example field-effect transistors, light-emitting diodes, and solar cells [1-4]. Organic electronic devices offer numerous favorable features, including light weight, cheap cost, flexibility, low-temperature device manufacture, chemical adaptability, and simple processing. The performance of many of the devices relies significantly on the charge carrier mobility of the organic materials [5]. Pentacene and its derivatives are regarded as a potential choice among organic π-conjugated materials owing to their strong charge carrier mobility and distinctive geometrical and electrical properties. However, pentacene has a few disadvantages. First, its insolubility demands the employment of vacuum deposition technologies. Second, pentacene is very susceptible to oxidation, resulting in the material's fast decomposition unless it is handled under strict oxygen exclusion [6]. These problems may be avoided by introducing substituents that improve stability, processability, and semiconductor device performance compared to traditional small molecule semiconductors. Until yet, several well-planned design of pentacene backbones have been manufactured; in particular, pentacene derivatives that provide sufficient performance for semiconductor devices frequently share a 6,13-substitution pattern. The pentacene core is more reactive at the 6- and 13-positions. Novel pentacene compounds were synthesized and investigated where the derivatives include unsymmetrical substitution based on a trialkylsilylethynyl group at the 6-position and various aryl groups added to the 13-position [7]. Anthony et.al. were the first to synthesize exceedingly soluble 6,13-disubstituted pentacene derivatives [8]. The effects of aryl substites on the resultant compound have been investigated on eight derivatives using x-ray crystallography and a variety of spectroscopic characterization methods. Their findings present a window of opportunity for comprehending the substitution-dependent properties of acenes and should assist their use in materials science [8, 9]. Additionally, it was shown by Vets et.al. that 6,13-diarylpentacenes are two orders more soluble than the parent pentacene, and are also very easy to synthesis [6]. Rohit Bhatia et.al. reviewed the various processes in synthesizing pentacene derivatives [9]. In this work, dispersion corrected Austin-Frisch-Petersson (APFD) formalism, and Marcus theory is used to analyze a series of pentacene derivatives substituted at the 6,13 position with aryl groups, which are Pent-a: 6,13-Bis(4-methoxyphenyl) pentacene, Pent-b: 6,13-Bis(4-acetylphenyl) pentacene, Pent-c: 6,13-Dithien-2-yl pentacene, Pent-d: 6,13-Bis(benzothien-2-yl) pentacene, Pent-e: 6,13-Bis(5-methoxythien-2-yl) pentacene, and compared the obtained result with its parent molecule pentacene. APFD is a hybrid functional that modifies the regular Austin-Frisch-Petersson functional by including dispersion adjustments and account for the influence of van der Waals interactions with extended range which are prevalent in nature [10]. Keeping this in mind theoretical exploration of the electronic as well as charge transport characteristics of the pentacene derivatives are further investigated.

II. METHODOLOGY

In recent years, DFT and TD-DFT have become a well-established technique for the theoretical analysis of molecular geometry together with electronic properties. At present, studies show great accuracy for a broad range of applications. DFT is used to expedite atomic calculations in

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the gas phase for the neutral, anion, and cation states separately. The whole set of calculations is performed using the quantum-chemical program Gaussian 16. The cationic and anionic state estimations are conducted utilizing unrestricted dispersion corrected Austin-Frisch-Petersson (APFD) formalism [11]. Based on the Marcus formalism, the charge transfer rate of pentacene derivatives at the molecular level were obtained [10, 12]. The optical absorption spectra were obtained for fifty excited states using TD-DFT method with LanL2MB basis set.

As because better electrical performance needs a stronger electronic coupling between adjacent molecules, Koopman's theory for the electron ($V_{electron}$) as well as hole (V_{hole}) were used to estimate the transfer integral, which is directly proportional to the rate of charge transfer [13]. The reorganization energy that is an crucial quantity for studying the charge transport characteristics because it is inversely proportional to the charge transfer rate. There are two fundamental types of reorganizational energy: internal and external. Experiments and theoretical analysis demonstrate, however, that the external reorganization energy contributes a minimal amount. In the case of a reversible charge transfer process, the relaxation energies are summed together to get the internal reorganization energies for the hole and electron.

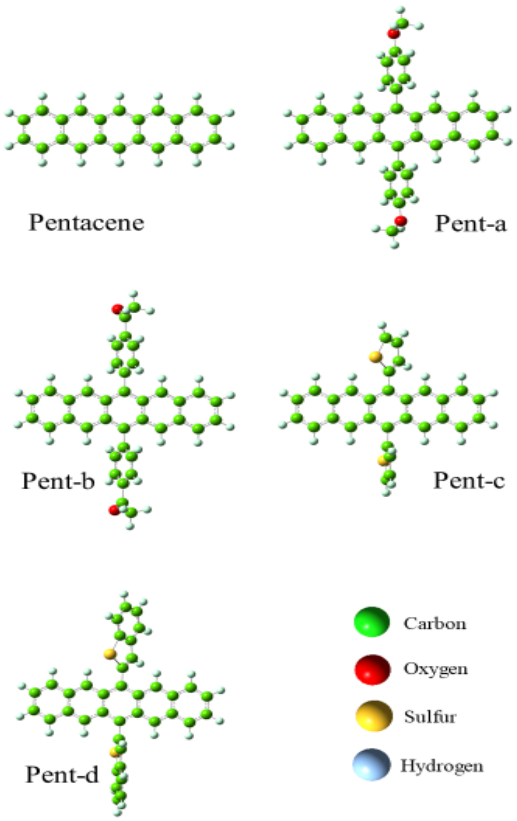

Fig. 1. Optimized structural geometries of Pentacene, Pent-a: 6,13-Bis(4-methoxyphenyl) pentacene, Pent-b: 6,13-Bis(4-acetylphenyl) pentacene, Pent-c: 6,13-Dithien-2-yl pentacene, Pent-d: 6,13-Bis(benzothien-2-yl) pentacene, Pent-e: 6,13-Bis(5-methoxythien-2-yl) pentacene.

III. Results and Discussions

A. Optimized Structural Geometry

The DFT/UAPFD molecular structures of pentacene and its four aryl-substituted derivatives have been shown in Fig.1. Among the derivatives, the optimized structure of Pent-b is the most symmetric in geometry. One of the side chains are twisted in Pent-c and Pent-d. The alignment of the derivatives in the film depends on the structural geometry of the derivatives.

B. Frontier Molecular Orbital, Electrostatic Potential and Electronic Energy Levels

The frontier molecular orbitals, HOMOs and LUMOs, are depicted in Fig. 2.

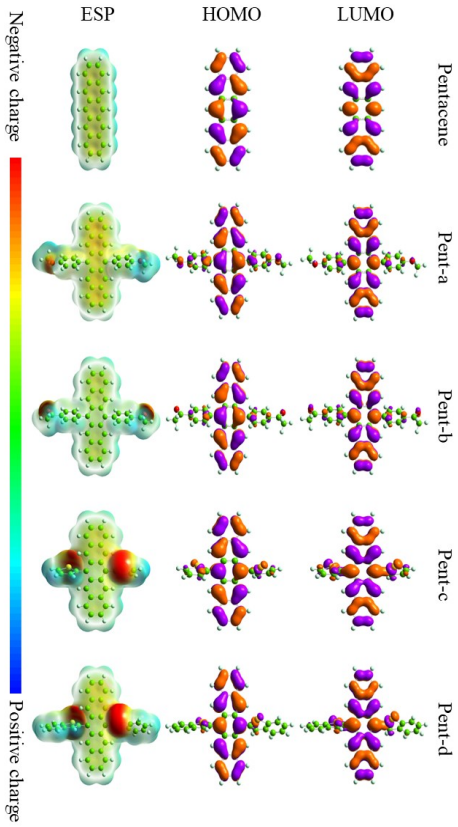

Fig. 2. Electronic density distribution of HOMO, LUMO and electrostatic potential for pentacene derivatives.

We notice that HOMO and LUMO of pentacene, Pent-a, Pent-b, Pent-c, and Pent-d are generally dispersed over the pentacene core. This suggests that the electron and hole transport occur along the same pathways in all the investigated molecules. The electrostatic potentials (ESP) mapped onto the surface of three-dimensional pentacene molecules. Negative charged regions are shown in red and positively charged regions in blue. We observe that, thienyl and benzothienyl groups in Pent-c and Pent-d have higher electron density than the central core. The ESP enables the prediction of electrophilic and nucleophilic sites. The energy gap, E_g is calculated theoretically from the energies of the HOMO and LUMO states. Fig. 3 shows the energies of HOMO, HOMO-1, LUMO, and LUMO+1. The E_g values ranges from 2.54 eV to 2.8 eV. Tuning the energy gap is important for required property in electronic devices.

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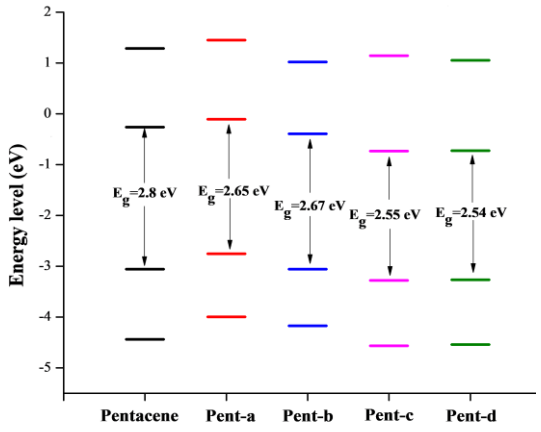

Fig. 3. Electronic structures of pentacene derivatives.

C. Charge Transport Properties

The electron and hole transport rates of pentacene molecules are shown in Fig. 4. Since pentacene has the smallest λ_{hole} of all its derivatives, its hole transport rate is the highest. Pent-c possesses higher $K_{electron}$ value among all the investigated pentacene derivatives and it may be used as an electron transporter. This is because thienyl group in Pent-c have higher electron density compared to other investigated pentacene.

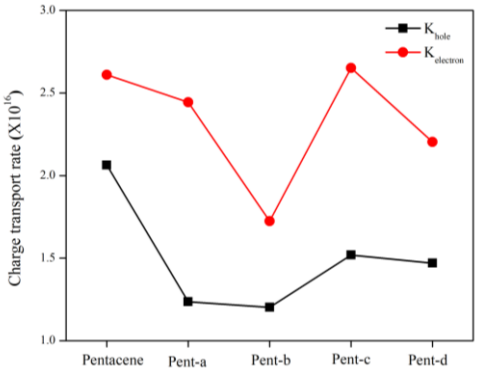

Fig. 4. Charge-carrier transport rates of the derivatives.

D. Optical Absorption Spectra

The calculated optical absorption peaks of pentacene and its four derivatives Pent-a, Pent-b, Pent-c, and Pent-d at visible range are observed at 2.61 eV, 2.43 eV, 2.46 eV, 2.32 eV and 2.32 eV, respectively. (Fig. 5) Another higher intensity peak around 5 eV and a weak peak or bump below 4.00 eV for all the compounds are observed. However, for Pent-b the high energy peak is much weaker compared to other pentacene molecules. The lower energy absorption is originated from π-π* transition.

Aryl substitution in the backbone of pentacene results in red-shift of the spectra compared to their parent pentacene molecule. From structure analysis we note that Pent-b is symmetrical and the high energy peak is much weaker than that of other compounds. The absorption spectrum of Pent-c and Pent-d are quite similar which is consistent with HOMO-LUMO energy gap. These pentacene derivatives were successfully synthesized by Vets et. al. [6]. The synthesized aryl pentacene derivatives show two orders higher solubility in THF than that of parent pentacene [14]. Therefore, these derivatives are feasible for solution processable spin coated thin-film device application. We conclude that, the choice of sidechains can be used to tune photon absorption energy which is essential for organic optoelectronic applications.

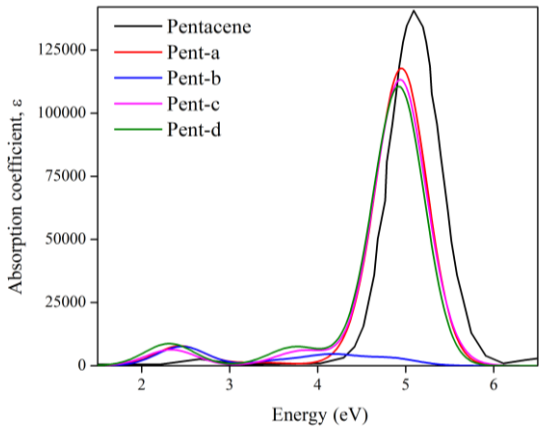

Fig. 5. Calculated optical absorption spectra of the Pentacene compounds.

IV. Conclusion

We have applied dispersion corrected Austin-Frisch-Petersson (APFD) formalism instead of B3LYP, and Marcus theory to calculate the charge carrier transport rate of pentacene and four of its aryl derivatives at the molecular level. APFD is a hybrid functional that modifies the regular Austin-Frisch-Petersson functional by including dispersion adjustments. The B3LYP functional does not account for the influence of van der Waals interactions with extended range, which are prevalent in nature. Optimized structural geometries, electronic structure with HOMO-LUMO energy gap and optical absorption spectra are presented. Our calculations suggest that Pent-c has the lowest LUMO energy that hinders photooxydation of devices that will act towards improving stability of devices. As the electron transport rate is higher for this derivative it can be used as electron transport layer in OLEDs. We anticipate that these findings will aid in experiments for the development of new types of OLEDs with improved efficiency and stability.

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References

[1] D. Di et al., “Efficient triplet exciton fusion in molecularly doped polymer light-emitting diodes,” Adv. Mater., vol. 29, no. 13, 2017.

[2] L. S. Grodd, E. Mikayelyan, T. Dane, U. Pietsch, and S. Grigorian, “Local scale structural changes of working OFET devices,” Nanoscale, vol. 12, no. 4, pp. 2434–2438, 2020.

[3] C. J. Bettinger and Z. Bao, “Biomaterials-based organic electronic devices,” Polym. Int., vol. 59, no. 5, pp. 563–567, 2010.

[4] A. Anctil, E. Lee, and R. R. Lunt, “Net energy and cost benefit of transparent organic solar cells in building-integrated applications,” Appl. Energy, vol. 261, no. 114429, p. 114429, 2020.

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[5] H. Li, R. Zheng, and Q. Shi, “Theoretical study of charge carrier transport in organic semiconductors of tetrathiafulvalene derivatives,” J. Phys. Chem. C Nanomater. Interfaces, vol. 116, no. 22, pp. 11886–11894, 2012.

[6] N. Vets, M. Smet, and W. Dehaen, “Reduction versus Rearrangement of 6, 13-Dihydro-6, 13-diarylpentacene-6, 13-diols Affording 6, 13- and 13, 13′-Substituted Pentacene Derivatives,” Synlett, no. 02, pp. 217–222, 2005.

[7] A. R. Waterloo, A.-C. Sale, D. Lehnherr, F. Hampel, and R. R. Tykwinski, “Aryl substitution of pentacenes,” Beilstein J. Org. Chem., vol. 10, pp. 1692–1705, 2014.

[8] J. E. Anthony, D. L. Eaton, and S. R. Parkin, “A road map to stable, soluble, easily crystallized pentacene derivatives,” Org. Lett., vol. 4, no. 1, pp. 15–18, 2002.

[9] R. Bhatia, D. Wadhawa, G. Gurtu, J. Gaur, and D. Gupta, “Methodologies for the synthesis of pentacene and its derivatives,” J. Saudi Chem. Soc., 2019.

[10] M. R. Hossain, A. Ullah, B. S. Mou, and N. Chawdhury, “Investigating the effect of sidechains in anthracene derivatives on charge transport behaviour by Quantum Chemical Method,” in 2021 International Conference on Electronics, Communications and Information Technology (ICECIT), 2021.

[11] A. Austin, G. A. Petersson, M. J. Frisch, F. J. Dobek, G. Scalmani, and K. Throssell, “A density functional with spherical atom dispersion terms,” J. Chem. Theory Comput., vol. 8, no. 12, pp. 4989–5007, 2012.

[12] X. Zhang et al., “Theoretical comparative studies on transport properties of pentacene, pentathienoacene, and 6, 13-dichloropentacene,” Journal of computational chemistry, vol. 36, no. 12, pp. 891–900, 2015.

[13] M. Ottonelli, M. Piccardo, D. Duce, S. Thea, and G. Dellepiane, “Koopmans’ transfer integral calculation: A comparison between the Hartree-Fock and the density functional results,” Energy Procedia, vol. 31, pp. 31–37, 2012.

[14] A. Maliakal, K. Raghavachari, H. Katz, E. Chandross and T. Siegrist, “Photochemical Stability of Pentacene and a Substituted Pentacene in Solution and in Thin Films,” Chem. Mater. vol. 16, no. 24, pp. 4980–4986, 2004.

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