International Journal of Advanced Engineering Research and Science (IJAERS) *[Vol-5, Issue-8, Aug- 2018]*
https://dx.doi.org/10.22161/ijaers.5.8.7 *ISSN: 2349-6495(P) | 2456-1908(O)*

Electronic Transitions and Photovoltaic Properties of New Compounds as Organic Dye Sensitizers for Solar Cell

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Abstract**—***This work deals with electronic and photovoltaic properties of new compounds as organic dye sensitized for solar cell. The ground state calculations are carried out by employing the B3LYP-DFT method and the TD-DFT for excitation properties at the Gaussian 09 package of programs. The results showed the HOMO and LUMO are slightly different and this suggests that different structures play significant roles on electronic properties and improving the electron accepting ability. The obtained values of energy gap and the open circuit voltage are the parameters manipulating to improving the quality of solar cell devices. Also, the results show these compounds can be used as organic sensitizers for solar cell due to possibility of the electron injection process from the compounds to the conduction band of TiO2.*

Keywords—HOMO, LUMO, Open circuit voltage and excitation energy.

I. INTRODUCTION

The increasing energy needs in the world gave the solar energy to has high importantly[1,2]. In solar cell, some of organic and inorganic materialshave been applied[3-7].Dye sensitized solar cell wasinitially developed by O'Regan and Grätzel[8].Low band gap polymers which are designed to improved match solar output have been studied, Polymers with alternating di-thiophene and thiadiazolothienopyrazine units and other polythiophene derivatives have been discovered by several research groups [9]. SanyinQu et al have developed new materials based on diketo-pyrrolo-pyrrole for solar cells applications [10]. Beside the experimental works, theoretical studies have been investigated to create an important source of valuable information which complements the experimental studies, thereby contributing to the understanding of the molecular electronic structure as well as the nature of absorption and emission[11]. Dyesensitized solar cells have involved much care due to their probable applications in coating and fabrication technologies, they are low cost and have high photoelectric conversion efficiency [12-14]. The contact between the electron donor and acceptor moieties in donor-acceptor can result in the hybridization of the highlying HOMO level of the donor and lowlying level of the acceptor, leading to small band gap material with new electronic structure. In recent years, interest in metalfree organic dyes as an alternative to noble metal complexes has increased due to their advantages, such as the variety of molecular structures, high molar extinction coefficients, simple synthesis, as well as low cost. Tian et al. have reported a series of donor-acceptor-π-bridge-acceptor (D-A-π-A) structural organic dyes incorporating Benzotiadiazole into the triphenylamine framework, resulting in red-shift in absorption and weakening the de-protonation effect on TiO2 film, which is beneficial for light-harvesting [15]. On the other hand, most recent papers are focused on the Carbazole (Cbz) [16-18], due to its significant photo-conductivity, photo-luminescence and hole transport properties. Current work, theoretical study by employing the DFT method on four conjugated compounds based on anthracene is described. Different electron subgroups were introduced to investigate their effects on the electronic structure.

II. METHOD

The relaxed structures of suggested different compounds series based on anthracenestudied in this work are four and they are presented in Figure 1. Initially, the suggested compounds are designed at the Gauss View 5.0.8 program and then relaxed by performing the three parameters Lee-Yang-Parr B3LYP hybrid functional density functional theory DFT method together with 6-31G basis sets at the Gaussian 09 package of programs[19]to study of their ground state and spectroscopic properties. The excited states properties and the transition states of the relax structures are studied by using the time dependent density functional theory TD-DFT[20].

III. RESULTS AND DISCUSSION

In Figure 1, it exposes that the phenyl rings at the two sides of anthracene is clear and the π-electron delocalization between the molecule units and aromatic rings is also clear. The effect of adding subgroups in phenyl rings are studied. In order to examine the effect of asymmetry in comparison with the corresponding symmetry compounds, compounds 1 and 4 are designed. The effect of the electron accepting and electron donating groups are also studied. It was found that the geometrical parameters from DFT calculations are in a good agreement with those obtained from the x-ray data for cyclic carbon compounds. The relax structures for the compounds in Figure 1 show they all of the similar conformation, they have quasi planar conformation. The results showed the consecutive units have like dihedral angles (between 180o and -180o). The inter-ring bond distances are around the value 1.421Ao and the C-C-C bonds are around 120o, the addition of number of subgroups does not change these parameters.

The total energy ET in a. u for the studied compounds was calculated and listed in Table 1. As seen, the Et is approximately independent on the position of the same subgroups in the compounds but depends only on the number of electrons in the compounds, this a sign to that the total energy is a reflection of the binding energy for each compound. Et is inversely proportional with the number of electrons, it decreased with increasing the number of electrons in the compound. In Table 1, the corresponding calculated values of virial ratio (-V/T) for the studied compounds showed they lie in the same range for such compounds, in which the experimental value for hydrogen atom (-V/T=2.0032). Above results indicate to good relax was found without any imaginary frequency for each one of the studied compounds by employing the DFT method. Figure 2 illustrates the Et for the compounds.

To interpretation and understanding of the behavior of the absorption spectra of the compounds, it is necessary to studying the electronic structure. Table 2 shows the calculated frontier orbital energies (High Occupied Molecular Orbital HOMO and Low Unoccupied Molecular Orbital LUMO) and LUMO-HOMO energy gap Egap of the studied compounds. The results in Table 2 noticed that all studied compounds display destabilization of the LUMO and stabilization of HOMO. The results showed the HOMO and LUMO are slightly different and this suggests that different structures play significant roles on electronic properties and improving the electron accepting ability, and the effect of symmetry and distribution of aromatic rings on the energies of HOMO and LUMO cannot be ignored. The ranking of LUMO energy is as:

$$2<4<3<1$$

The results showed the presence of the electron attracting subgroups in the compounds leads to lower the LUMO and therefore reducing the energy gap. Also, the presence of triple and double C-C bonds causes a lower of the LUMO and decrease the energy gap due to destabilization of LUMO energies, this result agree with the experimental data[3,21].

The calculated energy gaps were decreased in the following order : 1(3.438 eV) >4(2.818 eV) >3(2.616 eV) >2(2.599 eV). The compound 2 observes a lower energy gap than the other studied compounds due to asymmetric terminal ends in the compound. Inserting a triple C-C bonds between the anthracene and the phenyl rings in both donor and acceptor sides decreases the energy gap, this increases the conjugation length of the compound and therefore capable well charge transfer properties. The high energy gap for the first three compound is due to symmetric of adding subgroups in terminal ends of phenyl rings at the donating and accepting sites, in which the CH3 subgroup in compound 1 has the same behavior of the OCH3 subgroup. Figure 3 shows the LUMO-HOMO gap. The open circuit voltage Voc was calculated in Table 2 as the TiO2 is a good acceptor.

The contribution of the frontier molecular orbitals FMO is the key of determining the charge separated states of the compounds under study. Figure 4 illustrates the HOMO and LUMO distributions of the studied compounds. As shown, all the studied organic dyes have respectable electron separated states. It is strong localization of the HOMOs occurs on the phenyl donor subunits of the backbone of the compounds, and strong delocalization of the LUMOs occurs on the bridges between the subunits proving the flow of electron density along the backbone of the compounds. The electron density of LUMO is mainly localized on the acceptor units, so the electronic transitions of the studied compounds from HOMO to LUMO could lead to intra-molecular charge transfer from the donor units to the subgroups at the acceptor units through the conjugated bridge between the two sides.

Table 3 declare the results of the calculated values of chemical potential X, the global electrochemical hardness H and electrophilic index W of the studied compounds. As seen in Table 3, these compounds have low values of X in which indicates to that the electrons in the compounds under study have a large escaping tendency. The results showed all the studied compounds have low values of global hardness. The reducing of hardness is the main future as an indication to the band gap of the compounds to be rather more soft and leads to reducing the resistance of the compounds to lose an electron. In other words, these results refer to that these compounds have high ability to an electron transfer. Figures 5 and 6 illustrate the chemical potential and hardness of the compounds. The electrophilic index W is a factor to determine the ability of the molecule to interacts with other molecules or species. From Table 3 and figure 7, the order of W for the studied compounds is as:

2 > 4 > 3 >1

Figure 8illustrates the shapes of the total electron density ED distribution drawn from the calculations of the self-consistent field SCF. The shapes showed the distribution of ED completely depends on the point group symmetry for each compound, uniform distribution of ED was found around the anthracene back bone molecule with different areas of densities at the two sides of anthracene according to high/low ED due to presence phenyl rings at these areas. In the two ends of each compound, the ED was localized highly depending on large number of electrons in such end. The determine of the high ED area assistance to control the active site of electron transfer process.

Figure 9 illustrates the 2-D counter distribution and 3-D distribution of the electrostatic potential ESP surfaces of the studied compounds. The yellow color represents the ESP surface and the red color represents the surface dragged potential. As seen, the surface of ESP around the anthracene back bone is uniform and the potential was dragged towards the areas of highly electronegativity. In compounds 1 and 3, the ESP was distributed uniformly. While, in compounds 2 and 4, the ESP was dragged towards the active sites of high electronegativity.

The UV-Vis spectra of the compounds in present work were studied and analyzed using the TD-SCF method with the same hybrid functional and basis sets. The key factor for the compounds can have applications as the photovoltaic materials is the absorption spectra of the studied compounds equivalent to the solar spectrum. Table 4 illustrates the calculated values of absorption energy Eabs (eV), absorption wave length λmax (nm), the oscillator strength O.S and the molecular orbital character MOC %. As shown, the calculated wave length λmax of the compounds under study increases in the following order(see figure 10):

<1<3<2<4

IV. CONCLUSIONS

From above results, one can conclude that the used method for the relaxation of the studied compounds is a suitable theoretical investigation. The suggested organic compounds have energy gaps as for semiconductor materials. These compounds are appear absorption energy and wave length correspond to the solar spectrum.

Tables:

Table 1: The total energy Et and (-V/T) for the compounds.

Compound	E_t a. u	-V/T
1	-1384.30205	2.0057
2	-1611.62170	2.0056
3	-1675.54321	2.0056
4	-1574.07524	2.0056

Table 2: The HOMO, LUMO and Egap for the compounds.

Compound	HOMO eV	LUMO eV	E_{gap} eV	V_{oc}/TiO_2 eV
1	-5.2149	-1.7760	3.4389	1.8239
2	-4.7703	-2.1706	2.5997	1.4293
3	-4.7104	-2.0941	2.6163	1.5058
4	-4.9646	-2.1458	2.8187	1.4541
TiO_2	-5.928	-3.900		

Table 3: The X, H and W for the compounds.

Compound	X eV	H eV	W eV
1	3.4954	1.71945	3.5528
2	3.4704	1.29985	4.6327
3	3.4022	1.30815	4.4241
4	3.5552	1.4094	4.4841

Table 4: The absorption spectra calculations of the compounds.

Compound	**E_{abs} eV**	**λ_{max} nm**	**O.S**	**MO Character %**
1	2.5915	478.42	0.2821	HOMO→LUMO(99)
2	2.1891	566.36	1.0814	HOMO→LUMO(100)
3	2.2072	561.74	1.0573	HOMO→LUMO(100)
4	1.9782	626.75	0.0021	HOMO →LUMO (14) HOMO →L+1 (84)

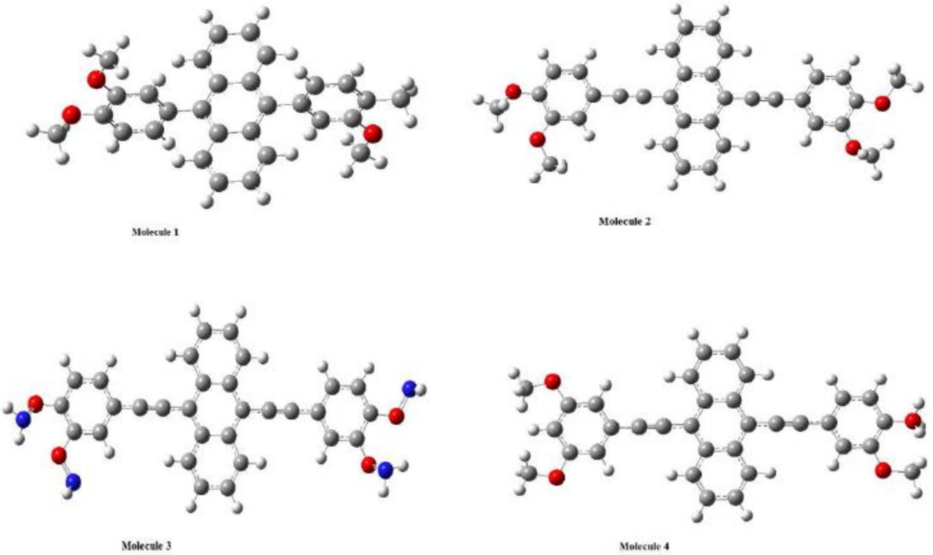


Fig. 1: The relax structure of the compounds.

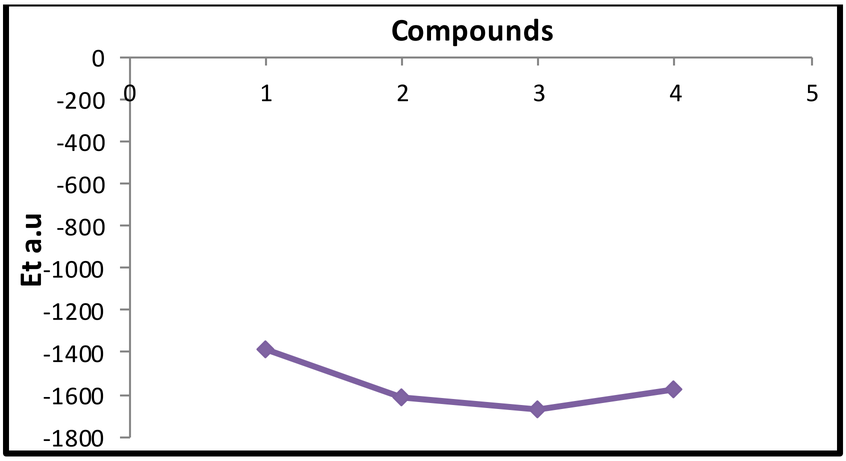


Fig. 2: Et of the compounds.

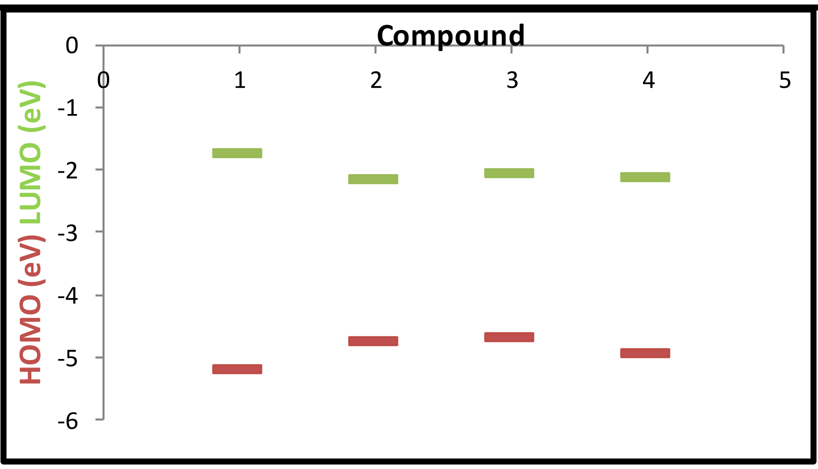


Fig. 3: LUMO-HOMO gap of the compounds.

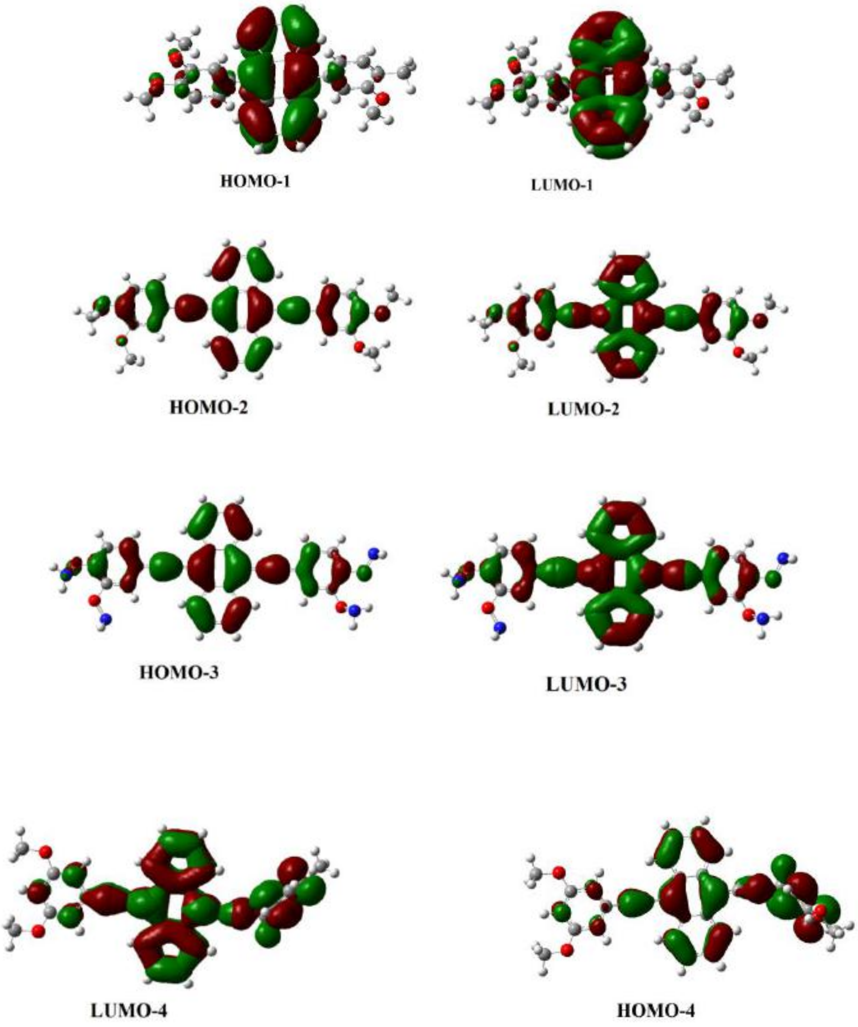


Fig. 4: LUMO and HOMO distribution of the compounds.

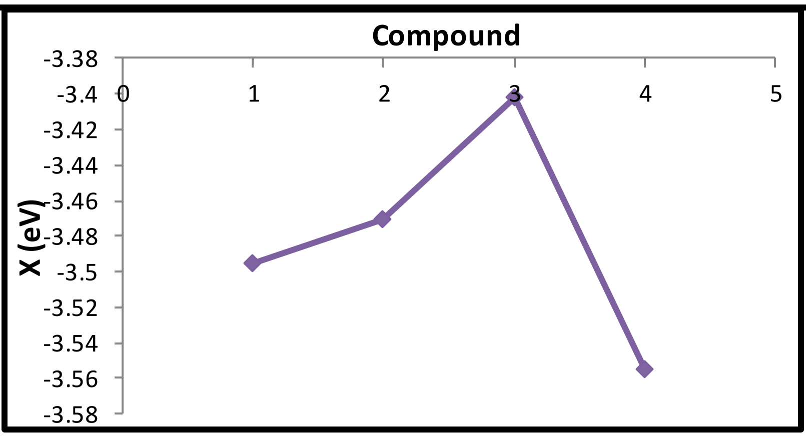


Fig. 5: Chemical potential of the compounds.

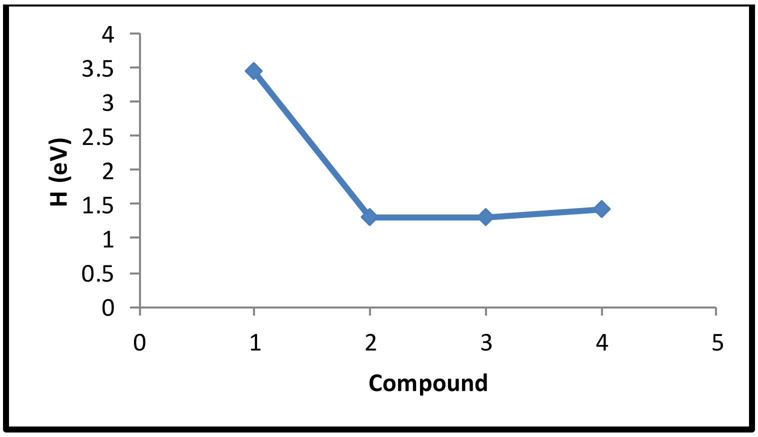


Fig. 6: Hardness of the compounds.

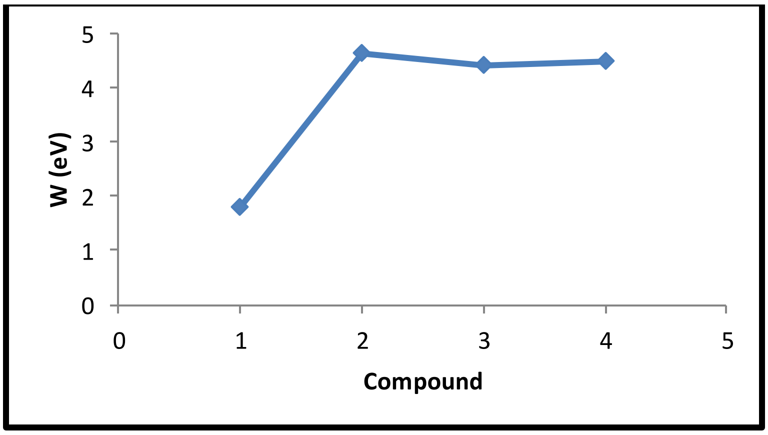
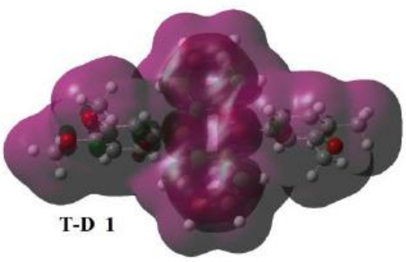
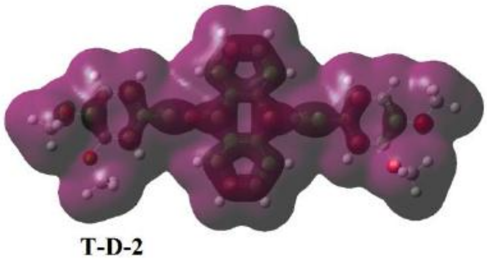


Fig. 6: Electrophilic index of the compounds.



T-D 1



T-D-2

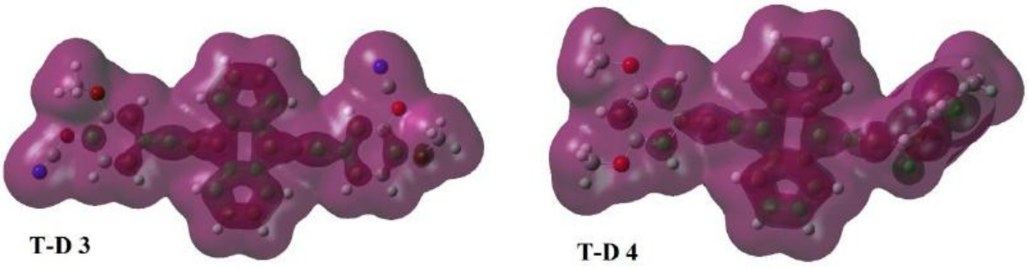
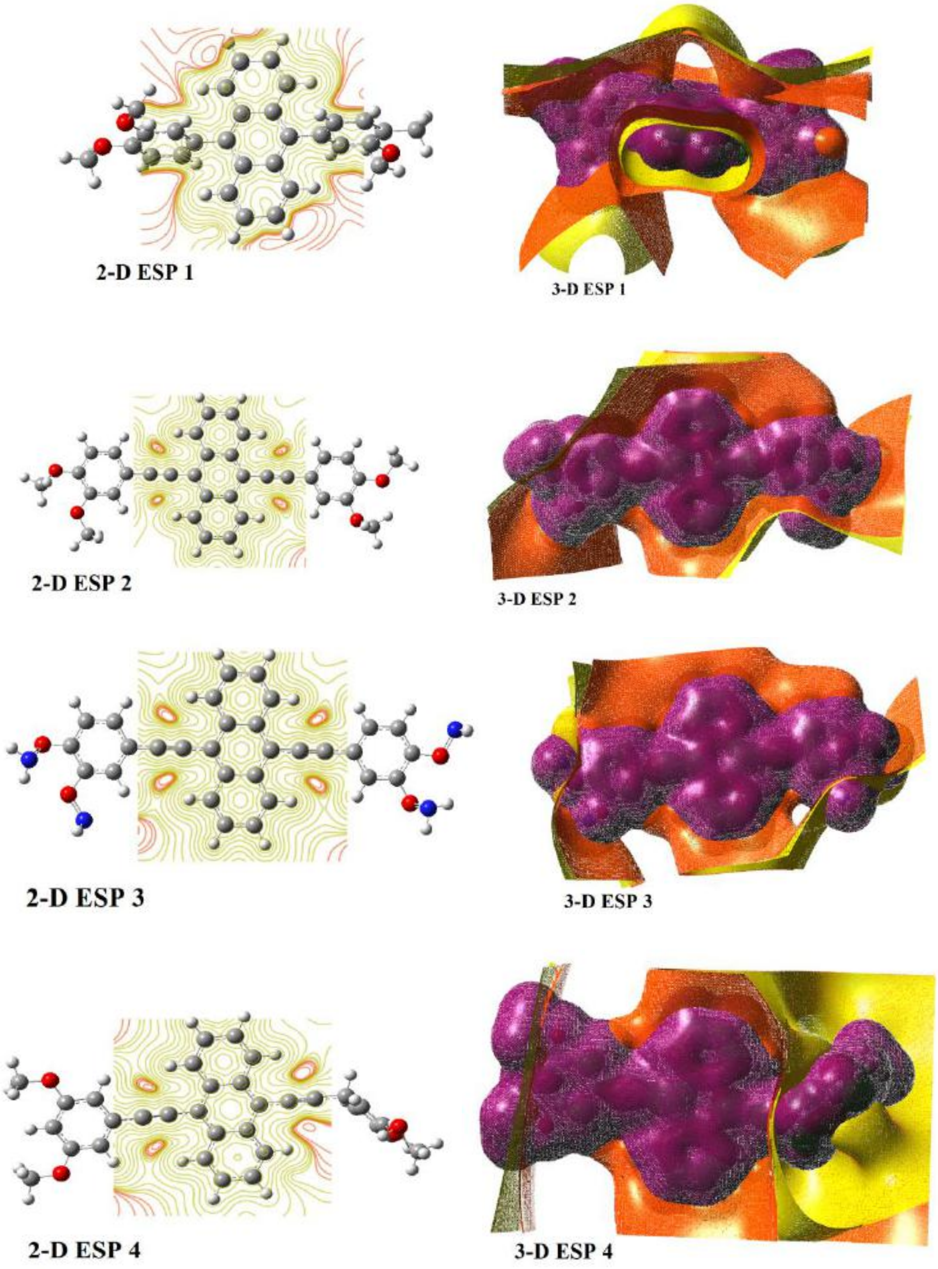

T-D 3 **T-D 4**

Fig. 8: Electron density distribution of the compounds.


2-D ESP 1 **3-D ESP 1**

2-D ESP 2 **3-D ESP 2**

2-D ESP 3 **3-D ESP 3**

2-D ESP 4 **3-D ESP 4**

Fig.9: Electrostatic potential distribution of the compounds.

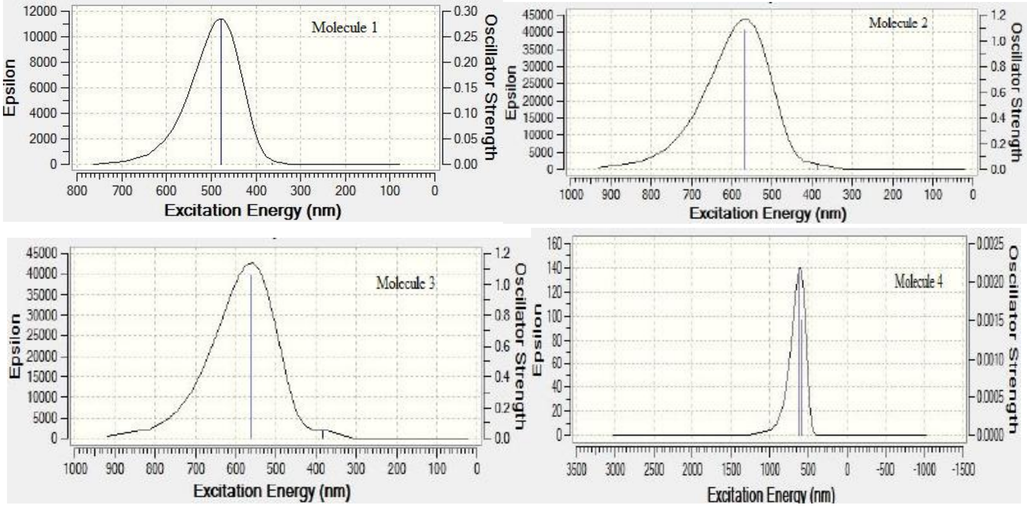


Fig. 10: UV-Vis spectra of the compounds.

REFERENCES

[1] M. Grätzel, *Phil. Trans. R Soc A.* 365 (2007) 993-1005.

[2] W.Katzenstein, J. Apt Environ. Sci. Technol. 43(2009) 253-258.

[3] C. W.Tang, , *Appl. Phys. Lett.* 48 (1986) 183-185.

[4] R.Liu, *J. Phys. Chem. C.* 11 (2009) 9368-9374.

[5] O. V.Prezhdo, W. R.Duncan, V.Prezhdo, *Acc. Chem. Res.* 41 (2008) 339-348.

[6] P. Peumans, V.Bulovic, S. R.Forrest, *Appl. Phys. Lett.* 76 (2000) 2650-2652.

[7] G.YuGao, J. Hummelen, J. C., Wudl, F., Heeger, *A. J., Science.* 270 (1995) 1789-1791.

[8] B.O'Regan, M.Grätzel, , *Nature.* 353 (1991) 737-740; Grätzel, M., Nature. 414 (2001) 338-344.

[9] M. M.Wienk, M. G. R.Turbiez, M. P.Struijk, M. J.Fonrodona, A. J.Rene Janssen, , Appl. Phys. Lett. 88 (2006),1019-1025.

[10] S.Qu, , B.Wang, , FA.Guo, , Li, J., Wu, W., Kong, C., Long, Y., Hua, J., *Dyes and Pigments*, 92 (2012) 1384-1394.

[11] S.Bouzakraoui, S.M.Bouzzine., M.Bouachrine, M.Hamidi, *Energy Mater. Sol. Cells.* 90 (2006) 1393-1402

[12] M.Gratzel, *Nature* 414 (2001) 338–344.

[13] M.J. Gratzel, *Photochem. Photobiol.* C 4 (2003) 145–153.

[14] R.Argazzi, N.Y.M.Iha. H.ZabriOdobel, F.Bignozzi, *Chem. Rev.* 248 (2004) 1299–1316.

[15] W.Zhu, Y.Wu, S.Wang, W.Li, Wang Z., H.Tian*AdvFunct. Mater.* 21 (2010) 756-63.

[16] G. Zotti,G.Schiavon, S.Zecchin, J. F.Morin, M.Leclerc, *Macromolecules.* 35 (2002) 2122.

[17] F.Garnier, G.Horowitz,X.Peng, D.Fichou, *Adv.Mater*2 (1990) 562.

[18] E.Gill R., Malliaras G. G., Wildeman J., Hadziioannou G., *Adv. Mater* 6 (1994) 132.

[19] M.J Frisch., G.W.Trucks, H. B.Schlegel,G. E.Scuseria, Robb M.A., Cheeseman J. R., Montgomery J.A., Vreven, T., Kudin, K. N. Jr., Burant, J. C., Millam, J. M., Iyengar, S. S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G. A., Nakatsuji, H., Hada, M, Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., M.Ishida, Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J. E., Hratchian, H. P., Cross, J. B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Ayala, P. Y., Morokuma, K., Voth, G. A., Salvador, P., Dannenberg, J. J., Zakrzewski, V. G., Dapprich, S., Daniels, A. D., Strain, M. C., Farkas, O., Malick, D. K., Rabuck, A. D., Raghavachari, K., Foresman, J. B., Ortiz, J. V., Cui, Q., Baboul, A. G., Clifford, S., Cioslowski, J., Stefanov, B. B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R. L., Fox, D. J., Keith, T., Al- Laham, M. A., Peng, C. Y., Nanayakkara, A., Challacombe, M., Gill, P. M. W., Johnson, B., Chen, W., Wong, M. W., Gonzalez, GAUSSIAN 09, Revision B.04, Gaussian, Inc. Pittsburgh PA. 2009.

[20] A. D.Becke, J. Chem. Phys. 98 (1993) 5648-5653.

[21] A. Faeq Mohammed and I. Hamid Abbood, (2017), International Journal of Advanced Engineering Research and Science, Vol-4, Issue-7,82-86.