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Electronic and Spectral Properties of Polymeric Composites

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Annotation: The aim of the present work is to present a theoretical study based on the hybrid function of three parameters Lee-Yang-Parr B3LYP of the density functional theory DFT quantum mechanical approach together with the Stuttgart Dresden triple zeta SDD basis sets. All calculations are carried out by employing the used method at the Gaussian 09 package of programs. The studied compounds are three. The electronic structure of the compounds includes the structural, electronic, spectroscopic properties.

The results show that the SDD basis sets are efficient strongly suggested for polymers and give good relax for the structures of the studied polymer –dye compounds. The total energy is independent on the position of the dye in the compounds, it depends only on the number of electrons in each compound.

From the calculations, the results showed the studied compounds show destabilization of LUMO and stabilization of HOMO, they both changed significantly to suggest different structures play important roles in electronic properties. The effect of symmetry and distribution of dye rings has an influence on the calculation of HOMO and LUMO.

In general, most of the studied (PMMA-dye) compounds have electronic transition with wave length lies in the range of ultraviolet spectrum. The compounds in this paper have an application as photovoltaic materials.

1.1 Introduction

This is the time of nanotechnology. But today there is nothing more significant than energy, since ,the absence of energy means a major problem to the present development, i.e not enough food warm shelter and connection to the Internet, counting the consumption of nanotechnology products. The growth of contemporary trends of energy demands promising new technologies and even new physical and chemical processes for the founding and process of effectual systems to make, accrue, transform and transport of energy into its various forms [1]. many organic and inorganic semiconductors have been used to make solar cells, The selection was mostly based on known materials as, till lately, experimental data was the main source for screening materials for ,solar cell [2]. The competence of solar cells is partially dependent on their project as a whole attractive into consideration a diversity of factors such as the intensity of concentrated sunshine and the stacking of multi-junction cells. In a study conducted by Massachusetts Institution of Technology (MIT), a new system was created that uses sunshine to heat an absorber-emitter expedient that is placed over the photovoltaic cells (PV) [3]. The consequences of this temperature change have previously augmented the frequency and severity of usual disasters and are probable to have more devastating effects for persons and other life forms in all parts of earth within the next decades. Solar cells are devices which convert solar energy straight into power, either straight through the photovoltaic effect, or circuitously by first converting the solar energy to heat or chemical energy. Meetings of cells used to make solar modules which are used to detention energy from sunlight, are known as solar panels. The energy generated from these solar modules, referred .to as solar power

Cells are described as photovoltaic cells when the light source is not unavoidably sunshine (lamplight, artificial light, … etc.). The quantity of power available from a PV expedient is resolute by the type and area of the material [4]. Second generation solar cells include of thin films .of materials like formless silicon, cadmium telluride and copper indium (gallium) dieseline [5] Since the late 1970s, amorphous silicon solar cells have been used to power small devices such as calculators and watches. Solar cells made from amorphous silicon typically convert between .of incident light energy into electricity (this is referred to as the conversion efficiency) %(6-3) Despite having small conversion competence, this thin film technology was used over other types of solar cells due to relatively good performance in inside light, and the aptitude to manufacture ,it in lightweight and supple form factors, facilitation integration into products such as solar fabrics cylindrical products, and lightweight charging mats [6]. A solar cell is a photonic device that converts photons with specific wavelengths to electricity. After Alexander Edmond Becquerel discovered the photo electrochemical (photovoltaic) effect in 1839 while he was investigating the effect of light on metal electrodes engrossed in electrolyte, research in this area sustained and technology developed to produce many types and structures of the materials presently used in photovoltaic technology. First and second generations photovoltaic cells are mainly constructed from semiconductors including crystalline silicon, III-V compounds, cadmium telluride, and copper indium selenite/sulfide. Low cost solar cells have been the subject of intensive investigation work for the last three decades. Amorphous semiconductors were proclaimed as one of the most promising materials for low cost energy production. However, dye sensitized solar cells DSSCs emerged as a new class of low cost energy conversion devices with simple manufacturing procedures. General comparison between semiconductor based solar cells and dye .sensitized solar cells is presented in table 1.1[7]

Table 1.1: Comparison between semiconductor based solar cell and the dye sensitized .solar cell DSSCs [7]

Property	Semiconductor solar cells	DSSCs
Transparency	Opaque	Transparent
Pro-environment (Material (and Process	Normal	Great
Power Generation Cost	High	Low
Power Generation Efficiency	High	Normal
Color	Limited	Various

The first generation of solar cell research was built about silicon Si because of it is availability and use in the emerging semiconductor industry. Intrinsic semiconductors, such as, Si are be doped with either donor or acceptor impurity atoms to create n-type and p-type extrinsic semiconductors, respectively. The carrier (electron or hole) concentration and consequently the material conductivity is controlled by varying the density of impurity atoms. Heavy semiconductor doping is undesired since it causes a narrowing of the band gap due to impurity .sub-bands and is likely to increase defect states resulting in higher recombination.[8]

production of energy from the sun with renewable material such as in dye-sensitized solar cells (DSSCs) has attracted a considerable quantity of care since O'Regan and Grätzel published their pioneering work in 1991.13. Easily invented and low-cost, these devices paved the way to a new generation of financial photovoltaic modules, appearing as a promising other to silicon-based solar cells, Low costs and higher functionalities were fundamentally attained by separating light harvesting and charge parting, as plants do in natural photosynthetic processes.[9]. Solar energy is one of the most interested and practical other sources of energy against the conservative relic fuels. Crystal-like silicon based solar cells are dominant in the photovoltaic industry and include about 90% of solar cell production worldwide. Low cost is still one of the main goals for solar cell manufacturing while maintaining a stable high conversion efficiency. Utilized materials and .processing techniques are the major components that need to be considered for cost reduction.[10]

1.2 Poly methyl methacrylate(PMMA)

Poly(methyl methacrylate) (PMMA), also known as acrylic, or acrylic glass, as well as by the trade names Crylux, Plexiglas, Acrylite, starigIas, Lucite, Perclax, and Perspex, among several others (see elow), is a transparent thermoplastic often used in sheet form as a lightweight or shatter-resistant alternative to glass. The same material can be used as a casting resin or in inks and .coatings, among many other uses

Although not a type of familiar silica-based glass, the substance, like many thermoplastics, is ,often technically classified as a type of glass (in that it is a non-crystalline vitreous substance) hence its occasional historic designation as acrylic glass. Chemically, it is the synthetic polymer of methyl methacrylate. The material was developed in 1928 in several different laboratories by many chemists, such as William Chalmers, Otto Röhm, and Walter Bauer, and was first brought to market in 1933 by German Röhm & Haas AG (as of January 2019, part of Evonik Industries) and its partner and former U.S. affiliate Rohm and Haas Company under the trademark ,Plexiglas[11]. PMMA is an economical alternative to polycarbonate (PC) when tensile strength flexural strength, transparency, polishability, and UV tolerance are more important than impact strength, chemical resistance, and heat resistance.[12] Additionally, PMMA does not contain the potentially harmful bisphenol-A subunits found in polycarbonate and is a far better choice for laser cutting.[13] It is often preferred because of its moderate properties, easy handling and ,processing, and low cost. Non-modified PMMA behaves in a brittle manner when under load especially under an impact force, and is more prone to scratching than conventional inorganic .glass, but modified PMMA is sometimes able to achieve high scratch and impact resistance

:Most important advantages polymer PMMA[14]

It is characterized by high flexibility and is a material with high transparency and high refractive-1 .index, which made this material important for use with organic dyes

.It is a polymer called thermoplastic-2

It is transparent at temperatures below Tg-3

1.3 Potassium permanganate

Potassium permanganate is an inorganic compound with the chemical formula $KMnO_4$. It is a purplish-black crystalline salt, that dissolves in water as K+ and MnO_4 −an intensely pink to .purple solution[15]

Potassium permanganate is widely used in the chemical industry and laboratories as a strong oxidizing agent, and also as a medication for dermatitis, for cleaning wounds, and general ,disinfection. It is on the World Health Organization's List of Essential Medicines.[16] In 2000 worldwide production was estimated at 30,000 tons.[17,18]

Potassium permanganate can be used to quantitatively determine the total oxidizable organic material in an aqueous sample. The value determined is known as the permanganate value. In analytical chemistry, a standardized aqueous solution of KMnO4 is sometimes used as an oxidizing titrant for redox titrations (permanganometry)[19]. As potassium permanganate is titrated, the solution becomes a light shade of purple, which darkens as excess of the titrant is added to the solution. In a related way, it is used as a reagent to determine the Kappa number of wood pulp. For the standardization of KMnO4 solutions, reduction by oxalic acid is often used.[20,21] In agricultural chemistry, it is used for estimation of active carbon in soil.[22]

Aqueous, acidic solutions of KMnO4 are used to collect gaseous mercury in flue gas during stationary source emissions testing.[23] In histology, potassium permanganate was used as a bleaching agent[24]

1.4 Previous Studies

JIE XU *et al*.(2009) studied series of indoline dyes with promising efficiency for dye-sensitized solar cells (DSSCs) using the density functional theory at the B3LYP/6-31g (d) level. The ground-state geometries, electronic structures and absorption spectra of these dyes are computed. The calculated results indicate that the energy levels of the HOMOs and LUMOs of these dyes are advantageous for electron injection. Their intense and broad absorption bands as well as favorable .excited-state energy levels are key factor for their outstanding efficiencies in DSSCs[25]

Sipke H. Wadman *et al.* (2010) prepared a series of (cyclometalated) ruthenium complexes to investigate the viability of cyclometalation as a general tool in the design of new sensitizers for dye sensitized solar cells. In this series, cyclometalation results in a red shift as well as in a broadening of the electronic absorption features and is accompanied by a cathode shift in the .RuII/RuIII redox process. The complexes are photo stable in both the Ru(II) and the Ru(III) state They applied TD-DFT for calculations. The complexes with the C,N,NO-bonding motif possess ,an excited state associated with the cyclometalated ligand, allowing efficient charge injection while the complex with the N,C,NO-bonding motif possesses a more isolated excited state located on the remote ligand. The results showed that the covalent carbon-to-ruthenium bond can be utilized as a tool to shift the operational threshold of the individual sensitizer for dye-sensitized solar cells toward lower energy, as long as care is taken that the nature of the excited state is appropriate for electron injection[26]. **Michal sokolsky *et al*.**(2010) proved that the dye-sensitized solar cell (DSSC) have a good chance to become a notable competitor for solar cells based on today technology of p-n junction. The principle of operation of DSSC solar cells in comparison with conventional semiconductor solar cells where light absorption and charge carrier transport are done by the semiconductor is different. In this paper, by using dyes which have broad absorption band, the solar cell is capable to harvest large fraction of sunlight. So, the basic

.construction and mode of operation of solar cells based on dyes is described[27]

Katja Vozel *et al.* (2011) introduced an application of p-n junctions within solar cells. They gave the upper limit to the solar cell efficiency. Also, they described three generations of solar cells, crystalline silicon solar cells, thin-film solar cells and photo electrochemical cells by means .of their operational principles and physics behind[5]

Rashmi Swami,(2012) designed some organic devices as well placed to meet the needs of both the electronics and energy industries because their manufacture does not require expensive processing steps and they can be adapted to a range of applications. He showed that there has been significant interest in this field over recent years and there are now many research groups world- ,wide investigating the semiconducting properties of conjugated materials and their use in LEDs photovoltaic and transistors. This activity of creating electricity through the use of organic solar cells is an example of one way scientists are trying to alleviate some of the dependence on non-renewable resources. It is the purpose of his research proposal to explore that with a little human .ingenuity, other ways to create energy can be attained [4]

M. Malek Shahi Byranv *et al*. (2012) studied various characteristics of dye-sensitized nanostructured TiO2 solar cells, such as working principle, electron transport and electron lifetime. The study avoids detailed mathematical and spectroscopic discussion, but rather tries to .summarize the key conclusions relevant to materials design[28]

A.Ali and A. Al-Mowali (2014) have investigated optoelectronic properties and Electronic states of poly furfuryle alcohol (PFA), rhodamine B (Rh B) dye and their blends (PFA Rh B) .It is carried out by using the density functional theory (DFT). The electronic states indicate that the oligomers of FA are insulators and Rh B is a wide band gap semiconductor. Their blends have a narrow band gap of about 0.75 eV. The optoelectronic properties are studied using TDDFT, which indicates that the chain length of poly furfuryl alcohol is an effective parameter to control both energies and intensities of absorption in which longer chain causes absorption with high intensity within long wavelength. A single broad band of electron excitations is more like 8-oligomer-RhB case, which centers at wavelengths about 599 nm and 625 nm. This band of absorption covers the whole visible .region of spectrum [29]

S. Bagheri and S. Majid (2015) have studied the optical properties of dyes with different types of polymer as solar cells with density functional theory (DFT) and time-dependent (TDDFT) .calculations

,Theoretical calculations allow us to quantify factors such as light harvesting efficiency (LHE) electron injection driving force and the weight of the LUMO orbital on the carboxylic group (QLUMO) related to the short-circuit photocurrent density. The factors affecting the short-circuit current density (Jsc) and open-circuit photovoltage (Voc), allow us to estimate the performance .of the dyes[30]

Si. Mohamed *et al.*(2016) have studied the electronic properties of Polythiophene (PTh) and its derivatives are polymer-based materials with a π-conjugation framework. Their properties are ,based on molecular structure; the derivatives contain different substitutes in the 3 and 5 positions such as electron-donating or electron withdrawing groups. All molecular geometries were optimized at B3LYP/6-31G(d,p) level of theory. The energy gap (Egap) between the HOMO and LUMO levels is related to the π-conjugation in the PTh polymer backbone. the DFT calculations were performed for the nonsubstituted and 3,5-substituted variants to investigate the stability geometries and electrical properties. The theoretical calculations show that the substituted forms .are stable, have low Egap, and are in good agreement with the experimental observations[31]

Grant Vonder Haar, (2017) studied designing for solar cells and determined the most efficient design for commercial and residential use while finding the most cost-effective materials to produce these cells. He updates on the materials involved in high efficiency cells, and discussed the different materials involved in solar cell manufacturing. This study has allowed him to determine that gallium arsenide compounds combined with crystalline silicon cells are the most effective at absorbing and storing solar energy. He also determined that factors such as multi- .junction cells and the concentration of light increase the cell's efficiency[3]

S. Dheivamalar and K. Bansura Banu (2019) have designed solar cells by using DFT. The geometrical framework of NiZn5O6 and ANiZn5O6 were optimized using the B3LYP/6-31G exchange-correlation functional method with 6-31G (d,p) basis set using the Gaussian 09 program The TD-DFT computations were employed to evaluate the excitation energy, UV-Vis electronic . transition, light harvesting ability and oscillator strength of photosensitizer at CAM-B3LYP/6-6-31G level with/- LUMO energies were analyzed at the B3LYP/31G level. The HOMO optimized structures. The Gauss sum program was used to obtain DOS results .The dipole moment, chemical parameters and polarizability were predicted from the B3LYP/6-31G functional in Gaussian 09 program. In further, molecular electrostatic potential (MEP) analysis and Mulliken charge distribution of each atom in the various sites of A-NiZn5O6 were also .investigated by the Gaussian 09 program[32]

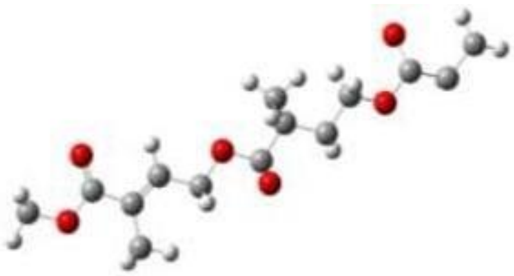
R. Jimenez *et al*.(2020) have analyzed The molecular structure of the difluoride boron compounds has been optimised by the DFT/B3LYP method, using the 6–31G** basis set. Since the long alkyl chain constitutes a hindrance to run the calculations and it has not a great effect over the electronic properties of the compounds, a methyl group was used instead to reduce the calculation times. They displays the electronic distribution in the frontier orbitals HOMO, HOMO- .HOMO-2, LUMO and LUMO. It attracts attention that the electron density is highly localized ,1 The HOMO and HOMO-1 are located over the benzene group, whereas the HOMO-2 is over the .pyridyne one. By contrast, the LUMO and LUMO are located over the diketonate group[33]

1.5 Aim of The Study

Design of some new compounds as organic polymer -dye sensitizers for solar cells and study of their electronic transitions

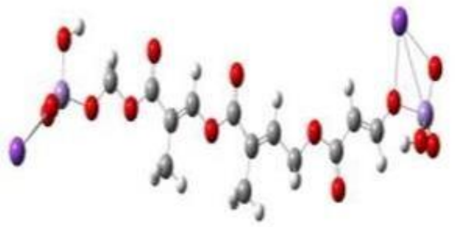
3.2 Structural Properties

In Figure 3.1 The effect of adding potassium permanganate to the *Poly* (methyl methacrylate) (PMMA) are studied. The effect of the electron accepting and electron donating groups are studied. All the geometrical parameters have been calculated by employing the B3LYP hybrid function together with SDD basis sets at the Gaussian 09 program... Table 3.1 illustrates the bond distances and angles in each compound. The inter-ring bond distances are around the value .1.421A^{o}



pure

1



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.Figure 3.1: The relax structure of the compounds

(Table 3.1: The geometrical parameters for)PMMA- potassium permanganate

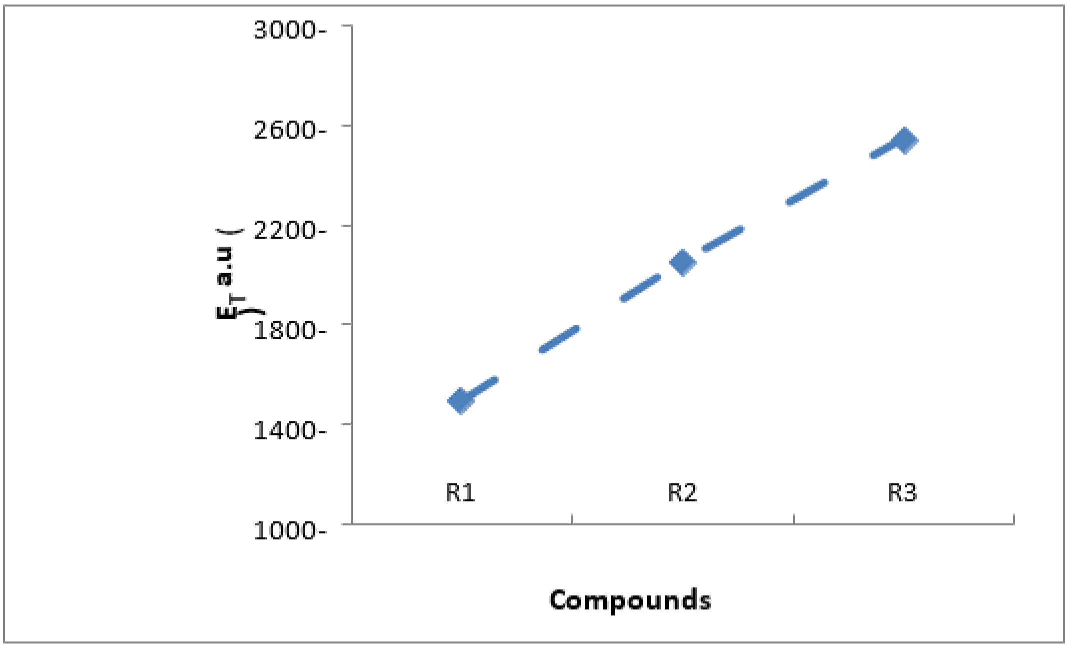
Compound	Bound		Bound	
	Length	Value A	Angle	Value degree
Pure	C—C C═O C—H C—O	(1.53749) (1.24420) (1.09477) (1.47241)	C—C—C C—C—H C—O—C O—C—H	(118.35195—118.34743) (119.586882—110.89353) (118.94369—118.83947) (111.26271—105.30951)
1	C—C C═O C—H C—O Mn-O K-O	(1.55235) (1.24569) (1.09493) (1.38237) (1.60122) (2.70377)	C—C—C C—C—H C—O—C O—C—H Mn—O—K O—K—O	(118.31833—118.31716) (119.60058—118.82933) (119.39488—119.38966) (111.04558—104.93436) (91.75399) (60.55756)
2	C—C C—H	(1.54650) (1.08779)	C—C—C C—C—H	(118.36494—118.31315) (119.59482—118.58671)
	O—C C═O Mn-O K-O	1.23570 (1.47513) (1.60122) (2.70377)	C—O—C O—C—H Mn—O—K O—K—O	(118.85483—118.29065) (111.31039—105.34343) (91.75399) (60.55756)

3.3 Total Energy

The total energy E_T in a. u for the studied)**PMMA- Potassium permanganate)** was calculated and listed in Table 3.2. As seen from mentioned Table, the E_T is approximately 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. E_T is inversely proportional with the number of electrons, it decreased with increasing the number of electrons in the compound. Figure 3.2 shows the E_T for the studied compounds. In other hand, the corresponding calculated values of viral ratio (-V/T) for the studied compounds in Table 3.2 showed they lie in the same range for such compounds, in which the experimental value for hydrogen atom (-V/T=2.0032) [43]. Above results indicate to good relax was found without any imaginary frequency for each one of the studied compounds .by employing the DFT method

. Table 3.2: The total energy E_T and (-V/T) for the (PMMA- potassium permanganate)

Compound	E_T a. u	V/T-
Pure	1493.2-	2.0056
1	2049.98-	2.0055
2	2539.81-	2.0053



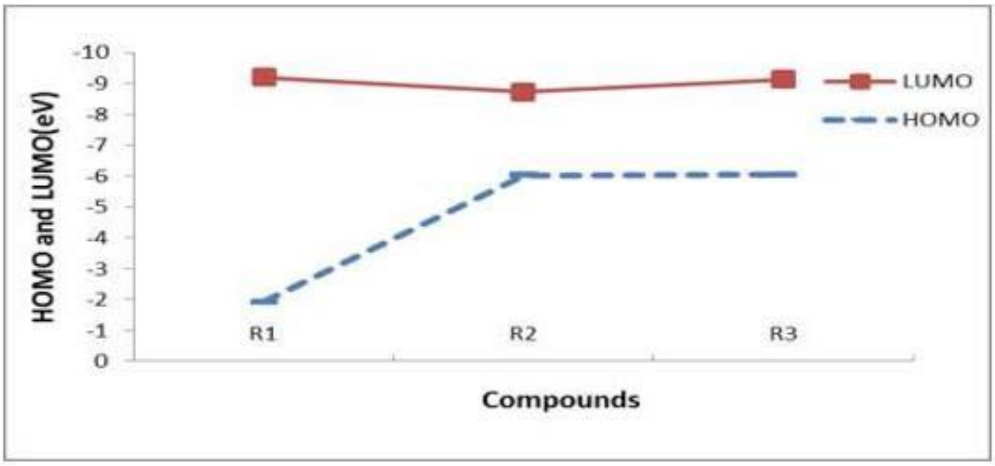
.(Figure 3.2: Total energy of the)PMMA-dye

3.4 Electronic States and Energy Gap

To interpretation and understanding the behavior of the absorption spectra of the compounds, it is necessary to studying the electronic structures for the studied compounds. Table 3.3 shows the calculated frontier orbital energies (High Occupied Molecular Orbital HOMO and Low Unoccupied Molecular Orbital LUMO) and LUMO-HOMO energy gap E_{gap} of the each compound.. The energies of HOMO and LUMO of the studied compounds are changed meaningfully as in Table 3.3 .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

.(Table 3.3: The HOMO, LUMO and E_{gap} for the)PMMA-dye

Compound	HOMO eV	LUMO eV	Egap eV
Pure	1.9237-	7.2761-	**5.3523**
1	6.0253-	2.6857-	**3.3396**
2	6.0376-	3.0955-	**2.9421**



.(Figure 3.3: EHOMO and ELUMO of the)PMMA-dye

The results showed the adding dye to the polymer in the compounds leads to lowering the LUMO and therefore reducing the energy gap. Also, the presence of double C-O bonds causes a lower of the LUMO and decreasing the energy gap due to destabilization of both HOMO and LUMO energies, this result agree with the experimental data [44]. Figure 3.3 illustrates the HOMO and LUMO energies of the studied compounds

The energy gap E_{gap} for the studied compounds was obtained from the separation LUMO-HOMO energy by using the B3LYP/SDD-DFT calculations. Figure 3.4 shows the Energy gaps of the .(PMMA-dye)

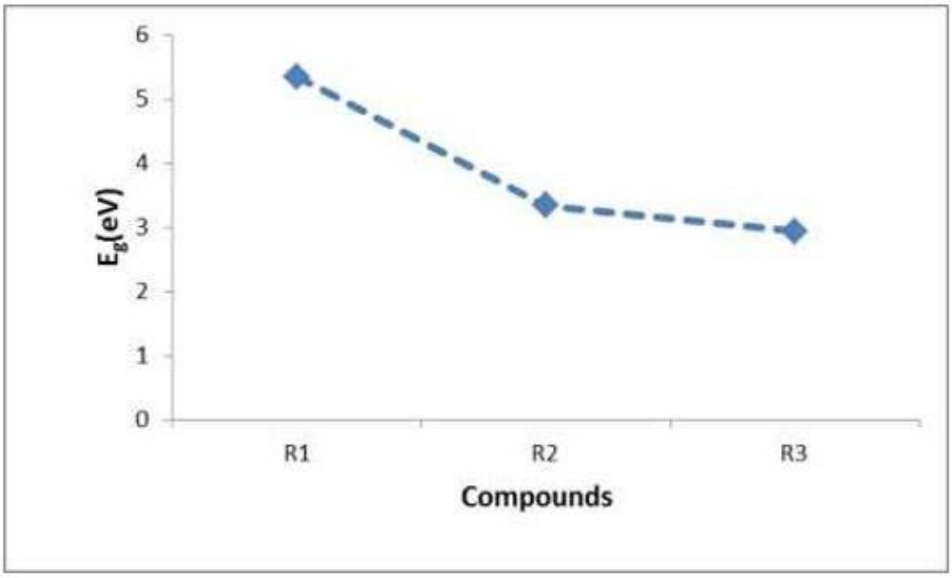
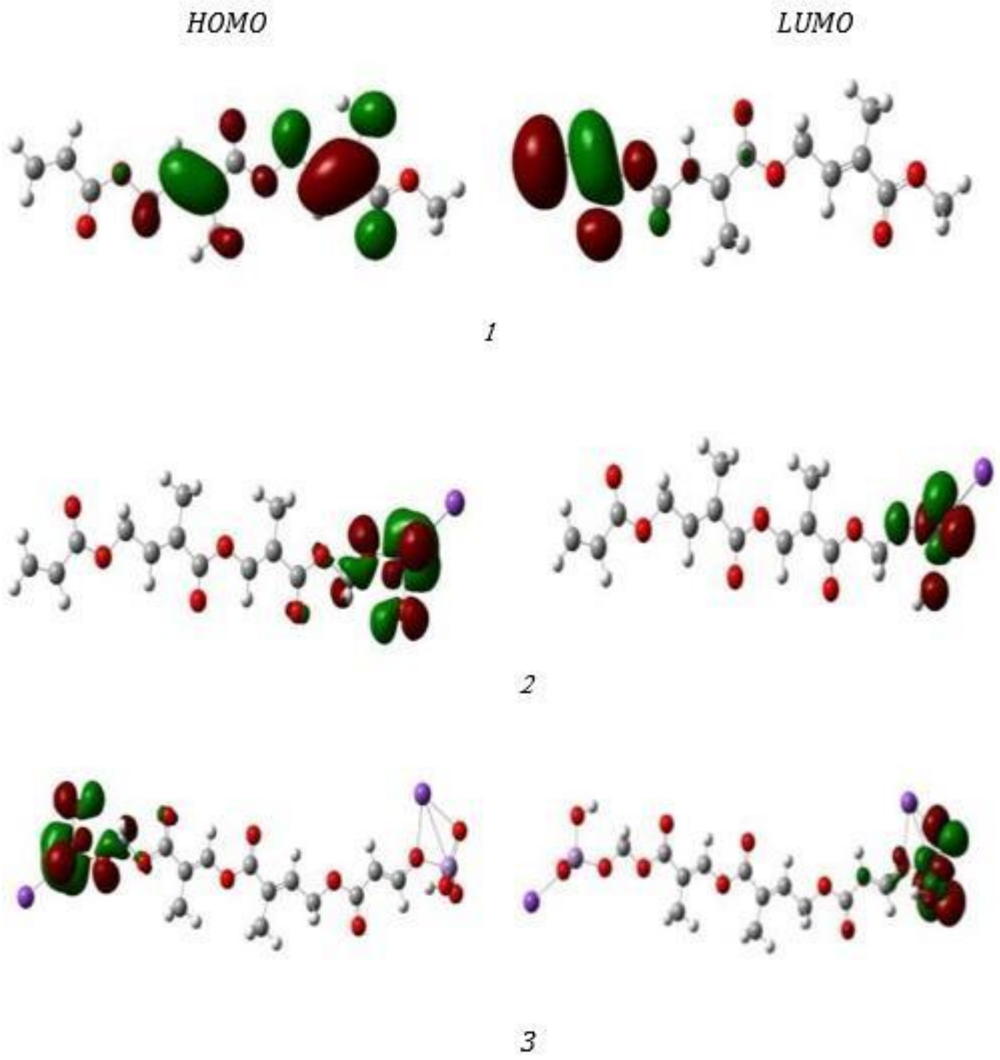


Figure 3.4: Energy gaps of the)PMMA-.(dye

The contribution of the frontier molecular orbitals FMO^s is the key of determining the charge separated states of the compounds under study. Figure 3.5 illustrate the electronic structures of the HOMO and LUMO of the studied compounds. As shown, all the studied organic polymer-dyes have respectable electron separated states. From the distribution of HOMO and LUMO in Figure 3.5 , it is strong localization of the HOMO^s occurs on the dye donor of the backbone in the compounds, and it is strong delocalization of the LUMO^s occurs on the bridges between the subunits proving the flow of electron density along the backbone in 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 acceptor units through the conjugated bridge between the two sides

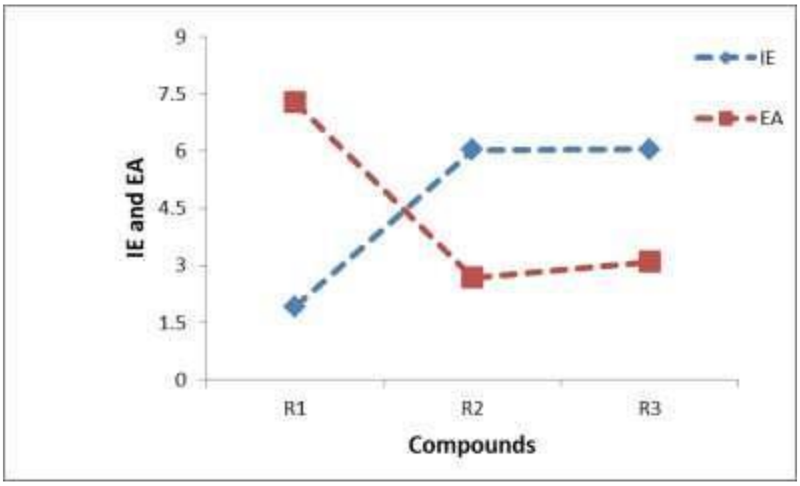


.HOMO and LUMO distribution of the (PMMA-dye))

According to Koopman^{s} theorem, the Ionization Energy IE and the Electron Affinity EA are the negative sign of the HOMO and LUMO energies, respectively. The values of IE and EA for the studied compounds are listed in Table 3.4. the results showed, compound 1 has the lower IE in comparison with the other compounds, but this indicates to that compound 1 has high ability to donating an electron to becomes action in comparison with the others. Above result can be discussed in terms of the low separation between the two edges of valence and conduction bands for the mentioned compound. On the other hand and for the same reason, the large separation between the two edges in the compound pure make from this compound to need high energy to .donating an electron in comparison with the others

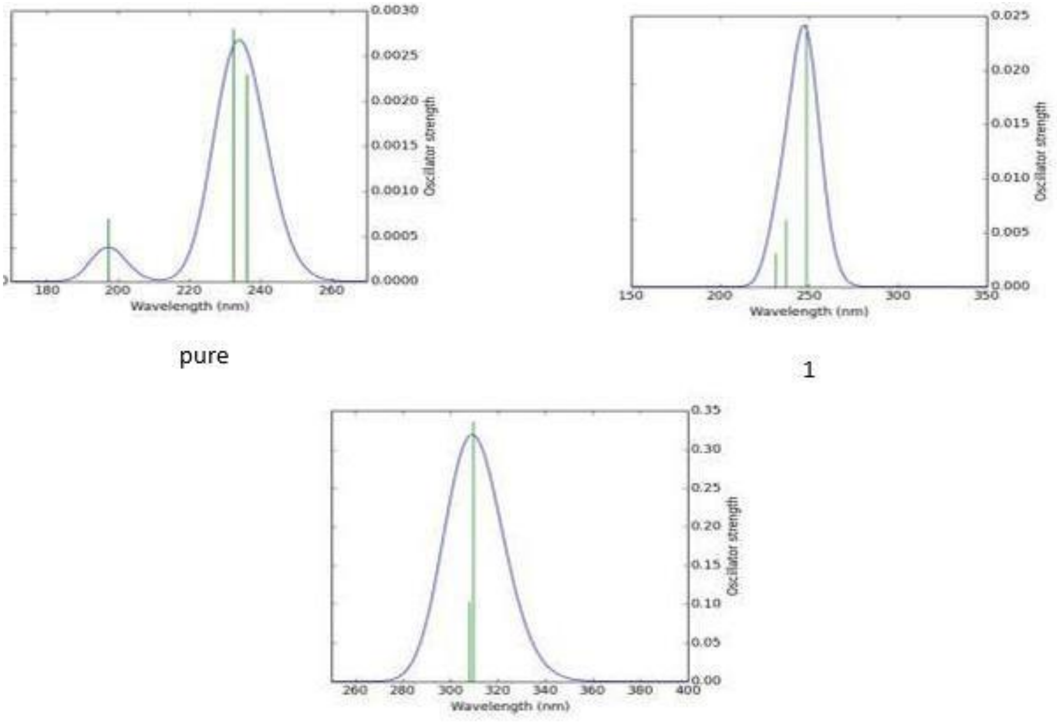
Table 3.4: The IE and EA for the compounds

Compound	PMMA-dye	
	IE eV	EA eV
pure	1.9237	7.2761
1	6.0253	2.6857
2	6.0376	3.0955



.Figure 3.6 shows the IE and EA of all (PMMA-dye) studied

From the founded relax molecular structures with the B3LYP/SDD-DFT method, the Ultraviolet-Visible UV-Vis spectra of the compounds under study were studied and analyzed using the time .dependent-self-consistent field TD-SCF method with the same hybrid functional and basis sets Table 3.5 indicate the excitation energies of the main band, oscillator strength and electronic transitions HOMO to LUMO for (PMMA-dye) compounds. The type of transition from nonbonding (n) to anti-bonding (π^*) $n \rightarrow \pi^*$ is in the region (400-750) nm. For the region (250-nm wave length, the transition is from bonding (π) orbital to anti-bonding (π^*) $\pi \rightarrow \pi^*$ due (400 to double bounds. In the region (150-250) nm, the type of transition is $n \rightarrow \sigma^*$; this is the lone pair electron or non-bonding electrons. If the region is less than 150 nm, the transition will be from a bonding (σ) to an anti-bonding (σ^*) $\sigma \rightarrow \sigma^*$ because of the single bounds in the compounds. The energy required to excite an electron from the ground state σ to excited state σ^* is larger. In general, the required transition energy for electron transition from orbital to others is the higher in $\sigma \rightarrow \sigma^*$ transition, and then $n \rightarrow \sigma^*$. At the end, the low required energy for the transition is at $^*n \rightarrow \pi^*$ and then at $\pi \rightarrow \pi$



pure

1

2

.Figure 3.7: UV-Vis Spectra of the (PMMA-dye)

Excitation energy, oscillator strength and electronic transitions HOMO→LUMO for(PMMA-dye)

Complexes	Excitation Energy (cm)$^{-1}$	Wave Length (nm)	Oscillator Strength	Transitions HOMO→LUMO	Types of Transition
Pure	42361.33776	236.0643	0.0023	HOMO→LUMO (%46) HOMO→LUMO+1 (%49) HOMO-1→LUMO+1 (%3)	$^{*}n \rightarrow \sigma$
	43040.46128	232.3395	0.0028	HOMO-1→LUMO (%73) HOMO-1→LUMO+1 (%21) HOMO→LUMO+1 (%3)	$^{*}n \rightarrow \sigma$
	50726.97808	197.1337	0.0007	HOMO→LUMO (%51) HOMO→LUMO+1 (%44) HOMO-1→LUMO (%2) HOMO-1→LUMO+1 (%3)	$^{*}n \rightarrow \sigma$
1	40255.4096	248.4138	0.0243	H-1→LUMO+3 (15%) HOMO→LUMO(77%) HOMO-LUMO+1(4%)→1	$^{*}n \rightarrow \sigma$
	42234.7078	236.7720	0.0062	H-3→L+1(70%) H-2→L+1 (11%) H-3→LUMO (3%) H-3→L+2 (4%) H-3→L+3 (8%)	$^{*}n \rightarrow \sigma$
	43252.5865	231.2000	0.0031	H-2→L+1 (17%) H-2→L+2 (62%) H-3→L+1 (3%) H-3→L+2 (8%) H-2→L+3 (6%)	$^{*}n \rightarrow \sigma$
D	32292.2427	309.6718	0.337	H-1→L+1 (15%) HOMO→LUMO (%46)	$^{*}\pi \rightarrow \pi$
2				HOMO→L+1 (17%) H-2→LUMO (2%) H-2→L+1 (6%) H-1→LUMO (9%)	
	32472.9121	307.9489	0.1029	H-1→LUMO (16%) H-1→L+1 (46%) HOMO→LUMO (%18) H-3→LUMO (2%)	$^{*}\pi \rightarrow \pi$

				H-3→L+1 (5%) ,H-2→LUMO (3%) HOMO→L+1 (4%)	

Reference

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