GSC Advanced Research and Reviews

eISSN: 2582-4597 CODEN (USA): GARRC2

Cross Ref DOI: 10.30574/gscarr

Journal homepage: https://gsconlinepress.com/journals/gscarr/

(RESEARCH ARTICLE)

Check for updates

Electronic structures and photovoltaic properties of a novel phthalocyanine and titanium dioxide phthalocyanine for dye sensitized-solar cells

Fares A. Yasseen * and Faeq A. Al-Temimei

University of Kufa, Faculty of Science, Department of Physica, Najaf, Iraq.

GSC Advanced Research and Reviews, 2021, 06(03), 107–115

Publication history: Received on 06 February 2021; revised on 09 March 2021; accepted on 11 March 2021

Article DOI: https://doi.org/10.30574/gscarr.2021.6.3.0046

Abstract

In the present work, geometries, electronic structures, photovoltaic and optical properties have been carried out on a series of structures formation of phthalocyanine and Titanylphthalocyanine dyes, which are replaced by several subgroup. A density functional theory (DFT) approach together with hybrid function (B3LYP) at SDD basis set was used for the ground state properties in the gas phase. The time-dependent density functional theory (TD-DFT)/ B3LYP was used to investigate the excitation properties of new dyes and analyzed the trends in their optical and redox characteristics. Theoretical principles of HOMO and LUMO energy levels of dyes is requisite in analyzing organic solar cells, thus, HOMO, LUMO levels, open circuit voltage, energy gap, light harvestings efficiency, electron regeneration and electron injection have been calculated and discussed. The outcome of the efficiency, the considered dyes explain absorption energy and wavelength properties that correspond to the solar spectrum requirements. According to results, all the considered materials have a good property and possibility of electron injection procedure from the dyes to conduction band of TiO2, PC60BM or PC60BM. As a result, the molecular changes affect the electronic properties of dye molecules for solar cells. Also, a study of new dyes sensitizers showed that designed materials will be excellent sensitizers. Theoretical designing will prae a way for experimentalists to synthesize the efficient sensitizers for solar cells clearer.

Keywords: Phthalocyanine; Titanylphthalocyanine; Solar cells, DFT; Photovoltaic properties

1. Introduction

Phthalocyanines are organic days that have received a great deal of interest during the 20th century as the second most imperative class of colourant due to their tectorial power and better properties, for example, remarkable stability to light, acids and alkalis. Since their discovery, phthalocyanines (Pcs) have been used in various applications which include photovoltaic energy conversion, dye-sensitized solar cells, semiconductors, transistor sensors, and catalysis[1,2]. Metal-phthalocyanine (MPc) complexes are extremely encouraging species for organic electronics because of their remarkable organ electronic properties, air stability and minimal cost[3].

They have been studied significantly with each theoretical technique and experimental. Further, more than 70 phthalocyanines with various electronic properties have been synthesized and studied, since their physical and chemical properties can be varied by changing the metal ion in the center of phthalocyanines (e.g., Cu, Pb, Zn, TiO, Fe) or different ligand attachment as functional groups to the terminal organic rings[4,5]. The properties connected to such as a structure explain both scientific and technological importance for the phthalocyanine molecules. Their stability and widely changing physical and chemical properties create them an attractive to be played a more important role in applications sensors[6]. Global research into conjugate organic molecules has been a major topic in the fields of physics, materials science and chemistry. Most researches in this field are focused mostly on the electronic properties and

* Corresponding author: Fares A Yasseen
University of Kufa, Faculty of Science, Department of Physica, Najaf, Iraq.

structure of the MPc, such as vanadyl-phthalocyanine (VOPc), titanyl-phthalocyanine (TiOPc) and chlor-gallium phthalocyanine (GaClPc)[7,8,9]. Titanyl phthalocyanine (TiOPc), in specific, has become of importance due to its semiconducting as well photoconductivity. TiOPc is known to form different polymorphs that are responsible for variances in stacking types and molecular position in systematic solid films[9,10]. In this paper, we will make quantum chemical investigated and designed of the neutral and doped of phthalocyanine and Titanyl phthalocyanine which is replaced by a various group that has been used to find appropriate candidates for creating improved solar cells. The chemical structures of the phthalocyanine, Titanyl phthalocyanine and derivatives are shown in Figure 1.

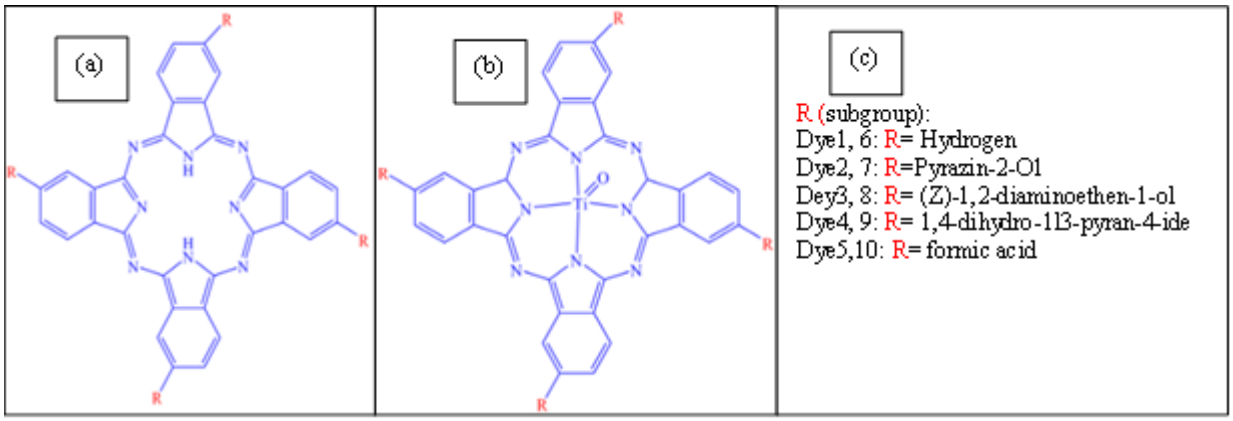

Figure 1 Chemical structure of (a) the phthalocyanine, (b) Titanyl phthalocyanine dye and (c) different subgroup.

2. Theoretical Methodology

The geometry optimizations of the neutral and doped of phthalocyanine and Titanyl phthalocyanine were done by DFT "density function theory" at the B3LYP "three-parameter compound functional of Beckes" with the SDD "Stuttgart Dresden triple zeta ECPs (Effective-Core Potential)" basis set[11]. The SDD basis sets the possible quality for the system of interest for heavy metals uses relativistic ECPs, it is powerfully recommended for the heavy metals. The electronic excitation energy was calculated for the relax molecules done by TD-DFT/B3LYP method with SDD basis sets. The geometry structures of neutral and dope dyes are optimized without any limitations[11,12]. TD-DFT method has been verified to be reliable for calculating spectra properties of many metal complexes. These compute processes have been successfully applied to another conjugate molecules[11,13]. All the DFT calculations reported in this work implemented using Gaussian 09 software package with Gauss View 5.0.8 software to insert and plot elemental structure of particles[14,15].

3. Results and discussion

3.1. Optimized Geometry of Structures

The DFT calculations are taken into account in all interactional corrections between the electrons in the structure of molecules. Therefore, the theoretical DFT method is considered reliable and effective in determining the geometrical optimization of the structure. The results have shown that the virial ratio (-V/T) extends from 2.0032 to 2.00511 that is compatible with the experimental value for a hydrogen atom. Also, the molecules are in minima energy without any imaginary frequencies. The geometric distances of the studied molecules indicate that dihedral angles of the consecutive units between 180o and -180o and the bond distances of inter-ring are around the value 1.423Å. It is also clear that adding many subgroups does not change these parameters. The range band lengths of all dyes are; C ─ C = 1.4408 - 1.4410, C ¨ C = 1.3892 - 1.4231, C ─ H = 1.0830 - 1.0947, O ─ C = 1.3792 - 1.4692, N ─ C = 1.1771 - 1.1771, N ─ H = 1.0227 -1.0239 and O ─ H = 1.0213 - 1.0238 Å. Å. Moreover, N – C – C. The angles correspond well to the experimental data, with the bond angles and the bond lengths of pyrazine and benzene. The bond angles and bond lengths between carbon and hydrogen atoms are also consistent with experimental data for aromatic carbon[16,17]. This result implies that the appropriate selection of the base group (SDD) are efficient strongly suggested to describe and relax the molecules under study. The results of the geometry optimizations of the neutral and doped of phthalocyanine and Titanyl phthalocyanine structures labelled from 1 to 10. We found that adjustment several associated combinations does not variation the geometric parameeters. Figure 2. demonstration that all studied molecules in this work have planar geometries.

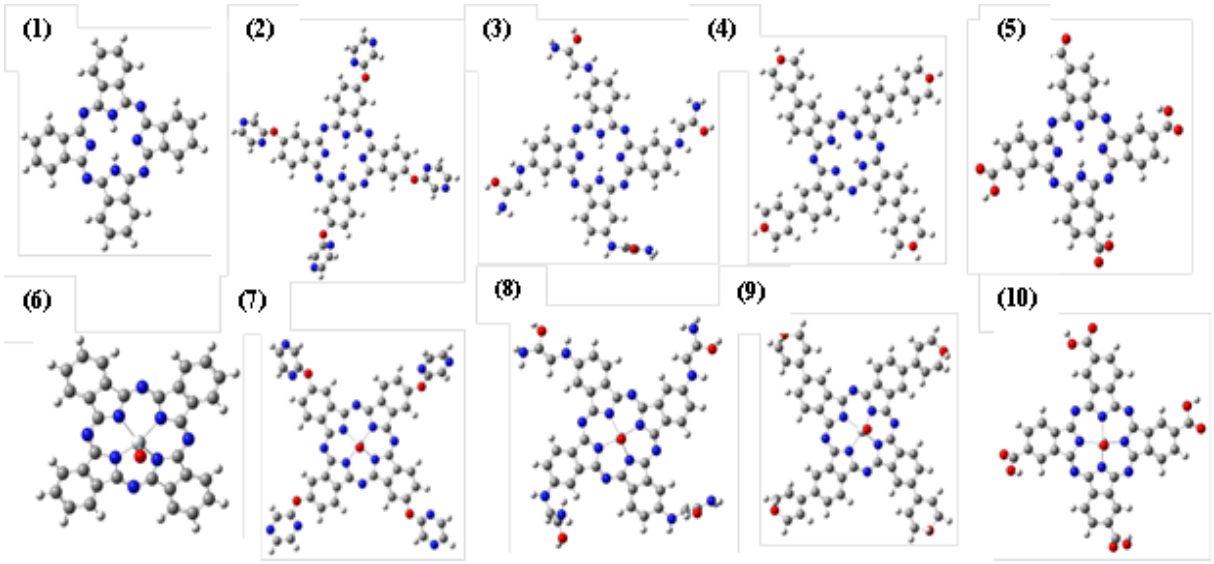

Figure 2 The optimizations of the phthalocyanine and Titanyl phthalocyanine and derivatives.

3.2. The Electronic Structure

The contribution of the frontier molecular orbital (FMO) is very important in determining the states of charge separation of the investigated particles because the relative arrangement of the occupied orbital and the hypothetical orbit provides a reasonable qualitative indication of the excitation properties[18]. Energy levels in the molecular orbitals from HOMO to LUMO of dyes are shown in Table 1.The distribution of electron density and energy levels at HOMO, LUMO and E_{gap} were influenced by the deformed structures. The LUMO energies change significantly with the presenting of subgroups. This means that the nature of substitution plays major roles in electronic properties and the effect of structural differences. The contrast of HOMO and LUMO energies is visible. The band gap computed from phthalocyanine and derivatives is classified in the following order: 4>5>3>2>1. Also, the bandgap of Titanylphthalocyanine and derivatives are classified in the following order: 10>7>6>9>8. The E_{gap} significant parameter was converted to be the absorption wavelength.

Table 1 Energies Values of E_{LUMO}, E_{HOMO} and E_{gap} in eV of all dyes under study.

Dyes	**No.**	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**E_{gap} (eV)**
Pc	1	-5.684	-4.007	1.678
PcO($C_4H_4N_2$)	2	-4.979	-3.023	1.956
PcNHCH($OHNH_2$)	3	-4.979	-2.993	1.986
PcO(C_5H_5O)	4	-5.511	-3.301	2.210
Pc(COOH)	5	-5.197	-3.178	2.019
TiOPc	6	-5.442	-3.069	2.373
TiOPcO($C_4H_4N_2$)	7	-5.470	-3.020	2.450
TiOPcNHCH($OHNH_2$)	8	-5.466	-3.428	2.038
TiOPcO(C_5H_5O)	9	-5.440	-3.347	2.093
TiOPc(COOH)	10	-5.549	-3.428	2.121
PC60BM		-6.100	-3.700	
PC70BM		-5.800	-3.830	
TiO_2		-5.928	-4.000	

From the previous analysis, we realized that the LUMO energy levels of all studied particles are much higher than the edge of the ITO conduction band (-4.7 eV). Therefore, the studied particles have strong ability to inject electrons into ITO electrodes. The test phenomenon is completely in agreement with the previous article. Besides, the LUMO energy levels are higher than the reduction potential energy of the I^-/I_3^- electrolyte (-4.80 eV) indicating that the oxidized dyes could be efficiently regenerated from the reduced species in the electrolyte to give an efficient charge separation [6,10]. Furthermore, the LUMO levels of dyes are higher than the conduction band of PC60BM, PC70BM or TiO_2, indicate the ability of dyes to inject electrons into PC60BM, PC70BM or TiO_2. Figure 3 represents the 3D distribution of HOMOs and LUMOs of the compounds studied due to LCAOs-MOs "Linear Combination of Atomic Orbital-Molecular Orbitals" according to the coordination of each dye in the ground state.

In general, as shown in Fig. 3. HOMO of current molecules in the neutral form have a π-bonding,d an-antibonding method between successive subunits whereas LUMO possesses an ant-antibonding and link-character in the middle of the subunits while inverting in the case of the doped forms.

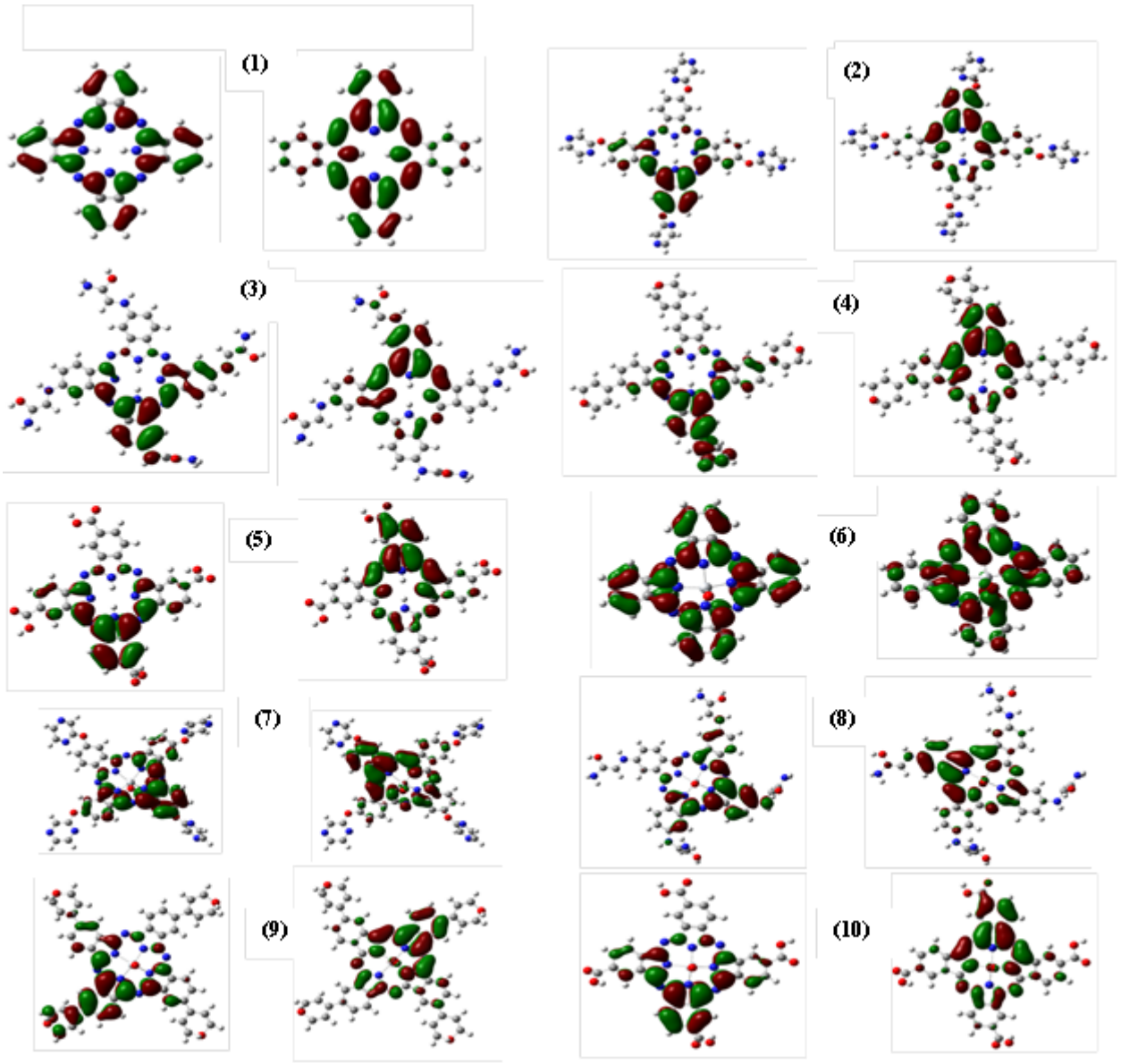

Figure 3 HOMO and LUMO frontier orbital distribution of the calculated dyes obtained at B3LYP/SDD level.

3.3. The photovoltaic properties

To examine the photoelectric properties of the performed particles, it is scientifically important to measure the potential for electronic transition from the excited state to the LUMO receptors of the dyes 'conduction band'. It is necessary to note from Table 1 that the energies of the LUMO level of the dyes are greater than the energies of the LUMO "conduction

band" level of the receiver PC60BM (-3.7 eV), PC70BM (-3.83eV) and TiO2 (-4.00 eV) [19,20]. HOMO energy levels for all of the dyes performed are higher than PC60BM (-6.1eV), PC70BM (-5.8eV), and TiO2 (-5.928eV) conduction band edge, indicating that the photo-excited electron goes from dyes (1-10) to PC60BM, PC70BM and TiO2 which may be sufficient to be useful in PV devices.

It is revealed that the open circuit voltage Voc is linearly dependent on the HOMO power of the donor and the LUMO of the receiver[19,21]. Table 2 shows the calculation of VOC to examine the relationship between the energy of VOC and LUMO energy of the studied dyes which depend on electron injection from the LUMO level to the conduction band of PC60BM, PC70BM or TiO2 as follows[20,21]:

$$V_{oc} = \left| E_{HOMO}\ (Donor) \right| - \left| E_{LUMO}\ (Acceptor) \right| - 0.3 \qquad (1)$$

The outcome values of Voc to the Eq. (1) in the range (1.251-1.957 eV) for PC60BM; (1.121 -1.827 eV) for PC70BM and (1.051 - 1.051 eV). These values of dyes are sufficient for probable electron injection. As a result, all current molecules can be used as utilized as sensitizers for solar cells as electron injection is possible from the studied compound to LUMO for PC60BM, PC70BM or TiO2.

Table 2 The Voc (eV)/ PC60BM, Voc (eV)/ PC70BM and Voc (eV)/ TiO2 (in eV) of all dyes under study.

Dyes	**No.**	**V_{oc} (eV)/ PC60BM**	**V_{oc} (eV)/ PC70BM**	**V_{oc} (eV)/ TiO_2**	**LHE**
Pc	1	1.441	1.311	1.241	0.6650
PcO($C_4H_4N_2$)	2	1.470	1.340	1.270	0.3705
PcNHCH($OHNH_2$)	3	1.711	1.581	1.511	0.6369
PcO(C_5H_5O)	4	1.440	1.310	1.240	0.5102
Pc(COOH)	5	1.692	1.562	1.492	0.6786
TiOPc	6	1.684	1.554	1.484	0.4325
TiOPcO($C_4H_4N_2$)	7	1.251	1.121	1.051	0.4071
TiOPcNHCH($OHNH_2$)	8	1.478	1.348	1.278	0.5523
TiOPcO(C_5H_5O)	9	1.711	1.581	1.511	0.6444
TiOPc(COOH)	10	1.957	1.827	1.757	0.4098

The performance of a solar cell that is the conversion of solar to electric efficiency is reliant on light-harvesting efficiency "LHE" that helps in light absorbance by the dye-sensitized PC60BM, PC70BM or TiO2sfilm. The LHE can be counted with the assistance of the oscillator strength (O. S) from TD-DFT method depending on the following Eq. [17,19,20].

$$LHE = 1 - 10^{-O.S} \qquad (2)$$

Where O.S is the oscillator strength of adsorbed dye molecules related to the maximum absorption wavelength λmax. We can see in Table 2 that the group of LHE dyes is under study 0.6786-0.3705 this values, which could harvest more light leading to betters performance of the cell. The LHE values for the dyes are in a narrow range. This means that all the dyes will give similar photocurrent.

Additionally, the electron injection from the dyes to the surface of TiO2, oxidation potential energy ($E_{OX}^{dye^*}$), oxidation potential energy (E_{OX}^{dye}) in the base case the free energy change (ΔG_{inj}°) are other important factors that impact electron injection. The theoretical values of these parameters were calculated from the following equations [15,18,20]: The negative sign

$$\Delta G_{inj}^{\circ} = E_{OX}^{dye^*} - E_{CB}^{TiO_2} \qquad (3)$$

$$E_{OX}^{dye^*} = E_{OX}^{dye} - E_{00} \quad (4)$$

Where: E_{00} is vertical excitation energy and the 0-0 transition energy accrue between the ground state and the excited state. To evaluation the 0-0 "absorption" line, we need both the singlet ground state (S_0) and the first singlet excited state (S1) In this work, the $E_{CB}^{TiO_2}$ represents the conduction band(-4.0 eV) and redox potential in the electrolyte $E_{OX}^{electrolyte}$ is 4.8 eV [20].The specific efficiency of the dye can be calculated by the driving force of dye regeneration (ΔG^{regen}), can be described by [19,20]:

$$\Delta G^{regen} = E_{OX}^{dye} - E_{OX}^{electrolyte} \quad (5)$$

Table 3 appearances that the $E_{OX}^{dye^*}$ value increases in the order: 2<3<5<7<6<9<4<8<10<1, illuminating that dye2 is the most easily oxidized types and phthalocyanine (dye1) is the smaller. The computed results in Table 3. indication that the E_{OX}^{dye} values of the designed dyes are matched well with that of the parent dye (phthalocyanine). The E_{OX}^{vdye} value for all dyes is slightly lower than that for phthalocyanine. Also, Table 3 presents the values ΔG_{inj}° for all dyes are a negative sign. This means that the process of spontaneous charge transfer arises after the photon absorbs the dye molecules and electron injection from the dye to TiO_2[18,20,22]. The ΔG_{inj}° values of the checked dyes increase in order:2<3<5<7<6<9<4<8<10<1. As a result, arrange the driving force for electron injection from the oxidizing dye into CB of TiO_2 is 2>3 >5>7>6 >9>4>8 >10>1, illuminating that dye2 has the smallest ΔG_{inj}° value, while dyes 1,10,8 and 4 have the largest values in specific demonstrations an important driving force for electron injection into TiO_2. Also, computed ΔG^{regen} of dyes is listed in Table 3. It can be noticed that the phthalocyanine is higher ΔG^{regen} (0.884 eV) compared with other dyes in this study, which would lead to a higher short circuit current density than phthalocyanine.

Table 3 The E_{OX}^{dye}, $E_{OX}^{dye^*}$, ΔG_{inj}° and ΔG^{regen} (in eV) of all dyes under study computed in the gas phase.

Dyes	**No.**	$\mathbf{E_{OX}^{dye}}$	$\mathbf{E_{OX}^{dye^*}}$	$\mathbf{\Delta G_{inj}^{\circ}}$	$\mathbf{\Delta G^{regen}}$
Pc	1	5.684	3.804	-0.196	0.884
PcO(C4H4N2)	2	4.979	2.962	-1.038	0.179
PcNHCH(OHNH2)	3	4.979	3.109	-0.891	0.179
PcO(C5H5O)	4	5.511	3.478	-0.522	0.711
Pc(COOH)	5	5.197	3.279	-0.721	0.397
TiOPc	6	5.442	3.362	-0.638	0.642
TiOPcO(C4H4N2)	7	5.470	3.326	-0.674	0.670
TiOPcNHCH(OHNH2)	8	5.467	3.508	-0.492	0.667
TiOPcO(C5H5O)	9	5.440	3.446	-0.554	0.640
TiOPc(COOH)	10	5.550	3.532	-0.468	0.750

3.4. The Absorption properties

The absorption of a new material which matches the solar spectrum is an important factor for the application as a photoelectric material, and a good PV material should have wide and strong visible absorption properties. The excitation state of the molecules were studied and examined using TD-DFT/B3LYB with SDD basis sets. As confirmed in Table 4 the values of absorption energy ($\lambda_{Labs.}$ in eV), absorption wavelength (λ_{max} in nm), oscillators strength (O.S), the main assignment (HOMO→LUMO) and the transition characters %. We can report, the calculated wavelength λ_{max} of dyes understudy in the range from 578.422to 663.051nm. Furthermore, the results indicated that the lowest singlet electronic excitation is described as a typical $n \rightarrow \pi^*$ transition, where required the low energy. In general, the type of additional subgroup plays a significant role in the absorption properties of the dyes.

Table 4 The excitation state properties of the dyes understudy at TD-DFT/B3LYB/SDD level.

Dyes	No.	Transition	E_{abs} (eV)	λ_{max} (nm)	O.S	Main assignment	Type transition
Pc	1	$S_0 \rightarrow S1$	1.9807	659.582	0.475	HOMO→LUMO	$n \rightarrow \pi^*$
PcO($C_4H_4N_2$)	2	$S_0 \rightarrow S1$	2.0691	614.741	0.201	HOMO→LUMO	$n \rightarrow \pi^*$
PcNHCH($OHNH_2$)	3	$S_0 \rightarrow S1$	2.0982	663.051	0.440	HOMO→LUMO	$n \rightarrow \pi^*$
PcO(C_5H_5O)	4	$S_0 \rightarrow S1$	2.3657	609.925	0.310	HOMO→LUMO	$n \rightarrow \pi^*$
Pc(COOH)	5	$S_0 \rightarrow S1$	2.1298	646.291	0.493	HOMO→LUMO	$n \rightarrow \pi^*$
TiOPc	6	$S_0 \rightarrow S1$	2.4991	596.102	0.246	HOMO→LUMO	$n \rightarrow \pi^*$
TiOPcO($C_4H_4N_2$)	7	$S_0 \rightarrow S1$	2.5978	578.422	0.227	HOMO→LUMO	$n \rightarrow \pi^*$
TiOPcNHCH($OHNH_2$)	8	$S_0 \rightarrow S1$	2.1912	632.929	0.349	HOMO→LUMO	$n \rightarrow \pi^*$
TiOPcO(C_5H_5O)	9	$S_0 \rightarrow S1$	2.2196	621.974	0.449	HOMO→LUMO	$n \rightarrow \pi^*$
TiOPc(COOH)	10	$S_0 \rightarrow S1$	2.2589	614.442	0.229	HOMO→LUMO	$n \rightarrow \pi^*$

Figure 4 characterized the relation between the E_{gap} and E_{abs} for all dyes, and we can note the E_{abs} (eV) is more than E_{gap} for all dyes and this resulted indicated the easy of accruing the excitation and transitions. The oscillators strength for an electronic transition is proportional to the transition moment.

This arrangement is related according to the terminal and molecular properties of the neutral and doped phthalocyanine and Titanyl phthalocyanine structures. This remarkable point is viewed by investigating the electronic and absorption results. All current molecules contain energy vacuoles of semiconductor materials. Those remarkable points are seen both in investigating the electronic structure and absorption properties.

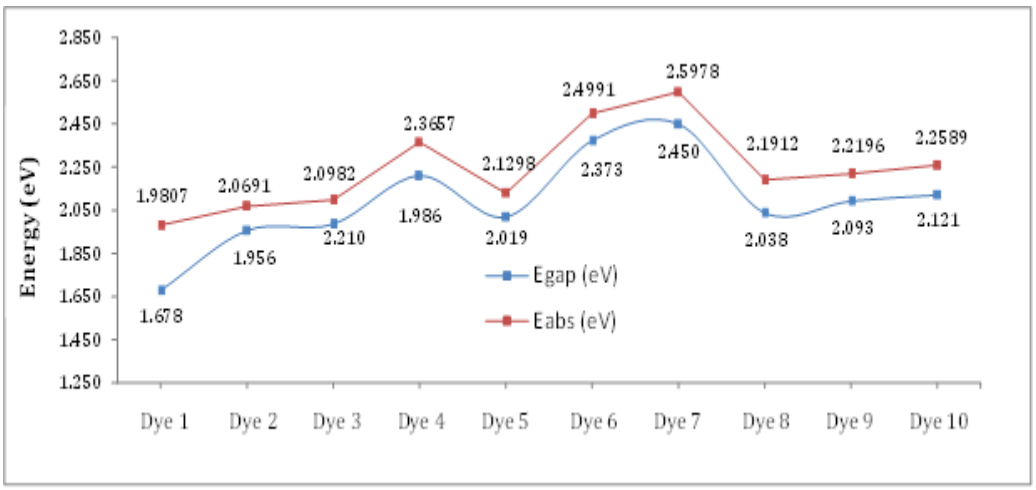

Figure 4 Described the relation between the E_{gap} and E_{abs} for all dyes under study.

4. Conclusion

According to study findings, the optimized structures to all studied dyes explain that they quasi-planar conformation and the geometric parameters are in good agreement with the experiment data. The calculation of HOMO and LUMO of the studied dyes revealed that they had energy gaps similar to that of the semiconductor materials, considering different structures, where the molecular changes affect the electronic properties. The LUMO energy levels of all dyes are higher than the conduction band of PC60BM, PC70BM or TiO_2, both HOMO and LUMO levels of the dyes agree well with the requirement for an efficient photosensitizer, The electron from the dyes can be injected into the conduction band of PC60BM, PC70BM or TiO2, and subsequent regeneration in a sensitive organic solar cell. In addition, these dyes are

better for them V_{oc}, and all the dyes will give similar photocurrent for the reason that the LHE values for the dyes are in a narrow range. However, regarding the predicted photovoltaic properties parameters, dyes showed better electron injection efficiency with of negative values of ΔG°_{inj} and larger values ΔG^{regen} these values for dyes are advantageous. It can be concluded that based on the efficiency results, the studied dye appearance absorption energy and wavelength characteristics correspond to the requirements of the solar spectrum. Based on the study findings, all the considered molecules can be used as sensitizers.

Compliance with ethical standards

Acknowledgments

We would like to thank our friends for their invaluable support.

Disclosure of conflict of interest

The authors declare no conflict of interest.

Statement of consent

Written consent was obtained from all participants and the study was approved by the Scientific Committee in Physics department of the Faculty of Science, University of Kufa.

References

[1] D. Gounden, G. N. Ngubeni, M. S. Louzada, S. Khene, J. Britton, and N. Nombona, "Synthesis, spectroscopic and DFT characterization of 4β-(4-tert-Butylphenoxy) phthalocyanine Positional Isomers for Non-linear Optical Absorption," *South African J. Chem.*, vol. 70, no. Mcd, pp. 49–59, 2017, doi: 10.17159/0379-4350/2017/v70a8.

[2] S. U. Lee, "Influence of exchange-correlation functional in the calculations of vertical excitation energies of halogenated copper phthalocyanines using time-dependent density functional theory (TD-DFT)," *Bull. Korean Chem. Soc.*, vol. 34, no. 8, pp. 2276–2280, 2013, doi: 10.5012/bkcs.2013.34.8.2276.

[3] J. J. Fu and Y. Liao, "Structure of chloroaluminum phthalocyanine (CLALPc) on SiO2(100) surface: A combined molecular dynamics(MD) and density functional theory (DFT-D) study," *J. Chem. Pharm. Res.*, vol. 6, no. 5, pp. 347–351, 2014.

[4] N. L. Tran, F. I. Bohrer, W. C. Trogler, and A. C. Kummel, "A density functional theory study of the correlation between analyte basicity, ZnPc adsorption strength, and sensor response," *J. Chem. Phys.*, vol. 130, no. 20, pp. 1–7, 2009, doi: 10.1063/1.3134743.

[5] F. A. Al-Temimie, "Electronic structure, photovoltaic and absorption properties of designed photo-efficient new organic dyes with D-π-A framework," Jul. 2020.

[6] P. Agarwala and D. Kabra, "A review on triphenylamine (TPA) based organic hole transport materials (HTMs) for dye sensitized solar cells (DSSCs) and perovskite solar cells (PSCs): Evolution and molecular engineering," *J. Mater. Chem. A*, vol. 5, no. 4, pp. 1348–1373, 2017, doi: 10.1039/c6ta08449d.

[7] T. Niu, J. Zhang, and W. Chen, "Molecular ordering and dipole alignment of vanadyl phthalocyanine monolayer on metals: The effects of interfacial interactions," *J. Phys. Chem. C*, vol. 118, no. 8, pp. 4151–4159, 2014, doi: 10.1021/jp4101653.

[8] A. Gerlach *et al.*, "Orientational ordering of nonplanar phthalocyanines on Cu(111): Strength and orientation of the electric dipole moment," *Phys. Rev. Lett.*, vol. 106, no. 15, pp. 1–4, 2011, doi: 10.1103/ Phys Rev Lett.106.156102.

[9] X. Liu, Y. Wei, J. E. Reutt-Robey, and S. W. Robey, "Dipole-dipole interactions in TiOPc adlayers on Ag," *J. Phys. Chem. C*, vol. 118, no. 7, pp. 3523–3532, 2014, doi: 10. 1021/jp4096612.

[10] R. Skonieczny, J. Makowiecki, B. Bursa, A. Krzykowski, and M. Szybowicz, "Characterization of titanyl phthalocyanine (TiOPc) thin films by microscopic and spectroscopic method," *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*, vol. 191, pp. 203–210, 2018, doi: 10.1016/j.saa.2017.10.034.

[11] M. C. Koch, W., Holthausen, *A Chemist's Guide to Density Functional Theory*, Second Edi. Wiley–VCH Verlag GmbH,Weinheim, 2001.

[12] F. A. Mohammed and H. I. Abbood, "Electronic structure of vanadium tetrachloride di-hydroxyl metal complex," *J. Eng. Appl. Sci.*, vol. 13, no. 23, pp. 9825–9830, 2018, doi: 10.3923/jeasci.2018.9825.9830.

[13] M. C. Zerner, "Semiempirical Molecular Orbital Methods," *Rev. Comput. Chem. Publ. Inc*, vol. 2, pp. 313–365, 1991, [Online]. Available: VCH Publishers Inc.

[14] M. J. et al Frisch, "Gaussian 09, Revision A. 02 Gaussian." Inc. Wallingford CT, Wallingford, 2009.

[15] M. M. Roy, D. D., Todd, A.K., John, "Gauss View 5.0.8. Gaussian." Inc. Gaussian, Inc., Wallingford, 2009.

[16] L. Pauling, *The Nature of the Chemical Bond*. United States: Cornell University Press, 1960.

[17] F. A. AL-Temimei and A. H. Omran Alkhayatt, "A DFT/TD-DFT investigation on the efficiency of new dyes based on ethyl red dye as a dye-sensitized solar cell light-absorbing material," *Optik (Stuttg).*, vol. 208, p. 163920, 2020, doi: 10.1016/j.ijleo.2019.163920.

[18] L. Yang, J. K. Feng, and A. M. Ren, "Theoretical studies on the electronic and optical properties of two thiophene-fluorene based π-conjugated copolymers," *Polymer (Guildf).*, vol. 46, no. 24, pp. 10970–10981, 2005, doi: 10.1016/j.polymer.2005.09.050.

[19] N. A. Wazzan, "A DFT / TDDFT investigation on the efficiency of novel dyes with ortho - fluorophenyl units (A1) and incorporating benzotriazole / benzothiadiazole / phthalimide units (A2) as organic photosensitizers with D – A2 – π – A1 configuration for solar cell ," *J. Comput. Electron.*, no. 0123456789, 2019, doi: 10.1007/s10825-019-01308-4.

[20] H. Tian *et al.*, "Effect of different electron donating groups on the performance of dye-sensitized solar cells," *Dye. Pigment.*, vol. 84, no. 1, pp. 62–68, 2010, doi: 10.1016/j.dyepig.2009.06.014.

[21] F. A. Al-Temimei, F. Salih Abbas, and A. S. Alaboodi, "New π-Conjugated Materials Based on Thienopyrazine As Organic Dye Sensitizers for Organic Photovoltaic Device Applications," *J. Phys. Conf. Ser.*, vol. 1294, no. 2, 2019, doi: 10.1088/1742-6596/1294/2/022003.

[22] A. Fitri, A. T. Benjelloun, M. Benzakour, M. McHarfi, M. Hamidi, and M. Bouachrine, "Theoretical investigation of new thiazolothiazole-based D-π-A organic dyes for efficient dye-sensitized solar cell," *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*, vol. 124, pp. 646–654, 2014, doi: 10.1016/j.saa.2014.01.052.