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Photovoltaic properties of Zn-Complexed-phtalocyanine and derivatives for DSSCs application

L. Louazri[1], A. Amine[2], S. M. Bouzzine[3], M. Hamidi[4], M. Bouachrine[5]
[1,2]*LCBAE/CMMBA, Faculty of Sciences, Moulay Ismail University, Meknes, Morocco.*
[3]*Centre Régional des Métiers d'Education et de Formation, BP 8, Equipe d'Electrochimie et Environnement, Faculté des Sciences et Techniques, Université Moulay Ismaïl, B.P. 509 Boutalamine, Errachidia, Morocco.*
[4]*Equipe d'Electrochimie et Environnement, Faculté des Sciences et Techniques, Université Moulay Ismaïl, B.P. 509 Boutalamine, Errachidia, Morocco.*
[5]*MEM, ESTM, Moulay Ismail University, Meknes, Morocco.*

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**Corresponding author. E-mail:* mbouach@hotmail.com

Abstract

Recent improvement in the dye-sensitized design demonstrated an increase of energy conversion efficiency of solar cells, use Sensitizers low band gap, extended zinc phthalocyanines have shown particular promise because of the efficient photoinduced electron transfer and strong absorption The purpose of in this paper to a DFT Study alternative sensitizers such as Zn phthalocyanine substituted with different acid for dye sensitized solar cell (DSSC). Density functional theory (DFT) was used to determine the ground state geometries of phtalocyaninr of four categories of phthalocyanines defined by the connecting positions of anchoring groups, symmetrically substituted phthalocyanines, $(PcZn(CHC(COOHCN))_8$, $PcZn(COOH)_8$, $PcZn(COOH)_4$, $PcZn(CHC(COOHCN))_4$. The time dependant density functional theory (TDDFT) was used to calculate the excitation energies. The LUMO energies of all the dyes were above the conduction band of TiO2, The HOMO-LUMO energy gaps of new design dyes were smaller as compared PcZn. All new design dyes were strongly red shifted as compared to PcZn. The improved light harvesting efficiency (LHE) and free energy change of electron injection ΔGinject of new designed sensitizers revealed that these materials would be excellent sensitizers. This theoretical designing will the pave way for experimentalists to synthesize the efficient sensitizers for solar cells.

Keywords: Dye-sensitized Solar Cells; phtalocyanine ; DFT; Photovoltaic; Optoelectronic properties.

Introduction

Dye-sensitized solar cells (DSSCs) have attracted significant attention as a low-cost alternative to conventional solid-state photovoltaic devices [1–6]. Dye-sensitized solar cells (DSSCs) have attracted an ever-increasing attention in scientific research and in practical applications since the first report by O'Regan and Grätzel in 1991, because of its potential advantages, such as low cost and highly efficient conversion of sunlight into electricity [1–3]. In particular, these DSSC are composed of a wide band gap semi-conductor (typically TiO2) sensitized with molecular dyes, able to capture light in the visible region of the spectrum, and a redox electrolyte (typically Iodide/triiodide) (I^-/I^-_3) [7–11].

In DSSCs, incoming light causes electronic excitations of the dye sensitizers leading to electrons injection to the conduction band of nanocrystalline metal oxide. Then, the dyes regain electrons from redox couple in electrolyte solution [12]. In general, a power conversion efficiency dye sensitizer has the following characteristics: the highest occupied molecular orbital (HOMO) energy must be located below the HOMO energy of electrolyte to accept the electron from a redox electrolyte pair (I^-/I^-_3), and the lowest unoccupied molecular orbital (LUMO) should have a higher energy than that of the conduction band of semi-conductor (TiO2).

The polypyridylruthenium complexes are the most successful charge-transfer sensitizers employed in these cells, with the highest solar-to-electric power conversion efficiencies over 12% achieved under simulated sunlight. However, the main drawback of the ruthenium complex-based sensitizers is the lack of absorption in the red region of the visible spectrum [13], which limits the further increase of the efficiencies of this type of sensitizer There are still some factors that can influence the performances of phthalocyanine-based DSSCs. The energy matching between the lowest unoccupied molecular orbital (LUMO) of the sensitizers and the band edge of the semiconductor TiO2 is one of the key factors that influence the electron injection of DSSC. The LUMOs of the phthalocyanine sensitizers described above are generally too low to provide perfect electron injection. On the contrary, phthalocyanine (Pc) and metallophthalocyanine (MPc) exhibit comparatively high molar extinction coefficients of approximately 10^5 $cm^{-1}M^{-1}$ in the Q band lying at 600–700 nm and are considered very good near infrared sensitizers. Changing the ligand PcZn, has the effect of further increasing the efficiency of solar cells [14].

DSSCs using zinc phthalocyanine ZnPc sensitizers reported to date is 4.6% [15]. Additionally, the peripheral substituents also play important roles in tuning the molecular orbital energy levels, increasing the solubility and reducing the aggregation of zinc phthalocyanine complexes used in DSSC [16–19]. These factors should be considered in further optimization of the phthalocyanine sensitizers. In this paper, for new molecular structures were designed to find appropriate candidates for creating improved solar cells. The structures of the sensitizers zinc phthalocyanine substituted ZnPc-R(R=,-COOH,-CNCOOH) are shown in Fig. 1.

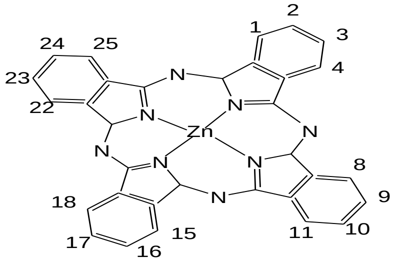
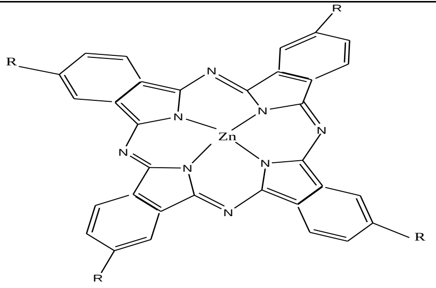
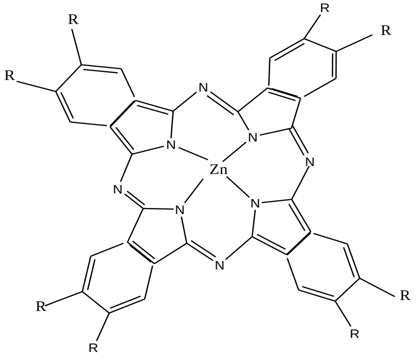
PcZn	
PcZnR$_4$ R:COOH , CHC(COOHCN)	
PcZnR$_8$ R:COOH , CHC(COOHCN)	

Figure 1: Chemical structures of macromolecules PcZnR

The calculated parameters including LUMO and HOMO their difference HOMO–LUMO represents gap energy, light-harvesting efficiency (LHE) and injection driving force ($\Delta G^{\text{injection}}$). Furthermore, the estimated values of photoelectric open (Voc) circuit thereon have been presented. The calculated results of these dyes reveal that the **PcZn(CHC(COOHCN))$_8$** dye can be used as a potential sensitizer for TiO_2 nanocrystalline solar cells due to its best electronic and optical properties and good photovoltaic parameters.
In this paper, the PcZnR sensitizers were investigated using the density functional theory **DFT (B3LYP/6-31G*).** and time-dependent density functional theory (TDDFT) method.

2. Methodologies and computation

DFT method of three-parameter compound of Becke (B3LYP) [20] was used in all the study of the neutral and polaronic compounds. The 6-31G (d) basis set was used for all calculations [21]. To obtain the charged structures, we start from the optimized structures of the neutral form. The calculations were carried out using the Gaussian 03 program [22]. The geometry structures of neutral and doped molecules were optimized under no constraint. We have also examined HOMO and LUMO levels; the energy Egap is evaluated as the difference between the HOMO and LUMO energies. The ground state energies and oscillator strengths were investigated using the TD/DFT, calculations on the fully optimized geometries. In fact, these calculation methods have been successfully applied to other conjugated molecules [23].

2.1.Theoretical background

The description of the electron transfer from a dye to a semiconductor, the rate of the charge transfer process can be derived from the general classical Marcus theory [24-28].

$$K_{\text{inject}} = \frac{|V_{RP}|^2}{h\left(\pi/\lambda K_B T\right)^{1/2} \exp\left[-\left(\Delta G^{\text{inject}} + \lambda\right)^2 / 4\lambda K_B T\right]} \qquad (1)$$

In Eq. (1), k_{inject} is the rate constant (in S^{-1}) of the electron injection from dye to TiO_2, k_{BT} is the Boltzmann thermal energy, h the Planck constant, $-\Delta G^{\text{injection}}$ is the free energy of injection and λ is the reorganization energy of the system, $|V_{RP}|$ is the coupling constant between the reagent and the product potential curves. Eq (1) revealed that larger $|V_{RP}|$ leads to higher rate constant which would result better sensitizer. The value of $|V_{RP}|$ defines the adiabatic or non adiabatic character of the electron transfer. The use of the Generalized Mullikene-Hush formalism (GMH) allows evaluating $|V_{RP}|$ for a photoinduced charge transfer [26, 27]. The explained that $|V_{RP}|$ can be evaluated as:

$$|V_{RP}| = \frac{\Delta E_{RP}}{2} \qquad (2)$$

The injection driving force can be formally expressed within Koopmans approximation as:

$$\Delta E_{RP} = \left[E_{HOMO}^{dye} - E_{ox}^{dye}\right] = -[E_{ox}^{dye} - E_{BC}^{TiO_2}] \qquad (3)$$

Here $E_{BC}^{TiO_2}$ is the conduction band edge. It is often difficult to accurately determine $E_{BC}^{TiO_2}$ because it is highly sensitive to the conditions, e.g. the pH of the solution. Thus we used experimental value corresponding to conditions where the semiconductor is in contact with aqueous redox electrolytes of fixed pH 7.0, $E_{BC}^{TiO_2} = -4$ eV [29-31].
Whereas the HOMO energy is related to the potential of first oxidation ($-E_{HOMO}^{dye} = E_{ox}^{dye}$) We propose to establish a reliable theoretical scheme to evaluate the dye's excited state oxidation potential and quantify the electron injection onto a titanium dioxide (TiO_2) surface. The free energy change (in electron volts, eV) for the electron injection can be expressed as [30]:

$$\Delta G^{\text{injection}} = E_{\text{ox}}^{\text{dye}*} - E_{\text{BC}}^{\text{TiO}_2} \qquad (4)$$

Here $E_{\text{ox}}^{\text{dye}*}$ is the oxidation potential of the dye in the excited state and $E_{\text{BC}}^{\text{TiO}_2}$ is the reduction potential of the semiconductor conduction band. Two models can be used for the evaluation of $E_{\text{ox}}^{\text{dye}*}$ [24,32,33]. The first implies that the electron injection occurs from the unrelaxed excited state. For this reaction path, the excited state oxidation potential can be extracted from the redox potential of the ground state, $E_{\text{ox}}^{\text{dye}}$ which has been calculated by DFT-B3LYP/6-31G* approach using the restricted and unrestricted formalisms and the vertical transition energy corresponding to the photoinduced
intramolecular (ICT).

$$E_{\text{ox}}^{\text{dye}*} = E_{\text{ox}}^{\text{dye}} - \lambda_{\text{max}}^{\text{ICT}} \qquad (5)$$

Here $\lambda_{\text{max}}^{\text{ICT}}$ is the energy of the ICT. Note that this relation is only valid if the entropy change during the light absorption process can be neglected. For the second model, one assumes that electron injection occurs after relaxation. Given this condition, $E_{\text{ox}}^{\text{dye}}$ is expressed as [33] :

$$E_{\text{ox}}^{\text{dye}*} = E_{\text{ox}}^{\text{dye}} - E_{0-0}^{\text{dye}} \qquad (6)$$

Here E_{0-0}^{dye} is the 0-0 transition energy between the ground state and the excited state. To estimate the 0-0 “absorption” line, we need both the S_0 (singlet ground state) and the S1 (first singlet excited state)
Where in this equation is the energy of intermolecular charge transfer (ICT). The light harvesting efficiency (LHE) was determined by formula [34].

$$\text{LHF} = 1 - 10^{-\text{f}} \qquad (7)$$

Where f is the oscillator strength of the dye. TDDFT calculations provide the oscillator strength directly.

3. Results and Discussion

How the computability of the absorption spectra relative to these new materials with the solar spectrum is an important factor for the application as a photovoltaic material. In this context, good photovoltaic material should have broad and strong visible absorption characteristics. In fact, we have calculated the UV-Visible spectra of the studied compounds using TD-DFT starting with optimized geometry obtained at B3LYP/6-31(d) level. The corresponding simulated UV–Vis absorption spectra of PcZnR, presented as oscillator strength against wavelength, are shown in Figure 2. As illustrated in table 1, we can find that the values of calculated absorption λ abs(nm) and oscillator strength (O.S) and LHF Light Harvesting Efficiency of the studied compounds PcZnR. The calculated wavelength λabs of the studied compounds decreases in the following order $PcZn(CHC(COOHCN))_8$ > $PcZnCHC(COOHCN)_4$ > $PcZn(COOH)_8$ > $PcZn(COOH)_4$. This bathochromic effect is obviously due to increased pi-delocalization which enhances with the nature of anchoring groups. Indeed, cyanoacrylate provokes delocalization as the acid. In addition, we note that there is a distribution of energy level corresponding to π-π* transition. This interesting point is seen both by analyzing electronic and absorption results. Excitation to the S1 state corresponds exclusively to the promotion of an electron from the HOMO to the LUMO. The absorption wavelengths arising from S0-S1 electronic transition increase progressively with the increasing of conjugation lengths. It is reasonable, since HOMO-LUMO transition is predominant in S0-S1 electronic transition; the results are a decrease of the LUMO and an increase of the HOMO energy, cyanoacrilique only gives rise to a HOMO levels of the acid.
Data in table II shows that there is a bathochromic shift when passing from Molecule $PcZn(COOH)_4$ (600.05nm) to Molecule $(CHC(COOHCN))_8$ (709.43nm). Those interesting points are seen both in the studying the electronic and absorption properties.

Light Harvesting Efficiency (LHE) and Oscillator Strength. The light harvesting efficiency (LHE) is the efficiency of dye to response the light. It is another factor which indicates the efficiency of DSSC. The light harvesting efficiency (LHE) of the dye should be as high as feasible to maximize the photo-current response.

Table 1: Absorption spectra data obtained by TD-DFT methods for the molecules Mi (1 to 4) compound at B3LYP/6-31G (d) optimized geometries.

	transition	**λ_{abs}(nm)**	**E_{S0-S1}**	**O .S**	**LHF**	**MO /character**
$PcZn(COOH)_4$	$S_0 \longrightarrow S_1$	600.05	2.0662	0.4809	0.669	HOMO -LUMO
	$S_0 \longrightarrow S_2$	599.58	2.0679	0.4759	0.665	HOMO-LUMO+1
$PcZn(COOHCN)_4$	$S_0 \longrightarrow S_1$	646.01	1.9192	0.5939	0.745	HOMO -LUMO
	$S_0 \longrightarrow S_2$	613.05	2.0224	0.6359	0.768	HOMO –LUMO+1
	$S_0 \longrightarrow S_3$	494.71	2.5062	0.0435	0.095	HOMO –LUMO+2
$PcZn(COOH)_8$	$S_0 \longrightarrow S_1$	616.47	2.0112	0.5521	0.719	HOMO -LUMO
	$S_0 \longrightarrow S_2$	612.99	2.0226	0.5505	0.718	HOMO –LUMO+1
PcZn $(CHC(COOHCN))_8$	$S_0 \longrightarrow S_1$	709.43	1.7479	0.7161	0.807	HOMO -LUMO
	$S_0 \longrightarrow S_2$	704.81	1.7591	0.7248	0.811	HOMO –LUMO+1
	$S_0 \longrightarrow S_3$	579.39	2.1399	0.0004	0.001	HOMO –LUMO+2

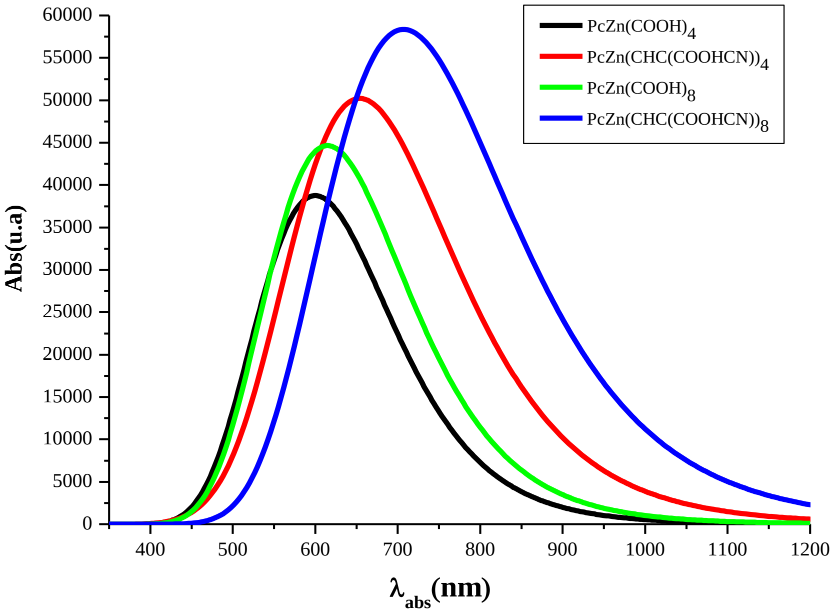


Figure 2: Simulated UV–visible optical absorption spectra of title compounds with calculated data at the TD-DFT/B3LYP/6- 31G(d).

This study was carried out to design new sensitizers for DSSC application.. We designed a new series of dyes by structural modification phthalocyanine substitution at 2 (3), 9 (10), 16 (17) and 23 (24) figure 1. The newly designed dyes geometries were optimized using DFT- B3LYP/6-31G*méthod.

The distribution pattern of highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of new sensitizers are shown in Figure 3.

From figure 3 it is clear that HOMO orbital distribution for substituted phthalocyanine molecule is well developed on all the molecules by a strong distribution on the central core consequently thes substitution are lightly covered. The LUMO are plated on the central core and the two phenyls symmetrically for the two other phenyls LUMO are less developed.

The Highest occupied molecular orbitals energy (E_{HOMO}), lowest unoccupied molecular orbitals (E_{LUMO}) and HOMO-LUMO energy gap (Egap) are given in Table 2. the energy gaps of the substituted phthalocyanine are in the following order $PcZn(COOH)_8$ < $PcZn(CHC(COOHCN))_8$ < $PcZn(CHC(COOHCN))_4$< $PcZn(COOH)_4$. We can note that the substitution by eight groups leads to lower gaps comparing to the substitution by four groups.

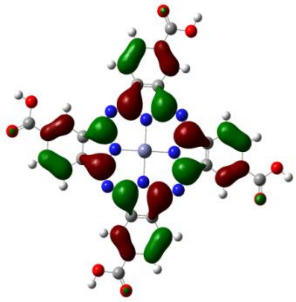
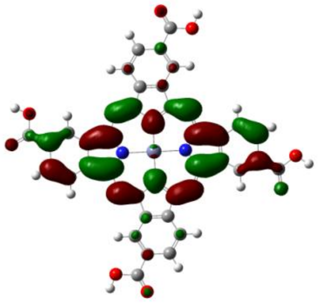
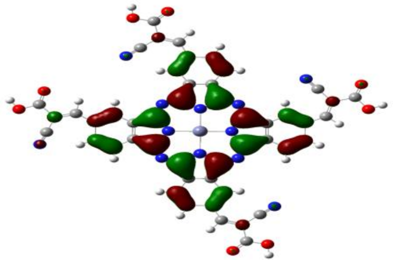
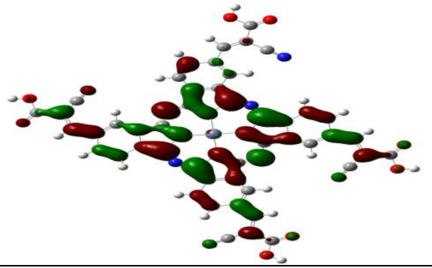
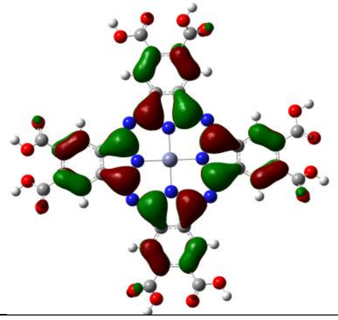
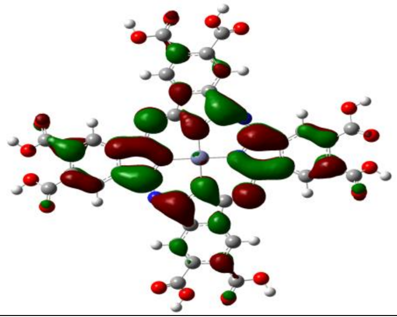
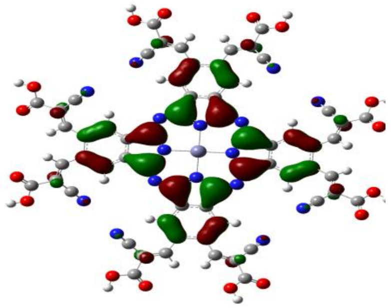
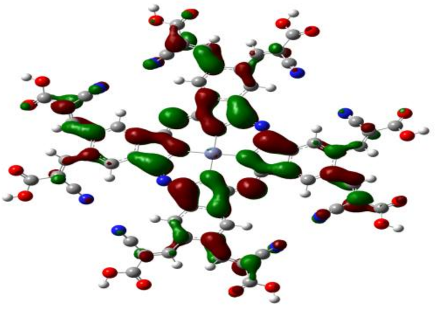
Molecules	**HOMO**	**LUMO**
PcZn(COOH)$_4$		
PcZnCHC(COOHCN)$_4$		
PcZn(COOH)$_8$		
PcZn(CHC(COOHCN))$_8$		

Figure 3: Obtained isodensity plots of the frontier orbital HOMO and LUMO of the studied compounds obtained at B3LYP/6-31(d) level.

Accordingly, the large donor acceptor area can favors charge separation and, hence, increases the conversion efficiency of the cell [35].To evaluate the possibilities of electron, transfer from the studied molecules to the conductive band of the proposed acceptors, the HOMO and LUMO levels are compared.

From the data in table2, we noted that the LUMO energy levels of the studied molecules are much higher than that of the ITO conduction band edge (-4.7 eV). Thus, the studied molecules PcZnR have a good ability to inject electrons into ITO electrodes. The experiment phenomenon is quite consistent with previous literature [36]. Furthermore the LUMO energy levels are higher than the reduction potential energy of the I^-/I_3^- electrolyte (−4.80 eV). The energy level diagram of the HOMO and LUMO of the dyes, E_{BC} of TiO_2 and redox potential energy of the electrolyte are presented in Figure 4. The HOMO and the LUMO energy levels of the donor and acceptor components are very important factors to determine whether effective charge transfer will happen between donor PcZnR and acceptor TiO_2. To evaluate the possibilities of electron transfer from the excited studied molecules to the conductive band of the acceptor TiO_2, the HOMO and LUMO levels were compared figure 4.

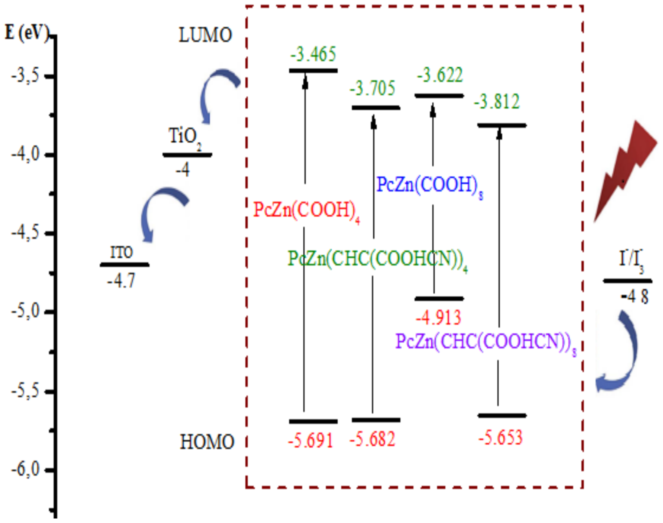


Figure 4: Schematic energy diagram of dyes, TiO$_2$ and electrolyte (I^-/I_3^-), E_{HOMO} and E_{LUMO} of the dyes PcZnR.

It is important to note that the LUMO levels of the dyes are higher than that of the conduction band of TiO$_2$ (-4.0 eV, [37]). The LUMO energy levels of all dyes are much higher than that of TiO$_2$ conduction band edge suggesting that the photo-excited electron transfer from PcZnR to TiO$_2$ may be sufficiently efficient to be useful in photovoltaic devices.

The power conversion efficiency (η) was calculated according to the following Eq.(8):

$$\eta = FF\,\frac{V_{oc}\,J_{sc}}{P_{inc\,.}} \qquad (8)$$

Where $P_{inc.}$ is the incident power density, *Jsc* is the short-circuit current, Voc is the open-circuit voltage, and *FF* denotes the fill factor.

The relationship between V_{OC} and E_{LUMO} of the dyes based on electron injection (in DSSCs)from LUMO to conduction band of semiconductor TiO$_2$ (E_{CB}), can be expressed as [38].

$$V_{OC} = E_{LUMO}\,(\text{Donnor}) - E_{LUMO}\,(\text{accepteur})\,| \qquad (9)$$

The obtained values Voc of the studied dyes calculated according to the Eq. (9), range from (0.188 to 0.535) of TiO$_2$. (Tab.2) these values are sufficient for a possible efficient electron injection.

Table 2: Energy values of E_{LUMO} (eV), E_{HOMO} (eV), Egap, and V_{OC} (eV) (OPEN CIRCUIT voltage) of the zinc phtalocyanine obtained by B3LYP/6-31G (d).

Molecules	**E_{HOMO} (ev)**	**E_{LUMO} (ev)**	**Egap (ev)**	**Voc (ev)**
PcZn(COOH)$_4$	-5.691	-3.465	2,226	0.535
PcZn(CHC(COOHCN))$_4$	-5.682	-3.705	1.977	0.295
PcZn(COOH)$_8$	-4.913	-3.622	1.291	0.378
PcZn(CHC(COOHCN))$_8$	-5.653	-3.812	1.841	0.188
TiO$_2$	-	-4		

Free Energy Change of Electron Injection. We have used mathematical equations to estimate the dye's excited state oxidation potential and free energy change of electron injection to titanium dioxide (TiO$_2$) surface. λ_{max}, ΔG^{inject} , λ_{max}^{ICT} , E_{ox}^{dye} and $E_{ox}^{dye\,*}$ are presented in Table 3.

The electron injection free energy change ΔG^{inject}, ground and excited state oxidation potentials computed in gas phase were calcuted using DFT- B3LYP/6-31G* method. Basis set was used for all calculations: E_{ox}^{dye} can be estimated as negative $E_{HOMO,}$ $E_{ox}^{dye\,*}$ is calculated based on Eq. (2), ΔGinject was estimated using Eq. (1).

For all the designed dyes, we found that ΔG^{inject} values are negative. PcZn(COOH)$_8$ showed the lowest value. This is an important result because a negative value of this parameter is an indication of spontaneous electron injection from the dye to TiO$_2$ [39].

Table 3: Calculated absorption spectra λmax, $|V_{RP}|$, ΔGinject, oxidation potential, intramolecular charge transfer energy of dyes at TDDFT/B3LYP/6-311+G* level of theory.

Molecules	λ_{max} **(nm)**	$|V_{RP}|$	$\Delta G^{injection}$	E_{ox}^{dye*}	E_{ox}^{dye}	λ_{max}^{ICT}
PcZn(COOH)$_4$	600.05	0.845	-0.3752	3,6248	5.691	2.0662
PcZn(CHC(COOHCN))$_4$	646.01	0.841	-0.2372	3,7628	5.682	1.9192
PcZn(COOH)$_8$	616.47	0.456	-1.0982	2.9018	4.913	2.0112
PcZn(CHC(COOHCN))$_8$	709.43	0.8265	-0,0947	3.9053	5.653	1.7479

Conclusion

This study is a correlation structures-properties for various compounds based on phtalcyanine. The study supports the effect of substituted groups on structural and optoelectronic properties of these materials. Moreover, calculations show that the studied materials can be used as active layers in Dye-sensitized solar cells (DSSCs). From the presented results some concluding remarks can be carried out:

- The studied molecules can be used in organic-sensitized solar cell because the electron injection process from the studied compounds (D) to the conduction band of TiO_2 (A) and the subsequent regeneration is possible LUMO (D)> LUMO (A).
- The substitution by eight groups leads to lower gaps compared to the substitution by four groups.
- For all the designed dyes, we found that ΔG_{inject} values are negative. PcZn(COOH)$_8$ showed the lowest value. This is an important result because a negative value of this parameter is an indication of spontaneous electron injection from the dye to TiO2.
- The light harvesting efficiency (LHE) is the efficiency of dye to response the light. The light harvesting efficiency (LHE) of the dye should be as high as feasible to maximize the photo-current response. We have noted that the following compound PcZnR has the highest value
- The computed λ_{max} of PcZn(CHC(COOHCN))$_8$ is 709 nm. This compound has the highest absorption value near the IR range which confirms their excellent optoelectronic properties,
- This calculation procedure can be used as a model system for understanding the relationships between electronic properties and molecular structure and also can be employed to explore their suitability in electroluminescent devices and in related applications. Finally, the procedures of theoretical calculations can be employed to predict the electronic properties on the other compounds, and further to design novel materials for sensitizers for solar cells.

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