

Insight into incident photon to current conversion efficiency in chlorophylls

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Abstract

Photovoltaic properties of the natural dyes of chlorophylls consist of Chl a, Chl b, Chl c2, Chl d, Phe a, Phe y and Mg-Phe a, were studied in the gas phases and water. The extension of the π -conjugated system, the substitution of the central Mg²⁺ and proper functional groups in the chlorophyll structures can amplify the charge transfer and photovoltaic performance. Chl a shows more favorable dynamics of charge transfer than other studied chlorophylls. Chl d, Phe a, Phe y and Mg-Phe a, have a greater rate of the exciton dissociation in comparison with Chl a, Chl b, and Chl c2 originated from a lower electronic chemical hardness, a lower exciton binding energy, and a bigger electron-hole radius. As a result, better efficiencies of the light-harvesting and energy conversion of the chlorophylls mainly appear in the Soret band. The LHE values of the chlorophylls in water show that solvent favorably affects the ability of light-harvesting of the photosensitizers. Finally, based on the energy conversion efficiency, Chl a, Phe a, and Mg-Phe a, are proposed as the best candidates for using in the dye-sensitized solar cells.

1 INTRODUCTION

Energy demand is dramatically increasing with the development of human society and the use of fossil fuels leads to serious environmental problems. ^[1,2] Solar energy is the most fundamental renewable energy source accessible today having clean and safe characteristics. ^[3] The photovoltaic cell is an electrical device that converts the light energy directly into electricity. ^[4] The first dye-sensitized solar cell (DSSC) was fabricated by O'Regan and Grätzel in 1991. ^[5]

A DSSC consists of a photosensitizer, an electrolyte, a titanium dioxide layer coated photoanode electrode, a counter electrode used as a cathode. ^[6] After photon absorption by a photosensitizer, an electron is excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The excited electron enters the conduction band (CB) of TiO₂, which flows via the external load to the counter electrode to reduce the redox electrolyte (I/I_3^-), thereby regenerating the oxidized dye and completing the whole circuit. ^[7]

The molecular structure of the dye is one of the parameters that affect the photovoltaic performance of the DSSC, such as light-harvesting efficiency. ^[8] Natural dyes are abundant and safe material without environment threat ^[9] that cut down the high cost of the metal complex photosensitizers. ^[10] The ratio of the power conversion efficiency (PCE) to the cost of the dye in the natural-DSSCs (NDSSCs) is larger than that of ruthenium-based solar cells. ^[11] Natural dyes can be extracted from the flowers petals, leaves, roots and barks in the form of anthocyanin, flavonoid and chlorophyll pigments. ^[12-14]

Previous studies on the natural dyes of red-cabbage, curcumin and red perilla used in the solar cells showed that the energy conversion efficiency of the solar cell fabricated by using a mixture of red-cabbage and curcumin is higher than that of the solar cells using one kind of these dyes. ^[15] Also, the ratio of the PCE to the cost of the extracted cabbage is more than the synthetic ruthenium dye-based solar cell. ^[11] Moreover,

to improve the spectroscopic properties, the ratio of cabbage to curcumin was changed. The abstained results showed that the maximum absorption at 430 and 550 nm are related to curcumin and red cabbage, respectively. The greater efficiency of the solar cell was produced when the ratio of the extract of cabbage to the curcumin was 70:1.^[15]

In the case of betalain derivatives including betanin, betaxanthin, and betanidin extracted from the red beetroot, electron transfer affects the energy conversion efficiency.^[16] Among the betalain derivatives, betaxanthin represented a more efficient electron transfer, but due to the undesirable recombination of electron transfer to TiO₂ with the oxidized dye, light-harvesting efficiency (*LHE*) decreases.^[16]

Some efficient push-pull systems, such as azo-bridged coumarin-purpurin based systems (CM1-CM7) were studied.^[17] On the basis of the results, the substitution of the donor moiety (coumarin) and solvent affect the optoelectronic and photovoltaic properties of the D- π -D- π -A systems. Among these dyes, CM6 was preferred because of a proper band gap, polarizability, spectroscopic behavior and light-harvesting efficiency. Moreover, the interaction of the dyes with (TiO₂)₆ showed that these dyes are efficient photosensitizers for DSSCs.^[17]

The influences of the chemical structure of the sensitizers on the photovoltaic properties were investigated.^[17-20] For example, polypyridyl dyes based on Cr²⁺ and V³⁺ show better performance in comparison with ruthenium- and other scarce metal-based polypyridyl dyes due to the moderate *LHE*, high efficiencies of electron and hole injection, which make them promising alternatives to scarce Ru²⁺ metal ion.^[18]

Also, theoretical insights into the effect of polycyclic aromatic hydrocarbons (PAHs) on monascus pigments (MPs) and as a photosensitizer for solar cells showed that the presentence of the PAHs reduces the electronic band gap and the electron injection efficiency of MPS.^[19] Also, the absorption peaks of the MPs-fluorene, MPs-naphthalene, and MPs-anthracene appear in the visible region. The results confirm that these dyes can be used as a photosensitizer in the solar cells.

The flavylum compounds consist of anthocyanin pigments (callistephin, chrysanthemine, oenin, myrtilin) and anthocyanidin pigments (peonidin, petunidin) were investigated to identify their potential of application as the photosensitizer in the solar cell.^[20] According to the obtained results, the peonidin dye is the preferred photosensitizer for DSSC because of good short-circuit current density, more ability to harvest light, the lower energy barrier for the electron injection, and favorable optic characteristics.^[20]

Generally, natural dyes including chlorophyll, carotenoid, flavonoid, and anthocyanin are a relatively easy extract from the natural products in comparison with the synthetic dyes.^[21] Chlorophylls belong to the natural photosynthetic dye, which efficiently harvests the light and the photosynthesis.^[22,23] Chlorophyll derivatives are applied as the photosensitizers in the DSSCs because of their ability to absorb blue and red light.

Moreover, Chang et al. Compared the photovoltaic performance of anthocyanins, N719 dye, and chlorophyll extracted from pomegranate leaves and berries.^[24] The maximum adsorption of chlorophyll in the wavelengths of 412-665 nm and N719 in the wavelength range of 500-600 nm. Also, in this experimental study, the combination of chlorophyll and anthocyanin pigments was evaluated and the combination of these pigments changes the absorption spectrum to 540-665 nm, which improves the NDSSC efficiency.

In this work, some metal-free and metal-based chlorophyll derivatives, such as **chlorophyll a**, **b**, **c2** and **d** (**Chl a**, **Chl b**, **Chl c2**, and **Chl d**, respectively) and pyropheophorbide-based chlorophylls, such as **Phe a**, **Phe y** and **Mg-Phe a**, are investigated. Since the optoelectronic characteristics of the photosensitizers are dependent on their rational design, molecular engineering is of great importance through the computational modeling of the NDSSCs.

Here, natural bond orbital (NBO) analysis, density functional theory (DFT) and time-dependent DFT (TD-DFT) methods are the main techniques to access the molecular orbital information, excited state properties, and charge transfer (CT) processes. Moreover, the behaviors of the exciton, the rate of free charge production and correlations of the energy conversion efficiency of the chlorophylls and DFT reactivity indices were evaluated through the computational approaches.

2 COMPUTATIONAL DETAILS

All calculations were performed by the Gaussian 09 program.^[25] The ground and excited states of the chlorophyll-based dyes were investigated through DFT and TD-DFT methods at M062X/6-31G++(d) level of theory, respectively. This function has the least deviation in calculating the distance between the HOMO and LUMO that shows good accuracy in calculating the oxidation potential in comparison with the experimental data.^[26,27] The non-equilibrium version of the conductor-like polarizable continuum model (CPCM) was applied to evaluate the difference between the gas phase and water.^[28] Also, to obtain DFT reactivity indices, such as the electronic chemical hardness, η , the electronic chemical potential, μ , and the electrophilicity index, ω , Koopman's theorem, and NBO analysis were used. The charge transfer distance, D_{CT} , and the overlap of e-h distribution, S , were obtained from the Multiwfn program.^[29]

The performance of the NDSSCs was determined by the incident photon conversion to the current efficiency ($IPCE$) affected by the possibility of electron transfer between the frontier energy levels of the sensitizers and TiO_2 /photosensitizer interface, which is theoretically obtained by Equation (1)^[30]:

$$IPCE = LHE(\lambda) \cdot \Phi_{\nu\theta} \cdot \eta_{\text{coll}} \quad (1)$$

where LHE is the light-harvesting efficiency, η_{coll} is the electron collection efficiency, and $\Phi_{\nu\theta}$ is the net electron injection efficiency, which is related to Gibbs energy of electron injection, $\Delta G_{\nu\theta}$. The LHE of the sensitizer can be expressed by Equation (2)^[31]:

$$LHE = 1 - 10^{-f} \quad (2)$$

where f is the oscillator strength of the dye molecule at the maximum absorption.

Electron injection from the excited states of the dye to the TiO_2 surface, $\Delta G_{\nu\theta}$, is given by Equation (3)^[32]:

$$\Delta G_{\nu\theta} = E_{O\Xi, \delta\psi\epsilon^*} - E_{CB(TiO_2)} \quad (3)$$

where $E_{CB(TiO_2)}$ is the conduction band energy of TiO_2 , and E_{OX, dye^*} is the excited state oxidation potential of the photosensitizer. The driving force of the electron transfer from the photosensitizer toward semiconductor, eV_{OC} , is derived from Equation (4)^[33]:

$$eV_{OC} = E_{LUMO(dye)} - E_{CB(TiO_2)} \quad (4)$$

Exposed to radiation, an exciton as the Frenkel type is generated by a Coulomb energy between the electron and hole. The material-dependent constant, a , which shows the ratio of the Coulomb and exchange interactions between the excited electron and hole is evaluated through Equation (5)^[34]:

$$E_B = \frac{(\alpha-1)^2 \mu_x e^4 k^2}{2\alpha^2 tsh^2 \epsilon^2} \quad (5)$$

where E_B (EBE) is the electron-hole binding energy, ϵ is the dielectric constant of the donor component, \hbar is the reduced Planck's constant, $k = (4\pi\epsilon_0)^{-1} = 9 \times 10^9 \text{ Nm}^2\text{C}^{-2}$, ϵ_0 is the vacuum permittivity, e is the electronic charge, and μ_x is the reduced mass of the exciton.

The rate of the photon absorption for a singlet excitation, R_a^S , is given by the transition matrix element and Fermi's golden rule, according to Equation (6)^[35]:

$$R_a^S = \frac{4ke^2(E_{LUMO} - E_{HOMO})^3 a_x^2}{3c^3 \epsilon^{1.5} tsh^4} \quad (6)$$

where c is the light speed and a_x is the exciton radius. For the singlet excitons, a_x is given by Equation (7)^[36]:

$$a_x = \frac{\alpha^2 \mu}{(\alpha-1)^2 \mu_x} a_0 \quad (7)$$

where μ is the reduced mass of the electron in the hydrogen atom and a_0 is the Bohr radius. The exciton dissociation rate, R_d , is obtained from Equation (8)^[37]:

$$R_d = \frac{8\pi^2}{3tsh^3 \epsilon^2 E_B} [E_{LUMO}^D - E_{CB}^A - E_B]^2 (tsh\omega_\theta) \mu_x a_x^2 \quad (8)$$

where ω_v is the frequency of the incident phonon to the photosensitizer.

CT indices contain the corresponding effective CT distance, D_{CT} , and S as another quantity shows the overlap extent of electron-hole distribution. According to Equation (9), D_{CT} is defined as the distance between two barycenters (r_+ and r_-), which is an important factor to estimate the CT length^[38]:

$$D_{CT} = |r_+ - r_-| \quad (9)$$

Another quantity, which evaluates the overlap extent between the electron-hole,

is S_{\pm} that is estimated according to Equation (10)^[39]:

$$S_{\pm} = \int \sqrt{\frac{C_+(r)}{A_+}} \sqrt{\frac{C_-(r)}{A_-}} dr \quad (10)$$

where the normalization factor, A , is introduced so that the integrals of $C_+(\mathbf{r})$ and $C_-(\mathbf{r})$ are equal to the integrals of $\rho_+(\rho)$ and $\rho_-(\rho)$, based on total densities of the ground and excited states.

Polarizability character is the response of the dye to an applied electric field of the incident light. The polarizability tensors ($a_{\xi\xi}$, $a_{\xi\psi}$, $a_{\psi\psi}$, $a_{\xi\zeta}$, $a_{\psi\zeta}$, $a_{\zeta\zeta}$) are applied to evaluate the isotropic polarizability (Equation (11))^[40]:

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (11)$$

The excited-state lifetime, τ , is also evaluated as^[41]:

$$\tau = \frac{1}{2\pi\nu_{\max.}} \quad (12)$$

where τ is the excited-state lifetime and $\nu_{\mu\alpha\xi}$ is the maximum frequency of the absorbed photon and $\nu_{\mu\alpha\xi}$ is the maximum frequency of the absorbed photon.

3 RESULTS AND DISCUSSION

3.1 Structural properties and charge transfer processes

The structures of the natural dyes based on chlorophyll consist of set **a** : **Chl a**, **Chl b**, **Chl c2**, and set **b** : **Chl d**, **Phe a**, **Phe y**, and **Mg-Phe a**, were optimized at M06-2X/6-31++G(d) level of theory. The optimized structures within natural sources and frontier energy levels are shown in Figure 1.

The frontier energy levels calculated by NBO analysis provides knowledge of the electronic transitions, which is important to evaluate the performance of the applied photosensitizers in the NDSSCs. According to Figure 1, the presence of the central Mg^{2+} and various functional groups on the chlorophyll structure affects the energy of the frontier molecular orbitals. Considering Figure 1, the energy gaps between the lowest unoccupied molecular orbital of the photosensitizer and the CB of the semiconductor are more than 0.2 eV, which sufficient enough to transfer the electron. Also, the highest occupied molecular orbital levels of the chlorophylls are lower than the reduction potential of F/I_3^- electrolyte (-4.8 eV), which leads to an acceptable dye regeneration and suppress their electron recombination.

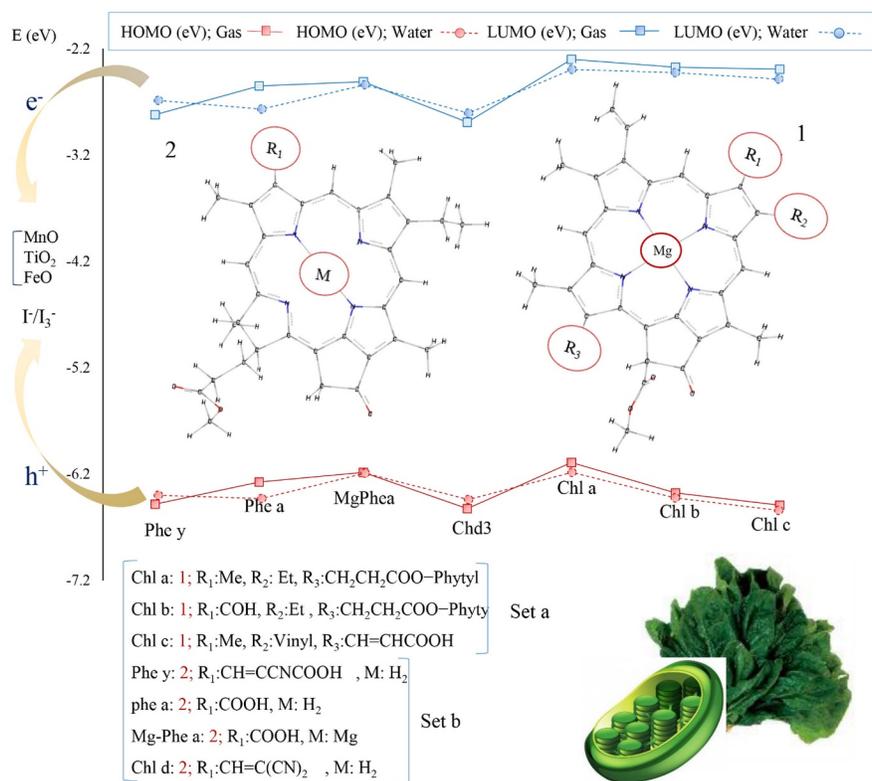


FIGURE 1 The energy diagram of the studied chlorophylls and the optimized structures within natural sources

To investigate the photovoltaic processes in the NDSSCs, DFT reactivity indices, electron driving force, eV_{OC} , the oxidation potential of the excited dyes, E_{OX,dye^*} , the coupling constant of chlorophylls and TiO₂, V_{RP} , a change in the Gibbs energy of electron injection, $\Delta\Gamma_{\nu\theta}$ and the exciton binding energy, EBE, were calculated and represented in Table 1. Moreover, the exciton radius, a_x , the rate of photon absorption for a singlet excitation, R_a , the rate of the exciton dissociation, R_d , light-harvesting efficiency, LHE , and the energy conversion efficiency, $IPCE$, the polarizability of the chlorophylls, a , the excited state lifetime, τ , and the charge transfer indices are reported in Table 2.

TABLE 1 The electronic chemical hardness, η , electronic chemical potential, μ , electrophilicity index, ω , electron driving fo

Dye in the gas phase

Phe a

Phe y

Mg-Phe a

Chl d

Chl a

Chl b

Chl c2

According to Table 1, the Gibbs energy of electron injection at the chlorophyll/TiO₂ interface has a negative character. Also, the electron driving force predominates to the exciton binding energy, EBE and the rate of the exciton dissociation, R_d , is faster than the exciton formation rate, R_a . These results show that the

primitive photovoltaic processes are efficiently occurring in the studied chlorophyll-based solar cells.

TABLE 2 Exciton radius (a_x ; Å), the rate of a photon absorption (R_a ; s⁻¹), rate of the exciton dissociation (R_d ; s⁻¹), light

Dye in the gas phase

Phe a

Phe y

Mg-Phe a

Chl d

Chl a

Chl b

Chl c2

Figure 2 shows the correlation of the reactivity indices and photovoltaics parameters. **Chl a**, **Chl b**, and **Chl c2** have a lower electrophilicity, which leads to a decrease in their tendency of electron reception and enhancement of the electron migration toward TiO₂. Set **a** of the chlorophylls also has greater polarizability in the case of the applied electric field of the incident radiation. Moreover, a decrease in the electronic chemical potential increases the ability of the chlorophylls to drive the electronic charges.

A decrease in the electronic chemical potential develops the light-harvesting efficiency and the ability of the electricity production in the natural dyes (Figure 2C). **Chl a**, **Chl b**, and **Chl c2** having a central Mg²⁺ show better intermolecular charge transfer (ICT). On the other hands, the existence of a longer π -conjugated system and resonance amplification in the chlorophyll structures improve their photovoltaic performance. In addition, Table 2 shows that softer chlorophyll derivatives, such as **Chl d** and **Phe y** are better candidates for coupling with TiO₂. The greater excited-state lifetime of the Chl d and Phe y within a bigger coupling constant with TiO₂ reduce the charge recombination.

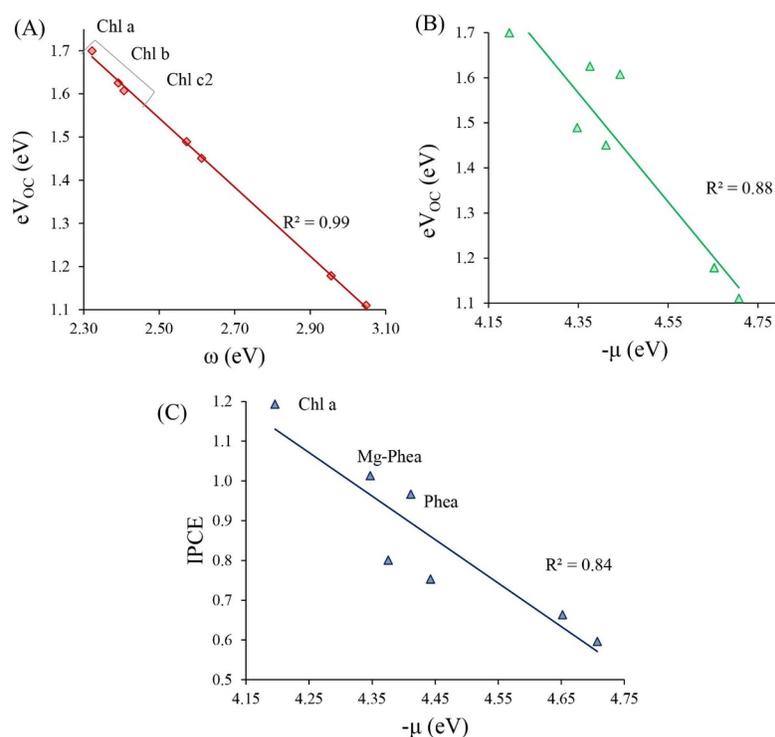


FIGURE 2 Linear correlations of the electron driving force vs. the electrophilicity (A) and electronic chemical potential of the chlorophylls (B). The correlation of energy conversion efficiency and μ (C)

In Figure 3, the changes of the energy barrier of the electron transfer at the chlorophyll/ TiO_2 interfaces and energy conversion efficiency of the NDSS show a harmony. According to these trends, $IPCE$ is dependent on the $[?]G_{inj}$ greater than LHE . Moreover, **Chl a**, **Mg-Phe** and **Phe a** chlorophylls have a lower excited state oxidation potential, $E_{OX(dye^*)}$, and greater negative character of the Gibbs energy of electron injection, which increases the final efficiency of the NDSSCs ($IPCE$). According to the experimental data, phe a-like structure (the phe a structure having vinyl group ($R_1 = CH=CH-COOH$)) shows the highest efficiency in comparison with other pigments that demonstrates a more favorable electron transfer, especially in 400nm and 690 nm.^[42]

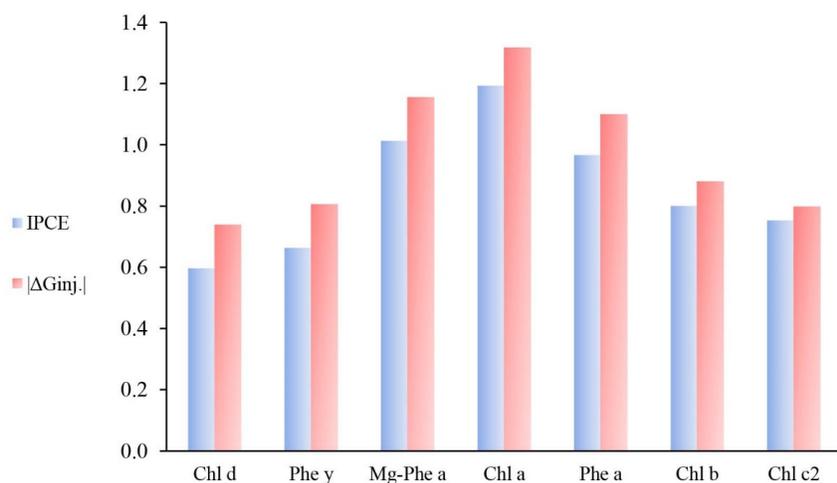


FIGURE 3 Theoretical changes of the Gibbs energy of the electron injection and the energy conversion efficiency

The rate of the exciton dissociation in the studied chlorophylls, R_d , are affected by the band gap (Figure 4A) and the exciton binding energy (Figure 4B). Also, the exciton binding energy and R_d are related to the exciton radius, and the electronic chemical hardness of the chlorophylls, respectively (Figure 4C and 4D).

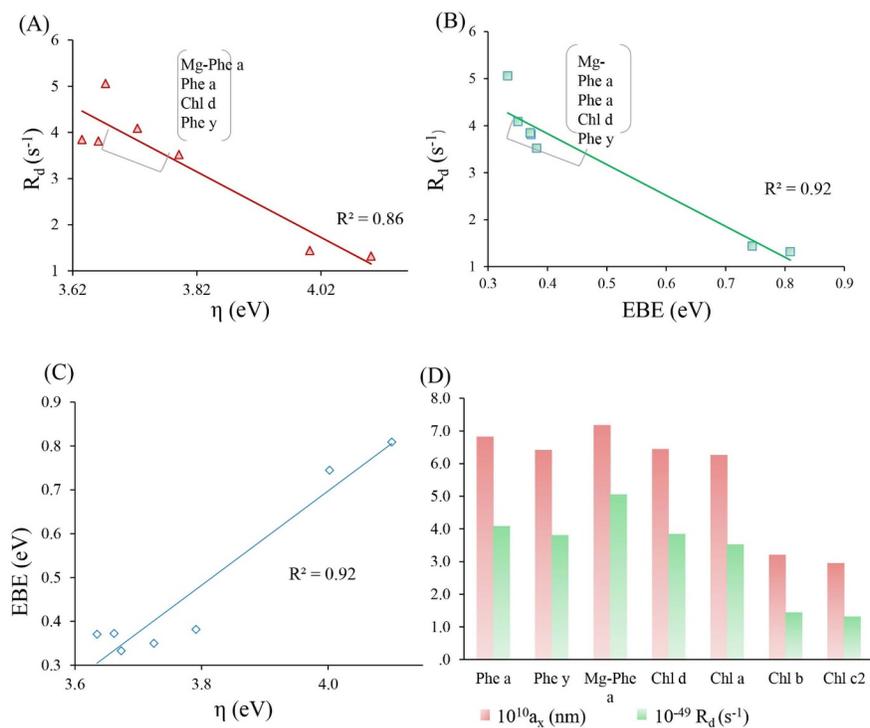


FIGURE 4 The rate of the exciton dissociation as a function of the band gap (A) and the exciton binding energy (B). EBE and R_d change vs the electronic chemical hardness of the chlorophylls (C) and exciton radius (D)

According to Figure 4, free charges are produced faster in set **b** (**Chl d** , **Phe a** , **Phe y** , and **Mg-Phe a**) in comparison with set **a** (**Chl a** , **Chl b** , and **Chl c2**) originated from a greater softness of the materials and an easier separation of the electron-hole in set **b** . Such an easier separation of the exciton is due to a bigger radius and lower binding energy of the electron-hole.

3.2. UV-Visible spectroscopy of the studied chlorophylls

The TD-DFT calculations based on the M06-2X functional and 6-31++G(d) basis set were used for simulating the UV-Vis absorption spectra of the chlorophyll derivatives. The UV-Vis absorption spectra, which are extracted directly from the output of the TD using the frontier molecular orbital transition configuration contributed to the maximum absorption peaks, are displayed in Figure 5 and the corresponding data are represented in Table 3.

The studied chlorophylls show two main absorption peaks consist of the Soret band in 300-450 nm and Q band with a wavelength >450 nm. In the Soret band, chlorophyll **c2** in the gas phase and water has the most intense absorption peak and the highest red shift in the absorption wavelength. In the Q-band, **Chl d** and **Phe y** in the gas phase show more proper spectroscopic properties originated from a higher probability of the electron transfer between their frontier molecular, tighter band gap (Figure 5A and Table 3), lower overlap of the electron-hole distribution, S , and a longer charge transfer distance, D_{CT} .

According to Figure 5B, the absorption peaks in the water represent the red shift with a greater intensity relative to the gas phase. Also, comparing the LHE values of the chlorophylls in the gas phase and water shows that solvent favorably affects the ability of the light-harvesting of the photosensitizers.

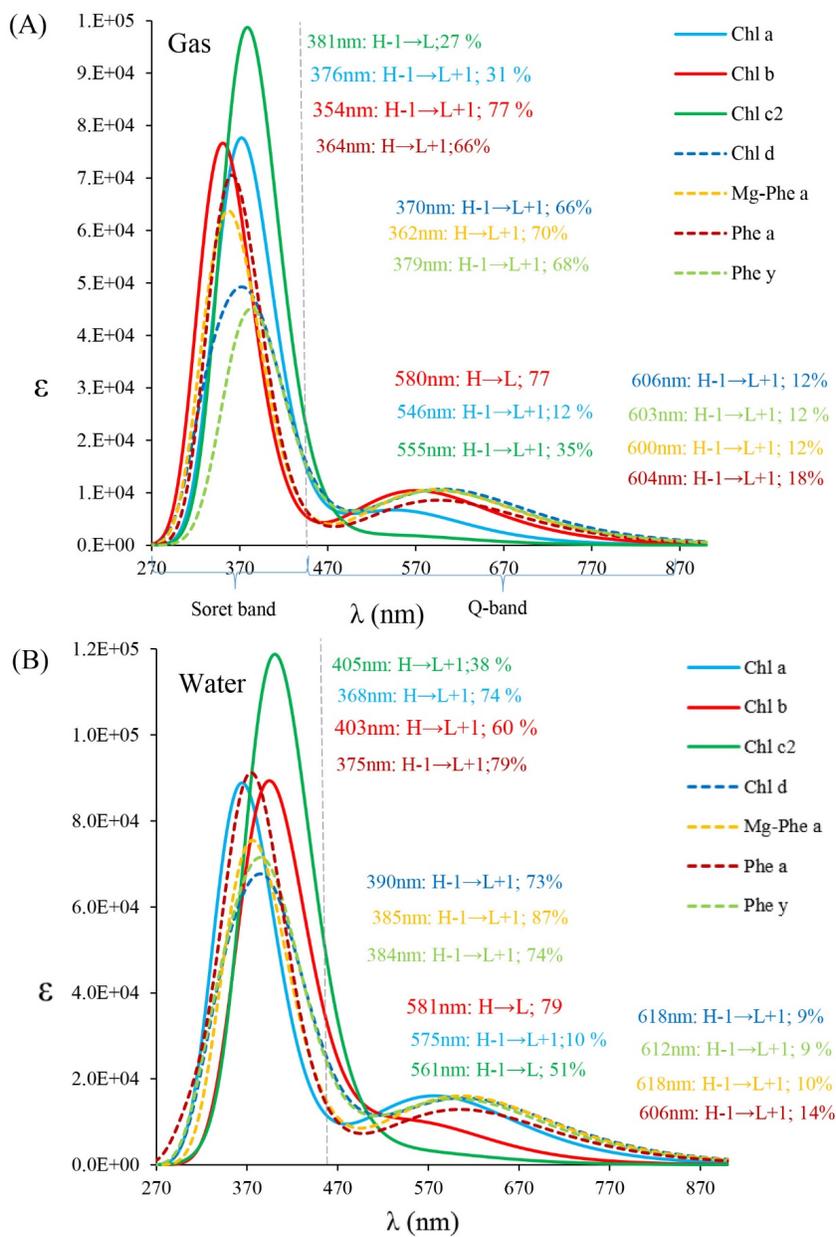


FIGURE 5 The simulated absorption spectra of the studied chlorophylls within the frontier molecular orbital transition configuration contributed to the maximum absorption peaks calculated at the TD-DFT/M062X/6-31++G(d) level of theory

TABLE 3 Theoretical vertical excited energies, E_{0-0} , the maximum absorption wavelength (nm), light-harvesting efficiency,

Dye in Gas
Phe y

Phe a

TABLE 3 Theoretical vertical excited energies, E_{0-0} , the maximum absorption wavelength (nm), light-harvesting efficiency,

Mg Phe

Chl d

Chl a

Chl b

Chl c2

Dye in water

Phe y

Phe a

Mg Phe a

Chl d

Chl a

Chl b

Chl c2

According to Figure 5A and Table 3, the maximum absorption wavelength in the studied pigments in the gas phase is related to the H-1 - L + 1 transition. Chl a also shows the highest percentage of transfer and IPCE for H-1 - L + 1 compared to other pigments at 338 nm.

LHE changes as a function of the electric transition dipole moment, $r_{k,k'}$, are shown in Figure 6A. This Figure shows that the chlorophylls in set **a**, having a higher electric dipole moment, show a more probable charge transfer between the molecular orbitals. According to quantum mechanics, a higher $r_{k,k'}$ means greater oscillating strength and intrinsic transition probability, which can increase the ability of the chlorophylls to harvest the light.

To evaluate the NDSSCs efficiencies, light-harvesting and energy conversion efficiency of the chlorophylls efficiency were illustrated as the function of the maximum absorption wavelength (Figures 6B and 7, respectively). **Chl a**, **Chl b**, and **Chl c2** have a greater ability of the light-harvesting and electron transfer

between the molecular orbitals (Figure 6B).

According to the results, a higher energy conversion efficiency is mainly appeared in the Soret band, which is according to the maximum oscillating strength. Finally, the dyes based on **Chl a**, **Phe a** and **Mg-Phe a** are the preferred dyes because of the lower energy barrier of the charge transfer and higher *IPCE*(Figure 7).

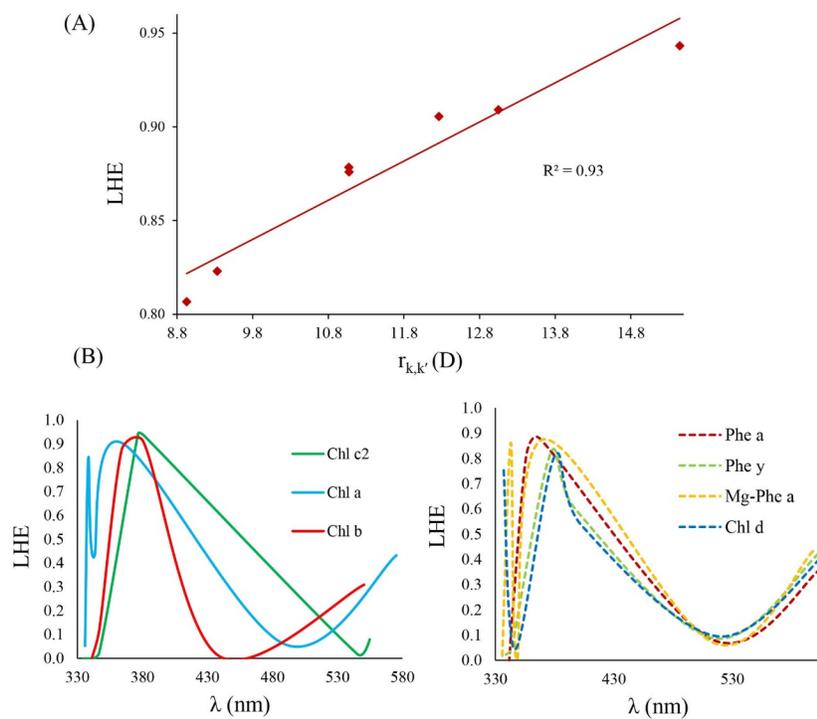


FIGURE 6 The correlation of *LHE* as a function of $r_{k,k'}$ (A). *LHE* values of the chlorophylls according to the maximum absorption wavelength (B)

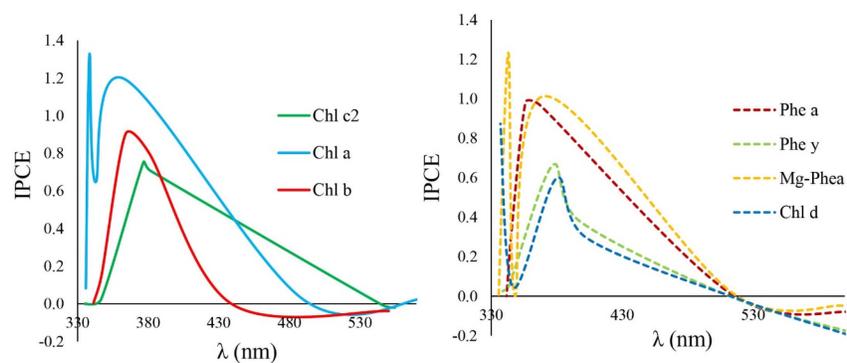


FIGURE 7 Theoretical behavior the *IPCE* values of the chlorophylls against to maximum absorption wavelength

According to the electronic density distribution of the frontier molecular orbitals (Figure 8), structural modification of the chlorophylls does not affect the HOMO-LUMO distribution property. Because they are mainly distributed in the central ring of the chlorophylls. The energy conversion efficiency is mainly affected by the dynamics of the charge transfer, such as the Gibbs energy of the electron injection from the chlorophylls to TiO_2 .

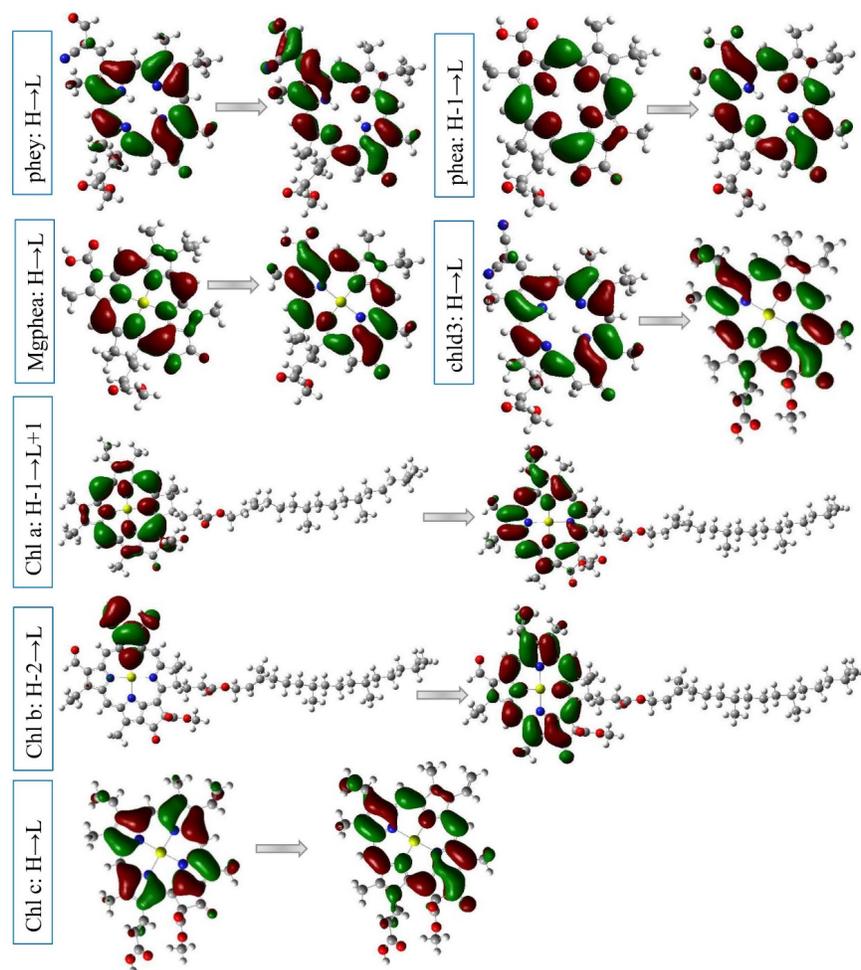


FIGURE 8 Electron density distribution of the frontier MOs in the studied chlorophylls

4 CONCLUSION

In this research, the feasibility of using of chlorophylls **a** ,**b** , **c2** , **d** , and the pyropheophorbide-based chlorophylls (**Phe a** , **Phe y** , and **Mg-Phe a**) in the NDSSCs was performed, dynamically and kinetically. The insertion of Mg^{2+} and various functional groups in the chlorophyll structure affect the energy levels of the corresponding molecular orbitals, DFT reactivity indices, and the photovoltaic processes. The studied chlorophylls can be considered as the efficient photosensitizers in the NDSSCs due to negative value of the Gibbs energy of the electron injection, the predominance of the electron driving force, eV_{OC} , to the exciton binding energy, EBE, and their ability in the generation of free charges. Based on the results, a decrease in the electrophilicity index and the electronic chemical potential of the chlorophylls increases the electron driving force and the energy conversion efficiency. Also, **Chl a** has the lowest energy barrier of the charge transfer at the dye/ TiO_2 interface and the highest *IPCE* . Meanwhile, **Chl d** ,**Phe a** , **Phe y** , and **Mg-Phe a** represent more favorable kinetic behavior in the charge transfer process because of a tighter band gap and a lower exciton binding energy. In the Soret and Q bands, chlorophyll **c2** , **Chl d** (and **Phe y**) derivatives have preferred spectroscopic properties, respectively. Comparing the LHE values of the chlorophylls in the gas phase and water shows that solvent favorably affects the ability of the light-harvesting of the photosensitizers. On the basis of the obtained results, **Chl a** , **Phe a** , and **Mg-Phe a** have a higher capacity to produce the electricity, which makes them the best candidate for the NDSSCs.

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