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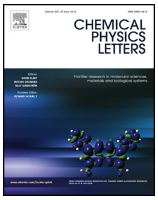

Substituents role in zinc phthalocyanine derivatives used as dye-sensitized solar cells. A theoretical study using Density Functional Theory

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ABSTRACT

A series of zinc phthalocyanine dyes with different electron-donating and electron-withdrawing substituents and using the COOH as the anchor group that interacts with the semiconductor (TiO_2) surface, were studied employing DFT and TDDFT methodologies. Their HOMO and LUMO orbital energies and, the redox mediator position would facilitate the injection process toward the conduction band of TiO_2. We tested the effect of some electron-donating or electron-withdrawing substituents over zinc phthalocyanine dyes in terms of the Hammett parameters ($\Sigma\sigma$). We obtained a linear correlation between the substituents properties versus the free energy change of the electron-injection (ΔG^{inject}) process.

1. Introduction

Grätzel [1,2] proposed Dye Sensitized Solar Cells (DSSC) in 1991. These DSSC involves adsorbing a dye on the semiconductor surface (ZnO_2 and/or TiO_2) which acts as a collector of solar energy [3,4]. In these DSSC the photon-induced excitation leads to one electron transfer from dyes to the semiconductor. The semiconductor titanium dioxide has a large band gap which can be excited by ultraviolet radiation. The dye extends the absorption to longer wavelengths, to the visible region. In the DSSC the absorption and transport functions necessary to load the operation of a solar cell are separated and can be constructed portable, multiform, semitransparent, colored and with decorative panels. So far, they have achieved efficiencies of up to 11.2% on a laboratory scale, while for industrially larger modules efficiency performed only up to 7%. Nowadays, there are numerous research groups involved in improving the efficiency and effectiveness and stability of these devices to maintain a reasonable photo conversion [5–7]. The efficiency of the cell depends on the photophysical properties of the semiconductor, the dye and the electrolyte regenerator. In this letter, we studied dye properties with the aim to proposing it as novel sensitizers in designing new solar cells [8–11].

The highest efficiencies have been obtained so far in cells with ruthenium complexes absorbing the light [12–14]. However, more recently the trend is that pure organic dyes are invoked as sensitizers in DSSCs. Organic dyes have significant advantages as compared to ruthenium complexes, because they can be easily modified and with a much lower cost [15,16]. It is possible to introduce functional group with different inductive characteristic

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in the skeleton of the chromophores by modifying their photochemical and photophysical properties and adjusted to optimize the efficiency of DSSCs. These modified dyes will have higher molar extinction coefficients, thus facilitating the process of capturing sunlight.

In recent years, research on DSSCs has been achieved in order to synthesize new structures that might show improved molecular properties. The use of organic dyes as sensitizers for solar cell design generated research focused on various organic substances containing appropriate structural characteristics [17,18]. In this work, we propose inorganic sensitizers to be adsorbed over the surface of the semiconductor TiO_2 through the carboxylic group (COOH) [18]. The characteristics to consider good sensitizers, are that the electronic injection that should be as efficient as possible, the energy of the LUMO (Lowest Unoccupied Molecular Orbital) orbital of the dye should be above the lower limit of the TiO_2 conduction band, and the energy of the HOMO (Highest Occupied Molecular Orbital) orbital of the dye must be below the potential of the redox mediator to generate efficient regeneration of the oxidized dye.

Metal Phthalocyanines (MPcs) and other macrocyclic transition metal complexes of similar structure represent a class of inorganic materials that attracts great attention in several diverse fields of science and industry. Phthalocyanines possess an intense absorption in the Q-band (around 700 nm), as well as promising electrochemical, photochemical, and thermal properties, and are thus of interest to utilize it as photosensitizers for DSSC [17]. The MPcs generally have a large variety of features that offers extraordinary versatility. These features include, intense colors (exhibit efficient energy absorption), redox activity, high thermal and chemical stability, and are not toxic. All these properties make the MPcs excellent mediators in charge transfer processes [19]. Thus, MPcs are used as pigments [20,21], in photoconductive surface, in electrochemical devices, in industrial sensors, in batteries, and in electrocatalytic processes [22–25]. The MPcs are also used, as reagents for peptide synthesis, as supports for gas chromatography, photocopying techniques and as precursors of new mixed valence compounds [19,26,27].

The molecular orbital energy levels and spectral properties of MPcs compounds can be tuned by varying the size of their π-conjugated system or by introducing different types of substituents on their peripheral positions, as proposed here [7,28,29]. Modifications of the macrocycle periphery, such as, the introduction of donor or acceptor moieties are the most common way of producing a red-shift of the Q-band absorption.

The effect of the substituent was quantified according to the sum of the Hammett parameters ($\Sigma\sigma$). These parameters were defined by Hammett and analyzed by Hansch and co-workers [30] from benzoic acids ionization constant, as follows:

$$\sigma_X = \log(K_X) - \log(K_H)$$

where K_H is the benzoic acid ionization constant in water at 25 °C and K_X is the corresponding constant for a *meta* or *para* substituted benzoic acid. Therefore, in our work we used $\Sigma\sigma$ which represent the sum of the contributions of the ionization constant of the substituent in *para* position relative to the central metal [30].

The substituents (R) used in this work for a family of zinc-phthalocyanine carboxyl complexes ($ZnPcR_3COOH$), comprise the electron-donating substituents $N(C_3H_7)_2$, $N(CH_3)_2$, $NH(CH_3)_2$, NH_2, OCH_3, OCH_2CH_3, $C(CH_3)_3$, CH_3, $CH{=}CH_2$ ($-C_2H_3$), C_6H_5, and the H is used as reference, and the electron-withdrawing substituents $CH{=}CH{-}CH{=}CH_2$ (C_4H_5), F, Cl. The function of the carboxylic acid group ($-COOH$) in the structure is to adsorb the sensitizer into the semiconductor surface (TiO_2) and to provide intimate electronic coupling between its excited state and the conduction band of the semiconductor.

2. Models and computational details

DFT (Density Functional Theory) and TD-DFT (Time-Dependent Density Functional Theory) methods have been proven suitable for calculating the energy minimized structure, electronic distribution, molecular orbitals and electronic absorption spectra of a series of phthalocyanines derivates. All the calculations were carried out with the TURBOMOLE v6.5 program [31]. The molecular structure optimizations and frequency calculations of the unsymmetrical $ZnPcR_3COOH$ sensitizers were calculated with the B3LYP functional. The vibrational frequency calculations were performed for each dye finding positive frequencies which indicate their local minima. The B3LYP functional is adopted in this work because the data calculated deliver values closer to the experimental values. This functional have been extensively used in analogous work [32]. The augmented correlation-consistent valance-triple-zeta (aug-cc-pVTZ) basis sets were employed for C, N, O and H, and def2-SV(P) as basis set for zinc atom. The excitation energies were obtained by means of the TD-DFT formalism [33,34], which is based on the Random-Phase Approximation (RPA) method [35]. For consistency, we used here the same B3LYP functional obtaining reasonable results. The excitation spectra have been simulated from the optimized geometry of the theoretical model, using a broadening factor σ (FWHM) of 0.5 eV.

3. Results and discussion

3.1. Molecular structure

The molecular structures of zinc-phthalocyanine carboxyl complexes ($ZnPcR_3COOH$) family with peripheral substituent R were all optimized. Here we used the sum of the Hammett parameters ($\Sigma\sigma$) [30] for classifying the substituent as electron-donating groups (negative values) or electron-withdrawing groups (positive values), and using the $-H$ (value zero) as reference, as has been

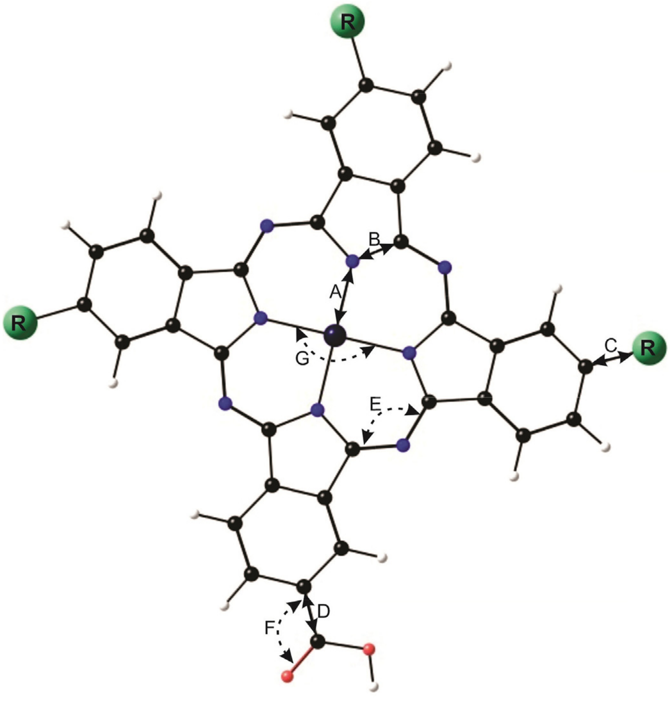

Figure 1. General molecular structure of the zinc-phthalocyanine carboxyl complexes ($ZnPcR_3COOH$). R = substituent. A–D classified as bond distances. E–G classified as bond angles.

explained in previous works [36–38]. We analyzed the bond distances A–D (see Figure 1). The results for the A–C distances obtained in our calculations are quite close with those found in literature for the Zinc-phthalocyanine (ZnPc) which show for A bond distance 2.024–2.028 Å, and for the B distance 1.366–1.399 Å [39,40], confirming the validity of the method used in this research. In general, the results show that the nature of the substituents does not cause any significant changes in bond distances classified as A and B. The carbon-substituent distance (distance C in Figure 1) and carbon-COOH of all the molecules used, shows differences that can be attributed to inductive factors and or steric effect due to the size of the substituent, compared against the hydrogen substituent which is used as reference. The analysis of bond angles, classified as E–G does not show any significant changes, indicating that the structure of $ZnPcR_3COOH$ is almost rigid.

3.2. *Molecular orbital energy levels of the $ZnPcX_3COOH$ series*

Studies by Mizuseki et al. [41] suggest that charge transport can be associated with the spatial distribution and composition of the frontier orbitals. The isosurface plots of the frontier molecular orbitals (MOs), HOMO and LUMO are shown in Figure 2. In general, the frontier MOs shows no significant contribution from the R substituent. The HOMOs are centered on the pyrrolinic rings of the phthalocyanines, and the LUMOs are located in the central ring of the phthalocyanines. The absorption band positions of the TiO_2 sensitizers are intimately related with dye energy gaps (HOMOs and LUMOs). For this reason, to explore electron-injection efficiency, it is necessary to search for dyes with smaller energy gaps to facilitate electronic excitation, thus contributing to obtain a higher short-circuit current density J_{sc} at higher overall power conversion efficiency [29]. We propose that to obtain an efficient electronic injection, the energy of the LUMO of the dye should be above the lower limit of the TiO_2 conduction band. Furthermore, for the oxidized dye regeneration to be efficient, the HOMO energy of the dye should be below the redox potential of the redox mediator. The typical electrolytes used are I_3^-/I^- or Co^{2+}/Co^{3+} in an organic solvent, which is regenerated by catalyst (usually metallic Pt) at the counter-electrode, closing the circuit. [17,42,43]. In Table 1, we provide the molecular orbital energy of all the dyes respect to $ZnPcH_3COOH$ (our reference) and the Hammett parameters. As can be seen, all the Zinc substituted phthalocyanines present the LUMO

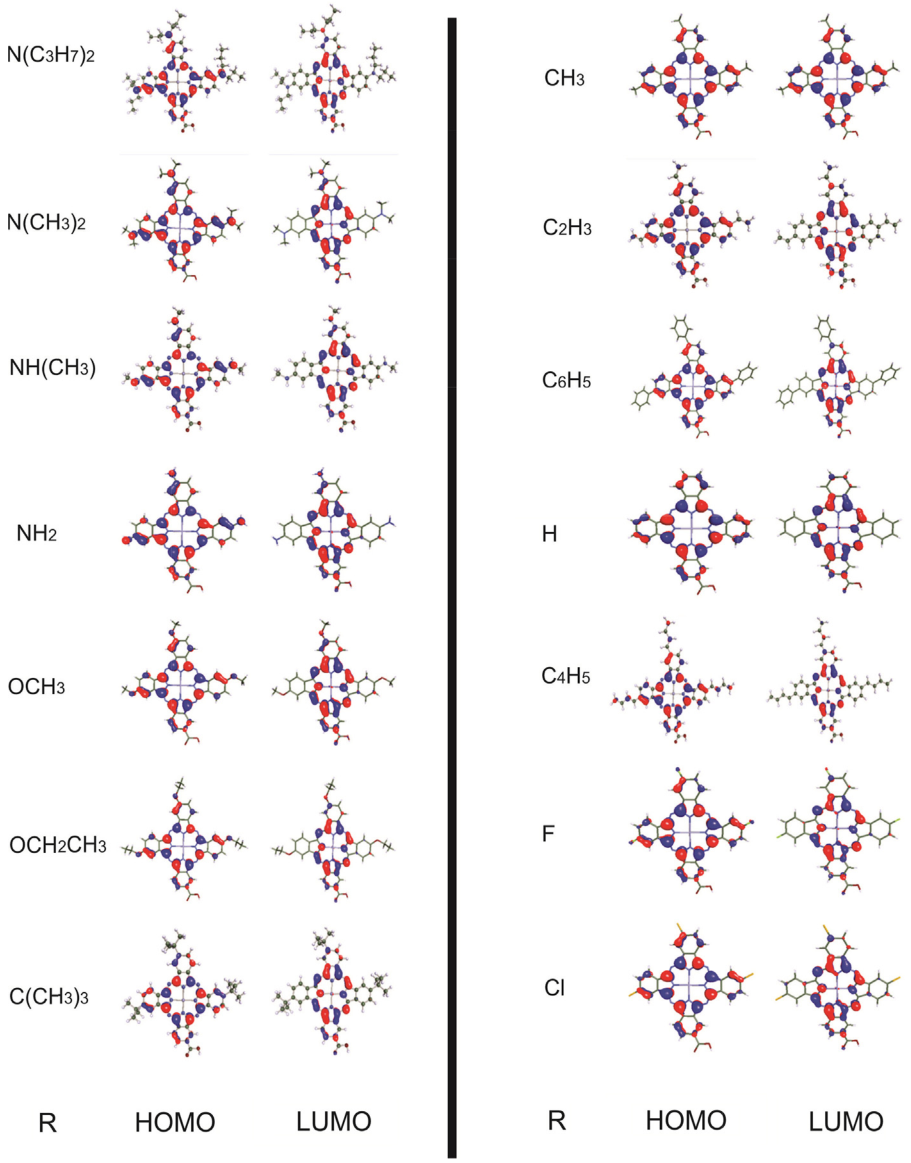

Figure 2. Caculated frontier MO isosurfaces of $ZnPcR_3COOH$ (R = substituent in figure).

Table 1

The LUMO and HOMO energy levels as the sum of the Hammett parameters, Q Band, excited state oxidation potential (E^{dye^*}) of the dye and free energy change for electron injection (ΔG^{inject}) of $ZnPcR_3COOH$.

	$\Sigma\sigma$	LUMO energy (eV)	HOMO energy (eV)	Q band (eV)	f[a]	Assignment[b,c]	E^{dye^*} (eV)	ΔG^{inject} (eV)
$N(C_3H_7)_2$	−2.790	−2.5305	−4.5087	1.9163	0.71	242a → 243a (93.3%)	2.5924	−1.41
$N(CH_3)_2$	−2.490	−2.5414	−4.5230	1.9373	0.33	194a → 195a (93.3%)	2.5857	−1.41
$NH(CH_3)$	−2.100	−2.5382	−4.5111	1.9649	0.60	182a → 183a (93.7%)	2.5462	−1.45
NH_2	−1.980	−2.6266	−4.6570	1.9806	0.27	170a → 171a (93.3%)	2.6764	−1.32
OCH_3	−0.810	−2.8269	−4.9028	2.0292	0.45	182a → 183a (93.9%)	2.8736	−1.13
OCH_2CH_3	−0.720	−2.7965	−4.8686	2.0160	0.45	194a → 195a (93.9%)	2.8526	−1.15
$C(CH_3)_3$	−0.600	−2.9361	−5.0644	2.0630	0.65	206a → 207a (93.7%)	3.0014	−1.00
CH_3	−0.510	−2.9555	−5.1078	2.0733	0.65	170a → 171a (93.2%)	3.0345	−0.97
C_2H_3	−0.120	−3.0928	−5.2143	2.0226	0.70	179a → 180a (91.3%)	3.1917	−0.81
C_6H_5	−0.03	−3.0490	−5.1727	2.0292	0.81	218a → 219a (93.3%)	3.1435	−0.86
H	0.000	−3.1896	−5.3211	2.0664	0.60	158a → 159a (93.8%)	3.2547	−0.75
C_4H_5	0.120	−3.0901	−5.1575	1.9556	1.4	200a → 201a (77.8%) 200a → 202a (16.0%)	3.2019	−0.80
F	0.180	−3.2465	−5.4115	2.1194	0.61	170a → 171a (93.2%)	3.2921	−0.71
Cl	0.690	−3.2986	−5.4584	2.0908	0.63	182a → 183a (93.0%)	3.3676	−0.63

[a] Oscillator strength.

[b] Values are $|coeff|^2 \times 100$.

[c] Transition type $\pi \rightarrow \pi^*$.

energy above the TiO_2 conduction band allowing efficient charge injection, and the HOMO of the some dyes present lower energy than the potential redox of the electrolyte, allowing efficient regeneration of the oxidized dye by the electrolyte. These results allow us to quantify only the efficiency of the first stage and not the complete cycle of the solar cell.

The molecular orbital energy levels of these $ZnPcR_3COOH$ are illustrated in Figure 3, which are sorted by the Hammett Parameters. The Hammett and the frontier orbital energies are shown in Table 1. The data for the energy gaps are marked at the appropriate orbital energy levels, and also the relative positions of the conduction band of TiO_2 and the redox potential of the mediator redox are shown. The values of the HOMO and LUMO energies are given in Table 1 according to the $\Sigma\sigma$. It is noted from this table the variation of the energy gaps of these macrocyclic when the carbon, oxygen, nitrogen or halogen served as the bridging atom that directly connects to the Pc rings with the respective substituent. The substituents with nitrogen atoms linked directly to the phthalocyanine rings possess the LUMO energy above the TiO_2 conduction band at an adequate distance for electron injection. This is contrary to the situation when halide substituents linked to the phthalocyanine rings which show the LUMO energy too close to the TiO_2 conduction band. The same effect was observed in other theoretical studies [29,40].

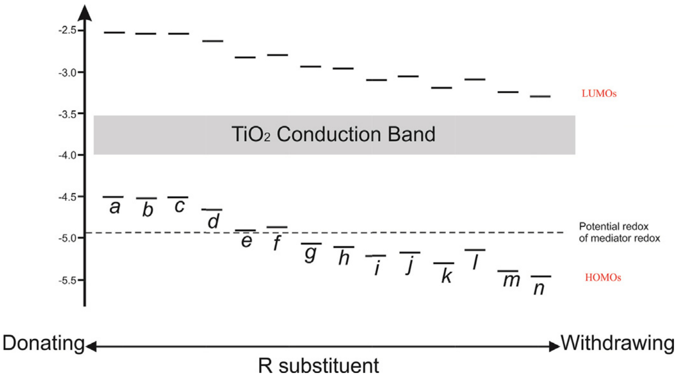

Figure 3. Molecular orbital energy level of complex. (The mediator redox used as reference is I_3^-/I^-. (Redox potential −4.90 vs vacuum [42]). The substituent R are $a = N(C_3H_7)_2$, $b = N(CH_3)_2$, $c = NH(CH_3)_2$, $d = NH_2$, $e = OCH_3$, $f = OCH_2CH_3$, $g = C(CH_3)_3$, $h = CH_3$, $i = CH{=}CH_2$ ($-C_2H_3$), $j = C_6H_5$, $k = H$, $l = CH{=}CH-CH{=}CH_2$ (C_4H_5), $m = F$, $n = Cl$.

3.3. Electronic absorption spectra

The calculated UV–vis absorption spectra of all the dyes are illustrated in Figure 4 and are arranged according to the Hammett parameters. According to Gouterman and coworkers [44], the metallophthalocyanines are characterized by two electronic transitions, $^1E_u \leftarrow {}^1A_{1g}$ (π–π^*) which correspond to the Soret band

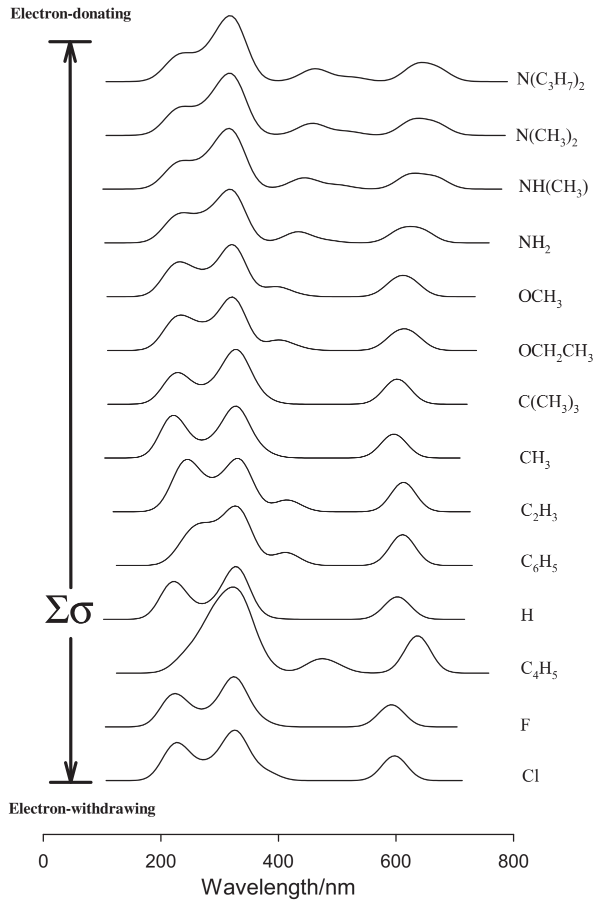

Figure 4. Electronic absorption spectra of $ZnPcR_3COOH$ (R = substituent). Using a broadening σ (FWHM) of 0.5 eV.

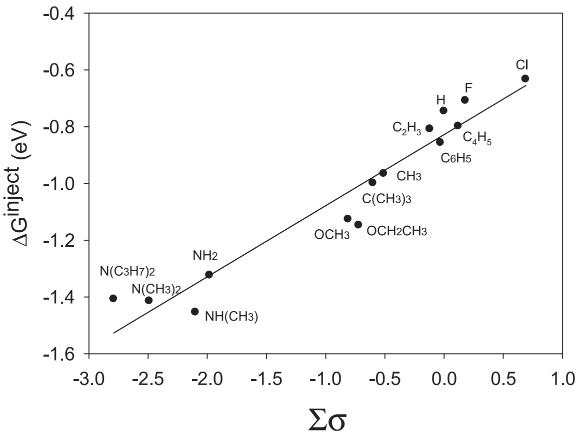

Figure 5. Plot ΔG^{inject} versus sum of the Hammett Parameters of the substituents on the ligand R (regression $r^2 = 0.93$).

(448–320 nm), which is due to the transition from the orbital a_{2u} (π) to the LUMO orbital e_g (π^*), and the Q-band (750–600 nm) arising from the $a_{1u}(\pi)$ (HOMO) toward the LUMO orbital. The latter transition is highly sensitive to the central metal ion, its valence states and the solvent used [45–48]. Our calculated results are shown in Figure 4. Here, the B and Q bands appear in the expected regions. Analysis of the spectra show that the molecules have very similar absorption bands and the only difference lies in the position of the signals. In the case of molecules with electron-donating substituent, the Q band shows a red shift, whereas with the electron-withdrawing substituent, the Q band displaces to the blue, respect to the hydrogen substituent (R = H). The exception arises with the electron withdrawing C_4H_5 substituent due to its π-conjugation is causing an intensity enhancement and a small red shift of the absorption spectrum, thus, increasing the possibility of electron transfer. On the other hand, the positions of the Q-bands of molecules with nitrogen substituent are situated in regions of longer wavelength than for the other substituents.

3.4. Absorption properties

Based on some published papers of other authors [32,49,50], we can relate fundamental theoretical parameters with the experimental controls such as open-circuit (V_{oc}) and short circuit current density (J_{sc}) [2]. The photo-induced electron injection in DSSCs can be viewed as a charge transfer (CT) process. Using the Marcus theory for electron transfer [51], the CT can be associated with the free energy change for electron injection (ΔG^{inject}) [42], affecting the electron injection rate and therefore the J_{sc} and V_{oc} in DSSCs. In general, the greater the ΔG^{inject} ($\Delta G < 0$), the greater electron-injection efficiency (Φ^{inject}) [43] and it can be calculated as $\Delta G^{\text{inject}} = E^{\text{dye}*} - E_{\text{CB}}$ [18,43]. E_{CB} is the reduction potential of the conduction band (CB) of the TiO_2.

In this work, we propose to establish a theoretical scheme, focusing in a first stage, to quantify the electron-injection into a titanium dioxide surface (which has an experimental value of $E_{\text{CB}} = -4.00$ eV vs. vacuum), widely used in several theoretical research [43,49,52–55]. In this scheme, E^{dye^*} is the dye excited state oxidation potential, and it is determined by the redox potential of the ground state of the dye (E^{dye}), and the vertical transition energy ($\lambda_{\max}$): $E^{\text{dye}^*} = E^{\text{dye}} - \lambda_{\max}$. The calculated E^{dye^*} and ΔG^{inject} of the Q-bands for $ZnPcR_3COOH$ dye (in gas phase) are shown in Table 1. These values are linked to the sum of the Hammett parameters $\Sigma\sigma$. To quantify the effect of the R substituent in the periphery of the Zinc phthalocyanines, we plotted the ΔG^{inject} (associated with Q band) versus the sum of the Hammett parameters ($\Sigma\sigma$), these are shown in the Figure 5. A linear response with $r^2 = 0.93$ it is obtained. The large absolute value of free energy for electron-injection is favorable for fast electron-injection and is directly proportional to the experimental values of J_{SC} and V_{OC}. These results allow us to propose adequate substituted zinc dyes that are of potential interest for designing highly efficient dye-sensitized solar cells.

4. Conclusions

In this work we presented novel unsymmetrical zinc phthalocyanine sensitizer candidates calculated by means of the DFT/TDDFT method in gas phase. The effect of the introduction of π-conjugation of the donor (C_4H_5) moiety produced a red-shifted spectra with higher oscillator strengths for the Q-bands. All of the $ZnPcR_3COOH$ dyes can provide driving forces for injecting an electron into the TiO_2 surface and for being regenerated by the mediator redox. The results of ΔG^{inject} show that the donor group linked to the phthalocyanine by using nitrogen as a bridging atom could lead to a more favorable process than groups that uses oxygen or carbon element as a bridge. These complexes based on molecules with adequate absorption bands and using the appropriate substituent have the potential for providing better performance facilitating the electronic transfer to obtain greater efficiency.

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