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## Original Research Article

# Computational investigations of a novel photoactive material for potential application in dye sensitized solar cells

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Computational study

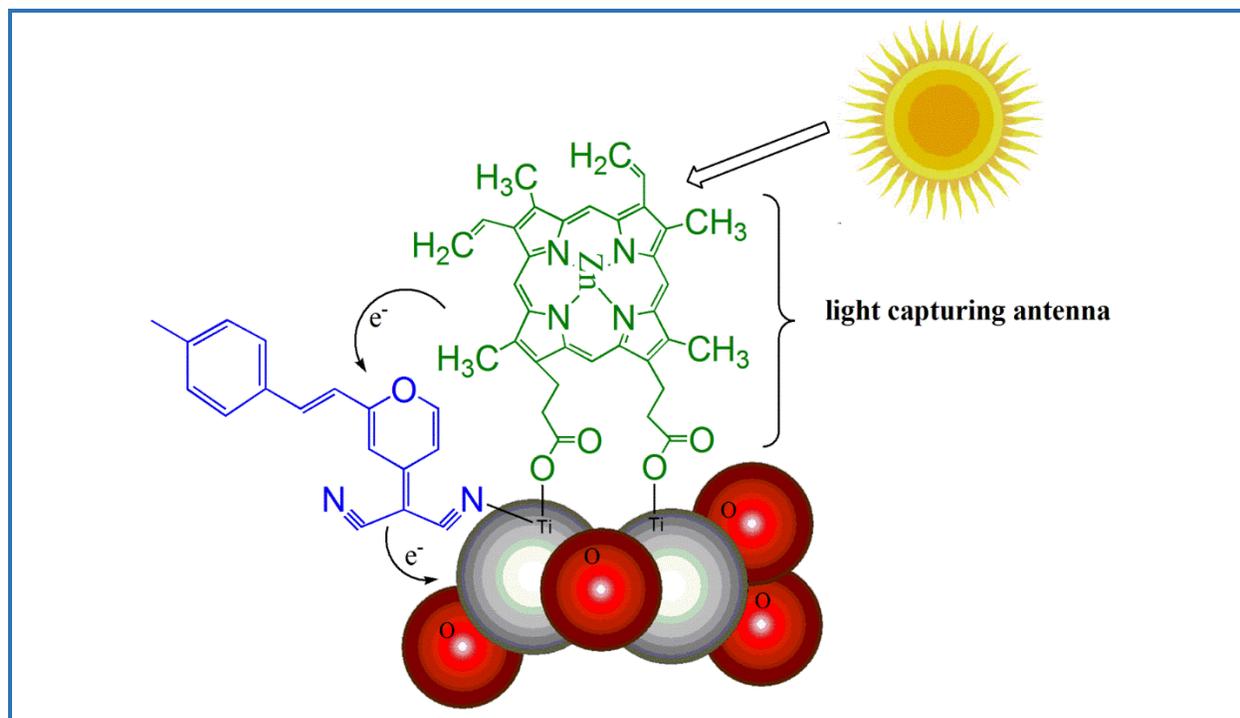
Co-adsorption

Dye sensitized solar cells

### ABSTRACT

In the present work, semiempirical computational methods were employed to investigate the properties of a complex formed by co-adsorption of protoporphyrin IX zinc (II) and 4-(dicaynomethylene)-6-(P-methylstyryl)-4H-pyrane in order to elucidate its potential as a sensitizer in dye sensitized solar cells. At first, PPZ-TiO<sub>2</sub> adsorption complex was formed via -COO- anchoring groups to determine its adsorption energy; electronic absorption spectrum. Then it was compared to the reported literature. Afterwards, 4-(dicaynomethylene)-6-(P-methylstyryl)-4H-Pyrane was co-adsorbed onto TiO<sub>2</sub> along with protoporphyrin IX zinc (II). The computational calculations were done to obtain the total energy, energies of HOMO/LUMO and also the theoretical electronic absorption spectrum of the compound. The results showed that the new complex has the potential to be used as an efficient light absorbing antenna in dye sensitized solar cells with an adsorption energy of -31714.5 kcal/mol and can provide a material with broad absorption range up to 615 nm. In addition, the HOMO/LUMO energy levels of the two dyes adsorbed on TiO<sub>2</sub> were found optimal for the flow of electrons in a cascade manner to the inorganic core materials.

## Graphical Abstract



## Introduction

Solar energy is a prime renewable energy source where the sunlight can be trapped to produce electricity by fabricating efficient solar cell devices. Dye sensitized solar cell (DSSCs) can serve as the most efficient and cheapest source of energy in this regard. Many studies have been conducted to find the best donor-acceptor material [1–6]. A DSSC usually consists of an inorganic core material which is sensitized with a donor-type material, referred to as dye and serves to absorb the visible light [7–9]. They are also termed as hybrid solar cells since they are the hybrid of inorganic and organic material. Since semiconductor materials such as TiO and ZnO have a limited absorption spectrum and suffer from charge recombination problem [10, 11], the adsorption/co-adsorption of the suitable dyes is expected to increase the performance of the solar cell. An enormous number of dyes have to be dealt with to find out the best donors however it is very difficult to experiment with such a large number of dyes and fabricate solar cells.

Computational methods provide an easy approach where many dyes can be easily tested without the waste of chemicals to find out the best working material for DSSCs [12]. The selected dyes can then be used to fabricate the solar cell materials in laboratory. An extensive research is going to be done on employing the computational techniques like Density Functional Theory (DFT) [13–15]. However, we have utilized a less time-consuming and easy semiempirical method using

Hyperchem Professional 07 software [16] in order to evaluate the potential of a novel complex for application in hybrid solar cells. For this purpose we first studied the adsorption of protoporphyrin IX zinc (II) which is known to be adsorbed on  $\text{TiO}_2$  via  $-\text{COO}^-$  groups, however the photovoltaic efficiency of the material was reported to be only 0.6% [17]. We believe that the efficiency could be enhanced by co-adsorption with another dye with the aim of extending the absorption range of the material. The results of our computational calculations are discussed in detail in the forthcoming sections.

## Experimental

### *Materials and methods*

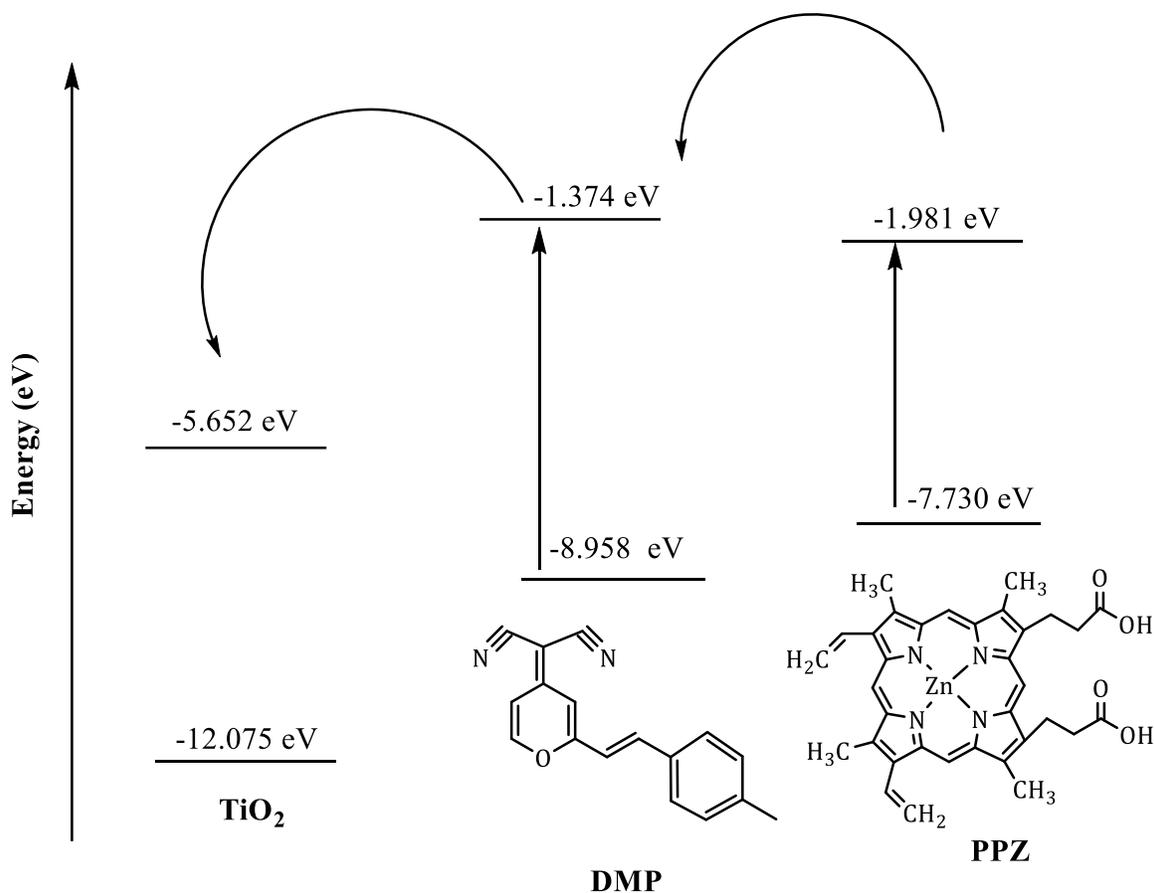
Hyperchem Professional 07 was employed to perform the computational calculations, and the semiempirical PM3 method was also used to optimize the molecules. In this sense, theoretical absorption spectra were calculated using ZINDO/s option of the semiempirical method. The investigated dyes include a porphyrin derivative, Protoporphyrin IX Zinc (II) and 4-(Dicaynomethylene)-6-(P-Methylstyryl)-4H-Pyrane. The  $1 \times 1$  crystal structure of  $\text{TiO}_2$  built with Crystal Builder option in Hyperchem was employed for adsorption studies. Single point energy calculations were then performed on the optimized dye,  $\text{TiO}_2$  and their adsorbed complexes in order to obtain the total energy and energies of the highest and lowest unoccupied molecular orbital.

## Results and discussion

PPZ, which can be regarded as a carboxylic acid functionalized Zn-metallated porphyrin while DMP is a pyran dye which was adsorbed individually and simultaneously onto  $\text{TiO}_2$  crystal. The chemical structures of PPZ and DMP are shown in [Scheme 1](#).

In order to investigate the adsorption of PPZ and DMP on  $\text{TiO}_2$ , we first computed the  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  values of dyes as well as  $\text{TiO}_2$  to determine the probable transfer of electron from dye to the  $\text{TiO}_2$ . The values were obtained using semiempirical PM3 method in Hyperchem Professional 07 where these molecules were first optimized and then subjected to single point energy calculations. The optimized structures of the molecules are shown in [Figure 1](#). The single point energy calculations on the optimized structures provided us with the  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  values which were found to be -7.730 and -1.981 eV, respectively. For DMP, the  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  values were observed at -8.958 and -1.374 eV, respectively. PPZ has HOMO, located higher (more positive) in energy, as compared to DMP where the LUMO is more negative.  $E_{\text{HOMO}}/E_{\text{LUMO}}$  values are related to the oxidation/reduction potentials of the compounds where more positive values demonstrate facile

oxidation (Removal of electron) or reduction (Addition of electron) since electrons can be easily added and removed. The literature survey shows similar  $E_{\text{HOMO}}/E_{\text{LUMO}}$  values of various porphyrin derivatives which are modulated by the functional groups as well as central metal attached to the porphyrin structure [18]. Following the above stated procedure, we determined the  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  values for  $\text{TiO}_2$  crystal which were found to be -12.075 and -5.652 eV, respectively. An energy level diagram constructed based on these values is shown in Scheme 1.

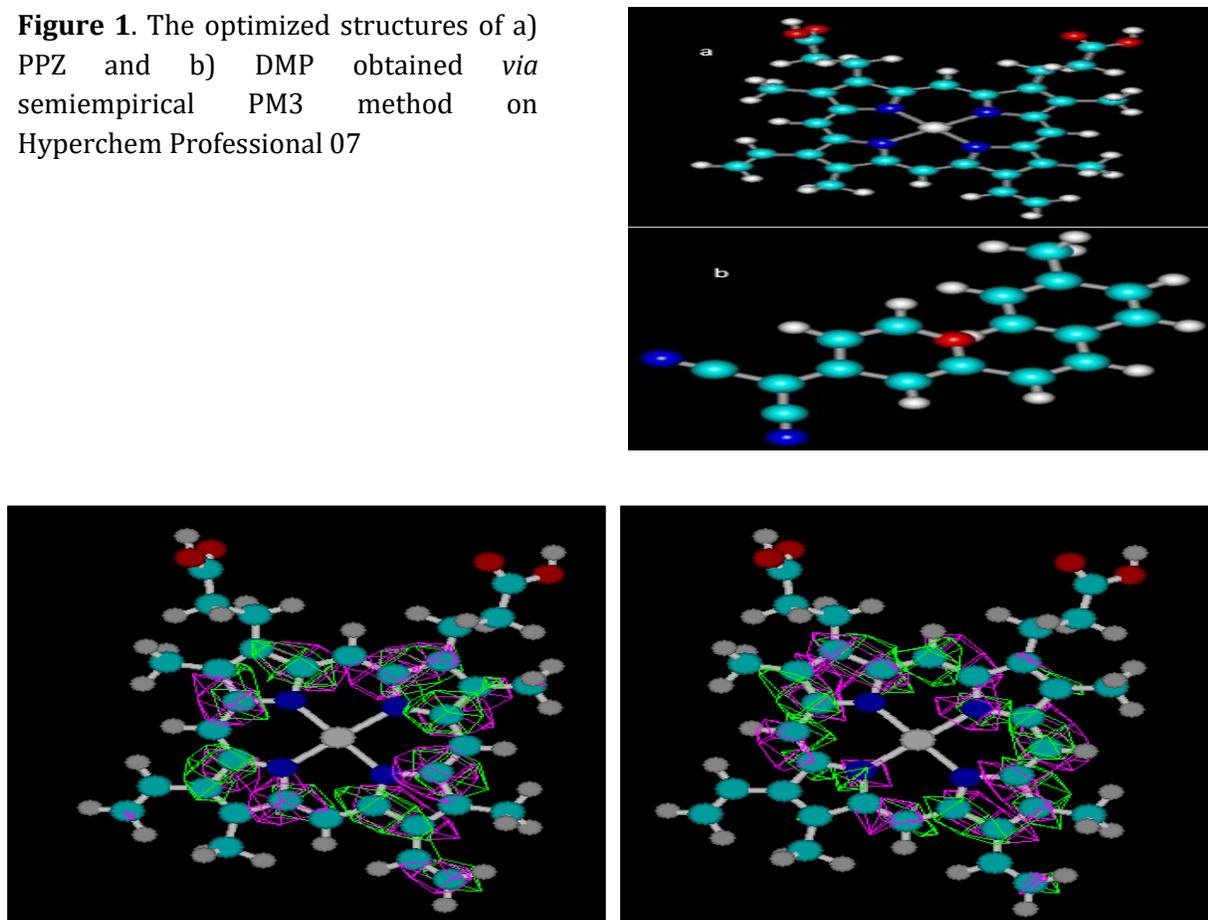


**Scheme 1.** The chemical structures of protoporphyrin IX zinc (II). (PPZ) 4-(dicaynomethylene)-6-(P-methylstyryl)-4H-pyrane (DMP) and the flow of electron from PPZ to  $\text{TiO}_2$  in a cascade manner based on their  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  values

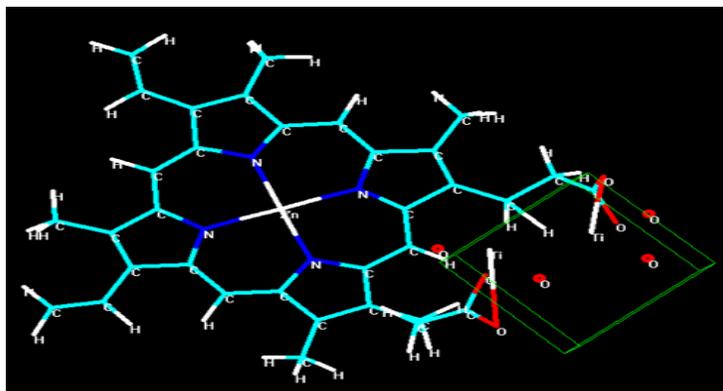
The values of  $E_{\text{HOMO}}/E_{\text{LUMO}}$  are quite suitable to provide an electron path where an excited electron from the HOMO of PPZ (As a result of light absorption) can be transferred to DMP and finally to the LUMO of  $\text{TiO}_2$  resulting in the flow of electron in a cascade manner. The graphical representation of the HOMO and LUMO of PPZ and DMP are displayed in Figure 2 and 3, respectively.

Theoretical electronic absorption spectra were also determined for PPZ, DMP and TiO<sub>2</sub>, individually. This was done by first optimizing the molecules using semiempirical PM3 method and, then, using ZINDO/s option for single point energy calculations. ZINDO/s was chosen for this study

**Figure 1.** The optimized structures of a) PPZ and b) DMP obtained *via* semiempirical PM3 method on Hyperchem Professional 07



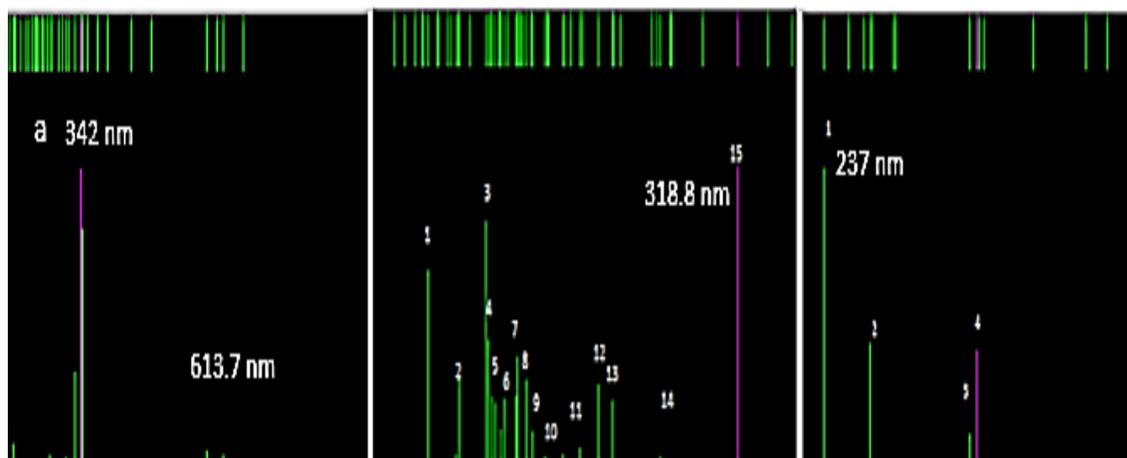
**Figure 2.** The graphical representation of HOMO (left) and LUMO (right) orbital of PPZ obtained using semiempirical PM3 calculations



**Figure 3.** Adsorption of PPZ on TiO<sub>2</sub> crystal forming PPZ-TiO<sub>2</sub> complex

-ecause it is known to yield better results for electronic absorption spectrum as compared to that of the TD-DFT method [16–19]. The electronic absorption spectrum of the porphyrin derivative PPZ, compared to the spectrum of DMP and TiO<sub>2</sub>, is shown in Figure 4. The upper peaks in all spectra show forbidden transitions in the molecules.

The longest wavelength peaks for PPZ, DMP were found to be at 613.7 and 318.8 nm while  $\lambda_{\max}$  is located at 342 and 318.8 nm, respectively. Computational calculations show that the DMP and TiO<sub>2</sub> possess a great absorption intensity in the ultraviolet region while PPZ has a slight absorption intensity in the visible region. Literature survey reveals that the absorption spectra of porphyrin derivatives typically has  $\lambda_{\max}$  situated between 350 nm to 430 nm [20]. Thus, our computational findings are in accordance with the reported literature. In this sense, the electronic absorption of DMP matches well with its already reported theoretical absorption spectrum, although the experimental absorption spectrum is red-shifted which can be attributed to the solvent affects [17].



**Figure 4.** Electronic absorption spectrum of a) PPZ, b) DMP and c) TiO<sub>2</sub> determined using ZINDO/option of semiempirical method

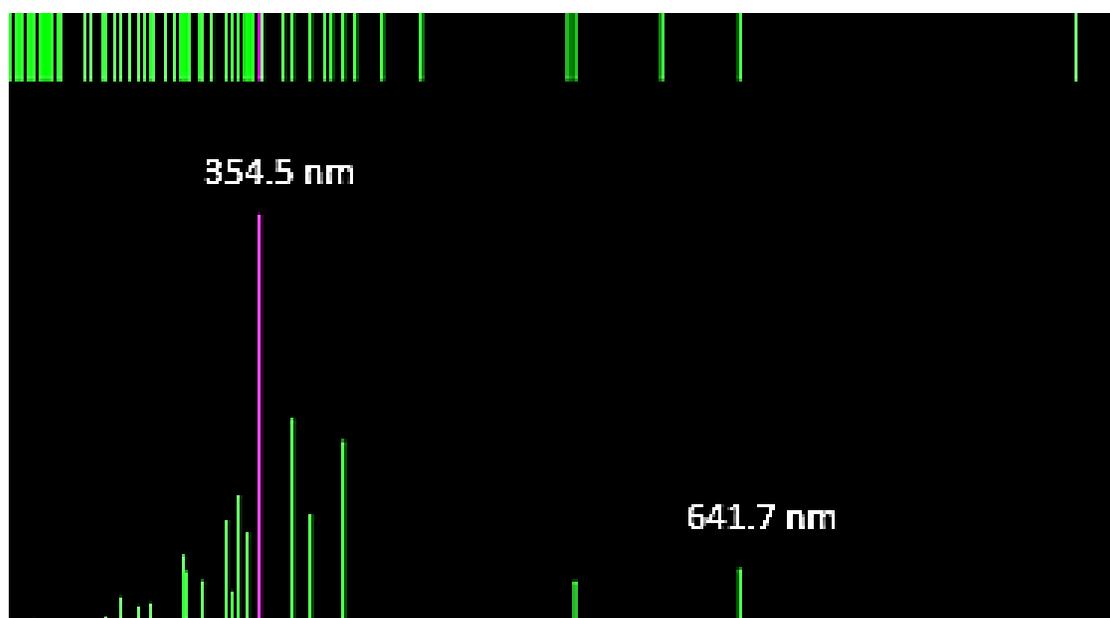
### Adsorption studies

Adsorption of the PPZ and DMP was first done individually on TiO<sub>2</sub> crystal structure. The  $E_{\text{HOMO}}/E_{\text{LUMO}}$  values, total energies and theoretical absorption spectra were evaluated for the resulting complexes. At first, PPZ was adsorbed on TiO<sub>2</sub> with the help of two -COOH groups. Since the central core of PPZ (Scheme 1) is already occupied by a Zn metal so its central metalation with Ti<sup>4+</sup> is not probable as reported for the free base porphyrins [20, 21]. The -COOH groups were used as anchoring entities on TiO<sub>2</sub> to form an adsorption complex. For his purpose, the proton of -COOH was removed and oxygen was bonded with titanium in the crystal structure. The second -COO<sup>-</sup> was also bonded in the same way with the other Ti<sup>4+</sup> of the crystal (As shown Figure S3). The complex

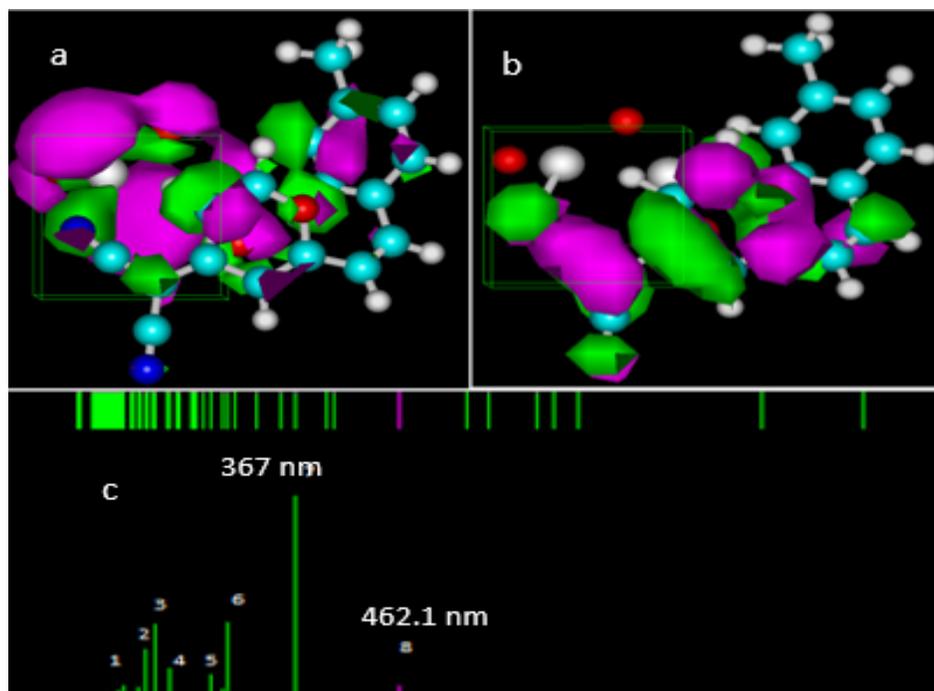
was then optimized and single point energy calculations were performed to obtain the total energy and the energies of the HOMO and LUMO which were found to be -8.513 eV and -2.892 eV, respectively. The electronic absorption spectrum of the complex PPZ-TiO<sub>2</sub> is displayed in Figure 5. The most bathchromically shifted peak is located at 641.7 nm while  $\lambda_{\text{max}}$  was found to be 354.5 nm considerably red-shifted (11.8 nm) as compared to the un-adsorbed PPZ ( $\lambda_{\text{max}} = 342.7$  nm).

The adsorption energy of PPZ on TiO<sub>2</sub> was determined from the total energies of PPZ, TiO<sub>2</sub> and PPZ-TiO<sub>2</sub> complexes using the equation  $E_{\text{ads}} = (E_{\text{PPZ}} + E_{\text{TiO}_2}) - E_{\text{PPZ-TiO}_2}$ . The total energy of PPZ was found to be -178188.2 kcal/mol as obtained from single point energy calculations. Whereas the total energy of the complex PPZ-TiO<sub>2</sub> was determined to be -222831.1 kcal/mol, considering the values and  $E_{\text{TiO}_2}$  i.e. -31777.6 kcal/mol,  $E_{\text{ads}}$  was estimated to be -12865.3 kcal/mol.

After studying the adsorption of PPZ on TiO<sub>2</sub>, DMP was anchored on TiO<sub>2</sub> via nitrogen atom. For this purpose, the nitrogen atom was bonded with one titanium of TiO<sub>2</sub>. The complex which was formed in this way was optimized using semiempirical PM3 method as total energy of the molecule along with  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  values was estimated (Figure 6). The  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  of DMP-TiO<sub>2</sub> were found to be -9.738 eV and -2.592 eV, respectively. Absorption range was enhanced up to 462.1 nm after sensitization (Figure 6). The  $\lambda_{\text{max}}$  is also considerably red-shifted (367 nm) as compared to pure TiO<sub>2</sub> or DMP. The experimental absorption spectrum of DMP which was adsorbed on TiO<sub>2</sub> using dimethylformamide as solvent shows  $\lambda_{\text{max}}$  around 387 nm, which is very close to our theoretical calculations [17]. This also affirms that our computational method is accurate enough to provide an estimate of the experimental phenomena.



**Figure 5.** The theoretical electronic absorption spectrum of PPZ-TiO<sub>2</sub>

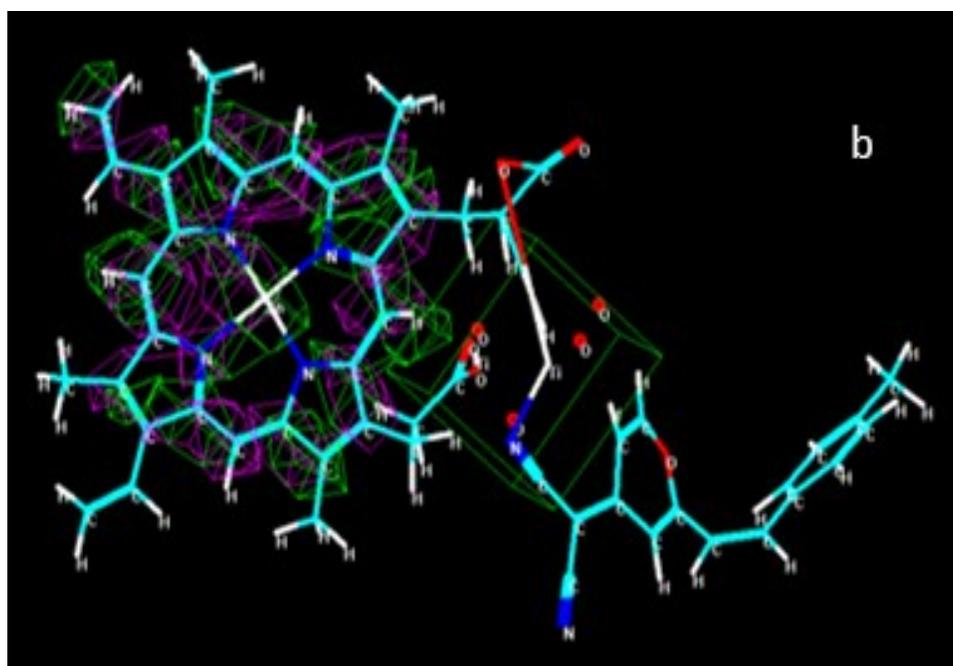
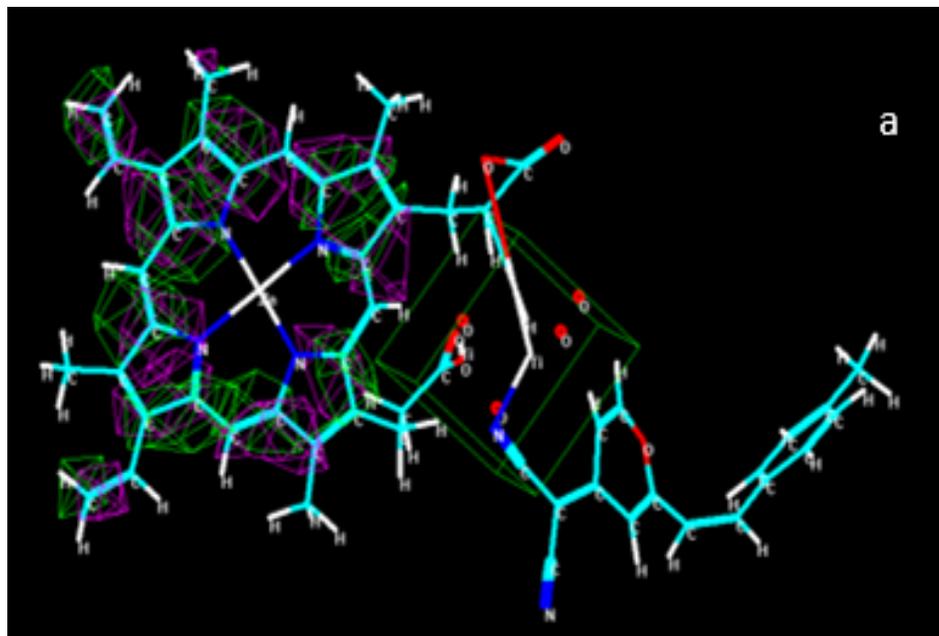


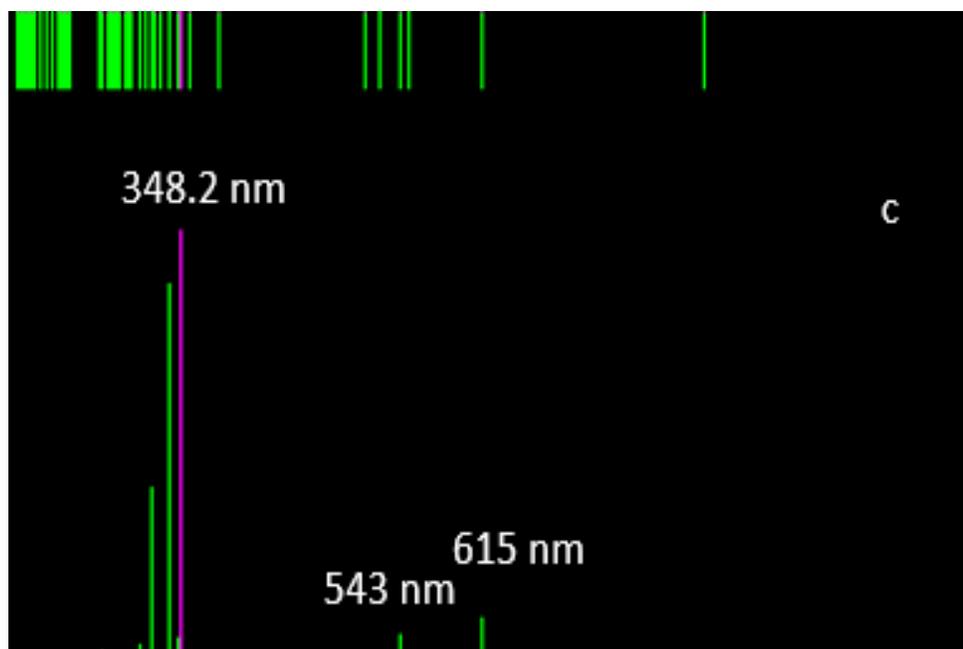
**Figure 6.** The graphical representation of a) HOMO, b) LUMO of PPZ-DMP-TiO<sub>2</sub>, c) theoretical absorption spectrum of DMP-TiO<sub>2</sub> using ZINDO/s option

Afterwards, we performed our calculation on a co-adsorbed complex where both PPZ and DMP were adsorbed on TiO<sub>2</sub> crystal. PPZ was attached in the same way *via* two -CO<sub>2</sub> groups while DMP was attached with one nitrogen atom to one of the titanium of the crystal (As shown in Figure 7). The complex which was formed in this way can be designated as PPZ-DMP-TiO<sub>2</sub> in the forthcoming explanation. Optimization and single point energy calculation using semiempirical PM3 method provided the energies of HOMO/LUMO orbital which were found to be -8.057 and -2.407 eV, respectively.

The electronic absorption spectrum of PPZ-DMP-TiO<sub>2</sub> is displayed in Figure 7 where a considerable red-shift is observed. A band in visible region can be seen located between 543–615 nm whereas the maximum absorbance in DMP-TiO<sub>2</sub> was observed at 462.1 nm. Thus, co-adsorption of PPZ and DMP on TiO<sub>2</sub> is expected to broaden the absorption spectrum of the material. In addition, the incorporation of DMP can enhance the photovoltaic performance by suppressing the charge recombination since the excited electrons in PPZ will prefer to go into the HOMO of DMP rather than reuniting with the holes in PPZ (Scheme 1). From there the electrons will continue their path to the HOMO/LUMO of TiO<sub>2</sub>. It is important to mention that the charge recombination has remained a major setback in increasing the efficiency of DSSCs [20]. The total energy of PPZ-DMP-TiO<sub>2</sub> came out to be -243120.4 kcal/mol which can be used to calculate the adsorption energy of the

complex. For this purpose, we added the total energies of  $\text{TiO}_2$  (-31777.6 kcal/mol), PPZ (-178188.2 kcal/mol) and DMP (-64869.1 kcal/mol) molecules and subtracted the total energy from the computationally obtained total energy of the co-adsorbed complex, PPZ-DMP- $\text{TiO}_2$ . The adsorption energy in this case was found to be -31714.5 kcal/mol. Moreover, If we compare this adsorption energy with DMP- $\text{TiO}_2$  (-147.7 kcal/mol) we can see that our suggested co-adsorbed complex is much more energetically feasible. The comparison of the obtained parameters using computational calculations for the two dyes is given in [Table 1](#).





**Figure 7.** The graphical representation of a) HOMO, b) LUMO of PPZ-DMP-TiO<sub>2</sub>, c) electronic absorption spectrum of PPZ-DMP-TiO<sub>2</sub> obtained using semiempirical ZINDO/s method

**Table 1.** The parameters obtained from the computational calculations on PPZ, DMP, TiO<sub>2</sub> and their adsorption complexes

Molecule	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	Total Energy/Adsorption Energy (kcal/mol)
TiO <sub>2</sub>	-12.075	-5.652	-31777.6
PPZ	-7.730	-1.981	-178188.2
PPZ-TiO <sub>2</sub>	-8.513	-2.892	-12865.3
DMP	-8.958	-1.374	-64869.1
DMP-TiO <sub>2</sub>	-9.738	-2.592	-147.7
PPZ-DMP-TiO <sub>2</sub>	-8.057	-2.407	-31714.5

## Conclusion

Computational study of the complex formed by co-adsorption of protoporphyrin IX zinc (II), (PPZ) and 4-(dicaynomethylene)-6-(*P*-methylstyryl)-4*H*-pyrane (DMP) onto TiO<sub>2</sub> crystal was done using semiempirical PM3 and ZINDO/s method in order to evaluate its potential as suitable material for DSSCs. The values of the total energies,  $E_{\text{HOMO}}/E_{\text{LUMO}}$  and theoretical absorption spectra manifest its potential as light absorbing antennas. The absorption spectrum was broadened to 615 nm by the addition of DMP to the already studied PPZ-TiO<sub>2</sub> complex. The adsorption energy of PPZ-

DMP-TiO<sub>2</sub> indicates much higher stability as compared to PPZ-TiO<sub>2</sub>. The study shows that the adsorption complex can serve as an efficient material for future use in DSSCs.

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### Disclosure statement

No potential conflict of interest was reported by the authors.

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