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Orginal Research Article

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

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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)-4*H*-pyrane to elucidate its potential as sensitizer in dye sensitized solar cells. At first, PPZ-TiO_2 adsorption complex was formed via -COO^- anchoring groups to determine its adsorption energy, electronic absorption spectrum. Then it was compared with the reported literature. Afterwards 4-(dicaynomethylene)-6-(P-methylstyryl)-4*H*-Pyrane was co-adsorbed onto TiO_2 along with protoporphyrin IX zinc (II) and computational calculations were done to obtain total energy, energies of HOMO/LUMO and 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 two dyes adsorbed on TiO_2, were found optimal for the flow of electrons in a cascade manner to the inorganic core materials.

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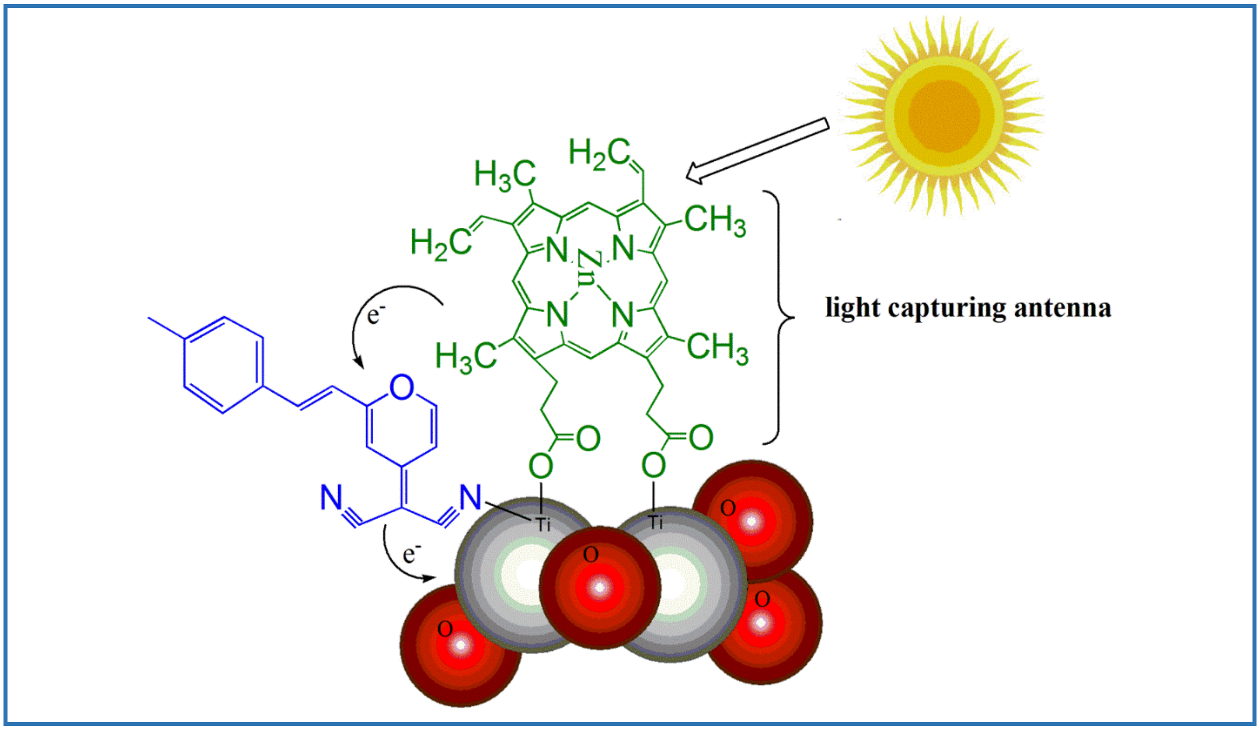
Graphical Abstract



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 consist 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 material such as TiO and ZnO have a limited absorption spectrum and suffer from charge recombination problem [10, 11], the adsorption/co-adsorption of 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 on employing computational techniques like Density Functional Theory (DFT) in this regard [13–15]. However, we have utilized a less time consuming and easy semiempirical method using

Hyperchem Professional 07 software [16] 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 adsorb on TiO_2 via $-COO^-$ 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

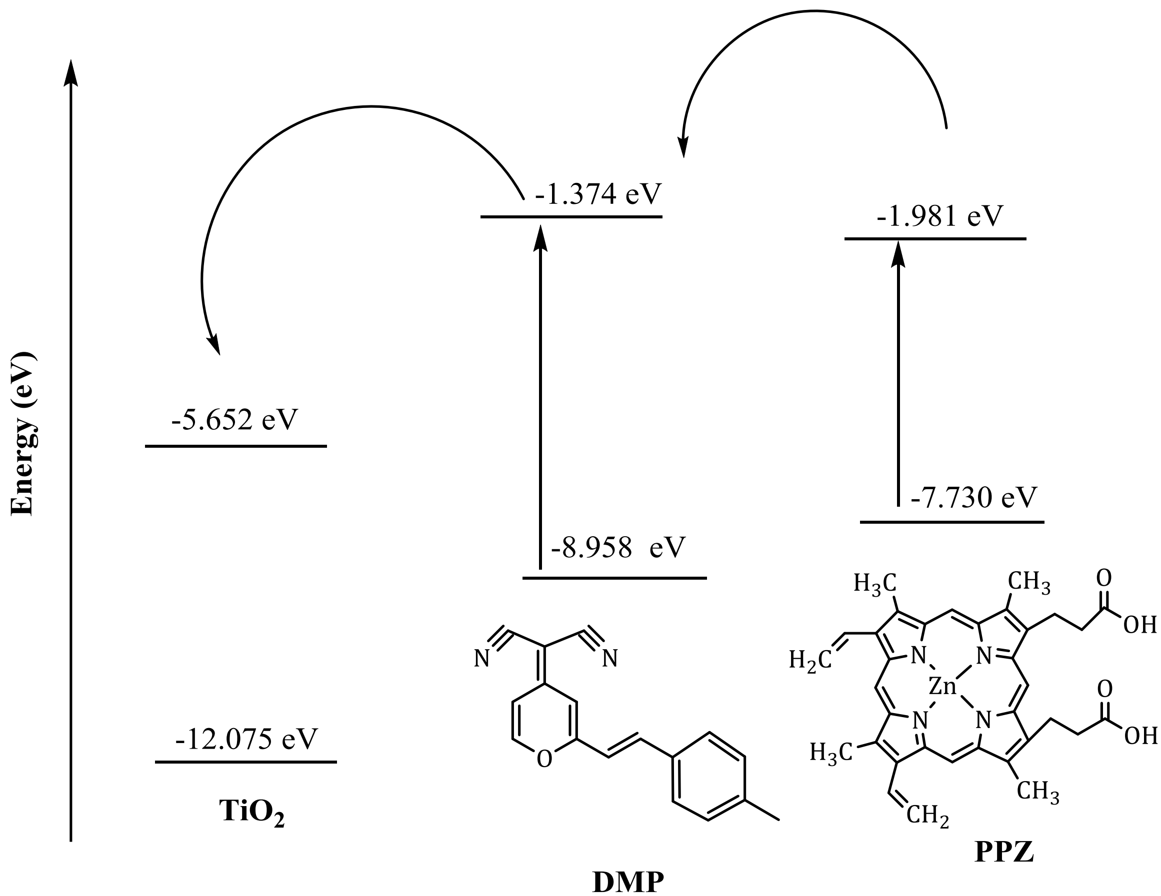
Materials and methods

Hyperchem Professional 07 was employed to perform the computational calculations, and the semiempirical PM3 method was used to optimize the molecules. Theoretical absorption spectra were calculated using ZINDO/s option of the semiempirical method. The dyes investigated include a porphyrin derivative, Protoporphyrin IX Zinc (II) and 4-(Dicaynomethylene)-6-(P-Methylstyryl)-4*H*-Pyrane. A 1×1 crystal structure of TiO_2 build with Crystal Builder option in Hyperchem was employed for adsorption studies. Single point energy calculations were then performed on the optimized dye, TiO_2 and their adsorbed complexes to obtain, total energy and energies of the highest and lowest unoccupied molecular orbital.

Results and discussion

PPZ, is a carboxylic acid functionalized Zn-metallated porphyrin while DMP is a pyran dye which were adsorbed individually as well as simultaneously onto TiO_2 crystal. The chemical structures of PPZ and DMP are shown in Scheme 1.

To investigate the adsorption of PPZ and DMP on TiO_2 we first computed the E_{HOMO} and E_{LUMO} values of dyes as well as TiO_2 to determine the probable transfer of electron from dye to the TiO_2. The values were obtained by 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_{HOMO} and E_{LUMO} values which were found to be -7.730 and -1.981 eV respectively. For DMP, the E_{HOMO} and E_{LUMO} values were observed at -8.958 and -1.374 eV respectively. PPZ has HOMO located higher (more positive) in energy compared to DMP whereas the LUMO is more negative. E_{HOMO}/E_{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_{HOMO}/E_{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_{HOMO} and E_{LUMO} values for TiO_2 crystal and 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.

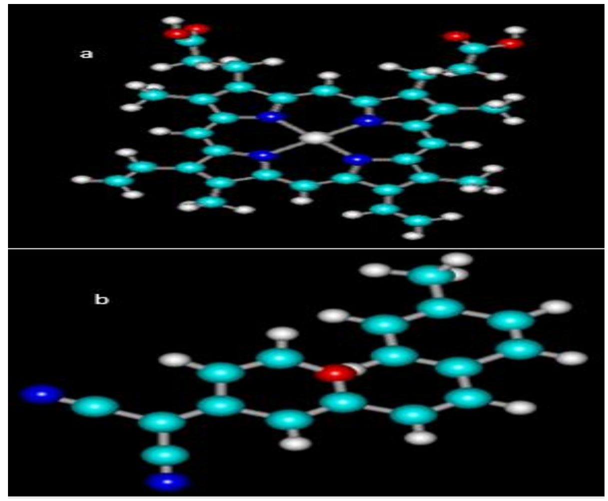


Scheme 1. The chemical structures of protoporphyrin IX zinc (II). (PPZ) 4-(dicaynomethylene)-6-(P-methylstyryl)-4*H*-pyrane (DMP) and the flow of electron from PPZ to TiO_2 in a cascade manner based on their E_{HOMO} and E_{LUMO} values

The values of E_{HOMO}/E_{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 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_2 individually. This was done by first optimizing the molecules using semiempirical PM3 method and then using ZINDO/s option for singe point energy calculations. ZINDO/s was chosen for this study b

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



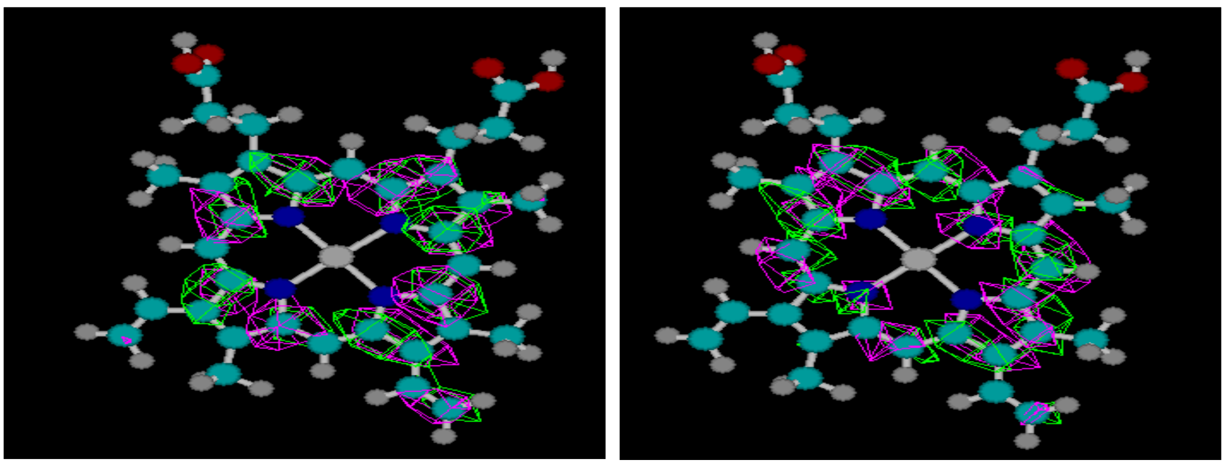


Figure 2. The graphical representation of HOMO (left) and LUMO (right) orbital of PPZ obtained using semiempirical PM3 calculations

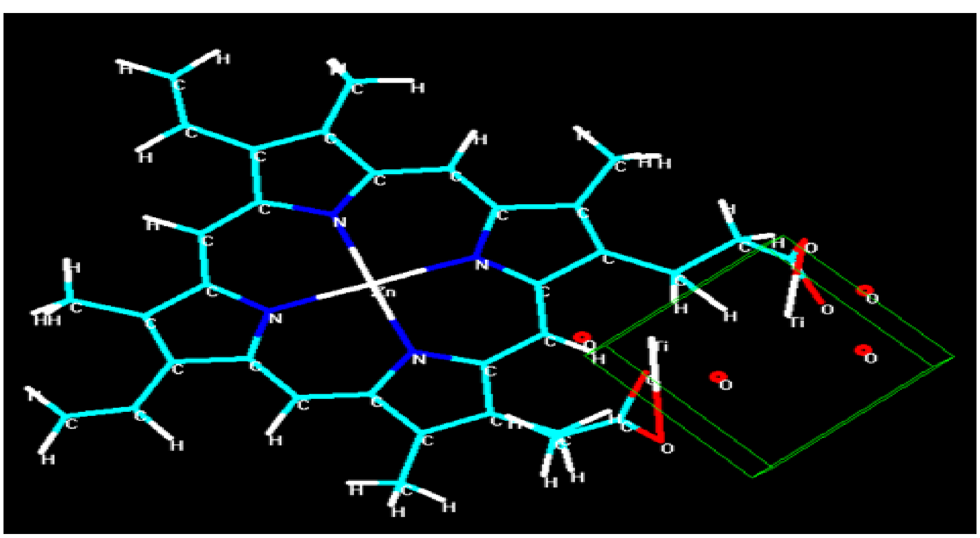


Figure 3. Adsorption of PPZ on TiO_2 crystal forming PPZ-TiO_2 complex

-ecause it is known to yield better results for electronic absorption spectrum compared to TD-DFT method [16–19]. The electronic absorption spectrum of the porphyrin derivative PPZ compared with the spectrum of DMP and TiO_2 is shown in Figure 4. The upper peaks in all spectra shows forbidden transitions in the molecules.

The longest wavelength peaks for PPZ, DMP were found to be at 613.7 and 318.8 nm while λ_{max} is located at 342 and 318.8 nm, respectively. Computational calculations show that, the DMP and TiO_2 are absorbing 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 λ_{max} situated between 350 nm to 430 nm [20]. Thus, our computational findings are in accordance with the reported literature. The electronic absorption of DMP matches well with its already reported theoretical absorption spectrum however the experimental absorption spectrum is red shifted which can be attributed to the solvent affects [17].

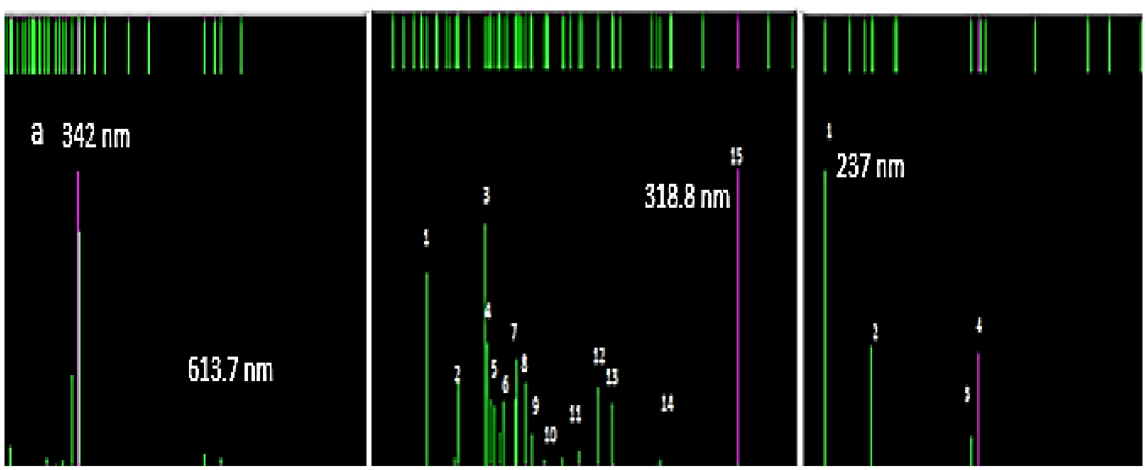


Figure 4. Electronic absorption spectrum of a) PPZ, b) DMP and c) TiO_2 determined using ZINDO/s option of semiempirical method

Adsorption studies

Adsorption of the PPZ and DMP was first done individually on TiO_2 crystal structure. The E_{HOMO}/E_{LUMO} values, total energies and theoretical absorption spectra were evaluated for the resulting complexes. At first, PPZ was adsorbed on TiO_2 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^{4+} is not probable as reported for the free base porphyrins [20, 21]. The -COOH groups were used as anchoring entities on TiO_2 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 $-COO^-$ was also bonded in the same way with the other Ti^{4+} of the crystal (As shown Figure S3). The complex was then optimized and single point energy calculations were performed to obtained 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_2 is displayed in Figure 5. The most bathchromically shifted peak is located at 641.7 nm while λ_{max} was found to be 354.5 nm considerably red shifted (11.8 nm) compared to the un-adsorbed PPZ (λ_{max} = 342.7 nm).

The adsorption energy of PPZ on TiO_2 was determined from the total energies of PPZ, TiO_2 and PPZ-TiO_2 complex using the equation $E_{ads} = (E_{PPZ} + E_{TiO2}) - E_{PPZ\text{-}TiO2}$. 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_2 was determined to be -222831.1 kcal/mol. By putting these values and E_{TiO2} i.e. -31777.6 kcal/mol, E_{ads} was estimated to be -12865.3 kcal/mol.

After studying the adsorption of PPZ on TiO_2, DMP was anchored on TiO_2 via nitrogen atom. For this purpose, one of the nitrogen was bonded with one titanium of TiO_2. The complex formed in this way was optimized using semiempirical PM3 method and total energy of the molecule along with E_{HOMO} and E_{LUMO} values was estimated (Figure 6). The E_{HOMO} and E_{LUMO} of DMP-TiO_2 were found to be -9.738eV and -2.592 eV respectively. Absorption range was enhanced up to 462.1 nm after sensitization (Figure 6). The λ_{max} is also considerably red shifted (367 nm) as compared to pure TiO_2 or DMP. The experimental absorption spectrum of DMP adsorbed on TiO_2 using dimethylformamide as solvent shows λ_{max} around 387 nm, close to our theoretical calculations [17]. This also affirms that our computational method is accurate enough to provide an estimate of the experimental phenomena.

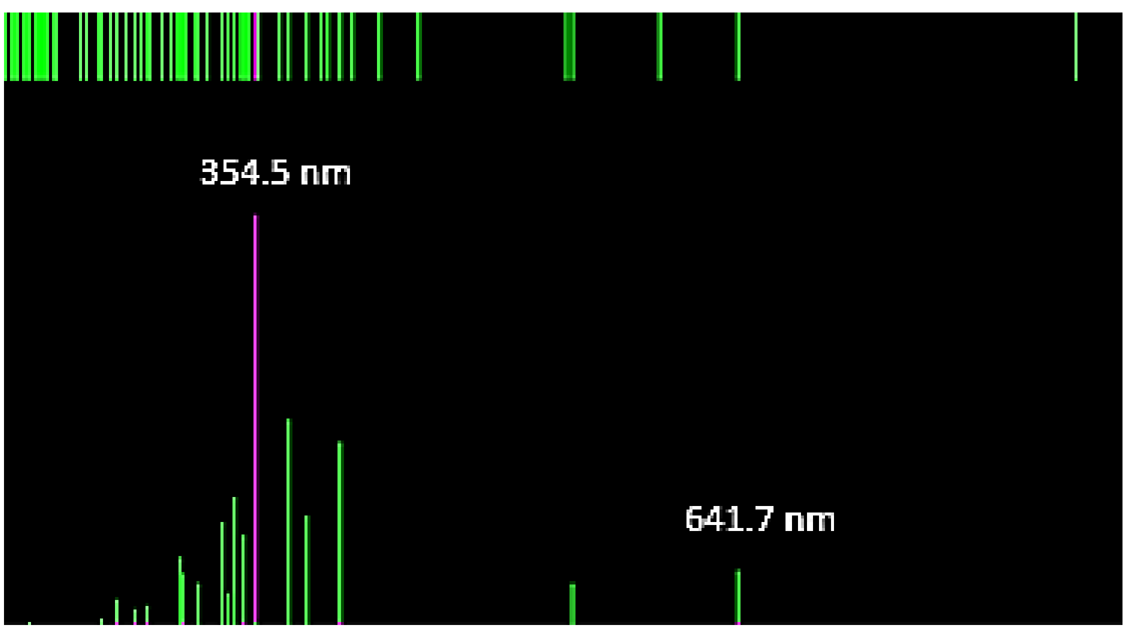


Figure 5. The theoretical electronic absorption spectrum of PPZ-TiO_2

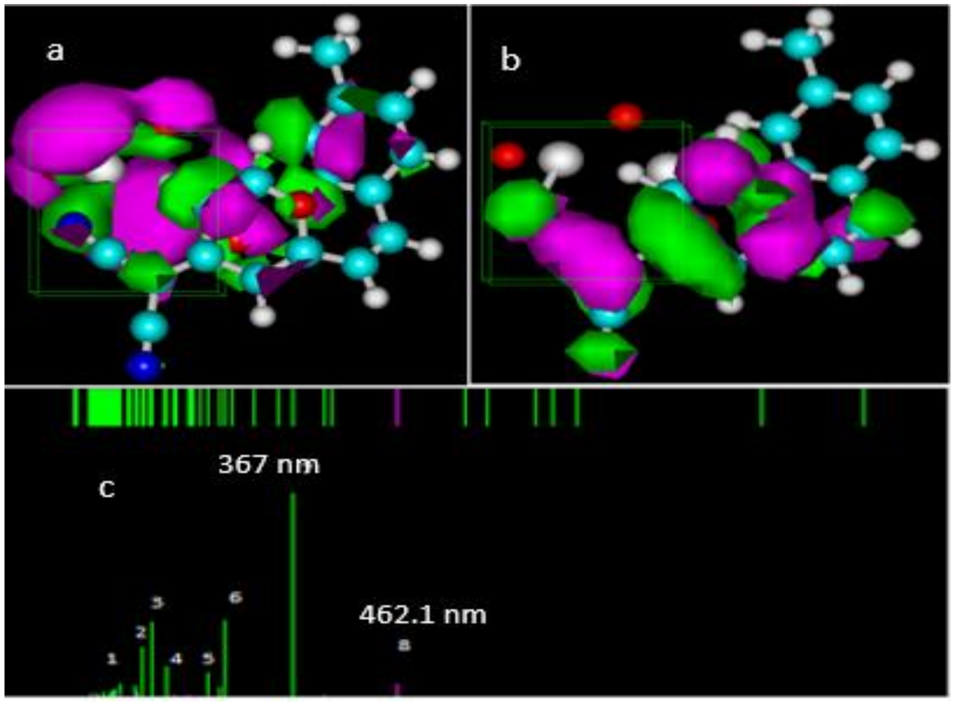
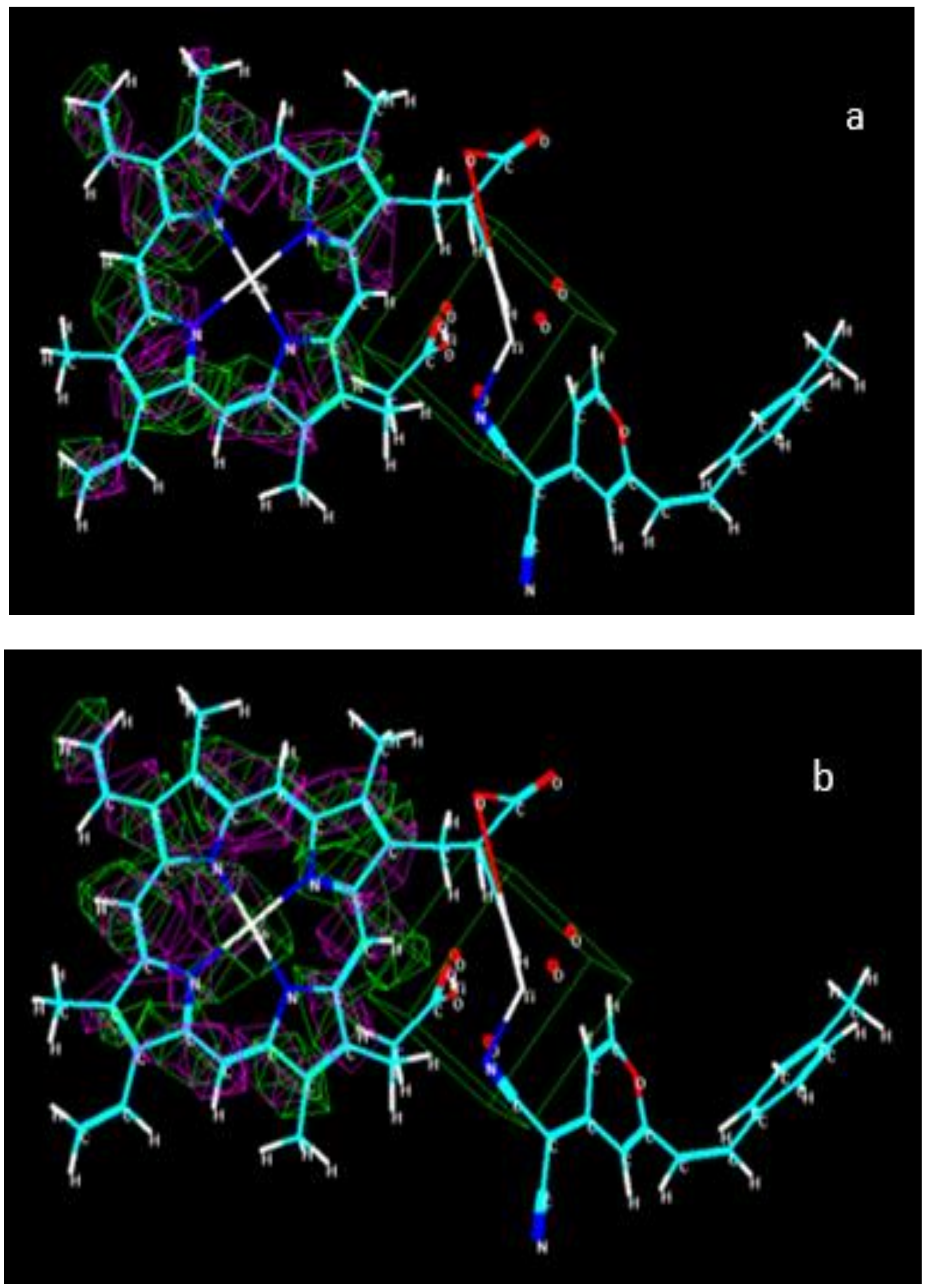


Figure 6. The graphical representation of a) HOMO, b) LUMO of PPZ-DMP-TiO_2, c) theoretical absorption spectrum of DMP-TiO_2 using ZINDO/s option

After wards we performed calculation on a co-adsorbed complex where both PPZ and DMP were adsorbed on TiO_2 crystal. PPZ was attached in the same way *via* two –CO_2 groups while DMP was attached with one nitrogen atom to one of the titanium of the crystal (As shown in Figure 7). The complex formed in this way is designated as PPZ-DMP-TiO_2 in the forthcoming explanation. Optimization and single point energy calculation using semiempirical PM3 method provided the energies of HOMO/LUMO orbital and which were found to be -8.057 and -2.407 eV respectively.

The electronic absorption spectrum of PPZ-DMP-TiO_2 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_2 was observed at 462.1 nm. Thus, co-adsorption of PPZ and DMP on TiO_2 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_2. It is important to mention here that charge recombination has remained a major setback in increasing the efficiency of DSSCs [20]. The total energy of PPZ-DMP-TiO_2 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 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-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-TiO_2 (-147.7 kcal/mol) we can see that our suggested co-adsorbed complex is much more energetically feasible. The comparison of the parameters obtained using computational calculations for the two dyes is given in Table 1.



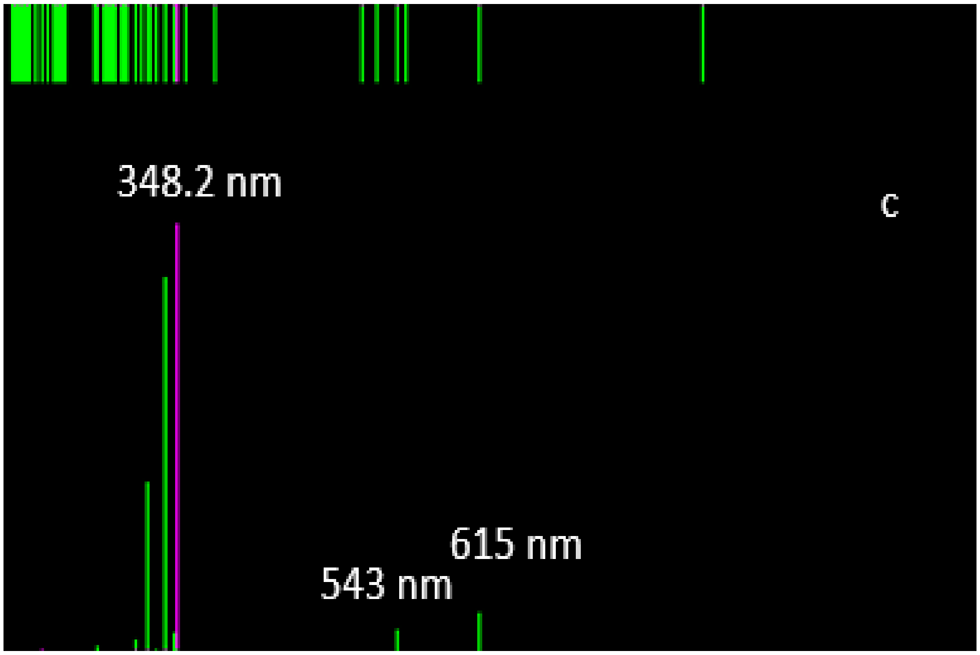


Figure 7. The graphical representation of a) HOMO, b) LUMO of PPZ-DMP-TiO_2, c) electronic absorption spectrum of PPZ-DMP-TiO_2 obtained using semiempirical ZINDO/s method

Table 1. The parameters obtained from the computational calculations on PPZ, DMP, TiO_2 and their adsorption complexes

Molecule	E_{HOMO} (eV)	E_{LUMO} (eV)	Total Energy/Adsorption Energy (kcal/mol)
TiO_2	-12.075	-5.652	-31777.6
PPZ	-7.730	-1.981	-178188.2
PPZ-TiO_2	-8.513	-2.892	-12865.3
DMP	-8.958	-1.374	-64869.1
DMP-TiO_2	-9.738	-2.592	-147.7
PPZ-DMP-TiO_2	-8.057	-2.407	-31714.5

Conclusion

Computational study of complex formed by co-adsorption of protoporphyrin IX zinc (II). (PPZ) and 4-(dicaynomethylene)-6-(P-methylstyryl)-4*H*-pyrane (DMP) onto TiO_2 crystal was done using semiempirical PM3 and ZINDO/s method to evaluate its potential as suitable material for DSSCs. The values of total energies, E_{HOMO}/E_{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_2 complex. The adsorption energy of PPZ-DMP-TiO_2 indicates much higher stability as compared to PPZ-TiO_2. 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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