

Computational Investigations of a Novel Charge Transfer Complex for Potential Application in Dye-Sensitized Solar Cells

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ABSTRACT: *The computational study of a novel charge-transfer complex as a photoactive blend for potential application in dye-sensitized solar cells was carried out using the semiempirical method. The adsorption of two natural dyes, 1S,3R,4R,5R-3-(3,4-dihydroxyphenyl)acryloyloxy)-1,4,5-trihydroxycyclohexane carboxylic acid (DHTH) and 2-Phenyl-4H-chromen-4-one (PCO) was achieved independently on to 1×1×1 TiO₂ crystal to form TiO₂-DHTH and TiO₂-PCO adsorption complexes. Semiempirical calculations were performed on the optimized molecules, as well as on the adsorption complexes, to obtain the total energies and E_{HOMO}/E_{LUMO} values, manifesting a flow of electron from DHTH/PCO to TiO₂. The theoretical electronic absorption spectra calculated via ZINDO/s method revealed a large bathochromic shift to 810 nm and 526 nm for TiO₂-DHTH and TiO₂-PCO, respectively, indicating the formation of a charge-transfer complex. Subsequently, the co-adsorption of PCO and DHTH on TiO₂ was accomplished with the aim to minimize the possible charge recombination in the photoactive blend. The semiempirical PM3 calculations evidenced high stability of the co-adsorption complex, TiO₂-PCO-DHTH, with the total energy of -200678.578 kcal/mol. The positions of HOMO and LUMO orbitals as obtained from single-point energy calculations, coincided accurately with our proposition of electron flow in a cascade manner from DHTH to PCO and finally to TiO₂. The theoretical electronic absorption spectrum of TiO₂-PCO-DHTH evinced absorption range of 351.8-800 nm demonstrating the high potential of TiO₂-PCO-DHTH to be used as a photoactive blend for solar cells.*

KEYWORDS: *Computational study; Co-adsorption; Charge transfer complex; Dye-sensitized solar cells.*

INTRODUCTION

Dye Sensitized Solar Cells (DSSCs) are classified as third generation organic solar cells because they offer additional functionalities such as flexibility and

transparency, which are not offered by the first two generation devices built using single crystalline silicon (first generation) or thin films (second generation).

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1021-9986/2020/6/19-27

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The DSSCs mimic photosynthesis process in which the light absorbed by a green pigment, called chlorophyll, and subsequent photo-induced electron transfer generate fuel (starch). In the DSSCs, dye molecule absorbs light and subsequent charge generation produces photovoltaic effect. They are named as bi-functional solar cells because of their transparency and flexibility-so that they can be used as windows of buildings and automobiles, and generation of photo-current simultaneously. Moreover, DSSCs could be fabricated at low cost, in different colors, on a transparent glass and on flexible substrates which have a huge potential in the commercial market, especially for "low-density" applications such as rooftop solar collector and other small electronic gadgets. Another important feature is its operational hours at both ambient light and full sun condition without much impact on efficiency and also its ability to work at wider angles; while the other traditional solar cells would fail at illumination below a certain range. Thus, DSSCs have a very low cutoff which make them more attractive field in the solar cell technology. The DSSCs could operate between 10 to 1 in a day whereas the traditional silicon solar cells merely operate for 6 to 8 hours [1].

The DSSC mainly comprises of a photoanode or Working Electrode (WE), which is made of Metal Oxide Semiconductor (MOS) deposited on a Transparent Conducting Oxide (TCO) glass substrate (typically Fluorine-doped Tin Oxide, FTO), a thin layer of dye molecules anchored on the MOS film, an electrolyte solution consists of iodide-triiodide (I^-/I_3^-) species, and the cathode substrate made of platinum coated FTO. When light shine on the DSSC, electrons are excited from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO) of the anchored dye molecule. These excited electrons are then injected into the MOS, giving rise to the charge separation. The resulting electrons diffuse in the Conduction Band (CB) of the MOS and empty state (holes) in the dye molecule's HOMO diffuse to the electrolyte. The free electrons permeate through the porous MOS and move to the external circuit through the FTO. After passing through the external circuit (load), the electrons return to the system to regenerate the electrolyte component that was used to reduce the oxidized dye molecule [2-5].

Several researchers are investigating the blends of organic and inorganic materials for their potential

application in DSSCs. Recently ZnO based dye sensitized solar cells have been reported by Zhang and its group using Eosin Y dye with and efficiency of 1.31% [6]. High efficiency dye sensitized solar cells are also reported recently consisting of the composite materials made from TiO_2 , SnO_2 and ZnO nanocrystals using N719 and N3 dyes [7-10]. The highest photovoltaic efficiency (IPCE) was found to be 61.9 % [11]. Another recent research article manifested a 3 % power conversion efficiency of SnO_2 based dye sensitized solar cells [12]. Similarly Sule *et al.* [13] synthesized a boron dibenzopyrromethene (dibenzo-BODIPY)-conjugated phenothiazine dye with cyanoacrylic acid which showed an absorption coefficient of 638 nm yielded efficiency of 7.69%. Bodipy dyes [14] and Porphyrin [15] were also studied for application in DSSC. 4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran and porphyrin dye adsorbed on mesostructured TiO_2 have shown to produce the DSSCs with power conversion efficiency of 4.5 % [16].

The inorganic semiconductor materials such as TiO , ZnO and SnO_2 etc. are sensitized with dyes since they have a limited absorption spectrum and suffer from charge recombination problem [17-20]. The adsorption/co-adsorption of suitable dyes is expected to increase the performance of the solar cells [21]. However, a large number of sensitizers have to be dealt with to find out the optimum electron donors. 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 [22]. The selected dyes can then be used to fabricate the solar cell materials in laboratory. An extensive research is going on using computational techniques like Density Functional Theory (DFT) in this respect [23-27]. However, we have utilized a less time consuming and easy semi-empirical method using Hyperchem Professional 08 software [26, 28] to evaluate the potential of a novel complex for application in hybrid solar cells.

In the present work we have employed two dyes namely (1S, 3R, 4R, 5R-3-(3, 4-dihydroxyphenyl) acryloyloxy)-1, 4, 5-trihydroxycyclohexane carboxylic acid (DHTH) and 2Phenyl-4H-chromen-4-one (PCO) to form a co-adsorption complex on to $1 \times 1 \times 1$ TiO_2 crystal. The total energy, E_{HOMO}/E_{LUMO} values and spectroscopic properties of the complex were evaluated to get insight into the stability and absorption spectrum of the co-adsorption

complex to find out its potency for application in hybrid solar cells.

EXPERIMENTAL SECTION

The dyes used for adsorption on TiO_2 include (1S,3R,4R,5R-3-(3,4-dihydroxyphenyl) acryloyloxy)-1,4,5-trihydroxycyclohexane carboxylic acid (DHTH) and 2-Phenyl-4H-chromen-4-one (PCO). Semiempirical PM3 method was employed to optimize the compounds by selecting 'Polak Ribiere' algorithm and RMS gradient of 0.1 kcal/Å Mol (75 maximum cycles). Single point energy calculations were performed using PM3 method to obtain $E_{\text{HOMO}}/E_{\text{LUMO}}$ and total energy of the molecules. Theoretical electronic absorption spectra were predicted by selecting ZINDO/1 and ZINDO/s options of the semiempirical method using 3 occupied and 3 unoccupied electrons. Hyperchem Professional 08 was employed for all computational measurements.

RESULTS AND DISCUSSION

The chemical adsorption of dyes (1S,3R,4R,5R-3-(3,4-dihydroxyphenyl) acryloyloxy)-1,4,5-trihydroxycyclohexane carboxylic acid (DHTH) and 2-Phenyl-4H-chromen-4-one (PCO) (Scheme 1) was first performed independently on to TiO_2 crystal to form adsorption complexes designated as TiO_2 -DHTH and TiO_2 -PCO respectively in the forthcoming section. The choice of the dyes was made based on their HOMO and LUMO energy values as obtained from the computational calculations. For this purpose, the molecules were first optimized and subjected to single point energy calculations using semiempirical PM3 method. These calculations provided us the total energies and $E_{\text{HOMO}}/E_{\text{LUMO}}$ values enabled us to predict electron flow in a cascade manner from DHTH to PCO and finally to TiO_2 . The energy level diagram is represented in Scheme 1.

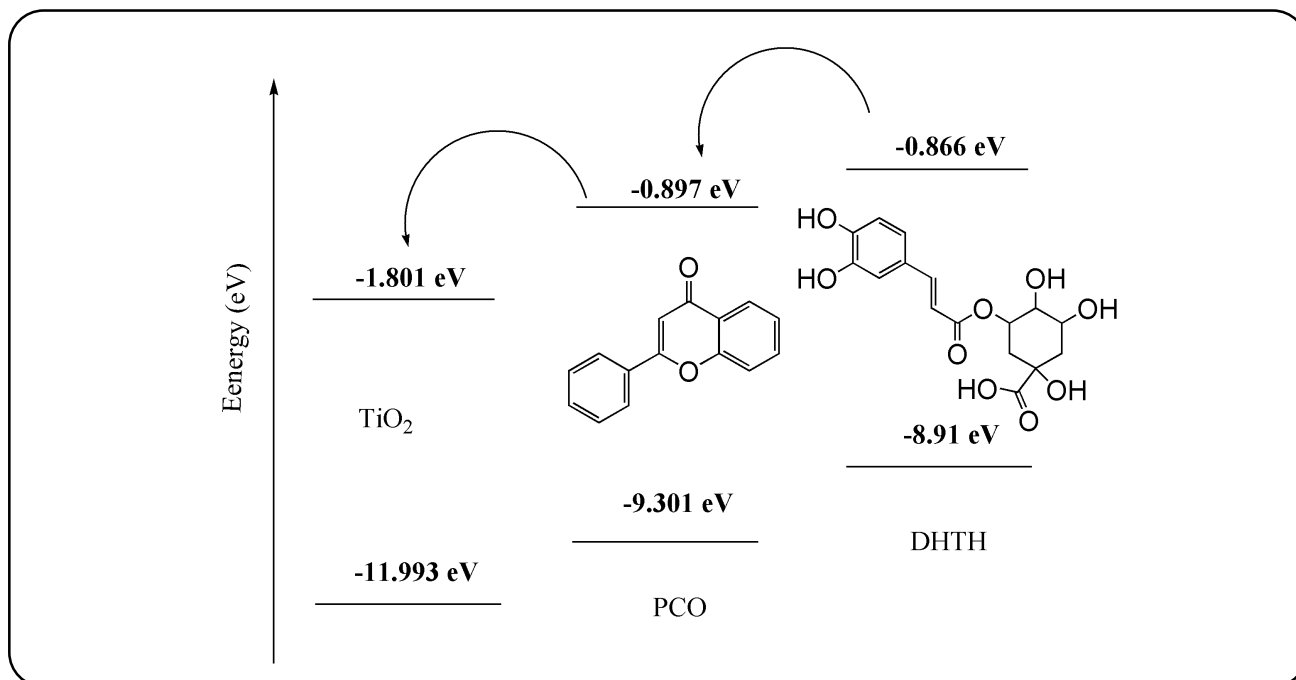
The graphical representation of the HOMO and LUMO of PCO and DHTH obtained through single point energy calculations is displayed in Fig. 1.

The spectroscopic properties of un-adsorbed dyes were also evaluated to see the effect of adsorption afterwards, by calculating the theoretical electronic absorption spectra for PCO and DHTH independently, through ZINDO/s and ZINDO/1 option of the semiempirical method (Fig. 2). The calculated absorption spectra via ZINDO/s method revealed the highest wavelength absorption peak at 281 nm

for PCO, closer to the literature quoted absorption peaks of the related compounds (see Fig. 2) [29, 30]. The theoretical absorption spectrum obtained by selecting ZINDO/1 option of the semiempirical method, displayed λ_{max} and highest absorption at 141 nm, contradicting with the literature quoted values and establishing that ZINDO/s is more accurate in predicting the spectroscopic properties of the molecules. Similarly, we calculated the absorption spectrum for pristine DHTH molecule using both ZINDO/s and ZINDO/1 options of the semiempirical method and compared the theoretical results with the literature reported values of the closely related compounds. The absorption peaks of DHTH were located in the range of 181-288 nm by employing ZINDO/s option, proximate to the literature quoted values [31, 32] whereas ZINDO/1 option resulted in an absorption spectrum in the range of 124-145 nm. We therefore choose ZINDO/s option to further investigate the spectroscopic properties of the adsorption complexes of dyes on TiO_2 . The absorption spectrum was also obtained for pristine TiO_2 crystal displaying λ_{max} at 191.5 nm and a minor absorption peak at 519 nm (see Fig. 2).

After evaluating the electrochemical and optical properties of the dyes and TiO_2 independently, we investigated the adsorption of each dye on TiO_2 . The adsorption of PCO on TiO_2 was accomplished via attachment with doubly bonded oxygen. For this purpose, one of the double bonds was removed and oxygen was bonded with Ti^{4+} of TiO_2 crystal. The adsorbed structure, designated as TiO_2 -PCO, was then optimized, and single point energy calculations were performed to obtain the total energy of the adsorbed structure (see Fig. 3) which was found to be -89957.539 kcal/mol. Similarly, DHTH was also adsorbed separately on TiO_2 via -OH group where proton was removed, and oxygen was bonded with Ti^{4+} of TiO_2 crystal (ref. Fig. 3). The resulting adsorbed complex was labelled as TiO_2 -DHTH. The total energy of TiO_2 -DHTH, determined using single point energy calculations, was found to be -142588.156 kcal/mol.

It is to be noted that the total energy of the complex TiO_2 -DHTH is much more negative compared to the TiO_2 -PCO predicting the former to be more stable as compared to the latter. The high stability could be attributed to the facile -O-Ti bonding in the adsorption complex formed using DHTH where the proton of -OH can be easily removed, as in the case of PCO, the double bond has to



Scheme 1: The energy level diagram showing a cascade flow of electrons from DHTH to PCO and finally to TiO_2 based on $E_{\text{HOMO}}/E_{\text{LUMO}}$ values obtained using semiempirical PM3 calculations.

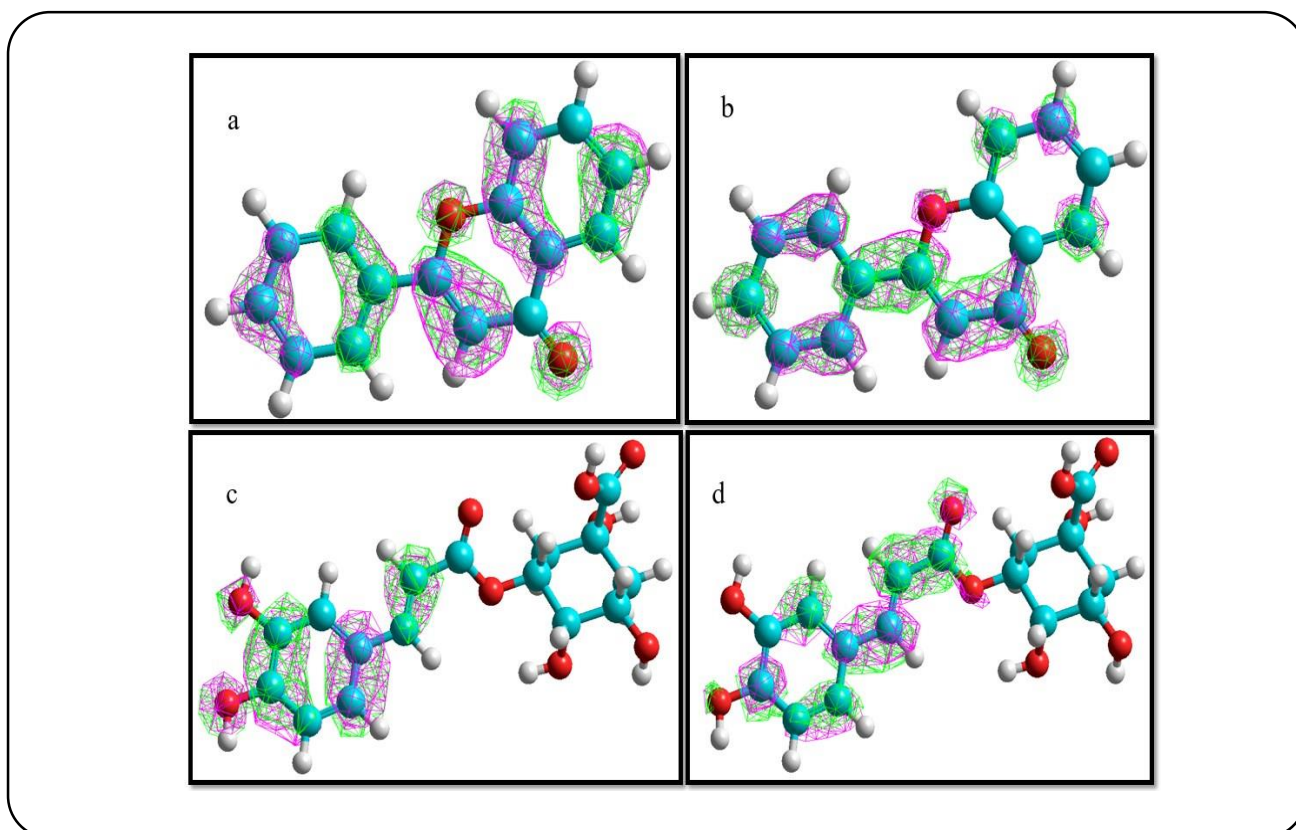


Fig. 1: The graphical representation of the HOMO (a) and LUMO (b) of PCO and HOMO (c) and LUMO (d) of DHTH.

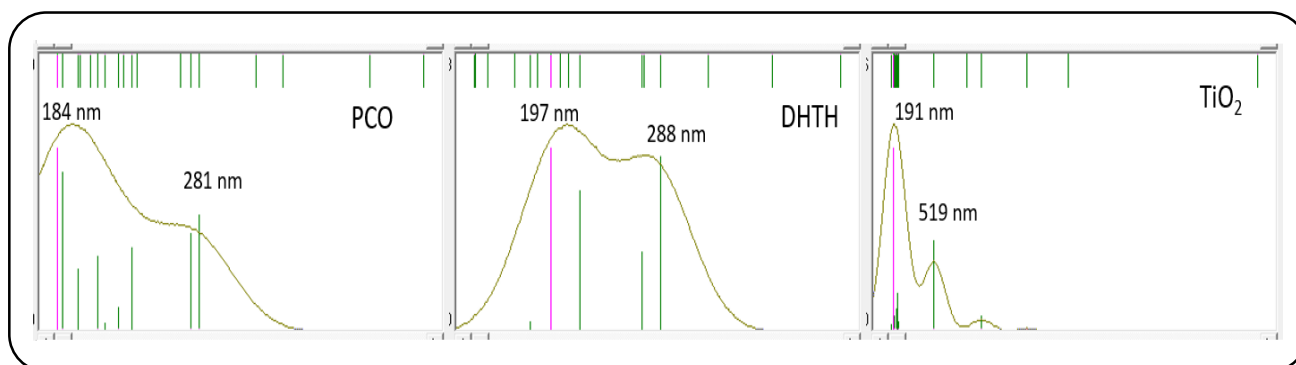


Fig. 2: Theoretical electronic absorption spectra of PCO, DHTH and TiO_2 obtained using semiempirical ZINDO/s method.

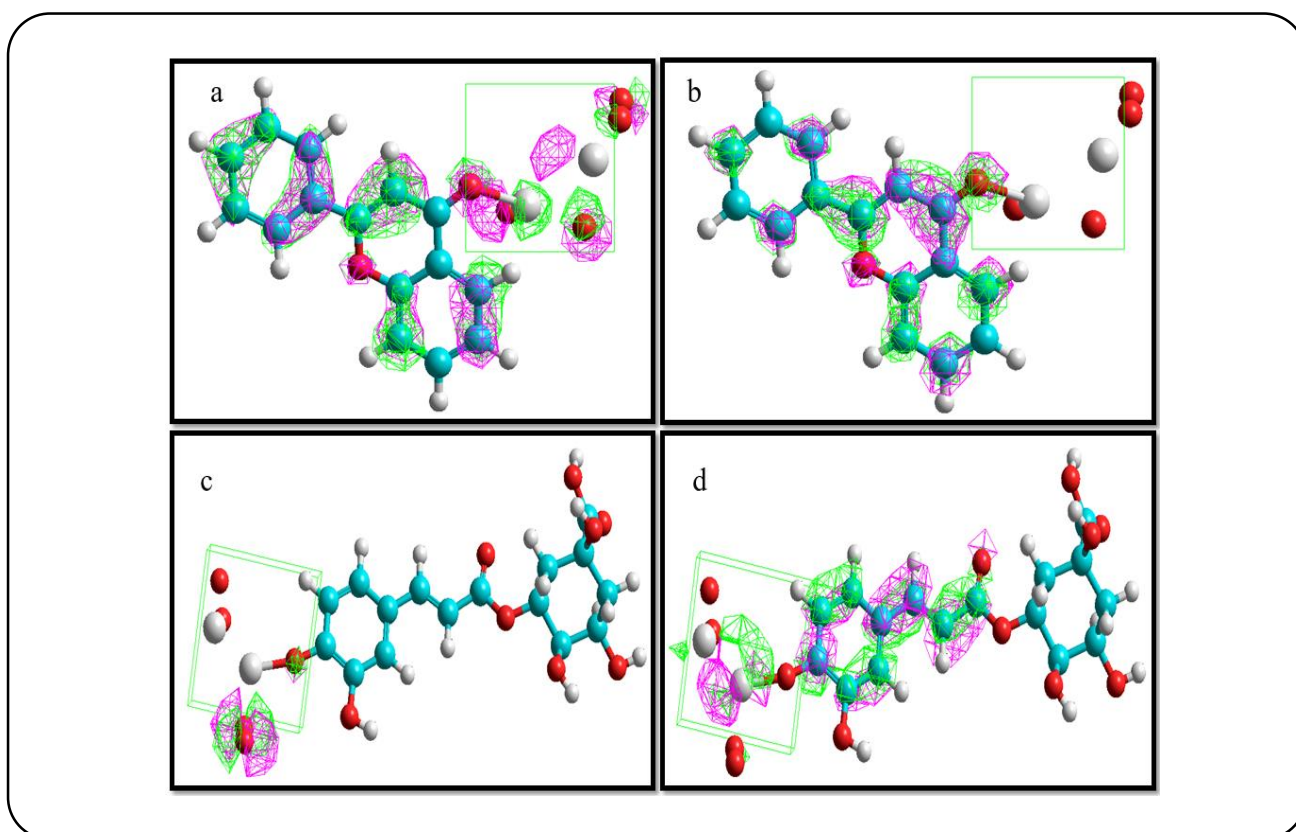


Fig. 3: The graphical representation of the HOMO (a) and LUMO (b) of TiO_2 -PCO and HOMO (c) and LUMO (d) of TiO_2 -DHTH.

converted to single bond for $-\text{O}-\text{Ti}$ bonding and considerably less facile.

The spectroscopic properties of the adsorption complexes TiO_2 -PCO and TiO_2 -DHTH were evaluated using semiempirical ZINDO/s method. The theoretical electronic absorption spectra of the two adsorption complexes obtained in this way are displayed in Fig. 4 and can be compared with the absorption spectra of un-adsorbed dyes. It is interesting to note that the absorption

spectrum of TiO_2 -PCO is considerably red shifted with the absorption extending up to 526 nm as compared to the absorption of un-adsorbed PCO (281 nm).

The considerable red shift might be the result of charge transfer from PCO to TiO_2 resulting in charge transfer transitions [33]. The theoretical absorption spectrum of TiO_2 -DHTH also shows large red shift up to 810 nm as compared to the 288 nm of the un-adsorbed dye. The large red shift is a strong indication of charge transfer between

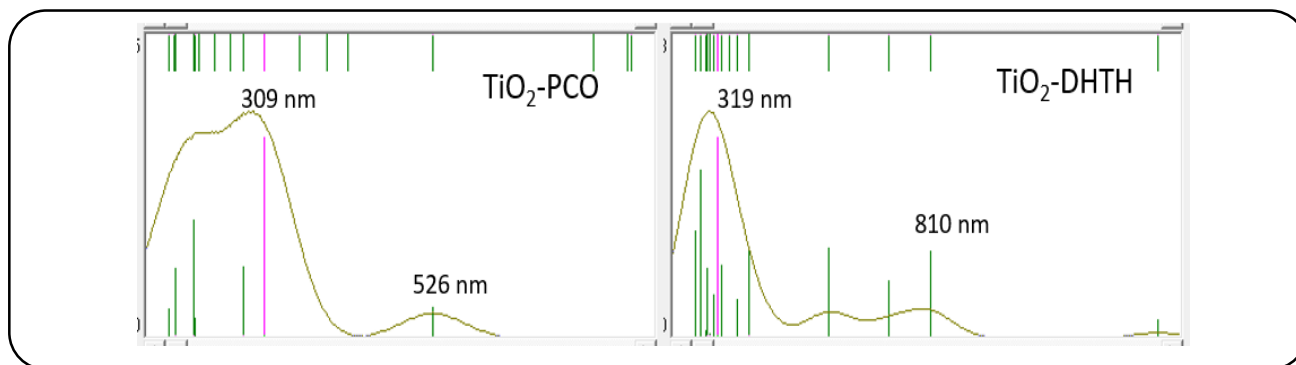


Fig. 4: The theoretical electronic absorption spectra of $\text{TiO}_2\text{-PCO}$ and $\text{TiO}_2\text{-DHTH}$ determined using semiempirical ZINDO/s method.

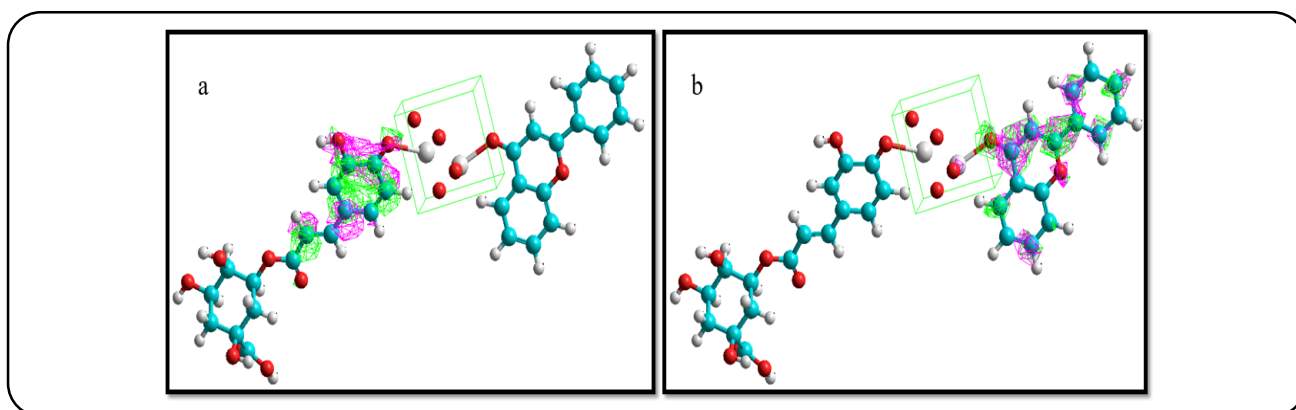


Fig. 5: The graphical representation of the HOMO (left) and LUMO (right) of $\text{TiO}_2\text{-PCO-DHTH}$ manifesting the electron transfer from DHTH to PCO.

dye and TiO_2 [34]. The extension of the absorption range shows the high potential of these dyes to be used in DSSCs.

Subsequently we investigated the co-adsorption of PCO and DHTH on $1 \times 1 \times 1$ TiO_2 crystal to evaluate the spectroscopic properties of the resulting complex, designated as $\text{TiO}_2\text{-PCO-DHTH}$ in the forthcoming sections. The aim of co-adsorption in hybrid solar cells is to cover the broad absorption range as well as reduce the charge recombination rate which is a major setback in achieving high efficiency. The co-adsorption was achieved by attaching PCO with Ti^{4+} of TiO_2 via doubly bonded oxygen after breaking one bond, and DHTH to the other Ti^{4+} of TiO_2 via $-\text{OH}$ group after removing proton. The total energy of the complex obtained from single point energy calculation was found to be -200678.578 kcal/mol. Based on the total energy values we can predict and compare the stabilities of $\text{TiO}_2\text{-PCO}$, $\text{TiO}_2\text{-DHTH}$ and $\text{TiO}_2\text{-PCO-DHTH}$ where the co-adsorption complex is found to be more stable owing to the most negative total energy.

The graphical representation of the HOMO and LUMO orbitals in $\text{TiO}_2\text{-PCO-DHTH}$ is manifested in Fig. 5. It is

very interesting to note that the location of the orbitals coincides accurately with our proposition of electron flow in a cascade manner from DHTH to PCO and finally to TiO_2 . This can be understood by considering $\text{TiO}_2\text{-PCO-DHTH}$ as one moiety where HOMO is located on the DHTH side of the molecule whereas the LUMO is situated on the PCO structure.

The spectroscopic properties of the co-adsorption complex were then determined by calculating theoretical electronic absorption spectrum where λ_{max} was found to be located at 803 nm (see Fig. 6). The absorption range of the co-adsorption complex was evidenced to be in the range of 351.8-800 nm covering the most part of the visible light.

CONCLUSIONS

- The co-adsorption of two dyes namely (1S,3R,4R,5R-3-(3,4-dihydroxyphenyl) acryloyloxy)-1,4,5-trihydroxycyclohexane carboxylic acid (DHTH) and 2-Phenyl-4H-chromen-4-one (PCO) was achieved on $1 \times 1 \times 1$ TiO_2 crystal structure and its electrochemical

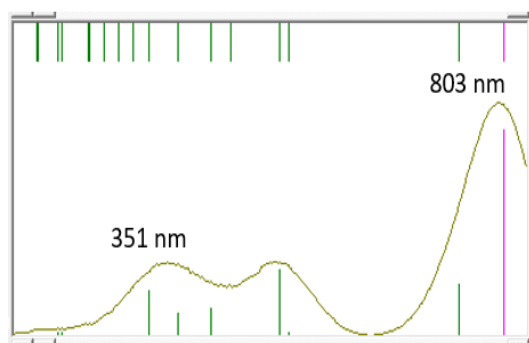


Fig. 6: The theoretical electronic absorption spectra of TiO_2 -PCO-DHTH determined using semiempirical ZINDO/s method.

and spectroscopic properties were evaluated using semi-empirical computational method.

- It was found that the co-adsorption complex formed by the simultaneous adsorption of two dyes on TiO_2 resulted in a photoactive charge transfer complex where electron transfer can take place in a cascade manner from DHTH to PCO to TiO_2 .

- The spectroscopic analysis shows a broad absorption range of the material up to 803 nm demonstrating its high potential for application in hybrid solar cells.

- The stability of the materials was evident from large negative total energy of be -200678.578 kcal/mol as obtained from the single point energy calculations.

Nomenclature

DHTH	(1S,3R,4R,5R-3-(3,4-dihydroxyphenyl)acryloyloxy)-1,4,5-trihydroxycyclohexane carboxylic acid
PCO	2-Phenyl-4H-chromen-4-one
TiO_2 -DHTH	(1S,3R,4R,5R-3-(3,4-dihydroxyphenyl)acryloyloxy)-1,4,5-trihydroxycyclohexane carboxylic acid adsorbed on TiO_2
TiO_2 -PCO	2-Phenyl-4H-chromen-4-one adsorbed on TiO_2
TiO_2 -PCO-DHTH	2-Phenyl-4H-chromen-4-one and (1S,3R,4R,5R-3-(3,4-dihydroxyphenyl)acryloyloxy)-1,4,5-trihydroxycyclohexane carboxylic acid adsorbed on TiO_2
HOMO	Highest occupied Molecular orbital
LUMO	Lowest Unoccupied Molecular orbital

Acknowledgments

The authors are highly thankful to the Women University Swabi, and National University of Technology, Islamabad, Pakistan for providing computational chemistry laboratory facilities.

Received : Jun. 11, 2019 ; Accepted : Sep. 27, 2019

REFERENCES

- [1] Fakharuddin A., Jose A., Brown M.T., Fabregat-Santiago F., Bisquert J., [A Perspective on the Production of Dye-Sensitized Solar Modules](#), *Energy Environ. Sci.*, **7**(12): 3952-3981 (2014).
- [2] Erten-Ela S., Cagatay Cakir A., [Dye Sensitized Solar Cells for Conversion of Solar Energy into Electricity](#), *Energy Sources, Part A*, **37**(8): 807-816 (2015).
- [3] Oregan B., Grätzel M., [A Low-Cost, High-Efficiency Solar Cell Based on Dye-Sensitized Colloidal \$\text{TiO}_2\$ Films](#), *Nature*, **353**(6346): 737- 740 (1991).
- [4] Grätzel M., [Photoelectrochemical Cells](#), *Nature*, **414**(6861): 338- 344 (2001).
- [5] Ragoussi E.M., Torres T., [New Generation Solar Cells: Concepts, Trends and Perspectives](#), *Chem. Commun.* **51**(19): 957-3972 (2015).
- [6] Zhang L., Konno A., [Development of Flexible Dye-Sensitized Solar Cell Based on Pre-Dyed Zinc Oxide Nanoparticle](#), *Int. J. Electrochem. Sci.*, **13**(1): 344-352 (2018).
- [7] Wali Q., Fakharuddin A., Jose A., [Tin Oxide as a Photoanode for Dye-Sensitized Solar Cells: Current Progress and Future Challenges](#), *J. Power Sources*, **293**: 1039-1052 (2015).
- [8] Wali Q., Bakr H.Z., Manshor A.N., Fakharuddin A., Jose R., [\$\text{SnO}_2\$ - \$\text{TiO}_2\$ Hybrid Nanofibers for Efficient Dye-Sensitized Solar Cells](#), *Solar Energy*, **132**: 395-404 (2016).
- [9] Bakr H.Z., Wali Q., Ismail J., Elumalai K.N., Uddin A., Jose R., [Synergistic Combination of Electronic and Electrical Properties of \$\text{SnO}_2\$ and \$\text{TiO}_2\$ in a Single \$\text{SnO}_2\$ - \$\text{TiO}_2\$ Composite Nanofiber for Dye-Sensitized Solar Cells](#), *Electrochim. Acta*, **263**: 524-532 (2018).
- [10] Bakr H.Z., Wali Q., Yang S., Yousefsadeh M., Padmasree P.K., Ismail J., Ab Rahim H.M., Yusoff M.M., Jose R., [Characteristics of \$\text{ZnO}\$ - \$\text{SnO}_2\$ Composite Nanofibers as a Photoanode in Dye-Sensitized Solar Cells](#), *Ind. Eng. Chem. Res.*, **58**(2): 643-653 (2018).
- [11] Mao X., Zhou R., Zhang S., Ding L., Wan L., Qin S., Chen Z., Xu J., Miao S., [High Efficiency Dye-Sensitized Solar Cells Constructed with Composites of \$\text{TiO}_2\$ and the Hot-Bubbling Synthesized Ultra-Small \$\text{SnO}_2\$ Nanocrystals](#), *Scientific Reports*, **6**: 19390 (2016).

- [12] Kunzmann A., Valero S., Sepúlveda E.A., Rico-Santacruz M., Lalinde E., Berenguer R.J., García-Martínez J., Guldi M.D., Serrano E., Costa D.R., [Hybrid Dye-Titania Nanoparticles for Superior Low-Temperature Dye-Sensitized Solar Cells](#), *Adv. Energy Mater.*, **8(12)**: 1702583 (2018).
- [13] Erten-Ela S., Ueno Y., Asaba T., Kubo Y., [Synthesis of a Dibenzo-BODIPY-Incorporating Phenothiazine Dye as a Panchromatic Sensitizer for Dye-Sensitized Solar Cells](#), *New J. Chem.*, **41(18)**: 10367-10375 (2017).
- [14] Çakmak Y., Kolemen S., Buyuktemiz M., Dede Y., Erten-Ela S., [Synthesis and Dye Sensitized Solar Cell Applications of Bodipy Derivatives with Bis-Dimethylfluorenyl Amine Donor Groups](#), *New J. Chem.*, **39(5)**: 4086-4092 (2015).
- [15] Yella A., Lee W.H., Tsao N.H., Yi C., Chandiran K.A., Nazeeruddin K.M., Diau W.G.E., Yeh Y.C., Zakeeruddin M.S., Grätzel M., [Porphyrin-Sensitized Solar Cells with Cobalt \(II/III\)-Based Redox Electrolyte Exceed 12 Percent Efficiency](#), *Science*, **334(6056)**: 629-634 (2011).
- [16] Hardin E.B., Yum J.H., Hoke T.E., Jun C.Y., Péchy P., Torres T., Brongersma L.M., Nazeeruddin K.M., Grätzel M., McGehee D.M., [High Excitation Transfer Efficiency From Energy Relay Dyes In Dye-Sensitized Solar Cells](#), *Nano Lett.*, **10(8)**: 3077-3083 (2010).
- [17] Huang S., Schlichthörl G., Nozik A., Grätzel M., Frank A., [Charge Recombination in Dye-Sensitized Nanocrystalline TiO₂ Solar Cells](#), *J. Phys. Chem. B*, **101(14)**: 2576-2582 (1997).
- [18] Palomares E., Clifford N.J., Haque A.S., Lutz T., Durrant R.J., [Control of Charge Recombination Dynamics in Dye Sensitized Solar Cells by the Use of Conformally Deposited Metal Oxide Blocking Layers](#), *J. Am. Chem. Soc.*, **125(2)**: 475-482 (2003).
- [19] Wali Q., Fakharuddin A., Ahmed I., Ab Rahim H.M., Ismail J., Jose R., [Multiporous Nanofibers of SnO₂ by Electrospinning for High Efficiency Dye-Sensitized Solar Cells](#), *J. Mater. Chem. A*, **2(41)**: 17427-17434 (2014).
- [20] Erten-Ela S., [Characterization and Performance Evaluation of Dye Sensitized Solar Cell Using Nanostructured TiO₂ Electrode](#), *Int. J. Photoenergy*, **2014**: 6 (2014).
- [21] Morandeira A., López-Duarte I., O'Regan B., Martínez-Díaz V.M., Forneli A., Palomares E., Torres T., Durrant R.J., [Ru \(II\)-Phthalocyanine Sensitized Solar Cells: the Influence of Co-Adsorbents Upon Interfacial Electron Transfer Kinetics](#), *J. Mater. Chem.*, **19(28)**: 5016-5026 (2009).
- [22] Kim G.B., Chung K., Kim J., [Molecular Design Principle of All-Organic Dyes for Dye-Sensitized Solar Cells](#), *Chem. - Eur. J.*, **19(17)**: 5220-5230 (2013).
- [23] Lee H.G., Kim S.Y., [Theoretical Study of an Asymmetric A-II-D-II-D-II-A' Tribranched Organic Sensitizer For Dye-Sensitized Solar Cells](#), *J. Korean Phys. Soc.*, **69(3)**: 381-385 (2016).
- [24] Wielopolski M., Moser E.J., Marszalek M., Zakeeruddin S., Grätzel M., [II-Conjugated Donor-Acceptor Systems as Metal-Free Sensitizers For Dye-Sensitized Solar Cell Applications](#), *EPJ Web of Conferences*, 08013 (2013).
- [25] El-Shishtawy M.R., Asiri M.A., Aziz G.S., Elroby A.S., [Molecular Design of Donor-Acceptor Dyes for Efficient Dye-Sensitized Solar Cells I: A DFT Study](#), *J. Mol. Model.*, **20(6)**: 2241 (2014).
- [26] Munir S., Begum M., Nosheen, [Computational Investigations of a Novel Photoactive Material for Potential Application in Dye Sensitized Solar Cells](#), *Asian J. Green Chem.*, **3(1)**: 91-102 (2019).
- [27] Ocakoglu K., Sogut S., Sarica S., Guloglu P., Erten-Ela S., [Influences of the Electron Donor Groups on the Properties of Thiophene-Pyrrole-Thiophene and Tert-Butyl Based New Ruthenium II Bipyridyl Sensitizers for DSSCs and DFT Studies](#), *Synth. Met.*, **174**: 24-32 (2013).
- [28] Liu N.J., Chen R.Z., Yuan F.S., [Study on the Prediction of Visible Absorption Maxima of Azobenzene Compounds](#), *J. Zhejiang Univ. Sci. B*, **6(6)**: 584 (2005).
- [29] Sancho I.M., Almandoz C.M., Blanco E.S., Castro A.E., [Spectroscopic Study of Solvent Effects on the Electronic Absorption Spectra of Flavone and 7-Hydroxyflavone In Neat and Binary Solvent Mixtures](#), *Int. J. Mol. Sci.*, **12**: 8895-8912 (2011).
- [30] Solovchenko A., [Photoprotection of Plants via Optical Screening](#), *Semantic Scholar*, **2016**: 5032169 (2016).

- [31] Navarra G., Moschetti M., Guarrasi V., Mangione M., Militello V., Leone M., [Simultaneous Determination of Caffeine and Chlorogenic Acids in Green Coffee by UV/Vis Spectroscopy](#), *J. Chem.*, **2017**: 6435086 (2017).
- [32] Belay A. Gholap A., [Characterization and Determination of Chlorogenic Acids \(CGA\) in Coffee Beans by UV-Vis Spectroscopy](#), *Afr. J. Pure Appl. Chem.*, **3(11)**: 34-240 (2009).
- [33] Munir S., Shah M.S., Hussain H., Siddiq M., [Adsorption of Porphyrin and Carminic Acid on TiO₂ Nanoparticles: a Photo-Active Nano-Hybrid Material for Hybrid Bulk Heterojunction Solar Cells](#), *J. Photochem. Photobiol.*, **153**: 397-404 (2015).
- [34] Shahzad N., Shah M.S., Munir S., Hana A., Jabeen U., Nosheen E., Habib B., Khan U.A., Hassan Z., Siddiq M., [Charge-Transfer Complexation at Carminic Acid-Cds Interface and its Impact on the Efficiency of Dye-Sensitized Solar Cells](#), *J. Electron. Mater.*, **44(4)**: 1167-1174 (2015).