TITLE: Development of efficient solar cells using combination of QSPR and DFT approaches

GRANT NO.: DE-SC0018322

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RESEARCH ACCOMPLISHMENT

Section A: Exploration of effective photosensitizers for dye-sensitized solar cell (DSSC) and polymer solar cell (PSC) using QSPR and DFT

The awarded research project aimed to design and determine the effective organic dye-sensitizers from the ensemble of chromophores for the dye-sensitized solar cell (DSSC) and fullerene-derivatives (FDs) as acceptor for polymer solar cell (PSC) followed by explore the electron transfer mechanism using the combined quantitative structure-property relationship (QSPR) analysis in conjunction with density functional theory (DFT) and time-dependent DFT (TDDFT)-based calculations. Based on our proposal we have employed different *in silico* approaches to design photo-efficient organic dye-sensitizers for DSSCs and FDs as acceptor for PSCs with exhaustive screening methodology.

1. Study on DSSC

To understand the primary electron transfer mechanism and photo-physical properties of 273 arylamine organic dyes (AODs) from 11 diverse chemical families explicit to iodine electrolyte used to build the QSPR model equation **[1]**. The direct QSPR models enable identification of the essential electronic and structural attributes necessary for quantifying the molecular prerequisites of 11 classes of AOD, responsible for high PCE of DSSCs. The identified properties from the corresponding QSPR models of the Tetrahydroquinoline, N,N'-dialkylaniline and indoline were employed in the designing of 'lead dyes'. Followed by, a series of electrochemical and photo-physical parameters were computed for designed dyes to check the required variables for electron flow of DSSCs.

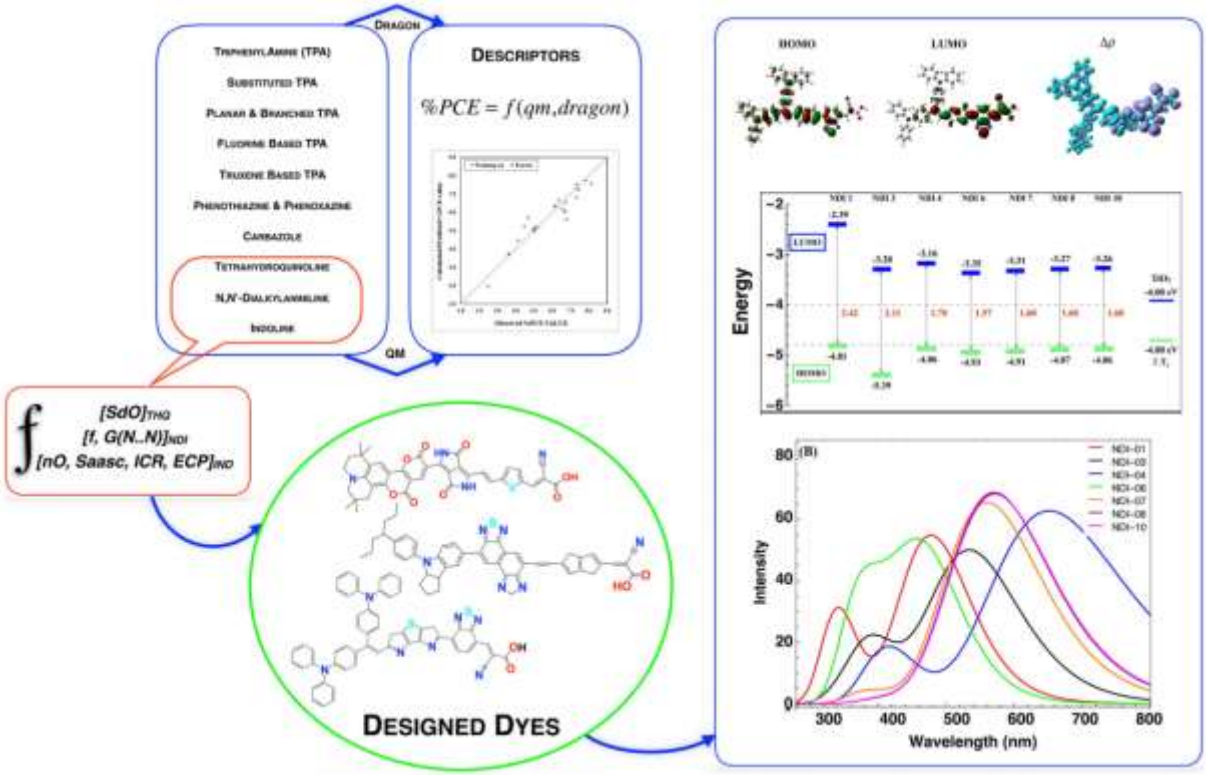

Figure 1.1: Schematic of the work published in *NPJ Computational Materials*.

Quantum chemical properties of the designed dyes such that electrochemical parameters, absorption spectra and contour plots of HOMO and LUMO of each lead dyes helped us to check required electrochemical environment for fast electron transfer rate in the composite DSSCs system to support their better PCE. The combined computational techniques yielded 7 promising 'lead dyes' each for all 3 chemical classes considered. Significant (130%, 183% and 46%) increment in predicted %PCE was observed comparing with the existing dye with highest experimental %PCE value for tetrahydroquinoline, N,N'-dialkylaniline and indoline, respectively maintaining required electrochemical parameters.

Proposed novel seven 'lead' dye-sensitizers from Tetrahydroquinoline (THQ) family were further investigated to reveal the photophysical properties like electron injection, charge transfer and separation of the isolated dyes as well the interface of the dye and TiO_2 semiconductor. We have performed systematic, comprehensive investigations to evaluate seven 'lead THQ dyes' to explore their potential applications as photosensitizers for DSSCs. Compelling photophysical properties such as electron injection driving force, electron injection time, and dye regeneration were studied for the isolated dyes under the DFT and TD-DFT frameworks. Index of spatial extent (S, D, and Δq), the strength of charge transfer and separation along with the charge transfer process is explored. Results from isolated dyes can be summarized as follows: THQ9 emerged among the top three dyes concerning charge transfer characteristics (S, τ, qCT, λ_{total}) while giving lower value for open circuit voltage (V_{OC}), and electron injection energy (ΔG_{inject}) than other considered dyes. We also compute the non-covalent redox shuttle interactions to elucidate the charge recombination process and we found that all the designed dyes are feasible to overcome this process. Thus, will provide higher PCE values. We have performed periodic DFT calculations including van der Waals density functional to understand the interfacial behavior of dye and semiconductor. Outcomes from periodic DFT calculations indicates that all of the designed dyes have optimal interfacial behavior. Introspecting the geometrical interface structures, PDOS, planar averaged charge density and potential energy difference of dye@TiO_2 system; we infer that there is robust electronic coupling between all dyes and TiO_2 surface. The PCEs of THQ7, THQ8, and THQ9 dyes are better than for the other four dyes when dye@TiO_2 are considered, due to their lowest adsorption energy, lower band gap and higher Bader charge. Interestingly, the other four dyes also possess all required electrochemical parameters to act as efficient and improved dye sensitizers for DSSCs, compared to the products exist dyes of THQ family. Therefore, the insertions of double bonded oxygen to the aromatic carbon certainly improve the photovoltaic performance and energy conversion efficiency of sensitizers **[2]**.

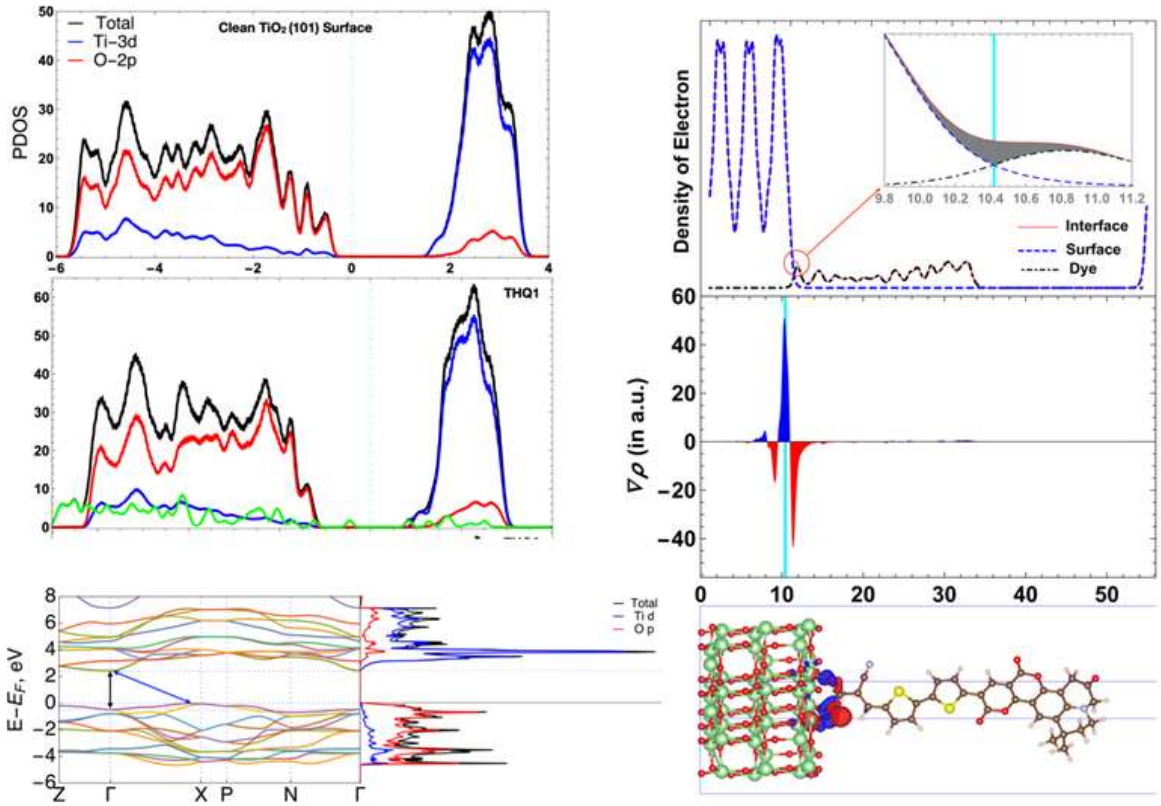

Figure 1.2: Overview of the work published in *Scientific Reports*.

Designed D-A-π-A based Indoline (IND) dyes have been comprehensively investigated using computational approaches to evaluate their prospect of application in future DSSCs. An array of optoelectronic properties of the isolated dye and dyes adsorbed on a TiO_2 cluster that simulates the semiconductor were explored by DFT and TDDFT methods. We modified the D-π-A framework with the inclusion of one internal acceptor unit in between donor and π-bridge. We used pyrido[3,4-b]pyrazine and benzothiadiazole unit as an internal acceptor. Effects of structural modification via molecular design on different photophysical properties should balance optimal J_{SC} and V_{OC} values. The various key parameters associated with the V_{OC} and J_{SC} such as vertical dipole moment (μ_{normal}), shift of the conduction band edge (CBE) of semiconductor, excited state life time (τ), photostability of the dyes after electron transfer, driving force of electron injection (ΔG_{inject}), and exciton binding energy ($_{Eb}$) were computed along with natural population analysis (NPA) based analysis was conducted to explore the atomic charge distribution at interface. Due to the widened optical absorption, longer excited state lifetime, highest photostability, highest vertical dipole moment and lowest exciton binding energy, IND3 would exhibit the better optical and electrical properties than the other considered dyes. The presence of Pyrazine based internal acceptor unit in IND3 is responsible for the enhancement of above-mentioned properties. Based on the Marcus theory calculation, the ability of hole transfer of IND5, IND7, IND9 and IND10 would be higher than the electron transfer arising from their lower hole reorganization energies, whereas IND5 is the best candidate for intra-molecular charge transfer (ICT) with the lowest reorganization energy (λ_{total}). Also, the optical gap of IND5 would leverage higher values of J_{SC}. Our study showed that presence of internal acceptor such as pyrido[3,4-b]pyrazine would influence greater the V_{OC}, compare to the benzothiadiazole moiety. Considering the balance between the V_{OC} and J_{SC} along with the all calculated characteristics, the IND3, IND5 and IND10 are the most suited among the designed dyes to be used as potential candidates for the photo efficient DSSCs **[3]**.

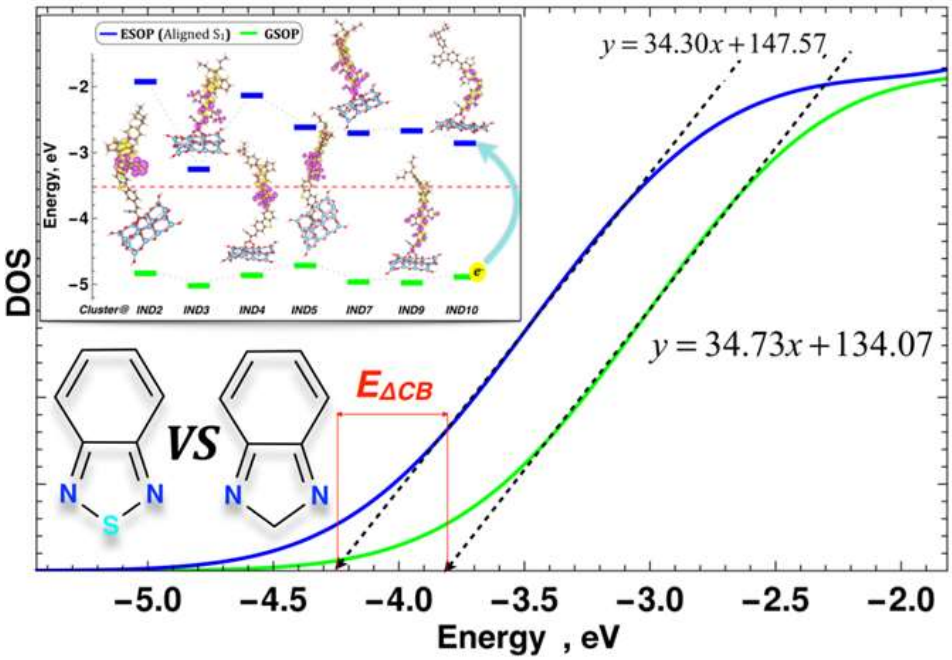

Figure 1.3: Overview of the JPCC work.

We have performed chemometric modeling of PCE data of DSSCs using the biggest available data set till date. It comprises around 1200 dyes covering 7 chemical classes **[4]**. To extract the best structural features required for higher PCE, we have developed multiple QSPR models. The partial least squares (PLS) models for the Triphenylamine, Phenothiazine, Indoline, Porphyrin, Coumarin, Carbazole and Diphenylamine datasets have been developed using descriptors derived from the best subset selection method. Among the models obtained from the best subset selection, we have selected five models in each dataset based on the Mean Absolute Error (MAE) values. The models were validated both internally and externally followed by the consensus predictions using the developed PLS models employing "Intelligent Consensus Predictor" tool to examine whether the quality of predictions of the test set compounds can be

improved. The quality of predictions for the respective external sets showed that the consensus models are better than the individual models in most of the cases. From the insights of the developed models, we concluded that attributes like a packed structure toward higher conductivity of electrons, auxiliary donor fragment of aromatic tertiary amines, number of thiophenes inducing the bathochromic shift and augmenting the absorption, presence of additional electron donors, enhancement of electron-donating abilities, number of non-aromatic conjugated C(sp2) which helps as conjugation extension units to broaden the absorption and highly conjugated π-systems exert positive contributions to the PCE. On the contrary, features negatively contributing to PCE are the followings: fragments which lower the tendency of localized π–π* transition, fragments related to larger volume and surface area of dyes along with hydrophobicity resulting in poor adhesion, fragment RC=N causing dye hydrolysis, steric hindrance for π electronic mobility, fragments enhancing polarity, *etc*. The developed models are useful for quick prediction of PCE of new/untested dyes along with designing of new dyes employing the deep mechanistic structural insights **[4]**.

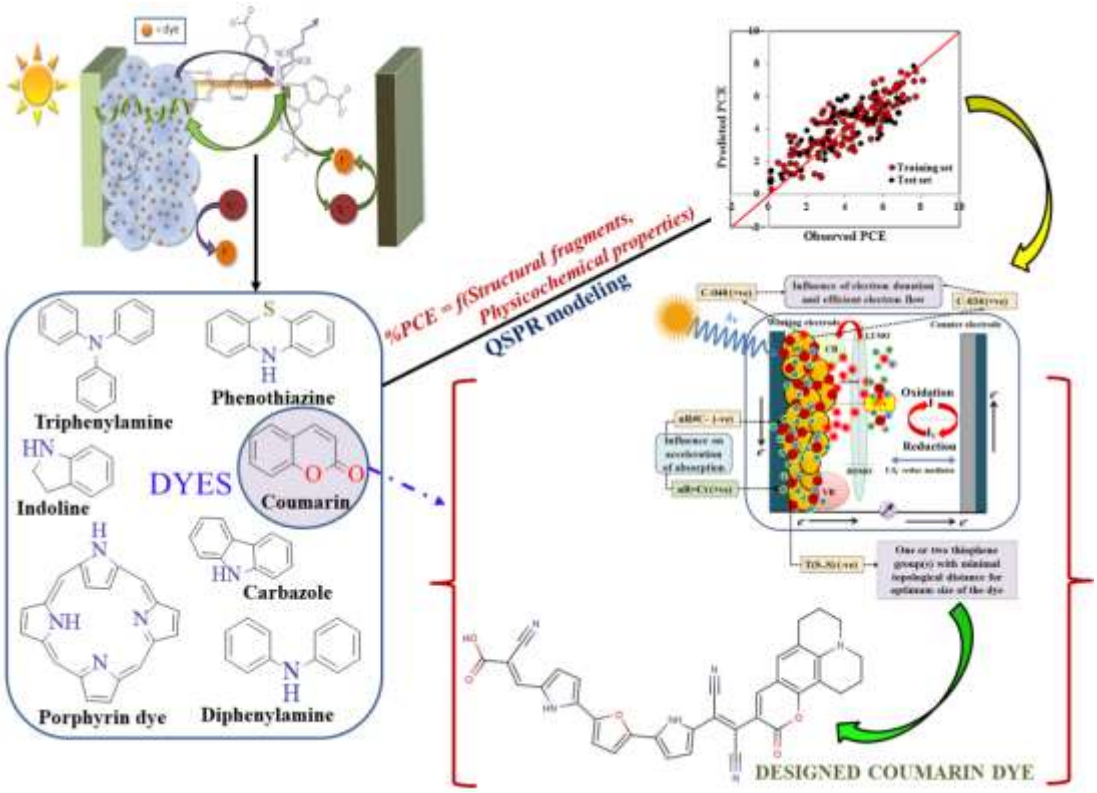

Figure 1.4: Overview of the Nano Energy work

2. Study on PSC

Ten novel FDs of C_{60} and C_{70} had been designed as acceptor for PSC by employing QSPR model which was developed strategically with reasonably big pool of experimental PCE data. The QSPR model was checked and validated with stringent parameter and reliability of predicted PCE values of all designed FDs. The predicted PCE of FDs range from 7.96 to 23.01 **[5]**. The obtained encouraging results led us to do the additional theoretical analysis of the energetics and UV-Vis spectra of isolated dyes employing DFT and TD-DFT calculations using PBE/6-31G(d,p) and CAM-B3LYP/6-311G(d,p) level calculations, respectively. Frontier orbital energies and UV-Vis absorption spectra of the isolated poly(3-hexylthiophene (P3HT) oligomer, PCBM and FDs were analyzed to estimate the optoelectronic properties of four FDs as an acceptor in future PSCs. Exciton binding energy plays the pivot role at interface when excitons to diffuse and dissociated into electrons on LUMO level of the acceptor. The big off-set of LUMO energy levels will hinders this process. FD4 is the best C_{60}-derivatives candidates for PSCs as it has the lowest exciton binding energy, up-shifted LUMO energy level that assist to increase V_{OC} and strong absorption in the UV region. The FD4 is the best C_{60}-derivatives candidates for PSCs as it has the lowest exciton binding energy, up-shifted LUMO energy level to increase V_{OC} and strong absorption in the UV region. In case of C_{70}-derivatives, FD7 is potential candidate for future PSCs due to its strong absorption in UV-Vis region

and lower exciton binding energy with higher V_{OC}. By trading off the computed optoelectronic properties, our analysis supports our QSPR model which predict highest PCE values for FD4. The structural analysis concluded the following points: (1) Ortho directing groups in the benzene rings and aromatic rings like phenyl, thiophene, pyrrole attached to the fullerene are significant features for better PCE of PSCs. and (2) Saturated carbon chains, (3) or higher –ortho substituents in benzene rings and a higher number of attachments in the parent fullerene core need to be avoided for higher PCE along with structural fragments with a lower solvent accessible surface area of polar atoms.

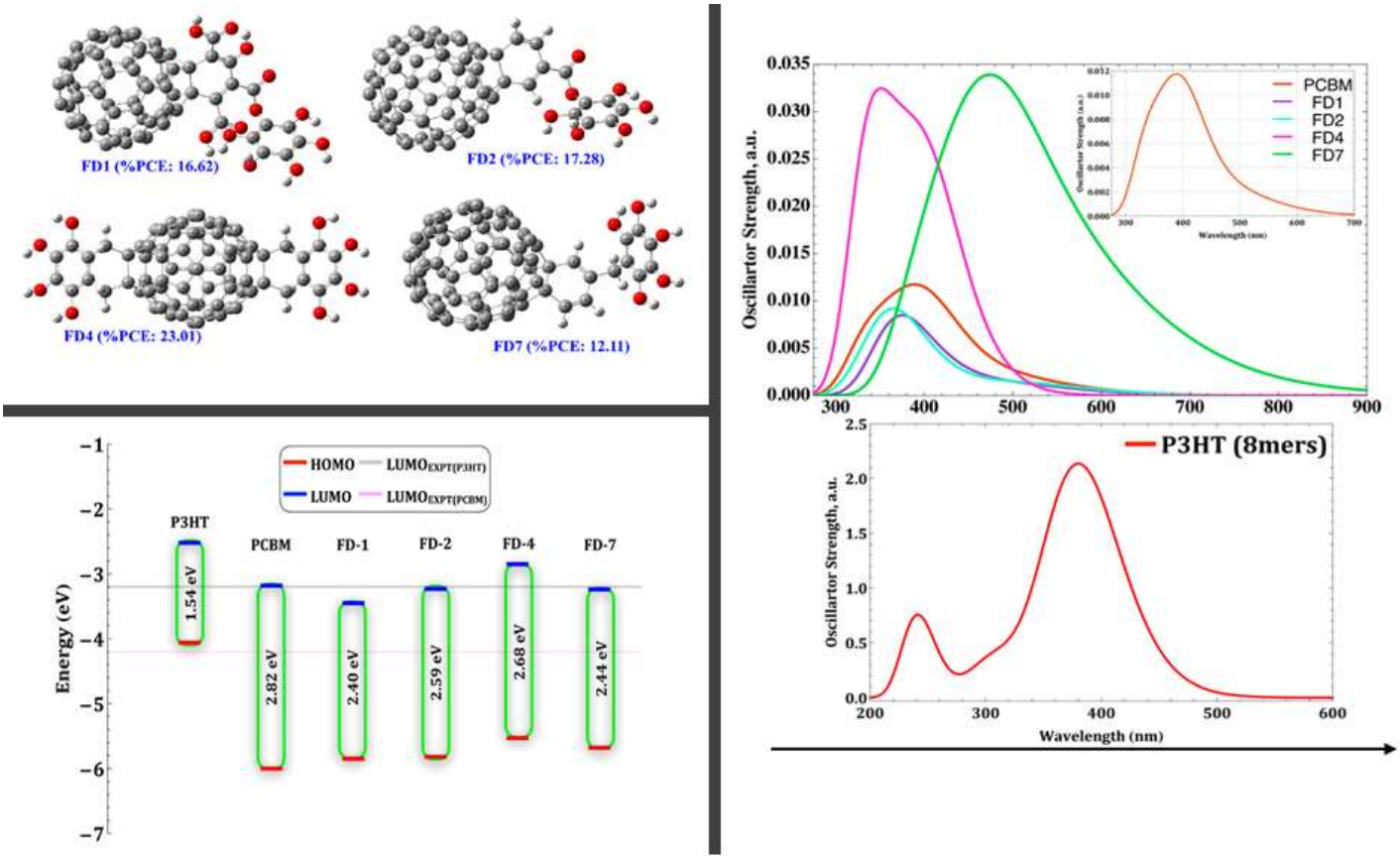

Figure 1.5: (Left top) Potential lead acceptor FD derivatives for PSC; (Left bottom) Computed energy diagram of the four FDs along with [6,6]-phenyl-C61-butyricacidmethylester (PCBM) and P3HT. Simulated absorption spectra of PCBM, four FDs [Right top] and P3HT [Right bottom] with the use of TD/CAM-B3LYP/6-311G(d,p) level of theory in chlorobenzene solvent.

References:

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2. Roy, J. K.; Kar, S.; Leszczynski, J. *Scientific Reports*, **2018**, *8*, 10997. **[Publication under DOE project]**
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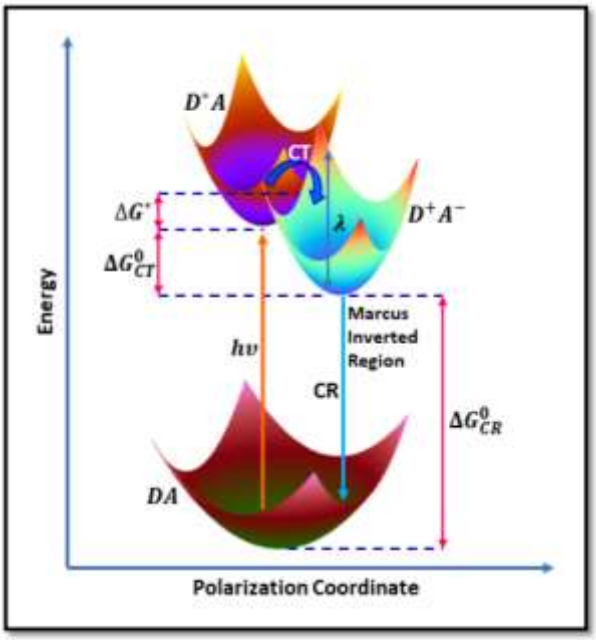
4. Krishna, J. G.; Ojha, P. K.; Kar, S.; Roy, K.; Leszczynski, J. *Nano Energy*, **2020**, *70*, 104537. **[Publication under DOE project]**
5. Roy, J. K.; Kar, S.; Leszczynski, J. *Materials*, **2019**, *12*, 2282. **[Publication under DOE project]**

Section B: Unveiling the Mechanism of Photoinduced Exciton Transfer and Charge Carrier-Transport for dye-sensitized solar cell (DSSC): First-Principles Approach

ABSTRACT: In our previous work (Published in ***J. Phys. Chem. C*** *2020, 124, 2817−2836*), we have assessed the competence of inclusion of spacer units in the metal-free D-π-A organic dyes concerning the augmentation of dye-sensitized solar cell (DSSC) efficiency through the excited state simulations of the charge injection and recombination processes at the dye-semiconductor interface. We selected five recently synthesized DSSC photosensitizers, which were proposed to exhibit higher short-circuit current densities and power conversion efficiencies compared to earlier metal-free organic dyes using I^-/I_3^- as redox shuttle. These D-π-A dyes comprise triphenylamine (TPA) as donor (D) unit, cyanoacrylic acid (CAA) as acceptor (A) unit, and highly planar tetrathienoacene (TTA) core as π-bridge unit. The TTA core of these dyes contain a long alkyl substituent (R = *n*-$C_{15}H_{31}$) to suppress dye aggregation and charge recombination on TiO_2 surface. All these dyes contain thiophen (T) as spacer unit between the π-bridge and the D/A units so that the orientation effect of thiophene on the performance of DSSC could be monitored. Within the framework of time-dependent density functional theory, we have estimated the crucial factors controlling the rates of photoinduced charge-transfer and energy-transfer processes, including electronic coupling, reorganization energy, and threshold energy barrier in semi-classical Marcus formalism. The evaluation of fluorescent state appeared to be the crucial step while explaining the ultrafast electron injection process and the charge recombination at the Marcus inverted region, as revealed by the obtained results. The electron- and hole-hopping mechanisms were critically analyzed through the estimations of electronic coupling between the dye's excited state and the conduction band of the semiconductor employing different computational strategies such as Generalized Mulliken-Hush method, Förster-Dexter formalism, and semi-classical Marcus theory. The time scales for electron injection between the dye and the TiO_2 surface were further computed by accounting the effect of adsorption on the relative alignment of electronic states of the photosensitizers and the lifetime broadening using the Newns-Anderson model. The retardation of charge recombination has been revealed to be assisted by the insertion of thiophene moiety between the π-bridge and the acceptor units. The estimated cold electron injection efficiencies deploying Onsagar-Braun theory, that rely on the computations of cold electron injection lifetime and cold electron lifetime, showed linear correlation with the experimental photovoltaic parameters of the DSSC comprising short-circuit current density, open-circuit voltage, and power conversion efficiency. The outcomes of the latest work establish a basis for unravelling the mechanism of intricate dynamical processes upon photoexcitation of the sensitizers, as well as devising plausible routes for functional DSSC materials.



[Schematic representation of the potential energy diagram for the photo-induced charge-transfer (CT) and charge-recombination (CR) processes depicting Gibbs free energy barriers for the corresponding elementary processes within the semi-classical Marcus theory of the charge transfer kinetics]

SIGNIFICANCE: The computational study, as revealed by the published article ***J. Phys. Chem. C*** *2020, 124, 2817−2836*, provides the basis for unveiling the mechanism of exciton formation and migration processes from a specified state of the D-π-A based DSSC photosensitizers to the acceptor states of the TiO_2 semiconductor, which in turn rely on the meticulous excited state geometry optimization and estimation of the electronic coupling. The semi-classical analysis of the interfacial charge transfer process using Marcus model demonstrates an ultrafast photoelectron injection at a time scale of *pico-second*, which corroborates well with the experimental cold electron injection lifetimes. The calculated lifetimes for the charge recombination process are in conformity with the results obtained from the electrochemical impedance spectroscopy. The combined strategies comprising applications of the rate theories and electronic structure calculations could pave the way for designing effective DSSC photosensitizers through the optimization of photoinduced charge-transfer and energy-transfer processes. The theoretical approaches are new in the sense that it exclusively considers the

photoluminescence properties to unravel the DSSC characteristics (as opposed to the earlier theoretical approaches based on absorption property calculations).

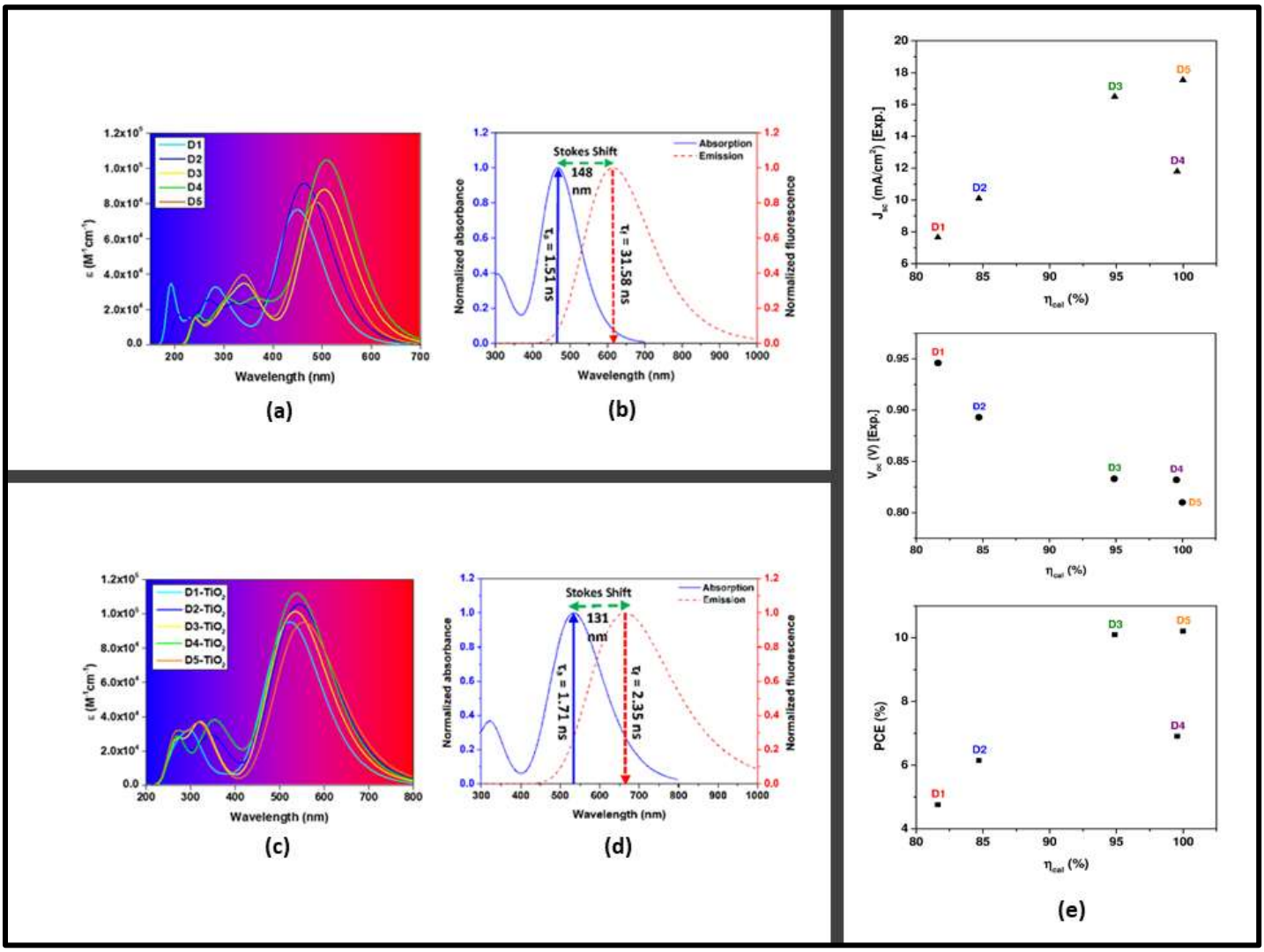


Figure B.1. Delineation of simulated absorption spectra in ortho-dichlorobenzene (o-DCB) solvent for the DSSC sensitizers **(a)** and the dye/TiO_2 complexes **(c)** at the TD-CAM-B3LYP/6-31G(d) level of theory; The layouts **(b)** and **(d)** compare the simulated absorption and emission spectra along with photophysical properties of a selected dye (D3) and D3-TiO_2 complex, respectively. The panel **(e)** shows the variation of calculated cold electron injection efficiency (η_{cal}) with respect to the experimental DSSC performance parameters: short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), and power conversion efficiency (PCE).

Publication under DOE project

- First-Principles Approach for Assessing Cold Electron Injection Efficiency of Dye-Sensitized Solar Cell: Elucidation of Mechanism of Charge Injection and Recombination. P. N. Samanta, D. Majumdar, S. Roszak, J. Leszczynski, ***J. Phys. Chem. C*** **2020**, 124, 2817−2836.