Donor-Acceptor Polymer for the Design of *All-Solid-State* Dye-Sensitized Solar Cells

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Abstract

Density functional theory study has been carried out to design a new *All-Solid-State* dye-sensitized solar cell (SDSC), by applying a donor-acceptor conjugated polymer instead of liquid electrolyte. The typical redox mediator (I^{1-}/I^{3-}) is replaced with a narrow band gap, hole transporting material (HTM). The electronic and optical properties predict that donor and acceptor moieties in the polymeric body have increased the visible light absorption and charge transporting ability, compared to their parent polymers. A unique "upstairs' like band energy diagram is created by packing N3 between HTM and TiO_2. Upon light irradiation on the proposed configuration, electrons will move from the dye to TiO_2 and from HTM to dye (to regenerate dye), simultaneously. Our theoretical simulations prove that the proposed configuration will be highly efficient as the HOMO level of HTM is 1.19 eV above the HOMO of sanitizer (dye); providing an efficient pathway for charge transfer. High short-circuit current density and power conversion efficiency is promised from the strong overlapping of molecular orbitals of HTM and sensitizer. A low reorganization energy of 0.21 eV and exciton binding energy of 0.55 eV, confirm the high efficiency of HTM. Finally, a theoretical open-circuit voltage of 1.49 eV would results high quantum yield while, the chemical stability of HTM towards oxidation can be estimated from its high ionization potential value (4.57 eV).

Introduction

When Sun strikes the earth for an hour, if that energy is properly harvest then it can fulfill whole the world energy demand for a year, but unfortunately, we are not able to harvest it properly [1, 2]. Solar energy technology in the market is mostly Silicon-based photovoltaic cells, which is a promising renewable energy technique for [3]. Silicon-based solar cells are ideal, but having a high cost and high operation temperature limits its portability and versatility, so, it is an urgent need to replace Si with a better and efficient material for photovoltaic applications [4-6]. Thin film solar technology based on CdTe, p-GaAs/n-GaAs, and ZnO/CdS/CuInSe$_2$ etc., exhibiting ~ 20% efficiency, however, this is more expensive and having elements which are not earth abundance and toxic for environment [7].

Dye-sensitized solar cell (DSSC) is considered as the best way forward to fulfill our energy requirements due to it's low-cost, easy fabrication and environmentally friendly [8]. A basic DSSC is consist of molecular dye, adsorbed on a mesoporous wide band gap semiconductor oxide (frequently TiO$_2$), a redox couple (I^{1-}/I^{3-}) usually liquid electrolyte and a p-type hole collector/counter electrode [9, 10]. The dye molecule (photosensitizer) absorb light and injects its excited electrons into the conduction band of TiO$_2$ and become oxidized. The redox electrolyte act as an intermediate to transfer hole from dye to counter electrode for regeneration of dye [11-13]. Although, highly efficient DSSCs have been reported but they are facing long-term performance and durability problems which are stem to liquid electrolytes; the I^{1-}/I^{3-} redox couple, leads to serious problems such as electrode corrosion and electrolyte leakage [14-16]. The crucial solution would be the purely solid-state cells, given the expected issues of any liquid electrolyte, such as leakage, heavyweight and complex chemistry.

Chung, *et al* [17] has designed an SDSC model with all inorganic material using TiO$_2$, Dye, and CsSnI$_3$, where an efficient e$^-$/h$^+$ transferring occurred due to the development of a better

band diagram of the mixing constituents [17]. The efficiency of this combination is found to have exceeded over the performance of a liquid electrolyte Grätzel cell [17]. The valance band (VB) edge positions of all these three interacting materials had sufficient gaps and are best suitable for h^+ transferring, however, conduction band (CB) edge levels; where the e^- of the excited dye can go to either side ($CsSnI_3$ or TiO_2), has not proper energy gap difference (upstairs). Moreover, $CsSnI_3$ is used as hole collector to regenerate dye but contains less abundant earth metals and also has processing issue similar to the thin film solar cell, making it expensive to fabricate.

Solid state hole transporting material (HTM)-based DSSC, termed as all solid-state DSSC (SDSC), has overcome the liquid electrolyte problems [17], but facing the challenge of modest conversion efficiency [18, 19]. Some HTM has a weak interaction with the dye which leads to the interruption of the hole-conducting path between HTM and dye molecule. So, designing of an efficient, flexible and cost-effective HTM is needed for the high-performance SDSC.

Conjugated organic polymers (COPs) are promising emerging materials and are considered to be superior over other materials (inorganic semiconductors) due to their possibility of processing to form useful, tunable, robust structures, having material diversity, mechanical flexibility, light weight, low-temperature processing, roll to roll printing (just like a newspaper printing) and large-area capability [20-23]. Photovoltaic is one of the efficient applications of COPs, especially in the form of donor-acceptor co-polymer, possess low band gaps are much suitable for solar energy harnessing technique [24]. These narrow band gap materials have better absorption capability within the active region of solar spectrum especially in the near-infrared region which consequently increases the generation of photocurrent.

Using our previous experience of COPs, here for the first time we are proposing an efficient all-solid-state organic-inorganic hybrid DSSC, preliminary based on their band edge positions

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(Fig 1), where COP is used as HTM [25-27]. A series of different COPs, such as *3,4*-ethylenedioxythiophene (EDOT), *3,4*-ethylenedioxyselenophene (EDOS), *2,1,3*-bezothiadizole (BOD), *2,1,3*-benzoselenadiazole (BSD), and their combination in the form of donor-acceptor moieties are used (Scheme 1) [28, 29], has been simulated to replace electrolyte in the conventional DSSC.

To design an ideal configuration for the SDSC, which would be cheap, easy to handle, environmental friendly and responsible for high efficiency, a perfect upstairs energy level diagram of the interacting materials is required where the band edge positions of TiO_2, Dye and HTM should have difference of at least of 0.50 eV (Fig 1). The HTM used in this work is a donor-acceptor co-polymer; a combination of EDOS and BSD moieties.

Methods

Quantum mechanical study of the molecular $(TiO_2)_{28}$ cluster, N3, EDOS, BSD, EDOS+BSD (HTM) and their non-bonded interacting systems are carried out with the help of density functional theory (DFT). *GAUSSIAN 09* [30] is used for the DFT calculations [31] while the results are visualized through *Gabedit* [32], *GaussSum* [33], and *GaussView* [34]. DFT and time-dependent DFT (TD-DFT) calculations are used for the electronic properties simulations of the mentioned materials, to predict an efficient model for SDSC. Different oligomeric chain lengths of EDOS, BSD and HTM from monomers up to nine repeating are considered and extended to polymers, using second order polynomial fit equation [31]. Prior to property simulations of the interacting systems such as N3-HTM, N3-TiO_2, and HTM-N3-TiO_2; the DFT method was confirmed through correlation of the HTM simulated HOMO, LUMO and band gaps with experimental data (see Table S1) [28, 35]. Hybrid functional such as B3LYP has been successfully applied for this type of polymers and has been found to be superior over other functionals [35-38]. In the case of inter-molecular study of the proposed model, N3 was

sandwiched between TiO_2 and HTM and then optimized at B3LYP functional with LanL2DZ basis set. The interaction energy of these three components is simulated with the help of inter-molecular energy simulation as explained elsewhere [25-27, 39, 40]. The quantitative and qualitative behavior of charge transferring phenomena of the entitled complexes are simulated at natural bonding orbital (NBO) analysis. The prediction of stability, electroactivity, conductivity and donor/acceptor nature are estimated from ionization energy (IP), electron affinity (EA), and band gap analysis. UV-vis spectra and ΔSCF energy gap (optical gap) were simulated in a solvent medium such as chlorobenzene, using a conductor like polarized continuum model (CPCM) at TD-B3LYP/LanL2DZ level which unveils our results regarding the optical and electrical properties.

Results and Discussion

The 84 atoms cluster of titanium dioxide [$(TiO_2)_{28}$] is used as a representative of the [101] surface of anatase [41-45]. The choice of a molecular cluster of $Ti_{28}O_{56}$ contrast to periodic calculations is that the excited states within TD-DFT are not generally implemented and in any case standard continuum solvation models are not applicable due to the impossibility of defining an infinite solvation cavity [41-43]. The major part of this paper is devoted to the hole transporting material (HTM), its applicability in SDSC and the corresponding efficiency. However, HTM interaction with dye, $N3-TiO_2$, and $HTM-N3-TiO_2$ systems are also highlighted. Charge transferring phenomena, electron-hole exchange and band edge positions of these systems are simulated and discussed in their respective parts.

Geometrical and Electronic Properties of HTM. The light absorption capability of a chemical substance can be predicted from its dihedral angles, UV-vis absorption spectra, conjugation of π-electrons, and planarity. As discussed elsewhere [46, 47], oligomers up to seven or eight repeating units represent the characteristics of their infinite polymer so that is why the chain

length is restricted to nine repeating units. Our current simulations on the nine repeating units of HTM also shows a similar trend and corroborates its polymeric properties. The optimized geometric structure of HTM is given in Fig 2, where an ideal dihedral angle of 180° (Table S2) is because of donor and acceptor moieties; which has planarized the geometry of the resulting polymer through establishing a delocalized π-electronic cloud density over its polymeric backbone.

The electrons and holes carrying properties of a species can be precisely estimated from the contours of its molecular orbitals; where the electronic cloud density of the localized HOMO represent holes and the LUMO determines the facility with which the electron moves under the external electric biased. Both the HOMO and LUMO of HTM are fully covered by electronic cloud density (Fig.S1), a clear indication of the free availability of π-electrons in the HTM (Fig. 3). Moreover, this molecular orbital overlapping (delocalized π-electrons in HTM) of the C, H, O, N, and Se atoms provides an easy pathway for the movement of free electrons which make it as a donor species (hole donor) in the bulk heterojunction solar cell.

Reorganization Energy (λ) of HTM. The energy of geometrical distortion of a chemical species between the neutral and cationic state can be termed as reorganization energy (λ). Hole mobility in an organic semiconductor can be understand in term of its reorganization energy; lower the reorganization energy the faster will be the hole transfer and vice versa. The internal reorganization energy (λ) of HTM is 0.21 eV, which is simulated by the adiabatic potential energy surface method, using equation 1.

$$\lambda = \lambda_1 + \lambda_2 = (E_0^* - E) + (E_+^* - E_+) \tag{1}$$

where E_0 and E_+, represent energies of neutral and charged species in their lowest energy geometries, while E_0^* and E_+^* represent the energy of a neutral molecule at the geometry of charged molecule and charged molecule at the geometry of the neutral molecule.

Comparative analysis of the reorganization energy of HTM with the already reported hole transporting materials such as *N,N′*-diphenyl-*N,N′*-bis(3-methylphenyl)-(1,1′-biphenyl)-4,4′-diamine (0.33 eV) [48], ((*N,N′*-bis(2,4-dimethyl-phenyl)-*N*-(4′-((2,4-dimethylphenyl)(phenyl)amino)-[1,1′-bi-phenyl]-4-yl)-*N′*-phenyl-[1,1′-biphenyl]-4,4′-diamine (0.23), 4-(4-phenyl-4-*α*-naphthylbutadienyl)-*N,N*-di(4-tolyl)-phenylamine (0.24) [49] and silole-based organic semiconductors (0.50 eV) [50] shows that our proposed HTM has better hole transfer ability due to lower reorganization energy. This low reorganization energy of HTM can also be correlated to its fully planner geometrical structure, where an ideal dihedral of 180° is present.

Polaron and Exciton Binding Energy of HTM.

The combination of charge and the associated lattice distortion in a chemical substance can be appropriately termed as Polaron, denoted as E_p. Distortion in the polymeric back establishes when a π-conjugated polymer donates electronic charge density, this intra-molecular relaxation can also be referred to as a polaronic effect. The polaron-binding energy that relates to the reorganization energy; transfer of a charge from one molecule to other can be calculated from this formula $E_p = (1/2\ \lambda)$, where λ is the reorganization energy. A 0.105 eV polaron-binding energy is simulated for the proposed HTM, which evidences its ease of electron donation. In terms of molecular orbitals analysis, an electron−hole binding energy is that energy when an electron adds in the LUMO and only one (instead of two) electron in the HOMO.

The electron−hole exciton binding energy (E_b) is actually the energy difference between the neutral exciton and the two free charge carriers. This can be simulated as $E_b = E_{band\ gap} - E_{optical\ gap}$, or the difference between the electrical gap and optical gap of a particular HTM. For the simulations of these gaps, TD-DFT method at LanL2DZ level and CPCM solvent model is used. The energy required to fully separate the electron−hole pair against the Coulomb

attraction is known as exciton binding energy. In Figure 4, the E_b, optical and band gap are schematically illustrated [51]. A lower E_b is responsible for the charge separation (prevent electron/hole recombination) and high charge carrier mobility in a particular solar cell. The intra-molecular charge transfer (E_b) in HTM has a binding energy of 0.55 eV. The E_b of the investigated HTM is also compared with the already reported hole transfer materials which concluded its lower binding energy. So, an easier dissociation of free charge carriers can be promised in our HTM. Furthermore, binding energy can also be used for the determination of short-circuit current density in a solar cell; lower exciton binding energy of a particular HTM is responsible for its higher short-circuit current density and vice versa.

Partial Charge Difference Analysis. Partial charge difference on the conjugated backbone of HTM is simulated by using equation 2. NBO charge on a particular atom in the neutral as well as in the cationic state is considered for the charge transferring phenomena in HTM. Partial charge difference analysis of HTM predicts that H and Se atoms are responsible for the charge donation.

$$\Delta Q_X = \sum Q_{Xi}^+ - \sum Q_{Xi}^0 \tag{2}$$

Where ΔQ is a charge on particular X atom, either in cationic (X^+) or neutral state (X^0).

The partial charge difference of the atoms involved in HTM backbone is given in Table 1, which demonstrates that the ΔQ_H value is slightly larger than ΔQ_{Se} to about 0.05 e$^-$. Comparative analysis of the data of Table 1 led us to conclude that Se and H atoms are mainly involved for the charge transfer in HTM, however, H atom plays a significant role compared to Se atom. The partial charge difference of ΔQ_H is 0.296 e$^-$ while that of ΔQ_{Se} is 0.24 e$^-$. Partial charge difference values for N, O, and C are 0.026, 0.054 and 0 e$^-$, respectively. In summary, partial charge difference between the neutral and the corresponding cation state directly reflects the geometric structures, whether planner, zig-zag or curl.

UV-vis Absorption Spectra of HTM. The first allowed maximum electronic excitation energy of HTM (λ_{max}) at ca. 925 nm has strong evidence to be an efficient charge transporting material, as it can easily absorb in the visible region. Furthermore, it is expected that higher efficiency is associated with high absorption ability of solar radiation, especially in the visible part. The effect of the alternating donor and acceptor moieties in the polymeric backbone is found in the form of visible light absorption as can be seen from Fig 5. Furthermore, the vertical excitation energy of the isolated donor, acceptor and HTM increases with chain length elongation (Fig S2-S4). Oligomeric chain length elongation produces a single but strong feature in the visible region and confirms that this excitation (the one with low energy) is dominated by a single absorption during which an electron is transferred from π to π^* orbital. Analysis of the data of Table S3-S5 proves that chain length elongation shifts the strong absorption to lower energy with high intensity and high oscillator strength. Moreover, it is observed that the contribution of HOMO-LUMO transition decreases and new absorption from HOMO-1→LUMO+1, HOMO-2-LUMO, and HOMO-LUMO+2 excitations start to contribute (Table S2-S4). The strong transition (the one with high oscillator strength) of HTM in the visible region corresponds to the transitions from HOMO to LUMO (Table 2).

The UV-vis spectra of HTM has three absorptions band peaks; two in the visible and one near to the IR region of the spectrum, which is an indication of its efficient light-harvesting ability. Charge-transfer character occurs at the lower energy part of UV-vis absorption and a low-lying wide conduction band (Fig 3) [52].

HTM and N3 Interacting System. Inter-molecular charge transferring and dye regeneration is simulated from the interaction study of HTM and Dye. The interaction between N3 and HTM is purely non-dissociative but quite strong due to the establishment of non-covalent bonding. The carboxylic anchoring groups of N3 establishes non-covalent bonding with the N and Se of HTM (Fig 6) which is a clear evidence of their strong interaction. Two of the oxygen atoms of

N3 make an inter-molecular bond with the Se of HTM, each having non-bonding distances of 3.13 Å. Other atoms involved in this electrostatic type of interaction are H atoms which lead to hydrogen bonding i.e., H of N3 with Se at ca. 3.54 Å and two H atoms of N3 with N of HTM each having distance of 2.74 Å (Fig 6). The inter-molecular electrostatic energy of this interaction is -8.72 kcal/mol, which further confirms the evidence of charge transferring between HTM and N3. It is well-known from the literature that a good amount of this type of dye work as donor-π-electrons –acceptor where a large orbital density of the LUMO should cover the carboxylic anchoring groups and a small electronic cloud density cover their HOMO [11-16, 53]. This similar type of phenomenon is observed in the molecular orbitals of N3 (Fig.S5) which is consistent with the already reported work [11-16, 53]. The higher electronic cloud density at LUMO compared to that of HOMO shows that the charge injection is favored from HTM to dye and prevents charge recombination in the dye molecule. The energies of HOMO, LUMO, band gap and an optical gap of these three species, before and after interaction are listed in Table 2.

Frontier molecular orbitals of HTM-N3 are shown in Fig 7, where the π-electron donation from HTM towards dye can be seen. The position of HOMO level of HTM which is considerably above (0.61 eV) the HOMO of dye (N3); obviously evidences the hole injection from N3 to HTM. Furthermore, the HOMO and LUMO of HTM in the HTM-N3 system indicates how the transformation of π-electrons towards N3 is achieved. Frontier molecular orbital analysis led us to conclude that a nice overlap in the orbitals coupling of HTM and N3 occurs, which can lead to the high efficiency of the corresponding solar cell.

As discussed earlier, the electrons and holes carrying species can be more precisely determined from the contours of their HOMO and LUMO, respectively. Lower the HOMO energy level (more negative) of the HTM the higher will be its open-circuit voltage in the corresponding solar cells, and a high adiabatic IP ensures its high stability in terms of resistance towards

ionization. The high IP (4.57 eV) of HTM which is 1.19 eV above the HOMO of dye is responsible for the hole exchange as well as high chemical stability toward oxidation. The adiabatic IP and EA are obtained from the negative of the DFT orbital (HOMO and LUMO) energy; using Koopman's theorem. The electrical gap (band gap) is estimated from the difference of IP and EA while the optical gap is simulated from the ΔSCF TD-DFT calculation, where first allowed electronic excitation with higher oscillator strength is considered (Table 2). In a typical DSSC, dye provides an electron to a wide bandgap material (TiO_2) and then regenerates itself from the liquid electrolyte. In our proposed SDSC configuration the regeneration of dye has been achieved from HTM, due to its low reorganization energy (*vide supra*). So, when the charge moves to N3, relaxation energies is needed to remove this charge from HTM to regenerate the dye which is about 0.21 eV (eq. 1).

According to NBO charge analysis, HTM and N3 share about 0.184 e^- of electronic cloud density (Fig S6a), moreover, the individual charge (NBO) on each atom of this complex is shown in Fig S6b.

N3 and TiO_2 Interacting System. In order to understand the electron transferring phenomena in the proposed solar cell, we further investigated the MOs analysis of N3-TiO_2 system; as shown in Figure 8. Contours of the HOMO and LUMO of N3-TiO_2 system indicate that dye has delocalized π-electrons which are ready for donation. So, a clear and sophisticated picture of electron transformation is observed from N3 to mesoporous titanium dioxide. The estimated open circuit voltage of this solar cell is 1.49 eV which is simulated from the difference of the quasi-Fermi levels of the TiO_2 and the HOMO energy level of N3 (Table 2).

HTM, N3, and TiO_2 Interacting System. Finally, the three components are simultaneously interacted via non-covalent bonding interaction to find/confirm the net electron-hole transformation. The HTM-N3-TiO_2 complex is optimized with LanL2DZ pseudopotential,

using hybrid functional of DFT such as B3LYP (Fig 9). On the electrostatic energy surface, both dissociative and non-dissociative strong interactions are found among these three components as can be seen from Fig 9. The interaction of N3 with TiO_2 is dissociative where oxygen atoms of the carboxylic groups make covalent bonds with the Ti atom of TiO_2. However, the HTM and N3 interaction is non-dissociative but quite strong, due to the establishment of Hydrogen bonding (Se---H), see Fig 9. Furthermore, the HOMO and LUMO of this three components system are also simulated to find the contours of the electronic cloud density (Figure 10). Results of the HOMO and LUMO are also inconsistent with the previous results, where an ideal and classical phenomenon is justified. Based on these simulations, we can say that when light shines on the proposed configuration, the delocalized π-electrons of N3 would become activated and move to TiO_2 and ultimately would regenerate itself by sharing an electron from the HOMO of HTM.

An easy pathway for the movement of electrons in the said complex is made possible due to the alliance of the energy levels (HOMO and LUMO) of TiO_2, N3, and HTM; having an upstairs ladder like band diagram (Fig 1). Analysis of the data of Table 2 and Fig 10, led us to conclude that it is not unusual for the electron to shift from the LUMO of HTM to N3 or from N3 to TiO_2 under the applied biased. As the LUMO energy level of HTM is about 0.49 eV above the LUMO edge position of N3 while that of dye and TiO_2 has 0.85 eV of difference in their LUMOs energy levels.

In summary, if the proposed configuration of SDSC is exposed to light; the excited electrons of both of the dye and HTM become delocalize and move from the dye to nanoporous TiO_2 and consequently the oxidized dye would be regenerated from the HTM via exchanging of the electron.

Conclusion

It is believed that all-solid-state DSSC (SDSC) is cost effective and a stable solar cell compared to the classically reported one. We have carried out structural, electronic, optical, and charge-transport properties of a donor-acceptor-donor polymer; a Hole transporting material (HTM), N3 and TiO_2 for the design of an efficient SDSC. We proposed an ideal setup for an SDSC, where the HTM, N3, and TiO_2 are chosen, based on their upstairs like energy levels (band edge positions); having a difference of at least 0.50 eV. Our theoretical simulations prove that if we shine a light on the proposed setup, the electron would move from the dye to TiO_2 and from HTM to dye, to be regenerate. HOMO level of our investigated HTM lies about 1.19 eV above the sanitizer, provides an easy pathway for hole injection. Strong overlapped molecular orbitals of HTM with that of sensitizer and their lower reorganization energy (0.21 eV) which led to 0.55 eV exciton binding energy, responsible for high short-circuit current density and high power conversion efficiency. The theoretical open-circuit voltage of about 1.49 eV is responsible for high quantum yield. Moreover, the HTM is chemically stable to oxidation due to 4.57 eV of IP and has excellent transparency in the visible region of sunlight (λ_{max} of 925 nm).

Acknowledgments

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