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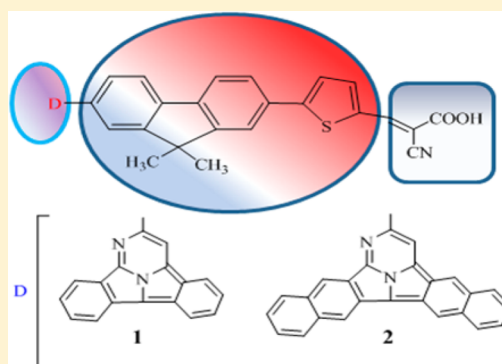
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Design of Efficient Metal-Free Organic Dyes Having an Azacyclazine Scaffold as the Donor Fragment for Dye-Sensitized Solar Cells

Abul Kalam Biswas,^{†,‡} Sunirmal Barik,[†] Anik Sen,[†] Amitava Das,^{*,§} and Bishwajit Ganguly^{*,†,‡}[†]Computation and Simulation Unit (Analytical Discipline and Centralized Instrument Facility) and [‡]Academy of Scientific and Innovative Research, Council of Scientific and Industrial Research Central Salt & Marine Chemicals Research Institute (CSIR-CSMCRI), Bhavnagar, Gujarat-364002, India[§]Academy of Scientific and Innovative Research, CSIR National Chemical Laboratory (NCL), Pune, Maharashtra-411008, India

S Supporting Information

ABSTRACT: The energy conversion efficiency of dye-sensitized solar cells derived from organic dye molecules has seen immense interest recently. In this work, we report a series of organic donor molecules with enhanced energy conversion efficiency using π -spacers and cyanoacrylic acid as an anchoring group (2–6). Density functional theory (DFT) and time-dependent DFT calculations of these molecules have been performed to examine their electronic structures and absorption spectra before and after binding to the semiconductor titanium dioxide surface. The computational results suggest that dyes 4 and 6 have a larger driving force ($\Delta G_{\text{inject}} = -1.66$ and -1.80 eV, respectively) and light-harvesting efficiency (LHE = 0.99) in the series of donor molecules studied. Thus, these dyes should possess a larger short-circuit photocurrent density (J_{sc}) compared to the other examined dyes. The reported ΔG_{inject} (-1.62 eV) and LHE (0.98) for compound 1, calculated with the same level of theory, were lower than those of the designed 4 and 6 dyes. Furthermore, the DFT calculations showed that the open-circuit photovoltage (V_{oc}) is improved with the vertical dipole moment and number of photoinduced electrons for 4 and 6. Dyes 4 and 6 are expected to exhibit high solar-energy-to-electricity conversion.



1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) have attracted considerable attention since O'Regan and Grätzel published their pioneering work in 1991.¹ These devices promise an appropriate alternative to silicon-based solar cells due to their low cost.^{2–10} Typical DSSCs are composed of organic or inorganic dyes adsorbed on the (101) surface of nanocrystalline anatase TiO_2 .¹¹ On exposure of such hybrid systems to solar radiation, photoinduced electron injection takes place from the appropriate excited state of the dye molecules into the conduction band of TiO_2 . This injected electron is transported to the external circuit, and the ground state of the dye molecule is regenerated through the redox reaction involving the I^-/I_3^- ion pair in an electrolyte. The highest power conversion efficiencies (PCEs) in DSSC devices are achieved by using metal-based dyes.^{12–24} Literature reports suggest that, among various dye molecules that have been utilized for designing an efficient DSSC, the best photostabilities and photocurrent conversion efficiencies are achieved by the sensitizer dye molecules derived from ruthenium(II)–polypyridyl complexes.²⁵ The ruthenium(II)–polypyridyl complexes have shown the highest PCEs because of their photophysical, photochemical, and electrochemical properties. Furthermore, intricacies involved in the synthesis and purification of the desired Ru(II)–polypyridyl complexes sometimes limit the scope of achieving the desired complexes with the anticipated

photocurrent conversion efficiency.²⁶ Metal-free organic sensitizers are still being argued as a viable alternative to conventional ruthenium(II)–polypyridyl-based dyes. Some recent reports reveal that metal-free dyes show comparable efficiencies for DSSC application.^{27–30} Major advantages of organic dyes over conventional ruthenium(II)–polypyridyl-based chromophores as photosensitizers are their lower cost, tunability, and higher molar extinction coefficients. The wider absorption of the solar emission spectrum and ease of synthesis and purification are additional advantages of organic dyes.³¹ Nonetheless, improving the efficiency of the DSSCs is a complex problem and a challenging task. There are various properties of a dye that actually contribute to determination of the actual efficiency of DSSCs, such as (i) choice of an appropriate anchoring functionality for efficient binding to the semiconductor surface, (ii) efficient absorption of solar radiation, (iii) efficient electron injection from its excited state into the semiconductor surface, (iv) efficient regeneration of the ground state of the sensitizer molecule, (v) stability toward photobleaching on irradiation, and (vi) slow charge recombination of the electron in the conduction band of TiO_2 and the photooxidized dye molecule.³² Thus, the engineering of

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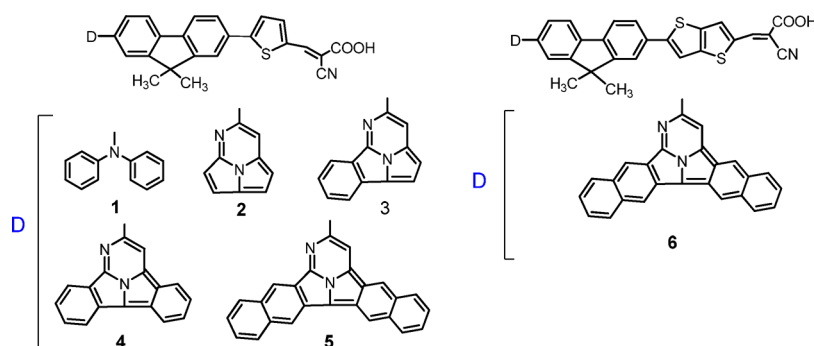


Figure 1. Molecular structures for organic dyes 1–6 having cyanoacrylic acid as the anchoring group.

sensitizers at the molecular level involves many parameters and remains a challenge for researchers.

With the advent of advanced user-friendly software and faster computing facilities, quantum chemical calculations are now more accurate in predicting the physical properties of organic systems. Thus, quantum chemical and density functional theory (DFT) studies could be utilized as a reliable tool for designing new organic dyes with the desired properties for DSSC application.³³ Minor alteration of any one or a combination of such properties in organic dyes could actually significantly influence the efficiency of DSSCs, and computational studies could be a good guide in developing an alternate/efficient strategy for designing efficient organic dyes with high cell performance. A few earlier reports have revealed that quantum chemical calculations are capable of predicting the electron injection rate of the dye adsorbed on the semiconductor by a range of methodologies with reasonable accuracy so that it compares well with the experimental observations.^{14,33–38} Such studies validate the methodologies used for theoretical calculations.³⁸

On the basis of the results of earlier reports, it has been argued that, for organic-molecule-based DSSCs, donor groups play an important role in the cell performance, and accordingly, a variety of donor groups such as dialkylamine groups,^{39,40} coumarins,^{41–45} carbazole,^{46,47} quinoxaline,^{48,49} difluorenylphenylamine,^{50–56} julolidine,⁵⁷ an electron-donating methoxy group containing a diphenylamine group,⁵⁸ di-*p*-tolylphenylamine,⁵⁹ and pyrrolidino⁶⁰ have been explored in designing DSSCs. In some cases the organic dyes containing the planar and sterically less hindered structures showed lower energy conversion efficiency due to the formation of aggregates on the TiO₂ surface.⁶¹ Grätzel and co-workers reported an organic dye containing a nitrogen-containing heterocycle of the ullazine group as the donor and a cyanoacrylic acid as the acceptor showed excellent efficiency.⁶²

In the present paper, we report electron-rich molecular units azacycl[3.2.2]azines 2–6 as donors (Figure 1) to be used as part of the dye sensitizers for DSSC applications. The synthetic feasibility of azacycl[3.2.2]azine has been demonstrated and reported in the literature.^{63,64} It is fabricated according to the following steps: The first step is cyclization reaction of the quaternary bromide of methylpyrimidine followed by reaction with dimethyl acetylenedicarboxylate. Then the resulting ester derivative is hydrolyzed with base followed by decarboxylation.^{63,64} Thus, the advantage of azacyclazine is that it is planar in structure and simple to manipulate in experimental studies and first-principle calculations. Azacyclazine is a 12- π -electron nitrogen-containing heterocyclic compound with a centralized positive charge on nitrogen (through donation of electron

density from the in-plane nitrogen to the π -plane of the ring) and a negative carbon atom. Thus, the electron-rich azacyclazine can be used as an excellent donor group. It is formed by the combination of electron-donating and -accepting groups in the same molecule and allows inter charge transfer. We have examined the role of azacycl[3.2.2]azine and its derivatives as donor functionalities in designing dye molecules for DSSCs. The π -spacers that are used in dyes 2–5 are fluorene and thiophene. The π -spacer groups are attached between the chromophore and the anchoring group. Such π -spacers help to shift the absorption band into the visible region via extended π -conjugation.⁶⁵ Fluorene is extensively used in organic dyes due to its high molar extinction coefficient, ease of functionalization, relatively lower cost, and excellent electron transfer property.^{66–68} Thiophene is also a popular choice for use as a π -spacer unit and has been extensively used in DSSCs due to its high polarizability and tunable spectroscopy and electrochemical properties.⁶⁹ Dye 6 has been modeled with fluorene and thienothiophene as spacer units. The thienothiophene unit as a π -spacer also showed excellent efficiency in earlier studies.^{70,71} The anchoring group considered for all dyes 2–6 is cyanoacrylic acid. DFT and time-dependent DFT (TD-DFT) calculations have been performed to compute the electronic structures and absorption spectra of designed dyes 2–6. We have examined these dyes with the reported dye 1, which showed excellent efficiency with a diphenylamino group as the donor system.⁷² The DFT-calculated results reveal that designed dyes 4 and 6 can function as efficient DSSCs for solar energy conversions.

2. COMPUTATIONAL METHODOLOGIES

The energy conversion efficiency (η) of a solar cell device is determined by the open-circuit photovoltage (V_{oc}), short-circuit current density (J_{sc}), and fill factor (FF), as compared to the incident solar power (P_{inc}), and is generally expressed through the following equation:

$$\eta = FF \frac{V_{oc} J_{sc}}{P_{inc}} \quad (1)$$

The V_{oc} of DSSCs is calculated by the following equation:⁷³

$$V_{oc} = \frac{E_c + \Delta CB}{q} + \frac{kT}{q} \ln \left(\frac{n_c}{N_{CB}} \right) - \frac{E_{redox}}{q} \quad (2)$$

Here, q is the unit charge, E_c is the conduction band edge of the semiconductor substrate, K is the Boltzmann constant, T is the absolute temperature, n_c is the number of electrons in the conduction band, N_{CB} is the density of accessible states in the

conduction band, E_{redox} is the reduction–oxidation potential of the electrolyte, and ΔCB is the shift of the conduction band edge of the semiconductor when the dye is adsorbed on it and can be expressed as⁷⁴

$$\Delta\text{CB} = -\frac{q\mu_{\text{normal}}\gamma}{\epsilon_0\epsilon} \quad (3)$$

where μ_{normal} is the dipole moment of the individual dye molecules perpendicular to the surface of the semiconductor substrate, γ is the dye surface concentration, and ϵ_0 and ϵ are the vacuum permittivity and the dielectric permittivity, respectively. It is evident from eqs 2 and 3 that the larger the μ_{normal} and n_c of a dye the higher the V_{oc} .

Another important parameter, J_{sc} in DSSCs is determined by the following equation:⁷⁵

$$J_{\text{sc}} = \int_{\lambda} \text{LHE}(\lambda) \Phi_{\text{inject}} \eta_{\text{collect}} d\lambda \quad (4)$$

where $\text{LHE}(\lambda)$ is the light-harvesting efficiency at a given wavelength, Φ_{inject} is the electron injection efficiency, and η_{collect} denotes the charge collection efficiency. $\text{LHE}(\lambda)$ can be calculated with

$$\text{LHE} = 1 - 10^{-f} \quad (5)$$

where f is the oscillator strength of the adsorbed dye molecule related to λ_{max} . Φ_{inject} is associated with the driving force ΔG_{inject} of electrons injected from the excited states of the dye molecules to the semiconductor substrate. It can be calculated as⁷⁶

$$\Delta G_{\text{inject}} = E^{\text{dye}*} - E_{\text{CB}} \quad (6)$$

where $E^{\text{dye}*}$ is the oxidation potential of the excited dye and E_{CB} is the reduction potential of the CB of the semiconductor. Here we use a widely used experimental value, -4.00 eV (vs vacuum).⁷⁶ $E^{\text{dye}*}$ can be expressed as⁷³

$$E^{\text{dye}*} = E^{\text{dye}} - \lambda_{\text{max}} \quad (7)$$

where E^{dye} is the redox potential of the ground state of the dye and λ_{max} is the vertical transition energy. Thus, from eq 4 we can say that the larger the LHE and ΔG_{inject} the higher the J_{sc} .

The gas-phase geometry optimization in the ground state of compounds 2–6 before and after binding to TiO_2 was performed with the density functional theory using Becke's three-parameter hybrid functional with the correlation formula of Lee, Yang, and Parr (B3LYP).^{77,78} All systems were fully optimized with the 6-31G* basis set for the C, H, O, N, and S atoms and effective core potential (ECP) LANL2DZ and its associated basis set for the Ti atom. Harmonic vibrational frequency calculations were performed to confirm that the optimized structures were minima, as characterized by positive vibrational frequencies. Preat et al. showed that this method could provide a reasonable geometry equivalent to the geometry optimized in MP2 with much lower computational cost.⁷⁹ TD-DFT calculations were performed with the conductor-like polarizable continuum model (CPCM)⁸⁰ at the CAM-B3LYP/6-31+G* level for simulating the absorption spectra of the isolated dyes in tetrahydrofuran (THF) solution.^{81,82} The optimized free dyes were further used for the calculation of the oxidation potential at the C-PCM-B3LYP/UB3LYP/6-311G** level of theory of the neutral and cationic dyes in the ground state.⁷⁷ The atomic charge calculations were performed by natural population analysis at

the CPCM-B3LYP/6-31G* level for nonmetals and the LANL2DZ level for the Ti atom in Gaussian 09.⁸³ The CPCM-B3LYP/6-31G* level of theory was used for the calculation of the dipole moment of the TiO_2 -bound dyes.

3. RESULTS AND DISCUSSION

We have examined a series of metal-free organic dyes with azacyclazine and substituted azacyclazine as donor groups. The

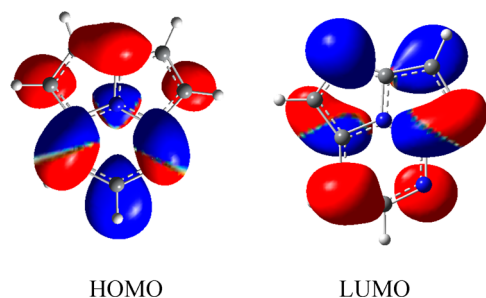


Figure 2. Frontier molecular orbitals of azacycl[3.2.2]azine at the CAM-B3LYP/6-31+G*//B3LYP/6-31G* level of theory in the gas phase with an isodensity surface of 0.02.

π -spacers of dyes 2–5 are fluorene and thiophene. Furthermore, we have designed dye 6 with fluorene and thienothiophene as π -spacers. Cyanoacrylic acid is the anchoring group used in all dyes 2–6. As discussed above, the LHE and Φ_{inject} of the dyes are directly related to the J_{sc} (eq 4), which is one of the factors responsible for augmenting the efficiency of the cell. Note that the larger vertical μ_{normal} of the adsorbed dyes pointing outward from the TiO_2 surface can significantly enhance the V_{oc} to affect the efficiency of the dye-sensitized solar cells.⁸⁴ The V_{oc} is further influenced by the number of electrons transferred from the excited-state dye molecule to the conduction band of the TiO_2 surface.

We first examined the 12- π -electron azacycl[3.2.2]azine donor containing dye 2, which can be achieved experimentally.^{63,64} A previous report has described the synthesis of azacyclazine following the cyclization reaction of the quaternary bromide of methylpyrimidine and then the reaction of this intermediate with dimethyl acetylenedicarboxylate in the presence of palladium on charcoal catalyst, resulting in the precursor ester derivative.^{63,64} This ester derivative on hydrolysis with base produced the desired dicarboxylated derivative.^{63,64} We have employed this compound for its structural and electronic properties and compared its data to the previously reported experimental data for the simple organic dye molecule 1 with good efficiency. The resonance structure consisting of a centralized positive charge due to the donation of electron density from the in-plane nitrogen indicates the potential donating strength as well as electron-stabilizing properties of this nitrogen-containing heterocycle. Frontier molecular orbital analysis of the donor group of compound 2 suggests that, in the highest molecular orbital (HOMO), the orbital coefficients are largely delocalized on the nitrogen center and around the periphery of the ring. However, in the lowest unoccupied molecular orbital (LUMO), the orbital coefficient is only localized on the periphery of the ring (Figure 2). The absorption spectrum of the compound showed slightly blue shifted absorption ($\lambda_{\text{max}} = 417$ nm) compared to that of dye 1 ($\lambda_{\text{max}} = 434$ nm) (Table 1, Figure 3). The calculated ΔG_{inject} (-1.26 eV, Table 1) of dye 2 is lower than

Table 1. Key Parameters for Deducing ΔG_{inject} (eV) of the Examined Dyes 1–6

dye	state	λ_{max}	main configuration	f	LHE	E^{dye}	ΔG_{inject}
1	$S_0 \rightarrow S_1$	434	H – 1 \rightarrow L (0.32) H \rightarrow L (0.59)	1.63	0.98	5.24	–1.62
2	$S_0 \rightarrow S_1$	417	H – 1 \rightarrow L (0.41) H \rightarrow L (0.52)	1.82	0.98	5.72	–1.26
3	$S_0 \rightarrow S_1$	421	H – 1 \rightarrow L (0.49) H \rightarrow L (0.44)	1.95	0.99	5.51	–1.43
4	$S_0 \rightarrow S_1$	428	H – 1 \rightarrow L (0.48) H \rightarrow L (0.41)	2.03	0.99	5.24	–1.66
5	$S_0 \rightarrow S_1$	465	H – 1 \rightarrow L (0.24) H \rightarrow L (0.39) H \rightarrow L + 2 (0.51)	1.74	0.98	4.89	–1.78
6	$S_0 \rightarrow S_1$	465	H – 1 \rightarrow L (0.29) H \rightarrow L (0.34) H \rightarrow L + 2 (0.49)	2.20	0.99	4.88	–1.80

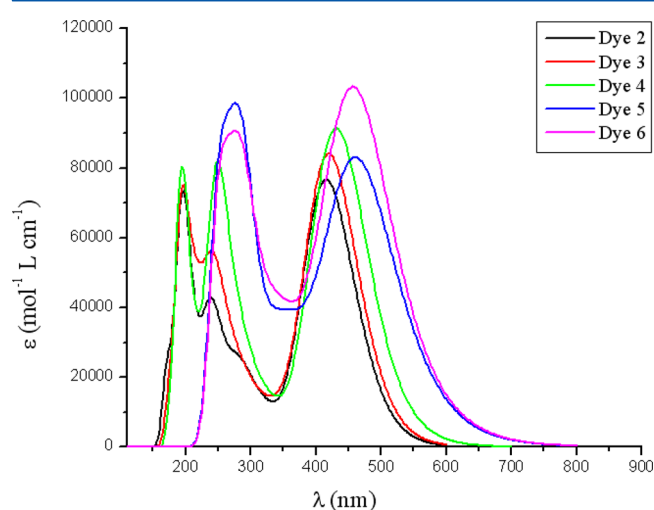
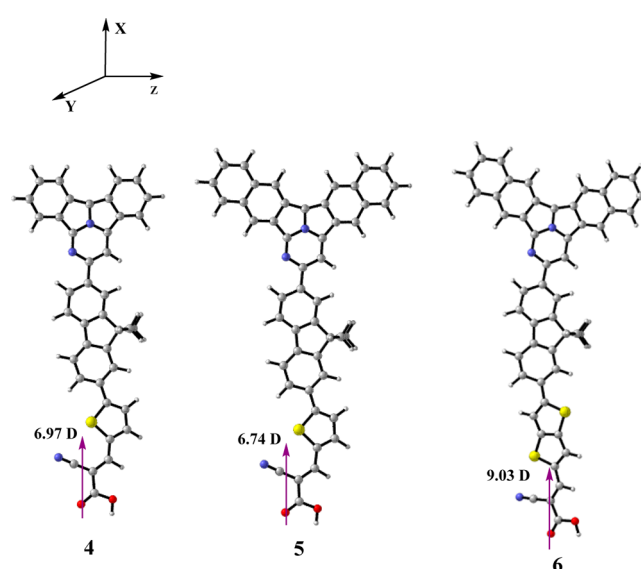


Figure 3. Calculated absorption spectra of dyes 2–6 in THF by TD-CAM-B3LYP/6-31+G* at the B3LYP/6-31G*-optimized geometries.

that of dye 1 (–1.62 eV, Table 1); however, it maintains a similar light-harvesting efficiency (0.98, Table 1). Thus, one could expect that dye 2 may possess a lower J_{sc} than dye 1. The atomic charge distribution analysis of dye 1 showed that the number of electrons transferred from the dye to the semiconductor after photoexcitation is lower (0.063 e, Table 2) than that of the reference dye 1 (0.083 e, Table 2). We have also calculated the vertical dipole moment of the dye at the geometry bound to the semiconductor. Here the dipole moment along the x -axis of the dye is μ_{normal} . The calculated μ_{normal} of dye 2 (7.25 D, Table 2) is larger than that of the

Figure 4. Vertical dipole moments of dyes 4–6 at the C-PCM-B3LYP/6-31G* level of theory in THF solvent. The TiO_2 surface is parallel to the yz plane.

reference dye 1 (6.94 D, Table 2). The V_{oc} of a dye depends on μ_{normal} and electron transfer process. The calculated results suggest that V_{oc} of dye 2 and reference dye 1 would not differ much (Table 2). However, the overall efficiency of a cell with dye 2 would not be better than that of a cell with dye 1, as the J_{sc} of dye 2 is lower than dye 1.

We have extended the π -conjugation by incorporating a phenyl group into the appropriate position of donor group 3

Table 2. Atomic Charge Distribution (e) of the Donor, π -Spacer (Fluorene and Heteroaromatic Ring), Acceptor (2-Cyanoacrylic Acid), and $\text{Ti}(\text{OH})_3 \cdot \text{H}_2\text{O}$ of the Six Dye– TiO_2 Combinations at the C-PCM-B3LYP/6-31G* Level^a

dye	S_0				μ_{normal}	S_1				Δq
	D	π	A	Ti		D	π	A	Ti	
1	–0.119	0.327	–0.636	0.429	6.94	0.337	0.267	–0.949	0.346	0.083
2	0	0.199	–0.629	0.431	7.25	0.342	0.215	–0.915	0.368	0.063
3	–0.449	0.143	–0.631	0.432	7.03	0.327	0.060	–0.951	0.350	0.082
4	–0.248	0.193	–0.631	0.432	6.97	0.694	–0.072	–0.971	0.345	0.087
5	0.008	0.189	–0.631	0.432	6.74	0.778	0.144	–0.979	0.344	0.088
6	–0.492	–0.205	–0.638	0.432	9.03	0.798	–0.149	–0.991	0.347	0.085

^aD = donor, π = π -spacer, A = acceptor, and Ti = $\text{Ti}(\text{OH})_3 \cdot \text{H}_2\text{O}$.

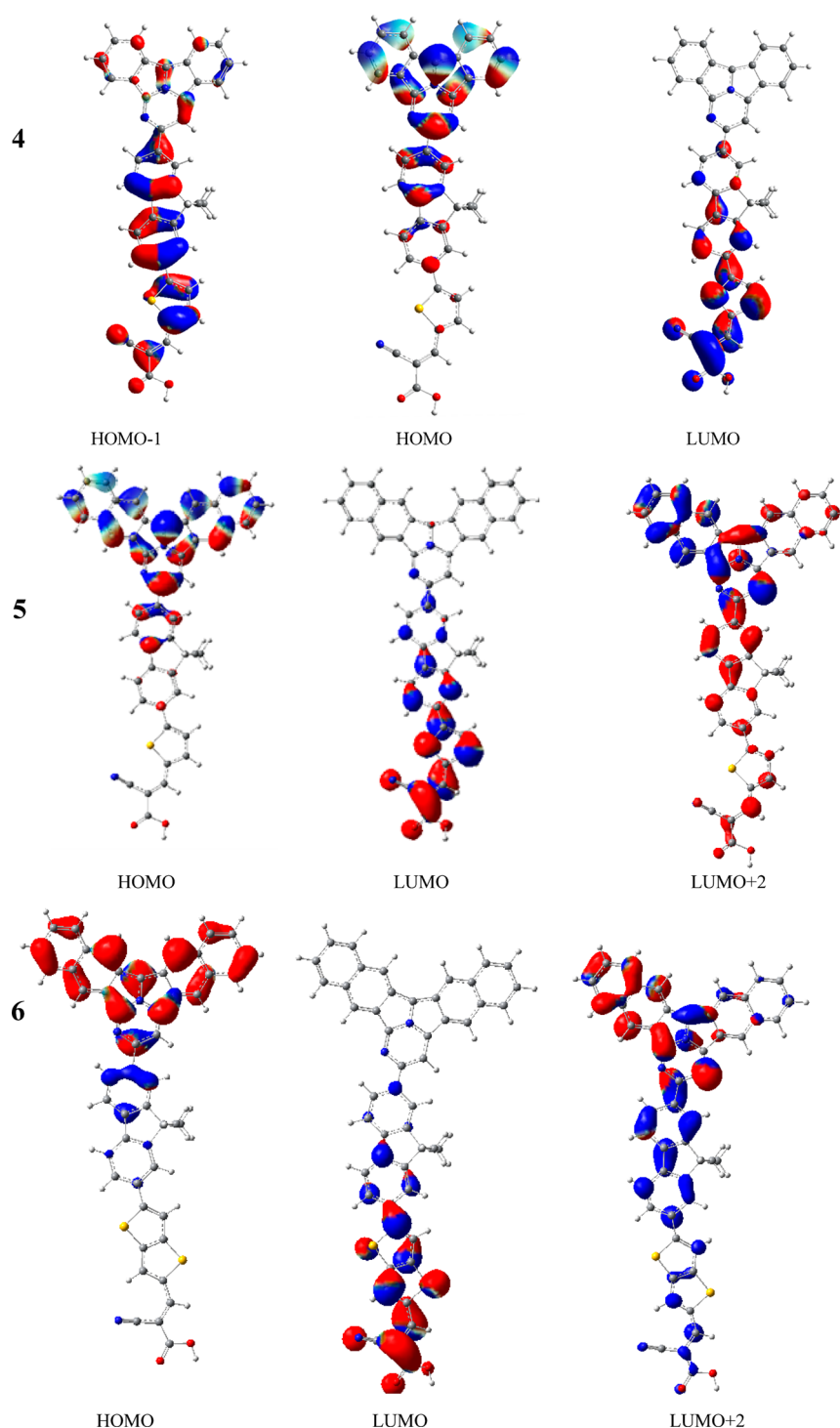


Figure 5. Frontier molecular orbitals of dyes 4–6 at the CAM-B3LYP/6-31+G*//B3LYP/6-31G* level of theory in the gas phase with an isodensity surface of 0.02.

(Figure 1). The better electronic conjugation will help to improve the absorption spectra and to decrease the HOMO–LUMO energy gap. As expected, dye 3 showed a slightly better absorption spectrum ($\lambda_{\text{max}} = 421$ nm) than dye 2 ($\lambda_{\text{max}} = 417$ nm); however, the value is lower than that of dye 1 ($\lambda_{\text{max}} = 434$ nm) (Table 1). The calculated results showed that dye 3 has a lower V_{oc} as well J_{sc} than dye 1. The effect of π -conjugation enhances the ability of the azacycl[3.2.2]azine donor group; hence, two phenyl groups were introduced into donor group 4 (Figure 1). The calculated results showed that compound 4 has

a higher LHE value (0.99) and also a similar absorption spectrum compared to dye 1 ($\lambda_{\text{max}} = 428$ nm) (Figure 3, Table 1). The ΔG_{inject} of compound 4 is -1.66 eV, which is much higher than those for dyes with donor groups 2 and 3 and also the reported dye 1 (-1.62 eV, Table 1). These calculated results suggest that the J_{sc} would be much better in this case. Dye 4 also showed higher electron transfer (0.087 e) than the previous cases (Table 2). The μ_{normal} calculated for 4 (6.97 D, Table 2, Figure 4) is also better and comparable to that of dye 1 (6.94 D, Table 2). The combination of electron injection and

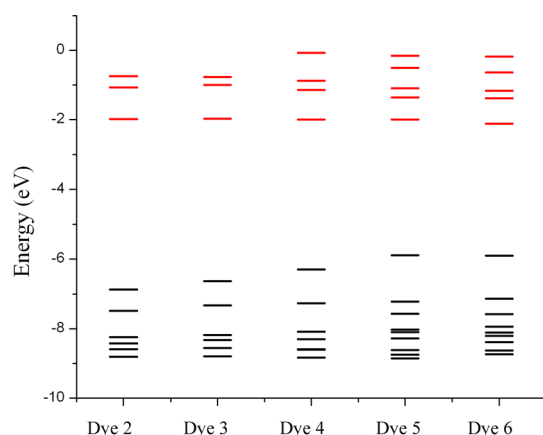


Figure 6. Calculated energy levels of the molecular orbitals of dyes 2–6. The red bars represent virtual orbitals, and the black bars denote filled orbitals.

vertical dipole moment would enhance the V_{oc} significantly for dye 4. A DSSC using dye 4 can exhibit a higher V_{oc} and J_{sc} compared to those using dyes 1, 2, and 3. Thus, the overall energy conversion efficiency should be better in this case. In these calculations, we have used $Ti(OH)_3 \cdot H_2O$ as the semiconductor surface, which is also employed in earlier studies to illustrate the properties of the semiconductor surface.⁷⁵ However, we have expanded the TiO_2 surface with the $(TiO_2)_6$ cluster model to examine the dipole moments, absorption spectra, and main configurations of the spectra for 2 and 4 as representative cases (Tables S1 and S2, Supporting Information). The calculated results revealed that the trend of the $(TiO_2)_6$ cluster model is similar to that obtained with the simple $Ti(OH)_3 \cdot H_2O$ model. We have performed our further studies with the $Ti(OH)_3 \cdot H_2O$ model.

Furthermore, the 12- π -electron azacycl[3.2.2]azine donor was extended with two naphthalene groups (dye 5, Figure 1) to achieve a higher efficiency of the cell. The DFT-calculated results reveal that dye 5 can have a much higher absorption spectrum ($\lambda_{max} = 465$ nm, Table 1, Figure 3) than dye 4. Compound 5 showed a superior J_{sc} compared to 1, as reflected in the larger ΔG_{inject} (−1.78 eV) (Table 1). The electron transfer process is also much higher in this case (Table 2). Therefore, these calculated results suggest that dye 5 can exhibit much better efficiency in cell performance.

The role of π -spacer groups in achieving cell efficiency is well documented.⁷⁰ We have undertaken the opportunity to examine the efficiency of dye 5 with thienothiophene as a spacer unit (dye 6, Figure 1). The efficiency of dye 6 should have a higher value compared to those of dyes 1 and 4 (Tables 1 and 2).

From TD-DFT calculations, it has been observed that in the case of dye 4 the favorable contribution to the first absorption peak occurring from HOMO − 1 to LUMO indicates their strong overlap (Table 1, Figure 5). In the case of dyes 5 and 6, the favorable contributions occurred from HOMO to LUMO + 2 (Table 1, Figure 5). Figure 6 shows the calculated energy levels for the molecular orbitals of dyes 2–6. Expectedly, the conjugative effect raises the HOMO energy by ~ 0.91 eV and lowers the LUMO energy by ~ 0.18 eV and, consequently, enhances the λ_{max} values in these cases (Figure 6). The HOMO frontier orbitals do not shift in position when these donor groups are used. It has been observed that the HOMO is localized on the donor part and does not change with the

elongated spacer unit. Note that the energy level of the HOMOs is ~ -6.5 eV, which is sufficiently lower than the redox potential of the I^-/I_3^- electrolyte (−4.6 eV). Such a situation can provide an advantage for the regeneration of dyes for further use.⁷¹

4. CONCLUSIONS

We have reported a series of organic donor molecules with augmented energy conversion efficiency using π -spacers and cyanoacrylic acid as an anchoring group (2–6). The DFT and TD-DFT calculations of these molecules suggest that dyes 4 and 6 have larger driving forces ($\Delta G_{inject} = -1.66$ and -1.80 eV, respectively) and light-harvesting efficiency (LHE = 0.99) in the series of donor molecules studied. Thus, these dyes should possess larger J_{sc} values compared to the other examined dyes. The calculated results also revealed that designed dyes 4 and 6 have higher J_{sc} values compared to the reported dye 1 ($\Delta G_{inject} = -1.62$ eV, LHE = 0.98) calculated with the same level of theory. Furthermore, dyes 4 and 6 showed improved vertical dipole moment and number of photoinjected electrons. The DFT calculations showed that dyes 4 and 6 have better V_{oc} values compared to dye 1 and can exhibit high cell performance. Dyes 4 and 6 are expected to exhibit high solar-energy-to-electricity conversion. We hope that dyes 4 and 6 will stimulate chemists to develop new dyes for dye-sensitized solar cells.

■ ASSOCIATED CONTENT

Supporting Information

Optimized molecular structures and the Cartesian coordinates of dyes 2–6 before and after adsorption in the gas phase. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: a.das@ncl.res.in. Fax: 00-91-20-25902629.

*E-mail: ganguly@csmcni.org. Fax: 00-91-278-2567562.

Notes

The authors declare no competing financial interest.

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