

Effect of Inserting Azabenzenes Linkers into TPA-Based Dye Sensitizers for Use in Solar Cells: DFT and TDDFT Calculations

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Abstract: Density functional theory (DFT) and time-dependent density functional theory (TDDFT) were used to study optical and electrochemical properties of a new series of dye sensitizers for use in dye-sensitized solar cells (DSSCs). The dyes include triphenylamine (TPA) unit as an electron donor and cyanoacrylic acid moiety as an electron acceptor/anchoring groups with different π -linkers. The effect of linkers on the performance of these dyes as photo-sensitizers was investigated. The linkers are benzene and azabenzenes and their hydrocarbon parent systems. The results indicated that the highest occupied molecular orbital (HOMO) is delocalized over the TPA unit and π -linker while lowest unoccupied molecular orbital (LUMO) is localized on the electron acceptor and π -linker. The HOMO level of the investigated dyes is located below the HOMO level of the I/I_3^- redox couple while the LUMO is situated above the conduction band of TiO_2 . The gradual insertion of nitrogen at benzene bridge decreases HOMO-LUMO energy gap. This ensures good electron injection and dye regeneration. They also introduce gradual red shift by increasing nitrogens at benzene bridge which is an indicator for enhancing photocurrent. The results suggest the possibility of design of efficient photovoltaic organic materials in DSSCs from the selected dyes.

Keywords: DSSCs, Triphenylamine (TPA), Azabenzenes, TD-DFT, π -linkers, FMO

Introduction

Since its invention¹, dye-sensitized solar cells (DSSCs) have drawn considerable attention for being among the most promising renewable energy devices²⁻⁶. They boast the traditional silicon-based solar cells in cost and in some other advantages¹⁻⁴. Although their photon-to-current conversion efficiency (PCE) is less than the conventional solar cells, the price/performance ratio

may be good enough to allow them for competence as a cheap source for generating electricity. The chemical stability problem is one of the drawbacks behind the lack of their entry into commercial applications at the current time⁵.

The components of DSSCs (dye sensitizers, anode, cathode and electrolyte) affect the PCE⁷⁻¹³. The requirements for an efficient solar cell sensitizers include: (1) the dye should contains anchoring groups with strong adsorption capacity to the semiconductor surface, (2) a wide absorption range in the UV/Vis to near-IR region to collect more photons from the solar spectrum, (3) proper energy level alignment of the excited state of the dye with the conduction band edge of the semiconductor and the redox level of the electrolyte with the ground state of the dye, (4) fast charge transfer from the dye to the semiconductor, with low loss of photoelectrons and (5) electrochemical and thermal stability^{6,14,15}.

The metal-free organic dyes with good performance in DSSC usually have a donor-bridge-acceptor (DBA) structure^{11,12}. In the DBA dyes, the π -electron delocalization from the electron donor to the electron acceptor through a linker can affect the performance of DSSC¹⁶. Therefore, the π -conjugated linker between the donor and acceptor moieties plays an important role not only in tuning and modifying the optical properties of DSSC devices under the sun light irradiation, but also in controlling the intramolecular electron transfer and electron injection from the excited dye to the conduction band of the semiconductor electrode.

Improving efficiency of dyes in the UV/Vis region requires a good conjugation across the donor and anchoring group which determines the large intramolecular charge transfer character of the electronic transition. The dye aggregation and charge recombination can lead to lower the efficiency in organic sensitizers¹⁷⁻¹⁹. Triphenylamine (TPA) function as electron donor and the cyanoacrylic acid moiety as electron acceptor were used widely in DSSCs²⁰⁻⁴⁴. TPA shows a steric hindrance that can prevent unfavorable dye aggregation at the semiconductor surface¹⁹. Appropriate DBA systems are required to design efficient metal-free sensitizers for DSSCs, whose properties can be tuned by structural modifications. TPA-based DSSCs have been extensively investigated by both experimental and theoretical investigations²⁰⁻⁴⁴. The π -bridges have a significant effect compared to enhancing donor ability of TPA^{45,46}.

Computational chemistry plays a vital role in the design and development of DSSCs. It has been reported that density functional theory (DFT) and its time-dependent (TD) extension are good tools for the treatment of electronic structures and absorption spectra of different systems⁴⁷. The long-range "Coulomb attenuating method" (CAM)⁴⁸⁻⁵¹ Becke three-parameters DFT with the correlation functional of Lee *et al.*, (B3LYP)⁵⁰⁻⁵² has been applied to investigate excitation energies for TPA-based dyes³⁰.

Different groups calculated ground state geometries of the TPA-based dyes at B3LYP⁵²⁻⁵⁴ with double and triple zeta basis sets including diffuse and polarization functions²⁰⁻⁴³. B3LYP bond lengths do not depend on the basis set and are almost identical to the MP2/6-31G(d,p) values³².

This study aims at investigating the effect of inserting π -conjugated linkers in the organic dye sensitizers derived from TPA and cyanoacrylic. The π -conjugated linkers were benzene and azabenzenes, as shown in Figure 1.

The energy gap between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) and the relevant energy gaps (E_g), the absorption spectra within near-UV to visible region, the related oscillator strength (f), light harvesting energy (LHE) and free energy of injection (ΔG^{inject}) of these dyes have been calculated and compared with the available experimental data, if any.

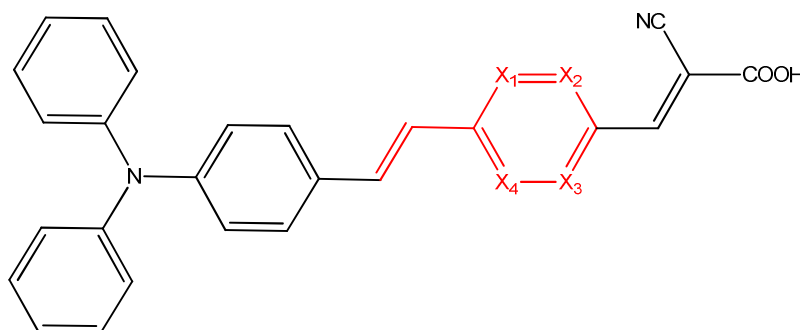
Computational details

The ground state geometries of the investigated dyes were optimized at the three-parameter B3LYP functional⁵²⁻⁵⁴ with the 3-21G(d) basis set followed by single point energy calculations in dichloromethane using polarizable continuum model (PCM)^{55,56} and 6-31+G(d,p) basis set. As the B3LYP hybrid functional underestimates vertical excitation energies, especially for larger dye molecules, the TD-CAM-B3LYP/6-31+G(d,p) level has been used to calculate the excitation energies for the selected dyes⁴⁷⁻⁵¹. The combination of TD-CAM-B3LYP with the split-valence basis sets with polarization and diffuse functions guarantees accurate absorption spectra²⁷. The calculations have been carried out in dichloromethane to match the experimental conditions⁴⁴. All calculations have been conducted with the Gaussian 09 program⁵⁷.

Results and Discussion

Electronic structure

Figure 1 displays the structures of the investigated dyes. The energies of the frontier molecular orbitals (FMO) for the selected dyes are collected in Table 1. The 2-cyano-5-(4-*N,N'*-diphenylamine) penta-2,4-dienoic acid (**a**) has an energy gap of 2.74 eV. Inserting benzene ring, as a π -linker, between 3-, 4- positions (**0N**) decreases the energy gap to 2.28 eV. Gradual replacement of the CH groups of the benzene linker with nitrogen atoms destabilizes the HOMO level and stabilizes the LUMO level, thus a remarkable decrease in the HOMO-LUMO energy gap was observed. Evidently, the presence of four nitrogen atoms in **4N** significantly lowers the energy gap (ca. 1.91 eV) compared to one, two, or three nitrogen atoms (**1N**, **2N**, **3N**, respectively). Therefore, the E_g decreases in the following order: benzene > pyridine > pyrazine > 1,2,4-triazine > 1,2,4,5-tetrazine.



N;2-Cyano-5-(4-*N,N'*-diphenylamine) penta-2,4-dienoic acid, **0N**; $X_1, X_2, X_3, X_4 = \text{CH}$, **1N**; $X_2, X_3, X_4 = \text{CH}$, $X_1 = \text{N}$, **2N**; $X_2, X_4 = \text{CH}, X_1, X_3 = \text{N}$, **3N**; $X_4 = \text{CH}, X_1, X_2 \& X_3 = \text{N}$, **4N**; $X_1, X_2, X_3, X_4 = \text{N}$

Figure 1. Structures of the selected triphenylamine dyes

Table 1. The HOMO, LUMO and HOMO-LUMO energies (eV) of the selected dyes at the PCM-B3LYP/6-31+G (d,p)//B3LYP/3-21G(d) level

| Systems | E_{HOMO} | E_{LUMO} | E_g |
|-----------|-------------------|-------------------|-------|
| 0N | -5.30 | -3.02 | 2.28 |
| 1N | -5.36 | -3.17 | 2.19 |
| 2N | -5.42 | -3.35 | 2.07 |
| 3N | -5.48 | -3.52 | 1.96 |
| 4N | -5.56 | -3.65 | 1.91 |

Good sensitizers must have narrow band gaps with their LUMOs located just above the conduction band of the semiconductor photoelectrode such as TiO_2 where the HOMO below the HOMO of redox couple. The I^-/I_3^- redox couple is often used as dye regenerator in DSSCs, implying that the solar cells work in solvent phase. Stabilization of LUMO of the dye ensures high photo-to-current efficiency for a given dye as a sensitizer. The HOMO and LUMO energies of bare $(\text{TiO}_2)_{38}$ cluster are -7.23 and -4.1 eV, respectively, resulting in an E_g of 3.13 eV⁵⁸. Effective electron injection is expected when the energy gap between the LUMO of the dye and the conduction band of the TiO_2 is higher than 0.2 eV⁵⁹. An inspection of Figure 2 indicates that the LUMO energy level of **4N** is located above the conduction band of TiO_2 while the HOMO level is situated below the HOMO of the redox couple I^-/I_3^- of -4.8 eV⁵⁹. This could ensure an efficient electron injection and regeneration⁶⁰. Adding nitrogen atoms (**1N-4N**) stabilizes the dyes LUMO levels which could allow easy electron transfer to the semiconductor photoelectrode compared to **0N**. Previous theoretical work^{29,33,38,42} reported band gaps of 1.77, 2.5, 1.96 and 2.1 eV for other di- and triphenylamine-based dyes with different π -linkers and substitutions. These values are close to those calculated for our dyes at 1.9 to 2.19 eV and could suggest them as good sensitizers.

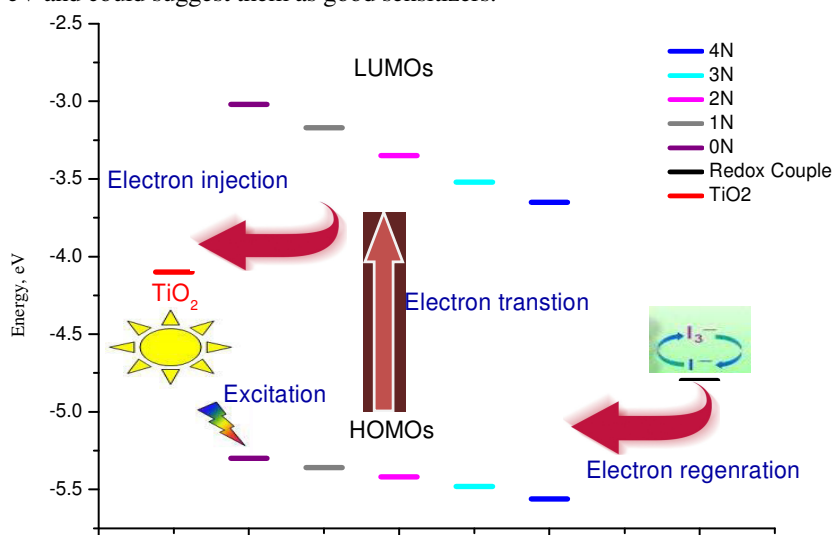


Figure 2. Sketch of PCM-B3LYP/6-31G+ (d, p)//B3LYP calculated energies of the HOMO and LUMO level of investigated compounds

The spatial distributions of HOMO and LUMO of **4N** in the S_0 state are displayed in Figure 3. The HOMO level is delocalized over TPA and π -linker while LUMO is localized on the acceptor and π -linker. This facilitates electron transfer through the dyes and guarantees good electron injection from the TPA unit to the TiO_2 conduction band³³.

As shown in Table 2, the projected density of state (PDOS) of all the dyes proves that the electron density is mainly located on donor and bridge moieties with a percentage (90-98%) for the HOMOs and an excellent electron charge transfer occurs at LUMO as the electron density is distributed at bridge and acceptor moieties with a percentage (87-92%). This is one of the features of good dyes as it's an indicator for the efficient electron transfer from HOMO to LUMO. For all dyes, TPA is a strong electron donor at HOMOs as the electron density is mainly concentrated on it and also acrylic acid is a good electron acceptor.

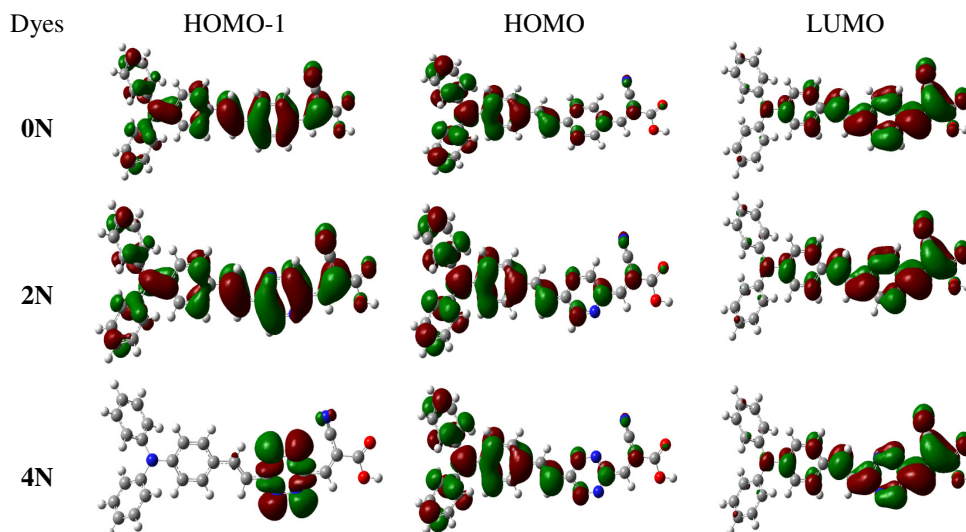


Figure 3. The HOMO-1, HOMO and LUMO spatial distribution of the designed sensitizers **0N**, **2N** and **4N**

Table 2. Calculated projected density of state (PDOS) of the investigated dyes

| Systems | HOMO | | | LUMO | | |
|-----------|-------|--------|----------|-------|--------|----------|
| | Donor | Bridge | Acceptor | Donor | Bridge | Acceptor |
| 0N | 81 | 16 | 3 | 8 | 39 | 53 |
| 1N | 84 | 14 | 2 | 7 | 37 | 56 |
| 2N | 82 | 15 | 3 | 10 | 42 | 48 |
| 3N | 83 | 14 | 3 | 8 | 37 | 55 |
| 4N | 84 | 14 | 2 | 10 | 40 | 50 |

Optical properties

The excited states in the near UV and visible regions were analyzed to determine the photophysical properties of the DBA dyes. Table 2 presents the calculated absorption spectra, oscillator strength (*f*) and assignments of transitions for the selected dyes in dichloromethane at the PCM-TD-CAM-B3LYP/6-31+G(d,p) level of theory. The absorption spectra are displayed in Figure 4. The observed absorption band at 441 nm for **0N** agrees well with the experimental value⁴⁴ of 438 nm. Previous calculations and experimental data of the DBA dyes in dichloromethane show two major absorption bands which were assigned to intramolecular charge transfer (ICT) and $\pi - \pi^*$ excitation²⁰⁻⁴⁴. For the investigated dyes, the first absorption band at ca. 400-550 nm originates from electron transfer from the donor to the acceptor moieties, which can be considered as an ICT band. The second absorption band at ca. 280-320 nm is attributed to $\pi - \pi^*$ electron transition within the entire dyes.

Compared to **0N**, replacing CH of the benzene linker by one, two and three nitrogen atoms significantly affects the UV/Vis spectra and produces red shift. For instance, replacement of benzene unit with pyridine results in 13 nm red shift in the absorption maximum. This is because pyridine is electron deficient relative to benzene which enhances the intramolecular charge transfer from TPA to cyanoacrylic acid unit. Figure 5 shows that increasing number of nitrogen atoms in the π -linker causes more red shift of the absorption

maxima relative to **0N** due to rising of electron deficiency⁶¹. Interaction of the sensitizers with the photoelectrode results in an energy alignment of both the dye and semiconductor. The PCE efficiency of a given DSSC depends on its constituents, photo anode, electrolyte, absorption spectra of the dye and its contact with the semiconductor electrode. The adsorption energies of similar systems with the same anchors were calculated between 20 and 30 kcal/mol which means good contact^{10,23,26}. The interaction between TiO₂ and dye causes stabilization of the dye LUMO and destabilization of the LUMO of the TiO₂ which leads to efficient electron transfer from the dye to the photoelectrode conduction band^{10,23,26}. The PCE of **0N** was estimated⁴⁴ as 9.1 %. Red shift is desirable for harvesting more photons. The new dyes show redshifted absorption spectra compared to **0N** and are expected to show higher efficiency and collect more photons.

Table 3. Absorption wavelength, assignment of electronic transitions, oscillator strength, and light harvesting energy for the singlet-singlet transition in Vis and near UV regions for the selected dyes in dichloromethane at PCM-TD-CAM-B3LYP/6-31+G(d,p)

| Systems | λ_{\max} , nm | f | LHE | Assignment |
|-----------|-----------------------|------|--------|--|
| 0N | 440.7 | 1.82 | 0.9849 | H \rightarrow L (61%), H-1 \rightarrow L (27%) |
| 1N | 453.9 | 1.72 | 0.9809 | H \rightarrow L (61%), H-1 \rightarrow L (25%) |
| 2N | 476.5 | 1.69 | 0.9796 | H \rightarrow L (62%), H-1 \rightarrow L (24%) |
| 3N | 477.1 | 1.50 | 0.9684 | H \rightarrow L (61%), H-1 \rightarrow L (22%) |
| 4N | 487.9 | 1.53 | 0.9705 | H \rightarrow L (63%), H-1 \rightarrow L (20%) |

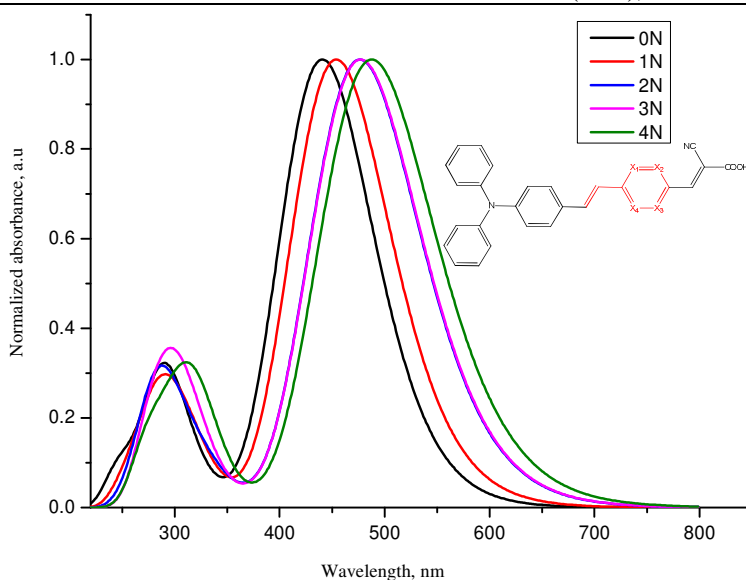


Figure 4. The calculated absorption spectra for the TPA dyes dissolved in dichloromethane at the PCM-TDCAM-B3LYP/6-31+G (d,p)//B3LYP/6-31+G(d,p) level of theory

The longest absorption wavelengths in the investigated dyes result from S₀ to S₁ electron transitions, HOMO \rightarrow LUMO. The HOMO represents π -orbital which is extended over the electron-donor and linker, while the LUMO is π^* that is localized on the linker of the electron-acceptor/anchoring, (Figure 4). This reveals an effective electron transition from the HOMO to LUMO and then electron transfer to the conduction band of the TiO₂ electrode.

It is known that a broad absorption covering the visible and some of the near-infrared region is favorable for good overlap with the solar spectrum to produce an enhanced photocurrent response^{34,35}. As shown in Figures 4 the new dyes (**1N-4N**) show a red shifted absorption band from 440 to 487 nm, which indicates an improved photo-to-current conversion compared to **0N**. Previously, absorption at 450, 548 and 474 nm was reported^{29,33,42} for TPA-based dye substituted at 3, 3' positions by 2-methoxy vinyl, polyene-diphenylaniline, 1,2-dimethyl vinyl groups, respectively. These values can be compared with our calculated absorption spectra which extend from 453 to 487 nm which cover a larger space of solar spectrum. This might ensure better performance for photon-to-current conversion once there is a good alignment between the LUMO of the dye and conduction band (CB) of the photoelectrode. These observations indicate that the selected dyes with different π -spacers could be good candidates in the DSSC devices.

Electron injection

The light-to-electricity conversion efficiency (η) of solar cell devices is determined from the open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF) and incident solar power (P_{inc}):

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

Usually, the standard AM1.5G solar spectrum $P_{inc} = 1000 \text{ W/m}^2$ is used for solar cell efficiency calculations. The short current density J_{sc} in DSSCs is determined from the following equation³²:

$$J_{sc} = fLHE(\lambda)\Phi_{inject}\eta_{collect}d\lambda \quad (2)$$

The light harvesting efficiency (LHE) of the dye sensitizer should be as high as possible to maximize photo-to-current conversion. LHE can be calculated from Eqn. (3)⁶²

$$LHF = 1 - 10^{-f} \quad (3)$$

Where f is the oscillator strength of the dye associated with the λ_{max}^{ICT} . The LHE parameter is related to light harvesting ability of the dye sensitizer and corresponds to the intramolecular charge transfer transition. The increased oscillator strength enhances the LHE value and therefore, gives rise to increase of the overlap with the solar spectrum, especially at the visible range.

Accurate $E_{CB}^{TiO_2}$ is difficult to be determined because of its sensitivity to the conditions e.g. the pH of the solution. Therefore, we used the experimental value of -4 eV where the semiconductor is in contact with aqueous redox electrolytes at pH 7.0⁶³⁻⁶⁵. Φ_{inject} is related to ΔG^{inject} of electron injection from the excited states of dye molecules to the semiconductor electrode. The ΔG^{inject} is calculated as follows⁶²:

$$\Delta G^{inject} = E_{ox}^{dye*} - E_{CB}^{TiO_2} = (E_{ox}^{dye} - E_{0-0}^{dye}) - E_{CB}^{TiO_2} \quad (4)$$

Where E_{ox}^{dye} and E_{ox}^{dye*} represent the oxidation potential of the dye in the ground and excited states, respectively, $E_{CB}^{TiO_2}$ is the conduction band edge of the semiconductor and E_{0-0}^{dye} is the 0-0 transition energy between the ground and the excited state. To estimate the

0–0 “absorption” line, we need both the S_0 (singlet ground state) and the S_1 (first singlet excited state) equilibrium geometries.

As shown in Table 3, insertion of nitrogen atoms in benzene bridge (**1N-4N**), the absorption wavelengths increase. The azabenzene derivatives have reasonable values of oscillator strengths and LHE which leads to higher photo-to-current efficiency as inferred from Eqs.1-3.

Table 4 lists the injection free energies of the investigated dyes and reveals that ΔG^{inject} decrease with increasing E_{ox}^{dye*} . **4N** has the largest E_{ox}^{dye*} and its ΔG^{inject} is smaller than the corresponding values for other dyes. However, The free energy of injections is large enough to guarantee efficient electron injection. On the other hand, too large ΔG^{inject} may introduce energy redundancy, resulting as smaller V_{oc} and large thermalization losses¹⁰.

Table 4. Calculated electronic properties of the selected dyes E_{ox}^{dye*} , E_{0-0}^{dye} and ΔG^{inject}

| Systems | E_{ox}^{dye} | E_{ox}^{dye*} | E_{0-0}^{dye} | ΔG^{inject} |
|-----------|----------------|-----------------|-----------------|---------------------|
| 0N | 5.30 | 2.61 | 2.689 | -1.39 |
| 1N | 5.36 | 2.67 | 2.652 | -1.33 |
| 2N | 5.42 | 2.82 | 2.549 | -1.18 |
| 3N | 5.48 | 2.87 | 2.549 | -1.13 |
| 4N | 5.56 | 2.98 | 2.765 | -1.02 |

Conclusion

The influence of π -linkers of a series of triphenylamine (TPA)-based dye sensitizers on their electronic and optical properties was studied for use in dye-sensitized solar cells (DSSCs) using DFT and TDDFT formalisms. The linker includes benzene and azabenzenes. The results indicated that the gradual insertion of nitrogen at benzene π -linker shows an enhanced spectral response (compared to **0N**) in the UV/Vis solar spectrum due to sharp lowering in the LUMO level and smaller HOMO-LUMO energy gap. HOMO and LUMO of the dyes are located above and below the conduction band of TiO_2 photoelectrode and the HOMO of the I/I_3^- redox couple, respectively, which could guarantee efficient electron injection and regeneration assuming a good alignment of energy levels among the constituents of the solar cell. The electron transfer from the LUMO of the dyes to the conduction band of the TiO_2 electrode can occur efficiently after HOMO to LUMO transition in the dye. The HOMO-LUMO energy gap decreases with increasing number of nitrogen atoms in the benzene linker. Tetrazine bridge seems more efficient as it shows a remarkable red shift in the absorption band compared to other dyes. The HOMO of the studied dyes is delocalized over the π -conjugated system with the highest electron density concentrated on the TPA moiety. On the other hand, the LUMO is localized on the anchoring group through the π -bridge. Compared to previous work, the new dyes give reasonable ΔG^{inject} . This ensures better electron injection. Our simulations could suggest the new dyes as efficient sensitizers in DSSCs.

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