

Triphenylamine Based Organic Dyes with Different Spacers for Dye-Sensitized Solar Cells: A First Principle Study

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ABSTRACT: The four novel metal-free organic dyes Ref. Dye, SP-SO, SP-OS and SP-OO, containing a Triphenylamine (TPA) unit as the π -bridge were designed and the impacts of the spacer on the photovoltaic performances were studied. The Geometry structure, energy levels, light-harvesting ability and ultraviolet-visible absorption spectra were calculated by using Density Functional Theory (DFT) and Time-Dependent-DFT. The results show that incorporating spacer with moderate electron-deficient ability can extend the absorption range (400-950 nm) and adjust the molecular orbital energy levels, improving the photovoltaic performance devices. The investigated dye reveals that SP-SO sensitizers showed absorbance in the visible region (400-950 nm) with higher oscillator strength (f) (1.1178 and LHE (0.9237).

KEYWORDS: DSSC, DFT, Electronic Absorption Spectra, Electron Injection Driving Force and Light Harvesting Efficiency.

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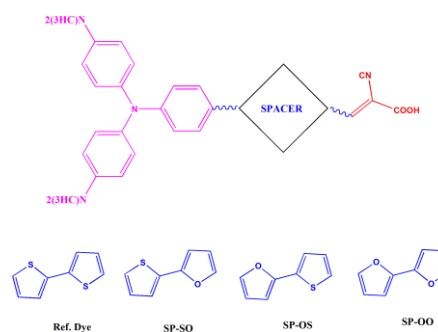
1. INTRODUCTION

The molecular compounds with non-linear optical (NLO) properties are currently drawing substantial attention, owing to their potential applications in optoelectronic devices for telecommunications and information storage [1-3]. The organic materials with good NLO properties have been the subject of extensive research from both experimental and computational points of view, because of the inherent disadvantages of the commonly used inorganic materials like lithium niobate in optoelectronic devices [4,5]. The contrasting feature is that the inorganic materials manifest NLO responses originating from suitable geometric perturbations of the key ions within a solid-state crystalline structural framework of the compound, whereas organic materials manifest the same on the transfer of electronic charge across the molecule [6].

Organic compounds, alternatively, have several benefits, such as large susceptibility, high laser damage threshold, very fast response time, low dielectric coefficient, better tailor ability, good process ability and large molecular NLO responses [7,8] and as a result, significant research efforts have been put forth on organic compounds both at industry and academic contextual. In order to modify the optical spectra along with NLO responses, alteration of molecular structure by substituent groups and substitution positions can be used as a useful scheme [9-11]. Carbazole derivatives have displayed promising properties ranging from electro-optics to dye-sensitized solar cells (DSSCs) [12-15]. Modulation of NLO properties of carbazole by

attaching various donor groups has already reported [16]. It seems applicable to TPA-based dyes and also the most studied compounds in the field of optics, owing to their high hole mobility and good photoconductivity [17-20].

Based on the above mentioned facts of TPA-based dyes, a theoretical study has been proposed in the present work to elucidate the effect of number of spacer units on NLO properties of organic dyes. The spacer moieties with TPA as donors have been designed quantum mechanically and are illustrated in Scheme 1. Time dependent density functional theory (TD-DFT) calculations have been performed to compute the NLO responses and absorption spectra of dyes. We hope that this work may facilitate the upcoming experimental studies to design new efficient organic dyes and may also provide guidelines towards the synthesis of efficient NLO compounds.



Scheme: Chemical Structure of the designed the dyes based on the TPA

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2. COMPUTATIONAL STRATEGY

All the calculations were performed through Gaussian 09w package [21]. Density functional theory (DFT) method was employed for ground state optimization, while the excited state calculates were carried out using Time-dependent DFT (TD-DFT) method. The DFT was treated according to hybrid functional B3LYP (Becke3-Lee-Yang-Parr hybrid unctional) with the 6-311++G(d,p) basis set [22]. The Conductor-like Polarizable Continuum Model (C-PCM) was used to optimize the excited state geometries [23]. The excitation energies, oscillator strengths and orbital contribution for the lowest 20 singlet-singlet transitions at the optimized geometry in the ground state were obtained by TD-DFT calculations using the same basis set as for the geometry minimization.

3. RESULTS AND DISCUSSION

3.1. Geometrical Structures of Dyes

The geometrical and electronic properties of Ref. Dye, SP-SO, SP-OS, and SP-OO dyes were studied by adopting DFT method and their optimized structures are shown in Figure 1. The dyes are fully optimized without any structural constrains. The selected geometric parameter values are furnished in Table 1. The D- π -A based molecular framework of the dyes is coplanar in structure that facilitates close packing and high coverage on the semiconductor surface [24]. This

feature will be verified by simulating the adsorption of the dyes on semiconductor surface.

Table 1 The HOMO and LUMO energy in eV at ground state obtained in B3LYP/6-311++G (d,p)

| Dye | HOMO | LUMO | Energy Gap |
|---------|-------|-------|------------|
| Ref-Dye | -5.01 | -2.98 | 2.03 |
| SP-SO | -5.15 | -2.62 | 2.53 |
| SP-OS | -5.11 | -2.54 | 2.57 |
| SP-OO | -5.16 | -2.42 | 2.74 |

3.2. Frontier Orbital levels of Isolated Dyes

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the dye sensitizer are essential to match the potential of iodide (I^-) / trioxides (I_3^-) redox couple and conduction band edge of the TiO_2 semiconductor which are illustrated in Figure 2. The HOMO and LUMO levels, corresponding energy and band gap values of the selected dyes are given in Table 2. The electron donating capacity of selected dyes varies based on the π -spacer of the energy gap, thus decreasing the oxidation potential. The energy gap is decreased gradually in the order of SP-SO > SP-OS > SP-OO > Ref.Dys.

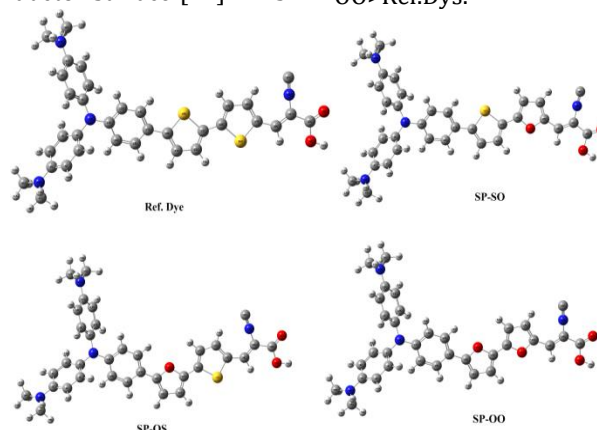


Figure 1. Optimized ground state geometries of the selected dyes in gas phase obtained at the B3LYP/6 311++G(d,p) level of theory

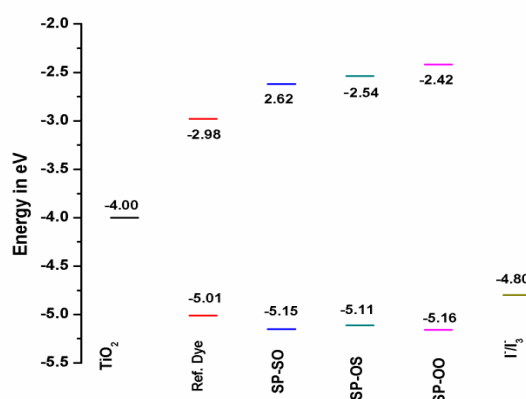


Figure 2. The frontier molecular orbital's of the designed dyes

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Figure shows the donor part of the fully occupied TPA entire localized part and delocalized to the acceptor part of the selected dyes. It is noteworthy that incorporation of spacer unit close to the acceptor group promotes the HOMO level of SP-SO and SP-OO dyes, which is ideal for electron injection to the TiO₂ conduction band. Despite this, the LUMO energy levels of all the dyes are considerably higher than the valance band of the TiO₂

[25]. Moreover, the HOMO energy levels of all the dyes are located slightly higher than the reduction potential energy of the I⁻/I₃⁻ redox electrolyte (-4.80 eV) [26]. The HOMO and LUMO energy level investigation of the dyes disclosed that the electron injection from the excited state of the dyes into the conduction band of the TiO₂ is highly feasible.

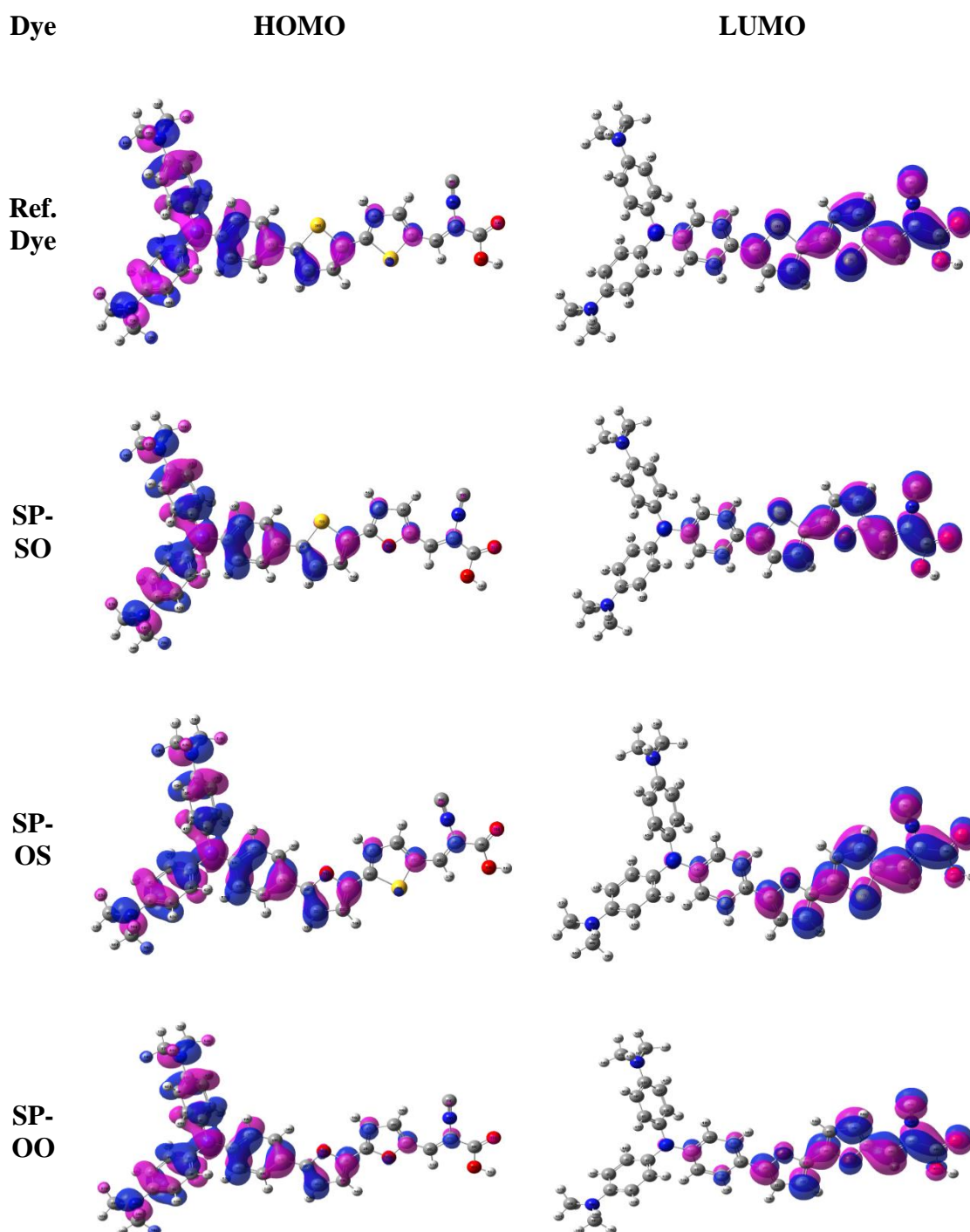


Figure 3 HOMO and LUMO energy level diagram of designed the organic sensitizers

3.3. Absorption Properties of Dyes

One of the functions of a sensitizer in DSSCs lies in its light absorption ability, which plays a crucial role in enhancing the short current density (J_{sc}), which is expressed in Eq. (1). An ideal sensitizer should absorb the solar radiation as much as possible in the visible and near-IR range. From the above-mentioned geometrical structures, we know that the rigid π -spacers will extend the π -conjugations of dyes; herein, we will further investigate the effects of such rigidified π -bridges on their absorption properties by means of TD-DFT calculations [27, 28].

Table 2. Absorption wavelength (in nm and eV), oscillator strength (f in a.u.), orbital transitions and light harvesting efficiency (LHE) of the studied dyes

| Dye | Wave length | | f | LHE | Main Contributions |
|---------|-------------|------|--------|---------|--------------------|
| | nm | eV | | | |
| Ref-Dye | 733 | 1.69 | 0.6413 | 0.7715 | H→L(100) |
| | 488 | 2.53 | 0.0697 | 0.14827 | H-2→L(89) |
| | 481 | 2.57 | 0.9989 | 0.8997 | H-2→L(11) |
| SP-SO | 688 | 1.80 | 0.6036 | 0.7508 | H→L(100) |
| | 465 | 2.66 | 0.0581 | 0.1232 | H-2→L(93) |
| | 462 | 2.68 | 1.1178 | 0.9237 | H-1→H(81) |
| SP-OS | 728 | 1.70 | 0.5231 | 0.70015 | H→L(100) |
| | 484 | 2.56 | 0.164 | 0.3145 | H-2→L(78) |
| | 477 | 2.59 | 0.7781 | 0.8333 | H-2→L(22) |
| SP-OO | 693 | 1.78 | 0.4975 | 0.68194 | H→L(100) |
| | 464 | 2.67 | 0.1311 | 0.2605 | H-2→L(82) |
| | 458 | 2.70 | 0.9422 | 0.8857 | H-2→L(18) |

H-HOMO, L-LUMO

$$J_{SC} = \int LHE(\lambda) \Phi_{INJ} \eta_{coll} d\lambda \quad (3.1)$$

$$LHE = 1 - 10^{-f} \quad (3.2)$$

The UV-vis absorption spectra of the dyes were simulated by TD-DFT method with functional B3LYP in acetonitrile solution and the resultant simulated spectra are shown in Figure 4. The maximum absorption wavelength (λ_{max}), oscillator strength (f), light harvesting efficiency (LHE) and major transition of the dyes are given in Table 3. The absorption spectra of the dyes have exhibited two distinct absorption bands in the ultraviolet and visible regions. The maximum absorption of the dyes are

decreased in the order of SP-SO > SP-OS > SP-OO > Ref.Dys. The maximum absorption peak of SP-SO dye is situated at 688 nm and showed broad absorption in the UV-visible region from 350 nm to 800 nm.

This can be attributed to the $\pi \rightarrow \pi^*$ and ICT transitions from the donor to the acceptor unit as evident from the TD-DFT results. The LHE is a crucial factor that highly influences the short current density and efficiency of DSSC. In the present study, the calculated LHE values of the modified dyes are very high when compared to the Ref. dye. The SP-SO dye exhibited highest oscillator strength (0.6036) and its corresponding wavelength is 462 nm. The dye modified with spacer moieties exhibited very lowest oscillator strength (0.4975) at the wavelength of 693 nm and its corresponding major transition is 100%.

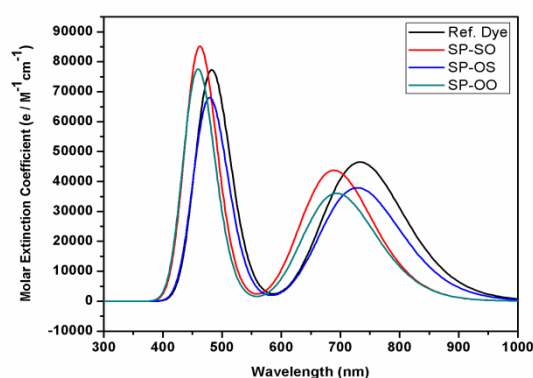


Figure 4 Simulated UV-Vis. absorption spectra of some selected dyes

3.4. NLO Properties-Computational Approach

The NLO properties of dyes are very crucial for device applications, such as optical devices, communication technology, optical switches and signal processing. The value of optical response depends on the electronic properties of the entire material.

In molecules, it depends on the linear response (polarizability) and non-linear responses (first and second hyperpolarizabilities). Hence, these properties must be calculated to evaluate the NLO potential of dye sensitizers.

The dipole moment is an important parameter towards the NLO properties. In the present study, the dipole moment was calculated using the following equation (3) [29]

$$\mu = (\mu_x + \mu_y + \mu_z)^{\frac{1}{2}} \quad (3.3)$$

Where, μ is total dipole moment and μ_x , μ_y , μ_z are the tensor components of selected dyes. The dipole moment is calculated using both gas phase and solvent mediums and their values are furnished in table 3. The polarizability and anisotropic polarizability were calculated using equations (4) & (5) [29, 30]

$$\alpha = \frac{1}{3} [\alpha_{xx} + \alpha_{yy} + \alpha_{zz}] \tag{3.4}$$

$$\Delta\alpha = \frac{1}{\sqrt{2}} \left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xz}^2 + 6\alpha_{xy}^2 + 6\alpha_{yz}^2 \right]^{1/2} \tag{3.5}$$

where, α_{xx} , α_{yy} and α_{zz} are polarizability tensor components. The values of anisotropic polarizability and mean polarizability of selected dyes are given in Table 3. The average polarizability of dyes were decreased in the order of SP-SO > SP-OS > SP-OO> Ref.Dys. Polarizability of TPA based pyrrole spacer moieties were higher over Ref. dye and comparative analysis of the designed dyes were evaluated both gas phase and solvent medium. Mostly, all the parameters of the selected dyes have exhibited high values for the solvent medium. The mean polarizability is essential to

gain high first hyperpolarizabilities [31]. NLO response of materials can be measured as first hyperpolarizability (β), which is related with intra molecular charge transfer (ICT), causing flow of electrons from donor moiety to acceptor group via π -conjugation. The communication of electronic density with an external electric field changes the dipole moment and NLO activity [32]. The first order hyperpolarizability was calculated using the equations (6) & (7) [33, 34].

$$\beta = \left[(\beta_{xxx} + \beta_{yyy} + \beta_{zzz})^2 + (\beta_{xxy} + \beta_{yyx} + \beta_{yzz})^2 + (\beta_{xxz} + \beta_{zyy} + \beta_{zzz})^2 \right]^{1/2} \tag{3.6}$$

Where, $\beta_{xxx}, \beta_{yyy}, \beta_{zzz}, \beta_{xxy}, \beta_{yyx}, \beta_{yzz}, \beta_{xxz}, \beta_{zyy}, \beta_{zzz}$ first order tensor components.

The values of first hyperpolarizabilities were calculated using B3LYP functional with 6-311++(d,p) basis set. The computed β values of selected dyes under gas phase and solvent medium are given in Table 3. The decreasing order of β under solvent medium for the selected dyes was SP-SO > SP-OS > SP-OO> Ref. Dye> . Among the spacers, the pyrrole based spacer disclosed higher β when compared to Ref. dye. Greater NLO response can be attributed to increase in charge transfer from donor to acceptor through π -spacer.

A desirable open circuit voltage (V_{oc}) is required to improve PCE of DSSC. The V_{oc} value was calculated using Eq. (3.8). The V_{oc} value is directly determined by shift in the conduction band edge of the semiconductor (ΔE_{CB}) [34-36].

$$eV_{OC} = E_{LOMO} - E_{CB} \tag{3.8}$$

The selected dyes with different π -spacers possibly present low charge recombination and increasing the efficiency of devise. The calculated open circuit voltage values are tabulated in the table 3. The binding energies of designed SP-OO dye are smaller than the Ref dye.

The values of β higher for the SP-SOand SP-OO dyes than that of the Ref Dye. This can be understood on the basis of higher electron pulling effect of thiazole based spacer, which facilitates in creating a stronger dipole and contribute to the first order Hyperpolarizability.

Based on the computational data, it could be inferred that larger V_{oc} value could be obtained with the SP-OO dye over other dyes owing to its slower charge recombination property and larger ΔE_{CB} . This future facilitates the design of SP-SO based dye sensitizer for high efficiency DSSCs.

3.5. Open-Circuit Voltage Analysis

Table 3 Static dipole moment (μ), mean Polarizability (α_0), Polarizability anisotropy ($\Delta\alpha$), First Hyperpolarizability (β_0) and Open circuit voltage (in eV) calculated at B3LYP level using 6-311++G(d,p) basis set

| Dye | Dipole Moment(μ) in Debye | Polarizability(α) ($\times 10^{-23}$ e.s.u) | Polarizability Anisotropy(Δ) ($\times 10^{-24}$ e.s.u) | Hyperpolarizability First order(β) ($\times 10^{-29}$ e.s.u) | eV |
|---------|---------------------------------|---|--|---|------|
| Ref-Dye | 14.88 | 3.77 10 | 2.97 | 0.18 | 0.21 |
| SP-SO | 15.17 | 3.75 | 1.13 | 2.04 | 0.35 |
| SP-OS | 13.05 | 2.38 | 3.34 | 1.34 | 0.31 |
| SP-OO | 13.65 | 3.57 | 2.40 | 1.61 | 0.36 |

4. CONCLUSION

The spacer alters the electronic properties of the TPA based sensitizers at D- π -A through DFT and TD-DFT method. The SP-SO based spacer units showed improvement in the Polarizability and Hyperpolarizability values of the selected dye. The NLO response of pyrrole based dye was higher than that of the other spacer moieties. DFT and TD-DFT studies disclosed that the HOMO level spread over TPA and π -spacer moieties and LUMO level spread over spacer unit and acceptor groups are ideal sensitizers for DSSCs. All the above mentioned structural modification can minimize the energy gap between HOMO and LUMO that lead to optical absorption at longer wavelength. Hence, the NLO properties of spacer modification for organic sensitizers will be helpful to design new compounds. The performance of different spacer units may play a vital role and ultimately predict the efficiency of optoelectronic and photovoltaic devices.

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