

1,3,4-Thiadiazole rings as π -spacers in triphenylamine based dyes: A density functional theory study of reactivity, UV/Visible spectra, structural and optical properties

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Abstract: The geometry, electronic structure, polarizability and reactivity of triphenylamine based organic dyes, which contain 1,3,4-thiadiazole rings as an electron donor-acceptor moiety, were studied using density functional theory (DFT), and the electronic absorption spectrum was investigated via time-dependent DFT (TD-DFT) with B3LYP/6-31G(d) level of theory. All the computations were done in gas phase at 298.15 K temperature and 1 atmosphere pressure. The results of computations indicate that the increasing number of 1,3,4-thiadiazole ring as π -spacer size in the structures of triphenylamine based dyes cause the more kinetic stability of molecules. And also, the UV-Visible spectra of molecules are gradually broadened and red-shifted increasing number of 1,3,4-thiadiazole units.

Keywords: Triphenylamine based dyes, Thiadiazole ring, Computational study, Time-dependent density functional theory, Electronic transitions.

Introduction

A dye is a colored substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber. Both dyes and pigments are colored because they absorb some wavelengths of light more than others. In contrast to dyes, pigments are insoluble and have no affinity for the substrate. Some dyes can be precipitated with an inert salt to produce a lake pigment, and based on the salt used they could be aluminum lake, calcium lake or barium lake pigments [1-8].

Organic dyes are extensively studied due to low cost, easy synthesis and fabrication. Easy structural modification of organic compounds enables to tune the chemical structures and properties for desired optical

response. These compounds with delocalized electrons are gaining much attention due to their large optical properties. It is considered that optical properties are associated with the intramolecular charge transfer (CT). Charge transfer takes place from donor to acceptor through π -spacer [9-12].

The five important properties of a dye are color, solubility, stability, reactivity and response to optic [13]. A particularly important method for understanding of the properties of a molecule is to model a molecular system prior to synthesizing that molecule in the laboratory. This is very useful mean because synthesizing a compound could need months of labor and raw materials, and generates toxic waste. A second use of computational chemistry is in understanding a problem more completely. There are some properties of a molecule that can be obtained

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theoretically more easily than by experimental means [14-16].

The present work was performed to show the effect of 1,3,4-thiadiazole rings number on stability, reactivity, optical properties and UV/visible spectra of organic dyes. Four triphenylamine dyes differing in π -spacer size were studied. Quantum mechanical computations were carried out to obtain the structural properties and absorption spectra of dyes. I hope my work would facilitate the future experimental studies to design and fast screen new efficient organic dyes.

Results and discussion

Relative energetic:

Scheme 1 indicates the structures of the triphenylamine based dyes presently considered. All considered compounds are presented in the Table 1. Table 2 shows the computed total energies of the structures at DFT theory (B3LYP) at the 6-31G(d) basis set. Total energies are corrected for zero-point vibrational energy (ZPVE). It can be seen from the data of the Table 2, the relative energies of the systems decreases in the following order: D3 > D2 > D1 > D0. Therefore, the stability of triphenylamine based dyes gradually increased on increase of 1,3,4-thiadiazole rings in π -spacer.

Electronic properties:

Electron density analysis for each one atom of the molecules indicates the reactivity of each atom in the structures, since they show the reactive regions as well as the nucleophilic and electrophilic attack in the molecules (Figure 1). Despite the fact that the molecular charge distribution remains unperturbed through the external test charge (no polarization occurs), the electrostatic potential of a molecule (MEP) is still a good guide in assessing the molecules reactivity towards positively or negatively charged reactants. The MEP was typically visualized through mapping its values onto the surface reflecting the molecules boundaries [17]. The three-dimensional electrostatic potential maps of the structures are shown in Figure 2. The red loops and the blue loops indicate negative and positive charge development for a particular system respectively. From the Figure 2, the negative charge is located on the nitrogen elements of the 1,3,4-thiadiazole rings and the nitrile and carbonyl groups as expected due to the electron withdrawing character of theirs. However, charge development on nitrile and carboxylic acid groups decreases with

increasing number of 1,3,4-thiadiazole rings in the structures.

Frontier molecular orbitals (FMOs) energies:

It is well known that global reactivity indices defined within conceptual DFT is a powerful tool to explain reactivity and the molecular properties [18]. Consequently, I have calculated global hardness, defined as $\eta = (I-A)/2$ and electronic chemical potential, defined as $\mu = -(I+A)/2$, where I and A denote ionization potential and electron affinity, respectively. In addition, global electrophilicity index, defined as $\omega = \mu^2/2\eta$, was also calculated. Following Koopman's theorem allows to evaluate μ as $(\epsilon_H + \epsilon_L)/2$ and η as $(\epsilon_L - \epsilon_H)/2$ where ϵ_H and ϵ_L indicate the energy of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively [19]. Energies of the HOMO and LUMO are important parameters in quantum chemical calculations. While the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity. Energy difference between HOMO and LUMO orbitals is called "energy gap" that is an important parameter for structural stability. Higher HOMO energy corresponds to the more reactive molecule in the reactions with electrophiles, while lower LUMO energy is essential for molecular reactions with nucleophiles. The HOMO is the orbital that donates electrons to the electron deficient species and the LUMO is the orbital that accepts electrons from electron rich species. A hard acid and/or base is associated with the large difference between ionization energy and electron affinity. The chemical hardness of a molecule is a good indicator of the chemical stability [20]. From the HOMO-LUMO energy gap, one can find whether the molecule is hard or soft. The molecules having large energy gap are known as hard and molecules having a small energy gap are known as soft. The soft molecules are more polarizable than the hard ones because they need small energy to excitation. Global electrophilicity index (ω) is estimated by using the electronegativity and chemical hardness parameters. A high value of electrophilicity describes a good electrophile while a small value describes a good nucleophile [19].

The calculated HOMO/LUMO energies, chemical potentials (μ), chemical hardnesses (η) and electrophilicity indexes (ω) of the compounds are collected in Table 3. We can see the HOMO energy of all dyes is -5.4 eV, but the LUMO energy of the molecules decreases in the following order: D0 > D1 > D2 > D3. Then, the reaction of compounds with

nucleophiles increases when the size of π -spacer increases. From the data of the Table 3, the HOMO-LUMO energies gap and chemical hardness of the molecules show the order of D0 > D1 > D2 > D3. It can be deduced that the kinetic stability and reactivity increases and decreases respectively with increasing of π -spacer size in triphenylamine based dyes. And also, the electrophilicity index order for the molecules is D3 > D2 > D1 > D0. This order gives us the same deduction of LUMO energies order of molecules.

Figures 3 and 4 show the correlation between chemical hardness (η) and total energy (E), electrophilicity index (ω) and total energy (E), respectively. It can be seen that the reactivity and electrophilicity of molecules increases with increasing the stability in molecules.

Density of states (DOS) of a system describes the number of states per interval of energy at each energy level that are available to be occupied. For atoms or molecules in gas phase, the density distributions are not discrete like a spectral density but continuous. A high DOS at a specific energy level means that there are many states available for occupation. A DOS of zero means that no states can be occupied at that energy level. In general a DOS is an average over the space and time domains occupied by the system [21, 22]. The DOS of investigated dyes (Figure 5) were calculated and created by convoluting the molecular orbital information with Gaussian curves of unit height and full width at half maximum (FWHM) of 0.3 eV using GaussSum 3. We can see from the DOS plots of the molecules, the LUMO density with energy in the range -5 eV to -12 eV increases, when the size of π -spacer increases.

Linear optical (LO) properties:

The development of optoelectronic materials and high efficient devices today points to the need of further improvement of the optical and transport properties. Therefore, the attempts to grow high quality crystals with low defect density or to design heterostructures for carrier confinement have been widely made [23]. Theoretically, the optical or electric reaction can be understood as the process of electron transitions between different energy states. The electronic energy band structure forms the basic frame for various electron movements in energy space. In principle, the strength of optical response depends on the electrical properties of the whole material, which for molecules can be related to the polarizability (α , linear response) [24]. Therefore, this is the property that should be measured in order to assess the optical

potential for molecules. The mean polarizability has been obtained using following formula [25]:

$$\alpha_{mean} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

Where α_{xx} , α_{yy} , α_{zz} are diagonal elements of polarizability matrix.

Values of mean polarizabilities and major contributing tensors of the molecules are given in Table 4. It can be seen from the data that the polarizability significantly increases on addition of 1,3,4-thiadiazole ring in π -spacer. Polarizability is dominantly determined by the x or y-direction transition. For example, the expression of dipole polarizability (x direction) is described in the following formula [25]:

$$\alpha_{xx} \propto \frac{(M_x^{gm})^2}{E_{gm}}$$

Where M_x^{gm} is transition moment between the ground and m^{th} excited state and E_{gm} is transition energy. We can see that the α value is directly proportional to the square of the transition moment and is inversely proportional to the transition energy. As a result, in general, the dye with a high value of M_x^{gm} will have a larger α value. And also, we can deduce that the M_x^{gm} is inversely proportional to the HOMO-LUMO energies gap.

UV-Vis spectra of molecules:

Time-dependent density functional theory (TD-DFT) combines the advantages of density functional theory and time-dependent formalism allowing the accurate determination of excited state properties. The technique can deal with the same accuracy for both medium and large molecules. TD-DFT is particularly well suited to low energy valence excited states which can be described by combinations of single excitations but should also work well for large, conjugated molecules. The main drawback of TD-DFT, inherent to any DFT approach, is the choice of the exchange correlation functional [26-28].

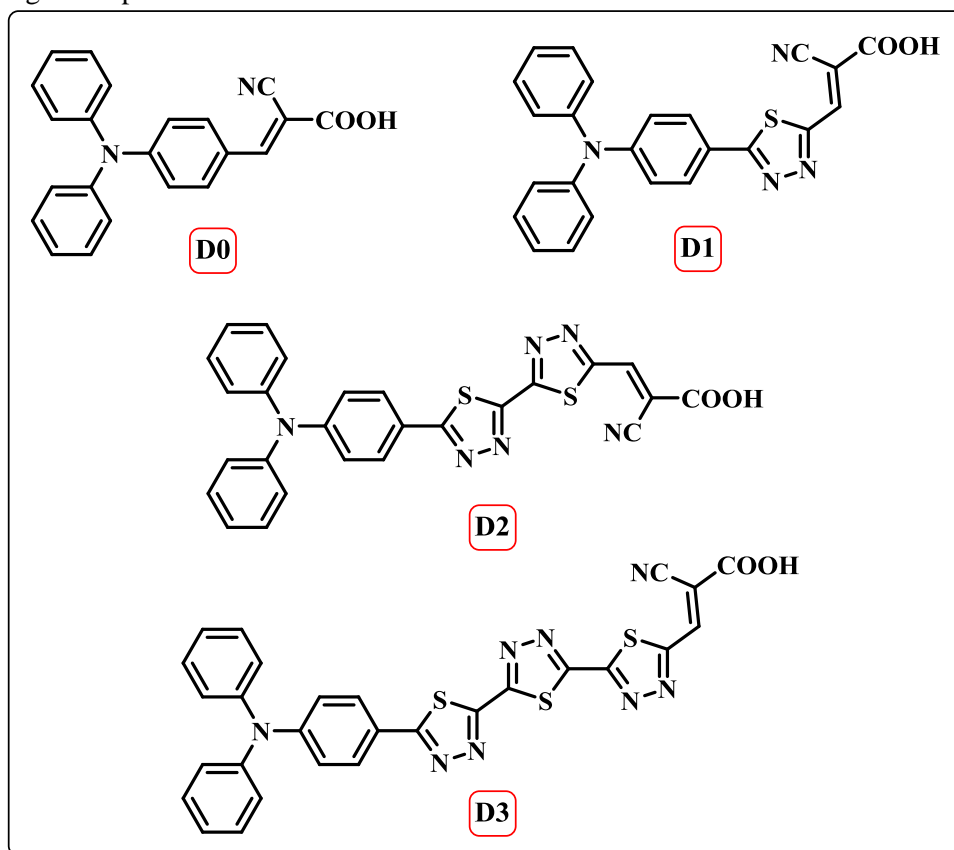
The calculated absorption wavelengths (λ), absorption energy, oscillator strengths (f) and nature of the transitions are collected in Table 5, while stimulated spectra are given in Figure 6. Computed λ_{max} of compound D0 (415 nm) is close to experimental λ_{max} (400 nm). This difference may due to the lack of direct solute-solvent interaction and the inherent approximations in the TD-DFT. This close agreement between computed and experimental values shows that used computational methodology is suitable to study designed dyes. Maximum absorption wavelength (λ_{max})

has seen significant red-shift. Molecule D3 with three 1,3,4-thiadiazole rings showed a λ_{\max} of 748 nm, while λ_{\max} for compound D0 having no 1,3,4-thiadiazole was 415 nm. Absorption energy significantly decreases from compound D0 to D3. Red-shifting of maximum absorption wavelength was in good agreement with energy gap. Maximum absorption wavelength is red-shifted with decrease of energy gap on the increase of number 1,3,4-thiadiazole units. Another factor that relates to efficiency of dyes is the performance of the dyes in responsibility to the incident light. Based on the light harvesting efficiency (LHE) of the dyes, the value has to be as high as possible to maximize the

photocurrent response. The LHE can be obtained by following formula [25]:

$$LHE = 1 - 10^{-f}$$

The LHE values are listed in Table 6. We can see the LHE order for the dyes is D0 > D1 > D2 > D3. Therefore, it can be deduced the light harvesting efficiency decreased with increase of 1,3,4-thiadiazole rings. The mentioned results show that increasing number of 1,3,4-thiadiazole in π -spacer is a valuable strategy to enhance the photovoltaic current. In dyes D0, D2 and D3 the HOMO to LUMO transition is most probable and low energy transition.



Scheme 1: Structure of studied triphenylamine based dyes.

Table 1: Studied molecules and their IUPAC names.

Dye	IUPAC name
D0	(E)-2-cyano-3-(4-(diphenylamino)phenyl)acrylic acid
D1	(E)-2-cyano-3-(5-(4-(diphenylamino)phenyl)-1,3,4-thiadiazol-2-yl)acrylic acid
D2	(E)-2-cyano-3-(5'-(4-(diphenylamino)phenyl)-[2,2'-bi(1,3,4-thiadiazol)]-5-yl)acrylic acid
D3	(E)-2-cyano-3-(5''-(4-(diphenylamino)phenyl)-[2,2':5',2''-ter(1,3,4-thiadiazol)]-5-yl)acrylic acid

Table 2: Calculated energies of the molecules.

Dye	Energy (hartree)	RE (kcal/mol)
D0	-1107.9140434	0.000
D1	-1691.7933696	-366390.116
D2	-2275.6717776	-732779.656
D3	-2859.5509926	-1099169.702

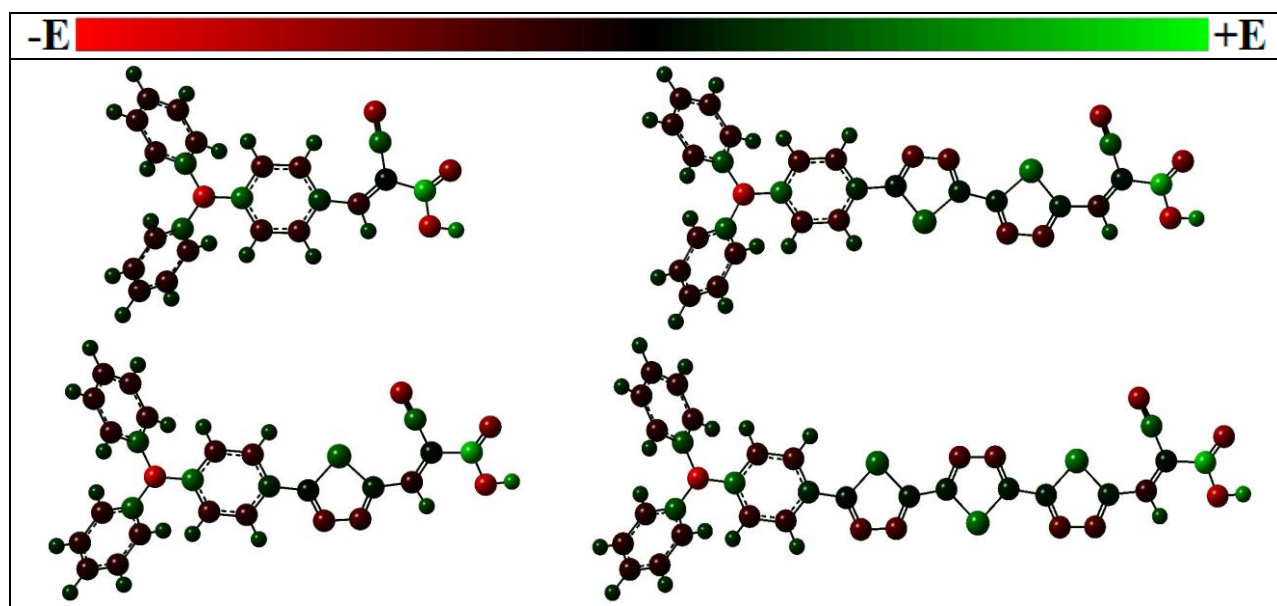
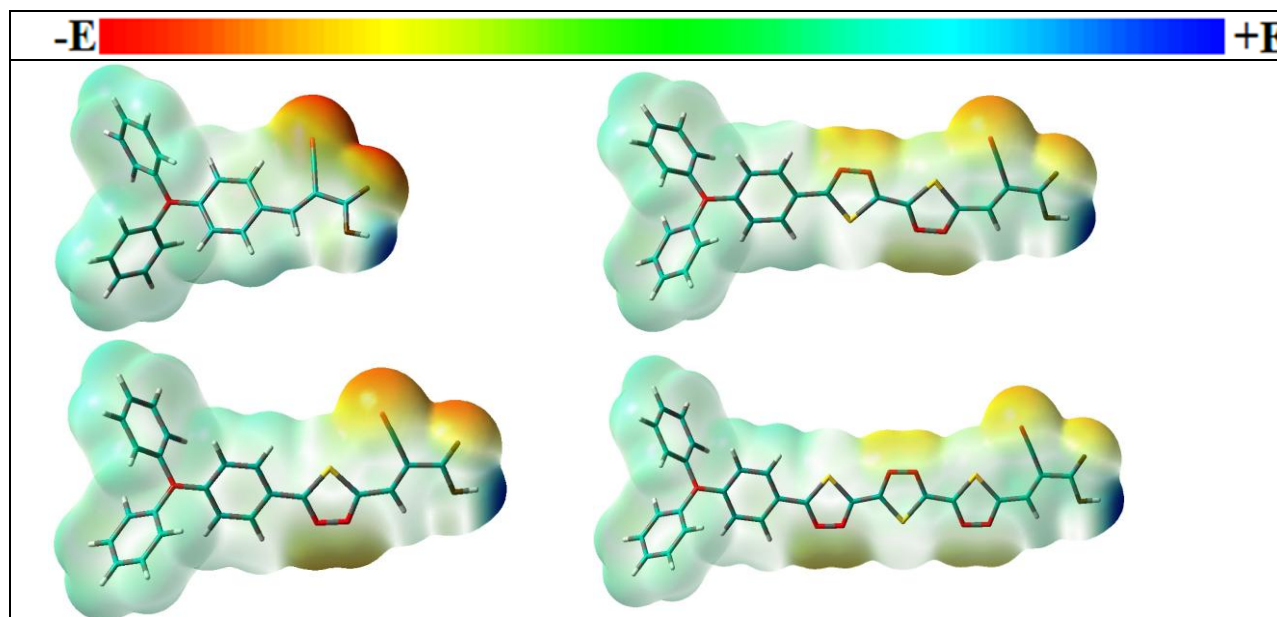
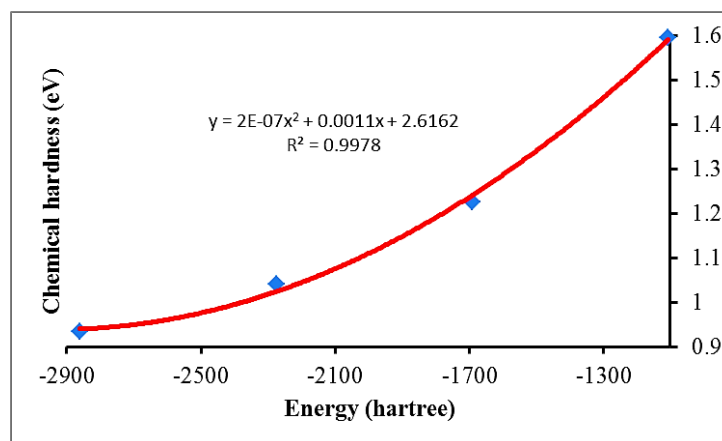
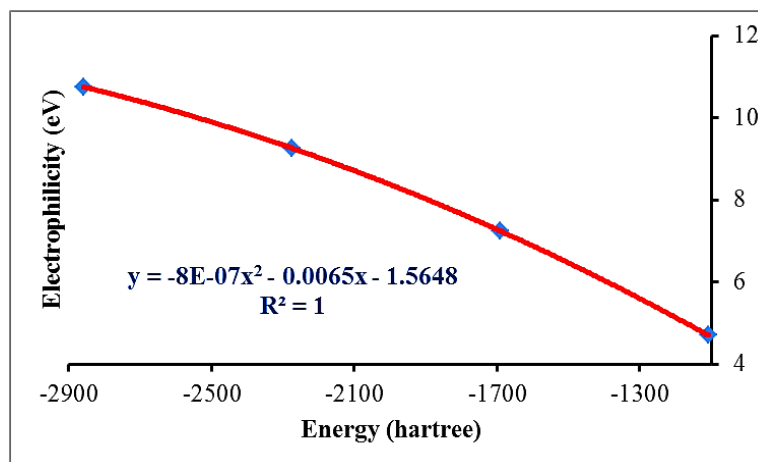
**Figure 1:** Electron density analysis of molecules.**Figure 2:** The 3-D electrostatic potential maps of the structures.

Table 3: HOMO/LUMO energies, chemical potentials (μ), chemical hardnesses (η) and electrophilicity indexes of the molecules obtained from B3LYP/6-31G(d) computations.

Dye	ϵ_{HOMO} (eV)	ϵ_{LUMO} (eV)	$\text{Gap}_{\text{H-L}}$ (eV)	μ (eV)	η (eV)	ω (eV)
D0	-5.47	-2.28	3.19	3.875	1.595	4.707
D1	-5.44	-2.99	2.45	4.215	1.225	7.252
D2	-5.43	-3.35	2.08	4.390	1.040	9.265
D3	-5.42	-3.55	1.87	4.485	0.935	10.757

**Figure 3:** Correlation between chemical hardness and total energy of studied dyes.**Figure 4:** Correlation between electrophilicity index and total energy of studied dyes.

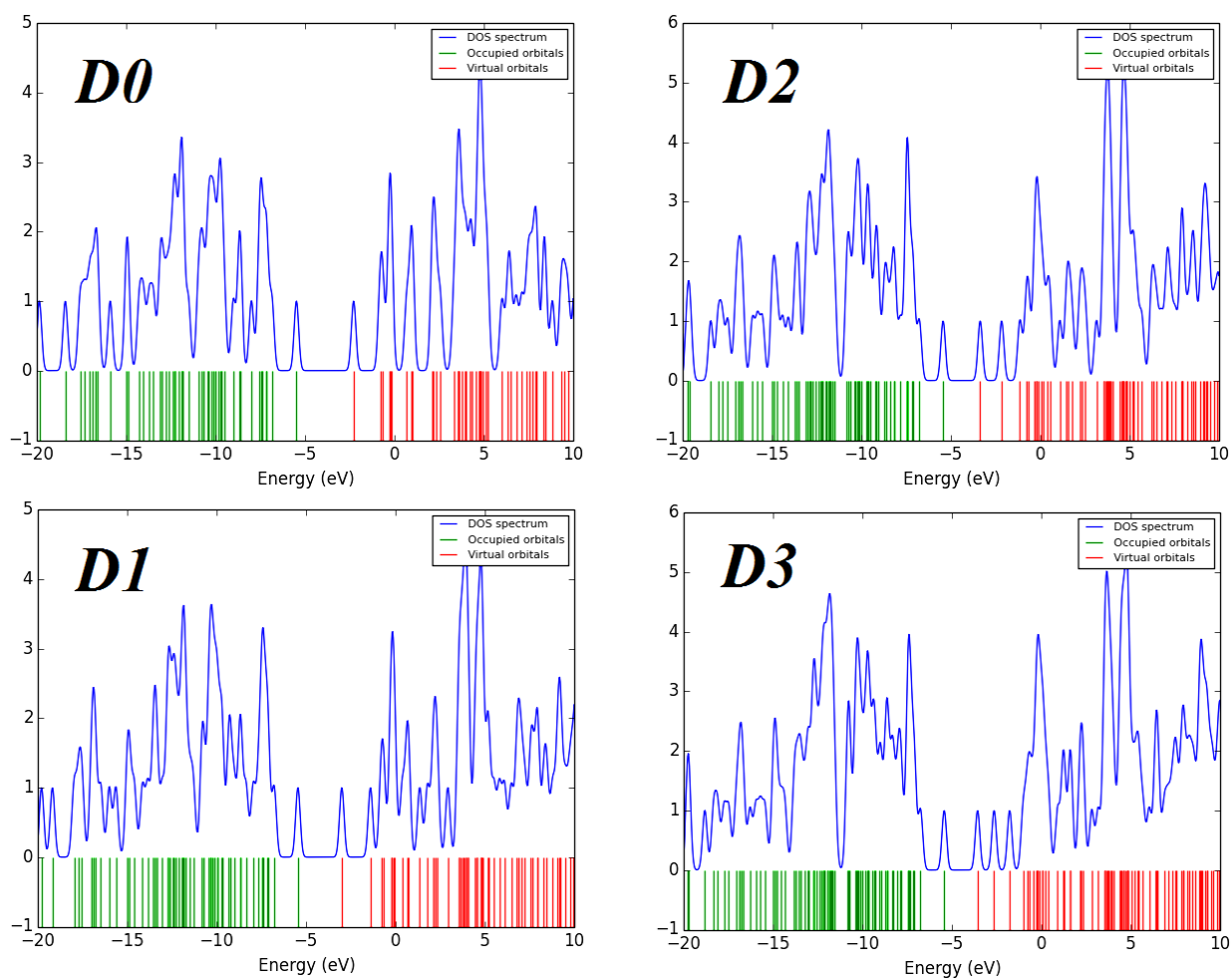


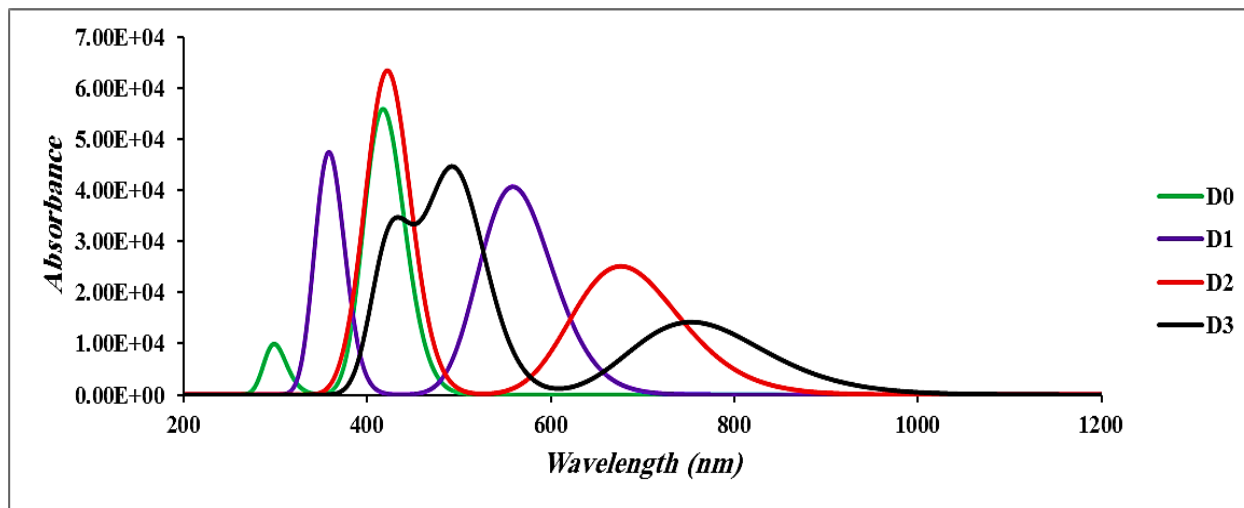
Figure 5: DOS plots of studied molecules in this work.

Table 4: Calculated mean polarizabilities α (a.u.) of the molecules obtained from B3LYP/6-31G(d) computations.

Dye	α_{xx}	α_{yy}	α_{zz}	α_{mean}
D0	474.062	276.193	146.153	298.803
D1	713.027	323.097	167.128	401.084
D2	945.856	358.879	189.165	497.967
D3	1134.572	405.592	210.004	583.390

Table 5: Computed absorption wavelengths (λ), absorption energy, oscillator strengths (f) and nature of the transitions.

Dye	λ (nm)	E (cm ⁻¹)	f	Transitions
D0	415.257	24081.46192	0.7721	H→L (82%), H→L+1 (79%), H→L+2 (80%), H-4→L (2%), H-4→L (2%), H→L+1 (8%), H-3→L (3%), H-2→L (6%), H→L+2 (5%)
	311.673	32084.95680	0.0243	
	296.313	33748.08352	0.1262	
D1	555.630	17997.57984	0.5622	H→L (88%), H-4→L (91%), H-1→L (65%), H→L+1 (26%), H-6→L (5%)
	366.121	27313.34784	0.0013	
	356.787	28027.96000	0.6541	
D2	671.996	14881.03200	0.3474	H→L (94%), H→L+1 (79%), H-1→L (77%), H-1→L (12%), H→L+1 (11%)
	422.445	23671.72944	0.8135	
	392.700	25464.71232	0.1561	
D3	747.653	13375.18448	0.1967	H→L (97%), H→L+1 (91%), H-1→L (89%)
	492.995	20284.17744	0.5956	
	425.869	23481.38128	0.4470	

**Figure 6:** Simulated UV-Vis spectra of molecules.**Table 6:** Computed maximum absorption wavelengths (λ_{\max}), absorption energy (E_g), oscillator strengths (f), light harvesting energy (LHE) and main transition nature of dyes.

Dye	λ_{\max} (nm)	E_g (eV)	f	LHE	Main transitions
D0	415.257	2.986	0.772	0.831	H→L

D1	555.630	2.231	0.562	0.726	H-4→L
D2	671.996	1.845	0.347	0.550	H→L
D3	747.653	1.658	0.197	0.365	H→L

Conclusion

In the present work, the four triphenylamine based dyes were designed and their stability, reactivity, optical properties and UV-Vis spectra have been determined and the following conclusions drawn:

(1) The stability of triphenylamine based dyes gradually increased on increase of 1,3,4-thiadiazole rings in π -spacer.

(2) The reaction of studied dyes with nucleophiles increases when the size of π -spacer increases.

(3) The kinetic stability and reactivity decreases and increases respectively with decreasing of π -spacer size in triphenylamine based dyes.

(4) The reactivity and electrophilicity of molecules increases with increasing the stability in molecules.

(5) The DOS plots of the dyes show that the LUMO density with energy in the range -5 eV to -12 eV increases, when the size of π -spacer increases.

(6) The polarizability significantly increases on addition of 1,3,4-thiadiazole ring in π -spacer.

(7) The transition moment of dyes is inversely proportional to the HOMO-LUMO energies gap.

(8) The computed λ_{\max} of compound compounds is close to experimental λ_{\max} .

(9) Absorption energy significantly decreased on increase of 1,3,4-thiadiazole rings in π -spacer.

(10) The light harvesting efficiency of dyes decreased with increase of 1,3,4-thiadiazole rings.

(11) Increasing number of 1,3,4-thiadiazole in π -spacer is a valuable strategy to enhance the photovoltaic current.

Theory and computational details

Density functional theory (DFT) calculations were performed for the triphenylamine based dyes using the Gaussian 03 quantum chemical package [29]. Structure optimizations have been performed at the B3LYP/6-31G(d) level. The choice of the level has already yielded satisfactory results and hence only this level has been used for the calculations. All the geometric parameters were allowed to be optimized, and no constraints were imposed on the molecular structure during the optimization process. The energies of the molecules were computed with a self-consistent field

(SCF) convergence of 10^{-8} a.u. for the density matrix. And also, all calculations were carried out in gas phase at room temperature.

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