The effect of substituted 2,5-Diphenyloxazole on DSSC performance: A theoretical study

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Abstract
Theoretical analysis of the 2,5-diphenyloxazole dye molecule and newly designed dyes were performed using Density Functional Theory. The ground state and excited state oxidation potential as well as electron injection from dyes to TiO2 are reported. Improved light harvesting efficiency and free energy change of electron injection of newly designed sensitizers reveal that these materials would be excellent sensitizers. This theoretical designing will pave way for the experimental list to synthesis the efficient sensitizers for solar cells. The study of structural, electronic and optical properties for these compounds could help to design more efficient functional photovoltaic organic materials.

Keywords: DSSC, LHE, DFT, 2,5-diphenyloxazole

Introduction
The synthesis and photophysics of Ir(III) complexes have been of great interest as these complexes represent the most effective tunable and sublimable phosphorescent materials for the fabrication of organic light emitting diode (OLEDs) [1, 2]. OLEDs are also utilized by experts in other photonic applications as sensors, probes, imaging agents and photosensitizers for electron and energy transfer [3], Oxazole derivatives are widely applied as efficient luminophores for liquid and plastic scintillators and dye-based lasers, and also as fluorescent probes and labels in biology and medicine [4-6]. Therefore, the study of solvation of these luminophores in solvents of various nature is of interest.
We have attempted to systematically study the structural, optoelectronic, photophysical properties and the better OLED performance in detail.First principle theoretical analysis is sometimes reliable in analyzing the electronic structures and the excited state transitions of transition metal complexes as there is always a significant level of uncertainty in all density functional theory [DFT] and time-dependent density functional theory (TDDFT) calculations, which heavily depend on the functional approximations used in the method [7-11].

Computational Details
Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations were performed to determine geometries, electronic structures and electronic absorption spectra of indigo base dyes. All the calculations, both in gas and solvent phase, were performed using Gaussian09 package. All calculations were performed by employing B3LYP functional and 6-311+G (d,p) basis set. Polarizable continuum model (PCM) was used to study solvent effects.

Results and discussion
The ground state structures for all molecules were with B3LYP/6-311+G level. The discussions about geometrical parameters of the molecules are neglected. The highest occupied molecular orbital energies (E_{HOMO}), the lowest unoccupied molecular orbital energies(E_{LUMO}) and dipole moment of all the dyes are computed at the B3LYP/6-311+G(d,p) level in the gas phase and in DMF are listed in table 1. Generally, the molecules having a large dipole moment, possesses a strong asymmetry in the distribution of electronic charge, therefore can be more reactive and be sensitive to change its electronic structure and its electronic properties under an external electric field. Through the Table 2, we can observe that the dipole moment (ρ) of compounds P1 and P4 are greater than others compounds, therefore we can say that these compound are more reactive that other compound, indeed, these compounds are more favourite to liberate the electrons to DIPO. This study was carried out to design new sensitizers for DSSC application. The designed dyes consist of following parts Donor(D), Pi-Square(π) and Acceptor (A) as shown in fig. 1. The chemical structure of 2,5-diphenyloxazole and newly designed dyes are shown in fig.2

Table 1: The E_{HOMO}, E_{LUMO}, energy gap (Eg) and dipole moment of 2,5-diphenyloxazole and newly designed dyes in eV at B3LYP/6-311+G level of theory

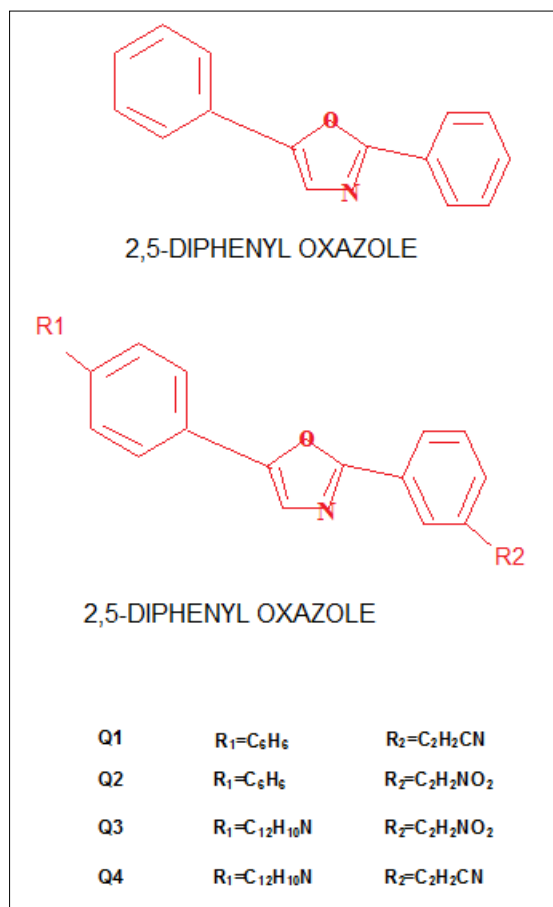| SYSTEM	GAS PHASE				DMF			
	E_{HOMO}	E_{LUMO}	E_{gap}	Dipole Moment	E_{HOMO}	E_{LUMO}	E_{gap}	Dipole moment
DIPO	-0.2117	-0.0782	3.6332	1.1367	-5.9006	-2.2686	3.6319	1.6446
DIPO1	-4.18596	-3.04607	1.1399	3.4988	-4.2561	-3.10756	1.1486	4.1731
DIPO2	-5.7517	-2.64306	3.1087	1.6872	-5.8548	-2.7141	3.1408	2.3644
DIPO3	-5.7607	-2.6580	3.1380	1.8419	-5.8682	-2.7187	3.1495	2.4962
DIPO4	-5.7735	-2.2175	3.5560	4.3006	-5.8627	-2.3094	3.5533	5.9383

*Dipole moment in Debyes

Table 2: Calculated absorption spectra λ_{max} nm, ΔG^{inject}, oxidation potential, intramolecular charge transfer energy of 2,5-diphenyloxazole and newly designed dyes at B3LYP/6-311+G level of energy

System	GAS PHASE					DMF				
	λ_{max}	ΔG^{inject}	E_{ox}^{dye*}	E_{ox}^{dye}	λ_{max}^{ICT}	λ_{max}	ΔG^{inject}	E_{ox}^{dye*}	E_{ox}^{dye}	λ_{max}^{ICT}
DIPO	366.18	0.8258	-3.1742	0.2117	3.3859	381.46	-1.349	2.650	5.901	3.250
DIPO1	8632.41	-0.042	4.042	4.186	0.144	11990.94	0.1528	4.153	4.256	0.1034
DIPO2	441.95	-1.053	2.946	5.752	2.806	447.34	-0.917	3.083	5.856	2.771
DIPO3	431.78	-1.110	2.889	5.761	2.872	439.28	-0.954	3.046	5.868	2.823
DIPO4	389.45	-1.410	2.589	5.774	3.184	393.28	-1.290	2.710	5.863	3.153

Table 3: Excitation energy (E), Light Harvesting Efficiency (LHE) and Average Light Harvesting Efficiency (LHF$_{Average}$) of 2,5-diphenyloxazole and newly designed dyes at B3LYP/6-311+G level of theory

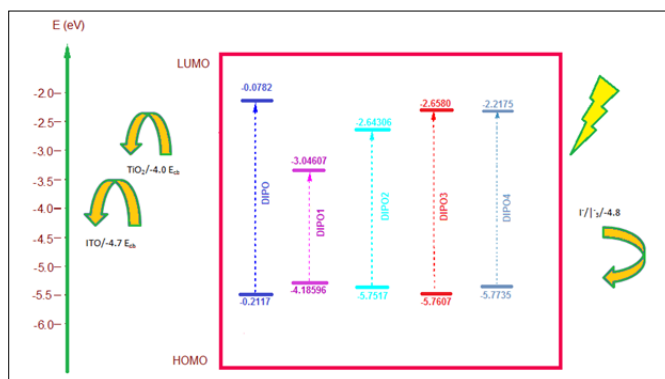| System	GAS PHASE				DMF			
	E (eV)	λ (nm)	LHE	LHE_{avg}	E (eV)	λ (nm)	LHE	LHE_{avg}
DIPO	3.3859	366.18	0.8720		3.2503	381.46	0.902	
	4.0319	307.51	0.0090	0.295	4.0537	305.85	0.039	0.315
	4.1968	295.43	0.0040		4.2089	294.58	0.003	
DIPO1	0.1436	8632.41	0		0.1034	11990.94	0	
	1.4705	843.1	0.269	0.101	1.4129	877.49	0.362	0.139
	1.9254	643.95	0.034		1.9362	640.35	0.054	
DIPO2	2.8054	441.95	0.638		2.7716	447.34	0.748	
	2.9922	414.35	0.699	0.535	2.9536	419.77	0.705	0.565
	3.5554	348.72	0.269		3.5595	348.32	0.242	
DIPO3	2.8715	431.78	0.718		2.8225	439.28	0.934	
	2.8825	430.13	0.678	0.506	2.8800	430.51	0.003	0.359
	3.3451	370.64	0.121		3.3508	370.01	0.138	
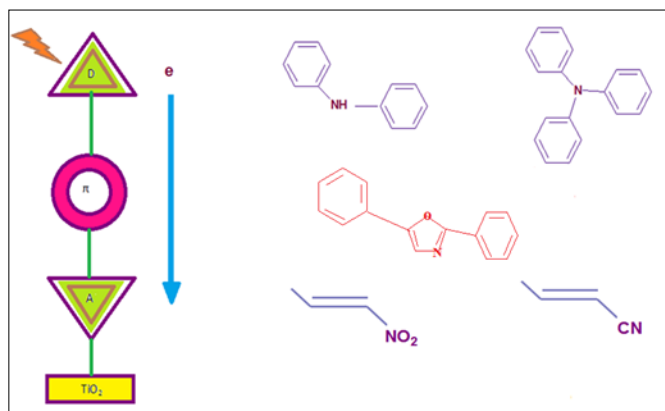
Fig 1: Different parts of D-π-a SYSTEM, d=donor, π= pi=spacer, A= acceptor

Fig 2: Chemical structure of 2,5-diphenyloxazole and newly designed dyes

Fig 3: Schematic energy diagram of dyes, TiO2 and electrolyte (I/I₃), E_{HOMO} and E_{LUMO} of the dyes are in gas phase
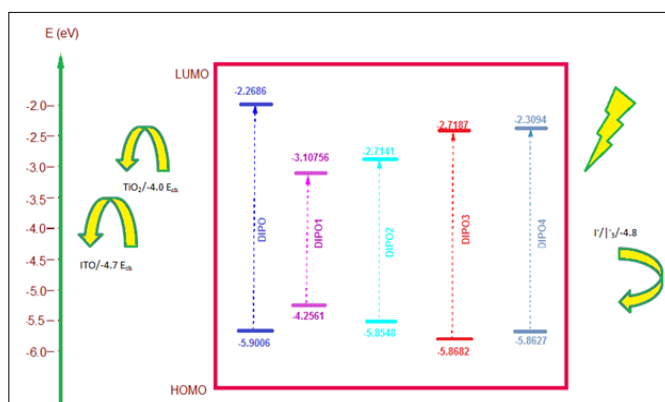
Fig 4: Schematic energy diagram of dyes, TiO2 and electrolyte (I/I₃), E_{HOMO} and E_{LUMO} of the dyes are in DMF

Effect of Solvent on HOMO-LUMO Energies The energy gap of DIPO and newly designed dyes in both gas phase and DMF are in the following order DIPO 1< DIPO2 < DIPO3 < DIPO4 < DIPO. This order can be explained on the basis of phenylamine variety and the anchoring group (Acceptor). Dipo has larger the energy gap because it has no acceptor and donor group. Substitution of the electron donating group in DIPO molecule has enhanced the electron donating ability in donor group while substitution of the electron withdrawing groups at acceptor side has increased electron accepting ability of acceptor. In other words substitution of the electron donating and electron withdrawing groups in the DIPO leads to efficient electron transfer, enhance the efficiency of dyes.

Spontaneous change transfer from the dye excited state to a conduction band of TiO_2 requires more positive potential LUMO energy than E $^{TiO2}_{CB}$ (-4.0ev) while spontaneous charge transfer requires more negative HOMO energy than reduction potential energy of I⁻/I⁻₃- electrolyte (-4.80ev). The energy level diagram of the HOMO and LUMO of the dyes, E_{CB} of TiO_2 and redox potential of the electrolyte are presented in fig.3 and fig.4. This indicates the spontaneous charge transfer and charge regeneration. From the fig.3 and fig.4, it is clear that the newly designed dyes are the good sensitizer.

Free Energy Change of Electron Injection and Oxidation Potential Energy.
We have used mathematical equations to estimate the dye's excited state oxidation potential and free energy change of electron injection to titanium dioxide (TiO2) surface. λ_{max}, ΔG_{inject} λ_{max} are presented in Table 2. The electron injection free energy change ΔG_{inject}, ground and excited state oxidation potentials computed in the gas phase and DMF. 6-311+G* basis set was used for all calculations. Can be estimated as negative E_{HOMO} is calculated and ΔG_{inject} was estimated. Its values are negative for all dyes. In parent molecule, ΔG_{inject} is -0.8258 in gas phase while it is −1.349 in DMF because of lowering of LUMO energy in solvent phase. In all newly designed dyes DIPO2, DIPO3 and DIPO4 ΔG_{inject} improved both in the gas phase and solvent phase as shown in Table 2. The negative ΔG_{inject} is an indication of spontaneous electron injection from the dye to TiO_2. For all newly designed dyes, ΔG_{inject} is more negative than 2,5-Diphenyl oxadiazole.

**Light Harvesting Efficiency (LHE) and Oscillator Strength.**
The light harvesting efficiency (LHE) is the efficiency of dye to response the light. It is another factor which indicates the efficiency of DSSC. The light harvesting efficiency (LHE) of

the dye should be as high as feasible to maximize the photocurrent response. The oscillator strength is directly obtained from TDDFT calculations. The DIPO dye has two main absorption peaks (366 and 308 nm in the gas phase, 381 and 301 nm in solvent phase DMF). Higher oscillator strength of three new designed sensitizers is due to better pi-conjugation. We have calculated the LHE of the main absorption peaks and then we have calculated the average LHE which is higher for the newly designed sensitizers than DIPO as shown in Table 3. These dyes will convert more light to electrical energy. The HOMO and LUMO composition of new sensitizers are depicted in Figure 5 and 6. The electron distribution of the HOMO orbital is delocalized on the π-system with the maximum electron density present on the Benzene rings and nitrogen of TPA in all newly designed sensitizers. It is noticed that the LUMO orbital have highest

compositions on anchoring group and benzene ring of the acceptor side in all newly designed sensitizers. Therefore, the electron will move from donor to acceptor during the HOMO-LUMO excitation resulted in light absorption.UV-VIS absorption spectra of DIPO, DIPO1, DIPO2 DIPO3 and DIPO4 are shown in Figures 7 and 8. Both consist of a very intense and well-separated absorption band in the 200-1350 nm region. The spectrum of DIPO is red-shifted in DMF. The spectrum of three new designed sensitizers DIPO1, DIPO2 DIPO3 and DIPO4 (11990.94nm, 447.34nm, 439.28nm and 393.28 nm) is marvellously red-shifted in comparison with that of DIPO1, DIPO2 DIPO3 and DIPO4 in the gas phase (8632.41 nm, 441.95nm, 431.78nm and 389.45 nm respectively). Solvent effect on the absorption spectrum of indigo is less. λ_{max} changed from 536 to 573 nm.
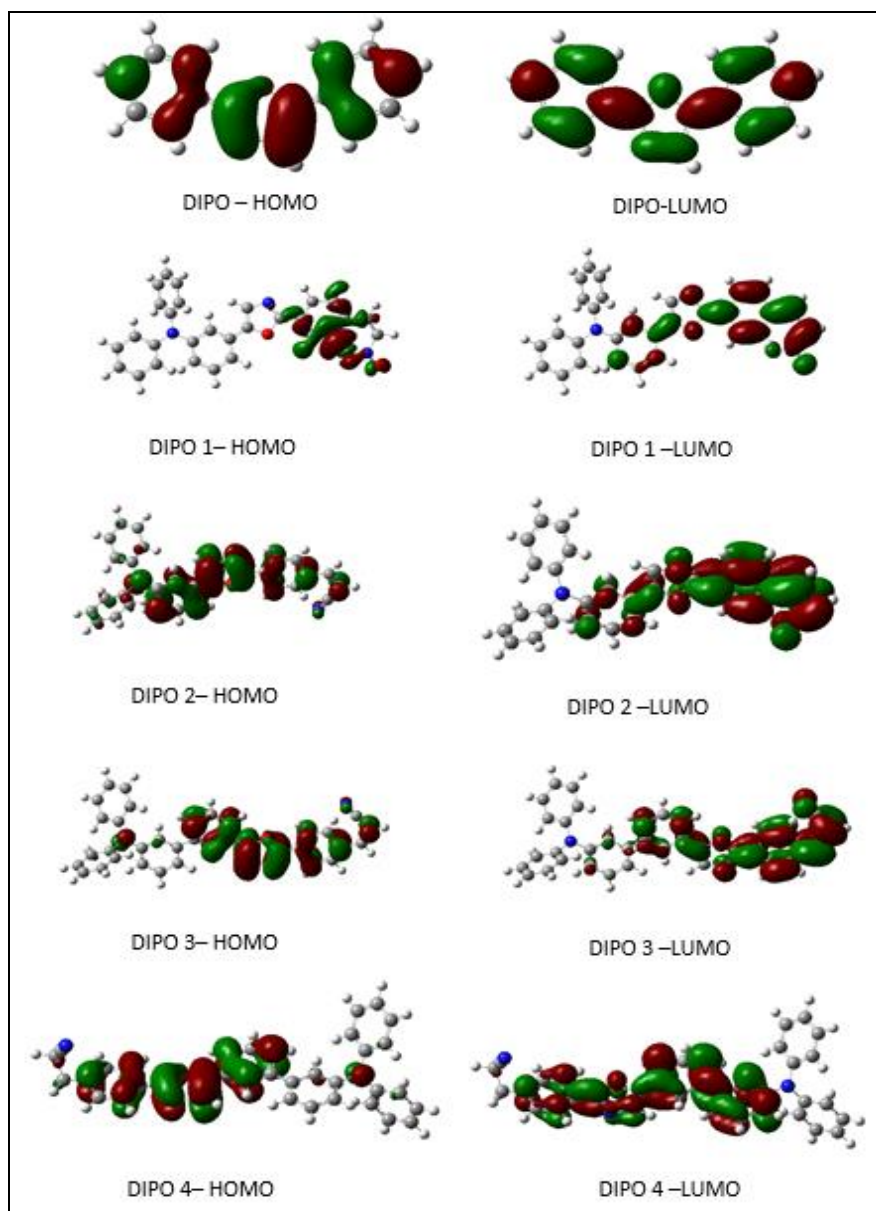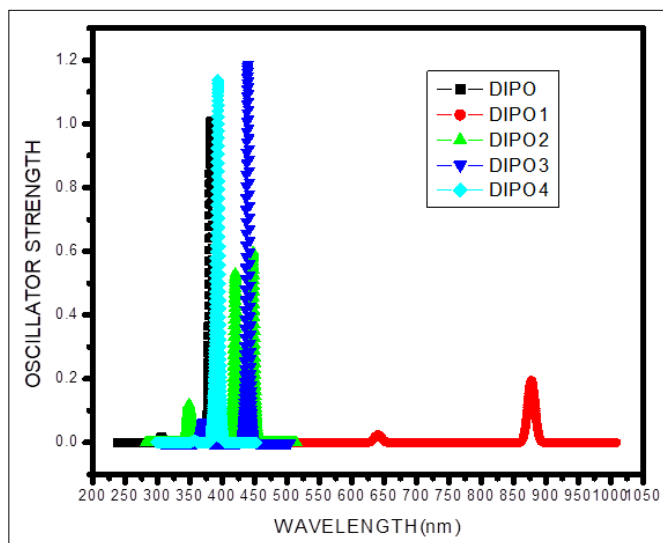

Fig 5: The HOMO and LUMO distribution pattern of dyesin gas phase at B3LYP/6-311+G level of theory
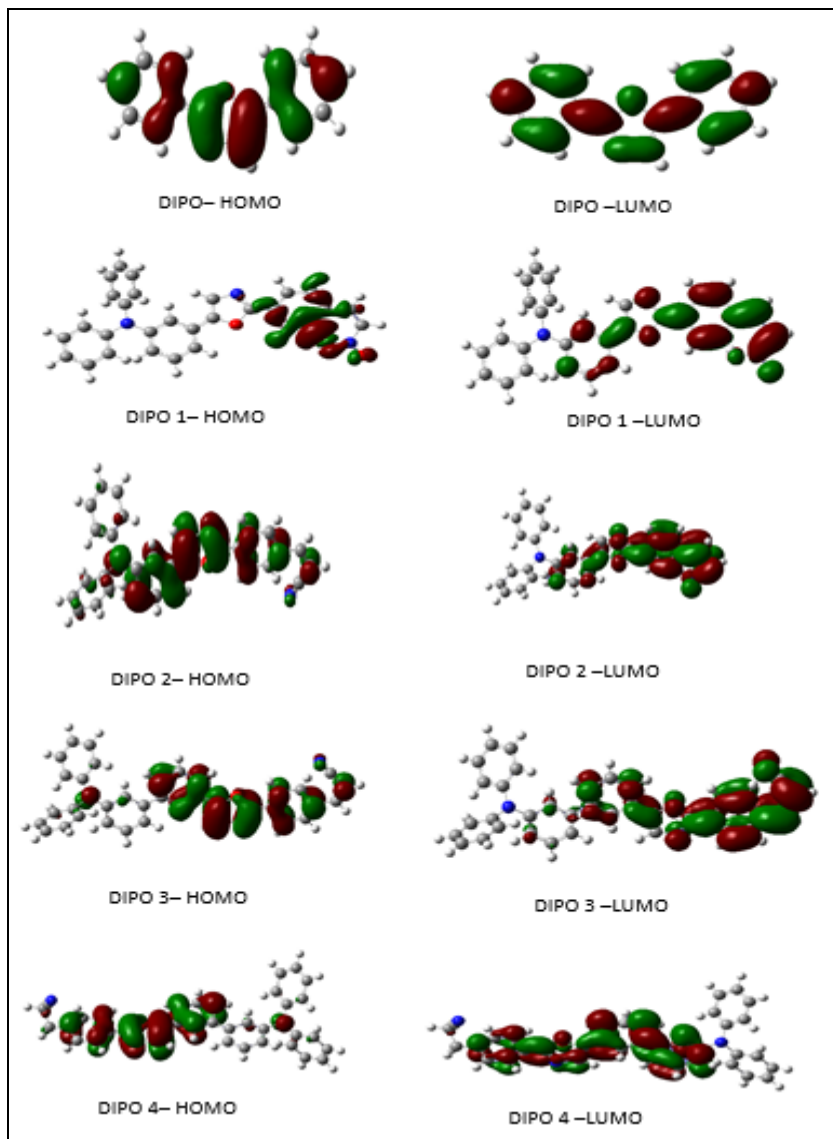
Fig 6: The HOMO and LUMO distribution pattern of dyes in DMFat B3LYP/6-311+G level of theory
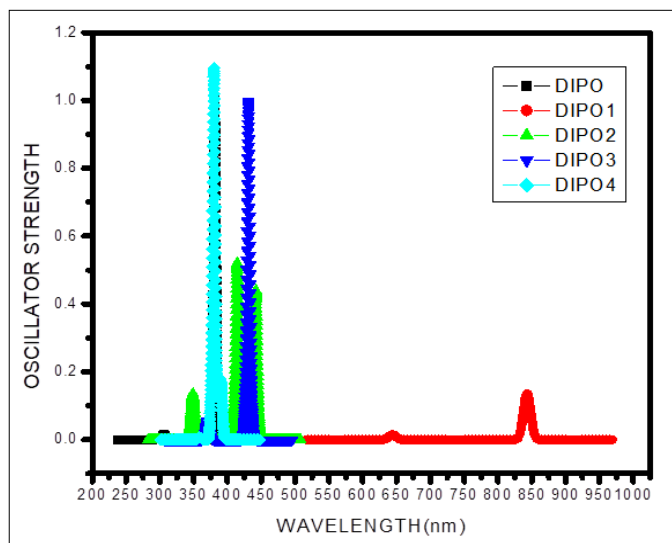
Fig 7: Simulated absorption spectra of dyes in Gas Phase at TDDFT/B3LYP/6-311+(d,p) level of theory

Fig 8: Simulated absorption spectra of dyes in DMF at TDDFT/B3LYP/6-311+(d,p) level of theory

Conclusion

In this study, we have used the DFT/B3LYP method to investigate theoretical analysis on the electronic properties of some 2,5-diphenyl-1,3-oxazole derivatives in alternate donor-acceptor structure. The modification of chemical structures can greatly modulate and improve the electronic and optical properties of molecules studied materials. All newly designed dyes DIPO1, DIPO2 DIPO3 and DIPO4 were highly red-shifted as compared to Indigo due to solvent effect. The ΔG_{inject} and LHE of newly designed photo-sensitizers were improved as compared to 2,5-diphenyl-1,3-oxazole. Electron donating groups on TPA side, electron withdrawing on acceptor side and indigo as a bridge promotes the electron injection and light harvesting efficiency. The steric hindrance of the TPA prevents the dye aggregation and recombination on the semiconductor surface. The theoretical results suggest that both the acceptor strength and the stable geometry contribute significantly to the electronic properties of alternating donor-acceptor conjugated copolymers. Finally, the procedures of theoretical calculations can be employed to predict the electronic properties of the other compounds, and further to design novel materials for organic solar cells.

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