

QUANTUM CHEMICAL STUDY OF ORGANIC DYE SENSITIZED SOLAR CELLS: 4,4-BIPYRIDINE DERIVATIVES

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ABSTRACT

The electronic structure and excitation properties of the Dipyrindyl dye molecule and its derivatives were performed using the Gaussian 09 software package. Calculations were performed based on the framework of density functional theory (DFT) with the Becke 3-parameter-Lee-Yang-Parr (B3LYP) functional, where the 6-311+ G (d,p) basis set was employed. The HOMO-LUMO energy gap, the improved light harvesting efficiency(LHE) and free energy change of electron injection of newly designed sensitizers revealed that this material would be an excellent sensitizer. Each of the molecules was theoretically analyzed and these could help in designing more efficient functional dye-sensitizers.

Keywords : DSSC, Dipyrindyl, Organic dyes

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INTRODUCTION

Dye-sensitized solar cells (DSSC) is a low cost solar cell and it attain more consideration because of its sky-scraping light to electricity conversion efficiency.¹⁻³ The sensitizer is a critical element in DSSC, which improves the power conversion efficiency and increases the stability of the devices. Searching and developing of renewable energy sources can be done only by solar cells, which serves as an answer to the global challenge. Photovoltaic technologies become the scientific topic of interest, in the systems of solar to electrical energy conversion cell. Dye sensitized solar cell(DSSC) are contemplated for this work. We evaluate dye properties with TiO₂. 4,4'-Bipyridine (4,4'-bipy) is mainly used as a precursor to the *N,N'*-dimethyl-4,4'-bipyridinium dication commonly known as paraquat. This species is redox active, and its toxicity arises from its ability to interrupt biological electron transfer processes. Because of its structure, 4,4'-bipyridine can bridge between metal centers to give coordination polymers. Among the various dyes being investigated, the dipyrindine has been considered due to its unique opto-electrical properties. As such, we consider it important to understand the similarities and scope between their properties which can be used for DSSC.

EXPERIMENTAL

GAUSSVIEW software was used to generate the molecular structures, and calculations were performed using GAUSSIAN 09W.⁴ Density functional theory (DFT) was implemented in the frequency and energy optimization. Time-dependent DFT (TD-DFT) was employed the same level of theory, the 6-311G (d, p) basis set and the Becke3-parameter -Lee-Yang-Parr (B3LYP) functional were employed. Polarizable continuum model (PCM) was used to study solvent effects.

The free energy change for electron injection onto a titanium dioxide surface is:

$$\Delta G^{inject} = E_{ox}^{dye*} - E_{CB}^{TiO_2} \quad (1)$$

where E_{ox}^{dye*} is the oxidation potential of the dye in the excited state and $E_{CB}^{TiO_2}$ is the energy of the conduction band of the TiO₂ (-4.0eV) semiconductor.⁵ The model used for the evaluation of E_{ox}^{dye*}

implies that the electron injection occurs from the unrelaxed excited state. For this reaction path, the excited-state oxidation potential can be extracted from the redox potential of the ground state E_{ox}^{dye} , and the absorption energy associated with the photo-induced ICT (λ_{max}^{ICT}) according to:

$$E_{ox}^{dye*} = E_{ox}^{dye} - \lambda_{max}^{ICT} \quad (2)$$

Where, λ_{max}^{ICT} is the energy of the intermolecular charge transfer.

The efficiency of DSSC 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 light harvesting efficiency (LHE) was determined by a formula.⁶

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

Where, f is the Oscillator's strength of the dye.

RESULTS AND DISCUSSION

New sensitizers for DSSC application was designed based on the study that was carried out. The designed dyes consist of following parts: Auxiliary Donor (AD), Donor (D), Pi-Spacer (π) and Acceptor (A) as shown in figure 1. We have made the structural modification of 4,4-Dipyridyl for designing the new dyes. The structure of Dipyridyl and newly designed dyes is shown in Figures- 1 and 2.

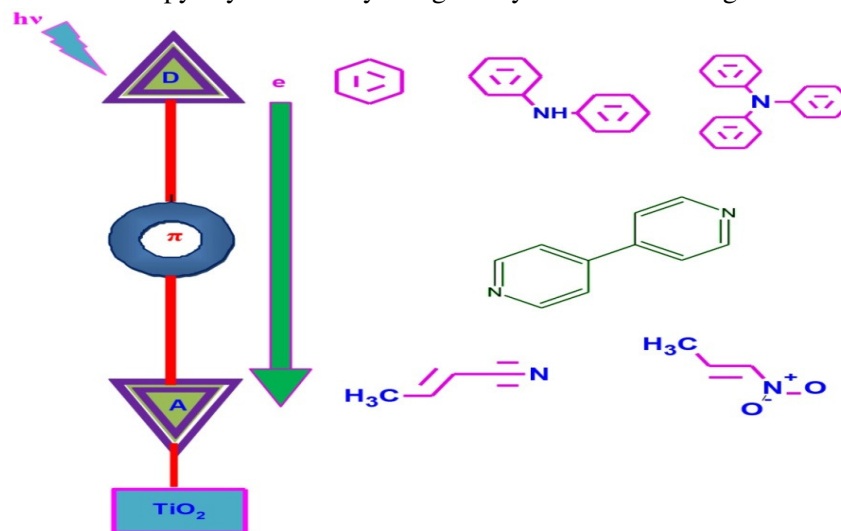


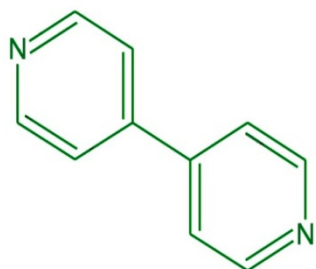
Fig.-1: Different parts of D- π -A system, D = donor, π = pi-spacer, A = acceptor

The ground state structures for all molecules were with B3LYP/6-311+G(d,p) level. The discussion about geometrical parameters of the ground state structure is neglected for all the molecules and they have not imaginary frequencies. The highest occupied molecular orbital energies (E_{HOMO}) and the lowest unoccupied molecular orbital energies (E_{LUMO}) of all dyes computed at the B3LYP/6-311+G(d,p) level in the gas and DMF are listed in Table-1. The distribution pattern of highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) are used to study the efficiency of sensitizers.

Table-1: The E_{HOMO} , E_{LUMO} and energy gap (E_g) of dyes in eV at B3LYP/6-311+G level of theory

System	Gas Phase			DMF		
	E_{HOMO}	E_{LUMO}	E_{gap}	E_{HOMO}	E_{LUMO}	E_{gap}
POT	-6.9239	-1.8484	5.0755	-6.9871	-1.9192	5.0678
POT1	-6.0929	-2.5540	3.5388	-6.0739	-2.5031	3.5707

POT2	-6.1944	-2.7685	3.4259	-6.1465	-2.9940	3.1524
POT3	-7.4336	-1.4438	5.9898	-5.9664	-2.9715	2.9949
POT4	-5.9661	-2.4329	3.5331	-5.9269	-2.4169	3.5100
POT5	-6.7703	-1.8028	4.9675	-6.8026	-1.9200	4.8825



DP1

R₁=C₂H₂CN

DP2

R₁= C₂H₂NO₂

DP3

R₁=C₂H₂CN

DP4

R₁= C₂H₂NO₂

DP5

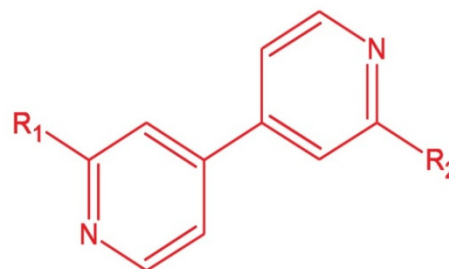
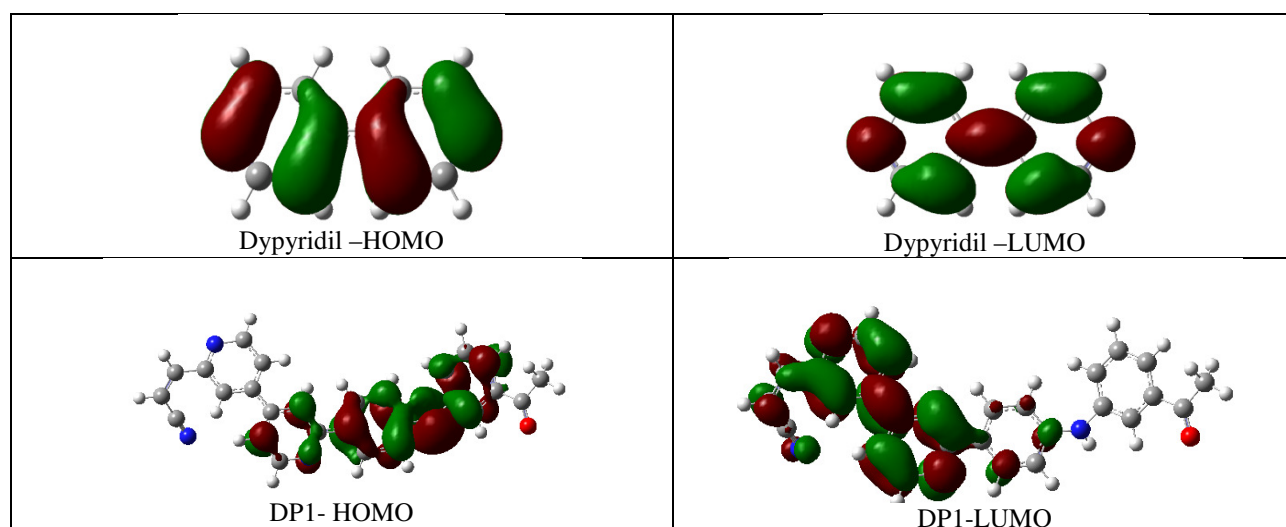
R₁=C₂H₂CNR₂=C₁₂H₁₀N-COCH₃R₂= C₁₂H₁₀N-COCH₃R₂=C₁₂H₁₀NR₂= C₁₂H₁₀NR₂=C₁₈H₁₄N

Fig.-2: Chemical structure of 4,4-Dipyridyl [DP] and newly designed dyes.

From the Figs.-3 and 4 it is clear that HOMOs are present on auxiliary group while LUMOs are present on the benzene ring of Dipyridyl near the anchoring group. Such electron density distribution is beneficial for efficient charge separation and electron injection. This indicates the charge transfer from donor to acceptor through Pi-spacer significance. Charge transfer from donor to acceptor proved that DP4 provides best dye which serves as brilliant sensitizers. By comparing the energy gaps of Dipyridyl and newly designed dyes, in both gas phase and DMF using Figs.-5 and 6, DP4 provides least energy gap. This may happen due to the substitution of the electron donating group, at DPA and with drawing groups and acceptor sides leads to efficient electron transfer which enhances the efficiency of dye DP4.



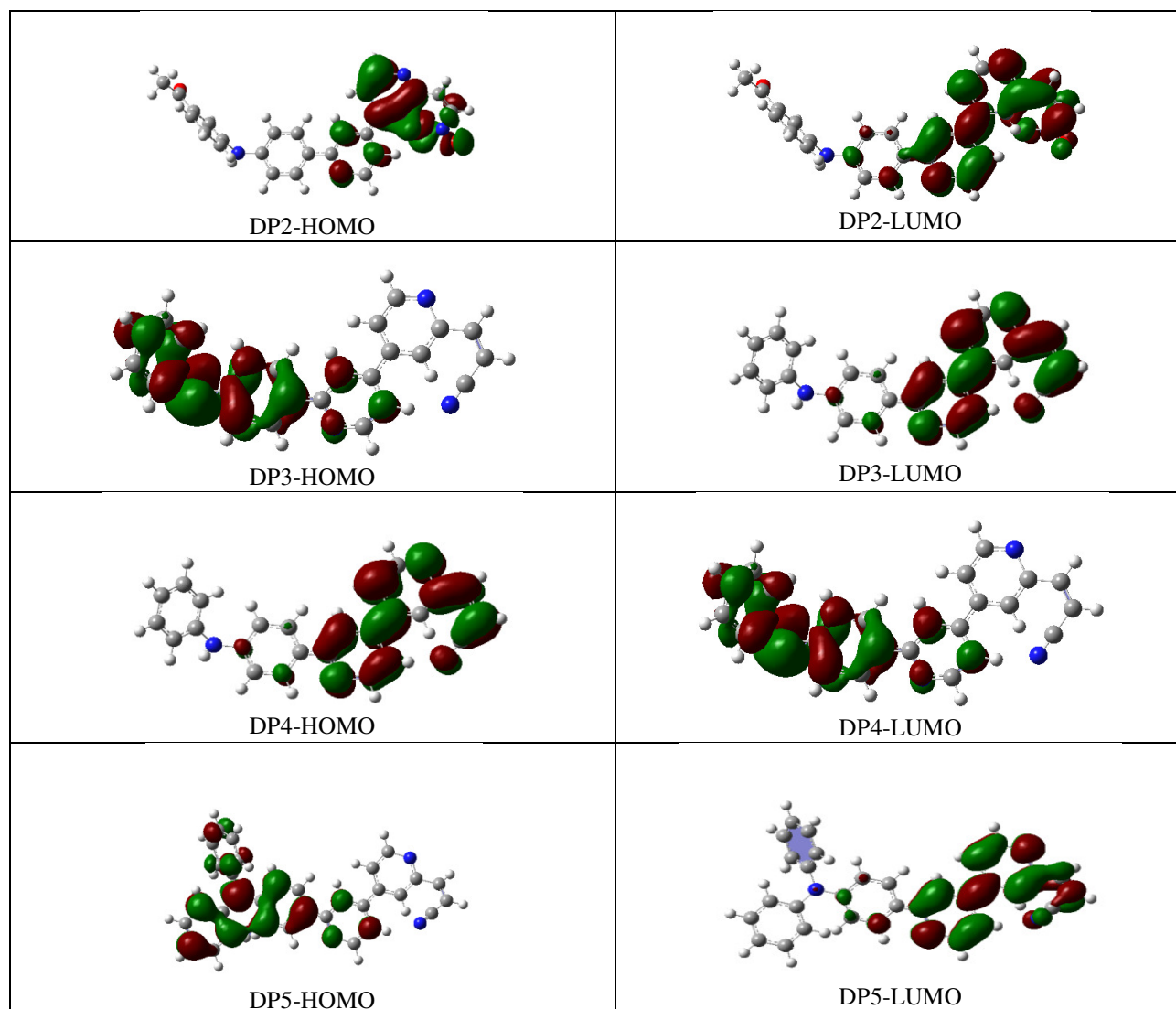
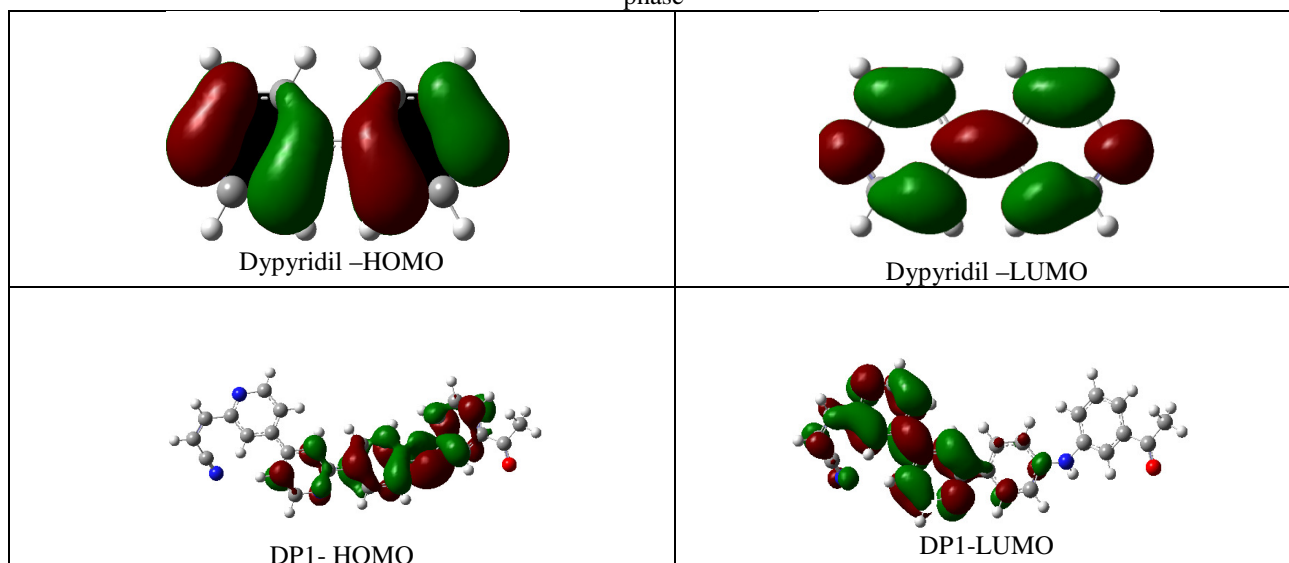


Fig.-3: The HOMO and LUMO distribution pattern of dyes at DFT / B3LYP/6-311+G(d,p) level of theory in gas phase



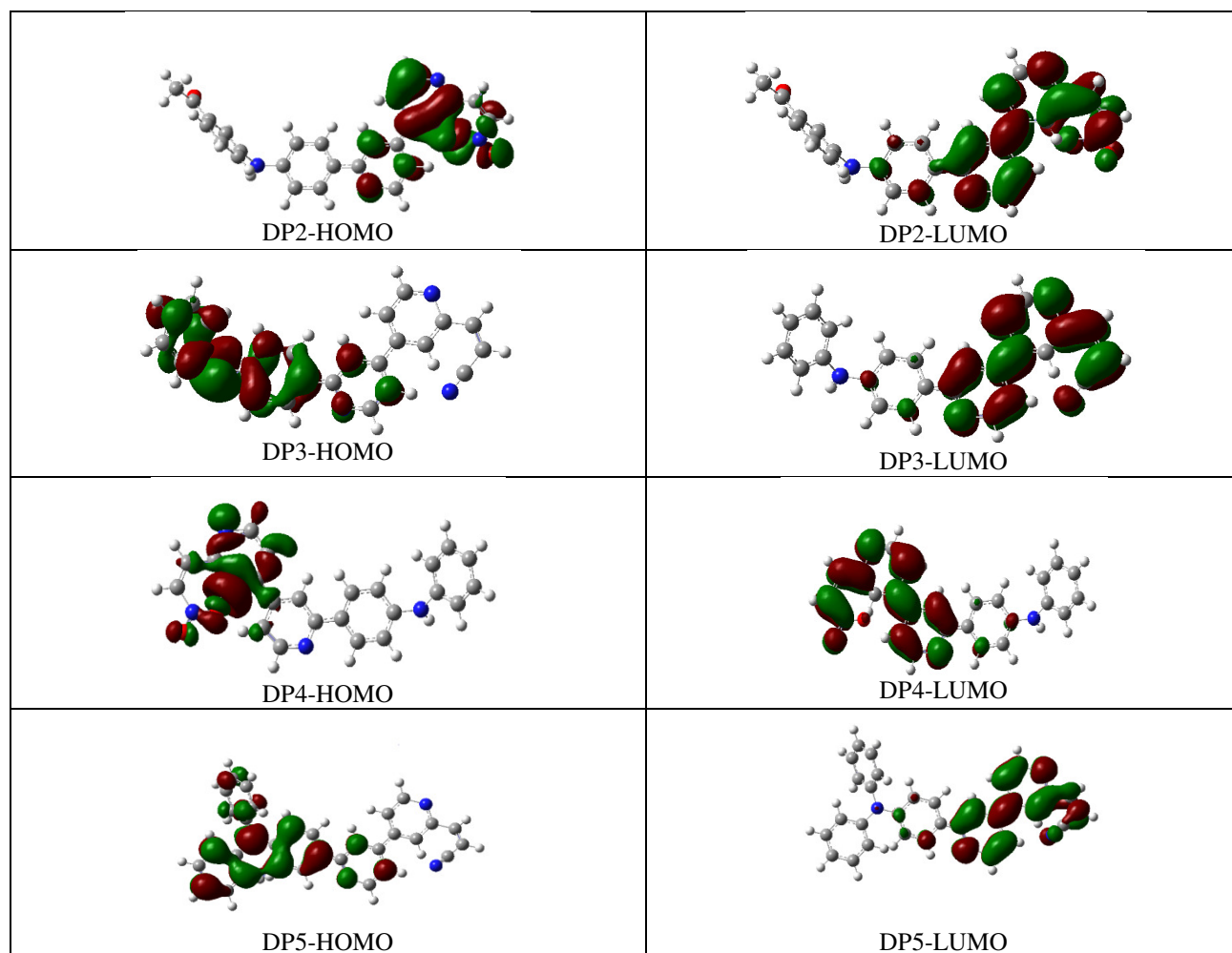


Fig.-4: The HOMO and LUMO distribution pattern of dyes at DFT / B3LYP/6-311+G* level of theory in PCM.

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 in titanium dioxide (TiO₂) surface. λ_{max} , ΔG^{inject} , λ_{max}^{ICT} , E_{OX}^{dye} , E_{OX}^{dye*} are presented in Table 2. The electron injection free energy change ΔG^{inject} , ground and excited state oxidation potential E_{OX}^{dye*} are computed in gas phase and DMF respectively. The 6-311+G* basis set is used for all calculations. E_{OX}^{dye} can be estimated as negative E_{HOMO} .^{7,8} E_{OX}^{dye*} is calculated based on Eq. (2) ΔG^{inject} was estimated using Eq.-1. Its values are negative for all dyes. In parent molecule ΔG^{inject} is -1.027 in the gas phase while it is -1.004 in DMF because of lowering of LUMO energy in solvent phase. In all new designed dyes DP1, DP2 and DP3 ΔG^{inject} improved in solvent phase as shown in Table 2. The negative ΔG^{inject} is an indication of spontaneous electron injection from the dye to TiO₂. For all newly designed dyes ΔG^{inject} is negative. The Order of ΔG^{inject} is: DP4>DP>DP1>DP3>DP2.

Table-2: Calculated absorption spectra λ_{max} nm, ΔG^{inject} , oxidation potential, intramolecular charge transfer energy of 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}
DP	306.85	-1.027	2.9723	7.0129	4.0406	308.31	-1.004	2.996	7.0175	4.0215
DP1	361.45	-1.337	2.623	6.0532	8.430	259.87	-0.5833	8.4167	8.1876	4.7709

DP2	447.59	-0.8884	3.116	5.8817	2.7701	280.35	-0.3812	3.6188	8.0143	4.4225
DP3	380.44	-1.4058	2.5942	5.8532	3.2590	266.05	-0.5235	3.4765	8.1368	4.6603
DP4	693.74	-1.2105	2.7895	4.5767	1.7872	704.68	-1.2309	2.7691	4.5285	1.7594
DP5	354.72	-1.995	2.005	5.5003	3.4953	355.68	-1.8675	2.1325	5.6183	3.4858

Light Harvesting Efficiency (LHE) and Oscillator Strength

The light harvesting efficiency (LHE), another factor which indicates the efficiency of DSSC; is the efficiency of dye to respond to the light and so it should be as high as to maximize the photo-current response⁹. The oscillator strength is directly obtained from TDDFT calculations. 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 sensitizer expect Dipyriddy in DMF as shown in Table-3. These dyes will convert more light to electrical energy.

Table-3: Excitation energy (E), Light Harvesting Efficiency (LHE) and Average Light Harvesting Efficiency ($LHE_{Average}$) of 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}
DP	3.6975	325.32	0	0.1438	3.8753	319.94	0.0009	0.1838
	3.8539	321.71	0.0080		3.9660	312.62	0.5404	
	4.0406	306.85	0.4232		4.0215	308.31	0.0101	
DP1	2.9948	414.00	0.0399	0.1432	4.3202	286.99	0.2914	0.5787
	3.3865	366.11	0.3681		4.4531	278.42	0.7821	
	3.4302	361.45	0.0214		4.7709	259.87	0.6627	
DP2	1.7297	716.80	0.0132	0.0102	3.5991	344.49	0.1284	0.4822
	1.9499	635.86	0.0144		4.1820	296.47	0.4031	
	2.7701	447.59	0.0029		4.4225	280.35	0.9151	
DP3	2.5448	487.20	0.0025	0.1703	4.1322	300.04	0.4032	0.6448
	3.2368	383.05	0.2828		4.3653	284.02	0.7133	
	3.2590	380.44	0.2255		4.6603	266.05	0.8176	
DP4	0.1711	7244.69	0.0007	0.0562	0.1404	8827.67	0.0069	0.0748
	1.4183	874.20	0.0890		1.3382	926.50	0.1234	
	1.7872	698.74	0.0789		1.7594	704.68	0.1002	
DP5	2.5705	482.33	0.0299	0.3444	2.5902	478.67	0.11508	0.4435
	2.9789	416.21	0.3517		3.0304	409.14	0.51938	
	3.4953	354.72	0.6517		3.4858	355.68	0.69612	

CONCLUSION

In conclusion, we have successfully and theoretically analyzed each of the molecules. As in thermodynamics, the spontaneous charge transfer process from the dye in an excited state to the conduction band of metal oxide needs the LUMO energy of the dye. It is a more positive potential than the conduction band energy of the metal oxide, while the HOMO energy of the dye must be more negative than reduce potential energy of the electrolyte. All newly designed dyes DP1, DP2, DP3, DP4 and DP5 were highly red compared to dipyriddy, due to solvent effects. The calculations show that all dyes can work for DSSC with TiO₂, because all have LUMO's less negative than TiO₂. The λ_G^{inject} and LHE of newly designed photo sensitizers were improved by comparing the LHE of all the dyes; DP5 has higher LHE, which we recommend for DSSC with TiO₂.

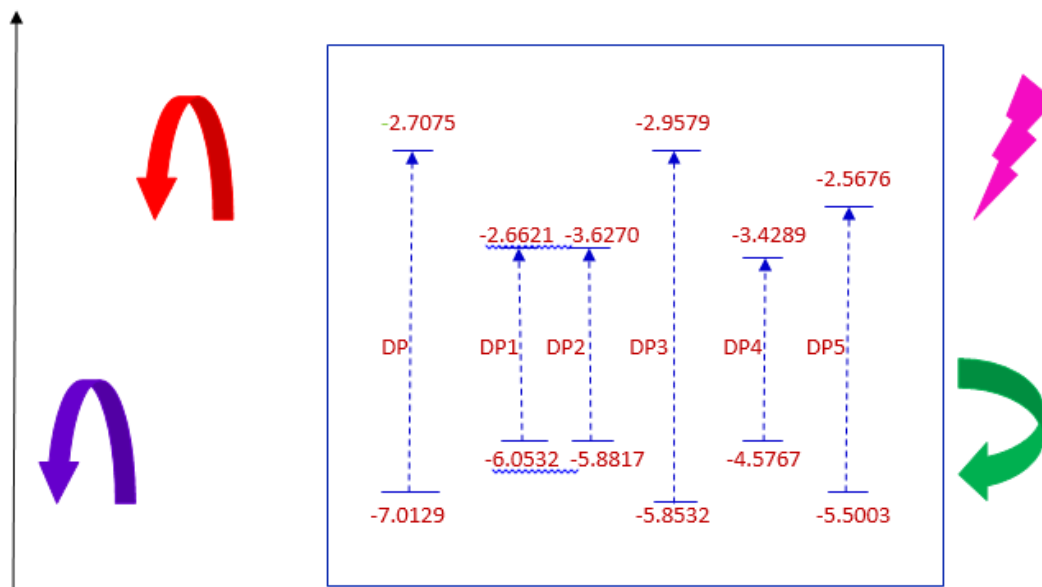


Fig.-5: Schematic energy diagram of dyes, TiO₂ and electrolyte (I⁻/I₃⁻). E_{HOMO} and E_{LUMO} of the dyes are in gas phase

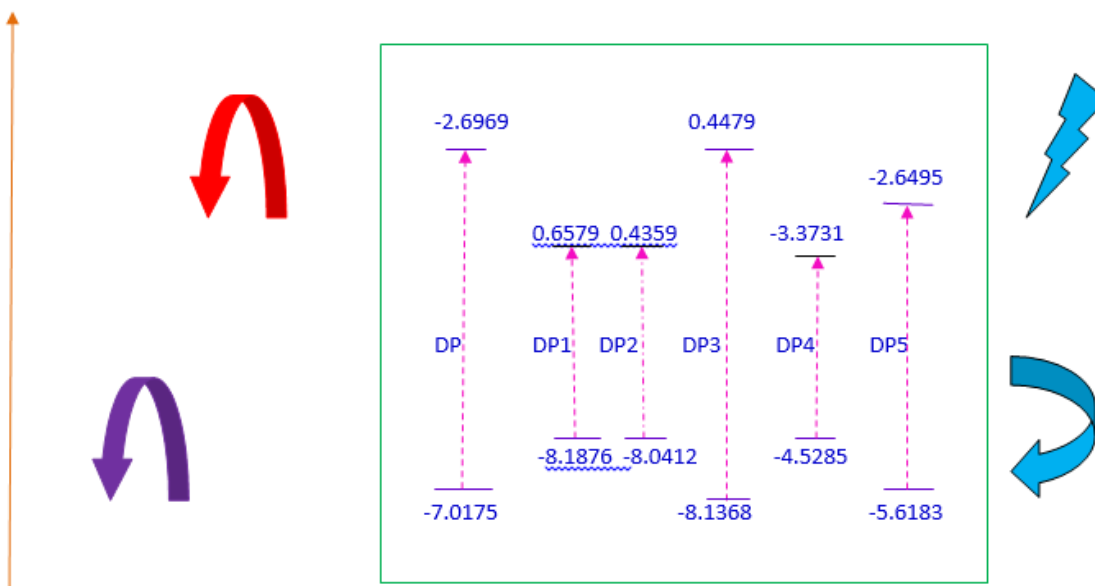


Fig.-6: Schematic energy diagram of dyes, TiO₂ and electrolyte (I⁻/I₃⁻). E_{HOMO} and E_{LUMO} of the dyes are in DMF

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[RJC-1598/2017]