Quantum chemical designing of efficient sensitizers using luminol dye

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ABSTRACT

Density functional theory (DFT) was used to determine the ground state geometries of Luminol and new design dyes (L1-Dye-1 L1-Dye-2, L1-Dye-3 and L1-Dye-4). The time dependant density functional theory (TDDFT) was used to calculate the excitation energies. All the calculations were performed in both gas and solvent phase. Theoretical analyses of the Luminol dye molecule and its derivatives with Chlorine (Cl), Sulfur(S), Selenium (Se) substituent were performed. Calculations were performed based on the framework of density functional theory (DFT) with the Becke3-parameter-Lee-Yang-Parr(B3LYP) functional, where the 6-311+G(d,p) basis set was employed. All this for study they properties for be used with metal oxides in dye-sensitized solar cells (DSSC). Each of the molecules was theoretically analyzed.

Introduction

Due to the global challenge for searching and developing of renewable energy source, photovoltaic technologies become a topic of interest in the design of solar to electrical energy conversion cell. Many multifunction solar cells has been successfully performed in the laboratory scale with up to 40% conversion efficiency [1].But their high production cost and toxicity to environment are problem to use as solar electricity in a very large scale[2-10].

The feasibility to develop a solar cell, organic molecules and polymers are two of the most alternatives. To investigate the electric and optical properties and the most favorite method; Density functional theory (DFT) is the method of choice according to an accurately describe and less computational cost in comparison to other high-level quantum approaches[11].

Time-dependent Density functional theory has been widely used to investigate excited state property because the high accuracy is reasonable to correlate in this work ,the electronic structure and optical properties, electronic transition, oxidation potential energy and electron injection force relevant to charge of the Luminal dyes were investigated using ab initio with computational methods were reported.

Luminescence based methods are widely accepted to study the biological system. Luminol is one of the most widely used chemiluminescent compounds because of its availability and low cost.

Luminol solutions are highly sensitive to light and incompatible with strong oxidizing agents, acids, bases, and reducing agents. The chemiluminescene properties of luminol are widely used as an analytical tool for environmental applications, immuno assay, monitoring of metabolic activities, detection of free radicals and forensic identification and detection of inorganic substrates. Due to its large number of applications, researchers have searched for some luminol derivatives to maximize the luminescence intensity and increase the range of emission wave length in the visible region.

Computational Details

DFT calculations were performed to determine geometries, electronic structures and electronic absorption spectra of Luminol base dyes. All the calculations, both in gas and solvent phase, were performed using Gaussian09 package[12]. All Calculations were performed by employing HF functions and 6-311+G basis set. Polarizable continuum model (PCM) was used to study solvent effects[13].

The free energy change for electron injection onto a titanium dioxide (Tio$_2$) surface and dye's excited state oxidation potential were calculated using mathematical equations. Following equation was used to calculate the free energy change for the process of electron injection.[14-15]

$$\Delta G^{inject} = E_{OX}^{dye*} - E_{CB}^{TiO2}$$

E_{OX}^{dye} Is the excited state oxidation potential of the dye. E_{CB}^{TiO2} Is the energy of conduction band of the TiO$_2$ semiconductor (-4.0 eV). E_{OX}^{dye*} Was determined using the following formula.

$$E_{OX}^{dye*} = E_{OX}^{dye} - \lambda_{max}^{ICT}$$

Where in this equation λ_{max}^{ICT} is the energy of intermolecular charge transfer (ICT). The light harvesting efficiency (LHF) was determined by formula[14]:

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

Where f is the Oscillator's strength of the dye. DFT calculations provide the oscillator strength directly.

Results and Discussion

The ground state structures for all molecules [fig.1]were with DFT/6-311+G (d,p) level. The discussion about geometrical parameters of the ground state structures is neglected; all molecules have not imaginary frequencies. The dipole moments for all molecules are equal to cero. The highest occupied molecular orbital energies (E$_{HOMO}$) and the lowest unoccupied molecular orbital energies (E$_{LUMO}$) of all dyes computed at the DFT/6-311+G(d,p) level in gas phase and solvent are liste in Table 1.

Effect of Solvent on HOMO-LUMO Energies

The distribution patterns of highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) are used to study the efficiency of sensitizers. The distribution pattern of highest occupied molecular orbitals

(HOMO) and lowest unoccupied molecular orbitals (LUMO) of new sensitizers are shownin Figure 4.The HOMO energy in DMF is greater than HOMO energy in gas phase. The LUMO energy in DMF is lesser than LUMO energy in gas phase. The DMF is an aortic polar solvent; it decreases the energy of LUMO and increases the energy of HOMO. Due these effects the energy gap becomes low in solvent phase as compared to gas phase, as shown in Table 1.
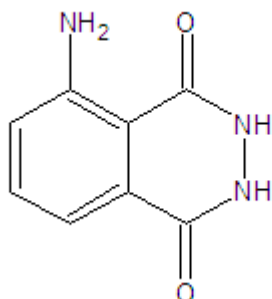

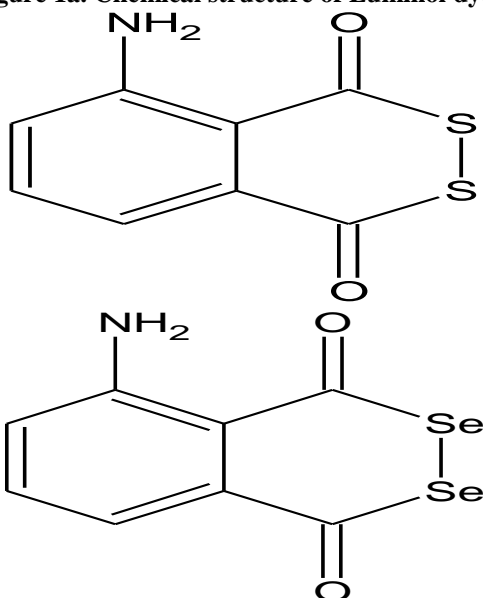**Figure 1a. Chemical structure of Luminol dye**

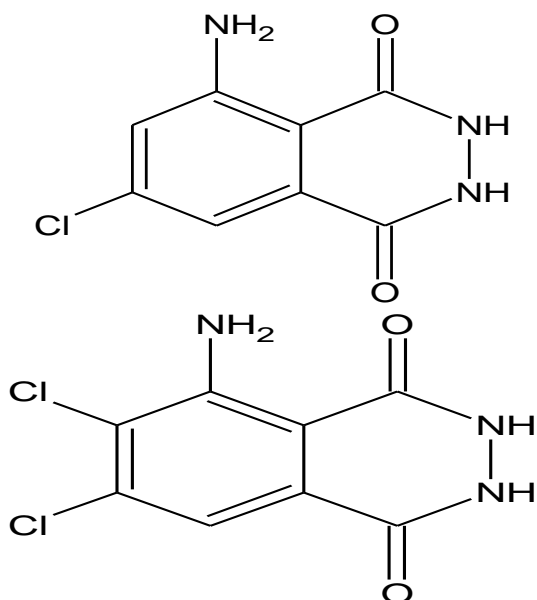**Figure 1b. Chemical structure of Donor Luminol dye**

Figure 1c. Chemiclal structure of Accepter Luminol dye

Luminol (Gas) – HOMO   Luminol (Gas) - LUMO   L1-Dye-1 (GAS) – HOMO   L1-Dye-1(GAS) – LUMO

L1-Dye-2 (GAS) – HOMO   L1-Dye-2(GAS) – LUMO   L1-Dye-3 (GAS) – HOMO   L1-Dye-3(GAS) – LUMO
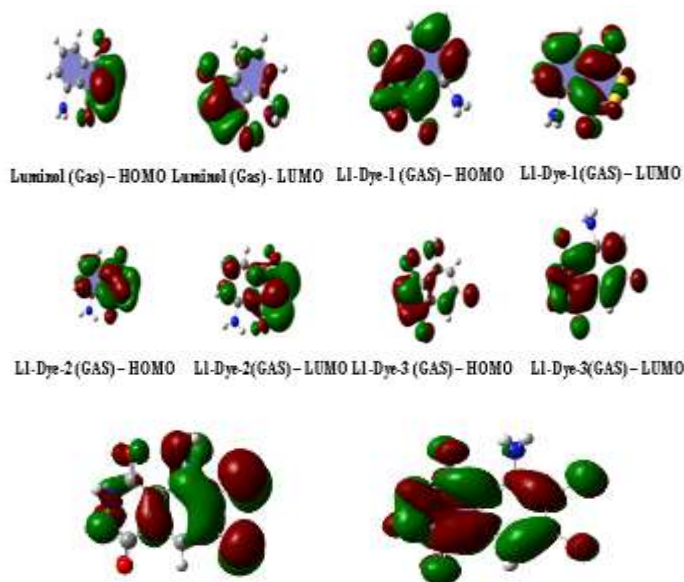
L1-Dye-4 (GAS) – HOMO   L1-Dye-4(GAS) – LUMO
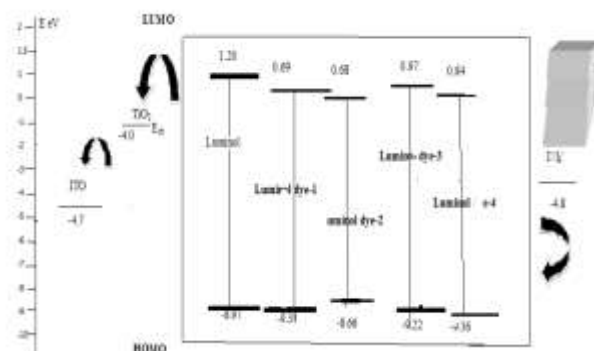**Fig 2. The HOMO and LUMO distribution pattern of dyes at DFT/B3LYP/6-3-11+G level theory.**

Figure 3. Schematic energy diagram of dyes, TiO$_2$ and electrolyte (I⁻/I$_3$).E$_{HOMO}$ and E$_{LUMO}$ of the dyes are in gas phase

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 (TiO$_2$) surface. Λmax, ΔG^{inject}, $\lambda_{max,}^{ICT}$ E_{OX}^{dye} and E_{OX}^{dye*} are presented in Table 2. The electron injection free energy change ΔG^{inject}, ground and excited E_{OX}^{dye*} state oxidation potentials computed in gas phase and DMF. 6-311+G basis set was used for all calculation. E_{OX}^{dye} can be estimated as value E$_{HOMO.}$ E_{OX}^{dye*} is calculated based on Eq.(2). ΔG^{inject} was estimated using Eq.(1). Its values are for all dyes. In parent molecule ΔG^{inject} is 0.174 in gas phase while it is 0.228 in DMF because of highering of HOMO energy in Solvent phase. In all new designed dyes ΔG^{inject} is higher value in DMF phase than that of ΔG^{inject} lowering value of gas phase. If ΔG^{inject} improved in new dyes both in gas phase and solvent phase as shown in table 2.

The values ΔG^{inject} is an indication of spontaneous electron injection from the dye to TiO$_2$.For all newly designed dyes ΔG^{inject} is more than luminal. Order of ΔG^{inject} is L1-Dye3<L1-Dye4<L1-Dye-2<L1-Dye1<Luminol. This is reflected from figures 3 and 4.

Table 1. The E$_{HOMO}$, E$_{LUMO}$ and energy gap (E$_g$) of dyes in eV at DFT/6-311+G level of theory

	Gas Phase			DMF		
	E$_{HOMO}$	E$_{LUMO}$	E$_{gap}$	E$_{HOMO}$	E$_{LUMO}$	E$_{gap}$
Luminol	-8.9735	1.2087	10.1816	-8.9931	1.1910	10.1842
L1-Dye-1	-9.3139	0.6955	10.0094	-9.1768	0.7053	9.8821
L2-Dye-2	-8.6660	0.6830	9.3490	-8.5977	0.6661	9.2639
L3-Dye-3	-9.2288	0.9774	10.2062	-9.1700	1.0258	10.1959
L4-Dye-4	-9.3659	0.8441	10.2100	-9.2878	0.9230	10.2108

Table 2. Calculated absorption spectra λ_{max}, ΔG^{inject}, oxidation potential, intramolecular charge transfer energy of dyes at DFT/6-311+G level of energy

	Gas Phase					DMF				
	λ_{max}	ΔG^{inject}	E_{ox}^{dye*}	E_{ox}^{dye}	λ^{ICT}	λ_{max}	ΔG^{inject}	E_{ox}^{dye*}	E_{ox}^{dye}	λ^{ICT}
	nm					nm	nm			nm
Luminol	258.3	0.174	4.174	8.973	4.799	260.5	0.234	4.234	8.993	4.759
L1-Dye-1	303.1	1.129	5.129	9.313	4.090	296.1	1.086	5.086	9.176	4.184
L1-Dye-2	316.4	0.749	4.749	8.666	3.917	309.5	0.593	4.593	8.597	4.004
L1-Dye-3	258.8	0.439	4.439	9.228	4.789	261.3	0.426	4.426	9.170	4.744
L1-Dye-4	258.4	0.568	4.568	9.365	4.797	260.1	0.522	4.522	9.287	4.765

Table 3. Excitation energy (E), Light Harvesting Efficiency (LHE) and Average Light Harvesting Efficiency (LHF$_{Average}$) of dyes at DFT/6-311+G level of theory

	Gas phase				DMF			
	E/ev	λ/nm	LHE	LHE$_{average}$	E/ev	λ/nm	LHE	LHE$_{average}$
Luminol	4.799	258.3	0.193	0.102	4.759	260.5	0.273	0.147
	5.414	229.0	0.012		5.534	224.0	0.021	
L1-Dye-1	4.090	303.1	0.003	0.116	4.184	296.1	0.019	0.165
	4.797	258.4	0.229		4.698	263.9	0.311	
L1-Dye-2	3.917	316.4	0.003	0.158	4.004	309.5	0.009	0.172
	4.305	287.9	0.313		4.276	289.9	0.334	
L1-Dye-3	4.789	258.8	0.2031	0.112	4.744	261.3	0.284	0.157
	5.383	230.3	0.0207		5.487	225.9	0.031	
L1-Dye-4	4.797	258.4	0.1966	0.106	4.765	260.1	0.294	0.156
	5.365	231.1	0.0159		5.460	227.0	0.018	

Table 4. Oscillator strength (f) and Transition character of dyes (H=HOMO, L=LUMO, L+1=LUMO+1,etc) at DFT/6-311+G level of theory (Major contribution in Paranthesis)

System	Gas phase			DMF		
	λ/nm	f	Transition Character	λ/nm	f	Transition Character
Luminol	258.3	0.093	H → L (100%)	260.5	0.139	H → L (100%)
	244.7	0.012	H-L → L+3(99%)	246.7	0.017	H-L → L+3(99%)
	229.0	0.005	H → L+1(94%)	224.0	0.009	H → L+1(92%)
L1-Dye-1	303.1	0.001	H → L (100%)	296.2	0.008	H → L (100%)
	295.6	0.004	H-1 → L+1 (94%)	289.1	0.011	H-1 → L+1 (93%)
	258.4	0.113	H → L+1 (88%)	263.1	0.162	H → L+1 (90%)
L1-Dye-2	316.4	0.001	H → L (99%)	309.1	0.004	H → L (99%)
	296.8	0.015	H+1 → L+3 (96%)	296.8	0.22	H-L → L+3 (96%)
	287.9	0.163	H → L+2 (90%)	289.9	0.177	H → L+2 (89%)
L1-Dye-3	258.8	0.095	H → L (100%)	261.3	0.144	H → L (100%)
	246.6	0.017	H-1 → L+1 (99%)	248.9	0.023	H-1 → L+1 (99%)
	230.3	0.009	H-1 → L+2 (89%)	225.9	0.014	H-1 → L+2 (88%)
L1-Dye-4	258.4	0.095	H → L(100%)	260.1	0.151	H → L (100%)
	249.2	0.039	H-1 → L+1 (91%)	250.9	0.048	H-1 → L+1 (91%)
	231.1	0.007	H-1 → L+3 (88%)	227.0	0.008	H-1 → L+3(93%)

**Light Harvesting Efficiency (LHF) and Oscillator Strength.**

The light harvesting efficiency (LHF) is the efficiency of dye to response the light. It is another factor which indicates the efficiency of DSSC. The light harvesting efficiency (LHF) of the dye should be as high as feasible to maximize the photo-current response.

The Oscillator strength is directly obtained from DFT calculations. The Luminol dye has two main absorption peaks (258 and 228 nm in gas phase, 260 and 224 nm in solvent phase DMF). Higher Oscillator strength of the four new designed sensitizers than luminol as shown in Table 3 these dyes will convert more light to electrical energy. The Oscillator strength and transitions character are given in Table 4. Only the transitions with considerable oscillator strengths are given. The electronic structures of the three new designed sensitizers are quite similar from one another. The HOMO and LUMO composition of new sensitizers are depicted in Figure 4. The electron distribution of the HOMO orbital is delocalized on the π-system with the electron density present on the Benzene Ring of the Luminol, In all new designed sensitizers. It is noticed that the LUMO orbital always highest compositions on anchoring group. Therefore, electron will move from HOMO donator to LUMO acceptor excitation resulted by light absorption.

Improve ΔG^{inject} and LHF of new designed sensitizers as compare to Luminol is due to the Replacement of hydrogen atom of Luminol at H with (Cl, Se,N,S) In the Benzene Ring This can be considerable by the distribution pattern of HOMO and LUMO of Luminol dervaties.It encourages the promotion of the electron injection.

Electronic absorption spectra

TD/DFT/6-311+G (d, p) methods were employed to simulate the optical property of the dyes. The computed vertical excited singlet states, transition energies and Oscillating strength of all dyes in gas phase and solvent medium are tabulated in table 4.The Graph plotted Wave length Vs Oascillator Strength are shown in figures 5 and 6.
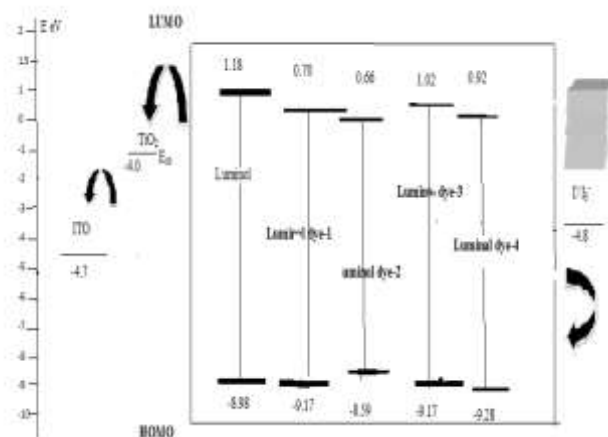
Figure 4. Schematic energy diagram of dyes, TiO$_2$ and electrolyte (I^-/I_3^-). E$_{HOMO}$ and E$_{LUMO}$ of the dyes are in DMF
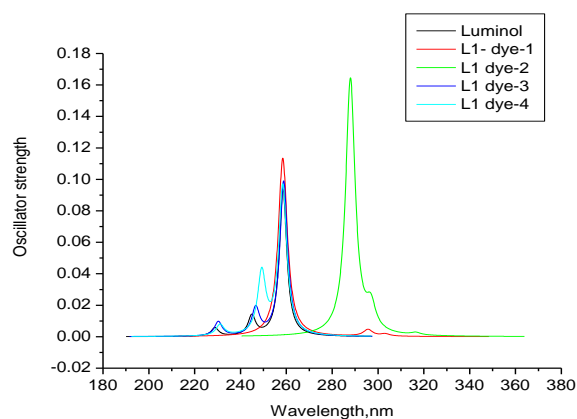
Figure 5. Simulated absorption spectra of dyes calculated in Gas phase at DFT/6-311+G level of theory
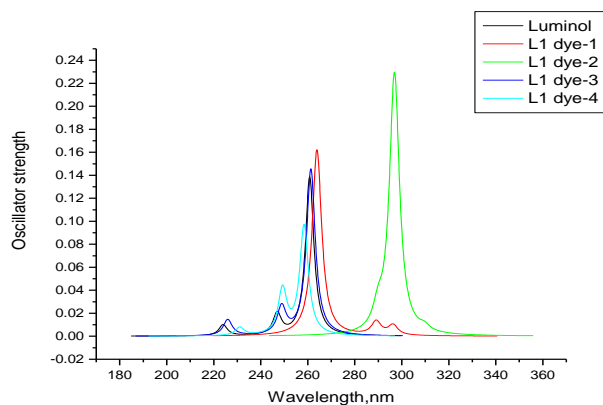
Figure 6. Simulated absorption Spectra of dyes calculated in DMF at DFT/6-311+G level of theory

The vertical excitation energies of the dyes are increasing ΔE_{exi} its value by the substitution. According transition to the character most of the dyes show the HOMO   LUMO transition as the first singlet excitation except for Luminol. The major contribution of the transition characters in gas phase differs from those solvent due to the effect of polar environment on the electronic energy level. The maximum (λ_{max}) wave length for UV-visible absorption spectra of all the dyes simulated in various media are shown in table (4). The calculated (λ_{max}) in gas phase and solvent medium is different by approximately red shift were found for all the dyes from gas phase and solvent phase.

Conclusions

Each of the molecules was theoretically analyzed. According to thermodynamic, the spontaneous charge transfer process from the dye in excited state to the conduction band of metal oxide, need that LUMO energy of the dye be more positive potential than conduction band energy of metal oxide, while the HOMO energy of the dye most be more negative than reduction potential energy of the I^-/I_3^- electrolyte. The calculations show that all dyes can work for DSSC with TiO_2, because all have LUMOS less negative than TiO_2 LUMO, while no one have less negative HOMO than the redox potential energy of electrolyte. L1-Dye-2 dye have the higher LHE of this dyes, which one recommended for DSCC with TiO_2 we expect that these dyes will be tested for DSSC.

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