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Quantum chemical designing of 2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxychromenium as a efficient sensitizer for dye sensitized solar cell

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In this study we have designed six metal free D–π–A system and evaluated their optimum properties for Dye sensitized solar cell (DSSC). The ground state geometries, electronic properties, light harvesting efficiency, and electronic absorption spectra of these dyes were studied using Density functional theory and Time dependant density functional theory. All these calculations were performed in the gas phase and Dimethylformamide, Dichloromethane as solvent. Our theoretical calculation reveals that the designed metal free organic dyes are good candidate for DSSC applications.

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Keywords: DFT, HOMO-LUMO, Dye sensitized solar cell

1. Introduction

The world’s energy consumption is constantly increasing and this makes a high demand for renewable energy sources to be developed. The biggest challenge for our global society is to discover ways to replace the gradually depleting fossil fuel supplies with renewable resources. In recent years dye-sensitized solar cells (DSSC) have received vital attention. The DSSC is a device for the conversion of visible light into electricity, based on the sensitization of wide band gap semiconductors [1]. The performance of DSSCs primarily depends on the dye used as the sensitizer [2].Organic dyes have a D–π–A dipolar structure, in which the donor (D) is a π-electron-rich moiety, the acceptor (A), is a π-electron-deficient moiety and a π-conjugated spacer as the connection between the donor and the acceptor [3]. Although experimental molecular modification is a viable approach for developing new dyes for DSSCs, the method is time consuming and costly. Theoretical calculation is another efficient tool for molecular design, and the results obtained from these methods are the most valuable guideline for the synthesis of new effective dyes [3].To design an appropriate organic sensitizers for DSSC, suitable D–π–A systems are needed whose properties can be altered by applying the drivable structural modifications[4].

This study was carried out to design novel sensitizers for DSSC application. The newly designed dyes consist of the following part as shown in the figure (1). Auxiliary donor (AD), donor (D), Pi-spacer (π) and acceptor. Chemical structure of cyanidin is shown in figure (2). The cyanidin are the basic structures of the anthocyanins. The anthocyanidins (or aglycons) consist of an aromatic ring [A] bonded to an heterocyclic ring [C] that contains oxygen, which is also bonded by a carbon–carbon bond to a third aromatic ring [B][5]. The structural modification of cyanidin as shown in figure (2a) is used to design new dyes. We have designed compounds by the substitution of Triphenylamine (TPA) and Diphenylamine (DPA) moiety in cyanidin as donor and NO_2 and CN moiety as electron acceptor. To estimate the effect of auxiliary donor on dyes efficiency, CH_3 groups have been introduced on TPA moiety as an auxiliary donor. The designed dyes were studied by the DFT and TD-DFT methods. This research would help the experimentalists to synthesize the efficient dyes for dye sensitized solar cells.

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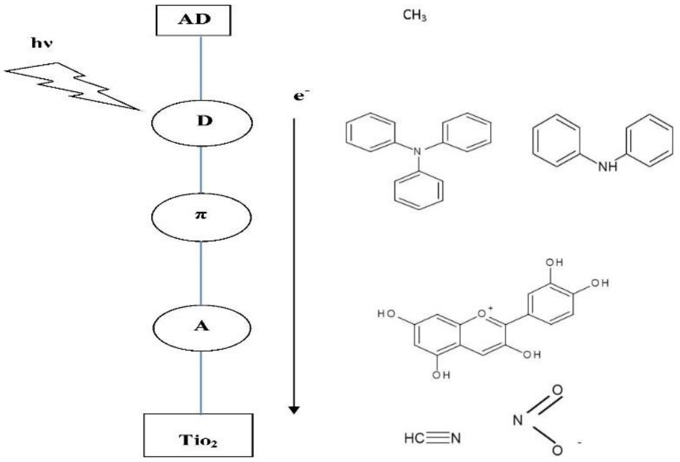


Fig. 1. Different parts of AD-D-π-A system. AD = auxiliary donor, D = donor, π = pi-spacer, A = acceptor.

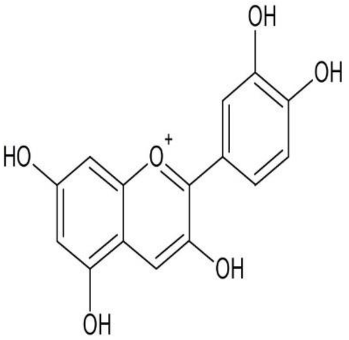


Fig. 2. Chemical structure of cyaniding.

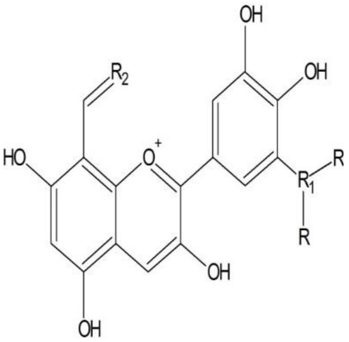


Fig. 2a.Chemical structure of newly designed dyes.

CY_1	$R_1= C_{12}H_{10}N$	$R_2= CN$	
CY_2	$R_1= C_{18}H_{14}N$	$R_2= NO_2$	
CY_3	$R_1= C_{12}H_{10}N$	$R_2= CN$	
CY_4	$R_1= C_{18}H_{14}N$	$R_2= NO_2$	
CY_5	$R_1= C_{12}H_{10}N$	$R_2= CN$	$R=CH_3$
CY_6	$R_1= C_{18}H_{14}N$	$R_2= NO_2$	$R=CH_3$

2. Theoretical background

All molecular calculation were performed in both gas and solvent phase using Density Functional Theory (DFT) using the B3LYP [Becke three-parameter Lee –Yang-Parr] exchange correlation functional [6].The basis set 6-311++G (d, p) was used for all calculations [7]. A newly designed functional, the long rang Coulomb attenuating method (CAM-B3LYP) considered long range interaction by comprising 19% of HF and 81% of B88 exchange at short –range and 65% of HF plus 35%of B88 at long range [8].Furthermore the CAM-B3LYP was also used and it was found to be sufficiently capable of predicting the excitation energies and the absorption spectra of the D-π- A molecule [9-12].In this work the vertical excitation energy and oscillator strength were stimulated using CAM-B3LYP.The inclusion of theoretical calculations is essential to predict the experimental spectra with a reasonable accuracy. Polarizable continuum model (PCM) was used to study the solvent effects [13].For the solvation effect, Dimethylformamide (DMF) and Dichloromethane (DCM) solvent phase were considered. All the calculation both gas and solvent phase were performed using Gaussian 09 package [14].

The free energy change(in eV) 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[15].

$$\Delta G^{\mathrm{inject}} = E_{\mathrm{ox}}^{\mathrm{dye}^*} - E_{\mathrm{CB}}^{\mathrm{TiO_2}} \tag{1}$$

In equation (1) $E_{ox}^{dye^*}$ is the excited state oxidation potential of the dye and $E_{CB}^{TiO_2}$ is the energy of conduction band of the TiO_2 semiconductor (−4.0 eV).The $E_{ox}^{dye^*}$ can be estimated by the following equation (2).

$$E_{\mathrm{ox}}^{\mathrm{dye}^*} = E_{\mathrm{ox}}^{\mathrm{dye}} - \lambda_{\mathrm{max}}^{\mathrm{ICT}} \tag{2}$$

In equation (2) λ_{max}^{ICT} is the energy of inter molecular charge transfer (ICT). According to Koopmans theorem, the ground state oxidation potential energy is associated to ionization potential energy. E_{ox}^{dye} can be estimated as negative E_{HOMO}. [19]

The light harvesting efficiency (LHE) of the dye sensitizer can be calculated from the following equation (3) [16, 18].

$$\mathrm{LHE} = 1 - 10^{-f} \tag{3}$$

Where f is the oscillator strength of dye. TDDFT calculations will provide the oscillator strength directly.

2.1. Electronic structure properties

The efficiency of the sensitizer was analysed by studying the distribution pattern of highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) [21].The distribution pattern of HOMO and LUMO of cyanidin and newly designed sensitizer in gas phase and in solvents phase were depicted in figure (3).The figure shows that HOMOs are localized on TPA and DPA unit and LUMOs are spread over on benzene ring of the cyanidin near the acceptor group. It is advantageous to have such electron density distribution for effective electron injection and charge separation. This shows how the charge is transfer from donor to acceptor through π spacer. Significant transfer from donor to acceptor revealed that these would have been an excellent sensitizer [23]. The HOMO energy (E_{HOMO}), LUMO energy (E_{LUMO}) and HOMO-LUMO energy gap (E_g) are given in table (1). In cyanidin the HOMO are delocalized over the entire molecule of cyanidin. The LUMO of cyanidin is dispersed throughout the molecule. The HOMOs are delocalized over the pi-conjugated system in newly designed dyes with the greatest electronic cloud mainly at the donor side and the LUMOs are spread over at the acceptor side.

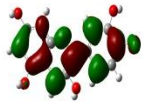
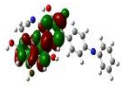
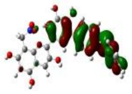
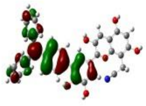
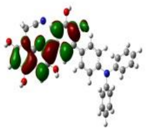
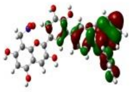
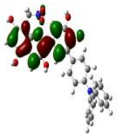
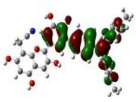
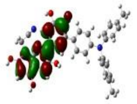
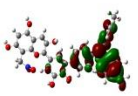
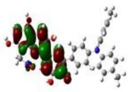
Dyes	HOMO	LUMO
Cyanidin		
CY1		
CY2		
CY3		
CY4		
CY5		
CY6		

Fig. 3. The HOMO and LUMO distribution pattern of dyes at B3LYP/6-311++G level of theory.

It has been found that the light stimulated HOMO-LUMO excitation has shifted the electron cloud from the TPA, DPA unit to the acceptor moiety and photo stimulated electron transfer from the dye to the Tio$_2$ electrode will occur significantly by the HOMO-LUMO transition. The energy gap of cyanidin and newly designed dyes in both gas and solvent (DMF, DMC) are in the following order: CY6<CY4<CY5<CY2<CY1<CY3<CY. Cyanidin has larger energy gap, since it has no donor and acceptor group. Substitution of the electron donating group at the third aromatic ring of cyanidin and withdrawing groups at the acceptor side enable effective electron transfer and enriches the efficiency of the dyes. According to previous studies [23, 24] the sensitizer which has small band gap value show high performance in DSSC. The light will be absorbed in a larger wavelength if the band gap is smaller and larger wavelength will absorb more light. As a result the electrons would be able to move easier from one orbital with a low energy level to other orbitals with higher energy levels, it will increase the response to light [27]. The HOMO and LUMO energies of the dyes were calculated in gas phase as well as in the solvent phase are shown in table (1).

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

Dye	GASPHASE			DMF			DCM		
	HOMO	LUMO	E $_{gap}$	HOMO	LUMO	E $_{gap}$	HOMO	LUMO	E $_{gap}$
CY	-9.9341	-6.7947	3.1394	-7.1035	-3.7639	3.3396	-7.2429	-3.9562	3.2866
CY-1	-7.3985	-6.4211	0.9774	-5.7585	-3.5859	2.1725	-5.8804	-3.8534	2.6269
CY-2	-7.454	-6.4907	0.9632	-5.7884	-3.6885	2.0999	-5.9119	-3.9497	1.9622
CY-3	-7.2448	-6.2657	0.9790	-5.5040	-3.5709	1.9331	-5.6368	-3.8275	1.8092
CY-4	-6.9171	-6.5209	0.3962	-5.5541	-3.704	1.8501	-5.6425	-3.9720	1.6705
CY-5	-6.9147	-6.242	0.6726	-5.3334	-3.5522	1.7812	-5.4447	-3.8093	1.6354
CY-6	-6.6453	-6.4948	0.1508	-5.3552	-3.6986	1.6566	-5.4341	-3.9641	1.4699

Spontaneous charge transfer from the dye excited state to conduction band of Tio$_2$ require more positive LUMO energy than E_{cb} ^{Tio}$_2$ (-4.0eV) while spontaneous charge regeneration needs more negative HOMO energy than reduction potential energy of the I^- / I^{-3} electrolyte (-4.8eV)[25,26].The energy level diagram of the HOMO and LUMO of the dyes, E_{cb} of Tio$_2$ and redox potential energy of the electrolyte in gas phase is represented in figure(4).All newly designed dyes LUMOs are exceed over the E_{cb} of Tio$_2$ whereas their HOMOs are lower than redox potential energy of the electrolyte in solvent phase. This shows the spontaneous charge transfer and charge regeneration.

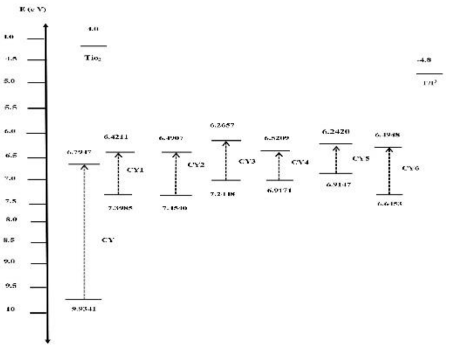


Fig. 4. Energy level diagram of dyes, Tio$_2$ and electrolyte (I^{-1}/I^{-3}), E_{HOMO} and E_{LUMO} of studied dyes are in gas phase.

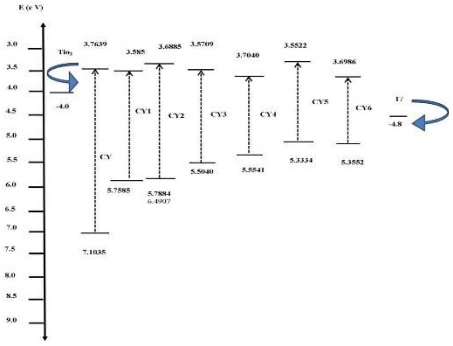


Fig. 5. Energy level diagram of dyes, Tio$_2$ and electrolyte (I $^{-1}$/I $^{-3}$), E$_{HOMO}$ and E$_{LUMO}$ of studied dyes are in DFM solvent phase.

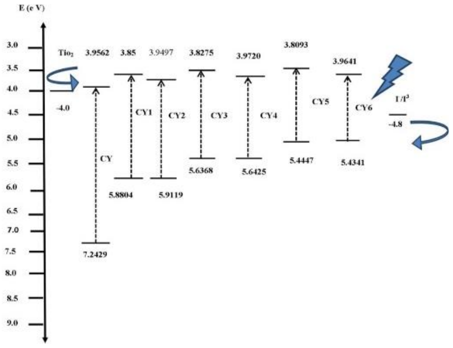


Fig. 6. Energy level diagram of dyes, Tio$_2$ and electrolyte (I $^{-1}$/I $^{-3}$), E$_{HOMO}$ and E$_{LUMO}$ of studied dyes are in DCM solvent phase.

2.2. Effect of solvent on HOMO-LUMO Energies

The solvation effect is taken into account in DFT calculation for analysing HOMO and LUMO, which reduces the variations between experiment and calculations. According to Priyasiri et al, the solvation effect calculation does not lead to significant changes in the band gap, but rather changes in the absolute value of both the HOMO and LUMO. This implies that the calculations in vacuum overestimate the energy level while having little effect on the band gap. Furthermore, when various polar solvents were considered for solvation effect, the energy level showed no significant difference [28]. In our studies Cyanidin and newly designed dyes showed similar results. The HOMO energy in solvent phase is greater than HOMO energy in gas phase. The LUMO energy in gas phase is lesser than LUMO energy in solvent phase. Furthermore, DMF and DCM are aportic polar solvents, they increase the energy of HOMO and LUMO. As a result of these effects, the energy gap in the solvent phase is lower than in the gas phase. Figures (5) & (6) shows the energy level diagram of HOMO and LUMO, E$_{cb}$ of Tio$_2$ and redox potential energy of the electrolyte in gas phase.

2.3. Absorption Properties

TDDFT calculations were performed with the CAM-B3LYP functional and 6-311++ G (d,p) basis set in gas and solvent phase to evaluate the electronic transition and optical properties of the newly designed dyes. The absorption wavelength λ_{max} and oscillator strength of cyanidin and newly designed dyes are stimulated in gas phase as well as in solvent phase are shown in table (2a) & (2b).Figure (7) shows the UV-Vis absorption spectra of cyanidin and newly designed dyes in gas as well as in solvent phase. The absorption spectra show that all are consists of a very intense and well separated absorption band in the visible and IR region. The spectrums of newly designed dyes are red shifted in wavelength. From this we revealed that it is essential to introduce the electron donating unit and electron withdrawing units to enhance the absorption spectrum.

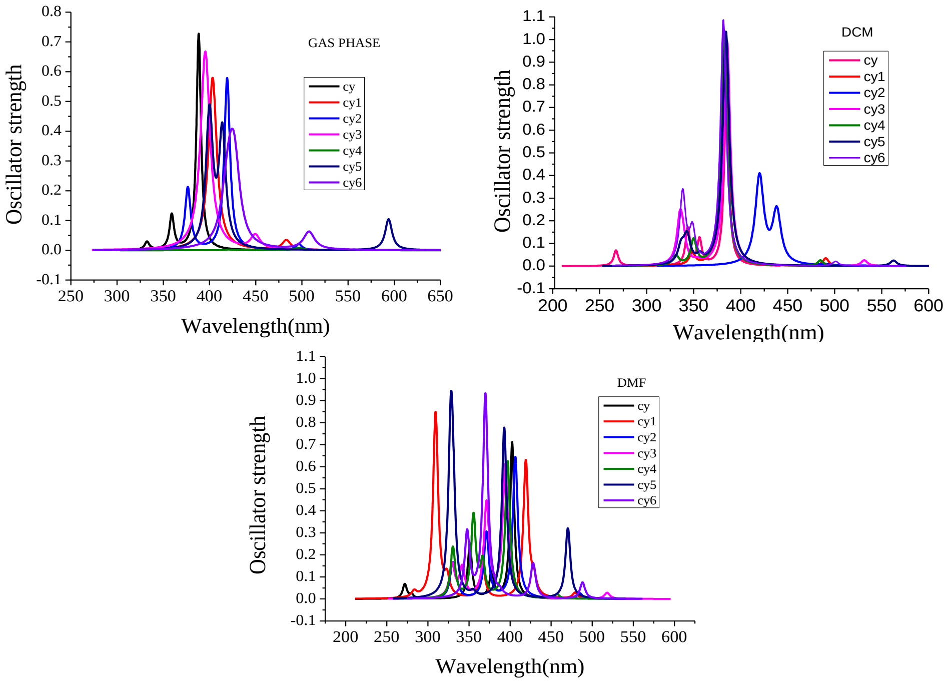


Fig. 7. Stimulated absorption spectrum of dyes in gas and solvent phase.

2.4. Free energy change of electron injection and oxidation potential energy

In this work the dyes free energy change of electron injection to titanium dioxide (Tio$_2$) surface and excited state oxidation potential are calculated using mathematical equation (1) & (2). The ground state oxidation potential ($E_{ox}{}^{dye}$) and excited state oxidation potential ($E_{ox}{}^{dye*}$) and the electron injection free energy change ΔG^{injet} are computed in gas phase as well as in solvent phase are presented in table (2a&2b). ΔG^{injet} values are negative for all newly designed dyes. In cyanidin and newly designed molecule ΔG^{injet} in gas phase showed endergonic type electron injection. The value of ΔG^{injet} is more negative than cyanidin for all newly designed dyes in solvent phase. In all newly designed dyes CY$_1$, CY$_2$, CY$_3$, CY$_4$, CY$_5$, CY$_6$ the ΔG^{injet} was improved in gas phase as well as solvent phase.The negative value of ΔG^{injet} which is favoured for electron transfer from the excited state of the dye molecule to conduction band of Tio$_2$ implies exergonic type electron injection.

2.5. Light harvesting efficiency (LHE) and oscillator strength

Light harvesting efficiency is another factor which indicates the efficiency of DSSC. The LHE of the dye should be high in order to maximize the photo-current response. The oscillator strength is obtained directly from TDDFT calculation. The higher oscillator strength is due to better π conjugation. The main absorption peaks are considered to calculate the dye's light harvesting efficiency [19]. The LHE and average value of LHE are shown in table (3a) &(3b). The light harvesting efficiency of all newly designed dyes was improved when compared to cyanidin. The maximum value of Light harvesting efficiency is calculated for CY6 which has the value of 0.7170 in solvent phase.

Table 2a. Calculated absorption spectra λ_{max}, intramolecular charge transfer energy, oxidation potential, ΔG^{inject} of dyes at B3LYP/6- 311+G(d,p) level of theory in gas phase.

DYE	GAS PHASE			
	λ_{max}	λ^{ICT}_{max}	E^{dye*}_{ox}	ΔG^{inject}
CY	454.34	2.7289	7.205	3.2051
CY-1	1997.90	0.6206	6.7779	2.7779
CY-2	2036.29	0.6089	6.8451	2.8451
CY-3	2085.14	0.5946	6.6502	2.6502
CY-4	1386.47	0.0981	6.819	2.8190
CY-5	4192.14	0.2958	6.6189	2.6189
CY-6	1919.28	1.8488	5.8488	1.8488

Table 2b. Calculated absorption spectra λ_{max}, intramolecular charge transfer energy, oxidation potential, ΔG^{inject} of dyes at B3LYP/6- 311+G(d,p) level of theory in solvent phase.

DYE	DMF				DCM			
	λ_{max}	λ^{ICT}_{max}	E^{dye*}_{ox}	ΔG^{inject}	λ_{max}	λ^{ICT}_{max}	E^{dye*}_{ox}	ΔG^{inject}
CY	436.53	2.8402	4.2633	0.2633	444.37	2.7901	4.4528	0.4528
CY-1	489.86	2.5310	3.2275	-0.7725	515.07	2.4071	3.4733	-0.5267
CY-2	531.28	2.3337	3.4547	-0.5453	556.60	2.2275	3.6844	-0.3156
CY-3	466.06	2.6603	2.8437	-1.1563	485.58	2.5533	3.0825	-0.9175
CY-4	570.43	2.1735	3.3806	-0.6194	612.27	2.0250	3.6175	-0.3825
CY-5	900.71	1.3765	3.9569	-0.0431	520.15	2.3836	3.0611	-0.9389
CY-6	622.05	1.9931	3.3621	-0.6379	676.08	1.8339	3.6002	-0.3998

Table 3a. Light Harvesting Efficiency (LHE) , average Light Harvesting Efficiency (LHE_{avg}) ,Oscillator Strength (f) and absorption Spectra (λ_{max}) of dyes at CAM-B3LYP/6-311+G(d,p) level of theory in gas phase.

DYE	GAS PHASE			
	λ_{max}	f	LHE	LHE_{avg}
CY	417.89 404.62	0.2657 0.1489	0.4576 0.2902	0.3739
CY-1	483.19 403.38	0.0324 0.5797	0.0718 0.7367	0.4042
CY-2	419.13 376.58	0.5778 0.2084	0.7357 0.3811	0.5584
CY-3	449.62 395.49	0.0464 0.6680	0.1013 0.7852	0.4431
CY-4	524.56 387.54	0.0129 0.7120	0.0292 0.8059	0.4175
CY-5	413.88 399.95	0.3873 0.4548	0.5900 0.6490	0.6195
CY-6	427.13 394.65	0.2425 0.7745	0.4278 0.8319	0.6298

Table 3b. Light Harvesting Efficiency (LHE) ,average Light Harvesting Efficiency (LHE_{avg}) ,Oscillator Strength (f) and absorption Spectra (λ_{max}) of dyes at CAM-B3LYP/6-311+G(d,p) level of theory in solvent phase.

DYE	DMF				DCM			
	λ_{max}	f	LHE	LHE_{avg}	λ_{max}	f	LHE	LHE_{avg}
CY	402.54 377.57	0.7101 0.1196	0.8050 0.2407	0.5228	384.85 356.16	0.7959 0.1117	0.8400 0.2267	0.5333
CY-1	419.18 366.79	0.6232 0.1465	0.7618 0.2868	0.5243	382.89 325.73	0.9450 0.0861	0.8864 0.1798	0.5331
CY-2	406.42 371.22	0.2990 0.0372	0.7719 0.4977	0.6348	382.27 329.58	0.9684 0.0940	0.8924 0.1946	0.5435
CY-3	394.18 371.39	0.6002 0.4275	0.7489 0.6263	0.6876	385.33 335.42	0.9904 0.1980	0.8977 0.3661	0.6319
CY-4	397.04 355.49	0.6216 0.3700	0.7609 0.5734	0.5813	382.33 349.87	1.0325 0.1090	0.9072 0.2219	0.5645
CY-5	392.91 327.74	0.7749 0.6521	0.8320 0.7772	0.6195	384.28 342.94	1.0327 0.1182	0.9072 0.2382	0.5727
CY-6	370.00 347.79	09255 0.2917	0.8812 0.4891	0.6815	381.53 338.27	10828 0.3159	0.9173 0.5168	0.7170

2.6. Electron coupling constant and open circuit voltage:

The electron coupling constant V_{RP} and open circuit voltage were calculated using equation (4) & (5) and it was shown in table (4).The difference between the energy of the LUMO of the dye and the energy of the conduction band of Tio_2 is regarded as the open circuit voltage [4].

$$V_{RP} = - \frac{\Delta G}{2} \tag{4}$$

$$V_{oc} = E_{LUMO} - E_{cb} \tag{5}$$

Since V_{oc} is directly proportional to the power conversion efficiency of the solar cell. The maximum value of open circuit voltage was calculated for CY5 which has the value of 0.4478 and it can be regarded as the most efficient sensitizer for DSSC. The open circuit voltages V_{oc} of the studied molecules are ranges from 0.2361eV to 0.4478eV.The anchoring group NO_2 as well as cyano group of the LUMO which leads the strong electronic coupling with the Tio_2 surface and enhance the electron injection efficiency.

Table 4. The electron coupling constants ($|V_{RP}|$) and open-circuit photovoltage (V_{oc}) in eV of Cyanidin dyes.

DYE	GAS PHASE		DMF		DCM	
	$\lvert V_{RP}\rvert$	V_{oc}	$\lvert V_{RP}\rvert$	V_{oc}	$\lvert V_{RP}\rvert$	V_{oc}
CY	2.3805	-2.7947	0.1316	0.2361	0.2264	0.0438
CY-1	1.3887	-2.4211	0.3862	0.4141	0.2633	0.1466
CY-2	1.4225	-2.4907	0.2726	0.3115	0.1578	0.0503
CY-3	1.3251	-2.2657	0.5781	0.4291	0.4587	0.1725
CY-4	1.4095	-2.5290	0.3097	0.2960	0.1912	0.0280
CY-5	1.3094	-2.6242	0.02155	0.4478	0.4694	0.1907
CY-6	0.9244	-2.4948	0.3189	0.3014	0.1999	0.0359

3. Conclusion

We have designed novel organic D -π -A system for Dye sensitized solar cell. To evaluate their optimum properties all these designed dyes have been investigated using DFT calculations. The opto electronic, electrochemical and photovoltaic properties were investigated both in gas as well as in solvent phase. All newly designed sensitizer have appropriate HOMO and LUMO levels relative to the redox couple and the Tio_2 conduction band. All newly designed dyes CY1-CY6 the value of λ^{max} was highly red shifted as compared to cyanidin due to solvent effect. The light harvesting efficiency (LHE), free electron injection ΔG^{inject} and open circuit voltage V_{oc} were improved as compared to cyanidin. This study shows that the introduction of electron donor and acceptor on π bridge promotes the electron injection and light harvesting efficiency. We suggested that the newly dyes are good candidates for DSSC applications.

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