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Modifications of the molecular structure of Aurantinidin dyes for DSSCs

Obasuyi Aanuoluwapo Raphael, Daniel Glossman-Mitnik, Norma Flores-Holguín
Laboratorio Virtual NANOCOSMOS, Centro de Investigación en Materiales Avanzados SC (CIMAV), Chihuahua, México

ABSTRACT

Two modifications for Aurantinidin dye were done, a design of D-π-A structure of Aurantinidin was done by the additions of donor and acceptor moiety. The modifications produce high light harvesting efficiency (LHE), driving force of electron injection (ΔG_{inject}), reorganization energy (ΔG_{reg}) and V_{OC}. These critical parameters have a close relationship with the short-circuit current density (J_{SC}) and open-circuit photovoltage (V_{OC}). The modifications improved the electron injection of the molecules

INTRODUCTION

High light-to-electricity conversion efficiencies, ease of fabrication, and low production costs are factors that has made Dye Sensitized Solar Cells (DSSCs) attracting considerable attention[1]. DSSC is a photovoltaic device which has a unique property: it uses molecules to absorb photons and convert them to electric charges without the need of intermolecular transport of electronic excitation. The recombination of charge carriers in DSSC occurs across the phase boundary thereby, separating the electron from the hole conductor medium. This helps to modify the interface in other to retard the back-electron-transfer reaction. Almost all the organic sensitizers applied in DSSCs have three important parts: 1) the electron donor, 2) the electron acceptor, and 3) the linker units for the pi conjugation to enhance the molar absorption coefficient[2].

THEORETICAL BACKGROUND

The electron injection efficiency ϕ_{inject} is related to injection driving force ΔG_{inject} of electrons injecting from the excited dyes to the semiconductor substrate. Therefore, the free energy change (eV) for the electron injection can be expressed as[3,4]

$$\Delta G_{inject} = E_{ox}^{dye*} - E_{CB}^{TiO_2}$$

$$E_{ox}^{dye*} = E_{ox}^{dye} - \lambda_{\max}^{ICT} \qquad -E_{HOMO}^{dye} = E_{ox}^{dye}$$

Dye Regeneration is $\Delta G_{reg} = E_{ox}^{dye} + E_{redox}^{Electrolyte}$

Light harvesting efficiency is $LHE = 1 - 10^{-A} = 1 - 10^{-f}$

Open Circuit Voltage is $V_{oc} = E_{LUMO} - E_{CB}$

COMPUTATIONAL STUDIES

The geometry optimizations of the structures have been computed using Density Functional Theory (DFT) with Gaussian09 package[5]. The MN12SX functional [6] and the 6-311+G(d,p) basis set[7] were used for the analysis of the structures. This basis set has been chosen because it has been shown that return a converged λ_{max} for a series of calculations, while a smaller basis set would give a too short λ_{max} (in nm)[8].

RESULTS AND DISCUSSIONS

Geometry Optimization

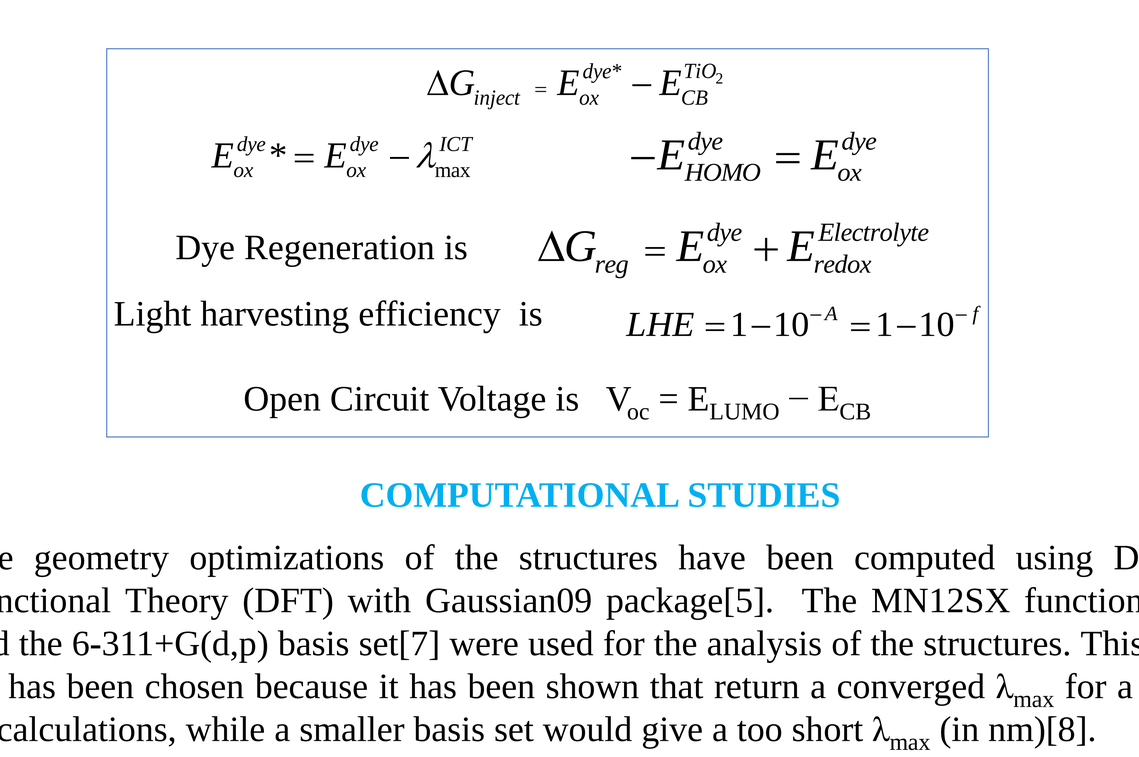

Figure 1: Structure of the Modified Molecules

Optical Properties

Table 2: Absorption wavelength (nm), Oscillator strength and transition level for modified molecules

Dyes	MN12-SX/6-311+G(d,p)		
	λ(nm)	f	Transition (%)
D-π-A(1)	553.6	0.3866	H - L (88)
	501.3	0.0259	H – L+1 (15)
	478.1	0.0048	H - L +1(32)
	457.6	0.0573	H - L +1(76)
D-π-A(2)	534.5	0.4066	H - L (82)
	502.3	0.0297	H - L (22)
	435.6	0.1054	H - L (72)
	400.4	0.0054	H - L (84)

The LUMO levels of the dyes lie above the conduction band (CB) of the TiO_2 (-4.0 eV), indicating that excited state of the dyes could quickly and efficiently inject electrons into the TiO_2 conduction band. The HOMO levels of dyes are below the redox potential of I- /I-3 electrolyte (-4.85 eV), indicating that the oxidized dyes could quickly get electrons from the electrolyte. The oscillator strength of the absorption (f) should be high. The HOMO of the D-π-A(1) and D-π-A(2) dyes are distributed mainly over the entire diphenylamine donor part, while the LUMOs are mainly delocalized over the π spacer and acrylic acid. The results show that the modification of the dyes promote light harvesting efficiency (LHE), high values of ΔG inject, the reorganization energy (ΔG_{reg}) is low and high Voc which will lead to faster electron transfer.

Frontier orbitals

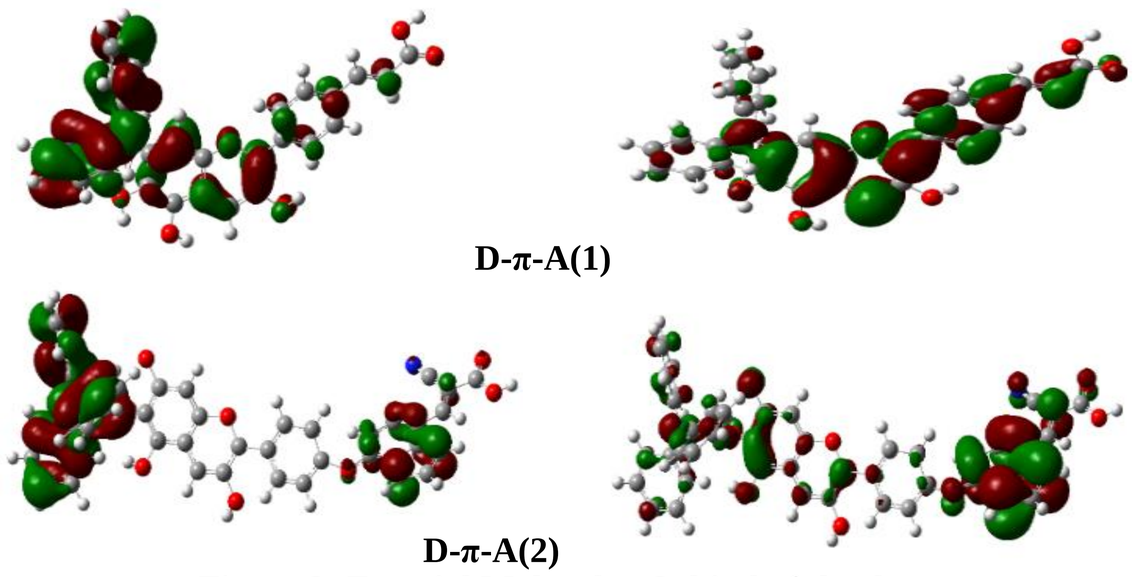

Figure 2: Frontial Molecular Orbital of the dyes

Electron Injection

Table 3: Calculated electronic properties of the dyes

Dyes	LHE	ΔG_{inject}	E_{ox}^{dye*}	E_{ox}^{dye}	ΔG_{reg}	Voc
D-π-A(1)	0.5894	-2.22	1.78	4.02	-0.83	1.45
D-π-A(2)	0.6079	-2.30	1.70	4.07	-0.78	1.46

CONCLUSIONS

Modification of the structures were done by adding units connected by a vinyl and using regular electron acceptor and electron donor moieties to the original structure. The modifications improved the electron injection of the molecules with a high light harvesting efficiency (LHE), driving force of electron injection (ΔG_{inject}), reorganization energy (ΔG_{reg}) and open-circuit photovoltage (V_{OC}). which shows that the modified molecules are good sensitizers for electron injection into the conduction band of the semiconductor material. D-π-A(2) shows better injection ability due to the double aromatic ring they possess.

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