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Research Article

DFT study of small D-π-A systems for DSSCs applications: High efficiency based on fluorene derivatives

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ABSTRACT

In this study, small D-π-A systems (F1-3, CBz1-3, DB1-2) have been investigated by Gaussian03 using DFT method. The fluorene derivatives have been found the best candidate for DCCSc applications. Geometric and electronic properties of all systems were investigated at B3LYP/6-31G(d) level, and absorption spectra were simulated by Time-Dependent Density Functional Theory (TD-DFT) at the same level. The fluorene derivative has the cyano acrylic acid group which is used as electron acceptor group for the attachment of the dye on the TiO2 surface and has two di-methoxyphenylamine as the electron acceptor. Simulated absorption value showed that this dye could harvest light in the visible spectrum. Calculated band gap energies for this new dye comparable to the small molecules dyes is considered very efficient. All these proprieties make the studied fluorene derivative in this article a good compound for organic dye-sensitized solar cells.

Keyword: Fluorene; Carbazol; D-π-A dyes; Dye-sensitised solar cell, photovoltaic performance.

INTRODUCTION

Dye-sensitised solar cells (DSCCs) have been a subject of a great deal of interest for its simple preparation process; the production costs are the low and high efficiency of converting solar energy into electricity[1-4]. Metal-free organic DSCs have received more and more attention for their variety, high molar extinction coefficients, simple preparation process, and low cost in comparison to Ru complexes [5].

Small molecule configured as donor–(p-bridge)–acceptor (D–p–A) with judicious selection of donor, acceptor, and p-bridge subunits are considered as a simple and effective molecular architecture to meet to a high photovoltaic performance [6]. Electron transfer from the donor to acceptor happens rapidly upon photo-excitation to generate a charge-separated species, and then the negative charge located on the acceptor is injected into the semiconductor.

In many dyes designed and synthesised by chemists, the amine derivatives act as the electron donor while a 2-cyanoacrylic acid or dicyano vinyl moiety acts as the electron acceptor [7-8]. These groups are connected by p-conjugated bridges such as the vinyl unit or thiophene chain. The p-conjugated bridge influences not only the region of light absorbed by the DSSCs but also the degree of electron injection from the dye's excited state to the TiO2

surface. Consequently, even a small change in the conjugated bridge of the dye can cause a significant change in the solar cell performance. Moreover, Shen et al [7] in previous reports have proved that p-conjugated bridge has a great influence on the molecular structure and photoelectronic properties of the metal-free organic dye. Changes in the electron-donating nature and structural variations of amine unit can result in a variety of electronic properties. The best of our knowledge, aromatic hydrazones and bis methoxy difenylamine compounds until now are few studied as photoactive dyes for DSSCs. Therefore, we became interested in designing metal-free organic dyes with hydrazine and bis methoxy difenylamine moiety to make use of their excellent hole-transport property for the electron donor. In here, we have investigated novel metal-free dyes consisting of an N, N-diphenylhydrazone, bis methoxy difenylamine as donors, a dicyanovinyl moiety as the electron acceptor, and different Pi-conjugated bridges (Figure 1).

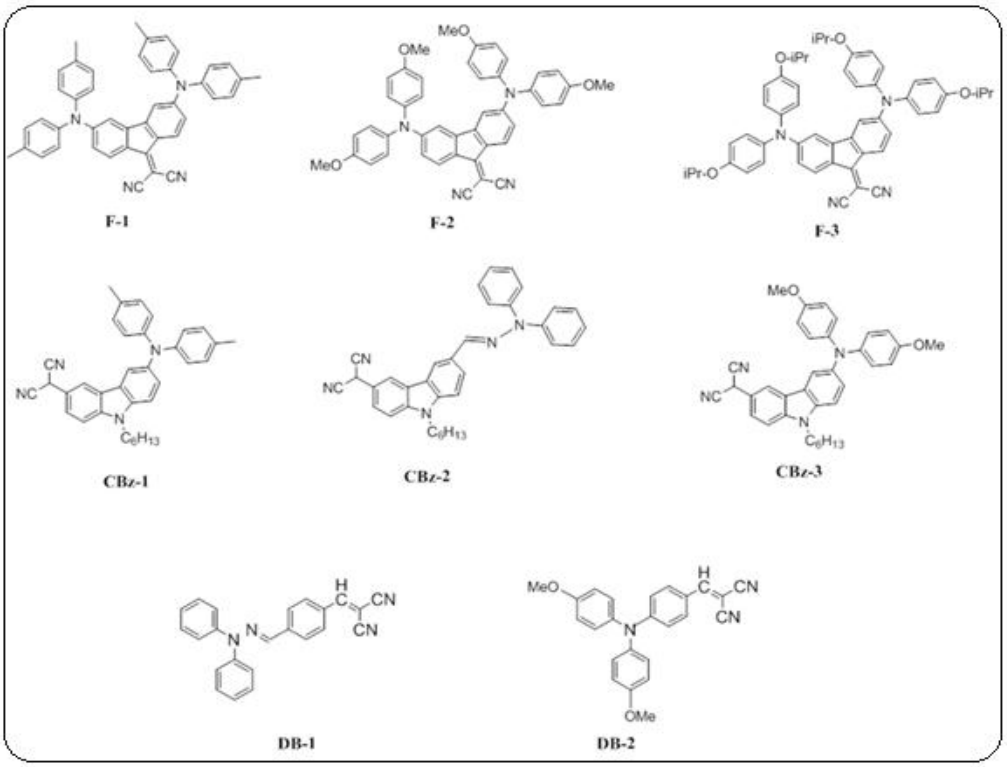

Fig. 1: Structures of D-π-A studied systems

EXPERIMENTAL SECTION

Molecular modelling methods

The Density Functional Theory (DFT) with Becke's Three-parameter Functional and the Lee-Yang-Parr Functional (B3LYP) [9] and 6-31G (d) basis set [10-12] was employed to investigate the geometry and electronic properties of the studied compounds. The calculations were performed with the Gaussian 03 program [13]. DFT-B3LYP/6-31G (d) has been found to be an accurate formalism for calculating the geometrical, electronic structures, absorption and emission properties of many organic molecules [14-17]. The energy of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels and gap energies and oscillator strengths (f) were also examined for the stable structures. The fully DFT optimised structure of the ground state were utilised to calculate the excited state energies using TD-DFT [18].

RESULTS AND DISCUSSION

The optimised structures of all studied compounds are shown in figure 2. All the molecular geometries have been calculated with the hybrid B3LYP function combined with 6-31G (d) basis sets using Gaussian 09 program.

From the optimised geometry of all studied structures, the absorption wavelength,

Excitation energies and oscillator strengths have been calculated using the time-dependent density functional theory (TD-DFT) method at the same level. Table 1 shows the values of the main calculated absorption wavelength λ_{abs}, lowest excitation energies, and oscillator strengths (f). The results illustrated in table 1 show that the structure of the derivative of fluorene F-2 is the compound that needs the lowest excitation energy. It is worth to note that the methoxy and isopropyloxy groups in F-2, F-3 and CBz-3 influence effectively on the decrease of excitation energy since we have seen that F-1, CBz-3 which have a methyl group show an excitation energy more than F-2, F-3 and CBz-1 respectively. We have also observed that the substitution of diphenylamine in CBz-1 by diphenylhydrazine in CBz-2 decreases the requested excitation energy. The same observation has been noted in the case of DB-1 and DB-2. In the other hand, as shown the table 1, the structures which have the maximum wavelength situated in the near-IR are F-2, F-3, F-1 respectively. Indeed the dye should have a broad absorption spectrum, and maximum wavelength situated preferably in the near-IR for better harvesting incident photons. Therefore, considering the excitation energies for all studied compounds, we have observed here that the fluorene derivative F-2 is the good candidate for DSSCs applications.

Table1: Absorption wavelength λabs (nm), Excitation energies and oscillator strengths obtained by the TDDFT/B3LYP/6-31G(d) method.

Molecule	Absorption λ_{max} (nm)	E_{ex} (ev)	f
F-1	604.39	2.05	0.23
F-2	620.79	1.99	0.25
F-3	619,66	2	0.25
CBz-1	369.68	3.35	0.53
CBz-2	381.63	3.24	1.03
CBz-3	387	3.20	0.52
DB-1	478.33	2.59	0.68
DB-2	439.17	2.82	0.73

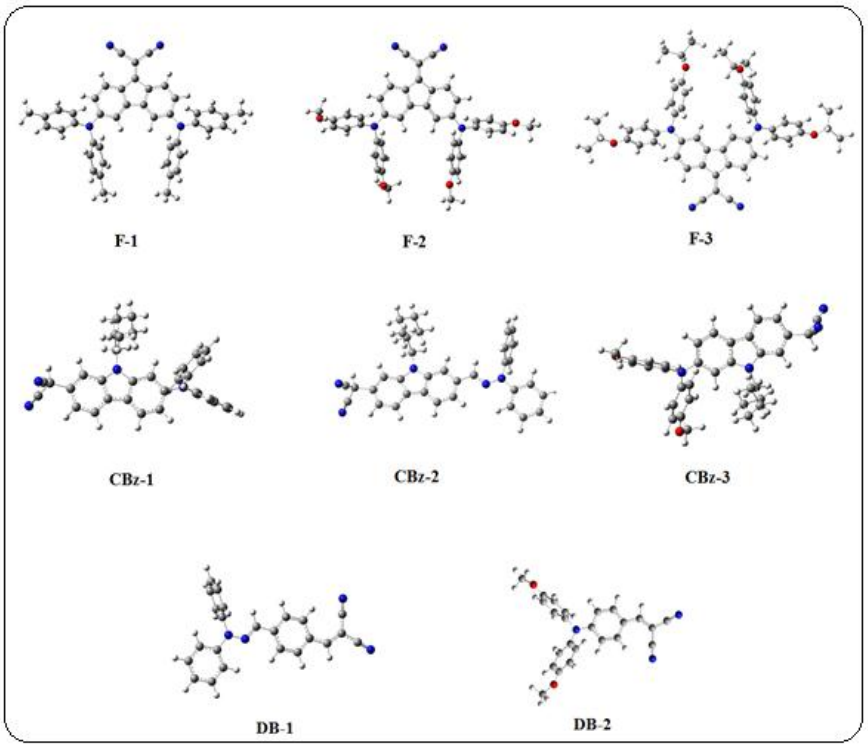

Fig.2: Geometry optimised structures using the B3LYP functional and the 6-31G(d)

The theoretical knowledge of the HOMO and LUMO energy levels of the studied structures give us more details regarding energy gap which enable us to save time and money in choosing the adequate organic materials to optimise photovoltaic devices properties. Therefore, the HOMO and LUMO energies level have been calculated by B3LYP/6-31G (d) level and the values of frontier orbital energy gaps between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are listed in Table 2.

Table 2: Values of HOMO (eV), LUMO (eV) and E_g (eV) energy calculated by B3LYP/6-31G (d) level.

Molecule	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)
F-1	-5.13	-2.61	2.51
F-2	-4.92	-2.47	2.45
F-3	-4.84	-2.39	2.45
CBz-1	-5.06	-1.28	3.78
CBz-2	-5.08	-1.52	3.56

Examining the energy gap of studied compounds, we observe that the energy gap of F-2 is much smaller than that of the other compounds. Molecule F-1 with this lowest energy gap is expected to have most outstanding photophysical properties. It has been observed also that the group methoxy in F-2 decreases the energy gap compared with F-1. The group isopropyloxy in F-3 does not make a difference in energy gap compared with F-2. Therefore, F-2 seems more useful for application namely in organic synthesis laboratories. In figure 3, we show the calculated electronic energies of frontier orbitals and corresponding surface isodensity plots for all dyes; the E_{LUMO} values were located above the conduction band edge (E_{cb}) of TiO2 (-4.0 eV versus vacuum). The E_{HOMO} values were below the energy of the redox species of iodide/ triiodide (-4.8 eV versus vacuum) [19]. Consequently, HOMO-LUMO excitation moved the electron distribution from the donor side (diarylamine or diphenylhydrazine) to the acceptor side (the cyano acrylic acid group), ensuring efficient charge separation by photo-excitation of dye. Furthermore, it was proved that these relative matchings of electronic levels of sensitizers would lead to energetically favourable electron injection as well as regeneration of oxidised dye during DSSC operation.

The Voc (open circuit voltage) of all studied systems have been calculated theoretically according to the equation:

$V_{oc} = E_{LUMO} - E_{CB}$

In fact, to effectively inject the electron into the CB of TiO2, The LUMO levels in the eneretic diagram of the dyes must be positioned above the CB energy (E_{cb}) of the semiconductor, by at least 0.2 eV [20]. As is illustrated in table 3, the obtained values of Voc all systems are positive which permit us to conclude that all studied dyes efficient for DSCCs applications.

Table 3: Values of V_{oc} of all studied systems

Molecule	F-1	F-2	F-3	CBz-1	CBz-3	CBz-3	DB-1	DB-2
V_{oc} (eV)	1.39	1.53	1.61	2.72	2.48	2.86	1.2	1.69

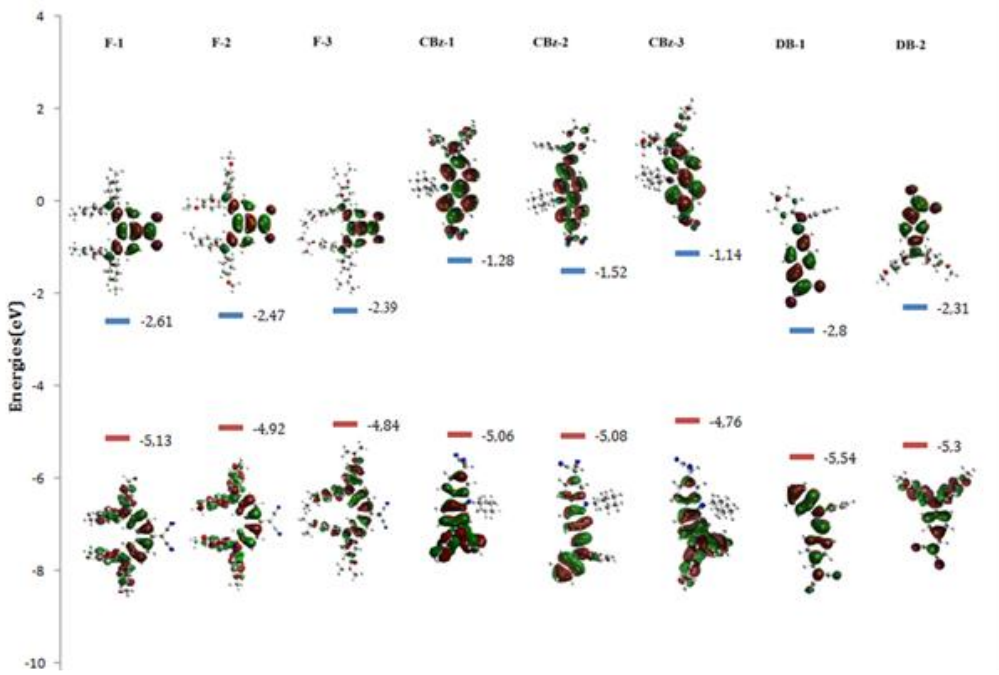

Fig. 3: Density function theory calculated HOMO and LUMO orbitals for all studied molecules with band gaps. DFT calculations were performed at a B3LYP/6-31G (d) level for the geometry optimisation.

CONCLUSION

In this study, different small D-π-A dyes based on Fluorene, Carbazole and phenyl were designed, and their geometries and electronic proprieties were studied by the quantum chemical method using the density functional theory. The results of optimised structures have demonstrated the influence of p- conjugated bridge on the photoelectronic proprieties of the dyes. We have also shown the impact of electron donating and withdrawing group on the performance of the D-π-A systems.

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CONFLICT OF INTEREST STATEMENT

The authors declare that they have no conflict of interests.

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