

Theoretical Studies Of Photovoltaic Properties For Design Of New Azo-Pyrrole Photo-Sensitizer Materials As Dyes In Solar Cells

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Abstract

Since the pyrrole derivatives are actively studied in connection with several application areas in optic and electronic, we aim to investigate new Azo-Pyrrole as useful photovoltaic sensitizer materials. Thus, DFT study was reported upon three compounds (APS, APC1, APC2). We present materials with low gap ($E_g < 2\text{eV}$), exhibiting open circuit voltage (V_{oc}) in the range 0.75–0.85 eV, with favorable absorption properties: Light Harvesting Efficiency ($LHE > 0.75$) and maximal absorption λ_{max} from 410 nm to 480 nm. In fact, this method constitutes a good approximation to characterize the dye molecules and gives helpful findings for the design of new dyes.

1. Introduction

Recent developments pointed out that organic semi-conducting materials can be used in several technological applications, due to some unique properties especially the potential of combining the domain of electronics with the benefits of the organic industry advances. Among the photovoltaic applications of these materials are there uses in renewable energy production. The Dye Sensitized Solar Cells (DSSC) constitute third generation solar cells for clean energy and low cost fabrication, with promising for lightweight and flexible cells since they can be made of different substrates such as plastics, ceramics and glass. The concept of photoelectrochemistry observed at green plants in nature, have been extended by Grätzel [1-2], through adsorption of dye molecules on the nanocrystalline TiO_2 electrodes, that leads the conceiving of the dye sensitized solar cells (DSSC). The quality of these cells is closely linked to the choice of the dye, the oxidant or the solvent. The best solar-to-electric power conversion efficiency has been achieved, 11.5% [3] with functioning lifetime of 20 years. In this context, much effort has been made in advancing the scientific knowledge, of processes occurring on dye molecules [4-6]. The π -conjugative molecules composed of such as: coumarin, indoline, thiophene, squaraine, phthalocyanine, triphenylamine and perylene derivatives have been developed as puissant sensitizers for DSSC [7-17].

In this paper, theoretical study by using Density Functional Theory (DFT), on three conjugated compounds based on 2-styryl-5-phenylazo-pyrrole is reported (Figure 1). The azo-photosensitizers show good candidates as dyes in DSSC, they exhibit high molar extinction coefficients. In fact, the high extinction coefficient is suitable parameter for the thin TiO_2 films required in solid state devices since the photovoltaic performance is constrained by mass transport and insufficient pore filling. Additionally, these compounds (APS, APC1 and APC2) have been successfully synthesized by Microyannidis et al [18].

The DSSC are characteristically composed of a semi-conductor with large band gap, the TiO_2 is mostly used sensitized with molecular dyes. The nanoporous TiO_2 not only acts as support for dye sensitizer but also function as electron acceptor and electronic conductor. Also, sustained conversion of light energy is facilitated by regeneration of the reduced dye sensitizer either via a reversible redox couple (Ox/Red), the Iodide/Triiodide couple (I^-/I_3^-) constitutes the typical regenerator electrolyte in DSSCs [19]. The electrolyte function is transferring the positive charge to the counter electrode before returning to the reduced form. The efficiency of

the DSSC is related to a large number of parameters such as light harvesting efficiency (LHE), short circuit photocurrent (J_{sc}), open circuit photovoltage (V_{oc}) [20-21]. To this end, we have performed the electronic structure calculations of the studied azo-dyes in the framework of time dependent DFT (TD-DFT). This investigation has been achieved with the aim of steering next syntheses towards compounds more useful as active photovoltaic sensitizer materials.

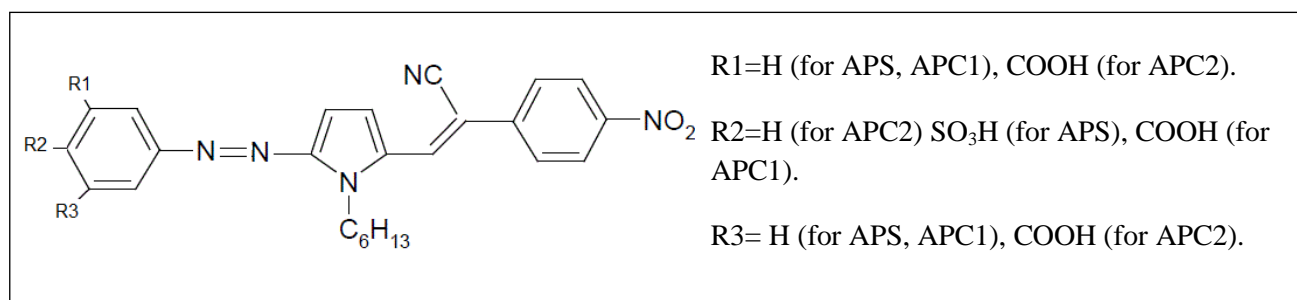


Figure 1: Studied azo dyes APS, APC1 and APC2.

2. Method and computations:

To evidence comparatively the effect of the structure of the compounds on the optoelectronic properties, we have carry out theoretical investigation on the structure of three Azo-Pyrrole dyes based on 2-styryl-5-phenylazo-pyrrole substituted of: Sulfonic acid (APS), Carboxylic acid (APC1), and Carboxylic diacid (APC2). The synthesis of the dyes was discussed by Microyannidis et al [18]. Three-parameters compound DFT method of Becke (B3LYP) was used in this study. So, the calculations were carried out using the GAUSSIAN program. Time dependent DFT (TD-DFT) calculations have been performed, in order to obtain detailed informations about the excited states [22], also to find the most interesting absorption properties [23-24]. It is well known that the judicious choice of functional is crucial to describe accurately the absorption of organic dyes. In other works [25-26], the Coulomb-attenuating method (CAM-B3LYP) has been used to describe the intramolecular charge-transfer states of organic dyes, it provides reliable results with discrepancy of 0.09 eV [27], but also it is more time-consuming as price of the limitation of this computational procedure. Hence, we adopted the B3LYP functional under 6-31(G,d) level in the following for investigating optical and photovoltaic properties. It is proved in previous studies that B3LYP functional gives results in good agreement with experimental values ($R^2=0.98$) [28-29].

3. Results and discussion:

3.1 Geometric structures:

It is generally appreciated that the morphology of conductive polymers plays a fundamental role in defining the characteristics of the material. in this context, the dihedral angles have been theoretically calculated in order to investigate the effect of the substituent on the geometries and electronic properties, the optimized structures of several studied compound were compared (Figure 2).

An accurate representation of the bond rotations in the chain is extremely important, since the properties of compounds depend strongly on the conformational statistics of chains. In Table 1, we list the theoretical calculated inter-ring torsion angles, between the hexyl-pyrrole and the other units. For the side of cyanovinylene 4-nitrophenyl, the angles are evaluated to be about ($\theta_2 \approx 180^\circ$) leading to quasi planar conformation. Whereas, due to the substituent effect on phenyl-azo side, the dihedral is changed with a slight decrease going from APC2, APC1 to APS. We note that APC2 almost has the perfect co-planarity ($\theta_1 \approx \theta_2 \approx 180^\circ$) which is an interesting structural characteristic to be taken into account in the interpretation of properties. This feature can significantly influence the electronic structure of the compounds by allowing the extension of the π -conjugation.

3.2 The optoelectronic properties:

The onset potentials of the oxidation and reduction, given by the cyclic voltammogram, can be used to determine the experiment LUMO and HOMO energy levels [30-31], and the potential difference HOMO-LUMO can be used to estimate the energy Gap. The LUMO and HOMO energy levels in (eV) corresponding to the electrochemical potentials versus Saturated Calomel Electrode (vs. SCE) are obtained by adding 4.4 V to the potentials [32]. Theoretically, we found HOMO and LUMO levels using DFT calculation upon optimized structures of these dyes, the calculated gap energies are also reported on Table 2 in the neutral and doped state.

Traditionally and until now, charged state in conjugated molecules has been discussed in terms of one-electron band model.

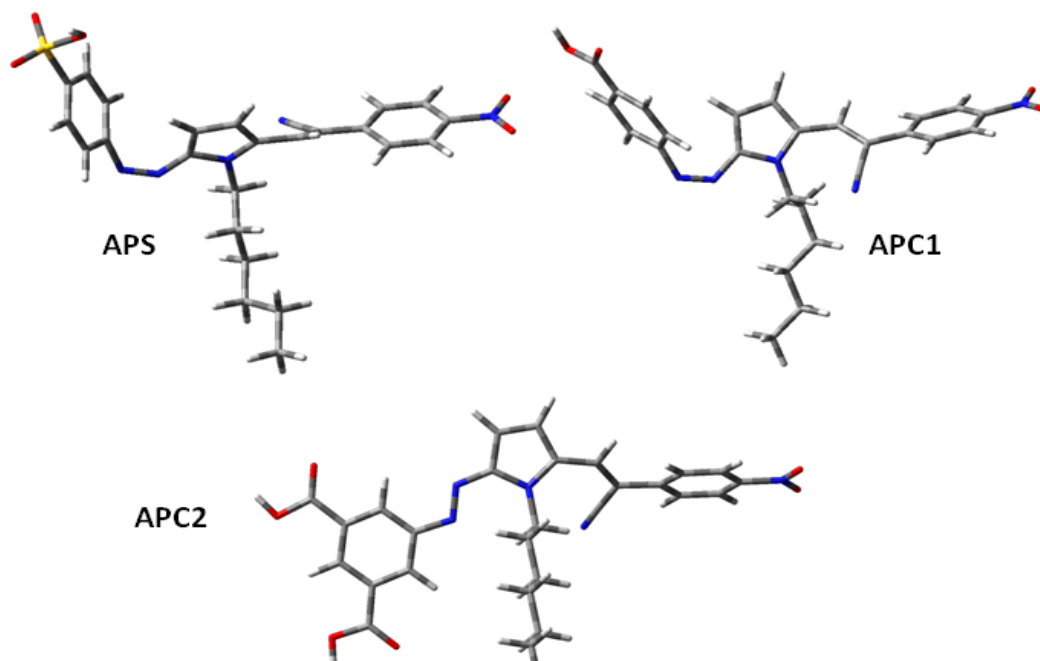


Figure 2: Optimized Structures for studied compounds obtained with B3LYP functional and (6-31 (G,d)) basis set.

Table 1: Inter-ring dihedral θ_i ($^\circ$) of studied compounds obtained by B3LYP/6-31G(d) calculations.

Angles ($^\circ$)	APS	APC1	APC2
θ_1	7.81	9.86	178.38
θ_2	179.61	178.54	179.78

The Sulfonic acid (SO_3H) does not raise the HOMO energy of the corresponding dye (APS). However, the HOMO level of APC2 (-6.032 eV) is higher than the others dyes. Thus, the diacid groups ($-\text{COOH}$) for APC2 is effective for raising the HOMO energy levels of the corresponding dye. This result suggests the acid units stabilize the quinoid forms. The present obtained Gap values show clearly that all dyes have a small gap without significant changes ($E_G \approx 1.5$ eV), we note also that doping is one reliable process for reducing the band Gap.

The favourable electronic and optical properties play an important role for the gain of higher solar-to-electricity conversion efficiency. To catch the electron from a redox electrolyte, the HOMO level of the dye should be sufficiently positive compared to the (I^-/I_3^-) redox couple potential ($E = -4.8\text{eV}$) permitting efficient dye regeneration. Additionally, the LUMO level of the dye should be sufficiently greater than the potential of the conduction band edge of the TiO_2 . Since the redox process is fast, the electrons of semi-conductor are hindered to return into the dye (in the S^+ state) which is slower than the previous phenomena. However, by broadening the absorption spectra the difference in the potentials of the HOMO and the LUMO energy levels is decreased, so the light absorption in the visible region should be efficient [34-38]. The 1-Hexylpyrrole is the central unit of the studied dyes which is connected with cyanovinylene 4-nitrophenyl at one side and with substituted phenyl at the other side of the pyrrole ring. Both these terminal moieties extended the absorption band of the dyes into the near infrared region, which is a desirable feature for PV applications [39]. The optical absorption parameters cited in Table 3 of APS, APC1 and APC2 show respectively a maximum peak at 412 nm (3.0 eV), 417 nm (2.96 eV), and 468 nm (2.65 eV). Basically, these peaks correspond to the $\pi-\pi^*$ interband transition. Moreover, the energy corresponding to the $\pi-\pi^*$ transition is depending on the delocalization of the π -electrons system.

Table 2: Energy values (eV) of the MOs, the Band Gap Width E_G , and Oxidation potential E_{ox} , calculated for the optimized structure of studied compounds.

	Neutral State			Doped State
	HOMO	LUMO	E_G	E_G
APS	-6.265	-3.247	3.02	1,48
APC1	-6,034	-3,152	2,89	1.50
APC2	-6,032	-3,204	2,83	1.67

Table 3: Calculated absorption parameters of the studied compounds obtained by B3LYP (6-31/G(d)) level.

Properties	Main Configuration	λ_{max} (nm)	Activation energy (eV)	O.S
APS	Homo-1 \rightarrow Lumo (0.45)	412.15	3.00	0.7833
APC1	Homo -1 \rightarrow Lumo (0.41)	417.80	2.96	0.6253
APC2	Homo \rightarrow Lumo (0.70)	468.38	2.65	1.2428

This delocalization is determined by the effective conjugation length, which depends on the amount of structural and conformational defects in the molecular backbone and the interaction between backbones. The strongest absorption peaks arise from $S_0 \rightarrow S_1$, as shown in Table 3, which correspond to the dominant promotion of an electron from HOMO to LUMO with minor promotion from HOMO-1 to LUMO. Also, the modification of the Oscillation Strength (O.S) values is observed when comparing the dyes, the higher value is corresponding to APC2 (O.S=1.24).

We present the calculated absorption spectra of the studied compounds in Figure 3 below. The spectra appear to be significantly influenced by the substitution at the phenyl ring. The positions of the absorption bands are approximately the same for APS and APC1. Due to the co-planarity of APC2, as proven by DFT calculations, the second introduction of the carboxylic acid group in compound APC1 extends the conjugation of the π -electrons from the pyrrolic rings to the benzene ring as well (compare APC1 with APC2). Thus, a bathochromic shift of $\Delta\lambda_{max}=50$ nm for the low-energy band of $S_0 \rightarrow S_1$ transition is observed.

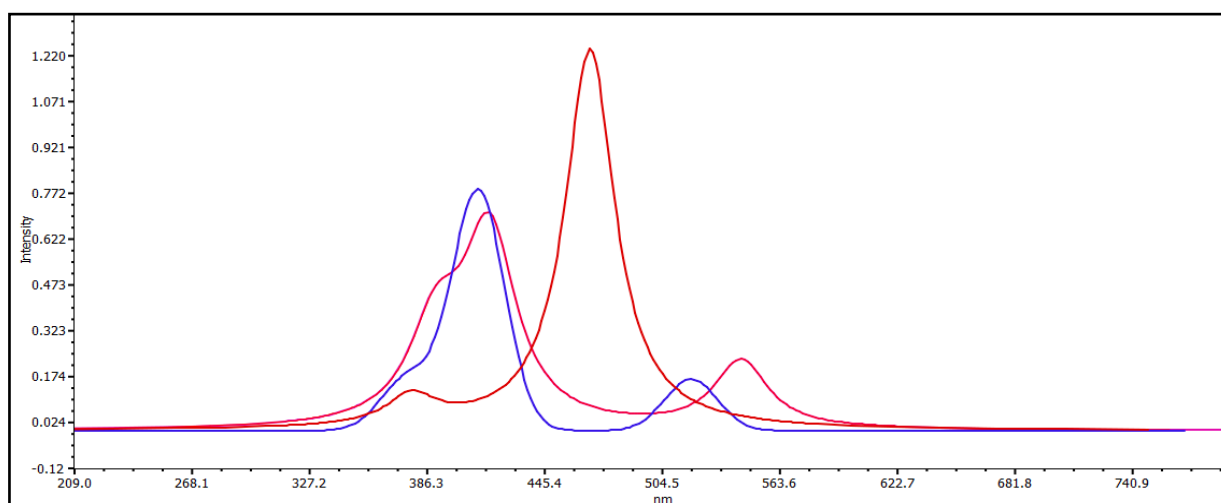


Figure3: Absorption spectra for studied compounds using TD-DFT/B3LYP calculations.

3.3 Photovoltaic properties:

In order to report a theoretical study on photovoltaic properties on a series of dye molecules, we aim to see the photosensitizer effects on the open circuit photovoltage (V_{oc}) and the short-circuit current density (J_{sc}) of the cell through discussing the key factors affecting them when the relationship among these values and electronic structures for the dyes is still unknown. The V_{oc} and J_{sc} values present experiment values deduced from the (J–

V) characteristics of the DSSC under illumination intensity of 100mW/cm². Basically, the power conversion efficiency η of the cell is expressed using the Fill Factor (FF) and the Incident Solar Power P_{inc} [40]:

$$\eta = FF \frac{V_{oc} J_{sc}}{P_{inc}} \quad ; P_{inc} \text{ is the incident power} \quad \text{Eq. 1}$$

The short-circuit current density in DSSCs, it is determined as:

$$J_{sc} = \int_{\lambda} LHE(\lambda) \Phi_{inj} \eta_{collect} d\lambda \quad \text{Eq. 2}$$

Where LHE is the light harvesting efficiency corresponding to the oscillator strength (*OS*) at a given wavelength, Φ_{inj} is the electron injection efficiency, and $\eta_{collect}$ is the charge collection efficiency. The greater LHE is related to the larger (*OS*) due to the relationship:

$$LHE = 1 - 10^{-OS} \quad \text{Eq. 3}$$

For the electron injection efficiency Φ_{inj} , it is closely associated to the driving force ΔG_{inj} of the electron injection from the photoexcited states of dyes to semiconductor surface [41-42], which is generally expressed as:

$$\Delta G_{inj} = E^{dye^*} - E_{CB} \quad \text{Eq. 4}$$

It is generally accepted that E^{dye^*} value can be evaluated by the difference between redox potential of the ground state of the dye and the vertical transition energy. Also, E_{CB} is the conduction band edge of TiO₂ ($E_{CB} = -4.0$ eV vs. Vacuum) [43].

Additionally, as mentioned in Eq. (1), beside J_{sc} the open circuit photovoltage V_{oc} could enhance the light-to-electricity efficiency [44]. Its expression represents the difference between the LUMO energy of the dyes and the conduction band (ECB) of the semi-conductor TiO₂:

$$V_{oc} = E_{LUMO} - E_{CB}(TiO_2) \quad \text{Eq. 5}$$

The Time Dependant DFT calculations have been performed in order to predict the excitation energies of the studied dyes. In Table 4, we list the theoretical photovoltaic properties of all dyes with the experiment values [18] of the open circuit voltage (V_{oc}) and the short-circuit photocurrent density (J_{sc}). It was found that V_{oc} values of all dyes are in the range 0.80 V, the results show also that studied compounds have good LHE (LHE > 0.76) in the increasing order APS, APC1 and APC2.

For deducing the driving force ΔG_{inj} of the electron injection from the photoinduced states of dyes to TiO₂ surface, E^{dye^*} was determined at (UB3LYP/6-31G(d)) level with the geometry of optimized organic dyes. This method is used specially for modeling the doped states, the compounds are treated as radical cations radical cations as open shell systems [45]. If the electron injection efficiency Φ_{inj} is closely related to the driving force ΔG_{inj} , both larger LHE with ΔG_{inj} could also improve short-circuit photocurrent density J_{sc} (Eq.2), that is observed in the case of APS. Thus, the greater J_{sc} of the dye APS measured in experiment was in part due to its higher driving force of the electron injection ($-\Delta G_{inj} = 4.6$ eV vs. Vacuum) with the LHE (LHE=0.83) as listed in Table 4. In summary, the former data reveals that the studied compounds can assure a beneficial effect on the process of photogeneration.

Table 4: The calculated photovoltaic parameters of the studied compounds. The $V_{oc/exp}$ and $J_{sc/exp}$ values are obtained from experiments reported elsewhere [18].

Properties	E^{dye^*}	ΔG_{inj}	LHE	V_{oc}	$V_{oc/exp}$	$J_{sc/exp}$
APS	-0.86	-4.9	0.835	0,753	0,69	10.8
APC1	-0.83	-4.8	0.763	0.848	0.61	8.5
APC2	-1.02	-5.0	0.943	0.796	0.63	9.6

Conclusion

In this work, we were carried out Ab-initio study using DFT and TD-DFT calculations of three Azo-Pyrrole dyes (APS, APC1 and APC2) so as to discuss the structural, electronic and absorption properties in order to

assess their performance especially in DSSC application. Firstly, the DFT optimization with the hybrid functional B3LYP, offered a description of molecular geometries with the different M.O energy levels. Among the studied dyes; APC2 presents the most co-planarity due to its dihedral angle which is about 180°. The band gap energy is about (1.5-1.6 eV) so it depends little on the type of Phenyl substituent. The dyes has also absorption in the visible part of the spectrum (λ_{\max} =412-468 nm). The analysis of the obtained results exhibits that these materials possess desired properties such as the low gap, favorable absorption, with high LHE and practical V_{oc} and J_{sc} .

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