



DFT and TD-DFT studies of the π -bridge influence on the photovoltaic properties of dyes based on thieno[2,3-b]indole

M. Hachi^{1*}, S. El Khattabi^{1,2*}, A. Fitri¹, A.T. Benjelloun^{1*}, M. Benzakour¹, M. Mcharfi¹,
M. Hamidi³, M. Bouachrine⁴

¹Laboratory of Materials Engineering, Modeling and Environment, Faculty of Sciences Dhar El Mahraz, University Sidi Mohamed Ben Abdallah, Fez, Morocco.

²Laboratory of Engineering, Systems and Applications, National School of Applied Sciences, University Sidi Mohamed Ben Abdallah, Fez, Morocco.

³Electrochemistry and Environment Team, Faculty of Science and Technology, Errachidia, University Moulay Ismail, Meknes, Morocco.

⁴LASMAR, Superior School of Technology, University Moulay Ismail, Meknes, Morocco.

Received 09 Jun 2017,
Revised 04 Nov 2017,
Accepted 14 Nov 2017

Keywords

- ✓ Thieno[2,3-b]indole
- ✓ Organic dyes;
- ✓ DSSC;
- ✓ DFT & TD-DFT;
- ✓ Optoelectronic properties;
- ✓ Photovoltaic properties.

hachimohamed1990@gmail.com
souad.elkhattabi@usmba.ac.ma
Phone: +212663086032
toumiba@gmail.com

Abstract

In this paper, a theoretical study has been conducted using the Density Functional Theory (DFT) and Time-Dependent Density Functional Theory (TD-DFT) methods on a series of ten organic donor- π -acceptor dyes, their π -conjugated bridge is based on the thiophene and benzene, the thieno[2,3-b]indole was used as an electron donor and the acid 2-cyanoacrylic was used as an electron acceptor group. The properties of all dyes, including frontier molecular orbitals (HOMO and LUMO), gap energy ($E_{\text{HOMO}} - E_{\text{LUMO}}$), intramolecular charge transfer, absorption and emission spectra and open-circuit voltage (V_{oc}) are investigated theoretically to confirm which dyes can produce great performance for dye-sensitized solar cell. The results of these investigations indicate how the electronic, optical and photovoltaic properties can greatly improve by increasing of the number of the thiophene and benzene on the bridge of dyes, leading us to suggest them as a good candidates for dye-sensitized solar cell.

1. Introduction

The development of energy use lately has brought the scientists to investigate other sources of renewable energies such as the conversion of solar energy to electric energy via solar cells. Among the latter, dye-sensitized solar cells (DSSCs), the most popular ones, are based on the conjugated molecules able to absorb two or more photons that go easily to their excited states. These conjugated organic molecules have been the subject of much research due to the growing interest in advanced photonic applications, low-cost concerns, and use of flexible and lightweight materials such as batteries [1], ElectroLuminescent (EL) devices [2], Organic Field-Effect Transistors (OFETs) [3] and photovoltaics [4]. The Dye-Sensitized Solar Cells (DSSCs) are anchored on TiO_2 semiconductor deposited on transparent conducting oxide glass such as Fluorine doped Tin Oxide (FTO), counter electrode of platinum and redox electrolyte. To date, DSSCs with the highest photo-electric conversion efficiency has achieved of 12.3% under AM 1.5 irradiation [5-6]. Generally, the configuration of organic dyes is push-pull, which is based on a dipolar, electron-donor, π -bridge spacer and electron-acceptor, with the acceptor ligand anchored on the semiconductor surface. The structure of (D- π -A) system can induce the Intra-molecular Charge Transfer (ICT) from the donor to the acceptor unit across the bridge, and then stimulate the excited electrons of the dye to inject into the conduction band of the semiconductor and eventually regenerate the excited dyes to the ground state by the redox couple. Recently, a new organic compound 3-(5-(8-butyl-8H-thieno[2,3-b]indole-2-yl) thiophen-2-yl)-2-cyanoacrylic acid have been successfully synthesized by R.A. Irgashev et al [7], in which the central thiophene is attached through conjugation of two groups, thieno[2,3-b]indole as donor and cyanoacrylic acid as acceptor, forming D- π -A (M1 compound). According to the values of the Power

Conversion Efficiency (PCE) = 0.79%[7] the uses of indole as donor moiety in this compound have not a remarkable effect on the conversion efficiency. It is well known, that the variation of the bridge has much high influence on the overall conversion efficiency [8], which would also affect the absorption properties and the degree of electron injection from the excited compounds to the conduction band of TiO_2 [9]. On the other hand, the thiophene moiety has been proved to be a good π -conjugated spacer because it serves to increase the intramolecular charge transfer efficiency and also serves to enhance the intensity of absorption [10-11].

In this study, we have designed from the M1 molecule (Figure1) nine compounds by increasing the number of thiophene (up to four thiophene) and switching position between thiophene and benzene. The theoretical analysis on the geometries and electronic properties of these new conjugated compounds, as shown in Figure 1, is reported and were investigated by the DFT method at B3LYP level with 6-31G(d,p) basis set. The effects of the ring structure and the substituents on the geometries and electronic properties of these materials are discussed with the aim of revealing the relationship between molecular structure and optoelectronic properties. Theoretical knowledge of the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) energy levels of the components is fundamental in study of organic solar cells, therefore, the HOMO, LUMO, gap energy and Voc (open-circuit voltage) of the studied compounds are calculated and reported.

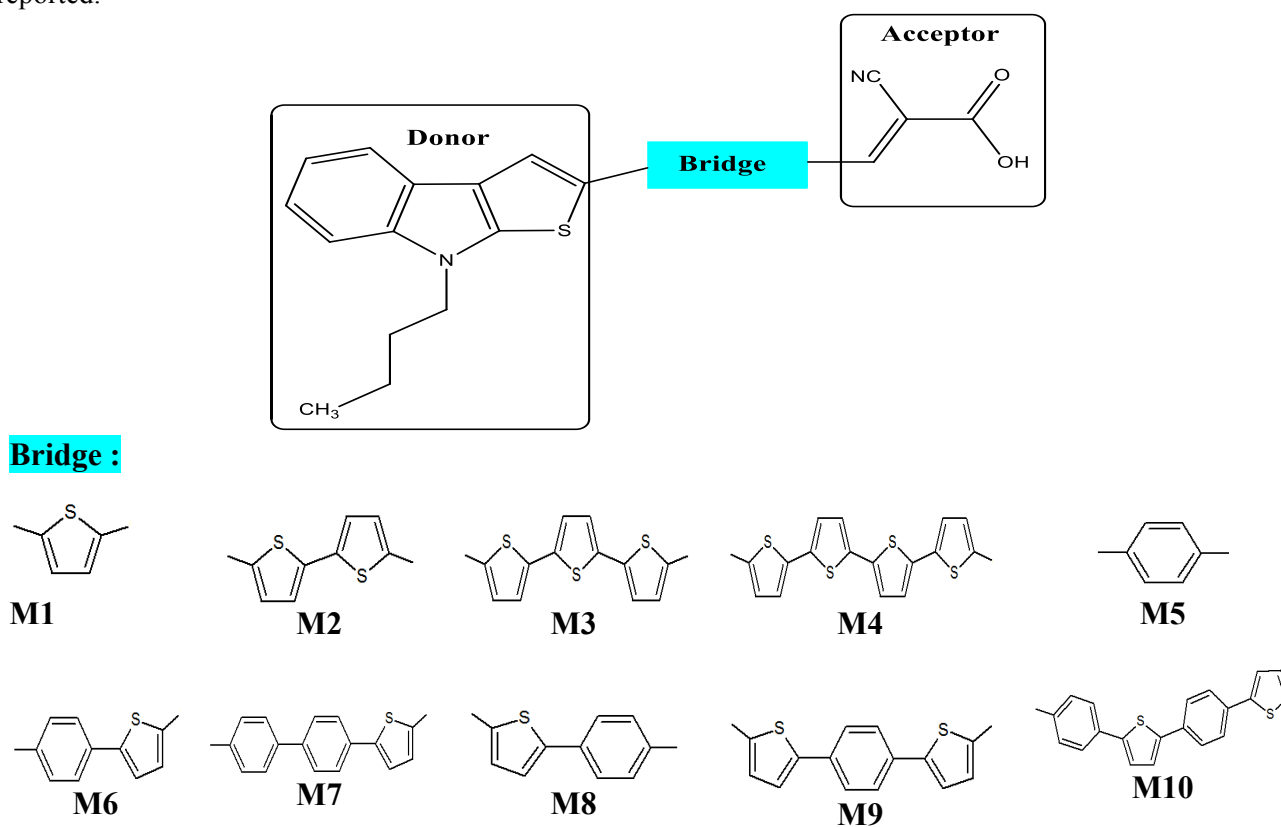


Figure 1: Sketches of studied compounds.

2. Computational details

All our molecular calculations were performed using the Gaussian09 software [12]. The ground state geometries of a series of D- π -A in their neutral states in gas phase are fully optimized with Density Functional Theory (DFT) method at the hybrid functional of exchange-correlation B3LYP (Becke three-parameter Lee–Yang–Parr)[13-15] and the basis set used for all atoms over all computations is the basis set of people with dual-polarized (6-31G(d,p) which have proved their effectiveness in the study of analogous systems [16-18]. At the same level of the theory the frequency calculations are performed to confirm the stationary nature of the optimized geometries at energy minimum. The optoelectronic properties of these D- π -A compounds are calculated by using Time-Dependent Density Functional Theory (TD-DFT) method. To check the reliability of the TD-DFT methodology, we use a variety of different functionals, including PBE0 [19-20], BHandHLYP[21], ω B97XD [22], M062X [23] and CAM-B3LYP [24] to evaluate the effect of different functional on the energies of the excited states. The 6-31G(d,p) basis sets were used for C, H, O, N, and S, in the TD-DFT calculations.

The inclusion of the solvent effect in theoretical calculations is important when seeking to reproduce or predict the experimental spectra with a reasonable accuracy. In this paper, the integral equation formalism polarizable continuum model (IEF-PCM) [25-26] was used to calculate the excitation energy. The oscillator strengths and excited state energies were investigated using TD-DFT calculations on the fully DFT optimized geometries.

3. Results and discussion

3.1. Functional effect

To verify whether the electronic properties of our compounds obtained by quantum computations (the HOMO level, the LUMO level and energy gap) are corresponding to our expectations, it was necessary to make the comparison between the electronic properties obtained theoretically and those obtained experimentally [7], in order to select a reasonable functional for DFT calculation. For that, we tested several functional on the reference compound M1.

Table 1: Energies of HOMO (E_{HOMO}), LUMO (E_{LUMO}) and the gap energy ($E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}}$) for M1 obtained by DFT with different functional level, compared with those obtained experimentally.

Functionals	$E_{\text{HOMO}}(\text{eV})$	$E_{\text{LUMO}}(\text{eV})$	$E_{\text{gap}}(\text{eV})/\text{RE}^*$
BHandHLYP	-6.114	-1.565	4.549/2.349
M062X	-6.373	-1.782	4.590/2.390
ω B97XD	-7.044	-0.931	6.113/3.913
PBE0	-5.494	-2.469	3.025/0.825
CAM-B3LYP	-6.422	-1.453	4.968/2.768
B3LYP	-5.252	-2.558	2.694/0.494
Exp.[7]	-5.600	-3.400	2.200

*RE: the relative error of the gap energy in (eV).

Based on the comparison of the values of HOMO level, LUMO level and gap (Table 1), we found that the gap energies of all functional are higher than the experimental ones except for B3LYP, where the gap energy is almost agrees with the one obtained experimentally with a reasonable margin of error ($\text{RE}=0.494$ eV). On the other hand, the gap obtained by the functional PBE0 in a recent study by Y. Wen et al.[27] for the M1 molecule is overestimated ($\text{RE}=0.880$ eV) than that we found by the B3LYP. This relative error calculated with PBE0 has the same order of magnitude as that obtained in this study ($\text{RE}=0.825$ eV). So, we can conclude that the functional B3LYP is undeniably appropriate to describe the electronic properties of the M1 compound. Thus, the function B3LYP will be used for the calculation of the electronic properties of the nine dyes designed.

3.2. Molecular design and geometric structures

All the molecular geometries have been obtained with the B3LYP/6-31G(d,p) of the studied compounds (M1 to M10) are plotted in Figure 2. The calculated vibrational spectrum in each molecule has no imaginary frequency, which means that the optimized geometry is located at the minimum point of the potential surface. The main optimized geometry parameters of the studied compounds in the ground state (S_0) are listed in Table 2. In the D- π -A molecules, the π -spacer is used as the bridge of intramolecular charge transfer (ICT), so, the bridge bonds between acceptor (A) and π -spacer, and donor (D) and π -spacer give an account of the interaction among themselves.

In order to indicate the molecular planarity clearly, two parameters were introduced: Φ_1 , Φ_2 . Here, Φ_1 is the torsional angle between D and π -spacer, Φ_2 is the torsional angle between A and π -spacer. Table 2 shows that Φ_2 is almost similar for all compounds (in the range 0.15 to 0.75°), while the values of Φ_1 vary between 12.08° and 19.27°, which indicates a tendency that is close to coplanarity for M1 as opposed to the other compounds, which is probably due to the steric effects of donor groups.

The bond length between the donor and acceptor groups is very important in the load transfer charge between the donor and acceptor group in the device solar cells, for the length bond fosters the intramolecular charge transfer when it is shorter. We report in table 2 the values of bond length(d_1, d_2) from all optimized compounds and show that these bonds are in the range of 1.418–1.461 Å showing especially more C=C character. These results show that the connection between donor moieties (D) and acceptor moieties (A) via π -bridge is crucial as it enhances the (ICT) character and makes the absorption spectra to red shift.

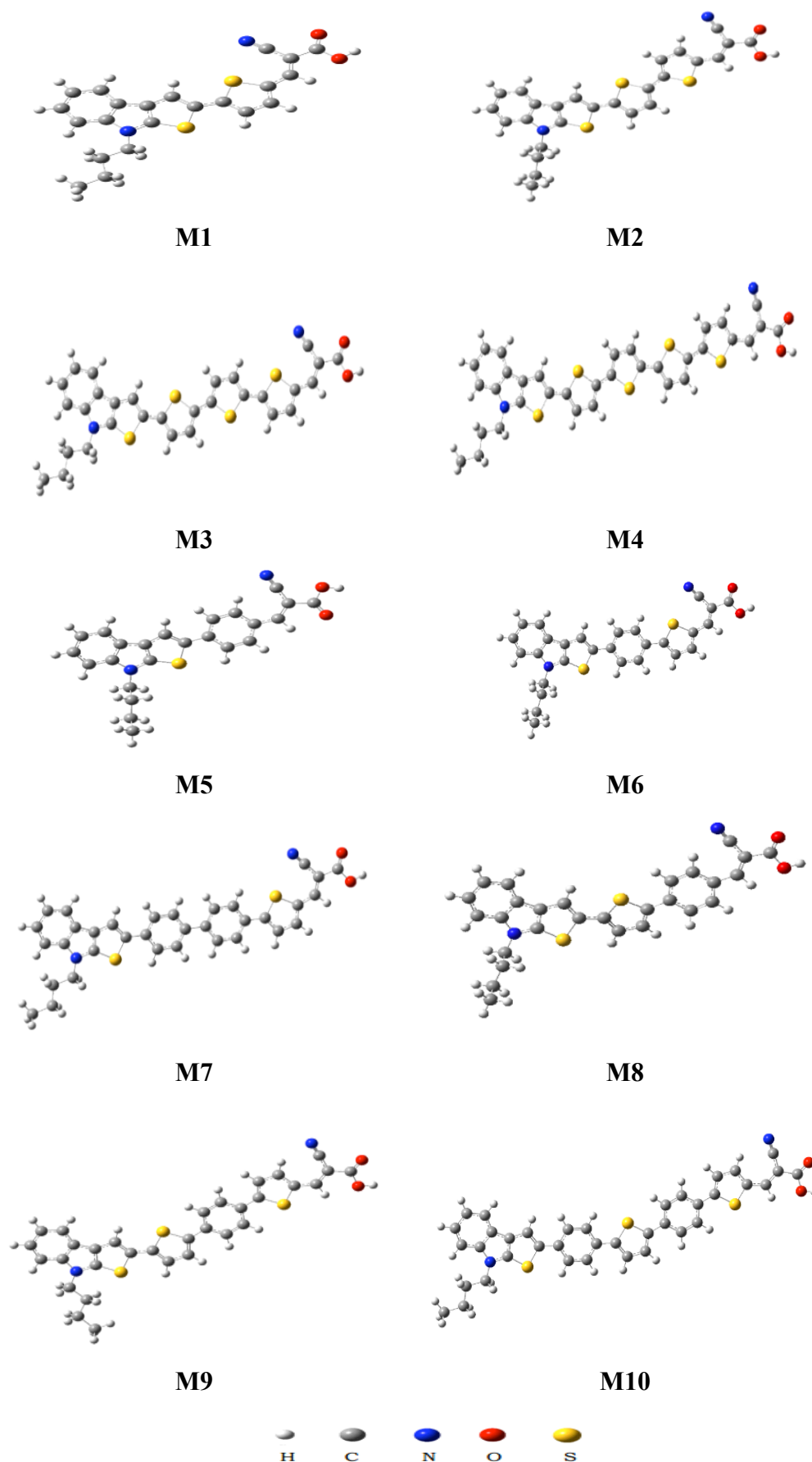
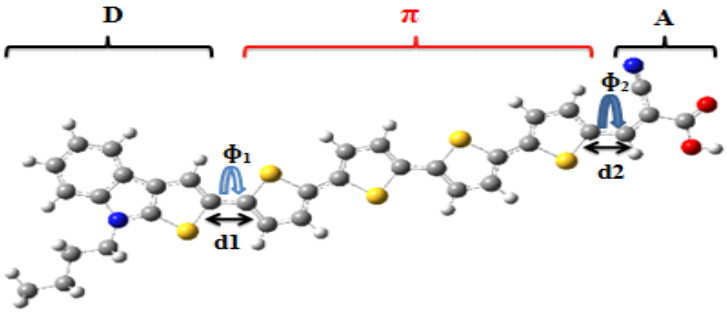


Figure 2: Optimized geometries of studied compounds at B3LYP/6-31G(d,p) level.

Table 2: Selected dihedral angle $\Phi(^{\circ})$ and distances d (Å) of studied compounds.


Compound	Φ_1	Φ_2	d1	d2
M1	2.44	0.15	1.435	1.418
M2	12.08	0.07	1.439	1.426
M3	14.20	0.11	1.440	1.424
M4	15.46	0.11	1.441	1.420
M5	13.74	0.02	1.453	1.444
M6	19.84	0.72	1.457	1.426
M7	23.36	0.75	1.461	1.426
M8	17.98	0.34	1.441	1.447
M9	18.26	0.69	1.442	1.426
M10	19.27	0.35	1.443	1.448

3.3. Frontier molecular orbitals and energy levels

The knowledge of the energy levels of Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) is crucial in the study of organic solar cells. Indeed, the energy levels HOMO and LUMO of the donor and acceptor for photovoltaic devices are very important factors that determine whether the charge transfer between the donor and acceptor is effective [28]. Table 3 shows detailed data of energy of the frontier orbital calculated by DFT for the studied molecules Mi (i=1 to10).

Table 3: Energy values of HOMO (E_{HOMO}), LUMO (E_{LUMO}) and gap (E_{gap}) of the studied compounds obtained by B3LYP/6-31G (d,p) level.

Compound	$E_{\text{HOMO}}(\text{eV})$	$E_{\text{LUMO}}(\text{eV})$	$E_{\text{gap}}(\text{eV})$
M1	-5.252	-2.558	2.694
M2	-5.116	-2.748	2.367
M3	-4.980	-2.803	2.177
M4	-4.871	-2.803	2.068
M5	-5.333	-2.503	2.830
M6	-5.197	-2.668	2.531
M7	-5.061	-2.667	2.395
M8	-5.116	-2.612	2.503
M9	-5.007	-2.721	2.286
M10	-4.925	-2.694	2.231
TiO ₂	-	-4.000	-

From the calculated parameters (E_{HOMO} , E_{LUMO} , E_{gap}), we note that the number and position of moieties that constitute the bridge (thiophene and benzene) have a remarkable effect on the gap energies of different compounds. Indeed, by increasing the number of thiophene, the energy gap that was in the range 2.694 to 2.068 eV decreases in the following order M1>M2>M3>M4. Moreover, the switching position between thiophene and benzene also leads to a decrease from 2.531 to 2.231 eV in the following order M6>M8>M7>M9>M10, but the introduction of one benzene moiety (M5) gave a higher value of gap energy (2.830 eV).

To make sure that the electron transfer is from the excited studied compounds to the conductive band of the acceptor TiO₂, the HOMO and LUMO levels were compared (Figure 3). It is important to note that the LUMO levels of the dyes are higher than that of the conduction band of TiO₂ (-4.0 eV, [29-32]). The HOMO energy levels of all compounds are much higher than that of TiO₂ conduction band edge, suggesting that the photoexcited electron transfer from Mi (i=1 to 10) compounds to TiO₂ may be sufficiently efficient to be useful in photovoltaic devices.

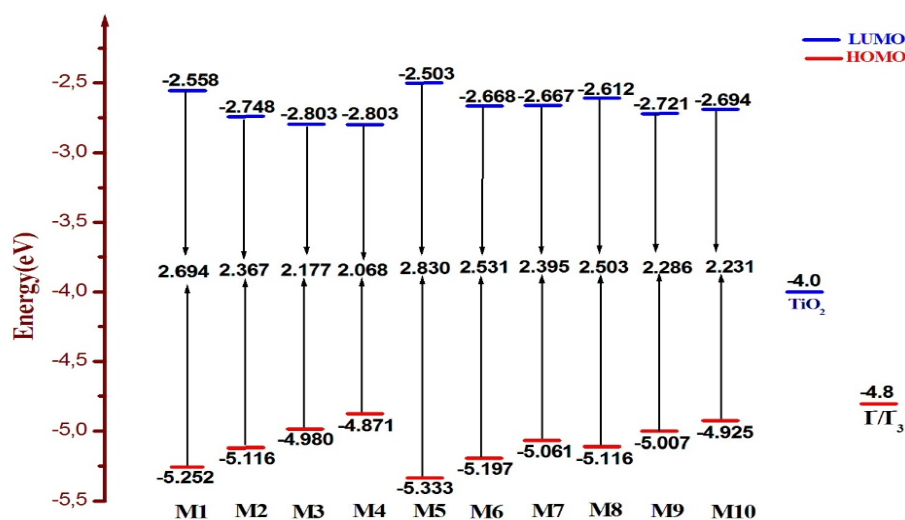


Figure 3: Schematic energy diagram of all compounds Mi (i=1-10), TiO₂ and electrolyte (I⁻/I₃⁻).

In Figure 4, we have plotted the contour plots of the HOMO and LUMO orbitals of all compounds in their optimized conformation obtained by B3LYP/6-31G(d,p) level. The Frontier Molecular Orbitals (FMOs) of all compounds have analogous distribution characteristics. All HOMOs show the typical aromatic features with electron delocalization for the whole conjugated molecule. The LUMOs are mainly concentrated on electron-deficient unit and the right of molecular chain. On the other hand, we notice that the HOMO orbital of all compounds presents a bonding character, whereas the LUMO orbital of all compounds presents an anti-bonding character.

3.4. Absorption spectra

The choice of the exchange-correlation functional is very important to describe precisely the excitation energy of the dyes, also to have more precise idea on the excited states which give rise to absorption spectra of the dyes under consideration. However, the choice of the hybrid function depends on the system. Here, five different exchange-correlation functionals, including three hybrid functionals (PBE0, M062X and BHandHLYP) and two long range corrected functionals (CAM-B3LYP and ω B97XD), were tested to study the functional influence on the vertical transition energy of M1.

The values of the vertical excitation energy and the absorption wavelength calculated by the functional hybrid PBE0 (which have 75% of PBE and 25% HF exchange) (Table 4) show that they agree with the experimental values and are better than those determined by M062X (54% HF Exchange) and BHandHLYP (50% of B88 and 50% of HF exchange). On the other hand, the long range corrected functionals CAM-B3LYP and the ω B97XD overestimates the vertical transition energy compared to the experiment. Thus, the PBE0 functional was employed to simulate the UV/Vis absorption spectra of the investigated dyes.

After choosing the adequate hybrid functional, we proceed to calculate the maximum wavelength of absorption spectrum (λ_{abs}), corresponding oscillator strength (OS) and the vertical excitation energy (ΔE). These calculations were simulated using TD-DFT with PBE0 functional and 6-31(d,p) basis set starting with the optimized geometry obtained using DFT/B3LYP/6-31(d,p) level. The obtained results are tabulated in table 5.

The simulated absorption spectra of the ten dyes in chloroform solution are displayed in Figure 5 and the corresponding data are presented in Table 5. All the dyes exhibit two transitions and cover a broad range (319-655 nm) of spectra. The results show that the successive introduction of the thiophene units between donor and acceptor units make the absorption peak more red shifted (M1: 505.17nm and M4: 655.52 nm). This bathochromic effect from M1 to M4 is obviously due to an increase of the π -delocalization.

On the other hand, the inverse effect is observed when substituting phenyl for thiophene (M1: 505.17nm > M5: 483.72 nm M3: 630.23nm > M7: 537.90 nm, M4: 655.52 nm > M10: 572.87). It is interesting to note that the maximal absorption wavelengths of the ten designed dyes are assigned to the electron transition HOMO $\rightarrow$ LUMO, as shown in Table 5. We conclude that the maximum of absorption which correspond to the transition from the HOMO to the LUMO can be assigned to the $\pi \rightarrow \pi^*$ transition.

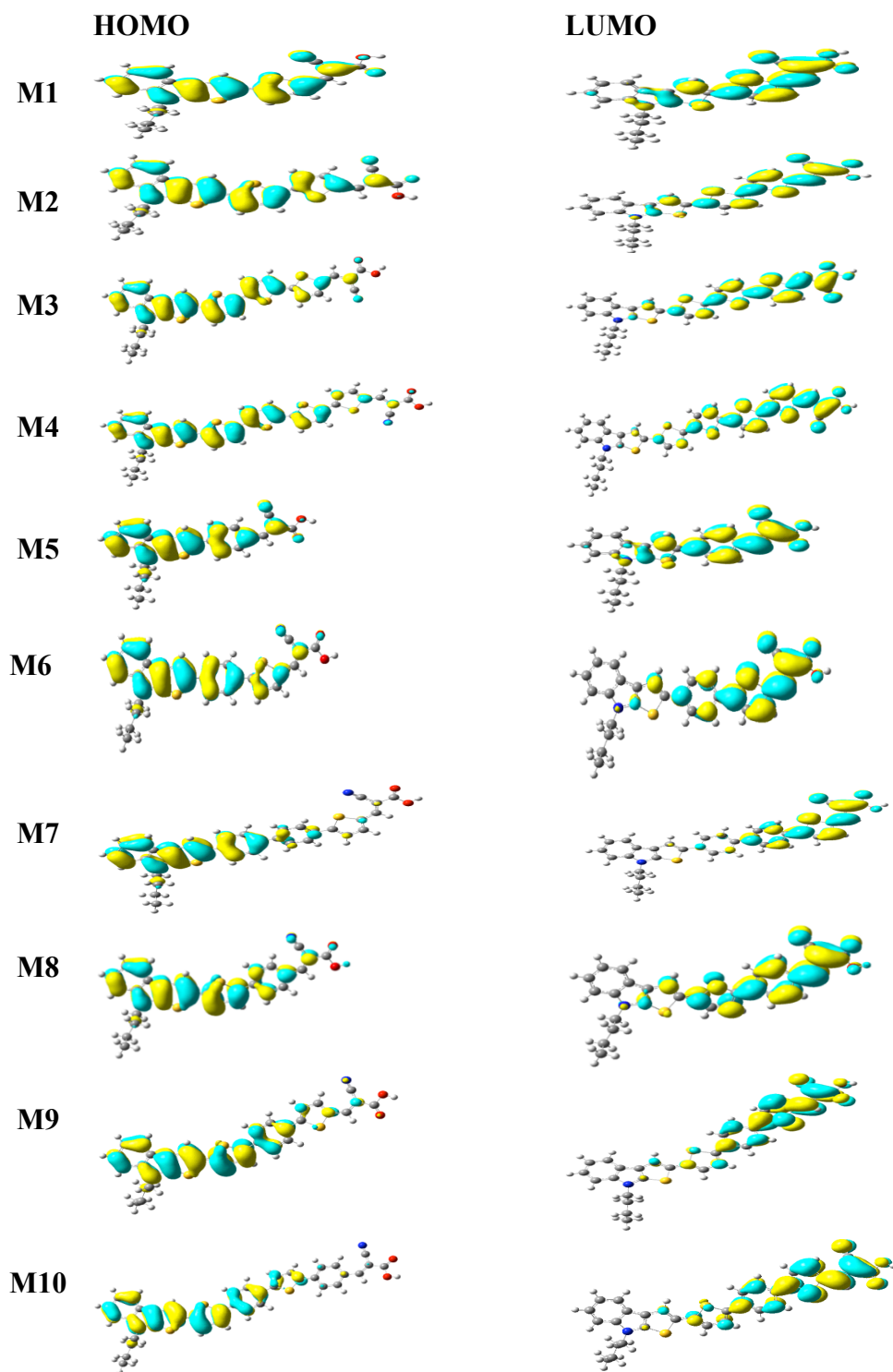


Figure 4: The contour plots of HOMO and LUMO orbitals of all dyes.

Table 4: The effects of functional on the estimated vertical excitation energy(ΔE), the absorption wavelength (λ_{abs}) of the M1 with 6-31G(d,p) basis set.

Functional	$\Delta E(\text{eV}) / \text{RE}^*$	$\lambda_{\text{abs}}(\text{nm}) / \text{RE}^{**}$
BHandHLYP	2.699 /0.529	459.30/44.70
M062X	2.675/0.535	463.45/40.55
ω B97XD	2.745/0.605	451.65/52.35
CAM-B3LYP	2.690/0.550	460.91/43.09
PBE0	2.454/0.314	505.17/1.17
Exp. [7]	2.140	504.00

RE*: the relative error of vertical excitation energy in (eV).

RE**: the relative error of the absorption wavelength in (nm).

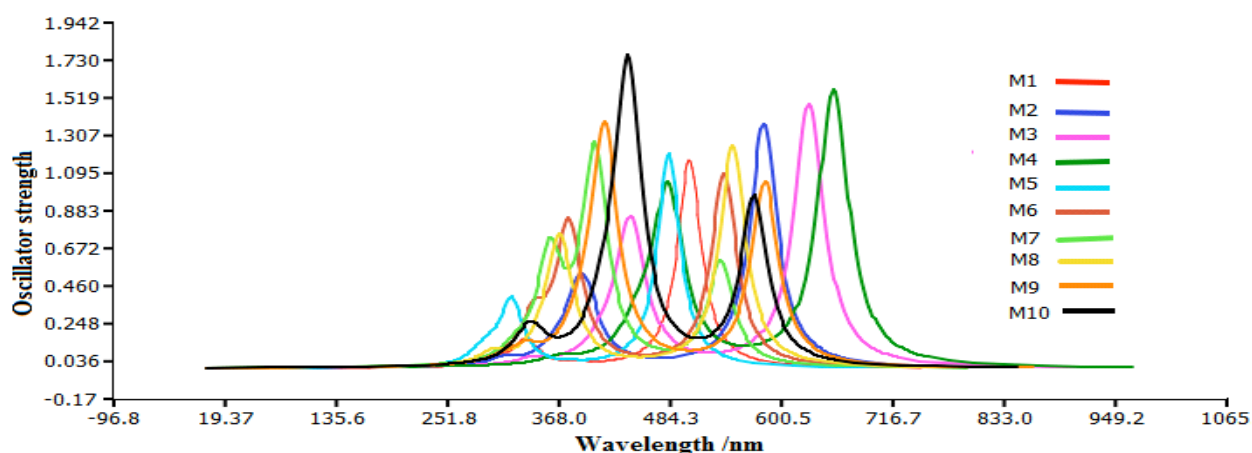


Figure 5: Simulated absorption spectra of the studied compounds in chloroform (CHCl_3) calculated by TD-DFT/PBE0/6-31G(d,p) level.

Table 5: Absorption spectra data of the Mi ($i=1-10$) compounds calculated with TD-DFT/PBE0/6-31G(d,p) level in chloroform solvent (CHCl_3).

Compound	Excited state	Main composition		λ_{abs} (nm)	ΔE (eV)	OS
M1	$\text{S0} \rightarrow \text{S1}$	HOMO $\rightarrow$ LUMO	0.70	505.17	2.454	1.174
M2	$\text{S0} \rightarrow \text{S1}$	HOMO $\rightarrow$ LUMO	0.70	582.78	2.128	1.374
M3	$\text{S0} \rightarrow \text{S1}$	HOMO $\rightarrow$ LUMO	0.70	630.23	1.967	1.482
M4	$\text{S0} \rightarrow \text{S1}$	HOMO $\rightarrow$ LUMO	0.69	655.52	1.891	1.559
M5	$\text{S0} \rightarrow \text{S1}$	HOMO $\rightarrow$ LUMO	0.70	483.72	2.563	1.205
M6	$\text{S0} \rightarrow \text{S1}$	HOMO $\rightarrow$ LUMO	0.70	541.38	2.290	1.089
M7	$\text{S0} \rightarrow \text{S1}$	HOMO $\rightarrow$ LUMO	0.70	537.90	2.305	0.588
M8	$\text{S0} \rightarrow \text{S1}$	HOMO $\rightarrow$ LUMO	0.70	550.41	2.253	1.245
M9	$\text{S0} \rightarrow \text{S1}$	HOMO $\rightarrow$ LUMO	0.70	584.02	2.123	1.037
M10	$\text{S0} \rightarrow \text{S1}$	HOMO $\rightarrow$ LUMO	0.70	572.87	2.164	0.946

3.5. Emission spectra

In order to study the photoluminescence emission (PL) properties of the studied compounds, the TD-DFT/PBE0 method was applied to the geometry of the lowest singlet excited state optimized at the PBE0 functional with the 6-31G(d,p) basis set. The emission spectrum data in chloroform solvent (CHCl_3) of these compounds is shown in Figure 6 and their corresponding emission parameters are presented in Table 6.

Table 6: Emission wavelengths (λ_{emis}), oscillator strengths (OS), Stokes shift (SS) and radiative lifetimes (τ) for all compounds obtained with TD-DFT/PBE0/6-31G (d,p).

Compound	Main composition		ΔE (eV)	λ_{emis} (nm)	OS	SS (nm)	τ (ns)
M1	HOMO $\rightarrow$ LUMO	0.70	2.243	552.65	1.344	47.48	3.42
M2	HOMO $\rightarrow$ LUMO	0.70	1.886	657.34	1.711	74.56	3.80
M3	HOMO $\rightarrow$ LUMO	0.70	1.685	735.45	1.908	105.22	4.26
M4	HOMO $\rightarrow$ LUMO	0.69	1.569	789.81	2.04	134.29	4.60
M5	HOMO $\rightarrow$ LUMO	0.70	2.319	534.64	1.310	50.92	3.28
M6	HOMO $\rightarrow$ LUMO	0.70	1.997	620.63	1.651	79.25	3.50
M7	HOMO $\rightarrow$ LUMO	0.70	1.867	663.94	1.045	126.04	6.34
M8	HOMO $\rightarrow$ LUMO	0.70	1.962	631.65	1.606	81.24	3.73
M9	HOMO $\rightarrow$ LUMO	0.70	1.754	706.9	1.555	122.88	4.83
M10	HOMO $\rightarrow$ LUMO	0.69	1.717	724.34	1.540	151.47	5.09

The normalized photoluminescence spectrum of the studied compounds shows a maximum at 552.65 nm with strongest intensity (OS=1.344) for M1, 657.34 nm (1.711) for M2, 735.45 nm (1.908) for M3, 789.81 nm (2.04) for M4, 534.64 nm (1.310) for M5, 620.63 nm (1.651) for M6, 663.94 nm (1.045) for M7, 631.65 nm (1.606) for M8, 706.9 nm (1.555) for M9 and 724.34 nm (1.540) for M10.

This could be regarded as an electron transition process that is the reverse of the absorption corresponding mainly to the LUMO → HOMO electron transition configuration. Also, the Stokes Shift (SS) of the compound can be calculated by taking the wavelength difference between the λ_{abs} of the absorption and the λ_{emis} of the emission peak. The relatively high values of stokes shift (SS) are obtained for M10 (151.47 nm) and the low values are obtained for M1 (47.48 nm), this indicate that the compounds which have a weak Stocks Shift present a minimal conformational reorganization between ground state and excited state. Indeed, this stops the intermolecular transfer charge and delaying the injection phenomenon from LUMO of the compounds to LUMO of TiO₂.

The inverse behavior observed in the absorption spectrum of M10, intense peak in blue shift at 441 nm and low red shift peak at 572 nm, in comparison with the other dyes is probably due to its high SS value.

We can also note that the radiative lifetimes τ (in ns) for spontaneous emission are obtained using the Einstein transition probabilities according to the following formula [33]:

$$\tau = \frac{c^3}{2(E_{\text{Flu}})^2 f} \quad (1)$$

where c is the velocity of light, E_{Flu} is the excitation energy and f is the oscillator strength OS. The radiative lifetimes of the study compounds are from 3.28 to 6.34 ns and increase in the following order: M5 < M1 < M6 < M8 < M2 < M3 < M4 < M9 < M10 < M7. Therefore, the Short radiative lifetimes lead to high light-emitting efficiency, while long radiative lifetimes facilitate electron and energy transfer.

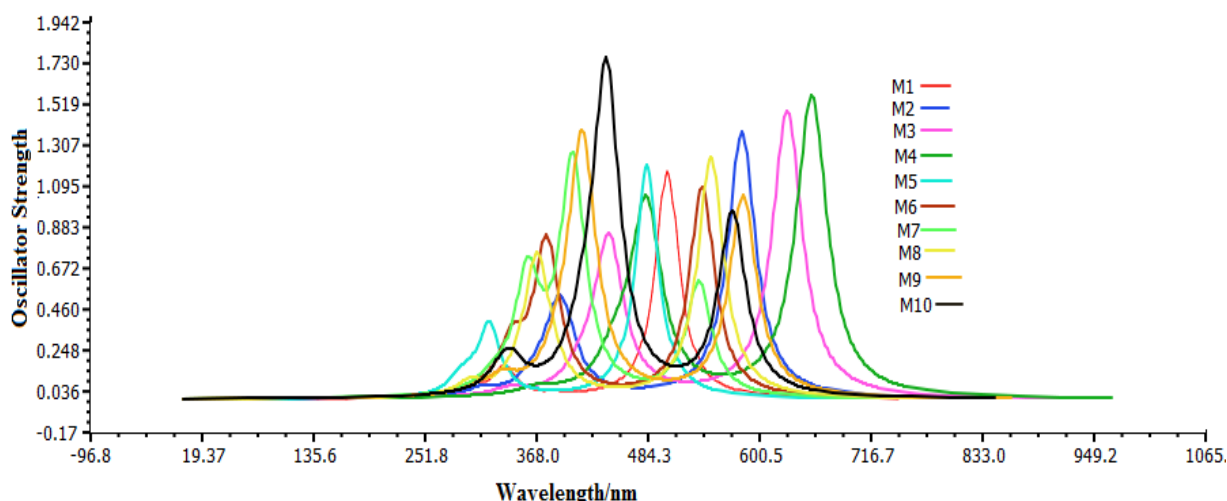


Figure 6: Simulated emission spectra of the studied compounds calculated with TD-DFT/PBE0/6-31G(d,p).

3.6. Photovoltaic properties

In order to evaluate the performance of a photovoltaic cell, the power conversion efficiency (PCE or η) can be calculated from the following (2)[34]:

$$\eta = \frac{FF \times V_{\text{oc}} \times J_{\text{sc}}}{P_{\text{in}}} \quad (2)$$

where P_{in} is the incident power density, J_{sc} is the short-circuit current, V_{oc} is the open-circuit voltage, and FF denotes the Fill Factor.

Among the parameter influence on the efficient of solar cells is the V_{oc} . Therefore, as part of this research, we will attempt to evaluate the value of V_{oc} for all compounds. The maximum open circuit voltage (V_{oc}) of DSSCs can be approximately estimated by the energy difference between the lower unoccupied molecular orbital (E_{LUMO}) of the dye and conduction band (E_{CB}) of the semiconductor TiO₂, taking into account the energy lost during the photo-charge generation. The theoretical values of open-circuit voltage V_{oc} have been calculated from the following expression (3) [35]:

$$V_{\text{oc}} = E_{\text{LUMO}}(\text{Donor}) - E_{\text{CB}}(\text{TiO}_2) \quad (3)$$

The obtained values of V_{oc} for the studied compounds calculated according to expression (3) range from 1.197(M3) to 1.496(M5) eV (Table 7), being sufficient for a possible efficient electron injection. Therefore, all the studied compounds can be used as sensitizers, because the electron injection process from the excited

molecule to the conduction band of the acceptor (TiO₂) and subsequent regeneration is possible in a dye sensitized solar cell

Table 7: Energy values of LUMO (E_{LUMO}), HOMO (E_{HOMO}) and the open circuit voltage V_{oc} of the studied compounds obtained by B3LYP/6-31G (d,p) level.

Compound	E_{HOMO} (eV)	E_{LUMO} (eV)	V_{oc} (eV)
M1	-5.252	-2.558	1.442
M2	-5.116	-2.748	1.252
M3	-4.980	-2.803	1.197
M4	-4.871	-2.803	1.197
M5	-5.334	-2.503	1.497
M6	-5.197	-2.667	1.333
M7	-5.061	-2.668	1.332
M8	-5.116	-2.612	1.388
M9	-5.007	-2.721	1.279
M10	-4.925	-2.694	1.306
TiO ₂	-	-4.00	-

3.6.1. Free energy change for the electron injection

The free energy change for the electron injection ΔG_{inject} for the dyes M_i (i=1 to 10) are represented in Table 8 can be expressed as [36]:

$$\Delta G_{\text{inject}} = E_{\text{ox}}^{\text{dye*}} - E_{\text{CB}}^{\text{TiO}_2} \quad (4)$$

Where $E_{\text{ox}}^{\text{dye*}}$ is the oxidation potential of the dye in the excited state, can be calculated by the equation [37]:

$$E_{\text{ox}}^{\text{dye*}} = E_{\text{ox}}^{\text{dye}} - \lambda_{\text{max}}^{\text{ICT}} \quad (5)$$

Where $E_{\text{ox}}^{\text{dye}}$ the oxidation potential energy of the dye in the ground state, while $\lambda_{\text{max}}^{\text{ICT}}$ is an electronic vertical transition energy.

The negative sign ΔG_{inject} values for all molecules confirm that the spontaneous charge transfer process arises following photon absorption of dye molecules. As indicated in (Table 8) the calculated values of ΔG_{inject} are decreased in the order M3>M2>M4>M6>M9>M8>M1>M5>M10>M7. It shows that M7 has the largest absolute value of ΔG_{inject} . Therefore, the larger absolute value of ΔG_{inject} is favorable for fast electron injection, and thus for improving J_{sc} and V_{oc} .

Table 8: Values of photovoltaic parameters of studies dyes obtained with B3LYP/6-31G(d,p) level.

Compound	$E_{\text{ox}}^{\text{dye}}$ (eV)	$\lambda_{\text{max}}^{\text{ICT}}$ (eV)	$E_{\text{ox}}^{\text{dye*}}$ (eV)	ΔG_{inject} (eV)	F	LHE
M1	5.252	2.454	2.798	-1.202	1.131	0.926
M2	5.116	2.128	2.988	-1.012	1.713	0.981
M3	4.980	1.967	3.013	-0.987	2.108	0.992
M4	4.871	1.891	2.98	-1.020	2.426	0.996
M5	5.333	2.563	2.770	-1.230	1.453	0.965
M6	5.197	2.290	2.907	-1.093	1.794	0.984
M7	5.061	2.305	2.756	-1.244	1.848	0.986
M8	5.116	2.253	2.863	-1.137	1.739	0.982
M9	5.007	2.123	2.884	-1.116	2.172	0.993
M10	4.925	2.164	2.761	-1.239	2.745	0.998

3.6.2. Light Harvesting Efficiency (LHE)

The efficiency of DSSC is related to the performance of the dyes responsible of the incident light. Based on the LHE of the dye, the value has to be as high as possible to maximize the photocurrent response.

The LHE is expressed as [38]:

$$\text{LHE} = 1 - 10^{-f} \quad (6)$$

The LHE values for all dyes are in narrow range 0.926(M1)-0.998(M10) (Table 8), but increase slightly with increasing the bridge length.

Conclusions

In this work, we have performed a detailed theoretical analysis on the geometries, electronic, optical and photovoltaic properties of ten D- π -A dyes by using DFT/TD-DFT. The modification concerning the bridge of chemical structures can effectively modulate and greatly enhance the electronic, optical and photovoltaic properties of the studied compounds. The concluding remarks are:

- The appropriate functional to predict the geometrical and electronics properties is B3LYP.
- The appropriate functional to predict the optical properties is PBE0.
- The absorption properties have been obtained by using TD/PBE0 calculations; the obtained absorption maximums are in the range of 505.17-655.52 nm and the simulated absorption spectra show that all the studied compounds absorb from the UV/Vis, arises from delocalized π - π^* transition.
- The HOMO, LUMO levels, and band gap of the studied compounds were well controlled by the bridge strength. The calculated band gap of the studied molecules was in the range of 2.830 to 2.068 eV, increases in the following order $M4 < M3 < M10 < M9 < M2 < M7 < M8 < M6 < M1 < M5$ and the results clearly indicated that the number and position of thiophene and benzene moieties that constitute the bridge decreased the Egap significantly.
- The obtained values Voc range from 1.197 to 1.496 eV of TiO_2 . These values are sufficient for a possible efficient electron injection.

Finally, we suggested that these compounds were good candidates for Dye-Sensitized Solar Cell (DSSC) applications. Also the procedures of theoretical calculations can be used as a model system to predict the electronic, optical and photovoltaic properties of the other compounds and further to design novel materials for organic solar cells.

References

1. X-G. Li, M-R. Huang, W. Duan, Y-L. Yang, *Chem. Rev.* 102 (2002) 2925.
2. R.E. Gill, G.G. Malliaras, J. Wildeman, G. Hadziioannou, *Adv. Mater.* 6 (1994) 132.
3. F. Garnier, G. Horowitz, X. Peng, D. Fichou, *Adv. Mater.* 2 (1990) 562.
4. G. Wang, S. Qian, J. Xu, W. Wang, X. Liu, X. Lu, F. Li, *Physica Part B.* 279 (2000) 116; M.M. Alam, S.A. Jenekhe, *Chem Mater.* 16 (2004) 4647.
5. A. Yella, H-W. Lee, H.N. Tsao, C. Yi, A.K. Chandiran, M.K. Nazeeruddin, E.W-G. Diau, C-Y. Yeh, S.M. Zakeeruddin, M. Grätzel, *Science.* 334 (2011) 629.
6. H-Q. Xia, J. Wang, F-Q. Bai, H-X. Zhang, *Dyes and Pigment.* 113 (2015) 87.
7. A.R. Irgashev, A.A. Karmatsky, A.S. Kozyukhin, K.V. Ivanov, A. Sadovnikov, V.V. Kozik, A.V. Grinberg, V.V. Emets, L.G. Rusinov, N.V. Charushin, *Synthetic Metals.* 199 (2015) 152.
8. H.W. Lin, Y.S. Wang, P.F. Yang, K.T. Wong, L.Y. Lin, F. Lin, *Org. Electron.* 14 (2013) 1037.
9. Z. Ning, Y. Fu, H. Tian, *Energy Environ. Sci.* 3 (2010) 1170.
10. Y.A. Duan, Y. Geng, H.B. Li, X.D. Tang, J.L. Jin, Z.M. Su, *Org. Electron.* 13 (2012) 1213.
11. Y.M. Cao, N. Cai, Y.L. Wang, R.Z. Li, Y. Yuan, P. Wang, *Phys. Chem. Chem. Phys.* 14 (2012) 8282.
12. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, J.J. E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Gaussian Inc., Wallingford, CT, (2009).
13. A.D. Becke, *J. Chem. Phys.* 98 (1993) 1372.
14. A.D. Becke, *Phys. Rev. A* 38 (1988) 3098.
15. C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
16. M. Bourass, A. Touimi Benjelloun, M. Benzakour, M. Mcharfi, M. Hamidi, S. Bouzzine, F. Serein Spirau, T. Jarroson, J-M. Sotiropoulos, M. Bouachrine, *J. Mater. Environ. Sci.* 7 (3) (2016) 700.

17. A. Fitri, A. Touimi Benjelloun, M. Benzakour, M. Mcharfi, M. Hamidi, M. Bouachrine, *J. Mater. Environ. Sci.* 7 (2016) 834.
18. A. Fitri, A. Touimi Benjelloun, M. Benzakour, M. Mcharfi, M. Hamidi, M. Bouachrine, *Spectrochim. Acta A: Mol. Biomol. Spectrosc.* 124 (2014) 646.
19. J.P. Perdew, K. Burke, M. Ernzerhof, *Physical Review Letters*. 77 (1996) 3865.
20. J.P. Perdew, K. Burke, M. Ernzerhof, *Physical Review Letters*. 78 (1997) 1396.
21. A.D. Becke, *J. Chem. Phys.* 98 (1993) 1372.
22. J.D. Chai, M. Head-Gordon, *J. Chem. Phys.* 128 (2008).
23. Y. Zhao, D.G. Truhlar, *J. Chem. Phys.* 124 (2006).
24. T. Yanai, D.P. Tew, N.C. Handy, *Chem. Phys. Lett.* 393 (2004) 51.
25. M. Cossi, V. Barone, *J. Chem. Phys.* 115(2001) 4708.
26. C. Adamo, V. Barone, *Chem. Phys. Lett.* 330 (2000) 152.
27. Y. Wen, W. Wu, Y. Li, W. Zhang, Z. Zeng, L. Wang, J. Zhang, *Journal of Power Sources*. 326 (2016) 193.
28. X. Ren, S. Jiang, M. Cha, G. Zhou, Z.S. Wang, *Chemistry of Materials*. 24 (2012) 3493.
29. W.L. Ding, D.M. Wang, Z.Y. Geng, X.L. Zhao, W.B. Xu, *Dyes Pigm.* 98 (2013) 125.
30. Z.L. Zhang, L.Y. Zou, A.M. Ren, Y.F. Liu, J.K. Feng, C.C. Sun, *Dyes Pigm.* 96 (2013) 349.
31. J. Preat, D. Jacquemin, C. Michaux, E.A. Perpète, *Chem. Phys.* 376 (2010) 56.
32. J. Zhang, H.B. Li, S.L. Sun, Y. Geng, Y. Wu, Z.M. Su, *J. Mater. Chem.* 22 (2012) 568.
33. V. Lukes, A. Aquino, H. Lischka, *J. Phys. Chem. A* 109 (2005) 10232.
34. M.R. Narayan, *Renew. Sust. Energy Rev.* 16 (2012) 208.
35. W. Sang-aroon, S. Saekow, V. Amornkitbamrung, *J. Photochem. Photobiol. A* 236 (2012) 35.
36. R. Katoh, A. Furube, T. Yoshihara, K. Hara, G. Fujihashi, S. Takano, S. Murata, H. Arakawa, M. Tachiya, *J. Phys. Chem. B* 108 (2004) 4818.
37. P.F. Barbara, T.J. Meyer, M. A. Ratner, *J. Phys. Chem. B* 100 (1996) 13148.
38. H.S. Nalwa, *Handbook of Advanced Electronic and Photonic Materials and Devices* Academi Press. San Diego, CA, (2001).

(2018) ; <http://www.jmaterenvironsci.com>