



Novel D- π -A organic dyes based on thieno[2,3-b]indole for efficient dye-sensitized solar cells: DFT and TD-DFT study

M. Hachi¹, A. Touimi Benjelloun¹, S. ElKhattabi^{1,2}, A. Fitri¹, M. Benzakour¹, M. Mcharfi¹

¹ *Equipe de Chimie Informatique et Modélisation, Laboratoire d'Ingénierie des Matériaux, de Modélisation et d'Environnement (LIMME), Faculté des Sciences Dhar El Mahraz, Université Sidi Mohammed Ben Abdellah, BP 1796 – 30000, Atlas – Fès, Fès.*

² *Ecole Nationale des Sciences Appliquées, Université Sidi Mohammed Ben Abdellah, Fès.*

Received 14 Jan 2019 ; Revised 21 Feb 2019, Accepted 28 Feb 2019

Keywords

Dye-sensitized solar cells (DSSC)
Thieno [2,3-b] indole
Dyes
TD-DFT
optoelectronic properties

Abstract

In this study, we evaluate the characteristics of new four dyes based on the 8-alkyl-8H-thieno [2,3-b] indole using DFT and TD-DFT quantum chemistry approach. This study mainly explores the impact of various changes of the π -conjugated D- π -A type organic dyes on the optoelectronic properties (λ_{max} , EHOMO, ELUMO, E_{gap}) as well as on the photovoltaic properties. The functional B3LYP and the 6-31G (d, p) basis set have been used to determine the optimized structures and the electronic properties (EHOMO, ELUMO, E_{gap}). On the other hand, PBE0 functional was used to describe optoelectronic properties such as the UV-visible spectrum for the various compounds studied. The calculated results reveal that dye M4 can be used as a potential sensitizer for TiO₂ nanocrystalline solar cells due to its best electronic and optical properties and good photovoltaic parameters.

1. Introduction

Dye-sensitized solar cells DSSCs have attracted significant attention in scientific and academic research and in industrial applications due to their high-power conversion efficiency, low costs, flexible devices, since the first report by O'Regan and Grätzel in 1991 [1-2]. DSSC class based on organic dyes is constructed with an extensive band gap (TiO₂) sensitized with organic dyes, ready to capture light in the visible region of the spectrum, electrolyte containing Iodide/triiodide redox couple, and a platinum counter electrode [3-4]. Over the past decades, the experimenters and the theorists Looking for news methods to improve the efficiency of dyes [5-9]. As we know, there are two categories of dyes; metal and metal free based organic dyes [10-11]. The power conversion efficiency (PCE) of the metal-based dyes class can exhibit 13% under AM 1.5 sunlight [12]. However, the fabrication of these class is limited by the rarity of noble metals, as well as environmental problems and time-consuming synthesis processes.

On the other side, the PCE of organic dye without metal can up to 14.3% [13]. Therefore, the development of the efficiency of this organic dye is an important strategy to improve the PCE of DSSCs. Recently, a new organic dye 3-(5-(8-butyl-8 H -thieno[2,3- b]indole-2-yl) thiophen-2-yl)-2-cyanoacrylic acid have been successfully synthesized by R.A. Irgashev et al [14], in which the central thiophene is located as bridge between two groups, thieno[2,3-b]indole as donor and cyanoacrylic acid as acceptor, forming D- π -A Dye. As we know the thiophene moiety and its derivatives is a good π -conjugated spacer because it is easy to synthesize and serves to increase the intramolecular charge transfer efficiency and also serves to enhance the intensity of absorption [15]. For that we decided in this work to study the impact of the increase in the number of thiophene in the bridge of the Donor- π -Acceptor organic dyes on the electronic properties and optical properties of four dyes sensitizers. The chemical structure of studied dyes are plotted in Figure 1 and their optimized structure calculated at DFT-B3LYP/6-31G(d,p) level are shown in Figure 2 (a).

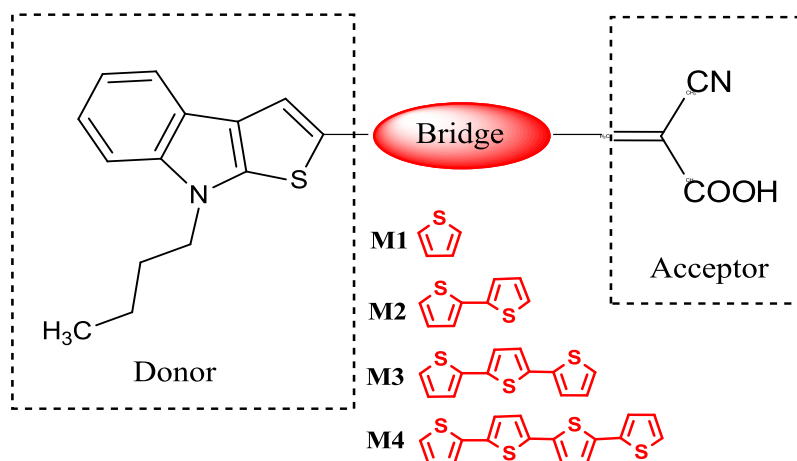


Fig.1. Chemical structure of studied dyes

2. Experimental details

The calculations were performed with the Gaussian09 software [16]. The geometries of the ground state and the energies of HOMO, LUMO and the gap (ELUMO - EHOMO) of dye sensitizers were calculated by using DFT (Density Functional Theory) [17] with the hybrid functional of exchange correlation B3LYP (Becke three-parameter Lee–Yang–Parr) and the basis set of People with double-polarized 6-31G (d, p). The energy of excited state and oscillator strengths (f) were investigated by using TD-DFT/PBE0 with 6-31G (d, p) basis set in chloroform solvent on the fully DFT optimized geometries [18] combining the integral equation formalism polarizable continuum model (IEF-PCM) [19].

3. Results and discussion

3.1. Geometric and electronic properties

Fig. 2 shows the optimized molecular structure and frontier molecular orbitals of studied dyes. As observed, the electron distributions of HOMOs are mainly localized on the electron donor groups and the bridge, whereas the electron distribution of LUMOs are mainly localized on the bridge and

acceptor units, which indicates that there are good electron-separated states between HOMOs and LUMOs. Therefore, we could expect that there would be intramolecular charge transfer when the transition occurs, which is beneficial for the photoexcitation electrons injection.

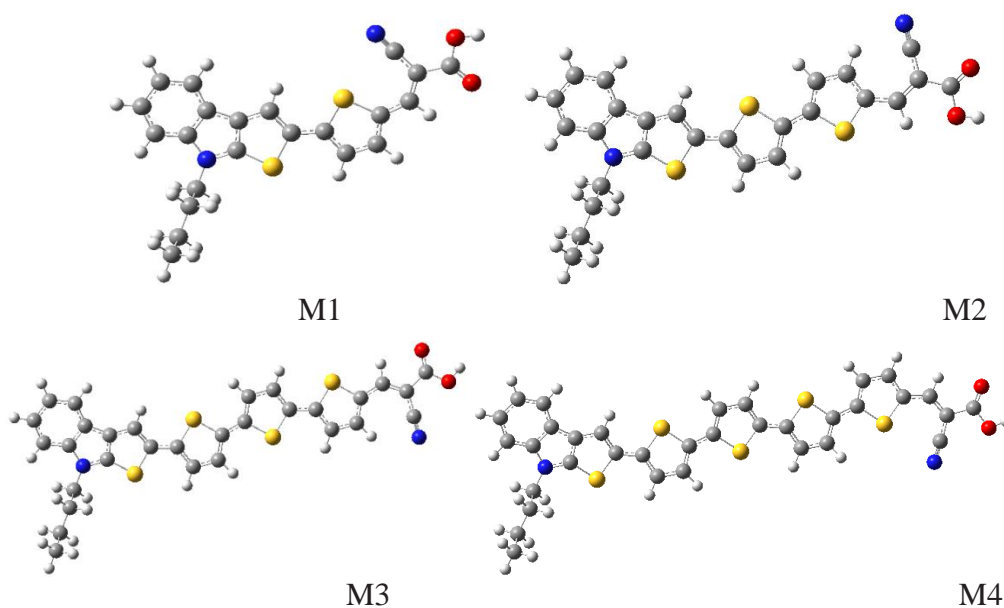


Fig. 2 (a)

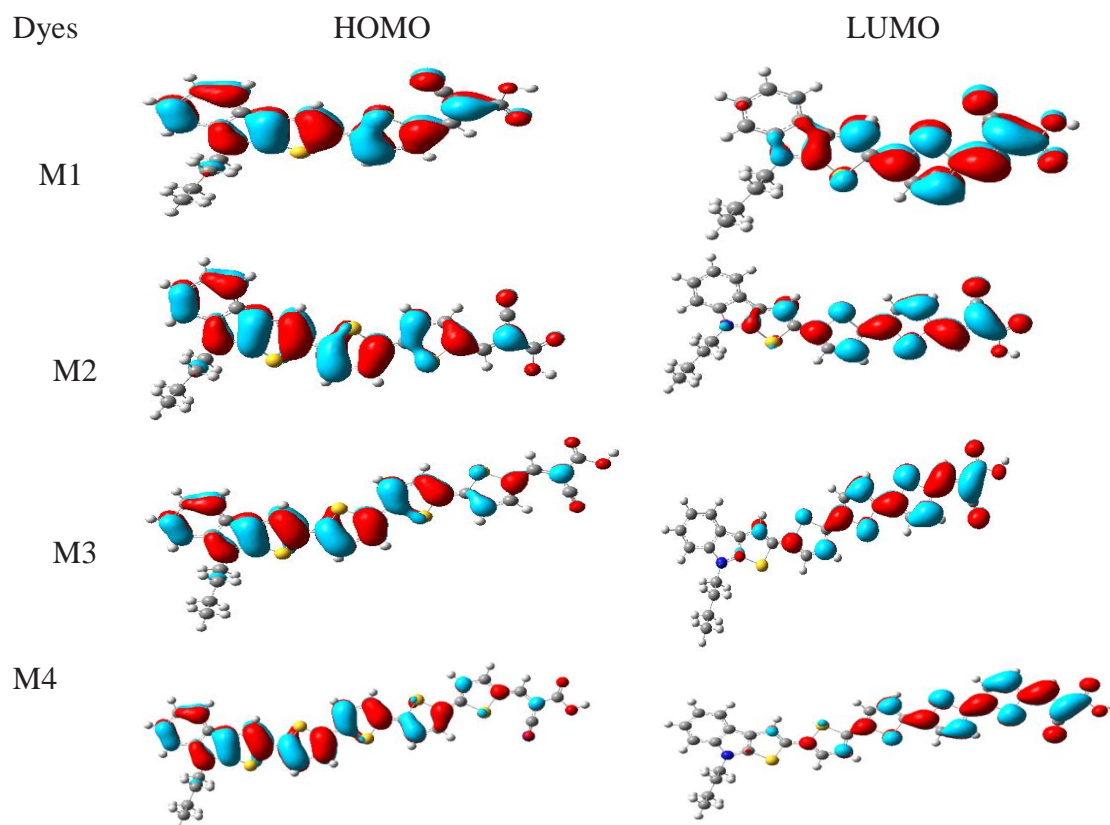


Fig. 2 (b)

Fig. 2. Molecular structure of studied dyes (a) and their frontier HOMO and LUMO orbitals (b) optimized with DFT at B3LYP/6-31G(d,p) level.

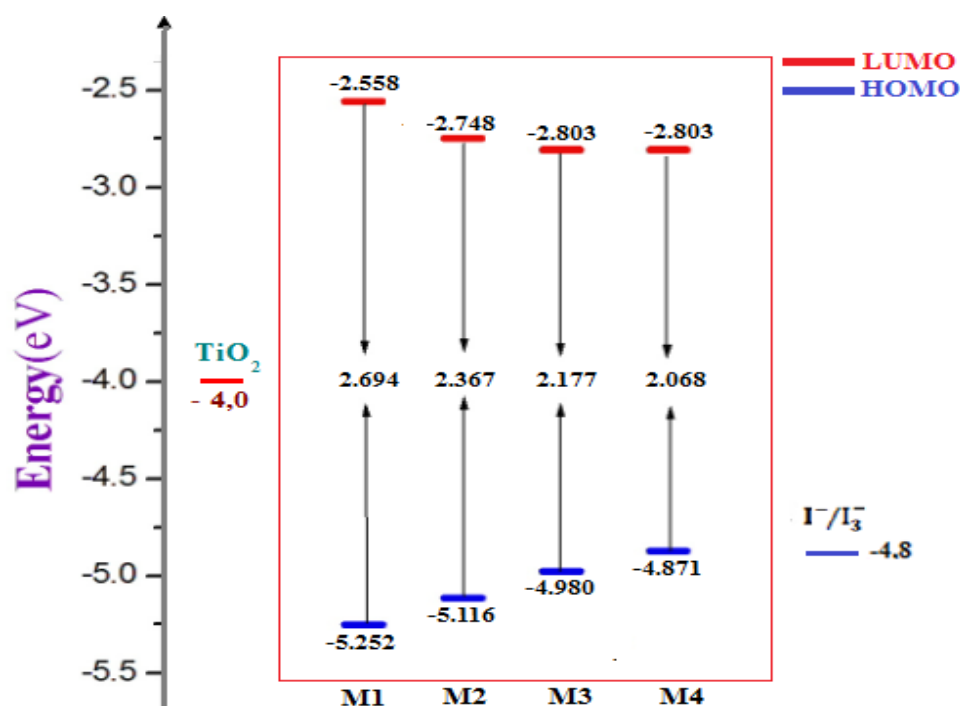


Fig. 3. Schematic energy diagram of all dyes, TiO₂ and electrolyte (I⁻/I₃⁻).

As shown in Fig. 3, the HOMO energies of all dyes are lower than that of I⁻/I₃⁻, so, the electrons lost by these molecules could be restored by getting electrons from the electrolyte. At the same time, the LUMO energy levels of all dyes are much higher than that of TiO₂ conduction band, which is responsible for an effective injection of excited electrons. There by, electron injection of excited molecules and, afterward, regeneration of the oxidized species is energetically permitted. This allows the application of the studied dyes in DSSC.

4. Ultraviolet-Visible Spectra

The simulated absorption spectra of four compounds is shown in fig4 and indicate that the strongest absorption in UV/vis ($\lambda_{\text{max}} > 400$ nm) correspond to electronic transition from the HOMO to LUMO of all compounds, it is found that the spectra of molecules of M1 to M4 gave absorption wavelengths about 505.17 to 655.52 nm.

5. Photovoltaic properties

From Table 1, we remark that the calculated values of ΔG_{inject} are decreased in the order M1>M2>M3>M4. It shows that M1 has the largest ΔG_{inject} value while M4 has the smallest, therefore, the negative sign of the free energy change for the electron injection ΔG_{inject} for all molecules confirm that the spontaneous charge transfer process arises following photon absorption of dye molecules.

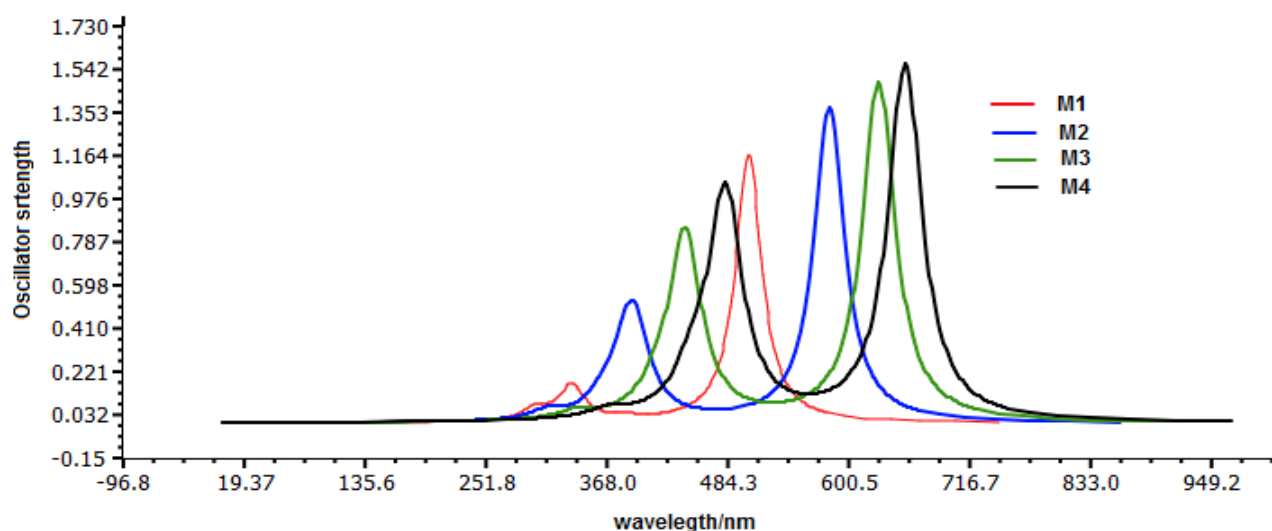


Fig. 4. Simulated absorption spectra of all dyes in chloroform.

Table 1: E_{ox}^{dye} , λ_{max}^{ICT} , E_{ox}^{dye*} , ΔG_{inject} , f and LHE values of all dye in the B3LYP/6-31G(d,p) level theory.

Dyes	E_{ox}^{dye} (eV)	λ_{max}^{ICT} (eV)	E_{ox}^{dye*} (eV)	ΔG_{inject} (eV)	f	LHE
M1	5.252	2.379	2.873	-1.127	1.131	0.926
M2	5.116	2.522	2.594	-1.406	1.713	0.981
M3	4.980	2.445	2.535	-1.465	2.108	0.992
M4	4.871	2.405	2.466	-1.534	2.426	0.996

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 values for all dyes are in narrow range 0.926–0.996 (Table 1), but increase slightly with increasing the bridge length. This means that all the sensitizers (except M1) give similar photocurrent.

6. Conclusion

In this research, we have performed a detailed theoretical analysis on the geometries and electronic properties of thieno[2,3-b]indole based. The modification concerning the bridge of chemical structures can effectively modulate and greatly enhance the electronic, optical and photovoltaic properties of studied dyes.

Finally, the theoretical results obtained suggest that calculation procedure can be used as a model system for understanding the relationships between electronic properties and molecular structure and a guiding tool to the synthesis process of these new systems. Also, these results confirmed that all systems can be applied as active compounds in DSSCs.

References

1. B. O'Regan, M. Grätzel, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films, *Nature*, 353 (1991) 737-740.
2. A. Hagfeldt, M. Grätzel, Molecular Photovoltaics *Acc. Chem. Res.*, 33(2000) 269-277.
3. M. Grätzel, Photoelectrochemical cells, *Nature*, 414 (2001) 338-344.
4. T.A. Heimer,, E.J. Heilweil, , C.A. Bignozzi,, G. Meyer, Electron Injection Recombination and Halide Oxidation Dynamics at Dye-sensitized TiO₂ Interfaces. *J. Phys. Chem. A*, 104 (2000), 4256-4262.
5. C. Dong, W. Xiang, F. Huang, D. Fu, W. Huang, , U. Bach, , Y.-B. Cheng, X.L. Li, Spiccia, Controlling interfacial recombination in aqueous dye-sensitized solar cells by octadecyltrichlorosilane surface treatment, *Angew. Chem. Int. Ed.*, 53 (2014), 6933–6937.
6. B. Xu, Y. Li, P. Song, F. Ma, M. Sun. Photoactive layer based on T-shaped benzimidazole dyes used for solar cell: from photoelectric properties to molecular design, *Sci. Rep.*, 7 (2017), 45688.
7. S. ElKhattabi, A. Fitri, , A.T. Benjelloun, M. Benzakour, , M. Mcharfi, M. Hamidi, M. Bouachrine, Theoretical investigation of electronic, optical and photovoltaic properties of alkylamine-based organic dyes as sensitizers for application in DSSCs. *J Mater Environ Sci.*, 9(3) (2018), 841–853.
8. A. Fitri, A.T. Benjelloun, M. Benzakour, M. Mcharfi, M. Hamidi, M. Bouachrine, Theoretical design of thiazolothiazole-based organic dyes with different electron donors for dye-sensitized solar cells, *Spectrochim Acta A Mol Biomol Spectrosc.*, 132 (2014), 232–238.
9. M. Hachi, S. El Khattabi, A. Fitri, A.T Benjelloun, , M. Benzakour, M. Mcharfi, , M. Hamidi, M. Bouachrine. DFT and TD-DFT studies of the π -bridge influence on the photovoltaic properties of dyes based on thieno[2,3-b]indole. *J. Mater. Environ. Sci.*, 4 (2018), 1200.
10. P.G. Bomben, K.C.D. Robson, B.D. Koivisto, C.P. Berlinguette, Cyclometalated ruthenium chromophores for the dye-sensitized solar cell. *Coord. Chem. Rev.*, 256 (2012), 1438.
11. M.K.R. Mishra, P. Fischer. Bäuerle, Metal-free organic dyes for dye-sensitized solar cells: from structure: property relationships to design rules, *Angew. Chem. Int. Ed.*, 48 (2009), 2474–2499.
12. Tavernelli, U. Rothlisberger, M.K. Nazeeruddin, M. Grätzel, Dye-sensitized solar cells with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers. *Nat. Chem.*, 6 (2014), 242–247.

13. K. Kakiage, Y. Aoyama, T. Yano, K. Oya, J.I. Fujisawa, , M. Hanaya Highly-efficient dye-sensitized solar cells with collaborative sensitization by silyl-anchor and carboxy-anchor dyes. *Chem. Commun*, 51 (2015), 15894–15897.
14. 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, (2015). *Synthetic Metals*. 199 (2015),152–158.
15. M.K. Nazeeruddin, Dye sensitized solar cells: Michael Grätzel Festschrift, a tribute for his 60th birthday: special issue. *Coord. Chem. Rev.*, 248 (2004), 1161-1164.
16. M.J. Frisch, et al. GAUSSIAN 09, Revision B.04. Gaussian, Inc., Pittsburgh PA (2009).
17. A. Fitri, A.T. Benjelloun, M. Benzakour, M. Mcharfi, M. Hamidi, M. Bouachrine, Theoretical investigation of new thiazolothiazole-based D-p-A organic dyes for efficient Dye-Sensitized Solar Cell, *Spectrochim. Acta A: Mol. Biomol.Spectros*, 124 (2014), 646-654.
18. W. Yaping, W. Wenpeng, L. Yuanyuan, Z. Weiyi, Z. Zhaoyang, W. Li, Z. Jinglai. First principles study of thieno[2,3-b]indole-based organic dyes for dye-sensitized solar cells: Screen novel p-linkers and explore the interface between photosensitizers and TiO₂. *Journal of Power Sources*, 326 (2016)., 193-202
19. J.P. Perdew, K. Burke, M. Ernzerhof. Generalized gradient approximation made simple, *Physical Review Letters*, 77(18) (1996), 3865–3868.

(2019) © JASES, USMBA Fez, Morocco