Theoretical investigations on the electronic absorption properties of phenothiazine based organic materials for dye-sensitized solar cells

S. Sambathkumar [a,*], D. Zych [b], E. Kavitha [c], P. Ramesh [a], R. Jagatheesan [a]

[a] Department of Chemistry, Vivekanandha College of Arts and Sciences for Women (Autonomous), Tiruchengode, Namakkal 637 205, Tamil Nadu, India
[b] Wroclaw School of Information Technology, Ks. M. Lutra 4, 54-239, Wrocław, Poland
[c] Department of Physics, NKR Government Arts College for Women, Namakkal 637 001, Tamil Nadu, India

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ABSTRACT

Herein, we present the theoretical investigations of three different D_2-π-A architectured phenothiazine (Pz) based organic materials with substituted imidazole as an auxiliary donor for the application of dye-sensitized solar cells (DSC's). Theoretical studies were performed by density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations. The optimized geometries and frontiers molecular orbitals of the proposed materials were calculated. Energy of frontier orbitals (eV), energy gaps (ΔE), wavelength maxima (λ_{max}), the electronic contribution of dyes and light-harvesting efficiency (LHE) with various hybrid potential and 6-31G(d,p) basis set in the chloroform by DFT/TD-DFT method were presented. Based on the electronic energy levels of the conduction band (CB) of TiO_2, dyes and I^-/I_3^- redox couple, the dyes are considered as promising solar energy materials for DSC's.

1. Introduction

Presently, DSC's have received considerable attention as promising alternatives to conventional silicon-based photovoltaic devices due to their low cost, easy manufacturing processes, and high-power conversion efficiencies [1,2]. As a critical component in DSC's, the sensitizer plays a vital role in the light-harvesting efficiency. As a promising alternative to traditional metal complexes, DSC's based on metal-free organic dyes have made remarkable progress [3] and they usually possess donor-π bridge-acceptor (D-π-A) structure. Among the donor moieties [4–7], the electron-rich nature of phenothiazine moiety provides a good relay for the electron migration from donor to acceptor, which can induce an efficient intramolecular charge transfer (ICT) even better than other amines [8]. Recently, D-D-π-A type of metal-free organic dyes has been reported and they exhibits red shift, broad and intense absorption in the visible region as well as better thermal stability as compared with traditional D-π-A configuration [9,10]. Upon introducing substituted imidazole as an additional donor, which enhances the red-shifted absorption [11]. Based on

the above discussion, we reported earlier Pz based D-D-π-A motifs and presently their electronic absorption performances have been analyzed systematically using DFT/TD-DFT calculations to understand the promising nature the proposed materials (shown in Scheme 1) for efficient DSC's.

2. Experimental section

The ground-state geometry of the Pz based organic materials is fully optimized using the DFT and TD-DFT calculations with the B3LYP, CAM-B3LYP, M06, wb97XD exchange- correlation functional implemented in the Gaussian 09 program with the 6-31G (d,p) basis set [12,13,16]. All of the calculations were performed with chloroform as the solvent in the PCM. All orbitals were computed at an isovalue of 0.03 e/bohr^3.

3. Results and discussion

3.1. Optimized structure of the materials

The optimized geometries of the proposed molecules, coded as **SP1**, **SP2** and **SP3** are shown in Fig. 1. The molecular design of the materials constituted with D-D-π-A architecture consisting of phe-

* Corresponding author.
E-mail address: sambathtacw@gmail.com (S. Sambathkumar).

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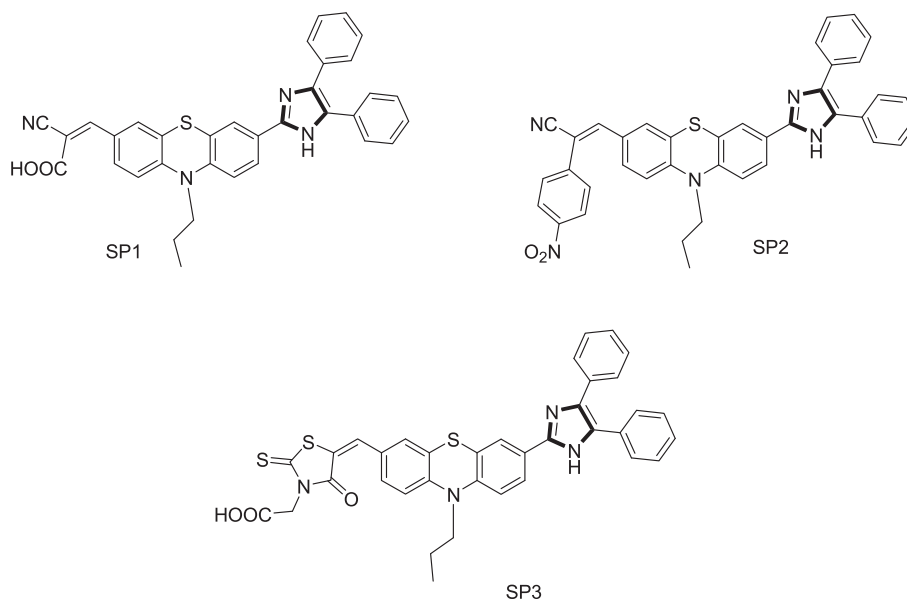
Scheme 1. Molecular structure of the proposed organic materials.
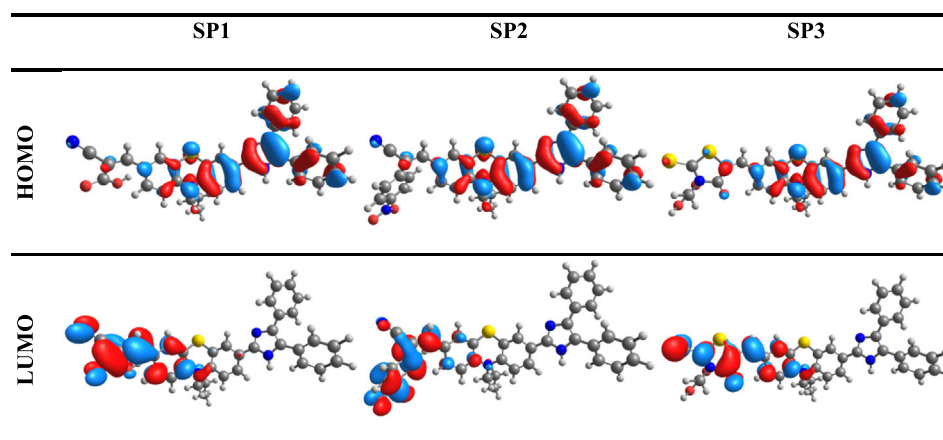

Fig. 1. The optimized structures B3LYP/6-31G(d,p) with HOMOs and LUMOs contours.

nothiazine is a core with 4, 5-substituted imidazole as a terminal donor with three different electron-withdrawing units such as, cyanoacetic acid, nitrophenyl acetonitrile and rhodanine acetic acid. Fig. 1.1 shows the top and side views of the optimized geometries of the dye molecules and their important bond parameters are presented in Table 1. The computed bond parameters reveal that these molecules found to show excellent delocalization of π-electrons. As can be seen from the Fig. 1, it is clear that all these molecules are not completely planar while the structures are slightly bent.

3.2. Frontier molecular orbital analysis

It is well known that the frontier molecular orbital analysis (FMO) is often used to obtain qualitative information about the optoelectronic properties of presented molecules. Thus, FMO analysis has been carried out and the results such as, energy of frontier orbitals (eV), energy gaps (ΔE), and electronic contribution of **SP1**-**SP3** molecules in a chloroform were presented in Table 1. The electron distribution of HOMO should be mainly localized on the donor part and LUMO should be mainly localized near the anchoring group [14]. As an example of titanium cluster, $(TiO_2)_9$ was used,

which allows to predict the consistent results of the proposed structures [15]. Fig. 2. Depicts the electronic energy levels of CB of TiO_2, dyes and I^-/I_3^- redox couple, which shows that the dyes are considered to have proper electronic energy levels as promising sensitizers in DSC's.

3.3. Insights on electronic absorption spectra

Theoretically calculated absorption spectra are shown in Fig. 3 with maxima of absorption calculated by various hybrid potential and 6-31G(d,p) with basis set in chloroform solution. Moreover, the significant differences in oscillator strengths for the lowest energy transitions affected the values of light-harvesting efficiency which were listed in Table 1. The electronic spectrum has red-shifted absorption and broadening, which indicates the π-π* transition and intramolecular charge transfer originates from donor to acceptor.

The power conversion efficiency (PCE) is an important parameter to characterize the performances of DSC's [12]. The LHE plays an important role in the enhancement of PCE of the DSC's, which has been derived from oscillator strength. The light-harvesting efficiency (LHE = 1-10^{-f}) of the dyes were ranged from 0.791 to 0.940
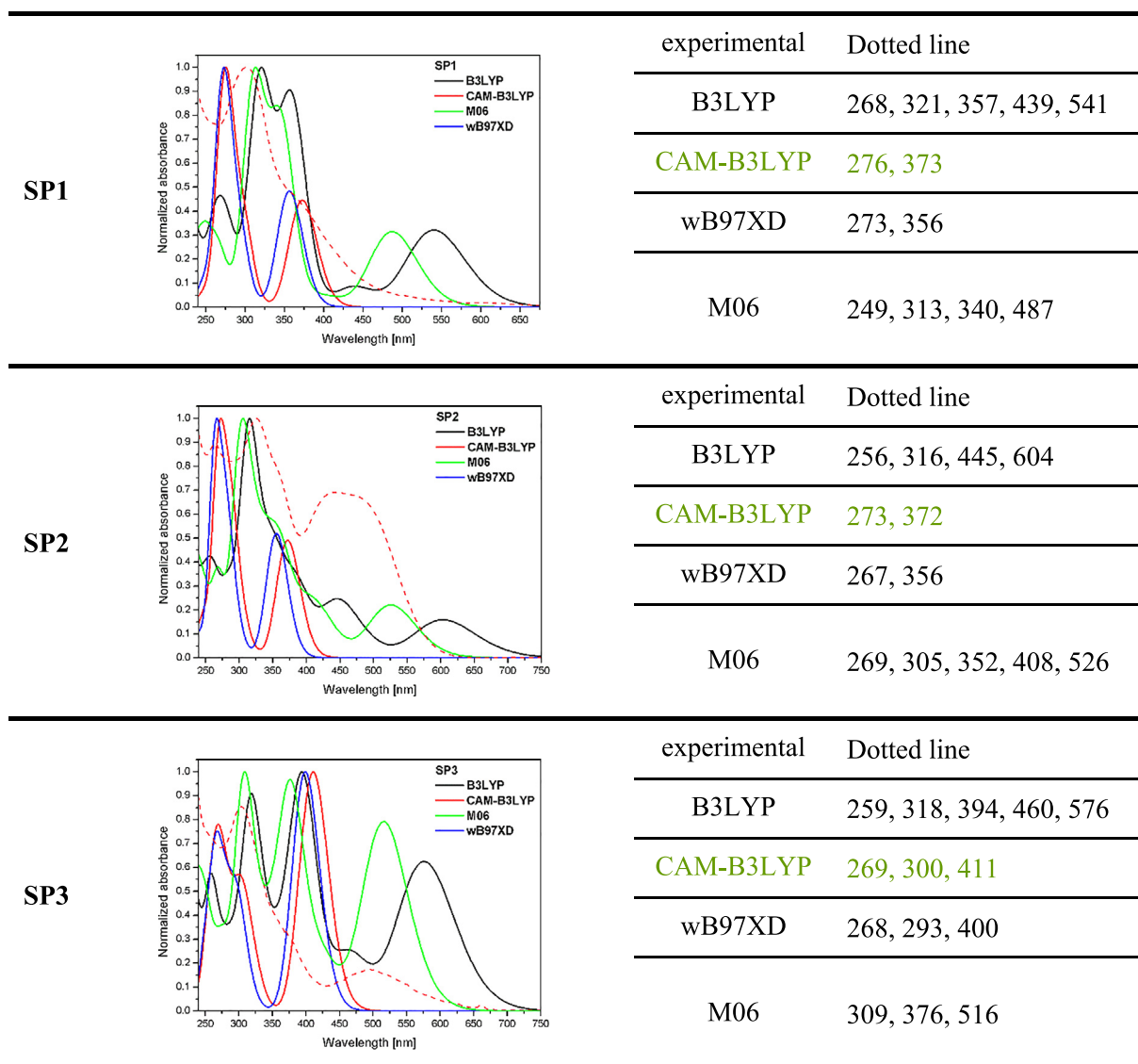
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Fig. 1.1. The B3LYP optimized geometries of **SP1**, **SP2** and **SP3**.

Fig. 2. Schematic energy levels of CB of TiO₂, dyes and I⁻/I₃⁻ redox couple.

as listed in Table 2. The observed result of the proposed structures shows a significant contribution in the performance of DSC's.

4. Conclusion

In summary, theoretical investigations on Pz based organic materials were made by DFT/TD-DFT methods. The frontier molecular orbital analysis was carried out and the obtained results were presented with respective of simulated absorption spectra of the molecules. The dyes have proper energy levels as promising for DSC's. The absorption spectra exhibits red-shifted absorption and broadening which enhance the light-harvesting efficiency. Hence, the present study is much important for the design and development of efficient sensitizers for DSC's.

Table 1
Selected bond parameters of the proposed dye molecules.

Parameters	SP1	SP2	SP3
C38-S1	1.777	1.777	1.775
C36-N1	1.418	1.418	1.398
C1-C29	1.460	1.461	1.447
C41-C59	1.446	1.450	1.447
C31-C34	1.389	1.389	1.389
C22-C24	1.396	1.396	1.396
C38-C40	1.417	1.416	1.418
C8-N1-C3	122.1	122.1	122.2
C38-S1-C32	99.2	99.2	99.6
C32-C30-C29	121.4	121.4	121.5
C31-C34-C36-N1	179.6	179.8	179.5
C29-C30-C32-S1	172.2	172.2	172.3
C9-C8-N1-C35	153.9	153.7	154.9

Table 2
Energy of frontier orbitals (eV), energy gaps (ΔE), wavelength maxima and transitions with electronic contribution of **SP1**-**SP3** molecules in the chloroform solution.

	B3LYP		CAM-B3LYP		wB97XD		M06	
	H	L	H	L	H	L	H	L
SP1	−5.23	−2.59	−6.49	−1.33	−7.09	−0.77	−5.55	−2.45
SP2	−5.16	−2.81	−6.42	−1.51	−7.03	−0.97	−5.47	−2.66
SP3	−5.14	−2.67	−6.39	−1.55	−6.99	−1.05	−5.46	−2.52
	ΔE (eV)							
	B3LYP		CAM-B3LYP		wB97XD		M06	
SP1	2.64		5.16		6.32		3.10	
SP2	2.35		4.91		6.06		2.81	
SP3	2.47		4.84		5.94		2.94	
	Calculated λ max (nm)		Oscillator strengths		Transitions (contribution)		LHE	
SP1	372.31		0.6808		HOMO->LUMO (52%), H-1->LUMO (35%),		0.791	
SP2	371.81		0.7602		HOMO->LUMO (41%), H-1->LUMO (22%), HOMO->L + 1 (16%)		0.826	
SP3	410.45		1.2189		HOMO->LUMO (55%), H-1->LUMO (32%)		0.940	

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	experimental	Dotted line
SP1	B3LYP	268, 321, 357, 439, 541
	CAM-B3LYP	276, 373
	wB97XD	273, 356
	M06	249, 313, 340, 487

	experimental	Dotted line
SP2	B3LYP	256, 316, 445, 604
	CAM-B3LYP	273, 372
	wB97XD	267, 356
	M06	269, 305, 352, 408, 526

	experimental	Dotted line
SP3	B3LYP	259, 318, 394, 460, 576
	CAM-B3LYP	269, 300, 411
	wB97XD	268, 293, 400
	M06	309, 376, 516

Fig. 3. Theoretically calculated maxima of absorption with various hybrid potential and 6-31G(d,p) basis set in the chloroform solution of **SP1**-**SP3**.

CRediT authorship contribution statement

S. Sambathkumar: Writing - original draft, Project administration. **D. Zych:** Software, Formal analysis, Data curation, Visualization, Writing - review & editing. **E. Kavitha:** Methodology. **P. Ramesh:** Resources. **R. Jagatheesan:** Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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