Asian Journal of Chemistry; Vol. 33, No. 10 (2021), 2373-2378

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2021.23340

Fused Thiazine Tethered Metal-Free Dyes for Dye Sensitized Solar Cells: A Computational Investigation

K. Gokula Krishnan, V. Saravanan, C. Udhaya Kumar and C. Ramalingan*

Department of Chemistry, School of Advanced Sciences, Kalasalingam Academy of Research and Education (Deemed to be University), Krishnankoil-626126, India

*Corresponding author: E-mail: ramalinganc@gmail.com; c.ramalingan@klu.ac.in

Received: 28 May 2021; *Accepted*: 21 July 2021; *Published online*: 20 September 2021; AJC-20509

Three novel cyanoacetamide decorated phenothiazines (**1a-c**) have been designed. Structural and photo-physical properties of the molecules **1a-c** have been investigated. To better realize the charge transport process involved in the dye-sensitized solar cells (DSSCs), computational studies have been performed using B3LYP and CAM-B3LYP method for the dyes **1a-c**. Theoretical findings for DSSCs include LHE (light-harvesting efficiency) and driving forces such as electron injection (ΔG^{inject}) and dye regeneration have been calculated to envisage the most appropriate dyes for the application of DSSC.

Keywords: Cyanoacetamide, Dye sensitized solar cells, Light harvesting efficiency, Phenothiazine.

INTRODUCTION

Dye sensitized solar cells (DSSCs) are one of the photovoltaic devices, which convert solar energy into direct electrical current using semiconductor metal oxides. A typical DSSC device with a dye possessing noble metal has been first established by O'Regan & Grätzel [1]. However, due to the low fabrication cost, high molar efficiencies, flexible structural modifications and relatively higher transparency, organic dyes have been fascinated attention in scientific research devoted to DSSCs. In the recent past, numerous research groups focused their interest on molecular design of organic dyes by varying electron-donor, acceptor/anchor and π-bridge/linker groups to enhance power conversion efficiency (η). Among the sensitizers based on donor/acceptor systems, the ones including triphenylamine [2], carbazole [3,4], fluorine [5,6], indoline [7,8], perylene [9,10], phenothiazine [11,12], tetrahydroquinoline [13,14], cyanoacrylic acid [15,16] and rhodanine-3-acetic acid [17] have been extensively studied.

As reported, phenothiazine dyes have been attracted much attention because of the property of charge transport carrier under light irradiation. Meanwhile, the non-planarity conformation of phenothiazine has effectively hinders the molecular aggregation and favours the creation of molecular excimers. During recent times, a diversity of approaches have been adopted to modify the phenothiazine core with different conjugating bridges, high molar absorptivity donor and acceptor moieties, which offered better overall power conversion efficiencies [18-25]. In most of the cases, the phenothiazine dyes have been integrated strong donor units at the positions 7 and 10 while acceptor/anchoring group at the position 3. However, the acceptor on the position 3 bearing π-bridge/linker scaffold is very plausible to enhance the electron flow to the anchor motif from the donor. Furthermore, the alkyl substituents surviving at the position 10 of the phenothiazine would improve both performance and stability. Based on the reports available in the literature as provided above, new hybrids having phenothiazine integrated cyanoacetamide backbone have been designed as sensitizers for efficient DSSCs.

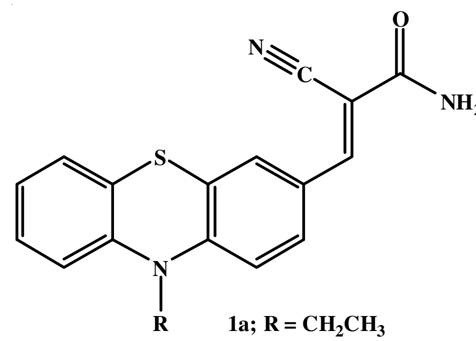
The present investigation reports computational studies of a series of aforementioned hybrid. In order to realize the connection between the chemical structure and their charge transport properties like optical and electronic characteristics of the dyes, computational studies have been executed. The DFT and time-dependent DFT have been adopted to compute the energies of vertical excitation, energies of band gap, strengths of oscillator (f) and light harvesting efficiency (LHE) of the dye molecules in ground state as well as excited state. Thus, the functionals, B3LYP [26] and CAM-B3LYP [27] with 6-311+g (d,p) basis sets have been utilized.

THEORETICAL ANALYSIS

The theoretical calculations for the dye molecules **1a-c** have been executed with the Gaussian 09 package [28]. The excited and ground state calculations have been accomplished by DFT and TD-DFT techniques. The hybrid functionals namely B3LYP (Becke3-Lee-Yang-Parr hybrid functional) and CAM-B3LYP (Coulomb-attenuating method-B3LYP) have been employed. The structures (optimized) of the dyes have been computed at DFT with 6-311+g(d,p) basis set while absorption spectra have been calculated using TD-DFT methodology with CAM-B3LYP/6-311+g(d,p) basis set. The solvation effect has been initiated by self-consistent reaction field (SCRF) using the conductor polarizable continuum model (CPCM) for both ground and excited state calculations.

RESULTS AND DISCUSSION

Designed molecules: The molecules have been designed in such a way that phenothiazine structural unit serves as electron donor and cyanoacetamide moiety serve as electron acceptor. The structures of the designed metal-free organic dyes are provided in Fig. 1.



1a; R = CH_2CH_3
1b; R = $(CH_2)_3CH_3$
1c; R = $(CH_2)_5CH_3$

Fig. 1. Structure of designed dyes (**1a-c**)

Structural analysis: The ground state optimized structures of the photo-sensitizers **1a-c** are shown in Fig. 2 and selected structural features are collected in Tables 1-3.

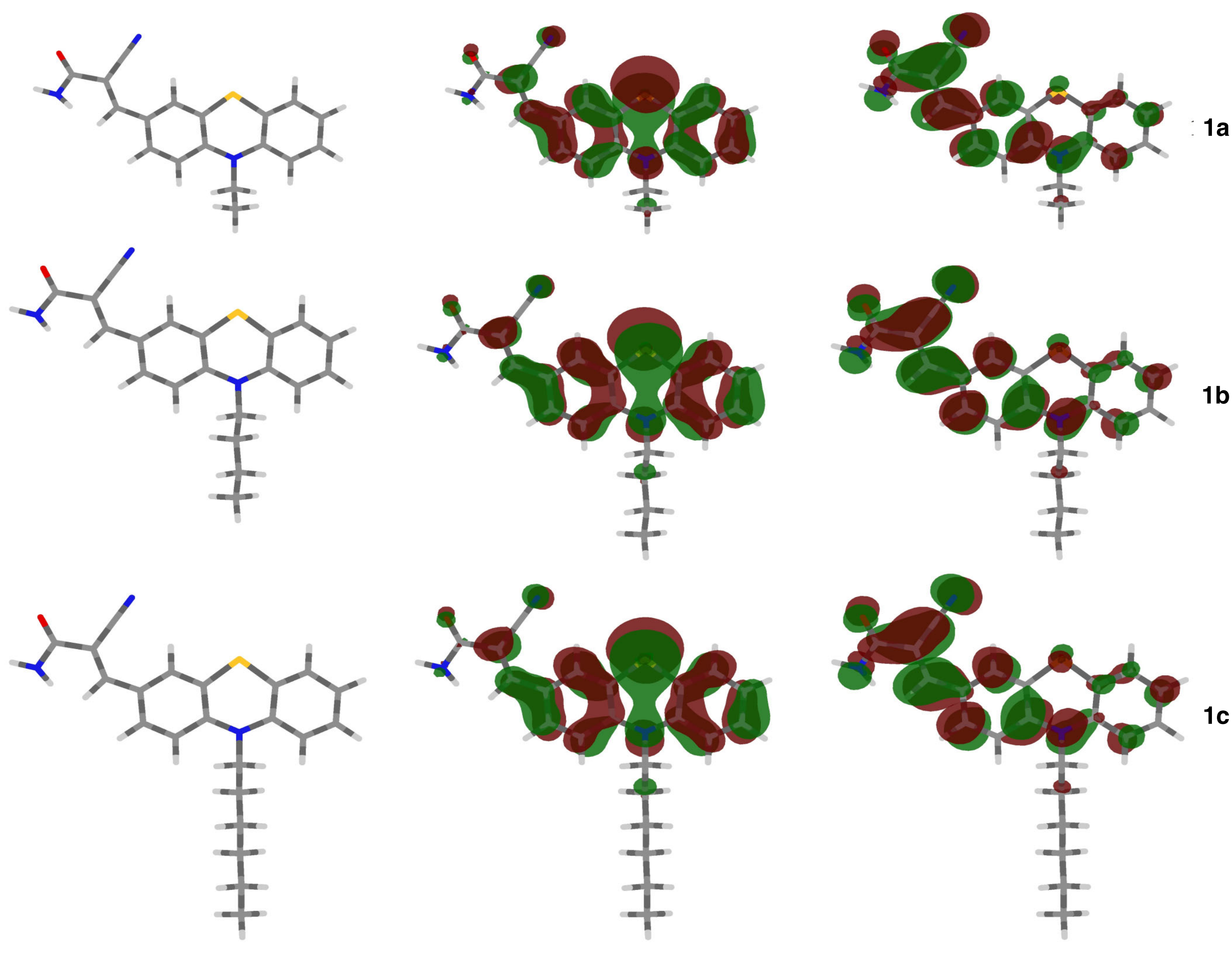


Fig. 2. Optimized structure and FMOs of phenothiazine-based dyes (**1a-c**)

TABLE-1
SELECTED BOND (Å) LENGTH OF DYES (**1a-c**)

1a	(Å)	**1b**	(Å)	**1c**	(Å)
C1-C2	1.507	C1-C2	1.506	C1-C2	1.507
C1-O4	1.221	C1-O4	1.221	C1-O4	1.221
C1-N5	1.380	C1-N5	1.380	C1-N5	1.380
C2-C3	1.364	C2-C3	1.364	C2-C3	1.364
C2-C22	1.434	C2-C24	1.434	C2-C26	1.434
C3-C8	1.451	C3-C8	1.451	C3-C8	1.450
C6-C7	1.387	C6-C7	1.387	C6-C7	1.387
C6-C19	1.410	C6-C19	1.410	C6-C19	1.410
C7-C8	1.407	C7-C8	1.407	C7-C8	1.407
C8-C9	1.413	C8-C9	1.412	C8-C9	1.413
C9-C10	1.387	C9-C10	1.387	C9-C10	1.387
C10-S11	1.777	C10-S11	1.777	C10-S11	1.777
C10-C19	1.419	C10-C19	1.419	C10-C19	1.419
S11-C12	1.776	S11-C12	1.777	S11-C12	1.776
C12-C13	1.395	C12-C13	1.395	C12-C13	1.395
C12-C17	1.409	C12-C17	1.410	C12-C17	1.409
C13-C14	1.394	C13-C14	1.394	C13-C14	1.394
C14-C15	1.391	C14-C15	1.391	C14-C15	1.391
C15-C16	1.395	C15-C16	1.396	C15-C16	1.395
C16-C17	1.405	C16-C17	1.405	C16-C17	1.405
C17-N18	1.421	C17-N18	1.421	C17-N18	1.421
N18-C19	1.400	N18-C19	1.400	N18-C19	1.400
C22-C23	1.164	C24-C25	1.164	C26-C27	1.164

The results of the optimized structures of the studied dyes **1a-c** imply that the dyes are having similar conformation. The dihedral angles and the bond angles between the planes C17-N18-C19 (122.1º)/C10-S11-C12 (99.4º) and S11-C12-C17-N18 (-6.5º)/S11-C10-C19-N18 (8.8º) make that the six-membered thiazine ring exists in butterfly conformation. Consequently, the core motif, phenothiazine tends to adopts as non-planer geometry and lower strain energy than the flat hexagonal shape. Since the non-planarity of the molecules normally suppresses J-aggregation and the molecules without J-aggregation would enhance the incident photon to energy conversion efficiency (IPCE) in DSSCs [29], the DSSC with the target dyes would provide better IPCE. The carbon-carbon bond lengths in the phenothiazine and acrylamide units lie between a double bonded C=C and a single bonded C-C distance, imply the existence of widespread delocalization throughout the molecules. In particular, carbon-carbon bond lengths of acrylamide are shorter than the phenothiazine ring, showing the flow of electrons transfer much easier from the donor to acceptor part further into semiconductor surface [30]. A distinctive bond length in alkyl chain (C-H) of dyes **1a-c** falls in the range ~1.08 Å, attained computationally. Further, increasing alkyl chain length may cause small effect on the geometrical parameters. Thus, the length of alkyl chain is increased (two carbons to six carbons) in the phenothiazine ring which would create a hydrophobic environment, consequently minimize aggregate formation and enhance power conversion efficiency [30].

Optical characteristics: The TD-DFT computations have been done for the dyes **1a-c** to acquire in sequence of the elect-

TABLE-2
SELECTED BOND ANGLE (°) OF DYES **1a-c**

1a	(°)	**1b**	(°)	**1c**	(°)
C2-C1-O4	121.7	C2-C1-O4	121.7	C2-C1-O4	121.7
C2-C1-N5	115.8	C2-C1-N5	115.8	C2-C1-N5	115.8
O4-C1-N5	122.5	O4-C1-N5	122.5	O4-C1-N5	122.5
C1-C2-C3	122.0	C1-C2-C3	122.0	C1-C2-C3	121.9
C1-C2-C22	114.0	C1-C2-C22	114.0	C1-C2-C22	114.0
C3-C2-C22	123.9	C3-C2-C22	123.9	C3-C2-C22	123.9
C2-C3-C8	132.2	C2-C3-C8	132.2	C2-C3-C8	132.2
C7-C6-C19	121.3	C7-C6-C19	121.4	C7-C6-C19	121.4
C6-C7-C8	122.0	C6-C7-C8	122.0	C6-C7-C8	122.0
C3-C8-C7	117.6	C3-C8-C7	117.6	C3-C8-C7	117.6
C3-C8-C9	125.6	C3-C8-C9	125.5	C3-C8-C9	125.6
C7-C8-C9	116.9	C7-C8-C9	116.9	C7-C8-C9	116.9
C8-C9-C10	121.4	C8-C9-C10	121.4	C8-C9-C10	121.4
C9-C10-S11	117.9	C9-C10-S11	117.8	C9-C10-S11	117.8
C9-C10-C19	121.6	C9-C10-C19	121.6	C9-C10-C19	121.6
S11-C10-C19	120.3	S11-C10-C19	120.4	S11-C10-C19	120.3
C10-S11-C12	99.4	C10-S11-C12	99.5	C10-S11-C12	99.4
S11-C12-C13	118.2	S11-C12-C13	118.1	S11-C12-C13	118.2
S11-C12-C17	120.7	S11-C12-C17	120.8	S11-C12-C17	120.8
C13-C12-C17	120.8	C13-C12-C17	120.9	C13-C12-C17	120.9
C12-C13-C14	120.8	C12-C13-C14	120.8	C12-C13-C14	120.8
C13-C14-C15	118.9	C13-C14-C15	118.9	C13-C14-C15	118.9
C14-C15-C16	120.5	C14-C15-C16	120.5	C14-C15-C16	120.5
C15-C16-C17	121.3	C15-C16-C17	121.3	C15-C16-C17	121.3
C12-C17-C16	117.5	C12-C17-C16	117.5	C12-C17-C16	117.5
C12-C17-N18	121.2	C12-C17-N18	121.2	C12-C17-N18	121.2
C16-C17-N18	121.3	C16-C17-N18	121.3	C16-C17-N18	121.3
C17-N18-C19	122.1	C17-N18-C19	122.2	C17-N18-C19	122.1
C6-C19-C10	116.8	C6-C19-C10	116.7	C6-C19-C10	116.7
C6-C19-N18	121.7	C6-C19-N18	121.6	C6-C19-N18	121.7

TABLE-3
SELECTED DIHEDRAL ANGLE OF DYES **1a-c**

1a	(°)	**1b**	(°)	**1c**	(°)
O4-C1-C2-C3	-151.4	O4-C1-C2-C3	151.1	O4-C1-C2-C3	151.1
O4-C1-C2-C22	24.7	O4-C1-C2-C22	-24.8	O4-C1-C2-C22	-24.9
N5-C1-C2-C3	26.5	N5-C1-C2-C3	-26.8	N5-C1-C2-C3	-26.8
N5-C1-C2-C22	-157.5	N5-C1-C2-C22	157.3	N5-C1-C2-C22	157.3
C1-C2-C3-C8	177.9	C1-C2-C3-C8	-177.7	C1-C2-C3-C8	-177.9
C22-C2-C3-C8	2.3	C22-C2-C3-C8	-2.2	C22-C2-C3-C8	-2.3
C2-C3-C8-C7	-176.2	C2-C3-C8-C7	175.3	C2-C3-C8-C7	175.6
C2-C3-C8-C9	4.0	C2-C3-C8-C9	-4.7	C2-C3-C8-C9	-4.6
C19-C6-C7-C8	-1.0	C19-C6-C7-C8	1.0	C19-C6-C7-C8	1.0
C7-C6-C19-C10	-1.2	C7-C6-C19-C10	0.9	C7-C6-C19-C10	1.1
C7-C6-C19-N18	179.8	C7-C6-C19-N18	179.9	C7-C6-C19-N18	-179.8
C6-C7-C8-C3	-178.6	C6-C7-C8-C3	179.0	C6-C7-C8-C3	178.7
C6-C7-C8-C9	1.2	C6-C7-C8-C9	-1.0	C6-C7-C8-C9	-1.1
C3-C8-C9-C10	-179.4	C3-C8-C9-C10	179.1	C3-C8-C9-C10	179.3
C7-C8-C9-C10	0.8	C7-C8-C9-C10	-1.0	C7-C8-C9-C10	-0.9
C8-C9-C10-S11	170.4	C8-C9-C10-S11	-170.5	C8-C9-C10-S11	-170.5
C8-C9-C10-C19	-3.1	C8-C9-C10-C19	3.0	C8-C9-C10-C19	3.1
C9-C10-S11-C12	153.7	C9-C10-S11-C12	-154.3	C9-C10-S11-C12	-154.0
C19-C10-S11-C12	-32.6	C19-C10-S11-C12	32.1	C19-C10-S11-C12	32.4
C9-C10-C19-C6	3.2	C9-C10-C19-C6	-2.9	C9-C10-C19-C6	-3.1
C9-C10-C19-N18	-177.8	C9-C10-C19-N18	178.1	C9-C10-C19-N18	177.8
S11-C10-C19-C6	-170.2	S11-C10-C19-C6	170.4	S11-C10-C19-C6	170.3
S11-C10-C19-N18	8.8	S11-C10-C19-N18	-8.5	S11-C10-C19-N18	-8.8
C10-S11-C12-C13	-153.5	C10-S11-C12-C13	153.8	C10-S11-C12-C13	153.7
C10-S11-C12-C17	31.5	C10-S11-C12-C17	-31.2	C10-S11-C12-C17	-31.3
S11-C12-C13-C14	-172.6	S11-C12-C13-C14	172.3	S11-C12-C13-C14	172.4
C17-C12-C13-C14	2.5	C17-C12-C13-C14	-2.6	C17-C12-C13-C14	-2.6
S11-C12-C17-C16	173.1	S11-C12-C17-C16	-172.7	S11-C12-C17-C16	-172.9
S11-C12-C17-N18	-6.5	S11-C12-C17-N18	6.8	S11-C12-C17-N18	6.7
C13-C12-C17-C16	-1.8	C13-C12-C17-C16	2.0	C13-C12-C17-C16	1.9
C13-C12-C17-N18	178.6	C13-C12-C17-N18	-178.4	C13-C12-C17-N18	-178.5
C12-C13-C14-C15	-1.1	C12-C13-C14-C15	1.1	C12-C13-C14-C15	1.1
C13-C14-C15-C16	-0.8	C13-C14-C15-C16	0.9	C13-C14-C15-C16	0.9
C14-C15-C16-C17	1.5	C14-C15-C16-C17	-1.4	C14-C15-C16-C17	-1.5
C15-C16-C17-C12	-0.1	C15-C16-C17-C12	0.0	C15-C16-C17-C12	0.0
C15-C16-C17-N18	179.4	C15-C16-C17-N18	-179.6	C15-C16-C17-N18	-179.5
C12-C17-N18-C19	-27.2	C12-C17-N18-C19	26.4	C12-C17-N18-C19	26.7
C16-C17-N18-C19	153.3	C16-C17-N18-C19	-154.0	C16-C17-N18-C19	-153.8
C17-N18-C19-C6	-155.2	C17-N18-C19-C6	155.7	C17-N18-C19-C6	155.5
C17-N18-C19-C10	25.8	C17-N18-C19-C10	-25.4	O4-C1-C2-C3	-25.5

ronic transitions between virtual and occupied orbitals using CAM-B3LYP method. The computed absorption spectra in dichloromethane solution of the dyes **1a-c** are given in Fig. 3. The calculated absorption maxima, oscillator strengths (f) and excitation energies are gathered in Table-4. A couple of major absorption bands have been observed around 390 and 300 nm for all the three dyes in dichloromethane as a solvent. The widest absorption range and higher light absorption ability of the synthesized dyes **1a-c** would favour for enhancing the photovoltaic efficiency.

Frontier molecular orbitals and dye regeneration analysis: The molecular orbitals and their respective energies of the organic sensitizers are significant quantum chemical parameters to offer the thermodynamic driving force for injection of electron. In DSSCs, it is well recognized that the HOMO energy level of the sensitizers must be lower than the redox potential of the electrolyte (I^-/I_3^-) while the LUMO level must be upper in energy than the conduction band (CB) of the

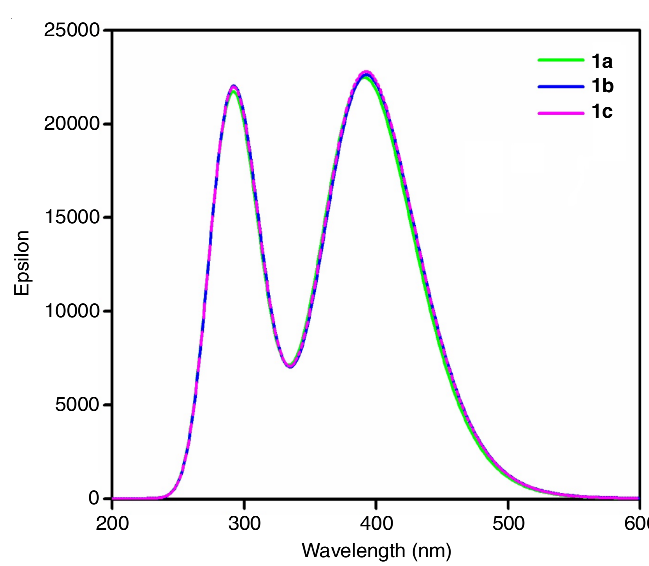


Fig. 3. Calculated UV-vis spectra of the dyes **1a-c** in dichloromethane

TABLE-4
EXPERIMENTAL AND CALCULATED PHOTOPHYSICAL DATA OF PHENOTHIAZINE-BASED DYES **1a-c**

Dyes	λ (nm)	E (eV)	f
1a	391.23 (H→L)	3.1691	0.5550
	300.32 (H-3→L)	4.1284	0.0019
	291.68 (H-3→L)	4.2507	0.5348
1b	392.73 (H→L)	3.1570	0.5585
	300.86 (H-3→L)	4.1209	0.0027
	292.04 (H-3→L)	4.2455	0.5415
1c	392.43 (H→L)	3.1594	0.5630
	300.76 (H-3→L)	4.1223	0.0028
	291.96 (H-3→L)	4.2466	0.5402

semiconductor (TiO_2) to attain finest performance. As seen in Fig. 1, the electron density of the HOMOs of the sensitizers **1a-c** is highly localized over the phenothiazine core along with very tiny on the cyanoacrylamide motif, whereas the electron density of the LUMO are nearly positioned on the cyanoacrylamide acceptor and slightly on the phenothiazine motif. Thus, the electron density distribution profile between the acceptor and donor indicates that the electron flow could be efficiently transferred into the semiconductor's CB. It is also noted that increasing the alkyl chain length from two carbons to four carbons/six carbons in the phenothiazine ring slightly reduce the HOMO-LUMO energy gap compared with the former one. On the whole, the small band gap energies and charge transfer profile suggest the fast electron transfer from dye into the CB of the semiconductor.

The driving force for dye regeneration of the synthesized photosensitizers **1a-c** has been computed and details are given in Table-5. It is found that the computed LUMO energies of the dyes **1a-c** are greater than the CB of TiO_2, which reveals that the electron transfer from the dye to CB of TiO_2 is more favourable. Likewise, the HOMO energy levels are found to be lesser than the redox potential of I^-/I_3^- and consequently, it provides fast regeneration of dye thereby avoiding recombination of charge between the photo-injected electrons and oxidized dyes in the semiconductor. As shown in Fig. 4, the energy levels of HOMO and LUMO of the dyes **1a-c** are well coincide with the necessity for a capable sensitizer, hence the synthesized

TABLE-5
CALCULATED FRONTIER MOLECULAR ORBITALS ENERGY VALUES OF PHENOTHIAZINE-BASED DYES **1a-c**

	HOMO	LUMO	ΔE (eV)	Dye regeneration driving force (eV)
1a	-5.7548	-3.6604	2.0944	0.9548
1b	-5.7488	-3.6601	2.0887	0.9488
1c	-5.7510	-3.6601	2.0909	0.9510

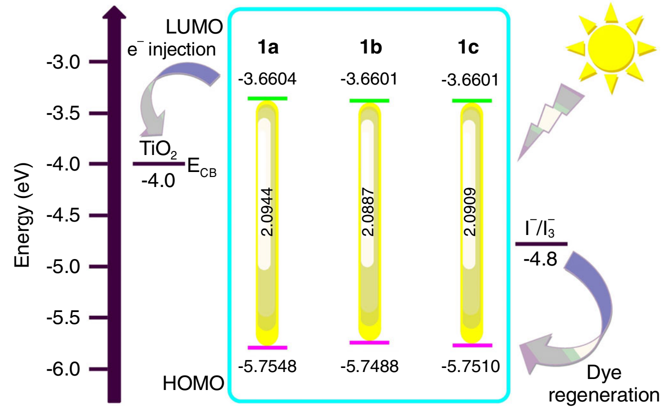


Fig. 4. FMOs energy levels of phenothiazine-based dyes **1a-c**

dyes could serve as potential candidates for DSSC application. The trend of dye regeneration of the photosensitizers **1a-c: 1a > 1c > 1b**.

Analysis of free energy of electron injection and light harvesting efficiency: In general, the photovoltaic efficiency of DSSCs [31,32] has been calculated from the incident photon to conversion efficiency (IPCE), which is straight away related to light harvesting efficiency (LHE), charge collection efficiency (η_c) and electron injection efficiency (Φ_{inj}).

$$IPCE = LHE \times \Phi_{inj} \times \eta_c \quad (1)$$

LHE can be expressed as:

$$LHE = 1-10^{-f} \quad (2)$$

where f is oscillator strength.

The Φ_{inj} is related to the free energy of electron injection

$$\Phi_{inj} \propto f(-\Delta G_{inject}) \quad (3)$$

Generally, the large ΔG_{inject} will result in the large Φ_{inj}, this lead to high PCE. The electron injection driving force (ΔG_{inject}) can be determined from the excited state oxidation potential of the dye and the ground state reduction potential of the CB of TiO_2 (-4.0).

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

$E_{ox}^{dye^*}$ can be derived from:

$$E_{ox}^{dye^*} = E_{ox}^{dye} - \Delta E \quad (5)$$

where E_{ox}^{dye} = ground state oxidation potential of the dye (*i.e.* $-E_{HOMO}$) and ΔE = energy of electronic vertical transition correspond to λ_{max}.

Table-6 shows the oscillator strength (f), driving force of electron injection (ΔG_{inject}) and light harvesting efficiency (LHE) and of three dyes **1a-c** obtained from TD-DFT calculations. The LHE and driving force of electron injection (ΔG_{inject}) can be obtained from the eqns. 2 and 4, respectively. The LHE of

TABLE-6
CALCULATED OXIDATION POTENTIAL, THE ELECTRONIC VERTICAL TRANSITION ENERGY ASSOCIATED WITH THE λ_{max}, LHE AND ΔG_{inject} OF PHENOTHIAZINE-BASED DYES **1a-c**

	λ (nm)	E (eV)	f	E_{ox}^{dye}	$E_{ox}^{dye^*}$	LHE	ΔG_{inject}
1a	391.23	3.1691	0.5550	5.7548	2.5857	0.7214	-1.4143
1b	392.73	3.1570	0.5585	5.7488	2.5918	0.7236	-1.4082
1c	392.43	3.1594	0.5630	5.7510	2.5916	0.7265	-1.4084

dye **1c** is higher (0.7265) than the dyes **1a** and **1b** (0.7214 and 0.7236). These results imply that the dye **1c** could harvest more light and leading to higher IPCE. The calculated ΔG_{inject} of all the three dyes **1a-c** are negative. This result clearly states that the CB of semiconductor lies lower than the excited state of the dyes (LUMO) and it favour for electron transfer. Thus, the LHE and ΔG_{inject} are associated with IPCE; one can find that the dye **1c** has higher LHE and electron injection driving force compared to the other dyes **1a** and **1b** which result in higher IPCE.

Conclusion

Three photosensitizers **1a-c** based on phenothiazine linked with cyanoacrylamide have been designed. Theoretical investigations reflect that the photosensitizers **1a-c** can be used as suitable candidates for making DSSCs, having its enhanced electronic and optical properties. The high LHE (0.7265) of the dye **1c** could harvest more light and leading to higher IPCE. The negative ΔG_{inject} of the dyes **1a-c** demonstrate thermodynamically favourable for electron injection from the dyes (LUMO) to the conduction band (CB) of TiO_2.

ACKNOWLEDGEMENTS

Financial assistance provided by Kalasalingam Academy of Research and Education, Anand Nagar, India is gratefully acknowledged.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. B. O'Regan and M. Grätzel, *Nature*, **353**, 737 (1991); https://doi.org/10.1038/353737a0
2. W. Zeng, Y. Cao, Y. Bai, Y. Wang, Y. Shi, M. Zhang, F. Wang, C. Pan and P. Wang, *Chem. Mater.*, **22**, 1915 (2010); https://doi.org/10.1021/cm9036988
3. Z.-S. Wang, N. Koumura, Y. Cui, M. Takahashi, H. Sekiguchi, A. Mori, T. Kubo, A. Furube and K. Hara, *Chem. Mater.*, **20**, 3993 (2008); https://doi.org/10.1021/cm8003276
4. K. Kakiage, Y. Aoyama, T. Yano, T. Otsuka, T. Kyomen, M. Unno and M. Hanaya, *Chem. Commun.*, **50**, 6379 (2014); https://doi.org/10.1039/c4cc02192d
5. S. Kim, J.K. Lee, S.O. Kang, J. Ko, J.-H. Yum, S. Fantacci, F. De Angelis, D. Di Censo, M.K. Nazeeruddin and M. Grätzel, *J. Am. Chem. Soc.*, **128**, 16701 (2006); https://doi.org/10.1021/ja066376f
6. A. Karuppasamy, K. Stalindurai, J.D. Peng, K.C. Ho and C. Ramalingan, *Electrochim. Acta*, **268**, 347 (2018); https://doi.org/10.1016/j.electacta.2018.02.134
7. T. Horiuchi, H. Miura, K. Sumioka and S. Uchida, *J. Am. Chem. Soc.*, **126**, 12218 (2004); https://doi.org/10.1021/ja0488277
8. D. Kuang, S. Uchida, R. Humphry-Baker, S.M. Zakeeruddin and M. Gratzel, *Angew. Chem. Int. Ed.*, **120**, 1949 (2008); https://doi.org/10.1002/ange.200705225
9. T. Edvinsson, C. Li, N. Pschirer, J. Schöneboom, F. Eickemeyer, R. Sens, G. Boschloo, A. Herrmann, K. Müllen and A. Hagfeldt, *J. Phys. Chem. C*, **111**, 15137 (2007); https://doi.org/10.1021/jp076447c
10. Y. Shibano, T. Umeyama, Y. Matano and H. Imahori, *Org. Lett.*, **9**, 1971 (2007); https://doi.org/10.1021/ol070556s
11. W. Wu, J. Yang, J. Hua, J. Tang, L. Zhang, Y. Long and H. Tian, *J. Mater. Chem.*, **20**, 1772 (2010); https://doi.org/10.1039/b918282a
12. A. Karuppasamy, K. Stalindurai, J.D. Peng, K.C. Ho and C. Ramalingan, *Phys. Chem. Chem. Phys.*, **18**, 30105 (2016); https://doi.org/10.1039/C6CP05722E
13. R. Chen, X. Yang, H. Tian, X. Wang, A. Hagfeldt and L. Sun, *Chem. Mater.*, **19**, 4007 (2007); https://doi.org/10.1021/cm070617g
14. R. Chen, X. Yang, H. Tian and L. Sun, *J. Photochem. Photobiol. Chem.*, **189**, 295 (2007); https://doi.org/10.1016/j.jphotochem.2007.02.018
15. L. Zhang and J.M. Cole, *ACS Appl. Mater. Interfaces*, **7**, 3427 (2015); https://doi.org/10.1021/am507334m
16. K. Stalindurai, A. Karuppasamy, J.D. Peng, K.C. Ho and C. Ramalingan, *Electrochim. Acta*, **246**, 1052 (2017); https://doi.org/10.1016/j.electacta.2017.06.151
17. K. Stalindurai, A. Karuppasamy, J.-D. Peng, K.C. Ho, A. Tamilselvan and C. Ramalingan, *Tetrahedron*, **73**, 278 (2017); https://doi.org/10.1016/j.tet.2016.12.019
18. Y. Hua, S. Chang, H. Wang, D. Huang, J. Zhao, T. Chen, W.Y. Wong, W.K. Wong and X. Zhu, *J. Power Sources*, **243**, 253 (2013); https://doi.org/10.1016/j.jpowsour.2013.05.157
19. Y. Hua, S. Chang, J. He, C. Zhang, J. Zhao, T. Chen, W.-Y. Wong, W.-K. Wong and X. Zhu, *Chem. Eur. J.*, **20**, 6300 (2014); https://doi.org/10.1002/chem.201304897
20. H. Tian, X. Yang, R. Chen, Y. Pan, L. Li, A. Hagfeldt and L. Sun, *Chem. Commun.*, **36**, 3741 (2007); https://doi.org/10.1039/b707485a
21. S.H. Kim, H.W. Kim, C. Sakong, J. Namgoong, S.W. Park, M.J. Ko, C.H. Lee, W.I. Lee and J.P. Kim, *Org. Lett.*, **13**, 5784 (2011); https://doi.org/10.1021/ol2023517
22. X. Yang, J. Zhao, L. Wang, J. Tian and L. Sun, *RSC Adv.*, **4**, 24377 (2014); https://doi.org/10.1039/c4ra01858c
23. S. Wang, H. Wang, J. Guo, H. Tang and J. Zhao, *Dyes Pigments*, **109**, 96 (2014); https://doi.org/10.1016/j.dyepig.2014.05.015
24. H.H. Gao, X. Qian, W.Y. Chang, S.S. Wang, Y.Z. Zhu and J.Y. Zheng, *J. Power Sources*, **307**, 866 (2016); https://doi.org/10.1016/j.jpowsour.2016.01.055
25. W.I. Hung, Y.Y. Liao, C.Y. Hsu, H.H. Chou, T.H. Lee, W.S. Kao and J.T. Lin, *Chem. Asian J.*, **9**, 357 (2014); https://doi.org/10.1002/asia.201301228
26. A.D. Becke, *J. Chem. Phys.*, **98**, 1372 (1993); https://doi.org/10.1063/1.464304
27. T. Yanai, D.P. Tew and N.C. Handy, *Chem. Phys. Lett.*, **393**, 51 (2004); https://doi.org/10.1016/j.cplett.2004.06.011
28. 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, Jr., 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, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski and D.J. Fox, Gaussian 09, Revision E.01, Wallingford CT (2009).
29. B. Nagarajan, S. Kushwaha, R. Elumalai, S. Mandal, K. Ramanujam and D. Raghavachari, *J. Mater. Chem. A Mater. Energy Sustain.*, **5**, 10289 (2017); https://doi.org/10.1039/C7TA01744H
30. A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, **110**, 6595 (2010); https://doi.org/10.1021/cr900356p
31. W. Fan, D. Tan and W.-Q. Deng, *ChemPhysChem*, **13**, 2051 (2012); https://doi.org/10.1002/cphc.201200064
32. W.L. Ding, D.M. Wang, Z.Y. Geng, X.L. Zhao and W.B. Xu, *Dyes Pigments*, **98**, 125 (2013); https://doi.org/10.1016/j.dyepig.2013.02.008