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Theoretical Analysis into the impact of π-spacers on Triphenylamine based Organic Sensitizers for Dye Sensitized Solar Cells (DSSCs)

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Abstract: In the present study, thirteen triphenylamine-based organic dye sensitizers with donor-π-acceptor patterns were created for utilization in dye sensitized solar cells (DSSCs). Theoretical computations such as DFT and TDDFT were employed to analyse the molecular structure of the dyes. Optimization was attained using the DFT/B3LYP approach with the 6-311++G (d,p) basis set to investigate structural and spectroscopic parameters. This study deals with the effect of different π-spacers. The electrochemical characteristics, electronic absorption spectra, energy levels, injection energy, light harvesting efficiency (LHE), frontier molecular orbitals, and dye generation energy were examined. All the created dyes are suitable for DSSC applications. The parameters such as low bandgap (2.30 eV), high light harvesting efficiency (0.972), strong oscillator strength, broad absorption spectrum and high electron injection energy made the dye P6 the best-performing one.

Keywords: Dye Sensitized Solar Cells, Organic sensitizers, Triphenylamine, Cyanovinyl, Light Harvesting Efficiency

1. Introduction

DSSCs have multiple features that include simple working methods, low cost and easy to assemble the cell [1]. Furthermore, DSSCs have pleasing properties like transparency, flexibility, attractive colours, non-hazardous and nature-friendly. DSSCs are low in weight and possess efficiency to be superior to the traditional solar cells which are silicon-based and can be utilised both outdoors and indoors. DSSCs can be used for outdoor purposes such as portable solar chargers for camping, solar-powered devices, and solar-powered vehicles, used as power sensors in irrigation systems and in remote monitoring devices [2-5]. DSSCs are used indoors instead of silicon-based solar cells because they can be made with lesser-cost materials and methods, which make them a good choice for collecting energy the inside [6]. The working of a DSSC is replicates the procedure of photosynthetic in plants. Light energy is transformed to electrical energy by dye sensitizers in DSSC. For this purpose, the dye molecules should be attached to the working electrode which is usually an array of semiconductors. The electron present in the dye needs to be injected in the semiconductor's conduction band in order to generate photocurrent [7].

Donor-π-Acceptor structured dyes have become popular owing to their convenient preparation and purification steps, high molar absorptivity, wider absorption spectra and ability to adjust the structure for specific features [8]. Several dyes have been made by changing the acceptor, donor and π-spacer to enhance the electron injection [9-11]. The donor groups are responsible of light collecting which is in accountable for highest occupied molecular orbital (HOMO) [12], oxidation potential and dye generation driving force [13], the acceptor groups have been assigned for managing lowest unoccupied molecular orbital (LUMO) [14] which controls electron injection into the conduction band [15,16]. The π-bridges are crucial for intramolecular charge transfer [17]. Triphenylamine has been analysed commonly due to the remarkable hole-transport characteristics, electron-donating capacity [18] and the best conversion efficiency [19]. Cyanoacrylic acid is an appropriate acceptor part because of its excellent binding capacity to the titanium dioxide surface [20]. Thiophene and its derivatives are often chosen as dyes in both organic solar cells and DSSC based on their excellent light absorbing characteristics in the near-infrared and visible regions of the electromagnetic spectrum [21], smaller energy gap, best power conversion efficiency (PCE) and best carrier transport

ability [22]. Cyanovinyl has a good electron-withdrawing nature that boosts charge transfer and lowers the band gap [23, 24] and it also stabilizes the LUMO level [25] and good option for π-spacer. Donor parts such as coumarin [26], carbazole [27], indoline [28, 29], phenothiazine [30], tetrahydroquinoline [31, 32], phenoxazine [33], cyanine [34], merocyanine [35] are employed frequently in the D-π-A pattern and used for strong photovoltaic sensitizers.

The theoretical methods such as DFT and TDDFT minimize the expense and time required for the development of innovative dyes experimentally by selecting the effective candidates prior to synthesis. By utilising simulations researchers can visualize frontier molecular orbitals and understand the functioning of electron transfer which is essential for boosting charge injection as well as the dye regeneration process in DSSCs [36, 37].

In this work, we discuss the computational investigations of a few organic dye molecules based on triphenylamine for usage in DSSC applications. The π-linkers in the sensitizer molecule include cyanovinyl, ethylene, and thiophene subunits, while the acceptor group is cyanoacrylic acid and the donor group is triphenylamine. The effects of π-spacer arrangements in the sensitizer are investigated. The electrical and optical properties and ground state optimised structure of thirteen organic dye molecules are investigated for DSSC applications using theoretical methodologies.

This study presented novel modifications of π-linkers and analysed their effect on the Frontier molecular orbitals of the dyes, absorption spectra, bandgap energies and charge transfer characteristics. The results demonstrated a direct correlation between the number and position of π-spacers which led to the stabilization of LUMO, the destabilization of HOMO and a significant reduction of the band gap that has not been previously reported.

2. Methods

DFT and TD-DFT approaches are considered crucial techniques for studying the electrical as well as optical features of dye sensitizers and that was applied to analyse the optoelectronic features. The Gaussian 09 W package was the software used for all the computations in the present study [38]. Using B3LYP [39] functional and 6-311++G(d,p) [40] basis set the optimised structure in the gas phase of the dyes was performed [41]. To simulate the solvent environment the polarizable continuum model of the SCRF [42] procedure in the solvent (chloroform) phase was employed ensuring accurate results compared to experimental data. The frequency computations were performed with an exact theoretical level and shown to be in the ground state that has the smallest potential energy for all the molecules. To draw molecular structural images the Gauss View 5.0 [43] program package was employed.

2.1 Geometrical structure of the dyes

Triphenylamine serves as the donor group and cyanoacrylic acid serves as the key acceptor group in the D-π-A (donor-π-acceptor) structure. The π-linker configurations are cyanovinyl, thiophene and ethylene used to design new dyes. The optimized D-π-A configurations are displayed in Figure 1. The π spacer combinations of thirteen dyes were shown in Figure2.

3. Results and Discussion

3.1 Analysis of Frontier Molecular Orbital (FMO)

The electron acceptor's LUMO and the electron donor's HOMO in electronic excitation are crucial parameters for electron transfer [44]. The analysis of FMO plays an important role in electrical and optical characteristics [45]. The HOMO and LUMO of dye sensitizers are displayed in figure 3. The HOMO is localized across the donor unit (triphenylamine) and has a negligible effect in the COOH group and small distribution on π-spacers in all dye sensitizers. Each dye sensitizer's LUMO is localized across the acceptor's OH group (cyanoacrylic acid) and π-bridge. The HOMO and LUMO are linked to dyes' electronic excitation [46] as well as transition properties [47]. Table 1 lists the energy Eigen values for the HOMO and LUMO. Both the LUMO and the HOMO should have well-overlapping orbitals and a good electron separated state. An atom with higher densities of HOMO should be capable of removing electrons more easily than one with higher densities of LUMO, which makes it simpler to acquire electrons. This process is quite evident in the energy spectrum for the gas phase given in Figure 4. It can be mentioned that all dyes are advantageous for DSSC applications.

3.2 Electronic structure of the sensitizers

The HOMO and LUMO play essential roles in the photoexcitation process. Figure 3 illustrates the distribution of electron density of designed sensitizers in gas phase. The electron density distribution for each dyes show that the HOMO electron density is primarily localised in the donor and π-spacer groups, while the LUMO is mostly localised in the acceptor group and π-linkers. It implies that the energy levels that are well-separated during photoexcitation allow an efficient intramolecular charge transition.

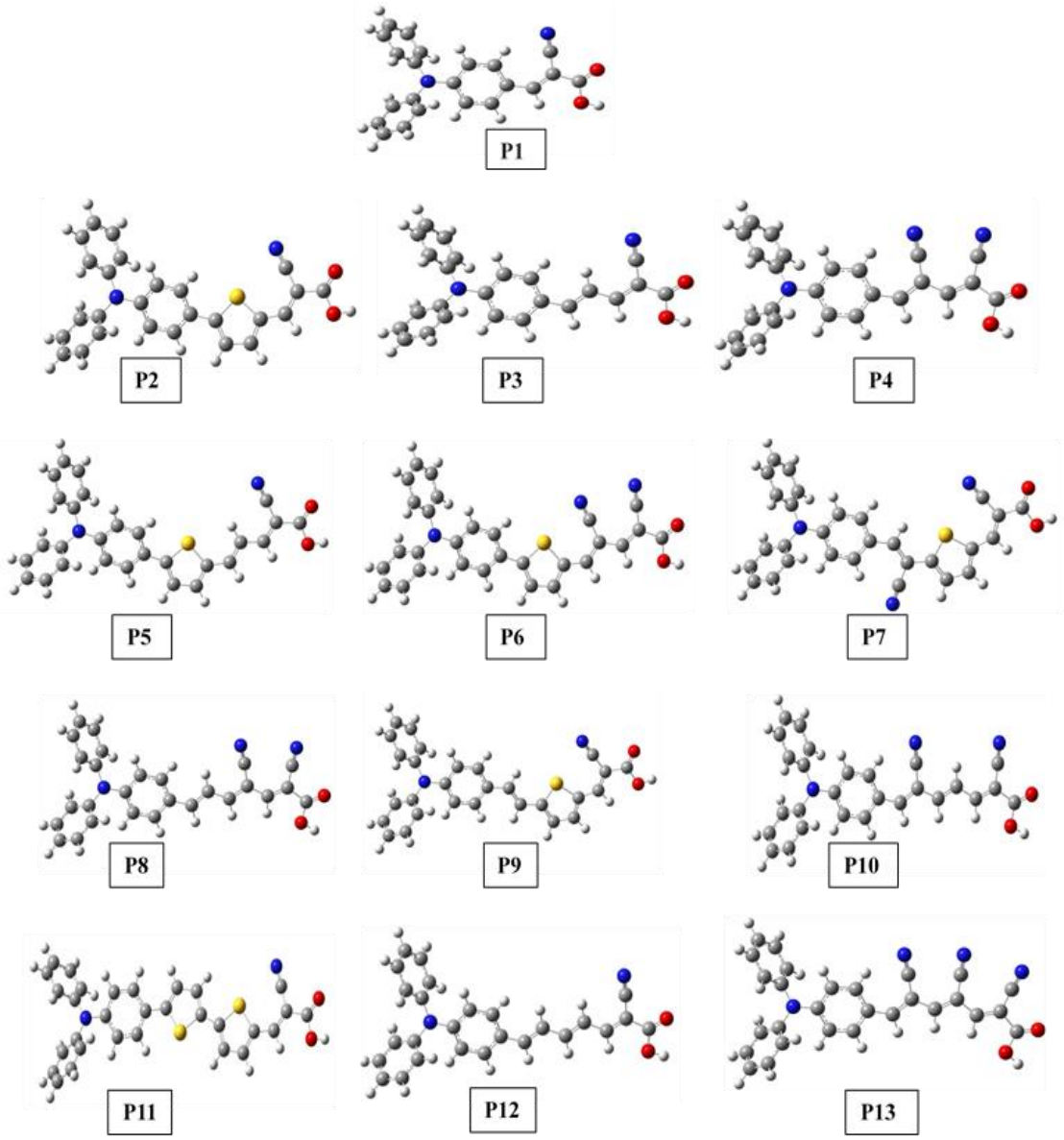

Figure 1. Optimized molecular structure of designed sensitizers

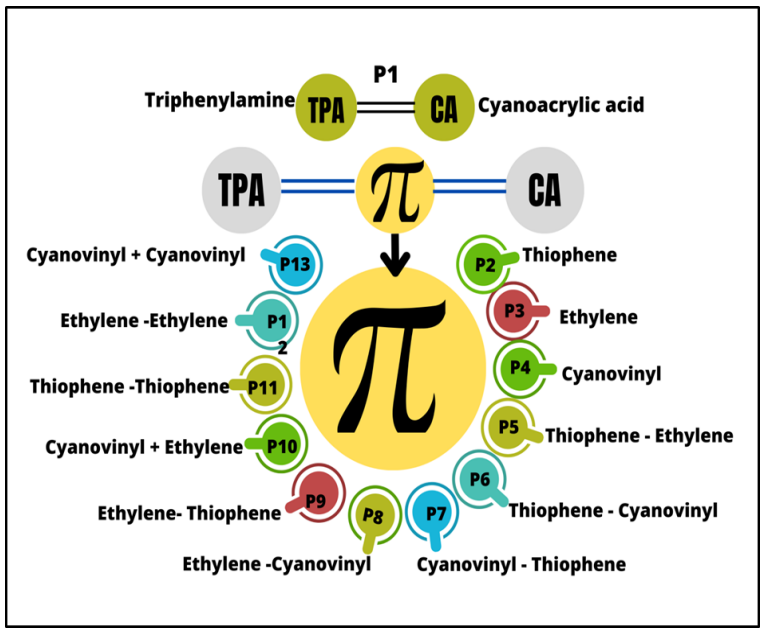

Figure 2. The π spacer combinations of dyes

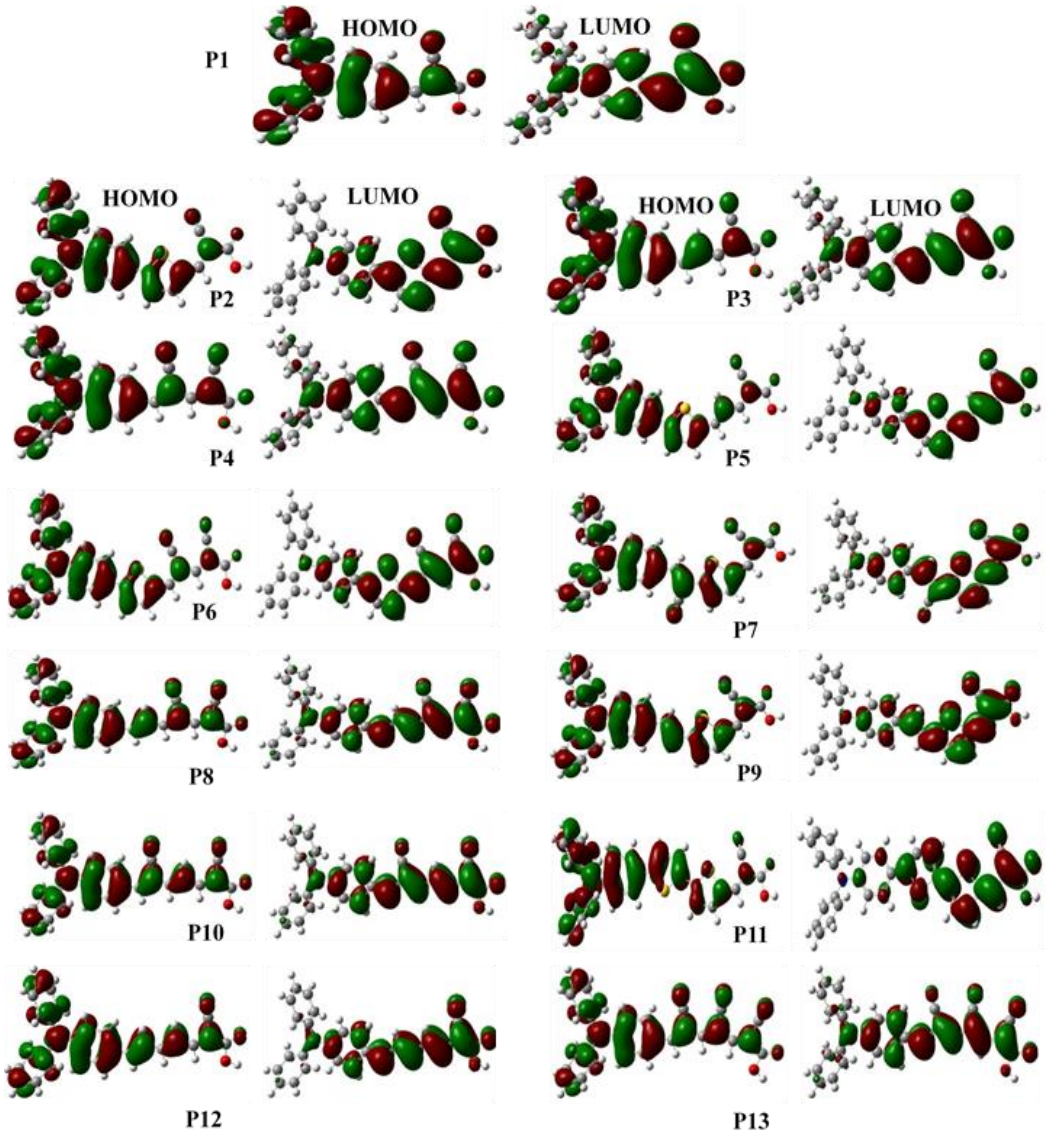

Figure 3. Frontier molecular orbital (FMO) of designed sensitizers

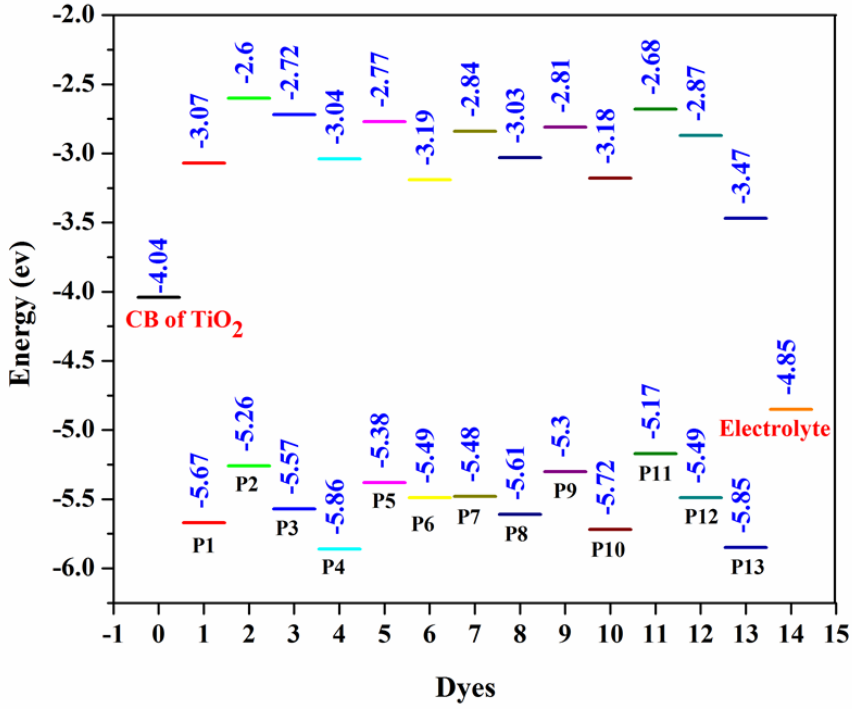

Figure 4 HOMO-LUMO energy level of dye sensitizers

Table 1. HOMO-LUMO and band gap values of dye sensitizers

Dye	Gas phase			Solvent phase		
	HOMO (eV)	LUMO (eV)	Band Gap (eV)	HOMO (eV)	LUMO (eV)	Band Gap (eV)
P1	-5.67	-3.07	2.60	-5.68	-2.59	3.09
P2	-5.26	-2.6	2.66	-5.42	-2.85	2.57
P3	-5.57	-2.72	2.85	-5.52	-2.8	2.72
P4	-5.86	-3.04	2.82	-5.78	-3.08	2.70
P5	-5.38	-2.77	2.61	-5.36	-2.98	2.38
P6	-5.49	-3.19	2.30	-5.48	-3.25	2.23
P7	-5.48	-2.84	2.64	-5.53	-3.16	2.37
P8	-5.61	-3.03	2.58	-5.61	-3.24	2.37
P9	-5.3	-2.81	2.49	-5.3	-2.97	2.33
P10	-5.72	-3.18	2.54	-5.64	-3.14	2.50
P11	-5.17	-2.68	2.49	-5.3	-2.98	2.32
P12	-5.49	-2.87	2.62	-5.41	-2.94	2.47
P13	-5.85	-3.47	2.38	-5.84	-3.41	2.43

The results from Table 1 indicate that increasing the number of π-linkers in the (D-π-A) pattern results in a decreased band gap energy which is caused by the expanded π-conjugation as well as the overlap of neighbouring π-orbitals. The P5 and P9 structures have the identical π-spacer configuration and chemical formula, whereas configurations P6 and P7, P8 and P10 also follow the same protocol but their band gap, LUMO and HOMO energies in the sensitizer are different from one another. Figure 4. shows the dye sensitizers' HOMO-LUMO energy level in the gas phase. The dyes' band gap energy in the gas phase falls between 2.30 eV and 2.85 eV, in the order P6<P3<P11=P9<P10<P8 <P1<P5<P12 <P7<P2<P4<P3. The dyes' band gap energy in the solvent phase falls between 2.23 eV and 3.09 eV, in the order P6<P11<P9<P7=P8<P5<P13<P12<P10<P2<P4<P3<P 1. The band gap of all the created dyes except P1 was less in the solvent phase compared to the gas phase.

3.3 Electronic Absorption Spectrum

The electronic absorption spectra and optical characteristics of the organic dye sensitizers may now be accurately simulated using the TD-DFT calculation. Figure 5, which depicts the gas phase, displays the simulated electronic absorption spectra of all 13 dyes. The dyes that absorb the maximum wavelengths (λ_{max}) for the dyes in the gas phase are provided in table 2. The λ_{max} values of the synthesised dyes range from 359 nm to 454 nm. P6 exhibits highest λ_{max} value (454 nm). The spectrum of absorption Figure 5 displays a red shift due to the π-orbital overlap and resonance conjugation. The range of electronic absorption spectrum of all the dyes in gas phase cover ranges from 200 nm to 650 nm that is sufficient for the sensitizer to absorb more sunlight. P6 is a dye sensitizer that has a broadening region than other dyes that are designed. The λ_{max} values in the gas phase of the 13 dye sensitizers are arranged as follows: P6>P7>P9>P8>P13>P11>P5>P10>P4>P12>P2>P3>P 1.

3.4 The oscillator strength (OS) and light harvesting efficiency (LHE)

Table 2, 3 lists the absorption spectral aspects of the 13 dyes in gas phase and solvent phase respectively. The main transition in all triphenylamine dyes is HOMO→LUMO. In all 13 configurations the HOMO→LUMO transition makes a larger contribution. This demonstrates how efficient the sensitizer is. Regardless of whether a transition is permitted or not, the oscillator strength takes it into account and indicates the intensity of the spectral band. All the 13 dye sensitizers have high oscillator strength values ranging from 0.985 to 1.978 in the gas phase and 1.117 to 2.119 in the chloroform phase.

The PCE is an essential measure to evaluate the efficiency of DSSCs [48]. The oscillator strength is used to compute the dyes' LHE. The 13 dye sensitizers' LHE values were determined using the equation LHE=1-10^{-f} [49] in which f represents the oscillator strength at the maximum wavelength. To improve the photocurrent performance, higher LHE values are essential [50]. Triphenylamine dye sensitizers have greater LHE values in the 0.897 and 0.999 range. The outcomes

demonstrate that the created sensitizers' light harvesting efficiency is suitable for DSSC applications.

3.5 Charge transfer properties

The dye regeneration driving force ΔG_{regen} is obtained from the change in HOMO energy and E_{OX}^{dye} of the electrolyte. The driving force of electron injection which is represented by ΔG_{inject} is obtained by the change in dyes'excited state energy and the energy of the conduction band of the semiconductor. The electron injection rate is closely linked to the oscillator strength (f). It is suitable to conclude that the electron injection ability from the excited state approaches to a unit in circumstances where ΔG^{inject} is larger than 0.2 eV [51].

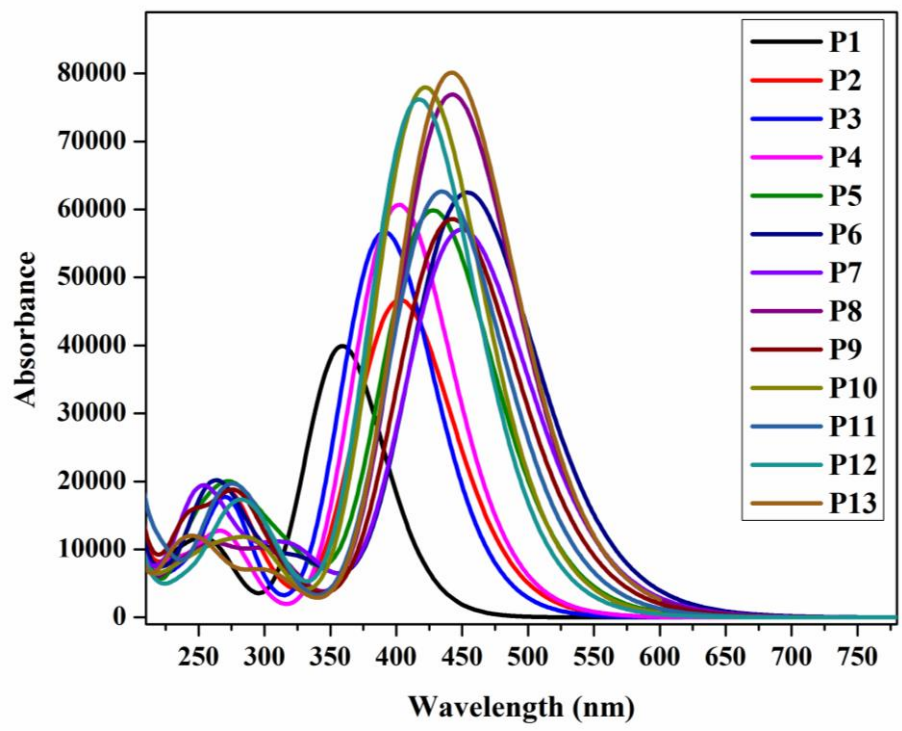

Figure 5 Electronic absorption spectrum of dye sensitizers in gas phase

Table 2. The absorption spectral aspects of six dyes in gas phase

Dye	Energy (eV)	λ_{max} (nm)	Oscillator strength	Electronic contribution	Light harvesting efficiency
P1	3.45	359	0.985	H→L (93%)	0.897
P2	3.08	403	1.158	H→L (83%)	0.931
P3	3.17	391	1.399	H→L (91%)	0.961
P4	2.95	420	1.498	H→L (93%)	0.969
P5	2.90	428	1.477	H→L (80%)	0.967
P6	2.73	454	1.542	H→L (84%)	0.972
P7	2.76	450	1.408	H→L (85%)	0.961
P8	2.81	442	1.898	H→L (92%)	0.988
P9	2.80	443	1.446	H→L (82%)	0.965
P10	2.94	422	1.925	H→L (91%)	0.989
P11	2.86	434	1.546	H→L (70%)	0.972
P12	2.97	417	1.881	H→L (90%)	0.987
P13	2.81	441	1.978	H→L (93%)	0.990

Table 3. The oscillator strength values of dye sensitizers both in gas and solvent phase

Dye	Gas Phase		Solvent Phase	
	λ_{max}	Oscillator strength	λ_{max}	Oscillator strength
P1	359	0.985	382	1.117
P2	403	1.158	427	1.270
P3	391	1.399	420	1.536
P4	420	1.498	433	1.642
P5	428	1.477	456	1.601
P6	454	1.542	487	1.680
P7	450	1.408	477	1.522
P8	442	1.898	482	2.033
P9	443	1.446	472	1.544
P10	422	1.925	455	2.068
P11	434	1.546	459	1.654
P12	417	1.881	451	2.017
P13	441	1.978	479	2.119

Table 4. Electrochemical aspects in the gas phase

Dye	E_{OX}^{dye} (eV)	λ_{max} (nm)	$E(\lambda_{max}^{ICT})$(eV)	E_{OX}^{dye*}(eV)	ΔG^{inject}(eV)	G_{dye}^{regen}(eV)
P1	5.67	359	3.45	2.22	-1.78	0.82
P2	5.26	403	3.08	2.18	-1.82	0.41
P3	5.57	391	3.17	2.40	-1.60	0.72
P4	5.86	420	2.95	2.91	-1.09	1.01
P5	5.38	428	2.90	2.48	-1.52	0.53
P6	5.49	454	2.73	2.76	-1.24	0.64
P7	5.48	450	2.76	2.72	-1.28	0.63
P8	5.61	442	2.81	2.80	-1.20	0.76
P9	5.3	443	2.80	2.50	-1.50	0.45
P10	5.72	422	2.94	2.78	-1.22	0.87
P11	5.17	434	2.86	2.31	-1.69	0.32
P12	5.49	417	2.97	2.52	-1.48	0.64
P13	5.85	441	2.81	3.04	-0.96	1.00

To efficiently inject charge, the dye's LUMOs are positioned above the conduction band edge [52]. TheE_{OX}^{dye} , λmax, E($\lambda_{\max}^{ICT}$), E_{OX}^{dye*}, ΔG^{inject}, and G_{dye}^{regen} for 13 dyes were computed by TD-DFT in gas phase and been listed in table 4. The evaluated ΔG^{inject} values are negative, indicating that the suggested sensitizers undergo spontaneous processes for both dye regeneration and charge injection [53]. Sufficient driving

force is crucial for dye regeneration and decrease the loss of electrons even further. It is discovered that all dye sensitizers have a higher regeneration driving force (ΔG_{reg}), which improves their inherent capacity to absorb electrons.

E_{ox}^{dye} -Redox potential of the iodide/triiodide electrolyte, E_{ox}^{dye*} -Oxidized potential of the dye in the excited state, ΔG_{inject} - driving force of electron injection and ΔG_{regen}-driving force of regeneration

4. Conclusion

The study of thirteen organic dye sensitizers incorporating triphenylamine donor fragments, cyanoacrylic acid functioning as the acceptor and varying π-conjugated spacers reveals their capability for DSSC applications theoretically. The band gap energies of all the dyes span from 2.30 eV to 2.85 eV in the gas phase and from 2.23 eV to 3.09 eV in the chloroform phase. The dyes show enhanced electron transfer because of the HOMO distribution in the triphenylamine donor and LUMO localization across the cyanoacrylic acid acceptor and π-linkers. In the gas phase the oscillator strengths crucial for light absorption fall within the range of 0.985 and 1.978 and the light harvesting efficiencies between 0.897 and 0.999. The dyes' HOMO lies below the reduction potential of the electrolyte (I^-/I_3^-), indicating the sensitizers' preferential thermodynamic regeneration. The findings demonstrate that all the dye sensitizers that were designed have the potential to be effective sensitizers for DSSC applications. P6 is prominent due its minimal band gap (2.38 eV in gas phase, 2.23 eV in solvent phase), higher λ_{max}(454 nm), and greater LHE (0.972) making it the leading dye for DSSC purposes. P6 assures effective charge transfer and reduces recombination of electrons with its desirable electron injection energy and significant dye regeneration driving force.

References

[1] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Dye-sensitized solar cells. Chemical Reviews, 110, (2010) 6595–6663. https://doi.org/10.1021/cr900356p

[2] Y.S. Tingare, N.S. Vinh, H.H. Chou, Y.C. Liu, Y.S. Long, T.C. Wu, T.C. Wei, C.Y. Yeh, New acetylene-bridged 9, 10-conjugated anthracene sensitizers: application in outdoor and indoor dye-sensitized solar cells. Advance Energy Materials, 7(8), (2017) 1700032. https://doi.org/10.1002/aenm.201700032

[3] S. Venkatesan, W.H. Lin, H. Teng, Y.L. Lee, High-efficiency bifacial dye-sensitized solar cells for application under indoor light conditions. ACS Applied Materials & Interfaces, 11, (2019) 42780–42789. https://doi.org/10.1021/acsami.9b14876

[4] M.C. Tsai, C.L. Wang, C.W. Chang, C.W. Hsu, Y.H. Hsiao, C.L. Liu, C.C. Wang, S.Y. Lin, C.Y. Lin, A large, ultra-black, efficient and cost-effective dye-sensitized solar module approaching 12% overall efficiency under 1000 lux indoor light. Journal of Materials Chemistry A, 6, (2018) 1995–2003. https://doi.org/10.1039/C7TA09322E

[5] J. Wu, Y. Xiao, Q. Tang, G. Yue, J. Lin, M. Huang, Y. Huang, L. Fan, Z. Lan, S. Yin, T. Sato, A Large-Area Light-Weight Dye-Sensitized Solar 312 Cell based on All Titanium Substrates with an Efficiency of 6.69% Outdoors. Advanced Materials, 24(14), (2012) 1884–1888. https://doi.org/10.1002/adma.201200003

[6] J. Gong, K. Sumathy, Q. Qiao, Z. Zhou, Review on dye-sensitized solar cells (DSSCs): advanced techniques and research trends, Renewable and Sustainable Energy Reviews 68, (2017) 234–246. https://doi.org/10.1016/j.rser.2016.09.097

[7] S.J. Sharma, K.K. Sonigara, H.K. Machhi, S.S. Soni, N. Sekar, Significance of anchoring group design on light harvesting efficiency of dye-sensitized solar cells and non-linear optical response. Journal of Molecular Structure, 1294, (2023) 136435. https://doi.org/10.1016/j.molstruc.2023.136435

[8] A. Mishra, M.K. Fischer, P. Bauerle, Metal-free organic dyes for dye-sensitized solar cells: from structure: property relationships to design rules. Angewandte Chemie International Edition, 48(14), (2009) 2474-2499. https://doi.org/10.1002/anie.200804709

[9] B. Nagarajan, S. Kushwaha, R. Elumalai, S. Mandal, K. Ramanujam, D. Raghavachari, Novel ethynyl-pyrene substituted phenothiazine-based metal free organic dyes in DSSC with 12% conversion efficiency. Journal of Materials Chemistry A, 5, (2017) 10289–10300. https://doi.org/10.1039/C7TA01744H

[10] J. Sivanadanam, R. Mukkamala, S. Mandal, R. Vedarajan, N. Matsumi, I.S. Aidhen, K. Ramanujam, Exploring the role of the spacers and acceptors on the triphenylamine-based dyes for dye-sensitized solar cells. International Journal of Hydrogen Energy, 43(9), (2018) 4691–4705. https://doi.org/10.1016/j.ijhydene.2017.10.183

[11] S. Mandal, G.R. Kandregula, V.N.B. Tokala, A computational investigation of the influence of acceptor moieties on photovoltaic performances and adsorption onto the TiO2 surface in triphenylamine-based dyes for DSSC application. Journal of Photochemistry and Photobiology A: Chemistry A, 401, (2020) 112745. https://doi.org/10.1016/j.jphotochem.2020.112745

[12] R. Kacimi , M. Raftani , T. Abram , A. Azaid , H.

Ziyat , L. Bejjit , M.N. Bennani , M. Bouachrine, Theoretical design of D-π-A system new dyes candidate for DSSC application. Heliyon, 7(6), (2021) e07171. https://doi.org/10.1016/j.heliyon.2021.e07171

[13] S.M. Feldt, G. Wang, G. Boschloo, A. Hagfeldt, Effects of driving forces for recombination and regeneration on the photovoltaic performance of dye-sensitized solar cells using cobalt polypyridine redox couples. The Journal of Physical Chemistry C, 115(43), (2011) 21500–21507. https://doi.org/10.1021/jp2061392

[14] A. Bourouina, M. Rekis, Comparison in optoelectronic properties of triphenylamine-imidazole or imidazole as donor for dye sensitized solar cells: theoretical approach. Journal of Molecular Modeling, 27, (2021) 225. https://doi.org/10.1007/s00894-021-04844-8

[15] K. Zaugg, J. Velasco, K.A. Robins, D.C. Lee, Understanding the electronic properties of acceptor–acceptor′–acceptor triads. ACS omega, 4(3), (2019) 5434-5441. https://doi.org/10.1021/acsomega.8b03554

[16] K.H. Chang, C.K. Tai, L. Chen, P.L. Yeh, B.C. Wang, Theoretical study of 5, 10-diphenylindeno [2, 1-a] indene (DPI) dyes for dye sensitized solar cells (DSSC). Research on Chemical Intermediates, 45, (2019) 77-90. https://doi.org/10.1007/s11164-018-3624-5

[17] D. Devadiga, M. Selvakumar, P. Shetty, M. Sridhar Santosh, R.S. Chandrabose, S. Karazhanov, The improved performance of dye-sensitized solar cells using co-sensitization and polymer gel electrolyte. International Journal of Energy Research, 45, (2021) 6584. https://doi.org/10.1002/er.6348

[18] P.B. Pati, W. Yang, S.S. Zade, New dyes for DSSC containing triphenylamine based extended donor: Synthesis, photophysical properties and device performance. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 178, (2017) 106-113. https://doi.org/10.1016/j.saa.2017.01.048

[19] J. Xu, L. Wang, G. Liang, Z. Bai, L. Wang, W. Xu, X. Shen, Conjugate spacer effect on molecular structures and absorption spectra of triphenylamine dyes for sensitized solar cells: density functional theory calculations. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 78(1), (2011) 287–293. https://doi.org/10.1016/j.saa.2010.10.008

[20] K.W. Park, L.A. Serrano, S. Ahn, M.H. Baek, A.A. Wiles, G. Cooke, J. Hong, An investigation of the role the donor moiety plays in modulating the efficiency of 'donor-π-acceptor-π-acceptor'organic DSSCs. Tetrahedron, 73(8), (2017)1098-1104. https://doi.org/10.1016/j.tet.2016.12.061

[21] [21] K.A. Wills, H.J. Mandujano-Ramírez, G. Merino, G. Oskam, P. Cowper, M. D. Jones, P.J. Cameron, S.E. Lewis, What di fference does a thiophene make? Evaluation of a 4,4′ -bis(thiophene) functionalised 2,2′ -bipyridyl copper(I) complex in a dye-sensitized solar cell. Dyes Pigments, 134, (2016) 419–426. https://doi.org/10.1016/j.dyepig.2016.07.023

[22] J. Cornil, D.A. dos Santos, D. Beljonne, J.L. Bredas, Electronic structure of phenylene vinylene oligomers: influence of donor/acceptor substitutions. The Journal of Physical Chemistry, 99(15), (1995) 5604-5611. https://doi.org/10.1021/j100015a051

[23] S. Manoharan, S. Anandan, Cyanovinyl substituted benzimidazole based (D–π–A) organic dyes for fabrication of dye sensitized solar cells. Dyes and Pigments, 105, (2014) 223-231. https://doi.org/10.1016/j.dyepig.2014.02.010

[24] S. Manoharan, J.J. Wu, S. Anandan, Synthesis of cyanovinyl thiophene with different acceptor containing organic dyes towards high efficient dye sensitized solar cells. Dyes and Pigments, 133, (2016) 222-231. https://doi.org/10.1016/j.dyepig.2016.05.052

[25] M. Xu, M. Zhang, M. Pastore, R. Li, F. De Angelis, P. Wang, Joint electrical, photophysical and computational studies on D-π-A dye sensitized solar cells: the impacts of dithiophene rigidification. Chemical Science, 3(4), (2012) 976-983. https://doi.org/10.1039/C2SC00973K

[26] M. Souilah, M. Hachi, A. Fitri, A.T. Benjelloun, S. El Khattabi, M. Benzakour, M. Mcharfi, H. Zgou, Coumarin-based D–π–A dyes for efficient DSSCs: DFT and TD-DFT study of the π-spacers influence on photovoltaic properties. Research on Chemical Intermediates, 47(2), (2021) 875-893. https://doi.org/10.1007/s11164-020-04302-9

[27] Z. Xu, Y. Li, Y. Li, S. Yuan, L. Hao, S. Gao, X. Lu, Theoretical study of T shaped phenothiazine/carbazole based organic dyes with naphthalimide as π-spacer for DSSCs. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 233, (2020) 118201. https://doi.org/10.1016/j.saa.2020.118201

[28] B. Seyednoruziyan, M.R. Zamanloo, M.D. Esrafili, A.N. Shamkhali, T. Alizadeh, S. Noruzi, Y-shape structured azo dyes with self-transforming feature to zwitterionic form as sensitizer for DSSC and DFT investigation of their photophysical and charge transfer properties. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 261, (2021) 120062. https://doi.org/10.1016/j.saa.2021.120062

[29] S. Ito, S.M. Zakeeruddin, R. Humphry-Baker, P. Liska, R. Charvet, P. Comte, K. Mohammad Nazeeruddin, P. Péchy, M. Takata, H. Miura, S.

Uchida, M. Gratzel, High-efficiency organic-dye-sensitized solar cells controlled by nanocrystalline-TiO2 electrode thickness. Advanced Materials, 18(9), (2006) 1202-1205. https://doi.org/10.1002/adma.200502540

[30] H. Tian, Yang X, Chen R, Pan Y, Li L, Hagfeldt A, Sun L, Phenothiazine derivatives for efficient organic dye-sensitized solar cells. Chemival Communications, 36, (2007) 3741. https://doi.org/10.1039/B707485A

[31] R. Chen, X. Yang, H. Tian, X. Wang, A. Hagfeldt, L. Sun, Effect of tetrahydroquinoline dyes structure on the performance of organic dye-sensitized solar cells. Chemistry of Materials, 19(16), (2007) 4007-4015. https://doi.org/10.1021/cm070617g

[32] R. Chen, X. Yang, H. Tian, L. Sun, Tetrahydroquinoline dyes with different spacers for organic dye-sensitized solar cells. Journal of Photochemistry and Photobiology A: Chemistry, 189(2-3), (2007) 295-300. https://doi.org/10.1016/j.jphotochem.2007.02.018

[33] H. Tian, I. Bora, X. Jiang, E. Gabrielsson, K.M. Karlsson, A. Hagfeldt, L. Sun, Modifying organic phenoxazine dyes for efficient dye-sensitized solar cells. Journal of Materials Chemistry, 21, (2011) 12462. https://doi.org/10.1039/C1JM12071A

[34] X. Ma, J. Hua, W. Wu, Y. Jin, F. Meng, W. Zhan, H. Tian, A high-efficiency cyanine dye for dye-sensitized solar cells. Tetrahedron, 64(2), (2008) 345-350. https://doi.org/10.1016/j.tet.2007.10.094

[35] K. Sayama, S. Tsukagoshi, K. Hara, Y. Ohga, A. Shinpou, Y. Abe, S. Suga, H. Arakawa, Photoelectrochemical properties of j aggregates of enzothiazole merocyanine dyes on a nanostructured TiO2 film The Journal of Physical Chemistry B, 106(6), (2002) 1363–1371. https://doi.org/10.1021/jp0129380

[36] C. Karnan, A. Ram Kumar, S. Selvaraj, Quantum Chemical Computational Studies on the Structural Aspects, Spectroscopic Properties, Hirshfeld Surfaces, Donor-Acceptor Interactions and Molecular Docking of Clascosterone: A Promising Antitumor Agent. International Research Journal of Multidisciplinary Technovation, 6(4), (2024) 32-53. https://doi.org/10.54392/irjmt2444

[37] A. Ram Kumar, S. Selvaraj, M. Azam, G.P. Sheeja Mol, N. Kanagathara, M. Alam, P. Jayaprakash, Spectroscopic, biological, and topological insights on lemonol as a potential anticancer agent. ACS omega, 8(34), (2023) 31548-31566. https://doi.org/10.1021/acsomega.3c04922

[38] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, D.J. Fox, (2009) Gaussian 09 (Verion Revision E. 01). Wallingford.

[39] A.D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior. Physical review A, 38(6), (1988) 3098. https://doi.org/10.1103/PhysRevA.38.3098

[40] A. Petersson, A. Bennett, T.G. Tensfeldt, M.A. Al-Laham, W.A. Shirley, J. Mantzaris, A complete basis set model chemistry. I. The total energies of closed-shell atoms and hydrides of the first-row elements. The Journal of chemical physics, 89(4), (1988) 2193-2218. https://doi.org/10.1063/1.455064

[41] P. J. Walsh, K.C. Gordon, D.L. Officer, W.M. Campbell, A DFT study of the optical properties of substituted Zn(II)TPP complexes. Journal of Molecular Structure: Theochem, 759(1-3), (2006) 17-24. https://doi.org/10.1016/j.theochem.2005.10.049

[42] G. Scalmani, M.J. Frisch, Continuous surface charge polarizable continuum models of solvation. I. General formalism. The Journal of chemical physics, 132(11), (2010) 114110. https://doi.org/10.1063/1.3359469

[43] Dennington, R., Keith, T., & Millam, J. Semichem Inc. Shawnee Mission KS, GaussView, Version, 5(8), (2009).

[44] S. Wei, K. Li, X. Lu, Z. Zhao, Y. Shao, Y. Dang, S. Li, W. Guo, Theoretical insight into electronic structure and optoelectronic properties of heterolytic Cu (I)-based complexes for dye-sensitized solar cells. Materials Chemistry and Physics, 173, (2016) 139–145. https://doi.org/10.1016/j.matchemphys.2016.01.049

[45] T.H. Wang, I.T. Wang, W.L. Huang, L.Y. Huang, A DFT study on structures, frontier molecular orbitals and UV–vis spectra of RuX (PPh3)(NHCPh2) L (X= Tp and Cp; L= Cl and N3). Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 121, (2014) 650-656. https://doi.org/10.1016/j.saa.2013.11.107

[46] M. Rezvani , M. Darvish Ganji , S. Jameh-Bozorghi , A. Niazi, DFT/TD-semiempirical study on the structural and electronic properties and absorption spectra of supramolecular fullerene-porphyrine- metalloporphyrine triads-based dye-sensitized solar cells. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 194, (2018) 57-66. https://doi.org/10.1016/j.saa.2017.12.073

[47] P. Pounraj, V. Mohankumar, M.S. Pandian, P. Ramasamy, The effect of different π-bridge configuration on bi-anchored triphenylamine and phenyl modified triphenylamine based dyes for dye sensitized solar cell (DSSC) application: A theoretical approach. Journal of Molecular Graphics and Modelling, 79, (2018) 235-253. https://doi.org/10.1016/j.jmgm.2017.12.004

[48] Z.J. Chermahini, A.N. Chermahini, H.A. Dabbagh, B. Rezaei, N. Irannejad, The effects of second electron acceptor group on the performance of tetrazole-based nanocrystalline TiO2 sensitizers in DSSCs. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 178, (2017) 79-85. https://doi.org/10.1016/j.saa.2017.01.061

[49] F. Zanjanchi, J. Beheshtian, Natural pigments in dye-sensitized solar cell (DSSC): a DFT-TDDFT study. Journal of the Iranian Chemical Society, 16, (2018) 795–805. https://doi.org/10.1007/s13738-018-1561-2

[50] P. Ferdowsi, Y. Saygili, W. Zhang, T. Edvinson, L. Kavan, J. Mokhtari, S.M. Zakeeruddin, M. Grätzel, A. Hagfeldt, Molecular Design of Efficient Organic D–A—A Dye Featuring Triphenylamine as Donor Fragment for Application in Dye-Sensitized Solar Cells. ChemSusChem, 11(2), (2018) 494-502. https://doi.org/10.1002/cssc.201701949

[51] L. Zhu, H. Yang, C. Zhong, C.M. Li, Modified triphenylamine-dicyanovinyl-based donor acceptor dyes with enhanced power conversion efficiency of p-type dye-sensitized solar cells. Chemistry An Asian Journal, 7(12), (2012) 279-285. https://doi.org/10.1002/asia.201200402

[52] S. Ramkumar, P. Manidurai, Tuning the physical properties of organic sensitizers by replacing triphenylamine with new donors for dye sensitized solar cells – a theoretical approach. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 173, (2017) 425–431. https://doi.org/10.1016/j.saa.2016.09.036

[53] X. Lu, S. Wei, C.M.L. Wu, S. Li, W. Guo, Can polypyridyl Cu(I)-based complexes provide promising sensitizers for dye-sensitized solar cells? A theoretical insight into Cu(I) versus Ru (II) sensitizers. The Journal of Physical Chemistry C, 115(9), (2011) 3753-3761. https://doi.org/10.1021/jp111325y

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Authors Contribution Statement

J. Jasmine Sharmila: Writing Original draft, conceptualization, Validation, computations. V. Mohankumar: Review & editing, computations. S. Sundaram: Formal analysis of data, Validation. P. Pounraj: Computations and Validation A. Umamaheswari: Review& edition, Validation, conceptualization, investigation, analysis. All authors have examined and approved the final manuscript.

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Data Availability

The data supporting the findings of this study can be obtained from the corresponding author upon reasonable request.

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