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TD-DFT and DFT Investigation on Electrons Transporting Efficiency of 2-Cyano-2-Pyran-4-Ylidene-Acetic Acid and 2-Cyanoprop-2-Enoic Acid as Acceptors for Thiophene-Based π-Linkers Dye-Sensitized Solar Cells

Great attention is being shifted to Dye-sensitized solar cells because of their structural and electronic tunability, high performance, and low cost compared to conservative photovoltaic devices. In this work, B3LYP/6-31G** level of theory was used to study the molecular architecture of the donor-π-acceptor (D-π-A) type. This architecture contains a series of dyes with the 2-cyano-2-pyran-4-ylidene-acetic acid (PLTP-dye) and 2-cyanoprop-2-enoic acid (CLTP-dye) units as acceptors; donor groups and thiophene-based π-linkers. The molecular and electronic properties, light harvesting efficiency, open circuit voltage (V_{OC}), injection force (ΔG^{inject}), regeneration force (ΔG^{regen}) and excitation state lifetime (τ_{esl}) were calculated. CLTP-dyes showed lower band gap, chemical hardness (η), chemical potential (μ), higher electrophilicity (ω) and electron denoting power (ω^-) than the corresponding PLTP-dyes. The ω^- demonstrated that PLTP-1, PLTP-2 and PLTP-3, CLTP-1, CLTP-2 and CLTP-3 should readily push electrons to the π-linker, which can lead to high intra-molecular charge transfer and photocurrent for the dyes. The Voc and ΔG^{inject} parameters favoured the CLTP-dyes over corresponding PLTP-dyes, and also dyes with the N,N-diphenylaniline donor have higher Voc, ΔG^{inject} values and longer wavelengths (λ_{max}) than the dyes with carbazole unit (N,N-diphenylaniline dyes > Carbazole dyes) in accordance with the calculated ω^-, although all the dyes have good regeneration and injection abilities.

Keywords: frontier orbitals, photoelectric properties, reactivity indices, TD-DFT, DFT, B3LYP, D-π-A type, dye-sensitized solar cells (DSSC).

Introduction

Increasing energy consumptions coupled with the global warming effect determined by energy supply from fossil resources has caused significant interest in renewable energy research. The energy released by the Sun to the Earth per hour exceeds the current world energy consumption per year; therefore, there is a daily growing in the development and use of solar renewable energy [1]. Consequently, efficient solar energy conversion devices or methods are required to provide a promising technology that can counterbalance the ever-growing energy demand needed for fast industrial development [2, 3]. However, solar photovoltaic cell has been considered to be one of the foremost prospective to cover a higher percentage of the future energy needs among other available renewable energy sources. In order to exploit this great benefit, a safe, cost-effective, efficient and ecofriendly method of harvesting solar energy are needed, and dye-sensitized solar cells (DSSCs) which belong to the third-generation solar cell technologies have the potential to meet these requirements. DSSCs invented by O'Regan and Grätzel in 1991, gave the broad view of using molecular components-based devices for the construction of a large-scale solar facility for electricity production, and thus put the solid-state technology to challenge by operating photovoltaic devices at molecular or nanoscale levels [4]. Although research is still ongoing, as well as pre-industrial technology in DSSCs is still low com-

pared to the performance of silicon devices; the efficiency is still below 13 % for DSSC [5]. Over the years, the applications of DSSCs have been intensively studied as a result of its potentially low cost of production, despite its current low efficiency and stability [6]. Designing of dye-sensitizers for DSSC have inform of donor (D)-π spacer-acceptor (A) to ensure intra-molecular charge transfer, usually from donor unit through π spacer to the acceptor unit [7, 8]. In an attempt to improve the dye-sensitizers importance, different types of dyes combinations have been developed, such as D–π–D–π–A, $(D–π–A)_2$, D–A–π–A, D–D–π–A, D–π–A–A and A–π–D–π–A [9–13].

Organic dyes with triphenylamine-based donor groups and the cyanoacrylic dyes as an acceptor/anchoring group are known for their outstanding properties, which have attracted much attention in DSSC technology [14–16]. Triphenyl moiety containing organic dyes possess unique characteristics such as the tunable frontier orbital energies, low dye aggregation, high molar absorption coefficients and non-planarity. These notable properties have made the triphenylamine (TPA) based sensitizers highly suitable for the DSSCs application [17]. However, these properties have led to a low recombination and back-reaction rate in the solar energy conversion process. Though, π-conjugated systems of the sensitizing dyes can be easily modified to obtain desired absorption wavelengths by adjusting the band gap of dyes [14, 15].

The cyanoprop-2-enoic acid has been a popular acceptor moiety for anchoring dye-sensitizers to TiO_2 surface in dye sensitized solar cells [16, 5]. However, other acceptor moieties used such dyes like the rhodamine-3-acetic acid in which the photovoltaic results were compared with those of the cyanoprop-2-enoic acid acceptor. The results revealed that dye with the rhodamine-3-acetic acid as an acceptor unit had the shorter wavelength, lower molar extinction coefficients and lower light capturing ability due to the weaker intra-molecular charge transfer ability [18]. Also, in some of our recent works, a series of dyes with the cyano-2-pyran-4-ylidene-acetic acid as acceptor were computationally modeled and studied. The results predicted very good optical properties, light harvesting efficiency and high circuit voltage, which were improved by the presence of fluorine atoms in the cyano-2-pyran-4-ylidene-acetic acid [19, 20]. Besides, several dyes of pyran derivatives have been investigated for absorption, light harvesting, intra-molecular charge transfer, regeneration and recombination properties using computational methods [21]; the results predict their applications as organic light emitting diode (OLED), bulk-heterojunction solar cells, and sensors [21–25].

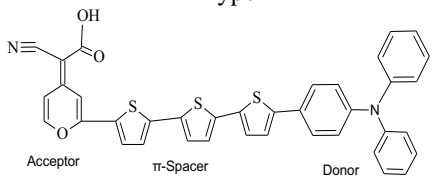
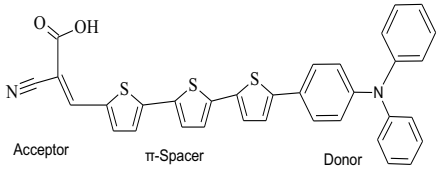
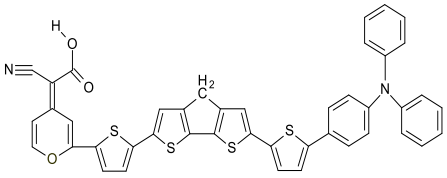
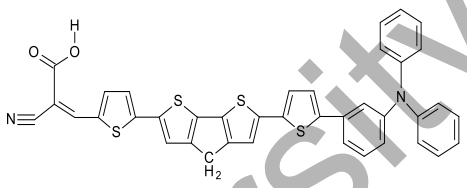
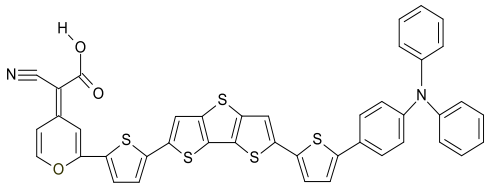
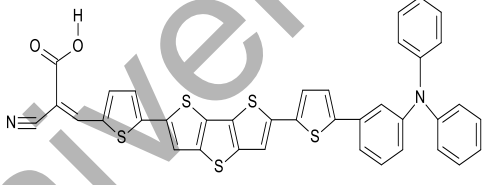
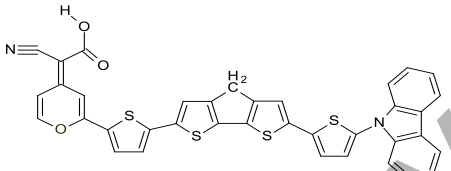
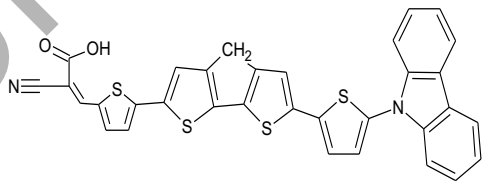
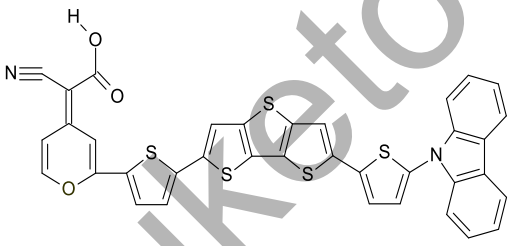
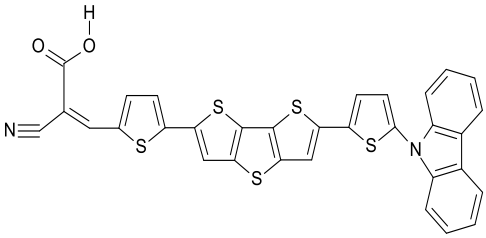
Density functional theory (DFT) methods continue to play a leading role in the design and research of the electronic structure, photocurrent and electron transport properties of dye-sensitizers for photovoltaic applications such as DSSCs development [26–31]. Therefore, in this present study, density functional theory was used to explore the electron transporting efficiency of the 2-cyano-2-pyran-4-ylidene-acetic acid (type A dyes) and the 2-cyanoprop-2-enoic acid (type B dyes) as the acceptor anchoring units for thiophene-based π-linkers for dye-sensitized solar cells as shown in Table 1. The effects of these acceptor units on intra-molecular charge transfer, electrons regenerating, electrons injecting and light harvesting efficiency of the dye sensitizers were studied. The roles of thiophene derivatives (bisthioeno[3,2-b,3-b]thiophene, 4H-cyclopenta[1,2-b,5,4-b]bisthiophene and terthiophene) as the π-linkers have thoroughly investigated and discussed.

Computational Details

The accuracy of DFT calculations depends on the selected functional and basis sets. It has been established that the polarized split-valence 6-31G(d, p) basis sets is sufficiently accurate for calculating the electronic excitation properties of organic dyes without extension of the basis sets [32, 33]; thus the designed D-π-A dyes were optimized using DFT of the three-parameter density functional, with Becke's gradient exchange correction [34] and the Lee, Yang, Parr correlation functional (i.e. B3LYP) [35] accounting the 6-31G(d, p) basis set. Frequency calculations were performed on the optimized structures of the dyes at the same levels of theory to reveal the stationary points as local minima, and none of the optimized structures of the dyes exhibited imaginary frequencies. The frontier orbital energies, reactivity indices, natural density analysis, photo-electronics properties, intra-molecular charge transfer properties, and injection and regeneration driving forces were calculated. All calculations were carried out using Spartan 14 software from Wavefunction Inc. (Spartan, 2014) [36], implemented on an Intel® Core TM i7-4520M CPU, 2.50 GHz computer.

Table 1

Schematic structure of the studied molecules: Type A is the 2-cyano-2-pyran-4-ylidene-acetic acid and Type B is the 2-cyanoprop-2-enoic acid as acceptor anchor, respectively

Type A	Type B
	
PLTP-1	CLTP-1
	
PLTP-2	CLTP-2
	
PLTP-3	CLTP-3
	
PLTP-4	CLTP-4
	
PLTP-5	CLTP-5

Results and Discussion

Frontier Molecular Orbital energies and reactivity indices

The frontier orbital energies, such as the HOMO and LUMO energies of dye sensitizers, are vital for modification the redox potential of the electrolyte and conduction-band edge of the semiconductor in DSSCs to achieve high harvesting and desired capability of the dye [37]. Designing low-molecular weight D–π–A dye sensitizers require fine tuning the properties of frontier orbitals because they are qualitative characteristics of organic dyes excitation properties [38, 26, 27, 29]. The frontier orbitals contour overlay is displayed in Figure 1 shows that the HOMOs overlaid are localized on the donor subunit extended over π-linker, and also the LUMOs overlaid are mainly on acceptor subunit with extension over π-linker. This means that there is a good interaction between the donor and acceptor groups through π-linker, which could facilitate intramolecular charge transfer from donor to acceptor unit [39].

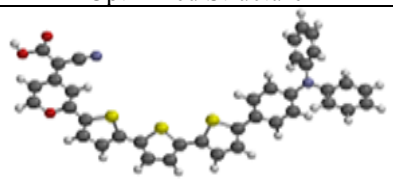
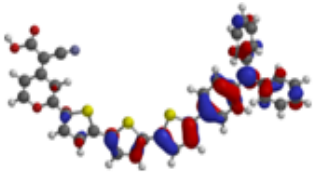
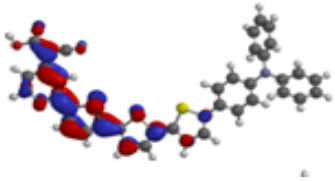
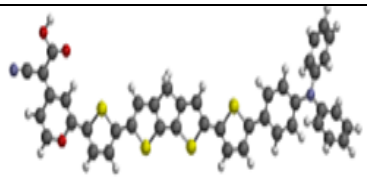
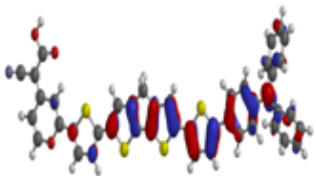
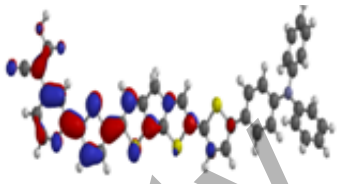
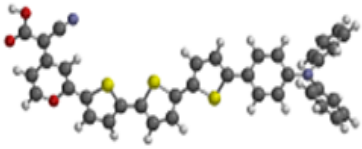
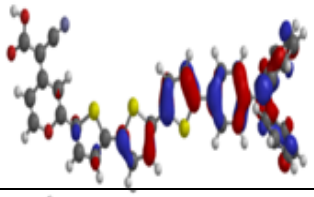
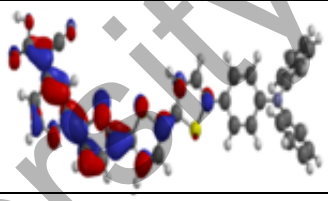
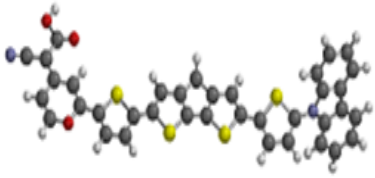
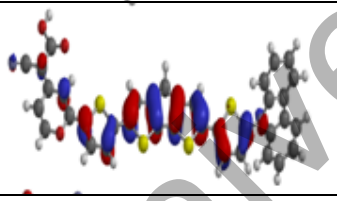
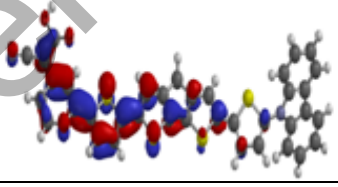
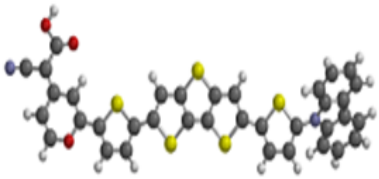
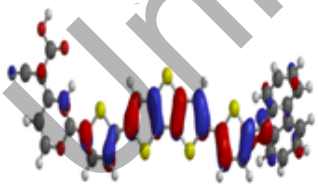
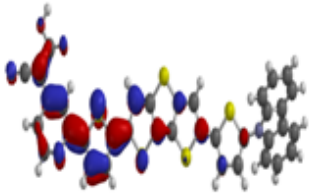
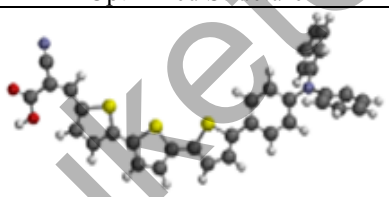
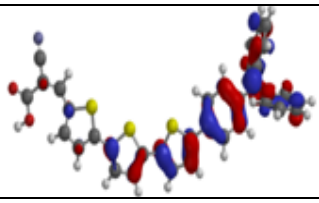
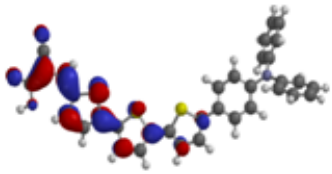
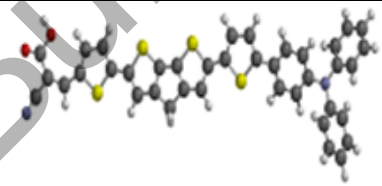
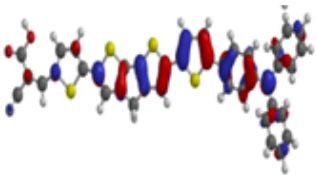
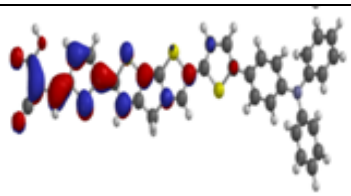
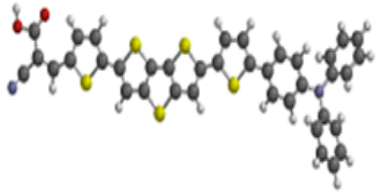
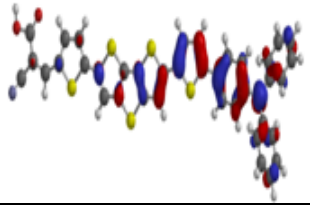
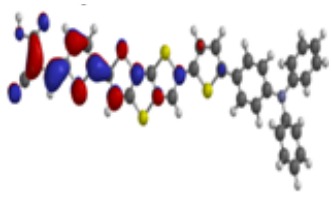
Mol	Optimized Structure	HOMO	LUMO
PLTP-1			
PLTP-2			
PLTP-3			
PLTP-4			
PLTP-5			

Figure 1*a*. The Contour Plots of the frontier orbitals of PLTPs dyes

Mol	Optimized Structure	HOMO	LUMO
CLTP-1			
CLTP-2			
CLTP-3			

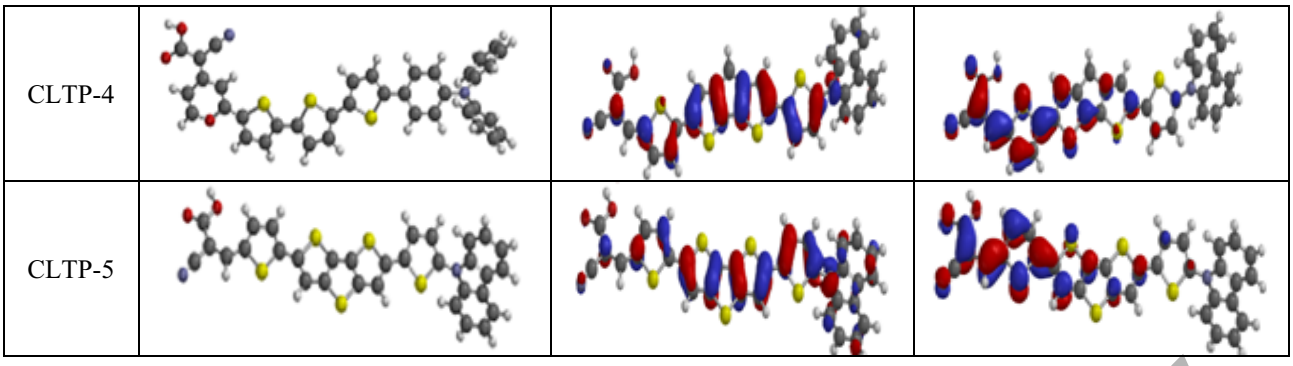
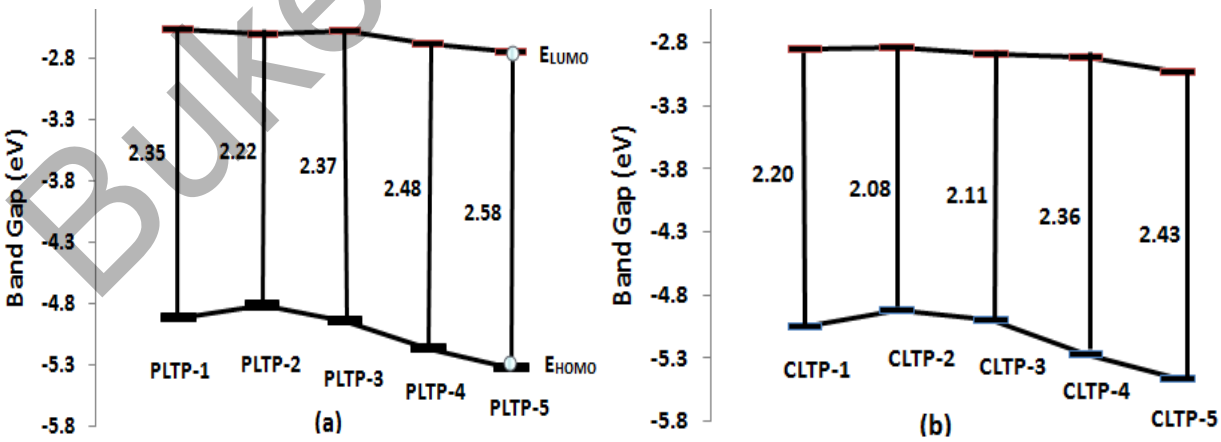


Figure 1*b*. The Contour Plots of frontier orbitals of CLTPs dyes

The electron accepting efficiency of the dye acceptors (types A and B) were examined by considering dyes with similar donors and π-conjugated linkers such as CLTP-1 and PLTP-1, CLTP-2 and PLTP-2, CLTP-3 and PLTP-3, CLTP-4 and PLTP-4, CLTP-5 and PLTP-5 (Lu et al., 2011 [40]). The HOMO, LUMO, and HOMO–LUMO energy gap (E_g) for the dyes were calculated as –4.92, –2.57 and 2.35 eV for PLTP-1; –5.04, –2.84 and 2.20 eV for CLTP-1, respectively. The CLTP-1 dye (Type B) with the 2-cyanoprop-2-enoic acid as acceptor unit showed a decrease in both the HOMO and LUMO energies by 0.12 and 0.27 eV, respectively, which resulted into lowering of Eg by 0.15 eV for CLTP-1 compare to PLTP-1. The calculated HOMO, LUMO, and Eg values for PLTP-2 were –4.82, –2.60, 2.22eV; and –4.91, –2.83 and 2.08 for CLTP-2, which also showed a reduction of the HOMO/LUMO by 0.09/0.23 eV resulting in a decrease of Eg by 0.14 eV for CLTP-2 over PLTP-2. Moreover, the HOMO, LUMO, and Eg for PLTP-3 were –4.94, –2.67, and 2.27 eV; and –4.99, –2.88 and 2.11 eV for CLTP-3; this led to a relative decrease in the HOMO/LUMO by 0.05/0.21 eV resulting in a reduction of Eg by 0.16 eV for CLTP-3 compare to PLTP-3 (Fig. 2).

Similarly, the HOMO, LUMO and Eg for CLTP-4 was lowered by 0.12 eV as compare to PLTP-4 due to a decrease in the HOMO/LUMO by 0.01/0.22 eV. This observation revealed that both the HOMO and LUMO of type B dye's orbitals are delocalized leading relative ease of π-electrons flow, thus lowering of Eg in CLTP dyes. The Eg values of the studied dyes can be ordered as PLTP-2 < PLTP-1 < PLTP-3 < PLTP-4 < < PLTP-5 for type A, and CLTP-2 < CLTP-3 < CLTP-1 < CLTP-4 < CLTP-5 for type B (Fig. 2). Generally, type B presented lower band gap than the corresponding type A; however, all the dyes are good photosensitized prospects, since their HOMO energy levels are lower than the redox potential of the I^-/I_3^- electrolyte (–4.8 eV) and LUMO energy levels are higher than the conduction band (CB) of the TiO_2 semiconductor (–4.0 eV) which ensures the injection of the electron from the dye to TiO_2 as well as dye renaissance [40; 41].



a — 2-cyano-2-pyran-4-ylidene-acetic acid; *b* — 2-cyanoprop-2-enoic acid as acceptor anchor, respectively

Figure 2. Energy band gap for the studied D–π–A dye sensitizers

Furthermore, the effect of π-linkers on the intramolecular charge transfer was investigated in the two-dye series; PLTP-1, PLTP-2 and PLTP-3 for type A, and CLTP-1, CLTP-2 and CLTP-3 for type B. The frontier energies (HOMO, LUMO and E_g) for PLTP-1, PLTP-2 and PLTP-3 were (–4.92, –2.57 and 2.35 eV), (–4.82, –2.60, 2.22 eV) and (–4.95, –2.58 and 2.37 eV), respectively. Therefore, the use of 4H-cyclopenta[1,2-b,5,4-b]bisthiophene as π-linker in PLTP-2 increases/decreases the HOMO/LUMO energy by 0.10/0.03 eV compare to PLTP-1 with terthiophene as π-linker, thereby causing delocalization of the LUMO orbital leading to reduction in the E_g by 0.13 eV. However, with bisthioeno[3,2-b,3-b]thiophene as π-linker in PLTP-3, the HOMO/LUMO was slightly decreased by 0.04/0.01 eV, thus PLTP-3 only increased in Eg by 0.02 eV. Also, similarly, the frontier orbital energies (HOMO, LUMO and Eg) for CLTP-1, CLTP-2 and CLTP-3 were (–5.04, –2.84, 2.20 eV), (–4.91, –2.83, 2.08 eV) and (–4.99, –2.88 and 2.11 eV), respectively. The electronic properties revealed that the HOMO/LUMO energies of CLTP-2 (with 4H-cyclopenta[1,2-b,5,4-b]bisthiophene as π-linker) increases by 0.13/0.01 eV, leading to lowering of Eg by 0.12 eV compare to CLTP-1. At the same time, with bisthioeno[3,2-b,3-b]thiophene as π-linker in CLTP-3, the HOMO/LUMO energies increases/decreases by 0.05/0.04 eV, which leads to reduction in Eg by 0.09 eV compare to CLTP-1 (Fig. 2). This suggests that dyes with 4H-cyclopenta[1,2-b,5,4-b]bisthiophene as linker could have superior photocurrent and charge transfer (CT) than dyes with terthiophene and bisthioeno[3,2-b,3-b]thiophene as π-linkers (Semire et al., 2017 [48]), It can be argued that higher HOMO energy together with the lower LUMO energy favors excitation of electrons in D–π–A organic dyes [21].

In addition, the efficiency of the donor subunits was also investigated by considering CLTP-2 and CLTP-4, PLTP-2 and PLTP-4 dyes. Comparing CLTP-2 and CLTP-4, the HOMO, LUMO energies, and Eg were –5.27, –2.91, 2.36 eV for CTP-4; and –4.91, –2.83 and 2.08 eV for CLTP-2. There is a stabilization of both the HOMO and LUMO orbitals by 0.36 and 0.08 eV, respectively leading to enhancement of Eg by 0.28 eV in CLTP-2 dyes compare to CLTP-4. Also, comparing PLTP-4 and PLTP-2, it can be noted that Eg enhanced by 0.26 eV as a result of stabilization of both the HOMO/LUMO by 0.35/0.09 eV. Therefore, N,N-diphenylaniline donor group donors/pushes more electrons readily towards π-linker than carbazole donor group, thus dyes bearing N,N-diphenylaniline donor group should have better intramolecular charge transfer and good photocurrent ability [20].

The natural bond orbital (NBO) analysis was performed on the optimized structure in the ground state in order to study the electron transfer mechanism as well as charge distribution of the studied D-π-A dyes. The calculated NBOs at the B3LYP/6-31G (d, p) level are listed in Table 2. The positive charges on the N,N-diphenylaniline moiety reveals an efficacious electron-donor unit and the large negative NBO charges on 2-cyano-2-pyran-4-ylidene-acetic acid/2-cyanoprop-2-enoic acid are evidence that electrons are enthralled in the acceptor unit. The NBO analysis, N-diphenylaniline donor group shows that the cyano-substituent attached to the acceptor unit of the dyes increases/decreases the natural bond orbital charges on both the acceptor and donor units. The trapping of electrons in the acceptor unit denotes that the NBO charges in the dye sensitizers are subjugated by acceptor moieties [42].

The dyes electronegativity (χ), chemical hardness (η), electrophilicity index (ω) and electron donating power (ω^-) were estimated from the ground state geometries of the optimized dyes at B3LYp/6-31G** level of theory for an N-electron system with total energy E as described in equations 1–4 [42, 43].

$$\chi = -\mu = \left(\frac{\delta E}{\delta N}\right)_{v(r)} \cong \frac{IP + EA}{2} \tag{1}$$

$$\eta = \left(\frac{\delta^2 E}{\delta N^2}\right)_{v(r)} \cong \frac{IP - EA}{2} \tag{2}$$

$$\omega = \frac{\mu^2}{2\eta} = \frac{(IP + EA)^2}{4(IP - EA)} \tag{3}$$

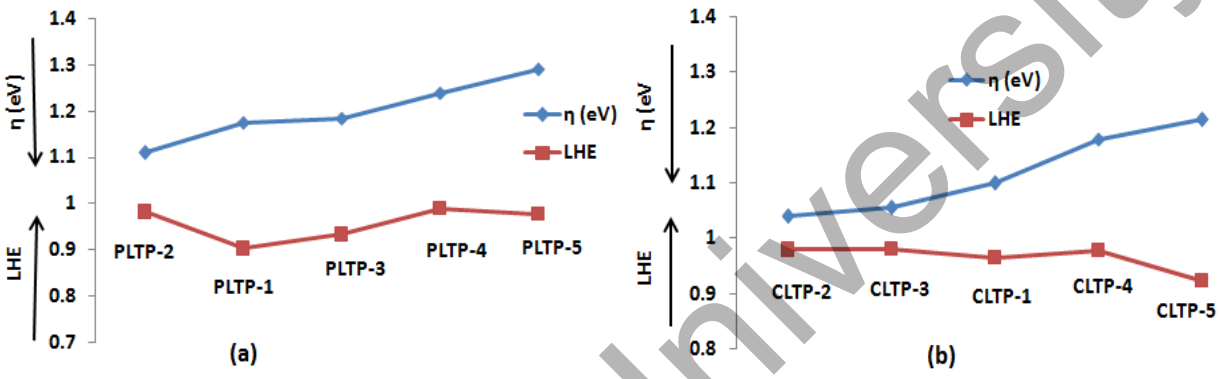
$$\omega^- = \frac{(3IP - EA)^2}{16(IP - EA)}, \tag{4}$$

where IP (vertical ionization potential) and EA (vertical electron affinity) are approximated to $-E_{HOMO}$ and $-E_{LUMO}$, respectively [45].

Table 2

Global Molecular Descriptors and Light Harvesting Efficiency (LHE)

MOL	q_{Donor}	π-linker	$q_{Acceptor}$	Δq(D-A)	μ (eV)	η (eV)	ω (eV)	ω^- (eV)
PLTP-1	0.126	–0.006	–0.120	0.246	–3.745	1.175	5.968	3.952
PLTP-2	0.142	–0.008	–0.138	0.280	–3.710	1.110	6.200	3.960
PLTP-3	0.141	–0.002	–0.140	0.281	–3.765	1.185	5.981	3.970
PLTP-4	0.152	0.019	–0.153	0.305	–3.930	1.240	6.227	4.142
PLTP-5	0.130	–0.004	–0.133	0.263	–4.040	1.290	6.325	4.247
CLTP-1	0.127	0.001	–0.125	0.252	–3.940	1.100	7.055	4.284
CLTP-2	0.033	–0.036	–0.172	0.205	–3.870	1.040	7.200	4.255
CLTP-3	0.135	–0.024	–0.164	0.299	–3.935	1.055	7.338	4.330
CLTP-4	0.143	–0.013	–0.132	0.275	–4.090	1.180	7.088	4.407
CLTP-5	0.142	–0.009	–0.136	0.278	–4.245	1.215	7.415	4.584



a — PLTPs; *b* — CLTPs

Figure 3: Relationship between light harvesting efficiency (LHE) and chemical hardness (η):

The thermodynamic stability of dye-sensitizers, a crucial parameter was adjudged by reactivity indices. Chemical hardness (η) is a parameter associated with molecular resistance to charge transfer with the surrounding [19]. According to [48] (Semire et al., 2017) it has a very close relation to intra-molecular charge transfer is favoured by low η for good dye-sensitizers. The η shows that type B (CLTP dyes) have lower chemical hardness compare to type A (PLTP dyes). The relationship between η and LHE has been described as a graph funnel-like shape [46]. Thus, as shown in Figure 3, low η and high LHE enhance good photocurrent in DSSCs [46] leading to a better short circuit current density (J_{SC}). Chemical potential (μ) is a parameter relating to charge transfer ability of a dye in its ground state, this is enhanced by high negative value of μ (Table 2). The electrophilicity (ω) describes the stabilization energy of a dye when an electronic charge is added to the dye from the surrounding, therefore, a high ω is desirable for good energy stabilization. All the dyes exhibit very good stabilization energy; however, type B (CLTP dyes) is more stabilized than type A (PLTP dyes). The electron denoting power (ω^-) is related to the ability of the dye to donate/push electrons through the linker/spacer to the acceptor unit of a dye. So, low value of ω^- corresponds to a better ability of donating/pushing electron density towards acceptor [46, 47]. Therefore, PLTP-1, PLTP-2 and PLTP-3 of type A and CLTP-1, CLTP-2 and CLTP-3 of type B will readily push electrons to the π-linker, leading to high intramolecular charge transfer and thus high photocurrent in DSSCs [48], suggesting higher electron-donating ability of dyes with N, N-diphenylaniline donor unit.

Theoretical view of the dye's efficiency

The light harvesting efficiency (LHE) is expected to be as high as possible for the dye sensitizers to have good performance in DSSC, also to enhance the photocurrent if the excited processes have a CT character. Therefore, the LHEs of the studied dyes are calculated as [49]:

$$LHE = 1 - 10^{-A} = 1 - 10^{-f}, \quad (5)$$

where *f* is the oscillator strength of the excited state associated to the λ_{max} and A is the absorption coefficient.

The LHE values reveal that PLTP-2, PLTP-4 and PLTP-5 for type A dyes, and CLTP-3, CLTP-2 and CLTP-4 for type B dyes are favoured for higher photocurrent (Table 3). Also, another key parameter of molecular global descriptors of solar cells is the open circuit voltage (V_{oc}) [35]. It is well known that the larger value V_{oc} corresponds to the better performance of solar cells [50]. V_{oc} is interrelated by the difference between the LUMO energy of the dye-sensitizer and the conduction band (the LUMO) of the electron acceptor (TiO_2; –4.0 eV), taking into account the energy lost during the photo-charge generation [51; 52]. The V_{oc} of the studied solar cell can be estimated by Equation (6) [44]:

$$V_{OC} = E_{LUMO} - E_{CB}^{TiO_2}. \quad (6)$$

The calculated V_{oc} values were 1.43, 1.40, 1.42, 1.31 and 1.25 for PLTP-1 to PLTP-5; and 1.16, 1.17, 1.12, 1.09 and 0.97 for CLTP-1 to CLTP-5, respectively (Table 3). This shows that V_{oc} values for type A dyes are higher than for the corresponding type B dyes; therefore, they are expected to present higher injection driving force and power conversion efficiency than type B. This also reveals that dyes with N,N-diphenylaniline donor unit have a higher V_{oc} value than dyes with carbazole unit (N,N-diphenylaniline dyes > Carbazole dyes) in line with calculated ω^- (Table 2).

The electron injecting ability (ΔG^{inject}) of the dyes were estimated for the two dyes series of dye-sensitizers (i.e. PLTPs and CLTPs) from the oxidation potential of the excited dye (E_{ox}^{dye*}) and the redox potential of the dye-TiO_2 couples [47]:

$$\Delta G^{inject} = E_{ox}^{dye*} - E_{CB}^{TiO_2}. \quad (7)$$

However, E_{ox}^{dye*} was calculated as the difference in the ground state oxidation potential of the dye and vertical electronic transition energy (λ_{max}^{ICT}) [14].

$$E_{ox}^{dye*} = E_{ox}^{dye} - \lambda_{max}^{ICT} \quad (8)$$

and the driving force of the dye regeneration known as regeneration efficiency (ΔG^{regen}) was estimated using Equation 9 [15].

$$\Delta G^{regen} = E_{ox}^{dye} - E_{redox}^{electrolyte}, \quad (9)$$

where 4.70 eV was taken as the value of $E_{redox}^{electrolyte}$ [44].

The negative values of injection driving force (ΔG^{inject}) show the ability of the dyes to inject electrons readily into TiO_2 surface as shown in Table 3. The ΔG^{inject} values show that PLTP-1, PLTP-3 for type A dyes, and CLTP-1, CLTP-2 and CLTP-3 for type B dyes are considered the best dyes, for they presented higher ΔG^{inject} values than PLTP-2, PLTP-4, PLTP-5, CLTP-4 and CLTP-5 (Table 3), signifying easy electrons injection into TiO_2. The positive values of dye regeneration drive force (ΔG^{regen}) suggest fast electrons transfer and thus ability to regenerate. However, it is necessary for ΔG^{regen} be as low as possible, making PLTP-2, CLTP-2, PLTP-1, PLTP-3 and CLTP-3 to be the candidate dyes for greater power conversion efficiency [53]. Another parameter to adjudge the suitability of a dye-sensitizer is the excitation state lifetime (τ_{esl}), a critical parameter for the charge-transport characteristics of a dye. It was predicted using Equation 10 [53; 54]:

$$\tau_{esl} = \frac{1.499}{fE^2}, \quad (10)$$

where E is the excitation energy of different electronic states in cm^{-1}, and f is the oscillator strength corresponding to the electronic state.

The τ_{esl} values reveal that CLPT-4 (2.576 ns), CLTP-5 (2.479 ns), PLTP-2 (2.998 ns) and PLTP-1 (1.647 ns) could be more stable in the cationic state, leading to long-lived excited state, higher charge transfer efficiency and improved efficiency of the dye-sensitizers than dyes with lower τ_{esl} [54].

Table 3

Calculated driving force of electron rejection and dye regeneration, LHE, Voc and excited state lifetimes (τ)

MOL	λ_{max}^{ICT}	f	E_{ox}^{dye*}	ΔG_{inj}	ΔG_{reg}	Voc	LHE	$\tau(ns)$
PLTP-1	2.714	1.0117	2.206	–1.794	0.22	1.43	0.9026	1.932
PLTP-2	2.041	1.7299	2.779	–1.221	0.12	1.40	0.9813	2.998
PLTP-3	2.731	1.1766	2.219	–1.781	0.25	1.42	0.9334	1.647
PLTP-4	2.319	1.9851	2.851	–1.149	0.47	1.31	0.9896	1.349

Continuation of Table 3

MOL	λ_{max}^{ICT}	f	E_{ox}^{dye*}	ΔG_{inj}	ΔG_{reg}	Voc	LHE	$\tau(ns)$
PLTP-5	2.368	1.6574	2.962	–1.038	0.63	1.25	0.9779	1.550
CLTP-1	2.701	1.4629	2.339	–1.661	0.34	1.16	0.9655	1.350
CLTP-2	2.465	1.6913	2.445	–1.555	0.21	1.17	0.9796	1.401
CLTP-3	2.502	1.7410	2.488	–1.512	0.29	1.12	0.9818	1.322
CLTP-4	2.279	1.0761	2.991	–1.010	0.57	1.09	0.9776	2.576
CLTP-5	2.284	1.1136	3.176	–0.824	0.76	0.97	0.9230	2.479

Photo-electronic Properties

The Beer–Lambert law states that absorbance at higher level denotes higher dye application. The study of the correlation between the DSSC photocurrent and the number of dye molecules has become trendy. In view of this, larger photocurrent can be attributed to increased adsorbed dye, ensuing in the increased harvesting of incident light [55–60]. Atomic information with reference to the electronic transitions can be obtained by investigating the molecular orbitals associated with each electronic transition, as calculated at TD-DFT/6-31G(d, p) level of theory (Tables 4). Absorptions in the visible and near-ultraviolet (UV) regions of the spectrum are the most important for photo to current conversion, so only the singlet → singlet transitions of the absorption bands with the wavelength longer than 300 nm are listed in the Table 4. The maximum absorbent wavelengths (λ_{max}) with probability of electron transition (oscillating strength, *f*) for the type A; PLTP-1, PLTP-2, PLTP-3, PLTP-4 and PLTP-5 were 579.02 (0.7881), 600.75 (1.7299), 570.36 (1.009), 528.81 (1.951) and 517.87 nm (1.6574), respectively, all arising from H→L orbital transitions. It is interesting to note that two major electronic transitions with highest *f* are arisen from the H→L and H-1→L orbitals' transitions (Table 4a). The maximum absorption transitions for type A dyes decreases in the following order: PLTP-2 > PLTP-1 > PLTP-3 > PLTP-4 > PLTP-5. Furthermore, the λ_{max} with oscillating strength, *f* for CLTP-1, CLTP-2, CLTP-3, CLTP-4 and CLTP-5 were 609.58 (0.7484), 626.50 (1.4056), 631.16 (1.0761), 537.94 (1.6503) and 536.83 (1.1136) nm, respectively, all arising from H→L orbitals' transitions as observed for type A. Similarly, the two major electronic transitions with highest *f* are arisen from the H→L and H-1→L orbitals' transitions (Table 4b), and the maximum absorption transitions for type B dyes decreases as follows: CLTP-3 > CLTP-2 > CLTP-1 > CLTP-4 > CLTP-5.

To compare the effect of π-linkers of electronic transitions as it relates to intramolecular charge transfer, PLTP-2 (CLTP-2) and PLTP-3 (CLTP-3) were considered. The 4H-cyclopenta[1,2-b,5,4-b]bisthiophene π-linker was changed in PLTP-2 (CLTP-2) to bisthioeno[3,2-b,3-b]thiophene as presented in PLTP-3 (CLTP-3). There was a shift in λ_{max} to shorter wavelength (blue-shift) by 30 and 4 nm, respectively; which may be due to easier delocalization of π-electrons for 4H-cyclopenta[1,2-b,5,4-b]bisthiophene π-linker than bisthioeno[3,2-b,3-b]thiophene leading to extension of π-conjugation [48]. To adjudge the effect of donor groups on intra-crossing charge transfer as it reflected in electronic transitions, PLTP-2 (CLTP-2) and PLTP-4 (CLTP-4) were considered. Replacement of N,N-diphenyalamine in PLTP-2 (CLTP-2) with carbazole in PLTP-4 (CLTP-4) shifted the λ_{max} to shorter wavelength (blue shift) of about 72 (90) nm, indicating that N,N-diphenylaniline pushes electrons more readily towards the linker than carbazole donor which is in line with the frontier orbital interactions and Eg energy earlier observed. Generally, **type B** dyes present lower energy energies and longer λ_{max} than the corresponding **type A** dyes, which may be linked to effective delocalization of π-electrons for 2-cyanoprop-2-enoic acid acceptor bearing dyes, and so enhance longer wavelength**.**

Table 4a

Absorption peaks, oscillation strength and molecular orbital's (MOs) involved in transitions calculated for PLTPs using B3LYP/6-31G (d, p)

λ, nm	OS	MOs involved in transition
PLTP-1		
350.57	0.2312	H-1 → L+1 (63 %)
367.83	0.2710	H → L +2 (81 %)
394.99	0.1113	H-2 → L (63 %), H-1 → L+1 (20 %),
428.85	0.2152	H → L+1 (81 %)
451.85	1.0117	H-1 → L (86 %)
579.02	0.7861	H → L (96 %)

Continuation of Table 4a

λ, nm	OS	MOs involved in transition
PLTP-2		
378.42	0.0970	H-1 → L+1 (54 %), H-2 → L (20 %)
392.12	0.0840	H → L+2 (66 %), H-3 → L (22 %)
409.36	0.0486	H-2 → L (49 %), H-1 → L+1 (35 %).
457.61	0.4318	H → L+1 (81 %)
486.49	1.2276	H-1 → L (89 %)
600.75	1.7299	H → L (97 %)
PLTP-3		
350.13	0.2415	H-1 → L+1 (66 %)
367.00	0.1481	H → L+2 (83 %)
394.57	0.0732	H-2 → L (64 %), H-1 → L+1 (18 %).
427.09	0.1730	H → L+1 (81 %)
449.08	1.1766	H-1 → L (88 %)
570.36	1.0098	H → L (98 %)
PLTP-4		
369.57	0.0049	H → L+2 (65 %), H-4 → L (29 %)
388.72	0.2378	H-3 → L (42 %), H → L+1 (26 %), H-1 →L+1 (17 %).
428.53	0.3541	H → L+1 (58 %), H-3 → L (38 %).
450.32	0.3635	H-1 → L (94 %)
528.81	1.9851	H→ L (94 %).
PLTP-5		
366.12	0.0335	H-4 → L (85 %)
389.08	0.2185	H-3 → L (36 %), H → L+1 (28 %), H-1 → L+1 (23 %)
419.26	0.2816	H → L+1 (53 %), H-3 → L (42 %)
444.03	0.5918	H-1 → L (95 %)
517.87	1.6574	H → L (96 %)

Table 4b

Absorption peaks, oscillation strength and molecular orbital's (MOs) involved in transition calculated for CLTPs using B3LYP/6-31G (d, p)

λ, nm	OS	MOs involved in transition
CLTP-1		
326.99	0.0694	H → L+4 (40 %), H-4 → L (18 %), H → L+3 (16 %)
339.04	0.0680	H → L+2 (45 %), H → L+3 (36 %).
361.61	0.2603	H-1 → L+1 (55 %), H-2 → L (32 %)
412.25	0.2996	H → L+1 (77 %)
454.06	1.4629	H-1 → L (83 %)
609.58	0.7484	H → L (97 %)
CLTP-2		
356.84	0.0086	H → L+2 (50 %), H-3 → L (20 %), H-1 → L+1 (14 %)
357.91	0.0060	H-2 → L (40 %), H → L+2 (29 %)
395.70	0.1449	H-1 → L+1 (63 %), H-2 → L (22 %)
449.92	0.5089	H → L+1 (77 %), H-2 → L (18 %)
497.36	1.6913	H-1 → L (86 %)
627.50	1.4056	H → L (94 %)
CLTP-3		
353.83	0.0073	H-2→ L (31 %), H-1 → L+1 (22 %), H → L+2 (13 %)
384.95	0.0672	H-3 → L (69 %), H-1 → L+1 (26 %)
390.88	0.2129	H-2→ L (40 %), H-1 → L+1 (30 %), H-3 → L (19 %)
442.01	0.6049	H → L+1 (79 %)
490.18	1.7410	H-1 → L (88 %)
631.16	1.0761	H → L (97 %)

Continuation of Table 4b

λ, nm	OS	MOs involved in transition
CLTP-4		
367.84	0.0226	H-1 → L+1 (81 %).
415.32	0.4898	H → L+1 (69 %), H-3 → L (28 %)
461.19	0.9159	H-1 → L (86 %)
537.94	1.6503	H → L (86 %)
CLTP-5		
370.99	0.1496	H-1 → L+1 (74 %)
382.82	0.0147	H-4 → L (68 %), H-3 → L (27 %).
405.72	0.6982	H → L+1 (72 %), H-3 → L (21 %).
462.95	1.1122	H-1 → L (88 %)
536.83	1.1136	H → L (89 %)

Conclusions

This paper reports a comprehensive computational investigations on the efficiency of the 2-cyano-2-pyran-4-ylidene-acetic acid and the 2-cyanoprop-2-enoic acid units as acceptor units connected through the thiophene-based π-linker dyes for the improvement of dye-sensitizers for DSSCs using the DFT(B3LYP/6-31G(d, p) method. The results revealed the following:

(1) Dyes with 4*H*-cyclopenta[1,2-b,5,4-b]bis-thiophene as a π-linker exhibit narrower band gap, and the longer absorption wavelength than others dyes in each dye series, indicating better intra-molecular charge transfer;

(2) Dyes with N,N-diphenyalamine as a donor unit presents lower band gaps, better the open circuit current (V_{oc}) and longer λ_{max} wavelength than dyes with the carbazole donor unit, indicating that N,N-diphenylaniline pushes electrons readily towards the π-linker than the carbazole donor; thus represents the better donor group;

(3) **Type B** dyes present lower band gaps and longer λ_{max} wavelength than the corresponding **type A** dyes, indicating effective delocalization of π-electrons in dyes with the 2-cyanoprop-2-enoic acid acceptor anchoring unit. This leads to better intra-molecular charge transfer, enhanced longer wavelength, higher V_{oc} value and injection force**.**

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