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# Manipulation of 2-[2-(10*H*-phenothiazin-3-yl)thiophen-3-yl]-10*H*-phenothiazine Based D-A- $\pi$ -A Dyes for Effective Tuning of Optoelectronic Properties and Intramolecular Charge Transfer in Dye Sensitized Solar Cells: A DFT/TD-DFT Approach

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#### K E Y W O R D S Molecular reactivity indices Frontier orbitals Optoelectronic properties DSSC

#### A B S T R A C T

Due to continuous growing in energy consumption brought on by economic development and population growth around the world, solar energy has emerged as one of the most important sources of renewable energy for human use. In this study, twelve metal-free organic dyes containing 2-[3-(10Hphenothiazin-3-yl)furan-2-yl]-10H-phenothiazine and its analogues as donor units inform of the D-A- $\pi$ -A structure (PBPD and PTPD) were theoretically studied for application in dye-sensitized solar cells (DSSCs). The structural, electrical, photovoltaic, and optical properties of the PBPD and PTDP dyes were carefully examined in relation to the impacts of changing the donor and  $\pi$ -spacer. The PBDP dyes showed band gaps ( $\Delta$ Eg) in the range of 1.75 (PBPD-4) to 2.09 eV (PBPD-3) while  $\Delta$ Eg values for PTPD dyes range from 1.87 eV (PTPD-4) to 2.33 eV (PTPD-3). The estimated open-circuit voltage (Voc) values ranged from 0.79 eV (PTPD-3) to 0.96 eV (PBPD-1 and PBPD-2) while the light gathering efficiency (LHE) values ranged from 0.766 (PTPD-2) to 0.968 (PBPD-6). The HOMO energies,  $\Delta Eg$  values, injection drive force ( $\Delta G^{inj}$ ), reorganization energies ( $\lambda$  total), and coupling constant ( $|V_{RP}|$ ) favoured PBPD dyes over PTPD dyes.



#### Introduction

The main source of energy for the world's continuously growing economies and populations has long been fossil fuels [1]. This has led to increase in greenhouse effect and environmental pollution, as well as nonrenewability associated with Fossil fuels, have been major concerned in recent time [2]. Therefore, continue depending on energies from these sources will eventually endanger bio- and ecosystems, and our world at large [3]. Consequently, a need to turn more promising, clean renewable, and limitless energy sources have become necessary. Solar energy fit in as most abundant renewable energy source, pollution-free, cheap, clean, unlimited, and large-scale production. support Thus, development in solar energy technologies among is Perovskite solar cells and organic solar cells [4-6].

In recent times, dye-sensitized solar cells (DSSCs) are now becoming more popular as new way to provide the needed energy demand to

meet the rising technological, industrial and population growth, due its reliability, cheap materials for construction, environmentally friendly, and biodegradable [7]. A typical DSSC structure has five basic components such as titanium (IV) oxide ( $TiO_2$ ), conducting glass substrate, dye sensitizers, redox electrolytes, and a counter electrode [8]. The properties of dye sensitizers are very crucial of effective performance of DSSCs, for it is the part of the cell that converts solar energy into electricity [9]. Various design of dye-sensitizers has been introduced such as metal based (e.g., rutheniumbased complexes and Co(II/III) tris(bipyridine)based dyes) and metal-free organic dyes [10]. The Ru dye-sensitizers are most prominent metal-based dye-sensitizers, and have been recorded to have displayed highest about 13% to 15% solar energy conversion efficiency [11] Also, some natural dyes such anthocyanins, flavonoids, chlorophylls, and carotenoids have been employed as dye-sensitizers [12].

Metal-free organic dyes, on the other hand, have recently received close attention due to their

structural flexibility, readily accessible, tunable electronic and optical properties, ease of purification, low processing cost, higher extinction coefficients, and environmental friendliness [13]. This is due to the high cost, limited access, and environmental pollution associated with Ru-based dye sensitizers [14].

The primary elements of metal-free dyesensitizers utilized in DSSCs are an electron donor (D) unit, an electron acceptor (A) unit, and a  $\pi$ -conjugated unit linking the donor and the acceptor to form a dipolar push-pull (D- $\pi$ -A) structure [15]. Several  $\pi$ -conjugated linkers such as thiophene and thiophene derivatives [16], furan derivatives [17], silole, and selenophenebased [18], have used in the molecular engineering of organic dye-sensitizers to improve optoelectronic properties and broaden absorption band, ensure regeneration and facilitate effective charge transfer to the semiconductor  $(TiO_2)$  from the dyes [19]. Also, many organic donors have reported like benzothieno-pyrrole [20], phthalocyanine [21], coumarin [22], indoline [23], quinoxaline and indoloquinoxaline [24], thieno[3,4-c]-pyrrole-4,6-dione [25], triphenylamine derivatives [26], benzothiadiazole [27], carbazole [28], diketopyrrolopyrrole [29], phenoxazine, and phenothiazine [5].

However, phenoxazine and phenothiazine have been reported to possess exceptional optical and electrical qualities suitable to be considered as donor units of dye-sensitizers for DSSCs utilization [30], although non-planarity of the system in the rings could hamper the pushing of electrons to  $\pi$ -linkers [31]. To overcome this challenge, auxiliary donor unit has been incorporated such as hexyl- and alkoxyphenylsubstituted phenothiazine, which led to solar energy conversion efficiency/power conversion efficiency (PCE) of 8.19 % [30]. Also, synthesis of dimers of both phenoxazine and phenothiazine was reported to have produced PCE of 5.87 and 6.40%, respectively [32]. Not quite long, the (E)- 3-(5-(7-(4-(bis(9,9-dimethyl-9H-fluoren-2-yl) amino)phenyl)-2,3-di-hydrothieno[3,4-

b][1,4]dioxin-5-yl)thieno[3,2-b]thiophen-2-yl)-2acid-based dye-sensitizer cyanoacrylic bisdimethylfluorenyl containing the amino groups donor units, 3,4as ethylenedioxythiophene, and thienothiophene as  $\pi$ -linkers with cyanoacrylic acid as an acceptor moiety were considered. The results revealed the absorption  $\lambda_{max}$  of the dyes centered around 481 nm with power conversion efficiency (PCE)  $\approx$ 5.65% [33]. These dyes were recently modified study the role of phenoxazine and to phenothiazine donor groups with 3substituted thiophene bearing electron withdrawing substituents on the optoelectronic characteristics of the dye-sensitizers [34]. The results showed that all the dyes displayed narrow energy gaps, broad UV-vis absorption spectra, red-shift, and enhanced regeneration ability compared to the reference dye. However, dyes containing 2-[3-(10H-phenothiazin-3yl)furan-2-yl]-10H-phenothiazine and 2-[3-(10Hphenoxazin-3-yl)furan-2-yl]-10H-phenoxazine as 3,4-ethylenedioxythiophene donors, coupled bisthieno[3,2-*b*:2',3'-*d*]thiophene  $\pi$ -linker with thiophene-3-carbonitrile showed outstanding optoelectronic properties [34].

Therefore, the major aim of this work is to modify these dyes with 2-[3-(10H-phenoxazin-3yl)thiophen-2-yl]-10H-phenoxazine, 2,3di(thianthren-2-yl)thiophene 2,3and di(thianthren-2-yl)furan as donor groups with 3,4-ethylenedioxythiophene (PBPD dyes)/1,3dihydro-2,1,3-benzothiadiazole (PTPD dyes), bisthieno[3,2-b:2',3'-d]thio-phene/thienothiophene, thiophene-3-carbonitrile as  $\pi$ -linkers, and cyanoacrylic acid as the acceptor as presented in Figure 1. The molecular and optoelectronic properties of these modeled dyes are calculated and analyzed via DFT and TD-DFT computational approaches to predict their usability and performance as dye-sensitizers for DSSC application.





Figure 1. 2D Schematic diagram of the designed dyes.

#### Computational details

The Spartan'14 quantum chemistry software package was used in this article to optimize and perform all molecular calculations [35]. On each modelled dye, a conformation search was conducted to determine the conformer with the lowest energy, which was then selected for optimization of the equilibrium geometry. Density Functional Theory (DFT) of the hybrid functional of exchange-correlation B3LYP with dual-polarized (6-31G(d,p) level of the theory [36] was utilized for all calculations. The optimized dye structures were used to estimate the reactivity descriptors of the dye-sensitizers, such as energy of the highest occupied molecular orbital (HOMO), energy of the lowest unoccupied molecular orbital (LUMO), and E<sub>(HOMO-LUMO)</sub> energy chemical hardness gaps,  $(\eta = \frac{E_{HOMO} - E_{LUMO}}{2} \approx \frac{I - A}{2}$ chemical potential  $(\mu = \left(\frac{E_{HOMO} + E_{LUMO}}{2}\right) \approx -\frac{I+A}{2}),$ global electrophilicity  $(\omega = \frac{\mu^2}{2n} = \frac{(I+A)^2}{4(I-A)}),$ electron

donating power  $(\omega^{-} = \frac{(3I+A)^2}{16(I-A)})$  and electron accepting power  $(\omega^{+} = \frac{(I+3A)^2}{16(I-A)})$ .

Furthermore, the excited state energies, absorption transitions, oscillator strength, and percentages of molecular orbitals involved in each electronic transition were calculated using the TD-DFT approach on fully optimized dye's structures [36].

## **Results and Discussion**

#### Frontier orbital analysis

Figure 2 displays the structures of the modeled dyes optimized at the B3LYP/6-31G(d,p) level of theory. The most desirable feature of a metal-free organic dye is that it has the ability to facilitate intramolecular charge transfer (ICT) from the donor to the anchoring group via the  $\pi$ -linker [36]. The HOMO, LUMO, and energy gap border orbitals, in particular, are important for a dye's ICT and photocurrent properties [36]. The energy values of the HOMO and LUMO orbitals, the energy gap and dipole moment are displayed in Table 1. The HOMOs of PBPD-1, PBPD-2 and PBPD-4 are localized on phenothiazinefuran/thiophene donor part extended to dihydrothieno[3,4-b][1,4]dioxine and thieno[3,2b]thiophene  $\pi$ -linkers, while PTPD-5 and PTPD-6 concentrated are on thianthrenefuran/thiophene donor part extended to dihydro-2,1,3-benzothiadiazole. The HOMOs of PBPD-3, PBPD-5, PBPD-6, and PTPD-3 are mainly on  $\pi$ -linkers extension, whereas PTPD-1 and PTPD-4 are fully localized on donor units (2-[3-(10H-phenothiazin-3-yl)furan-2-yl]-10H-

phenothiazine), as demonstrated in Figure 3. The electron-deficient acceptor on the right side of the dyes, where the LUMOs are mostly concentrated on thiophene-3-carbonitrile and cyanoacrylic acid. The HOMO orbitals of the dyes exhibit a bonding character, whereas the LUMO orbitals display an antibonding character (Figure 3).

A good dye-sensitizer should have its own HOMO energy less than the redox potential of  $I^{-}/I_{3}^{-}$ , to facilitate electrons from the electrolyte  $(I^{-}/I_{3}^{-})$  could reduce the oxidized molecules (photosensitizers) [5]. All the HOMO energies of the designed dyes are greater than the redox potential of the electrolyte (4.70 eV) [36]. In addition, the LUMO energy values of the dyes are expected to be at least 0.2 eV greater than the conduction band of  $TiO_2$  (-4.00 eV) to facilitate quick electrons injection into the TiO<sub>2</sub> semiconductor the dyes' excitation [36]. Thus, the LUMO energies of all studied dyes are higher than CB of  $TiO_2$  by 0.80-0.96 eV. Therefore, the designed dyes (PBPD and PTPD series) are appropriate for DSSC application and good choice as sensitizers. The proposed dyes' HOMO energy values are as follows: PBPD-4 (-4.83 eV) > PBPD-1 (-4.87 eV) > PBPD-2 (-4.89 eV) > PTPD-4 (-5.02 eV) > PTPD-1 (-5.03 eV) > PBPD-5 (-5.06 eV) > PBPD-6 (-5.11 eV) > PBPD-3 (-5.19 eV) > PTPD-5 (-5.33 eV) > PTPD-2 (-5.37 eV) > PTPD-6 (-5.37eV) and PTPD-3 (-5.54 eV), thus, PBPD-1, PBPD-2, PBPD-4, PBPD-5, PTPD-1 and PTPD-5 are expected to have capacity for good regeneration and performance [37].

Furthermore, the PBPD dyes have higher HOMO energies than their counterpart/corresponding PTPD dyes (Table 1).

The energy gap has a considerable impact on molecular activity. A dye-sensitizer with a small bandgap energy is better for electron excitation and has better absorption qualities. [36]. The energy gaps ( $\Delta$ Eg) of the dye-sensitizers can be arranged in ascending order as PBPD-4 (1.75 eV) < PBPD-1 (1.83 eV) < PBPD-2 (1.85 eV) < PTPD-4 (1.87 eV) < PTPD-1 (1.90 eV) < PBPD-5 (1.93 eV) < PBPD-6 (1.99 eV) < PBPD-3 (2.09 eV) < PTPD-5 (2.15 eV) < PTPD-2 (2.21 eV) < PTPD-6 (2.27 eV) < PTPD-3 (2.33 eV), as shown in Table 1 and



Figure 2. Optimized structures of designed dye-sensitizers.



Figure 3. The frontier orbitals overlay.

and Figure 4; thus, PBPD-1, PBPD-2, PBPD-4, PBPD-5, PBPD-6, PTPD-1, and PTPD-4 are expected to have excellent absorption qualities due to readiness of electron to move from the HOMO to the LUMO, thus suggesting that these molecules would have higher short-circuit current densities (Jsc) [36].

Likewise, the  $\Delta$ Eg of PBPD dyes are lower than their corresponding PTPD dyes, thus PBPD dyes are expected to have Jsc than their counterpart PTPD dyes. However, by substituting 2-[3-(10Hphenothiazin-3-yl)furan-2-yl]-10H-

phenothiazine (donor) in PBPD-1 with 2-[3-(10H-phenothiazin-3-yl)thiophen-2-yl]-10H-

phenothiazine (donor), as shown in PBPD-2,

leads to increase in  $\Delta$ Eg by 0.02 eV, and further increases  $\Delta$ Eg by 0.26 eV in PBPD-3, when it is replaced with 2,3-di(thianthren-2-yl)thiophene (donor). However, replacing thieno[3,2*b*]thiophene in PBPD-1 with bisthieno[3,2-*b*:2',3'*d*]thiophene in PBPD-4 lowers the  $\Delta$ Eg by 0.08 eV. On replacing 2,3-dihydrothieno[3,4*b*][1,4]dioxine in PBPD-1 with 1,3-dihydro-2,1,3benzothiadiazole as represented in PTPD-1 increased the  $\Delta$ Eg by 0.07 eV. It is also noted that bisthieno[3,2-*b*:2',3'-*d*]thiophene in PBPD-4 caused a reduction of  $\Delta Eg$  by 0.03 eV compared to PTPD-4.

Dye	НОМО	LUMO	DM	Eg
PBPD -1	-4.87	-3.04	19.55	1.83
PBPD-2	-4.89	-3.04	16.13	1.85
PBPD-3	-5.19	-3.10	15.01	2.09
PBPD-4	-4.83	-3.08	12.08	1.75
PBPD-5	-5.06	-3.11	15.01	1.95
PBPD-6	-5.11	-3.12	14.23	1.99
PTPD-1	-5.03	-3.13	10.00	1.90
PTPD-2	-5.37	-3.16	10.18	2.21
PTPD-3	-5.54	-3.21	8.920	2.33
PTPD-4	-5.02	-3.15	12.95	1.87
PTPD-5	-5.33	-3.18	10.28	2.15
PTPD-6	-5.47	-3.20	12.54	2.27

Table 1. Frontier orbital energies (eV) and dipole moment (Debye) of the designed dyes



Figure 4. The energy gap graph.

# Molecular indicators of the dye's response to the environment

The chemical reactivity characteristics of the dyes, including their electrophilicity index ( $\omega$ ), chemical hardness ( $\eta$ ), electron-donating power ( $\omega$ -), and electron-accepting power ( $\omega$ +) were calculated using DFT conceptual calculations. The ease of electron transfer through the molecule has been linked to low value of chemical hardness ( $\eta$ ) [36]. Also,  $\eta$  has been correlated to the light harvesting efficiency (LHE) and the DSSC's conversion efficiency [38]. The  $\eta$  values ranged 0.875 eV (PBPD-4) to 1.165 eV (PTPD-3) as shown in Table 2, indicating that PBPD -1 (0.915 eV), PBPD-2 (0.925), PBPD-5 (0.975 eV), PBPD-6 (0.995 eV), PTPD-1 (0.950 eV), PTPD-4 (0.935 eV), and PBPD-4 (0.875 eV) would have ease of electrons transfer property and enhanced DSSC's conversion efficiency. The electrophilicity index  $(\omega)$  is linked to the stabilization energy of a molecule that is saturated with electrons, and the electron giving power ( $\omega$ -) and electronaccepting power ( $\omega$ +) are connected to the molecular ability to give and accept electrons, respectively; thus, lower  $\eta$ , higher values of  $\omega$ and  $\omega$ + are preferrable for good dye sensitizers [39]. The  $\omega$  and  $\omega$ + values can be ordered as PTPD-3 < PTPD-2 < PTPD-6 < PBPD-3 < PTPD-5 < PBPD-6 < PBPD-2 < PBPD-5 < PBPD-1 < PTPD-1 < PTPD-5 < PBPD-4.

#### Electrostatic Potential Map of the studied dyes

The electron density is a crucial factor in predicting intermolecular interactions resulting from hydrogen bonding, as well as the reactivity of electrophilic and nucleophilic sites, which govern chemical processes. Figure 5 is the molecular electrostatic potential maps (MEPs) for the designed dyes; the red regions typify the negative potentials (the electron-rich area), which correspond to the responsive site for electrophilicity. The positive potentials (electronpoor area) are the blue regions, which correspond to the responsive site for nucleophilicity. The MEP energies are ordered as red, orange, yellow, and blue. Analysis in Figure 5 revealed that the carboxyl oxygen atoms and the cyano group (-CN) on the acceptor, as well as cyano group (-CN) on the cyano-thiophene, an auxiliary acceptor group on the dyes are highly negative regions (red colour); thus, the most advantageous sites for the electrolyte [4].

Dye	η	М	ω	ω	ω+
PBPD-1	0.915	-3.955	8.548	10.639	6.684
PBPD-2	0.925	-3.965	8.498	10.632	6.631
PBPD-3	1.045	-4.145	8.221	10.413	6.279
PBPD-4	0.875	-3.955	8.938	11.044	7.070
PBPD-5	0.975	-4.085	8.558	10.728	6.637
PBPD-6	0.995	-4.115	8.509	10.697	6.576
PTPD-1	0.950	-4.080	8.761	10.938	6.840
PTPD-2	1.105	-4.265	8.231	10.529	6.237
PTPD-3	1.165	-4.375	8.215	10.516	6.173
PTPD-4	0.935	-4.085	8.924	11.101	6.998
PTPD-5	1.075	-4.255	8.421	10.694	6.428
PTPD-6	1.135	-4.335	8.279	8.8601	6.253

Table 2. Reactivity properties of the designed dyes



**Figure 5.** Electrostatic potential maps on the molecular surfaces of the designed dyes.

#### UV-vis absorption

The transition characteristics were estimated based on the optimized structures of the dyes at the TD-DFT method, with a 6-31G (d,p) basis set. The electromagnetic spectrum's absorption in the near-ultraviolet (UV) and visible regions is very vital for photocurrent conversion in DSSC [40]. The electronic transition characteristics associated absorption with wavelengths, oscillator strength (f), and distinctive molecular orbital involvements are listed in Table 3. The absorption  $\lambda_{max}$  (longest wavelength) are 495.07 (737.80), 491.23 (723.84), 456.22 (630.09), 505.72 (763.99), 472 (681.25), and 472.15 (666.13) nm for PBPD-1, PBPD-2, PBPD-3, PBPD-4, PBPD-5 and PBPD-6, respectively. Others are 529.31 (715.75), 555.84 (624.95), 439.96 (578.36), 548.44 (722.46), 567.22 (632.64), and 423.93 (587.86) nm for PTPD-1, PTPD-2, PTPD-3, PTPD-4, PTPD-5, and PTPD-6, respectively. The electrons transition/transferring for dyes'  $\lambda_{max}$ are majorly from  $H \rightarrow L+1$  for PBPD-1 through PBPD-6 and PTPD-6; H-1→L for PTPD-2 and PTPD-5; H-3 $\rightarrow$ L for PTPD-1 and PTPD-4, and H- $4 \rightarrow L$  for PTPD-3. All the longest wavelengths of the dyes are from  $H \rightarrow L$  representing  $\pi \rightarrow \pi^*$ transitions. Furthermore, the replacement of 2-[3-(10H-phenothiazin-3-yl)furan-2-yl]-10H-

phenothiazine (donor) in PBPD-1 with 2-[3-(10H-phenothiazin-3-yl)thiophen-2-yl]-10H-

phenothiazine (donor) as displayed in PBPD-2 shifted the  $\lambda_{max}$  to shorter wavelength by 5 nm, and further shifted to shorter wavelength of 35 nm in PBPD-3 when it is replaced with 2,3di(thianthren-2-yl)thiophene (donor). However, replacing thieno[3,2-*b*]thiophene in PBPD-1 with bisthieno[3,2-b:2',3'-d]thiophene in PBPD-4 red shifted the  $\lambda_{max}$  by 10 nm, and also changing 2,3dihydrothieno[3,4-b][1,4]dioxine in PBPD-1 to 1,3-dihydro-2,1,3-benzothiadiazole as represented in PTPD-1 shifted the  $\lambda_{max}$  to a longer wavelength by 34 nm. It is also noted that bisthieno[3,2-b:2',3'-d]thiophene in PBPD-4 caused a red shift in  $\lambda_{\text{max}}$  by 19 nm compared to PTPD-4.

# Calculations of optoelectronic parameters affecting DSSC performance

The DSSCs performance can be measured as overall power conversion efficiency (PCE), whose value depends on the short-circuit current density (Jsc), the open-circuit photovoltage (Voc), the fill factor (FF), and incident solar power (Pin), as given in Equation (1) [40].

$$PCE = \frac{J_{sc}V_{oc}}{P_{in}}FF$$
(1)

And the charge collecting efficiency  $(\eta_{coll})$ , electron injection efficiency  $(\Phi_{inj})$ , and the lightharvesting efficiency (LHE) (at a certain wavelength) are determinants of the shortcircuit current density (J<sub>SC</sub>) for a DSSC, as shown in Equation (2) [36]:

$$J_{SC} = \int LHE(\lambda)\phi_{inj}\eta_{coll}\partial\lambda$$
(2)

It follows that the light harvesting efficiency (LHE) component of the dyes'  $J_{SC}$ , can be determined from the absorption coefficient (A), relates to the oscillator strength (f) of the excited state of the maximum wavelength (max) as follows [40]:

LHE = 
$$1 - 10^{-A} = 1 - 10^{-f}$$
 (3)

For a dye-sensitizer to effectively absorb the majority of photons in the UV-Visible region, and then inject photoexcited electrons into the CB of TiO<sub>2</sub>, the LHE value must be near to unity; thus, PTPD-2 < PTPD-3 < PTPD-5 < PBPD-1 < PTPD-1 < PBPD-2 < PTPD-4 < PTPD-6 < PBPD-4 < PBPD-3 = PBPD-5 < PBPD-6. The dye-sensitizer's opencircuit photovoltage, Voc estimated from the energy of the dye's  $E_{LUMO}$  and the photoanode's (TiO<sub>2</sub>) conduction band ( $E_{CB}$ ) is shown in Equation (4) [34].

$$V_{OC} = E_{LUMO} - E_{CB}^{TiO_2} \tag{4}$$

For a dye-sensitizer to effectively absorb the majority of photons in the UV-Visible region, and then inject photoexcited electrons into the CB of

Dye	$\lambda_{nm} = E eV$	f MO interactions	Dye	$\lambda_{nm} = E eV$	<i>f</i> M0 interactions
PBPD -1	437.612.83454.622.73495.072.51591.122.10618.702.00737.801.68	$\begin{array}{ccc} 0.0784 & \text{H-1} \rightarrow \text{L+1} \ (0.66), \\ & \text{H-2} \rightarrow \text{L+1} \ (0.22) \\ 0.3935 & \text{H-3} \rightarrow \text{L} \ (0.74) \\ 0.8568 & \text{H} \rightarrow \text{L+1} \ (0.85) \\ 0.4823 & \text{H-2} \rightarrow \text{L} \ (0.95) \\ 0.2751 & \text{H-1} \rightarrow \text{L} \ (0.96) \\ 0.5155 & \text{H} \rightarrow \text{L} \ (0.98) \end{array}$	PTPD -1	446.632.78464.652.67529.312.34592.082.09658.231.88715.751.73	$\begin{array}{ll} 0.1798 & \text{H-4} \rightarrow \text{L} (.68), \\ & \text{H} \rightarrow \text{L+1} (0.29) \\ 0.6334 & \text{H} \rightarrow \text{L+1} (0.79) \\ 0.9804 & \text{H-3} \rightarrow \text{L} (0.94) \\ 0.0295 & \text{H-2} \rightarrow \text{L} (0.95) \\ 0.0558 & \text{H-1} \rightarrow \text{L} (0.98) \\ 0.1864 & \text{H} \rightarrow \text{L} (0.99) \end{array}$
PBPD-2	449.422.76458.772.70491.232.53582.872.13640.921.93723.841.71	$\begin{array}{ccc} 0.0724 & \text{H-3} \rightarrow \text{L} \ (0.68), \\ & \text{H-1} \rightarrow \text{L+1} \ (0.15) \\ 0.2431 & \text{H-1} \rightarrow \text{L+1} \ (0.82) \\ 0.9813 & \text{H} \rightarrow \text{L+1} \ (0.86) \\ 0.7196 & \text{H-2} \rightarrow \text{L} \ (0.97) \\ 0.0707 & \text{H-1} \rightarrow \text{L} \ (0.99) \\ 0.5993 & \text{H} \rightarrow \text{L} \ (0.99) \end{array}$	PTPD-2	<ul> <li>426.48 2.91</li> <li>437.81 2.83</li> <li>472.50 2.62</li> <li>487.26 2.54</li> <li>555.84 2.23</li> <li>624.95 1.98</li> </ul>	$\begin{array}{ccc} 0.0534 & \text{H-4} \rightarrow \text{L} (0.71), \\ & \text{H} \rightarrow \text{L+1} (0.16) \\ 0.4640 & \text{H} \rightarrow \text{L+1} (0.61), \\ & \text{H-4} \rightarrow \text{L} (0.26) \\ 0.3163 & \text{H-3} \rightarrow \text{L} (0.97) \\ 0.3580 & \text{H-2} \rightarrow \text{L} (0.98) \\ 0.6316 & \text{H-1} \rightarrow \text{L} (0.93) \\ 0.2086 & \text{H} \rightarrow \text{L} (0.95) \end{array}$
PBPD-3	399.243.11428.322.90456.222.72476.212.60487.442.54630.091.97	$\begin{array}{ll} 0.0099 & \text{H-4} \rightarrow \text{L} \ (0.80) \\ 0.1113 & \text{H-3} \rightarrow \text{L} \ (0.65), \\ & \text{H} \rightarrow \text{L+1} \ (0.21) \\ 1.4093 & \text{H} \rightarrow \text{L+1} \ (0.63), \\ & \text{H-3} \rightarrow \text{L} \ (0.29) \\ 0.0967 & \text{H-2} \rightarrow \text{L} \ (0.98) \\ 0.3729 & \text{H-1} \rightarrow \text{L} \ (0.96) \\ 1.2837 & \text{H} \rightarrow \text{L} \ (0.97) \end{array}$	PTPD-3	420.552.95439.962.82477.552.60498.652,49556.032.23578.362.14	$\begin{array}{ccc} 0.2280 & H \rightarrow L+1 \ (0.42), \\ & H-1 \rightarrow L+1 (0.37) \\ 0.6153 & H-4 \rightarrow L \ (0.93) \\ 0.3293 & H-3 \rightarrow L \ (0.97) \\ 0.0870 & H-2 \rightarrow L \ (0.99) \\ 0.0859 & H-1 \rightarrow L \ (0.86) \\ 0.6909 & H \rightarrow L \ (0.87) \end{array}$
PBPD-4	457.432.71464.992.67505.722.45581.062.13653.181.90763.991.62	$\begin{array}{ccc} 0.0174 & \text{H-1} \rightarrow \text{L+1} \ (0.57), \\ & \text{H-3} \rightarrow \text{L} \ (0.31) \\ 0.1886 & \text{H-3} \rightarrow \text{L} \ (0,50), \\ & \text{H-1} \rightarrow \text{L+1} \ (0.40) \\ 1.2824 & \text{H} \rightarrow \text{L+1} \ (0.83) \\ 0.6017 & \text{H-2} \rightarrow \text{L} \ (0.98) \\ 0.0852 & \text{H-1} \rightarrow \text{L} \ (1.00) \\ 0.6439 & \text{H} \rightarrow \text{L} \ (0.99) \end{array}$	PTPD-4	457.652.71476.492.60548.442.26588.802.11662.131.87722.461.72	$\begin{array}{ccc} 0.1369 & \text{H-4} \rightarrow \text{L} (0.74), \\ & \text{H} \rightarrow \text{L+1} (0.16) \\ 0.6758 & \text{H} \rightarrow \text{L+1} (0.80) \\ 1.0855 & \text{H-3} \rightarrow \text{L} (0.93) \\ 0.0351 & \text{H-2} \rightarrow \text{L} (0.95) \\ 0.0641 & \text{H-1} \rightarrow \text{L} (0.99) \\ 0.2042 & \text{H} \rightarrow \text{L} (0.99) \end{array}$
PBPD-5	408.603.03440.832.81472.002.63477.522.60508.122.44681.251.82	$\begin{array}{ll} 0.0064 & \text{H-6} \rightarrow \text{L} \ (0.81) \\ 0.0545 & \text{H-3} \rightarrow \text{L} \ (0.69), \\ & \text{H} \rightarrow \text{L+1} \ (0.20) \\ 1.4127 & \text{H} \rightarrow \text{L+1} \ (0.65), \\ & \text{H-3} \rightarrow \text{L} \ (0.26) \\ 0.0101 & \text{H-2} \rightarrow \text{L} \ (0.29) \\ 0.7611 & \text{H-1} \rightarrow \text{L} \ (0.93) \\ 1.0391 & \text{H} \rightarrow \text{L} \ (0.98) \end{array}$	PTPD-5	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{lll} 0.0432 & \text{H-4} \rightarrow \text{L} \ (0.75) \\ 0.5501 & \text{H} \rightarrow \text{L+1} \ (0.66), \\ \end{array}$ $\begin{array}{lll} 0.1428 & \text{H-3} \rightarrow \text{L} \ (0.98) \\ 0.4813 & \text{H-2} \rightarrow \text{L} \ (0.97) \\ 0.7222 & \text{H-1} \rightarrow \text{L} \ (0.94) \\ 0.3104 & \text{H} \rightarrow \text{L} \ (0.96) \end{array}$
PBPD-6	<ul> <li>411.89 3.10</li> <li>441.63 2.81</li> <li>473.15 2.62</li> <li>488.88 2.54</li> <li>507.09 2.45</li> <li>666.13 1.86</li> </ul>	$\begin{array}{ccc} 0.0125 & \text{H-4} \rightarrow \text{L} \ (0.56), \\ & \text{H-6} \rightarrow \text{LUMO} \ (0.33) \\ 0.1467 & \text{H-3} \rightarrow \text{L} \ (0.66), \\ & \text{H} \rightarrow \text{L+1} \ (0.21) \\ 1.4913 & \text{H} \rightarrow \text{L+1} \ (0.64,), \\ & \text{H-3} \rightarrow \text{L} \ (0.29) \\ 0.0174 & \text{H-2} \rightarrow \text{L} \ (0.99) \\ 0.5115 & \text{H-1} \rightarrow \text{L} \ (0.95) \\ 1.0768 & \text{H} \rightarrow \text{L} \ (0.98) \end{array}$	PTPD-6	423.93 2.93 442.45 2.80 464.12 2.67 497.71 2.49 509.36 2.43 587.86 2.11	1.1357H $\rightarrow$ L+1 (0.74)0.4710H-4 $\rightarrow$ L (0.77)0.0173H-3 $\rightarrow$ L (0.83)0.2689H-2 $\rightarrow$ L (0.98)0.3074H-1 $\rightarrow$ L (0.99)0.8357H $\rightarrow$ L (0.99)

**Table 3.** Absorption wavelengths with molecular orbitals involve electronic transitions calculated at the TD-DFT/B3LYP/6-31G\*\* level

To understand a solar cell device's electric potential capability and PCE, as well as to prevent charge recombination in the dye, a high Voc value is required. The predicted Voc for the dyes ranged from 0.79 to 0.96 eV (Table 4), which means that PBPD-1/PBPD-2 (0.96 eV), PBPD-3 (0.90 eV), and PBPD-4 (0.92 eV) are predicted to exhibit higher electron injection power or higher injection driving force, which would boost the PCE of the dyes [34]. The free energy change electron injection ( $\Delta G$ )<sup>inject</sup>) for the dye-sensitizers calculated using the oxidation potential of an excited dye ( $E_{ox}^{dye*}$ ) and the redox potential of the dye-TiO<sub>2</sub> couples, in an excited state [36], as shown in Equation (5).

$$\Delta G^{\text{inject}} = E_{\text{ox}}^{\text{dye*}} - E_{CB}^{TiO_2}$$
(5)

Where,  $E_{ox}^{dye*}$  is the difference between the oxidation potential of the dye in its ground state  $(E_{ox}^{dye*})$  and the electronic vertical transition energy  $(\lambda_{max}^{ICT}, \text{ in eV})$  [34] and it is estimated as follows:

$$E_{ox}^{dye*} = E_{ox}^{dye} - \lambda_{max}^{ICT}$$
(6)

The  $\Delta G^{inject}$  reveals the dye's sensitivity to sunlight absorption which leads to the dye's excitation and subsequent transfer of electrons to the semiconductor TiO<sub>2</sub>'s conduction band. For the possibility of electron drive into the conduction band, a negative value of  $\Delta G^{inject}$  is preferrable [40]. It is interesting to note that  $\Delta G^{\text{inject}}$  values are all negative (between -0.604 and -1.634 eV) (Table 4), which suggested that all the dyes are thermodynamically satisfactory for electron injection to the TiO<sub>2</sub> semiconductor [34]. Moreover, the injection efficiency of the electrons in the excited state could be substantial, providing a significant driving force for electron injection process, when the absolute  $\Delta G^{inject}$  for dyes is larger than 0.2 eV [34]. The absolute Ginject values of the dyes could be ordered as PBPD-1/PTPD-6 > PBPD-3 > PBPD-4 > PBPD-2 > PBPD-5 > PTPD-5 > PBPD-6 > PTPD-3 > PTPD-1 > PTPD-4 > PTPD-2.

Also, the dye's regeneration ( $\Delta G^{\text{regen}}$ ) force is estimated using Equation (7) and the redox couple of  $I^-/I_3^-(\mathbf{E}_{\text{redox}}^{\text{electrolyte}})$  is taken be 4.70 eV [36].

$$\Delta G^{\text{regen}} = E_{\text{ox}}^{\text{dye}} - E_{\text{redox}}^{\text{electrolyte}}$$
(7)

The  $\Delta G^{regen}$  provides information on how charge is recovered in a solar cell system. To prevent charge recombination, this process must be fast [40]. As a result, a positive  $\Delta G^{regen}$  value is anticipated for efficient dye regeneration. The  $\Delta G^{regen}$  values for these dyes showed they all positive (0.13 eV, PBPD-4 to 0.84 eV, PTPD-3) and are favourable for sufficient charge regeneration (Table 4). Another parameter that is also very crucial, is an excited state lifetime  $(\tau_{esl})$  when measuring charge transfer efficiency. The higher the excited state  $(\tau_{esl})$ , the longer the dye can be held in the cationic state and the better it is for charge transfer [36]. The lifespan of the dye in its excited state can be calculated using the following Equation (8). where f is the oscillator intensity corresponding to the electronic state, and E is the excitation energy of the electronic states (cm<sup>-1</sup>) at particular *f*.

$$\tau_{\rm esl} = \frac{1.499}{f^{\rm E^2}}$$
(8)

The  $\tau_{esl}$  gives an estimated time for electrons to be pushed into the semiconductor substrate from the dye. The higher the optical stability of the dye in the excited state, the lesser the dye's lightemitting efficiency, and the longer the excited state lifetime [36]. The predicted  $\tau_{esl}$  values for designed dyes, as shown in Table 4, revealed that PTPD-8 (4.58 ns) > PTPD-3 (4.54 ns) > PTPD-5 (4.17 ns) > PBPD-1 = PTPD-1 (2.68 ns) > PTPD-4 (2.60 ns) > PBPD-2 (2.30 ns) > PBPD-4 (1.86 ns) > PBPD-5 = PTPD-6 (1.48 ns) > PBPD-6 (1.38 ns) > PBPD-3 (1.38 ns). Thus, there would be a delay in charge recombination process in dyes PTPD-8, PTPD-3 and PTPD-5, which can lead to improvement of the DSSCs efficiency.

Dye	λ <sub>max</sub> (nm)	F	$E_{ox}^{dye}$	$\lambda_{max}^{ICT}$ eV	$E_{ox}^{dye*}$	Voc	LHE	$\Delta G^{inject}$	$\Delta G^{regen}$	τ <sub>esl</sub> (ns)
PBPD-1	495.07	0.8568	4.87	2.504	2.366	0.96	0.861	-1.634	0.17	2.68
PBPD-2	491.23	0.9813	4.89	2.524	2.366	0.96	0.896	-1.528	0.19	2.30
PBPD-3	456.22	1.4093	5.19	2.718	2.472	0.90	0.961	-1.625	0.49	1.38
PBPD-4	505.06	1.2824	4.83	2.455	2.375	0.92	0.948	-1.567	0.13	1.86
PBPD-5	472.00	1.4127	5.06	2.627	2.433	0.89	0.961	-1.510	0.36	1.48
PBPD-6	473.15	1.4913	5.11	2.620	2.490	0.88	0.968	-1.312	0.41	1.41
PTPD-1	529.31	0.9804	5.03	2.342	2.688	0.87	0.895	-0.861	0.33	2.68
PTPD-2	555.84	0.6316	5.37	2.231	3.140	0.84	0.766	-0.604	0.67	4.58
PTPD-3	578.36	0.6909	5.54	2.144	3.396	0.79	0.796	-1.241	0.84	4.54
PTPD-4	548.44	1.0855	5.02	2.261	2.759	0.85	0.918	-0.856	0.32	2.60
PTPD-5	567.22	0.7222	5.33	2.186	3.144	0.82	0.810	-1.455	0.63	4.17
PTPD-6	423.93	1.1359	5.47	2.925	2.546	0.80	0.927	-1.634	0.77	1.48

Table 4. The parameters affecting dye-sensitizers' optoelectronic properties

In addition, the functionality of the DSSC device can be affected by the charge transfer rate (k); a dye-sensitizer should have an excellent charge transfer rate to be highly efficient [34]. The transfer rate (k) is estimated using Equation (9):

$$k = \left(\frac{\pi}{k_b \lambda T}\right)^{\frac{1}{2}} \frac{|V_{RP}|^2}{\hbar} exp\left(-\frac{\lambda}{4k_b T}\right)$$
(9)

Where,  $\lambda$ ,  $k_b$ , T, and  $V_{RP}$  are total reorganization energy, Boltzmann constant, temperature and coupling constant, respectively. And  $\lambda$  ( $\lambda = \lambda_{+} + \lambda_{+}$ ) is calculated from equation 10.  $\lambda$  is the addition of the electron-reorganization energies ( $\lambda_{-}$ ) and the hole-reorganization energies ( $\lambda_{+}$ );

$$\lambda_{\pm} = \left(E_0^{\pm} - E_{\pm}^{\pm}\right) + \left(E_{\pm}^0 - E_0^0\right) \tag{10}$$

Where,  $E_0^{\pm}$  is the energy of the neutral molecule computed in the optimum cationic/anionic state,  $E_{\pm}^0$  is the energy of the cation/anion with the geometry of the neutral molecule,  $E_{\pm}^{\pm}$  is the energy of the anion/cation calculated based on optimized anion/cation geometry and  $E_0^0$  is the energy of the neutral molecule.

The coupling constant  $(|V_{RP}|)$ , a variable that influences the rate of electron injection from the organic dyes into the semiconductor substrate [40]:

$$|V_{RP}| = \Delta E_{RP}/2 \tag{11}$$

Where,  $\Delta E_{RP}$  is estimated from Equation (12).

The reorganization energies,  $\lambda$ , coupling constant  $|V_{RP}|$  and charge transfer rate (k) values are displayed in Table 5. The computed  $\lambda$  total values for the designed dyes are in following order:

PTPD-5 (0.811 eV) > PTPD-2 (0.808 eV) > PTPD-6 (0.775 eV) > PTPD-1 (0.705 eV) > PTPD-4 (0.666 eV) > PBPD-1 = PTPD-3 (0.625 eV) > PBPD-2 (0.616 eV) > PBPD-4 (0.584 eV) > PBPD-3 (0.550 eV) > PBPD-5 (0.548 eV) > PBPD-6 (0.529 eV). These values suggested that PBPD dyes have lower  $\lambda$  total values than their counterpart PTPD dyes; thus, PBPD dyes should have good electron-transfer efficiency due to low values of  $\lambda$  [4]. Also, it is observed that dyes with lower  $\lambda$  values have higher LHE values (Figure 6) and lower  $\tau_{esl}$  (Table 4). The V<sub>RP</sub> also showed that PBPD-3, PBPD-6, PBPD-2, and PBPD-5 with higher  $V_{RP}$  values presented greater electrons transfer rate constant (k), as is presented in Table 5, and should result in a better sensitizer. Additionally, it is also noticed that dyes with higher  $\Delta G^{regen}$  driving forces displayed higher  $V_{RP}$ values (Figure 7).

$$\Delta E_{RP} = \left[ E_{LUMO}^{dye} + 2E_{HOMO}^{dye} \right] - \left[ E_{LUMO}^{dye} + E_{HOMO}^{dye} + E_{CB}^{TiO_2} \right] = E_{HOMO}^{dye} - E_{CB}^{TiO_2}$$
(12)

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<b>Fable 5.</b> Reorganization energies, $\mathcal{K}(ev)$ , coupling constant $ v_{RP} $ and that get transfer rate								
Dye	λ_	λ+	λ	$ \Delta E_{RP} $	$ V_{RP} $	<b>k</b> x10 <sup>12</sup>		
PBPD-1	0.345	0.281	0.626	0.87	0.435	1.44		
PBPD-2	0.322	0.294	0.616	0.89	0.445	1.67		
PBPD-3	0.315	0.235	0.550	1.19	0.595	6.02		
PBPD-4	0.314	0.270	0.584	0.83	0.415	2.04		
PBPD-5	0.313	0.235	0.548	1.06	0.530	4.88		
PBPD-6	0.313	0.216	0.529	1.11	0.555	6.56		
PTPD-1	0.399	0.304	0.703	1.03	0.515	9.01		
PTPD-2	0.399	0.409	0.808	1.37	0.685	5.34		
PTPD-3	0.370	0.256	0.626	1.54	0.770	4.51		
PTPD-4	0.374	0.292	0.666	1.02	0.510	1.30		
PTPD-5	0.371	0.440	0.811	1.33	0.665	4.88		
PTPD-6	0.355	0.420	0.775	1.47	0.735	8.66		

**Table 5.** Reorganization energies,  $\lambda$  (eV), coupling constant  $|V_{RP}|$  and charge transfer rate



**Figure 6.** The reorganization energies ( $\lambda$ ) and LHE of the designed dyes.



**Figure 7.** Reorganization drive force and coupling constant  $|V_{RP}|$  of the designed dyes.

#### Conclusion

The D-A- $\pi$ -A dyes were designed in such a way that 2-[3-(10H-phenoxazin-3-yl)thiophen-2-yl]-

10H-phenoxazine, 2,3-di(thianthren-2-yl)thiophene, and 2,3-di(thianthren-2-yl)furan as donor groups with 3,4-ethylenedioxythiophene (PBPD

dyes)/1,3-dihydro-2,1,3-benzothiadiazole (PTPD bisthieno[3,2-b:2',3'-d]thiophene dves) and /thienothiophene as acceptor and  $\pi$ -linker units, respectively connecting thiophene-3to carbonitrile (acceptor) and cyanoacrylic acid, an optoelectronic anchoring unit. The key properties such as absorption ( $\lambda$ max), light harvesting efficiency (LHE), open circuit current (Voc), regeneration ( $\Delta G^{regen}$ ), and injection ( $\Delta G^{inj}$ ) drive forces. excited state  $(\boldsymbol{\tau}_{esl}),$ total reorganization energy ( $\lambda$ ) and coupling constant  $(|V_{RP}|)$  were calculated using DFT and TD-DFT methods. The results showed that Dyes containing 1,3-dihydro-2,1,3-benzothiadiazole (PBDP dyes) have higher HOMO and LUMO energies than the corresponding dyes with 2,3dihydrothieno[3,4-b][1,4]dioxine (PTDP dyes), leading to lower energy band gap. Thus, PBDP dyes have lower energy band gaps, lower total reorganization energy ( $\lambda$ ), and higher injection drive force ( $\Delta G^{inj}$ ) than PTDP dyes counterparts. However, PTPD dyes are favoured by the excited state  $(\tau_{esl})$  and coupling constant  $(|V_{RP}|)$  than corresponding PBDP dyes. The optoelectronic characteristics of the dyes are controlled mainly by 3,4-ethylenedioxythiophene/1,3-dihydro-2,1,3-benzothiadiazole than subunit bisthieno[3,2-b:2',3'-d]thiophene/thienothiophene subunit. However, all the designed dyes are appropriate for DSSC application and good choice as sensitizers.

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#### **Disclosure statement**

The authors declare that they have no conflict of interest.

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