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The Effect of Π-Bridging on the Optoelectronic Properties of Organic Solar Cell Photosensitiser

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Abstract

Organic π-conjugated materials have been used as active materials in optoelectronic devices. The organic nature of these materials, when suitably modified, allows fabrication of flexible, lightweight and low cost optoelectronic devices. Recently, considerable attention has been paid to the modulation of organic dyes in order to create effective dye sensitized solar cell using theoretical methods. In this regard, four dyes sensitizer, containing tertiary aromatic amine as donor (D) and π-bridge were designed and theoretically investigated for dye-sensitized solar cells (DSSCs). These dyes were simulated using Density Functional Theory (DFT) and Time–Dependent Density Functional Theory (TDFT) to calculate their electronic properties, optical absorption properties (λ_{max}) and light harvesting efficiency (LHE). The electronic properties: Highest occupied molecular orbital (HOMO), Lowest unoccupied molecular orbital (LUMO) and Energy band gap (E_g) of these dyes were in the range of -4.99 to -6.04 eV, -2.41 to -2.56 eV and 2.48-3.48 eV respectively. While the λ_{max} peaks appear in two regions around 240–450 nm and 450–650 nm. The LHE values were in the range of 0.68–0.92. The results revealed that the nature and position of the π-bridged dye sensitisers, affects the electronic and light harvesting properties making the modelled π-bridged dye more proficient solar cell sensitisers than those without π-bridge. Thus, this work is a guide to the synthesis of more efficient organic solar cell sensitizers and helps to understand the structure–properties relationship of the new systems.

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INTRODUCTION

Renewable energy sources are solution for sustainable energy supply, especially by the direct utilization of solar energy. The organic type of photovoltaic technology is of interest in recent researches because it involves employment of π-conjugated materials (small oligomers, polymers and dyes) based on a planar backbone of sp^2-bonded atoms in the solar cell active layer. The π-conjugated organic materials of the dye solar cells are highly sought after, for study and use because of their solution-processable materials, ease of synthesis, low cost, mechanically flexible and high performance, compared to other technologies (Shaheen et al., 2005). The properties of organic π-conjugated materials can be "tuned" to allow for changes in the electronic structure and property of the systems. Most of these changes occur as a result of altering the E_g between the HOMO and the LUMO. Altering the E_g can be done by doping, increasing conjugation length, grafting onto the building blocks of the conjugated materials, or incorporating elements that are active participants in the conjugation (Roncali, 2007). The current challenges for organic photovoltaics most especially the dye sensitised solar cells (DSSCs) remain improved efficiency as well as cost-effectiveness, to compete with traditional silicon-based solar cells. Efficiency development in organic solar cell device is largely driven by the design of new organic sensitisers (π-conjugated molecules). Structural design is often dominated by costly and time-consuming synthetic procedures (Mishra *et al*., 2009). In addition, the synthesis and testing of these new materials for organic solar cells process involves a large degree of trial and error process. Therefore, synthetic chemists find it difficult to obtain high efficient organic sensitisers with desirable properties prior to the experiments on the assembled cell, without any support on the information of the new molecules (Zhang *et al*, 2012). Moreover, the structure-property relationships of new molecules are hardly obtained from “chemical intuitions” without accurate quantum mechanical calculations. In some cases, unsatisfactory results to the end of organic synthesis in laboratories indicate an urgent need to understand the physical origin of organic π-conjugated materials at molecular level before conducting experiment. Therefore, to overcome this delay in the development and synthesis of new organic sensitisers for efficient organic solar cells, advanced or high tech computational methods need to be utilised. In this article, the task was not just only to develop new sensitisers but to examine the effect of various π organic components on the properties of already well-established Donor-Acceptor (D-A) building blocks in order to obtain innovative molecular architectures Donor-π-Acceptor (D-π-A) and unique electronic properties. Therefore, unlike D-A sensitisers which have been widely used for many decades, D-π-A sensitisers incorporating benzene, thiophene, and phosphorus building blocks were introduced as the π-bridge between triphenylamine (TPA)-donor group and cyanoacrylic acid acceptor group as a model to compare with triphenylamine and cyanoacrylic acid acceptor group as shown in Figure 1.

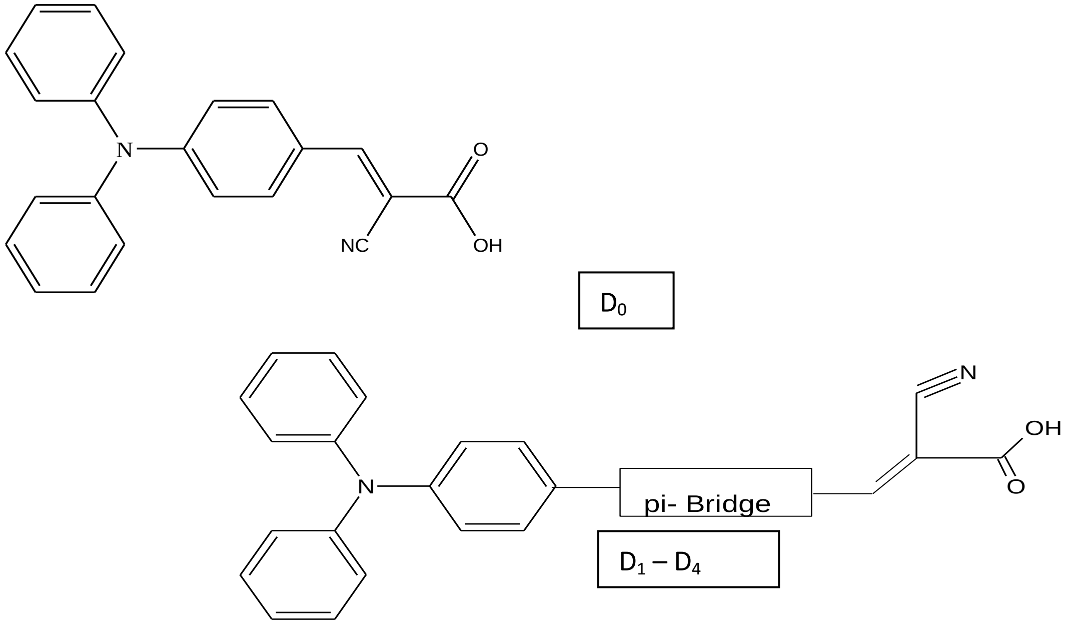


Figure 1: Structures of D_0 and $D_1 – D_4$ sensitisers

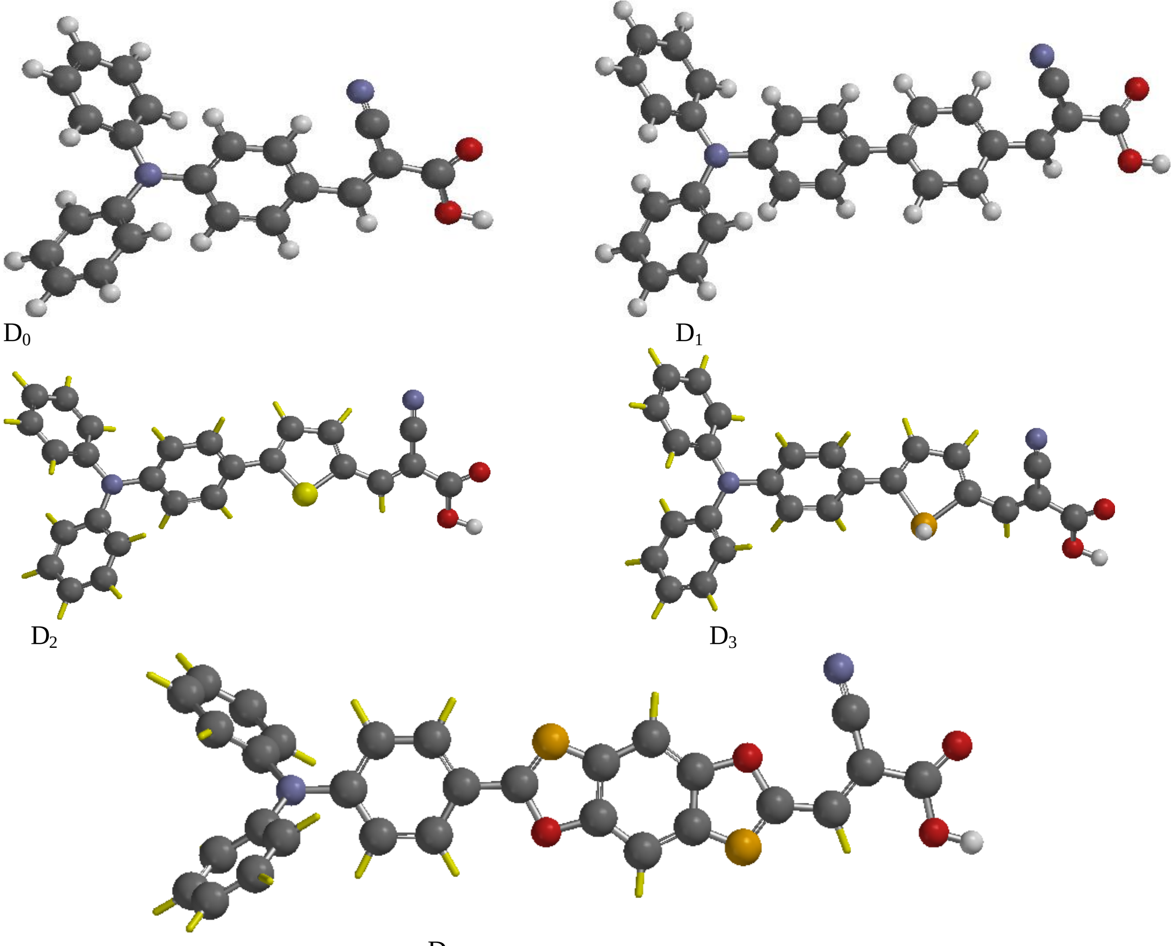
Computational methods

Molecular modeling techniques in quantum chemistry provide a competitive alternative to interpreting experimental data and even ensure the predictability of new materials arising from industrial interests and developments. The ground-state equilibrium geometry of the five triphenylamine dye sensitisers were fully optimized at the DFT level using the B3LYP hybrid functional with the 6-31G(d,p) basis set. The HOMO and LUMO levels were also calculated to provide easy access to the molecular orbital energies; determination of molecular orbital energies and charge population analysis were performed on the optimized structures of the studied dyes. Absorption transition calculations were carried out using the optimized geometry in ground state using TDDFT/6-31G(d,p) theory in gas phase. To understand electronic transitions, microscopic information about the electronic transitions was obtained by checking the molecular orbital (MO) corresponding to each electronic transitions, as calculated using the TD-DFT performed with the 6-31G(d,p) basis set and B3LYP functional level of theory (Oyeneyin *et al.*, 2018). All calculations were performed using Spartan 10 software (Shao *et al.*, 2011) implemented on an Intel_CoreTM i3-G42-247SB CPU, 2.30 GHz computer.

RESULTS AND DISCUSSIONS

Molecular Structures of Triphenylamine Cyanoacrylic Acid Derivatives (Modelled Dyes Sensitisers).The designed organic dye sensitisers (D_1-D_4) incorporating triphenylamine TPA (donor unit), benzene (D_1), thiophene (D_2), benzobis(1,3-

oxaphosphole) (D_3), and phosphole (π-bridge) units, and cyanoacrylic acid (CNCOOH acceptor unit) to form D-π-A dye sensitisers were optimized using DFT/B3LYP/6-31G(d,p) theory (Figure 2). Their properties were therefore compared with DFT/B3LYP/6- 31G(d,p) results of D_0 incorporating triphenylamine (TPA) (donor) unit, and cyanoacrylic acid (CNCOOH) (acceptor) unit, to form donor-pi-acceptor (D-A) dye sensitisers.


D_0

D_1

D_2

D_3

D_4

Figure 2: Optimized structures of the modelled dye sensitisers

Electronic Property of Modelled Dyes Sensitisers

The band gap energies, HOMOs, and LUMOs of organic sensitisers play a vital role in determining the thermodynamic driving force for the electrons injection (Umer *et al*., 2015). These energies of the dyes sensitisers are crucial in tuning the redox potential of both electrolytes and conduction band (CB) edge of TiO_2 in DSSCs in order to achieve the desired, harvesting capability of the dye molecule. Thus, the effect of organophosphorus group on the HOMO and LUMO levels was studied to find out the likelihood of the injecting charges to the CB of TiO_2 semiconductor and possible regeneration of the dye molecule. Table 1 provided the DFT calculation in CH_2Cl_2 and energy level alignment of the modeled dyes and TiO_2 semiconductor CB (−4.00 eV) (Asbury *et al.*, 2001) and the redox potential of I^-/I_3^-(−4.80 eV) (Asbury *et al.*, 2001). The excited and ground states energies of the modelled sensitisers, TiO_2 semiconductor and the redox level of the I_3^-/I^- electrolyte, were shown. Appropriate dyes for DSSC required suitable energy levels. For instance, the E_{LUMO} must be adequately negative with regard to the CB of TiO_2 for effective electron injection; and the E_{HOMO} should be sufficiently positive than the redox potential of I_3^-/I^- for efficient dye regeneration. Therefore, in evaluating the possibility of injecting electrons into the CB of the TiO_2 semiconductor and regenerating electrons from the electrolyte system, the orbital energy levels of the dyes were calculated.

The LUMO levels of D_1-D_4 were reduced when π-bridges were incorporated into D_0, and the HOMO levels of D_1-D_4 showed similar trend. The LUMO energy levels results showed that, changing of the π-bridges also affected the LUMO level in vacuum. In addition, the reduction in energy gaps of D_3-D_4 compared to D_1-D_2 was attributed to increase in the π-bridge unit. Therefore, the dyes of D_3-D_4 would be more efficient to extend the absorption wavelengths. However, with the stabilized molecular orbital energies, the energy gaps of these dyes were in the range of 2.489–3.48 eV. Energy band gaps of the designed dyes D_1–D_4 were smaller than the famous D_0 (2.56 eV). Sensitisers that have smaller energy gap values may demonstrate higher efficiency in the DSSCs (Guo, *et al.*, 2014). Thus, it could be concluded that the modelled molecules can have an improved light harvesting ability.

Table 1: Electronic Properties of Modelled Dyes (D_0, D_1-D_4) Systems

Dye Molecules	E_{HOMO} *(eV)*	E_{LUMO} *(eV)*	E_g *(eV)*	*λmax*	*LHE*
D_0	-6.04	-2.56	3.48	293/434	0.86
D_1	-5.53	-2.47	3.06	310/452	0.88
D_2	-5.24	-2.48	2.76	348/511	0.89
D_3	-4.99	-2.51	2.48	549/644	0.75
D_4	-5.00	-2.41	2.59	341/534	0.92

Electron Transfer Analysis and Electron Density Distribution of the Modelled Sensitisers

The effect of π-spacing on electron transfer processes of the modelled molecules required the evaluation of the charge transfer orientation in the orbital energy levels using electron densities distribution. The orientation of the charge transfer is related to the electron density distributions of orbital energy levels of the sensitisers. This molecular orbital contribution is important for assessing the charge-separation state of organic dyes. To generate an efficient charge-separated state, the HOMO must be localized on the donor subunit, and the LUMO must be localized on the acceptor subunit.

Density functional evaluation of the frontier molecular orbital distribution of the modelled systems (Figures 3) revealed a coplanar conformation between the D-π-A moieties. This is beneficial to the interaction between the electron donating TPA unit and the π-bridging molecules; in addition, it is beneficial to the injection of electrons due to the modified suitable energy level resulting from the introduction of the π-conjugated bridge. Figures 3 showed that the HOMO electron density plots of the dyes were distributed on the triphenylamine donor. The electron densities were little stretched from the electron donors and also delocalized on the π-bridges. While the LUMO plots of the dyes were quite different and mostly distributed on acceptors and π-bridges except for D_0 and D_1 systems. The electron densities in LUMOs of D_3-D_4 delocalized through the organophosphorus (π-bridge) and cyanoacrylic acid (acceptor). However, the electron densities in LUMOs of D_0 and D_1 delocalized the entire molecules

Comparison of LUMOs of D_0-D_2 and D_3-D_4 indicated that the LUMO of D_3-D_4 are more in electron density than D_2 (with thiophene as π-bridge), D_1 (with benzene as π-bridge) and D_0 (without π-bridge) respectively. This difference was predicted to be as a result of different strengths of π-bridge organophosphorus units. The organophosphorus unit combined with cyanoacrylic acid lowers the E_{LUMO} much more than the combined cyanoacrylic acid with phenylene and thiophene. This will definitely contribute to the increase of electron density localized on the acceptor unit. The electronic transition indicated that when electron at ground state was excited by photon from the sun light, electron would transfer from the triphenylamine ring (chromophore) towards the carboxyl group and a pronounced intramolecular charge separation, thus the LUMO orientation on the acceptor unit would favour electron injection, provided that similar molecular orbital distribution when the dye keen onTiO_2 surface (Ooyama *et al.*, 2013).

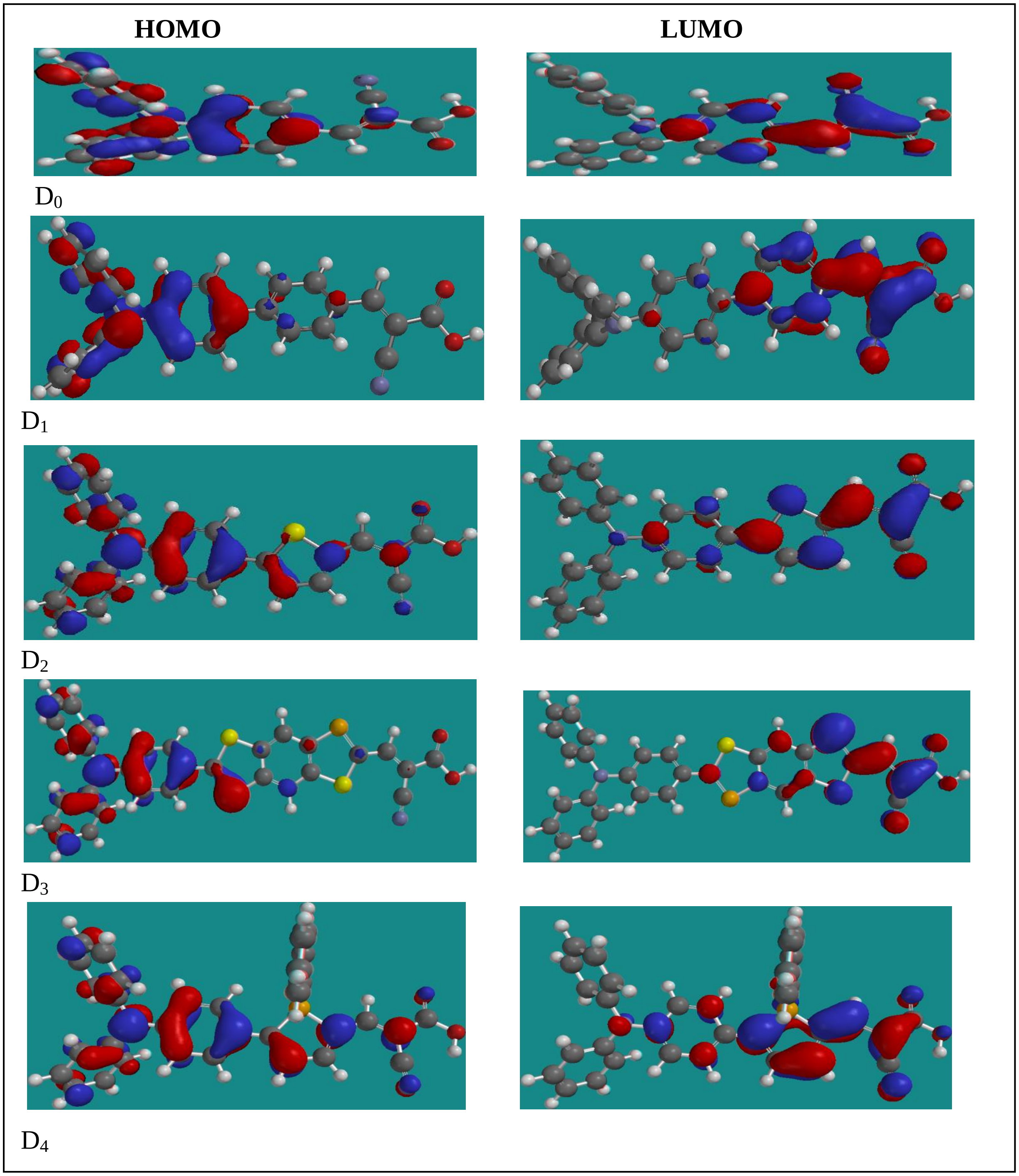


Figure 3: Frontier molecular orbital energy-level of modelled sensitisers containing benzene bridge (D_1), thiophene bridge (D_2) and phosphole bridges (D_3-D_4)

The effects of π-spacing organic unit on the distribution of electron were investigated on D_o, D_1 D_2, D_3 and D_4 sensitisers using energy gap. These modelled sensitisers were also divided into two fragments: the donor (TPA) and the conjunct bridge-acceptor fragments, and their orbital energy levels ($HOMO_{donor}$, $LUMO_{donor}$ $HOMO_{bridge\text{-}aceptor}$, and $LUMO_{bridge\text{-}aceptor}$) were calculated separately also listed in Table 2

Table 2. Molecular Orbital Energy Levels of Selected Compounds and Their Units

Molecules		E_{LUMO}	E_g	E_{HOMO}
TPA		-0.30		-4.95
CNCOOH		-2.62		-8.21
Bz-CNCOOH		-2.76		-7.07
Th-CNCOOH		-2.89		-6.82
BAP-CNCOOH		-3.44		-6.39
Ph-CNCOOH		-2.94		-6.51
TPA-CNCOOH	**(D_0)**	-2.56	3.48	-6.04
TPA-Bz-CNCOOH	**(D_1)**	-2.47	3.06	-5.53
TPA-Th-CNCOOH	**(D_2)**	-2.48	2.76	-5.24
TPA-BAP-CNCOOH	**(D_3)**	-2.51	2.48	-4.99
TPA-Ph-CNCOOH	**(D_4)**	-2.41	2.59	-5.00

Clearly, the $LUMO_{bridge\text{-}aceptor}$ of conjunct bridge-acceptor fragments were in the following order: CNCOOH (−2.62 eV) > Bz-CNCOOH (−2.76 eV) > Th-CNCOOH (−2.89 eV) > Ph-CNCOOH (−2.94 eV) > BAP-CNCOOH (-3.44). These values are properly positioned below the $LUMO_{donor}$ of the donor fragment (−0.3 eV). Similarly, the band gap of the D_o, D_1 $D_{2,}$ D_3 and D_4 sensitisers follow the same order with $LUMO_{bridge\text{-}aceptor}$ of conjunct bridge-acceptor fragments: D_o (3.48 eV) >D_1 (3.06 eV) >D_2 (2.76 eV) > D_4 (2.59 eV) > D_3 (2.48 eV). A larger influence was produced when the benzo(1,3-oxaphosphole) was incorporated into the sensitisers. The implication is that the presence of organophosphole as the π-bridge has meaningful effect in reducing the energy band gap and decreasing the E_{LUMO} of the sensitisers more than benzene and thiophene. It can be concluded that the position of the E_{LUMO} and the kind of π-bridge unit influences the electronic coupling since the more the contributions from the LUMOs of the dye and the more electrons delocalized on the acceptors, the stronger the coupling interaction between the sensitisers and TiO_2 will be. Therefore, the stronger coupling interaction between the sensitisers and TiO_2 will increase efficiency of electron injection because the strength of the interfacial interaction could influence the injection of electron from the excited dyes to the CB of TiO_2 surface. Furthermore, if this interaction between the excited dyes and the CB of TiO_2 semiconductor is strong enough, an ultrafast electron transfer can follow the initial excitation to the TiO_2 conduction band thereby retarding intramolecular thermalization and other competing processes (Le Baher and labat, 2010)

The direction of charge transfer in organic sensitisers is connected with electron density distribution of their molecular orbitals. As shown in Figure 3, electron transfer can be pictured as if electron is relocating from the LUMO of donor ($LUMO_{donor}$) through the LUMO of the π-bridge to the LUMO of the acceptor ($LUMO_{acceptor}$). In the modelled sensitisers, the energy drops of the modelled sensitisers ($LUMO_{donor}$–$LUMO_{bridge\text{-}acceptor}$) were in the following order: TPA-Ph-CNCOOH (0.864 eV) > TPA-Th-CNCOOH (0.4651 eV) >TPA-Bz-CNCOOH (0.0918 eV) > TPA-CNCOOH, (D_4> D_2> D_1> D_0) indicating that the incorporation of organophosphorus compounds (phospholes and heterophospholes) are more favourable for charge separation. The degree of energy barrier for reverse transfer should also follow this order; that is, the presence of organophosphorus compounds could weaken the reverse transfer process in solar cells. Therefore, energy levels of the π-bridge unit and donor unit are essential for effective charge separation and efficient the solar cell operation in general. It also worthy to note that, the lower the E_{LUMO} of the π-bridge of sensitisers (with the same TPA moiety), the more the localization of electron densities on the bridge-acceptor fragment. It was also discovered that organophosphorus pi-bridges are better pi-bridge unit for modeling of sensitisers.

Further investigation into the electron–transfer mechanism and the charge distribution of the modeled dyes, required the analysis of natural bond order (NBO). This analysis was carried out using the ground state optimized structures of the modelled sensitisers obtained at DFT/B3LYP/6–31G (d, p). The estimated NBO charges populated in each unit of the modeled sensitisers were shown in Table 3. Comparing the calculated NBO results of dyes D_3–D_4, the NBO charges of the electron donor were between 0.184 – 0.232 e^-. The positive charges of the donor group of all dyes revealed they were effective electron pushing unit. Contrarily, the negative charges in the π–conjugated bridge and acceptor/anchoring group showed that they were effective electron-pulling unit which trapped the electron in the acceptor unit of the molecular backbone. The data also suggested that charges on the acceptor unit are very close to each other. This could be as a result of the same type of acceptor unit used in all the modelled dyes molecules. However, the charges on the donors and the conjugated bridges are more flexible. During the excitation, the electrons on the donor group of dyes were transferred to the acceptor group, and the charge separation state was formed in dyes. Furthermore, the NBO charges of the acceptor/anchoring group were prominent in the sensitisers. That is, upon binding on the TiO_2 semiconductor, electrons could be successfully moved from the TPA unit to the acceptor unit and finally inject into the conduction band of TiO_2 (Asmae *et al.*, 2014).

Furthermore, the effluence of the π-bridge on the modelled dye sensitisers can be examined by determining the possible recombination process through the estimation of the atomic charges on nitrogen (q^N in $|e|$) of triphenylamine (TPA) donating group. As reported by Preat *et.al.*,(2009), far away positive charges on nitrogen of cationic triphenylamine moiety from the semiconductor surface after electron injection would effectively limit the recombination process (Preat *et.al.*, 2009). Therefore, to estimate *q*, charges derived from the electrostatic potential (Besler, *et al*., 1990) using B3LYP/6-31G(d) in gas-phase was utilized. For D_1-D_4, the difference in the charge (Δq^N) between the neutral (q_{dye}^N) -0.836 $|e|$ to -0.601$|e|$) and cationic species (q_{dye}^N +) -0.653$|e|$ to –0.511 $|e|$) amounted to 0.209 $|e|$ to 0.088$|e|$ as shown in Table 4. Therefore, it was assumed that a positive charge may not directly contact with TiO_2 semiconductor thereby effectively inhibiting the recombination reaction.

Table 3. The Ground State Charge Populations for the Modelled Dyes

Molecules	Donating unit	π-conjugated bridge unit	Acceptor Unit
D_0	0.181	-	-0.129
D_1	0.186	-0.014	-0.134
D_2	0.198	-0.016	-0.178
D_3	0.225	-0.123	-0.108
D_4	0.213	-0.119	-0.111

Table 4: Atomic Charges on Nitrogen (q^N in $|e|$) of the TPA Group

Molecules	Neutral Species (q_{dye}^N)	Cationic Species (q_{dye}^N +)	Variation of the Charge (Δq^N)
D_0	-0.596	-0.511	0.085
D_1	-0.601	-0.513	0.088
D_2	-0.624	-0.501	0.123
D_3	-0.836	-0.653	0.183
D_4	-0.750	-0.541	0.209

CONCLUSION

The electronic energy levels, optical absorption and the light harvesting efficiency of TPA sensitisers, namely: D_1, D_2, D_3 and D_4, were estimated to provide electronic information about the roles of π-bridges in the performances of sensitisers in the DSSC system. Structurally, the present theoretical work has shown that π-bridges TPA make significant changes to their structural properties making them to accommodate more outstanding optoelectronic properties. Consequently, the results obtained may provide structural guidelines on the choice of a suitable π-bridge to be used to further improved sensitisers in DSSC applications. In addition, the calculation procedure associated with this work could be used as: model for understanding the relationship between molecular properties and electronic structures, studying potential electronic device and evaluating their uses.

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