



# DFT computational investigation of tuning the electron donating ability in metal-free organic dyes featuring a thienylethynyl spacer for dye sensitized solar cells



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## ABSTRACT

The recent improvements in metal-free organic dye-sensitized solar cells (DSSCs) have been attributed to the ability to tune the optical and electronic properties through various structural modifications. Within the donor– $\pi$ -conjugated spacer–acceptor (D– $\pi$ –A) architecture, the electron-donating and accepting strengths have been proven to be major control variables for increasing the energy conversion efficiency. In the present study, a series of metal-free organic D– $\pi$ –A dyes for DSSCs were designed and investigated. In particular, the electron donating strength was modulated by adding electron donating groups to the donor side. The HOMO energy increased with a gradual increase in donor strength which was verified by an investigation of the bond distances between the nitrogen and carbon atom of phenyl ring connected with  $\pi$ -conjugated spacer. The net electron transfer from the donor to acceptor, calculated from natural bond orbital (NBO) analysis, also showed quantitative correlation with the bond distances. Finally, the absorption peak shifted to a longer wavelength with the increase of donor strength as well as  $\pi$ -conjugated spacer. Detailed analysis of the results supported that all properties investigated has a strong correlation with the bond distance between the nitrogen and the carbon atom in the phenyl ring attached to the  $\pi$ -conjugated spacer. Based on this apparent correlation, this bond distance from ground-state DFT calculations may be used as a descriptor for the high throughput screening of DSSC dyes instead of using computationally expensive TDDFT calculations.

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## 1. Introduction

The depletion of finite fossil fuels and global warming together with the increasing global demand for energy have promoted the search for clean, renewable, and cheap energy. Among the naturally abundant energy resources, the Sun radiates a huge amount of energy that can contribute to the current electrical and chemical needs, a power level of 1000 W/m<sup>2</sup> [1]. Accordingly, photovoltaic (PV) devices (or solar cells) have been developed extensively to meet the global energy demand. Of particular note has been the considerable progress in dye-sensitized solar cells (DSSCs) because of their distinctive features, including large flexibility in shape,

color, and transparency, as well as their good performance under low light conditions and different solar incident angles [2]. Over the last few decades, many researchers have focused on the design and synthesis of new photosensitizers, such as ruthenium(II)-polypyridyl complexes and metal-free organic dyes. Even if the ruthenium(II)-polypyridyl complexes allow high power-conversion efficiency in DSSCs, these photosensitizers have a couple of drawbacks, such as high cost of ruthenium metal, intricate synthesis and complicated purification steps. In contrast, metal-free organic dyes have several advantages including rich synthetic protocols, lower cost large-scale production and higher molar extinction coefficients [3]. More importantly, organic dyes composed of donor (D) and acceptor (A) groups separated by a  $\pi$ -conjugated bridge (D– $\pi$ –A) can be tuned by structural modifications with the incorporation of substituents into the chromophore skeletons.

So far, computational science has been considered as a generic approach to identify candidates for potential photosensitizers prior

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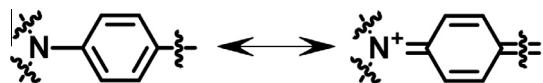
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to time-consuming expensive synthesis and tests in the development of DSSCs. Density functional theory (DFT) and time-dependent DFT (TDDFT) are considered efficient tools for examining the electronic and optical properties in the ground and excited states of virtual photosensitizers [4–6]. Previously, new metal-free organic dyes featuring a thienylethynyl spacer (Dye 6 and Dye 7) and their DSSC performance were reported [7]. Computational calculations provided molecular-level insights to better understand their geometric, optical and PV properties. Moreover, the theoretical predictions based on the DFT calculations coincided quite well with the experimental data [7]. For example, the acetylene and thiophene linker groups allowed the planar structure to be maintained while increasing the distance between the donor and acceptor groups. The addition of a second thiophene unit into the  $\pi$ -conjugated bridge also played an important role in modulating the optical and redox properties, which results improving the power-conversion efficiency of the DSSCs.

In this study, we further investigated the structural modification of Dye 6 and 7 by replacing the electron-donating groups [e.g. triphenylamine (TPA), 4,4'-dimethyltriphenylamine, 4,4'-dimethoxytriphenylamine, bis(4-dimethylaminophenyl)-phenylamine] with dimethyl-phenyl-amine units by DFT and TDDFT calculations. It is known that donor modifications with TPA can result in a high open circuit voltage and longer electron lifetime, which can contribute significantly to the solar cell efficiency [8,9]. Yang et al. reported that an increase in the donor size by the addition of alkoxy groups leads to better light harvesting efficiency and slower back electron transfer, which gives rise to higher PV performance [10]. Using reliable theoretical tools, our purpose was to investigate the donor effects on the geometrical structures and other properties of the TPA-based dye derivatives. As shown in Scheme 1, a partial double bond formed between the nitrogen atom in tertiary amine unit and the carbon atom in phenyl unit originates from resonance stabilization. This  $\pi$ -electronic delocalization causes bond shortening because of its partial double bond character as well as hybridization [11,12]. In this article, the correlation between the donor strength and this bond length was analyzed. The effectiveness of modifying the donor unit was also examined by a comparison with previous research [13–15].

To correctly reflect the excited state in the quantum chemistry calculation, the TDDFT calculations with a geometry optimization structure is inevitable. However, the excited state calculation imposes a practical limit to computational approach to modeling whole molecules with many atoms and electrons. Instead, we examined a geometric parameter by demonstrating the correlation with UV–Vis absorption properties as well as other properties relating with photo-conversion efficiencies of DSSCs. In other words, a geometric parameter obtained from DFT calculations was tested as a type of descriptor for predicting the optical properties, which can be used for the high-throughput screening of organic dyes for DSSC. To the best of the author's knowledge, this approach provides the first reported study about a correlation between the geometric and optical properties. Previous studies reported that energy transfer from the donor to acceptor is affected by the donor to acceptor distance [16] and electron donating substituents affect the C–C single bond length of butadienes [17]. Recently, Tigreros et al. demonstrated that N–C bond distances would change during photo-excitation process because electronic reorganization occurs [18]. However the correlation between the bond length and other properties, i.e. optical properties, were not



**Scheme 1.** Resonance structure in the donor unit composed of phenylamine derivatives.

examined. Natural bond orbital (NBO) analysis was also carried out to quantitatively determine the amount of charge transfer from electron-donating groups to electron-withdrawing groups in the organic dyes. Note that instead of using complicated calculation, the current approach using the interrelationship between the geometric and optical properties can be a good indicator for the design of new metal free D– $\pi$ –A dyes for use in DSSCs at less computational cost.

## 2. Computational methods

DFT and TDDFT calculations were performed using the Gaussian '09 software package [19]. The geometry of all dyes (shown in Fig. 1) was optimized using the B3LYP method with the 6-311G(d, p) basis set. The optimized structures were classified as local minima on their respective potential energy surfaces according to their vibrational frequencies. None of the vibrational frequencies in the optimized geometries generated negative frequencies in their ground state. The excitation energies and oscillator strengths for the lowest 20 transitions in the optimized ground state geometries were calculated using TDDFT with the functional CAM-B3LYP and 6-311G(d, p) basis set [5]. The solvation effect (ethanol,  $\epsilon = 35.68$ ) was introduced to both the ground and excited states by a self-consistent reaction field (SCRF) using the polarizable continuum model (PCM). Natural bond orbital (NBO) analysis was performed by calculating the orbital populations with the B3LYP/6-311G(d, p) method for the ground state and the CAM-B3LYP/6-311G(d, p) method for the excited state.

## 3. Results

The effect of tuning the electron-donating groups on the both geometrical structures and optical properties of derivatives of Dye 6 and 7 [7] were examined theoretically. Each of the new donor units, triphenylamine (TPA), 4,4'-dimethyltriphenylamine (DMT-TPA), 4,4'-dimethoxytriphenylamine (DMO-TPA) and bis(4-dimethylaminophenyl)-phenyl-amine (DMA-TPA) in ascending order of electron-donating strength, was replaced with the dimethyl-phenyl-amine (DPA) unit in the previous D– $\pi$ –A systems (Fig. 1). Substituents with which the para position of terminal phenyl group had been replaced are known as para-directors [20]. In addition, modified dyes were scrutinized theoretically in two groups (Sets 1, 2) regarding the effect of the additional second thiophene moiety as a  $\pi$ -spacer. The selected bond lengths in these systems (denoted as  $d_1$ ,  $d_2$ ,  $d_3$ ,  $d_4$  and  $d_5$  in Fig. 1) were examined thoroughly to determine the electron donating strength.

### 3.1. Geometric property

Fig. S1 illustrates the optimized ground-state geometries of Set 1 (KHS1 to KHS4) and Set 2 (KHSS1 to KHSS4). The cyanoacrylic acid group as an electron acceptor and the thiophene group as a  $\pi$ -conjugated bridge are laid in a same plane forming a fully coplanar structure, as given in the dihedral angles in Fig. S1. The phenyl ring connected to the acetylene linker is also located at the same plane. Importantly, the acetylene linker between the phenylamine and thiophene units reduces the steric hindrance between the hydrogen atoms of these rings. In addition, these coplanar structures would be favorable because it allows efficient charge transfer from the donor to acceptor units and stability of the dyes by including a strong  $\pi$ -conjugation effect [18,21]. It is noteworthy that such overall molecular geometries are rigid and are not affected even with the substituents of the donor group as DMT-TPA, DMO-TPA and DMA-TPA moieties. This enables us to account for molecular properties with different electron donor groups.

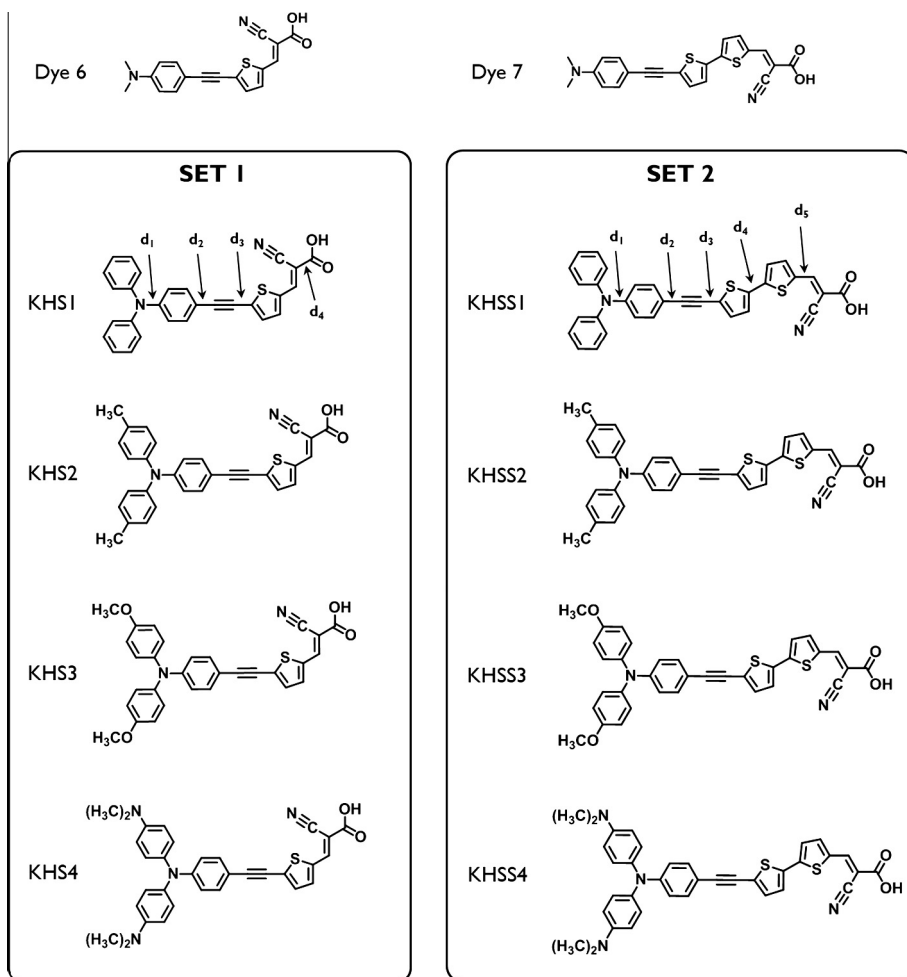


Fig. 1. Molecular structures of the dyes.

From the optimized structures of the eight molecules with different donor units in Fig. S1, one can see that the framework of the molecules are arranged in an almost perfectly coplanar deposition, meanwhile the internal phenyl rings in the TPA unit are not. These TPA units have a distorted three-dimensional structure with a dihedral angle between the phenyl rings of approximately 60 degrees which comes from the internal steric hindrance. Interestingly, the TPA unit and its substituents are also beneficial for a longer electron life-time and higher  $V_{oc}$  values due to the blocking effect by the steric hindrance of the nonplanar structure [9,10]. Bulky donor groups like TPA could prevent the approach of the electrolyte to the  $TiO_2$  surface and makes it possible to avoid undesirable back electron transfer.

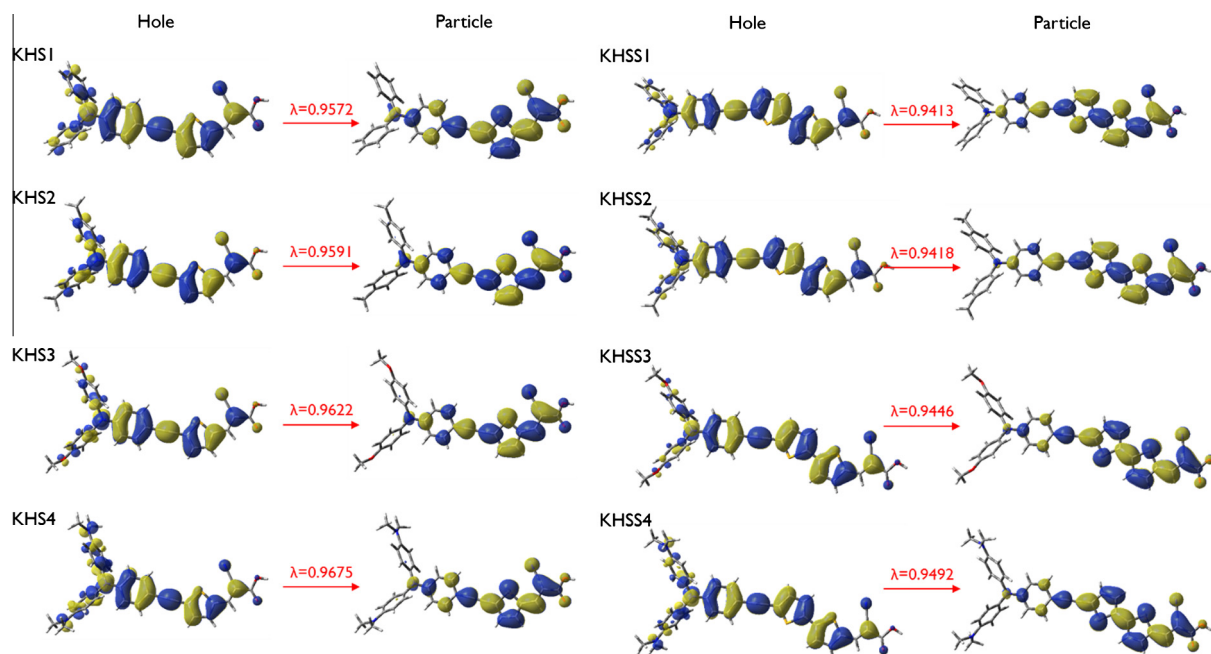
The calculated bond lengths in the optimized geometries are summarized in Table 1. The lengths ranged from 1.39 Å to 1.43 Å and these values were between those of single and double bonds (i.e. C–C: 1.530 Å, C=C: 1.339 Å [12], N–C: 1.471 Å [22] and N=C: 1.273 Å [23]). This indicates that resonance structures are built through all the planar configuration of the dyes, not only causing bond length shortening, but also inducing efficient electron transfer from the donor unit to the acceptor unit through the  $\pi$ -conjugation linker. **KHS4** and **KHSS4** had the lowest  $d_1$  value in Sets 1 and 2, respectively (see Table 1). When considering the TPA derivatives, the  $d_1$  values are consistently decreased with increasing donor strength. Therefore, the electron-donating strength has a direct influence on the  $d_1$  value. As mentioned earlier, geometric features can contribute more to the electronic structures, charge transfer and optical properties as follows.

**Table 1**  
Optimized geometrical parameters, bond lengths (in Å), of the organic dyes obtained by using B3LYP/6-311G(d, p) method.

Dyes	Selected bond lengths				
	$d_1$	$d_2$	$d_3$	$d_4$	$d_5$
KHS1	1.39932	1.41244	1.39580	1.41695	
KHS2	1.39595	1.41163	1.39524	1.41639	
KHS3	1.39094	1.41069	1.39460	1.41571	
KHS4	1.38586	1.40871	1.39313	1.41432	
KHSS1	1.40509	1.41579	1.39892	1.43727	1.41537
KHSS2	1.40017	1.41504	1.39853	1.43695	1.41511
KHSS3	1.39446	1.41426	1.39810	1.43626	1.41464
KHSS4	1.38898	1.41284	1.39719	1.43527	1.41397

### 3.2. Electronic structures

The electronic density distributions of the all dyes determined by natural transition orbitals (NTOs) analysis [24] are illustrated in Fig. 2. Since intramolecular charge transfer (ICT) likely occurs under light illumination, it is very important to examine electronic distribution during the electronic transition process [24,25]. NTOs could give detailed information about excited state transition aside from the mixed electronic configurations due to the multiple excitations among molecular orbitals [26]. Hole and particle transition orbitals represent the unoccupied and occupied NTOs, respectively. An eigenvalue  $\lambda$  refers to the fraction of the hole-particle pair contribution for the electronic transition. Importantly, HOMO  $\rightarrow$



**Fig. 2.** Natural transition orbitals (NTO) of the  $S_0 \rightarrow S_1$  transition for the organic dyes with TDDFT at the CAM-B3LYP/6-311G(d, p) level of theory;  $\lambda$  represents the fraction of the hole-particle contribution to the excitation.

LUMO excitation contribute most to the  $S_0 \rightarrow S_1$  transition, as can be seen in Table S2 from TDDFT calculation. This will be discussed in the next chapter.

The electron density of the hole NTOs for all of the dyes is localized on the phenylamine (D) moiety and is extended along the acetylene/thiophene bridge to the cyanoacrylic acid (A) moiety. On the contrary, the electron density of the particle NTOs is localized mainly on the acetylene/thiophene bridge to the cyanoacrylic acid (A) moiety. This indicates that photo-induced charge transfer is highly likely taken place for all of the organic dyes. Further, one can see that NTO eigenvalues for each dyes increase corresponding electron donors (from 0.9572 to 0.9675 in Set 1, from 0.9413 to 0.9492 in Set 2, respectively).

This electronic transition while absorbing visible light would allow net electron-transfer from the donor to acceptor, and sequentially to the  $\text{TiO}_2$  surface, where the acceptor is anchored. In this respect, the donating ability of the electron donor group is crucial for charge transfer, because more noticeable electronic density separation requires a stronger donor group as shown in Fig. 2. In addition, an insertion of additional thiophene unit into the  $\pi$ -bridge in Set 2 led to better ICT from D to A than Set 1 [7].

Excited state properties, especially oxidation potential of the dyes is required to understand driving force of interfacial charge flow from the sensitizers to the  $\text{TiO}_2$  surface. Fig. 3 shows the molecular orbital energies of all of the D- $\pi$ -A dyes from HOMO-3 to LUMO+3 levels calculated with B3LYP. Calculated potential of the dyes are summarized in Table S1. Delta SCF method was also applied under the same level of theory in order to compare the obtained energy values. By replacing the substituent on the para position of phenyl rings in TPA with the DMT, DMO and DMA moieties for stronger donor ability, the HOMO-LUMO energy gaps decrease in turn notably, which is favorable to absorb longer wavelength of visible light. Especially, **KHS4** and **KHSS4** have the minimum energy gap 1.89 eV and 1.75 eV, respectively. So it becomes obvious that replacement of strong electron-donating groups causes a notable decrease in the HOMO-LUMO gap of the dye sensitizers. Particularly, it can be seen that the HOMO levels increase gradually, while the LUMO levels remain almost constant.

The delta SCF approach, following Koopmans' theorem, the energy of the HOMO, LUMO level, and estimate energy gaps provide quite similar results with the conventional DFT calculation (see Table S1) [27,28]. The difference between the energy gaps is just around 0.24 eV.

In general, there are essential factors necessary for suitable dye sensitization process. First, the excited state redox potential has to match the energy of the conduction band (CB) edge of the  $\text{TiO}_2$ . In order to get insights into the quantitative analysis of the electron injection, free energy change could be estimated as follows [29]:

$$\Delta G_{\text{inject}} = E_{\text{dye}^*} - E_{\text{CB}} = E_{\text{dye}} + E_{0-0} - E_{\text{CB}}$$

where  $E_{\text{dye}^*}$  is the oxidation potential of the excited state of the dye,  $E_{\text{CB}}$  is the CB edge of the  $\text{TiO}_2$  (e.g., -3.74 eV [13]),  $E_{\text{dye}}$  is the redox potential of the ground state of the dye, and  $E_{0-0}$  is the vertical transition energy. Calculated  $\Delta G_{\text{inject}}$  values are 1.34, 1.38, 1.44, and 1.68 eV for **KHS1** to **KHS4** in Set 1, and 1.34, 1.39, 1.45, and 1.69 eV for **KHSS1** to **KHSS4** in Set 2, respectively. This reveals that these dyes have sufficient driving force for the electron injection of excited electrons into  $\text{TiO}_2$  CB. Second, HOMO level must fit the redox potential of the electrolyte. As illustrated in Fig. 3, the HOMO energies of these dyes lie below the iodide redox potential (-4.6 eV [24]), and this fulfills the energy criteria for the dye regeneration of the oxidized dyes by the electrolyte. Additional thiophene unit as a  $\pi$ -spacer in Set 2 is also conducive to lower the HOMO-LUMO energy gap, which is attributable to the improved  $\pi$ -conjugation in Set 2 compared to Set 1 including monothiophene [6].

### 3.2.1. NBO analysis: charge analysis

Natural bond orbital (NBO) analysis of the ground state was performed to determine the amount of charge populations on the overall dye molecules [30,31], as summarized in Table 2. The NBO charge  $q^{\text{Donor}}$ , represents the total amount of natural charges to the donor group. In the same way, the value  $q^{\text{Acceptor}}$  represents the total amount of natural charges to the acceptor group. A positive NBO value represents the TPA based derivatives being an electron donor unit, while negative NBO charge reveals that

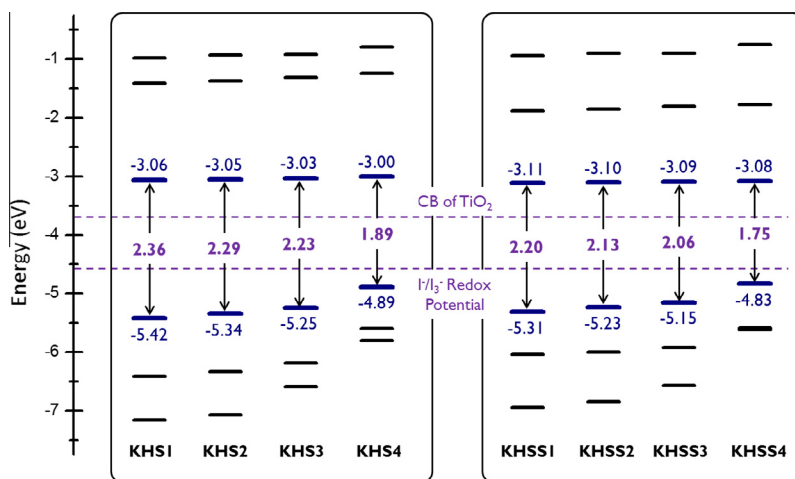


Fig. 3. Frontier molecular orbital energies of the modified dyes.

Table 2

The NBO analysis of metal-free organic dyes in the ground state where  $q^{\text{Donor}}$ ,  $q^{\pi\text{-spacer}}$ , and  $q^{\text{Acceptor}}$  denotes the total amount of natural charges on the donor group,  $\pi$ -spacer, and the acceptor group, respectively.  $\Delta q^{\text{D-A}}$  represents the charge variance between natural charges on the donor and the acceptor group.

Dyes	$q^{\text{Donor}}$	$q^{\pi\text{-spacer}}$	$q^{\text{Acceptor}}$	$\Delta q^{\text{D-A}}$
KHS1	0.0839	0.1106	-0.1946	0.2786
KHS2	0.0925	0.1062	-0.1987	0.2912
KHS3	0.1034	0.1007	-0.2041	0.3075
KHS4	0.1265	0.0891	-0.2156	0.3421
KHSS1	0.0548	0.1359	-0.1906	0.2454
KHSS2	0.0592	0.1449	-0.2042	0.2634
KHSS3	0.0694	0.1375	-0.2069	0.2763
KHSS4	0.0919	0.1102	-0.2151	0.3069

cianoacrylic acid attracts electrons as the electron acceptor unit. Hence it can be noticed that  $\pi$ -spacer (acetylene and thiophene fragment) act more like a donor unit since it shows positive NBO charge. For example, in molecules **KHS4** and **KHSS4**, the natural charges on donor,  $\pi$ -spacer and acceptor are 0.1265/0.0891/-0.2156 e and 0.0919/0.1102/-0.2021 e, respectively. These values are worthwhile to note that the dyes have the biggest charge variance between natural charges on the donor ( $q^{\text{Donor}}$ ) and acceptor ( $q^{\text{Acceptor}}$ ) group among other molecules in Set 1 and Set 2, respectively, as it is represented in  $\Delta q^{\text{D-A}}$  values. This illustrates that strong electron donating groups promote the natural charge separation between the donor and acceptor group of the D- $\pi$ -A organic dyes.

### 3.3. Optical property

The simulated absorption spectra are depicted in Fig. 4 and the corresponding features for the main peak of the spectra are listed in Table S2. A comparison of Fig. 4(a) with (b) shows that the addition of thiophene moieties in Set 2 caused a bathochromic shift from 10 to 20 nm compared to those in Set 1. The oscillator strength ( $f$ ), which corresponds to the molar extinction coefficient, is also increased by the addition of extra thiophene units (see Fig. 4 and Table S2), and these changes in optical behavior have been reported [7]. Accordingly, it is anticipated that all of the donor modified dyes examined have higher light absorption ability than the previous Dye 6 and 7, which is underpinned by the oscillator strength values listed in Table S2. Light-harvesting efficiency (LHE) is also examined for the following equation:

$$LHE = 1 - 10^{-f}$$

where  $f$  is the oscillator strength of the dye corresponding to absorption maximum ( $\lambda_{\text{max}}$ ). Since LHE value is directly related to short circuit current density  $J_{\text{sc}}$  [6,13], strong electron donor group encourages the efficient usage of incident light. Presumably, the efficiency of **KHSS4** would be higher than other designed dyes.

Furthermore, from **KHS1** to **KHS4** (Set 1) and from **KHSS1** to **KHSS4** (Set 2), bathochromic shifts of the  $\lambda_{\text{max}}$  values are observed, and **KHS4** and **KHSS4** showed the longest maximum wavelength at 482.71 nm (2.57 eV) and 492.95 nm (2.52 eV), respectively (33.29 nm and 24.41 nm redshifted compared to **KHS1** and **KHSS1**, respectively). This trend also agrees well with the HOMO-LUMO gaps. This suggests that replacing the donor group from TPA to the DMA-TPA unit provides an additional chance for extending the conjugation.

## 4. Discussion

The geometric, electronic and optical properties have been investigated theoretically. Intriguingly, the electronic and optical properties were closely related to the geometric property, especially to the bond length. Therefore, carbon-nitrogen bond length (denoted as  $d_1$ ) can be an indication of the electron-donating strength because the  $d_1$  value is most susceptible to the donor strength. Fig. 5 shows vertical excitation energy as a function of  $d_1$  distance, indicating a good correlation between them. **KHS4** and **KHSS4** showed the minimum excitation energy value and shortest  $d_1$  values due to the strongest donor, the DMA-TPA group. This is consistent with the longest wavelength absorption properties, and thus this makes **KHS4** and **KHSS4** promising candidates for future development of DSSC device. On the other hand, as the donor strength decreased from DMA-TPA to TPA, the vertical transition energies increase while the corresponding  $d_1$  length values increased. In our series of the organic dyes with the modified TPA derivatives as a donor group, almost linear dependence of theoretical excitation energy on the  $d_1$  length was observed.

In this respect, the NBO charge can also be interpreted as a function of  $d_1$  distance, as shown in Fig. 6.  $q^{\text{Donor}}$  and  $q^{\text{Acceptor}}$  were illustrated separately in Fig. 6(a) and (b), respectively, by using natural charges data from Table 2. In the NBO charge graph of the donor group (Fig. 6(a)), molecules with shorter  $d_1$  distance show more positive NBO charges. For example, **KHS4** and **KHSS4** have the most positive NBO charges with the shortest  $d_1$  distance in Set 1 and Set 2, respectively. In contrast, **KHS1** and **KHSS1** have the least positive NBO charges with the longest  $d_1$  distance in Set 1 and Set 2. On the other hand, in the NBO charge graph of the

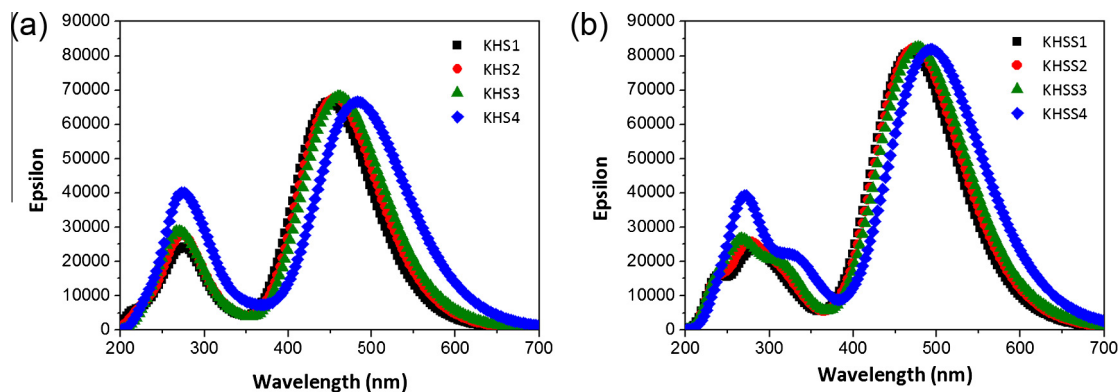


Fig. 4. Simulated absorption spectra of the modified dyes at the CAM-B3LYP/6-311G(d, p) level (a) Set 1 and (b) Set 2.

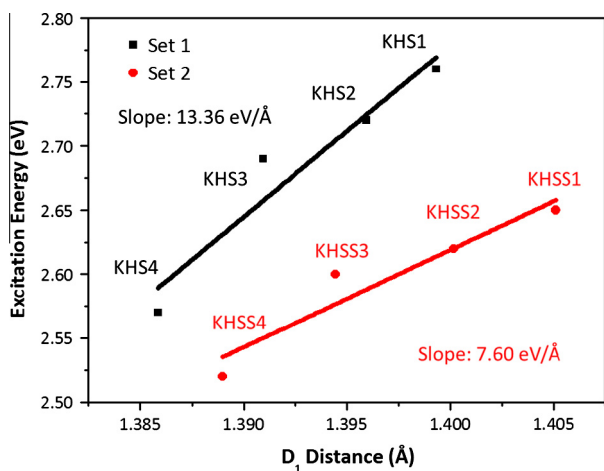


Fig. 5. Plots of the maximum absorption wavelength versus the  $d_1$  distance. The black squares represent Set 1 and the red circles represent Set 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

acceptor group (Fig. 6(b)), molecules with shorter  $d_1$  distance show more negative NBO charges. As discussed earlier, this indicates that the NBO charges of the donor and acceptor are separated each other. It should be noted that these NBO charges show linear relationship with the  $d_1$  bond distances.

Second order perturbation theory (SOPT) analysis within the NBO basis was also performed to characterize the direction and

amount of the charge separation between the donor and acceptor groups [13,32], and the results are listed in Table S3. In addition, Fig. S2 shows the conjugative interaction energy of the donor part (solid, left) and acceptor part (hollow, right) as a function of the  $d_1$  distance. In much the same way, KHS4 and KHSS4 have the highest conjugative interaction energy with the shortest  $d_1$  lengths among all other molecules in Sets 1 and 2, respectively. Therefore, the conjugation energy depends almost solely on the  $d_1$  distance, which is ascribable to the donor strength. These results show that the electronic charge separation can be a simple function of the  $d_1$  distance, because the electronic conjugation through the organic molecules depends on both the donor strength and electronic charge transfer.

Moreover, a linear tendency of the optical and electronic charge properties with the  $d_1$  distance were established in Figs. 5 and 6. Note that the angles of inclination of Set 1 (Fig. 5: 13.36 eV/Å, Fig. 6:  $-3.083$  e/Å, 1.521 e/Å) for each analysis are steeper than those of Set 2 (Fig. 5: 7.60 eV/Å, Fig. 6:  $-2.261$  e/Å, 1.398 e/Å). This means that the optical and electronic charge properties of the dyes with monothiophene (Set 1) as a  $\pi$ -spacer are more susceptible to the modifications of the donor strength than the dyes with bithiophene (Set 2). Although an additional thiophene unit would be beneficial for increasing the conjugated length, leading to an increase in absorption intensity and a bathochromic shift, it will not induce a dramatic alteration to their properties within the framework of the varying donating ability. However, more experimental and theoretical studies will be needed to determine the advantage of a longer  $\pi$  spacer in terms the final solar cell efficiency.

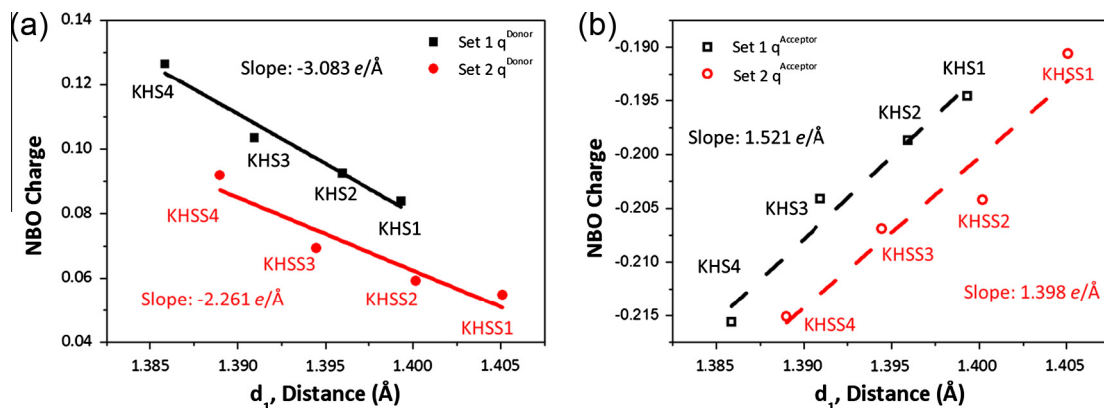


Fig. 6. Plots of the NBO charges versus the  $d_1$  distances. (a) Black solid squares represent Set 1 and red solid circle represent Set 2 in donor part, and (b) black hollow squares represent Set1 and red hollow circle represent Set 2 in acceptor part. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

## 5. Conclusion

In summary, eight new linear dye molecules were designed and the effects of substituted donor groups and the  $\pi$ -bridge moiety on enhancing PV properties were investigated. The DFT and TDDFT calculations showed that tuning the donor group plays a crucial role in determining the applicability of the photo-sensitizer from their structural, electronic and optical properties. **KHS4** and **KHSS4** were expected to show the best performance in each Set 1 and Set 2, respectively. An additional thiophene ring as a  $\pi$ -spacer (Set 2) brings a notable difference compared to a monothiophene containing dye (Set 1) with an increase in oscillator strength and a bathochromic shift. Importantly, we demonstrated a correlation between the geometric parameter  $d_1$  and the electronic and optical properties. As shown above, the geometric parameter  $d_1$  is related to the amount of charge transfer and the maximum absorption wavelength of UV-Vis spectra. A comparison of the donor-modified dyes (Set 1 and Set 2) showed that better ICT and a bathochromic shift coincided with a stronger electron donating group which contributed to the decreased  $d_1$  length. Therefore, short  $d_1$  parameter may work as a simpler and more reliably calculated descriptor of the performance of dye molecules in terms of the strong electron donating ability, charge transfer and optical properties. In other words, DFT calculation has been known to provide good prediction to molecular geometry in ground state. With the increase of molecular size for calculation, however, the reliability of the calculation results for other electronic properties is still questionable. Moreover, the TDDFT calculations incur high computational cost and the calculated optical properties often have questionable reliability. In contrast, the proposed relationship between the geometric parameter  $d_1$  and other properties provides a practical way for the high throughput screening of a huge number of candidates. This interpretation might be feasible for other research, such as that reported elsewhere [13–15], and it is expected that this theoretical tool can be an attractive method that will help us to the more efficient development of metal-free organic sensitizers for DSSCs by reducing the computational cost and time.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.comptc.2016.02.009>.

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