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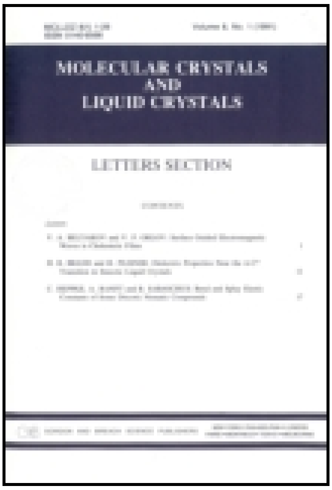

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# Theoretical Study of the Effect of Introducing $\pi$-Conjugation and/or an Electron Withdrawing Unit in a Heteroleptic Dual-Electron Donor-Based Dye Sensitizer

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*In this study, three triphenylamine (TPA)-based dye sensitizers with phenothiazine (PTZ) and TPA as dual-electron donors, benzothiadiazole (BTD) as an electron withdrawing unit, and cyanoacetic acid as an electron acceptor (dye1, dye2, dye3, dye4) were designed and investigated. To decrease the energy band gap of dye1, we added $\pi$-conjugation between the PTZ donor and the TPA donor in dye1 and/or BTD between the TPA and thiophen in dye1. Using density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations, we gained insight into the factors responsible for photovoltaic performance. Due to the different energy band gaps of each dye, the absorption spectra of the dyes each showed a different form. Among the dyes, dye4 showed the most red-shifted and broadest absorption spectra. It is expected that dye4 would have better photovoltaic properties than the others. This work indicates that adding $\pi$-conjugation or a withdrawing unit into dye would result in good photovoltaic properties for dye-sensitized solar cells (DSSCs).*

**Keywords:** D-A-$\pi$-A; dual donor; dual acceptor; electron withdrawing; DSSCs; DFT; TD-DFT

## 1. Introduction

In recent years, dye-sensitized solar cells (DSSC) have attracted much attention due to their low cost, easy fabrication and flexibility compared to conventional crystalline silicon based solar cells [1, 2]. During the past decade, the performance and stability of DSSC devices have been studied and developed [3–5]. Currently, zinc porphyrin dye has the best efficiency among DSSCs (over 12%) in conjunction with the Co(II/III)tris(bipyridyl)–based redox electrolyte and ruthenium polypyridyl dyes, which also have good efficiency of DSSCs (over 11%) in combination with a voltaic $I^-/I_3^-$ mixture as the electrolyte [6, 7] However, metal-based dyes, such as ruthenium or zinc complexes, are not suitable in terms of cost efficiency and environmental friendliness [8, 9]

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Thus, metal free organic dyes have received attention as alternatives to metal-based dyes, owing to their high molar extinction coefficient, simple synthesis and purification, low cost and environmental friendliness. The donor-$\pi$ conjugated linker-acceptor (D-$\pi$-A) structure is generally used for metal free organic dyes [10]. The dual-donors (D-D-$\pi$-A) or –acceptors (D-A-$\pi$-A) group of dyes can increase the photovoltaic performance of these dyes [11, 12]. The antenna group of hole transport materials can delay the charge-recombination process through the physical separation of the holes, moving them spatially away from the electrons in the semiconductor, thus improving the efficiency of DSSCs [13, 14]. In the D-A-$\pi$-A structure dye, the additional electron withdrawing unit can be treated as an electron trap where charge separation occurs, and facilitate the electron migration from the donor to the anchoring acceptor [15, 16].

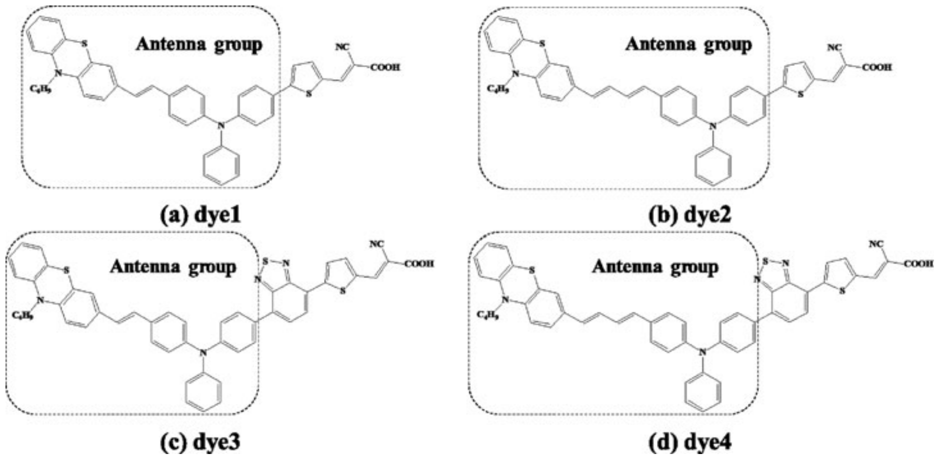
We designed four triphenylamine (TPA)-based dye sensitizers with phenothiazine (PTZ) as an electron donor, benzothiadiazole (BTD) as an electron withdrawing unit, and cyanoacetic acid as an electron acceptor (dye1, dye2, dye3, dye4) and investigated the effect of extending the $\pi$-conjugation length and substituting the electron withdrawing unit. Dye1 and dye2 have D-D-$\pi$-A structure and dye3 and dye4 have D-D-A-$\pi$-A structure. Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations were used to estimate the photovoltaic properties of the dyes [17]. This study was performed to determine whether a suitable $\pi$-conjugation length and electron withdrawing unit would provide good photovoltaic properties for DSSCs.

## 2. Computational Details

To gain insight into the factors responsible for the absorption spectrum and conversion efficiency, we performed DFT and TD-DFT calculations on the ground state of the dyes. This computational procedure allows us to provide a detailed assignment of the excited states involved in the absorption process. The geometries and energy levels of the molecular orbital (MO) were calculated using the DFT method, and the absorption spectrum was calculated at optimized ground state geometries using the TD-DFT method. Although the energy levels of the MO can predict the trend of the energy gap in the absorption spectrum, their data do not exactly match the absorption spectrum. Since the absorption process is time-dependent, the absorption spectrum in this study originates from the TD-DFT.

The geometries in the gas phase were optimized by the DFT method using the B3LYP exchange–correlation function with the 6-31G(d) basis set in the Gaussian 09 program package. The possible isomers of the organic dyes were calculated by initially setting the double bond torsional values to either cis or trans geometry. This doubles the number of possible conformations, and the lowest energy conformation is found by optimizing the molecular structure of the dyes in the gas phase. The electronic populations of the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO) were calculated to show the position of electron populations according to the calculated MO energy diagram.

TD-DFT calculations with the Coulomb attenuating (CAM) B3LYP/6-31G(d) level of theory were performed at ground-state optimized geometries by means of the C-PCM algorithm with the solvation effect of dichloromethane, as implemented in the Gaussian 09 program package. The absorption spectrum was calculated at optimized ground-state geometries for the lowest 30 singlet–singlet excitations up to a wavelength of 300 nm. The simulation of the absorption spectra was performed by a Gaussian convolution with fwhm = 0.35 eV.



**(a) dye1** **(b) dye2** **(c) dye3** **(d) dye4**

**Figure 1.** Molecular structure of the dyes: dye1, dye2, dye3, and dye4.

## 3. Results and Discussion

Figure 1 shows the schematic molecular structure of the dyes considered in this study. Dye1 was a TPA-based dye with TPA and PTZ as dual electron donors, thiophen as a π-conjugation linker, and cyanoactetic acid as an electron acceptor. For the efficient energy absorption, dye2 was obtained by extending the π-conjugation length between PTZ and TPA; dye3 was obtained by substituting BTD as an electron withdrawing unit between the TPA and thiophen; and dye4 was obtained by extending the π-conjugation length and substituting BTD as an electron withdrawing unit. We expected that the absorption spectra of dye2 at the short wavelength region would be red-shifted because of the increasing length of the π-conjugation; the absorption spectra of dye3 at the long wavelength region would be red-shifted because of an additional electron withdrawing unit; and the absorption spectra of dye4 would show both patterns of change.

To obtain the MOs and the electronic structures of the dyes, DFT calculations were performed at a B3LYP/6-31G(d) level for the geometry optimization of these dyes. The electron distribution of some frontier MOs for dye1, dye2, dye3, and dye4 are shown in Fig. 2. The electron population of dye1 and dye2 show similar patterns in which HOMO and HOMO-1 are delocalized over the dual donor part; the LUMOs are delocalized across the cyanoacetic acid and thiophene and partly on the TPA; and LUMO+1 is partly delocalized on each donor. The electron population of dye3 and dye4 also show similar patterns in which HOMO and HOMO-1 are delocalized over the dual donor part; the LUMOs are delocalized across the cyanoacetic acid, thiophene, BTD, and partly on the TPA; and LUMO+2 is delocalized in the same way as LUMO+1 of dye1 and dye2. The schematic-calculated MO energy levels of dye1, dye2, dye3, and dye4 are shown in Fig. 3. The HOMO energy levels of dye1, dye2, dye3, and dye4 are −4.89 eV, −4.85 eV, −4.86 eV and −4.80 eV, respectively, which did not differ much. However, the LUMO energy levels of dye1, dye2, dye3, and dye4 are −2.60 eV, −2.60 eV, −3.04 eV and −3.04 eV, respectively, where the LUMO energy levels of dye3 and dye4 decreased compared to those of dye1 and dye2. This result indicates that the energy band gap of dye3 and dye4 decreased by the LUMOs energy levels of the dyes to decrease, and the substitution of the electron withdrawing unit in the dye caused the LUMO energy levels of the dyes to decrease.

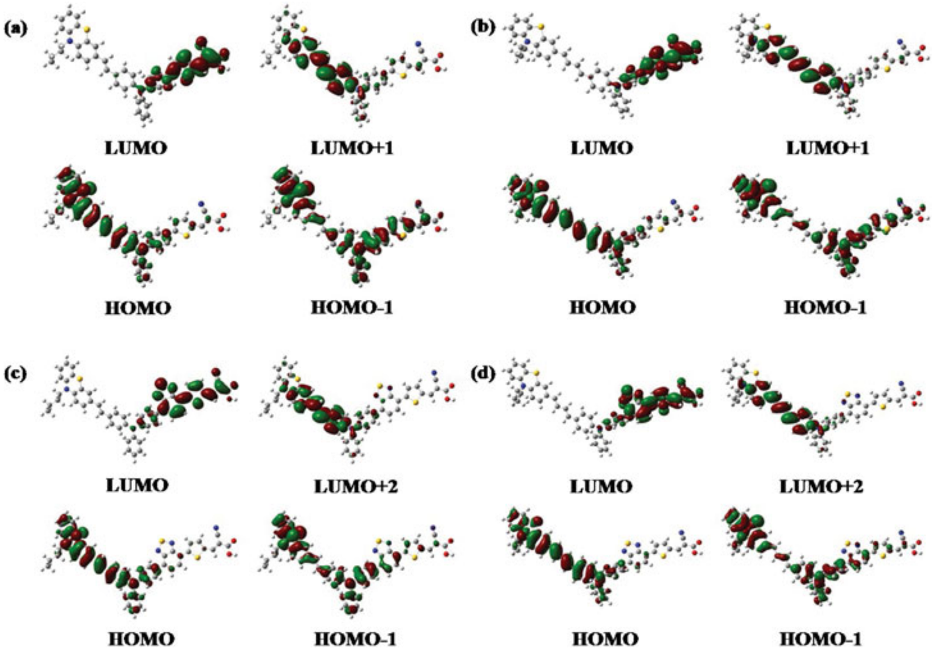


**Figure 2.** Electron distributions of MOs: (a) dye1, (b) dye2, (c) dye3, and (d) dye4.

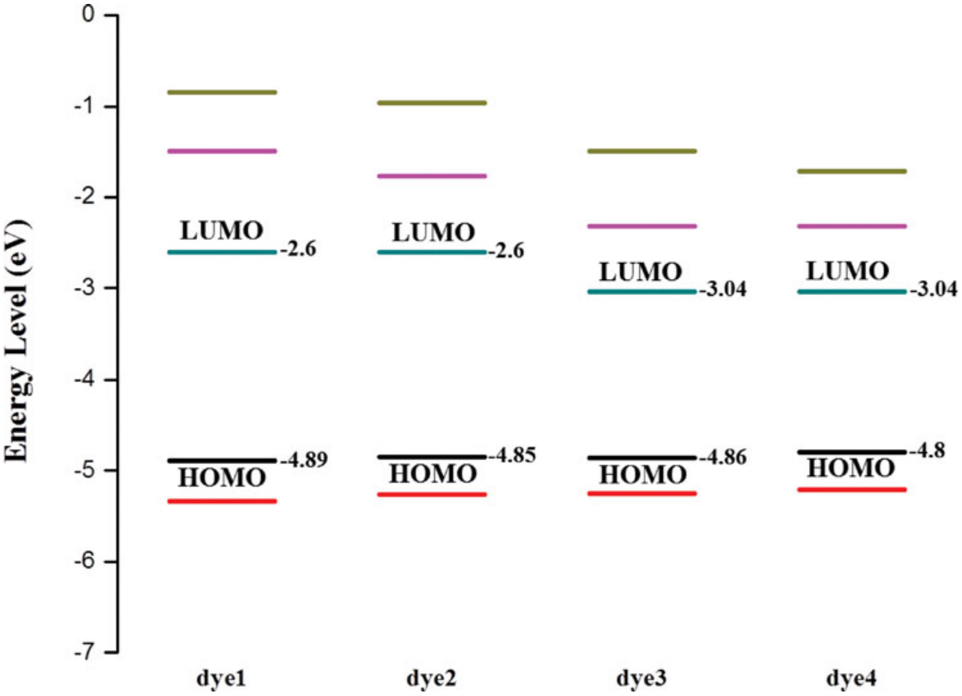


**Figure 3.** Schematic MOs energy levels of dye1, dye2, dye3, and dye4.

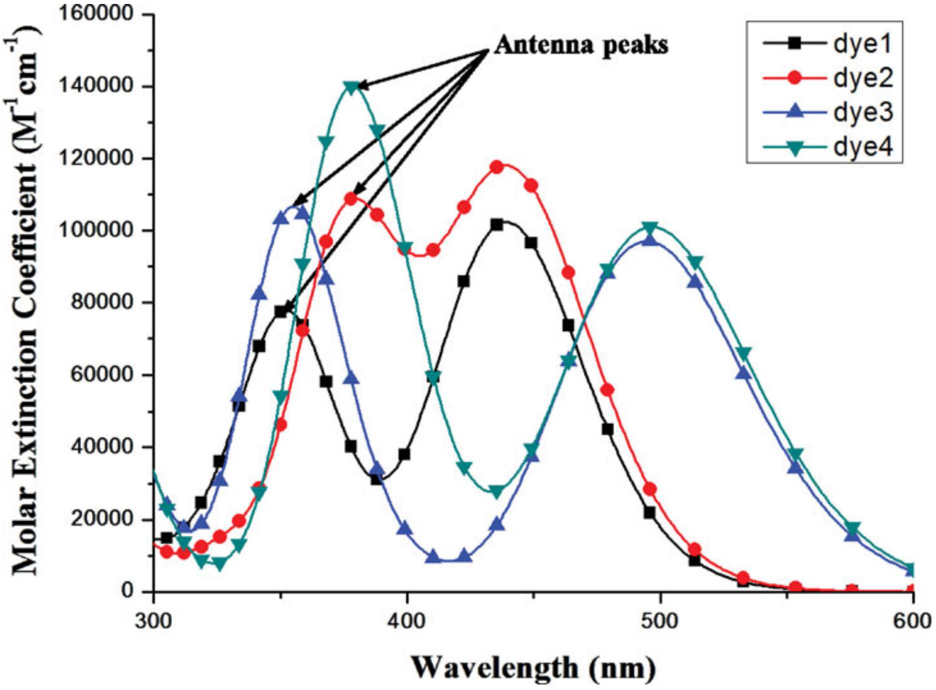


**Figure 4.** Calculated TDDFT UV-Vis absorption spectra of dye1, dye2, dye3, and dye4.

The UV-Vis absorption spectra of these four dyes, derived using TD-DFT calculations, are shown in Fig. 4. Table I shows the calculated absorption energy, oscillator, and major composition in terms of MO contributions to the dyes. The lowest energy absorption peaks of dye1, dye2, dye3, and dye4 are 439 nm, 441 nm, 495 nm, and 497 nm, respectively, which

**Table 1.** Calculated absorption energy, oscillator strength and major composition in terms of MO contributions of dye1, dye2, dye3, and dye4

| Dye | # of excited state | Calculated energy (nm) | Oscillator strength (f) | Major composition | Transition character |
|---|---|---|---|---|---|
| dye1 | 1 | 439 | 1.6463 | HOMO → LUMO (51%) | ICT |
| | | | | H-1 → LUMO (26%) | ICT + $\pi \rightarrow \pi^*$ |
| | 2 | 354 | 1.1872 | HOMO → L+1 (75%) | $\pi \rightarrow \pi^*$ |
| dye2 | 1 | 441 | 1.8385 | HOMO → LUMO (44%) | ICT |
| | | | | H-1 → LUMO (28%) | ICT + $\pi \rightarrow \pi^*$ |
| | 2 | 377 | 1.6758 | HOMO → L+1 (77%) | $\pi \rightarrow \pi^*$ |
| dye3 | 1 | 495 | 1.5622 | HOMO → LUMO (45%) | ICT |
| | | | | H-1 → LUMO (25%) | ICT + $\pi \rightarrow \pi^*$ |
| | 2 | 355 | 1.0977 | HOMO → L+2 (39%) | $\pi \rightarrow \pi^*$ |
| dye4 | 1 | 497 | 1.6256 | HOMO → LUMO (39%) | ICT |
| | | | | H-1 → LUMO (28%) | ICT + $\pi \rightarrow \pi^*$ |
| | 2 | 377 | 1.9261 | HOMO → L+2 (62%) | $\pi \rightarrow \pi^*$ |

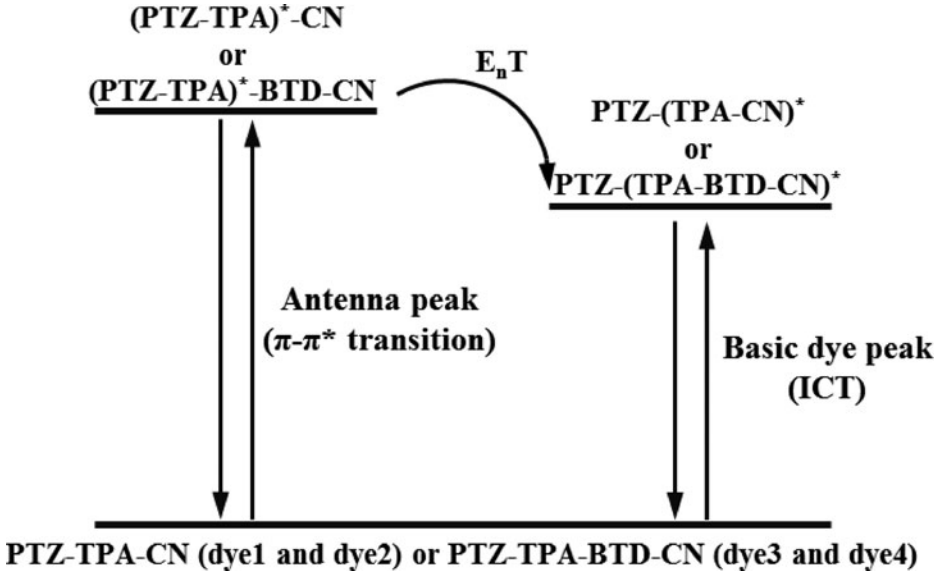


**Figure 5.** Schematic drawing of the intramolecular energy transfer (EnT) process of the dyes.

were ascribed to the HOMO → LUMO transition and the HOMO-1 → LUMO transition. The highest energy absorption peaks of dye1 and dye2 are 354 nm, 377 nm, 355 nm, and 377 nm, respectively, which were ascribed to the HOMO → LUMO+1 transition, and those of dye3 and dye4 are 355 nm and 377 nm, respectively, which were ascribed to the HOMO → LUMO+2 transition

In a study of the intramolecular energy transfer ($E_nT$) and the charge transfer (ICT) of TPA-based dye, the antenna group of the dye transferred the energy to the basic dye. This $E_nT$ process was occurred by Förster $E_nT$. For effective intramolecular $E_nT$, the emission band of the antenna group should be well overlapped with the absorption band of the basic dye [18]. In this study, we used PTZ-TPA group as an antenna group, and TPA-CN and TPA-BTD-CN dye as the basic dye, respectively. Figure 5 showed schematic drawing of the intramolecular $E_nT$ process of the dyes. The molar extinction coefficient of dye2 in the long wavelength region was higher than that of dye1. The absorption spectra of dye2 were also broader than that of dye1, even though the lowest peak of dye1 and dye2 were almost same. It means that the emission band of antenna group which has extended $\pi$-conjugation was better overlapped with the absorption band of TPA-CN than another antenna group which does not have extended $\pi$-conjugation, so dye2 has better intramolecular $E_nT$.

The absorption peaks of dual-donor-based dye were dominated by two types of transitions, an intramolecular charge transfer (ICT) and a $\pi \rightarrow \pi^*$ transition. As shown in Table I, the absorption peaks at the long wavelength region were dominated by the ICT, and the absorption peak at the short wavelength region was dominated by the $\pi \rightarrow \pi^*$ transition. The ICT takes place between the dual donor and acceptor, and the $\pi \rightarrow \pi^*$ transition takes place inside dual donors, which can be considered an antenna effect. We wanted the antenna peak, which was the highest energy absorption peak of dye, to be red-shifted by the extension of the $\pi$-conjugation length and the lowest energy absorption peak of dye to be red-shifted by the substitution of the electron withdrawing unit. As shown in Figure 4, the highest energy absorption peak of dye2 was red-shifted, the lowest energy absorption peak of dye3 was red-shifted, and the energy absorption of dye4 was red-shifted compared to dye1. Therefore, among the dyes, dye4 would have the best photovoltaic properties for DSSCs.

## 4. Conclusions

We designed and investigated four PTZ–TPA dual-donor-based dye sensitizers using DFT and TD-DFT calculations. Due to the different $\pi$-conjugation length and the substitution of an electron withdrawing unit, the energy absorption spectra of dyes showed different forms. In this study, we confirmed that the energy absorption ascribed to the $\pi \rightarrow \pi^*$ transition was bathochromic-shifted by the extension of the $\pi$-conjugation length. Due to the substitution of an electron withdrawing unit, the LUMO energy levels of the dyes decreased; thus, the energy absorption ascribed to the ICT was also bathochromic-shifted. This study shows that dye4 would have the best photovoltaic performance for DSSCs. However, this is not enough for a panchromatic dye sensitizer. Therefore, further studies are needed to investigate the energy absorption spectra of dye so it will be more red-shifted by controlling the $\pi$-conjugation length or by using a different $\pi$-conjugation linker, such as thiophen or benzene, between each donor or between an additional electron withdrawing unit and acceptor. We will also investigate the effect of substituting other kinds of electron withdrawing units, such as benzotriazole or quinoxaline, for a panchromatic dye sensitizer.

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