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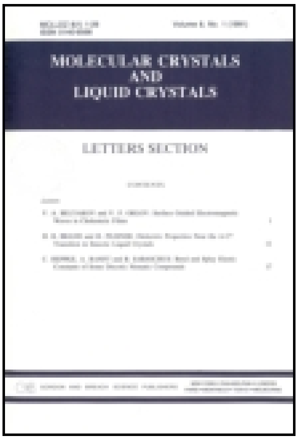

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Heteroleptic Dual Acceptor Organic Dyes with Rhodanine-3-Acetic Acid and Cyanoacrylic Acid

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Heteroleptic Dual Acceptor Organic Dyes with Rhodanine-3-Acetic Acid and Cyanoacrylic Acid

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Herein, as a photosensitizer for the dye-sensitized solar cells (DSSCs), we designed a novel organic dye with heteroleptic dual electron acceptors (rhodanine-3-acetic acid and cyanoacrylic acid) on each side of a triphenylamine-based organic dye. The density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations were used to estimate the photovoltaic properties of the dyes. It was found that the dyes with dual acceptor groups (DB-2, DB-3) showed stronger and more red-shifted intensities from the absorption spectra. Due to the proximity of the lowest unoccupied molecular orbitals (LUMO) to the anchoring carboxylic group, it was also shown that DB-3 with cyanoacrylic acid and rhodanine-3-acetic acid acceptors might be more effective in J_{sc} than DB-2 with rhodanine-3-acetic acid acceptors. From these results, it is suggested that the DB-3 dye with heteroleptic dual acceptors would show better photovoltaic performance than other dyes in this study as a dye sensitizer for DSSCs.

Keywords DSSCs; Triphenylamine; Heteroleptic dual acceptor; DFT; TD-DFT

Introduction

Dye-sensitized solar cells (DSSCs) have been of interest in scientific research and for practical applications due to the potential advantages of low cost, easy production, flexibility, and transparency relative to conventional crystalline silicon solar cells [1, 2]. Performance and stability of DSSC devices have been studied and significantly developed over the past decade [3–5]. Among the components of DSSCs, the sensitizer is a crucial element, which significantly influences the power conversion efficiency as well as the stability of the device. Up to now, the record for DSSC efficiency was held by a polypyridyl ruthenium sensitizer (11%) in combination with a voltaic iodide/triiodide mixture as an electrolyte [6]. However, ruthenium complex dyes are not suitable for the concerns of cost effectiveness and environmental friendliness because ruthenium is a rare and expensive metal, which limits the potentially wide application of these complexes.

Thus, interest in organic dyes as an alternative to noble metal complexes has increased because of the former's many advantages, such as diversity of molecular structures, high molar extinction coefficient, simple synthesis, low cost, and increased sensitivity to

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environmental issues [7, 8]. Numerous metal-free organic dyes for DSSCs, such as coumarin-[9], merocyanine-[10], indoline-[11], xanthene-[12], hemicyanine-[13], perylene-[14] and fluorene-[15] based organic dyes have been developed and have shown good DSSC performance.

Recently, it has been reported that metal free organic dyes for DSSCs have a general structure with a donor-linker-acceptor [16] and dual donor or dual acceptor groups of the dye sensitizers can increase photovoltaic performance [17, 18]. Also, it has been reported that the antenna group of hole transport materials can make the charge-recombination process slow through the physical separation of the holes spatially away from the electrons in the semiconductor, thus improving the efficiency of DSSCs [19, 20].

In this work, we designed a novel organic dye with heteroleptic dual electron acceptors (rhodanine-3-acetic acid and cyanoacrylic acid) on each side of a triphenylamine-based organic dye, as a photosensitizer for the DSSCs. The density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations were used to estimate the photovoltaic properties of the dyes [21]. Specifically, structural, electronic, and optical properties of some triphenylamine-based dyes were investigated with the introduction of dual electron acceptor groups. We have suggested the high performance dye sensitizer as a DSSC device among the presented triphenylamine-based dyes.

Computational Methods

We performed DFT and TD-DFT calculations on the ground state of the triphenylamine-based dyes to get insight into the factors responsible for the absorption spectral response and the conversion efficiency. This computational procedure allowed us to provide a detailed assignment of the excited states involved in the absorption process.

The geometries in the gas phase were optimized by the DFT method using the B3LYP (Becke, three-parameter, Lee-Yang-Parr) exchange-correlation function with a 6-31G(d) basis set in the Gaussian 03 program package. The 6-31G(d) basis set (defined for the atoms H through Zn) is a valence double-zeta polarized basis set that adds to the 6-31G set six d-type Cartesian-Gaussian polarization functions on each of the atoms Li through Ca and ten f-type Cartesian Gaussian polarization functions on each of the atoms Sc through Zn. The 6-31G(d) basis set is often considered the best compromise of speed and accuracy and is the most commonly used basis set.

The lowest energy conformation was found by optimizing the molecular structure of the dyes in the gas phase. Electronic populations of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were calculated to show the position of the localization of electron populations along with the calculated molecular orbital energy diagram.

TD-DFT calculations with the B3LYP/6-31G(d) level of theory were performed at optimized ground-state geometries. The absorption spectrum was calculated at optimized ground-state geometries for lowest singlet-singlet excitations (from 10 to 20) up to a wavelength of 350 nm. Solvation effects were included by means of the polarizable continuum model. The simulation of the absorption spectra was performed by a Gaussian convolution with fwhm = 0.35 eV.

Results and Discussion

D5 has a molecular structure with triphenylamine as an electron donor and cyanoacrylic acid (**C**) moiety as an electron acceptor. On this dye, **DB-1** was designed by adding the other **C** moiety. **DB-2** was replaced with two rhodanine-3-acetic acid (**R**) moieties as electron acceptors, instead of **C** moieties (see Figure 1). To increase the power conversion efficiency, a new **DB-3** was designed with **C** and **R** moieties as a heteroleptic dual electron acceptor. DFT calculations were performed at a B3LYP/6-31G(d) level for the geometry optimization of the triphenylamine-based dyes in order to obtain molecular orbitals and electronic structures of **D5**, **DB-1**, **DB-2**, and **DB-3**.

Figure 2 shows the calculated molecular orbital energy diagram for triphenylamine-based dyes. Overall, energy gaps between the HOMOs and the LUMOs of **DB-1**, **DB-2**, and **DB-3** were decreased with additional electron acceptor groups, as shown in Figure 2. Specifically, the energy level decrements of LUMOs are mainly due to electron-withdrawing characteristics of electron acceptor groups. Through the introduction of dual electron acceptors, LUMO of **D5** was also split into LUMOs and LUMO+1s of **DB-1**, **DB-2**, and **DB-3**. The reduction of the energy gap of the dye showed a more red-shifted band in the absorption spectrum. The degeneracy of LUMO and LUMO+1 resulted in HOMO => LUMO (and LUMO+1) simultaneous transitions, enabling a more panchromatic absorption band in the long wavelength region.

Figure 3 shows the UV-Vis absorption spectra of the triphenylamine-based dyes by TD-DFT calculations. **D5** has an absorption energy band of HOMO => LUMO transition with a peak at 552 nm. By introducing dual electron acceptors, absorption energy bands of **DB-1**, **DB-2**, and **DB-3** were red-shifted with peaks at 597 nm, 619 nm, and 608 nm, respectively. Considering degeneracy and energy differences between LUMOs and LUMO+1s in Fig. 2, the HOMO => LUMO+1 transitions for the dyes with dual acceptors did not represent as apparent absorption bands. These transitions were involved in the largest absorption bands. Therefore, the second largest absorption bands between 400 nm and 500 nm resulted from the HOMO-1 => LUMO transition. From Figure 3, **DB-2** and **DB-3** show stronger and

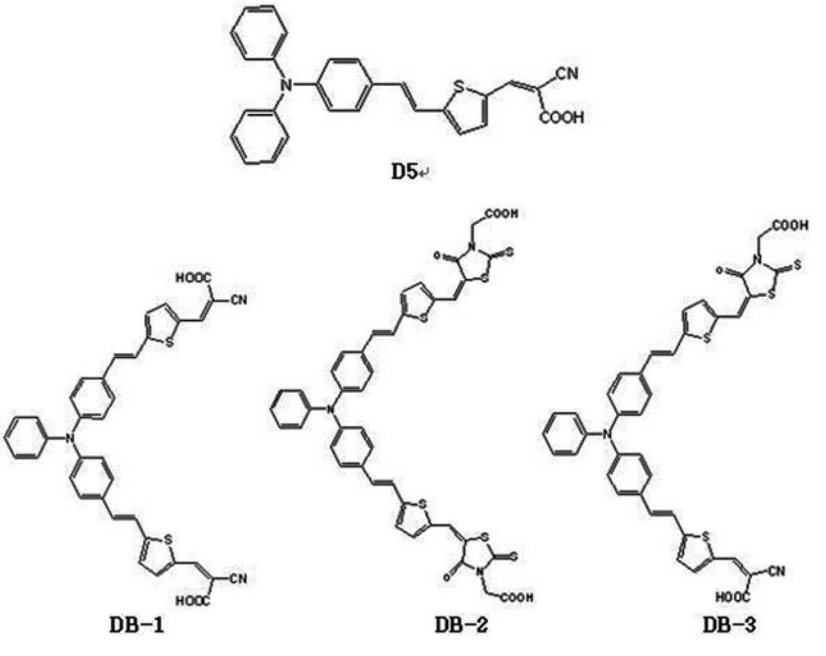

Figure 1. Schematic molecular structures of triphenylamine-based dyes: **D5**, **DB-1**, **DB-2**, and **DB-3**.

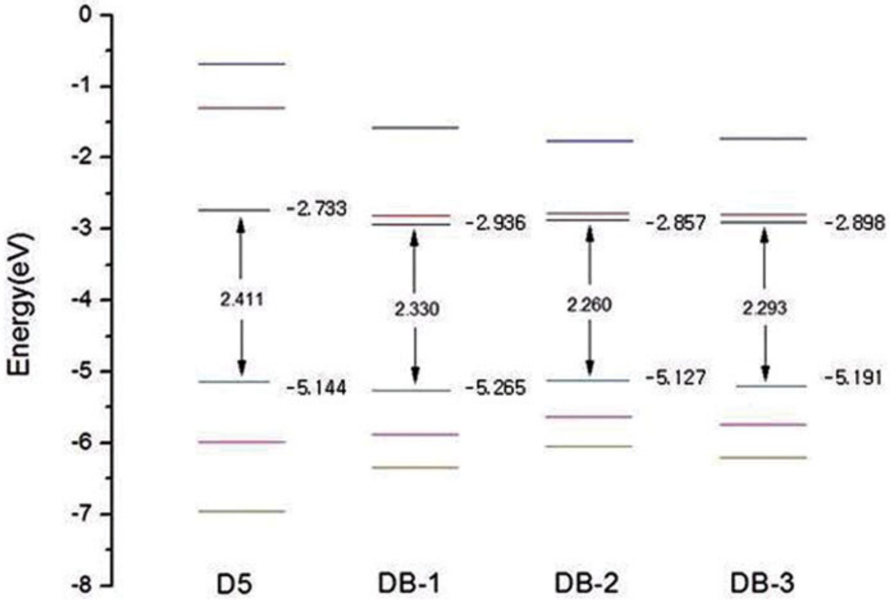

Figure 2. Schematic energy diagram for triphenylamine-based dyes.

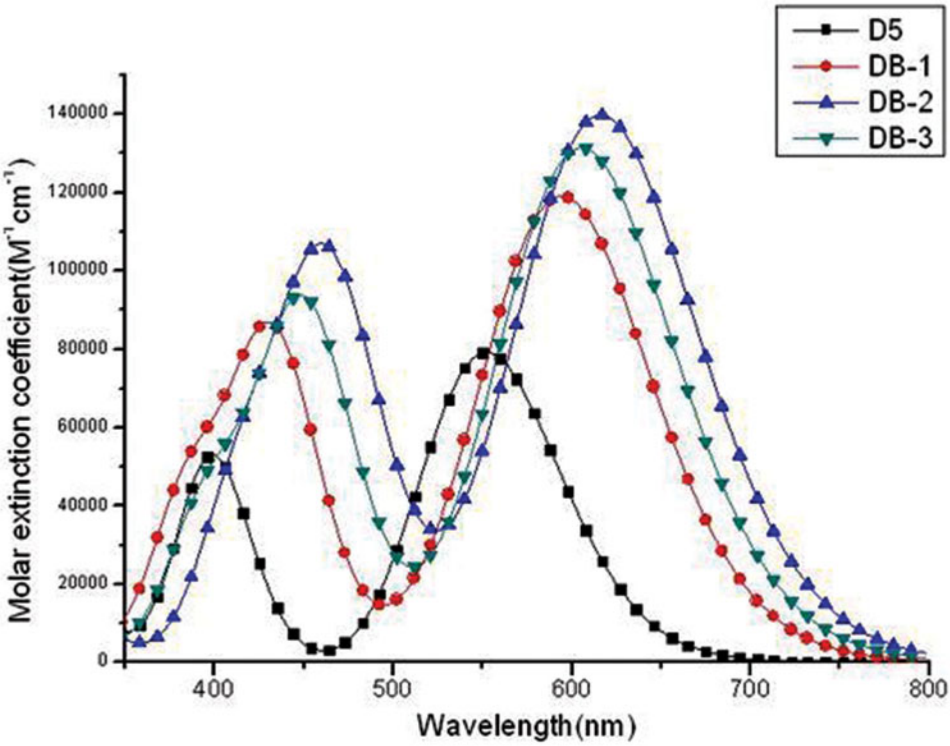

Figure 3. Calculated TD-DFT absorption spectra of triphenylamine-based dyes. The simulation of the absorption spectra was performed by a Gaussian convolution with fwhm = 0.35 eV.

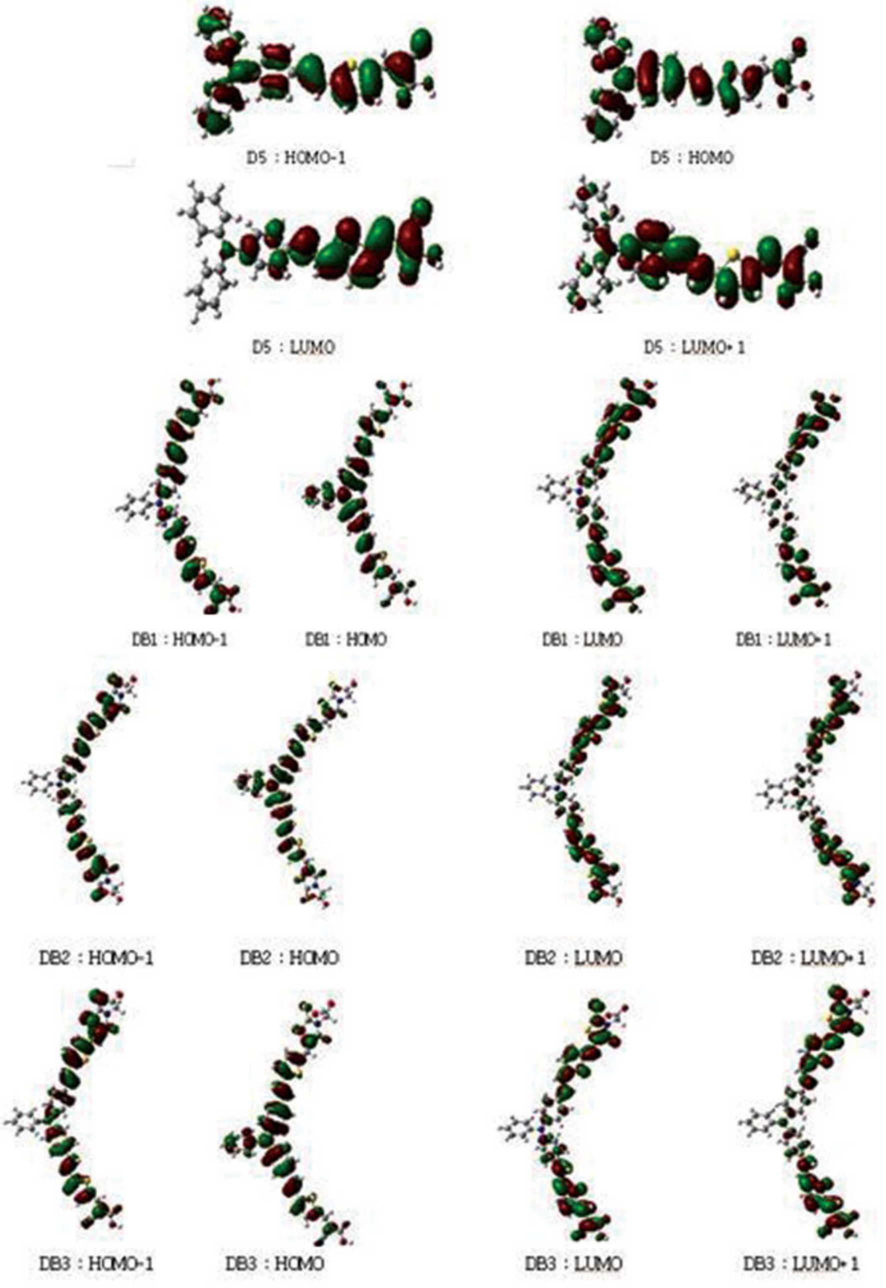

Figure 4. Frontier molecular orbitals (HOMO-1, HOMO, LUMO, LUMO+1).

more red-shifted absorption spectra, which resulted in higher absorptivity as a photovoltaic device.

Figure 4 shows the frontier molecular orbitals of triphenylamine-based dyes. The HOMOs of **D5** with a single electron acceptor are delocalized over the entire molecule however, the LUMOs are delocalized on the electron acceptor moiety. By introducing additional electron acceptors to the triphenylamine moiety, the HOMOs of the dyes (**DB-1**, **DB-2**, and **DB-3**) are also delocalized over the whole molecules with much weaker electron distributions on anchoring parts. The LUMOs of the dyes, however, are delocalized with relatively weaker populations on the electron-donating triphenylamine moiety.

The LUMOs of **D5**, **DB-1**, and **DB-3** are distinctively stretched out to the **C** moiety with the anchoring carboxylic group. On the other hand, the LUMOs of **DB-2** and **DB-3** are not stretched to the **R** moiety. It has been reported that for the dyes with dual electron acceptors, LUMO or LUMO+1 states stretched out to both anchoring parts are likely to ensure high electronic coupling between the excited states of the dyes and TiO_2 conduction band and to provide doubly folded paths for the electron transfer [18].

In Figure 4, another noticeable feature among the dyes with dual acceptors is the electron density of LUMOs near the carboxylic group. It has been reported that the closer the LUMO of the dye to its carboxylic group, the higher is the observed J_{sc} [22]. In this respect, the dye with dual acceptors of the **C** moiety showed higher performance in conversion efficiency compared with the dye with dual acceptors of the **R** moiety. Therefore, the photovoltaic performance of **DB-3** was superior to that of **DB-2**.

As stated previously, although **DB-2** with dual acceptors of the **R** moiety showed the best absorption property in the absorption spectra, its photovoltaic performance was not better than other dyes, **DB-1** or **DB-3**, with dual acceptors of the **C** moiety due to the electron density of LUMOs near the carboxylic group. Overall, **DB-3** with heteroleptic dual electron acceptors showed the best photovoltaic performance among the present dyes.

Conclusions

Some organic triphenylamine-based dyes were designed and studied theoretically for the potential devices of DSSCs. Specifically, structural, electronic, and optical properties of the triphenylamine-based dyes were investigated with the introduction of dual electron acceptor groups. Electronically, LUMO levels were degenerated due to the introduction of dual acceptors. In contrast, HOMOs were not nearly changed. The absorption spectra of DB-2 and DB-3 showed stronger and more red-shifted intensities by the addition of electron acceptor moieties. Moreover, due to the proximity of LUMOs to the anchoring carboxylic group, it was also shown that DB-3 with cyanoacrylic acid and rhodanine-3-acetic acid acceptors might be more effective in J_{sc} than DB-2 with rhodanine-3-acetic acid acceptors. Therefore, **DB-3** with heteroleptic dual electron acceptors showed the best photovoltaic performance among the present dyes. This study also suggests that dual electron acceptor groups should play a crucial role in improving the photovoltaic properties of DSSCs and give insight for developing more efficient organic dyes for DSSCs.

Acknowledgment

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