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Theoretical Study of Triphenylamine and Indoline-Based Dyes with Dual Donor and Dual Acceptor for Dye-Sensitized Solar Cells

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New triphenylamine and indoline-based dyes with dual donor and dual acceptor were designed and their electronic and optical properties were investigated by using density functional theory and time-dependent density functional theory calculations. The results showed that the homoleptic and heteroleptic dual acceptors of the dyes (C-TPA-In-C, R-TPA-In-C) intensified each absorption band between 450 and 600 nm, compared to the single acceptor of the reference dye (TPA-In-C). Considering overall properties, it is expected that the R-TPA-In-C dye with dual electron acceptor would show highest performance of the dyes in conversion efficiency for dye-sensitized solar cells.

Keywords Density functional theory; dual acceptor; dual donor; dye-sensitized solar cells (DSSCs); indoline; triphenylamine

1. Introduction

Dye-sensitized solar cells (DSSCs) have been attracted much attention 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 DSSC, the sensitizer is a crucial element, which significantly influences on the power conversion efficiency as well as the stability of the devices. 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 electrolyte [6]. However, since ruthenium is a rare and expensive metal, which limits the potentially wide application of these complexes. Therefore, the investigation of DSSCs using metal-free organic dyes has been focused for practical applications [7,8].

Numerous efficient organic dyes for DSSCs, such as hemicyanine-[9a], thienylfluorene-[9b], phenothiazine-[9c], merocyanine-[9d], coumarin-[9e], and indoline-[9f, 9g, 9h, 9i] based organic dyes, have been developed and their devices as DSSC showed good photovoltaic performance. The higher conversion efficiency value of the organic dye-sensitized solar cell based on indoline dye, 9%, was achieved in full sunlight by Ito et al

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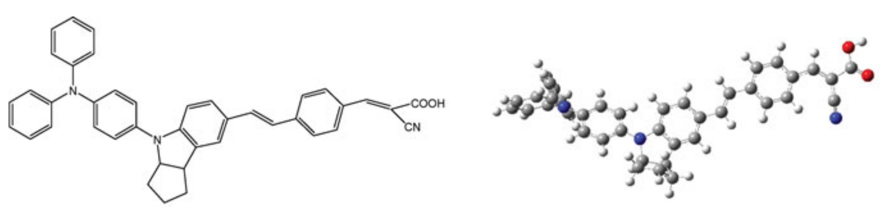
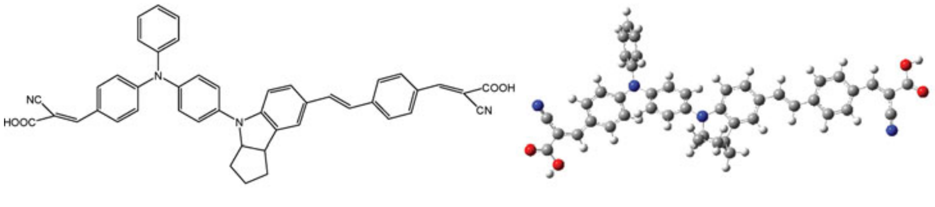
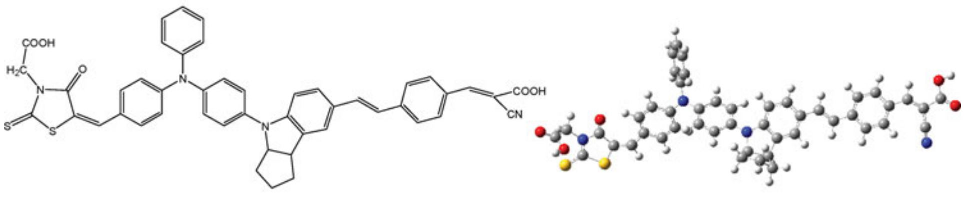


(a) TPA- In- C dye



(b) C- TPA- In- C dye



(c) R- TPA- In- C dye

Figure 1. Molecular structures (left) and their lowest energy conformational isomers (right) of TPA and indoline-based dyes: (a) the TPA-In-C dye, (b) the C-TPA-In-C dye, and (c) the R-TPA-In-C dye.

[9f, 9g]. This result suggested that the commercial application of organic dyes in DSSCs is promising.

Herein, we have designed new dye sensitizers (C-TPA-In-C, R-TPA-In-C) with dual donor (triphenylamine [TPA] and indoline moieties) and dual acceptor (the cyanoacrylic and rhodanine moieties). The C-TPA-In-C dye is composed of homoleptic electron acceptors (the cyanoacrylic moiety) and the R-TPA-In-C dye is composed of heteroleptic electron acceptors (the cyanoacrylic and rhodanine moieties) (Fig. 1). The properties of these two dyes were compared with those of the dye with single electron acceptor (the TPA-In-C dye). We have investigated charge transfer and absorption mechanism of the dyes to understand the role as a dye sensitizer. This theoretical study would give insight for developing more efficient dye for DSSCs.

2. Computational Methods

We perform density functional theory (DFT) and time-dependent DFT (TDDFT) calculations on the ground state of TPA and indoline-based dyes to get insight into the factors responsible for the absorption spectral response and the conversion efficiency. This computational procedure allows 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 exchange-correlation functional, together with a 6–31G(d) basis set in the Gaussian 03 program package. 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. Electronic populations of the highest occupied molecularorbital (HOMO) and lowest unoccupied molecularorbital (LUMO) were calculated to show the position of the localization of electron populations along with the calculated molecular orbital energy diagram.

TDDFT calculations with the B3LYP/6–31G(d) level of theory were performed at the ground-state-optimized geometries. Solvation effects were included by the conductor-like polarizable continuum model(C-PCM), as implemented in the G03 program package. Absorption spectrum was calculated at the ground-state-optimized geometries for 20 lowest singlet-singlet excitations (up to 350 nm). The simulation of the absorption spectra was performed by a Gaussian convolution with fwhm = 0.35 eV.

3. Results and Discussion

Figure 1 shows the molecular structure of TPA and indoline-based dyes with single or dual electron acceptors, namely, the TPA-In-C dye, the C-TPA-In-C dye and the R-TPA-In-C dye. These dyes have the common core structure of TPA and indoline moieties and cyanoacrylic moiety as an acceptor. The C-TPA-In-C and R-TPA-In-C dyes were designed by attaching the cyanoacrylic and rhodanine electron acceptors to the core structure, respectively. As shown in Fig. 1(b) and (c) on the right side, the lowest energy conformational isomers of the two dyes with dual acceptors have the planar structure from anchoring part with cyanoacrylic or rhodanine moieties to electron donor part of the core structure. It reflects strong conjugation between the dye sensitizer and TiO_2 film, consequently suggests smooth charge flow for DSSC devices.

The calculated TDDFT absorption spectra of TPA and indoline-based dyes are shown in Fig. 2. Major absorption peaks of the TPA-In-C dye are around 590 nm, 450 nm and 370 nm, which are ascribed to HOMO→LUMO, HOMO-1→LUMO and HOMO→LUMO+1 transitions, respectively (see Table 1). For the C-TPA-In-C dye, major absorption peaks were changed. The peak around 520 nm was intensified but blue shifted. This can be understandable by the introduction of homoleptic dual acceptor, which made HOMOs stabilized and created nearly degenerate LUMO and LUMO+1. Therefore, the peak around 520 nm was attributed to both HOMO→LUMO and HOMO→LUMO+1 instead of HOMO→LUMO alone. Likewise, the peaks around 420 nm and 360 nm were ascribed to HOMO-1→LUMO and HOMO-1→LUMO+1, HOMO→LUMO+2, respectively (see also Table 1).

For the heteroleptic electron acceptor of the R-TPA-In-C dye, major two peaks around 550 nm and 430 nm might be ascribed to HOMO→LUMO and HOMO→LUMO+1, HOMO-1→LUMO and HOMO-1→LUMO+1, respectively, from Table 1. The peak around 360 nm was attributed to HOMO-3→LUMO and HOMO→LUMO+2 instead of HOMO→LUMO+2 alone. Overall, the absorption bands of the R-TPA-In-C dye had stronger intensities compared to those of other two dyes. Therefore, it is expected that the R-TPA-In-C dye would show best absorbance as the dye sensitizer among the dyes in this study.

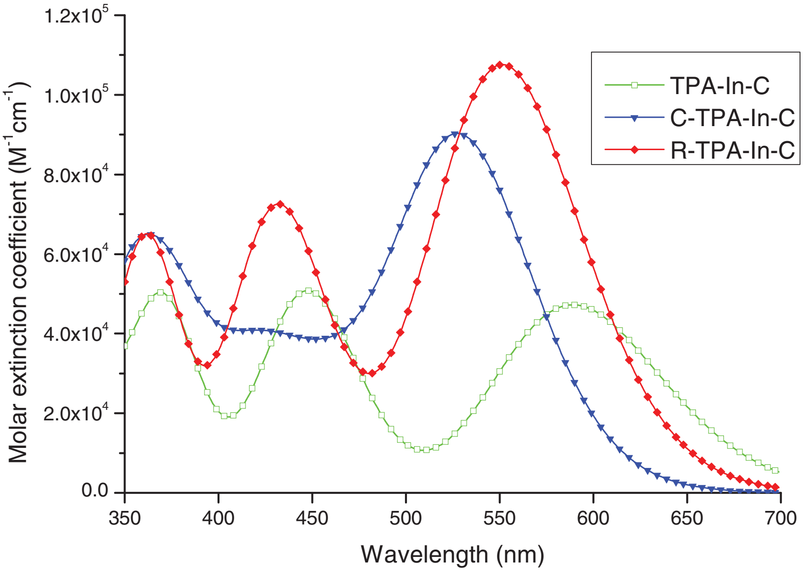


Figure 2. Calculated TDDFT absorption spectra of TPA and indoline-based dyes.

Figure 3 shows the calculated molecular orbital energy diagram for the TPA and indoline-based dyes, the TiO_2 nanoparticle model and I^-/I_3^- redox. To consider the molecular levels of the present dyes with the band edges of a model TiO_2 nanoparticle, we use a $Ti_{38}O_{76}$ cluster, and their HOMO and LUMO levels are calculated at −6.55 and −2.77 eV,

Table 1. Calculated TDDFT excitation energy (eV, nm), oscillator strength (f), major composition in terms of MO contributions of the TPA and indoline-based dyes

Dye	# of excited state	Calculated energy eV (nm)	Oscillator strength (f)	Major composition	Transition character
TPA-In-C	1	2.10(589)	0.6518	HOMO$_\rightarrow$ LUMO (92%)	ICT
	2	2.77(448)	0.6998	H-1$_\rightarrow$ LUMO (90%)	ICT
	3	3.34(370)	0.6635	HOMO$_\rightarrow$ L+1 (82%)	ICT + π-π^*
C-TPA-In-C	1	2.34(530)	1.2118	HOMO$_\rightarrow$ LUMO (91%)	ICT
	2	2.68(462)	0.3321	HOMO$_\rightarrow$ L+1 (90%)	ICT
	3	2.95(420)	0.4235	H-1$_\rightarrow$ LUMO (91%)	ICT
	4	3.28(377)	0.5607	H-1$_\rightarrow$ L+1 (85%)	ICT + π-π^*
	5	3.52(352)	0.5870	HOMO$_\rightarrow$ L+2 (64%)	ICT + π-π^*
R-TPA-In-C	1	2.24(553)	1.4128	HOMO$_\rightarrow$ LUMO (84%)	ICT
	2	2.39(518)	0.1118	HOMO$_\rightarrow$ L+1 (82%)	ICT
	3	2.81(441)	0.4485	H-1$_\rightarrow$ LUMO (89%)	ICT
	4	2.91(426)	0.5939	H-1$_\rightarrow$ L+1 (84%)	ICT + π-π^*
	5	3.42(363)	0.8148	H-3$_\rightarrow$ LUMO (43%), HOMO$_\rightarrow$ L+2 (44%)	ICT + π-π^*

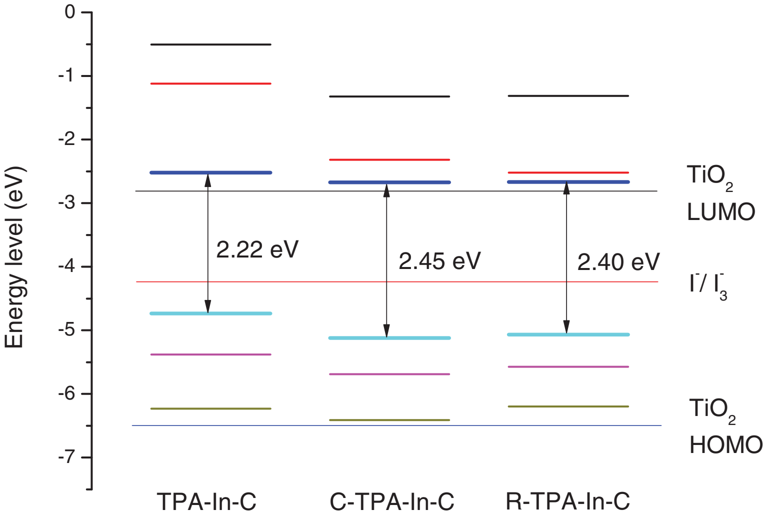


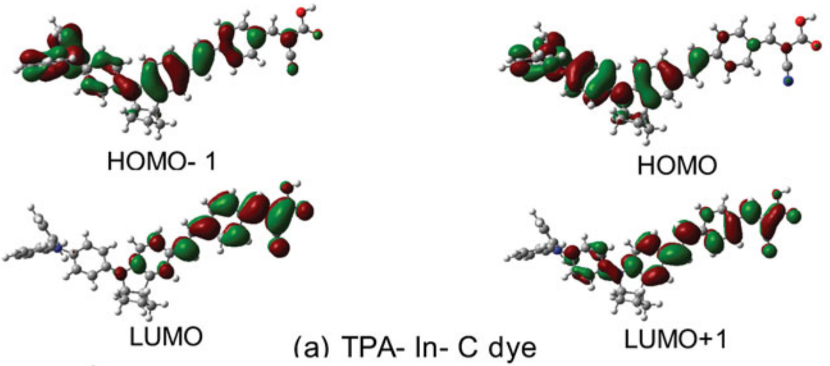
Figure 3. Schematic energy diagram for TPA and indoline-based dyes.

respectively [6]. The calculated LUMO levels for the present dyes are located above the TiO_2 LUMO level. This means that these dye sensitizers have sufficient driving force for electron injection to TiO_2. In addition, all HOMO levels of the dye sensitizers are located below the $I^-/I_3{}^-$ redox, ensuring that there is enough driving force for the dye generation reaction.

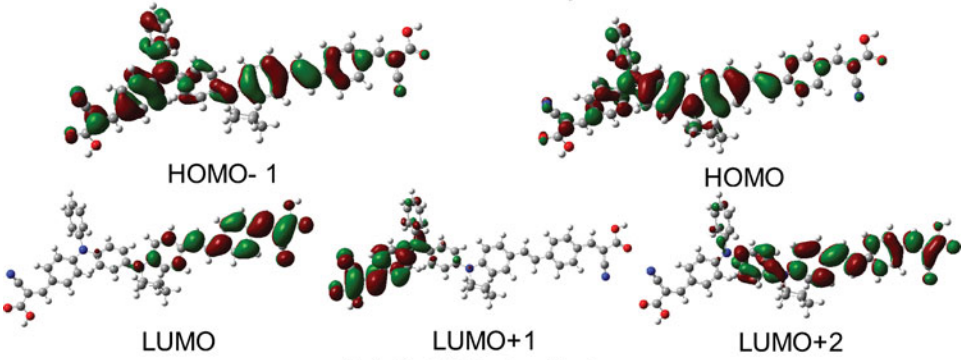
In Fig. 3, by the introduction of dual electron acceptors, most MO levels were stabilized compared to those of the TPA-In-C dye with single electron acceptor. Especially, HOMO levels were highly stabilized. This might be attributed to withdrawal tendency of an electron for both C-TPA-In-C and R-TPA-In-C dyes due to additional acceptors. For the C-TPA-In-C and the R-TPA-In-C dye with dual acceptors, new LUMO and LUMO+1 levels were nearly degenerated. This might be inferred from the fact that the cyanoacrylic and rhodanine moieties as electron acceptors had similar LUMO levels.

Electron distributions of some frontier MOs for the present dyes are shown in Fig. 4. Molecular orbital analysis confirmed that HOMO and HOMO-1 of the TPA-In-C dye are delocalized over the whole electron donor part with TPA and indoline moieties. The LUMO is mainly localized over the cyanoacrylic anchoring part. By the introduction of homoleptic dual acceptor, HOMO and HOMO-1 of the C-TPA-In-C dye are also delocalized over the whole electron donor part. However, its LUMO and LUMO+1 are different. As shown in Fig. 4(b), LUMO is localized over the cyanoacrylic moiety attached to the phenyl linker. However, LUMO+1 is localized over the cyanoacrylic moiety in opposite site. This was confirmed in Fig. 3 that energy levels of LUMO and LUMO+1 were degenerated for the C-TPA-In-C dye. By the introduction of heteroleptic dual acceptor, the shapes of MOs for the R-TPA-In-C dye are similar to those for the C-TPA-In-C dye. In this dye, however, LUMO+1 is localized over the rhodanine moiety instead of the cyanoacrylic one.

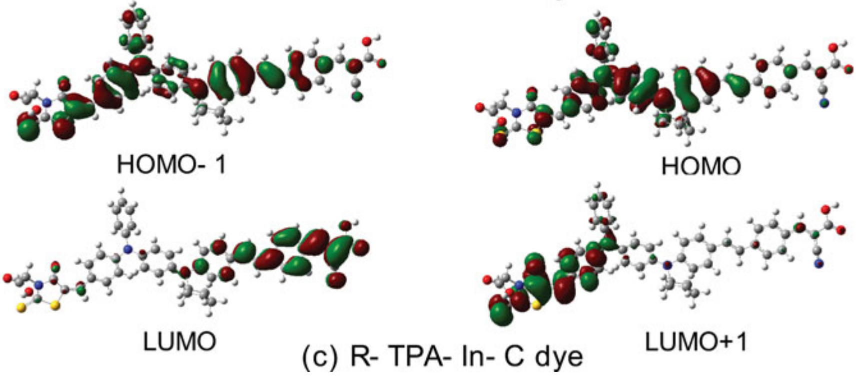
To get more insight into excitations giving rise to the optically active absorption bands in the visible region, we performed TDDFT calculations at the B3LYP/6–31G(d) level. In Table 1, we report calculated absorption energy, oscillator strength, and major composition in terms of molecular orbital contributions for the present dyes. Excitations above 350 nm in absorption energy were only considered in the table. The lowest and second lowest



(a) TPA- In- C dye



(b) C- TPA- In- C dye



(c) R- TPA- In- C dye

Figure 4. Electron distributions of some frontier molecular orbitals: (a) HOMO-1, HOMO, LUMO and LUMO+1 for the TPA-In-C dye, (b) HOMO-1, HOMO, LUMO, LUMO+1 and LUMO+2 for the C-TPA-In-C dye and (c) HOMO-1, HOMO, LUMO and LUMO+1 for the R-TPA-In-C dye.

excitations of the TPA-In-C dye were attributed to HOMO→LUMO, HOMO-1→LUMO and HOMO→LUMO+1 transitions. By the introduction of homoleptic electron acceptor, LUMO level was split into LUMO and LUMO+1 levels. Consequently, the second and the fourth lowest excitations of the C-TPA-In-C dye were attributed to HOMO→LUMO+1 and HOMO-1→LUMO+1 transitions. The oscillator strength of the C-TPA-In-C dye for HOMO→LUMO transition was intensified. By the introduction of heteroleptic electron acceptor, the excitation pattern was similar to that for homoleptic electron acceptor. For both the C-TPA-In-C dye and R-TPA-In-C dye, LUMO and LUMO+1 due to dual acceptors were fully used for these excitations. As shown in Table 1, most transitions had intramolecular charge transfer (ICT) or mixed ICT + π-π^* characters.

4. Conclusions

TPA and indoline-based dyes with dual electron acceptors were designed and investigated for their electronic and optical properties as DSSC devices. To get a better understanding of the role as a dye sensitizer, particularly of its electronic structure and excited-state properties, we performed DFT and TDDFT calculations. For these dye sensitizers, both dual donor and dual acceptor contributed to the transitions during absorption process. Especially, heteroleptic dual electron acceptor, both cyanoacrylic and rhodanine moieties, could be fully used for the photovoltaic properties of the R-TPA-In-C dye. This study suggests that the R-TPA-In-C dye with heteroleptic electron acceptor would show highest performance of the dyes in this study in conversion efficiency for DSSCs.

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