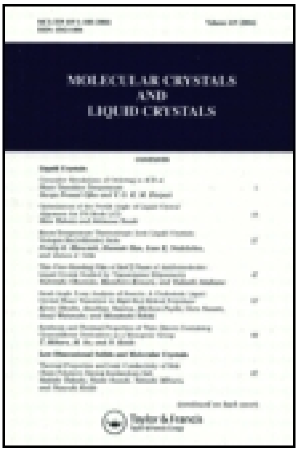

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Molecular Design and Computation of Dye Sensitizers with Multiple Electron Donor for DSSCs

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Herein, indoline-based dye sensitizers with dual and triple electron donors (the TPA-In and the POZ-TPA-In dye) were designed and their electronic and optical properties were investigated theoretically to enhance photovoltaic performance as dye-sensitized solar cells (DSSCs). To gain insight into the factors responsible for photovoltaic efficiencies, we perform the density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations for these dyes. This study shows that all electron donor moieties might contribute to absorption process even for the dye with triple electron donor. From DFT and TDDFT calculations as well as frontier orbital analysis, this result is attainable when HOMO levels of the POZ-TPA-In dye were manipulated appropriately. It suggests that dye sensitizer with multiple electron donor could show better photovoltaic properties in case of proper design of its MO levels and consequently increase the conversion efficiency for DSSCs.

Keywords dye-sensitized solar cells (DSSCs); multiple electron donor; indoline; DFT; TDDFT

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] 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

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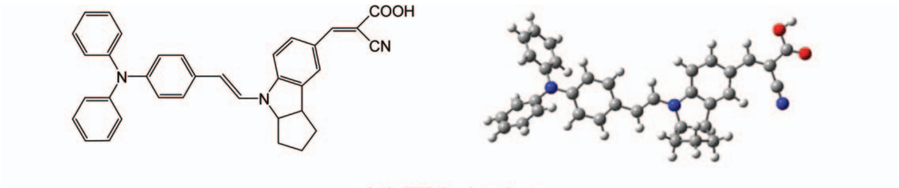
cell based on indoline dye, 9%, was achieved in full sunlight by Ito et al [9f, 9g]. This result suggested that the commercial application of organic dyes in DSSCs is promising.

Herein, we have designed indoline-based dyes with multiple electron donors (the TPA-In dye and the POZ-TPA-In dye). The TPA-In dye has dual electron donor, composed of triphenylamine (TPA) and indoline (In) moieties. The POZ-TPA-In dye with triple electron donor was composed of another phenoxazine (POZ) moiety besides TPA and indoline ones (Fig. 1). We have investigated charge transfer and absorption mechanism of the dyes to understand the role as a dye sensitizer. Especially, we have focused on the investigation for the feasibility of maximal utilization of the dye with triple electron donor. This theoretical study would give insight for developing more efficient dye for DSSCs.

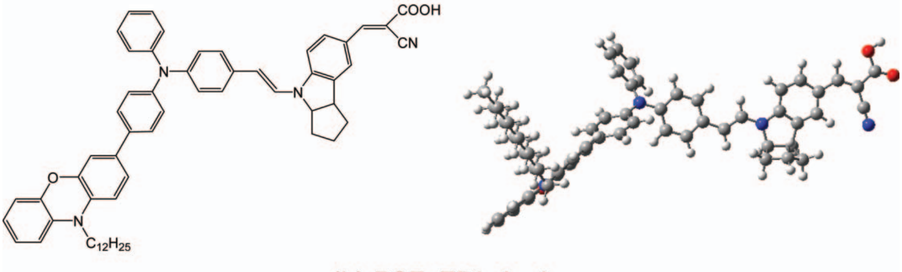
2. Computational Methods

We perform density functional theory (DFT) and time-dependent DFT (TDDFT) calculations on the ground state of DCM-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 function, 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 molecular orbital (HOMO) and 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.



(a) TPA- In dye



(b) POZ- TPA- In dye

Figure 1. Molecular structure of indoline-based dyes with multiple electron donor: (a) the TPA-In dye (b) the POZ-TPA-In dye.

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

Fig. 1 shows the molecular structure of indoline-based organic dyes with dual and triple electron donor, namely, the TPA-In dye and the POZ-TPA-In dye. These dyes have the common core structure of indoline moiety and cyanoacrylic acid as an acceptor. The TPA-In and POZ-TPA-In dyes were designed by adding TPA and POZ-TPA electron donors to indoline moiety, respectively. As shown in Fig. 1(b), optimized structures of these dyes have the planar structure from anchoring part with cyanoacrylic acid to electron donating group with indoline moiety. 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 indoline-based dyes are shown in Fig. 2. Major absorption peak of the In dye (this dye was partly considered) is around 370 nm, which is ascribed to HOMO → LUMO transition. For the TPA-In dye with dual electron donor, major absorption peaks are around 525 nm and 370 nm, which are ascribed to HOMO → LUMO and HOMO-1 → LUMO transitions, respectively (see Table 1). By the introduction of triple electron donor, major absorption peaks of the POZ-TPA-In dye appear around 545 nm, 485 nm and 390 nm (see also Table 1). These peaks are ascribed to HOMO → LUMO, HOMO-1 → LUMO and HOMO-2 → LUMO transitions with the characteristics of POZ, TPA and indoline moieties, respectively (see Fig. 4(b)). This implies that all electron donor moieties might contribute to absorption process even for the dye with triple electron donor. From Fig. 2, it is expected that the POZ-TPA-In dye would show better optical property as the dye sensitizer compared to the TPA-In dye.

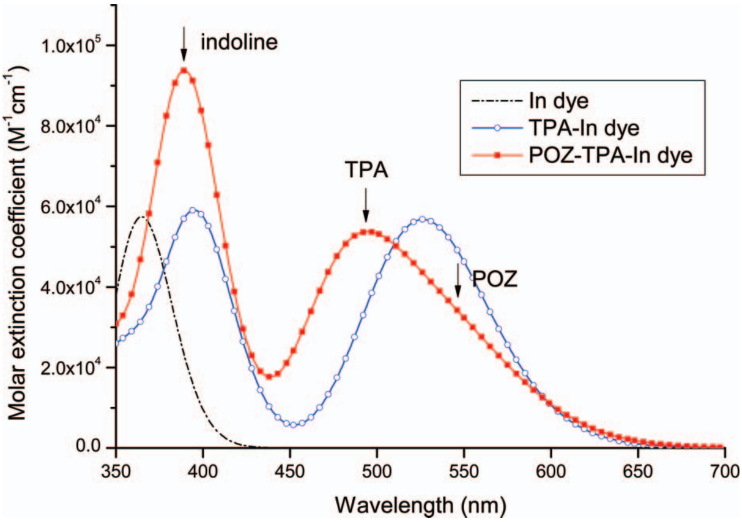


Figure 2. Calculated TDDFT absorption spectra of indoline-based dyes.

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

Dye	# of excited state	Calculated energy eV (nm)	Oscillator strength (f)	Major composition	Transition character
TPA-In	1	2.36 (526)	0.7837	HOMO → LUMO (89%)	ICT
	2	3.13 (396)	0.7934	H-1 → LUMO (82%)	ICT
	3	3.49 (355)	0.2981	HOMO → L+1 (76%)	$\pi \rightarrow \pi^*$
POZ-TPA-In	1	2.27 (546)	0.3293	HOMO → LUMO (98%)	ICT
	2	2.55 (487)	0.6543	H-1 → LUMO (92%)	ICT
	3	3.18 (390)	1.2135	H-2 → LUMO (56%)	ICT
	4	3.51 (353)	0.1351	HOMO → L+2 (44%), HOMO → L+1 (18%)	$\pi \rightarrow \pi^*$, $\pi \rightarrow \pi^*$

Fig. 3 shows the calculated molecular orbital energy diagram for the three 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, 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

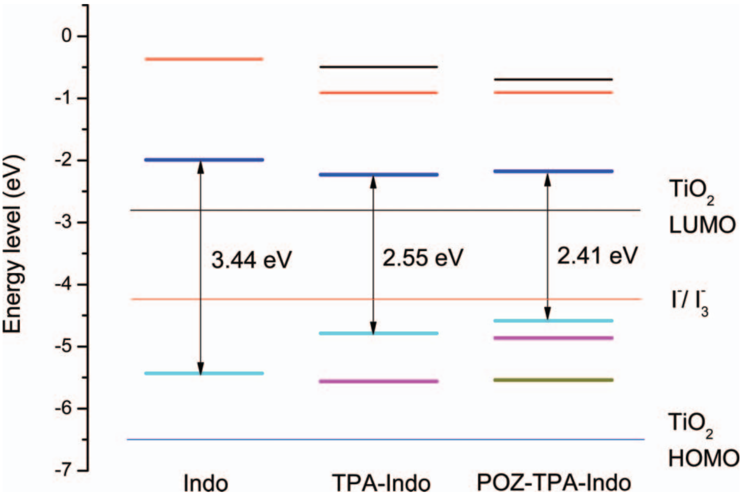


Figure 3. Schematic energy diagram for indoline-based dyes.

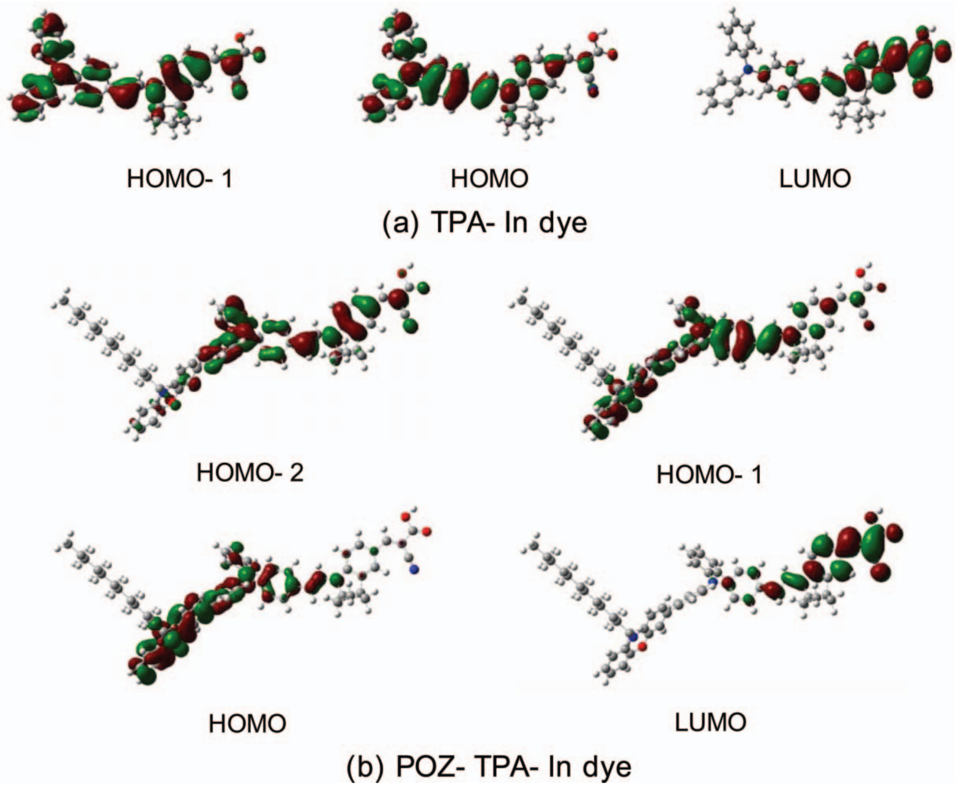


Figure 4. Electron distributions of some frontier molecular orbitals: (a) HOMO-1, HOMO and LUMO for the TPA-In dye and (b) HOMO-2, HOMO-1, HOMO and LUMO for the POZ-TPA-In dye.

below the I^-/I_3^- redox, ensuring that there is enough driving force for the dye generation reaction.

In Fig. 3, despite of the introduction of dual or triple electron donors, their LUMO levels were nearly unchanged. However, HOMO levels were considerably changed. This might be attributed to the tendency that HOMOs are likely to localize over electron donor part for the present dyes. For the TPA-In dye with dual electron donor, new HOMO level should be originated from TPA moiety since its HOMO-1 level was very similar to the HOMO level of the In dye with single electron donor. As shown in Fig. 2, HOMO → LUMO and HOMO-1 → LUMO transitions were represented as the lowest and the second lowest absorption bands, respectively. Likewise, new HOMO and HOMO-1 levels of the POZ-TPA-In dye should be originated from POZ and TPA moieties, respectively, compared with the HOMO level of the TPA-In dye. Therefore, even for triple electron donor, all electron donor moieties could contribute to the absorption as the dye sensitizer. This was confirmed in the spectrum for the POZ-TPA-In dye in Fig. 2. The optically maximal utilization of the POZ-TPA-In dye could be attainable when HOMO, HOMO-1 and HOMO-2 have relatively strong electron populations at POZ, TPA and indoline moieties, respectively. In other words, energy levels of donor moieties at which HOMOs localize have the following order: indoline $<$ TPA $<$ POZ.

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 dye are delocalized over the whole electron donor part with relative stronger electron populations on TPA and indoline moieties, respectively. The LUMO is mainly localized over the cyanoacrylic anchoring part. By the introduction of triple electron donor, HOMO, HOMO-1 and HOMO-2 of the POZ-TPA-In dye are also delocalized over the whole electron donor part. However, their electron distribution is different for each MO. Electron populations are relative stronger at POZ, TPA and indoline moieties for HOMO, HOMO-1 and HOMO-2, respectively. This also confirms that all donor moieties might contribute to the absorption. The LUMO of the POZ-TPA-In dye is also mainly localized over the cyanoacrylic anchoring part. This means that effective charge transfer is possible when the transition is related to this LUMO level.

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 excitation of the TPA-In dye was attributed to HOMO → LUMO transition and TPA moiety. By the introduction of triple electron donor, HOMO level was split into HOMO and HOMO-1 levels. Consequently, the lowest excitation of the POZ-TPA-In dye was attributed to HOMO → LUMO transition and POZ moiety with relatively weak strength. For the intramolecular charge-transfer (ICT) character, it has the tendency that the more physical separation between HOMO and LUMO increases, the weaker its oscillator strength is. Since the physical separation between HOMO and LUMO for POZ-TPA-In increased, compared to that for TPA-In in Fig. 4, the oscillator strength of the first excited state for POZ-TPA-In became relatively weak. The second lowest one was HOMO-1 → LUMO transition and TPA moiety. Transitions of HOMO-1 → LUMO for TPA-In dye and HOMO-2 → LUMO for POZ-TPA-In dye were related to indoline moiety. As shown in Table 1, most transitions had an ICT character.

4. Conclusions

Indoline-based dyes with dual and triple electron donors 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 dye sensitizers with triple electron donor as well as with dual donor, all electron donor moieties could contribute to the transitions during absorption process. For the maximal utilization of the dye sensitizer with triple electron donor, HOMO levels should be manipulated appropriately. The maximal absorption property of the POZ-TPA-In dye could be attainable when energy levels of donor moieties where HOMOs localize have the following order: indoline $<$ TPA $<$ POZ. This study suggests that the POZ-TPA-In dye with triple electron donor would show better performance compared to the TPA-In dye in conversion efficiency for DSSCs.

Acknowledgment

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References

[1] O'Regan, B., & Gratzel, M., (1991). *Nature*, *353*, 737.

[2] Gratzel, M. (2005). *Inorg. Chem.*, *44*, 6841.

[3] Kuang, D., Ito, S., Wenger, B., Klein, C., Moser, J. E., Humphry-Baker, R., Zakeeruddin, S. M., & Gratzel, M. (2006). *J. Am. Chem. Soc.*, *128*, 4146.

[4] Kuang, D., Klein, C., Ito, S., Moser, J. E., Humphry-Baker, R., & Zakeeruddin, S. M., & Gratzel, M. (2007). *Adv. Funct. Mater.*, *17*, 154.

[5] Kuang, D., Klein, C., Ito, S., Moser, J. E., Humphry-Baker, R., Evans, N., Duriaux, F., & Gratzel, C., Zakeeruddin, S. M., Gratzel, M. (2007). *Adv. Mater.*, *19*, 1133.

[6] Nazeeruddin, M. K., Angelis, F. D., Fantacci, S., Selloni, A., Viscardi, G., Liska, P., Ito, S., Takeru, B., &Gratzel, M. (2005) *J. Am. Chem. Soc.*, *127*, 16835.

[7] Horiuchi, T., Miura, H., Sumioka, K., & Uchida, S. (2004). *J. Am. Chem. Soc.*, *126*, 12218.

[8] L. Schmidt-Mende, Bach, U., Humphry-Baker, R., Horiuchi, T., Miura, H., Ito, S., Uchida, S., & Gratzel, M. (2005). *Adv. Mater.*, *17*, 813.

[9] (a) Wang, Z.-S., Li, F.-Y., Huang, C.-H. (2001). *J. Phys. Chem. B*, *105* 9210; (b) Thomas, K. R. J, Lin, J. T., Hsuc, Y.-C., Ho, K.-C. (2005). *Chem. Commun.* 4098; (c) Tian, H., Yang, X., Chen, R., Pan, Y., Li, L., Hagfeldt, A., Sun, L. (2007). *Chem. Commun.*, 3741; (d) Li, S.-L., Jiang, K.-J., Shao, K.-F., Yang, L.-M. (2006). *Chem. Commun.* 2792; (e) Wang, Z.-S., Cui, Y., Dan-oh, Y., Kasada, C., Shinpo, A., Hara, K. (2007). *J. Phys. Chem. C*, *111*, 7224; (f) Ito, S., Zakeeruddin, S. M., Humphry-Baker, R., Liska, P., Charvet, R., Comte, P., Nazeeruddin, Md.K., Pechy, P., Takata, M., Miura, H., Uchida, S. & Gratzel, M. (2006). *Adv. Mater.*, *18*, 1202; (g) Ito, S., Miura, H., Uchida, S., Takata, M., Sumioka, K., Liska, P., Comte, P., Pechy, P., & Gratzel, M. (2008). *Chem. Commun.* 5194; (h) Ham, H. and Kim, Y. (2010). *Thin Solid Films*, *518*, 6558.