



# Influence of conformation on the absorption spectra of flexible organic dyes used in dye-sensitized solar cells



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## ABSTRACT

We performed density functional theory (DFT) and time dependent-DFT (TD-DFT) calculations on indoline dye D149 to elucidate the influence and/or effect of conformation of flexible organic dyes on the light absorption spectra. Calculating the conformational energy for D149 showed that 16 kinds of conformations are possible in acetonitrile solvent. The TD-DFT calculations revealed that the 16 kinds of conformations result in two types of absorption spectra. The first type shows about 1.3 times higher oscillator strength than the second type in a long-wavelength region around 530 nm, whereas the second type shows about 1.7 times higher oscillator strength than the first type in a short-wavelength region around 390 nm. Which of the two types of absorption spectra occurs depends on whether the torsion angle between the indoline and rhodanine parts is 180° or 0°. Trying to control the torsion angle by computationally designing derivatives of D149, we demonstrated that introducing methyl, chloride, and hydroxyl groups in the indoline part enables us to fix the torsion angle on either 0° side or 180° side and thereby selectively obtain a dye with one of the two types of absorption spectra.

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## 1. Introduction

Using solar cells to convert sunlight into electrical power is one of the most promising approaches to sustainable energy production, and dye-sensitized solar cells (DSSCs) [1,2] are attractive alternatives to silicon-based solar cells. When a dye anchored to the surface of a TiO<sub>2</sub> semiconductor electrode in a DSSC absorbs sunlight, a ground-state electron in the dye transits to an excited state and is immediately injected from the LUMO orbital of the dye to the conduction band of the semiconductor electrode. Subsequently, the oxidized dye is regenerated on a microsecond time scale by a redox mediator in the electrolyte.

The performance of a DSSC is greatly dependent on the absorption spectrum of the dye. For high efficiency of the conversion of solar energy to electrical energy, the dye needs to absorb light of wavelengths in both the visible and near infrared regions, and the absorption strength needs to be high. Such dye can produce a large photoelectric current. In 1991, Grätzel and O'Regan [1] invented a DSSC with a ruthenium-based dye that can absorb light throughout the visible range of the solar spectrum. Its conversion efficiency was 7.1%, and its success was a step toward the practical use of DSSCs. DSSCs with a ruthenium-based dye, nanocrystalline TiO<sub>2</sub> electrode, and I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox electrolyte have a conversion

efficiency of about 11% under the AM1.5G condition, [3–5] but the use of a heavy metal like ruthenium is undesirable from an environmental perspective. Furthermore, since ruthenium is a rare metal, resource deficiency would be a concern in the commercial mass production of DSSCs with ruthenium-based dye.

Metal-free organic dyes are promising alternatives to ruthenium-based dyes because they are less expensive and are not as much of a resource problem. Their conversion efficiency is relatively high, and their structures are easy to modify. A DSSC using the indoline dye D149, [6–8] I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox electrolyte, acetonitrile solvent, and a nanocrystalline TiO<sub>2</sub> electrode 12.6 μm thick has been reported to have a conversion efficiency of 9.03%. [7] The molecular structure of D149 includes indoline and rhodanine parts (Fig. 1). The highest peak in the absorption spectrum of free D149 in tert-butyl alcohol/acetonitrile (1/1) solvent is at 526 nm, and other peaks are near 390 nm and 340 nm. [6] The absorption spectrum of D149 anchored to a TiO<sub>2</sub> electrode, on the other hand, is widely spread. The highest peak is shifted to 541 nm, the peak near 390 nm is shifted to near 400 nm, and the peak near 340 nm is nearly gone. [6] Geometrical, electronic, and optical properties of D149 have also been examined in studies using density functional theory (DFT) calculations and time-dependent DFT (TD-DFT) calculations. [9–21] For example, DFT/TD-DFT calculations have been used to investigate the effect of the dipole moment of the dye on the TiO<sub>2</sub> electrode, [9,14] the influence of the dye-aggregation, [12,18] and the properties of designed derivatives of D149. [13,17]

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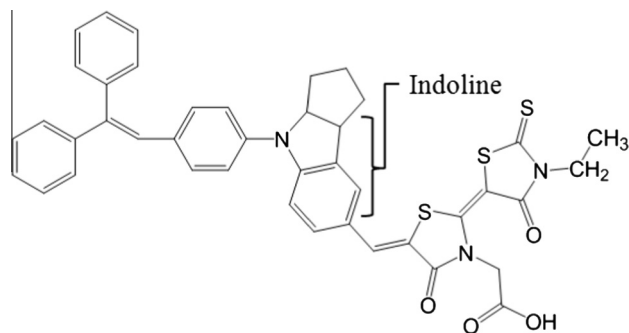


Fig. 1. Indoline dye D149.

The performance of DSSCs is well-known to be affected by the excited state quenching due to dye aggregation, charge recombination, etc., throughout various kind of dyes. For metal free organic dyes like D149, influence of the dye's conformation on the DSSC's performance should also be considered because metal-free organic dyes have several rotatable torsion angles and therefore the dyes undergo various conformational changes in a solvent. That is, the structure is not always the one with the lowest energy. Naturally, the influence of the conformation increases with the length of the dye's structure. It is expected that dye's conformation will be a major factor influencing the DSSC's performance with increasing utilization of metal free organic dyes.

In this study, the first purpose is to elucidate the influence of conformations of a flexible organic dye on the dye's absorption spectrum. For this purpose, the structural and optimal properties of the indoline dye D149, which is a representative flexible organic dye, was calculated by using quantum chemical calculations. Conformation search was performed using DFT calculations, and then excitation states of the generated conformations were calculated using TD-DFT calculations. The second purpose is to explore the feasibility of molecular design to control the conformation. We computationally designed D149 derivatives to control a torsion angle influencing the dye's absorption spectrum and found that the control of conformations makes it possible to obtain a specific absorption spectrum.

## 2. Methods

An *ab initio* quantum chemistry program GAMESS [22,23] was used for density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations.

The conformation search was performed using DFT at the level of the B3LYP hybrid three-parameter exchange–correlation functional [24,25] and the 6-31G(d) base set [26] with the polarizable continuum model (PCM) [27] for aprotic acetonitrile solvent. The DSSC using D149 were designed using acetonitrile-based solvent [6–8], and applying the PCM for acetonitrile is adequate for comparing calculation with experiment. The process of the conformation search was as follows: (1) the molecule was divided into partial structures, (2) energetically stable conformations for the partial structures were searched, (3) conformations of the whole structure were reproduced by combinations of the stable conformations of the partial structures, and (4) conformations of whole structures were structurally optimized.

The singlet–singlet excitation energies and oscillator strengths for searched conformations were calculated using TD-DFT at the level of the M05 exchange–correlation functional [28] and the 6-31G(d) base set [26] with the polarizable continuum model (PCM) [27] for aprotic acetonitrile solvent. The M05 was determined in preliminary TD-DFT calculations using a low-energy

conformation. The reliability of the M05 is shown in Table S-1 (Supplementary information), where errors against experimental data for 2.36 eV (526 nm), 3.18 eV (390 nm), and 3.64 eV (340 nm) [6] are compared among 18 exchange–correlation functionals. The error of the M05 for the minimum excitation energy is remarkably small, and errors for the other two excitation energies are also small. Considering the balance of these errors, we thought that choice of the M05 was reasonable.

## 3. Results and discussion

### 3.1. Conformation search and absorption spectra for D149

In the first step of the conformation search, D149 was divided into five parts connected by rotating bonds, and partial structures were modeled as shown in Fig. 2. For each partial structure, the conformational energies were calculated at each 15° step of torsion angle. At each torsion angle, the other internal degrees of freedom were optimized. Fig. 2 shows the results. The partial structures (a), (c), (d), and (e) have two stable torsion angles for which the energies are almost the same, whereas the partial structure (b) has two stable and two meta-stable torsion angles and we adopted only stable torsion angles for reproducing the whole structure. Note that in the partial structures (a) and (b), the two stable states 180° apart are identical because the benzene ring is simply reversed by 180° rotation. The lower energy barriers between two stable states for partial structures (a)–(e) are respectively 4.10, 1.98, 10.26, 6.52, and 5.05 kcal/mol. The energy barrier for partial structure (c) is so high that conformational change between the two states does not occur easily.

As a result of the partial structure calculation, 16 conformations for D149 were established by combining stable torsion angles of partial structures. Note that when the partial structures (a) and (b) were combined, only 30° was adopted for the partial structure (b) and both 30° and 150° were adopted for the partial structure (a), i.e., the partial structures (a) and (b) was combined in two ways. For the two rhodanine groups in D149, the trans orientation was adopted because the energy of the cis-isomer is significantly higher than that of the trans-isomer. [11] The torsion angles before and after structural optimization, conformational energies after the structural optimization and ratios relative to the lowest-energy conformation in 16 conformations are listed in Table 1. Differences between each energy and the lowest energy,  $\Delta E$ , are lower than 1.14 kcal/mol. When the ratio of the lowest-energy conformation is defined by 1, the ratio of the highest-energy one is 0.15 by  $\exp(-\Delta E/kT)$ , where  $k$  is the Boltzmann constant and temperature  $T$  is 300 K. These values indicate that the probability of even the highest-energy conformation is not negligible. Consequently, all the 16 conformations have a possibility of appearing in acetonitrile solvent.

Next, the singlet–singlet excitation energies and oscillator strengths for the 16 conformations were calculated by TD-DFT. The five lowest excitation energies and their oscillator strengths are listed in Table 2, and the absorption spectra that were simulated by a Gaussian convolution with an arbitrarily set full width at half-maximum (FWHM) of 10 nm are shown in Fig. 3. The absorption peaks calculated for all 16 conformations are near 360 nm, 390 nm, or 530 nm, and their locations are in good agreement with experimental results [6]. The calculated absorption spectra are of two types that clearly differ in oscillator strength. The first type shows about 1.3 times higher oscillator strength than the second type in a long-wavelength region around 530 nm, and the second type shows about 1.7 times higher oscillator strength than the first type in short-wavelength region around 360 nm and 390 nm. In classifying the conformations corresponding to

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