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# DFT Studies on the electronic structures of indoline dyes for dye-sensitized solar cells

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*Abstract*: A series of indoline dyes with promising efficiency for dye-sensitized solar cells (DSSCs) were studied using the density functional theory at the B3LYP/6-31g (*d*) level. The ground-state geometries, electronic structures and absorption spectra of these dyes are reported. The calculated results indicate that the energy levels of the HOMOs and LUMOs of these dyes are advantageous for electron injection. Their intense and broad absorption bands as well as favorable excited-state energy levels are key factor for their outstanding efficiencies in DSSCs.

*Keywords*: density functional theory; indoline dyes; dye-sensitized solar cells; electronic structures.

## INTRODUCTION

Due to the increasingly serious energy-demanding and environmental-concerning nature of conventional energy systems, new systems based on renewable sources have drawn more and more attention. Over the past years, significant emphasis has been put on the development and understanding of light-driven charge separation in molecular systems as methods of converting and storing solar energy. Dye-sensitized solar cells (DSSCs) have attracted widespread interest for the conversion of sunlight into electricity because of their high efficiency and low cost.[1–4]

Generally, transition metal coordination compounds (ruthenium polypyridyl complexes) are used as effective sensitizers, due to their intense charge-transfer absorption over the whole visible range and highly efficient metal-to-ligand charge transfer.[5] However, Ru polypyridyl complexes contain a heavy metal, which is undesirable from the environmental point of view.[6] Moreover, the synthesis processes of such complexes are complicated and costly. In addition to Ru com-

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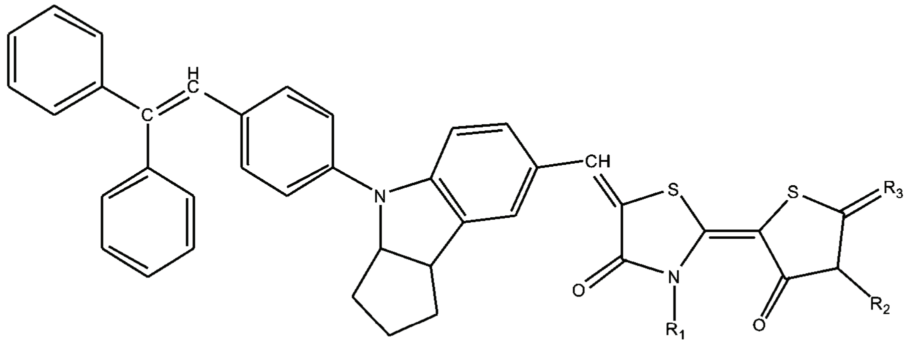
plexes, pure organic dyes as sensitizers are also under intensive investigation due to their high molar extinction coefficients, flexible structural modifications and low costs,[7] and some of them have reached good efficiency.[8–11] Indoline dyes have been reported as high-efficient sensitizers for DSSCs because of their strong and intense absorption bands in the visible region.[9,12,13]

An accepted model for a DSSC is as follows: a sensitizing dye molecule absorbs visible or near infrared light and injects an electron into a semiconductor from its excited state(s).[14] Once the electron is transferred into, for example, solid $TiO_2$, it proceeds through the semiconductor to an external circuit. Subsequently, the oxidized sensitizer receives an electron from an electron donor, such as an iodide ion, present in the electrolyte. Therefore, the performance of DSSC strongly depends on the following factors: 1) the absorption efficiency of the sensitizing dye for the solar light spectrum; 2) electron transfer, probably from the excited state of the sensitizing dye to $TiO_2$ (efficiency of the charge separation); and 3) probability of the electron transfer from the electron donor to the oxidized dye.[3] All these factors are closely associated with the structure of the ground and excited electronic states of the sensitizing dye. From this point of view, it is imperative to investigate the electronic structures of both the ground and excited states of the sensitizing dye molecule for an understanding of the mechanism of the charge separation and the electron transfer, which are the key processes in this type of solar cells. In order to design and synthesize more efficient sensitizing dyes, it is also necessary to understand the electronic structures of the existing efficient sensitizing dyes.

The density functional theory (DFT) has emerged as a reliable standard tool for the theoretical treatment of structures as well as electronic and absorption spectra. Its time-dependent extension, called time-dependent DFT (TD-DFT), can give reliable values for the valence excitation energies with standard exchange-correlation functionals. The computational cost of a TD-DFT calculation is comparative to that of a Hartree–Fock based single excitation theory, such as, configuration interaction singles (CIS) or the time-dependent Hartree–Fock (TD--HF) method, and maintains a uniform accuracy for open-shell and closed-shell systems. In recent years, TD-DFT has been extensively used to study the structures and absorption spectra of sensitizing dyes for DSSCs. Ru complexes have been widely investigated by TD-DFT calculations.[4,15–22] TD-DFT calculations have also been applied to the study of some pure organic dyes which act as sensitizers in DSSCs.[23–26] Zhang *et al*.[25] employed DFT and TD-DFT calculations to study the absorption spectra and electronic structures of a series of coumarin dyes. However, there have been relatively few attempts to investigate the electronic structures of indoline dyes.

In this study, a series of indoline dyes (shown in Fig. 1) were examined using DFT and TD-DFT. The ground-state geometries, electronic structures and

UV–Vis absorption spectra were obtained. The theoretical calculation studies provide an in-depth understanding concerning molecular structures and physical properties, which is helpful for the interpretation and prediction of optical absorption spectra of this series of indoline dyes at a molecular level.



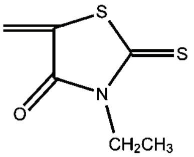
| Indoline Dye | R1 | R2 | R3 |
|---|---|---|---|
| 1 | —$CH_2COOH$ | —$CH_2CH_3$ | =S |
| 2 | —$CH_2COOH$ | —$CH_2COOH$ | =S |
| 3 | —$CH_2CH_2COOH$ | —$CH_2CH_3$ | =S |
| 4 | —$CH_2COOH$ | —$CH_2CH_3$ |  |

Fig. 1. Chemical structures of the indoline dyes D102, D131 and D149.

## COMPUTATIONAL METHOD

All the calculations were performed using the Gaussian 03 program package.[27] The ground-state geometries were fully optimized without any symmetry constrains at the DFT level of theory with the Becke[29] three parameters hybrid functional and the Lee, Yang and Parr correlational functional B3LYP[29] sing a standard 6-31g (d) basis set on all atoms. The excitation energies and oscillator strengths for the lowest 30 singlet-singlet transitions at the optimized geometry in the ground state were obtained in TDFT calculations using the same basis set as for the ground state. According to the calculated results, the UV–Vis absorption spectra were simulated by a Gaussian convolution with a full width at half-maximum of 0.4 eV (3200 cm$^{-1}$).[4] Solvation effects were introduced by the SCRF method, *via* the conductor polarizable continuum model (CPCM)[30,31] implemented in the Gaussian program, for both geometry optimizations and the TD-DFT calculations.

## RESULTS AND DISCUSSION

### *Molecular structures*

The framework of the indoline dyes in this study is formed by a phenylethenyl group, an indoline ring and two or three rhodanine rings. The optimized ground-state geometries of the four indoline dyes are shown in Fig. 2. The physical separation of the electron-donating (ED) and electron accepting groups (EA) for these dyes are quite similar (11.33±0.01 Å) although their substituent groups

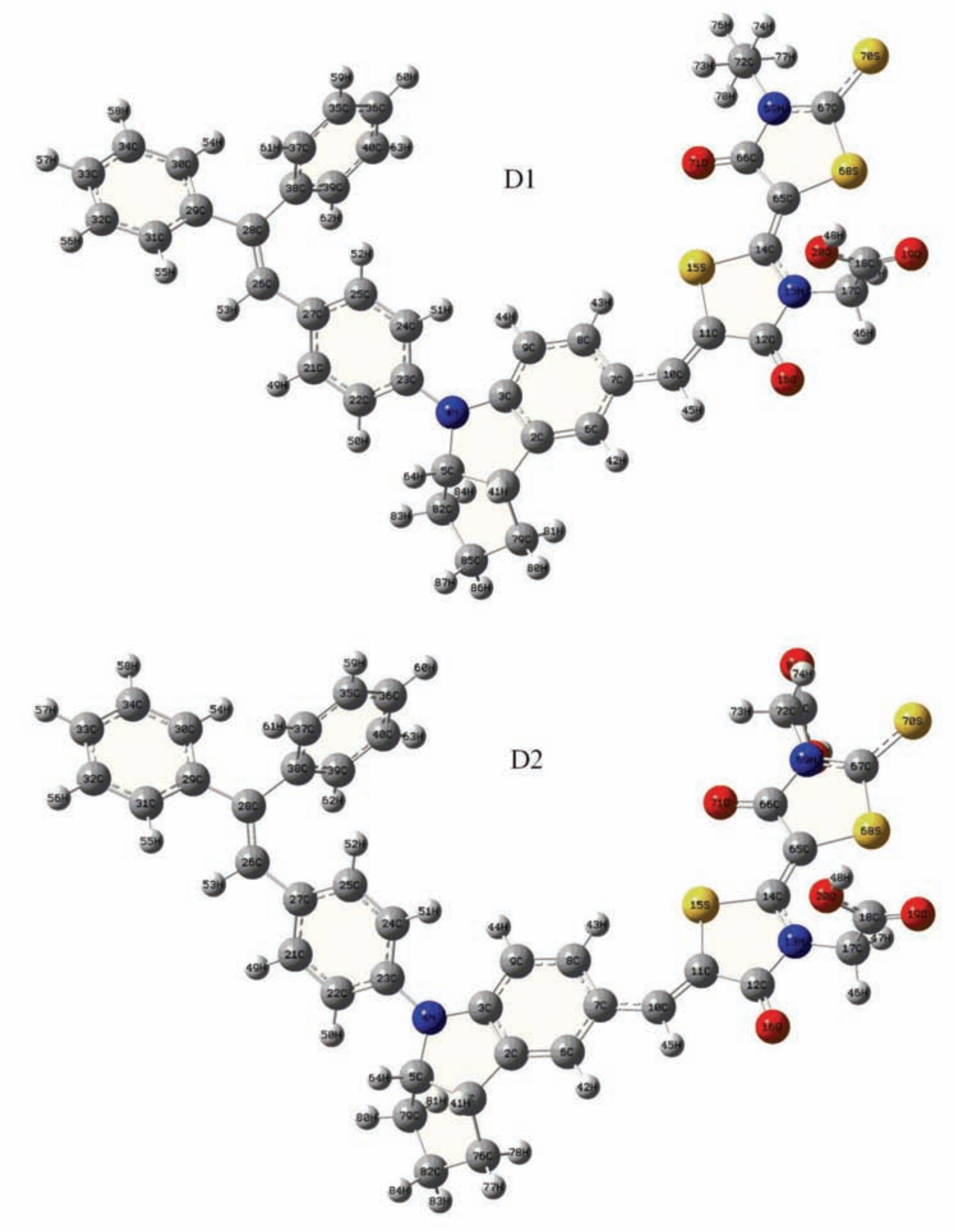


Fig. 2. Optimized ground-state geometries of the indoline dyes. (Continued on next page).

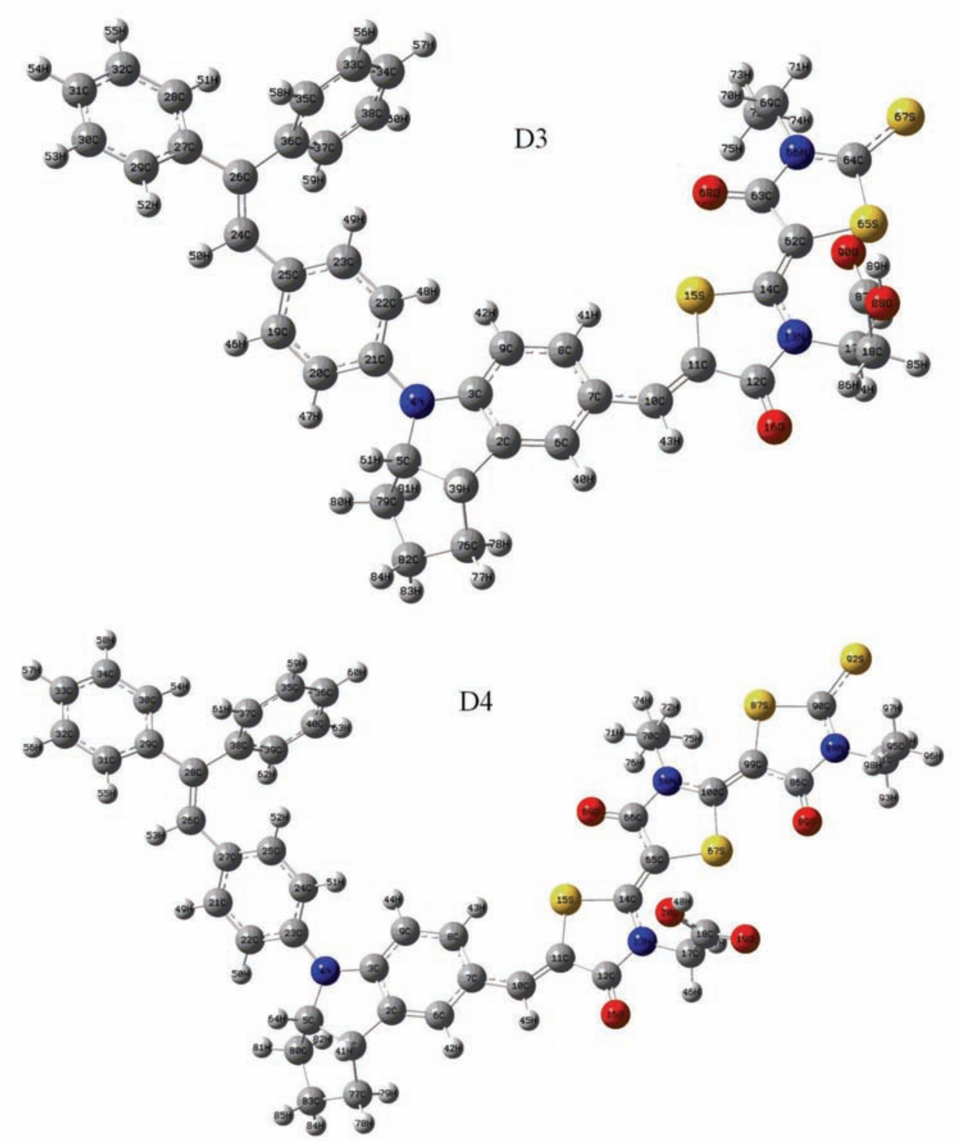


Fig. 2. Optimized ground-state geometries of the indoline dyes. (Continued).

differ from each other. The C10-C11 bond lengths for these dyes are 1.364–1.365 Å, exhibiting a delocalized π-bond character. The dihedral angles of the C–C and C=C bonds at the methine bridge between the indoline and rhodanine rings (∠C8–C7–C10–C11) for D1, D2, D3 and D4 are 3.50, –0.22, 3.88 and 1.59°, respectively. In comparison to D1, the rhodanine rings are distorted by 3.72° in response to the orientation of the second carboxyl group for D2 and by 1.91° in response to an increased rhodanine ring for D4, but very slightly in response to the increased methylene for D3. The N13-C17 bond for D1 (1.456 Å) are shorter than that for D3 (1.476 Å), indicating that the increased methylene in carboxyl group would be disadvantageous to the electron injection through the anchoring carboxyl group in DSSCs. The dipole moments for D1, D2, D3 and D4 are 14.562, 15.697, 13.035 and 15.227 D, respectively.

### *Electronic structures*

The molecular orbitals involved in the analyzed transitions were examined by the DFT method. The vertical excitation energy and oscillator strength along with the main excitation configuration are listed in Table I. The major electronic absorption bands are assigned to those excitations with significant oscillator strengths. The electronic structures of these dyes are quite similar although their substituent groups are distinct from one another. The HOMO and LUMO orbitals of D1 are shown in Fig. 3 as a representation. The electron distribution of the HOMO orbital is delocalized over the π-system with the highest electron density centered on the central nitrogen atom. It is noticed that the LUMO orbital have larger compositions of the terminal carboxyl group compared with the HOMO orbital. Therefore, the HOMO–LUMO excitation induced by light irradiation could shift the electron distribution from the middle of the molecule to the anchoring moieties, thus favoring electron injection from dye to $TiO_2$. The absolute energies of the HOMOs are –4.95, –4.98, –4.93, and –4.93 eV, while the absolute energies of the LUMOs are –2.56, –2.59, –2.50, and –2.56 eV for D1, D2, D3, and D4, respectively. The calculated energies of D1 herein are quite consistent

TABLE I. Excitation energy (E and calculated $\lambda$), oscillator strength ($f$) and main configuration of indoline dyes (H = HOMO, L = LUMO, L+1 = LUMO+1, *etc.*)

| Dye | $E$ / eV | $\lambda$ / nm | $f$ | Configuration | Assignment |
|---|---|---|---|---|---|
| D1 | 2.12 | 585.7 | 0.913 | H → L (+89 %) | π → π* |
| | 2.82 | 439.3 | 0.546 | H–1 → L (+75 %); H → L+1 (+16 %) | |
| | 2.95 | 420.0 | 0.386 | H → L+1 (+73 %); H-1 → L (+16 %) | |
| | 3.26 | 380.2 | 0.549 | H–2 → L (+68 %); H → L+2 (+19 %) | |
| D2 | 2.33 | 532.8 | 1.024 | H → L (+86 %) | π → π* |
| | 3.10 | 399.6 | 0.281 | H–1 → L (+91 %) | |
| | 3.48 | 356.3 | 0.202 | H → L+1 (+81 %); H → L+2 (+7 %) | |
| D3 | 2.13 | 581.1 | 0.944 | H → L (+89 %) | π → π* |
| | 2.83 | 437.5 | 0.520 | H–1 → L (+76 %); H → L+1 (+15 %) | |
| | 2.98 | 415.5 | 0.433 | H → L+1 (+74 %); H–1 → L (+14 %) | |
| | 3.25 | 381.1 | 0.522 | H–2 → L (+66 %); H → L+2 (+23 %) | |
| D4 | 2.08 | 596.7 | 1.103 | H → L (+90 %) | π → π* |
| | 2.65 | 467.7 | 0.701 | H–1 → L (+58 %); H → L+1 (+34 %) | |
| | 2.76 | 449.5 | 0.405 | H → L+1 (+58 %); H–1 → L (+31 %) | |
| | 3.07 | 403.3 | 0.163 | H–2 → L (+86 %) | |
| | 3.25 | 381.2 | 0.353 | H → L+2 (+72 %); H–1 → L+1 (+18 %) | |

with the experimental data (cited as D149, HOMO: –4.901 eV, LUMO: –2.873 eV).[32] For comparison, the HOMO level for N719 (calculated at the DFT level of theory in a water environment) is –5.3 eV with the LUMO at –2.7 eV.[33] The HOMO (conduction band) energy level of $TiO_2$ calculated for a $Ti_{38}O_{76}$ cluster exposing the anatase (101) surface[34] is located at –6.55 eV, and the corresponding LUMO at –2.77 eV.

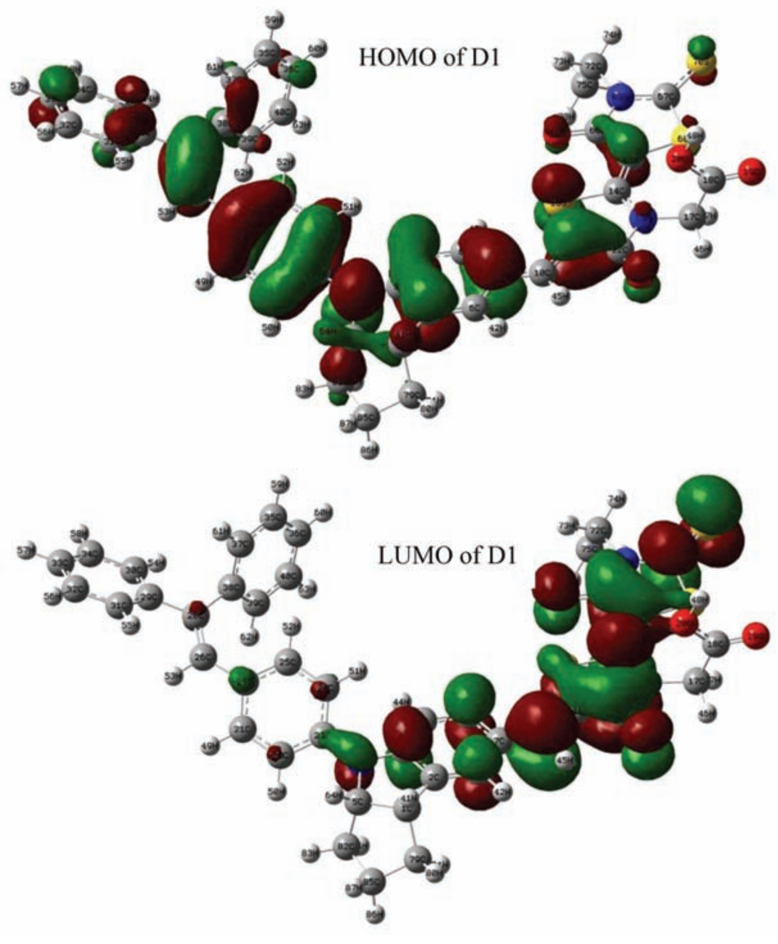


Fig. 3. HOMO and LUMO of the indoline dyes computed on the ground-stated geometries.

The HOMO and LUMO levels of a dye used in a DSSC must match with the conduction-band-edge energy level ($E_{cb}$) of the $TiO_2$ and the redox potential of electrolyte for an efficient charge separation and dye regeneration. The HOMO level has to be sufficiently more positive than the redox potential (0.40 V *vs.* NHE for $I^-/I_3^-$) and the LUMO of the dye has to be sufficiently more negative than the $E_{cb}$ of $TiO_2$. Usually, an energy gap of more than 0.2 V between the LUMO level of the dye and the $E_{cb}$ of $TiO_2$ (–0.50 V *vs*. NHE) is necessary for an effective electron injection from the excited dye to the conduction band of $TiO_2$.[24] The energy levels of the excited state of the four dyes are depicted in Fig. 4. The HOMO levels are more positive than the redox potential of $I^-/I_3^-$ (0.40 V *vs*. NHE), meaning that the resultant dye$^+$ can be deoxidized by $I^-$ in the electrolyte. The LUMO levels are sufficiently more negative than the $E_{cb}$ (–0.5 V *vs*. NHE) to inject electrons from the dyes. The relatively large energy gaps between the LUMO and the $E_{cb}$ values could improve the voltage and, consequently, the total efficiency.

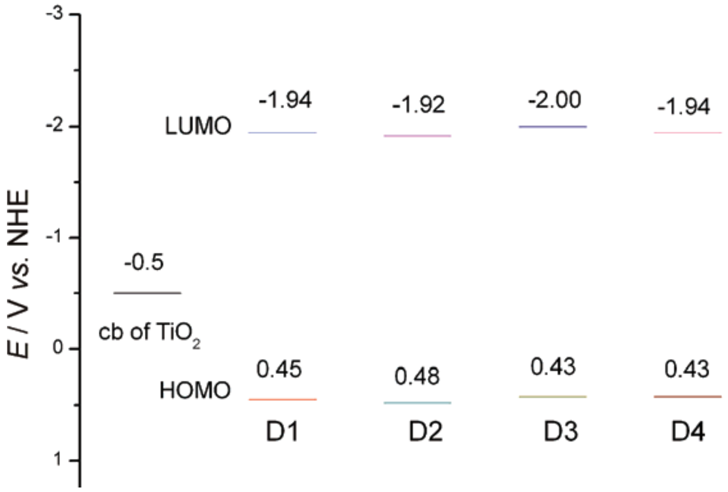


Fig. 4. Energy level diagram of the conduction bands of $TiO_2$, and the ground state and single excited states of the indoline dyes.

*UV–Vis absorption spectra*

The simulated absorption spectra of the four indoline dyes in solutions are shown in Fig. 5. The first optically allowed electronic transition of D1, D2, D3 and D4 are predicted to populate the HOMO → LUMO transitions at 585.7, 532.8, 581.1 and 596.7 nm, respectively. The observed experimental $\lambda_{max}$ values are at 526, 531, and 532 nm for D1, D2 and D3 (D4 has a slightly red-shifted absorption spectrum peak, but the $\lambda_{max}$ value is not valuable).[9] It seems that the calculated results did not reproduce the corresponding experimental spectra very well. The inclusion of the solvent is important to calculate spectra in good agreement with the experiment. However, the experimental data[9] were obtained in *tert*-butyl alcohol/acetonitrile (1/1); while the present calculation was carried out with only the solvation effect of acetonitrile.

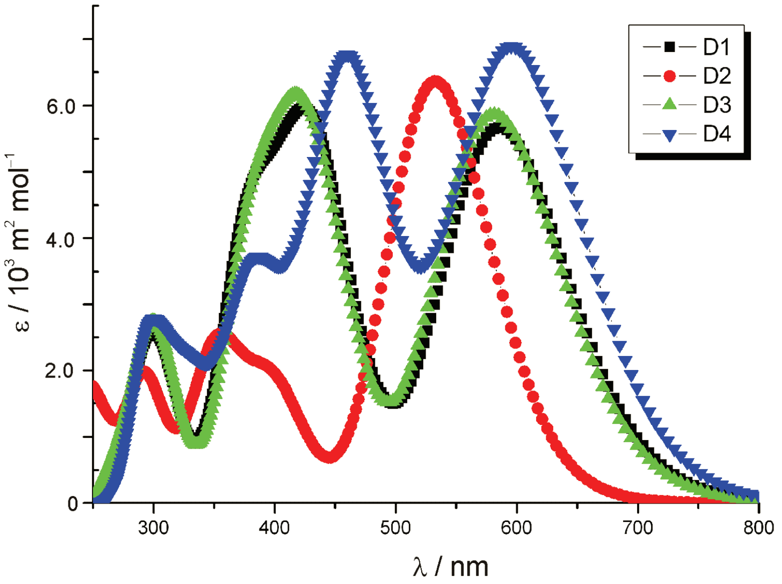


Fig. 5. Simulated absorption spectra of the indoline dyes.

## CONCLUSIONS

In this paper, the ground-state geometries and electronic structures of four indoline dyes in acetonitrile were investigated by DFT calculations. The high absorption coefficients of these dyes in visible region make them very suitable for efficient light harvesting. The absolute energies of the HOMOs are –4.95, –4.98, –4.93, and –4.93 eV, while the absolute energies of the LUMOs are –2.56, –2.59, –2.50, and –2.56 eV for D1, D2, D3, and D4, respectively, indicating that electron transfer from the excited dyes to the $TiO_2$ conduction band is available.

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## ИЗВОД

## DFT ИСПИТИВАЊА ЕЛЕКТРОНСКЕ СТРУКТУРЕ ИНДОЛНИХ БОЈА СОЛАРНЕ ЋЕЛИЈЕ ОСЕТЉИВЕ НА БОЈУ

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Серија индолних боја које имају обећавајућу ефикасност за соларне ћелије осетљиве на боју испитивана је помоћу теорије функционала густине на B3LYP/6-31g (d) нивоу. Приказани су геометрије основних стања, електронске структуре и апсорпциони спектри ових боја. Резултати израчунавања указују на то да су HOMO и LUMO енергетски нивои ових боја погодни за пријем електрона. Нихове интензивне и широке апсорпционе траке, као и фаворизовани енеггетски нивои ексцитованог стања су кључни фактори за њихову изузетну ефикасност у DSSC.

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