

Combination of Natural Dye (Crocetin) and Synthetic Dye (Indoline D205) for DSSCs Application

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Abstract: Dye-sensitized solar cells (DSSCs) are reckoned as emerging next-generation solar cells of a high potency. Co-sensitization of dyes facilitates widening of the light absorption range of a sensitizer and is one of possible options to improve overall DSSC performance. In this work, an effect of combination of the natural crocetin dye and synthetic metal free indoline D205 dye was studied. Molecular design of a complex formed from the individual dyes was attempted. The structures, vibrational and electronic spectra of the species were computed by DFT and TD-DFT B3LYP5 methods with mid-sized basis sets. The UV-vis absorption spectra were measured for individual dyes and their mixture in chloroform solutions. Electron density distribution of the frontier molecular orbitals and energy levels alignment were used for analysis of the electronic spectra and mechanism of transitions. The results indicated that the designed complex can be considered as a potential candidate for DSSCs application with improved properties compared to the individual dyes.

Keywords: Dye-Sensitized Solar Cells (DSSCs), IR and UV-Vis Spectra, Time-Dependent Density Functional Theory (TD-DFT), Crocetin, Indoline D205

1. Introduction

Dye-sensitized solar cells (DSSCs) are regarded as low cost next-generation solar cells, and significant progress has been made in their performance and stability since their discovering in 1991 by Michael Grätzel and Brian O'Regan [1]. Among the components of DSSC, the sensitizer is a crucial part as this mimic the function of chlorophyll in plant due to the fact that it significantly influences on the power conversion efficiency as well as the stability of the devices [2]. To date, the most efficient DSSCs are made using ruthenium dye complexes with reported power conversion efficiency of about 12% at the illumination of 100 mW cm⁻² (AM 1.5) [2-4]. Researchers have tested different types of sensitizers, including natural and synthetic dyes, so as to identify their ability to convert light into electricity. However, the DSSCs fabricated using natural dyes suffer from very low efficiencies [5] while the synthetic dyes are expensive in terms of synthetic route and utilization of heavy transition

metals [6, 7].

Experimental and theoretical studies of physical and chemical properties of dyes contribute to understanding of the relationship between structure, properties of dyes and performance of a solar cell and hence facilitate design and synthesis of novel dyes for DSSCs application [8-13]. Many efforts were focused on synthesis of suitable donor-acceptor dyes, design of solar cells with novel materials and architectures [14, 15]. For a dye to be useful in DSSC, the important criteria include the electron-donating part [16, 17], a unit to adjust the absorption spectrum [18], and the electron-acceptor part [19]. Combinations of dyes with shorter and longer wavelengths absorption were investigated aimed to increase the light absorption range and hence improve overall solar cell performance [20-23]. To our knowledge, no work about the combination of natural and synthetic dyes was reported in literature by now.

The aim of this work is to study an effect of combination of natural crocetin dye and synthetic metal free dye indoline

D205 considering them as sensitizers in DSSCs. The experimental part comprises measurements and analysis of UV-vis spectra of the individual dyes' solutions and their mixture. The theoretical part includes the computations of the vibrational and electronic spectra of the crocetin and indoline D205 molecules as well as a complex designed through combination of individual dyes.

2. Materials and Methods

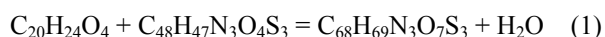
2.1. Experimental Details

The crocetin and indoline D205 dye samples were purchased in powder form with a stated purity of 97% (HPLC) from MedKoo Biosciences, Inc (USA) and Sigma-Aldrich Chemical Company (USA), respectively; and were used without further purification for solution preparation at room temperature.

For crocetin solution preparation, 0.7 mg of the crocetin powder was dissolved in 10 ml (7×10^{-2} g L⁻¹) of chloroform, and then 1 ml of the solution was added to 5 ml of chloroform resulting in 1.4×10^{-2} g L⁻¹ concentration. This was used as a sample for crocetin UV-vis spectra measurements. Also for indoline dye D205, 0.5 mg of the sample was dissolved in 50 ml of chloroform resulting in concentration 10^{-2} g L⁻¹, then 1 ml of this solution was added to 40 ml of chloroform, and the solution of indoline used for UV-vis spectra measurements had the concentration of 2.5×10^{-4} g L⁻¹. For the mixture preparation, 1 ml of the indoline dye D205 solution was added to 1 ml of crocetin dye solution. This was used as a sample for measurements of UV-vis spectra. The UV-vis spectra of the samples prepared have been recorded in the region around 200–800 nm using a single beam 2800 UV-vis spectrophotometer (Hitachi U-2000).

2.2. Computational Details

The density functional theory B3LYP5 with 3-21G basis set was used for the geometrical parameters optimization and computation of vibrational spectra. The initial coordinates of the crocetin C₂₀H₂₄O₄ and indoline D205 C₄₈H₄₇N₃O₄S₃ molecules were taken from Chem Spider [24]. The complex C₆₈H₆₉N₃O₇S₃ was designed through combination (etherification) of these two molecules. For the computation of the complex parameters the same approach, B3LYP5/3-21G, as for individual dyes was applied. The energy and enthalpy of the complex formation reaction



were computed with different basis sets, from 3-21G to 6-31G (d, p) with geometrical parameters optimized with the 3-21G basis set. The energies of the reaction $\Delta_r E$ were calculated as the difference between the total energies of the product and reactants:

$$\Delta_r E = \Sigma E_{\text{prod}} - \Sigma E_{\text{react}} \quad (2)$$

The enthalpies of the reactions $\Delta_r H^\circ(0)$ were obtained using $\Delta_r E$ and the zero-point vibration energy $\Delta_r \epsilon$:

$$\Delta_r H^\circ(0) = \Delta_r E + \Delta_r \epsilon \quad (3)$$

$$\Delta_r \epsilon = \frac{1}{2}hc (\Sigma \omega_{i \text{ prod}} - \Sigma \omega_{i \text{ react}}) \quad (4)$$

where h is the Plank's constant, c is the speed of light in the free space, $\Sigma \omega_{i \text{ prod}}$, and $\Sigma \omega_{i \text{ react}}$ are the sums of the vibration frequencies of the product and reactants, respectively.

The electronic spectra of the species both for vacuum and solvent (chloroform) were calculated at the TD-DFT B3LYP5/6-31G level of theory. The calculations were performed using the Firefly QC package [25], which is partially based on the GAMESS (US) [26] source code. The geometrical structures, vibrational and electronic spectra were visualized and analyzed using the Chemcraft [27] and Mac Mol Plt [28] software.

3. Results and Discussion

3.1. Molecular Structure of Individual Dyes and Complex

Equilibrium geometrical structures of crocetin and indoline molecules are shown in Figures 1, 2. In the crocetin, the middle part is composed of four methyl groups, and two carboxylic groups COOH attached at the ends. The molecular structure of the indoline dye D205 comprises diphenylethenyl, bicyclic indoline and two rhodanine groups [29]. The combination of two dyes through the chemical reaction (1) with elimination of water molecule leads to the formation of the complex; the optimized geometrical structure is shown in Figure 3. The selected geometrical parameters of the individual dyes are compared with those in the complex molecule in Tables 1, 2.

In the complex, the joining of the molecules occurs *via* a new chemical bond C19-O3-C23. One can suggest that formation of this bond is accompanied by detachment of the H-atom from H23-O1-C19 fragment of the crocetin (Figure 1) and hydroxyl O2-H3 from the carboxylic group of the indoline (Figure 2) to release water molecule. The bond C19-O3-C23 in the complex is specified with parameters $R(\text{C19-O3}) = 1.461 \text{ \AA}$, $R(\text{O3-C23}) = 1.385 \text{ \AA}$, $\angle \text{C19-O3-C23} = 119.2^\circ$; which are comparable with those of the ether C-O-C linkage, 1.40 \AA and 110° . In the vicinity of the new chemical bond, a slight elongation of the internuclear distances C-O and C=C, by $0.003\text{--}0.069 \text{ \AA}$, is observed while the bond lengths C=O and C-C are slightly decreased. Generally, from individual dyes to the complex, the difference in the respective parameters is in the range from -0.02 \AA to $+0.07 \text{ \AA}$ for bond lengths and $\pm 0.05^\circ$ for bond angles; bigger change is seen for crocetin moiety. The parameters of the remote parts of the complex remain practically the same as within the individual dyes.

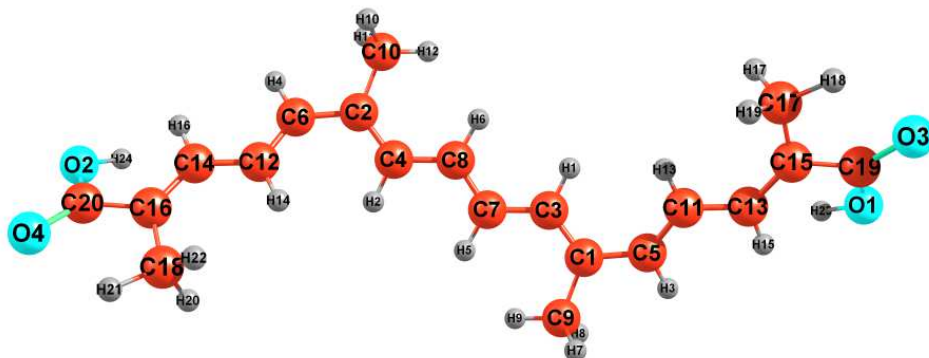


Figure 1. Optimized geometrical structure of the crocetin molecule.

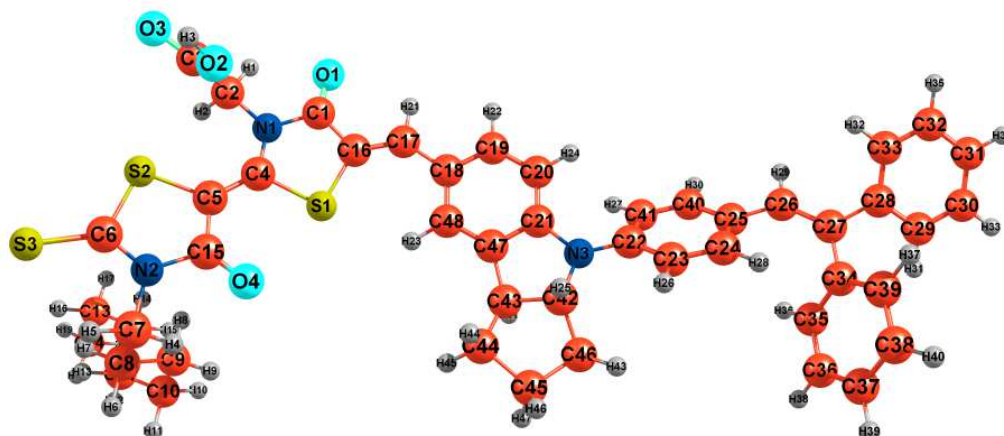


Figure 2. Optimized geometrical structure of the indoline dye D205 molecule.

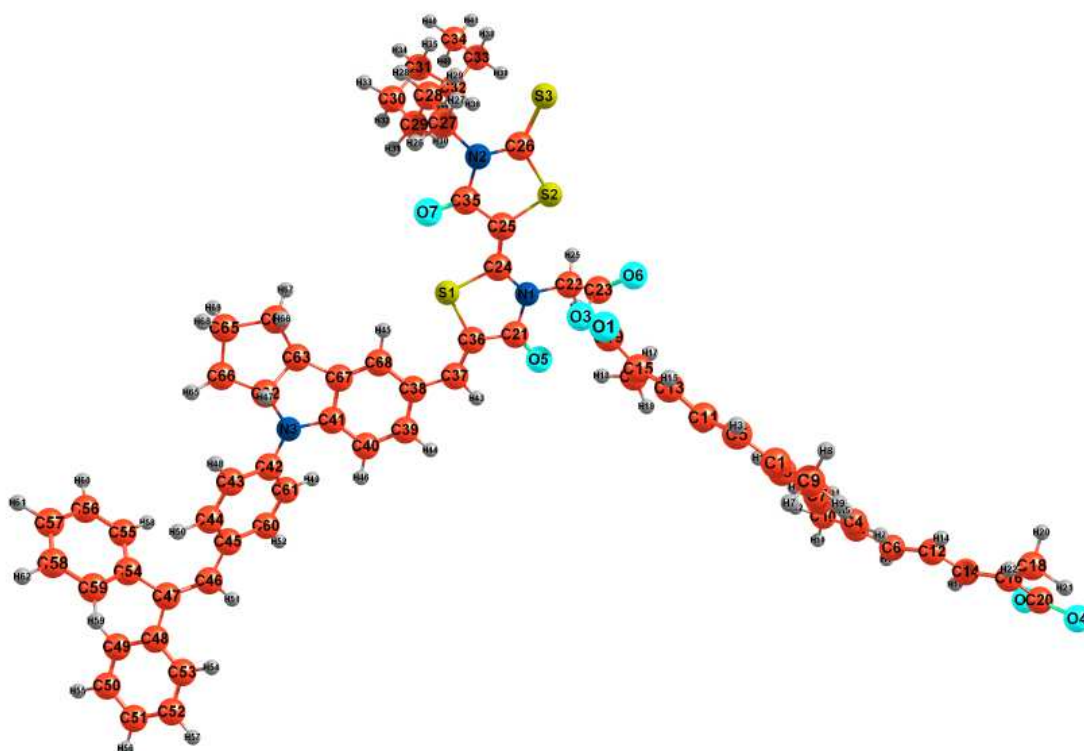


Figure 3. Optimized geometrical structure of the complex molecule.

Table 1. Comparison of selected geometrical parameters in crocetin and complex molecules.

Crocetin		Complex		Difference
Bond lengths, Å				
O3=C19	1.226	O1=C19	1.217	-0.009
O1-C19	1.392	O3-C19	1.461	+0.069
		O3-C23	1.385	
C15-C19	1.493	C15-C19	1.470	-0.023
C13=C15	1.356	C13=C15	1.361	+0.005
C11-C13	1.441	C11-C13	1.434	-0.007
C1-C5	1.458	C1-C5	1.455	-0.003
C16-C20	1.493	C16-C20	1.493	0.000
O4=C20	1.226	O4=C20	1.226	0.000
Bond angles, deg				
O1-C19=O3	119.5	O3-C19=O1	118.8	-0.7
C17-C15-C19	114.5	C17-C15-C19	119.9	+5.4
C13=C15-C19	120.3	C13=C15-C19	114.9	-5.4
C1-C5=C11	127.0	C1-C5=C11	128.3	+1.3
C18-C16-C20	114.5	C18-C16-C20	114.3	-0.2
O2-C20=O4	119.5	O2-C20=O4	119.5	0.0

Table 2. Comparison of selected geometrical parameters in indoline D205 and complex molecules.

Indoline D205		Complex		Difference
Bond lengths, Å				
C2-C3	1.523	C22-C23	1.525	+0.002
N1-C2	1.465	N1-C22	1.463	-0.002
C4=C5	1.355	C24=C25	1.358	+0.003
C1-C16	1.459	C21-C36	1.458	-0.001
C3-O2	1.372	C23-O3	1.385	+0.013
C3=O3	1.222	C23=O6	1.219	-0.003
C1=O1	1.238	C21=O5	1.241	+0.003
C17-C18	1.444	C37-C38	1.444	0.000
C16=C17	1.351	C36=C37	1.352	+0.001
S1-C4	1.848	S1-C24	1.846	-0.002
C19=C20	1.392	C39=C40	1.393	+0.001
C21-N3	1.409	C41-N3	1.407	-0.002
C35=C36	1.398	C55=C56	1.396	-0.002
Bond angles, deg				
C3-C2-N1	114.4	C23-C22-N1	113.9	-0.5
S2-C6=S3	122.0	S2-C26=S3	121.9	-0.1
C4=C5-S2	127.7	C24=C25-S2	128.1	+0.4
C4-S1-C16	89.7	C24-S1-C36	89.7	0.0
C16=C17-C18	131.5	C36=C37-C38	131.2	-0.3
Dihedral angles, deg				
C15-N2-C6-S3	178.9	C35-N2-C26-S3	179.4	+0.5
S1-C4-C5-S2	178.6	S1-C24-C25-S2	177.2	-1.4

The thermodynamic characteristics of the complex formation reaction (1) are given in Table 3. The thermodynamic functions, entropies $S^\circ(T)$ and enthalpy increments $H^\circ(T)-H^\circ(0)$, of the crocetin, indoline, complex and water molecules have been computed with OpenThermo software [30]; in calculations, the geometrical parameters and vibrational frequencies of the molecules were used as computed with the 3-21G basis set. The Gibbs free energies $\Delta_r G^\circ(T)$ of the reaction were calculated as follows:

$$\Delta_r G^\circ(T) = \Delta_r H^\circ(T) - T\Delta_r S^\circ(T) \quad (5)$$

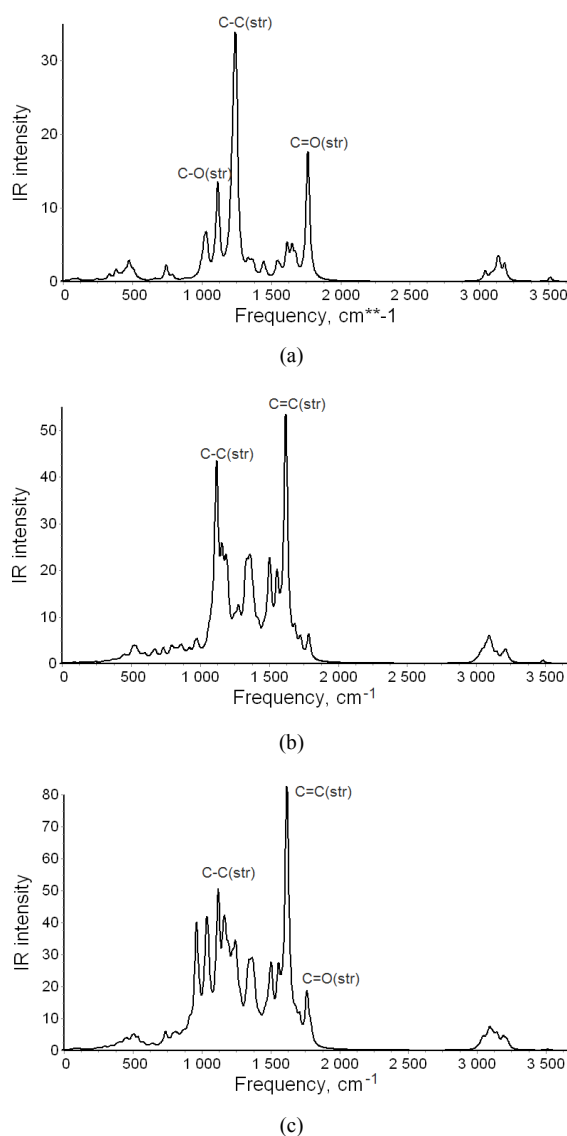
where $\Delta_r H^\circ(T)$ and $\Delta_r S^\circ(T)$ are the enthalpy and entropy of the reaction at temperature T ; $\Delta_r H^\circ(T) = \Delta_r H^\circ(0) + \Delta_r [H^\circ(T)-H^\circ(0)]$.

Table 3. The thermodynamic characteristics of reaction (1): energy $\Delta_r E$, zero point vibration energy $\Delta_r \epsilon$, enthalpies $\Delta_r H^\circ(0)$ and $\Delta_r H^\circ(298)$, Gibbs free energy $\Delta_r G^\circ(298)$.

Quantity, kJ mol ⁻¹	3-21G	6-31G	6-31G (d, p)
$\Delta_r E$	42.2	41.5	41.9
$\Delta_r \epsilon$	-8.83	(-8.83)	(-8.83)
$\Delta_r H^\circ(0)$	33.4	32.7	33.1
$\Delta_r H^\circ(298)$	38.1	36.4	36.8
$\Delta_r G^\circ(298)$	48.2	46.5	46.9

The values of $\Delta_r E$ computed with different basis sets do not change noticeably with the basis set extension. Positive values of enthalpies $\Delta_r H^\circ$ show endothermicity of the reaction. The entropy of the reaction is negative, $\Delta_r S^\circ(298) = -33.9 \text{ J mol}^{-1} \text{ K}^{-1}$, that points out a rising of the system's order. The Gibbs energy being positive at 298 K shows non-spontaneity of the complex formation through direct combination of the dyes' molecules.

3.2. Vibrational Spectra of the Species

**Figure 4.** IR spectra: (a) crocetin; (b) indoline D205; (c) complex.

Vibrational spectra of the species were calculated by DFT B3LYP5 method with 3-21G basis set. An absence of imaginary frequencies confirmed that the geometrical structures of the species corresponded to minima on the potential energy surfaces. The computed IR spectra are shown in Figure 4. The most intensive modes in the spectra are assigned to the vibrations 1220-1247 cm^{-1} (C-C stretching), 1615-1676 cm^{-1} (C=C stretching), 1115 cm^{-1} (C-O stretching and CH_3 bending), 1764 cm^{-1} (C=O stretching) of the crocetin molecule, and 1120 cm^{-1} (C-C stretching), 1618-1621 cm^{-1} (C=C stretching), 1156-1188 cm^{-1} (mostly C-N and C-C stretching), 1504 cm^{-1} and 1556 cm^{-1} (H-C-H bend in the six-member ring), 1786 cm^{-1} (C=O stretching) of the indoline molecule. Comparison of our results to experimental frequencies of crocetin [31], 1536 cm^{-1} (C=C stretching), 1165 cm^{-1} (C-C stretching) and 1020 cm^{-1} (C-C in-plane rocking), shows that our calculated frequencies are overrated by 7-8% which is typical for theoretical results of similar computational level.

IR spectrum of the complex (Figure 4c) apparently comprises the intensive modes which correspond to the crocetin moiety (1115 cm^{-1} C-O stretching and CH_3 bending, 1251 cm^{-1} C-C stretching), and indoline moiety (1121 cm^{-1} C-C stretching, 1154 cm^{-1} C-N and C-C stretching, 1616-

1619 cm^{-1} C=C stretching) being shifted slightly from the position in spectra of individual dyes. The frequencies in the range 1760-1790 cm^{-1} relate to stretching vibrations of two C=O groups, one from crocetin and another from indoline part. Also one can see the additional picks at 960 and 1167 cm^{-1} which are assigned to the C-O stretching motion of atoms in the new bond C19-O3-C23 between the moieties.

3.3. Electronic Spectra of the Species

For the three molecules under study, the electronic spectra were computed for vacuum and for chloroform solution using polarized continuum model. The vertical excitation energies (E_{ex}), wavelengths (λ), oscillator strengths (f) and electronic configurations of the transitions are listed in Table 4. The singlet-singlet ($S_0 \rightarrow S_{\text{ex}}$) excitations with nonzero oscillator strengths ($f > 0.001$) were taken into account.

In spectra of all species the bands of maximum wavelengths are seen in visible region. For the crocetin and indoline molecules, the excitations from the ground to first excited state are of the highest oscillator strength and attributed to the HOMO-LUMO (H \rightarrow L) transitions while for the complex the more probable transitions are to the second and third excited states and assigned mostly to H \rightarrow L+1 and H-1 \rightarrow L.

Table 4. Electronic spectra of crocetin, indoline D205 and complex molecules (TD-DFT B3LYP5/6-31G).

No of excited state	E_{ex} , eV	λ , nm	f	Electronic transition configuration
Crocetin, vacuum				
1	2.53	490	1.882	H \rightarrow L, 88 \rightarrow 89
3	3.82	325	0.050	H-1 \rightarrow L, 87 \rightarrow 89
5	3.87	321	0.021	H-3 \rightarrow L, 85 \rightarrow 89
6	3.93	316	0.053	H \rightarrow L+2, 88 \rightarrow 91
7	4.19	296	0.078	H-1 \rightarrow L+1, 87 \rightarrow 90
9	4.80	258	0.040	H-3 \rightarrow L+1, 85 \rightarrow 90
Crocetin, chloroform				
1	2.46	504	1.871	H \rightarrow L, 88 \rightarrow 89
3	3.77	329	0.066	H-1 \rightarrow L, 87 \rightarrow 89
4	3.88	320	0.100	H \rightarrow L+2, 88 \rightarrow 91
5	4.10	302	0.064	H-1 \rightarrow L+1, 87 \rightarrow 90
9	4.80	259	0.491	H-2 \rightarrow L, 86 \rightarrow 89
Indoline D205, vacuum				
1	2.37	520	1.042	H \rightarrow L, 218 \rightarrow 219
3	2.99	414	0.567	H-1 \rightarrow L, 217 \rightarrow 219
4	3.16	392	0.212	H \rightarrow L+1, 218 \rightarrow 220
5	3.39	366	0.227	H-3 \rightarrow L, 215 \rightarrow 219
6	3.58	347	0.092	H \rightarrow L+2, 218 \rightarrow 221
8	3.82	325	0.068	H-1 \rightarrow L+1, 217 \rightarrow 220
9	3.95	314	0.021	H-7 \rightarrow L, 211 \rightarrow 219
10	3.98	311	0.023	H-4 \rightarrow L, 214 \rightarrow 219
Indoline D205, chloroform				
1	2.16	574	0.807	H \rightarrow L, 218 \rightarrow 219
2	2.84	436	0.582	H-1 \rightarrow L, 217 \rightarrow 219
3	2.95	421	0.355	H \rightarrow L+1, 218 \rightarrow 220
5	3.34	371	0.126	H-2 \rightarrow L, 216 \rightarrow 219
6	3.53	351	0.343	H \rightarrow L+2, 218 \rightarrow 221
7	3.69	336	0.030	H-1 \rightarrow L+1, 217 \rightarrow 220
10	3.83	324	0.017	H-5 \rightarrow L, 213 \rightarrow 219
Complex, vacuum				
1	1.99	624	0.002	H \rightarrow L, 301 \rightarrow 302
2	2.33	531	1.666	H \rightarrow L+1, 301 \rightarrow 303
3	2.44	509	1.741	H-1 \rightarrow L, 300 \rightarrow 302
5	2.59	479	0.001	H-2 \rightarrow L, 299 \rightarrow 302
6	2.85	435	0.003	H-3 \rightarrow L+1, 298 \rightarrow 303

No of excited state	E_{ex} , eV	λ , nm	f	Electronic transition configuration
Complex, chloroform				
1	2.04	606	0.002	H→L, 301 →302
2	2.13	583	1.051	H→L+1, 301 →303
3	2.16	574	0.013	H-1→L+1, 300→303
4	2.32	533	2.017	H-1→L, 300 →302

The theoretical electronic spectra of the molecules are compared to our experimental UV-vis spectra of the dyes in chloroform solutions (Figures 5-7). The theoretical results for UV-vis spectra of crocetin indicate a slight red shift of the maximum wavelength from vacuum ($\lambda = 490$ nm) to chloroform solution ($\lambda = 504$ nm). In experimental UV-vis spectrum of crocetin (Figure 5c), the broad bands are observed with maxima at 286, 412, 436, and 462 nm, the latter two are overlapping resulting in highest intensity bands. This experimental spectrum does not contradict much to the theoretical results (Figures 5 a, b) and in a good agreement with data obtained in [32] where the peaks at 415, 433 and 462 nm were observed in the visible range of the spectrum for crocetin in chloroform.

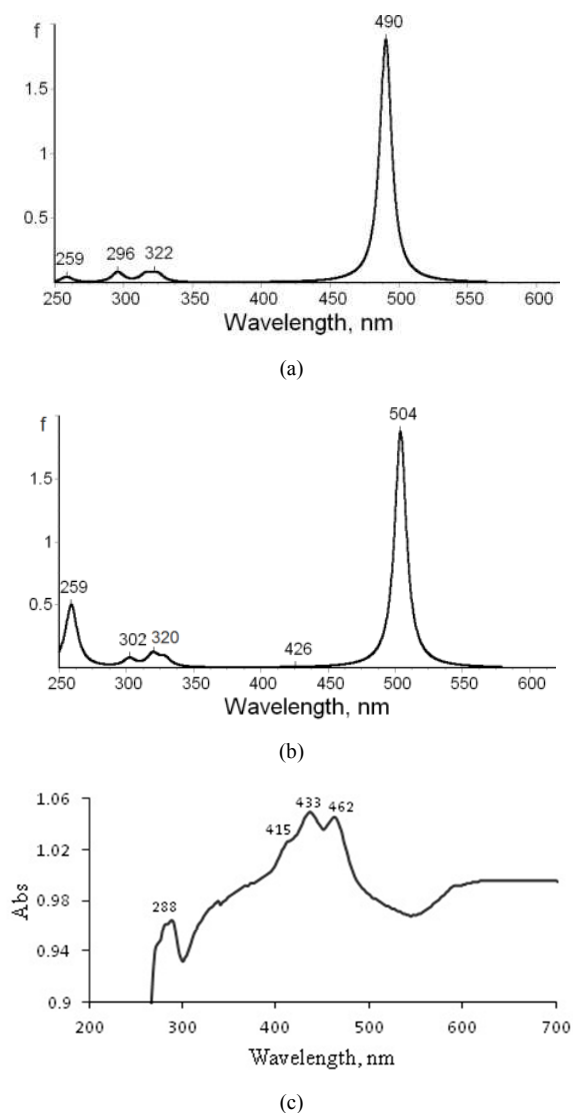


Figure 5. UV-vis spectrum of crocetin: (a) computed for vacuum; (b) computed for chloroform solution; (c) experimental for chloroform solution.

In the theoretical UV-vis spectra of indoline (Figures 6a, b), the peaks of high intensity are at 415 and 523 nm (vacuum) and at 435 and 577 nm (chloroform), thus the red shift is seen from vacuum to solution. In the experimental spectrum in chloroform (Figure 6c), the most intensive band lies in the UV region with three maxima at 288, 338, 370 nm and broad band of low intensity is observed in the range 500-600 nm. The appearance of the theoretical and experimental spectra looks different regarding intensities of the peaks, still accordance may be noted between wavelengths in spectra computed for indoline dye (523, 577 nm) and measured experimentally (~550-560 nm). Our experimental result agrees well with the value $\lambda = 554$ nm observed earlier in spectrum of indoline dye D205 in chloroform solution [33].

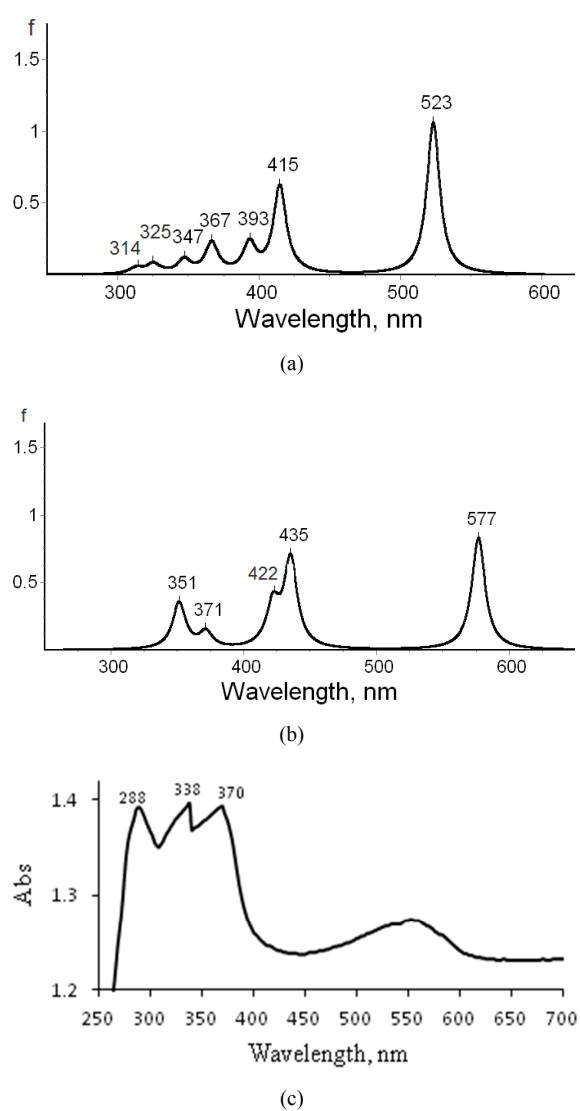


Figure 6. UV-vis spectrum of indoline: (a) computed for vacuum; (b) computed for chloroform solution; (c) experimental for chloroform solution.

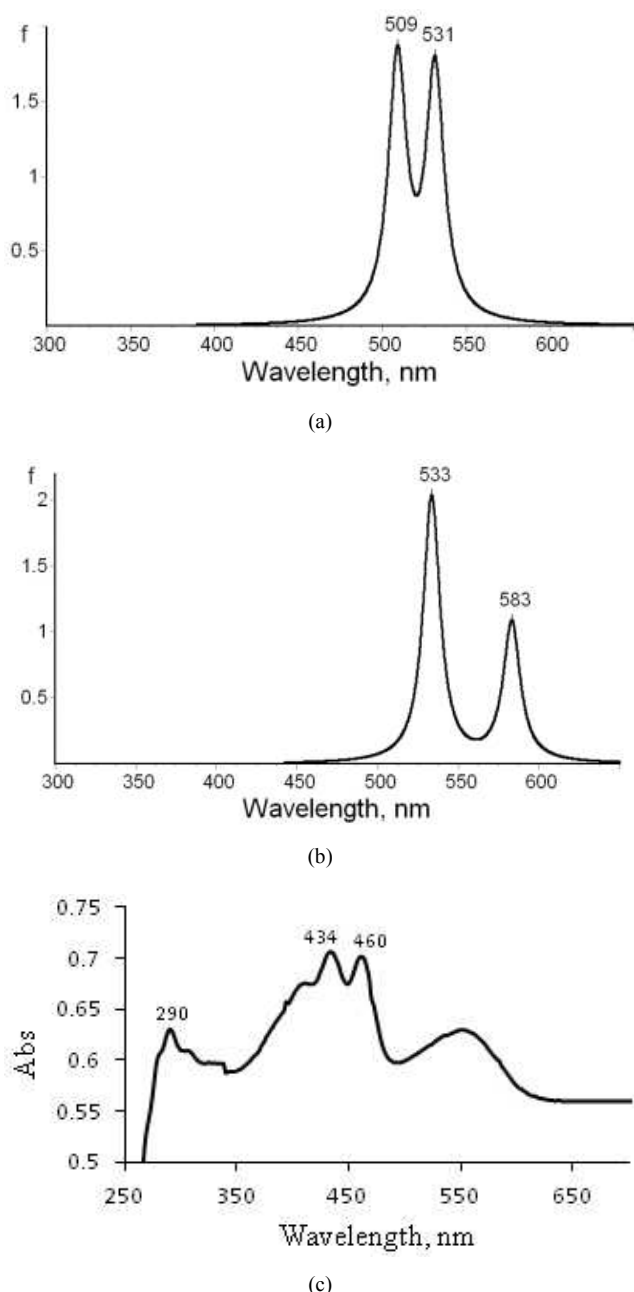


Figure 7. UV-vis spectra of the combination of two dyes, crocetin and indoline D205: (a) computed for the complex molecule in vacuum; (b) computed for the complex molecule in chloroform solution; (c) measured experimentally for the mixture of two dyes in chloroform solution.

The computed UV-vis spectrum of the complex contains two intensive peaks (Figures 7 a, b). Peaks at 531 nm (vacuum) and 583 nm (chloroform) correspond to those in spectra of the indoline D205 molecule: 523 and 577 nm for vacuum and chloroform, respectively. For the complex molecule, the peak at 509 nm (vacuum) or 533 nm (chloroform) does not correspond to any transition neither for crocetin nor indoline. One can suggest that this peak may relate to the new formed bond C19-O3-C23 in the complex molecule. That means that the combination of two dyes allows widening of the light adsorption in visible range and

thus improving the sensitizing ability of the dye.

In the experimental measurements of UV-vis spectrum of the mixture (Figure 7c), four maxima were identified, three in visible region (434, 460 and ~550 nm) and one in ultraviolet (290 nm). Two peaks among them resemble those in spectrum of individual crocetin, 436 and 462 nm (Figure 5c) while the other two peaks correspond to those in spectrum of individual indoline dye D205, 288 and ~554 nm (Figure 6c). If compare the theoretical spectrum of the complex molecule and experimental for the mixture, one can see that two sharp peaks in the former look like merged into one broaden band in the latter. However no strong evidence of chemical interaction between individual dyes in solution is noticed. This observation is in accordance with the conclusion based on thermodynamic approach (Table 3) that the reaction (1) of complex formation is not thermodynamically favorable being endothermic and non-spontaneous.

3.4. Analysis of Frontier Molecular Orbitals and Energy Levels Alignment

Useful information about electronic structure of molecules and mechanisms of chemical reactions can be revealed from analysis of molecular orbitals [34, 35]. For the crocetin and indoline D205 molecules in vacuum, the frontier orbitals isosurfaces and energies are shown in Figures 8, 9. The number of occupied orbitals is 88 for crocetin and 218 for indoline molecules. From the shape of the orbitals, it is seen that in crocetin, both HOMO and LUMO are delocalized and electron density is distributed along the carbon chain. In indoline, the frontier orbitals are more localized; HOMO is located mostly on the diphenylethenyl part and on the indoline ring and LUMO on the rhodanine rings. In the electronic spectra of both molecules, the excitation $S_0 \rightarrow S_1$ is specified with high oscillator strengths (Table 4), and HOMO \rightarrow LUMO transition contributes mostly to this first excited state transition.

The frontier and adjacent orbitals (HOMO, LUMO, H-1, and L+1) of the complex molecule in vacuum are displayed in Figure 10. The number of occupied orbitals is 301. The HOMO is located on the indoline part while LUMO is at the crocetin site (Figure 10a). This implies that when an electron transfers from the HOMO to LUMO, the electron density significantly decreases in the electron-donating indoline moiety, accompanied by increase in that of the electron-accepting crocetin site. Nevertheless, according to the results on oscillator strengths (Table 4), the most probable transitions are not HOMO \rightarrow LUMO, but H \rightarrow L+1 and H-1 \rightarrow L. As is observed in Figure 10b, the H-1 MO is located on the crocetin part of the complex, and L+1 MO on the indoline part. It means that the protruded picks of the electronic spectrum (Figure 7a) is attributed to the transitions within either crocetin or indoline sites in the complex molecule.

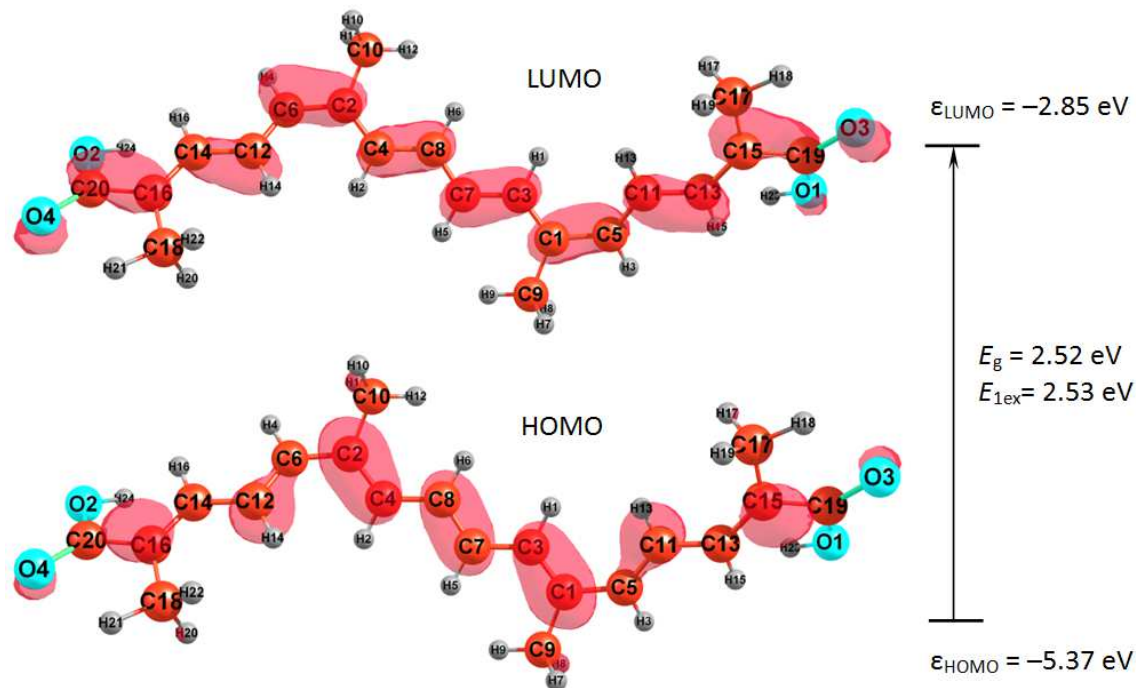


Figure 8. Frontier orbitals HOMO and LUMO in the crocein molecule.

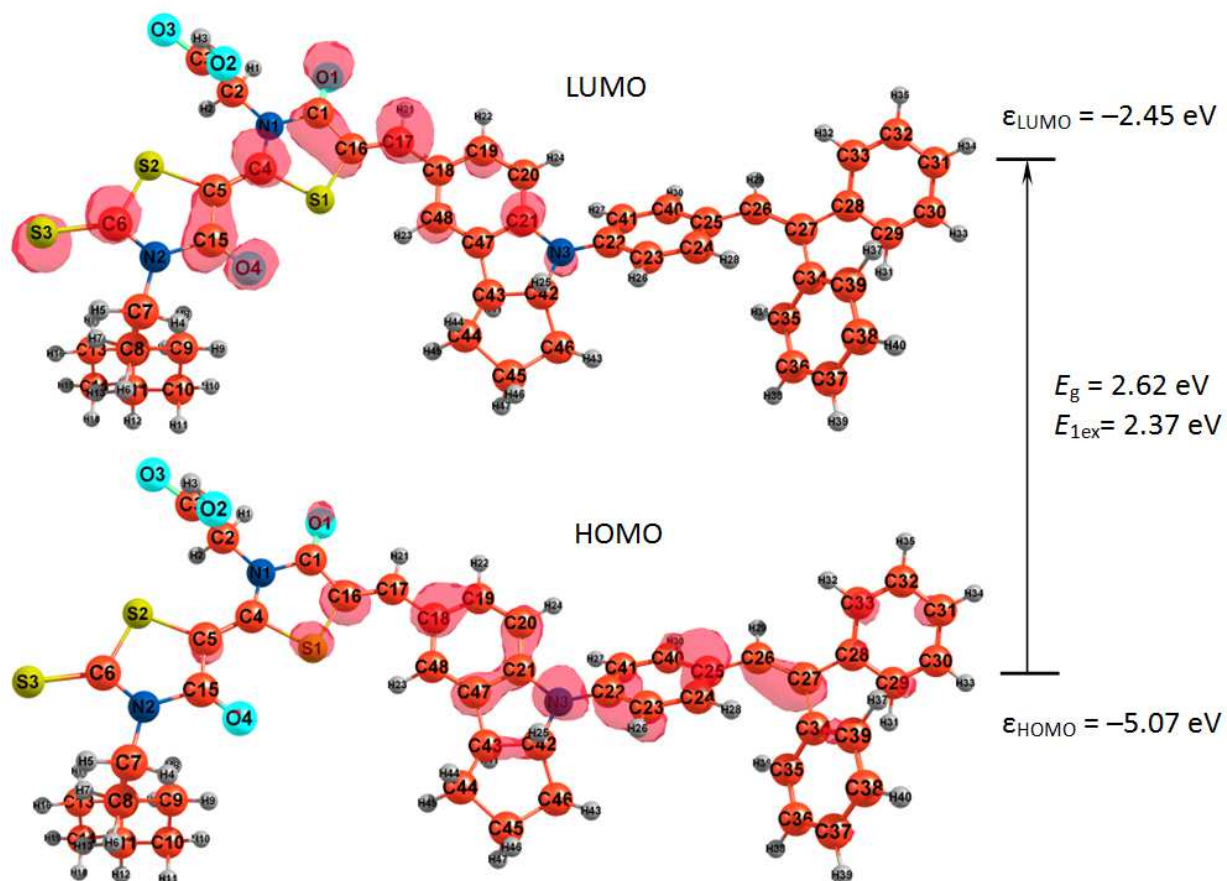
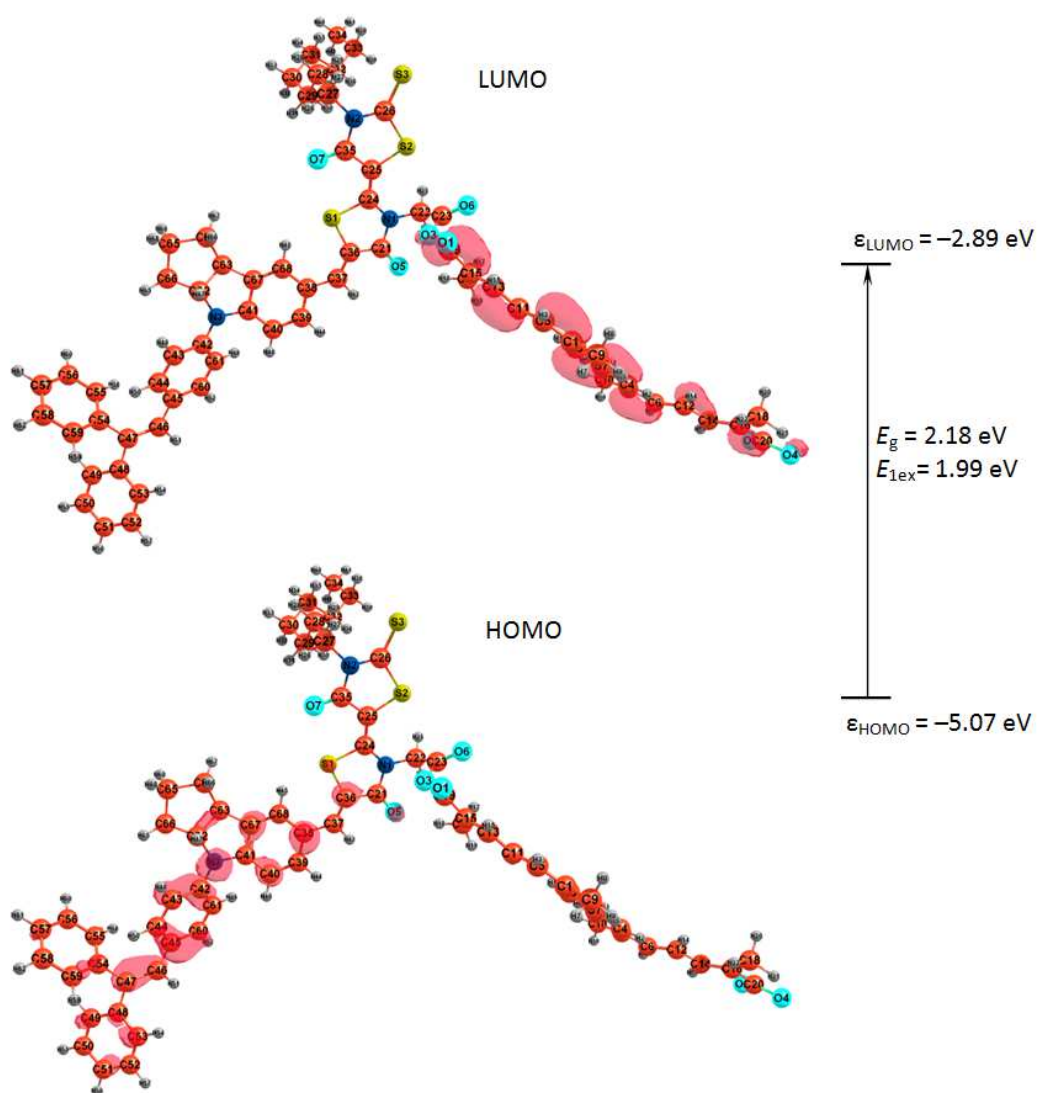
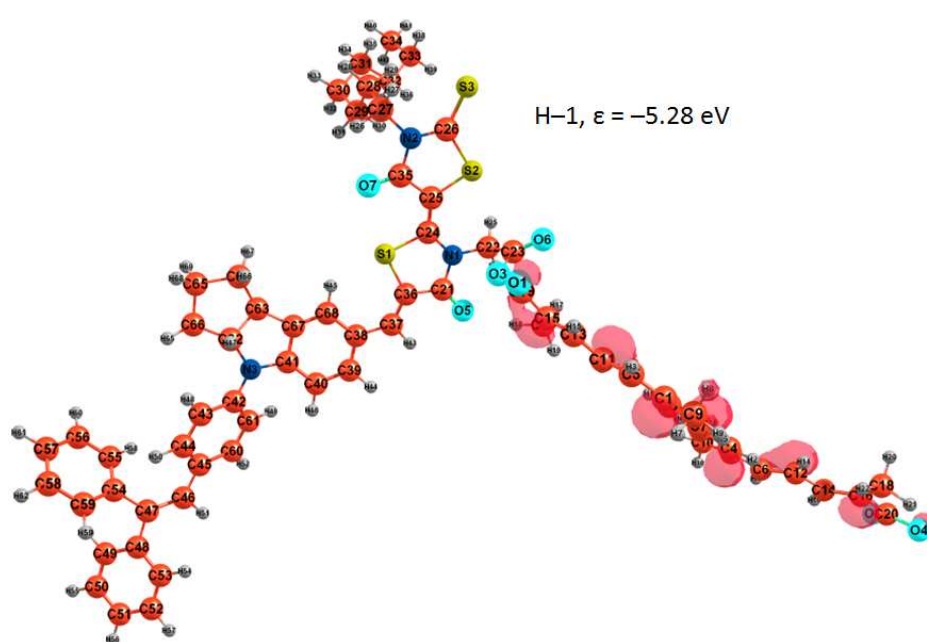


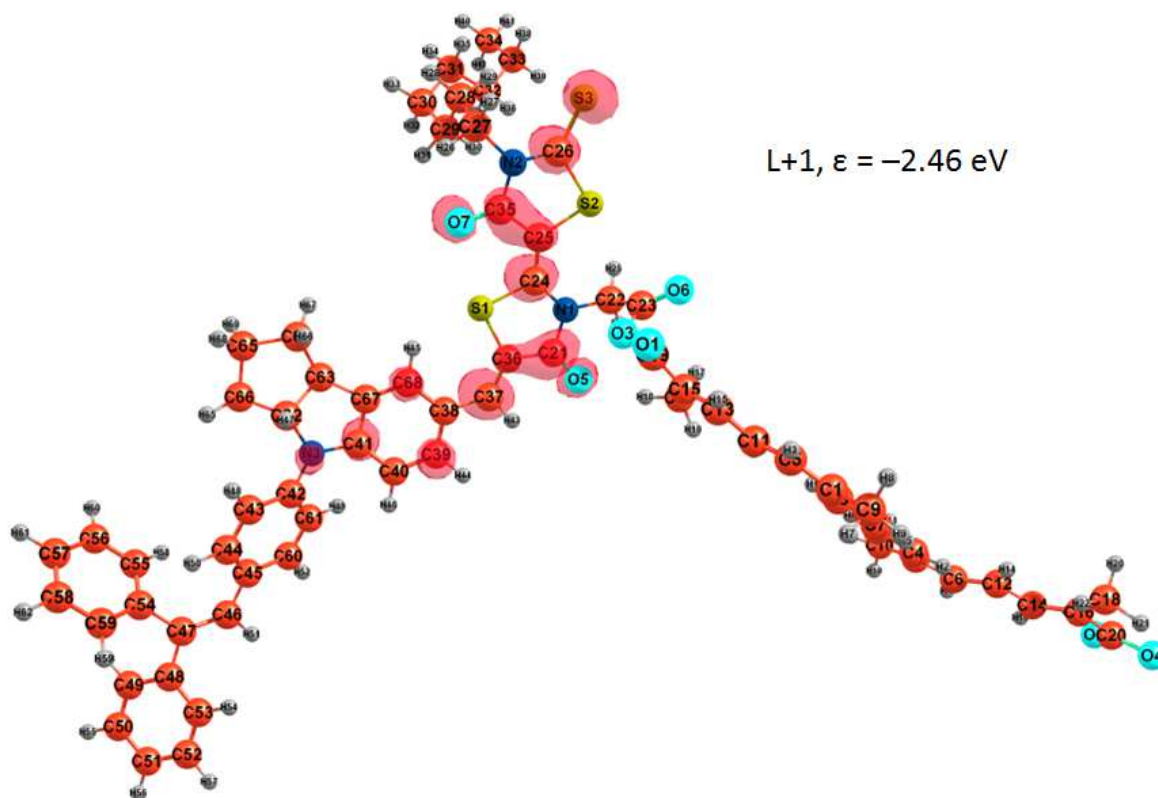
Figure 9. Frontier orbitals HOMO and LUMO in the indoline D205 molecule.



(a)



(b)



(c)

Figure 10. Frontier and adjacent MOs in the complex molecule: (a) HOMO and LUMO; (b) H-1; (c) L+1.

A proper energy level alignment between a dye, semiconductor and electrolyte is a fundamental requirement for a DSSC. The simplest way to consider this alignment is drawing the frontier MOs energy levels together with valence and conduction bands of a semiconductor. However more strict approach is to implement the excitation energies E_{ex} obtained by TD-DFT and calculate the excited state potentials ESP [36]. In our work, the values of ESP were found as sums of the ground state occupied MOs energies and respective excitation energies E_{ex} , $ESP = \epsilon(\text{HOMO}) + E_{\text{ex}}$. The calculated energies of frontier and adjacent molecular orbitals $\epsilon(\text{MO})$, excitation energies E_{ex} , energy differences between MOs E_{g} , and excited state potentials ESP are presented in Table 5. The values of E_{ex} and E_{g} correspond to transitions between the orbitals shown in respective column.

Although an analysis of the frontier orbitals is illustrative and useful for understanding of electron transfer mechanism, the values of excitation energies allow entire electronic spectra modeling and correct representation of electron transitions. As is seen, the values of energy gap between HOMO and LUMO (E_{g}) coincide with the first excitation energy (E_{ex}) for crocein molecule; this is valid for vacuum and chloroform solution. For indoline and complex molecules, these quantities differ, the values of E_{g} is bigger, as a rule, the difference approaches 0.5 eV. These differences result in lowering the ESP s compared to respective unoccupied orbitals.

Table 5. The energies of molecular orbitals $\epsilon(\text{MO})$, excitation energies E_{ex} , energy differences between MOs E_{g} , and excited state potentials ESP ; all values in eV.

MO	$-\epsilon(\text{MO})$	Transition	E_{ex}	E_{g}	$-ESP$
Crocein, vacuum					
88, H	5.37	H→L	2.53	2.52	2.84
89, L	2.85				
Crocein, chloroform					
88, H	5.12	H→L	2.46	2.46	2.66
89, L	2.66				
Indoline D205, vacuum					
218, H	5.07	H→L	2.37	2.62	2.70
219, L	2.45				
Indoline D205, chloroform					
218, H	5.11	H→L	2.15	2.37	2.96
219, L	2.74				
Complex, vacuum					
300, H-1	5.28	H→L	1.99	2.18	3.08
301, H	5.07	H→L+1	2.33	2.39	2.95
302, L	2.89	H-1→L	2.44	2.91	2.63
303, L+1	2.46				
Complex, chloroform					
300, H-1	5.18	H→L	2.04	2.24	3.09
301, H	5.13	H→L+1	2.13	2.36	3.00
302, L	2.89	H-1→L	2.32	2.29	2.86
303, L+1	2.77				

The diagram in Figure 11 shows the energy levels of HOMOs and ESP s of the molecules under study for chloroform solutions; the valence and conduction bands of the semiconductors TiO_2 [36, 37] and ZnO [38], redox level of the I^-/I_3^- electrolyte [37, 39, 40] are given for

comparison. According to requirements, the HOMO and LUMO levels of a dye must match with the conduction-band-edge energy level of the semiconductor and the redox potential of electrolyte for an efficient charge separation and dye regeneration [41]; the HOMO level of the sensitizer has to be lower than the redox potential and the first excited state of the dye has to be slightly higher than the conduction band of the semiconductor [42, 43]. As is observed on the diagram, all three molecules meet the criteria for sensitizers: HOMO levels lie below the redox level of the electrolyte, and the excited state potentials lie above or coincide with conduction bands of semiconductors. That is the injection of

electrons from the dyes to the conduction bands of TiO_2 or ZnO can occur. For the complex it is expected even higher performance due to the energy levels better meet requirements for sensitizer as the complex possesses smaller excitation energies (2.04, 2.13 and 2.32 eV for the complex compared to 2.46 eV for crocetin and 2.15 eV for indoline). Moreover, the transitions from H-1 to the first excited state and from HOMO to second excited state are of high probability to be involved in sensitizing semiconductor, and the two corresponding ESP levels (-2.86 and -3.00 eV) match well with the conduction band of ZnO (-2.96 eV).

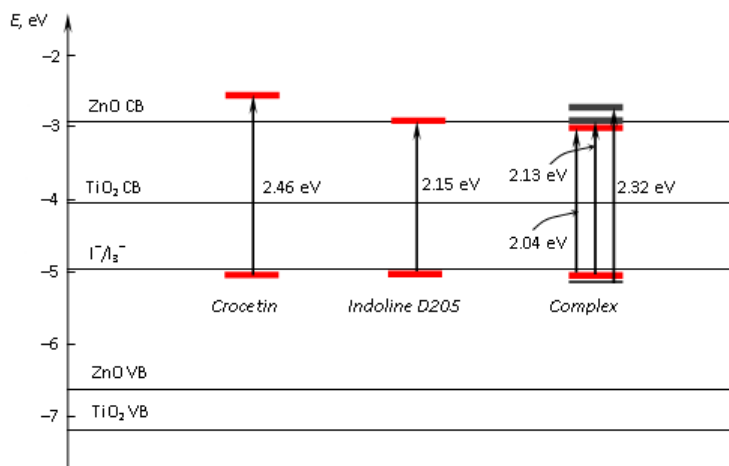


Figure 11. Energy level diagram of HOMOs and excited state potentials of crocetin, indoline D205 and complex molecules in chloroform.

4. Conclusion

Molecular design of solar cell sensitizer was done through the combination of two individual dyes, natural crocetin and synthetic indoline D205, aimed to improve optical properties of the materials. The properties of the complex molecule as well as individual dyes have been studied by DFT and TD-DFT methods. The equilibrium structures of the molecules, IR and electronic spectra were computed and analyzed. The thermodynamic approach indicated endothermicity and non-spontaneity of the direct joining of the components *via* C-O-C linkage. The absorption bands in experimental UV-vis spectra of the individual dyes are reproduced adequately by theoretical TD-DFT computations. The combination of two dyes results in widening of light absorption visible range and better energy level alignment with the conduction band of semiconductor ZnO and redox level of the I^-/I_3^- electrolyte. Thus the complex molecule designed might possess enhanced power conversion efficiency compared to that of individual dyes.

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