A DFT and TD-DFT Study on Emodin and Purpurin and their Functionalized Molecules to Produce Promising Organic Semiconductor Materials

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Abstract

Density functional theory (DFT) computations were done to explore the optical and electronic properties of two conjugated molecules, emodin and purpurin, as potential organic semi-conductors. The molecules were functionalized to explore the impact of functionalization on the electronic and optical properties. The properties calculated include reorganization energy (λ_h and λ_e), adiabatic ionization potential (IP), adiabatic electron affinity (EA), chemical hardness (n), HOMO and LUMO energies, and HOMO-LUMO energy gap (E_g) via B3LYP/6-3++G (d, p) method. In addition, the maximum absorption (λ_{max}) and oscillator strength (f) at the excited states in vacuum and solvent (Ethanol) were investigated using time-dependent density functional theory (TD-DFT). The introduction of functional groups to emodin was considered to convert the molecule from a p-type into an n-type material, while purpurin is considered as an n-type material, its functionalization with NO_2 and 2F resulted in a slight increase in λ_e values, which is considered detrimental for the process of charge-transport. However, the functionalized molecules have shown an increase in EA and a decrease in LUMO energy level, indicating their potential use as n-type materials. Furthermore, to have an understanding of the intermolecular interactions in emodin and purpurin molecules, Hirshfeld surface analysis and energy framework were studied.

Keywords: Organic semiconductors; Optical properties; Electronic properties; DFT; TD-DFT

Abbreviation

HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Occupied Molecular Orbital
λ	Reorganization energy
λ_{int}	Internal reorganization energy
λ_{ext}	External reorganization energy
IE	Adiabatic Ionization energy
EA	Adiabatic Electron affinity
Eg	Energy gap
DFT	Density functional theory
TD-DFT	Time Dependent - Density functional theory
η	Chemical Hardness
λ_{max}	Maximum Absorption
f	Oscillator Strength
Å	Bond lengths
°	Bond angles
B3LYP	Becke, 3-parameter, Lee-Yang-Parr

1 Introduction

The Earth receives a total quantity of radiant energy from the sun of 1370 W/m^2/s, with 343 W/m^2/s received per unit area of the Earth's surface [1]. The abundance and non-polluting characteristics of solar energy have made it a widely recognized renewable source of energy. The photovoltaic effect of solar cells can covert this solar energy into electrical energy. Organic solar cells are being increasingly attractive due to their low production cost [2–4], electronic features such as light absorption and emission, charge generation and transportation [5], tuning of molecular properties by modifying the length and type of functional groups [5–8].

The basic operating principle of organic solar cells is the initial absorption of incident photons that leads to the generation of free electrons and holes (excitons) [4, 9]. The Coulomb forces of attraction between the generated excitons are high owing to the low dielectric constant of organic semi-conductors. Therefore, the excitons dissociation requires a heterojunction that is created by two dissimilar organic semi-conductor materials; donor (n-type) and acceptor (p-type). A donor is defined as a material that has a high ionization energy (IP) and an acceptor is a material that has a high electron affinity (EA). Finally, upon the dissociation of excitons, the electron created is transferred to the cathode, and the hole is transferred to the anode to initiate current [9–11].

The most essential features of organic semiconductors are inclusive of abundance and low production cost, optimum energy gap (E_g) between HOMO and LUMO, strong light absorption, thermal and photo stability [12–14]. However, there remains the challenge of enhancing the proficiency of solar organic cells in comparison to inorganic solar cells. Several research efforts are being carried out on organic solar cell systems to improve their efficacy, processing and stability [9, 15, 16]. One of the approaches used is to enhance the optical and electronic properties of organic semi-conductor molecules by using functional groups to tune their properties [6]. For instance, it was stated that the introduction of electron-deficient atoms or groups increases the molecule electron affinity by reducing the molecular LUMO and thus resulting in better n-type organic semi-conductors. These functional groups include imides, amides, carbonyls, quinones and halogen atoms [9]. To increase the environmental stability and electron affinity of conjugated systems, imides and amides are introduced into the backbone of the molecule as strong electron-withdrawing groups [17]. In a study conducted by Zhenan *et al.*, a p-type material, metallopthalocyanine, was converted into an n-type air-stable material by functionalization with fluorine [18]. Other research showed the pentacene perfluorination converted it into an n-type material [19], while the chloro (Cl) and Nitro (N) functionalization of naphthalene and pentacene molecules provided a better material than perfluoropentacene and octafluoronaphthalene [6, 20]. The addition of the F and CN groups to 1,3,5-tripyrrolebenzene (TPB) have stabilized frontier molecular orbital and improved air stability [21]. In addition, the influence of functionalization on absorption was reported by R. Cardia *et al.* [5] in functionalized triisopropylsilylethynyl (TIPS), resulting in better visible region absorption. This improvement of absorption in the visible region was also shown by different sensitizers functionalized by OH, NH_2, OCH_3, CF_3, F, and CN [22].

Reorganization energy, which is known to influence the rate of charge transfer [23], is a critical element that dictates the efficiency of organic solar cells. The reorganization energy is often considered as the summation of internal and external influences. The internal reorganization energy (λ_{int}) is attributed to the change in equilibrium geometry of the donor and acceptor sites due to electron transfer, while the external reorganization energy (λ_{ext}) is attributed to the polarization effects that lead to the change in the surrounding media [8, 23, 24]. The external reorganization energies values are considered to be much smaller than the inner reorganization energies, and thus negligible [21,25,26].

The effect of functionalization on the reorganization energy has been reported by many studies. For example, Hutchison *et al*. [27] investigated the functionalization impact of oligomers of thiophene and furan in terms of reorganization energy. Others have revealed that the cyanation of pentacene gives smaller values of hole (75 meV) and electron reorganization energy (87 meV) than pentacene (94 and 133 meV,respectively) [28]. Oshi and co-workers discussed the increase of hole and electron reorganization energy in 7,7,8,8-Tetracyanoquinodimethane by electron-donating groups CH_3, OCH_3, and OH [8]. Thus, it is valuable to recognize the effect of functionalization on molecule's reorganization energy as it provides perception into charge transfer rate in organic semiconductor materials. Charge transport (at low temperatures) in organic semiconductors is described as band-like motion in which the charge is delocalized across the system. The charge transport technique at high temperatures is represented by a hopping mechanism where the charge transporters are localized to a single molecule, and jump from a molecule to a nearby molecule as described by the Marcus equation, which is given as follows: [7,29–32]

$$K = (4\pi^2/h)t^2(4\pi\lambda K_B T)^{-0.5} exp[-\lambda/4K_B T]$$

where t, λ and T represent the charge transfer matrix element, reorganization energy and absolute temperature, respectively. While h and K_B are the Planck and the Boltzmann constants respectively.

The charge transport rate from the equation is mostly affected by the reorganization energy and electronic coupling (transfer integral). The charge transport rate is determined by the transfer integral, which is influenced by the orientation and distance of the molecules. A lower reorganization energy land larger transfer integral lead to a faster charge transport rate. [31,33,34].

Quantum mechanics and molecular modeling give an understanding of the structure, optical and electronic properties relationships that lead to systematic molecular design [16, 17, 35–37]. In this investigation, the influence of functionalization on electronic and optical properties of two conjugated molecules, emodin (6-methyl-1,3,8-trihydroxyanthraquinone), and purpurin (1,2,4-Trihydroxyanthraquinone) are studied to understand their possible use in organic solar cells, figure 1 and figure 2, respectively. Also, some of the bond lengths (Å) along with the bond angles (°) of emodin and purpurin and their derivatives are presented in Table 4 and Table 5, respectively. Both molecules belong to the anthraquinones, which are considered to be the largest occurring quinones that are naturally abundant. They are used as natural colorants as well as in variety of other applications [38,39].

2 Materials and Methods

The structures of emodin and purpurin were optimized via DFT method [40] using Becke, 3-parameter, Lee–Yang–Parr (B3LYP) functional [41-44] and the 6-31++G (d, p) basis set. The B3LYP has been used in the calculation of reorganization energy in several studies [20, 33, 45,46]. The frequency calculations carried out at the same level of theory, reveal that all studied molecules have reached local minima with no imaginary frequencies. The performed calculations included λ for holes and electrons, adiabatic ionization potential (IP), and adiabatic electron affinity (EA), chemical hardness (n), HOMO and LUMO energy levels, and energy gap (E_g). The reorganization energies for holes (λ_h) and electrons (λ_e) are calculated as follows:

$$\lambda_e = (E_0^- - E_-) + (E_-^0 - E_0^0)$$
$$\lambda_h = (E_0^+ - E_+^+) + (E_+^0 - E_0^0)$$

where the E_0^- (E_0^+) represent the anionic (cationic) energy of the molecule in an optimized neutral structure, the $E_-^-(E_+^+)$ is the anionic (cationic) energy of the molecule in an optimized anion (cation) structure, the $E_-^0(E_+^0)$ is the neutral energy of the molecule in optimized anion (cation) structure and the E_0^0 is the neutral energy of the molecule in optimized neutral structure [34, 47, 48].

The IP and EA energies were calculated as per the following equation:

$$IP = E(M^+) - E(M^0)$$

$$EA = E(M^0) - E(M^-)$$

The $E(M^0)$, $E(M^-)$ and $E(M^+)$ represents the total energies of the neutral, anionic, and cationic state of the molecule [6]. The chemical hardness of the molecule, η, was calculated using $\eta = \frac{IP-EA}{2}$ [12,49].

The excited states of the molecules were determined using time-dependent density functional theory (TD- DFT) [50] utilizing the B3LYP functional with 6-31++ (d, p) basis set from ground state optimized geometry in vacuum and solvent (Ethanol). This gives the absorption spectra and oscillator strength. All calculations were done using Gaussian 09 program [51].

Furthermore, the intermolecular interaction of emodin and purpurin were investigated to determine the role of these interactions to the crystal lattice through Hirshfeld surface analysis [52]. To aid the interpretation of the interactions, d_ map, shape index and 2D fingerprint plots [52] were demonstrated. The 3D energy framework was represented by computing the interaction energies, electrostatic energy, polarization energy, dispersion energy, exchange-repulsion energy, and total intermolecular energy [53] at B3LYP/6-31G (d,p), and a 3.8 Å cluster was generated around the molecule. The calculations were done using the CrystalExplorer17 program [54]. Emodin and hydrated purpurin was used in the representation of the 3D energy framework.

3 Results and Discussion

3.1 Reorganization Energy

The λ_h and λ_e values of emodin and its functionalized molecules are listed in Table 1. For emodin, it can be observed that the λ_h value is smaller than the value of λ_e, 0.22 eV and 0.41 eV, respectively. The λ_h values increased upon the introduction of functional groups, with the lowest value being 0.38 eV for molecules 4 and 5, and the highest value being 0.40 eV for molecules 2 and 3. The λ_e showed only a slight change in values with an increase of 0.03 eV on F-functionalized molecule 4 and a decrease for molecules 3 (0.03 eV) and 5 (0.01 eV). The changes in λ_h and λ_e are due to the changes in structure during oxidation and reduction that are attributed to the C-X (functional groups), bonds contribution. As mentioned in section 1, the charge transfers rate increases with the decrease of reorganization energy. As such, emodin without functionalization is predicted to have the highest charge transfer rate and serves as a good candidate as a hole transport material and electron transport material upon the introduction of functional groups.

Purpurin λ_h and λ_e values are also listed in Table 1. Unlike emodin, the value of λ_e is smaller than λ_h value, 0.39 eV and 0.59 eV, respectively. Accordingly, purpurin without functionalization may act as a good electron transport material. The addition of functional groups has led into a minor decrease of λ_h in molecules 2, 3, 5 and 6 with λ_h values of 0.56, 0.56, 0.58, and 0.58 eV, respectively. The only increase was in Cl-functionalized molecule 4, with λ_h to be 0.60 eV. The changes in λ_e values are also minor, with the largest increase for molecules 2 and 6 by 0.03 eV and the smallest decrease for molecule 3 by 0.02 eV. While no change occurred in the Cl-functionalized molecules, 4 and 5. Based on the given data, purpurin is inclined to have a high charge transport rate as an electron transport material and its functionalized molecules may also have a similar charge transfer rate as electron transport materials.

In general, for halogenated molecules, the values for F show higher reorganization energy than Cl, in emodin and purpurin as a result of the higher electronegativity of Fluorine. This is in agreement with results of halogenated naphthalene [6] and tetracene [55]. It is suggested that the intra-ring functionalization of molecules may yield better results in minimizing the reorganization energy as it avoids the introduction of additional degrees of freedom for geometric relaxation [23]. Overall, the values of λ_h and λ_e are similar to those of proposed organic semiconductors [6–8,23]. The values of chemical hardness for the two molecules are also presented in Table 1. The chemical hardness (η) is defined as the resistance of the chemical potential to change in the number of electrons [47], the functionalized molecules show similar values of η to that of emodin and purpurin, indicating their stability.

3.2 Adiabatic Ionization Potential and Adiabatic Electron Affinity

The values IP and EA for emodin, purpurin, and their functionalized molecules are illustrated in Table 1. One of the concerns in n-type organic semiconductor systems is the lack of stability of their radical anions in the air, [56] and functionalization of molecules may be used to tune IP and EA values for a more stabilized molecule. The IP value of emodin is calculated to be 8.74 eV and the EA is 1.85 eV, and because of the similarity in structure, the IP and EA of purpurin have shown similar values to that of emodin with values of 8.43 eV and 1.85 eV, respectively.

The functionalization of emodin and purpurin results in a decrease of IP and an increase in EA values. The values of emodin IP are in the sequence of molecules 1> 3> 5> 4> 2 and for EA values 3> 5> 4> 2>1 and for purpurin the IP values are in the sequence of 1> 2> 3> 6> 5> 4 and for EA 2> 3> 5> 6> 4>1. The NO_2-functionalized purpurin has the highest IP and EA values due to the negative resonance effect and electron affinity of the NO_2 group. Electrons are withdrawn from the rings, leading to electron deficit at all positions of the fused rings. It is followed by the CN-functionalized molecule, which is attributed to the interactions of the nitrogen lone pair of electrons (negative resonance effect) with the π-electron clouds of the fused rings, as well as the inductive effect of the electronegative nitrogen atom. These results are in agreement with the NO_2 and CN functionalization of tetracene [7].

Similarly, the CN-functionalized molecule in emodin has the highest EA value, 2.33 eV. The 2Cl-functionalized purpurin molecule has a higher EA value than the 2F-functionalized molecule, that is accounted for by the higher ability of Cl to withdraw electrons, taking into consideration resonance and inductive effects. This is in agreement with halogenated pentacene [20] and naphthalene [6]. In addition, the Cl-functionalized emodin molecule also has a higher EA than the F-functionalized molecule.

3.3 HOMO and LUMO Energy, and Optical properties

The values of E_g, HOMO and LUMO of emodin, purpurin and their functionalized molecules are shown inTable 2. The molecules E_g falls within the range of organic semiconductors, 1.4 - 4.2 eV [34]. The functionalization of emodin and purpurin contributed to lowering the energy gap that predicts kinetic stability and an increase in conductivity.

The energy gap of emodin and its functionalized molecules ranged between 3.40 - 3.52 eV, the smallest E_g value was for CN-functionalized molecule 3, 3.40 eV, followed by Cl-functionalized molecule 5, 3.45 eV, and accordingly is predicted to have better conductivity. In addition, the LUMO energy levels and λ_e of CN and Cl-functionalized molecules also have the lowest values, which results in improved emodin functionality as an n-type material.

The overall LUMO values decreased except for the functionalized C_2H_2 molecule. The LUMO values ordered as molecule 1= 2> 4> 5> 3. The CN-functionalized molecule showed the lowest value, leading to the smallest energy gap value. The HOMO levels also decreased in value with the order of molecule 1= 2> 4> 5> 3. The HOMO and LUMO values of purpurin and its functionalized molecules are in the sequence of molecule 1> 4> 5> 6> 3> 2 and 1> 4> 6> 5> 3> 2, respectively. The E_g values range from 2.84 - 3.12 eV, emodin showed the highest E_g value of 3.12 eV with NO_2- functionalization. The value decreased into 2.84 eV to become the smallest E_g among the molecules, followed by the CN-functionalized molecule 3.

The decrease in E_g values of emodin and purpurin upon the addition of functional groups is in consistent with the results obtained for F, CN Cl, and NO_2functionalized tetracene and anthracene by [7]. Overall, the LUMO values of the molecules are in the range of typical n-type materials between -3.0 and -4.0 eV, lowering of LUMO also results in an increase in stability [23] and a higher ability to accept electrons [49]. Hence, thestudied molecules are proposed to be good n-type materials. The study of these frontier molecular orbitals (FMO), in qualitative manner, are insightful in predicting the electron transition [47]. Therefore, the HOMO and LUMO qualitative molecular representations of emodin, purpurin and their functionalized molecules in S_0 are represented in figures 3 and 4. For emodin and its functionalized molecules, the HOMO and LUMO are delocalized on one of the benzene rings and slightly on the functionalized benzene ring. This indicates a strong overlap between the HOMO and LUMO that leads to strong optical absorption due to electron excitation S_0-S_1. For purpurin, the HOMO and LUMO are delocalized on one of the benzene ring, the transition is mainly within the non-functionalized benzene ring. The electrostatic potential (ESP) is useful in predicting the reactive sites of the molecule. The ESP of the molecules increases in the order of red> orange> yellow > green> blue. The reactive sites of the emodin, purpurin and their functionalized molecules are also shown in figure 5. In general, the addition of the functionalization resulted in an increase in reactivity in the site except for molecule 2 in emodin.

The oscillator strengths of emodin, purpurin and their functionalized molecules are presented in Table 3. Oscillator strength expresses the probability of absorption of electromagnetic radiation, the higher the oscillator strength is for a molecule the higher the expected absorption. In this study, the strongest absorption for emodin corresponds to excited state S_1 with a value of 413.28 nm ($f = 0.1139$) in a vacuum.For molecule 2, the strongest absorption was at excited state S_1 with a value of 429.11 nm ($f = 0.1427$) in the solvent. The strongest absorption in molecule 3 corresponds to 439.71 nm ($f = 0.1168$) in the solvent atexcited state S_1. The excited state S_1 shows the strongest absorption for molecule 4 with a value of 425.47 nm ($f = 0.1283$) in the solvent. Finally, molecule 5 also shows the strongest absorption at excited state S_1 with a value of 434.66 nm ($f = 0.146$) in the solvent.

For purpurin, the excited state (S_1) corresponds to the maximum absorption with values of 461.81 nm ($f = 0.194$) in the solvent. For NO_2- functionalized molecules, the strongest absorption value is 541.1 nm ($f = 0.0944$) in the solvent at excited state S_1. For molecules 3, 1022.69 nm ($f = 0.297$) in the solvent at excited state S_1. For the 1Cl-functionalized molecule at excited state S_1 with a value of 466.58 nm ($f = 0.2031$) in the solvent. As for the 2Cl-functionalized molecule, which also corresponds to excited state S_1 with a value of 473.32 nm ($f = 0.2028$) in the solvent. For molecule 6, the strongest absorption takes place in a vacuum with a value of 456.44 nm ($f = 0.1241$). It can be noticed from the given values in Table 3, that the solvent resulted in a redshift of the maximum absorption. Moreover, the decrease in the E_g values also resulted in a red shift in the maximum absorption, as listed in Table 2.

3.4 Hirshfeld Surface Analysis

The Hirshfeld surface analysis aids in the quantification and visualization of intermolecular interactions by utilizing different colors and intensities in graphical representation. Hirshfeld surface analysis has been used to investigate various intermolecular interactions in the crystal structure of organic molecules and complexes [57, 58]. The dnorm (normalized

contact distance) maps of emodin and purpurin are depicted in figure 6. The contacts with shorter distances (close contacts) than the Van der Waals radii are represented by red surfaces, while the blue surfaces represent contacts with longer distances (distance contact). The white surfaces denote distance equivalent to the sum of Van der Waals radii. The red regions in emodin and purpurin appears to originate from the -OH groups in the molecules. The red regions of the molecules may act as donors in intermolecular reactions. Thereby, it is expected that their functionalized molecules with electronegative groups would adhere more sites that act as donors. The shape-index of emodin and purpurin on the Hirshfeld surface is presented in figure 7. The red and blue regions represent the donor and acceptor groups of the molecule, the adjacent red and blue triangles denote π-π stacking interaction among the structures.

The 2D fingerprint plots and fragment patches of emodin and purpurin are illustrated in figures 8 and 9, respectively. The de and di on the plots represent the distances to the nearest atom center, external and internal to the surface. Points on the plot without contribution are gray colored and points with small contribution is blue colored through green to red for the points with the largest contribution. The most significant interaction in emodin is O--H/H--O that contributes 31.8 % to the overall surface. The second largest interaction is H--H with contribution of 30.1 % as pair wings, followed by C--H/H--C (15.9 %), C--C (10.9 %) and O--C/C—O (9.1 %). In purpurin, the O--H/H--O interactions dominated with a contribution of 41%, while the H--H and C--C interactions were 26.6% and 22.3%, respectively. Both molecules have other small contributions; emodin O--O (2.2%) and purpurin C--H/H--C (5.5%), O--O (2.8%) and C--O/O--C (1.9%).

3.5 Energy Frameworks

The calculated interaction energies energy E_{tot} (kJ mol^{-1}) namely, electrostatic (E_{elec}), polarization (E_{pol}), dispersion (E_{dis}), exchange-repulsion (E_{rep}) are used to generate 3D representation of the major interactions in the form of energy frameworks. figure 10 The interaction energies relative strength in individual directions are represented by exhibited cylinder-shaped energy frameworks, the size of the interactions that are less than 5 kJ mol^{-1} have been excluded. It can be seen that the intermolecular interactions are dominated by dispersion forces in emodin and purpurin, figure 9 and figure 10, respectively.

4.4 Conclusion

In the present paper, the electronic and optical properties of emodin and purpurin were investigated utilizing DFT and TD-DFT methods, to learn about their possible use as organic semiconductors. The molecules were also functionalized by electronegative groups to appreciate the influence of functionalization on the optical and electronic properties of the molecules. There was an overall increase in reorganization energy due to the geometrical changes of the molecule upon oxidation and reduction processes. However, the decrease in E_g and LUMO energy levels of the molecules predicts the increase in stability and conductivity. Furthermore, an increase in EA values was also noted to reinforce the molecule's ability to accept electrons. Hence, the functionalization of emodin and purpurin strengthened the n-type properties of the molecules. The energy gaps of the molecules are within the range of semi-conductors (1.4 - 4.2 eV)

and the absorption ranges of the molecules are within the visible range. Based on the given data, we have concluded that emodin and purpurin along with their functionalized molecules are good candidates for organic semi-conductors. Also, the intermolecular interactions and 3D energy framework of emodin and purpurin molecules were studied through Hirshfeld surface analysis. It has been shown that the main interaction in the crystal structure of emodin and purpurin is O--H/H--O and dispersion energy was dominant in the 3D energy framework.

5 Acknowledgment

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Figure and Table legends

Figure 1: Structure and numbered atoms of emodin, 6-methyl-1,3,8-trihydroxyanthraquinone
Molecule 1: R15= R16= R17= R18= R19= R26= CH3
Molecule 2: R26= C2H5
Molecule 3: R15= CN
Molecule 4: R15= F
Molecule 5: R26= Cl

Figure 2: Structure and numbered atoms of purpurin, 1,2,4-Trihydroxyanthraquinone
Molecule 1: R17= R18= R19= R20= R21= H
Molecule 2: R18= NO2
Molecule 3: R18= CN
Molecule 4: R18= Cl
Molecule 5: R17= R18= Cl
Molecule 6: R17= R18= F

Figure 3: HOMO and LUMO of emodin molecule 1 – 5

Figure 4: HOMO and LUMO of purpurin molecule 1 – 6

Figure 5: ESP of emodin and purpurin

Figure 6: Hirshfeld surface of emodin and purpurin plotted over dnorm in the range of -0.4160 to 1.2016 and -1.7662 to 0.8459 a.u, respectively

Figure 7: Shape-index of emodin and purpurin on Hirshfeld surface

Figure 8: Emodin two-dimensional fingerprint plots and fragment patches (surface patches adjacent to neighboring surfaces are colored separately) for intermolecular interactions

Figure 9: Purpurin two-dimensional fingerprint plots and fragment patches (surface patches adjacent to neighboring surfaces are colored separately) for intermolecular interactions

Figure 10: Emodin and purpurin energy frameworks, coulomb energy (red), dispersion energy (green) and total energy (blue)

Table 1: λ_h and λ_e, IP, EA and η(in eV) of emodin and purpurin and their derivatives calculated at B3LYP/6-31++G (d,p)level of theory

Table 2: HOMO-LUMO Gap of Indigo, Alizarin and derivatives

Table 3: Maximum absorption and oscillator strength of emodin and purpurin along with their derivatives in presence andabsence of ethanol solvent

Table 4: Some of the bond lengths (Å) and bond angle (°) of emodin and its functionalized derivatives calculated at the B3LYP/6-31++G(d,p), for the structures and atom numbering, see Fig 1.

Table 5: Some of the bond lengths (Å)and bond angle (°) of purpurin and their functionalized derivatives calculated at the B3LYP/6-31++G(d,p), for the structures and atom numbering, see Fig 2.

Figures

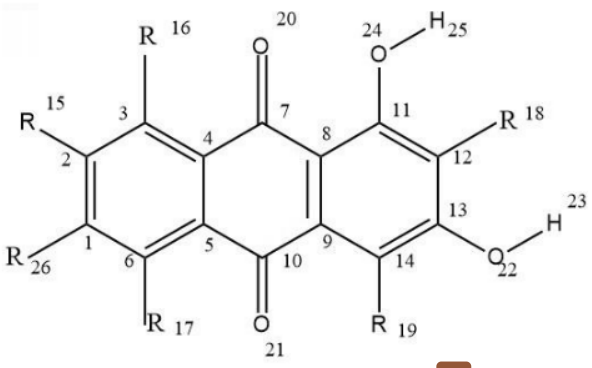


Figure 1: Structure and numbered atoms of emodin, 6-methyl-1,3,8-trihydroxyanthraquinone
Molecule 1: R15= R16= R17= R18= R19= R26= CH_3
Molecule 2: R26= C_2H_5
Molecule 3: R15= CN
Molecule 4: R15= F
Molecule 5: R26= Cl

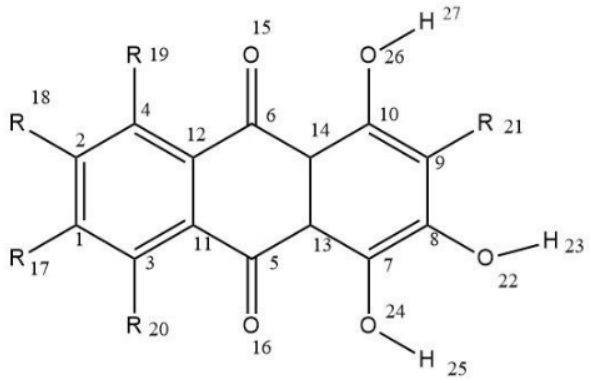


Figure 2: Structure and numbered atoms of purpurin, 1,2,4-Trihydroxyanthraquinone
Molecule 1: R17= R18= R19= R20= R21= H
Molecule 2: R18= NO_2
Molecule 3: R18= CN
Molecule 4: R18= Cl
Molecule 5: R17= R18= Cl
Molecule 6: R17= R18= F

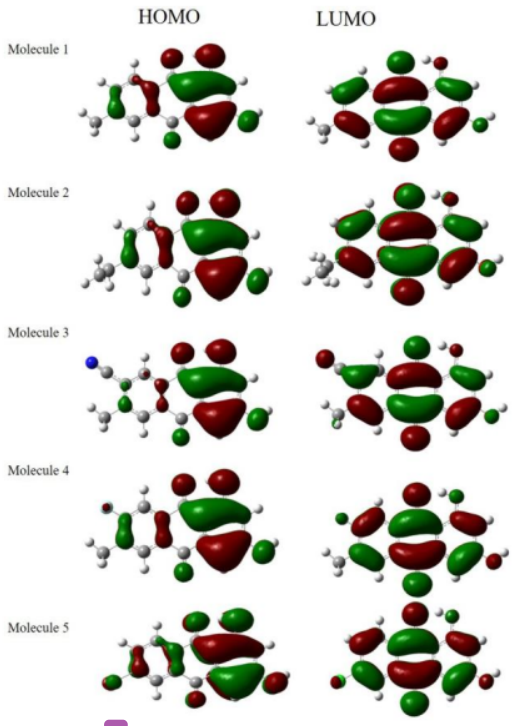


Figure 3: HOMO and LUMO of emodin molecule 1 – 5

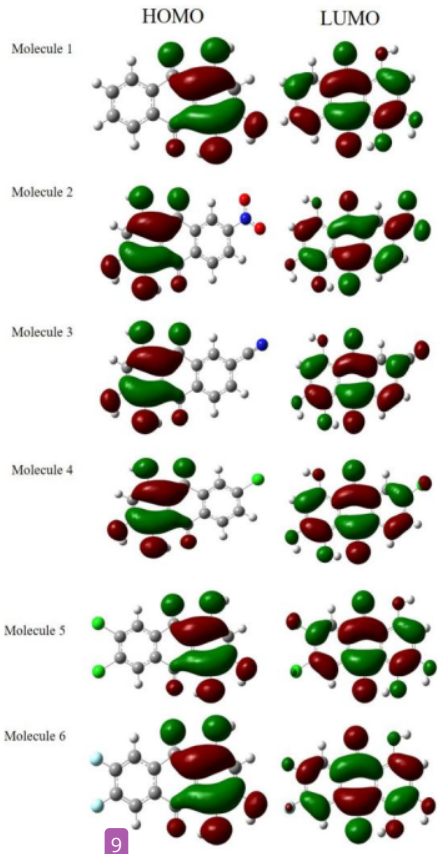


Figure 4: HOMO and LUMO of purpurin molecule 1 – 6

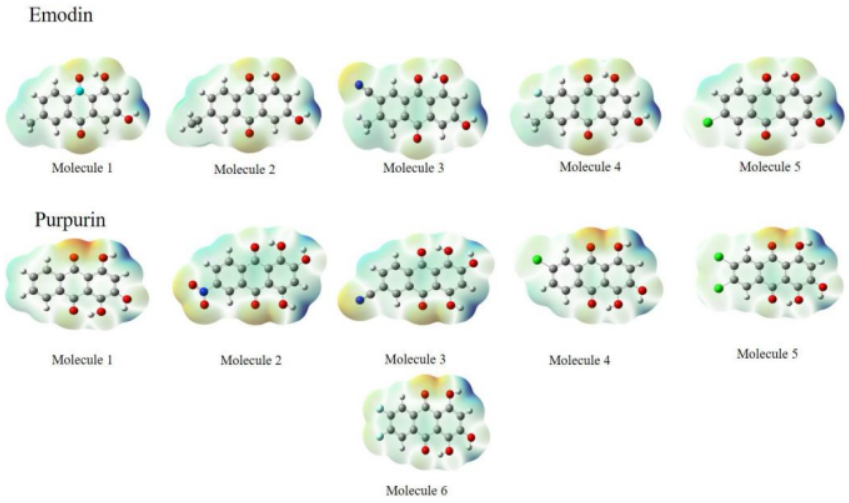
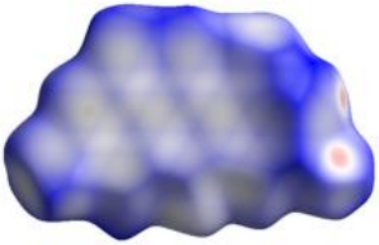


Figure 5: ESP of emodin and purpurin

Emodin



Purpurin

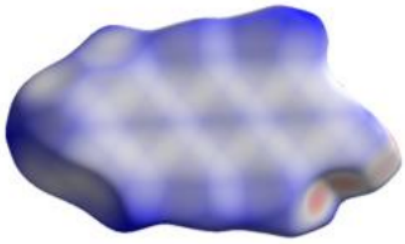


Figure 6: Hirshfeld surface of emodin and purpurin plotted over dnorm in the range of -0.4160 to 1.2016 and -1.7662 to 0.8459 a.u, respectively

Emodin

Purpurin

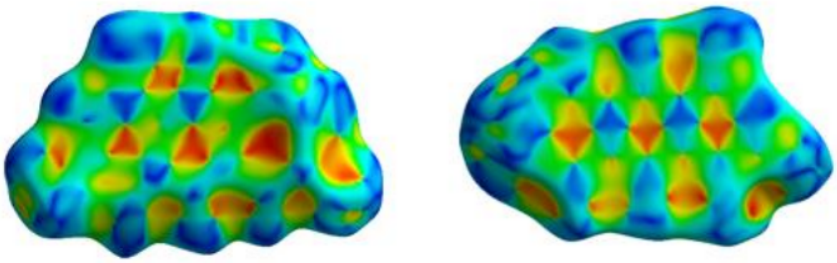


Figure 7: Shape-index of emodin and purpurin on Hirshfeld surface

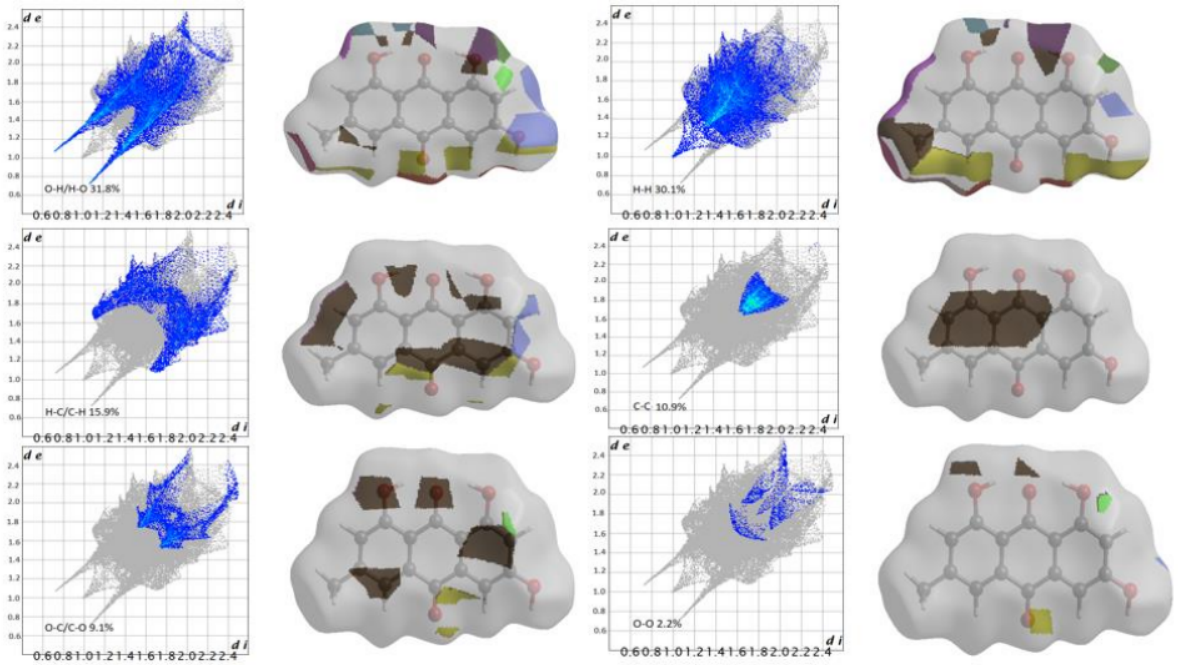


Figure 8: Emodin two-dimensional fingerprint plots and fragment patches (surface patches adjacent to neighboring surfaces are colored separately) for intermolecular interactions

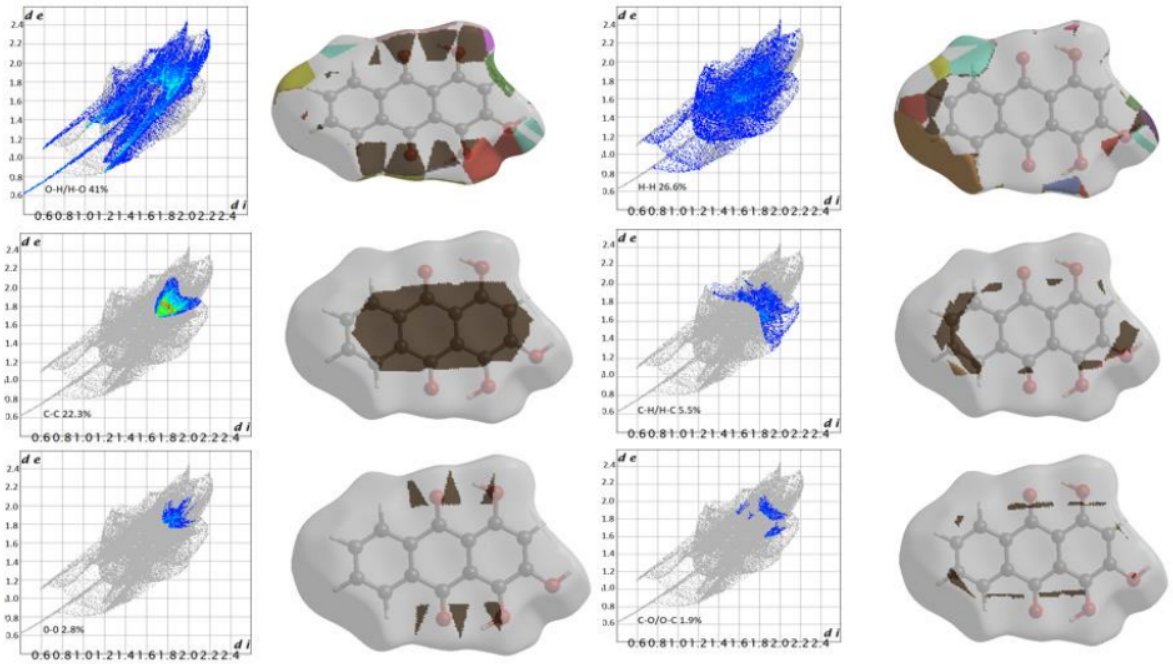


Figure 9: Purpurin two-dimensional fingerprint plots and fragment patches (surface patches adjacent to neighboring surfaces are colored separately) for intermolecular interactions

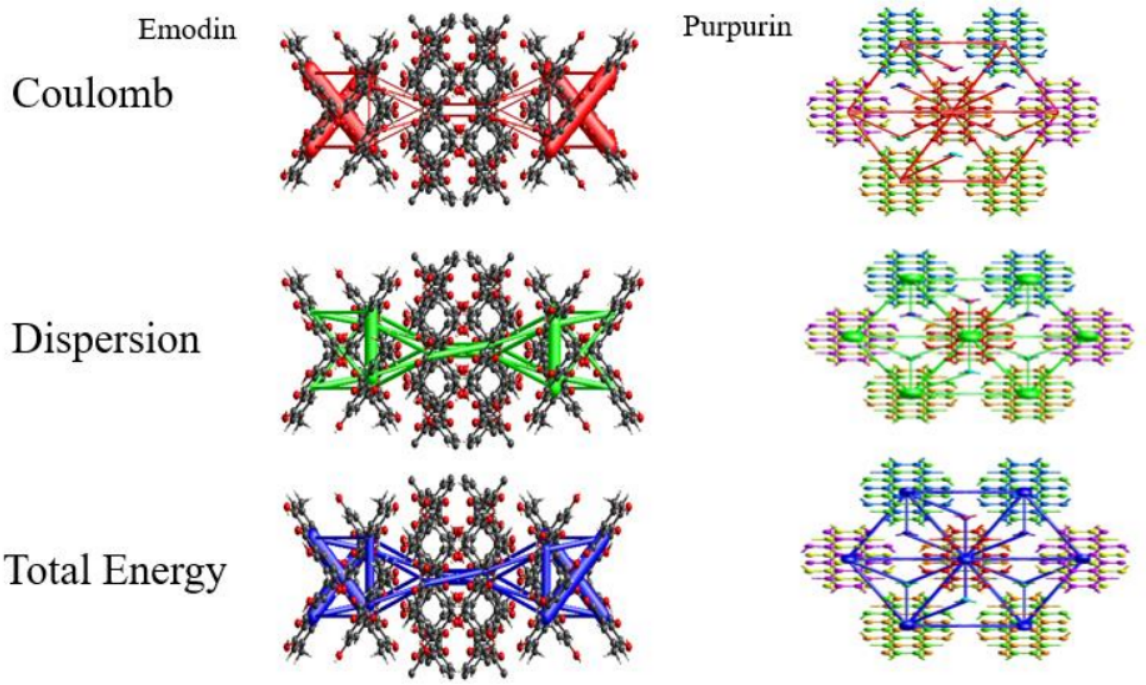


Figure 10: Emodin and purpurin energy frameworks, coulomb energy (red), dispersion energy (green) and total energy (blue)

Molecule	λ_h	λ_e	IP	EA	n
Emodin					
1 – None	0.22	0.41	8.74	1.85	3.44
2 – (1) Ethylene	0.40	0.41	8.13	1.87	3.13
3 – (1) CN	0.40	0.38	8.42	2.33	3.05
4 – (1) F	0.38	0.43	8.24	1.98	3.13
5 – (1) Cl	0.38	0.40	8.30	2.13	3.09
Purpurin					
1 – None	0.59	0.39	8.43	1.85	3.29
2 – (1) NO_2	0.56	0.42	8.06	2.59	2.74
3 – (1) CN	0.56	0.37	8.01	2.37	2.82
4 – (1) Cl	0.60	0.39	7.81	2.04	2.88
5 – (2) Cl	0.58	0.39	7.88	2.19	2.85
6 – (2) F	0.58	0.42	7.93	2.12	2.91

Table 1: λh and λe, IP, EA and η(in eV) of emodin and purpurin and their derivatives calculated at B3LYP/6-31++G (d,p) level of theory

Molecule	E_g(eV)	λ_{abs}	HOMO(eV)	LUMO(eV)	f
Emodin					
1 – None	3.52	413.28	-6.69	-3.18	0.1139
2 – (1) Ethylene	3.51	414.72	-6.69	-3.18	0.1173
3 – (1)CN	3.40	427.31	-7.01	-3.62	0.091
4 – (1)F	3.51	411.77	-6.81	-3.30	0.1063
5 – (1)Cl	3.45	421.43	-6.89	-3.44	0.1183
Purpurin					
1 – None	3.12	452.09	-6.31	-3.19	0.1274
2 – (1)NO_2	2.84	509.51	-6.68	-3.84	0.0797
3 – (1)CN	2.97	480.52	-6.63	-3.66	0.1138
4 – (1)Cl	3.09	455.57	-6.44	-3.35	0.1349
5 – (2)Cl	3.06	461.24	-6.53	-3.47	0.135
6 – (2)F	3.09	456.44	-6.54	-3.45	0.1241

Table 2: HOMO-LUMO Gap of emodin, purpurin and derivatives

Molecule	Excited State 1				Excited State 2				Excited State 3			
	λ_{max}(nm)	f	λ_{max}(nm)	f	λ_{max}(nm)	f	λ_{max}(nm)	f	λ_{max}(nm)	f	λ_{max}(nm)	f
Emodin	Without Solvent		With Solvent		Without Solvent		With Solvent		Without Solvent		With Solvent	
1 – None	413.28	0.1139	419.83	0	388.39	0	407.63	0.175	381.58	0.1036	380.18	0
2 – (1) Ethylene	414.72	0.1173	429.11	0.1427	413.11	0.0003	403.01	0	365.56	0.012	378.55	0.0356
3 – (1) CN	427.31	0.091	439.71	0.1168	417.29	0	408	0	362	0	386.1	0.039
4 – (1) F	411.77	0.1063	425.47	0.1283	409.61	0	399.56	0	356.28	0	380.94	0.0464
5 – (1) Cl	421.43	0.1183	434.66	0.146	412.82	0	402.54	0	360.14	0	383.27	0.026
Purpurin												
1 – None	452.09	0.1274	461.81	0.194	449.76	0	425.89	0	350.37	0	370.06	0.0317
2 – (1) NO_2	509.51	0.0797	541.1	0.0944	467.25	0	442.21	0	374.59	0.0096	401.81	0.0597
3 – (1) CN	480.52	0.1138	1022.69	0.0297	457.45	0	1011.86	0.001	357.24	0	693.33	0
4 – (1) Cl	455.57	0.1349	466.58	0.2031	446.72	0	423.55	0	366.79	0.0651	379.2	0.0608
5 – (2) Cl	461.24	0.135	473.32	0.2028	447.96	0	424.82	0	373.14	0.0318	382.31	0.0322
6 - (2) F	456.44	0.1241	708.01	0	444.04	0	478.79	0	365.57	0.0265	465.55	0

Table 3: Maximum absorption and oscillator strength of emodin and purpurin along with their derivatives in presence andabsence of ethanol solvent

Emodin	Molecule 1	Molecule 2	Molecule 3	Molecule 4	Molecule 5
Bond length (Å)					
C_1-C_2	1.404	1.406	1.416	1.400	1.399
C_2-C_3	1.393	1.392	1.403	1.386	1.391
C_3-C_4	1.399	1.400	1.393	1.396	1.400
C_4-C_5	1.410	1.409	1.409	1.409	1.408
C_5-C_6	1.397	1.398	1.396	1.398	1.398
C_6-C_1	1.401	1.399	1.399	1.399	1.392
C_4-C_7	1.483	1.483	1.487	1.485	1.485
C_7-C_8	1.457	1.457	1.455	1.455	1.455
C_8-C_9	1.420	1.419	1.421	1.420	1.420
C_9-C_{10}	1.497	1.497	1.495	1.498	1.496
C_{10}-C_{11}	1.421	1.421	1.422	1.421	1.421
C_{11}-C_{12}	1.402	1.402	1.402	1.402	1.402
C_{12}-C_{13}	1.392	1.392	1.392	1.392	1.392
C_{13}-C_{14}	1.407	1.407	1.408	1.407	1.407
C_9-C_{14}	1.385	1.385	1.384	1.384	1.384
C_7-O_{20}	1.250	1.251	1.249	1.249	1.250
C_{10}-O_{21}	1.226	1.226	1.225	1.227	1.225
Bond Angle (°)					
$C_1C_2C_3$	121.2	121.2	121.1	123.7	119.2
$C_2C_3C_4$	120.2	120.2	120.2	118.7	120.5
$C_3C_4C_5$	119.2	119.2	119.3	119.6	119.5
$C_4C_5C_6$	119.8	119.8	119.9	119.6	120.1
$C_5C_6C_1$	121.2	121.2	121.8	122.0	119.2
$C_6C_1C_2$	118.1	118.1	117.5	116.2	121.3
$C_5C_4C_7$	121.0	120.9	121.1	121.0	120.9
$C_4C_7C_8$	118.4	118.5	118.3	118.3	118.4
$C_7C_8C_9$	121.6	121.6	121.8	121.7	121.7
$C_8C_9C_{10}$	120.3	120.3	120.4	120.4	120.3
$C_9C_{10}C_5$	117.4	117.5	117.4	117.4	117.4
$C_{10}C_5C_4$	120.9	120.9	120.9	121.0	121.0
$C_9C_8C_{11}$	118.4	118.4	118.4	118.4	118.4
$C_8C_{11}C_{12}$	120.1	120.1	120.1	120.1	120.1
$C_{11}C_{12}C_{13}$	119.8	119.8	119.8	119.7	119.8
$C_{12}C_{13}C_{14}$	121.0	121.0	121.0	121.0	121.0
$C_{13}C_{14}C_9$	119.2	119.2	119.2	119.2	119.2
$C_{14}C_9C_8$	121.2	121.1	121.2	121.1	121.2

Table 4: Some of the bond lengths (Å) and bond angle (°) of emodin and its functionalized derivatives calculated at the B3LYP/6-31++G(d,p), for the structures and atom numbering, see Fig 1.

Purpurin	Molecule 1	Molecule 2	Molecule 3	Molecule 4	Molecule 5	Molecule 6
Bond length (Å)						
$C_1 - C_2$	1.401	1.398	1.410	1.401	1.409	1.401
$C_2 - C_4$	1.393	1.388	1.400	1.391	1.393	1.383
$C_4 - C_{12}$	1.400	1.398	1.397	1.398	1.396	1.400
$C_{12} - C_{11}$	1.407	1.405	1.405	1.406	1.405	1.406
$C_{11} - C_3$	1.403	1.403	1.403	1.403	1.399	1.404
$C_{12} - C_6$	1.503	1.506	1.506	1.505	1.503	1.503
$C_6 - C_{14}$	1.479	1.476	1.476	1.477	1.477	1.477
$C_{14} - C_{13}$	1.433	1.435	1.434	1.434	1.434	1.434
$C_{13} - C_5$	1.467	1.465	1.466	1.469	1.468	1.468
$C_5 - C_{11}$	1.474	1.480	1.478	1.472	1.475	1.474
$C_{14} - C_{10}$	1.408	1.408	1.408	1.408	1.408	1.408
$C_{10} - C_9$	1.409	1.410	1.410	1.409	1.410	1.410
$C_9 - C_8$	1.381	1.381	1.381	1.381	1.381	1.381
$C_8 - C_7$	1.416	1.417	1.417	1.416	1.417	1.417
$C_7 - C_{13}$	1.400	1.401	1.401	1.400	1.400	1.400
$C_6 - O_{15}$	1.228	1.227	1.227	1.227	1.227	1.228
$C_5 - O_{16}$	1.251	1.249	1.249	1.251	1.249	1.250
Bond Angle (°)						
$C_1C_2C_4$	120.3	122.6	120.3	121.5	120.0	120.9
$C_2C_4C_{12}$	120.2	118.7	119.9	119.3	120.5	119.3
$C_4C_{12}C_{11}$	119.3	119.5	119.5	119.8	119.3	119.6
$C_{12}C_{11}C_3$	120.2	120.5	120.3	119.9	120.2	120.5
$C_{11}C_3C_1$	119.9	120.1	120.1	120.3	120.1	118.9
$C_3C_1C_2$	119.9	118.4	119.6	119.0	119.6	120.5
$C_{12}C_6C_{14}$	117.4	117.2	117.2	117.2	117.1	117.2
$C_{11}C_{12}C_6$	122.0	122.2	122.1	122.1	122.2	122.2
$C_6C_{14}C_{13}$	119.9	120.0	120.0	119.9	120.0	119.9
$C_{14}C_{13}C_5$	121.7	121.8	121.8	121.7	121.8	121.8
$C_{13}C_5C_{11}$	118.7	118.7	118.7	118.7	118.5	118.6
$C_5C_{11}C_{12}$	120.0	119.9	119.9	120.1	120.1	120.1
$C_{13}C_{14}C_{10}$	117.9	117.9	117.9	117.9	117.9	117.9
$C_{14}C_{10}C_9$	120.6	120.6	120.6	120.6	120.6	120.6
$C_{10}C_9C_8$	120.9	121.0	121.0	120.9	120.9	120.9
$C_9C_8C_7$	119.8	119.7	119.7	119.8	119.8	119.8
$C_8C_7C_{13}$	119.8	119.7	119.8	119.8	119.7	119.7
$C_7C_{13}C_{14}$	120.8	120.8	120.7	120.7	120.7	120.7

Table 5: Some of the bond lengths (Å)and bond angle (°) of purpurin and their functionalized derivatives calculated at the B3LYP/6-31++G(d,p), for the structures and atom numbering, see Fig 2.

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