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Evaluation and visualisation of molecular orbitals of natural pigments by density functional theory for their application in photoelectrochemical devices

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The theoretical study of natural pigments such as delphinidin, petunidin and fuligorubin using density functional theory at the B3LYP/6-31G (d) level is presented to highlight their usefulness for photo electrochemical devices. Ground state geometries, electronic transition energies, oxidation potentials and the essential parameters for their photoelectrochemical behaviour are reported. The ground state oxidation potentials are calculated to be 1.31, 1.68 and 1.25 V (vs. normal hydrogen electrode, NHE) and the excited state oxidation potentials are -1.35 , -1.12 and -1.51 V (vs. NHE), respectively. Deprotonation order is determined by calculating proton affinities at different sites which indicates the site of anchoring and charge flow direction.

Keywords: photosensitisers; natural pigments; density functional theory; ground and excited state oxidation potentials; photoelectrochemical devices

1. Introduction

Spectral tuning of semiconductor–electrolyte interfaces is the key to the success of photoelectrochemical devices. A photosensitiser interposed at the interfaces of the photo electrochemical (PEC) device can bring about the required spectral tuning to match the solar spectrum. The required features of such photosensitisers are perfect anchoring to the surface of the semiconductor, absorption of light and photo-induced electron release into the conduction band of the semiconductor. Special attention is focused on development of dyes to harvest a larger region of the solar spectrum [1]. A potential photosensitiser should absorb all light in the solar spectrum spanning over visible, UV and IR regions of wavelength. In addition, it must carry attachment groups to graft it firmly to the semiconductor oxide surface. Upon excitation it should inject electrons into the solid with a quantum yield of unity [2]. The energy level of the excited state should be well matched to the lower bound of the conduction band of the oxide to minimise energetic losses during the electron transfer reaction. Its redox potential should be sufficiently high that it can be regenerated via electron donation from the redox electrolyte or the hole conductor. Naturally available dyes with fastness to sunlight have been successfully used in the textile industries.

Dyes obtained from natural products can be used as photosensitisers with an acceptable efficiency [3,4]. Natural pigments from plants, such as chlorophyll, carotenoids [5,6] and anthocyanins [7] have been extensively studied as photosensitisers for the dye sensitised solar cell (DSSC).

2. Computational methods

The optimised geometries of the singlet ground state of three natural pigments delphinidin, petunidin (commonly found anthocyanins [8]) and fuligorubin (a red pigment from slime mould *Fuligo septica* [9]) were carried out using density functional theory (DFT) calculations with B3LYP/6-31G (d) basis set. The structures of the pigments are given in Figure 1. The excitation energies and oscillator strengths at the optimised geometry in the ground state were determined using the time dependent DFT (TDDFT) calculations with the same basis set as that for the ground state. All calculations were performed with the Gaussian 03 programme package [10].

3. Results and discussion

3.1 Ground state geometries and optical properties

The ground state geometries of delphinidin, petunidin and fuligorubin were optimised in the ground state in order to reveal their exact electronic structure. Their optimised structures were found to be non-planar. The first optically allowed electronic transitions of delphinidin, petunidin and fuligorubin are predicted to populate the 2^1A states (a Highest Occupied Molecular Orbital (HOMO) \rightarrow Lowest Unoccupied Molecular Orbital (LUMO) transition). The theoretical and experimental absorbance maxima of the three dyes are given in Table 1.

As seen in Figures 2 and 3, HOMOs of delphinidin and petunidin are primarily localised on A and C rings, while the LUMO has character on the B ring. During the optical

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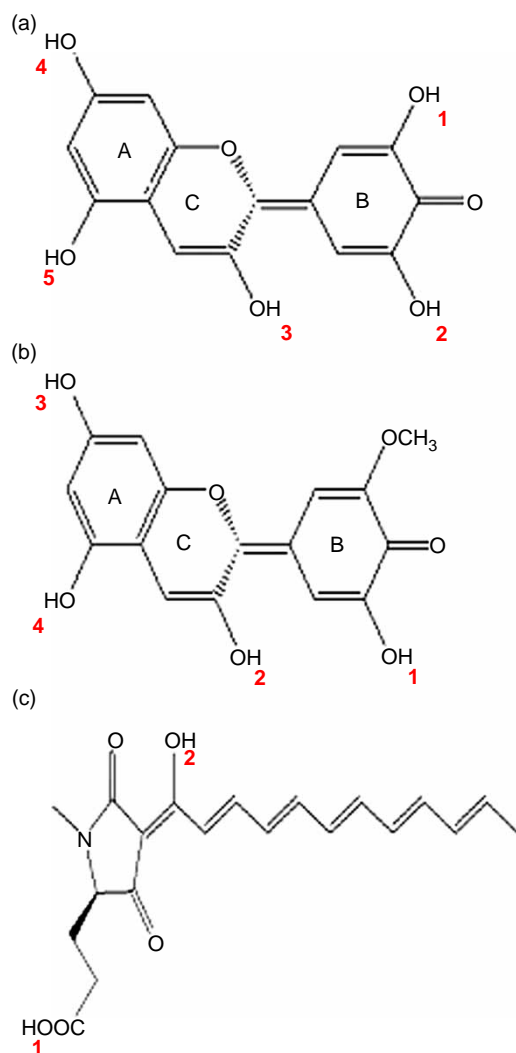


Figure 1. Structures of delphinidin (a), petunidin (b) and fuligorubin (c).

transition, electron density is increased in B ring while it is decreased in A ring. The hydroxy substituents of B ring are assumed to be the anchoring groups to the semiconductor layer. Thus, the spatial overlap of the delphinidin and petunidin LUMO with the conduction band of the semiconductor and the enhanced excited state

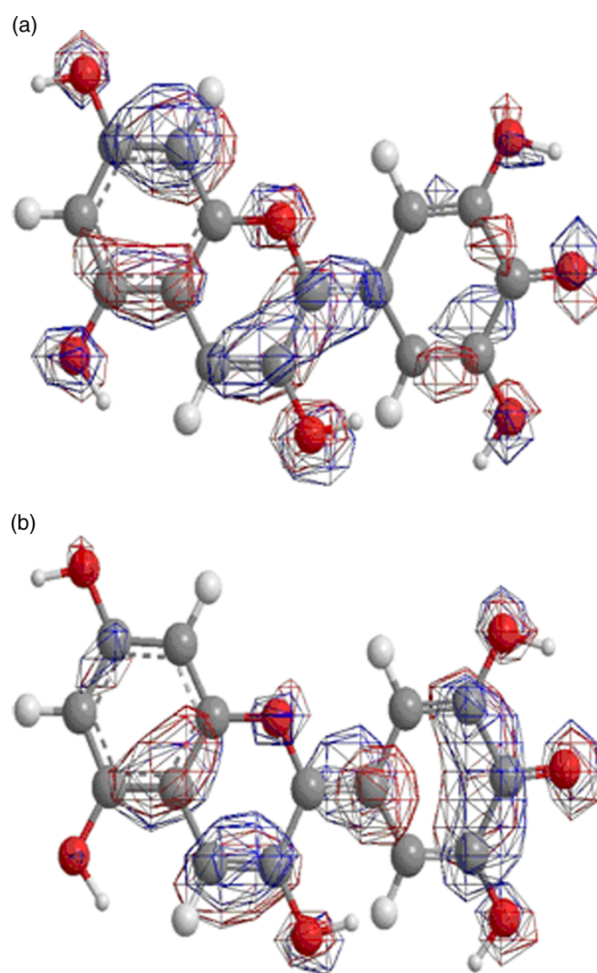


Figure 2. HOMO (a) and LUMO (b) of delphinidin.

electron density at the B ring can favour efficient electron injection in the PEC devices.

In the case of fuligorubin, HOMO \rightarrow LUMO photo-excitation moves the electron density from the polyene chain to the anchoring moiety (Figure 4), thus favouring electron injection from the dye to semiconductor.

An important thermodynamic requirement of the dyes to be used in DSSC technology is that the HOMO level of the dye has to be sufficiently positive in the redox potential

Table 1. Redox and spectral characteristics of natural pigments by TDDFT.

Dye	Oxidation potential		Theoretical λ_{\max} (nm)	Experimental λ_{\max} (nm)	f^a	C^a
	HOMO (V vs. NHE)	LUMO (V vs. NHE)				
Delphinidin	1.31	− 1.35	467.26	508	0.6456	0.56
Petunidin	1.68	− 1.12	442.86	506	0.7802	0.57
Fuligorubin	1.25	− 1.51	450.16	450	1.9692	0.61

^a The dominant configuration (HOMO–LUMO) coefficients (C) and oscillator strength (f) are presented.

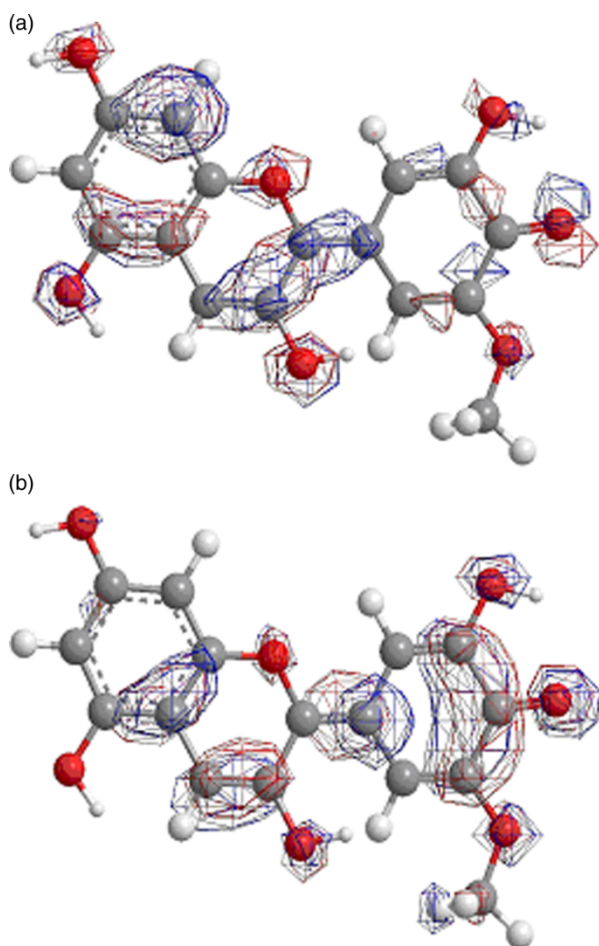


Figure 3. HOMO (a) and LUMO (b) of petunidin.

and the LUMO of the dye has to be sufficiently more negative than the conduction band edge of the semiconductor (E_{CB}). The HOMO level of delphinidin, petunidin and fuligorubin are 1.31, 1.68 and 1.25 V versus normal hydrogen electrode (NHE), respectively (Table 1). The LUMO levels of the dyes of delphinidin, petunidin and fuligorubin are -1.35 , -1.12 and -1.51 V versus NHE, respectively (Table 1).

Importantly, the calculated excited state oxidation potentials are all more negative than the conduction band edge of TiO_2 (0.5 V vs. NHE) [11], and hence a thermodynamically favourable excited state electron injection from the dyes to TiO_2 is expected.

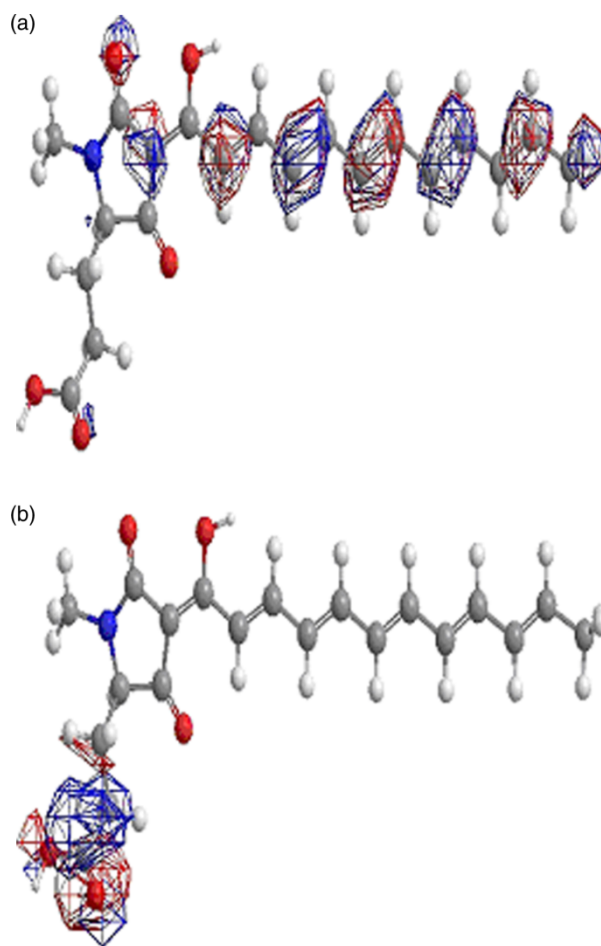


Figure 4. HOMO (a) and LUMO (b) of fuligorubin.

3.2 Deprotonation of delphinidin, petunidin and fuligorubin

The deprotonation order (proton affinity, PA) has been studied by comparing the energy difference between the optimised and protonated and deprotonated structures (Table 2). In the case of delphinidin and petunidin, though deprotonation order predicts the possibility of displacing the hydrogens on A and C rings, the stable mononuclear bidentate coordination structure of the quinoidal delphinidin and petunidin with the metal ions upon adsorption to the semiconductor would compensate and make the anchoring of hydrogen on the B ring favourable [12]. The deprotonation order in the

Table 2. Thermodynamic evaluation of deprotonation of natural pigments by TDDFT.

Dye	Deprotonation				
	PA($-\text{H}_1^+$) Kcal/mol	PA($-\text{H}_2^+$) Kcal/mol	PA($-\text{H}_3^+$) Kcal/mol	PA($-\text{H}_4^+$) Kcal/mol	PA($-\text{H}_5^+$) Kcal/mol
Delphinidin	355.61	339.73	324.799	323.7322	326.9325
Petunidin	356.3	326.24	325.36	327.874	—
Fuligorubin	350.61	452.52	—	—	—

case of fuligorubin predicts that the carboxyl group is the anchoring group rather than the hydroxyl group as the deprotonation energy is 102 Kcal/mol higher when the hydrogen on the hydroxyl group is removed.

4. Conclusions

Using TDDFT calculations, we have reported the ground state geometries and electronic structures of three natural dye molecules in the gas phase: delphinidin, petunidin, fuligorubin. The TDDFT calculations show that the dominant electronic transitions populate the 2^1A state (a HOMO \rightarrow LUMO transition) at, 467.26, 442.86 and 450.16 nm, respectively. The ground state oxidation potentials are calculated to be 1.31, 1.68 and 1.25 V (vs. NHE), respectively, and the excited state oxidation potentials are -1.35 , -1.12 and -1.51 V (vs. NHE), respectively, making the electron transfer from the dye molecules to the TiO_2 conduction band thermodynamically favourable. This study throws light on the utilisation of biologically safe and cheap natural sources as semiconductor sensitizers that would definitely enhance the environmental and economic benefits of solar energy conversion by simplifying the steps involved in the preparation and purification of synthetic dyes. It also paves way for effective screening of the potential photosensitisers before employing them in service conditions.

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