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RESEARCH ARTICLE

Density functional theory (DFT) and time-dependent density functional theory (TDDFT) studies of selected ancient colourants as sensitizers in dye-sensitized solar cells

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Abstract: Ancient dyes such as brazilin, brazilein, haematoxylin and haematein have wide applications such as dyestuff, microscopy stains, and also as traditional and modern medicines. However these dyes have not yet been explored as sensitizers in dye sensitized solar cells. In the present work theoretical studies of these dyes have been performed using concepts such as density functional theory and time-dependent density functional theory, with Gaussian'09W software at B3LYP/6-31g(d) level. All the calculations are with the inclusion of geometric optimization and solvation effect of ethanol. Various energy levels of the dyes, electron cloud density, dominant energy transition states, optical properties and deprotonation order (proton affinity) of the dyes were obtained. This information was helpful to evaluate the feasibility of the dyes in dye sensitized solar cell (DSSC) applications. The dominant energy transition state of all dyes was found to be HOMO → LUMO at the first excitation state. For all four dyes electron clouds at the lowest unoccupied molecular orbital (LUMO) level were found to be localized near or at the most probable hydroxyl group that may anchor to the semiconductor. Among the four dyes, brazilein and haematein displayed excellent optical properties (λ max, oscillator strength, absorption band at visible spectrum) exhibiting their potential in DSSC application.

Keywords: Brazilein, brazilin, DFT, DSSC, haematein, haematoxylin.

INTRODUCTION

Dye-sensitized solar cells (DSSC) are solar devices that convert light energy into electrical energy and have received much attention, research and development due to the low cost, high efficiency and the ease of preparation (Liu, 2008; Wang *et al.*, 2013). The solar cell was first reported by O'regan and Grätzel (1991). The highest photon-conversion efficiency was achieved by Yella and co-workers (2011) at 12 %.

A DSSC consists of a photo-sensitizer (dye), an electrolyte (contain redox couple), metal oxide semiconductors and a counter electrode. An ideal dye relevant to DSSC application should possess the ability to be excited to the lowest unoccupied molecular orbital (LUMO) level by visible light, anchor strongly onto the metal oxide semiconductor (typically by the hydroxyl group or carboxyl group), and inject electrons into the semiconductor where the electrons will then flow into the external load (Calogero *et al.*, 2013; Wang *et al.*, 2013).

Many natural dyes and pigments have been extracted from flowers (e.g. *Bougainvillea, Hibiscus*); leaves (e.g. spinach, holly); fruits (e.g. dragon fruit); and seeds (e.g. coffee) during the past decades, used as photosensitizers and tested for the photon-to electrical conversion efficiency in the DSSC research (Narayan, 2012).

Brazilin (C.I 75280) and haematoxylin (C.I 75290) are some of the natural colourants that have been used in the Mediterranean region thousands of years ago (Melo, 2009). Brazilin was reported to be identified in centuries-old textile samples found in the Mount Athos, Greece (Karapanagiotis *et al.*, 2011), and the historical uses as dyestuff and traditional medicines were well-described by Puchtler and co-workers (1986). In the past decades brazilin, haematoxylin and its derivative forms have

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*Corresponding author (piyasiri.ekanayake@ubd.edu.bn) been widely used as microscopy stains for biological samples (Puchtler *et al.*, 1986) and for colourimetric detection of metals such as tin, aluminium and molybdate (Sastry *et al.*, 1989). In the recent years these dyes have been widely studied in pharmaceutical research, which includes uses as anti-convulsant (Baek *et al.*, 2000), immunosuppressant (Ye *et al.*, 2006), anti-inflammatory drug (Wu *et al.*, 2011), as well as in HIV (Ishii *et al.*, 2012) and cancer drug research (Kim *et al.*, 2012).

Brazilin is extracted from red wood such as *Caesalpinia brasiliensis*, *C. echinata* and *C. sappan,* and haematoxylin is extracted from *Haematoxylum campechianum* (Puchtler *et al.*, 1986; Melo, 2009; Ishii *et al.*, 2012; Tong *et al.*, 2014). The molecular structure of brazilin and haematoxylin are almost similar, with haematoxylin possessing one hydroxyl group more than brazilin (Figure 1). Both brazilin and haematoxylin can be oxidised in lye, alkaline solutions or by oxidizing agents to yield brazilein and haematein, respectively (Livingstone, 1987; Ishii *et al.*, 2012). Brazilin and haematoxylin are not considered as dyes under treatises on staining (Culling, 1963; Puchtler *et al.*, 1986) because both dyes are colourless when in pure form (Weigl *et al.*, 2009). However, the oxidized forms of brazilin and haematoxylin are coloured (Rosenberg, 2008).

So far brazilin, haematoxylin and their oxidized forms have not been explored for DSSC applications. Moreover, these dyes possess hydroxyl groups, which can serve as an anchoring group to the semiconductor (Calogero *et al.*, 2013). The main aim of this theoretical study was to investigate the possibility of using such dyes as photo-sensitizers in DSSC applications.

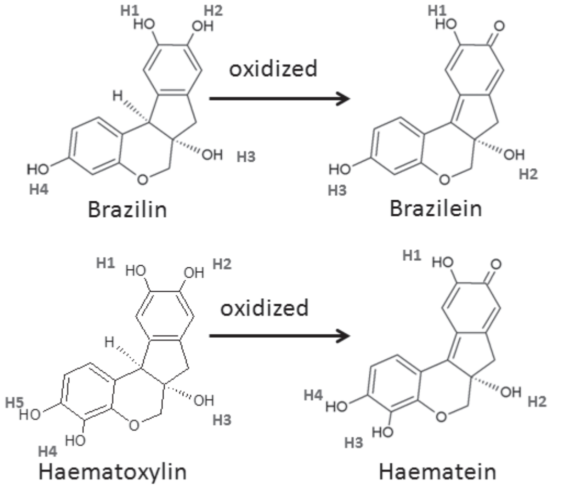

Figure 1: Molecular structure of brazilin, brazilein, haematoxylin and haematein. The hydroxyl groups of the dyes are labelled as H1, H2, H3, H4 and H5.

COMPUTATIONAL DETAILS

Spartan'10 software package was used for constructing the structure of the molecules and obtaining the molecular geometric coordinates (Deppmeier *et al.*, 2011). Both density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations were carried out using Gaussian'09W software package (Frisch *et al.*, 2010). B3LYP hybrid functional and 6-31g(d) basis set were applied to DFT and TDDFT calculation. Molecular geometric optimizations were carried out using B3LYP/6-31g(d) level of theory with the inclusion of solvation effect of ethanol. The molecular orbital plots were visualised at isovalue of density of 0.03 using GaussView Version 5 (Dennington *et al.*, 2009). Deprotonation order (proton affinity) was performed using B3LYP/6-31g(d) levels in gas phase (without solvation effect).

RESULTS AND DISCUSSION

Energy levels

The main reason for including the solvation effect of ethanol in the calculation is because brazilin and haematoxylin are extracted in ethanol from redwood samples (Ye *et al.*, 2006). Table 1 summarizes the results of DFT and TDDFT calculations of the dyes with the inclusion of geometric optimization and solvation effect of ethanol at B3LYP/6-31g(d) level of theory.

DFT calculates the energy levels of the dye molecule at particular transition states. The band gap of brazilein and haematein were 2.94 eV and 2.95 eV, respectively, whereas brazilin and haematoxylin were 5.47 eV and 5.45 eV. The similarities of the energy levels (brazilin *vs* haematoxylin, and brazilein *vs* haematein) may be due to their similar molecular structures (Figure 1).

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the oxidized dyes (brazilein and haematein) were almost equal, while a similar pattern was observed for energy levels of non-oxidized dyes (brazilin and haematoxylin).

For efficient injection of the electron of the excited dye into the metal oxide semiconductor e.g. TiO_2, the LUMO level of the dye needs to be higher than the conduction band edge of the semiconductor (Lee & Yang,

Table 1: DFT and TDDFT calculation of the dyes with inclusion of geometric optimization and solvation effect of ethanol at B3LYP/6-31g(d) level of theory.

	DFT Calculation			TDDFT Calculation				
Photosensitizer	HOMO (eV)	LUMO (eV)	Band gap (eV)	Excitation state	Calculated energy (eV)	(nm)	Oscillator strength (f)	*Transition state (coefficient)
Brazilin	- 5.66	- 0.19	5.47	1	4.80	258	0.138	H-3 → L + 3 = 0.26 H → L = 0.65
				2	5.01	247	0.031	H-1 → L + 1 = 0.52
				3	5.07	245	0.002	H → L + 1 = 0.69
Brazilein	- 5.55	- 2.61	2.94	1	2.86	434	0.701	H → L = 0.68
				2	3.34	372	0.125	H-1 → L = 0.68
				3	3.45	360	0.032	H-3 → L = 0.64
Haematoxylin	- 5.64	- 0.19	5.45	1	4.80	259	0.146	H → L = 0.64
				2	4.93	252	0.014	H-1 → L = 0.56
				3	5.11	243	0.0001	H-1 → L = 0.37 H-1 → L + 1 = 0.31
Haematein	- 5.57	- 2.62	2.95	1	2.86	434	0.534	H → L = 0.62
				2	2.89	429	0.182	H-1 → L = 0.63 H → L = 0.28
				3	3.36	370	0.207	H-2 → L = 0.68

*Coefficients higher than 0.2 were only listed in the table

2011; Calogero *et al.*, 2013). The band edge of TiO_2 is approximately at - 4.2 eV (relative to vacuum) (Heera & Cindrella, 2010) and the LUMO energy level of brazilin, haematoxylin, brazilein and haematein were - 0.19 eV, - 0.19 eV, - 2.61 eV and - 2.62 eV, respectively, indicating that the LUMO levels of all four dyes are higher than the conduction band edge of TiO_2.

The HOMO level of the dye needs to be sufficiently lower than the redox couple to ensure the efficient regeneration of the dye (Calogero *et al.*, 2013). The most widely used redox couple in the electrolyte of DSSC is the I^-/I^{3-} pairs where the estimated energy level is at - 4.8 eV (relative to vacuum) (Lee & Yang, 2011). The HOMO of brazilin, haematoxylin, brazilein and haematein were - 5.66 eV, - 5.64 eV, - 5.55 eV and - 5.57 eV, respectively, which are more negative than the energy level of the redox couple.

Optical properties

TDDFT calculation simulated the optical properties of the dyes. The first excitation state of all four dyes were predominantly a HOMO → LUMO transition ($\pi \rightarrow \pi^*$-type electron cloud transition), and all yield the highest oscillator strength (Table 1, Figure 2). The energy transition for the second excitation state is HOMO - 1 → LUMO, while at the third excitation state, all four dyes displayed different energy transition states.

The absorption bands of both brazilin and haematoxylin were in the UV region, whereas brazilein and haematein absorption bands were at the visible spectrum region. The estimated molar extinction coefficient ε of brazilin, brazilein, haematoxylin and haematein were 6600, 30200, 6400 and 31000 M^{-1} cm^{-1}, and the peak absorbance maxima λ_{max}, were 258 nm, 434 nm, 259 nm and 434 nm, respectively. The oxidized analogues of the dyes (brazilein and haematein) were observed to produce stronger absorption bands than the non-oxidized dyes (brazilin and haematoxylin).

Both brazilin and haematoxylin were reported to have the same λ_{max} at 292 nm (experimental UV-vis data). Thier oxidized analogues (brazilein and haematein) were reported to have their λ_{max} at 445 nm (Bettinger & Zimmermann, 1991; Dong *et al.*, 1997; Gulmini *et al.*, 2013). The suggested reason for brazilin and haematoxylin to have the same UV-vis absorption maxima may be due to the similarity in the chemical structure (Figure 1), and the same reason is suggested for the oxidized analogues of the dyes. These reported experimental UV-vis data are close to the theoretical values obtained by TDDFT calculation. Furthermore, the absorption band pattern of the experimental UV-vis absorption spectra of both haematoxylin and haematein (not shown here) (Bettinger & Zimmermann, 1991) resemble the UV-vis absorption spectra (Figure 2) derived from TDDFT.

Oscillator strength *f*, is the strength of the transition of the dye from one energy state to another (i.e. from HOMO to LUMO) and is related to light harvesting efficiency (LHE) (Wang *et al.*, 2013). The value of the oscillator strength determines the capability of the dye as a photo-sensitizer. A higher oscillator strength indicates the more usefulness of the dye as a photo-sensitizer (Heera & Cindrella, 2010). The oscillator strength (at first excitation state) of brazilein and haematein were 0.701 and 0.534, respectively, while brazilin and haematoxylin were 0.138 and 0.146. At the second and third excitation states, the oscillator strength of all four dyes were much lower than at the first excitation state. It was deduced that the oxidized dyes (brazilein and haematein) are better photo-sensitizers than non-oxidized dyes (brazilin and haematoxylin).

Deprotonation (proton affinity)

Deprotonation is the energy difference between the optimized protonated and deprotonated molecules, usually calculated in the gas phase. No solvation effect is included in the calculation because the solvation sphere is artificially restricted (Qin & Clark, 2007; Liu, 2008).

The hydroxyl (-OH) group and the carboxyl group (-COOH) are the two common functional groups of a natural dye that anchors the dye molecules to the metal oxide semiconductor such as TiO_2 (Heera & Cindrella, 2010; Calogero *et al.*, 2013). By calculating the proton affinity, it can be determined as to which of the hydroxyl groups of a dye is the most probable anchor group. The group with the lowest value of the proton affinity indicates the most probable group that anchors to the metal oxide semi conductor (Qin & Clark, 2007; Heera & Cindrella, 2010).

Brazilin molecule contains four hydroxyl groups. The deprotonation order of brazilin starting from the lowest energy value was $H2 < H1 \approx H4 < H3$ (Table 2). As H2 of brazilin has the lowest energy, it is the most probable anchoring group. Brazilein contains only three hydroxyl groups, and the deprotonation order was $H3 < H1 < H2$, thus H3 is the most probable anchoring group of brazilein.

Haematoxylin contains five hydroxyl groups, and the deprotonation order is $H2 < H5 < H1 < H4 < H3$. The most probable anchoring group is H2. The deprotonation energy values of H2 and H5 are close (difference of 5.2 Kcal mol^{-1}), and thus H5 may also be favourable as an anchoring group. Haematein contains four hydroxyl groups and the deprotonation order is $H4 < H3 < H1 < H2$. The most probable anchoring group of haematein is H4.

Electronic structure

The model of electronic structure of the dyes as seen in Figure 3, displays the density of the electron clouds at different energy levels. The information regarding where the electron clouds are concentrated will be useful to predict whether the electron transfer system is efficient. Brazilin molecule consists of two major units, which are the 3,4-dihydro-*2H*-chromen-3,7-diol unit (CMD) and the 2,3-dihydro-*1H*-indene-5,6-diol unit (IDD) (Figure 1). At HOMO - 1 level, the π-type electron cloud was localized in the CMD unit, while at HOMO level, the π-type electron clouds shifted to the IDD unit (Figure 3). At LUMO level, the π*-type (anti-bonding) electron clouds delocalized over the entire molecules, with much denser electron clouds localized at the IDD unit. LUMO - 1 level displayed the same electron cloud pattern as LUMO level, except that denser electron clouds were found to localize in the CMD unit. As previously mentioned the first excitation state of the dye is a HOMO → LUMO transition. The injection of electrons to the metal oxide semiconductor is mostly facilitated by the dense electron clouds localized near to the anchoring group (H2 hydroxyl group) at the LUMO level.

Brazilein dye consists of a CMD unit and a 6-hydroxyl-2,3-dihydro-*5H*-inden-5-one unit (HDI). At HOMO - 1 and HOMO level, π-type electron clouds were observed to delocalize over the entire molecule. At LUMO level, the delocalization of π*-type electron clouds over the entire molecules were observed. The electron cloud covering the anchoring group (H3 hydroxyl group) at LUMO level can facilitate the injection of the electrons into the metal oxide semiconductor. At LUMO - 1, the π*-type electron clouds delocalized over the entire molecule, and a higher density of electron cloud is observed at the CMD unit.

Table 2: Energy values of the deprotonation order (proton affinity) of the oxidized and non-oxidized dyes in Kcal mol^{-1}

Sensitizers	Deprotonation order (Kcal mol^{-1})				
	$-H1^+$	$-H2^+$	$-H3^+$	$-H4^+$	$-H5^+$
Brazilin	341.1	326.1	358.1	341.7	
Brazilein	334.1	344.0	313.0		
Haematoxylin	341.7	326.7	359.9	347.0	331.9
Haematein	334.8	345.0	330.2	306.2	

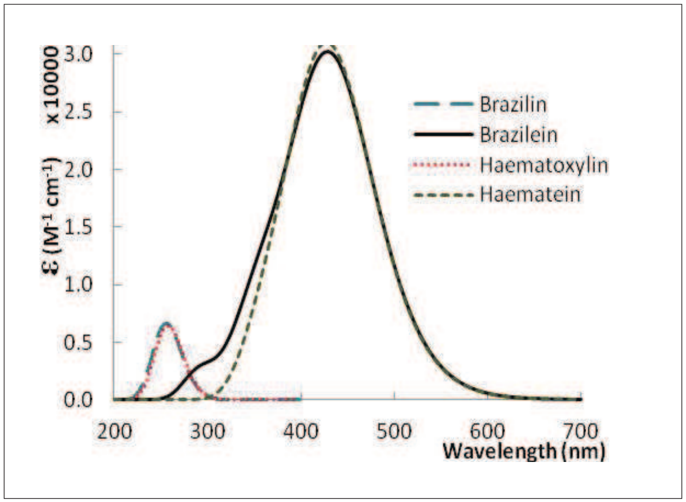

Figure 2: Simulated UV-vis absorption spectra of brazilin, brazilein, haematoxylin and haematein

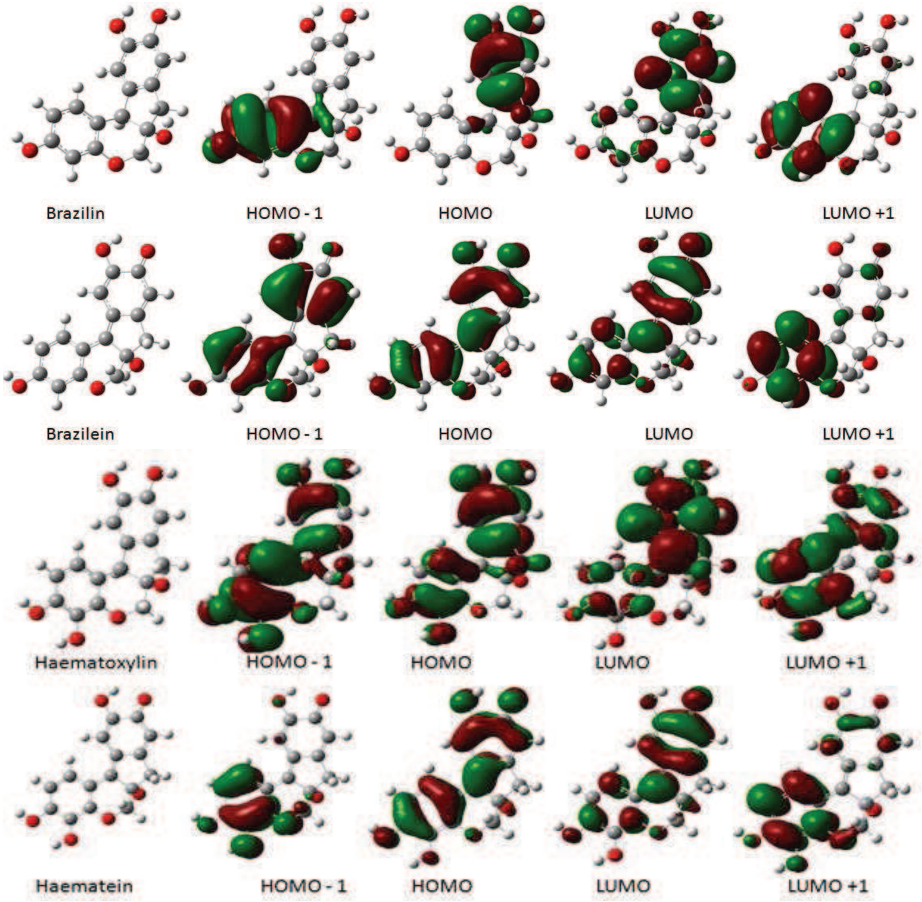

Figure 3: Electron structures of the dyes, at various energy levels. Models were visualized using GaussView 5 at isovalue of density = 0.03

Haematoxylin consists of a 3,4-dihydro-*2H*-chromen-3,6,7-triol unit (CMT) and an IDD unit. Delocalization of the electron clouds was observed for HOMO – 1, HOMO, LUMO and LUMO +1 level. HOMO -1 and HOMO level electron clouds are π-type, whereas LUMO and LUMO +1 are π*-type. The density of the electron clouds was observed to be higher in the IDD unit of LUMO while it was higher in the CMT unit at LUMO + 1 level. With a dense electron cloud localized close to the anchoring group (H2 hydroxyl group) during LUMO, electron transfer to the metal oxide semiconductor is favourable for HOMO → LUMO transition.

Haematein consists of a CMT unit and a HDI unit. Localization of π-type electron at the CMT unit was observed at HOMO -1, while at HOMO level delocalization of the π-type electron cloud was observed over the entire molecule. At LUMO level, π*-type electron clouds are delocalized over the entire molecule. As the anchoring group (H4 hydroxyl group) is covered by electron clouds at LUMO level, electrons can be injected into the metal oxide semiconductor. Lastly, at LUMO + 1 level, the π*-type electron cloud was localized in CMT unit, and with lower density of electron cloud localized at the 2-hydroxylcyclohexa-2,5-dien-1-one unit of HDI unit exposing the cyclopentene ring.

When taking both the deprotonation energies and the electronic structure into account, it is possible to deduce which particular anchoring group of the molecule is the most favourable (Ekanayake *et al.*, 2013). The hydroxyl anchoring group with the lowest deprotonation energy of brazilin, haematoxylin and their oxidized analogues are covered with electron clouds at LUMO level, thus these anchoring groups are deduced to be the most profitable to attach to the metal-oxide semiconductor.

CONCLUSION

All four dyes displayed a HOMO → LUMO transition at the first excitation state. The hydroxyl groups of the dyes brazilin, brazilein, haematoxylin and haematein that have a potential to anchor to the semiconductor are H2, H3, H2 and H4 group, respectively. At LUMO level, the electron clouds of all four dyes appear near or at the anchoring group of the dyes, which facilitates electron injection into the metal oxide semiconductor. The LUMO of all four dyes is higher than the conduction band edge of TiO_2, which is favourable for efficient electron injection. The HOMO level of the four dyes is lower than the redox couples (I^-/I^{3-}), which helps to regenerate the dye. Of the four dyes investigated, the analysis of calculated optical properties revealed that brazilein and haematein have the potential as sensitizers in dye sensitized solar cells.

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