

## Structural Studies of Plant Pigments Used in Dye Sensitized Solar Cells

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### Introduction

In the modern world, there exists a high demand for pure and clean sources of energy. Solar cells can be identified as a good candidate for this category. The use of natural dyes as sensitizers for solar cells is justified by the need to produce energy which is at the same time reliable, safe and eco-friendly (O'Regan and Gratzel, 1991). Generally, anthocyanins are considered as suitable natural pigments to be used in dye sensitized solar cells.

Anthocyanins are water soluble pigments which can be found in most land plants with a few exceptions such as cacti and the group containing the beet. These pigments reflect the red to blue range of the visible spectrum. Therefore, they are responsible for the red, purple and blue colours in many fruits, vegetables, grains and flowers.

Anthocyanins can be divided into sugar free anthocyanin aglycons and anthocyanin glycosides with sugar moieties attached. There are many types of anthocyanins present in nature which are named according to the types and positions of functional groups attached to the central core of the anthocyanin molecule. The most abundant anthocyanin in nature is cyanin.

The use of anthocyanins in dye sensitized solar cells can be justified, as the structure of the molecule suggests possible anchorage to titanium dioxide.

This paper presents the structural study of natural pigments used in dye sensitized solar cells with the aid of Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy and theoretical calculations of vibrational modes using hybrid Hartree-Fock/density functional theory (HF/DFT).

### Materials and methods

Pigments were extracted from three sources namely purple yam, pomegranate seeds and spinach seeds. The pigment from purple yam

was extracted in a 50% methanol solution, while pigments from pomegranate and spinach were extracted by squeezing the seed coats and filtering the juice. Further, a purification method was followed in order to isolate anthocyanins from any impurities, which may have been present in the extracted pigment. UV-Visible spectroscopy was used to identify the presence of anthocyanins in all three pigment samples.

In order to analyze the pigment samples using DRIFT spectroscopy, they were converted from liquid form to powder form by mixing with potassium bromide (KBr) powder followed by drying. Spectra corresponding to the pigment alone and the pigment adsorbed onto TiO<sub>2</sub> were separately obtained for each sample. Hybrid HF/DFT calculations were done using the B3LYP method within Gaussian 03 to quantify the vibrational properties of the pure pigment and the pigment adsorbed to TiO<sub>2</sub>.

### Results

The cyanidin models in Figure 1 were used in the theoretical calculations carried out. Model A corresponds to the pure cyanidin molecule, while model B is the molecule after binding with Ti. In Figures 2, 3 and 4, experimental and calculated spectra corresponding to each sample studied were compared.

The encircled area in the experimental spectra in Figure 2 shows the disappearance of the band around 1077 cm<sup>-1</sup>, which corresponds to the free OH bending mode. Similarly, the encircled area of the calculated spectra in Figure 2 also shows the disappearance of the band around 1100 cm<sup>-1</sup>.

The encircled area of the experimental spectra in Figure 3 shows the downward shift of the band around 1400 cm<sup>-1</sup>, which corresponds to the OH bending and C-C stretching mode. Similarly, the encircled area in the calculated spectra in Figure 3 also shows the clear downward shift of the band around 1400 cm<sup>-1</sup> after adsorption onto TiO<sub>2</sub>.

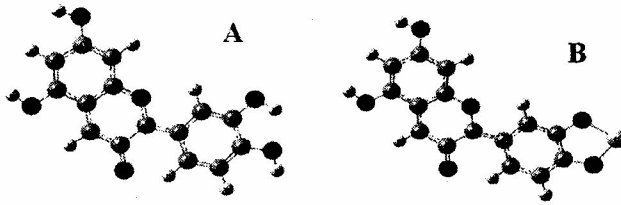


Figure 1. Cyanidin models used in vibrational mode calculations

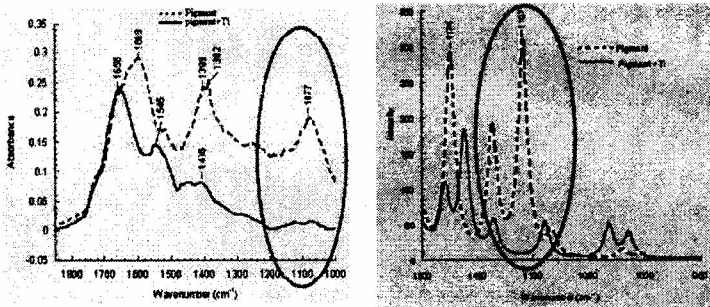


Figure 2. Experimental DRIFT spectra for spinach (left) and calculated spectra for the cyanidin models (right)

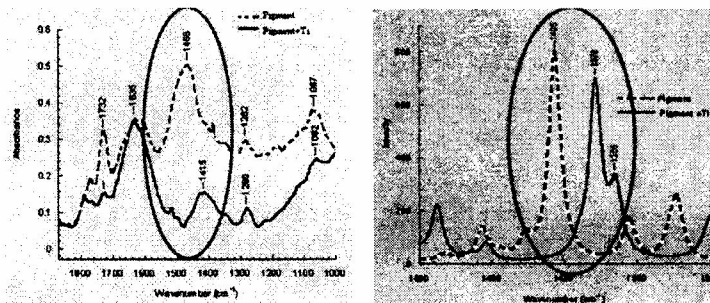


Figure 3. Experimental DRIFT spectra for purple yam (left) and calculated spectra for the cyanidin models (right)

The encircled area of the experimental spectra in Figure 4 shows the downward shift of the band around  $1700\text{ cm}^{-1}$ , which mainly corresponds to the C=O stretching mode, after adsorption onto  $\text{TiO}_2$ . The encircled area of the calculated spectra in Figure 4 also shows the downward shift of the band around  $1700\text{ cm}^{-1}$  after adsorption onto  $\text{TiO}_2$ .

## Conclusions

From both experimental and theoretical results, it can be concluded that:

1. Experimental results for all the pigments well agree with the theoretical results calculated for the cyanidin model.

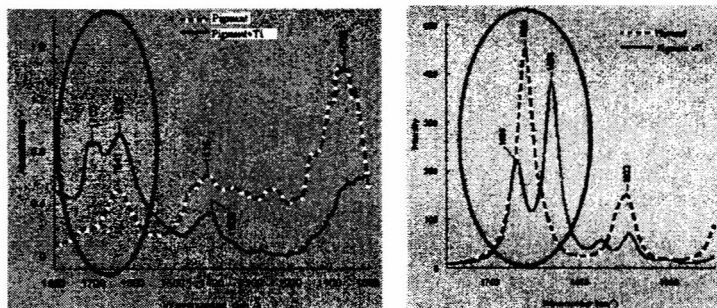


Figure 4. Experimental DRIFT spectra for pomegranate (left) and calculated spectra for the cyanidin models (right)

2. A band corresponding to the free OH bending mode around  $1100\text{ cm}^{-1}$  disappears after adsorption to  $\text{TiO}_2$ . This proves that the anchoring to Ti is through hydroxyl groups of cyanidin.
3. The band corresponding to the OH bending and C-C stretching around  $1400\text{ cm}^{-1}$  shifts downwards upon adsorption to Ti. Similarly, another band around  $1700\text{ cm}^{-1}$  mainly corresponding to C=O and C=C stretching modes splits upon adsorption. These shifts and splits are mainly due to the change in electron

density of the cyanidin molecule upon adsorption to Ti.

#### Acknowledgements

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#### References

- O'Regan, B. and Gratzel, M. (1991) A low-cost, high efficiency solar cell based on dye-sensitized colloidal  $\text{TiO}_2$  films, *Nature*, 353, 737.