

# Water Soluble Porphyrin based Solar Cell

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**Abstract.** Porphyrins are organic chromophores with structure very close to naturally occurring pigment in leaves – Chlorophyll. In addition, blood cells are red due to iron porphyrins. These versatile porphyrins are simple to synthesize and easy to modify for different applications. By introducing ionic charges they could be made water soluble. Water Soluble Porphyrins (WSP) are known to interact with DNA and their application includes medical and catalysis. Currently harvesting solar energy has become the top priority in research. Different types of porphyrins are also being studied at present as potential sensitizer. Here we report unique way of using 3 different types of WSP for harvesting sunlight. Our simple strategy is to utilize positively charged WSP to decorate negatively charged tin oxide nanoparticles. This kind of anion-cation interaction led to a strong interaction between them. We used UV-visible absorption spectroscopy, Fluorescence spectroscopy, to investigate their strength of interaction. In order, to understand their effectiveness in solar energy harvesting, we conducted photo electrochemical experiment on WSP modified tin oxide electrodes. Our results showed Incident Photon Conversion Efficiency (IPCE) around 91 % at 450 nm. In other word, 91 out of 100 photons corresponding to 450 nm light is converted to current.

## 1. Introduction

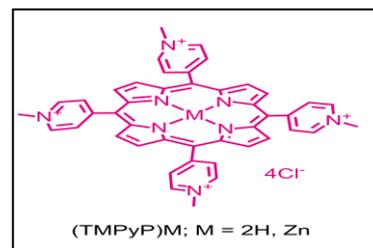
Energy related research is one of the highly discussed subjects due to pronounced energy consumption and raising global environmental issues. One of the feasible solutions is finding ways to decrease the consumption of fossil fuels and increase the usage of renewable energy resources. Of available natural resource solar energy is very promising because of its availability and high energy density (1000 mW/cm<sup>2</sup>).

To harvest solar energy, highly energy efficient solar cells are needed. Solar cells are broadly classified as inorganic solar cell, dye sensitized solar cells and organic solar cells. Most of the research is now focused on adapting different techniques and strategies in building efficient but less expensive solar cells. In dye sensitized solar cell, dyes play a very important of absorbing sunlight<sup>1</sup>. Here we report water soluble porphyrin as the potential sensitizer for preparing efficient solar cell. We used anion-cation supramolecular interaction in order to build the solar cell. In such cells, our dye outperforms the other reported dye in light harvesting efficiency.

## 2. Experiment

Water soluble porphyrins shown in the scheme 1 were synthesized using and characterized using NMR. In order to understand their interaction with SnO<sub>2</sub> nanoparticle, which possesses a negative charge UV-Visible absorption, fluorescence and steady state lifetime measurement, were performed in water. Stability of the interaction was tested by adding an ionic salt such as lithium perchlorate. To prepare solar cells nanocrystalline tin dioxide (SnO<sub>2</sub>) were drop casted on to a conducting glass surface and heated at 400°C for 30 minutes in air. Then the electrodes were sensitized using the water soluble porphyrins. Then absorption spectrum of the electrodes was measured to understand the nature of interaction. Photoelectrochemical experiments were carried out to check the performance of the cell using AM1.5 solar simulator. Incident Photon Conversion Efficiency (IPCE) was calculated using the following formula.

$$IPCE(\%) = \frac{I_{sc}(A) \times 1240}{P_{in}(W) \times \lambda (nm)} \times 100$$
 Where  $I_{sc}$  is short circuit current,  $P_{in}$  is incident light power density at a particular wavelength ( $\lambda$ ) respectively.



Scheme -1 Structure of water soluble porphyrins Tetra n Methyl-Pyridyl Porphyrin (H<sub>2</sub>TMPyP) & Zinc Tetra n Methyl-Pyridyl Porphyrin ZnTMPyP.

### 3. Results, Discussion, and Significance

Inherently SnO<sub>2</sub> nanoparticles are negatively charged and so when positively charged porphyrin (H<sub>2</sub>TMPyP and ZnTMPyP) was added during a titration, it showed a strong 1:1 binding complex as shown Fig. 1a (UV absorption spectrum for H<sub>2</sub>TMPyP). Similar results were obtained for ZnTMPyP also. Calculated binding constant was  $1.8 \times 10^4$  and  $1.77 \times 10^4 \text{ M}^{-1}$  for ZnTMPyP and H<sub>2</sub>TMPyP respectively. Also strong binding resulted in a 40-50 nm red shift in the H<sub>2</sub>TMPyP absorbance spectrum. This large shift is attributed to flattening of porphyrin molecule upon adsorption on SnO<sub>2</sub> surface<sup>2</sup>. From the fluorescence spectrum (Fig 1b.) we confirmed that the intensity of the porphyrin emission bands decreased with continuous addition of SnO<sub>2</sub> when it was excited at 517 nm. Quenching of fluorescence indicated efficient electron transfer from the porphyrin to SnO<sub>2</sub> upon excitation. This was confirmed as the lifetime of the electrons in excited state decreased in presence SnO<sub>2</sub> from 4.9 ns to 3.5ns Fig. 1c. Additional experiments were performed to visualize the stability of electrostatically adsorbed porphyrin dyes onto to SnO<sub>2</sub> surface by monitoring the recovery of fluorescence due to addition of LiClO<sub>4</sub> (red line in Fig. 1d). Calculations showed 80% of quenched porphyrin (black line in Fig.1d) could be recovered. This effect can also be seen visually Fig.1d inset where under UV lamp H<sub>2</sub>TMPyP (1) red emission light turns off in presence of SnO<sub>2</sub> (3) and recovered back when LiClO<sub>4</sub> was added (2) to the solution. The recovery effect can attributed to the fact that stronger ion binding nature of Li<sup>+</sup> to SnO<sub>2</sub> releases H<sub>2</sub>TMPyP back in to the solution confirming purely electrostatic interaction between SnO<sub>2</sub> and H<sub>2</sub>TMPyP.

Photoelectrochemical experiments were performed as illustrated in Fig 1e using 2 electrodes – a dye sensitized SnO<sub>2</sub> electrode and platinum foil separated with a spacer and a redox mediator comprised of Iodide and Iodine in acetonitrile. Fig.1f shows the image of porphyrin modified SnO<sub>2</sub>. Photocurrent switching with respect to time for ZnTMPyP (green), H<sub>2</sub>TMPyP (blue) bound SnO<sub>2</sub> and Plain SnO<sub>2</sub> (pink) electrodes of the same thickness are shown in Fig.1g. It is very evident that SnO<sub>2</sub> upon ZnTMPyP and H<sub>2</sub>TMPyP modification generates photocurrent up to 5mA/cm<sup>2</sup> and 4mA/cm<sup>2</sup> respectively. To understand the reason behind such high photocurrent generation process, Incident Photon to Current conversion Efficiency was calculated for entire visible portion of sunlight from 400- 800 nm as shown in Fig 1h. Shape of IPCE spectrum resembles the shape of solution absorbance spectrum and also ZnTMPyP outperforms H<sub>2</sub>TMPyP in absorbing higher wavelength light where the energy density of sunlight is higher. It is worth mentioning that the IPCE conversion of 90% at 450 nm achieved in our system using water soluble porphyrins is the highest obtained so far. Having found this efficient system research is going on to improve the material property so that highly energy efficient solar cell could be obtained in near future.

### 4. Conclusions

Here we reported an efficient light harvesting system by taking advantage of ionic interactions between positively charged water soluble porphyrins and negatively charged tin dioxide nanoparticles. A systematic solution based study revealed strong electrostatic binding event resulted in good electronic interaction between them. As a result, very high photocurrent generation and highest photon conversion efficiency was observed.

**5. Acknowledgement:** We thank WSU, NSF, and NSF-EPSCOR for funding and support.

1. B. Oregan and M. Gratzel, *Nature*, 1991, **353**, 737-740.
2. Z. Chernia and D. Gill, *Langmuir*, 1999, **15**, 1625-1633.

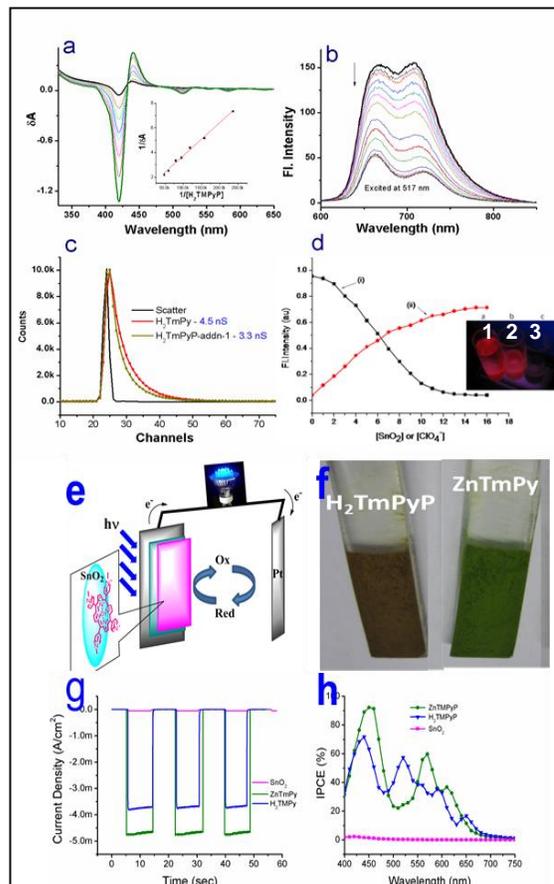


Figure 1. (a) Change in UV absorbance upon addition of H<sub>2</sub>TMPyP to SnO<sub>2</sub> (inset: binding constant determination using Benesi-Hildebrand plot). (b) Fluorescence change upon addition of SnO<sub>2</sub> to H<sub>2</sub>TMPyP. (c) Steady state lifetime measurement (d) Effect of adding Lithium perchlorate (e) Scheme of solar cell construction (f) Picture of porphyrin adsorbed electrodes (g) Photocurrent switching experiment (h) Incident Photon Conversion Efficiency (IPCE) spectrum of the surface modified electrodes H<sub>2</sub>TMPyP-blue, ZnTMPyP-green, unmodified SnO<sub>2</sub>-pink