

WICHITA STATE UNIVERSITY

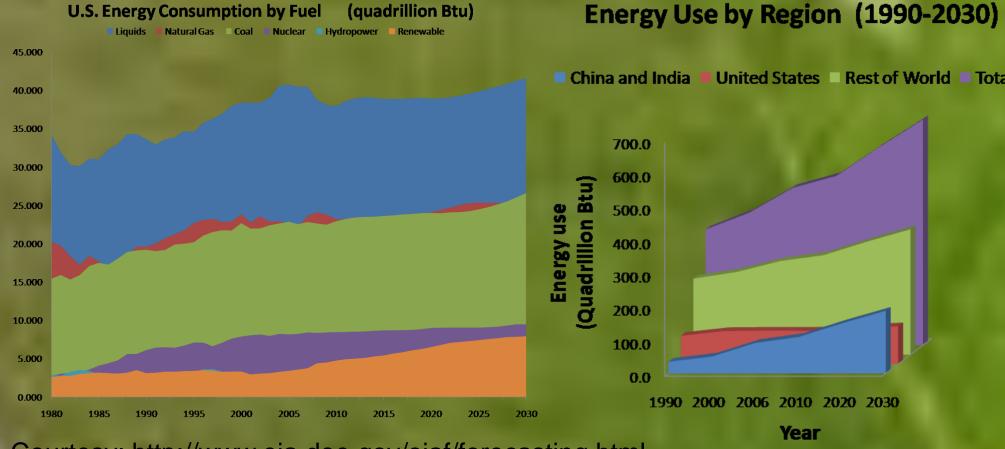
Abstract

Exploring sustainable energy resources are becoming important due to the predicted oil depletion and soaring CO₂ levels in the atmosphere. Of available alternatives, solar energy finds special attention due to its vast availability and high power density of 1000 watts per square meter. Various mechanisms have been carefully employed to harvest the solar power including semiconductor silicon based photovoltaic, inorganic/organic dye sensitized or bulk heterojunction solar devices. Some of the latter devices utilize donor-acceptor supramolecular systems designed based on natural photosynthesis. Here, self-assembly of energy donor and acceptor is proved to be an important criterion.

In the present study, we demonstrate an elegant method of self-assembly to modify TiO₂ surface using coordinating ligands followed by immobilization of a variety of photosensitizers and dyads. This method, in addition of testing the photoelectrochemical behavior of simple zinc tetrapyrroles also allows us to introduce fairly complex structures involving more than one donor and/or acceptor entities. As will be demonstrated, of all macrocycles studied, a biomimetic zinc porphyrin-ferrocene dyad markedly improves the current-voltage performance of the photoelectrochemical cell due to an electron transfer-hole migration mechanism. Incident photon-to-current efficiency value up to 37%, highest value reported for this type of devices is obtained for the electrode modified with the dyad, highlighting the importance of photocells built based on biomimetic principles for efficient harvesting of solar energy.

Introduction

Are We in need of More Energy?

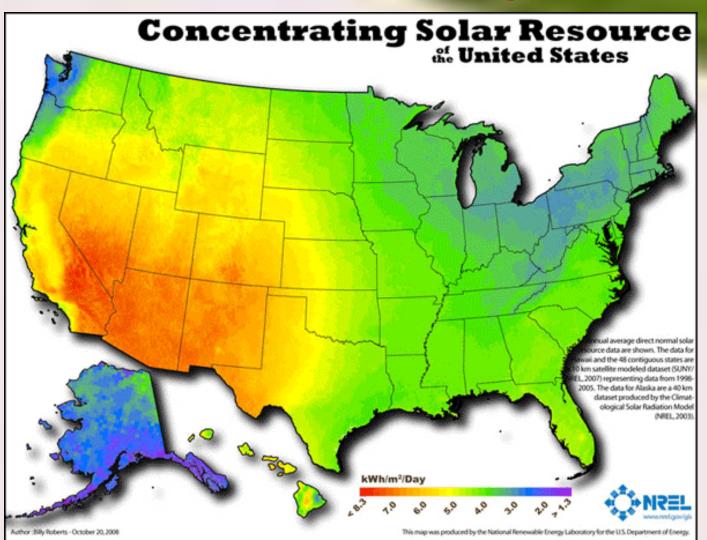


Courtesy: http://www.eia.doe.gov/oiaf/forecasting.html

1 BTU = 1 055.05585 joules

 Increase in the energy consumption per year necessitates alternate energy source

Why Should Attempts be Made to Harvest Solar Energy???

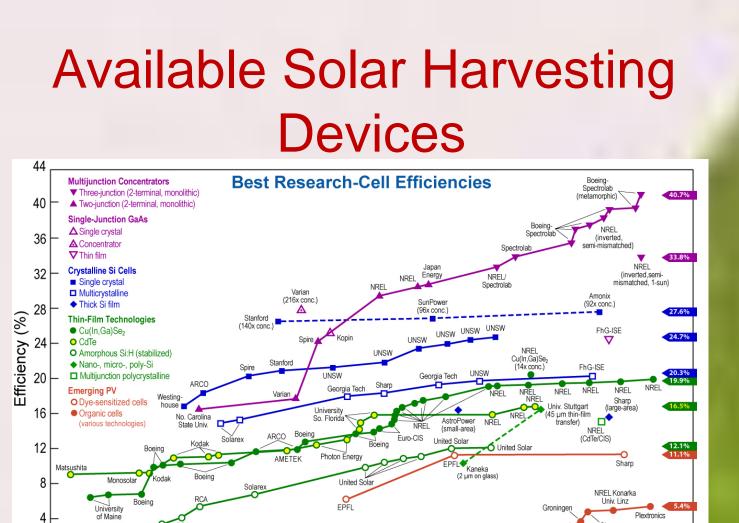


•Widely available •More powerful (1000 W/m²)

>Dye could be self assembled on a TiO₂ surface by adapting axial ligation

Advantage > No need for acid functional group Possible to assemble different dyes on TiO₂ layer covering entire visible region (400-800 nm)

Solar Energy Harvesting Device – Biomimetic Solar Cell Navaneetha K. Subbaiyan* and Francis D'Souza **Department of Chemistry, Wichita State University**



Courtesy: http://en.wikipedia.org/wiki/Solar_cells

 Inorganic PV devices are efficient but expensive.

•Dye Sensitized Solar Cells (DSSC) are made up of Titanium dioxide (TiO_2) . • Organic Solar Cells are less efficient.

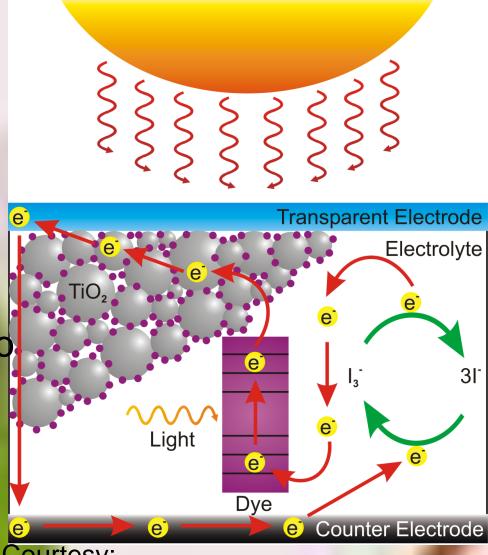
How does a DSSC Work?

•Dye absorb sunlight and inject electron into TiO₂ resulting in photo current

•Maximum 11% efficiency reported till now

•Dye should contain acid functional group to adsorb on TiO₂

• A Dye should absorb visible light (400-800 nm) – Research Target



http://upload.wikimedia.org/wikipedia/commons/ f/fd/Dye_Sensitized_Solar_Cell_Scheme.png

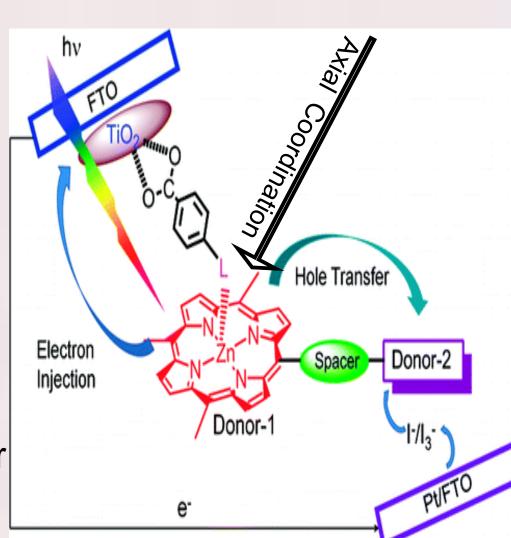
Natural Photosynthesis



Self Assembly ofelectron donor-

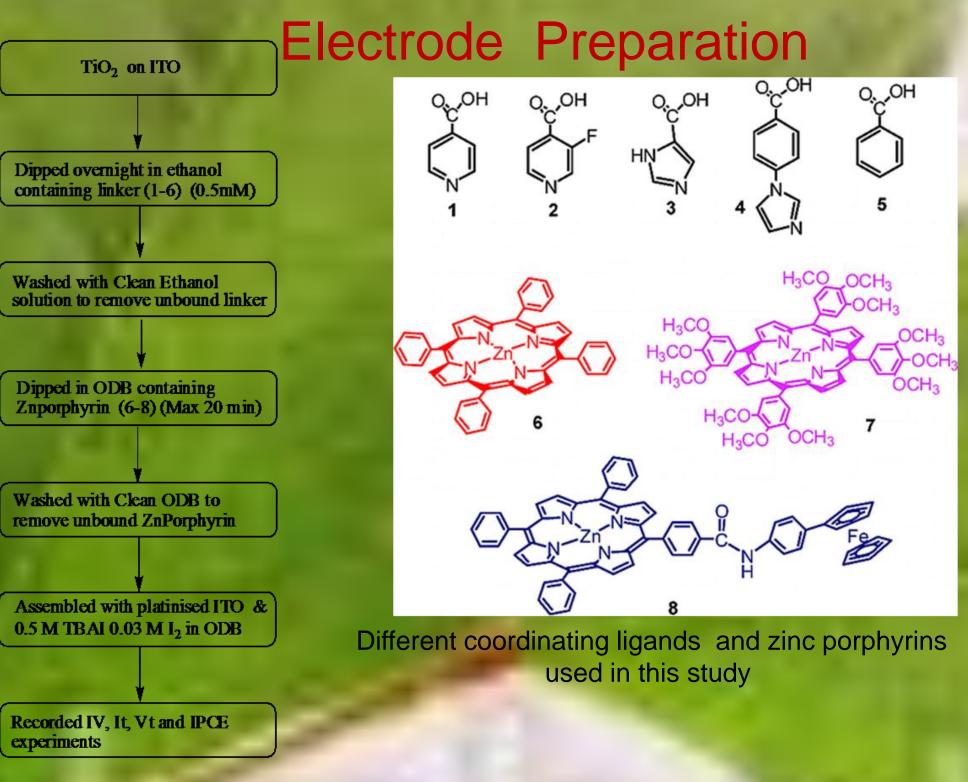
Pigments in leaves are self assembled to trap sunlight

Our Approach- Self Assembly

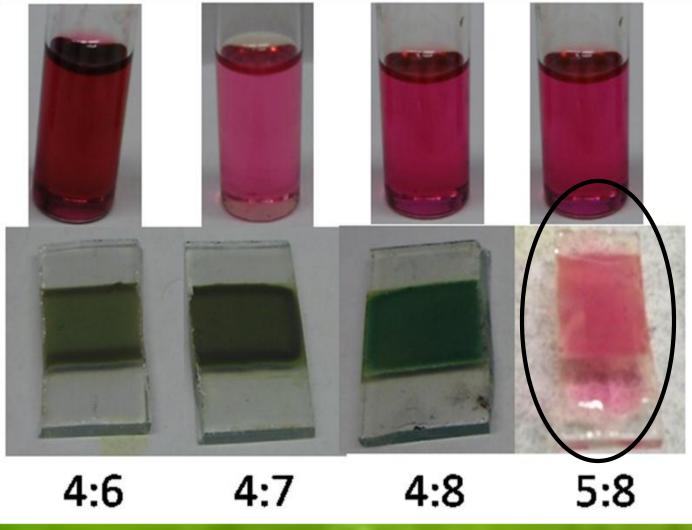


≥ -0.5 0 -1.0. 5 -1.5

Supramolecular Solar Cells: Surface Modification of Nanocrytalline TiO₂with **Coordinating Ligands To Immobilize** Sensitizers and Dyads via Metal-Ligand **Coordination for Enhanced Photocurrent** Generation



Axial Coordination on TiO₂ Surface



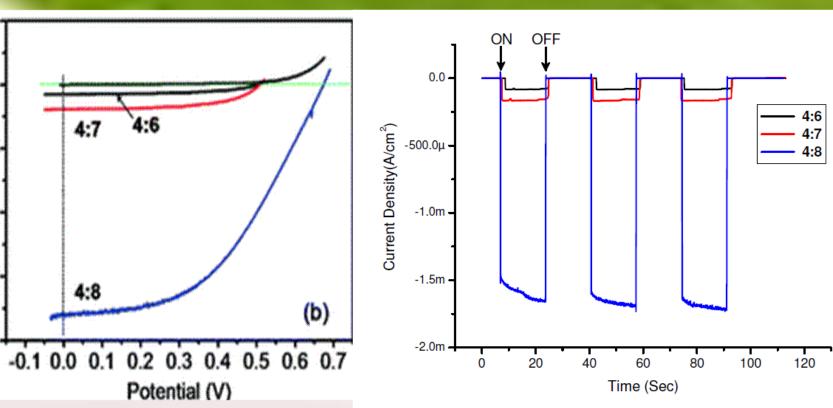
Evidence for axial ligation occurrence

Green color confirms axial coordination and lack of ligand in **5:8** shows simple adsorption

Photoelectrochemical studies

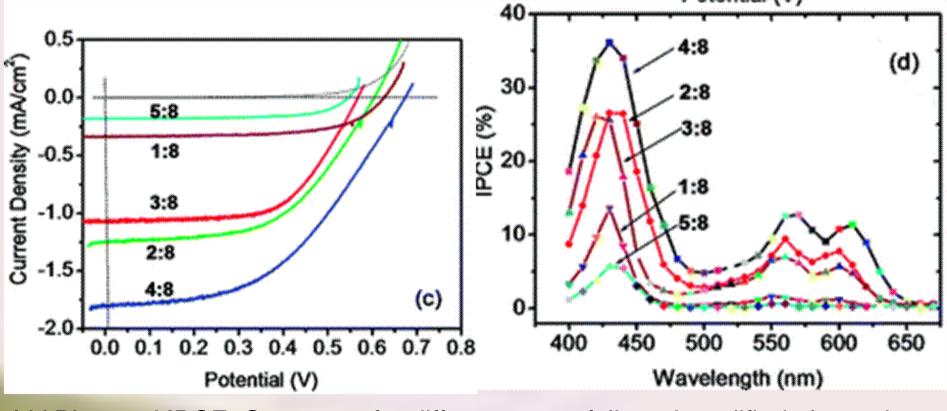
Different types of zinc porphyrin modified electrodes (versatility of this method)

- Zn porphyrin- ferrocene (8) showed better photo response than other two compounds
- Current switching experiment shows that it is reproducible indicating the stability of the supramolecular photoelectrochemical system



I-V plot and I-t plot for different porphyrin modified electrodes using ligand 4

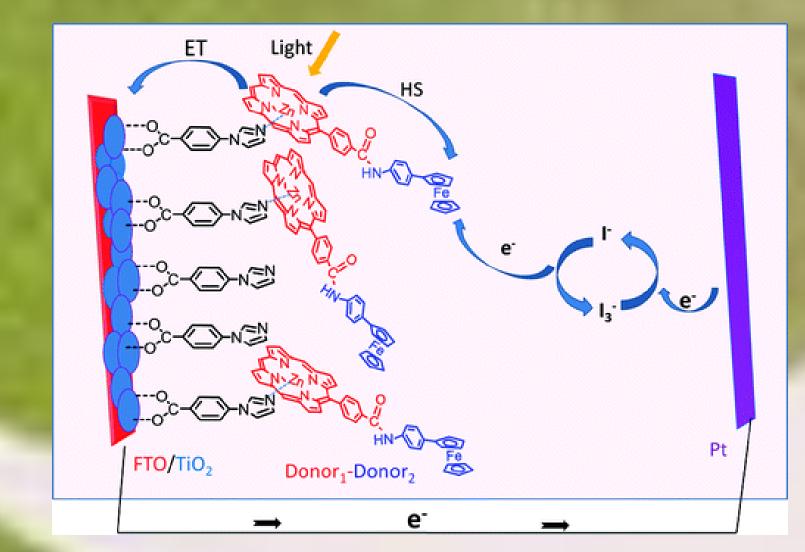
Influence of Different Coordinating Ligands



I-V Plot and IPCE Spectrum for different type of ligand modified electrode

Strength of coordination varies depending on type of ligands and so their on binding constant (4>2>3>1) Highest performance by (4:8) system (36% Incident Photon Coversion Efficiency) due to strong binding and better charge separation.

Mechanism for high performancevectorial electron transfer



Proposed mechanism for Photocurrent generation of the Dyad

•Electron injection from zinc porphyrin into TiO₂ nanoparticle

• Ferrocene donates the electron to porphyrin cation to prevent back electron transfer resulting in better performance.

Conclusion

* Self assembly of different types of dye molecules is possible by using axial ligation technique.

Increased charge separation facilitates better performing solar cell.

☆Highest IPCE value of 36% was obtained in current study.

Set to improve the performance using different dyes are under study.

Acknowledgements

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