

Molecules for Converting Sunlight into Electricity

Dye Sensitized Nanocrystalline-TiO₂ based Photovoltaics

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Ravi Mosurkal is a postdoctoral research associate at Center for Advanced Materials, University of Massachusetts, Lowell, USA. His main research interests are design and synthesis of novel molecular materials for photonics and optoelectronics applications. Currently he is involved in developing efficient photosensitizer dyes for molecular photovoltaics.

The dream of generating electricity from sunlight in large scale at low cost may not be that far from reality in this century. Rapidly emerging solar energy technology using low cost dye sensitized photovoltaic cells on plastics would be a real boost for the third world countries. Though the conventional silicon solar cells are efficient in converting solar energy into electricity until now, the non conventional solar cells based on molecular photosensitization by colored materials in wide band gap semiconductors is a fast growing field of basic scientific and industrial research. Present state-of-the-art cells using molecular dyes shows energy conversion efficiencies of 10-11%. In this article, we present the concept of dye-sensitized photovoltaic (DSPV) cell and the progress in current research. The important contributions of molecular dyes that are used as photosensitizers in these photovoltaic or solar cells are also described.

The conversion of light into electricity was first discovered in 1839 by Edmund Bequerel. He observed the generation of electricity when two electrodes were put in a conducting solution and exposed to light. In the late 19th century many other materials including silicon that convert light into electric energy were discovered. But the efficiency of the solar cells was too low because of the lack of high purity silicon. In 1940-50, when silicon of high purity was produced, a solar cell with 4% efficiency was developed at the Bell Laboratories in USA. The present silicon solar cells have an efficiency up to 30%.

In an entirely different historical background, photography, using dyes with silver halide grains was first discovered in 1873 by Vogel. Since then many scientists have been attracted to-

wards photoelectric molecules. The first observation of injecting electrons by a dye molecule into the conduction band of the semiconductor substrate was reported in 1960's. From then on the concept of dye sensitization developed gradually. Highly efficient sensitization of titanium dioxide (TiO_2) by a ruthenium dye was first published in 1985, which led to the development of a new concept of generating electricity from sunlight. This approach of generating electricity from sunlight has many advantages over silicon solar cell technology. The DSPV cells are much cheaper to manufacture compared to crystalline silicon solar cells. They can be made in transparent modules to integrate into windows and sunroofs. They maintain their performance even in shaded conditions and higher temperatures unlike silicon solar cells. Though various other wide band gap semiconductors such as SnO_2 , ZnO , Nb_2O_5 , WO_3 , SrTiO_3 , etc. were studied, TiO_2 is chosen as an optimum semiconductor for DSPV cells because TiO_2 has many advantages including its long term thermal and photo-stability. It is cheap, abundant, non-toxic, biocompatible and widely used in healthcare products (e.g. toothpaste) and paints. In 1988, Michael Gratzel and others discovered that TiO_2 is the best suited semiconductor for chemisorbing the dyes for efficient light harvesting and energy conversion.

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A schematic diagram of a typical DSPV cell is shown in *Figure 1*. From left to right, the cell components are described as follows. (i) transparent and conducting SnO_2 substrate (ii) titanium dioxide film, photosensitizer dye (adsorbed as shown in *Figure 2*) (iii) redox electrolyte (iodine and potassium iodide mixture in acetonitrile solution) for regenerating the oxidized dye and (iv) conducting SnO_2 counter electrode. All of the components in the device are very important for fabricating an efficient DSPV cell. However, the design and synthesis of ideal dyes for efficient photosensitization has always been the thrust of the research in this area.

The nanocrystalline TiO_2 film is generally prepared as follows. Commercially available colloidal TiO_2 powder with particle size



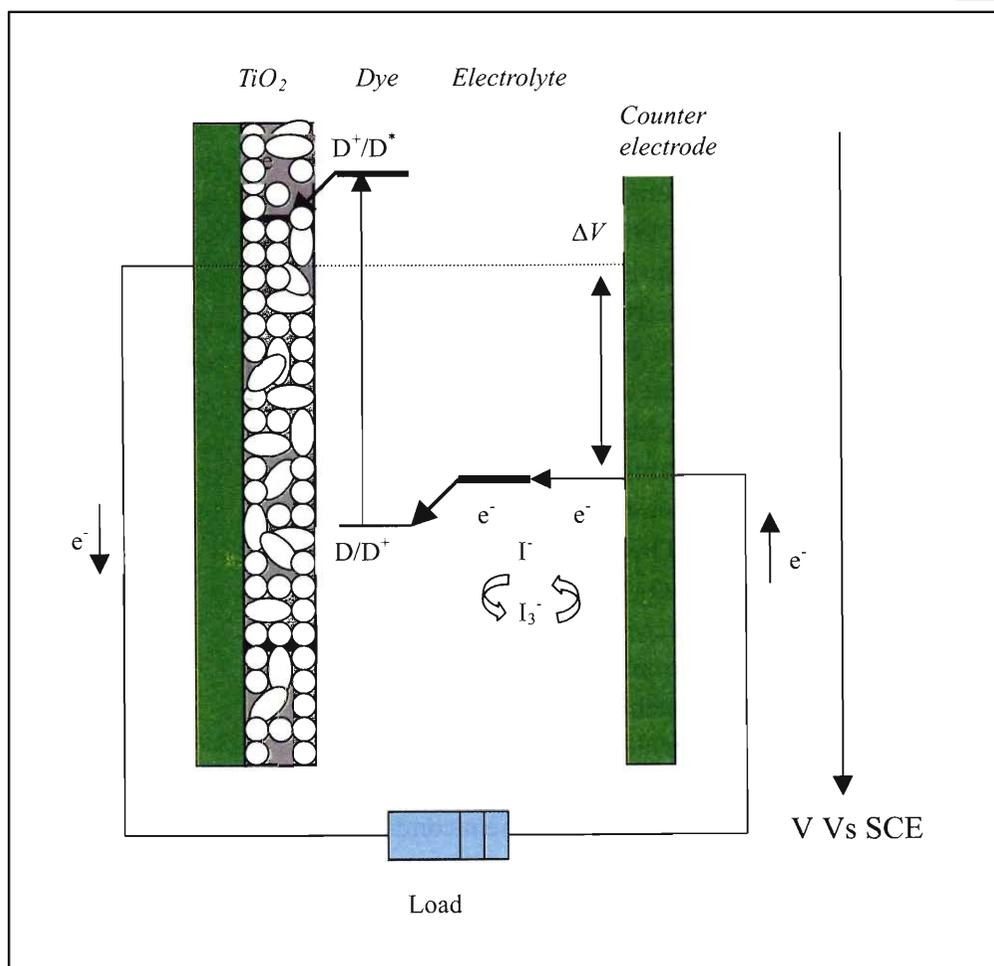


Figure 1. A schematic diagram of dye-sensitized photovoltaic cell.

25-30 nm is made into thin paste in nitric or acetic acid (pH 3-4) by grinding thoroughly. This paste is spread on a conductive SnO₂ substrate and sintered at 450°C for 30 minutes to achieve maximum porosity and surface area in the film. The particle-to-particle contact established in the film after sintering forms the pathway for the conduction of electron that is injected by the dye. After cooling, the TiO₂ plate is soaked in the dye solution in ethanol (~10⁻⁵M) for 3-4 hours or until the substrate is stained with the dye. As shown in *Figure 2*, a monolayer of the dye is formed on the surface of the TiO₂ and the plate becomes colored. The counter electrode can be another SnO₂ plate with a carbon/graphite coating on the conductive side. The carbon

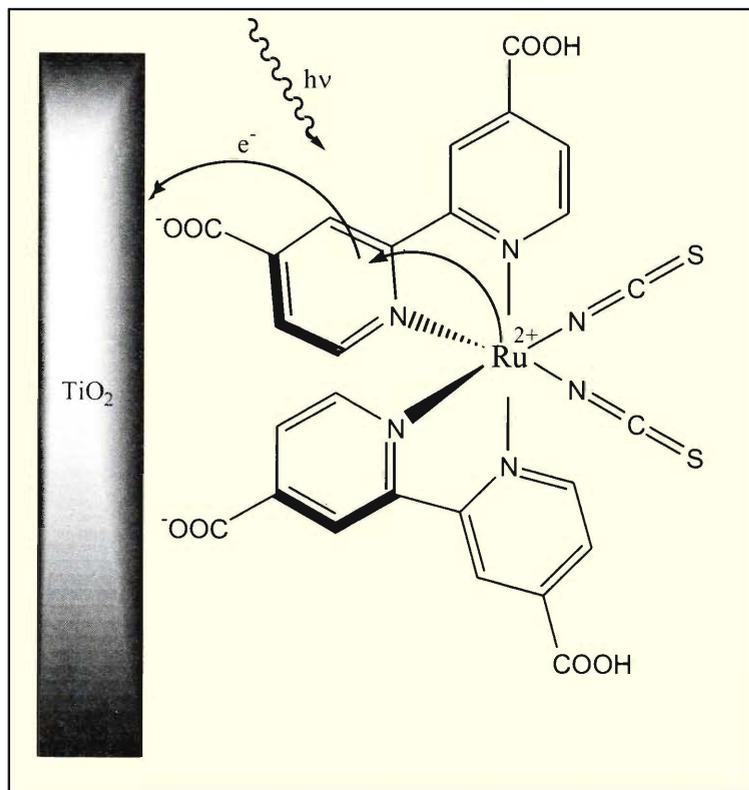


Figure 2. Chelation of the dye onto TiO₂ through carboxylic acid groups.

coating serves as a catalyst in the electrolyte regeneration reaction. Platinum coated SnO₂ substrate is also used as a counter electrode.

The dye stained TiO₂ plate is washed with ethanol and dried and TiO₂ side is faced up. The counter electrode is placed on top of it, facing the conductive side with the TiO₂ film. The plates are held together with binder clips with offset of 4 mm strip of uncoated TiO₂. The contacts are made with crocodile clips at the uncoated portion of the glass plates. Then one or two drops of electrolyte solution are introduced from the edges of the plates in between the two electrodes. This sandwich type solar cell (Figure 3) is exposed to the natural sunlight or simulated AM1.5 (Air Mass 1.5) solar light in lab using xenon or tungsten halogen lamp (100 mWcm⁻²) through the TiO₂ coated plate. AM1.5 light is the average solar light that reaches the earth's atmosphere at an angle of 48° (1/cos 48 = 1.5).

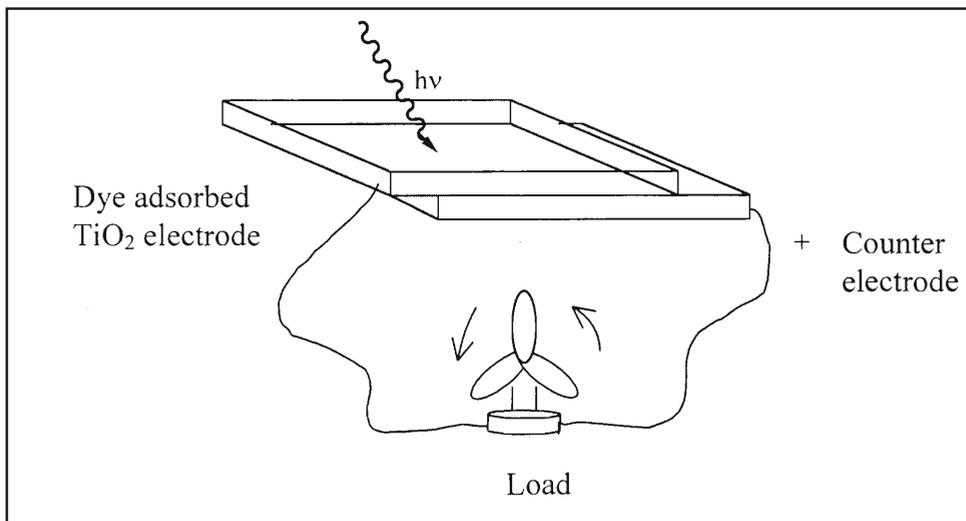


Figure 3. Sandwich type DSPV cell.

The negative electrode is TiO_2 coated SnO_2 and the positive electrode is SnO_2 . The resulting current and voltages are measured using a multimeter. A typical I - V curve measured for a ruthenium dye is shown in *Figure 4*.

The efficiency of an electrical power generating electrochemical solar cell is directly related to the fill factor that is calculated from the I - V power characteristics. The experimental I - V curve

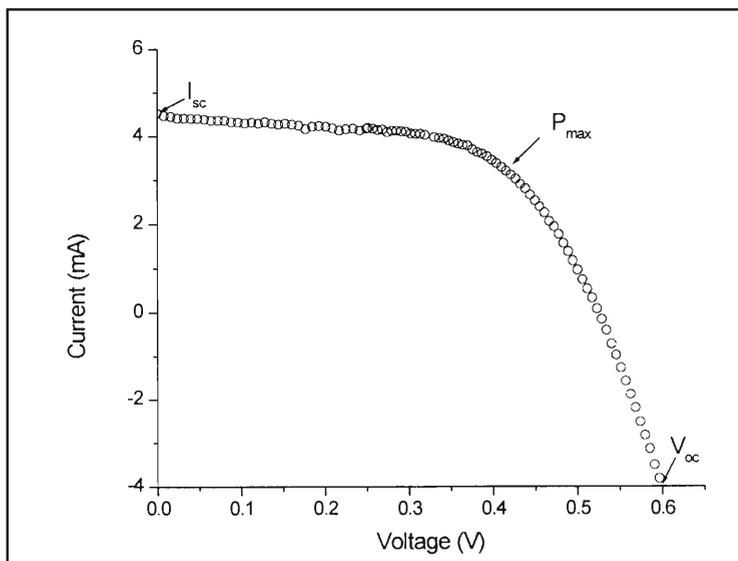


Figure 4. Typical current-voltage (I - V) curve, characteristic of a DSPV cell.

is obtained by measuring the current flowing across a standard resistor. The ratio of the areas under the experimental curve to the ideal curve gives the fill factor. Alternatively, a point in the experimental curve can be chosen to give the V_{\max} and I_{\max} and the fill factor is given by, Fill factor (ff) = $(V_{\max} \times I_{\max}) / V_{oc} \times I_{sc}$ where V_{\max} and I_{\max} are the maximum photovoltage and photocurrent density generated. V_{oc} is the photovoltage developed under open circuit conditions and I_{sc} is the short circuit current density.

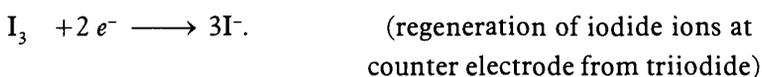
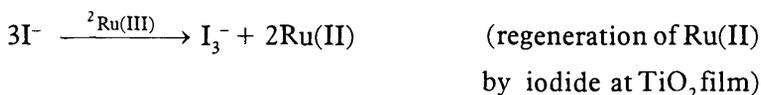
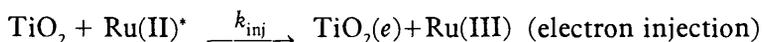
This regeneration of the dye by the electrolyte intercepts the recapture of the conduction band electron by the oxidized dye.

As shown in the diagram (*Figure 2*) when the light is illuminated on the device, the dye attached to TiO_2 is photo-excited and injects an electron into the conduction band of TiO_2 . Due to the nanocrystalline, high porous and sponge-like nature of TiO_2 , it is possible for the light to penetrate through the hundreds of monolayers of adsorbed dye molecules. The electron transfer takes place via metal-to-ligand charge transfer (MLCT) transition. Chelating groups such as carboxylic acids are grafted onto TiO_2 with strong electronic coupling between $3d$ orbitals of TiO_2 and Π^* orbitals of bipyridine ligand acts as bridging units for efficient electron transfer. The dye behaves exactly as chlorophyll does in natural photosynthesis in plants. In plants, the sunlight is absorbed by chlorophyll and this energy is used to split water into hydrogen ions and oxygen. Ultimately, the electron is accepted by carbon dioxide and carbohydrates are synthesized. In the case of DSPV cells, the dye absorbs the light and utilizes this light energy to induce electron transfer. Photo-injected electrons percolate rapidly through the TiO_2 film and are quantitatively collected by the conducting SnO_2 glass support. TiO_2 serves the same role as carbon dioxide in photosynthesis. In another analogy, TiO_2 acts as silver halide grain in color photography except that here the electrons from the dye produce electricity rather than forming an image. The dye is reduced back to its original state by the electrolyte. This regeneration of the dye by the electrolyte intercepts the recapture of the conduction band electron by the oxidized dye. The iodide is regenerated by reduction of triiodide at the counter



electrode (Figure 1) and the circuit is completed through the external load. Thus the solar cell is regenerative.

The whole process of heterogeneous electron transfer and regeneration of the DSPV cell takes places as follows.



The performance of a DSPV cell mainly depends on two processes. (i) the electron injection from photo-excited dye to the conduction band in ultra fast time (typically it occurs within $\sim 10^{-12}$ - 10^{-15} s⁻¹) (ii) the slower recombination of the injected electron with the oxidized dye ($\sim 10^{-6}$ s⁻¹) and (iii) the regeneration of the dye by electrolyte before recombination ($\sim 10^{-8}$ s⁻¹). The performance of the DSPV cell can be quantified on a macroscopic level with parameters such as incident photon-to-current efficiency (IPCE), open circuit photovoltage (V_{oc}) and short circuit photocurrent (I_{sc}) and the overall efficiency of the cell (η_{cell}). IPCE is defined as the product of the quantum yield for charge injection (ϕ), the efficiency of collecting electrons in the external circuit (η_c) and fraction of radiant power absorbed by the material or 'light harvesting efficiency' (LHE), (1)

$$\text{IPCS}(\lambda) = \text{LHE}(\lambda) \times \phi \times \eta_c, \quad (1)$$

where ϕ and η_c can be rationalized on the basis of kinetic parameters, LHE depends on the active surface area of the semiconductor and on the cross-section for the light absorption of the dye. In practice the IPCE measurements are performed with monochromatic light and calculated according to (2).

LHE depends on the active surface area of the semiconductor and on the cross-section for the light absorption of the dye.



$$\text{IPCE}(\lambda)\% = \frac{1.24 \cdot 10^3 \times \text{Photocurrent density} (\mu\text{A}\cdot\text{cm}^{-2})}{\text{Wavelength}(nm) \times \text{Intensity of incident light} (W\cdot m^{-2})} \quad (2)$$

and the overall efficiency of the PV cell (η_{cell}) is given by (3)

$$\eta_{\text{cell}} = \frac{I_{\text{sc}} \times V_{\text{oc}} \times ff}{I_s}, \quad (3)$$

where I_s is the intensity of incident light. The maximum open circuit voltage attainable in the DSPV cell is the difference between the Fermi level of the solid (TiO_2) under illumination and the Nernst potential of the redox couple in the electrolyte.

The main requirements for developing efficient dyes for photosensitization are as follows:

(i) The low lying excited state energy level of the dye should be compatible with TiO_2 conduction band.

(ii) The redox potential of the dye molecule should match with the mediator redox couple in the electrolyte.

(iii) The absorbance spectrum of the dye should have large overlap with the solar spectrum or the absorption of visible light of all colors and near IR region (400-900 nm)

(iv) Chelating groups such as carboxylic acids, sulphonic acids or phosphonic acid for grafting the dye on the semiconductor surface should be present.

(v) The dye should be able to inject electrons into the conduction band of TiO_2 with a quantum yield of unity.

As mentioned earlier, the conversion efficiency depends on energy matching and fast electron transfer between the sensitizing dye and the semiconductor, as well as the dye and the redox species. Insight into the Highest occupied molecular orbital (HOMO) – Lowest unoccupied molecular orbital (LUMO) energy levels of the dyes by theoretical calculations using semi

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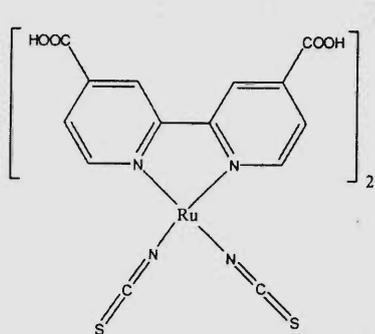
Suggested Reading

- [1] Greg P Smestad and Michael Gratzel, Demonstrating electron transfer and nanotechnology: A natural dye-sensitized nano-crystalline energy converter, *J. Chem. Edu.*, Vol.75, pp. 752-756, 1998.
- [2] Anders Hagfeld and Michael Gratzel, Molecular Photovoltaics, *Acc. Chem. Res.*, Vol.33, pp.269-277, 2000.
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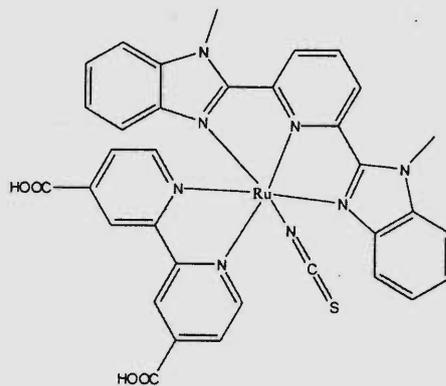
Most efficient and stable sensitizers are carboxylated Ru(II) polypyridyl complexes.

empirical or ab initio programs is therefore useful in understanding the potential of the dyes to optimize these cells.

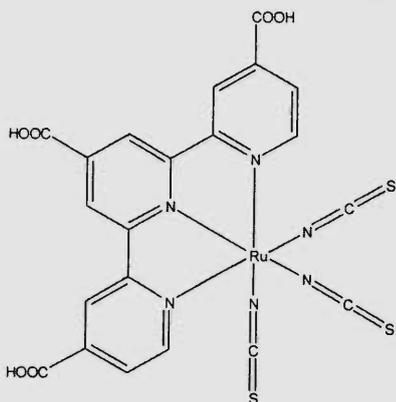
Figure 5 shows the structures of some of the best photosensitizer dyes reported in the literature. Gratzel and others announced the first DSPV cell with an overall efficiency of 10% in 1988. They used cis-di(thiocyanato)bis(2, 2'-bipyridyl, 4, 4'-carboxylate) ruthenium (II), best known as N3 (Figure 5a), attached to a nanocrystalline TiO₂ film by chemisorption. N3 showed IPCE value of 85% and was very stable upon illumination over a long period of time. They also claim that it can undergo nearly 10⁷ redox cycles without any loss of performance. Since then various structural modifications have been done on ruthenium complexes (e.g. Figures 5b and 5e) to find a better photosensitizer dye. Other transition metal (e.g. Fe, Rh, Os) complexes, organic molecular dyes such as perylene derivatives (Figure 5f), chlorophyll derivatives, phthalocyanines, anthocyanines extracted from black berries (Figure 5d) and related natural porphyrines have also been studied as photosensitizer dyes in DSPV cells. Presently most efficient and stable sensitizers are carboxylated Ru(II) polypyridyl complexes. N3 dye has been the main focus of study due to its high efficiency. Although, the unique performance of N3 is difficult to rationalize, it is an ideal photosensitizer with the quantum yield for injection of an electron near unity and occurs within femtoseconds. The only disadvantage that one could find in N3 is the lack of near IR absorption. Since the solar spectrum of AM1.5 contains the near IR region, the dye absorption in this region is also important. Recently, Gratzel and others reported a modified version of N3, which is known as 'black dye' (Figure 5c), that could be a promising candidate for DSPV cell due to its panchromatic absorption (400-920 nm) with the photovoltaic overall efficiency (cell) of 10.4% and IPCE value of 70%. The future of DSPV cells depends on the design and synthesis of dyes, which can absorb entire visible light with optimum HOMO-LUMO energy levels that match with the conduction band of TiO₂ and redox potential of the electrolyte. Semi-empirical quantum



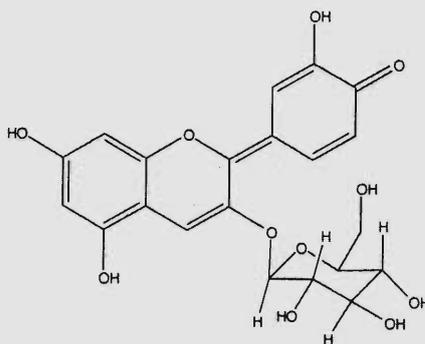
(a)



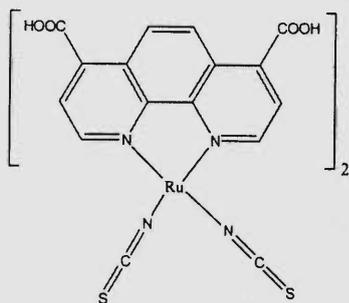
(b)



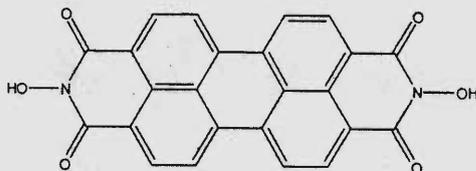
(c)



(d)



(e)



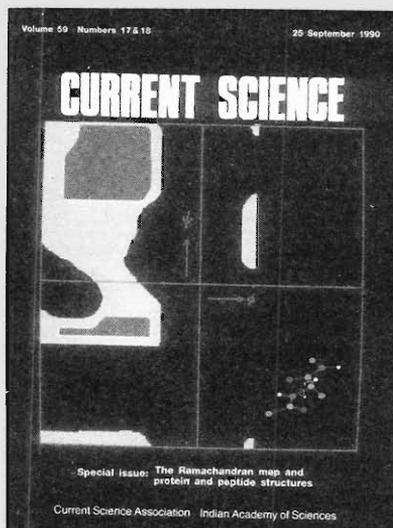
(f)

Figure 5. The structures of some dyes used in DSPV cells.

chemical methods can be used to calculate the absorption spectrum of the dyes accurately. These theoretical studies may be very useful in screening various dyes to ultimately choose optimal ones.

In conclusion, the dye-sensitized solar cells or DSPV cells have many advantages over the conventional silicon solar cells. There is a great possibility of fabricating low cost transparent solar cells using low to medium purity materials. These cells can also be used for splitting water into oxygen and hydrogen by sunlight for photosynthesis. More importantly, the environment friendliness and biocompatibility of these cells make them very valuable for future solar cell technology. The Sustainable Technologies of Australia recently announced that they have developed the technique for manufacturing a power module of DSPV cells, which can produce approximately 20V under low light conditions. Currently, our group at Lowell is active in developing the technology for the fabrication of all solid-state DSPV cells incorporating polyelectrolytes.

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