

AN OVERVIEW ON THE SOME PHENOTIAZINE DERIVATIVE MOLECULES USED IN ORGANIC DYE-SENSITIZED SOLAR CELLS

Özgül Birel¹

Abstract

The aim of this review article is to give a short and simple information about photovoltaic performance and structure of the some phenothiazine (PTZ) dyes used in dye-sensitized solar cells (DSSC). The dye chromophore is a heart component in the DSSC device to improve the conversion efficiency to electric energy of the solar cells. It describes the some electrochemical, spectral properties and structure of the phenothiazine dyes used in dye based-solar cells.

Key Words: Dye-sensitized solar cells, Phenothiazine

¹ Luleburgaz Higher Vocational School, Kirklareli University, Luleburgaz, Kirklareli, TURKEY
Chemistry Department, Faculty of Science, Mugla University, Mugla, TURKEY
ozgulhakli@yahoo.com; ozgulbirel@mu.edu.tr

Introduction

Solar cells, also called photovoltaic cells, is an electronic device used to generate electricity directly from sunlight. Dye-sensitized solar cells (DSSCs) have attracted alternative to the conventional photovoltaic cell due to low-cost electricity production from sun light, high power conversion efficiency for solar energy. DSSCs are promising alternatives to silicon-based photovoltaic technologies for solar energy conversion (Maheswari, 2015; Thomas, 2008).

The typical DSSC is a sandwich structure device consisting of a porous layer of titanium dioxide (TiO_2) nanoparticles having wide band gap suitable for generation of useful voltage, a dye called as sensitizer, an electrolyte containing a suitable redox couple and a Pt coated counter electrode. The light-to-energy conversion performance of solar cell depends on the relative energy levels of the semiconductor and molecular structure of dye. Organic dyes such as triphenylamine, coumarin, indoline, carbazole, squaraine and phenothiazine used in solar cells are attracted molecules due to the advantages of easier preparation and purification (Hua,2013;Longo,2003).

In photoelectrochemical cell based on organic dye-sensitized, under the illumination of sunlight, light adsorbed by sensitizer excites an electron. An electron injects to the conduction band of the semiconductor electrode. By losing an electron the dye is oxidized. The free electron travels through the layer of TiO_2 and flow through the external circuit to arrive at the counter- electrode. The oxidized dye is then reduced by the electron from an electrolyte ion to get its original state. Thus, the dye is restored to original state by electron donation from electrolyte containing usually the solution of an organic solvent or ionic liquid solvent containing I_3^-/I^- redox system. The rate of electron injection must be faster than the decay of the dye excited state. Also, the rate of reduction of the the oxidized sensitizer by the electron donor in the electrolyte. The iodide is regenerated by reduction of triiodide at the counter electrode. Thus circuit is completed and the process can continue without permanent chemical change. The process leads to direct conversion of sunlight into electricity. The photocurrent yield depends on the spectral and redox properties of the dye, its excited state lifetimes, the efficiency of charge injection, the ionic conductivity of the electrolyte and the properties of the semiconductor electrode to collect and channel the electrons through the external circuit (Longo,2003).

The main parts of dye sensitized solar cell are illustrated schematically in Figure 1.

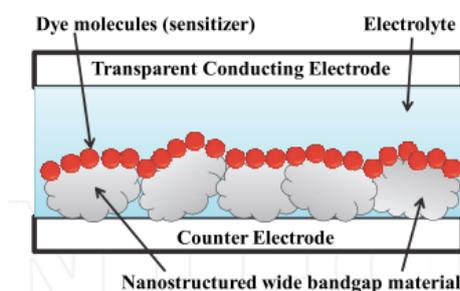


Figure 1: Schematic of the structures of dye-sensitized solar cell (Jasim, 2011)

Dye-Sensitized Solar Cell Materials

The basic structure of dye-sensitized solar cells consists of semiconductor oxide film, the sensitizer, electrolyte and a platinum counter electrode. Semiconductor oxide film electrode has nanostructured mesoporous surface deposited on a glass or a flexible substrate. The dye adsorbed on the surface of the semiconductor acts as the sensitizer. Electrolyte contains a redox couple. The operating mechanism of the solar cells is shown in Figure 2.

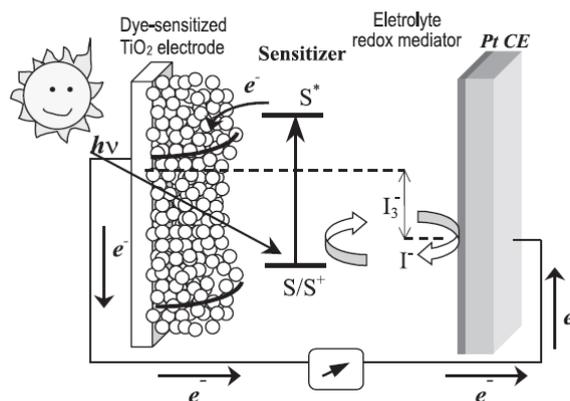


Figure 2: Operating mechanism of Dye-sensitized solar cell diagram (Longo,2003)

The operating of DSSC;

1. Firstly the sensitizer absorbs the photon to get excited.
2. The excited sensitizer injects an electron into the conduction band of the semiconductor and it gets oxidized.
3. Semiconductor film layer collects the excited electron from the conduction band and the electrons flow from the external load to the counter electrode.
4. Finally the oxidized dye molecule is reduced by gaining electrons from the electrolyte solution (Nazeeruddin, 2011).

The basic structure of dye-sensitized solar cells;

1. A support coated with nanostructured mesoporous semiconductor oxide film.
2. The nanoporous semiconductor film, usually TiO_2
Although semiconductor oxides used in dye-sensitized solar cell include TiO_2 , ZnO , SnO_2 , Nb_2O_5 etc.(Kong,2007), TiO_2 or titanium (IV) oxide becomes the best choice in semiconductor due to some advantages such as low cost, widely available, biocompatible, cheap, thermally stable, chemically inert and non-toxic. It is also a common additive in many food, personal care, and other consumer products used by people (Kong,2007;Weir,2012). TiO_2 particles which are used as a photoanode to absorb sunlight for application in dye-sensitized solar cell, particularly in anatase form due to its larger bandgap to permit significant collection of visible light, is a well-known n-type semiconductor. In a typical DSSC the particle size of TiO_2 anatase is in the range of 10-25 nm with a film thickness of 5-15 μm (Gratzel,2013). The semiconductor is responsible for providing the surface for dye adsorption, for accepting electrons from the excited dye and for conducting them towards the external circuit (Andrade,2010).
3. A sensitizer, organic dye
The dye should be present long stability, good adsorption to the semiconductor's surface, high solubility in the corresponding solvent and no toxicity (Andrade,2010). The dye should have a broad absorption spectrum in the visible range in order to capture solar radiation. Dye sensitizers serve as the solar energy absorber. The sensitizers used in dye based solar cell are divided into two types according to their structure: organic and inorganic dye. Inorganic dyes contain a transition metal in the structure. Ruthenium-based sensitizer which have high conversion efficiency are the most commonly used as sensitizer early on and still now the most commonly used sensitizer (Kong,2007). Compared with metallic organic dyes, metal free organic dyes are inexpensive, easy to synthesize with molar extinction coefficients, their tunable absorption and electrochemical properties through suitable structure design. Organic dye anchored to TiO_2 surface absorbs the photon to get oxidized state by losing the its electron. An electron injects to semiconductor. Oxidized organic dye accepts an electron from the redox couple in the electrolyte (Iqbal,2013).
The sensitizer is very important component in DSSCs (Wu,2010). The organic dyes generally consist of electron donor(D) (a molecule that can donate electrons to another compound), electron acceptor(A) (a molecule that can accept electrons), conjugated spacer(π) between donor and acceptor, and surface

anchoring groups. With the electron withdrawing and donating effects of acceptor and the donor moieties, the absorption of the visible light are red shifted and leads to improving the light harvesting. Metal free organic dyes with D-A- π -A structures are reported to exhibit better performance than of D- π -A (Basheer,2014).

The sensitizers anchored on the surface of semiconductor film electrode with carboxylate group or phosphonate group, which enable the electron injection into the conduction band of the semiconductor. Organic dye was adsorbed on the TiO₂ surface. Organic dye is used as a photoanode to absorb the sunlight. Dye-derived nanocrystalline titania films are photoanode. It is very important the structure of organic dye for solar cell efficiency. For example; the role of the carboxylate groups attached to dye is to allow immobilization of dye to the film surface via the formation of bidentate coordination and ester linkages. The isothiocyanato (-NSC) groups enhance its response the visible light absorption. Generally, organic dye has the general structure of Donor (D)- π conjugation bridge-acceptor (A). With the electron withdrawing and donating effects of acceptor and the donor moieties, the absorption response of the visible light are red-shifted, which improves the light harvesting and short circuit photocurrent of the solar cell. The conjugation structure of a dye molecule plays important role for its absorption spectrum to match with the solar emission spectrum (Kong,2007).

4. An electrolyte

The electrolyte is one of the key components for dye-sensitized solar cells. Electron injection depends on the reducing ability of the electrolyte (Nwanya,2011). The electrolyte reduces oxidized dye and transport holes in the cell. An electrolyte contains a redox mediator. The main redox couple used is triiodide/iodine. Iodide/triiodide-based redox electrolyte has been the most widely used and efficient electrolyte. Though liquid electrolyte has achieved high efficiency, there are some disadvantages such as evaporation of electrolyte, health hazards, thermal stability problems, sealing problems. The pores of the nanocrystalline TiO₂ film are filled with a liquid electrolyte containing the iodide/triiodide redox couple in a non-aqueous electrolyte, such as acetonitrile (Ojah, 2013).

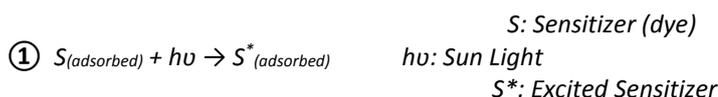
5. A counter electrode

A transparent counter electrode is placed over the nanocrystalline TiO₂ and the edges of the cell are sealed.

Steps of Operating Principle of Dye-Sensitized Solar Cells

Solar energy conversion and storage can be achieved by photo-electrochemical processes (Longo,2003).

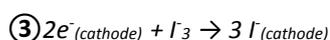
1. When illuminated, light is absorbed by the dye adsorbed on the surface of the TiO₂ transparent film. It leads to the excited sensitizer (S*).



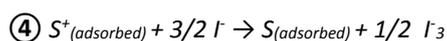
2. Excited sensitizer transfers an electron within a short time into the conduction band of the semiconductor, TiO₂. This leads to an effective charge separation (S⁺).



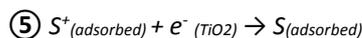
3. The injected electron flows through the semiconductor network to arrive at the back contact and then through the external load to the counter electrode to reduce the redox mediator. The oxidized sensitizer (S⁺) is regenerated by accepting electrons from the iodide ion. The triiodide redox mediator diffuses towards the counter electrode and is reduced to iodide.



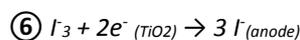
4. This completes the circuit.



Some undesirable reactions are the recombination of the injected electrons either with oxidized sensitizer,

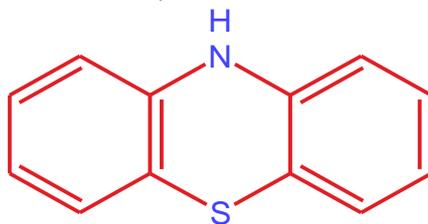


or with the oxidized redox couple at the TiO_2 surface (Nazeeruddin,2011).



Some Phenothiazine Derivative Dyes Used in Dye-Based Solar Cells

Phenothiazine (PTZ) are a molecule with electron-rich nitrogen and sulfur heteroatoms in the central ring in a heterocyclic structure with high electron-donating ability (Scheme 1). PTZ is even better donor than triphenylamine, tetrahydroquinoline, carbazole and iminobenzyles. The electron rich nature of a phenothiazine makes it a good electron donor during a photo-excited charge transfer transition. Phenothiazine ring with nonplanar with a butterfly conformation in the ground state can sufficiently inhibit molecular aggregation and the formation of intermolecular excimers. The structural features of a phenothiazine dye make it a promising type of sensitizer for DSSC applications. Phenothiazine is a potential hole transport semiconductor in organic devices (Wu,2010;Chang,2012;Dai,2015;Hua,2013).

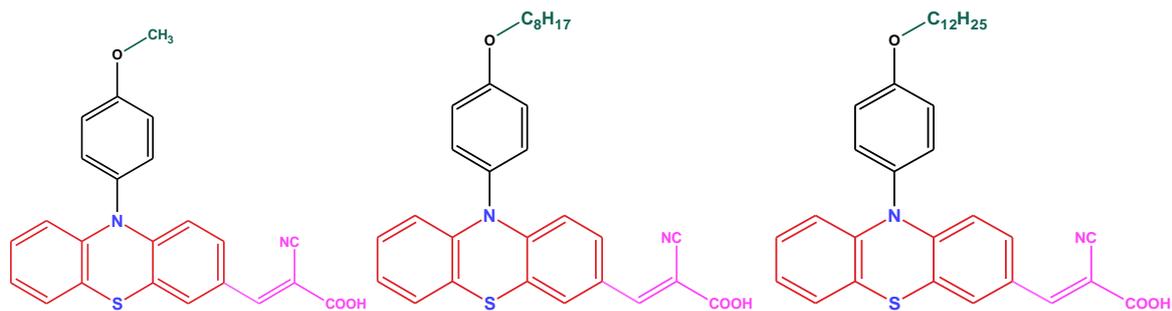


Scheme 1: Molecular Structure of phenothiazine

Usually, N-substituted simple phenothiazines are colorless and can not absorb visible light. However, further introduction of electron withdrawing groups into aromatic rings in phenothiazines can induce shift of the absorption band into the visible light region. It has been reported that phenothiazine-based dyes with a directly connected anchoring group showed higher visible light harvesting efficiencies in dye-sensitized solar cells than typical donor-acceptor type dyes with additional π -conjugated bridges (Lee,2012).

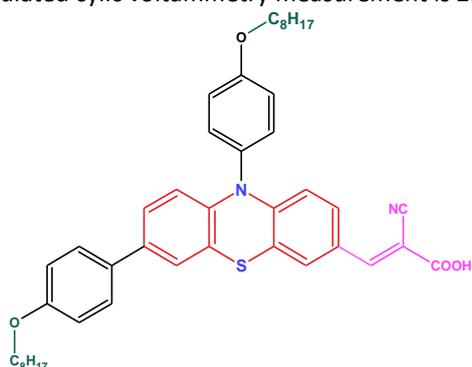
Phenothiazine for dye based-dyes are promising organic sensitizer for DSSCs because of their excellent photoresponse in the visible region.

Iqbal et al. have synthesized some novel phenothiazine chromophores with different alkoxy chain lengths and increased conjugation the following (Scheme 2 and Scheme 3). The main aims of modifications of these phenothiazines were made for the enhancement of the light harvesting capabilities and reduction of aggregation. It has been reported that alkoxy groups besides electron donating also reduce aggregation of dyes in TiO_2 films. Aromatic rings do not only increase the light harvesting capacity but also reduce surface aggregation. As known, phenothiazine is a strong electron donor. Cyanoacrylic acid is a electron acceptor group linked to phenothiazine molecule. The UV spectra of the phenothiazine dyes in solvent mixture exhibit two distinct bands, one at 306-324 nm which correspond to π - π^* transition and the other at 420-459 nm which assign to an intramolecular charge transfer (ICT) between the central phenothiazine and the cyanoacetic acid. The average band gap value of dyes is 2.50 eV. The requirement for appropriate electron injection from the excited state to the conduction band of titanium dioxide is 0.2 eV. Photovoltaic performance of these dyes 4.53, 4.79 and 4.54%, respectively.



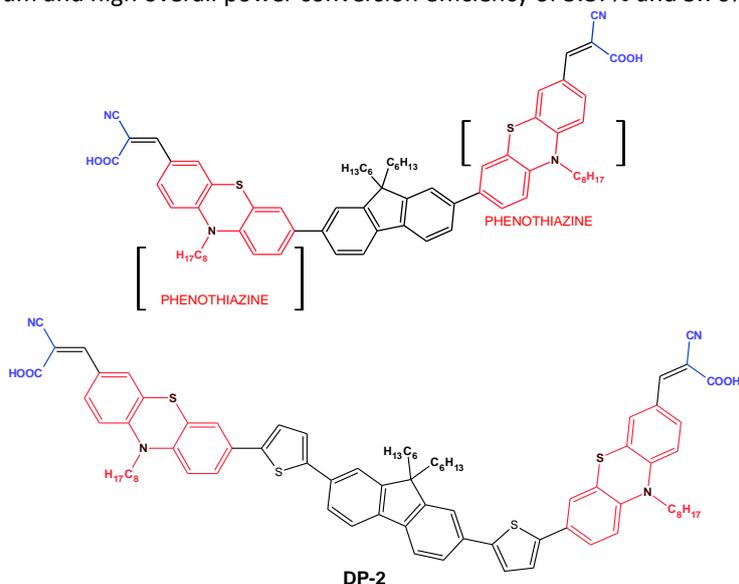
Scheme 2: Structures of molecules synthesized by Iqbal et al.

Also they have synthesized bilateral phenothiazine molecule following. This dye exhibits a maximum efficiency of 5.73%. The band gap value calculated cyclic voltammetry measurement is 2.37 eV. (Iqbal,2013).



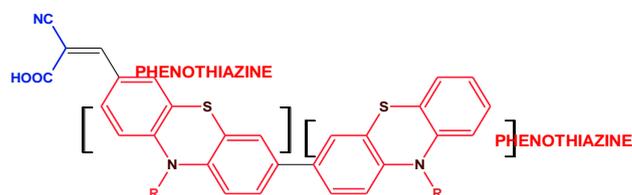
Scheme 3: Structure of molecule synthesized by Iqbal et al.

Dai et al. have synthesized a new di-anchoring organic dye based on phenothiazine featuring A-D- π -D-A (acceptor-donor- π -linker-donor-acceptor) configuration with fluorene as the π linker (Scheme 4). Phenothiazine di-anchoring dye contains N-octylphenothiazine as the donor, cyanoacetic acid as the acceptor. The hydrophobic alkyl chains on the fluorene moiety can not only improve the solubility, but also reduce dye aggregation and effectively suppress the charge recombination. The adsorption in shorter wavelengths ranging from 280-380 nm is from aromatic π - π^* electronic transitions of the phenothiazine unit. The absorption in longer wavelengths in the range of 380-550 nm is attributed to the intramolecular charge from the donor to the acceptor, which provides efficient charge separation in the excited state. DP-2 with two thiophene groups displayed one more absorption band compared with other dye molecule. These molecules exhibit a red shift of the absorption spectrum and high overall power conversion efficiency of 5.87% and 5.70% (Dai,2015).



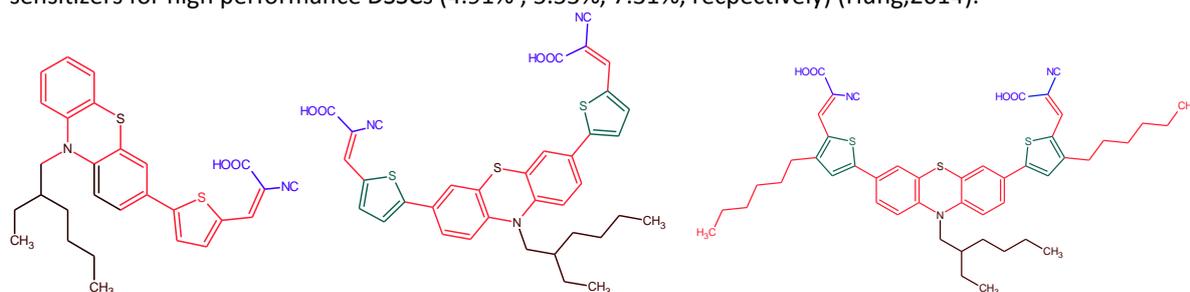
Scheme 4: Structures of molecules synthesized by Dail et al.

Chang et al. have prepared phenothiazine dye containing cyanoacrylate group attached to one side of the dye, acting as an electron acceptor following (Scheme 5). The nitrogen atom of compound is substituted by two kinds of linear chains. The dye synthesized by Chang et al. exhibit broad absorption in the range of 250–600 nm. The short wavelength region at 250–330 nm is attributed to localized $\pi-\pi^*$ and $n-\pi^*$ transitions, while the long wavelength region in the range of 459–496 nm is derived from intramolecular charge-transfer transitions (ICT). The intensity of UV transition increases with the number of phenothiazine units. The conversion efficiency of dye is 7.38% (Chang, 2012).



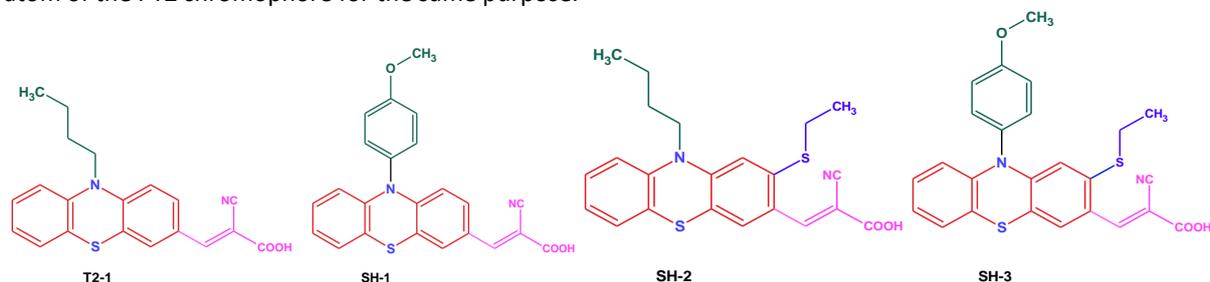
Scheme 5: Structure of molecule synthesized by Chang et al.

Hung et al. have designed a series of new phenothiazine-based dyes including various π spacers (thiophene derivatives) following (Scheme 6). These dyes exhibited broader spectral response ranges and higher absorptivity. UV/Vis absorption spectra of this phenothiazine's dyes show two distinct bands. The band located at a shorter wavelength is attributed to an aromatic $\pi-\pi^*$ transition, and the band at a longer wavelength is assigned to an intramolecular donor \rightarrow acceptor charge transfer transition. These dyes could be used as the sensitizers for high performance DSSCs (4.91%, 5.53%, 7.31%, respectively) (Hung, 2014).



Scheme 6: Structures of molecules synthesized by Hung et al.

Kim et al. have investigated the effect of N-substitution and ethylthio substitution on the performance of phenothiazine donors in dye-sensitized solar cells (Scheme 7). N-substituents are added to the phenothiazine to suppress dye aggregation and an ethylthiol is added as an additional donor function. Hydrophobic ethylthiol groups are expected to suppress electron recombination between electrons injected on the TiO_2 surface and I_3^- ions in the electrolyte. An aliphatic butyl chain or an aromatic methoxyphenyl ring is also introduced on the N atom of the PTZ chromophore for the same purpose.

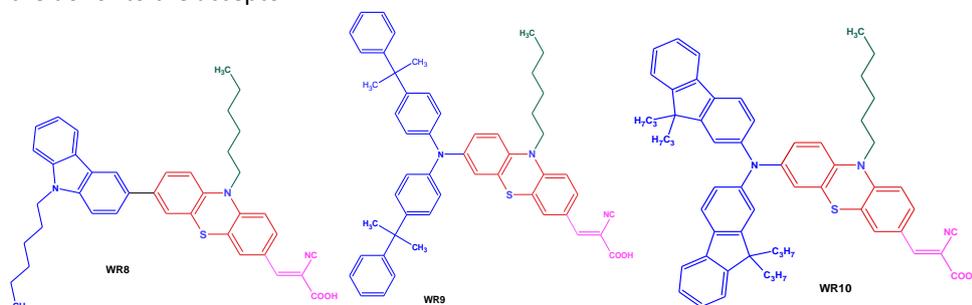


Scheme 7: Structure of molecule synthesized by Kim et al.

A butyl chain or methoxyphenyl ring is introduced on the phenothiazine moiety to improve its solubility and electron density. Addition of N-methoxyphenyl rings resulted in more planar structures of the PTZ moieties that led to red-shifted absorption maxima by 20 nm compared with those of the dyes with N-butyl chains. The ethylthio unit also red shifted λ_{max} by 16 nm compared with the corresponding structure without ethylthiol due to the extension of electron delocalization over the whole molecule. The band gap values are 2.26 eV, 2.18 eV,

2.17 eV, 2.12 eV for 1, 2, 3, 4 molecules of phenothiazine, respectively. The best overall conversion efficiency showed molecule 1 (6.02%) (Kim,2013).

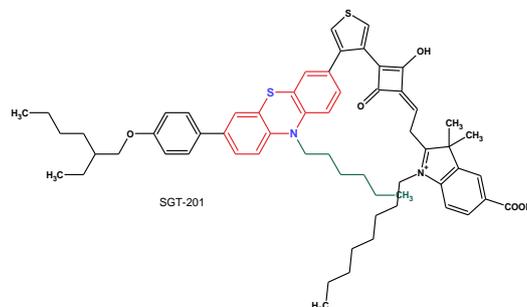
Wang and co-workers have reported influence of the terminal electron donor in D-D- π -A phenothiazine dyes for dye-sensitized solar cells (Scheme 8). Studies have demonstrated that the performance of DSSCs strongly depends on the nature of sensitizers. On general, organic sensitizers are constituted with the donor- π -acceptor (D- π -A) configuration. This push-pull structure can induce an efficient intramolecular charge transfer (ICT) from the donor to the acceptor.



Scheme 8: Structures of molecules synthesized by Wang et al.

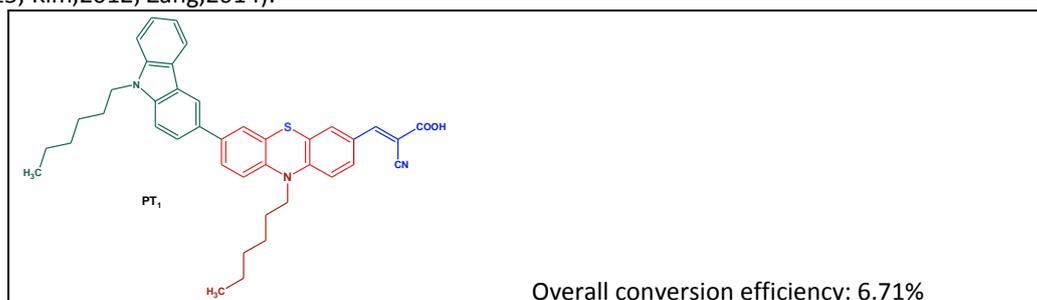
The excellent photoelectric function of the carbazole unit makes it a promising type of terminal electron donor for PTZ dyes. Electrochemical data are 2.24, 2.28, 2.36 eV for WR8, WR9, WR10, respectively. The HOMO levels of these dyes are more positive than I^-/I_3^- redox couples and LUMO levels of these dyes are much more negative than the conduction band of the TiO_2 level. WR8 shows the best overall conversion efficiency of 7.13% (Wang,2014).

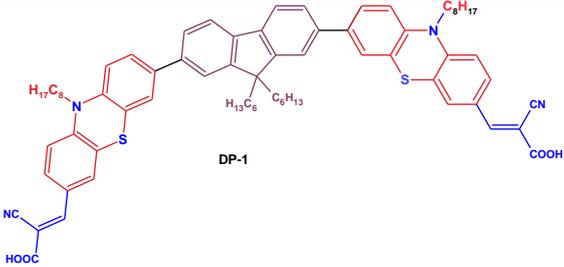
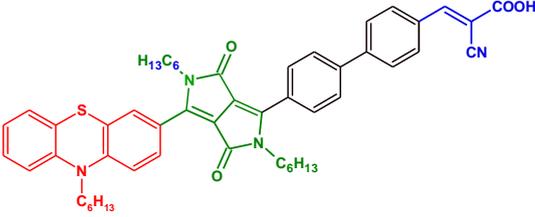
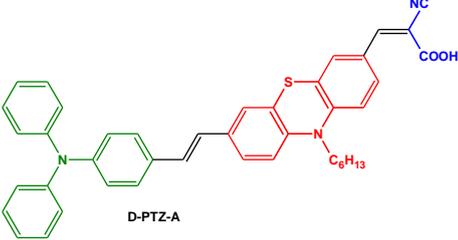
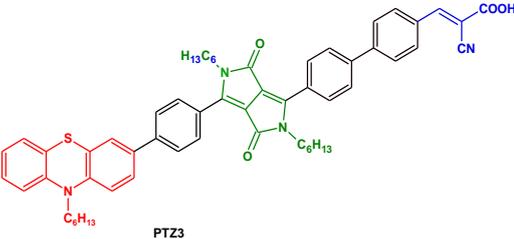
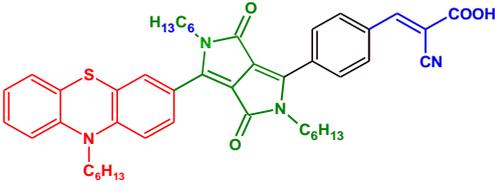
Bae et al. have synthesized unsymmetrical squaraine near-infrared (NIR) sensitizer with π -bridge unit, based on the donor- π -squaraine core-acceptor structural motif for dye-sensitized solar cells (Scheme 9). Squaraines have received much attention as photosensitizers due to their sensitizing abilities in the NIR region, extremely high molar absorption coefficient for DSSCs. Recently, use of extended aromatic or heterocyclic units has allowed us to red-shifted the absorption maxima of the squaraine dye to the longer wavelength region. By the introduction of π -bridge groups, such as phenyl, thienyl and pyrrole groups between the donor and acceptor groups in the squaraine dyes, the moiety has been shown to lead to a red shift in the absorption maximum (Bae,2015).



Scheme 9: Structure of molecule synthesized by Bae et al.

Other some phenothiazin molecules and their photovoltaic performance are shown following (Hua,2013; Dai,2015; Kim,2012; Zang,2014).



 <p style="text-align: center;">DP-1</p>	Overall conversion efficiency: 5.70%
 <p style="text-align: center;">PTZ1</p>	Overall conversion efficiency: 5.16%
 <p style="text-align: center;">D-PTZ-A</p>	Overall conversion efficiency: 4.6%
 <p style="text-align: center;">PTZ3</p>	Overall conversion efficiency: 4.56%
 <p style="text-align: center;">PTZ2</p>	Overall conversion efficiency: 3.26%

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