

# Phthalocyanines: potential alternative sensitizers to Ru(II) polypyridyl complexes for dye-sensitized solar cells

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**This review reports possible alternative sensitizers such as phthalocyanines to Ru(II) polypyridyl complexes for dye-sensitized solar cell (DSSC) applications. DSSCs are currently of great interest because of low cost, easy of fabrication upon flexible substrate and environment-friendly compared to conventional solid-state p-n photovoltaic devices. The sensitizer is one of the key components in achieving high efficiency and durability of the device. Ru(II) polypyridyl complexes are widely used as sensitizers for DSSC with an efficiency >11%. However, ruthenium complexes are expensive due to rarity of the metal and lack of absorption in the red region of the visible spectrum. In this regard, phthalocyanines are found to be potential alternative sensitizers to ruthenium complexes based on electronic, physical and thermal properties.**

**Keywords:** Photovoltaic devices, phthalocyanine, redox electrolyte, ruthenium, solar cells.

AS the utilization of fossil fuels increases year by year, their resources will be exhausted very soon and current forecasts suggest that alternatives must make a major contribution in the near future<sup>1</sup>. In this regard, clean and renewable energy is an alternative to fossil fuels. Most of the renewable energy options must rely on a net input of energy into the earth, and since the sun is our only external energy source, harnessing its energy, which is clean and infinities the main objective of all alternative energy strategies<sup>2</sup>. It is remarkable that a mere 1 h of solar irradiation onto the Earth's surface is equal to the total yearly human energy consumption. Therefore, if we could accomplish harvesting merely a tiny fraction of the solar energy reaching the Earth, we would solve many of our problems not only in energy, but global, environmental and political.

A solar cell is a device that directly converts the light energy into electrical energy through the process of photovoltaics. Solar cells are broadly divided into three generations<sup>3-5</sup>. First-generation solar cells are the larger, silicon-based photovoltaic cells that have, and still do, dominate the solar-panel market. Monocrystalline and

polycrystalline solar cells fall under this category. They are dominant due to their high efficiency, despite their high manufacturing costs, a problem that second-generation cells hope to remedy. Second-generation cells, also called thin-film solar cells, are significantly cheaper to produce than first-generation cells, but have lower efficiency. Amorphous silicon (a-Si), Cd-Te, Ga-As and CIGS are examples of this generation of solar cells. The materials that are used in both generations of solar cells are either cost effective or hazardous. To overcome these problems, scientists have developed excitonic solar cells, which are fall in the third-generation solar cells. Third-generation solar cells are the cutting edge of solar technology. Still in the research phase, third-generation solar cells have moved well beyond silicon-based cells. The excitonic solar cells are broadly divided into nanocrystalline, dye-sensitized solar cells (DSSCs) and organic/polymer solar cells. Of these, DSSCs are on the verge of commercialization. This review will discuss alternative sensitizers such as phthalocyanines for DSSCs.

## Nanocrystalline dye-sensitized solar cells

The first observation of injecting electrons by a dye molecule into the conduction band of the semiconductor substrate was reported<sup>6</sup> in 1960s. From then on the concept of dye sensitization developed gradually. But, the efficiency of the device was very low until 1991, when O'Regan and Grätzel<sup>7</sup> reported the sensitization of nanocrystalline TiO<sub>2</sub> using a Ru(II) polypyridyl complex with an efficiency ( $\eta$ ) of 7.1%. This approach of generating electricity from sunlight has many advantages over first- and second-generation solar-cell technologies. The DSSC devices are easy to fabricate 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 NiO, ZnO, SnO<sub>2</sub>, WO<sub>3</sub>, etc. have been studied, TiO<sub>2</sub> has many advantages, including its long-term thermal and photostability. It is low-cost, abundant, non-toxic, biocompatible and widely used in healthcare products (e.g. toothpaste) and paints<sup>8-10</sup>.

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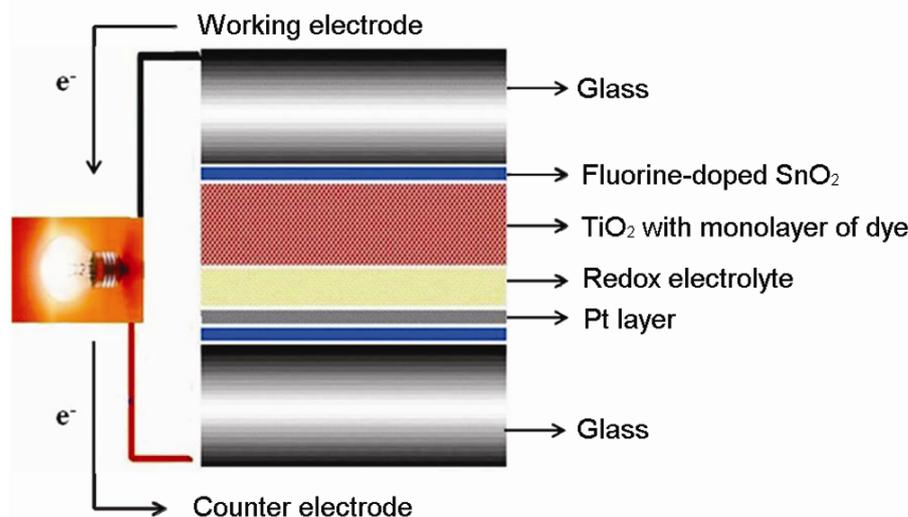


Figure 1. Schematic structure of a dye-sensitized solar cell device.

### Operating principle

A schematic diagram of a typical DSSC device is given in Figure 1. The device has three primary parts. On the top of the device is a transparent glass plate coated with a conductive layer of fluorine-doped tin dioxide ( $\text{SnO}_2:\text{F}$ ). On the back of this conductive plate is a thin layer (typically 6–10  $\mu\text{m}$  thick) of nanocrystalline  $\text{TiO}_2$  (of 20–25 nm particle size), which forms into a highly porous structure with an extremely high surface area. On top of this layer, another layer of  $\text{TiO}_2$  (of 400 nm particle size) was laid (light scattering layer).  $\text{TiO}_2$  absorbs only in the UV region of the solar spectrum. The plate was then immersed in dye solution (typically a Ru(II) polypyridyl complex). After soaking the film in the dye solution, a thin layer of the dye was left covalently bonded to the surface of  $\text{TiO}_2$ . On another conductive glass plate, a thin layer of platinum was laid, which acts as a cathode. The two electrodes were held to each other by heating with a hot-melt polymer film (Surlyn, 50  $\mu\text{m}$  thickness) to create the space between the electrodes. A drop electrolyte was injected in that space.

When light is illuminated on the device, the sensitizer gets photo-excited and the electron in the excited state of the sensitizer is injected (metal-to-ligand charge transfer of sensitizer, MLCT) into the conduction band of nanocrystalline  $\text{TiO}_2$ . Due to the nanocrystalline and highly porous nature of  $\text{TiO}_2$ , it is possible to anchor more dye on the  $\text{TiO}_2$  surface, thereby reflecting in efficiency. The dye behaves exactly as chlorophyll does in natural photosynthesis of plants. The oxidized dye is subsequently reduced by electron donation from an electrolyte (typically  $\text{I}^-/\text{I}_3^-$  in volatile organic solvent). The injected electron flows through the semiconductor network to arrive at the back contact and then through the external load to the counter electrode. At the counter electrode, reduction of

triiodide in turn regenerates iodide, which completes the circuit.

Almost all the elements of the DSSC device need further improvement before commercialization of this technology. The sensitizer is one of the key components in achieving high efficiency and durability of the DSSC device. The widely used charge-transfer sensitizers employed so far in such cells are bis(tetrabutylammonium)-cis-di(thiocyanato)-bis(4,4'-dicarboxy-2,2'-bipyridine)-Ru(II) (the N719 dye) and trithiocyanato 4,4'4''-tricarboxy-2,2' : 6',2''-terpyridine Ru(II) (the black dye), generating solar-energy-to-electricity conversion efficiencies ( $\eta$ ) of >11% under AM 1.5 irradiation and stable operation for millions of turnovers<sup>11,12</sup>. A number of modifications have been done on Ru(II) polypyridyl complexes in order to further improve the efficiency and durability of the device<sup>13–17</sup>. Even though, Ru(II) polypyridyl complexes are more dominant in DSSC, they are expensive due to the rarity of the metal, less durable due to the presence of two or three-NCS group in its molecular structure, and the absorption maximum of ruthenium complexes are limited at around 550 nm. As Ru(II) sensitizers are exclusive, metal-free sensitizers such as synthetic organic dyes and natural dyes are important for DSSC applications<sup>18–20</sup>. Since these sensitizers do not contain noble metals, there are no concerns about resource limitation. However, organic dye-based DSSCs are not useful for rooftop applications as these molecules do not withstand high temperatures. For a light-harvesting system, the essential requirements are that the sensitizing dye absorbs light over a wide wavelength range, preferably one that encompasses the visible spectrum to near-IR, binds strongly to the semiconductor surface (needs to have an anchoring group), has appropriately high redox potential for regeneration following excitation and is stable over many years of exposure to sunlight.

Based on electronic, thermal and redox properties, phthalocyanines are found to be alternative sensitizers to Ru(II) polypyridyl complexes for DSSC applications<sup>21</sup>. Phthalocyanines are tetra pyrrolic cyclic organic molecules, which can find applications in several fields<sup>22</sup>. They are 18- $\pi$  electron aromatic systems and possess an intense Soret-band at 350 nm and Q-band in the 650–700 nm region. Providing good absorption in the red/near-IR region of the solar spectrum, phthalocyanines can be tuned to be transparent over a large region of the visible spectrum, thereby enabling the possibility of using them as ‘photovoltaic windows’: a red/near-IR absorbing photovoltaic cell in the place of a window will allow visible light to enter a building while harvesting the solar power from the red/near-IR part of the spectrum. In addition to directly generating power, this also reduces the solar heating of buildings, thereby reducing the demand for, and power consumption of, air-conditioning units.

### Phthalocyanines without anchoring groups

Although it is known that the anchoring groups on the phthalocyanine macrocycle are necessary for adsorption of the sensitizer on nanocrystalline TiO<sub>2</sub>, the sensitization of TiO<sub>2</sub> was made without anchoring groups. The adsorption of phthalocyanine sensitizer on nanocrystalline TiO<sub>2</sub> was done using two different methods<sup>23,24</sup>. The first method involves physical adsorption occurring directly from the solution onto the previously sintered TiO<sub>2</sub> nanoparticles. The second method involves the physical mixing of the sensitizer with TiO<sub>2</sub> nanoparticles and the resulting nanoparticles are made into a paste. Aranyos *et al.*<sup>25</sup> have reported a series of phthalocyanines with aryl groups connected at the peripheral positions showing surprising sensitization of the nanocrystalline TiO<sub>2</sub> electrode. The aryl group connected at peripheral positions (**1**) are designated to facilitate the adsorption of dyes at the surface of the nanoparticles. These sensitizers have shown reasonable incident photon to current conversion efficiencies (IPCEs) of 4–9%. Myristic acid co-adsorbent was used<sup>26,27</sup> for the sensitization of aluminium(III) 2,9,16,23-tetraphenoxy phthalocyanine (**2**) for nanocrystalline TiO<sub>2</sub>. The co-adsorbent reduces the aggregation of phthalocyanine on the nanocrystalline TiO<sub>2</sub> surface; as a result the test cell efficiency improves. The overall conversion efficiency of phthalocyanine sensitizers without anchoring was very low, which is not sufficient to replace Ru(II) complexes.

### Phthalocyanines anchoring groups at axial position/s

Aggregation is one of reason for the low efficiency of DSSC based on phthalocyanine sensitizers because of the rapid non-radiative deactivation of the dye excited states

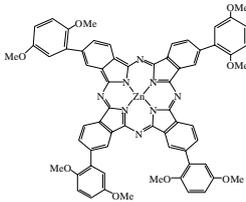
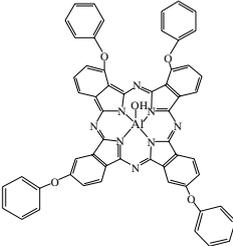
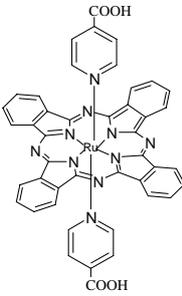
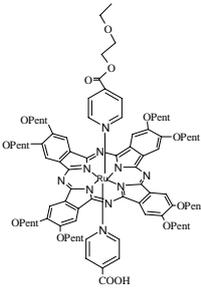
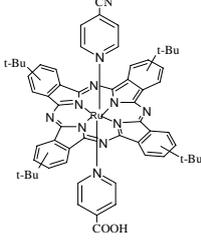
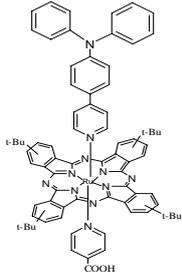
in aggregates. Axial coordination has been proved to hinder the aggregation of phthalocyanine efficiently. The use of axial carboxylated ligands as binding moieties for phthalocyanines in DSSC has been demonstrated several times over the last few years<sup>28–34</sup>. Nazeeruddin *et al.*<sup>28</sup> have utilized axial positions of (1,4,8,11,15,18,22,25-octamethyl phthalocyanine)Ru(II) having bis-(3,4-dicarboxypyridine) as anchoring groups. The resulting DSSC had an IPCE of over 60% in the near-IR region. The major drawback of this dye was the tedious synthesis, poor yield as well as desorption due to the coordinate mode of binding of pyridine ligand to Ru(II). Yanagisawa *et al.*<sup>29</sup> have compared the sensitization properties of an axially anchoring phthalocyanine (**3**) with that of a peripherally substituted phthalocyanine (**4**) under similar test cell conditions. The axially substituted phthalocyanine showed an overall conversion efficiency of 0.61%, which is better than that of the peripherally substituted phthalocyanine, 0.58%. The low efficiency of **4** was attributed to the pentyloxy groups at the peripheral position, which may reduce the stability of the adsorption of phthalocyanine on the surface of TiO<sub>2</sub>.

Axially substituted ruthenium phthalocyanines were studied using transient absorption experiments<sup>30,31</sup>. The ruthenium phthalocyanine has either 4-cyanopyridine (**5**), which is electron withdrawing group or triphenyl amine (**6**) which is an electron releasing group present at the axial position. The other ligand 4-carboxy pyridine acts as an anchoring group. The work reveals surprisingly that the electron injection from triplet state of ruthenium phthalocyanine. The long lifetime of the triplet state leads to an efficient electron injection occurring in hundreds of nanoseconds with an IPCE of 45%. Palomares *et al.*<sup>32</sup> used axial positions of titanium(IV) phthalocyanines for DSSC applications. Unlike in Ru(II) phthalocyanines, they connected anchoring 4-carboxy catechol at the axial position by covalent bond. By using covalent bond, desorption from the surface of nanocrystalline TiO<sub>2</sub> could be minimized. IPCE was found to be 19% and  $\eta$  0.2%. The poor efficiency is due to the poor injection of electron transfer from S<sub>1</sub> state of phthalocyanine to the conduction band of TiO<sub>2</sub>. Zannotti *et al.*<sup>33</sup> have used iron-based bridged phthalocyanines which contain 4-carboxy pyridine at the axial position for sensitization of nanocrystalline TiO<sub>2</sub>. These sensitizers show poor performance in DSSC.

### Phthalocyanines anchoring groups at peripheral position/s

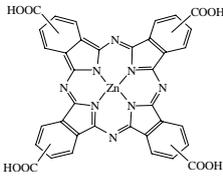
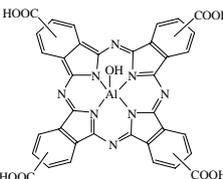
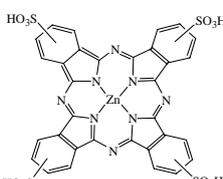
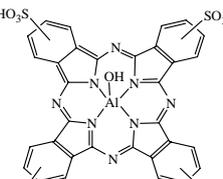
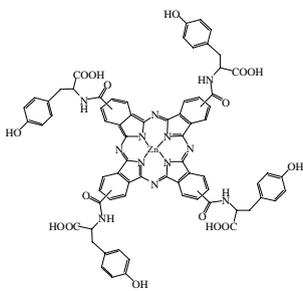
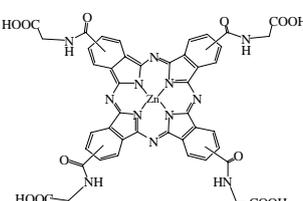
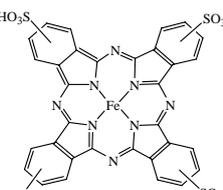
Though anchoring groups at axial position/s of a metallo phthalocyanine minimized aggregation of the macrocycle, their efficiency remained well below 1%. Moreover, desorption of the sensitizer takes place quickly from the surface of the nanocrystalline TiO<sub>2</sub> due to either coordinate

**Table 1.** Photovoltaic data of various phthalocyanines

Sl. no.	Phthalocyanine structure	IPCE <sup>a</sup> (%)	$J_{SC}^a$ (mA/cm <sup>2</sup> )	$V_{OC}^a$ (V)	FF <sup>a</sup>	$\eta^a$ (%)
1		9	0.24	0.360	0.540	0.47 <sup>b</sup>
2		1 1.5	0.026 0.061	0.186 0.225	0.404 0.400	<0.1 <sup>b</sup> <0.1 <sup>c</sup>
3		21	3.15	0.360	0.540	0.61 <sup>b</sup>
4		7	2.61	0.340	0.650	0.58 <sup>b</sup>
5		45	0.90	0.566	—	— <sup>d</sup>
6		—	—	—	—	— <sup>d</sup>

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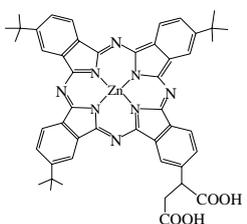
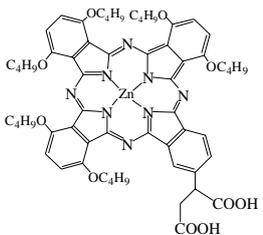
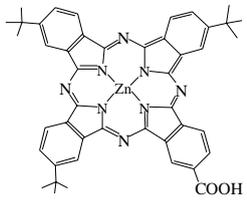
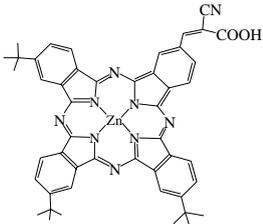
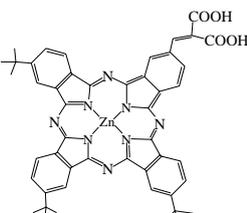
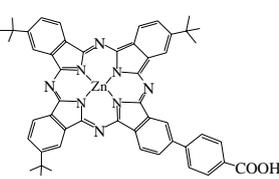
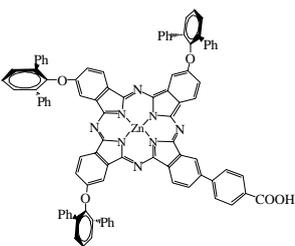
Table 1. (Contd)

Sl. no.	Phthalocyanine structure	IPCE <sup>a</sup> (%)	$J_{SC}^a$ (mA/cm <sup>2</sup> )	$V_{OC}^a$ (V)	FF <sup>a</sup>	$\eta^a$ (%)
7		43	5.40	0.416	– <sup>d</sup>	1.00 <sup>a</sup>
8		13	1.10	0.466	– <sup>d</sup>	0.42 <sup>a</sup>
9		30	0.48	0.453	– <sup>d</sup>	0.77 <sup>a</sup>
10		10	0.60	0.382	– <sup>d</sup>	0.14 <sup>a</sup>
11		24	2.25	0.360	0.670	0.54 <sup>b</sup>
12		6	0.61	0.320	0.680	0.13 <sup>b</sup>
13		– <sup>c</sup> – <sup>c</sup>	5.16 6.94	0.980 0.940	0.610 0.630	3.08 <sup>b</sup> 4.10 <sup>e</sup>

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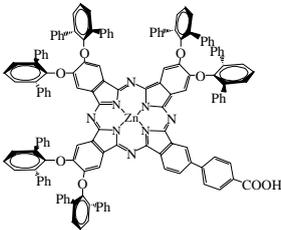
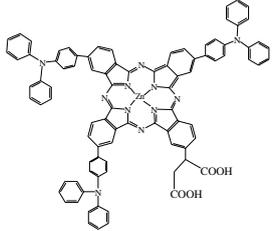
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**Table 1.** (Contd)

Sl. no.	Phthalocyanine structure	IPCE <sup>a</sup> (%)	$J_{sc}^a$ (mA/cm <sup>2</sup> )	$V_{oc}^a$ (V)	FF <sup>a</sup>	$\eta^a$ (%)
14		75	6.50	0.635	0.743	3.05 <sup>b</sup>
		41	4.04	0.570	0.670	1.52 <sup>f</sup>
		45	2.10	0.720	0.520	0.87 <sup>g</sup>
15		25	2.81	0.525	0.764	1.13 <sup>b</sup>
16		80	7.60	0.617	0.750	3.52 <sup>b</sup>
		72	16.20	0.666	0.720	7.74 <sup>h</sup>
17		47	5.63	0.557	0.750	2.35 <sup>b</sup>
18		70	9.15	0.600	0.720	3.96 <sup>b</sup>
19		30	5.30	0.580	0.740	2.30 <sup>b</sup>
20		52	4.80	0.580	0.770	2.10 <sup>b</sup>

(Contd)

Table 1. (Contd)

Sl. no.	Phthalocyanine structure	IPCE <sup>a</sup> (%)	$J_{SC}$ <sup>a</sup> (mA/cm <sup>2</sup> )	$V_{OC}$ <sup>a</sup> (V)	FF <sup>a</sup>	$\eta$ <sup>a</sup> (%)
21		78	10.4	0.30	0.700	4.60 <sup>b</sup>
22		27	3.36	0.460	0.689	1.05 <sup>b</sup>

<sup>a</sup>IPCE, Incident photon to current conversion efficiency;  $J_{SC}$ , Current density;  $V_{OC}$ , Open circuit voltage; FF, Fill factor;  $\eta$ , Efficiency.

<sup>b</sup>Redox electrolyte is  $I^-/I_3^-$  in volatile organic solvent.

<sup>c</sup>Myristic acid used as co-adsorbent.

<sup>d</sup>Photovoltaic data not reported.

<sup>e</sup>TiO<sub>2</sub> electroded treated with dil. HNO<sub>3</sub>.

<sup>f</sup>Non-volatile redox electrolyte: 0.9 M 1-butyl-3-*n*-methylimidazolium iodide, 0.1 M I<sub>2</sub>, 0.5 M *n*-methylbenzimidazolium iodide and 0.1 M lithium saccharide in  $\gamma$ -butyrolactone.

<sup>g</sup>Hole transport material 2,2',7,7'-tetrakis(N,N-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene.

<sup>h</sup>Photovoltaic data-based co-sensitization of organic and phthalocyanine sensitizers.

nature of the anchoring ligand to metallo phthalocyanine or without the anchoring group. Therefore, anchoring groups at the peripheral position of either the free base or metallo phthalocyanine may give better efficiency. Anchoring groups at peripheral positions of phthalocyanines are divided into two classes – symmetrical and unsymmetrical.

### Symmetrical phthalocyanines

A great variety of symmetrical phthalocyanines having anchoring groups either –COOH or –SO<sub>3</sub>H at peripheral positions of either the free base or metallo phthalocyanines have been reported. But, their efficiency has remained below 1%. Shen *et al.*<sup>34</sup> first reported sensitization of nanocrystalline TiO<sub>2</sub> with zinc tetracarboxy phthalocyanine (**7**) and the efficiency was very low<sup>34</sup>. Deng *et al.*<sup>35</sup> used gallium tetrasulphonated phthalocyanine as sensitizer for DSSC and conversion efficiency was very low. The poor conversion of light into electrical energy using gallium tetrasulphonated phthalocyanine was due to the formation of dimer on the surface of nanocrystalline TiO<sub>2</sub>.

The anchoring group and the distance from the macrocycle as well as central metal ion of the phthalocyanine

cavity played a major role in achieving high efficiency<sup>36</sup>. Grätzel and co-workers have used either sulphonic acid or carboxylic acid groups as anchoring groups and zinc(II) (**7**, **9**) or aluminum(III) (**8**, **10**) as central metal ion of phthalocyanine for the sensitization of nanocrystalline TiO<sub>2</sub>. Both sulphonic acid and carboxylic acid groups could achieve a stable binding to the surface of TiO<sub>2</sub>, which did not present significant influence on the electron injection. The macrocycle having carboxylic acid anchoring group and zinc(II) as central metal ion showed better conversion efficiency than the corresponding sulphonic acid anchoring group with aluminum(III) as central metal ion under similar test-cell conditions. The maximum efficiency that was observed in this series was 1% using **7** as the sensitizer. The poor  $\eta$  of phthalocyanines might be due to the aggregation and poor electron injection from excited state of macrocycle into the conduction band of semiconductor. To avoid the aggregation of phthalocyanines, Grätzel and co-workers used chenodeoxycholic acid as co-adsorbent to minimize the aggregation of phthalocyanines. This however, affects the efficiency of the test cell device. Sundstrom and co-workers used zinc(II) phthalocyanines substituted with amino acids for the sensitization of nanocrystalline TiO<sub>2</sub> (refs 37 and 38). Phthalocyanine substituted with tyrosine (**11**) shows better photovoltaic efficiency of 0.54% than

the glycine (**12**) derivative, whose efficiency was only 0.13%. Balaraju *et al.*<sup>39</sup> used iron tetrasulphonic acid phthalocyanine (**13**) for sensitization of nanocrystalline TiO<sub>2</sub>. They used PEDOT : PSS-coated FTO counter electrode rather than Pt counter electrode and the TiO<sub>2</sub> surface was treated with dilute HNO<sub>3</sub>. The device showed an overall conversion efficiency of up to 4.1%. Except in **13**, all other symmetrical phthalocyanines with anchoring groups either sulphonic acid or carboxylic acid groups had efficiency less than 1%. This efficiency is not sufficient for the commercialization of DSSC technology.

### Unsymmetrical phthalocyanines

The low efficiency of DSSC devices incorporating phthalocyanines as sensitizers was probably due to the lack of solubility of phthalocyanine macrocycle in common organic solvents, aggregation due to the planarity of macrocycle and poor electron injection from excited phthalocyanine to the nanocrystalline TiO<sub>2</sub> conduction band. One of the essential requirements for the light-harvesting system of a molecular/semiconductor junction is that the phthalocyanine sensitizer must possess directionality of its electronic orbitals in the excited state. This directionality should be arranged to provide an efficient electron transfer from the excited dye to the TiO<sub>2</sub> conduction band by good electronic coupling between the lowest unoccupied molecular orbital (LUMO) of the dye and the Ti 3d orbital.

Yanagisawa *et al.*<sup>40</sup> used two unsymmetrical phthalocyanines with different metal ions at the phthalocyanine central cavity. The zinc phthalocyanine-based sensitizer showed an overall conversion efficiency of 0.03%, whereas Ru(II) phthalocyanine-based sensitizer showed an efficiency of 0.40%. The low efficiency of these phthalocyanines was probably due to rupture in the conjugation between the macrocycle and the anchoring group, thereby resulting in poor electron injection from the excited state to the conduction band of TiO<sub>2</sub>. In order to further improve the efficiency of the DSSC device based on phthalocyanine sensitizers, unsymmetrical phthalocyanines have been designed based on the 'push-pull' concept<sup>41-45</sup>. These phthalocyanines have either three bulky *-tert*-butyl groups (**14**) or six alkoxy groups (**15**) in the molecular structure, which serves to increase the solubility of macrocycle in common organic solvents, minimizes the aggregation, acts as electron releasing ('push') and tunes the LUMO level of the phthalocyanine that provides directionality in the excited state. It also has two carboxylic acid groups which serve to graft the sensitizer onto the nanocrystalline TiO<sub>2</sub> and act as electron withdrawing ('pull')<sup>41,42</sup>. The sensitizers **14** and **15** have IPCEs of 75% and 25% respectively, with overall conversion efficiencies of 3.05% and 1.13% respectively, using volatile liquid redox electrolyte. The high efficiency of

the sensitizer, when compared to other phthalocyanine-based sensitizers is due to the directionality of the excited state electron from the sensitizer to the conduction band of the semiconductor TiO<sub>2</sub>. Using the durable redox electrolyte (high boiling point solvents such as  $\gamma$ -butyrolactone), the unsymmetrical sensitizer **14** showed a conversion efficiency of close to 2% and the device was stable even after 1000 h when continuously exposed to heat and light<sup>43</sup>. The sensitizer **14** was also tested using hole-transporting material 2,2',7,7'-tetrakis(N,N'-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-MeOTAD), and showed<sup>39</sup> an overall conversion efficiency of 0.87%. In another study<sup>46</sup>, the sensitizer was further redesigned having only one anchoring carboxylic acid group rather than two (**16**). This sensitizer showed an overall conversion efficiency of 3.52%. The high efficiency of **16** over **14** is probably due to the fact that the excited state lifetime is less in the former, so that the recombination of excited electron with oxidized phthalocyanine is less. Further, the distance and orientation of the anchoring group to the phthalocyanine macrocycle was also calculated<sup>47</sup>. The unsymmetrical phthalocyanine-bearing insulating spacer showed poor performance, whereas those having conductor spacer showed good performance.

Giribabu *et al.*<sup>44</sup> redesigned the sensitizer **14** by adopting 'push-pull' and extended- $\pi$  conjugation concept and reported the sensitizer **17**. The anchoring group in this sensitizer is a cyano acetic acid group. This sensitizer showed broader absorption compared to sensitizer **14**. However, the overall conversion of sensitizer **17** was 2.35% using liquid redox electrolyte. Garcia-Iglesias *et al.*<sup>48</sup> reported another sensitizer (**19**) having dicarboxylic acid group on extended- $\pi$  conjugation rather than cyano acetic acid group, with an overall conversion efficiency of 3.96%. The improved efficiency was due to the slow recombination process. Aggregation is one of the reasons for low efficiency of symmetrical phthalocyanines when compared to unsymmetrical phthalocyanines. The co-adsorbent chenodeoxycholic acid was used to further reduce the aggregation phenomenon in unsymmetrical phthalocyanines.

In order to further improve the efficiency of unsymmetrical phthalocyanines, one has to reduce the aggregation phenomenon further. Taya and co-workers<sup>49</sup> have further redesigned the phthalocyanine molecule by introducing bulky *-tert*-butyl **19** or phenoxy groups **20** and **21** in its peripheral sites. The absorption spectra of **19** both in solution and on TiO<sub>2</sub> showed a broader absorption around 600 nm, suggesting the formation of aggregation on the surface. In contrast, the sensitizers **20** and **21** showed a sharp Q band both in solution and on TiO<sub>2</sub>, indicating a significant decrease in aggregation. The IPCE of **19-21** was 30%, 52% and 78% respectively, at 700 nm. The overall conversion efficiency of **21** was 4.6%, which is the highest efficiency among phthalocyanine-based sensitizers. This is due to the lesser aggrega-

tion of phthalocyanine on the TiO<sub>2</sub> surface than that of other phthalocyanine-based sensitizers.

Phthalocyanines have sharp Q-band in the 650–700 nm region. In order to further improve the efficiency of phthalocyanine-based sensitizers, one has to improve absorption in 500–600 nm region. Torres and co-workers<sup>46</sup> have used the co-sensitized concept by mixing a phthalocyanine and an organic sensitizer, whose absorption is around 550 nm. Such types of cocktail sensitizers have shown an overall efficiency of 7.74%. Giribabu *et al.*<sup>45</sup> reported a cocktail sensitizer based on zinc phthalocyanine and bulky organic molecules, triphenyl amine (**21**). The presence of bulky triphenyl amine groups further reduces the aggregation of the macrocycle. The absorption spectrum broadens due to the presence of triphenyl amine groups. It has an IPCE of 37%, with an overall conversion efficiency of 1.05%. The low efficiency of **22** is probably due to the low energy transfer efficiency from triphenyl amine moiety to the phthalocyanine macrocycle.

Though phthalocyanine-based sensitizers have low efficiency compared to Ru(II) polypyridyl complexes for DSSC applications, they are low-cost and no concern about their resources. The sensitizer is the one of the expensive components of the DSSC device. Through various modifications of the phthalocyanine macrocycle, the efficiency has been increased from 0.1% to 4.6%. But, this efficiency may be increased up to 6% either by re-designing the phthalocyanine macrocycle or by tuning the redox electrolyte. If Ru(II) complexes are replaced with phthalocyanine sensitizers, then the cost of the device can be drastically reduced and its durability increased.

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