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Review

Porphyrins in bio-inspired transformations: Light-harvesting to solar cell

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ABSTRACT

Almost two decades after the outstanding X-ray crystallographic studies of light-harvesting antenna complex LH_2 of the photosynthetic bacterium *Rhodopseudomonas acidophila*, a plethora of artificial mimics have been developed. It is well known that, in green plants, sophisticated self-assembled polypyrrolic architectures of photosynthetic units lead to efficient photo-induced electron transfer and by subsequent processes solar energy is stored in terms of chemical fuel in a very efficient way. The beauty and accuracy of light harvesting as well as the electron transfer process in natural photosynthesis are sources of inspiration for chemists, physicists and researchers of other disciplines to design artificial systems in order to convert solar energy into electricity or other forms of energy. More importantly, the understanding of the fundamentals of these processes is necessary in order to improve the design and the efficiency of artificial photoconversion systems, especially for photovoltaic applications. Porphyrins being ubiquitous in most of the natural pigments are an important building block for developing artificial molecular assemblies for solar photoconversion. The simplest mimicking unit of the natural photosynthetic center could be a

Abbreviations: BDP, boron dipyrrin; CDCA, chenodeoxycholic acid; CIGS, copper indium gallium selenide; CNT, carbon nanotube; CS, charge seperation; C_{60}, fullerene-C_{60}; D–A, donar–acceptor; DSSC, dye-sensitized solar cell; EET, excited electron transfer; GO, graphene oxide; HFIP, 1,1,1,3,3,3-hexafluoro-2-propanol; LH, light harvesting; NIR, near infra-red; OPV, organic photovoltaics; Pc, phthalocyanine; PCE, power conversion efficiency; PSU, photosynthetic unit; RGO, reduced graphene oxide; SWNH, single wall carbon nanohorn; SWNT, single wall carbon nanotube; TCPP, tetra(4-carboxyphenyl)porphyrin; TMPyP, 5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrin tetra(*p*-toluenesulfonate); TPP, tetraphenylporphyrin.

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porphyrin-derivative where an electron donor and an electron acceptor moiety are covalently linked or self-assembled *via* weak interactions. Intrinsic light-harvesting properties of porphyrins made them the best choice as sensitizers for organic photovoltaics, especially in photo-electrochemical dye-sensitized solar cells (DSSCs) or in hybrid solar cells. It is worth mentioning that, twenty years after the discovery of DSSC by Grätzel, a porphyrin based sensitizer has exhibited one of the highest efficiency (11.9%) reported so far. In this review, our aim is to highlight mostly the recent studies on porphyrin based bio-inspired materials for solar energy utilization.

1. Introduction

Efficient production of clean and sustainable energy is the most formidable scientific challenge in the next half-century [1,2]. The demand for energy is increasing with growing global population which is projecting toward 10.6 billion by 2050 [3]. In addition, limited resources of fossil fuels and the harmful effects of combustive carbon emissions compelled researchers to find carbon-free and environmentally friendly energy sources [4]. Sunlight is the most abundant and one of the cleanest sources of energy. Therefore, the utilization of solar energy in terms of solar fuels or electricity has attracted much attention by the scientific community. Nature harnesses solar energy very efficiently *via* the photosynthetic process. The basic route of the natural photosynthesis is that first light is captured by antenna systems made of pigment–protein complexes. The captured excitation energy is transferred to the pigments in the reaction center proteins where the photo-induced electron transfer gives rise to electrochemical potential energy. Then, redox processes in catalytic sites lead to water splitting and fuels such as carbohydrates.

This natural phenomenon of sunlight harvesting and its utilization served as the inspiration for research in various disciplines. As a result, artificial antenna systems were developed and new materials for solar cell devices were produced [5,6]. Toward these efforts, a considerable amount of pioneering research was carried out and remarkable success was achieved. The "artificial leaf" by Nocera et al. [5], serves a good example of these discoveries. Similar practices include the generation of bioelectricity by direct extraction of photosynthetic electrons from a living algal cell *Chlamydomonas reinhardtii* as reported by Ryu et al. [7], and a self-repairing artificial light-harvesting complex reported by Strano et al. [8]. However, all the synthetic systems reported to date need to be optimized in order to reach the near impeccable functions of all natural systems [9,10]. Concerning the mechanism of photosynthesis, the absorption of light induces the electronic excitation at the membrane containing an array of macrocyclic tetra-pyrrole derivatives such as chlorophylls, carotenoids *etc*., then undergoes a rapid photo-induced charge separation and efficiently transforms solar energy into chemical potentials. Therefore, it is necessary to understand the functional mechanisms of the natural light harvesting unit in order to built an efficient artificial photosynthetic fuel production system [11–15]. Thus, the light harvesting antenna model must be able to absorb sunlight along the whole visible and the near IR spectrum. Then to transform the light energy into chemical energy by water splitting to hydrogen fuel or to "electrical energy" for future applications of sunlight transformations [16,17].

Various cells (silicon, organic dye-sensitized) can mimic the fundamental principles of the natural photosynthetic units. For example solar cells capture sun radiation in terms of excited state electron–hole pairs followed by charge separation, which is in turn converted to electrical energy. The state of the art single crystal silicon solar cells is the most commonly used photovoltaic technology at present exhibiting 25% efficiency in the laboratory and 22% efficiency on an industrial scale [18]. Silicon based solar cells display high efficiencies and long stabilities, but have high energy costs due to silicon purification and solar cells manufacture. Therefore, the effort of the scientific community is focused on the preparation of solar cell systems with low cost and high efficiencies. Photovoltaics based on Si-thin film, organic semiconductors, dye sensitized cells, *etc.* are cost effective alternatives of single crystal silicon cells. Si-thin films may offer a cheaper substitute of crystalline silicon cell but suffer from relative low efficiencies and availability of the resource materials. In this regard, dye-sensitized solar cells (DSSCs) a pioneering discovery by O'Regan and Grätzel in 1991 [19], became a viable and promising technology. Their low cost, simple fabrication process, compatibility with flexible materials and good longevity are some of the major advantages in the field of solar energy conversion [20–28]. Ruthenium polypyridyl complexes served as a leading player in advancing DSSC technology and showed the best efficiencies (up to 11%) on ruthenium based systems under standard air-mass (AM) 1.5 illuminations [29–45]. However, the high cost toxicity and low stability of the ruthenium complexes led researchers to search for alternate chromophores such as, porphyrins, phthalocyanins and other organic dyes.

Porphyrins as photosensitizers on DSSC are particularly interesting. Owing to appropriate LUMO and HOMO energy levels and very strong absorption of the Soret band in the 400–450 nm region, as well as the Q-bands in the 500–700 nm region, porphyrin derivatives can be suited as panchromatic photosensitizers for DSSCs and are potential candidates to replace ruthenium dyes. Introducing appropriate substituents in four *meso* and eight *beta* positions of the porphyrin, allows tailoring of the spectroscopic response as well as electrochemical potentials, which in turn, could be reflected in the efficiency of solar cells. Remarkably, a discovery by Grätzel and Diau et al., reported a porphyrin sensitizer that achieved 12.3% efficiency using Co(II)/Co(III) based redox mediator [46]. As our research interests lie in exploring different aspects of porphyrins [47–56] while, the underlying subject of this review is on bio-inspired materials for solar energy utilization, we will restrict our discussion on porphyrin based systems.

2. Bioinspired light harvesting by porphyrin containing antenna systems

Natural light harvesting antennae consist of chromophores such as, chlorophylls, carotenoids, luteine, *etc.* Chlorophylls have very high molar extinction coefficient (~100,000 $M^{-1}\,cm^{-1}$) [57,58] owing to their highly conjugated monomeric units that are assembled in special orientation in the antenna complex. The crystal structure of the light-harvesting antenna complex LH_2 from the purple bacterium *Rhodopseudomonas acidophila* revealed the circularly arranged assemblies of carotenoids and bacteriochlorophyls embedded in two symmetric rings (B850 and B800) [59]. This finding triggered the design and synthesis of covalent or non-covalent linked cyclic porphyrins for structural mimicking of the photosynthetic unit (PSU). Moreover, the photophysics of these multi-chromophoric systems give the fundamental insight into light induced energy transfer and electron transfer processes. Numerous artificial antenna systems based on donor–acceptor (D–A) architectures have been constructed, and relevant to natural photosynthesis photophysical studies are reported [8,60–71].