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Creating Electrochemical Gradients by Light: From Bio-inspired Concepts to Photoelectric Conversion

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Light is harvested by natural photosynthetic systems to generate electrochemical gradients that power various reactions. Implementing nature's lessons in photosynthesis holds great promise for technological advances. With a focus on designs and concepts, recent progress in generating electrochemical gradients by light, mimicking the two general types of photosynthetic centers in nature that make use of either light-induced charge separation or photo-isomerization are summarized here. Light induced electrochemical gradients pave new ways for photoelectric conversion. While extensive research in this direction has focused on light-induced charge separation, recent work has shown that energy conversion based on photo-isomerization is very promising. Photoswitchable compounds have been found in nature, such as the retinal molecule in bacteriorhodopsin. These compounds may form an attractive molecular basis for future progress in this field.

1. Introduction

There is ongoing research interest in learning from natural biochemical machinery to advance current technology. Solar energy arrives on Earth at an annual rate of ca. 120'000 terawatts which is significantly higher than the current annual worldwide energy consumption rate of ca. 15 terawatts.[1-3] Making efficient use of solar energy is a promising solution for the increasing global energy demand.[4-8] Developing highly efficient solar cells has therefore become an extremely popular area in fundamental and applied science.[9-12]

Solar energy is harvested in nature by living organisms to produce (electro)chemical energy for almost all life on Earth. Photosynthesis is one of the most fundamentally important biological processes. In chlorophyll based photosynthetic centers, absorption of sunlight creates an electronic excitation in the peripheral antenna of photosynthetic systems (PSI and PSII) and the subsequent transfer of the excitation energy to reaction centers (RC).[13, 14] During the photoreaction, a proton gradient across the cell membrane is formed to generate proton-motive force, which eventually results in the production of adenosine triphosphate (ATP) by ATP synthase.[6, 13] These RCs are one of the most advanced photovoltaic devices developed by nature, with a quantum yield of ca. 100%,[13] while this does not yet guarantee a high conversion efficiency.[15]

Some archaea, such as *Halobacterium halobium*, do not possess the oxygenic photosynthetic system of green plants.[16, 17] These microorganisms have instead developed photoproteins such as bacteriorhodopsin (bR), proteorhodopsin and halorhodopsin in the cell membrane to delocalize H^+ and Cl^- and ATP upon light absorption.[18-21]

Nature seems to find its own way to harness solar energy by converting it to electrochemical and chemical energy. Either way, electrochemical gradients are formed after light absorption that are utilized to power various biological processes.[13, 16] An electrochemical gradient is a convenient energy form for biosystems. From a technological angle, following the generation of electrochemical gradient is the potential for its conversion to electrical energy in the form of an electric current.[7, 22] The concepts of light triggered electrochemical gradients and photoelectric conversion are therefore linked.

There has been extensive research work on mimicking the natural photosynthetic center in recent years.[4-6, 23] In this perspective article, recent results on light-induced electrochemical gradients in bio-inspired artificial light harvesting systems and their implication for photoelectric conversion are discussed. We are focusing on fundamental mechanisms, potentials and limitations, with an

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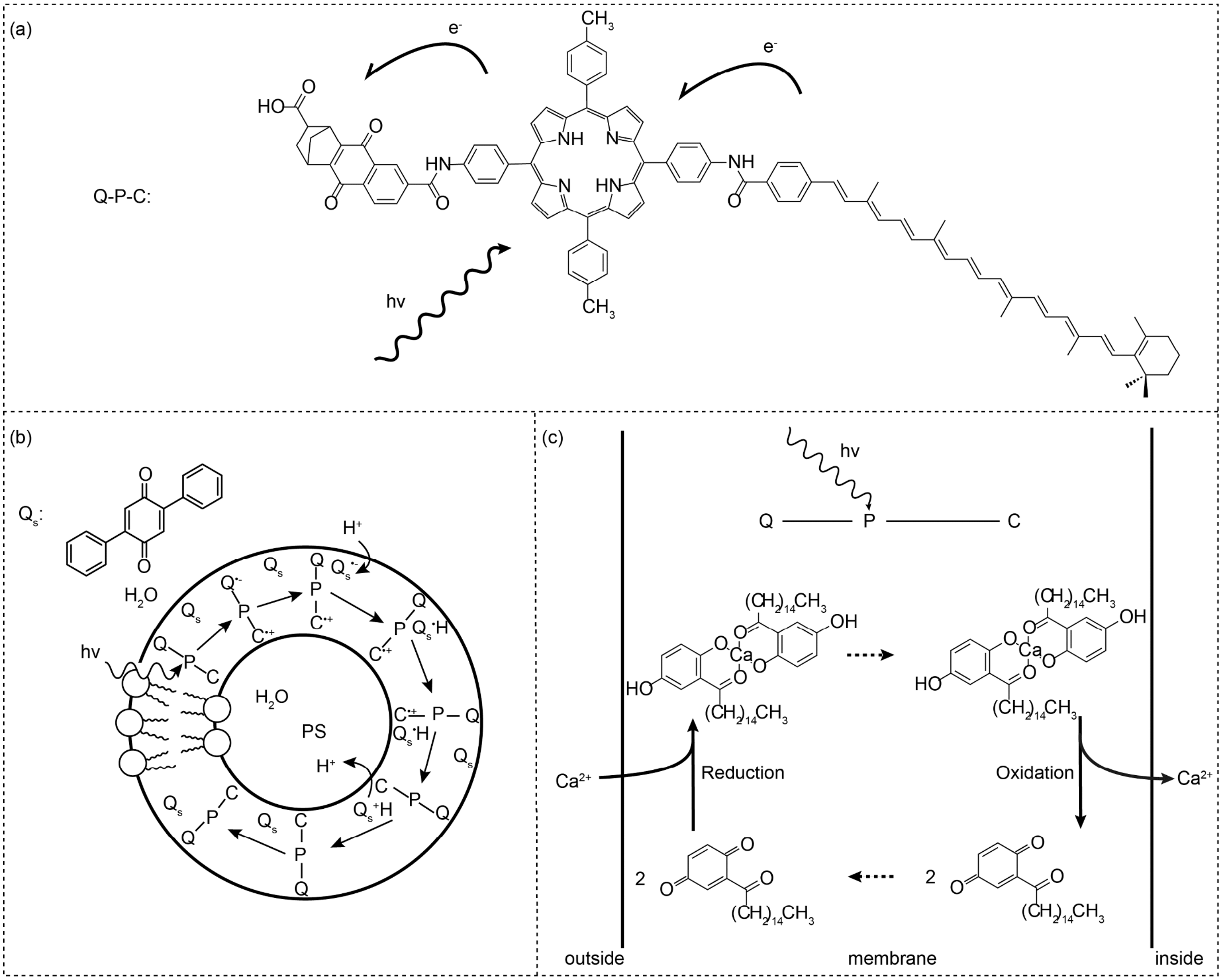

Figure 1. (a) Light induced charge separation in carotenoid polyene (C)-tetraarylporphyrin (P)-carboxylated norbornene (Q) triad. (b) Light-induced proton pumping across the bilayer lipid membrane containing oriented Q-P-C and Q_s. (c) Schematic representation of a liposome-based, light-powered transmembrane Ca^{2+} pump. The Q-P-C artificial reaction centre crosses the membrane, with its hydrophilic quinone moiety near the external interface. The shuttle molecule for Ca^{2+} is oxidized at the inner side and reduced at the outer side by the charge separated Q-P-C. Adapted from reference 25 and 27.

emphasis on chemical principles. Conventional semiconductor based solar cells as well as dye sensitized solar cells (DSSC) are not the focus of this review.

2. Mimicking Nature: Producing Electrochemical Gradients by Light-induced Charge Separation

Light-induced charge separation is ubiquitous in natural photosynthetic processes. Efficient electron transport and hole movement enable long distance charge separation and the generation of electrochemical gradients. In photoproteins of green plants, numerous chromophores are used to achieve the separation of charge and to avoid back reactions.[24]

Although a direct duplication of the natural system is not possible owing to its high complexity, artificial light driven ion pumps have been attempted. A molecular triad Q-P-C containing carotenoid (C), porphyrin (P) and naphthoquinone (Q) moieties as shown in Figure 1 has been devised to make artificial photosynthetic centers and transport ions across biological lipid bilayer.[25-27] The triad undergoes photoinduced electron transfer from the excited singlet state of the porphyrin moiety to first yield the intermediate species $Q^{\bullet-}$-$P^{\bullet+}$-C, and subsequently the long range charge separated species $Q^{\bullet-}$-P-$C^{\bullet+}$. The generation of the intermediate $Q^{\bullet-}$-$P^{\bullet+}$-C has a quantum yield of nearly 1 while the conversion from $Q^{\bullet-}$-$P^{\bullet+}$-C to $Q^{\bullet-}$-P-$C^{\bullet+}$ has to compete with the charge recombination step ($Q^{\bullet-}$-$P^{\bullet+}$-C to Q-P-C) and results in an overall quantum yield of 0.15.[28]

As illustrated in Figure 1 (b), a light controlled artificial proton pump has been proposed by doping liposomes with Q-P-C and 2,5-diphenylbenzoquinone (Q_s), which acts as a shuttle for protons.[25] In this design, Q-P-C must align uniformly to result in the

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unidirectional transport of H^+. Active transport of Ca^{2+} has been achieved by replacing Q with a chelator molecule for Ca^{2+}, as shown in Figure 1 (c).[27] The transport of Ca^{2+} also results in an increase of the transmembrane potential.

Reported by Imahori and co-workers., light irradiation on a similar ferrocene (Fc) –phorphyrin (P) -C_{60} molecular triad yielded $Fc^{\bullet+}$-P-$C_{60}^{\bullet-}$ with a lifetime of ca. 0.01 ms and a quantum yield of 0.25-0.99. The compound was used to control the transport of K^+ across a cell membrane.[29]

As shown in Figure 2, Matile et al. reported on a blue, red-fluorescent rigid-rod photosystem in which the π-stack supports sufficient charge separation for conversion into electrochemical gradients.[30] The photoproduction of proton gradients was achieved with lipid bilayer vesicles loaded with quinone acceptor and surrounded with the electron donor EDTA. The establishment of the proton gradient differs from the molecular triad approach since there is no shuttle for protons within the membrane. The pH change inside the vesicles is a result of electron infusion and the resulting reduction of entrapped quinone molecules. The concept has been adapted to devise multifunctional photosystems (see below).

Transition metal ion complexes that exhibit metal to ligand charge transfer (MLCT) have been employed to create transmembrane gradients as well. Hurst and co-workers reported on the transport of pyrylium ions in vesicle based photocatalytic systems containing tris(2, 2'-bipyridine)-Co(III) ion and zinc porphyrin.[31, 32] Hvasanov *et al.* demonstrated a light driven proton pump across a polymer bilayer.[33] Ruthenium(II)-terpyridine was linked to cytochrome c and coupled to cytochrome c oxidase to drive the electron transport chain.

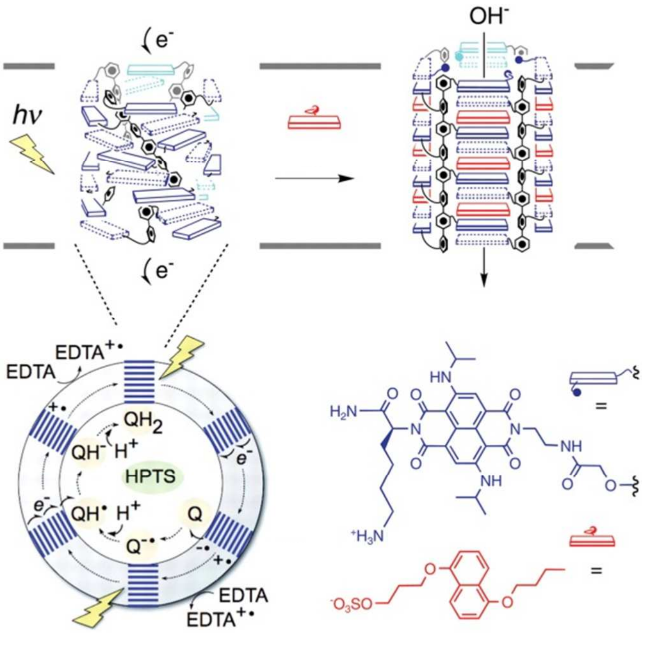

Figure 2. Photoproduction of H^+ gradient across lipid bilayers using π-stacked rigid-rod fluorescent supramolecules. Reproduced from reference 30 with permission. Copyright: The American Association for the Advancement of Science.

To summarize, the generation of intra/intermolecular long range charge separation in artificial light harvesting systems has been achieved in the past few decades. Charge recombination must be suppressed as much as possible. Although only a few examples are reported, this direction should be continued due to the insight it can provide to further solar energy utilization.

3. Photo-isomerization for Ion Transportation

Bacteriorhodopsin (bR), a retinal containing photochromic protein with a molecular weight of 26784 daltons produced by halobacteria, is the second biggest photosynthetic system.[16] Conceptually similar to the biological machinery of vision, the bR photosynthetic system works differently from the more developed chlorophyll system of green plants. As shown in Figure 3, light is absorbed by bR with an absorption maximum at 568 nm (B_{568}) and causes the photoisomerization of the protein-bound all-trans retinal about its 14–15 single bond to the 13-cis isomer (K_{590}). K_{590} has a reduced pKa and rearranges the proton conductive pathways, resulting in the proton displacement from the inner side of the cell membrane to the outer surroundings.[34] After photoisomerization, the retinal molecule is released from the protein and a new molecule takes its place. Freely dissolved retinal does not absorb in the visible range, thereby efficiently localizing the light absorption step in the membrane protein.

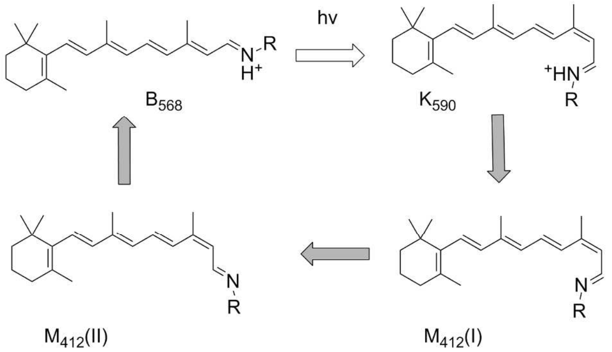

Figure 3. Proton pump cycle of bR in *Halobacterium halobium*, with dark arrows showing the dark transitions.

Other photochromic proteins such as proteorhodopsin and halorhodopsin share similar mechanisms.[21, 35, 36] Unlike in the chlorophyll system, it is the photo-isomerization after light absorption that results in the affinity change for H^+ and the electrochemical gradient.

Since photo-isomerization usually causes changes in molecular light absorption, some of the compounds are also called photochromic compounds, or molecular photoswitches. The rhodopsin based photosynthetic centers in nature are much younger than the chlorophyll based ones found in green plants.[37] Why did nature take such a long time to evolve this second photosystem? As far as the number of different models is concerned, natural photochromic proteins are rather rare. Indeed, not many molecular varieties exist that can undergo photo-isomerization, even taking synthetic ones

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into account. Figure 4 shows the core structures of some well-known photochromic compounds.

Photochromic compounds are sensitive to photons and many of them transform upon UV light radiation, since the energy required to relocate atoms is rather high. Only a few chemicals can be switched by visible light from their thermally stable state.[38-40] Nature has developed retinal, which is sensitive to visible light in its protein bound form. The likely reason lies in the emission maximum of sunlight, which is similar to this absorption maximum in its protein bound form.

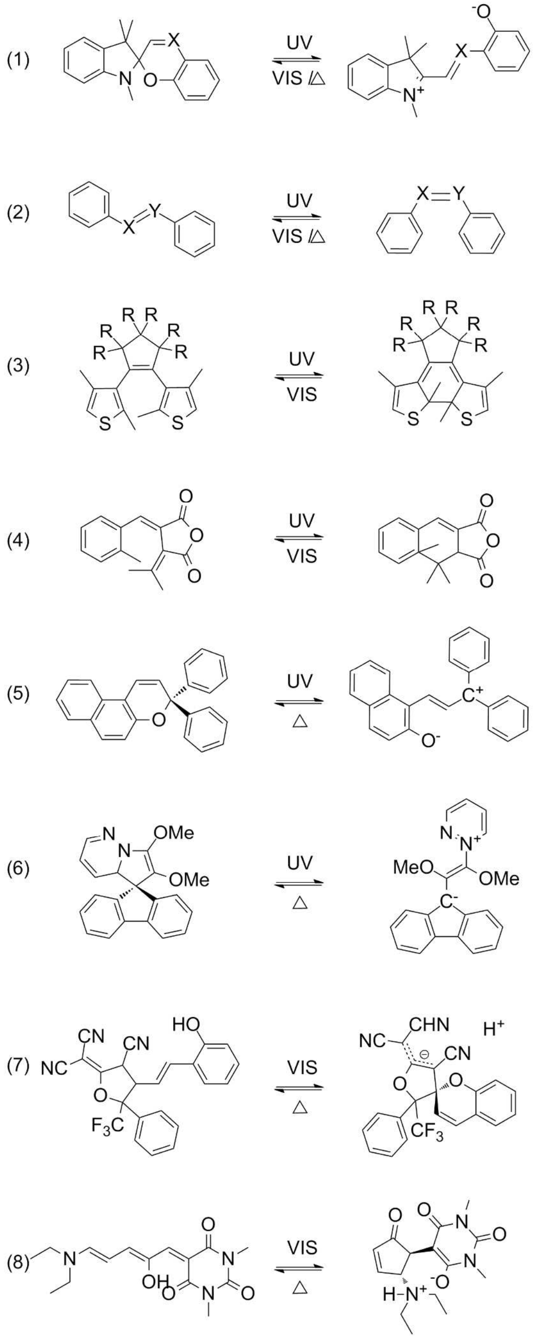

Figure 4. Photo-isomerization of some well-known photoswitchable compounds. (1) spiropyran (X=C) and spirooxazine (X=N), (2) azobenzene (X=Y=N), stylbene (X=Y=C) and Shiff base (X=C, Y=N), (3) diarylethene (R=F or H), (4) fulgide, (5) chromene (6) dihydroindolizine (7) visible light responsive photoacid from reference 38, (8) visible light switchable compound form reference 39.

A limited number of artificial systems to transport ions and create electrochemical gradient that resemble bR have been reported. In order to create an ion flux based on the photochromic compounds, the compound's affinity for a certain ion must change upon light irradiation. For example, azobenzenes, diarylethenes and spiropyrans (Sp) are widely studied compounds that can be used to make so-called photo-controllable molecular switches.[41]

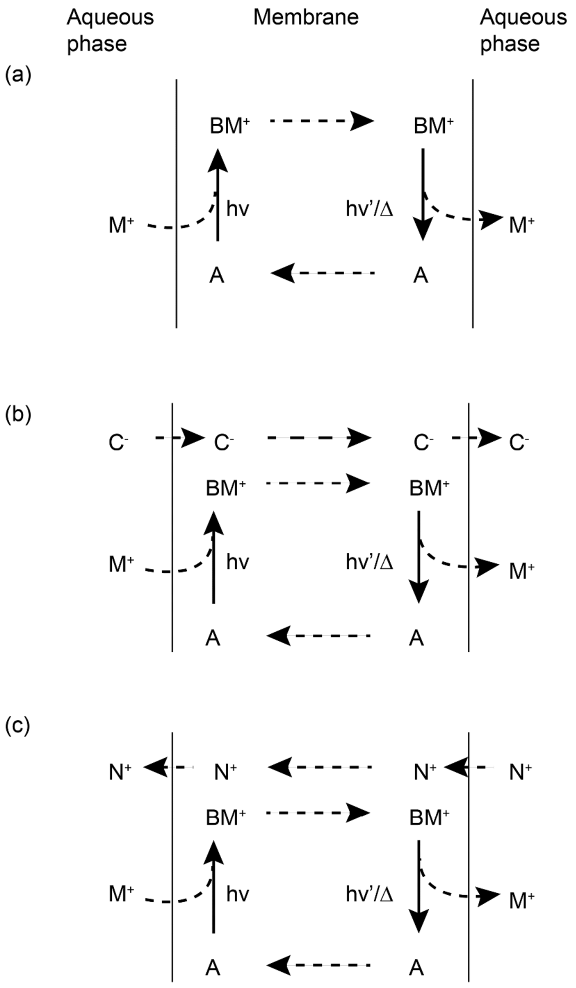

Figure 5. Light induced ion transport across a liquid membrane containing a photoswitchable compound that undergoes a photoreaction from A to B. B has a higher affinity for M$^+$ and carries M$^+$ across the membrane where it is converted back to A, either thermally (Δ) or catalyzed by light of a different wavelength (hv'). (a) Transporting M$^+$ with no interfering ions, (b) Co-transport of M$^+$ and a lipophilic anion C$^-$, (c) Counter-transport of M$^+$ and N$^+$.

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In principle, as shown in Figure 5, light triggered transportation of ions can be induced by incorporating molecular switches into membranes, thereby separating two chambers containing the interactive ions. In the simplest approach (Figure 5 (a)), ions are transported directly by the photo-responsive carriers, resulting in a net charge separation. Electrochemical gradients will form within the membrane and an electric potential difference will arise at the two sides of the membrane. In less energetically challenging designs (Figure 5 (b) and (c)), the electrochemical gradient is coupled to a counter acting or co-transporting ion flux, without net charge accumulation at the two membrane sides. The conteracting flux will cause a diminished electric potential difference.

Kumano *et al.* used azobenzene bridged crown ether to transport K^+ across a thick plasticized poly(vinyl chloride) (PVC) membrane, accompanied by co-transport of chloride or p-toluenesulfonate ions.[42] The *cis* isomer exhibits a higher affinity for K^+ and thus facilitates the K^+ uptake at the UV side. Sakamoto *et al.* reported on several azacrown modified spiropyrans as photo-responsive carriers for alkali metal ions.[43] These molecules were shown to transport alkali metal ions across dichloromethane membrane in the presence of the picrate ion, which was co-transported to provide visual perception of the transportation. Azobenzenes were also embedded in vesicles as modulators for potassium ion permeation.[44]

Bakker and colleagues reported that the photo-isomerization of spiropyrans results in two structures of very different basicity.[45] The light induced basicity change highly resembles the photo-properties of the retinal compounds in natural bR. Chloride ions can be co-extracted into a polymeric membrane together with H^+ by UV light illumination, generating a electrochemical gradient of Cl^- at the aqueous-polymeric phase boundary.[46] Later, nanospheres containing Sp and other receptors (ionophores) were shown capable of modulating the surrounding K^+ concentration.[47] Recently, it was demonstrated that H^+ can be relocated by polymeric liquid membrane embedded with Sp, forming an artificial proton pump (Figure 6).[48] This is the first time that photoswitchable compounds were used to create a proton pump in rather thick (ca. 25 µm) polymeric membrane, converting light to electrochemical energy and later to current. In order to increase the proton transport rate, asymmetric light illumination was required, while only one sided illumination is needed in photovoltaic cells and natural photosynthetic systems. Proton pumping was still observed with just one sided UV or visible light irradiation but the gradient was much smaller.

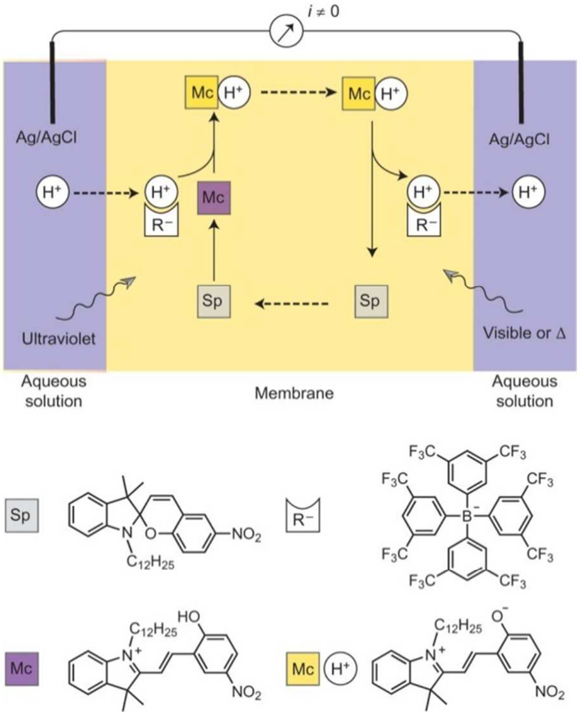

Figure 6. Scheme showing the photocurrent generation principle based on a photoisomerization induced proton pump. The left side of the membrane is illuminated with UV light while the right side is irradiated with visible light or kept in the dark. The aqueous solutions both contain 0.1M HCl. The Dashed arrows represent mass transport of the species.

4. From Artificial Photosynthesis to Photoelectric Conversion

4.1 Utilizing Light-induced Charge Separation: A Chemical Approach

If charged species are transported across a membrane without any counteracting flux, an electrochemical potential difference will establish between the two sides of the membrane. Electrochemically, this gradient can be used to generate electric energy, given that the two chambers separated by the membrane are connected through an external load (Figure 6).

Despite the conceptual elegance of electrochemical gradients created by charge separation in liposomes and polymersomes, direct conversion from light energy to electrical energy requires alternative designs. After light induced charge separation, electrons or holes must move toward an electrode, as in DSSC.[49]

Self-assembled monolayers (SAMs) are expected to provide a promising avenue for this purpose. There have been so far many examples of light-induced energy/electron transfer on gold electrodes and semiconductors. Early on, photocurrent generation in metal bisphosphonate multilayer thin films with a power conversion efficiency of 0.05% were reported.[50] Later, molecular triads with a long lived long range charge separated state were self-assembled on gold electrodes to generate photocurrents.[51] Similarly, gold electrodes modified with mixed self-assembled monolayers of porphyrin-ferrocene-thiol triad, boron-dipyrrin and ferrocene-porphyrin-fullerene triad were used to convert light to current with efficiencies near 1%.[52] Fullerenes or ruthenium tris(bipyridyl) complexes modified self-assembled monolayers on gold electrodes able to modulate the photocurrent generation were also reported.[53] However, efficient energy conversion (overall efficiency 1%-10%)

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from light to current was hampered due to the difficulty in assembling the donor-acceptor linked molecules unidirectionally.

Matile and co-workers reported on a zipper assembly of photoactive rigid-rod naphthalenediimide π-stack architectures on gold nanoparticles and gold electrodes, representing a different approach to achieving highly ordered long range charge separation.[54] Upon light illumination, electrons and holes can move across the π-stack in opposite directions, similar to the process reported in the photoproduction of H^+ gradients in lipid bilayers. Later, the same group proposed a self-organizing surface-initiated polymerization (SOSIP) to create ordered functional photosystems on transparent conductive glass surfaces.[55] Despite the fact that the efficiency so far is not yet sufficient for practical use, the conceptual design to achieve self-organized photosystem is quite elegant.

4.2 Photoprotein Modified Electrode

On the other hand, it has long been recognized that the natural RC pigment proteins can be utilized *in vitro*. Instead of mimicking the natural photoinduced charge separation, researchers have taken one step back and introduced photoprotein-modified electrodes.

As reported by Welland and co-workers, such photoelectrochemical cells are typically constructed with a conductive glass anode modified with photoprotein, an electrolyte solution containing the electron transducer, and a platinum cathode.[56] Figure 7 shows the vacuum potentials for the key components. Upon light irradiation, a charge separation is formed to produce P^+-Q_B^-. While P^+ is reduced at the fluorine-doped tin oxide (FTO) electrode, Q_B^- is oxidized by the redox mediator *N,N,N',N'*-tetramethyl-p-phenylenediamine (TMPD), which later delivers the electrons to the Pt counter electrode. These photoelectrochemical cells can produce direct current upon continuous illumination and also alternating current in response to discontinuous illumination.[57] Despite the extremely high yield of primary charge separation and the relative large open-circuit voltage (ca. 0.21 V), the external power conversion efficiency is relatively low. One possible reason is the buried location of the electron transfer molecules inside the RC, which could increase the intermolecular distance and cause elevated electron-tunneling barrier.

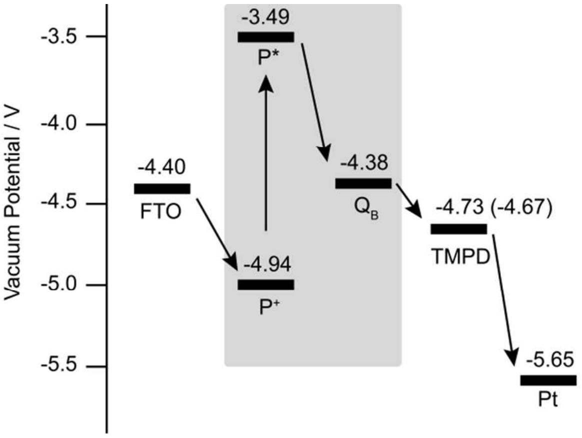

Figure 7. Vacuum potentials of key components of a photoelectric cell composed of a photoprotein modified FTO electrode, a Pt counter electrode and TMPD as redox shuttle, adapted from reference 56.

As in the artificial photosynthetic centers, the orientation and alignment of the RC is very important. An additional mediator could also help reduce the electron-tunneling barrier. For instance, incorporating cytochrome c into the immobilized RC can significantly improve the electron transfer process between RC and the gold electrode.[58]

In conceptually similar work, Yaghoubi *et al.* showed that the photosynthetic reaction center can be immobilized through a carboxylic acid terminated cytochrome c linker for applications in photoprotein-based bio-photovoltaic devices.[59] Choi *et al.* have reported on bio-photodiodes with self-assembled heterolayers containing green fluorescent proteins, cytochrome c or organic molecules such as viologen through Langmuir-Blodgett techniques.[60, 61]

Construction of solar cells with bR has attracted attention in recent years because of bR's high long term stability and bio-functionality against thermal, chemical, and photochemical degradation.[22] Following the early reconstruction of bR in proteoliposomes to generate electric potentials[62], Thavasi *et al.* studied the feasibility of bR as bio-photosensitizer in excitonic solar cells.[63] Recently, bR was molecularly linked to quantum dots to introduce photovoltaic devices towards improvement in solar cell effiency.[64] The theoretical efficiency limit for such photovoltaic device should obey the Shockley–Queisser limit.[65]

In conclusion, bR is now becoming a promising candidate in photoelectric conversion. However, the variety of photoproteins that can be fixed on an electrode remains limited. Construction of the electrodes requires attention since the unidirectional orientation of the protein array is the key to obtaining a high efficiency.

4.3 Photo-Isomerization for Photoelectric Conversion: How Far Can It Go?

At the heart of every photoelectric conversion device lies the photon to electrical transduction mechanism. How to generate a photovoltage and make the most efficient use of it? In natural systems, relocation of ionic species can influence the electrostatic fields and build up the electric potential difference. However, in electrochemical cells, electrode potentials are closely related to the concentration (more strictly, the activity) of the redox active species by the Nernst equation. A photovoltage is formed when a photoreaction changes the concentration of the redox active species, which defines the electrode potential. Current will flow once the two electrodes are connected. The steady state photocurrent density can be limited by a number of factors including electrode material, light intensity, photoreaction rate, electrode reaction kinetics, mass transport, and the ohmic drop from the solvent.[66]

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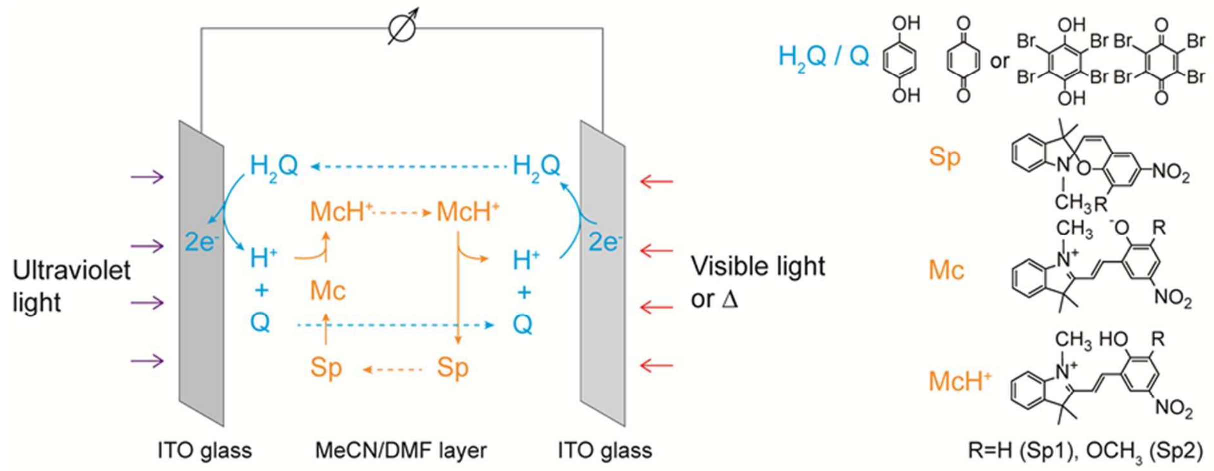

Figure 8. Photoelectric cell based on PCET and a photo-isomerization reaction. Ultraviolet light (UV) is introduced from one side where Sp is transformed to Mc. The opposite side where the ring-opened form is transformed back to Sp is illuminated by visible light or left in dark (Δ). A photovoltage is formed with the electrode potential at the UV side lower than the other. Tetrabutylammonium hexafluorophosphate is used as supporting electrolyte.

Previous photoelectric conversion methodologies involve mostly utilization of charge separation processes after light absorption. Photo-isomerization, the process that occurs in photochromic proteins, seems to be much less explored. There are very few reports on photoelectric conversion based on photo-isomerization mechanism. Previously it has been proposed that spiropyran can be used in photoelectric conversion.[48] As shown in Figure 6, a polymeric membrane doped with Sp and ion exchanger has been shown to transport H^+ under asymmetric light illumination. The pumping of H^+ creates an electrochemical gradient across the membrane. Therefore, when the two sides of the membrane are connected to appropriate electrode elements, current will flow. In addition to direct current, alternating current can be produced by applying alternating UV and visible light to one side of the membrane. Nevertheless, the design requires two aqueous solutions bracketing the membrane and acting as source and sink for proton transport, and additional Ag/AgCl elements as ion to electron transducers. These elements cannot renew themselves and will place a limit on the efficiency of the photoconversion system.

Soon afterward, Xie and Bakker proposed a new approach in which photoswitchable compounds can be used together with proton-coupled electron transfer (PCET) reactions for photoelectric conversion.[67] As shown in Figure 8, the electrode potential is defined by the PCET redox pair, quinone/hydroquinone. Since for a PCET redox couple, the redox potential also depends on H^+ concentration, changing the local pH will result in an change on this potential.[68, 69] The redox potential is therefore related to the specific form of Sp at the electrode. At the UV side, the photomerocyanine (Mc) prevails, with a much higher basicity than the ring-closed form. On the opposite side, Mc is converted back to Sp upon visible light illumination.

Unfortunately, the efficiency for this initial device is ca. 0.02%, limited mainly by the large PCET redox barrier at the electrode surface.[67] In that work, ITO glasses act merely as conductive and optically transparent substrates. A thin coating of catalyst on the ITO substrate, resulting in minimal attenuation of the incident light, would be most promising to effectively catalyse the PCET reaction. On the other hand, other photo-isomerizable compounds inducing a basicity change could also be explored. Azobenzene based photoswitches that exhibit large acidity changes upon light irradiation were reported by Jullien and co-workers.[70] Visible light sensitive reversible photoacids were also recently introduced.[38, 40] Excited state photoacids such as 8-Hydroxypyrene-1,3,6-trisulfonic acid (HPTS) could potentially be promising as well for this purpose.[23]

Similar to the light driven proton pump bR, the molecular isomerization of photochemical compounds is not only driven by photon energy but also thermal energy.[71] The influence of temperature on such photoelectric devices should be studied carefully. Photoelectric conversion based on photo-isomerization reactions is a young topic and there is much to be explored. As more photoswitchable compounds are being discovered, the field is expected to become more active.

5. Concluding Remarks

There are two general types of photosynthetic systems in nature: the older chlorophyll system in green plants and the more recent bR system in *Halobacterium halobium*. Artificial photosystems converting light energy to electrochemical gradients and electrical energy have been widely explored with a significant focus on mimicking the chlorophyll based one. In these approaches, light absorption results in a charge separation state followed by electron and hole transport. However, artificial photosystems that implement lessons from the other photosynthetic system bR have been less explored. It has taken nature more than a billion years to develop the bR photosystem[37], so perhaps making efficient use of solar energy through photo-isomerizing molecules can be time consuming as well. Nevertheless, its potential and importance should not be overlooked.

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Admittedly, the varieties of photoswitchable molecules are not yet sufficiently versatile, and there has been comparably slow progress to diversify the available molecular toolbox. With some key developments summarized in this perspective article, we expect that efficient energy conversion devices based on photo-isomerization reactions will eventually be realized.

Acknowledgements

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