Photoelectric Conversion Based on Proton-Coupled Electron Transfer Reactions

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Ⓢ Supporting Information

ABSTRACT: Making efficient use of solar energy is one of the biggest challenges of our time. In nature, solar energy can be harvested by photosynthesis where proton-coupled electron transfer (PCET) plays a critical role. Here, PCET is utilized for the first time to directly convert light energy to electrical energy. Quinone/hydroquinone PCET redox couples were used to produce a photovoltage along with spiropyrans, photoswitchable compounds that undergo reversible transformation between a ring-closed (Sp) and ring-opened form (Mc). The Mc form is more basic than the Sp form, and the open-circuit voltage (V_{oc}) is related to the proton concentration and that of the Sp/Mc ratio controlled by light. V_{oc} values from 100 to 140 mV were produced. In addition to direct current (J_{sc} ca. 9 $\mu A\ cm^{-2}$), alternating current in the range of 0.1 to 200 Hz was also produced by manipulating the input light.

Proton-coupled electron transfer (PCET) reactions are ubiquitous in chemistry and play important roles in many enzymatic pathways that control life.[1−3] Light-driven reduction of CO_2 by water in photosynthesis and oxidation of glucose by oxygen in respiration are quintessential examples of PCET reactions in nature. Because of the enormous potential it holds for catalysis and energy conversion, there has been extensive fundamental research and growing understanding of the importance of various PCET reactions.[4−6]

A PCET reaction involves both electron transfer and proton transfer from or to a substrate, such as the redox reaction of the quinone/hydroquinone pair (Q/H_2Q in eq 1).

$$H_2Q \underset{+2e^-}{\overset{-2e^-}{\rightleftharpoons}} 2H^+ + Q \tag{1}$$
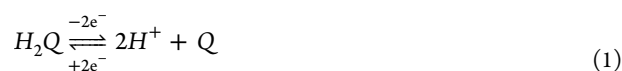
The reduction of plastoquinone occurs in the electron transport chain in light dependent reactions in photosynthesis.[7] Other examples that involve metal complexes acting as a catalyst have been established.[8−11]

PCET reactions have been widely studied for applications in chemical science. They become essential in artificial photosynthesis to produce solar fuels, thereby converting light energy to chemical energy.[12,13] They have also been recently used to achieve long-range charge separation in artificial light-harvesting systems.[14] However, photoelectric conversion on the basis of PCET reactions has not been reported before. Considering the enormous importance of solving the energy problem, the development of efficient solar cells is clearly one of the biggest scientific opportunities of our time. In this work, we show for the first time that PCET can be used to directly convert light energy to electrical energy.

Specifically, a Q/H_2Q pair was placed in contact with an indium tin oxide (ITO) electrode. The redox potential of Q/H_2Q at the ITO surface is defined by the Nernst equation as shown in eq 2, where $[Q]$ and $[H_2Q]$ are the concentrations of Q and H_2Q, respectively.

$$E = E^\circ + \frac{RT}{2F}\ln \frac{[Q][H^+]^2}{[H_2Q]} \tag{2}$$

To produce the photovoltage, a photochromic spiropyran (Sp) was added to bring about a Q/H_2Q redox potential change at the electrode. Under UV light irradiation, Sp will undergo a ring-opening reaction to form the ring-opened merocyanine (Mc) form,[15,16] which is much more basic than the Sp form.[17] Based on this light induced basicity increase, photoswitchable ion sensors and potassium nanocages have recently been reported.[18−20] We subsequently introduced an artificial light controlled proton pump in a polymeric membrane to convert light energy to electricity.[21] Despite the conceptual elegance of this approach, the design required 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 are not optically transparent and will place a limit on the efficiency of the photoconversion system. The direct photoelectric conversion of a proton gradient to electrical current proposed here requires just a single solution phase that is sandwiched between two transparent electrodes.

As shown in Figure 1, the photoelectric cell is composed of two ITO glass electrodes separated by a thin layer (2 mm thick) of organic liquid (acetonitrile (MeCN) or N,N-dimethylformamide (DMF)) containing spiropyran, the Q/H_2Q redox pair, and supporting electrolyte tetrabutylammonium hexafluorophosphate ($Bu_4N^+PF_6^-$). One of the electrode sides is illuminated with UV light (365 nm ± 10 nm), and the other with visible light (>409 nm) or left in darkness. On the UV side, Sp will transform into the Mc form and reduce the local H^+ concentration because Mc is more basic than Sp. Therefore, the electrode potential at the UV side will decrease. The ring-opened form then diffuses to the opposite side where it will be converted back to the Sp form, resulting in an effective recycling process. At steady state, gradients will be established with an excess of Q and McH$^+$ on
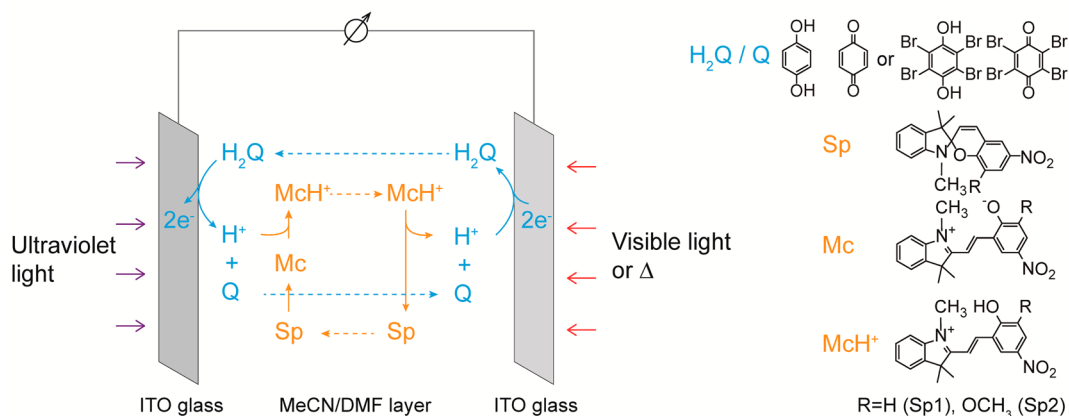
Figure 1. Schematic illustration of PCET based solar cell. Ultraviolet light (UV) is introduced from one side where Sp is transformed to Mc. The opposite side where the ring-opened form is transformed back to Sp is illuminated by visible light or left in dark (Δ). A photovoltage is formed with the electrode potential at the UV side lower than the other. Tetrabutylammonium hexafluorophosphate is used as supporting electrolyte.
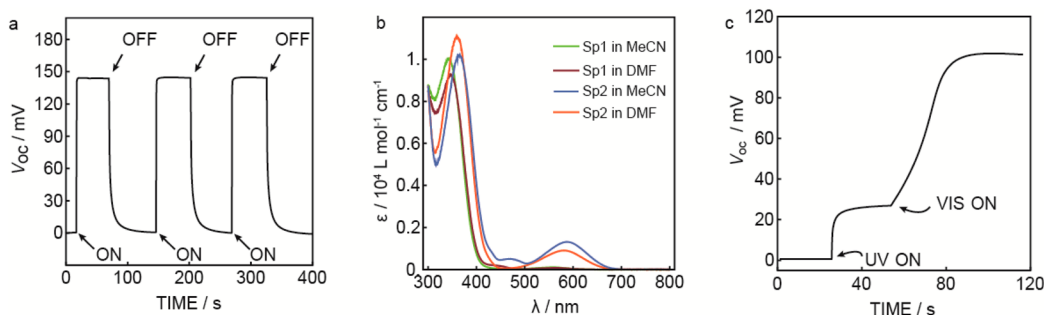

Figure 2. (a) Open-circuit voltage (V_{oc}) evolution for a composition containing Sp1 (0.04 M), Q (0.01M), H$_2$Q (0.01 M), and Bu$_4$N$^+$PF$_6^-$ (0.1 M) in MeCN with ultraviolet light irradiation (UV, 365 nm $\pm$ 10 nm, 5 mW cm^{-2}). (b) Absorption spectra of Sp1 and Sp2 in MeCN and DMF. (c) Open-circuit voltage evolution for a composition containing Sp2 (0.03 M), BrQ (0.01), BrH$_2$Q (0.01), and Bu$_4$N$^+$PF$_6^-$ (0.1M) in MeCN with UV (365 nm $\pm$ 10 nm, 5 mW cm^{-2}) at one side and visible light (VIS, >409 nm, 10 mW cm^{-2}) at the other.

the UV side while H$_2$Q and Sp prevail on the opposite side. The concentration asymmetry produces a photovoltage according to eq 2.

The light induced open-circuit voltage using Sp1 and unsubstituted Q/H$_2$Q in MeCN is shown in Figure 2a. Upon UV irradiation, a V_{oc} of ca. 140 mV was immediately observed, while the V_{oc} dropped back to zero after UV was switched off. When the light input intensity was increased, a higher V_{oc} was observed (Supplementary Figure S1). No visible light was required on the other side of the ITO surface in this case. Spiropyrans are known to undergo light and thermally driven ring-opening reactions.[22] As shown in Figure 2b (see Figure S2 for spectra after light illumination), no intense absorbance around 550 nm was observed for Sp1 in both MeCN and DMF, indicating that the spontaneous ring-closing reaction is sufficiently fast. Instead, visible light may partially leak into the UV illuminated side and suppress the activation of Sp. On the other hand, for the methoxyl substituted Sp2 (see Figure 1 for structure), intense absorption peaks that originated from the Mc form were observed in both MeCN and DMF (Figure 2b). In this case, visible light illumination on the opposite side was able to further increase the open-circuit voltage, as shown in Figure 2c. Since the ring closing reaction is in fact much slower than the ring-opening reaction,[16] the V_{oc} increase after applying visible light was slower compared with the increase upon UV irradiation. In DMF, a similar voltage increase was observed (see Supplementary Figure S3), but the V_{oc} value was smaller

compared with the one in MeCN. In the absence of the PCET redox pairs, no photovoltage was observed. Moreover, decreasing the cell thickness to 0.5 mm caused cross-irradiation of both UV and VIS on the ITO glass and diminished the photovoltage, while increasing the thickness did not enhance the photovoltage.

A rapid PCET redox reaction rate at the ITO surface is very important in view of achieving a high short-circuit current density (J_{sc}) and improved efficiency. The J_{sc} for the unmodified Q/H$_2$Q pair was low (ca. 0.6 μA cm^{-2}), indicating a rather high PCET activation barrier. However, a structural modification of the PCET redox pair could potentially lower the reaction barrier and increase the current density. For instance, the bromide substituted quinone/hydroquinone pair (BrQ/BrH$_2$Q; see Figure 1 for structure) was found to exhibit a much higher redox rate than the unsubstituted Q/H$_2$Q. In a linear voltammetric scan (Figure 3 a), BrH$_2$Q/BrQ showed higher cathodic and anodic current densities than H$_2$Q/Q in the overpotential range of 0 to 0.15 V. The short-circuit photocurrent with BrH$_2$Q/BrQ and Sp2 in MeCN is shown in Figure 3b. The current increased immediately upon UV illumination. Subsequently, likely because of the accumulation of Mc and McH$^+$ on the nonilluminated side of the cell, the current density started to drop after reaching a maximum. Indeed, illumination by visible light on the other side was able to accelerate the conversion from the ring opened forms to Sp and, thus again, increase the current density. A current density
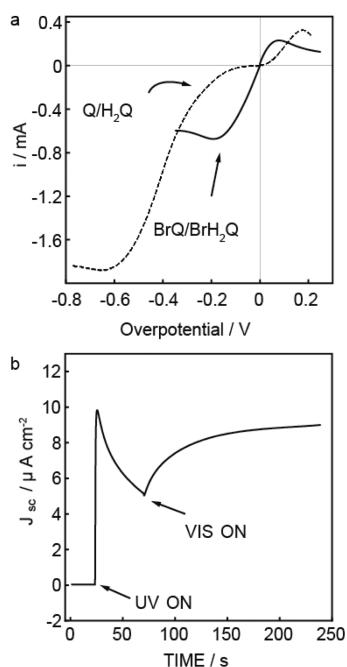
Figure 3. (a) Linear scan voltammetry of Q/H_2Q (0.01 M) and BrQ/BrH_2Q (0.01 M) in MeCN containing 0.02 M tridodecylmethyl-ammonium chloride, reference electrode: Ag/AgCl. (b) Short circuit current density (J_{sc}) for PCET based solar cell containing 0.01 M BrQ/BrH_2Q, 0.03 M Sp2 and 0.1 M $Bu_4N^+PF_6^-$ in MeCN. Energy input: UV 5 mW cm^{-2}, VIS 10 mW cm^{-2}.

of ca. 9 μA cm^{-2} was obtained when the system reached steady state.

The current photoelectric conversion cell exhibited a linear $J-V$ curve, and thus the fill factor[23] is ca. 50%. Therefore, the efficiency[23] of the current system (0.02%) is not yet comparable with existing solar cells. Compared with the previously reported proton pump based system, the lower efficiency is mainly due to a larger electrode reaction barrier compared with Ag/AgCl.[21] Nevertheless, there are ways that can potentially increase efficiency, such as surface modification on the electrode material to reduce the PCET reaction barrier, structural modification on the redox pair, and the light sensitive dye to enhance the quantum yield and increase the light triggered basicity change. While the photostability of spiropyran is known to be limited, the photoelectric cell was surprisingly robust. No drastic deterioration was observed even after light exposure for several hours. Of course, spiropyrans are not the only compounds that exhibit a light induced basicity change. Other compounds such as azobenzenes[24] have also been reported to possess similar properties and thus, in principle, are also suitable for this type of application.

In addition to direct current, we demonstrate here that alternating current (AC) can be obtained through the control of light. Although alternating current can be obtained in other ways with excellent efficiencies, a chemically innovative approach using light can result in new unanticipated directions. Light induced alternating current has been reported by discontinuous illumination or by switching the wavelength of the input light.[21,25] However, the frequencies achieved so far are quite low (0.1 to 0.2 Hz). For the PCET based system, alternating current was achieved by illuminating the ITO on both sides with discontinuous UV light (Figure 4). AC was also produced through alternatingly illuminating one ITO surface with UV and visible light (see Supplementary Figure S4). Compared to previous systems, a much wider range of alternating frequency from 0.1 Hz up to 200 Hz was achieved with the PCET based solar cell (see Supplementary Figure S5 for 200 Hz AC acquired in fast chronoamperometry mode).

In conclusion, photoelectric conversion using proton-coupled electron transfer reactions was introduced here for the first time. In order to utilize the PCET reactions, spiropyrans that showed a basicity increase upon UV
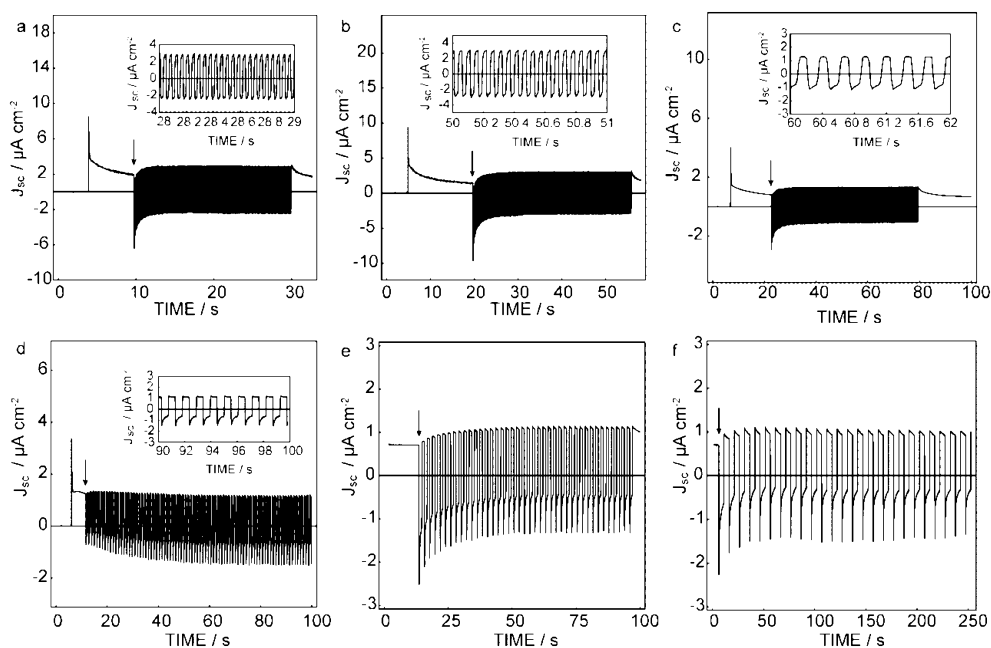

Figure 4. Alternating current generation from PCET based solar cell containing 0.01 M Q/H_2Q, 0.04 M Sp1, and 0.1 M $Bu_4N^+PF_6^-$ in MeCN with different frequencies: (a) 24 Hz, (b) 20 Hz, (c) 5 Hz, (d) 1 Hz, (e) 0.5 Hz, (f) 0.1 Hz. One of the two ITO electrodes was illuminated with discontinuous UV light from DG-4 while the other constantly with UV light.

illumination were utilized to alter the local proton concentration in organic solutions containing the PCET redox couple. Since the redox potentials are dependent on the proton concentration for PCET, a photovoltage was produced between the two transparent electrodes. In addition to direct current, alternating current with frequencies from 0.1 to 200 Hz was achieved with the photoelectric conversion cell. Besides spiropyran, the principle should work with other materials that exhibit light induced basicity changes as well.[26,27] A catalyst deposited on the ITO should potentially be able to lower the PCET redox barrier, increasing the attainable photocurrent. Further efforts (chemical modification on the PCET redox pair, light sensitive compounds, electrode materials, and reaction media) are envisioned to help improve the characteristics of photoelectric conversion systems based on this principle. We estimate that this work opens up new possibilities for photoelectric conversion that could take advantage of PCET reactions.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Additional information as noted in the text including the detailed experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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