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Authors

White, William
Luo, Simon
Bhide, Rohit
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Evaluation of the role that photoacid excited-state acidity has on photovoltage and photocurrent of dye-sensitized ion-exchange membranes

William White,[1] Simon Luo,[1] Rohit Bhide,[1] Christopher D. Sanborn,[1] Mikhail S. Baranov,[2,3]
Kyril M. Solntsev,[4,5] and Shane Ardo[1,6,7*]

[1]Department of Chemistry, University of California Irvine, Irvine, CA, 92607 USA

[2]Institute of Bioorganic Chemistry, Russian Academy of Sciences, Miklukho-Maklaya 16/10, Moscow 117997, Russia

[3]Pirogov Russian National Research Medical University, Ostrovitianov 1, Moscow 117997, Russia

[4]School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, USA

[5]New York University Abu Dhabi, P.O. Box 129188, Abu Dhabi, United Arab Emirates

[6]Department of Materials Science & Engineering, University of California Irvine, Irvine, CA 92607, USA

[7]Department of Chemical & Biomolecular Engineering, University of California Irvine, Irvine, CA 92607, USA

* corresponding author: ardo@uci.edu

ABSTRACT

Light-driven ion pumps can be fabricated from ion-exchange membranes infiltrated with water as the protonic semiconductor. Absorption of visible light and generation of mobile charge carrier protons are accomplished using photoacids that are covalently bonded to the membranes. Prior results from our work suggest that the photoacid excited-state acidity is not large enough to result in significant yields for conversion of light into mobile protons. Herein we compare a series of photoacid-bearing membranes that are even stronger acids in their excited states, and we determine that excited-state acidity does not correlate with photovoltage. By assessing the photoresponse of a series of bipolar membranes fabricated by laminating a photoacid-bearing cation-exchange membrane to an anion-exchange membrane, no clear trend was observed between net built-in electric potential and photovoltaic performance. This suggests that other properties dictate the effectiveness of these light-driven proton pumps.

Keywords: light-driven proton pump, ionic solar cell, photoacid, ion-exchange membrane, dye sensitization, desalination

(1) INTRODUCTION

Ion pumps are ubiquitous in Nature, yet there are few examples of artificial ion pumps. Using light to drive proton pumping is particularly interesting because it is analogous to the process that occurs for electrons and holes in electronic solar cells and it can be used for direct light-driven desalination of salt water.[1–4] Recent demonstrations of artificial light-driven proton pumps used light-activated molecules to initiate proton transport through ionically conductive membranes.[2,5–7] Several membranes have been engineered for use as light-driven proton pumps, and similar across these demonstrations is incorporation of reversible photoacids to sensitize the membranes to absorption

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of visible light. Long-lived (non-excited-state) photoacids have been reported,[6] which undergo proton transfer from a metastable state that reverts back to the ground state on the timescale of microseconds to minutes. Förster-type (excited-state) photoacids have also been reported by us and others,[2,5] which perform proton transfer from an excited state on the femtosecond to nanosecond timescale and where proton transfer is driven by the fact that the excited-state pK_a, pK_a*, is smaller than the ground-state pK_a.[8,9] In our prior work, we showed that 8-hydroxypyrene-1,3,6-tris(2-aminoethylsulfonamide) (HPTSA) covalently bonded to a membrane with a perfluorosulfonic acid (PFSA) backbone absorbed visible light, performed excited-state proton transfer, and exhibited photovoltaic action as a single membrane[5] and when laminated to an anion-exchange membrane to form a bipolar membrane[2] (Figure 1).

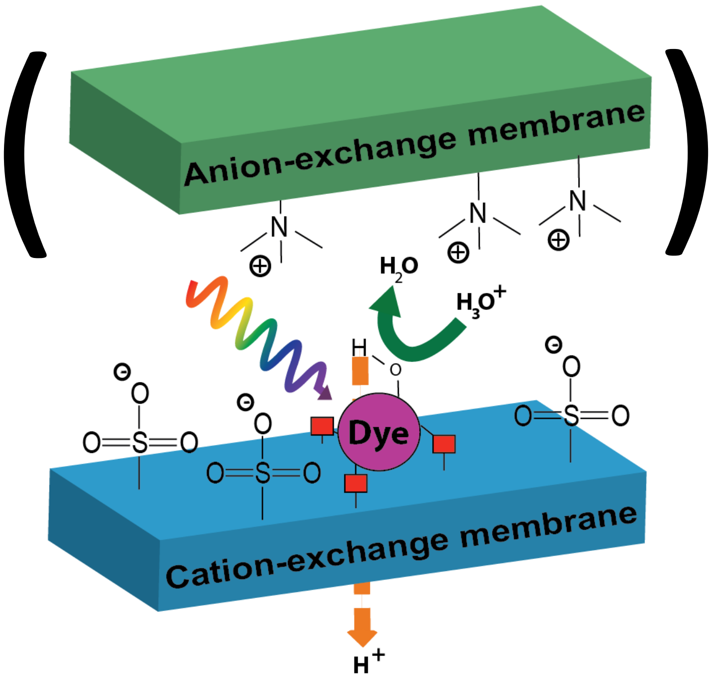

Figure 1. Diagram representing a photoacid-sensitized cation-exchange membrane. Our data are consistent with a process where upon absorption of light the photoacid dye releases a proton that then transports through the cation-exchange membrane. Addition of an anion-exchange membrane to form a bipolar membrane structure resulted in a significantly larger photovoltage.

The most effective way to generate large photovoltages in electronic solar cells is to fabricate buried electrostatic junctions between two electronic semiconductors. To mimic an electronic pn-homojunction structure using ion-exchange membranes and water as the protonic semiconductor, a single photoacid-dye-sensitized cation-exchange membrane was laminated to an anion-exchange membrane to form a bipolar membrane.[2] Both HPTSA-PFSA and its bipolar membrane analog exhibited internal quantum yields of < 5% for conversion of photons into ionic current,[2,5] suggesting that opportunities exist to improve materials performance. One observation was that many HPTSA-PFSA membranes did not effectively perform excited-state proton transfer, as evidenced by wetted membranes exhibiting photoluminescence spectra dominated by emission from protonated photoacids.[2,5] This observation suggests that incorporation of photoacids into polymers results in a local microenvironment that does not support excited-state proton transfer, behavior that we also recently observed from wetted HPTSA-modified conical nanopores in poly(ethylene terephthalate).[10] Therefore, photoacids with more acidic excited states may overcome this issue. There are many different Förster-type photoacidic molecules, with derivatives of naphthol, pyrene, and phenylcyanine being some of the most well studied. Their ground-state acidities are similar, with pK_a values in the range of 3 to 5, while their excited-state acidities are far more variable, with pK_a* values in the range of 1 to < –5,[7–13] and most being more acidic than HPTSA.

The aim of the work reported herein was to optimize the photovoltaic performance of these membranes and to show generality in photoacid-driven photovoltaic behavior. To do this, we covalently bonded a series of photoacids to PFSA with acidities measured in water that were stronger (lower pK_a*) than previously reported HPTSA. Our hypothesis was that by using photoacids that were stronger acids in their excited states, the yield for photogeneration of protons would increase and this would result in an increase in the magnitude of the open-circuit photovoltage, short-circuit photocurrent, and internal quantum yield for conversion of photons into ionic current.

(2) EXPERIMENTAL

Sec. 2.1. Materials. All chemicals were reagent grade and were used without further purification unless stated otherwise. The following reagents were used as received from the indicated suppliers: sulfuric acid (95%, Fisher Scientific), sodium hydroxide (> 95%, Macron Fine Chemicals), potassium hydroxide (88%, Fischer Scientific), perchloric acid (70%, Alfa Aesar), sodium chloride (99 %, Sigma), potassium chloride (99 %, Sigma), Nafion sulfonyl fluoride poly(perfluorosulfonyl fluoride) membrane (2 mil (50.8 μm) thick, EW = 1100, C.G. Processing), and 1-aminopyrene (97 %, Accel Pharmtech) (AP).[13] *N*-(2-aminoethyl)-2,7-dimethoxyacridine-9-carboxamide (DMACA) and 8-hydroxypyrene-1,3,6-tris(2-aminoethylsulfonamide) (HPTSA) were synthesized as previously reported in the literature.[14] 2-(4-((2-aminoethyl)amino)-4-oxobutyl)-5,5,6,8-tetrafluoro-7-hydroxy-1-oxo-2,5-dihydro-1*H*-5l4-benzo[c]imidazo[5,1-f][1,2]azaborinin-4-ium (*p*-DiFBDI) was synthesized as previously reported in the literature.[15]

Sec. 2.2. pH titrations of *N*-(2-aminoethyl)-2,7-dimethoxyacridine-9-carboxamide (DMACA) in solution. Two stock solutions of 4 µM DMACA in 1 M HCl(aq) and in 1 M NaOH(aq) were prepared and mixed in various ratios to form working solutions in the pH range of 0 to 14. Electronic absorption spectra and photoluminescence spectra were recorded as a function of pH using an Agilent Cary-60 UV-Vis Spectrophotometer and Agilent Cary Eclipse Fluorescence Spectrophotometer, respectively. So that each sample absorbed approximately an equal number of photons irrespective of pH, photoexcitation occurred at an approximate isosbestic point of DMACA (385 nm). To correct for minor differences in absorption at the excitation wavelength, photoluminescence values were scaled by the absorptance (α) at 385 nm, assuming zero reflectance, as follows,

$$\alpha = 1 - \%\mathrm{T} = 1 - 10^{-\mathrm{Abs}} \tag{1}$$

where %T is the fraction of transmitted light and Abs is the absorbance. Values for pK_a and pK_a* were calculated by fitting the absorbance at 390 nm and photoluminescence at 580 nm to the weighted sum of one or two Henderson–Hasselbalch equations, respectively,

$$y = \frac{1}{1 + 10^{(\mathrm{p}K_\mathrm{a} - \mathrm{pH})}} \tag{2}$$

where pH is the independent variable and each pK_a is a fitted parameter.

Sec. 2.3. Synthesis of photoacid-bearing membranes. In general, each photoacid-bearing PFSA membrane was synthesized using a previously reported procedure,[5] except with different amounts of dye added to ensure that the membranes were deeply colored. Some modifications to the procedure were made to bind AP, because it was a substantially worse nucleophile than the dyes that contained primary amines. Reactions that used less than 1.0 molar equivalent of AP with respect to the amount of sulfonyl fluoride in the PFSA precursor membrane material did not result in membranes with appreciable absorbance, and therefore at least 2.0 molar equivalents were used. Membranes with 1.2 molar equivalents of DMACA, 1.2 molar equivalents of HPTSA, and 1.0 molar equivalents of *p*-DiFBDI-PFSA were also synthesized.

Sec. 2.4. Bipolar membrane preparation. Bipolar membranes where constructed by annealing each previously synthesized photoacid-bearing cation-exchange membrane to a Neosepta AHA anion-exchange membrane. Prior to annealing, the photoacid-bearing cation-exchange membrane was soaked in 20 mL of 1 M HCl(aq) for at least 5 min and the anion-exchange membrane was soaked in 20 mL of 1 M NaOH(aq) for at least 5 min. The membranes were placed separately on a Teflon sheet (1 in^2 area, 1 mm thick) and rinsed with copious amounts of water, then patted dry with a Kim Wipe. The rinsed membranes were then stacked and annealed at 90 $^\mathrm{o}$C under 1 ton of pressure for 1 h.

Sec. 2.5. Electrochemical procedures. The electrochemical H-cell and electrochemical procedure were previously described in detail in the literature,[2,5] with several relevant modifications noted here to allow for *operando* spectroscopic characterization: holes for insertion of reference electrodes are doubled to 1 cm in diameter; holes for insertion of the current-carrying electrodes are now inline both 1 cm away from the center of the reference electrode hole and are each displaced 0.5 cm off-center of the KEL-F block; and the simple compression screw is replaced with a hollow PEEK screw with a 1.86 cm^2 area circular hole and accompanying borosilicate glass window (Figure 2). For measurements of single membranes, one side of the membrane was wetted by 1 M H_2SO_4(aq) and the other side of the membrane was wetted by 1 M NaOH(aq). These electrolytes were added to the electrochemical cell and replaced once before measuring the open-circuit photovoltage (V_oc) and the photocurrent at near-zero applied bias ($J_\mathrm{ph\text{-}sc}$). Both V_oc and $J_\mathrm{ph\text{-}sc}$ were acquired in a 35 min experiment consisting of three stages: a 5 min period in the dark, a 15 min period of illumination, and another 15 min period in the dark. For measurements of bipolar membranes, one side of the membrane was wetted by 10 mM $HClO_4$(aq) and the other side of the membrane was wetted by 10 mM KOH(aq). To ensure that bipolar membranes were nearly fully equilibrated with the contacting electrolytes, the open-circuit potential in the dark (E_oc) was monitored over 45 min during which the electrolyte was replaced three times. If E_oc did not appear to reach a steady-state value, the electrolyte was replaced one additional time, and then E_oc was recorded followed by measurements of V_oc and $J_\mathrm{ph\text{-}sc}$ under illumination for 15 to 60 min and subsequent dark times of 20 to 90 min. V_{oc} and $J_{ph\text{-}sc}$ values were calculated in the same manner as in our previous reports,[2,5] by subtracting an exponential–linear combination fit of the dark regions before and after a period of illumination to the following function,

$$y = at + be^{ct} + d \tag{3}$$

where t is the independent variable, time, and the fitted parameters are a, b, c, and d.

As previously, all photoelectrochemical experiments used a laser diode powered by a DC power supply to generate 405 nm illumination that had been calibrated prior to each experiment using a silicon photodiode (Thorlabs FSD100).[2,5] The laser diode beam shape was expanded to approximately fill the wetted area of the membrane (1.86 cm^2). The incident photon-to-current-efficiency external quantum yield (EQY) was calculated by dividing $J_{ph\text{-}sc}$ by the current density expected when every incident photon is absorbed, separated into a positive and negative charge, and collected as current. The internal quantum yield (IQY) was calculated by dividing EQY by the absorptance at the excitation wavelength, as follows,

$$\mathrm{IQY} = \frac{\mathrm{EQY}}{\alpha} = \frac{J_{\mathrm{ph-sc}}}{\alpha F \Phi} \tag{4}$$

where F is the Faraday constant and Φ is the incident photon flux in units of mol cm^{-2} s^{-1}.

Sec. 2.6. Membrane characterization. Electronic absorption spectra of membranes were collected in the electrochemical H-cell and under experimental condition using an Agilent Cary-60 UV-Vis Spectrophotometer with a resolution of 1 nm and baselined against a spectrum taken using the electrochemical cell filled with 1 M NaCl(aq) and no membrane. The absorptance spectrum for each membrane assumed zero additional reflectance beyond the baseline spectrum and thus was calculated using Equation 1.

Further characterization of the membranes was not performed, because prior attempts to characterize bonds between photoacids and PFSA using Fourier transform infrared (FTIR) spectroscopy with attenuated total internal reflectance (ATR) and X-ray photoelectron spectroscopy (XPS) yielded inconclusive results.[5] Ion-exchange capacity measurements were conducted by soaking the membrane in 1 M HCl(aq), followed by 1 M NaCl(aq) and measuring the change in pH of the solution.[5] Ion-exchange capacity measurements conducted on AP-PFSA, DMACA-PFSA, and Nafion were within experimental error the same, likely because binding of AP and DMACA each removed one protic group from the membrane, but AP and DMACA each have one protic group and so the net change in the number of protic groups was zero. By visual inspection, immersion of photoacid-bearing PFSA membranes in 1 M HCl(aq) or 1 M NaOH(aq) did not result in significant leaching of photoacids into the solution, supporting that photoacids incorporated into PFSA were stable over the time required to conduct an experiment.

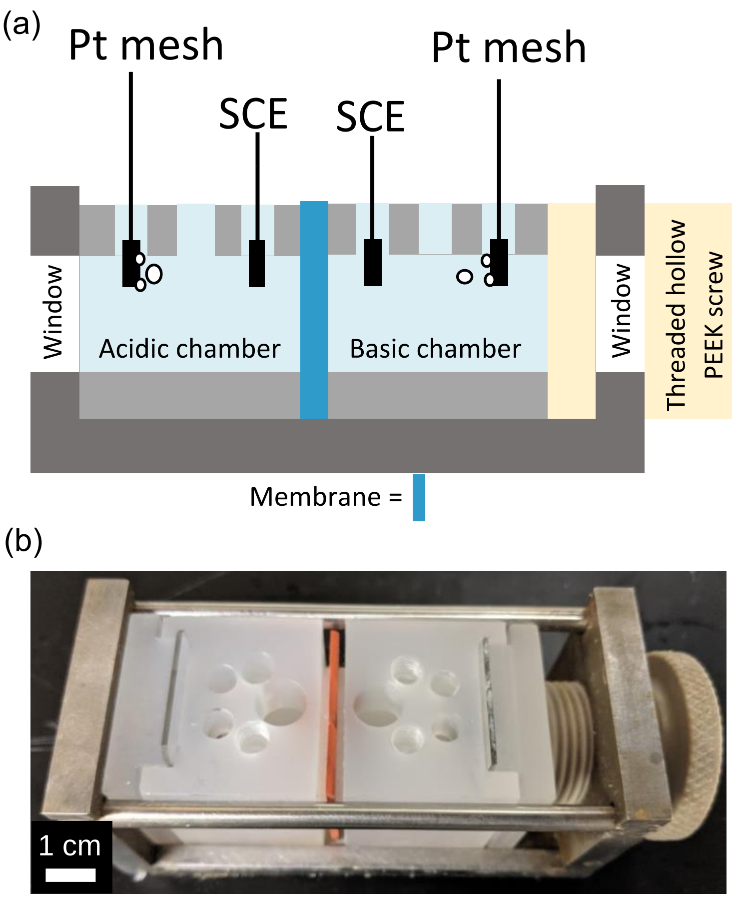

Figure 2. (a) Diagram of the electrochemical H-cell indicating the general placement of the electrodes and the membrane. (b) Digital photograph of a dry electrochemical cell incorporating a red silicone sheet to indicate where the membrane would be located and where the largest holes are 1 cm in diameter.

(3) RESULTS AND DISCUSSION

Sec. 3.1. Weakly photoacidic dye molecule. The DMACA molecule was synthesized and tested for its ability to perform excited-state proton transfer in aqueous solutions. Acid–base titrations of the pH with detection by absorbance and photoluminescence helped to quantify pK_a and pK_a*, respectively (Figure 3). Absorption data exhibited two inflection points suggesting that there are two pK_a values, 3.3 ± 0.1 and ~8, while photoluminescence data exhibited three inflection points suggesting that there are three pK_a* values, 1.8 ± 0.1, 3.2 ± 0.2, and ~8. The data above pH 8 were not fitted, because our prior studies suggested that deprotonation of free ammonium groups occurred in this pH range and their pK_a values did not change upon photoexcitation.[10] The coincidence of the two largest pK_a values and two largest pK_a* values suggest that DMACA is not a photoacid; observation of an additional (smallest) pK_a* value is suggestive that DMACA might be slightly photoacidic with a Δp$K_a = 1.8 - 3.3 = -1.5$. Additional studies are needed to verify these hypotheses. Irrespective, we postulate that DMACA will exhibit poorer photovoltaic performance when incorporated into PFSA than a photoacid like HPTSA whose pK_a value decreased by a larger magnitude on transitioning from its ground state to its excited state. Moreover, DMACA-modified PFSA may serve as a more optimal control membrane than Ru(bpy)$_3^{2+}$ ionically associated into Nafion, where bpy is 2,2'-bipyridine (Ru(bpy)$_3^{2+}$/Nafion), because DMACA is organic like the photoacids and DMACA contains functional groups for covalent bonding to PFSA.[5]

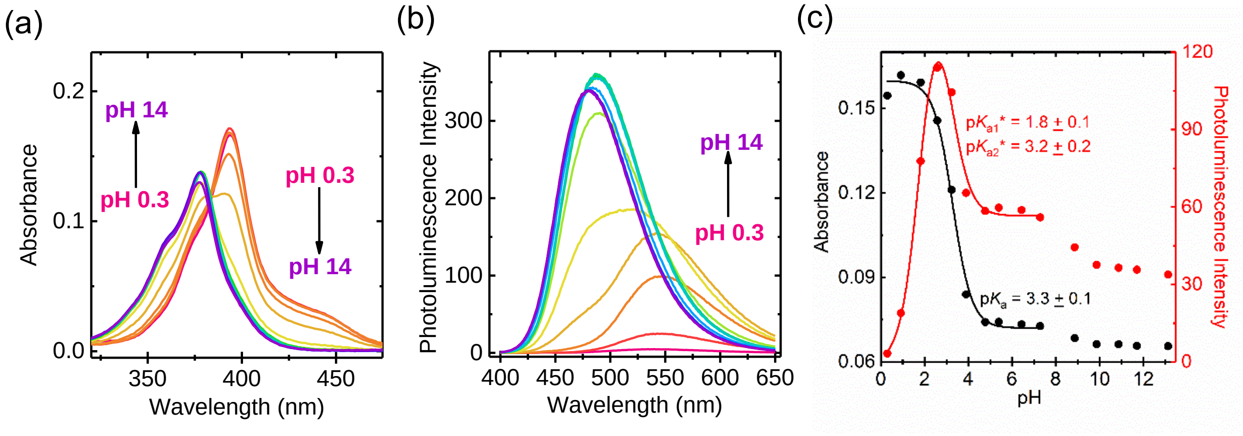

Figure 3. Acid–base titration data for DMACA dissolved in 1 M ionic strength aqueous solutions with pH values that range from 0.3 (red) to ~14 (purple): (a) absorbance spectra; (b) photoluminescence spectra after optical excitation at 385 nm; (c) absorbance measured at 390 nm (black) and corrected photoluminescence intensity measured at 580 nm (red) as a function of pH, and displayed with nonlinear least-squares best fits to scaled linear combinations of Equation 2.

Sec. 3.2. Photoacid-sensitized ion-exchange membranes. Several new photoacids were covalently bonded to PFSA via coupling chemistry,[2,5] and resulted in membranes that absorbed a substantial amount of visible light (Figure 4). Excited-state acidity generally increased on going from HPTSA-PFSA to AP-PFSA to *p*-DiFBDI-PFSA. However, photovoltaic performance was found to be rather insensitive to the acidity of the excited state, except for DMACA-PFSA, which performed significantly worse than the other membranes (Figure 5). Also, notably for AP-PFSA, several membranes were evaluated at different dye loadings; however, there was no clear in trend in performance based on the amount of dye added (Table 1).

The best control material reported previously was [Ru(bpy)$_3$]$^{2+}$/Nafion, which was used to show the effect that a non-protic dye had on performance and whose photoexcitation would favor local heating of the membrane or electron-transfer redox chemistry with O_2 or water. While [Ru(bpy)$_3$]$^{2+}$/Nafion exhibited minimal photoresponse, [Ru(bpy)$_3$]$^{2+}$ exhibited substantial degradation in the dark and light after prolonged exposure to concentrated acidic or alkaline electrolyte. DMACA-PFSA membranes reported herein did not degrade substantially after prolonged exposure to experimental conditions and exhibited a similar photoresponse as [Ru(bpy)$_3$]$^{2+}$/Nafion, suggesting that DMACA-PFSA may be a reasonable control material.

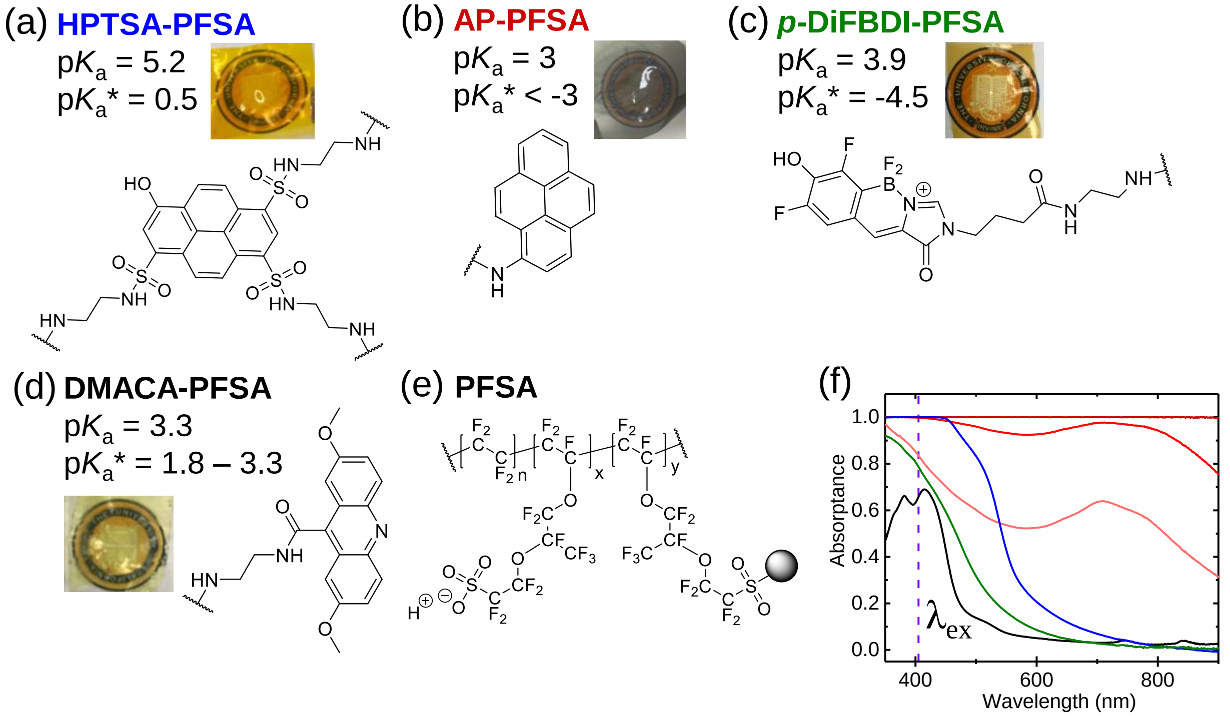

Figure 4. Photoacid-modified PFSA membrane abbreviations, pK_a and pK_a* reported for each photoacid in aqueous solution, digital photographs, and chemical structures of the photoacid unit: (a) 8-hydroxypyrene-1,3,6-tris(2-aminoethylsulfonamide) (HPTSA), (b) 1-aminopyrene (AP), 2-(4-((2-aminoethyl)amino)-4-oxobutyl)-5,5,6,8-tetrafluoro-7-hydroxy-1-oxo-2,5-dihydro-1*H*-5l4-benzo[c]imidazo[5,1-f][1,2]azaborinin-4-ium (*p*-DiFBDI), and (d) *N*-(2-aminoethyl)-2,7-dimethoxyacridine-9-carboxamide (DMACA), (e) PFSA polymer showing binding region to photoacids as a grey sphere, and (f) color-coded absorptance spectra of the four membranes in panels a – d, including three photoacid concentrations for AP-PFSA as shades of red and the excitation wavelength (λ_{ex}) used for photoelectrochemical measurements as a vertical dashed line.

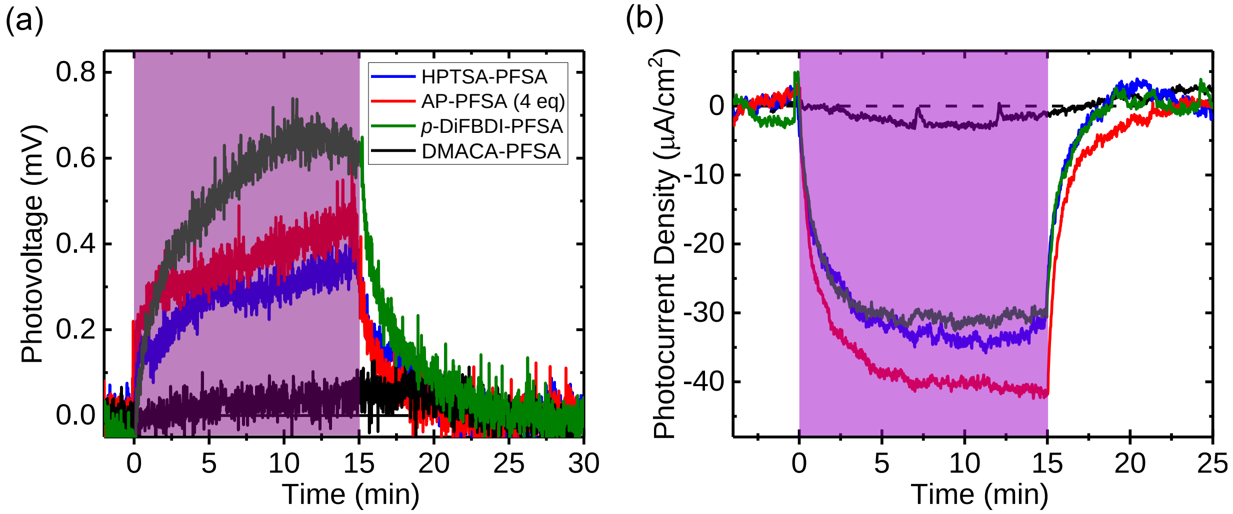

Figure 5. (a) Open-circuit photovoltage (V_{oc}) and (b) photocurrent at near-zero applied bias ($J_{ph\text{-}sc}$) measured for HPTSA-PFSA (blue), AP-PFSA (red), *p*-DiFBDI-PFSA (green), and DMACA-PFSA (black) during alternating illumination with 405 nm light (purple bars) and in the dark. Each membrane was wetted by 1 M H_2SO_4(aq) on one side of the membrane and by 1 M NaOH(aq) on the other side of the membrane.

Table 1. Photoelectrochemical properties of photoacid-bearing PFSA membranes under the conditions described in Figure 5, including the best-performing HPTSA-PFSA reported to-date.

Membrane	V_{oc} **(mV)**	$J_{ph\text{-}sc}$ **(μA/cm^2)**	**IQY (%)**	**Reference**
HPTSA-PFSA (0.1 eq)	+1.0	-100	4	ref. 5
HPTSA-PFSA (1.2 eq)	+0.4	-30	0.6	this work
AP-PFSA (2 eq)	+0.6	-20	0.3	this work
AP-PFSA (4 eq)	+0.5	-40	0.6	this work
AP-PFSA (7 eq)	+0.5	-40	0.6	this work
p-DiFBDI-PFSA (1.0 eq)	+0.6	-30	0.6	this work
DMACA-PFSA (1.2 eq)	+0.0	-2	0.05	this work

Results using HPTSA-PFSA, AP-PFSA, *p*-DiFBDI-PFSA, and DMACA-PFSA provide conclusive evidence that the photovoltaic effect initiated from photoacids bound to PFSA is generalizable and is not likely due to non-radiative excited-state deactivation processes that result in heating of the membrane or other excited-state chemistry. However, decreasing pK_a* from 0.5 in HPTSA[10] to < –3 in AP[13] and *p*-DiFBDI[15] did not result in a significant change in V_{oc} or $J_{ph\text{-}sc}$, which indicates that charge photogeneration, separation, and collection may not be limiting factors in overall photovoltaic performance.

Sec. 3.3. Photoacid-sensitized bipolar membranes. Following our previous demonstration that the addition of a second ion-selective membrane of opposite charge selectivity resulted in an increased V_{oc}, a larger data set of HPTSA-PFSA bipolar membranes was collected (Figure 6). A trend reported previously was that as the magnitude of the dark E_{oc} value increased so did the membrane performance.[2] This seemed like a reasonable correlation, because E_{oc} is a

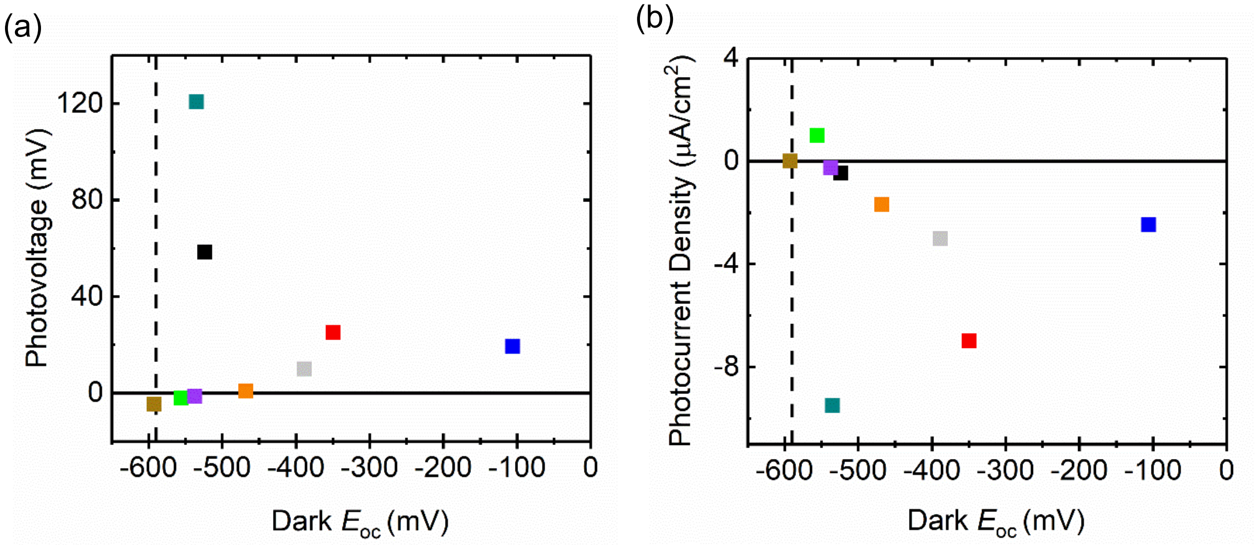

Figure 6. (a) Open-circuit photovoltage (V_{oc}) and (b) photocurrent density at near-zero applied bias ($J_{ph\text{-}sc}$) measured for 9 different bipolar membranes consisting of HPTSA-PFSA laminated to Neosepta AHA, and each represented by a different colored point. Each membrane was wetted by 10 mM $HClO_4$(aq) and 10 mM KOH(aq), which resulted in a ten orders-of-magnitude difference in proton concentration across the membrane that is expected to result in E_{oc} = 590 mV, and is shown as vertical dashed lines.

measure of the net electrostatic potential difference across the membrane and a larger built-in electrostatic potential results in better performance in electronic solar cells. Moreover, a large-magnitude dark E_{oc} value suggests that the ion-exchange membrane is highly selective for its respective charges and exhibits good interfacial contact with no holes to serve as effective ionic shunts. The value of E_{oc} predicted using the Donnan equation, based on the proton concentration on both sides of the membrane,[2,16,17] is shown as vertical dashed lines in Figure 6. The larger data set reported in Figure 6 is not consistent with the expected trend. In fact, as the dark E_{oc} approaches the value expected based on Donnan exclusion there is a change in the sign of V_{oc} from an expected positively-signed value to a negatively-signed value. The negatively-signed value is consistent with a faster net rate for loss of mobile charge carriers upon illumination. While atypical, useful work can still be performed using this non-equilibrium state except that the device would pass charges in directions that are opposite of that expected for a traditional electronic solar cell. Additional experiments are required in order to more clearly identify the mechanisms that are responsible for proton-transfer behavior of photoacids dissolved in solution and bonded to hydrated ion-exchange membranes under the aforementioned experimental conditions.

(4) CONCLUSIONS

Several new photoacid-sensitized ion-exchange membranes were synthesized and characterized, and each was shown to exhibit photovoltaic action. This observation indicates that the previously reported photovoltaic action from HPTSA-PFSA is generalizable to more than one photoacid dye. An improved control dye was synthesized, bonded to PFSA, and characterized, and was found to exhibit a much smaller photoresponse than all PFSA membranes containing bound known photoacids. This observation further supports that a compound undergoing photoinduced proton transfer is responsible for the large photoresponse observed by photoacid-bearing PFSA; however, there was no clear trend between excited-state acidity of the photoacid and the photovoltage of photoacid-bearing PFSA. Moreover, data obtained from an increased sample size of photoacid-bearing PFSA bipolar membranes indicate that dark E_{oc} does not correlate with typical photovoltaic parameters. To progress this technology a greater understanding of the mechanisms responsible for the observed photoresponse is needed and perhaps novel photoacids or photobases with substantially different acidities than those reported herein need to be synthesized and evaluated.

(5) ACKNOWLEDGMENTS

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