Electronic Supplementary Information for

Clarification of Mechanisms of Protonic Photovoltaic Action Initiated by Photoexcitation of Strong Photoacids Covalently Bound to Hydrated Nafion Cation-Exchange Membranes Wetted by Aqueous Electrolytes

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Donnan Theory and the Capacity for Ion Exclusion. Donnan theory is used to quantify spatial distributions of ions and electric potentials across a membrane interface, or across a thin, porous membrane separator when specifically in the presence of other charged species that cannot cross the interface, and a single salt species, e.g., HCl(aq). Transport of each mobile ion, e.g., H\(^+\) and Cl\(^-\), down its gradient in electrochemical potential results in formation of a space–charge region, due to the charged species that cannot cross the interface, whose single associated electric potential difference satisfies electrochemical equilibrium for each mobile ion. In this case, the electrochemical potential of H\(^+\) on either side of the membrane interface is equal, which also satisfies the condition that the electrochemical potential of Cl\(^-\) on either side of the membrane interface is equal, as follows,

\[
\bar{\mu}_i^s = \bar{\mu}_i^m \tag{S1}
\]
\[
\mu_i^s + z_i F \phi^s = \mu_i^m + z_i F \phi^m \tag{S2}
\]
\[
\mu_i^{0,s} + RT \ln a_i^s + z_i F \phi^s = \mu_i^{0,m} + RT \ln a_i^m + z_i F \phi^m \tag{S3}
\]

where \(\bar{\mu}_i\) is the electrochemical potential of species \(i\), \(\mu_i\) is the chemical potential, \(z_i\) is the valency, \(F\) is the Faraday constant, \(\phi\) is the electric potential, \(\mu_i^{0}\) is the standard chemical potential, \(a_i\) is activity, and the superscripts \(s\) and \(m\) refer to species in the solution phase and in the membrane phase, respectively.\(^{31}\) Assuming the reasonable assumption that \(\mu_i^{0}\) in each phase is the same, the interfacial (int) Donnan (D) electric potential difference between the bulk quasi-neutral region of the solution \textit{versus} the bulk quasi-neutral region of the membrane, \(\phi^\text{int}_D\), is calculated as follows,

\[
RT \ln a_i^s + z_i F \phi^s = RT \ln a_i^m + z_i F \phi^m \tag{S4}
\]
\[
\phi^s - \phi^m = \phi^\text{int}_D = \frac{RT}{z_i F} \ln \frac{a_i^m}{a_i^s} \tag{S5}
\]
\[
\phi^\text{int}_D = \frac{RT}{F} \ln \frac{a_{\text{H}^+}^m}{a_{\text{H}^+}^s} = \frac{RT}{F} \ln \frac{a_{\text{Cl}^-}^s}{a_{\text{Cl}^-}^m} \tag{S6}
\]
where **Equation S6** is the same as **Equation 1** in the main text, and which leads to the following equation,

\[ a_{H^+}^m a_{Cl^-}^m = a_{H^+}^s a_{Cl^-}^s \quad (S7) \]

Since cation-exchange membranes, like Nafion, contain negatively charged fixed groups (R\(^-\)), the following charge conservation relationships exist,

\[ a_{H^+}^s = a_{Cl^-}^s \quad (S8) \]
\[ a_{H^+}^m = a_{R^-}^m + a_{Cl^-}^m \quad (S9) \]

which when coupled with **Equation S7**, result in the following equations,

\[
(a_{Cl^-}^m)^2 + a_{R^-}^m a_{Cl^-}^m - (a_{Cl^-}^s)^2 = 0 \quad (S10)
\]

\[
a_{Cl^-}^m = \frac{-a_{R^-}^m + \sqrt{(a_{R^-}^m)^2 + 4 (a_{Cl^-}^s)^2}}{2} = \frac{a_{R^-}^m}{2} \left( 1 + 4 \left( \frac{a_{Cl^-}^s}{a_{R^-}^m} \right)^2 - 1 \right) \quad (S11)
\]

If the square root term is approximated to two non-zero terms in the Maclaurin series, an approximation for the activity of mobile anions in the membrane can be calculated as follows,

\[
a_{Cl^-}^m \approx \frac{a_{Cl^-}^m}{2} \left( 1 + 2 \left( \frac{a_{Cl^-}^s}{a_{R^-}^m} \right)^2 - 1 \right) = \frac{(a_{Cl^-}^s)^2}{a_{R^-}^m} \quad (S12)
\]

where **Equation S12** is the more general version of **Equation 5** in the main text based on species concentrations, and which indicates that \( a_{Cl^-}^s \ll a_{R^-}^m \) must be satisfied in order to achieve significant Donnan exclusion of coion anions, e.g. Cl\(^-\), from the membrane to result in primarily cationic conduction.

**Impact of the Choice of Potential-Sensing Electrodes.** Our prior studies of HPTSA-modified PFSA used two nominally identical saturated calomel electrodes (SCEs) to sense potential differences across the membrane as a function of ionic current passing through the membrane.\(^{S2-S4}\) The reduction potential of these *photoinactive* SCEs was dictated by the activity of Cl\(^-(aq)\) near the
electrode surface, which was fixed based on the concentration of Cl\(^{-}\) (aq) present in the fritted tube, resulting in measured values for the open-circuit potential \(E_{oc}\) being equal to the net electric potential difference across the membrane (see Equation 6 in the main text). For our work herein, experiments were initially conducted using SCEs. Although initial values of \(E_{oc}\) (Figure S1a) were in agreement with Donnan theory, i.e. \(~59\) mV per difference in pH between the room temperature acidic aqueous electrolytes that wetted the membrane, measured \(E_{oc}\) values changed over time and were unstable on the timescale of hours (Figure S1b and S3a). To quantify the open-circuit photovoltage \(V_{oc}\), a time-dependent baseline was simulated by best-fitting \(E_{oc}\) values measured in the dark to a sum of two exponential decays (Figure S3a). For several HPTSA-modified PFSA with high dye density \((\text{OD}_{405\text{nm}} > 4)\), measured values for \(V_{oc}\) after 60 min of illumination were positive in sign (Figure S1c and S3a), consistent with a decrease in the net built-in electric potential across the membrane and behavior that is expected based on the theory of electronic solar cells. We observed similar behavior in our prior studies.\(^{52-54}\) It was apparent that higher
concentrations of HPTSA used to synthesize DSM-VH resulted in larger deviations between experimental $E_{oc}$ values and those predicted by Donnan theory, since HPTSA replaces fixed charge groups in PFSA, but no clear correlations were apparent among $V_{oc}$ values and dye density. Results from a series of follow-on measurements supported that these analyses and trends were complicated, at least in part, by transient changes in the concentration of KCl(aq) that wetted the membrane due to the slow introduction of KCl(aq) into the concentrated and dilute electrolyte chambers via diffusion from the saturated KCl(aq) SCEs. Leakage of salt from the SCEs was supported by measurements of the conductance of an aqueous electrolyte containing an immersed SCE (Figure S3b).

To further investigate the impact of transient salt leakage on measured electric potential differences, $E_{oc}$ values were measured between two so-called leak-free Ag|AgCl|KCl(aq, 3.4 M) electrodes (Innovative Instruments, LF-2) with timed introduction and removal of SCEs or a fritted tube filled with saturated KCl(aq) into both the concentrated and dilute electrolyte chambers in order to replicate the salt-leakage behavior from SCEs used as sensing electrodes in prior experiments (Figure S3c). Before Event 1, no KCl(aq) source was present and $E_{oc}$ values were found to be rather stable and illumination resulted in an increase in the magnitude of $E_{oc}$ values,

Figure S2. Current density versus potential data obtained from four-electrode stepwise chronoamperometry measurements of DSM-H1 using two Ag/AgCl potential-sensing wires under conditions of 100 mM HCl||10 mM HCl(aq) (pHCl 1||2) in the dark. The area-specific resistance calculated from the slope of these data equals $\approx 76 \ \Omega\cdot\text{cm}^2$, which agrees well with the expected bulk-electrolyte-limited area-specific resistance of $\approx 25 \ \Omega\cdot\text{cm}^2$, given that in the dilute electrolyte (10 mM HCl; $\sigma \approx 4 \ \text{mS cm}^{-1}$) the electrode–membrane spacing was $\approx 1 \ \text{mm}$.
resulting in negative values for $V_{oc}$. At Event 1, KCl(aq) sources were immersed into each electrolyte and shortly thereafter the rate of change of $E_{oc}$ with respect to time increased significantly. This was accompanied by a change in the sign of $V_{oc}$ values under illumination, where now the magnitude of $E_{oc}$ values decreased, behavior that is consistent with effects that occur in traditional electronic solar cells, and that we observed previously.\textsuperscript{52-54} At Event 2, KCl(aq) sources were carefully removed, so as to not significantly agitate the solution, and the sign of $V_{oc}$ values remained unchanged. At Event 3, the electrolyte in each chamber was homogenized by cycling the solutions with a pipette, resulting in behavior similar to that occurring prior to Event 1, where $V_{oc}$ values were opposite (“reverse”) of those that occur in traditional electronic solar cells.

**Figure S3.** (a) Open-circuit potential ($E_{oc}$) over time measured between two salt-leaking saturated calomel electrodes (I-SCEs) positioned across DSM-H1 under conditions of 10 mM||1 mM HClO$_4$(aq) (pHClO$_4$ 2.23). The inset shows values for the open-circuit photovoltage ($V_{oc}$) baseline corrected for changes in $E_{oc}$ values over time using a sum of two exponential decays to best-fit $E_{oc}$ values measured in the dark, highlighting their generally positive values. Short-circuit photocurrent measurements (data not shown) were performed during regions where $E_{oc}$ values were not recorded. (b) Conductance measured over time for a 1 mM KCl(aq) solution containing an I-SCE as a KCl leakage source, and with standard reference values measured for KCl(aq) indicated. (c) $E_{oc}$ over time measured between two so-called leak-free Ag/AgCl electrodes (lf-Ag/AgCl) across DSM-H1 under conditions of 100 mM||10 mM KCl(aq) (pKCl 1.2) and in the presence of an external KCl(aq) source. At Event 1, an SCE (black dataset) and a fritted tube filled with saturated KCl(aq) (red dataset) were introduced into the dilute electrolyte chamber as passive KCl(aq) leakage sources. At Event 2, the respective KCl(aq) sources were removed. At Event 3, the electrolyte in each chamber was homogenized by cycling the electrolyte with a pipette. Positive $V_{oc}$ values are dominant during transient salt introduction and/or homogenization; negative $V_{oc}$ values are dominant for the quiescent homogenized solutions. Regions colored in purple indicate the times when the membrane was illuminated.
This supports that leakage of salt into the electrolytes and its transient interaction with membrane|solution interfaces were responsible for effects observed in our prior work.\textsuperscript{S2–S4}

A single-junction sensing electrode, for example an SCE, features a redox couple whose chemical potential is dictated by an internal reference electrolyte, typically containing high concentrations of salt and other species when appropriate. This internal reference electrolyte is separated from the experimental electrolyte by a ceramic frit that somewhat slows exchange of electrolyte species but is insufficient at doing so for our studies (Figures S3a). Therefore, we considered using double-junction sensing electrodes, which each contain a fritted chamber filled with experimental electrolyte that is placed between the single-junction sensing electrode and the experimental electrolyte to decrease the rate of cross-contamination between the internal reference electrolyte and the experimental electrolyte. We also considered using so-called leak-free Ag|AgCl|KCl(aq, 3.4 M) sensing electrodes, which each contain a somewhat conductive (<10 kΩ), but non-porous, junction to slow cross-contamination. We observed that leak-free electrodes exhibited long equilibration times that resulted in less-certain baseline values for $E_{oc}$ when the electrolyte was not KCl and/or when the electrolyte concentration was less than 10 mM ($pX = 2$). Moreover, in the absence of a membrane, theoretical $E_{oc}$ values and $E_{oc}$ values measured between a double-junction sensing electrode or a leak-free sensing electrode \textit{versus} an Ag/AgCl wire each immersed in a single aqueous electrolyte differed significantly (Table S1). These disparities are likely the result of liquid-junction potentials that formed between the internal reference electrolyte and experimental electrolyte and are too large for accurate measurement of membrane potentials. Because Ag/AgCl wires immersed into a chloride-containing electrolyte rapidly reach electrochemical equilibrium and cannot form a liquid-junction potential, they were determined to be the potential-sensing electrode of choice for our studies.
Table S1. Open-circuit potential ($E_{oc}$, in mV) measured for various electrodes (left electrode: SCE, leak-free Ag/AgCl(KCl) electrode, custom single-junction or double-junction acidic Ag/AgCl(HCl) electrode) versus an Ag/AgCl wire immersed into beakers containing solutions of various concentrations of Cl$^-$(aq) (right electrode), calculated values (in mV), and differences (in mV) attributed to liquid-junction potentials that form across electrode frits ($\phi_{LJ}^{\text{frit}}$).

| Electrochemical Cell Line Notation (Compartment A || Compartment B || Compartment C (if necessary)) | $E_{oc}$ (measured) | $E_{N,\text{redox}}^\circ$ (see first row) | $-\frac{RT}{F} \ln Q$ (with $T = 25$ °C; see Equation 4) | $\phi_{LJ}^{\text{frit}}$ (calculated using Equations 4 and 6) |
|---------------------------------------------------------------|----------------------|-------------------------------------------|--------------------------------------|---------------------------------------------|
| Pt(s) | Hg$\text{Cl}_2$(s) | Hg(l) | KCl(aq, sat’d) || KCl(aq, sat’d $\approx 4.8$ M) | AgCl(s) | Ag(s) | +45 | +45 | 0 | 0 |
| Pt(s) | Hg$\text{Cl}_2$(s) | Hg(l) | KCl(aq, sat’d) || KCl(aq, 10 mM) | AgCl(s) | Ag(s) | -97 | +45 | -159 | +17 |
| Pt(s) | Hg$\text{Cl}_2$(s) | Hg(l) | KCl(aq, sat’d) || KCl(aq, 10 mM) | AgCl(s) | Ag(s) | -143 | +45 | -218 | +30 |
| Ag(s) | AgCl(s) | KCl(aq, 3.4 M) || KCl(aq, 10 mM) | AgCl(s) | Ag(s) | -108 | 0 | -150 | +42 |
| Ag(s) | AgCl(s) | KCl(aq, 3.4 M) || HCl(aq, 10 mM) | AgCl(s) | Ag(s) | -133 | 0 | -209 | +76 |
| Ag(s) | AgCl(s) | HCl(aq, 1 M) || HCl(aq, 10 mM) | AgCl(s) | Ag(s) | -180 | 0 | -118 | -62 |
| Ag(s) | AgCl(s) | HCl(aq, 1 M) || HCl(aq, 10 mM) | AgCl(s) | Ag(s) | -289 | 0 | -178 | -111 |
| Ag(s) | AgCl(s) | HCl(aq, 1 M) || HCl(aq, 10 mM) || -198 | 0 | -118 | -80 |
| Ag(s) | AgCl(s) | HCl(aq, 1 M) || HCl(aq, 10 mM) || -313 | 0 | -178 | -135 |

For subsequent experiments and results described in the main text, Ag/AgCl wires were utilized as sensing electrodes to eliminate sources of salt leakage. Use of Ag/AgCl wires limited electrolyte options to those that contained Cl$^-$, e.g. HCl(aq) and KCl(aq), but resulted in $E_{oc}$ values that were quite stable on the order of $>10$ h for conditions where differences in the concentration of HCl across the membrane were as large as two orders-of-magnitude, i.e. pHCl 1$\|3$ (Figure S4a). Although coion crossover was greatly attenuated with this setup, osmosis was not, so much so that after 5 h, transport of water from the dilute electrolyte chamber to the concentrated electrolyte
The chamber was visibly evident (Figure S5a). Because osmosis and transient introduction of salt are each dynamic processes that should result in similar effects on $E_{oc}$ values, the effects of osmosis on $V_{oc}$ values were also assessed. For this, we compared $V_{oc}$ values obtained under conditions of pHCl 1||3, where an osmotic pressure of 44 atm existed, to $V_{oc}$ values measured under equiosmolar conditions, where to account for the van’t Hoff factor of HCl(aq), 198 mM of sucrose – a solute that under the aqueous conditions studied is non-dissociable, non-reducing, and uncharged – was introduced to the 1 mM HCl(aq) solution (Figure S5b). The resulting $V_{oc}$ behavior both with and without added osmolyte was essentially the same, suggesting that transient osmotic processes do not explain the observed “reverse” photovoltaic behavior.

AgCl wires are also known to undergo photochemical reactions, and therefore Ag/AgCl wires were initially sheathed in Teflon tubing and suspended above the illumination path to prevent direct photochemical responses. However, light that was scattered by the glass Luggin–Haber
capillaries and through the bottom opening of the tubing were sufficient to induce a noticeable change in $E_{oc}$ values upon illumination (Figure S4b). Therefore, the Teflon tubing was wrapped in opaque black polyolefin heat-shrink tubing and the bottom of the Teflon tubing was sealed with silicone (Figure S4c). Slits were made on the side of the tubing at the bottom/top to allow solution/air to enter/exit the sheath and using this setup, we did not observe any noticeable changes in $E_{oc}$ values upon illumination of unmodified Nafion under conditions of pHCl 2||3 (Figure S4b).

*Electric Potential Differences Measured using Ag/AgCl Wires.* Open-circuit potential, $E_{oc}$, values measured between two sensing electrodes report directly on the difference in the electrochemical potential of electrons in the wires.\(^{56}\) When these electrons are equilibrated with species in solution via redox reactions, $E_{oc}$ reports indirectly on electrochemical potentials of solution species. For the Ag/AgCl reaction the following reduction reaction results in the following relations at electrochemical equilibrium,
\[
\text{AgCl} + e^{-} \rightleftharpoons \text{Ag}^{+} + \text{Cl}^{-} \quad (S13)
\]

\[
\bar{\mu}_{\text{AgCl}}^{\beta} + \mu_{e}^{\alpha} = \bar{\mu}_{\text{Ag}}^{\alpha} + \bar{\mu}_{\text{Cl}^{-}}^{\gamma} \quad (S14)
\]

\[
\bar{\mu}_{e}^{\alpha} = \bar{\mu}_{\text{Cl}^{-}}^{\gamma} \quad (S15)
\]

\[
\mu_{e}^{\alpha} + RT \ln a_{e}^{\alpha} + z_{e}F \phi^{\alpha} = \mu_{\text{Cl}^{-}}^{\gamma} + RT \ln a_{\text{Cl}^{-}}^{\gamma} + z_{\text{Cl}^{-}}F \phi^{\gamma} \quad (S16)
\]

where \( \mu_{\text{AgCl}}^{\beta} = \mu_{\text{AgCl}}^{\alpha} = \mu_{\text{AgCl}}^{o,\beta} = 0 \) and \( \mu_{\text{Ag}}^{\alpha} = \mu_{\text{Ag}}^{\gamma} = \mu_{\text{Ag}}^{o,\alpha} = 0 \) because AgCl and Ag are not charged, meaning \( z = 0 \), their activity is assumed to be constant at one, and their standard chemical potential is arbitrarily chosen to be equal to zero, respectively. \textbf{Equation S16} and \textbf{Equation S3} look remarkably similar, except that only the latter equality holds for two different species, including electrons in phase \( \alpha \) whose relative electrochemical potential \textit{versus} electrons in a second wire is sensed directly by a voltmeter as \( \Delta G = \mu_{e}^{\alpha,\text{WE}} - \mu_{e}^{\alpha,\text{CE}} = -FE_{oc} \), where \( \Delta G \) is the Gibbs free energy difference, WE stands for “at the working electrode,” and CE stands for “at the counter electrode.” Again, assuming the reasonable assumption that \( \mu_{i}^{\gamma} \) in each phase is the same, and not expanding \( \bar{\mu}_{e}^{\alpha} \) in \textbf{Equation S16}, \( E_{oc} \) can be written as follows,

\[
E_{oc} = -\left( \frac{RT}{F} \ln a_{\text{Cl}^{-}}^{\gamma,\text{WE}} + z_{\text{Cl}^{-}}\phi^{\gamma,\text{WE}} \right) + \left( \frac{RT}{F} \ln a_{\text{Cl}^{-}}^{\gamma,\text{CE}} + z_{\text{Cl}^{-}}\phi^{\gamma,\text{CE}} \right) \quad (S17)
\]

\[
E_{oc} = \frac{RT}{F} \ln \frac{a_{\text{Cl}^{-}}^{\gamma,\text{CE}}}{a_{\text{Cl}^{-}}^{\gamma,\text{WE}}} - z_{\text{Cl}^{-}}(\phi^{\gamma,\text{WE}} - \phi^{\gamma,\text{CE}}) \quad (S18)
\]

\[
E_{oc} = E_{N}^{\text{redox}} + \sum \phi_{i} \quad (S19)
\]

where \textbf{Equation S19} is the same as \textbf{Equation 6} in the main text, \( E_{N}^{\text{redox}} \) stands for the net Nernst redox potential of the WE \textit{versus} the CE (\textbf{Equation 4} in the main text), and \( \phi_{i} \) is any contribution to differences in electric potential between nearer to the WE \textit{versus} nearer to the CE, including Donnan potentials (\textbf{Equations 1 and 2} in the main text) and liquid-junction potentials. Notably, although Donnan theory is based on electrochemical equilibrium to form a Donnan electric potential difference across \textit{each interface of a membrane}, \( \phi_{D}^{\text{int}} \), this does not result in
electrochemical equilibrium across the entire membrane when two or more mobile ions are present that do not react chemically over the timescale of transport, e.g. H⁺ and Cl⁻. Moreover, when multiple mobile salt species are present, e.g. HCl(aq) and KCl(aq), it is highly unlikely that a value for \( \phi_D^{\text{int}} \) exists that results in electrochemical equilibration across a single interface and in which case the Henderson and Goldman equations and their associated theories are more applicable to approximating values for the membrane potential, \( \phi_i \).

**Independence of Illumination Direction on Open-Circuit Photovoltage.** Using a custom automated setup we measured the effect of equal illumination intensity and beam profile incident from either direction of the cell in an alternating fashion (Figure S6), using only one motorized flipper mirror (Thorlabs, MFF101). Results were the same as we reported previously in that there was no illumination-direction dependence to the observed sign or magnitude of \( V_{oc} \) values.

**Comparison of HPTSA-modified PFSA to its Methoxylated Analog, MeOPTSA-modified PFSA.** A shortcoming of the non-photoacidic light absorbers used as negative controls, i.e. \([\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}\) ionically associated into Nafion and carbon cloth affixed to Nafion, were that the light-absorbing species were not covalently bound.

![Figure S6. Open-circuit photovoltage (\( V_{oc} \)) measured for DSM-H1 under conditions of 100 mM HCl||1 mM HCl (pHCl 1||3) in the dark and illuminated with 170 mW/cm² of 405 nm laser light demonstrating the independence of illumination direction (incident on the side with the dilute electrolyte (Event 1) or incident on the side with the concentrated electrolyte (Event 2)) on the sign and magnitude of the open-circuit photovoltage (\( V_{oc} \)) while illuminated (purple bars). Each measurement was baseline corrected for drift of the open-circuit potential by subtracting a line that spanned from the beginning of the first illumination event to the beginning of the fifth illumination event.](image-url)
Figure S7. (a) Open-circuit photovoltage ($V_{oc}$) over time measured between two Ag/AgCl wires positioned across various light-absorbing PFSA or Nafion membranes under conditions of 100 mM || 1 mM HCl(aq) (pHCl 1||3) and with data grouped based on illumination cycle timing. Each measurement was baseline corrected for drift of the open-circuit potential by subtracting a line that spanned from the beginning of the first illumination event to the beginning of the sixth illumination event. Purple bars indicate times of 405 nm laser excitation (2 min each) with increasing intensity over time due to decreasing attenuation from a neutral density filter (1 ND, 0.6 ND, 0.4 ND, 0.2 ND, 0.1 ND, no filter). (b) Final illumination events in the absence of a neutral density filter, each at a similar irradiance of 140 mW/cm$^2$, where the condition of 1 Sun equivalent excitation occurs for an irradiance of 31.3 mW/cm$^2$.

Figure S8. Open-circuit photovoltage ($V_{oc}$) over time measured between two Ag/AgCl wires positioned across (a) DSM-H1 and (b) Nafion NR-212 with ionically associated [Ru(bpy)$_3$]$^{2+}$ under conditions of 100 mM||1 mM HCl(aq) (pHCl 1||3). Each measurement was baseline corrected for drift of the open-circuit potential by subtracting a line that spanned from the beginning of the first illumination event to the beginning of the sixth illumination event. Purple bars indicate times of 405 nm laser excitation (2 min each) with increasing intensity over time due to decreasing attenuation from a neutral density filter (1 ND, 0.6 ND, 0.4 ND, 0.2 ND, 0.1 ND, no filter). The maximum irradiance used for DSM-H1 was 166 mW/cm$^2$ and for [Ru(bpy)$_3$]$^{2+}$/Nafion was 141 mW/cm$^2$, and the condition of 1 Sun equivalent excitation for DSM-H1 occurs for an irradiance of 31.3 mW/cm$^2$. The legend indicates the chronological order of trials (T) taken on the same membrane, each with refreshed electrolyte. (c) $V_{oc}$ across DSM-H1 when both electrolytes included 1 mM Fe(ClO$_4$)$_x$(aq) where $x = 2$ or 3, and illuminated with 145 mW/cm$^2$ of 405 nm laser light (purple bar). Each measurement was baseline corrected for drift of the open-circuit potential by subtracting the open-circuit potential value just prior to the illumination event.
to the membrane. Therefore, we aimed to improve on these negative controls by developing a new dye where the photoacidic hydroxyl group in HPTSA was replaced with a methoxy group, resulting in the non-photoacidic molecule abbreviated MeOPTSA. To synthesize MeOPTSA, HPTS was first converted into MeOPTS via reaction with methyl iodide. Success of this reaction was supported by data obtained using FTIR–ATR spectroscopy (Figure S9a) and NMR spectroscopy (Figure S10), which indicated a lack of a broad shoulder associated with the photoacidic hydroxyl group in the range of 2900 – 3400 cm\(^{-1}\) and the presence of a singlet at a chemical shift of ~4.4 ppm that integrates to ~3 times larger than signals arising from single protons and is consistent with the methyl group on MeOPTS, respectively. Acid–base titrations with spectroscopic detection also supported that MeOPTS is not photoacidic, given similarities between the absorption and photoluminescence spectra when dissolved in aqueous acidic solutions versus alkaline solutions, and compared to protic HPTS under the same conditions (Figure S9b,c). MeOPTS was then converted into its trisulfonamide variant, MeOPTSA, via the same protocol used to convert HPTS to HPTSA.
Figure S10. $^1$H-NMR spectra of MeOPTS (inset: structure with labeled peaks) dissolved in D$_2$O(l) after being subjected to the following conditions for 24 h: (a) in the dark under ambient conditions and (b) illuminated from the bottom of the NMR tube with ~20 mW of 405 nm diode light from a generic presentation pointer. The peak at 4.8 ppm is due to H$_2$O impurity.
Covalent bonding of MeOPTSA to PFSA resulted in a small bathochromic shift of its strongest absorption feature (Figure S11a), but the overall electronic absorption spectrum remained qualitatively similar to that observed for MeOPTS(aq). Increasing the pH of the aqueous electrolyte in contact with MeOPTSA-modified PFSA from 2 to 13 resulted in a small hypsochromic shift of its strongest absorption feature, consistent with deprotonation of free ammoniums on HPTSA/MeOPTSA that were not crosslinked with PFSA. Under conditions of pHCl 2||3, MeOPTSA-modified PFSA exhibited small positive $V_{oc}$ values (Figure S11b), consistent with a decrease in the magnitude of the built-in electric potential as observed with traditional electronic solar cells. The small magnitude of $V_{oc}$ values can be rationalized, because 60% less photons were absorbed by MeOPTSA-modified PFSA as compared to other non-photoacidic controls, but the sign of the $V_{oc}$ values was unexpected. Positive values for $V_{oc}$ were only observed sporadically using $[\text{Ru}^{II}(\text{bpy})_3]^{2+}$/Nafion (Figure S8b) and in the presence of a
constant source of salt, e.g. in the presence of a salt-leaking SCE (Figure S3). The stability of MeOPTS was evaluated for MeOPTS in D$_2$O(l) in an NMR tube by illuminating it for 24 h at ~20 mW with a generic 405 nm presentation pointer, equivalent to ~1.9 h of constant illumination at the irradiance used in the electrochemical experiments. Changes in relative integrated signal intensities and/or the presence of new peaks, e.g. due to methanol at 3.34 ppm, were not observed (Figure S10), suggesting that MeOPTS is photostable over the timescale of our experiment. This may indicate that mechanisms for generating photovoltages with modified PFSA may be different between MeOPTSA-modified PFSA and other non-photoacidic negative control dye molecules.

![Figure S12. (a) Open-circuit photovoltage (V$_{oc}$) as a function of irradiance from 405 nm laser light measured between two Ag/AgCl wires positioned across Nafion membranes containing various photoabsorbers under conditions of 10 mM||1 mM HCl(aq) (pHCl 2||3). HPTSA ("DSM" datasets) was covalent bound to PFSA, [Ru(bpy)$_3$]$^{2+}$ was ionically associated into commercial Nafion NR-212, and carbon cloth was affixed to one side of commercial Nafion. Optical densities at 405 nm were >4, except for DSM-L, which was 0.664. Data and error bars for each DSM-X are the mean ± standard deviation of three trials while each negative control measurement was only performed once. (b) V$_{oc}$ over time measured between two Ag/AgCl wires positioned across Nafion NR-212 with ionically associated [Ru(bpy)$_3$]$^{2+}$ under conditions of 10 mM||1 mM HCl(aq) (pHCl 2||3). Each measurement was baseline corrected for drift of the open-circuit potential by subtracting a line that spanned from the beginning of the first illumination event to the beginning of the sixth illumination event. Purple bars indicate times of 405 nm laser excitation (2 min each) with increasing intensity over time due to decreasing attenuation from a neutral density filter (1 ND, 0.6 ND, 0.4 ND, 0.2 ND, 0.1 ND, no filter). The maximum irradiance used was 170 mW/cm$^2$ and the condition of 1 Sun equivalent excitation occurs for an irradiance of 31.3 mW/cm$^2$. The legend indicates the chronological order of trials (T) taken on the same membrane, each with refreshed electrolyte.](image-url)
Transient Dye Characterization. Kinetics data for the reprotonation of ground-state deprotonated HPTSA(aq) were analyzed in order to obtain both the forward and backward rate constant for ground-state proton transfer with H⁺(aq) (Reaction 11 in the main text). The integrated rate equation for an analogous process has been reported previously, but for clarity, we show the derivation here for our specific case, which starts with the following differential rate equation,

\[
\frac{d[PA^-]}{dt} = -k_{+2}[PA^-][H^+] + k_{-2}[PAH]
\]  

(S20)

where \(k_{+2}\) is the rate of proton association, \(k_{-2}\) is the rate of proton dissociation, [PA⁻] and [PAH] are the concentration of ground-state deprotonated/protonated photoacids, respectively, and [H⁺] is the concentration of free (unbound) protons. Due to the dilute conditions used in this experiment, activity coefficients for each species are reasonably assumed to be unity. Although reaction rates are dependent on the concentration of protons and photoacid species, our transient absorption...
spectroscopy measurements only report on the change in concentration of ground-state deprotonated photoacids generated from pulsed-laser excitation, such that Equation S20 can be recast as follows,

\[
\frac{d([\text{PA}^-]_{eq} + \Delta[\text{PA}]_t)}{dt} = -k_2[\text{PA}^-]_t([H^+]_{eq} + \Delta[H^+]_t) + k_{-2}([\text{PAH}]_{eq} + \Delta[\text{PA}]_t)
\]  

(S21)

where the $[X]_{eq}$, $\Delta[X]$, and $[X]_t$ are written as such to indicate the equilibrium concentration, transient non-equilibrium change in concentration, and transient non-equilibrium total concentration, respectively. Colors and bold text are used to clarify subsequent substitutions using the following conservation of mass relation (Equation S22), the fact that experiments were conducted under conditions where a negligible concentration of $H^+(aq)$ was photogenerated relative to its equilibrium concentration (Equation S23), and the equilibrium expression that results from setting $\frac{d[\text{PA}^-]}{dt}$ equal to zero in Equation S20 (Equation S24),

\[
\Delta[\text{PA}^-]_t = [\text{PA}^-]_t - [\text{PA}^-]_{eq} = -\Delta[\text{PAH}]_t
\]

(S22)

$[H^+]_t \approx [H^+]_{eq}$, and thus $\Delta[H^+]_t \approx 0$  

(S23)

\[
k_{-2}[\text{PAH}]_{eq} = k_{+2}[\text{PA}^-]_{eq}[H^+]_{eq}
\]

(S24)

Substituting these equations into Equation S21 leads to the following,

\[
\frac{d[\text{PA}^-]_t}{dt} = (-k_2[\text{PA}^-]_t[H^+]_{eq} + 0) + (k_{+2}[\text{PA}^-]_{eq}[H^+]_{eq} - k_{-2}[\text{PA}^-]_t + k_{-2}[\text{PA}^-]_{eq})
\]

(S25)

\[
\int_{[\text{PA}^-]_{eq} + \Delta[\text{PA}^-]_t}^{[\text{PA}^-]_{eq} + \Delta[\text{PA}^-]_t} \frac{1}{-(k_{+2}[H^+]_{eq} + k_{-2})[\text{PA}^-]_t + (k_{+2}[H^+]_{eq} + k_{-2})[\text{PA}^-]_{eq}} d[\text{PA}^-]_t = \int_0^t dt
\]

(S26)

where subsequent substitution using the following four relations, $c = [\text{PA}^-]_{eq}$; $y_i = c + \Delta[\text{PA}^-]_t$; $y_o = c + \Delta[\text{PA}^-]_o$; $k_{obs} = k_{+2}[H^+]_{eq} + k_{-2}$, $y = [\text{PA}^-]_t$, leads to the following integrated rate equations,

\[
- \frac{1}{k_{obs}} \int_{y_o}^{y_i} \frac{1}{y - c} dy = - \frac{1}{k_{obs}} \ln \left( \frac{y_i - c}{y_o - c} \right) = t
\]

(S27)

\[
y_t - c = (y_o - c)e^{-k_{obs}t}
\]

(S28)

\[
\Delta[\text{PA}^-]_t = \Delta[\text{PA}^-]_o e^{-(k_{+2}[H^+]_{eq} + k_{-2})t}
\]

(S29)
This resulting equation implies that transient absorption kinetic data obtained from photoacids that undergo Reaction 11 in the main text should be fit well by a single decaying exponential function, as observed in Figure 6 in the main text, with an observed rate constant equal to \( k_{\text{obs}} \), and represented by Equation 13 in the main text.

**Average Number of OH\(^-\) Encounters by a Photogenerated H\(^+\) in Protonated Nafion.** The largest volume that any given photogenerated H\(^+\) in HPTSA-modified PFSA will stochastically encounter before it interacts with a side of the membrane is a hemisphere with a radius that is equal to the thickness of the membrane (50.8 \( \mu \)m), assuming that H\(^+\) exhibit similar through-plane and in-plane diffusion coefficients. Using this volume (2.7 x 10\(^{-10}\) dm\(^3\)), and the approximate concentration of OH\(^-\) of 10\(^{-14}\) M (mol/dm\(^3\)), based on a perceived concentration of ~1 M H\(^+\) (approximately the concentration of sulfonates in Nafion NR-212) and an assumed autoprotolysis equilibrium constant of that of bulk water, \( K_w = 10^{-14} \), a photogenerated H\(^+\) within Nafion would encounter on average only ~1.7 OH\(^-\) molecules during transport across the entire 50.8 \( \mu \)m thick membrane.

**Photovoltaic Action using Neutral Salt Water.** Studies reported herein intentionally utilized molecules consisting of protic salts and photoacid dyes to perform excited-state proton transfer in
single-membrane constructs. The proton-centric nature of our systems enabled us to glean detailed mechanistic information about materials function. Ultimately, we would like to use our photoactive materials for direct light-driven desalination of salt water. However, detailed studies of their function when in the presence of pH-neutral aqueous salt solutions were not performed due to the complexity of having multiple ions present (i.e. H\(^+\) and salt ions), use of photoacids that only photogenerate mobile protons, and small magnitude \(V_{oc}\) values observed in the presence of acid only. Notwithstanding, as an initial proof-of-concept we evaluated DSM-H1 in the dark and under illumination while in the presence of significant amounts of aprotic salts, i.e. KCl, under near-neutral pH conditions (Figure S15). Inconsistent behavior was observed at early times, which also used the lowest intensity light of those examined, that may be a consequence of initial equilibration of the salt solution with photogenerated H\(^+\) from the photoacids, even though the membrane had been soaked in 100 mM KCl(aq) for 24 h prior to measurements. In future work, we plan to explore this parameter space in more depth in order to better understand design guidelines for light-driven ion pumps for use in small-footprint autonomous desalination devices.

![Figure S15. Open-circuit potential (Eoc) over time measured between two Ag/AgCl wires positioned across DSM-H1 under conditions of 100 mM||1 mM KCl(aq) (pKCl 1||3). The legend indicates the chronological order of trials (T) taken on the same membrane. Purple bars indicate times of 405 nm laser excitation (2 min each) with increasing intensity over time due to decreasing attenuation from a neutral density filter (1 ND, 0.6 ND, 0.4 ND, 0.2 ND, 0.1 ND, no filter). The maximum irradiance used was 120 mW/cm\(^2\) and the condition of 1 Sun equivalent excitation occurs for an irradiance of 31.3 mW/cm\(^2\).](image)
References


(S7) P. Henderson, Zeitschrift für Phys. Chemie, 1907, 59, 118.


