Supporting Information for:

Preparation and characterization of crosslinked poly(vinylimidazolium) anion exchange membranes for artificial photosynthesis

Blaine M. Carter¹, Laura Keller², Matthias Wessling²,³, and Daniel J. Miller¹†

†Corresponding Author, Tel: +1 (510) 495-2353 E-mail: danieljmiller@lbl.gov

¹Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, Berkeley, CA 97420, United States

²RWTH Aachen University, Chemical Process Engineering, Forckenbeckstr. 51, 52074 Aachen, Germany

³DWI – Leibniz Institute for Interactive Materials, Forckenbeckstr. 50, 52074 Aachen, Germany

Fig. S1. ¹H (500 MHz, CDCl₃) of compound ii
Fig. S2. $^{13}\text{C}$ (500 MHz, CDCl$_3$) of compound ii
Fig. S3. $^1$H (500 MHz, DMSO-$d_6$) of monomer 1
Fig. S4. $^{13}$C (500 MHz, DMSO-$d_6$) of monomer 1
Fig. S5. $^1$H (500 MHz, DMSO-$d_6$) of monomer 2
Fig. S6. $^{13}$C (500 MHz, DMSO-$d_6$) of monomer 2
Due to the non-selective chemistry, the first reaction step produces monomer 1 that cannot be separated from monomer 1a. Since monomer 1a contains a unique CH proton at 9.19 ppm, but both monomer 1 and 1a contain a CH proton at 9.61 ppm, the ratio of monomer 1a and 1 is given by:

$$\frac{\text{monomer 1a}}{\text{monomer 1}} = \frac{I_{CH \text{ at } 9.19 \text{ ppm}}}{(I_{CH \text{ at } 9.61 \text{ ppm}} - I_{CH \text{ at } 9.19 \text{ ppm}})/2}$$

The mol % of monomer 1a can be calculated as follows:

$$\text{monomer 1a (mol %)} = \frac{I_{CH \text{ at } 9.19 \text{ ppm}}}{I_{CH \text{ at } 9.19 \text{ ppm}} + (I_{CH \text{ at } 9.61 \text{ ppm}} - I_{CH \text{ at } 9.19 \text{ ppm}})/2}$$

$$= \frac{2 I_{CH \text{ at } 9.19 \text{ ppm}}}{I_{CH \text{ at } 9.19 \text{ ppm}} + I_{CH \text{ at } 9.61 \text{ ppm}}}$$
Fig. S8. $^{13}C$ (500 MHz, DMSO-$d_6$) of monomer 1a
Due to the non-selective chemistry, the first reaction step produces monomer 2 that cannot be separated from monomer 2a. Since monomer 2a contains a unique CH proton at 9.13 ppm, but both monomer 2 and 2a contain a CH proton at 9.52 ppm, the ratio of monomer 2a and 2 is given by:

\[
\frac{\text{monomer } 2a}{\text{monomer } 2} = \frac{I_{CH \text{ at } 9.13 \text{ ppm}}}{(I_{CH \text{ at } 9.52 \text{ ppm}} - I_{CH \text{ at } 9.13 \text{ ppm}})/2}
\]

The mol % of monomer 2a can be calculated as follows:

\[
\text{monomer } 2a \text{ (mol %)} = \frac{I_{CH \text{ at } 9.13 \text{ ppm}}}{I_{CH \text{ at } 9.13 \text{ ppm}} + (I_{CH \text{ at } 9.52 \text{ ppm}} - I_{CH \text{ at } 9.13 \text{ ppm}})/2} = \frac{2 I_{CH \text{ at } 9.13 \text{ ppm}}}{I_{CH \text{ at } 9.13 \text{ ppm}} + I_{CH \text{ at } 9.52 \text{ ppm}}}
\]
Fig. S10. $^{13}$C (500 MHz, DMSO-$d_6$) of monomer 2a
Fig. S11. Temperatures used to prepare membranes at different prepolymerization solvent contents. Curing was performed by photopolymerization.

<table>
<thead>
<tr>
<th>Prepolymerization solvent content (wt. %)</th>
<th>Solvent</th>
<th>Monomer</th>
<th>Polymerization temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.50</td>
<td>Water</td>
<td>1 or 1a</td>
<td>80</td>
</tr>
<tr>
<td>25.00</td>
<td>Water</td>
<td>1 or 1a</td>
<td>20</td>
</tr>
<tr>
<td>37.50</td>
<td>Water</td>
<td>1 or 1a</td>
<td>20</td>
</tr>
<tr>
<td>50.00</td>
<td>Water</td>
<td>1 or 1a</td>
<td>20</td>
</tr>
<tr>
<td>31.25</td>
<td>Methanol</td>
<td>1 or 1a</td>
<td>45</td>
</tr>
<tr>
<td>37.50</td>
<td>Methanol</td>
<td>1 or 1a</td>
<td>35</td>
</tr>
<tr>
<td>43.75</td>
<td>Methanol</td>
<td>1 or 1a</td>
<td>35</td>
</tr>
<tr>
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<td>1 or 1a</td>
<td>25</td>
</tr>
<tr>
<td>25.00</td>
<td>Methanol</td>
<td>2 or 2a</td>
<td>40</td>
</tr>
<tr>
<td>31.25</td>
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<td>35</td>
</tr>
<tr>
<td>37.50</td>
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</tr>
<tr>
<td>50.00</td>
<td>Methanol</td>
<td>2 or 2a</td>
<td>25</td>
</tr>
</tbody>
</table>
Fig. S12. Representative ATR FTIR spectra of monomer 1 before and after polymerization. Polymer was dried in a vacuum oven to remove solvent prior to measurement.
Fig. S13. Representative ATR FTIR spectra of monomer 2 before and after polymerization. Polymer was dried in a vacuum oven to remove solvent prior to measurement.
Fig. S14. Representative ATR FTIR spectra of monomer 1 and 1a before and after polymerization. Polymers were dried in a vacuum oven to remove solvent prior to measurement.
Fig. S15. Representative ATR FTIR spectra of monomer 2 and 2a before and after polymerization. Polymers were dried in a vacuum oven to remove solvent prior to measurement.
2.10 Thermal characterization

Differential scanning calorimetry (DSC) was performed on dried polymer films using a TA Instruments Q20 (New Castle, DE). All samples were dried under vacuum (< 1 Torr, 40 °C) for a minimum of 24 h before analysis. To erase the thermal history of the samples, they were heated to 200 °C at 10 °C/min or 20 °C/min, held isothermally for 5 min, and then cooled to -80 °C at 5 °C/min or 10 °C/min and held isothermally for 5 min. This cycle was repeated and the second cycle was used for analysis.

Thermogravimetric analysis (TGA) was performed on dry polymer films using a TA Instruments Q50 (New Castle, DE). All samples were dried under vacuum (< 1 Torr, 40 °C) for a minimum of 24 h before analysis. Samples were equilibrated at 25 °C, then heated to 500 °C at 5 °C/min and held isothermally for 5 min.