### **Supporting Information**

### Design guidelines for membrane-separated organic electrosynthesis: the case of adiponitrile electrochemical production

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#### Membrane conductivity equilibration time



**Figure S1.** Measurements of Nafion conductivity equilibration time for varying AN concentrations. The electrolyte for conductivity measurements contained 0.5 M Na<sub>3</sub>PO<sub>4</sub>, 0.02 M tetrabutylammonium hydroxide, and 0.03 M EDTA at 25 °C.

#### Flow cell dimensions



Figure S2. Dimensions of end plates, flow plates and flow pattern of the flow reactor



# Permeability measurements at steady state

**Figure S3.** Effect of flow rate on the flux of organic species from cathodic to anodic chamber with Nafion 117. The catholyte contained 0.5 M Na<sub>3</sub>PO<sub>4</sub>, 0.02 M tetrabutylammonium hydroxide, and 0.03 M EDTA and 0.6 M AN. The anolyte consisted of 1 M H<sub>2</sub>SO<sub>4</sub>.



#### EIS measurements for membrane conductivity

**Figure S4**. (a) Bode diagram, (b) proposed equivalent circuit, and (c) Nyquist plot for 10 mV sinus amplitude from 7 MHz to 1 Hz. Electrolyte contained 0.5 M Na<sub>3</sub>PO<sub>4</sub>, 0.02 M TBA hydroxide, 0.03 M EDTA, and 1.3 M AN.

The equivalent circuit for membrane conductivity in solution with the four electrode setup described in the manuscript has been previously proposed<sup>1</sup>, with the behavior characteristic of systems with two time constants. The circuit identifies the resistance for the membrane and solution ( $R_{m+s}$ ), as well as resistance and capacitances of the electrical double layer (EDL) and diffusion in the boundary layer (DBL).  $R_{m+s}$  was thus found from the far right intercept of the Nyquist plot. Values were further corroborated with linear sweep voltammetry, obtaining the membrane resistance from the slope of the graph.

# SAXS holder design



Figure S5. Design and main dimensions of sample holder for SAXS experiments

### References

1. J. C. Jansen, *Encyclopedia of Membranes*, Springer-Verlag Berlin Heidelberg, Italy (2016).