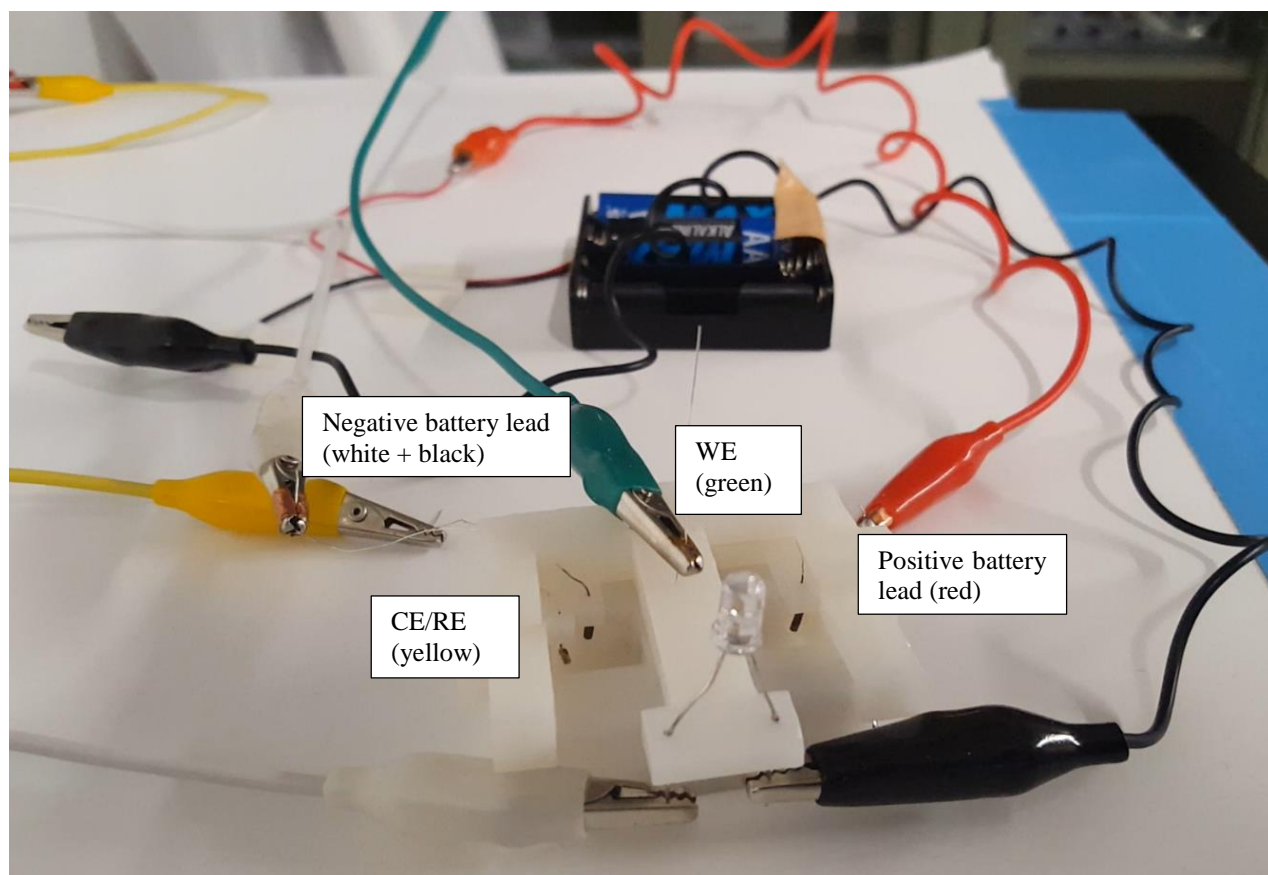**Supplementary Figure 1. Membrane, SEM imaging, and setup.** Suspended PPy(DBS) formed across the pores of gold-sputtered track-etched polycarbonate filter (Au/PCTE). SEM image of PPy(DBS) of charge densities 0.15 and 0.25 C/cm^2 on a PCTE substrate, showing loss of transparency of pores underneath polymer with increasing thickness. Schematic of bicameral device with membrane as septum and associated applied potentials and resulting currents.
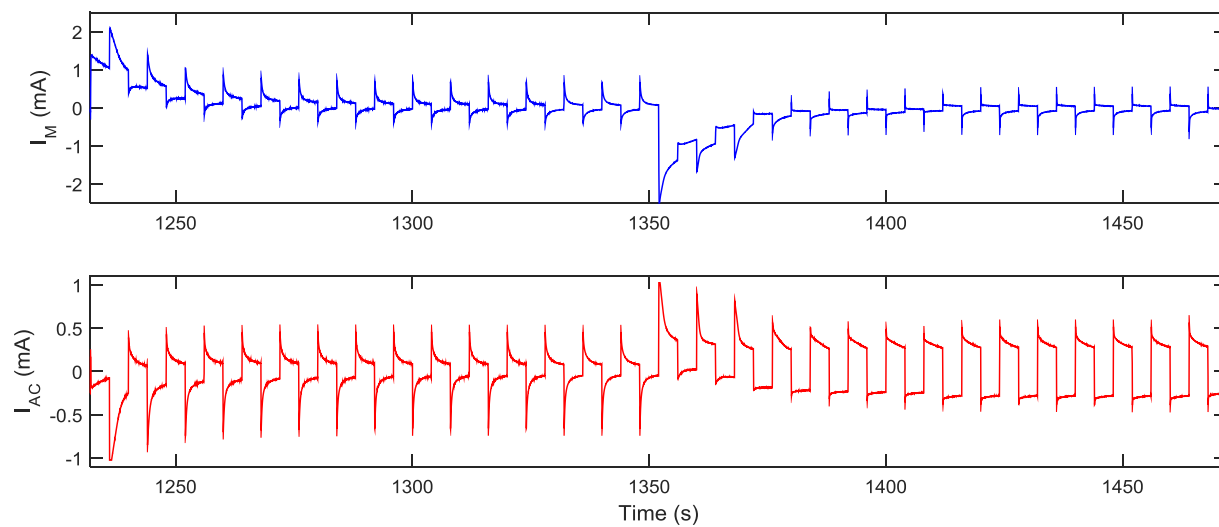
Supplementary Figure 2. Unprocessed temporal current response of membrane and transmembrane. Interplay between the currents exist as a result of interplay current in the form of double-layer formation at membrane and Ag/AgCl electrode within a single chamber of bicameral device.
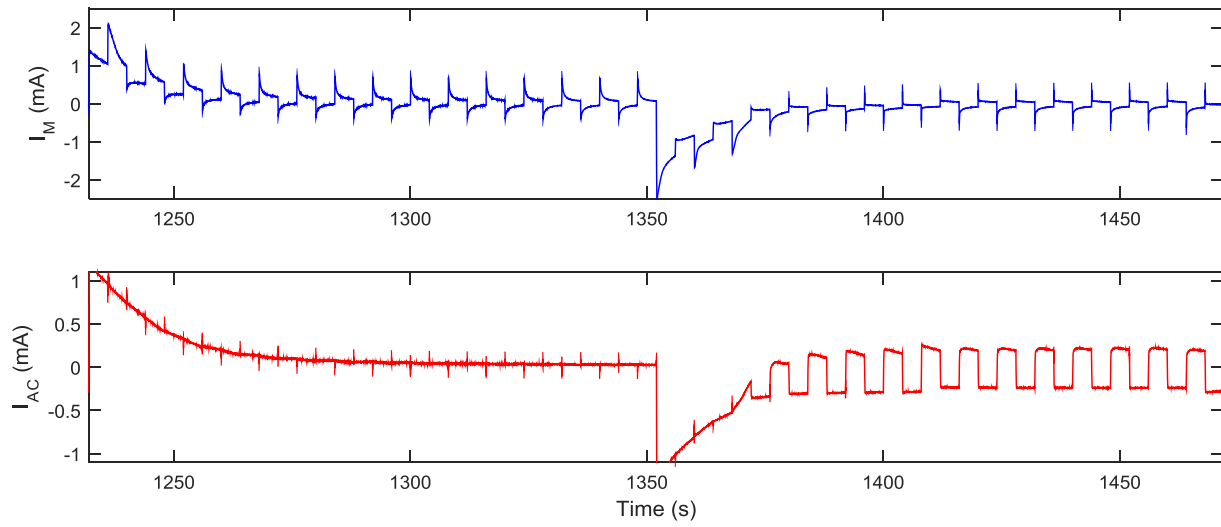
Supplementary Figure 3. Corrected temporal current response of transmembrane. Steady-state membrane current is superposed onto transmembrane current to give true transmembrane current without interplay current.

Supplementary Figure 4. LED circuit electron flow control. A closed circuit is created with 2-AA batteries, an LED, and a bicameral device containing ionic solution and with the smart membrane separator as the septum, electron flow controlled by potential applied to PPy(DBS) of membrane separator.
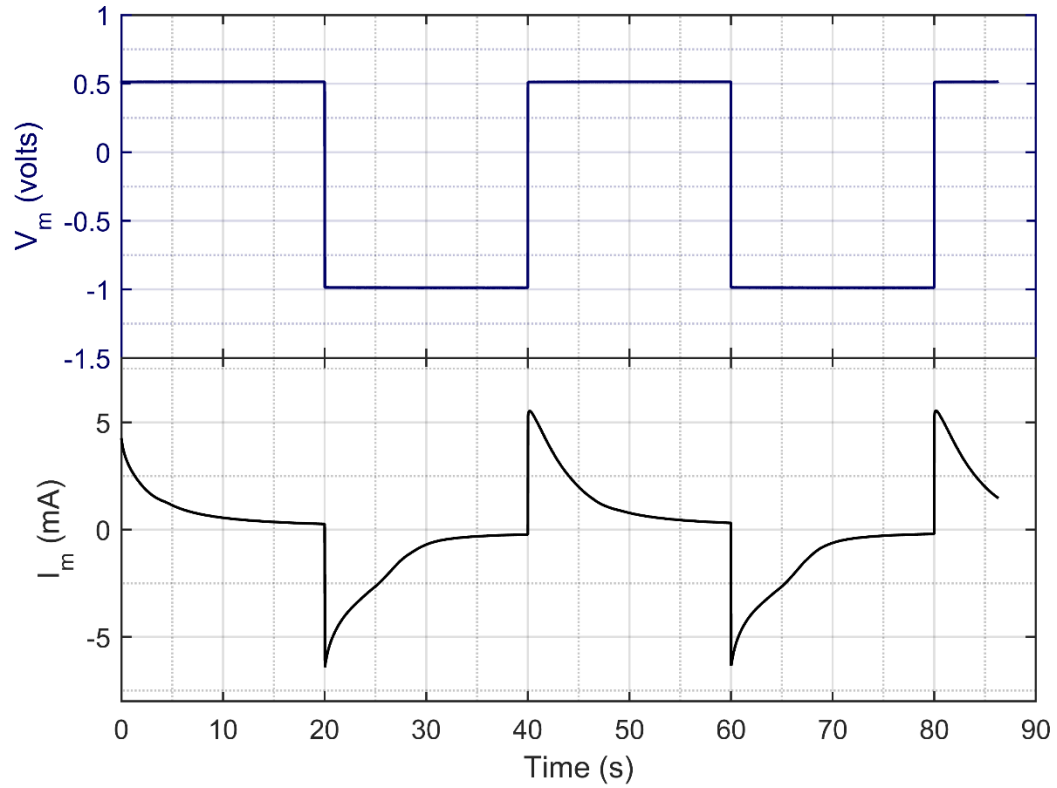
Supplementary Figure 5. Membrane voltage and current for 25 mHz LED circuit. Applied membrane potential during 20 second on (-1V), 20 second off (+0.5V) testing of LED circuit and resulting membrane current.
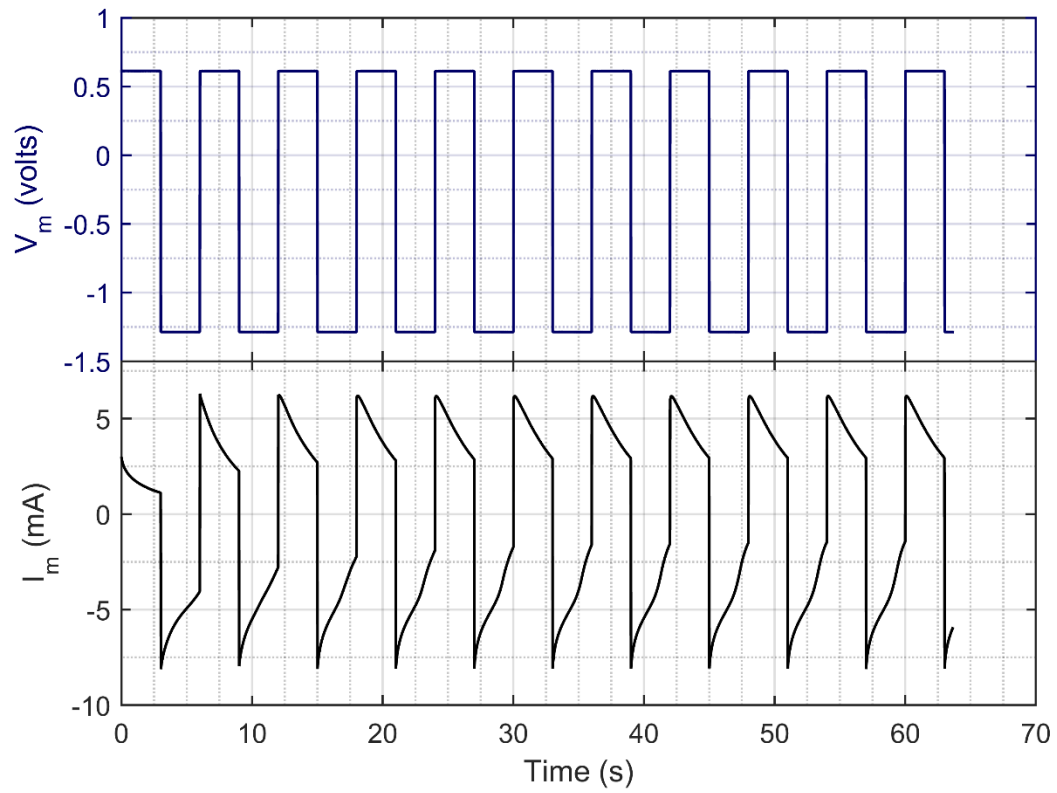
Supplementary Figure 6. Membrane voltage and current for 167 mHz LED circuit. Applied membrane potential during 3 second on (-1.3V), 3 second off (+0.6V) testing of LED circuit and resulting membrane current.
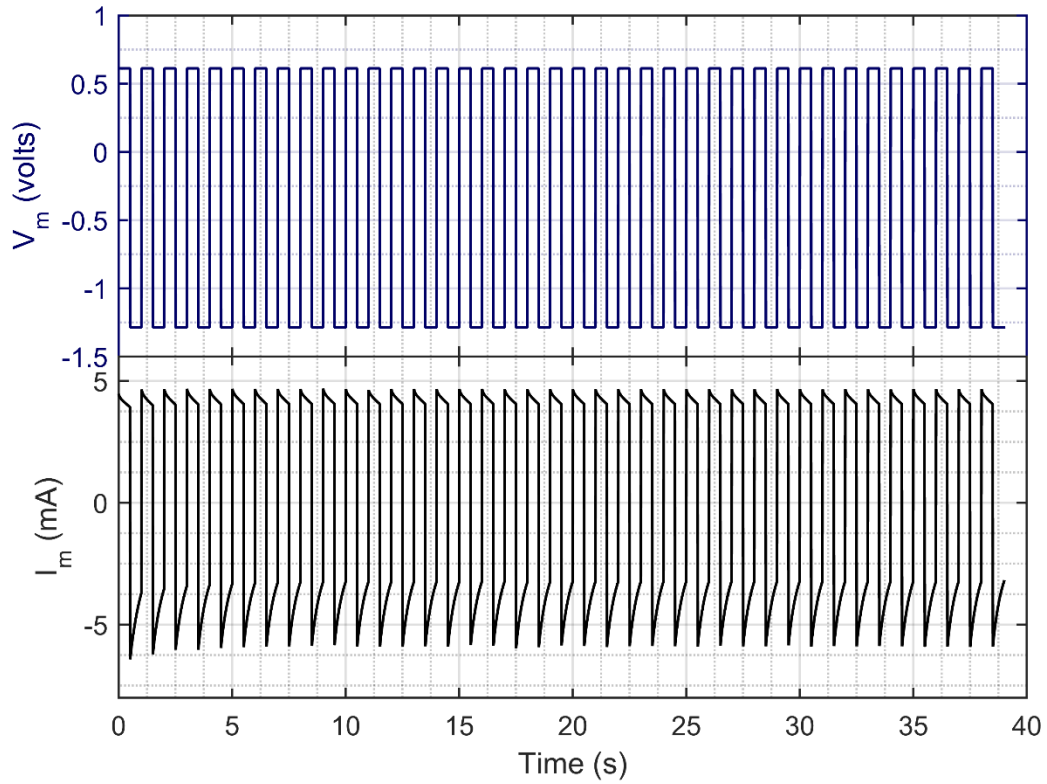
Supplementary Figure 7. Membrane voltage and current for 1 Hz LED circuit. Applied membrane potential during 0.5 second on (-1.3V), 0.5 second off (+0.6V) testing of LED circuit and resulting membrane current.
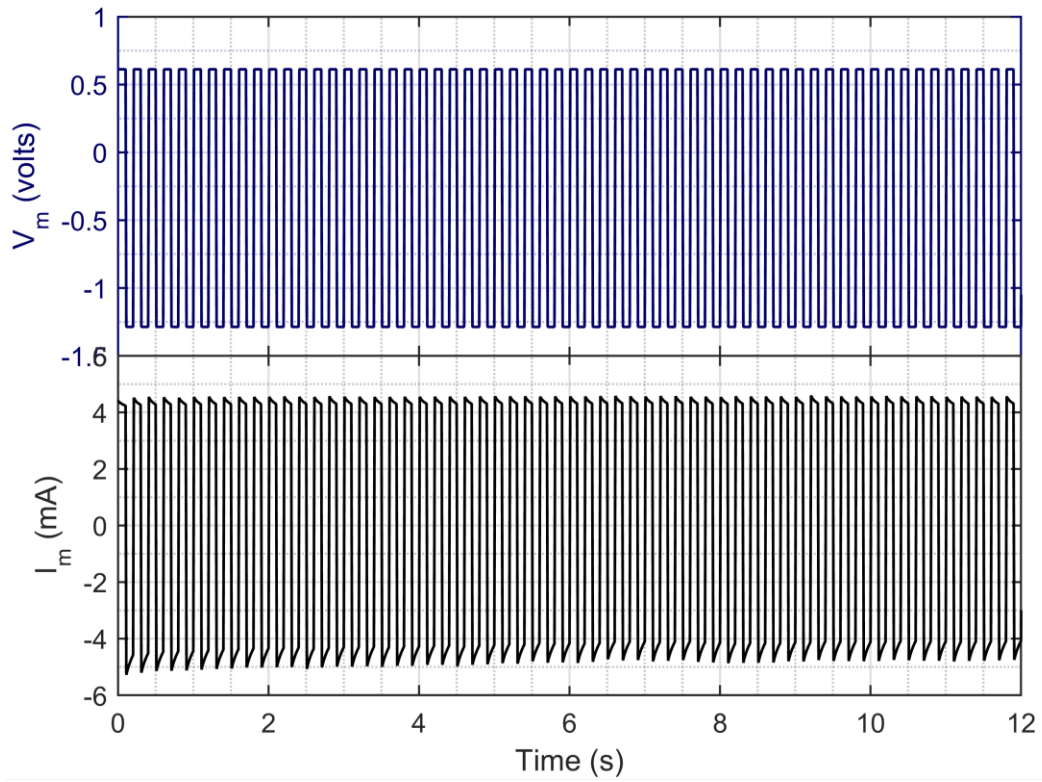
Supplementary Figure 8. Membrane voltage and current for 5 Hz LED circuit. Applied membrane potential during 0.1 second on (-1.3V), 0.1 second off (+0.6V) testing of LED circuit and resulting membrane current.
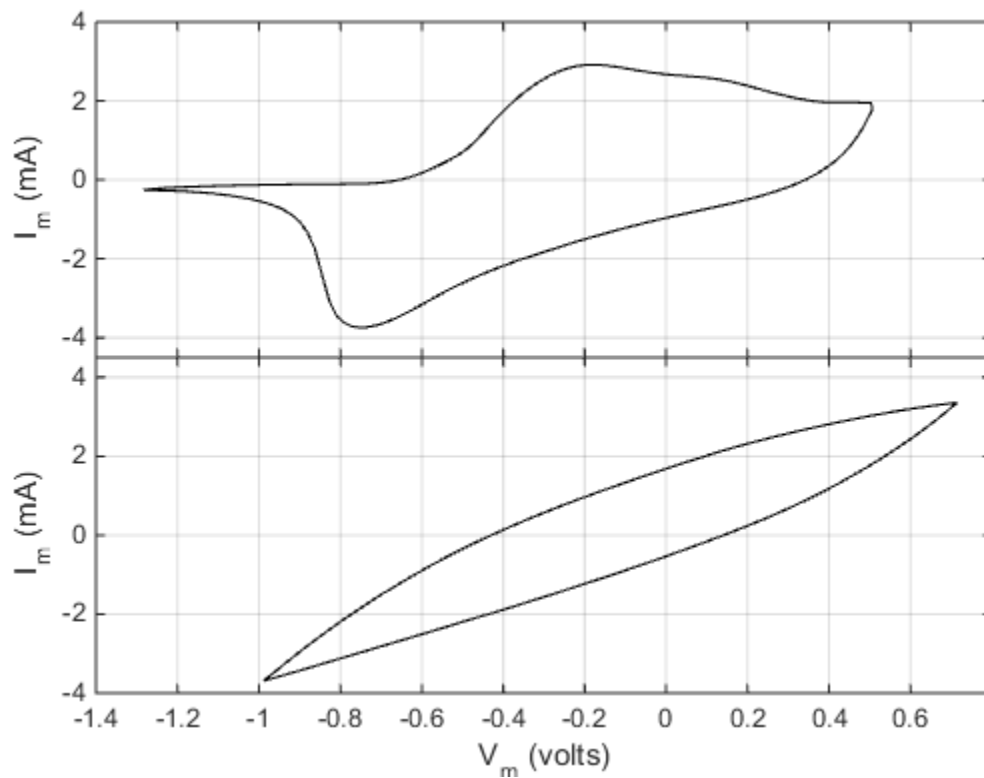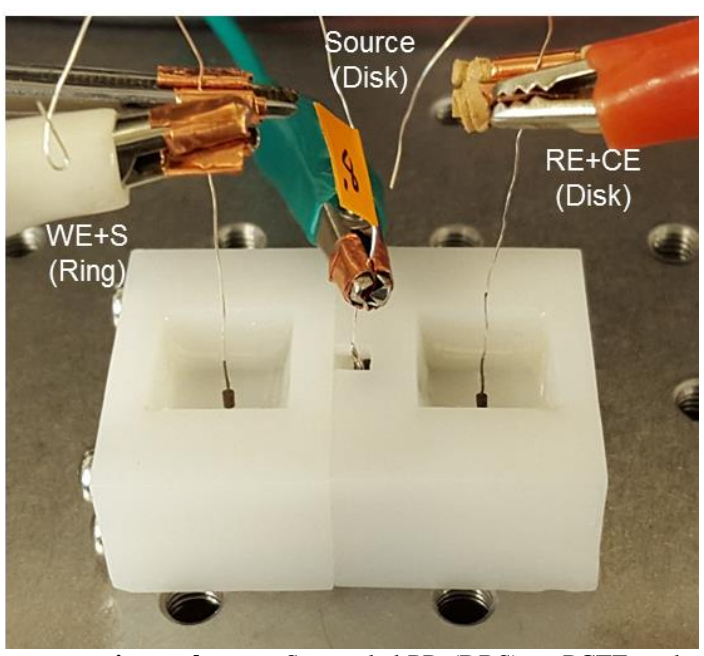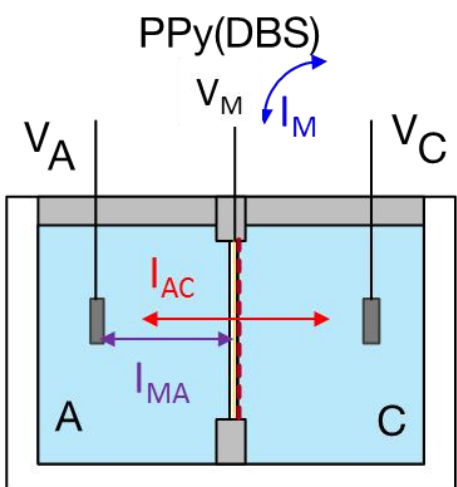
Supplementary Figure 9. Membrane cyclic voltammogram (CV) for constant variable control LED circuit. Typical CV for membrane for 50 mV/s scan rate and resulting CV for LED circuit testing from on (-1V) to off (+0.7V) for 300 mV/s scan rate.
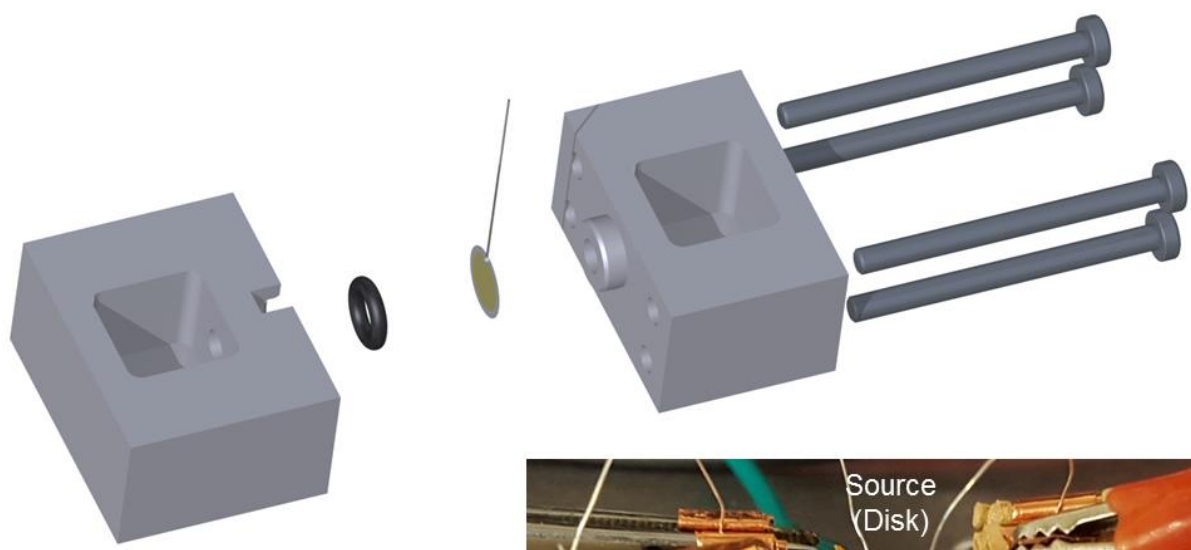
Supplementary Figure 10. Controlled Ion transport experimental setup. Suspended PPy(DBS) on PCTE as the septum in a bicameral device. The PPy(DBS) is attached as the disk working electrode, and Ag/AgCl pellets attached as the ring working and counter/reference electrodes to a bipotentiostat. Schematic of applied potentials and resulting currents.

Supplementary Note 1. Membrane preparation and experimental characterization. A polycarbonate track-etched (PCTE) membrane (Isopore – EMD Millipore) with 600 nm diameter pores and a 50nm sputtered gold layer is used as the substrate for electropolymerization of PPy(DBS). This substrate, as well as a gold foil strip and an Ag/AgCl pellet (World Precision Instruments), are connected as the working, counter, and reference electrodes, respectively, to a Potentiostat (PARSTAT 4000) and submerged in an aqueous solution of 100mM sodium dodecylbenzenesulfonate (NaDBS) and 200mM pyrrole (Sigma Aldrich). Chronoamperometry (CA) is performed with a 0.42 V constant potential applied to the cell to monitor the electropolymerization current and charge over time until the desired polymer areal density is reached.

The newly formed polymer is subsequently rinsed with DI water, dried with nitrogen gas, and submerged as the working electrode in an aqueous solution of desired ion type and concentration, along with an Ag/AgCl pellet as the counter/reference electrode. The polymer is conditioned by application of a cyclic voltammetry (CV) function to induce redox reactions, cycling between -1.3 and 0.5V at a scan rate of 50 mV/s, in which distinct reduction and oxidation current peaks are visible. This function is continued until the same number of ions (monitored by charge) ingress/egress the polymer for each cycle. At this point, typically after about 20 cycles, the polymer is considered to be fully conditioned and in equilibrium.

To assess transmembrane ionic flow of a smart membrane separator, a bicameral device was designed and manufactured to allow for use and electrical connection of the membrane as the septum. Both chambers are filled with aqueous solution and an Ag/AgCl pellet is submerged in each chamber. The membrane and two pellets are electrically connected to a bipotentiostat as the disk working, ring working, and counter/reference electrodes, respectively, for application of the membrane and transmembrane potentials. See Supplementary Fig. 10 for an exploded view, cross-sectional schematic, and final assembly demonstrating the electrode setup and the active membrane separated chamber assembly.

Supplementary Note 2. Bipotentiostat correction to calculate transmembrane current. A potential V_M between 0 V and -1.1 V is applied to the membrane with respect to the RE/CE electrode at potential V_C to either oxidize or reduce the polymer, respectively. A potential V_A in the form of a square wave is applied to the WE/S electrode also with respect to the RE/CE electrode, resulting in an overall transmembrane potential V_{AC}. The resulting currents at the membrane (I_M) and the WE/S electrode (I_{AC}) are subsequently measured. These currents are a direct result of the motion of ions into and across the membrane. An example of this data is shown in Supplementary Figure 3.

There also exists an interplay between the membrane and transmembrane currents. Upon investigation of the internal circuitry of the bipotentiostat, the potential difference between V_A and V_M allows a double-layer of ions to build up on the electrode or membrane within a single chamber. This manifests as an interplay current between the WE/S electrode and the membrane, denoted by I_{MA}. In order to get accurate measurements of the transmembrane current, this interplay current must be removed from the signal.

To remove the interplay current I_{MA}, it must first be determined. The measured current I_{AC} contains the transmembrane and interplay currents at all times, and since the transmembrane current is the unknown variable desired to determine, the interplay current cannot be resolved from the measured I_{AC}. The measured current I_M contains the redox current of the membrane and the interplay currents. During transients of the membrane redox state, the redox current is not known and therefore the interplay current cannot be determined. However, once the redox event has terminated and the membrane is in a steady-state condition, the redox current diminished to zero. It is therefore known that the measured current I_M at steady-state redox conditions is equal to the interplay current I_{MA}.

$$I_M^{SS} = I_{MA}$$

With the interplay current known in steady-state redox conditions, the true transmembrane current can now be determine in these same conditions. Since the interplay current at the membrane will be equal to and opposite of the interplay current at the WE/S electrode, the principle of superposition can be used to remove it from the measured I_{AC}. The corrected transmembrane currents is then equated by

$$I_{AC}^C = I_{AC}^M + I_M^{SS}$$

And shown in Supplementary Figure 4. From this it can be seen that the steady-state transmembrane current is close to zero in the oxidized membrane state and is a non-zero square wave in the reduced membrane state, following closely to the square wave potential V_{AC} being applied.

Supplementary Note 3. Demonstration in an application – LED experiment. The membrane is placed as the septum in a bicameral device, of which both chambers are filled with a 500mM LiCl aqueous solution. The only path between the two chambers is through the polymer membrane. With the polymer as the working electrode, an Ag/AgCl pellet is submerged in the chamber in which the polymer side of the membrane is exposed as the counter/reference electrode.

An electrical/ionic circuit is created with two AA batteries and an LED bulb. The circuit is run through the ionic solution, such that the negative lead and positive lead are attached to separate Ag/AgCl pellets. The negative lead Ag/AgCl pellet is submerged in the chamber with the polymer side of the membrane exposed, and positive in the chamber with the backside of the membrane exposed. The circuit functions such that if ions are able to travel across the membrane, the circuit is closed and the AA batteries should light up the LED bulb, and if ions are unable to travel across the membrane, the circuit is open and the LED will not light up.

With this circuit in place, the following potentiostatic functions are applied to the polymer membrane:

- CA square wave at -1 and 0.5 V and 40 second cycle time (25 mHz)
- CA square wave at -1.3 and 0.6 V and 6 second cycle time (167 mHz)
- CA square wave at -1.3 and 0.6 V and 1 second cycle time (1 Hz)
- CA square wave at -1.3 and 0.6 V and 0.2 second cycle time (5 Hz)
- CV between -1 and 0.7 V and 0.3 V/s scan rate