Electronic Supplementary Information

"Voltage-Controlled Current Loops with Nanofluidic Diodes Electrically Coupled to Solid State Capacitors"

ADDITIONAL EXPERIMENTAL DATA

Figure S1 shows a typical FESEM image of the polyimide membrane surface corresponding to the cone large opening (base).The pore density of the samples used in the experiments is of the order of 10^4 cm^{-2}.

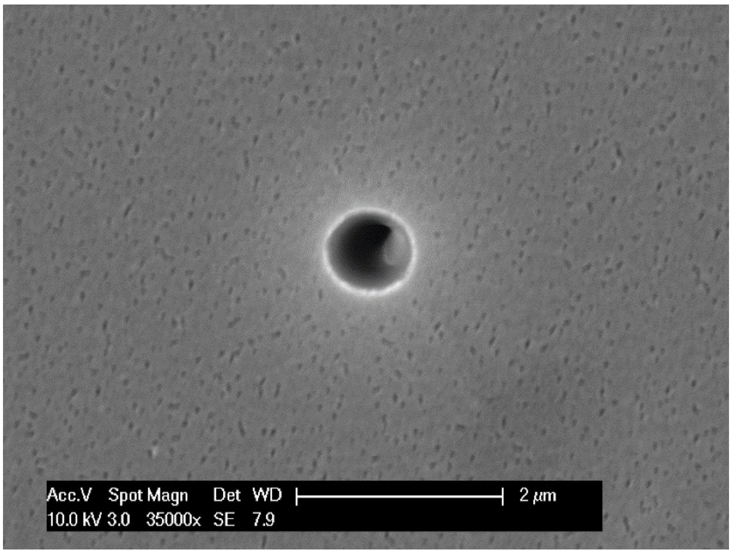

Figure S1

In order to characterise the multipore membranes used in the experiments, the individual current-voltage (*I*–*V*) curves in 0.1 M KCl were measured several times. Figures S2 and S3 show the steady-state *I*–*V* curves of the membranes 1 and 2 used in the half-wave multiplier of Figure 1a. The measurements were conducted within a two month period using different cells and electrodes and showed a good reproducibility.

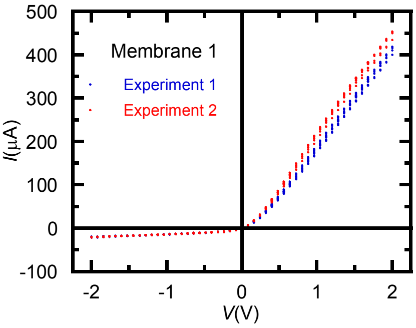

Figure S2

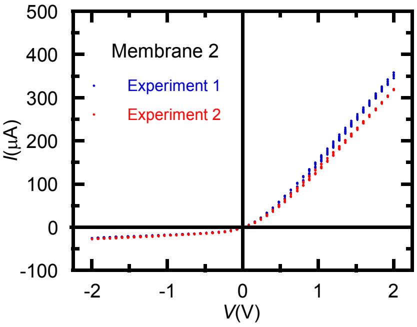

Figure S3

The two samples show similar rectification properties, with a high current state for $V > 0$ when the current enters the membrane pores through the pore tip, and a low current regime for $V < 0$ when the current enters the membrane pores through the pore base. It has been demonstrated extensively that the negatively charged carboxylate residues on the conical pore walls lead to an asymmetric electric potential which is responsible for the electrical rectification observed. The effect of this surface charge can be checked further in the experiments of Figure S4.

Figure S4 shows the I–V curve of membrane 1 in 0.1 M KCl (pH = 7) and 0.1 M HCl solutions. At low pH values, however, the protonation of the carboxylate groups changes the sign of the fixed charges and reverses the rectification properties (Figure S4). The high current values observed for the 0.1 M HCl solution case are due to the high mobility of protons, and possible adsorption of protons to the pore walls.

Membrane transport properties can also be probed by means of reversal potential, V_{rev}, measurements. This potential difference is established when a membrane is in contact with a salt concentration gradient. Reversal potential is a measure of membrane selectivity; for KCl at room temperature and 10 fold concentration gradient, it is equal to 58 mV when the membrane transports only one type of ions, and approaches zero when the membrane is not selective. Values between 58 mV and zero indicate partial selectivity. Figure S5 shows the reversal potential of membrane 1 for the two multipore membrane positions indicated where c_L (left) and c_R (right) are the KCl concentrations of the two chambers separated by the membrane. All measurements were performed at pH = 7 in this case. The results of Figure S5 confirm the cation selectivity of the membranes and reveal that the magnitude of reversal potential depends strongly on the direction of the applied salt gradient. In addition, V_{rev} decreases when the concentration of the electrolyte facing the pore tip is relatively high compared to the concentration of fixed charge groups.

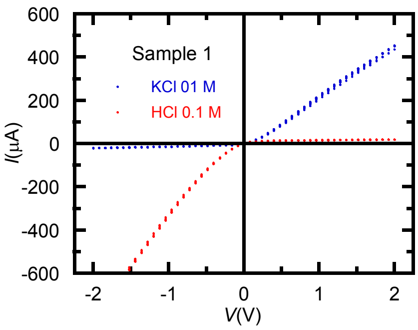

Figure S4

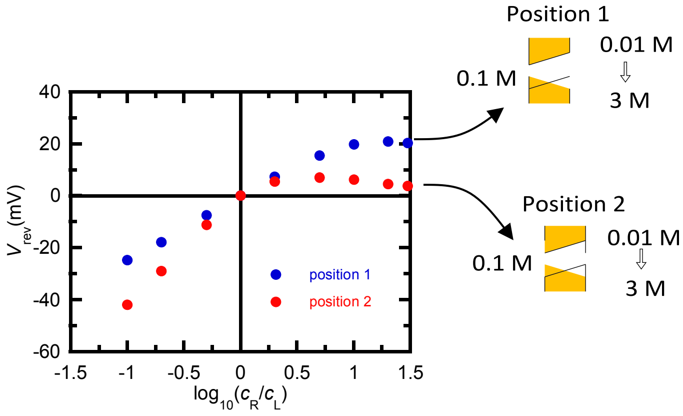

Figure S5

REPRODUCIBILITY OF THE EXPERIMENTAL VOLTAGE-CONTROLLED CURRENT LOOPS

Irradiated polymer membranes can be stable over years and nanoporous membranes are functional after etching (at least) over weeks. In order to check further both the stability of the nanofluidic diodes electrically coupled to the capacitors and the reproducibility of the voltage-controlled current loops in Figures 1e and 1f, the experiments were conducted several times. Figures S6–S8 show the transient voltage-controlled current loops for $V_0 = 2$ V. In experiment 1 (Figure S6), the capacitors were initially charged while in experiments 2 and 3 (Figures S7 and S8), the initial charge of the two capacitors was set to zero.

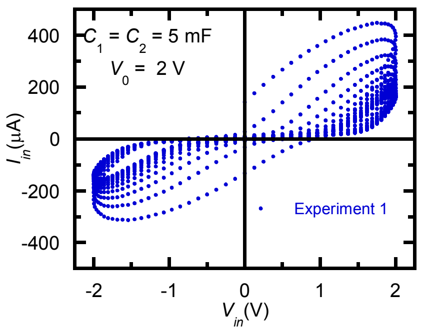

Figure S6

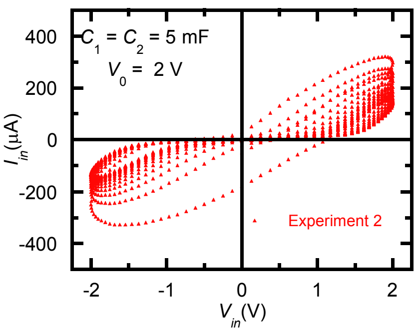

Figure S7

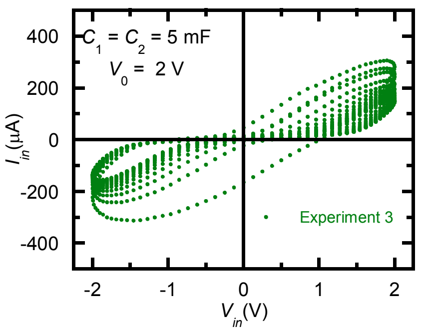

Figure S8

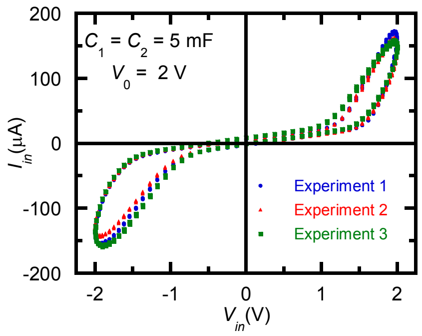

Figure S9

Finally, Figure S9 shows the steady-state voltage-controlled current loops for the three experiments above. The measurements were conducted within a two month period using different cells and electrodes showed a good reproducibility.

EQUIVALENT CIRCUIT EQUATIONS

The equivalent circuit of Figure 1b can be described in terms of the following equations:

$$V_{\text{in}} = \frac{q_1}{C_1} - V_1(-I_1)\,, \tag{1}$$

$$V_{\text{in}} = \frac{q_1}{C_1} + V_2(I_2) + \frac{q_2}{C_2}\,, \tag{2}$$

$$I_{\text{in}} = \frac{dq_1}{dt}\,, \tag{3}$$

$$I_2 = \frac{dq_2}{dt}\,, \tag{4}$$

$$I_{\text{in}} = I_1 + I_2\,. \tag{5}$$

In Eqs. (1)-(5), q_1 and q_2 are the charges on the plates of the capacitors C_1 and C_2, respectively, and V_1 $(-I_1)$ and $V_2(I_2)$ are the current-dependent voltage drops across the respective nanofluidic diodes. These voltages are obtained from the experimental I–V curves of the membrane samples in Figures S2 and S3. The model results of Figures 2b and 6b have been obtained by integrating Eqs. (1)–(5) with the boundary conditions q_1 $(0) = q_2(0) = 0$ and allowing the system to reach the steady state.