

## Supporting Information

### Nanoporous Membranes with Electrochemically Switchable, Chemically Stabilized Ionic Selectivity

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All reference numbers refer to references cited in the manuscript itself.

**Synthesis of 1:** 4-nitrophenyl diazonium tetrafluoroborate:

4-nitrophenyl diazonium tetrafluoroborate was obtained from Sigma-Aldrich and recrystallized from water before its use.  $^1\text{H}$  NMR 500 MHz,  $(\text{CD}_3)_2\text{SO}$ :  $\delta$  8.92 (d,  $J = 9.3$  Hz, 2H), 8.71 (d,  $J = 9.3$  Hz, 2H).

**Synthesis of 2:** 4-(1-(2,5-dimethoxybenzyl)-1*H*-1,2,3-triazol-4-yl)benzenediazonium tetrafluoroborate:

**2-(bromomethyl)-1,4-dimethoxybenzene**

The product was synthesized according to the procedure in Ref 27.

**2-(azidomethyl)-1,4-dimethoxybenzene**

A small flask was charged with 1.0 gram of 2-(bromomethyl)-1,4-dimethoxybenzene (5.17 mmoles) and 10 mL of dry DMF. To this solution was added 1 gram of sodium azide (15.4 mmoles) and the solution was stirred at room temperature for 2 hours. The solution was diluted with 50 mL of water and was extracted 2 x 25 mL of ethyl acetate and dried over magnesium sulfate. Filtration and subsequent rotary evaporation yielded the azide in near quantitative yield. <sup>1</sup>H NMR 500 MHz, CDCl<sub>3</sub>: δ 6.82 (s, 3H), 4.31 (s, 2H), 3.80 (s, 3H), 3.95 (s, 3H).

**4-(1-(2,5-dimethoxybenzyl)-1*H*-1,2,3-triazol-4-yl)aniline**

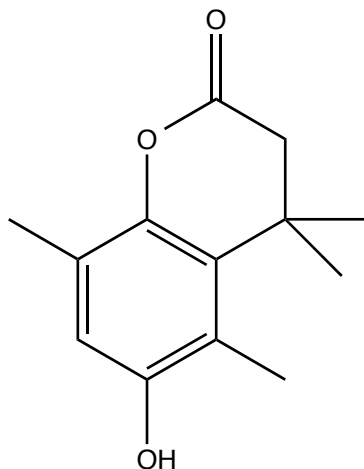
A small flask was charged with 0.61g of para-ethynyl aniline (5.21 mmoles) and 2-(azidomethyl)-1,4-dimethoxybenzene 1.0 g (5.2 moles) and 0.12 grams of tris(triphenylphosphine)copper (I) bromide 129 μmoles and 4 mL of dry DMSO. The solution was magnetically stirred 24 hours. Aqueous workup followed by column chromatography (2:1 ethyl acetate/hexane R<sub>f</sub> 0.3) followed by recrystallization from benzene yielded 0.76 grams of product (2.50 mmoles 50%).<sup>27</sup> <sup>1</sup>H NMR 500 MHz (CD<sub>3</sub>)<sub>2</sub>SO: δ 8.61 (s, 1H), 7.46 (pseudo d, 2H), 6.97 (m, 1H), 6.89 (m, 1H), 6.71 (d, 1H), 6.57 (pseudo d, 2H), 5.64 (s, 2H), 3.76 (s, 3H), 3.66 (s, 3H). MS: m/z calc. 311.15 (C<sub>17</sub>H<sub>19</sub>N<sub>4</sub>O<sub>2</sub><sup>+</sup>), found 311.11.

**4-(1-(2,5-dimethoxybenzyl)-1*H*-1,2,3-triazol-4-yl)benzenediazonium**

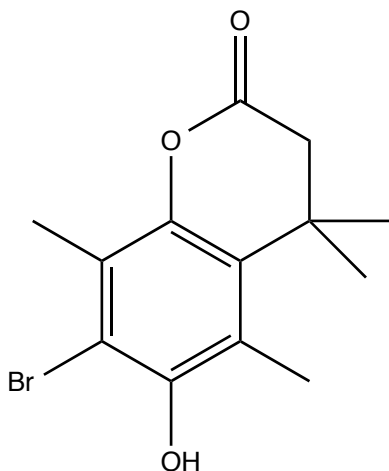
**tetrafluoroborate.** A small flask was charged with 75 mg of 4-(1-(2,5-dimethoxybenzyl)-1*H*-1,2,3-triazol-4-yl)aniline, 2 mL of ethanol, and 0.25 mL of 48% tetrafluoroboric acid and the solution was cooled to 0 °C. To the solution was added 0.25 mL of t-butyl nitrite. A precipitate formed after 30 minutes. To the suspension was added 5 mL of cold diethyl ether. The solids were collected by filtration, washed with additional ether, and dried under vacuum. <sup>1</sup>H NMR 500 MHz (CD<sub>3</sub>)<sub>2</sub>SO: δ 8.9 (s, 1H), 8.68 (pseudo d, 2H), 8.41 (pseudo d, 2H), 6.9-7.0 (m, 3H), 5.60 (s, 2H), 3.75 (s, 3H), 3.69 (s, 3H). MS: m/z calc. 294.12 (C<sub>17</sub>H<sub>16</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup>), found 294.09 (N<sub>2</sub> leaves phenyl radical).

### Synthesis of 3, “trimethyl lock,”

4-(6-methoxy-4,4,5,8-tetramethyl-2-oxochroman-7-yl)benzenediazonium tetrafluoroborate:

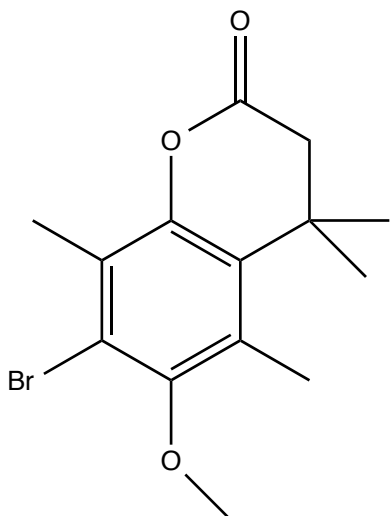


**6-hydroxy-4,4,5,8-tetramethylchroman-2-one** was synthesized according to reference 29.



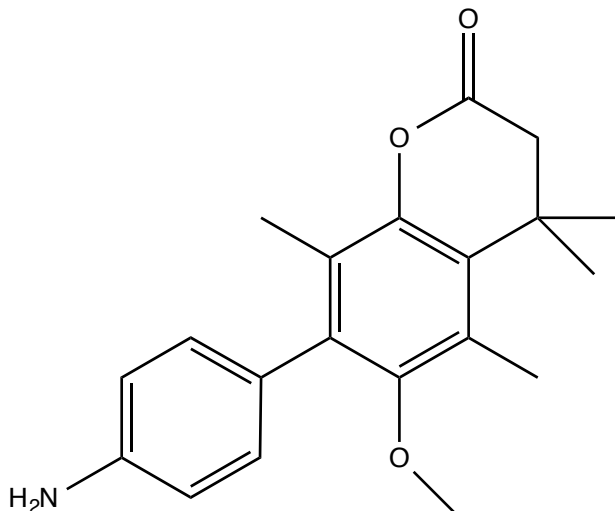
**7-bromo-6-hydroxy-4,4,5,8-tetramethylchroman-2-one** was synthesized by a variation of the preparation described in reference 33. Briefly, 1.62 grams of 6-hydroxy-4,4,5,8-tetramethylchroman-2-one (7.36 mmole) was dissolved in glacial acetic acid. Bromine, 2.59 grams (16.3 mmoles, 2.2 eq's) was dissolved in 5 mL of glacial acetic acid and slowly added to the lactone at room temperature. The mixture was stirred 12 hours then concentrated under vacuum to an oil which was then dissolved in 30 mL of methylene chloride and extracted with aqueous saturated sodium thiosulfate and then dried over magnesium sulfate. Filtration and rotary evaporation yielded 2.15 grams of crude product which was recrystallized from 1:1 hexane:methylene chloride. Presumably, the

initial product was the quinone (3-(4-bromo-2,5-dimethyl-3,6-dioxocyclohexa-1,4-dien-1-yl)-3-methylbutanoic acid) which upon reductive aqueous work up cyclized to the lactone.  $^1\text{H NMR}$  500 MHz  $\text{CDCl}_3$ :  $\delta$  5.60 (br, 1H), 2.53 (s 2H), 2.39 (s, 3H), 2.34 (s 3H), 1.43 (s, 6H).



**7-bromo-6-methoxy-4,4,5,8-tetramethylchroman-2-one**

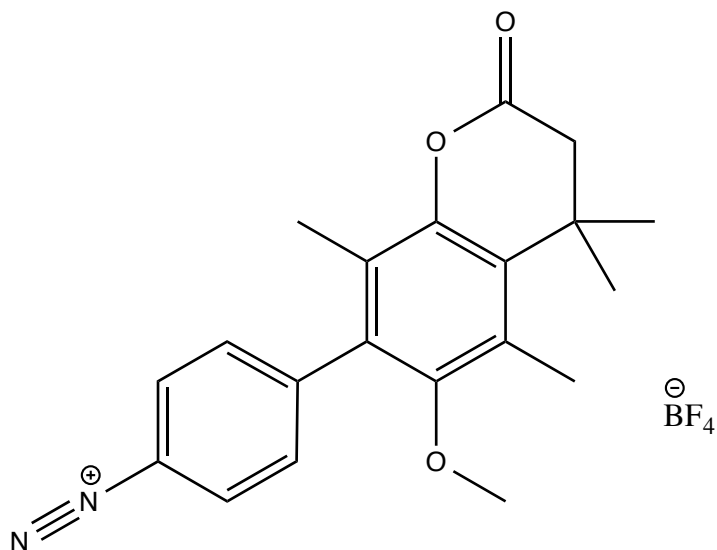
1.05 grams of 7-bromo-6-hydroxy-4,4,5,8-tetramethylchroman-2-one (3.36 mmoles) was dissolved in approximately 20 mL of acetone and treated with a 20 fold excess of methyl iodide and 20 equivalents of potassium carbonate and catalytic 18-C-6. The reaction mixture was refluxed overnight and provided the product in quantitative yield after aqueous work up using ethyl acetate.  $^1\text{H NMR}$  500 MHz  $\text{CDCl}_3$ :  $\delta$  3.73 (s, 3H), 2.55 (s, 2H), 2.42 (s, 3H), 2.37 (s, 3H), 1.45 (s, 6H).



### 7-(4-aminophenyl)-6-methoxy-4,4,5,8-tetramethylchroman-2-one

A Schlenk flask was charged with 1.01 g of 7-bromo-6-methoxy-4,4,5,8-tetramethylchroman-2-one (3.19 mmol) and 1.00 grams of 4-aminophenylboronic acid pinacolate ester (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline) (4.57 mmol, 1.4 eq's) and 1.44 grams of potassium carbonate (10.4 mmol) and 0.25 grams of 18-C-6 (0.9 mmol). The flask was evacuated and back filled with argon. To the solids was added 10 mL of 1,4-dioxane, 10 mL of ethanol, 10 mL of water, and 10 mL of toluene. The solution was rapidly degassed. To the flask was rapidly added 136 mg of bis(diphenylphosphino)ferrocene palladium (II) chloride (0.2 mmol) and 0.50 mg of tetrakis(triphenylphosphine)palladium (0) (0.043 mmol) where upon the reaction mixture turned black. The solution was refluxed overnight after which time it was yellow. After cooling the reaction mixture was diluted with additional water and then extracted with ethyl acetate; drying over magnesium sulfate followed by filtration and concentration under vacuum provided a black solid. The solid was dissolved in 30 mL of benzene to which was added 20 mL of 1N HCl. The solids which were isolated by centrifugation were suspended in ethyl acetate to which was added 30 mL of 1 N NaOH. Extraction followed by drying and concentration provided a dark solid that by NMR was product and starting borate ester. The solids were dissolved in a minimum of methylene chloride and filtered through a flash plug of silica gel (1 inch) on a fritted glass funnel using 500 mL of methylene chloride. This provided 0.85 grams of colorless product contaminated with a trace of the starting borate ester which was removed by washing a methylene chloride solution of the product with 1 N NaOH. The product was recrystallized from ethyl acetate/hexane to provide 0.60 grams of crystals in the first crop followed by a second crop of 0.100 grams (2.2 mmol, 67%).

$^1\text{H NMR}$  500 MHz  $\text{C}_6\text{D}_6$ :  $\delta$  7.07 (pseudo d, 2H), 6.48 (pseudo d, 2H), 3.15 (s, 3H), 2.25 (s, 3H), 2.22 (s, 3H), 2.12 (s, 2H), 1.02 (s, 6H). MS: m/z calc. 326.18 ( $\text{C}_{20}\text{H}_{24}\text{NO}_3^+$ ), found 326.14.



**4-(6-methoxy-4,4,5,8-tetramethyl-2-oxochroman-7-yl)benzenediazonium tetrafluoroborate:**

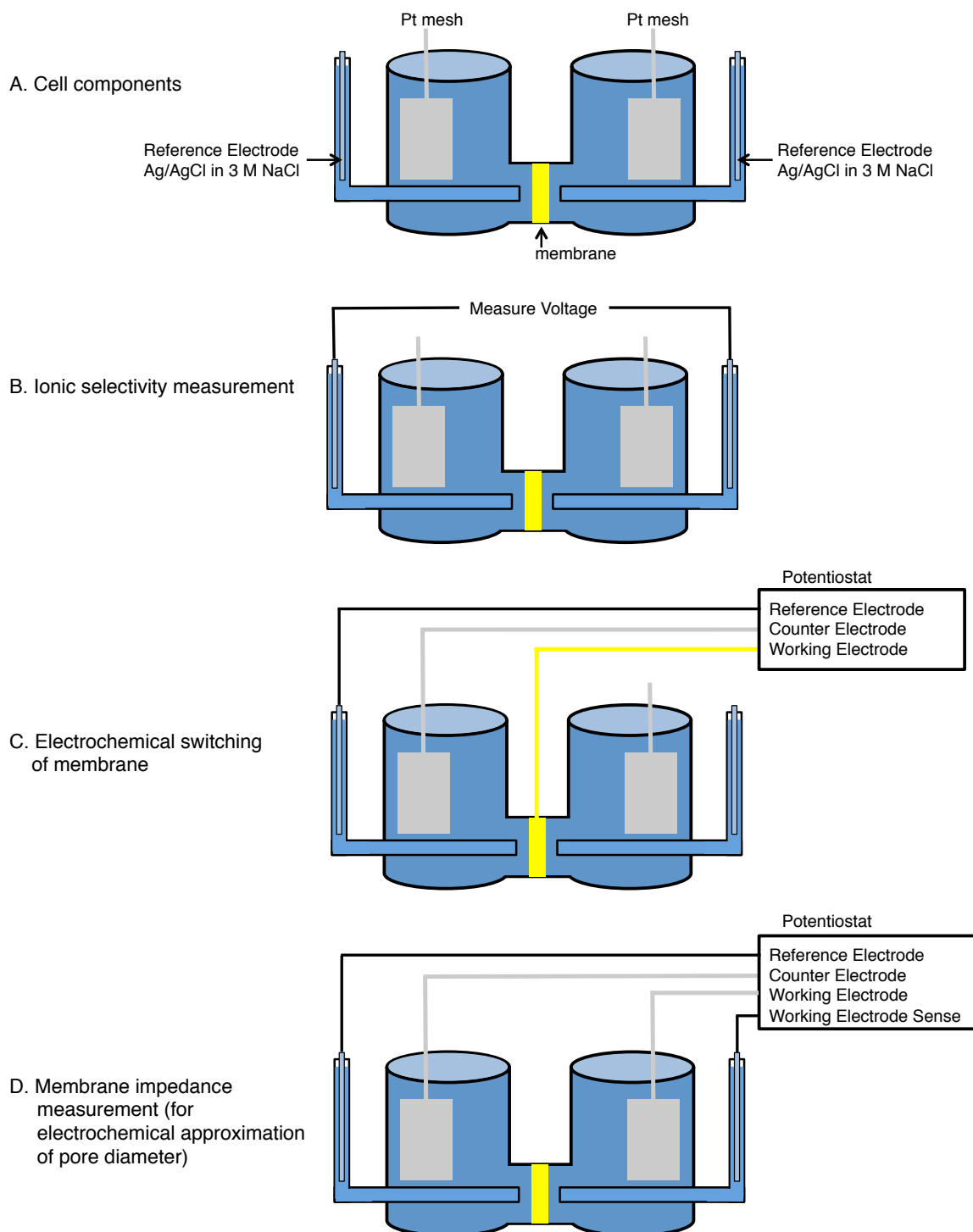
The starting aniline was diazotized by dissolving the aniline in ethanol followed by addition 3-5 fold excess of 48% tetrafluoroboric acid. This solution was cooled to 0 °C after which a 5 fold excess of t-butyl nitrite was added. Stirring at 0 °C for 30 minutes followed by addition of ethyl ether provided a solid which was collected by filtration washed with additional ether and dried and used without additional purification. MS: m/z calc. 309.15 (C<sub>20</sub>H<sub>21</sub>O<sub>3</sub><sup>+</sup>), found 309.11 (N<sub>2</sub> leaves phenyl radical).

## Electroless Gold Plating of Polycarbonate Membranes

After the nanopores were shaped, the membranes were subjected to UV-ozone cleaning for 10 minutes per side. Immediately thereafter, they were rinsed in methanol, then water. Membranes were sonicated for 5 minutes in a solution of 0.03 M  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (Aldrich,  $\geq 98\%$ ) and 0.07 M trifluoroacetic acid (Aldrich,  $\geq 99\%$ ) in 1:1, by volume, methanol-water. Subsequent rinsing in water was followed by ultrasonic agitation for 5 minutes in 0.03 M ammoniacal silver nitrate ( $\text{AgNO}_3$  Aldrich, 99.995%;  $\text{NH}_4\text{OH}$ , Fisher 20%). The pretreated membranes were then placed for 2 hours in an aqueous solution of 40:1 diluted (by volume) gold plating solution (Oromerse Part B, Technic Inc., Cranston, RI), 0.625 M formaldehyde (Aldrich, 37 wt% in water), and 0.127 M  $\text{Na}_2\text{SO}_3$  (Aldrich,  $\geq 98\%$ ) prechilled to 3 °C. To prevent cross-contamination, each membrane was placed in freshly cleaned glassware with fresh solutions for each step of this process.



## Electrochemical Test Cell Setup

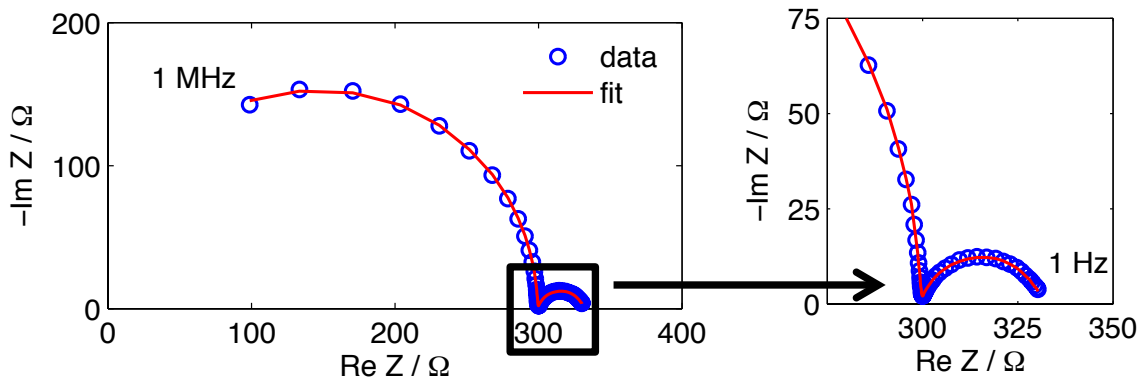


**Figure S1:** Schematic of the electrochemical cell used in this work. Membranes were sealed between two glass NW-15 vacuum flanges, and reference electrodes are contained in Luggin probes 1 cm from the membrane face.

## Electrochemical Method for Approximating Nanopore Diameter

For dimensions where a statistically relevant sample size was not easily measured in SEM, the pore diameter was calculated by measuring the solution resistance in the pore via electrochemical impedance spectroscopy, following similar work in refs. 36-37. The membrane was placed in a U-shaped cell filled with 1 M or 0.1 M KCl. High surface area platinum mesh electrodes were placed on each side of the cell, acting as current source and sink. Ag/AgCl reference electrodes housed in Luggin probes were placed 1 cm from each side of the membrane. Using a Solartron Modulab system, the frequency was scanned over 1 MHz – 1 Hz, with 10 mV RMS AC voltage, and 0 V DC. The cell conductivity was calibrated at 1, 0.1, and 0.01 M aqueous KCl. Impedance data was fit with an equivalent circuit consisting of two parallel RC networks linked in series. The first RC network is associated with the bulk solution resistance and cell capacitance. The second RC network is related to the membrane solution resistance and capacitance. Using the software ZPlot (Scribner Associates, South Pines, NC), individual fitting errors were less than 2%, and overall fit, judged by  $\chi^2$ , was better than  $5 \times 10^{-4}$ .

Example data and the equivalent circuit are provided in Figure S2. Here two arcs are clearly seen in the impedance plane. Only the high frequency arc appears when the membrane is absent from the cell, confirming that the high frequency response is attributed to the bulk solution, while the lower frequency response is due to the membrane.



**Figure S2:** Typical impedance response of gold-plated nanoporous membrane in aqueous 0.1 M KCl.

To calculate the nanopore radius, the following equations were employed. The resistance,  $R$ , of a cylindrically-shaped material may be written:

$$R = \frac{\rho l}{\pi r^2}$$

Where  $\rho$  is the bulk resistivity of the conductor,  $l$  is the cylinder length (membrane thickness), and  $r$  is the cylinder radius. Approximating a nanoporous membrane as an array with  $N$  cylinders in parallel, the total resistance of the membrane,  $R_m$  may be written:

$$R_m = \frac{\rho l}{N\pi r^2}$$

Similarly, the resistance of a membrane with conical nanopores may be written as follows<sup>8</sup>:

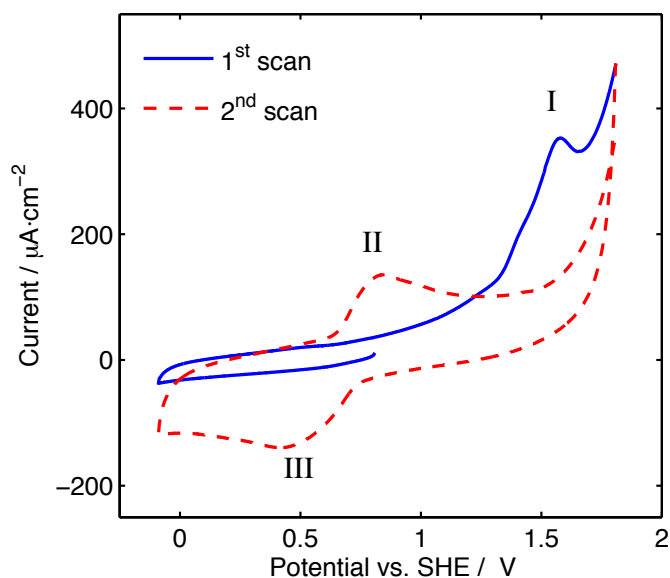
$$R_m = \frac{\rho l}{N\pi r_{tip} r_{base}}$$

The value  $R_m$  was extracted from the resistance of the low frequency arc in the impedance data.  $r$  was determined for membranes with cylindrical nanopores. For membranes with conical nanopores,  $r_{base}$  was determined via SEM, and  $r_{tip}$  was solved for. Membrane thickness, as measured in SEM, was 6  $\mu\text{m}$  for membranes with cylindrical nanopores, and 10  $\mu\text{m}$  for those with conical nanopores.

## Additional Cyclic Voltammograms (CVs) of **2**

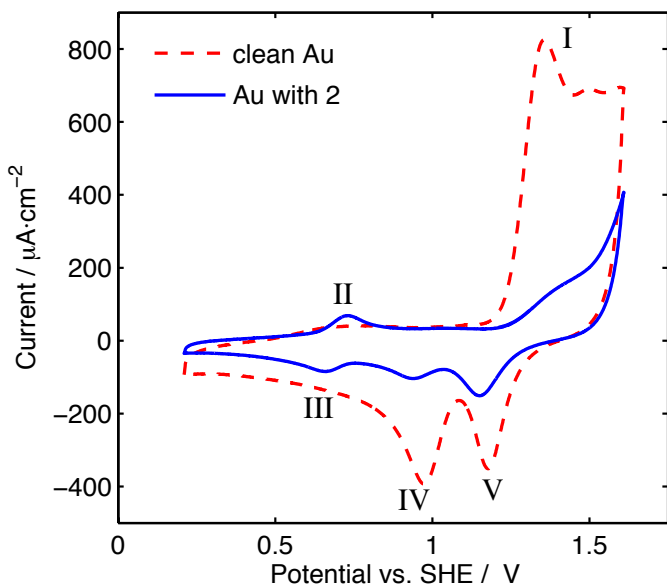
As shown in Figure S3, oxidation of the methoxy groups in **2 $\alpha$**  to form **2 $\beta$**  is readily seen at peak I on the first scan of CVs of **2** assembled onto glassy carbon. On the gold substrates of Figure 3B in the original text, the methoxy oxidation peak (peak I in Figure S3) is obscured by gold oxidation. Peaks II (**2 $\gamma$**   $\rightarrow$  **2 $\beta$** ) and III (**2 $\beta$**   $\rightarrow$  **2 $\gamma$** ) remain unchanged from a gold substrate.

Glassy carbon electrodes (MF-2070, BASi, West Lafayette, IN) were successively polished in 1.0  $\mu\text{m}$ , then 0.05  $\mu\text{m}$  alumina polish (Buehler) and sonicated in deionized water for 15 minutes before assembly of **2**.



**Figure S3:** CVs of a glassy carbon surface coated in **2**. Argon-deaerated 0.5 M  $\text{H}_2\text{SO}_4$ . 100 mV/s scan rate.

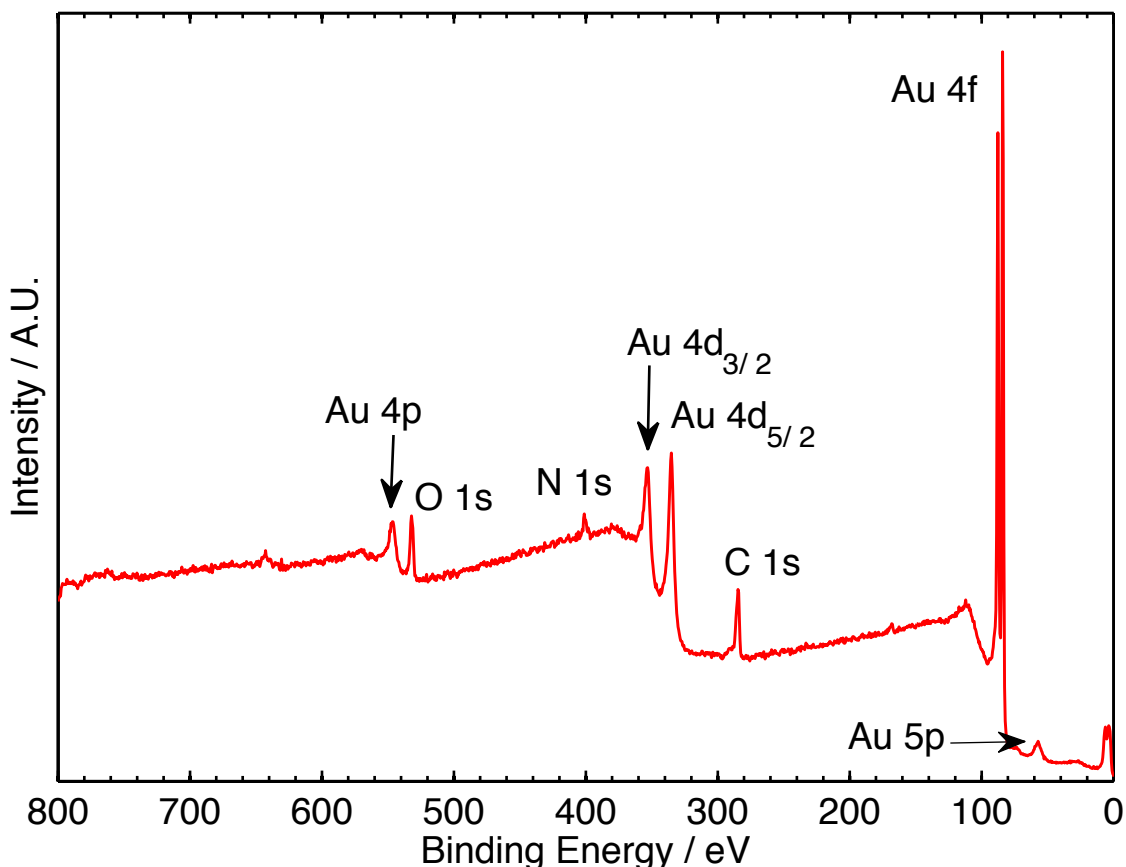
In Figure S4, the gold surface functionalized with **2** from Figure 3B is compared to a clean gold surface. Here it is seen that the gold oxidation peak I and corresponding reduction peaks IV and V are suppressed, consistent with passivation of the gold surface with  $2\alpha$ . Further, peaks II ( $2\gamma \rightarrow 2\beta$ ) and III ( $2\beta \rightarrow 2\gamma$ ) are not inherent to the gold substrate, but rather are a feature of **2**.



**Figure S4:** CVs of a clean gold surface (dotted red line) and a gold surface coated in **2** (solid blue line) in argon-deaerated 0.5 M  $\text{H}_2\text{SO}_4$ . 5<sup>th</sup> scan for each. 100 mV/s scan rate.

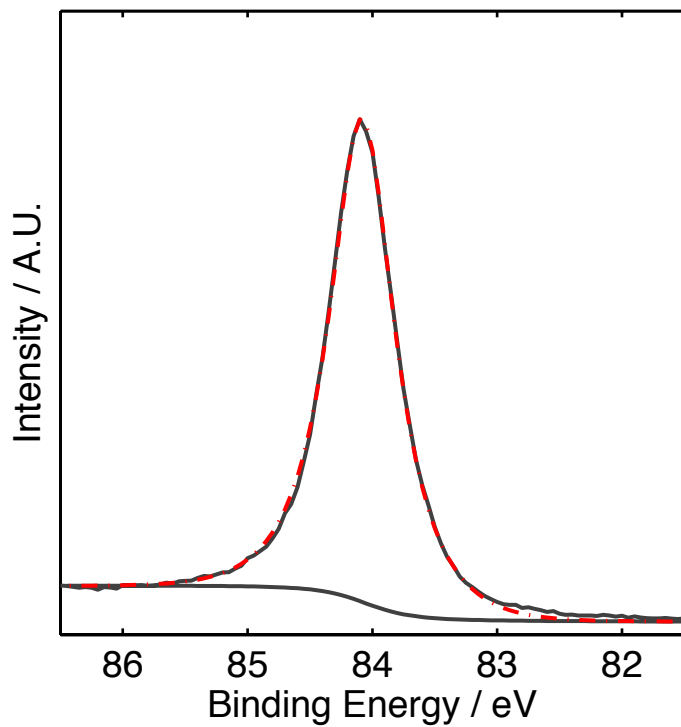
## Additional X-Ray Photoelectron Spectroscopy (XPS) Data

An XPS survey spectrum typical of the gold-coated glass slides functionalized with diazonium molecules used throughout this report is presented in Figure S5. Peaks characteristic of oxygen, nitrogen, and carbon, attributed to the diazonium molecules, are seen. Additionally, several peaks attributed to the gold thin film substrate are observed.



**Figure S5:** XPS survey spectrum typical of gold-coated glass slides functionalized with electrochemically switchable molecules used throughout this report.

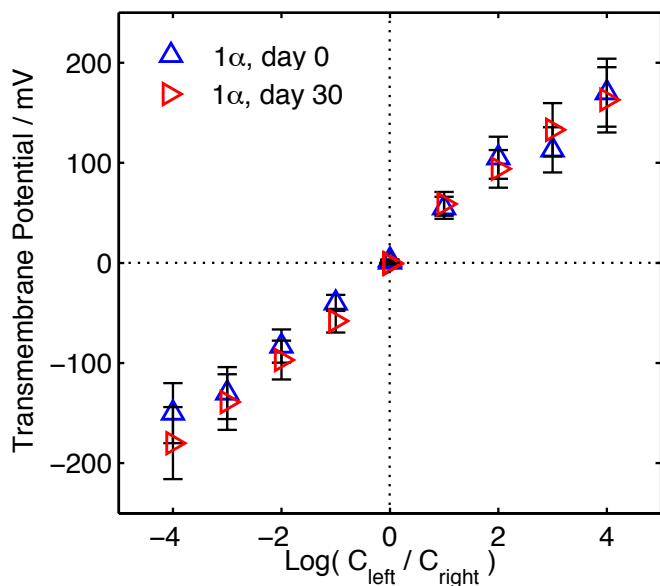
Closer examination of the gold  $4f_{7/2}$  peak, presented in Figure S6, reveals that all gold is in the metallic state, regardless of diazonium molecule or electrochemical treatment required to switch between states. The gold  $4f_{7/2}$  and  $4f_{5/2}$  peaks were well separated, with no overlap, allowing peak fitting to only the gold  $4f_{7/2}$  peak. Across all samples a single Gaussian-Lorentzian peak was observed at  $84.03 \pm 0.03$  eV (FWHM  $0.63 \pm 0.01$  eV), consistent with the binding energy of metallic gold readily found in standard XPS tables.



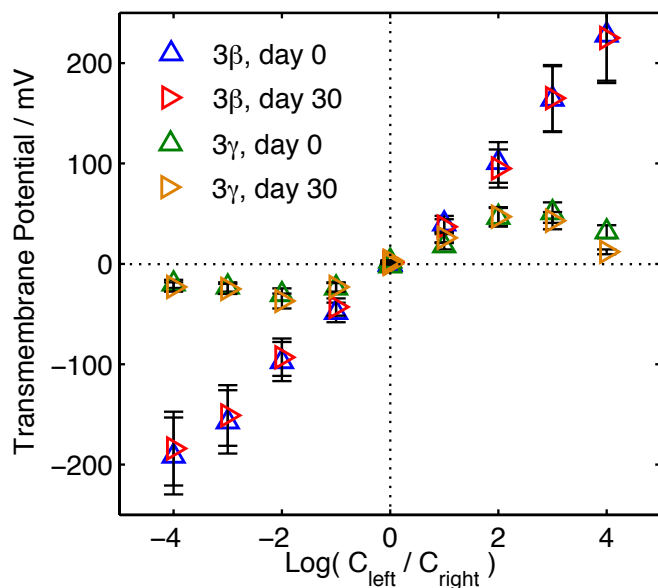
**Figure S6:** Au  $4f_{7/2}$  XPS spectrum (solid line) and peak fit (dashed red line) typical of gold-coated glass slides functionalized with the electrochemically switchable molecules used throughout this report.

## Ionic Selectivity Measurements after 0 and 30 Days

After 30 days of storage in 0.1 mM NaCl, the ionic selectivity of the membranes were statistically unchanged. In Figure S7 ionic selectivity measurements of  $1\alpha$  are shown after 0 and 30 days. In Figure S8 ionic selectivity measurements of  $3\beta$  and  $3\gamma$  are shown after 0 and 30 days.



**Figure S7:** Ionic selectivity measurements of  $1\alpha$  after 0 and 30 days.



**Figure S8:** Ionic selectivity measurements of  $3\beta$  and  $3\gamma$  after 0 and 30 days.