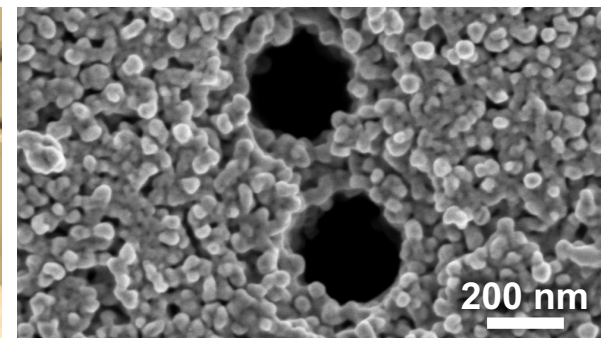
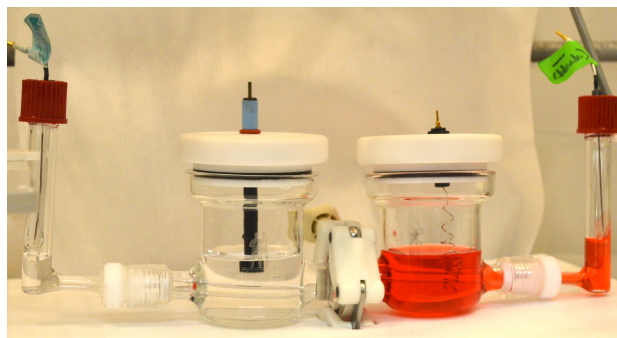
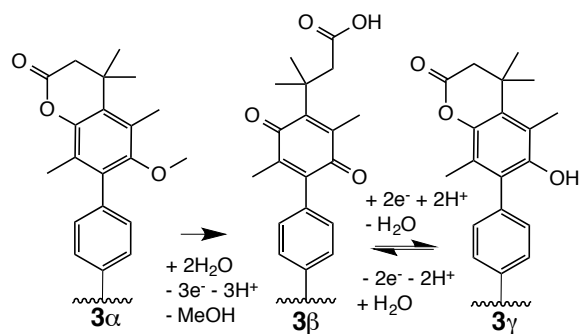


Exceptional service in the national interest



Diazonium Functionalized Nanoporous Membranes for Electrochemically Switchable Ionic Separations

Leo J. Small, David R. Wheeler, Erik D. Spoerke

MRS Spring 2017, Symposium SM7
19 April 2017

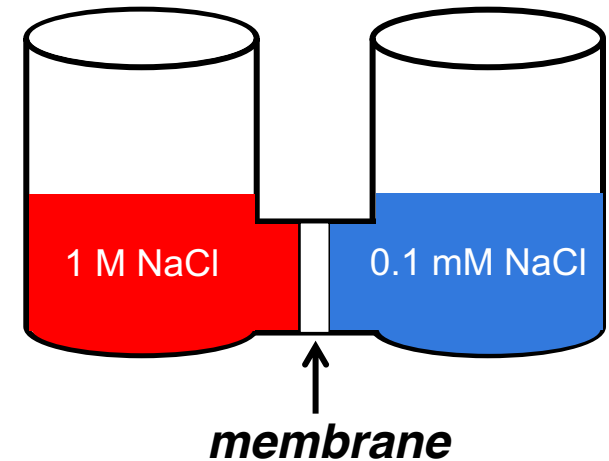
Motivation

Goal: Maintain an ionic gradient without external stimulus,
and ***release this gradient on demand via voltage pulse.***

- No constant voltage, light, chemical, etc. needed.
- Chemical separations, power sources, drug delivery

Strategy: Ionic diode with ***switchable ionic selectivity***

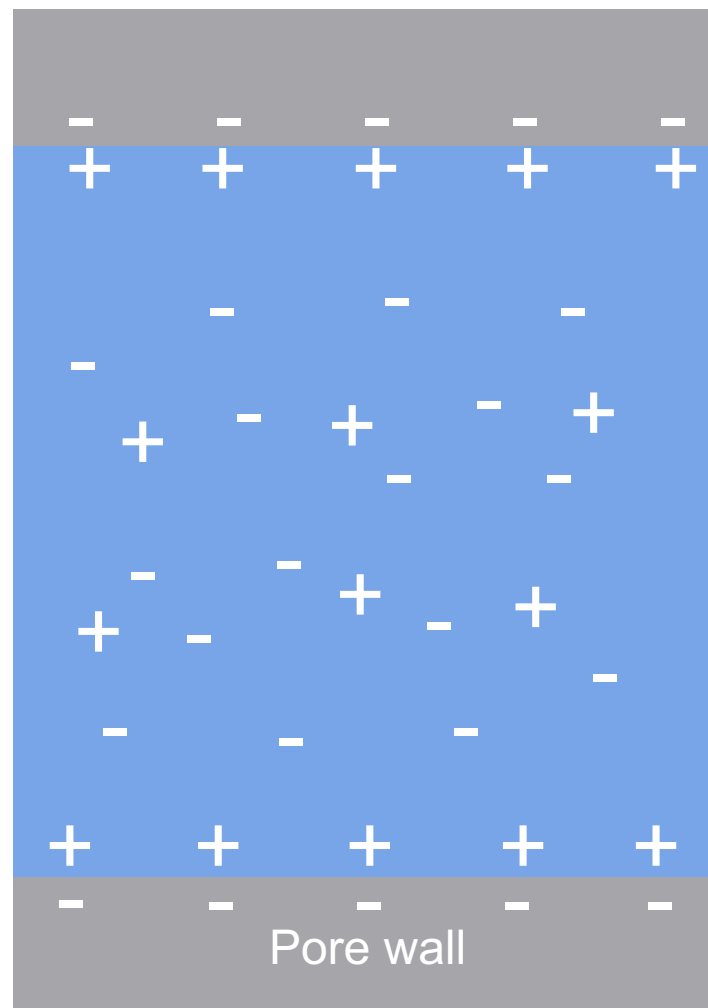
- Diode: charge moves in one direction
- Ionic selectivity: only 1 type of charge (+/-) can move
- ***Switch ionic selectivity to release ionic gradient***



***How can we create a membrane with stable,
switchable ionic selectivity?***

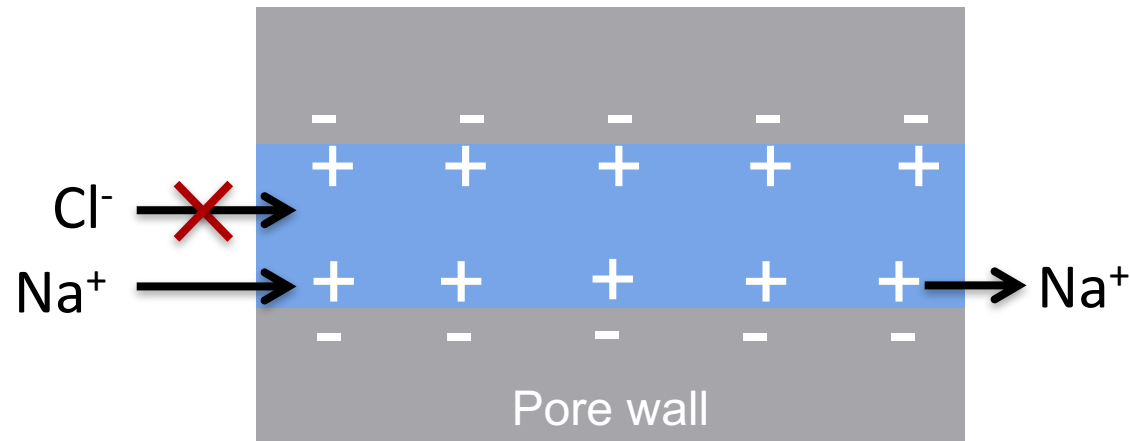
Ionic Selectivity in Nanopores

- Electrochemical double layer at the solid-liquid interface
 - pore diameter
 - wall surface charge



Ionic Selectivity in Nanopores

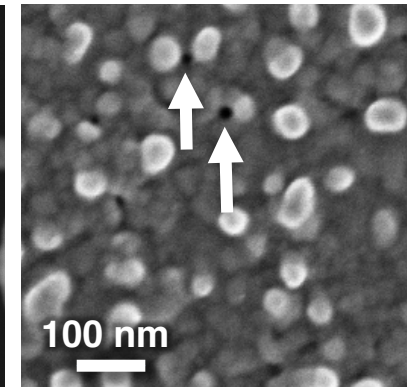
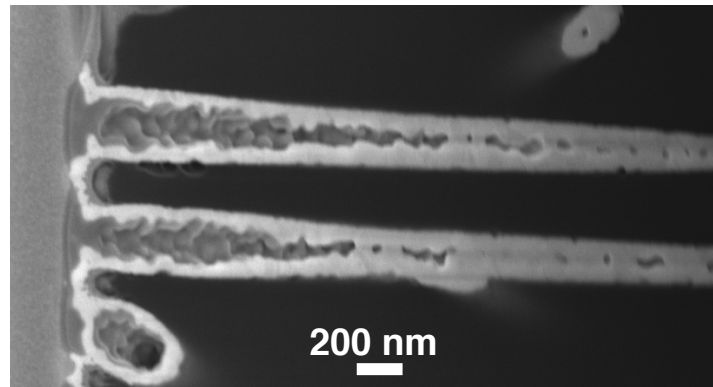
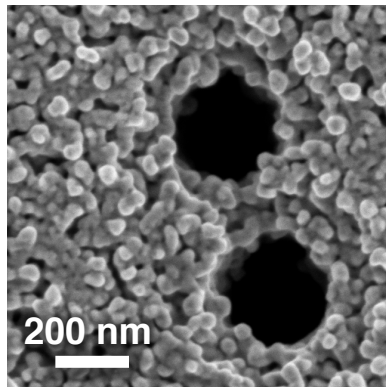
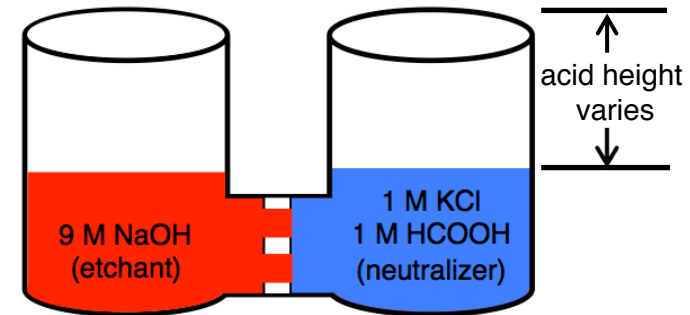
- Double layer size controls ion distribution in nanopore
 - ~ 10 nm @ 0.1 mM
 - < 1 nm @ 1 M



Overlapping double layers facilitate highly ion-selective transport.

Gold-Plated Polycarbonate Nanopores

- Polycarbonate films 5-10 μm thick ion-tracked by Sterlitech Corp.
- Chemically etch ion tracks under pressure¹
 - +300 Pa \rightarrow cones 275 nm x 3 nm
 - -20 Pa \rightarrow cylinders 42 \pm 6 nm
- Metallize with electroless gold^{2,3}
 - 6 nm diameter cylinders



Evaluating Ionic Selectivity

- Measure the voltage when the membrane separates different salt concentrations

$$V_m = 0.059 \cdot (t_+ - t_-) \cdot \log \frac{a_{right}}{a_{left}}$$

t_+ = cation transference number

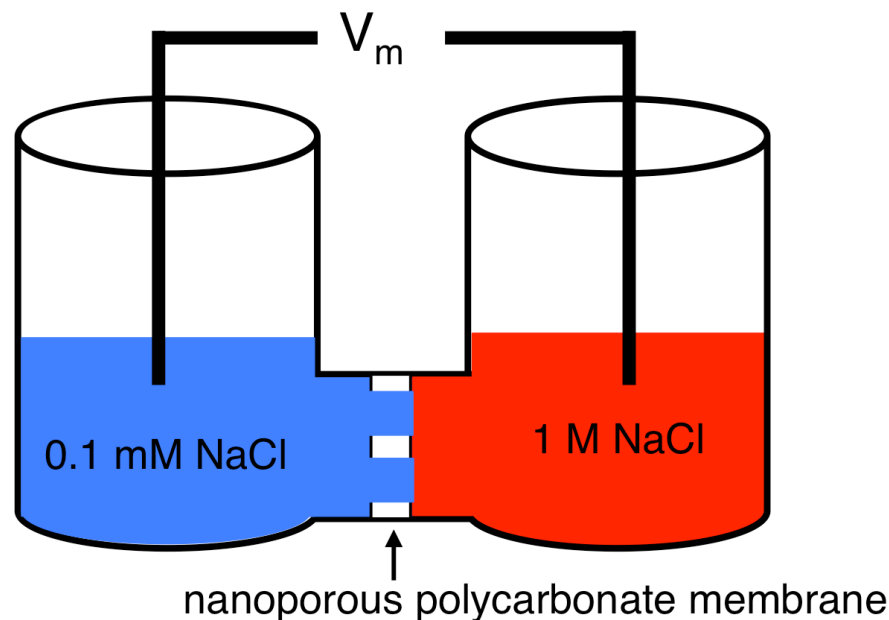
t_- = anion transference number

V_m , in Volts

25 °C

1:1 salt

Measured by Ag/AgCl wires



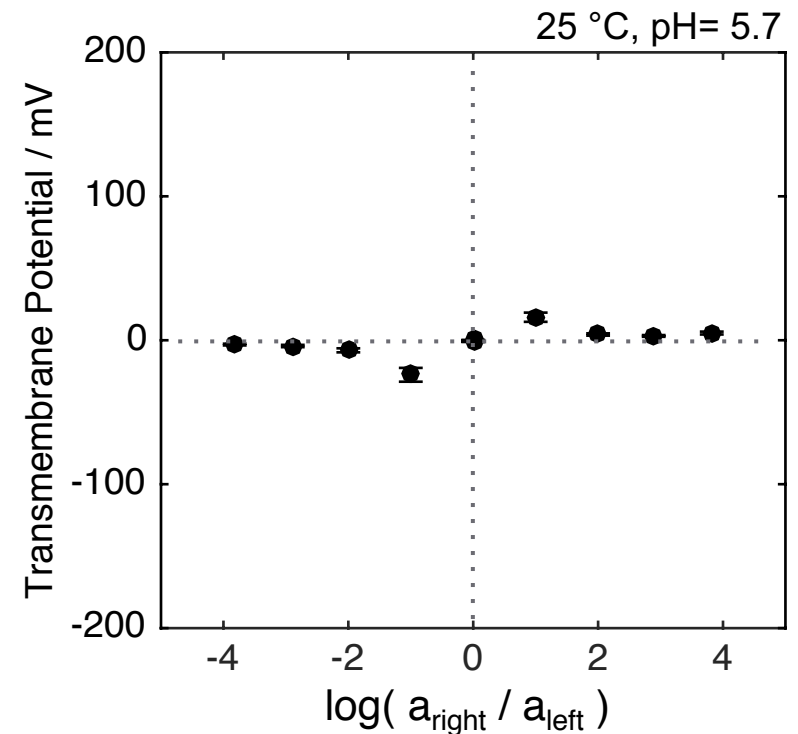
Ionic Selectivity of Nanoporous Polycarbonate

- Measure the voltage when the membrane separates different salt concentrations

$$V_m = 0.059 \cdot (t_+ - t_-) \cdot \log \frac{a_{right}}{a_{left}}$$

● polycarbonate $(t_+ - t_-)$
0.34

Larger slope = greater ionic selectivity



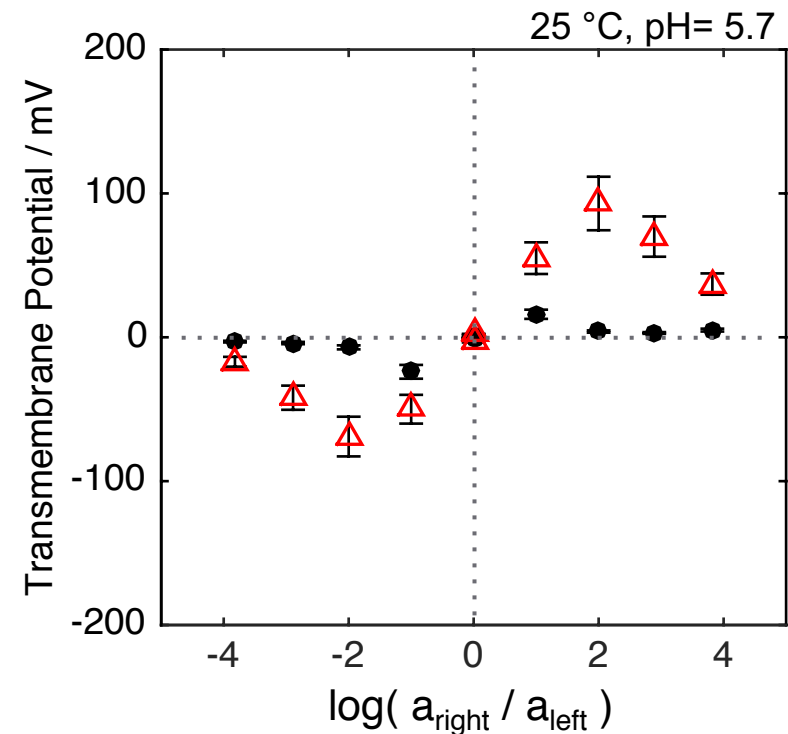
Gold Plating Increases Ionic Selectivity

- Measure the voltage when the membrane separates different salt concentrations

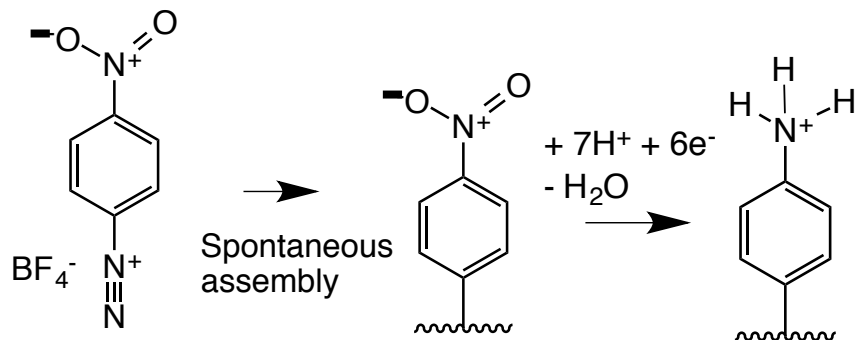
$$V_m = 0.059 \cdot (t_+ - t_-) \cdot \log \frac{a_{right}}{a_{left}}$$

	$(t_+ - t_-)$
● polycarbonate	0.34
△ gold-plated polycarbonate	0.73

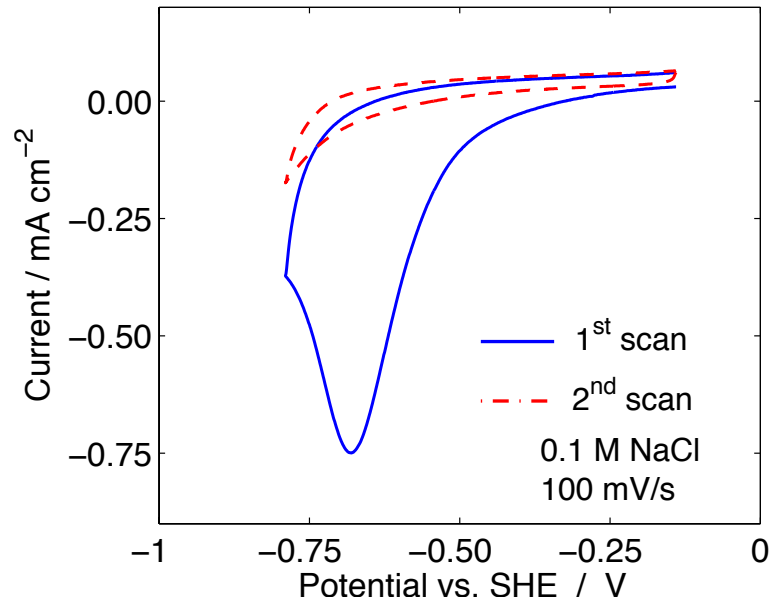
Smaller pore size and increase surface charge increase ionic selectivity.



Nitrophenyl Diazonium: Spontaneous Assembly and Irreversible Reduction



Irreversible electrochemical reduction via cyclic voltammetry



Surface	Contact Angle (°)
nitro	63
amine	47

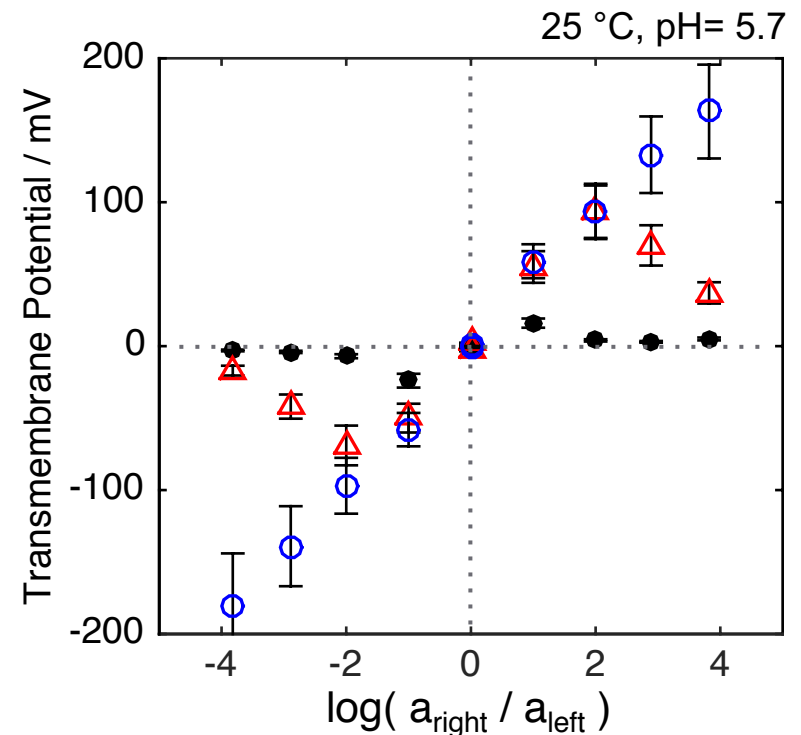
Two monolayers of nitrophenyl have spontaneously assembled onto electroless gold.

Nitrophenyl Surface Is Cation-Selective

- Measure the voltage when the membrane separates different salt concentrations

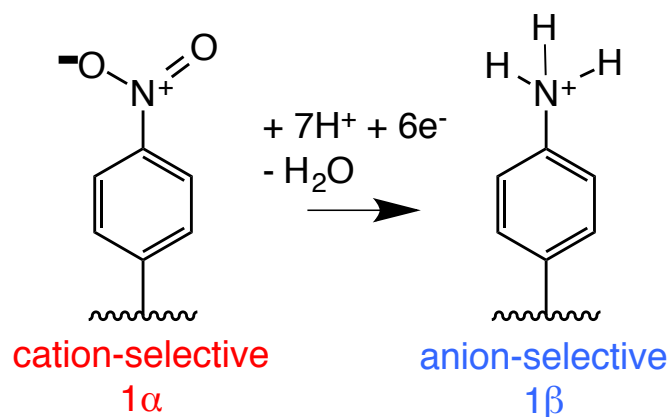
$$V_m = 0.059 \cdot (t_+ - t_-) \cdot \log \frac{a_{right}}{a_{left}}$$

	$(t_+ - t_-)$
● polycarbonate	0.34
△ gold-plated polycarbonate	0.73
○ nitrophenyl on gold	0.79

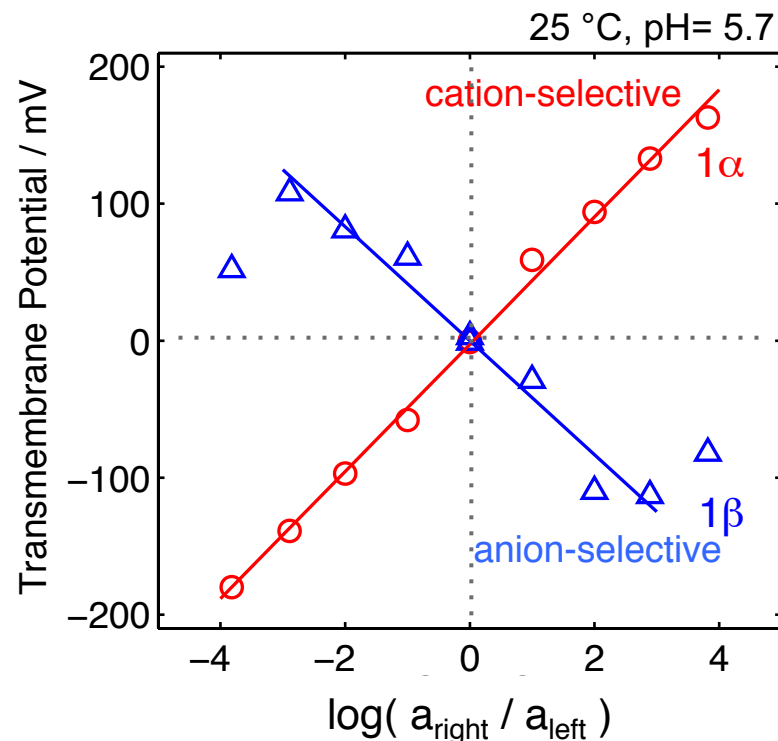


Ionic Selectivity Switches upon Reduction of Nitrophenyl to Aminophenyl

Irreversible electrochemical reduction



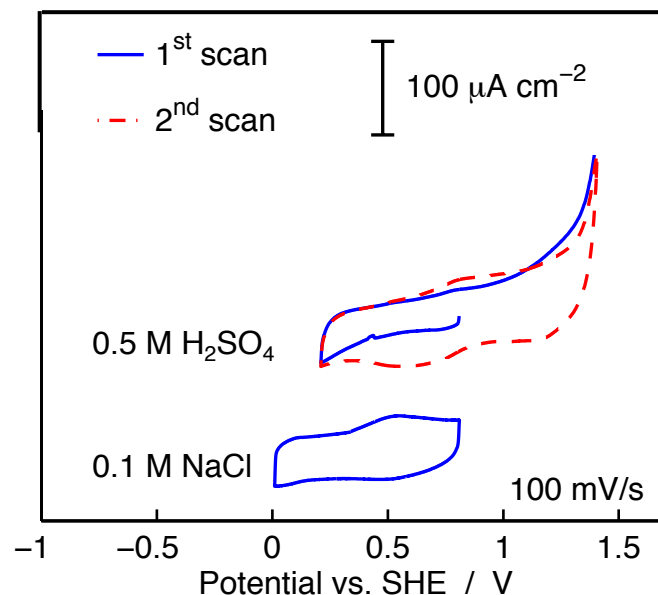
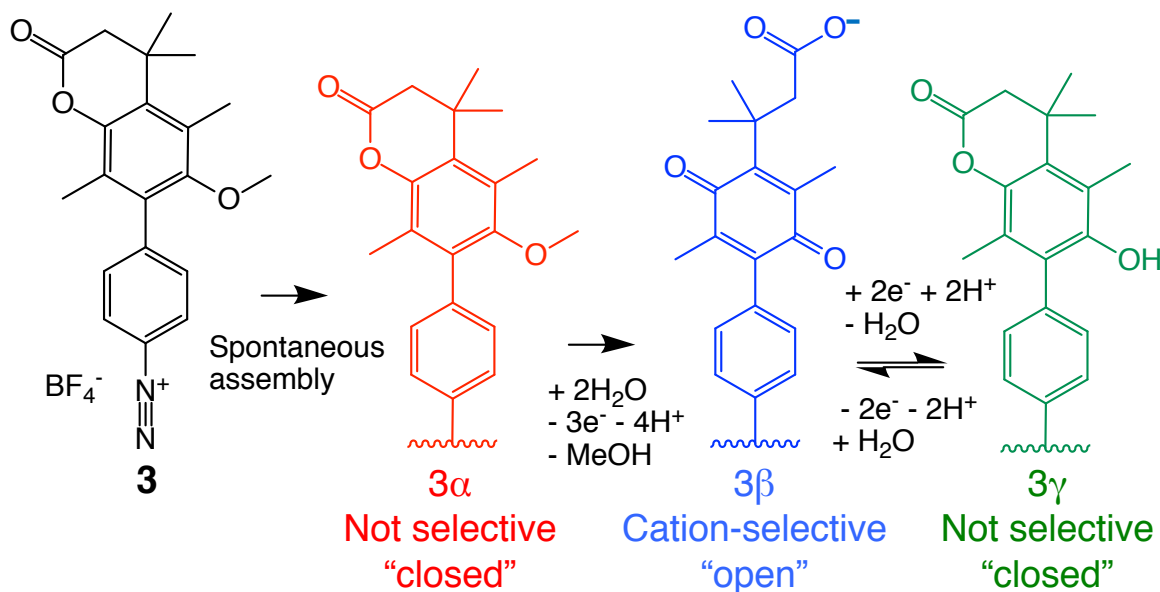
Reduction of nitrophenyl to aminophenyl enables transition from cation-selective to anion-selective membrane.



Surface	Slope
1α	+0.79
1β	-0.70

Trimethyl Lock: Hiding a Carboxylic Acid

Reversible electrochemical redox



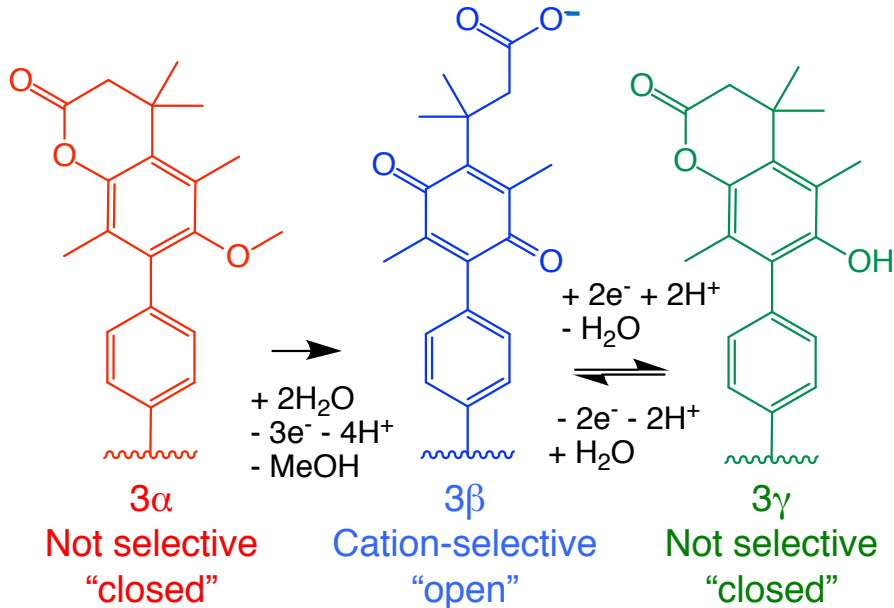
~0.2 monolayers of trimethyl lock have been deposited onto electroless gold.

Surface	Contact Angle (°)
3α	76
3β	64
3γ	77

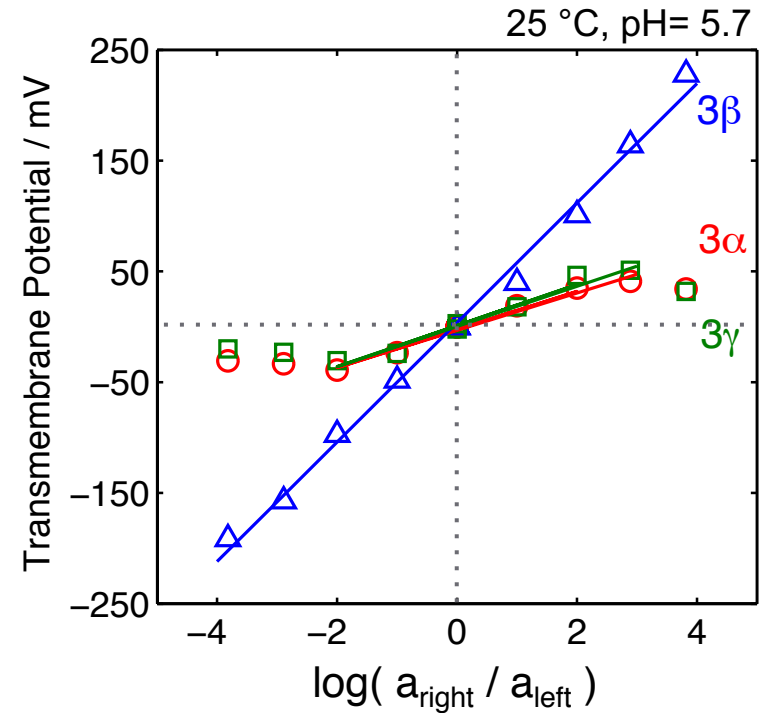
Molecules synthesized by D.R. Wheeler

Exposed Carboxylic Acid Increases Selectivity

Reversible electrochemical redox



Exposing carboxylic acid in "open" trimethyl lock increases surface charge, increasing ionic selectivity 8x.

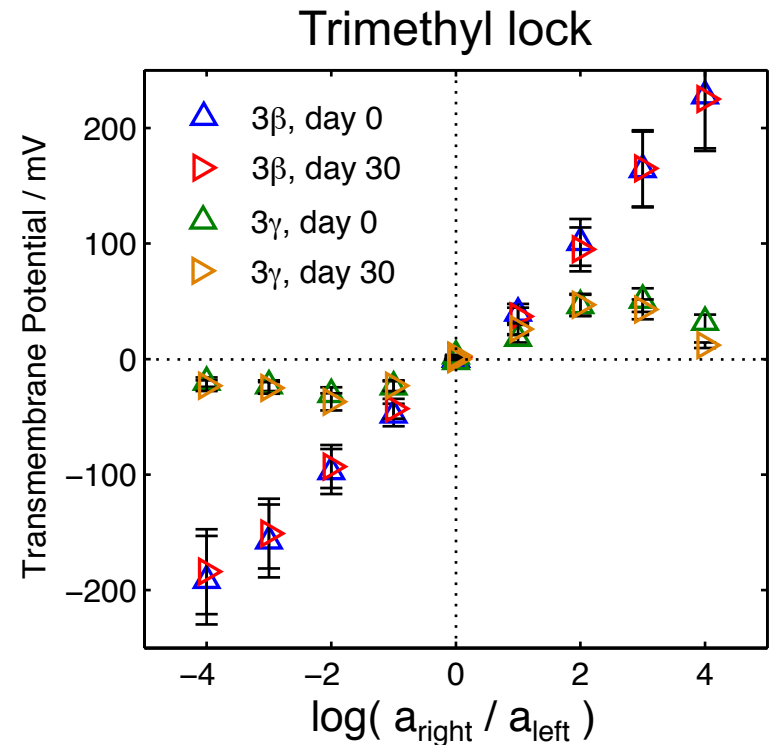
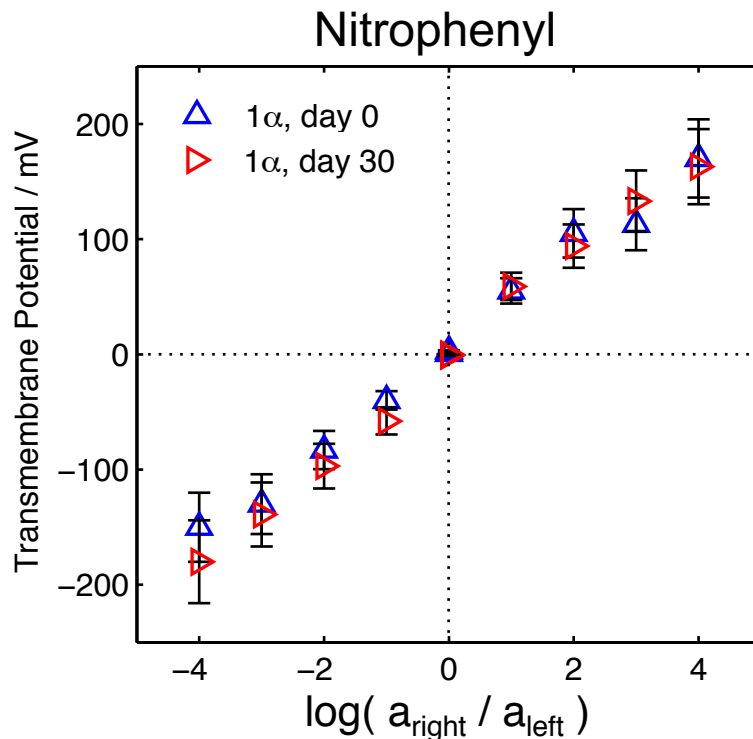


Surface	Slope
3α	0.29
3β	0.91
3γ	0.31

Molecules synthesized by D.R. Wheeler

Electrochemically Switched States Are Stable >30 Days

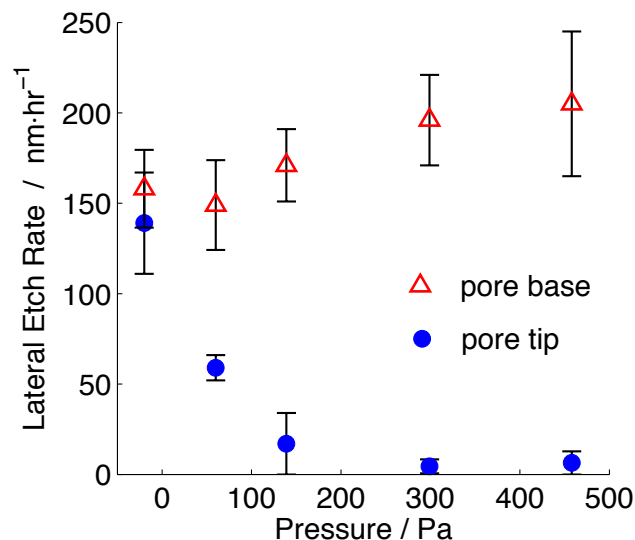
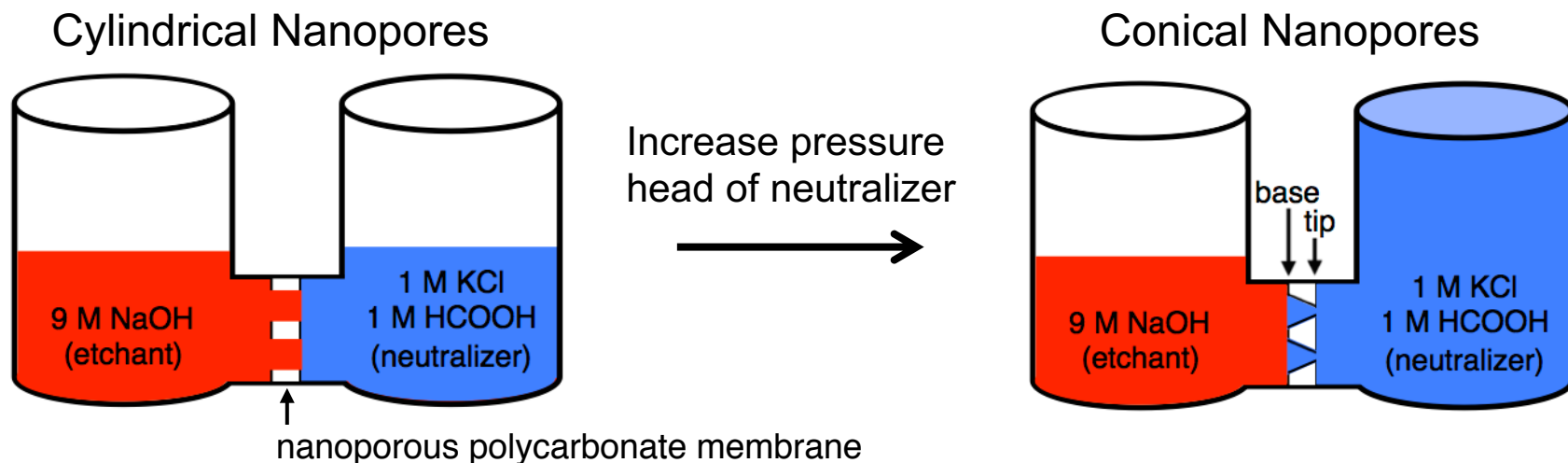
- Repeat ionic selectivity test after 30 days
- Membranes stored in 0.1 mM NaCl
- Electrochemical state retained ***without maintained stimulus!***



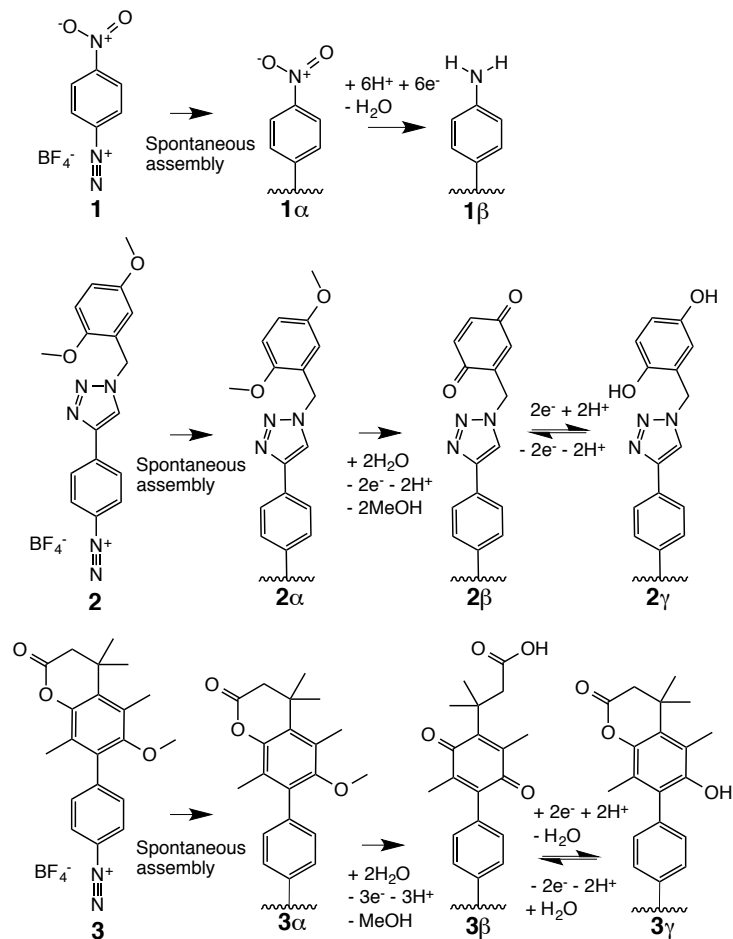
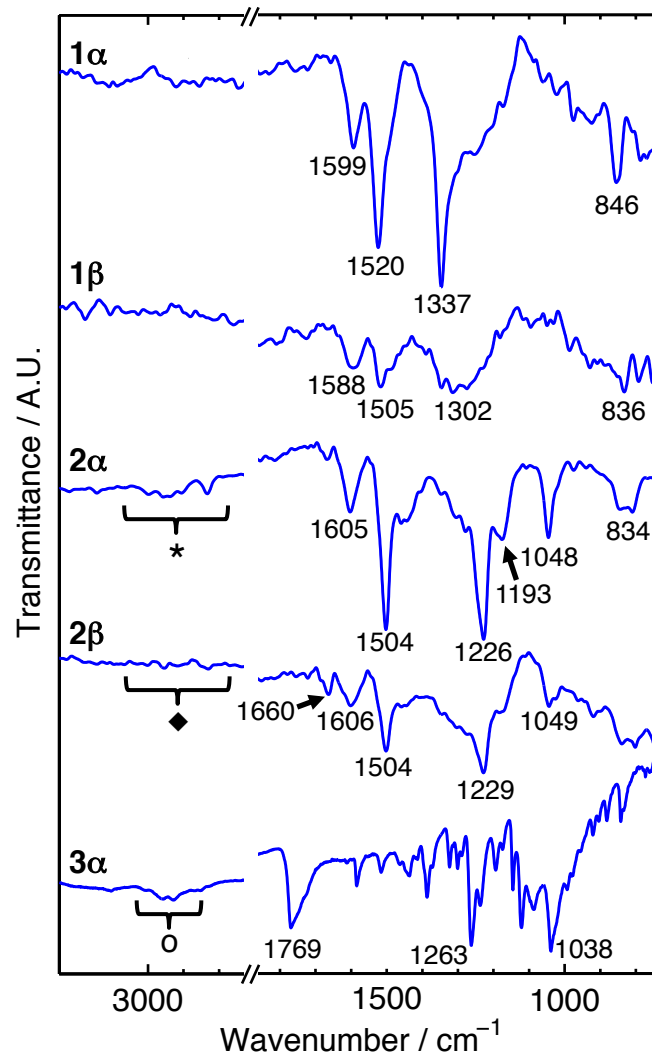
- ***Electrochemically switchable, chemically stabilized*** chemistries can be used to control the surface charge and ionic selectivity nanoporous membranes.
- These chemistries are stable >30 days without continuously applied stimulus.
- Investigation of higher flux membranes will allow industrial separations and water purification (e.g. electrodialysis) applications.

Extra Slides

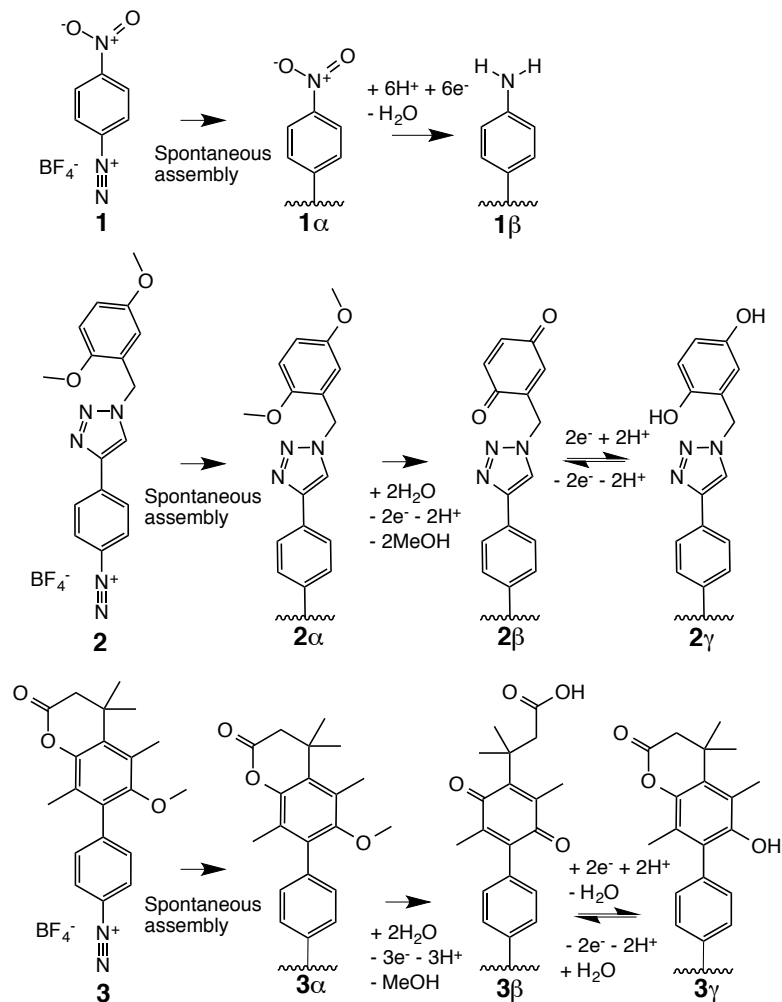
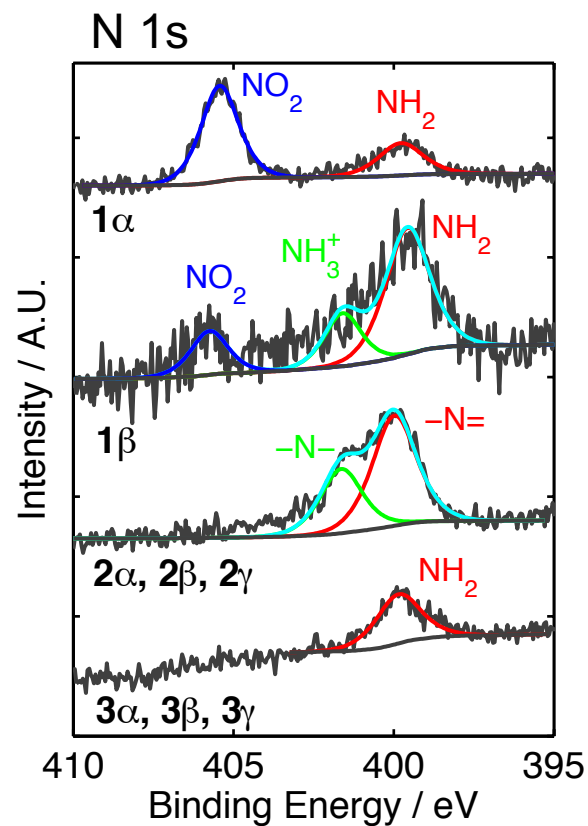
Pressure-Biased Chemical Etching



Elevated pressure increases neutralizer concentration in nanopores, minimizing etch rate at one side.



Molecules assembled on 150 nm Au / 20 nm Ti / glass witness coupons.



Revised Electroless Gold Plating

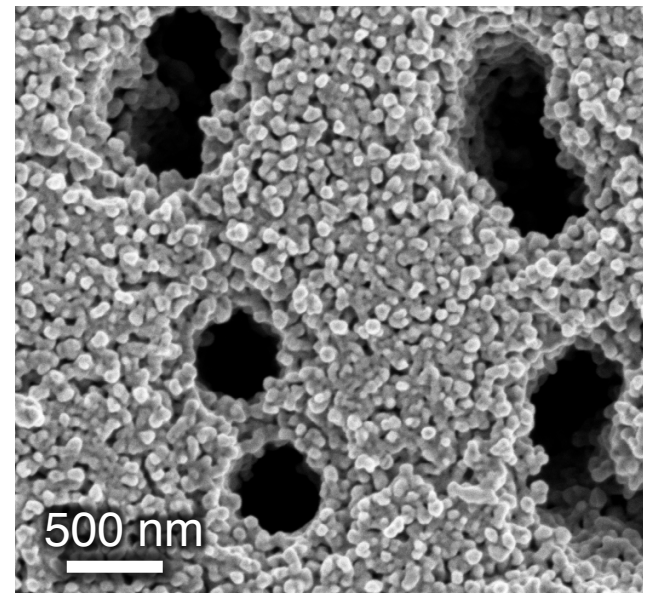
1. **Etch** in 9 M NaOH for 5 min.
2. Rinse in H₂O.
3. **UV-ozone clean** 10 min per side
4. **Sensitize under ultrasonication** in 0.07 M trifluoroacetic acid, 0.03 M SnCl₂.
5. Rinse in H₂O.
6. **Activate under ultrasonication** in 0.03 M AgNO₃, NH₄OH.
7. Rinse in H₂O.
8. Electrolessly plate Au from AuNaSO₃ + CH₂O at 3 °C.

initial
gold



optimized
gold

Improved surface preparation enables uniform gold coverage across polycarbonate surface.

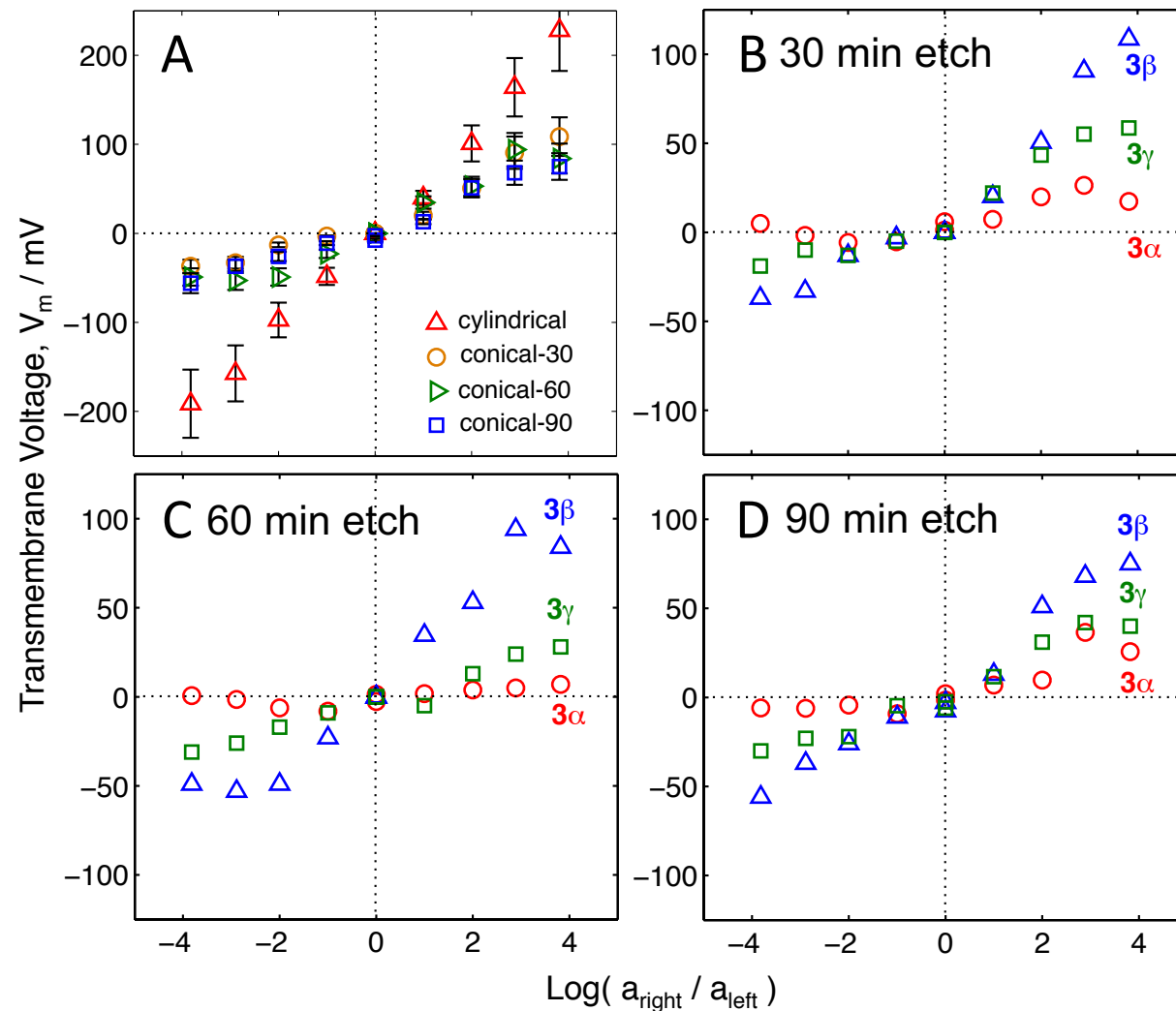


Diazonium Assembly Conditions

- **1** (nitrophenyl) and **2** (quinone)
 - 1 mM in 1:1: H₂O:EtOH
 - 4 h in dark
 - Rinse in DI H₂O, then soak in 0.1 mM NaCl 24 h

- **3** (trimethyl lock)
 - 1 mM in 2-propanol
 - 24 h in dark
 - Rinse in DI H₂O, then soak in 0.1 mM NaCl 24 h

Conical Response to Concentration Gradients Sandia National Laboratories



Etch Time (min)	D_{base} (nm)	D_{tip} (nm)	$V_{\text{forward}} / V_{\text{reverse}}$
0	6.1	6.1	1.2
30	70	1.5	2.9
60	180	1.0	1.7
90	225	2.5	1.3

2.9, 1.7, 1.3,