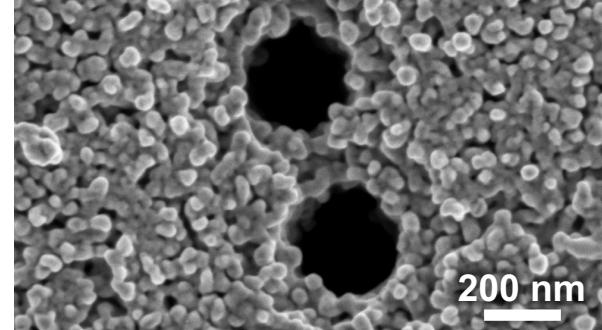
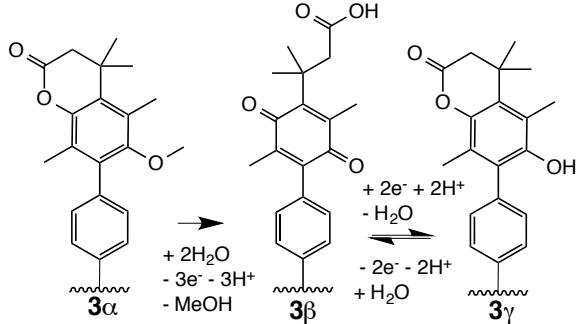


*Exceptional service in the national interest*



## Diazonium Functionalized Nanoporous Membranes for Electrochemically Switchable Ionic Separations

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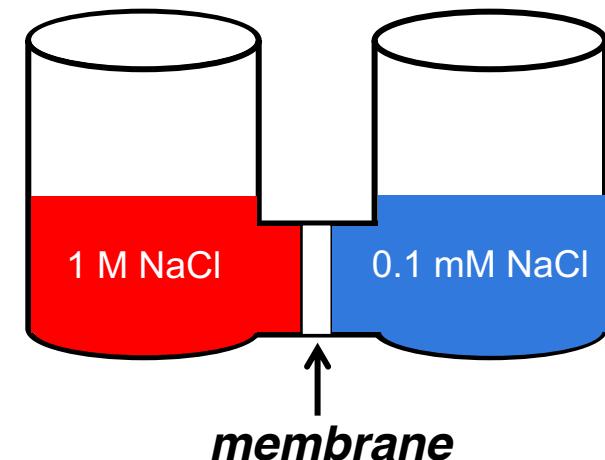
# Motivation

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***

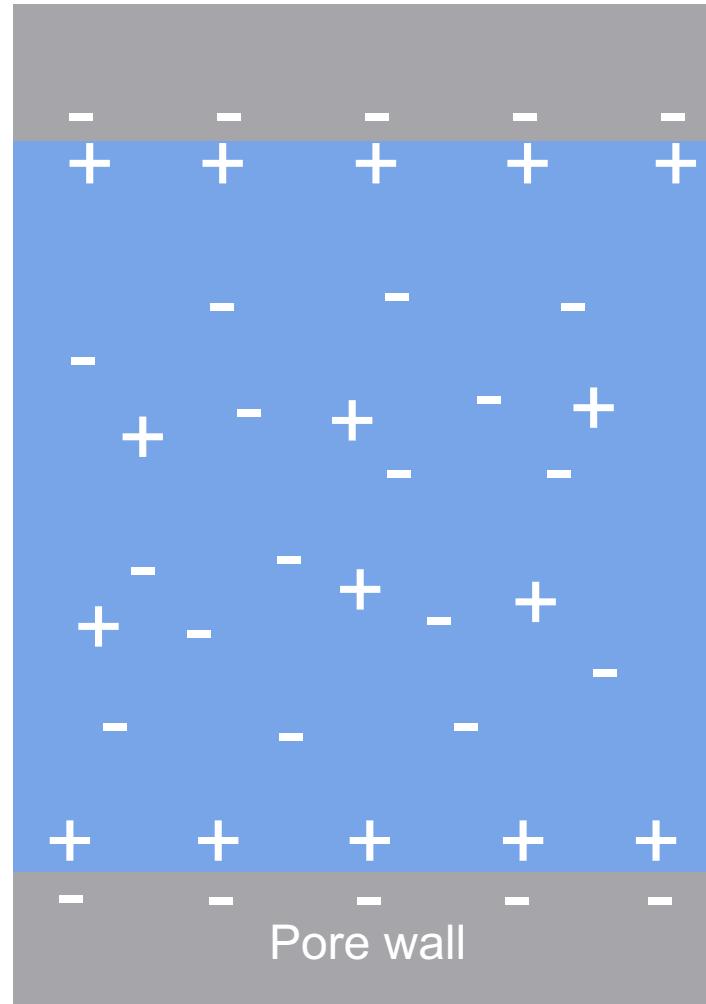
- Diode: charge moves in one direction
- Ionic selectivity: only 1 type of charge (+/-) can move
- ***Switch ionic selectivity to release ionic gradient***



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

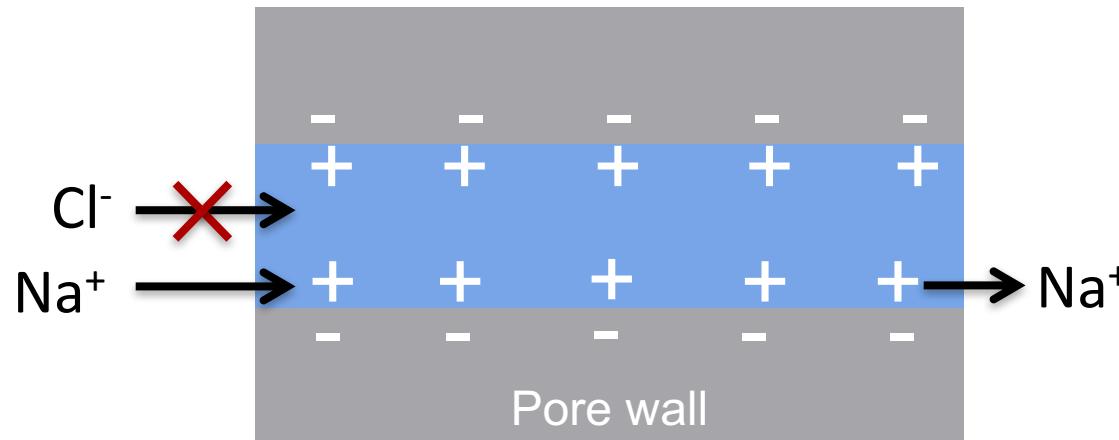
# Ionic Selectivity in Nanopores

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



# Ionic Selectivity in Nanopores

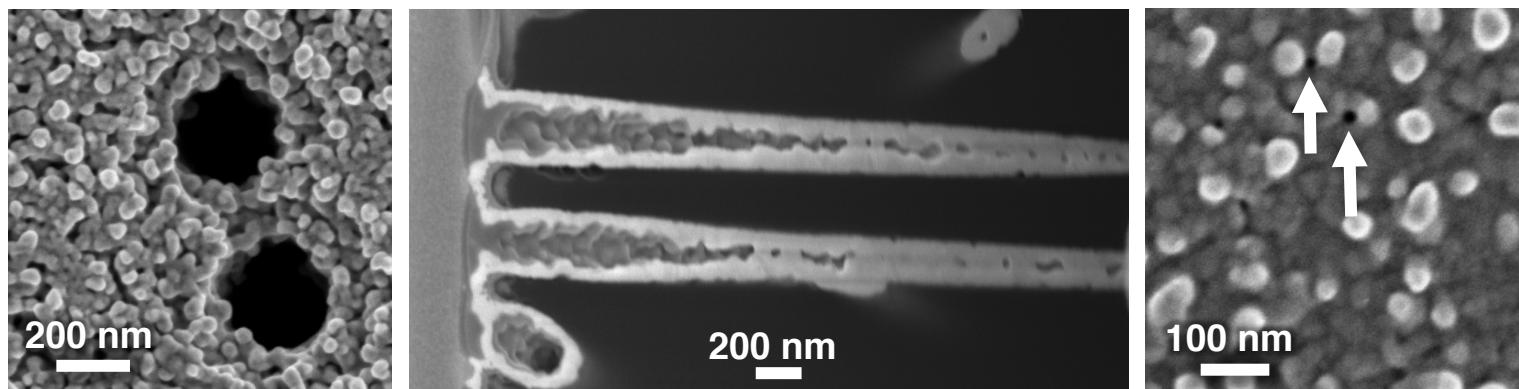
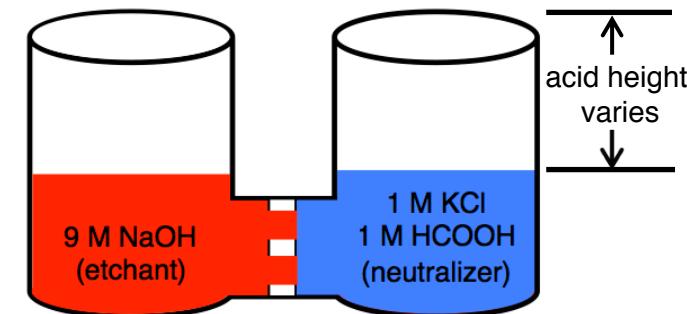
- Double layer size controls ion distribution in nanopore
  - $\sim 10 \text{ nm} @ 0.1 \text{ mM}$
  - $<1 \text{ nm} @ 1 \text{ M}$



***Overlapping double layers facilitate highly ion-selective transport.***

# Gold-Plated Polycarbonate Nanopores

- Polycarbonate films 5-10  $\mu\text{m}$  thick ion-tracked by Sterlitech Corp.
- Chemically etch ion tracks under pressure<sup>1</sup>
  - +300 Pa  $\rightarrow$  cones 275 nm x 3 nm
  - -20 Pa  $\rightarrow$  cylinders 42  $\pm$  6 nm
- Metallize with electroless gold<sup>2,3</sup>
  - 6 nm diameter cylinders



# Evaluating Ionic Selectivity

- Measure the voltage when the membrane separates different salt concentrations

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

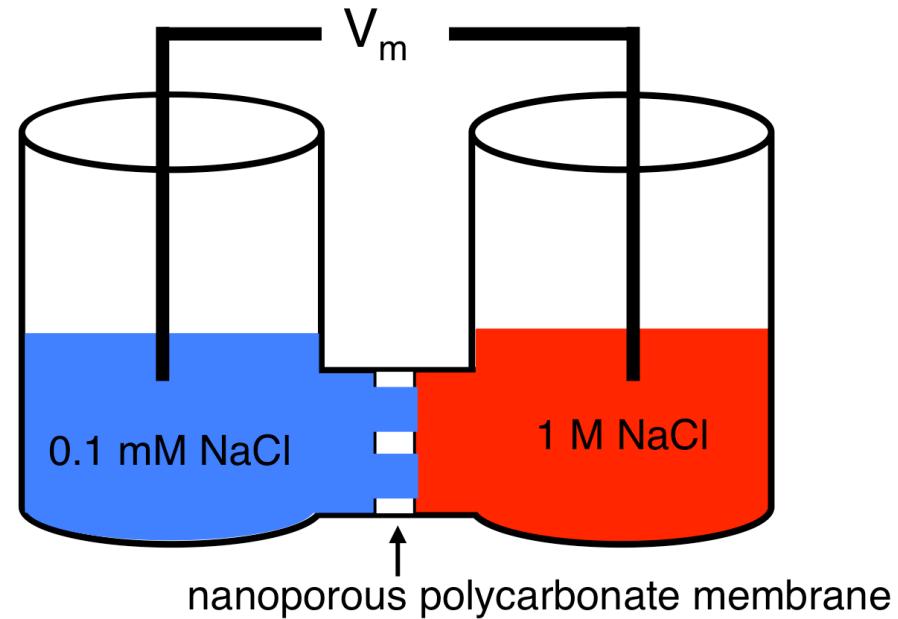
$t_+$  = cation transference number  
 $t_-$  = anion transference number

$V_m$ , in Volts

25 °C

1:1 salt

Measured by Ag/AgCl wires



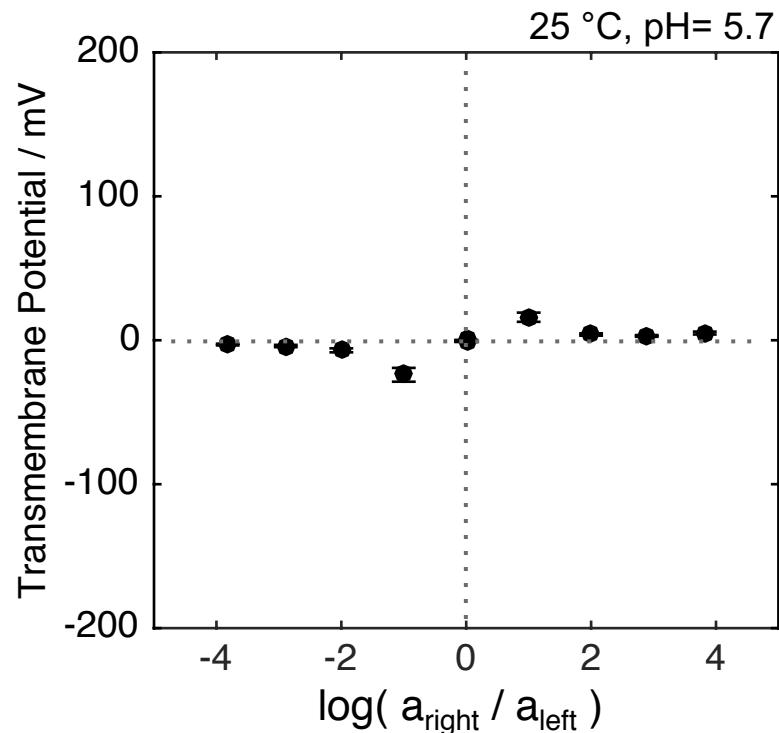
# Ionic Selectivity of Nanoporous Polycarbonate

- 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**



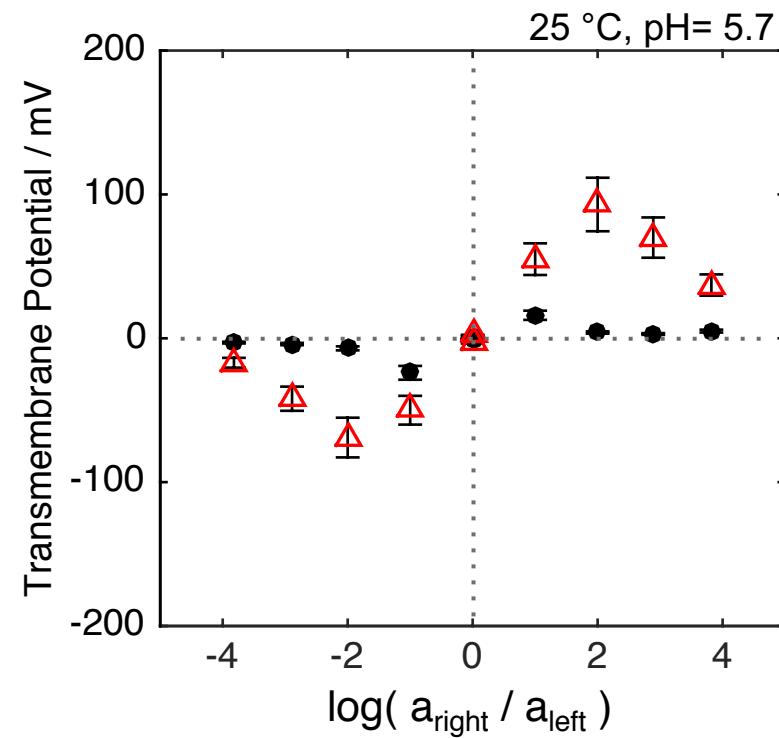
# Gold Plating Increases Ionic Selectivity

- Measure the voltage when the membrane separates different salt concentrations

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

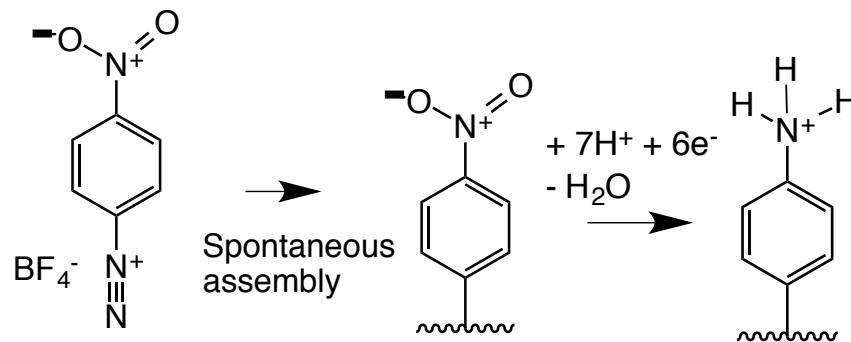
$(t_+ - t_-)$

- polycarbonate 0.34
- △ gold-plated polycarbonate 0.73

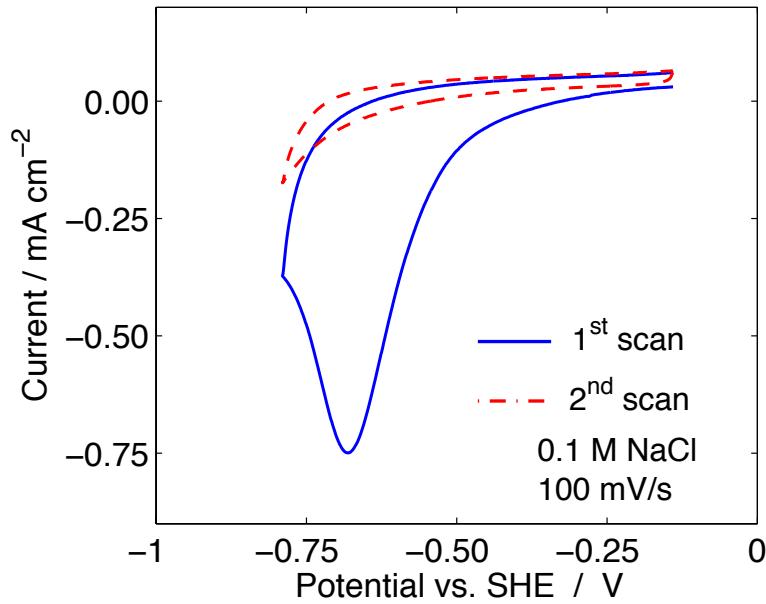


***Smaller pore size and increase surface charge increase ionic selectivity.***

# 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.***

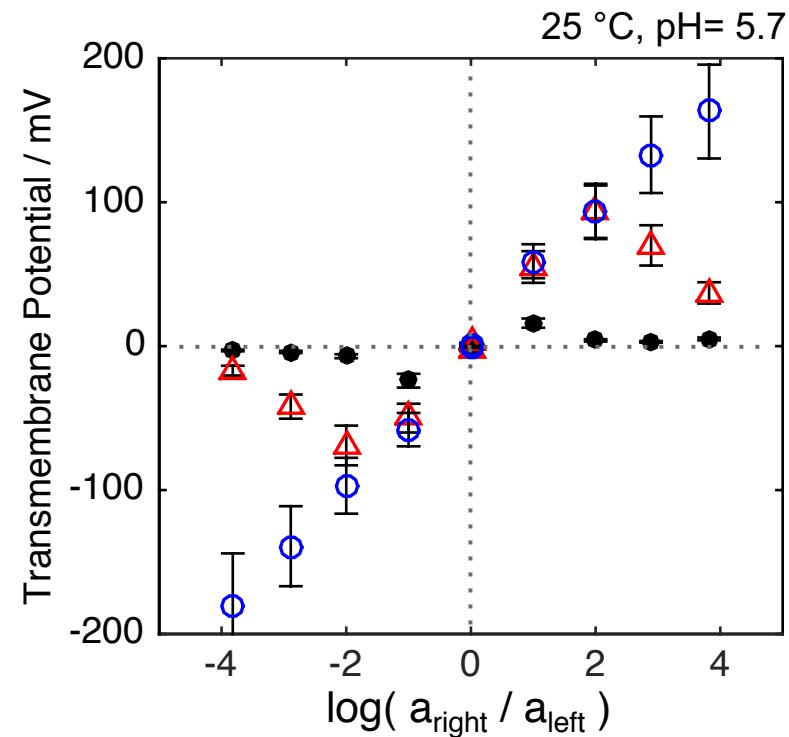
# Nitrophenyl Surface Is Cation-Selective

- Measure the voltage when the membrane separates different salt concentrations

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

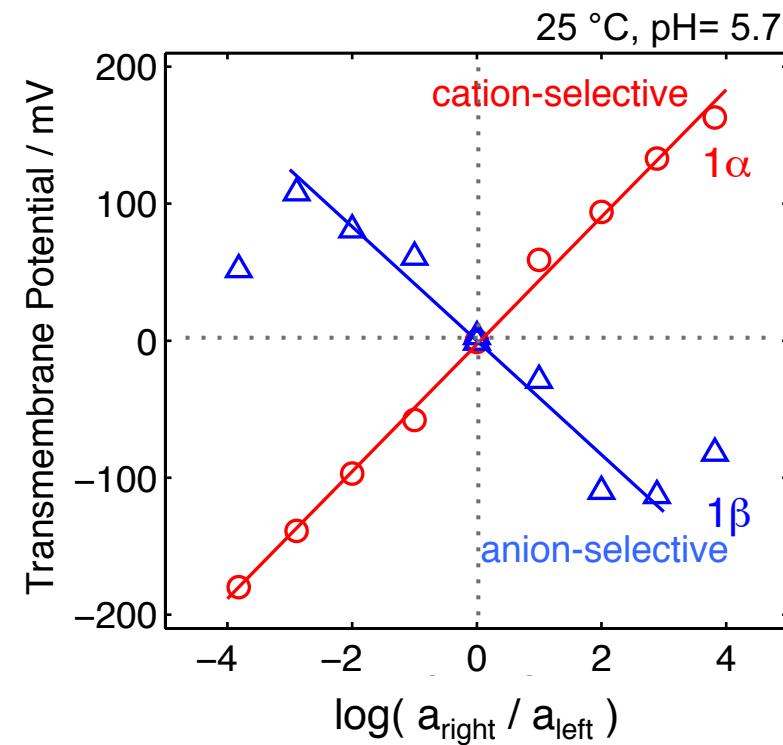
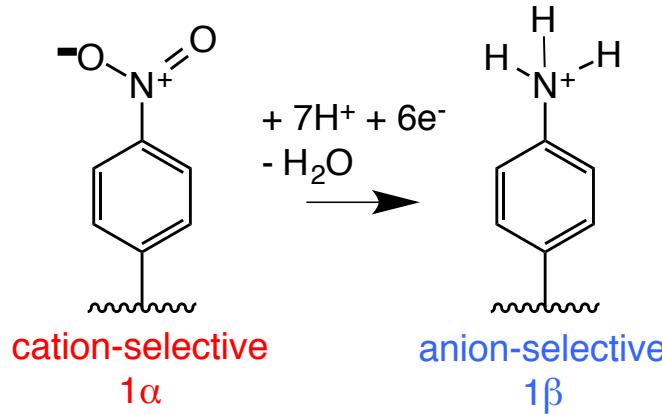
$(t_+ - t_-)$

● 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

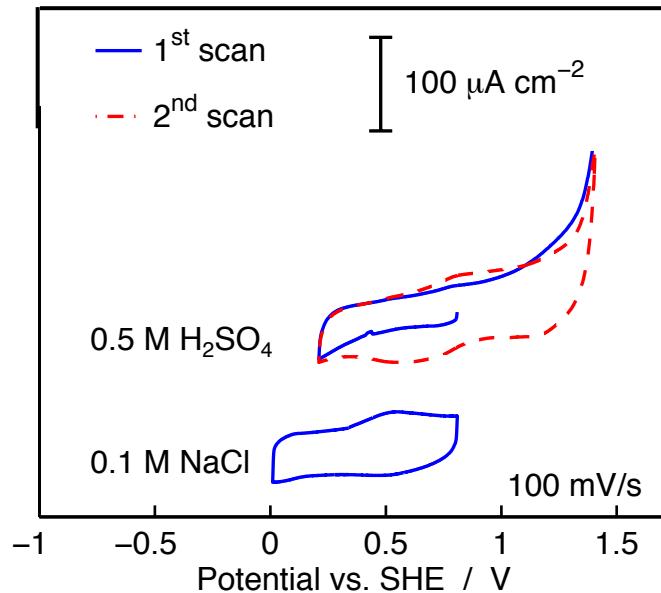
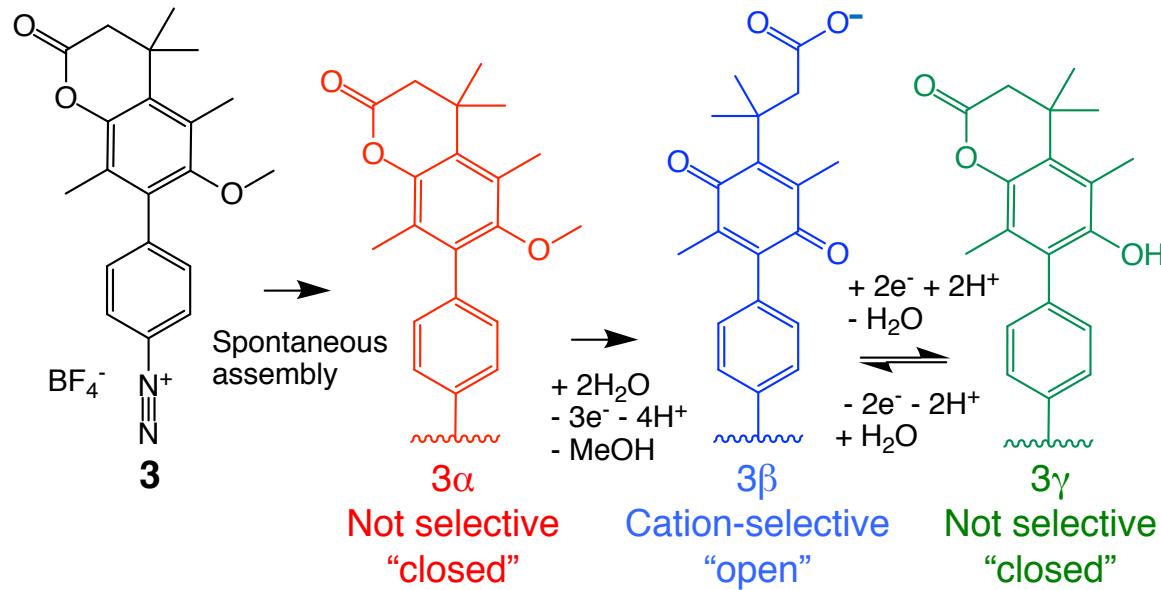


***Reduction of nitrophenyl to aminophenyl enables transition from cation-selective to anion-selective membrane.***

Surface	Slope
$1\alpha$	+0.79
$1\beta$	-0.70

# Trimethyl Lock: Hiding a Carboxylic Acid

## Reversible electrochemical redox



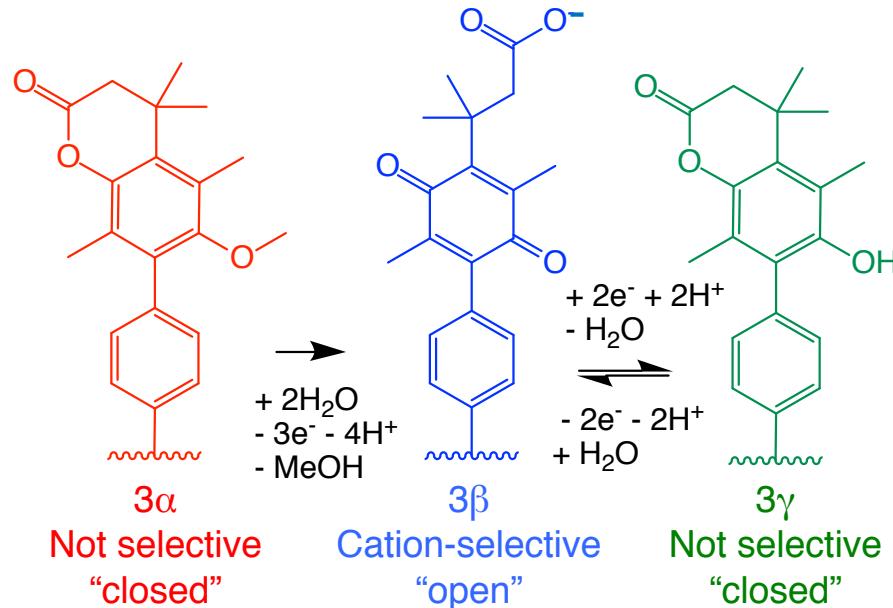
**~0.2 monolayers of trimethyl lock have been deposited onto electroless gold.**

Surface	Contact Angle (°)
3 $\alpha$	76
3 $\beta$	64
3 $\gamma$	77

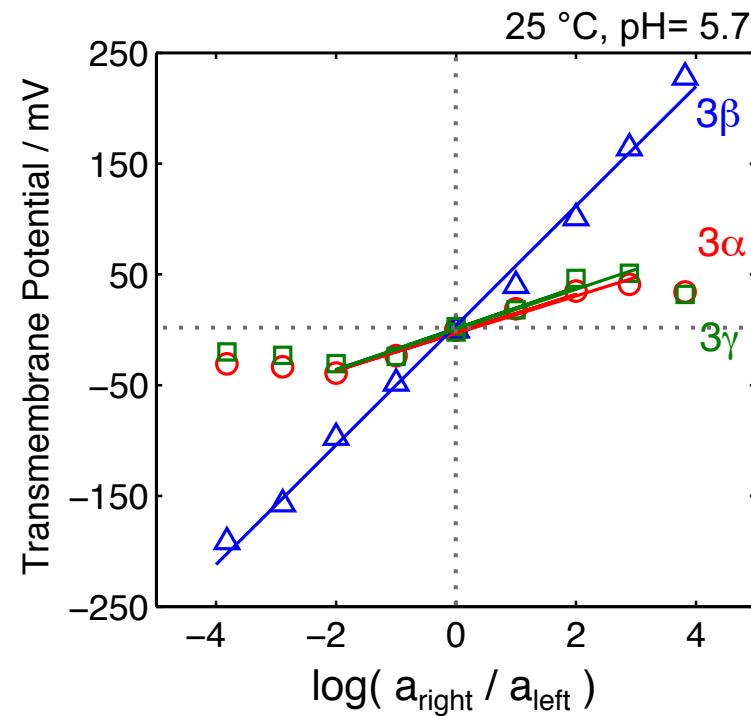
Molecules synthesized by D.R. Wheeler

# Exposed Carboxylic Acid Increases Selectivity

Reversible electrochemical redox



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

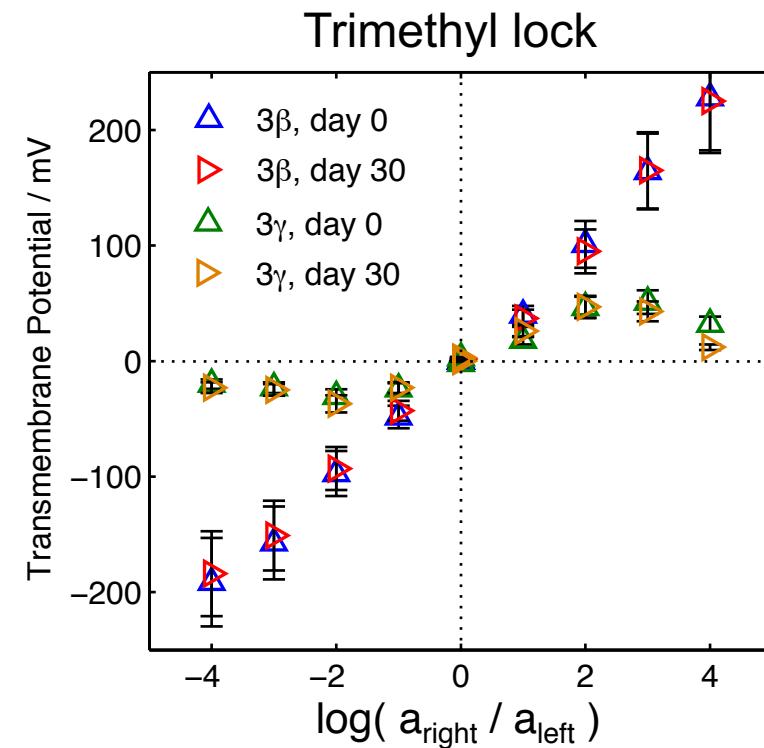
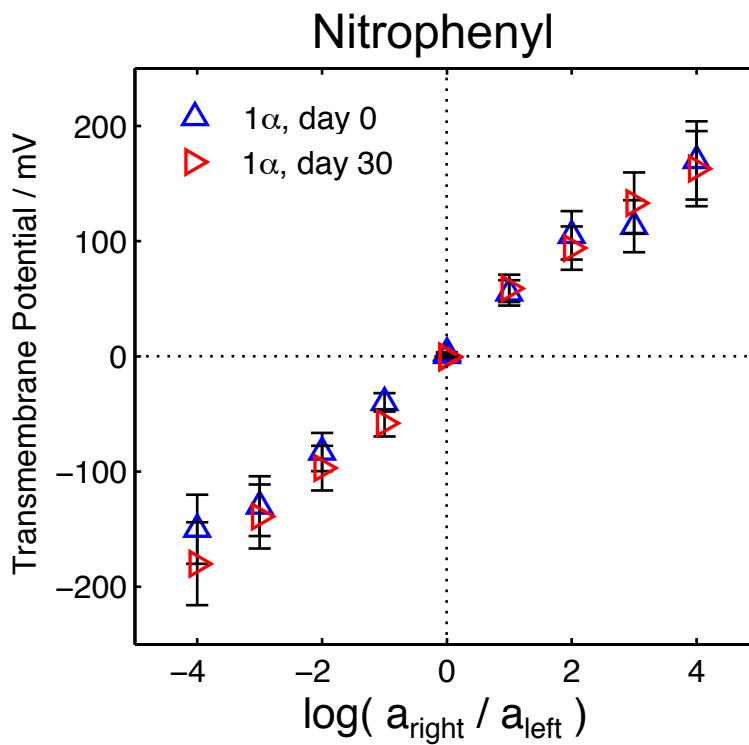


Surface	Slope
3α	0.29
3β	0.91
3γ	0.31

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!***



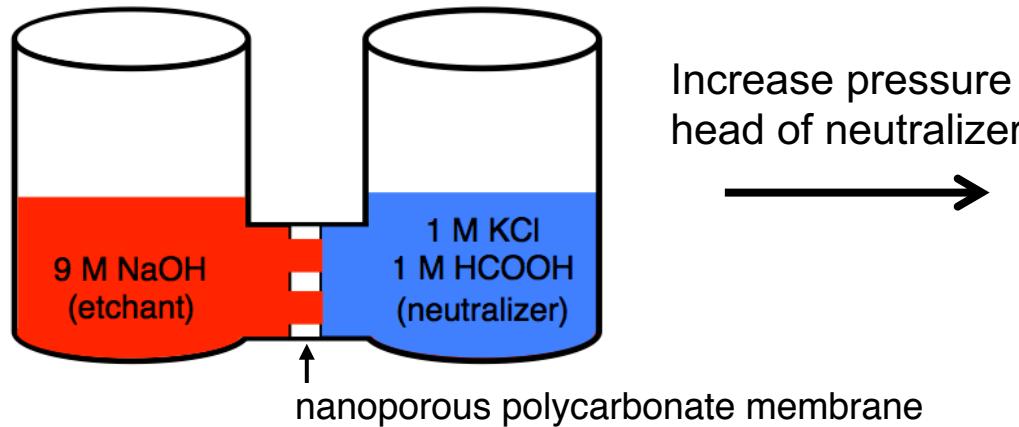
# Moving Forward

- ***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.

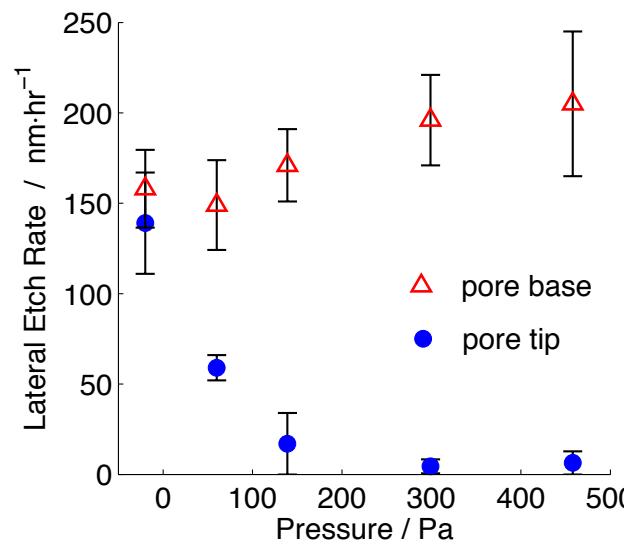
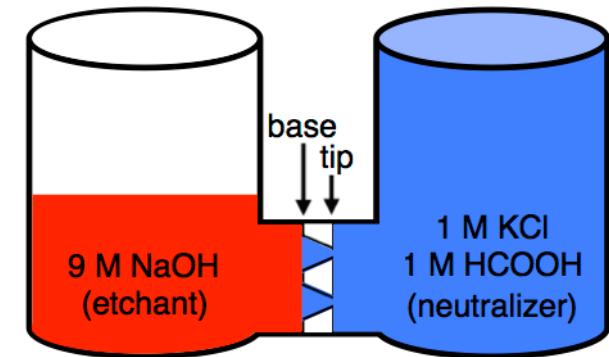
# Extra Slides

# Pressure-Biased Chemical Etching

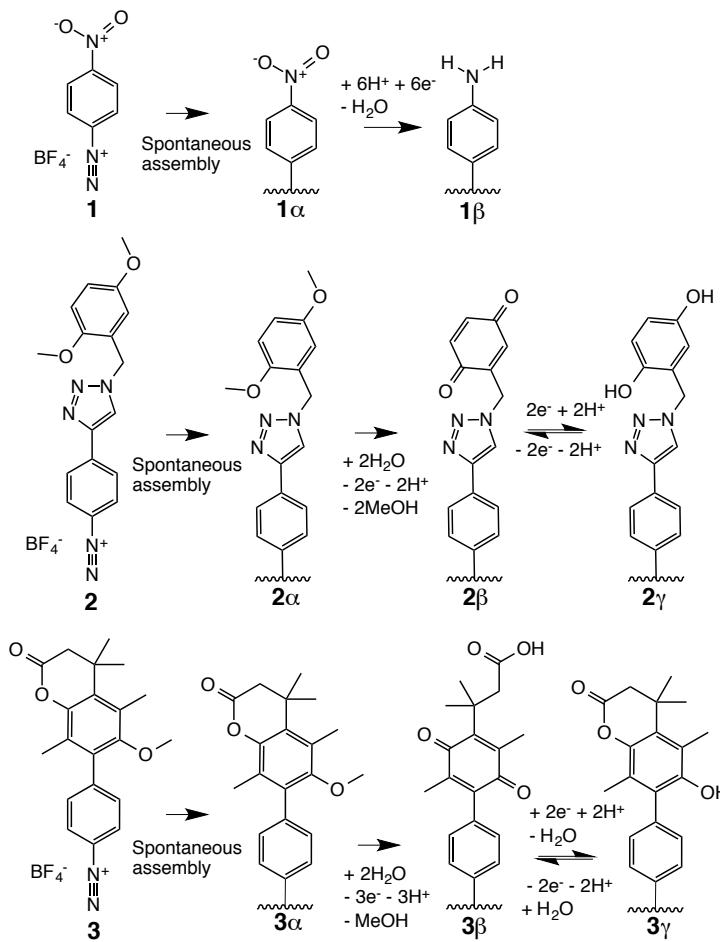
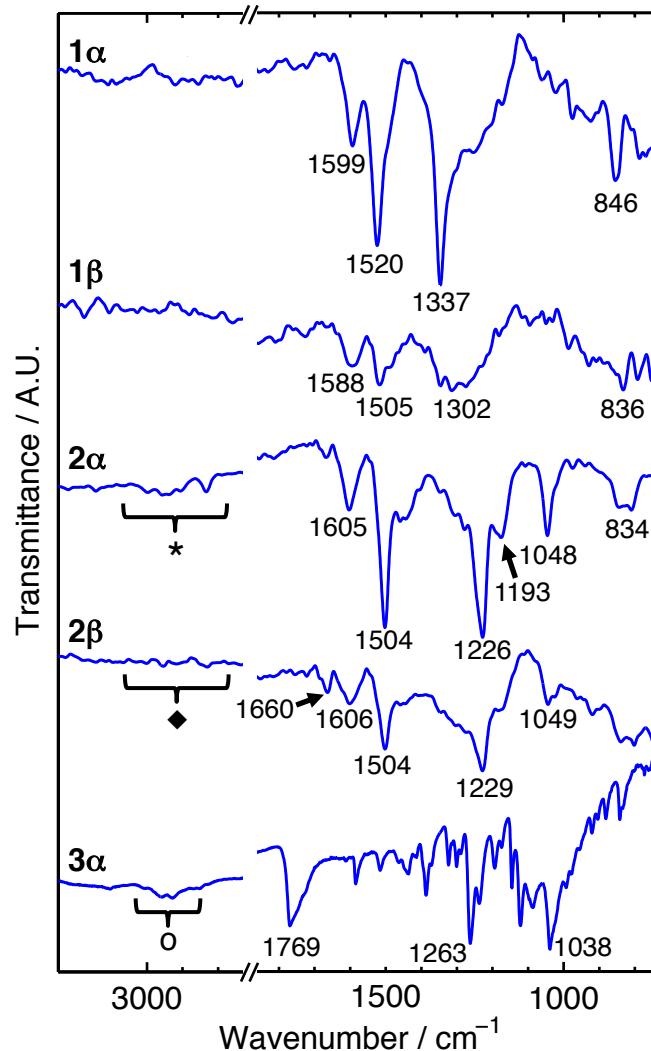
Cylindrical Nanopores



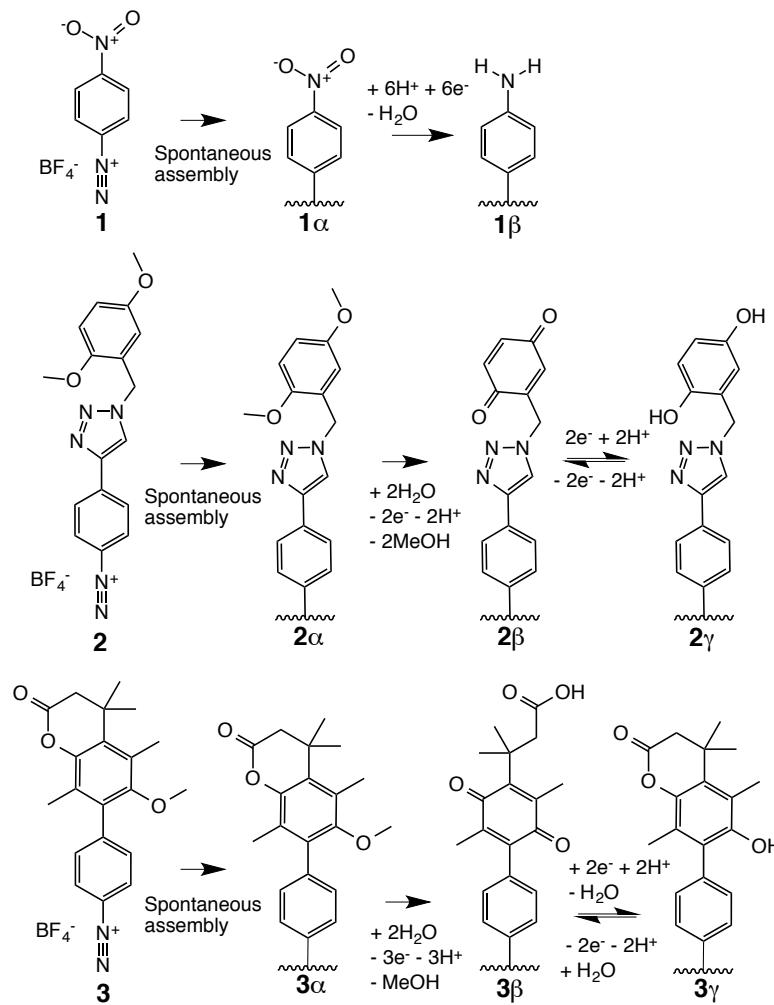
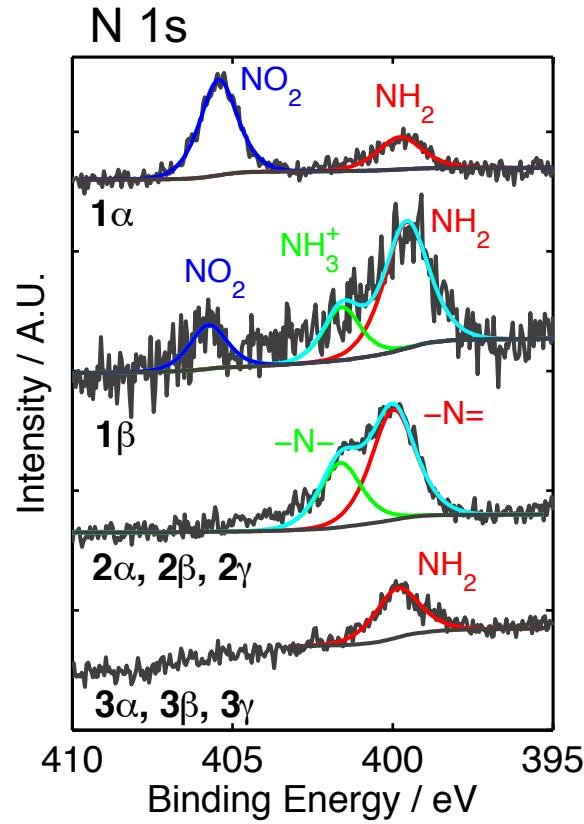
Conical Nanopores



***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.

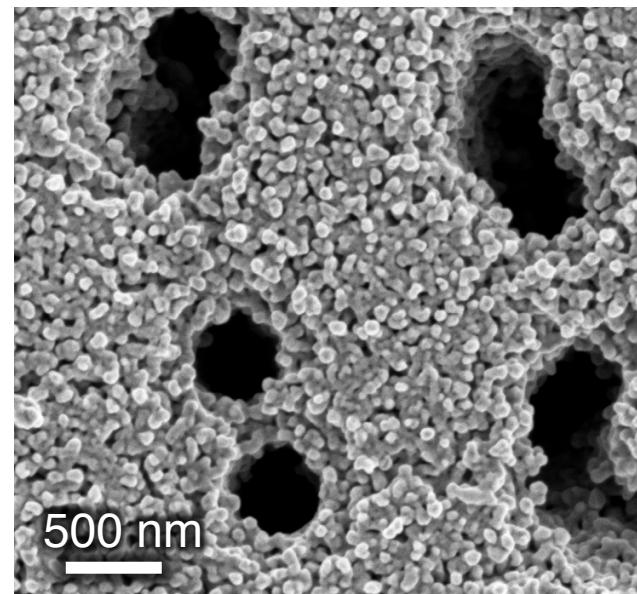


# Revised Electroless Gold Plating

1. **Etch** in 9 M NaOH for 5 min.
2. Rinse in H<sub>2</sub>O.
3. **UV-ozone clean** 10 min per side
4. **Sensitize under ultrasonication** in 0.07 M trifluoroacetic acid, 0.03 M SnCl<sub>2</sub>.
5. Rinse in H<sub>2</sub>O.
6. **Activate under ultrasonication** in 0.03 M AgNO<sub>3</sub>, NH<sub>4</sub>OH.
7. Rinse in H<sub>2</sub>O.
8. Electrolessly plate Au from AuNaSO<sub>3</sub> + CH<sub>2</sub>O at 3 °C.



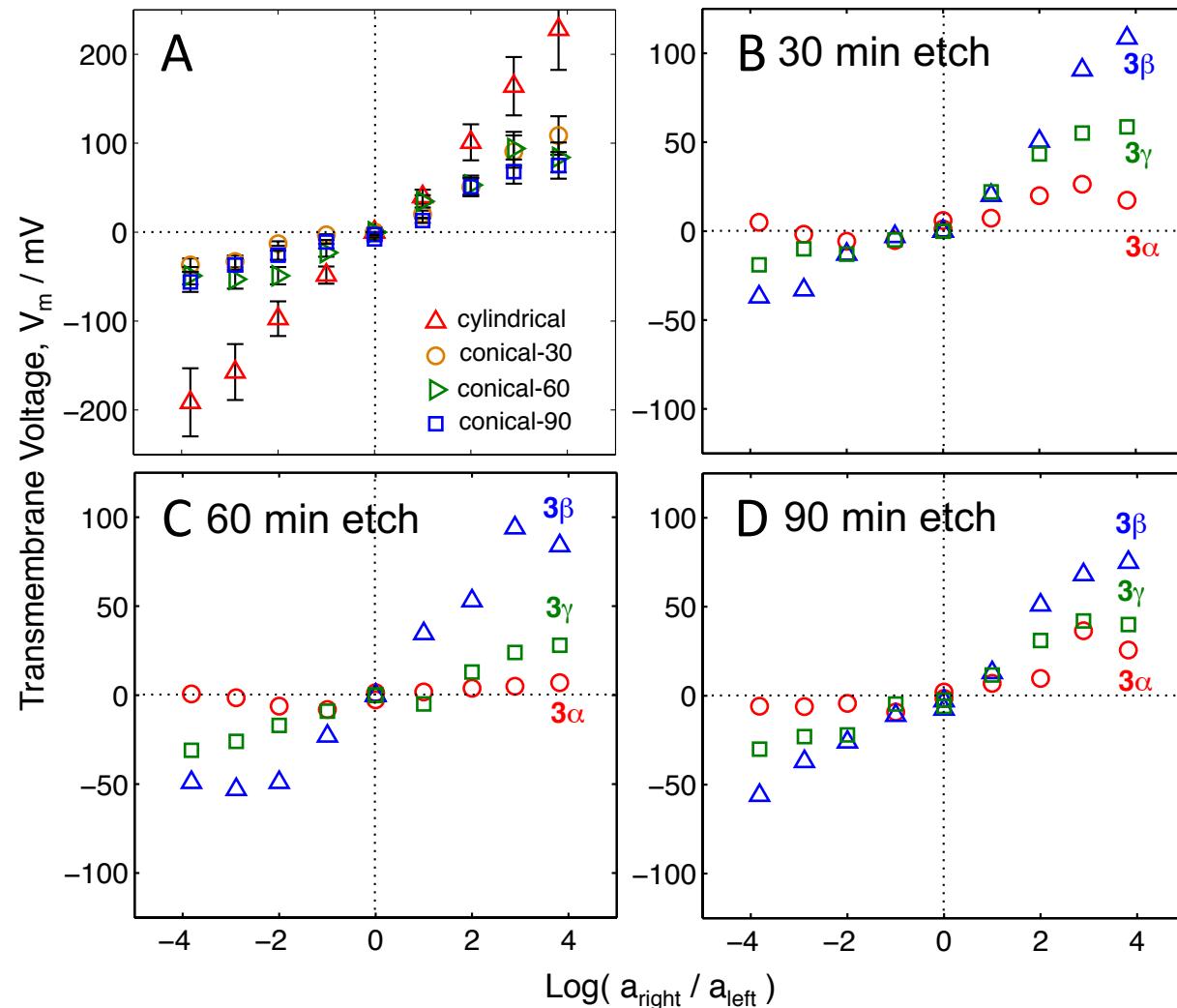
***Improved surface preparation enables uniform gold coverage across polycarbonate surface.***



# Diazonium Assembly Conditions

- **1** (nitrophenyl) and **2** (quinone)
  - 1 mM in 1:1: H<sub>2</sub>O:EtOH
  - 4 h in dark
  - Rinse in DI H<sub>2</sub>O, then soak in 0.1 mM NaCl 24 h
  
- **3** (trimethyl lock)
  - 1 mM in 2-propanol
  - 24 h in dark
  - Rinse in DI H<sub>2</sub>O, then soak in 0.1 mM NaCl 24 h

# Conical Response to Concentration Gradients



Etch Time (min)	$D_{base}$ (nm)	$D_{tip}$ (nm)	$V_{forward}/V_{reverse}$
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,