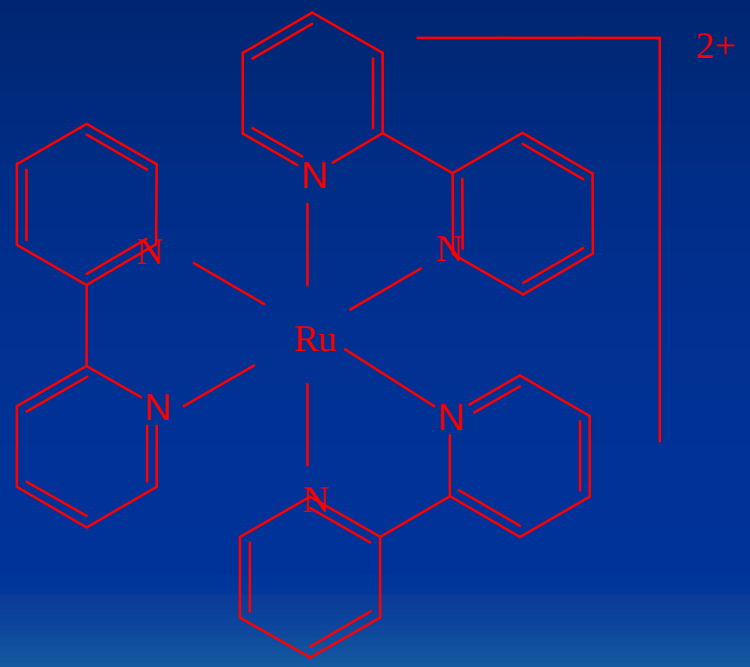
ECL Mechanism of $Ru(bpy)_3^{2+}$/TPrA System

Wujian Miao

ECL: ***E***lectro***c***hemi***l***uminesence
or ***E***lectrogenerated ***C***hemi***l***uminesence



$Ru(bpy)_3^{2+}$

$(CH_3CH_2CH_2)_3N$:

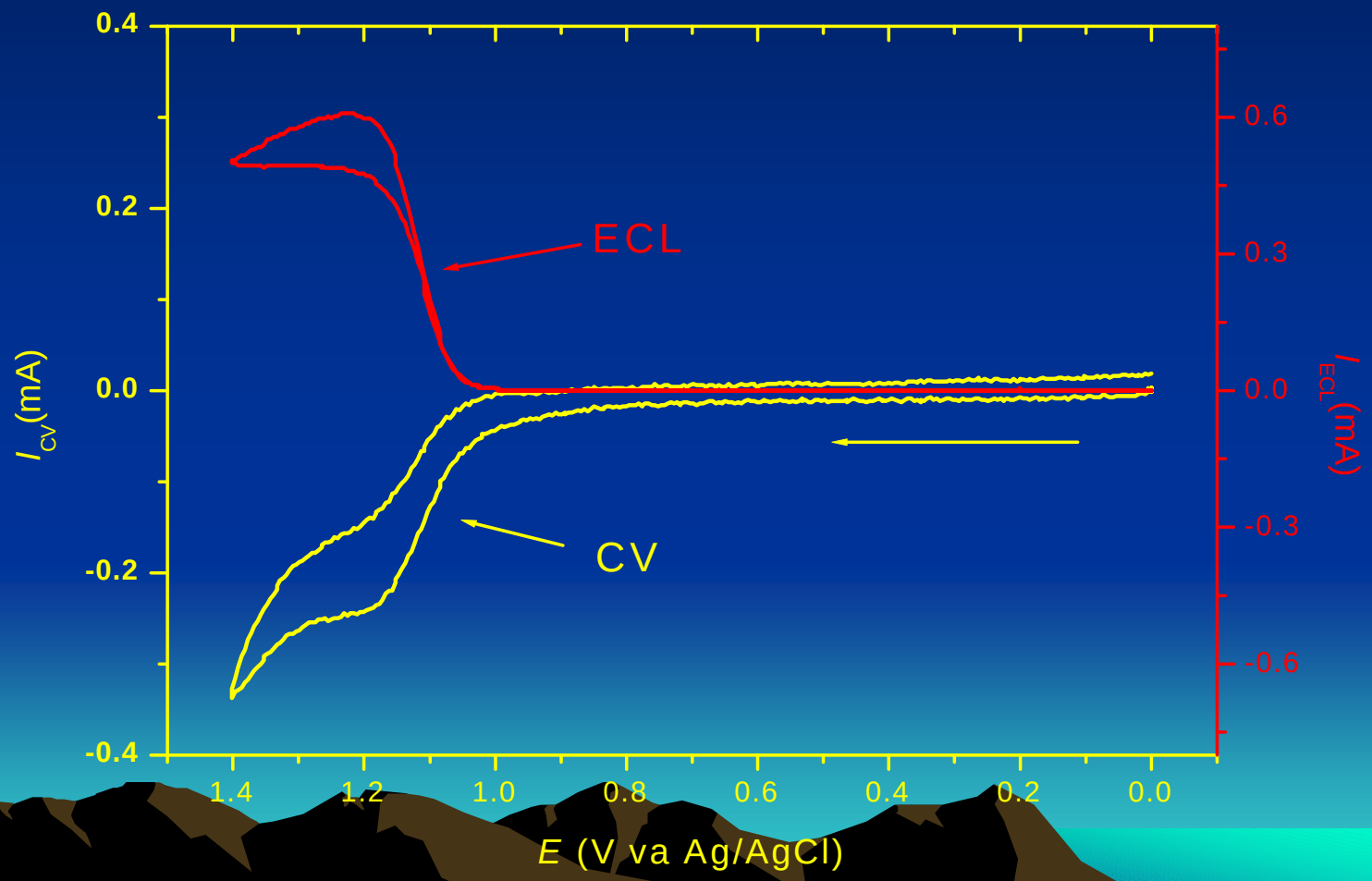
(***T***ri***Pr***opyl ***A***mine)

TPrA

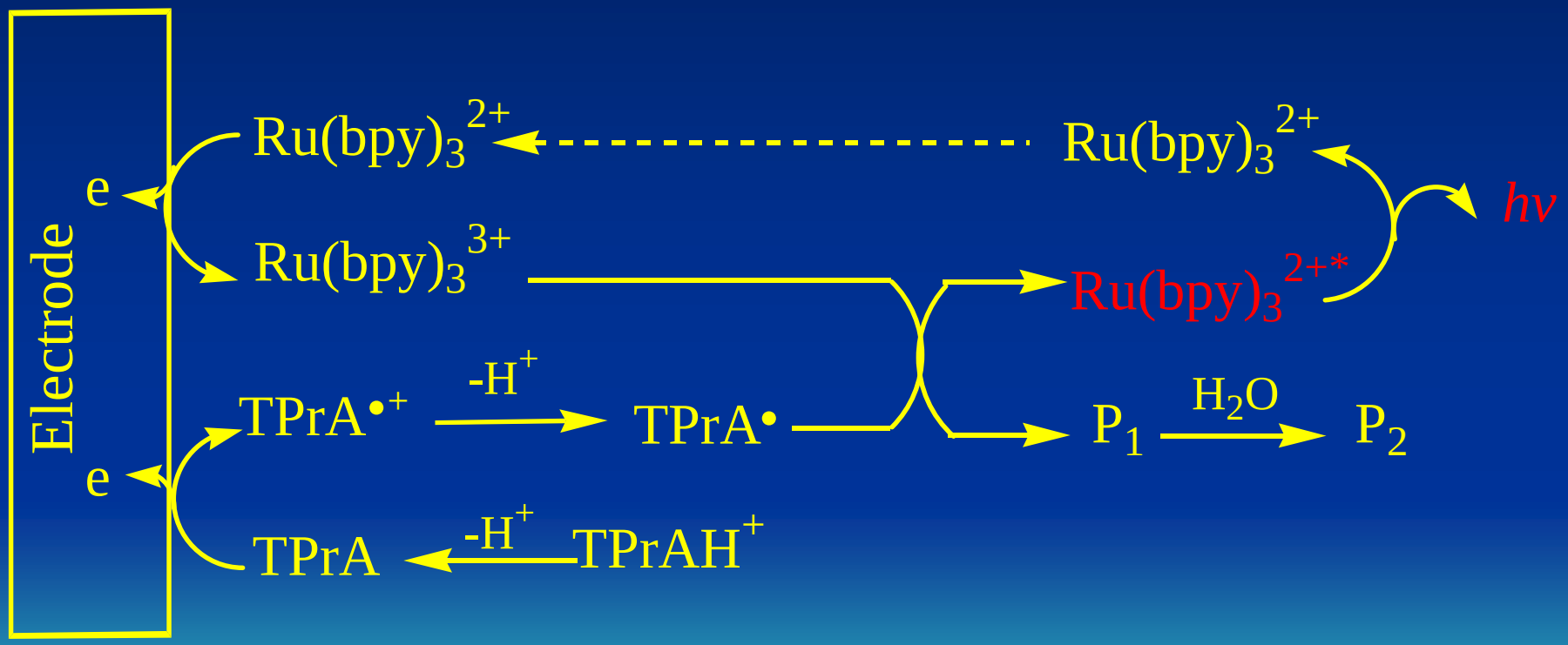
(As coreactant)

I_{ECL} & I_{CV} ~ E Profiles for $Ru(bpy)_3^{2+}$(1 mM) /TPrA (10 mM) System

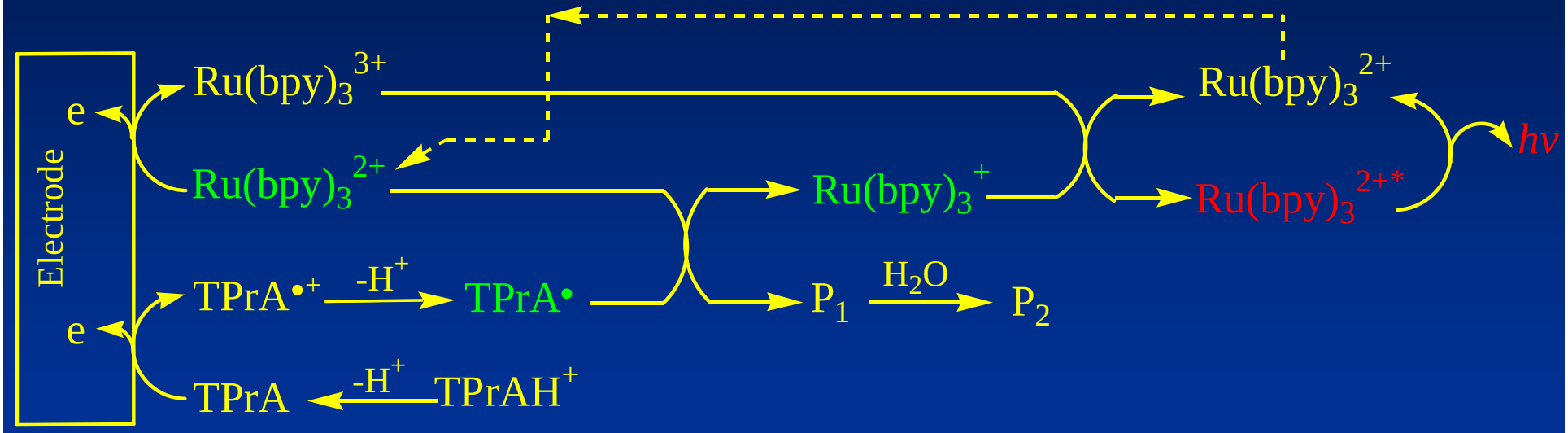
(3 mm GC, 0.10 M PBS, pH 7, 100 mV/s)

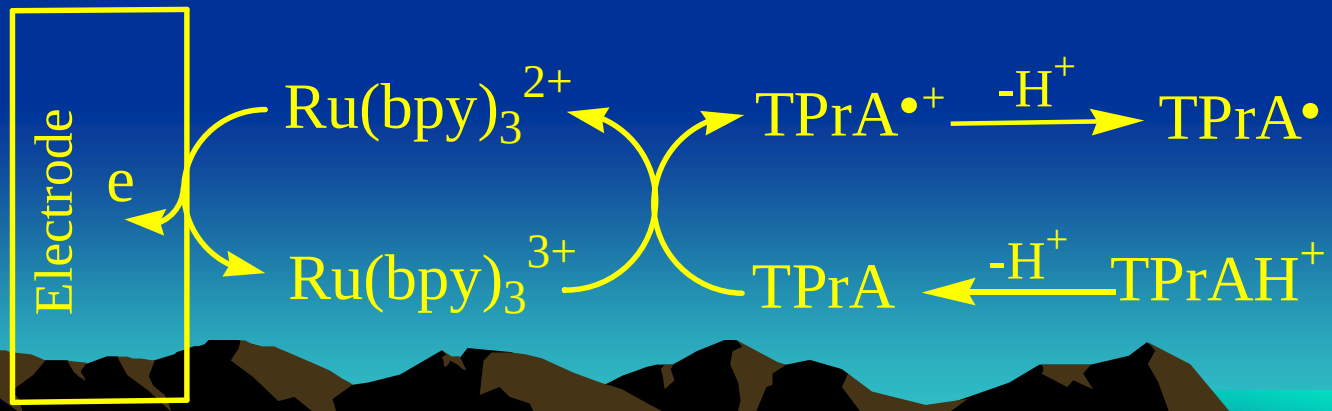


Direct $Ru(bpy)_3^{2+}$ Oxidation Routes



Alternatively





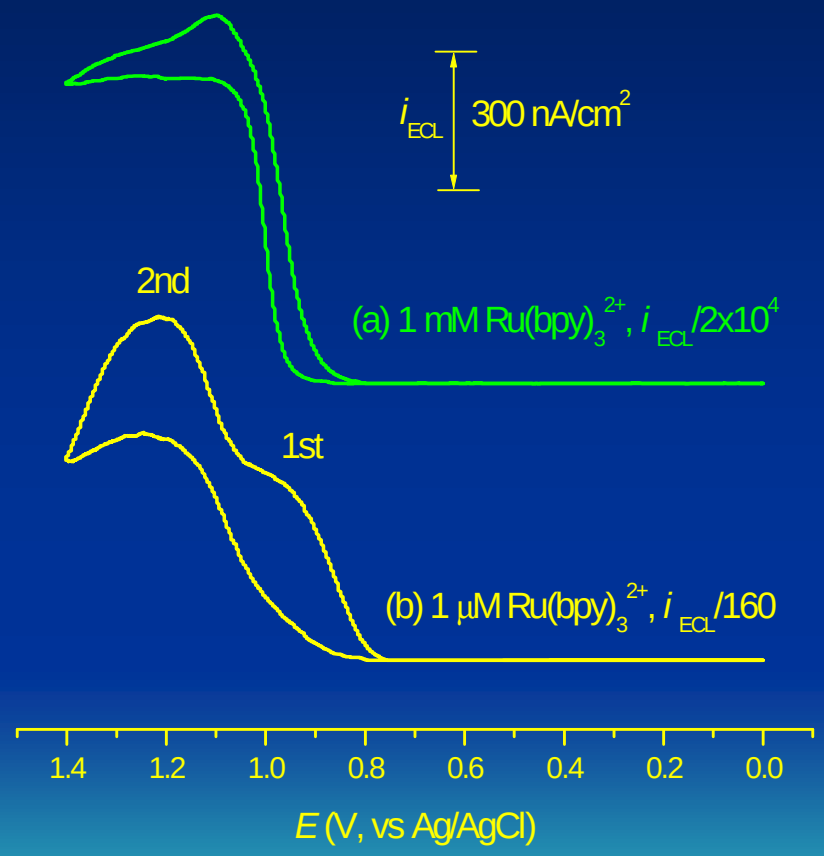
Problems with the Direct $Ru(bpy)_3^{2+}$ Oxidation Mechanism

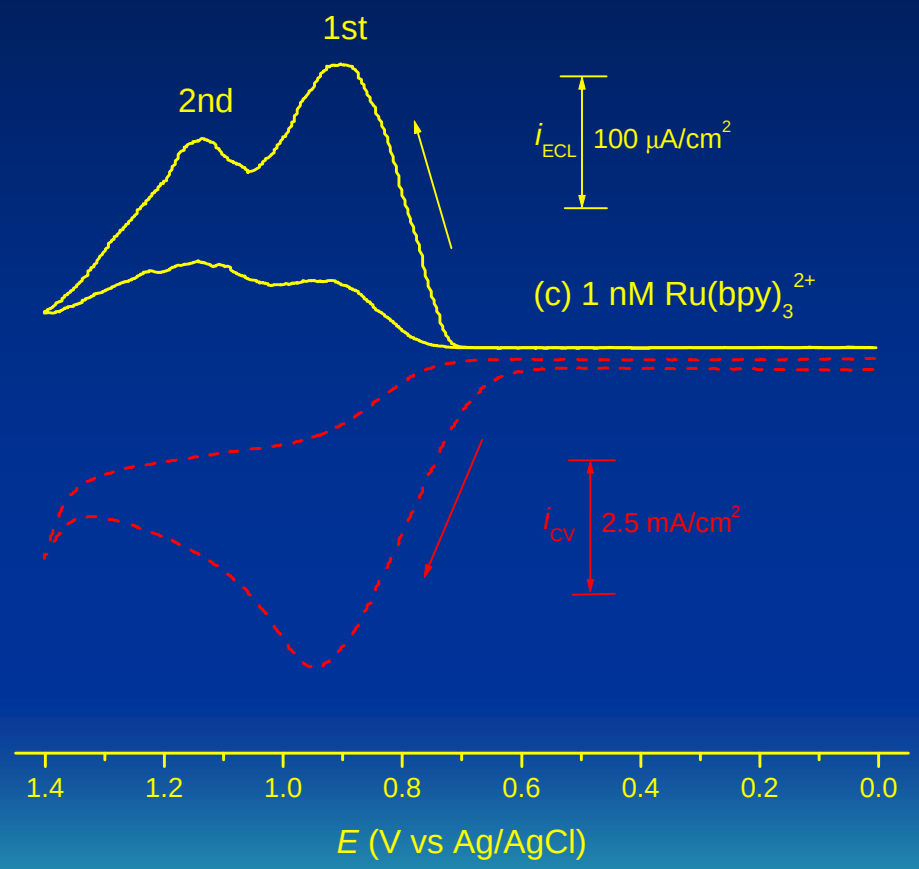
1. Mysterious ECL Pre-wave;

2. ECL at Labeled Magnetic Beads;

3. Proof of Energetic and Existence of Intermediates.

$Ru(bpy)_3^{2+}$ Concentration Effects on i_{ECL}- E Profiles

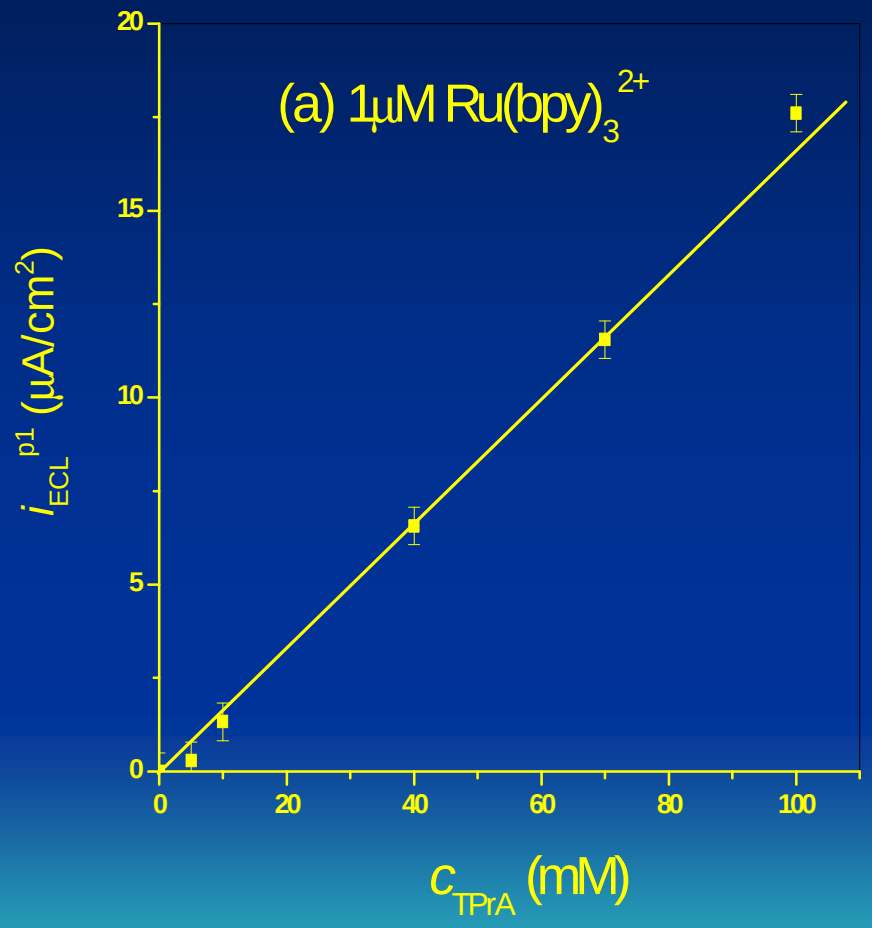


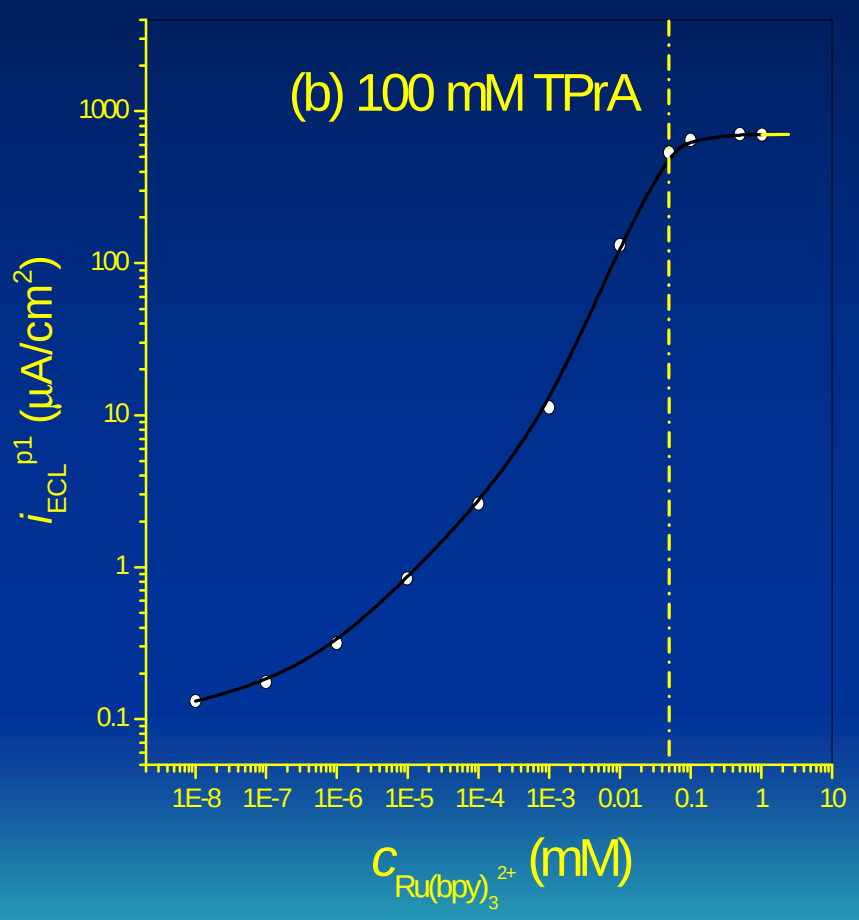


0.10 M TPrA + 0.20 M PBS
pH 8, v = 20 mV/s, 3 mm GC

0.10 M TPrA/0.10 M Tris/0.10 M $LiClO_4$
pH 8, v = 50 mV/s, 3 mm GC

1st ECL Peak Intensity vs c_{TPrA} & $c_{Ru(bpy)_3^{2+}}$

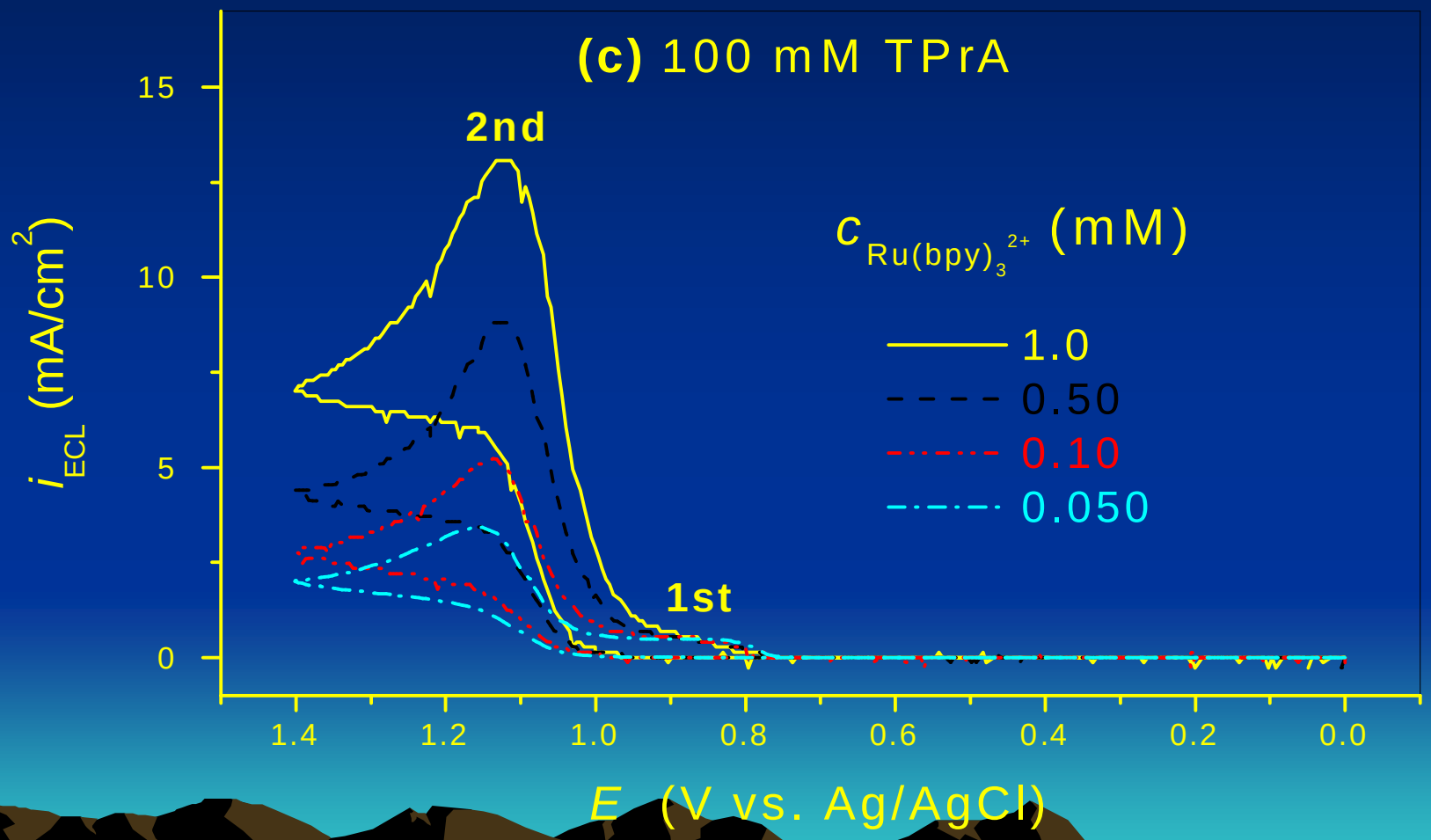




0.20 M PBS, pH ~ 8, 100 mV/s, GC

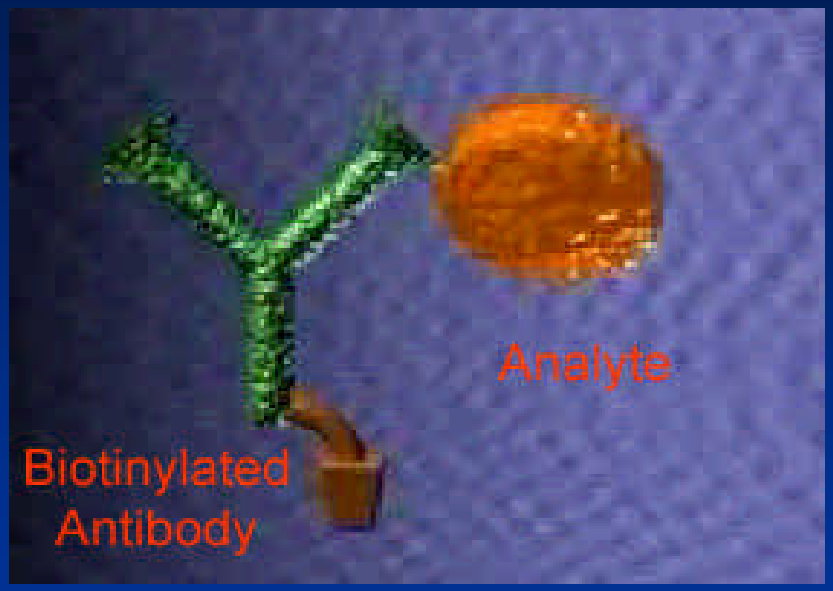
1st & 2nd ECL Responses

When $c_{Ru(bpy)_3^{2+}}$ >= 0.050 mM

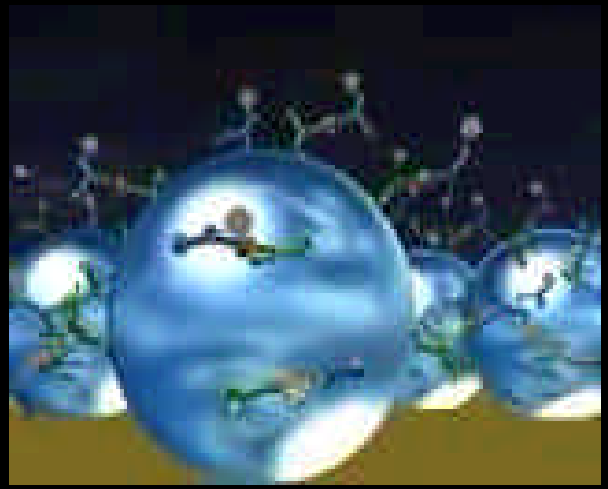


0.20 M PBS, pH ~ 8, 100 mV/s, GC

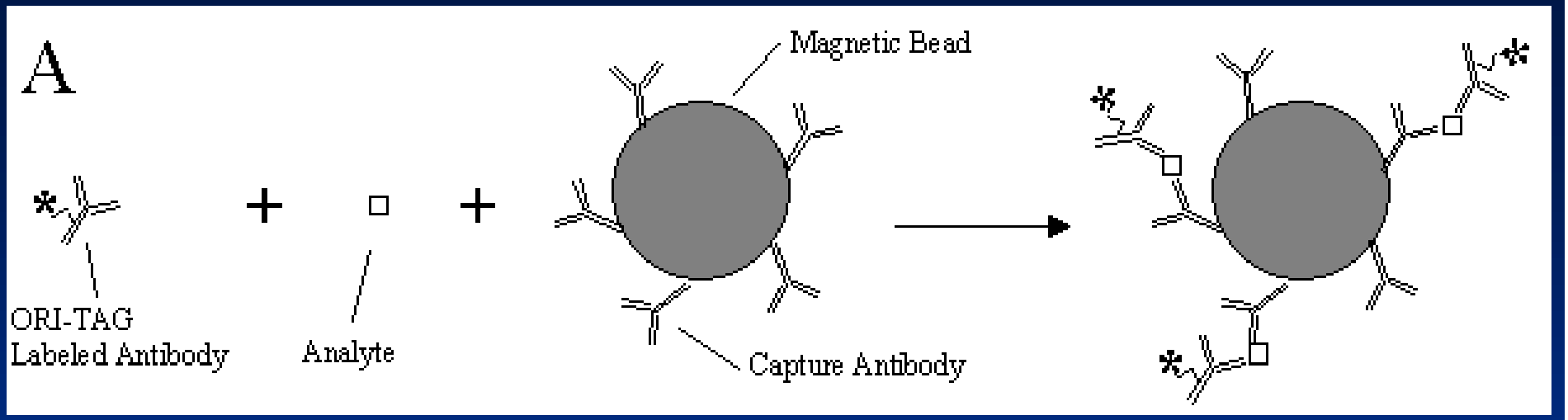
ECL at Labeled Magnetic Beads



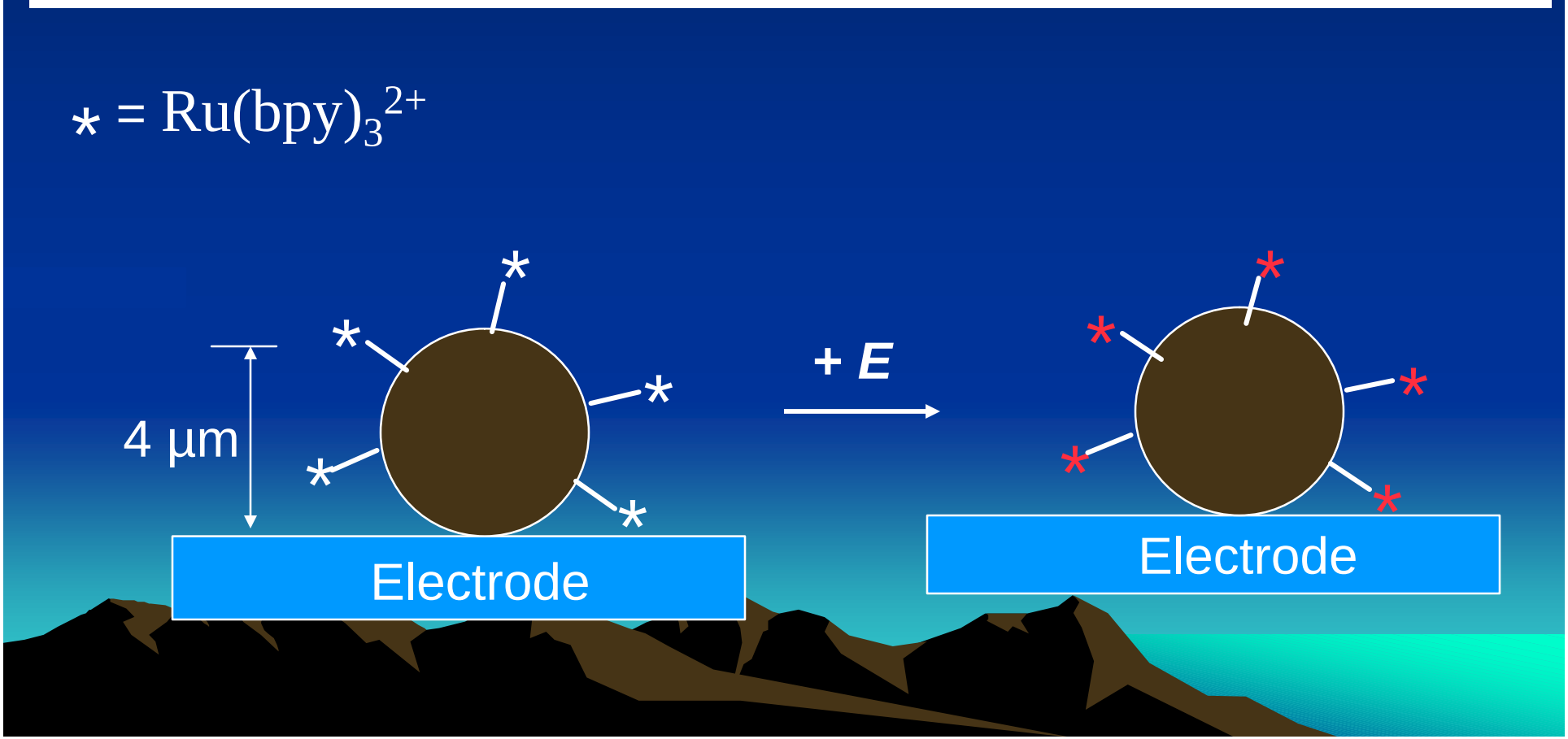

Electrode



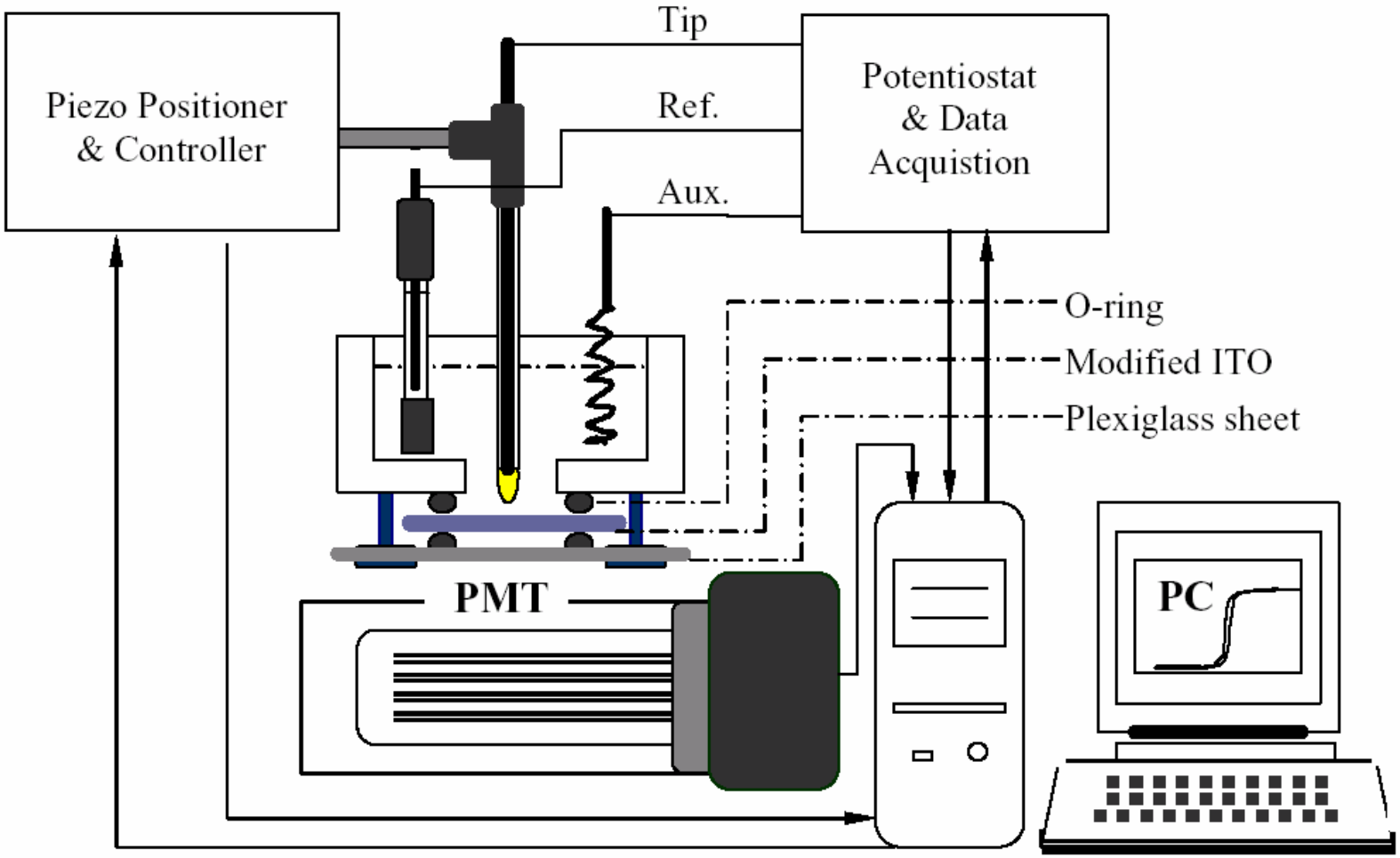

PMT Detector


A
Magnetic Bead
ORI-TAG
Labeled Antibody
Analyte
Capture Antibody

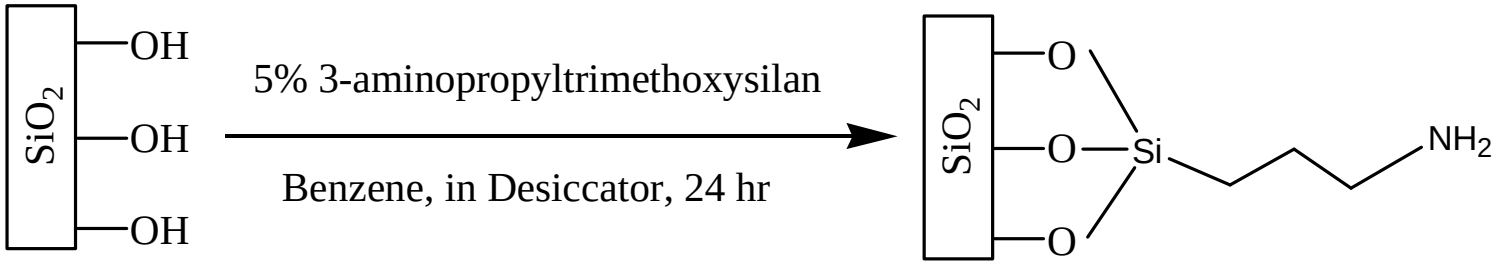
$* = Ru(bpy)_3^{2+}$


4 µm
Electrode
+ E
Electrode

SECM-ECL Experimental Set-Up

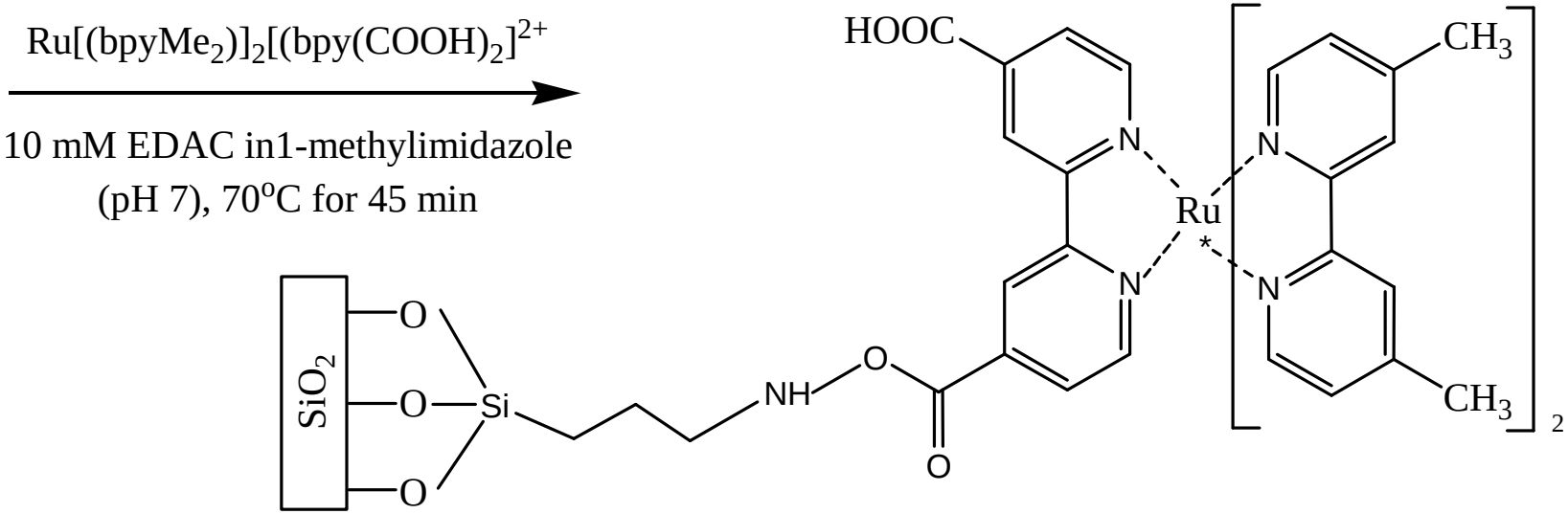


Silanization



ITO

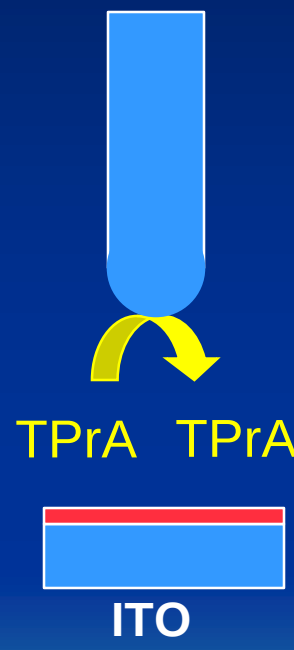
Schematic Structure of Silanized ITO Surface

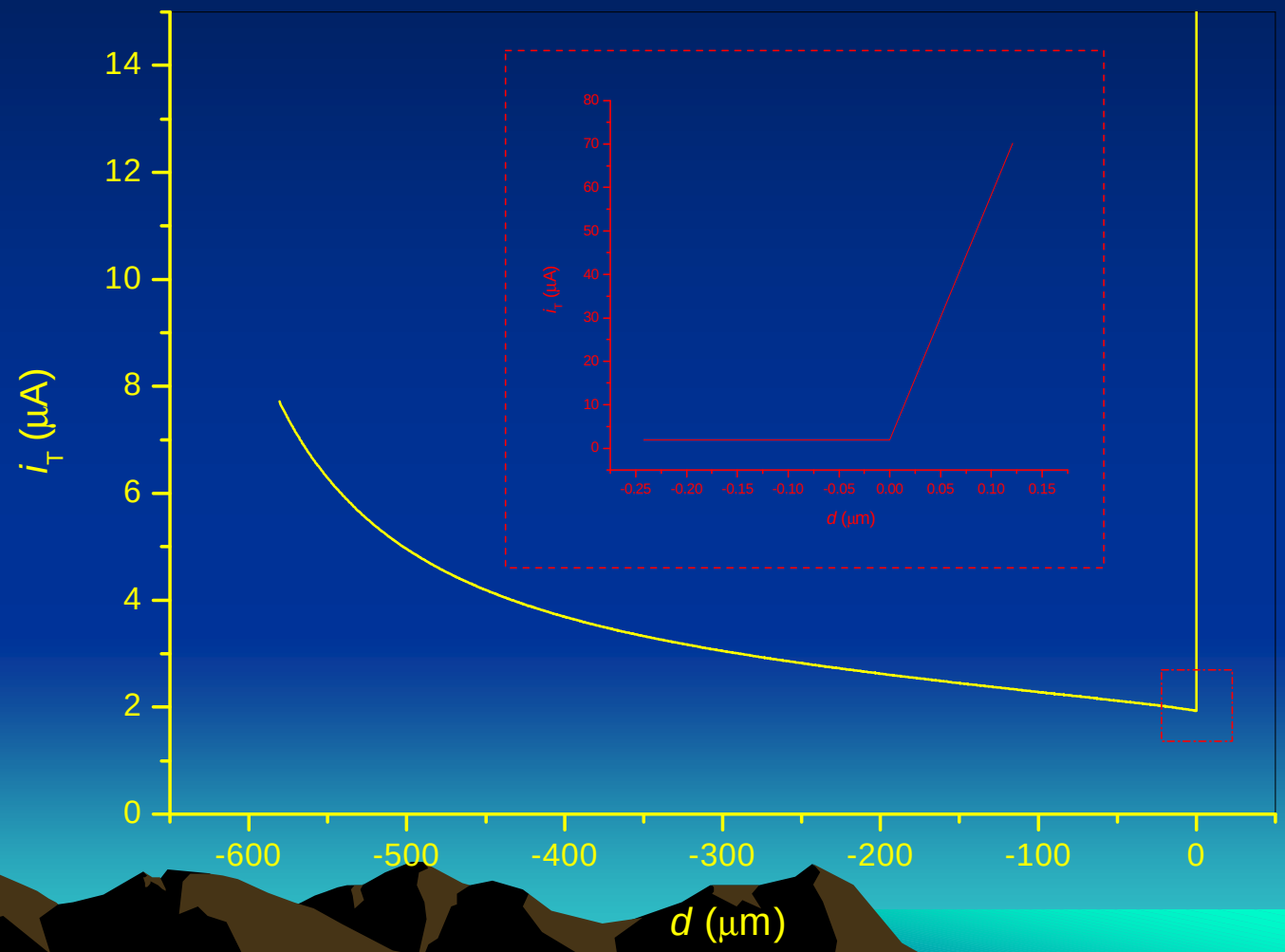


ITO/OSiRu^{II}

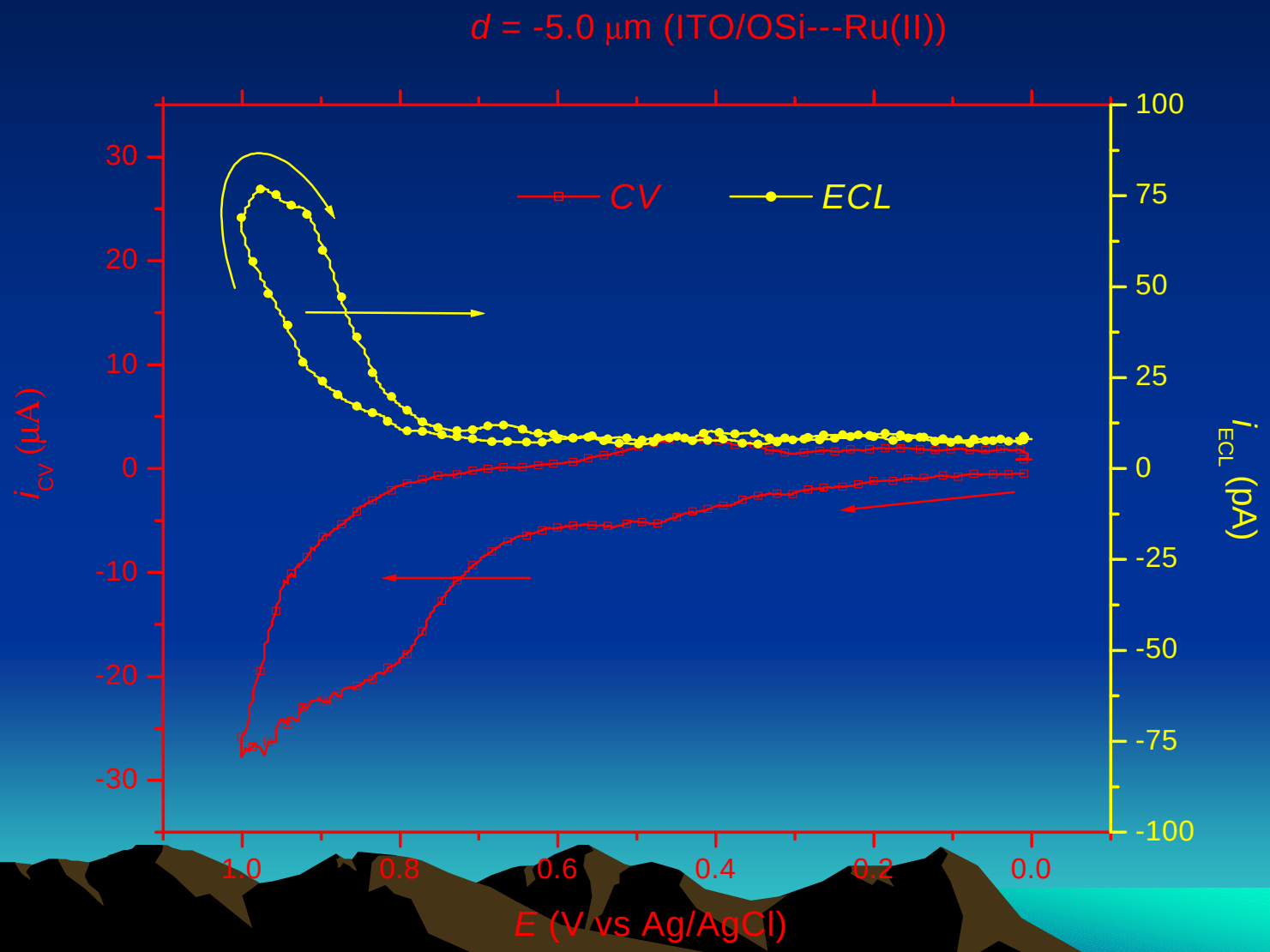
Approach curve (tip current vs. distance)

(f =1.5 mm hemispherical Au at +0.85 V vs Ag/AgCl, in 10 mM TPrA+100 mM $LiClO_4$+100 mM Tris buffer (pH = 8) Soln)



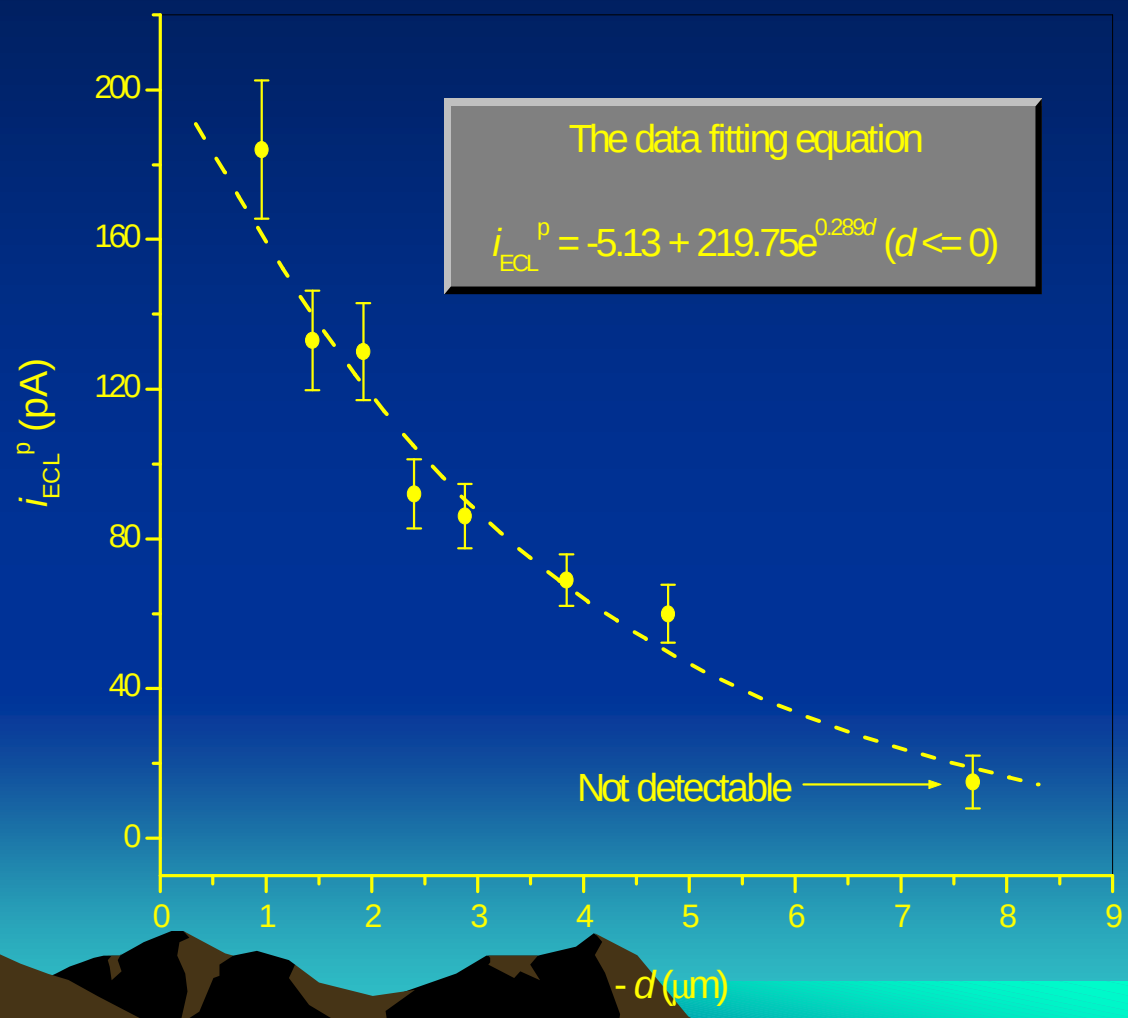


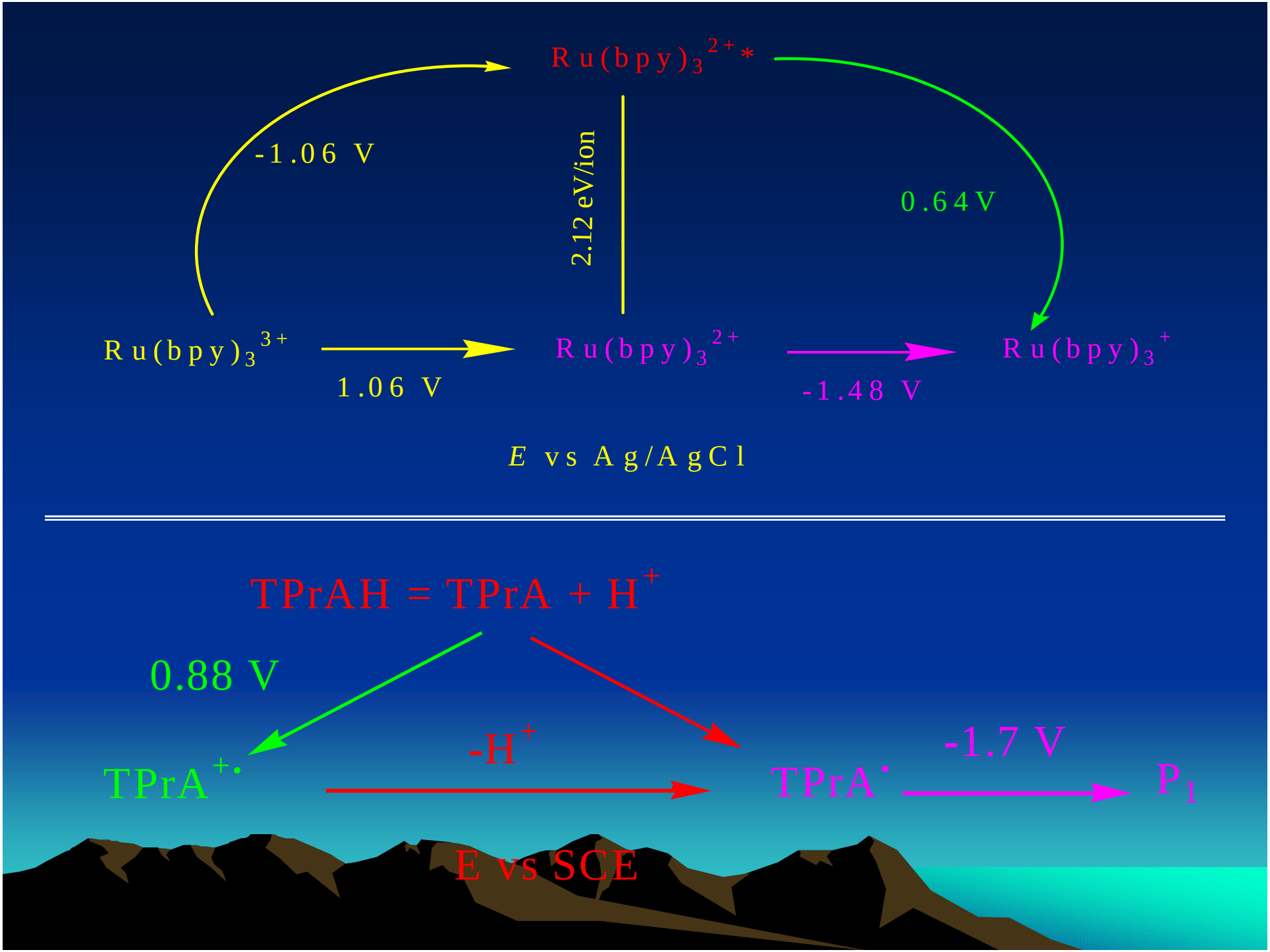
ECL Detection Without Touching with $Ru(bpy)_3^{2+}$/ITO



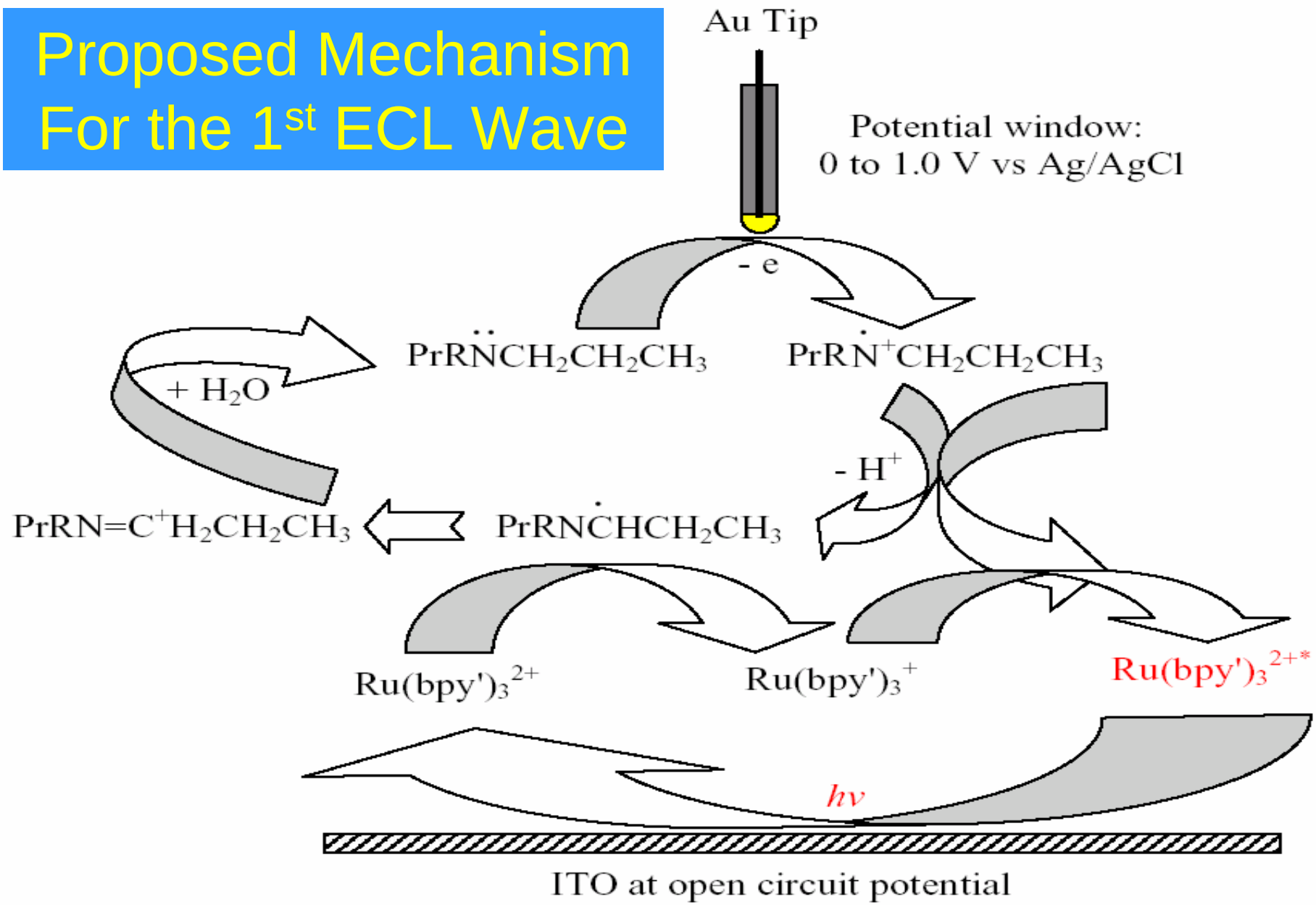
Tip ~ Substrate Separation Effect on ECL Intensity

- *d* (mm)	ECL Intensity (pA)
0.96	184
1.44	133
1.92	130
2.40	92
2.88	86
3.84	69
4.80	60
7.68	Not detectable



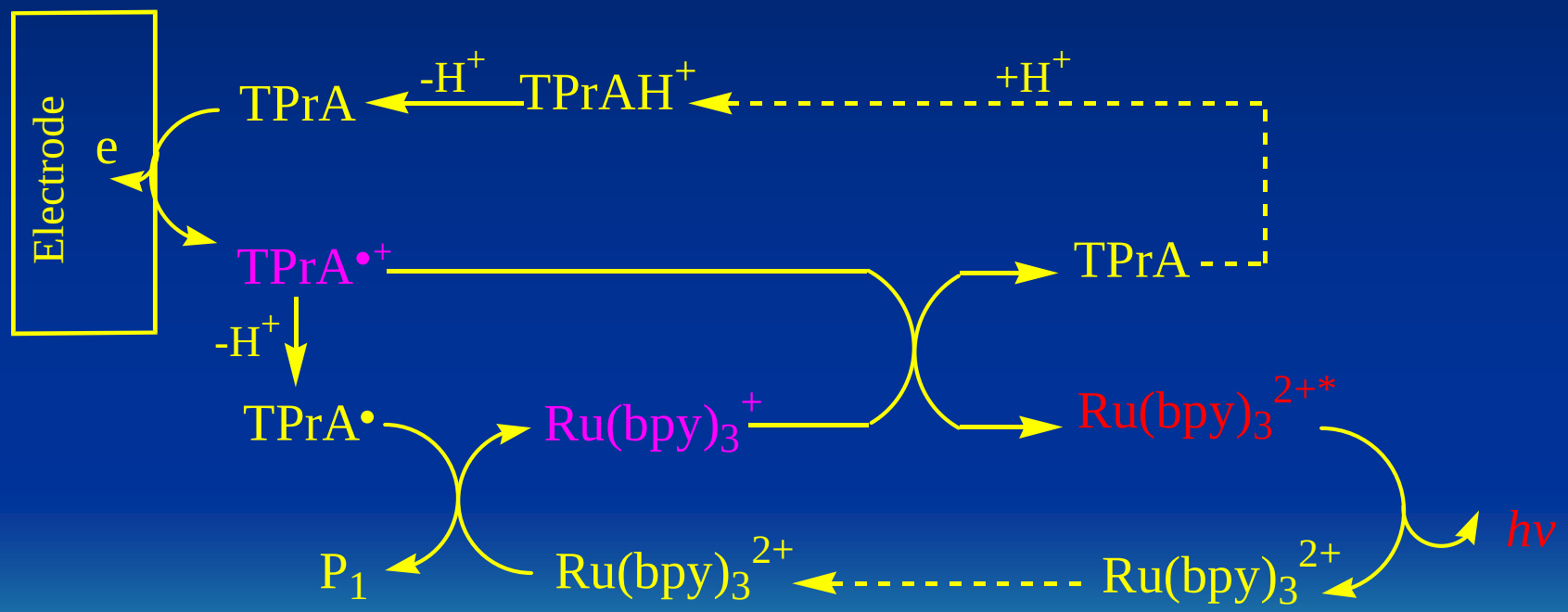

Ru(bpy)3 2+*
-1.06 V
2.12 eV/ion
0.64V
Ru(bpy)3 3+
1.06 V
Ru(bpy)3 2+
-1.48 V
Ru(bpy)3 +
E vs Ag/AgCl
TPrAH = TPrA + H+
0.88 V
-H+
-1.7 V
TPrA+•
TPrA•
P1
E vs SCE

Proposed Mechanism For the 1st ECL Wave



R: Pr = $CH_2CH_2CH_3$ & H

A New Route for the Generation of $Ru(bpy)_3^{2+*}$ in $Ru(bpy)_3^{2+}$/TPrA System



Reaction Processes Involved for the Oxidation of TPrA

$$TPrAH^+ \underset{}{\overset{pK_a = 10.4}{\rightleftharpoons}} TPrA + H^+$$

$$TPrA \xrightarrow{k_s} TPrA^{\bullet +} + e$$

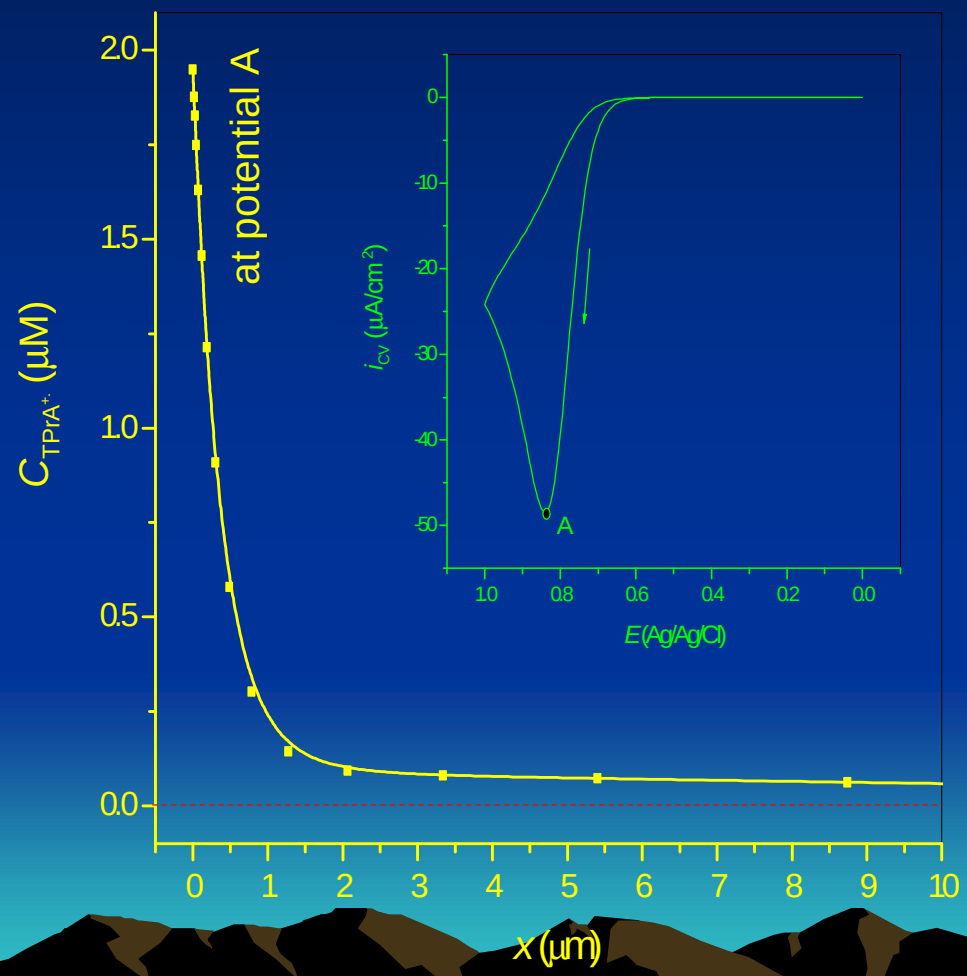
$$TPrA^{\bullet +} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} TPrA^{\bullet} + H^+$$

$$TPrA^{\bullet} \xrightarrow{k_s} P1 + e$$

$$P1 + H_2O = P2$$

and $$TPrA^{\bullet +} + TPrA^{\bullet} = TPrA + P1$$

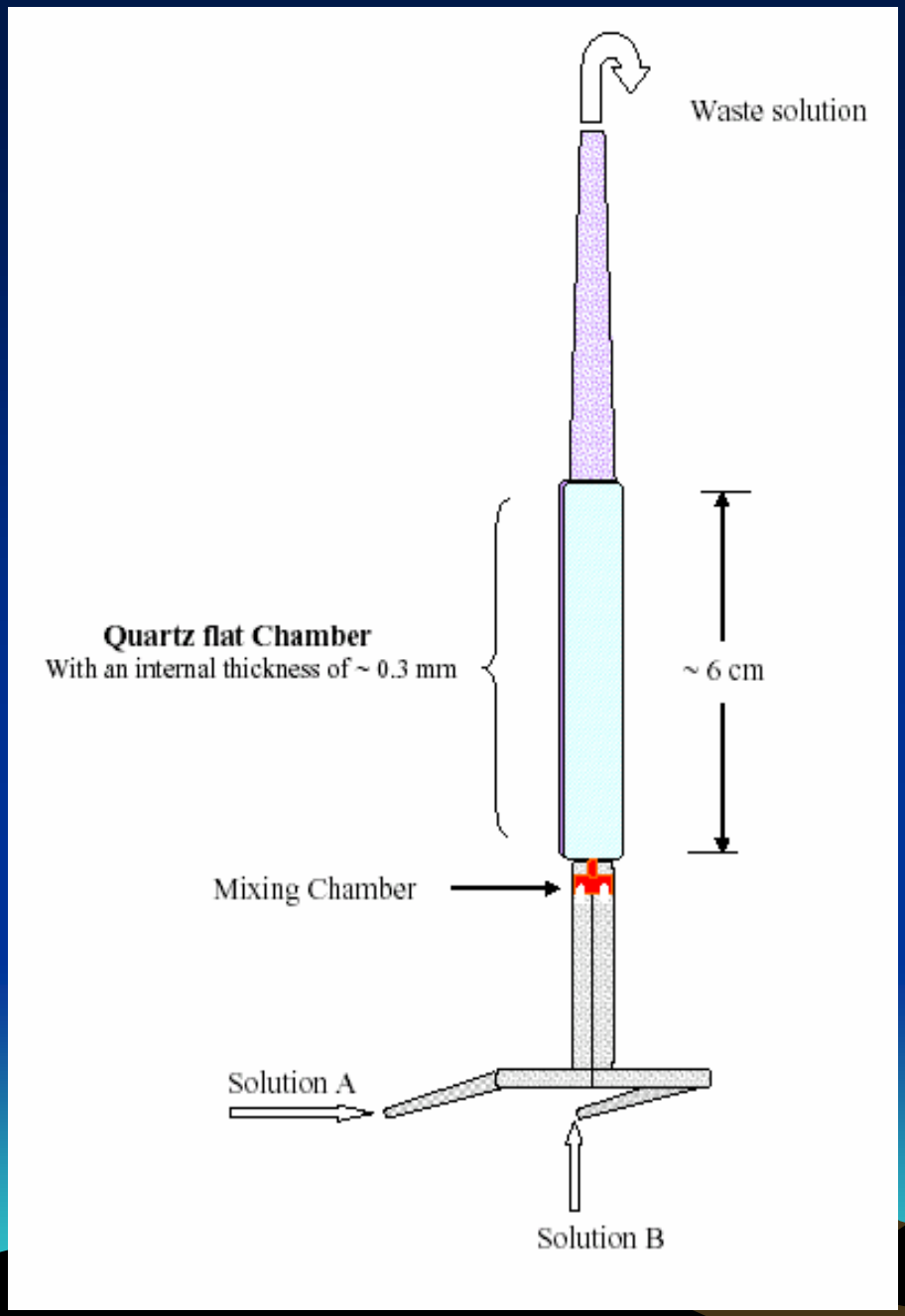
Half-life of $TPrA^{+\cdot}$ Cation Radical Based on CV Simulation



$$TPrA^{+\bullet} \xrightarrow{k_f} TPrA^{\bullet} + H^+$$

$$k_f = 3500$$

$$t_{2/1} = 0.693/k_f \sim 0.2 \text{ ms}$$



EPR Detection of $TPrA^{+\cdot}$

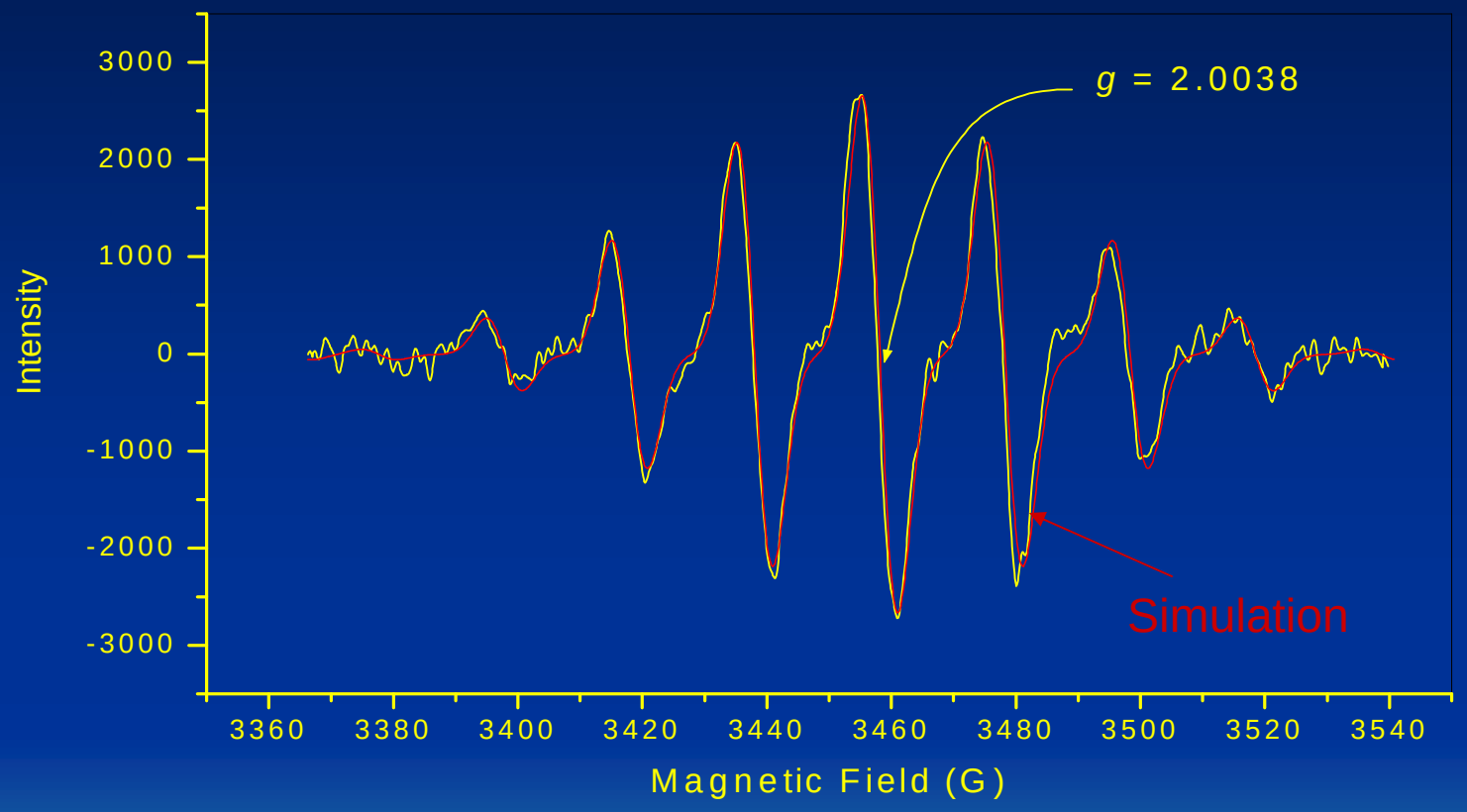
Solution A: 0.03 M $Ru(bpy)_3^{3+}$ Freshly Generated By Oxidized $Ru(bpy)_3^{2+}$ Using Cl_2

Solution B: 0.10 M TPrA at pH 7

Flow Rate: 2 to 5 mL/s

EPR Reference: Fremy's Salt ($K_2[NO(SO_3)_2]$)

EPR of $TPrA^{+\cdot}$ obtained by mixing 0.03 M $Ru(bpy)_3^{3+}$ and 0.10 M TPrA (pH = 7) solutions in a quartz flat EPR cell

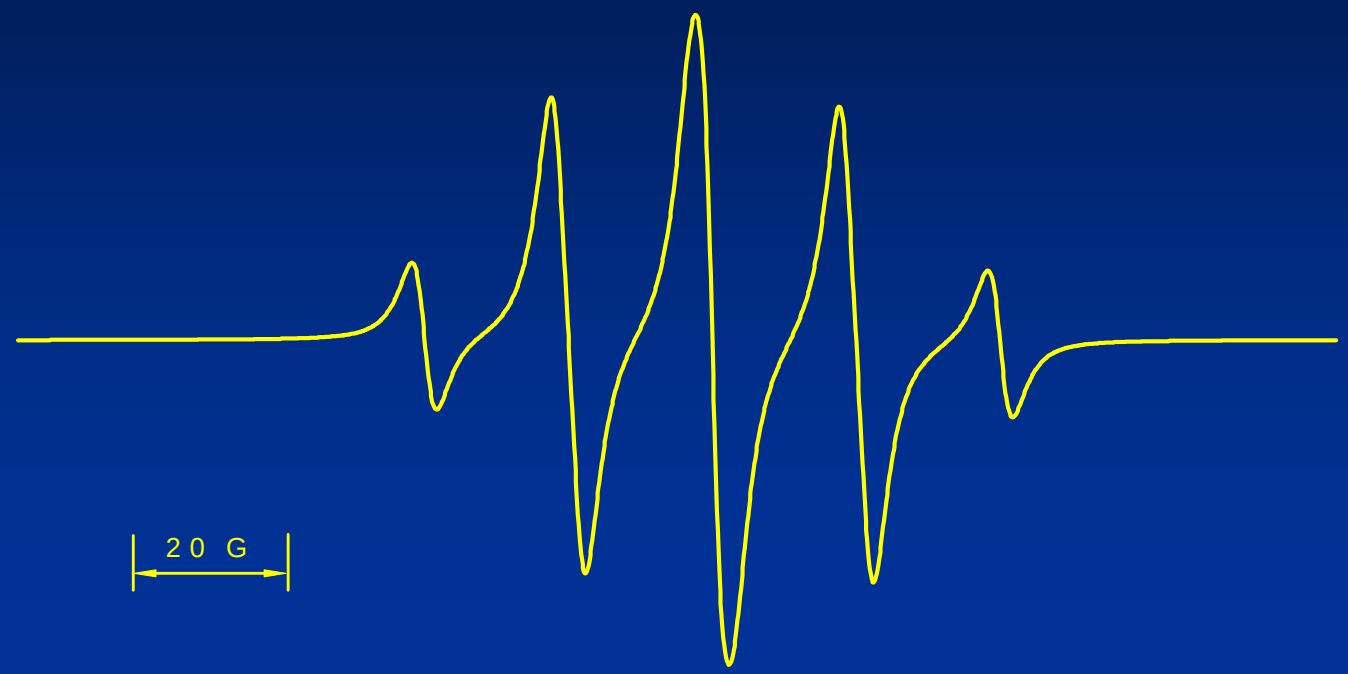


Simulation Parameters:

^{14}N (1N, I = 1), Hyperfine = 19.87G,

α–^{1}H (6H, I = 0.5), Hyperfine = 20.05 G

Simulated EPR for TPrA$^{\cdot}$



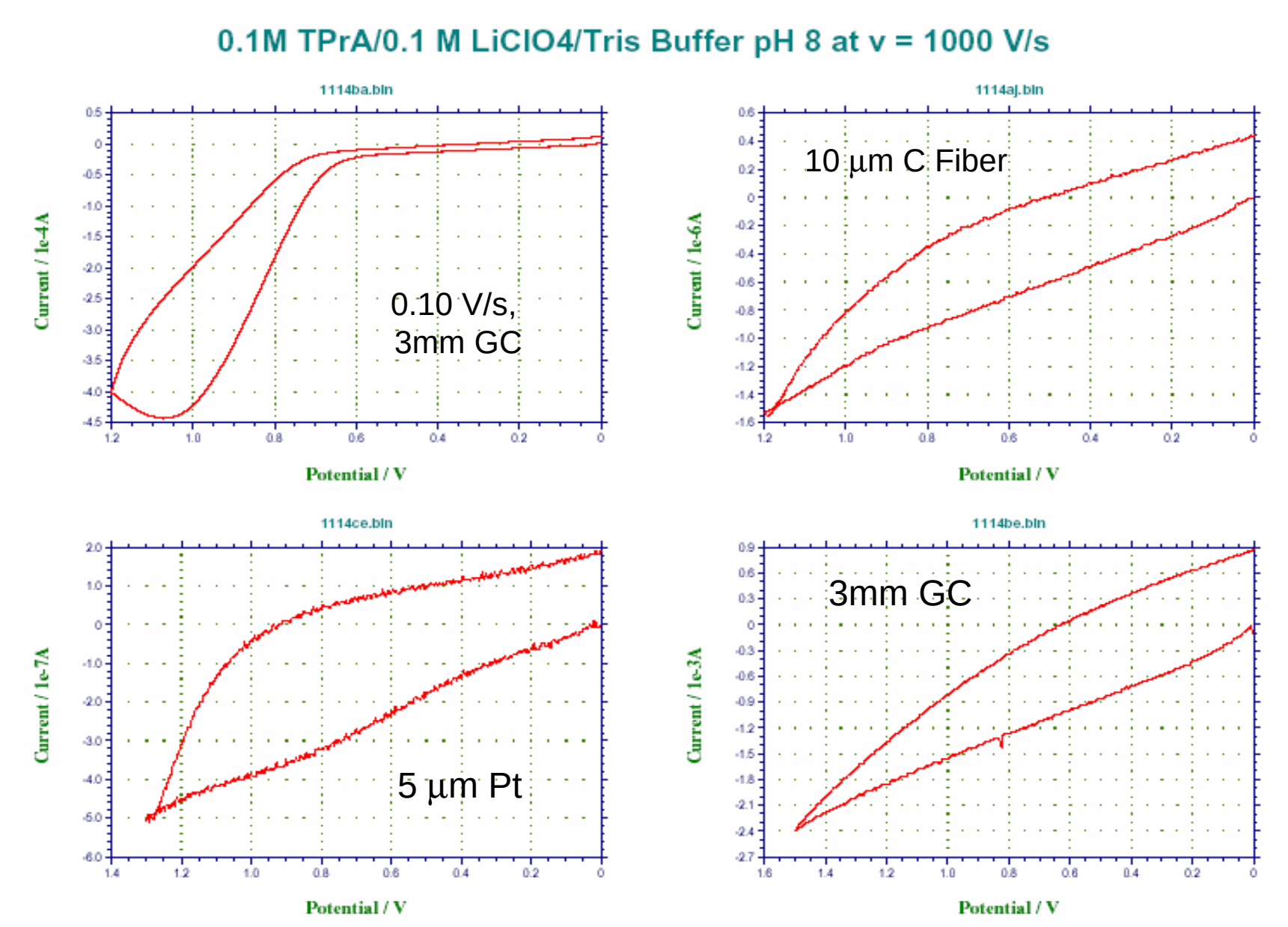
$(CH_3CH_2CH_2)_2N\text{-}C^{\cdot}H\text{-}CH_2CH_3$

Parameters used for the carbon free radical simulation:

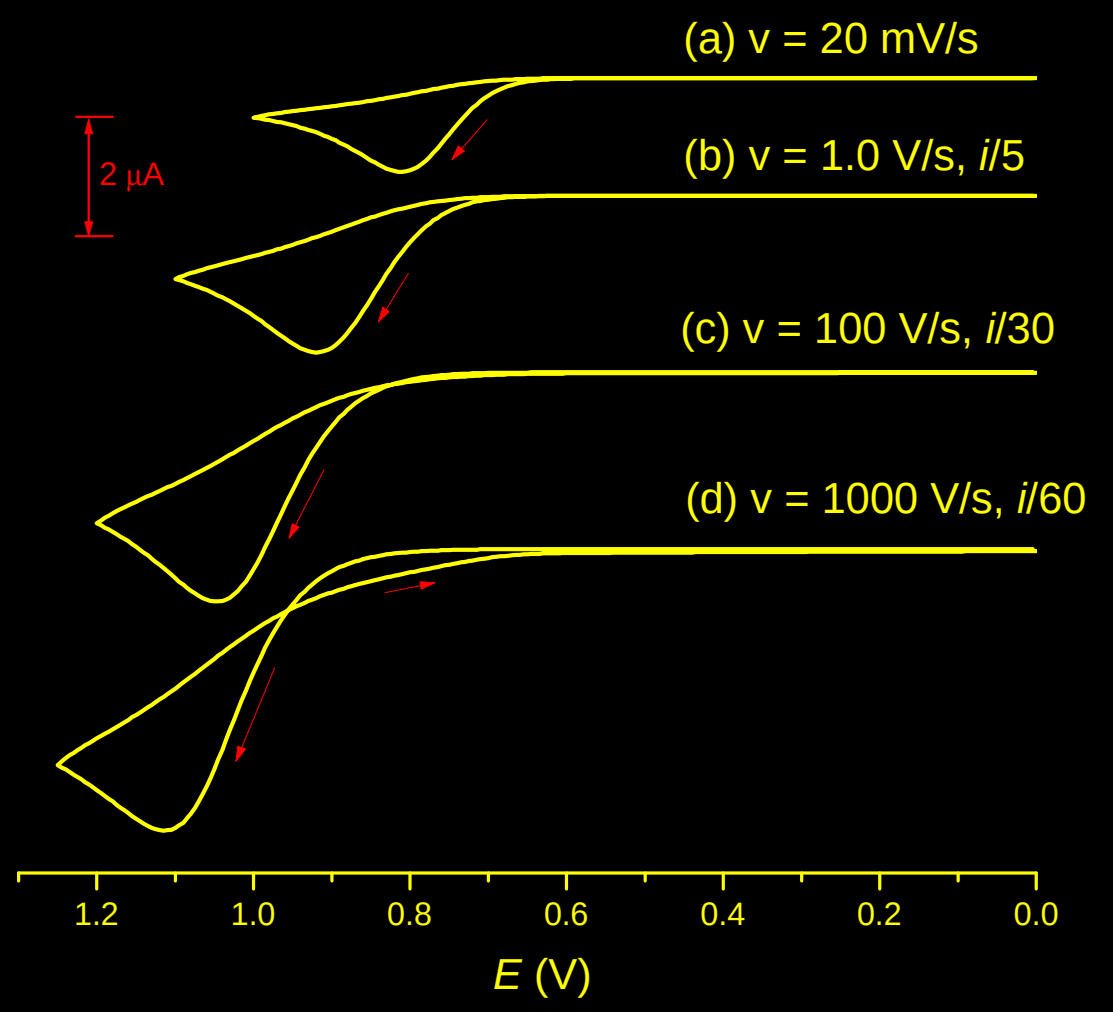
^{13}C (1, I = 1/2, hyperfine 20 G),

α ^{1}H (1, I = 1/2, hf = 20 G), β ^{1}H (2, I = 1/2, hf = 18 G)

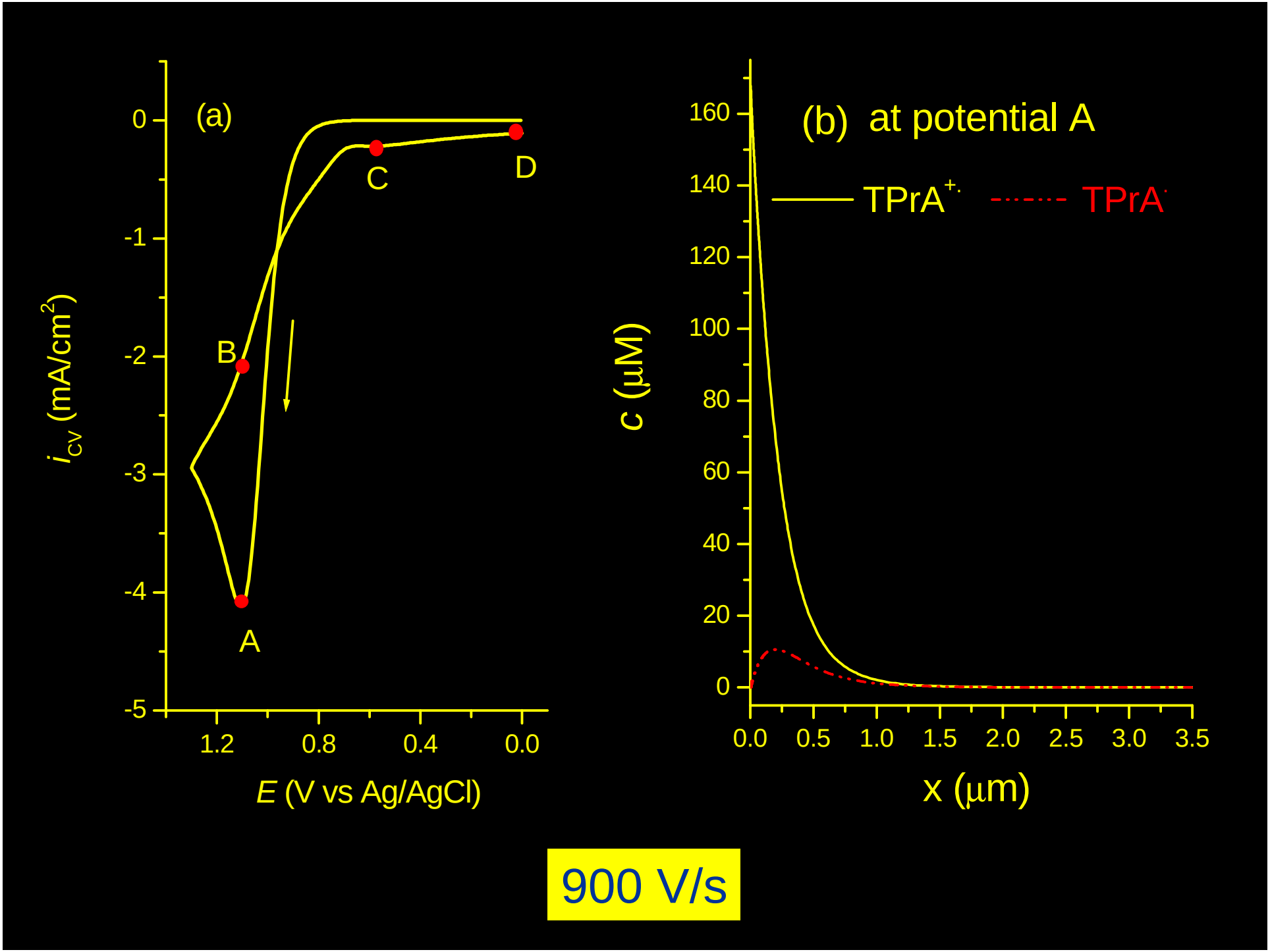
Fast Scan Cyclic Voltammetry

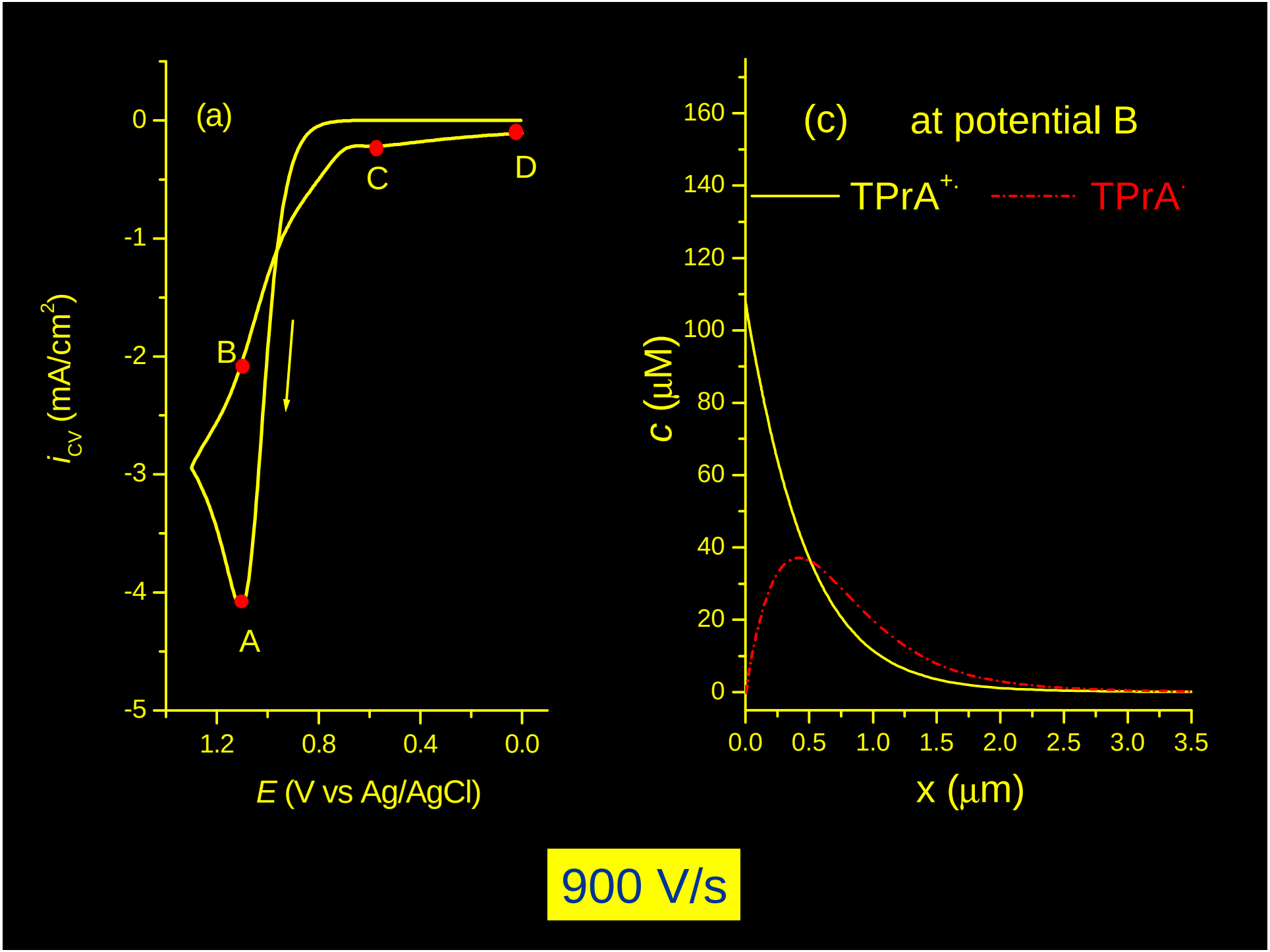


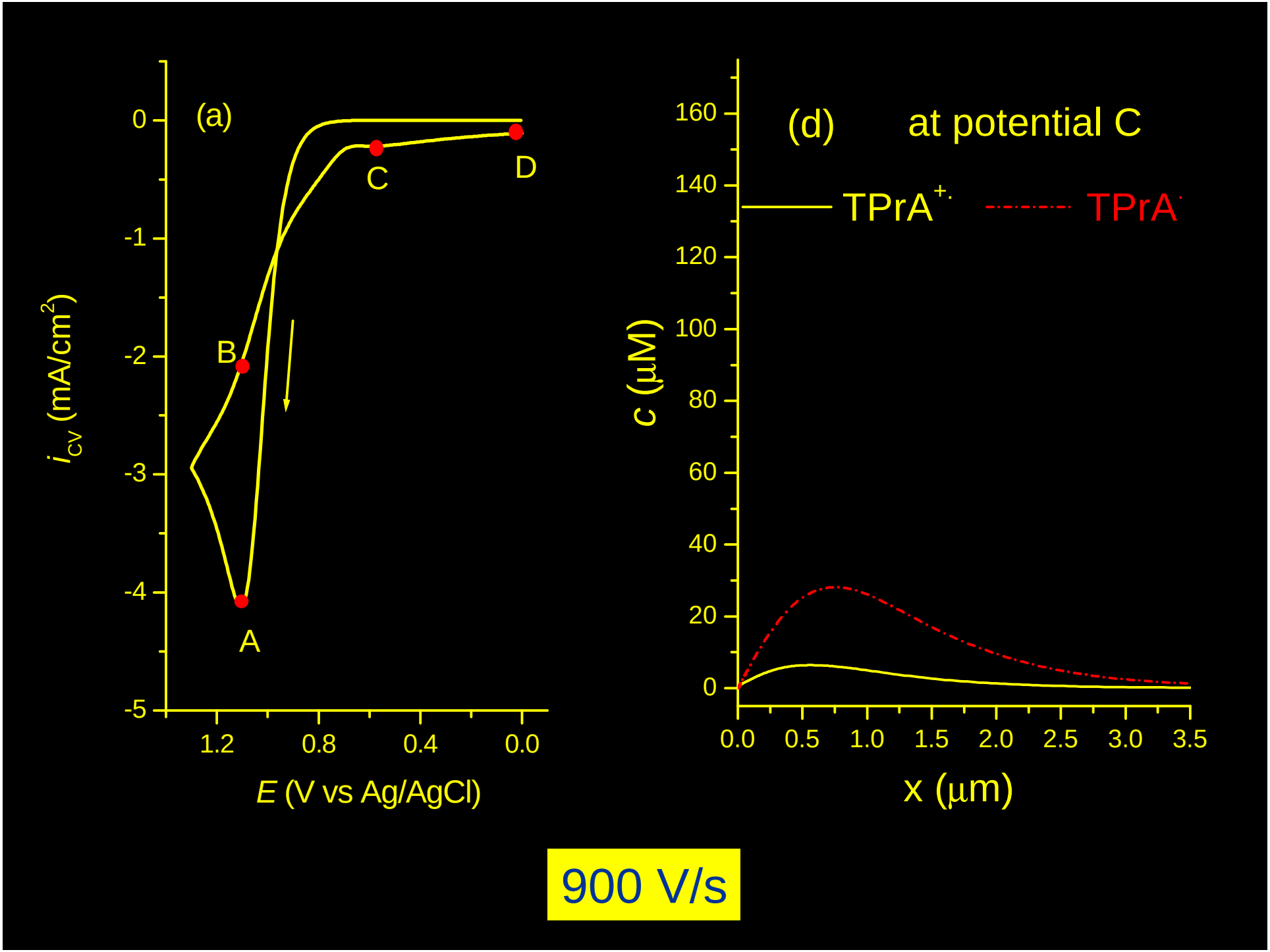
Fast Scan CV Digital Simulations

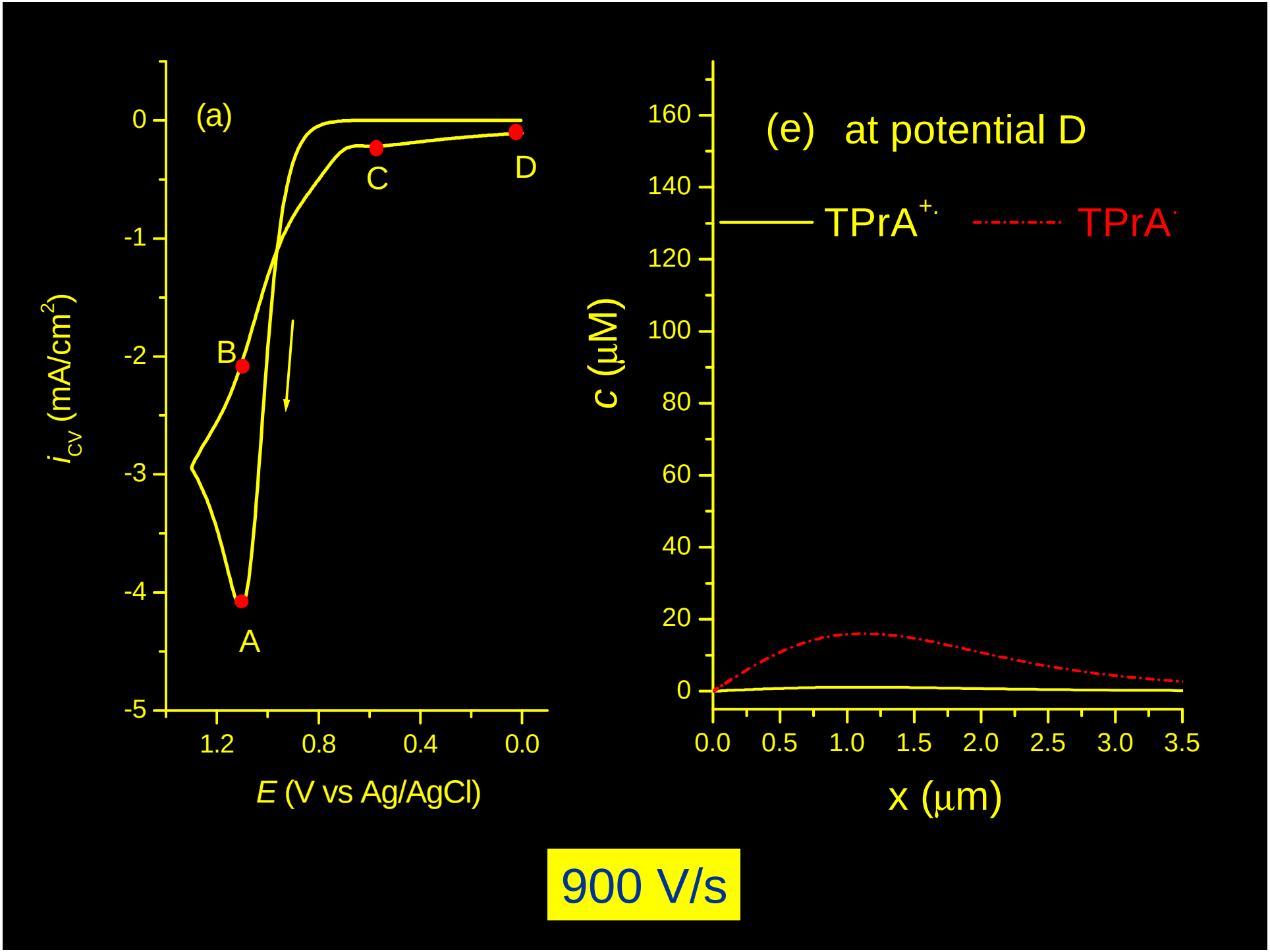


TPA_sim_E&i


(a)
0
-1
-2
-3
-4
-5
i_{CV} (mA/cm^2)
A
B
C
D
1.2
0.8
0.4
0.0
E (V vs Ag/AgCl)
(b) at potential A
160
140
120
100
80
60
40
20
0
c (μM)
TPrA$^{+\cdot}$
TPrA$^{\cdot}$
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
x (μm)
900 V/s


(a)
0
-1
-2
-3
-4
-5
i_{CV} (mA/cm^2)
A
B
C
D
1.2
0.8
0.4
0.0
E (V vs Ag/AgCl)
(c) at potential B
TPrA$^{+\cdot}$
TPrA$^{\cdot}$
160
140
120
100
80
60
40
20
0
c (μM)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
x (μm)
900 V/s


(a)
0
-1
-2
-3
-4
-5
i_{CV} (mA/cm^2)
A
B
C
D
1.2
0.8
0.4
0.0
E (V vs Ag/AgCl)
(d)
at potential C
TPrA$^{+\cdot}$
TPrA$^{\cdot}$
160
140
120
100
80
60
40
20
0
c (μM)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
x (μm)
900 V/s


(a)
0
-1
-2
-3
-4
-5
A
B
C
D
i_{CV} (mA/cm^2)
1.2
0.8
0.4
0.0
E (V vs Ag/AgCl)
(e) at potential D
TPrA$^{+\cdot}$
TPrA$^{\cdot}$
160
140
120
100
80
60
40
20
0
c (μM)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
x (μm)
900 V/s

Conclusions

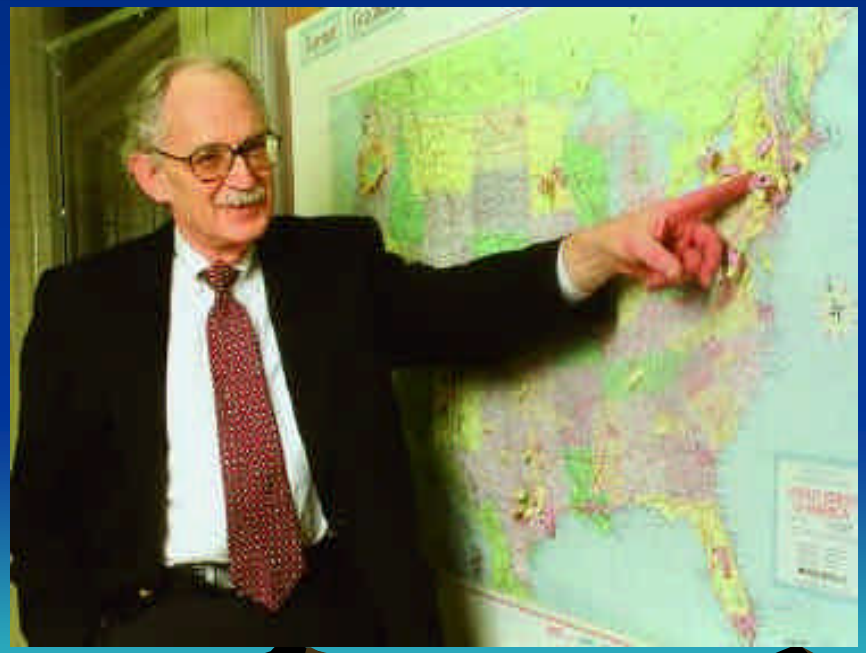
$TPrA^{+\cdot}$ **is sufficiently stable in neutral aqueous solution to oxidize $Ru(bpy)_3^{+}$ to generate $Ru(bpy)_3^{2+*}$;**

Under some ECE conditions, fast scan CV will not show short-lived species;

The ECL behavior of the $Ru(bpy)_3^{2+}$/TPrA system is complicated and involves several paths to the generation of excited state.

Acknowledgement

Dr Allen J Bard



Mr Jai-Pil Choi