

Electrogenerated Chemiluminescence of the  
Tris(2,2'-bipyridine)ruthenium(II)/Tri-*n*-propylamine (TPrA)  
System: Crucial Role of the Long Lifetime of TPrA<sup>•+</sup> Cation  
Radicals Suggested by Electrode Surface Effects

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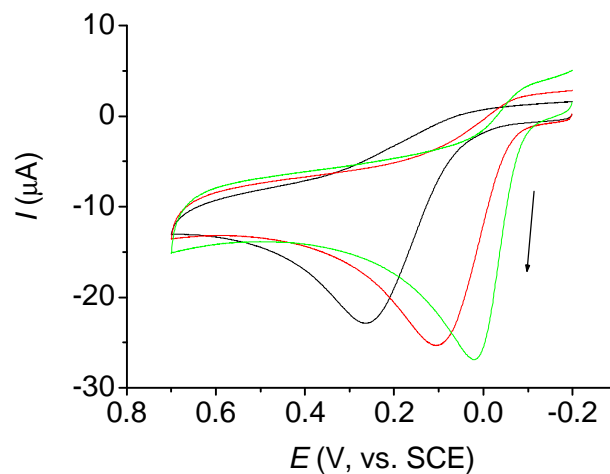
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Supporting Information

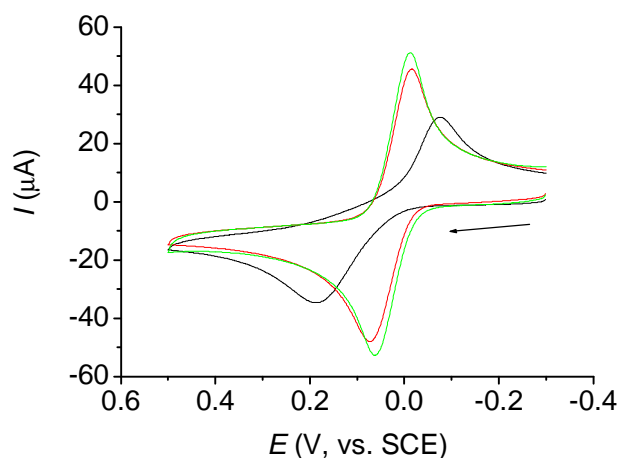
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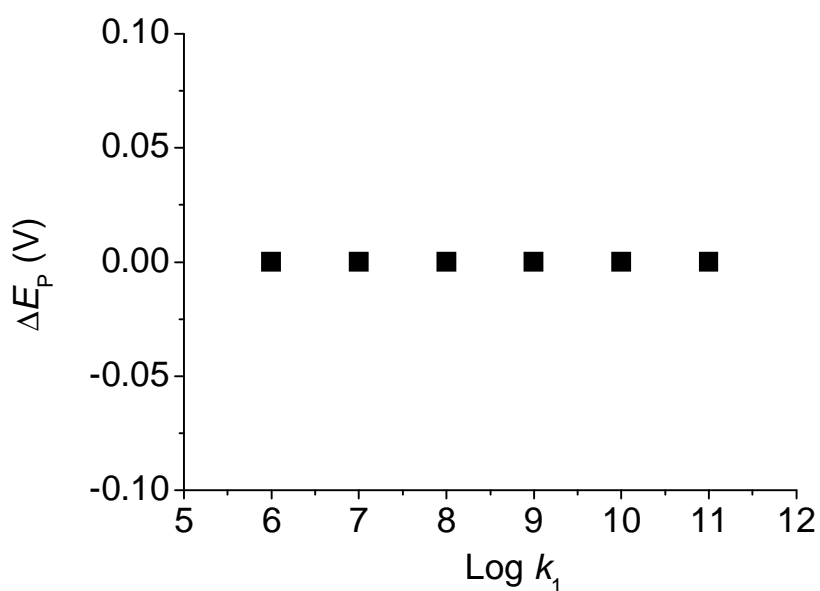
E-mail address: [ybzu@ibn.a-star.edu.sg](mailto:ybzu@ibn.a-star.edu.sg) (Y. Zu).



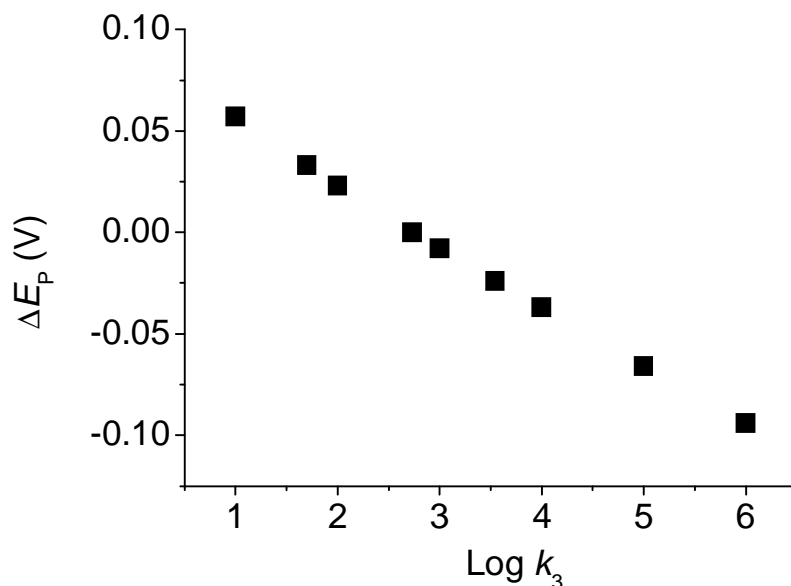
**Figure S1.** CV curves of 1 mM ascorbic acid in 0.15 M PBS (pH 7.5) at a freshly polished GCE (black line), and GCEs pretreated in potential ranges from -0.2 to 1.8 V (red line) or from -0.2 to 2.4 V (green line) for 10 cycles. Scan rate, 100 mV/s.



**Figure S2.** CV curves of 1 mM hydroquinone in 0.15 M PBS (pH 7.5) at a freshly polished GCE (black line), and GCEs pretreated in potential ranges from -0.2 to 1.8 V (red line) or from -0.2 to 2.4 V (green line) for 10 cycles. Scan rate, 100 mV/s.



**Figure S3.** Digital simulation (based on the CECE mechanism, eq.1 – eq.4 in the Introduction Section) of the shift of TPrA oxidation peak potential as a function of Log  $k_1$  (the rate constant of reaction 1). Parameters used in the simulation:  $E^0(\text{E1}) = 0.9 \text{ V vs SCE}$ ,  $k^0(\text{E1}) = 0.6 \text{ cm/s}$ ,  $k_3 = 540 \text{ s}^{-1}$ ,  $E^0(\text{E2}) = -1.7 \text{ V vs SCE}$ ,  $k^0(\text{E2}) = 10 \text{ cm/s}$ ,  $\alpha_1 = \alpha_2 = 0.5$ .  $C(\text{TPrA}) = 10 \text{ mM}$ . All species were assumed to have a diffusion coefficient of  $5 \times 10^{-6} \text{ cm}^2/\text{s}$  except for  $\text{H}^+$  ( $D_{\text{H}^+} = 5 \times 10^{-5} \text{ cm}^2/\text{s}$ ). Potential scan rate,  $100 \text{ mV/s}$ . The potential changes are calculated based on the  $E_p$  value when  $k_1 = 1 \times 10^{8.2} \text{ M}^{-1} \text{ s}^{-1}$ .



**Figure S4.** Digital simulation (based on the CECE mechanism, eq.1 – eq.4 in the Introduction Section) of the shift of TPrA oxidation peak potential as a function of Log  $k_3$  (the rate constant of reaction 3). Parameters used in the simulation were:  $k_1 = 10^{8.2} \text{ M}^{-1} \text{ s}^{-1}$ ,  $E^0(\text{E1}) = 0.9 \text{ V vs SCE}$ ,  $k^0(\text{E1}) = 0.6 \text{ cm/s}$ ,  $E^0(\text{E2}) = -1.7 \text{ V vs SCE}$ ,  $k^0(\text{E2}) = 10 \text{ cm/s}$ ,  $\alpha_1 = \alpha_2 = 0.5$ .  $C(\text{TPrA}) = 10 \text{ mM}$ . All species were assumed to have a diffusion coefficient of  $5 \times 10^{-6} \text{ cm}^2/\text{s}$  except for  $\text{H}^+$  ( $D_{\text{H}^+} = 5 \times 10^{-5} \text{ cm}^2/\text{s}$ ). Potential scan rate, 100 mV/s. The potential shifts were calculated based on the  $E_p$  value when  $k_3 = 540 \text{ s}^{-1}$ .