Supporting Information for Journal of the American Chemical Society article: *"Cyclic Transmembrane Charge Transport Mediated by Pyrylium and Thiopyrylium Ions"*, Rafail F. Khairutdinov and James K. Hurst, Department of Chemistry, Washington State University, Pullman, WA, USA 99164-4630

Derivation of Kinetic Equations for Transmembrane Diffusion of Neutral Pyrylium Radicals. All experiments reported were made under conditions where on average less than 0.6 TPP° or $TPTP^{\circ}$ radicals per vesicle were generated by the laser pulse. Under these conditions, the rate equations describing the radical decay are:

$$d[Pyr^{\circ}]_e / dt = -\tau_o^{-1}[Pyr^{\circ}]_e + \tau^{-1}\left(-[Pyr^{\circ}]_e + [Pyr^{\circ}]_i\right) \quad \text{(S1)}$$

$$d[Pyr^{\circ}]_i / dt = -(nk_q + \tau_o^{-1})[Pyr^{\circ}]_i + \tau^{-1}\left(-[Pyr^{\circ}]_i + [Pyr^{\circ}]_e\right) \quad \text{(S2)}$$

where the concentration subscripts i and e refer to the intravesicular and extravesicular location of the radicals, τ_o is the characteristic time for decay of Pyr° in the absence of $Co(bpy)_3^{3+}$, τ is the characteristic time for transmembrane diffusion of Pyr°, k_q is the rate constant of $(Pyr^{\circ})_i$ oxidation by $Co(bpy)_3^{3+}$ and n is the number of $Co(bpy)_3^{3+}$ ions located within a particular vesicle. Equations S1 and S2 can be solved analytically to give for the total (intravesicular and extravesicular) concentration of Pyr°:

$$\frac{[Pyr^{\circ}](t)}{[Pyr^{\circ}](0)} = F(t, \tau_o, \tau, nk_q) \equiv A_1(\tau_o, \tau, nk_q)e^{-\lambda_1 t} + A_2(\tau_o, \tau, nk_q)e^{-\lambda_2 t} \quad \text{(S3)}$$

where $A_1(\tau_o,\tau,nk_q)$ and $A_2(\tau_o,\tau,nk_q)$ are constants and

$\lambda_{1,2} = \dfrac{-(2/\tau_o + 2/\tau + nk_q) \pm \sqrt{4/\tau^2 + n^2k_q^2}}{2}$. Recognizing that the number of $Co(bpy)_3^{3+}$ within the population of vesicles follows the Poisson distribution, one obtains:

$$\frac{[Pyr^{\circ}](t)}{[Pyr^{\circ}](0)} = \sum_{n=0}^{\infty}\frac{m^n}{n!}\exp(-m)F(t, \tau_o, \tau, nk_q) \quad \text{(S4)}$$

where $m = [Co(bpy)_3^{3+}]/[ves]$ is the average number of $Co(bpy)_3^{3+}$ ions per vesicle. The characteristic decay time is the first moment of the decay kinetics, so we have:

$$\tau' = \int_0^{\infty}\frac{[Pyr^{\circ}](t)}{[Pyr^{\circ}](0)}dt = \sum_{n=0}^{\infty}\frac{m^n}{n!}\exp(-m)\int_0^{\infty}F(t, \tau_o, \tau, nk_q)dt \quad \text{(S5)}$$

where τ' is the experimentally observed characteristic time for Pyr° decay.

If $k_q >> \tau^{-1}$, τ_o^{-1}, it follows from Equation S5 that

$$\tau' = \frac{\tau_o}{\tau_o + \tau}(\tau + \tau_o e^{-m}) \quad \text{(S6)}$$

and the characteristic decay time changes from τ_o in the absence of $Co(bpy)_3^{3+}$ to $\tau_o\tau/(\tau_o+\tau)$ at large $Co(bpy)_3^{3+}$ concentrations. When $\tau_o >> \tau$, $\tau' = \tau$, i.e., the rate of decay equals the rate of transmembrane diffusion of Pyr^o.

If $k_q << \tau^{-1}$, τ_o^{-1} or $\tau_o^{-1} << k_q << \tau^{-1}$, it follows from Equation S6 that $\tau' = \tau_o$, so that the characteristic decay time remains unchanged upon addition of $Co(bpy)_3^{3+}$.

Only the first limiting case, $k_q >> \tau^{-1}$, can account for the experimental data (Figure 11). Consequently, the experimental decay time measures the characteristic time for transmembrane diffusion of Pyr^o.

Figure S1. Kinetics of $TPTP^+$ hydrolysis in DHP vesicles. Reactions were monitored by changes in absorption at 400 nm in 40 mM acetate buffer, pH 11. Conditions: $[TPTP^+]/[vesicle] = 160$ (1) and $[TPTP^+]/[vesicle] = 30$ (2). Solid lines are best fits to a sum of two exponents with $\tau_1 = 13.5$ s and $\tau_2 = 353$ s (1) and to a single-exponential rate law with $\tau = 13.5$ s (2).

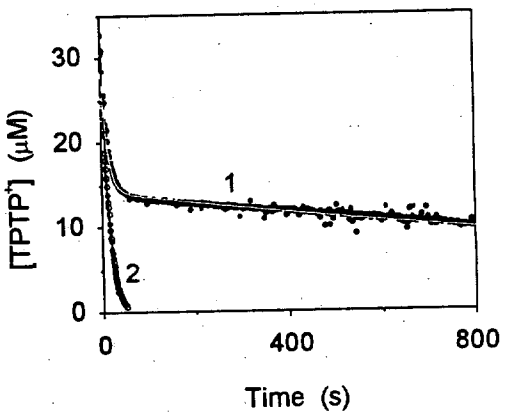

Figure S2. Emission spectra of $TPTP^+$. Conditions: in 40 mM acetate buffer, pH 5.0 (1), and bound to DHP vesicles at $[TPTP^+]/[vesicle] = 30$ (2) and $[TPTP^+]/[vesicle] = 160$ (3); $\lambda_{ex} = 400$ nm.