Supporting Information

For

External Electric Field Effect on Fluorescence Spectra of Pyrene in Solution

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With the kinetic model (Birk's model) shown in the text, it is given below how Eqs. (6) – (10) can be derived.

The quantum yield of monomer fluorescence is expressed in the form

$$\Phi_M = \frac{k_{fM}Y}{k_M Y + [c]k_{DM}k_D} \tag{1}$$

It is assumed that the radiative rate constant (k_{fM}) is independent of the electric field, and the field-induced change in the field-dependence rate constant is denoted by Δk. Then, the fluorescence quantum yield of the monomer fluorescence in the presence of electric field (Φ_M^F) is given by

$$\Phi_M^F = \frac{k_{fM}Y^F}{k_M^F Y^F + [c]k_{DM}^F k_D^F} = \frac{k_{fM}(Y+\Delta Y)}{(k_M+\Delta k_M)(Y+\Delta Y)+[c](k_{DM}+\Delta k_{DM})(k_D+\Delta k_D)} \tag{2}$$

Eq. (2) can be rewritten in the form

$$\Phi_M^F = \frac{k_{fM}(Y+\Delta Y)}{Z+\Delta Z} = \frac{k_{fM}(Y+\Delta Y)}{Z}\left(\frac{1}{1+\frac{\Delta Z}{Z}}\right) \tag{3}$$

where $Z = k_M Y + [c]k_{DM}k_D$, $\Delta Z = k_M \Delta Y + \Delta k_M(Y+\Delta Y) + [c]k_{DM}\Delta k_D + [c]\Delta k_{DM}(k_D + \Delta k_D)$. It would be reasonable to suppose that $\Delta Z << Z$. By using the relation, $\frac{1}{1-x} = \sum_{n=0}^{\infty} x^n$, and $|x| < 1$, Eq. (3) becomes

$$\Phi_M^F = \frac{k_{fM}(Y+\Delta Y)}{Z}\left(\frac{1}{1-(-\frac{\Delta Z}{Z})}\right) = \frac{k_{fM}(Y+\Delta Y)}{Z}\left(1+(-\frac{\Delta Z}{Z})+(-\frac{\Delta Z}{Z})^2+\cdots\right) \tag{4}$$

We may neglect $(\Delta Z/Z)^n$ with $n \geqq 2$, that is much smaller than $\Delta Z/Z$, and the following relation can be obtained:

$$\Phi_M^F \approx \frac{k_{fM}(Y+\Delta Y)}{Z}(1-\frac{\Delta Z}{Z}). \tag{5}$$

Using Eqs. (1) and (4) we obtain the following expression of $\Delta\Phi_M/\Phi_M$:

$$\frac{\Delta\Phi_M}{\Phi_M} = \frac{\Phi_M^F - \Phi_M}{\Phi_M} = \frac{\frac{k_{fM}(Y+\Delta Y)}{Z}(1-\frac{\Delta Z}{Z}) - \frac{k_{fM}Y}{Z}}{\frac{k_{fM}Y}{Z}} = \frac{\Delta Y}{Y} - \frac{\Delta Z}{Z} - \frac{\Delta Z}{Z}\frac{\Delta Y}{Y}. \tag{6}$$

By assuming that $\Delta Z\Delta Y/YZ$ is relatively small, the $\Delta\Phi_M/\Phi_M$ can be expressed in the form of

$$\frac{\Delta\Phi_M}{\Phi_M} \approx -\frac{\Delta Z}{Z} + \frac{\Delta Y}{Y}. \tag{7}$$

Then, the observed $\Delta I_M/I_M$, which is equivalent to $\Delta\Phi_M/\Phi_M$, can be roughly expressed as follows:

$$\frac{\Delta I_M}{I_M} \approx -(\frac{Y\Delta k_M + k_M\Delta k_{MD} + k_M\Delta k_D + [c]k_{DM}\Delta k_D + k_D[c]\Delta k_{DM}}{Z}) + \frac{\Delta k_{MD} + \Delta k_D}{Y} \tag{8}$$

Further simplification is made for Eq. (8) by assuming that $[c]\Delta k_{DM}\Delta k_D/Z$ and $\Delta k_M\Delta Y/Z$ are negligibly small. Then,

$$\frac{\Delta I_M}{I_M} \approx -\frac{k_D}{Z}[c]\Delta k_{DM} + \frac{[c]k_{DM}k_D}{YZ}\Delta k_{MD} - \frac{[c]k_{DM}k_{MD}}{YZ}\Delta k_D - \frac{Y}{Z}\Delta k_M \quad (9)$$

The quantum yield of excimer fluorescence can be represented by

$$\Phi_D = \frac{k_{fD}[c]k_{DM}}{k_M Y + [c]k_{DM}k_D} \quad (10)$$

Then, the yield of excimer fluorescence in the presence of electric field can be given by

$$\Phi_D^F \approx \frac{k_{fD}[c]k_{DM}^F}{k_M^F Y^F + [c]k_{DM}^F k_D^F} = \frac{k_{fD}[c](k_{DM} + \Delta k_{DM})}{(k_M + \Delta k_M)(Y + \Delta Y) + [c](k_{DM} + \Delta k_{DM})(k_D + \Delta k_D)} \quad (11)$$

By rearranging the above equation, the following can be obtained:

$$\Phi_D^F = \frac{k_{fD}[c](k_{DM} + \Delta k_{DM})}{Z + \Delta Z} = \frac{k_{fD}[c](k_{DM} + \Delta k_{DM})}{Z}\left(1 + (-\frac{\Delta Z}{Z}) + (-\frac{\Delta Z}{Z})^2 + \cdots\right) \quad (12)$$

Then $\Delta\Phi_D/\Phi_D$ can be expressed as

$$\frac{\Delta\Phi_D}{\Phi_D} = \frac{\frac{k_{fD}[c](k_{DM} + \Delta k_{DM})}{Z}(1 - \frac{\Delta Z}{Z}) - \frac{k_{fD}[c]k_{DM}}{Z}}{\frac{k_{fD}[c]k_{DM}}{Z}} = \frac{[c]\Delta k_{DM}}{[c]k_{DM}} - \frac{\Delta Z}{Z} - \frac{\Delta Z}{Z}\frac{[c]\Delta k_{DM}}{[c]k_{DM}} \quad (13)$$

On the assumption that $\Delta Z \Delta k_{DM} / Z k_{DM}$ is relatively small,

$$\frac{\Delta\Phi_D}{\Phi_D} \approx -\frac{\Delta Z}{Z} + \frac{[c]\Delta k_{DM}}{[c]k_{DM}} \quad (14)$$

The observed $\Delta I_D/I_D$, which is equivalent to $\Delta\Phi_D/\Phi_D$, can be expressed with the assumption that $[c]\Delta k_D \Delta k_{DM} / Z$ and $\Delta k_M \Delta Y / Z$ are relatively small:

$$\frac{\Delta I_D}{I_D} \approx -\left(\frac{Y\Delta k_M + k_M \Delta k_{MD} + k_M \Delta k_D + [c]k_{DM}\Delta k_D + k_D[c]\Delta k_{DM}}{Z}\right) + \frac{[c]\Delta k_{DM}}{[c]k_{DM}} \quad (15)$$

By rearranging the above equation,

$$\frac{\Delta I_D}{I_D} \approx \frac{k_M Y}{[c]k_{DM} Z}[c]\Delta k_{DM} - \frac{k_M}{Z}\Delta k_{MD} - \left(\frac{[c]k_{DM} + k_M}{Z}\right)\Delta k_D - \frac{Y}{Z}\Delta k_M \quad (16)$$

A combination between $\Delta I_M/I_M$ and $\Delta I_D/I_D$ gives the following relation:

$$
\begin{cases}
\dfrac{\Delta I_M}{I_M}\underline{\dfrac{k_M Y}{[c]k_{DM}Z}} = -\dfrac{k_D}{Z}\underline{\dfrac{k_M Y}{[c]k_{DM}Z}}[c]\Delta k_{DM} + \dfrac{[c]k_{DM}k_D}{YZ}\underline{\dfrac{k_M Y}{[c]k_{DM}Z}}\Delta k_{MD} \\
-\dfrac{[c]k_{DM}k_{MD}}{YZ}\underline{\dfrac{k_M Y}{[c]k_{DM}Z}}\Delta k_D - \dfrac{Y}{Z}\underline{\dfrac{k_M Y}{[c]k_{DM}Z}}\Delta k_M \\
\\
\dfrac{\Delta I_D}{I_D}\underline{\dfrac{k_D}{Z}} = \dfrac{k_M Y}{[c]k_{DM}Z}\underline{\dfrac{k_D}{Z}}[c]\Delta k_{DM} - \dfrac{k_M}{Z}\underline{\dfrac{k_D}{Z}}\Delta k_{MD} - (\dfrac{[c]k_{DM}+k_M}{Z})\underline{\dfrac{k_D}{Z}}\Delta k_D - \dfrac{Y}{Z}\underline{\dfrac{k_D}{Z}}\Delta k_M
\end{cases}
\tag{17}
$$

that is,

$$
\begin{aligned}
&\frac{\Delta I_M}{I_M}\frac{k_M Y}{[c]k_{DM}Z} + \frac{\Delta I_D}{I_D}\frac{k_D}{Z} = -(\frac{k_M k_{MD}}{ZZ} + \frac{k_M k_D + [c]k_{DM}k_D}{ZZ})\Delta k_D - \frac{Y}{Z}(\frac{k_M Y + [c]k_{DM}k_D}{[c]k_{DM}Z})\Delta k_M \\
&= -(\frac{k_M Y + [c]k_{DM}k_D}{ZZ})\Delta k_D - \frac{Y}{Z}(\frac{Z}{[c]k_{DM}Z})\Delta k_M = -\frac{1}{Z}\Delta k_D - \frac{Y}{Z[c]k_{DM}}\Delta k_M
\end{aligned}
\tag{18}
$$

and, we get

$$
\Delta k_D + \frac{Y}{[c]k_{DM}}\Delta k_M = -\frac{k_M Y}{[c]k_{DM}}\frac{\Delta I_M}{I_M} - k_D\frac{\Delta I_D}{I_D} \tag{19}
$$

If $[c]$ is extremely small, i.e., 0, the following relation can be obtained from Eq. (19) :

$$
\frac{\Delta I_M}{I_M} \approx -\frac{\Delta k_M}{k_M} \tag{20}
$$

Then, Δk_M can be derived from the results at very low concentration experiments.

Supporting Figures

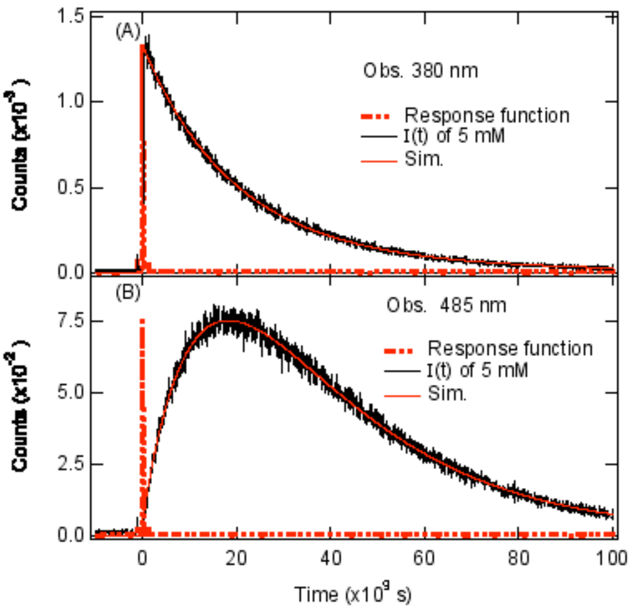

Figure S1. Fluorescence decay of monomer fluorescence at 380 nm (upper) and excimer fluorescence at 485 nm (lower) of pyrene solution at concentration of 5 x 10^{-3} M. Black line shows the observed decay, thin line shows the simulated decay, and chain line shows the response function of the scattered light. Excitation wavelength was 300 nm.

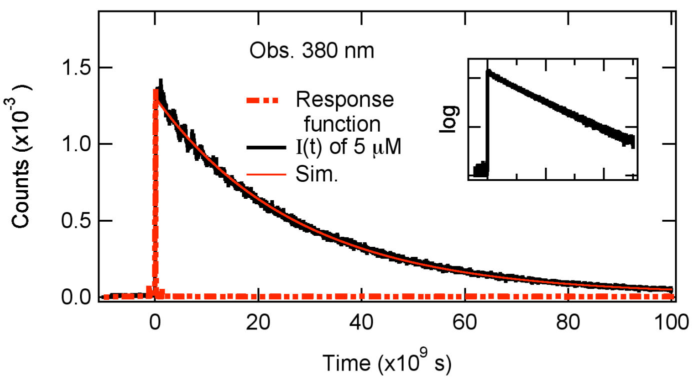

Figure S2. Fluorescence decay of monomer fluorescence of pyrene solution at a low concentration of 5 x 10^{-6} M. The decay in the logarithmic scale is shown in the inlet.