Appendix 1

A1. Estimation of binding constant from the absorption spectra

When a fluorophore (represented as A) and phase transfer catalyst (represented as B) interact to form a complex (denoted as C), the complexation process can be written as

\[ A + B \rightleftharpoons C \]  \hspace{1cm} (1)

The equilibrium concentration (indicated by the subscript, e) and the total concentration (indicated by the subscript, t) of a species are related as

\[ [A]_e = [A]_t - [C]_e \quad \text{and} \quad [B]_e = [B]_t - [C]_e \]

In the experimental condition, when \([B]_t \gg [A]_t\); \([B]_e\) can be equated to \([B]_t\).

The formation constant \((K)\) of the complex, \(K = \frac{[C]_e}{[A]_e[B]_e} \)  \hspace{1cm} (2)

Replacing \([B]_e\) by \([B]_t\) and \([A]_e\) as \([A]_t - [C]_e\)

We can write \(\frac{[A]_t[B]_t}{[C]_e} = \frac{1}{K} + [B]_t\)  \hspace{1cm} (3)

Taking into consideration the fact that the phase transfer catalyst, B does not contribute to the absorption in the spectral range studied, the total absorbance \((OD_t)\) at any given wavelength is the sum of that due to the complex and the probe. The total OD at any specific wavelength \((OD_t)\) can be expressed as, \(OD_t = \varepsilon_A[A]_e + \varepsilon_C[C]_e\), where \(\varepsilon\) is the molar extinction coefficient.

This can be transformed as, \(OD_t = \varepsilon_A[A]_e + (\varepsilon_C - \varepsilon_A)[C]_e = OD_A + OD_C\)
Where, $OD_A$ stands for the initial OD due to A at any given wavelength ($= \varepsilon_A[A]$), and $OD_C$ represents the OD at the same wavelength (at equilibrium) due to the complex ($= \varepsilon_C[C]$).

We can write, $[C]_e = \frac{\varepsilon_A OD_C[A]_s}{\varepsilon_k OD_A}$ \hspace{1cm} (4)

Where, $\varepsilon_k$ stands for $(\varepsilon_C - \varepsilon_A)$

Substituting the expression for $[C]_e$ from equation (4) into equation (3), we obtain

$$\frac{OD_A}{OD_t - OD_A} = \frac{1}{[B]_l} \left( \frac{1}{K \varepsilon_k} \right) + \frac{\varepsilon_A}{\varepsilon_k}$$ \hspace{1cm} (5)

**A2. Estimation of binding constant from the emission spectra**

Assuming a similar equilibrium between A and B (equation 1), we can rewrite the expression of the formation constant ($K$) as obtained in equation (2)

$$K = \frac{[C]_e}{[A]_e[B]_e}$$

replacing $[B]_e$ by $[B]_l$;

$$K = \frac{[C]_e}{[A]_e[B]_l}$$

If $I_A$ and $I_C$ represent the intensity of the light absorbed by fluorophore, A and complex, C respectively, then we can write

$$\frac{I_C}{I_A} = \frac{\varepsilon_C [C]_e}{\varepsilon_A [A]_e} = K \frac{\varepsilon_C [B]_l}{\varepsilon_A}$$
Assuming an identical molar extinction coefficient of the fluorophore \( \varepsilon_A \) and complex \( \varepsilon_C \), we can write

\[
\frac{I_C}{I_A} = K[B],
\]

We can express the overall fluorescence intensity (or quantum yield), \( \phi \) of the system (where both the fluorophore and the complex are emitting species) as,

\[
\phi = \frac{\phi_A I_A + \phi_C I_C}{I_A + I_C}
\]

where, \( \phi_A \) and \( \phi_C \) correspond to the individual emission intensity at a particular wavelength due to uncomplexed fluorophore and the complex, respectively.

Substituting the expression for \( \frac{I_C}{I_A} \) (from equation 6) in equation (7), we obtain,

\[
\phi = \frac{\phi_A + \phi_C K[B]}{1 + K[B]}
\]

Subtracting \( \phi_A \) from both sides we obtain

\[
\phi - \phi_A = \frac{K[B](\phi_C - \phi_A)}{1 + K[B]}
\]

Dividing equation (8) by \( \phi_A \) and then rearranging the same we get

\[
\frac{\phi_A}{\phi - \phi_A} = \left[ \frac{1}{K[B]} \right] \frac{1}{\phi_C - \phi_A} + \frac{\phi_A}{\phi_C - \phi_A}
\]
A1. Derivation of fluorescence response function of monomer and excimer

According to scheme 3, the time-dependence of $M(1)^*$ can be written as,

$$\frac{d}{dt}[M(1)^*] = -(k_1 + k_M)t$$

On integration we get,

$$\frac{[M(1)^*]}{[M^*]_0} = f_1 \exp(-(k_1 + k_M)t)$$

where, $f_1$ is the fraction of molecule originally present in $M(1)$ form and $[M^*]_0$ is the initial concentration of $[M(1)^*]$ at time, $t = 0$ after excitation with a $\delta$-function light flash.

Similarly, for the other species $M(2)^*$ we can write,

$$\frac{[M(2)^*]}{[M^*]_0} = f_2 \exp(-(k_2 + k_M)t)$$

The overall monomer response function, $I_M(t)$ will be the sum of the contributions from $M(1)^*$ and $M(2)^*$.

$$I_M(t) = k_{FM} \frac{[M(1)^*] + [M(2)^*]}{[M^*]_0} = k_{FM} [f_1 \exp(-(k_1 + k_M)t) + f_2 \exp(-(k_2 + k_M)t)]$$

For the excimer ($D^*$), the rate equation takes the form,

$$\frac{d[D^*]}{dt} = k_1 [M(1)^*] + k_2 [M(2)^*] - k_D [D^*]$$
Substituting the value of $[M(1)*]$ and $[M(2)*]$ in equation (4)

\[
\frac{d[D*]}{dt} + k_D[D*] = [M*]_0[k_1f_1 \exp(-(k_1 + k_M)t) + k_2f_2 \exp(-(k_2 + k_M)t)]
\]

Multiplying both sides by $\exp(k_Dt)$ and on integration we get

\[
\frac{[D*]}{[M*]_0} = \frac{k_1f_1}{(k_D - k_1 - k_M)} \exp(-(k_1 + k_M)t) + \frac{k_2f_2}{(k_D - k_2 - k_M)} \exp(-(k_2 + k_M)t)
\]

\[
- \left[ \frac{k_1f_1}{(k_D - k_1 - k_M)} + \frac{k_2f_2}{(k_D - k_2 - k_M)} \right] \exp(-k_Dt)
\]

Using equation (5), we obtain the following time-dependent response function of the excimer,

\[
I_D(t) = k_{FD} \frac{[D*]}{[M*]_0}
\]

\[
= \frac{k_{FD}k_1f_1}{(k_D - k_1 - k_M)} \exp(-(k_1 + k_M)t) + \frac{k_{FD}k_2f_2}{(k_D - k_2 - k_M)} \exp(-(k_2 + k_M)t)
\]

\[
- \left[ \frac{k_{FD}k_1f_1}{(k_D - k_1 - k_M)} + \frac{k_{FD}k_2f_2}{(k_D - k_2 - k_M)} \right] \exp(-k_Dt)
\]