

## Supporting Information

### A. General expression for electric field induced fluorescence quench $Q_F$

Equation (6) in the text defines the magnitude of electric field induced fluorescence quench as follows

$$Q_F = \frac{\phi_0 - \phi(F)}{\phi_0} \quad (\text{A1})$$

Derivation of this equation follows from the standard definition of fluorescence intensity ( $I(\tilde{\nu}) = \varepsilon(\tilde{\nu}) \cdot C \cdot l \cdot k \cdot \phi_f$ ) as described in the text. When experimental conditions are chosen such that the electric field effect on  $\varepsilon(\tilde{\nu})$  is negligible, such as when exciting at a zero-crossing of the electroabsorption spectrum, any changes to  $I(\tilde{\nu})$  are derived from electric field effects on the radiative ( $k_r$ ) and nonradiative ( $k_{nr}$ ) excited state relaxation rates. The following definitions were

used:  $\phi_F = \frac{k_r(F)}{k_r(F) + k_{nr}(F)}$ ,  $\phi_0 = \frac{k_r}{k_r + k_{nr}}$ , and  $k_r(F)$  is the radiative relaxation rate in the electric field and  $k_{nr}(F)$  is the corresponding nonradiative relaxation rate. As described in the text, field effects on the radiative relaxation rate have been found negligible; therefore,  $k_r(F) = k_r$ .

### B. Fluorescence quench as a function photophysical parameters

Fluorescence quench can be parameterized with the radiative and nonradiative rate constants by substituting the definitions of  $\phi_F$  and  $\phi_0$  into  $Q_F$ .

$$Q_F = \frac{\left( \frac{k_r}{k_r + k_{nr}} \right) - \left( \frac{k_r}{k_r + k_{nr}(F)} \right)}{\left( \frac{k_r}{k_r + k_{nr}} \right)} \quad (\text{B1})$$

This expression can be simplified by writing

$$Q_F = 1 - \left( \frac{k_r + k_{nr}}{k_r + k_{nr}(F)} \right) \quad (\text{B2})$$

and then

$$Q_F = \frac{k_{nr}(F) - k_{nr}}{k_r + k_{nr}(F)} \quad (\text{B3})$$

To allow for substitution of the analytical expressions for intersystem crossing ( $k_{isc}$ ) or internal conversion ( $k_{ic}$ ) into  $Q_F$ ,  $k_{nr}$  is factored out and the resulting expression simplified to give,

$$Q_F = \frac{k_{nr}}{k_{nr}} \times \left( \frac{k_{nr}(F)/k_{nr} - 1}{k_r/k_{nr} + k_{nr}(F)/k_{nr}} \right) \quad (\text{B4})$$

$$Q_F = \frac{\left( \frac{k_{nr}(F)}{k_{nr}} - 1 \right)}{\left( A + \frac{k_{nr}(F)}{k_{nr}} \right)} \quad (\text{B5})$$

Where  $A$  is a fit parameter defined as  $k_r/k_{nr}$ . Following the prescription in the text, the analytical expressions for  $k_{isc}$  or  $k_{ic}$  (eqns. 9 and 11) can now be introduced to yield eqns. (10) and (13).

### C. Fluorescence quench as a function of $k_{isc}$

Substitution of eq. (9) into  $Q_F$  is straightforward. The general expression relating  $k_{isc}$  to  $S_1 \rightarrow T_n$  energy gap is

$$k_{isc} \propto C \cdot \exp \left[ -\frac{(E_{ST} + \lambda)^2}{4\lambda RT} \right] \quad (\text{C1})$$

The singlet-triplet energy gap,  $E_{ST}$ , is sensitive to the Stark shift of  $S_1$  defined in the text by eq. (8). When the electric field is applied,  $E_{ST}$  shifts by  $\Delta\Delta\tilde{\nu}$  to give  $E_{ST} - \Delta\Delta\tilde{\nu}$ . The negative sign indicates the Stark shift is always to lower energy as

defined by eq. (8). Substituting this expression for  $E_{ST}$  into  $k_{isc}$  the following expression for the field effect on  $k_{isc}$  is derived,

$$k_{isc}(F) \propto C \cdot \exp \left[ -\frac{(E_{ST} - \Delta\tilde{\nu} + \lambda)^2}{4\lambda RT} \right] \quad (C2)$$

Equation (10) is expressed by substituting the expressions for  $k_{isc}$  and  $k_{isc}(F)$  into the general expression for fluorescence quench,  $Q_F$ , and simplifying,

$$Q_{ISC} = \frac{\left( \exp \left[ \frac{1}{4} \cdot \Delta\tilde{\nu} \cdot \frac{(2 \cdot E_{ST} - \Delta\Delta\tilde{\nu} - 2 \cdot \lambda)}{\lambda \cdot R \cdot T} \right] - 1 \right)}{\left( A + \exp \left[ \frac{1}{4} \cdot \Delta\tilde{\nu} \cdot \frac{(2 \cdot E_{ST} - \Delta\Delta\tilde{\nu} - 2 \cdot \lambda)}{\lambda \cdot R \cdot T} \right] \right)} \quad (C3)$$

#### D. Fluorescence quench as a function $k_{ic}$

Following a similar prescription,  $Q_{IC}$  can be derived by substituting eq. (11),

$$k_{ic} = C \cdot \exp \left( -\frac{\gamma}{\hbar\omega_m} \cdot E_g \right) \quad (D1)$$

into the general expression for fluorescence quench and by modifying the argument of the exponent in  $k_{isc}$  from  $E_g$  to  $E_g - \Delta\Delta\tilde{\nu}$  to express internal conversion as a function of Stark shift,  $k_{isc}(F)$ . Equation (13) directly follows,

$$Q_{IC} = \frac{\left( \exp \left[ \frac{\gamma}{\hbar\omega_m} \cdot \Delta\Delta\tilde{\nu} \right] - 1 \right)}{\left( A + \exp \left[ \frac{\gamma}{\hbar\omega_m} \cdot \Delta\Delta\tilde{\nu} \right] \right)} \quad (D2)$$

#### E. Modification to analytical expression for $\gamma$ .

The original expression for  $\gamma$  as taken from Ref. 104 is

$$\gamma = \ln \left( \frac{2\Delta E}{n\hbar\omega_m\Delta Q^2} \right) - 1 \quad (E1)$$

where  $\Delta E$  is the energy gap,  $n$  is the vibrational quantum number,  $\omega_m$  is the frequency of the dominant normal vibrational mode, and  $\Delta Q^2$  is the displacement between the minima of the ground and excited state potential energy surfaces.  $\Delta Q$  is related to the reorganization energy  $\lambda$  by

$$\lambda = n\hbar\omega_m S, \text{ where } S = \frac{\Delta Q^2}{2}$$

Substituting the expression for  $S$  and solving for  $\Delta Q$  yields

$$\Delta Q = \frac{2\lambda}{n\hbar\omega_m} \quad (\text{E2})$$

Equation 13 then follows.