Associated Content

Of the manuscript entitled

Energy transfer cascade in bio-inspired Chlorophyll-a / Polyacrylamide hydrogel: way towards a new class of biomimetic solar cell

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Average excited state lifetime was calculated from the formula

$$\tau_{avg} = \frac{a_1\tau_1^2 + a_2\tau_2^2 + a_3\tau_3^2}{a_1\tau_1 + a_2\tau_2 + a_3\tau_3} \qquad (13)$$

The reduced radiative lifetime was calculated from the equation

$$k_{rad} = \frac{\phi}{\tau_{avg}} \qquad (14)$$

This is related to exciton coherence of porphyrin species and extends over approximately 4 monomers in PaaChl_soak. Here ϕ is quantum yield determined using Chl-a in ethanol as a reference solution from the equation

$$\phi = \phi_{ref}\frac{\eta^2}{\eta_{ref}^2} \times \frac{I}{I_{ref}} \times \frac{A_{ref}}{A} \qquad (15)$$

Here ϕ_{ref} is quantum yield of the reference solution taken to be 0.25, I_{ref} and I are integrated fluorescence of PaaChl and Chl-a respectively. A_{ref} and A represent absorbance of PaaChl and Chl-a, whereas η_{ref}^2 and

η^2 stands for refractive indices of PaaChl and Chl-a respectively. We calculated the non-radiative decay rate following the equation

$$k_{nonrad} = \frac{1 - \phi}{\tau_{avg}} \qquad (16)$$

High dipole strength calculated from the equation

$$|\vec{\mu}^2| = k_{rad}\frac{3\epsilon_0 hc^3}{16\pi^3 v^3 n} \qquad (17)$$

Fluorescence decay of PaaChl was measured for parallel and perpendicular positions of emission polarizer relative to excitation polarizer and the value of anisotropy was calculated using the relation

$$r(t) = \frac{I_{\parallel}(t) + GI_{\perp}(t)}{I_{\parallel}(t) - 2GI_{\perp}(t)} \qquad (18)$$

Where $I_{\parallel}(t)$ and $I_{\perp}(t)$ are decay for parallel and perpendicular positions of the emission polarizer as a function of time. The G factor for the present setup was calculated to be 0.70. The anisotropy decay curve of PaaChl_soak was bi-exponentially fitted using the function

$$y = a_1 e^{-\frac{x}{t_1}} + a_2 e^{-\frac{x}{t_2}} \qquad (19)$$

Where as that of PaaChl_*in situ* could not be fitted. The initial anisotropy value is written as

$$r_0 = r_f d_N d_\beta \qquad (20).$$

Here r_f is fundamental anisotropy, typically taken as 0.4 for single photon excitation systems, d_N is depolarization factor of instrument, same as the G factor and d_β is depolarization due to orientation of absorption and emission dipoles. Depending on these three factors r_0 can vary from -0.5 to 1.[37] Strong dipolar interactions among porphyrin molecules in close vicinity, gives rise to the initial anisotropy of

0.5. The orientation angle of emitting and absorbing dipoles of ordered assembly were calculated using the relation

$$r_0 = \frac{3}{2}cos^2\theta - \frac{1}{2} \qquad (21)$$

The angle between adjacent dipoles was calculated to be 33° [Table. 3.]. High initial anisotropy value together with fast decay time suggests that among many other possible paths, excitation transport *via* hopping among interactive supramolecular species is prominent within the swelled sample. Rate of hopping was calculated from the equation

$$k_{hopp} = \frac{1}{N\tau_{ET}} \qquad (22)$$

N is the number of fluorophores taking part in depolarization and τ_{ET} represents excitation transfer time calculated from anisotropy data fitting. The effective interaction radius R_0^6 was also calculated by help of the equation

$$R_0^6 = 8.857 \times 10^{-5}\frac{\kappa^2 \phi J}{n^4} \qquad (23)$$

Where J is overlap integral between absorption and emission spectra of chlorophyll doped hydrogel and its value is ~120 × 10^{14} mole^{-1}cm^{-1}nm^4. κ^2 is taken as 2/3 for usually assumed random orientation of chromophores. ϕ is fluorescence quantum yield of PaaChl. From this value, distance between two adjacent chlorophyll assemblies was calculated using the equation

$$d^6 = \frac{R_0^6}{k_{hopp}\tau_{avg}} \qquad (24)$$

All these calculated values are tabulated in Table.2 and Table.3.