**Solutions of Week 7 Assignment**

1. The specific intermolecular interaction that leads to the sixth power dependence in the efficiency of energy transfer with intermolecular distance is

(a) Exchange energy

(b) **Coulombic interaction**

(c) Van der Walls interaction

(d) Nuclear interaction

Ans: (b) Coulombic interaction between donor and acceptor molecule leads to the sixth power dependence in the efficiency of energy transfer.

2. The FRET efficiency measured between a rhodamine dye molecule and a cyanine dye on either end of a 15 base strand of DNA is $E = 75\%$. Given that 50% transfer distance between the two dyes take place when $r = 60 \, \text{Å}$. Considering Forster mechanism, the distance between two dyes in the DNA is

(a) 40 Å

(b) **50 Å**

(c) 60 Å

(d) 70 Å

Ans: Efficiency of energy transfer ($E$) is given by

$$E = \frac{1}{1 + \left(\frac{r}{R_0}\right)^6}$$

Here as at $r = 60 \, \text{Å}$, $E = 0.50$, thus $R_0 = 60 \, \text{Å}$.

Now for 75% FRET efficiency, $E = 0.75$.

Thus using $E = 0.75$ and $R_0 = 60 \, \text{Å}$ in the first equation we can find that $r = 50 \, \text{Å}$.

3. Melittin (a protein) contains one tryptophan. The emission intensity ratio of melitin and dansyl labeled melitin is 1:0.56. Given that the $R_0$ value for the tryptophan-dansyl pair is 23.6 Å. The distance between tryptophan and dansyl group in melittin is
(a) 32 Å
(b) 24 Å
(c) 16 Å
(d) 8 Å

Ans: (b) FRET efficiency (E) is given by,
\[ E = \frac{1}{1 + \left(\frac{r}{R_0}\right)^6} = 1 - \frac{I_{DA}}{I} \]

Here tryptophan of melittin protein is the donor and dansyl is the acceptor. According to the problem, \( \frac{I_{DA}}{I} = 0.56 \) and \( R_0 = 23.6 \) Å.

Using these two values in the first equation one can find \( r = 24 \) Å.

4. When \( \theta_D = \theta_A = 45^\circ, \theta_T = 60^\circ \), The orientation factor (\( \kappa^2 \)) is
(a) 0
(b) 0.25
(c) 0.5
(d) 1

Ans: (d) \( \kappa^2 = (\cos \theta_T - 3 \cos \theta_D \cos \theta_A)^2 \)

Now putting the given values of \( \theta_D, \theta_A \) and \( \theta_T \) in the above equation \( \kappa^2 \) can be calculated and in this case it will be 1.

5. Consider a case where the lifetime of the donor is 2 ns in the absence of acceptor, whereas the lifetime of donor in presence of the acceptor is 1 ns. If the efficiency of energy transfer is 50% when the distance between the donor and the acceptor becomes 40 Å, the distance between the donor and acceptor is
(a) 20 Å
(b) 30 Å
(c) 40 Å
(d) 50 Å
Ans: (c) FRET efficiency ($E$) is given by,

$$ E = \frac{1}{1 + \left( \frac{r}{R_0} \right)^6} = 1 - \frac{\tau_{DA}}{\tau} $$

Here, $\frac{\tau_{DA}}{\tau} = \frac{1}{2}$ and $R_0 = 40 \text{ Å}$ thus $r = 40 \text{ Å}$

6. For an isotropic orientation of the donor and acceptor, the orientation factor ($\kappa^2$) is

(a) 0
(b) 0.33
(c) 0.66
(d) 1

Ans: (c) Go through the lecture 32 from 10:00 to 12:30 min.

7. Consider the following table:

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$pK_a$</th>
<th>$pK_a^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>8.0</td>
<td>2.5</td>
</tr>
<tr>
<td>B</td>
<td>7.0</td>
<td>8.5</td>
</tr>
<tr>
<td>C</td>
<td>10.0</td>
<td>4.0</td>
</tr>
<tr>
<td>D</td>
<td>4.0</td>
<td>8.5</td>
</tr>
<tr>
<td>E</td>
<td>2.0</td>
<td>6.5</td>
</tr>
</tbody>
</table>

The excited state proton transfer is more favorable than in the ground state for

(a) A and B
(b) C and D
(c) A and C
(d) B, D and E
Ans: (c) Excited state proton transfer process becomes more favorable when the $pK_a$ of a molecule decreases upon photoexcitation. And in the above case only molecule A and C satisfies the requirement.

8. A weak organic acid in its dissociated form ($A^-$) absorbs at 375 nm with a molar extinction coefficient of $4.48 \times 10^3$ L mol$^{-1}$ cm$^{-1}$. The undissociated form of the acid (HA) does not absorb at 375 nm. A $3.0 \times 10^{-3}$ M solution of this weak acid in water has an absorbance of 0.231 at 375 nm in a 5 mm cell. The $pK_a$ of the above weak acid is

(a) 1.53
(b) 3.66
(c) 4.82
(d) 5.44

Ans: (d) $HA \rightleftharpoons H^+ + A^-$

Concentration of the dissociated form ($A^-$) can be calculated from the absorbance at 375nm.

$A = \varepsilon cl$

$A = 0.231, l = 0.5 \text{ cm}$ and $\varepsilon = 4.48 \times 10^3$ L mol$^{-1}$ cm$^{-1}$

:. Thus concentration of $A^-$, $c = 1.031 \times 10^{-4}M$

$$K_a = \frac{[A^-][H^+]}{[HA]}$$

$[A^-] = [H^+] = 1.031 \times 10^{-4}M$

$[HA] = 3.0 \times 10^{-3}M$

:. $K_a = 3.66 \times 10^{-6}M$

:. $pK_a = 5.44$

9. A weak organic acid in its dissociated form ($A^-$) absorbs at 375 nm with a molar extinction coefficient of $4.48 \times 10^3$ L mol$^{-1}$ cm$^{-1}$ and emits at 415 nm. The undissociated form of the acid (HA) does not absorb at 375 nm and emits at 360 nm. At 375 nm, a $3.0 \times 10^{-3}$ M solution of this weak acid in water has an absorbance of 0.231 at 375 nm in a 5 mm cell. The excited state $pK_a$ ($pK_a^*$) of the above weak acid is
(a) -4.6

(b) -2.2

(c) +3.1

(d) +5.4

Ans: (b) 

\[ pK_a^* = pK_a + \frac{N_a h (\nu' - \nu'')}{2.303RT} \]

\[ \nu' = \frac{c}{\lambda_{HA}} \text{ and } \nu'' = \frac{c}{\lambda_{A^-}} \]

\[ \lambda_{HA} = 360 \text{ nm and } \lambda_{A^-} = 415 \text{ nm} \]

\[ pK_a = 5.44 \text{ (from the previous problem)} \]

Now from the first equation we can calculate 

\[ pK_a^* = -2.2 \]

10. Consider a 2-step irreversible proton transfer reaction. The fluorescence transient of the excited protonated species has decay time constant \( \tau_1 \) and the fluorescent transient of the excited deprotonated species has a rise time constant 0.5 ps and decay time constant 800 ps. Then \( \tau_1 = \)

(a) 0.25 ps

(b) 0.5 ps

(c) 0.75 ps

(d) 1.0 ps

Ans: (b) For a 2-step irreversible proton transfer reaction the decay time constant of the protonated species is equal to the rise time constant of the deprotonated species. Thus \( \tau_1 = 0.5 \) ps. Go through lecture-35 for clarification.