

Molecular Photonics

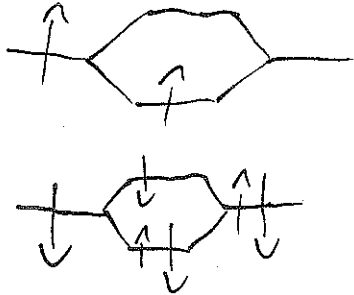
Exercise 3

Timo Bretten

ID C7A2MRNL7

1) An excimer is an excited state dimer

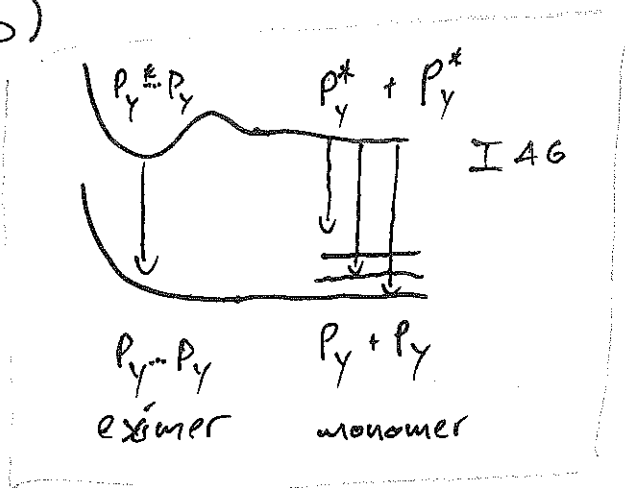
a)



Dimer \rightarrow two species

Excimer \rightarrow dimer with (at least) one species excited, here: the one on the left

b)



An excimer is lower in energy than the corresponding ~~dimer~~ excited dimer, because the excitation can be shared between two molecules, i.e. is less

localised. Thus excimer fluorescence will be red-shifted (\rightarrow less energetic) compared to monomer emission

Excimer emission is smoother, because distinct vibronic levels are overlayed by continuous "dimer-levels": depending on how close the two monomers are when forming the dimer, the energetic position of the ground state will change, leading to many dense vibrational levels

- a) At higher concentrations (2nd spectrum), excimers are more likely to form and excimer fluorescence shows up in the spectrum. Monomer fluorescence is reduced accordingly.
- b) At higher concentrations, the trend will continue: more excimer fluorescence, less monomer fluorescence. In the crystal, the monomer fluorescence will vanish altogether.
- c) If pyrene would be bound to two different biomolecules, their co-location in the cell could be investigated: if they are far away from each other, monomer fluorescence of pyrene should dominate in an image of the cell taken after excitation. When the biomolecules are close together a situation comparable to the case of pyrene in high concentration is reached, that is excimer fluorescence could be seen.

I think the problem of calibrating to relate a given ratio 'monomer/excimer fluorescence' is not an easy one to solve



(- cell with monomer-fluor. in the EPR (black) and excimer fluor. in the core)

3) parallel transition dipoles: blue shift; $\uparrow\uparrow \rightarrow$ allowed
 1) $\uparrow\downarrow \rightarrow$ forbidden



11) inline transition dipoles: red shift; δ -aggregate



$\uparrow\uparrow \rightarrow$ forbidden
 $\uparrow\downarrow \rightarrow$ allowed

11) coplanar transition dipoles:



energy of observed fluorescence is ϕ -dependent

11) oblique transition dipoles: band splitting

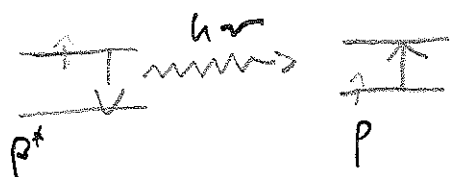


$\uparrow\uparrow \rightarrow$ allowed
 $\uparrow\downarrow \rightarrow$ forbidden

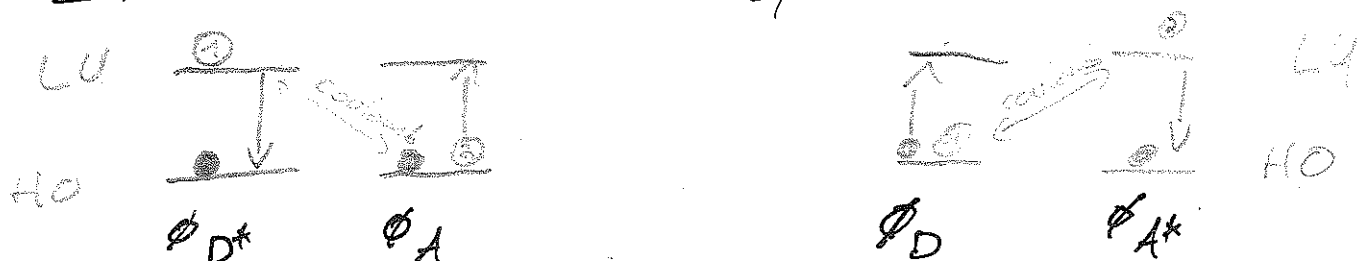
a) For a state to be allowed, a net dipole has to exist. Thus, for "parallel" $\uparrow\uparrow$ is allowed and for inline $\Rightarrow\Rightarrow$ is allowed and for coplanar and oblique there is no forbidden state, because there's always a dipole. If you take into account coulombic-repulsion it becomes clear why $\uparrow\uparrow$ is higher in energy than $\uparrow\downarrow$ and similar arguments hold for all other cases: $\Rightarrow\Rightarrow > \Rightarrow\downarrow$; $|\nearrow| > |\searrow|$; $|\swarrow| > |\nwarrow|$

4)

I) radiative : one molecule emits, the other absorbs



II) Förster resonance energy transfer (FRET)



The mechanism is coulombic so there is no orbital overlap necessary


III) Dexter energy transfer



Overlap is necessary since the exchange is direct

b) FRET is most common

c) At extremely high concentrations, the molecular overlap can become much more probable, thus the Dexter mechanism can dominate.

b) When you compare the spectrum of the dimer to the monomer, one clearly sees band-splitting: 

So the naphthalenic moieties of dimer 1 resemble the oblique situation.

The higher-energy emission comes from the excited state where the transition dipoles face each other, the energy of emission is lower compared to the monomer emission when the transition dipoles in the excited state face away from each other.

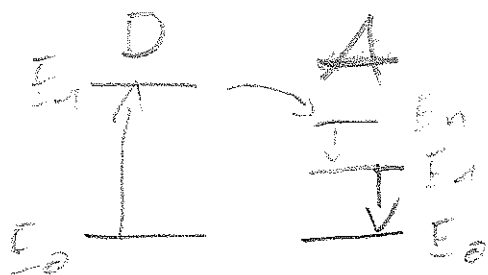
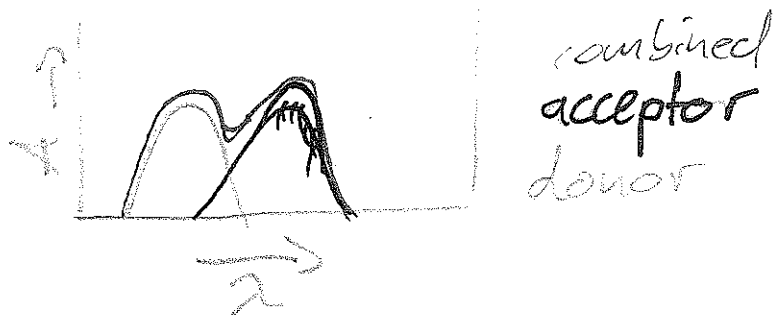
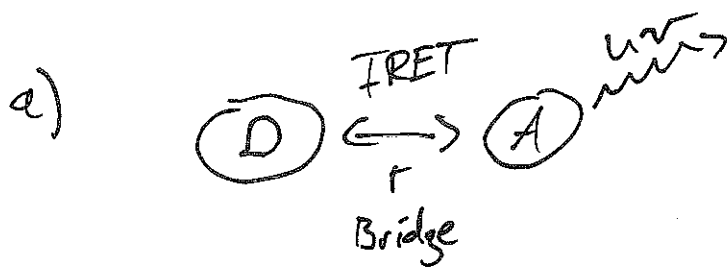
Increasing the distance of the naphthalenes decreases the coulombic interaction, thus the band-splitting decreases until the monomeric emission-spectrum is nearly completely recovered in shape (not intensity of course)

It was early in the morning... of course I meant "extinction" instead of "emission" everywhere above.

Excuse this lapse, please!

5) By UV/vis when:

- combined absorption ($D+A$) remains nearly unchanged compared to
- enhanced acceptor emission when donor is excited and its emission is quenched

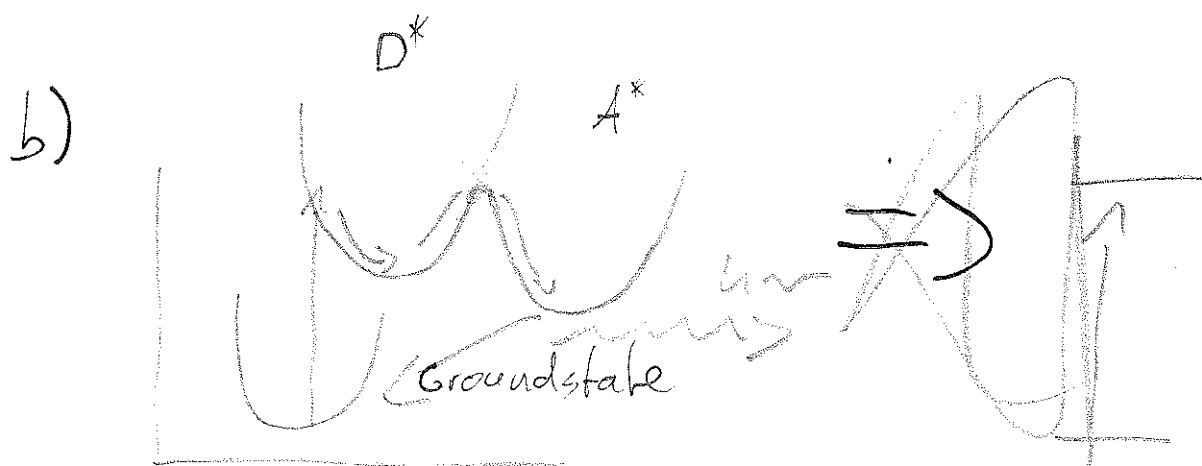


acceptor - increasing the length of

o) a The spectrum of 4 is the sum of the spectra of 2 & 3

when excited with $\lambda = 750\text{nm}$ only a will absorb, so there will only be emission in the long wavelength region.

However, when excited with $\lambda = 380\text{nm}$ intra-molecular energy transfer can take place (from 3 to 2) so again we will have strong emission in the long-wavelength region, but this time alongside some emission in the region of 3 as well



c) For this system, an efficiency of 99% was found and generally, the efficiency goes as $1/R^6$. This can be checked by introducing rigid spacer chains between the donor and acceptor (increasing the length of