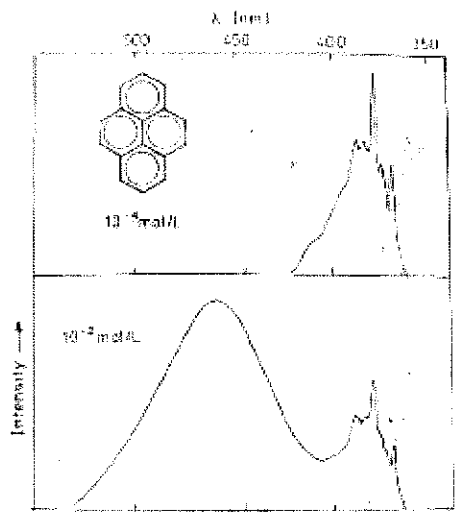
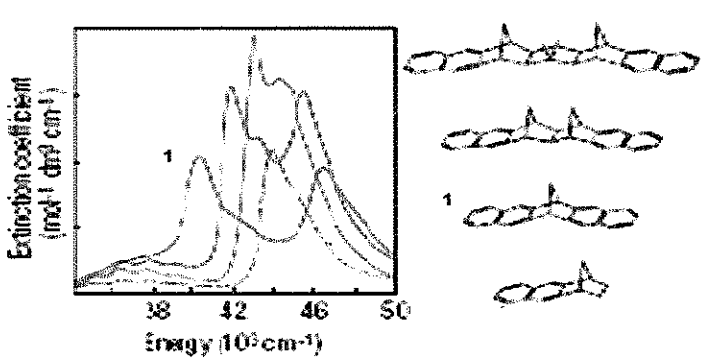
Molecular Photonics
Exercise 3

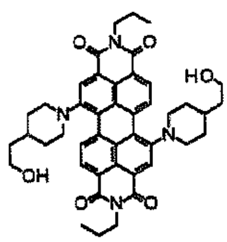
1. What is an excimer?
   a. Draw a MO scheme that represent excimer formation.
   b. Draw schematically the potential energy curves that represent excimer formation and the differences between monomer and excimer fluorescence. Explain the expected differences in the shape and wavelength.
2. In the two UV-vis/Fluorescnces spectra of pyrene below there are major differences.
   a. Suggest an explanation (notice the concentrations).
   b. What changes can one expect in the fluorescence spectra at higher concentrations? Suggest what will happen to the fluorescence spectrum of pyrene in crystal form.



   c. Suggest one biochemical application for pyrene excimers.
3. Draw the four situations of exciton energy level splitting using Kasha's theory. (Kasha et al. *Pure Appl. Chem.* **1965**, *11*, 371-392.)
   a. Explain shortly the reason for the energy stabilization and allowedness of each level.
   b. Explain using the answer to question **3a** the spectrum below what can be said regarding the relative position in space of the naphthalenic moieties of dimer **1**. (monomer's trace is in black),



4. What are the three mechanisms for energy transfer between two molecules?
   a. Draw schemes and explain each mechanism.
   b. Which one is the most common?
   c. In what specific case the answer for question **4b** is not the dominating mechanism? Explain.
5. By what means one can detect energy transfer between molecules?
   a. Give an example for a system like this. Draw schematically the molecular system and the spectra of the different components.
6. Compound **2** is a perylene diimide derivative. Compound **3** is a coumarine derivative. Compound **4** is the combination of both. The figure below shows the UV-vis spectra of all the three compounds. The spectrum of **4** is the sum of the spectra of **2** and **3**. (Fréchet et al. *J. Am. Chem. Soc.* **2002**, *124*, 11848-11849)
   a. Describe shortly what will be observed in the emission spectra when compound **4** will be excited at 380 nm and 750 nm.



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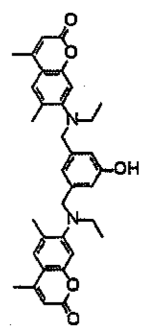

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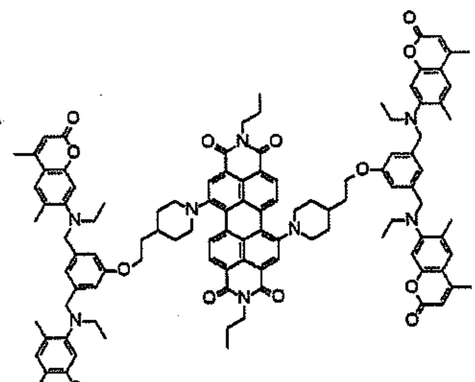

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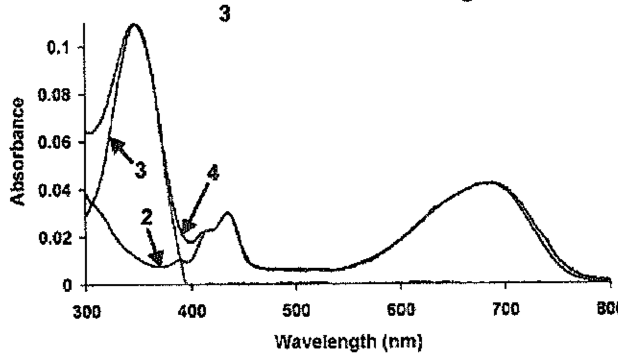

   b. Draw a schematic energy level diagram that describes the photophysical processes that occur in this system.
   c. What is the energy transfer efficiency that was found for the system by Fréchet and coworkers? What will happen to it if the distance between **2** and **3** will increase? Suggest a general way to check that. What dependency on the distance will be found?

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Molecular Photonics Ex. 3

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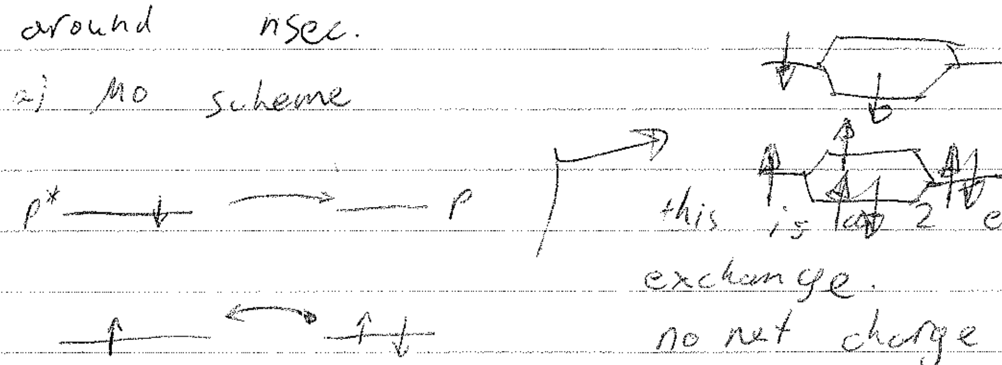
(031741184)

1) An excimer is an excited state dimer. The dimer is buid out of two species at least one of them is excited. Eximer lifetime is around nsec.

a) MO scheme



this is 2 electron exchange. no net charge redistribution.

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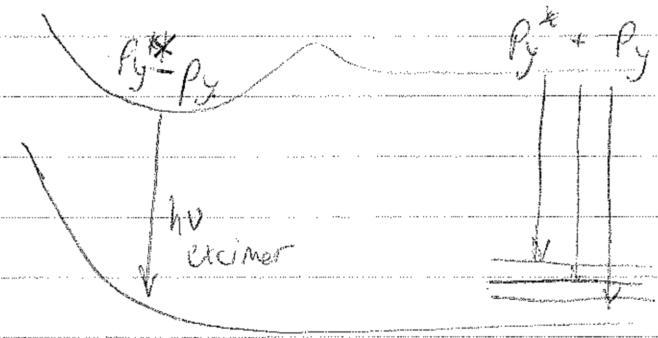
b) Potential energy curve



The flourescence of the excimer will be red shifted (less energetic) relative to the monomer emission and will also be smooth. The monomer flourescence on the other hand will have vibration levels and thus will have secondary peaks in it.

why?

-4

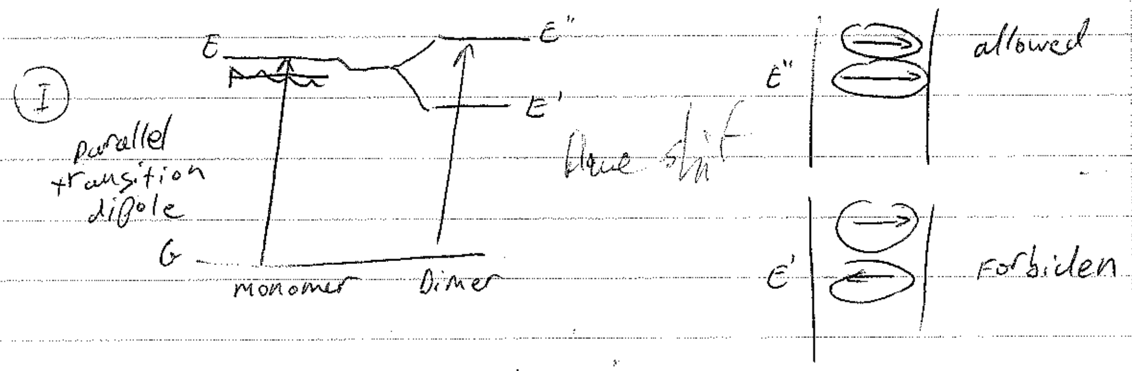
2) a) The second spectra exhibit an excimer flourescence while the monomer flourescence is reduced. This phenomenon accure when conc. is high and there is a bigger probability for excimer formation

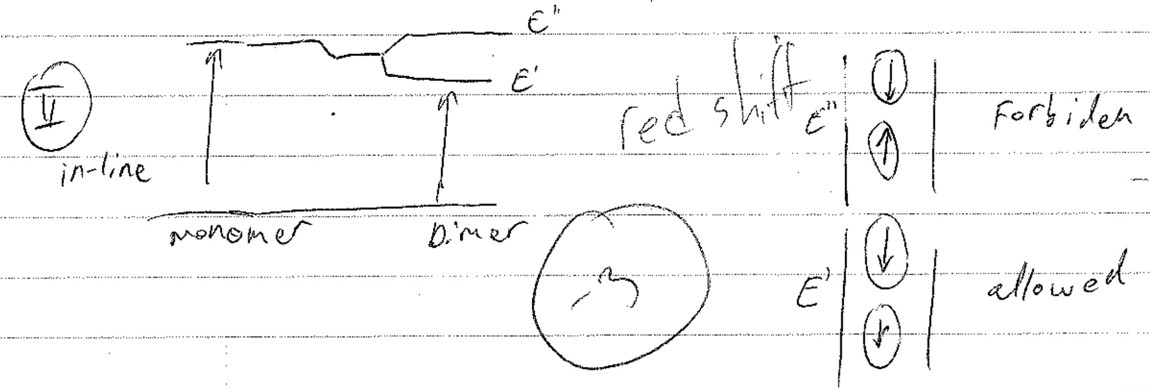
ex 3 cont. 1

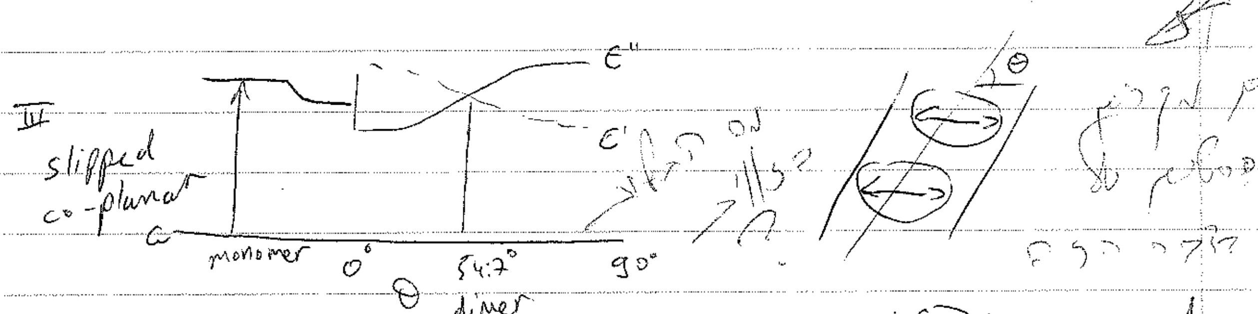
b. At higher concentration one can expect the monomer flourescence at 380nm to vanish alltogether and only the excimer will be visible at 460nm.

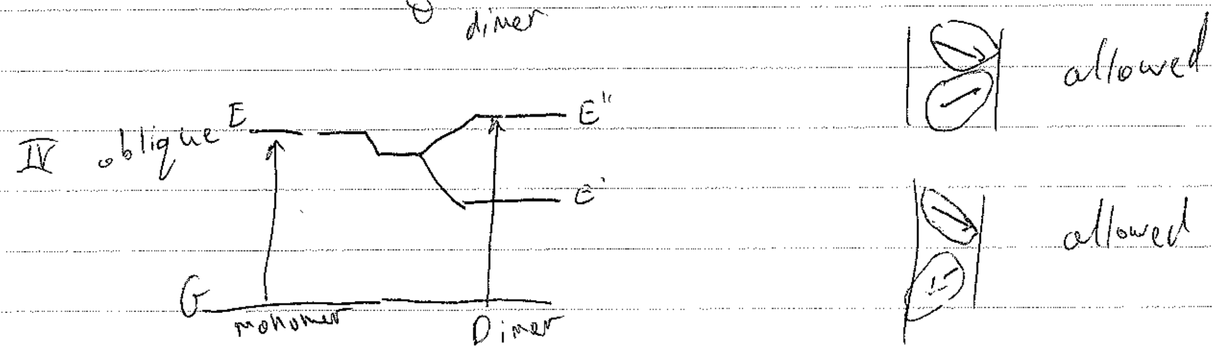
c. An application to the pyrene excimer is evaluating the distance between biomolecules. You should be ~~som~~ more specific (-2)

3)







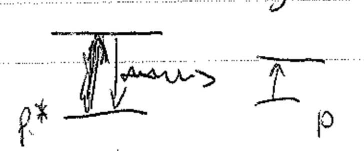


ex. 3 - cont. II

3) a. only a state with a net dipole is allowed for transition.
in the parallel transition dipole this: ⇄ state is more stable since there is less coloumbic repulsion but this is forbidden.
the other level: ⇉ is allowed but higher in energy.
In the in-line in E'' ↓↑ there is a repulsion and no net dipole and this is why it's forbidden.
In the slipped and oblique transition dipole there is always net dipole and the state are all allowed

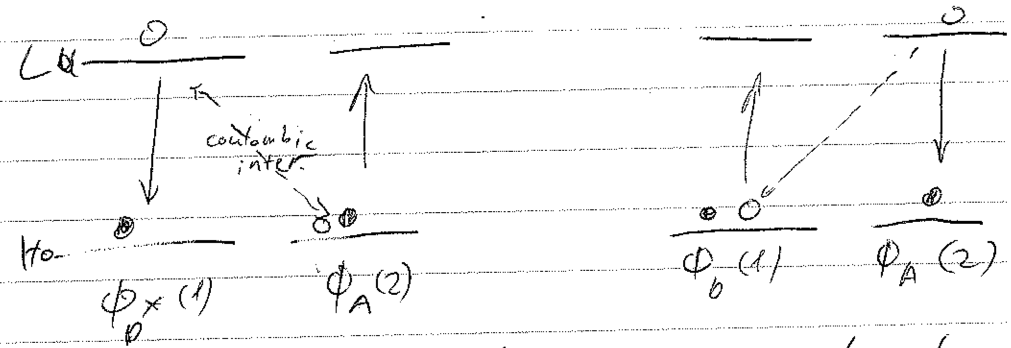
b. Naphtaleneic moities of dimer. this situation resmbles the oblique transition dipole were both levels are allowed but when the dipoles are facing one each other the energy will be higher than the monomer excited state wile when dipoles are facing other sides level is lowered compared to monomer level.
~~main~~ Taking the naphtalenes apart from one each other repulsion decrease until eventually there is no interaction and we are back to the monomer excition.

4) Energy transfer:
I. radiative transfer - one molecule emit light while the other absorbs the light and get the energy



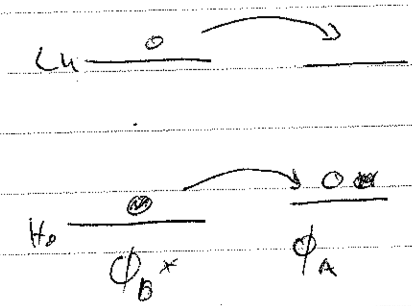
4) energy transfer

II (Forster) FRET



coulombic mechanism no direct orbital overlap necessary

III Dexter energy transfer mechanism



electron exchange - Direct orbital overlap is necessary.

b) <u>suprisingly</u> FRET is the most common mechanism while the "trivial" radiative transfer is very rare.

c) when one deals with high concentrations then radiative energy transfer <u>becomes</u> more frequent. ↑ this is not the answer at all

-4

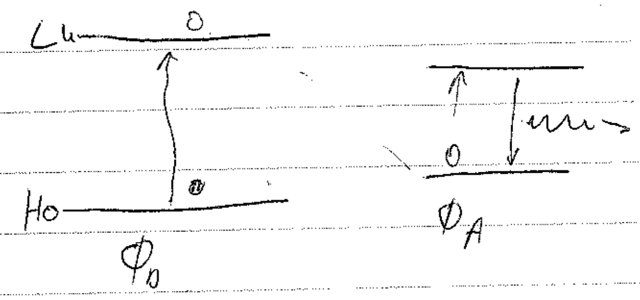
במקרה [illegible]

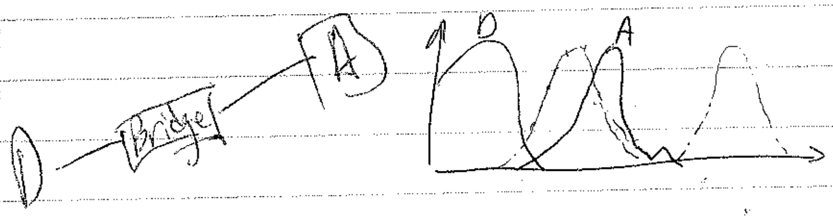
ה- FRET [illegible]

מכיוון [illegible] במקרה שלהם

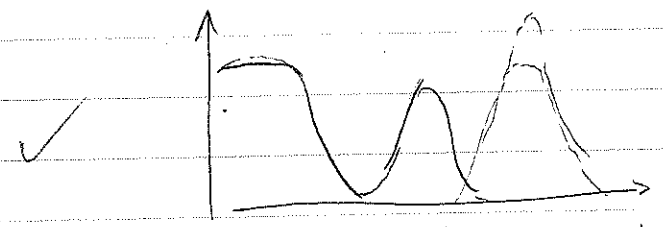
[illegible] DEXTER

5) energy tranfer is observed by uv-vis/ flowrescence spectroscopy.





no transfer / isolated molecule

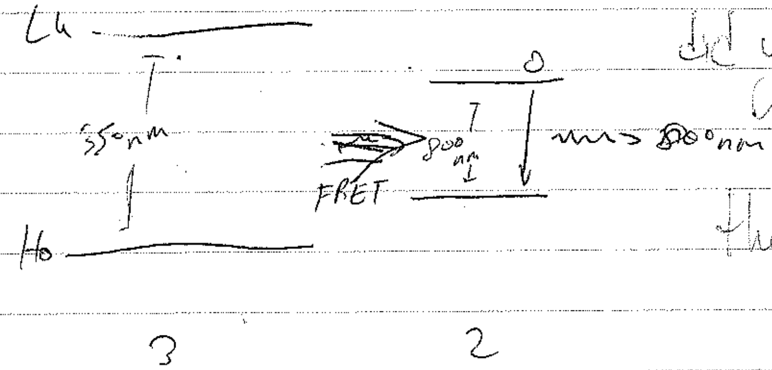


FRET

light is absorbed in the Donor ~~spe~~ molecule but emission of the donor is highly reduced while the acceptor emission is increased by energy transfered to is from the Donor.

6) a) when compound 4 will be excited with 380 nm both 2 and 3 species will be excited. Energy from 3 will be transfered to 2 and I expect to get high flowrescence in the 800nm region, and ~~when~~ small emission in the green where 3 emits when excited with 750 nm, I expect emission in the 800 nm region only because only 2 is excited.

6) b.



did you look at the article sent with the exercise? -2

c. Frecet and coworkers found 99% efficiency of energy transfer in this system. taking the donor and acceptor apart from one eachother by introducing longer rigid chains between them will reduce efficiency like $\frac{1}{R^6}$