House of the Estates, Helsinki
2 – 4 September 2013

Randomness and order in the exact sciences

Self- and co-assembling soft materials

Photochemistry in organized thin films

Helge Lemmetyinen

Laboratory of Chemistry
Department of Chemistry and Bioengineering
Tampere University of Technology,
FINLAND

TAMPERE UNIVERSITY OF TECHNOLOGY
Department of Chemistry and Bioengineering

Why and how do chemical reactions occur?

Thermodynamics determines the equilibrium state of a dynamic system, that depends on absolute energies of reactants and products

Thermodynamics does not tell how fast or how a reaction takes place - time, molecular structures, their environment, and geometrical relations between reacting species are not parameters in thermodynamic equations

Thermodynamics only deals with energies between the reacting system and its environment during the process is taking place

What are the *processes* between *individual molecules and atoms* yielding products, *e.g.* "mechanism" or "chemistry" of a reaction, this is a subject of "*chemical kinetics*"

From Kinetics to Dynamics:

For reaction orientated collisions needed – not random

$$2\ BrNO \longrightarrow Br_2 + 2\ NO$$

(a)

(b)

(c)
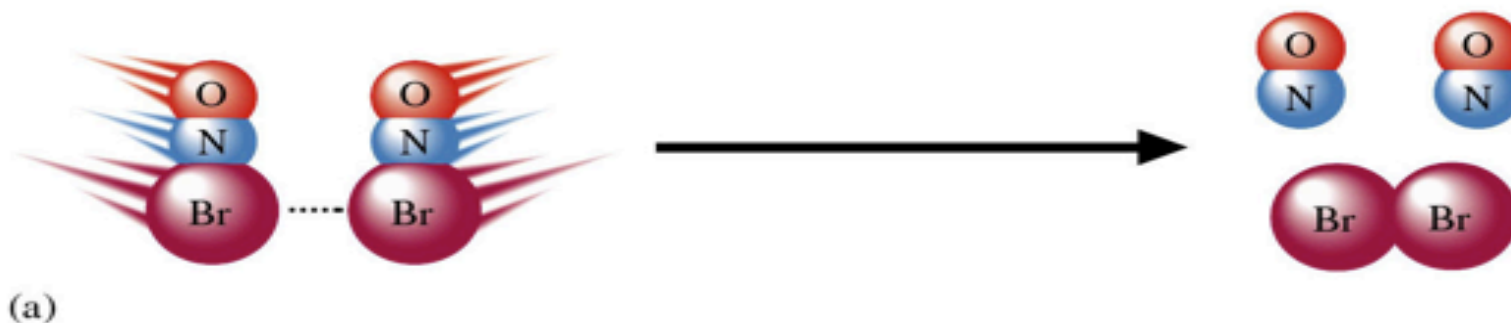
No reaction

From Kinetics to Dynamics

Reactive species need energy

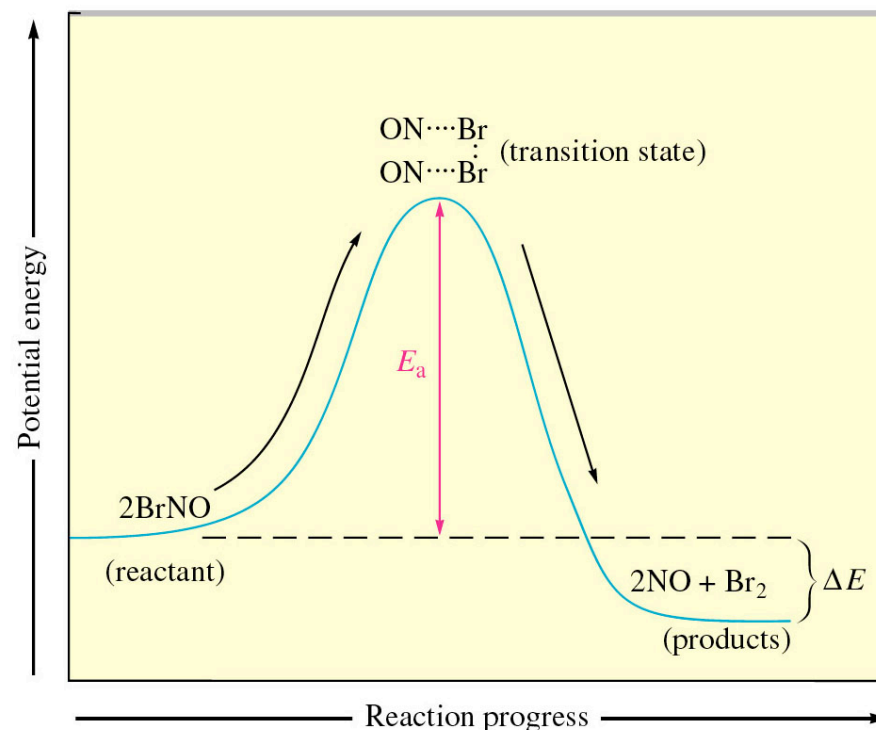**Svante Arrhenius (1889):**

$$k = Ae^{\frac{-E_a}{RT}}$$

or

$$\ln k = -\frac{-E_a}{RT} + C$$

The rate constant, $k(T)$, does not provide a detailed molecular picture of the reaction.
We need to know:
how reagent molecules approach, collide, exchange energy, break bonds and make new ones, and finally separate into products

From Kinetics to Dynamics

Henry Eyring and Michael Polanyi (1931):
   Potential energy surphase

Eyring, Polanyi and Evans (1935):
   Transition-state theory

$$k = Ae^{\frac{-E_a}{RT}} = (\frac{k_BT}{h})(\frac{Q^{\#}}{Q_AQ_B})e^{\frac{-E_a}{RT}}$$

The fastest reaction at room temperature:

$$k = (\frac{k_BT}{h}) \approx 6x10^{12}s^{-1}$$

or $\tau = 170$ fs

The time scale of molecular vibrations is typically 10 - 100 fs

H. Eyring & M. Polanyi

Hirschfelder *etal*
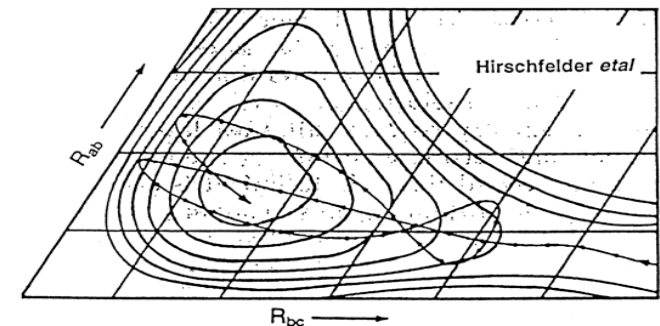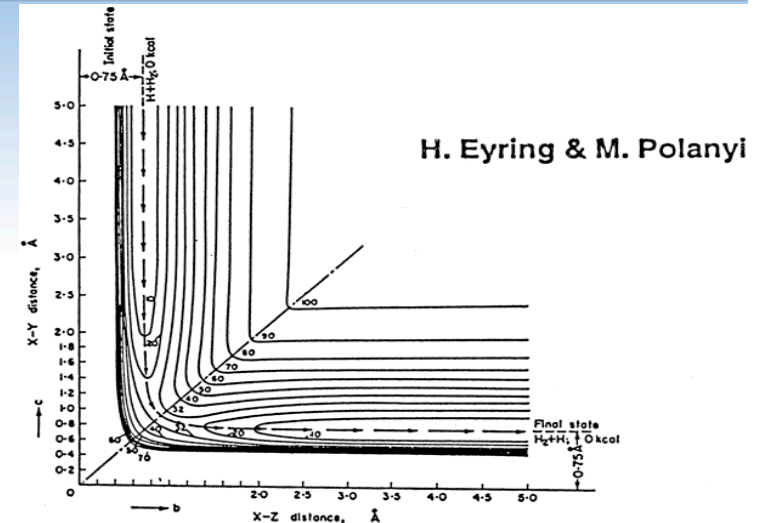
Mater Waves Particle-type Control & Dynamics

de Broglie (1924)

Einsteins's light wave/particle

$$E = h\,\nu \qquad\qquad E = c\,p$$

$$\lambda = h/p \qquad\qquad p = m\,v$$

Schrödinger (1926)

The Wave Equation – Stationary waves

$$H\,\Psi = E\,\Psi$$
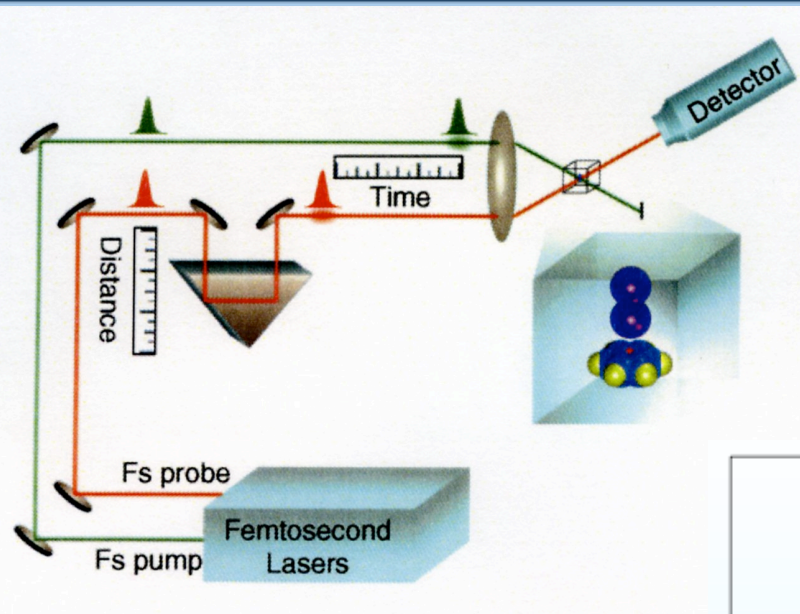
Schrödinger (1926)

Micro- to Macro Mechanics

Quantum to Newton Mechanism

Femtochemistry & Quantum limit (h): Particle Type

$$\lambda = h/p; \qquad \Delta x\,\Delta p \geq h/2\pi \qquad \Delta t\,\Delta E \geq h/2\pi$$

$$\Delta x = p/m\,\Delta t = v\,\Delta t \qquad \Delta t \approx 10\ \text{fs} \qquad \Delta x = 0{,}01\ \text{nm}$$

$$\Delta t \approx 10\ \text{ps} \qquad \Delta x = 10\ \text{nm}$$

Femtochemistry – Nobel Laureate in Chemistry 1999
Ahmed H. Zewail
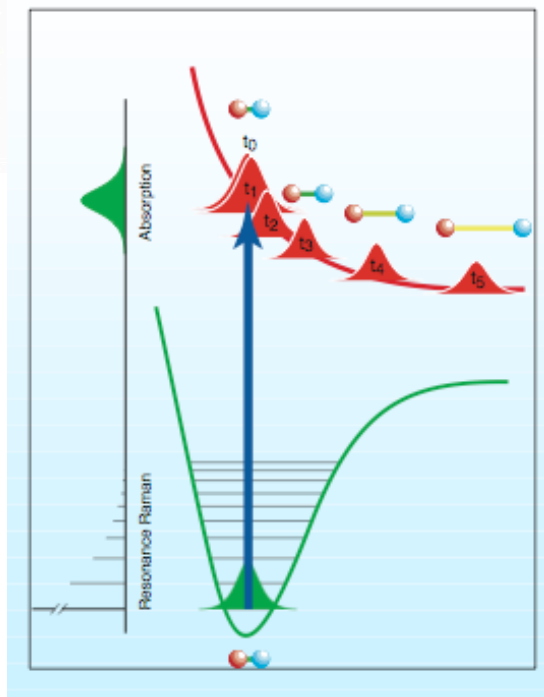
Observation of atomic motions in a molecule?
Reactions in organized thin films?

The distance of atoms in a molecule is about 0.1 nm
The size of an organic molecule, *e.g.* chlorophyll ring is about 1 nm
The thickness of biological membrane, two molecular layers, is about 2 nm
The average time required for atomic motion is about 10 - 150 fs

Concerning the chemical reactions the pertinent questions are

How does the energy put in into a reactant molecule distribute among the different degrees of freedom and how fast does this happen?

What are the speeds of the chemical changes connecting individual quantum states in the reactants and products?

What are the detailed nuclear motions that chart the reaction trough its transition states, and how rapid are these motions?

Those questions concern random systems
How do reactions takes place
in organized and ordered systems, as in solid films?

How function the parameters determining the rates and efficiencies
of reactions in films?

distance	short and fixed
orientation	fixed and static
time	fast
spatial distribution	fixed or variable
"freedom"	limited

How do the reactions take place when reacting species or molecular groups
are (already) close to each other?

Does the reacting species or molecular moieties recognize the presence
of the counter part, if does, how?

TAMPERE UNIVERSITY OF TECHNOLOGY
Department of Chemistry and Bioengineering

Photochemical processes for capturing energy

Let's take one example:
Electron transfer (ET) is the fastest (and simplest) chemical reaction

Rates of ET reactions are mainly controlled by

- the distances
- temperature
- mutual orientations (anisotropy) between the reactants
- environment viscosity and polarity
- organization: membranes, vesicles, micelles, layers, wires
- natural and artificial (supra)molecular structures

Two ways of ET processes
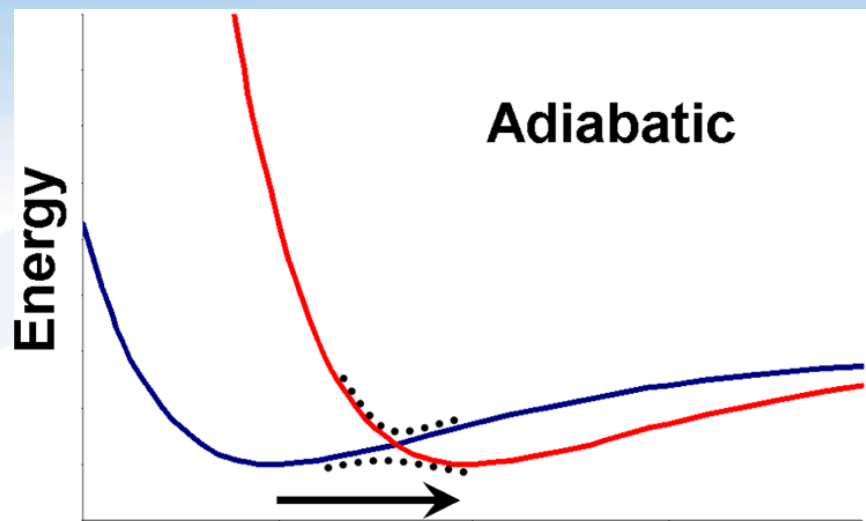
Adiabatic process can be accurately described by a single electronic wave function
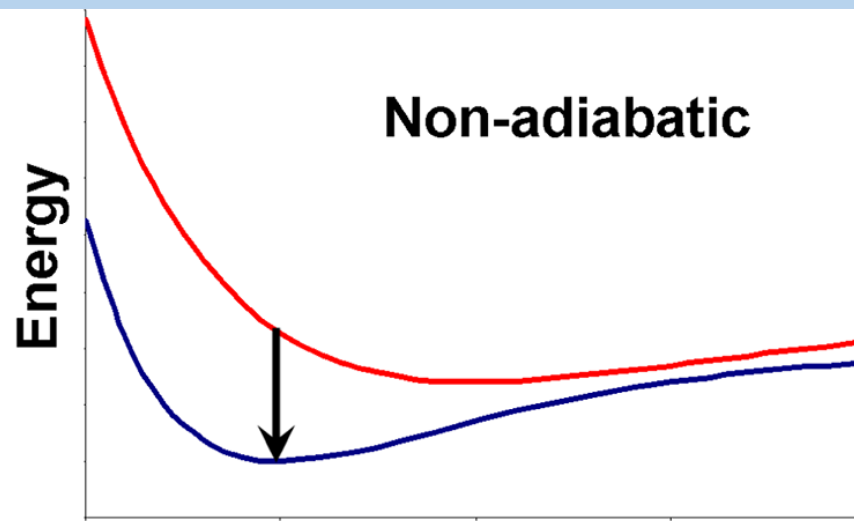
Nonadiabatic processes involve at least two electronic states, and cannot be described by a single potential energy surface.

Marcus ET theory for adiabatic process (Nobel Price 1993)
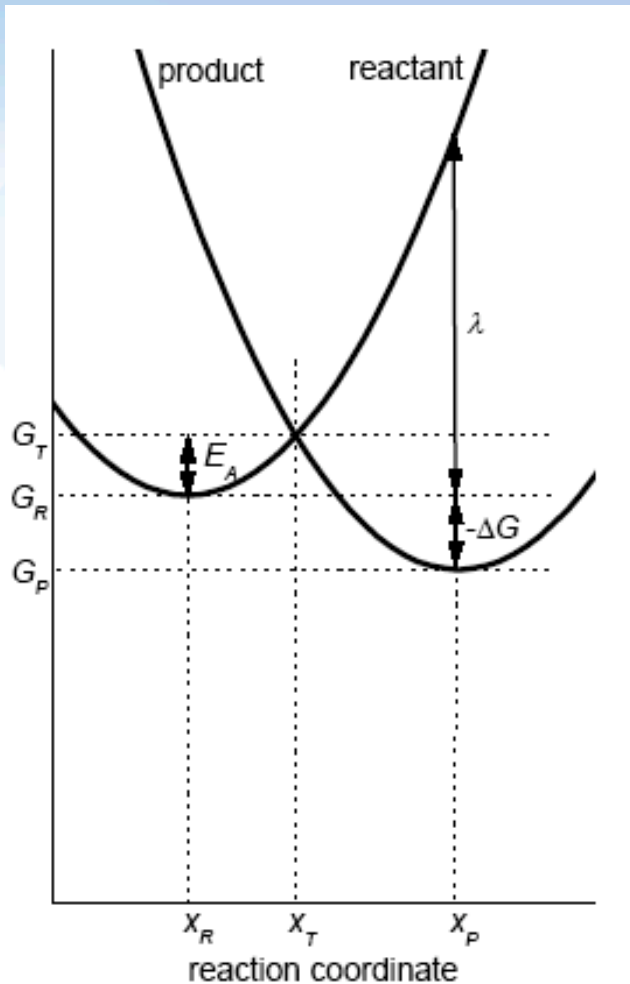
$$E_A = G_T - G_R = \frac{(\Delta G + \lambda)^2}{4\lambda}.$$

$$k_{ET} = \kappa_{el} \nu_n \exp\left(-\frac{E_A}{k_B T}\right),$$

$$k_{ET} = \kappa_{el} \nu_n \exp\left[-\frac{(\Delta G + \lambda)^2}{4\lambda k_B T}\right].$$

The Marcus theory works well for the one step ET and BET.

However, more complex reactions, with one or more intermediate steps, may be difficult to interpret quantitatively with the 1-dimensional model.

Paradoxes of ET reactions

Electron transfer (ET) reactions can proceed *at different distances*
- in loose reactant pairs (long range ET)
    - Marcus theory and radiationless transition theory
        a) transition state between two potential minima, that of initially excited (LE) and charge transfer (CT) states
- in tight pairs (contact ET)
    - strong electronic coupling between LE and CT states
    - reaction is no more a single elementary step trough a transition state
    b) formation of intermediate state(s) with partial CT: excimer or exciplex

LE   CT

(a)   (b)
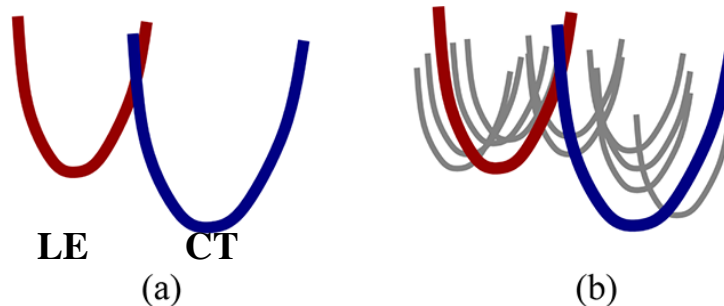
Examples in solution: 1) Photo-induced electron transfer reaction pheophytin-fullerene derivative:

Parametres: orientation, distance, spatial distrbution, environment

e⁻
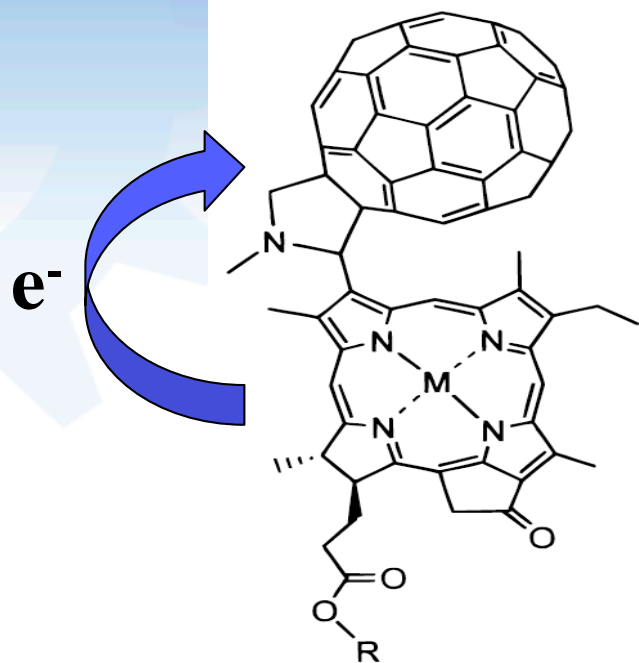
PF: M = 2H, R = H

*J. Am. Chem. Soc., **121**, 1999, 3978*
Lemmetyinen, Tkachenko et al..
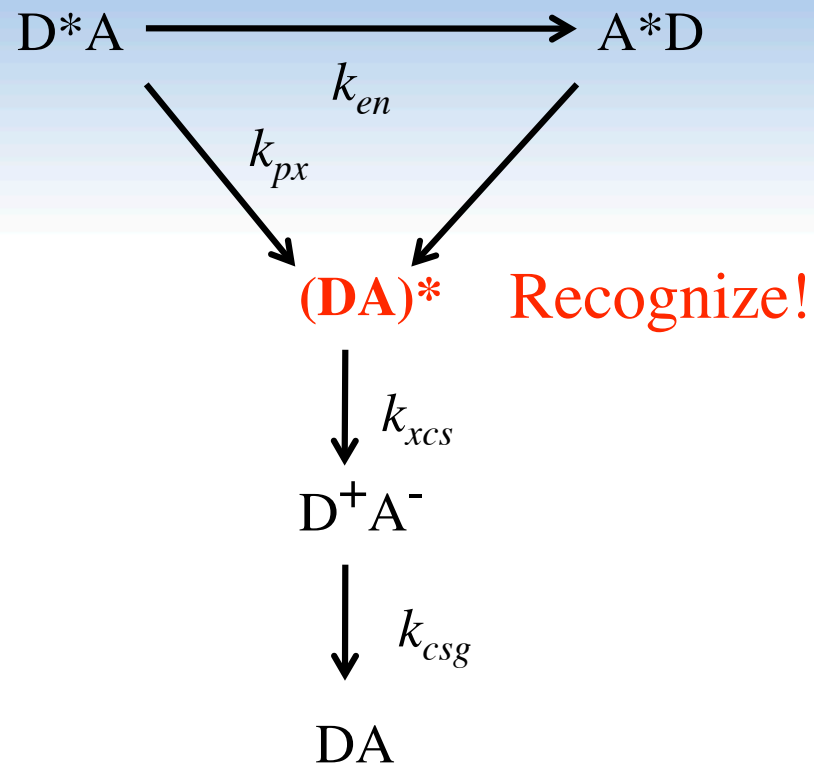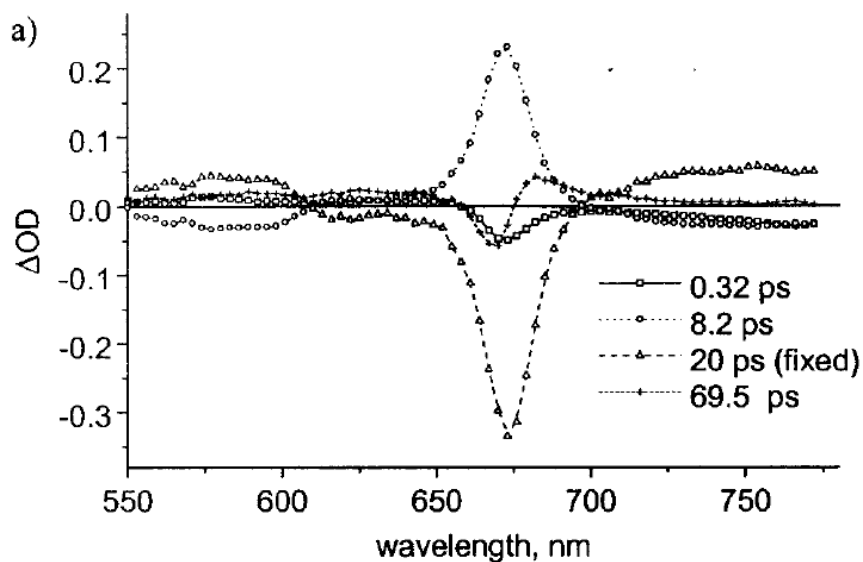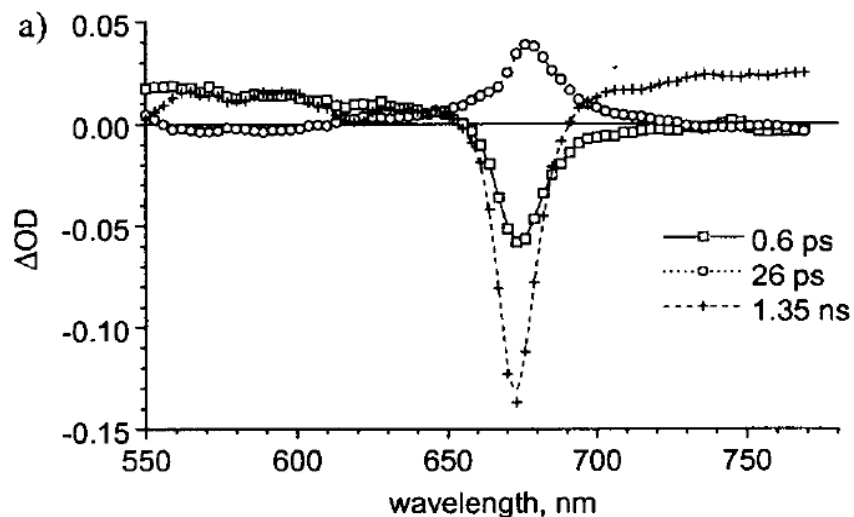
Reference Pheopytin: τ_1 = 4 – 5 ns

|	toluene	benzonitrile
PaF: τ_1 =	0.59 ps	0.54 ps
τ_2 =	8.5 ps	4.4 ps

Pheophytin-fullerene derivatives:
Time-resolved component spectra:
in non-polar toluene three components
in polar benzonitrile four components

$$D*A \xrightarrow{} A*D$$

k_{en}

k_{px}

(DA)* Recognize!

k_{xcs}

$D^{+}A^{-}$

k_{csg}

DA

0.35 ps = k_{en}	energy transfer
8 ps = k_{px}	exciplex formation
19 ps = k_{xcs}	CT-state formation
65 ps = k_{csg}	CT-state recombination

The role of the exciplex in the ET and BET reactions:
it reduces the activation energy between the reactants and reaction product, the CT state or radical ions
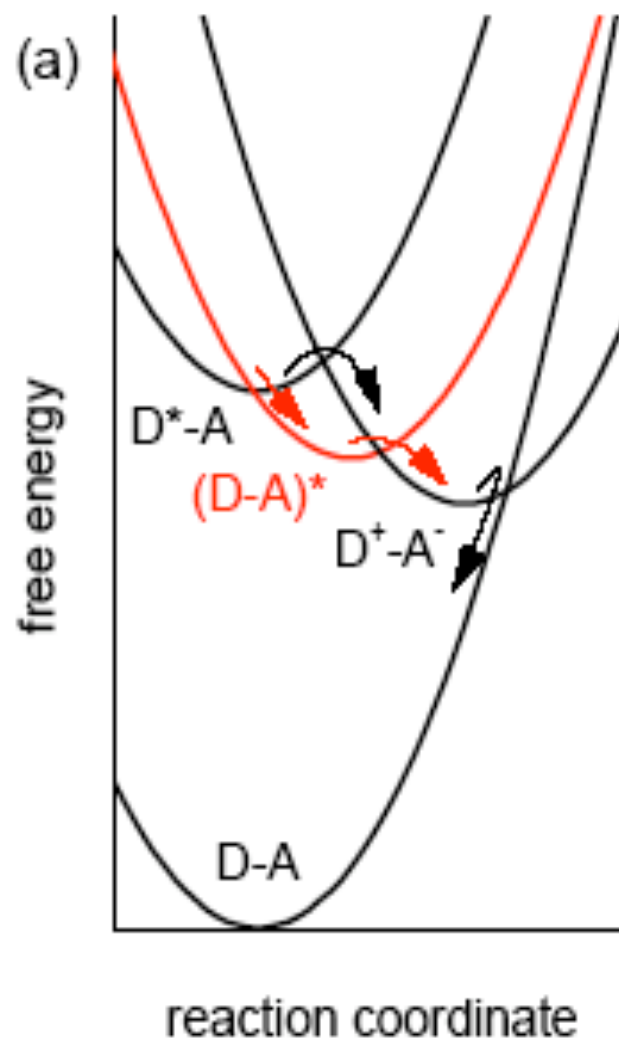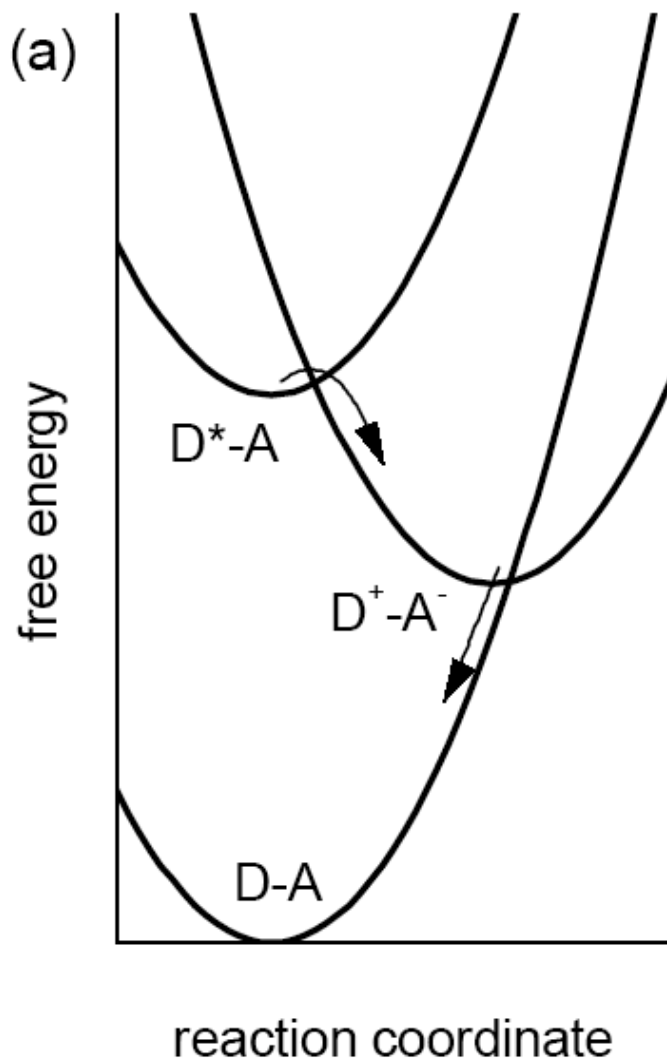
Three-dimensional surfaces for the ET reaction: free energy, distance and solvent polarization

a) Mixing of states D*A and D$^+$A$^-$ is not taken into account
b) Mixing of states is taken into account

a)

b)

TAMPERE UNIVERSITY OF TECHNOLOGY
Department of Chemistry and Bioengineering

A topographic surface for the ET reaction: free energy, distance and solvent polarization:

As *r* decreases exciplex formation occurs, mainly in non-polar solvent, but can be stabilized by solvation

No (or small) activation energy is needed for exciplex and ion formation!

NO TEMPERATURE DEPENDENCE !?

J. Phys. Chem. A, 111, 2007, 9240
Murata & Tachiya
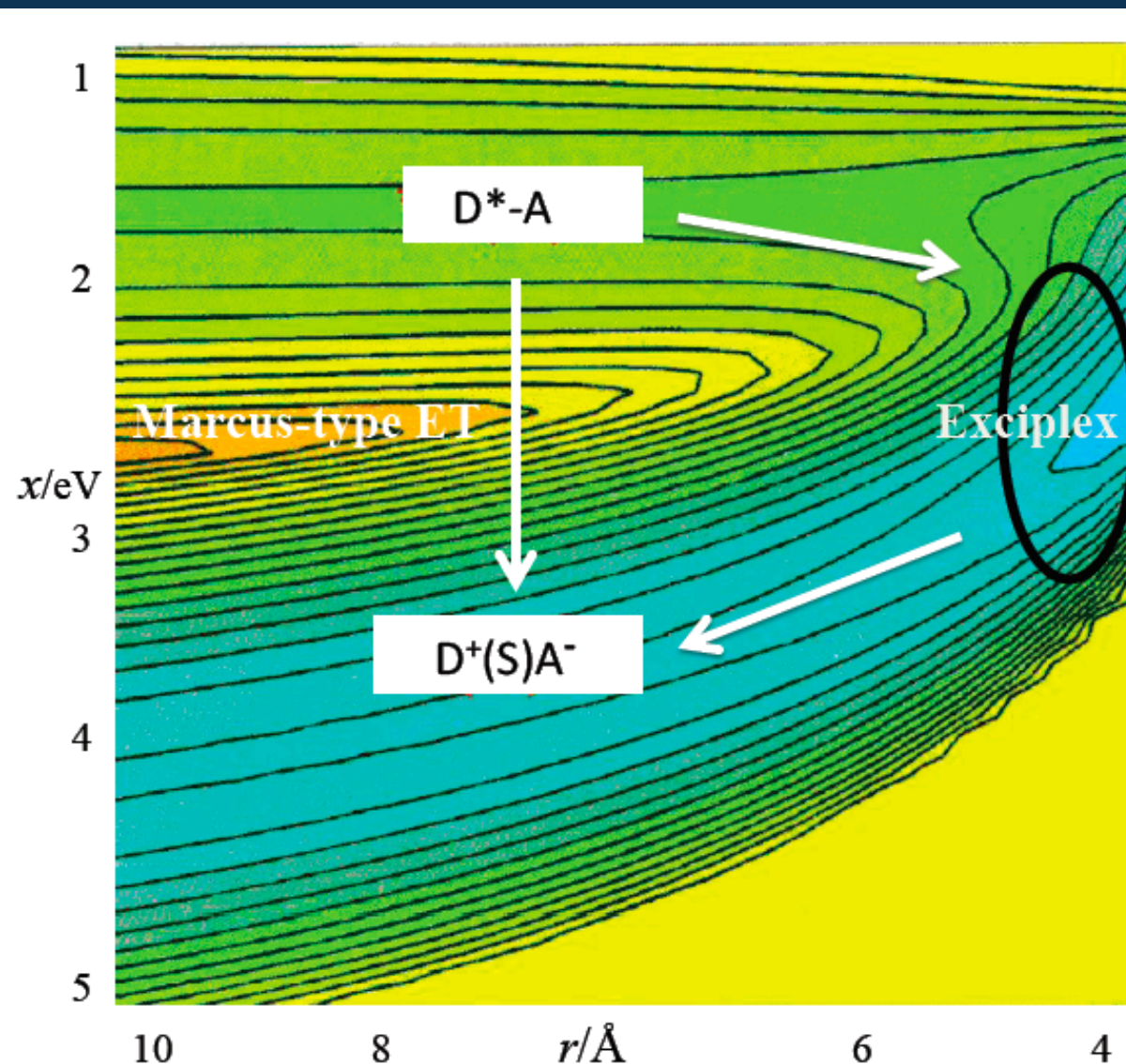
More examples: A series of electron donor-acceptor compounds has been studied
Orientation, distance, spatial distrbution, environment

Porhyrin-porphyrin-fullerene triad
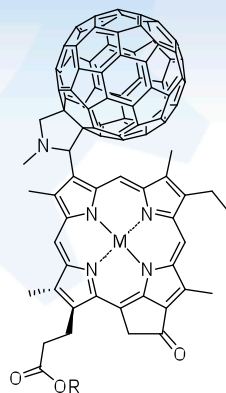
Chlorophyll-fullerene dyad
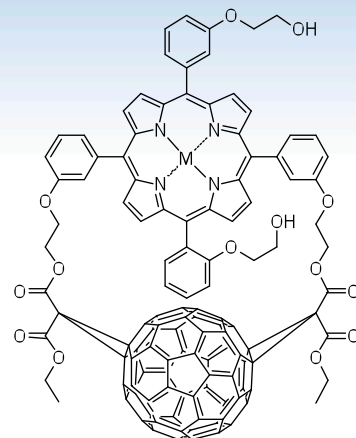
Porphyrin-fullerene dyad

Phthalocyanine-fullerene dyad
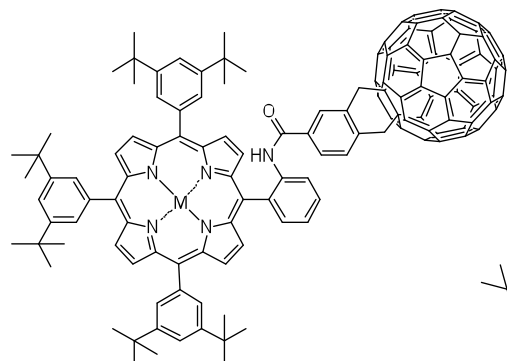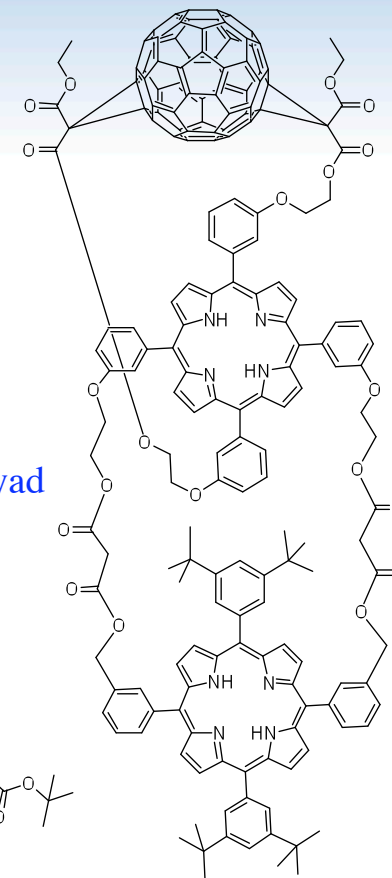
Porphyrin-fullerene dyad
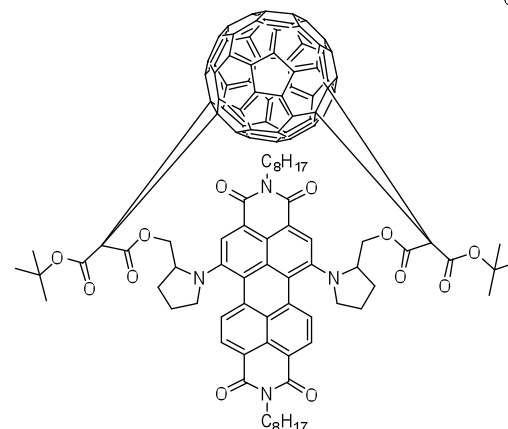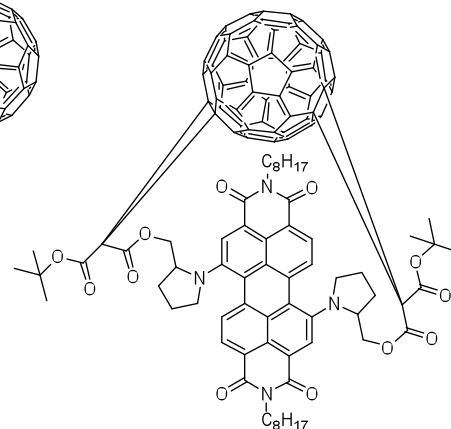
Two isomers of perylenediimide-fullerene dyads

… and more…:

Orientation, distance, spatial distrbution, environment

PF: M = 2H, R = H

PaF

PbF
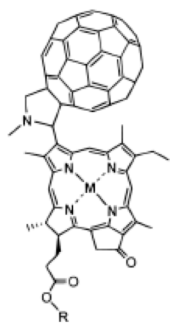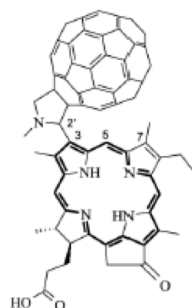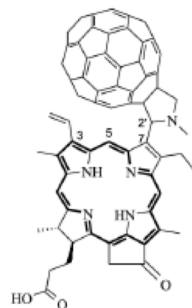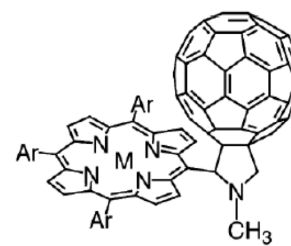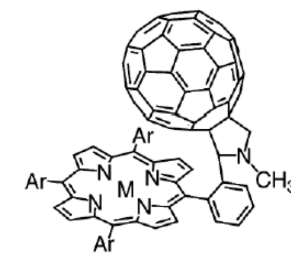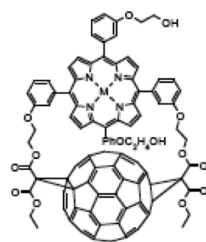
DHD6ee, M = 2H
ZnDHD6ee, M = Zn
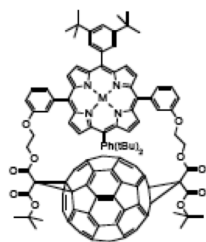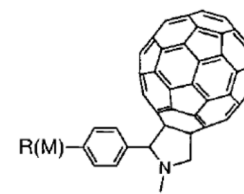
ZnTBD6be, M = Zn
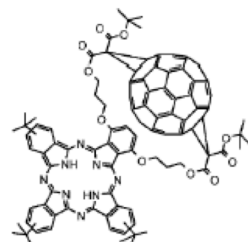
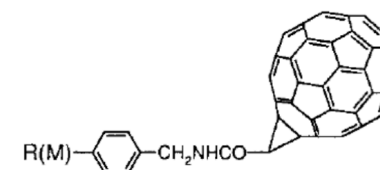MPc-F: M = , 2H, Zn
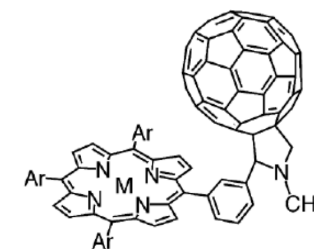
MP-m-F: M = 2H, Zn

MP-p-F: M = 2H, Zn
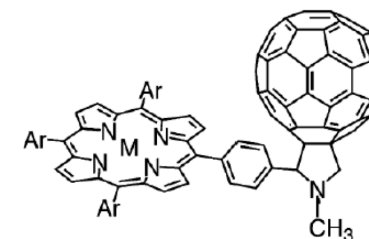
-o-F: M = 2H, Zn
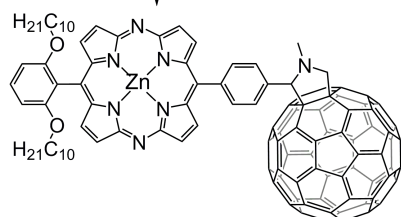
MP-: M = 2H, Zn

MP-S-F

MP-C-F

Submitted JACS 1.9.2013
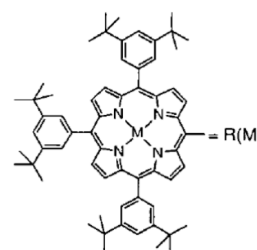
To conclude: covalently linked with two chains
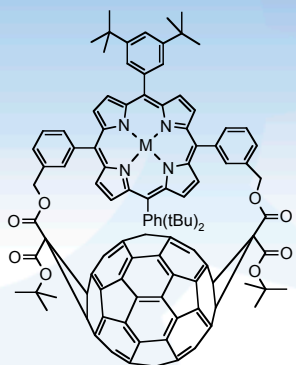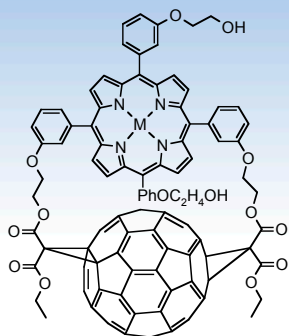
TBD4be **DHD6ee**
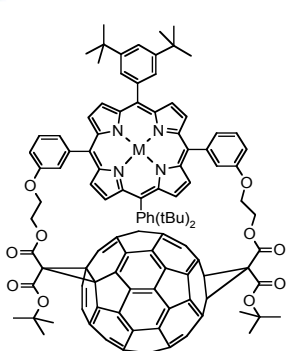
TBD6be **ZnD7mee**
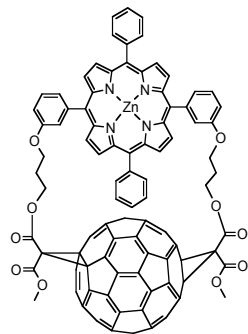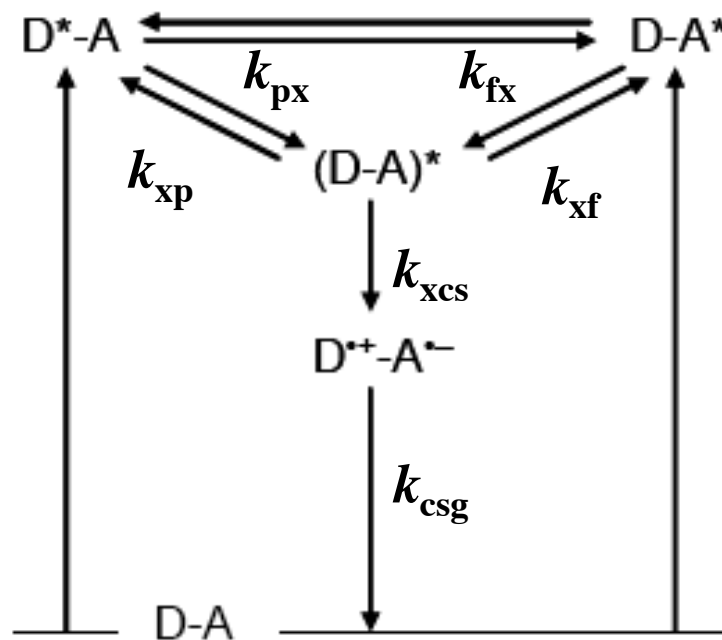
k_{px} = 10 -20 x 10^{12} s^{-1} *e.g.* 50-100 fs

k_{xcs} = 0.8 - 1.4 x 10^{12} s^{-1} *e.g.* 0.7- 1.3 ps

k_{csg} = 16 - 20 x 10^{9} s^{-1} *e.g.* 50 - 60 ps

CONCLUSIONS:

ET reactions can occur in solutions by various different mechanisms depending on diffusion, solvent, time, and orientation:

1. In the **first few ps** the reaction rate is controlled by the distance and fluctuations of orientations and displacements of reactant molecules.

2. During the following **10 – 50 ps** ET depends on distance, time, and spatial distribution of the quencher molecules related to the excited molecule.

3. Finally the reaction becomes diffusion controlled, when the distance increase between the reactive molecules.

These observations open new possibilities to handle, explain, and understand ET reactions in different nanostructures and supra-molecular solid arrangements.

# Electron transfer reactions in artificial solid molecular films

Methods for film preparations
- **spin-coating**
- **casting**
- **dropping**
- **vacuum-evaporation**
- **Langmuir-Blodgett and Langmuir-Schäfer deposition**

Experimental methods
- **time-reso fluorescence (fs-ns)**
- **time -resolved absorbance (fs – ms)**
- **time-resolved MDCM-method (ns – s)**

Knowing the mechanism in solutions open new possibilities to handle, explain, understand and control the ET reactions in different nanostructures, molecular assemblies, supramolecular arrangements, and MOLECULAR THIN FILMS
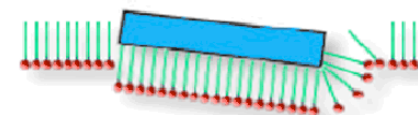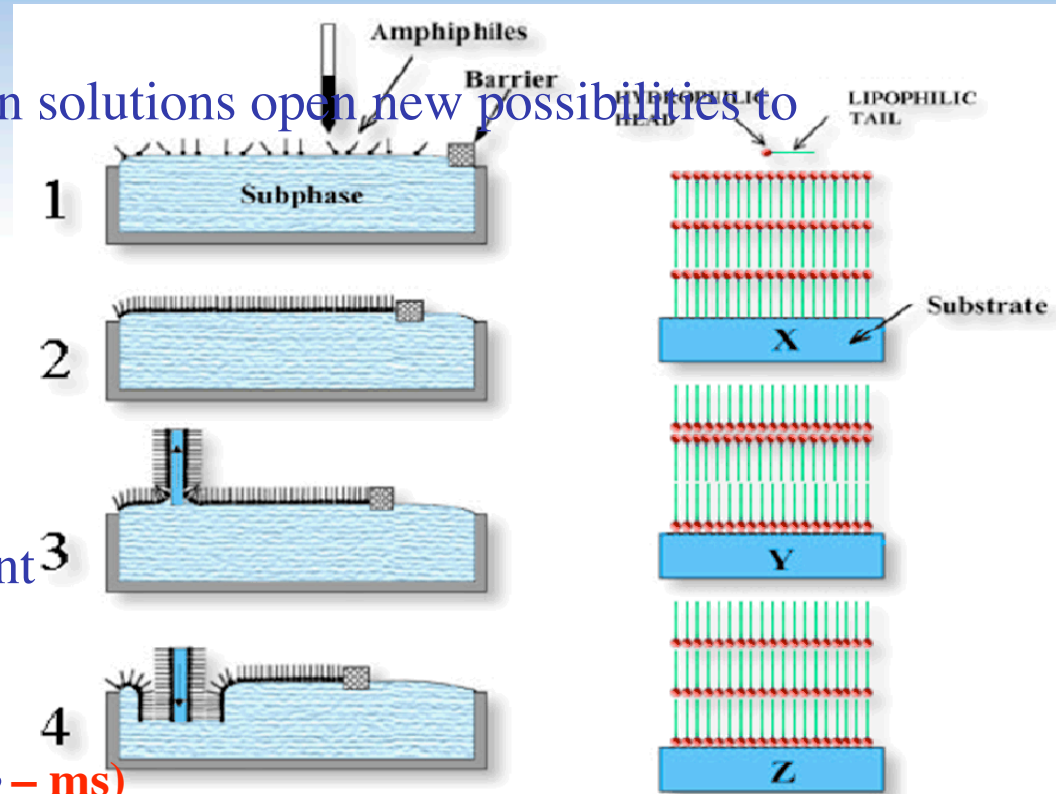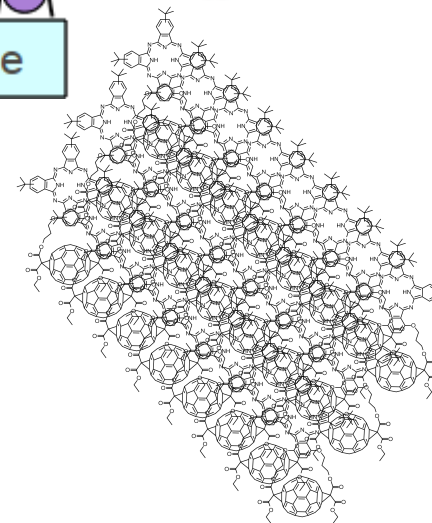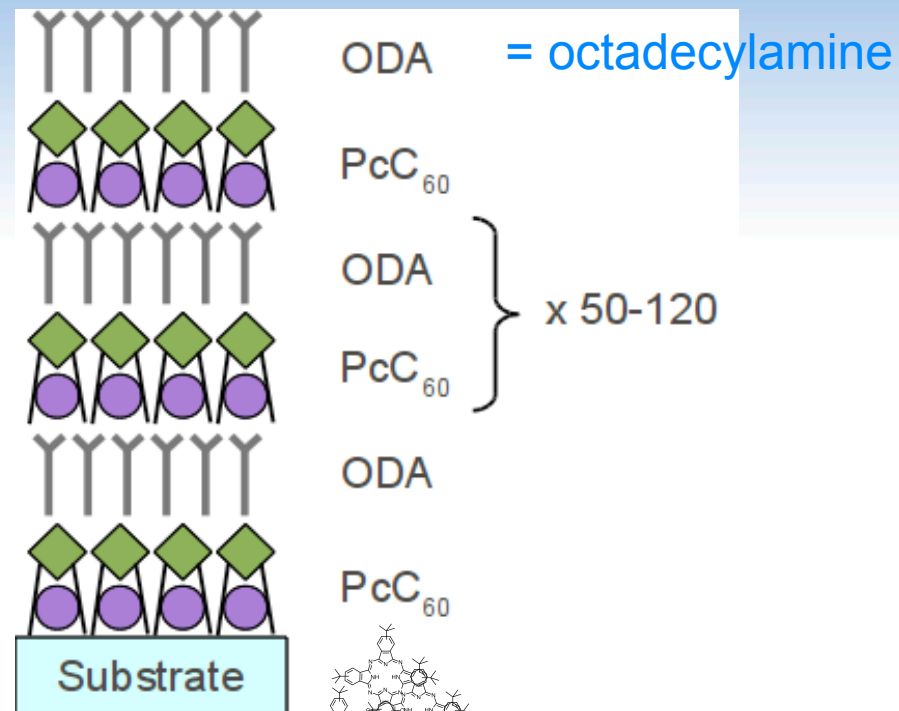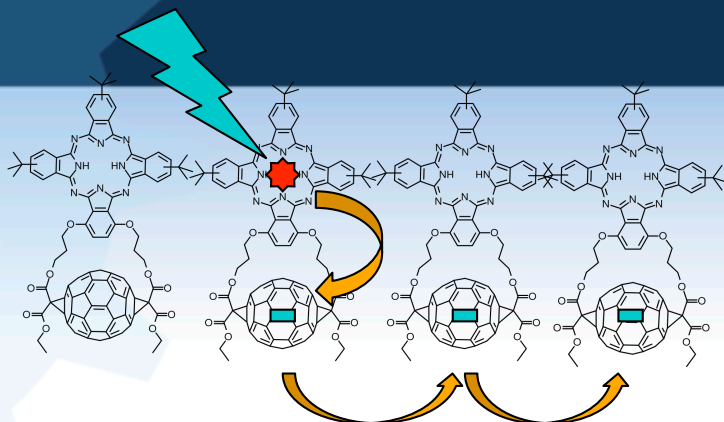

Langmuir-Schaefer

Multilayer films of phthalocyanine-fullerene dyad, *para*-PcF
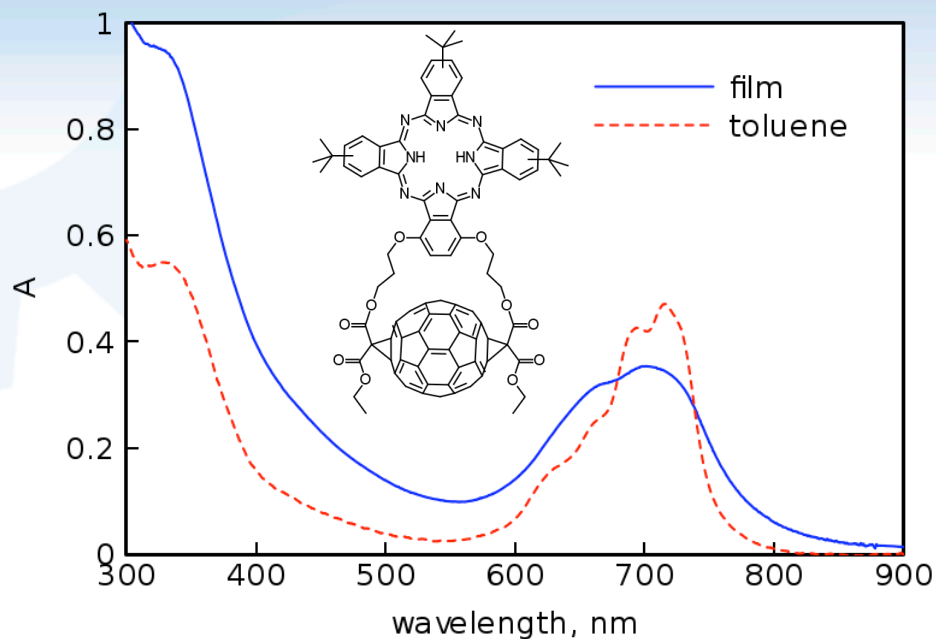
Absorption spectra of phthalocyanine-fullerene dyad multilayer LS film and in toluene.

ODA = octadecylamine

PcC$_{60}$

ODA

PcC$_{60}$ } x 50-120

ODA

PcC$_{60}$

Substrate

Vectorial and lateral electron transfer processes in organized solid films of *para*-PcF: femtosecond pump-probe measurements

1. Excitation of the electron donor

2. Intra-molecular electron transfer to acceptor

3. Formation of the charge separation state
   0.8 ps

4. Inter-molecular charge hopping from acceptor to acceptor
   35 ps

5. Formation of long-living CS-film

6. Recombination of the CS-film
 $\gg 2\ \mu s$

Legend:
- 0.8 ps
- 35 ps (av.)
- $\gg$ 3 ns
- at 0 ps
- at 10 ps

x-axis: wavelength, nm (600, 700, 800, 900, 1000)
y-axis: ΔA (0.02, 0.01, 0, -0.01, -0.02, -0.03, -0.04)

TAMPERE UNIVERSITY OF TECHNOLOGY
Department of Chemistry and Bioengineering

Vectorial and lateral electron transfer processes take place in solutionsin time scale less than one ns, but in organized solid films μs – ms time scales
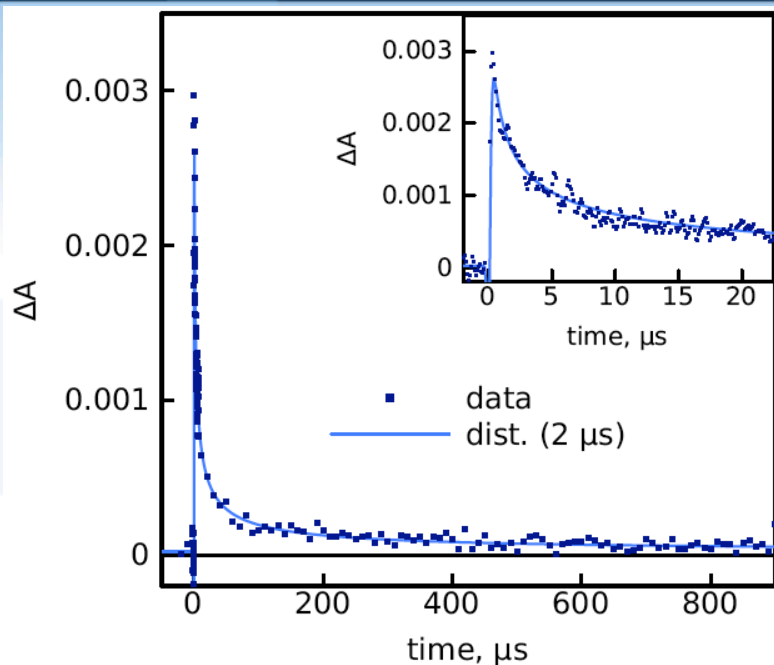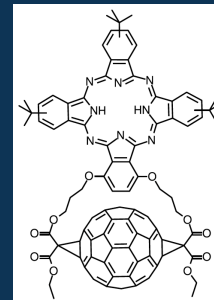
Transient absorption decay at 510 nm of multi-layer PcC dyad. Flash-photolysis
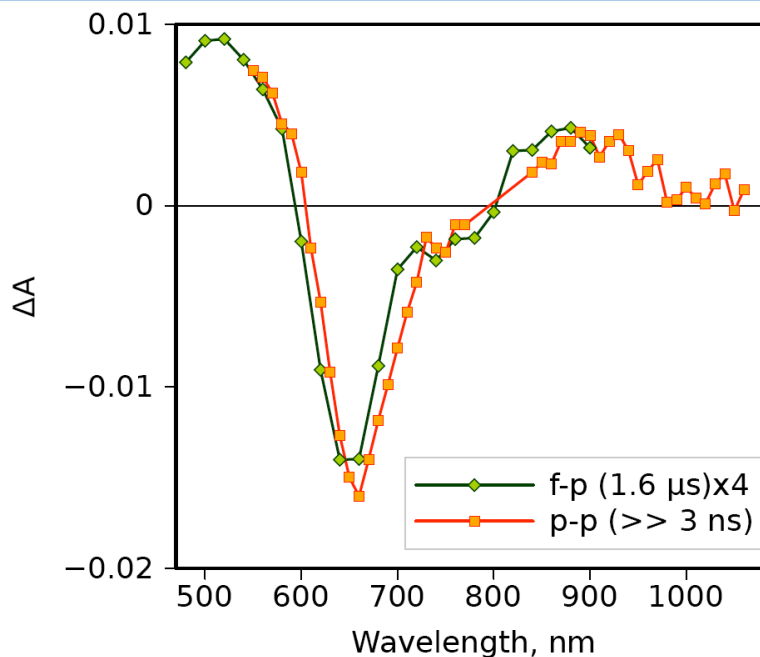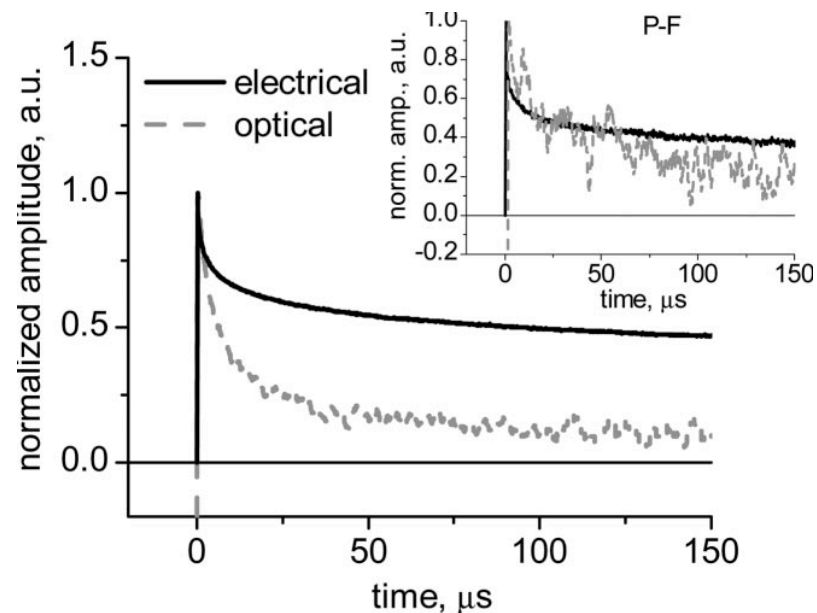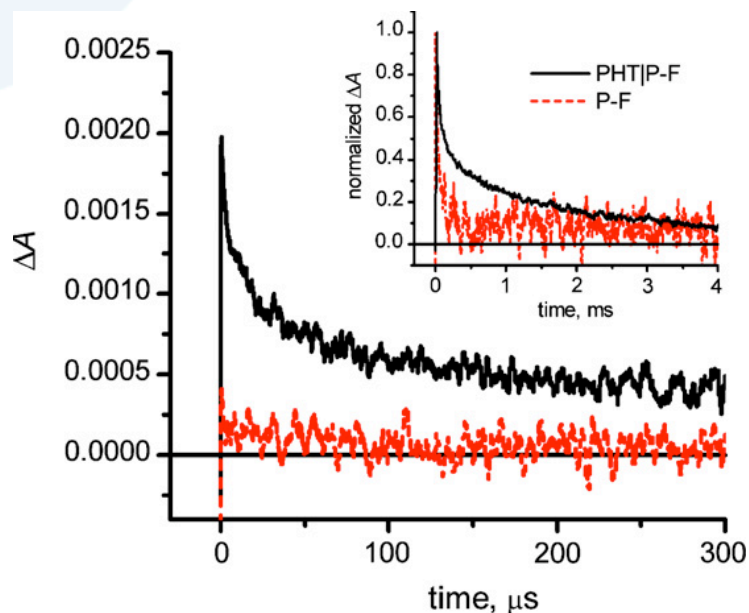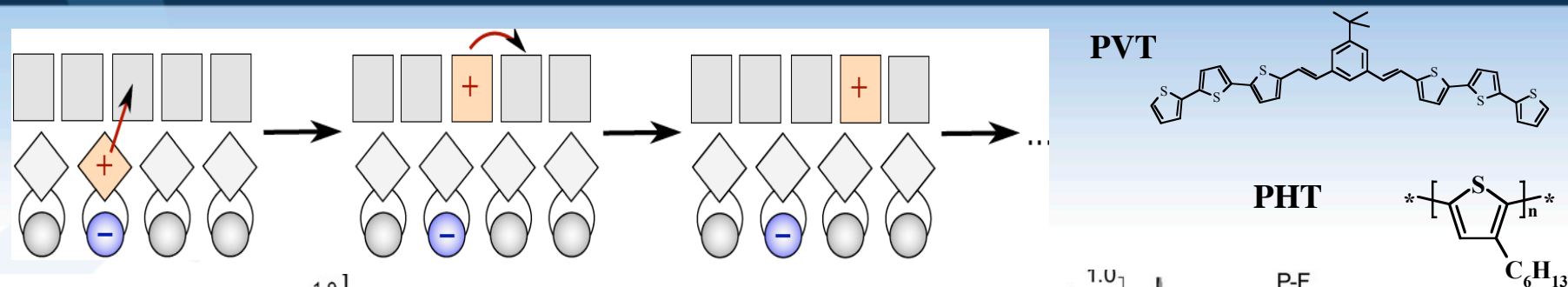
Comparison of the spectra measured by pump-probe and flash-photolysis methods

H. Lehtivuori, T. Kumpulainen, M. Hietala, A. Efimov, H. Lemmetyinen, A. Kira, H. Imahori, N. V. Tkachenko, *J. Phys. Chem. C*, **2009**, *113* (5), 1984-1992.

TAMPERE UNIVERSITY OF TECHNOLOGY
Department of Chemistry and Bioengineering

Optical decay (left) and electrical decay curves (right) of PVT(or PHT) | DHD three layer systems
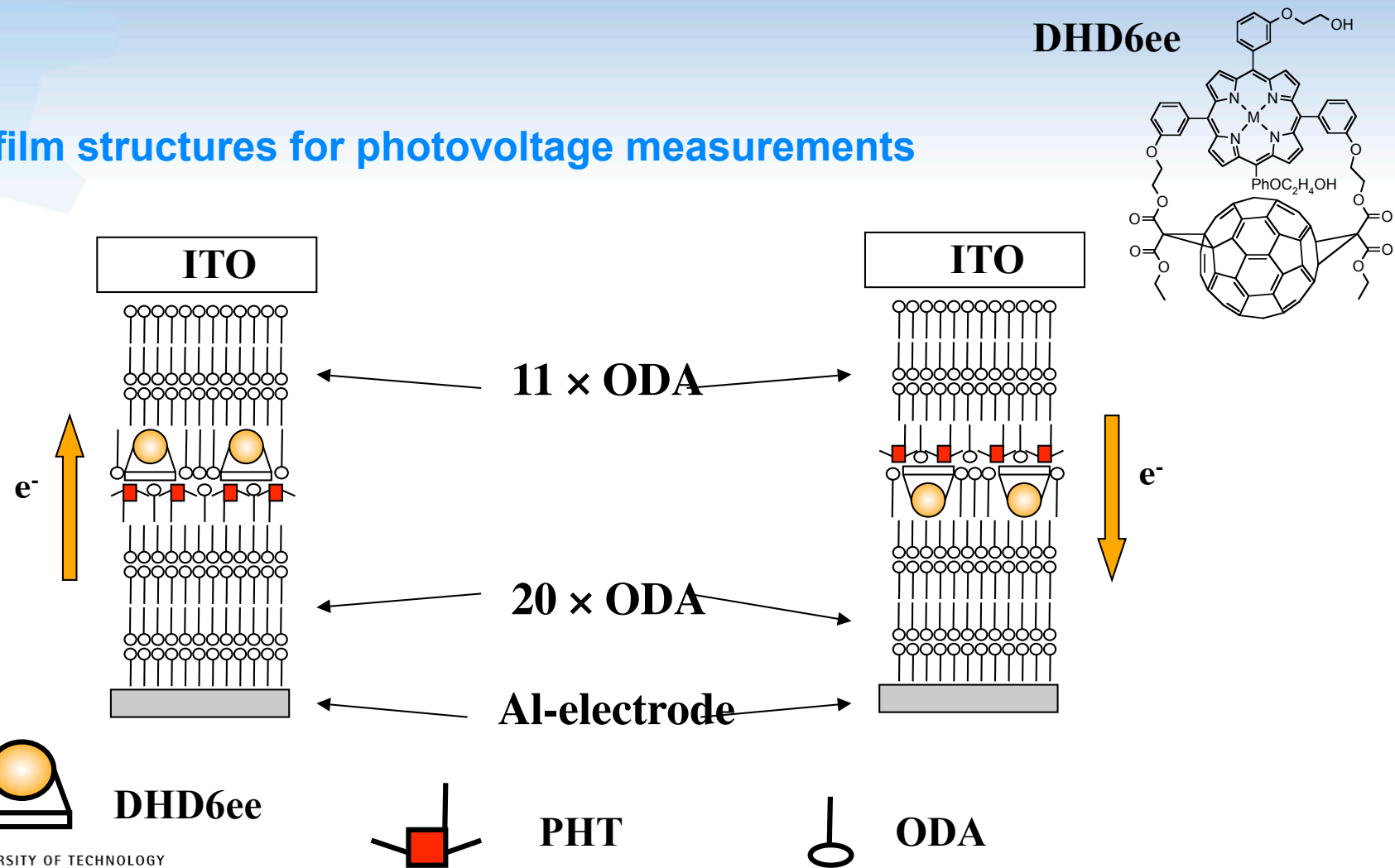

PVT

PHT

Kaunisto, Chucharev, Tkachenko, Lemmetyinen, *Chem. Phys. Lett.*, **460**, 2008, 10256

Kaunisto, Chucharev, Tkachenko, Efimov, Lemmetyinen, *J. Phys. Chem.*, **113**, 2009, 3819
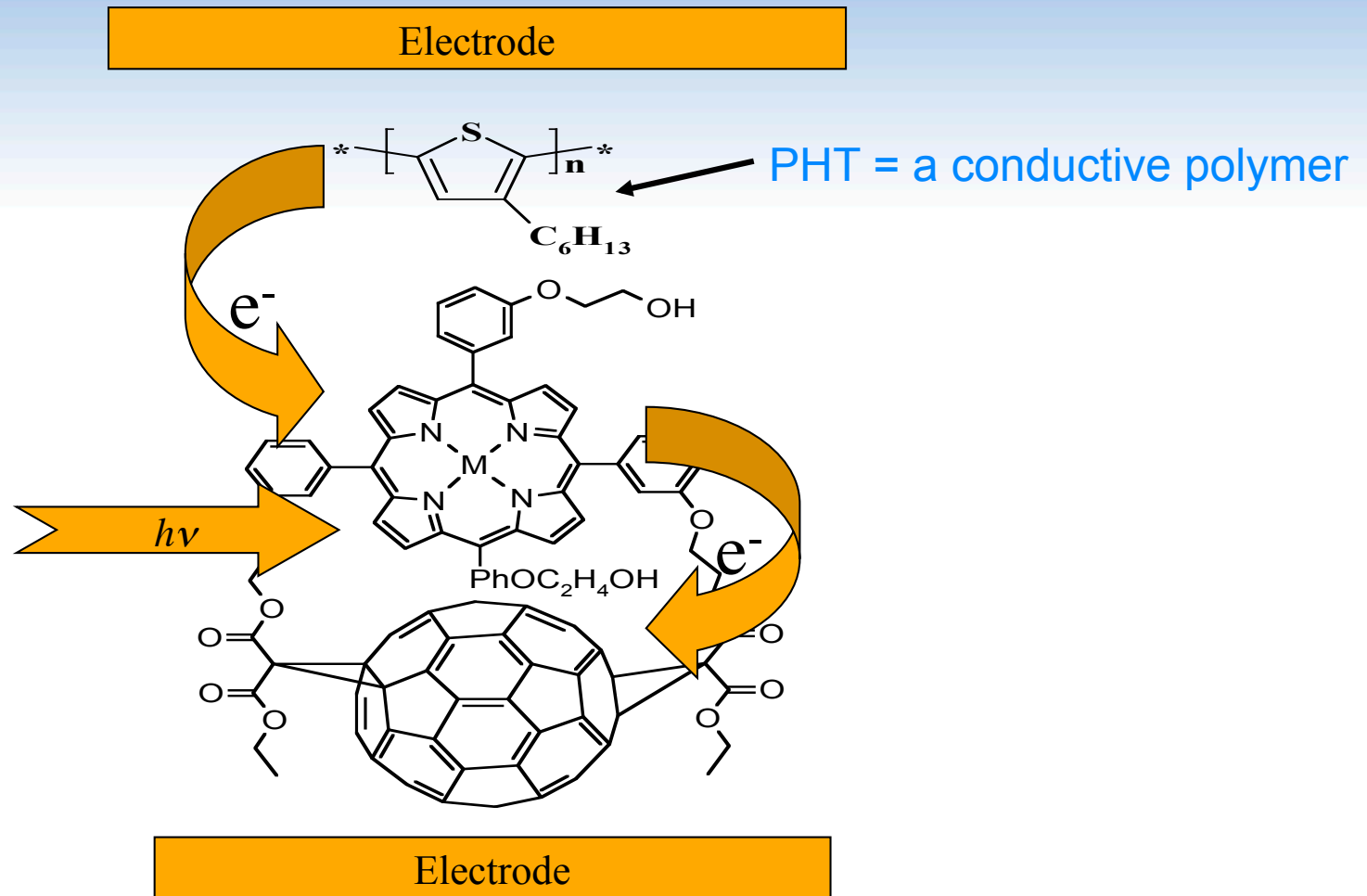
Orientation of molecular thin films were obtained by using the Langmuir-Blodgett technique:
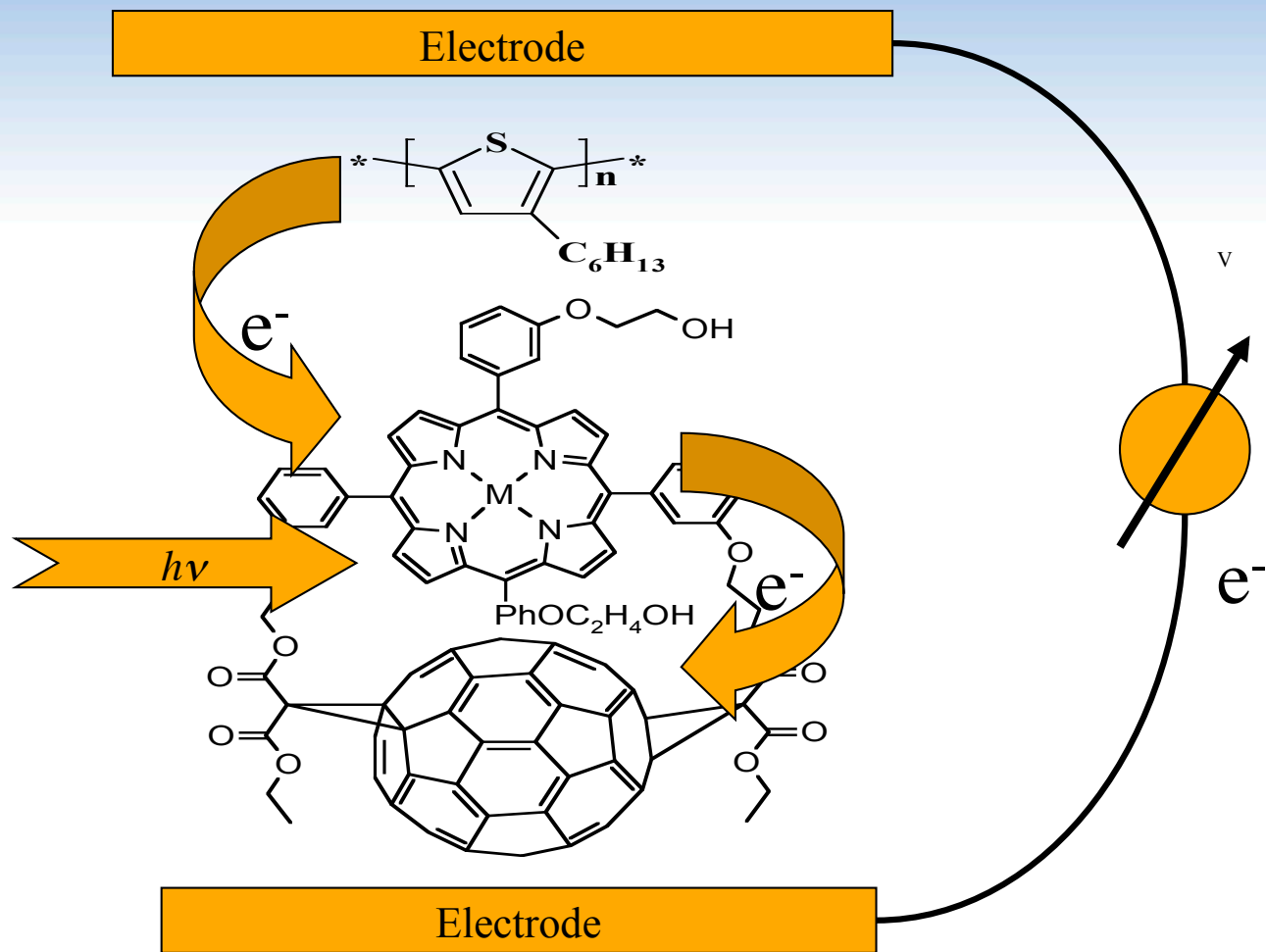
DHD6ee

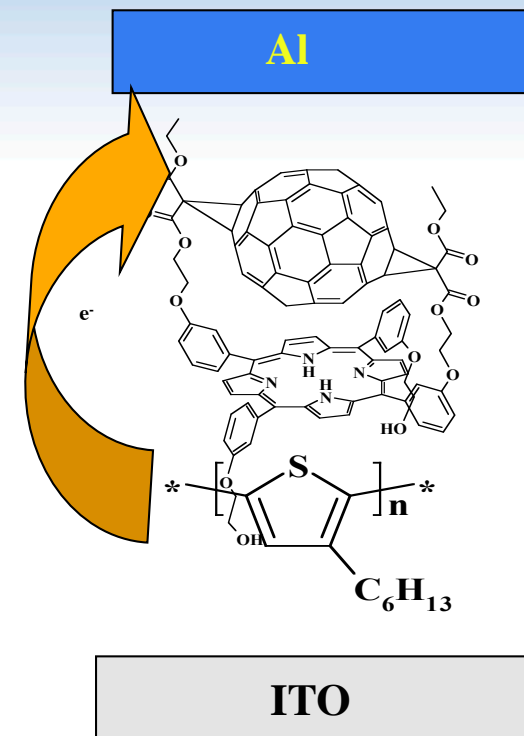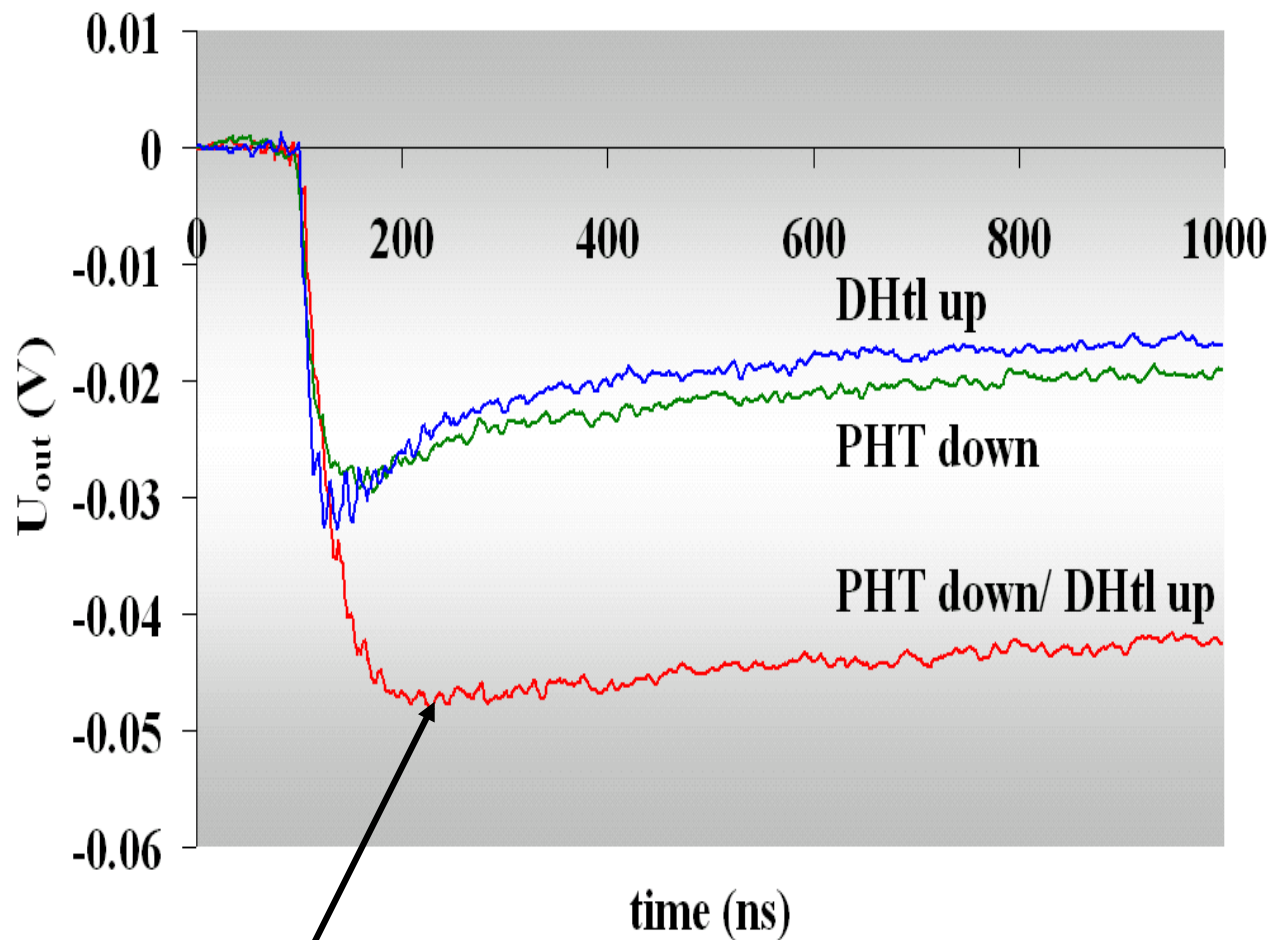## The LB-film structures for photovoltage measurements

Molecules in self-assembled or organized phase: in 2D films vectorial electron transfer takes place …

PHT = a conductive polymer

... and create photovoltage or photocurrent!

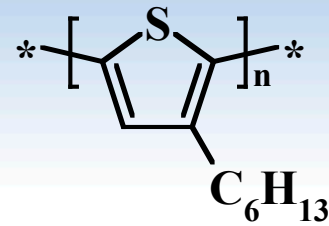# Intensity of the photovoltage signals depends on number of electrons moving and on the distance of the movement
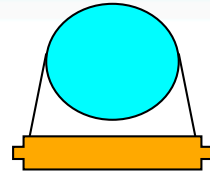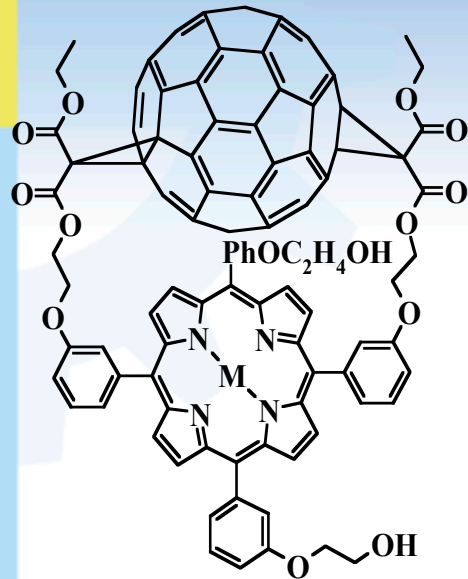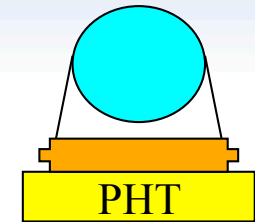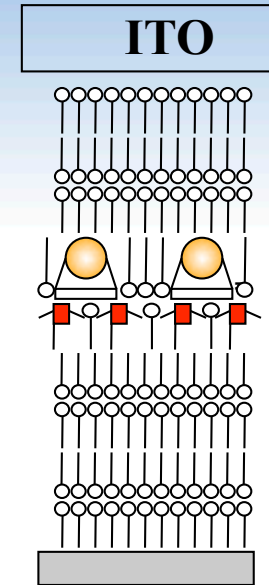

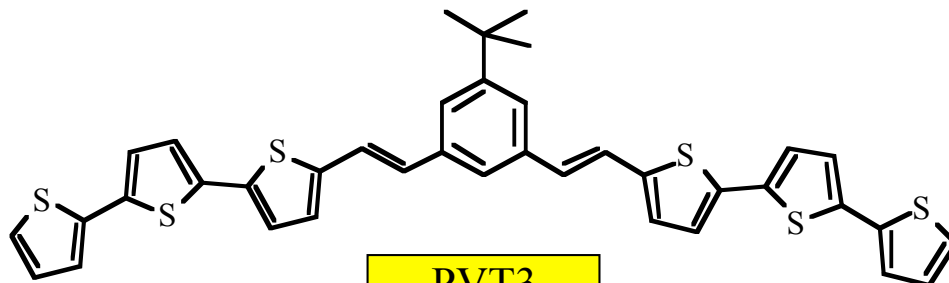(a lower excitation intensity was used)

Molecular Engineering: Building a device:

The elements for preparing of supramolecular film structures

PHT

ITO

PHT
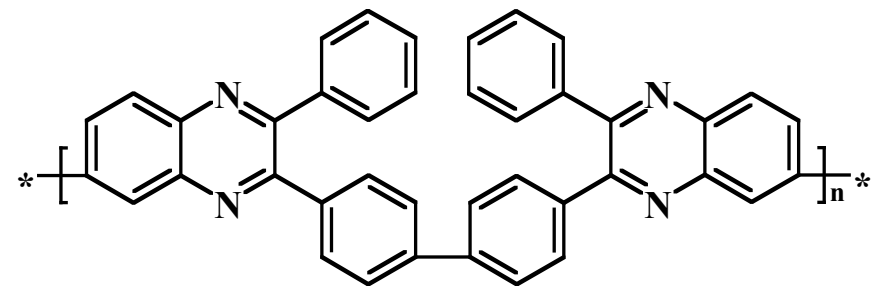
PVT3

PPQ

Photovoltage signals for PVT3/Dyad/PPQ film systems:

As number of layers increases the signal intensity and life time increase
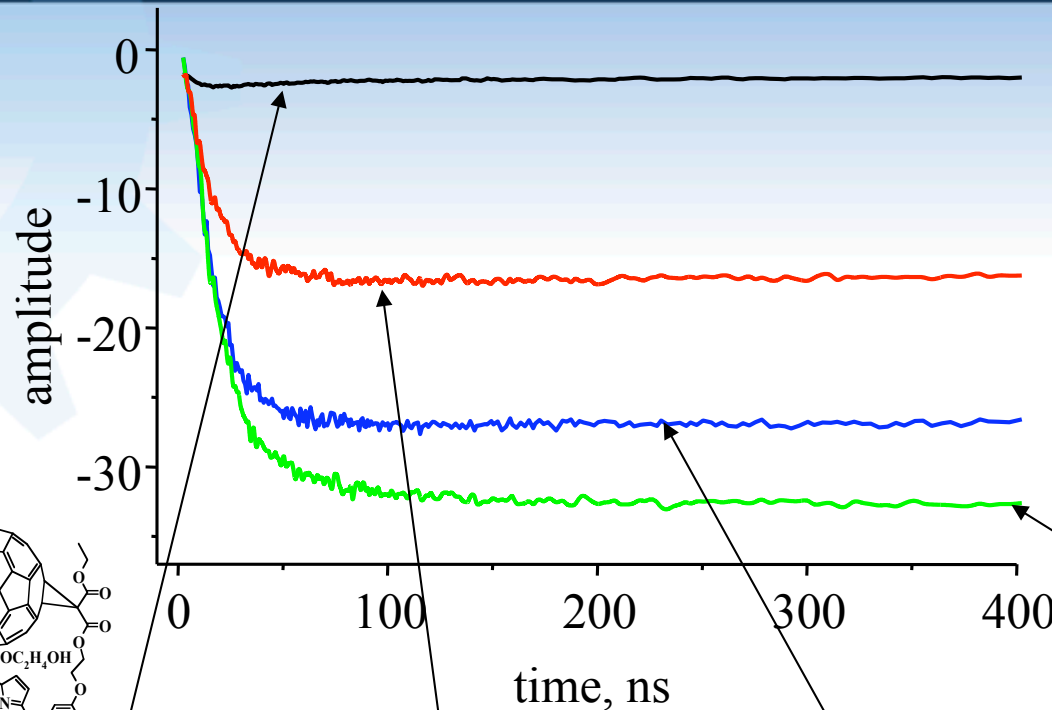
- PVT3 acts as an energy donor to the porphyrin moiety
- PPQ acts as electron acceptor from fullerene anion radical
- PHT acts as an electron donor to porphyrin cation radical
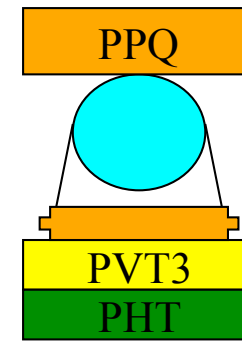
Lifetimes are in time scale of of seconds!

CARBON NANO TUBES, FULLERENE AND DYE MOLECULES IN SELF-ORGANIZED MOLECULAR ARRANGEMENTS

Donor covalently linked on the surface of nano tube

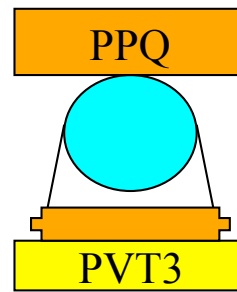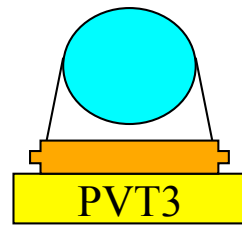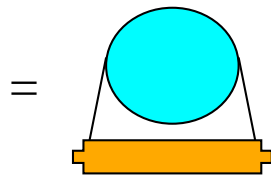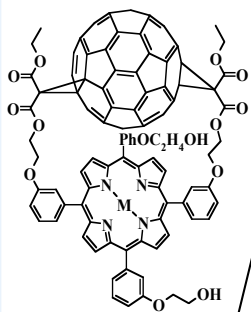1) Porphyrin-NT composites with a "long" flexible bridge to SWNT, have showns photoinduced charge separation

NT--P* → NT$^{-\cdot}$--ZnP$^{+\cdot}$ → NT—P
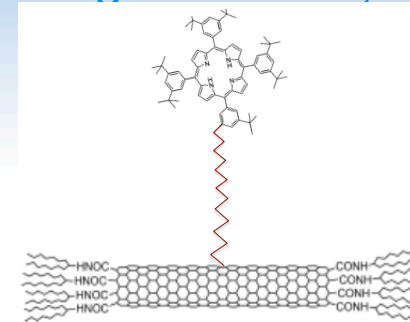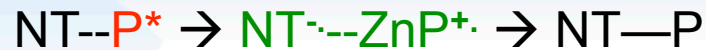
2) Porphyrin-NT composites with a "short" rigid bridge to SWNT form exciplex and decays directrly to the ground state

NT-P* → (NT-P)* → NT--P
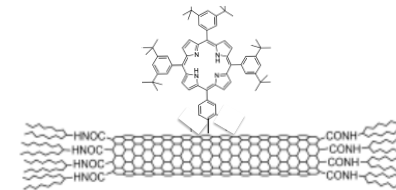
Therefore, the separation distance and spatial orientation between porphyrin and SWNT are crucial factors to control the relaxation processes from the excited states.

D-A pair on the surface of nano tube

H₂Por–C₆₀ H₂Por–ref C₆₀–ref f-SWNT
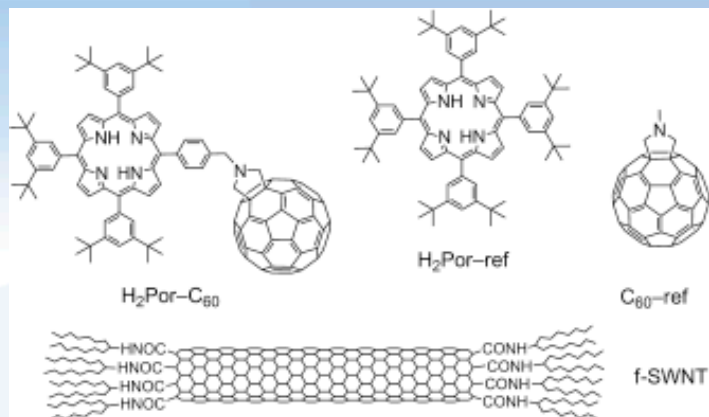
Covalently linked electron D (porphyrin) and A (C_{60}) yield a long-lived charge-separated state efficiently
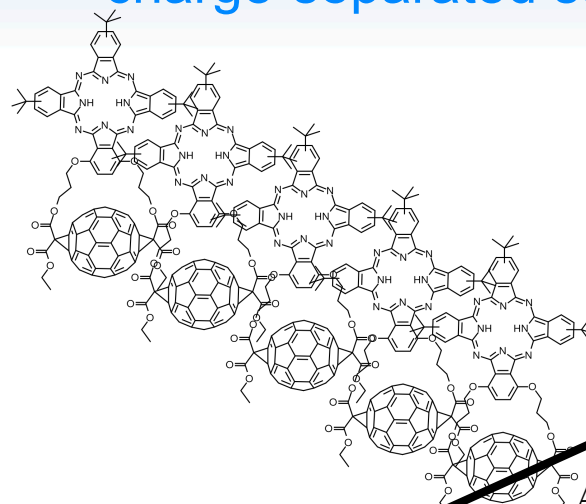
AAAAA
DDDDD
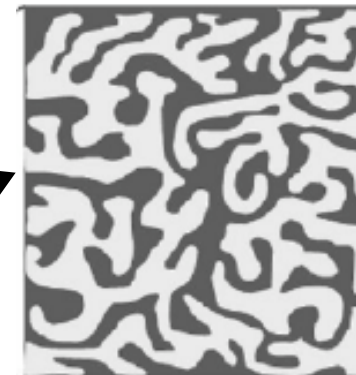
Mixing D-A –pair, in a suitable solution, intermolecular porphyrin–porphyrin (D-D) and C_{60}–C_{60} (A-A) interactions yield to a formation of nanograins, where D and A moieties are arranged separately.

TAMPERE UNIVERSITY OF TECHNOLOGY
Department of Chemistry and Bioengineering

Formation of porphyrin–porphyrin (D-D) and C_{60}–C_{60} (A-A) nanograins on the surface of nanotubes.

Adding of NTs cross-links the nanograins in the mixed solvent enhancing the electric communication between the grains
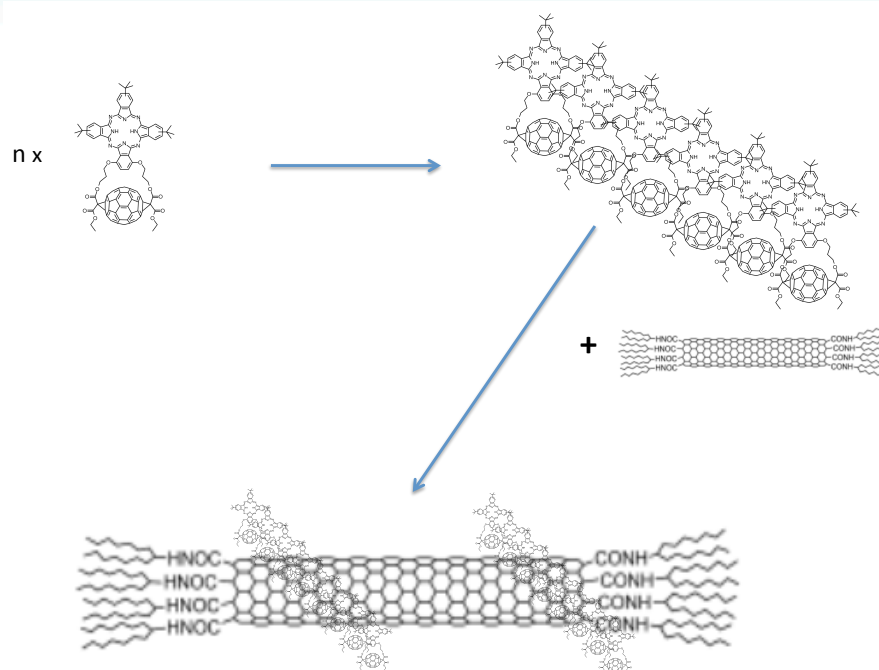
Electrophoretic deposition of the nanograins onto a nanostructured SnO$_2$ electrode fabricates a desirable **H$_2$Por-C$_{60}$-NT** film on the electrode. (step 2)

Step 1: Formations of the nanograins in the mixed
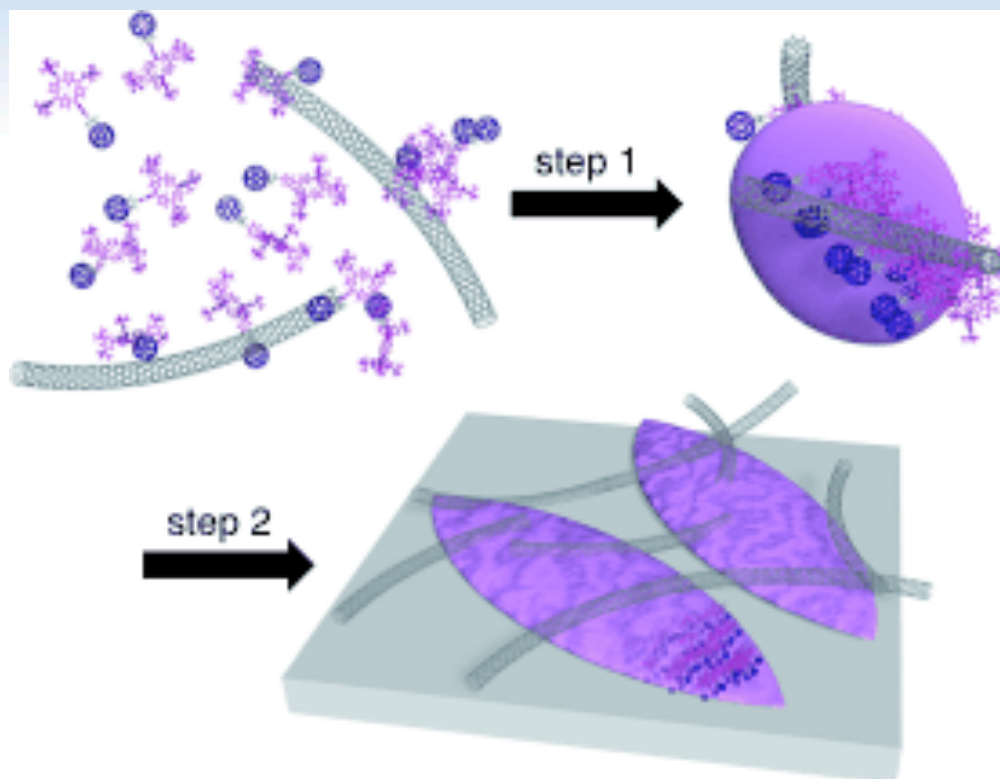
FE-SEM images on solid FTO/SnO$_2$
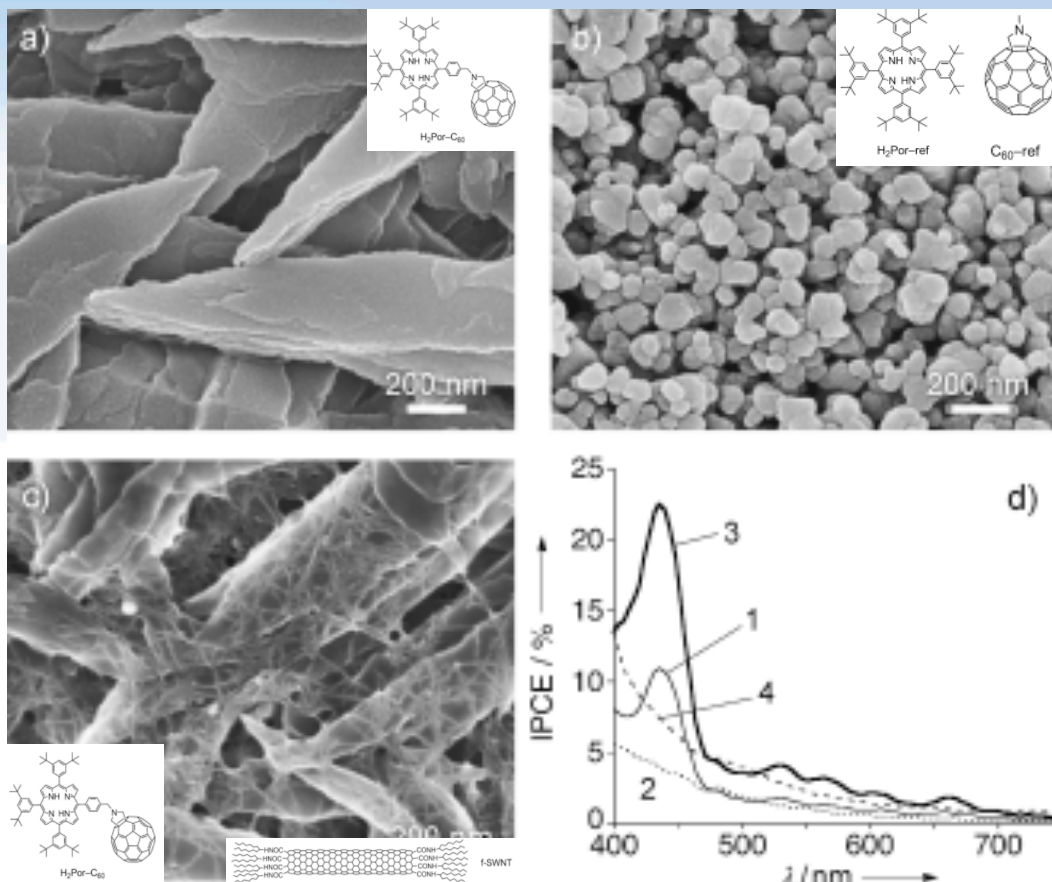
FE-SEM images of FTO/SnO$_2$/films
a) H$_2$Por–C$_{60}$
b) H$_2$Por-ref + C$_{60}$-ref
c) H$_2$Por–C$_{60}$+ NT electrodes
d) Corresponding photocurrent action
 spectra of
1) H$_2$Por–C$_{60}$
2) H$_2$Por-ref + C$_{60}$-ref
3) H$_2$Por–C$_{60}$+ NT electrodes
4) H$_2$Por-ref + C$_{60}$-ref + NT

IPCE=incident photon to current efficiency

Donor covalently linked on the surface/acceptor inside of nano tube

C_{60}@NT

C_{60}@NT-PhI

C_{60}@NT-ZnP

Ar=

solution

f-SWNT
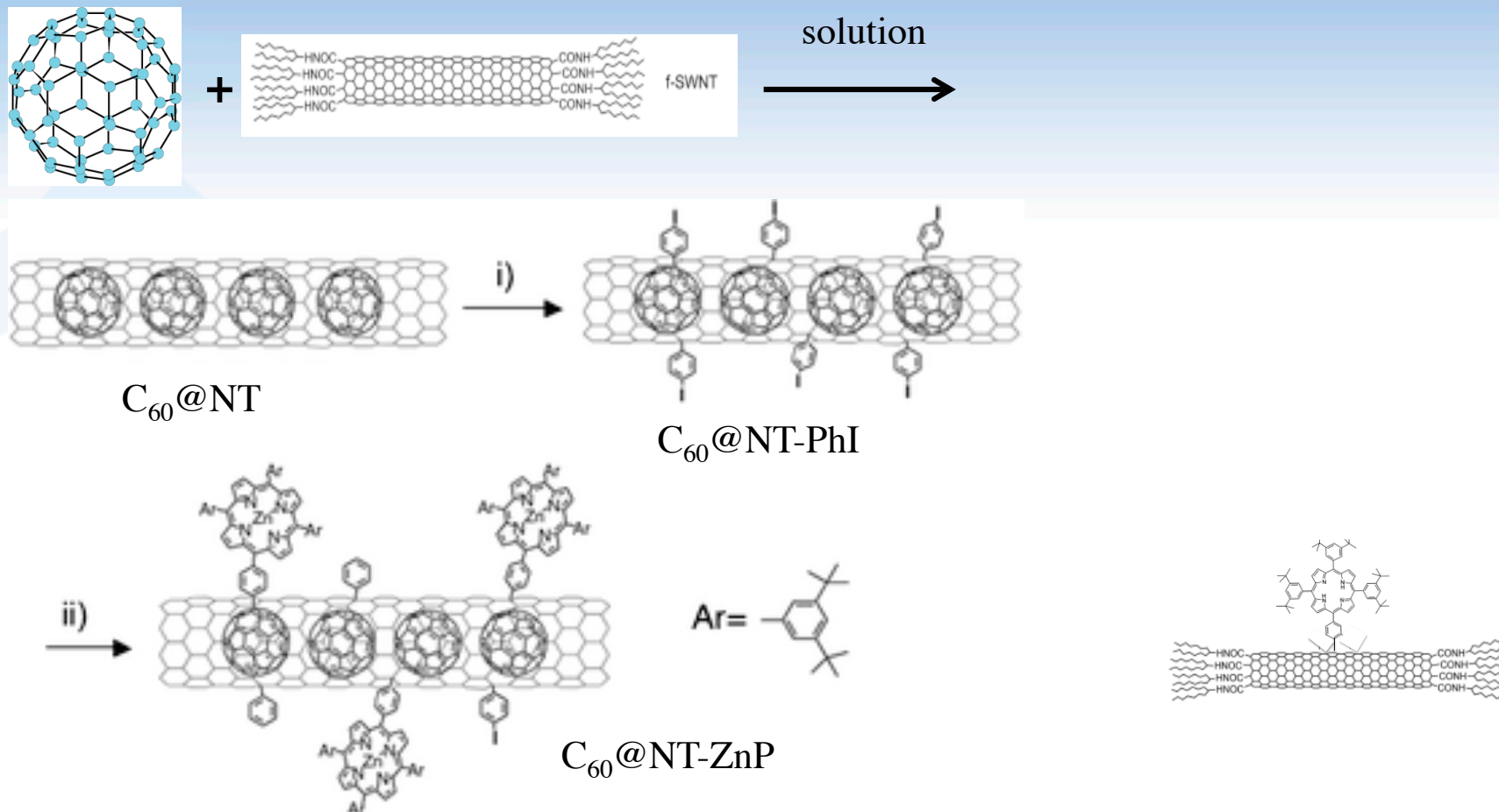
Absorption and emission spectra of components forming Donor-Acceptor system separated by NT

C$_{60}$@NT-PhI
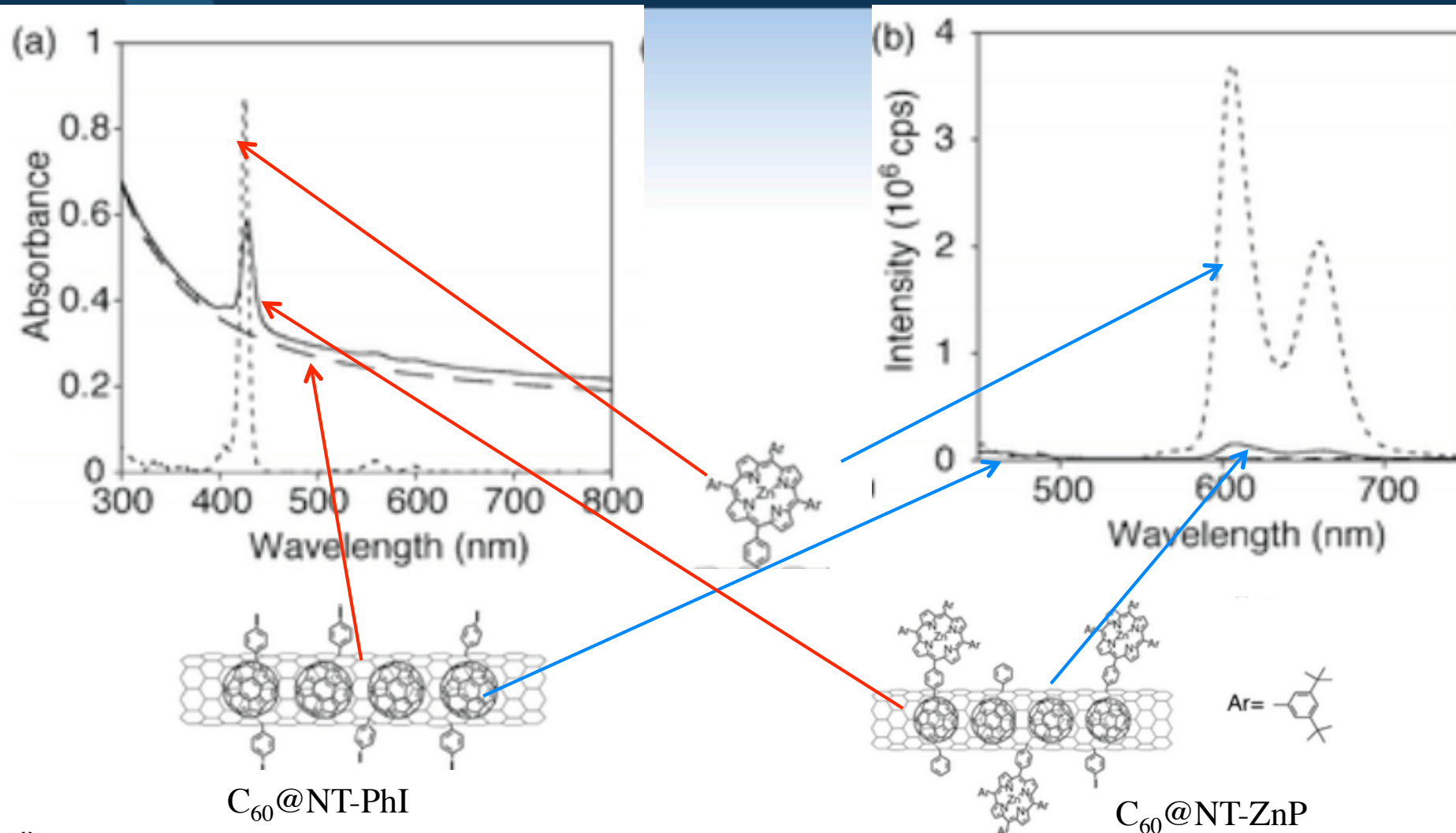
C$_{60}$@NT-ZnP

The porphyrin emission decays and transient absorption spectra of C_{60}@NT-ZnP and ZnP-ref

$\tau = 2.0$ ns

C_{60}@NT-ZnP

$\tau < 70$ ps

Ar=
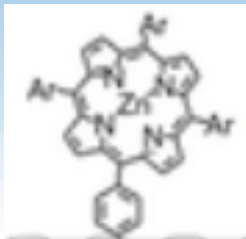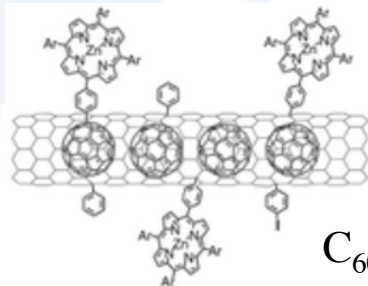
C_{60}@NT-ZnP* $\rightarrow$ C_{60}@(NT-ZnP)* $\rightarrow$ $C_{60}^{-\cdot}$@NT-ZnP$^{\bullet+}$
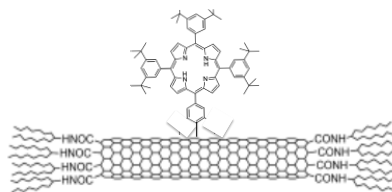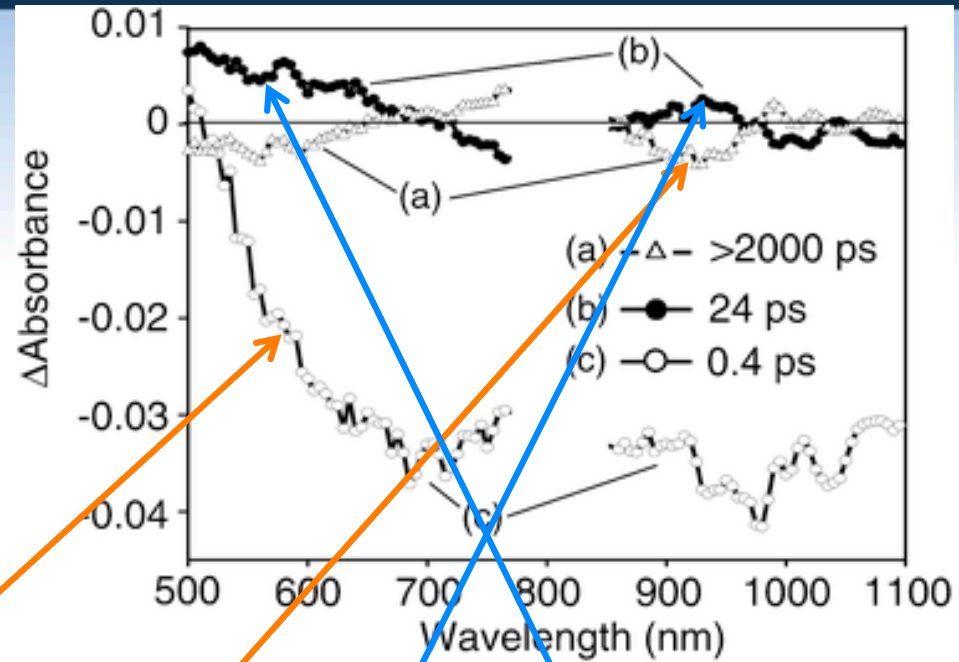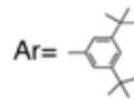
Why we do all this research?

We have a dream…

PF: M = 2H, R = H

carbon dioxide + water $\xrightarrow[\text{chlorophyll}]{\text{light energy}}$ carbohydrates + oxygen

$CO_2 + H_2O \xrightarrow[\text{chlorophyll}]{\text{light energy}} C_6H_{12}O_6 + O_2$

$6CO_2 + 6H_2O \xrightarrow[\text{chlorophyll}]{\text{light energy}} C_6H_{12}O_6 + 6O_2$
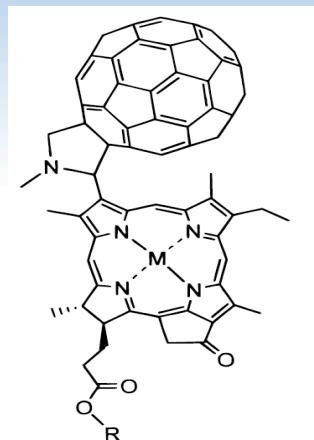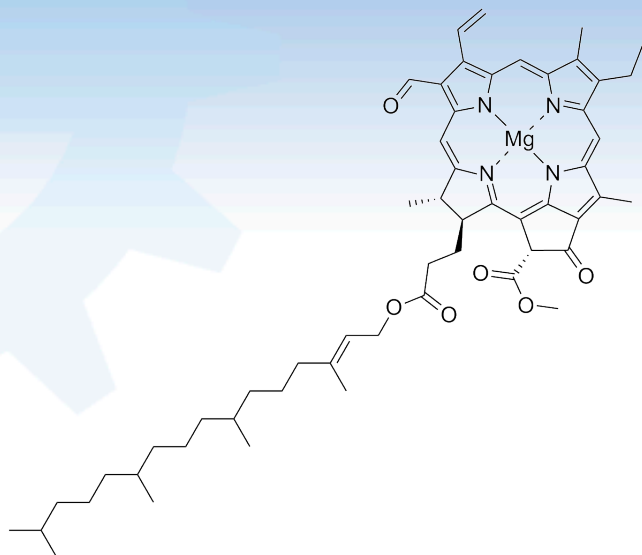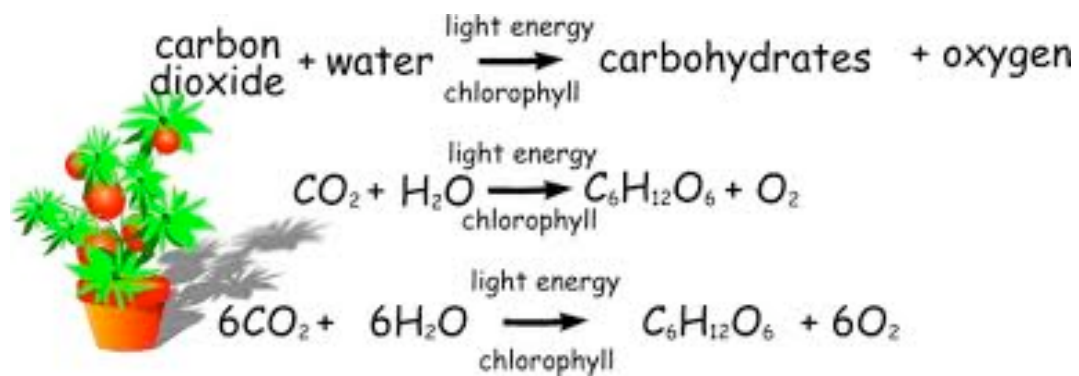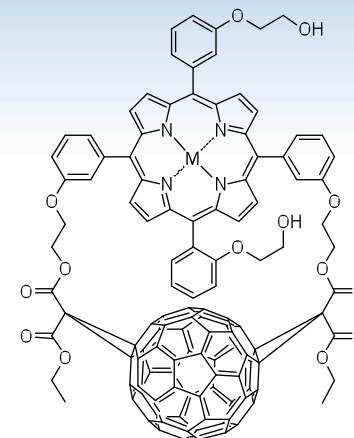
… and not only we!

Jimmy Stewart on Photosynthesis

A memorable scene from the 1938 movie adaptation of the play

"*You Can't Take It With You*",

starring Jimmy Stewart, Jean Arthur, Lionel Barrymore, and Edward Arnold

World Energy Production
1970 to 2100
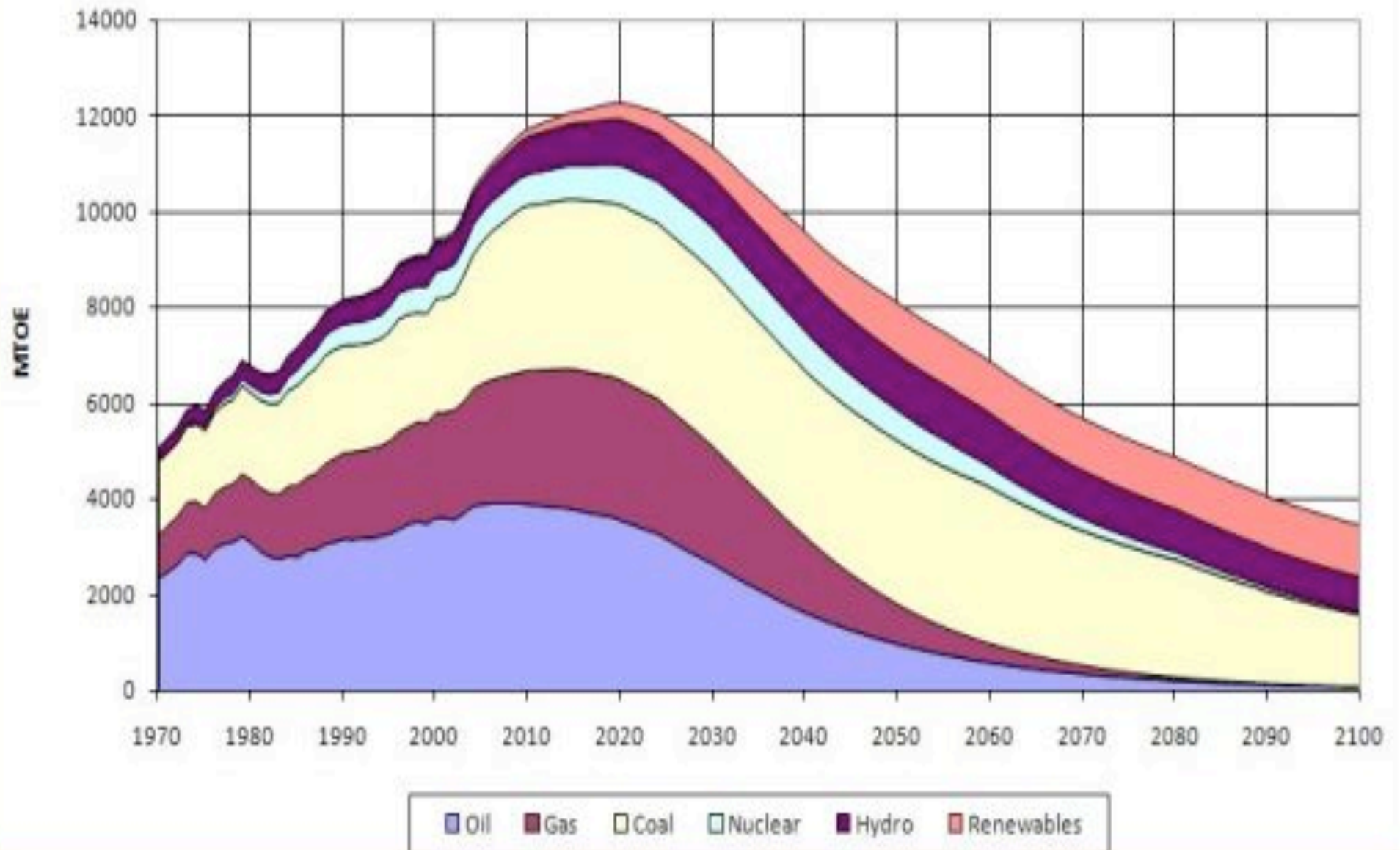
Word energy consumtion annually

2004	$5{,}0 \cdot 10^{20}$ J	$15{,}0 \cdot 10^{12}$ W	15 TW
2010	$5{,}4 \cdot 10^{20}$ J	$17{,}1 \cdot 10^{12}$ W	17 TW
2020	$7{,}1 \cdot 10^{20}$ J	$22{,}5 \cdot 10^{12}$ W	23 TW
2040			45 TW

In next 25 years (2015-2040) we need more energy 25 TW

$\approx$ 25 000 nuclear power plants (1 GW)

$\approx$ 1000 power plants/year

Figure 1 - Evolution of global cumulative installed capacity 2000-2011 (MW)

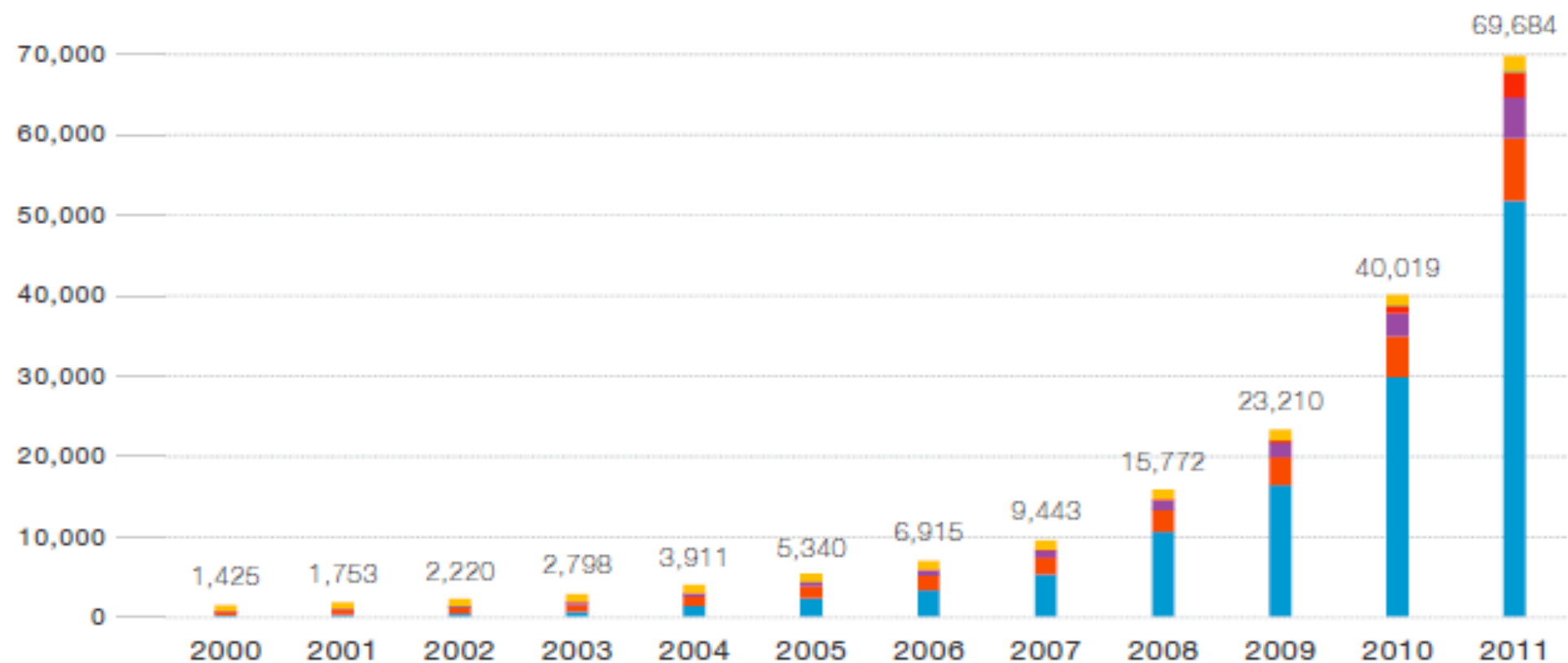|	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
ROW	751	807	887	964	993	1,003	1,108	1,150	1,226	1,306	1,209	1,717
MEA	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	21	205	336
China	19	30	45	55	64	68	80	100	145	373	893	3,093
America	146	177	222	287	379	496	645	856	1,205	1,744	2,820	5,053
APAC	355	491	677	902	1,178	1,475	1,797	2,080	2,643	3,409	5,116	7,769
Europe	154	248	389	590	1,297	2,299	3,285	5,257	10,554	16,357	29,777	51,716
Total	1,425	1,753	2,220	2,798	3,911	5,340	6,915	9,443	15,772	23,210	40,019	69,684

Figure 12 - European cumulative scenarios until 2016 - Moderate and Policy-Driven (MW)
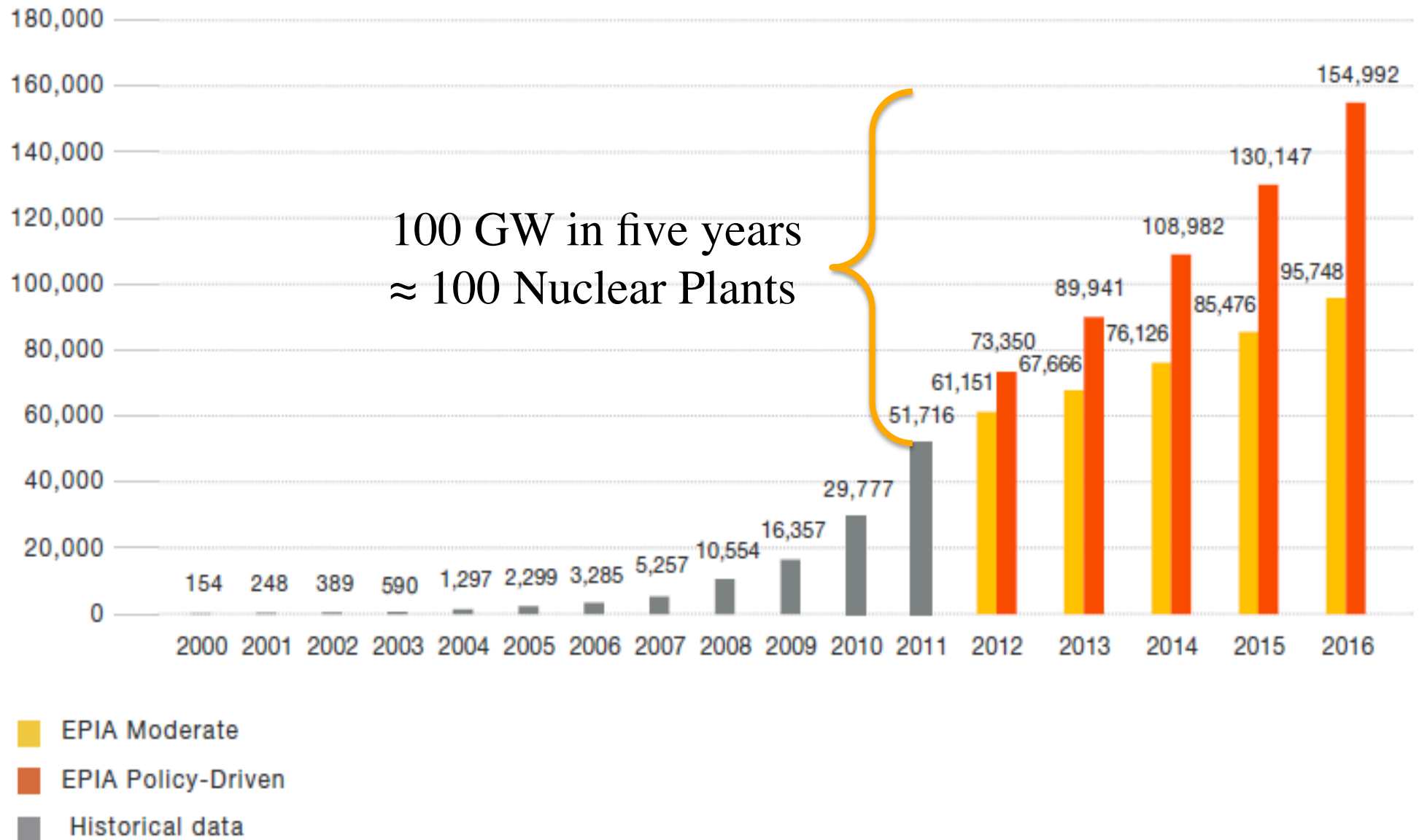
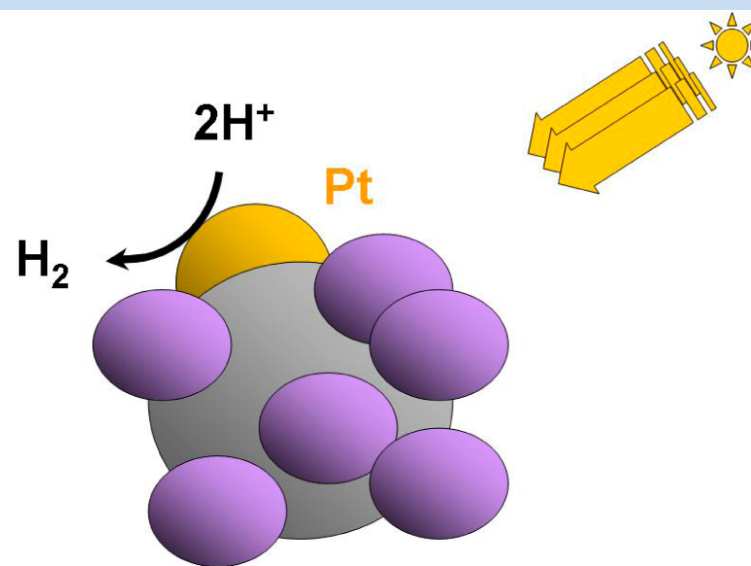# Schematic representation of photovoltaic (a) and photochemical (b) cells.
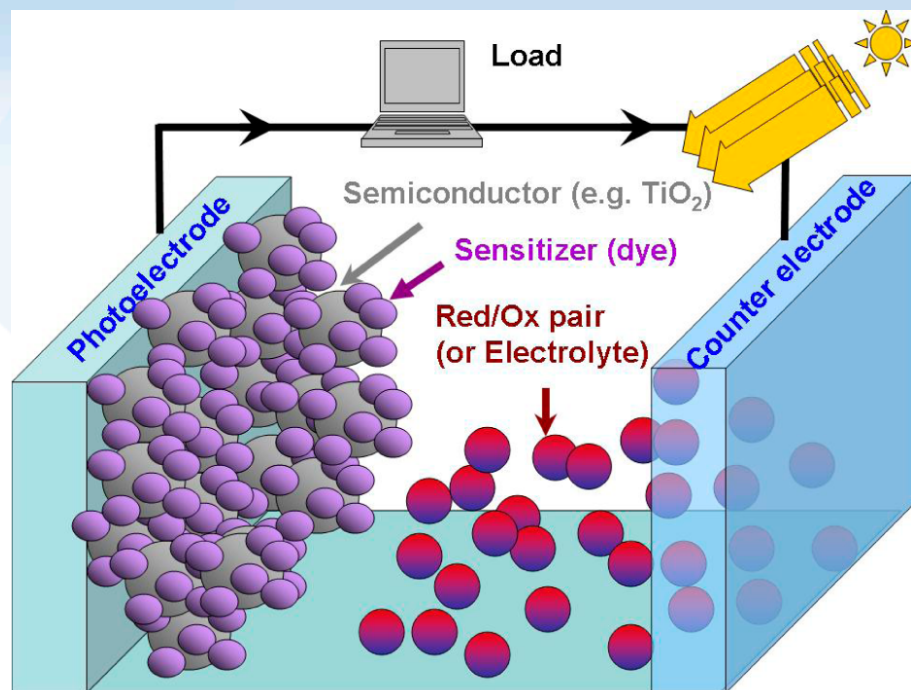
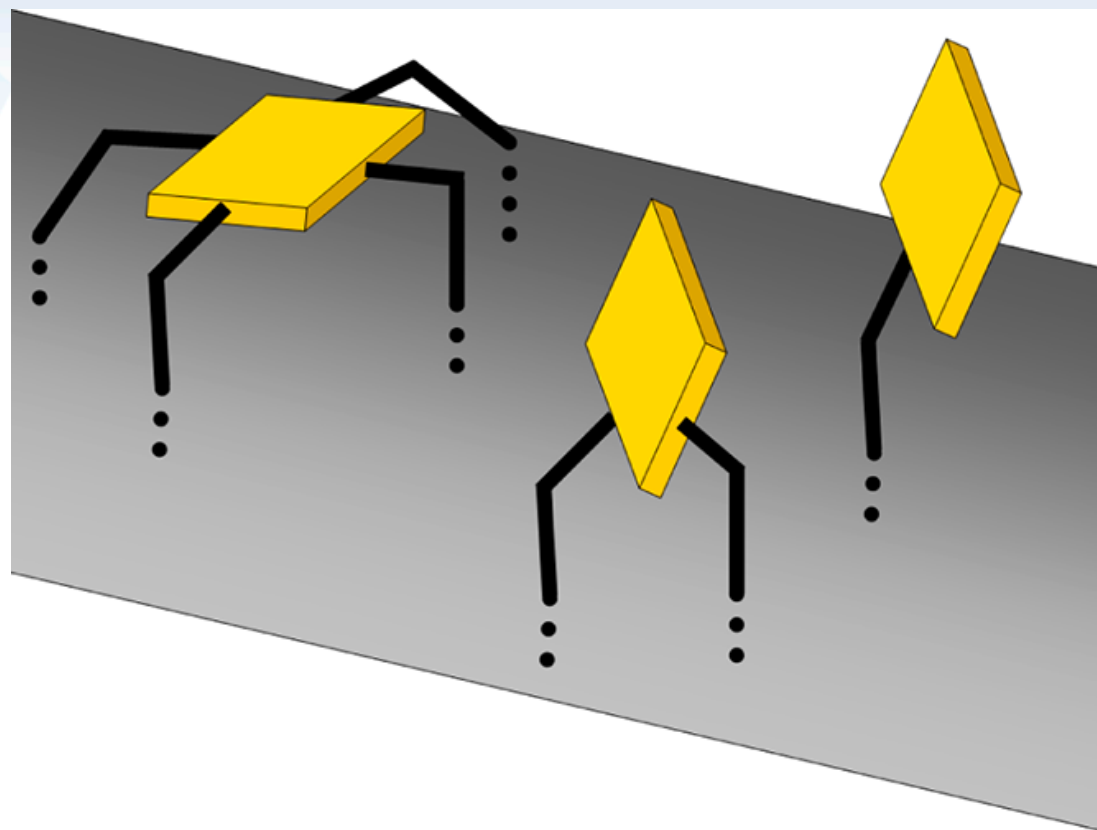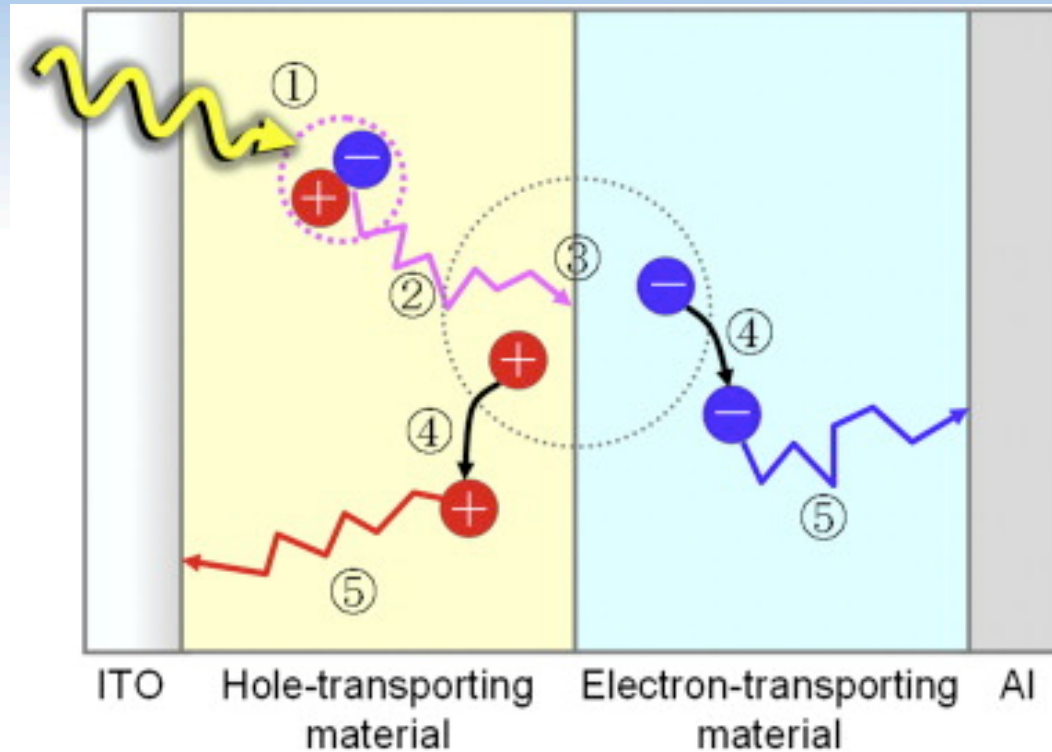(a)   (b)

Binding modes of porphyrins and phthalocyanines

Photovoltaic conversion processes in bilayered organic solar cells:
1) exciton generation, 2) exciton diffusion, 3) charge transfer,
4) charge dissociation, and 5) charge transport.

Schematic of a bulk heterojunction solar cell and the simplified energy level diagram of a donor/acceptor interface
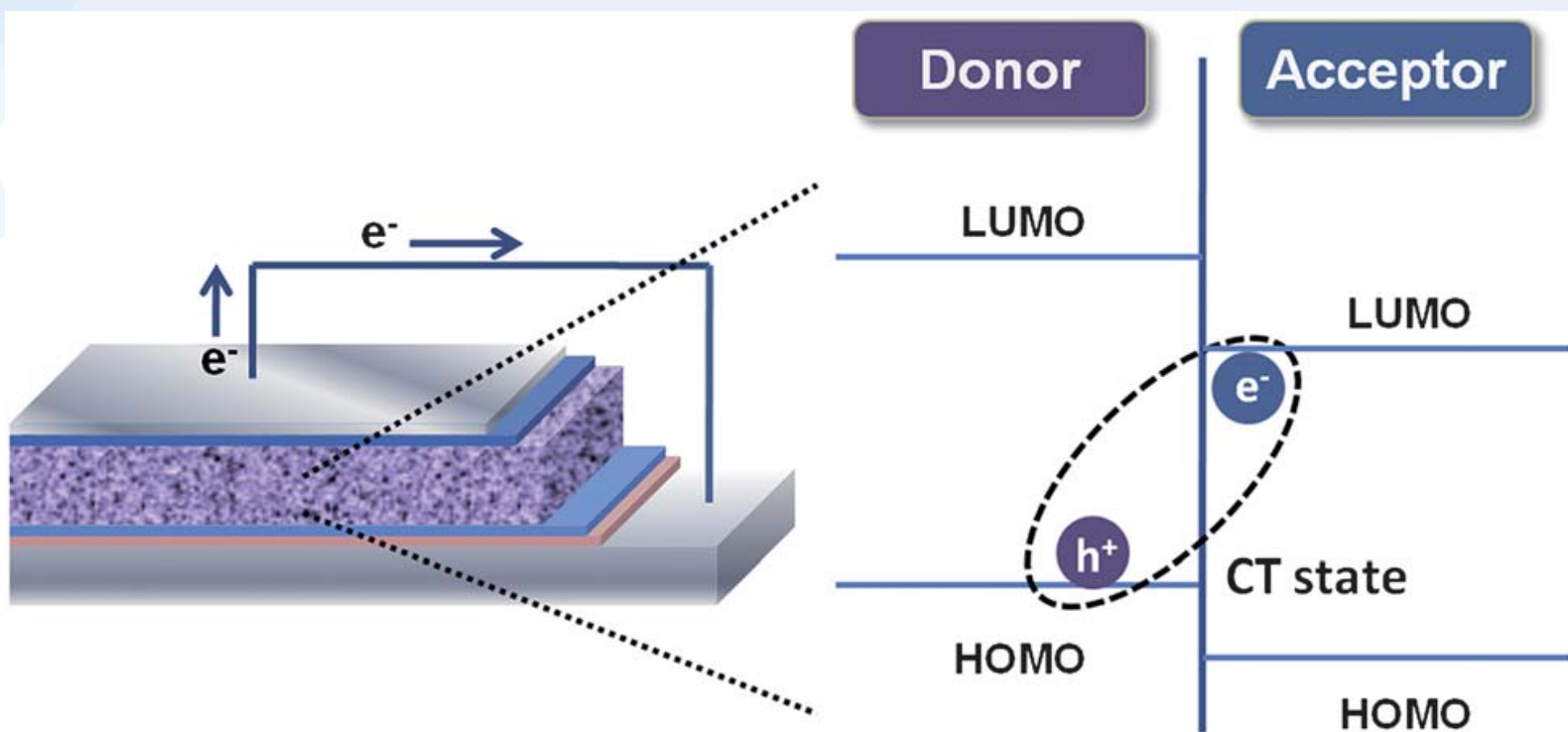
Conjugated polymers employed in polymer/fullerene solar cells:
a) MEH-PPV, b) MDMO-PPV, c) RR-P3HT, d) RRa-P3HT, e) C_{60},
f) PCBM, g) [70]PCBM.
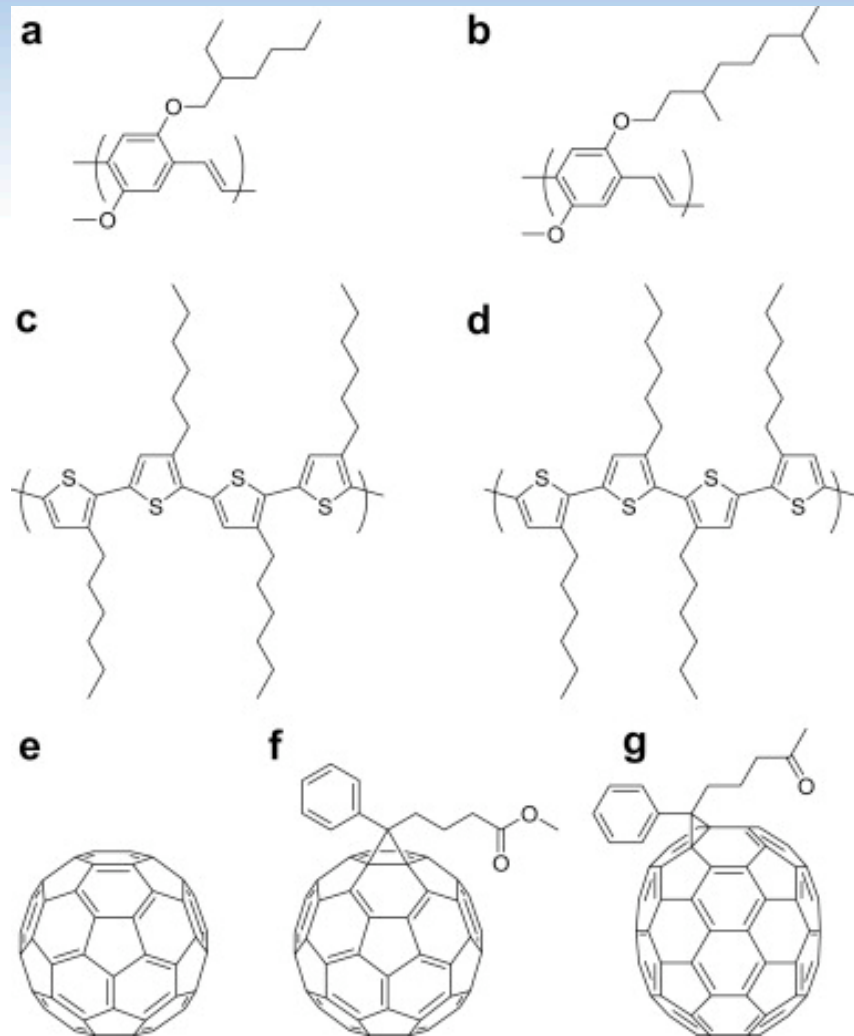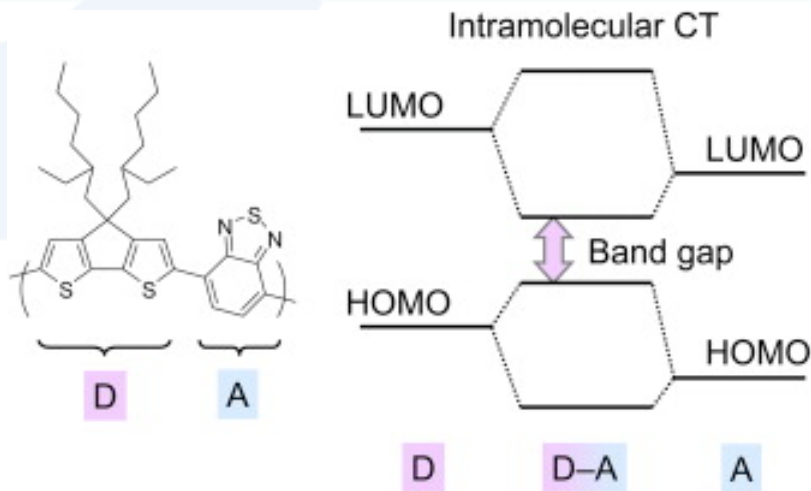
Organic solar cell configurations

LAYERED

− +

Al or Au

ITO

PLASTIC or GLASS

BULK HETEROJUNCTION

− +

Al or Au

ITO

PLASTIC or GLASS
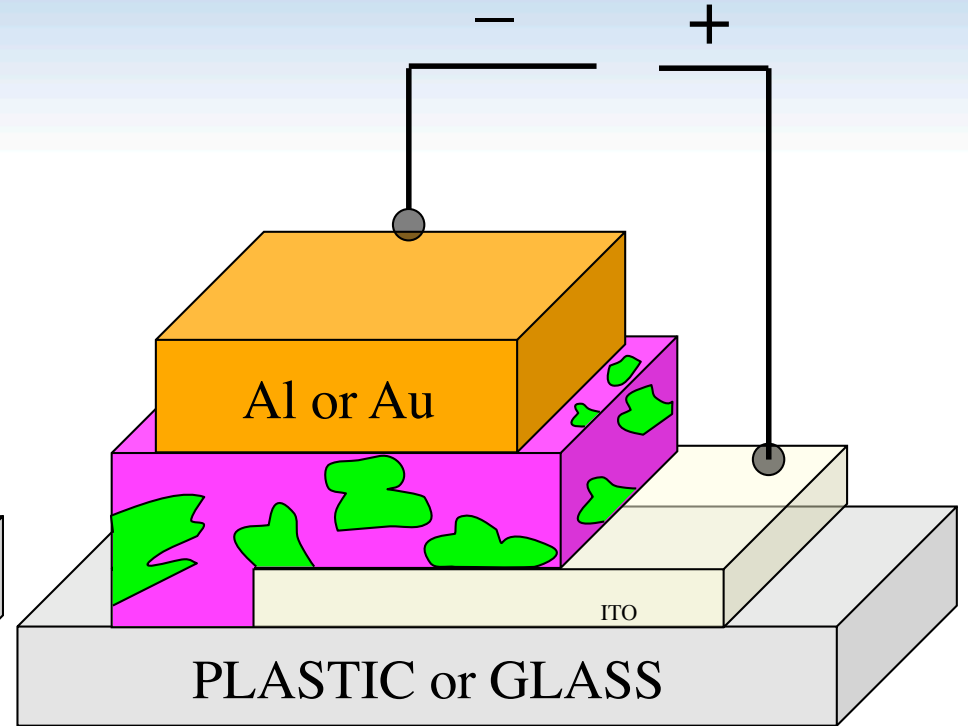
Electron donor (HTL)

Electron acceptor (ETL)

Zn-benzothiazole as buffer layer

Alq3

ZnBT2
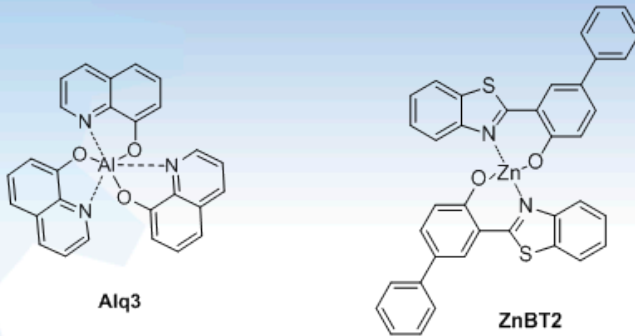
Sample lifetime is one year at ambient conditions.

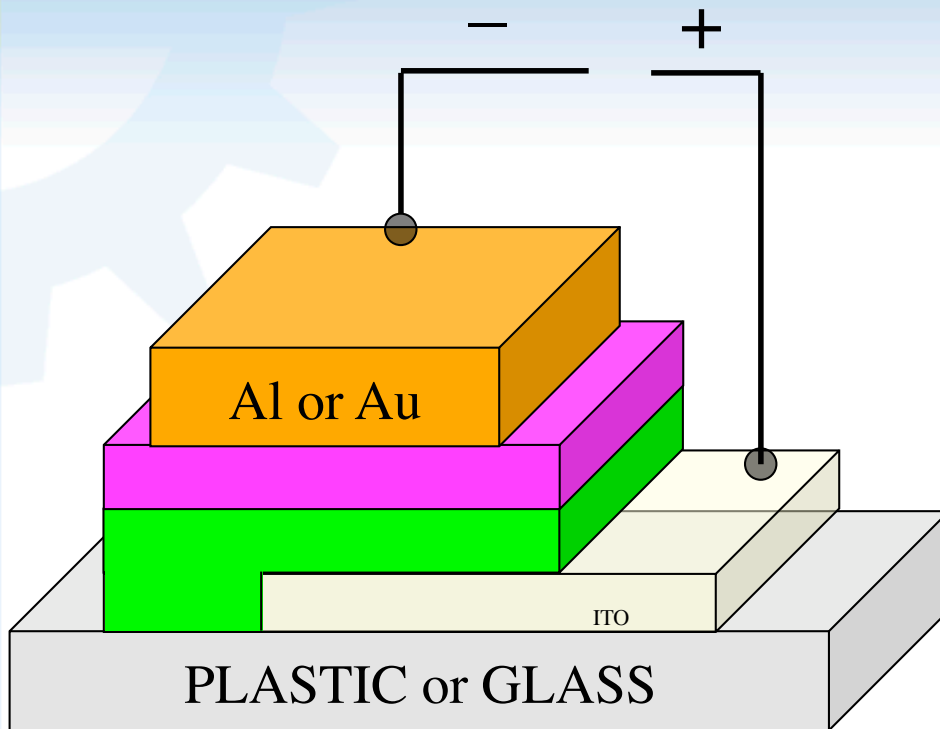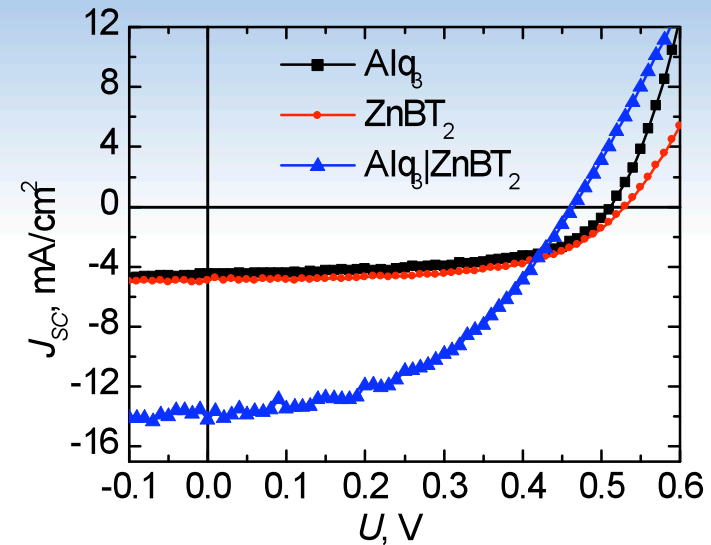| Sample structure	J_{SC}, mA/cm²	U_{OC}, V	FF	η
ITO|ZnO|PHT:PCBM|Alq$_3$|Au	4.45	0.49	0.59	2.77
ITO|ZnO|PHT:PCBM|ZnBTZ$_2$|Au	4.95	0.53	0.61	3.26
ITO|ZnO|PHT:PCBM|Alq$_3$|ZnBTZ$_2$|Au	14.18	0.46	0.53	**6.70**

Doping the bulk heterojunction

P3HT:PCBM   1,7-PyPDI

Buffer|Metal

BHJ blend

ZnO

ITO
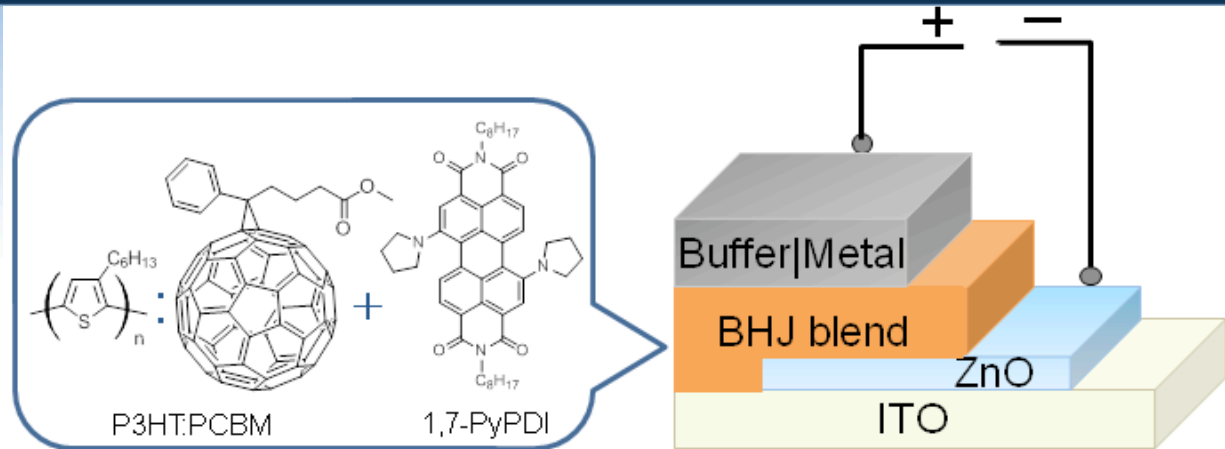
1,7-PyPDI	J_{SC} (mA/cm^2)	U_{OC} (V)	FF	(%)
0	9.73	0.56	0.52	2.83
0.01	11.37	0.55	0.52	3.25
0.02	10.93	0.55	0.53	3.19
0.03	**12.57**	**0.55**	**0.55**	**3.8**
0.04	11.37	0.55	0.58	3.63
0.05	11.23	0.56	0.58	3.65
0.1	10.37	0.56	0.62	3.6
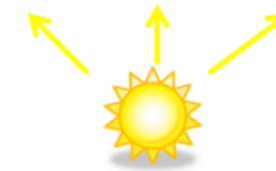
Optimum concentration
of doping compound
(PDI) is 3 % (by weight)

TAMPERE UNIVERSITY OF TECHNOLOGY
Department of Chemistry and Bioengineering

Acknowledgements

Prof. Helge Lemmetyinen, Prof. Nikolai Tkachenko, Drs Elina Vuorimaa, Alexander Efimov, Terttu Hukka

Marjo Ikonen, Ahmed Mayouf, Elina Vuorimaa, Andrei Tauber, Ramin Vatanparast, Tapio Jussila, Kirsi Lehto, Mika Lahtinen, Visa Vehmanen, Tero Kesti, Vladimir Chukharev, Irmeli Tuukkanen, Tommi Vuorinen, Veer D.S. Dhaka, Teemu Toivonen, Marja Niemi, Kimmo Kaunisto, Heli Lehtivuori, Anne Kotiaho, Paola Vivo, Kalle Lintinen, Pekka Aittala, Alexey Veselov, Somnath Day, Rajee Dubey, Ali H. Al-Subi

TAMPERE UNIVERSITY OF TECHNOLOGY
Department of Chemistry and Bioengineering

Acknowledgements

P. Hynninen, H. Tenhu, J. Keinonen, R. Serimaa, M. Yliperttula, A. Urtti (Helsinki),
H. Stubb, J. Peltonen, R. Österbacka, A. Ivaska, C. Kvarnsröm (Åbo),
K. Rissanen (Jyväskylä), O.E.O. Hormi (Oulu)
M. Pessa, M. Guina, M. Kauranen , T. Rantala (Tampere),
M. Linder, H. Lipsanen (Aalto)

M. G. Kuzmin, A.S. Alekseev, V.V. Savransky, V.F. Plyusnin,
M.V. Kovalchuk, (Russian),
C. Varma, J. Cornelisse (The Netherlands)
A. Persoons, M. Van der Auweraer, F.D. Schryver (Belgien),
Y. Sakata, H. Imahori, S. Fukuzumi, O. Ito, (Japan),
P.V. Kamat, D.I. Schuster, F. D'Souza, L. Ehcegoyen (USA),
D.M. Guldi, F. Würthner, O. Wenger (Germany) M.J. Crossley (Australia),
B. Albinson (Sweden), E. Vathey (Swizerland), A. Benniston (G-B),
M. Vasilescu (Rumania)

TAMPERE UNIVERSITY OF TECHNOLOGY
Department of Chemistry and Bioengineering

Thank you!