FINNISH-JAPANESE WORKSHOP ON FUNCTIONAL MATERIALS
Espoo-Helsinki 25. – 26. May, 2009

THEMATIC WORKING GROUP:

MATERIALS FOR NEW ENERGY SOLUTIONS, SOLAR CELL & BATTERY

Fast spectroscopy – Synthesis of functional molecules – Function in supramolecular structures

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FINLAND

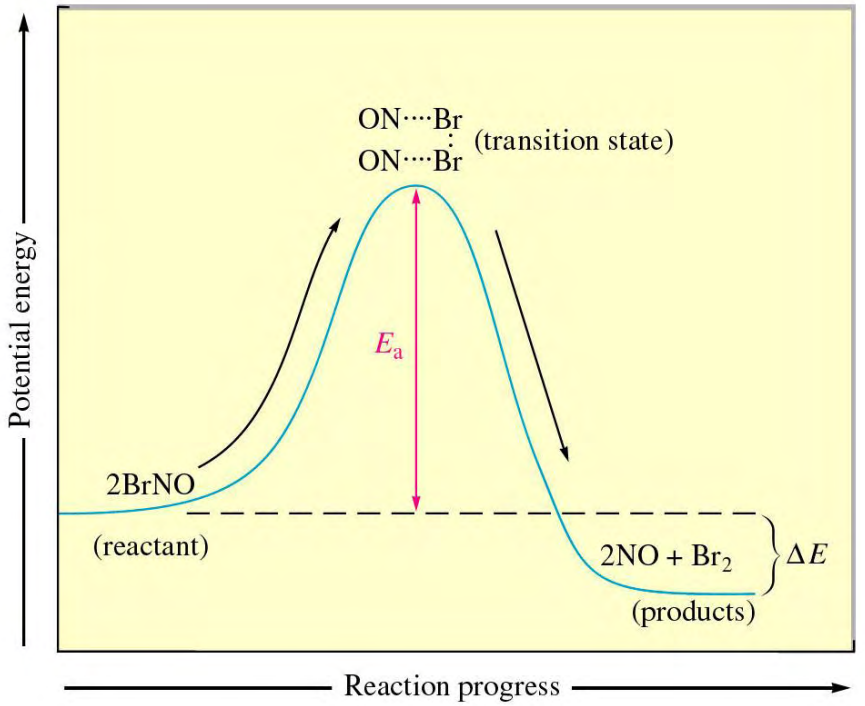
From Kinetics to Dynamics

Svante Arrhenius (1889): $k = A \exp(-E_a/RT)$

or

$\ln k = -E_a/RT + C$

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):

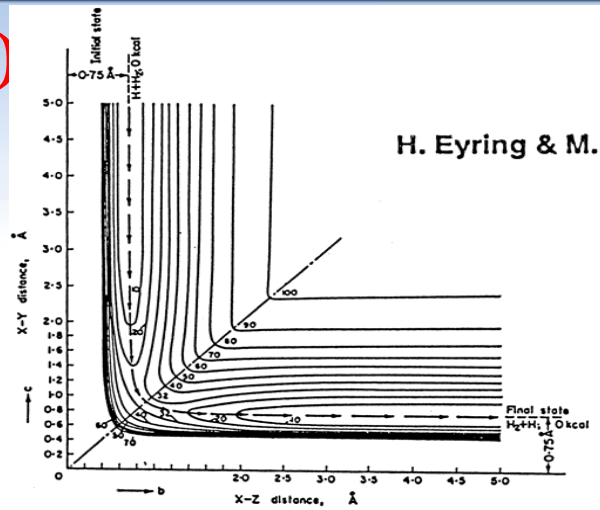
Transition-state theory

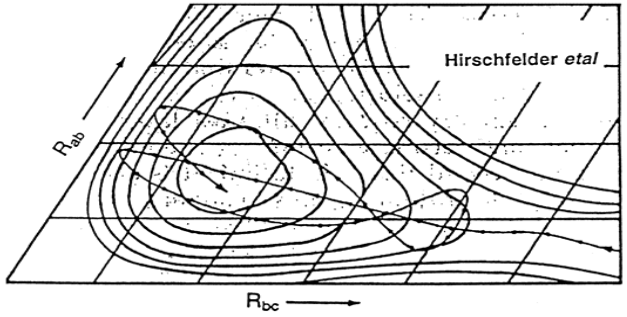
$k = (\boldsymbol{k}T/h)\,(Q^{\ddagger}/Q_A Q_B)\,\exp(-E_o/kT)$

The fastest reaction at room temperature:

$k = (\boldsymbol{k}T/h) \approx 6 \times 10^{12}\ s^{-1}$

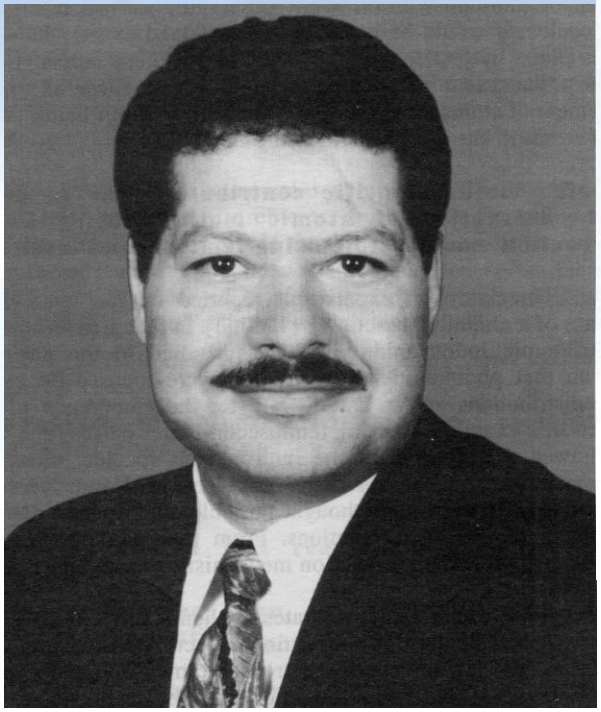
or $\tau = 170$ fs

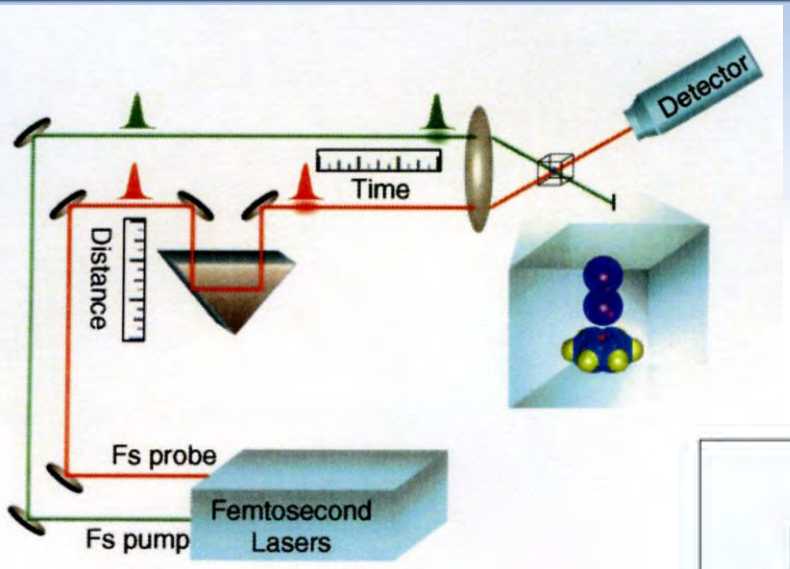


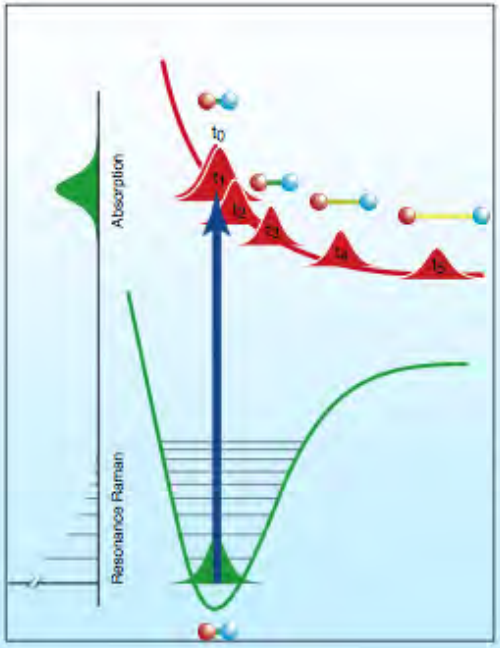


The time scale of molecular vibrations is typically 10 - 100 fs

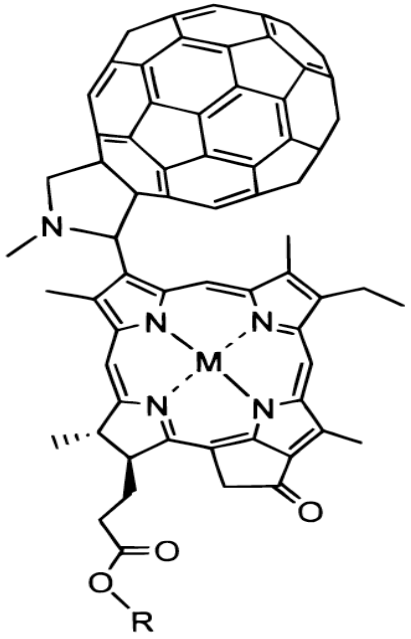
Femtochemistry – Nobel Laureate in Chemistry 1999
Ahmed H. Zewail



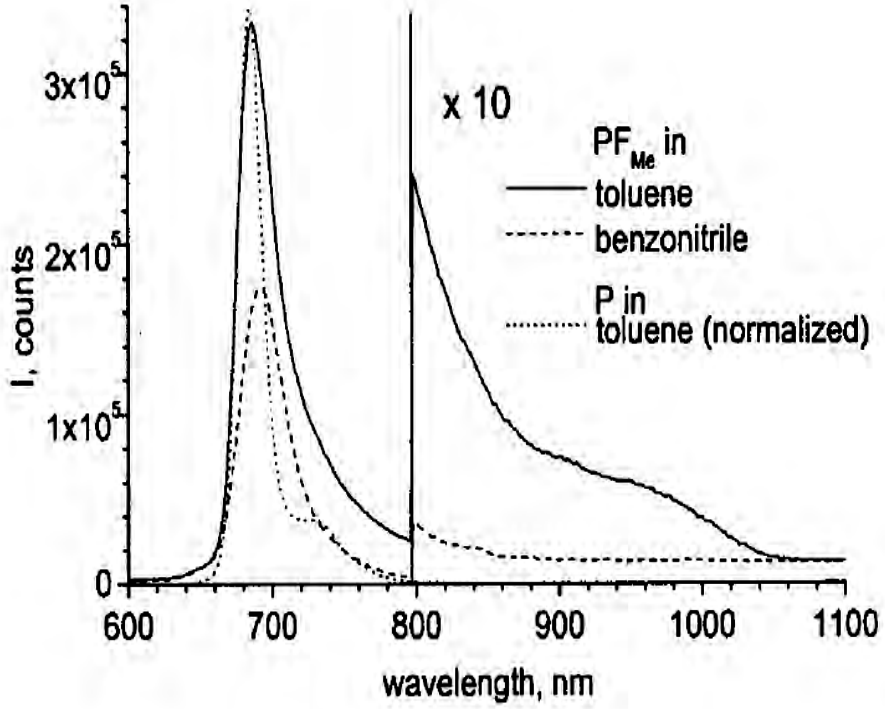




Ultra-fast Spectroscopy at TUT: Photo-induced Electron Transfer reaction Pheophytin-fullerene derivative: fluorescence spectra and lifetimes



PF: M = 2H, R = H



J. Am. Chem. Soc., ***121***, 1999, 3978
Lemmetyinen, Tkachenko et al.

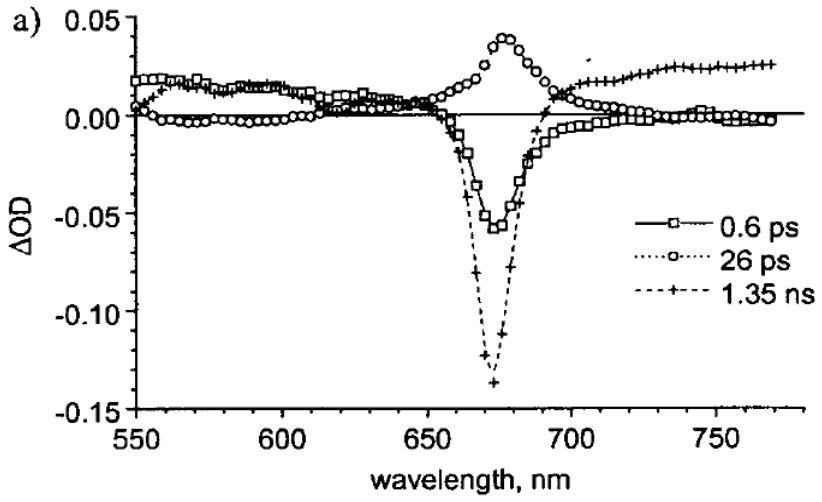
Reference Pheopytin: τ_1 **= 4 – 5 ns**

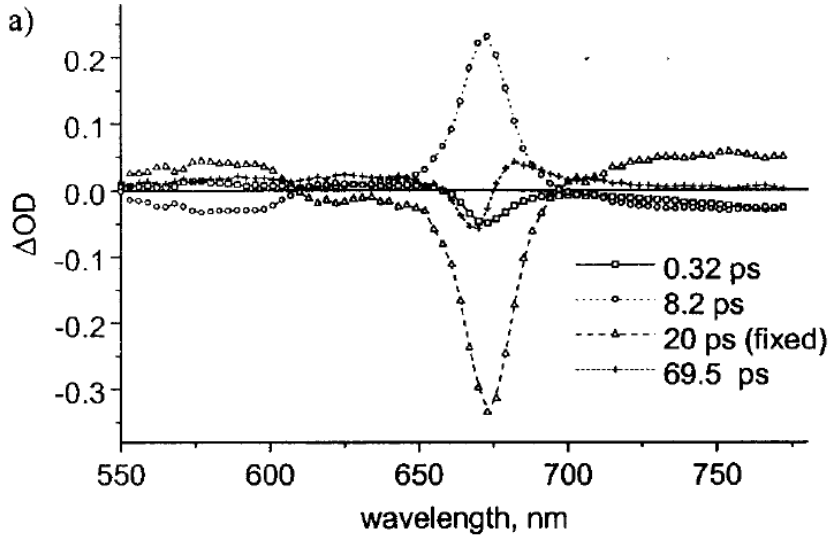
		toluene	benzonitrile
PaF:	τ_1 =	**0.59 ps**	**0.54 ps**
	τ_2 =	**8.5 ps**	**4.4 ps**

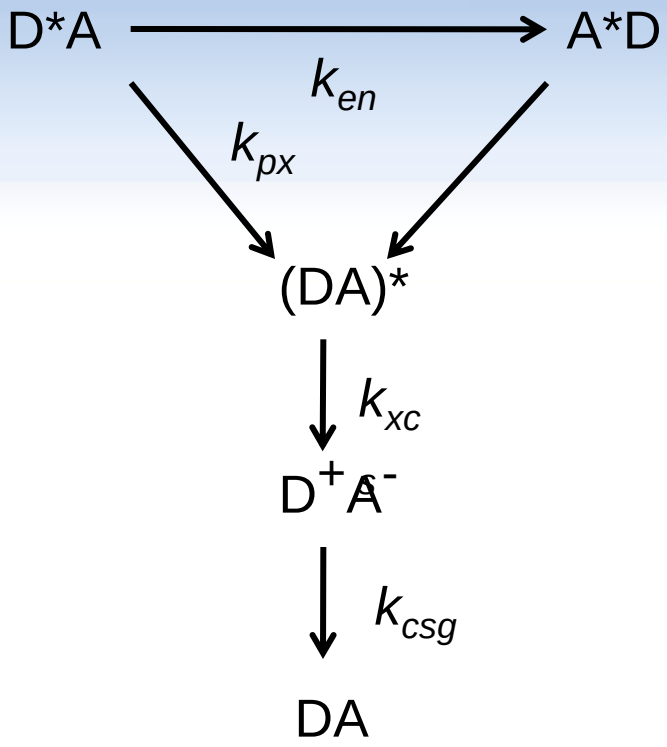
Pheophytin-fullerene derivatives:

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

J. Am. Chem. Soc., ***121***, 1999, 3978
Lemmetyinen, Tkachenko et al.







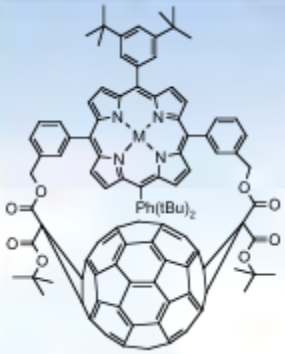
0.35 ps = k_{en} energy transfer

8 ps = k_{px} exciplex formation

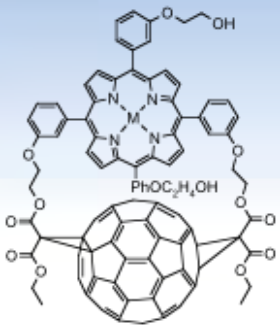
19 ps = k_{xcs} CT-state formation

65 ps = k_{csg} CT-state recombination

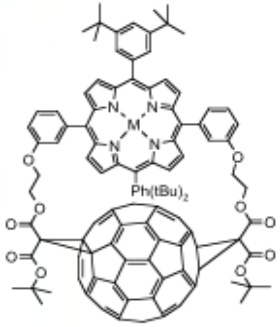
Porphyrin-fullerene series: covalently linked with two chains



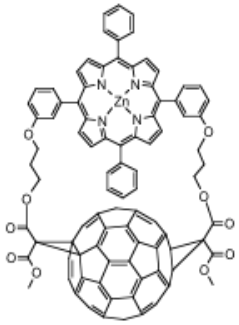
TBD4be



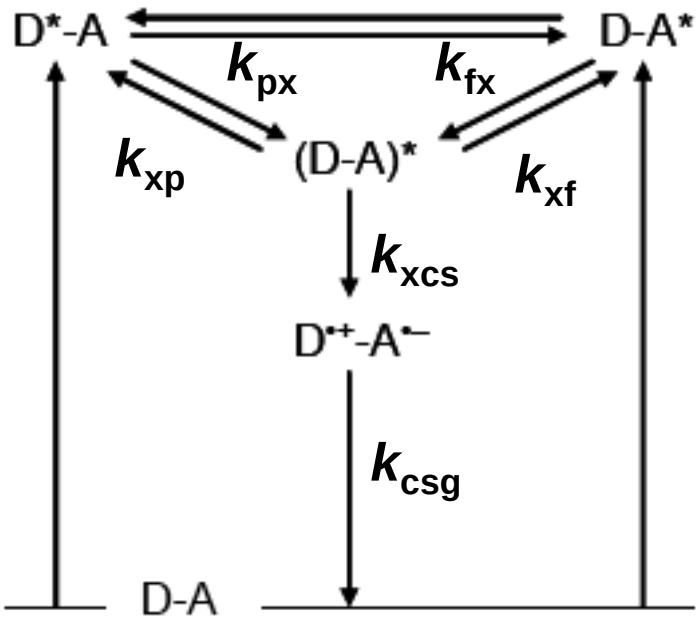
DHD6ee



TBD6be



ZnD7mee



k_{px} = 10 -20 x 10^{12} s^{-1} *e.g.* 50-100

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

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

J. Phys. Chem., B, ***108***, 2004, 16 377
Lemmetyinen, Tkachenko, Guldi et al.

Joint publications on Electron-Transfer and Solar Cells with Groups of Prof. Fukuzumi (Osaka) and Imahori (Kyoto) 2000 -2009

N.V. Tkachenko, C. Guenther, H. Imahori, K. Tamaki, Y. Sakata, S. Fukuzumi, and H. Lemmetyinen: Near infra-red emission of charge-transfer complexes of porphyrin-fullerene films, *Chem. Phys. Lett.*, *326*, 2000, 344-350.

Hiroshi Imahori, Nikolai V. Tkachenko, Visa Vehmanen, Koichi Tamaki, Helge Lemmetyinen, Yoshiteru Sakata, and Shunichi Fukuzumi: An Extremely Small Reorganization Energy of Electron Transfer in Porphyrin-Fullere Dyad, *J. Phys. Chem. A*, *105*, 2001, 1750-56.

Visa Vehmanen, Nikolai V. Tkachenko, Hiroshi Imahori, Shunichi Fukuzumi, and Helge Lemmetyinen: Charge-transfer emission of compact porphyrin-fullere dyad analyzed by Marcus theory of electron-transfer, ***Spectrochimic. Acta, A 57***, 2001, 2227-2242.

Tero J. Kesti, Nikolai V. Tkachenko, Visa Vehmanen, Hiroko Yamada, Hiroshi Imahori, Shunichi Fukuzumi, and Helge Lemmetyinen: Exciplex intermediates in photoinduced electron transfer of porphyrin-fullerene dyads, ***J. Am. Chem. Soc., 124***, 2002, 8067-8077.

Joint publications on Electron-Transfer and Solar Cells with Groups of Prof. Fukuzumi (Osaka) and Imahori (Kyoto) 2000 -2009

Chem. Phys. Lett., **366**, 2002, 245-252

J. Phys. Chem., 107, 2003, 8834-8844

J. Am. Chem. Soc.,126, 2004,1600-1601

J. Phys. Chem., B 109, 2005, 15368-15375

J. Phys. Chem., B 109, 2005, 18465-18474

J. Phys. Chem., A, 109, 2005, 4662-4670

Langmuir, ***22***, 2006, 5497-5503

Org. Lett., ***8***, 2006, 4425-4428

J. Phys. Chem. C, **111**, 2007, 13618-13626

Langmuir 23, 2007, 13117-13125

J. Phys. Chem., A, 112, 2008, 6884-6892

Chem. Asian. J., 3, 2008, 2065-2074

Photochem. Photobiol. Sci., **2**, 2003, 251-258

J. Phys. Chem., 107, 2003, 12511-12518

Langmuir, ***21***, 2005, 6385-6391

Chem. Eur. J., 11, 2005, 7265-7275

J. Mater. Chem., 15, 2005, 4564-4554

Langmuir, 21, 2005, 5383-5390

Chem. Phys., 326, 2006, 3-14

J. Phys. Chem. C, 111, 2007, 6133-6142

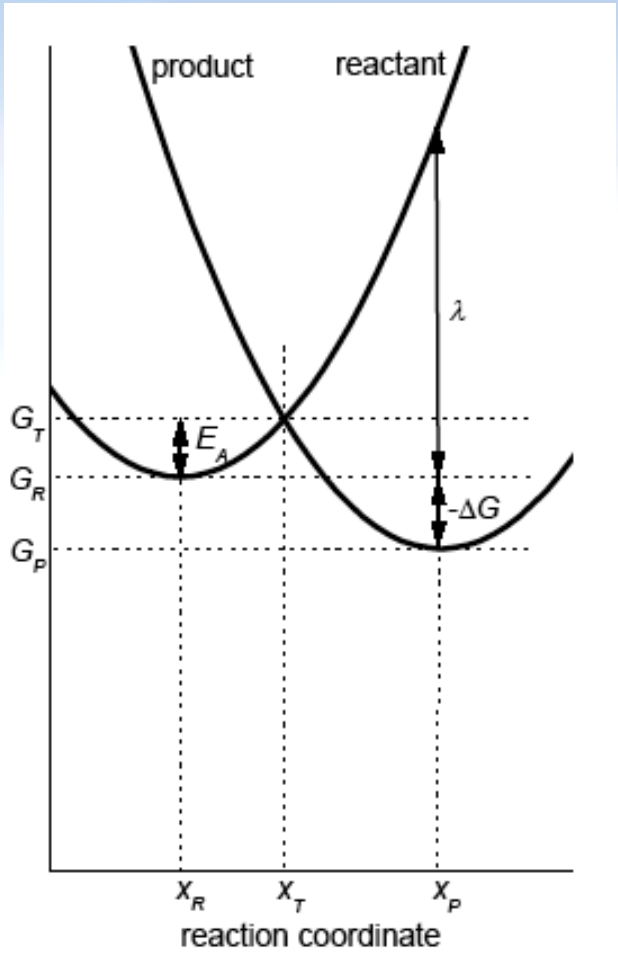
Chem. Eur. J. 13, 2007, 10182-10193

J. Phys. Chem. C, 112 (26), 2008, 9896–9902

J. Phys. Chem. B, ***112***, 2008, 16517-16524

J. Phys. Chem. C, **113,** 2009, 1984-

Marcus electron transfer theory



$$E_A = G_T - G_R = \frac{(\Delta G + \lambda)^2}{4\lambda}.$$

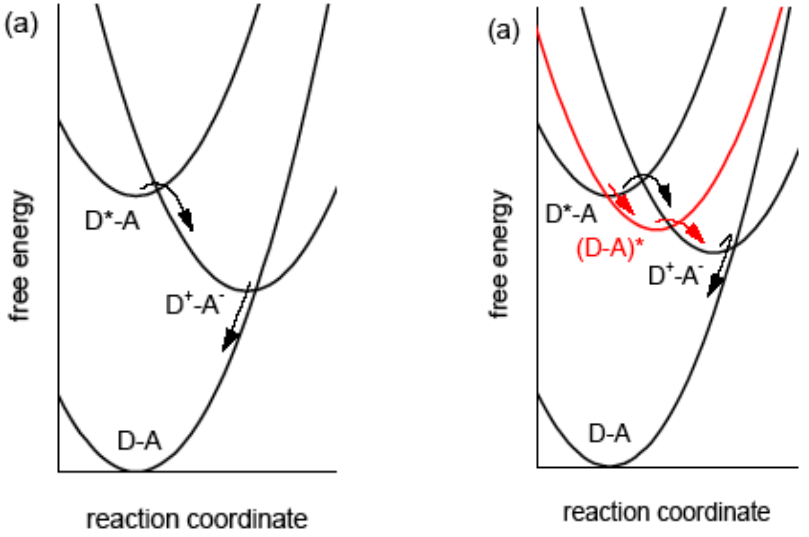
$$k_{ET} = \kappa_{el} \nu_n \exp\left(-\frac{E_A}{k_B T}\right),$$

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

Marcus electron transfer theory and more complex multistep reactions

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

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

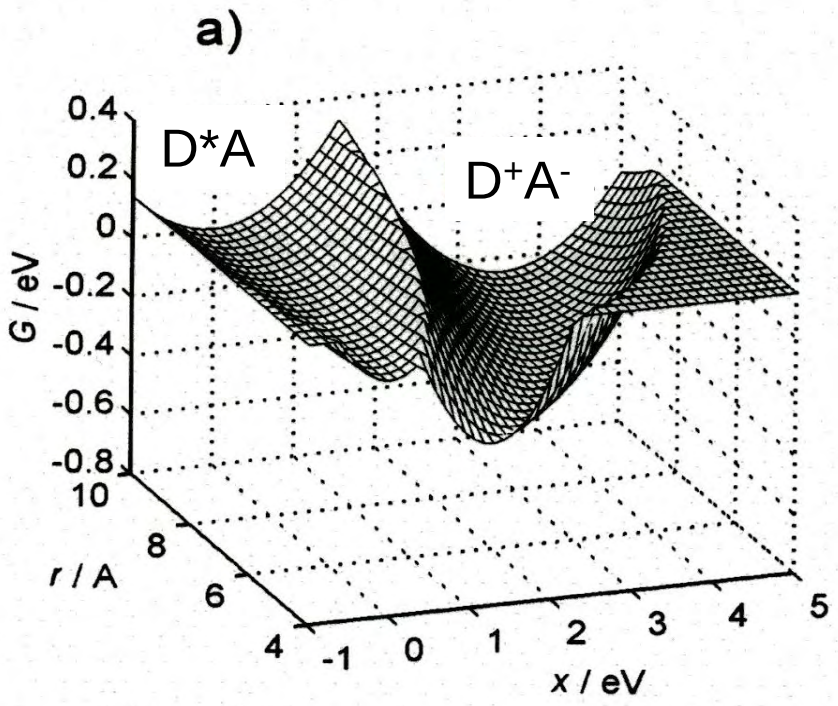


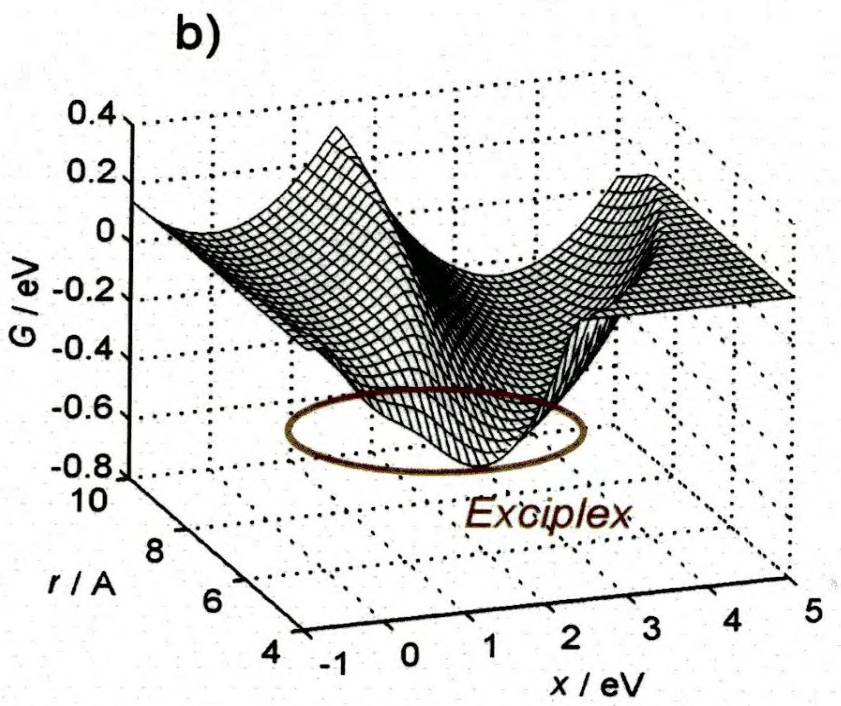
A series of electron donor-acceptor compounds were studied

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





J. Phys. Chem. A, 111, 2007, 9240
Murata & Tachiya

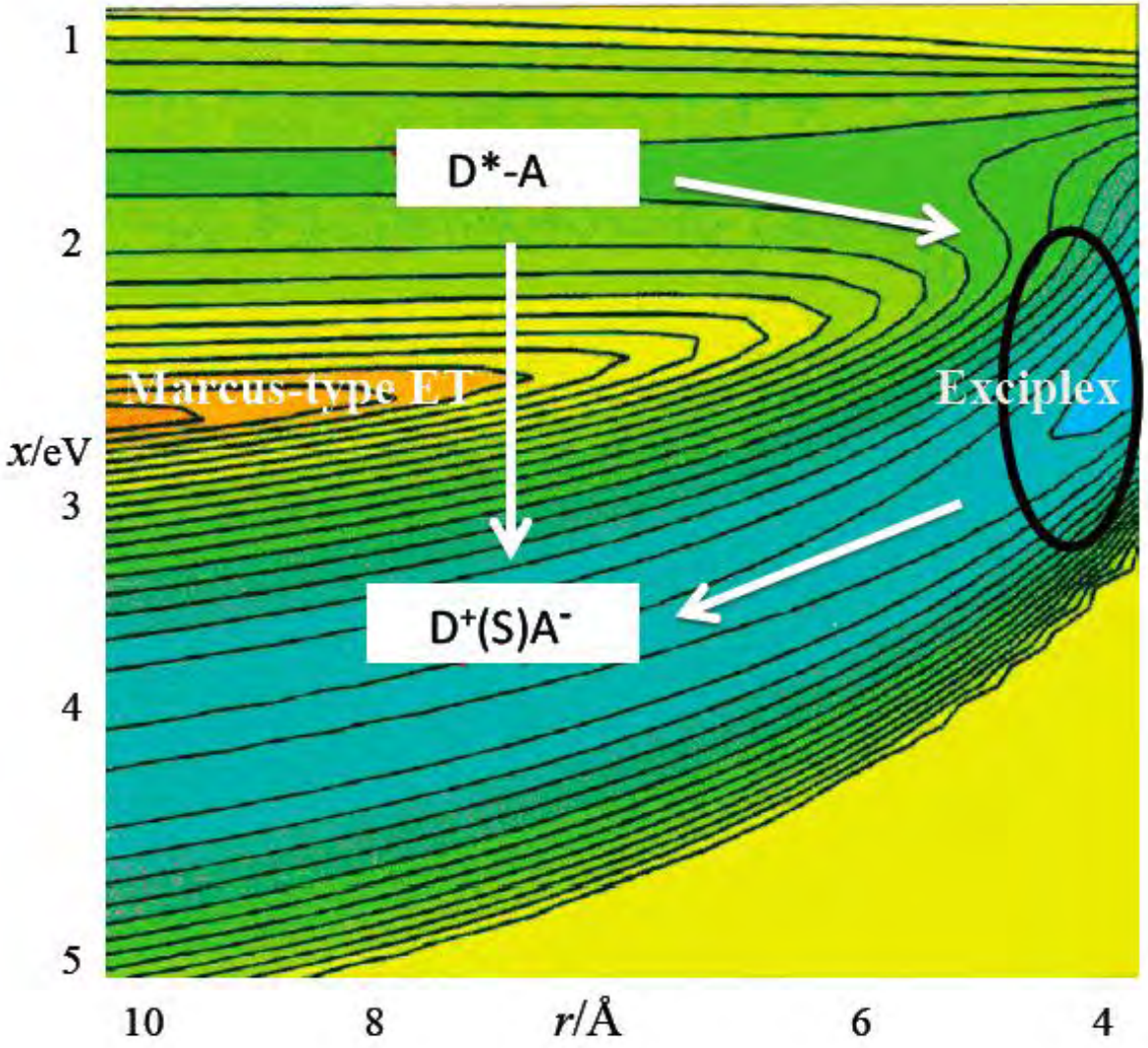
A topographic surface for the ET reaction: free energy, distance and solvent polarization:

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 !?

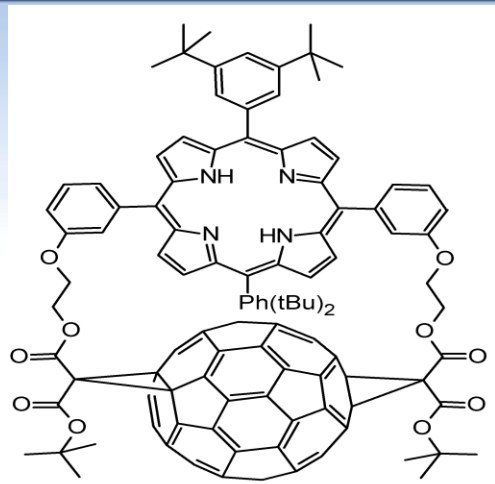
J. Phys. Chem. A, 111, 2007, 9240
Murata & Tachiya



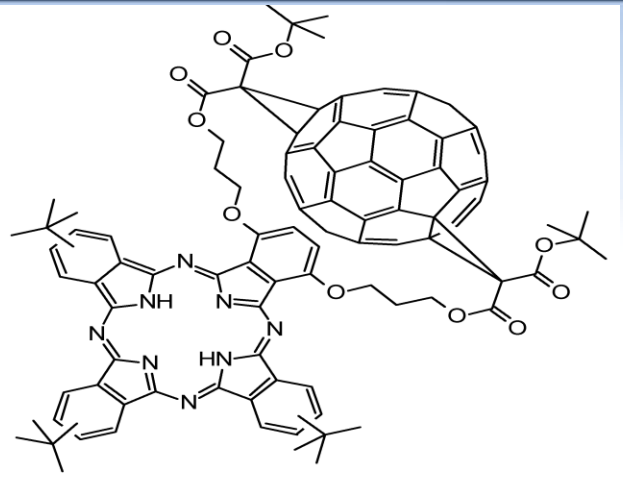
Studies of temperature dependent ultrafast photoinduced charge transfer in donor-acceptor pairs forming exciplexes

All the compounds, except P-BQ form exciplex as a transient state

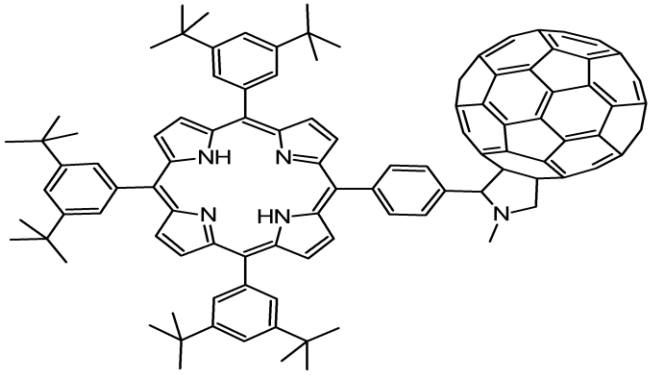
Will be published in Hiroshi Masuhara Festschrift, ***J. Phys. Chem. C.***, June 20



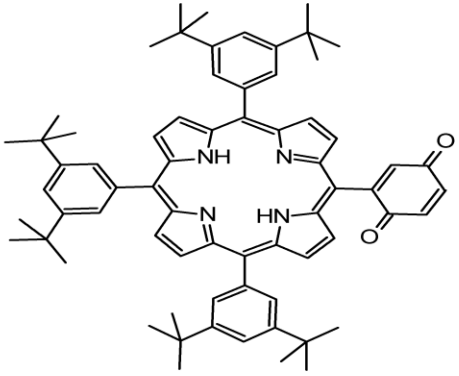
TBD6e



H_2Pc-F

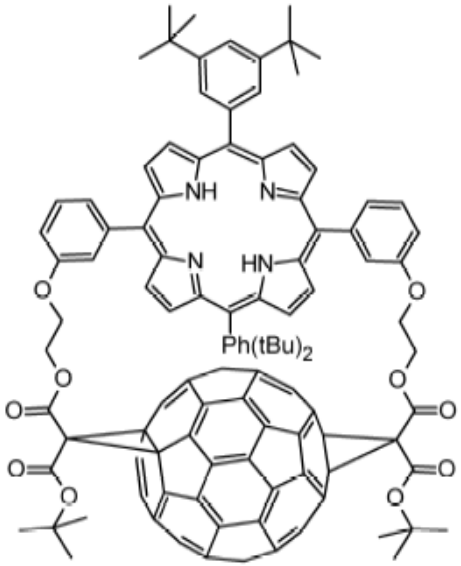


H_2P-S-F

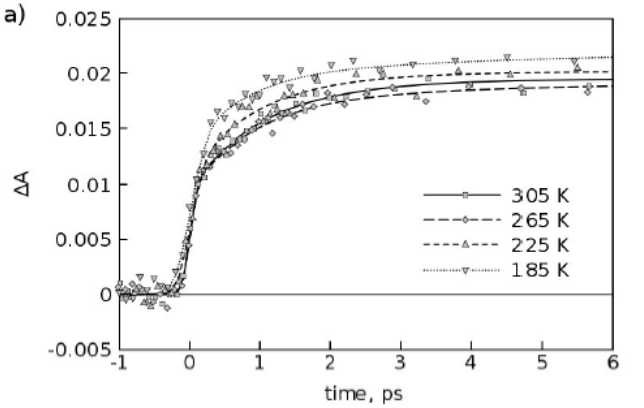


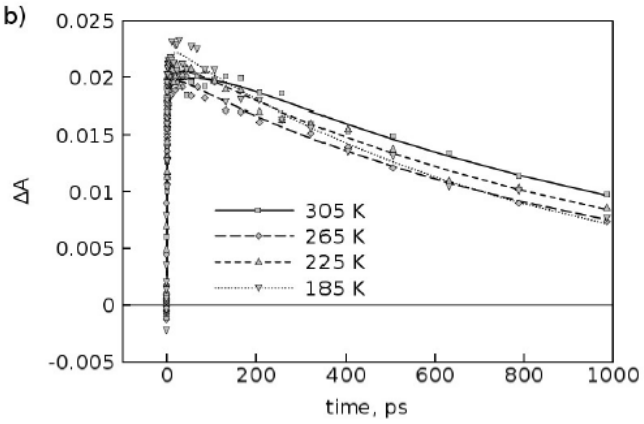
P-BQ

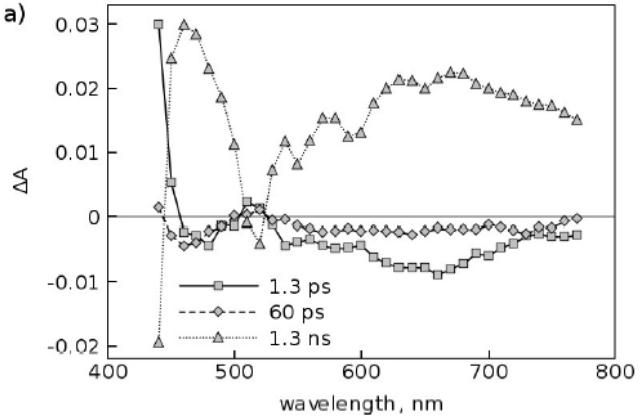
Left: a) Formation of exciplex and b) decay of the CT state of TBD6e in THF at different temperatures.
Right: The component spectra and their lifetimes of transient states of TBD6e in THF at temperatures of a) 305 K and b) 205 K.

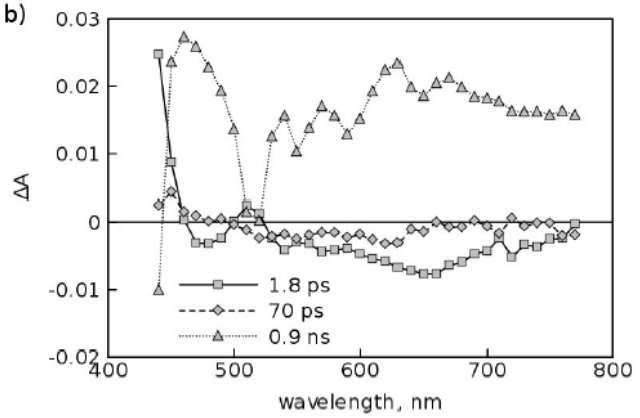


TBD6e

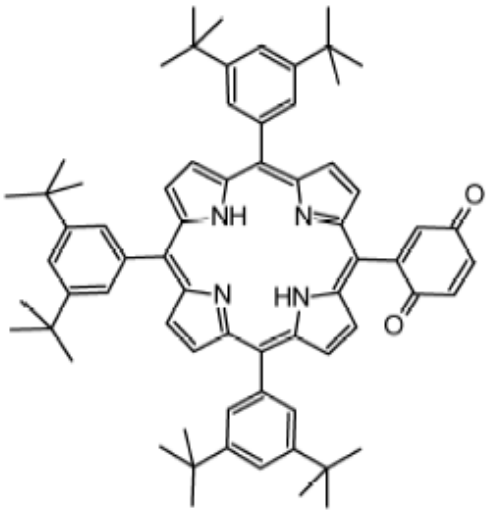




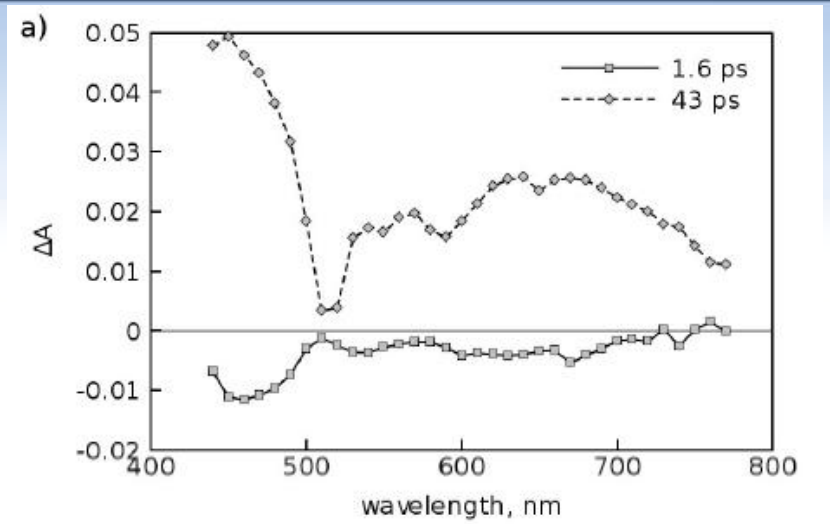


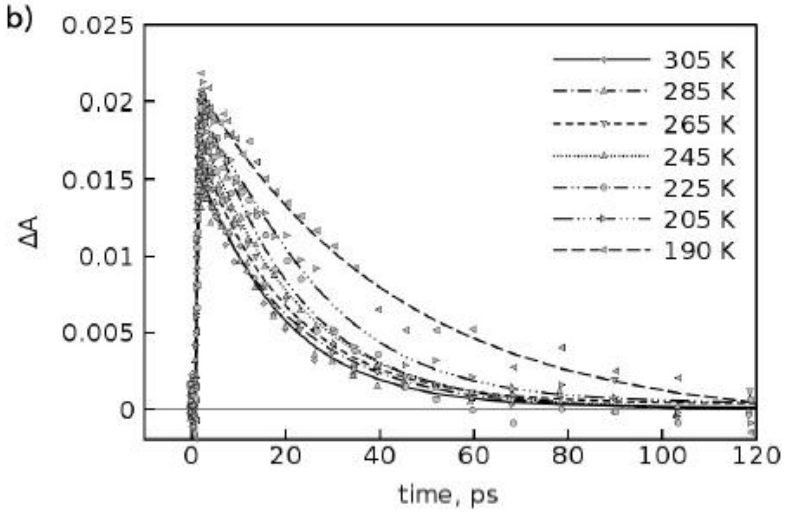


a) The component spectra and their lifetimes of transient states of P-BQ in toluene at temperature of 190 K and b) decays of the CT state of P-BQ at different temperatures



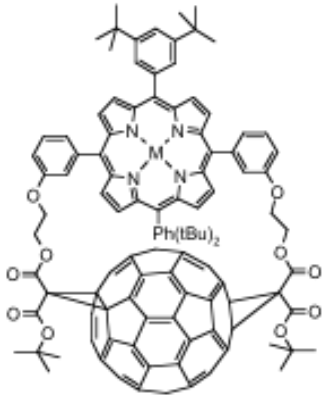
P-BQ





Comparison of micro-and pico-second time-scales for a double-bridged porphyrin-fullerene dyad in solid film

DHD6ee



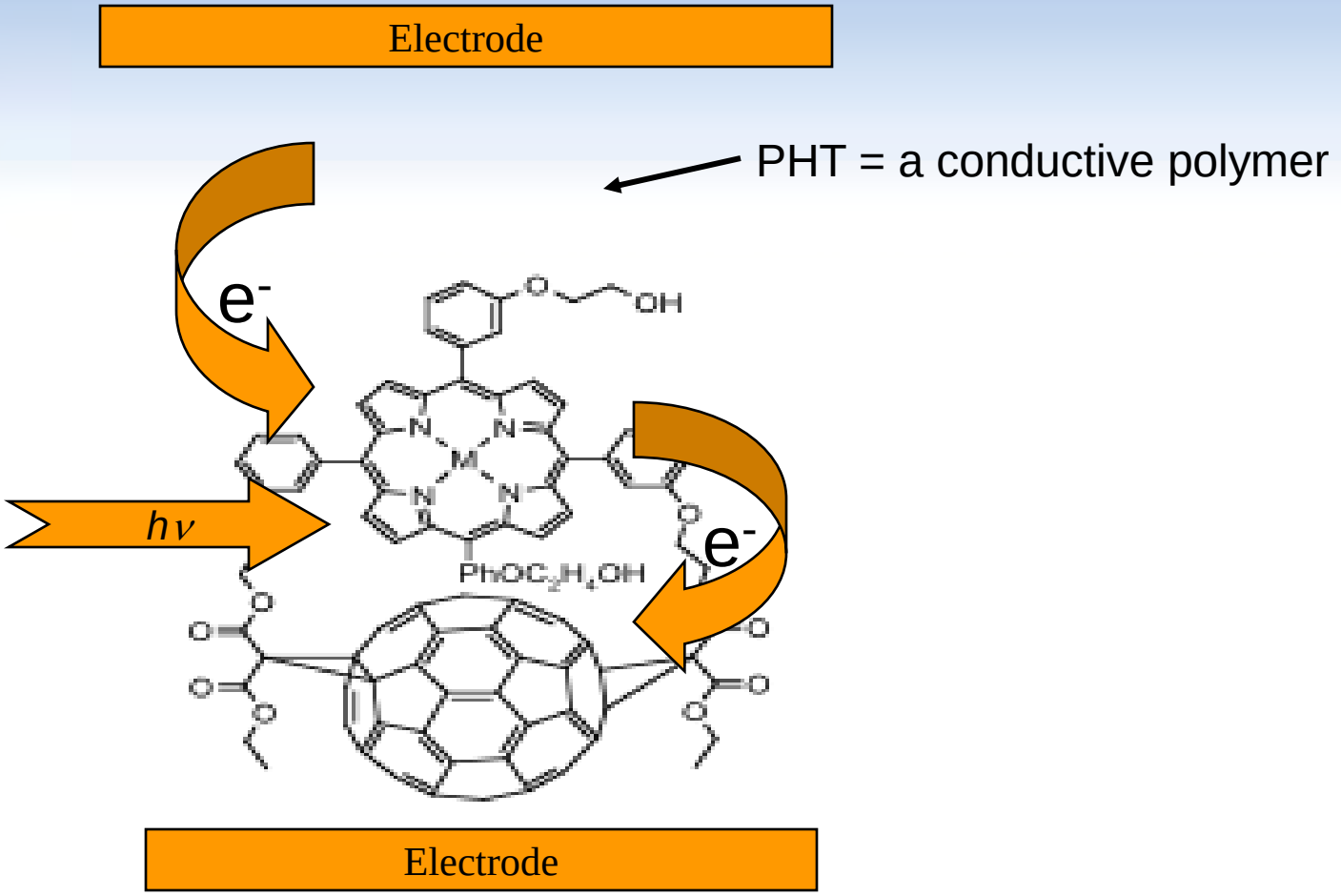
TBD

Superposition of radical cation of porphyrin and radical anion of fullerene in ps and μs time-scales

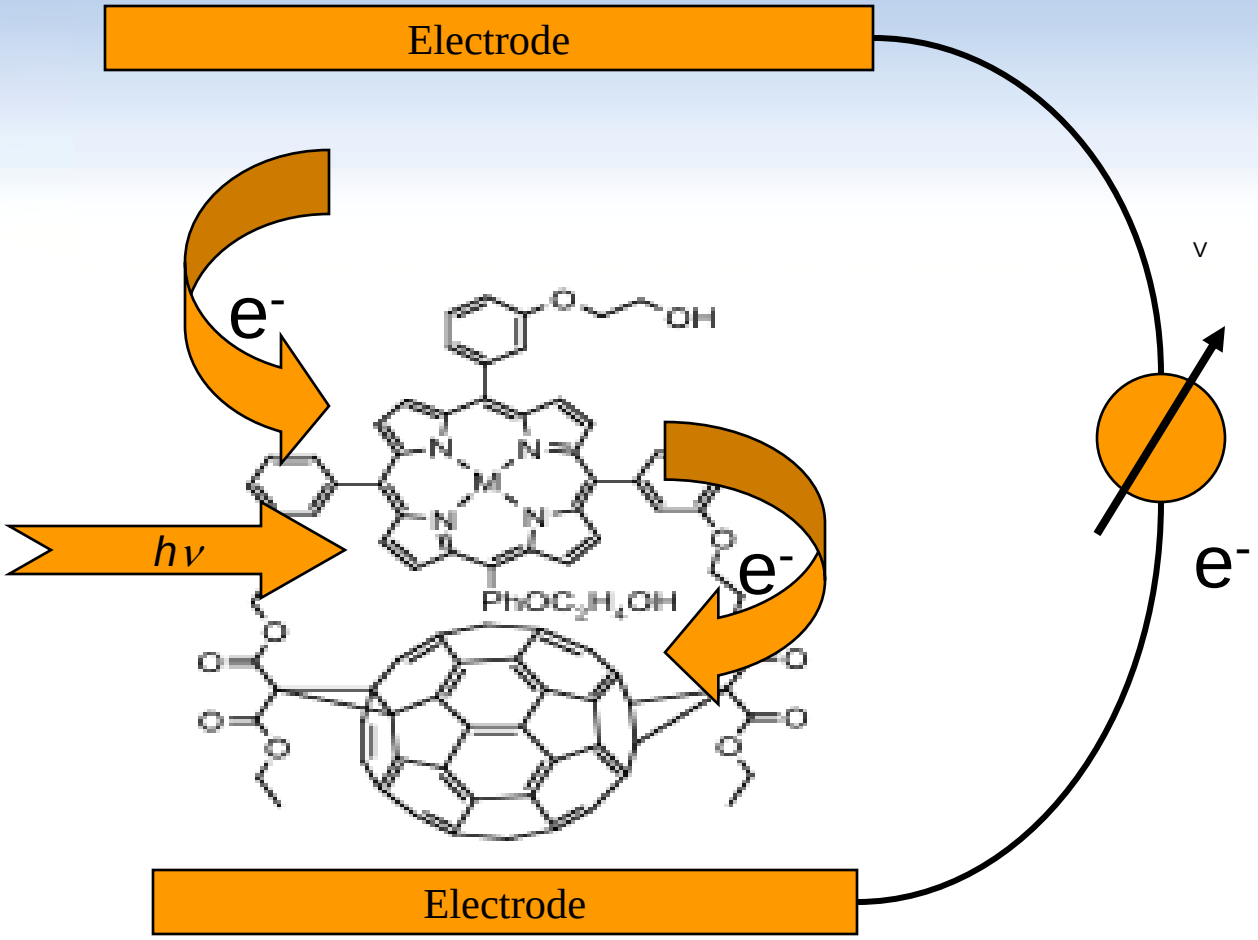
$$Pc^{*} - C_{60} \longrightarrow Pc^{+} - C_{60}^{-} \rightleftharpoons Pc'^{+} - C'^{-}_{60}$$

TAMPERE UNIVERSITY OF TECHNOLOGY
Department of Chemistry and Bioengineering

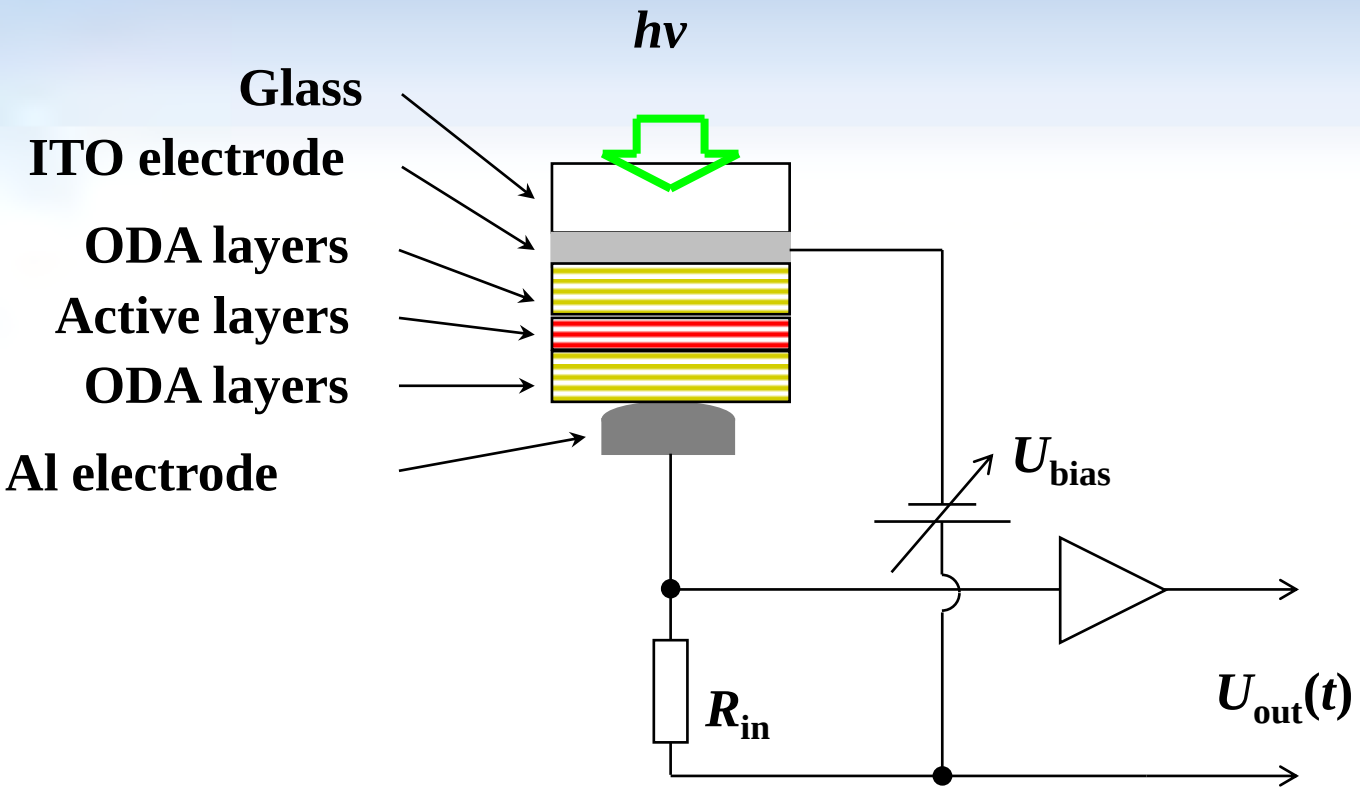
Molecules in self-assembled or organized phase: in 2D films vectorial electron transfer takes place and …



... and thus create photovoltage or photocurrent ?

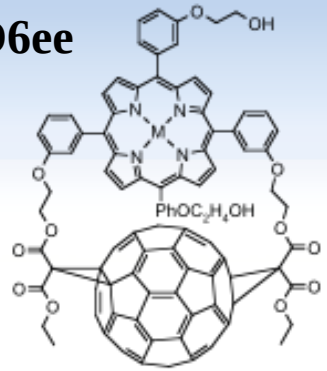


Vectorial electron transfer in solid films was measured by applying a Maxwell displacement charge measurement technique (Transient Photovoltage)

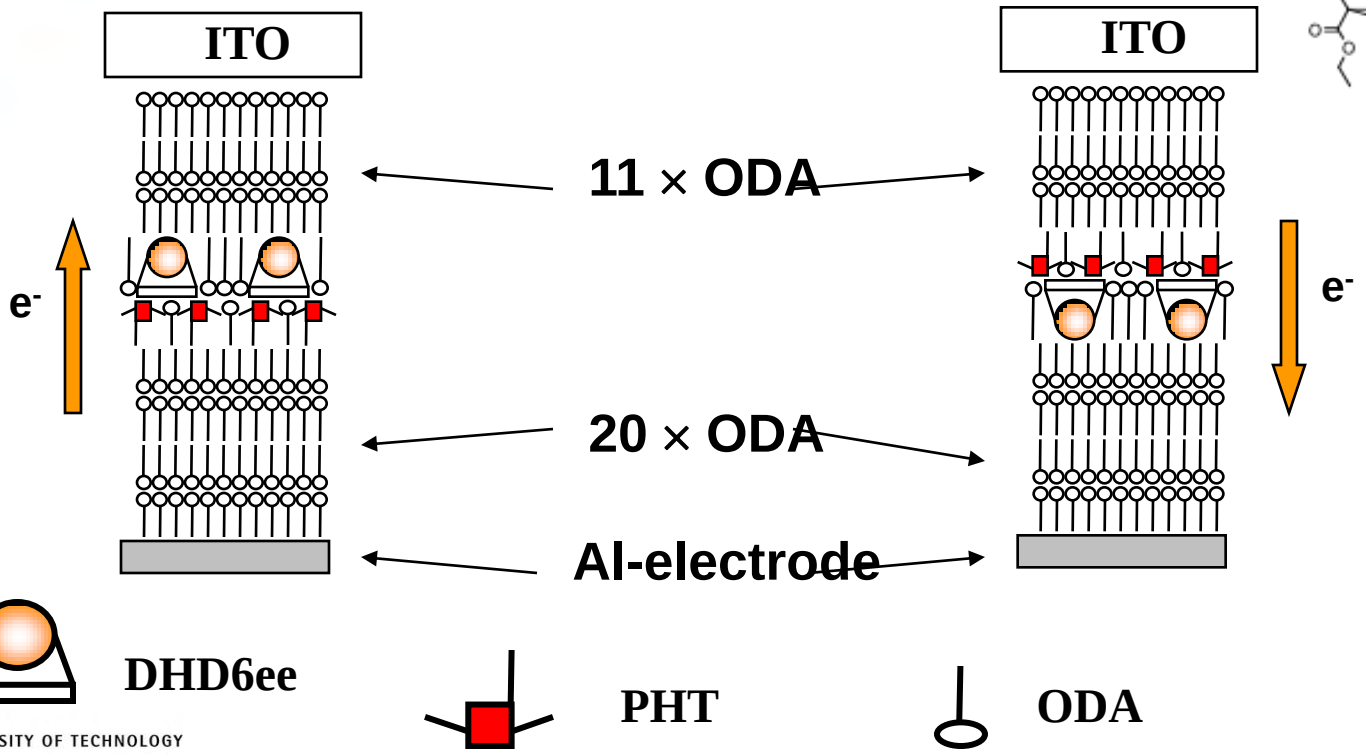


Orientation of molecular thin films were obtained by using the Langmuir-Blodgett technique:

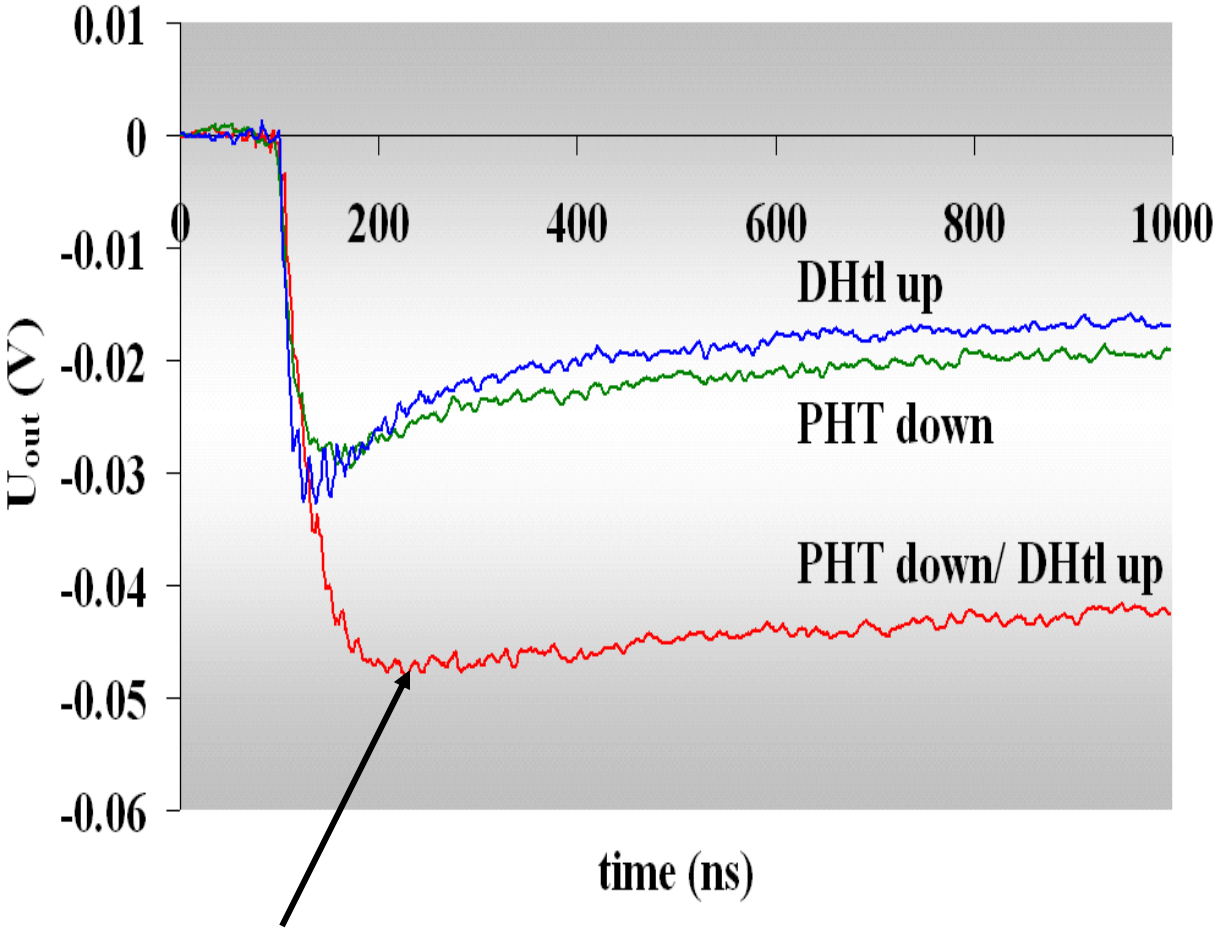
DHD6ee

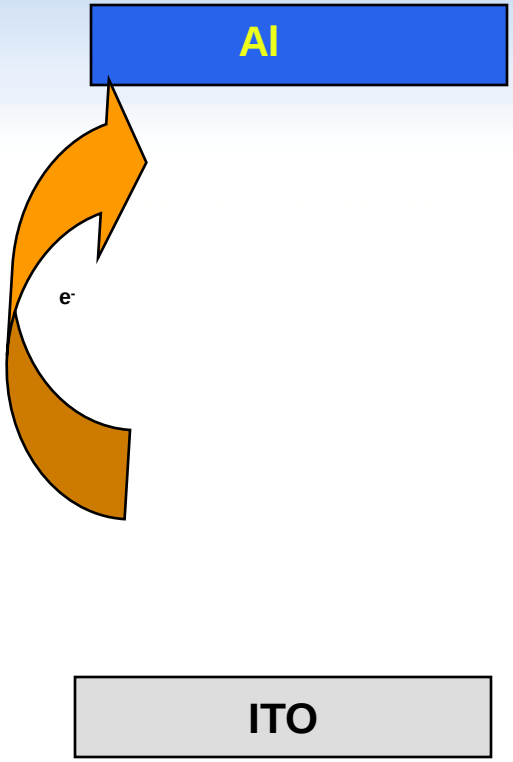


The LB-film structures for photovoltage measurements



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



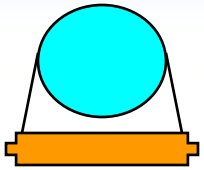


(a lower excitation intensity was used)

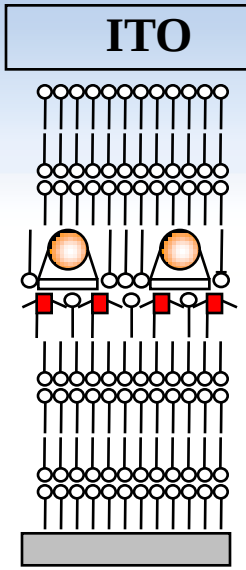
Molecular Engineering: Building a Device:

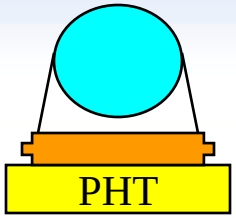
The elements for preparing of supramolecular film structures

=



PHT

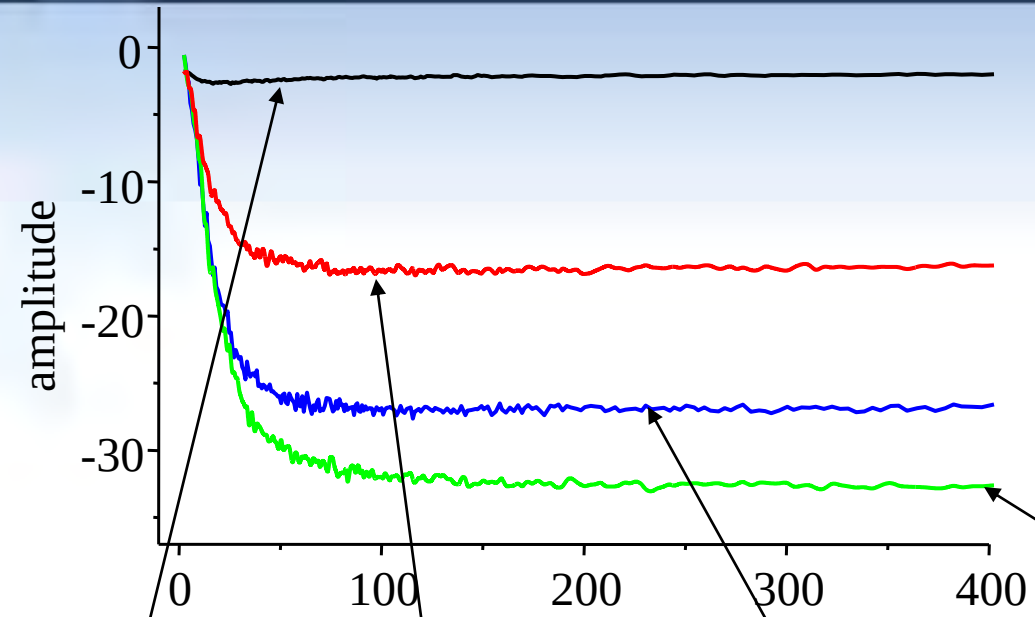




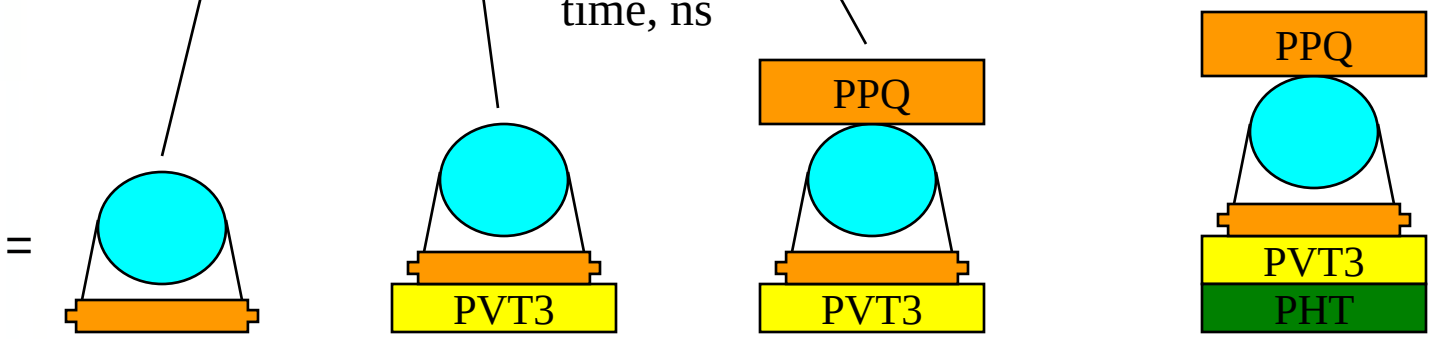
PVT3 =

PPQ =

Sensitivity **hotovoltage signals for PVT3/Dyad/PPQ film systems**



- 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



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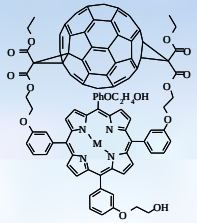
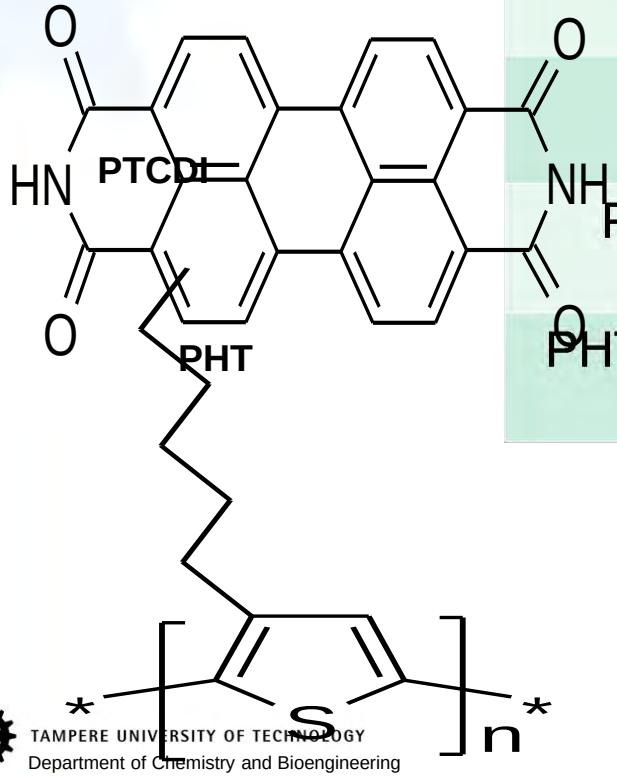
Lifetimes are in time scale of tens of seconds!

Sensitivity of the photovoltage signals PHT/P-F/PTCDI film systems

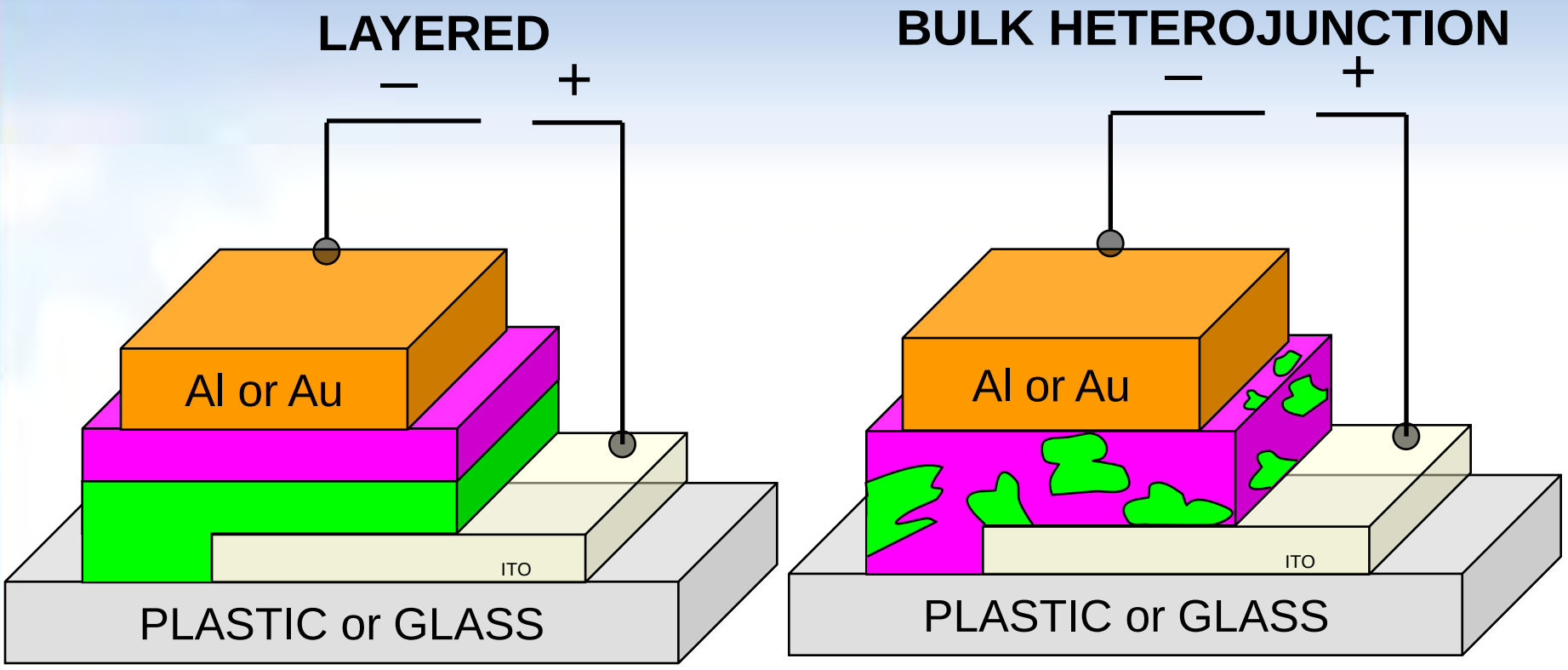


P-F

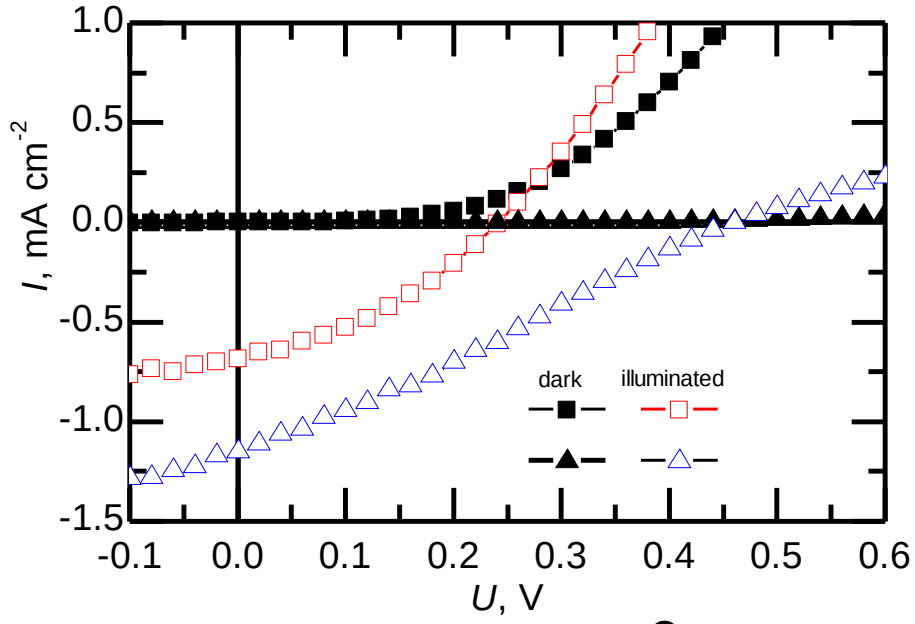


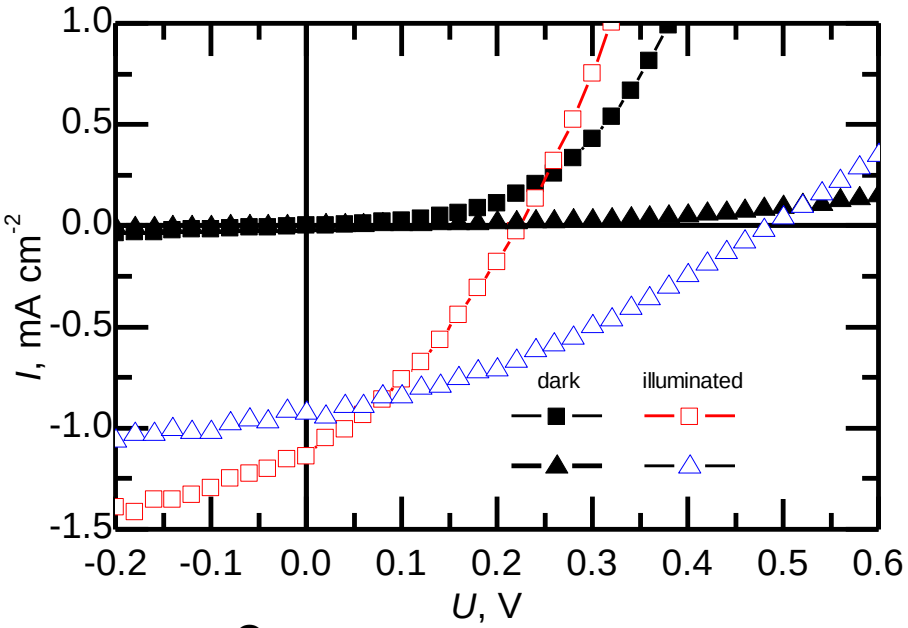
Structure	λ, nm	S_{max}, V cm^2 mJ^{-1}
P-F	430	-1.2
	532	--
PTCDI	430	-63
	532	-97
PHT	430	-13
	532	-29
P-F|PTCDI	430	-1610
	532	-814
PHT|P-F|PTCDI	430	-3000
	532	-2891

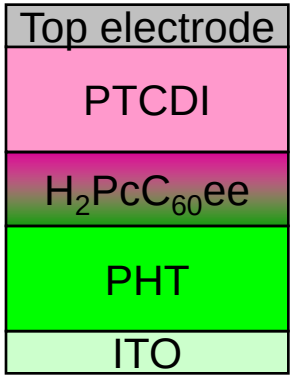
Organic solar cell configurations

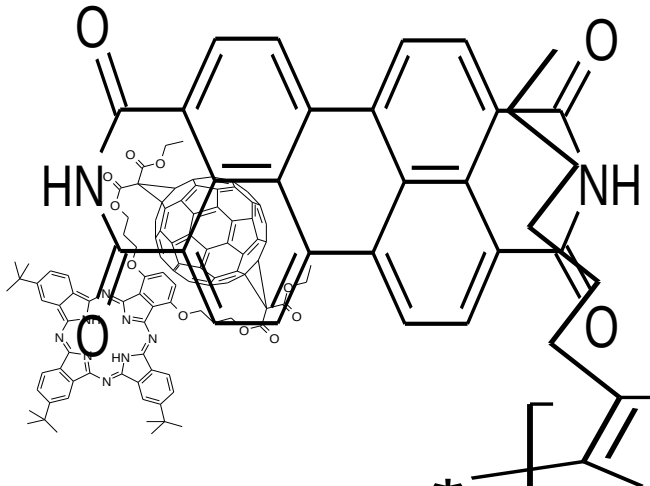


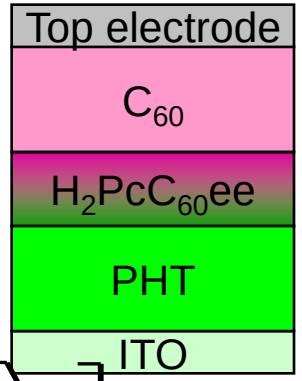
I-V characteristics of multilayered cells containing $H_2PcC_{60}ee$







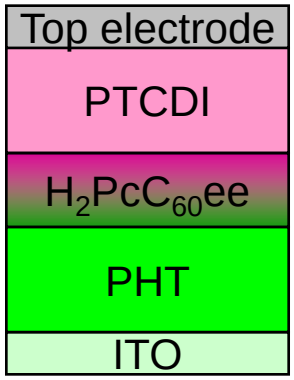


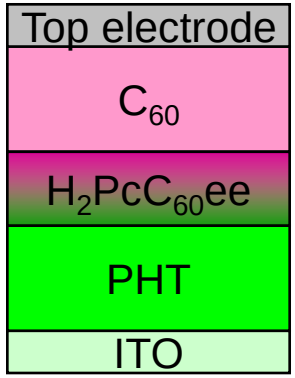


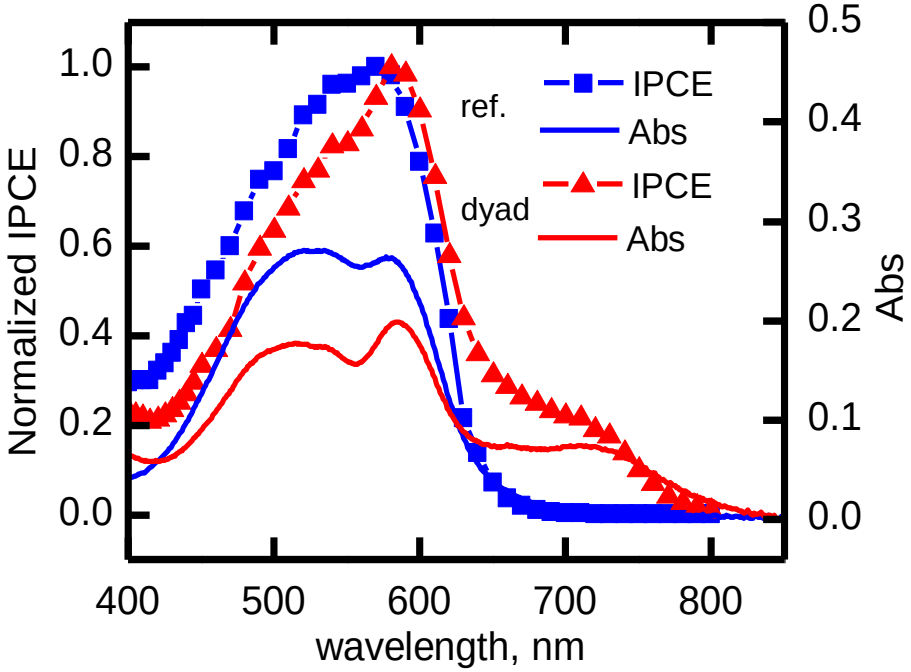
Photovoltaic parameters

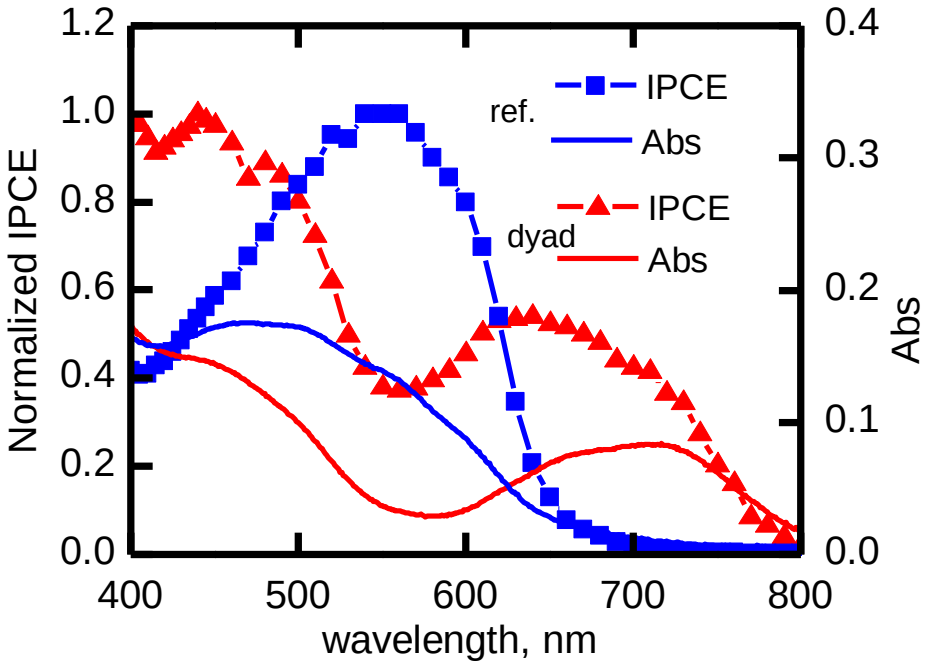
Structure	I_{sc}, mA/cm^2	U_{oc}, V	*FF*	η, %	IPCE, %
PHT|PTCDI|Alq_3	0.69	0.25	0.35	0.12	3.18
PHT|H_2PcC_{60}ee|PTCDI|Alq_3	1.15	0.45	0.28	0.32	5.33
PHT|C_{60}|Alq_3	1.14	0.21	0.35	0.18	4.82
PHT|H_2PcC_{60}ee|C_{60}|Alq_3	0.93	0.50	0.34	0.30	3.94

Action and absorption spectra: comparison





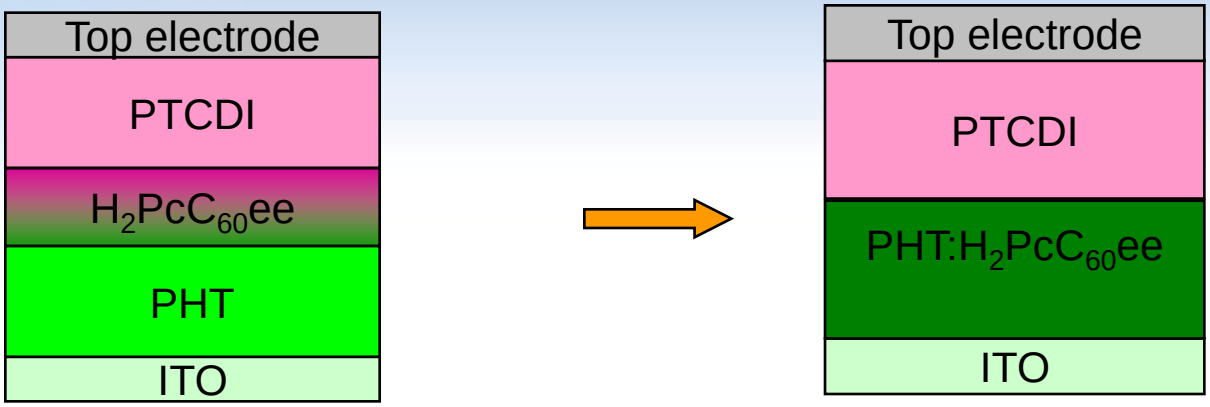




Monochromatic light: quantum yields

Structure	λ, nm	I_{sc}, mA/cm^2	*Abs.*	Φ_{EXT}, %	$\Phi_{INT,}$ %
PHT|PTCDI|Alq_3	540	70.0	0.311	26.0	50.8
	580	75.2	0.316	26.5	51.3
	700	0.25	0.018	0.11	2.60
PHT|H_2PcC_{60}ee|PTCDI|Alq_3	540	29.7	0.217	11.0	28.0
	580	37.3	0.263	13.2	29.0
	700	6.25	0.076	2.67	16.6
PHT:H_2PcC_{60}ee|PTCDI|Alq_3	540	60.9	0.253	22.6	51.2
	580	74.3	0.252	26.2	**59.5**
	700	4.04	0.05	1.73	16.1

Mixing of PHT and $H_2PcC_{60}ee$



Structure	I_{sc}, mA/cm^2	U_{oc}, V	*FF*	η, %	IPCE, %
PHT:$H_2PcC_{60}ee$|PTCDI|Alq_3	2.50	0.33	0.24	**0.40**	11.1

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