Exciton diffusion and interfacial charge separation in porphyrin/TiO_2 bilayers

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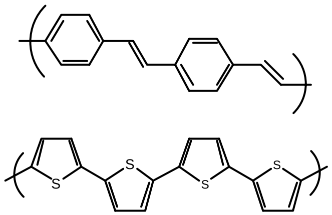
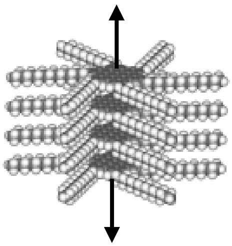
Research in Delft on opto-electronic properties of materials

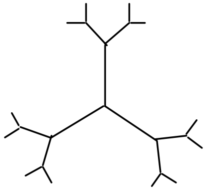


conducting polymers

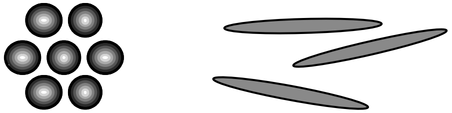


discotic liquid crystals

DNA



supra-molecular assemblies



inorganic nanoparticles, nanorods

composite systems

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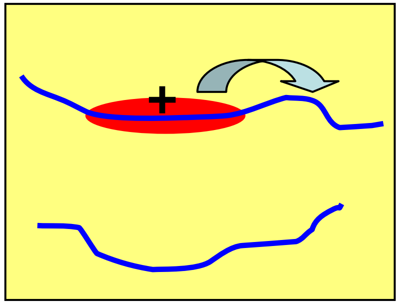
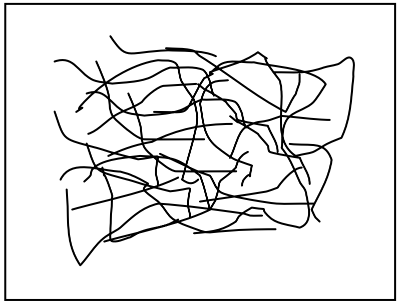
Sample morphologies

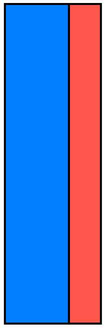
dilute solution / gel

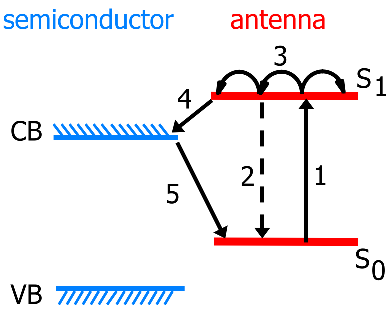


bulk solid

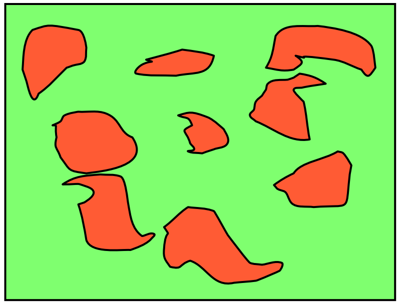


thin film on (active) substrate





heterogeneous blends

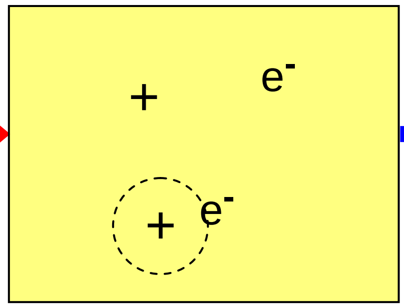


Dynamics of charge carriers and excitons

Formation (fsec - nsec)

Radiation pulse

- e^- accelerator
- lasers



Time-resolved detection

Detection (microwave, THz, optical)

Charge carriers

- mobility, trapping, recombination
- optical abs. spectra

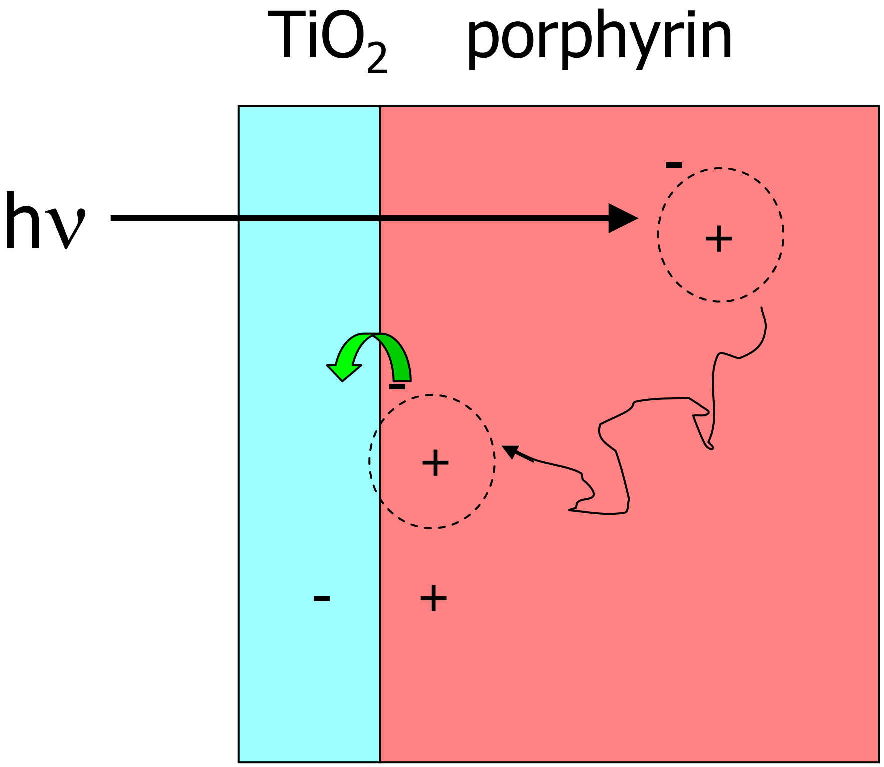
Excitons

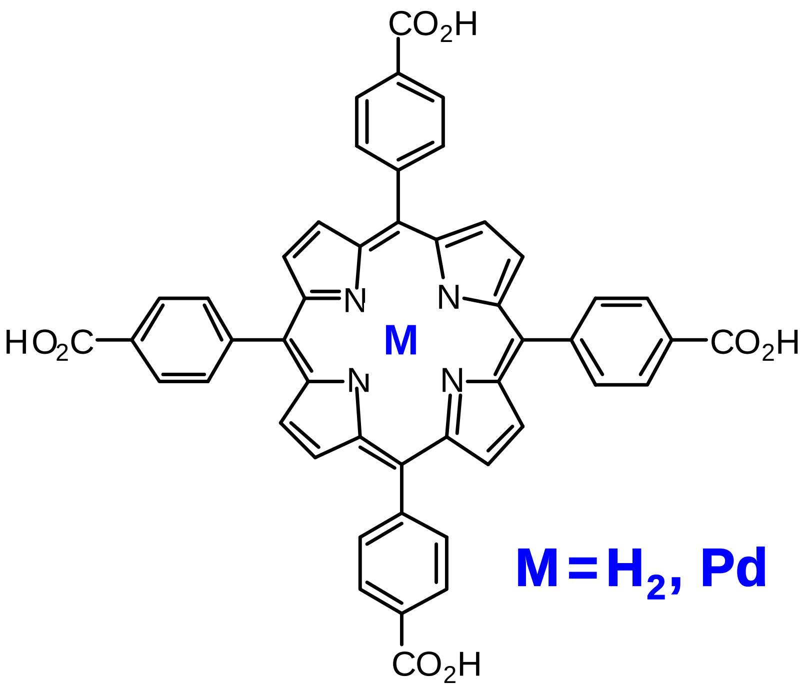
- dissociation, diffusion and decay
- polarizability, opt. abs. spectra

Theory

- electronic structure calculations (HF, DFT etc.)
- quantum mechanical calcs. on charge and exciton motion
- Monte Carlo simulations of hopping transport

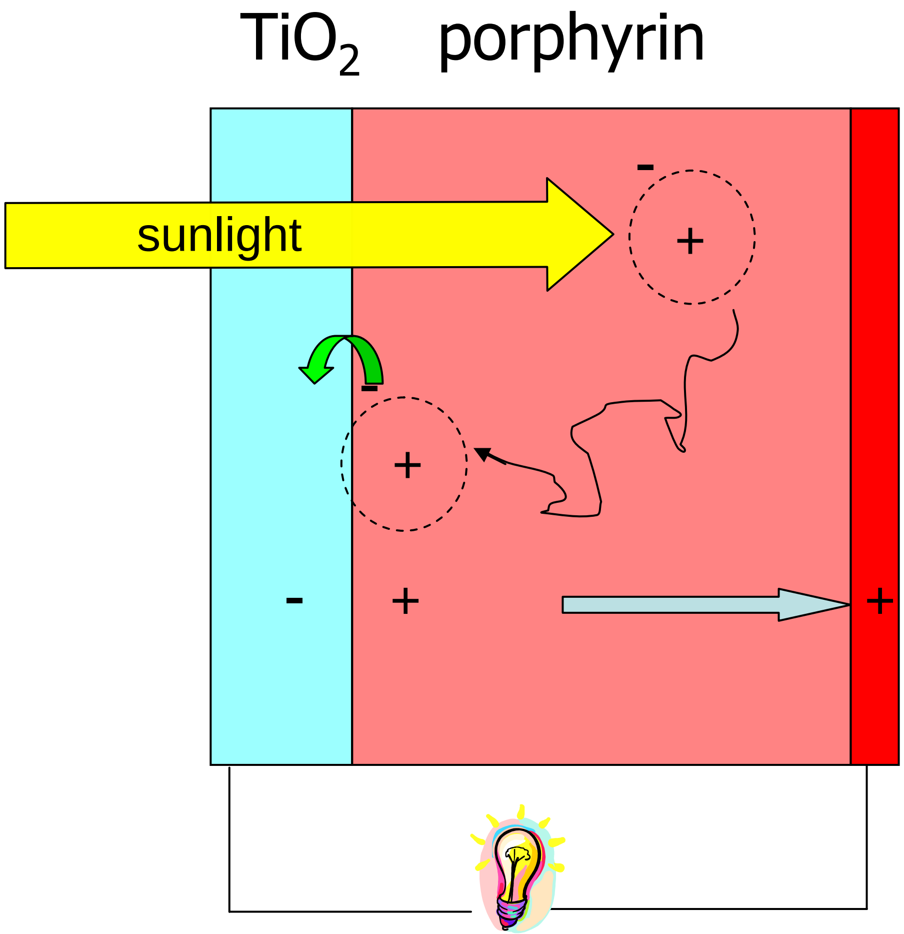
Exciton diffusion in bilayer model systems





5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin (TPPC)

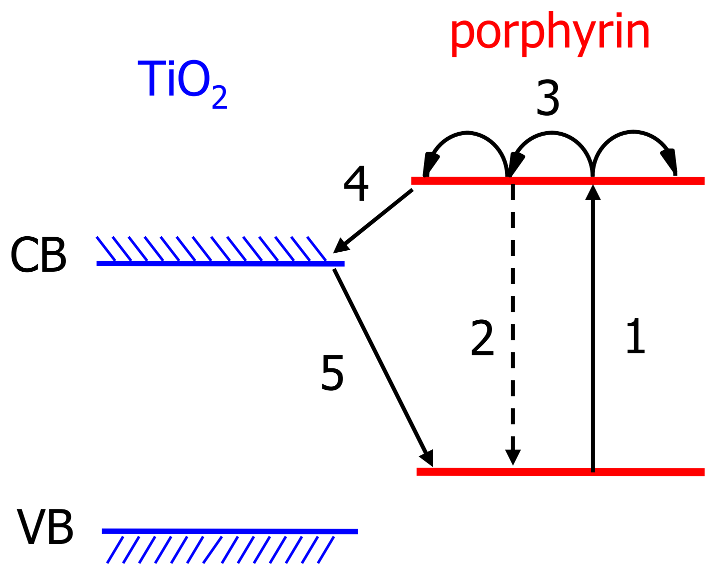
Simple bilayer dye-sensitized solar cell



Requirements:

- efficient light absorption
- large exciton diffusion length
- efficient charge separation at interface
- escape of charge from recombination
- mobile charges

Relevant processes



1: photo-excitation
2: (non)radiative decay
3: exciton diffusion and annihilation
4: interfacial electron transfer
5: interfacial charge recombination

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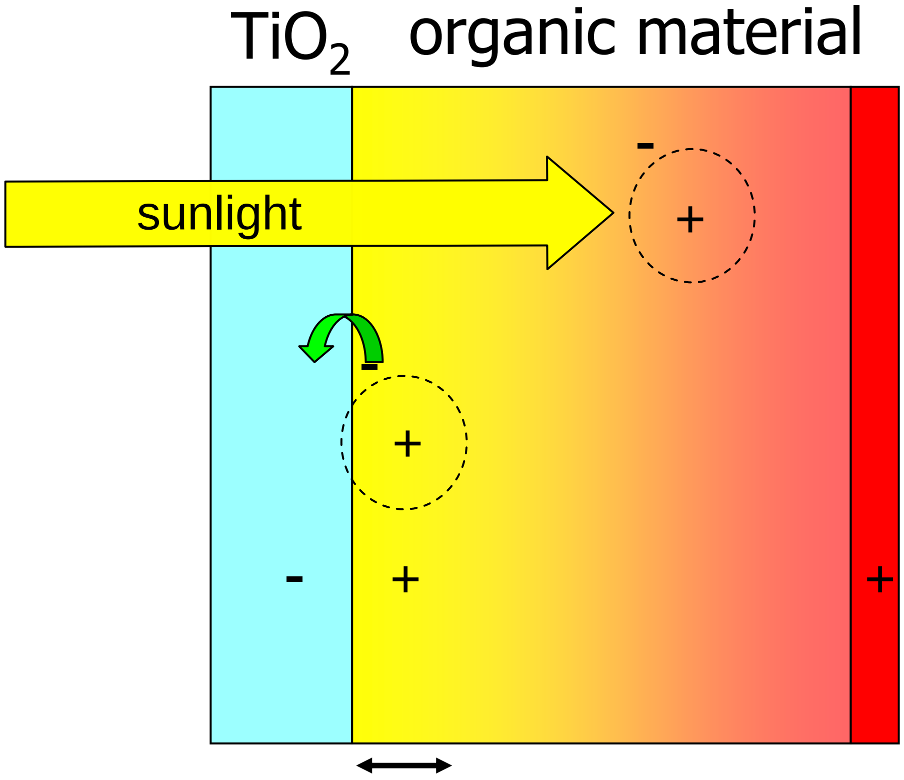
Bilayer is inefficient due to small exciton diffusion length



only small fraction of excitons reaches interface

exciton diffusion length $\Lambda_E = \sqrt{(D_E * \tau_E)} < 10$ nm

light penetration depth $\Lambda_{h\nu} \sim 100$ nm

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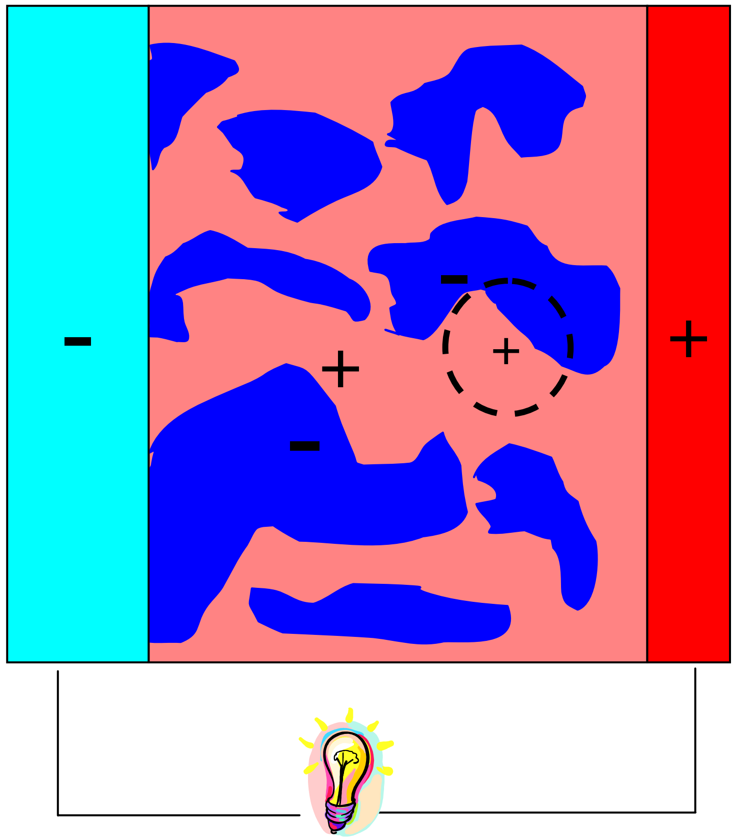
In heterogeneous structure Λ_E can be short



Disadvantages:

- percolation paths needed
- recombination losses
- exciton quenching on trapped charges

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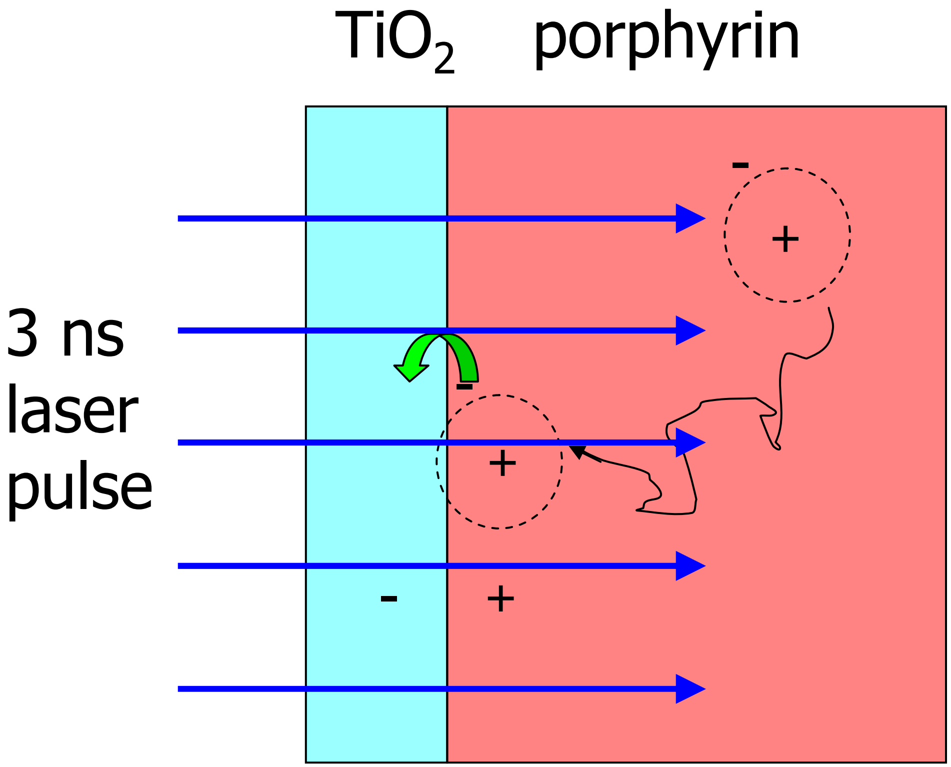
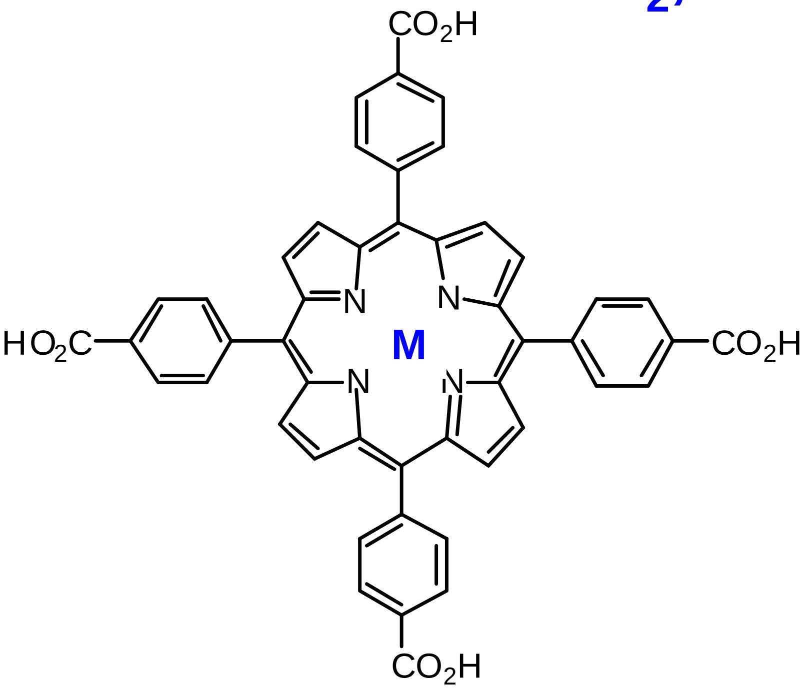
Exciton diffusion and charge separation in bilayer model systems: effect of Pd

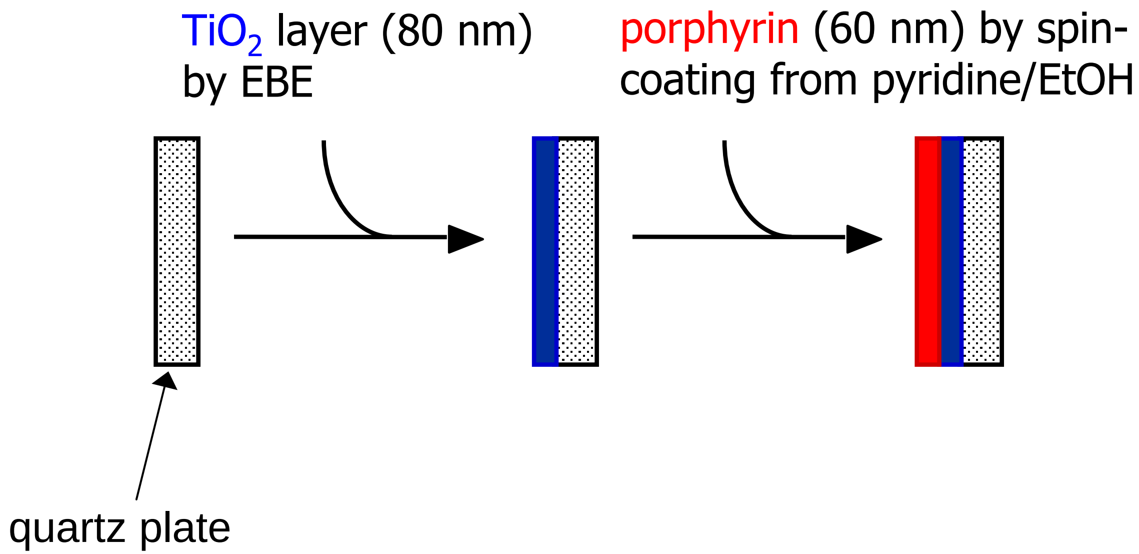


M=H$_2$, Pd



5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin (TPPC)

Layer preparation



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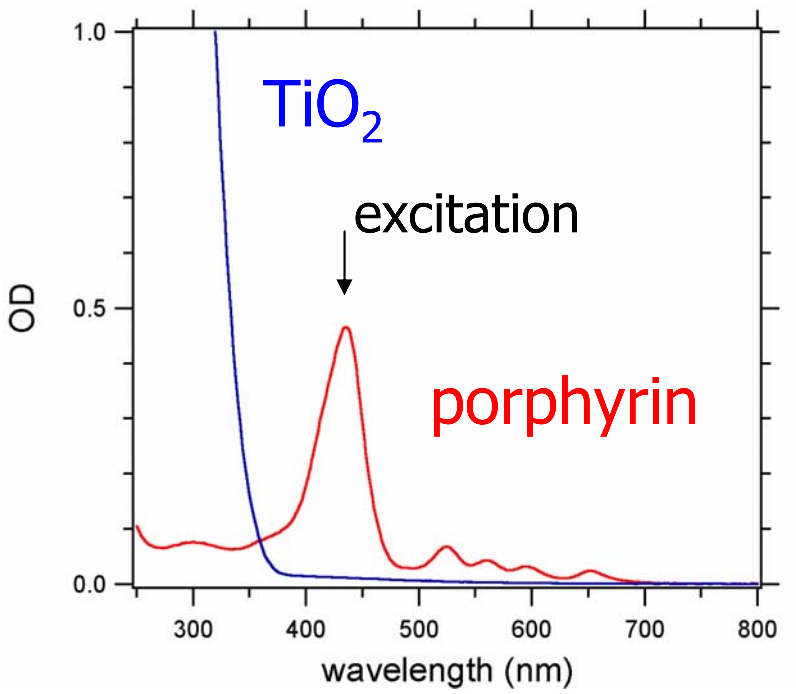
Absorption spectra



Selective excitation of porphyrin (400-700 nm) or TiO_2 (300 nm)

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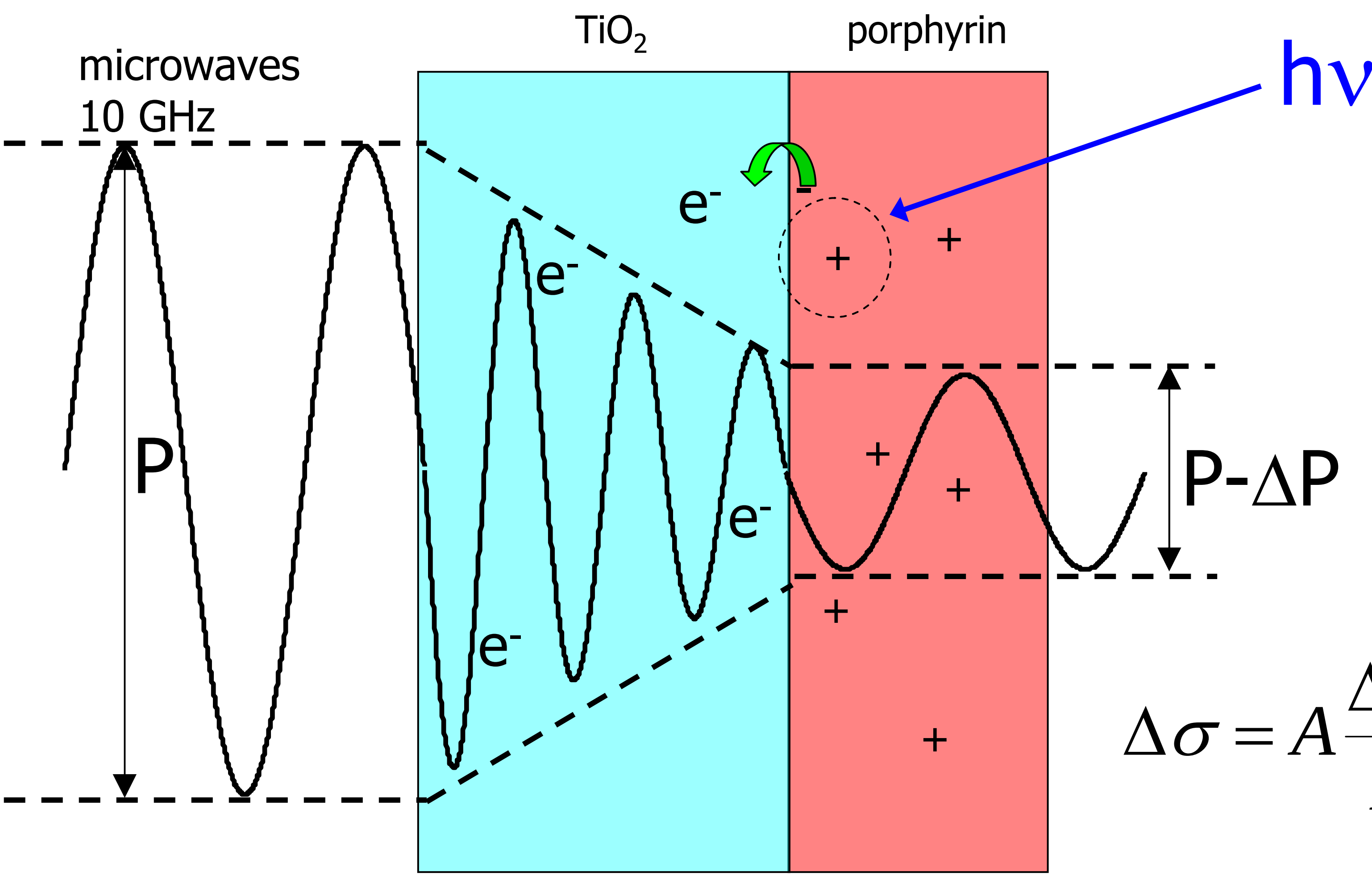
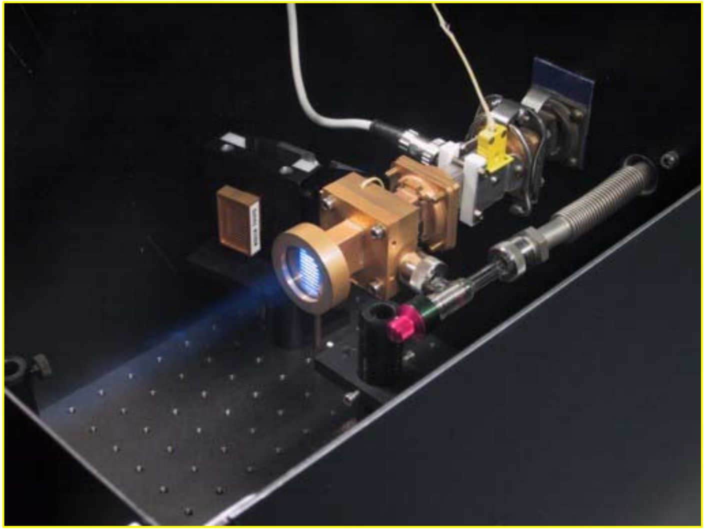
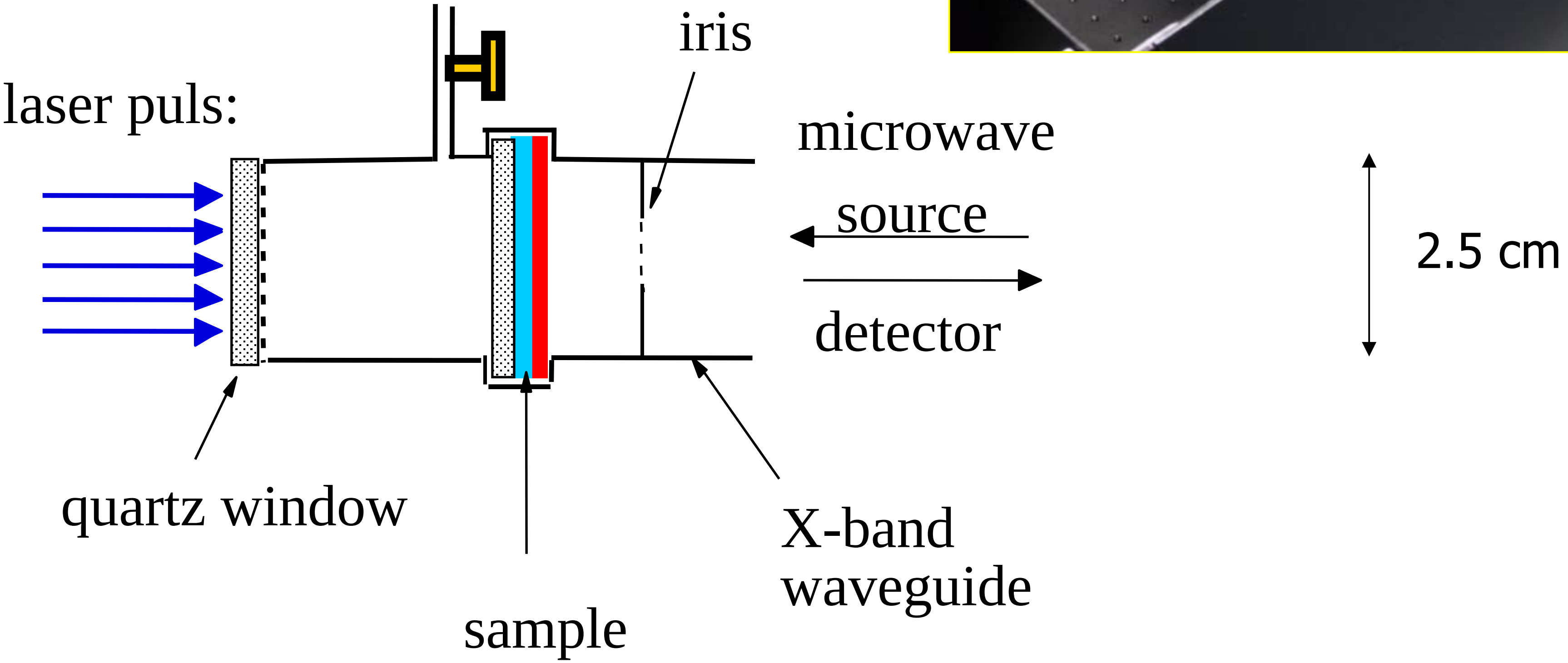
Time-resolved microwave conductivity measurements probe mobile electrons in TiO_2



$$\Delta\sigma = A\frac{\Delta P}{P} = e n \mu_{-}$$

Measurement cell





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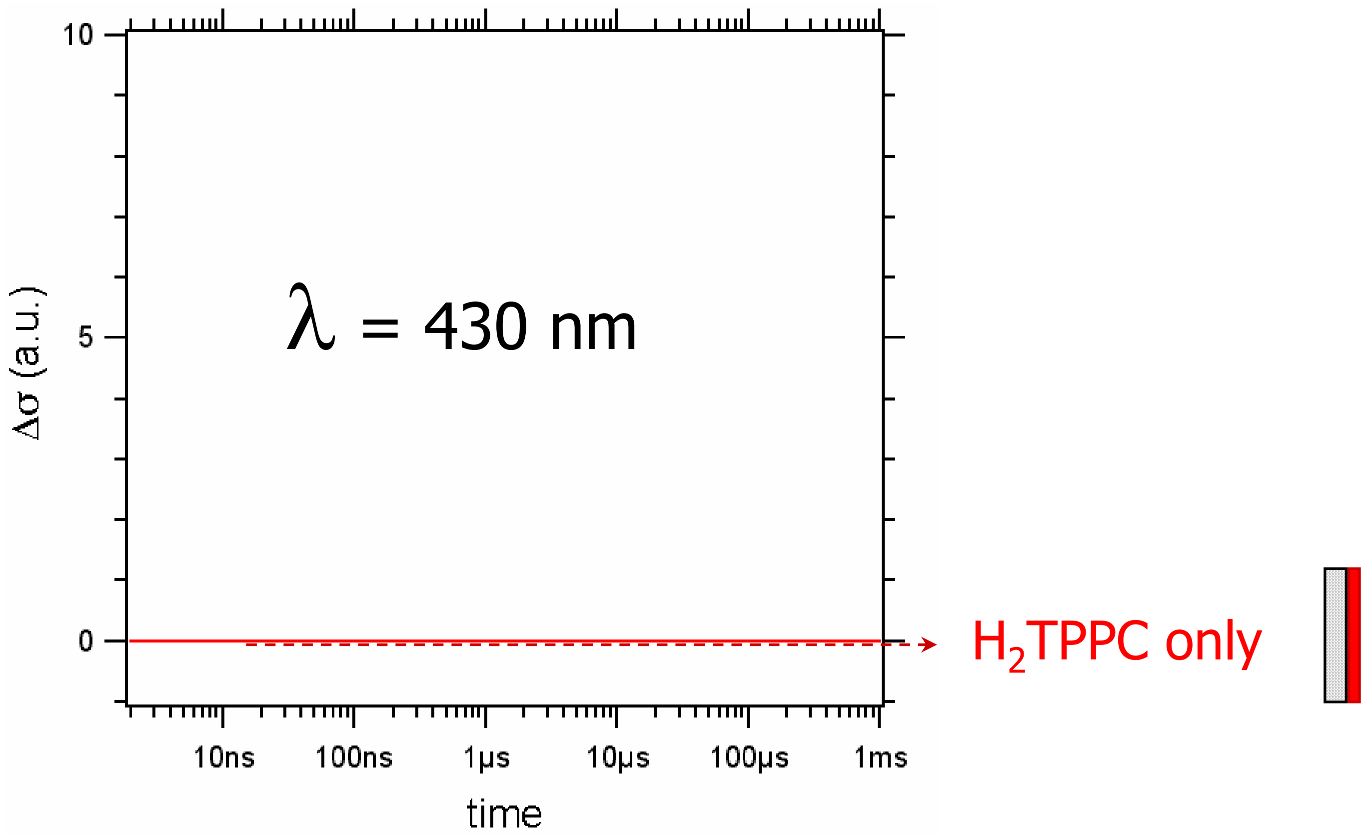
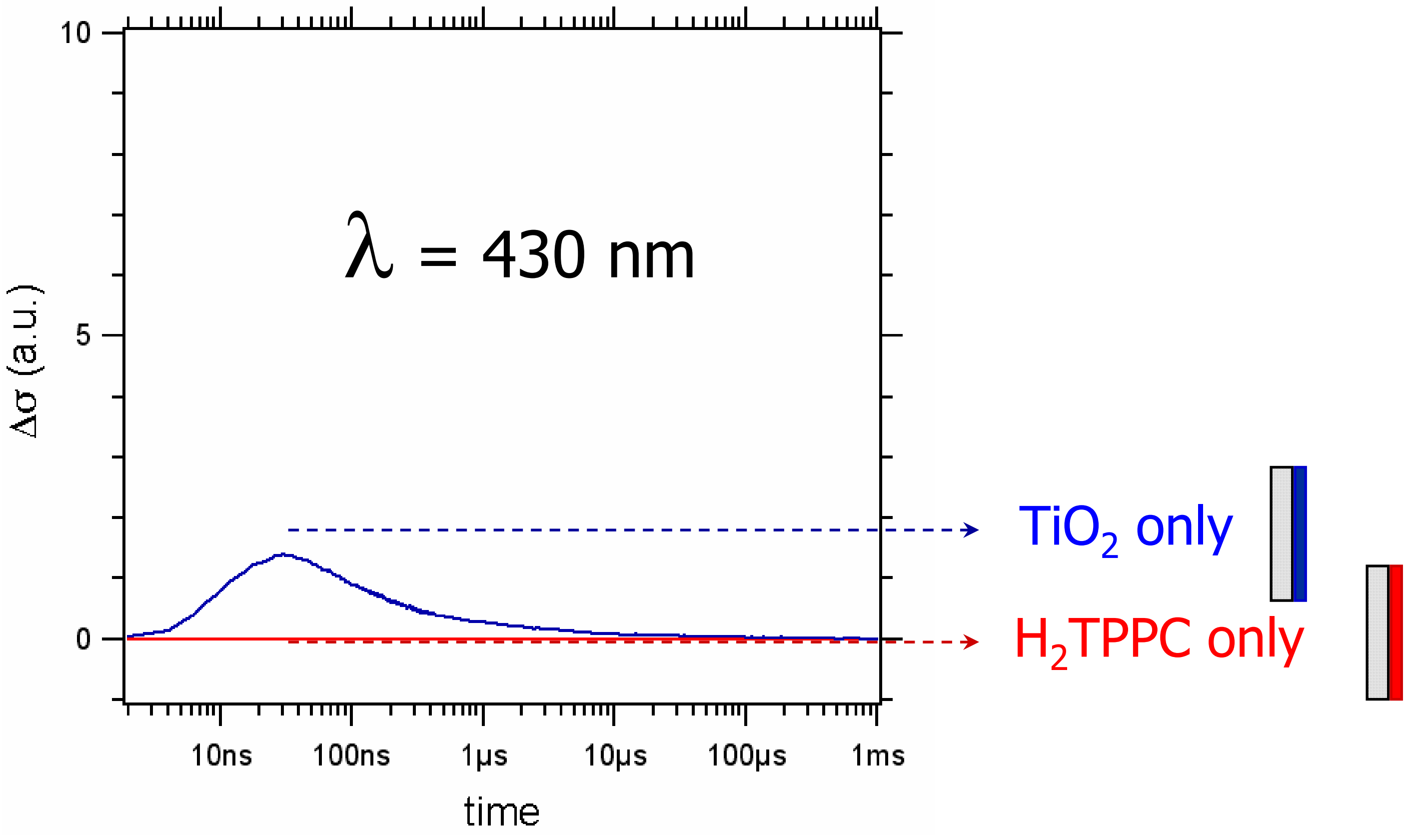
Porphyrin on quartz: no photoconductivity



TiO_2: small short lived photoconductivity



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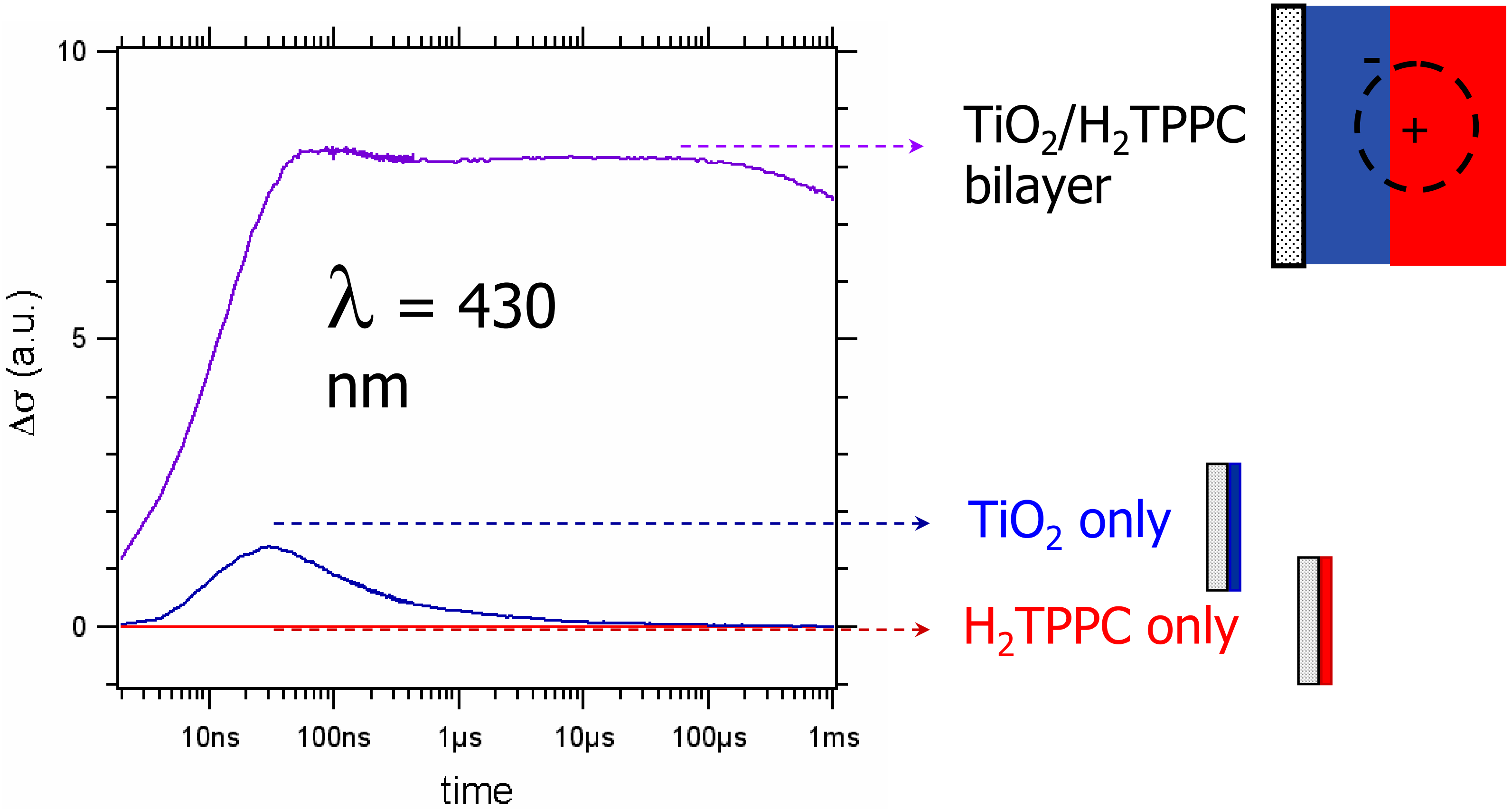
Porphyrin / TiO_2 bilayer: long-lived photoconductivity



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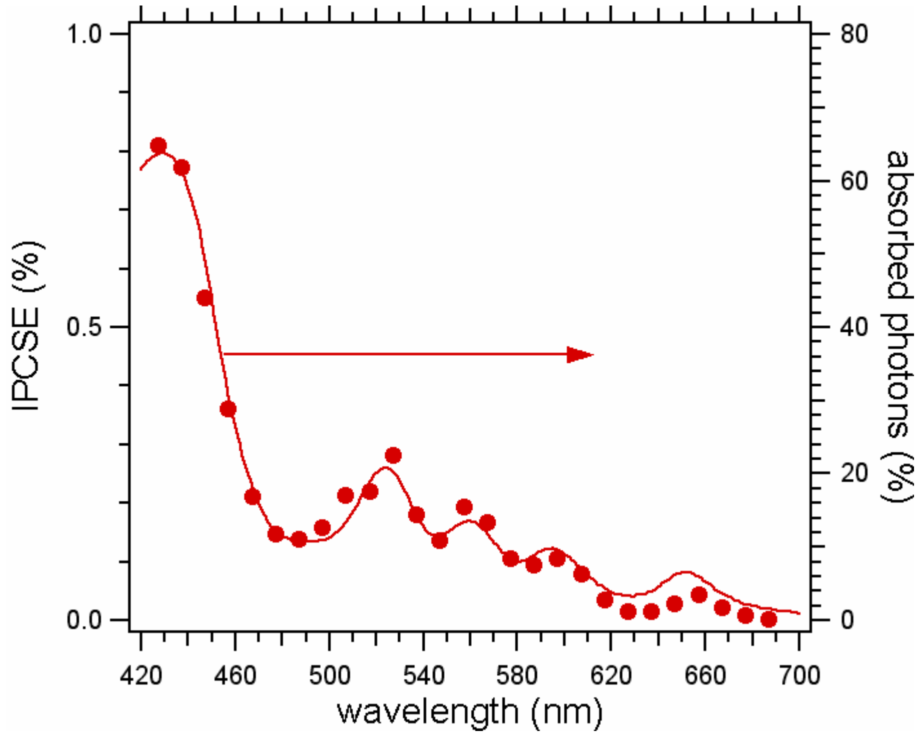
Porphyrin / TiO_2 bilayer: wavelength dependence

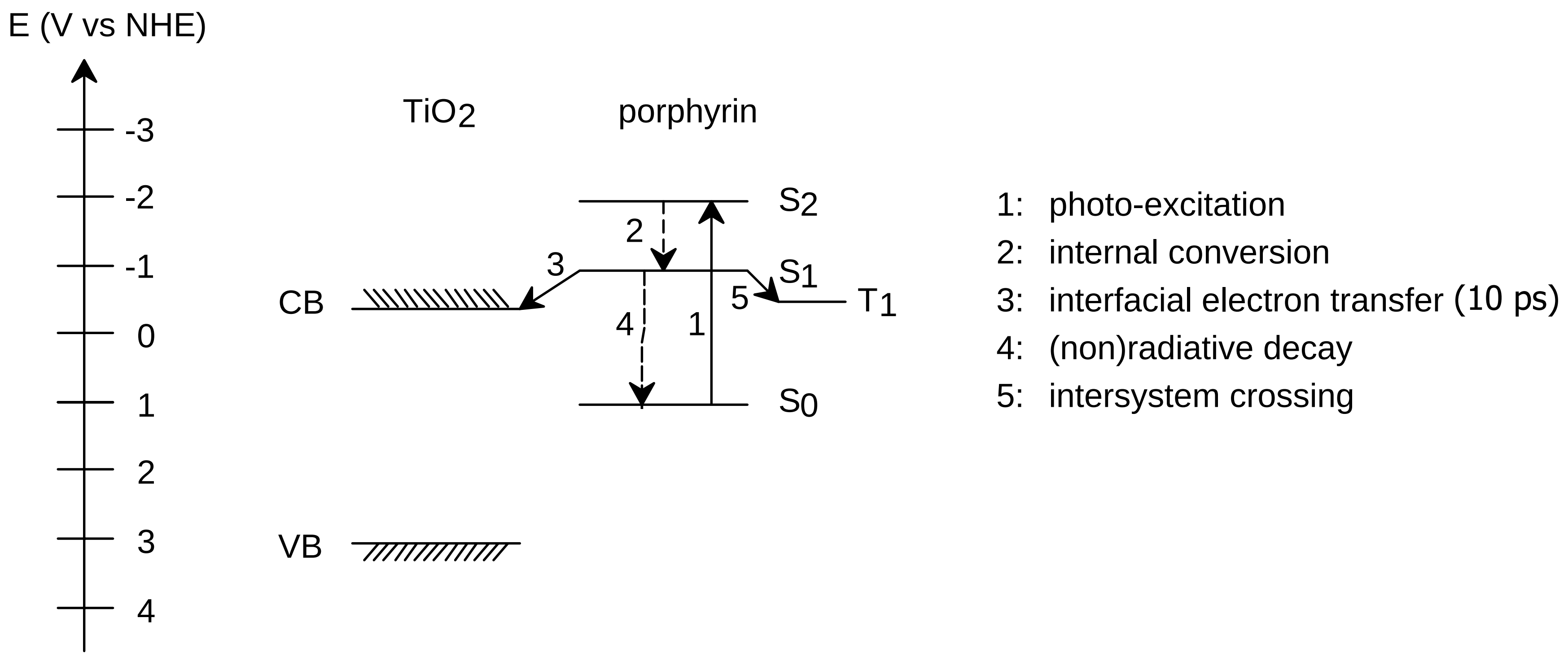
$$\text{IPCSE} = \frac{\text{no. of charges}}{\text{no. of incident photons}}$$



- No preferential charge separation at specific wavelength
- IPCSE < 0.8 % (F_a=0.6 at 430 nm)
- Exciton diffusion length only 1-2 monolayers of porphyrin

Kroeze, J. E.; Savenije, T. J.; Warman, J. M., *J. Photochem. Photobiol. A-Chem.* **2002,** 148, 49-55.

In H_2TPPC photoconductivity results from singlet excitons



Singlets (τ=11 ns) undergo intersystem crossing to triplets (ϕ=0.78, τ=0.4 ms) which diffuse via slow Dexter mechanism

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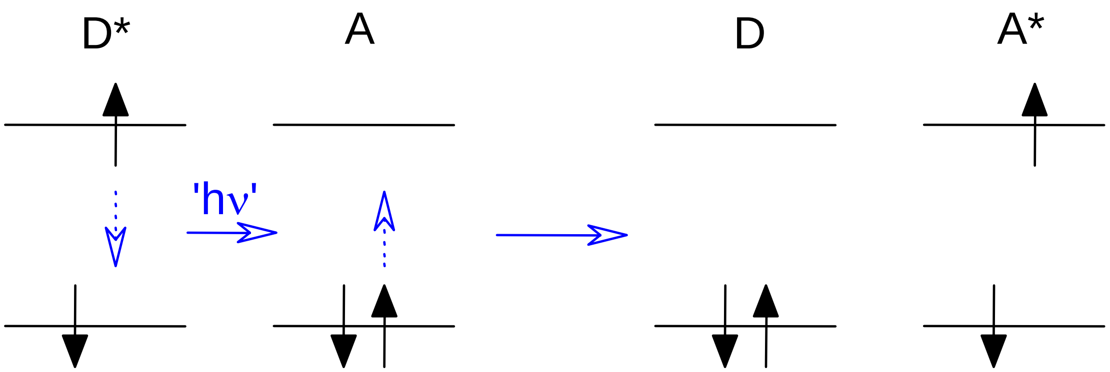
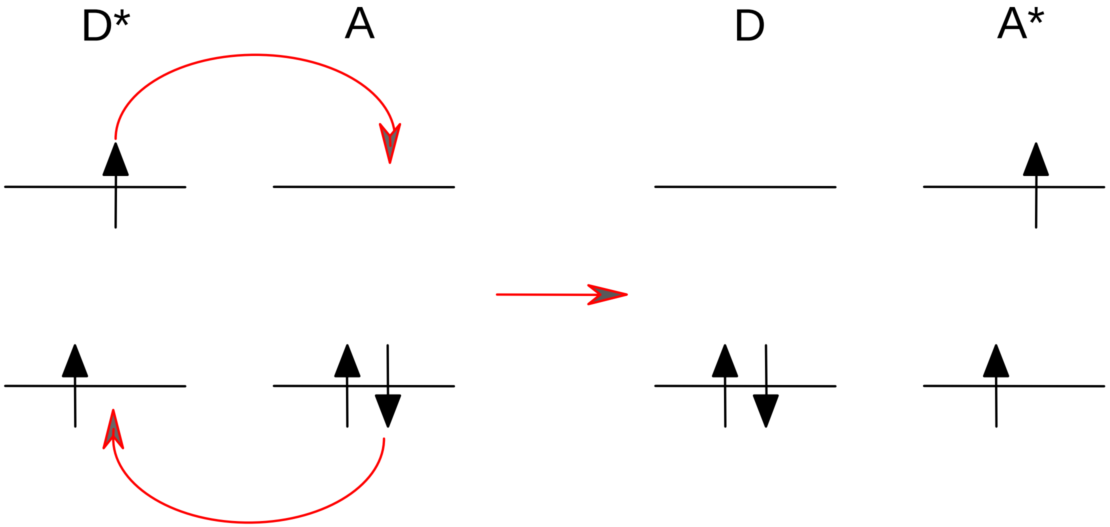
Singlet:
Förster energy transfer



Triplet:
Dexter energy transfer



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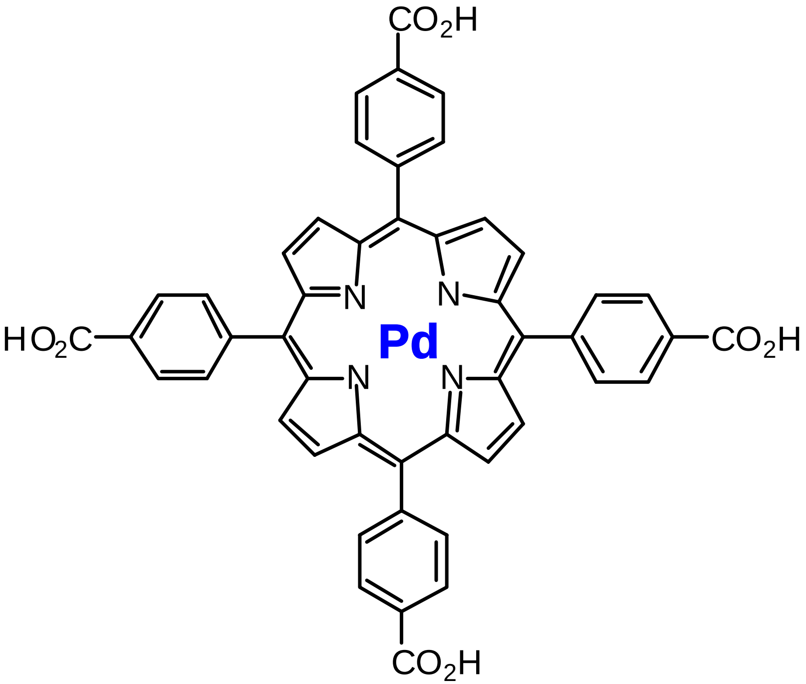
Mixing of singlet and triplet by spin orbit couling due to heavy metal

Excitons in Pd substituted porphyrin: - long lifetime due to triplet character
- diffusion via singlet character



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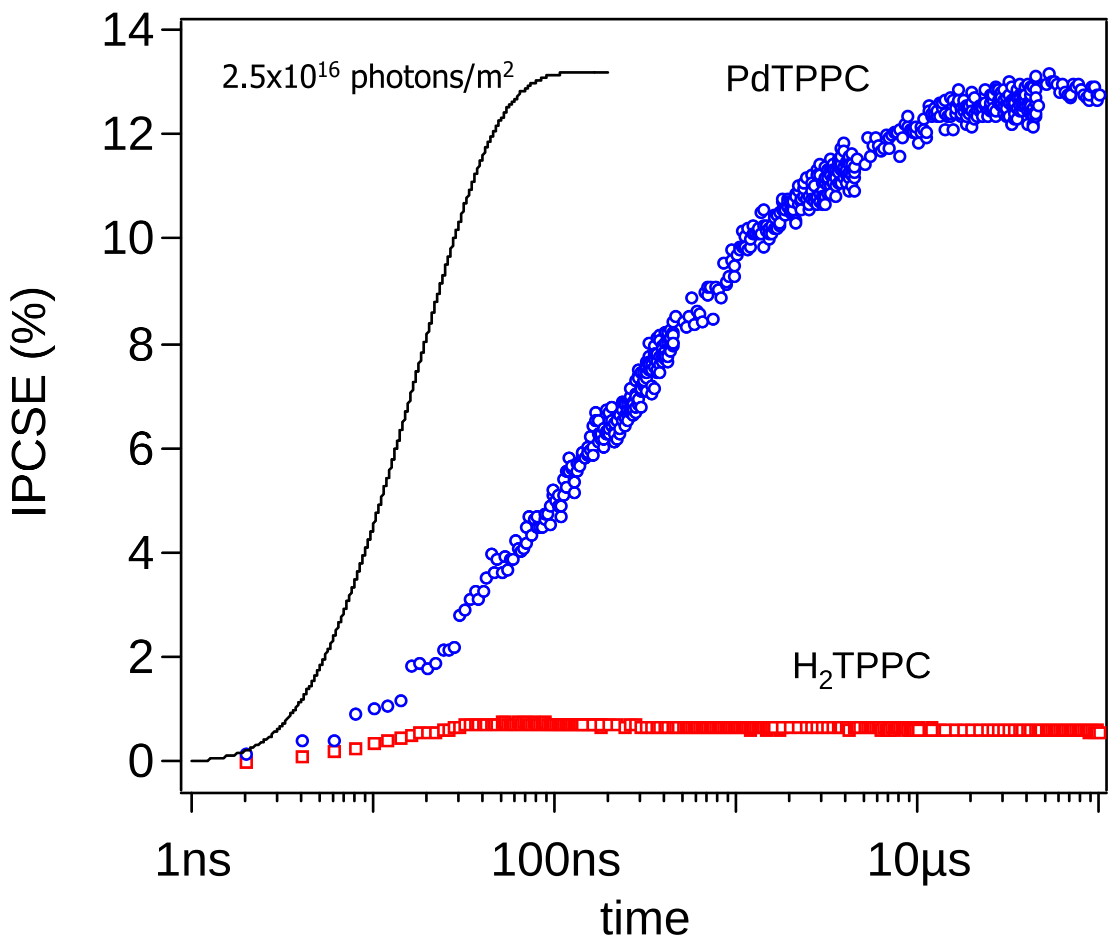
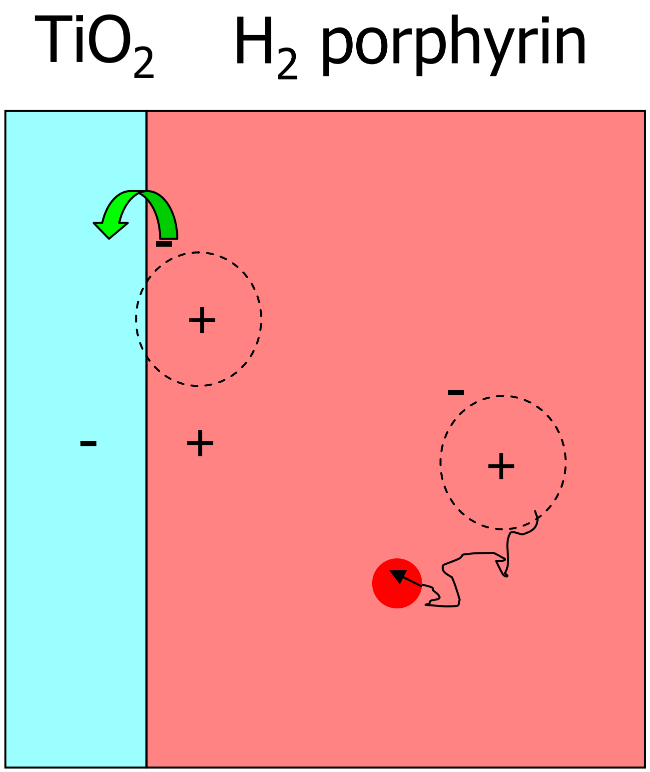
Pd substitution enhances IPCSE on longer times to 12 % due to diffusion of excitons with mixed singlet / triplet character

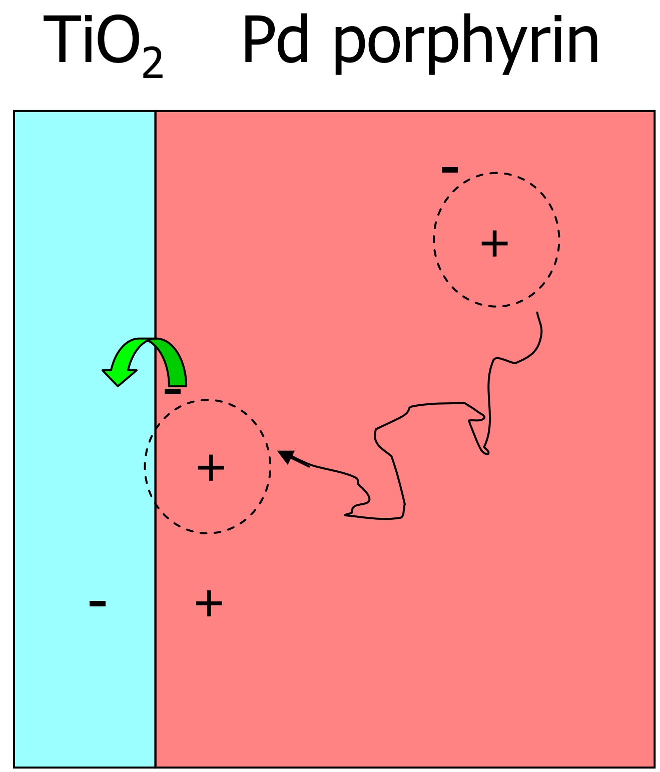


	H_2TPPC	PdTPPC
τ_S (ns)	11	~ 10^{-2}
τ_T (ms)	0.4	0.29
ϕ_T	0.78	~1
k_P (s^{-1})	0.0067	61
$E(S_0)$ (eV)	-5.5 [-1.1]	-5.7 [-1.3]
$E(S_1)$ (eV)	-3.6 [0.8]	-3.5 [0.9]
$E(S_2)$ (eV)	-2.6 [1.8]	-2.7 [1.7]
$E(T_1)$ (eV)	-4.1 [0.3]	-3.9 [0.5]

Kroeze, J. E.; Savenije, T. J.; Warman, J. M. *Adv. Mater.* **2002**, *14*, 1760-1763.

Enhanced diffusion length in PdTPPC





In PdTPPC diffusion via singlet and triplet

$$\Psi_{exc} = c_S \Phi_S + c_T \Phi_T$$

$$\Lambda = \sqrt{D\tau}$$

$$D = \delta^2 k_{hop} = \delta^2 \left[P_s^2 k_{Forster} + (1 - P_s) k_{Dexter} \right] \qquad \tau = \frac{1}{P_s k_{rad} + k_{nrad}}$$

$$\Lambda = \sqrt{\frac{\delta^2 \left[P_s^2 k_{Forster} + (1 - P_s) k_{Dexter} \right]}{P_s k_{rad} + k_{nrad}}}$$

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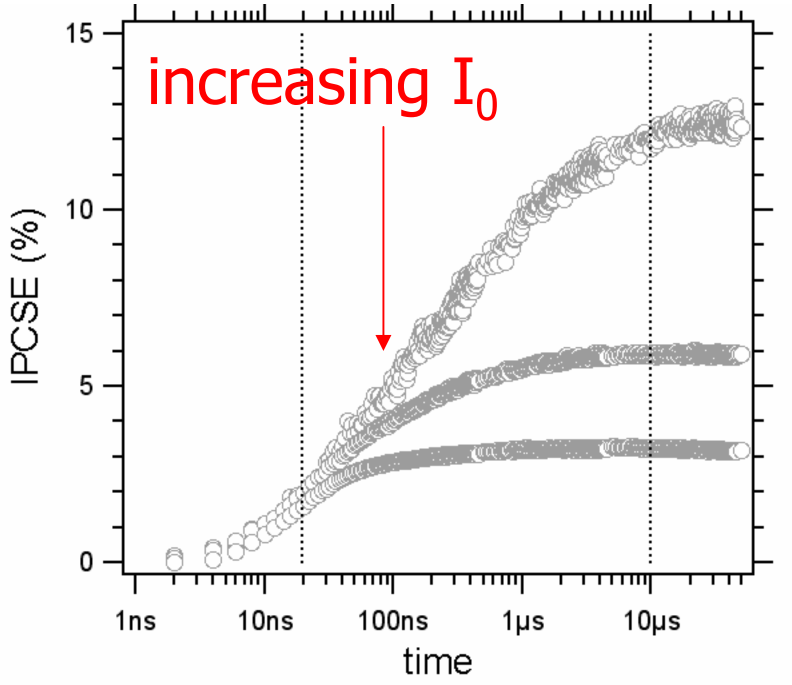
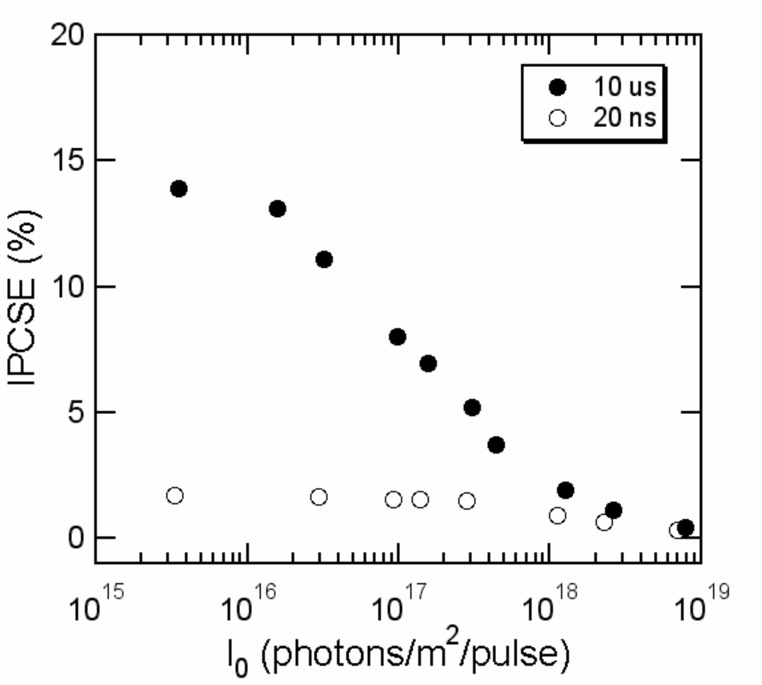
Effect of laser intensty on conductivity in PdTPPC / TiO_2 bilayer





Strong influence of $I_0 \rightarrow$ bimolecular exciton-exciton annihilation

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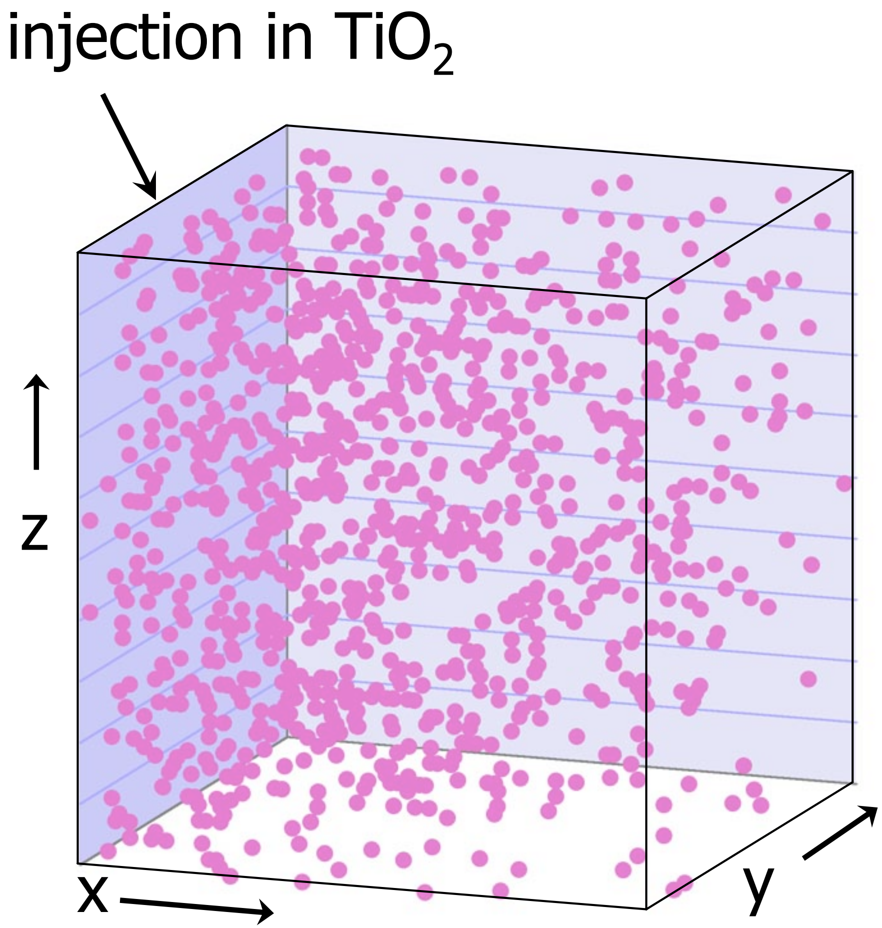
Monte Carlo computer simulations



- 3D excitation profile; Lambert-Beer along x
- Exciton mean lifetime τ and diffusion coefficient D
- Excitons peform 3D random walk
- Annihilation if 2 excitons within distance R_{ann}
- Electron injection with chance ϕ_{inj} at TiO_2 interface
- Output: charge separation efficiency *vs* time

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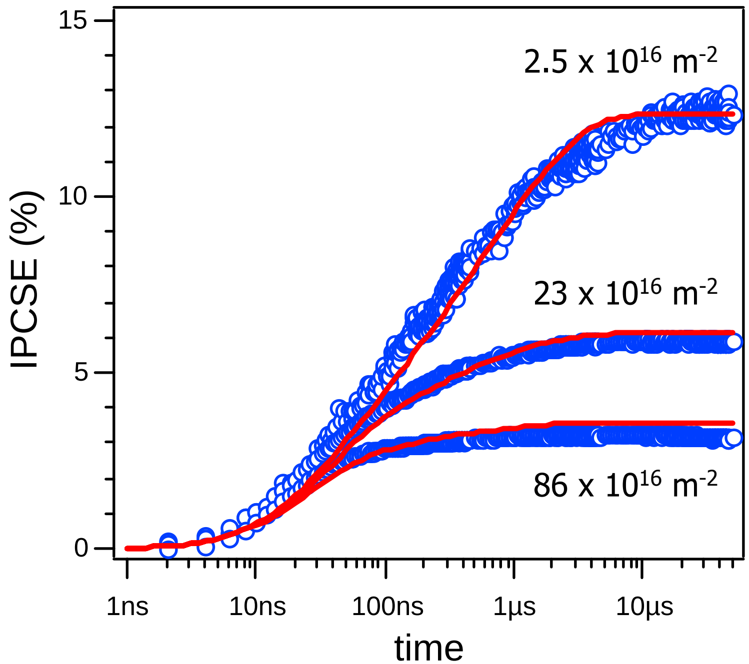
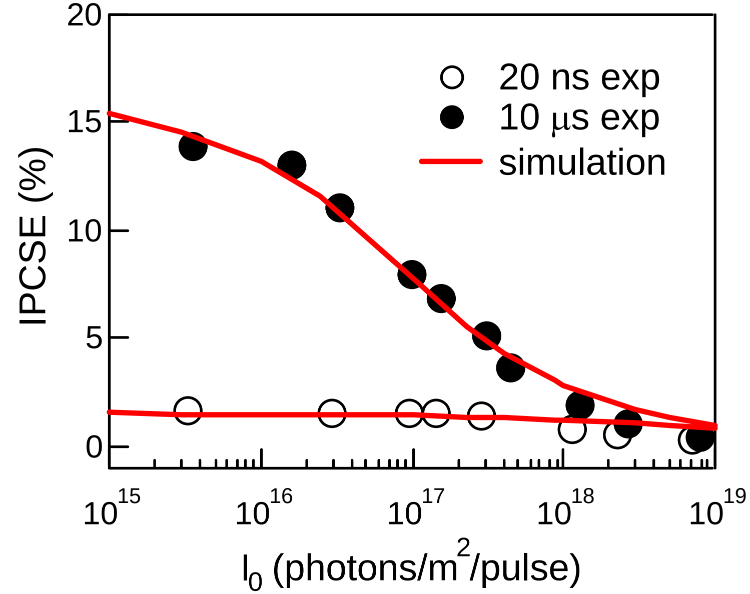
Triplet exciton diffusion in PdTPPC simulated





- $D = 8\times10^{-11}$ m^2/s (5 ns hopping time for d=1.5 nm) , $\tau \geq 10$ µs
- Exciton diffusion length ≥ 28 nm!
- $\phi_{inj} = 0.4$
- $R_{ann} = 1.5$ nm

Kroeze, J. E.; Savenije, T. J.; Candeias, L. P.; Warman, J. M.; Siebbeles, L. D. A. *Solar Energy Mater. Solar Cells* **2004**, in press.

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$D = 8 \times 10^{-11}\ m^2/s$ for triplets in PdTPPC

<u>literature:</u>

$D = 2.8 \times 10^{-8}\ m^2/s$ for singlets in lc porphyrin derivative
$D = 10^{-8} - 10^{-6}\ m^2/s$ for singlets in conjugated polymers

$D = 10^{-12}\ m^2/s$ for triplets in ZnTPPC

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Conclusion

- Singlet-triplet mixing due to heavy atoms enhances exciton diffusion length

- Simple bilayer devices may become competitive with designs based on mesoporous nanocrystalline materials

Acknowledgments

Dr. J.E. Kroeze, Dr. T.J. Savenije and Dr. J.M. Warman

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