Electronic Excitation Energy Transfer

Gion Calzaferri
Department of Chemistry and Biochemistry,
University of Bern, Freiestrasse 3, CH-3012 Bern

Part 1: An experimental approach

Energy Collection, Transport, and Trapping by Supramolecular Organization of Dyes in Hexagonal Zeolite Nano Crystals

Part 2: Theoretical concepts

Förster Energy Transfer Theory

Electronic Excitation Energy Transfer

Part 1: An experimental approach

Energy Collection, Transport, and Trapping by Supramolecular Organization of Dyes in Hexagonal Zeolite Nano Crystals

In the antenna system of a leaf, the energy of the sunlight is transported by chlorophyll molecules for the purpose of energy transformation.

The aim of this work is to develop a similar light transport in an artificial system in which dye loaded zeolite L crystals adopt the antenna function and to find out if and how this can be used in photoelectronic devices.

Organic dyes have the tendency to form aggregates even at low concentration.

Aggregates are known to cause fast thermal relaxation of electronic excitation energy.

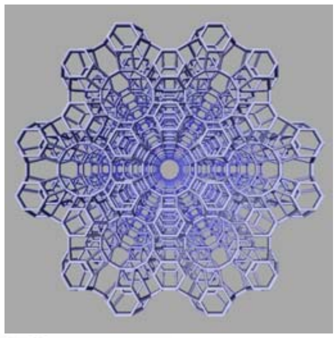
The role of the zeolite (host) is to prevent this aggregation,
to superimpose a specific organization,
and also to strongly improve the stability of the dyes.

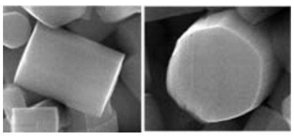
First paper on this subject:
Thionine in the Cages of Zeolite L
G. Calzaferri and N. Gfeller, J. Phys. Chem., 96 (1992) 3428

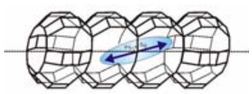
1 Zeolite L is an ideal host for supramolecular organization of dyes

Its crystals consist of one-dimensional channels.

Zeolite L belongs to the family of classical zeolites which are alumosilicates.

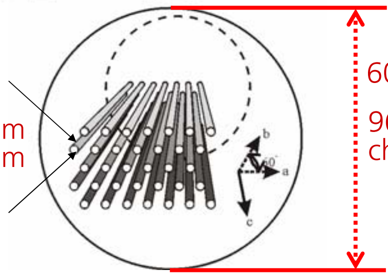






30 nm – 7000 nm

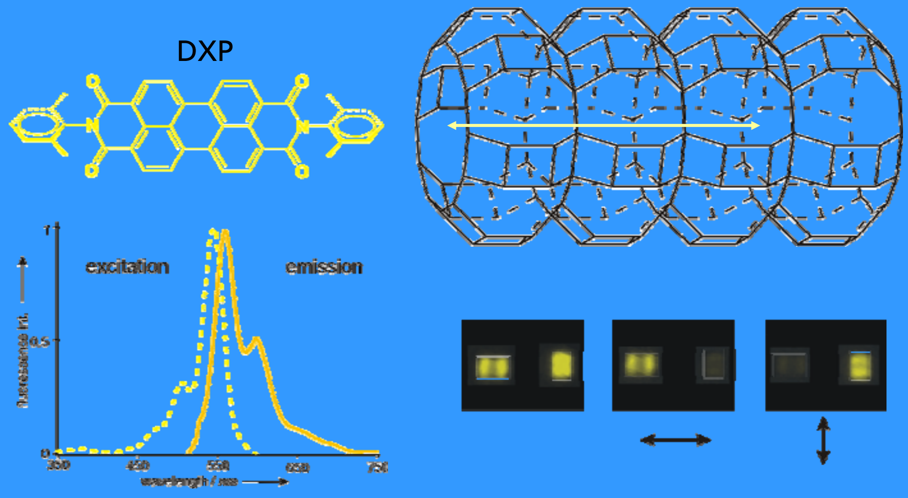
3×10^4 nm^3 – 7×10^{11} nm^3



Consequences:
very high concentration of organized monomers
(up to about 0.4 mol/L)
30 nm crystal → 4800 dyes

60 nm ⟶ 38'000 dyes

1 Zeolite L is an ideal host for supramolecular organization of dyes

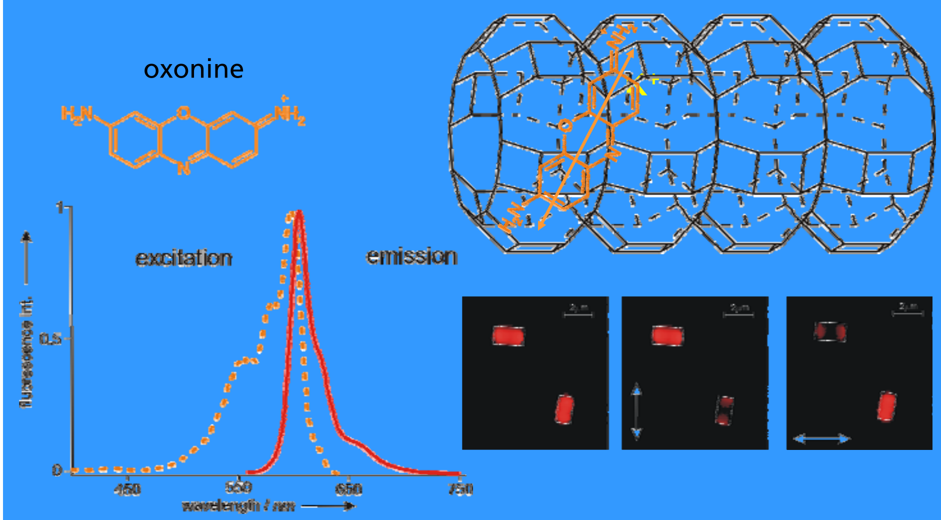


S. Brasselet, K. Komorowska, Cachan internal report

Nano-bulbs

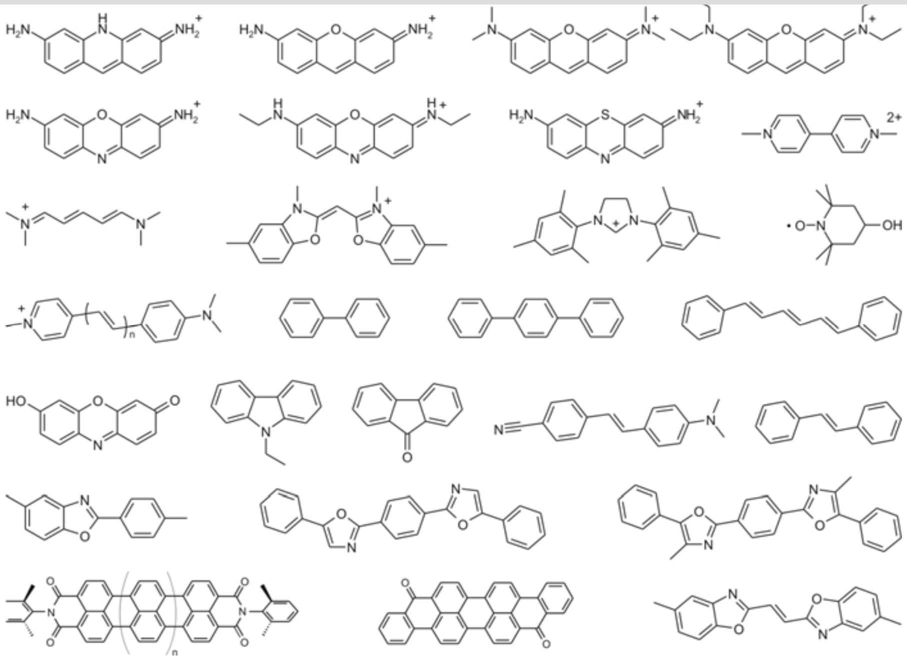
Stefan Huber, Gion Calzaferri, ChemPhysChem, 2004, 5, 293.

1 Zeolite L is an ideal host for supramolecular organization of dyes

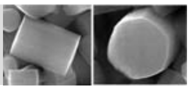


S. Megelski, A. Lieb, M. Pauchard, A. Drechsler, S. Glaus, Ch. Debus, A.J. Meixner, G. Calzaferri
J. Phys. Chem. B 105, 2001, 25

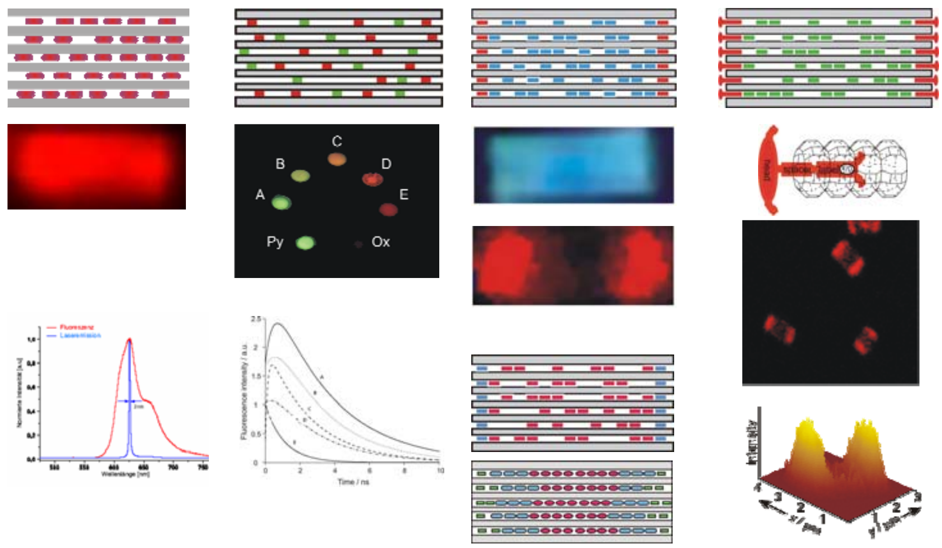
1 Zeolite L is an ideal host for supramolecular organization of dyes



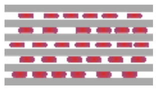
2 Overview, dye-zeolite L materials

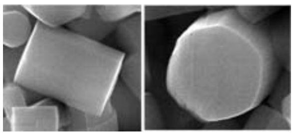


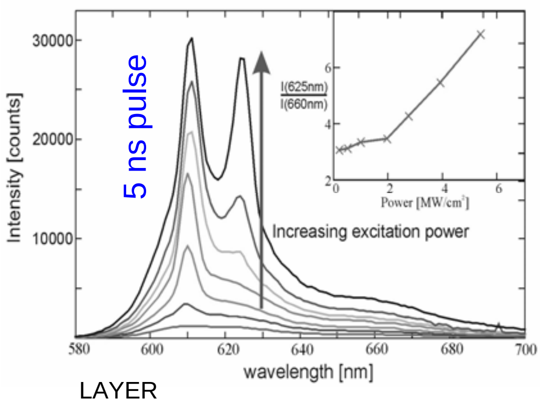
single dye material | mixed dye material | antenna material | stopcock plugged antenna material



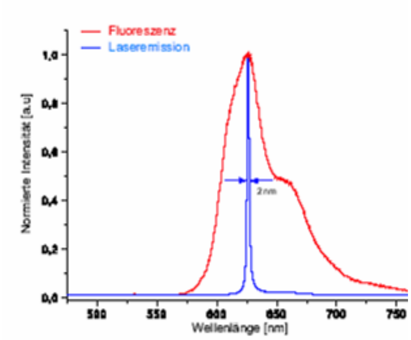
2 Overview, dye-zeolite L materials: nanolasers?







LAYER

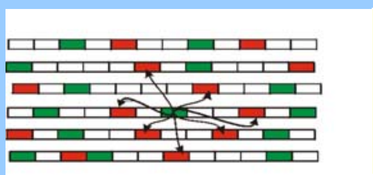


Single Crystal (about 1000 nm)

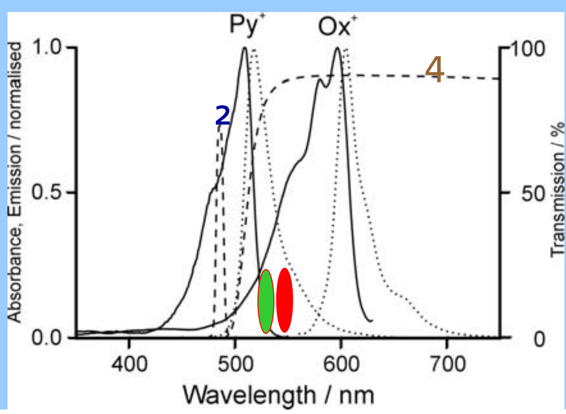
G. Calzaferri, C. Leiggener, S. Huber, D. Brühwiler, M.K. van Veen, A. Zabala Ruiz, C. R., Chimie (2005) in press

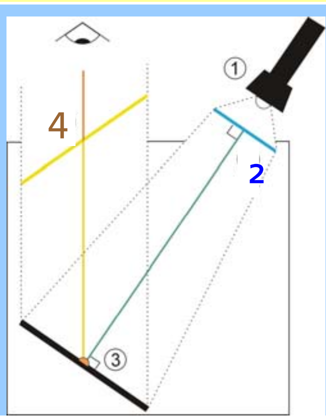
9

2 Overview, Dye-zeolite L materials:
A Förster energy transfer demonstration experiment

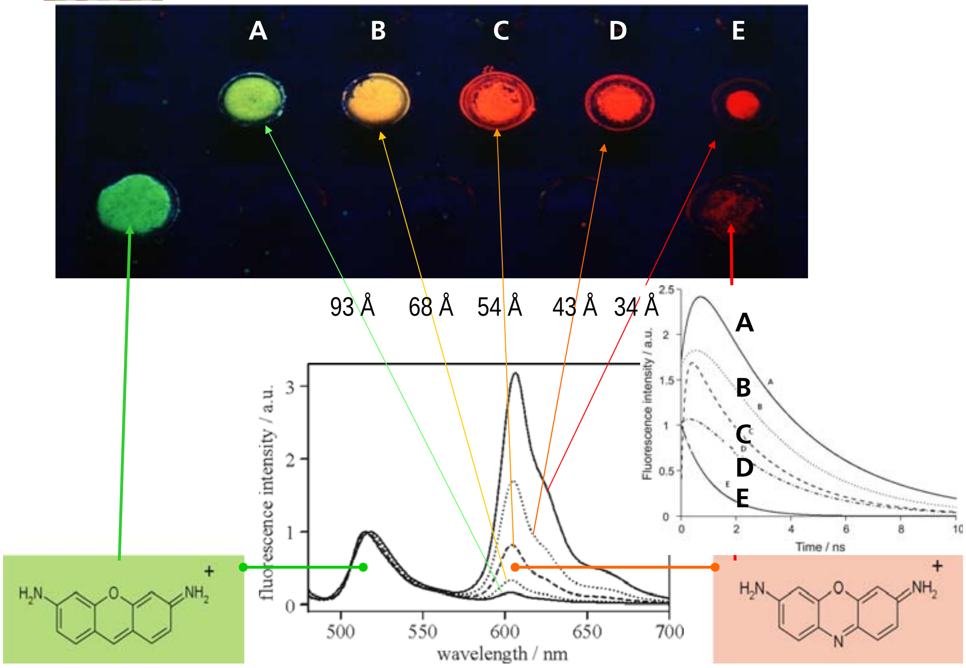


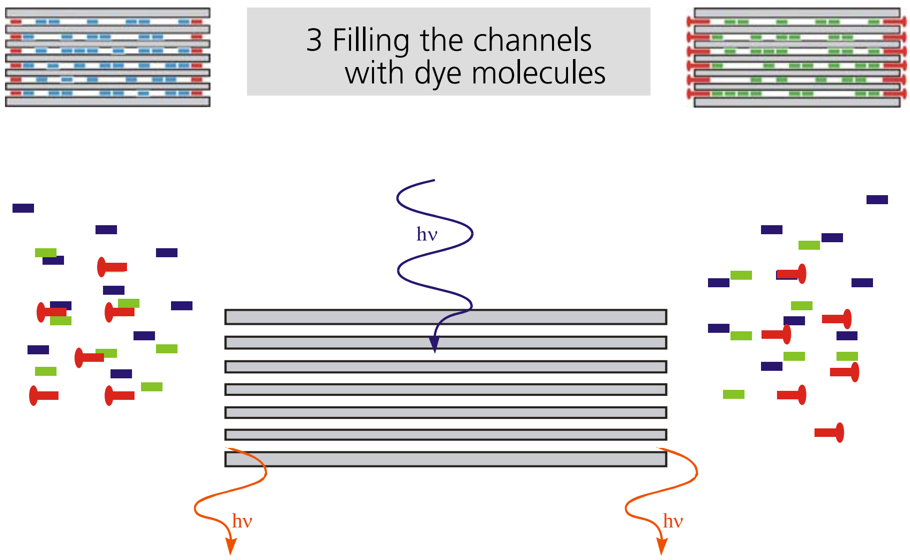
$$\frac{\kappa^2}{R^6} \cdot J$$





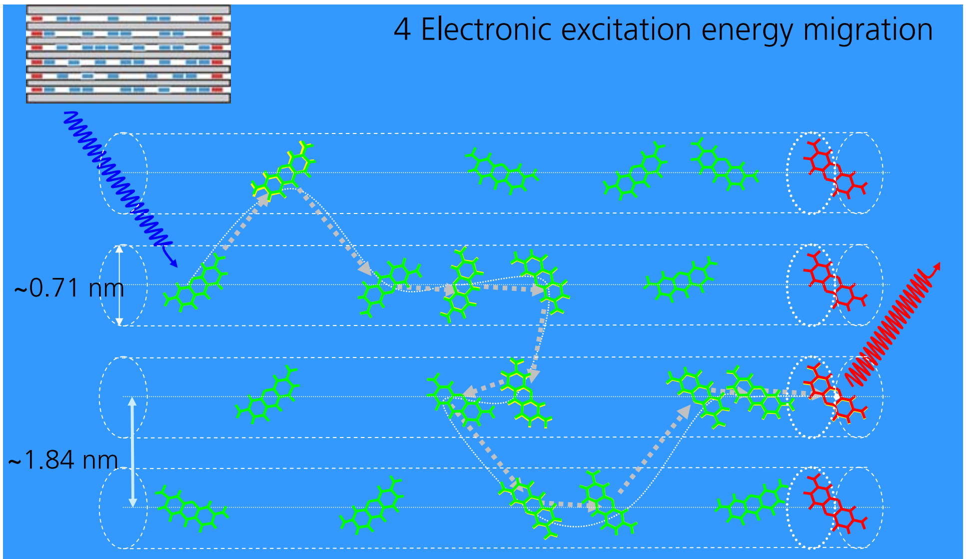
2 A Förster energy transfer demonstration experiment





Host-Guest Antenna Materials
G. Calzaferri, S. Huber, H. Maas, C. Minkowski, *Angew. Chemie, Int. Ed.* 2003, 42, 3732

4 Electronic excitation energy migration

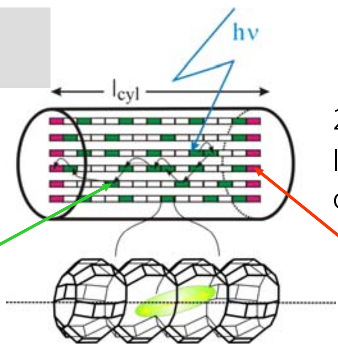


k_{EnT} up to 3×10^{13} s^{-1}

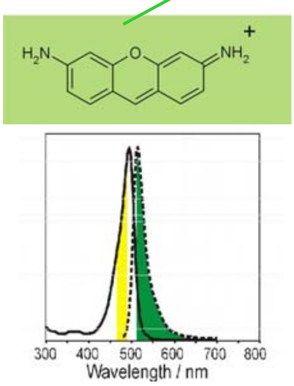
Electronic Excitation Energy Migration in a Photonic Dye-Zeolite Antenna

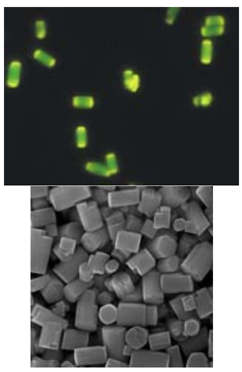
J. Phys. Chem. B 1997, 101, 1396
CHEMPHYSCHEM 2003, 4, 567

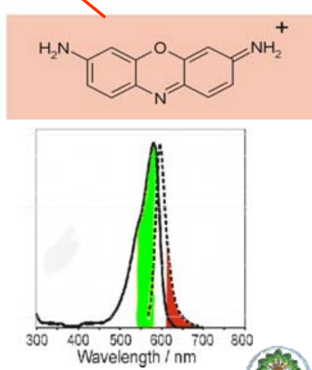
4 Electronic excitation energy migration



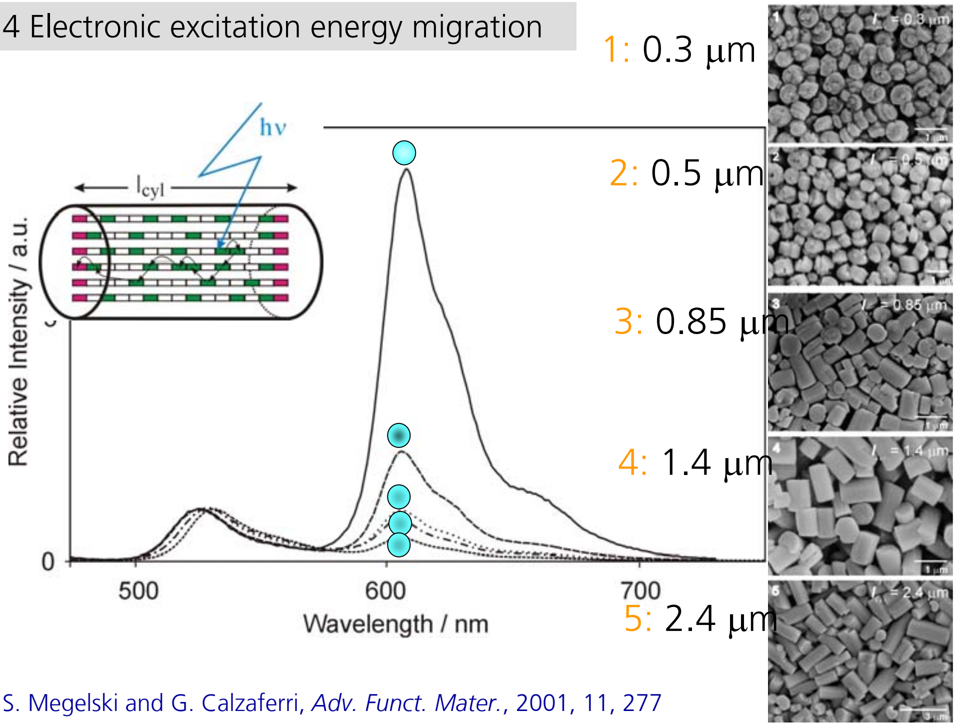
2 Parameter:
length of the cylinder
occupation probability





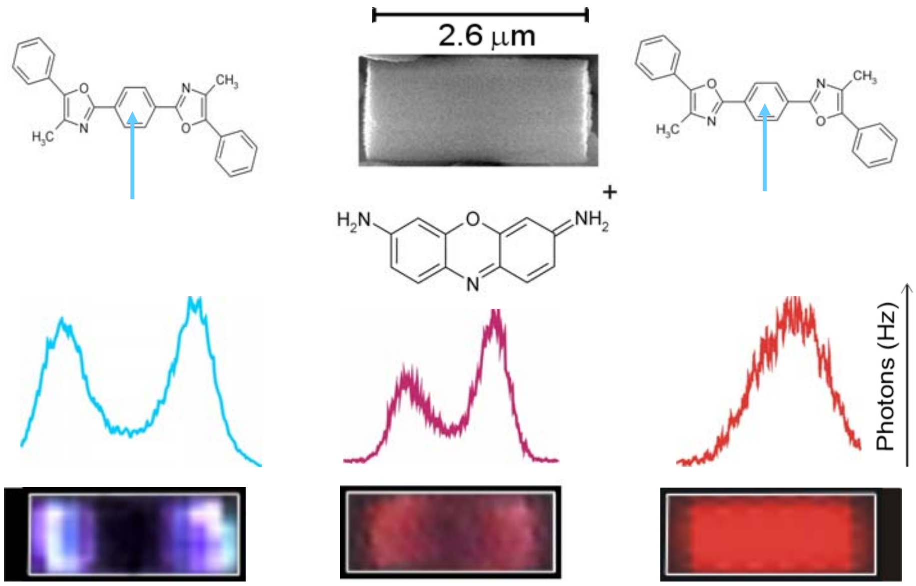


4 Electronic excitation energy migration



S. Megelski and G. Calzaferri, *Adv. Funct. Mater.*, 2001, 11, 277

4 Electronic excitation energy migration

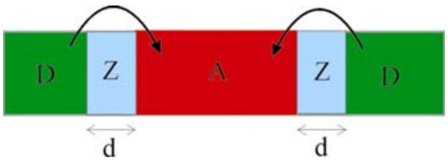


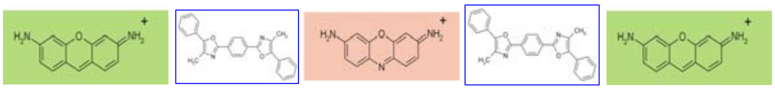
M. Pauchard, S. Huber, **R. Méallet**, H. Maas, **R. Pansu**, G. Calzaferri
Angew. Chem. Int. Ed. 40 (2001) 2839

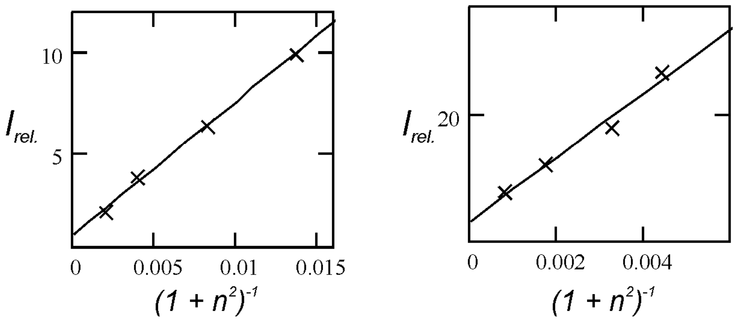
4 Electronic excitation energy migration along a specified axis

Claudia Minkowski, Gion Calzaferri, Angew. Chem. in press

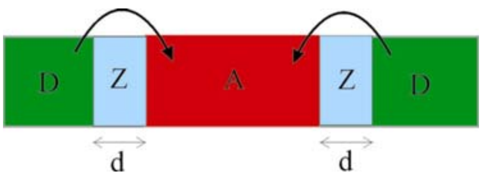
$$P \propto \left[1 + \left(\frac{R}{R_0}\right)^{\alpha}\right]^{-1}$$

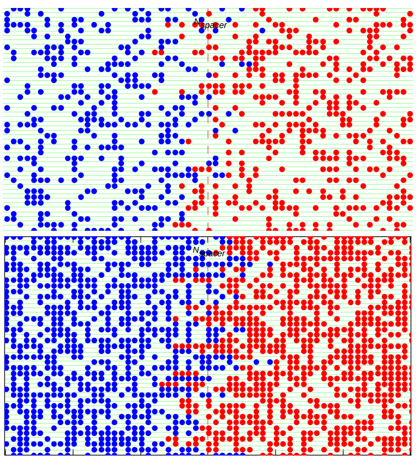






4 Electronic excitation energy migration along a specified axis: Phase boundary





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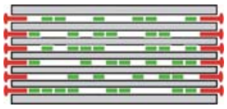
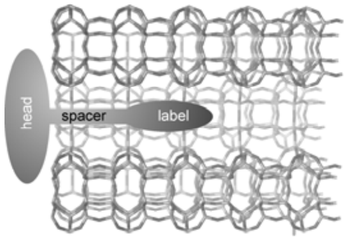
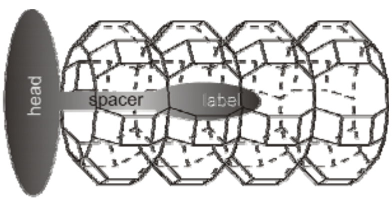


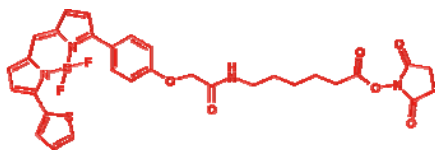
5 The stopcock principle
Functional stopcocks

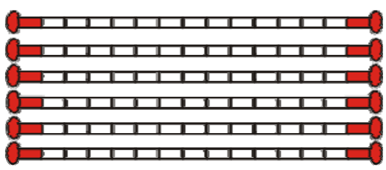


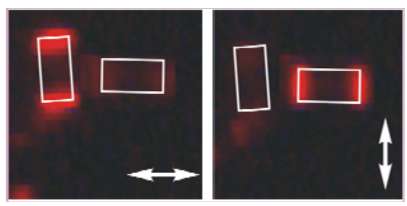
Trapping Energy from and Injecting Energy into Dye-Zeolite Nanoantennae
H. Maas, G. Calzaferri, Angew. Chemie, Int. Ed. 2002, 41, 2284

5 The stopcock principle: *Functional stopcocks*









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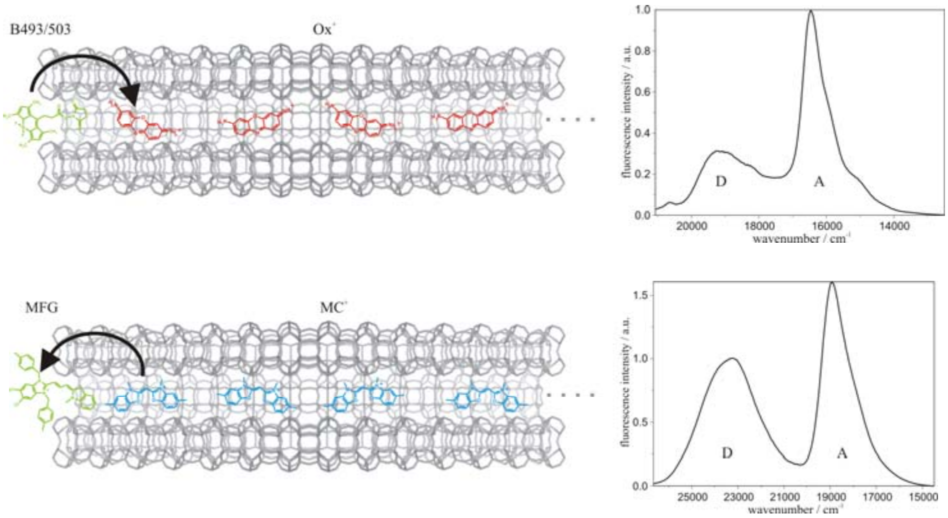
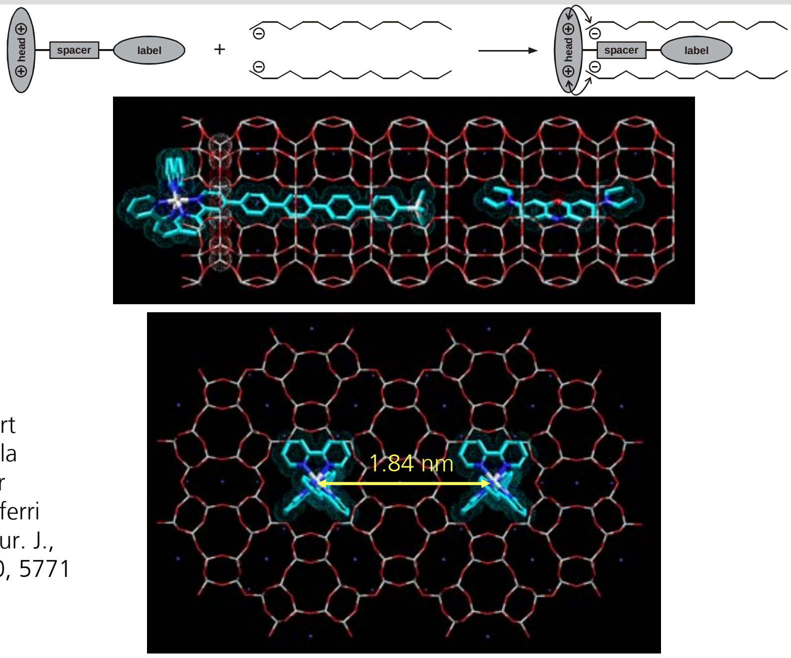
5 The stopcock principle: *Functional stopcocks*



Trapping Energy from and Injecting Energy into Dye-Zeolite Nanoantennae
H. Maas, G. Calzaferri, Angew. Chemie, Int. Ed. 2002, 41, 2284
Constructing dye-zeolite photonic nanodevices
Huub Maas and Gion Calzaferri, The Spectrum 16 (3) 2003, 18-24

21

5 The stopcock principle: *Functional stopcocks*



O. Bossart
L. De Cola
S. Welter
G. Calzaferri
Chem. Eur. J.,
2004, 10, 5771

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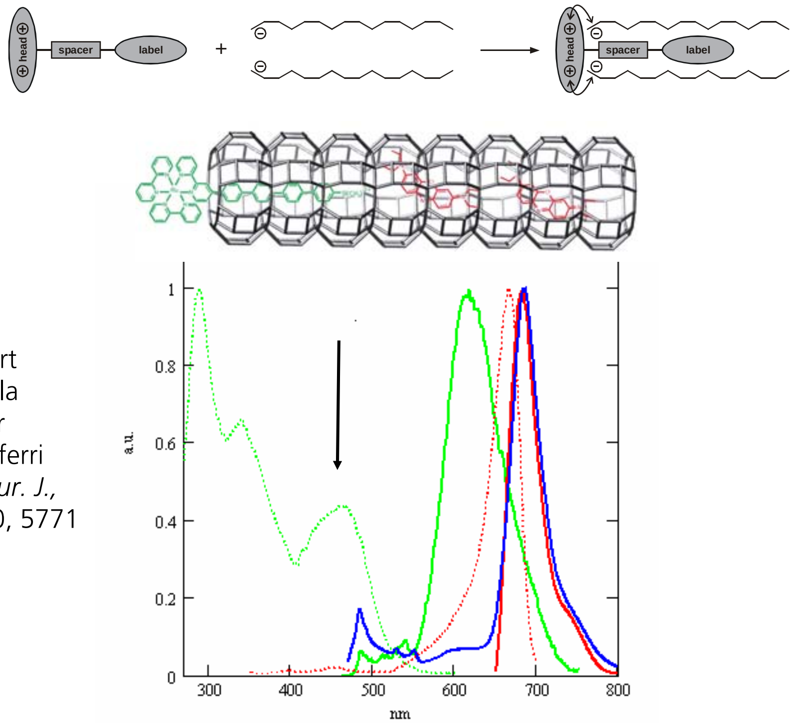

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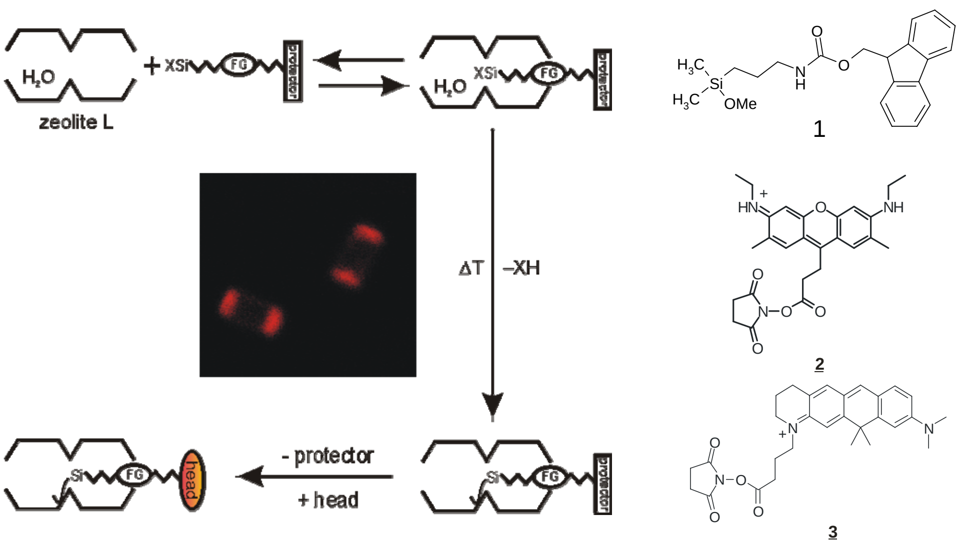
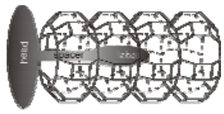
5 The stopcock principle

5 The stopcock principle: *Functional stopcocks*



Sequential Functionalization of the Channel Entrances of Zeolite L Crystals
S. Huber, G. Calzaferri, Angew. Chem. Int Ed. (2004)., 43, 6738

5 The stopcock principle
Functional stopcocks



The following types of stopcock-zolite L materials have been demonstrated by us:

I) <u>Reversible Stococks.</u> (Only weakly bound.)

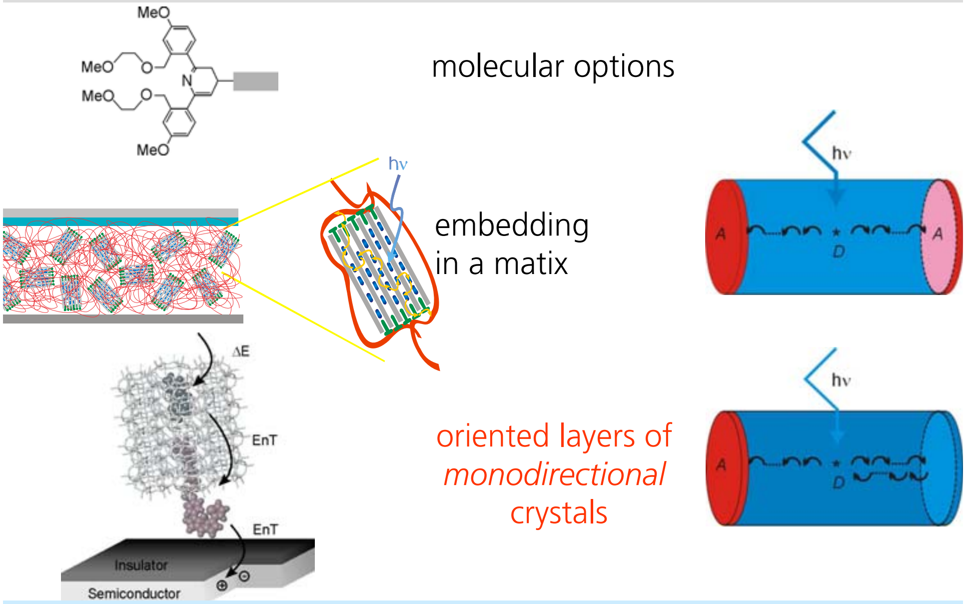
II) <u>Covalently bound stopcocks.</u> (Bonding via –Si-O-Si- and –Si-O-Al- .)

- **IIA) Covalently bound** (reaction via –Si(OR)$_3$ that cannot enter the channels)
- **IIB) Reaction of the stopcock inside of the channel**
- **IIC) Sequentielle functionalization.** ***This is a very flexible principle.***

III) <u>Electrostatically bound stopcocks.</u> We distinguish between two types:

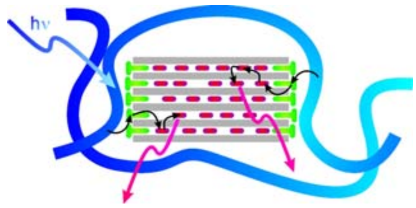
- **IIIA) Positively charged head.**
- **IIIB) positively charged tail.** The tail can bare one or more positive charges.

6 Coupling to an external device through a stopcock unit

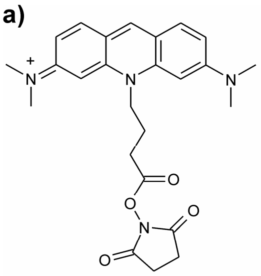


We have experimental evidence that these three principles work.
The next step is to test and optimize the materials for specific purposes.

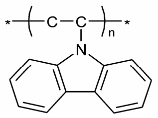
6 Coupling to an external device: EnT from polymer via stopcock to guest



a)

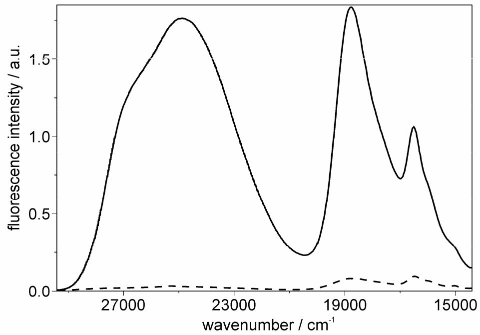


b)

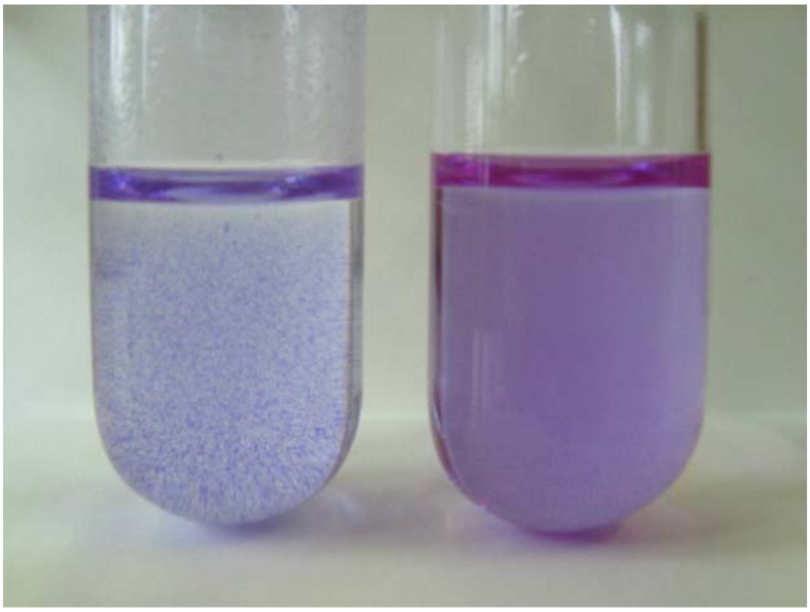


c)

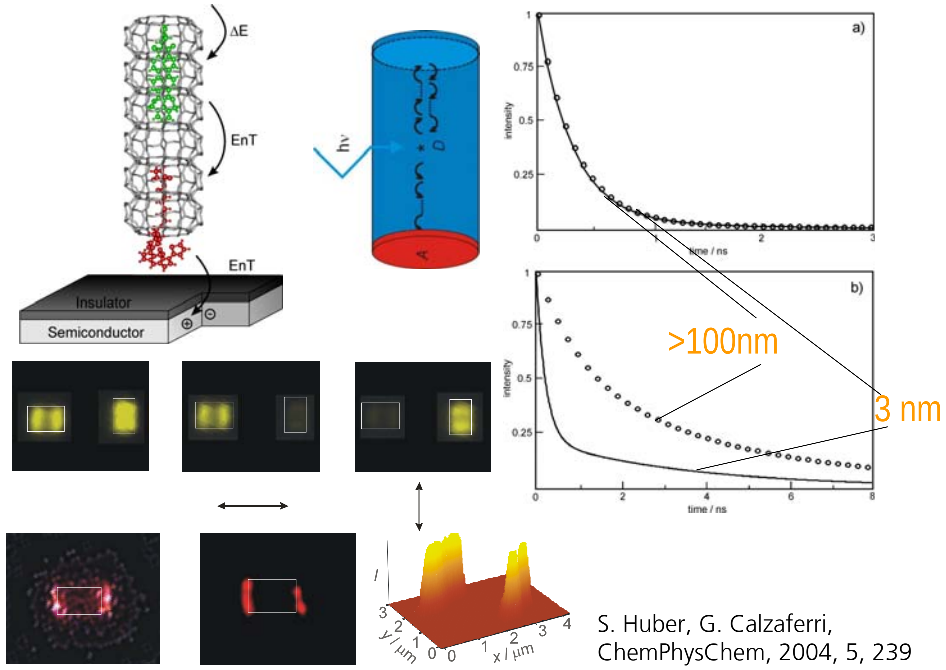
Constructing Dye-Zeolite Photonic Nanodevices
H. Maas, G. Calzaferri, The Spectrum, 16, 2003, 18



6 Functionalization of the external surface leads to solubilization

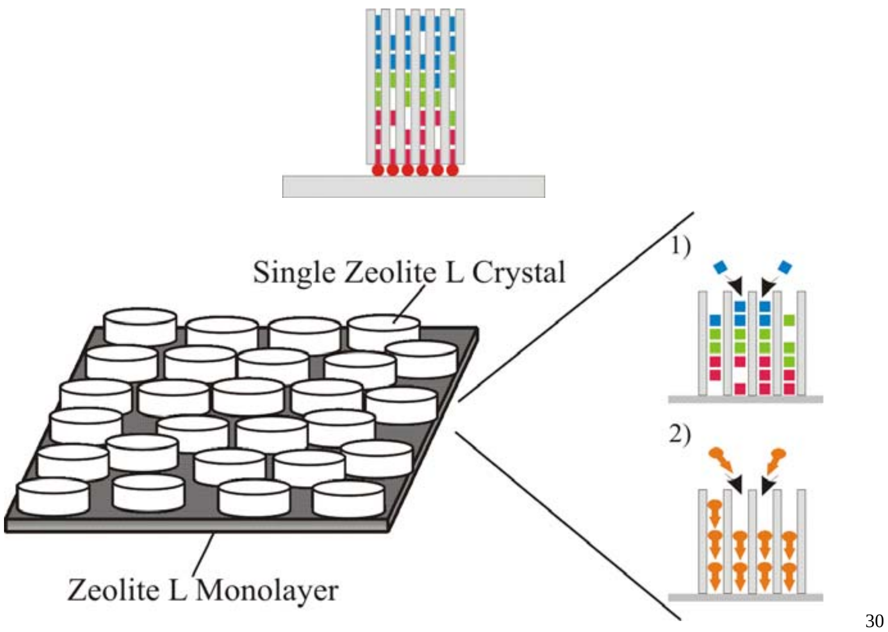


6 Coupling to an external device: EnT from an antenna via stopcock to a semiconductor



S. Huber, G. Calzaferri,
ChemPhysChem, 2004, 5, 239

7 Monodirectional materials



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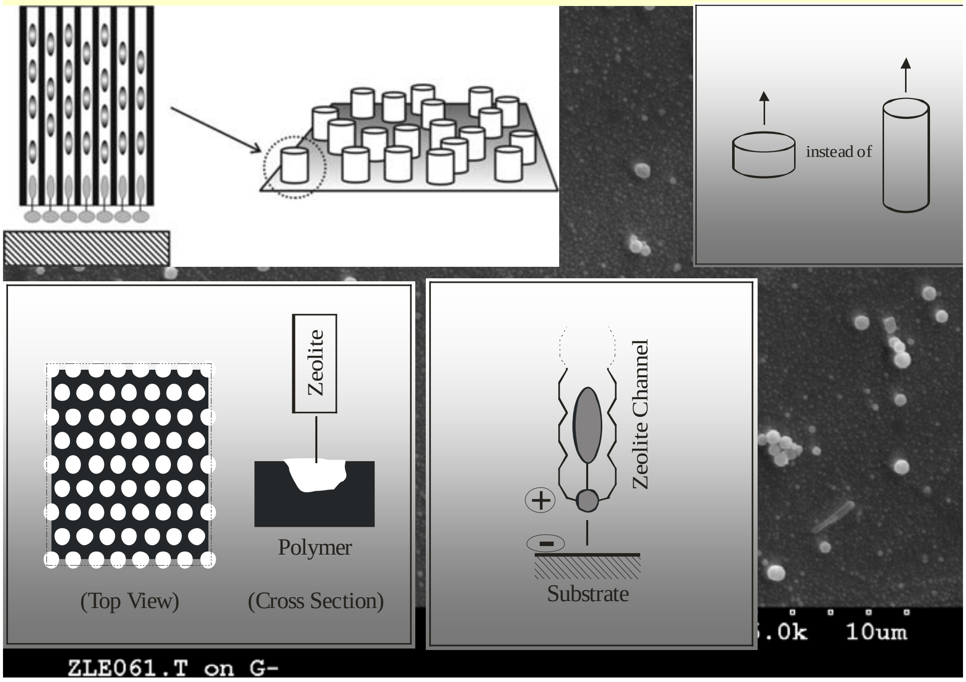
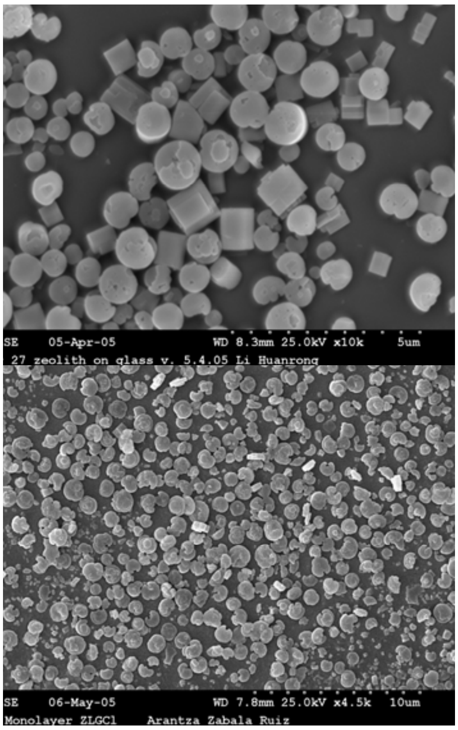
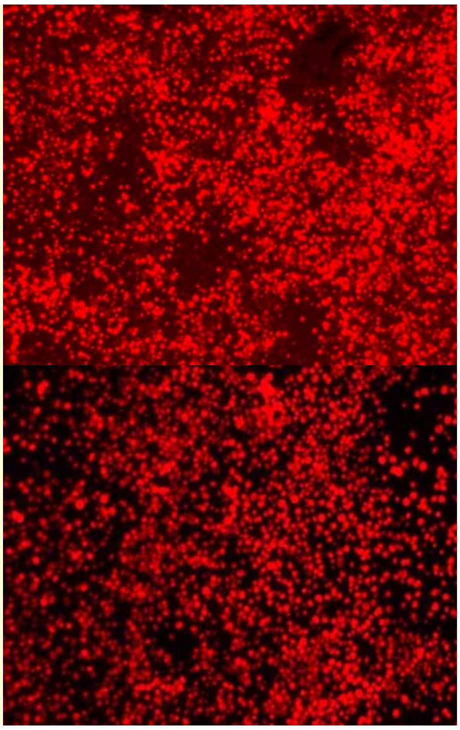
7 Monodirectional materials





7 Monodirectional materials

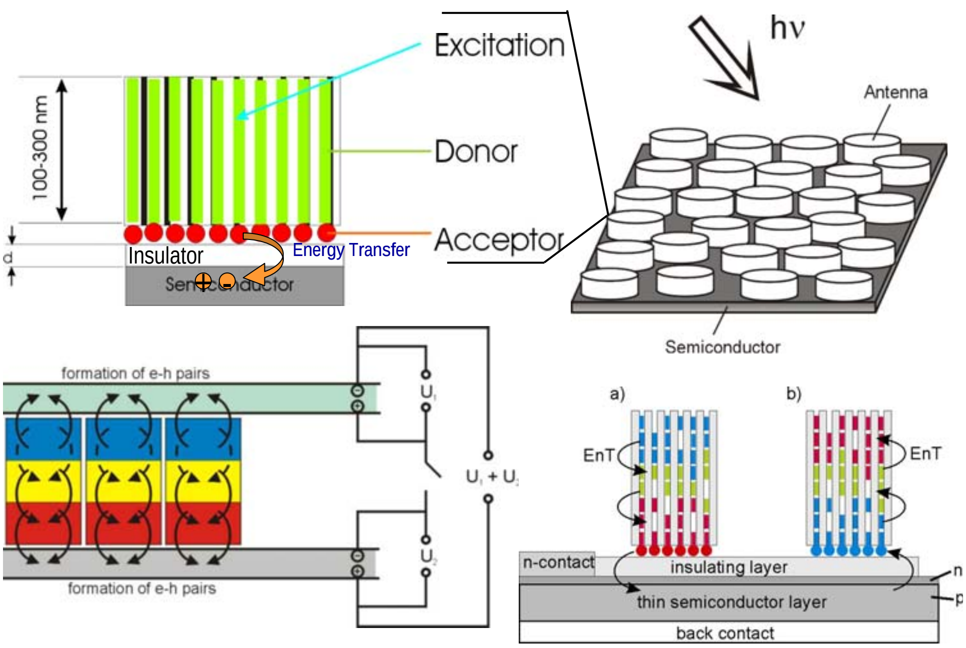


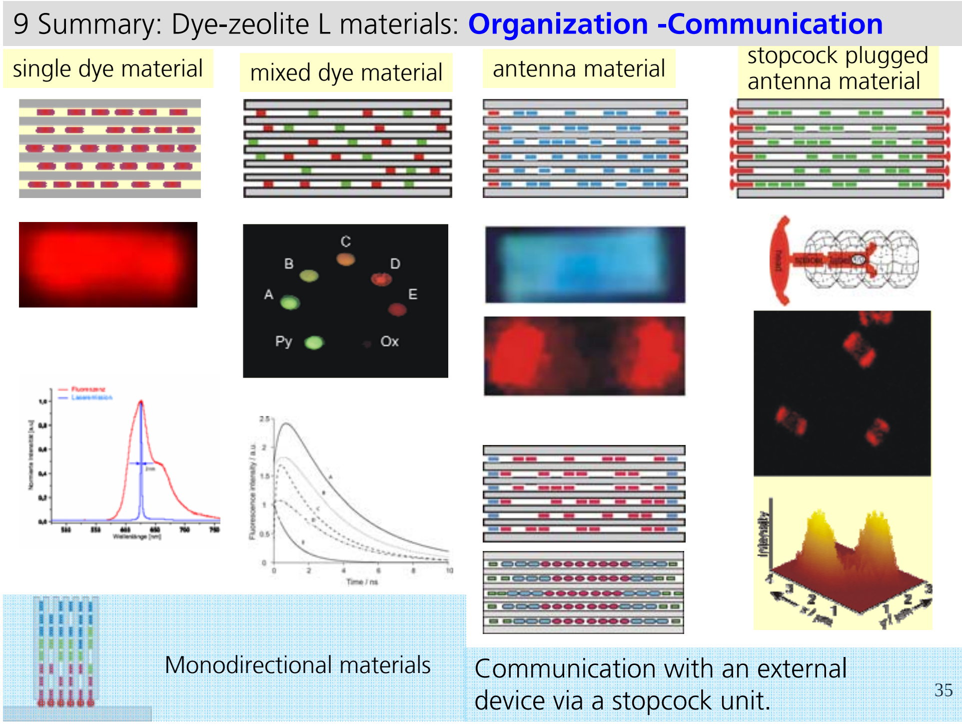
8 Challenges for developing new photonic devices for solar energy conversion

Antenna sensitized solar cells
sensitization via electronic excitation energy transfer

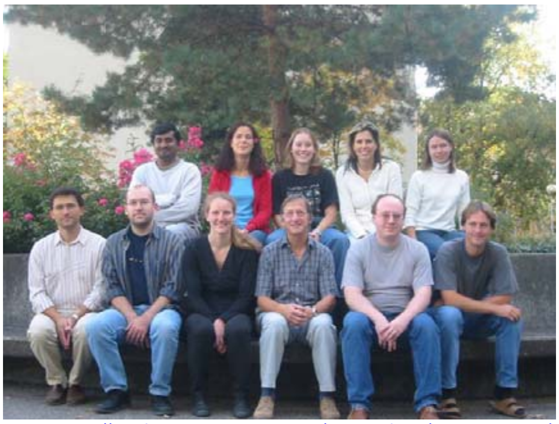
Sensitized thin film solid state solar cells	Sensitized plastic solar cells	Dye sensitized solar cells
embedding 30 nm crystals oriented layers of *monodirectional* ~200 nm crystals	sensitization of the polymer sensitization of e.g. the C_{60}, C_{70} unit Stability Spectral range Costs	oriented layers of *monodirectional* ~200 nm crystals Stability Spectral range Costs
	Redox systems based solar cells	

8 Antenna sensitized solar cells: Solid state thin film devices





I would like to thank all those who have contributed to make this research a success.



Dr. Rodrigo Queiroz de Albuquerque
Dr. Takayuki Ban,
Olivia Bossart,
Dr. André Devaux,
Dr. Stephan Glaus,
Katsiaryna Lutkouskaya,
Dr. Claudia Leiggener,
Dr. Huub Maas,
Dr. Silke Megelski,
Dr. Marc Pauchard,
Dr. Marieke van Veen,
Arantzazu Zabala Ruiz,
Dr. Dominik Brühwiler,
Dr. Antonio Currao,
Dr. Niklaus Gfeller,
Dr. Stefan Huber,
Dr. Abderrahim Khatyr,
Dr. Huanrong Li
Dr. Marc Meyer,
Claudia Minkowski,
Dr. Michel Pfenniger,
Dr. Mikalai Yastkou,
René Bühler

NRP 47: Energy collection, transport and trapping by supramolecular organization of dyes in hexagonal zeolite nanocrystals
BFE: Photochemische, Photoelektrochemische und Photovoltaische Umwandlung und Speicherung von Sonnenenergie
NF: Luminescent molecules and quantum dots in the cavities and channels of zeolites
EU: Nanochannel (European Union Research Training Network *Nanochannel*)
CLARIANT: Dye-loaded zeolite L materials
Fruitful collaboration with scientists in Belarus, Belgium, France, Germany, Italy, Japan, Netherlands, and Switzerland is acknowledged.

Light-harvesting host-guest antenna materials for quantum solar energy conversion devices

Gion Calzaferri
Department of Chemistry and Biochemistry, University of Bern, CH-3012 Bern
gion.calzaferri@iac.unibe.ch

In natural photosynthesis, light is absorbed by photonic antenna systems consisting of a few hundred chlorophyll molecules. These devices allow fast energy transfer from an electronically excited molecule to an unexcited neighbour molecule in such a way that the excitation energy reaches the reaction centre with high probability. Trapping occurs there. The anisotropic arrangement of the chlorophyll molecules is important for efficient energy migration. In natural antennae the formation of aggregates is prevented by fencing the chlorophyll molecules in polypeptide cages. A similar approach is possible by enclosing dyes inside a microporous material and by choosing conditions such that the cavities are able to uptake only monomers but not aggregates. In most of our experiments we have been using zeolite L as a host because it was found to be very versatile. Its crystals consist of an extended one-dimensional tube system and can be prepared in wide size range. We have filled the individual tubes with successive chains of different dye molecules and we have shown that photonic antenna materials can be prepared, not only for light harvesting within the volume, but also for radiationless transport of electronic excitation energy to a target molecule fixed at the ends of the nanochannels as well as with an injector molecule fixed at their „entrances". The molecule which has been excited by absorbing an incident photon transfers its electronic excitation to another one. After a series of such steps the electronic excitation reaches a luminescent trap. The energy migration is in competition with spontaneous emission, radiationless decay, quenching, and photochemically induced degradation. Fast energy migration is therefore crucial if a trap should be reached before other processes can take place. - The supramolecular organization of the dyes inside the channels is a *first stage of organization*. It allows light harvesting within a certain volume of a dye-loaded nano-crystalline zeolite and radiationless transport to both ends of the cylinder or from the ends to the centre. The *second stage of organization* is the coupling to an external acceptor or donor stopcock fluorophore at the ends of the zeolite L channels, which can trap or inject electronic excitation energy. The *third stage of organization* is the coupling to an external device via a stopcock intermediate. The wide-ranging tunability of these highly organized materials offers fascinating new possibilities for exploring excitation energy transfer phenomena, and challenges for developing new photonic devices for solar energy conversion and storage.

Details can be found in the publications 1-28.

37

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