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

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

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.

## 1. Introduction

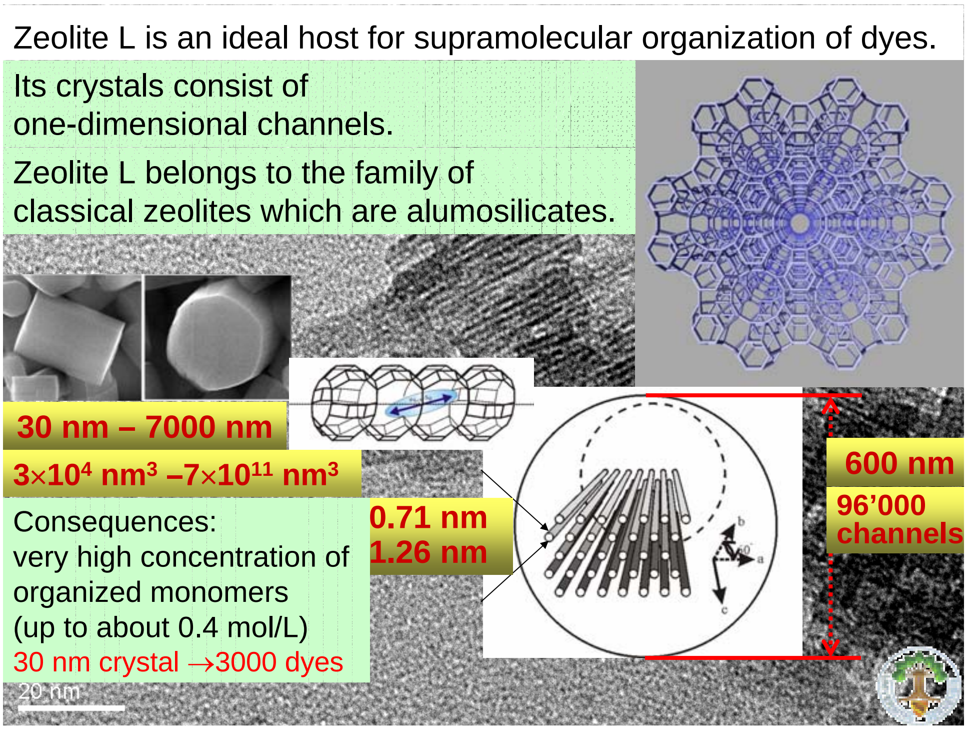
- Zeolite L, an ideal host for supramolecular organization of dyes
- Filling the channels with dye molecules
- Some dyes which have been inserted in zeolite L
- Orientation of the dyes in the channels
- Dye loaded zeolite L crystals as nanolasers?
- Radiationless transfer of electronic excitation energy
- Förster energy transfer, a demonstration experiment
- Intrazeolite diffusion kinetics monitored by energy transfer

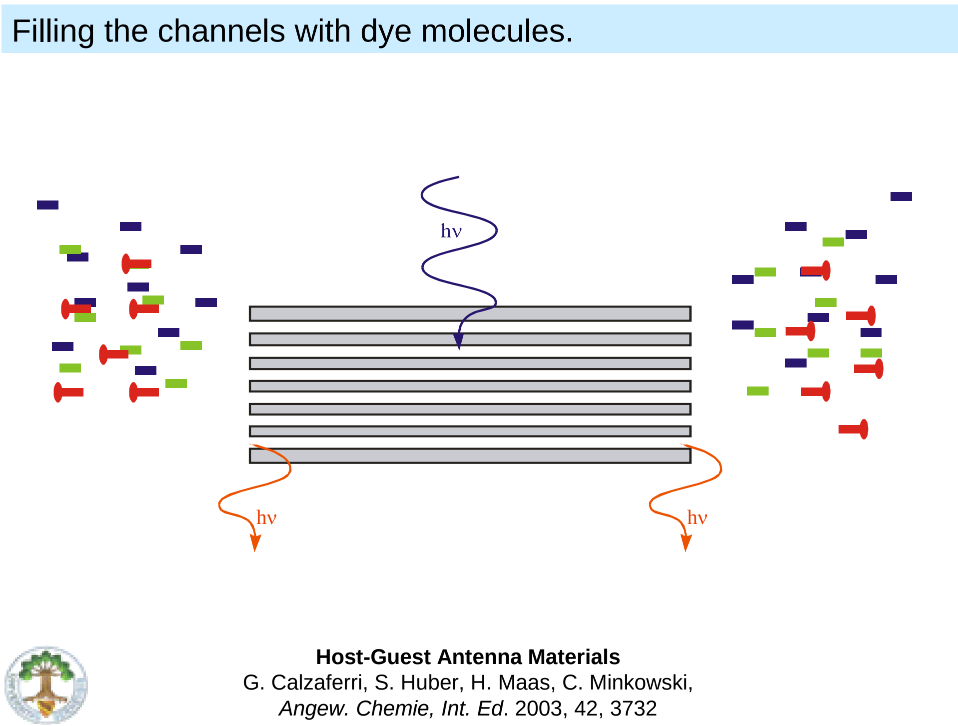
## 2. Light-harvesting host-guest antenna materials

**Three stages of organization**

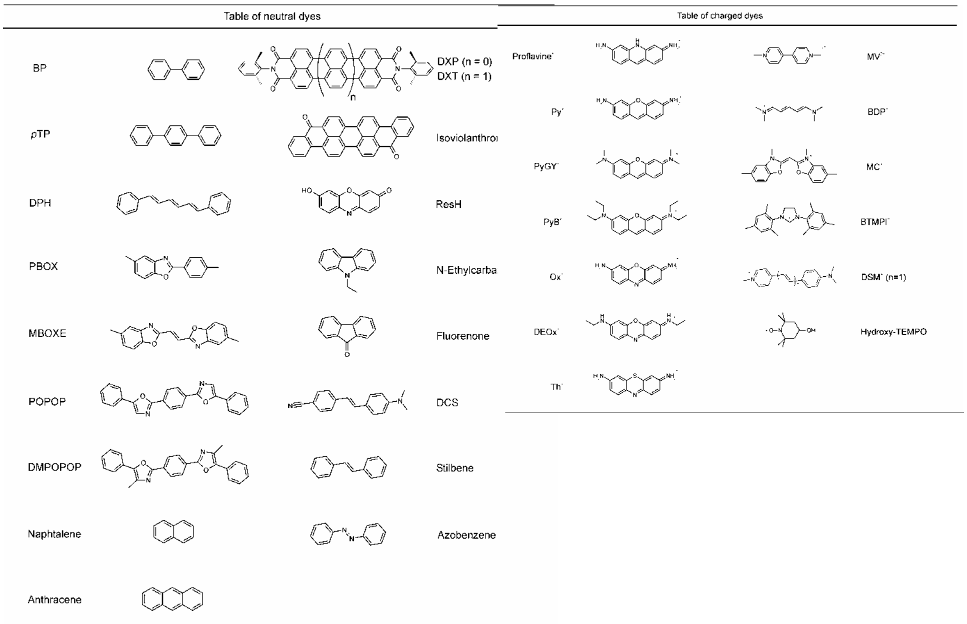
- Electronic excitation energy migration
- One dimensional energy transfer; phase boundary
- External trapping (The stopcock principle)
- Coupling to an external device
- Monodirectional materials

## 3. Challenges for developing antenna sensitized devices for solar energy conversion and LED's

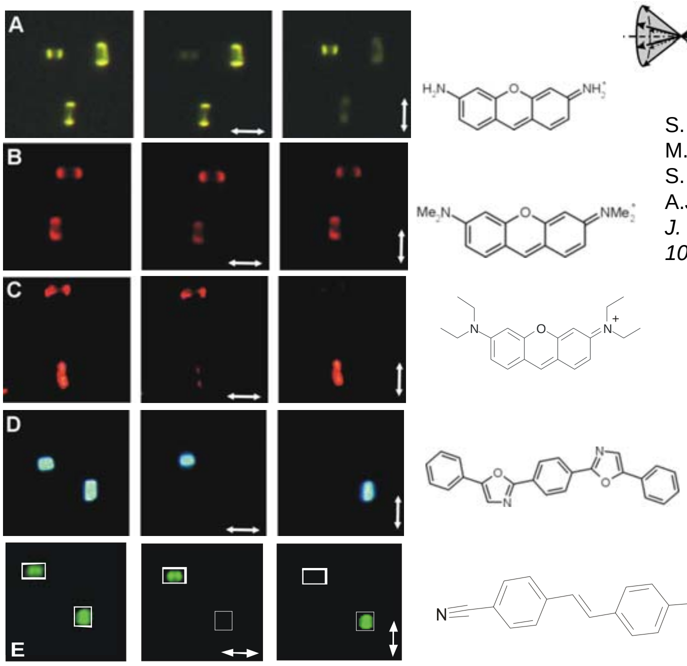

Zeolite L is an ideal host for supramolecular organization of dyes.
Its crystals consist of one-dimensional channels.
Zeolite L belongs to the family of classical zeolites which are alumosilicates.
30 nm – 7000 nm
3×10⁴ nm³ –7×10¹¹ nm³
Consequences:
very high concentration of organized monomers
(up to about 0.4 mol/L)
30 nm crystal →3000 dyes
0.71 nm
1.26 nm
600 nm
96’000 channels
20 nm

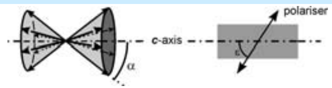

Filling the channels with dye molecules.
hν
hν
hν
Host-Guest Antenna Materials
G. Calzaferri, S. Huber, H. Maas, C. Minkowski,
Angew. Chemie, Int. Ed. 2003, 42, 3732

## Some dyes which have been inserted in zeolite L




## Orientation of the dyes in the channels

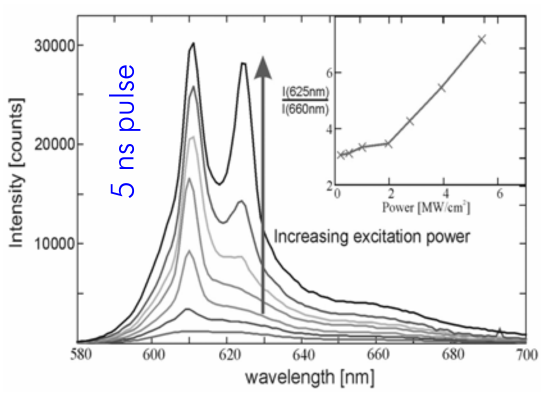


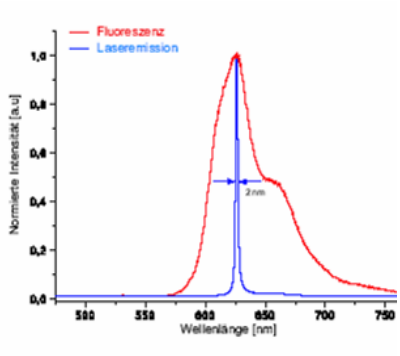




S. Megelski, A. Lieb,
M. Pauchard, A. Drechsler,
S. Glaus, Ch. Debus,
A.J. Meixner, G. Calzaferri
*J. Phys. Chem. B*
*105*, 2001, 25

S. Brasselet
ENS Cachan

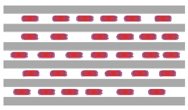
## Dye loaded zeolite L crystals as nanolasers?

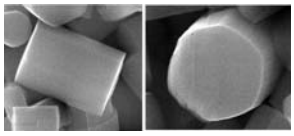


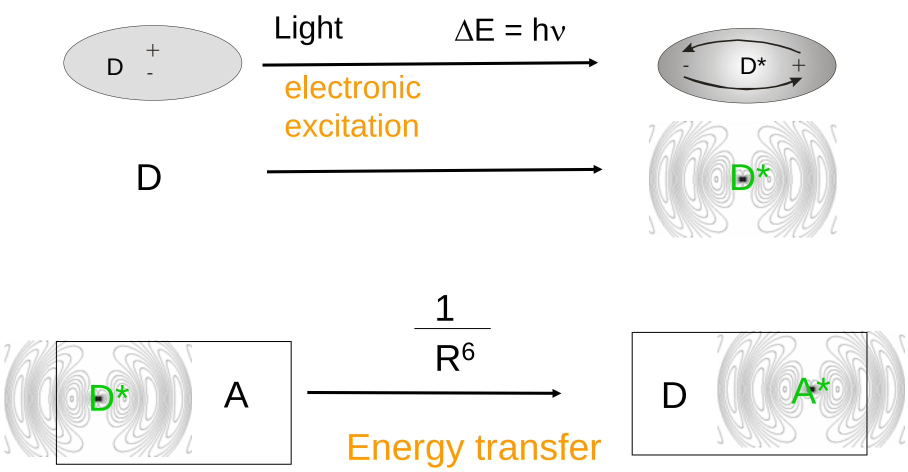

Prof. Franco Laeri 2003
with samples from us

Calzaferri, Leiggener, Huber, Brühwiler, Zabala Ruiz
Proceedings European Coatings Conference,
Smart Coatings III, Berlin, June 7-8, **2004**, 93-109

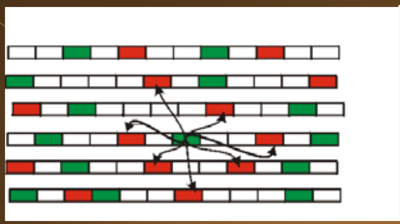




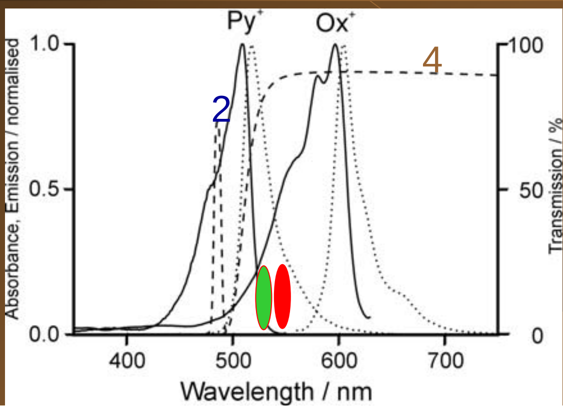
## Radiationless transfer of electronic excitation energy
## Förster energy transfer

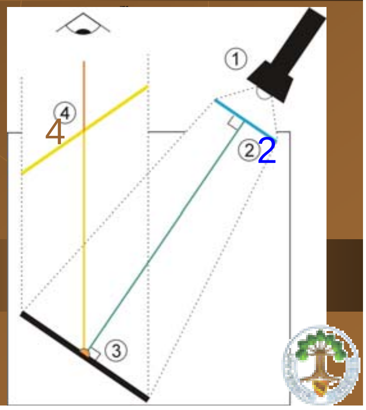


## Förster energy transfer, a demonstration experiment

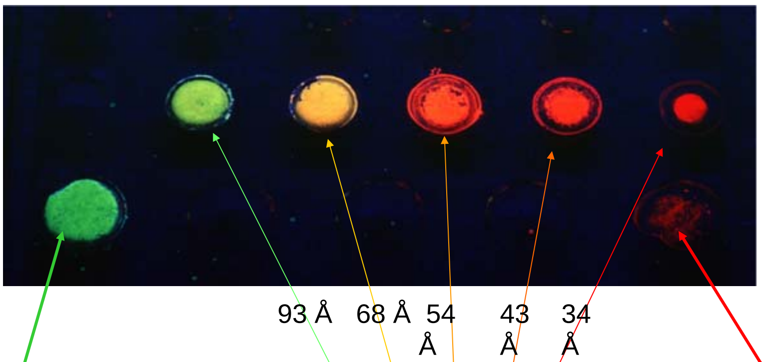


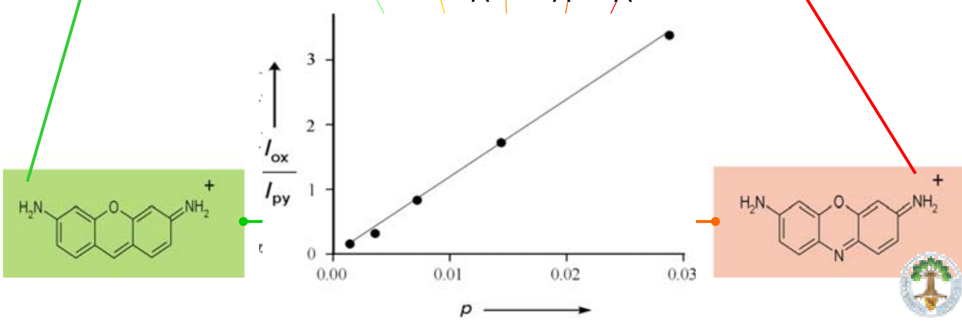
$$\frac{\kappa^2}{R^6}\cdot J$$



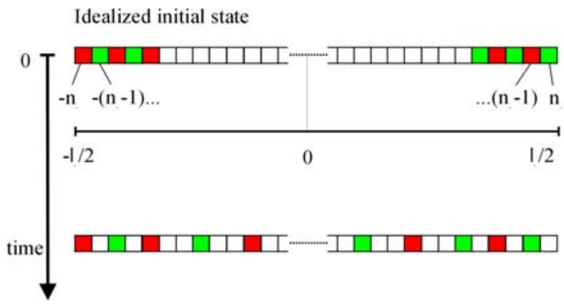




## Förster energy transfer, a demonstration experiment



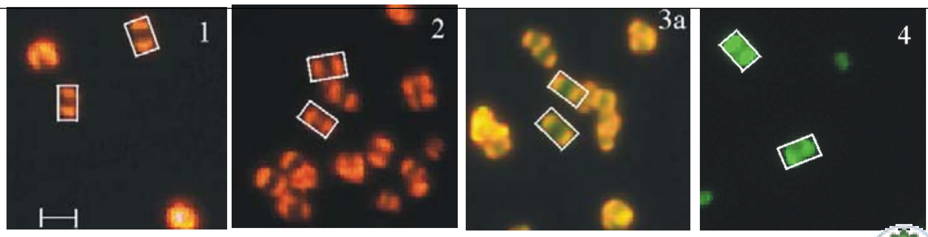



## Intrazeolite diffusion kinetics monitored by energy transfer




$$\frac{I_F^A}{I_F^D}(t) = C\frac{(p^0)^2}{\sqrt{8\pi}}\frac{1}{\sqrt{Dt}}$$

$D_{85\,°C} \sim 10^{-15}\ cm^2s^{-1}$




M. Pfenniger, G. Calzaferri, *CHEMPHYSCHEM* 2000, (4) 211

## 2. Light-harvesting host-guest antenna materials: organization

Inorganic-inorganic host-guest systems
with ordered guest are known.
The order is imposed by the host.

Can these systems also be regarded as being *organized*?

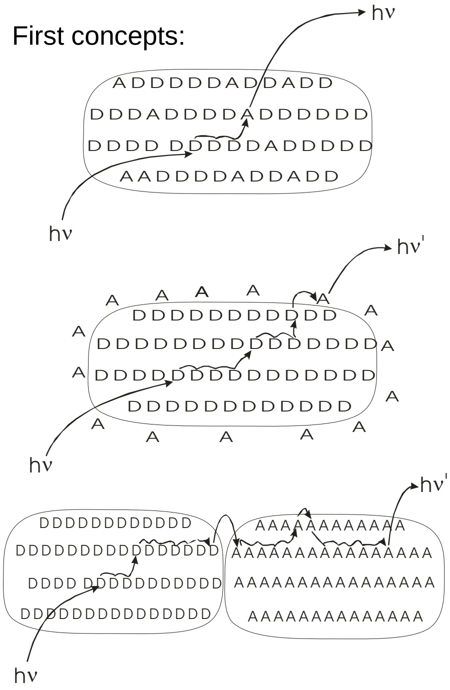
*Organization* implies transfer of a signal in a specific way
to a specific place.

### Question

Is it possible to address the ordering in zeolite based host-guest systems on a molecular level in order to realize *organization*
and, if yes,
how can this be achieved?

I discuss this question for inorganic-organic host-guest systems where the host is zeolite L.

First concepts:

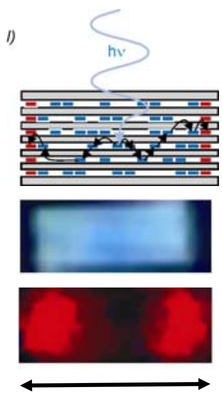



The early concept we developed to make use of the possibilities of zeolite-dye host-guest materials are illustrated in this figure. It was presented as a poster at IPS-10, 1994 in Interlaken, Switzerland, and is still valid and useful for some experiments and practical applications.

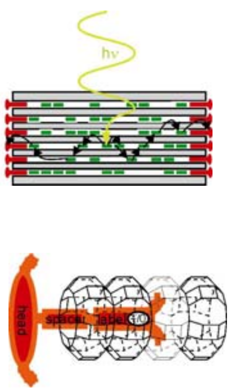
We have, however, learned to use the specific structure of the materials in a more sophisticated and challenging way in order to reach a much higher stage of organization than possible by this early concept.

F. Binder, G. Calzaferri, N. Gfeller, Solar Energy and Solar Cells, 38 (1995) 175

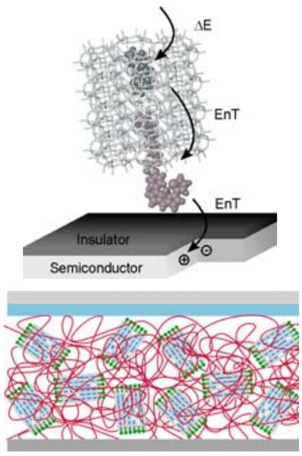
## Light-harvesting host-guest antenna materials:
## Three stages of organization



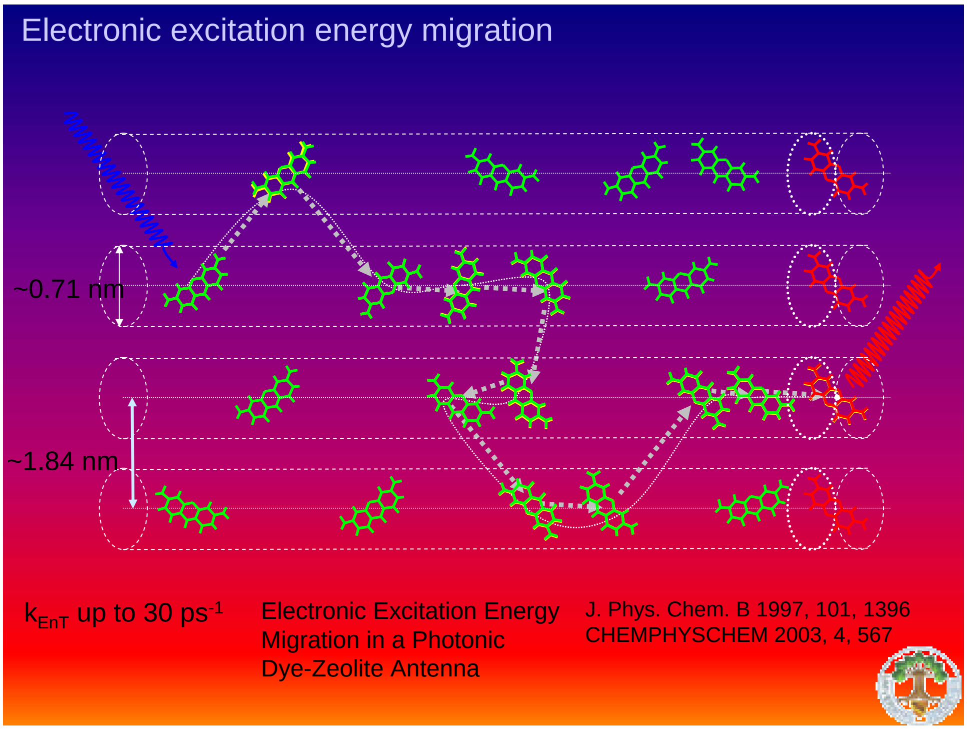

*Supramolecular organization of molecules inside the channels.*

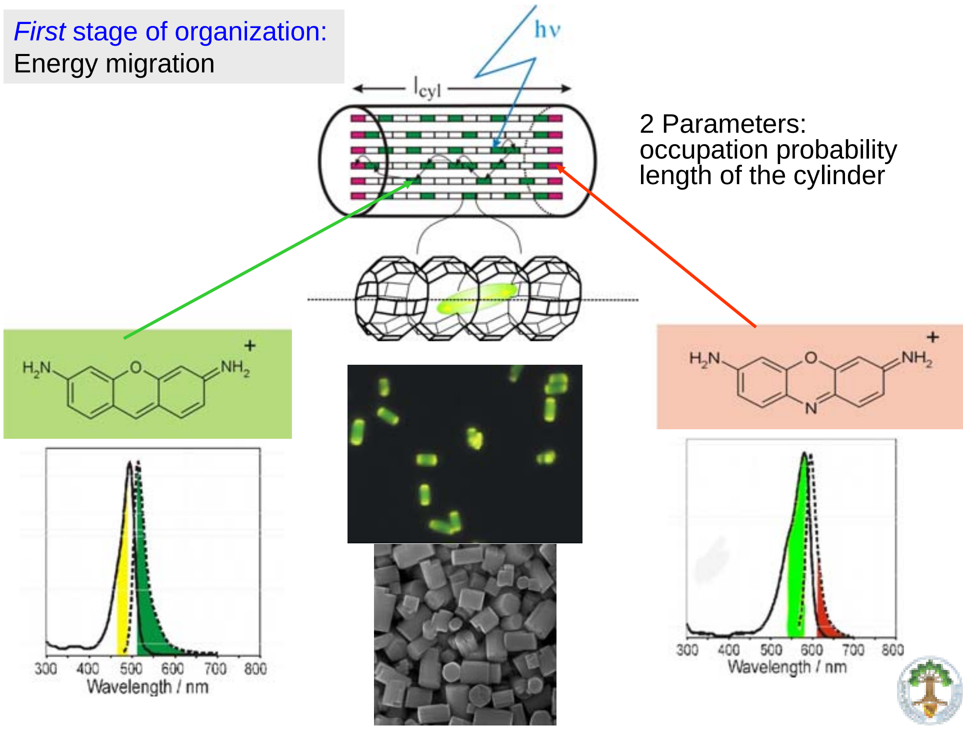



*Coupling to an external acceptor- or donor preferably a stopcock.*

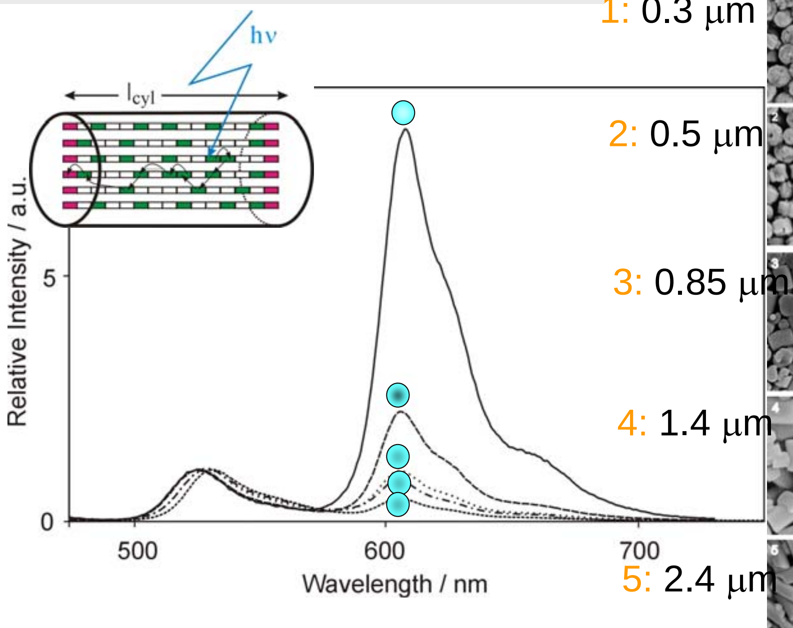


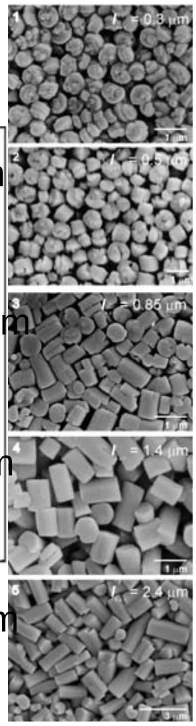

*Coupling to an external device preferably through a stopcock unit.*


Electronic excitation energy migration
~0.71 nm
~1.84 nm
$k_{EnT}$ up to 30 $ps^{-1}$
Electronic Excitation Energy
Migration in a Photonic
Dye-Zeolite Antenna
J. Phys. Chem. B 1997, 101, 1396
CHEMPHYSCHEM 2003, 4, 567


*First* stage of organization:
Energy migration
hν
$l_{cyl}$
2 Parameters:
occupation probability
length of the cylinder
$H_2N$
O
$NH_2$
+
300 400 500 600 700 800
Wavelength / nm
$H_2N$
O
N
$NH_2$
+
300 400 500 600 700 800
Wavelength / nm

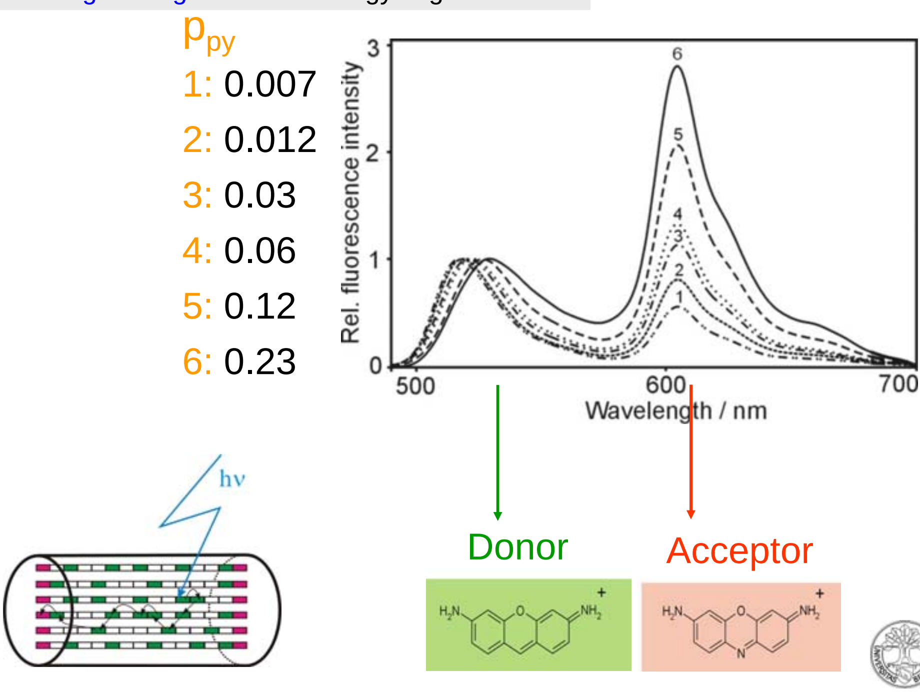
*First* stage of organization: Energy migration



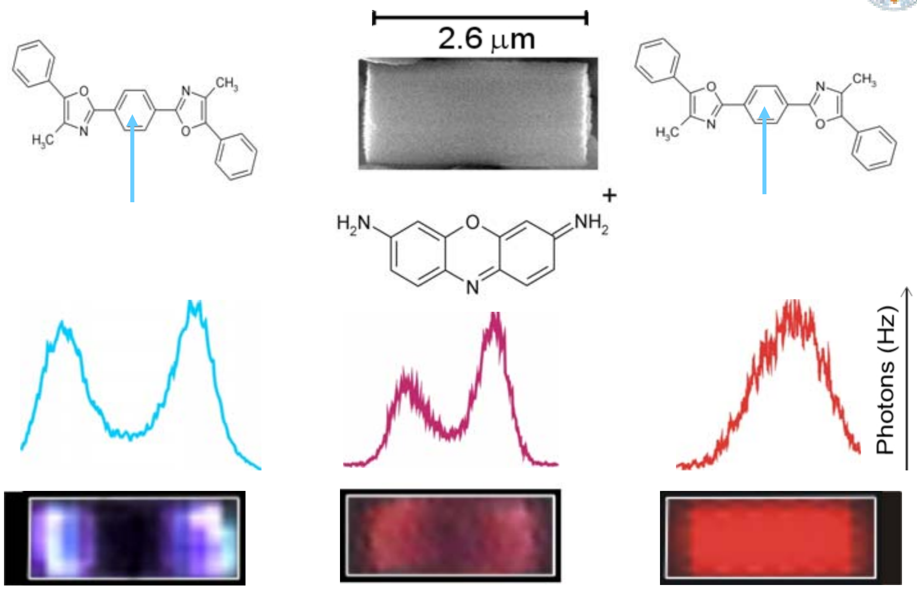



S. Megelski and G. Calzaferri, *Adv. Funct. Mater.*, 2001, 11, 277

*First* stage of organization: Energy migration

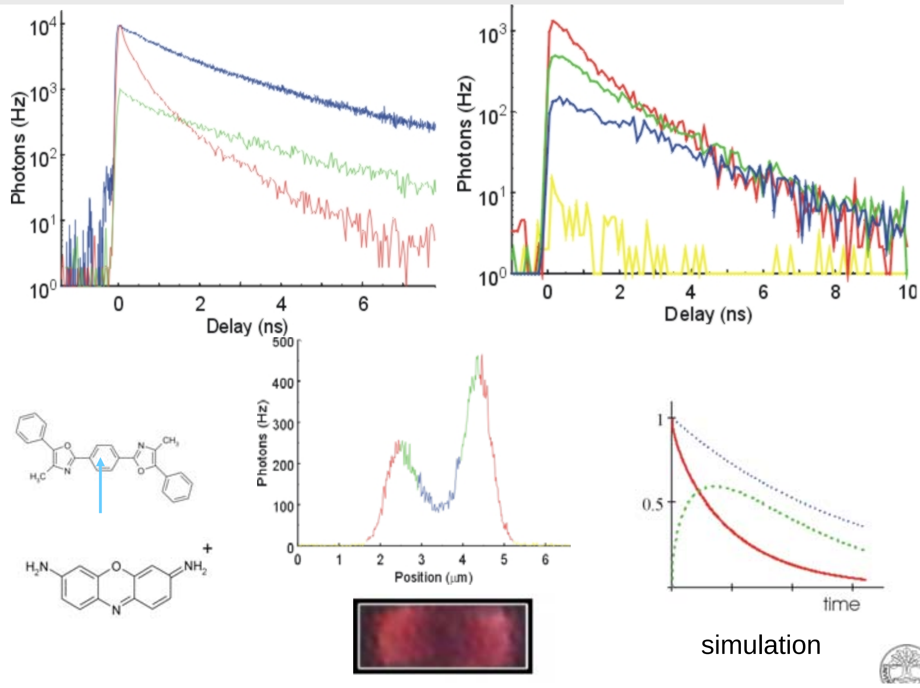


*First* stage of organization: Mechanism of the Energy Migration

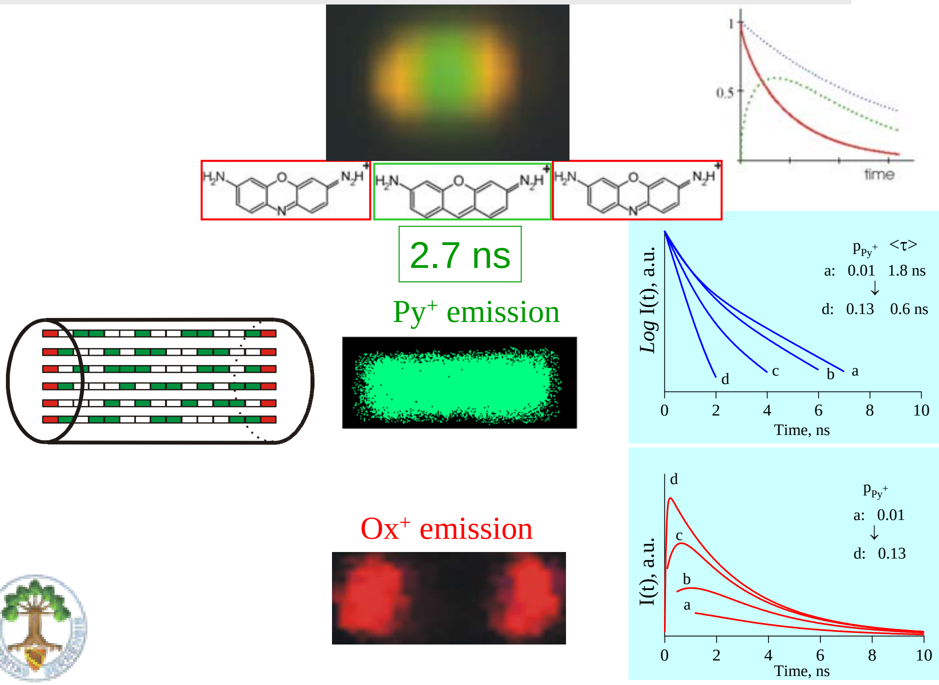



M. Pauchard, **S. Huber**, R. Méallet, H. Maas, R. Pansu,G. Calzaferri, Angew. Chem. Int. Ed. 40 (2001) 2839

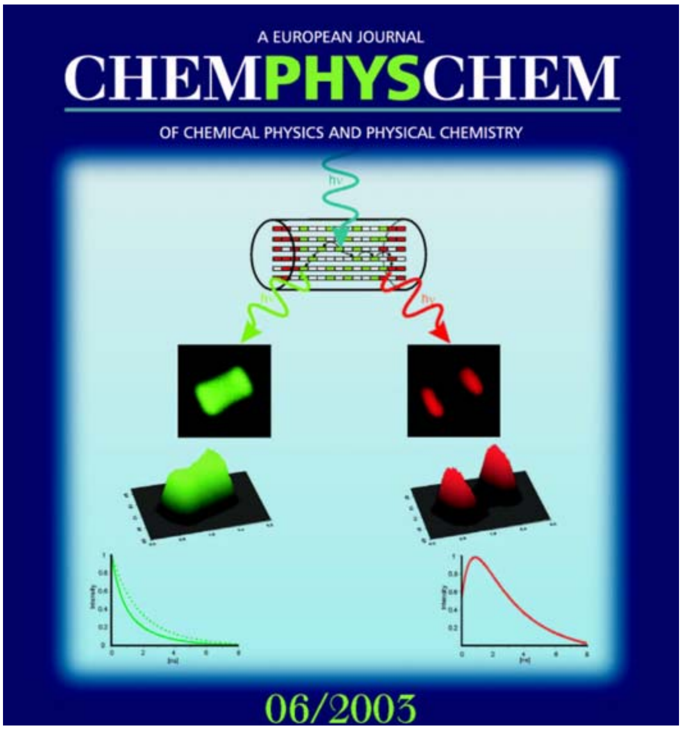
*First* stage of organization: Mechanism of the Energy Migration



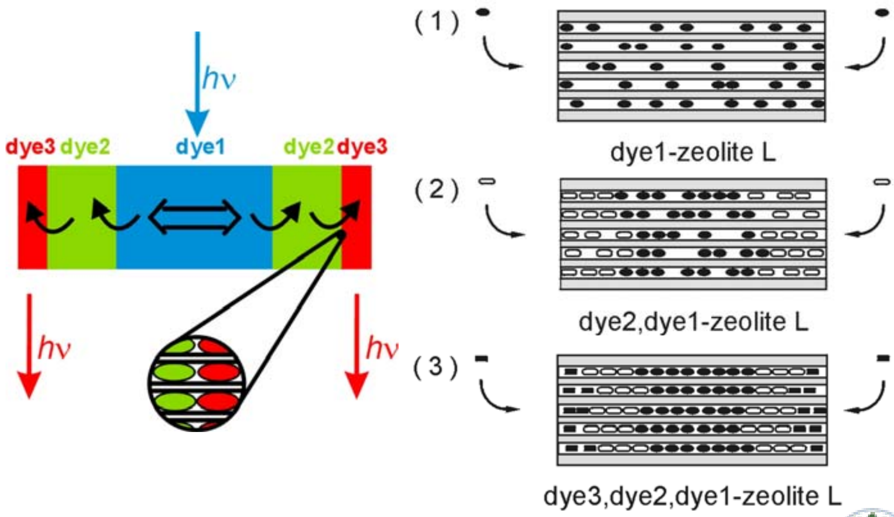
*First* stage of organization: Mechanism of the Energy Migration



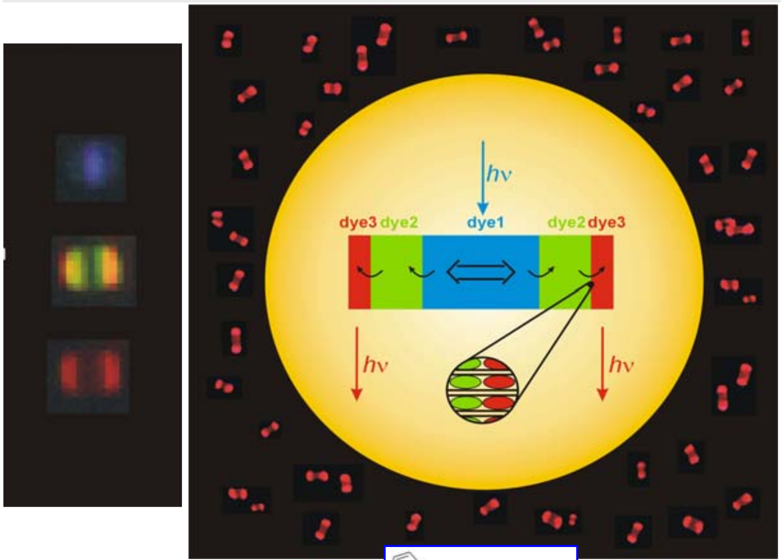

First stage of organization: Mechanism of the Energy Migration



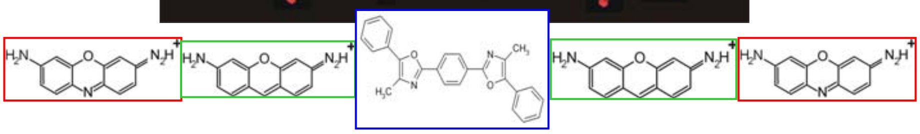
First stage of organization



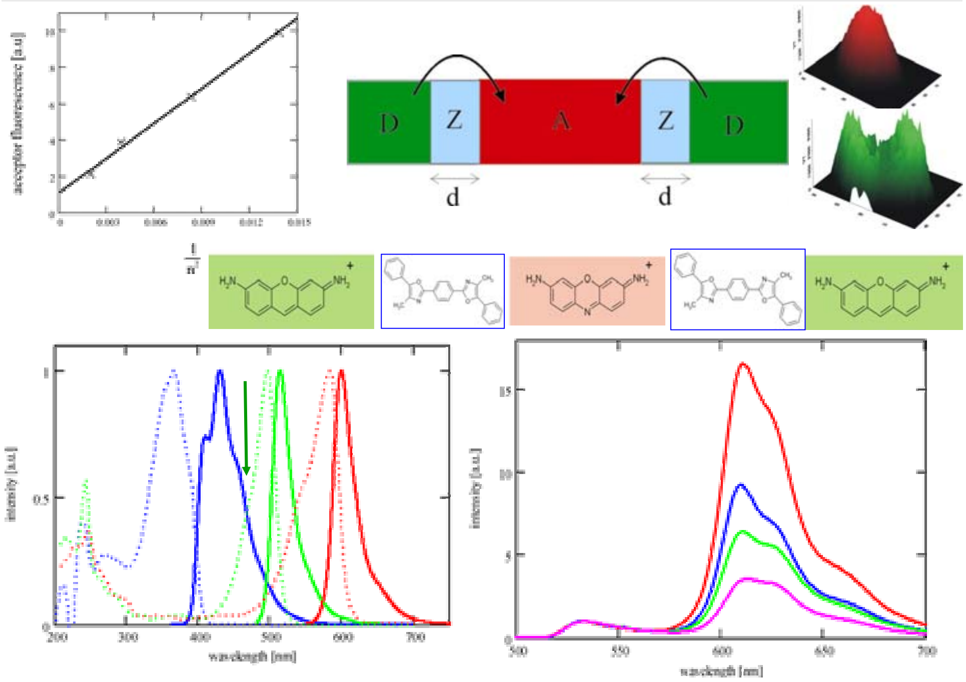

**Dye-Loaded Zeolite L Sandwiches as Artificial Antenna Systems for Light Transport**

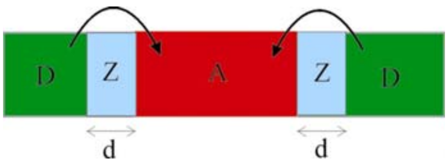



M. Pauchard,
A. Devaux,
G. Calzaferri
*Chem. Eur. J.*
2000, *6*, 3456

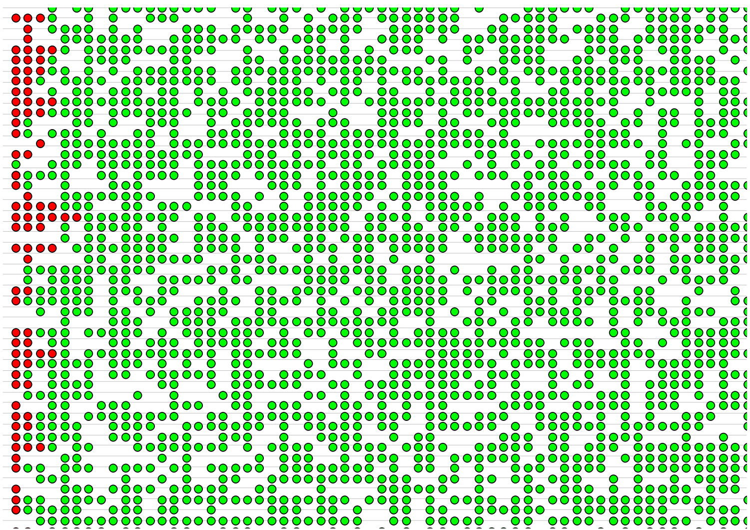


First stage of organization: One dimensional energy migration



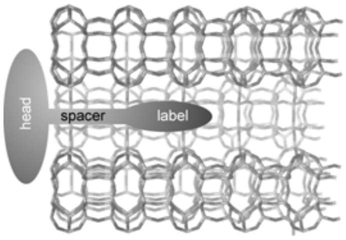



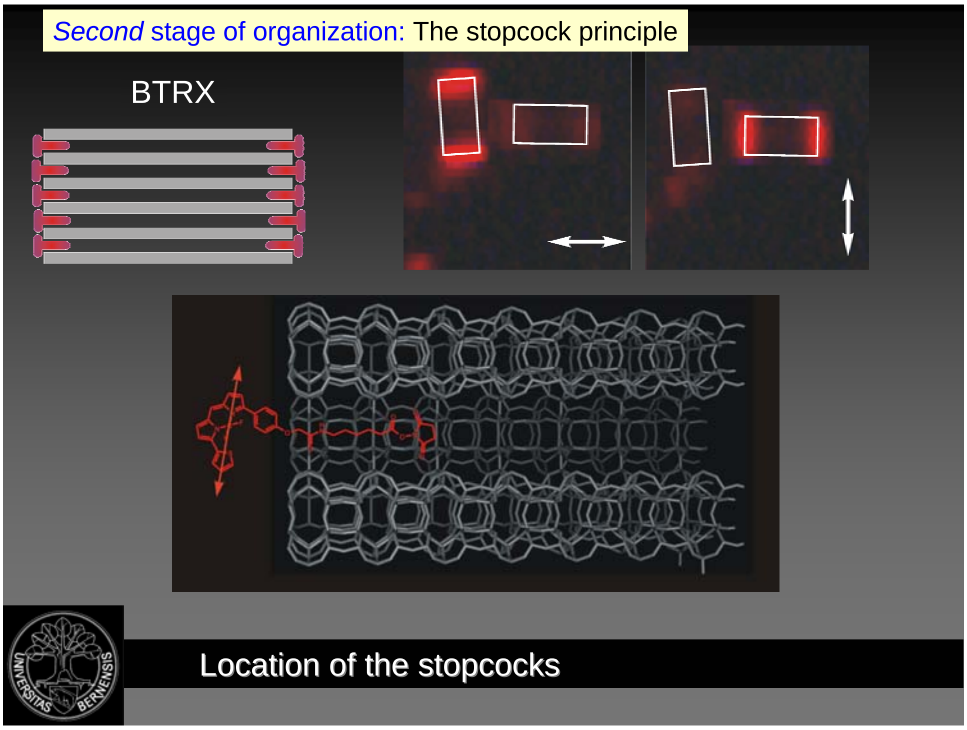

First stage of organization:
Phase boundary



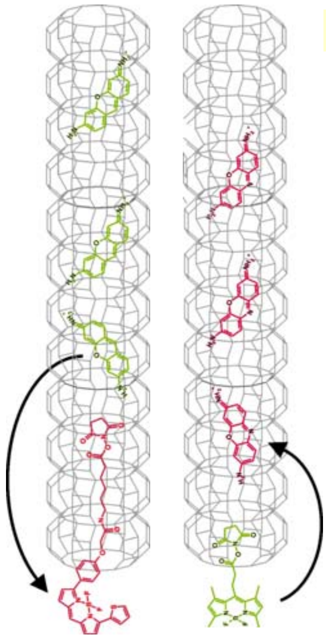
## The stopcock principle

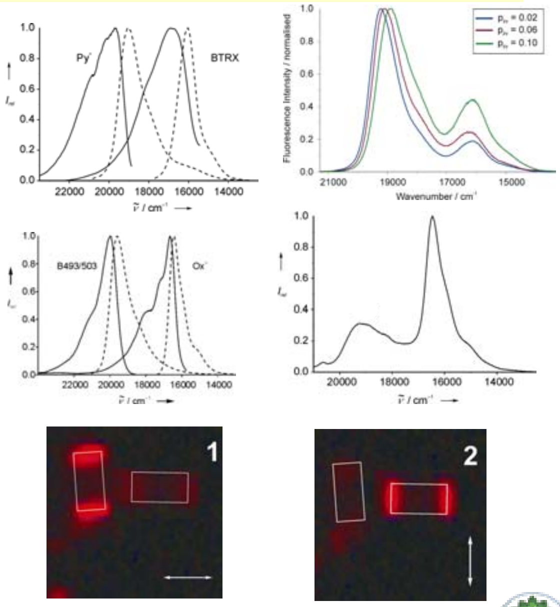
### *Functional stopcocks*



## The stopcock principle: First important success

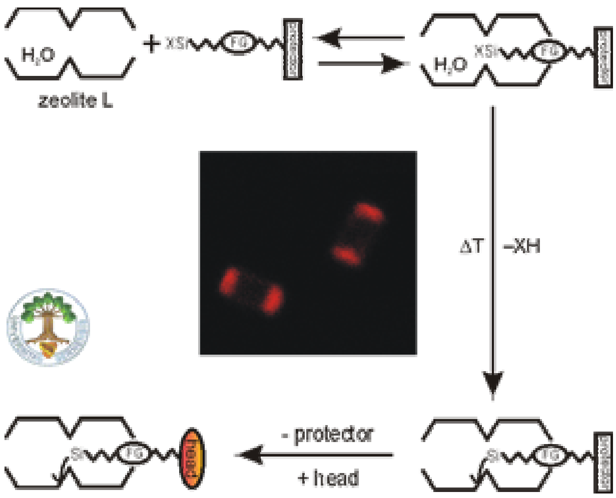


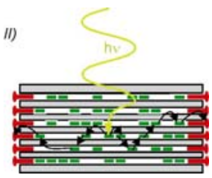


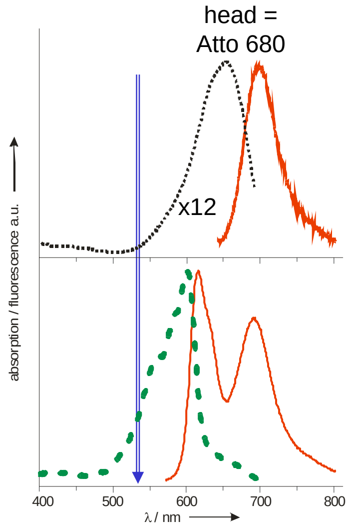

Huub Maas, Gion Calzaferri *Angew. Chem. Int. Ed. 41*, 2002, 2839
Abderrahim Khatyr, Huub Maas, Gion Calzaferri *JOC. 67*, 2002, 7605

## The stopcock principle, a general reaction principle

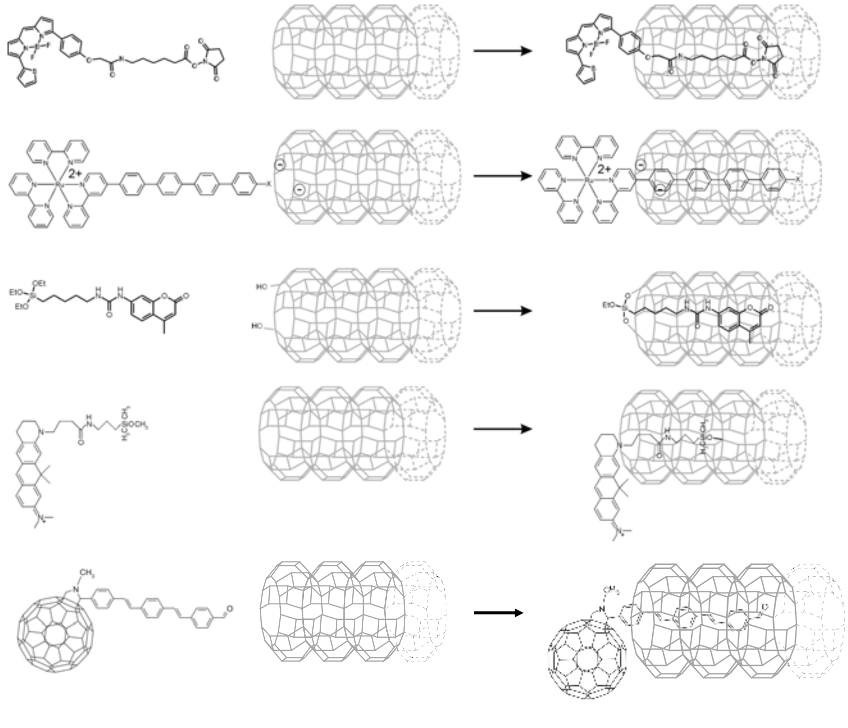
Sequential Functionalization of the Channel Entrances of Zeolite L Crystals
*Stefan Huber and Gion Calzaferri*
*Angew. Chemie, 2004, in press*



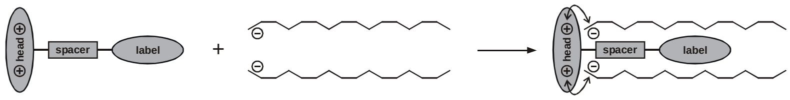



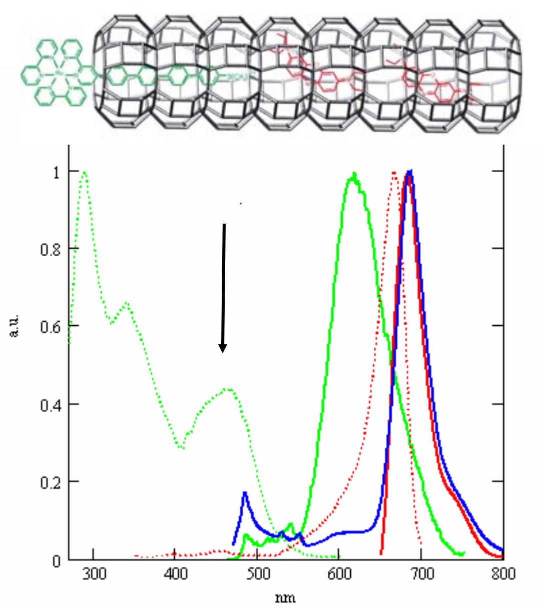



The stopcock principle



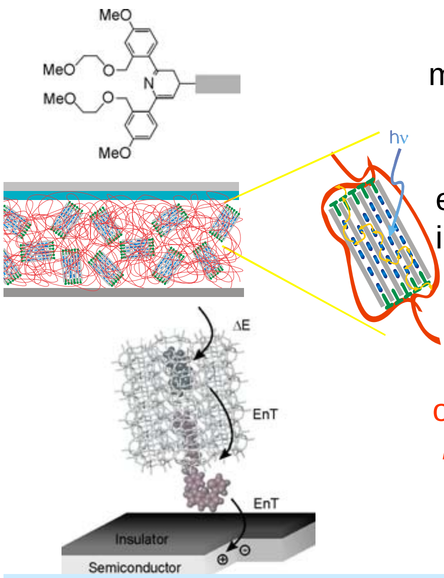
The stopcock principle




Olivia Bossart
Luisa De Cola
Steve Welter
Gion Calzaferri
*Chem.Eur.J.* 2004, *10*,…

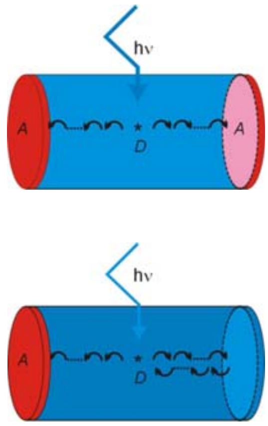
Third stage of organization: Coupling to an external device through a stopcock unit




molecular options

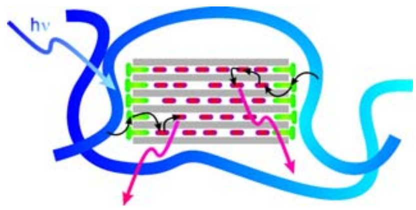
embedding
in a matix

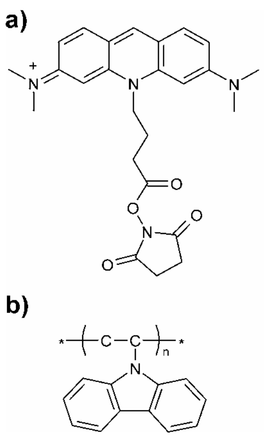
oriented layers of
*monodirectional*
crystals



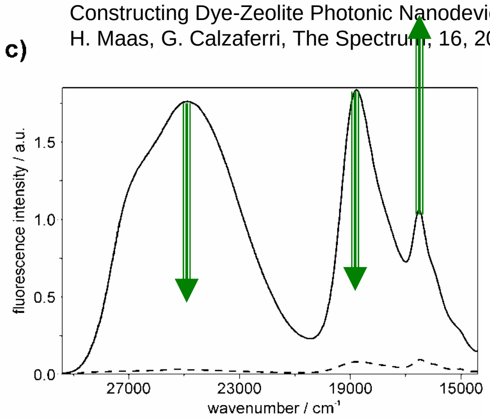

We have experimental evidence that these three principles work.
The next step is to test and optimize the materials for specific devices.

Third stage of organization: EnT from polymer via stopcock to guest

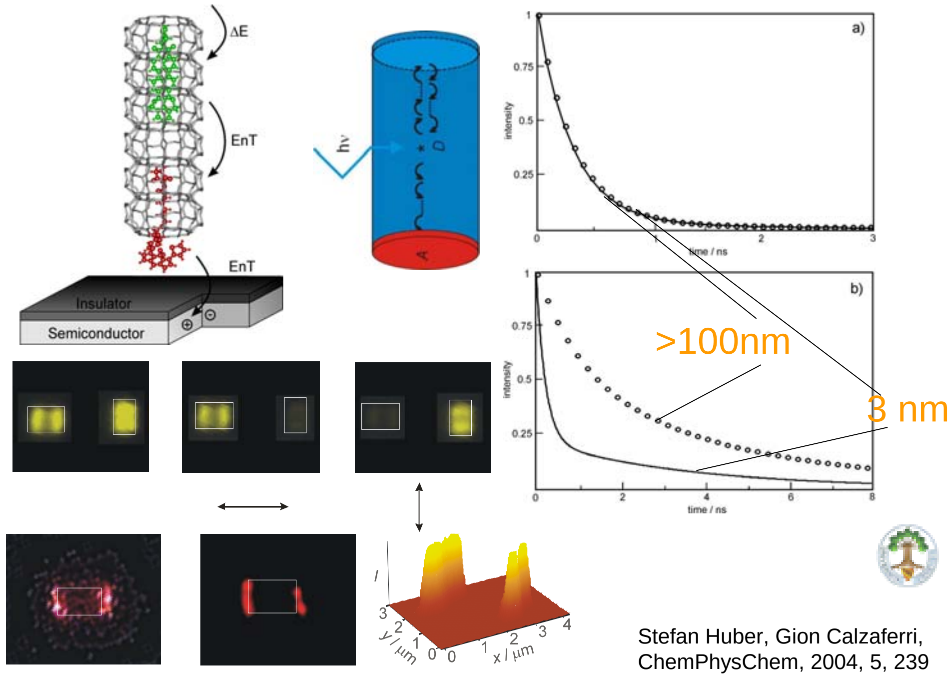



Constructing Dye-Zeolite Photonic Nanodevices
H. Maas, G. Calzaferri, The Spectrum, 16, 2003, 18

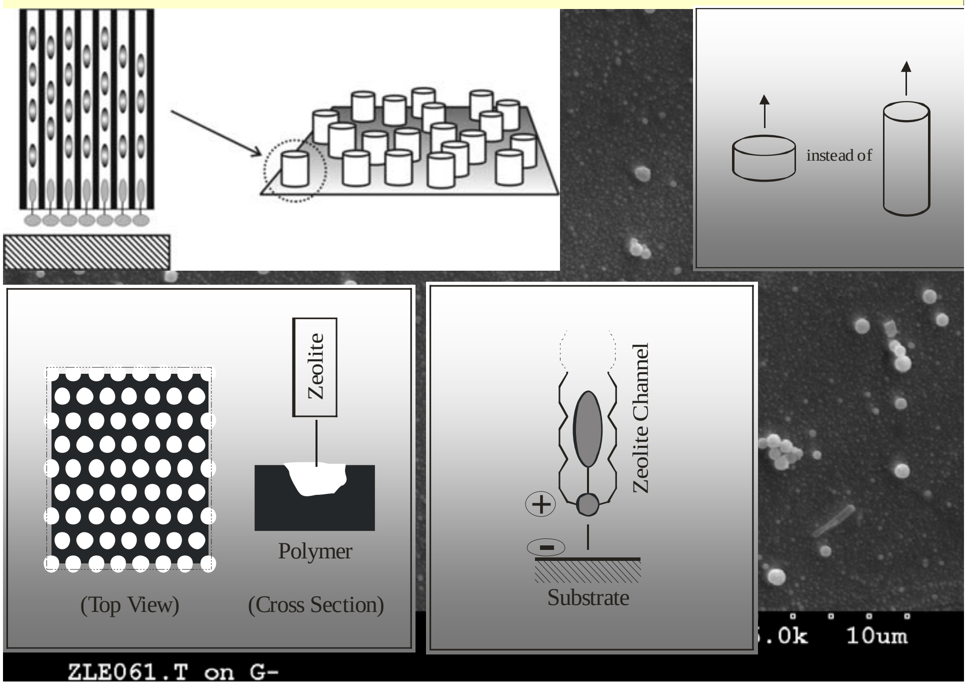


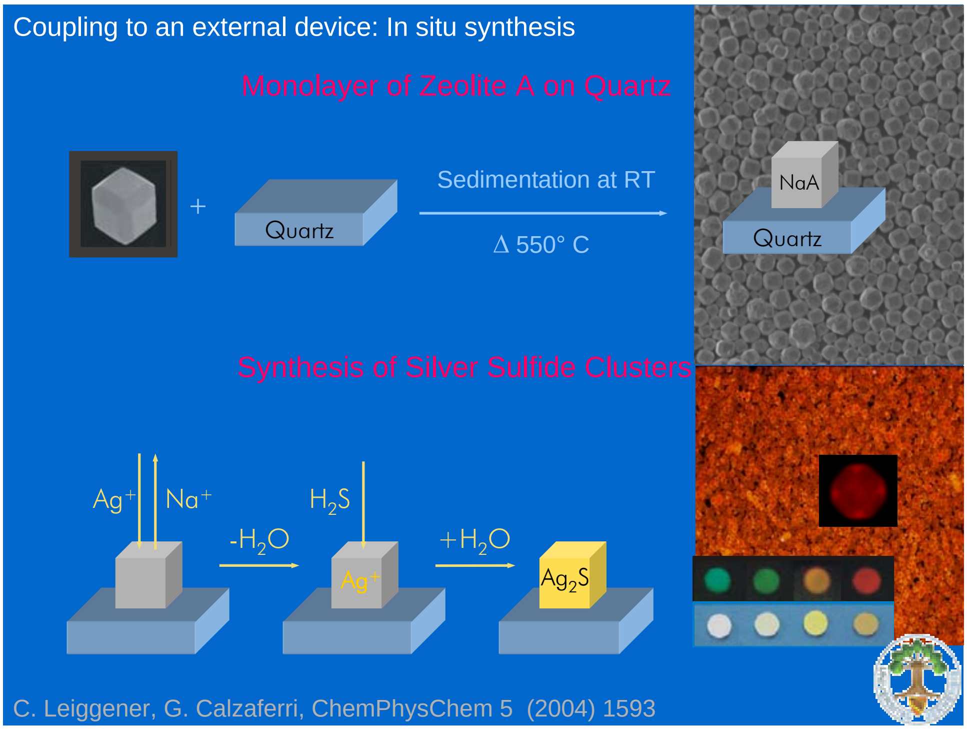
Third stage of organization: EnT from an antenna via stopcock to a semiconductor

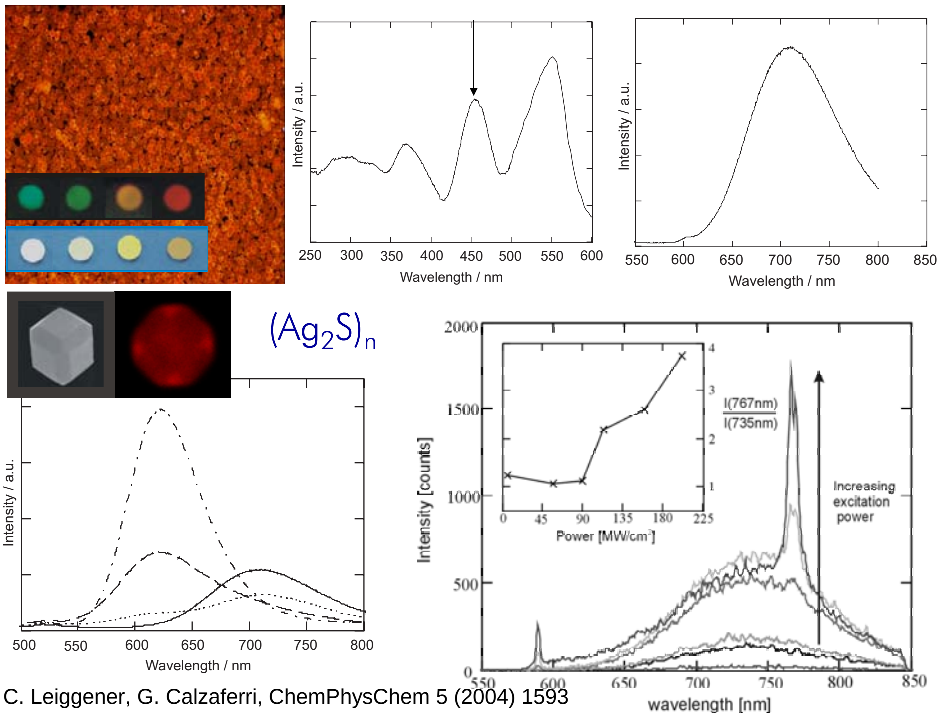



Stefan Huber, Gion Calzaferri, ChemPhysChem, 2004, 5, 239

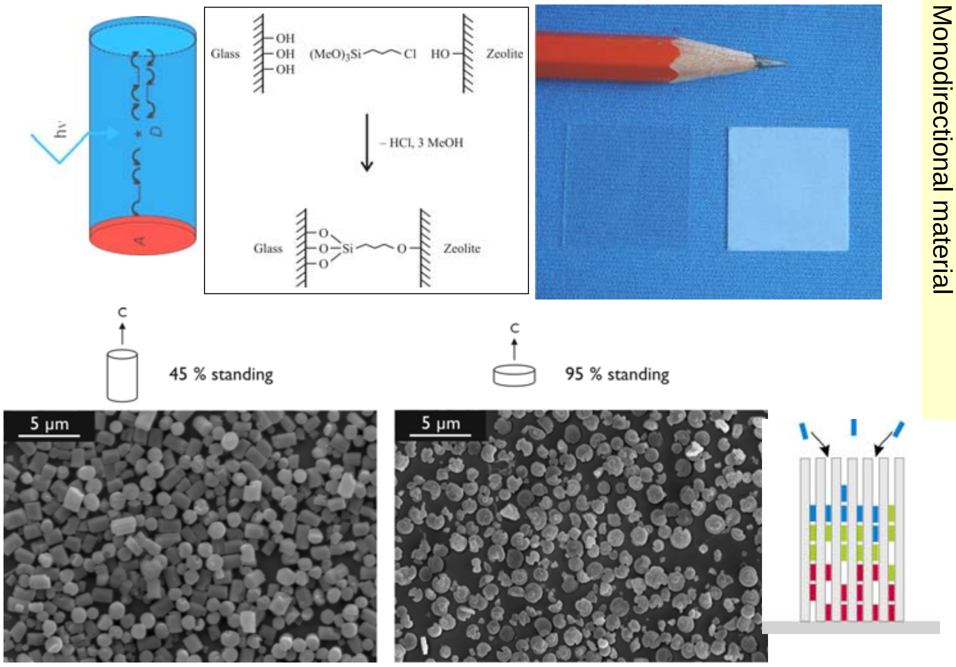
Monodirectional materials






C. Leiggener, G. Calzaferri, ChemPhysChem 5 (2004) 1593




Monodirectional material

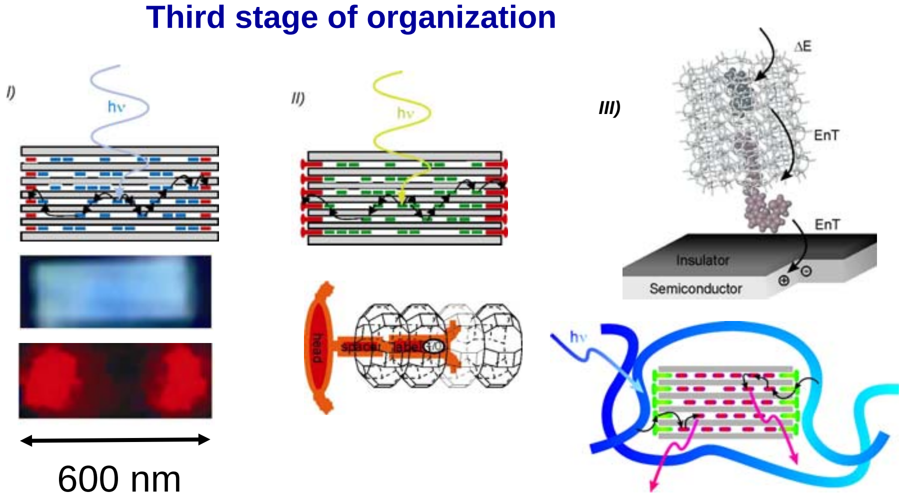
A. Zabala Ruiz, D. Brühwiler, G. Calzaferri Monatshefte für Chemie, 2004, in press

Summary

**First stage of organization**

**Second stage of organization**

**Third stage of organization**



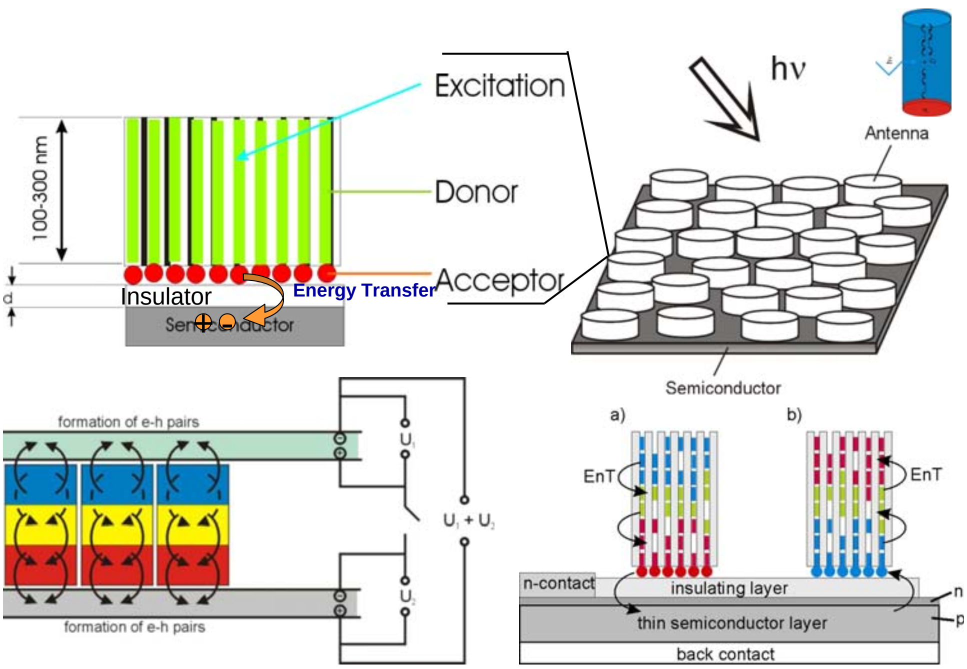
## 3. Challenges for developing new photonic devices for solar energy conversion

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<br><br>oriented layers of *monodirectional* 300 - 600 nm crystals | sensitization of the polymer<br><br>sensitization of the $C_{60}$, $C_{70}$ unit | oriented layers of *monodirectional* 300 - 600 nm crystals<br><br>can reduce the amount of Ru needed by 2-3 orders of magnitude |
| | Redox systems based solar cells | |

**Antenna sensitized solar cells:** Solid state thin film devices



# Light-harvesting host-guest antenna materials for new photonic devices

1. **Zeolite L, an ideal host for supramolecular organization of dyes**
2. **Host-guest antenna materials: Three stages of organization**
3. **Challenges for developing new photonic devices**
4. **Conclusions**

*J. Mater. Chem. 2002, 12, 1*
*Angew. Chemie, Int. Ed*. **2003**, *42*, 3732-3758
*Microporous, Mesoporous Materials*, **2004**, *72*, 1-23

Functionalized host-guest antenna materials have been developed over the last twelve years. Zeolite L was used as a host in all experiments I have presented. Other zeolites could be used as well.

A next step consists in testing the applicability of these materials.

Functional pigments, molecular probes, optical electronics.

Solar energy materials for thin film solid state, redox-based, and **low cost tandem solar cells.**

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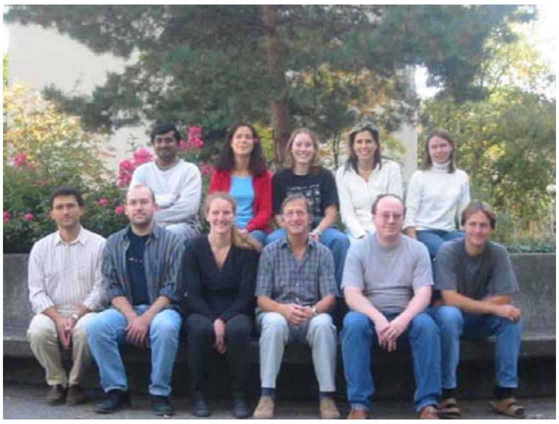

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NRP 47: Energy collection, transport and trapping by supramolecular organization of dyes in hexagonal zeolite nanocrystals
EU: Nanochannel (European Union Research Training Network *Nanochannel*)
NF: Luminescent molecules and quantum dots in the cavities and channels of zeolites
BFE: Photochemische, Photoelektrochemische und Photovoltaische Umwandlung und Speicherung von Sonnenenergie

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