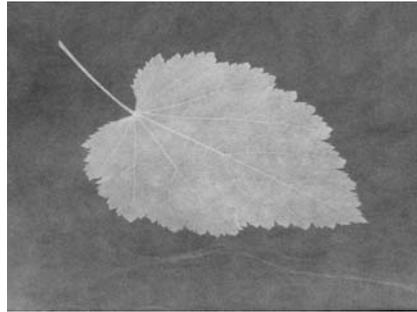


Transformation and Storage of Solar Energy

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Transformation and Storage of Solar Energy, Berner Chemische Gesellschaft, Bern, January 31, 2007, Gion Calzaferri

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Lecture presented by Gion Calzaferri
at the Berner Chemische Gesellschaft
January 31, 2007

Transformation and Storage of Solar Energy

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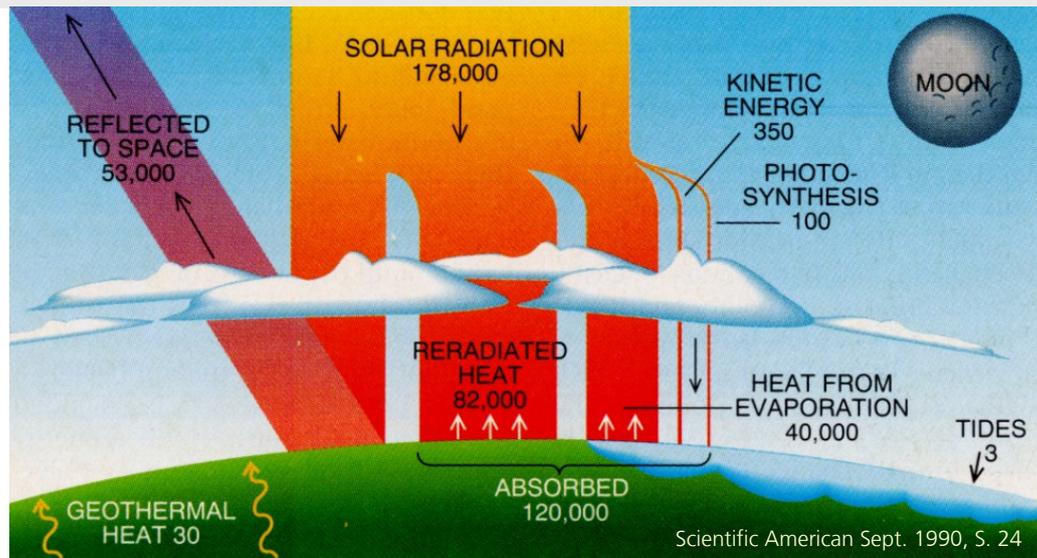
7 Summary

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In the introduction I put our research into a broader context. (1)
Then I will start focusing on „Quantum Solar Energy Conversion“, (2)
trying to learn a few things from green plants, (3)
and discuss how an artificial antenna system can be made.(4)
After this I will become more ambitious and look into
„Organization and Communication“ (5)
before asking
“if the material we have now in hands is actually of any use for
Solar Energy Conversion Devices“? (6)
And at the end I will summarize what has been said

1. Introduction



Solar radiation striking the earth: 178'000 TW. (1 TW = 10^{12} Watt)
This is approximately 14'000 times our actual „technical power consumption“.
30 % immediately reflected back to space. 50 % absorbed by the earth.
20 % creates wind and powers the water cycle.
0.056 % drives the photosynthesis of green plants.

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Solar radiation striking the earth amounts to 178'000 terawatt, or is about 14'000 times the world actual "technical power consumption" (0.007%) which is in the order of 13 terawatt.

20 % creates wind and powers the water cycle.

0.056 % drives the photosynthesis of green plants – our food and oxygen source.

The geothermal contribution is small with respect to the solar radiation – but is nevertheless nearly three times more than the

actual "technical power consumption" –

while the contribution of the tides (earth-moon gravitational energy) appears to be less important.

This is the basic information to be considered when thinking about renewable energy sources.

1. Introduction

Interaction of light with matter

reflection/re-, di-fraction

absorption

scattering/NLO

absorbed IR light goes into kinetic energy of the nuclei
while visible and near UV light is stored as kinetic energy of the electrons

KINETIC ENERGY OF THE ELECTRONS

transformation
into heat

emission as
light quanta

generation of
electron-hole pairs

reagent for
material changes

random
movements
of the atoms

luminescence

photocurrent

photochemical
reactions

thermo chemistry

lighting

optoelectronics

photochemistry

wind, water cycle, climate

photosynthesis and environmental photochemistry

thermal solar energy conversion

quantum solar energy conversion

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We focus on solar radiation striking the earth, hence, we should consider the "Interaction of light with matter".

Light can be reflected, it can be scattered or absorbed.

The energy of absorbed infrared light goes in a first step into specific movements of the nuclei, while visible and near UV light is stored for a short time as **kinetic energy** of the electrons.

In a next step the kinetic energy of the nuclei and some of the electrons is transformed into heat, which is random movement of the atoms. It drives **thermo chemistry** and is used for **thermal solar energy conversion**. It is this part of the energy input which drives the wind, the water cycle and hence, controls the climate.

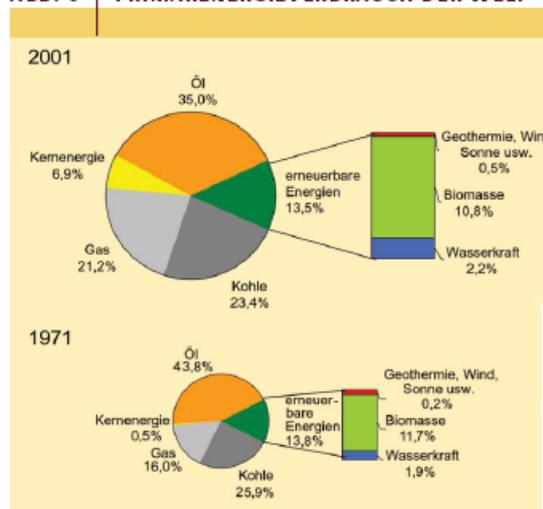
Stored kinetic energy of the electrons can be emitted as light quanta, this is luminescence and plays e.g. an important role in **lighting**.

Stored kinetic energy of the electrons can generate electron-hole pairs in semiconductors which can then lead to a photocurrent. This process is the basis of modern **optoelectronics**.

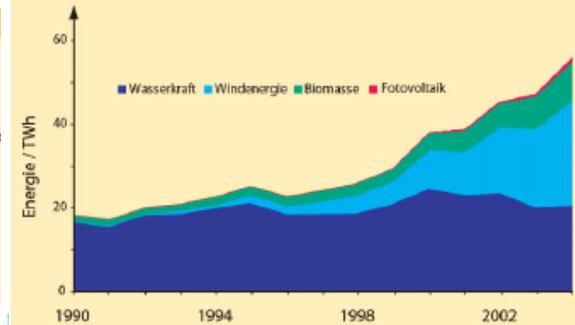
Finally, stored kinetic energy of the electrons can be used as a reagent for material changes, which is nothing else than photochemical reactions and hence the basis of **photochemistry**. These processes are used in quantum solar energy devices and they are the basis of natural **photosynthesis**.

1. Introduction

ABB. 6 | PRIMÄRENERGIEVERBRAUCH DER WELT



Electricity produced from renewables in Germany



20 TW of power (world's mid-century projected demand), requires 0.16 % of Earth's land with 10%-eff. solar panels.

<http://www.erneuerbare-energien.de/>

HARALD KOHL, Phys. Unserer Zeit, 37 (2006) 126

Nicola Armaoli, Vincenzo Balzani
Angew. Chem. Int. Ed. 46 (2007) 52

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Having understood this, we now look at the „technical energy consumption“ of the world.

It is interesting to see, that **the percentage of renewable energy to the total energy consumption remained constant** in the period from 1971 to 2001, despite of the fact that the total energy consumption nearly doubled during this period.

The amount of renewable energy in Germany increased by a factor of nearly 4 since 1990, despite of the fact that hydropower remained constant. Interestingly, the main growth started less than 10 years ago.

How much land is needed, if we would like to supply our “technical energy consumption“ at the year 2050 exclusively by means of a 10 % efficiency process? It corresponds just to the 6 red spots shown on this map. From this you can guess that it is probably less than the land we are covering by highways, streets and parking lots.

Hence, land is an important but certainly not a limiting issue on a global scale.

1. Introduction



Wilhelm Ostwald, 1853 – 1932

Nobel price in Chemistry 1909

Vergeude keine Energie – verwende sie.

1911 "Die Mühle des Lebens"

Beschreibt die Rolle der Sonne für die Existenz des Lebens auf der Erde und begründet die Forderung, dass der Mensch seinen Energiebedarf primär durch Sonnenenergie decken soll.

Transformation (and Storage) of Solar Energy

has become a respectable business with an annual growth rate of about 40 %.

Politics - economy

Technology - engineering

Science?

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It is interesting to read that Wilhelm Ostwald, who is often considered as being the father of physical chemistry, argued already 100 years ago why humanity should supply its energy consumption mainly by means of solar energy.

Nowadays transformation of solar energy has become a respectable business with an annual growth rate of about 40 %.

It has become a political and economic issue

Technology and engineering have advanced rapidly for the last few years.

Hence, we should ask: **Is there any scientific challenge left?**

I do not try to treat this question in a general way but focus on "Quantum solar energy conversion".

As a consequence we immediately meet the father of modern photochemistry, namely Giacomo Ciamician.

2 Quantum solar energy conversion

Giacomo Ciamician, Professor for Chemistry at the University of Bologna 1889 – 1922.

Inspired by the ability of green plants to transform solar energy in chemical energy, he predicted already 100 years ago, that the future of fossil fuels would be in chemical fuels **produced by artificial photosynthesis**.



Giacomo Ciamician, *Science*, New Series, Vol. 36, No. 926. (Sep. 27, 1912), pp. 385-394.

The first serious attempts to promote the technical utilization of solar energy on a large scale, however, came as a consequence of the first oil crisis 1973-74.

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Inspired by the ability of green plants to transform solar energy in chemical energy, he predicted already 100 years ago, that the future of fossil fuels would be in chemical fuels **produced by artificial photosynthesis**.

In October 1973 a new war between Israel and its Arabic neighbors broke out. On October 16 of the same year the oil exporting countries decided to use oil as a weapon, when it was clear the Arabic attack did not lead to the expected victory. Oil-exports were stopped immediately. As a consequence our societies became finally aware of their enormous dependence on oil.

This was the beginning of the first serious attempts to promote the technical utilization of solar energy.

2 Quantum solar energy conversion

Melvin Calvin, Nobel price in Chemistry 1961

The best quantum-converting machine we know is the green plant with its chloroplasts.

IPS-0, Boston 1974. IPS = International conference on Photochemical transformation and storage of solar energy

Today we are going back to the „green machine“ by converting plant carbohydrate into a more useful liquid fuel through an alcohol fermentation process.



The final stage in reverting to the „green machine“ will be the synthetic generation of chloroplast's **quantum-capturing and converting function**, so ultimately we will require neither plants nor land on which to grow them.

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In this context let me mention Melvin Calvin, who received the Nobel price in chemistry for his contributions to the understanding of the carbon dioxide fixation by green plants. He said:

The best quantum-converting machine we know is the green plant with its chloroplasts. Today we are going back to the „green machine“ by converting plant carbohydrate into a more useful liquid fuel through an alcohol fermentation process.

The final stage in reverting to the „green machine“ will be the synthetic generation of chloroplast's **quantum-capturing and converting function**, so ultimately we will require neither plants nor land on which to grow them. **(Calvin did not advise to synthesize chloroplasts but to mimic their function).**

Better utilization of biomass is highly desirable, however, I am deeply skeptical about agriculture for fuel production – which may often not even survive a serious thermodynamic efficiency analysis.

2 Quantum solar energy conversion

The Swiss National Science Foundation launched 1976 a research program
Erzeugung und Speicherung chemischer Energieträger.

Ernst Schumacher encouraged me to participate in this project.



Ernst Schumacher,
1976 University of Bern

So, I installed 1980 together with my brother and sisters a small photovoltaic panel on the Maiensäss of my father.

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1076, the Swiss National Science Foundation launched a research program
Erzeugung und Speicherung chemischer Energieträger.

Ernst Schumacher encouraged me to participate in this project. I did, and by now never lost interest in this subject.

It is natural that I first wanted to learn about the then available technical possibilities and how well they work.

As a consequence, I installed a small photovoltaic panel on the Maiensäss of my father, together with my brother and sisters. This was 1980.

2 Quantum solar energy conversion



1750 müM, Winter 1981

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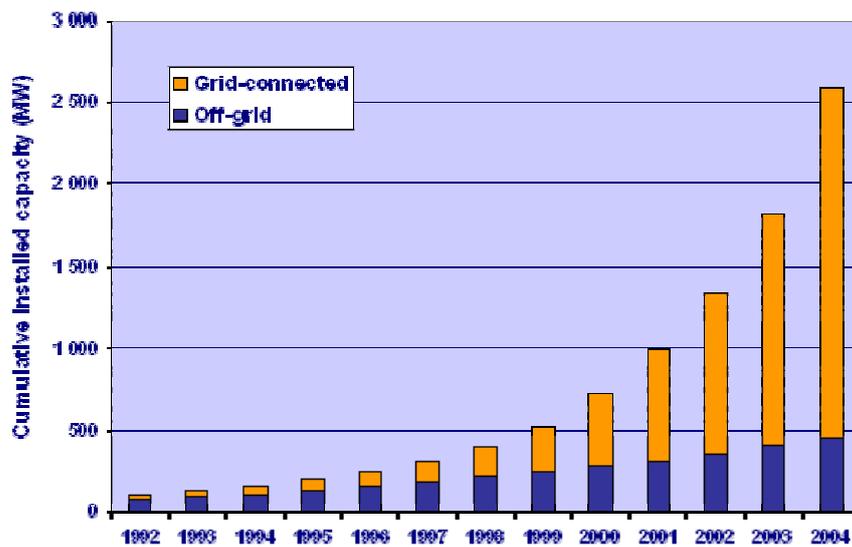
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You see it here.

Photo activity of plants is sleeping in deep winter. However, artificial photoactive devices can still work well, and they provide us e.g. with electrical power.

In this picture you see a small silicon solar cell panel. We installed it 27 years ago and it still works as well as it did then, transforming solar energy into electrical energy with an efficiency of about 14 %.

2 Quantum solar energy conversion



S. Nowak, IEA-PVPS, 20th EUPVSEC, Barcelona, Juni 2005 (www.iea-pvps.org).

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Solar cell market has been increasing very fast over the last 15 years. 2005 about 1.4 GW power was newly installed and 2006 nearly 2 GW peak power was added.

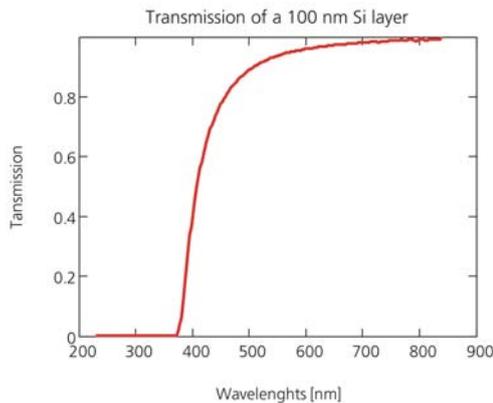
2 Quantum solar energy conversion

Durability of good solar cells: more than 25 years

The best tandem solar cells have nowadays an efficiency of close to 40 %.

Is there room for science ?

- 1) Storage as a chemical fuel is still a challenge!
- 2) Concentrators are needed for realizing the effectiveness of available tandem cells.
- 3) The future belongs to thin layer solar cells!



European Society for Quantum
Solar Energy Conversion
<http://www.esqsec.unibe.ch>

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The durability of good solar cells is more than 25 years. (This corresponds to the guarantee one can get from the manufacturer.)

The world record efficiency of Tandem Solar cells is close to 40 %.

With these facts in mind – **high stability, fast growth rate, impressive maximum efficiency** - we should ask:

Is there any room left for innovative science?

- 1) Storage as a chemical fuel is still a challenge!
- 2) Concentrators are needed to realize the effectiveness of available tandem cells.
- 3) However, the future belongs to thin layer solar cells!

This viewgraph shows the transmission of a 100 nm silicon layer.

Little of the incoming light of longer wavelengths than 450 nm is absorbed in a 100 nm silicon layer.

Making efficient and stable thin layer solar cells of not very toxic materials remains a considerable challenge.

So let us see what we can learn from green plants.

3. Learning from green plants

In natural photosynthesis, sunlight is absorbed by organized chlorophyll molecules and transported to the reaction center.

That's where all life begins!

An important aspect of natural photosynthesis is the production of oxygen!

Molecular oxygen is a prerequisite of all animal and human life.

Without oxygen only primitive organisms have ever existed.



Figur aus
Bild der Wissenschaft,
April 1990, S. 92.

[Photoelectrochemical oxidation of Water – photoelectrochemical watersplitting](#)

Currao, Vanga, van Veen, Schropp, Calzaferri, *Photochem. Photobiol. Sci.* 2004, 3, 1017.

Vanga, Currao, Calzaferri, *J. Phys. Conf. Ser.* 2007, *in press*.

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In natural photosynthesis, sunlight is absorbed by organized chlorophyll molecules and transported to the reaction center.

That's where all life begins!

An important aspect of natural photosynthesis is the production of oxygen!

Molecular oxygen is a prerequisite of all animal and human life.

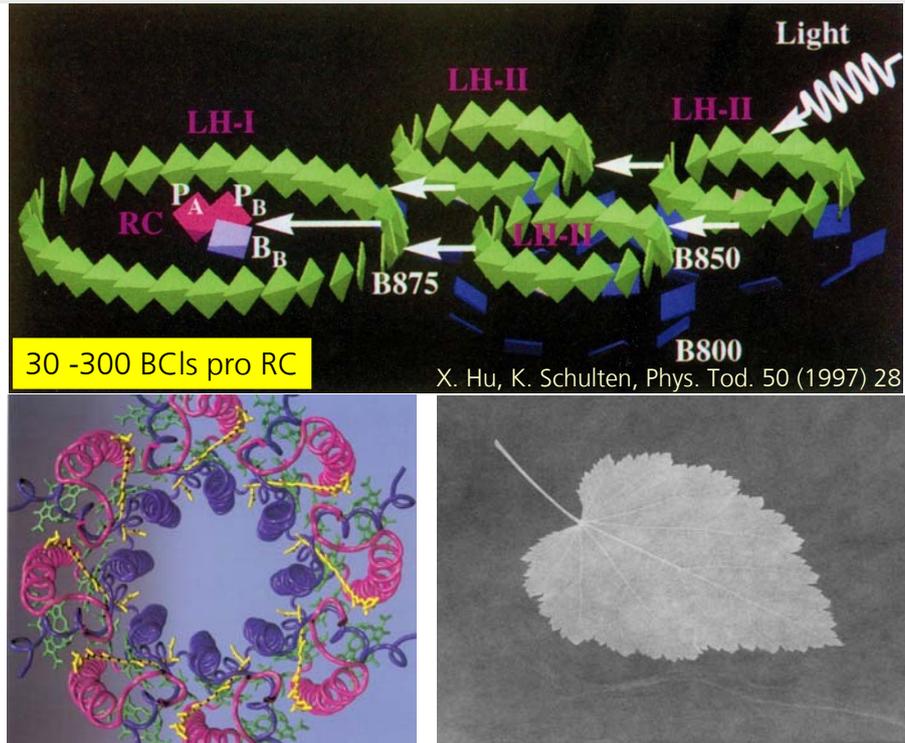
I show you a water plant, producing oxygen under irradiation, as you see from the bubbles.

Without oxygen, only primitive organisms have ever existed.

We have been working on photochemical oxidation of water to oxygen with visible light and we have devised a reversibly working photo electrochemical water splitting process the efficiency of which is, however, still too low.

I must skip this interesting topic today in order to ask:

3. Learning from green plants



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What can we learn from green plants?

The overall efficiency of green plants for solar energy conversion is much lower than that of commercially available solar cells. However, their antenna system is cleverly designed and works at maximum efficiency.

The detailed structure of the antenna system of purple bacteria has been resolved. It consists of regular arrangements of chlorophyll molecules held at fixed positions by means of proteins.

Light absorbed by any of these chlorophyll molecules is transported to the reaction center providing the necessary energy for the chemical processes to be initiated.

A green leaf consists of millions of such antenna devices.

Synthesizing this in the laboratory would be a hopeless task – at least regarding the current possibilities of chemists.

What to do?

First we must understand the basic principle on which such an antenna works.

This understanding comes from the work of Theodor Förster.

RC = Reaktionszentrum

PA,PB Special Pair

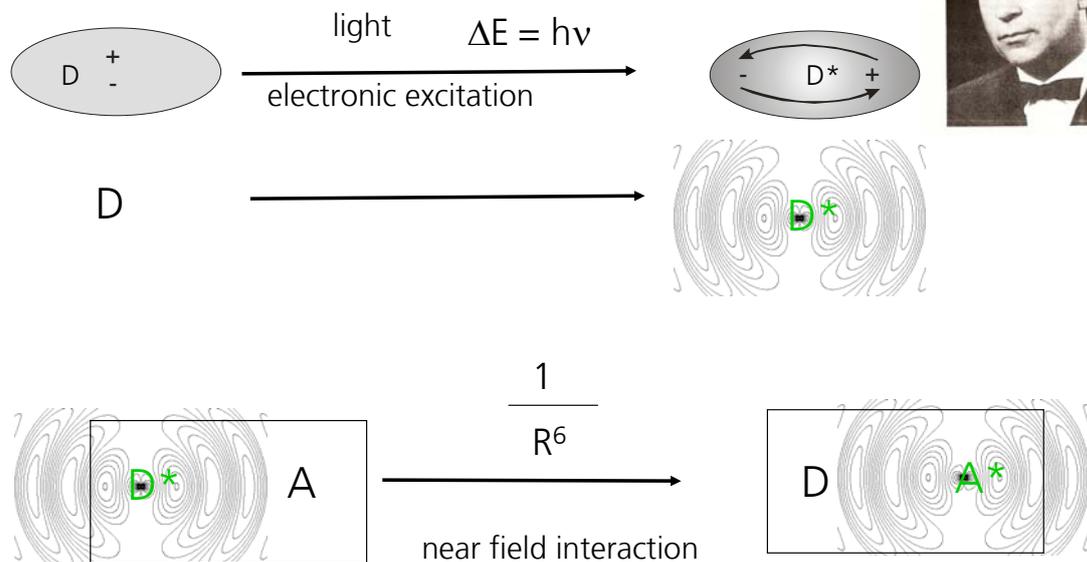
B800 etc : Die Zahlen geben die Absorptionskante in nm an

Blau: α -Helices, bestehend aus 56 Aminosäuren

Lila: α -Helices, bestehend aus 45 Aminosäuren

3. Learning from green plants

Understanding the antenna system of green plants.
Th. Förster, Ann. Phys. 2, 55, 1948



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We think of a molecule D as consisting of nuclei and electrons. The energy of a photon absorbed by D is transformed into kinetic energy of an electron. This causes an alternant current and, as a consequence, an oscillating field.

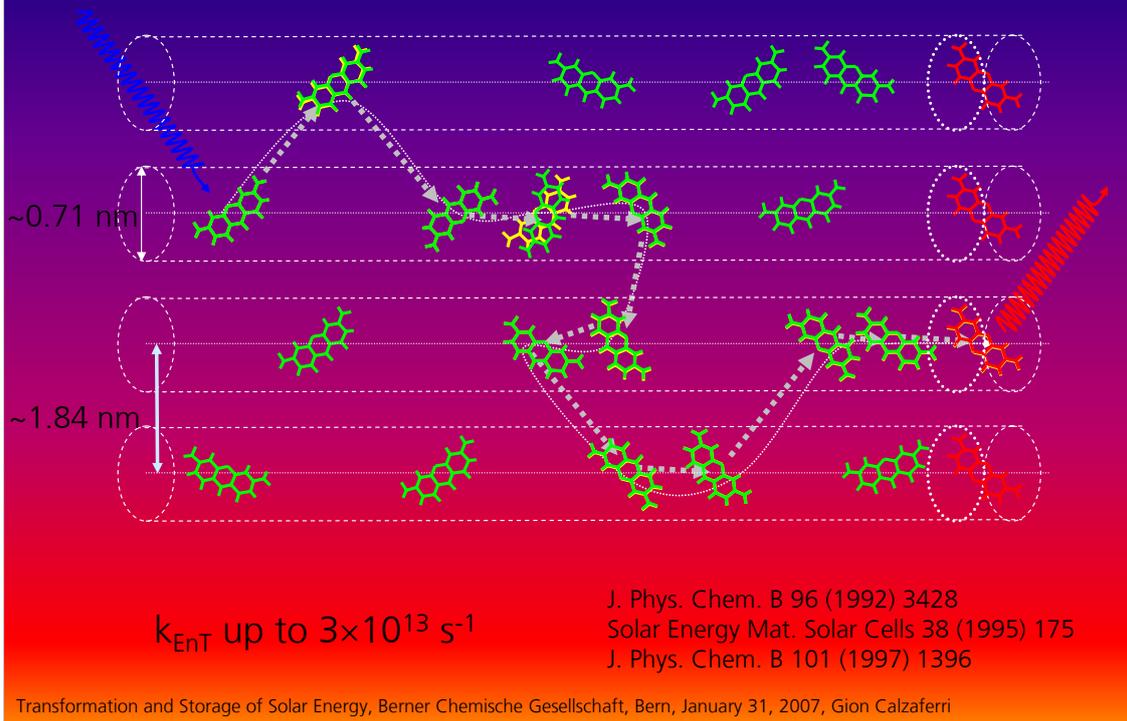
An acceptor molecule A in the neighborhood of the excited molecule feels the oscillating field over a considerable distance and can capture the excitation energy of D^* , provided that it bears states that are in resonance with the donor. The main interaction of the donor and the acceptor is of dipole-dipole type and therefore proportional to 1 over the distance R power to the 6.

We must multiply this with a geometry factor that takes into account the relative orientation between donors and acceptor and the degree of resonance.

This principle works not exclusively for chlorophyll molecules but for any exciton, either in molecules, clusters, quantum dots or semiconductors.

Having understood this, we can try to design an artificial system. I started with it about 17 years ago.

4. An artificial antenna system



Our design of a model that mimics the key functionality of the antenna system of green plants was inspired by experience I had with different zeolite materials. From this I deduced that a one-dimensional channel system had the advantage of being the simplest possible choice.

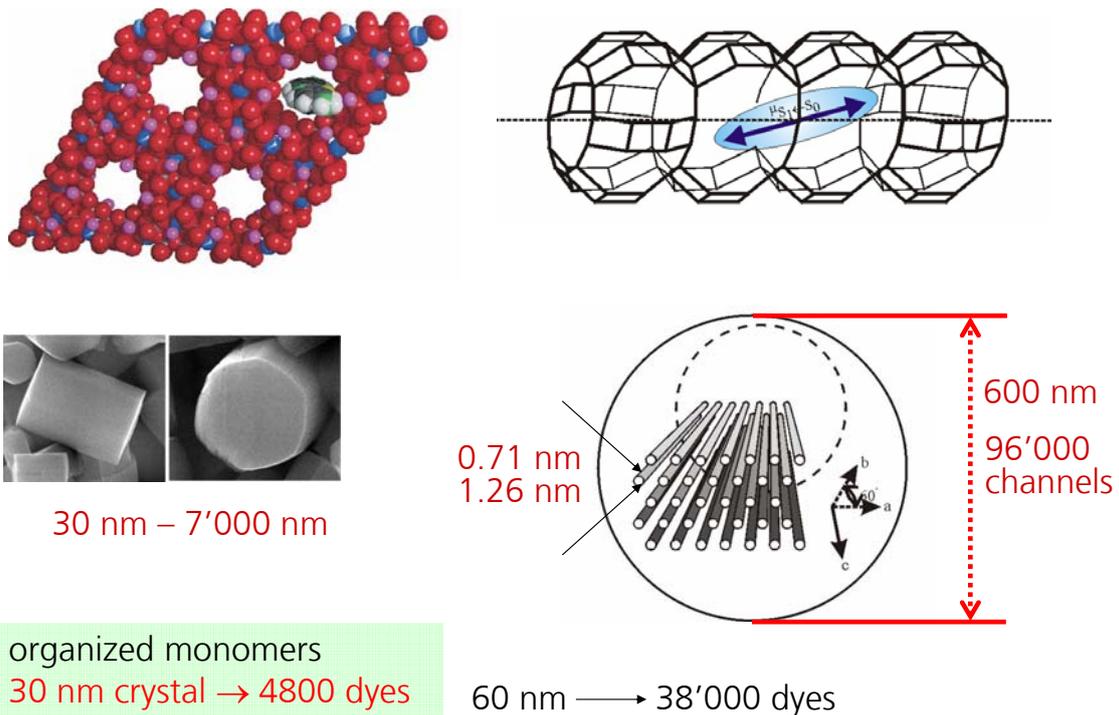
So I considered zeolite L. The numbers given here correspond to the channel opening and the distance between the centers of two channels. We theoretically studied cylinders containing green donor molecules and at one end red acceptors – as shown here -. The red acceptors should mimic the “entrance of the reaction center RC”.

Light absorbed by one of the green molecules is hopping among them randomly until it is caught by an acceptor, which can be seen by monitoring the luminescence of the red dye.

We estimated that rate constants could be in the order of 10^{13} s^{-1} .

This was a system worthwhile to be tried in the laboratory.

4. An artificial antenna system



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Look at this van der Waals picture that shows a dye molecule entering a channel of zeolite L. It illustrates that there are dye molecules that can enter but that the space is so tight, that once inside they cannot pass each other.

We have learned how to synthesize zeolite L crystals in the size range of 30 nm up to about 7000 nm, which means that we can cover about 7 order of magnitude in terms of volume. The SEM images illustrate a top and a side view of good crystals.

This is a side view of a channel with a molecule inside. The double arrow indicates a possible orientation of the molecules electronic transition moment which can also be oriented parallel to the channel axis, perpendicular to it, or at any angle in-between, depending on the length and the shape of the molecule.

It is useful to imagine zeolite L as consisting of a bunch of strictly parallel channels as indicated here. The openings which molecules must pass have a diameter of 0.71 nm and the largest diameter inside is 1.26 nm.

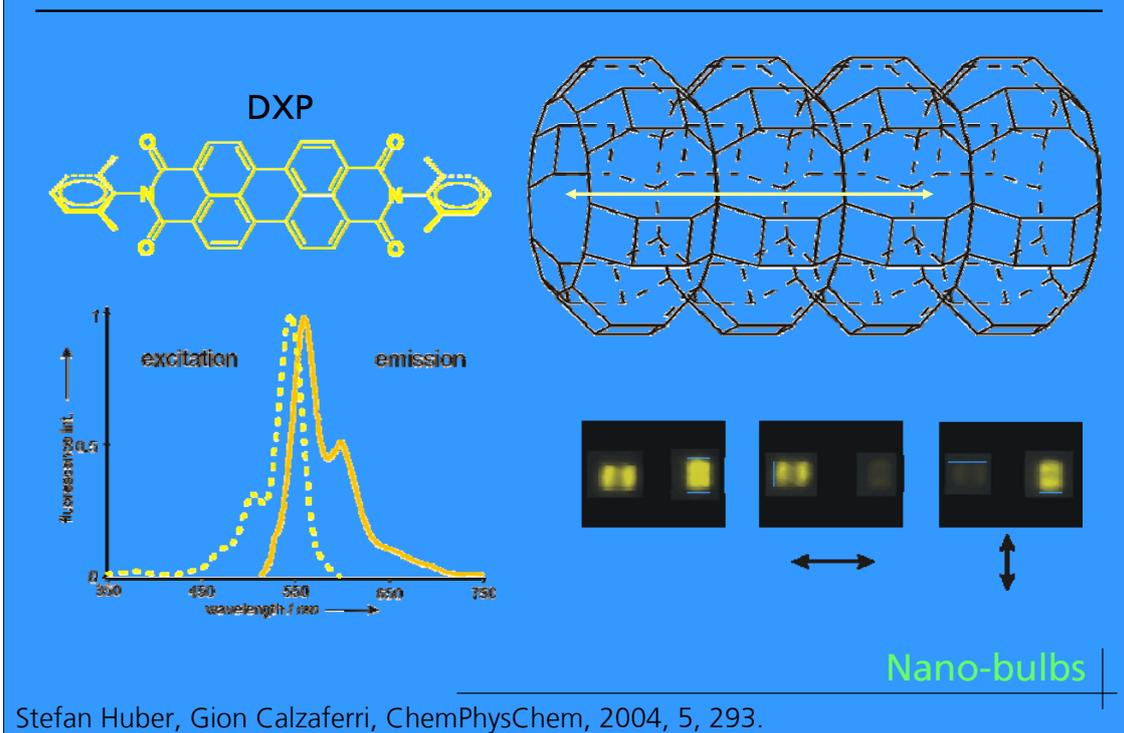
Of how many channels does a zeolite L crystal of 600 nm diameter consists? It is easy to calculate this number and it turns out that a crystal of 600 nm diameter consists of roughly 100'000 strictly parallel channels. Please keep this number in mind: 600 nm diameter corresponds to 100'000 channels!

An important consequence is that this material allows to realize extremely high concentrations of well oriented dye molecules that behave as monomers.

As an example, a 30 nm crystal can bear nearly 5'000 monomeric dye molecules and a 60 nm crystal can host nearly 40'000 monomers. **This is extremely interesting! And the basis of all what I have to tell you from now on.**

4. An artificial antenna system

Insertion of dye molecules into the channels of zeolite L



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

Insertion of dyes into the channels of zeolite L can be realized in different ways. By cation exchange, if we have cationic dyes, or from the gas phase, if we want to insert a neutral dye such as DXP. For DXP we dry the zeolite under vacuum and then sublime the dye at 300 °C.

You can see that the dye loves to go in under these conditions and that the electronic transition moment is oriented along the channel axis as we know by looking at the fluorescence of two crystals which are oriented perpendicularly to each other through a polarizer.

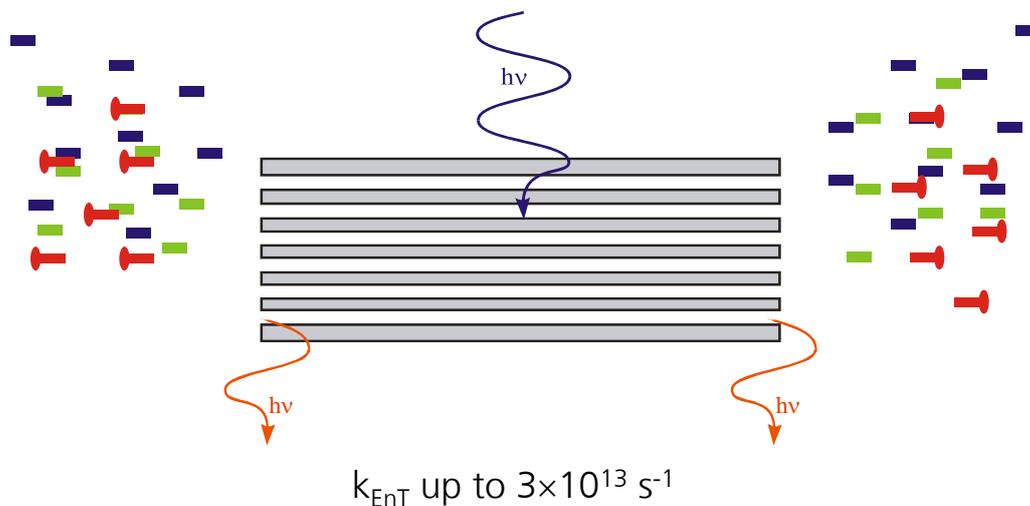
If the polarizer is only transparent in the direction indicated by this arrow, the luminescence of the crystal oriented perpendicular to it vanishes. If we turn the polarizer by 90 ° it becomes bright, but the luminescence of the crystal we have seen before disappears.

The fact that the molecules are there as monomers can be demonstrated by measuring the absorption and the fluorescence spectra.

However, we have to be careful with this argument because we soon observe optical saturation.

4. An artificial antenna system

Increasing organization: *Sequential insertion of dyes*



Dye-Loaded Zeolite L Sandwiches as Artificial Antenna Systems
M. Pauchard, A. Devaux, G. Calzaferri *Chem. Eur. J.* 2000, 6, 3456.
Photon-Harvesting Host-Guest Antenna Materials
G. Calzaferri, S. Huber, H. Maas, C. Minkowski
Angew. Chem.Int Ed. 2003, 42, 3732.

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Now I would like to increase the organization and hence the complexity.

I show you a cartoon which symbolizes zeolite L. The gray bars are the walls and the empty space in between are the channels. I will use this kind of cartoon more often.

I show you how a crystal can be filled with more than one type of dyes.

We start with blue dye molecules and let them slip into the channels.

Next, why not allowing a green dyes to slip in? Please pay attention too what happens!

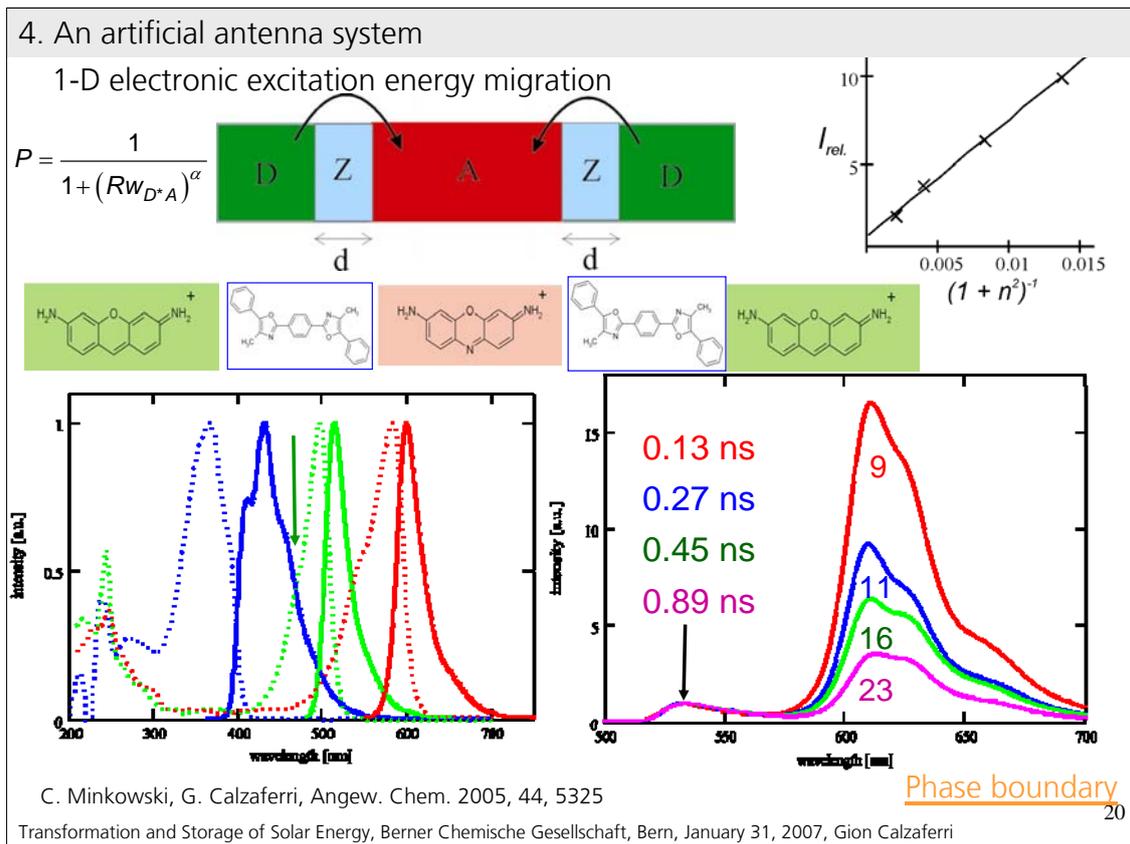
You can see how they push the blue ones deeper into the channels because there is not enough space available to pass them.

In a next step we add stopcock molecules. They close the channels and they allow efficient communication with the outside world.

Light is absorbed by blue molecules in the middle of the crystal, transported to both ends where it is emitted as red light.

Transport goes to both ends. That's why we call this bidirectional antenna.

Many of such materials have been made in my own and recently also in other laboratories.



An important question concerns the dimensionality of the near-field interaction driven excitation energy transport. To investigate this we, have prepared zeolite L crystals symbolized by this rectangle, where we have in the middle red acceptor molecules, followed by spacers Z and followed by donors D.

The idea of this experiment was, to investigate the distance dependence of the energy transfer probability from D to A for varying thickness d of the spacer layer.

To prepare this material we have first inserted the red acceptors A, we have then inserted DMPOPOP, which can act as a spacer Z, as I will show, followed by the donors D.

Here you see the fluorescence spectra as solid lines and the excitation spectra as dotted lines of the individual dyes. It is obvious, that the blue spacer Z does not absorb, if we excite the material at a wavelength indicated by this green arrow, hence, it acts as a spacer.

The result of this experiment is shown in this part of the picture. The numbers 9, 11, 16, 23 indicate the average number of molecules Z in the spacer layer.

The small band at about 530 nm is the emission of the green donor D and the band at 620 nm is that of the acceptor. You can see that the amount of energy transferred to the acceptor decreases with increasing thickness of the spacer layer and the lifetime of the donor luminescence decreases with decreasing layer thickness.

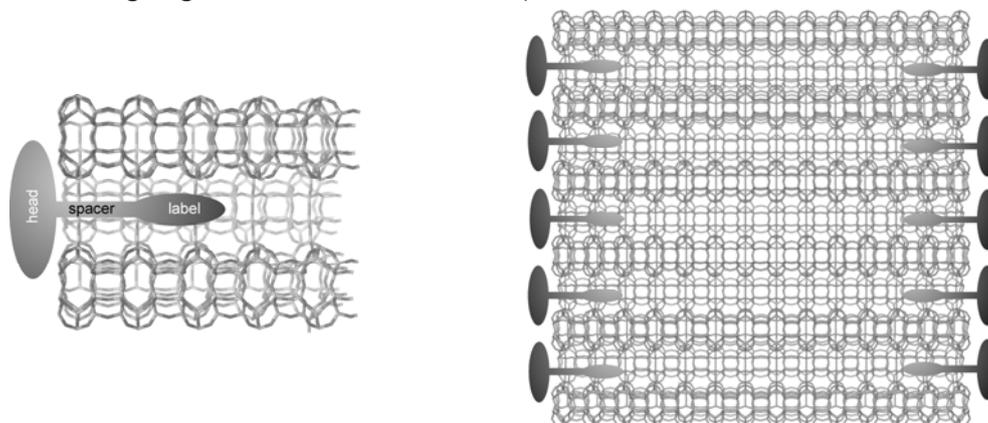
This clearly indicates that the process is controlled by near-field interaction.

The probability P for energy transfer from D to A is proportional to $1 / (1 + \text{weighted donor-acceptor distance } R w_{D^*A})^\alpha$, where α is equal to six for a 3-D event, 4 if it is 2-D and 2 in the 1-D case. What we found in three experiments with different donors and acceptors was always $\alpha = 2$.

This is the first experimental prove given in the literature for quasi 1-D electronic excitation energy transport.

4. An artificial antenna system

Increasing organization. Functional stopcocks



I) Reversible stopcocks

II) Electrostatically bound stopcocks

III) Covalently bound stopcocks (Bonding via $-\text{Si-O-Si}-$ and $-\text{Si-O-Al}-$.)

Trapping Energy from and Injecting Energy into Dye-Zeolite Nano-antennae

H. Maas, G. Calzaferri, *Angew. Chemie, Int. Ed.* 2002, 41, 2284

G. Calzaferri, US + EU patent, (priority date 2000, granted US 2005, EU 2006)

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I wanted to envisage controlled communication with the outside world. To achieve this, we had to do something. What we did was to invent nano-stopcocks.

This are molecules that consist in principle of a label, a spacer and a head that is too large to enter the channels, as indicated by this cartoon.

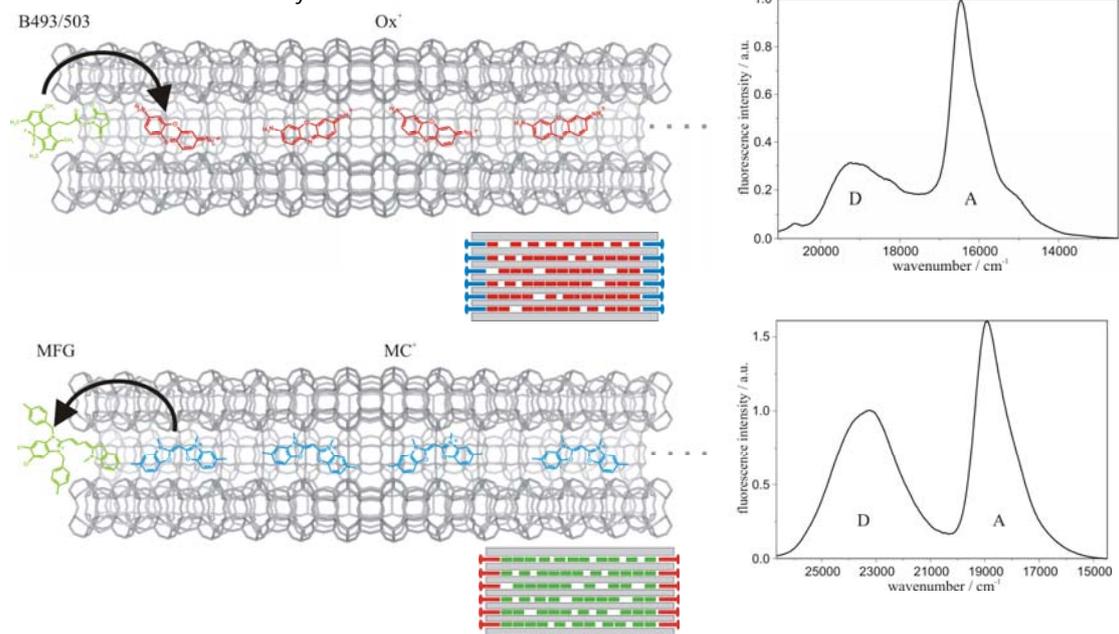
Imagine you have a 600 nm diameter zeolite L crystals and you want to close each channel with a stopcock. This would mean adding roughly 200'000 stopcocks.

It is clear, that such a problem is best solved by chemical means, which is by means of methods dealing with a large number of objects, and not by a physical approach which would address one channel opening after the other.

Over the last 5 or 6 years we have developed methods for attaching reversible stopcocks, electrostatically bound stopcocks, and covalently bound stopcocks and we have realized several bidirectional antenna materials with electronic excitation efficiencies of more than 95 %.

4. An artificial antenna system

Artificial antenna system: First success



Trapping Energy from and Injecting Energy into Dye-Zeolite Nanoantennae

H. Maas, G. Calzaferri, *Angew. Chemie, Int. Ed.* 2002, 41, 2284

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Let me explain some of our very early successes with this approach. We inserted the red luminescent molecule as acceptor and the green bodypy stopcock as donor. Excitation of the donor D lead to a considerable fluorecence of A, caused by near-field interaction.

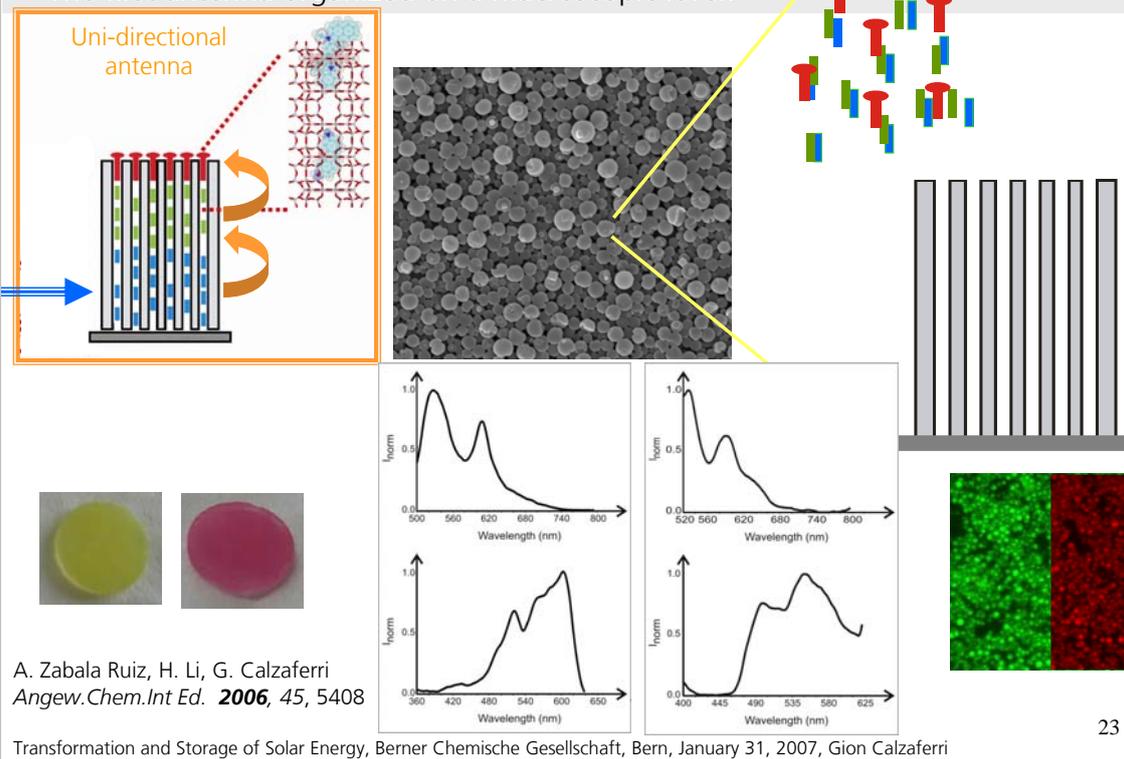
In the next experiment we wanted to transfer excitation energy from the inside to the outside. The spectra prove that energy transfer from the molecules insid to the stopcock takes place.

Hence, we can either inject excitation energy from the stopcocks to molecules inside of the crystal or we can transfer excitation energy from molecules inside of the crystal to acceptors attached as stopcocks.

Sophisticated methods for synthesizing such materials have been developed in my group over the last four years.

4. Artificial antenna system.

The first antenna organized on a macroscopic level!



When Arantza joined my group in May 2002 I told her that my dream would be to make a material as indicated by this cartoon namely an uni-directional antenna, where light is absorbed by the blue dyes transported to the green dyes and from there to the stopcocks.

In order to synthesize such a system we had to learn how to make good monolayers of standing zeolite L crystals on a substrate –

The channels had to be filled with dyes, as shown in this cartoon and eventually the channels had to be closed by adding stopcocks.

Making a cartoon is easy - realizing this material is not – but it works!

You see here a monolayer containing the green luminescent dye pyronine, if we add oxonine, the material becomes red.

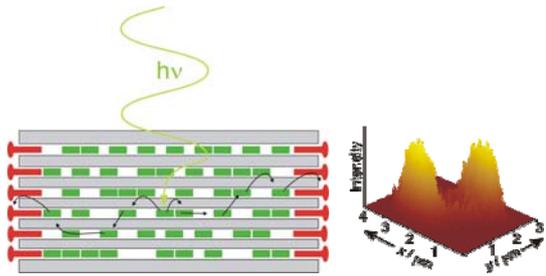
Such dye loaded monolayers are strongly colored.

These are the first excitation and absorption spectra we could measure about two years ago. They show that energy transfer works well.

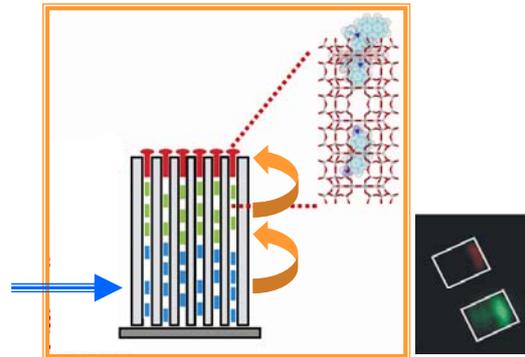
I will skip the detailed explanation of these data and just summarize that they add to the proof, that the material with the properties indicated in the cartoon – top left – can be made.

4. An artificial antenna system.
The first antenna organized on a macroscopic level!

Bi-directional antenna



Uni-directional antenna



We can synthesize bi-directional and uni-directional antenna materials.

Hence, we are able to organize molecules by means of a well chosen host.

Can the resulting nano-objects be organized in order to realize a desired macroscopic property?

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We can synthesize bidirectional and we can synthesize uni-directional antenna materials.

Hence, we are able to organize molecules by means of a well chosen host.

EnT stopcocks can be regarded as having a comparable function to the special pair in natural antenna systems.

Can the resulting nano-objects be organized in order to realize a desired macroscopic property?

This question leads us to the next chapter.

5. Organizing the crystals and communication

Bossart, Calzaferri
Chimia **60**, **2006**, 179

Yunus, Spano, Bolognesi, Botta, Patrinoiu, Brühwiler, Zabala Ruiz, Calzaferri
Adv. Func. Mater. **2006**, **16**, 2213

Suárez, Devaux, Bañuelos, Bossart, Kunzmann, Calzaferri
Adv. Func. Mater. **2007**, ...

Cucchi, Spano, Giovanna Catellani, Tonin, Calzaferri Botta, *SMALL*, **2007**, **3**, 305

O. Bossart, PhD, Dec. 1, 2006

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Lets start with bidirectional crystals. The simplest way is to embed them randomly in an acceptor medium. Zeolite crystals are highly scattering light because of their size and their refractive index of about 1.5, as you can recognize by the white color of this zeolite L monolayer. The scattering disappears if we cover this layer in the right way with a polymer.

You see two perfectly transparent samples which contain dye loaded zeolite. The fact that we found a way to solve the scattering problem opens an interesting field of applications.

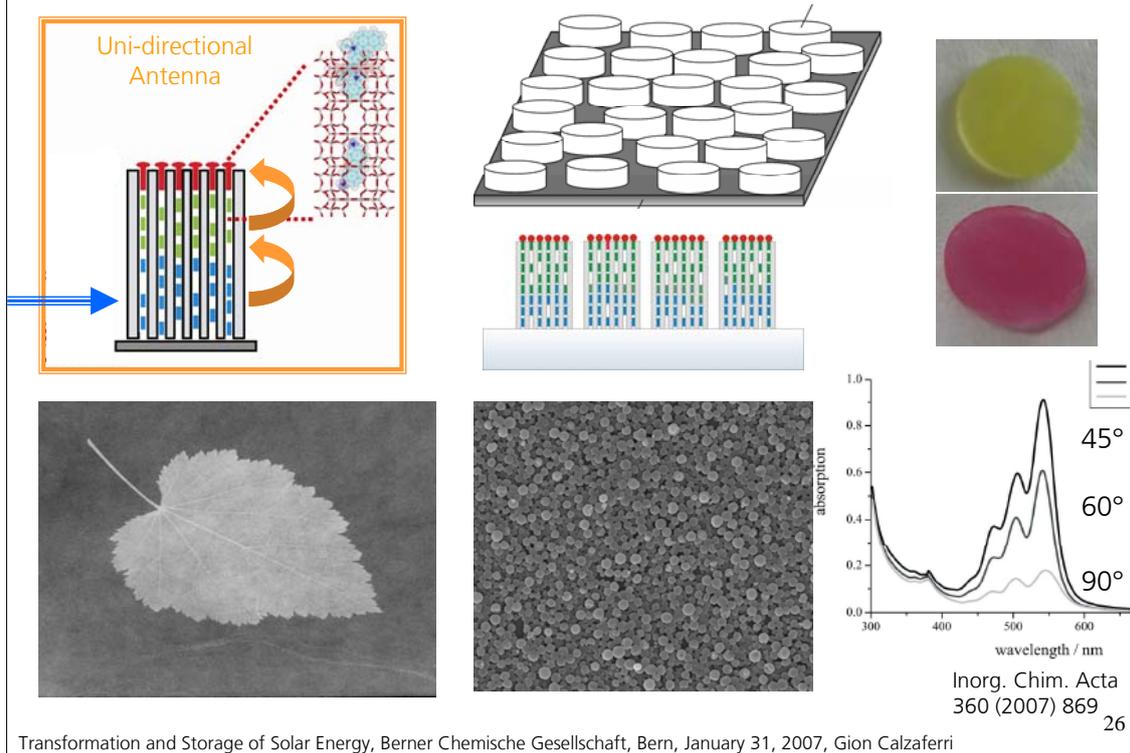
Zeolite crystals can be aligned under different conditions. Here you see blue luminescence of crystals through a polarizer oriented as indicated by the double arrow. If I turn the polarizer by 90 degree, the red luminescent crystals appear, turning the polarizer once more, we have the blue luminescence, and so on.

Fluorescent electro spun nano-fibres embedding dye-loaded zeolite crystals can be made which offer some new challenges.

The dye loaded zeolites can be arranged in hexagonal pattern which offer more complex light polarization properties.

Olivia Bossart wanted to know what happens if you dip flower petals into a suspension containing zeolite L crystals. Here you see one of the observations she made (on horned pansy). Look at the change of the pattern when changing the orientation of the polarizer through which we observe the luminescence.

5. Organizing the crystals – communication



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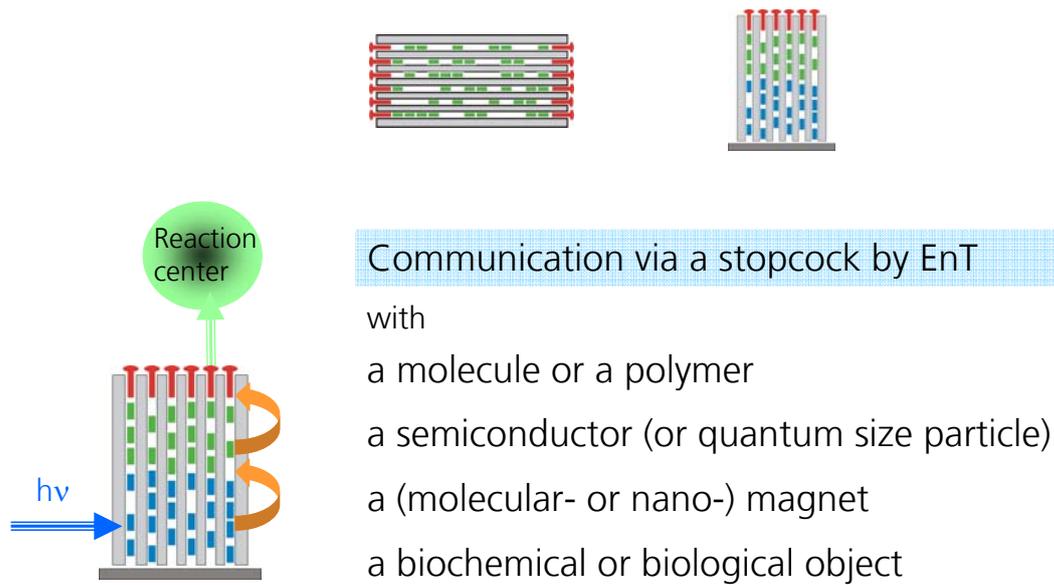
What about the unidirectional antenna, which indeed do mimic first important steps of the antenna system of green leaves?

Green leaves do not consist of one antenna, but of thousands and millions of them! A way to mimic this is to orient all the crystals on a layer, as indicated by this cartoon!

Here we are lucky, because in order to prepare the unidirectional antenna, we first had to prepare layers of oriented zeolite L crystals and then fill them with dyes as indicated by this cartoon. (The diameter of the crystals shown in this SEM image is in the order of 1 micrometer.)

These photographs of 2 samples made by Simon Fahrni illustrate that such monolayers can have high light-absorptivity. One can measure absorption spectra of them at different incident angle, as you can see here as an example for a layer containing DXP and they show the expected behavior.

5. Organizing the crystals - communication



Photonic antenna system for light harvesting, transport and trapping
G. Calzaferri, M. Pauchard, H. Maas, S. Huber, A. Khatyr, T. Schaafsma
J. Mater. Chem. 2002, **12**, 1-13.

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Having solved all these problems, lets become a bit more ambitious and try to communicate with a reaction center, as indicated by this cartoon!

What can we communicate with?

We can communicate with a molecule or a polymer

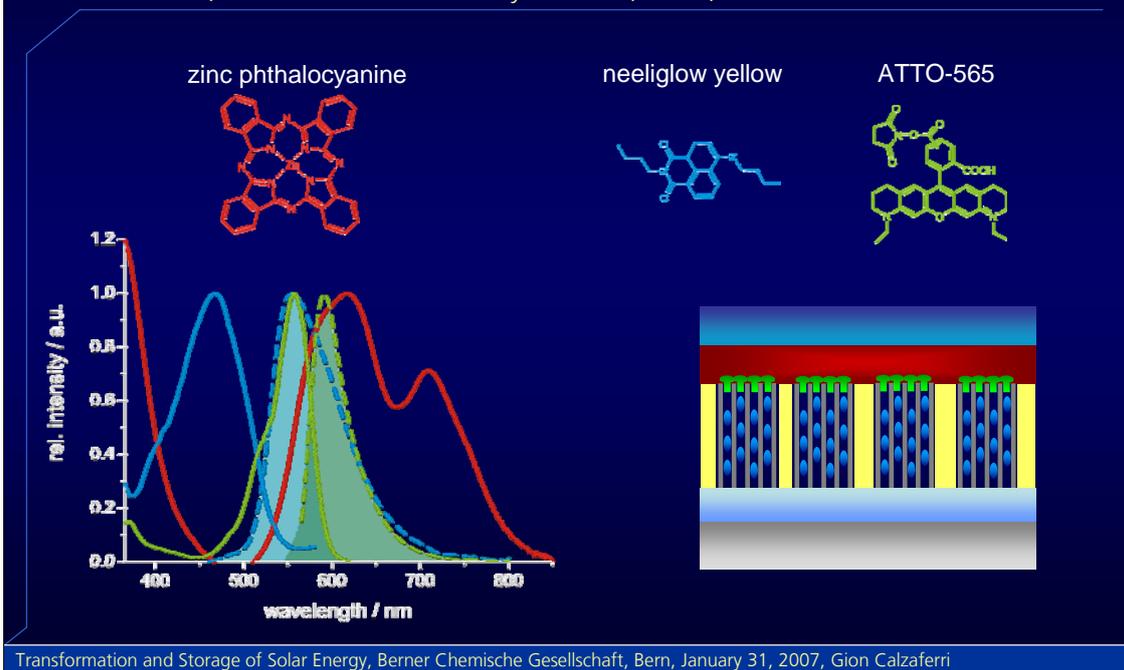
Or with a semiconductor

Or with a molecular magnet

Or – we should also have something for our biochemists - we can try to communicate with a biochemical or a biological object.

5. Organizing the crystals – communication with a molecule

Energy Transfer from Dye-Zeolite L Antenna Crystals to Bulk Silicon
Stefan Huber, Gion Calzaferri *ChemPhysChem* 5, 2004, 239-242.



Sometime ago we have demonstrated that electronic excitation energy can be transferred to silicon through an approximately 3 nm thin silicon dioxide layer, while this does not work when the thickness of the layer is in the order of 100 nm or more, as expected if near-field interaction controls the process.

Here I would like to show you results which might be of more interest to chemists.

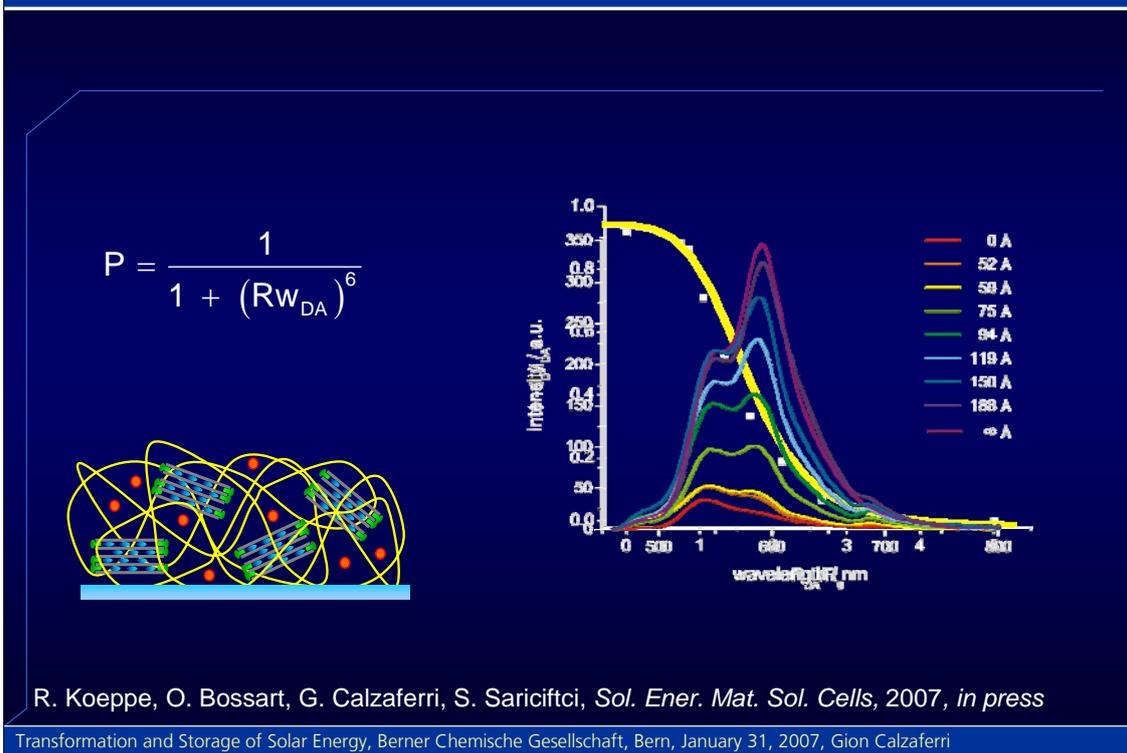
Zinc phthalocyanine can be used for manufacturing organic solar cells. It is an attractive material, however, the efficiency is still too low for being used. One of the reasons for this is the lack of absorption between 400 and 500 nm. One can try to overcome this problem by integrating the antenna material.

First experiments were made by using neeliglow yellow as absorbing dye and ATTO-565 as stopcock. Spectral overlap is perfect so that energy transfer should work well.

A sophisticated device consists of a zeolite antenna monolayer followed by the solar cell part.

In order to know if this works, one has to check how well the energy transfer from the antenna to the device works.

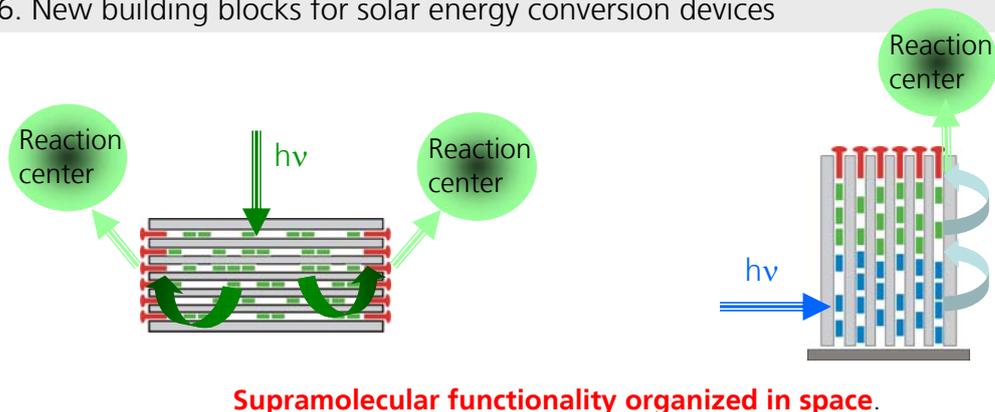
5. Organizing the crystals – communication with a molecule



In fact it works well. The probability for energy transfer is proportional to 1 divided by 1 plus the weighted distance between the donor and the acceptor power to the 6. In this cartoon the zinc phthalocyanine which is the acceptor is marked as red spots.

The fluorescence intensity of the donor decreases with decreasing donor acceptor distance. Plotting this intensity versus the weighted donor to acceptor distance and comparing it with theory shows that Förster energy transfer is fast and efficient.

6. New building blocks for solar energy conversion devices



Supramolecular functionality organized in space.

We have highly organized antenna available, which can communicate to an external object where a specific task is performed.

Is this of any use for solar energy conversion devices?

[Antenna sensitized thin film solar cells](#)

Antenna sensitized thin film [organic solar cells](#)

Antenna sensitized thin film [Si solar cells](#)

[Luminescent concentrators](#)

[Color changing media](#)

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We found a way to organize molecules such that they perform a specific task and that information flows in a chosen direction: this means that we have achieved **supramolecular functionality organized in space**.

This cartoon is a way to summarize the results for a bidirectional antenna. Light is absorbed by the dyes inside of the channels, transported to the stopcock and from there it goes to a reaction center where electron-hole pairs are created or some other task is performed. - The uni-directional system is even more sophisticated, because information or energy flow in only one direction.

Expressing these results in a different way I can say:

We have highly organized antenna available, which can communicate to an external object where a specific task is performed.

Is this of any use for solar energy conversion?

The answer seems to be YES, despite of the many remaining questions.

In any solar energy device, photons must first be absorbed and the excitation energy should reach the right spot. We have contributed to a new solution of this important problem. The new material and concept can now be tested for developing antenna sensitized [thin film solar cells](#),

namely: Antenna sensitized thin film organic solar cells
and Antenna sensitized thin film Si solar cells

for developing a new generation of [luminescent concentrators](#)
and for applications as [color changing media](#).

I wonder if some of our material or concepts survive the demanding step into solar energy applications.

7. Summary

1 Introduction

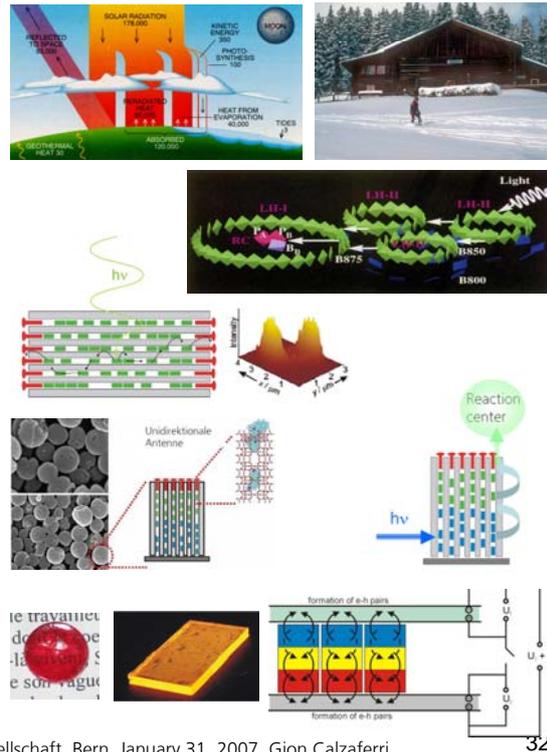
2 Quantum solar energy conversion

3 Learning from green plants

4 An artificial antenna system

5 Organization - communication

6 New building blocks for SEC devices



Transformation and Storage of Solar Energy, Berner Chemische Gesellschaft, Bern, January 31, 2007, Gion Calzaferri

I summarize what I have explained during past hour.

In the introduction I put our research in a broader context. (1)

Then we started focusing on „Quantum Solar Energy Conversion“, (2)

learnt from green plants about the basic principles of their antenna, (3)

and – based on this – we have discussed how an artificial antenna system can be made. (4)

I have then shown that they can be organized so that they work on a macroscopic scale and that they are able to communicate with different objects. (5)

I concluded that the antenna materials developed in my research group is ready for being tested as building blocks in solar energy devices. (6)

I have not spoken about the possibility of realizing tandem solar cells based on the new material.

However, what might be more important is, that we have realized:

supramolecular functionality organized in space.

Quantum solar energy conversion leaves plenty of room for ambitious functional materials research, and we may be surprised to see what kind of devices will come to the market within the next 10 to 20 years.



Let me thank all those who have contributed to this research. Without them, little would have been achieved.

I cannot show everybody who has contributed in one picture.

But my thanks go also to those who are not shown.

Of course I also thank for the money we have received for this research.

And finally I would like to thank you for your kind attention.