Mimicking the antenna system of green plants

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ABSTRACT

Artificial photonic antenna systems have been realised by incorporating organic dyes in a nanoporous material. We have been using zeolite L in most of our experiments as it has proven to be a very versatile host. Its crystals are cylindrically shaped porous aluminosilicates featuring hexagonal symmetry. The size and aspect ratio of the crystallites can be tuned over a wide range. A nanometre sized crystal consists of many thousand one-dimensional channels oriented parallel to the cylinder axis. These can be filled with suitable organic guests. Geometrical constrains of the host structure lead to supramolecular organisation of the guests in the channels. Thus very high concentrations of non- or only very weakly interacting dye molecules can be realised. A special twist is added to these systems by plugging the channel openings with a second type of fluorescent dye, which we call stopcock molecule. The two types of molecules are precisely tuned to each other; the stopcocks are able to accept excitation energy from the dyes inside the channel, but cannot pass it back. The supramolecular organisation of dyes inside the zeolite channels is what we call the first stage of organization. It allows light harvesting within the volume of a dye-loaded zeolite L crystal and also radiationless energy transport to either the cylinder ends or centre. The second stage of organisation represents the coupling to an external acceptor or donor stopcock fluorophore at the ends of the zeolite L channels, which can then trap or inject electronic excitation energy. The third stage of organization is realised by interfacing the material to an external device via a stopcock intermediate. We observed that electronic excitation energy transfer in dye-zeolite L materials occurs mainly along the channel axis. This important finding means that macroscopically organised uni-directional materials can be prepared. In order to achieve this, we prepared oriented zeolite L monolayers, filled them with luminescent dyes, and finally added a stopcock. The new materials offer unique possibilities as building blocks for optical, electro-optical and sensing devices.

Keywords: FRET, host-guest materials, supramolecular chemistry, luminescence, nanochannel, solar energy, dyes/pigments

1. INTRODUCTION

Our design of a model that mimics the key functionality of the antenna system of green plants is based on specific properties of different zeolite materials.[1] We reasoned that a one-dimensional channel system has the advantage of being the simplest possible choice. As a consequence, we considered to use zeolite L, which was well known, as the host.[2-4] In a theoretical and preliminary experimental study, we examined cylinders containing green emitting donor molecules and at ends red emitting acceptors and we carried out many experiments based on this.[5-9] Host-guest interactions in zeolites has been recently review.[10] Our reasoning can be illustrated by means of Figure 1.[11] The donor molecules are represented in green and the acceptors in red. The donor that has been excited by absorbing an incident photon transfers its electronic excitation to an unexcited neighbor. After series of such steps, the electronic excitation reaches a luminescent trap (acceptor molecule) and is then released as fluorescence. The acceptors are thought to mimic the "entrance of the reaction center RC" of the natural antenna. The dimensions given in Figure 1 correspond to the pore opening and the distance between the centers of two channels in zeolite L. The largest energy transfer rate constant is observed if the electronic transition dipole moments are oriented parallel to the channel axis. We observed quasi one dimensional energy transfer in such systems which is important for realizing a very efficient light harvesting material.[12]
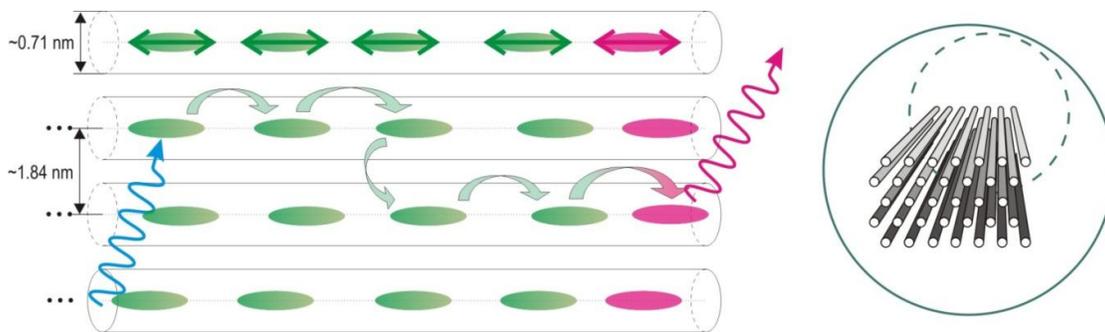
Figure 1. Scheme of an artificial photonic antenna. The chromophores are embedded in the channels of the host. The green dyes act as donor molecules which absorb the incoming light and transport the electronic excitation energy via Förster resonance energy transfer (FRET) to the red acceptors shown at the ends of the channels on the right. The process can be analyzed by measuring the emission of the red acceptors and comparing it with that of the donors. Right: Top view of a bunch of such strictly parallel channels.[11]

2. STOPCOCK PRINCIPLE

We invented nano-stopcocks to realize communication of the dyes inside the zeolite channels with the outside world. These are molecules that consist in principle of a label, a spacer and a head as shown in Figure 2. The head of these molecules is too large to enter the channels. Since stopcock molecules are located at the interface between the interior of a zeolite L crystal and the surroundings, they can be considered as mediators for communication between dye molecules inside the nanochannels and objects outside of the crystals. Fluorescent stopcocks can be used to extract or inject electronic excitation energy into or from the zeolite L crystals by means of FRET. Stopcock molecules can also prevent penetration of small molecules such as oxygen and water or hinder encapsulated molecules, cluster and cations from leaving the channels.[13,14] Imagine a 600 nm diameter zeolite L crystal and *that* you want to close each channel with a stopcock as schematically shown in Figure 2 (middle) – this would mean adding roughly 200'000 stopcocks. It is clear that such a problem is best solved by chemical means, which is by methods dealing with a large number of objects, and not by a physical approach which would address one channel opening after the other. Depending on the type, stopcocks can be bound either by physisorption, by electrostatic interaction, by covalent bonding or by a combination of electrostatic and covalent bonding. A selection of stopcocks successfully used so far can be found in ref. [11].

Figure 2. Stopcock principle. Left: A channel entrance with a schematically represented stopcock molecule. Middle: Schematic representation of a zeolite crystal plugged with stopcock molecules at the channel entrances. Right: Confocal fluorescence microscopy images of an ATTO680-zeolite L crystal. The two images indicate that only the base of the crystal is modified with ATTO680. The zeolite crystal is marked with a rectangle in the image on the left side.

The best way to find out if and where the molecules are attached to a crystal is fluorescence microscopy – if possible in confocal mode – on crystals of different size. Figure 2(right) shows as an example ATTO-680 covalently attached to both ends of a zeolite L crystal. The red luminescence on both crystal bases comes from the attached ATTO-680.[15] Stopcock plugged antenna are dye loaded zeolite crystals where either the donors or the acceptors are stopcock molecules.
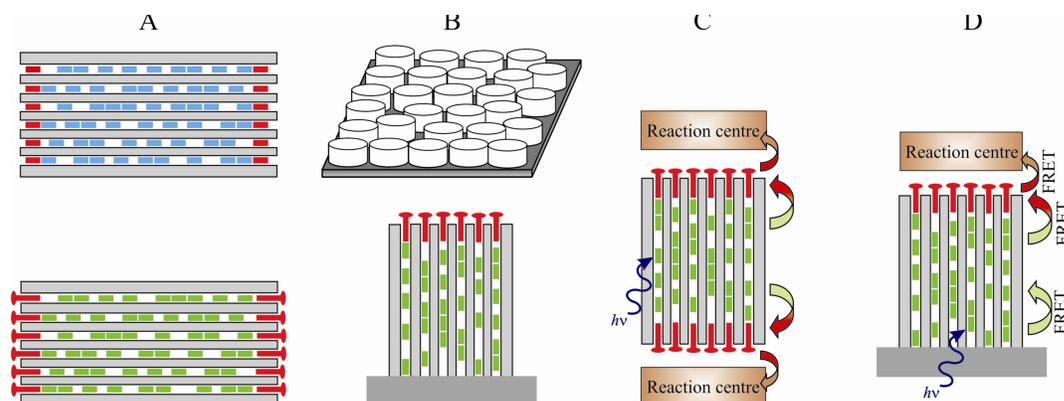
Figure 3. Representation of materials that have been successfully prepared fulfilling the criteria of different stages of supramolecular organisation. The length of the cylindrically shaped crystals is in the order of 50 nm up to a few hundred nm. A: Antenna materials are obtained by the consecutive insertion of different dye molecules. Bidirectional stopcock-plugged antenna materials are obtained by modifying the channel entrances with specific stopcock molecules. B: Oriented monolayers of standing zeolite L crystals on a substrate (top).[16,17] C and D: Interfacing antenna crystals to a reaction centre via stopcock molecules. Bidirectional (C) and monodirectional (D) electronic excitation energy transport materials connected to a photoelectronic or photochemical reaction centre. The excitation energy from the dyes in the channels (green rectangles) is transported via FRET to the stopcock molecules (red) located at the entrances. From there, the electronic excitation energy is transferred radiationless by near field interaction (FRET) to a reaction centre.

The stopcock principle outlined above allows for the communication of dyes inside the channels with external species like a molecule, a polymer matrix, a semiconductor, a quantum sized particle, a molecular- or a nano-magnet, and a biochemical or a biological object. This principle is illustrated in Figure 3 for a bidirectional (C) and a monodirectional (D) electronic excitation energy transport material.[11] Here, we describe an energy transfer material in which solvent green (SG5) was inserted into the channels of zeolite L from the gas phase and the bodipy dye BNCO[18,19] was attached to the channel entrances according to a procedure described in ref. [20], Scheme 1, as an example. The organization of the obtained material corresponds to the principle illustrated in Figure 3A. When handling SG5 care must be taken in order to avoid hydrolysis which affects the spectroscopic properties.[21]
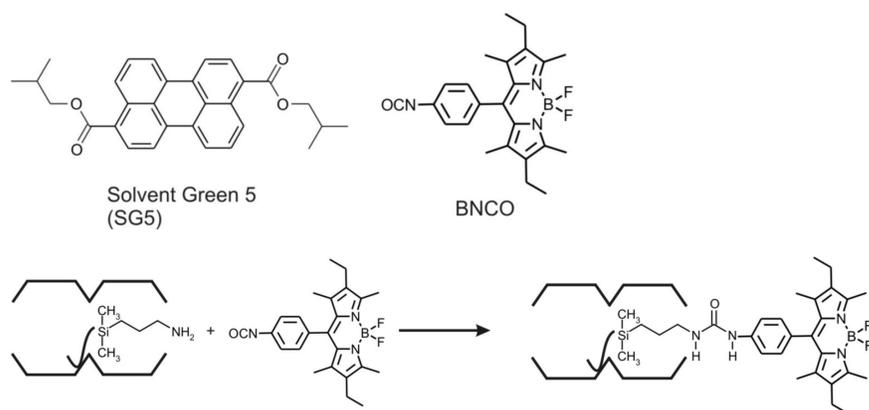
Scheme 1. Structure of the dyes (top) and covalent binding of the BNCO to the channel entrance (bottom).[20]

Figure 4 shows the result of an energy transfer experiment of a system as explained in Figure 3 (A, bottom). The fluorescence spectrum of SG5 and the excitation spectrum of BNCO shown on the left indicate a large spectral overlap which is essential for efficient Förster resonance energy transfer (FRET).[22] We report on the right of Figure 4 the excitation and the fluorescence spectra of the bidirectional BNHCO-,SG5-zeolite L antenna material. It shows that energy transfer from SG5 to the bodipy attached to both sides of the cylindrically shaped crystals is nearly quantitative. Similar experiments have also been made on monolayers of standing zeolite L crystals corresponding to the organization seen in Figure 3B.[11]
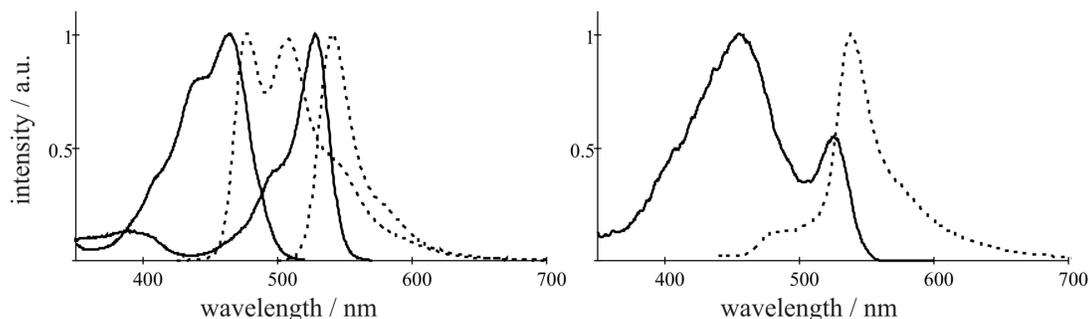

Figure 4. Energy transfer experiment. Left: Excitation (solid) and emission (dashed) spectra of SG5 in ethanol and of BNCO in CH_2Cl_2. The emission spectrum of SG5 in zeolite L was recorded upon excitation at 410 nm; the excitation spectrum was detected at 560 nm. The emission spectrum of BNCO was recorded upon excitation at 460 nm; the excitation spectrum was detected at 600 nm. Right: Excitation (solid) and emission (dashed) spectra of BNC-,SG5-zeolite L. The emission spectrum was recorded after selective excitation of SG5 at 430 nm. The excitation spectrum was detected at 640 nm.

3. NEW BUILDING BLOCKS FOR QUANTUM SOLAR ENERGY CONVERSION DEVICES

An antenna material which absorbs all light in the right wavelength range and transfers the electronic excitation energy by radiationless energy transfer (FRET) to well organized acceptors offers a unique possibility for developing dye sensitized solar cells, luminescent solar concentrators or colour changing media. The concepts are explained in Figure 5.

The principle of this kind of sensitised solar cell functions by first absorbing light over a broad spectral range in the zeolite antenna material. The excitation energy migrates radiationless among the inserted dyes towards the stopcock molecules. From there FRET to the semiconductor takes place across a very thin insulating layer. The injected electronic excitation energy can now be used for driving the charge separation process in the active medium. Finally, the resulting electrical current is collected via appropriate contacts. We show in Figure 5 two

strategies that can be followed. B refers to thin layer silicon cells and C to organic solar cells where the design must match the short free path lengths of the charge carriers in such devices.[8,15,23] Phthalocyanine stopcocks into which the insulating layer, needed to prevent electron transfer, is directly integrated as substutuents are especially attractive.[24] Energy can also be transferred from an appropriately chosen semiconductor to the antenna composites by reversing the current and putting a voltage over the semiconductor. The dye-zeolite composites on the semiconductor surface subsequently lose their energy by emitting light. The colour of the emission can be tuned by adapting the ratio of blue, yellow, and red fluorescent dyes, which means that white light emission is possible. High energy efficiency and easily adaptable emission spectra are expected for (O)LEDs made by using this principle.[8,11]

A luminescent solar concentrator (LSC) is a transparent plate containing luminescent chromophores.[25] Light enters the face of the plate and is absorbed and reemitted by these centers. A fraction of the luminescent light is trapped by total internal reflection and guided to the edges of the plate where it can be converted to electricity by a photovoltaic device. As the edge area of the plate is much smaller than the face area, the LSC operates as a concentrator of light. A major loss in conventional LSC is the overlap between absorption and emission spectra as can be seen e.g. in Figure 4 (left). Self-absorption therefore becomes an important loss mechanisme.[26] A solution to this is to use antenna material as explained in Figures 3A, 3B and 5A. Absorption and emission spectra are separated by employing an absorbing dye present in large amount and a monolayer of an emitting dye.[24,27] A further advantage of using this material is that the photo-stability of many dyes can be considerably improved by embedding into the channels of zeolite L which protects them due to confinement. We show in Figure 5D an experiment where DXP was used as absorbing dye and ATTO 565 as emitter. The thickness of the active layer, which is embedded between two glass plates, is in the order of a few micrometers and light scattering has been suppressed by a procedure reported in ref. [28].
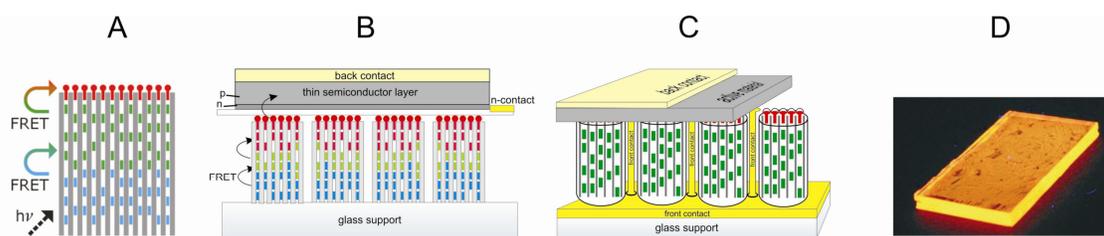

Figure 5. New building blocks for solar energy conversion devices. **A:** We show on the left the principle of these new building blocks, consisting of nanochannels containing two types of dye molecules (blue and green) and stopcocks (red). Light absorbed by the blue and also the green molecules travels to the stopcock heads radiationless by near field interaction (FRET). **B** and **C:** Principle of dye sensitized solar cells. Arranging crystals, of a length of 50 nm up to a few hundred nm, with their *c*-axes perpendicular to the surface of a semiconductor allows transport of the excitation energy towards the zeolite-semiconductor interface by FRET. Stopcock molecules are placed only at one channel end to. The semiconductor layer can be very thin, because the electron-hole pairs form near the surface. The transfer of electrons from the antenna to the semiconductor is prevented by introducing a thin insulating layer, preferably directly into the stopcock. Scheme B shows a principle related e.g. to thin layer silicon devices. Scheme C is related to organic or plastic solar cells. The white area on top of the head is an insulating part directly integrated into the stopcock. The zeolite material is enlarged with respect to the rest of the device. D: Small fluorescent concentrator (2cm x 1cm) with DXP as donor and ATTO 565 as acceptor which acts as emitter dye.

REFERENCES

[1]   D. W. Breck, *"Zeolite Molecular Sieves"*, John Wiley & Sons, New York (1974).
[2]   S. Ernst, J. Weitkamp, "Synthesis of large pore alumisilicates", *J. Catal. Today*, **19**, 27–60 (1994).
[3]   Ch. Baerlocher, W. M. Meier, D. H. Olson, *"Atlas of Zeolite Framework Types"*, Elsevier, Amsterdam, 5th edn (2001).
[4]   T. Ohsuna, B. Slater, F. Gao, J. Yu, Y. Sakamoto, G. Zhu, O. Terasaki, D. E. W. Vaughan, S. Qiu, C. R. A. Catlow, "Fine structures of zeolite-Linde-L (LTL): Surface structures, growth unit and defects", *Chem. Eur. J.*, **10**, 5031–5040 (2004).
[5]   N. Gfeller, G. Calzaferri, "Energy migration in dye-loaded hexagonal microporous crystals", *J. Phys. Chem.*, **101**, 1396–1408 (1997).
[6]   S. Megelski, G. Calzaferri, "Tuning the size and shape of zeolite L based inorganic/organic host/guest composites for optical antenna systems", *Adv. Funct. Mater.*, **11**, 277–286 (2001).
[7]   G. Calzaferri, M. Pauchard, H. Maas, S. Huber, A. Khatyr, T. Schaafsma, "Photonic antenna system for light harvesting, transport and trapping", *J. Mater. Chem.*, **12**, 1–13 (2002).
[8]   G. Calzaferri, S. Huber, H. Maas, C. Minkowski, "Host-guest antenna materials", *Angew. Chem. Int. Ed.*, **42**, 3732–3758 (2003).
[9]   G. Calzaferri, S. Huber, A. Devaux, A. Zabala Ruiz, H. Li, O. Bossart, L.-Q. Dieu, "Light-harvesting host-guest antenna materials for photonic devices", in *Proc. of SPIE, Org. Optoelectronics and Photonics II*, **6192**, 619216-1–9 (2006).
[10]   T. Bein, "Host-guest interactions is zeolites and periodic mesoporous materials", *Studies in Surface Science and Catalysis, Vol. 168: Introduction to Zeolite Chemistry*, eds J. Cejka, H. van Bekkum, A. Corma, F. Schüth, Elsevier, Amsterdam, 3d revised edn, pp. 611–658 (2007).
[11]   G. Calzaferri, K. Lutkouskaya, "Mimicking the Antenna System of Green Plants", submitted for publication
[12]   C. Minkowski, G. Calzaferri, "Förster-type energy transfer along a specified axis", *Angew. Chem. Int. Ed.*, **117**, 5459–54630 (2005).
[13]   G. Calzaferri, "Dye-loaded zeolite materials", *US and EU patent*, WO 02/36490 A1, prior. date (2000).
[14]   H. Maas, G. Calzaferri, "Trapping energy from and injecting energy into dye-zeolite nanoantennae", *Angew. Chem. Int. Ed.*, **41**, 2284–2287 (2002).
[15]   S. Huber, G. Calzaferri, "Energy transfer from dye-zeolite L antenna crystals to bulk silicon", *ChemPhysChem*, **5**, 239–242 (2004).
[16]   A. Zabala Ruiz, H. Li, G. Calzaferri, "Organizing supramolecular functional dye-zeolite crystals", *Angew. Chem. Int Ed.*, **45**, 5282–5287 (2006).
[17]   H. Li, Y. Wang, W. Zhang, B. Liu, G. Calzaferri, "Fabrication of oriented zeolite L monolayers employing luminescent perylenediimide-bridged Si(OEt)$_3$ precursor as the covalent linker", *Chem. Commun.*, 2853–2854 (2007).
[18]   R. Ziessel, C.Goze, G.Ulrich, M. Césario, P. Retailleau, A. Harriman, J. P. Rostron, "Intramolecular energy transfer in pyrene-bodipy molecular dyads and triads", *Chem. Eur. J.*, **11**, 7366–7378 (2005).
[19]   G. Ulrich, R. Ziessel, A. Harriman, "The Chemistry of Fluorescent Bodipy Dyes: Versatility Unsurpassed", Angew. Chem. Int. Ed. **47**, 1184-1201 (2008).
[20]   S. Huber, G. Calzaferri, "Sequential functionalization of the channel entrances of   zeolite L Crystals", *Angew. Chem. Int. Ed.*, **43**, 6738–6742 (2004).
[21]   R. Q. Albuquerque, G. Calzaferri, "Proton activity inside the channels of zeolite L", *Chem. Eur. J.*, **13**, 8938–8952 (2007).
[22]   Th. Förster, „Zwischenmolekulare Energiewanderung und Fluoreszenz", *Ann. Phys.*, **437**, 55–75 (1948).
[23]   R. Koeppe, O. Bossart, G. Calzaferri, N.S. Sariciftci, "Advanced photon harvesting concepts for low energy gap organic solar cells", *Sol. Energy Mater. Sol. Cells*, **91**, 986–995 (2007).
[24a]   D. Brühwiler, L.-Q. Dieu, G. Calzaferri, "Nanochannel materials for quantum solar energy conversion devices", *Transformation and Storage of Solar Energy, Special Issue CHIMIA*, **61**, 820–822 (2007).
[24b]   L.-Q. Dieu, A. Devaux, I. López-Duarte, M. V. Martínez-Díaz, D. Brühwiler, G. Calzaferri, T. Torres, "Novel phthalocyanine-based stopcock for zeolite L", *Chem. Commun.*, 1187-1189 (2008).
[25]   J. S. Batchelder, A.H. Zewail, T. Cole, "Luminescent solar concentrators. Theory of operation and techniques for performance evaluation", Applied Optics, **18**, 3090-3110 (1979).
[26]   P. Kittidachachan, L. Danos, T. J.J. Meyer, N. Alderman, T. Markvart, "Photon Collection Efficiency of Fluorescent Solar Collectors", *CHIMIA*, **61**, 780–786 (2007).

[27]   Gion Calzaferri, Arantzazu Zabala Ruiz, Huanrong Li, Stefan Huber, "Oriented zeolite material and method for producing the same", PCT/CH2006/000394; priority US 60/698,480 and CH 1266/05 (2005).
[28]   S. Suárez, A. Devaux, J. Bañuelos, O. Bossart, A. Kunzmann, G. Calzaferri, "Transparent zeolite-polymer materials with adaptable properties", *Adv. Funct. Mater.*, **17**, 2298–2306 (2007).