

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

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## ABSTRACT

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 are of cylindrical shape and consist of an extended one-dimensional tube system. They 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. Moreover, fluorescent dye molecules can be bound covalently to the channel entrances. Dependent on the spectral properties of these stopcock molecules, the electronic excitation energy is transported radiationless to the stopcock fixed at the ends of the nanochannels or injected from the stopcock to the dyes inside the zeolite. The radiationless energy migration is in competition with spontaneous emission, thermal deactivation, quenching, and photochemically induced degradation. Fast energy migration is therefore crucial for an efficient antenna material. - The supramolecular organization of the dyes inside the channels is a *first stage of organization*. It allows light harvesting within the volume of a dye-loaded zeolite L crystal 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.

**Keywords:** zeolites, monolayers, host-guest systems, FRET, dyes/pigments, solar cells, artificial antenna, luminescence, unidirectional.

## 1. INTRODUCTION

Plant photosynthesis, the conversion of light into chemical energy, is greatly fascinating. As a radio uses an antenna to absorb electromagnetic waves from the atmosphere, plants use their chlorophyll to capture certain wavelengths of visible light and pass its energy on to their photosynthetic apparatus.<sup>[1,2]</sup> Such "photonic antennas" would also be great for technical applications, particularly for a new, more efficient generation of solar cells. Several interesting attempts are presented in the literature, e.g. panchromatic chromophore mixtures in an AlPO<sub>4</sub>-5 molecular sieve, faujasite incorporated dye molecules, or polymer embedded iridium complexes that show interesting luminescence properties.<sup>[3-6]</sup> Promising results were obtained with artificial photonic antennae, where a strongly fluorescent dye is introduced in the linear channels of zeolite crystals in order to capture light. When the fluorescent dye is irradiated, a small portion of the energy released in this process is dispersed as vibrations throughout the molecules, the rest of the energy is emitted as fluorescence. When the dye molecules are inserted in the parallel channels of the crystals, they are neatly packed right up against each other. This allows them to transfer the excitation energy directly - without conversion into light - from

molecule to molecule. Furthermore, the openings of the channels are plugged with a second type of fluorescent dye, so called stopcock molecules.<sup>[7]</sup> The two types of molecules are precisely tuned to each other; the stopcocks are thus also able to accept excitation energy from the dyes inside the channel, but they are not able to pass it back. The stopcocks can re-emit the energy as fluorescence on the surface of the little crystals, or, in a more advanced setup, transfer it radiationless to a photoelectronic or a photochemical device. This receiving antenna can alternatively be made into a transmitter if the two fluorescent dyes are more or less switched. The stopcocks capture energy from outside, which they then pass on to the molecules inside the crystals. These then fluoresce, which is useful e.g. for making light emitting diodes.<sup>[8,9]</sup>

## 2. RESULTS AND DISCUSSION

### 2.1. Host Material

Zeolites are porous silicates of different size, shape and geometry that can uptake a large variety of guest molecules. Promising results were obtained with colloidal materials where mesoporous spheres are used as a template to prepare zeolite monoliths.<sup>[10,11]</sup> Zeolite L is a crystalline aluminosilicate with hexagonal symmetry.<sup>[12-17]</sup> Its anionic framework and the positions of the charge-compensating cations are illustrated in Fig. 1. The crystals consists of cancrinite cages ( $\epsilon$ -cages) linked by double 6-membered rings. These units form columns in the  $c$  direction which are connected, and thus form a 12-membered ring with a free diameter of 0.71 nm. This gives rise to one-dimensional channels running through the whole crystal, with a largest free diameter of 1.26 nm and a unit cell length of 0.75 nm. The main channels are linked via nonplanar 8-membered rings which form an additional two-dimensional channel system with ring opening of about 0.15 nm. The centre-to-centre distance between two main channels is 1.84 nm. The hexagonal structure of the zeolite L material is visible in the scanning electron microscopy picture. This also illustrates that the shape of the crystals can be described well by assuming cylinder morphology. The number of channels lying parallel to the  $c$  axis is equal to  $0.265(d_c)^2$ , where  $d_c$  is the diameter of the cylinder in nanometres. As an example, a crystal with 550 nm diameter consists of about  $8 \cdot 10^4$  parallel channels. Zeolite L has an anionic framework. Four different cation sites (A, B, C, D) have been reported. The water molecules in the large cavities of zeolite L have been reported to behave like an intercrystalline liquid, whereas they seem to build clusters around the cations in the smaller pores.<sup>[15]</sup> The stoichiometry of zeolite L with monovalent cations is  $(M)_9[Al_9Si_{27}O_{72}] \cdot nH_2O$ , where  $n$  equals 21 in fully hydrated materials, and 16 at about 22 % relative humidity. We have synthesized zeolite L crystals in the size range of 30  $\mu$ m up to about 7000 nm.<sup>[16]</sup>

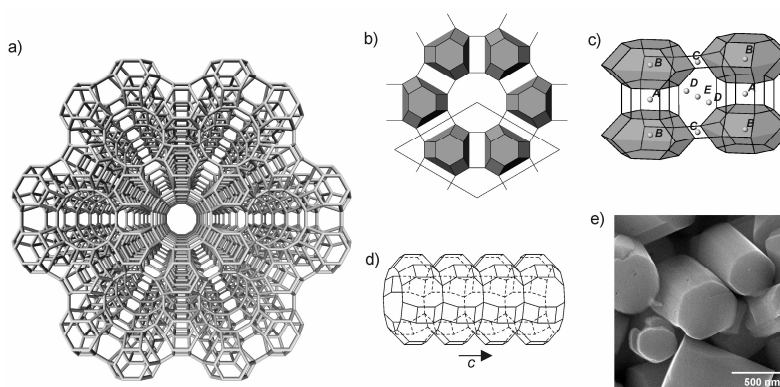
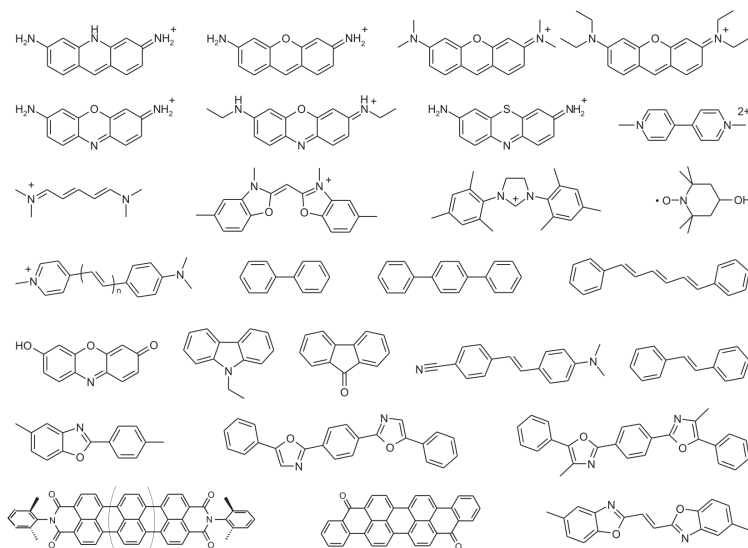


Figure 1. Zeolite L framework: a) projection along the  $c$  axis, b) with the cancrinite cages highlighted as polyhedra, c) section showing the different cationic positions A to E, d) side view of the 12-ring channel, e) scanning electron microscopy image of zeolite L crystals.

Scheme 1 lists some of the dye molecules that have been incorporated in the channels of zeolite L.



Scheme 1. Some dyes that have been incorporated in the channels of zeolite L.

## 2.2. Dye-Loaded Zeolite L Materials

The incorporation of guest molecules in the cavities of molecular sieves leads to a large variety of highly interesting materials. We now present materials where molecules – as listed in Scheme 1 – are incorporated in the channels of zeolite L.<sup>[8,18,19]</sup> The cationic dyes can be incorporated in the channels via ion exchange, the neutral dyes are inserted from the gas phase. Materials that have been synthesized by us can be divided into four categories, depending on the stage of organization of the dye molecules; Fig. 2.

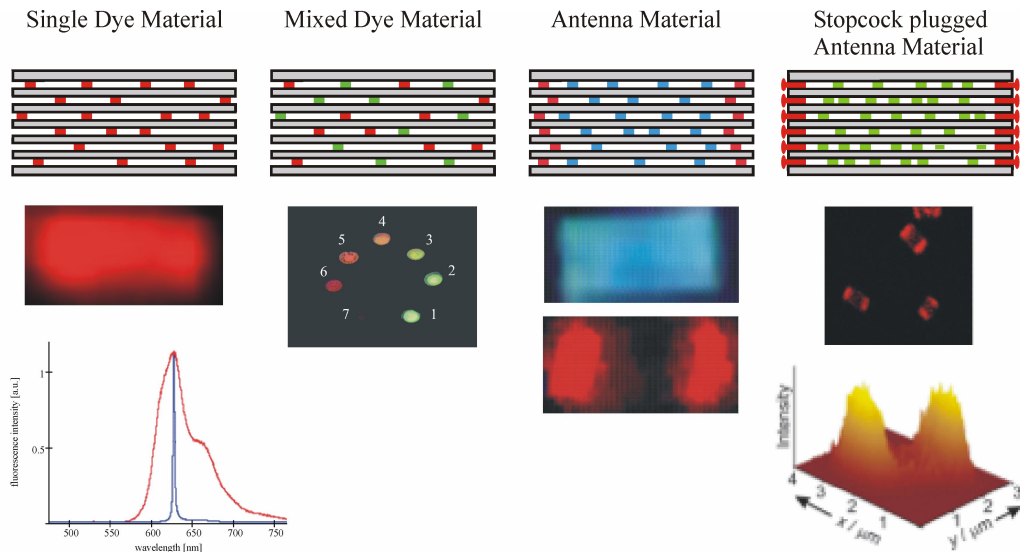


Figure 2. Overview of dye-zeolite L materials. *Single dye material*. Top: Zeolite L crystal loaded with one kind of dye. Middle: Fluorescence microscopy image of a zeolite L crystal containing red emitting dyes. Bottom: Fluorescence of an  $\text{Ox}^+$ -loaded zeolite L crystal after electronic excitation. By increasing the excitation power, the crystal starts to show lasing, as illustrated by the narrow emission band with a FWHM of 2 nm; the crystal has a length of about 1000 nm. *Mixed dye material*. Top: Zeolite L crystal loaded randomly with two different kinds of dyes. Bottom: Photograph of the fluorescence of dye-loaded zeolite L layers upon monochromatic irradiation at 485 nm and observation through a cut-off filter. 1 and 7 are references loaded with  $\text{Py}^+$  and  $\text{Ox}^+$ . Probes 2 to 6 contain a 1:1 mixture of  $\text{Py}^+$  and  $\text{Ox}^+$  with increasing overall concentration from 2 to 6. *Antenna material*. Top: Zeolite L crystal consecutively loaded with different dye molecules. Bottom: Fluorescence microscopy image of such a zeolite L crystal,

containing blue emitting dyes in the middle (middle) and red emitting dyes at the channels endings (bottom). *Stopcock plugged antenna material*. Top: Zeolite L crystal loaded with one kind of dye molecule and then sealed with a stopcock molecule. Middle: confocal microscopy image of the red emission of the stopcock molecules located at the channel endings. Bottom: Confocal microscopy image of the local fluorescence intensity of a crystal with fluorescing stopcocks at the channel endings.

*Single dye materials* contain zeolite L crystals that are filled with only one kind of dye molecule. Interesting photophysical properties of the dye molecules can be studied, e.g. polarisation experiments, since the host lattice implies a strict arrangement of the guest molecule,<sup>[20]</sup> light-induced reorganization like photoisomerization,<sup>[21]</sup> or changes in the conformation of the guest molecules due to steric constraints imposed by the zeolite.<sup>[22]</sup> Furthermore, such crystals can act as nanolasers, see Fig. 2 *bottom*, where the dye molecules start to emit laser light by increasing the excitation power.<sup>[23]</sup>

*Mixed dye materials* consist of zeolite L crystals randomly filled with different dye molecules. This can only be realized when the dyes enter the channels at about the same speed. If the spectral properties of the dyes are such that the emission spectra of one dye (donor) has a large overlap integral with the excitation spectra of the other dye (acceptor), Förster type energy transfer from one dye to the other can be observed. A visual demonstration of the energy transfer is based on the observation that  $\text{Py}^+$  and  $\text{Ox}^+$  are inserted in zeolite L at about equal rates. It is therefore possible to control the mean distance between donors  $D$  and acceptors  $A$  by varying the concentration. Electronically excited donors transfer their energy to the acceptors with a rate that depends on their distance.<sup>[24]</sup> The picture in Fig. 2 *bottom* shows 7 luminescent samples of zeolite L crystals. They were filled with equal amounts of  $\text{Py}^+$  (donor) and  $\text{Ox}^+$  (acceptor), increasing the overall dye amount from sample 2 to 6. Due to their favourable spectral properties and their high fluorescence quantum yields, this donor-acceptor pair exhibits remarkable excitation energy transport capability via  $\text{Py}^+$  energy carriers to luminescent  $\text{Ox}^+$  traps. In all cases  $\text{Py}^+$  was selectively excited at  $485 \pm 5$  nm, where the absorption of  $\text{Py}^+$  is strong and that of  $\text{Ox}^+$  very weak. The two references 1 and 7 are loaded with only  $\text{Py}^+$  and  $\text{Ox}^+$ , respectively. As can be seen, only the  $\text{Py}^+$ -zeolite L sample 1 is excited. The other samples contain a 1:1 mixture of  $\text{Py}^+$  and  $\text{Ox}^+$  with increasing concentrations. We observe in 2 mainly the green luminescence of  $\text{Py}^+$ . This means that the energy transfer is unimportant. But the yellow colour of 3 is due to a mixture of green and red luminescence which means that energy transfer is significant in this sample. It becomes more and more important with increasing concentration, from sample 5 on, the red luminescence stemming from  $\text{Ox}^+$  is dominant.

For the *antenna materials*, the dyes are incorporated consecutively in the channels of zeolite L. Since the conditions are such that the dyes cannot glide past each other, the crystal is divided into compartments where the density of one dye is dominant. If first a donor is incorporated and then an acceptor, the energy after selective excitation of the donor is transported from the middle to the channel endings, if an acceptor is incorporated first and then a donor, the excitation energy of the donor is transported from the endings to the middle of the crystal. According to this, crystals also containing three different dyes can be synthesized.<sup>[25]</sup>

For the *stopcock plugged antenna materials*, as the name says, the channels are enclosed with “plugs” – so called stopcock molecules.

### 2.3. The Stopcock Principle

Stopcock molecules have a narrow label which can penetrate the channels of zeolite L, and a head that is too large to be inserted, see Fig. 3. Label and head are connected by an inert flexible spacer. Due to this shape they are able to plug the channel entrances in a champagne-cork manner.

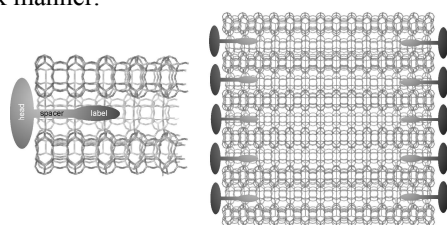


Figure 3. Stopcock principle. *Left*: typical shape of a stopcock with a label that penetrates the channel and a head that is too large to enter. Label and head are connected with an inert flexible spacer. *Right*: A few channels that are plugged with stopcocks.

These stopcock molecules connect the guest molecules inside, with materials or molecules outside of the zeolite channels since they act as extensions of the interior of the zeolite crystal.<sup>[7,8,26]</sup> This can be a reaction centre of i) molecular dimension, e.g. a head of a stopcock molecule which changes its properties as a function of the pH, or the

presence of a specific molecule, ii) macromolecular dimension like photoinducing or conducting polymers, quantum dots or semiconductors, and iii) macroscopic dimension like semiconductors, conductors, and quantum wells. Furthermore, they can prevent small molecules like H<sub>2</sub>O or O<sub>2</sub> from diffusing into the channels.<sup>[8]</sup> — Communication via energy transfer can be achieved by using stopcocks containing a strongly fluorescing unit. Such stopcock molecules can either trap the electronic excitation energy (acceptor stopcock) from a donor inside the channels, or inject electronic excitation energy to an acceptor inside the channels (donor stopcock). We distinguish between different types of stopcock molecules, depending on the way they are linked to the channel entrances. *Reversible stopcocks* are only weakly bound to the zeolite framework.<sup>[7,27]</sup> They are attached by adsorption. An example is the green fluorescing B493/503 molecule that can inject its excitation energy to the red emitting Ox<sup>+</sup> molecules inside the zeolite, see Fig. 4 *top*, left. Fig. 4 *top*, right shows the emission spectra of 30 nm long Ox<sup>+</sup>-zeolite crystals modified with one B493/503 molecule per channel after exciting the B493/503. The Ox<sup>+</sup> loading was chosen to be low, so that 3.5 times more donor molecules were present than acceptor molecules.<sup>[28]</sup> According to this, another reversible stopcock, the green fluorescing MFG, is presented in Fig. 4, *middle*, left. Its emission spectrum overlaps with the excitation spectrum of Ox<sup>+</sup>, and therefore, energy transfer from the stopcock to the Ox<sup>+</sup> molecules inside the channels is expected. The emission spectrum of MFG modified Ox<sup>+</sup>-zeolite L after selectively exciting MFG is shown in Fig. 4, *middle*, right. The crystals are 30 nm long, the average loading of Ox<sup>+</sup> was again low, every channel modified with a MFG molecules at each side.<sup>[29]</sup> The MFG stopcock can be used as energy trap for blue emitting donor dyes like MC<sup>+</sup> inside the channels, see Fig. 4, *bottom*, left. After selectively exciting the MC<sup>+</sup> of MFG modified MC<sup>+</sup>-zeolite L crystals, the emission spectrum of Fig. 4, *bottom*, right, is obtained. The crystal length is also 30 nm; every channel contains approximately 2 MC<sup>+</sup> in the middle and one MFG at every channel entrance.<sup>[28]</sup>

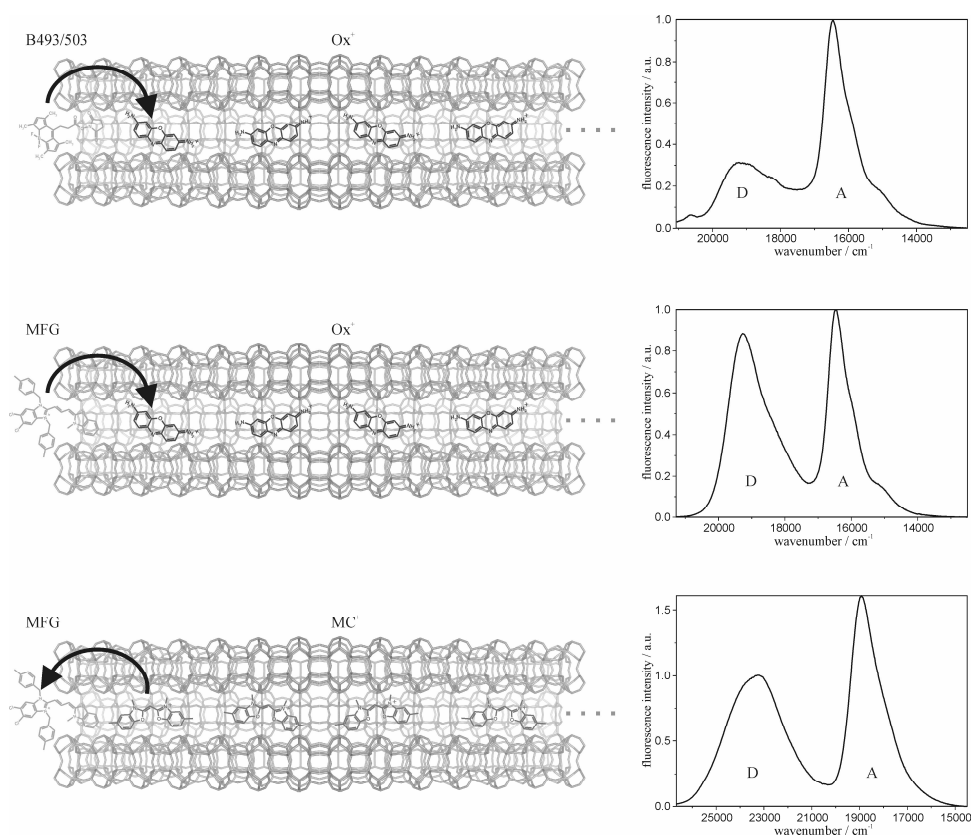


Figure 4. Electronic excitation energy transfer from donor-stopcocks to acceptors inside the zeolite channels, and vice versa. The emission coming from the donors is denoted with D and that of the acceptors with A. Left: Scheme of three stopcock plugged antenna systems, *top* and *middle* with donor stopcocks that inject their excitation energy into the channels, *bottom* with an acceptor stopcock that traps the excitation energy from inside the channel. Right: corresponding emission spectra after selective excitation of the donor. The donors were selectively excited at 21740 cm<sup>-1</sup> (*top*), 22000cm<sup>-1</sup> (*middle*), and 28570 cm<sup>-1</sup> (*bottom*).

*Covalently bound stopcocks* form a bonding via  $-\text{Si-O-Si}-$  and  $-\text{Si-O-Al}-$  where we distinguish between a) covalently bound stopcocks that react via  $-\text{Si}(\text{OR})_3$  and that cannot enter the channels,<sup>[26]</sup> b) reaction of the stopcock in the channel,<sup>[30]</sup> and c) sequential functionalization, a very flexible principle.<sup>[31]</sup>

*Electrostatically bound stopcocks* contain either a positively charged head, or a positively charged tail, where the tail can bare one or more positive charges.<sup>[32,29]</sup>

#### 2.4. Förster Type Energy Transfer along a Specified Axis

One-dimensional electronic excitation energy transfer has been discussed in a number of theoretical studies, see e.g. ref [33]. We have recently observed electronic excitation energy in a quasi-one-dimensional manner in dye-zeolite L materials.<sup>[34]</sup> This observation is of considerable interest for developing highly anisotropic opto-electronic devices.

#### 2.5. Unidirectional materials

Special arrangements of zeolite crystals containing guest species constitute another hierarchy of structural order and are important for the development of specific applications.<sup>[8,9]</sup> We have developed methods for generating robust monolayers of zeolite L crystals having the channels perpendicular to the surface of the substrate and we have shown that subsequent insertion of dye molecules in the open channel is possible.<sup>[35]</sup> In these systems which we illustrate in Fig. 5 electronic excitation energy is transported in one direction. Such a unidirectional photonic antenna is optimal for coupling to an external e.g. macroscopic device.

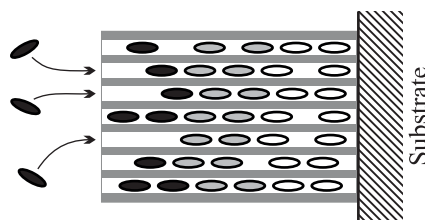


Figure 5. Strategy for synthesizing unidirectional photonic antennae. Attachment of the base of zeolite L crystals to a substrate allows filling of the channels from one side only.

#### 2.6. Coupling to external devices

In view of practical applications the coupling of dye-zeolite composites to external devices is of special interest. The coupling of bidirectional antennae (see Fig. 2) to a luminescent or photoconductive polymer offers possibilities for the development of novel LED materials. When embedding zeolite crystals in polymer films, methods to covalently anchor dye molecules on the outer surface of the zeolite can be employed to enhance the contact area between polymer and zeolite. Such grafting procedures which use silane reagents to couple the dyes to the surface of the crystals have been applied to immobilize dye molecules in mesoporous silica.<sup>[36]</sup> We have recently prepared a polymer embedded, surface modified  $\text{Ox}^+$ -zeolite L, for which we observed transfer of electronic excitation energy from the photoconductive polymer to the dye molecules at the external zeolite surface and ultimately to the  $\text{Ox}^+$  molecules located in the channels. Energy transfer from dye-zeolite crystals to bulk silicon has also been demonstrated.<sup>[30]</sup>

### 3. CONCLUSIONS

The great flexibility of these highly organized materials offers fascinating possibilities both for the exploration of excitation energy transfer phenomena and for the development of new photonic devices for solar energy conversion and storage. A dye-sensitized solar cell which employs energy transfer instead of electron injection is of great interest. The advantage of such a cell is that the dyes do not require regeneration. This is in contrast to cells working by electron injection, in which the dyes have to be regenerated by a redox couple. A dye-zeolite composite prepared as a unidirectional antenna opens possibilities for novel sensitized solar cells. Arranging small composite crystals with their *c*-axes perpendicular to the surface of a semiconductor allows transport of the excitation energy towards the zeolite-semiconductor interface by energy migration. Stopcock molecules are placed at the channel ends to allow energy

transfer. Only a very thin semiconductor is needed in this case, because the electron-hole pairs form near the surface. The transfer of electrons from antenna to semiconductor can be prevented by introducing a thin insulating layer. Energy can also be transferred from the 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 color of the emission can be tuned by adapting the ratio of blue, yellow, and red fluorescent dyes, hence also white light emission is possible. Higher energy efficiency is expected for such a system compared to conventional LEDs.

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## REFERENCES

- (a) G. Kodis, P.A. Liddell, L. de la Garza, P.Ch. Clausen, J.S. Lindsey, A.L. Moore, T.A. Moore, D. Gust, J. Phys. Chem. A, **106**, 2036-, 2002.  
(b) R.K. Clayton, Photosynthesis Res., **73**, 63-, 2002.  
(c) T. Ritz, A. Damyanovic, K. Schulten, ChemPhysChem, **3**, 243-, 2002.  
(d) W. Lubitz, Phys. Chem. Chem. Phys. **4**, 5539-, 2002.
- A.N. Macpherson, P.A. Liddell, D. Kuciauskas, D. Tatman, T. Gillbro, D. Gust, T.A. Moore, A.L. Moore, J. Phys. Chem. B, **106**, 9424-, 2002.
- M. Ganschow, Ch. Hellriegel, E. Kneuper, M. Wark, C. Thiel, G. Schulz-Ekloff, Ch. Bräuchle, D. Wöhrle, Adv. Funct. Mater., **14**, 269-, 2004.
- S. Hashimoto, T. Mutoh, H. Fukumura, H. Masuhara, J. Chem. Soc., Faraday Trans., **92**, 3653-, 1996.
- R. Hoppe, G. Schulz-Ekloff, D. Wöhrle, Ch. Kirschhock, H. Fuess, L. Uytterhoeven, R. Schoonheydt, Adv. Mater., **7**, 61-, 1995.
- X. Gong, J.C. Ostrowski, D. Moses, G.C. Bazan, A.J. Heeger, Adv. Funct. Mater., **13**, 439-, 2003.
- H. Maas, G. Calzaferri, Angew. Chem. Int. Ed., **41**, 2284-, 2002.
- G. Calzaferri, S. Huber, H. Maas, C. Minkowski, Angew. Chem. Int. Ed., **42**, 3732, 2003.
- (a) D. Brühwiler, G. Calzaferri, Micropor. Mesopor. Mater., **72**, 1-, 2004.  
(b) G. Calzaferri, M. Pauchard, H. Maas, S. Huber, A. Khatyr, T. Schaafsma, J. Mater. Chem. **2002**, 1, 1.
- L. Tosheva, V.P. Valtchev, Chem. Mater., **17**, 2494, 2005.
- A. Dong, N. Ren, W. Yang, Y. Wang, Y. Zhang, D. Wang, J. Hu, Z. Gao, Y. Tang, Adv. Funct. Mater., **13**, 943-, 2003.
- Ch. Baerlocher, W.M. Meier, D.H. Olson, Atlas of zeolite Framework Types, 5th ed., Elsevier, Amsterdam, 2001.
- T. Ohsuna, B. Slater, F. Gao, J. Yu, Y. Sakamoto, G. Zhu, O. Terasaki, D. E. W. Vaughan, S. Qiu, C.R. Catlow, Chem. Eur. J., **10**, 5031-, 2004.
- O. Larlus, V. P. Valtchev, Chem. Mater., **16**, 3381-, 2004.
- D.W. Breck, Zeolite Molecular Sieves, John Wiley & Sons, New York, 1974.
- (a) S. Megelski, G. Calzaferri, Adv. Funct. Mater., **11**, 277-, 2001.  
(b) A. Zabala Ruiz, D. Brühwiler, G. Calzaferri, Monatshefte für Chemie, **136**, 77-, 2005.
- M. Tsapatsis, AIChE Journal, **48**, 654-, 2002.
- S. Hashimoto, M. Hagiri, N. Matsubara, S. Tobita, Phys. Chem. Chem. Phys., **3**, 5043-, 2001.
- B.-L. Su, V. Norberg, C. Hansenne, Langmuir, **16**, 1132-, 2000.
- S. Megelski, A. Lieb, M. Pauchard, A. Drechsler, S. Glaus, C. Debus, A.J. Meixner, G. Calzaferri, J. Phys. Chem. B, **105**, 25-, 2001.
- (a) K. Hoffmann, F. Marlow, J. Caro, Adv. Mater., **9**, 567-, 1997.  
(b) K. Hoffmann, U. Rensch-Genger, F. Marlow, Micropor. Mesopor. Mater., **41**, 99-, 2000.  
(c) K. Hoffmann, U. Rensch-Genger, F. Marlow, in: F. Laeri, F. Schüth, U. Simon, M. Wark (Eds.), „Host-Guest Systems Based on Nanoporous Crystals”, Wiley-VHC, 501-, 2003.

22. (a) H.L. Casal, J.C. Scaiano, *Can. J. Chem.*, **62**, 628-, 1984.  
(b) H.L. Casal, J.C. Scaiano, *Can. J. Chem.*, **63**, 1308-, 1985.  
(c) J.C. Scaiano, H. García, *Acc. Chem. Res.*, **32**, 783-, 1999.
23. G. Calzaferri, O. Bossart, D. Brühwiler, S. Huber, C. Leiggenger, M. K. van Veen, A. Zabala Ruiz, C. R. Chimie, **9**, 214-, 2006.
24. (a) M. Pfenniger and G. Calzaferri, *ChemPhysChem*, **4**, 211-, 2000.  
(b) K. Lutkouskaya, G. Calzaferri, *J. Phys. Chem B*, in press, 2006.
25. M. Pauchard, S. Huber, R. Méallet-Renault, H. Maas, R. Pansu, G. Calzaferri, *Angew. Chem. Int. Ed.*, **40**, 2839-, 2001.
26. (a) T. Ban, D. Brühwiler, G. Calzaferri, *J. Phys. Chem. B*, **42**, 16348-, 2004.  
(b) D. Brühwiler, G. Calzaferri, *C. R. Chimie*, **8**, 391-, 2005.
27. A. Khatyr, H. Maas, G. Calzaferri, *J. Org. Chem.*, **67**, 6705-, 2002.
28. H. Maas, Dissertation, Universität Bern, 2003.
29. H. Maas, G. Calzaferri, *The Spectrum*, **16**, 18-, 2003.
30. S. Huber, G. Calzaferri, *ChemPhysChem*, **5**, 239-, 2004.
31. S. Huber, G. Calzaferri, *Angew. Chem. Int. Ed.*, **43**, 6738-, 2004.
32. O. Bossart, L. De Cola, S. Welter, G. Calzaferri, *Chem. Eur. J.*, **10**, 5771-, 2004.
33. (a) J. Klafter, J.M. Drake, "Molecular Dynamics in Restricted Geometries", John Wiley & Sons, 1989.  
(b) S.E. Webber, *Chem. Rev.*, **90**, 1469-, 1990.  
(c) J. Klafter, A. Blumen, *J. Chem. Phys.*, **80**, 875-, 1984.  
(d) P. Levitz, J.M. Drake, *Phys. Rev. Letters*, **58**, 686-, 1987.  
(e) J.P.S. Farinha, J.G. Spiro, M. A. Winnik, *J. Phys. Chem. B*, **105**, 4879-, 2001.  
(f) M. Hopmeier, W. Guss, M. Deussen, E.O. Göbel, R.F. Mahrt, *Phys. Rev. Letters*, **82**, 4118-, 1999.
34. (a) C. Minkowski, G. Calzaferri, *Angew. Chem. Int. Ed.*, **44**, 5325-, 2005.  
(b) C. Minkowski, R. Pansu, M. Takano, G. Calzaferri, *Adv. Funct. Mater.*, **16**, 273-, 2006.
35. (a) G. Calzaferri, A. Zabala Ruiz, H. Li, S. Huber, Patentschrift 01266/05, 2005.  
(b) S. Huber, A. Zabala Ruiz, H. Li, G. Calzaferri, "Optical spectroscopy of inorganic-organic host-guest nanocrystals organized as monolayers", manuscript in preparation.
36. A. Devaux, Z. Popović, O. Bossart, L. De Cola, A. Kunzmann, G. Calzaferri, *Micropor. Mesopor. Mater.*, **90**, 69-, 2006.