

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

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## ABSTRACT

Dye-loaded zeolite L host-guest materials were already successfully used in the realisation of efficient light-harvesting antenna systems. A new hierarchy of structural order is introduced by arranging the zeolite L crystals into densely packed, oriented monolayers on a substrate. In device engineering, a high degree of supramolecular organisation is a prerequisite for achieving desired macroscopic properties. The methods we developed to synthesise such monolayers, to fill them with dyes and to terminate them with a luminescent stopcock will be discussed as well as their influence on the design of novel materials. By subsequent insertion of two different types of dye molecules in a zeolite L monolayer, the first unidirectional antenna system was realised. UV-VIS absorption as well as NIR luminescence spectroscopy was carried out on dye-loaded zeolite L monolayers. We also report a novel concept for the preparation of thin layer, silicon based solar cells.

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

## 1. INTRODUCTION

Artificial photonic antenna systems have been realised by incorporating organic dyes in a microporous material. By choosing the appropriate host and insertion conditions, one can ensure that guest molecules inside of the system will only be present as monomers. We have been using zeolite L in most of our experiments as it has proven to be a very versatile host material.<sup>1</sup> Zeolite L crystals are cylindrically shaped, porous aluminosilicates featuring a hexagonal symmetry. They have an electronic absorption spectrum similar to that of pure quartz.<sup>2</sup> 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, like fluorescent dye molecules, allowing the creation of strongly luminescent materials. Geometrical constraints of the hosts framework lead to supramolecular organisation of the guests in the channels. Thus very high concentrations of monomeric dye molecules can be realized. The short distances between them lead to fast radiationless Förster type energy migration where the excitation energy is directly transferred from molecule to molecule, without conversion into light. 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.<sup>3</sup> These 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 stopcocks can re-emit this energy as fluorescence from the crystal surface or, in a more advanced setup, transfer it radiationlessly to a photoelectronic or a photochemical device. Such a "receiving antenna" can alternatively be turned into a "transmitter" if the positions of the two dyes are reversed. The stopcocks now capture energy from the outside and transfer it to the molecules located inside the crystals.

Energy migration is in competition with spontaneous emission, radiationless decay, quenching, and photochemically induced degradation. Fast energy migration is therefore crucial if a trap should be reached before other processes can take place. - The supramolecular organization of 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 organization* 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 recently have observed that electronic excitation energy transfer in dye-zeolite L materials

occurs along a well specified axis.<sup>4</sup> This important finding means that organized, unidirectional materials as shown in Figure 1 (right) can be prepared. In order to achieve this, we have developed methods to synthesize zeolite L monolayers, fill them with dyes, and to finally add a stopcock. These procedures and their repercussions on the design of novel materials will be discussed in the present article.

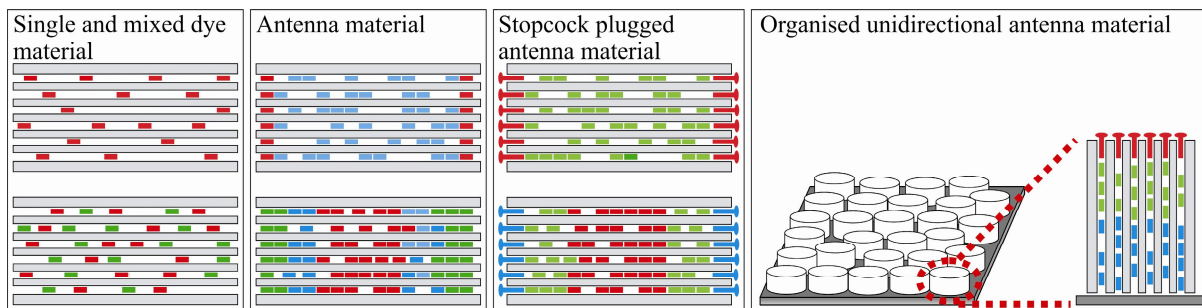


Figure 1. Schematic representations of materials fulfilling the criteria of the different stages of supramolecular organisation. All materials depicted here have been successfully prepared. Far left: *Single and mixed-dye materials* are obtained by loading zeolite crystals with either one kind of dye (top) or with two randomly mixed dyes (bottom). Middle left: *Antenna materials* in which the crystal channels are consecutively loaded with different dye molecules. Two different arrangements are shown. Middle right: *Stopcock-plugged antenna material* obtained by modifying zeolites loaded with either one (top) or with two types of dye (bottom) with a specific closure molecule. The stopcock molecules feature a head that is too large to pass the pore opening and a tail that fits in the channel. Far right: *Organized unidirectional antenna material*. An oriented monolayer of zeolite L crystals on a substrate is shown. The enlargement illustrates the unidirectionality achieved after consecutive insertion of two different dyes and the final addition of a stopcock molecule.

## 2. RESULTS AND DISCUSSION

In this section, we review some recent developments that will prove useful in the design and preparation of future photonic devices. The section starts with discussing the solubilisation of nanosized zeolite L crystals and the preparation of homogenous, oriented monolayers on a glass substrate. Next, we report the preparation of a unidirectional antenna system as well as a new design concept for creating thin layer solar cells. All dyes that were used in this study are summarised in Table 1.

The dye molecules are positioned at sites along the large, one-dimensional channels of zeolite L. The length of such a site corresponds to a number  $s$  multiplied by the unit cell length, so that one molecule fits exactly into one site. The value of  $s$  depends on the size of the molecule and the length of the primitive unit cell (0.75 nm in the case of zeolite L). A site can either be occupied by a molecule or be empty. Under equilibrium conditions, all sites have the same probability of being occupied by a molecule. The occupation probability  $p$  is equal to the ratio of the occupied to the total number of equivalent sites. For example, a zeolite L channel with a length of 700 nm contains 932 unit cells. A molecule like Ox has a length around 1.5 nm, so  $s$  is equal to 2 and the number of sites in such a channel will correspond to 466. If we now fill half of these sites with an Ox molecule, the occupation probability  $p$  will be 0.5 Ox molecules per site ( $p = 0.5$ ).

Abbreviation	Structural Formula	Abbreviation	Structural Formula
Ox		Py	
Ox1		Cy02702	
MeAcr		JCG	
Ru-ph4-TMS		DTCI	
Qu			

Table 1. Dye molecules used in this study

### 2.1 Solubilisation of nanosized, dye loaded zeolite L crystals

A zeolite L crystal of 30 nm length and diameter consist of about 9600 unit cells which can be filled with molecules of appropriate size. If, due to its length, a dye occupies two unit cells, then such a crystal can host up to 4800 of them. The geometric constrains imposed by the host framework ensure that all these molecules will behave as monomers, as orbital overlap is prevented. We have calculated that for a crystal filled with donor molecules and modified at one channel entrance with a single acceptor, the trapping efficiency of electronic excitation can be above 95%.<sup>5</sup> This makes such host-guest materials interesting for a wide range of applications. A drawback of these small particles is their tendency to aggregate and their pronounced Rayleigh scattering. Embedding dye zeolite materials in polymer matrices has been discussed by Schneider et al.<sup>6</sup> Successful solubilisation and refractive index matching experiments with nanosized, dye loaded zeolite L crystals were recently reported.<sup>7</sup> This work has been extended and conditions for obtaining stable and transparent suspensions were found in many additional situations. An example is shown in Figure 2 where we show that benzoic-acid ethyl ester is able to solubilise the zeolite crystals well. Due to the refractive index matching, the suspension in this solvent is clear, while a similar amount of crystals dispersed in methanol exhibits strong light scattering.

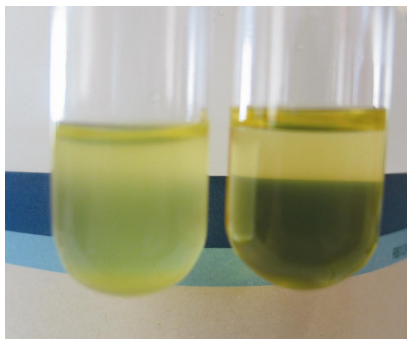


Figure 2. Solubilisation experiment with 30 nm long dye-loaded zeolite L crystals. Comparison of a suspension of JCG-zeolite L ( $p=0.5$ ) in methanol (left) and in benzoic-acid ethyl ester (right).

## 2.2 Oriented zeolite L monolayers

The motivation behind the development of densely packed zeolite monolayers came first from the domain of electrochemistry.<sup>8</sup> An early method for post synthetic orientation of zeolite crystals was reported by Caro et al.<sup>9</sup> They observed that crystals of ALPO4-5 and ZSM-5 can be oriented in a parallel arrangement upon application of an electric field of  $2\text{--}3\text{ kV cm}^{-1}$ . This method, however, can only be applied on crystals that are larger than  $20\text{ }\mu\text{m}$  and have an aspect ratio of at least four to five. Large ZSM-5 crystals (several tenths of  $\mu\text{m}$ ) with a uniform size distribution were successfully aligned in the grooves of etched silicon wafers by Scandella et al.<sup>10</sup> Feng and Bein were among the first to report on the growth of oriented molecular sieve crystals on a substrate.<sup>11</sup> High quality close-packed monolayers of size selected zeolite A crystals of a few  $\mu\text{m}$  in size were prepared by sedimentation.<sup>12</sup> This versatile method was also used for realizing the first ship in a bottle synthesis of luminescent clusters in a perfect zeolite A monolayer on quartz.<sup>13</sup> Another important contribution was the covalent bonding between zeolite A or ZSM-5 and a substrate (usually glass) using a variety of linker molecules.<sup>14-15</sup> Recently, the interest in zeolite monolayer materials has greatly increased as new application fields have been envisaged. The applications span a wide range of uses such as membranes, chemical sensors, low-k dielectrics, and hosts for supramolecular organization of guest molecules or nanostructures.<sup>1,16-18</sup> Organising dye loaded zeolite L crystals into oriented monolayers on a substrate gives access to a new hierarchy of structural order. Different procedures for preparing such materials have been recently described.<sup>19-20</sup> In Figure 3, we show a typical good zeolite L monolayer that was prepared on a quartz plate according to one of these procedure. The densely packed crystals are oriented in such a manner, that their channels are perpendicular to the surface of the substrate. The obtained material is quite robust and can be subjected without problems to further physical or chemical modifications, like loading dyes in or grafting molecules to the zeolites.

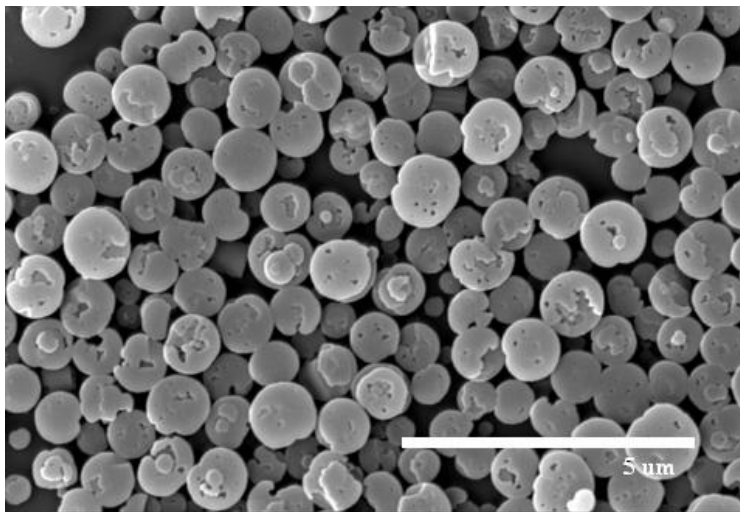


Figure 3. SEM image of a Zeolite L monolayer on a quartz substrate after calcination. The layer was prepared by using 3-(triethoxysilyl)propyl isocyanate as a covalent linker between the crystals and the substrate.<sup>19</sup>

Quartz plates bearing a zeolite L layer as shown in Figure 3 exhibit strong light scattering. They, however, become fully transparent when immersed in toluene. This important observation allows the measurement of high quality absorption spectra from such layers. As an illustration, we present in Figure 4 the spectra obtained from monolayers loaded with small amounts of Ox. Figure 4 A) shows a comparison of the absorption spectra of the same layer, recorded in air (solid line) and in toluene (dashed line). The Ox-loading in this sample was about 0.004 dyes per site, which corresponds to a concentration of  $1.5 \times 10^{-6}$  M. The Ox absorption band is hardly visible when the sample is measured in air, due to the intense scattering. The same band is, however, very well resolved when the layer is immersed in toluene, despite the exceedingly low Ox concentration.

The  $pK_{a1}$  and the  $pK_{a2}$  of Ox are 11.3 and -1.2.<sup>21-22</sup> We found that the  $pK_{a2}^*$  of the electronically excited Ox is about 1.2. The doubly protonated Ox is non-fluorescent and it exhibits a large spectral overlap with the fluorescence of the luminescent Ox. This means that the pH inside of the zeolite L channels must be kept within an optimal range if a strongly luminescent material is desired. Zeolite L channels can, depending on the pre-treatment, become very acidic. This is illustrated in Figure 4 B) where absorption spectra of monolayers immersed in toluene are shown for the three different Ox loadings of 0.004, 0.007, and 0.012 molecules per site. We observe in all cases an additional band around 650 nm which does not belong to the Ox. Comparing these with the absorption spectrum of Ox in 2M hydrochloric acid - shown in Figure 4 C) as dashed line - we find that this peak stems from the doubly protonated Ox. This indicates that the acidity inside of the channels corresponded in this case to more than that of 2M hydrochloric acid. In Figure 4 D), we show that the 650 nm band can be fully eliminated by immersing the layer for a few seconds in alkaline ethanol. Other important applications for this new and fast possibility to obtain good quality absorption spectra are given in ref. 23.

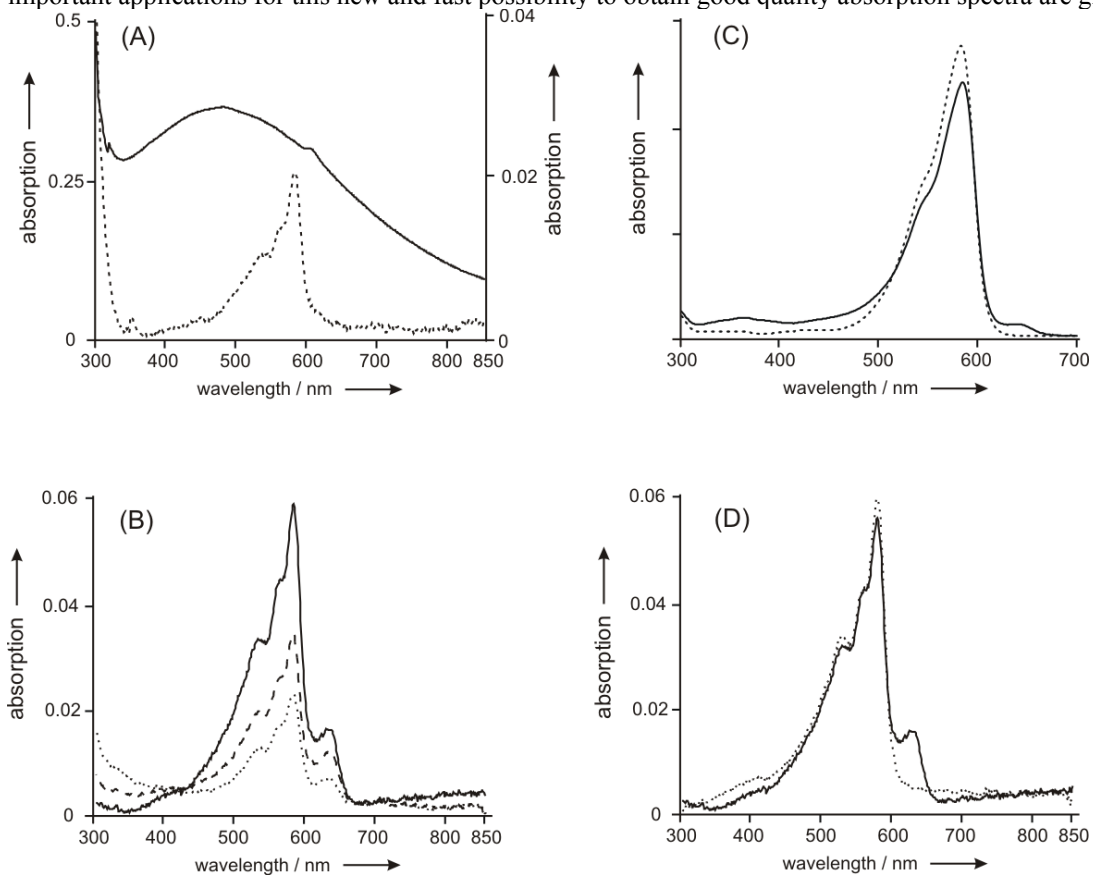


Figure 4. Absorption spectra of Ox-zeolite L monolayers and of Ox in solution. A) Absorption spectra of an Ox-zeolite L monolayer measured in air (solid) and in toluene (dotted). B) Absorption spectra of an Ox-zeolite L monolayer in toluene after first insertion of Ox (dotted;  $p = 0.004$ ), after second insertion (dashed;  $p = 0.007$ ) and after third insertion ( $p = 0.012$ ). C) Absorption spectra of Ox in water (dotted) and in 2M HCl (solid). D) absorption spectra of an Ox-zeolite L monolayer in toluene measured after loading (solid) and after short immersion into an alkaline ethanol solution (dotted).

### 2.3 Unidirectional antenna systems

In device chemistry, a high degree of supramolecular organisation is usually required for achieving desired macroscopic properties. The possibility to arrange zeolite L crystals in densely packed, oriented monolayers gives access to such a higher level of structural organisation. The materials described in the previous section expand our options for the creation of photonic devices. We will focus here on the description of only one example: the unidirectional antenna system. Zeolite L has proven to be an ideal host for the realisation of light-harvesting antenna materials for several reasons. The supramolecular organization of dyes inside the one-dimensional channel system has been realised. It has been demonstrated that the dye-loaded zeolite materials can be interfaced with the environment (be it a polymer or a semiconductor) via stopcock molecules. Lastly, we also developed methods for the solubilisation of small zeolite crystals.

The new hierarchy of structural order attained by organising supramolecular functional dye-zeolite crystals into oriented monolayers has led to the successful realisation of a unidirectional antenna system. After the monolayer preparation, the zeolite channels can be sequentially filled with different dyes. In such a material, the Förster energy transfer process can only occur in one direction. This is shown schematically in the upper part of Figure 5. The lower part of the same Figure presents fluorescence microscopy images proving that the desired material has actually been obtained. We prepared a DTCl, MeAcr<sup>+</sup>-zeolite L monolayer, by first inserting MeAcr<sup>+</sup> (green dye) followed by DTCl (red dye) in the zeolite channels of an already prepared monolayer, taking care that the crystals were not completely filled. Some crystals were then broken free from the monolayer for the optical microscopy investigation. This was done by scratching the layers with a spatula. Fluorescence can only be detected at one end of the crystals. This was true for a reasonable large amount of the zeolite L crystals present in the sample. This observation proves that after calcination of a zeolite L monolayer, dyes can enter the channels only from one side. Such a material forms the basis for systems where excitation energy is transported in one direction only. Thus largely extending the possibilities to make use of the quasi 1D-electronic excitation energy transport in dye loaded zeolite L systems that has recently been observed.<sup>24</sup>

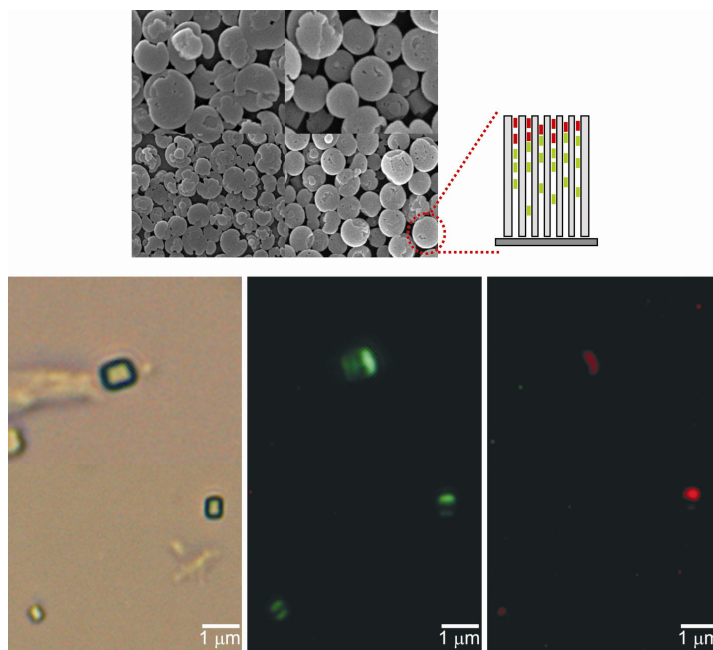


Figure 5. Experimental realisation of a unidirectional antenna material. Upper part: SEM images of two zeolite L monolayers at two different magnifications. The inset shows a schematic representation of the prepared antenna material. Lower part: Fluorescence microscopy images of DTCl, MeAcr<sup>+</sup>-zeolite L crystals removed from a zeolite L monolayer. Left: Under white light. Middle: Specific excitation of MeAcr<sup>+</sup> at 470–490 nm. Right: Specific excitation of DTCl at 545–580 nm.

In another experiment, an oriented monolayer was prepared from Ox1-loaded zeolite L crystals that were afterwards modified with Ru-ph4-TMS stopcocks. This donor-acceptor pair was chosen because of the efficient energy transfer that was recently observed between them.<sup>25</sup> The aim of the experiment was to see, whether a unidirectional energy transfer

between the dye and the stopcock could be realised in a monolayer system. First results we obtained for such an experiment are shown in Figure 6. The excitation (dashed) and emission (solid) spectra of Ru-ph4-TMS (in green) and of Ox1 (in red) are shown in Figure 6 A). The energy transfer experiment in a monolayer sporting this acceptor-donor pair is depicted in Figure 6 B). The emission spectrum resulting from the selective excitation of the Ru<sup>3+</sup> complex at 450 nm is shown as a solid line. The excitation spectrum, shown as a dashed line, was detected at the emission maximum of Ox1 (710 nm). The luminescence spectra show very nicely that energy transfer from Ru-ph4-TMS to Ox1 takes also place in this type of system.

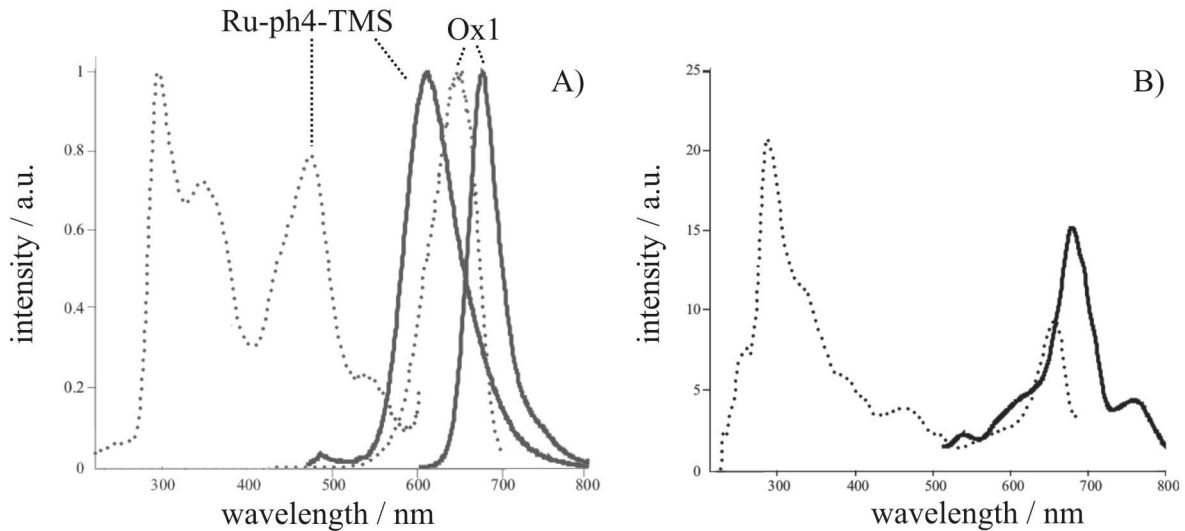


Figure 6. A) Excitation (--) and emission (–) spectra of Ru-ph4-TMS and Ox1. There is a large spectral overlap between the emission spectrum of the donor Ru-ph4-TMS and the excitation spectrum of the acceptor Ox1, a prerequisite for Förster resonance energy transfer. B) Excitation (--) and emission (–) spectra of a zeolite monolayer containing Ox1 in the channels and modified with Ru-ph4-TMS at the channel ends. The emission spectrum was observed after excitation at 450 nm, where Ru-ph4-TMS is selectively excited. The excitation spectrum was recorded at 710 nm.<sup>25</sup>

#### 2.4 A new concept for preparing thin layer, silicon based solar cells

The major drawback of silicon for the production of solar cells, being an indirect bandgap material, is its low absorptivity at wavelengths longer than 500 nm. Therefore, solar cells based on monocrystalline silicon need a thickness of 200  $\mu\text{m}$  to 300  $\mu\text{m}$  in order to be able to absorb enough sun light. An antenna material which absorbs all light in the right wavelength range and transfers it by radiationless energy transfer to the semiconductor appear to be an attractive solution for overcoming this problem.<sup>26</sup> The new highly organized zeolite L materials reported here offer a unique possibility for developing such dye sensitized solar cells or luminescent solar concentrators. The 6-stage strategy we are currently pursuing for the preparation of silicon based thin layer solar cells is sketched in Figure 7. In a first step, a densely packed, oriented zeolite L monolayer is deposited on a glass substrate (step A). The channels of these crystals are then sequentially filled with appropriate dyes. In this scheme we used three dyes: the first absorbs in the blue spectral range, the second in the green and the final one in the red (step B). In the next step, the channel openings of the dye-loaded zeolites are sealed with stopcock molecules that are optimised for efficient energy transfer to the semiconductor. Step D) consists in adding a thin insulating layer (around 2 nm in thickness) and the necessary electrical contacts. The system is now ready for the deposition of the semiconductor layer and its doping (step E). These two processes will usually be done by vapour deposition techniques. The cell is finalised by adding a back contact in the last stage F. The so prepared sensitised solar cell functions by first absorbing light over a broad spectral range in the zeolite antenna material. The excitation energy migrates radiationlessly among the inserted dyes towards the stopcock molecules. From there, Förster energy transfer to the semiconductor takes place across the insulating layer. The injected energy can now be used for the charge separation process in the silicon layer. Finally, the resulting electrical current is collected via the appropriate contacts.

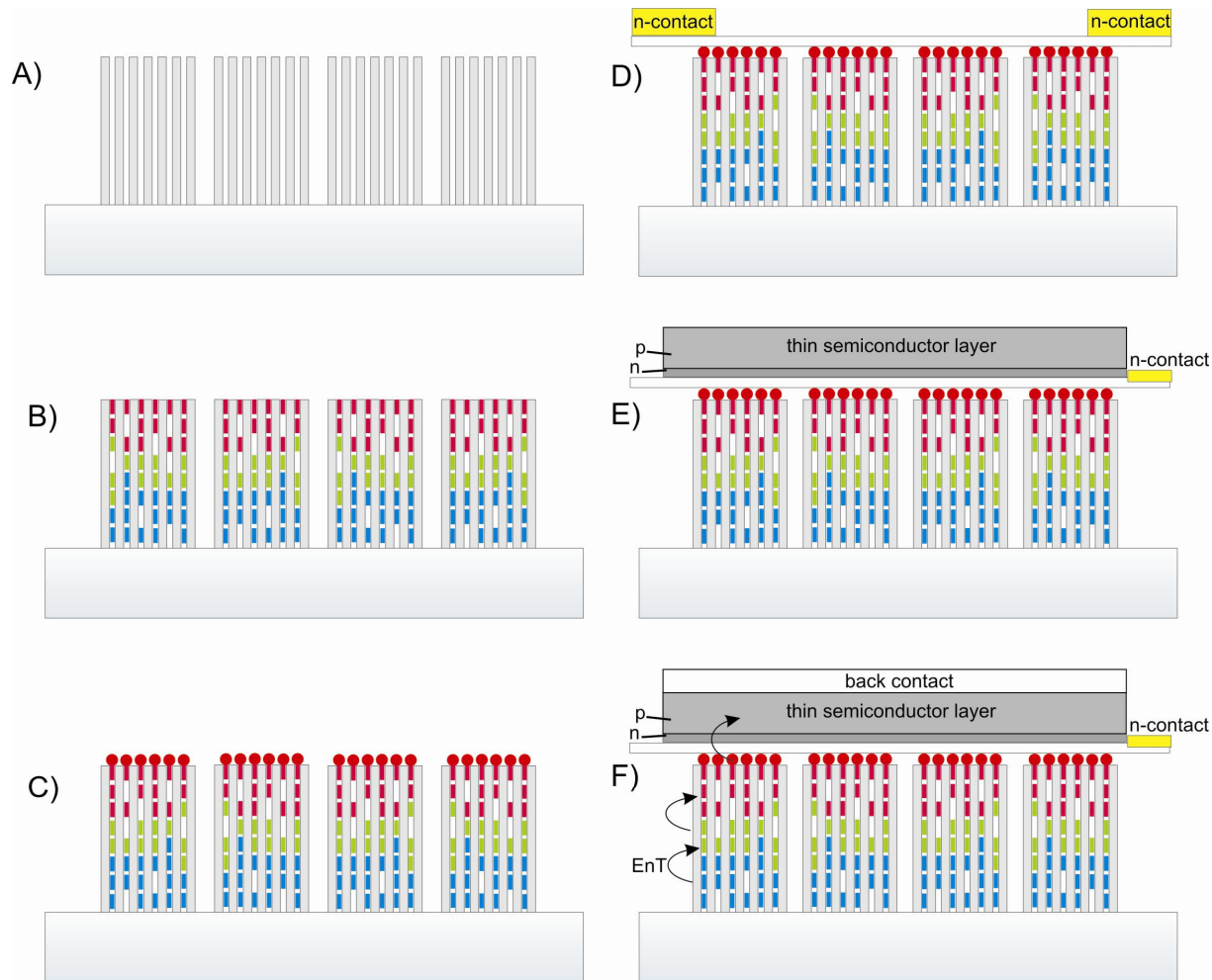


Figure 7. Six-step strategy to build an antenna sensitized solar cell. A) Formation of a zeolite L monolayer. B) Consecutive insertion of dyes. We illustrate this with three dyes. In practice, two dyes are expected to be sufficient. C) Addition of the stopcock molecules which are optimized for efficient energy transfer to the semiconductor. D) Addition of a very thin insulating layer (2 nm to 5 nm) and the necessary electrical contacts. E) Addition of the semiconductor and doping, both usually done by a vapour deposition process. F) Finalised cell with back contact.<sup>20</sup>

We are currently in the process of studying the different reaction steps separately. In these studies NIR luminescence spectroscopy plays an important role, as the stopcock molecule should have its emission maximum in this range for optimum energy transfer to the silicon. Another use for this technique will be to monitor the charge recombination processes in the semiconductor layer. Some recently recorded NIR spectra are summarised in Figure 8. All spectra were excited around 460 nm with an argon ion laser. The partial systems include a silicon covered zeolite L monolayer, and a similar monolayer with crystals terminated by a quinolinium derivative (Qu) as a stopcock molecule.

In Figure 8 A), we show the NIR luminescence spectrum of a thin layer of silicon (75 nm thick) deposited on zeolite L monolayer. The clearly resolved band around 1062 nm can be attributed to the silicon, proving that we are able to directly excite the silicon layer at 540 nm and to detect its luminescence in air at room temperature. The emission spectrum of a monolayer of zeolite L crystals terminated with Qu, given in Figure 8 B), features a broad band at 960 nm. For comparison, we show in Figure 8 C) the absorption and emission spectra of Qu solution in 1-butanol ( $7.4 \times 10^{-6}$  M). The absorption spectrum shows three peaks: a very intense one at 521 nm and two weaker luminescence bands at 780 nm and 860 nm. The luminescence spectrum of this solution, excited at 540 nm, exhibits also a very broad band around 930 nm. These spectral characteristics make Qu a candidate for the stopcock molecule in our intended application.



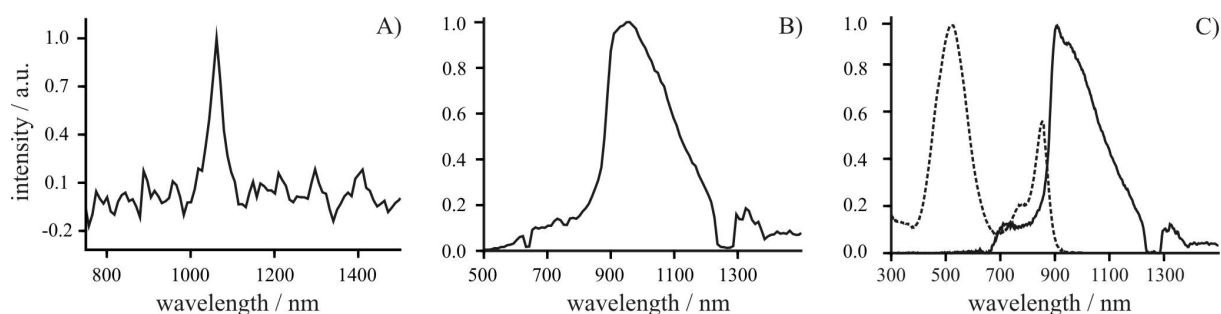


Figure 8. A) NIR emission spectrum of a 75 nm thick silicon layer deposited on a zeolite L monolayer. B) Luminescence spectrum of zeolite L monolayer, where the channels are terminated with the dye Qu. C) Absorption (dashed) and emission (solid) spectra of a Qu solution in 1-butanol ( $7.4 \times 10^{-6}$  M). All luminescence spectra were excited with an argon ion laser around 460 nm.

### 3. CONCLUSIONS

The great flexibility of these highly organised 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 that employs energy transfer instead of electron injection is of great interest. The main 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 monodirectional 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 only at one channel end to allow energy transfer. The semiconductor layer can be very thin, because the electron-hole pairs form near the surface. The transfer of electrons from antenna to semiconductor is prevented by introducing an insulating layer.

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. Higher energy efficiency is expected for such a system compared to conventional LEDs.

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### REFERENCES

- (a) G. Calzaferri, S. Huber, H. Maas, C. Minkowski, "Photon-harvesting host-guest antenna materials", *Angew. Chem. Int. Ed.*, **42**, 3732-3758, 2003.
  - (b) G. Calzaferri, O. Bossart, D. Brühwiler, S. Huber, C. Leiggenger, M. K. van Veen, A. Zabala Ruiz, "Light-harvesting host-guest antenna materials for quantum solar energy conversion devices", *C. R. Chimie*, **9**, 214-225, 2006.

2. (a) Ch. Baerlocher, W.M. Meier, D.H. Olson, *Atlas of Zeolite Framework Types*, 5th ed., Elsevier, Amsterdam, 2001.  
 (b) T. Ohsuna, B. Slater, F. Gao, J. Yu, Y. Sakamoto, G. Zhu, O. Terasaki, D. E. W. Vaughan, S. Qiu, C.R. Catlow, "Fine structures of zeolite-Linde-L (LTL): surface structures, growth unit and defects", *Chem. Eur. J.*, **10**, 5031-5040, 2004.  
 (c) A. Zabala Ruiz, D. Brühwiler, T. Ban, G. Calzaferri, "Synthesis of zeolite L: tuning size and morphology", *Monatshefte für Chemie / Chemical Monthly*, **136**, 77-89, 2005.  
 (d) S. Megelski, G. Calzaferri, "Tuning the size and shape of zeolite L based inorganic/organic host/guest composites for optical antenna systems", *Adv. Funct. Matter.*, **11**, 277-286, 2001.  
 (e) O. Larus, V.P. Valtchev, " ", *Chem. Mater.*, **16**, 3381-, 2004.  
 (f) Y.-Jo Lee, J.S. Lee, K.B. Yoon, " ", *Micropor. Mesopor. Mater.*, **80**, 237-, 2005.
3. (a) H. Maas, G. Calzaferri, "Trapping energy from and injecting energy into dye-zeolite nano Antenna", *Angew. Chem. Int. Ed.*, **41**, 2284-2288, 2002.  
 (b) G. Calzaferri, "Dye loaded zeolite material", USPatent 6,932,919 B2, Aug. 23, **2005**, Priority Date Nov. 3, 2000; Licensed by Clariant International LTD.
4. C. Minkowski, G. Calzaferri, "Förster type energy transfer along a specified axis", *Angew. Chem. Int.*, **44**, 5325-5329, 2005.
5. N. Gfeller, G. Calzaferri, "Energy migration in dye-loaded hexagonal microporous crystals", *J. Phys. Chem. B*, **101**, 1396-1408, 1997.
6. J. Schneider, D. Fanter, M. Bauer, C. Schomburg, D. Wöhrle, G. Schulz-Ekloff, "Preparation and optical transparency of composite materials from methacrylate ester copolymers and faujasites with an embedded azo dye", *Micropor. Mesopor. Mater.*, **39**, 257-263, 2000.
7. A. Devaux, Z. Popović, O. Bossart, L. De Cola, A. Kunzmann, G. Calzaferri, "Solubilisation of dye-loaded zeolite L nanocrystals", *Micropor. Mesopor. Mater.*, **90**, 69-72, 2006.
8. (a) J. Li, G. Calzaferri, "Silver Zeolite 4A Modified Electrodes: Intrazeolite Effect", *J. Chem. Soc. Chem. Commun.*, 1430-1431, 1993.  
 (b) J. Li, K. Pfanner, G. Calzaferri, "Silverzeolite A Modified Electrodes: An Intrazeolite-Ion-Transport Mechanism", *J. Phys. Chem.*, **99**, 2119-2126, 1995; *ibid* 12368-12468.
9. J. Caro, G. Finger, J. Kornatowski, J. Richter-Mendau, L. Werner, B. Zibrowius, "Aligned molecular sieve crystals", *Adv. Mater.*, **4**, 273-276, 1992.
10. L. Scandella, G. Binder, J. Gobrecht, J. C. Jansen, "Alignment of single-crystal zeolites by means of microstructured surfaces", *Adv. Mater.*, **8**, 137-139, 1996.
11. (a) S. Feng, T. Bein, "Growth of oriented molecular sieve crystals on organophosphonate films", *Nature*, **368**, 834-836, 1994.  
 (b) T. Bein, "Synthesis and applications of molecular sieve layers and membranes", *Chem. Mater.*, **8**, 1636-1653, 1996.
12. Ph. Lainé, R. Seifert, R. Giovanoli, G. Calzaferri, "Convenient preparation of close-packed monograin-layers of pure zeolite A microcrystals", *New. J. Chem.*, **21**, 453-460, 1997.
13. C. Leiggenger, G. Calzaferri, "Monolayers of zeolite A containing luminescent silver sulfide clusters", *ChemPhysChem*, **5**, 1593-1596, 2004.
14. (a) S. Y. Choi, Y. -J. Lee, Y. S. Park, K. Ha, K. B. Yoon, "Monolayer assembly of zeolite crystals on glass with fullerene as the covalent linker", *J. Am. Chem. Soc.*, **122**, 5201-5209, 2000.  
 (b) K. Ha, Y. -J. Lee, H. J. Lee, K. B. Yoon, "Facile assembly of zeolite monolayers on glass, silica, alumina, and other zeolites using 3-halopropylsilyl reagents as covalent linkers", *Adv. Mater.*, **12**, 1114-1117, 2000.  
 (c) A. Kulak, Y. -J. Lee, Y. S. Park, K. B. Yoon, "Orientation-controlled monolayer assembly of zeolite crystals on glass and mica by covalent linkage of surface-bound epoxide and amine groups", *Angew. Chem. Int. Ed.*, **39**, 950-953, 2000.  
 (d) A. Kulak, Y. S. Park, Y. -J. Lee, Y. S. Chun, K. Ha, K. B. Yoon, "Polyamines as strong molecular linkers for monolayer assembly of zeolite crystals on flat and curved glass", *J. Am. Chem. Soc.*, **122**, 9308-9309, 2000.  
 (e) G. S. Lee, Y. -J. Lee, K. Ha, K. B. Yoon, "Orientation-controlled monolayer assembly of zeolite crystals on glass using terephthaldivarboxaldehyde as a covalent linker", *Tetrahedron*, **56**, 6965-6968, 2000.  
 (f) Y. S. Chun, K. Ha, Y. -J. Lee, J. S. Lee, H.S. Kim, Y. S. Park, K. B. Yoon, "Diisocyanates as novel molecular binders for monolayer assembly of zeolite crystals on glass", *Chem. Commun.*, 1846-1847, 2002.

15. a) K. Ha, Y. -J. Lee, D. Y. Jung, J. H. Lee, K. B. Yoon, "Micropatterning of oriented zeolite monolayers on glass by covalent linkage", *Adv. Mater.*, **12**, 1614-1617, 2000.  
 b) K. Ha, Y. -L. Lee, Y. S. Chun, Y. S. Park, G. S. Lee, K. B. Yoon, "Photochemical pattern transfer of continuous zeolite films on glass by direct dipping in synthesis gel", *Adv. Mater.*, **13**, 594-596, 2001.
16. J. Choi, S. Ghosh, Z. Lai, M. Tsapatsis, "Uniformly a-oriented MFI zeolite films by secondary growth", *Angew. Chem. Int. Ed.*, **45**, 1154-1158, 2006.
17. G. Shu, J. Liu, A. S. Chiang, R. W. Thompson, "Transparent zeolite films with regular surface patterns", *Adv. Mater.*, **18**, 185-189, 2006.
18. J. S. Lee, K. Ha, Y.-J. Lee, K.B. Yoon, "Ultrasound-aided remarkably fast assembly of monolayers of zeolite crystals on glass with a very high degree of lateral close packing", *Adv. Mater.*, **17**, 837-841, 2005.
19. A. Zabala Ruiz, H. Li, G. Calzaferri, manuscript submitted for publication
20. G. Calzaferri, A. Zabala Ruiz, H. Li, S. Huber, Patentschrift 01266/05, 2005.
21. H. Musso, H.-G. Matthies, H. Krämer, P. Hocks, "Orcein pigments. XI. The constitution of the aminoorceimines", *Chem. Ber.*, **93**, 1782-1788, 1960.
22. L. Michaelis, S. Garnick, "Oxidation-reduction equilibrium, over the whole pH range, of oxonine and some related dyestuffs", *J. Am. Chem. Soc.*, **63**, 1636-1643, 1941.
23. S. Huber, A. Zabala Ruiz, H. Li, G. Calzaferri, "Optical spectroscopy of inorganic-organic host-guest nanocrystals organized as monolayers", manuscript in preparation.
24. C. Minkowski, R. Pansu, M. Takano, G. Calzaferri, "Energy Collection, Transport, and Trapping by Supramolecular Organization of Dyes in Hexagonal Zeolite Nano Crystals", *Adv. Func. Mater.*, **16**, 273-285, 2006.
25. O. Bossart, L. De Cola, S. Welter, G. Calzaferri, "Injecting electronic excitation energy into an artificial antenna system by a Ru<sup>2+</sup> complex", *Chem. Eur. J.*, **10**, 5771-5775, 2004.
26. (a) T. Förster, "Zwischenmolekulare Energiewanderung und Fluoreszenz", *Ann. Phys. Chem. B*, **2**, 55-75, 1948.  
 (b) T. Förster, *Fluoreszenz organischer Verbindungen*, Vandenhoeck & Ruprecht, Göttingen, 1951.  
 (c) S. Jang, M. D. Newton, R. J. Silbey, "Multichromophoric Foerster resonance energy transfer", *Phys. Rev. Letter*, **92** (21), 218301/1-218301/4, 2004.