

Technology as we know it is a product of industry and manufacturing. Industry acquires a lot of its resources from nature. For example, trees are chopped in forests, ore is mined in mountains, and sand is extracted from the soil. Then, these raw natural materials are processed into products which we consider useful. Trees are manufactured into lumber and finally become furniture. Ore is processed into molten iron, and then steel is fabricated. Silicon is exploited from sand and then chips are produced from silicon. All the processes used in these manufacturing steps are crude steps like cutting, stirring, baking, spraying, etching, grinding, and many more.

Nature is often not crude, though. Trees for example make wood and leaves, but for that they do not carry out any of these crude processes. Instead they gather solar energy using molecular devices, the antenna systems in the chloroplasts of the leaves. The solar energy obtained in this way is converted in a magnificent way by tiny molecular machines. With the collected energy they process carbon dioxide and water into oxygen and molecular building blocks. Other molecular machines combine these molecular building blocks to form roots, leaves, trunks, branches, twigs, solar collectors, and more complex molecular machinery. If we just take a good look at a leaf then we see that it is even more sophisticated than the space shuttle and it is made without any noise, heat, or toxic waste. Even better, pollutants are consumed in the process. This example shows that we have by far not reached the technology of these natural biological systems.¹

Although we are still far away from designing a tree, we can study the individual molecular machines that nature has evolved and try to learn from them. One of the most studied and intriguing systems of nature is the photosynthetic system in chloroplasts. It is amazing how efficiently solar energy is harvested and stored into energy rich molecules. The natural photon harvesting antenna has served as an example for the research in our group.

An artificial photonic antenna system works analogously as the natural photonic antenna and consists of an organized multicomponent arrangement in which several chromophoric molecular species absorb the incident light and transport the excitation energy (not charges) to a common acceptor component. Numerous imaginative attempts to build artificial photonic antennae have been presented in literature.² However, mostly the number of molecules that form the light harvesting antenna system is very low and the molecules are organized on a primitive level.

In natural photosynthesis, light is absorbed by an antenna system of a few hundred chlorophyll molecules. It allows a fast energy transfer from an electronically excited molecule to unexcited neighbor molecules in a way that the excitation

energy reaches the reaction center with high probability. Trapping occurs there. The anisotropic arrangement of chlorophyll molecules is important for the efficiency of the energy migration to the reaction center.^{3,4} The formation of aggregates is prevented by fencing the light absorbing chlorophyll molecules in polypeptide cages. This is necessary because aggregates are known to quench the luminescence and in this way also break up the energy migration mechanism. A similar approach is possible by enclosing light absorbing dye molecules inside a microporous material by choosing conditions such that the volume of the cages or channels is able to uptake only monomers but not aggregates.² Our approach to build an artificial photonic antenna is based on this principle. We use zeolite crystals with a narrow channel structure as a host for guest dye molecules. In this way it is possible to have very small molecular distances, just like in the natural antenna systems, and to specifically organize the dye molecules which mimic the function of chlorophyll.

Supramolecular chemistry deals with the association of two or more chemical species and is based on molecular non-covalent interactions. These interactions often give the supramolecular structure new chemical and physical properties. We speak of functional supramolecular chemistry when such a supramolecular structure or supermolecule is able to perform a function that the isolated molecules are unable to perform on their own. On one hand the objects of supramolecular chemistry are defined by the nature of the individual components, and on the other hand by the type of interactions which hold them together. These interactions can be hydrogen bonding, electrostatic forces, Van der Waals forces, metal ion coordination, etc.^{5,6}

The roots of supramolecular chemistry are found in biological processes where individual molecules combine to make new supermolecules that are able to perform some new function. The combination of such individual biomolecules often happens by a so-called “key-lock” principle and is very selective. Only in the last few decades chemists try to construct such complex supramolecular structures themselves. However, most intermolecular forces still cannot be controlled in such a way that the final structure of a supramolecular assembly can be reliably predicted. This is mostly due to the fact that non-covalent bonds are much less stable and directional than covalent bonds. A second difficulty is that even though it is relatively easy to design large systems with optimal functionalities on paper, it is often very difficult to synthesize such large complex systems.

A very important and intriguing part of supramolecular chemistry is concerned with host-guest systems. The biological analogy is found with molecular complexes that are

formed in the first step of enzymatic catalysis.⁷ The function of the complexes there is to orient the reactants and catalysts in such a way that the final reaction occurs in an efficient way. Chemists have used model systems to mimic such molecular complexes, which more or less started the field of host-guest chemistry.^{8,9} Later on they also tried to design new special hosts, mostly for catalytic purposes.

Numerous different hosts have been studied. Here, we restrict ourselves to inorganic hosts. Especially inorganic materials that have layers, pores, cavities and channels are interesting. We can distinguish between host-guest systems in the classical supramolecular way, where we have no covalent bonds, and systems where the guests are covalently bound to the host. In the next section the rare earth elements will be picked out and on the basis of these guest ions, the significance of supramolecular chemistry and host-guest systems is demonstrated. Although this is just an example and the rare earth elements are unique, similar property changes are

and the emissive rates are slow. This results in long-lived and line-like emission bands. As a consequence, direct excitation of the lanthanide ions is unfavorable. The comparatively fast thermal relaxation of the excitation energy is a problem when using lanthanide ions for luminescence. This non-radiative relaxation may occur by interaction of the electronic levels of the lanthanide ion with suitable vibrational modes of the environment. The efficiency of these processes depends on the energy gap between the ground and excited states as well as the vibrational energy of the oscillators. Different ways to overcome the difficulty of low absorptivity have been used. The most important ones are shown in Figure 1: a) matrix excitation followed by energy transfer to the lanthanide ion, b) ligand \rightarrow metal charge transfer followed by lanthanide f-f emission, and c) ligand-centered absorption followed by energy transfer from the ligand to the lanthanide ion.¹¹

Because direct excitation of the lanthanide ions is unfavorable, coordinating ligands are often used as sensitizers. After

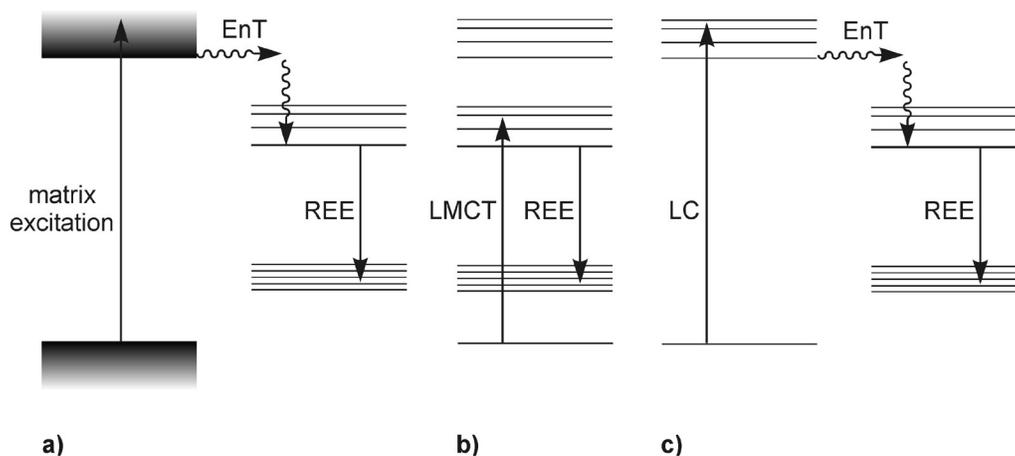


Figure 1. Three paths to efficient lanthanide luminescence (EnT = energy transfer; REE = rare earth emission; LMCT = ligand \rightarrow metal charge transfer absorption; LC = ligand-centered absorption). a) A matrix is excited above the band gap energy and, after energy transfer, the lanthanide ion emits. b) Ligand \rightarrow metal charge transfer absorption can lead to an excited lanthanide ion which in turn luminesces. c) Ligand-centered absorption excites a ligand which transfers its electronic excitation energy to a lanthanide ion that fluoresces.

observed for many other guests upon the formation of host-guest systems.

The research work on the unique luminescent properties of rare earth elements hosted in different matrixes is strongly motivated by their technological importance in optoelectronic devices.¹⁰ The materials emit over the entire spectral range of interest. Their optical transitions involve 4f orbitals, which are well shielded from their chemical environment by 5s² and 5p⁶ electrons. The f-f transitions are parity forbidden and, as a result, the absorption coefficients are very low

absorption of light by the ligands, the electronic excitation energy is transferred and results in a luminescence of the lanthanide ion, see Figure 1c.

If a suitable host is used, fast thermal relaxation can be prevented. Zeolites possess pore structures and these enable them to act as a host for molecules and ions. The cations which are normally present in the pores of zeolites have a charge-compensating function and can generally be exchanged. Rare earth ions and some of their complexes can be inserted by ion exchange. Ligands can protect the lanthanide ions from

the water molecules, which are present in zeolites under ambient conditions. The zeolite framework itself only has low vibration quanta which are not expected to contribute much to non-radiative deactivation of the excited state of the lanthanide ion. Ligands containing organic chromophores can be used to excite the lanthanide ion by the mechanisms shown in Figure 1b and c. However, conventional ligands do not usually give rise to inert complexes because the lanthanide ions are unable to form strong coordination complexes due to their electronic configuration. Depending on the solvent, this situation leads to a competition of the coordination sites between the ligands and solvent molecules. Lanthanide ions inside zeolite pores that are not complexed must be excited by sensitization of another species. For this, one can use, for example, Ce^{3+} ions which have allowed f-d transitions.¹²

Another strategy is to use the high porosity of glass films derived from sol-gel processes to incorporate inorganic lumophores, which act as light-harvesting centers.¹³ These can efficiently collect photons and subsequently transfer their energy to the lanthanide ions to produce intense luminescence. The luminescence can be activated or enhanced by the presence of a molecule to be sensed. The target molecule must diffuse through the porous network of the film and bind to the

generated optically, which results in photoluminescence, or electrically, which gives electroluminescence.

It turns out that the use of host-guest systems is a clever way to obtain efficiently luminescent lanthanide ions.¹¹ The unique interactions between host and guest result in a material which has properties that the individual components cannot show separately.

Because of their well-defined internal structure with uniform cages, cavities or channels, zeolites are extremely well suited as host materials.¹⁵ Zeolites are inorganic microporous and microcrystalline materials built up of corner shared tetrahedra and capable of complexing or adsorbing small and medium-sized organic molecules.¹⁶ Typical crystal sizes are in the 0.05-10 μm range. The structures can be thought of as sponge-like material with channels and cages that extend periodically and regularly across their entire structure. Many different zeolite framework structures with various geometrical properties are known, some of which are shown in Figure 2.

Figure 2 shows that although the various zeolites are chemically very similar, they have totally different geometrical properties. Depending on the application of the material, different zeolites can be considered. The framework structures of zeolites have the advantage over organic framework hosts

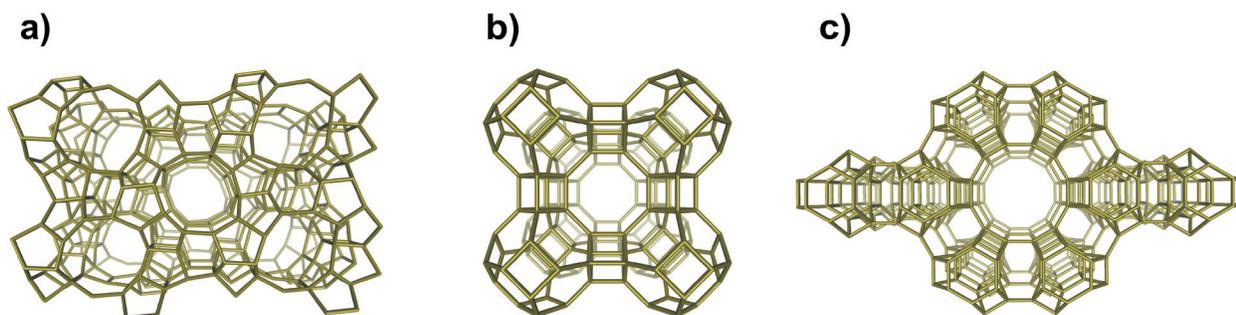


Figure 2. Three examples of zeolite frameworks: a) MFI, having a two-dimensional channel system; b) LTA, having cages; c) LTL, having a one-dimensional channel system.

lanthanide ion, thus increasing the emission of the light-harvesting centers. The sensors work by simply monitoring the emission intensity from the lanthanide centers.

The difficulties of low absorptivity and non-radiative relaxation can also be overcome by encapsulating the lanthanide ions in a semiconductor matrix. Charge carriers in a semiconductor can recombine at a lanthanide-related trap site in the matrix and transfer their recombination energy to the lanthanide ion, which then becomes excited and subsequently emits. Therefore, the lanthanides have been studied as emission amplifiers for semiconductors, which have an intrinsic indirect band gap, such as silicon.¹⁴ The charge carriers can be

of high mechanical and thermal stability. There are approximately 40 naturally occurring and well over a 100 synthetic forms of zeolites.

A wide spectrum of guests in zeolites has been studied. If guest molecules or clusters are encapsulated in these host materials and subjected to constrained dimensions, the properties and reactivities of the incorporated materials change. This can lead to very interesting applications like gas separation, selective catalysis, removal of pollutants and ion exchangers, data storage, quantum electronics and non-linear optics, chemoselective devices, nano reaction chamber, or energy conversion systems.

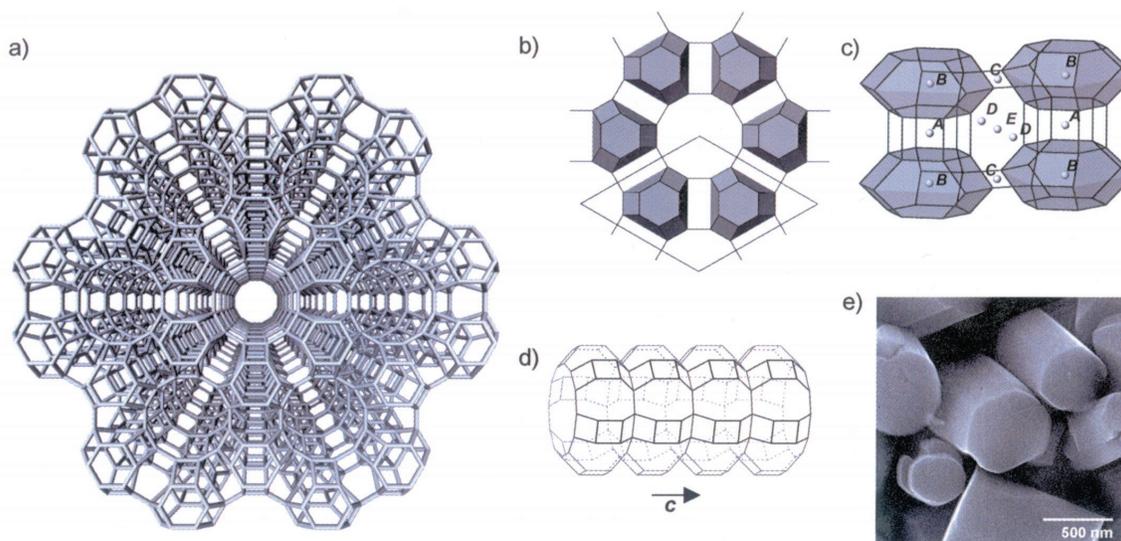


Figure 3. Zeolite L framework. a) Projection along the crystal c -axis showing 7 main channels. b) Projection along the c -axis with the cancrinite cages highlighted as polyhedra and the unit cell framed. c) Section showing the different cationic positions A to E. d) Side view of the 12-ring channel along the c -axis. e) Scanning electron microscopy picture of zeolite L crystals.

The insertion of organic dye molecules into zeolites is of interest because of the unusual chemical, physical, and photophysical properties in the host environment. The inorganic host stabilizes the incorporated dyes, yielding composite materials with improved thermal, mechanical, and optical resistances, as well as optical transparency which is similar to that of quartz for pure materials.¹⁷ Additionally, the zeolite can incorporate guest molecules in a geometry that is related to its pore structure. This results in extremely anisotropic materials. Chromophore-loaded zeolites have been investigated for different purposes such as interfacial electron transfer, micro-lasers, second harmonic generation, frequency doubling, and optical bistabilities giving rise to spectral hole burning.

Our experiments have been focused on zeolite L as a host. The reason for this is that neutral as well as cationic dyes can be inserted into the channels of zeolite L and that synthesis procedures for controlling the morphology of zeolite L crystals in the size regime of 30 nm to about 3000 nm are available. Many results obtained with zeolite L are valid for other nanoporous materials as well. Zeolite L is a crystalline aluminosilicate with hexagonal symmetry. Due to the aluminum atoms, its framework is anionic. The positions of charge compensating cations in the zeolite L structure are illustrated in Figure 3.

The crystals consist of so-called cancrinite cages (ϵ -cages) linked by double 6-rings. These units form columns in the crystal c -direction which are interconnected and thus give rise to 12-rings with a free open diameter of 7.1 Å. As a

consequence, zeolite L consists of one-dimensional channels, running through the whole crystal, with a widest diameter of about 12.6 Å, and a unit cell length in the crystal c -direction of 7.5 Å. The main channels are linked by non-planar 8-rings which form an additional two-dimensional channel system with a ring opening of about 1.5 Å. Four different charge compensating cation sites (A, B, C, and D) have been reported. A is in the center of the double 6-ring unit, B is in the center of the ϵ -cage, C lies midway between the centers of two adjacent ϵ -cavities, and D is inside the main channel near the wall of the 8-ring. Dehydrated zeolite L shows an additional cation site which is located midway between two neighboring sites A and is indicated as site E, see Figure 3c. The stoichiometry of the unit cell of zeolite L with monovalent cations is $(M_9)[(SiO_2)_{27}(AlO_2)_9] \cdot nH_2O$, where n equals 21 in fully hydrated material and 16 at about 20% relative humidity. The hexagonal morphology of zeolite L is visible in the scanning electron microscopy picture shown in Figure 3e.

The geometrical constraints imposed by the host determine the organization of the dyes. We focus on systems consisting of organic dye molecules in hexagonally arranged linear channels. The primitive vector c corresponds to the channel axis while the primitive vectors a and b are perpendicular to it enclosing an angle of 60°. The channels run parallel to the central axis of the cylinder.¹⁸

We consider the supramolecular organization of the dyes inside the channels as a *first level of organization*, shown in Figure 4a. It allows light harvesting within a certain volume of

a dye-zeolite and radiationless energy transport to both ends of the cylinder or from the ends to the center. This first stage is well mastered.¹⁹ A *second level of organization* is the coupling to an external acceptor or donor stopcock fluorophore at the ends of the zeolite L channels which can trap electronic excitation energy from donor molecules inside the crystal or inject electronic excitation energy to acceptors inside the channels, see Figure 4b. We have shown that this works for several different stopcock fluorophores.²⁰ A *third level of organization* is coupling of the dye-zeolite L systems to the environment for

example with a luminescent polymer. This is interesting for OLED research and is shown in Figure 4c.

Green emitting mitofluor green (MFG) stopcocks can be combined with oxonine (Ox⁺) inside the zeolite L channels in order to inject electronic excitation energy from the MFG stopcocks to Ox⁺ molecules inside the zeolite. This is schematically shown in Figure 5.

The emission spectrum of MFG adsorbed on zeolite L and the excitation spectrum of Ox⁺ in zeolite L are shown in Figure 6a. There is a nice spectral overlap region, so we can

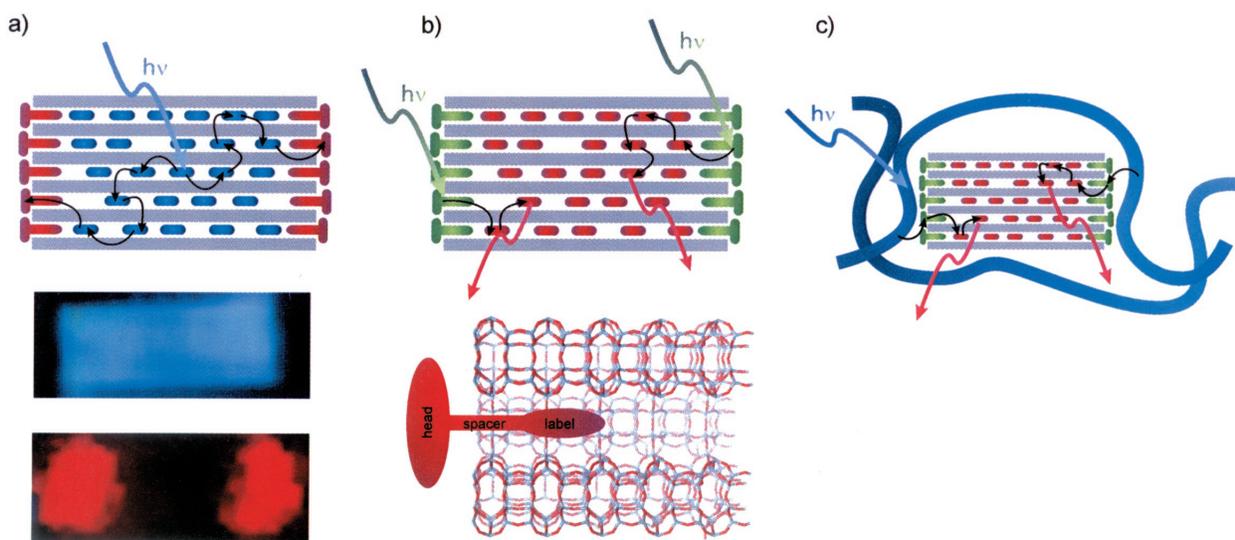


Figure 4. a) Dye-zeolite L antenna; blue emitting donors inside the zeolite L transfer electronic excitation energy to red emitting acceptors at the left and right of the cylindrical crystal. The lower part shows a crystal of about 2 μm long containing DMPOPOP in the middle part and Ox⁺ at both ends as seen in an optical microscope.¹⁹ b) Inverse antenna system with stopcock molecules as energy injectors and a schematic picture of a stopcock at the end of a zeolite L channel. The stopcock consists of a head, a spacer, and a label. c) Energy transfer from a luminescent polymer into a stopcock modified dye-zeolite L system. The luminescent polymer is drawn as a blue ribbon.

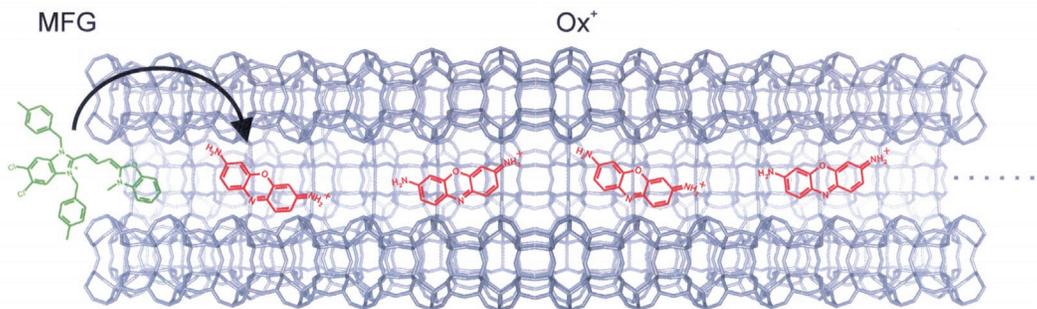


Figure 5. Ox⁺-zeolite L modified with MFG stopcocks for injection of electronic excitation energy.

expect efficient energy transfer. The system shown in Figure 5 was prepared with low Ox^+ loading so that 4.5 times more MFG donor was present than Ox^+ acceptor. When MFG was selectively excited at 22000 cm^{-1} the emission spectrum of Figure 6b was obtained, which shows a considerable Ox^+ fluorescence contribution around 16000 cm^{-1} . This combination thus proves to be successful for energy injection.

A system which approaches the schematic drawing of Figure 4c has been studied recently. Zeolite nanocrystals were modified with amino groups through siloxane linkages and then reacted with ATTO-TEC 495. The structural formula of ATTO-TEC 495 is shown in Figure 7a. The succinimidyl ester is able to react with the amino groups on the zeolite surface yielding peptide linkages. The luminescent polymer which

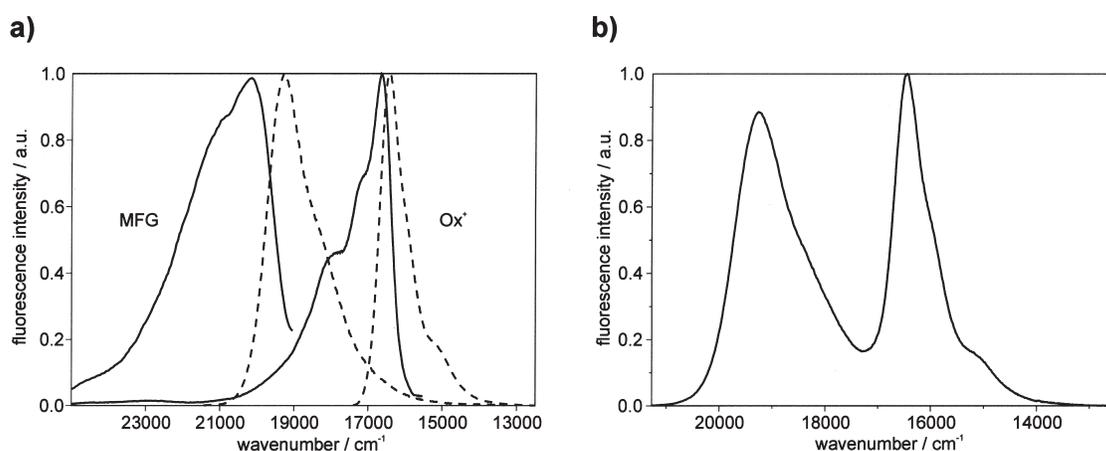


Figure 6. a) Fluorescence (dashed) and fluorescence excitation (solid) spectra of Ox^+ -zeolite L nanocrystals and MFG modified zeolite L nanocrystals; the molar extinction coefficients are $\epsilon_{\text{Ox}^+}(\lambda_{\text{max}}) \approx 84100\text{ cm}^{-1}\text{M}^{-1}$, $\epsilon_{\text{MFG}}(\lambda_{\text{max}}) \approx 119000\text{ cm}^{-1}\text{M}^{-1}$; the spectral overlap between MFG and Ox^+ is $J_{\text{MFG-Ox}^+} \approx 1.9 \times 10^{-13}\text{ cm}^{-3}\text{M}^{-1}$; the Ox^+ occupation probability was $p_{\text{Ox}^+} = 0.008\text{ site}^{-1}$; the crystals with MFG were modified with two molecules per channel. All spectra have been scaled to the same height. b) Fluorescence spectrum of MFG modified Ox^+ -zeolite L nanocrystals. MFG was selectively excited at 22000 cm^{-1} ; the Ox^+ occupation probability was $p_{\text{Ox}^+} = 0.009\text{ site}^{-1}$. The crystals were modified with two MFG molecules per channel.

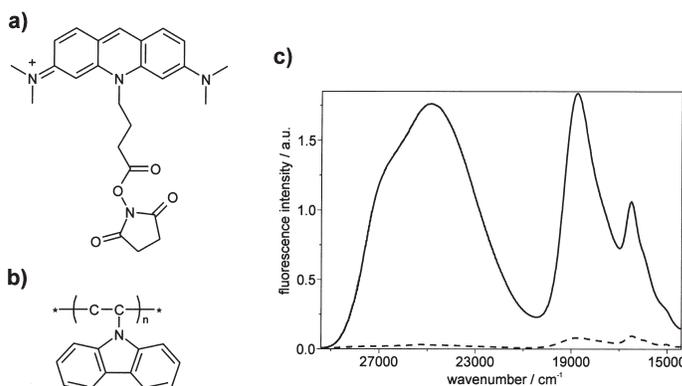


Figure 7. a) Chemical structure of ATTO-TEC 495 with amino reactive succinimidyl ester. b) Chemical structure of poly(*N*-vinylcarbazole), PVK. c) Fluorescence spectra of ATTO-TEC 495 modified Ox^+ -zeolite L embedded in PVK (solid) and of ATTO-TEC 495 modified Ox^+ -zeolite L (dashed). Both samples contained an equal amount of ATTO-TEC 495 modified Ox^+ -zeolite L and were excited at 30300 cm^{-1} . $p_{\text{Ox}^+} = 0.10\text{ site}^{-1}$. The crystals were modified with ATTO-TEC 495 in such a way that each molecule of ATTO-TEC 495 had an area of 25 nm^2 at its disposition. This corresponds to 0.012 molecules per unit cell.

was used for embedding the dye-zeolite crystals was poly(*N*-vinylcarbazole) PVK. The structure of PVK is shown in Figure 7b. It is a photoconductive polymer and emits in the blue. The optical properties of ATTO-TEC 495 are pretty similar to those of MFG. Its absorption maximum in ethanol lies at 20080 cm⁻¹ and its emission maximum at 19048 cm⁻¹. The spectral overlap regions between PVK and ATTO-TEC 495 and between ATTO-TEC 495 and Ox⁺ are large. This dye is thus expected to trap electronic excitation energy from PVK, and pass it on to Ox⁺.

Once the ATTO-TEC 495 molecules are covalently bound on the zeolite external surface, the crystals can be treated in a rough way without washing off the dye molecules. The crystals were embedded in PVK by preparing a polymer/dye-zeolite suspension in dichloromethane. Then, solid state layers were prepared by evaporating the solvent. The result is a solid state dye-zeolite embedded polymer layer. Figure 7c shows the emission spectra of ATTO-TEC 495 modified Ox⁺-zeolite L embedded in PVK, and of ATTO-TEC 495 modified Ox⁺-zeolite L. Both layers were excited at 30300 cm⁻¹. The amount of donor carbazole monomers segments exceeds the amount of Ox⁺ acceptor molecules about 30 times.

Figure 7c shows that we can transfer electronic excitation energy from the photoconductive polymer PVK to the ATTO-TEC 495 molecules on the zeolite external surface, and even to the Ox⁺-molecules which are inside the zeolite channels. This system is a proof that even on a third level of organization it is now possible to communicate between the different components. Each component has its own function and is organized in a different manner, and together these components form a photonic nanodevice.²¹

References

- Drexler, E.; Peterson, C. *Unbounding the Future: the Nanotechnology Revolution*; William Morrow and Company, Inc.: New York, 1991.
- Calzaferri, G.; Maas, H.; Pauchard, M.; Pfenniger, M.; Megelski, S.; Devaux, A. In *Advances in Photochemistry*, Vol. 27; Neckers, D. C., Von Bünau, G., Jenks, W. S., Eds.; John Wiley & Sons, Inc.: Hoboken, 2002; pp 1-50.
- Ritz, T.; Damjanovic, A.; Schulten, K. *Chem. Phys. Chem.* **2002**, *3*, 243.
- Hu, X.; Schulten, K. *Phys. Today* **1997**, *50*, 28.
- Lehn, J.-M. *Science* **1985**, *227*, 849.
- Lehn, J.-M. *Angew. Chem., Int. Ed.* **1988**, *27*, 89; *Angew. Chem.* **1988**, *100*, 91.
- Cram, D. J.; Cram, J. M. *Science* **1974**, *183*, 803.
- Cram, D. J. *Angew. Chem., Int. Ed.* **1988**, *27*, 1009; *Angew. Chem.* **1988**, *100*, 1041.
- Pedersen, C. J. *Angew. Chem., Int. Ed.* **1988**, *27*, 1021; *Angew. Chem.* **1988**, *100*, 1053.
- Jüstel, T.; Nikol, H.; Ronda, C. *Angew. Chem., Int. Ed.* **1998**, *37*, 3084; *Angew. Chem.* **1998**, *110*, 3250.
- Maas, H.; Currao, A.; Calzaferri, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 2495; *Angew. Chem.* **2002**, *114*, 2607.
- Kynast, U.; Weiler, V. *Adv. Mater.* **1994**, *6*, 937.
- Rudzinski, C. M.; Young, A. M.; Nocera, D. G. *J. Am. Chem. Soc.* **2002**, *124*, 1723.
- Polman, A. *J. Appl. Phys.* **1997**, *82*, 1.
- Suib, S. L. *Chem. Rev.* **1993**, *93*, 803.
- Breck, D. W. *Zeolite Molecular Sieves: Structure, Chemistry, and Use*; John Wiley & Sons: New York, 1974.
- Schulz-Ekloff, G.; Wöhrle, D.; Van Duffel, B.; Schoonheydt, R. A. *Microporous Mesoporous Mater.* **2002**, *51*, 91.
- Ohsuna, T.; Horikawa, Y.; Hiraga, K. *Chem. Mater.* **1998**, *10*, 688.
- Calzaferri, G.; Pauchard, M.; Maas, H.; Huber, S.; Khatyr, A.; Schaafsma, T. J. *Mater. Chem.* **2002**, *12*, 1.
- Maas, H.; Calzaferri, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 2284; *Angew. Chem.* **2002**, *114*, 2389.
- Calzaferri, G.; Huber, S.; Maas, H.; Minkowski, C. *Angew. Chem., Int. Ed.* **2003**, *42*, 3732; *Angew. Chem.* **2003**, *115*, 3860.

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