

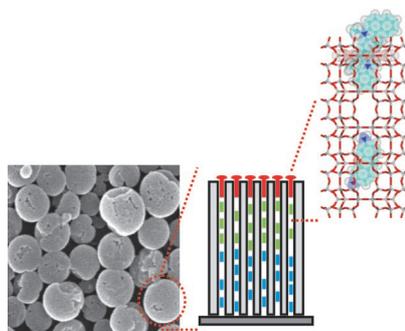
Reprint

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Monolayers

## Organizing Supramolecular Functional Dye–Zeolite Crystals



**Unidirectional antennas:** Dyes in the open channels of the robust monolayers of zeolite L crystals on a glass substrate create a hierarchical order (see picture). Coupling the dye-loaded monolayers to an external acceptor or donor stopcock dye at the channel ends enables electronic excitation energy to be trapped from donor molecules inside the crystal or to inject it to an acceptor inside the channels.

A. Zabala Ruiz, H. Li,  
G. Calzaferri\* \_\_\_\_\_ 5282–5287

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## Organizing Supramolecular Functional Dye–Zeolite Crystals\*\*

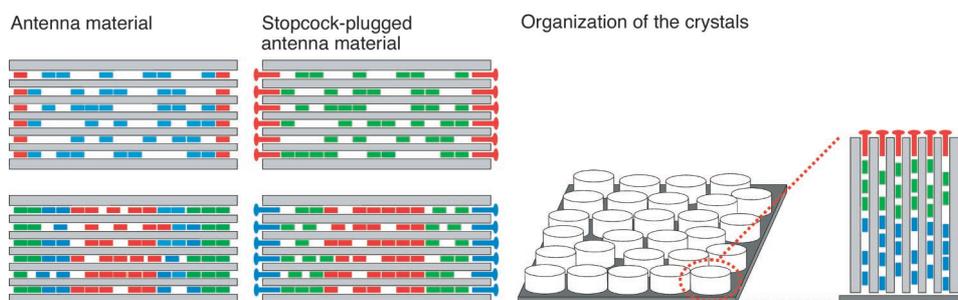
Arantzazu Zabala Ruiz, Huanrong Li, and Gion Calzaferri\*

Sunlight is absorbed in the antenna system of a green leaf where it is transported by supramolecularly organized chlorophyll molecules for the purpose of energy transformation. The aim of our research is to develop a similar transport of light in an artificial system in which dye-loaded zeolite L crystals adopt the antenna function and to find out if and how this can be used in photoelectronic devices. Organic dye molecules have the tendency to form aggregates even at low concentration. These aggregates are known to generally cause fast thermal relaxation of electronic excitation energy. The main role of the zeolite as a host is to prevent this aggregation and to superimpose a specific organization.<sup>[1]</sup> We have shown that zeolite L<sup>[2]</sup> is an ideal host for this purpose. Supramolecular organization of dyes inside the one-dimensional channels of this material has been realized and their communication via stopcock molecules with molecules in the environment with a polymer or a semiconductor as well as solubilization of dye-loaded zeolite L crystals has been demonstrated.<sup>[3,4]</sup>

We know that in chemical devices a high degree of supramolecular organization is important for attaining the desired macroscopic properties.<sup>[5]</sup> A possibility for achieving a high level of organization is the controlled assembly of the zeolite crystals into oriented structures and the preparation of monodirectional materials. In the case of cylindrically shaped zeolite L, this implies the alignment of many crystals on a surface, and has the consequence of the alignment of a large

number of one-dimensional channels. An overview of the antenna material, of the stopcock-plugged antenna material, and of the desired organization of the zeolite L crystals resulting in monodirectional functional materials is illustrated in Figure 1.

The preparation of dense monolayers of zeolite crystals in the nanometer to micrometer size regime was first reported for zeolite A<sup>[6]</sup> and later considerably improved and also extended to other types of zeolites.<sup>[7]</sup> As a general rule, we can state that the successful assembly of small zeolite crystals



**Figure 1.** Different stages of organization. Left: Supramolecularly organized dye–zeolite crystals. Middle: Stopcock-plugged dye–zeolite crystals. Right: Organization of supramolecular functional dye–zeolite crystals in oriented monolayers.

largely depends on the availability of a narrow size distribution and a well-defined morphology. The successful assembly of oriented zeolite L monolayers, which can then be modified to result in organized supramolecular functional materials, offers a new challenge. Table 1 gives an overview of the different ways of preparing such monolayers on a substrate. An underlying principle that has to be respected is that the interaction between the base of the cylindrically shaped zeolite L crystals and the substrate must be stronger or preferably much stronger than that between the coat of the crystals and the substrate and, importantly, any interaction between the zeolite crystals. Working with an excess of crystals, fixing them in the right way to the substrate, and washing away the excess material has, under these conditions, a high chance of leading to the desired material. Subsequent insertion of dye molecules into the channels and the addition of stopcocks is only possible if the channels are not blocked or damaged during the preparation of the monolayer. The procedure leads to materials with exciting properties, for example, to systems where electronic excitation energy is transported in one direction only.

The preparation of zeolite L monolayers was carried out with two types of medium-sized cylindrically shaped zeolite L crystals: 1  $\mu\text{m}$  average length of average aspect ratio (length to diameter ratio) 1.0, and 200 nm average length of average aspect ratio 0.3.<sup>[8]</sup> Different chemical procedures were followed depending on the reagents used. The incorporation of the dyes and the attachment of stopcock molecules at the channel ends, after calcining the monolayers of oriented zeolite L crystals, led to monodirectional materials. The molecules that have been used as covalent linkers to synthesize the zeolite L monolayers, the dyes that have been

[\*] Dipl.-Chem. A. Zabala Ruiz, Dr. H. Li, Prof. Dr. G. Calzaferri  
 Departement für Chemie und Biochemie  
 Universität Bern  
 Freiestrasse 3, 3012 Bern (Switzerland)  
 Fax: (+41) 31-631-3994  
 E-mail: gion.calzaferri@iac.unibe.ch

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