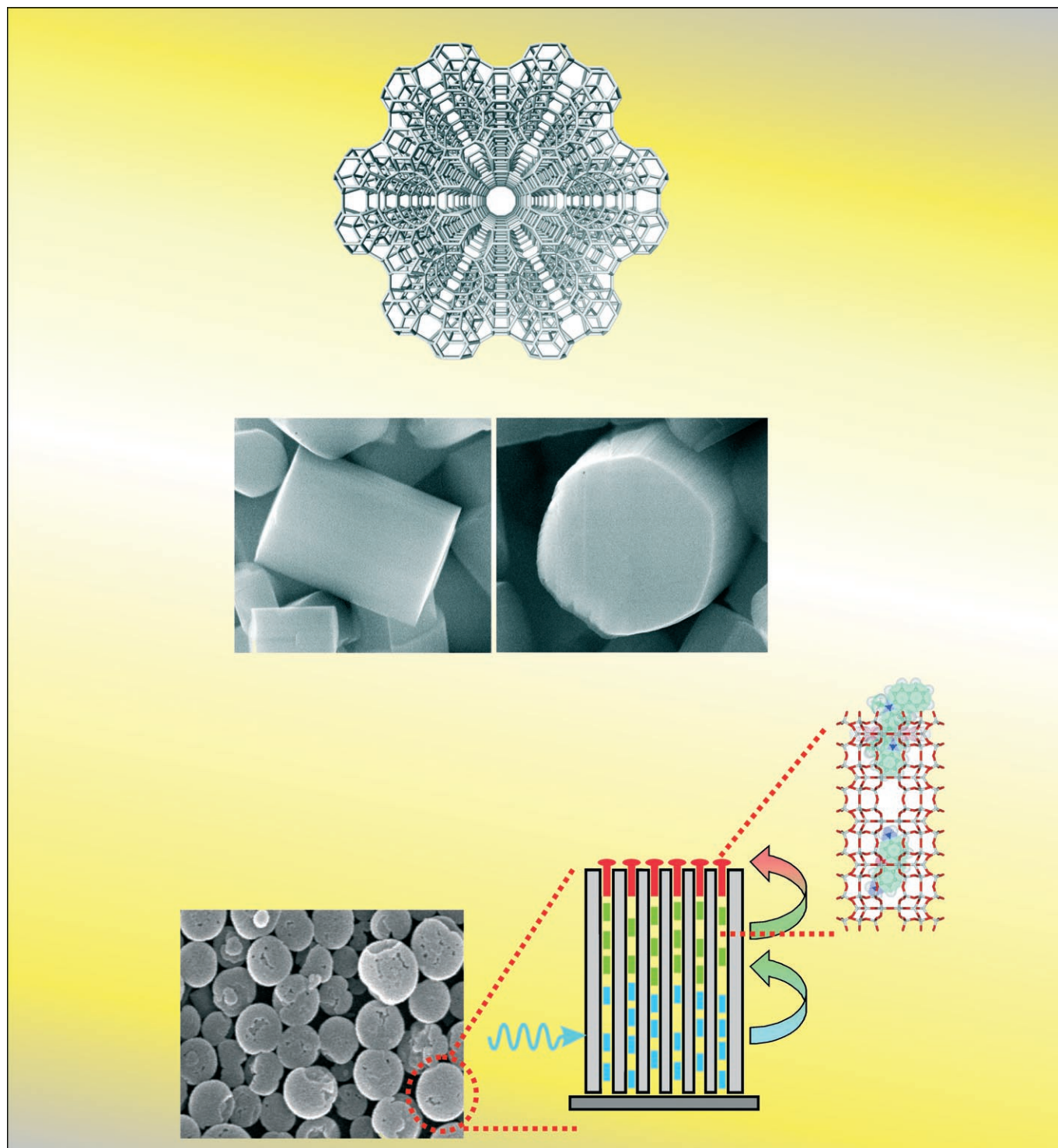


Dye-Modified Nanochannel Materials for Photoelectronic and Optical Devices

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Abstract: Artificial photonic antenna systems have been realised by incorporating organic dyes into zeolite L. The size and aspect ratio of the cylindrically shaped zeolite crystals can be tuned over a wide range, adding to the versatility of this host material. A 600 nm sized crystal, for example, consists of about 96 000 one-dimensional channels oriented parallel to the cylinder axis. Geometrical constraints imposed by the host structure lead to supramolecular organisation of the guests, allowing high concentrations of non- or only very weakly interacting dye molecules. A special twist is added to these systems by plugging the channel openings with a second type of fluorescent dye, a so-called stopcock molecule. The two types of molecules are precisely tuned to each other; the stopcocks are able to accept excitation energy from the dyes in the channels, but cannot pass it back. The supramolecular organisation of dyes in the zeolite channels corresponds to a first stage of organisation, allowing light-harvesting within the volume of a cylindrical crystal and radiationless energy transport to either the cylinder ends or centre. The second stage of organisation represents the coupling to an external acceptor or donor stopcock fluorophore at the channel entrances, which can then trap or inject electronic excitation energy. The third stage of organisation is realised by interfacing the material to an external device through a stopcock intermediate. We observed that electronic-excitation-energy transfer in dye-zeolite L materials occurs mainly along the channel axis and we have shown that macroscopically organised materials can be prepared. The new materials offer unique possibilities as building blocks for optical, electro-optical and sensing devices.

Keywords: dyes/pigments • FRET (fluorescence resonant energy transfer) • host-guest chemistry • luminescence • supramolecular chemistry • zeolites

Introduction

One-dimensional channel materials are very attractive hosts for supramolecular organisation of guests.^[1,2] They are often, at least conceptually, the simplest possible choice for obtaining a specific organisational pattern. A large variety of systems have been realised by using zeolite L as a host and luminescent dye molecules as guests.^[2-4] Zeolite L consists of strictly parallel channels arranged in a hexagonal framework as shown in Figure 1. Its stoichiometry is $[M]^+_9 \cdot [(AlO_2)_9(SiO_2)_{27}] \cdot nH_2O$, in which M^+ are monovalent ions compensating the negative charge resulting from the aluminium atoms and n is 21 in fully hydrated materials, and 16 at about 22% relative humidity.^[5] Zeolite L currently seems to be the only nanochannel material that can be synthesised in a size range starting from about 30 nm up to a few thousand nm and with different aspect ratios from disc-shaped to elongated crystals.^[6] In a theoretical study, we examined cylinders containing donor and acceptor molecules in an arrangement as shown in Figure 1F.^[7] The donors are represented in green and the acceptors in red. The donor that has been excited by absorbing an incident photon transfers its electronic excitation radiationlessly by means of Förster resonance energy transfer (FRET) to an unexcited neighbour.^[8] After a series of such steps, the electronic excitation reaches a luminescent trap (acceptor molecule) and is then released as fluorescence. The acceptors are thought to mimic the “entrance of the reaction centre” of the natural antenna. The dimensions given in Figure 1F correspond to the pore opening and the distance between the centres of two channels in zeolite L. The largest energy-transfer rate constant is observed if the electronic transition dipole moments (ETDM) are oriented parallel to the channel axis. Quasi one-dimensional energy transfer, an important requirement for an efficient light-harvesting material, was observed, and the first unidirectional antenna system realised on a macroscopic scale has been reported.^[9,10] In the following, we will present selected features of these new materials specifically concerning their unique possibilities as building blocks for optical, electro-optical and sensing devices. Table 1 shows the structure of the dyes that were used as guest molecules for the materials discussed in this article.

Organisation

Antenna systems are supramolecular arrangements in which electronic excitation of molecules occurs in a given volume and in which the electronic excitation energy is then transported by near-field interactions (FRET) to a well-defined location. Sequential insertion of dyes into zeolite L channels is an excellent concept for preparing such systems.^[11] Communication of the dyes in the channels with the outside world is established by stopcocks, consisting in principle of a label, a spacer and a head as shown in Figure 2.^[12] The

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