

AFMDC6  
ISSN 1616-301X  
Vol. 16, No. 17  
November 3, 2006

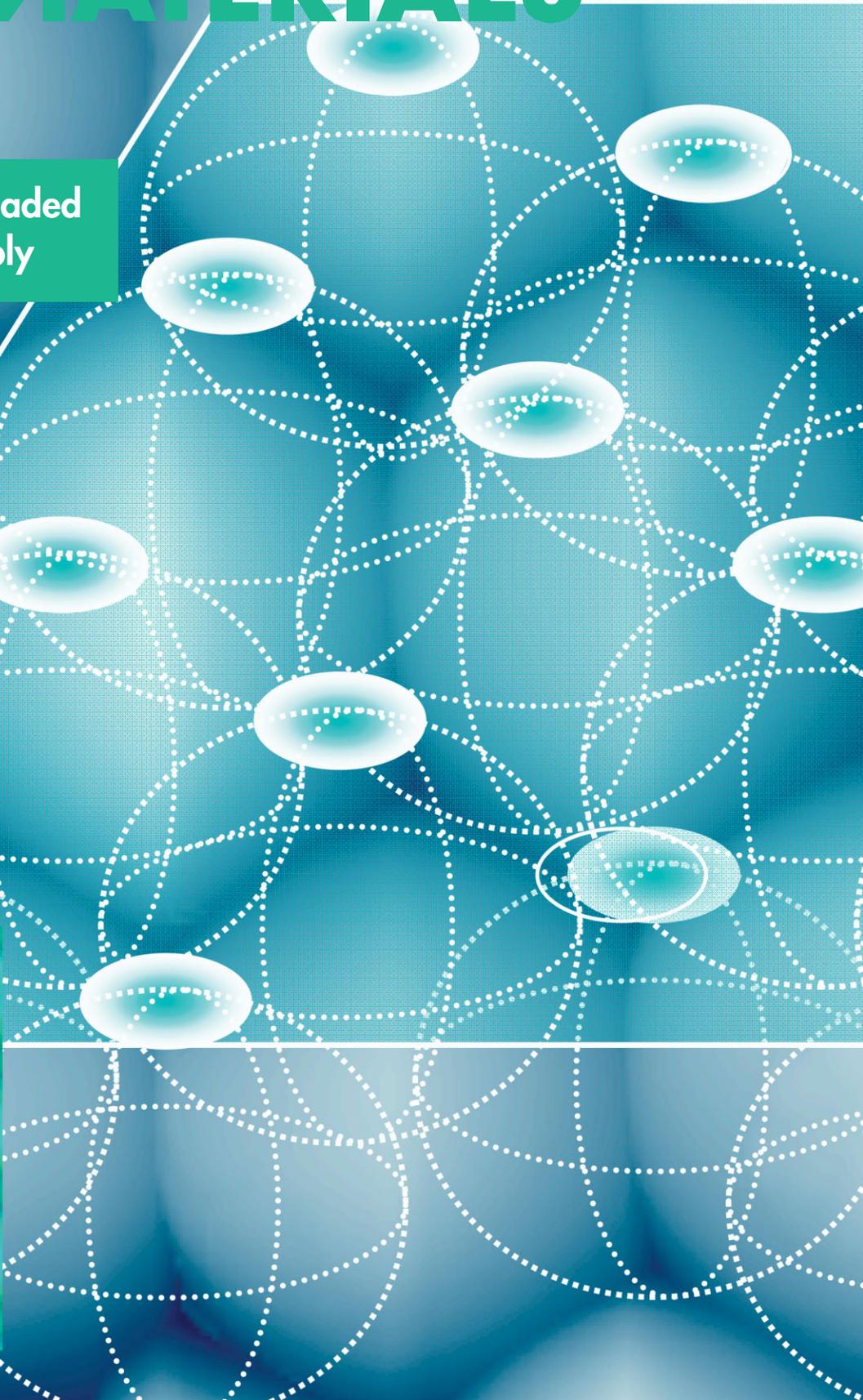
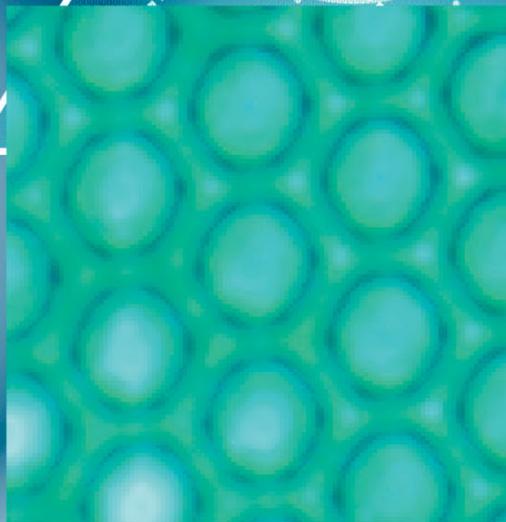


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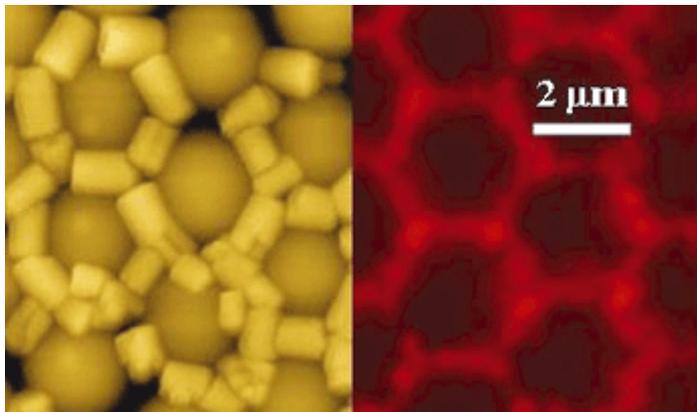
# ADVANCED FUNCTIONAL MATERIALS

Organization of Dye-Loaded  
Zeolites by Autoassembly



## Hexagonal Network Organization of Dye-Loaded Zeolite L Crystals by Surface-Tension Driven Autoassembly

S. Yunus, F. Spano, G. Patrinoiu, A. Bolognesi, C. Botta, D. Brühwiler, A. Zabala Ruiz, G. Calzaferri



**Highly fluorescent dye-loaded zeolite L crystals** are organized in an hexagonal network (see figure left and inside cover) by a surface-tension-driven autoassembly process. The resulting film displays a regular hexagonal pattern of polarized fluorescence (figure right), reflecting the polarization properties of the dye molecules inserted in the parallel nanochannels of the zeolite crystals.

DOI: 10.1002/adfm.200600255

# Hexagonal Network Organization of Dye-Loaded Zeolite L Crystals by Surface-Tension-Driven Autoassembly\*\*

By Sami Yunus,\* Fabrizio Spano, Greta Patrinoiu, Alberto Bolognesi, Chiara Botta, Dominik Brühwiler, Arantzazu Zabala Ruiz, and Gion Calzaferri

Highly fluorescent dye-loaded zeolite L crystals, approximately 1.4  $\mu\text{m}$  long and 650 nm in diameter, are organized in a hexagonal network by a surface-tension-driven autoassembly process. A polydimethylsiloxane (PDMS) film presenting a trigonal ordering of spherical protuberances, including a polystyrene (PS) hexagonal network occupying their interstices, is chosen as the platform for the assembly. The overall wettability and the difference in surface tension between PDMS and PS surfaces are found to offer good conditions for ordering micrometric dye-loaded zeolite L crystals in a 2D hexagonal network. The resulting film displays a regular hexagonal pattern of polarized fluorescence, reflecting the polarization properties of the dye molecules inserted in the parallel nanochannels of the zeolites.

## 1. Introduction

Hierarchically organized structures, presenting successive ordering from the molecular up to the millimeter scale are subject to great interest, owing to the direct relationship between the molecular arrangements (i.e., orientation of molecules) and the macroscopic geometry or properties.<sup>[1–3]</sup> This is one aspect that makes nanotechnology so appealing and promising in many technological fields, for example in nano- and microelectronics.

Zeolite L crystals containing oriented fluorophores in their parallel nanochannels<sup>[4]</sup> possess extremely efficient fluorescent properties that make them ideal host–guest structures for the exploitation of energy-transfer and energy-funneling processes in the fields of optoelectronics and photonics, provided that

they can be properly organized. Self-assembly strategies in the organization of matter make hierarchical ordering especially attractive from fundamental and economic points of view, by avoiding expensive techniques such as photolithography. Assembling zeolite crystals into well-defined macroscopic structures is of particular interest, considering that zeolites are ideal host materials for supramolecular organization.<sup>[5]</sup> The generation of zeolite patterns adds a further level of organization, thus extending the ordering from the molecular to the macroscopic scale. Large zeolite crystals (longer than 100  $\mu\text{m}$  long) can be aligned by an electric field,<sup>[6]</sup> or by mechanically shaking them into the grooves of a microstructured surface.<sup>[7]</sup> However, single crystals in the size regime of 100  $\mu\text{m}$  are not accessible for most zeolite types, and are furthermore not practical for most purposes. For smaller crystals, a distinct interaction between the crystals and specific parts of the substrate is necessary to achieve ordering into defined patterns. Micropatterning of monolayers of micrometer-sized ZSM-5 crystals has been demonstrated by Yoon and co-workers, through covalent bonding of the crystals to pretreated glass substrates.<sup>[8]</sup>

Herein, we introduce a novel approach towards micropatterning of small zeolite crystals employing a surface-tension pattern. As demonstrated and calculated by Whitesides and co-workers, strategies implying self-assembly by minimization of interfacial free energy can be applied to position small objects at the micrometric scale.<sup>[9]</sup> We show that zeolite L crystals containing oriented fluorophores in their parallel nanochannels<sup>[10]</sup> can be well organized in an hexagonal arrangement on polydimethylsiloxane (PDMS) films obtained through molding of self-assembled, ordered, macroporous polystyrene (PS) films. We have found, in this precise case and at this scale length (approximately micrometer scale), that surface-tension interactions should be considered as the tool of choice for manipulation at the micrometric scale.<sup>[11,12]</sup> With this simple method, based on self-assembling processes, we have been able to hierarchically organize molecular dyes at a macroscopic level, reaching a fair 2D chromophore organization.

[\*] Dr. S. Yunus,<sup>[+]</sup> Dr. F. Spano, Dr. G. Patrinoiu,<sup>[++]</sup> Dr. A. Bolognesi, Dr. C. Botta  
Istituto per lo Studio delle Macromolecole, CNR  
Via E. Bassini 15, 20133 Milano (Italy)  
E-mail: yunus@pcpm.ucl.ac.be

Dr. S. Yunus,<sup>[+]</sup> Dr. F. Spano, Dr. G. Patrinoiu,<sup>[++]</sup> Dr. A. Bolognesi, Dr. C. Botta  
Polo Scientifico Tecnologico, CNR  
Via Fantoli 16, 20133 Milano (Italy)

Dr. D. Brühwiler,<sup>[+++]</sup> A. Z. Ruiz, Prof. G. Calzaferri  
Department of Chemistry and Biochemistry  
University of Bern  
Freiestrasse 3, CH-3000 Bern 9 (Switzerland)

[+] Present address: Laboratoire de Physico-Chimie et de Physique des Matériaux, Université Catholique de Louvain, Place Croix du Sud 1, 1348 Louvain-la-Neuve, Belgium.

[++] Present address: I. G. Murgulescu Institute of Physical Chemistry, Spl. Independentei 202, 77208 Bucharest, Romania.

[+++] Present address: Institute of Inorganic Chemistry, University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzerland.

[\*\*] The authors acknowledge financial support from the European Commission through the Human Potential Program (RTN 'Nanochannel', Contract No. HPRN-CT-2002-00323 and Nanomatch, Contract No. MRTN-CT-2006-035884).