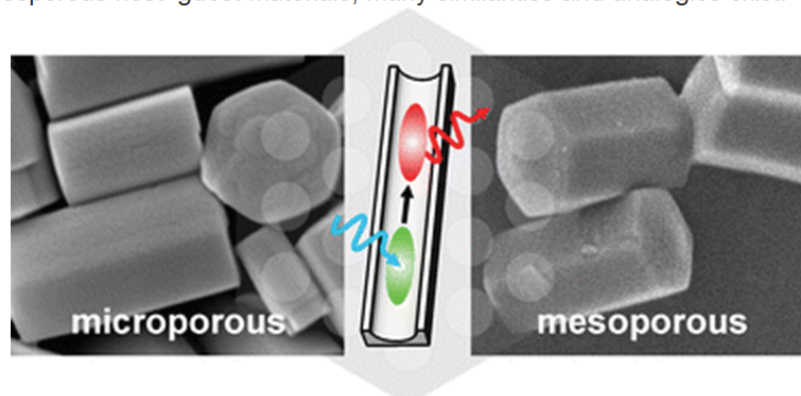


Nanochannels for supramolecular organization of luminescent guests

Dominik Brühwiler, Gion Calzaferri, Tomás Torres, Jan Hinrich Ramm, Nando Gartmann, Le-Quyenh Dieu, Ismael López-Duarte and M. Victoria Martínez-Díaz

Zeolites and mesoporous silica are versatile host materials for the supramolecular organization of a large variety of guests. The inclusion of luminescent molecules, complexes, or nanoclusters into ordered one-dimensional channel systems is particularly intriguing, as the resulting host–guest compounds may exhibit unique properties such as optical anisotropy, efficient energy transfer, and enhanced stability. Several levels of organization have been realized for zeolite L, extending from the interior of a given crystal to the channel entrances and the external surface as well as from the microscopic to the macroscopic scale. The diverse chemistry that is involved in the development of a highly organized and functional host–guest material is illustrated by the design of molecules which are able to selectively adsorb at the channel entrances and establish communication between included guests and external objects. The importance of phthalocyanines as chromophores for this particular concept is exemplified. Based on the extensive research on zeolite L, possibilities and recent developments in the field of mesoporous silica hosts are discussed, revealing that despite the obvious differences between microporous and mesoporous host–guest materials, many similarities and analogies exist.



Nanochannels for supramolecular organization of luminescent guests

Dominik Brühwiler,^{*a} Gion Calzaferri,^{*b} Tomás Torres,^{*c} Jan Hinrich Ramm,^a Nando Gartmann,^a Le-Quyenh Dieu,^a Ismael López-Duarte^c and M. Victoria Martínez-Díaz^c

Received 9th April 2009, Accepted 4th June 2009

First published as an Advance Article on the web 14th July 2009

DOI: 10.1039/b907308f

Zeolites and mesoporous silica are versatile host materials for the supramolecular organization of a large variety of guests. The inclusion of luminescent molecules, complexes, or nanoclusters into ordered one-dimensional channel systems is particularly intriguing, as the resulting host–guest compounds may exhibit unique properties such as optical anisotropy, efficient energy transfer, and enhanced stability. Several levels of organization have been realized for zeolite L, extending from the interior of a given crystal to the channel entrances and the external surface as well as from the microscopic to the macroscopic scale. The diverse chemistry that is involved in the development of a highly organized and functional host–guest material is illustrated by the design of molecules which are able to selectively adsorb at the channel entrances and establish communication between included guests and external objects. The importance of phthalocyanines as chromophores for this particular concept is exemplified. Based on the extensive research on zeolite L, possibilities and recent developments in the field of mesoporous silica hosts are discussed, revealing that despite the obvious differences between microporous and mesoporous host–guest materials, many similarities and analogies exist.

1. Introduction

Zeolites, which according to IUPAC nomenclature are named (for historical reasons) microporous materials, are actually nanoporous, with pore sizes between 0.4 and 2 nm. By the same classification, materials with pore sizes in the range of 2 to 50 nm are referred to as mesoporous materials.¹ Zeolites are crystalline

and can in general be regarded as thermally and chemically robust hosts for enclosing guests and protecting them from reactive environments as well as allowing them to establish a new, very specific and often complex order, which results in organized objects with unique properties. Guests can travel through the extended cavity and channel system, experiencing potentially size-selective chemical processes and leaving the host as a new species.^{2–4} Summarizing the amazing variety of properties of zeolites, many of which have been exploited in hundreds of applications, is beyond the scope of this article, because not only the structure and composition, but also the size and morphology of the crystals, surface modifications, and external parameters such as the surrounding medium, temperature, and pressure may be of considerable influence. Most zeolites can be considered as having 3D channel systems, others bear a 2D

^aInstitute of Inorganic Chemistry, University of Zürich, Winterthurerstrasse, 190, 8057 Zürich, Switzerland. E-mail: bruehwi@aci.uzh.ch

^bDepartment of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland. E-mail: gion.calzaferri@iac.unibe.ch

^cDepartamento de Química Orgánica, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain. E-mail: tomas.torres@uam.es



Dominik Brühwiler

Dominik Brühwiler received his PhD from the University of Bern in 2001, followed by a post-doctoral stay at the Lawrence Berkeley National Laboratory. Since 2004, he is leading a research group at the University of Zürich specializing in the synthesis, functionalization, and organization of microporous and mesoporous materials.



Gion Calzaferri

Gion Calzaferri is emeritus professor of physical chemistry at the University of Bern (Switzerland). He is the 2007 recipient of the Theodor Förster lectureship, awarded jointly by the German Chemical Society and the German Bunsen Society for Physical Chemistry. His research focuses on supramolecularly organized molecules, clusters, and complexes in zeolites, and on artificial antenna systems for light harvesting.

channel structure and some have 1D channels. An example of each type is illustrated in Fig. 1. For other framework types and structures we refer to the excellent source provided online by the International Zeolite Association.⁵

This article focuses on the well-developed platform of zeolite L host systems. However, many of the reported concepts can in principle be applied to other nanoporous hosts, such as mesoporous materials or zeolites with frameworks other than zeolite L. Despite the obvious differences of microporous and mesoporous silicate-based hosts, the properties of the resulting host–guest composites are often similar and may include optical anisotropy, efficient energy transfer or the ability to respond to external stimuli. Throughout this article we will therefore take brief excursions into the field of host–guest systems based on mesoporous silica, illustrating that the step from micro- to mesopores opens a variety of new possibilities to create advanced functional materials.

The most popular mesoporous host materials are of the MCM-41⁶ and SBA-15⁷ type, featuring, in an ideal model, hexagonally arranged channels. Cage-type mesostructures with 3D pore systems, such as SBA-16,^{7,8} are particularly interesting

for the introduction of guests by a ship-in-a-bottle approach. An overview of the various types of mesoporous silica and their respective syntheses can be found in a recent review by Wan and Zhao.⁹

Besides the pore size, there are further essential differences between zeolites and mesoporous silica. The pore walls of mesoporous silica are amorphous, providing a large number of surface silanol groups, which can be used to covalently attach functional moieties, such as chromophores or catalytically active species.¹⁰ Functionalized pore walls can also provide an optimized environment for guests. The pore size of mesoporous silica can be tuned by employing a specific structure-directing agent (SDA), by adjusting the synthesis conditions such as temperature and aging time, or by the addition of swelling agents. While mesoporous silica particles often feature irregular morphology, the preparation of particles with more regular shape, such as spheres¹¹ or hexagonal fibers,¹² is possible (Fig. 2).

The design of structurally organized and functionally integrated artificial systems that are capable of elaborating the energy and information input of photons to perform functions such as processing and storing of information, sensing of microscopic environments on a nanoscale level, opening and closing of pore entrances or transformation and storage of solar energy is an important topic of materials science and one of the most fascinating challenges of modern photochemistry.^{13–15} The electronic transition dipole moment (ETDM) of the chromophores plays an important role for the description and understanding of such systems.¹⁶ Increasing complexity of the individual objects has been realized by embedding several active molecules or chromophores into the cavities/channels and also by modifying the external surface of the respective host material.^{3,17–20}

Zeolites and mesoporous silica are attractive hosts for the preparation and investigation of hierarchically organized structures, presenting a successive ordering from the molecular up to the macroscopic scale, thus highlighting the relationship between molecular arrangements and macroscopic properties.^{14,21–26} The simplest composites consist of a host accommodating a guest, which can be a molecule, a complex or a cluster. Ideally, the guest is only in contact with the host and not able to escape under the conditions specific to the given application. Such materials can be used as pigments, luminophores, nano- or micro-sized



**Tomás Torres (below),
M. Victoria-Martínez-Díaz (right)
and Ismael López-Duarte (left)**

Tomás Torres, M. Victoria-Martínez-Díaz and Ismael López-Duarte are, respectively, Full Professor, Associate Professor and Ph.D. Student of the Department of Organic Chemistry at the Autònoma University of Madrid (UAM). The Torres group has a multi-disciplinary character at the interface of chemistry, physics and materials science. In addition to various aspects of synthetic, and supramolecular chemistry, the group is currently exploring several areas of

application of phthalocyanines, including organic and hybrid solar cells, with a focus on nanotechnology.



**Le-Quyenh Dieu (left), Jan Hinrich Ramm (middle) and
Nando Gartmann (right)**

Le-Quyenh Dieu (left) studied chemistry at the University of Bern and is currently working towards her PhD. Her research focuses on photonic antenna systems based on dye-zeolite inclusion compounds with phthalocyanine stopcocks. Nando Gartmann (right) obtained his MSc (Chemistry) from the University of Zürich. An important part of his PhD project concerns the selective functionalization of external and internal surfaces of mesoporous silica and the analysis of functional group distributions. Jan Hinrich Ramm (middle) studied chemistry at the TU Bergakademie Freiberg. His current PhD work involves the synthesis of multi-functionalized mesoporous silicas as advanced host materials for luminescent guests.