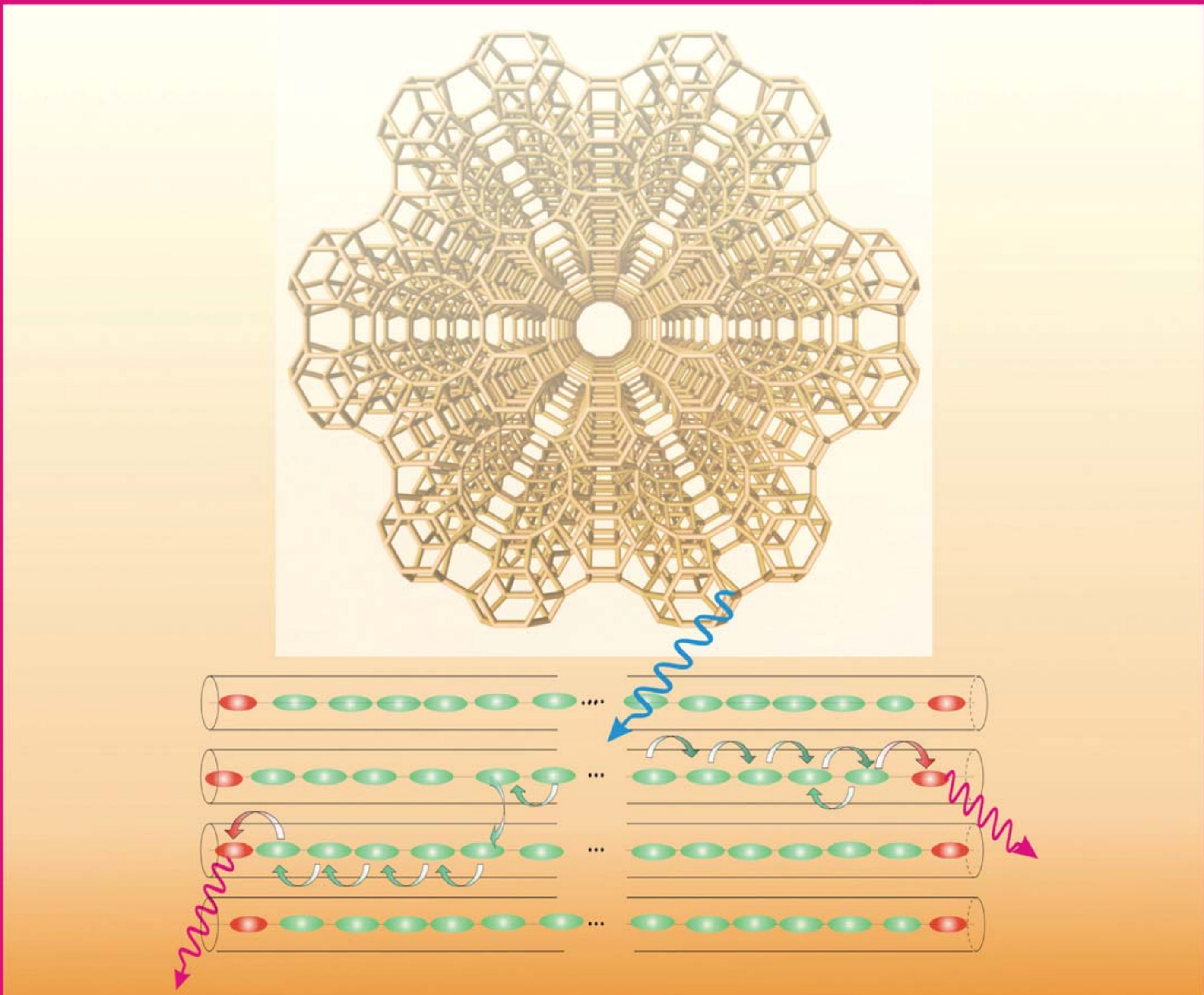
Langmuir

The ACS Journal of Surfaces and Colloids

APRIL 17, 2012
VOLUME 28, NUMBER 15
pubs.acs.org/Langmuir



Artificial Antenna Built by Embedding Fluorescent Dyes in One-Dimensional Nanochannels

(see p. 5A)

ACS Publications
MOST TRUSTED. MOST CITED. MOST READ.

www.acs.org

Langmuir
Editorial
pubs.acs.org/Langmuir

Biographical Sketch

Gion Calzaferri is emeritus professor of physical chemistry at the University of Berne, Switzerland. His research focuses on supramolecularly organized molecules, clusters, and complexes in zeolites, on artificial antenna systems for light harvesting, and on photochemical transformation and storage of solar energy. Research stays and invited professorships at NREL, Golden, Colorado, at Cornell University, at Ecole Normale Supérieure de Cachan, at University of Münster/Westfalen, and at other places mark his interest in international collaboration and scientific exchange. Gion is the author/coauthor of about 280 scientific publications and patents, and 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.

Published: March 28, 2012

dx.doi.org/10.1021/la300947d | Langmuir 2012, 28, 6201−6201

Cover illustration figure by Gion Calzaferri. The figure illustrates the channel arrangement of a hexagonal framework acting as a host, and below it a side view of the artificial antenna built by embedding fluorescent dye molecules in these channels: donors in the middle part and acceptors at both ends. The donors are electronically excited by absorbing a photon. This causes transfer of electronic excitation energy via FRET to the acceptors located at both ends of the one-dimensional channels, where the energy is trapped and can be released as fluorescence or can be transferred to another target. For more information, see “Nanochannels: Hosts for the Supramolecular Organization of Molecules and Complexes” by Gion Calzaferri on pages 6216-6231.

Langmuir

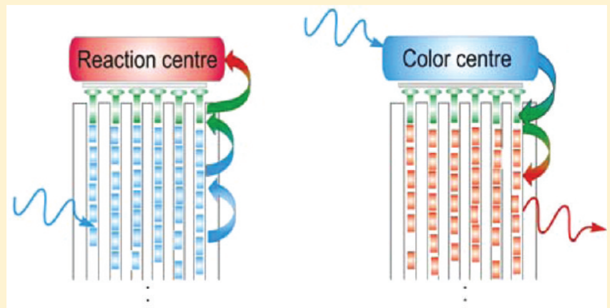
Invited Feature Article

pubs.acs.org/Langmuir

Nanochannels: Hosts for the Supramolecular Organization of Molecules and Complexes

Gion Calzaferri*

Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland



ABSTRACT: Nanochannels have been used as hosts for supramolecular organization for a large variety of guests. The possibilities for building complex structures based on 2D and especially 3D nanochannel hosts are larger than those based on 1D nanochannel hosts. The latter are, however, easier to understand and to control. They still give rise to a rich world of fascinating objects with very distinguished properties. Important changes are observed if the channel diameter becomes smaller than 10 nm. The most advanced guest−nanochannel composites have been synthesized with nanochannels bearing a diameter of about 1 nm. Impressive complexity has been achieved by interfacing these composites with other objects and by assembling them into specific structures. This is explained in detail. Guest−nanochannel composites that absorb all light in the right wavelength range and transfer the electronic excitation energy via FRET to well-positioned acceptors offer a unique potential for developing FRET-sensitized solar cells, luminescent solar concentrators, color-changing media, and devices for sensing in analytical chemistry, biology, and diagnostics. Successful 1D nanochannel hosts for synthesizing guest−host composites have been zeolite-based. Among them the largest variety of guest−zeolite composites with appealing photochemical, photophysical, and optical properties has been prepared by using zeolite L (ZL) as a host. The reasons are the various possibilities for fine tuning the size and morphology of the particles, for inserting neutral molecules and cations, and for preparing rare earth complexes inside by means of the ship-in-a-bottle procedure. An important fact is that the channel entrances of ZL-based composites can be functonalized and completely blocked, if desired, and furthermore that targeted functionalization of the coat is possible. Different degrees of organizational levels and prospects for applications are discussed, with special emphasis on solar energy conversion devices.

1. INTRODUCTION

Materials bearing channels of uniform diameter in the range of a few nanometers play an important role in nature, science, and technology. They are found as single tubes of different lengths, as fragile assemblies of single tubes, and also as robust arrangements of many tubes. The latter can exist as noncrystalline or crystalline objects of different morphologies and variable size. Assemblies always show a degree of polydispersity in their size, shape, surface structure, charge, and functionality that is manifest in the achievable degree of their structural perfection and the nature and population of defects in the assembled system. Perfect monodispersity is a privilege of molecules. But even molecules, the size and connectivity of which are exactly defined, give rise to a huge variety of fluctuating states, especially when in contact with a solvent or another environment, as has been beautifully visualized in single-molecule spectroscopy and in advanced computer simulations. The extent of importance of the polydispersity of the objects depends on the properties that we are studying. We shall not often explicitly refer to this aspect, but it is advisible to keep it in mind.[1−15]

The prefix nano has its origin in the Greek word nanos, meaning dwarf. In science, it denotes a factor of 10^{-9}. The diameter of a gold atom is about 0.3 nm (nm). A sphere of 100 nm diameter can host a huge number of atoms or molecules, for example, 3.09×10^7 gold atoms or 1.75×10^7 water molecules. This changes dramatically when crossing the 10 nm limit, where a sphere can host 30 880 gold atoms or 17 500 water molecules, but the number reduces to 31 gold atoms or 17 water molecules in a 1 nm sphere. Understanding the size range below 10 nm is especially fascinating and challenging. The diameter of the nanochannels that we shall explore is mainly in this range, with special emphasis on the 1 nm world, and their length can be somewhere between 10 nm and a few thousand nm. Nanochannels can assemble to nanometer- or micrometer-sized packages, and they can act as hosts for the supramolecular organization of guests, namely, molecules and complexes. A higher level of organization can be realized by interfacing the particles with other objects and by assembling them into specific structures, thus realizing successive ordering from the molecular up to the macroscopic scale. This makes guest−nanochannel composites appealing for utilization in nano/microelectronics, optics, photonics, sensing, biology, and diagnostics.

Nanochannels can be 1D, meaning that one channel does not have more than two entrances that can be opened or closed

Received: January 6, 2012
Revised: February 16, 2012
Published: February 28, 2012

