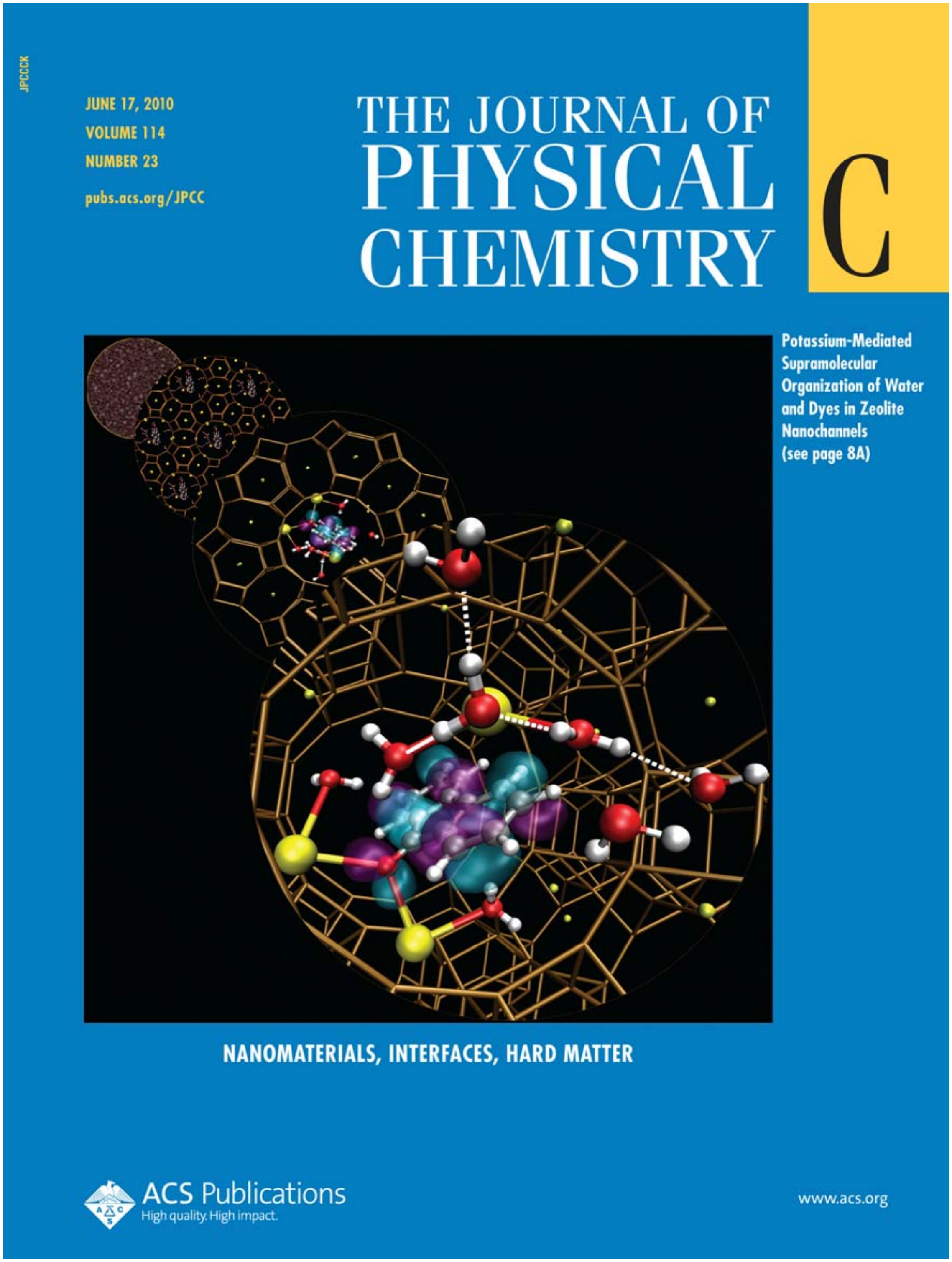
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Potassium-Mediated
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Nanochannels
(see page 8A)

NANOMATERIALS, INTERFACES, HARD MATTER

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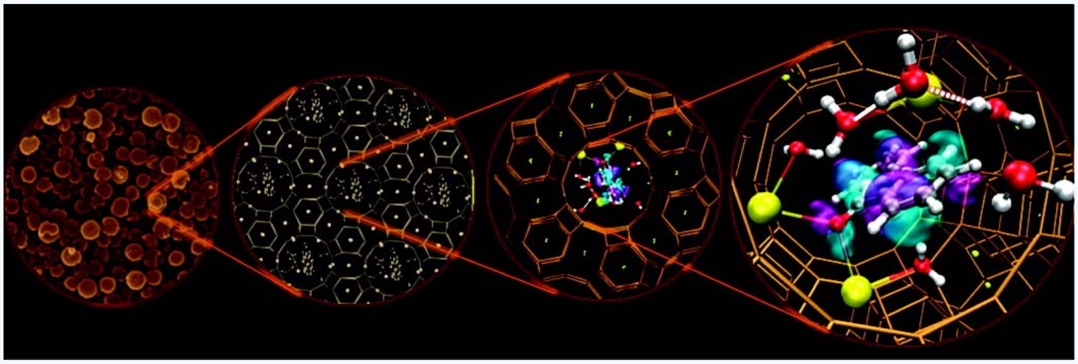
Potassium-mediated supramolecular organization of water and dyes in zeolite nanochannels. Computational studies show that interaction with potassium extraframework cations stabilizes the carbonylic dye fluorenone inside zeolite L, leading to a water-resistant dye-zeolite composite. The material is based on the supramolecular organization of neutral dyes; K^+ mediates the dye/water cohabitation in nanochannels, while the water hydrogen bond network modulates the dye electronic excitation properties and orientation dynamics. The image shows a magnification starting from zeolite L crystals arranged as an oriented monolayer to the framework and finally the molecular structure of the guest inside a nanochannel.



The development of functional materials based on the supramolecular organization of photoactive species in nanosized porous matrices requires a deep knowledge of host–guest interactions and of their influence on material properties and stability. Extensive first-principles investigations on the fluorescent dye fluorenone inside zeolite L, both at dry conditions and in the presence of water, have unraveled the molecular origin of the peculiar stability of this composite in humid environments, a fundamental prerequisite for practical applications. Results of first-principles molecular dynamics simulations, structural optimizations, and TDDFT calculations, validated by comparison with experimental data, provide a comprehensive picture of the structure, energetics, electronic excitation properties, and room-temperature behavior of the fluorenone/zeolite L composite and predict a substantial optical anisotropy for this material also maintained upon contact with water. The interaction of the fluorenone carbonyl group with the zeolite extraframework potassium cations is responsible for the dye stabilization in zeolite L nanochannels and features itself as a general leitmotiv regarding important properties of carbonyl functionalized photoactive species in hydrophilic matrices.

Interactions, Behavior, And Stability of Fluorenone inside Zeolite Nanochannels

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1. Introduction

Zeolites and mesoporous silica are successful host matrices for the supramolecular organization of a large variety of guests as well as key components of a novel promising class of hierarchically organized multifunctional hybrid materials.[1] The inclusion of photoactive molecules, complexes, or clusters into ordered one-dimensional channel systems is particularly intriguing, as the resulting host−guest compounds may exhibit peculiar properties, such as optical anisotropy, efficient energy transfer, nonlinear optical properties, enhanced stability, or specific photoactivity, thus opening the way for their exploitation in some of the most challenging fields of modern chemistry and material sciences. Novel perspectives have been disclosed by these materials in several research areas of interest, among which solar energy harvesting, processing/storing of information, and advanced sensing technology for analytics and diagnostics at the nanoscale are only some representative examples.[1−7] The zeolite-based materials are more advanced, with respect to organizational level and realization of practical applications, than materials based on mesoporous hosts.[1] Zeolite L (Figure 1) configures itself as an ideal host matrix because its arrays of parallel channels with small pore openings and cage diameters impose severe space restrictions and geometrical constraints to the guest species; as a result, very high concentrations of well-oriented photoactive molecules, which essentially behave as monomers, can be obtained. Considerable organization has been realized for organic dye−zeolite L composites, 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.[8] Diverse chemistry has been involved in the development of highly organized and functional host−guest materials, particularly also the design of molecules that are able to selectively adsorb at the channel entrances and establish communication between included guests and external objects.

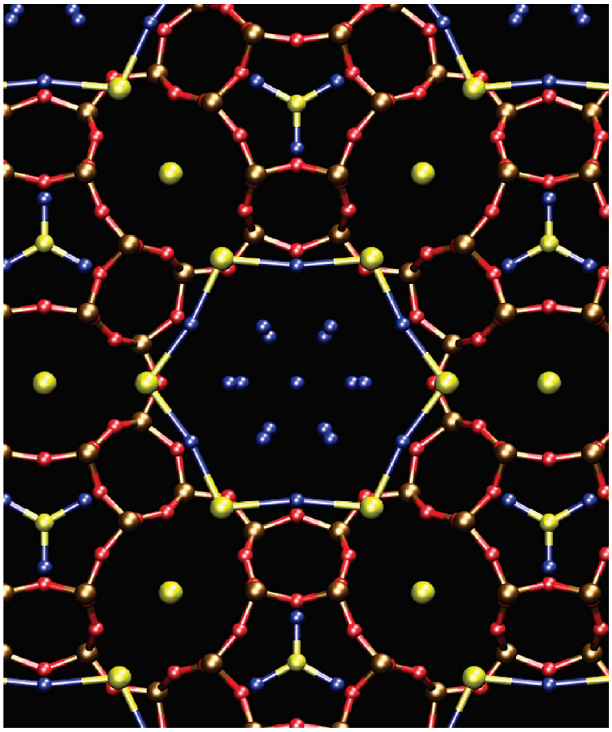

Figure 1. Ball-and-stick representation of perlialite ($K_{12}[Al_{12}Si_{24}O_{72}]\cdot 20H_2O$), the potassium-rich natural zeolite with an LTL framework topology, projected along the *c* axis, evidencing the location of the water sites in the 12-membered-ring channel. Color code: brown, T tetrahedral framework sites (Si or Al); red, framework O; yellow, K^+ sites; blue, water sites. Both K^+ and water sites have partial occupancy. The blue−yellow lines represent water−potassium coordination distances (2.77 Å).

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