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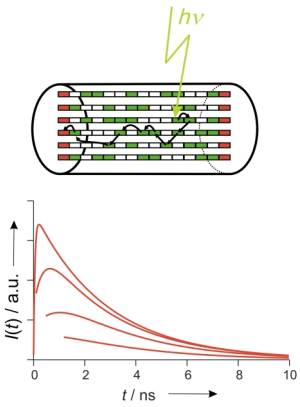

Seeing red with Zeolite: Electronic excitation energy migration in a host–guest material has been investigated by time-resolved fluorescence experiments and by Monte Carlo calculations. The main characteristic of the time evolution of acceptor,donor–zeolite L crystals is that the acceptor intensity is first built up before it starts to decay. This intensity increase becomes faster with increasing donor loading (see graphic), a fact which beautifully shows that the crystals behave as photonic antenna in which excitation energy is transported preferentially along the channels by a Förster-type mechanism until it reaches the acceptor, where it is emitted.

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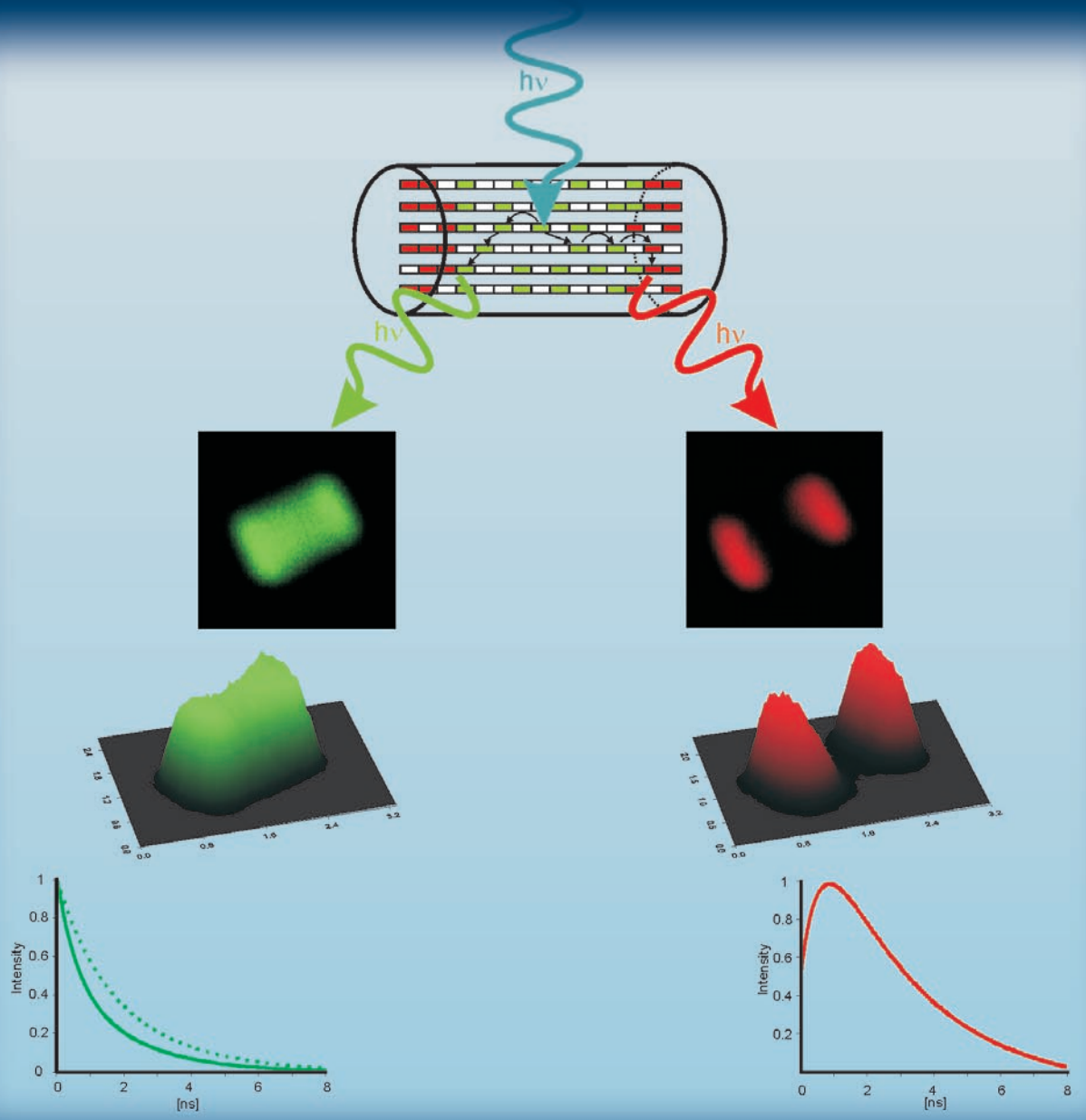

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Electronic Excitation Energy Migration in a Photonic Dye – Zeolite Antenna

Mikalai M. Yatskou, Marc Meyer, Stefan Huber, Michel Pfenniger, and Gion Calzaferri*[a]

Electronic excitation energy migration in a photonic antenna host – guest material has been investigated by time-resolved fluorescence experiments and by Monte Carlo calculations. The host consists of a linear channel system (zeolite L). The channels are filled with energy transporting dyes (donors) in their middle section and by one or several monolayers of a strongly luminescent trapping dye (acceptors) at each end of the channels. Excitation energy is transported among the donors in a series of steps until it reaches an acceptor at one end of the channels, or it is somehow trapped on its way, or it escapes by spontaneous emission. We describe the organization of dyes in the channels by means of Monte Carlo simulation and we report time-resolved data on a variety of pyronine-, oxonine-, and oxonine,pyronine – zeolite L materials. In the latter, the pyronine acts as donor and oxonine as acceptor. We find that the luminescence decay of crystals containing only one kind of dye is single exponential for moderate loading if measured under oxygen-free conditions, but biexponential otherwise. The main characteristic of the time evolution of oxonine,pyronine – zeolite L crystals is that the acceptor intensity is first built up before it starts to decay. This intensity increase becomes faster with increasing donor loading, a fact that beautifully supports the interpretation that the crystals behave as photonic antenna in which excitation energy is transported preferentially along the channels by a Förster-type mechanism until it reaches the acceptor, where it is emitted as red luminescence.

KEYWORDS:

energy migration · host – guest systems · Monte Carlo simulations · time-resolved fluorescence · zeolites

1. Introduction

The advanced understanding of the natural photosystem of green plants has encouraged chemists to synthesize increasingly complex organized materials in order to mimic some of their natural functions.[1–3] Plants are masters of efficiently transforming sunlight into chemical energy. In this process, every plant leaf acts as a photonic antenna, in which photonic energy is absorbed in the form of sunlight and transported by chlorophyll molecules for the purpose of energy transformation. In natural photosynthesis, light is absorbed by a photonic antenna system of a few hundred chlorophyll molecules arranged in a protein environment. These devices allow a fast energy transfer from an electronically excited molecule to unexcited neighbor molecules in such a way that the excitation energy has a high probability of reaching the reaction center; trapping occurs there. It has been reported that the anisotropic arrangement of chlorophyll molecules is important for efficient energy migration (EM).[4, 5] In natural antenna systems, the formation of aggregates is prevented by fencing the chlorophyll molecules in polypeptide cages.[6] A similar approach is possible by enclosing dyes inside a microporous material and by choosing conditions such that the volume of the cages and channels is able to uptake monomers only, and not aggregates.[7] Other attempts to build an artificial antenna have been presented in the literature.[8] Multinuclear luminescent metal complexes,[9–11] multichromophore cyclodextrins,[12] Langmuir – Blodgett films,[13–15] and dyes in polymer matrices,[16–18] and dendrimers[19] have been investigated. Sensitization processes in silver halide photographic materials[20] and also the spectral sensitization of polycrystalline titanium dioxide films in some cases bear aspects of artificial antenna systems.[21–23] Our approach is based on zeolites bearing a channel structure as a host material.[24] The transport of light is made possible by specifically organized dye molecules which mimic the natural function of chlorophyll. In most of our experiments, we have used zeolite L because it was found to be very versatile for this research. Zeolite L crystals consist of an extended one-dimensional tube system.[25, 26] We have filled each individual tube with successive chains of different joint, but noninteracting, dye molecules. Other procedures for preparing dye – zeolite materials have been reported.[27] Light shining on the cylinder is first absorbed and the energy is then transported by the dye

[a] *Prof. Dr. G. Calzaferri, Dr. M. M. Yatskou, M. Meyer, S. Huber, Dr. M. Pfenniger*
Department of Chemistry and Biochemistry
University of Bern
Freiestrasse 3, 3012 Bern (Switzerland)
Fax: (+41) 31-631-39-94
E-mail: gion.calzaferri@iac.unibe.ch

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