Fine-Tuning of Fluorescence Resonance Energy Transfer Efficiency into Zeolite L nanochannels

L. Gartzia-Rivero, J. Bañuelos-Prieto, I. López-Arbeloa

Dpto Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV-EHU), Aptdo 644 48080, Bilbao, Spain leire.gartzia@ehu.es

One of the most fascinating topics of the modern photochemistry is the design of nanostructured artificial photonic systems capable of harvesting and transporting the light to the reaction center and with the desired energy (mimicking the natural process of photosynthesis) [1]. The incorporation of organic photoactive guests into one-dimensional channel materials, such as Zeolite L, gives rise to well organized multifunctional dye-doped hybrid materials. The rigid environment of the solid host protects the organic molecule against chemical or photochemical attacks and increases its thermal resistance. Moreover, geometrical constrains imposed by the framework lead to a supramolecular organization of the guests into the channels, with a preferred orientation along the zeolite L channels.

Nowadays, there is a wide variety of commercially available laser dye families that emit in the ultraviolet (UV), visible (Vis) and near-infrared (IR) regions susceptible to be located by their size in nanoporous materials. In these sense, doping the host's channels with different fluoropohores leads to a hybrid ordered antenna systems for light-harvesting (Figure 1). In these systems light from the UV/Vis/NearIR is harvested and transported to the desired reaction center with the adequate energy via successive energy transfer processes [2]. However, it still remains a challenge to organize multiple cromophores with well-defined interchromophore distances and control their relative orientations and the exact ratio of donors to acceptors, which are the key factor that determine the efficiency of FRET (Förster resonance energy transfer).

The present work deals about the development of antenna devices where laser dyes (C165 and DMPOPOP in the blue region, BODIPYs in the green-yellow and Oxazines in the red) are allocated into the zeolite L nanopores, an alluminosillicate with one-dimensional channels running along the crystal and a pore diameter of about 7.1 Å. The pores of the host are filled with a high amount of dyes, exclusively in monomeric form and aligned in a preferential orientation, thus giving rise to an organized photoactive material (Figure 1).

The obtained organized dye-doped material has been fully characterized by several photophysical techniques: steady-state, time-resolved and confocal fluorescence microscopy. The intermolecular energy transfer between dyes takes place into zeolite L channels directly from donor excited molecules to an acceptor unexcited neighbor, via FRET mechanism, or after energy migration among the donors. In order to control the efficiency of the energy transfer process we have combined different dyes together with a fine selection of their relative proportions. Just modifying both parameters, the energy transfer efficiency can be maximized favoring the red emission (antenna system), or alternatively the FRET can be partial, reaching a tunable emission in the blue, green and red regions (white-light emitting devices) [3] (Figure 2).

References

[1] P. K. Dutta, R. Varghese, J. Nangreave, S. Lin, H. Yan, Y. Liu, J. Am. Chem. Soc., **133** (2011) 11985-11993.

[2] G. Calzaferri, R. Méallet-Renault, D. Brühwiler, R. Pansu, I. Dolamic, T. Dienel, P. Adler, H. Li, A. Kunzmann, J. Am. Chem. Soc., **12** (2011) 580-594.

[3] L. Gartzia-Rivero, J. Bañuelos-Prieto, V. Martínez-Martínez, ChemPlusChem, Vol 77, 1 (2012) 61-70

Figures



Figure 1. Nanostructured antenna system based on Zeolite L channel filled with different fluorophores.



Figure 2. Normalizad time-resolved emission spectra of C165, PM546, Ox4 doped zeolite L, together with the fluorescence images under 350/50 nm excitation and emission recorded with different band passes (400 nm, 515 nm, 580 nm and 665 nm respectively).