

TOWARD MOLECULAR WIRES CONFINED IN ZEOLITE CHANNELS FOR AN EFFECTIVE TRANSPORT OF ELECTRONIC EXCITATION ENERGY

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Sunlight is the fundamental energy source sustaining life on Earth. Green plants are provided of very sophisticated and highly efficient tools to exploit light, they are able to harvest sunlight and to transport electronic excitation energy by means of a particular “antenna system” to reaction centres (natural photosynthesis). The antenna consists of regular arrangements of chlorophyll molecules held at fixed positions by means of proteins. Light absorbed by any of these molecules is transported - by radiationless energy transfer (FRET) - to reaction centres, providing the energy necessary for the chemical processes to be initiated. A green leaf consists of millions of such well-organized antenna devices. A long-standing challenge has been the development of an artificial system able to mimic the photosynthetic system. Artificial antenna systems can be realized once several organized chromophores are able to absorb the incident light and to channel the excitation energy to a common acceptor component¹⁻³. Artificial antenna can be built by incorporating dyes into the one-dimensional channels of zeolite L (ZL). ZL crystals feature strictly parallel nano sized channels arranged in hexagonal symmetry. These channels can be filled with high concentration of suitable guests. The geometric constraints imposed by the host structure allow achieving supramolecular organization of photoactive guests¹. It has been shown², that the properties of the dye-ZL systems depend on the molecular packing inside the channels, controlling the intermolecular and the dyes/framework interactions. In this work we present a study on the optical properties of a two-dyes antenna system in which fluorenone molecules (donor molecule) and thionine (acceptor molecule) are organized in Zeolite L porosities.

To interpret the optical properties of the hybrids a detailed structural study at atomistic level was mandatory. Due to the impossibility of studying from the structural point of view a two-dyes system, two “one-dye” hybrids (ZL/fluorenone and ZL/thionine) were firstly synthesized and characterized to investigate the intermolecular and the dyes/framework interactions⁴.

The results of thermogravimetric, IR, and X-ray structural refinements carried out for the one-dye system ZL/FL established that 1.5 molecules per unit cell is the maximum FL loading, in contrast with the data reported previously in literature⁵ and that the FL carbonyl group strongly interacts with a K⁺ of the ZL. The FL distribution at maximum loading can be considered as a self-assembly of planar dye molecules into a noncovalent nanoladder. (Fig 1)

FL molecules organized in such a single, continuous nanostructure of dye molecules did not exhibit significant electronic interactions. Indeed, both absorption (recorded in the diffuse reflectance mode) and photoemission electronic spectra of ZL/FL systems with different FL loading scaled almost linearly in intensity with the amount dye hosted in the unit cell (ranging from 0.5 to 1.5), without significant changes of the spectral profiles. Noticeably, the combination and steady state and time resolved photoluminescence data indicated that even at the maximum loading ca. 90% of FL molecules are photoluminescent, with significant increase

in the average quantum yield with respect to FL molecules in solution. Such a finding clearly indicates that excited states coupling (Davydov splitting) is not contributing to the optical properties of the material.

The structural study of the ZL/TH system revealed that the maximum possible loading of TH is equal to 0.3 molecules per unit cell in agreement with the TGA and literature data⁶. Short distances between the carbon, sulfur and nitrogen atoms and two water molecule sites, in turn at bond distance from the oxygen atoms of the main channel, suggested a water-mediated Th-ZL interactions⁷. Moreover, IR spectroscopy provided evidence of the interaction of the aromatic rings with the environment. This likely resulted in an increase of the rate of non-radiative decay of Th molecules in the electronic excited state, because only ca. 5% of Th molecules hosted in the ZL channel appeared photoluminescent.

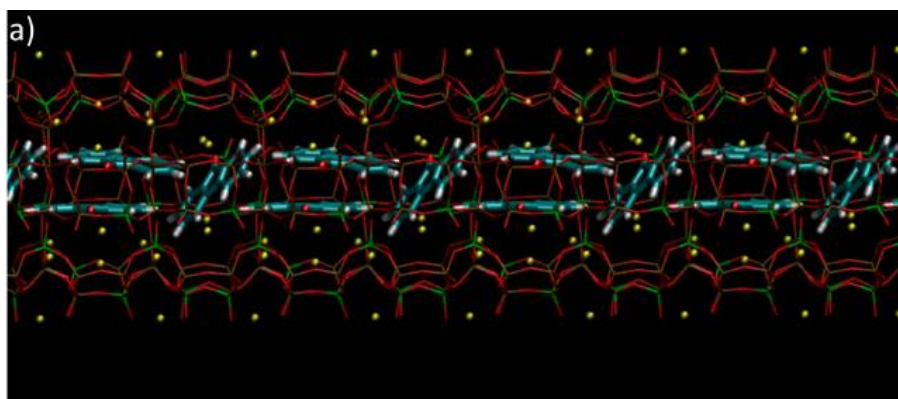


Figure 1. Graphical representation of the minimum energy structure calculated for the ZL/1.5FL model

The occurrence of energy transfer from excited FL molecules forming the noncovalent nanoladder in the ZL channels and Th, in the ground state, deposited on the external surface of ZL particles are currently under investigation.

In conclusion, we have here presented a study on the physico-chemical properties of dense molecular wires encapsulated in the one-dimensional pores arrays of Zeolite L. Concerning the optical properties of our composites, no evidence of Davydov splitting emerged from our study, indicating that one of the main competitors of the FRET mechanism is not operative notwithstanding the close packed arrangement of FL. We believe that this feature is of overwhelming relevance in view of application of such a system in artificial antenna systems.

References

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