

Artificial antenna system based on one-directional FRET between AC and PY dyes within AIPO-36 nanochannels

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Abstract

The encapsulation of dyes into nanostructured ordered systems is a good tactic to provide new functional materials with interesting optical, chemical and electrical properties.^[1] A great variety of solid matrices with different 1-, 2- or 3-dimension arrays are suitable to induce an anisotropy orientation on the guest molecules. In this sense, nanotubes and nanostructured tubular systems with elongated pores can act as a powerful ordering framework in one dimension for the guest species. Specifically, microporous aluminophosphates (AIPO) present zeolitic structures. The open nature of the structure of zeotypes made them very interesting as host materials.^[2] The structure of these solids is built by a three-dimensional arrange of corner-sharing tetrahedra characterized by the presence of channels of molecular dimensions, where different molecules can be encapsulated. Therefore, aluminophosphates are good hosts to get 1D highly ordered ALPO/dye functional materials. They also exhibit different pore sizes depending on the type of AIPO₄, which provides de advantage of choosing one type or another according to the application.

These materials are usually prepared using organic compounds which are denominated structure directing agents (SDAs) that remain occluded within the structure at the end of crystallization. As dye molecules are not very different to typical SDAs used in zeolite-type hosts synthesis, this gives the opportunity to study the in situ incorporation of the dye during synthesis of the material.

One of the types of aluminophosphates usually used as host is AIPO-5 (AFI) with 7.3 x 7.3 Å sized pores. However, in previous work it has been demonstrated that for xanthene-type dye guests, AIPO-5 system is high enough to accommodate H-type dimers resulting in a drastic quenching of the emission of the sample.^[3] However, by a slight reduction of pore size of the host, i.e., AIPO-36 unidirectional channels with pore size of 7.3 x 6.4 Å, those dyes tend to conform J-aggregates. These aggregates are characterized by a fluorescent emission shift to the red range of the UV/Visible light spectrum. In this sense, PyronineY (PY) dye occluded into AIPO-36 crystals (ATS) show a multicolour emission under the optical fluorescence microscope (Figure A), from red (J-aggregates) to yellow (monomers and aggregates) and to green (monomers).^[4]

This material was thought to be interesting for light harvesting as the excitation energy can be transported along the crystal due to the particular arrangement of the PY species within the nanochannels: the green PY monomers can act as energy transfer donors to the red-shifted PY aggregates which behave as acceptor at the other end of the crystal needle (see Figure 1).

In order to increase the range on UV/Visible collection range for a more efficient antenna system, Acridine (AC) dye, with a characteristic UV absorption band and blue emission is co-adsorbed together with the PY dye into the host material (Figure B). In this work, ATS crystals hosting two dyes are synthetize for different AC:PY relative concentrations in order to achieve an efficient energy transfer between the two dyes that will offer an antenna system working in the whole UV/Visible light range.

References

- [1] Schulz-Ekloff, G.; Wöhrlé, D.; van Duffel, B.; Schoonheydt, R.A. *Microporous Mesoporous Mater.* **51** (2002), 91.
- [2] D. Brühwiler, G. Calzaferri, *Microporous Mesoporous Mater.* **72** (2004) 1-23.
- [3] R. García, V. Martínez-Martínez, L. Gómez-Hortigüela, I. López-Arbeloa, J. Pérez-Pariente, *Microporous Mesoporous Mater.*, (2013) <http://dx.doi.org/10.1016/j.micromeso.2013.01.025>
- [4] V. Martínez-Martínez, R. García, L. Gómez-Hortigüela, J. Pérez-Pariente, I. López-Arbeloa (Submitted).

Figures

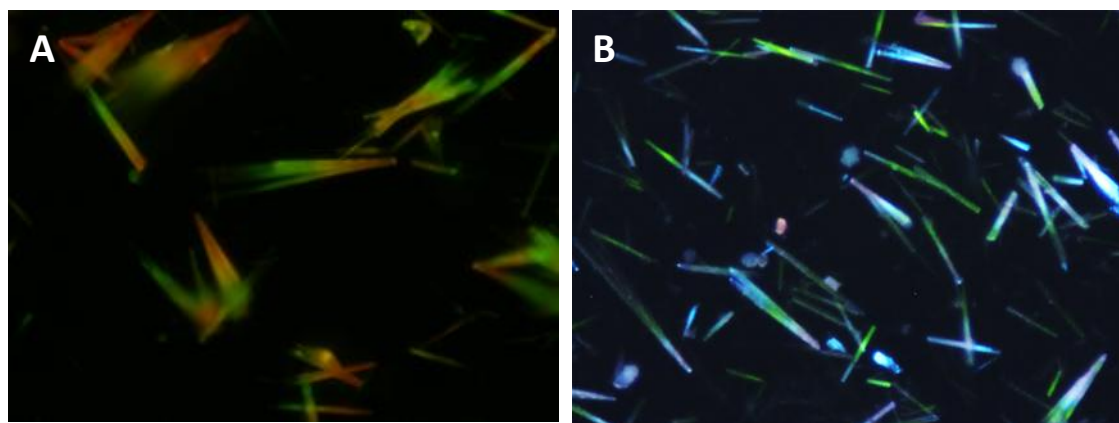


Figure: Real color fluorescence images of A) PY dye and B) AC and PY dyes into AIPO-36 crystals