# One dimensional Ordered Materials for Optical Applications: Pyronine Y dye into Aluminophosphates with different nanopore size

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## Abstract

The encapsulation of dyes into nanostructured ordered systems is a good strategy to provide new functional materials with interesting optical, chemical and electrical properties. In this regard, 1D-ordered clays, zeolites and zeotypes microporous materials are very interesting host materials due to the open nature of their frameworks with well-defined internal channels. These hybrid nanomaterials are characterized by a high organization degree where the photoactive molecule is aligned in a preferred position due to the geometrical restrictions imposed by the solid framework inducing highly monomeric and anisotropic dye distributions [1].

Generally, materials for optical applications require a high dye concentration. In those cases many dyes in adsorbed-state are aggregated [2]. Therefore, the incorporation of dye molecules in monomeric species is crucial, avoiding their tendency to self-associate since aggregates quench the fluorescence. In the cases, that aggregation cannot be totally suppressed, J- type aggregates (head-to-tail dyes), characterized by red-shifted emission respect to the monomers should be favored in detriment of H-aggregates (dyes in sandwich-like configuration) which are usually non-fluorescent and also quench the monomer emission.

The present work shows a computer-aided rational choice of 1D- magnesioaluminophosphate nanoporous hosts to occlude a xanthene-type dye, Pyronine Y (PY) in order to prepare highly fluorescent hybrid materials by preventing dye aggregation.

Thus, Pyronine Y (PY) dye is occlued into different unidirecctional aluminophosphates with different size pore (Figure): i) MgAPO-5 (AFI structure-type) with a 12-ring system of cylindrical channels with a diameter of 7.3 Å; ii) MgAPO-36 (ATS structure-type), which possesses a 12-ring elliptical channel system with slightly smaller dimensions, 6.7 x 7.5 Å; iii) and MgAPO-11 (AEL structure-type) with a 10-ring channel system of even smaller dimensions, 4 x 6.5 Å. Pyronine Y dye with a molecular size of (13.7 Å x 6.2 Å x 3.2 Å) will fit with its longer axis mainly aligned along the channel direction of the three materials under study.

PY/MgAPO-5 crystals show green emission under the optical fluorescence microscope (Fig. 1a) and high dichroic ratio values (Table) indicative of the encapsulation of PY molecules within the nanopores. The two life-times measured (Table) and the absence of new fluorescence bands for this sample confirms the co-existence of monomers and H-aggregates in this structure [3].

In contrast, formation of H-aggregates is suppressed by the encapsulation of PY within channels of smaller dimensions, such as those in PY/MgAPO-36 (ATS). The crystals of this sample show a multicolour emission under the optical fluorescence microscope from red (J-aggregates) to yellow (monomers and aggregates) to green (monomers). This system offers an antenna system that can harvest and transmit light in a wide range of the visible spectrum. DFT calculations show that only the channels in AFI are large enough to host the H-aggregates of PY.[4]

**Table.** Main photophysical parameters of PY/MgAlPO; $\lambda_{exc}$: excitation maxima wavelength; $\lambda_{fl}$: fluorescence maxima wavelength; $\tau_{fl}$: lifetimes $\Phi_{fl}$: quantum yield; D: fluorescence dichroic ratio.

| Material | $\lambda_{exc}$(nm) | $\lambda_{fl}$(nm) | $\tau_{fl}$ (ns)(%) | $\Phi_{fl}$ | D |
|---|---|---|---|---|---|
| MgAlPO-5 | 534 | 550 | 1.3(35) 3.1(65) | 0.4 % | 11-15 |
| MgAlPO-36 | 539 | 560/610/660 | 0.5-0.7(40) 1.7-2.0(50) 4.0-4.2 (10) | 1% | 3-5 |
| MgAlPO-11 | 523 | 537 | 2.95 | 21 % | 40 |
| Py (aq) | 548 | 568 | 2 | 22 % | 1 |
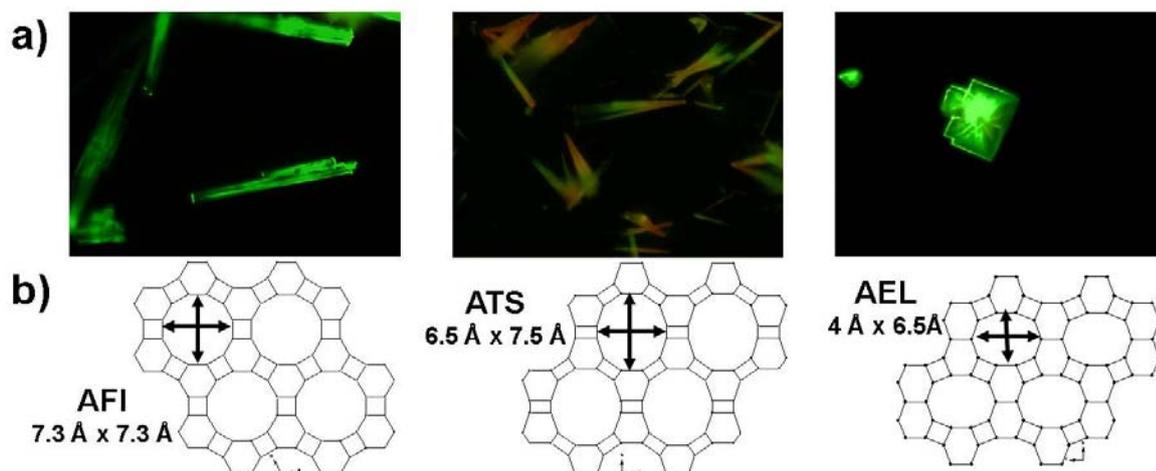
**Figure**. Fluorescence images of PY into the different MAPO structures (a), together with the view along the straight channels of the different structures (b).

The channels of MgAPO-11 have the appropriate dimensions to completely suppress the formation of aggregated species. The intense green color and the measurement of an unique lifetime indicate that monomers are only present within the channels. The absolute quantum yield of the sample is similar to that recorded in diluted solution of PY, being more than one order of magnitude higher than those obtained for MgAlPO-5 or MgAlPO-36. Moreover, a huge anisotropic response to the linear polarized light is derived in this material with dichroic ratios ≥ 40. DFT shows that the AEL nanochannels are optimal to prevent PY aggregation since, on the one hand, their small dimension avoid aggregates which involve stacking (H- and some J-aggregates), and on the other hand, their particular topology comprising side-pockets of size commensurate to that of PY impedes the dye to site close to each other in J-type coplanar configuration, hence forcing PY to arrange exclusively as monomers. Our multi-approach work shows now how one can fine-tune the optical properties of host-guest materials by rationally selecting the appropriate framework with the aid of modeling tools [4].

In this work, we used a combination of synthesis work, advanced spectroscopic characterization and modeling tools in order to rationally select the most appropriate one-dimensional nanoporous aluminophosphate framework to incorporate the fluorescing dye Pyronine Y (PY) as monomers directly during the synthesis of the solids (crystallization inclusion). We report experimental evidences and modeling insights of how the "cage effect" of nanochannels, i.e. the pore size and their particular topology, can tune the optical properties of the hybrid composite material by controlling the aggregation state of the occluded dye. This study provides an essential contribution to the rational design and development of new optical materials.

## References

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