

## TUNING THE PHOTOPHYSICS OF ITQ-51 ZEOTYPIC STRUCTURE

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The results presented in this work demonstrate the feasibility of occluding dyes into restricted nanocavities of zeotypic materials to promote new and/or enhanced photophysical processes in organic fluorophores. In this way, the design and proper selection of the components that make up the photoactive hybrid systems are crucial to establish the perfect combination and improve the photophysical properties, such as the fluorescence efficiency, which will determine the final emissive properties of the photoactive material and, therefore, its best field of application. The most important factors to consider in the design are the type (channels or cages) and dimensions of the host nanochannels, and the molecular size and intrinsic properties of the guest dyes.

Therefore, as the host framework, a Mg-doped ITQ-51 zeotype [1] with an extra-large pore opening of 9.3 Å x 10.6 Å has been selected. In particular, this framework has blue fluorescent properties and has been synthesized without the need to incorporate additional dyes into the synthesis gel, due to the intrinsic emissive characteristics of the template (DMAN, Figure 1a) guiding the crystallization. In addition, it has been demonstrated that this material shows photophysical changes over time, due to the fact that the structure-directing organic agent (DMAN) employed for its crystallization exhibits a redistribution within the unidirectional IFO channels, favoring the formation towards thermodynamically more stable aggregates.

Based on this starting fluorescent zeotype (DMAN/ITQ-51), the fluorescence range of the material has been broadened by the simultaneous occlusion of different active guests by the *crystallization inclusion* method, giving rise to artificial antennas (an efficient method demonstrated in other previous works).[2] By combining suitable FRET dye pairs with properties in the green and red regions of the visible spectrum, such as R123 (Rhodamine 123) and NB (Nile Blue, Figure 1b-c), different emissive properties (green or red fluorescence) have been induced compared to the starting structure, allowing to develop possible efficient lasers in different areas of the spectrum. In these systems, the resultant fluorescence color emission is highly dependent on the probability of FRET processes between the simultaneously occluded dyes in the restricted space of the zeotype channels. Likewise, distribution, concentration and relative proportions of the dyes play a key role in improving FRET efficiency, and consequently influence the final emissive properties of the resultant material.

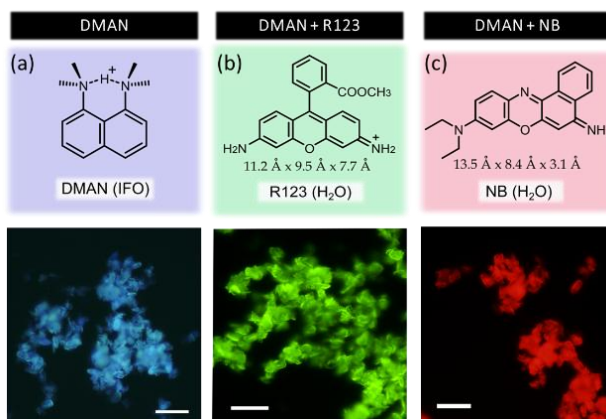


Figure 1. Selected molecular structures for energy transfer within Mg-doped ITQ-51 channels with their molecular dimensions (a) DMAN (structure-directing agent), (b) Rhodamine 123 (R123), and (c) Nile Blue (NB), and the fluorescence image of the as-synthesized particles below. Scale = 20 μm.

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- [2] García, R., Martínez-Martínez, V., Sola Llano, R., López-Arbeloa, I., & Pérez-Pariente, J., The Journal of Physical Chemistry C, 2013, 117(45), 24063–24070.