SELF-ORGANIZATION, PHOTOLUMINESCENCE AND EMERGENCE IN AMIDE-FUNCTIONALIZED ORGANIC/INORGANIC HYBRIDS

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Complex structures, such as living organisms or highly structured materials, share in common the fact that their inherent complexity may be accounted for by the tangled organization of a vast number of simple units. The complex behaviour arises not necessarily due to the atomic structure of the system, but to the orderly assembly of all, or part, of its constituents [1]. Self-assembly of synthetic soft-matter components such as polymers, liquid crystals, surfactants, colloids and organic/inorganic hybrids results in regular hierarchically-organized structures [2-4]. Silsesquioxanes and organosilanes are examples in which hierarchically-ordered self-assembly architectures with well-defined morphologies at the macroscopic scale are induced by weak interactions between the organic spacers (hydrogen bonding, hydrophobic interactions and π-π interactions) [4]. However, up to the present, the self-assembly of the simpler alkylsilanes has only been reported sporadically [5].

We have recently introduced a hierarchically-structured amide cross-linked alkyl/siloxane hybrid (named *mono-amidosil,* Fig. 1), where self-assembly is driven by intermolecular hydrogen bonding between amide groups; van der Waals interactions between all-*trans* alkylene chains assuming a partially interdigitated packing mode and an entropic term related to the phase separation between the alkyl chains and the siloxane nanodomains [6]. This *mono-amidosil* hybrid is the first example of a photoluminescent bilayered suprastructure displaying unique nanoscopic sensitivity. The self-organization in the *mono-amidosil* is determinant for the emergence of a thermally-actuated optical memory effect induced by a reversible order-disorder phase transition of the alkyl chains (Fig. 1) [6].

Although the relationship between structural complexity and self-assembly mechanisms has been given much consideration, the essential role played by higher organizing principles in determining emergent physical phenomena in soft-matter complex structures, has been largely unexplored.

The aim of this work is to discuss the nanoscopic (~150 nm) sensitivity of the *mono-amidosil*'s light emitted as an emergent property of the hybrid host determined by the self-organization process (induced by the reversible order-disorder phase transition of the alkyl chains). This phase transition provokes a hysteretic behaviour of the emission energy which presents a slow relaxation accurately described by a logarithmic law (typical of the time evolution of a variety of strongly interacting materials). The connection between the concepts of self-organization and emergence [7] will be also addressed.

References:

[1] R. B. Laughlin, D. Pines, Proc. Natl. Acad. Sci. USA, **97** (2000) 28.
[2] A.Von Blaaderen, Nature, **439** (2006) 545.
[3] K. Vallé, P.Belleville, F. Pereira, C. Sanchez, Nature Mater., **5** (2006) 107.
[4] J. J. E. Moreau, B. P. Pichon, M. Wong Chi Man, C. Bied, H. Pritzkow, J.-L. Bantignies, P. Dieudonné, J.-L. Sauvajol, Angew. Chem. Int. Ed., **43** (2004) 203.
[5] A. Shimojima, N. Umeda, K. Kuroda, Chem. Mater., **13** (2001) 3610.
[6] L. D. Carlos, V. de Zea Bermudez, V. S. Amaral, S. C. Nunes, N. J. O. Silva, R. A. Sá Ferreira, J. Rocha, C. V. Santilli, D. Ostrovskii, Adv. Mater., **19** (2007) 341.
[7] P. A. Corning, Complexity, **7** (2002) 18.

Figures:

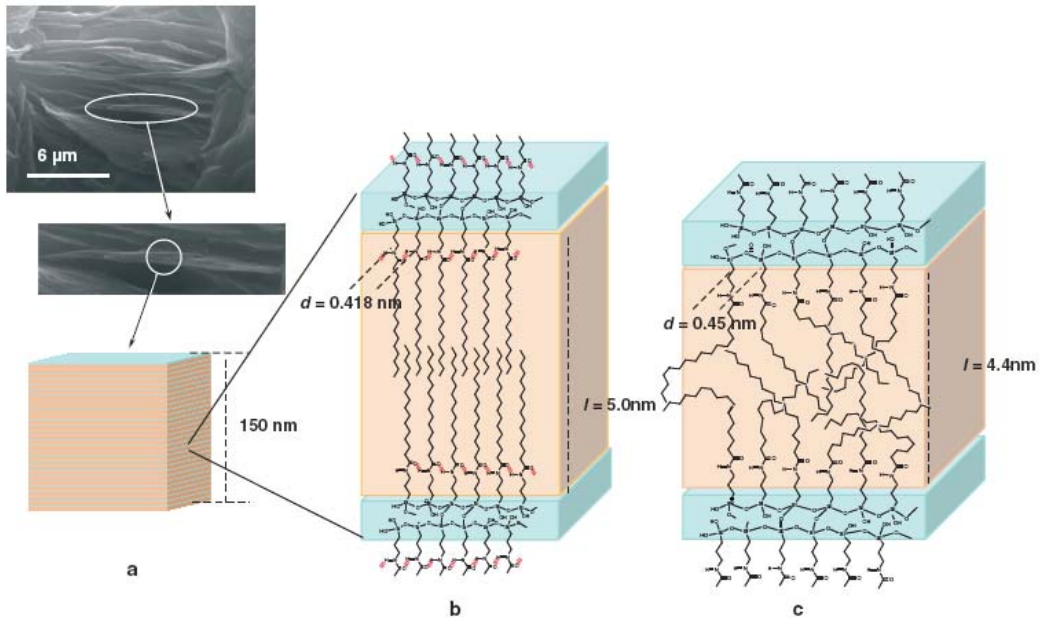

Figure 1. SEM image and schematic representations of the structure of mono-amidosil hybrid. a) Lateral portion of a crystallite composed of a stack of bilayers. b-c) Bilayer at room temperature and at 120 ºC, respectively.