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MAPPING MOLECULAR DIFFUSION IN NANO-CHANNEL SYSTEMS BY TRACKING INDIVIDUAL FLUORESCENT MOLECULES

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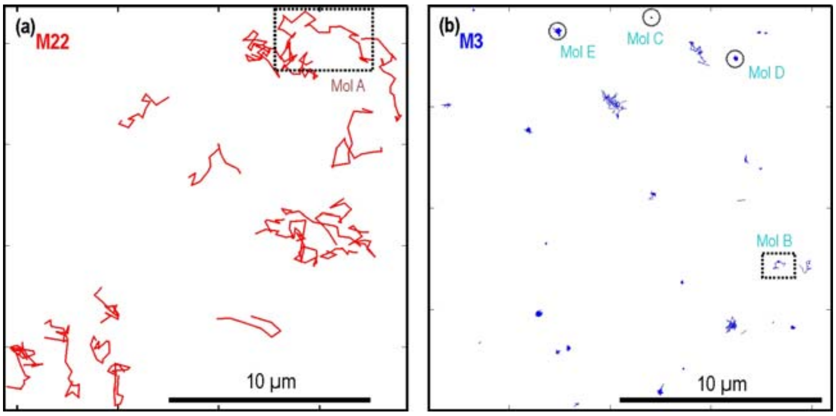
Sol-gel derived hybrid materials have great potential in many areas, including sensors, laser materials, molecular sieves, catalysis and photocatalysis. For example, dye-doped silica xerogel monoliths have oxidative and disinfectant properties due to photosensitised production of singlet oxygen on exposure to visible light in air[1]. It is therefore important to understand the dynamics of the organic phase, often a large dye molecule, in the pore system of the host. Immediate questions are the rates of translational and rotational diffusion, physical trapping and chemical tethering to the host material, clustering, and the homogeneity and isotropy of these phenomena throughout the material. Well established techniques for characterising porous materials, such as N_2 adsorption porometry are not fully relevant to the dynamics of the much larger dye molecules. Techniques such as PFG NMR may be difficult to deploy and may require considerable assumptions to extract dynamical information from the recorded data. One would like to be able to follow directly the motion of the large organic molecules in the pore system.

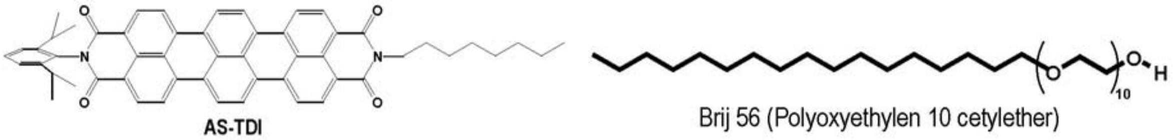
In single particle tracking, usually performed with an epifluorescence microscope, individual particles are tracked from frame to frame in a video recording. Particle tracking is slower (ms-minutes), than in fluorescence correlation spectroscopy (μs)[2], but much more informative, and requires no previous assumptions about the diffusive process.

We present data on tracking individual fluorescent dye molecules in amorphous silica xerogel monoliths[3] with different porosities, and in templated, spin-cast silica thin films[4]. Diffusion in the amorphous xerogels is faster in materials with wider pores. More surprising is dynamical trapping in regions of size 50nm-1μm. Furthermore, a tenfold spatial heterogeneity of the diffusion coefficient on micron lengthscales is also revealed by this technique.

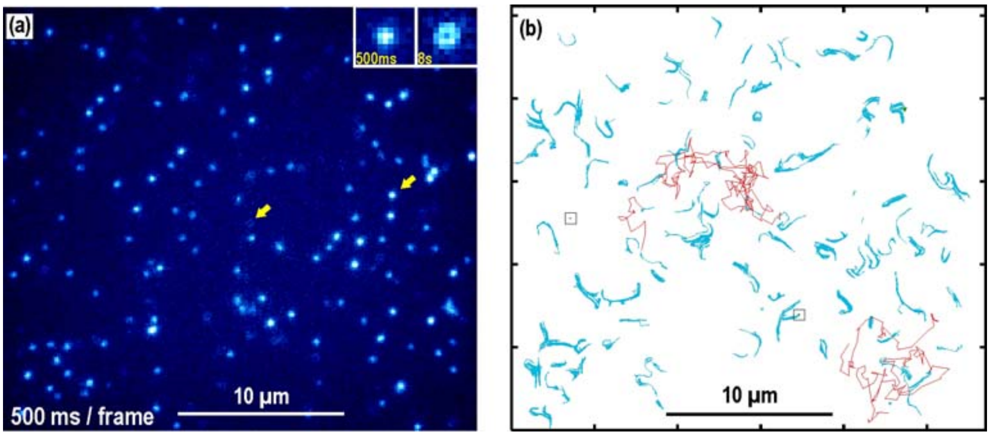


Sample single molecule tracks (streptocyanine dye) in amorphous silica xerogel monoliths with (a) *wide, 22nm and* (b) *narrow (3nm) pores.*

Diffusion of the dye in templated silica thin films clearly maps the topology and practical connectivity of channels in domains of different mesophases and molecules passing between them or escaping and re-entering to and from the surface. It also reveals dynamical heterogeneities, both between different parts of the sample and within the same spot.



Terrylene diimide dye and Brij 56 template.



(a*) Epifluorescence video frame of single terrylene diimide molecules in a Brij56- templated silica thin film, in which a hexagonal and a lamellar mesophase happen to coexist. The doughnut-shaped diffraction spot in the lamellar phase shows molecular orientation parallel to the optical axis.* (b*) Tracks of individual molecules in the mesophases are qualitatively and quantitatively different: oriented diffusion in bundles of channels in the hexagonal phase (blue), isotropic, much slower motion in the lamellar phase (box), isotropic fast diffusion at the sample surface (red).*

References:

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