# Imogolite and imogolite-like tubular nanocristals. Formation mechanism, properties and applications

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Imogolites are aluminosilicate nanotubes naturally occurring in volcanic soils (Yoshinaga and Aomine, 1962). Getting inspiration from this natural clay, it is possible to prepare synthetic aluminosilicate or aluminogermanate nanotubes of formula $(OH)_3Al_2O_3Si_xGe_{(1-x)}(OH)_y(CH3)_{(1-y)}$ which are monodisperse in diameter (from 2 to 4 nm depending on composition) and polydisperse in length from several tens of nanometers up to several microns (Thill et al. 2012, Amara et al, 2013). The formation mechanism of y=1 nanotubes has been the subject of recent discoveries especially for the aluminogermanate nanotubes. The existence of Double-walled nanotubes has been discovered and their formation mechanism has been explained. A better understanding of the imogolite precursors (proto-imogolite) has been achieved and the growth kinetic of the nanotubes has been studied *in situ* and modeled. In particular, a scenario based on the nanomechanical behaviour of proto-imogolite has been proposed to explain the co-existence in various proportion of imogolite and allophane. The synthesis of hybrid nanotubes (y=0) with coexisting hydrophobic (internal) and hydrophilic (external) surfaces has been achieved recently (Bottero et al. 2011). By replacing the tetraethoxysilane precursor by methyltriethoxysilane, nanotubes possess a hydrophobic nanocavity covered with $Si\text{-}CH_3$ groups instead of Si-OH. These nanotubes are easily dispersed in aqueous solutions and are able to trap small organic molecules (Amara et al. 2015, Picot et al, 2016). We have recently expended the chemical composition of the internal hybrid surface by introducing 5% of various Si-R groups. We illustrate the effect of this internal surface doping on the optical properties of a trapped organic molecule (Nile Red) (Figure 1).

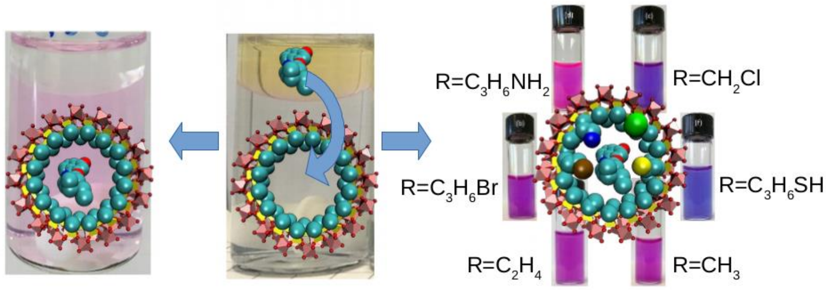


*Figure 1 : Liquid liquid extraction of Nile Red and impact of internal surface doping with Si-R groups on the optical properties of encapsulated molecules.*

Concerning the external surface modification, we have also explored the most classically used reaction with phosphonic acids (PA). This reaction is often applied to make the external surface hydrophobic. We show that PA react with imogolite but we observe the formation of a new composite material which is a mixture of intact imogolite nanotubes and a lamellar AlPO phase. Their is not actual proof of a successful grafting of intact nanotube to our knowledge.

In this conference, a review of the recent discoveries on imogolite formation mechanism will be made in detail. We will also present the synthesis of the hydrid janus nanotubes. These hybrid nanotubes have promising properties especially for trapping photoactive or RedOx active molecules.


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