Supporting Information for

Behaviour of hybrid inside/out janus nanotubes at an oil/water interface. A route to self-assembled nanofluidic?

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TGA measurements.

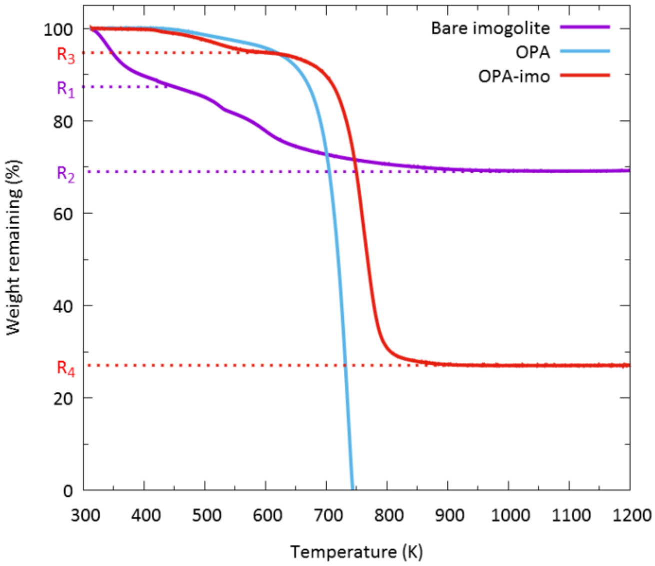

Figure S1. TGA curves of bare imogolite, OPA and OPA-imo.

TGA curve of bare imogolite shows two steps: the first one, up to 450 K, comes from the release of water adsorbed onto the sample (between and in the nanotubes), whereas the second one, between 450 K and 1000 K, originates from the dehydroxylation of the wall that leads to irreversible structural transformations.[1,2] For the OPA-imo sample, two losses of weight are also observed: in the same temperature ranges. However, as indicated by the TGA curve of OPA demonstrating its full decomposition at 750 K, the second step between 450 and 1000 K combines the wall dehydroxylation process and the degradation of the grafted phosphonic acid. Assuming that the dehydroxylation extend is not affected by the grafted molecules, it is possible to estimate the amount of phosphonic acid. For the bare imogolite, the initial mass can be decomposed into three contributions with $1 = \Phi_i + \Phi_{sw} + \Phi_w$ where Φ_i is the mass fraction of powder remaining up to 1000 K, Φ_{sw} is the mass fraction of structural water lost at about 600 K and Φ_w is the mass fraction of adsorbed water. In the case of the grafted imogolite, the mass fractions are noted $1 = \Phi'_i + \Phi'_{sw} + \Phi'_w + \Phi'_{OPA}$ with Φ'_{OPA} the mass fraction of grafted OPA. Then, it is possible to obtain from the TGA curves several experimental mass ratios noted as dotted lines on the Figure S1:

$R_1 = \Phi_i + \Phi_{sw}$
$R_2 = \Phi_i$
$R_3 = \Phi'_i + \Phi'_{sw} + \Phi'_{OPA}$
$R_4 = \Phi'_i$

We make the assumption that the grafting of OPA onto the surface of imogolite does not modify the amount of structural water that is eliminated at 600 K, which gives $\Phi_i/\Phi_{sw} = \Phi'_i/\Phi'_{sw}$. Using the two first experimental ratio R_1 and R_2, we can write:

$$\Phi'_{sw}/\Phi'_i = R_1/R_2 - 1 \qquad (1)$$

The amount of grafted OPA is compared to the amount of imogolite before dehydroxylation. Using R_3, we have:

$\Phi'_{OPA}/(\Phi'_i+\Phi'_{sw}) = R_3/(\Phi'_i+\Phi'_{sw}) - 1.$

Combining this expression with equation 1, we obtain the desired OPA ratio:

$\Phi'_{OPA}/(\Phi'_i+\Phi'_{sw}) = R_2R_3/(R_1R_4) - 1$

Finally, the weight ratios obtained from TGA curves and shown in figure S1 for bare imogolite and OPA-imo are $R_1 = 0.87$, $R_2 = 0.69$, $R_3 = 0.95$ and $R_4 = 0.27$.

SAXS measurements.

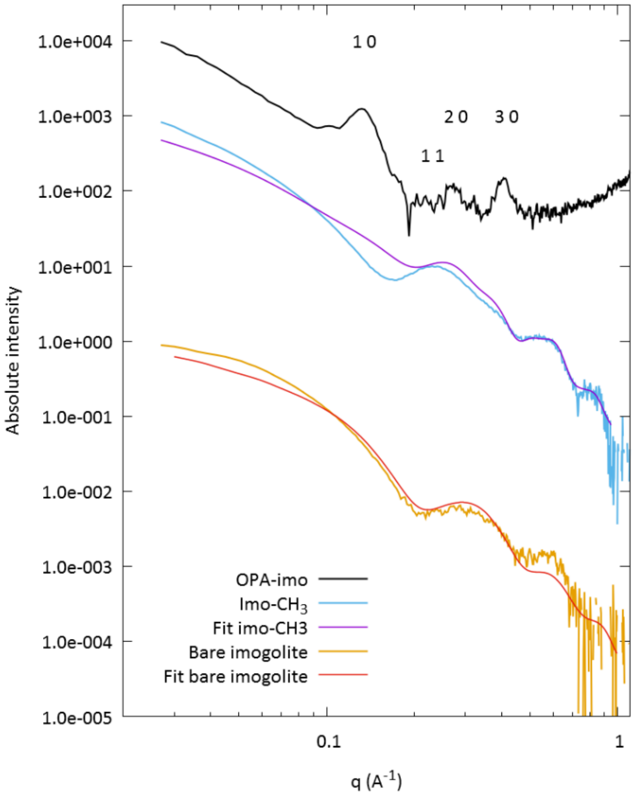

Figure S2. SAXS curves of OPA-imo, imo-CH_3 and bare imogolite with their respective fit. Intensity of imo-CH_3 and its fit is multiplied by a factor 200 and OPA-imo by 400 000.

The calibrated scattered intensities are compared to form factors of hollow cylinders assuming a homogeneous scattering length density. The scattering length density of the imogolite wall is proportional to the electron density of the nanotubes that is obtained by:

$$\rho = \frac{2n_e N}{\pi e(2r_i + e)T}$$

With n_e the number of electrons per imogolite structural unit, N the numbers of structural units per circumference, T the period of repeat distance along the tube axis, r_i the internal radius and e the imogolite wall thickness.

The damping of the scattering oscillations for the bare imogolite is due to the presence of a large proportion of proto-imogolite. A fit of the experimental scattered intensity is obtained when the nanotubes are mixed with more than 90 % of proto-imogolite consisting of small nanotube pieces of less than 5 nm.[3]

For imo-CH_3, we also consider that the nanotubes are associated in poorly organised bundles.[4] This curve also displays damped oscillations of the form factor. The fit is also obtained by considering a mixture of nanotubes and proto-imogolite. However, particle agglomeration may also induce nanotube deformation and scattering oscillation damping.

Pickering emulsions with bare imogolite.

Figure S3. Emulsion test with bare imogolite, hexane and water. Left photo $\Phi_w = 0.2$ and right photo $\Phi_w = 0.8$. For both $C_{\text{bare imogolite}} = 1.09$ g L^{-1}.

Figure S3 shows picture of emulsion prepared with bare imogolite, water and hexane. Photos were taken one day after stirring. Hexane-in-water emulsions are obtained for both Φ_w indicating a stabilisation from bare imogolite. Creton et *al.* showed that, by molecular dynamics simulations, the external surface of imogolite exhibits a hydrophobic behaviour (the internal surface remaining hydrophilic).[5] They explain that the low proton reactivity of the (001) surface of Gibbsite is conserved even after the curving of this layer (by the bonding of with silicon tetrahedron). Hence, this hydrophobic external surface can stabilise an oil/water interface.

Viscosity measurements.

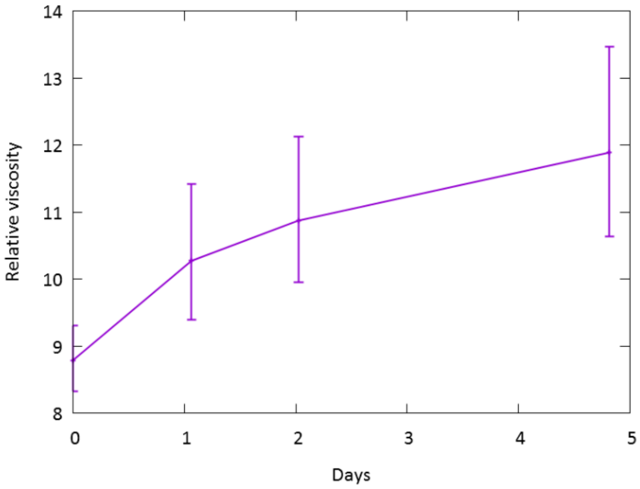

Figure S4. Evolution of the viscosity for an imo-CH_3 in contact with hexane at 20°C.

Figure S4 shows the evolution of the relative viscosity of an imo-CH3 phase in contact with hexane at 20°C.

References

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