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Engineering the self-assembly of proteins and polymers with fluorous interphases and halogenated molecules.

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The peculiar characteristics of halogen atoms offer powerful tools to direct the self-assembly of materials.
The omniphobicity of highly fluorinated compounds dictates their tendency to segregate into separate *fluorous*[1] phases in order to avoid unfavorable interactions, sometimes giving rise to unique interfacial structures,[2] and has been exploited in separation, catalysis and biotechnological applications[3]. However, it also becomes an issue when the need arises to compatibilize fluorous and non-fluorous (hydro- or lipophilic) phases. In the first part of this talk we will show how hydrophobins[4], *i.e.* natural fungal proteins endowed with non-ordinary surface activity and self-assembly features, can act as environmentally friendly surfactants to prepare stable dispersions of fluorous droplets[5] and nanoparticles[6], as well as fluorous coatings on poorly reactive polymer surfaces. We will also show how selective chemical modification of hydrophobins can further enhance their affinity towards fluorous phases[7].

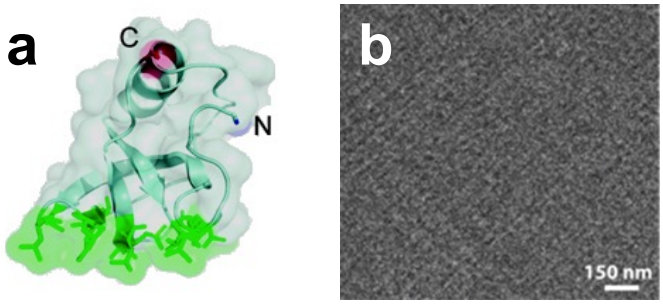

Figure 1. a) Structure of the hydrophobin HFBI. The green highlighted patch is composed uniquely by hydrophobic amino acids; b) TEM image of a polymer/fluorous mesogen complex. The alignment shown persists over mm-scale distances[9].

In the second part of the talk, we will see how heavier halogens (Cl, Br, I) can help direct the self-assembly of materials by means of halogen bonding, *i.e.* a highly directional, non-covalent interaction with strength comparable to hydrogen

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bonding[8]. When used in synergy with the fluorous segregation effect, halogen bonds can direct self-assembly in a number of polymeric systems, *e.g.* enabling nanostructure alignment up to the millimetre scale[9].

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