Synthesis of Photoluminescent Organic-Inorganic Ureasil Nanoparticles for Imaging Applications

Ilaria Meazzini[1*], Steve Comby[1], François-Xavier Turquet[1], Judith E. Houston[1] and R. C. Evans[1]

[1]*School of Chemistry, Trinity College, The University of Dublin, Dublin 2, Ireland.*

[*]*meazzini@tcd.ie*

In recent years, nanoparticles (NPs) have attracted significant interest in various fields of research and are now considered as a powerful platform for the development of novel imaging probes/agents. The main reason for such interest comes from the unique properties of NPs like large surface areas, easy functionalisation and enhanced optical properties, that can be further tuned and controlled precisely by their design and the materials they consist of [1]. In particular, organic-inorganic (O-I) hybrid NPs have attracted much attention for this purpose as they offer the possibility of combining the advantageous properties of the two classes of components into one material, for example the stability of silica with the hydrophobicity of organic domains, ideal for incorporation of organic dyes [2].

Here, we present the synthesis of a new class of O-I *ureasil* hybrid NPs consisting of a di-branched polyamine block *co*-polymer bound to a siloxane precursor through urea bridges. *Ureasils* are well-known Class II O-I hybrids [3], but to the best of our knowledge this is the first time they have been used for the preparation of NPs. This novel synthetic approach, which combines nanoprecipitation [4] and the Stöber method [5], allows us to obtain NPs with a relatively low colloidal stability in water media, which can be greatly improved by addition of tetraethylorthosilicate (TEOS), yielding a core-shell nanostructure. Dynamic light scattering measurements show that the NPs have an average size of 150 nm and good polydispersity indices (< 0.2). Although ureasils are photoluminescent in the solid-state, their low photoluminescence quantum yields in solution necessitates the doping of these NPs with a fluorophore (*e.g.* Coumarin C153) if they are to be utilised for imaging. The incorporation process needs to be efficient and to preserve the photophysical properties of the fluorophore, while maintaining the stability of the NPs. We have investigated two routes for dye incorporation: (i) a non-covalent approach, where organic dyes are encapsulated in the NPs through hydrophobic interactions and (ii) a covalent approach, where we covalently grafted the dye to either the organic or the siliceous domains of the NPs.

Approach (i) was applied to efficiently incorporate Coumarin C153 into the NP cores (Fig. 1). As a consequence of the incorporation (*i.e.* change in the polarity of the environment) Coumarin C153 emission shifted from green to blue. While the investigation of the incorporation of Fluorescein isothiocyanate through approach (ii) is still in progress, these preliminary results represent a promising step towards the preparation of a new class of luminescent O-I hybrid NPs.

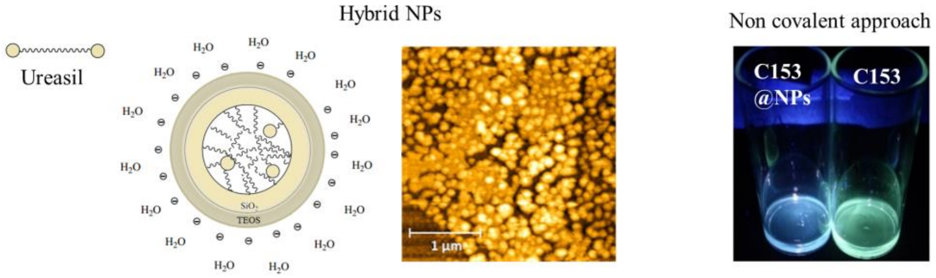

Figure 1. Model structure of the hybrid NPs, AFM image of a sample of un-doped NPs and picture of a solution of Coumarin C153 embedded in the NPs and dissolved in water (λ_{ex} = 365 nm).

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