

Assembly of fluorinated quantum dots at water/oil interface driven by proteins

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Controlled assembly of nanoparticles at fluid-fluid interfaces can increase their utility for a large range of applications. Here we demonstrate that selectively functionalizing of quantum dots with fluorinated hydrophobic ligands is an elegant way to do this, as protein interactions provides structure control.

Fluorinated quantum dots (QD_F) are adsorbed to a fluid-fluid interface driven by their interaction with proteins. This behavior has been observed with CdSe/ZnS QDs coated with HS-C₁₁-TEG-O-F ligands and dispersed in dichloromethane (DCM) when put in contact with an aqueous BSA solution. The interaction of BSA molecules with highly hydrophobic QD_F nanoparticles, which are highly hydrophobic due to the fluor atoms, is favored when the pH of aqueous phase is at the isoelectric point (pI) of the protein, and therefore the protein has a net charge of zero. This observation seems to indicate that the interaction between QD_F nanoparticles and BSA molecules may happen through the hydrophobic interaction of the fluor atoms of the ligand owing to their “superhydrophobic” character and the hydrophobic pockets of the BSA structure. This dependence of the QD_F@BSA interfacial activity on pH suggests that pH can be used as a means of triggering changes to QD_F@BSA assemblies and the jammed state of the assemblies.

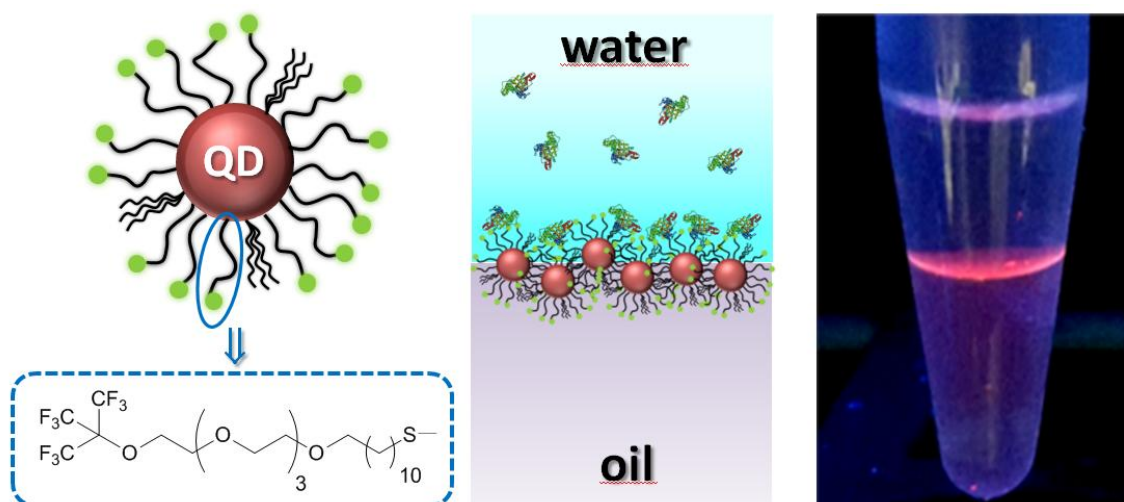


Fig. 1. Fluorinated CdSe/ZnS QDs are assembled at the water/oil interface after their interaction with BSA protein.

Interestingly, the kinetic of the adsorption of QD_F nanoparticles to the water/DCM interface is influenced by the amount of BSA in the aqueous solution, which has been studied by surface tension measurements. The higher the BSA amount is, the faster the QD_F nanoparticles adsorb at the interface. In the absence of BSA, the QD_F nanoparticles stay preferably dispersed in the organic phase. The protein-nanoparticle interaction supplies the driving force for the efficient assembly of the nanoparticles at the water/oil interface, leading to the reduction of the interfacial tension between the two fluids.

This work would inspire new concepts for the design and assembly of hybrid nanomaterials with potential application in sensing and multimodal imaging thanks to the fact that such nanoparticles are highly fluorescent and active in fluorine-19 nuclear magnetic resonance (¹⁹F NMR).