CHARACTERIZATION OF THE ORGANIC COATING OF COLLOIDAL QUANTUM DOTS USING NMR SPECTROSCOPY

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Colloidal inorganic nanocrystals surface-coated with organic stabilizing shells offer nanoscale platforms with unique photophysical properties. The organic coating strongly affects the physical properties of the cores while promoting steric stabilization in solution phase. Limited information is available about the molecular arrangements of the ligands on those nanomaterials. We hereby combine a few solution phase NMR spectroscopy techniques, namely $^1$H, $^{31}$P, heteronuclear single quantum coherence (HSQC), and diffusion ordered spectroscopy (DOSY) to probe the composition of the capping layer on colloidal CdSe-ZnS core-shell quantum dots, which have been grown via the “hot injection” route. We first probe the structure of a few sets of hydrophobic QDs and develop an understanding of the ligand shell structure and stoichiometric composition. We then expand the investigation to hydrophilic QDs ligated with a few sets of lipoic acid-based ligands containing one or two lipoic acid anchors and one or two polyethylene glycol blocks. For this, we combine the proton signatures of the ligands with diffusion ordered spectroscopy (DOSY) to distinguish surface-coordinated ligands those free in the medium. Quantification of the ligand shell was carried out by comparing the sharp $^1$H-signature(s) of the terminal groups in the ligands to an external standard, to extract estimates for the density of ligands for a few different size QDs. We found that both the molecular architecture and the surface curvature of the QDs play an important role in the surface coverage. Given the non-invasive nature of NMR as an analytical technique, the extracted information on the molecular arrangements on the ligands for hydrophobic and hydrophilic media is highly valuable. Such information has great implications for nanocrystal use in devices, bio-conjugation and energy and charge transfer interactions.

Keywords: Quantum dots, organic coating, Steric stabilization, NMR spectroscopy

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