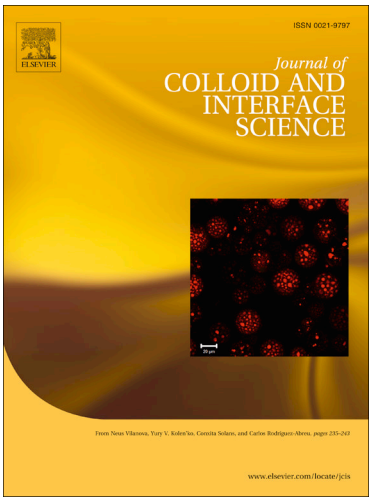

Hydrogen bond-induced bright enhancement of fluorescent silica cross-linked micellar nanoparticles

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Hydrogen bond-induced bright enhancement of fluorescent silica cross-linked micellar nanoparticles

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This work demonstrated the synthesis and design of ultra-bright and ultra-small fluorescent nanoparticles, which were prepared by encapsulating 4-(diphenylamino)benzaldehyde (DPB) in silica cross-linked micellar nanoparticles (SCMNPs). The DPB-doped SCMNPs (DPB-SCMNPs) exhibited ultra-bright fluorescence in an aqueous medium that was 22 times brighter than that of free DPB molecules in an organic solvent. For the first time, density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations were used to confirm that the enhanced brightness of the DPB-SCMNPs was due to a hydrogen bond-induced mechanism. In addition, the 3D fluorescence spectra and the Commission Internationale de L'Eclairage (CIE) diagram were employed to determine the optical properties and emission colour of the DPB-SCMNPs. Moreover, the DPB-SCMNPs were water-soluble, monodisperse and ultra-small (~12 nm) and should be robust and stable in aqueous media and biological systems.

† Footnotes relating to the title and/or authors should appear here.

Introduction

Fluorescence measurements have recently attracted much interest as a non-invasive and highly sensitive technique that can be used in various biological applications, such as intracellular tracking and biolabelling.[1-4] These in vivo applications require fluorescent materials that are ultra-small and exhibit good dispersity and stability to improve their penetration ability and cellular uptake in aqueous media.[5-7] Organic dyes and quantum dots (QDs) are the most common ultra-small species; however, they have several disadvantages, limiting their use in in vivo sensing.[8, 9] For example, organic dyes are small enough to penetrate biological tissues, but their inadequate stability and brightness hinder their use in aqueous media and intracellular environments. QDs exhibit stable fluorescence and are less than 10 nm in size; however, the long-term toxicity of QDs is a considerable disadvantage.[10] Moreover, even if nanocrystals, carbon dots and nanoclusters are ultra-small, they are hard to functionalize with different moieties and load with drugs for medical use.[11, 12] Thus, it is very important that ultra-small fluorescent nanomaterials are designed to be multifunctional and biocompatible for practical applications.

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One effective strategy is to incorporate fluorescent species into various nanomaterials,[13-23] such as mesostructured silica nanoparticles,[24-27] to improve their biocompatibility[7, 28-30] and fluorescence stability[10, 31, 32] in aqueous media.[29, 33] Mesostructured silica nanoparticles have unique pore structures with confined spaces, which can help stabilize the fluorescence of organic dyes and thus enhance the brightness of the nanoparticles. For example, a series of ultra-bright silica nanoparticles ranging from microscale (10 μm) to nanoscale (20-50 nm) in size were synthesized by encapsulating rhodamine 6G in their mesoporous channels.[8, 9, 34] The brightnesses of the different rhodamine 6G-doped mesoporous silica nanoparticles were 20-770 times higher than that of a single rhodamine 6G molecule. However, due to their poor dispersity and large sizes, these silica nanoparticles had difficulty penetrating cell membranes and eliminating from the body.

Compared to conventional mesoporous silica nanoparticles, ultra-small (~12 nm) silica cross-linked micellar nanoparticles (SCMNPs) are ideal scaffolds for encapsulating fluorescent species for biological applications.[6, 35-37] SCMNPs have mesostructured hydrophobic cores and hydrophilic tails that can encapsulate and stabilize Ir complexes, organic dyes and QDs to make them water-compatible for intracellular sensing.[29, 38-40] To enhance the sensing ability of an SCMNPs-based system, a fluorescence resonance energy transfer (FRET) process was introduced into dye-doped SCMNPs to amplify the Cu^{+} sensing signal.[41] Recently, our group also prepared several dye-doped