From macro to nano crystals of cyclodextrin metal-organic frameworks and their use as optical functional materials

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Cyclodextrins (CDs) are a family of naturally abundant, cyclic oligosaccharides, consisting of cone-shaped molecules, with a hydrophobic internal and hydrophilic external surface. Through the coordination of CDs with alkali metal ions (Na⁺, Rb⁺, Cs⁺, K⁺,….) biocompatible, porous metal-organic frameworks (CD-MOFs) can be obtained. These CD-MOFs are attractive materials for practical applications as they can be considered as biocompatible, biodegradable, inexpensive MOF alternatives.

We present our work on designing macro and nano crystals, including core-shell type crystals, of γ-cyclodextrin MOFs (γ-CD-MOFs) and used them as platforms for the encapsulation of different dye molecules for the purpose of developing optical ratiometric thermometers. Both visible, as well as near-infrared emitting dye molecule combinations, are explored, opening a wide range of unique optical γ-CD-MOFs macro/nano crystals. The dyes were added to the reaction medium allowing them to build in during the growth of the crystals. We also show a well optimized route to prepare core-shell type crystals which are synthesized in two steps, allowing to incorporate one of the dyes in the core and a second one in the shell. Last, their use as ratiometric thermometers is presented, where the ratio of the emission bands of two dyes is used to create a thermometric calibration curve. The materials show very good performance in the physiological temperature range, reaching very high relative sensitivity values of up to 5%K⁻¹.

Figure 1. a) Space-filling representation of the cuboidal arrangement of six γ-CD tori, portrayed in different colors, in the crystal structure of γ-CD-MOFs, b) microscopy photographs of macro γ-CD-MOF crystals with mixed dyes (rhodamine B and fluorescein), c) SEM images of nano γ-CD-MOF crystals, d) diagram showing the flow-process employed for the synthesis of core-shell γ-CD-MOF crystals, e) microscopy photographs of macro γ-CD-MOF crystals with a core-shell structure, where rhodamine B is in the core and fluorescein is in the shell.