Use of confocal fluorescence microscopy to compare different methods of modifying metal–organic framework (MOF) crystals with dyes†

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Dye modified MOF microcrystals were characterized by fluorescence microscopy (FM) and confocal laser scanning microscopy (CLSM) which visualized the position and distribution of fluorescent dyes encapsulated into MOF crystals and provided proof for selective, post-synthetic covalent modification of the external surface of MOF crystals.

Metal organic frameworks (MOFs) are known for their intriguing structural motifs with large pore volume, high surface areas (up to several thousand m$^2$ g$^{-1}$), ordered pore channels and tuneable structures.$^1$ The wide-open porous structure provides free space for loading with guest molecules, which can amount up to 90% of the crystal volume, thus making MOFs promising host materials. The loading of guest molecules into MOF frameworks is an important area of research. Gases (most notably dihydrogen),$^2$ drugs,$^3$ metals$^4$ and metal-oxide nanoparticles,$^5$ hydrocarbons,$^6$ and even large molecules like C$_6$O$^7$ were already successfully accommodated into MOF frameworks, thereby generating potential for fascinating applications. In all cases, the loading itself could be verified by macroscopic methods. Recently, computational molecular dynamics simulations of guest molecule diffusion in MOFs have been performed.$^8$ However, major challenges are the experimental determination of the distribution of guest molecules or post-synthetically implemented functional groups at a MOF crystallite and achieving control of the distribution of these species within the bulk of the MOF crystallite or on the outer surface.

Using coloured or luminescent dyes with different sizes and functional groups as models for guest molecules hosted by MOFs is a conceivable method to investigate and visualize the loading of MOFs. For example, Yaghi et al. used three different dyes to simulate functions such as artificial photonic antenna, solid-state lasing, and novel light-emitting diodes.$^8$ Qiu and co-workers incorporated Rhodamine 6G dye molecules into Cd-MOFs (JUC-48) for a potential temperature-sensor.$^9$ However again, it could not be established that the dye molecules were evenly distributed inside the crystals. Fluorescence or UV-Vis spectroscopy is a common method to quantify the dye loading in solid porous crystals macroscopically, nevertheless, it does not allow for determining the dye’s distribution between the bulk and the surface of the crystal.$^9,10$ Kondo et al. reported on the immobilization of fluorescent functional group monolayers on the PCP microcrystal external surface by coordination bonding.$^{11}$ Recently we demonstrated a related surface layer selective and covalent post-synthetic functionalization of a MOF thin film.$^{12}$ The control of (permanent) modification of the external surface of MOF crystallites, nanoparticles or thin films represents an important aspect of the upcoming field of MOF surface chemistry.$^{13}$

In this communication, we compare the use of fluorescence microscopy (FM) and confocal laser scanning microscopy (CLSM) to characterize dye-modified MOF single crystals for determination of the distribution of dyes adsorbed by individual MOF microcrystals (MOF-mc) and we compared the results from the two imaging techniques. We selected IRMOF-1 and the amino-functionalized IRMOF-3, fluorescein and fluorescein-isothiocyanate (FITC), respectively, in order to investigate the influence of different factors such as pore size and reactive functional groups at the linkers and at the dye on the distribution of the dye molecules between the volume and the external surface of the MOF-mc. Two methods of modification with dyes being smaller or larger than the window size of the IRMOF pores were used, either the dye loading by diffusion at preformed MOF-mc or the in situ dye loading by crystallization of the MOFs from solvothermal mother solutions with the addition of the dye molecules (co-precipitation).

As our initial target, IRMOF-1 (cf. MOF-5, [Zn$_4$O(bdc)$_3$], bdc = 1,4-benzenedicarboxylate) cubic crystals with a uniform size of ca. 100 µm were produced from a diethylformamide (DEF) solution of