Controlled growth and composition of multivariate metal-organic frameworks-199 via a reaction-diffusion process

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In this paper, we exploit our prior successful synthesis of MOF-199 single crystals using the reaction-diffusion framework (RDF), to synthesize multivariate metal-organic frameworks (MTV-MOFs) version with enhanced properties. The MTV-MOFs are synthesized by creating defects within the MOF-199 crystal structure by integrating organic linkers entailing different functional groups. Accordingly, 5-aminoisophthalic acid (NH2-BDC) and 5-hydroxyisophthalic acid (OH-BDC) are separately mixed with 1,3,5-benzenetricarboxylic acid (BTC) in three different starting ratios of X-BDC:BTC (1:3, 1:1) and 3:1). The effects of this linker on the morphology of the synthesized MTV-MOFs, their thermal stability, and their surface area are investigated. The extent of the incorporation of the linkers in the framework is elucidated via 1H-NMR spectroscopy and it is shown that the incorporation varies as a function of the location along the tubular reactor, a characteristic of RDF. The enhanced properties of the synthesized MTV-MOFs are further demonstrated by measuring its adsorptive capability for methylene blue (MB) and rhodamine B (Rh B) in aqueous solution, and compared with that of the as-synthesized MOF-199. The kinetic and thermodynamic studies reveal that MTV-MOFs with the ratio of X-BDC:BTC (1:1) exhibit the best uptakes of MB (263 mg/g) for X = OH and Rh B (156 mg/g) for X = NH2. The adsorbents are also easily regenerated for three consecutive cycles without losing their efficiency. We finally demonstrate that MTV-MOFs can be designed to tune the dye removal selectivity and enhance the removal capacity of both MB and RhB in a binary aqueous solution of these dyes.