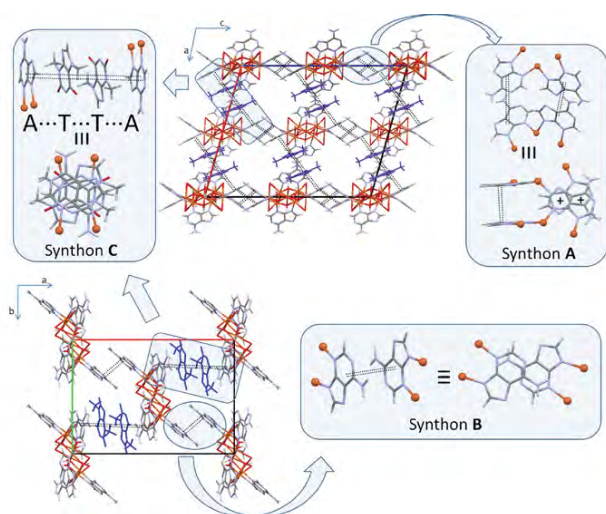


1 and strong intradimeric antiferromagnetic interactions in compounds 2 and 4.



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Keywords: SMOFs, supramolecular interactions, π - π stacking

MS32-P06

Temperature-dependent supramolecular isomerism of lutetium-aminoterephthalate metal-organic frameworks: synthesis, crystallography and physical properties

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Polymorphism or supramolecular isomerism is becoming an increasingly important subject in the field of crystal engineering, as it may facilitate the design of porous polymeric materials with targeted physical properties.^[1] In this context, the unique properties of MOF polymorphs, displaying both different crystal structures and identical molecular composition, allow for the derivation of structure-property relationships solely based on structural parameters or topology of the polymeric network. There are various key factors governing the formation of MOFs' polymorphic forms, including reaction time, temperature, concentration of precursors, pH, solvent, modulators, and so on. Although numerous individual factors^[2] or their conjunction^[3] affect the occurrence of polymorphic forms, temperature is the one of the most important variables. The study of polymorphism is not only important in producing novel materials with target properties but may also be helpful in developing a fundamental understanding of the factors influencing crystal growth, such as reaction temperature.

In this line, we present the investigation on the relationship between the crystal structures and gas adsorption / fluorescence properties of lutetium(III) 2-aminoterephthalate MOFs isomorph series. Three supramolecular isomers of lutetium metal-organic framework, $\{\text{Lu}_2(\text{H}_2\text{O})_4(\text{ATA})_3 \cdot 4\text{H}_2\text{O}\}_n$ (Lu-ATA@RT), $\{\text{Lu}_2(\text{H}_2\text{O})_2(\text{C}_3\text{H}_7\text{NO})_2(\text{ATA})_3\}_n$ (Lu-ATA@100) and $\{\text{Lu}_2(\text{C}_3\text{H}_7\text{NO})(\text{ATA})_3\}_n$ (Lu-ATA@150), have been obtained from the reaction of $\text{Lu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with 2-aminoterephthalic acid (ATA) at different temperatures. The resulting structures of Lu-ATA MOFs depend on the temperature applied during the synthesis, revealing a temperature-susceptible supramolecular isomerism. Single-crystal X-ray diffraction analyses suggest that new compounds with formula $\{\text{Lu}_2(\text{S})_x(\text{ATA})_3\}_n$ (S = solvent: H_2O , DMF) display different three-dimensional architectures which consist on dinuclear lutetium building units. The supramolecular isomer Lu-ATA@RT, formed at room temperature, has a *pcu*-net topology while its double interpenetrated analogue, Lu-ATA@100, assembles at 100 °C under hydrothermal conditions. Hydrothermal synthesis at 150 °C affords formation of the dense Lu-ATA@150 cage-

like framework displaying a new hexagonal-packed net topology. All Lu-ATA isomeric phases are porous and display different gas-uptake behaviour towards carbon dioxide as a function of polymeric network arrangement. The luminescent properties of Lu-ATA frameworks in solid state as well as in suspension in the presence of different solvents reveal a solvent dependent emission.

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MS32-P07

Nanosheets of non-layered aluminium metal-organic frameworks through a surfactant-assisted method

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During the last decade, the synthesis and application of metal-organic framework (MOF) nanosheets has received growing interest,^[1] showing unique performances for different technological applications.^[2] Despite the advances reported, the applicability of the synthetic methods developed so far is mainly restricted to MOFs possessing a layered structure. These MOFs consist of stacked 2D layers, being more prone to the formation of nanosheets. However, this subfamily of compounds only embodies a small fraction of the MOF structures reported to date, severely limiting the potential of this promising type of 2D nanomaterials. To the best of our knowledge, only one very recent example has been reported so far on the top-down exfoliation of 3D MOFs.^[3] However, top-down approaches are often associated with particle fragmentation and re-aggregation of the detached sheets. A bottom-up approach for the synthesis of 3D MOF has never been reported.

Within this context, we present a bottom-up surfactant-assisted synthetic approach for the fabrication of free-standing nanosheets of various non-layered 3D Al-containing MOFs, broadening the scope of MOF nanosheets application. Surfactant-assisted pre-organization of the metallic precursor prior to MOF synthesis allows for the manufacture of non-layered Al-containing MOF lamellae. These MOF nanosheets are shown to exhibit a superior performance over other crystal morphologies for both chemical sensing and gas separation. Gas separation behaviour of MOF nanosheets embedded in polymer matrix was explored for CO₂/CH₄ mixture and compared to the nanoparticle-containing composite. The NH₂-MIL-53(Al) nanolamellae/Matrimid® mixed matrix membrane showed a 10-fold increase in CO₂ permeability along with a doubled selectivity in the separation of CO₂/CH₄ mixtures. Moreover, sensing studies on NH₂-MIL-53(Al) nanolamellae-coated device suggested the enhanced sensing performance towards different types of alcohols. As revealed by electron microscopy and diffraction, this superior performance arises from the shorter diffusion pathway in MOF nanosheets, whose one-dimensional channels are oriented along the shortest particle dimension.