Modulated Synthesis of Thorium-Based Metal–Organic Frameworks for Radionuclide Remediation

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Systematic investigations on the modulated synthesis of thorium based metal-organic frameworks (Th MOFs) by a variety of modulators, including formic acid, trifluoroacetic acid, nitrate acid, hydrochloric acid, etc., were first time conducted, affording large single crystals of a series of Th MOFs with superior quality. With increased equivalents of modulator versus thorium, the products transform from intergrown to single crystals with increasing sizes. In the meanwhile, a strategy based on linking Th^{IV} cations and polycarboxylate ligands with variable lengths into extended networks allows for design new Th MOFs whose porosity and functionality could be varied systematically. Isoreticular Th MOFs with void volumes incrementally varied from 45.3% for $Th_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(FUM)_6(H_2O)_6\cdot G$ (H_2FUM = fumaric acid) to the record-high 74.0% for $Th_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(ABDC)_6(H_2O)_6\cdot G$ (H_2ABDC = 4,4-azobenezenedicarboxylic) among all thorium compounds were obtained. Notably, $Th_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(PEDA)_6(H_2O)_6\cdot G$ (H_2PEDA = 1,4-phenylenediacrylic acid) exhibit a Brunauer-Emmett-Teller (BET) surface area of 3396.5 m^2/g, which is the higest among all Th complexes. Furthermore, several obtained Th MOFs such as $Th_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(BPDC)_6(H_2O)_6\cdot G$ (H_2BPDC = biphenyldicarboxylic acid) can serve as effective adsorbents to capture radioactive iodine, a key fission product in nuclear waste stream, in aqueous or gas forms. This work sheds light on the design and build of thorium and other actinide MOFs with composition variety, hierarchical complexity, void turnability, for the potential applications in nuclear industry relevant applications, e.g. radionuclide remediation.