Title:	A rational design and green synthesis of 3D metal organic frameworks containing a rigid heterocyclic nitrogen-rich dicarboxylate: structural diversity, CO2 sorption and selective sensing of 2,4,6-TNP in water†
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Abstract:	A heterocyclic fluorogenic linker, thiadiazole dicarboxylate (H2tdz), offering diverse coordination modes has been utilized to synthesize two three-dimensional (3D) metal organic frameworks {[Cd2(tdz)2(4,4′-bpy)2]·6.5H2O}n (1) and [Cu(tdz)(4,4′-bpy)]n (2) from a one-pot self-assembly reaction under ambient conditions in high yields. MOFs 1 and 2 are structurally characterized by elemental analysis, FTIR and UV-Vis spectroscopy, single crystal and powder X-ray diffraction, and thermogravimetric analysis. Their single crystal molecular structures reveal that 1 contains a permanent pore along the b-axis with dimensions of 14.576 × 17.567 Å2 while 2 forms a 3D two-fold interpenetrated structure with an extensively reduced pore size. The effect of interpenetration has been further elaborated by a comparison of their CO2 uptake capacities at 263 K, 273 K and 298 K. The uptake value of CO2 for non-interpenetrated 1 (24.8 cm3 g−1) is much higher compared to that of interpenetrated 2 (5 cm3 g−1) at 298 K. Furthermore, to obtain an insight into the adsorbate–adsorbent interaction owing to the presence of the polar thiadiazole moiety and polarizable CO2 molecules, the isosteric heat of adsorption (Qst) was calculated for 1 (29.1 kJ mol−1) and 2 (23.4 kJ mol−1). Thermal and chemical stabilities of 1 in water were ascertained by variable temperature powder X-ray diffraction (VT-PXRD) analysis. MOF 1 having a d10 metal center was utilized to harness the availability of nitrogen atoms in the tdz2− linker for the selective sensing of nitrophenols in water with a detection limit for TNP as low as 1.4 ppm. Moreover, 1 is found to be stable and recyclable up to four cycles.
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