Dalton Transactions



PAPER



Cite this: *Dalton Trans.*, 2019, **48**, 16604

A stimuli responsive multifunctional ZMOF based on an unorthodox polytopic ligand: reversible thermochromism and anion triggered metallogelation†

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A novel Cd(II)-ZMOF with a unique sodalite topology has been successfully designed and synthesized using a flexible polytopic compartmental ligand. The microporous complex contains 1D hexagonal channels with large void space for the accommodation of guest molecules. This work demonstrates a new paradigm for designing and functionalizing zeolite-type frameworks. The triconnected linker forms coordination polymer gels in the presence of Cd²⁺ and the gelation was controlled by the presence of specific anions. They possess good thermal stability and exhibit thixotropic behavior. Optical properties revealed that the complex is exclusively thermochromic and undergoes a reversible transition at 80 °C, changing its color from yellow to orange red. Owing to the large voids in the framework, the complex can serve as a host for use in dye adsorption. Thus this paper offers a new MOF material with exceptional chromic behavior, gelation properties and adsorption capability for the development of high performance multifunctional materials.

Received 8th July 2019, Accepted 24th September 2019 DOI: 10.1039/c9dt02820j

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1. Introduction

Zeolitic Metal–Organic Frameworks (ZMOFs), a burgeoning class of porous Metal–Organic Frameworks (MOFs), have been researched extensively over the past decade due to their great potential to act as crystalline multi-functional materials formed by the deliberate assembly of judiciously selected organic ligands and inorganic metal nodes. MOFs have found their way into many applications, such as catalysis, gas storage and separation, sensing, drug delivery, adsorption, magnetism and so on.^{1–6} In particular, their unparalleled large surface areas, adjustable pore sizes and structured pore surface properties make them promising materials with outstanding applications. MOFs vary in dimensionality from two to three including open, permanently porous, and aesthetic framework structures.

Porous ZMOFs are topologically related to inorganic zeolites. The linkers serve to substitute the oxygen (O^{2-}) that bridges the tetrahedral units in traditional zeolites and pre-

serve the intended angle of connectivity (with an average M-L-M angle of \sim 144°), adorning and expanding the native zeolitenet topology with distinct properties. The desirability associated with these compounds relies, in part, on their porosity, with homogeneously-sized and -shaped openings and voids and forbidden interpenetration. ^{7,8} To date, there have been four synthetic routes towards building ZMOFs: (1) the 'edge expansion' approach, (2) from metal–organic cubes or squares, (3) from supertetrahedral building blocks and (4) *via* organic tetrahedral nodes. Among these approaches, the 4 + 2 strategy is particularly popular and well explored, which involves the use of a longer ditopic organic linker bridging 4 connected tetrahedral nodes (T-nodes). ⁹

Controllable synthesis of MOFs is a great challenge and highly structured molecular architectures make use of bottom-up methods using ligands programmed with appropriate coordination information. Among the large family of known ZMOFs, the sod-type materials are momentous for their unique structural characteristics and properties.^{7,10} Most of the reported sod-ZMOFs are constructed by the assembly of imidazolate derivatives and different metal ions.^{10,11} Therefore, it is an imperative and perplexing task to explore appropriate organic linkers and suitable metals for the preparation of sod type ZMOFs.

In this endeavor, in contrast to linkers functionalized by carboxylate, nitrogen or phosphate donors, we have investigated a compartmental polytopic ligand, namely 2,3-butane-

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 $[\]dagger$ Electronic supplementary information (ESI) available: CCDC 1911379. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/C9DT02820J