



## Tetrazole anchored triazole: Potential structure and function directing tecton in Metal-organic frameworks

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Dynamic microporous metal-organic frameworks (MOFs) which offer unlimited opportunity in terms of architecture, porosity, endurance and properties have found applications in separation science, gas storage technology, sensors, catalysis, drug delivery etc. <sup>[1]</sup>. In continuation of our modular approach to functional metal-organic frameworks,<sup>[2]</sup> we introduce two different tectons: the first based on tetrazole, L1 = 5-(4H-1,2,4-triazol-yl)-2H-tetrazole<sup>[3]</sup> and the second based on a natural amino acid, L2 = 3-hydroxy-2-[1,2,4]triazole-4-yl-propionic acid, as a bi-functional bridging ligand and as anion. Synthesis involving ternary components of L1, zinc and phen/phen-dione leads to a 2D network [Zn(phen)<sub>2</sub>(L1)]BF<sub>4</sub> (**1**) which crystallizes in a centrosymmetric space group (Pnma). A mononuclear inclusion complex [Zn(2,2'-bpy)<sub>3</sub>]<sub>2</sub>(L1)(BF<sub>4</sub>)<sub>3</sub>·10H<sub>2</sub>O (**2**) that crystallizes in a non-centrosymmetric space group (P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>) was also obtained.

We have studied gas adsorption/storage applications and fluorescence properties of these materials. TGA-DTA of **1** shows exceptional thermal stability up to 200°C whereas **2** which is dehydrated at 100°C, begins to collapse after 110°C. **1** shows little preference for both N<sub>2</sub>(g) and H<sub>2</sub>(g). Type-I isotherm with a low specific surface area of 11 m<sup>2</sup>/g for N<sub>2</sub>(g) and a non-reversible low H<sub>2</sub>(g) uptake of 8 cm<sup>3</sup>/g was evidenced. In the inclusion complex **2**, the hanging-up of **L1** in the matrix dictates a larger separation of mononuclear entities thus creating sufficient spaces in the host crystal packing. This structural impact is seen in the BET results. Degassed at 30°C under high vacuum, the activated phase of **2** shows a specific surface area of 40 m<sup>2</sup>/g from N<sub>2</sub>(g) isotherm and a H<sub>2</sub>(g) uptake of 33 cm<sup>3</sup>/g. When subjected to a dynamic vacuum at 110°C the surface area increases to 49 m<sup>2</sup>/g. Upon excitation (λ<sub>ex</sub> = 345 nm), **1** emits strong emissions at 373, 392 nm assigned to intra-ligand fluorescence from the capping ligand whereas the shoulder band at 415 nm arises from a charge-transfer transition.

A comparison between the role of neutral and anionic duality of 1,2,4 amino-acid scaffold and the asymmetric triazole-tetrazole tecton, in these coordination polymers is presented.

**Keywords:** porous MOFs; amino-acids derivatives; phenazine; 4-R-1,2,4-triazole

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