A theoretical study of the zinc oxide cluster models of CPO-27-Zn

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Zinc oxide is a well-known semi-conductor with a wide, size-dependent band gap of 3.37 eV and lots of effort has been put in to tune the band gap by changing the particle size [1]. Recently, it has attracted a lot of attention because of its unique catalytic, electrical, and optoelectronic properties [2] as well as LED applications and piezoelectric and pyroelectric properties [3]. Clusters possess different properties compared to bulk and film due to the size effect and a large surface-to-volume ratio [4], and they are essential for the development of fundamental understanding of materials at nanoscale.

Porous materials are applicable for gas storage and adsorption because of high surface area and pore volume [6]. In this presentation, the main focus will be on the microporous coordination polymer Zn_2(dhtp)-$(H_2O)_2]\cdot 8\,H_2O$, hereafter termed CPO-27-Zn, which was first prepared by Dietzel et. al in 2007 [5]. Each zinc atom is coordinated by six oxygen atoms where five stem from the organic ligand 2,5-dihydroxoterephthalic acid (dhtp) and the remaining oxygen stem from the water molecule resulting in infinite, one-dimensional, helical chains of *cis*-edge sharing ZnO_6 octahedra, which are linked by the organic ligand in such a way that a six-ring chelate complex is formed, resembling a honeycomb (fig. 1). Upon heating, the coordination number of Zn is reduced to five as the water molecule is removed, thereby changing the coordination polyhedra from octahedra to square pyramids. Because the unit cell of CPO-27-Zn contains a large number of atoms, there is a need to make smaller cluster models that will be representative for the system. A major part of the project is to achieve knowledge about how the HOMO-LUMO gap changes with the ZnO chain length and the size of the organic ligand. The cluster calculations will be performed using Gaussian and ADF (Amsterdam Density Functional) and the periodic calculations using VASP (Vienna Ab-initio Simulation Package).

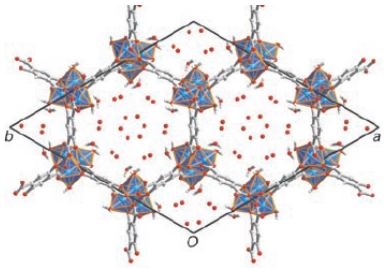

Figure 1: Unit cell of the crystal structure of CPO-27-Zn along [001]. The figure is taken from ref. [6].

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