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Tuning the high-pressure phase behaviour of ultra-compressible zeolitic imidazolate frameworks – From discontinuous to continuous pore closure by linker substitution

Zeolitic imidazolate frameworks (ZIFs), a very important subfamily of metal-organic frameworks (MOFs), are constructed from tetrahedrally coordinated M2+ (Zn2+ or Co2+) ions, which are interlinked by imidazolate linkers[1]. Recently, we discovered that the prototypical ZIF-4 (chemical composition M(im)2, im−= imidazolate) undergoes a phase transition from an open pore (op) to a closed pore (cp) phase under hydrostatic pressure[2]. Here we further present the high-pressure (HP) behaviour of a series of isostructural ZIF-4 derivatives, named ZIF-62, with the general chemical composition M(im)2-x(bim)x (bim−= benzimidazolate, 0.02 < x < 0.35). The ZIF-62 materials crystallize in the space group Pbca and feature the same network topology (cag) as the original ZIF-4, however, some of the im−linkers are substituted by the bulkier bim−linkers. HP-PXRD experiments were performed at beamline I15 of Diamond Light Source in the pressure range from ambient up to 4000 bar using silicon oil as a non-penetrating pressure transmitting medium and a hydraulic pressure cell[3]. Under hydrostatic pressure, all ZIF-62 derivatives reversibly contract from the op to the cp phase only by rotations about the imidazolate-metal bonds (Fig. 1). Crystal symmetry and network topology are preserved. With increasing bim−-concentration, the threshold pressure for the op-cp phase transition increases from 700 bar to 1300 bar and the overall volume contraction across the transition decreases from 25% to 17% of the initial volume. Most importantly, the 1st order (discontinuous) transition transfers to a 2nd order (continuous) transition for x > 0.30. Thus, the void space and pore openings of ZIF-62 can be tuned continuously by the application of mechanical pressure –a unique feature which might be useful for adjusting and enhancing the gas separation performance of these flexible MOFs.

Fig. 1. Structural models of ZIF-62 with the composition Zn(im)1.65(bim)0.35 at ambient pressure (left) and 4000 bar (right). The void space available for CO2 molecules (kinetic diameter = 3.30 Å) is shown in gold.

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