High Connectivity Framework Polymers: A New Co-ordination Chemistry

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The concept of a co-ordination number and its relationship to specific co-ordination geometries describing the number and relative dispositions of ligands bound to a metal cation within a metal complex is very well established. In contrast, understanding which specific topology is associated with a particular connectivity of a metal ion within a framework polymer is less well developed, particularly for highly-connected nets. For example, 2-connected systems are commonly associated with linear or zig-zag chains, 3-connected with ladder, brick-wall or herringbone motifs, 4-connected with (4,4) square or adamantoid cages, and 6-connected with cubic or alpha-polonium nets. Higher order frameworks of 5-, 7- and 8-connectivity are exceedingly rare, and we have developed, for the first time, a general route to such systems via the use of lanthanide nodes and N-oxide bridging ligands [1]. The use of N-oxide ligands as linkers in such systems is based upon the complementarity of hard lanthanide ions, showing relatively high co-ordination numbers, with hard O-donors. Furthermore, N-oxides do not impose severe steric constraints on binding up to eight such ligands to a lanthanide centre.

[1] Hill R.J., Long D-L., Champness N.R., Hubberstey P., Schröder M., *Acc. Chem.. Res*., 2005, *in press and references therein.*

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