Cyclic alpha-peptoids hold the attention of both synthetic and supramolecular chemists for their biostability and potential diversity but also for their elegant and intriguing architectures.[1] Peptoids differ from peptides in the side chains, which are shifted by one position along the peptide backbone to the nitrogen atom to give N-substituted oligoglycine. The lack of the amide proton prevents the formation of NH•••OC hydrogen bonds and weaker interactions, as CH•••OC hydrogen bonds and CH-pi interactions, play a key role. Inter-annular CH•••OC hydrogen bonds can provide face to face or side by side arrangement of macrocycles mimicking beta-sheet secondary structure in proteins.[2] In particular, the role of side chains in the solid state assembly of peptoid macrocycles will be discussed to show how they can promote the formation of a peptoid nanotube by acting as pillars, extending vertically with respect to the macrocycle planes. [3] Examples of the solid state assembly of free and metallated cyclic peptoids will be reported to show their extreme versatility as building blocks for designing new materials, with novel chemical properties and defined biological activities. In particular the first crystal structure of a recently synthesized novel cyclic alpha-peptoid, containing open channels with a radius of approximately 7 Å, will be discussed as a case of the successful engineering of cyclopeptoid crystals. In figure it is shown the channel void surface as seen along the a axis (0.0003 au, CrystalExplorer 3.1). The results of recent variable temperature high resolution XRPD measurements performed at ESRF beamline ID31 will be also reported to highlight the unusual thermal stability of this class of compounds and how the mobility of the side chains may be exploited to prepare new functional materials. EU FP7-People-IRSES grant number 319011 is gratefully acknowledged.