Pyramidal ligands based on the cyclootriveratrylene (=CTV) host have rigid molecular cavities. These ligands can form either discrete or polymeric metal-ligand systems, thus creating metallo-supramolecular assemblies or coordination polymers with specific molecular recognition sites. The pyramidal shape of these ligands results in assemblies with distinctive “star-burst” shapes or stellated polyhedra. Discrete metallo-supramolecular assemblies or “star-burst” prisms with these ligands include [MnL2]2+ capsules, different types of [Ag2L2]4+ tetrahedra, and a series of giant [Pd4L4]25+ stella octangulosa (pictured below). A further, and unexpected, trend in this chemistry is the formation of topologically non-trivial assemblies. Capsules forming triply interlocked [2]catenanes have been found with 2,2’-bipyridine or 3-pyridyl derived ligands, and a [Pd4(NO3)2(H2O)2L4]8+ “Solomon’s cube” assembly has a unique molecular topology akin to a self-entangled cube. The pyramidal shape of the ligands also leads to both known and unusual topologies within coordination polymers, including chains or nets of linked capsules, 2D nets of 4.8 topology, and highly complicated and unusual 3D networks, amongst others. The structural and some solutions chemistry of these supramolecular assemblies and coordination polymers will be presented.

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