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Coordination-Driven Self-Assembly of Discrete Molecular Nanotubular Architectures

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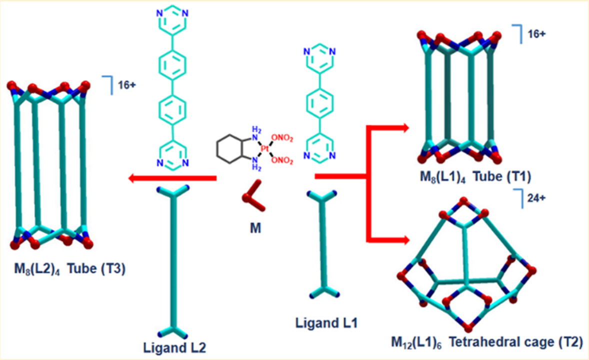
Ⓢ *Supporting Information*

ABSTRACT: Two new $\mathbf{M_8L_4}$ tetrafacial nanotubes (**T1** and **T3**) of different lengths have been synthesized in water using ligands **L1** and **L2**, respectively, with acceptor *cis*-[(*dch*)Pt$(NO_3)_2$] (**M**) using coordination-driven self-assembly [where *dch* is 1,2-diaminocyclohexane, **L1** is 1,4-di(pyrimidin-5-yl)benzene, and **L2** is 4,4′-di(pyrimidin-5-yl)-1,1′-biphenyl]. In addition to complex **T1**, a tetrahedral cage of composition $[M_{12}(L1)_6]$ (**T2**) was also formed in the self-assembly reaction of ligand **L1** with *cis*-[(*dch*)Pt$(NO_3)_2$]. The precise composition of the products (**T1** and **T2**) in solution was confirmed by ^{1}H NMR and ESI−MS. Pure tube **T1** was separated out by a crystallization technique and fully characterized by ^{1}H NMR and X-ray diffraction. Temperature- and concentration-dependent NMR studies indicated no equilibrium between **T1** and **T2** in the solution phase, and the proportion of **T1** and **T2** in the mixture depends on the temperature of the reaction. In contrast to ligand **L1**, the self-assembly of the longer ligand, **L2**, with *cis*-[(*dch*)Pt$(NO_3)_2$] gave only tetrafacial tube $[M_8(L2)_4]$ (**T3**) without any tetrahedral cage.



INTRODUCTION

Supramolecular architectures synthesized through various self-assembly approaches have been found to be quite interesting in terms of both their diverse structural features and applications in recognition, catalysis, separation, drug delivery, and sensing. Among other synthetic self-assembly approaches, coordination-driven self-assembly based on the metal−ligand coordination bond as a driving force has emerged as a convincing tool for forming a plethora of coordination architectures with fascinating applications.[1] This approach is endowed with numerous synthetic advantages which include the reversible nature of the bond, an inherent self-correction mechanism, a one-pot reaction, and high yields of the desired products. Highly ordered structures such as tetrahedrals,[2] octahedrals,[3] cubes,[4] cuboctahedrals,[5] dodecahedrals,[6] and others[7] have been produced through the judicious combination of donors with suitable acceptors that are held together by metal−ligand bonds. The formation of a single discrete metallocage as an exclusive product is generally observed in many cases. Nevertheless, in some cases, both equilibrium and non-equilibrium mixtures of products are also formed.[8] The final outcome of the self-assembly is decided by many other external factors such as the nature of the solvent,[9] pH,[10] temperature,[11] the coordination environment of the metal ions,[12] and steric constraints.[13] The ratio of the products in an equilibrium mixture is determined by a delicate balance between entropy and enthalpy. While smaller self-assembled structures are favored by entropy because a great number of such assemblies are formed from the same number of building blocks, larger assemblies are enthalpy-favored with minimal possible conformational strain and other steric constrains. As a result of this balance, smaller assemblies having the ligand flexibility to reduce the possible strain end up as the major component in an equilibrium, while larger assemblies end up as minor products. However, with rigid ligands the larger assemblies are favored by a high enthalpy gain, and it overcompensates for the entropic loss to become the major component of the mixture. Mainly the pyridyl-based symmetric and rigid organic donors have been used to construct such molecular architectures owing to their well-behaved and easy prediction of product structure. Interestingly, pyrimidine-based donors remained less explored because of the weak coordinating ability of endocyclic N atoms. The parent pyrimidine molecule is a π-electron poor heteroaromatic and is weakly basic in nature. Because of the relatively low basicity, the nitrogen binding sites of the pyrimidine form weak coordination bond with the transition-metal ions. However, few examples of metal complexes with pyrimidine-based ligands are reported in the literature.[14] The relatively robust nature of the Pt(II)−N bond as compared to the Pd(II)−N bond encouraged us to explore the Pt(II) acceptors in combination with pyrimidine-based ligands, possibly to achieve stable molecular architectures. Molecular nanotubular structures are of particular importance with their

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