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A Pd_{24} Pregnant Molecular Nanoball: Self-Templated Stellation by Precise Mapping of Coordination Sites

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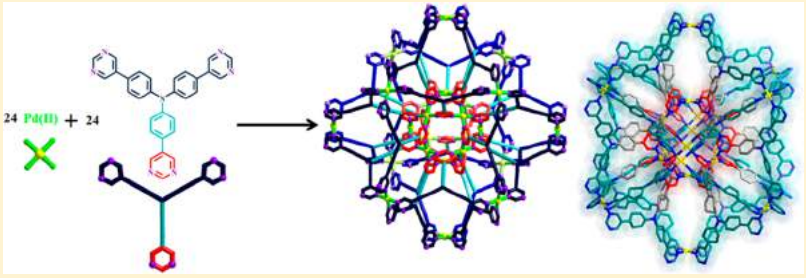
Supporting Information



ABSTRACT: We found that Pd(II) ion (**M**) and the smallest 120° bidentate donor pyrimidine ($\mathbf{L_a}$) self-assemble into a mononuclear $\mathbf{M(L_a)_4}$ complex (**1a**) instead of the expected smallest $\mathbf{M_{12}(L_a)_{24}}$ molecular ball (**1**), presumably due to the weak coordination nature of the pyrimidine. To construct such a pyrimidine bridged nanoball, we employed a new donor tris(4-(pyrimidin-5-yl)phenyl)amine (**L**); which upon selective complexation with Pd(II) ions resulted in the formation of a pregnant $\mathbf{M_{24}L_{24}}$ molecular nanoball (**2**) consisting of a pyrimidine-bridged Pd_{12} baby-ball supported by a Pd_{12} larger mother-ball. The formation of the baby-ball was not successful without the support of the mother-ball. Thus, we created an example of a self-assembly where the inner baby-ball resembling to the predicted $\mathbf{M_{12}(L_a)_{24}}$ ball (**1**) was incarcerated by the giant outer mother-ball by means of geometrical constraints. Facile conversion of the pregnant ball **2** to a smaller $\mathbf{M_{12}(L_b)_{24}}$ ball **3** with dipyridyl donor was achieved in a single step.

INTRODUCTION

Inspired by the incredible emergence of precise assembly in well-defined large structures of multiple proteins subunits,[1] chemists have explored various creative approaches to prepare polyhedral molecular architectures with specific Platonic and Archimedean geometries having desired functions.[2] Careful control over coordination interaction of exomultidentate ligands with transition metal ions has been pursued with special attention to fabricate several topologically similar derivatives such as "cubes",[3] "balls",[4] and "spheres"[5] with structural resemblance to spherical virus capsids. Since the vertices and edges of these architectures are occupied by metal ions and organic ligands respectively, understanding the underlying principles is crucial to effectively map a particular structure by designing appropriate donor and acceptor units.[6] However, due to relatively flexible and weak nature of the coordination bond, sometimes other factors (e.g., template,[7] solvents,[8] bent angle,[9] etc.) may influence the self-assembly leading to unprecedented architectures. For example, Fujita and co-workers have shown that slight change in ligand bent angle can result into incommensurable difference in the final structures; from cuboctahedron to rhombicuboctahedron.[9] Therefore, a more precise understanding of the interplay of these several effects is necessary for the preparation of desired architectures by control self-assembly.

On the other hand, supramolecular self-selection depends on specific instructions like coordination environment of metal ions,[10] steric constraints,[11] and geometrical complementarity[12] which are encoded in building components. This represents a novel approach to build-up functionally integrated and structurally organized supramolecular architectures from multiple subunits. Moreover, lability of coordination interactions allows reversible associations of the building units by continuous exchange which is associated with error-checking and thus often leads to the formation of predominant thermodynamic product(s).[13] Several external stimuli, like solvent,[14] pH[15] and temperature,[16] can sometimes also decide the fate of certain recognition process. However, influence of electronic properties of the subunits and entropic factor to guide such self-selection process in complex mixture of competing species has been investigated in limited number of systems.[17,18]

Based on the previous results,[19a] the outcome of the self-assembly of a square planar Pd(II) ion with any 120° bidentate rigid donor (X) should be a $Pd_{12}X_{24}$ cuboctahedral cage. Pyrimidine ($\mathbf{L_a}$) is considered to be the shortest 120° bidentate donor with two donor nitrogens separated by a single carbon atom. Hence, self-assembly of pyrimidine ($\mathbf{L_a}$) with square

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