

Self-sorting of Pd<sub>12</sub> Self-assembled tetrahedral homo-chiral nano-cages with polytetrazole linkersProdip Howlader<sup>1</sup>, Partha Sarathi Mukherjee<sup>1</sup><sup>1</sup>Indian Institute Of Science, Bangalore, India

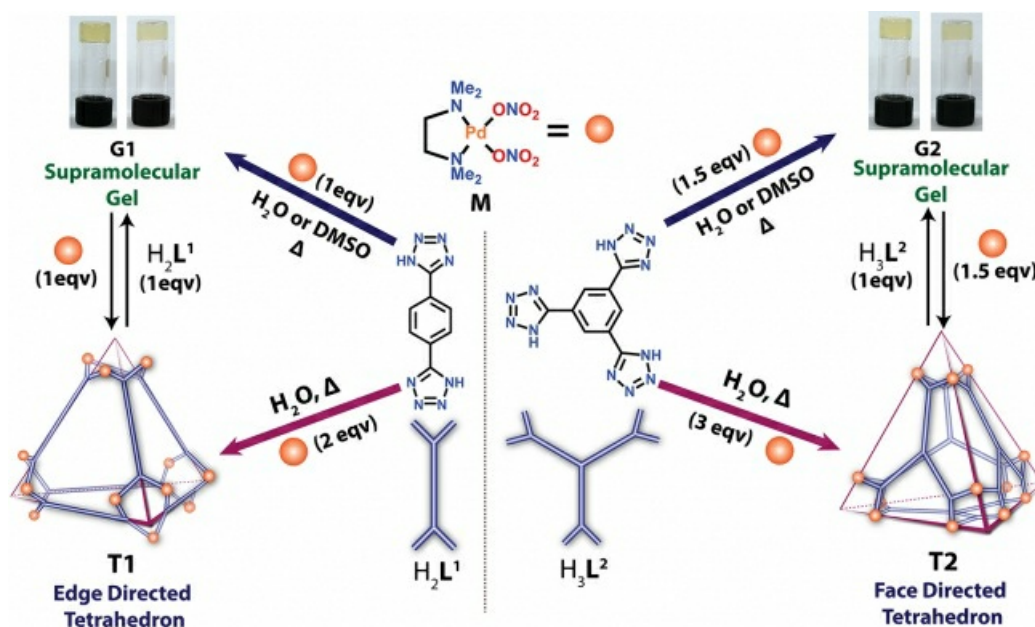
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Coordination-driven self-assembly strategy inspired chemists in past two decades to design basic 3D structures of high symmetry and well defined shapes and sizes. Tetrahedron is one of the common 3D geometries.<sup>1</sup> Several tetrahedral molecular cages have been reported using mainly octahedral metal ions with a few examples of analogous cages of lanthanides with higher coordination number, though their solubility is restricted to organic solvents in majority of the cases. Due to geometric restriction, square planar metal ion like Pd(II) has not been explored much for the design of regular tetrahedral cages. Herein, we discuss the reactions of a cis-blocked Pd(II) 90° acceptor [cis-(tmeda)Pd(NO<sub>3</sub>)<sub>2</sub>] (M) with 1,4-di(1H-tetrazol-5-yl)benzene (H<sub>2</sub>L<sup>1</sup>) and [1,3,5-tri(1H-tetrazol-5-yl)benzene] (H<sub>3</sub>L<sup>2</sup>) in 1:1 and 3:2 molar ratios respectively, which yielded soft metallogels G1 and G2 [tmeda = N,N,N'-tetramethylethane-1,2-diamine] in both water and organic solvent like DMSO. Post-metallation of the gels G1 and G2 with 1 equivalent amount of M yielded highly water-soluble edge and face directed self-assembled Pd<sub>12</sub> tetrahedral nanocages T1 and T2, respectively.<sup>2</sup> Single crystal XRD data of both T1 and T2 shows that each vertex of the tetrahedron is occupied by a Pd<sub>3</sub> unit and they are connected by the tetrazole unit along the face or the edge direction respectively. Such facile conversion of Pd(II) gels to discrete tetrahedral metallogels is unprecedented. Interestingly, the coordination modes of the tetrazole units conjure 'symmetry breaking' into these assemblies. Single crystal XRD structures showed that the handedness of the Pd<sub>3</sub> vertices formed by the tetrazole units are responsible for the 'symmetry breaking' which led to the formation of homo-chiral (all the vertex have the identical handedness) assembly having T symmetry. Moreover, distinct self-sorting of these two tetrahedral cages of similar size was observed in the self-assembly of M with a mixture of H<sub>2</sub>L<sup>1</sup> and H<sub>3</sub>L<sup>2</sup> in aqueous medium. Moreover, the edge directed tetrahedral cage (T1) has open windows as compared to the face directed one (T2), therefore T1 was used to perform Michael addition reactions of a series of water insoluble nitro-olefins assisted by the encapsulation into the cage in an aqueous medium in a homogeneous manner. The same set of reactions were previously carried out with a water insoluble urea functionalized molecular prism in a heterogeneous fashion.<sup>3</sup>

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