



Cite this: *Chem. Commun.*, 2018, 54, 4814

Received 22nd February 2018,  
Accepted 6th April 2018

DOI: 10.1039/c8cc01487f

rsc.li/chemcomm

## Preparation of a chiral Pt<sub>12</sub> tetrahedral cage and its use in catalytic Michael addition reaction†

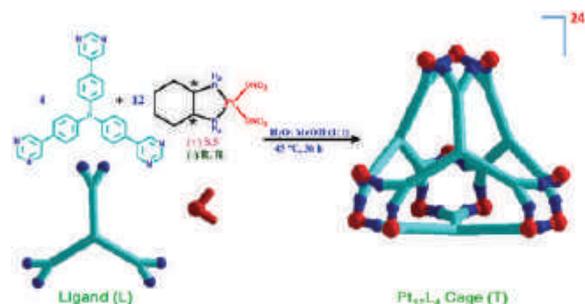
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**The reaction of chiral *cis*-[(1*S*,2*S*)-*dch*]Pt(NO<sub>3</sub>)<sub>2</sub> (**M**) [where (1*S*,2*S*)-*dch* = (1*S*,2*S*)-1,2-diaminocyclohexane] with a hexadentate ligand (**L**) in 3 : 1 stoichiometric ratio yielded a [12+4] self-assembled chiral M<sub>12</sub>L<sub>4</sub> molecular tetrahedron (**T**). The cage **T** features an internal 3D nanocavity with large open 'windows', enabling it to catalyze Michael addition reactions of a series of nitrostyrene derivatives with indole in a 9 : 1 water : methanol mixture.**

The general concept of "cavity-directed synthesis", which deals with molecular containers having confined space with size comparable to that of reactants, to alter the profile of the chemical reactions is well established.<sup>1</sup> Enzymes, which are nature's molecular containers, possess molecular pockets capable of binding substrates through non-covalent interactions and catalyze many important enzymatic reactions.<sup>2</sup> Initially, covalent hosts such as cyclodextrins, carcerands and hemicarcerands as molecular containers attracted much focus with diverse applications.<sup>3</sup> Over the last two decades, with the advent of coordination-driven self-assembly, the focus has greatly shifted to exploiting weak metal–ligand coordination for the self-assembly of molecular containers from individual components. The simple yet dynamic nature of coordination driven self-assembly has led to the construction of various capsules and cages with nanometer-size cavities capable of various applications.<sup>4–7</sup> The shape and size of inner cavity of the coordination cages, even those not possessing definite covalent interactions between the catalyst and substrate, play a paramount role in altering the reactivity and properties of the contained molecules.<sup>3b,8</sup> Large rate enhancement, modulation in selectivity, or shifts in the thermodynamic properties of encapsulated guests have been achieved by appropriate choice of substrates and host cages.<sup>1a,9</sup> Tetrahedral clusters, as the basic platonic polyhedrons feature many interesting

host–guest chemical properties owing to their intrinsic structural beauty.<sup>10</sup> Several tetrahedral molecular cages have been reported recently by mostly employing octahedral metal ions or lanthanides with higher coordination number. The solubility of such tetrahedral cages is largely restricted to organic solvents.<sup>11</sup> However, due to geometric restrictions, very few tetrahedral cages have been reported with square planar metal ions (such as Pd(II) acceptors) through coordination driven self-assembly.<sup>12</sup> The relative kinetic inertness of Pt–N bonds makes it more difficult to achieve large architectures from amine-blocked Pt(II) acceptors. In many cases, self-assembly of amine-blocked Pt(II) acceptors leads to a mixture of products. However, such Pt(II) architectures are more appealing as molecular vessels for diverse chemical reactions due to their better stability compared to analogous Pd(II) counterparts.

Herein, we report the synthesis of an unusual chiral M<sub>12</sub>L<sub>4</sub> tetrahedral cage **T** by treating the exo-hexadentate ligand tris-(4-(pyrimidin-5-yl)phenyl)amine (**L**) with chiral *cis*-[(1*S*,2*S*)-*dch*]Pt(NO<sub>3</sub>)<sub>2</sub> (**M**) in a 1 : 3 stoichiometric ratio in 1 : 1 water : methanol mixture (Scheme 1). The formation of a tetrahedral cage of Pt(II) in the present study as the single product is unique because an analogous hexadentate tripyrimidine ligand with *cis*-blocked Pd(NO<sub>3</sub>)<sub>2</sub> yielded a hexahedron cage. Since the Pt(II)–pym bond is stronger than the Pd(II)–pym bond,<sup>13</sup> the tetrahedral cage **T** attains thermodynamic stability through the positive cooperative effect of only 24 Pt(II)–pym coordination



Scheme 1 Schematic representation of the synthesis of tetrahedral cage **T**.

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† Electronic supplementary information (ESI) available. CCDC 1824959. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8cc01487f