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Neutral Polyhedral pd(II) Cages Supported by tris(imido)phosphate trianions

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Polyhedral cages derived from metal-ligand coordination bonds are a notable class of materials in supramolecular chemistry. Traditionally, these cages were obtained as charge-separated assemblies, cationic or anionic, by choosing geometrically tailored metal ions as nodes and neutral organic donor ligands as directional bridging motifs. Conversely, in recent years tremendous attention has been accorded to the use of multi-metallic scaffolds or clusters as vertices for obtaining charge neutral nanocages which are termed as metal-organic polyhedra (MOPs). However, rational routes to access these kinds of MOPs have been restricted to a small number of systems owing to the lack of precise control over the assembly of such cluster motifs and the limited availability of suitable auxiliary groups that can specifically protect some of the metal-coordination sites in these clusters for the exclusive formation of MOPs. In this effort, our group has developed a facile route for preparing polyhedral building unit (PBUs) consisting of three Pd(II) atoms cis-protected by tris(imido)phosphate trianions, analogous to orthophosphate ion. These PBUs self-assemble in presence of suitably chosen wide-angle chelating linkers such as oxalate dianions and pyrazine dicarboxylate anions to yield stable neutral cages in tetrahedral and cubic topology. These cage assemblies offer excellent platforms for studying host-guest chemistry in solution as well as in the solid-state. Also, by employing suitable bridging ligands containing additional functionalities the cages can undergo post-assembly reactions to yield heterobimetallic cages and 3D-frameworks. Further, by employing PBUs containing chiral imido(phosphate) trianions, enatipure cages have been prepared that show chiral recognition and separation.

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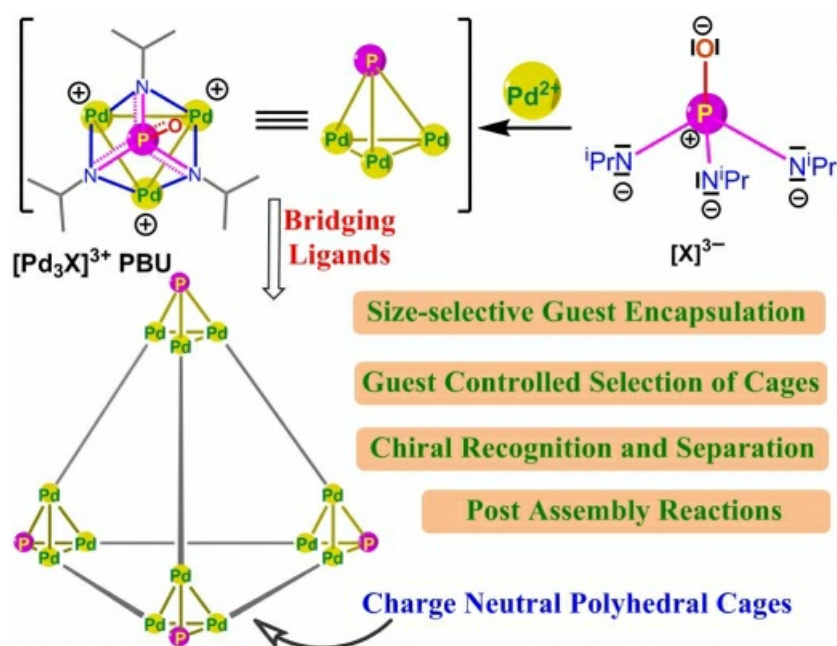
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