Discrete polyoxometalates: from geochemistry via crystal engineering to functional materials

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Polyoxometalates (POMs) are a class of discrete, anionic metal-oxides with an enormous structural diversity and a multitude of interesting properties leading to potential applications in different areas including catalysis, nanotechnology and medicine [1]. Noble metal-containing POMs are in particular attractive for homogeneous and heterogeneous catalytic applications. However, the number of well characterized noble-metal POMs is rather small [2]. POMs based exclusively on Pd^{2+} addenda (polyoxopalladates, POPs) were discovered in 2008 [3]. The area of POP chemistry has developed rapidly ever since, due to the fundamentally novel structural and compositional features of POPs, resulting in unprecedented electronic, spectroscopic, magnetic, and catalytic properties [4]. In terms of POP structural types, the symmetrical 12-palladate nanocube $\{MPd_{12}L_8\}$ and the 15-palladate nanostar $\{MPd_{15}L_{10}\}$ are the most abundant. Especially for the $\{MPd_{12}L_8\}$ nanocube, many derivatives with various central guests including *d* and *f* block metal ions and various capping groups are known [4]. We demonstrated the use of $\{MPd_{12}L_8\}$ as discrete molecular precursors for the formation of supported palladium metal nanoparticles as hydrogenation catalysts, and we discovered an important dependence of the catalytic properties on the type of internal metal guest and external capping group [5]. We also managed to construct 3D coordination networks using externally functionalized POPs, resulting in metal-organic framework (MOF)-type assemblies (POP-MOFs) with interesting sorption and catalytic (C-C coupling) properties [6].

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