The chemistry of polyoxometalates based hybrids and polycarboxylic acid complexes in view of crystal engineering concepts

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At present, research into polyoxometalates (POMs) is a hot topic in many scientific fields, mainly because of their vast range of potential applications. Recently, the coordination ability of POMs has attracted the attention of the scientific community because it allows them to behave as unusual inorganic ligands. Currently, the design and assembly of hybrid inorganic–organic compounds has become an area of rapid growth due to their structural diversities as functional materials. POMs, as a unique class of inorganic metal oxide clusters, possess intriguing structures, unexpected reactivity and abundant potential applications. To date, a great deal of POMs-based hybrid compounds constructed from various metal ions and different kinds of POMs have been reported. A direct consequence of this ability is the assembly of high-dimensional architectures, which have been reported during the past decade. Thus, this presentation considers the latest achievements in the construction of hybrid inorganic-organic materials based on POMs, with a specific focus on their various coordination modes, particularly Keggin-type anions, which are widely available in our research group. [1-4] Herein, we describe the fascinating architectures of POMs-based hybrid compounds constructed using metal ions and different kinds of POMs. Complementing, the important role of POMs, the choice of adequate ligands is fundamental to modulate the properties of hybrids inorganic-organic as highlighted in this presentation. In addition to the important role of POMs, the choice of adequate ligands is important to modulate the properties of hybrid inorganic-organic materials. Moreover, flexible ligands with strong coordination capacity have been used for construction of POMs-based compounds with attractive topologies and different dimensionality. Thus, this presentation puts into perspective latest research on this topic focusing to the construction of hybrid inorganic-organic materials based on flexible ligands. Remarkably, they provide to POMs-based systems the flexibility and conformational freedom necessary to satisfy the coordination environment of the metal centers creating unprecedented topologies, such as entangled structures. In addition, this presentation also describes recent works devoted to analyze how the negative charge of POMs influences the supramolecular assembly of hybrid inorganic–organic materials. In second part of this talk, we report the syntheses and X-ray crystal structures of supramolecular frameworks based on polycarboxylic acid and amines prepared under ambient/solvothermal conditions using the proton-transfer mechanism in views of crystal engineering concepts. [5-7] The solid state architecture of the complexes has been analyzed and the energetics of the noncovalent interactions has been studied by means of high level DFT calculations. The evaluation of the binding energies associated with each noncovalent interaction is useful for rationalizing their mutual influence in the crystal packing.

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