

Charge-driven assembly of Water-soluble Ionic Metal-Organic Polyhedra with Enzymes

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Metal-organic polyhedra (MOPs) are a fascinating class of compounds, that can be used as elementary bricks for the realization of complex organized materials. MOPs are zero-dimensional analogues of MOFs, with a high intrinsic porosity, but also the capability to be dispersed as molecularly defined single entities in selected solvents and recombined in a controlled manner. However, their typically low solubilities and stabilities in water preclude most application in association with biological systems. This calls for the design of new MOPs, that would enable the design bio-hybrid MOP-based systems. One promising application is for the immobilization of catalytically active enzymes. Recently, this domain saw a strong interest in the use of MOFs as immobilization matrix, combining high activity enabled by the MOF microporosity as well as good stabilization performances. In this context, establishing a novel strategy that provides a general way to build microporous networks able to integrate a wide variety of enzymes in mild conditions (i.e. aqueous medium, room temperature, neutral pH with minimal salts or additive,...) is extremely relevant for a wide range of applications.

Hereby, we describe for the first time how MOPs can act as an efficient immobilization matrix for enzyme [1]. The targeted design of MOPs with Rh-centers and pending arms bearing either cationic or anionic groups offered both a good solubility in water, as well as a high affinity for enzymes with an isoelectric point (pI) below or above 7, respectively.

Using BSA, we demonstrate the formation of assemblies with cationic MOPs, that were obtained either in a colloidal state or as precipitated powder, depending on the initial MOP-to-protein ratio. Assemblies were obtained by simple mixing of BSA and MOP aqueous solutions, without additive nor chemical modification required. The method was then transposed to Catalase, that has also a pI below 7. In this case, immobilization resulted in a significant maintenance of catalytic activity with a reduction by only one Log, on par with that of other MOF immobilization systems. Furthermore, the immobilization in a solid material enabled recyclability for the enzyme. Meanwhile, Cytochrome C, with a peroxidase activity and a pI above 7, we used anionic MOPs to prepare assemblies. In this case, the activity was not only maintained, but was even significantly improved for the immobilized enzyme, by a factor 44. This effect was attributed to interaction between Cytochrome C and the highly ionic network of MOPs surrounding it.

As such, MOPs offer a powerful and versatile way to immobilize proteins and notably catalytically active enzymes. The very mild assembly conditions, as well as MOP intrinsic porosity, contribute to the high activity of the enzymes after immobilization.

[1] Submitted