Catalytic activity of enzymes immobilized with ionic metal-organic cages

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Enzyme immobilization is a powerful strategy to harness their high catalytic activity and exquisite selectivity while allowing to work with a solid-state material that can easily be manipulated, increasing greatly stability and recyclability. We recently developed a new strategy for immobilization for proteins, relying on their charge-driven co-assembly with ionic metal-organic cages (MOCs).[1] This technique allows a very mild immobilization, at neutral pH and without chemical modification needed. Furthermore, the intrinsic porosity of the cages, acting as spacers, is expected to greatly help the mass transport within the MOC-enzyme composite. While the principles of immobilization are discussed in another presentation for the archetypal protein **BSA** (non-enzymatic), we discuss here the maintenance of a catalytic activity for enzymes when immobilized with MOCs.

We first consider the activity of bovine liver catalase (**Cat**), catalyzing the disproportionation of H_2O_2 into O_2 and H_2O. The composite formed spontaneously by mixing cages and **Cat**, and with a mass ratio of MOC to **Cat** of 20:80. **Cat** maintained a significant fraction activity of its activity when immobilized, with only a decrease by a factor 12 (Figure 1A). Furthermore, the composite could be recycled several times, with only minimal loss of catalytic activity.

In addition, we demonstrated the maintenance of catalytic activity for Horse heart cytochrome C (**CytC**), acting as a peroxidase. In this case, the MOC to **CytC** mass ratio in the composite was 24:75. Activity was evaluated by following the oxidation of ABTS by H_2O_2. Remarkably, the activity of **CytC** was not only maintained, but even increased by a factor 40 upon immobilization with MOCs (Figure 1B). A likely reason for this effect is the distortion of the active site of the enzyme when placed in a strongly ionic environment.

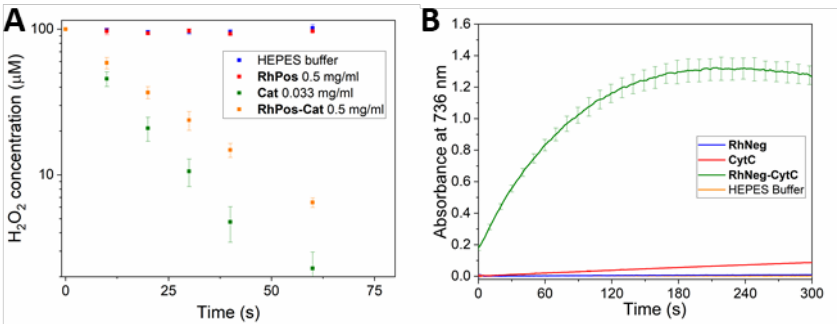

Figure 1. *Catalytic activity of **Cat** (A) and **CytC** (B).*

1) *Submitted*