Inside or outside the box? Confinement-driven and surface catalysis with coordination cages

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Coordination cages, consisting of a self-assembled combination of metal ions and ligands into a porous, three-dimensional arrangement are attractive candidates for catalysis applications.[1,2] Much as enzymes control reactivity through trapping the substrates in their cavities, coordination cages are able to include one or two guests and direct them through various supramolecular interactions towards reaction-ready configurations, while also lowering the activation energy of various reactions due to the confinement effect.

More recently though, surface catalysis has also been explored for these assemblies.[3] Even if to a lesser extent compared to the hollow cavity of a coordination cage, the cage exterior provides an anisotropic environment which is suitable for various chemical transformations.[4] Even more, the cage can be employed both as a platform and a “nanoreactor” when both cavity-bound and surface-bound guests are employed concomitantly.

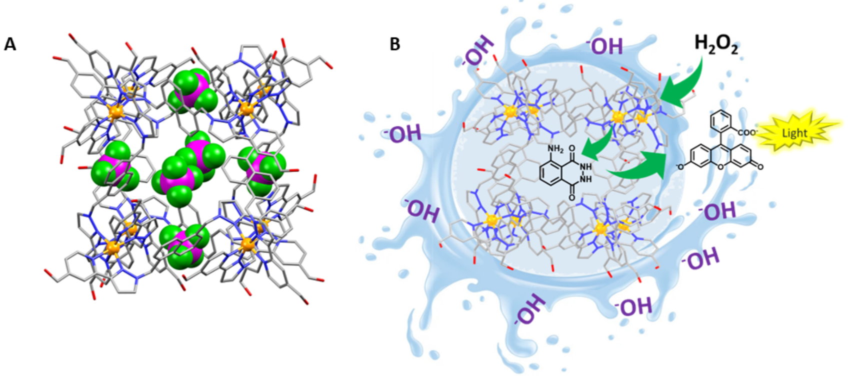

Figure 1. A. Molecular structure of the $[Co_8L_{12}](BF_4)_{16}$ cage determined by single-crystal X-ray diffraction (The H atoms were removed for clarity). B. Schematic representation of the oxidation of luminol and generation of chemiluminescence resonance energy transfer in the presence of the cage.

The high hydrophobic surface of the cage with the general formula $Co_8L_{12}^{16+}$, (where L is a pyrazole-pyridine-type ligand) (Figure 1A), as well as its high positive charge, allows it to act as a co-locator of both the fluorescein diacetate substrate and the hydroxide anions, promoting ester hydrolysis and formation of the fluorescein dianion, whose formation can be monitored by UV-Vis. We have found that the hydrophobic effect leads to a high association constant of 15000 (±2000) M^{-1}, while the rate of the reaction is accelerated 50 times compared to the uncatalyzed reaction.[4] Moreover, the Co^{2+} ions, in the presence of the surface bound hydroxide ions and reactive oxygen species catalyse the oxidation of cavity-bound luminol to generate chemiluminescence (Figure 1B). The cage acts as both a nanoreactor and as a platform for bringing all the components together so when an additional guest is bound to the surface, the cavity-bound luminol can transfer its excitation energy to the surface-bound fluorescein in the first example of Chemiluminescence Resonance Energy Transfer (CRET) involving coordination cages.[5]

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