Encapsulating hydrogenase active site analogues in peptide-based supramolecular hydrogels: a photochemical study

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Synthetic inorganic compounds inspired by the active site of the hydrogenase (H_2-ases) enzymes have attracted much scientific attention as a result of their ability to catalyse the reversible reduction of protons to form dihydrogen. It is anticipated that these systems will ultimately offer a more economic and renewable alternative to the platinum-based approach currently used in fuel cells. These bio-inspired compounds are however limited in terms of technological applications by oxygen sensitivity and a reduced catalytic rate in comparison to the native enzyme. In an effort to address some of these issues we have incorporated hydrogenase model compounds (e.g. Fig. 1(a)) into low molecular weight (LMW), peptide based, hydrogels that are able to modify both the chemical stability and photochemistry of the encapsulated molecule, offering potential new routes to exploitation of these systems.[1]

LMW hydrogelators, and in particular self-assembled oligopeptide-based gels, have shown great potential in encapsulating enzymes with retention or improvement of catalytic activity.[2] These materials are generally low-cost, biocompatible and highly tuneable. We have successfully incorporated a range of [FeFe]-H_2-ase active site mimics into Fmoc-dipeptide hydrogels containing only 1% gelator in aqueous environments (Fmoc = 9-fluorenylmethoxycarbonyl, Fig. 1(b)). Fourier transform infrared (FTIR) and UV_{pump}-IR_{probe} time-resolved infrared spectroscopy (TRIR, Fig. 1(c)) experiments have been carried out and both show results that differ with respect to data obtained in the solution phase. Both FTIR and TRIR experiments show results that are consistent with an immobile, but strong hydrogen bonding environment in the gel phase that restricts dynamic processes such as photo-induced isomerisation while maintaining the fast vibrational relaxation rates observed in solution,[3] confirming the gel's unique properties. In addition, the chemical stability of the encapsulated species was observed to be improved relative to solutions.

In summary, encapsulating hydrogenase active site mimics in LMW hydrogels induces significant changes in their photochemistry and chemical stability. Since understanding and ultimately controlling the mechanistic role of ligands near Fe centres is likely to be crucial in exploiting artificial hydrogenases, these gels may offer a new option for future materials design involving catalysts.

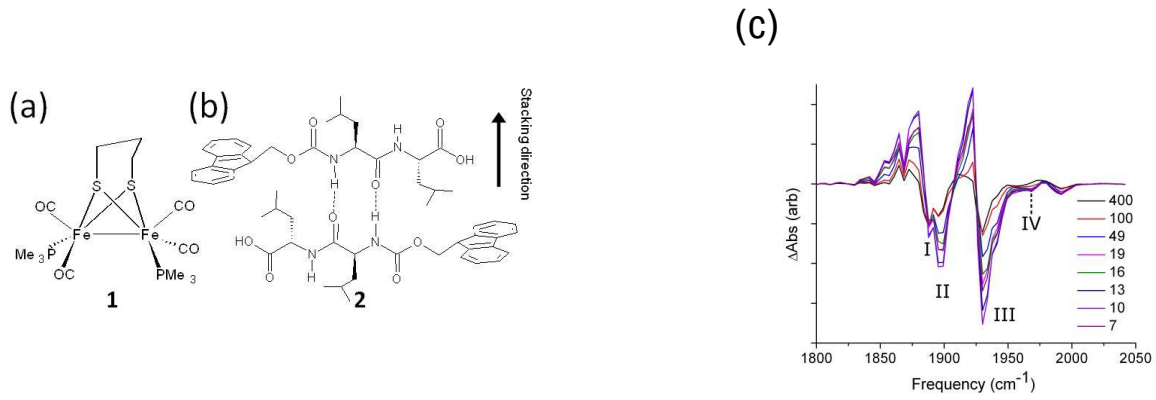

Fig. 1. (a) Chemical structure of one of the H_2-ase active site mimics studied. (b) Chemical structure and schematic diagram of the β-sheet-type stacking of the peptide-based gelator (Fmoc-Leu-Leu). (c) TRIR difference spectra of the hydrogenase-inspired model compound shown in (a) encapsulated in a peptide hydrogel (b). The data range shown corresponds to UV_{pump}-IR_{probe} time delays of 1-400 ps.

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