Exploring novel features of [FeFe]-hydrogenase models through non-biomimetic modifications and reactivity: a DFT viewpoint.

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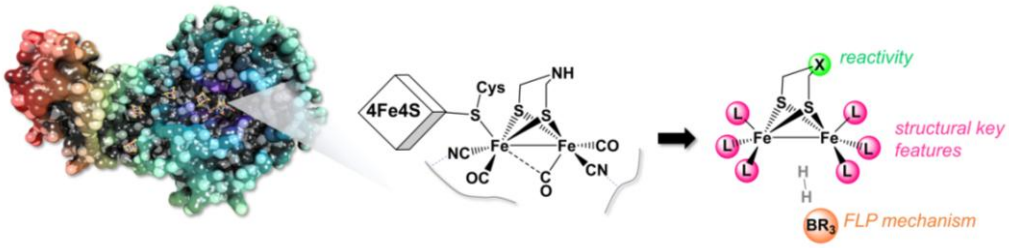
[FeFe]-hydrogenases are enzymes that catalyze the reversible formation of H_2 with surprising turnovers, being capable of producing up to 7500 molecules of H_2 per second.[1,2] This makes them particularly promising in the context of carbon-free energy storage/production, avoiding, at the same time, the costly and non-sustainable exploitation of rare metals. Their active site consists in a unique organometallic iron-sulfur cluster which has inspired the design and the synthesis of a plethora of diiron dithiolato biomimetic compounds.[3,4] Remarkably, this approach led to the development of active catalysts for H_2 production and oxidation that, however, do not reach yet the efficiency of the natural system. Thus, an alternative and promising strategy would be extending catalysts design by going beyond the structural and mechanistic paradigms provided by Nature. Here we present combined experimental-theoretical strategies to i) modulate *structural* key features through modification in the *first* Fe's coordination sphere, ii) modulate *reactive* features through modification in the *second* Fe's coordination sphere[5] and iii) unravel novel *mechanisms* by taking advantage of unnatural Frustrated Lewis Pair reactivity.



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