

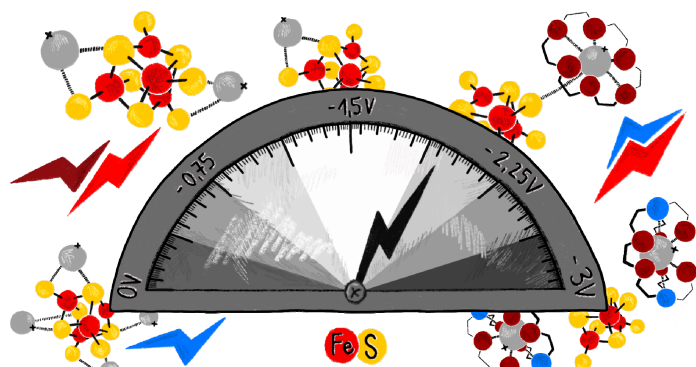
EXPLOITING EXTREMELY VARIABLE REDOX CHEMISTRY AT CUBANE-TYPE IRON-SULFUR CLUSTERS

Liam Grunwald,^a Mariko Inoue,^a Paula Cendoya Carril,^a Martin Clemancey,^b
Daniel Klose,^a Michael Wörle,^a Gunnar Jeschke,^a Genevieve Blondin^b
and Victor Mougel^{a,*}

^aDepartment of Chemistry and Applied Biosciences, ETH Zürich, CH-8093, Zürich.

^bUniversity of Grenoble Alpes, CNRS, CEA, IRIG, PMB, CEA Grenoble, F-38054, Grenoble Cedex

Cubane-type iron-sulfur clusters are some of Nature's most ancient and versatile cofactors [1]. However, seemingly simple, their main function is electron transfer. Recently, we demonstrated that the use of a bulky terphenyl thiolate ligand promoting the encapsulation of alkali-cations in the vicinity of the cubane allowed the syn-



thesis and study of a complete series of $\text{Fe}_4\text{S}_4(\text{SR})_4$ complexes, that covers all oxidation states accessible by one-electron transformations of the individual Fe-atoms ($[\text{Fe}_4\text{S}_4]^{4+}$ – $[\text{Fe}_4\text{S}_4]^0$) – formerly one of the major challenges in the field of bioinorganic chemistry [2,3]. The redox potential of these Fe_4S_4 complexes and Fe_4S_4 -containing enzymes alike is often conceived as a static parameter, which is incompatible with some of Nature's more elaborate electron transfer mechanisms, particularly conformationally gated ones [4,5]. Thus, we further developed and rationalized our strategy, leading us to present here the case of a synthetic $\text{Fe}_4\text{S}_4(\text{SR})_4$ model complex exhibiting dynamically modular redox potentials on-demand. Using extensive cyclic voltammetry studies and state-of-the-art spectroscopic techniques, we unravel the influence of cation-packing on the cluster's electrochemical properties, chemical stability and spectroscopic fingerprint. Most significantly, we demonstrate that alkali-ion- $[\text{Fe}_4\text{S}_4(\text{SR})_4]$ assemblies act as molecular storage units for electrical energy, that can be liberated by cation removal. This can be used to control the occurrence of a formerly “uphill” electron transfer and, thus, highlights the relevance of these complexes as functional chemical models for a unique class of Fe_4S_4 -containing ATPases, which have come to be known as “archerases” [4,5].

[1] H. Beinert, R. H. Holm, E. Münck, *Science* **277**, 653–659 (1997).

[2] S. C. Lee, W. Lo, R. H. Holm, *Chem. Rev.* **114**, 3579–3600 (2014).

[3] L. Grunwald, et al. *Proc. Natl. Acad. Sci. U. S. A.* **119**, 1–14 (2022).

[4] H. L. Rutledge, F. A. Tezcan, *Chem. Rev.* **120**, 5158–5193 (2020).

[5] S. H. Knauer, W. Buckel, H. Dobbek, *Biochemistry* **51**, 6609–6622 (2012).