

that heterochiral window pairing is a key stabilizing factor, the exploration of the energy landscapes of such organic reticular nets is particularly challenging due to the presence of solvent and multiple-tecton compositions.

By focusing on chiral recognition events between tectons of different shapes and connectivity, the team has uncovered a new way of accessing novel porous topologies and propagating them as isorecticular nets. Their work opens new avenues for controlling the packing of hierarchical and modular architectures while producing materials with potentially new functionalities. Organic tectons may be regarded as analogues of the secondary

building units found in zeolites and MOFs, and their assembly through non-covalent chiral recognition is a versatile approach towards the control of hierarchical porosity and the computationally guided conception of new solids. □

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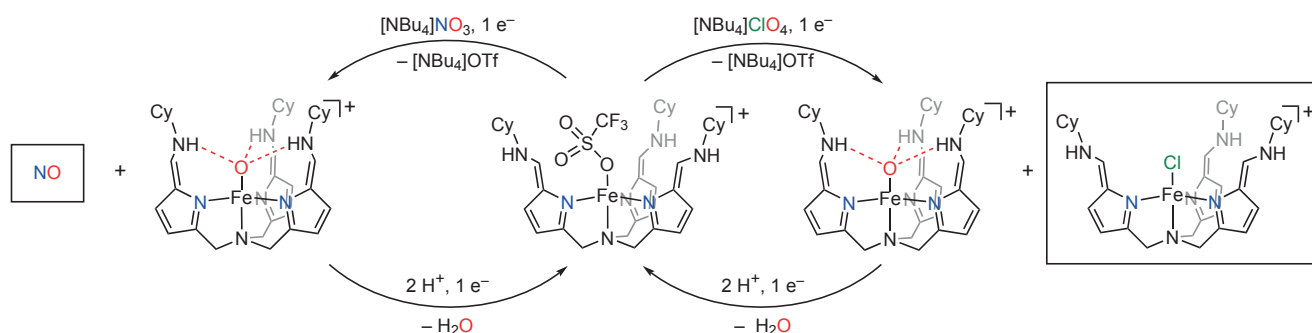
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#### References

1. Cheetham, A. K., Férey, G. & Loiseau, T. *Angew. Chem. Int. Ed.* **38**, 3268–3292 (1999).
2. Brunet, P., Simard, M. & Wuest, J. D. *J. Am. Chem. Soc.* **119**, 2737–2738 (1997).
3. Férey, G. *et al. Science* **309**, 2040–2042 (2005).
4. Banerjee, R. *et al. Science* **319**, 939–943 (2008).
5. Eddaoudi, M. *et al. Science* **295**, 469–472 (2002).
6. Tan, J. C., Bennett, T. D. & Cheetham, A. K. *Proc. Natl Acad. Sci. USA* **107**, 9938–9943 (2010).
7. Slater, A. G. *et al. Nat. Chem.* **9**, 17–25 (2017).
8. Dolbecq, A. *et al. J. Am. Chem. Soc.* **131**, 16078–16087 (2009).
9. Woodley, S. M. & Catlow, R. *Nat. Mater.* **7**, 937–946 (2008).
10. Mellot-Draznieks, C., Dutour, J. & Férey, G. *Angew. Chem. Int. Ed.* **43**, 6290–6296 (2004).
11. Wilmer, C.E. *et al. Nat. Chem.* **4**, 83–89 (2012)

## BIOINORGANIC CHEMISTRY

# Nitrate NO more



There are many examples of how nature breaks down small molecules effortlessly. However, such reactions pose a significant challenge to chemists and thus the enzymatic cleavage of strong bonds is a prominent source of inspiration for small-molecule chemistry. One class of reactions that has proven reluctant to translate into the flask is the reduction of oxyanions. In particular, nitrates ( $\text{NO}_3^-$ ) and perchlorates ( $\text{ClO}_4^-$ ) are difficult to reduce, demanding harsh reaction conditions to furnish NO and  $\text{Cl}^-$ , respectively. These oxyanions are water-supply pollutants that are critical — but problematic — to remove in a practical manner. Now, a team from the University of Illinois at Urbana-Champaign led by Alison Fout has demonstrated a bio-inspired approach to carrying out these reductions catalytically

(*Science* **354**, 741; 2016). Fout and co-workers looked to natural systems for inspiration, noting that their active sites featured redox-active heme centres surrounded by extended hydrogen-bonding networks that work in tandem to stabilize the high-valent iron-oxo intermediates. Previously, Fout and co-workers had synthesized azafulveneamine ( $\text{N(afa}^{\text{Cy}})_3$ ) iron complexes and observed structural and electronic characteristics similar to those of metalloenzyme active sites, wherein ligand tautomerization triggers the formation of the hydrogen bonds necessary to carry out multi-electron redox in a stoichiometric fashion.

Now, the group has found that the triflate salt of these complexes,  $\text{N(afa}^{\text{Cy}})_3\text{FeOTf}_2$ , is effective for transient coordination of nitrate and perchlorate to the metal, forming intermediates

that readily react to form the desired iron nitrosyl and chloride complexes. Comparison to the redox-inert zinc analogues showed that the secondary coordination sphere was not involved in coordinating the oxyanions. It was, however, required for reduction, playing a significant role in stabilizing the metal-oxo centre. The team then demonstrated catalytic reductions, resulting in 3.5 turnovers for nitrate and 3 turnovers for perchlorate — while low, even a few turnovers for such challenging reactions is impressive. Although there is work to come in developing a more practical reduction process, these results show that well-designed small-molecule catalysts can handle even the toughest of redox reactions.

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