

pancreatic ribonucleases retain Gly 38.

In a different study published last year⁴, an active ancestral molecule was deduced from a consensus sequence of F-type L1 retroposons that are dispersed in the mouse genome. These modern L1 sequences are transcriptionally and transcriptionally inactive, apparently because of the accumulation of mutations, but the recreated F-type monomer had transcriptional activity⁴. Although in most instances the consensus sequence is not a valid ancestral sequence (see figure), this approach appeared to work for L1. This is probably because the L1 sequences integrated into the mouse genome within the last few million years⁴, so their evolution-

ary history may be better represented by a starburst than by a strictly bifurcating tree.

To date, the cases where ancestral sequence reconstruction seems to have worked involve sequences that are fairly closely related. As sequences become available from a greater variety of species, we should be able to reconstruct ancestral molecules going further back in time: perhaps — in the future — to the very root of the 'tree of life'. □

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CATALYSIS

Electron transfer branches out

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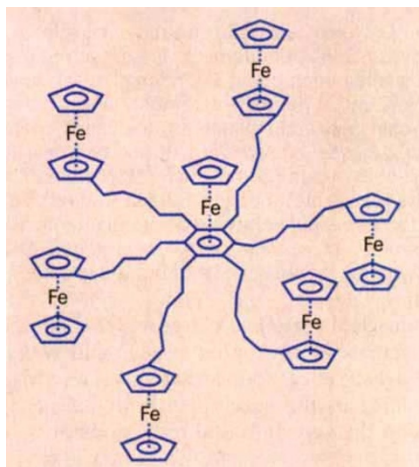
THE production of molecules that can act as multielectron catalysts is a challenge for organic chemists, but it is a goal that remains largely unrealized. Nevertheless, ingenious syntheses of new molecules¹⁻³ that show multielectron redox reactions could be bringing the goal closer.

In work published in December¹, Astruc and co-workers describe the synthesis of an interesting polynuclear iron-containing species which has six ferrocene units (FeCp₂, where Cp is cyclopentadiene) attached to the benzene (Bz) of a BzFeCp core (see figure). This 'molecular tree' can serve as an electron reservoir, where each FeCp₂ unit can be oxidized to FeCp₂⁺, to provide an overall six-electron (6e) reaction. Cyclic voltammetric measurements in *N,N*-dimethylformamide show that the individual FeCp₂ units out on the branches do not interact appreciably with one another or with the central core, and thus are oxidized at a potential near that of free FeCp₂ in a single 6e wave. The BzFeCp core, in contrast, is oxidized at fairly negative potentials and its 1e wave serves as a convenient internal standard. The authors suggest possible applications of this substance in multielectron redox (electron transfer) catalysis and molecular electronic devices.

This molecule is only one of many that show multielectron redox reactions — examples are linear polymers, supra-molecular species and dendrimers. The latter consist of large molecules with units linked to form star-shaped or hyper-branched patterns; Astruc and colleagues' molecule could be thought of as the core of such a dendrimer. Electroactive groups can be incorporated within or on the periphery of the molecule to provide multiple redox centres. Such molecules

differ structurally from the more familiar (and easier to synthesize) linear polymers and oligomers with pendant redox groups.

One such supermolecule is a decanuclear ruthenium polypyridine complex⁴ containing linked Ru(bpy)₃²⁺-like units (bpy is 2,2'-bipyridine). Molecules such as these are of interest because the photochemical and electrochemical processes of



Ru(bpy)₃²⁺ have potential applications in energy conversion and chemiluminescent analytical methods.

Very different dendrimeric molecules have been synthesized by Miller and co-workers². In these species, redox-active imide (A) groups were attached around the periphery of the molecule. Depending upon the size of the dendrimer it was possible to incorporate from 6 to 192 A groups per molecule and reduce these to the radical anions (A⁻). In these molecules, as opposed to the molecule of Astruc and co-workers¹, the cyclic voltammetry suggests interactions among the electroactive groups, ascribed by the authors to possible π -stacking of the radical

anions. Electrochemical investigations are useful in determining the extent of interactions between electroactive groups and whether a molecule with *n* identical electroactive centres undergoes electron transfer in a single *n*-electron wave, as is typical for linear polymers with pendant groups, or in closely spaced waves at different potentials⁵.

The real pay-off with such molecules will come with the synthesis of species that can act as multielectron catalysts for useful redox reactions. Such catalysts have long been sought for the efficient reduction of dioxygen to water or dinitrogen to ammonia under ambient conditions in ways that mimic biological reductions catalysed by enzymes. For example, an effective electrocatalyst for O₂ reduction that allows the reaction to occur at potentials near that of the O₂/H₂O couple would find application in fuel cells for the direct conversion of fuels to electricity. Present-day fuel cells use expensive platinum-based electrocatalysts for this function. Similarly, a good N₂ catalyst would be useful in the production of fertilizer under less extreme conditions than those that are currently employed.

But these reactions, and indeed most interesting multielectron reactions, are complicated. For example, reduction of O₂ to H₂O requires not only the addition of four electrons, but also addition of four protons and cleavage of the O–O bond. A catalyst for this process will require a more complex structure than the type of molecules described above; it will have to provide not only the needed four electrons, but also sites that bind O₂ and its reduction intermediates. Simple multielectron transfer catalysts do not work well. There has been some success with metal porphyrin-based materials as oxygen reduction catalysts — for example, last year's report³ of a Co porphyrin with three pendant Ru(NH₃)₅²⁺ groups that shows electrocatalytic behaviour for O₂ reduction — but not, as yet, anything to rival platinum.

In the real world, of course, the cost of such catalysts is an important factor. Many of the more exotic molecules, such as those discussed here, are difficult to synthesize and thus expensive. At present, indeed, they often cost more than the noble metal catalysts they hope to replace. □

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