

report the synthesis of a beautifully simple series of oligoferrocene macrocycles (**cyclo**[*n*], *n* = 5, 6, 7, 9, see Fig. 1a) via copper-mediated Ullmann coupling reactions of linear iodinated ferrocene precursors under high-dilution conditions⁹.

Each cyclopentadienyl (Cp) ligand is connected to that of a neighbouring ferrocene unit through direct Cp–Cp linkages. Investigation of the electrochemical properties of **cyclo**[5], **cyclo**[6] and **cyclo**[9] revealed that individual redox events corresponding to successive one-electron oxidations of ferrocene units could be assigned. For example, for **cyclo**[9] a series of six waves was observed within the electrochemical window of the solvent, corresponding to seven different stable redox states. The difference between the potentials of successive redox waves for each species provides a measure of the extent of interaction between the metal sites (which is related to the position of the comproportionation equilibrium between the mixed-valence state and the isovalent states).

The linear correlation between the Gibbs free energies of interaction (ΔG_{int}) and the number of electrons removed from the **cyclo**[*n*]^{*m*+} rings is indicative of delocalization of the positive charge between the ferrocene units. This suggests that, on the electrochemical timescale, delocalization of positive charge exists across the iron centres of the entire macrocycle. This is also reflected in the oxidation potentials: the larger the ring,

the more facile oxidation is to a given oxidation state, because the positive charge is accommodated by a larger number of ferrocene units. Albrecht, Long and colleagues conclude that the **cyclo**[*n*]^{*m*+} (*n* = 5, 6, 9) compounds may belong in the Robin–Day class II regime, as indicated by the nature of the intervalence charge-transfer bands in **cyclo**[6]⁺ and **cyclo**[6]²⁺ observed by UV-vis/near IR spectroscopy. Further determination of the rate of electron transfer between the metal centres on different timescales — by methods such as Mössbauer, electron spin resonance, IR and photoelectron spectroscopy — presents an interesting avenue for future investigation.

One of the ferrocene macrocycles, **cyclo**[6], which might be considered to be a kind of organometallic analogue of benzene, was also characterized crystallographically (Fig. 1b). Adjacent ferrocene units were found to be twisted with respect to one another in the solid-state structure, with both *anti* and *syn* conformations present (Fe...Cp–Cp...Fe angles of 164, 138 and 48°, respectively). Such torsion decreases the efficacy of electron transfer between the $d_{x^2-y^2}$ orbitals of neighbouring iron atoms via the antibonding π orbitals of the fulvalene ligand framework, which may suggest why cations of **cyclo**[6] exhibit a lesser degree of delocalization than that of the monocation of biferrocenylene (3), where torsion is negligible^{10,11}.

If the yields (currently <2%) of Albrecht and Long's **cyclo**[*n*] compounds can be improved, these macrocycles may have

fascinating and important applications in host–guest chemistry. Conformational flexibility (often common in larger rings) is expected in solution as a result of virtual free rotation about the Cp–Fe–Cp axis in each ferrocene unit¹², and the introduction of an anionic guest molecule to chemically oxidized **cyclo**[*n*]⁺ may lead to particularly interesting studies. In addition, the design and study of soluble high molar mass polymeric analogues of these oligomers with ferrocene (or other metallocene) repeat units is an extremely appealing prospect¹³. □

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DENSITY FUNCTIONAL THEORY

Fixing Jacob's ladder

Density functional theory calculations can be carried out with different levels of accuracy, forming a hierarchy that is often represented by the rungs of a ladder. Now a new method has been developed that significantly improves the accuracy of the 'third rung' when calculating the properties of diversely bonded systems.

Roberto Car

Density functional theory (DFT) is the method of choice for calculating the electronic structure of molecules and materials in applications involving large systems and/or extensive sampling of geometries. It comes in several 'flavours', each relying on various approximations, which means that although DFT methods can typically describe bonds of a similar kind reasonably well, they have difficulties dealing with diversely bonded systems. Now, writing in *Nature Chemistry*, Jianwei Sun

and co-workers have made a major contribution to overcome this limitation by devising a new functional and creating a new flavour of DFT that is computationally efficient and works equally well for covalent and metallic bonds as it does for ionic, hydrogen and even intermediate-range van der Waals bonding¹.

The electronic ground-state energy, and how it changes with nuclear positions, determines the geometries of molecules and materials as well as the relative stability

of isomers, different phases of matter, and chemical reactants and products. Knowing the quantum-mechanical energy of the electrons requires knowledge of the wavefunction, and the computational cost of calculating it grows exponentially with the number of electrons (*N*) in the system. Walter Kohn, the father of DFT, likened the computational cost of calculating the wavefunction to an 'exponential wall' of quantum mechanics in his 1998 Nobel Prize address²: it means that accurate

calculations rapidly become impractical as molecular size increases. DFT is an alternative way to determine electronic structure in which the basic variable is not the wavefunction but instead it is the electron density, a much simpler quantity that can, in principle, be calculated exactly. Its use eliminates the exponential wall, however the devil is in the 'in principle' qualification because the intricacy of the interacting quantum state of the electrons has been transferred from the wavefunction to a term within the functional form known as the 'exchange-correlation' energy. Unfortunately, we do not know how to calculate the exchange-correlation energy exactly, and therefore it must be approximated. Finding good functional approximations is a difficult 'art' and a major goal of DFT research.

The simplest approximation for the exchange-correlation energy used in DFT is the 'local density approximation' (LDA), which approximates the exchange-correlation energy density at a given position as a function of the electron density at that same local position. At the next level of sophistication comes the 'generalized gradient approximation' (GGA), for which the energy density approximation also depends on the gradient of the density at that given position. A level above this is 'meta-GGA', for which the energy density depends also on the local kinetic energy density of the calculated Kohn–Sham orbitals. The LDA, the GGA and the meta-GGA scale with N^3 , which is the same as Hartree theory, which crudely approximates the wavefunction. Higher-order approximations such as hybrid functionals further improve the accuracy, but at the price of non-locality in the density dependence and higher computational cost.

Although the bonding description in GGA improves substantially over LDA, earlier parameterizations of meta-GGA have been met with mixed success. Now, Sun and co-workers introduce a new parameterization that makes meta-GGA systematically superior to GGA and equivalent to (or sometimes even better than) hybrid functionals. The new parameterization can recognize metallic bonds, covalent single bonds and even intermediate-range van der Waals bonds arising in the presence of a small overlap between density distributions. The new exchange-correlation functional satisfies all of the 17 known exact constraints appropriate to a semilocal functional¹, a condition that is impossible to meet within GGA. Using exact results as much as possible in the construction of a



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Figure 1 | The hierarchy of DFT approximations represented by Jacob's ladder. The development of the SCAN functional by Sun and co-workers means that the meta-GGA rung has moved up almost to the same level as the rung associated with hybrid functionals.

functional is the trademark philosophy of one of the senior researchers responsible for these advances: John Perdew. He and his many collaborators have been using this approach for over 30 years. It avoids empirical fitting and guarantees good transferability. The new functional called SCAN (strongly constrained and appropriately normed), dramatically improves the description of the electronic structure of broadly diverse systems such as: van der Waals and hydrogen-bonded systems; covalent and metallic structures; and ionic bonded ferroelectric and multiferroic materials.

Sun and co-workers provide a few examples to illustrate the performance of SCAN. When using GGA, water hexamer clusters do not have the correct energy ordering: open structures are more stable than compact ones. Hybrid functionals that are able to handle van der Waals interactions correct the trend but still miss the relative stability of prism and cage structures. SCAN is instead surprisingly good with relative energies and they are amazingly close to those of accurate but expensive quantum chemistry methods. Structural phase transitions in the presence of a metal–insulator transition provide another example. Using LDA and GGA, the high-pressure metallic phase of crystalline silicon has a calculated energy that is too close to that of the low-pressure covalent diamond-like phase. This leads to an underestimation of the transition pressure. SCAN corrects this error. Also, ferroelectric and multiferroic materials derive their unusual properties from a

combination of ionic and covalent bonding that is challenging to model within LDA or GGA. Again SCAN works well in this situation and is almost as good as a hybrid functional that was especially designed for this class of materials.

However, some limitations remain, for example SCAN does not include long-range van der Waals interactions. These may be negligible in small clusters but are important in bulk water phases. Adding these effects would be relatively straightforward following one of the approaches available in the GGA context. The addition of long-range van der Waals interactions, although more physically representative, would increase the binding energy and could in fact worsen the almost perfect agreement with experiment of the ice structures that Sun and co-workers describe (in Fig. 1a of their Article). A more serious difficulty affecting all semilocal functionals, and not just SCAN, is the self-interaction error, which arises from spurious interactions between electrons. The error is larger for more localized electrons, leading to an artificial enhancement of covalency. This effect also leads to an overestimate in the strength of hydrogen bonds in liquid water and may lead to underestimates in chemical reaction barriers; therefore SCAN is not expected to do better than GGA in this respect.

How to eliminate the self-interaction error is an open problem. A popular image to illustrate the hierarchy of DFT approximations is that of Jacob's ladder connecting the earth to heaven (Fig. 1). Successive rungs correspond to better approximations that bring us closer to the 'heaven' of chemical accuracy. The first three rungs are, respectively, LDA, GGA, and meta-GGA. With the advent of SCAN the meta-GGA rung moved up almost to the same level as the fourth rung associated with hybrid functionals. These functionals have been devised to partially correct the self-interaction error³ and hybridization of the SCAN functional could be a possible way of achieving this goal. Thus, the development of SCAN is not only important in itself and for its applications, but also because it can lead to a significant retooling of Jacob's ladder. □

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