

Guest Editorial

“Seek, and ye shall find” (Matthew 7:7)

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The preparation and characterisation of organic molecular magnets is a non-trivial task which touches on many contemporary issues within chemistry. As a number of authors have alluded to in their articles within this Special Issue, the design of organic ferromagnets merely requires ‘a stable organic radical with a three-dimensional network of ferromagnetic interactions’. This simple statement belies substantial synthetic problems.

Free radicals are often considered to be extremely reactive and may exhibit limited tolerance towards oxygen and/or water. Despite their sensitivity, a number of families of stable organic radicals have been identified which have proved to be suitable building blocks in the design of molecular materials. The majority are based on π -delocalised functional groups containing group 15/16 elements such as N/O/S. Here the electronegative nature of these elements, coupled with π -delocalisation produces a lowering of the orbital energy, i.e. some thermodynamic stabilisation. In addition there is often some steric protection of the radical centre in order to enhance stability. Amongst the more fashionable free radicals used in the design of magnetic materials are the persistent nitroxide and nitronyl nitroxide radicals, as well as verdazyl and thiazyl radicals. Yet the formation of a stable radical itself does not infer any form of magnetically ordered phase. Organic radicals are normally considered as Heisenberg-like spins (i.e. little anisotropy) and, as a consequence, a three-dimensional network of magnetic interactions is required if the material is to undergo bulk magnetic order [1]. In order to achieve a bulk ferromagnet the dominant exchange interaction in all three dimensions must be ferromagnetic. The nature of the intermolecular interaction is not well understood and is still a matter of some debate; A number of theories were put forward in the 1960’s, of which those proposed by McConnell have received greatest attention [2]. Recently, however, the McConnell I mechanism has proved inadequate to describe the magnetic behaviour of the most common group of organic radicals,

the nitronyl nitroxides [3]. Indeed the total exchange interaction between radicals depends on a number of contributions (direct exchange, superexchange, double exchange, dipolar interactions etc.) [4]. Each of these interactions has its own dependency upon the intermolecular separation and geometry, as well as the spin-density distribution on individual molecules. The intentional design of an organic ferromagnet therefore implicitly requires the complete three-dimensional control of the solid state structure. Whilst the control of solid state structure through the use of robust intermolecular interactions (crystal engineering) has been extremely popular in recent years, only the fool-hardy would believe that they can reliably predict the structures of their compounds in three dimensions. Indeed a series of blind tests held by the CCDC indicated mixed performances in the ability of current software to reliably predict crystal structures of molecular compounds [5]. This is further inhibited by the propensity of polymorphism (crystallisation in more than one form) in many molecular species [6].

Given the limited structural control currently available, we might consider the synthesis of an organic ferromagnet to be entirely fortuitous. Yet we should not let this preclude the pleasure of the search. Even if we do not find our own Holy Grail, we might find something of interest along the way; 'Beauty is', as they say, 'in the eye of the beholder'. For example chemists have also become increasingly aware that they can often provide model compounds to test fundamental theories in physics e.g. in low dimensional magnetic behaviour e.g. Kagome lattices [7] and spin ladders [8]. In addition, chemists may design materials in which the physical properties can be tailored at the molecular level. This opens up the possibility of generating new 'smart' or 'multifunctional' materials in which the magnetic behaviour can be incorporated with another desirable property. These two properties may be either dependent or independent of one another, leading to materials whose physical properties can be tuned by the application of an external stimulus such as heat, light or pressure.

The articles in this Special Issue reflect basic design strategies for the generation of stable radicals (including charge-transfer salts, fullerenes and novel thiazyl radicals) and magnetic studies on more well-established radicals such as nitronyl nitroxide and thiazyl radicals. The importance of theoretical calculations to model exchange interactions in organic systems and their extensions to polynuclear transition metal clusters are also described. These studies coupled with the move towards novel multifunctional materials illustrate the vibrant and diverse nature of organic molecular magnetism. Whilst the construction of complex solid state architectures is still some way off, we should not forget to marvel at the simple towers, pyramids and other basic structures which we may make along the way.

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