Development of functionalized molecule-based magnetic materials

Abstract: The main purpose of our integrated project was to explore new frontiers of molecular magnetism as well as to further improve our insight into molecule-based magnetic materials. We continued our synergetic strategy to combine the expertise brought into the group by scientists from three continents and a broad range of scientific fields as for example chemical synthesis, theoretical modeling and experimental investigation and manipulation.

Magnetocalorics aims at the development of new refrigerant materials based on magnetic molecules for sub-Kelvin refrigeration. In this very active field we could achieve a large number of impressive results. We obtained the largest magnetocaloric effect (MCE) reported so far for liquid-helium temperatures [A1] and designed one the very first examples of 3D molecule-based magnetic coolers containing Gd(III) [A2]. We investigated the role of the relative magnetic density in the MCE; this article was featured on the back cover of the Journal issue and selected as "VIP" paper [A3]. Other examples include lanthanide-free and cobalt-containing magnetic molecular refrigerants [A4-A13]. Extremely local coolers, i.e. cooling on the molecular level, could be designed by means of isolated molecules on surfaces [A14].

Quantum computing needs as an indispensible prerequisite long coherence times of the manipulated quantum states. Our investigations therefore focused on the synthesis and experimental investigation of promising new molecular magnetic qubits. By varying systematically each structural component of the molecular nanomagnet Cr7Ni, we identified and minimised the mechanisms of decoherence of the electron spin, thereby achieving a phase memory time exceeding 15µs at low temperatures [B1]. In order to couple several qubit-units chemical control of spin propagation between heterometallic rings was investigated [B2]. In a broader sense this addresses the issue of control of spin entanglement at the supramolecular level [B3-B5]. Phonons are one of the sources of decoherence; we investigated by means of NMR the decay of the time correlation function of molecular observables [B6]. From the theory point of view investigations of the time evolution are rather involved; some classical simulations are published in [B7].

Single molecule magnets (SMM) which exhibit bistability and hysteretic behavior are candidates for next-generation storage devices. Within the project we follow routes of rational design of e.g. C3-symmetric molecular magnets in order to prevent losses through quantum tunneling and thus increase bistability [C1-C4].

New magnetic molecules have been synthesized, among them redox controlled magnetic {Mn_{13}} Keggin systems (cover and "VIP") as well as a cyanide-bridged [CoFe] chain with three-way switching properties [D1-D17]. We could also demonstrate the first use of a flow system for the discovery of new cluster compounds and for the scale up of other cages previously only available in very small yields [D18]. Some of the large variety of theoretical modeling procedures are described in a chapter [D19] of a book on molecular magnetism which was edited by R.E.P. Winpenny.

New experimental tools such as four dimensional inelastic neutron scattering open new gateways to a better understanding of magnetic correlations [E1,E2]. Figure 1 shows the high intensity resolution that can be achieved in three dimensional Q-space[E1]. Together with modern EPR techniques [E3] such methods deliver a much more accurate picture of the internal magnetic structure than gross measurements such as magnetic susceptibility.

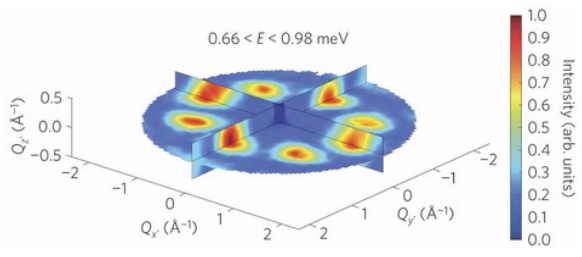

Fig. 1: Constant-energy plots of the neutron scattering intensity for a Cr8 ring [E1].

Deposition of magnetic molecules on surfaces is a new scientific goal in order to being able to address single molecules by means of e.g. tunneling microscopy. Since many interesting molecules are fragile, and the details of the interactions with the surface are a priori unknown we first aimed at the control of self assembling of molecular rings on surfaces [F1-F4].

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