A look at molecular nanosized magnets from the aspect of inter-molecular interactions

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Nanosized molecular magnetic materials such as single-molecule magnets and single-chain magnets are recent attractive research targets in the fields of materials chemistry and physics, not only because of their fundamental fascination, but also because of their potential applications as ultimate memory devices or in quantum computations. In this paper, we give our personal perspectives on these materials. In particular "*magnetic assemblies of single-molecule magnets*", in which inter-molecular interaction is an essential factor in determining their properties, will be focused on together with related compounds reported recently.

Introduction

In the early 1990s, polynuclear discrete clusters exhibiting slow relaxation of molecule-derived magnetization were discovered and have since been called single-molecule magnets (SMMs).[1–3] Today, more than one hundred SMMs are known. A SMM is a superparamagnet known as a single-domain nano-particle.[4]

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Nevertheless, its size-defined feature tailored by a bottom-up design allows us to evaluate quantitatively the origin of slow dynamics[1,2,3] and quantum phenomena.[5,6] The slow relaxation of the magnetization is due to uniaxial anisotropy of the molecule, which enables the direction of the molecular magnetization to be fixed, similar to the dipole of N (*i.e.*, spin up) and S (*i.e.*, spin down) in classical permanent magnets at low temperatures in which the thermal activation for spin reversal is suppressed. Thus, the relaxation time (τ) obeys the thermally activated Arrhenius relation as:

$$\tau(T) = \tau_0 \exp\left(\frac{\Delta}{k_B T}\right) \qquad (1)$$

As the uniaxial anisotropy is referred to as the zero-field splitting parameter (D) of a given molecule with a spin ground state (S_T), the energy barrier for the magnetization reversal, Δ, can be simply described as $|D|S_T^2$ for integer S_T and $|D|(S_T^2 - 1/4)$ for half-integer S_T.[2,3] Thus, the properties of SMMs are determined by the intrinsic nature of the individual molecules. In this regard, we speculate that the inter-SMM interactions are exclusively responsible for the intrinsic properties of SMMs, and their long-range correlations produce magnetic domains seen in classical bulk magnets or spin glass-like materials. However, recent energetic research on various kinds of SMM materials and their related compounds has shown that the inter-SMM interactions act to modulate the intrinsic properties of SMMs (*e.g.*, quantum tunneling magnetization) and to create new magnetic systems including other nanosized magnetic materials even in such correlated systems as single-chain magnets (SCMs). At the same time, the tuning of inter-molecular (SMM) interactions demonstrates the possibility of switching from an original nanosized magnetic system to a correlated system, for example, from SMM to SCM or from such nanosized magnets to a bulk magnet and *vice versa*. Inter-molecular interaction has been generally treated as a nuisance, but today, it has established itself as an important functional tool, tunable at will, in the design of nanosized magnetic materials and their dimensionally-expanded compounds.

Inter-SMM interactions tune intrinsic properties of SMMs

Despite the lack of correlation in a 3D molecular arrangement, the inter-SMM interaction, albeit very weak, can perturb the intrinsic properties of individual SMMs, pointing to the possibility of tuning SMM properties through the inter-SMM interaction.[7,8] This intriguing peculiarity was theoretically and experimentally revealed by Wernsdorfer *et al.* in a sample of dimerized Mn$_4$ SMMs with the individual $S_T = 9/2$ ground state, $[\mathrm{Mn^{III}}_3\mathrm{Mn^{IV}O_3Cl_4(O_2CEt)_3(py)_3}]_2$ (py = pyridine), weakly interacting through hydrogen bonds and Cl$\cdots$Cl contacts (Fig. 1).[9] In general, SMM displays quantum tunneling of magnetization (QTM) between its quantized energy sublevels ($M = -S_T, -S_T + 1, -S_T + 2, \cdots, S_T$) which is clearly visualized in the field dependence of the magnetization as a staircase structure with a QTM-observable field of H_z given by $H_z \approx n|D|/g\mu_B$ (n = 0, 1, 2, 3, $\cdots$), where g is the electronic g-factor and μ_B is Bohr magneton.[10] Looking at this equation, QTM between the ground states should occur at static zero field (n = 0), but $[\mathrm{Mn^{III}}_3\mathrm{Mn^{IV}O_3Cl_4(O_2CEt)_3(py)_3}]_2$ does not reveal it. Why? This is due to the effect of inter-SMM interaction in the dimerized molecules. At this time, the quantized energy sublevels of the respective molecules interact coherently to produce superposition states.[11] When the influence of the exchange interaction is taken into account, the QTM-observable field is given by:

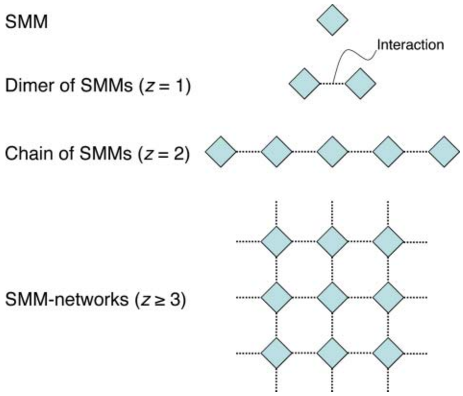

Fig. 1 Schematic representations of SMM assemblies in which individual SMMs interact mutually. The z value is the approximate number of neighboring interacting molecules in a mean-field consideration. The magnetic system varies depending on whether a correlation is made or not (see text).

$$H_z \approx \frac{n|D|}{g\mu_B} \pm \frac{2|J|}{g\mu_B} S_T \qquad (2)$$

where the Hamiltonian is $H = -2JS_{T1}{\cdot}S_{T2}$, and $2|J|S_T/g\mu_B$ means the exchange-bias field, H_{bias}, which allows the QTM-observable field for QTM between the ground states to shift from zero field. For example, the QTM from (M_1, M_2) = (−9/2, −9/2) to (−9/2, 9/2) was observed at −0.33 T shifted from the zero field, deriving $J/k_B \approx -0.04$ K.[5] Note that this applies also to cases exhibiting mean-field interactions (Fig. 1). In such cases, H_{bias} is described by:[12]

$$H_{bias} \approx \frac{2z|J|S_T}{g\mu_B} \qquad (3)$$

where z is the number of neighboring molecules interacting with a given molecule. Thus, even very weak inter-SMM interactions are able to exert a significant influence on the quantum properties of the original SMM, and allow highly refined tuning of QTM in the SMMs by controlling i) the strength of the interaction (the degree of lack of correlation) and ii) the number of molecules interacting with a given molecule (z).

Importantly, the aforementioned story is limited to the case in which materials are characterized as SMMs and not correlated systems. The correlation among SMM molecules would not only create new materials but also offer us an experimentally unexplored field to confirm and expand existing theoretical models. The creatable materials are strongly dependent on the dimensionality of the correlation; personally, we find low-dimensional correlated systems quite interesting. Before we discuss 1D systems, we look at the cases of 2D and 3D correlation among SMMs.

From SMMs to classical magnets

The 3D correlation among SMM molecules results in a long-range ordered classical antiferromagnet or ferromagnet, and their spin glass-like forms. One example of conversion between

SMM and antiferromagnet is achieved by crystal packing of molecules and has been seen in a set of Mn^{III} salen-type out-of-plane dimeric compounds, $[Mn^{III}_2(saltmen)_2(H_2O)_2](ClO_4)_2$[13] and $[Mn^{III}_2(saltmen)_2(ReO_4)_2]$[14] (saltmen^{2-} = N,N'-(1,1,2,2-tetramethylethylene)bis(salicylideneiminate)). Although both compounds possess an $S_T = 4$ ground state and a large negative D value, the former is an antiferromagnet due to 3D antiferromagnetic correlation among the molecules ($zJ/k_B \approx -0.8$ K),[13] whereas the latter is an SMM with negligible inter-molecular interactions ($|zJ/k_B| < 0.1$ K).[14]

One of the advantages in the design of classical ferromagnets using SMM building blocks is that anisotropy able to hold the direction of magnetization can be tuned to create a hard magnet with a relatively large coercivity. This might be somewhat advantageous for currently desired applications. However, 3D magnets designed using SMM building blocks are still a rarity[15] and only one that has been rationally designed is known so far: $[Mn^{II}_2Mn^{III}_2(hmp)_4(OH)_2Mn^{II}(dcn)_6]\cdot 2MeCN\cdot 2THF$ (Hhmp = hydroxymethylpyridine; Hdcn = dicyanamine).[16] The double-cuboidal $[Mn^{II}_2Mn^{III}_2(hmp)_4(OH)_2]^{4+}$ SMM building blocks with $S_T = 9$ acting as a hexadentate coordination acceptor are connected with $[Mn^{II}(dcn)_6]^{4-}$ to form a 3D network (Fig. 2). The exchange interaction between the Mn_4 SMM building block and the isolated Mn^{II} ion *via* the dcn linker is very weakly antiferromagnetic with $J/k_B \approx -0.037$ K. Nevertheless, this material exhibits 3D long-range order at $T_c = 4.1$ K (ferrimagnet). Unfortunately, the coercive field is very small ($H_c = 28$ Oe at 1.9 K) despite use of the SMM building block. Nevertheless, this result shows that even with such a very small interaction, it is possible to yield long-range order in an SMM network.

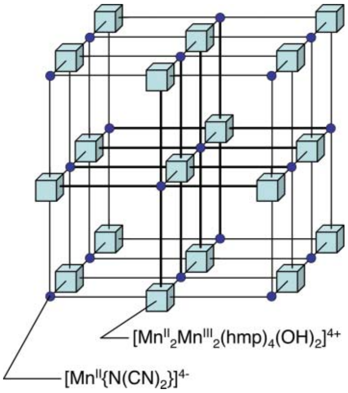

Fig. 2 Schematic representation of the 3D network of $[Mn^{II}_2Mn^{III}_2(hmp)_4(OH)_2Mn^{II}(dcn)_6]\cdot 2MeCN\cdot 2THF$ (Hhmp = hydroxymethylpyridine; Hdcn = dicyanamine).[16]

The dicyanamide anion in the $\mu_{1,5}$-bridging mode yields a weak superexchange owing to the presence of conjugating/resonance π-orbitals, but is liable to localize on the terminal N atoms of the five-atom N–C–N–C–N linkage. Thus, most chemists may think that it is not a very good candidate for a magnetic mediator producing a strong long-range correlation because of the need for long-distance superexchange. However, the high-dimensional dicyanamide bridge has made possible the production of classical magnets assembling with several transition metal ions,[17] as well as the above 3D SMM compound. The magnetic properties of SMM assemblies directly connected by dicyanamide anions have been investigated in three 2D network compounds of double-cuboidal $Mn^{II}_2Mn^{III}_2$ SMMs similar to those used in the above 3D compound.[18] Common to the three compounds is the fact that the Mn_4 SMM building blocks act as tetradentate coordination acceptors, forming a 2D quasi-square-lattice network with formula $[Mn_4](dcn)_2$ (Fig. 3). However, their magnetic properties are completely different from each other: The first compound exhibits SMM behavior despite its 2D bridging network; the second one reveals two relaxation modes, each of which includes SMM, and short-range order relaxations separated at a crossover point at 2.18 K; and the third one experiences long-range order at 4.6 K (a canted antiferromagnet). Why is it that these compounds exhibit different behaviors despite having a similar dcn-bridged network? The difference in magnitude of antiferromagnetic exchange *via* the dcn linker is not the main reason; rather, the arranged angle (θ) made by the two kinds of Mn_4 SMM orientations in the 2D network is closely associated with their correlation (Fig. 3). The arranged angle θ was estimated to be approximately 80°, 63°, and 18°, respectively, from their structures (for the third compound, the angle of 11° was approximately estimated from the magnetization).[18] In the Ising limit at 0 K, the H_c field at which the applied field overcomes the mean-field effect, *i.e.*, the antiferromagnetic interactions among Mn_4 SMMs, can be expressed as:[18]

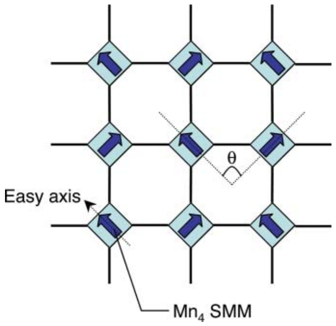

Fig. 3 Schematic representation of a 2D network constructed with formula $[Mn_4](dcn)_2$, where $[Mn_4]^{2-}$ is double-cuboidal $Mn^{II}_2Mn^{III}_2$ SMM and dcn$^-$ is the dicyanamide anion. The two kinds of orientation of the Mn_4 SMM unit yield an angle variation (θ) between the two easy axes.

$$H_c = \frac{2\,|zJ|\,S_T}{g\mu_B}\,\frac{\cos(\theta)}{\cos(\theta/2)} \qquad (4)$$

In fact, H_c was observed at 3800 Oe and 8200 Oe for the second and third compounds, respectively, and eqn (4) leads approximately to $zJ/k_B \approx -0.05$ K and -0.06 K, respectively. The theoretical critical temperature in a zero field for a 2D square-lattice Ising model[19] can be calculated from:

$$T_c = 0.56730 \times \frac{2\,|zJ|\,S_T^2\cos(\theta)}{k_B} \qquad (5)$$

The introduction of experimentally obtained values into eqn (5) finally leads to $T_c = 2.1$ K and 5.4 K, respectively. These values are in good agreement with the experimental values. Thus, the correlation behavior on the SMM networks is indirectly associated with "the anisotropic nature of SMMs", and use of high-spin SMMs as building blocks with zJ of only several Kelvin shows promise in creating high T_c magnets even in 2D networks.

From SMMs to SCMs

More than a decade after the discovery of SMM, a magnetically isolated chain system exhibiting SMM-like magnetization relaxation was reported by Gatteschi and co-workers.[20] The unique compound is a ferrimagnetic chain composed of an alternating arrangement of [Co$^{\rm II}$(hfac)$_2$] possessing an effective $S_{\rm eff} = 1/2$ Ising-type spin[21] and a nitronylnitroxide radical having an $S_{\rm rad} = 1/2$ isotropic spin (hfac = hexafluoroacetylacetonato), and the observed magnetization relaxation is interpreted based on Glauber dynamics theoretically proposed in 1963, which predicts spin dynamical behavior on an Ising chain.[22,23] In Glauber dynamics, the relaxation time ($\tau_{\rm Ising}$) for the Ising spin ($S_{\rm Ising}$) is represented by the following Arrhenius notation (as $H = -2JS^2_{\rm Ising}\sum_i \sigma_i{\cdot}\sigma_{i+1}(\sigma_{\rm i} = \pm 1)$):

$$\tau_{\rm Ising} = \tau_{\rm i}\exp\left(\frac{8JS^2_{\rm Ising}}{k_{\rm B}T}\right) \qquad (6)$$

where $\tau_{\rm i}$ is a pre-exponential factor introduced phenomenologically to describe the intrinsic reversal dynamics of each Ising spin and $8JS_{\rm Ising}{}^2$ corresponds to an energy barrier (Δ) for the Ising spin reversal. Importantly, Glauber dynamics for the Ising chain is simply represented as a function of the inter-Ising spin exchange coupling J. Note that Gatteschi's compound obeyed a finite chain form of this relation, in which $8JS_{\rm Ising}{}^2$ is changed to $4JS_{\rm Ising}{}^2$ (*vide infra*).[24]

One year after Gatteschi's report, the first ferromagnetic-type chain was reported by us and the research group of Clérac.[25] This compound, [Mn$^{\rm III}_2$(saltmen)$_2$Ni$^{\rm II}$(pao)$_2$(py)$_2$](ClO$_4$)$_2$ (pao$^-$ = pyridine-2-aldoximate), exhibits similar slow relaxation of the magnetization and is named as a single-chain magnet for a class of compounds exhibiting similar behavior.[25] Our compound is a Mn$^{\rm III}_2$Ni$^{\rm II}$ heterometallic chain with a [–Mn$^{\rm III}$–ON–Ni$^{\rm II}$–NO–Mn$^{\rm III}$–(O$_{\rm Ph}$)$_2$–] repeat unit, where Mn$^{\rm III}$–(O$_{\rm Ph}$)$_2$–Mn$^{\rm III}$ is an out-of-plane [Mn$^{\rm III}_2$(saltmen)$_2$]$^{2+}$ dimeric moiety with a bi-phenolate bridge and ON–Ni$^{\rm II}$–NO is a Ni$^{\rm II}$ oximate unit acting as a linear-type linkage. Due to strong antiferromagnetic coupling between Mn$^{\rm III}$ and Ni$^{\rm II}$ ions *via* the –ON– bridge ($J_{\rm Mn\text{-}Ni}/k_{\rm B} \approx -20$ K), the trinuclear unit of [Mn$^{\rm III}$–ON–Ni$^{\rm II}$–NO–Mn$^{\rm III}$] is assumed to be an $S = 3$ unit, and weak ferromagnetic interaction between the units *via* the –(O$_{\rm Ph}$)$_2$– bridge ($J_{\rm trimer}/k_{\rm B} \approx +0.7$ K) produces an $S = 3$ ferromagnetic chain at temperatures less than 10 K. One feature essential to its being an SCM is the existence of uniaxial anisotropy in the unit, wishing ultimately to be an Ising unit. Indeed, the trinuclear [Mn$^{\rm III}$–ON–Ni$^{\rm II}$–NO–Mn$^{\rm III}$] unit has strong uniaxial anisotropy with $D/k_{\rm B} \approx -2.5$ K, in which the easy axis of magnetization is directed to the Mn–Ni–Mn axis, namely, it corresponds to the chain axis.[26] This chain aspect, *i.e.*, the anisotropic $S = 3$ regular chain, was also confirmed by high-field and high-frequency EPR measurements.[27]

With the requirement of the Ising limit, $|D/J| > 4/3$, the relaxation time for a SCM ($\tau_{\rm SCM}$) made from effective uniaxial anisotropic spins ($S > 1$) is expressed as:

$$\tau_{\rm SCM1} = \tau_0 \exp\left(\frac{8JS^2 + |D|\,S^2}{k_{\rm B}T}\right) \qquad (7)$$

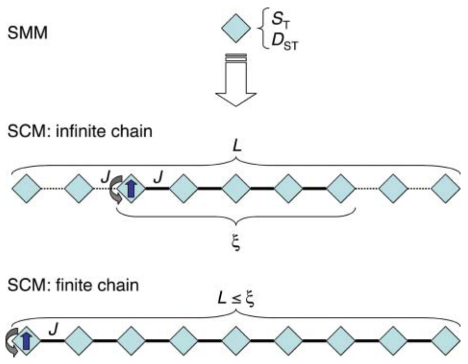

Fig. 4 Schematic representations of spin reversal in SCMs. According to either the infinite chain regime ($L \gg \xi$) or the finite chain regime ($L \ll \xi$), the total correlation energy affecting the spin reversal is changed between $8JS^2$ and $4JS^2$, respectively.

In this notation, ($8JS^2 + |D|S^2$) corresponds to the energy barrier of the magnetization relaxation in a SCM (= $\Delta_{\rm SCM1}$).[28] Eqn (7) can be applied to an infinite chain, *i.e.*, $L \gg$ correlation length ξ (Fig. 4). If $L \ll \xi$, which means a finite chain regime, eqn (7) will be converted into

$$\tau_{\rm SCM2} = \tau_0 \exp\left(\frac{4JS^2 + |D|\,S^2}{k_{\rm B}T}\right) \qquad (8)$$

where the energy barrier of the magnetization relaxation is ($4JS^2 + |D|S^2$) (= $\Delta_{\rm SCM2}$) (Fig. 4).[26–29] Considering the range of $|D/J| \gg 4/3$ with the real D (< 0) value observable in typical first-transition metal complexes, the J value is assumed to be very small. Such a chain would have a narrow domain wall so that $|D|S^2$, which is identical to that of a SMM, is added as the inherent exchange energy for one-spin reversal in addition to the correlation energy of $8JS^2$ or $4JS^2$, as seen in eqn (6) and (7). Thus, these notations accurately support the assumption that SCMs in general are a *magnetically arranged chain of uniaxial anisotropic spins*, and lead us to imagine that SMMs can be converted into an SCM system that has a one-dimensional arrangement of SMM units as a function of inter-SMM interactions.

Experimentally, the relaxation dynamics of our Mn$_2$Ni SCMs is well interpreted in eqn (7) and (8). The observed experimental values of Δ are 72 K and 55 K across a crossover around 2.7 K, in good agreement with the proposed values of $\Delta_{\rm SCM1}/k_{\rm B} \approx 73$ K and $\Delta_{\rm SCM2}/k_{\rm B} \approx 48$ K, respectively, using magnetic parameters J and D. The anisotropic component, $|D|S^2$, is expected to be approximately 23 K; if $J = 0$ is achieved, the trinuclear unit could be an SMM. This hypothesis was confirmed in two discrete Mn$^{\rm III}_2$Ni$^{\rm II}$ trinuclear SMMs, [Mn$_2$(5-Rsaltmen)$_2$Ni(pao)$_2$(phen)](ClO$_4$)$_2$ (phen = 1,10-phenantholine; R = Cl, Br), which have an $S_{\rm T} = 3$ ground state and $D_{\rm ST}/k_{\rm B} = -2.4$ K, and have a very similar bridging scheme to the Mn$^{\rm III}_2$Ni$^{\rm II}$ SCM unit.[29] Such correlation between SMM and SCM can be similarly seen in a set of Mn$^{\rm III}_2$Fe$^{\rm III}$ trinuclear SMMs: (NEt$_4$)[Mn$_2$(salmen)$_2$(MeOH)$_2$Fe(CN)$_6$], with an $S_{\rm T} = 9/2$ ground state, and Mn$^{\rm III}_2$Fe$^{\rm III}$ ferromagnetic SCM, (NEt$_4$)[Mn$_2$(5-MeOsalen)$_2$Fe(CN)$_6$] (salmen^{2-} = *rac*-*N*,*N*′-(1-methylethylene)bis(salicylideneiminate); 5-MeOsalen^{2-} = *N*,*N*′-ethylenebis(5-methoxysalicylideneiminate)).[30] Although the direct conversion between an SMM unit and the SCM produced from it remains an issue for future work (Can it be accomplished with external stimuli? See Conclusion), these examples demonstrate that the 1D correlation among SMM units produces dramatic changes in the magnetic system.

Various magnetic systems appear in 1D SMM arrangements

The aforementioned SCMs are a typical case of regular chains with only one kind of exchange coupling. However, depending on the symmetry of the building blocks used or the packing effects in their assemblies, various chain arrangements can be produced. For instance, it is possible to derive an alternating arrangement with J_1 and J_2, using an asymmetrical SMM building block, where the units connect in head-to-head/tail-to-tail coordination modes (Fig. 5a) (when the units connect in a head-to-tail mode, the chain will be a regular chain; see Fig. 5).[26b] In such a case, the energy barrier of SCMs, Δ_1, would be expressed as $\Delta_1 = 4(J_1 + J_2)S^2 + |D|S^2$, when $J_1 \approx J_2$ (Δ_2 is assumed in several cases). If $J_1 \gg J_2$, that is, a dimerized chain is assumed, Δ_1 would be changed to $\Delta_1 = 8J_2S^2 + 2|D|S^2$, which defines the occurrence of a double spin-flip in a 1D chain (Fig. 5a). Furthermore, although the chain arrangement is accomplished, if $J_2 \approx 0$, Δ_1 is no longer expressed as a function of exchange interaction, but should be expressed as $2|D|S^2$ for the correlated dimer of a SMM (Fig. 5b). Moreover, if J_1 is also very weak, the system can be simply considered as a single SMM unit with an energy barrier of $|D|S^2$ (Fig. 5c). In these cases, the very weak J_2 (and J_1 for the last case) could perturb the properties of the SMM (see the second section).[26b]

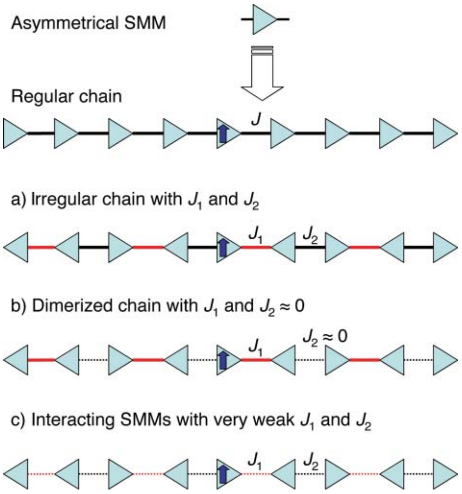

Fig. 5 Various assembly features using asymmetrical SMM units. The same-direction arrangement (head-to-tail arrangement) of the molecular vector provides a regular chain with one kind of J, whereas the alternating arrangement that has counteracting molecular vectors between neighboring units (head-to-head/tail-to-tail arrangement) results in an irregular chain with two kinds of J, *i.e.*, J_1 and J_2 (a–c). At this time, the magnitude of J_1 and J_2 strongly affects the relaxation dynamics of the chain.

Thus, tuning of the intra-chain exchange interaction makes it possible to change the relaxation dynamics of a 1D arranged compound. However, it is actually very difficult to synthesize rationally the respective systems. One reasonable way is to investigate systematically a family of chains having the same bridging lattice but changeable outer complexing ligands. Along this line, we are currently investigating a family of $Mn^{III}{}_2M^{II}$ 1D systems possessing the same bridging scheme of $[–Mn^{III}–ON–M^{II}–NO–Mn^{III}–(O_{Ph})_2–]_n$. As shown in the SCM $[Mn_2(saltmen)_2Ni(pao)_2(py)_2](ClO_4)_2$, the exchange coupling J (or corresponding J_1 and J_2) between quasi-Ising $[Mn^{III}–M^{II}–Mn^{III}]$ units (which are SMMs as $M^{II} = Ni^{II}$) is regulated by the nature of the $Mn^{III}–(O_{Ph})_2–Mn^{III}$ bridge in the out-of-plane Mn^{III} saltmen dimeric moiety. Fortunately, the exchange interaction in the Mn^{III} saltmen dimers, $[Mn_2(R\text{-saltmen})_2(X)_2]^{n+}$, is changeable at will according to (i) their bridging structure, (ii) the R substituents of the saltmen ligand, and (iii) the ligand field from the opposite axial ligand group X.[13,31] Therefore, assembling systems with the bridging scheme $[–Mn^{III}–ON–M^{II}–NO–Mn^{III}–(O_{Ph})_2–]_n$ offer a good tool for the investigation of relaxation dynamics in real systems.

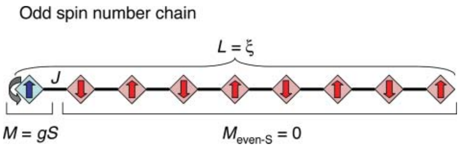

Fig. 6 Schematic representation of antiferromagnetically coupled odd--spin-numbered segments. Even-spin-numbered segments cancel their total magnetization. $M_{\text{total}} = g\sum_{n/2}(S_i + S_{i+1})$ as $S_i + S_{i+1} = 0$, whereas odd-spin-numbered segments retain the magnetization of only one spin $M_{\text{total}} = gS + g\sum_{(n-1)/2}(S_i + S_{i+1})$ as $S_i + S_{i+1} = 0$ (no thermal excitation of spin is present).

Antiferromagnetically coupled SCMs

In the absence of a spin canting arrangement, the antiferromagnetic chains of SMM building blocks are also able to display slow relaxation of the magnetization. This may sound strange because the magnetization arising from constituting spins is progressively cancelled with decreasing temperature (when all spin excitations are neglected at $T > 0$). For example, a strongly antiferromagnetically correlated integer S system, or even the Heisenberg system, may lead to a singlet ground state; this phenomenon is called the Haldane gap effect.[32] In contrast, in weakly correlated systems or even integer S systems, segments of finite chains possibly composed of odd spin number should be magnetically active and experience relaxation of the magnetization (Fig. 6). In this case, the relaxation dynamics could be expressed as a function of exchange coupling similarly to ferromagnetic-type SCM systems. Clérac *et al.* were the first to explain this behavior in a chain of antiferromagnetically coupled Mn_4 SMMs, where Mn_4 SMM is a double-cuboidal $Mn^{II}{}_2Mn^{III}{}_2$ cluster with $S_T = 9$ and $|D|S_T{}^2 \approx 23$ K (used as well in the network compounds mentioned in the previous paragraph) and the exchange interaction between Mn_4 units is $J/k_B \approx -0.08$ K.[33] Although the observed signals are small, the ac susceptibilities of χ' and χ'' are strongly frequency-dependent, and the estimated relaxation times obey the Arrhenius relation with $\tau_0 = 7 \times 10^{-11}$ s and $\Delta/k_B = 47$ K. This Δ value disagrees with the value of $|D|S_T{}^2$ for the isolated unit, but can be treated as $\Delta = 4|J|S^2 + |D|S^2$ for terminal spin reversal on segments with odd spin number. The estimated Δ value following this relation is 49 K, in excellent agreement with the experimental value. Thus, even antiferromagnetic correlation in an SMM 1D arrangement can lead to slow relaxation of the magnetization similar to that observed in SCMs. A 1D arranged

SMM, $[Mn_7O_8(O_2SePh)_8(O_2CMe)(H_2O)]$, reported by Christou and co-workers, also showed similar behavior.[34]

The relaxation of the magnetization in the antiferromagnetic chain of Mn_4 SMMs demonstrates its polydispersity attributed to the distribution of segment size, consequently inducing asymmetrical Cole–Cole plots (χ'' *vs* χ' plot).[33] Notably, in addition to the size-dependent polydispersity, mixing of the intrinsic relaxation of individual original SMM building blocks may have to be considered. In the ac susceptibility data of an antiferromagnetic chain of SMMs designed recently by our group ($J/k_B \approx -0.1$ K), the presence of another relaxation mode in addition to the SCM relaxation mode was detected, which was active in the higher frequency region than the SCM one. Finally, the relaxation mode was concluded to be due to the intrinsic relaxation of the SMM building block, and a system in which the relaxation dynamics was coherently changed from SMM to SCM was discovered.[35] To summarize, the antiferromagnetic correlation in SMMs with a 1D arrangement enables conversion into an SCM system, in which finite segments with odd spin number are active because of the net magnetization corresponding to one SMM unit (Fig. 6).

Many issues concerning the dynamics of magnetization relaxation in both ferromagnetic-type and antiferromagnetic-type SCM systems await evaluation. Nevertheless, studies of weakly correlated systems, or interacting 1D arrangements in some cases,[36] will further reveal the unique behavior of anisotropic spins. An intermediate compound between SMM and SCM might be discovered. In addition, we must consider the case of strongly correlated 1D systems. In such a case, another problem would emerge: this is discussed in the next section.

Strong correlation in 1D arrangement

The first approach in designing an SCM would be to assemble anisotropic metal ions and bridging ligands and to linearly connect them. This is a simple and good choice because the degree of anisotropy of the used metal ion and the intra-chain exchange interaction between them only become a subject of discussion. In the Ising limit, *i.e.*, $|D/J| \ll 4/3$, eqn (7) and (8) are ruled out in explaining the SCM relaxation dynamics, but the correlation energy $8JS^2$ or $4JS^2$ would remain as a component in order to express the energy barrier along Glauber dynamics.[37] The case possessing a strong J value has a broad domain wall. Therefore, a different kind of inherent exchange energy for one spin reversal, instead of $|D|S^2$ in the narrow domain wall case, needs to be considered.[38,26,28] Meanwhile, the case in which SMM building blocks are magnetically assembled is not so simple because it contains two kinds of intra-chain magnetic pathways: the intra-cluster (J_{intra}) and inter-cluster (J_{inter}) exchanges. Ideally, the former produces a spin ground state (S_T) for the SMM building block and the latter plays the role of J to assess SCM behavior of the produced chain. Nevertheless, such a system is only accomplished when $J_{\text{intra}} \gg J_{\text{inter}}$, as discussed in the previous sections. In the case of $J_{\text{intra}} \ll J_{\text{inter}}$, the pre-organized SMM building block would no longer be defined as a unit of the assembled chain, and it is difficult to evaluate quantitatively SCM dynamics. As far as we know, there are few studies of strongly correlated SCM systems at the experimental level.[20,37]

Conclusion and perspectives: What is next in this subject?

In this paper, we stress that inter-SMM interaction (and correlation) is a powerful tool not only for the modulation of intrinsic physical phenomena of original SMMs but also for the creation of new materials. The magnetic properties of this kind of material can be changed by the following factors: i) *interaction* or *correlation*, ii) the strength of interaction, iii) the dimensionality of correlation, and iv) the range of correlation (short or long range for 2D and 3D networks; the correlation length and its relation to the finite chain length for 1D systems). Therefore, quantitative evaluation of the observed properties remains the most important task in understanding the produced materials. Meanwhile, what is the next step from the viewpoint of molecular design? Here, we would like to introduce a few topics currently being tackled in our group.[39] The first topic is about the production of SMM-network compounds induced with external stimuli. Considering that inter-SMM interaction is another tunable parameter in materials design, if the inter-SMM interaction could be switched with an external stimulus, the conversion between a SMM and its magnetic network would be achieved. Currently, we are giving much attention to photo-irradiation and chemical and artificial pressures as external stimuli (for the latter, a few examples can be found in ref. 40 and 41). To obtain photo-induced SMM-network compounds, the molecular pre-design is very important because molecules used in photo-irradiation must have a photoactive site that induces electron transfer concomitantly with electron excitation to create/break (ON/OFF) the magnetic pathway between SMMs (or between anisotropic spins for SCMs). One way is to use a photoactive bridging ligand that acts as a shunt for magnetic pathways (Fig. 7a). Meanwhile, the photo-induced metal-to-metal electron transfer reaction must be highly effective to design, for example, photo-induced SCMs (Fig. 7b). The well-known work of Ohkoshi and co-workers on cyano-bridged magnetic materials would provide much information for the design of such compounds.[42]

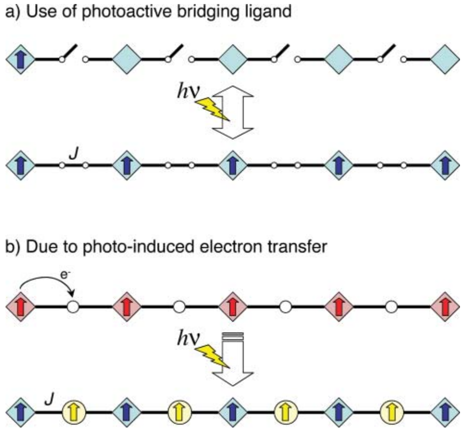

Fig. 7 Proposed design of photo-induced SMM-network compounds.

The second topic is about hybridized materials having SMM or SCM properties, one target being magnetic molecular conductors.[43] The groups of Day[44] and Coronado[45] respectively have been energetically working on this subject. One of the goals in the coexistence of SMM properties with high conductivity is to tune the SMM properties using interactions with itinerant electrons of the conducting sublattice. Even if the inter-SMM interaction is as weak as ∼ −0.1 K, such an interaction crucially affects the original SMM properties (Fig. 8). Therefore, SMM would also act as a sensitive magnetic sensor in this kind of material. Another point worth noting is that SMM and SCM possess strong anisotropic nature, in addition to the artificial high spin state in SMM. These characteristics have inspired us to imagine the creation of giant magnetoresistance or spintronics materials.

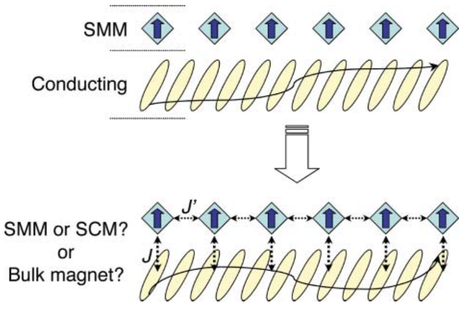

Fig. 8 Proposed design of conducting-hybridized SMMs. Concomitant interaction between SMM units and conducting electrons (J) would lead to interaction among SMM units (J').

In summary, the inter-SMM interaction is an important factor to understand not only the SMM building block itself but also the produced SMM assembly. Controlling the interactions from the initial anisotropic single ion in the ligand field (0D), to SMMs (0D) and SCMs (1D), and finally to 2D and 3D networks would give us a complete picture of dynamic variation straddling both quantum and classical regimes (Fig. 9). Finally, we would like to stress that more studies on molecular nanosized magnetic materials would increase the possibility of discovering new materials having novel physical properties.[46]

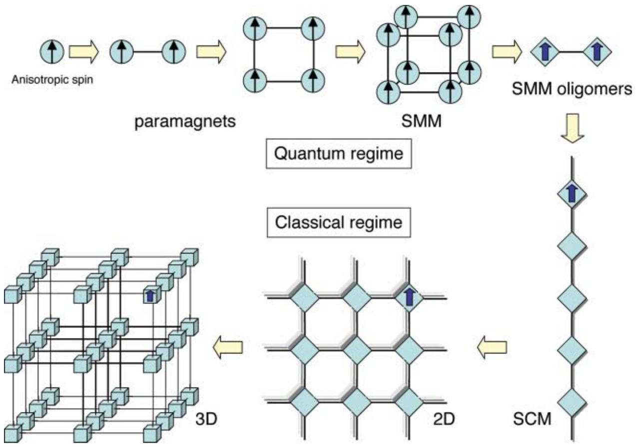

Fig. 9 Schematic representation of the construction of SMM assemblies. Controlling the interaction reveals a complete picture of dynamic variation straddling both quantum and classical regimes.

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