Stable two-dimensional ferromagnets made of regular single-layered lattices of single-molecule nanomagnets on substrates

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We propose that stable two-dimensional (2D) ferromagnets can be made of regular single-layered lattices of single-molecule nanomagnets with enough uniaxial magnetic anisotropy on appropriate substrates by controlling the inter-nanomagnet magnetic interaction. Our Monte Carlo simulated results show that such ideal 2D ferromagnets are thermodynamically stable when the anisotropy is strong enough. If the anisotropy energy equals 80 K, approximately that of the Mn$_{12}$, the $T_c$ varies from zero to 15 K depending on different inter-nanomagnet coupling constants. Such stable spin systems, experimentally accessible, should be promising for information applications.

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Single-molecule (SM) nanomagnets attract huge interest because they show quantum tunnelling, interference, and coherence effects at ultra-low temperatures and have various potential applications, such as magnetic information storage and quantum computation[1, 2, 3, 4, 5, 6, 7, 8]. An SM nanomagnet usually has large spin $S$ and strong uniaxial anisotropy, and there is an easy axis for spin orientation[8]. Hence it must overcome an effective energy barrier $U_{\text{eff}}$ to achieve a spin reversal at low enough temperature. For example, the famous Mn$_{12}$ SM nanomagnet ($[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Br})_{16}(\text{H}_2\text{O})_4\cdot 4\text{CH}_2\text{Cl}_2]$) has $S = 10$ and its spin reversal energy barrier $U_{\text{eff}}$ is up to 74 K[8, 9]. The record-breaking value of $U_{\text{eff}}$ is 86.4 K in the case of $[\text{Mn}_6^{\text{II}}\text{O}_2(\text{Et-sao})_6(\text{O}_2\text{CPh(Me})_2)_2(\text{EtOH})_6]$, which has $S = 12[10]$.

SM magnets can be made to form single isolated magnets, dimers, and other clusters[1, 2, 3, 4, 5]. Through chemical methods, they can be synthesized in the form of three-dimensional (3D) crystalline structures and two-dimensional (2D) networks[3, 10, 11, 12, 13]. The basic building blocks in these structures are single magnets. The effective inter-magnet magnetic interactions usually are antiferromagnetic (AF) and cannot be easily controlled. Thus, it is quite difficult to make stable ferromagnets from such systems of SM magnets. Fortunately, single layers of SM nanomagnets have recently been achieved on gold and silicon surfaces[14, 15, 16].

This breakthrough makes us believe that stable ideal 2D ferromagnets can be made from regular 2D lattices of SM nanomagnets, although Mermin-Wagner theorem allows no finite-temperature phase transition in 2D isotropic Heisenberg spin systems[17, 18].

Here we show that stable 2D ferromagnets can be made of regular single-layered lattices of SM nanomagnets with enough uniaxial anisotropy on appropriate substrates by controlling the inter-nanomagnet magnetic interaction. The spin of the nanomagnet is described as a large spin. The easy axis is perpendicular to the 2D spin lattice. We describe the 2D ferromagnets by a 2D quantum Heisenberg model with the uniaxial anisotropy and relatively weak ferromagnetic (FM) inter-spin coupling. This model is reasonable and liable because the dipolar spin interaction almost is reduced to a purely AF one and the inter-spin coupling can be controlled by choosing right substrates and manipulating the inter-nanomagnet distances[19]. We reduce the quantum spin operators to classical variables because both the spin value and the anisotropy energy are large enough[8, 9, 10], and then use Monte Carlo method to simulate the many-body physical properties with various parameters[20, 21]. Our results prove that stable 2D ferromagnets can be made of such SM nanomagnets for experimentally-accessible parameters. More detailed results will be presented in the following.

SM nanomagnets such as the Mn$_{12}$ have large spins and their inter-spin exchange interactions usually are very weak compared to their anisotropy energies[8, 9, 10, 11, 12, 13]. When put on appropriate surfaces, such SM nanomagnets can have the same uniaxial anisotropy energy and adjustable inter-spin interactions[14, 15, 16]. Thus, the 2D ferromagnets can be described by the Hamiltonian

$$H = -K \sum_i (S_i^z)^2 - \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

where $K$ describes the uniaxial anisotropy with the easy axis ($z$ direction) perpendicular to the 2D lattice, the $\vec{S}_i$ is the spin operator at site $i$ in the lattice, and $J_{ij}$ is the inter-spin coupling constant between $\vec{S}_i$ and $\vec{S}_j$. This perpendicular anisotropy and the 2D lattice structure make the dipolar spin interaction almost reduced to an AF one, and thus $J_{ij}$ can vary from AF to FM interaction. Here we are interested mainly in the FM case. The latter summation is over spin pairs between $i$ and $j$.

Because the spin $S$ is very large and we are interested in the equilibrium properties, we can reasonably treat the quantum spin operator $\vec{S}_i$ as a classical vector $S\hat{s}_i$, where $\hat{s}_i$ is a unit vector.
We investigate the equilibrium properties of this model using Monte Carlo (MC) methods \cite{20, 21}. Both Metropolis and cluster algorithms are used \cite{22, 23}. We take an \( L \times L \) square lattice and limit \( J_{ij} \) to nonzero \( J (> 0) \) only for the nearest spin pairs without losing main physics. As usual, we use a periodic boundary condition. For convenience, we use a special unit that the Boltzmann constant \( k_B \) is set to 1. We use the parameter \( D = K/J \) to describe the strength of the anisotropy energy relative to the exchange constant. As we prove, the system is already in equilibrium after 100,000 MC steps (MCS). The average magnetization \( M \), the fourth-order Binder’s cumulant \( U_4 \), the specific heat \( C \), and the magnetic susceptibility \( \chi \) are calculated by averaging over 50,000 MCS after thermodynamical equilibrium is reached \cite{20, 21}. Ten copies of such average values are used to calculate the final results.

In Figure 1 we present average magnetizations \( M \) as functions of temperature \( T \) for 16 \( D \) values from 0.05 to 500. We have \( M = 1 \) at \( T = 0 \) because the magnetization \( M \) is normalized to 1. The magnetization \( M \) for all the higher temperatures increases with \( D \). There is a spinodal point in the specific magnetization curve for a given \( D \) value. When \( D \) becomes larger, the spinodal point shifts rightward to higher temperature, which means that the phase-transition temperature \( T_c \) increases with increasing \( D \). In order to determine \( T_c \) more accurately, we actually use the unique intersection point of the various \( U_4 - T \) curves of different \( L \) values. This method is the best approach to obtain accurate phase-transition temperature \cite{20, 21}. The calculated \( T_c \) as function of \( D \) is presented in Figure 2. In order to emphasize the \( T_c \) of large \( D \) values, we use logarithmic scale in the main plot and linear scale in the inset. Our results show that \( T_c \) increases with \( D \), converging to 2.269, the Ising limit \cite{24, 25}, when \( D \) is infinite. For \( D = 0 \) we obtain \( T_c = 0 \), which is consistent with established conclusion that there is no finite-temperature phase-transition for 2D isotropic model \cite{17, 18}. A nonzero \( D \) is necessary to a finite \( T_c \).

We describe the deviation of the normalized spin vector from the easy axis by the parameter \( d_m \) defined as

\[
d_m = 1 - \langle (\vec{s}^2) \rangle / \langle (\vec{s}^2) \rangle,
\]

where \( \vec{s} = (1/L^2) \sum \vec{s}_i \) and \( \langle A \rangle \) is the average value of \( A \). We present \( d_m(T) \) for various \( D \) values in Figure 3. It is clear that \( d_m \) is zero or tiny at low temperature. When \( D \) approaches to zero, we obtain \( d_m \leq 2/3 \). For a given \( D \), \( d_m \) increases with \( T \), reaching a maximum \( d_{mc} \) at \( T_c \). \( d_{mc} \) decreases with increasing \( D \), being already less than 0.02 for \( D = 30 \). For \( D \geq 100 \), \( d_m \) is actually zero in the temperature window in Figure 3. Indeed, when \( D \) is very large, the Hamiltonian is similar to the 2D Ising model, but it is equivalent to the 2D Ising model only when \( D \) is infinite.

It is established that the inter-spin interaction can be changed experimentally and even adjusted intentionally for special purposes \cite{19}. This means that \( J \) can be changed actually from a few K to zero. Considering that the parameter \( K \) in Eq. (1) can be nearly 80 K \cite{10}, we conclude that the anisotropy parameter \( D \) can be 10 or much larger. Accordingly, \( T_c \) is \( 1.8 \sim 2.269J \). With \( K = 80 \) K, \( T_c \) equals 2.2 K if \( J = 1 \) K, and 14.4 K if \( J = 8 \) K. Because the 2D ferromagnets are in the regime of large \( D \), the spin deviation \( d_m \) is very small, smaller than 0.001, when \( T \) is at \( T_c \), and can be considered zero when \( T \) is substantially below \( T_c \). Therefore, the spin is nearly in the Ising limit in well-ordered FM states and such spin systems should be stable enough to carry information.

![Figure 1](image1.png)

**FIG. 1**: (color online). Normalized magnetizations \( M \) as functions of temperature \( T \) for given anisotropy parameters from \( D=0.05 \) to 500.

![Figure 2](image2.png)

**FIG. 2**: (color online). The \( D \) dependence of Curie temperature \( T_c \) with \( D \) from 0.05 to 500. The dash line indicates \( T_c \simeq 2.269 \), the Ising limit. The inset shows \( T_c \) as a function of \( D \) in linear scale.

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In summary, we propose that stable 2D ferromagnets can be made of regular single-layered lattices of SM nanomagnets with enough uniaxial magnetic anisotropy on appropriate substrates by controlling the inter-nanomagnet magnetic interaction. The quantum spin operator for them can be naturally reduced to a classical spin variable because the spin value and the anisotropy energy are so large. Our Monte Carlo simulated results show that such ideal 2D ferromagnets are stable because the deviation of the spins from the easy axis is smaller than 0.1% in the ferromagnetic state when the anisotropy is strong enough. If the anisotropy energy equals 80 K, approximately that of the famous Mn$_{12}$, the $T_C$ varies from zero to $\sim$15 K according to the different inter-spin coupling constants. Our 2D model is reasonable and reliable because the dipolar inter-spin interaction almost can be reduced to an AF one due to the perpendicular easy axis and the 2D spin lattice. Therefore, such stable spin systems should be promising for information applications.

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