Spin Amplification, Reading, and Writing in Transport through Anisotropic Magnetic Molecules

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Inelastic transport through a single magnetic molecule weakly coupled to metallic leads is studied theoretically. We consider dynamical processes that are relevant for writing, storing, and reading spin information in molecular memory devices. Magnetic anisotropy is found to be crucial for slow spin relaxation. In the presence of anisotropy we find giant spin amplification: The spin accumulated in the leads if a bias voltage is applied to a molecule prepared in a spin-polarized state can be made exponentially large. For one ferromagnetic and one paramagnetic lead the molecular spin can be reversed by applying a bias voltage even in the absence of a magnetic field. We propose schemes for reading and writing spin information based on our findings.

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Introduction.—Recently, a number of fascinating experiments have studied transport through magnetic molecules. The current through a molecule weakly coupled to metallic leads shows steps as a function of bias voltage when additional molecular transitions become energetically available. The differential conductance dI/dV then shows peaks. Zeeman splitting of the energy levels and of the peaks in dI/dV has been observed for magnetic molecules [1, 2]. Magnetic anisotropy partially lifts the degeneracy of molecular levels, leading to fine structure of the peaks even for vanishing magnetic field, which has been observed for Mn_{12} complexes [3]. Some of the fine structure peaks show negative differential conductance (NDC) [3]. The Kondo effect has also been found for single molecules [1, 2]. The Zeeman splitting [4] as well as spin blockade and NDC [3, 5] in magnetic molecules have been investigated theoretically. Transport through magnetic molecules has also been studied in the STM geometry, where the coupling to the substrate is much stronger [6].

Magnetic molecules are interesting for applications that combine spintronics [7, 8], i.e., the idea to use the electron spin in electronic devices, with molecular electronics, i.e., the utilization of molecules as electronic components [9]. We study processes that are relevant for the utilization of magnetic molecules as memory cells. In this context it is crucial that the stored information *persists* over sufficiently long times and that one can *read out* and *write* the information. The read out process would naturally utilize the interaction of electrons tunneling through the molecule with its local spin. The works mentioned above lay the ground for a study of this aspect. On the other hand, the other two aspects—persistence and writing—have received little attention.

In the present Letter, we consider current-induced spin relaxation and propose schemes for reading and writing the molecular spin electronically. We show that the spin transmitted from one lead to the other before the molecular spin relaxes can be made very large. This interesting effect of *spin amplification* forms the basis of our proposed read-out mechanism. *Magnetic anisotropy* is a key ingredient for this effect and for molecular memory devices in general. Since in the absence of a magnetic field the spin polarization vanishes in the steady state, we expect any spin polarization to decay in time. For memory applications this relaxation should be slow. This can be accomplished by an easy-axis anisotropy, which introduces an *energy barrier* for a change of spin direction [3]. Typical molecules we have in mind are planar complexes of magnetic ions, e.g., porphyrin complexes like heme.

Theory.—We consider a magnetic molecule with one orbital coupled to a local spin $\mathbf{S}$, described by the Hamiltonian

$$\begin{aligned} H_{\mathrm{mol}} &= (\epsilon - eV_g)\,\hat{n} + \frac{U}{2}\,\hat{n}(\hat{n}-1) - J\,\mathbf{s}\cdot\mathbf{S} \\ &\quad - K_2\,(S^z)^2 - B(s^z + S^z). \end{aligned} \tag{1}$$

Here, $\hat{n} \equiv c_\uparrow^\dagger c_\uparrow + c_\downarrow^\dagger c_\downarrow$ is the number operator ($c_\sigma^\dagger$ creates an electron in the orbital) and $\mathbf{s} \equiv \sum_{\sigma\sigma'} c_\sigma^\dagger(\boldsymbol{\sigma}_{\sigma\sigma'}/2)c_{\sigma'}$ is the corresponding spin operator. Easy-axis magnetic anisotropy is assumed ($K_2 > 0$) for the local spin of length $S \geq 1$. We define the total spin operator $\mathbf{S}_{\mathrm{tot}} \equiv \mathbf{s} + \mathbf{S}$.

The molecule is weakly coupled to two leads L (left) and R (right) with Hamiltonians $H_\alpha = \sum_{\mathbf{k}\sigma} \epsilon_{\alpha\mathbf{k}\sigma}\, a_{\alpha\mathbf{k}\sigma}^\dagger a_{\alpha\mathbf{k}\sigma}$ where $a_{\alpha\mathbf{k}\sigma}^\dagger$ creates an electron in lead α. The hybridization of the molecular orbital with the leads is described by Hamiltonians $H_{\mathrm{hyb},\alpha} = \sum_{\mathbf{k}\sigma}(t_\alpha\, a_{\alpha\mathbf{k}\sigma}^\dagger c_\sigma + \mathrm{h.c.})$.

The unperturbed Hamiltonian H_{mol} is easily diagonalized. The eigenstates fall into sectors with $n = 0, 1, 2$ electrons. Since $[S_{\mathrm{tot}}^z, H_{\mathrm{mol}}] = 0$ the eigenvalue m of S_{tot}^z is another good quantum number. For $n = 0$, 2 we obtain $2(2S+1)$ eigenstates $\{|0,m\rangle, |2,m\rangle\}$ with energies $\epsilon(0,m) = -K_2 m^2 - Bm$ and $\epsilon(2,m) = 2(\epsilon - eV_g) + U - K_2 m^2 - Bm$, respectively. For $n = 1$ we find the eigenstates, in terms of spin states of the electron and the local spin,

$$\begin{aligned} |1,m\rangle^\pm &= \mp\frac{\sqrt{2\Delta E \mp (2K_2 - J)m}}{2\sqrt{\Delta E}}\,|\downarrow\rangle|m+1/2\rangle \\ &\quad + \frac{J\sqrt{S(S+1) - m^2 + 1/4}}{2\sqrt{\Delta E}\sqrt{2\Delta E \mp (2K_2 - J)m}}\,|\uparrow\rangle|m-1/2\rangle, \end{aligned} \tag{2}$$

with energies

$$\epsilon^\pm(1,m) = \epsilon - eV_g - Bm + \frac{J}{4} - K_2\Big(m^2 + \frac{1}{4}\Big) \pm \Delta E(m) \tag{3}$$

where $\Delta E(m) \equiv [K_2(K_2 - J)m^2 + (J/4)^2(2S+1)^2]^{1/2}$.

There are two orthogonal states $|1,m\rangle^{\pm}$ for $-S+1/2 \le m \le S-1/2$. For the fully polarized states $|1,-S-1/2\rangle$ and $|1,S+1/2\rangle$ the upper (lower) sign applies if $K_2 - J/2$ is positive (negative).

The hybridization is treated as a perturbation. The derivation follows Refs. [4, 10, 11, 12] and is not repeated here. We obtain coupled rate equations

$$\dot{P}^i = \sum_{j\neq i} P^j R_{j\to i} - P^i \sum_{j\neq i} R_{i\to j} \tag{4}$$

for the probabilities P^i of the molecular many-body states $|i\rangle$. The steady state P_0^i is the solution for $\dot{P}^i = 0$.

The transition rates $R_{i\to j}$ are written as a sum over the two leads and the two spin directions, $R_{i\to j} = \sum_{\sigma\alpha} R^{\sigma\alpha}_{i\to j}$, with

$$\begin{aligned} R^{\sigma\alpha}_{i\to j} &= \frac{1}{\tau_0}\big[f(\epsilon_j - \epsilon_i + e s_\alpha V/2)\,|C^\sigma_{ij}|^2 \\ &\quad + f(\epsilon_j - \epsilon_i - e s_\alpha V/2)\,|C^\sigma_{ji}|^2\big], \end{aligned} \tag{5}$$

where $s_{\mathrm{L,R}} = \pm 1$, $1/\tau_0 \equiv 2\pi\,|t|^2\,D v_{\mathrm{uc}}/\hbar$ is the typical transition rate in terms of the density of states D (for one spin direction) of the leads and their unit-cell volume v_{uc}, V is the bias voltage, ϵ_i is the energy of state $|i\rangle$, $f(x)$ is the Fermi function, and $C^\sigma_{ij} \equiv \langle i|c_\sigma|j\rangle$.

The occupation and spin in a state described by probabilities P^i are given by $n = \sum_i n_i P^i$ and $m = \sum_i m_i P^i$, respectively. Here, n_i (m_i) is the occupation (polarization) in state $|i\rangle$. The current through lead α is

$$I^\alpha = -e\, s_\alpha \sum_{ij} (n_i - n_j)\left(R^{\uparrow\alpha}_{j\to i} + R^{\downarrow\alpha}_{j\to i}\right) P^j, \tag{6}$$

where we count currents from left to right as positive. The *steady-state* currents $\langle I^\alpha\rangle$ through the two leads are equal since the occupation is constant in time. The current scale is e/τ_0, where the rate $1/\tau_0$ comes from the transition rates. Comparing this to typical experimental currents of $0.1\,\mathrm{nA}$ [1, 13], we obtain $\tau_0 \sim 1.6\,\mathrm{ns}$. The *spin* current

$$I^\alpha_s = \frac{s_\alpha}{2} \sum_{ij} (n_i - n_j)\left(R^{\uparrow\alpha}_{j\to i} - R^{\downarrow\alpha}_{j\to i}\right) P^j \tag{7}$$

is generally nonzero if the molecule is prepared in a spin-polarized state. The molecule relaxes exponentially towards the steady state, which for $B = 0$ is nonmagnetic. We can thus define the *total transmitted spin*

$$\Delta S^\alpha[\mathbf{P}] = \int_0^\infty dt\, I^\alpha_s(t,\mathbf{P}), \tag{8}$$

which depends on the probabilities $\mathbf{P} = (P^1,\ldots)$ at $t = 0$.

To evaluate Eq. (8) we require the time dependence of $\mathbf{P}$. We rewrite the rate equations (4) in matrix form, $\dot{\mathbf{P}} = A\,\mathbf{P}$, where A has the components $A_{ij} = R_{j\to i}$ for $i \neq j$ and $A_{ii} = -\sum_{k\neq i} R_{i\to k}$. The solution is $\mathbf{P}(t) = e^{At}\,\mathbf{P}(0)$, which allows to calculate occupation, polarization, and (spin) current as functions of time for given initial conditions.

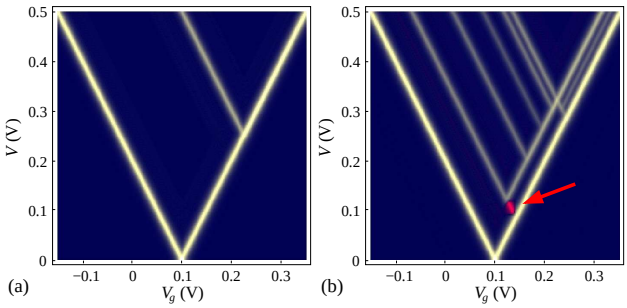

FIG. 1: (color online). dI/dV as a function of gate voltage V_g and bias voltage V. Yellow (red) colors denote positive (negative) differential conductance. In (a) results for an isotropic molecule are shown, the parameters are $T = 0.002$, $S = 2$, $\epsilon = 0.2$, $U = 1$, $J = 0.1$, $K_2 = B = 0$. Energies are here and in the following given in electron volts. Coulomb blockade is found to the left and right of the V-shaped region, whereas within this region a nonzero steady-state current is flowing. The satelite line results from the exchange splitting of energy levels for $n = 1$. In (b) an anisotropy of $K_2 = 0.04$ has been assumed, leading to a complex splitting of the dI/dV peaks. We find one peak with NDC (arrow).

Results.—As noted above, the anisotropy partially lifts the degeneracy of molecular levels. The resulting fine structure of the peaks in dI/dV is shown in Fig. 1. One of the peaks exhibits NDC. At the low temperature assumed in Fig. 1 this can be understood as follows: The transitions that become energetically possible at the corresponding bias have rather small transition rates $R^{\sigma\alpha}_{j\to i}$ due to small matrix elements C^σ_{ji}. Equation (6) shows that the current is an average over the transition rates. For this particular transition the result is that the current for higher bias voltage is *smaller*. This mechanism is different from the one for Mn_{12} complexes [3]—in our case there is no blocking state in which the molecule becomes trapped due to suppressed outgoing transition rates. On the contrary, the probabilities P^i are equal for all accessable states.

We now turn to the relaxation of the molecular spin. For a molecule prepared in state $|0,2\rangle$ at time $t = 0$, Fig. 2(a) shows the time dependence of occupation and spin polarization. The occupation approaches the constant value $\langle n\rangle$ on the timescale τ_0, the typical time for a single tunneling event.

The spin polarization shows a quite different behavior with two distinct timescales. Initially, $m(t)$ approaches a "quasi-steady" state on the timescale τ_0, which in this case has *higher* polarization since the state $|1,5/2\rangle$ has significant weight. Then, $m(t)$ decays to zero more slowly. This decay is slow because the molecule must pass through several intermediate states to reach a state with opposite spin polarization, essentially performing a one-dimensional random walk, as indicated in the level scheme, Fig. 2(b). For anisotropies $K_2 \gtrsim 0.04$ the decay becomes much slower since two of the transitions needed to reverse the spin, denoted by the crosses in Fig. 2(b), become higher in energy than $eV/2$ and are thus forbidden for $T \to 0$ and thermally activated for $T > 0$.

Importantly, in the regime of thermally activated (slow) spin relaxation a sizeable steady-state current is flowing since transitions between the states $|0,\pm 2\rangle$ and $|1,\pm 5/2\rangle$ are still

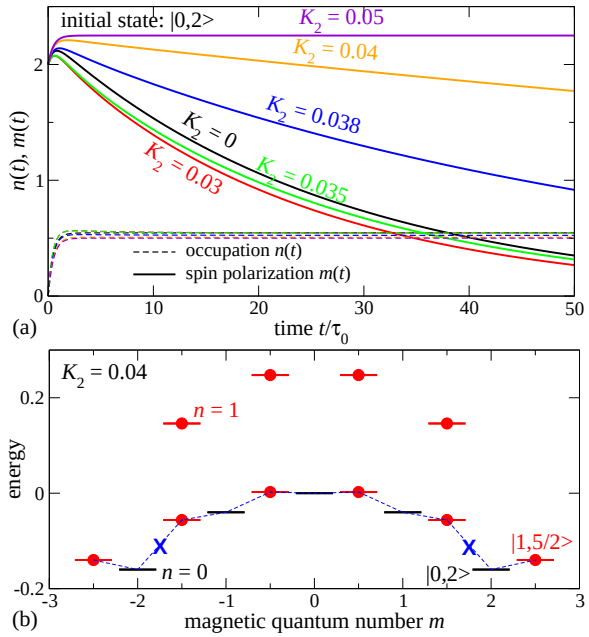

FIG. 2: (color online). (a) Occupation $n(t)$ and spin polarization $m(t)$ for bias $V = 0.2\,\mathrm{V}$, and $T = 0.002$, $S = 2$, $\epsilon = 0.12$, $U = 1$, $J = 0.1$, and $B = 0$ for various anisotropies K_2. In this and the following figures we absorp the gate voltage into ϵ. The molecule is in state $|0,2\rangle$ at time $t = 0$. (b) Molecular energy levels for states with $n = 0$ (black bars) and $n = 1$ (red bars with circles) for the parameters from (a) and $K_2 = 0.04$. Active transitions are denoted by dashed lines. The crosses denote the transitions that next become thermally suppressed for larger K_2 or smaller bias V.

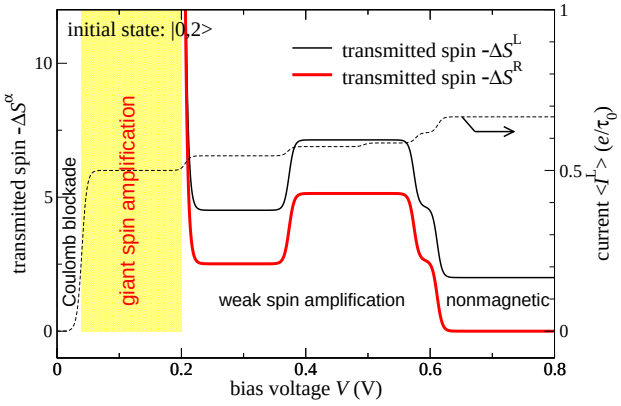

FIG. 3: (color online). Total transmitted spin through the left and right leads for a magnetic molecule prepared in the $n = 0$ maximum spin state $|0,2\rangle$, as functions of bias voltage. The parameters are as in Fig. 2 with $K_2 = 0.04$. The steady-state current is also shown.

possible, see Fig. 2(b). As noted above, this should lead to a nonzero total transmitted spin, Eq. (8). This is indeed found in Fig. 3. Varying the bias voltage we observe four regimes:

(i) For small bias we are in the Coulomb blockade regime with exponentially small (for small T) steady-state current. However, we find that the total transmitted spin is exponentially *large*. While all transitions are thermally activated, the ones necessary to relax the spin have a much higher energy than the transition between $|0,2\rangle$ and $|1,5/2\rangle$, which dominates the current. However, the transmission takes exponentially long since this transition is also thermally activated.

(ii) For larger bias we find the most interesting regime. The spin relaxation rate is still small while the current is large. The bias is too small to overcome the energy barrier between spin up and down, see Fig. 2(b). Here the current is spin-polarized for an exponentially long time leading to an exponentially large transmitted spin $|\Delta S^\alpha|$ [the negative sign in Fig. 3 can be understood by considering the transition rates, Eq. (5), in detail]. The typical time $T_s^\alpha \equiv 1/|I_s^\alpha(t=0)|$ for one unit of spin to be transmitted is of the order of τ_0. If T_s^{R} is short compared to the spin relaxation time in the leads large opposite magnetizations will be accumulated in the leads. This effect is induced by the breaking of spin symmetry at $t = 0$ only through the polarization of a single quantum spin, and can thus be described as *giant spin amplification*. It is a promising method to *read out* the spin information. The magnetization in the leads could be detected with a pickup coil or by the magneto-optical Kerr effect [14, 15]. A strong amplification mechanism could also facilitate the reliable transfer of spin between individual molecules in a device.

(iii) Further increase of the bias leads to a regime where the transmitted spin is nonzero but not exponentially enhanced. Here, both spin relaxation rate and current are large. The bias is large enough to overcome the energy barrier. Figure 3 shows that the spin transmitted through the left lead is (in absolute value) larger by two than through the right lead. The reason is that the electrons flow from right to left and that the spin of the initial state has to leave the molecule for $t \to \infty$.

(iv) At large bias *all* transitions between states with $n = 0, 1$ are possible. The spin transmitted through the right, incoming lead, ΔS^{R}, essentially vanishes. The initial spin leaves the molecule through the left lead, leading to $\Delta S^{\mathrm{L}} \cong -2$. This is the nonmagnetic regime.

Finally, for molecular memory application one also needs to *write* the information, i.e., to switch the molecule to a predetermined state. An obvious idea is to apply a magnetic field to a molecule attached to the nonmagnetic leads considered so far. However, applying a field at zero bias does not work since all transitions remain thermally suppressed so that relaxation to the spin-polarized steady state is exponentially slow.

We find that reliable switching requires a *two-step scheme*: First one applies a magnetic field, which *tilts* the energy levels in Fig. 2(b), and a bias voltage that is just large enough to allow transitions in the desired direction but not in the opposite one at low temperatures. Since the Zeeman energy B is small this requires fine tuning of V on the scale B/e and cooling to $T \ll B$. Figure 4 shows the change of probabilities for all states with $n = 0, 1$ if one starts with $|0,-2\rangle$ and applies a positive B field to switch the molecule to spin up. The Zeeman energy is chosen as $2\,\mathrm{meV}$. The molecule crosses over from $|0,-2\rangle$ to a steady state essentially consisting of $|0,2\rangle$ and $|1,5/2\rangle$ on a timescale of the same order and of the same origin as the spin relaxation times, see Fig. 2. Note that in a molecular circuit one could apply a magnetic

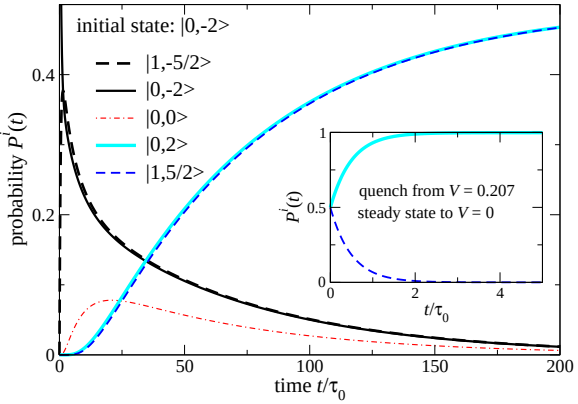

FIG. 4: (color online). Probabilities of molecular states after initial preparation in state $|0,-2\rangle$ as functions of time at the bias voltage $V = 0.207\,\mathrm{V}$. The probabilities of states with extremal spin polarization and of the representative intermediate state $|0,0\rangle$ are shown. A magnetic field ($B = 0.002$) leads to spin relaxation towards larger spin values. The parameters are $T = 0.0002$ (lower than before), $K_2 = 0.04$ and otherwise as in Fig. 2(a). Inset: Probabilities after the bias voltage is suddenly switched off in the steady state reached for $V = 0.207\,\mathrm{V}$.

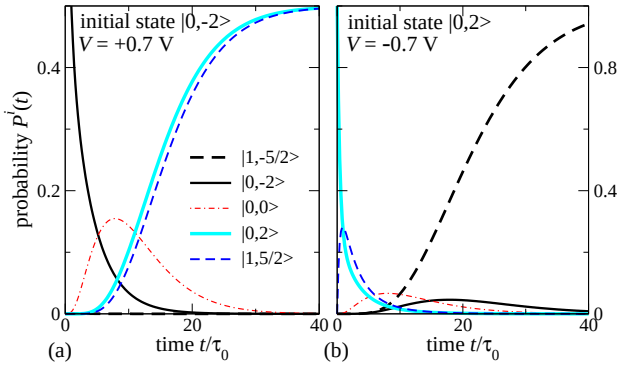

FIG. 5: (color online). Probabilities of molecular states after initial preparation in state (a) $|0,-2\rangle$ and (b) $|0,2\rangle$ as functions of time at the bias voltage (a) $V = 0.7\,\mathrm{V}$ and (b) $-0.7\,\mathrm{V}$. The right lead is ferromagnetic with a ratio of densities of states of $D^{\mathrm{R}}_{\downarrow}/D^{\mathrm{R}}_{\uparrow} = 0.001$. There is no applied magnetic field. The other parameters are as in Fig. 4 except for the *much higher* temperature $T = 0.02$.

field to many molecules and address a specific one with the bias voltage. In the second step the bias is switched off. The inset of Fig. 4 shows that the system then relaxes towards the target state $|0,2\rangle$ on the timescale τ_0.

This writing scheme is problematic because it requires to reverse a large magnetic field between switching events, which is a very slow process. It also requires very low temperatures. We can overcome these problems by using one ferromagnetic and one nonmagnetic lead: In this case one can write the spin information in *zero* magnetic field. The ferromagnetic lead R is modelled by different densities of states D^{R}_{σ} for $\sigma = \uparrow, \downarrow$ electrons. We set $D^{\mathrm{R}}_{\downarrow}/D^{\mathrm{R}}_{\uparrow} = 0.001$ so that the lead is essentially a halfmetallic ferromagnet. Figure 5 shows that one can switch the spin polarization in *both* directions on the timescale of typical spin relaxation times only by applying a bias voltage. For $V > 0$, Fig. 5(a), the electrons flow from right to left. Since $D^{\mathrm{R}}_{\downarrow}$ is small, nearly all electrons have spin up. Due to exchange scattering between electron spin and local spin, the latter is *increased*. For $V < 0$, Fig. 5(b), the electrons flow from left to right. Spin-down electrons are essentially trapped on the molecule until they perform a spin exchange with the local spin, which *decreases* the local spin. Importantly, no fine tuning of the bias voltage is required. Furthermore, the temperature need not be small—Fig. 5 is calculated with T close to room temperature.

If one lead is ferromagnetic, the current is generally spin-polarized even in the steady state. Then the total transmitted spin, Eq. (8), diverges. However, we can define the *excess* transmitted spin in a certain state relative to the steady state, $\Delta S^{\alpha}[\mathbf{P}] = \int_0^{\infty} dt\,[I^{\alpha}_s(t,\mathbf{P}) - \langle I^{\alpha}_s\rangle]$. This quantity exhibits spin amplification as in the case of nonmagnetic leads.

Conclusions.—We have studied the inelastic charge and spin transport through a magnetically anisotropic molecule weakly coupled to metallic leads. The three processes crucial for molecular memory applications—writing, storing, and reading information—can be implemented in such a device. The information storage is affected by spin relaxation, which can be very slow for large easy-axis anisotropy. Also due to the anisotropy, application of a bias voltage to a molecule in a spin-polarized state can lead to the transfer of an exponentially large spin from one lead to the other. We propose that this giant spin amplification could be used to read out the spin information. Finally, we also propose a scheme to write the information, which does not rely on the application of a magnetic field but uses one ferromagnetic lead.

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