Dynamic control of magnetic nanowires by light-induced domain-wall kickoffs

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Controlling the speed at which systems evolve is a challenge shared by all disciplines, and otherwise unrelated areas use common theoretical frameworks towards this goal. A particularly widespread model is Glauber dynamics,⁶ which describes the time evolution of the Ising model and can be applied to any binary system.⁴–⁷ Here we show, using molecular nanowires under irradiation, that Glauber dynamics can be controlled by a novel domain-wall kickoff mechanism. In contrast to known processes, the kickoff has unambiguous fingerprints, slowing down the spin-flip attempt rate by several orders of magnitude, and following a scaling law. The required irradiance is very low, a substantial improvement over present methods of magneto-optical switching.⁸–⁹ These results provide a new way to control and study stochastic dynamic processes. Being general for Glauber dynamics, they can be extended to different kinds of magnetic nanowires and to numerous fields, ranging from social evolution to neural networks and chemical reactivity.³,⁴

The Ising model, which describes networks of interacting objects that can assume only two values, is ubiquitous in scientific research, because it is applicable to any binary system. The evolution of Ising systems is normally described using Metropolis dynamics, which, in one dimension, can be solved exactly and is called Glauber dynamics. It finds extensive application in areas as different as social sciences,⁶ polymer⁴ and surface kinetics,⁴ neural networks,⁶ and magnetism.⁶–⁷ A recently-reported class of molecular magnetic nanowires, called single-chain-magnets (SCMs), are well-suited for exploring this dynamics: they have negligible interchain interactions and their molecular structure allows an in-depth study using analytical models.⁴ SCMs, along with single-molecule-magnets,⁶ constitute one of the only two classes of molecular materials that show magnetic hysteresis without the onset of three-dimensional magnetic ordering. Controlling the dynamics of these systems by light would be an extremely appealing result. Switching the magnetization of materials is a prerequisite for spintronics¹⁰–¹², quantum computation¹¹ and magneto-plasmonics,¹⁰ and its achievement in bulk systems, using electrons, electric fields, and laser pulses, represented scientific and technological breakthroughs. Decreasing the magnetization reversal energy, in particular, would make the manipulation of the information easier.¹⁰–¹⁵ Now new mechanisms need to be devised for nanomagnets,¹⁵ which are necessary for miniaturization and whose physics is different from that of bulk systems. Slow-relaxing magnetic molecules are model systems for these studies; they clearly show quantum phenomena and are candidates for spintronic and single-molecule devices.¹⁶ For these reasons, for the past twenty years, scientists have been trying to switch their dynamics by light; without success, so far. Here we introduce a new scheme of optical switching, which acts on the system by altering the magnetic intrachain exchange interaction, J, so as to kickoff a domain wall. In contrast to charge-transfer

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processes\(^{19,20}\), this principle can be applied to any Ising network, and does not need one to chemically design a material around it. Ising spins can assume only two values, \(S_i = \pm 1\), and the magnetization reversal starts with a single spin-flip, which needs to overcome a barrier associated with \(J\) (Fig. 1a). This creates a very narrow domain wall that, in Glauber dynamics, moves along the chain at no energy cost, by a random walk process. The resulting relaxation time is: \(\tau = \tau_0 e^{\Delta E/\kappa} \), where \(\kappa\) is the Boltzmann constant, \(\tau_0\) the inverse of the spin-flip attempt rate and \(\Delta E\) the nucleation energy cost. Our kickoff mechanism introduces a new element in the dynamics by turning \(J\) at a chain site into a lower value, \(J_{\text{exc}}\) (Fig. 1b). We propose to achieve this in SCMs by producing a localized electronic excitation (Frenkel exciton) by irradiation, so as to locally alter the spin density. If the exciton lifetime \(\tau_{\text{exc}}\) is longer than the inverse of the spin-flip attempt rate, the domain wall can nucleate at the irradiated site with a reduced energy barrier, \(\Delta E_{\text{exc}}\). After nucleation, the domain wall can freely propagate only when the exciton has disappeared, leading to an expected increase of the \(\tau_0\) parameter to a value close to \(\tau_{\text{exc}}\). The dynamics in the presence of light-induced kickoffs should thus follow a law: \(\tau_{\text{exc}} = \tau_{\text{exc}} e^{\Delta E_{\text{exc}}/\kappa} \), with \(\Delta E_{\text{exc}} < \Delta E\) and \(\tau_{\text{exc}} \gg \tau_0\) (see Supplementary Sections S3 and S4 for details and related movies).

The first SCM investigated is \([\text{Co(hfac)}_2(\text{NIT-PhOMe})]\) (ref. 21), where hfac is hexafluoroacetylacetonate and NIT-PhOMe stands for 2-(4'-p-methoxyphenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (Fig. 2a). The system is composed of Co(II) magnetic centres (effective \(S = 1/2\) and \(G \approx 7\) at low \(T\)) surrounded by hfac molecules and bridged by organic radicals (isotropic \(c = 1/2\) and \(g = 2\) centres). It crystallizes in the \(P3_1\) space group and the unit cell contains three repeating units, with the chains extending along the crystallographic axis \(c\). Its strongly Ising character has been confirmed experimentally\(^{21,22}\) and theoretically\(^{23}\) and the Hamiltonian for a chain of \(N\) spins is:

\[
H = -J \sum_{i=1}^{N/2} (S_{2i-1}S_{2i} + S_{2i+1}S_{2i}) - \mu_B H \sum_{i=1}^{N/2} (gS_{2i+1} + GS_{2i})
\]

Where \('\mu_B\', the Bohr magneton'. The exchange interaction \(J < 0\) is antiferromagnetic but the Landé factors of the Co and radical sites, \(G\) and \(g\), do not compensate each other, giving rise to a ferrimagnetic chain with an overall easy axis along \(c\). This is no complication for the dynamics, as the ferrimagnetic structure can be mapped onto a ferromagnetic one\(^2\). A convenient wavelength for irradiation is at 632.8 nm, where the absorption bands do not overlap and only one type of exciton is formed (see discussion in the Supplementary Section S2).

To measure the effect of light on SCMs we built a specialized set-up (Fig. 2b and Supplementary Section S1) in which the magnetic torque of a single crystal is measured as the capacitance variation produced by the deflection of a CuBe cantilever, which can be rotated with respect to the external magnetic field \(H\). The set-up overcomes current problems in photomagnetic studies: the high sensitivity of the set-up allows probing of tiny single crystals, thus ensuring that all chains are iso-oriented and that the whole crystal is irradiated. The CuBe cantilever minimizes undesired heating effects as it is reflecting, non-absorbing and a good heat conductor.

A crystal of \([\text{Co(hfac)}_2(\text{NIT-PhOMe})]\) is placed with the \(c\) axis along the cantilever beam direction (Fig. 2b). The torque signal at 10 K (Fig. 2c) is zero for \(c\parallel H\) (\(\theta = 0°\)) and for \(c\perp H\) (\(\theta = 90°\)), indicating an anisotropic paramagnet. The many peaks observed are due to the non-collinear orientation of the Co(II) axes in the chain (Fig. 2a) and will be discussed elsewhere, being of no interest for the kickoff process (Supplementary Section S3). On lowering \(T\), a non-zero signal is observed for \(c\perp H\) (Fig. 2c), owing to the magnetization dynamics becoming slower than the measurement time. This signal increases as \(H\) rises and, for high fields, the curves become steep around \(c\perp H\) (Fig. 2d). For low fields the curve shows a plateau at \(c\perp H\), and this field range, being the less sensitive to errors in \(\theta\), is best suited to investigate the slow relaxation.

From the exponential decay of this signal we extracted the magnetization relaxation time \(\tau\) (Supplementary Section S5). In the absence of irradiation, we obtained the same Arrhenius law reported in the literature\(^{22}\) (\(\Delta E/\kappa_B = 153 \pm 7\) K and \(\tau_0 = 3.8 \pm 0.6 \times 10^{-11}\) s). Irradiation immediately induces a much faster decay (Fig. 3a) and, as soon as light is turned off, the behaviour is completely reversed to the slower dynamics. Under continuous irradiation (Fig. 3b), the decay becomes biexponential (Supplementary Section S1), and two Arrhenius plots can be
simultaneously extracted. One Arrhenius plot can be reproduced with the same parameters as the non-irradiated system (Fig. 3c) and corresponds to the chains that relax via the standard Glauber mechanism, even under irradiation. The second Arrhenius plot (Fig. 3d) shows a different energy barrier, $\Delta E_{\text{exc}}/k_B = 105 \pm 7$ K, which is largely independent of the laser irradiance $I$. The intercept $\tau_{\text{exc}}^0$ decreases continuously on increasing $I$ (from $1.4 \times 10^{-7}$ s for 0.425 $\mu$W cm$^{-2}$ to $2.7 \times 10^{-8}$ s for 1.7 $\mu$W cm$^{-2}$), but always remains orders of magnitude higher than $\tau_0$, the value for the non-irradiated case.

First of all we quantify laser-induced heating. The chains that relax with the normal mechanism are intermingled with the fast-relaxing ones, and experience the same thermal bath. Acting as an internal thermometer, they offer the most accurate way of probing the temperature of the sample. Heating would shift the Arrhenius plot; however the shift detected under maximum irradiation corresponds to a temperature rise of less than 70 mK, which is negligible for the scale of the effects we are investigating (Fig. 3c). Heating also contrasts with all our observations about the faster process. First, heating increases the spin-flip rate and would lead to a decrease in $\tau_0$, whereas a marked increase is observed. Second, for any activated process, heating can shift the Arrhenius plot, but cannot alter the barrier. Third, the switching from one dynamics to the other is faster than the time resolution of our apparatus (500 $\mu$s), whereas heating effects normally have a slower onset.

In contrast, all data agree with the kickoff mechanism. Frenkel excitons are created with a probability $\partial P(I)/\partial t = (\varepsilon \rho n(1-r))I/\hbar \nu$, where $t$ is time, $\varepsilon$ the absorption cross section, $\rho$ the fraction of absorbing sites, $\hbar \nu = 1.96$ eV the irradiation energy, $n$ the refractive index, $r$ the reflection coefficient and progressive photons absorption along the optical path in the crystal can be accounted for. Writing the rate equation for the number of ‘up’ (non-reversed) spins in a chain, $N^\uparrow$:

$$N^\uparrow(t + dt) = N^\uparrow(t) - P(I)N^\uparrow(t) \frac{dt}{\tau_0 e^{\Delta E/k_B T}} - [1 - P(I)]N^\uparrow(t) \frac{dt}{\tau_0 e^{\Delta E/k_B T}}$$
is used, and this scaling behaviour is indeed observed (Fig. 4b). Eventually, we are able to explain the $\Delta E_{\text{exc}}$ value and understand the nature of the Frenkel exciton by ab initio methods. Calculations were performed with an occupation-restricted multiple active space on one repeating unit of CoPhOMe (Supplementary Section S6). The results indicate an electronic transition between triplet states, involving a spin density transfer between localized $\pi^*$ orbitals of the radical and a simultaneous excitation of Co(II) to a low-spin configuration. The resulting electron redistribution during the exciton lifetime affords a theoretical ratio $J/f_{\text{exc}} = 1.3$, in good agreement with the experimental observation $\Delta E/\Delta E_{\text{exc}} = 1.4 \pm 0.1$.

These results demonstrate that the dynamics of the Ising model can be controlled using external stimuli that locally alter the exchange interaction. In our experimental demonstration we switched molecular nanowires with light, using powers thousands of times lower than in previous optical switching methods.\textsuperscript{26} This manipulation of stochastic dynamic processes is extremely clean, leading to fingerprint signatures and scaling laws. These observations can be used, in material science, to better study domain-wall displacements\textsuperscript{28} and solitons in discrete lattices\textsuperscript{29} and constitute a starting point to control correlated spin systems with external stimuli. Attempts are under way to use the mechanism in combination with high-resolution imaging\textsuperscript{29–30}, so as to obtain real-time control and reading of inorganic nanowires and self-assembled chains of magnetic adatoms. For nanoelectronics\textsuperscript{12,16} and molecular spintronics\textsuperscript{9}, the kickoff affords external control of molecular spin-valves\textsuperscript{31} and a magnetic fingerprint in single molecule measurements\textsuperscript{9}. It can also be applied to the dynamics of mechanical switches and the related study of phasons\textsuperscript{4} and order–disorder transitions.

These results are not limited to materials science, but are expected to affect all areas where Glauber dynamics is employed. When mapped onto scale-free networks, they could be used even for the modelling of opinion dynamics\textsuperscript{9}. In polymer kinetics\textsuperscript{4} they can model the reduced activation energy at some specific sites, such as those influenced by a catalyst. As regards biological problems, the fields of neural networks\textsuperscript{5} and biomembranes make heavy use of Ising models, and several natural processes can produce preferential sites for nucleation.

Received 26 April 2011; accepted 23 October 2012; published online 2 December 2012

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**Acknowledgements**

We acknowledge financial support from Italian MIUR, German DFG (SPP1601, SFB-TRR21), the Humboldt Stiftung (Sofja Kovalevskaja award) and the Baden-Württemberg Stiftung (Kompetenznetz Funktionelle Nanostrukturen). We thank K. Kern, D. Wiersma, J. Wrachtrup and R. Sessoli for helpful discussions, L. Cavigli and M. Gurioli for the depletion control measurements and L. Sebeke for the movies.

**Author contributions**

F.E.H., E.H. and L.B. developed the experimental set-ups and performed the torque measurements. L.B., M.G.P. and A.R. developed the kickoff model. F.T. performed the *ab initio* calculations. L.B. devised the experiment, synthetized the samples and wrote the paper. All authors discussed the results and contributed to the manuscript.

**Additional information**

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to L.B.

**Competing financial interests**

The authors declare no competing financial interests.