Electronic Supplementary Information:

Selective and Directional Actuation of Elastomer Films Using Chained Magnetic Nanoparticles

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Preparation and Characterization of Chained Magnetic Polymer Nanocomposite Films:

Oleic acid-functionalized magnetite (Fe_3O_4) magnetic nanoparticles (MNPs) with an average size of 29 nm were synthesized according to an established method.[S1] 0.71 g of iron (III) acetylacetonate and 0.41 g of 4-biphenylcarboxylic acid were dissolved in a mixture of 2 mL of oleic acid and 10 mL of benzyl ether in a 100-mL, three-necked, round-bottomed flask. The mixture was degassed under vacuum at room temperature for 1 h and backfilled with nitrogen. The flask was then heated at a rate of 15 °C min^{-1} and held at 290 °C for 30 min before cooling to room temperature. Excess methanol (12-15 mL) was added to 10 mL of the MNP stock solution, and the mixture was centrifuged at 8418 *g* for 5 min. The sedimented MNPs were resuspended in 5 mL of tetrahydrofuran (THF) and centrifuged again (no methanol added). The purified MNPs were suspended in THF. For characterization by TEM, a small volume of the purified MNPs was further diluted in THF, which was drop cast onto a Cu TEM grid coated with an ultrathin carbon film. The MNP size was measured using ImageJ by averaging measurements taken of each MNP in two orthogonal directions. A histogram of the size measurements for 112 MNPs is presented in Figure S1. The average MNP size was 29.4 ± 3.5 nm.

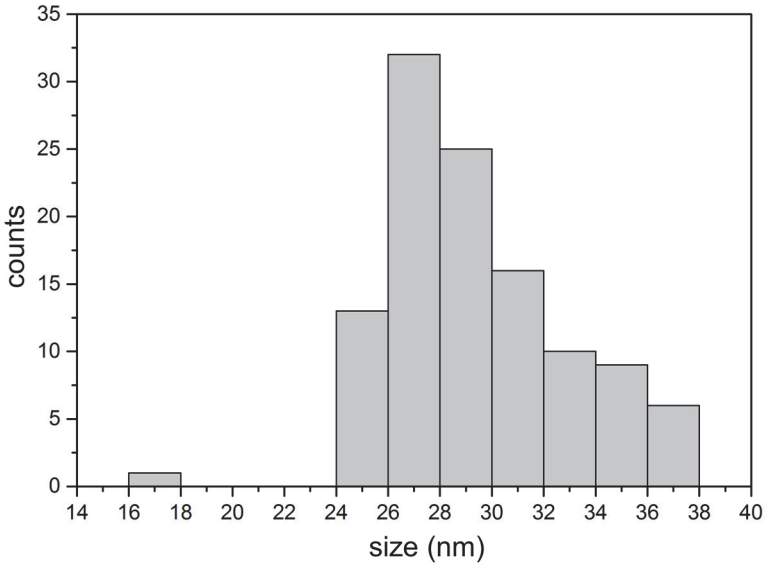


Figure S1. Histogram of measurements of the MNP size from TEM images.

Irogran PS455-203, a thermoplastic polyurethane (TPU) provided by Huntsman Corporation, was used as the elastomer for film preparation. Irogran was dissolved in THF containing the MNPs and cast in a poly(tetrafluoroethylene) (PTFE) boat in a uniform 200 Oe (15.9 kA/m) magnetic field (generated by a GMW 3472-70 electromagnet with a pole cap separation of 60 mm) to obtain the chained samples, which contained 4.0 wt% of Fe_3O_4 MNPs. This value is based on the saturation moment measured by SQUID magnetometry performed at 300 K using a Quantum Design MPMS 3 SQUID VSM.

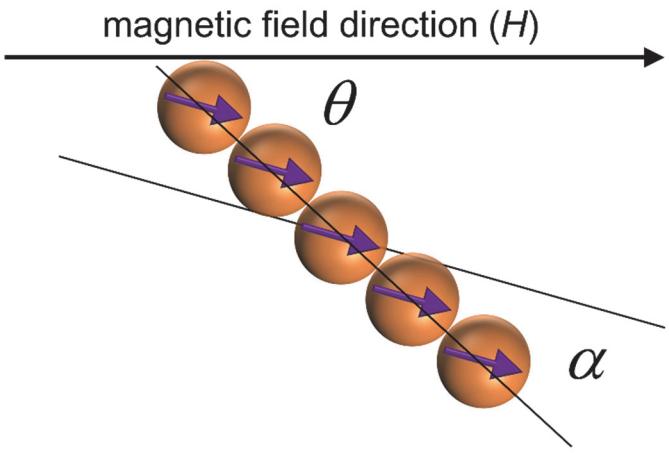
Alignment and Bending Studies:

To study the response in uniform magnetic fields, a cross-shaped sample with average arm length of 20 mm, width of 4 mm, and thickness of 121 μm was mounted by its center on a stage. The entire assembly was placed between the poles of a GMW 3472-70 electromagnet with a pole cap separation of 60 mm. The position of a parallel arm at different applied fields was monitored to give the dependence of the bending angle, θ, on the applied magnetic field strength, H. θ was measured at the middle of the arm. In another experiment, the sample was rotated at a rate of 3.7 rpm under a static applied field of 7.2 kOe (570 kA/m). For studying actuation in a magnetic field gradient, the sample was pinned flat on a rotating stage (1.2 rpm), and a FeNdB permanent magnet was positioned above the edge of the sample. The bending behavior of each arm was observed as it passed under the magnet.

Modelling Actuation Behavior in Uniform Magnetic Fields:

MNPs are treated as single-domain, spherical nanoparticles assembled into parallel, non-interacting chains of one MNP width. Magnetocrystalline anisotropy and thermal energy are neglected, giving these MNPs zero coercivity and eliminating the effect of superparamagnetism randomizing the MNP magnetization directions. The magnetization behavior of MNPs without dipolar coupling in this model is a step function, matching a Langevin function describing a superparamagnet at 0 K temperature. In this model and the associated experiments, dipolar interactions among MNPs, alignment of the magnetic moments within the magnetic field, and gravity determine the behavior.

When the sample arm (and hence the chains) is at a given bending angle, θ, with respect to the horizontal external field, H, the individual MNP dipoles are rotated by a moment angle, α, where $\alpha < \theta$, as depicted below:



The magnetic dipolar interaction energy, E_{12}, between two neighboring MNPs is given by:[S2]

$$E_{12} = \frac{\mu_0}{4\pi}\left(\frac{m_1 m_2}{d^3}\right)\left(\widehat{m_1}\cdot\widehat{m_2} - 3\left(\widehat{m_1}\cdot\hat{d}\right)\left(\widehat{m_2}\cdot\hat{d}\right)\right),$$

where m_1 and m_2 are the moments of the MNPs, whose unit vectors denote their orientations, and d is the center-to-center interparticle separation, for which the unit vector denotes the axis of their separation. For a chain of identical MNPs, depicted above,

$$\overrightarrow{m_1} = \overrightarrow{m_2} = \vec{m}... \text{ and } \widehat{m_1}\cdot\hat{d} = \cos\alpha \text{ gives}$$

$$E_{12} = \frac{\mu_0}{4\pi}\left(\frac{m^2}{d^3}\right)\left(1 - 3\cos^2\alpha\right).$$

Therefore the net energy for the interaction of each MNP with its two nearest neighbors is $2E_{12}$. For infinitely long chains (i.e., more neighbors at distances of $2d$, $3d$, $4d$,...):

$$E_{1\infty} = 2RE_{12}, \text{ where } R = \sum_1^\infty \frac{1}{n^3} = 1.20.$$

It should be noted that $\sum_1^{20} \frac{1}{n^3} = 1.20$ is 99.9% of the value of the infinite sum expressed above. Consequently, the magnetic interactions for each MNP within our long, finite MNP chains can be approximated using the interactions within infinite chains, where edge effects would apply to substantially less than $20d$ (< 1 μm) at the edges of the film. While edge effects could potentially be significant for μm-scale samples, they can be neglected for our macroscale arms with an average length of 20 mm. The total magnetic dipolar interaction energy, E, for N MNPs within parallel, non-interacting chains is thus given by:

$$E = \frac{0.6\mu_0 N}{\pi}\left(\frac{m^2}{d^3}\right)\left(1-3\cos^2\alpha\right).$$

The (clockwise) torque on the moments caused by chaining is denoted by:

$$T_m = -\frac{dE}{d\alpha} = -\frac{1.8\mu_0 N}{\pi}\left(\frac{m^2}{d^3}\right)\left(\sin 2\alpha\right).$$

This is physically equivalent to generating an opposite torque by the moments on the chains,

$$T_c = \frac{1.8\mu_0 N}{\pi}\left(\frac{m^2}{d^3}\right)\left(\sin 2\alpha\right).$$

T_c acts to rotate the chains and hence the sample arm toward horizontal (counterclockwise). The gravitational torque (clockwise) acting on sample length L and mass w is given by:

$$T_g = -\frac{gwL}{2}\sin\left(90^\circ-\theta\right).$$

T_g opposes T_c to rotate the sample arm (and the chains) downward (clockwise). Mechanical equilibrium gives a relationship between θ and α:

$$T_g + T_c = 0$$

$$-\frac{gwL}{2}\sin\left(90^\circ-\theta\right) + \frac{1.8\mu_0 N}{\pi}\left(\frac{m^2}{d^3}\right)\left(\sin 2\alpha\right) = 0$$

$$\sin 2\alpha = \frac{gwL\pi d^3}{3.6\mu_0 N m^2}\cos\theta.$$

The Zeeman energy for N MNPs in the configuration shown above is given by:

$$E_z = -Nm\mu_0 H\cos(\theta-\alpha).$$

The magnetic torque (T_H) acting on the moments due to the external magnetic field, H, is obtained as the derivative of the Zeeman energy:

$$T_H = -\frac{dE_z}{d\alpha} = Nm\mu_0 H\sin(\theta-\alpha).$$

T_H acts to rotate the moments (counterclockwise) toward the field direction, and the torque on the moments caused by chaining (T_m) acts to align them (clockwise) with chain axis. For equilibrium of the magnetic moments,

$$T_H + T_m = 0$$

$$Nm\mu_0 H\sin(\theta-\alpha) - \frac{1.8\mu_0 N}{\pi}\left(\frac{m^2}{d^3}\right)(\sin 2\alpha) = 0$$

$$H = \frac{1.8m}{\pi d^3}\frac{\sin 2\alpha}{\sin(\theta-\alpha)}.$$

In experiments, the chains are multiple MNPs wide, giving a significant number of side-by-side interactions along with head-to-tail interactions. The effect of side-by-side interactions is to make the total dipolar interaction energy, E, more positive (less favorable). Decreasing the effective moment of the MNPs would give a similar effect. We have thus defined an effective moment,

$$m' = \gamma m = \gamma M_s V,$$

where the disorder parameter, $0 \leq \gamma \leq 1$. M_s is the saturation magnetization and V is the MNP volume, $V = \pi d^3/6$. Therefore, NV is the total volume of MNP core material, which is equal to the weight fraction of MNPs (f) multiplied by the weight of sample (w) and divided by the density (ρ) of Fe_3O_4:

$$NV = \frac{fw}{\rho}$$

$$w = \frac{\rho NV}{f}.$$

The equations describing magnetic and mechanical equilibrium for disordered chains can thus be rewritten,

$$H = 0.3\gamma M_S \frac{\sin 2\alpha}{\sin(\theta - \alpha)}, \text{ where } \sin 2\alpha = \frac{g\rho L}{0.6\mu_0 f \gamma^2 M_s^2} \cos\theta.$$

Since the effects of coercivity and thermal energy are neglected, there is no dependence on the MNP size. From magnetometry measurements of the parallel configuration at 300 K (Figure 1c), the saturation moment is 2.956×10^{-3} emu, and the remanent moment is 1.315×10^{-3} emu. The disorder parameter is thus calculated as $\gamma = 1.315 \times 10^{-3} / 2.956 \times 10^{-3} = 0.445$. Inserting the following values for physical constants and fixed experimental parameters, g = 9.8 m s^{-2}, ρ = 5240 kg m^{-3}, L = 0.02 m, f = 0.0402, M_S (at 20 °C) = 480,000 A m^{-1}, $\mu_0 = 4\pi \times 10^{-7}$ kg m s^{-2} A^{-2}, and 1 Oe = $1000/4\pi$ A m^{-1}, gives:

$$H = 0.598 \frac{\cos\theta}{\sin(\theta - \alpha)} \text{kOe}, \text{ where } \sin 2\alpha = 0.742 \cos\theta.$$

Photos and Schematics of Inward Bending of Parallel Arms Alternating with Lifting:

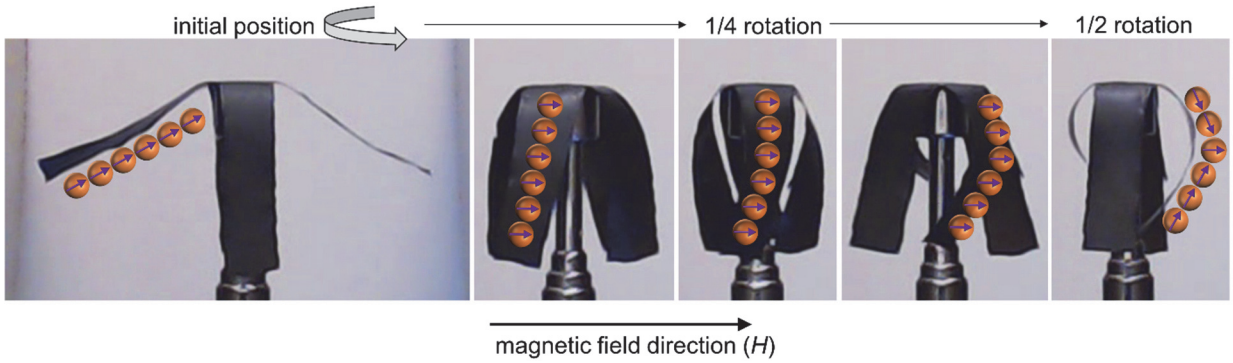


Figure S2. Alternating lifting and bending of parallel arms of the rotating cross in a uniform 3.1 kOe (250 kA/m) field with schematic overlays of the magnetization of chains within the composite. Twisting at ¼ rotation causes inward bending at ½ total rotation.

Modelling Dependence of the Mechanical Bending on the Orientation of the Magnetic Moments:

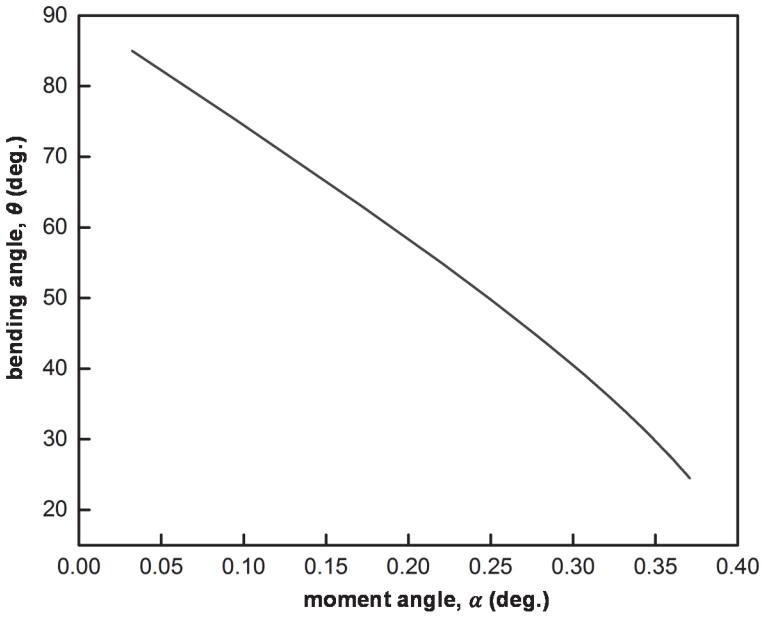


Figure S3. Plot of the calculated dependence of the bending angle, θ, on the moment angle, α, measured with respect to the chain direction for the disordered chains using the relationship, $\sin 2\alpha = 0.742 \cos\theta$.

References:

(S1) D. Kim, N. Lee, M. Park, B. H. Kim, K. An and T. Hyeon, *J. Am. Chem. Soc.*, 2009, **131**, 454–455.

(S2) M. F. Hansen and S. Mørup, *J. Magn. Magn. Mater.*, 1998, **184**, L262–274.