# Supporting Information

All reagents and solvents were purchased from Sigma Aldrich (Gillingham, UK) and used without further purification.

Glucose and glucose oxidase from Aspergillus niger (EC 1.1.3.4, 156 U/mg) and type I peroxidase from horseradish (EC 1.11.1.7, 52 U/mg) were purchased form Sigma-Aldrich (Gillingham, UK). The substrate reagent B containing 3,3′,5,5′-tetramethylbenzidine (TMB) was purchased from BD Biosciences (Oxford, UK).

## Synthesis of low molecular weight compounds

1. The molecular magnet $[(C_3H_7)_2NH_2][Cr_7NiF_8(CH_3(CH_2)_3CHEtCO_2)_{16}]$ (**1**) was prepared according to a literature procedure developed in the group of Winpenny [1]. The protected bifunctional initiator used to start the episulfide emulsion polymerization, S,S'-[ethane-1,2-diylbis(ozyethane-1,1-diyl)] diethanethioate, was prepared according to a literature procedure developed in the group of Tirelli [2]

**Preparation of cross-linked nanoparticles**. 80 mg of Pluronic F127 were dissolved in 10 mL of degassed MilliQ water in a 25 mL Radley's Carousel parallel reactor tube. The system was continuously stirred at 1,000 rpm for 10 min under an argon atmosphere. In a separate vial, under argon atmosphere, the protected bifunctional initiator (0.013 g, 0.061 mmol) was mixed with 0.5 M $CH_3ONa$ in methanol (245 μL) for 10 minutes, to deprotect it. The deprotected initiator and propylene sulphide (PS, 0.4 g, 5.48 mmol, corresponding to 45 PS equivalents per thiol group; overall DP = 90) were then added to the reaction flask, the reaction mixture was further stirred for 10 min, and 2 equivalents of DBU (0.018 g, 0.112 mmol) were finally added to initiate the polymerization. The reaction mixture was stirred under inert conditions for 2 h; the pH was lowered to 9.5 by the addition of acetic acid, and 0.5 equivalents of tetra-functional cross-linker pentaerythritol tetraacrylate (0.03 mmol, 0.010 g) dissolved in dichloromethane (0.3 mL) were then added to the reaction mixture. After 1 minute the pH was brought to 7.4 by adding 5 mL of PBS (50 mM, pH 7.4), in order to minimize the hydrolysis of the cross-linkers. The suspension was additionally stirred for 16 h before purification by ultrafiltration (Amicon Ultrafiltration Cell Model 8200, Millipore, UK) against MilliQ water through 300 kDa MWCO regenerated cellulose membranes (Spectrum Laboratories, UK). For any further use, the concentration of nanoparticles was determined gravimetrically after freeze drying samples of their dispersions. ATR

FT-IR (thin film): 2956 ($\nu_{as}$ $CH_3$), 2920 ($\nu_{as}$ $CH_2$), 2856 ($\nu_s$ $CH_2$), 1740 ($\nu$ C=O), 1450 ($\delta_{as}$ $CH_3$), 1372 ($\delta_s$ $CH_3$), 1170 ($\nu_{as}$ C-O-C, ester), 1100 ($\nu_{as}$ C-O-C in Pluronic F-127), 800-600 $cm^{-1}$ ($\nu$ C-S in PPS).

**Loading of $[(C_3H_7)_2NH_2][Cr_7NiF_8(CH_3(CH_2)_3CHEtCO_2)_{16}]$ (1) in PPS nanoparticles**. The above preparative procedure was modified by adjusting the pH of the reaction mixture to 7.4 after polymerisation, dissolving $[(C_3H_7)_2NH_2][Cr_7NiF_8(CH_3(CH_2)_3CHEtCO_2)_{16}]$ (0.006 g, 0.002 mmol) in THF (0.8 mL) and adding it to the reaction mixture. The dispersion was then left to stir for 10 minutes. The pH was then brought to 9.5 and the tetra-functional cross-linker added. The molecular magnet loading was measured by UV-Vis spectroscopy: an aliquot (typically 3 mL) of the nanoparticle dispersion was freeze-dried and then redispersed in 1 mL THF. The solution was sonicated for 5 minutes and then filtered through a 0.22 μm PTFE filter to remove any colloidal object and its absorption at 615 nm was measured with a UV/Vis spectrophotometer Perkin Elmer Lambda 25 (Perkin Elmer, UK) using the calibration below. EPR spectra were recorded at 5 K on a Bruker EMX spectrometer at Q-band (approximately 34 GHz).

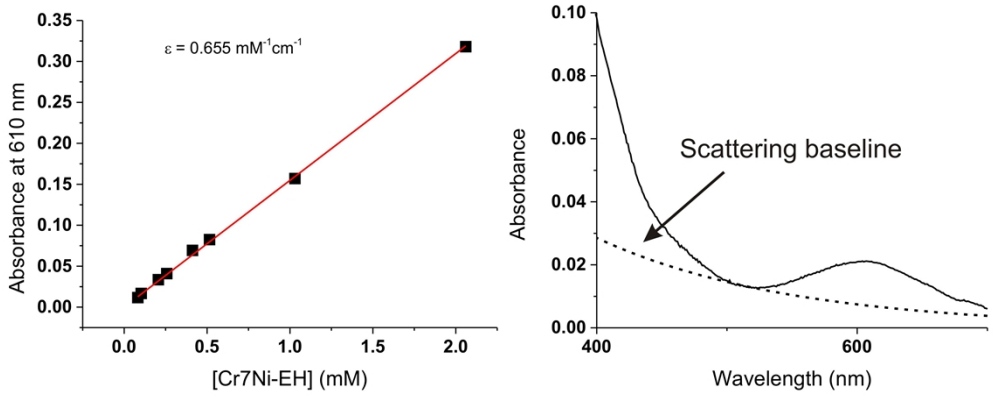


**Figure 1SI**. *Left:* Calibration curve for the absorbance of **1** in THF solution. The calculated extinction coefficient; ε = 0.655 $mM^{-1}cm^{-1}$. ***Right:*** Vis spectrum of loaded nanoparticles (solid line) and scattering baseline used to correct the absorbance values of **1**.

## $T_1/T_2$ relaxivity measurements

Relaxivity measurements of water protons were performed on a Bruker Advance II 400MHz NMR spectrometer. $T_1$ measurements were performed using the t1ir, inversion recovery, pulse sequence. $T_2$ measurements were performed using the Car-Purcel-

Meilboom-Gill (CPMG) inversion-recovery pulse sequence. The water peak intensities were then fit to a monoexponential function using Wolfram Mathematica.

**Oxidation experiments with direct $H_2O_2$ addition**

900 μL of PPS nanoparticles (loaded or unloaded at a concentration of 2.2 mg/mL - solutions contained 10% $D_2O$ for NMR experiments) were introduced into a 1.5 mL Eppendorf tube. 100 μL of a $H_2O_2$ solution (5, 1 or 0.5% in PBS (x5) at pH 7.4) was added, for a final concentration of 0.5, 0.1 or 0.05 respectively (final nanoparticle concentration: 2 mg/mL). The system was left to react for 15, 30, 45, 60 or 120 min. KI (0.013 g, 0.078 mmol) was then added to neutralise the $H_2O_2$. Measurements were then performed on the sample.

**Oxidation experiments with enzymatic production of $H_2O_2$**

The reaction between oxygen and glucose mediated by glucose oxidase (EC 1.1.3.4) allows the *in situ* generation of hydrogen peroxide. Four vials containing 400 μL of a 2.5 mg/mL dispersion of nanoparticles and four with the same volume of plain buffer as a control were prepared. 50 μL of glucose 10, 5, 1 and 0.5 mM respectively were added followed by 50 μL of a 2.69 mg/mL solution of glucose oxidase (final nanoparticle concentration: 2 mg/mL). All the solutions were prepared in PBS (x5). The samples were incubated 1.5 hours at 37 °C and then analysed. The conversion of glucose was quantitative in all cases, as confirmed by the analysis of the hydrogen peroxide produced in the control samples (1, 0.5, 0.1 and 0.05 mM). Specifically, 100 μL of each solution (both the samples to be tested and the standards prepared for the calibration curve) were pipette in a 96-well plate, 50 μL of a freshly prepared 1 mg/mL solution of type I horseradish peroxidase and 50 μL of Substrate reagent B containing 3,3′,5,5′-tetramethylbenzidine were then added and the absorbance values at 420 and 650 nm were recorded on a BIOTek® Synergy 2 multi-mode microplate reader (NorthStar Scientific Ltd., Leeds, UK). If necessary, the samples were subsequently diluted with PBS in order to ensure the readings to be in the linear range of the calibration curve.

**Table 1SI:** $T_2$ values as a function of the exposure to $H_2O_2$ [a].

| | $T_2$ (msec) | | | $T_1$ (msec) | |
|---|---|---|---|---|---|
| | PBS | in $H_2O_2$ (0.5% wt.) | after $H_2O_2$ (KI treated[b]) | PBS | after $H_2O_2$ (KI treated[b]) |
| Control | 3400 ± 93 | 54 ± 2 | 2242 ± 28 | | |
| Nanop.s | 2840 ± 32 | 54 ± 3 | 2333 ± 17 | | |
| Nanop.s + **1** | 659 ± 9 | 56 ± 3 | 333 ± 4 | 3100 ± 80 | 3280 ± 83 |

[a] 30 minutes incubation in the presence of 0.5% wt. $H_2O_2$.
[b] $T_2$ of water protons 90 minutes after the addition of KI, which allows for the complete degradation of residual $H_2O_2$ (see Figure 2SI).

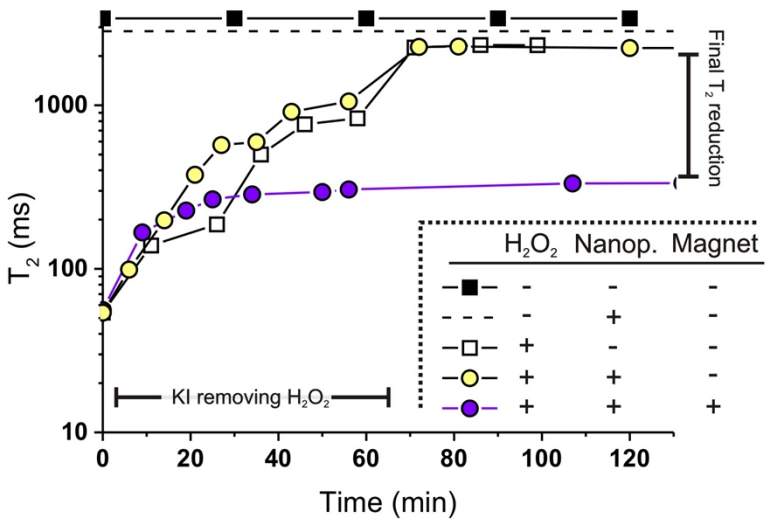


**Figure 2SI.** The presence of unloaded particles has a negligible effect on $T_2$ (dashed line). On the contrary, the presence of $H_2O_2$ (0.5%)lowers the water $T_2$ to values in the region of 50-60 ms, irrespective of the presence of loaded or unloaded particles (empty and colored symbols at time zero). The removal of hydrogen peroxide by KI brings $T_2$ back to values comparable to those of pure water in the absence of particles (empty squares) or in the presence of unloaded particles (yellow circles). However, when magnet-loaded (8.42 nmol of **1**/mg) particles where exposed to $H_2O_2$ and then treated with KI (purple circles) a clear effect of final $T_2$ reduction was apparent.

## References


1. A. McRobbie, A. R. Sarwar, S. Yeninas, H. Nowell, M. L. Baker, D. Allan, M. Luban, C. A. Muryn, R. G. Pritchard, R. Prozorov, G. A. Timco, F. Tuna, G. F. S. Whitehead and R. E. P. Winpenny, *Chemical Communications*, 2011, **47**, 6251-6253.
2. L. Wang, G. Kilcher and N. Tirelli, *Macromolecular Bioscience*, 2007, **7**, 987-998.