Experimental Section

Measurements

IR spectra (200-4000cm^{-1}) were recorded by diffuse reflectance using a Perkin Elmer Spectrum One FT-IR spectrophotometer. Raman spectra were measured with a Renishaw 1000 micro-Raman system. The excitation wavelength was 514.5 nm from an Ar+ ion laser (Laser Physics Reliant 150 Select Multi-Line) with a typical laser power of ~ 20 W cm^2 in order to avoid excessive heating. The 100x magnifying objective of the Leica microscope was capable of focusing the beam into a spot of approximately 1 μm diameter. Transmission electron microscopy (TEM) images were taken on a Hitachi H-7000. The TEM was operated at a beam voltage of 100 kV. Samples for TEM were prepared by deposition and drying of a drop of the powder dispersed in ethanol or distilled water onto a formvar coated 400 mesh copper grid. UV-Visible absorption spectra (200-700nm) were recorded using a Cary 300 scan UV-Vis spectrophotometer. Fluorescence spectra were performed on a LS-50B Perkin Elmer luminescence spectrometer, with a 150W Xenon lamp.

^{1}H T_1 measurements (NMRD) were made in the frequency range 10kHz-20MHz using a Spinmaster Fast Field Cycling Relaxometer operating at a measurement frequency of 9.25MHz. X-Ray powder diffraction was performed using a Siemens-500 X-Ray diffractometer.

Materials

Methanol was dried over magnesium turnings prior to use. Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and ammonium hydroxide (NH_4OH, 0.88M) were obtained from BDH Chemicals. Ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), 4, 4', 4'', 4'''-(21H, 23H-porphine-15, 10, 15, 20-tetrayl) tetrakis (benzoic acid) were all obtained from Aldrich.

3 mM phosphate buffer, pH 7.2, was made up of potassium dihydrogen phosphate (0.023 g; 1.66×10^{-4} mol), potassium hydrogen phosphate (0.023 g; 1.33×10^{-4} mol) and sodium chloride (0.876 g; 1.49×10^{-2} mol) dissolved in 100 mL Millipore water. The pH of the buffer was tested and found to be 7.2.

Preparation of octaaminopropylsilsesquioxane hydrochloride ($T_8NH_3^+Cl^-$)

Concentrated HCl (20 mL) was added to a stirring solution of 3-aminopropyltriethoxysilane (15 mL; 0.063 mol) in dry methanol (200 mL). This mixture was stirred at room temperature for 1 hour, then left to stand in a stoppered round bottomed flask for five weeks. The product began to crystallise out of solution after three weeks. The filtrate was reduced to approximately ¾ of its original volume. The product was obtained in 29.7% yield (2.73g) by filtering the reaction mixture, washing with cold, dry methanol and dried under vacuum.

^{1}H NMR (400 MHz, DMSO-d_6, 25°C): δ 8.25 (s, NH_3, 24 H), 2.83 (t, CH_2N, 16 H), 1.78 (m, $SiCH_2CH_2$, 16 H), 0.78 (t, $SiCH_2$, 16 H). ^{13}C NMR (100 MHz, DMSO-d_6, 25°C): δ 41.01 (s, CH_2N), 20.62 (s, $SiCH_2CH_2$), 8.40 (s, $SiCH_2$). ^{29}Si NMR (300 MHz, MeOH, 25°C): δ -66.4 (s). Mass spectrum: calc. For $C_{24}H_{72}Cl_8N_8O_{12}Si_8$, $[M + H - 8\ HCl]^+$ *m/z* 881.29, found 881.29.

NMRD analysis

The effect of these nanoparticle composites on the water proton spin-lattice relaxation time T_1 has been measured by NMR dispersion (NMRD), allowing the determination of the frequency dependence of the relaxivity r_1 via equation 1 {where T_1(water) is the native relaxation time of the supporting fluid (water) and r_1 is independent of the concentration of the magnetic fluid}.

$$R_{1(obs)} = \frac{1}{T_{1(obs)}} = \frac{1}{T_{1(water)}} + \frac{1}{T_{1(para)}} = \frac{1}{T_{1(diam)}} + r_1[Fe] \quad (1)$$

Preparation of cells for visualisation

Samples were prepared for confocal imaging by fixing the glass coverslip slide with 3% Glutaraldehyde in 0.1M Sodium Cacodylate buffer (pH 7.2). This fixation process was carried out for 1 hour at room temperature. Following this, confocal microscopy slides were fixed on glass slide and imaged.

IR spectra

An IR spectrum of the dried magnetite-$T_8NH_3^+Cl^-$ nanocomposite shows a stretch at 3367 cm^{-1} which incorporates the contributions from both symmetrical (ν_1) and asymmetrical (ν_3) modes of the O-H bonds which are attached to the surface iron atoms. The presence of an adsorbed water layer is confirmed by a stretch for the vibrational mode of water found at 1619 cm^{-1}. Asymmetric Si-O-Si stretches appear at 1261 and 986 cm^{-1}. The N-H wagging and Fe-O vibrations occur at 810 and 584 cm^{-1} respectively. For the porphyrin treated magnetite-$T_8NH_3^+Cl^-$ nanocomposite the stretches at 3367 cm^{-1} and 1603 cm^{-1} remain for OH groups bound to and water molecules associated with the nanoparticle surface respectively. A carbonyl stretch for the benzoic acid is found at 1527 cm^{-1}. Combined contributions for C-H and C-C stretches occur between 1388 and 1089 cm^{-1}. Asymmetric Si-O-Si stretches from the $T_8NH_3^+Cl^-$ stabiliser occur at 1021 cm^{-1}. The N-H wagging and Fe-O stretches occur at 803 and 582 cm^{-1} respectively.

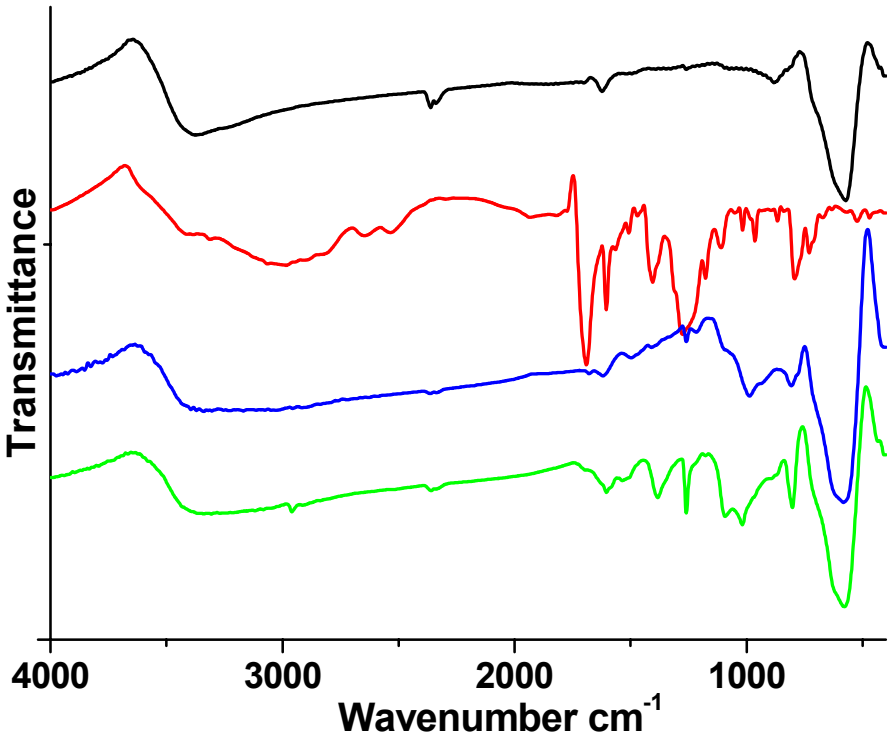

Figure 1S: IR spectra of (from top to bottom) magnetic nanoparticles, porphyrin complex, $T_8NH_3^+Cl^-$ -magnetite nanocomposite and porphyrin-$T_8NH_3^+Cl^-$ - magnetite nanocomposite.

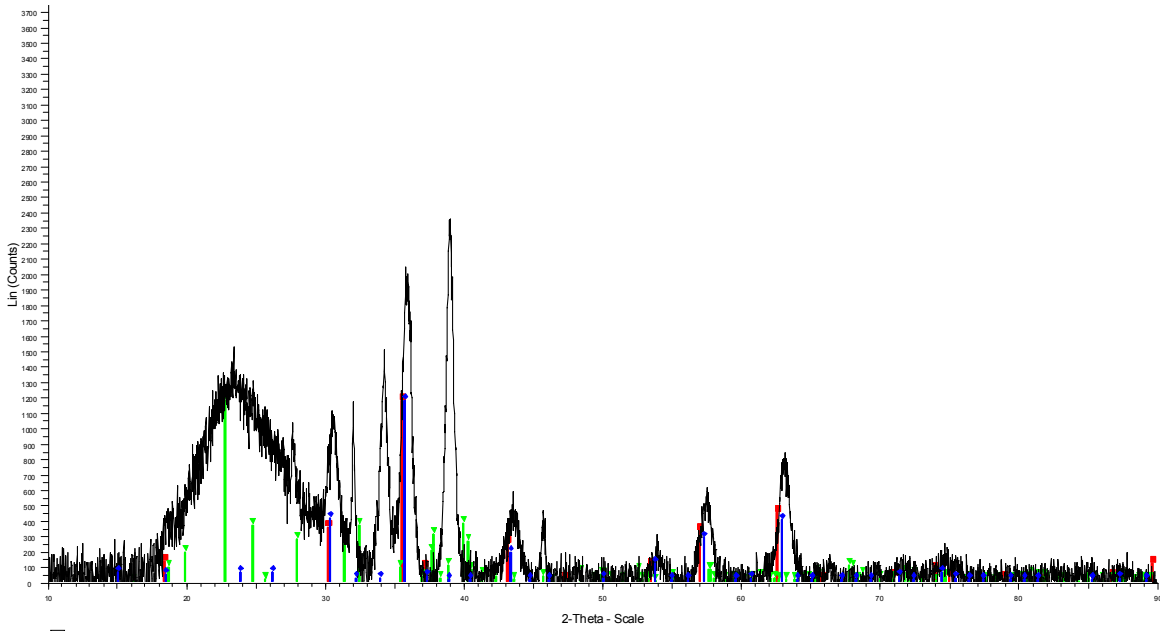

Figure 2S: XRD pattern of porphyrin-$T_8NH_3^+Cl^-$ - magnetite nanocomposite, which overlaps with the JCPDS data for magnetite. The peaks at 30.5 and 34.5 degrees 2θ appear due to the tungsten lamp present in the XRD machine.

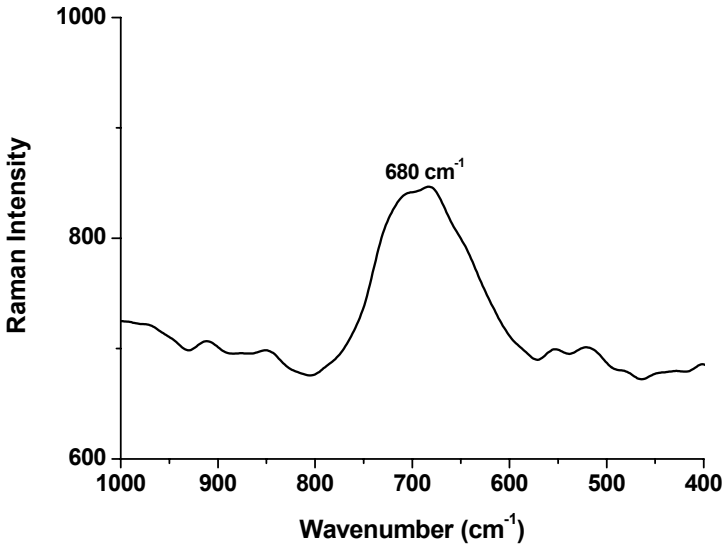

Figure 3S: Raman spectrum of magnetite nanoparticles showing typical peak for magnetite at 680 cm^{-1}.

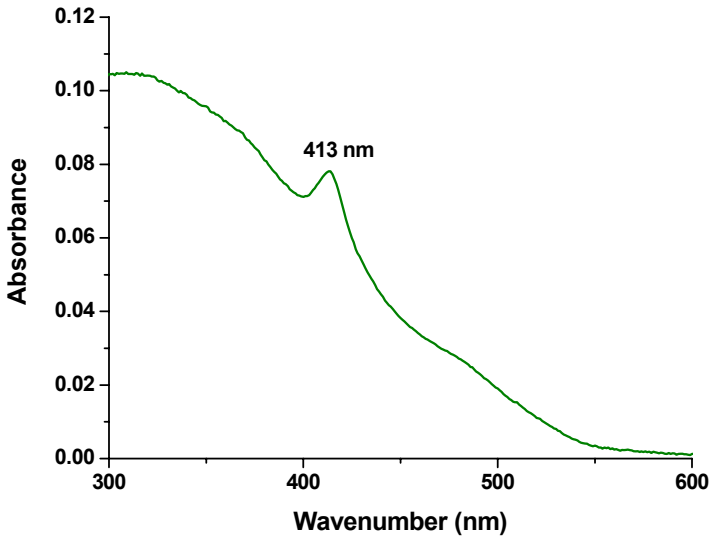

Figure 4S: UV spectrum of porphyrin-$T_8NH_3^+Cl^-$ -magnetite nanocomposite, showing porphyrin peak at 413 nm

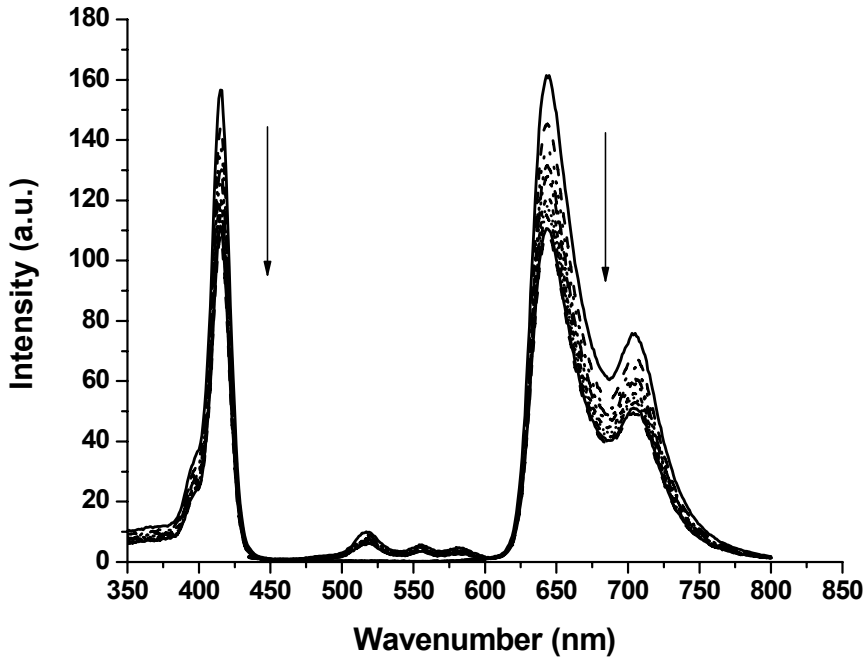

Figure 5S: Fluorescence spectra (emission and excitation) of porphyrin complex with increasing concentration of $T_8NH_3^+Cl^-$. Fluorescence intensity decreases with increasing $T_8NH_3^+Cl^-$ concentration, as seen in spectra for magnetite-$T_8NH_3^+Cl^-$-porphyrin nanocomposite. This observation is due to the interaction of ammonium cations with porphyrin carboxylate groups.[1]

1. A. Flores-Villalobos, H. Morales-Rojas, S. Escalante-Tovar and A.K. Yatsimirsky, *J. Phys. Org. Chem.,* 2002, **15**, 83.

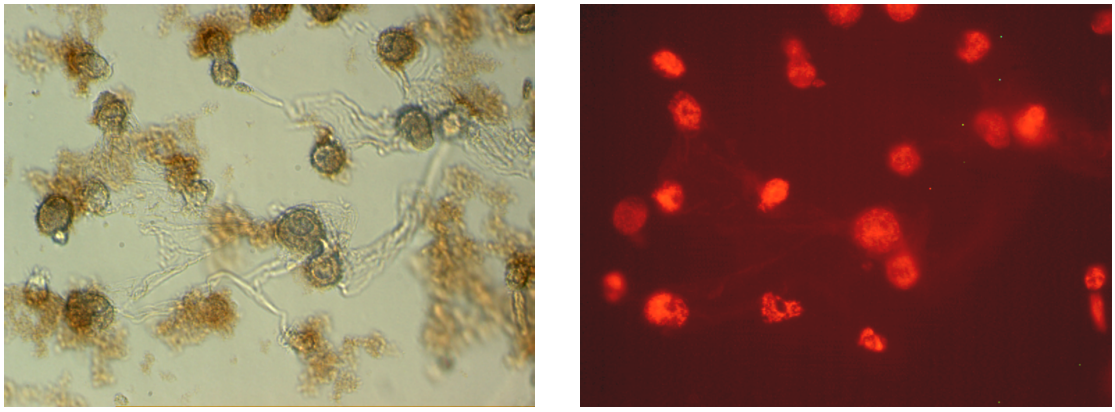

Figure 6S: Porphyrin-$T_8NH_3^+Cl^-$ -magnetite nanocomposites in cultures of macrophages. Left, transmitted light microscopic image of the THP-1 cells interacting with nanocomposite particles. Right, corresponding fluorescent image of the same microscopic field (λ_{ex}= 488 nm, λ_{em}= 650 nm).

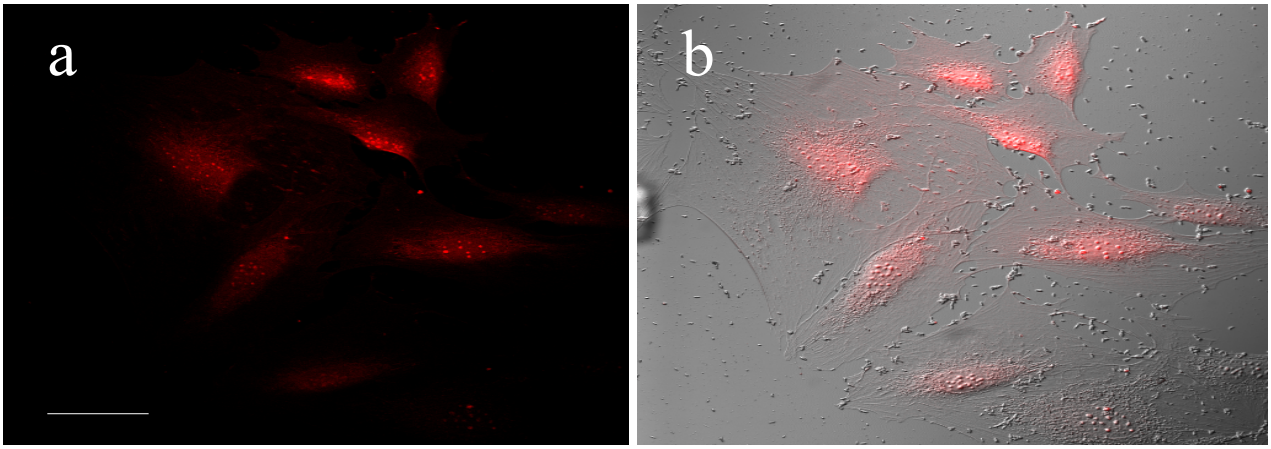

Figure 7S: MC3T3-E1 cell population with internalized nanoparticles. A) Confocal image and B) overlay with phase contrast (mag. x 40, Scale bar = 50 μm). Cells were incubated for 30 minutes at physiological conditions (37°C, 5% CO_2 and 95% RH).

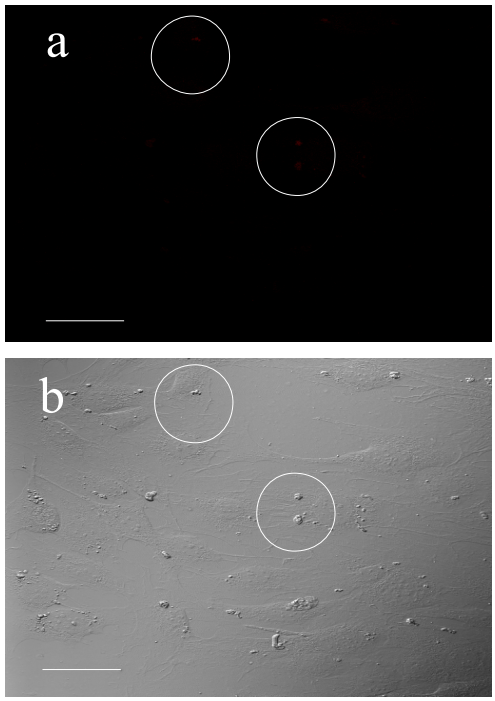

Figure 8S: MC3T3-E1 cells cultured for two days in cell medium mixed with porphyrin (concentration). A) Confocal image showing no uptake by cells of porphyrin dye. Only external big clusters are fluorescent (see circles). B) Matching phase contrast image. (mag. x 40, scale bar = 50 μm).