Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Ce^{3+} Sensitized $GdPO_4:Tb^{3+}$ with Iron Oxide Nanoparticles: A Potential Biphasic System for Cancer Theranostics

Niroj Kumar Sahu, Naorem Shanta Singh, Lina Pradhan, Dhirendra Bahadur*

Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai-400 076, India

**Email:dhirenb@iitb.ac.in*

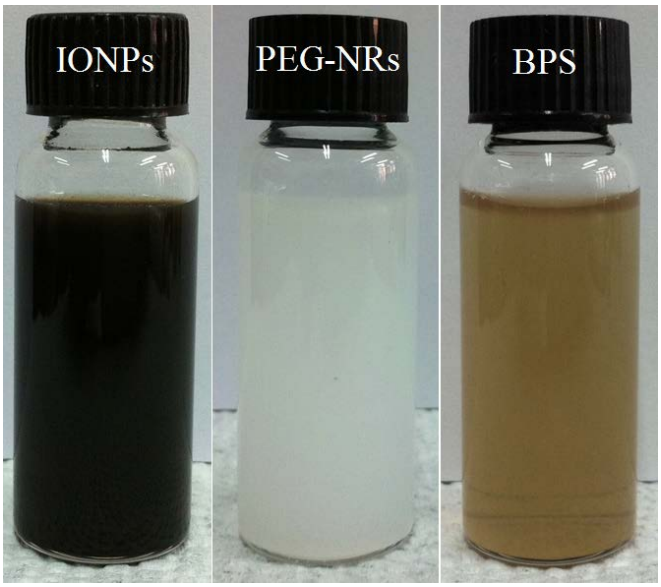

Fig. S1 Visual photographs of individual water dispersed solutions of IONPs, PEG-NRs and BPS.

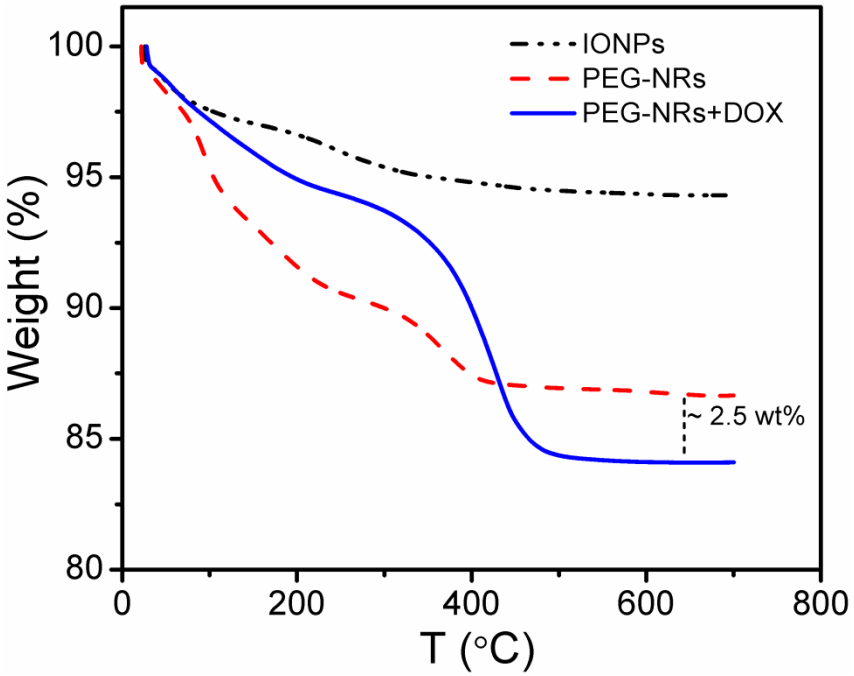

Fig. S2 Weight loss profile of as-synthesized PEG-NRs, IONPs and PEG-NRs+DOX (as indicated in the legend of the graph) with heating. The TG curve was obtained in N_2 with a heating rate of 10 °C/min.

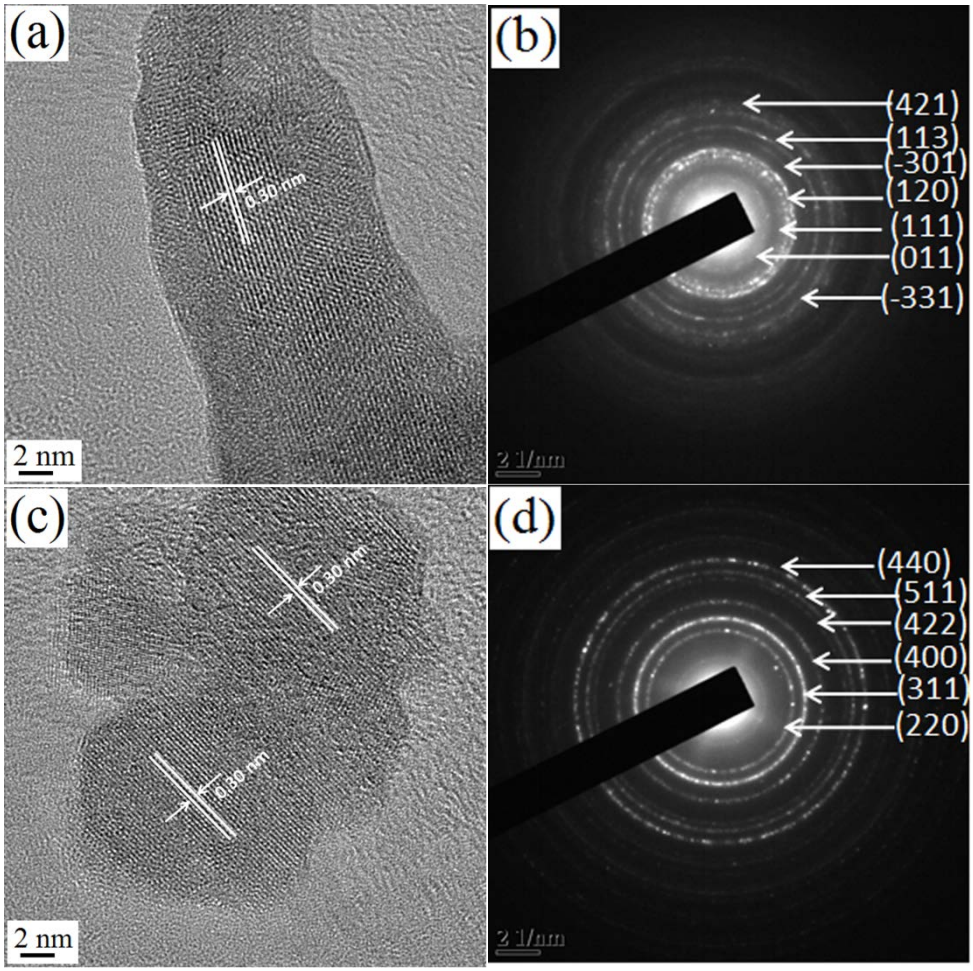

Fig. S3 HRTEM images of (a) PEG-NRs and (c) IONPs are showing the inter-planar spacing and their respective SAED patterns (b and d) show the diffracted planes.

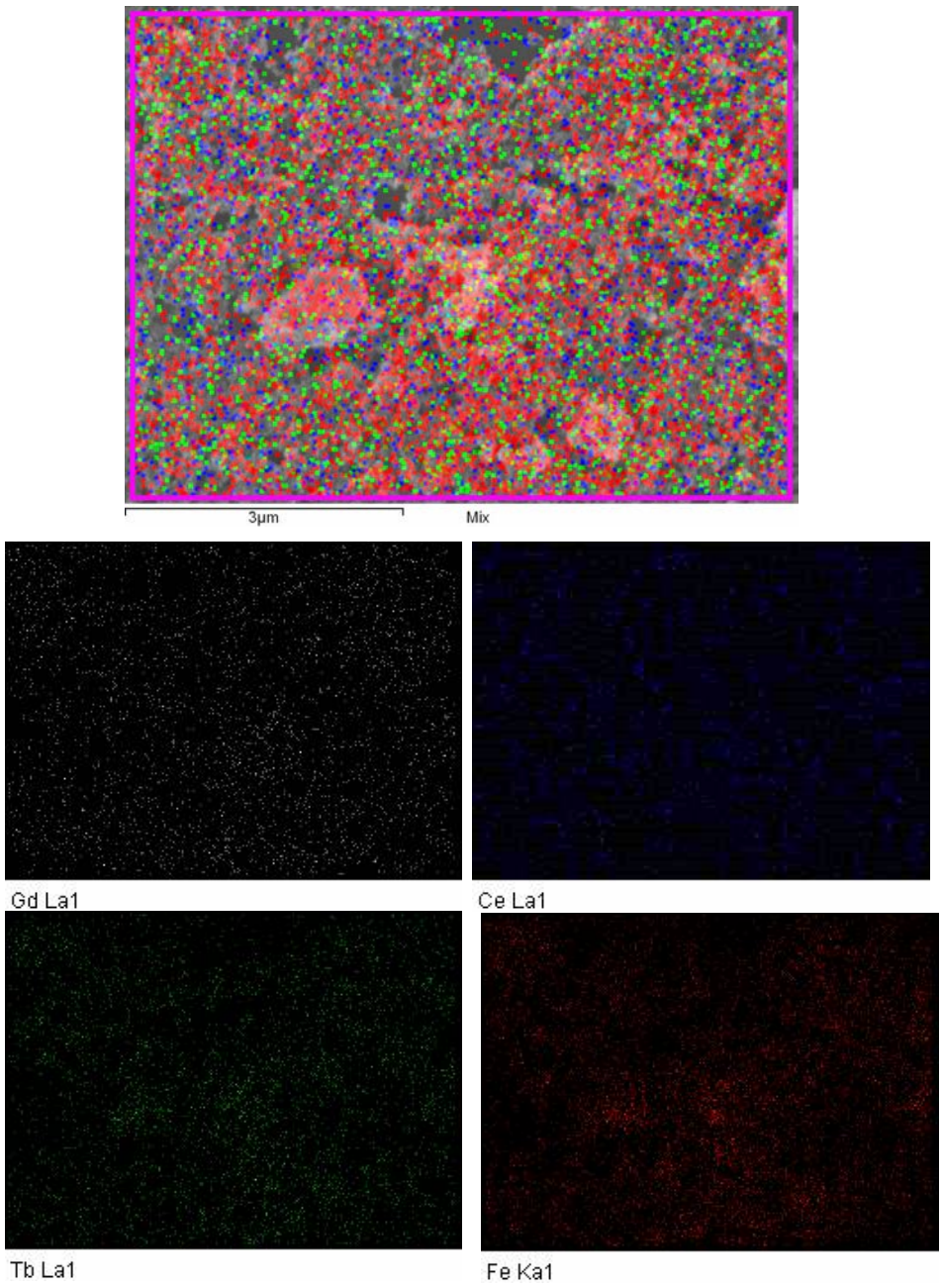

Fig. S4 EDX mapping of the BPS showing the distribution of Gd, Ce, Tb and Fe in the sample.

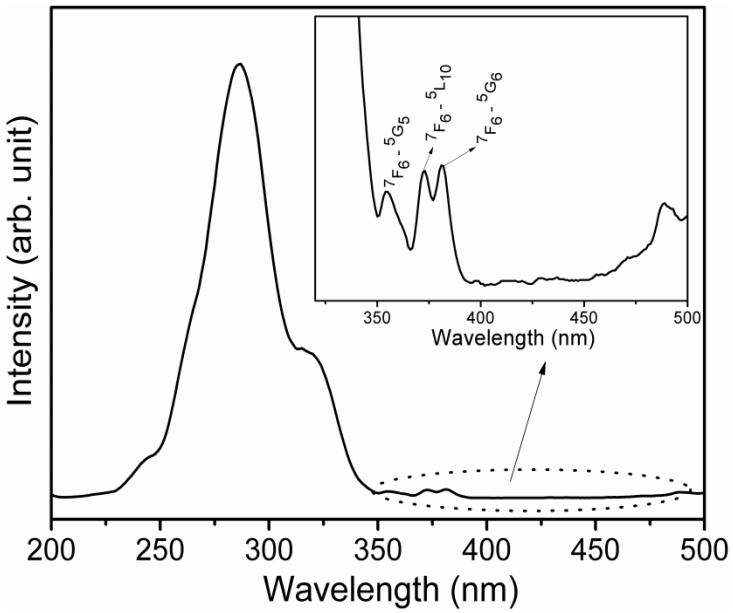

Fig. S5 Excitation spectrum of PEG-NRs recorded with a monitoring emission at 544 nm. A part of the spectrum is magnified and is shown in the inset.

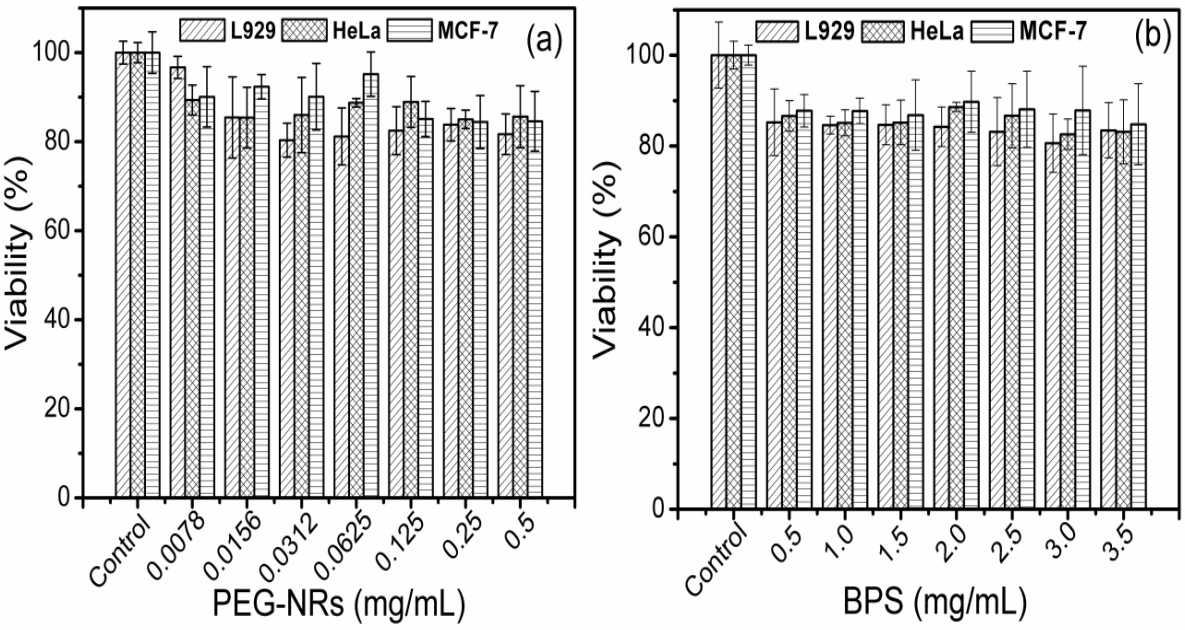

Fig. S6 Viability of L929, HeLa and MCF-7 cells after incubation with different concentration of (a) PEG-NRs and (b) BPS for 24 h.

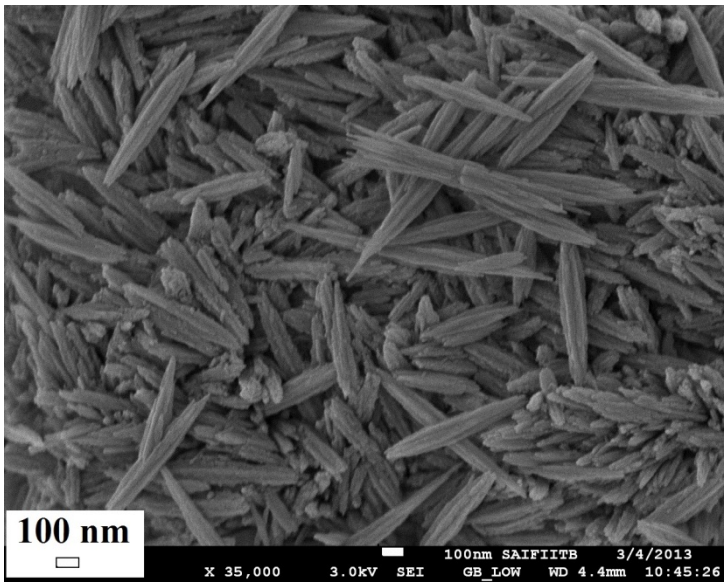

Fig. S7 FESEM image of $GdPO_4$ nanoparticles coated with PEG-3000.

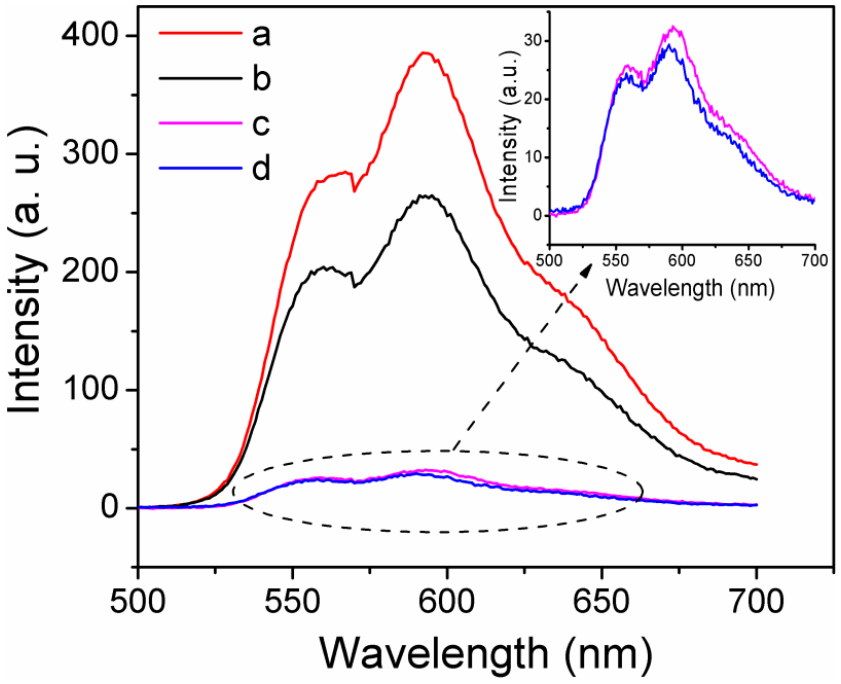

Fig. S8 Fluorescence spectra of (a) DOX solution (50 µg/mL) and the supernatants (unloaded part) after loading of DOX in (b) PEG-3000 coated $GdPO_4$ nanoparticles, (c) PEG-NRs and (d) BPS. 50 µg of DOX and 10 mg of the particles were incubated for 24 h in all cases. The excitation wavelength is 470 nm and the emission range is scanned between 490 and 700 nm. Inset is the magnified one of the encircled plots.

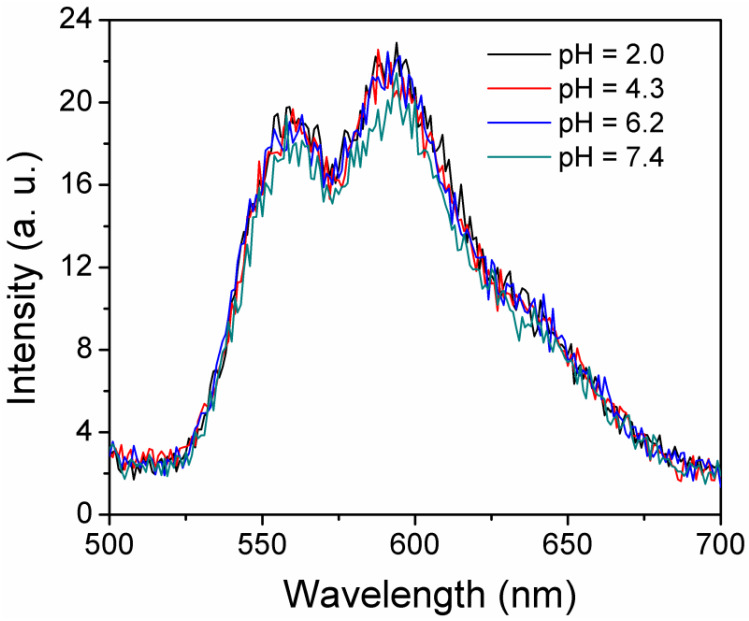

Fig. S9 Fluorescence spectra of the 1 mL DOX solution (10 µg/mL) at different pH of 2.0, 4.3, 6.2 and 7.4.

To confirm whether there is any influence of pH on fluorescence intensity of DOX, we have recorded the fluorescence spectra of the 1 mL DOX solution (10 µg/mL) at different pH of 2, 4.3, 6.2 and 7.4. No significant variation in intensity was found (Fig. S9). Hence it indicates that the mechanism of drug loading and release is dependent on the change in the nature of the chemical bonding of the drug molecule with the functionalized nanoparticles in different pH environments.

Table S1. Zeta potentials and hydrodynamic diameter of PEG-NRs, IONPs and BPS.

Sample	Zeta potential (mV)	Hydrodynamic diameter (H_d, nm)
PEG-NRs	-26.9	100.7
IONPs	-37.2	118.2
BPS	-31.3	344.3

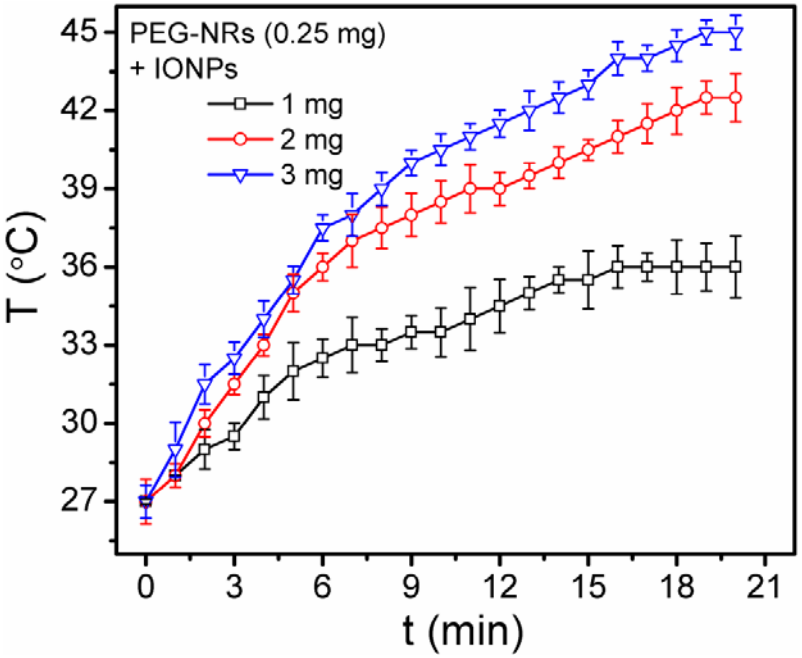

Fig. S10 Temperature (T) versus time (t) plot for an aqueous suspension of biphasic mixture of IONPs with PEG-NRs under ACMF (250 kHz, 460 Oe).

Magnetic fluids (colloidal suspension of magnetic nanoparticles) under an AC magnetic field produce heat loss (power dissipation) by (i) hysteresis loss, (ii) Brownian rotational loss, (ii) Néel's spin relaxation and (iv) eddy current. The heat loss due to hysteresis is ruled out as the magnetic nanoparticles are superparamagnetic in nature and that due to eddy current is negligible as the resistivity of the magnetite NPs is very high ($\rho \sim 10^2$ ohm-cm). So the major contribution of power dissipation (heat loss) comes from the Brownian motion and Néel's spin relaxation. The total heat/power dissipation (P) can be expressed as:

$$P = \mu_0 \pi \chi'' f H_0^2 \qquad (1)$$

Where, μ_0 is the permeability of free space, $f=\omega/2\pi$ is the frequency of the AC magnetic field and χ'' is the imaginary part of the magnetic susceptibility ($\chi = \chi' + \chi'' = M/H$)

$$\chi'' = \frac{\omega\tau}{1+(\omega\tau)^2}\chi \qquad (2)$$

Where τ is the total relaxation contributed from Brownian rotational and Néel's spin relaxations. In Brownian rotational relaxation (τ_B), the magnetic moment aligns with the magnetic field (H) and the particle rotates under an AC field. Brownian relaxation at a particular temperature (T) is given by:

$$\tau_B = \frac{4\pi\eta r_h^3}{k_B T}, \qquad (3)$$

Where, η is the dynamic viscosity of carrier liquid and r_h is the hydrodynamic radius of the magnetic nanoparticles. During rotation, collision with the surrounding medium generates heat. The Néel's spin rotational relaxation (τ_N) is due to the rotation of magnetic spin of a domain from 0 to 180 º which is given by the equation,

$$\tau_N = \tau_0 e^{\frac{K_u V}{k_B T}} \qquad (4)$$

where, K_uV (K_u = anisotropy constant, V = particle volume) is the effective anisotropy energy and the k_BT (k_B = Boltzmann's constant) is the thermal energy at temperature T.

The total relaxation (s) is expressed as,

$$\tau^{-1} = \tau_N^{-1} + \tau_B^{-1} \qquad (5)$$

The heating ability of the water-stable NC suspension was measured from the time-dependent calorimetric measurements using instrument (EASY HEAT, EZLI5060) with 6 cm diameter (4 turns) coil. To maintain the temperature of the coil at ambient temperature, a cooled water circulation surrounding to the coils is provided. During the experiment, 1 mL of water suspended NC (1, 2 and 3 mg/ml of Fe_3O_4 along with 0.25 g of PEG-NRs) was taken in a plastic micro centrifuge tube (2 ml) and placed at the center of the coil to minimize the heat loss. The applied frequency was 250 kHz. Samples were kept under varying AC magnetic field (by varying the current, *i*) to reach the desired hyperthermia temperature. For the conducted experiments, the magnetic field was calculated from the relationship:

$$\mathrm{H} = \frac{1.257ni}{\mathrm{L}}\ \mathrm{Oe} \qquad (6)$$

Where, *n*, *i* and L denote the number of turns, applied current and the diameter of the turn in centimeters, respectively. Temperature was measured using an alcohol thermometer with an accuracy of ±0.5 ºC.

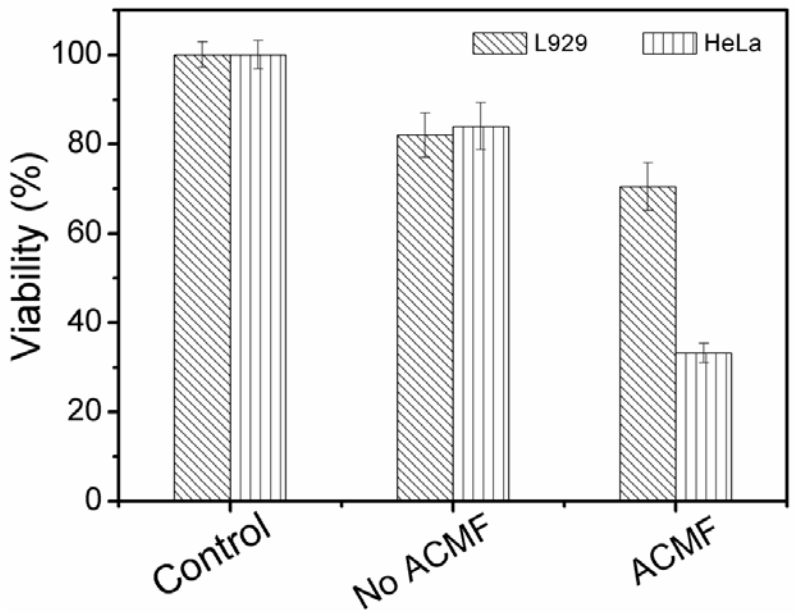

Fig. S11 Cell viabilities (%) of L929 and HeLa cells after incubation with BPS (2 mg IONPs + 0.25 mg PEG-NRs) with or without the exposure of ACMF.

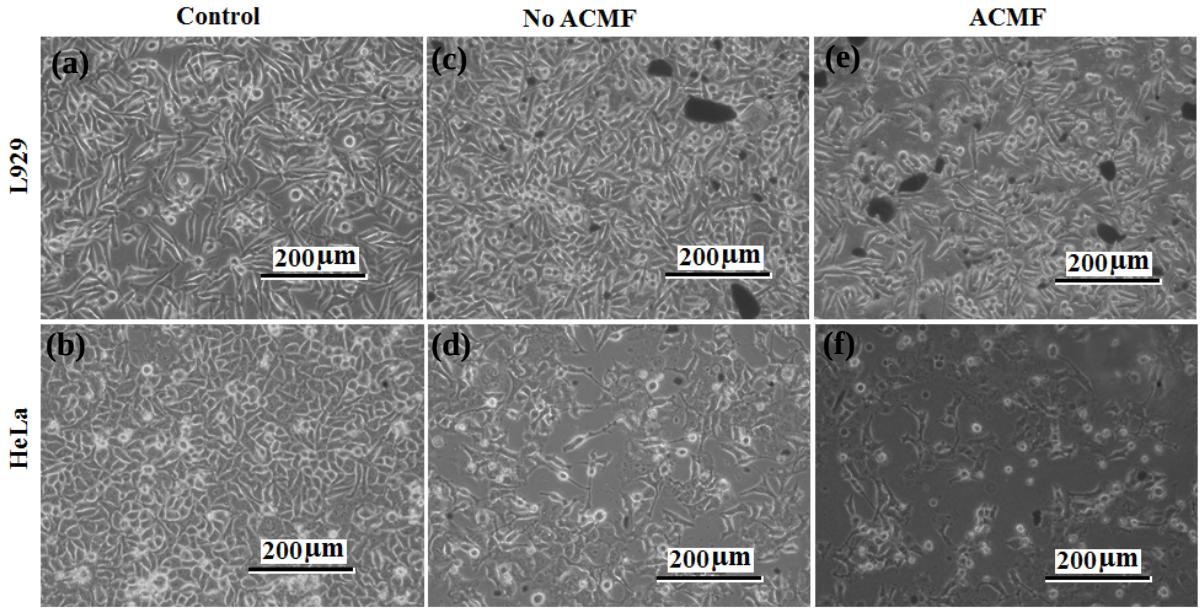

Fig. S12 Microscopic images of L929 and HeLa cells: (a& b) control, (c & d) after treatment with biphasic mixture of IONPs (2 mg) and PEG-NRs (0.25 mg) in absence of ACMF and (e & f) in presence of ACMF. All scale bars are of 200 µm.