Supplementary Information

Taking the Temperature of the Interiors of Magnetically Heated Nanoparticles

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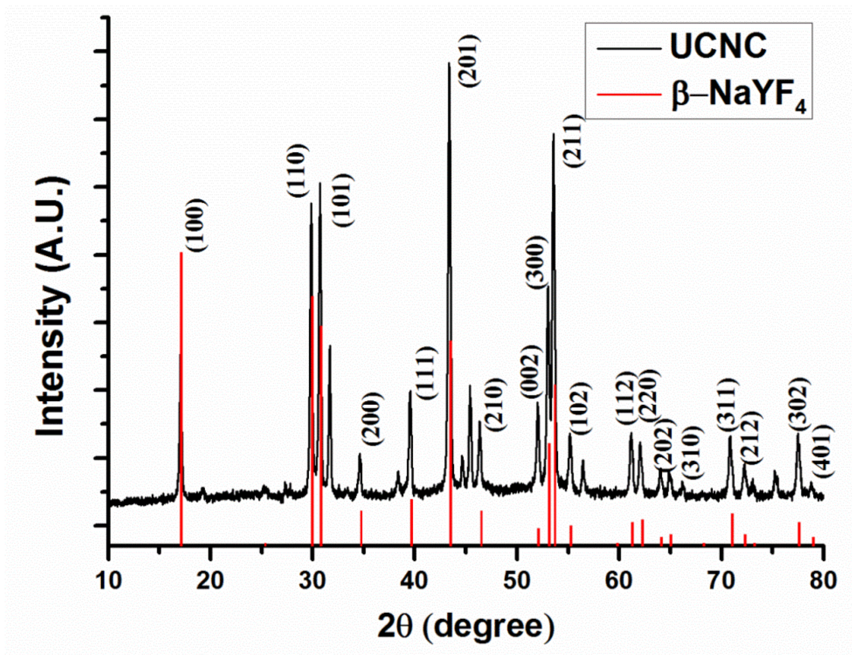

Figure S1. XRD pattern of the synthesized up-conversion nanocrystals (black curve) matches with that of the standard hexagonal $NaYF_4$ crystals (the red lines, JCPDs: 28-1192), confirming the lattice structure of the nanocrystals. The extra peaks belong to a small amount of YF_3 mixed in the matrix.

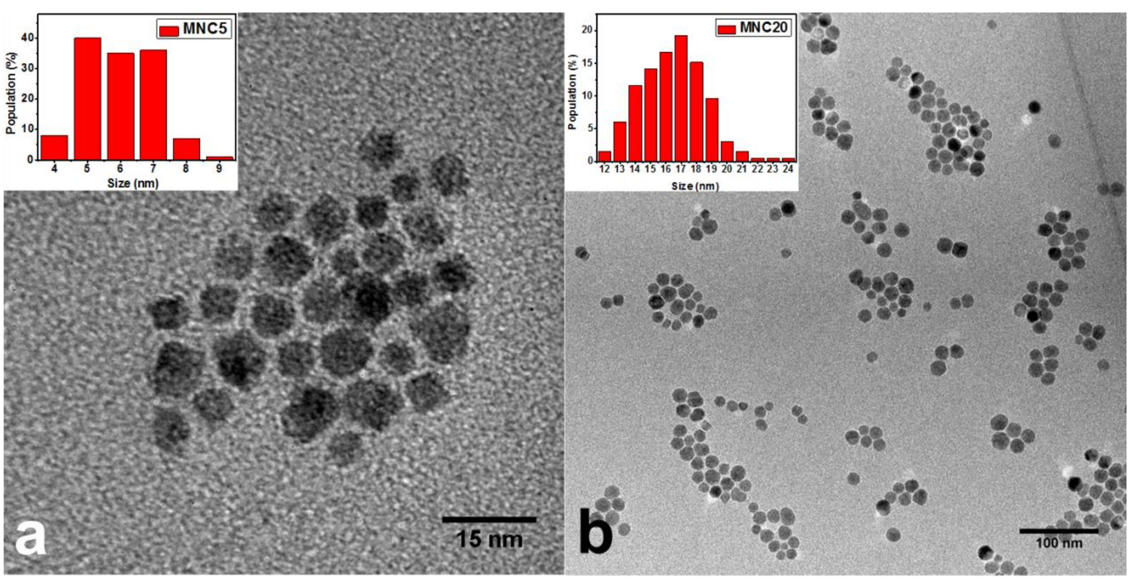

Figure S2. TEM images and size distribution analysis of MNCs. **a,** Small MNCs denoted as "MNC5" with an average diameter of 6.4 $\pm$1.0 nm. **b,** Large MNCs denoted as "MNC20" with an average size of 17 $\pm$2 nm.

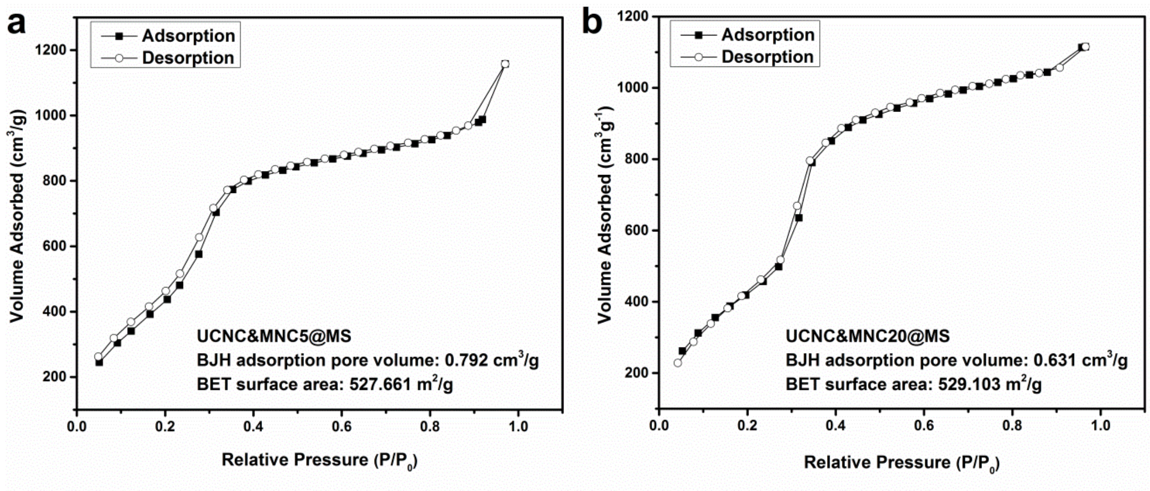

Figure S3. N_2 adsorption-desorption isotherms of the dual-core nanoparticles

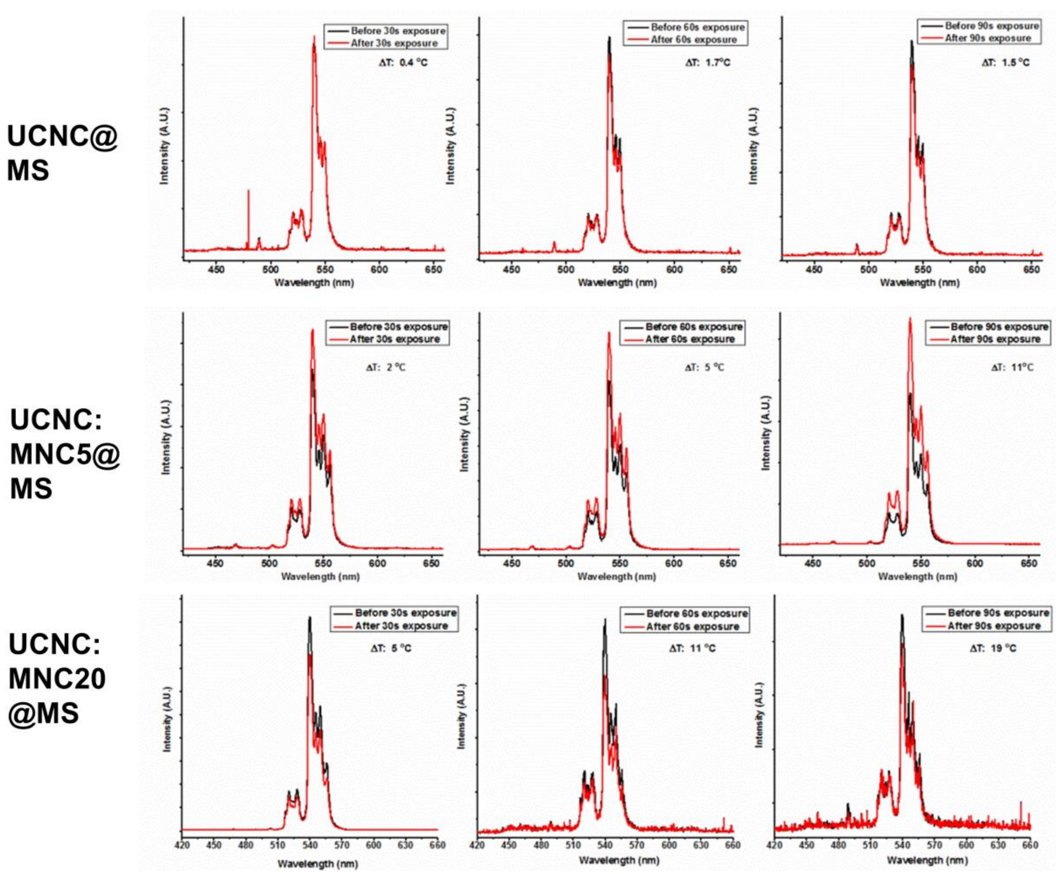

Figure S4. Luminescence spectra of samples before and after the OMF exposures. The three samples are UCNC@MS, UCNC:MNC5@MS, and UCNC:MNC20@MS. The exposure time is 30 s for the first column, 60 s for the second column and 90 s for the last column.

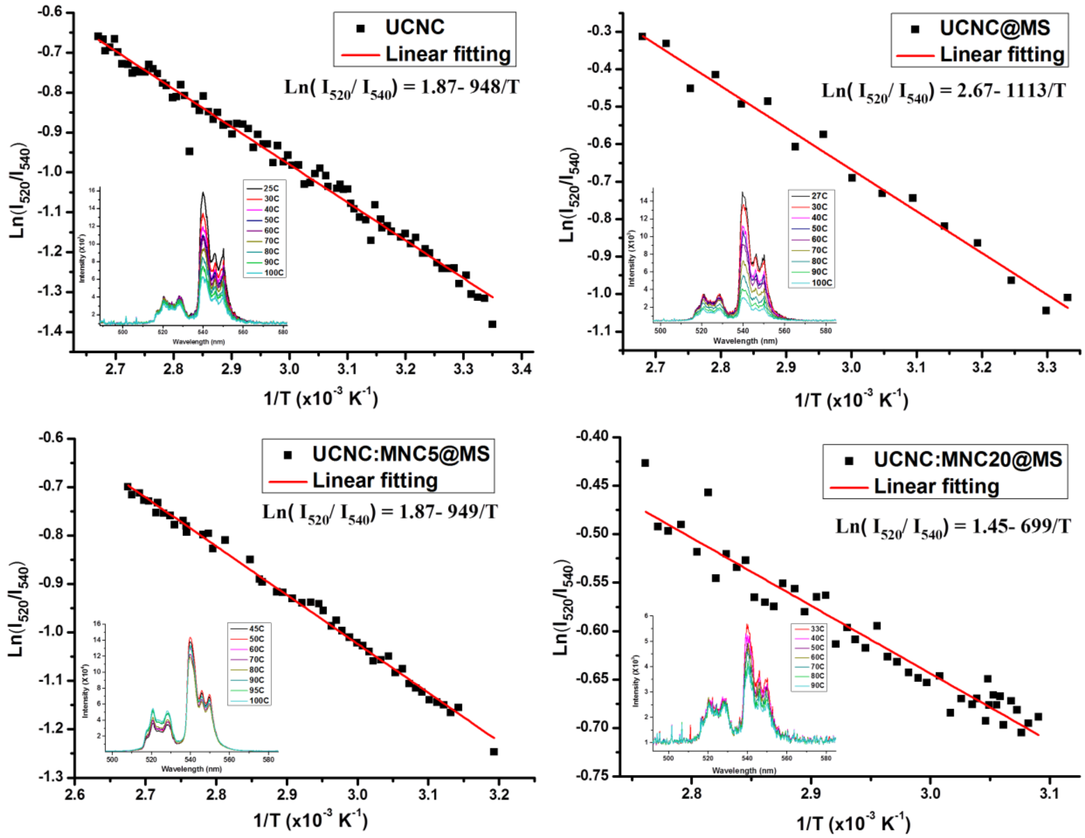

Figure S5. Intensity ratios between peak 520 nm and 540 nm are plotted versus the inverse of the temperature to generate linear working curves for sample UCNC (top left), UCNC@MS (top right), UCNC:MNC5@MS (bottom left) and UCNC:MNC20@MS (bottom right). Inset shows the luminescence spectra at different temperatures.

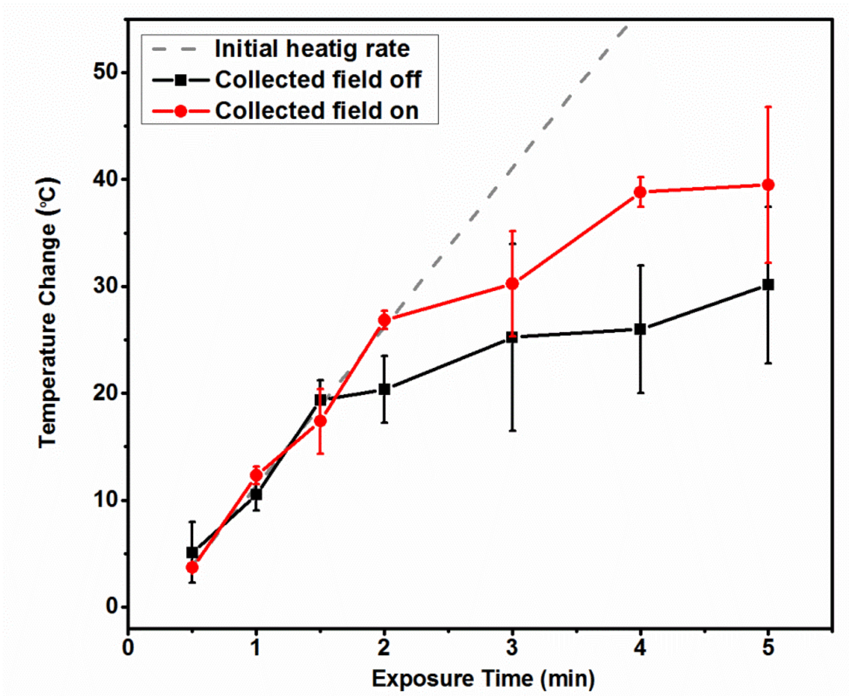

Figure S6. Nanoparticle heating effect as a function of oscillating magnetic field exposure time. The temperature increase is linearly related to the exposure time initially (grey dash line) and eventually saturates as the length approaches 5 min. The nanoparticle temperatures collected after the field is off (black squares) are smaller than those of the points that are collected while the field is on (red dots), and the distinct difference grows as the exposure time lengthens, as a result of the faster heat dissipation rate.

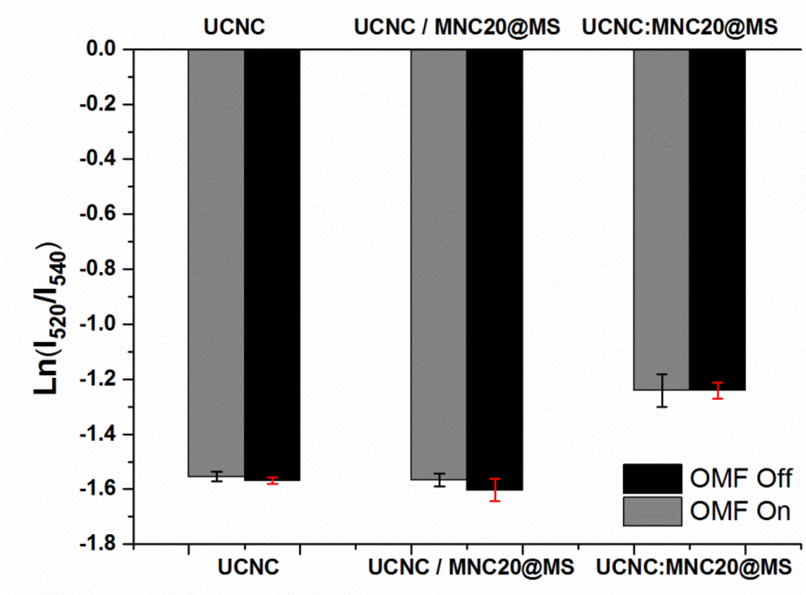

Figure S7. Experiment results confirm that the UCNC emission intensity ratios are not influenced by the OMF when no heating effect is placed, since the oscillating frequency (~375 kHz) is several orders slower than the electron transitions. UCNC are nanocrystals without any silica coating. UCNC/ MNC20@MS have 20 nm magnetic nanocrystals embedded in MSNs and the MSNs are mixed with UCNC in the solution. UCNC:MNC20@MS are the dual-core MSNs that have both the UCNC and MNC embedded for nano temperature detection. OMF off: 10 spectra were collected every two minute for every sample. The laser was turned on for 1 s every time. The averages of emission intensity ratios were calculated together with the errors. OMF on: similar to the field off group, and the OMF was turned on briefly during the spectrum collection.

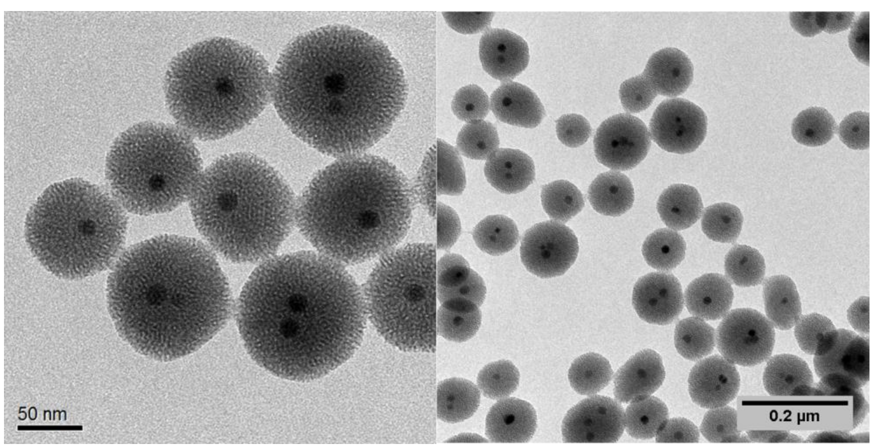

Figure S8. TEM images of MNC20@MS at different magnifications.

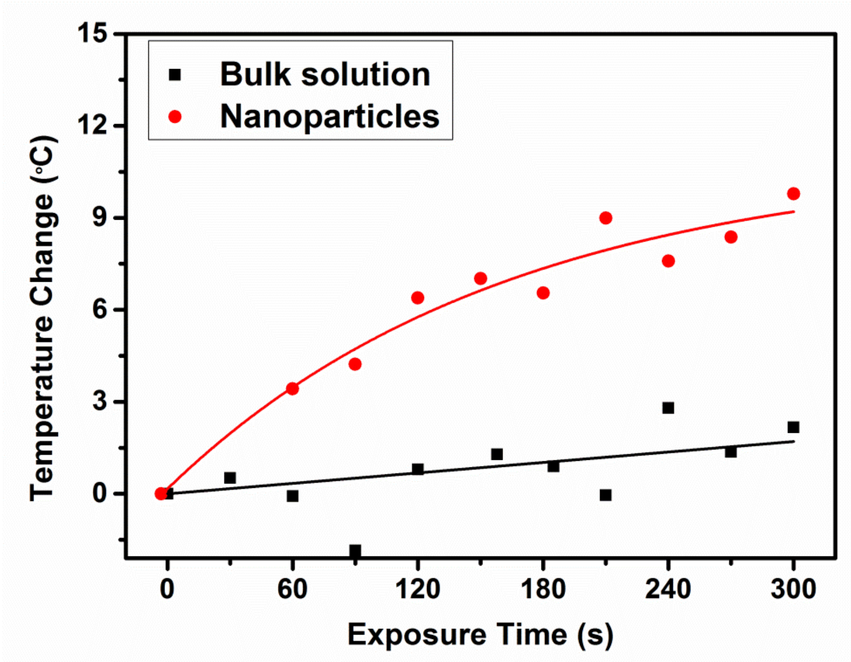

Figure S9. UCNC&MNC20@MS nanoparticle interior temperature compared with that of the solution during the exposure to the oscillating magnetic field. The solution temperature increases by about one degree over time while the nanoparticle interior was nine times larger, confirming the temperature gradient exists. The induction power of the field in this experiment was reduced to 25% of the maximum.

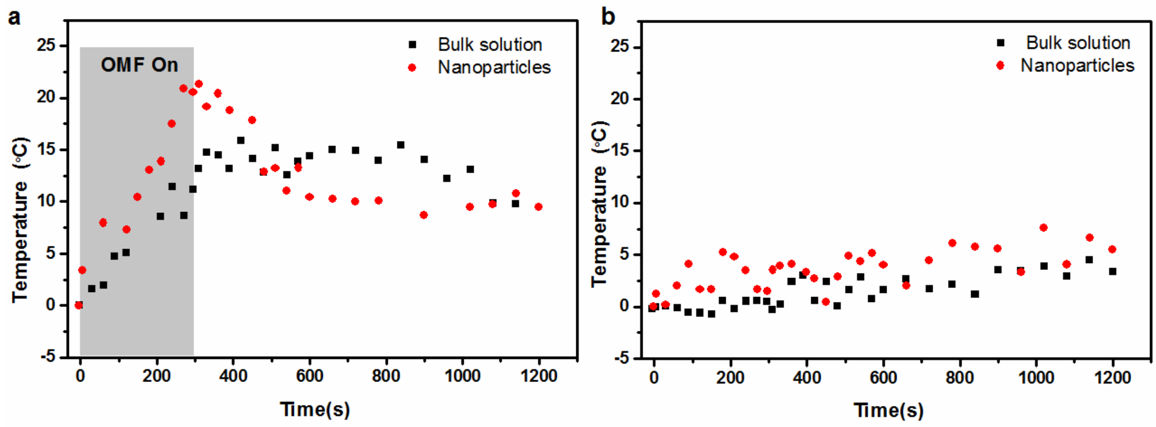

Figure S10. Temperatures of the nanoparticles and the bulk solution when placed in an ice bath. **a,** Five minute OMF exposure. We observed much smaller temperature increases for both the nano and bulk environment, compared to when the system was in ambient air. The nanoparticles temperature still grew more than the bulk solutions, confirming the local heating effect. **b,** Control group with no OMF applied. For both the nanoparticles and the solution, the temperature remained stable initially and slowly warmed up in the later stage. Thus, the heating effect in **a** origins from the nanoheaters in the MSNs. Due to the limitation of the experimental setup, the ice bath is rather small to sustain under the heating from the nanoheaters, that the solution temperature was raised too.

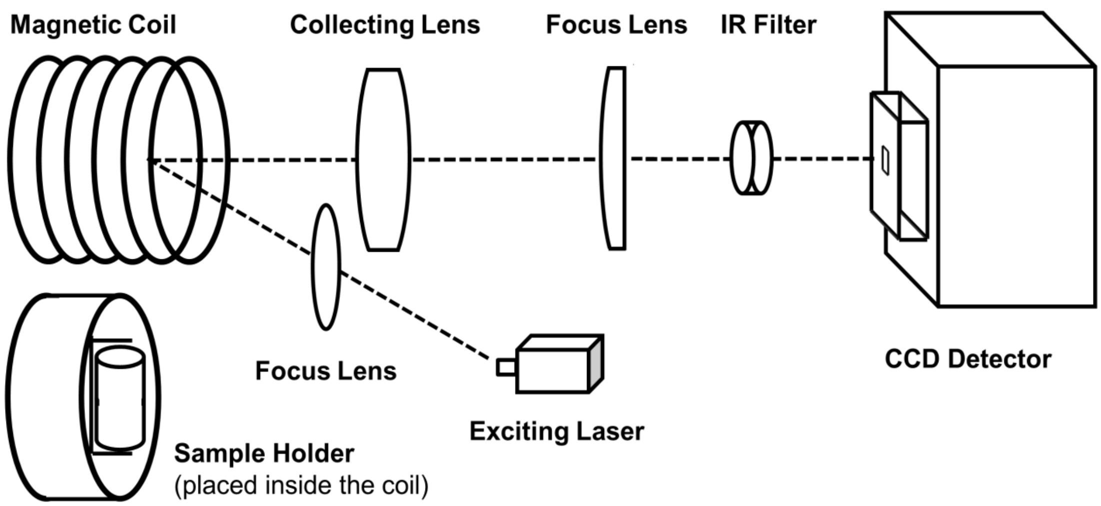

Figure S11. Illustration of the experimental setup for luminescence detection

Table S1. Statistical analysis result of the nanocrystal ratios between UCNCs and MNCs in the two samples and the average distance between the two types of nanocrystals*

Sample	Nanocrystal ratio (UCNC:MNC)				Average distance between UCNC and MNC
	1:1	1:2	1:3 or more	MNC only	
UCNC&MNC5@MS	67.77 %	10.74 %	9.09 %	12.40 %	8.0 ± 1.5 nm
UCNC&MNC20@MS	65.03 %	12.57 %	1.09 %	21.31 %	9 ± 2 nm

***Analyses are based on about 150 UCNC&MNC5@MS nanoparticles and 230 UCNC&MNC20@MS nanoparticles.

Systematic Error Propagation

For UCNC, the linear equation correlating the temperature and the luminescence intensity ratio is :

$Ln\frac{I_{520}}{I_{540}} = A - \frac{B}{T}$, where $A = 2.00061 \pm 0.02834$, $B = 1009.02004 \pm 9.72607$

For the intensity ratio part, the peak area calculations have a coefficient of determination (R^2) that is at least 0.99. Thus, the systematic error of the intensity ratio calculation is:

$$\because \delta\left(\frac{I_{520}}{I_{540}}\right) = 0.01\left(\frac{I_{520}}{I_{540}}\right)$$

$$\therefore \delta\left(Ln\frac{I_{520}}{I_{540}}\right) = \sqrt{\left(\frac{\partial Ln\frac{I_{520}}{I_{540}}}{\partial\frac{I_{520}}{I_{540}}}\right)^2 \times \delta\left(\frac{I_{520}}{I_{540}}\right)^2} = \frac{\delta\left(\frac{I_{520}}{I_{540}}\right)}{\frac{I_{520}}{I_{540}}} = 0.01$$

$$T = \frac{B}{A - Ln\frac{I_{520}}{I_{540}}}$$

$$\delta T = \sqrt{\left(\frac{\partial T}{\partial Ln\frac{I_{520}}{I_{540}}}\right)^2 \delta\left(Ln\frac{I_{520}}{I_{540}}\right)^2 + \left(\frac{\partial T}{\partial A}\right)^2 (\delta A)^2 + \left(\frac{\partial T}{\partial B}\right)^2 (\delta B)^2}$$

$$= \sqrt{\left(\frac{B}{\left(A - Ln\frac{I_{520}}{I_{540}}\right)^2}\right)^2 \delta\left(Ln\frac{I_{520}}{I_{540}}\right)^2 + \left(\frac{B}{\left(A - Ln\frac{I_{520}}{I_{540}}\right)^2}\right)^2 (\delta A)^2 + \left(\frac{1}{\left(A - Ln\frac{I_{520}}{I_{540}}\right)}\right)^2 (\delta B)^2}$$

$$= \sqrt{\frac{1}{\left(A - Ln\frac{I_{520}}{I_{540}}\right)^2}\left(\frac{B^2\delta\left(Ln\frac{I_{520}}{I_{540}}\right)^2 + B^2(\delta A)^2}{\left(A - Ln\frac{I_{520}}{I_{540}}\right)^2} + \left(\frac{\delta B}{B}\right)^2 B^2\right)}$$

$$= \frac{B}{A - Ln\frac{I_{520}}{I_{540}}}\sqrt{\frac{\delta\left(Ln\frac{I_{520}}{I_{540}}\right)^2 + (\delta A)^2}{\left(A - Ln\frac{I_{520}}{I_{540}}\right)^2} + \left(\frac{\delta B}{B}\right)^2}$$

$$\frac{\delta T}{T} = \sqrt{\frac{\delta\left(Ln\frac{I_{520}}{I_{540}}\right)^2 + (\delta A)^2}{\left(A - Ln\frac{I_{520}}{I_{540}}\right)^2} + \left(\frac{\delta B}{B}\right)^2}$$

At 25 ^{o}C, $\frac{\delta T}{T} = 0.013$, the systematic error is about 1.3 %.

Detection sensitivity calculation

For UCNC:

$$Ln\frac{I_{520}}{I_{540}} = 1.87 - \frac{948}{T}$$

$$S = \frac{d(\frac{I_{520}}{I_{540}})}{dT} = \frac{I_{520}}{I_{540}} \times \frac{948}{T^2}$$

$$\because T = 298.15\ K,\ \frac{I_{520}}{I_{540}} = 0.270$$

$$\therefore S = 28.8 \times 10^{-4} / K$$

Similarly, the detection sensitivity for UCNC@MS under room temperature is 43.2×10^{-4} /K; UCNC&MNC5@MS: 28.7×10^{-4} /K; UCNC&MNC20@MS: 32.1×10^{-4} /K.

Specific absorption rate (SAR) calculation

From Figure 4b, during a 5 min OMF exposure, the bulk solution was heated by about 20 K and the nanoparticles were heated by 42 K. The particle concentration was 10 mg/ml. The field oscillating frequency was 375 kHz and the magnetic field strength was about 20 – 24 kA/m.

Heat absorbed by 1 ml toluene solution:

155.96 J/(mol·K) × 1 ml × 0.87 g/ml × 20K / 92.14 g ·mol^{-1} =29.45 J

Hear absorbed by the silica nanoparticles (Ignore the heat capacity differences between silica and the nanocrystals, given their small volume fractions.)

0.703 J/(g·K) × 10 mg ×42 K = 0.2953 J

Total heat absorbed:

29.452 J + 0.2953 J= 29.747 J

Assuming the MNC radius is 10 nm, UCNC radius is 15 nm and the silica particle radius is 50 nm, and their densities are 5.17 g/cm^3, 4.21 g/cm^3 [1] and 2.05 g/cm^3, respectively. Iron oxide weight percentage of the 10 mg assembled nanoparticles is:

$5.17 \times 4\pi/3 \times 10^3 / (5.17 \times 4\pi/3 \times 10^3 + 4.21 \times 4\pi/3 \times 15^3 + 2.05 \times 4\pi/3 \times (50^3 - 10^3 - 15^3))$

= 1.94 %

The specific absorption rate regarding to the iron oxide nanocrystal weight is:

29.747J / 300s / (10 mg ×1.94 %) = 511 W/g ≈ 500 W/g

Heating Center Distance Estimation

The heating center MNCs are encapsulated in MSNs. Assuming that the MNCs are located in the center of the silica nanoparticles and that all the silica nanoparticles are perfectly separated without any interconnection, the average distance between the MNCs would depend on the concentration of nanoparticles in the solution (10 mg/ml in this study).

Average nanoparticle weight for UCNC&MNC20@MS:

$5.17\ g/cm^3 \times 4\pi/3 \times 10^3\ nm^3 + 4.21\ g/cm^3 \times 4\pi/3 \times 15^3\ nm^3 + 2.05\ g/cm^3 \times 4\pi/3 \times (50^3 - 10^3 - 15^3)\ nm^3)$

$= 1.117 \times 10^{-15}$ g

In 1 ml of particle solution, the number of dual-core nanoparticles is:

$10\ mg / (1.117 \times 10^{-15}\ g) = 8.953 \times 10^{12}$

Average volume occupied by a single nanoparticle is:

$1\ ml / (8.953 \times 10^{12}) = 0.1172\ um^3$

Assuming the nanoparticles are in cubic structures next to another cubic with a nanoparticle inside it, then the average distance between particle centers is the length of these cubic edge:

$(0.1172\ um^3)^{1/3} = 0.489$ um

Thus, the estimated average distance between heating centers are about 489 nm. However, there is a small portion of particles that have two MNCs embedded. The average distance between these heating centers would be about 10-20 nm. On the other hand, some nanoparticles may be interconnected with other nanoparticles, in which case, the heating MNCs would be separated by the two silica shells and the gap between silica surfaces, probably around 100 nm.

References

1. Cheng, L.; Yang, K.; Zhang, S.; Shao, M.; Lee, S.; Liu, Z. Highly-Sensitive Multiplexed *in vivo* Imaging Using Pegylated Upconversion Nanoparticles. *Nano Res.* **2010**, *3*, 722-732.