Supplementary Material (ESI) for Chemical Communications

Electronic Supporting Information.

Fabrication of Silica-Coated Magnetic Nanoparticles with Highly Photoluminescent Lanthanide Probes

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Experimental

1. Fabrication of $SiO_2@Fe_3O_4$/BDA Nanoparticles

The ferrite nanopartcles (NPs) were prepared on the basis of reported methods with minor modifications in water phase.[1-2] De-ionized water was used for all procedures. Briefly, an acidified solution of $FeCl_2$ (2g in 5mL of water) was added to another acidified solution of $FeCl_3$ (3.2g in 20mL of water) at room temperature, which was then stirred vigorously for 1 h. The ammonium hydroxide (30 mL) solution was slowly added to the mixed solution, resulting in precipitation of NPs. The precipitate was centrifuged and the supernatant was decanted to afford the ferrite particles (Fe_3O_4). Fe_3O_4 NPs were washed a couple of times with methanol.

25 mg of ferrite NPs dispersed in 50 mL of water were stabilized by the addition of 1 mL of PVP (polyvinylpyrrolidone) solution. The PVP-stabilized Fe_3O_4 NPs were separated using an aqueous acetone (water/acetone=1/10, v/v) and washed a couple of times with methanol. 80 mg of the PVP-stabilized ferrite NPs were added to a solution containing 4 mL of DI water and 20 mL of 2-propanol. In order to fabricate the silica-coated ferrite NPs, 1 mL of TEOS (tetraethylorthosilicate) and 0.5 mL of NH_4OH were added to the reaction mixture and then stirred for 12 h. The silica-coated ferrite, $SiO_2@Fe_3O_4$, NPs were separated by using a permanent magnet and washed a couple of times with ethanol.

The BDA (0.24 g in 30 mL of water) solution was added to the $SiO_2@Fe_3O_4$ NPs (20 mg) dispersed in 20 mL of water, which was then stirred for 24 h. The BDAanchored NPs ($SiO_2@Fe_3O_4$/BDA) were isolated using a permanent magnet. Trivalent lanthanum chlorides (1 mmol) dissolved in 50 mL of water was added to the $SiO_2@Fe_3O_4$/BDA NPs (20 mg) dispersed in 20mL of water, which was stirred for 12 h to make complete binding of lanthanides ions to the BDA molecule. To remove the non-binding lanthanide ions, the resulting NPs were separated by using a magnet and washed a couple of times with ethanol.

2. Powder X-ray diffraction (XRD)

The XRD data of the $SiO_2@Fe_3O_4$ NPs were taken using a Rigaku RAD diffractometer equipped with Cu Kα radiation. All the peaks coincide well with the cubic spinel phase typical of Fe_3O_4. The XRD data also suggests that the silica shell consists mainly of amorphous phase rather than polycrystalline one.

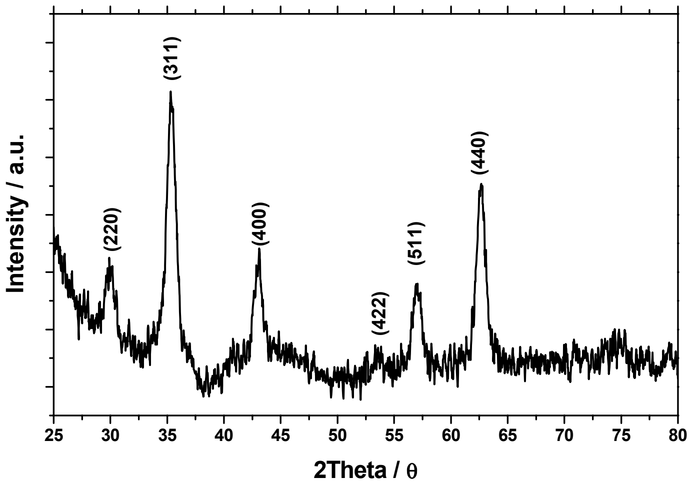

Figure S1. X-ray powder diffraction pattern of silica-coated ferrite NPs, $SiO_2@Fe_3O_4$

3. TEM images

TEM images were obtained using a Tecchnai G2 F30 S-TWIN operated at 300 keV.

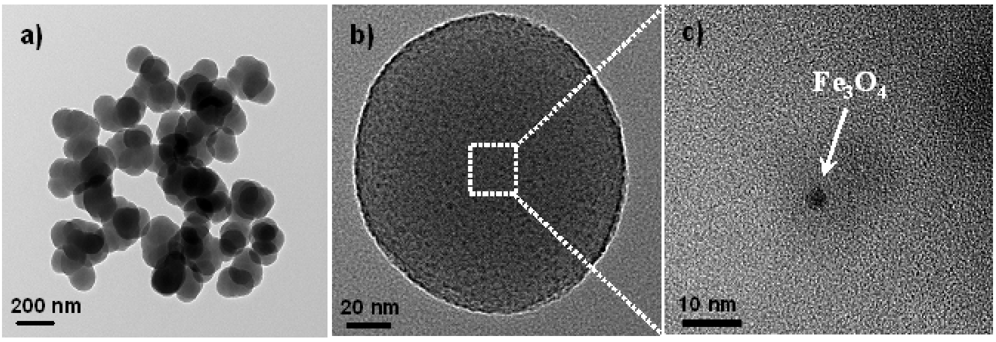

Figure S2. a) Representative TEM image of the silica-coated ferrite NPs, $SiO_2@Fe_3O_4$, b) a TEM image of one $SiO_2@Fe_3O_4$ NP, and c) an expanded view of a high resolution

TEM image for the same NP.

4. Absorption and Emission spectra

The absorption spectra were measured with a Perkin-Elmer Lambda 35 UV-Vis spectrophotometer. The steady-state fluorescence spectra were recorded with Fluorolog 3-11 spectrofluorometer (Jobin Yvon Inc.). As shown in Figure S3a, the characteristic peak corresponding to BDA is clearly observed in the two samples at the very similar position (~ 295 nm), indicating that BDA is covalently linked to the silica surface of $SiO_2@Fe_3O_4$. A noticeable feature is that the fluorescence spectra show distinctive difference between free BDA and bounded BDA molecules (Figure S3b). The $SiO_2@Fe_3O_4$/BDA NPs have their emission maximum at 420 nm, which is largely red-shifted compared to the free BDA molecules. This peak shift might be due to the conformational change of BDA molecules followed by their linkage to the oxide surface.

In order to measure the emission of Ln^{3+} ions bounded to the $SiO_2@Fe_3O_4$/BDA, $SiO_2@Fe_3O_4$/BDA NPs (5 mg) were added to the 10 mL aqueous solution of $LnCl_3$ and then the mixed solutions was stirred for 24 h to make complete binding of lanthanides ions to the BDA molecule. The emission spectra of $SiO_2@Fe_3O_4$/BDA/Ln^{3+} dispersed in DI water were measured with Fluorolog 3-11 spectrofluorometer (Jobin Yvon Inc.). The concentration of Ln^{3+} in all sample solutions was adjusted to be $1x10^{-5}$ M.

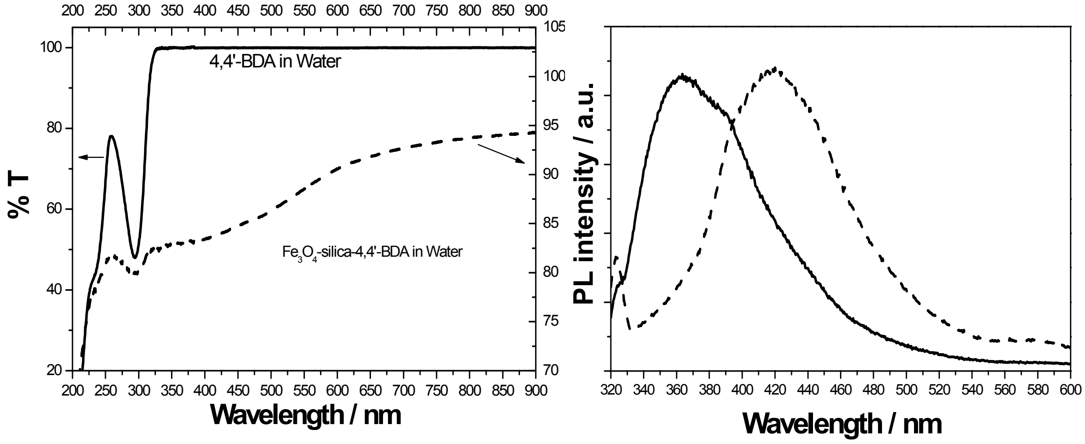

Figure S3. UV-visible absorption and the normalized emission spectra of BDA molecules (black) and $SiO_2@Fe_3O_4$/BDA NPs (red).

5. Raman spectrum and magnetization data.

Raman spectrum was taken with MICRO Raman spectrometer LabRAM HR

(Horiba Jobin Yvon Inc.) using the 633 nm line of a He-Ne laser. The field-dependent magnetization measurements were carried out using a SQUID magnetometer (Quantum Design).

References.

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2. T. J. Meyer, G. J. Meyer, B. W. Pfennig, J. R. Schoonover, C. J. Timson, J. F. Wall.; C. Kobusch. X. Chen, B. M. Peek, C. G. Wall, W. W. Ou, B. W. Erikson, C. A. Bignozzi, *Inorg. Chem.* 1994, **33**, 3952-3964.