Advanced Functional Materials

Multifunctional Mesostructured Silica Microspheres from Ultrasonic Aerosol Spray

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Supporting Information

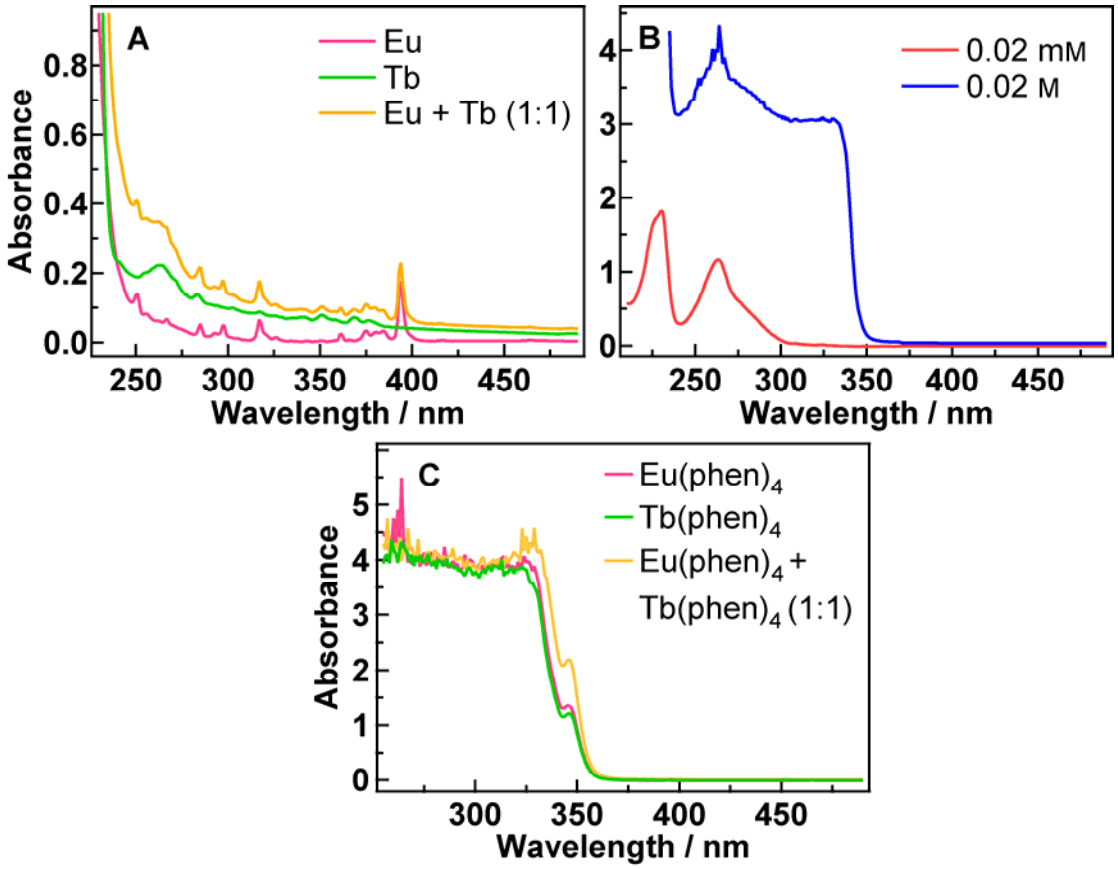

Figure S1. A) Absorption spectra of ethanolic solutions of $EuCl_3$, $TbCl_3$, and $EuCl_3$–$TbCl_3$ mixture (1:1 molar ratio). The concentrations of $EuCl_3$ and $TbCl_3$ are 0.1 M, and the total concentration of $EuCl_3$ and $TbCl_3$ in the mixture solution is 0.1 M. B) Absorption spectra of 1,10-phenanthroline (phen) dissolved in ethanol at two different concentrations. C) Absorption spectra of ethanolic solutions of $[Eu(phen)_4]^{3+}$, $[Tb(phen)_4]^{3+}$, and $[Eu(phen)_4]^{3+}$–$[Tb(phen)_4]^{3+}$ mixture (1:1 molar ratio). The concentrations of $[Eu(phen)_4]^{3+}$ and $[Tb(phen)_4]^{3+}$ are 5.0 μM, and the total concentration of $[Eu(phen)_4]^{3+}$ and $[Tb(phen)_4]^{3+}$ in the mixture solution is 5.0 μM.

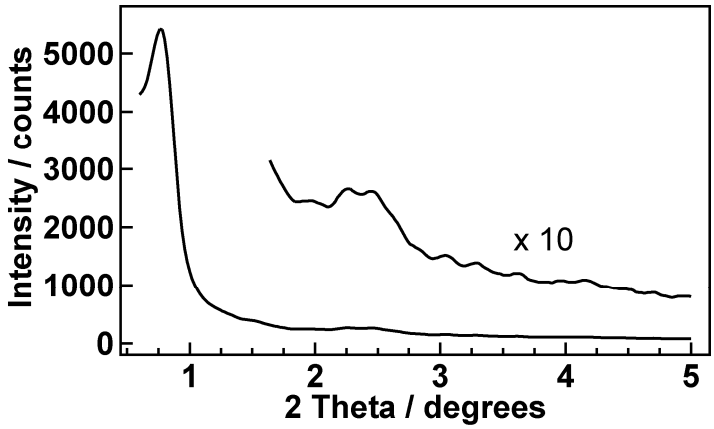

Figure S2. Small-angle XRD pattern of mesostructured silica microspheres doped with rare earth ion–phenanthroline complexes. There are one strong peak at $2\theta = 0.77°$ and one weak peak at $2\theta = 2.36°$. The corresponding *d*-spacings are 11.5 and 3.7 nm, respectively.

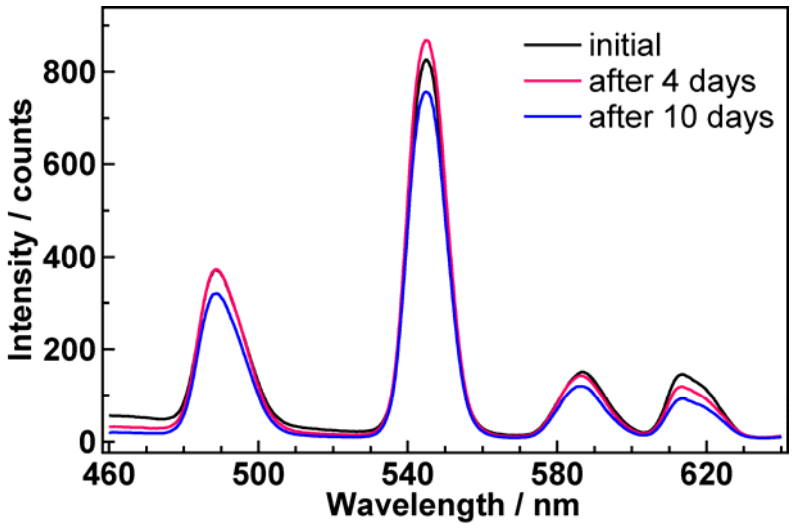

Figure S3. Photoluminescence spectra of mesostructured silica microspheres doped with 1 mol % of $[Eu(phen)_4]^{3+}$ and 1 mol % of $[Tb(phen)_4]^{3+}$. The excitation is at 330 nm. The microspheres were dispersed in water at a concentration of 0.5 wt %. The first spectrum was taken right after the dispersion of the microspheres in water. After the microspheres were kept in water for 4 days, they were precipitated by centrifugation and re-dispersed in the same volume of water and then the second spectrum was taken. After the microspheres were kept in water for 6 more days, they were processed again by centrifugation and re-dispersion, and then the third spectrum was recorded. The spectral shape and intensity remain almost unchanged, indicating that these microspheres are highly stable in terms of their luminescence when dispersed in aqueous solutions. It is also noted that the relative intensities among the luminescence peaks when the microspheres are dispersed in water are different from those when the microspheres are in powder form. The intensity ratio of the former to the latter becomes smaller as the emission wavelength gets longer, probably due to the luminescence quenching caused by the hydroxyl groups of water.

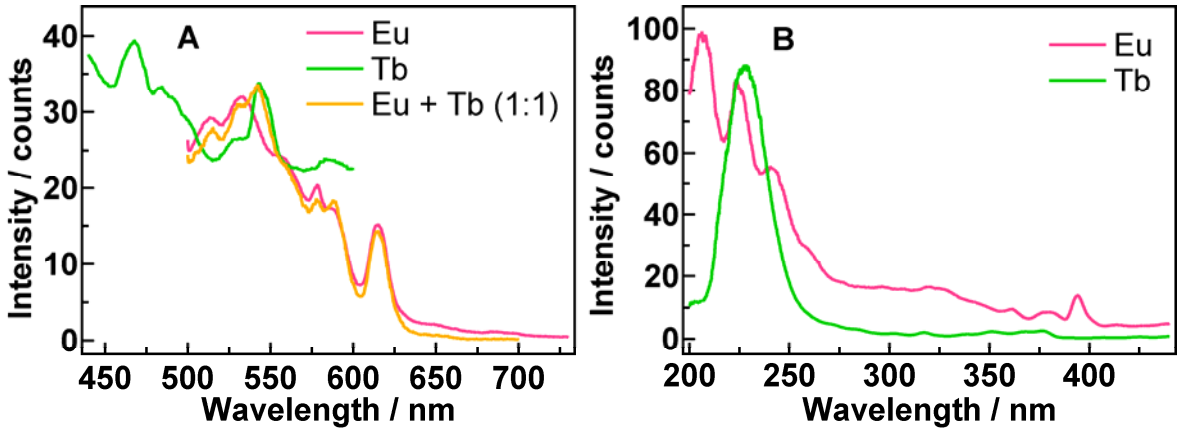

Figure S4. A) Photoluminescence spectra of mesostructured silica microspheres doped with 1 mol % of Eu, 1 mol % of Tb, and 1 mol % Eu + 1 mol % Tb, respectively. The excitation is at 330 nm. B) Photoluminescence excitation spectra of the Eu- and Tb-doped silica microspheres. The detection wavelengths are 616 and 545 nm, respectively.

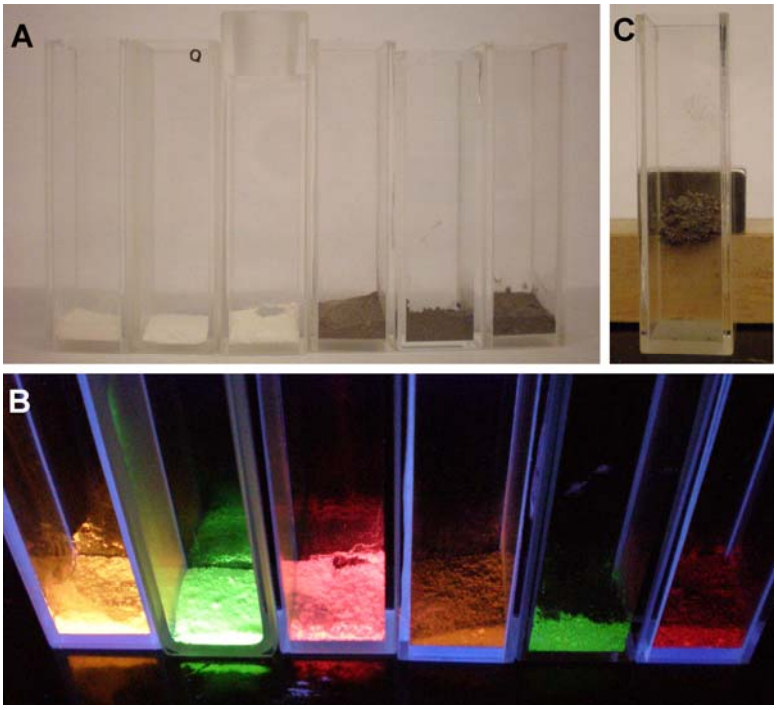

Figure S5. A) Digital image of mesostructured silica microsphere samples doped with rare earth ion–phenanthroline complexes. The image was taken under ambient light. The left three samples do not contain Fe_3O_4 particles. The right three samples contain Fe_3O_4 particles. The samples from left to right in each group are doped with 1 mol % of $[Eu(phen)_4]^{3+}$ + 1 mol % of $[Tb(phen)_4]^{3+}$, 1 mol % of $[Tb(phen)_4]^{3+}$, and 1 mol % of $[Eu(phen)_4]^{3+}$, respectively. B) Digital image of the same samples taken under illumination with a UV lamp at 254 nm. C) Representative digital image showing multifunctional silica microspheres containing rare earth ion–phenanthroline complexes and Fe_3O_4 particles are attracted to the side wall of a quartz cuvette by a magnet without falling down. The image was taken under ambient light.

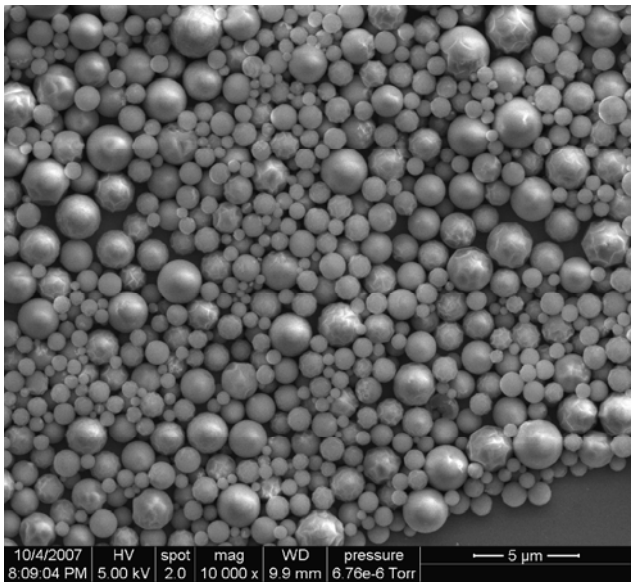

Figure S6. SEM image of mesostructured silica microspheres containing magnetic Fe_3O_4 particles. The sample is as-prepared without undergoing size separation by centrifugation.

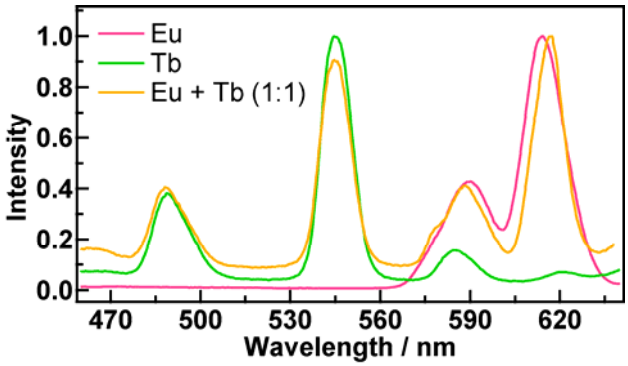

Figure S7. Photoluminescence spectra of the three microsphere samples shown in Figure 4. The excitation is at 330 nm.

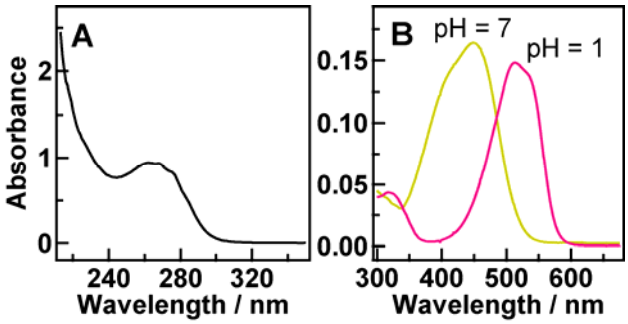

Figure S8. A) Absorption spectrum of the photoacid generator dissolved in ethanol at 0.1 mM. B) Absorption spectra of the pH-sensitive dye dissolved in water solutions at two different pH values and 0.01 mM. 1 M of HCl was used to adjust the pH of the solution to 1, and a standard KH_2PO_4/NaOH buffer solution was used to adjust the pH of the solution to 7.