Supplementary Material (ESI) for Chemical Communications

Electronic supplementary information (ESI)

Study on the high-efficiency fluorescent microcapsules doped with rare earth complex by LbL self-assembly

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Materials

Poly(sodium 4-styrenesulfonate) (PSS, M.W. ~70,000) and poly(allylamine hydrochloride) (PAH, M.W. ~70,000) were obtained from Sigma-Aldrich Inc., U.S.A.. All commercial polyelectrolytes were used without further purification. Monodispersed weakly cross-linked melamine formaldehyde (MF) particles with a diameter of 5.43 ± 0.16 μm were purchased from Microparticles GmbH, Berlin, Germany. $Eu(DBM)_3Phen$ was synthesized according to literature methods (*J. Am. Chem. Soc.* 1964, **86**, 5125). NaCl, ethanol, NaOH and HCl were all of analytical reagents. Water used in all experiments had a resistivity higher than 18 MΩ·cm.

Methods

PAH aqueous solution (2.0 $mg \cdot mL^{-1}$) containing 0.5 M NaCl and PSS aqueous solution (2.0 $mg \cdot mL^{-1}$) containing 0.5 M NaCl were adjusted to neutral by using NaOH or HCl solution, respectively. In 1mL PSS solution at neutral pH, PSS layer was firstly assembled on MF particles (approximately 10^8 particles) for 20 min. The dispersion was centrifuged at 3000 rpm for 5 min. The supernatant was removed and 2 mL water was added to wash the microcapsules. The particles were then re-dispersed in water by gentle shaking. The centrifugation/wash cycle was repeated twice. The PAH layers were assembled in the same way. EuC layer was assembled by adding 1mL EuC saturated ethanol solution into the 0.2mL $(PSS/PAH)_3PSS$ microcapsule suspension. Twenty minutes later, the supernatant ethanol was removed and another PAH layer was assembled. By continuing to assemble a second EuC layer, fluorescent $[(PSS/PAH)_3/PSS/EuC/PAH/EuC]$ microcapsules on MF were obtained. For hollow fluorescent microcapsules, the template MF core was dissolved by 0.1 M HCl solution after assembling $(PSS/PAH)_3PSS$ layers. Then, EuC was fabricated in the shell and hollow microcapsules of $[(PSS/PAH)_3/PSS/EuC/PAH/EuC]$ were assembled.

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The ζ-potential of the MF microparticles was measured on a Powereach JS94H microelectrosphoretic instrument (China). Each value was averaged for five parallel measurements. The fluorescence emission spectra of EuC doped microcapsules were measured with a Perkin Elmer LS55 Luminescence Spectrometer (U.S.A.). The excitation wavelength used throughout the experiments was 350 nm. The excitation and emission slit width was adjusted to 10 nm and 5nm, respectively. Fluorescence microscopy images were obtained with a mercury lamp and a 60 × oil immersion objective and captured by a DP70 CCD camera (Japan) on an Olympus IX 81 instrument (Japan). Excitation filter for light between 330-385 nm was used. Emission filter cuts light below 610 nm. SEM analysis was performed using a JEOL JSM-6700F instrument (Japan) at an operation voltage of 3 KeV. Microcapsules were also observed under a JEM-100CXII TEM (Japan) onto 230-mesh copper grid covered with Formvar. The samples were observed under an accelerating voltage of 100 KV and a vacuum of 10^{-6} Torr. The morphology and roughness measurement of hollow EuC self-assembled microcapsules in dried state were performed using a Nanoscope IIIa Multimode AFM (Digital Instruments Inc., U.S.A.) at room temperature. Tapping mode was utilized at a scan rate of 0.5 Hz with a silicon cantilever having resonance frequency about 200 kHz.

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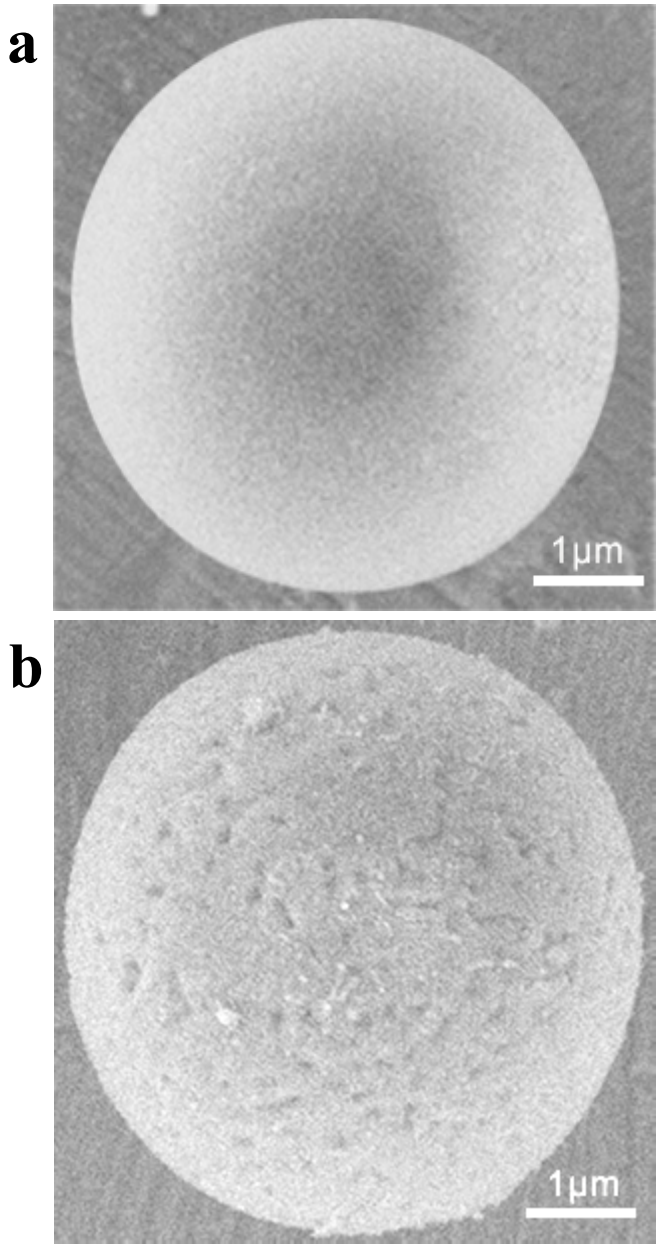

Fig. S1 SEM images of (a) bare MF particle and (b) $(PSS/PAH)_3/PSS/EuC/PAH/EuC]$ microcapsule self-assembled on MF.

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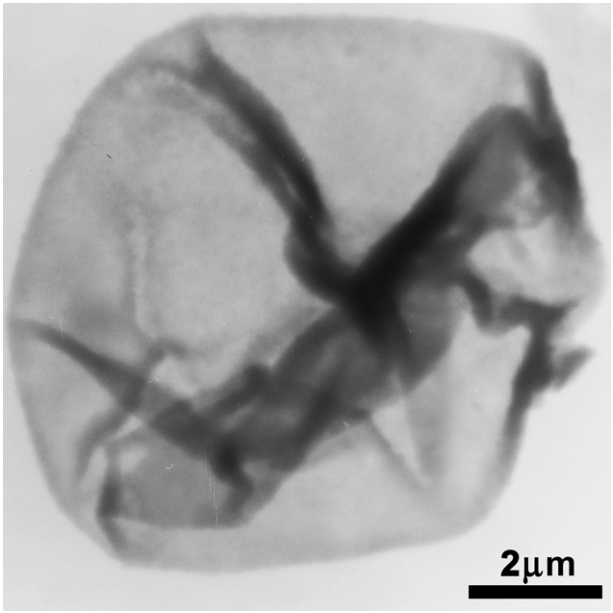

Fig. S2 TEM image of the luminescent intact hollow microcapsule [$(PSS/PAH)_3$/PSS/EuC/PAH/EuC]

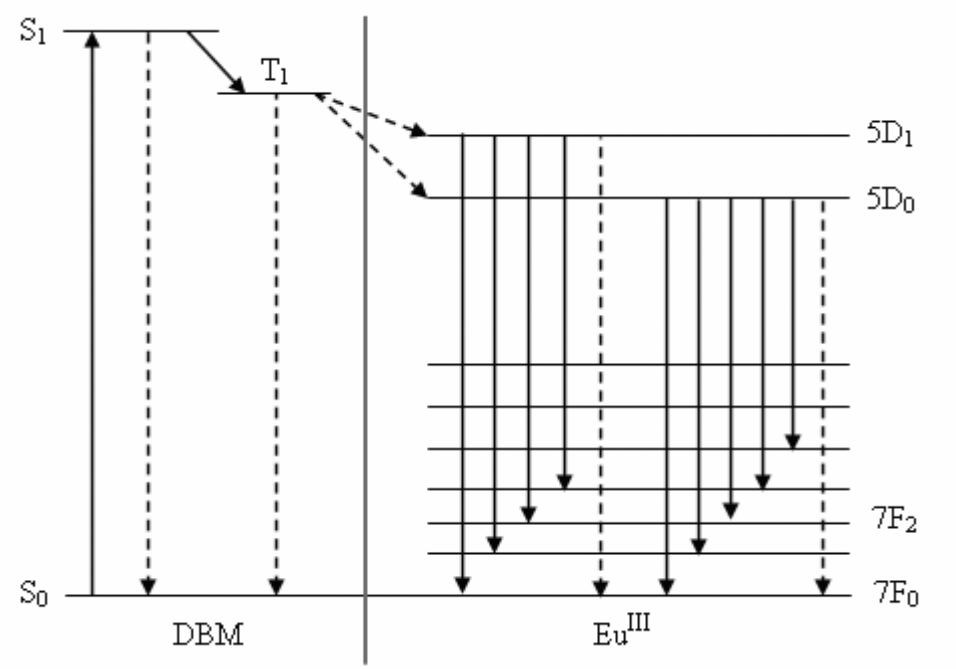

Fig. S3 Luminescence radiation for Eu^{III} along with the singlet and triplet levels of DBM.

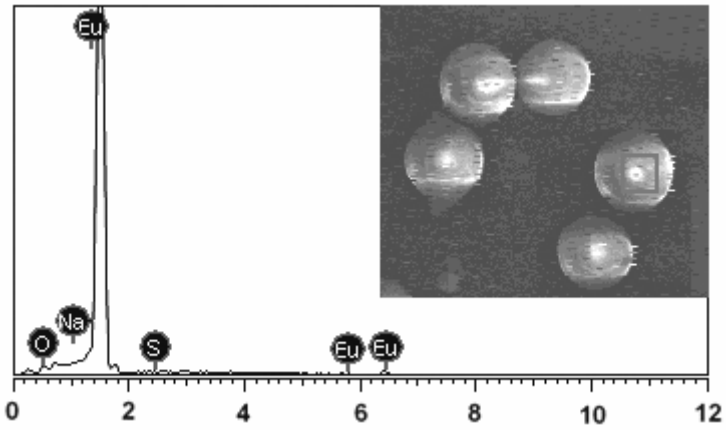

Fig. S4 EDS analysis of [$(PSS/PAH)_5$/PSS/EuC/PAH/EuC] microcapsules self-assembled on MF.

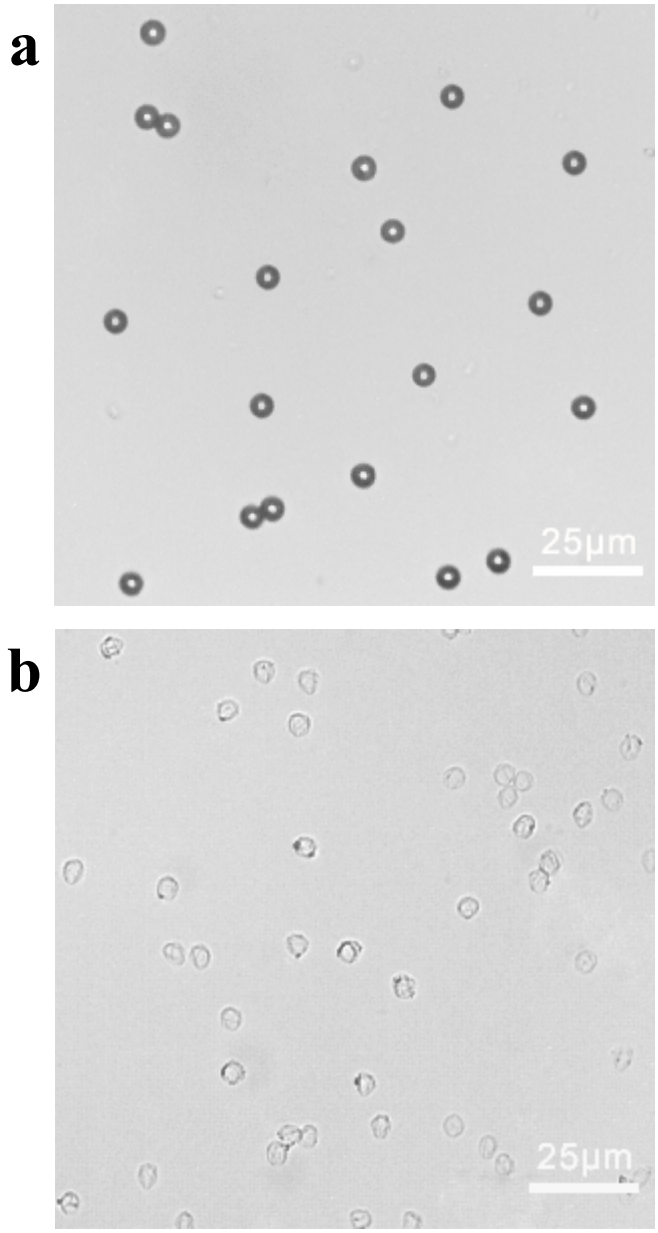

Fig. S5 Optical micrographs of (a) [$(PSS/PAH)_3$/PSS/EuC/PAH/EuC] microcapsules assembled on MF and (b) hollow EuC doped microcapsules dispersed in pure water after the core removal.