Supporting Information

Solvothermal Synthesis of Hierarchical Eu_2O_3 Nanostructures Templated by PS-*b*-PMAA: Morphology Control via Simple Variation of Water Content

Ying Xiao[a], Xiaoyan Wang[a, b], Thomas Wagner[c], Jürgen Thiel[c], Yuan Yao[d], Yichao Lin[a], Ezzeldin Metwalli[d], Rui Liu[e], Hans Jürgen Butt[c], Peter Müller-Buschbaum[d], Jian-Qiang Meng[b], Liang Chen[a], Ling-Dong Sun[e], Chun-Hua Yan[e], and Ya-Jun Cheng*[a]

[a] Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, 1219 Zhongguan West Rd, Zhenhai District, Ningbo, Zhejiang Province 315201, P. R. China

E-mail: chengyj@nimte.ac.cn

[b] Tianjin Polytechnic University, State Key Laboratory of Hollow Fiber Membrane Materials & Processes, Tianjin 300387, P. R. China

[c] Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128, Mainz, Germany

[d] Technische Universität München, Physik-Department, Lehrstuhl für Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching, Germany

[e] Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials Chemistry and Applications & PKU-HKU Joint Lab on Rare Earth Materials and Bioinorganic Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China

Experiments

Materials

All chemicals and materials addressed in this work were used without further purification. DMF of analytical grade and concentrated HCl (37 %) were received from Sinopharm Group Co., Ltd. Europium (III) nitrate hexahydrate was purchased from Alfa Aesar. The amphiphilic block copolymer polystyrene-*block*-poly (methacrylic acid) (PS-*b*-PMAA) was synthesized in house via a sequential anionic polymerization. The repeating units were 59 for PS and 256 for PMAA with a polydispersity index of 1.05 for PS. Analytical grade of N, N′-dimethyl formamide (DMF), polypropylene glycol (PPG), polypropylene glycol (MDI) and glycerol were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Si (100) wafers (Shanghai JunHe Electronic Materials Co., Ltd.) were used as substrate for spin coating the solutions after solvothermal treatment.

Synthesis of PS-*b*-PMAA

Purification of the monomers: Methyl methacrylate (MMA) was mixed with a few drops of triethyl aluminum until a stable yellow solution was obtained, and then distillated. Styrene was added to Flourenyl lithium and distillated.

Polymerization: In a reactor tetrahydrofuran (THF) was distilled with calculated amount of initiator (*sec*. BuLi) and cooled with dry ice/acetone (The entire reaction took place at -80 °C). Then the calculated amount of styrene was added to the reactor. The solution turned dark and was stirred for a few minutes. Sample solution was taken out for analysis by GPC from the reaction mixture. The reaction mixture was

treated with a slight excess (<10 %) of diphenyl ethylene and stirred for 10 minutes at -80 °C. Then the calculated amount of methyl methacrylate was added. The reaction mixture was yellow and stirred further for about 20 minutes at -80 °C. Finally, the reaction mixture was mixed with a few ml of methanol and thus terminated.

Hydrolysis: The polymer synthesized was dissolved in THF and mixed with around 100 ml of HCl and stirred for 24 hr. The extent of hydrolysis was monitored by NMR.

Sample Preparation and Characterization

Sample solutions were prepared according to the following procedure: 0.1 g of PS-*b*-PMAA was mixed together with *ca*. 0.5 g of Europium (III) nitrate hexahydrate, 8.0 g of DMF, and certain amount of H_2O within five minutes. The solutions were stirred for 15 minutes to dissolve the salt completely. The solution was then transferred into a Teflon-lined autoclave of 25 ml capacity and heated for 12 h at 170 °C. After the autoclave was cooled to room temperature naturally, the white precipitates were centrifuged and washed several times with DMF. The obtained white precipitates were then dispersed in the mixture of *ca.* 5 g PPG and *ca.*0.1 g glycerol by ultrasonication (Qsonica, Q700, ultrasonication for 3 minutes), followed by the addition of *ca*. 3.7 g of MDI. By gentle heating, Europium oxide/PU composites were prepared. Finally, the composite was calcined at 800 °C for 4 h in air with a ramp rate of 5 K/min starting from room temperature. After calcination, the samples were cooled to room temperature naturally in furnace.

Films of the pure DBC PS-*b*-PMAA were prepared as following: In order to

study the self-assembly behavior of the DBC PS-*b*-PMAA in the solvothermal process the samples were prepared without Europium (III) nitrate hexahydrate. 0.1 g of PS-*b*-PMAA was mixed together with *ca*. 8.0 g of DMF, and different amounts of H_2O within five minutes. The solutions were stirred for 15 minutes and then transferred into a Teflon-lined autoclave of 25 ml capacity and heated for 12 h at 170 °C. The polymer solutions obtained after solvothermal process were spin coating onto the Si (100) wafers for 60.0s using a spin coater (KW-4A, Institute of Microelectronics of Chinese Academy of Sciences) to get films for a characterization of the morphology.

AFM images were recorded in tapping mode using a Digital Instruments Scanning force microscope (Dimension 3100V, Veeco) equipped with Bruker cantilevers (spring constant ranging between 20-80 N/m and resonate frequency of 278 – 327 kHz).

Scanning electron microscopy (FESEM) images were obtained on Hitachi S 4800 scanning electron microscope (Tokyo, Japan) at an acceleration voltage of 4 kV.

Transmission Electron Microscopy (TEM) experiments were conducted by putting a drop of aqueous suspension containing the powder on a carbon-supported copper grid and measured with a JEOL JEM-2100F TEM operated at 200 kV.

The X-ray photoelectron spectroscopy (XPS) was recorded on an AXIS UTLTRADLD system (Shimadzu Japan) with Ag radiation.

Fourier-transform infrared (FT-IR) spectroscopy was applied to investigate the complexation between Europium ions and PS-*b*-PMAA. The solution prepared with

0.5 g $Eu(NO_3)_3 \cdot 6H_2O$,8.0 g DMF and 0.2 g H_2O was dried at 80°C for 12 hours to remove the solvents. The spectra were recorded from solid powder KBr pellets on a Thermo Nicolet 6700 spectrometer (Madison, America) with the wavenumber range from 4000 cm^{-1} to 400 cm^{-1}. The spectrum of each sample was an average of 32 scans at 4 cm^{-1} resolution.

Small-angle X-ray scattering (SAXS) measurements were performed on a Ganesha 300XLSAXS-WAXS system (SAXS LAB ApS, Copenhagen/Denmark). The X-ray radiation was produced at 50 kV/0.6 mA from a Cu anode with a wavelength of 0.154 nm. The sample-to-detector distance was 406 mm. The sample powder was put into a glass capillary which functioned as a holder and allowed X-ray transmission (SAXS) experiments. The 2D SAXS/WAXS data were radially averaged and presented in logarithmic scattering intensity versus the magnitude of the scattering vector, $q = 2\pi\lambda^{-1}\sin(2\theta)$, where 2θ is the scattering angle. The SAXS data were fitted using ″SASfit″software[1].

Photoluminescence was measured with F-4600 FL Spectrophotometer with a excitation wavelength of 254 nm. The wavelength scan starts from 550 nm to 700 nm with a scan speed of 240 nm/min.

The Nitrogen adsorption-desorption isotherm was measured on ASAP 2020M apparatus at 77.3 K. In a general procedure, the dry sample (~200 mg) was loaded into the glass analysis tube. Then fix the glass tube to the degas port to be heated and evacuated, including two stages, initially to 90 °C at 10 K/min and hold the temperature for 30 min then to 200 °C for 8 h. After this, the outgas rate was less than

5 μm Hg. The sample was then backfilled with N_2 before transferred to the analysis port. N_2 adsorption-desorption isotherm was measured at 77.3 K and the range of relative pressures between 0 and 1.0. The BET surface area was calculated over the range of relative pressures between 0.05 and 0.20.

Reference

1. Joachim Kohlbrecher (2010), SASfit: A Software package SASfit for fitting small-angle scattering curves, PSI.

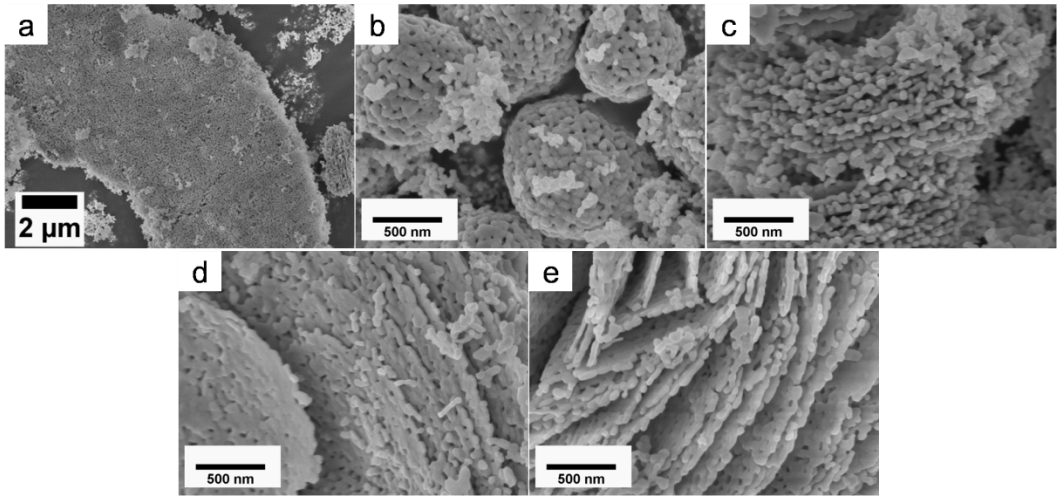

Figure S1. SEM images of the hierarchical Eu_2O_3 nanostructured powders prepared with different mass ratios of H_2O/DMF: (a) 0; (b) 2.5 wt%; (c) 5.0 wt%; (d) 10 wt%; (e) 20 wt%.

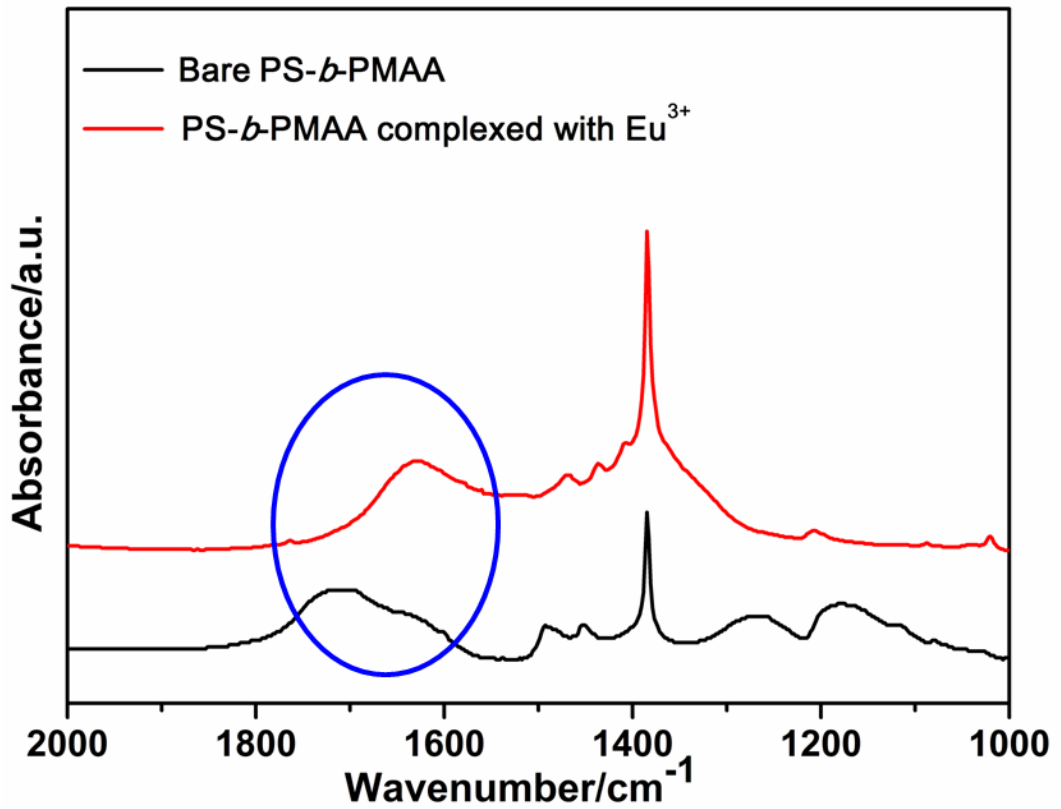

Figure S2. FT-IR profiles of pure PS-*b*-PMAA DBC (black) and PS-*b*-PMAA DBC complexed with Europium Nitrate (red). The marked regions indicate the red shift of the carbonyl stretching band (1716 cm^{-1} vs. 1648 cm^{-1}).

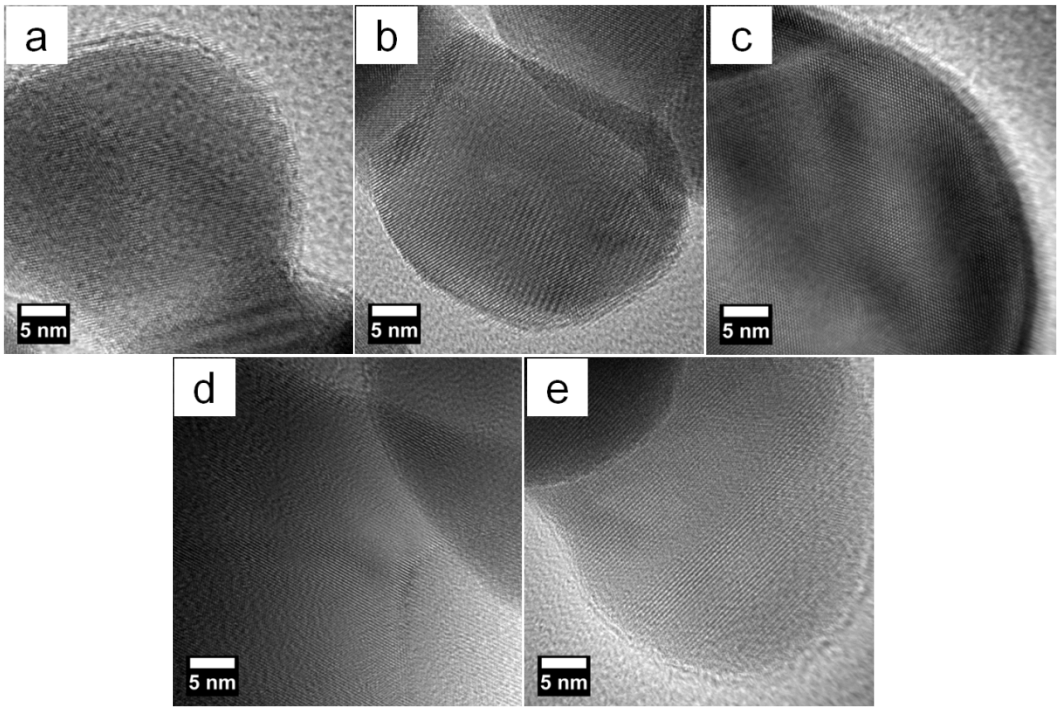

Figure S3. HRTEM images of the hierarchical Eu_2O_3 nanostructured powders prepared with different mass ratios of H_2O/DMF: (a) 0; (b) 2.5 wt%; (c) 5.0 wt%; (d) 10 wt%; (e) 20 wt%.

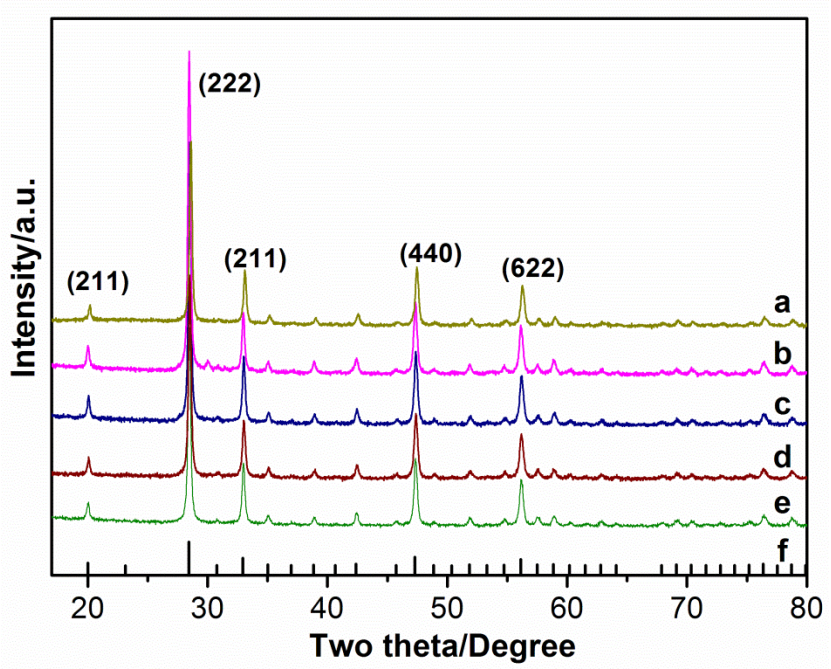

Figure S4. XRD patterns of the hierarchical Eu_2O_3 nanostructured powders prepared with different mass ratios of H_2O/DMF: (a) 0; (b) 2.5wt%; (c) 5.0 wt%; (d) 10 wt%; (e) 20 wt%; (f) standard XRD pattern of Eu_2O_3.

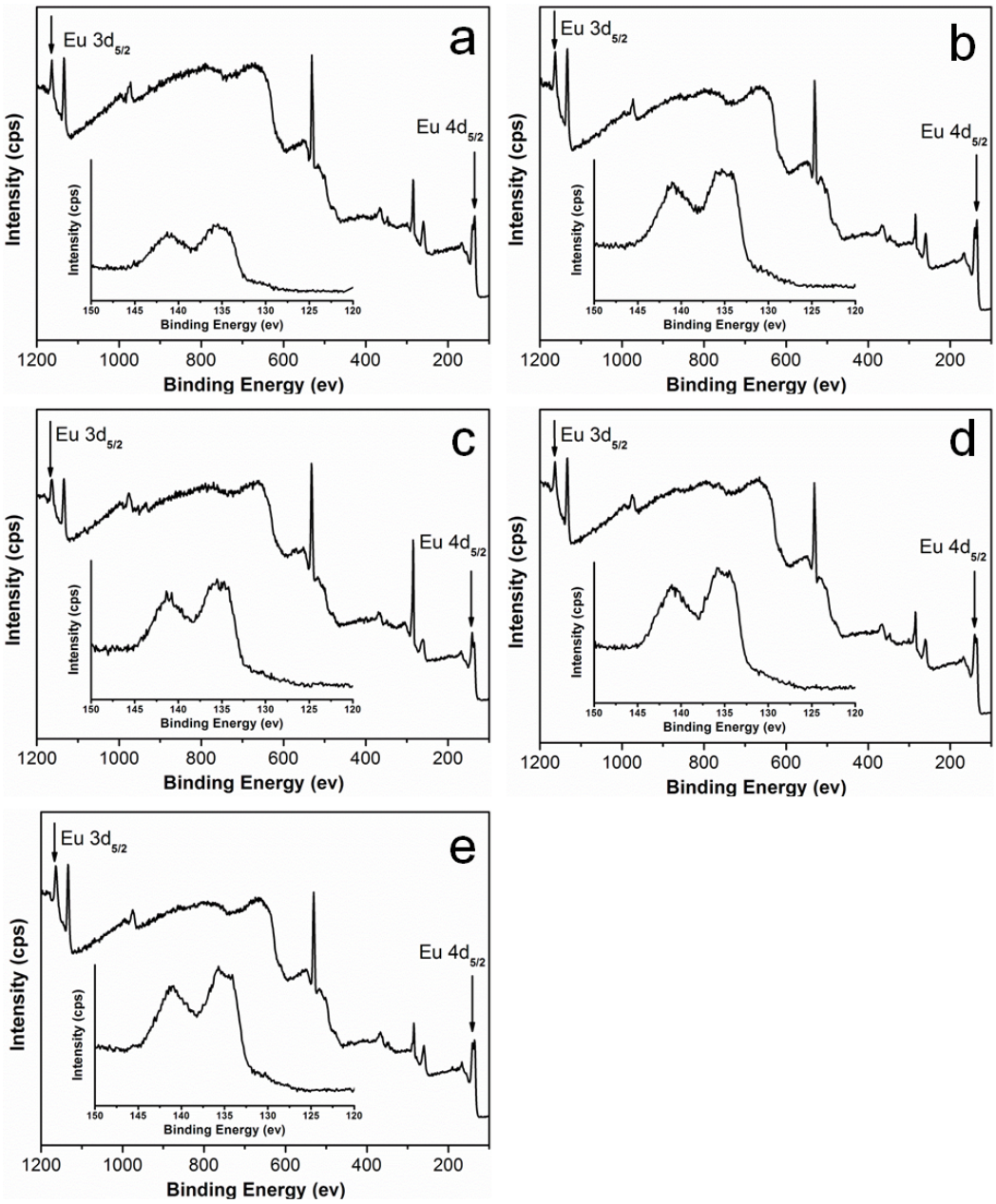

Figure S5. XPS profiles of the hierarchical Eu_2O_3 nanostructured powders prepared with different mass ratios of H_2O/DMF: (a) 0; (b) 2.5wt%; (c) 5.0 wt%; (d) 10 wt%; (e) 20 wt%. Inset: detailed XPS of the 4d electron of Eu^{3+}.

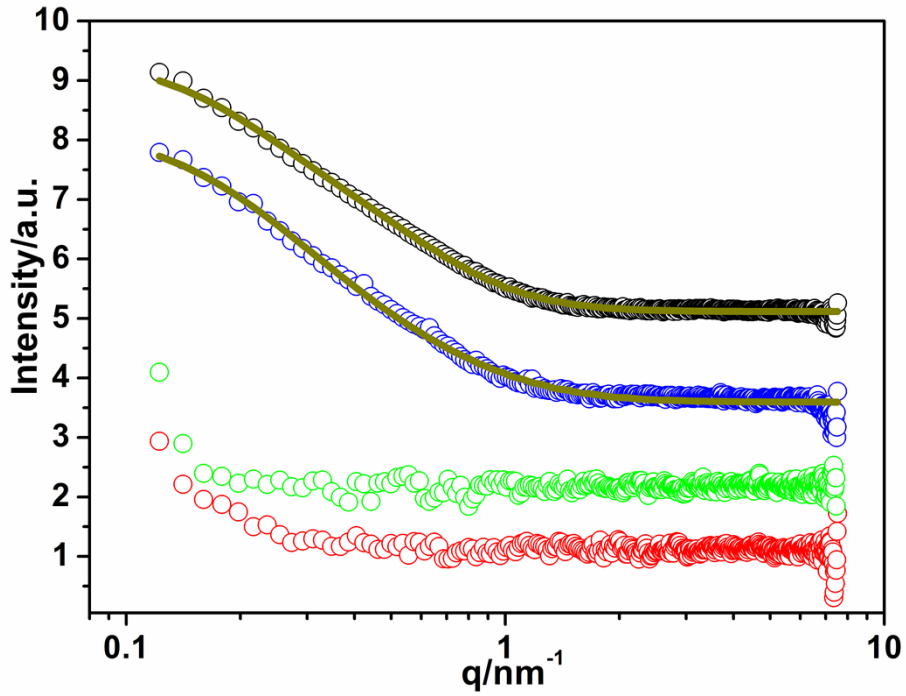

Figure S6. Small angle x-ray scattering (SAXS) data (open circles) of the hierarchical Eu_2O_3 nanostructured powders prepared with different mass ratios of H_2O/DMF: (black) 2.5 wt%; (red) 5.0 wt%; (green) 10 wt%; (blue) 20 wt%; and shown together with simulated curves (dark yellow solid lines).

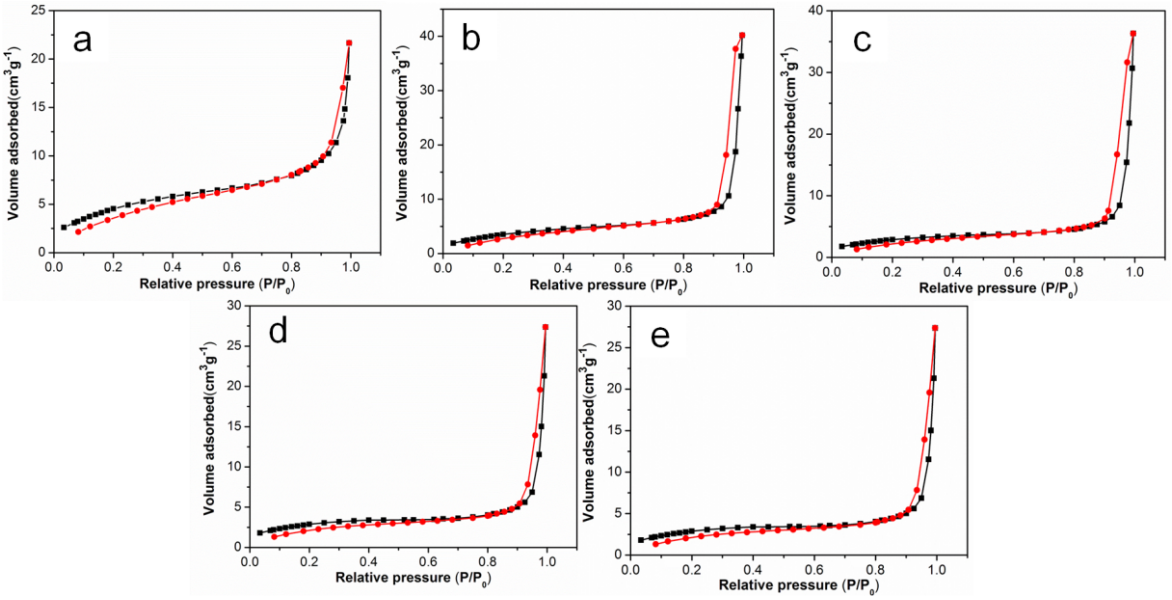

Figure S7. Nitrogen physisorption isotherms of the micro-nano Eu_2O_3 powder prepared with different mass ratios of H_2O/DMF: (a) 0; (b) 2.5 wt%; (c) 5.0 wt%; (d) 10 wt%; (e) 20 wt%.

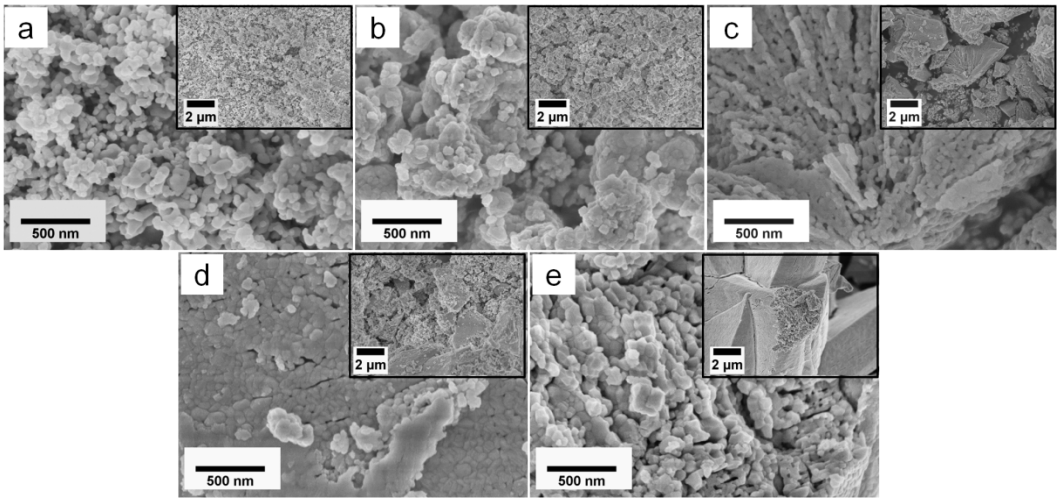

Figure S8. SEM images of Eu_2O_3 synthesized with different mass ratios of H_2O/DMF (without PS-*b*-PMAA): (a) 0; (b) 2.5 wt%; (c) 5.0 wt%; (d) 10 wt%; (e) 20 wt%, insets: low-magnification SEM images.

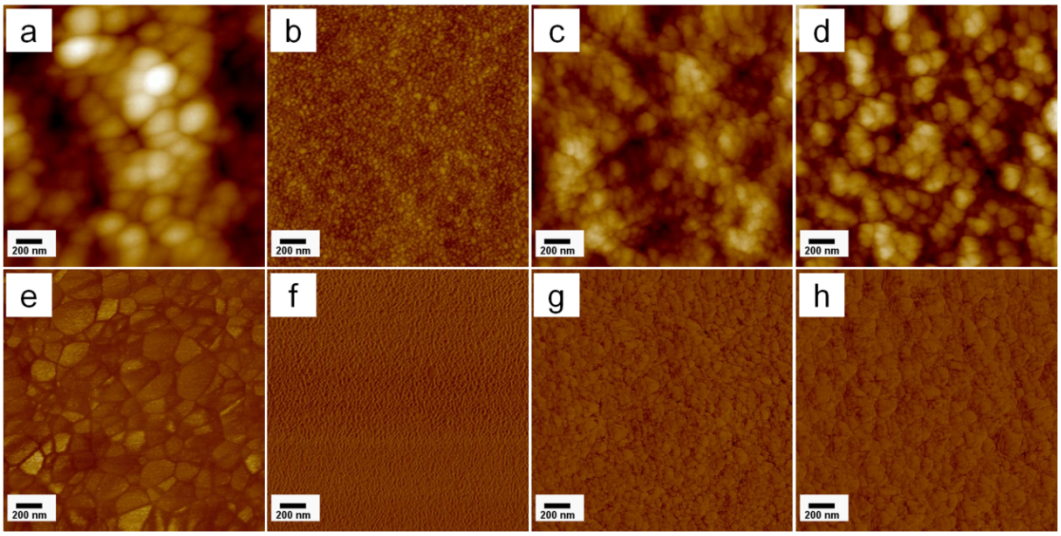

Figure S9. AFM height (a-d) and phase (e-h) images of pure PS-*b*-PMAA DBC films spin coated on Si substrate after solvothermal reaction for 12 hours at 170 °C with different mass ratios of H_2O/DMF: (a, e) 2.5 wt%; (b, f) 5.0 wt%; (c, g) 10 wt%; (d, h) 20 wt%. Height scale: 40 nm, phase scale: 40 nm.