

Terbium-Based Infinite Coordination Polymer Hollow Microspheres: Preparation and White-Light Emission

Sheng-Liang Zhong,^{*a} Rong Xu,^a Lin-Fei Zhang,^a Wen-Gang Qu,^b Gui-Qi Gao,^b Xi-Lin Wu,^b and An-Wu Xu^{*b}

^a College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang, Jiangxi.330022, The People's Republic of China. Fax: + 86 791 8120386; E-mail: zslxhx@yahoo.com.cn

^b Division of Nanomaterials and Chemistry, Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, Anhui. 230026, The People's Republic of China. Fax: (+86) 0551-3600246; E-mail: anwuxu@ustc.edu.cn

TABLE S1: Samples and Corresponding Experimental Parameters

Sample	Reaction time (h)	Reaction Temperature (°C)	c(Tb(NO ₃) ₃) (mM)	c(H ₃ BTB) (mM)	Volume of DMF (mL)	Total volume (mL)	Main morphology and size distribution
Tb-BTB-1	12	150	4	4	8	12.5	hollowspheres, 260–500 nm
Tb-BTB-2	12	150	2	2	8	12.5	solid spheres, 350 nm–1 μm
Tb-BTB-3	12	150	8	8	8	12.5	spheres with nanopetals on the surface, ca. 500 nm
Tb-BTB-4	12	150	1	4	8	12.5	spheres (aggregated), ca. 500 nm
Tb-BTB-5	12	150	2	4	8	12.5	monodisperse hollow spheres, 450 nm–1 μm
Tb-BTB-6	12	150	8	4	8	12.5	spheres 270–550 nm; flower-like nanostructures, 1–2 μm
Tb-BTB-7	12	150	16	4	8	12.5	spheres 520–670 nm; flower-like nanostructures, 1.5–2.4 μm
Tb-BTB-8	12	150	4	4	12.5	12.5	microspheres, 2–4 μm; nanoparticles, ca. 500 nm
Tb-BTB-9	12	150	4	4	6	12.5	flower-like nanostructures
Tb-BTB-10	12	150	4	4	4	12.5	flower-like nanostructures
Tb-BTB-11	12	60	4	4	8	12.5	solid spheres, 600 nm–1 μm
Tb-BTB-12	12	80	4	4	8	12.5	solid spheres, 1–1.7 μm
Tb-BTB-13	12	120	4	4	8	12.5	solid spheres with smooth surface, 800 nm–1.3 μm
Tb-BTB-14	12	180	4	4	8	12.5	hollowspheres, 150–900 nm
Tb-BTB-15	1	150	4	4	8	12.5	solid spheres, 150–450 nm
Tb-BTB-16	2	150	4	4	8	12.5	solid spheres, 700–900 nm
Tb-BTB-17	6	150	4	4	8	12.5	solid and hollowspheres, 500–1000 nm
Tb-BTB-18	24	150	4	4	8	12.5	hollowsphere, ca. 1.2 μm
Tb-BTB-19	48	150	4	4	8	12.5	hollow spheres, 1.5 μm

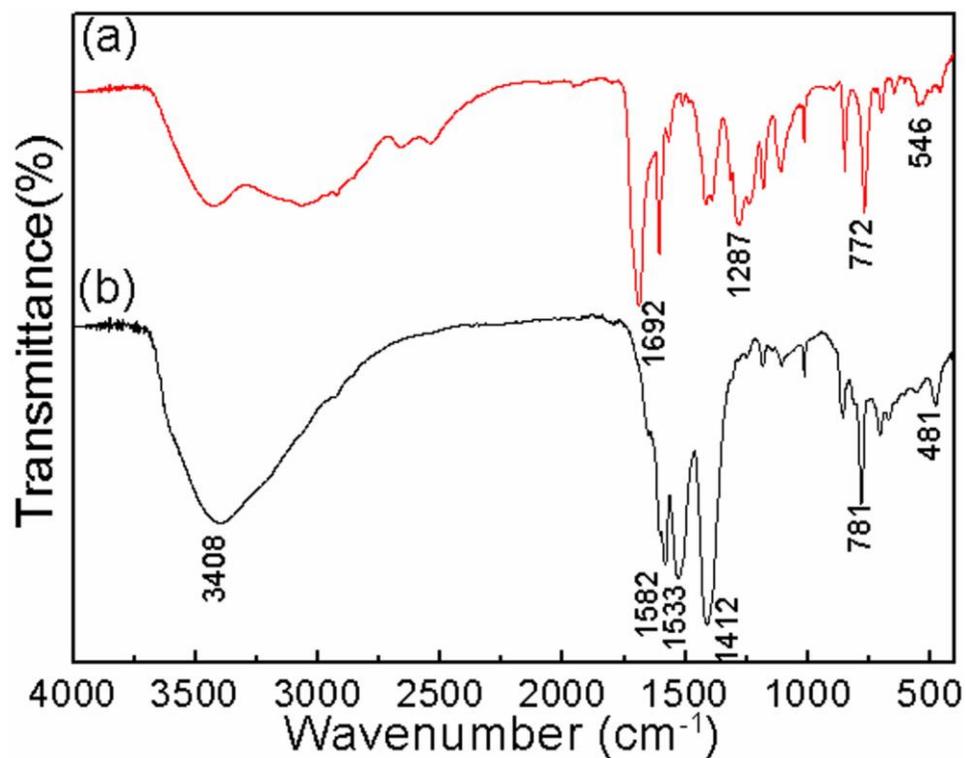


Fig. S1. FT-IR spectra of (a) H₃BTB; (b) Tb-BTB-1.

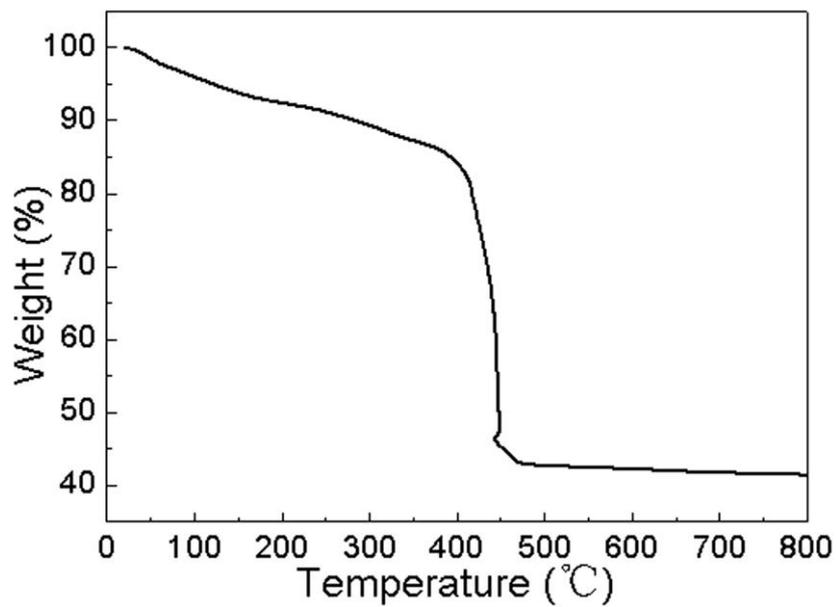


Fig. S2. TG curve of the Tb-BTB-1.

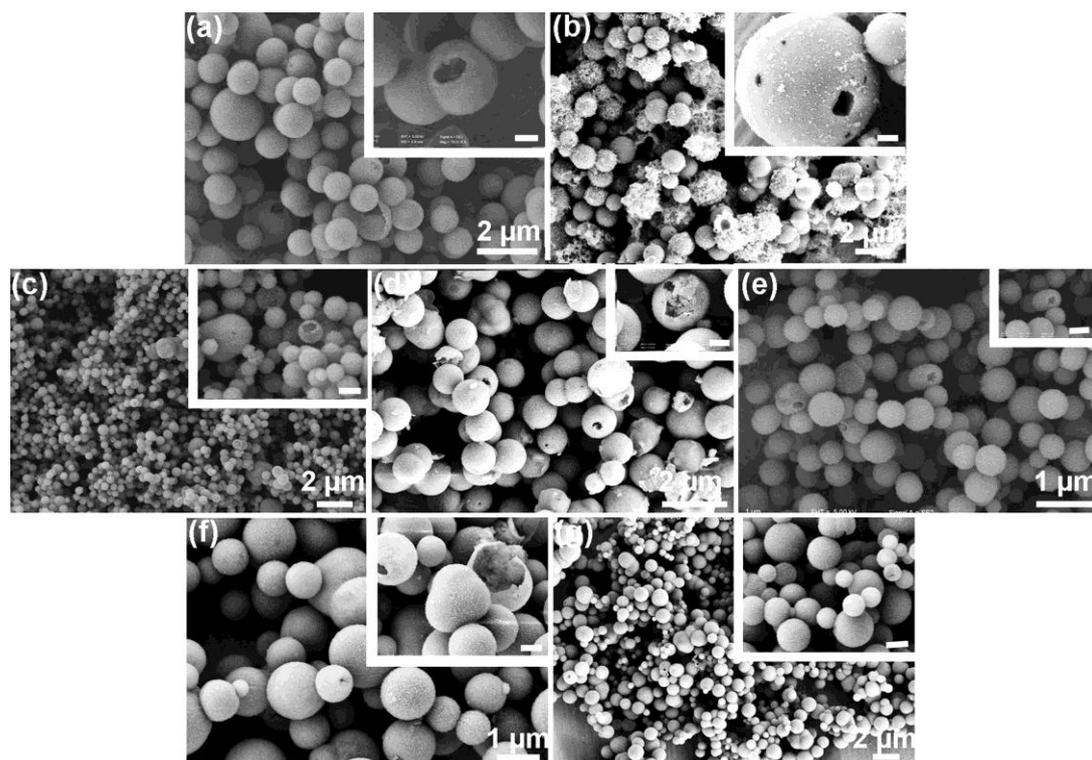


Fig. S3. SEM images of the as-synthesized Ln-BTB. (a) La-BTB; (b) Ce-BTB; (c) Pr-BTB; (d) Nd-BTB; (e) Sm-BTB; (f) Eu-BTB; (g) Gd-BTB. The scale bar of each inset is 500 nm.

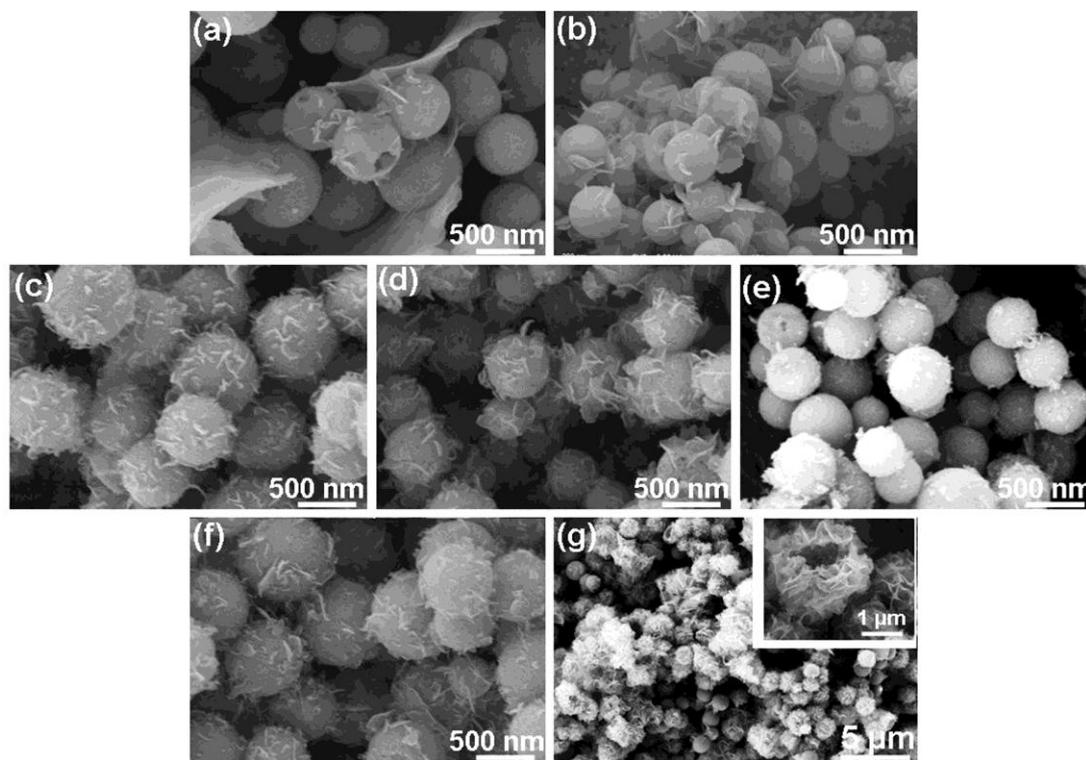


Fig. S4. SEM images of the as-synthesized Ln-BTB. (a) Dy-BTB; (b) Ho-BTB; (c) Er-BTB; (d) Tm-BTB; (e) Yb-BTB; (f) Lu-BTB; (g) Y-BTB.

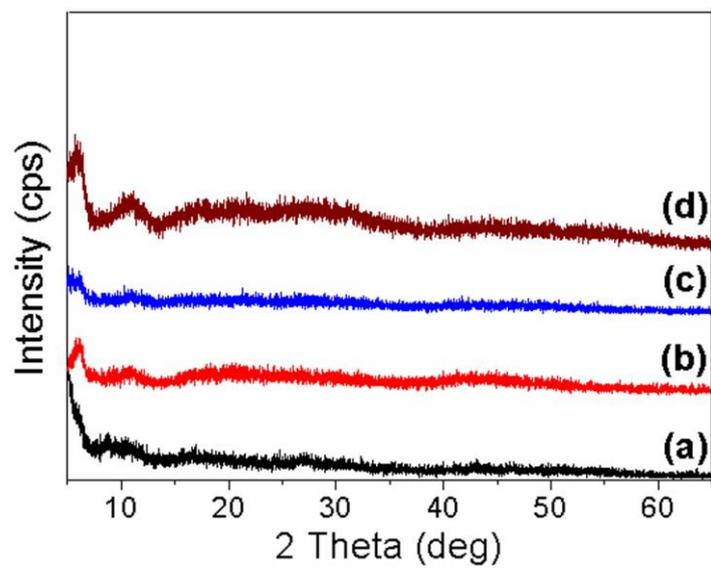


Fig. S5. Typical PXRD patterns of the as-synthesized Ln-BTB complexes (a) Y-BTB; (b) La-BTB; (c) Gd-BTB; (d) Lu-BTB.

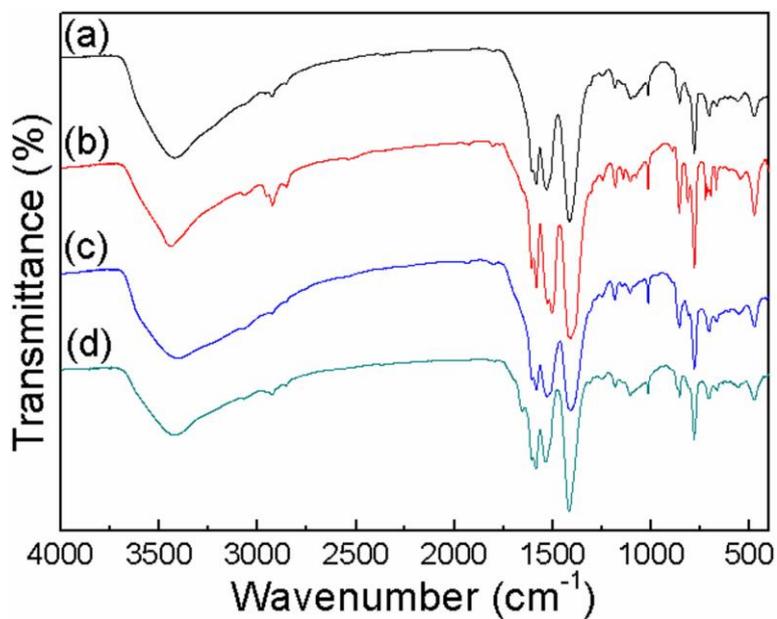


Fig. S6. Typical IR spectra of the as-synthesized Ln-BTB of complexes (a) Y-BTB; (b) La-BTB; (c) Gd-BTB; (d) Lu-BTB.

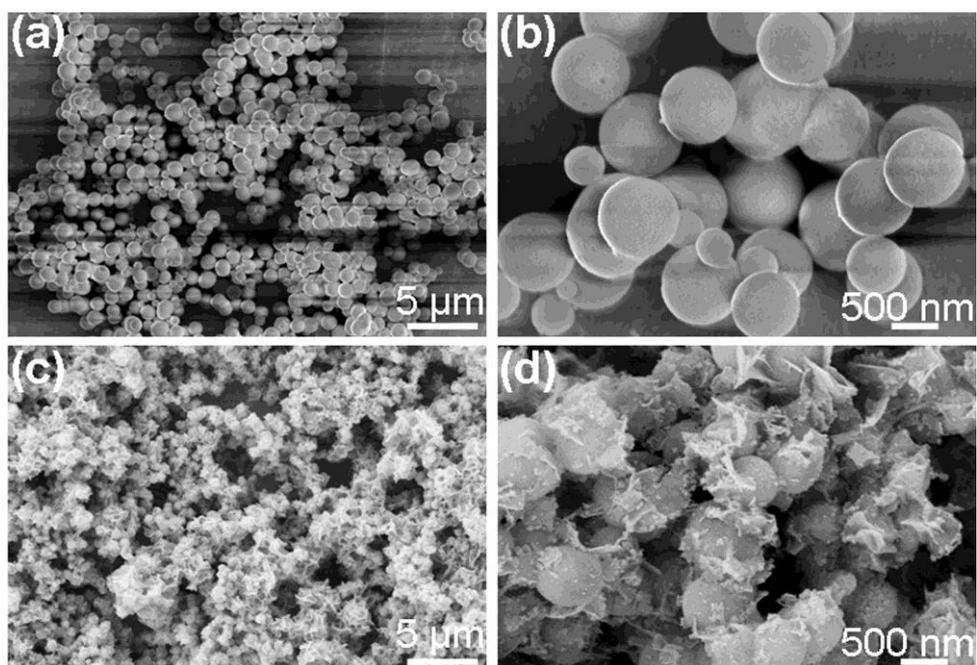


Fig.S7. SEM images of products prepared at different concentrations of Tb^{3+} and H_3BTB with other conditions remaining unchanged: (a, b) 2 mM (Tb-BTB-2); (c, d) 8 mM (Tb-BTB-3).

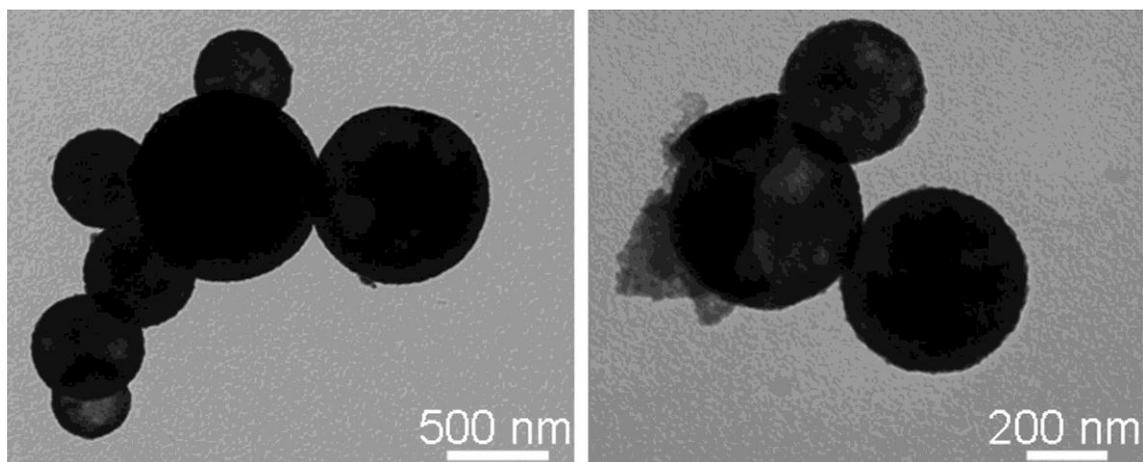


Fig. S8. TEM images of Tb-BTB-2.

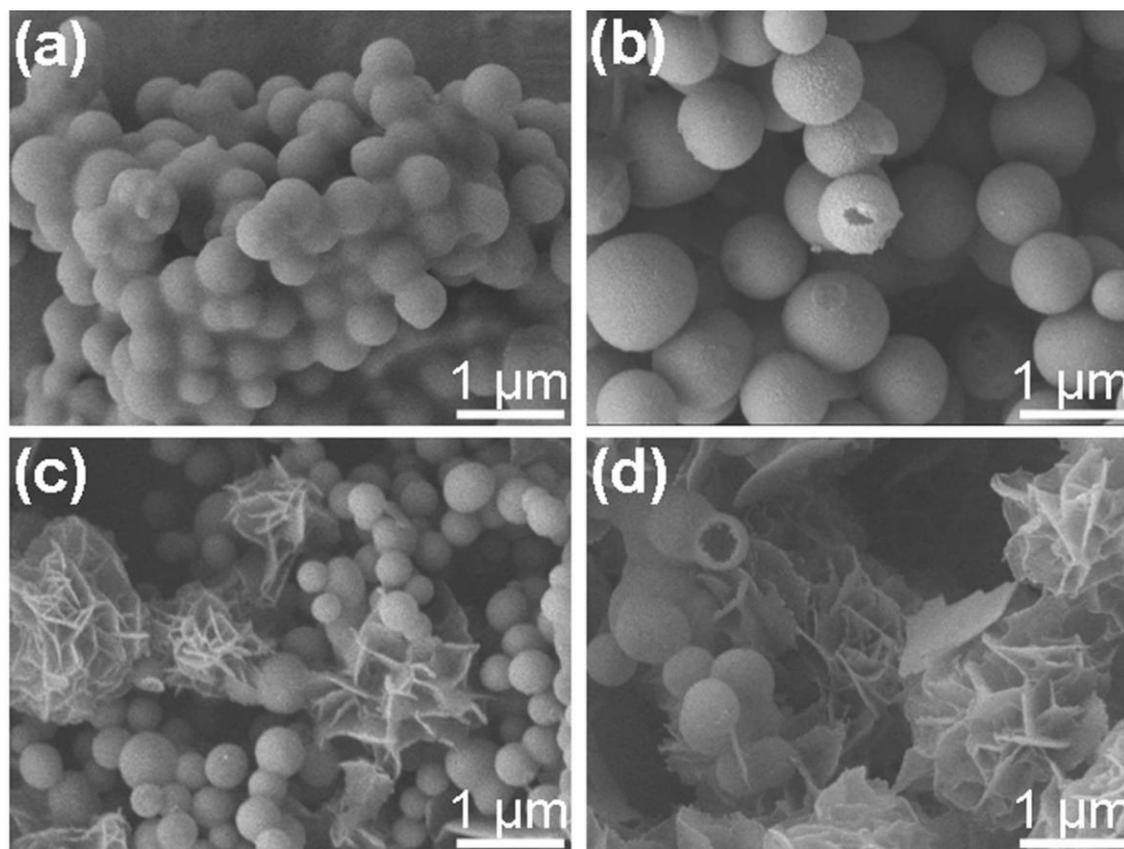


Fig. S9. SEM images of products prepared with various molar ratio of Tb^{3+} to H_3BTB : (a) 1: 4 (Tb-BTB-4); (b) 1: 2 (Tb-BTB-5); (c) 2:1 (Tb-BTB-6); (d) 4:1 (Tb-BTB-7). This result indicated that low molar ratio of Tb^{3+} to H_3BTB is in favor of the formation of pure hollow spheres.

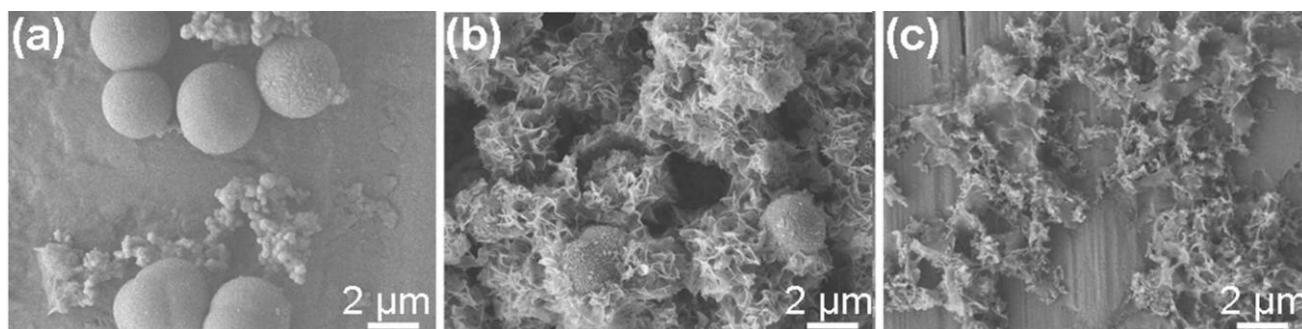


Fig. S10. SEM images of products prepared with different volume of DMF: (a) 12.5 mL (Tb-BTB-8); (b) 6 mL (Tb-BTB-9); (c) 4 mL (Tb-BTB-10).

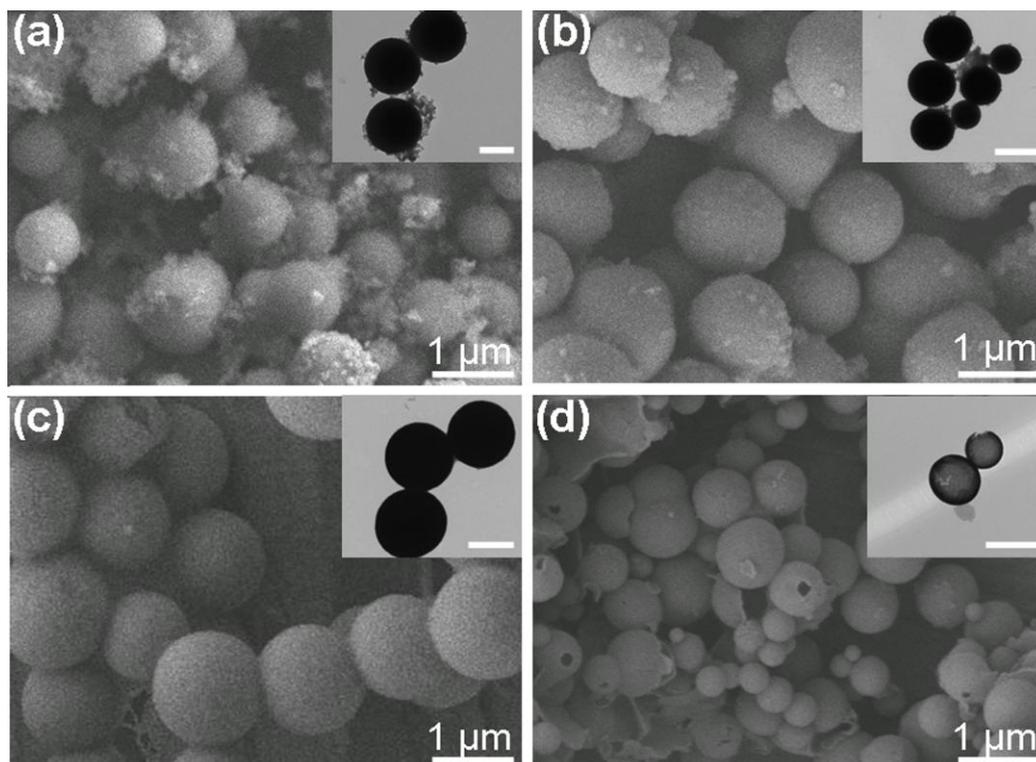


Fig. S11. SEM and TEM images of as-prepared products at different temperature : (a) 60 °C (Tb-BTB-11); (b) 80 °C (Tb-BTB-12); (c) 120 °C (Tb-BTB-13); (d) 180 °C (Tb-BTB-14). The scale bar of each inset is 1 μm.

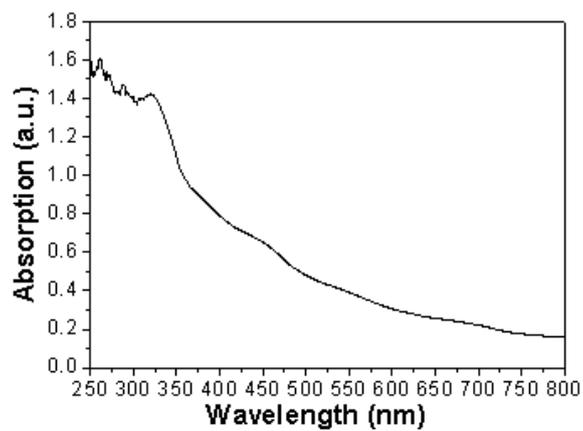


Fig. S12. UV/Vis absorption spectrum of the H₃BTB ligand.

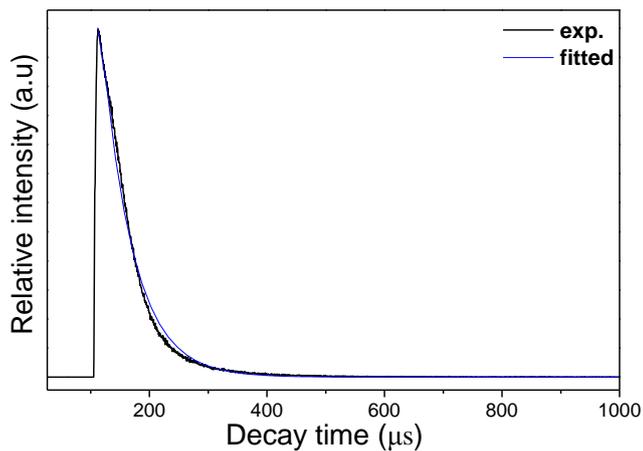


Figure S13. Decay curve of Tb-BTB-1.

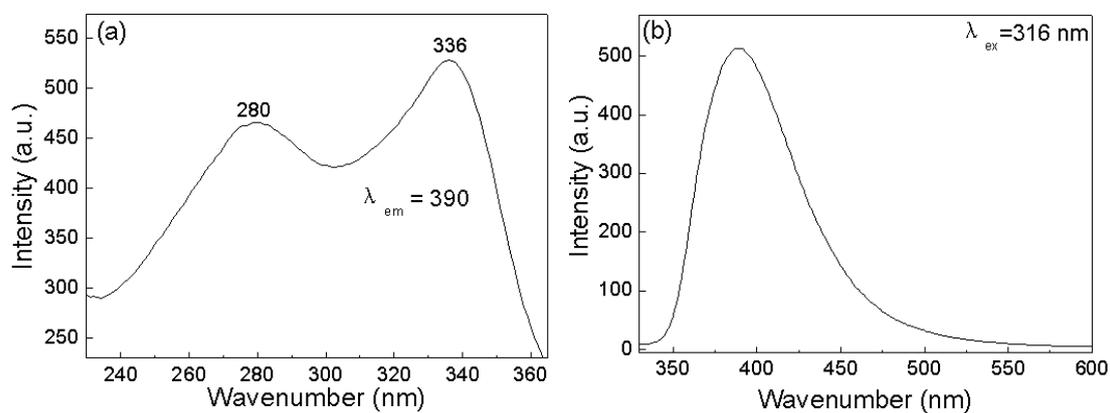


Fig. S14. (a) Excitation and (b) emission spectra of the H₃BTB ligand.

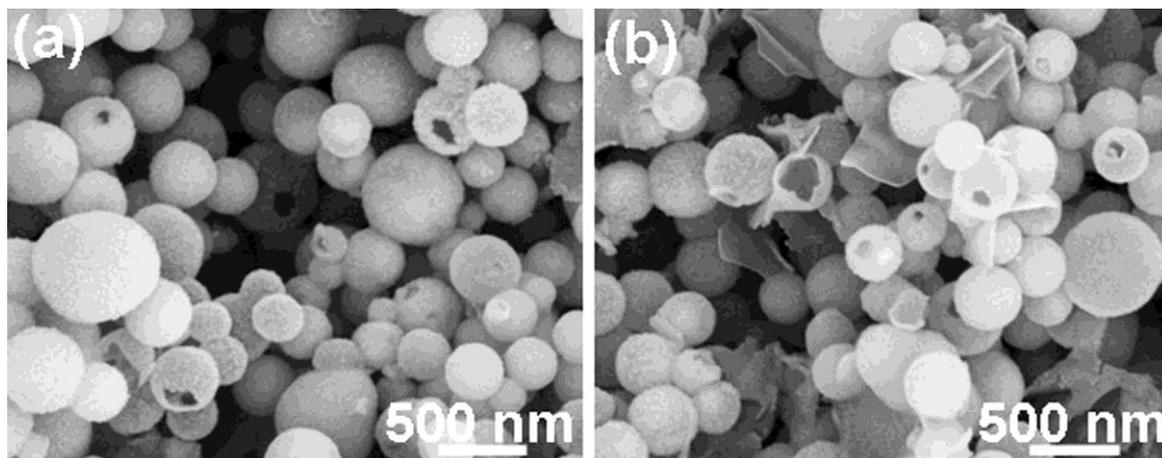


Fig. S15. SEM images of the Eu³⁺-doped Tb-BTB complexes: (a) Tb-BTB-1:0.05% Eu³⁺ and (b) Tb-BTB-1:10% Eu³⁺.

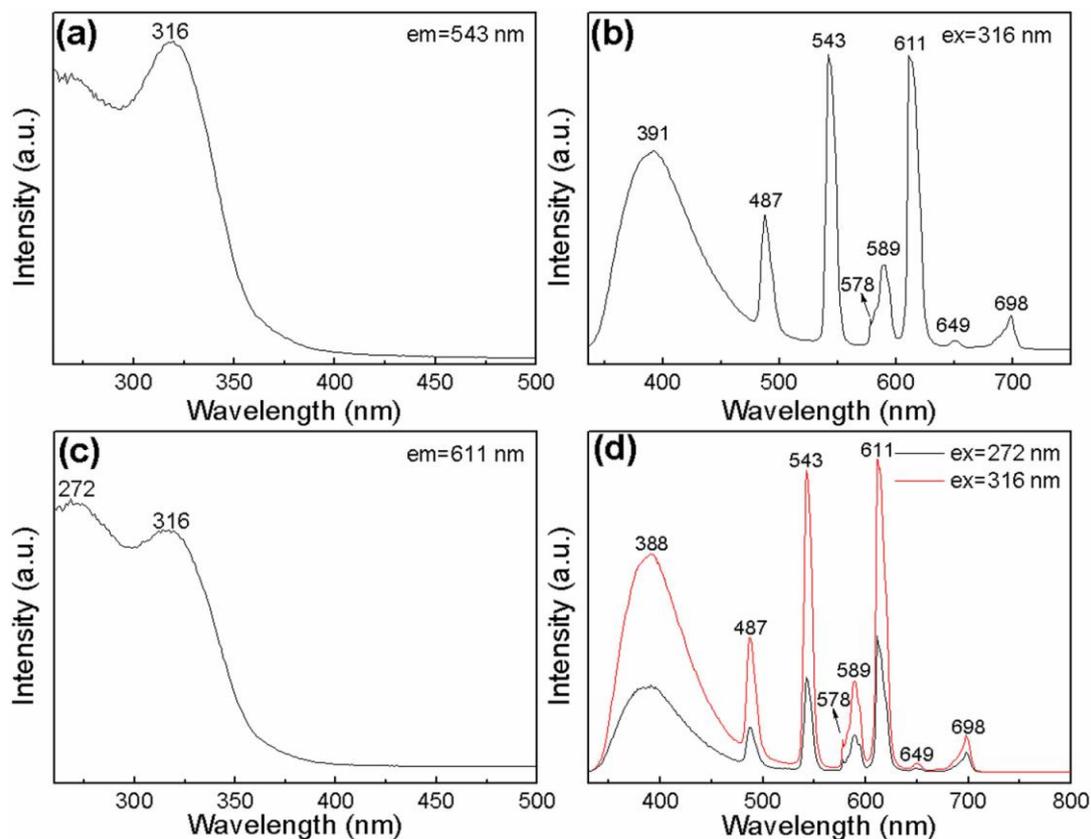


Fig. S16. Excitation and emission spectra of the Tb-BTB-1:0.3%Eu³⁺ hollow spheres.

Table S2. Chromaticity coordinates (x, y) of the Eu³⁺ doped Tb-BTB-1 hollowspheres under 316 nm excitation.

sample	Chromaticity coordinate (x)	Chromaticity coordinate (y)
Tb-BTB-1	0.2217	0.324
Tb-BTB-1:0.05%Eu ³⁺	0.2582	0.3105
Tb-BTB-1:0.1%Eu ³⁺	0.2776	0.2865
Tb-BTB-1:0.3%Eu ³⁺	0.3369	0.292
Tb-BTB-1:0.5%Eu ³⁺	0.4429	0.3323
Tb-BTB-1:5%Eu ³⁺	0.5789	0.3256
Tb-BTB-1:10%Eu ³⁺	0.6016	0.3266