Supporting Information

π−System Based Coordination Polymer Hollow Nanospheres for Selective Sensing of Aromatic Nitro Explosive Compounds

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Figures and Captions.

S1. Molecular stacks (TbBTB)

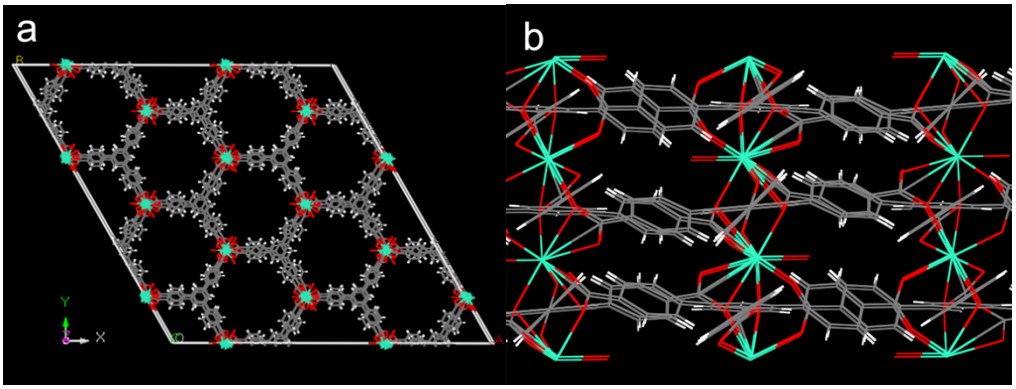


Fig. S1 (a) Direct view of MIL-103 along z axis. Space group: R32 (CCDC-28584). Cell parameters: a=28.5344(8), c=12.2148(5), V=8613.0(5) A^3. (b) The enlarged view along y axis. Tb is coordinated with one water oxygen atom and eight carboxylate oxygen atoms of 6 separate BTB ligands.[1]

S2. Synthesis, composition and microstructure

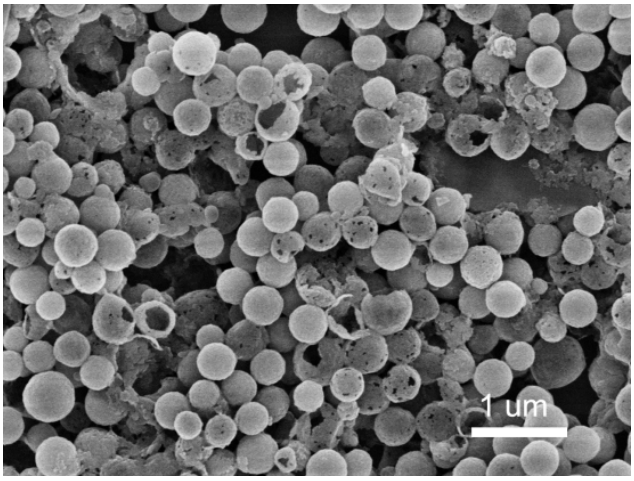


Fig. S2 Low magnification FESEM image of the obtained TbBTB hollow spheres.

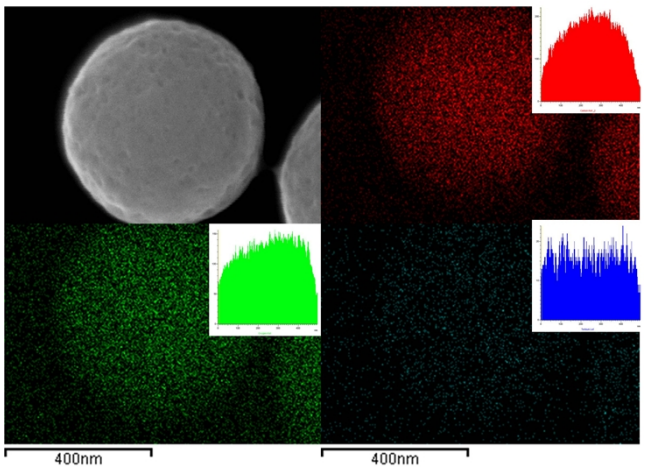


Fig. S3 EDX Mapping results of a single sphere. Red, green and blue represent C , O, Tb, respectively.

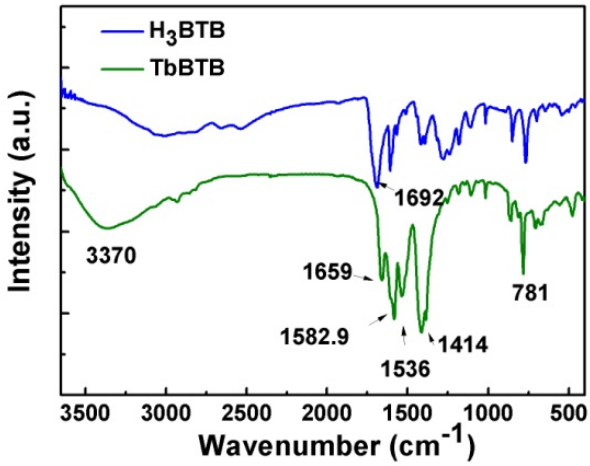


Fig. S4 FT-IR spectra of H_3BTB and TbBTB nanospheres.

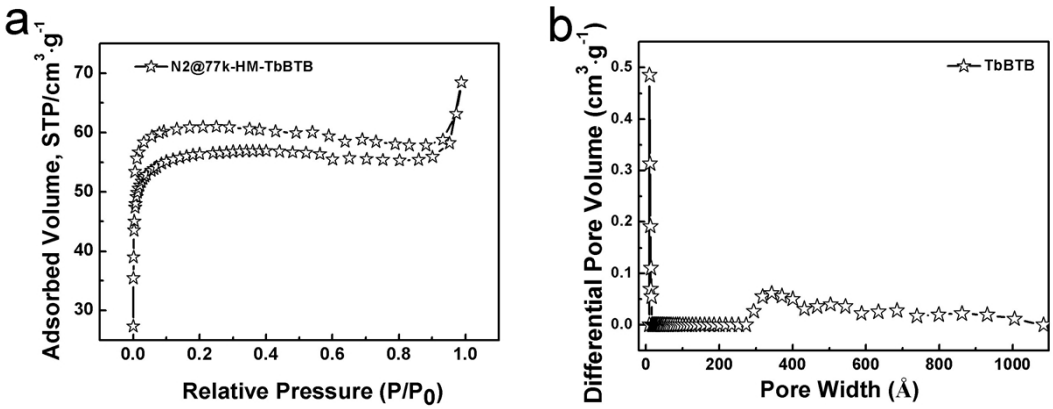


Fig. S5 (a) N_2 adsorption/desorption isotherm (b) Pore width distribution of the nanospheres.

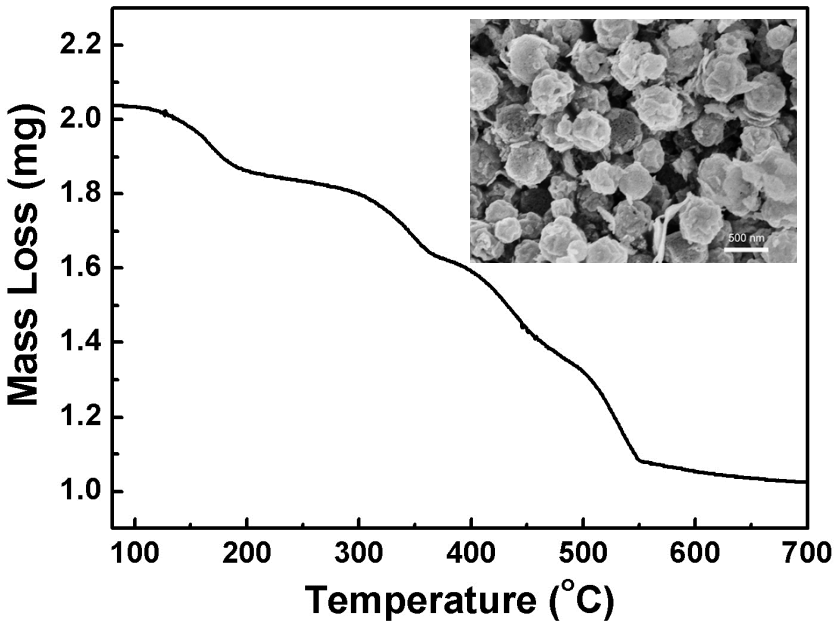


Fig. S6 Thermogravimetic (TG) curve of TbBTB nanospheres. The inset is corresponding FESEM image of the product obtained after thermal analysis.

S3. Fluorescence sensing tests

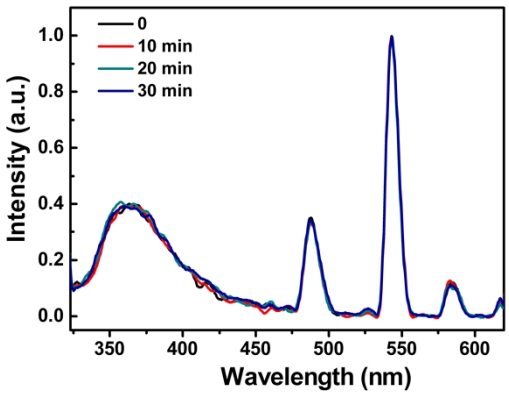


Fig. S7 Time-dependent fluorescence spectra of the DMF dispersion of TbBTB nanospheres dispersed in DMF.

Table S1. Reported sensing performance of lanthanide based MOF for 2,4-DNT.

Sensing materials	Sensitivity (Quenching efficiency; Ksv&Concentration Scale)	Literatures
$Eu_2(BDC)_3(H_2O)_2\cdot(H_2O)_2$ (BDC=benzene-1,4-dicarboxylate)	2,4-DNT: 0.83 mM (150ppm), 56% Ksv: no value	H. Xu, F. Liu, Y. Cui, B. Chen and G. Qian, *Chem. Commun.*, 2011, **47**, 3153-3155
$[Tb(TTCA)(DMA)(H_2O)]\cdot 7DMA\cdot 9.5H_2O$ (TTCA=triphenylene-2,6,10- tricarboxylate; DMA= N,N-dimethyl acetamide)	2,4-DNT: 4mM, 82% 1mM, 59% Ksv: no value	Y.-N. Gong, L. Jiang and T.-B. Lu, *Chem. Commun.*, 2013, **49**, 11113-11115
Eu-MFDA Space group: $P2_1/c$ (H2MFDA = 9,9-dimethylfluorene-2,7-dicarboxylic acid)	2,4-DNT: 1mM, 46 % Ksv: $1.31*10^3$ M^{-1}@0~50mM	X. Zhou, H. Li, H. Xiao, L. Li, Q. Zhao, T. Yang, J. Zuo and W. Huang, *Dalton Trans.*, 2013, **42**, 5718-5723
Eu-MFDA Space group: *Pnna*	2,4-DNT: 1mM, 36.5% Ksv: $1.58*10^3$ M^{-1}@0~50mM	X. Zhou, L. Li, H. Li, A. Li, T. Yang and W. Huang, *Dalton Trans.*, 2013, **42**, 12403-12409
$[Y_{1.8}Eu_{0.2}(PDA)_3(H_2O)_1]\cdot 2H_2O$	2,4-DNT: 20 μM, 50% Ksv: nonlinear@>20μM Ksv: 5.01×10^4@0~20μM	D. K. Singha, P. Majee, S. K. Mondal and P. Mahata, *Eur. J. Inorg. Chem.*, 2015,

		8, 1390-1397

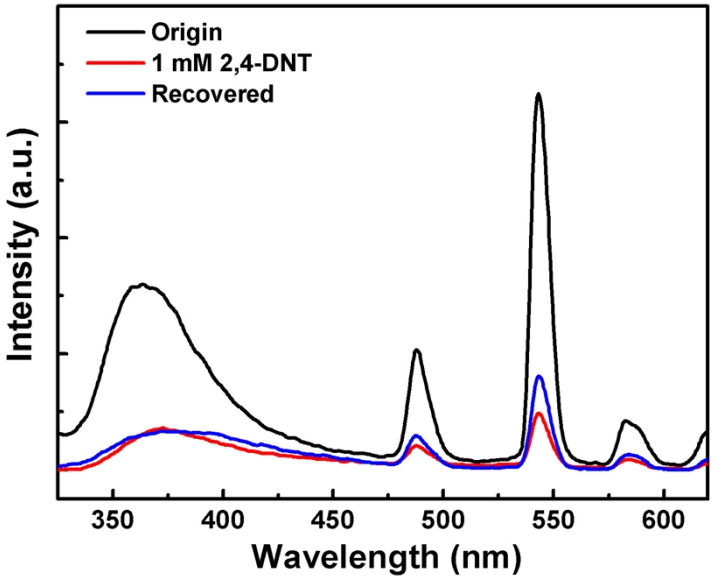


Fig. S8 The fluorescence quenching and recovery test of TbBTB nanospheres. The black, red and blue curves represent the fluorescent spectra of the original TbBTB nanosphere dispersion, the dispersion in 1 mM DNT and the recovered dispersion after removing the DNT, respectively.

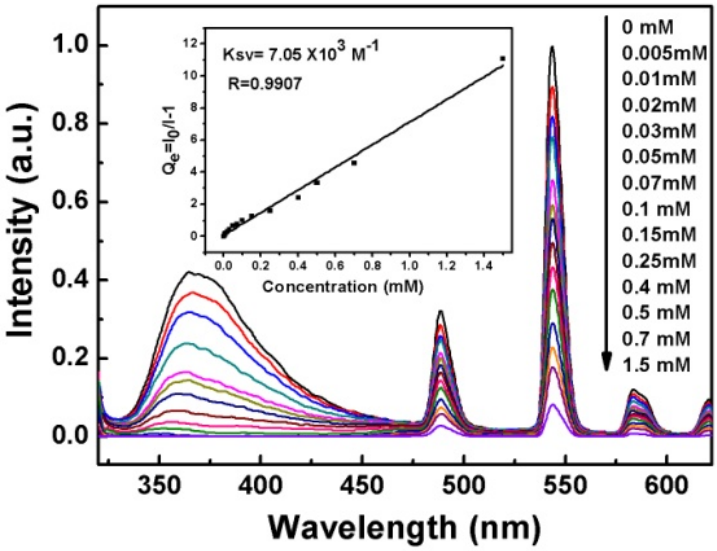


Fig. S9 Concentration-dependent luminescence responses of TbBTB nanospheres for PA. The inset is the corresponding Stern-Volmer plot.

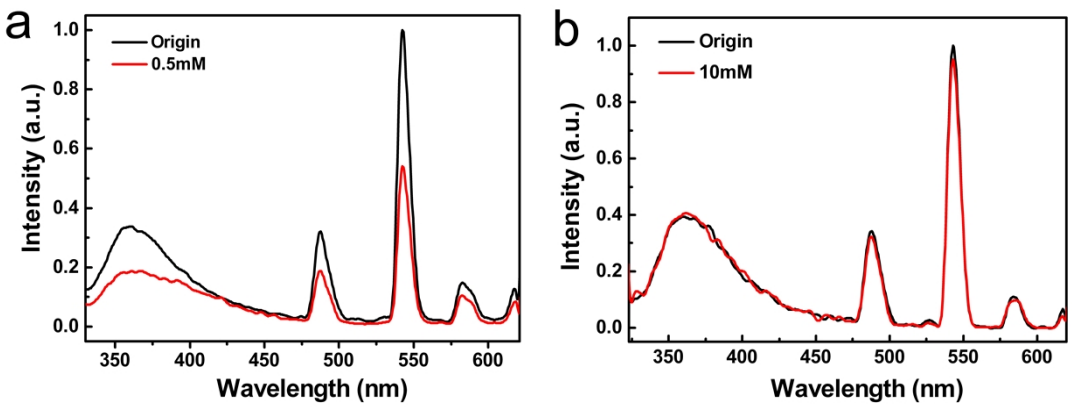


Fig. S10 (a) Fluorescence spectra of the MeCN dispersion of TbBTB hollow spheres with (red line) /without (black line) 2,4,6-Trinitrotoluene (TNT) (TNT: 5.0×10^{-4} M; LUMO: -3.930 eV, HOMO: -8.810 eV) [2], λ_{ex} = 314 nm (b) Fluorescence spectra of the DMF dispersion of TbBTB hollow spheres with (red line) /without (black line) MeCN (MeCN: 10 mM). λ_{ex} = 314 nm.

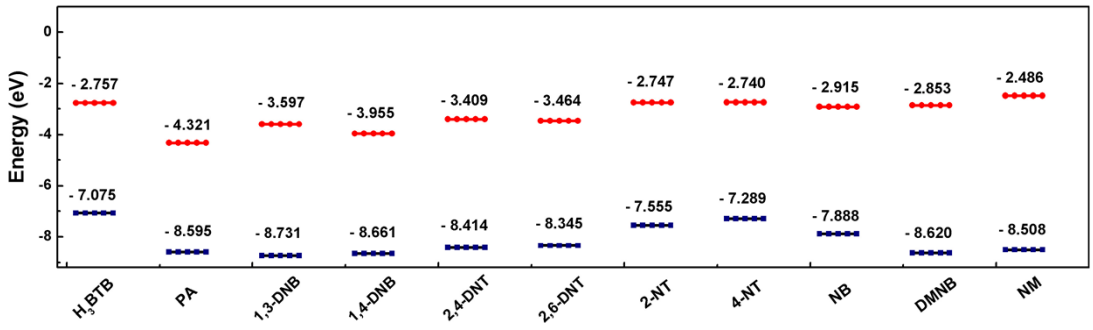


Fig. S11 HOMO and LUMO energies of the analyte targets by calculation via Gaussian 09 at the B3LYP/6-31G* level or by reference. [2]

S4. Formation of the structures

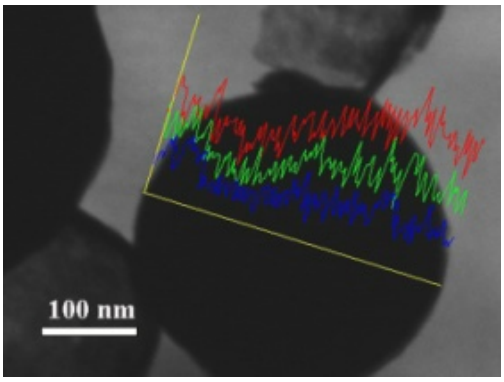


Fig. S12 Stacking elements TEM image of a solid sphere. Red, green and blue represent C , O, Tb, respectively.

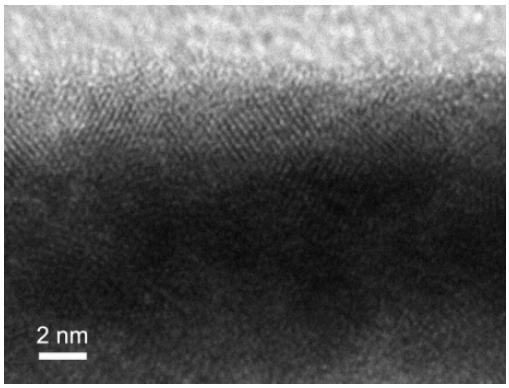


Fig. S13 HRTEM image of the solid sphere.

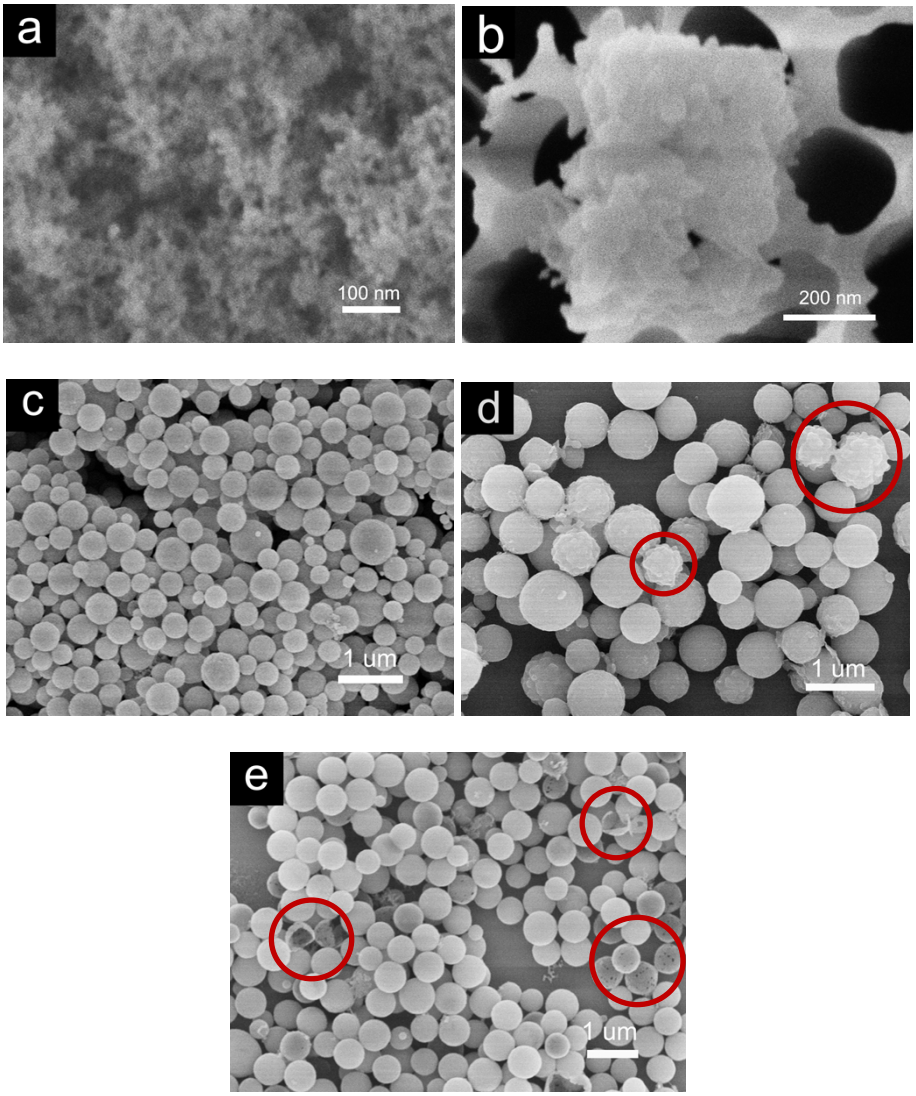
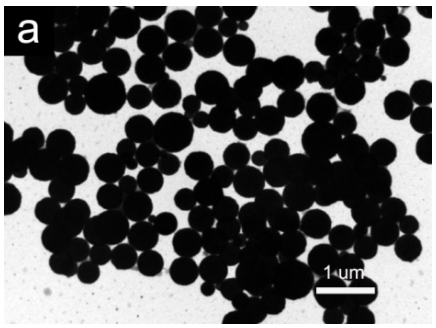


Fig. S14 FESEM images of the obtained TbBTB nanospheres at different reaction time of (a) 0.5, (b) 1, (c) 4, (d) 12 and (e) 20 h.



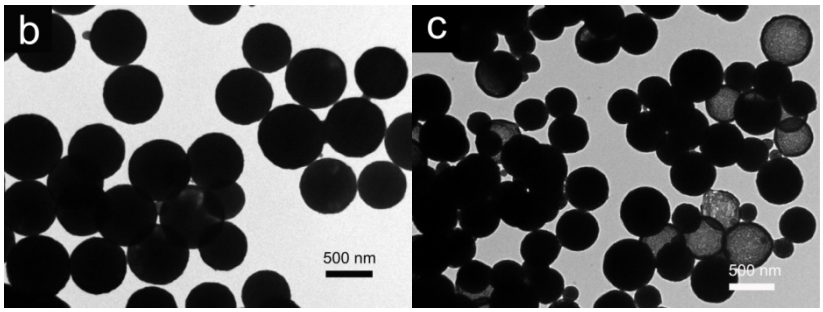


Fig. S15 TEM images of the obtained TbBTB nanospheres at different reaction time of (a) 4, (b) 12 and (c) 20 h.

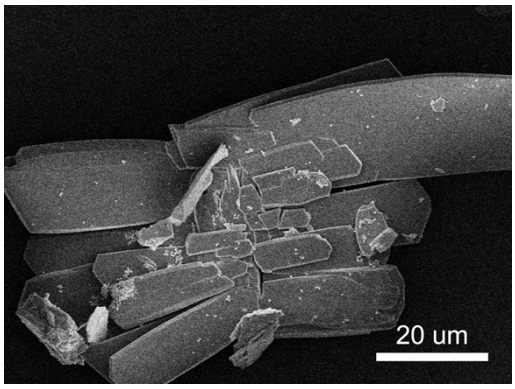


Fig. S16 FESEM image of the product obtained after 7 days.

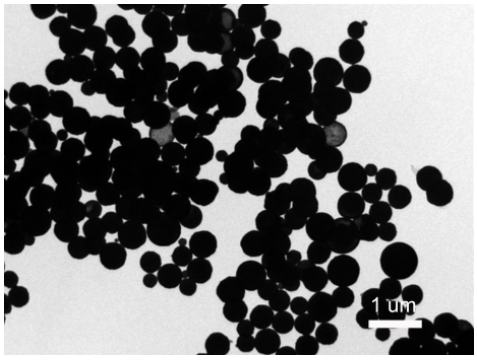


Fig. S17 TEM image of the product obtained by aging the nanospheres formed at 4h in the solvent without any other reactants at 120 ^{o}C for 20h.

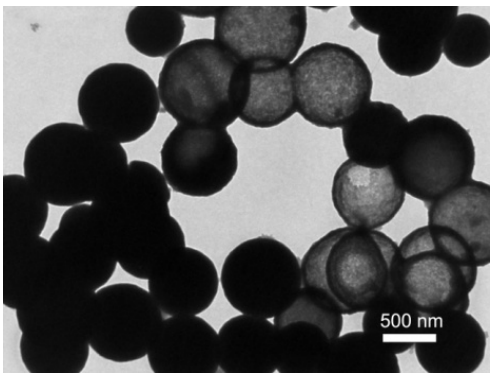


Fig. S18 TEM image of products prepared for 36h at the same condition as the literature (0.05 mmol H_3BTB and 0.05 mmol $Tb(NO_3)_3$ were dissolved in the mixed solvent of 12.5 mL DMF and H_2O (v:v = 8 : 4.5), heated at 150 °C for 36 h).[3]

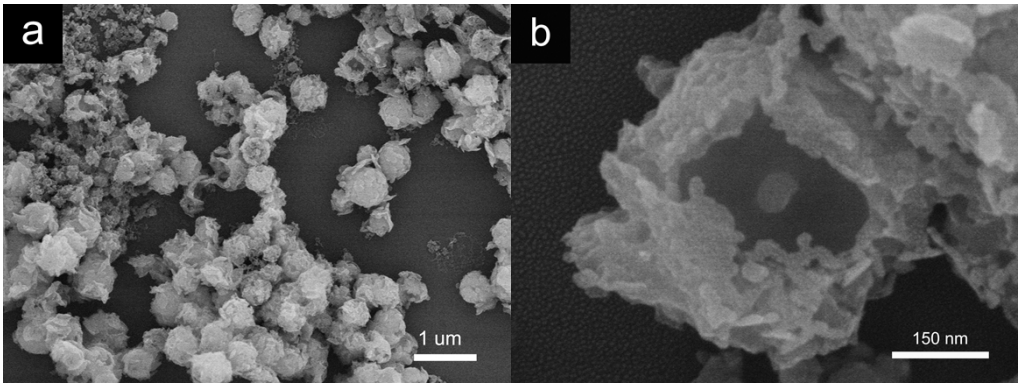


Fig. S19 (a) Low and (b) high magnification FESEM images of the obtained products at 140 °C in the reaction system employed in the experimental section.

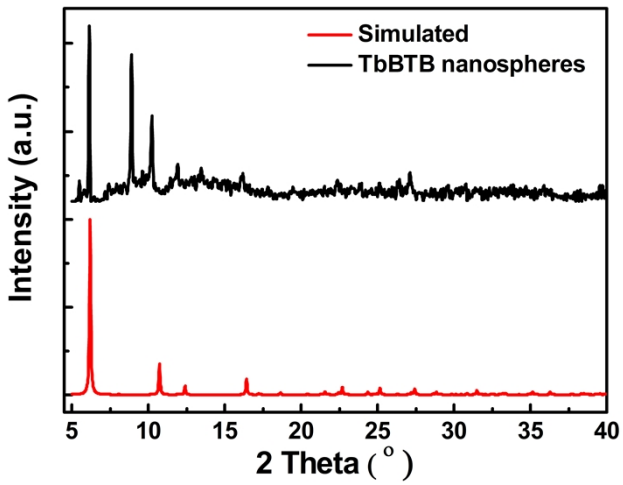


Fig. S20 X-ray diffraction pattern of (a) TbBTB single crystal (red line) and (b)

TbBTB nanospheres (black line).

References

1. Devic, T.; Serre, C.; Audebrand, N.; Marrot, J.; Férey, G., MIL-103, a 3-D lanthanide-based metal organic framework with large one-dimensional tunnels and a high surface area. *Journal of the American Chemical Society* 2005**, 127**, 12788-12789.
2. Hu, Z.; Deibert, B. J.; Li, J., Luminescent metal–organic frameworks for chemical sensing and explosive detection. *Chemical Society reviews* 2014, **43**, 5815-5840.
3. Zhong, S.-L.; Xu, R.; Zhang, L.-F.; Qu, W.-G.; Gao, G.-Q.; Wu, X.-L.; Xu, A.-W., Terbium-based infinite coordination polymer hollow microspheres: preparation and white-light emission. *Journal of Materials Chemistry* 2011, **21**, 16574-16580.