Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supplementary Information

Micro-crystals of metal-organic frameworks constructed from pyrene-based organic linkers and lanthanide ions for tunable white light emission

Jeehyun Park and Moonhyun Oh*

Department of Chemistry, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, Korea

*Corresponding Author

Telephone number: 82-2-2123-5637

Fax number: 82-2-364-7050

Email address: moh@yonsei.ac.kr

General

All chemicals and solvents were obtained from commercial sources and were used as received. All SEM images were acquired using a Hitachi SU 1510 SEM. The EDX spectra were obtained using a Hitachi SU 1510 SEM equipped with a Horiba EMAX Energy E-250 EDS system. X-ray diffraction studies were carried out using a Rigaku Ultima IV equipped with a graphite monochromated $Cu_{k\alpha}$ radiation source (40 kV, 40 mA). The IR spectra of solid samples were obtained using a Jasco FT/IR 4200 spectrometer as KBr pellet. TGA measurements were conducted using a Shimadzu TGA-50 in an oxygen atmosphere at a heating rate of 5 ℃ min^{-1}. Emission spectra were obtained using a Perkin Elmer LS 55 fluorometer using quartz cells (10 × 4 mm light path). Metal analysis was conducted using a Perkin Elmer NexION300 inductively coupled plasma-mass spectrometer (ICP-MS).

Preparation of CPP-17 of a three-dimensional framework $[Gd_3(BDC)_{4.5}(S)_a]_n$

A coordination polymer precursor solution was prepared by mixing 1,4-benzenedicarboxylic acid (H_2BDC, 4.98 mg, 0.030 mmol) and $Gd(NO_3)_3 \cdot 6H_2O$ (14.895 mg, 0.033 mmol) in 7.5 mL of DMF/THF cosolvent (2:1 v/v). The resulting precursor solution was placed in an oil bath (140 ℃) for 20 min. After 20 min, the resulting particles were isolated and subsequently washed several times with DMF and acetonitrile *via* centrifugation-redispersion cycles. Each successive supernatant was decanted and replaced with fresh solvent. IR for CPP-17 (KBr pellet cm^{-1}): 1666 (s), 1641 (w), 1569 (s), 1505 (m), 1404 (s), 1312 (w), 1254 (w), 1158 (w), 1107 (w), 1019 (w), 886 (w), 820 (w), 752 (s), 677 (m), 515 (m).

Preparation of a series of CPP-17-X (X = a-e), $[Gd_3(BDC)_{4.5-x}(L)_x(S)_a]_n$

The precursor solutions were prepared by mixing $Gd(NO_3)_3 \cdot 6H_2O$ (14.895 mg, 0.033 mmol) with the mixture of H_2BDC and 2-(pyrene-1-carboxamido)terephthalic acid (H_2L) (0, 2.49, 3.74, 4.73, or

4.86 mg of H_2BDC were used for CPP-17-a ~ CPP-17-e, respectively, and 12.27, 6.14, 3.07, 0.61, or 0.31 mg of H_2L were used for CPP-17-a ~ CPP-17-e, respectively) in 7.5 mL of DMF/THF cosolvent (2:1 v/v). The resulting precursor solution was placed in an oil bath (140 ℃) for 20 min. After 20 min, the resulting particles were isolated and subsequently washed several times with DMF and acetonitrile *via* centrifugation-redispersion cycles. Each successive supernatant was decanted and replaced with fresh solvent.

Preparation of a series of CPP-17-Y (Y = i-viii), $[Eu_{3-y}Tb_y(BDC)_{4.5}(S)_a]_n$

The precursor solution was prepared by mixing H_2BDC (4.98 mg, 0.030 mmol) and a mixture of $Eu(NO_3)_3 \cdot 5H_2O$ and/or $Tb(NO_3)_3 \cdot 5H_2O$ at different ratios (the ratios of $Eu(NO_3)_3 \cdot 5H_2O$ and $Tb(NO_3)_3 \cdot 5H_2O$ were 1:0, 0.5:0.5, 0.3:0.7, 0.1:0.9, 0.075:0.925, 0.05:0.95, 0.025:0.975, or 0:1 for CPP-17-i ~ CPP-17-viii, respectively, with the total amount maintained at 0.03 mmol) in 7.5 mL of DMF/THF cosolvent (2:1 v/v). The resulting precursor solution was placed in an oil bath (140 ℃) for 20 min. After 20 min, the resulting particles were isolated and subsequently washed several times with DMF and acetonitrile *via* centrifugation-redispersion cycles. Each successive supernatant was decanted and replaced with fresh solvent.

Preparation of CPP-17-e-iv

A coordination polymer precursor solution was prepared by mixing H_2BDC (4.86 mg, 0.029 mmol), 2-(pyrene-1-carboxamido)terephthalic acid (H_2L, 0.31mg, 0.00075 mmol), and a mixture of $Eu(NO_3)_3 \cdot 5H_2O$ (1.41mg, 0.0033mmol) and $Tb(NO_3)_3 \cdot 5H_2O$ (12.92mg, 0.0297mmol) in 7.5 mL of DMF/THF cosolvent (2:1 v/v). The resulting precursor solution was placed in an oil bath (140 ℃) for 20 min. After 20 min, the resulting particles were isolated and subsequently washed several times with DMF and acetonitrile *via* centrifugation-redispersion cycles. Each successive supernatant was decanted and replaced with fresh solvent.

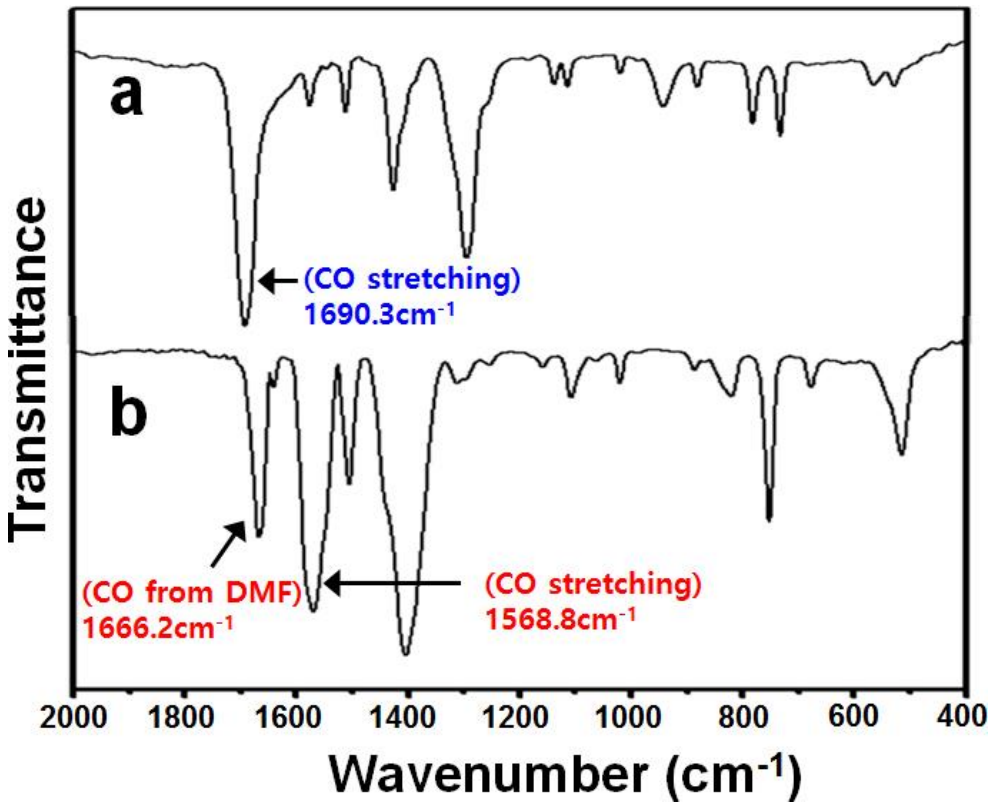

Fig. S1 IR spectra of (a) H_2BDC and (b) CPP-17 of $[Gd_3(BDC)_{4.5}(S)_a]_n$.

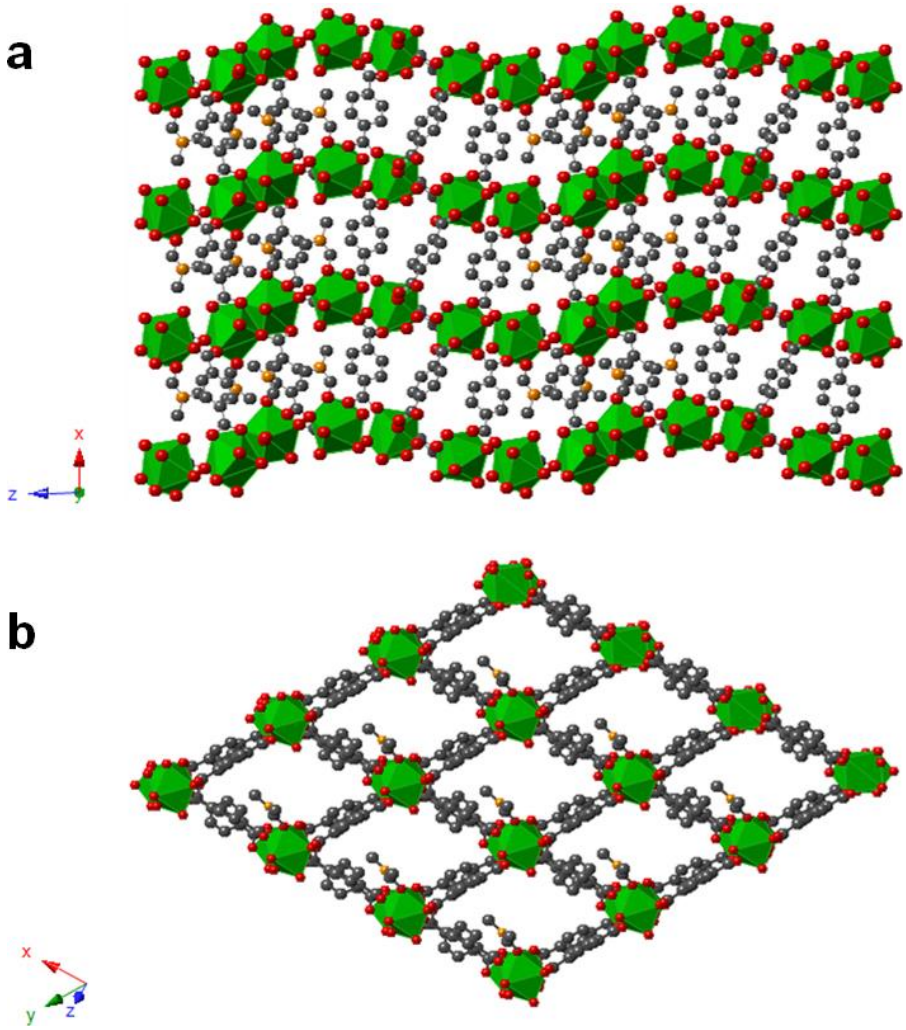

Fig. S2 (a,b) Ball-and-stick representations of 3D framework of $[Tb_3(BDC)_{4.5}(S)_a]_n$. Polyhedra; terbium, gray; carbon, red; oxygen, orange; nitrogen. Hydrogen atoms and guest molecules are omitted for clarity.

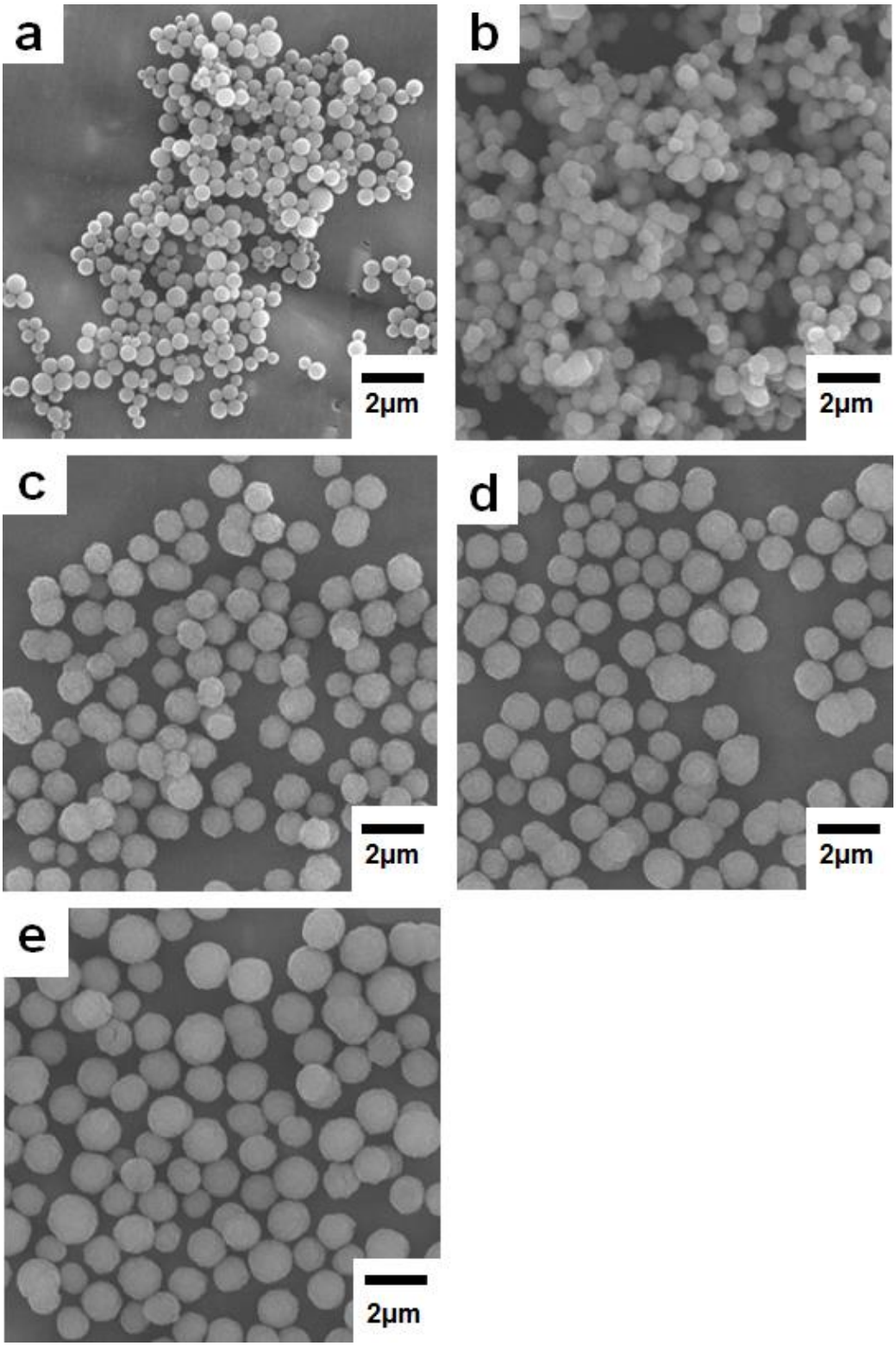

Fig. S3 SEM images of a series of CPPs (CPP-17-X, X = a-e; $[Gd_3(BDC)_{4.5-x}(L)_x(S)_a]_n$) with various ratios of L^{2-}:BDC^{2-} prepared using various initial amounts of H_2L and H_2BDC (a = 1:0, b = 0.5:0.5, c = 0.25:0.75, d = 0.05:0.95, e = 0.025:0.975). (a) CPP-17-a, (b) CPP-17-b, (c) CPP-17-c, (d) CPP-17-d, and (e) CPP-17-e.

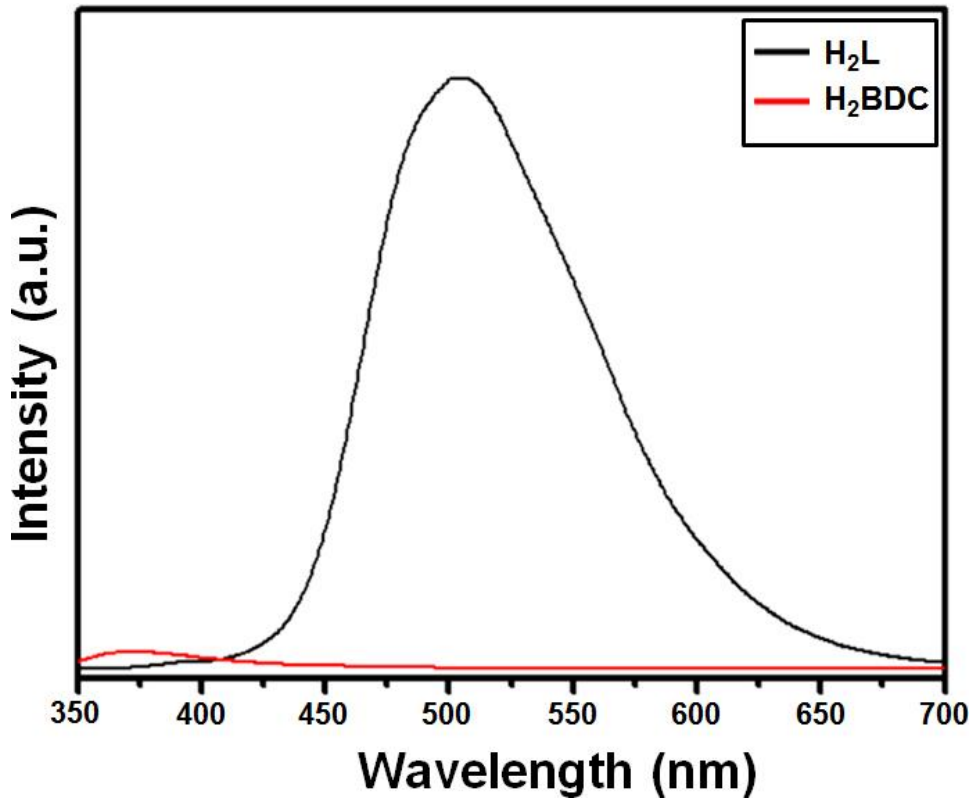

Fig. S4 Emission spectra of H_2L and H_2BDC in CH_3CN (c = 1.0 x 10^{-4} M, λ_{ex} = 310 nm).

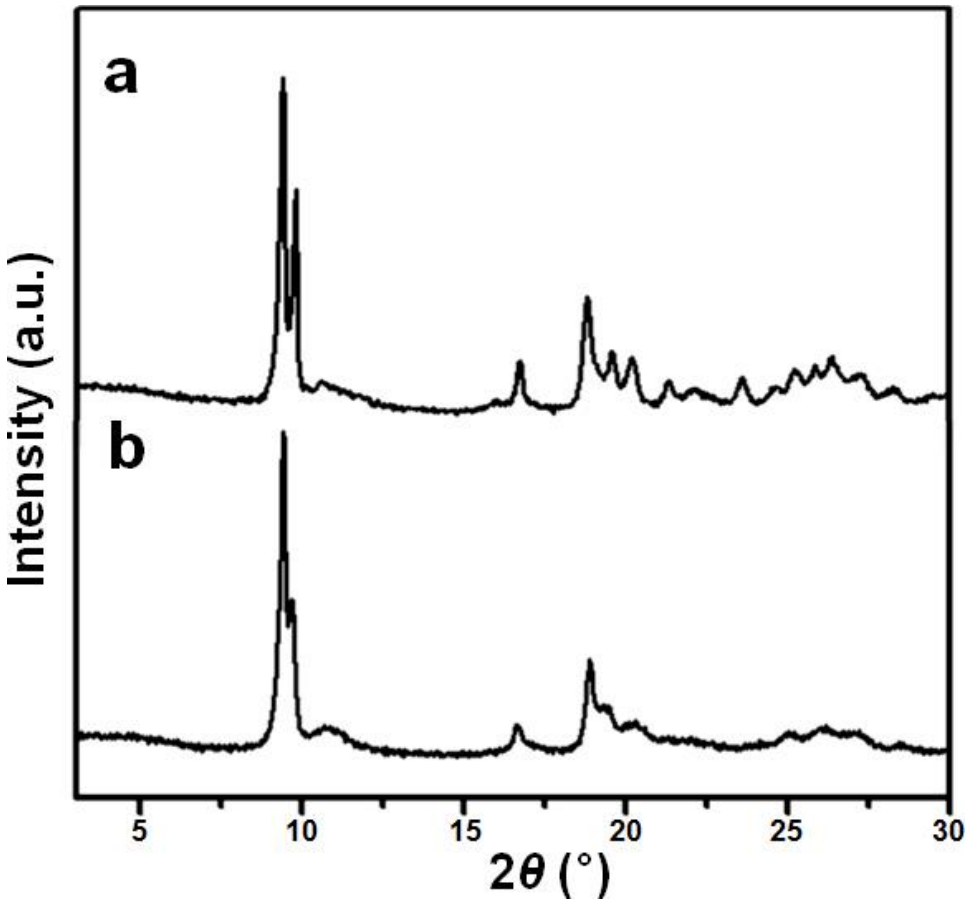

Fig. S5 PXRD patterns of (a) CPP-17 and (b) CPP-17-e.

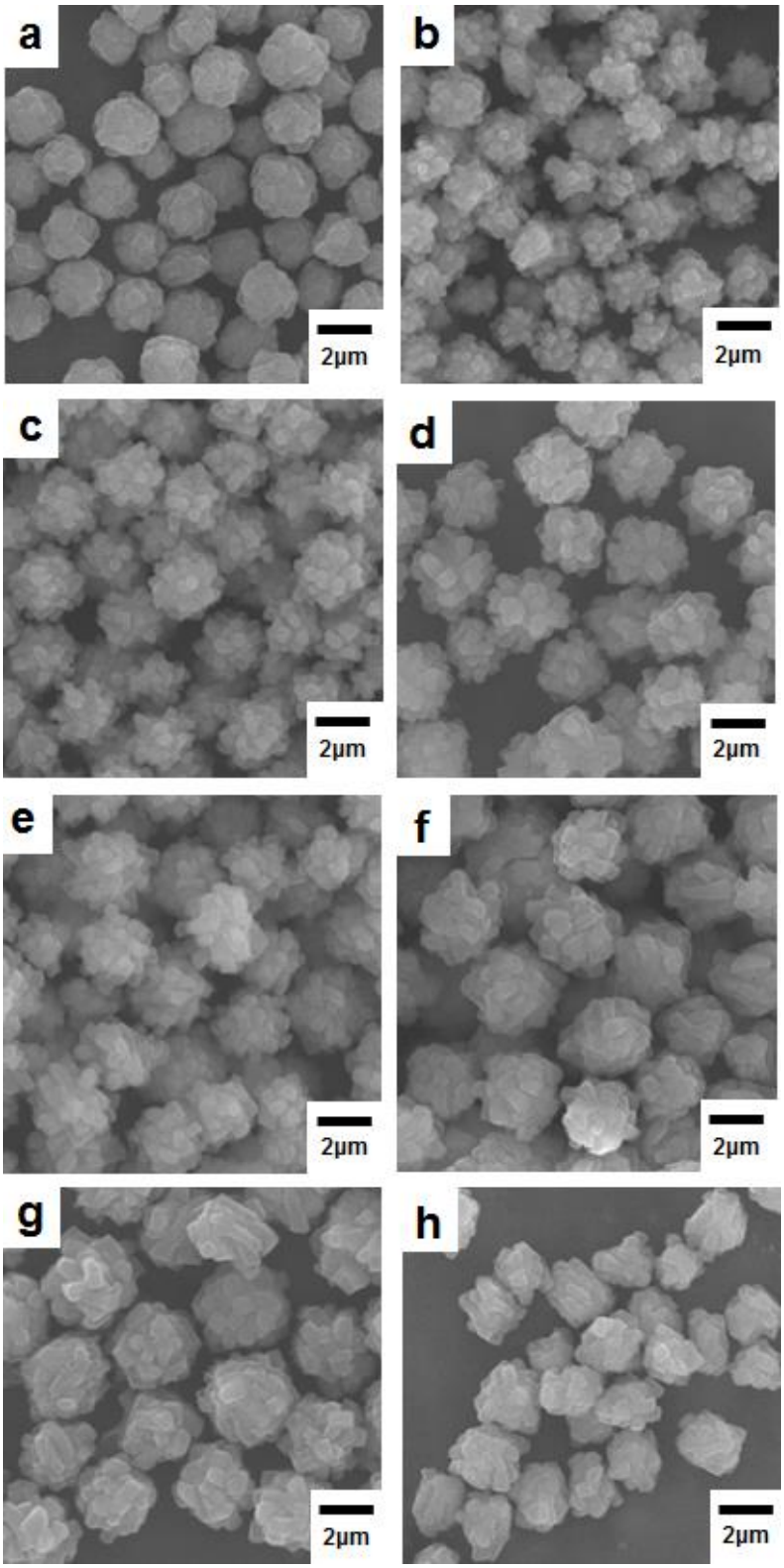

Fig. S6 SEM images of a series of CPPs (CPP-17-Y, Y = i-viii; $[Eu_{3-y}Tb_y(BDC)_{4.5}(S)_a]_n$) prepared using different ratios of Eu^{3+}:Tb^{3+} (i = 1:0, ii = 0.5:0.5, iii = 0.3:0.7, iv = 0.1:0.9, v = 0.075:0.925, vi = 0.05:0.95, vii = 0.025:0.975, viii = 0:1). (a) CPP-17-i, (b) CPP-17-ii, (c) CPP-17-iii, (d) CPP-17-iv, (e) CPP-17-v, (f) CPP-17-vi, (g) CPP-17-vii, and (h) CPP-17-viii.

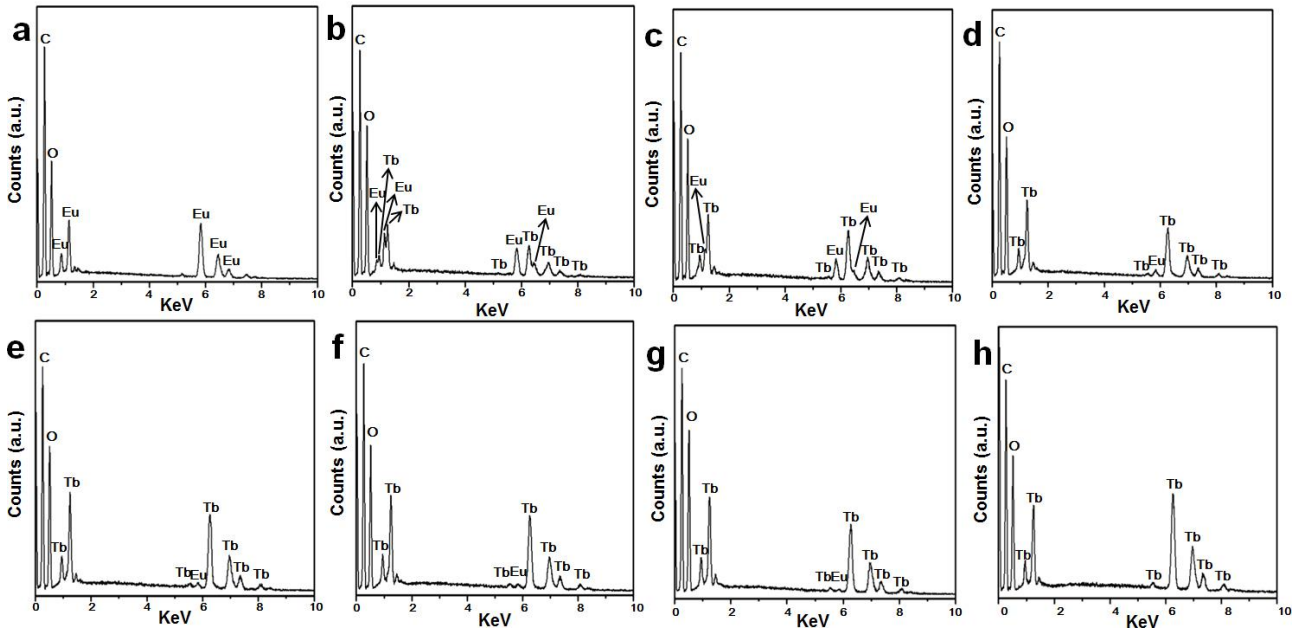

Fig. S7 EDX spectra of a series of CPP-17-Y (Y = i-viii). (a) CPP-17-i, (b) CPP-17-ii, (c) CPP-17-iii, (d) CPP-17-iv, (e) CPP-17-v, (f) CPP-17-vi, (g) CPP-17-vii, and (h) CPP-17-viii.

Table S1 The relative amounts of Eu^{3+} and Tb^{3+} incorporated within a series of CPP-17-Y (Y = i-viii; $[Eu_{3-y}Tb_y(BDC)_{4.5}(S)_a]_n$) determined by ICP analysis.

CPPs	Eu^{3+} (%)	Tb^{3+} (%)
CPP-17-i	100	0
CPP-17-ii	45.9	54.1
CPP-17-iii	26.6	73.4
CPP-17-iv	8.7	91.3
CPP-17-v	6.4	93.6
CPP-17-vi	4.2	95.8
CPP-17-vii	2.1	97.9
CPP-17-viii	0	100

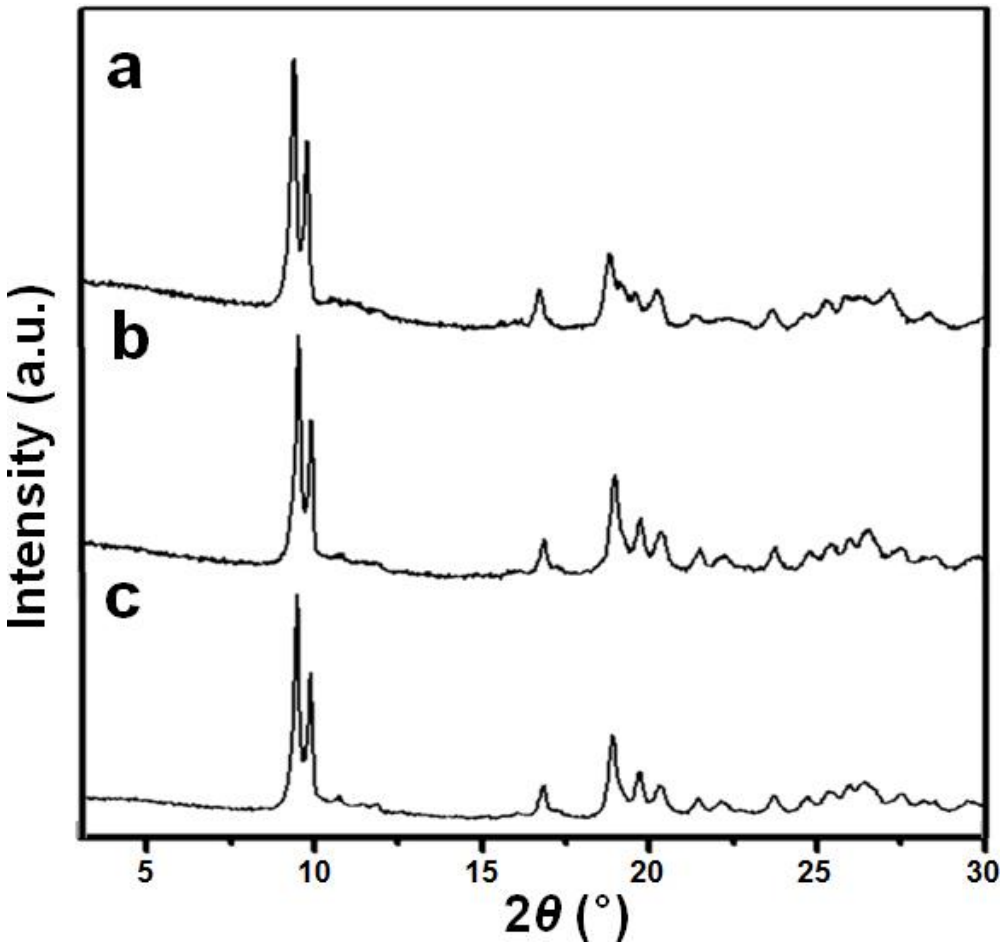

Fig. S8 PXRD patterns of (a) CPP-17-i, (b) CPP-17-iv, and (c) CPP-17-viii.

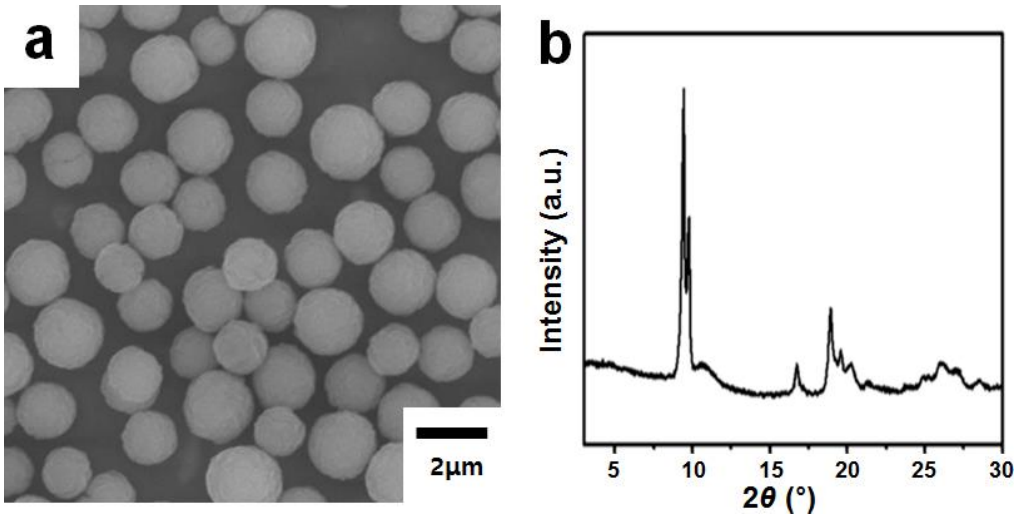

Fig. S9 (a) SEM image and (b) PXRD pattern of CPP-17-e-iv.