Supplementary Information

Effect of phosphonates on lanthanide separation for surface-grafted porous zirconia

Miho Otaki,*[a] Topi Suominen,[a] Valtteri Suorsa,[a] Sami Hietala [b] and Risto T. Koivula [a]

[a] *Department of Chemistry — Radiochemistry Unit, A. I. Virtasen Aukio 1, P.O. Box 55, FI-00014 University of Helsinki, Finland*

[b] *Department of Chemistry, A. I. Virtasen Aukio 1, P.O. Box 55, FI-00014 University of Helsinki, Finland*

*Corresponding author, Email: miho.otaki@helsinki.fi

Detailed procedure of MP-AES measurements

The concentration of the stable lanthanides was determined by an Agilent microwave plasma atomic emission spectrometer (MP-AES 4200). Samples were diluted to concentrations below 10 mg/L with 5%(w/w) HNO_3, and a linear calibration curve was established by 0, 0.5, 1, 5, and 10 mg/L standard solutions. The quality of measurement was controlled by the internal standard method. For single and binary lanthanide solutions, Y was used as the internal standard. For the lanthanide mixture solution, two internal standards of Li and Be were used.

Table S1. Reaction conditions for hybrid synthesis and Lu^{3+} uptake of the resulted materials at pH 3. (EOS: end of synthesis.)

Matrix	Ligand	Solvent	Reaction time	pH at EOS	Uptake (μmol/g)	Measurement method
SG85	ATMP	Milli-Q	1 day	1.45	82	MP-AES
SG85	ATMP	0.5 HCl	1 day	0.32	92	MP-AES
SG85	ATMP	0.5 HCl	3 days	0.36	96	MP-AES
SG85	ATMP	1 M HCl	3 days	0.04	110	Gamma counting
SG85	DTPMP	0.2 M HCl	1 day	0.73	88	MP-AES
SG85	DTPMP	0.5 M HCl	1 day	0.39	99	MP-AES
SG85	DTPMP	0.5 M HCl	3 days	0.45	99	MP-AES
SG85	DTPMP	1 M HCl	3 days	-0.05	117	Gamma counting

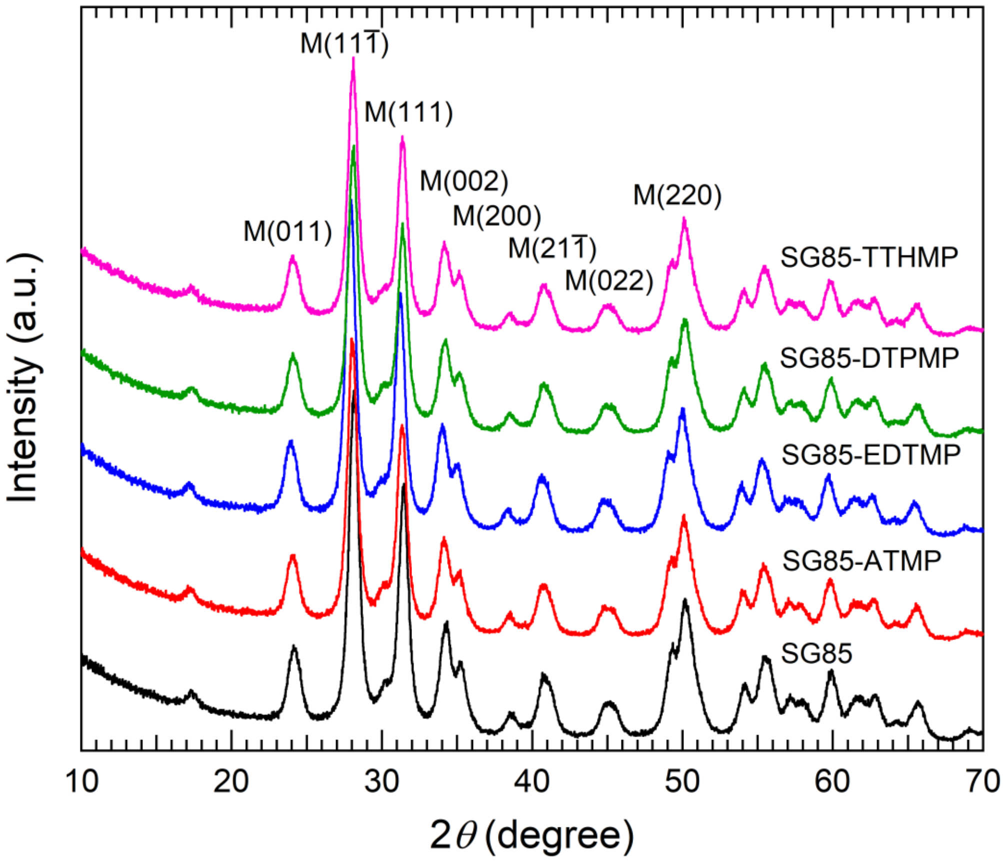
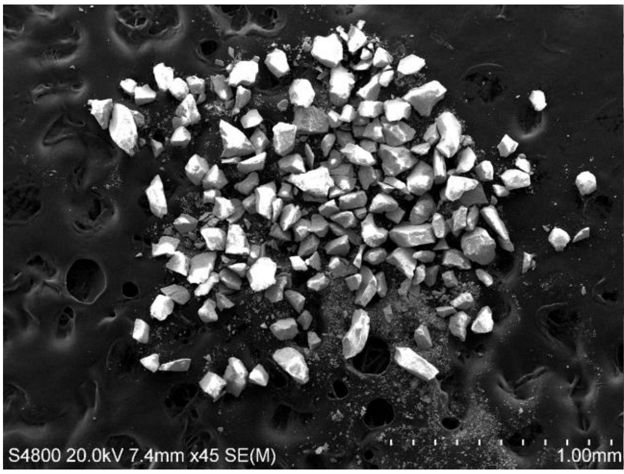


Figure S1. Powder XRD patterns of the bare porous zirconia (SG85) and hybrid materials.

(a)



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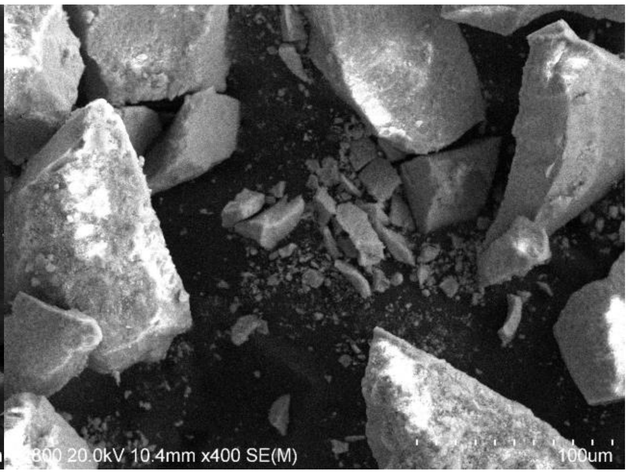
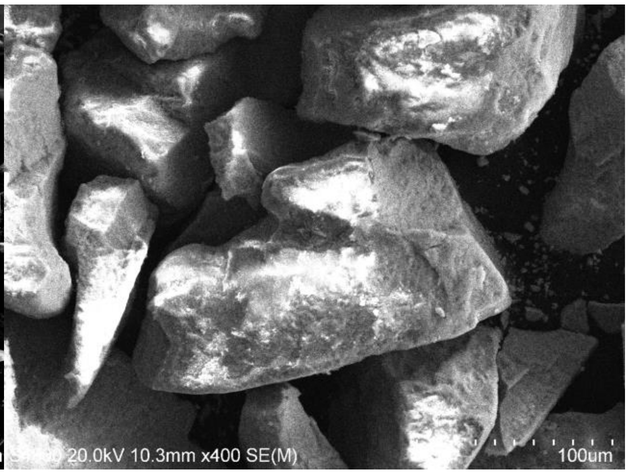
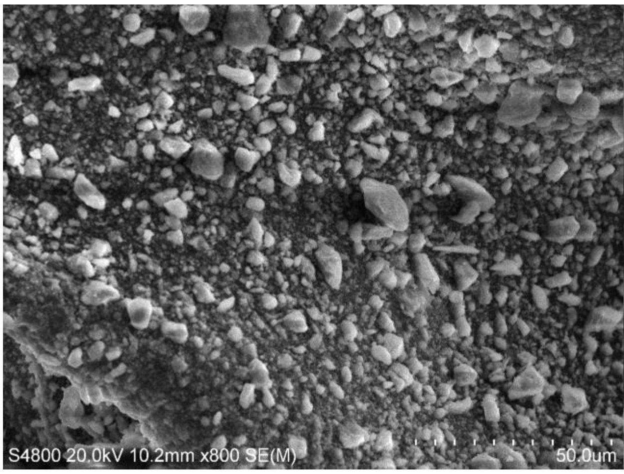


(c)

(d)



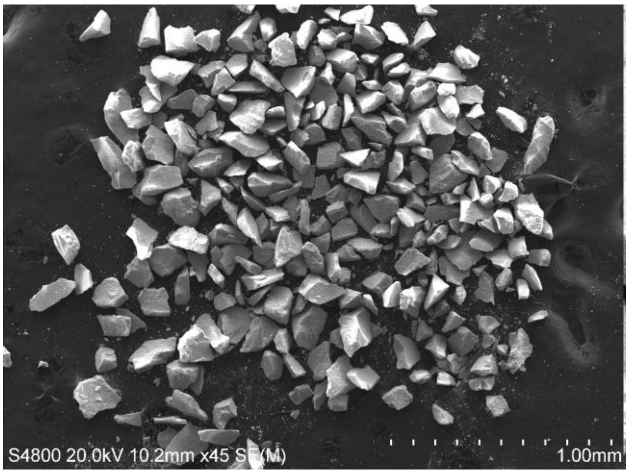
(e)

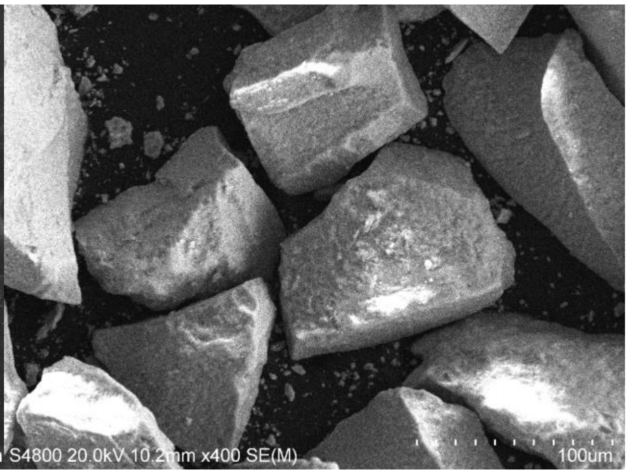


(f)

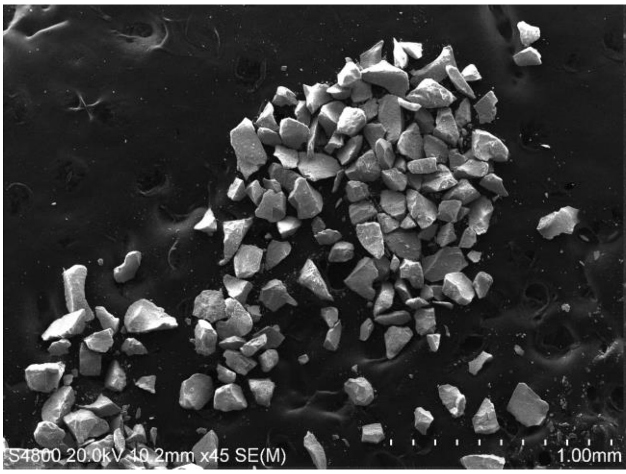
Figure S2. SEM image of (a)–(b) SG85 porous zirconia, (c)–(d) SG85-ATMP, (e)–(f) SG85-EDTMP, (g)–(h) SG85-DTPMP and (i)–(j) SG85-TTHMP.

(g) (h)





(i) (j)



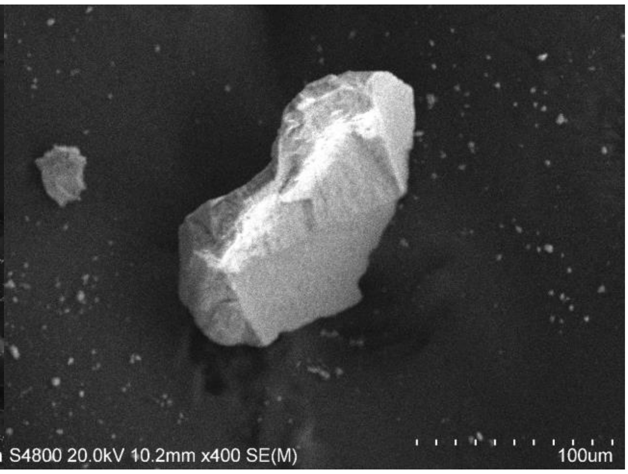


Figure S2. (Continued).

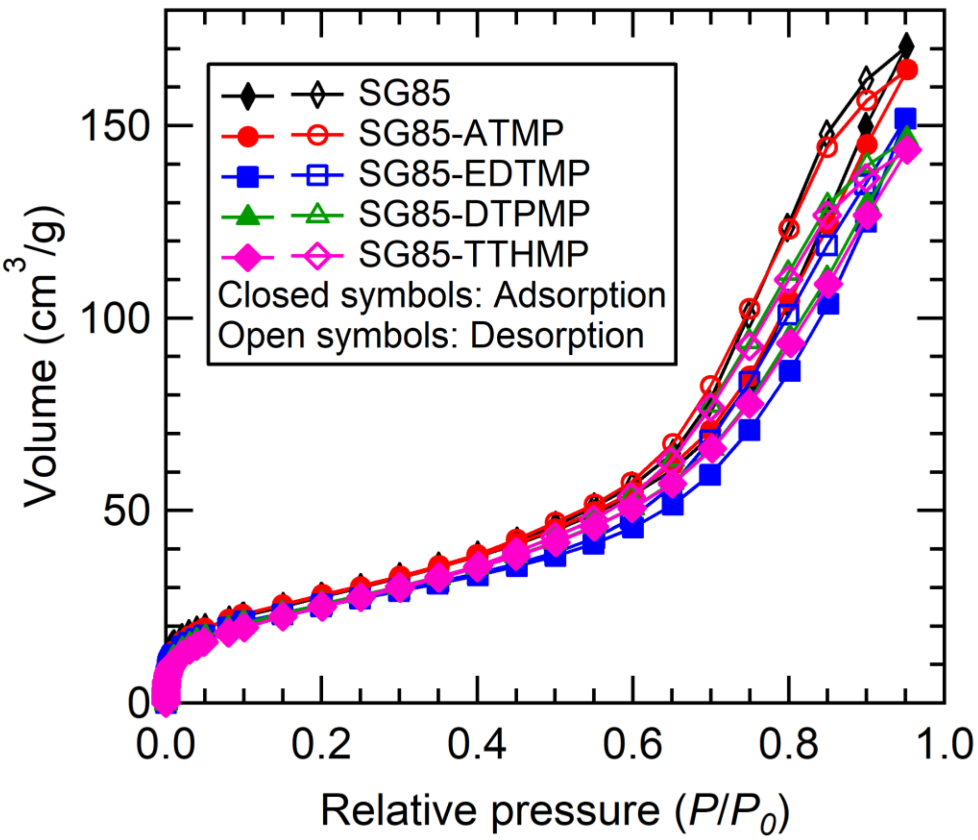


Figure S3. Nitrogen adsorption-desorption isotherms of the bare porous zirconia and synthesized hybrid materials.

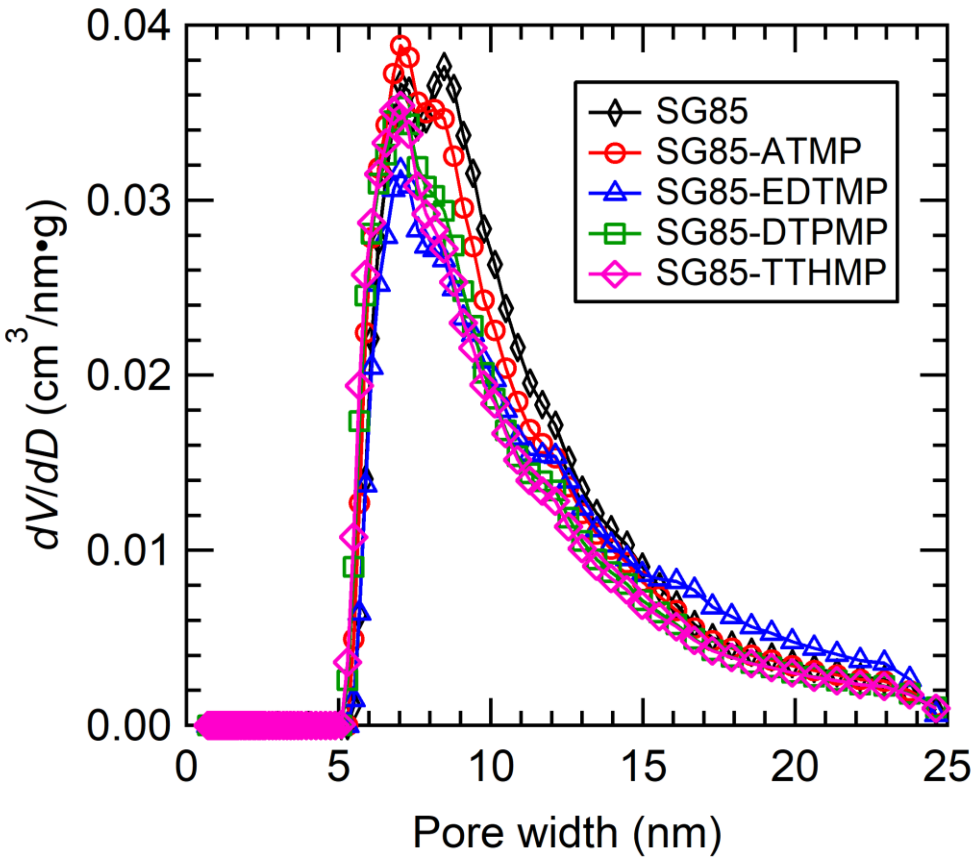


Figure S4. Pore size distributions of the bare porous zirconia and synthesized hybrid materials, calculated using the DFT.

Table S2. Surface areas, pore volumes, and pore sizes of the bare porous zirconia and synthesized hybrid materials. Surface areas were determined by the BET method, and pore volumes and sizes by the DFT calculation.

	Surface area (m^2/g)	Pore volume (cm^3/g)	Mode pore width (nm)	Mean pore width (nm)
SG85	102.61	0.252	8.462	9.69
SG85-ATMP	103.17	0.244	7.032	9.44
SG85-EDTMP	91.89	0.223	7.032	10.06
SG85-DTPMP	96.32	0.217	7.032	9.27
SG85-TTHMP	95.56	0.213	7.032	9.21

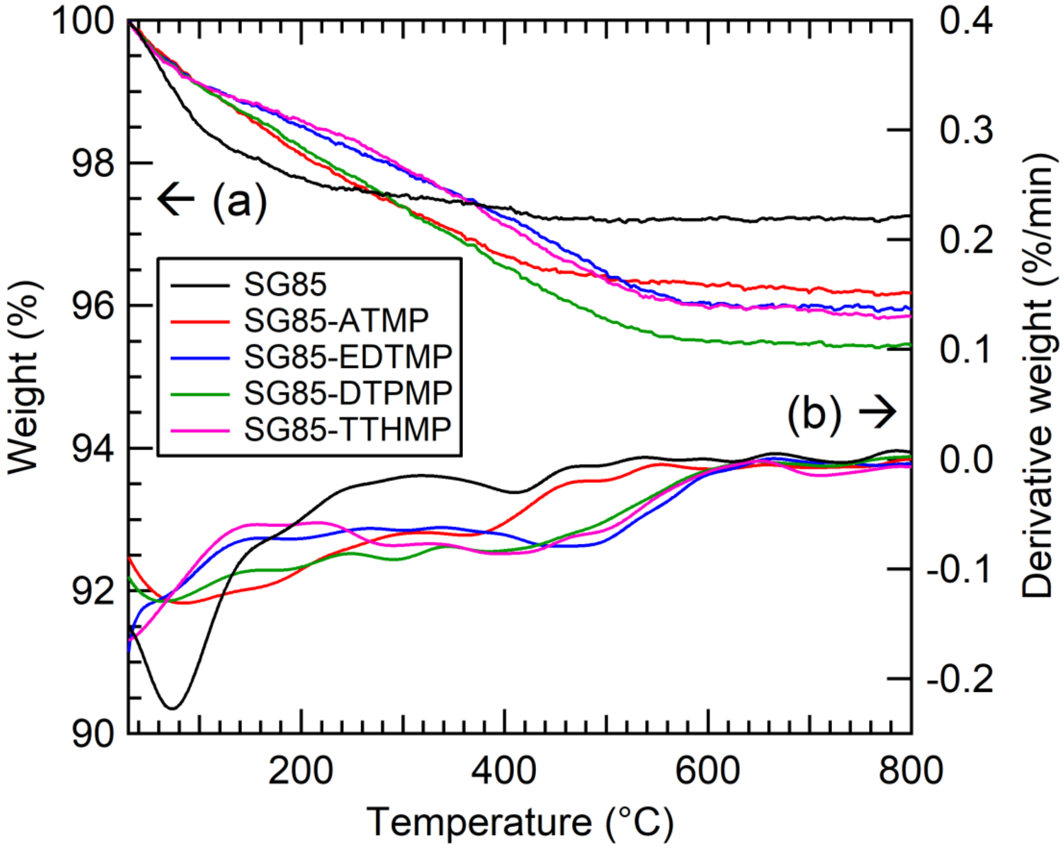


Figure S5. (a) TGA and (b) derivative TG of the bare porous zirconia and synthesized hybrid materials.

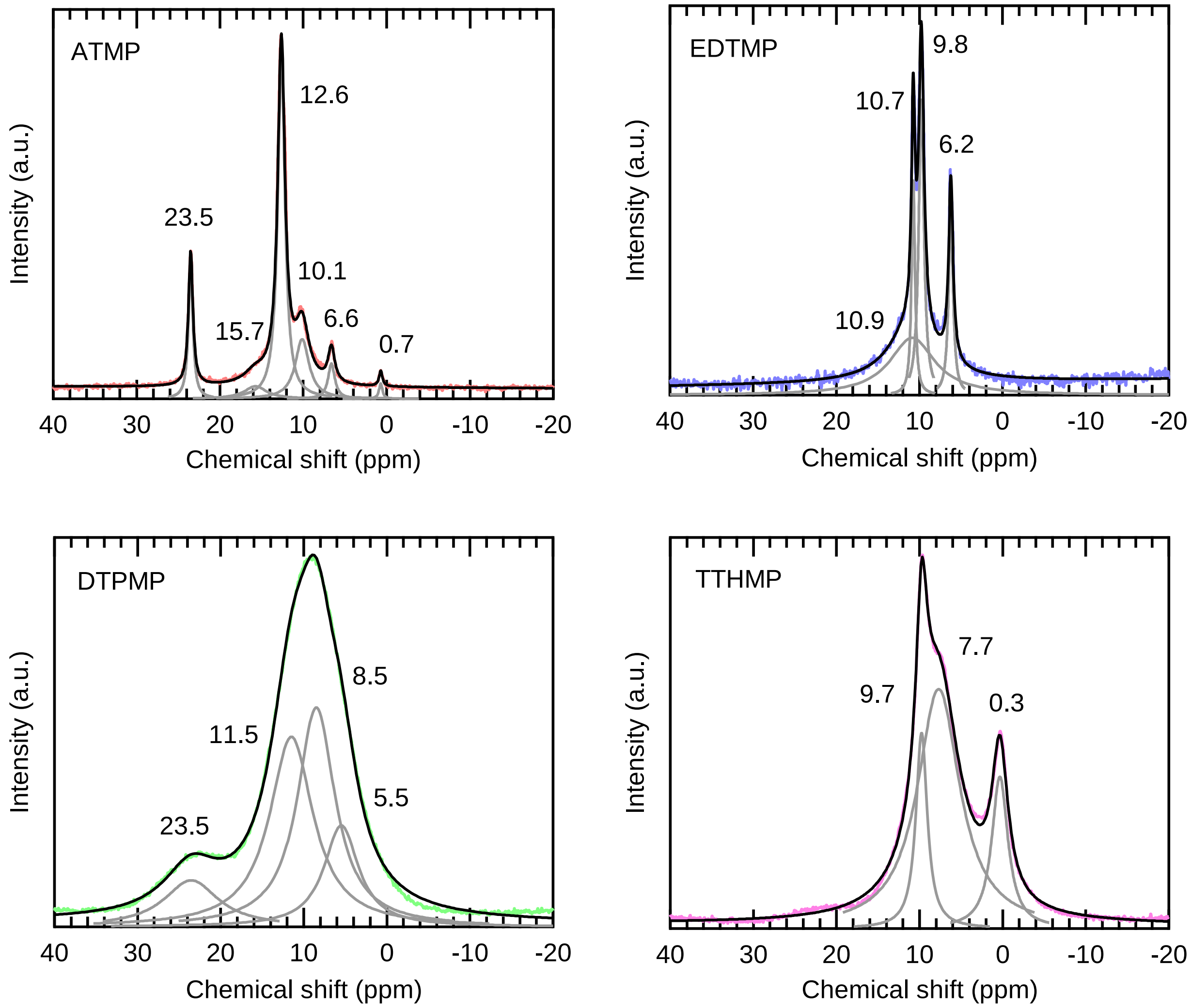


Figure S6. Solid-state ^{31}P MAS NMR spectra of the raw ligands. The intensive peaks at 7.7-12.6 ppm are possibly assigned to the phosphonic acid groups of the ligands. Other peaks are considered to be impurities such as methylphosphonates (~24 ppm), phosphate monoester (~6 ppm) and orthophosphates (~0 ppm).[*1]

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*1. P. Sannigrahi and E. Ingall, *Geochem Trans*, 2005, **6** (3), 52–59. DOI: 10.1186/1467-4866-6-52

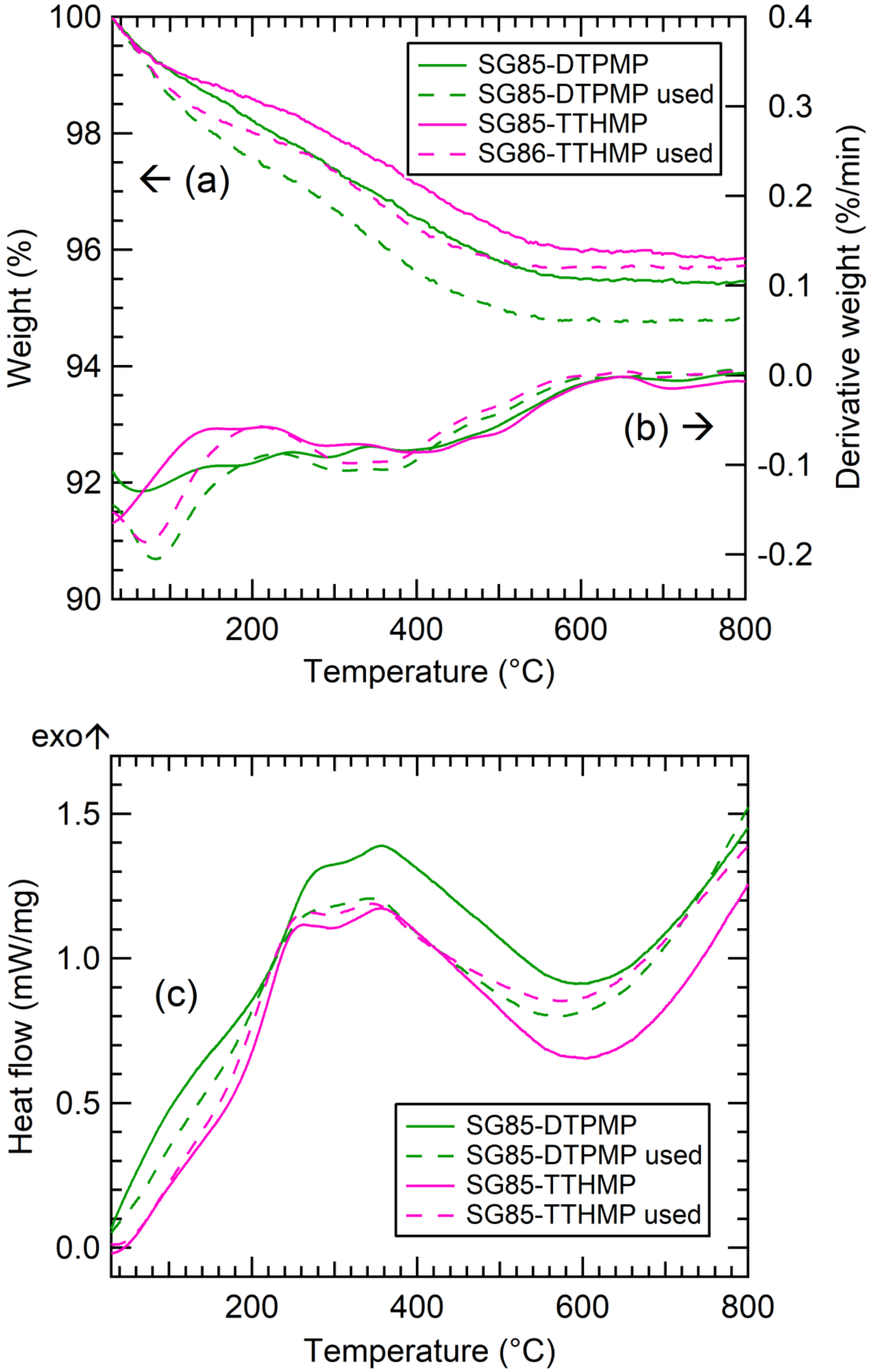

Figure S7. (a) TGA, (b) derivative TG, and (c) DSC of the as-synthesized materials and ones after 5-cycle column runs (used materials).

K_d values for intra-lanthanide selectivity assessment

Ln-selectivity of material was studied in a batch mode. 20 ± 0.2 mg of material was equilibrated for 72 h with 10 mL of two types of Ln^{3+}-containing solution: all-Ln solution and binary Ln solutions. The all-Ln solution was prepared to contain 0.04 mM of nitrate of lanthanides (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, in total 0.56 mM of Ln^{3+}) and 10 mM $NaNO_3$. The binary Ln solution was prepared to contain 0.2 mM $La(NO_3)_3$, 0.2 mM of nitrate of one of other Ln (Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or Lu, in total 0.4 mM of Ln^{3+}), and 10 mM $NaNO_3$. Pm was not used since it does not have stable isotopes. For both types of solutions, pH was adjusted to 3.3 before equilibration so that pH became about 3 after equilibration. The concentration of the stable lanthanides was determined by MP-AES. The results are summarized in Table S3 and S4.

Table S3. K_d values for each Ln excluding Pm at equilibrium pH 3–3.1. Initial solution: 0.04 mM equimolar mixture of Ln^{3+} (La–Lu excluding Pm) in 10 mM $NaNO_3$; Batch factor: approximately 500 mL/g; Equilibrium time: 3 d.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
SG85-ATMP	69.4 ± 2.4	134.0 ± 2.0	144.9 ± 5.6	159.3 ± 4.9	328.4 ± 6.3	351.9 ± 3.9	296.7 ± 3.5	339.2 ± 4.5	332.1 ± 3.6	278.0 ± 3.5	309.4 ± 4.7	374.3 ± 5.6	650.1 ± 6.3	763.8 ± 7.4
SG85-EDTMP	60.9 ± 2.1	97.7 ± 1.6	96.9 ± 2.3	107.9 ± 4.1	210.5 ± 5.2	224.8 ± 3.1	191.0 ± 2.5	219.3 ± 3.3	220.0 ± 4.6	188.1 ± 2.9	215.8 ± 4.1	271.6 ± 3.8	500.2 ± 5.4	610.8 ± 6.2
SG85-DTPMP	44.7 ± 1.9	90.6 ± 1.8	101.0 ± 1.9	116.7 ± 4.1	230.8 ± 5.3	249.0 ± 3.0	209.0 ± 2.7	259.6 ± 3.5	280.4 ± 3.2	262.1 ± 3.6	352.5 ± 5.0	507.5 ± 6.1	1244.4 ± 12.0	1743.5 ± 15.6
SG85-TTHMP	16.6 ± 2.0	37.4 ± 2.4	44.5 ± 2.2	51.9 ± 3.9	102.2 ± 4.6	112.5 ± 3.1	94.1 ± 2.5	123.2 ± 3.0	142.3 ± 3.8	142.3 ± 3.1	215.4 ± 4.2	344.5 ± 5.4	946.1 ± 10.4	1393.1 ± 14.5

Table S4. K_d values for each Ln excluding Pm at equilibrium pH 3–3.1. Initial solution: 0.2 mM equimolar mixture of La and one of the other stable lanthanides (Ce–Lu excluding Pm) in 10 mM $NaNO_3$; Batch factor: approximately 500 mL/g; Equilibrium time: 3 d.

		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
SG85-ATMP	La + Ce	256.2 ± 5.2	534.8 ± 9.2												
	La + Pr	242.5 ± 5.0		648.6 ± 10.2											
	La + Nd	222.1 ± 3.9			674.5 ± 12.1										
	La + Sm	183.7 ± 3.3				1023.1 ± 19.4									
	La + Eu	167.3 ± 2.9					1045.8 ± 18.5								
	La + Gd	167.8 ± 3.3						889.3 ± 16.6							
	La + Tb	178.5 ± 5.0							1043.9 ± 16.6						
	La + Dy	188.2 ± 3.1								1059.4 ± 17.6					
	La + Ho	192.8 ± 4.0									931.1 ± 15.1				
	La + Er	202.2 ± 4.0										1029.9 ± 16.5			
	La + Tm	188.4 ± 5.0											1093.2 ± 18.5		
	La + Yb	176.8 ± 4.7												1214.7 ± 26.2	
	La + Lu	173.6 ± 4.0													1259.7 ± 20.7
SG85-EDTMP	La + Ce	195.4 ± 3.7	415.8 ± 7.2												
	La + Pr	181.1 ± 3.7		492.7 ± 7.8											
	La + Nd	146.1 ± 2.8			430.6 ± 7.3										
	La + Sm	124.6 ± 3.1				599.8 ± 11.7									

Table S4. (Continued).

		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
SG85-EDTMP	La + Eu	108.5 ± 3.0					587.0 ± 9.4								
	La + Gd	124.4 ± 2.2						576.7 ± 10.1							
	La + Tb	121.3 ± 3.4							648.0 ± 11.8						
	La + Dy	123.8 ± 2.2								653.5 ± 11.1					
	La + Ho	124.7 ± 4.2									587.2 ± 10.4				
	La + Er	129.7 ± 3.4										639.7 ± 11.7			
	La + Tm	120.1 ± 2.9											660.8 ± 12.4		
	La + Yb	112.6 ± 3.6												720.1 ± 14.6	
	La + Lu	108.4 ± 3.8													702.4 ± 13.4
SG85-DTPMP	La + Ce	200.5 ± 3.7	470.1 ± 8.7												
	La + Pr	191.1 ± 3.8		568.1 ± 10.1											
	La + Nd	183.3 ± 3.2			592.5 ± 12.5										
	La + Sm	142.1 ± 3.2				848.8 ± 15.3									
	La + Eu	131.7 ± 3.2					838.4 ± 15.0								
	La + Gd	144.5 ± 2.8						766.0 ± 14.9							
	La + Tb	140.6 ± 3.2							967.7 ± 15.0						
	La + Dy	144.1 ± 3.9								1066.9 ± 17.4					
	La + Ho	131.7 ± 3.5									950.3 ± 17.1				
	La + Er	125.3 ± 2.8										1059.3 ± 19.4			
	La + Tm	103.3 ± 2.2											1357.2 ± 21.7		
	La + Yb	109.0 ± 3.2												2069.3 ± 38.6	
	La + Lu	86.0 ± 2.2													1765.7 ± 19.2
SG85-TTHMP	La + Ce	118.3 ± 2.8	286.6 ± 5.0												
	La + Pr	107.1 ± 3.0		335.5 ± 9.2											
	La + Nd	102.9 ± 3.4			344.2 ± 6.2										
	La + Sm	86.4 ± 2.8				490.3 ± 11.5									
	La + Eu	81.1 ± 2.9					468.7 ± 7.8								
	La + Gd	84.9 ± 3.9						445.2 ± 8.8							
	La + Tb	77.4 ± 2.8							558.9 ± 9.4						
	La + Dy	69.6 ± 2.2								569.6 ± 10.0					
	La + Ho	52.1 ± 2.5									524.3 ± 9.5				
	La + Er	60.3 ± 1.9										622.6 ± 11.3			
	La + Tm	42.5 ± 2.0											799.5 ± 14.1		
	La + Yb	38.4 ± 2.0												911.6 ± 21.4	
	La + Lu	29.3 ± 2.5													859.1 ± 13.8