- Supporting Information -

EXAFS Investigation of Adsorption and Separation Phenomena of Metal Ions in Organic Resin

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This supporting information includes the distribution coefficient data, EXAFS spectra and their structural parameters obtained from the curve fits, and the description about the estimation of bond distances from the EXAFS data.

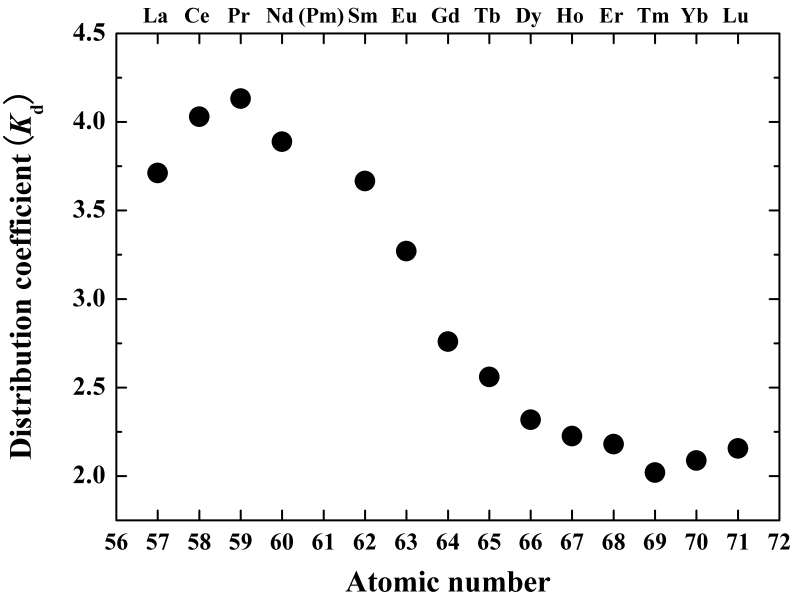

Figure S1. Distribution coefficients of lanthanides for tertiary pyridine resin in conc. HCl / MeOH mixed solution: conc. HCl / MeOH = 5 / 5 (vol/vol), the values are obtained in batch experiments.

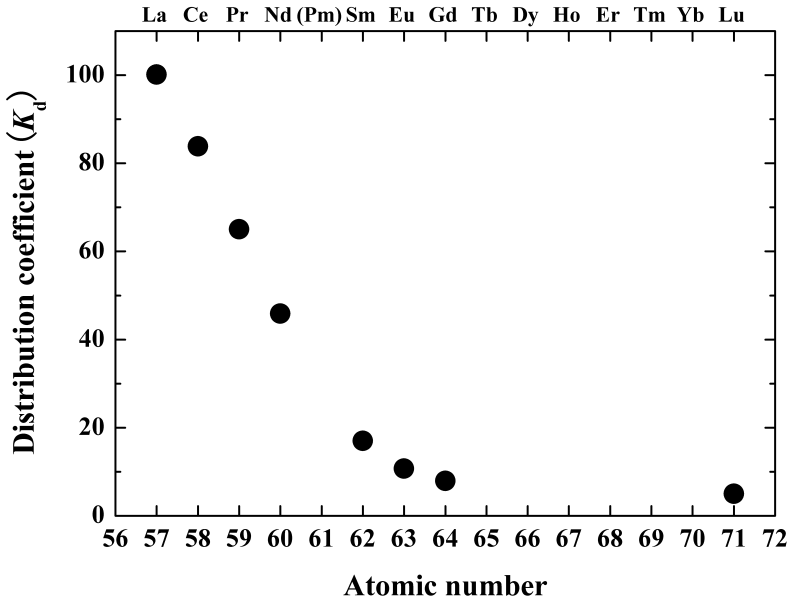

Figure S2. Distribution coefficients of lanthanides for tertiary pyridine resin in conc. HNO_3 / MeOH mixed solution: conc. HNO_3 / MeOH = 5 / 5 (vol/vol), the values are obtained in batch experiments.

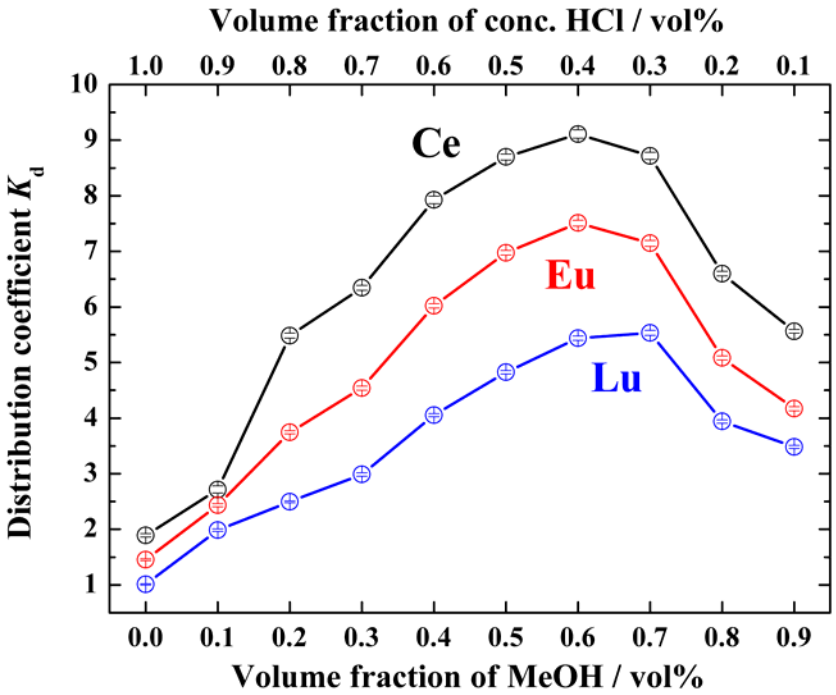

Figure S3. Distribution coefficients of lanthanides for tertiary pyridine resin in different compositions of conc. HCl / MeOH mixed solution: the values are calculated from chromatography experiments.

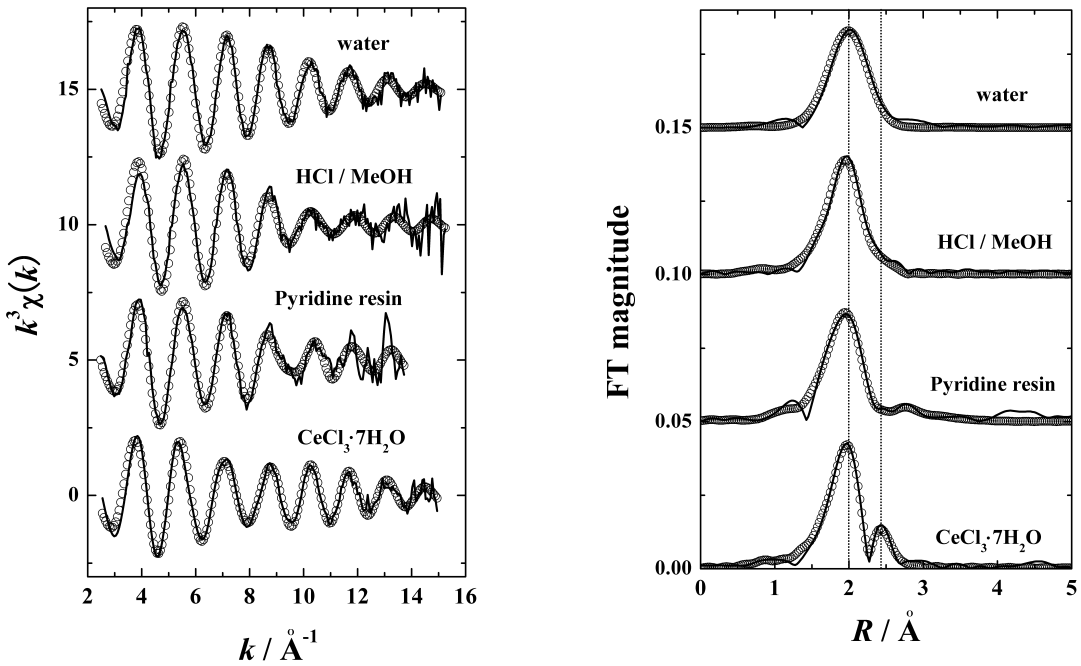

Figure S4. k^3-weighted Ce K-edge EXAFS spectra (left) and their corresponding Fourier transforms (right): Solvent; conc. HCl / MeOH = 5 / 5 (vol/vol), FTs; phase shifts are not corrected.

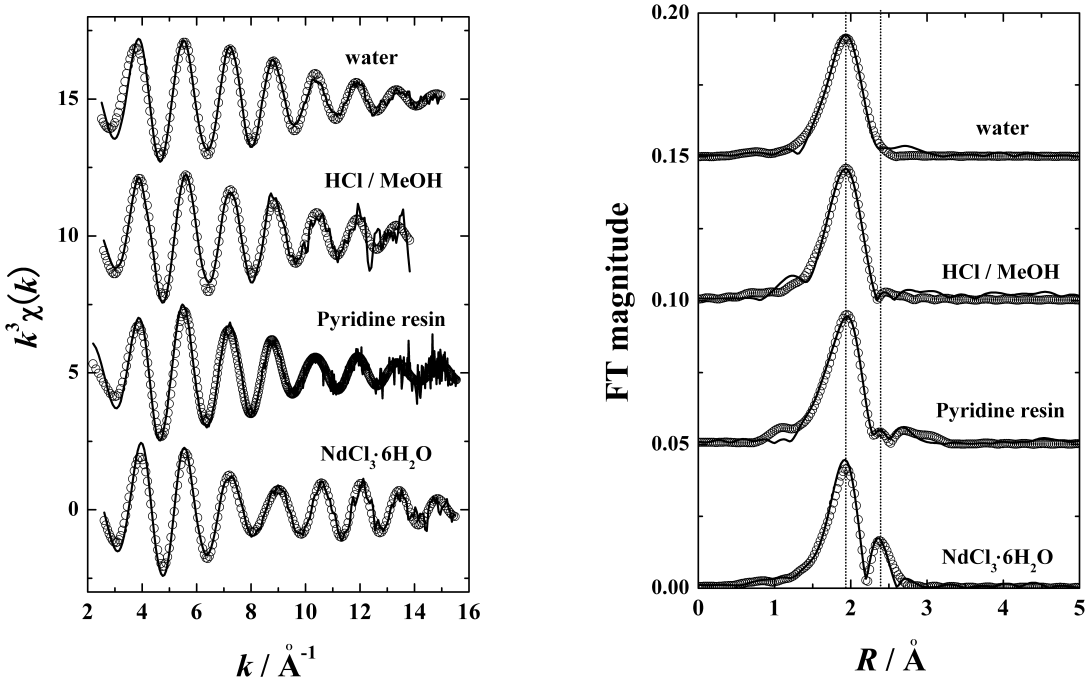

Figure S5. k^3-weighted Nd K-edge EXAFS spectra (left) and their corresponding Fourier transforms (right): Solvent; conc. HCl / MeOH = 5 / 5 (vol/vol), FTs; phase shifts are not corrected.

Table S1. EXAFS structural parameters obtained for HCl solution system

	Sample	Shell	R / Å[a]	N[b]	σ^2 / Å^{2}[c]	ΔE_0 / eV[d]	S_0^2(fixed)	F-values[e]
	water	O	2.55	9.5	0.0077	-0.77	0.9	0.914
	HCl /MeOH	O	2.55	9.6	0.0083	-0.25	0.9	0.866
		O or N	2.52	8.3	0.0066			
La	Pyridine resin	Cl	2.91	1.0	0.0070	1.08	0.9	0.953
		C	3.53	1.8	0.0021			
	Hydrated $LaCl_3$	O	2.55	7.0	0.0065	-0.85	0.9	0.853
		Cl	2.91	2.0	0.0096			
Ce	water	O	2.53	9.6	0.0080	-2.45	0.9	0.923
	HCl /MeOH	O	2.52	9.6	0.0091	-0.77	0.9	0.866
		O or N	2.53	9.0	0.0072			
	Pyridine resin	Cl	2.90	0.6	0.0057	5.80	0.9	0.784
		C	3.48	2.0	0.0020			

	Hydrated $CeCl_3$	O	2.53	7.0	0.0064	-3.53	0.9	0.987
		Cl	2.90	2.0	0.0095			
Nd	water	O	2.47	9.5	0.0079	-6.19	0.9	0.941
	HCl /MeOH	O	2.48	9.6	0.0086	-1.25	0.9	0.727
	Pyridine resin	O or N	2.49	9.0	0.0080	-0.65	0.9	0.825
		Cl	2.81	0.5	0.0051			
		C	3.46	1.5	0.0053			
	Hydrated $NdCl_3$	O	2.47	6.0	0.0060	1.79	0.9	0.472
		Cl	2.81	2.0	0.0073			

[a] Estimated standard deviations; R(Ln-O or N) ± 0.005 Å, R(Ln-Cl) ± 0.008 Å, R(Ln-C) ± 0.01 Å. [b] Estimated standard deviations; N(O or N) ± 10%, N(Cl) ± 20%, N(C) ± 20%. [c] Estimated standard deviations; $\sigma^2 \leq \pm$ 0.0005 Å^2. [d] Estimated standard deviations; $\Delta E_0 \leq \pm$ 0.01 eV. [e] F-value is a measure of curve-fit and defined as $F = \sum k^6(\text{data} - \text{fit})^2/(N_{pts} - N_{var})$, where N_{pts} and N_{var} are the number of data points and that of floating variables, respectively.

Calculation of Ln-N distance from Ln-C distance

As shown in Figure S6, we can apply the Pythagorean theorem for the calculation of Ln-N distance from the obtained Ln-C distance. The angle Ln-M-C makes a right angle and, hence, we can obtain the following equation:

$$(R_N + c)^2 + (b/2)^2 = R_C^2 \quad \ldots\ldots(1).$$

Assuming that a = 1.34 Å and b = 2.30 Å, we can calculate the Ln-N distance, R_N, by using the following equation:

$$R_N = \sqrt{(R_C^2 - 1.15^2)} - 0.67 \ldots\ldots(2).$$

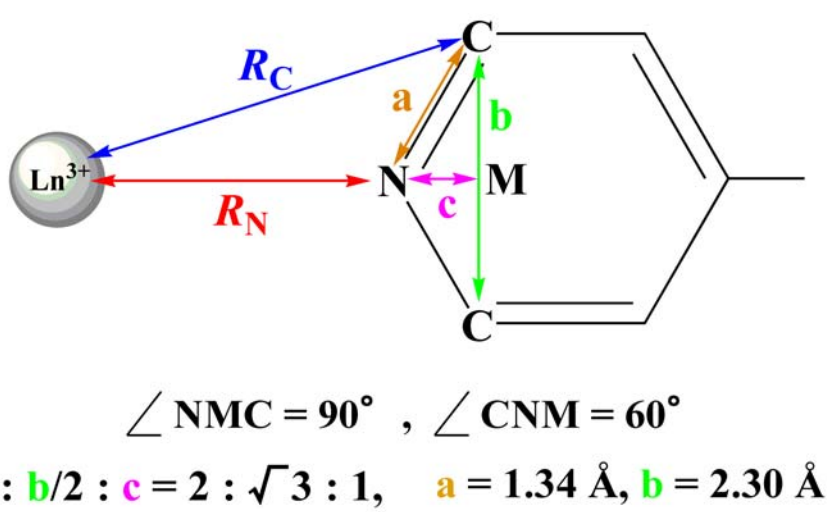

Figure S6. Coordination geometry of pyridine group to Ln cation.

Table S2. EXAFS structural parameters obtained for HNO_3 solution system

	Sample	Shell	R / Å[a]	N[b]	σ^2 / Å^{2c}	ΔE_0 / eV[d]	S_0^2(fixed)	F-values
Nd	HNO_3 / MeOH	O_{hyd}	2.50	5.5	0.0045	8.18	0.9	0.943
		O_{co}	2.63	3.9	0.0045			
		N	3.07	1.9	0.0059			
		O_{dist}	4.26	1.9	0.0006			
		MS (N-O_{dist}-N)	4.30	1.9	0.0012			
	Pyridine resin	O_{hyd}	2.49	2.1	0.0045	8.23	0.9	0.699
		O_{co}	2.61	7.9	0.0045			
		N	3.05	3.9	0.0059			
		O_{dist}	4.26	3.9	0.0006			
		MS (N-O_{dist}-N)	4.31	3.9	0.0012			
Sm	water	O_{hyd}	2.44	8.6	0.0074	4.48	0.9	0.543
	HNO_3 / MeOH	O_{hyd}	2.42	4.7	0.0044	8.18	0.9	0.191
		O_{co}	2.54	3.8	0.0028			
		N	2.97	1.9	0.0010			
		O_{dist}	4.20	1.9	0.0022			
		MS (N-O_{dist}-N)	4.20	1.9	0.0049			
	Pyridine resin	O_{hyd}	2.42	4.1	0.0044	8.23	0.9	0.760
		O_{co}	2.53	3.9	0.0028			
		N	2.96	1.9	0.0010			
		O_{dist}	4.20	1.9	0.0022			
		MS (N-O_{dist}-N)	4.20	1.9	0.0049			

[a] Estimated standard deviations; R(Ln-O_{hyd}) ± 0.005 Å, R(Ln-O_{co}) and R(Ln-N) ± 0.01 Å, R(Ln-O_{dist}) and R(MS) ± 0.02 Å. [b] Estimated standard deviations; N(O_{hyd}) ± 10%, N(NO_3) ± 15%. [c] Estimated standard deviations; $\sigma^2 \leq \pm$ 0.0005 Å^2. [d] Estimated standard deviations; $\Delta E_0 \leq \pm$ 0.01 eV.