Supporting Information

Selective collection of Yb(III) over La(III) and Eu(III) from aqueous solution by bis(tetramethylammonium) salt crystals of *p-tert*-butylcalix[4]arene-1,3-diphosphonic acid

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Contents:

I. General

Inductively coupled plasma optical emission spectra (ICP-OES) were measured using a Thermo Fisher Scientific iCAP6500. ^{1}H NMR spectra were measured on a 400 MHz spectrometer using CD_3OD as a solvent. SEM-EDX analysis was performed using HITACHI S-4800 and HORIBA EX-250. ESI-MS measurement was performed using Bruker solariX. **H4L** was prepared as previously reported.[1] Reagent-grade chemicals and solvents were used as purchased. Stock solutions of each Ln(III) [La(III), Eu(III) and Yb(III)] were prepared by dissolving $YbCl_3·6H_2O$, $EuCl_3·6H_2O$ and $LaCl_3·7H_2O$ in an aqueous solution of HCl, respectively.

II. Preparation of bis(tetramethylammonium) salt [(Me₄N)₂H₂L]

To a stirred solution of **H₄L** (100.0 mg, 129 µmol) in methanol (30 mL) was added Me₄NOH (25% in H_2O, 101.4 µL, 284 µmol), and the mixture was stirred at room temperature for 24 h. The resulted solution was concentrated by evaporation and anhydrous tetrahydrofuran (15 mL) was added to solution. The precipitation was collected by filtration and dried in vacuo (0.5−1.0 kPa) at 60 ºC to give **(Me₄N)₂H₂L** as a colorless powder (92.0 mg, 77 %). **(Me₄N)₂H₂L**: mp 308.7−311.4 °C (decomp.); ^{1}H NMR (400 MHz, CD₃OD) δ (ppm): 0.85 (s, 18H), 1.33 (s, 18H), 3.22 (s, 24H), 3.43 (d, 4H, J = 14.0 Hz), 5.45 (d, 4H, J = 14.0 Hz), 6.71 (d, 4H, J = 3.60 Hz, Ar*H*), 7.08 (s, 4H); ^{13}C NMR(100 MHz, CD₃OD) δ (ppm): 31.3, 32.3, 34.6, 34.8, 38.5, 38.5, 56.0, 56.1, 56.1, 126.8, 126.9, 126.9, 131.0, 141.9, 143.6, 143.7, 150.9, 150.9, 152.3 ; IR (KBr) cm⁻¹: 3386, 2960, 1487, 1149, 1037. Anal. Calcd for C₅₂H₈₈N₂O₁₂P₂ [**(Me₄N)₂H₂L·(H₂O)₄**]: C, 62.76; H, 8.91; N, 2.81. Found: C, 62.44; H, 9.00; N, 3.09.
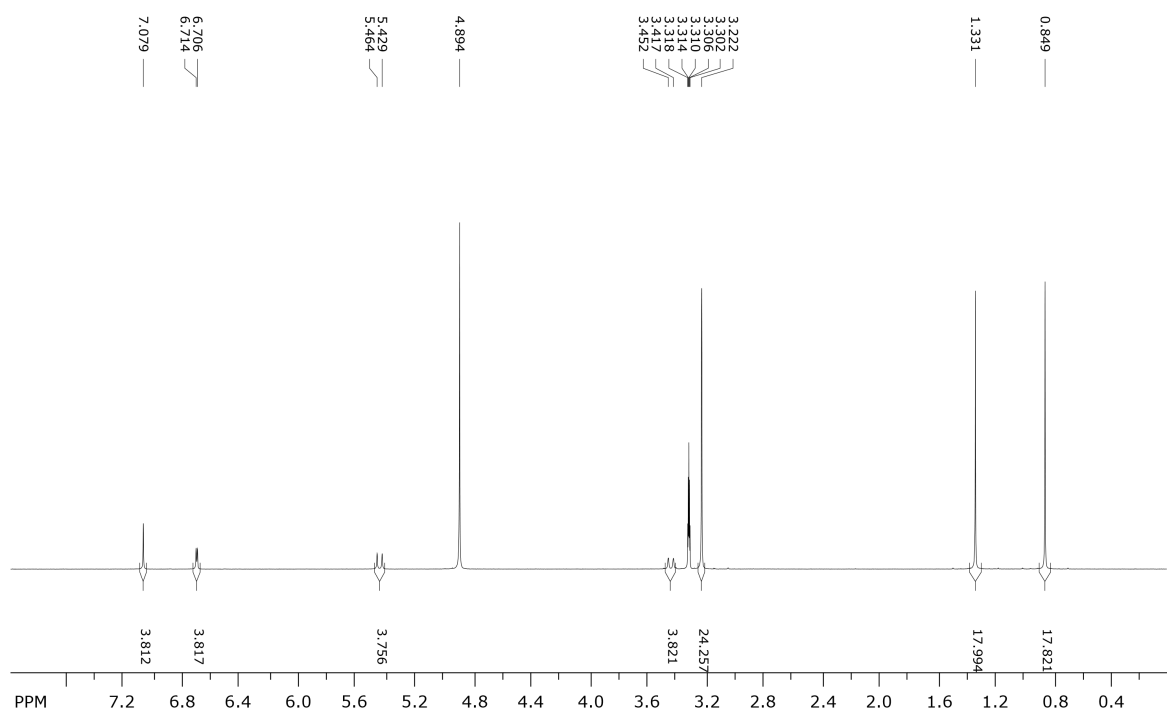
Figure S1. ^{1}H NMR spectrum of **(Me₄N)₂H₂L** (CD₃OD, 400 MHz).
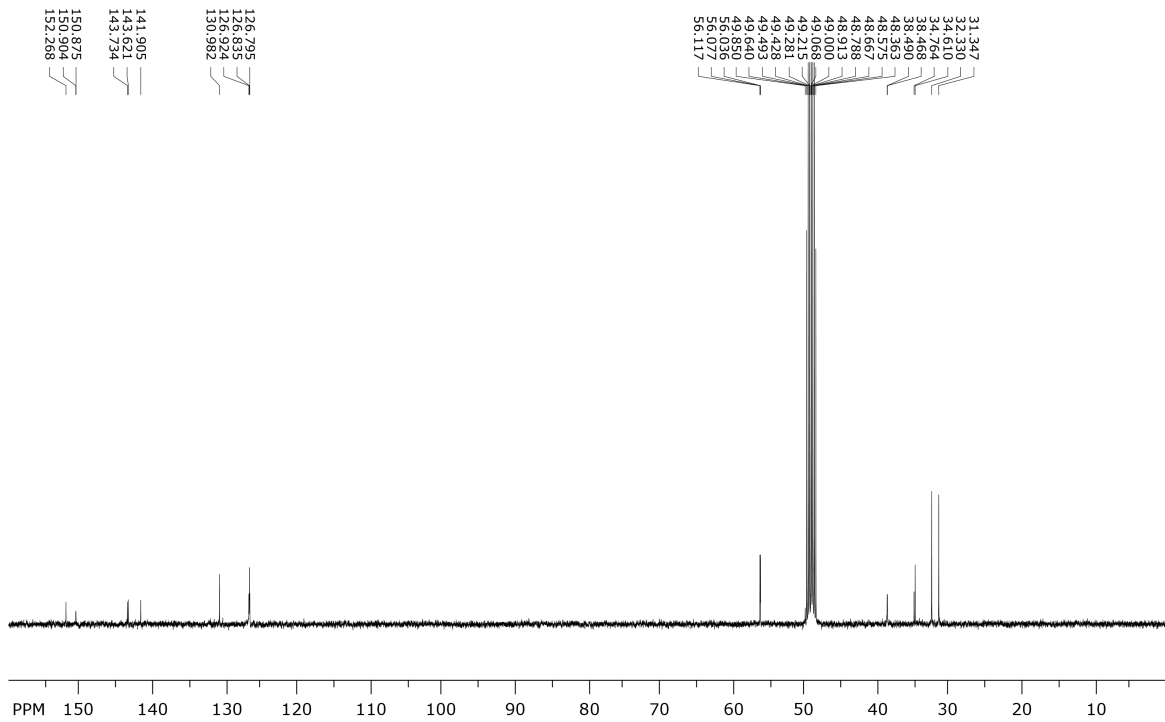
**Figure S2.** ^{13}C NMR spectrum of **(Me₄N)₂H₂L** (CD₃OD, 100 MHz).

III. Single-crystal XRD analysis of **H₄L** and **(Me₄N)₂H₂L**

Single crystals of **H₄L**·$(H_2O)_{0.2}$ were accidentally obtained by leaving a solution of **H₄L** in the mixture of CH_3CN with H_2O containing NaOH (0.005 M) after addition of 0.01 M HCl solution containing $YbCl_3$. This crystal has different packing structure compared to previously reported crystal[1] of **H₄L** due to the difference of included solvent. Single crystals of [**(Me₄N)₂H₂L**]·$MeOH$·H_2O were prepared by vapor diffusion of tetrahydrofuran to methanol solution of **(Me₄N)₂H₂L**.

Single-crystal X-ray diffraction data were collected on a Bruker APEX-II with a CCD diffractometer equipped with a multilayered confocal mirror and a fine-focus rotating anode, using Mo−$K\alpha$ radiation (λ = 0.71073 Å). The structure was solved by the direct method by SHELXL-97[2] and refined by the least-squares method on F^2 using SHELXL-2017.[3] Yadokari-XG 2009 was used as a GUI for SHELXL-97 and SHELXL-2017.[4] In the refinement of [**(Me₄N)₂H₂L**]·$MeOH$·H_2O, θ_{max} was set in 23.5º due to weak diffraction.
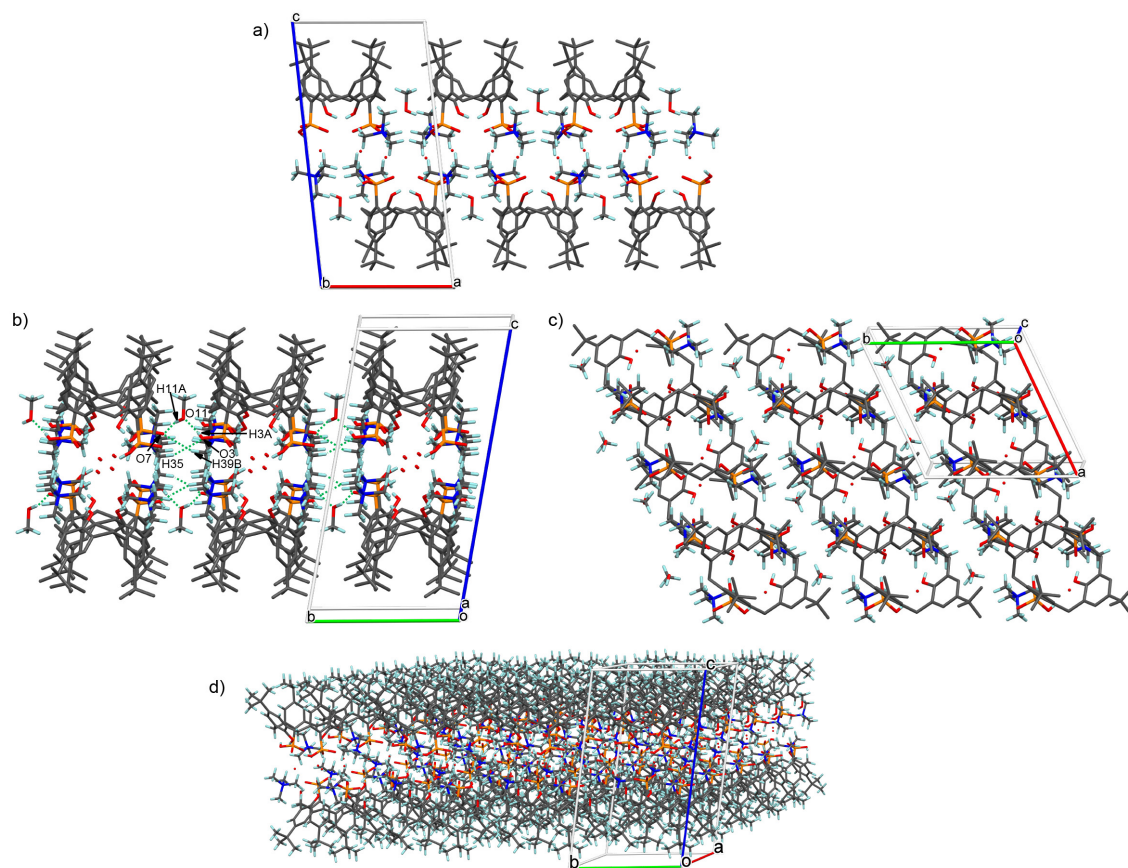
Figure S3. X-ray structure of [**(Me₄N)₂H₂L**]·MeOH·H₂O : cross-sections of sheet structure parallel to the *a-c* plane (a), the *b-c* plane (b), and the *a-b* plane (c) and a sheet structure parallel to the *a-b* plane (d). Each H_2O molecule are disordered at two positions. In (a, b), selected hydrogen atoms and disordered atoms for *tert*-butyl groups are omitted for clarity. Green dotted lines represent intermolecular hydrogen bonds. Selected distances: O3···H35 (2.482 Å), O7···H11A (1.814 Å), O7···H39B (2.508 Å), O11···H3A (1.836 Å).
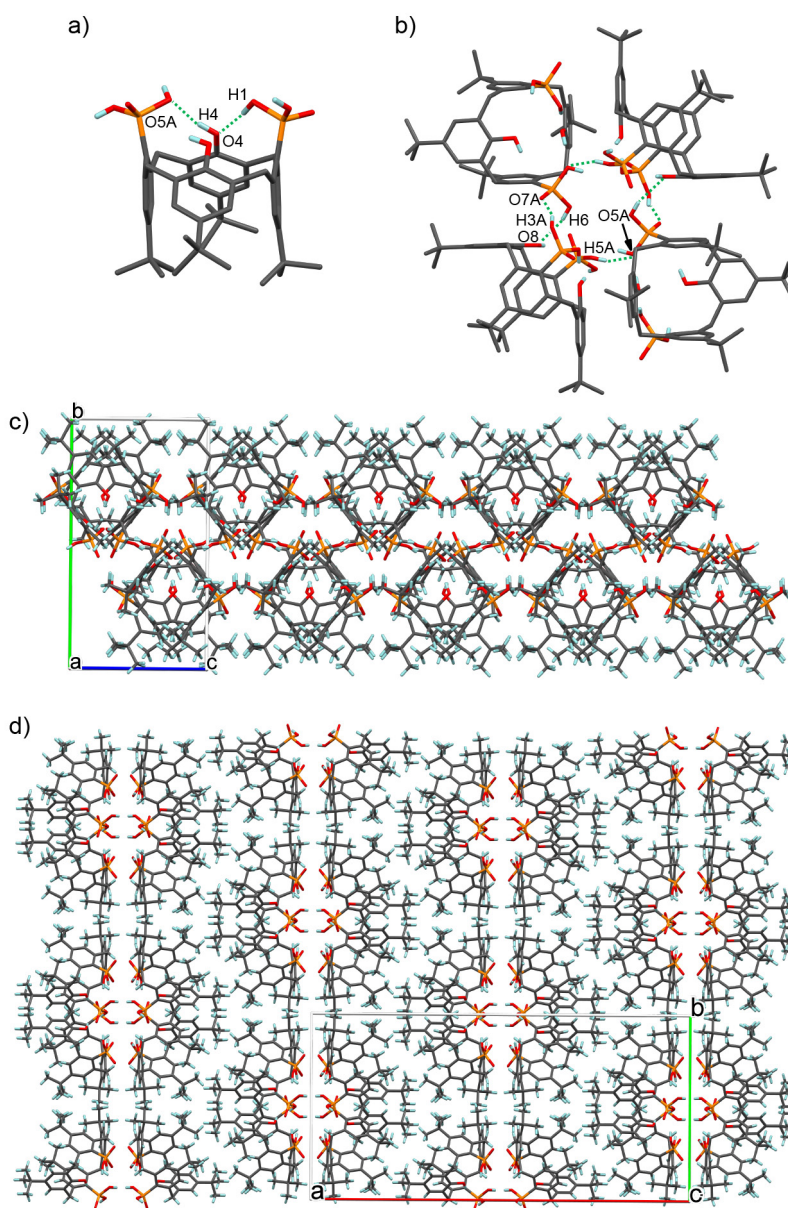
Figure S4. X-ray structure of **H₄L**·(H₂O)$_{0.2}$: side view of **H₄L** (a), an aggregate of selected four molecules (b), a columnar structure along the *c* axis (c), and parallel cross-section to the a–*b* plane (d). In (a, b), selected hydrogen atoms, disordered atoms and solvent molecules are omitted for clarity. Green dotted lines represent intra- and intermolecular hydrogen bonds. Selected distances: (a) O4···H1 (1.784 Å), O5A···H4 (1.852 Å), (b) O5A···H5A (1.779 Å), O7A···H3A (1.643 Å), O8···H6 (2.198 Å).

Table S1. Crystallographic Data for **H₄L** and **(Me₄N)₂H₂L**

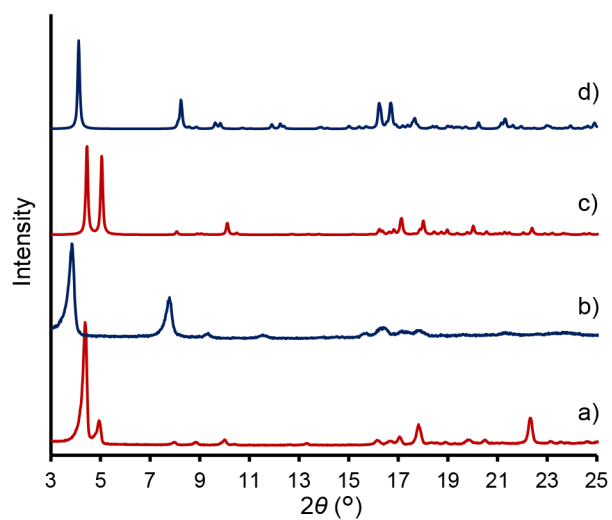|	**H₄L·(H₂O)₀.₂**	**[(Me₄N)₂H₂L]·MeOH·H₂O**
Empirical formula	$C_{44}H_{58.4}O_{8.2}P_2$	$C_{53}H_{86}N_2O_{10}P_2$
Formula weight	780.44	973.17
Crystal system	monoclinic	triclinic
Space group	$C2/c$	$P\bar{1}$
a, b, c / Å	40.637(6), 19.488(3), 10.9137(16)	11.762(10), 12.090(10), 21.684(18)
α, β, γ / °	90, 102.487(2), 90	96.168(13), 93.167(13), 114.670(11)
V / Å³	8439(2)	2769(4)
Z	8	2
F(000)	3344	1056
T / K	223(2)	223(2)
ρ_{calc} / gcm⁻³	1.229	1.167
Reflections collected	24095	11621
Independent reflections	9571 [R_{int} = 0.1057]	8093 [R_{int} = 0.1573]
μ (Mo Kα) / mm⁻¹	0.154	0.133
Data / restraints / parameters	9571 / 736 / 656	8093 / 460 / 693
R_1, wR_2 ($I > 2\sigma(I)$)	0.0730, 0.1333	0.0893, 0.2102
R_1, wR_2 (all data)	0.1919, 0.1872	0.2487, 0.2716
Goodness-of-fit on F^2	1.004	0.826
Largest diff. peak and hole / e·Å³	0.330 and -0.394	0.755 and -0.314
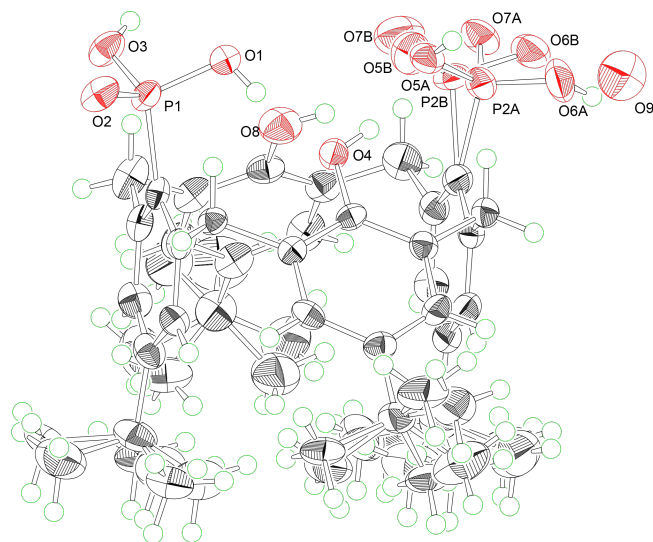
Figure S5. ORTEP drawing of **H₄L**·(H₂O)₀.₂ with 50% probability ellipsoids (CCDC 2262871).
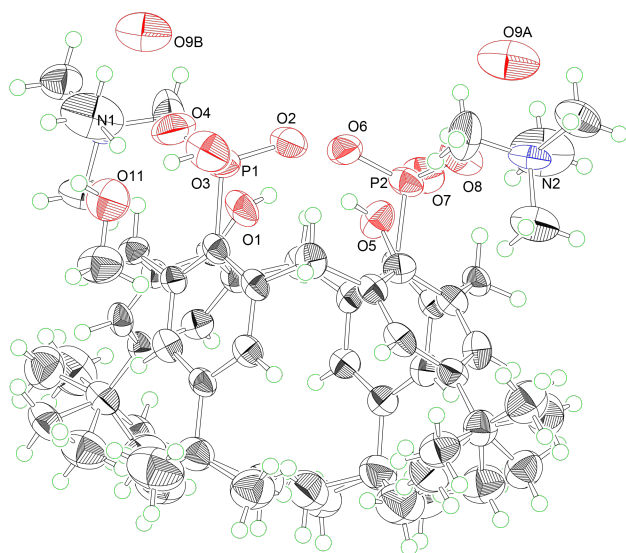
Figure S6. ORTEP drawing of [**(Me₄N)₂H₂L**]·MeOH·H₂O with 50% probability ellipsoids (CCDC 2262872).

IV. PXRD analysis

Data were collected on a powder X-ray diffractometer using CuKα radiation at increments of 0.02° and an exposure time of 1.2 s/step in the angular range 3–30° (2θ) at room temperature. The PXRD patterns of crystals of **(Me₄N)₂H₂L**, in which each peak was observed at same region as shown in Fig. S7b, may slightly shift depending on the measurements.

Figure S7. PXRD patterns of compound **H₄L** and **(Me₄N)₂H₂L**: experimental data of compound **H₄L** (a) and **(Me₄N)₂H₂L** (b) and simulation from XRD data of **H₄L**·(H₂O)$_{0.2}$ (c) and [**(Me₄N)₂H₂L**]·MeOH·H₂O (d).
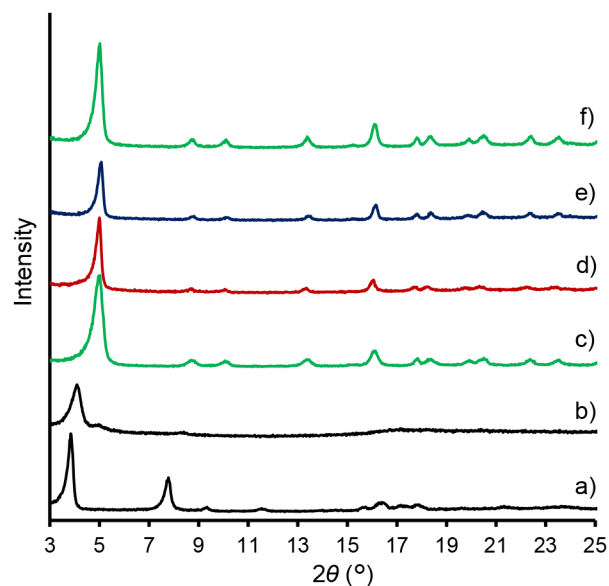
Figure S8. Changes in the PXRD pattern of **(Me₄N)₂H₂L** (a) after extraction of Yb(III) for 1 h (b) and 24 h (c), La(III) for 168 h (d), Eu(III) for 24 h (e) and competitive extraction of Ln(III) for 24 h (f). Samples were prepared under the following conditions: Aq. phase (2 mL): $[\text{Metal}]_{aq,init} = 3.0 \times 10^{-3}$ M (6.0 μmol), [HCl] = 0.01 M. Solid phase: **(Me₄N)₂H₂L** (6.0 μmol). 60 °C.

V. Extraction experiment of Ln(III)

Powdery crystals of compound **H₄L** or compound **(Me₄N)₂H₂L** (6.0 µmol) were placed in a screw cap vial (3.5 mL) equipped with a stir bar and suspended by the addition of an aqueous solution (2 mL) containing HCl (0.001–0.05 M) and La(III), Eu(III), and Yb(III) ($[\text{Metal}]_{aq,init}$). The suspension was stirred at fixed temperature. After the crystals were removed by filtration using membrane filter (1.0 µm pore size), the concentration of the metal species remaining in the aqueous phase, $[\text{Metal}]_{aq}$, was measured by ICP-OES. The percentage of extraction ($E\%$) was calculated according to eq 1.

$$E\% = ([\text{Metal}]_{aq,init} - [\text{Metal}]_{aq})/[\text{Metal}]_{aq,init} \times 100\% \qquad (1)$$

where $[\text{Metal}]_{aq}$ is the concentration of the metal ion in the aqueous phase after the extraction. The ratio selectivity, $r\%(\text{Ln})$, for the selectively extracted Ln(III) was calculated from $E\%(\text{Ln})$ of each Ln(III) according to Eq 2.

$$r\%(\text{Ln}) = E\%(\text{Ln})/[E\%(\text{La}) + E\%(\text{Eu}) + E\%(\text{Yb})] \times 100\% \qquad (2)$$

Table S2 The residual ratio (%) of Me₄N⁺ in the crystal of **(Me₄N)₂H₂L** after treatment with aqueous solution of HCl in the absence of Ln(III). [a]

[HCl] / M	Time / min	The residual ratio (%) of Me₄N⁺ [b]
0.01	30	25
0.01	60	19
0.05	30	6
0.05	60	5

[a] Conditions: Aq. phase (1 mL): [HCl] = 0.01–0.05 M. Solid phase: **(Me₄N)₂H₂L** (3.0 µmol), 30 ℃.
[b] Estimated by ¹H NMR analysis. The residual ratio (%) of Me₄N⁺ in **(Me₄N)₂H₂L** before the treatment with aqueous solution of HCl was defined as 100 %.

Table S3. Competitive extraction of light rare earth ions [Ln^1(III)] and Yb(III) with crystals of **(Me₄N)₂H₂L**.^{a}

Ln^1(III)	E%	
	Ln^1(III)	Yb(III)
La(III)	0	48
Pr(III)	1	40
Ce(III)	6	47

^{a} Conditions: Aq. phase (2 mL): [Metal]$_{aq,init}$ = 3.0 × 10^{-3} M [6.0 μmol each for Ln^1(III) and Yb(III)], [HCl] = 0.01 M. Solid phase: **(Me₄N)₂H₂L** (6.0 μmol), 60 ºC, 48 h.

Table S4. Dependence of E% on the molar equivalent of each Ln(III) to **(Me₄N)₂H₂L** for the competitive extraction of La(III), Eu(III) and Yb(III) with crystals of **(Me₄N)₂H₂L**.^{a}

Molar equivalent of each Ln(III) to **(Me₄N)₂H₂L**	E%			r%(Yb)
	La(III)	Eu(III)	Yb(III)	
0.33	10	53	95	60
0.5	0	24	80	77
1	1	7	47	85
2	0	3	23	88
3	0	3	14	82

^{a} Conditions: Aq. phase (2 mL): [Metal]$_{aq,init}$ = 1.0 × 10^{-3}–9.0 × 10^{-3} M (2.0–18.0 μmol for each metal ions), [HCl] = 0.01 M. Solid phase: **(Me₄N)₂H₂L** (6.0 μmol), 60 ºC, 24 h.

Table S5. E % of La(III), Eu(III) and Yb(III) with crystals of **(Me₄N)₂H₂L**.[a]

Ln(III)	Time	$E\%$
La(III)	1	48
La(III)	24	48
La(III)	48	49
Eu(III)	1	58
Eu(III)	24	53
Eu(III)	48	57
Yb(III)	1	53
Yb(III)	24	57
Yb(III)	48	54

[a] Conditions: Aq. phase (2 mL): $[\text{Metal}]_{aq,init} = 3.0 \times 10^{-3}$ M (6.0 μmol), [HCl] = 0.01 M. Solid phase: **(Me₄N)₂H₂L** (6.0 μmol), 60 ºC, 24 h.

Table S6. Dependence of $E\%$ on the molar equivalent of Yb(III) to **(Me₄N)₂H₂L** for the extraction of Yb(III) with crystals of **(Me₄N)₂H₂L**.[a]

Molar equivalent of Yb(III) to **(Me₄N)₂H₂L**	$E\%$(Yb)	Molar equivalent of Yb(III) collected to **(Me₄N)₂H₂L**
0.25	99	0.25
0.5	99	0.50
1	54	0.54
2	25	0.50
3	17	0.51

[a] Conditions: Aq. phase (2 mL): $[\text{Metal}]_{aq,init} = 0.75 \times 10^{-3}$–$9.0 \times 10^{-3}$M (1.5–18.0 μmol for metal ions), [HCl] = 0.01 M. Solid phase: **(Me₄N)₂H₂L** (6.0 μmol), 60 ºC, 24 h.

VI. ESI-MS measurement
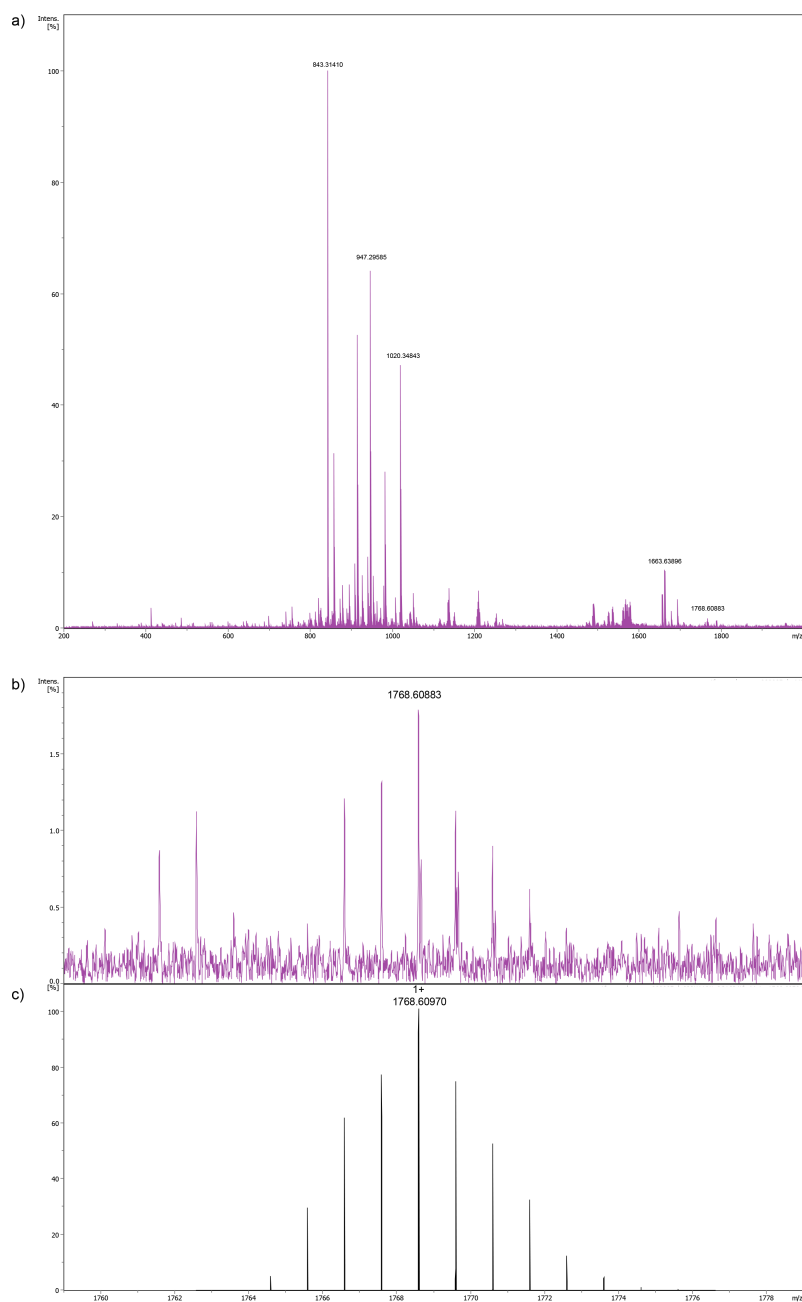
Figure S9. ESI-MS spectra of crystals after collection of Yb(III) (a), isotopic distribution patterns of experimental (b) and theoretical (c) for $C_{88}H_{112}Na_2O_{16}P_4Yb$ [M−H+2Na]$^+$. Samples were prepared under the following conditions: Aq phase (2 mL) : [HCl] = 0.01 M, [Yb(III)]$_{aq,init}$ = 3.0 × 10^{-3} M. Solid phase : **(Me₄N)₂H₂L** (6.0 μmol). 60 ºC, 48 h.

VII. Back-extraction of Yb(III)

Forward extraction was achieved from 2 mL of 0.01 M HCl containing Yb(III) [[Metal]$_{aq,init}$ = 3.0 × 10^{-3} M: 6.0 μmol] with the crystals of **(Me$_4$N)$_2$H$_2$L** (6.0 μmol). It was confirmed that saturated amount of Yb(III) was extracted to the crystals by the measurement of the residual metal ion concentration [Metal]$_{aq}$ in the aqueous phase by ICP-OES. Obtained crystals of Yb(III) complex were placed in a screw cap vial (30 mL) was suspended by addition of 10 mL of methylisobutylketone and 10 mL of aqueous solution of 5 M acids (HCl, H$_2$SO$_4$ and H$_3$PO$_4$) and the resulting suspension was shaken for 24 h at 300 strokes per min at ambient temperature. After the aqueous phase was separated by centrifugation, the concentration of the metal ions in the aqueous phase, [Metal]$_{aq}$′, was measured by ICP-OES. Back extraction percentage ($E\%_{back}$) defined as eq 3 was calculated.

$$E\%_{back} = (5 \times [Metal]_{aq}')/([Metal]_{aq,init} - [Metal]_{aq}) \times 100\% \quad (3)$$

Table S7. Back-extraction of Yb(III) extracted with crystals of **(Me$_4$N)$_2$H$_2$L**.

Acid	$E\%_{back}$
HCl	100
H$_2$SO$_4$	100
H$_3$PO$_4$	94

VIII. References

[1] N. Morohashi, T. Hayashi, Y. Nakamura, T. Kobayashi, S. Tanaka and T. Hattori, *Chem. Lett.*, 2012, **41**, 1520–1522.

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[3] K. Wakita, *Yadokari-XG*, *Software for Crystal Structure Analyses*, 2001.

[4] C. Kabuto, S. Akine, T. Nemoto and E. Kwon, *Nippon Kessho Gakkaishi*, 2009, **51**, 218–224.