

Supporting Information for

Unraveling Cooperative Interactions between Complexed Ions in Dual-Host Strategy for Cesium Salt Separation

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S1. General Information

All starting materials and solvents were ordered from commercial sources (Beijing InnoChem, Aladdin, Macklin Science & Technology Co., Ltd.) and used without further purification. ^1H and ^{13}C NMR spectra were recorded on Bruker AVANCE AV II-400/500 MHz spectrometer at 298 K. ^1H NMR chemical shifts were reported relative to residual solvent peaks (^1H NMR: 2.50 ppm for DMSO- d_6 , 7.26 ppm for CDCl_3 ; ^{13}C NMR: 39.52 ppm for DMSO- d_6 , 77.1 ppm for CDCl_3). High resolution mass spectrometry data were obtained by Bruker micro TOF-Q II ESI-Q-TOF LC/MS/MS. Single crystal X-ray data were measured on Bruker D8 Venture Photon II diffractometer. The anion concentration in aqueous solution was recorded by Shine ion chromatography (CIC-D100, China). All aqueous solutions were prepared by using ultrapure water (18.25 $\text{M}\Omega\cdot\text{cm}$).

The Cesium phosphate salts are not commercially available and were prepared by acid-base reaction from corresponding cesium hydroxide and phosphoric acid. The phosphoric acid (H_3PO_4) was placed in a small vial and certain amounts of hydroxide was added. The mixture was diluted to 1 mL and the prepared solution was used directly. Cs_3PO_4 (water): H_3PO_4 was mixed with three equivalents of CsOH (40% wt, H_2O).

S2. X-ray diffraction single crystal structures

$[\text{Cs}(18\text{-Crown-6})]_2\text{SO}_4$ (12 μL or 18 μL , 0.625 mol/L, prepared by mixing Cs_2SO_4 with 2 equivalents of 18-Crown-6) was added to a suspension of **L** (16 mg) in acetonitrile (1 mL) and acetone(1 mL). After stirring overnight at room temperature, the solution was centrifugated. The obtained clear solution was used for crystal growing. Slow vapor diffusion of diethyl ether into above-mentioned solution provided yellow crystals of **L**•18-crown-6• Cs_2SO_4 within one week.

$[\text{Cs}(18\text{-Crown-6})]_2\text{CO}_3$ (9 μL , 0.625 mol/L, prepared by mixing Cs_2CO_3 with 2 equivalents of 18-Crown-6) was added to a suspension of **L** (12 mg) in acetonitrile (1 mL) and acetone(1 mL). After stirring overnight at room temperature, the solution was centrifugated. The obtained clear solution was used for crystal growing. Slow vapor diffusion of diethyl ether into above-mentioned solution provided yellow crystals of **L**•18-crown-6• Cs_2CO_3 within one week.

$[\text{Cs}(18\text{-Crown-6})]_3\text{PO}_4$ (22 μL , 0.616 mol/L, prepared by mixing Cs_3PO_4 with 3 equivalents of 18-Crown-6) was added to a suspension of **L** (12 mg) in acetonitrile (1 mL) and acetone(1 mL). After stirring overnight at room temperature, the solution was centrifugated. The obtained clear solution was used for crystal growing. Slow vapor

diffusion of diethyl ether into above-mentioned solution provided white crystals of L•18-crown-6•Cs₃PO₄ within one week.

Table S1 Crystal data details for obtained structures

Complex	L•18-C-6•Cs ₂ SO ₄	L•18-C-6•Cs ₂ CO ₃	L•18-C-6•Cs ₃ PO ₄
Empirical formula	C ₇₈ H ₈₄ Cs ₂ N ₁₆ O ₃₁ S	C ₆₁ H ₇₂ Cs ₂ N ₁₆ O ₂₁	C ₁₈₂ H ₂₆₈ Cs ₆ N ₃₆ O ₇₁ P ₂
CCDC	2411573	2411574	2411575
Formula weight	2039.49	3882.54	3882.54
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1
<i>a</i> (Å)	15.3688(19)	19.0373(8)	15.4237(2)
<i>b</i> (Å)	21.192(3)	22.1519(9)	16.2180(2)
<i>c</i> (Å)	29.312(4)	19.0940(8)	22.8955(3)
<i>α</i> (deg)	90	90	77.3610(10)
<i>β</i> (deg)	104.965(5)	116.5470	88.8450(10)
<i>γ</i> (deg)	90	90	86.5290(10)
<i>V</i> (Å ³)	9223(2)	7203.2(5)	5577.95(13)
<i>Z</i>	4	4	1
<i>T</i> (K)	180	180	180
<i>F</i> (000)	4152.0	3312.0	2540.0
<i>D</i> _{calc.} /cm ³	1.469	1.094	1.475
Total no. of data	17017	13284	19654
Completeness to <i>θ</i>	0.999	1.000	1.000
<i>θ</i> range	2.229-25.436	2.191-25.421	2.221-25
<i>μ</i> /mm ⁻¹	0.900	1.094	1.081
Data/restraints/ Parameters	17017/88/1167	13284/51/909	19654/995/1406
GoF on <i>F</i> ²	1.027	1.041	1.081
<i>R</i> 1	0.0510	0.0627	0.0384
<i>wR</i> 2	0.061	0.1765	0.1042

Table S2 Hydrogen bonding information in the crystal structure of L·18-C-6·C₈H₁₆SO₄

<i>D-H...A</i>	<i>d (D-H)</i>	<i>d (H...A)</i>	<i>d (D...A)</i>	$\angle DHA$
N2-H2...O28	0.88	2.12	2.924	151
N3-H3...O30	0.88	2.05	2.872	155
N4-H4...O30	0.88	2.08	2.873	149
N5-H5...O31	0.88	2.43	2.766	103
N6-H6...O28	0.88	1.93	2.77	159
N7-H7...O39	0.88	2.16	2.941	148
N8-H8...O29	0.88	1.96	2.941	158
N9-H9...O30	0.88	2.18	2.941	151
N10-H10...O28	0.88	2.38	2.941	107
N11-H11...O28	0.88	1.9	2.941	164
N12-H12...O31	0.88	2.13	2.941	151

Table S3 Hydrogen bonding information in the crystal structure of L·18-C-6·C₈H₁₆CO₃

<i>D-H...A</i>	<i>d (D-H)</i>	<i>d (H...A)</i>	<i>d (D...A)</i>	$\angle DHA$
N2-H2...O19	0.88	2.12	2.924	151
N3-H3...O19	0.88	2.05	2.872	155
N4-H4...O21	0.88	2.08	2.873	149
N5-H5...O21	0.88	2.43	2.766	103
N7-H7...O21	0.88	1.93	2.77	159
N8-H8...O21	0.88	2.16	2.941	148
N9-H9...O20	0.88	1.96	2.798	158
N10-H10...O20	0.88	2.18	2.983	151
N12-H12...O20	0.88	2.38	2.765	107
N13-H13...O20	0.88	1.9	2.757	164
N14-H14...O19	0.88	2.13	2.936	151
N15-H15...O19	0.88	1.91	2.762	161

Table S4 Hydrogen bonding information in the crystal structure of L·18-C-6·Cs₃PO₄

<i>D-H...A</i>	<i>d (D-H)</i>	<i>d (H...A)</i>	<i>d (D...A)</i>	$\angle DHA$
N1-H1...O6	0.88	1.98	2.776	151
N3-H3...O10	0.88	1.97	2.819	162
N4-H4...O4	0.88	1.89	2.759	170
N5-H5...O4	0.88	1.92	2.773	162
N6-H6...O8	0.88	1.92	2.795	170
N7-H7...O10	0.88	2.04	2.829	149
N8-H8...O6	0.88	1.85	2.716	168
N9-H9...O8	0.88	1.91	2.769	164
N10-H10...O4	0.88	2.02	2.833	153
N12-H12...O8	0.88	2.44	2.784	104
N14-H14...O6	0.88	2.03	2.847	153
N14-H14...O10	0.88	2.48	2.812	103
N16-H16...O10	0.88	2.05	2.84	148

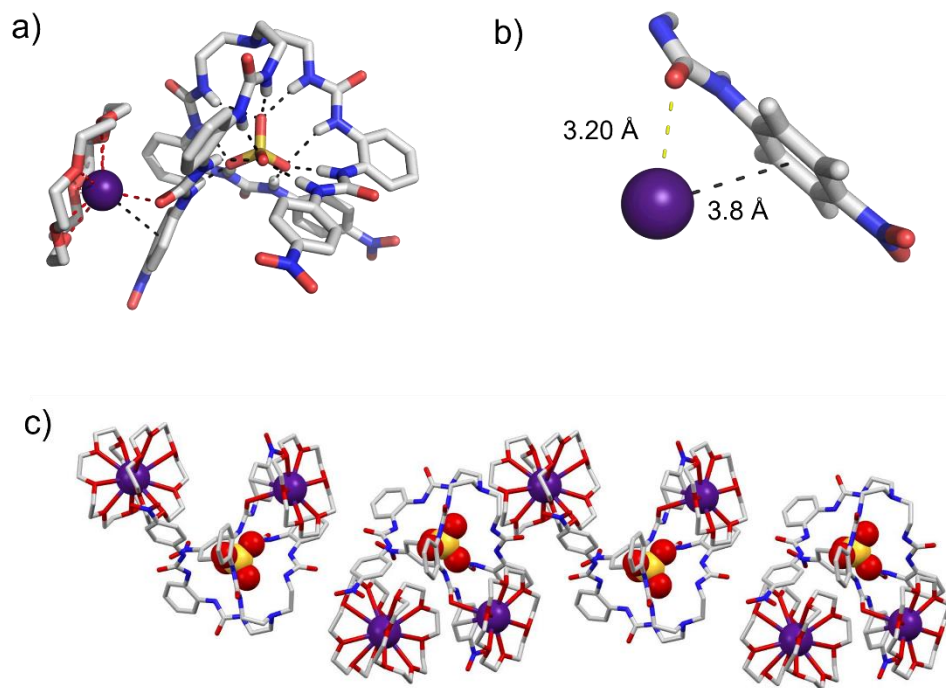


Figure S1. a) Single-crystal structure of the complex L·18-crown-6·Cs₂SO₄, the chemical stoichiometry is 1:1:1 (ligand: anion: 18-C-6), and the 18-C-6 complexed Cs is located outside the cavity. b) Cs enhances structural stability by facilitating ion- π interactions and oxygen interactions with the urea-carbonyl moiety of the ligand. c) Crystal

packing arrangement showing interactions among 18-crown 6 ether, Cs⁺, and L•SO₄²⁻ complex

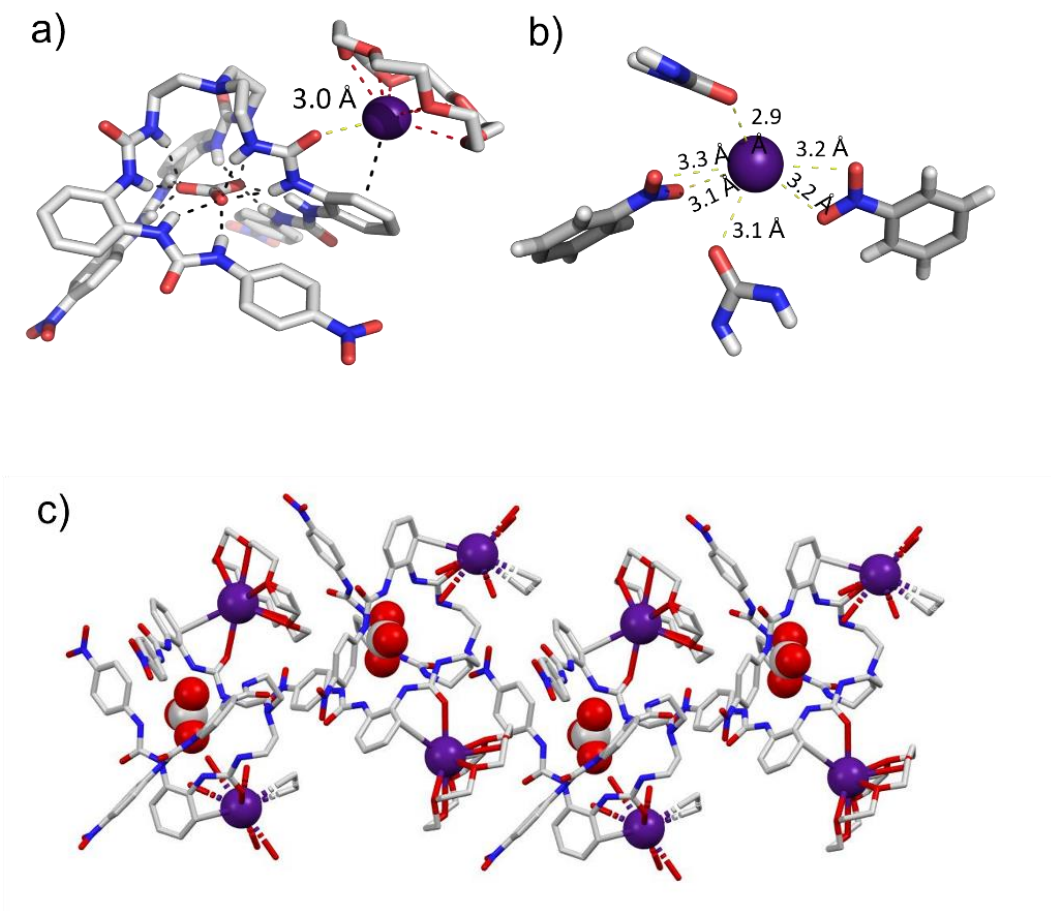


Figure S2. a) Single-crystal structure of the complex L•18-crown-6•Cs₂CO₃, the chemical stoichiometry is 1:1:1 (ligand: anion: 18-C-6), and the 18-C-6 complexed Cs is located outside the cavity. b) Cs enhances the structural stability by interacting with the adjacent ureido carbonyl oxygen atom and the terminal nitro group oxygen atom. c) Crystal packing arrangement showing interactions among 18-crown 6 ether, Cs⁺, and L•CO₃²⁻ complex

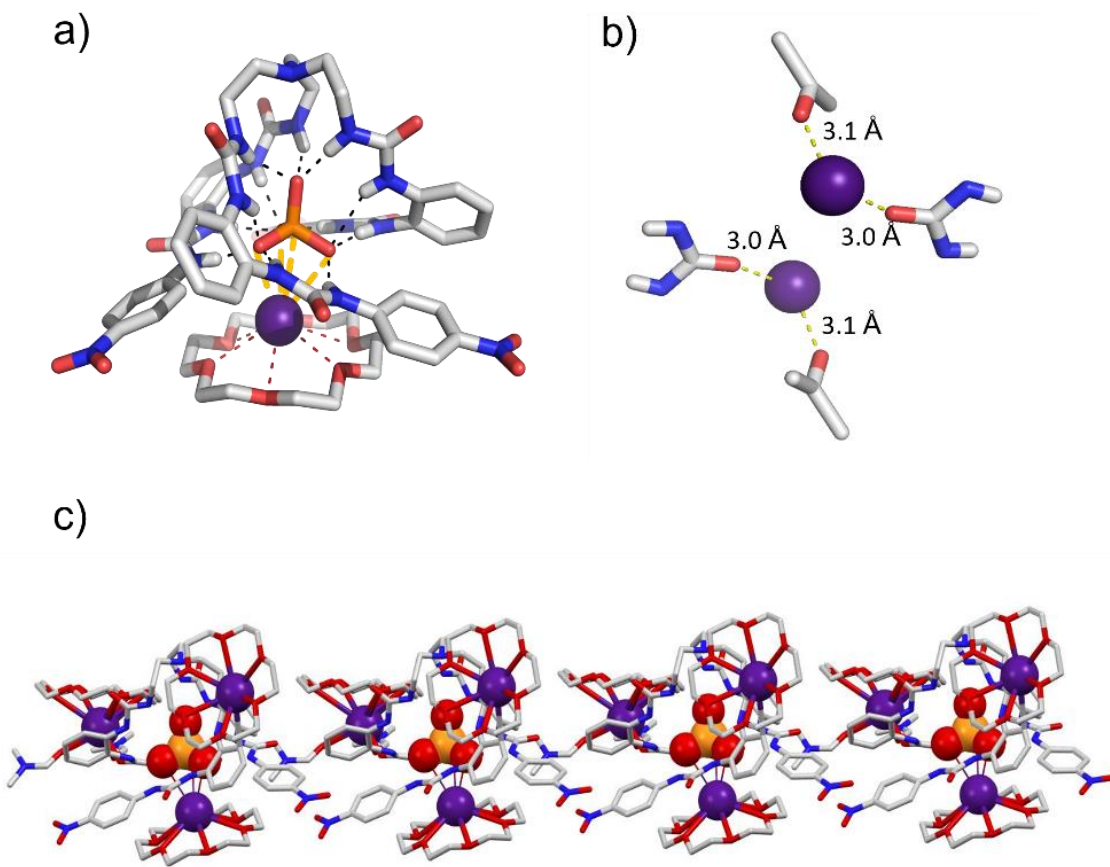


Figure S3. a) Single-crystal structure of the complex $L \cdot 18\text{-crown-6} \cdot \text{Cs}_3\text{PO}_4$, the chemical stoichiometry is 1:1:1 (ligand: anion: 18-C-6), and the 18-C-6 complexed with Cs is located inside the cavity. One oxygen atom of the phosphate group points towards the nitrogen atom of the TREN, with three oxygen atoms pointing downwards to form a tetrahedron. b) Cs enhances the structural stability by interacting with the ureido carbonyl oxygen atoms and acetone oxygen atoms. c) Crystal packing arrangement showing interactions among 18-crown 6 ether, Cs^+ , and $L \cdot \text{PO}_4^{3-}$ complex

S3. ¹H NMR Titration Studies

For a slow titration, such as titrating a ligand by adding carbonate anion as tetrabutylammonium salt (TBA₂CO₃), the equilibrium reaction equation can be represented as follows:



For the calculation, we define these:

$$x = [L \cdot (CO_3^{2-})] + [CO_3^{2-}]$$

$$y = [L \cdot (CO_3^{2-})]$$

$$a = [L]$$

the competitive equilibrium constant K can be represented as

$$K = \frac{[L \cdot (CO_3^{2-})]}{[L \cdot (CO_3^{2-})] \cdot [CO_3^{2-}]} = \frac{y}{(a-y) \cdot (x-y)} \quad (2)$$

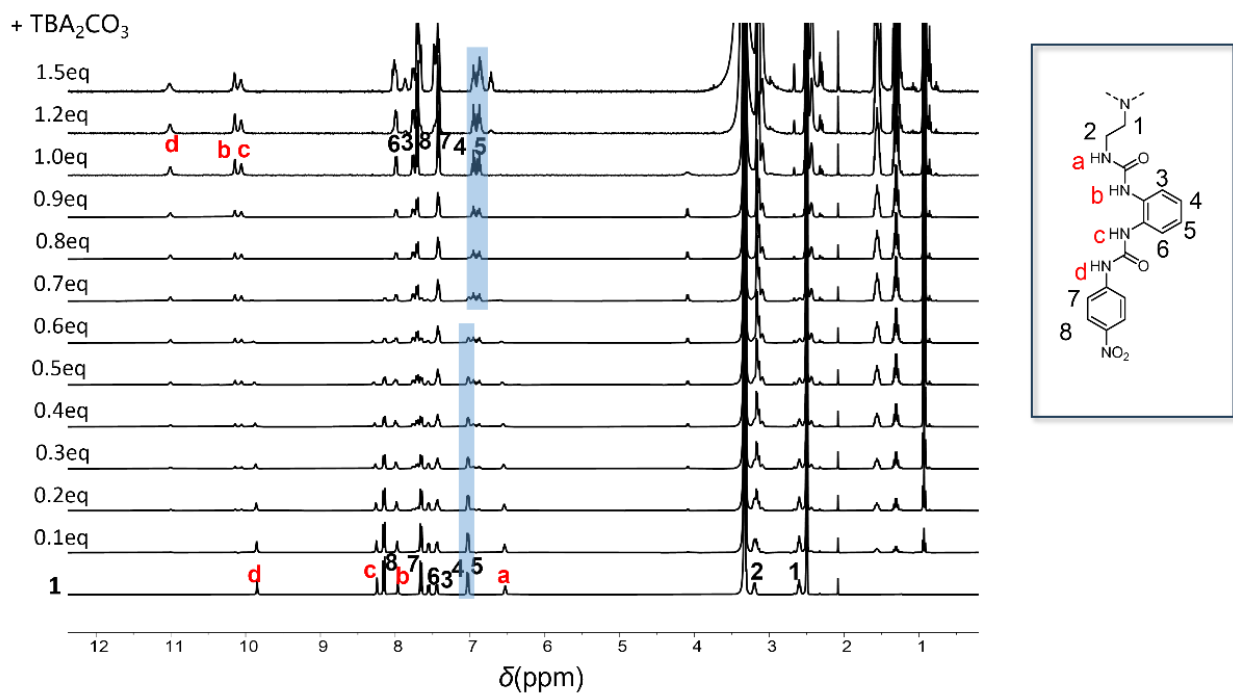


Figure S4. Stacked partial ¹H NMR spectra (400 MHz, 298 K, DMSO-*d*₆) of receptor L (2 mM) by adding carbonate anion as tetrabutylammonium salt (TBA₂CO₃, 50 mM).

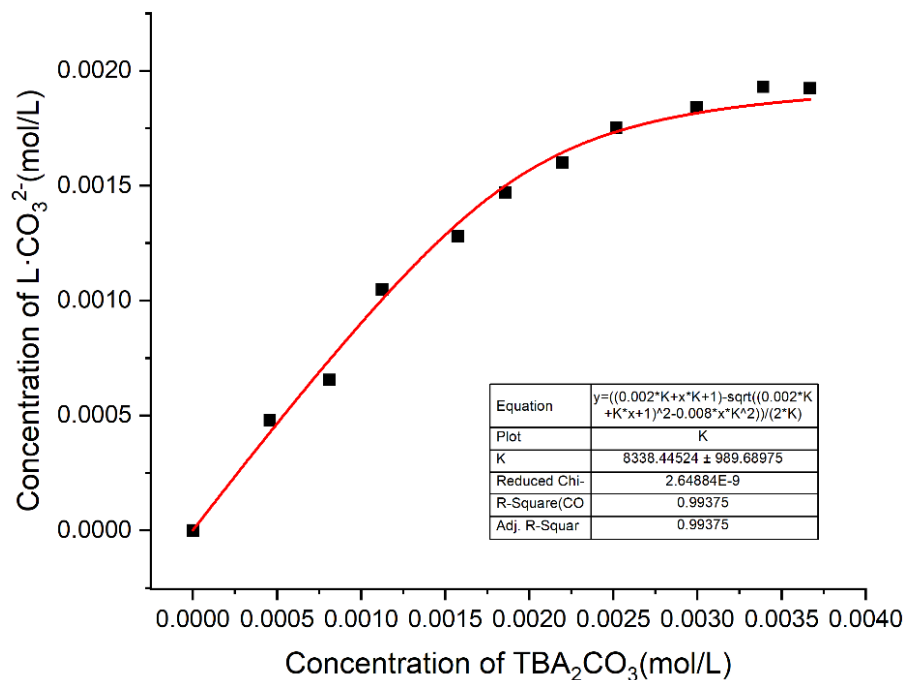


Figure S5. The fitting curve determined based on above-mentioned equation (2) using Origin.

+ TBANO₃

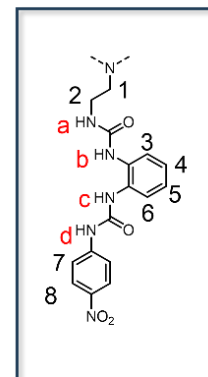
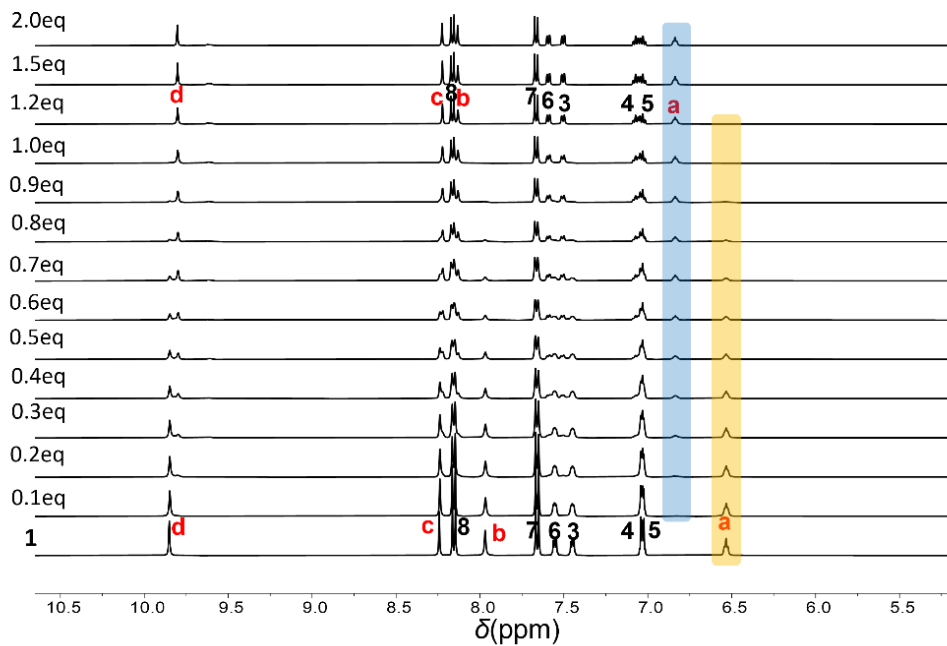


Figure S6. Stacked partial ¹H NMR spectra (500 MHz, 298 K, DMSO-*d*₆) of receptor L (2 mM) by adding nitrate anion as tetrabutylammonium salt (TBANO₃, 50 mM).

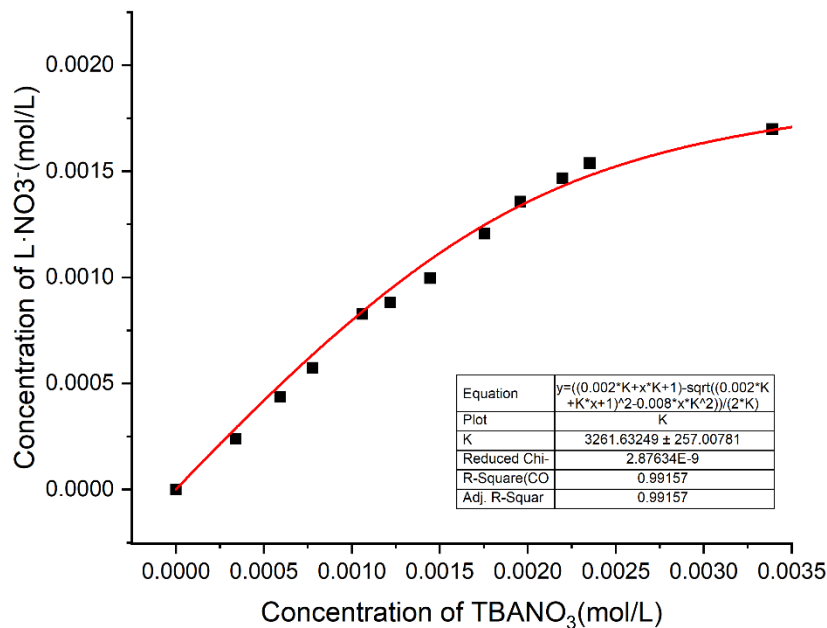


Figure S7. The fitting curve determined based on above-mentioned equation (2).

S4. Solid-liquid extraction experiments

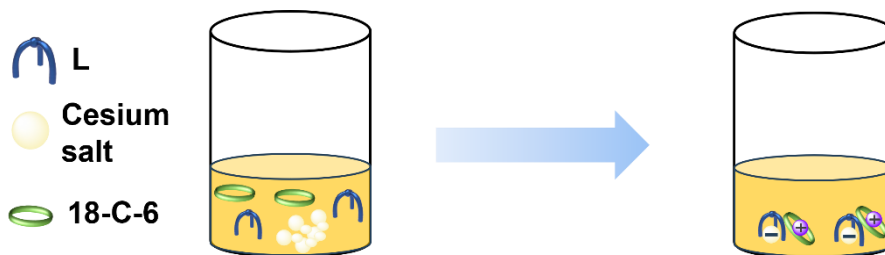


Figure S8. Diagram for solid-liquid extraction.

General solid-liquid extraction procedure: expose the acceptor solution (4 mM, 10 mL, CHCl_3) to a solid containing the target alkali metal cation (such as CsCl , CsNO_3 , Cs_2CO_3 , Cs_2SO_4 , Cs_3PO_4). The solution is a yellow suspension. Mix the prepared solution mixture and stir it at 30 °C for 0.5 hours at a stirring speed of 1500 r/min. The solution and the insoluble solid are separated by centrifugation. The organic layer is carefully collected and dissolved in $\text{DMSO-}d_6$ for ^1H NMR analysis. The bottom sediment is washed with regular CHCl_3 (2 mL \times 3) and redissolved in water (5 mL) by using a volumetric flask. An aqueous solution (0.5 mL) is taken and subjected to a 0.2 μM syringe filter, then the obtained aqueous solution is charged for ion chromatography to determine cation concentration.

Table S5. Summary of IC Results Involving ligands and 18C6 solid-liquid extractions of cesium ions.

Cesium salts	Initial concentration(mM)	After extraction(mM)	Extraction efficiency
CsCl	4.33	0.79	81.8%
CsNO ₃	5.16	3.29	36.2%
Cs ₂ CO ₃	8.74	3.39	61.2%
Cs ₂ SO ₄	8.03	4.76	40.8%
Cs ₃ PO ₄	13.46	ND	100%

Table S6. The IC results of different cations extracted by the solid-liquid extraction method with ligand and 18C6

Chloride salts	Initial concentration(mM)	After extraction(mM)	Extraction efficiency
NaCl	5.75	3.19	44.5%
KCl	2.49	0.77	69.1%
CsCl	4.38	0.39	91.2%
LiCl	1.92	ND	100%

Table S7. Summary of IC results from ligand solid-liquid extraction of cesium ions

Cesium salts	Initial concentration(mM)	After extraction(mM)	Extraction efficiency
CsCl	4.33	3.88	10.4%
CsNO ₃	5.16	4.48	13.2%
Cs ₂ CO ₃	8.74	7.87	10.0%
Cs ₂ SO ₄	8.03	7.72	3.9%
Cs ₃ PO ₄	13.46	12.78	5.0%

Table S8. Summary of IC Results from 18C6 solid-liquid extractions of cesium ions.

Cesium salts	Initial concentration(mM)	After extraction(mM)	Extraction efficiency
CsCl	4.33	1.40	67.7%
CsNO ₃	5.16	3.56	30.9%
Cs ₂ CO ₃	8.74	5.37	38.6%
Cs ₂ SO ₄	8.03	6.75	16.0%
Cs ₃ PO ₄	13.46	5.58	58.5%

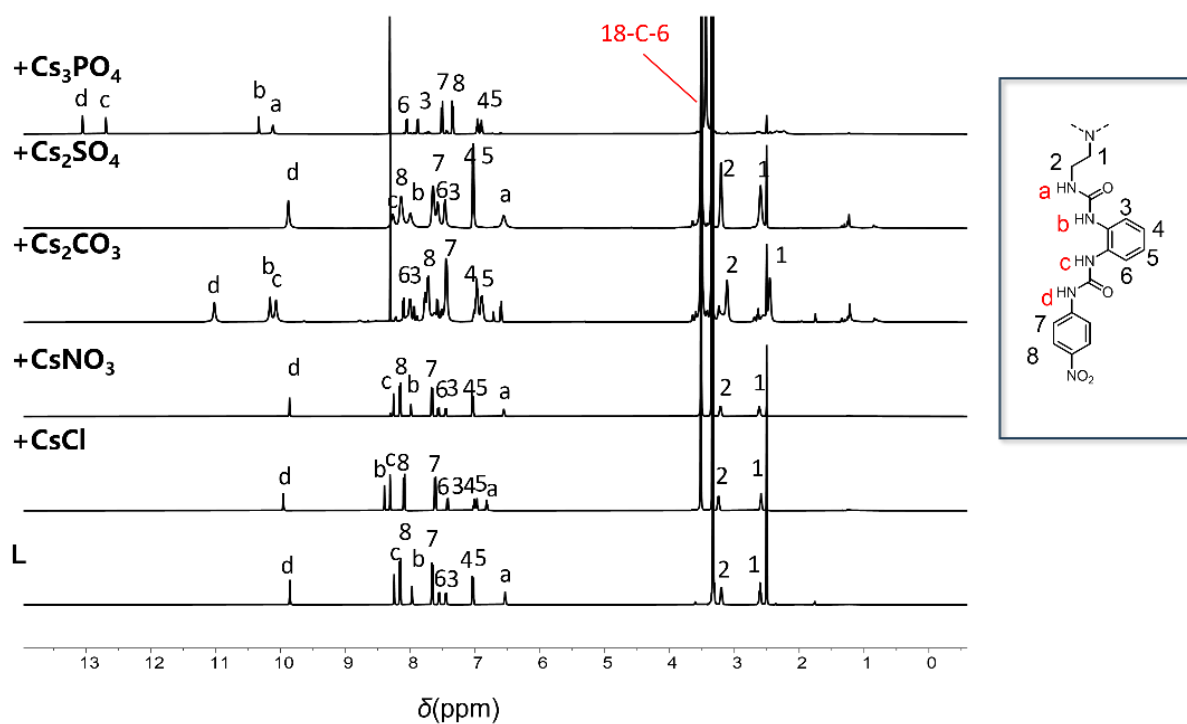


Figure S9. Partial ¹H NMR spectra of a 4.0 mM solution of free L recorded in the absence and presence of CsCl, CsNO₃, Cs₂CO₃, Cs₂SO₄, Cs₃PO₄ in DMSO-*d*₆. All spectra were recorded after allowing the solid phase and the organic phase to equilibrate for 0.5 h.

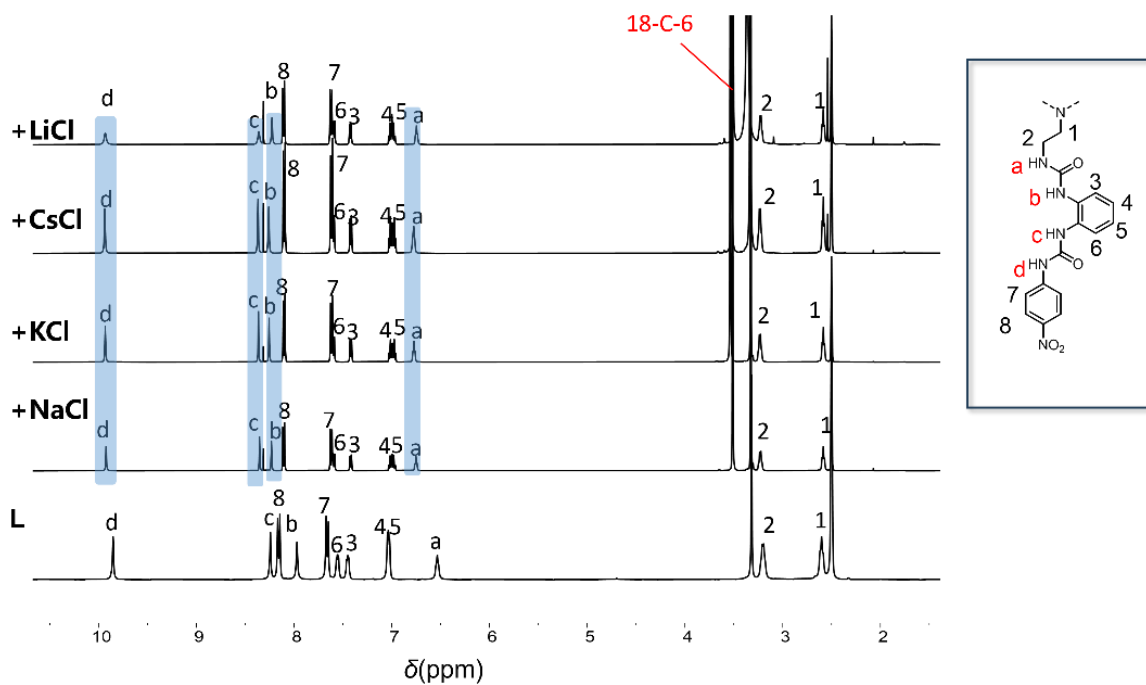


Figure S10. Partial ^1H NMR spectra of a 4.0 mM solution of free L^1 recorded in the absence and presence of CsCl , CsNO_3 , Cs_2CO_3 , Cs_2SO_4 , Cs_3PO_4 in $\text{DMSO-}d_6$.

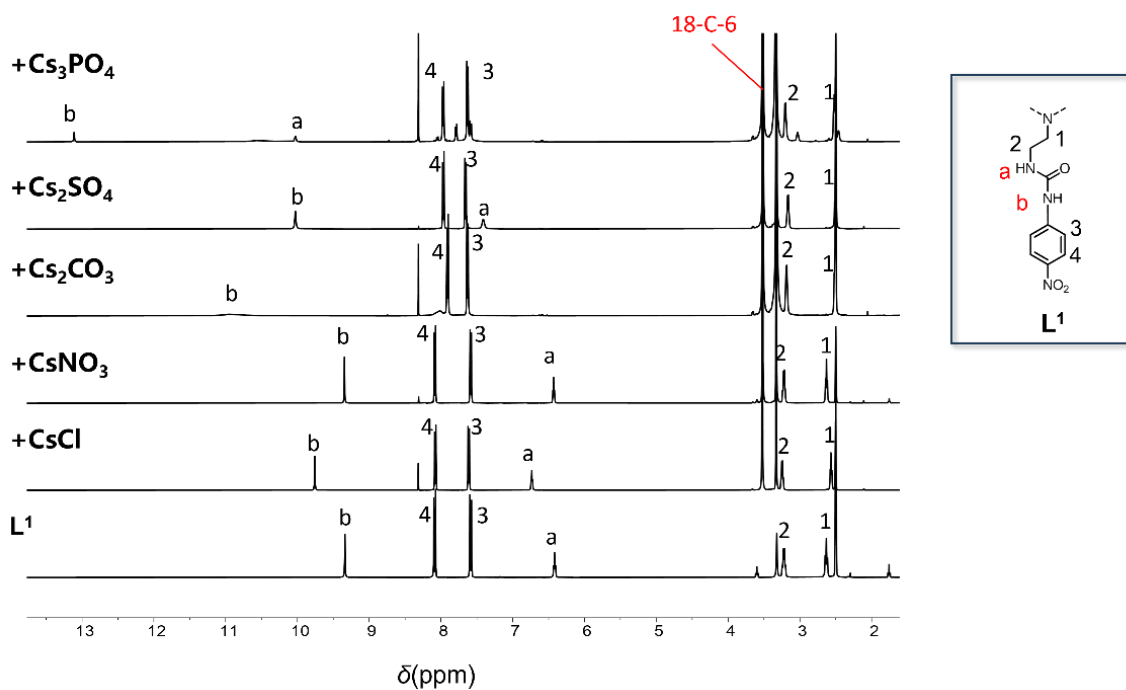


Figure S11. Partial ^1H NMR spectra of a 4.0 mM solution of free L recorded in the absence and presence of LiCl , CsCl , KCl , NaCl in $\text{DMSO-}d_6$.

S5. Mass Spectrometry

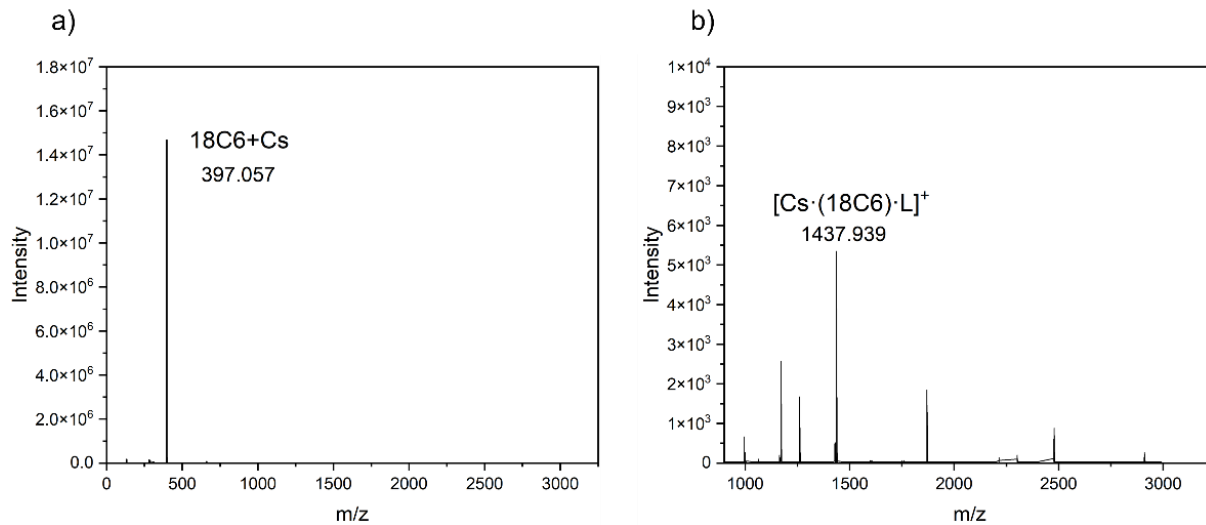


Figure S12. (a) Full and (b) partial ESI-MS spectra of $[\text{L} \cdot (18\text{C}6) \cdot \text{CsCl}]$ in CH_3CN (obtained from the complex $\text{L} \cdot (18\text{C}6) \cdot \text{CsCl}$).

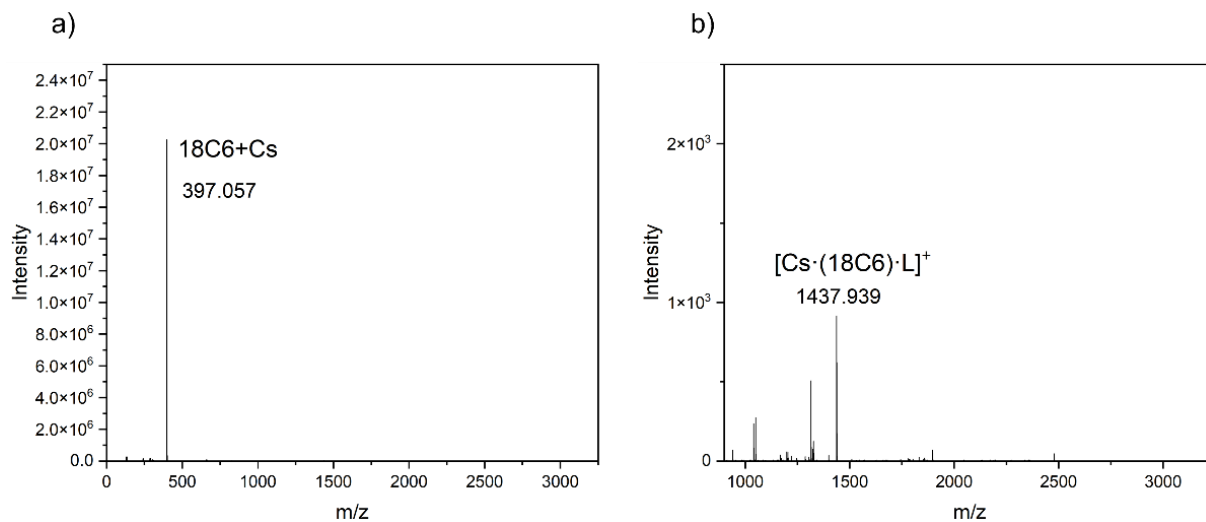


Figure S13. (a) Full and (b) partial ESI-MS spectra of $[\text{L} \cdot (18\text{C}6) \cdot \text{CsNO}_3]$ in CH_3CN (obtained from the complex $\text{L} \cdot (18\text{C}6) \cdot \text{CsNO}_3$).

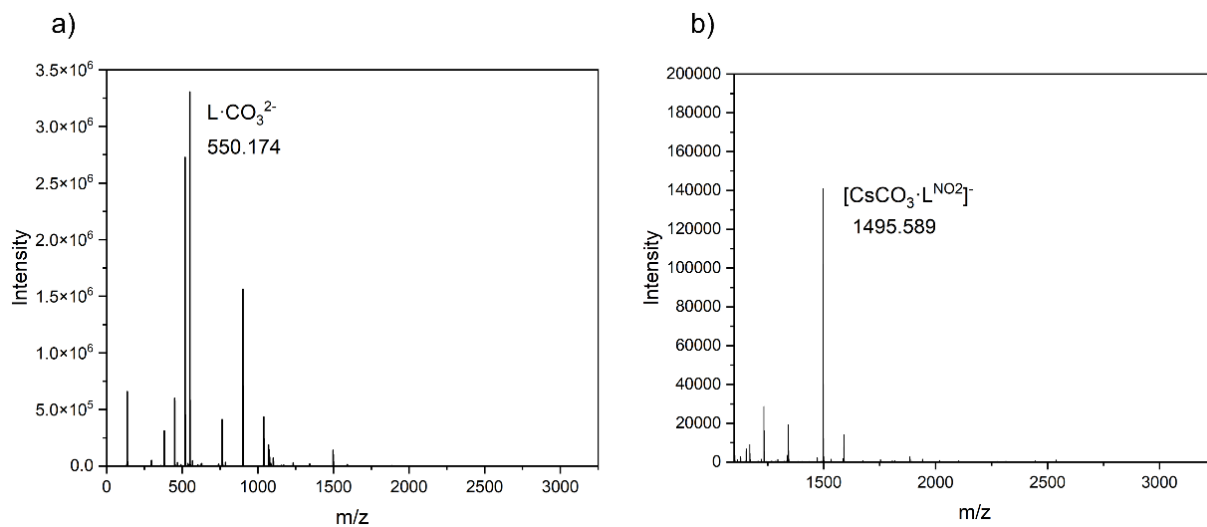


Figure S14. (a) Full and (b) partial ESI-MS spectra of $[L \cdot (18C6) \cdot Cs_2CO_3]$ in CH_3CN (obtained from the complex $L \cdot (18C6) \cdot Cs_2CO_3$)

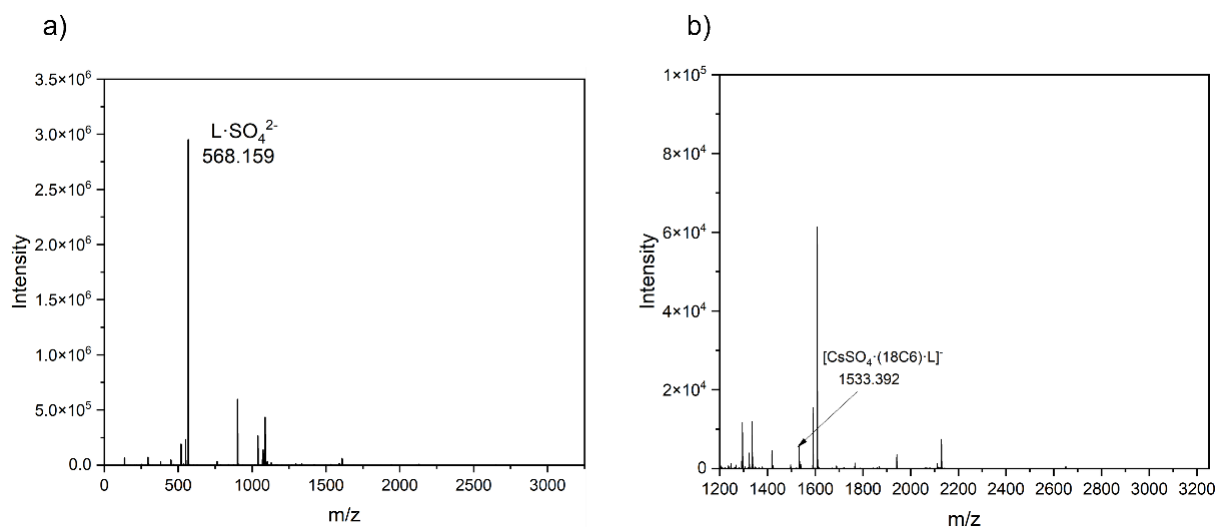


Figure S15. (a) Full and (b) partial ESI-MS spectra of $[L \cdot (18C6) \cdot Cs_2SO_4]$ in CH_3CN (obtained from the complex $L \cdot (18C6) \cdot Cs_2SO_4$)

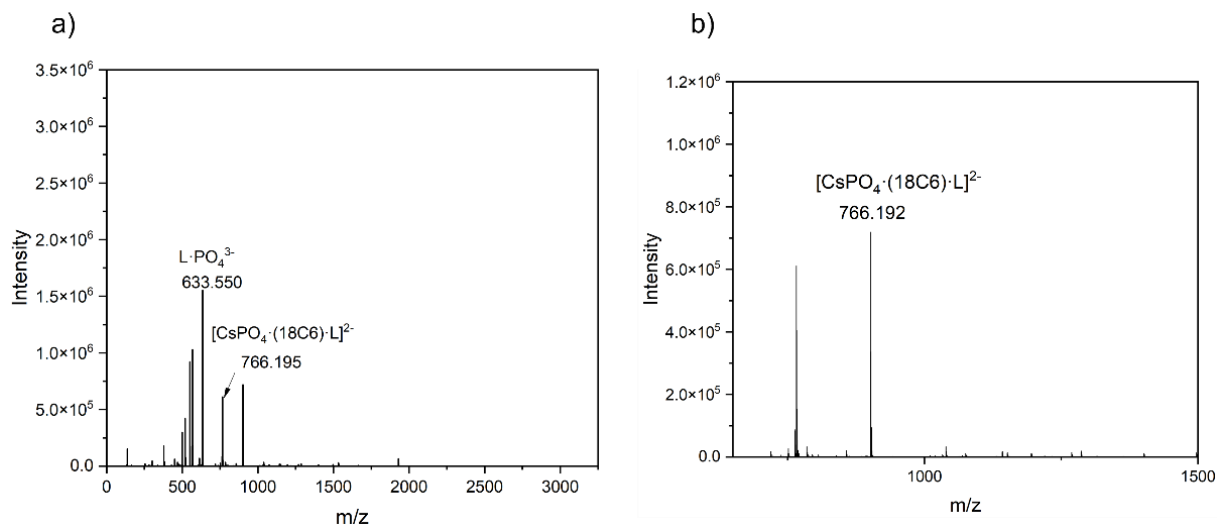


Figure S16. (a) Full and (b) partial ESI-MS spectra of $[L \cdot (18C6) \cdot Cs_3PO_4]$ in CH_3CN (obtained from the complex $L \cdot (18C6) \cdot Cs_3PO_4$)