Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Selective Recognition and Extraction of KBr via Cooperative Interactions with a Urea Functionalized Crown Ether Dual-host

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Experimental Section

Synthesis of L^1:

In a 50 ml round bottomed flask, 4′-aminodibenzo-18-crown-6 (100 mg, 0.27 mmol) was dissolved in 15 ml of dry DCM. The mixture was allowed to stir at 0°C temperature in nitrogen atmosphere for 15 min. 40 µL (0.3 mmol) of pentafluorophenyl isocyatate was dissolved in another 15 mL of dry DCM and taken in a 25 mL pressure equalizing funnel. This solution was added drop-wise for a period of 1 hour with constant stirring at 0°C temperature. After the addition, the reaction mixture was allowed to stir at room temperature in nitrogen atmosphere for another 12 h. The white precipitate was filtered, and washed three times with DCM. Then the precipitate was dried in vacuum to yield the desired product as white solid (145 mg, 92%). ESI-HRMS (+Ve): m/z calcd. for $C_{27}H_{25}F_5N_2NaO_7$ $[M + Na]^+$, 607.1479, found 607.1478. ^{1}H- NMR (300 MHz, DMSO-d_6): δ 8.88 (s, 1H, -N*H*), 8.39 (s, 1H, -N*H*), 7.13 (d, 1H, *J* = 1.8 Hz Ar-*H*), 6.95-6.83 (m, 6H, Ar-*H*), 4.06-3.99 (m, 8H, -O-CH_2), 3.82 (s, 8H, -O-CH_2). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 152.1 (-*C*=O), 148.0 (Ar-*C*), 147.9 (Ar-*C*), 143.6 (Ar-*C*), 132.6 (Ar-*C*), 120.8 (Ar-*C*), 113.0 (Ar-*C*), 112.6 (Ar-*C*), 110.7 (Ar-*C*), 104.8 (Ar-*C*), 69.1 (-O-*C*H_2), 69.0 (-O-*C*H_2), 68.9 (-O-*C*H_2), 68.03 (-O-*C*H_2), 67.8 (-O-*C*H_2), 67.7 (-O-*C*H_2).

^{1}H-NMR Titrations Studies Details:

Binding constants were obtained by ^{1}H-NMR (300 MHz) titrations of L^1 with different anions (as TBA-salt) such as Cl^-, Br^-, NO_3^- and HSO_4^- in CD_3CN at 25˚C. The initial concentration of L^1 was ~2 mM. Aliquots of anions were added from a stock solutions ~10-20 mM. Tetramethylsilane (TMS) in CD_3CN was used as an internal reference, and each titration was performed by 15-20 measurements at room temperature. All proton signals were referred to TMS. The association constant (*K),* values were calculated by fitting the change in the urea-NH chemical shift with a 1:1 association model with non-linear least square analysis. The equation $\Delta\delta = [([A]_0 + [L]_0 + 1/K) \pm \{([A]_0 + [L]_0 + 1/K)^2 - 4[L]_0[A]_0\}^{1/2}]\Delta\delta_{max}/2[L]_0$ was used to determine the *K* values.

Isothermal Titration Calorimetric (ITC) Studies Details:

The titrations were carried out at 298 K in freshly distilled acetonitrile. A solution of L in acetonitrile was placed in the measuring cell. This solution was then titrated with 30 injections of 10 µL of TBACl solution that was prepared in acetonitrile. An interval of 220 s was allowed between each injection, and the stirring speed was set at 329 rpm. The obtained data was processed by using Origin 7.0 software that was supplied with the instrument and was fitted to a one-site binding model. A blank titration of plain solvent was also performed and subtracted from the corresponding titration to remove any effect from the heats of dilution from the titrant.

Solid-Liquid Extraction Studies Details:

For solid-liquid extraction studies, **L** (1.2 mg) was dissolved in 1 ml CD_3CN/CH_3CN (2 mM concentration) in a 2 ml glass vial. Then excess of respective solid Na^+/K^+ salt (5 equivalents with respect to **L**) was added in the solution of **L**. The solid salts remain insoluble in CD_3CN/CH_3CN. The mixture was allowed to sonicate for 1hr on a sonicator bath at room temperature. Then the solution was filtered through Whatman-42 filter paper and filtrate was allowed to different studies like ^{1}H-NMR, ESI-MS and EDX."

Figure S1 ESI-MS (+ve) spectrum of ligand **L**.

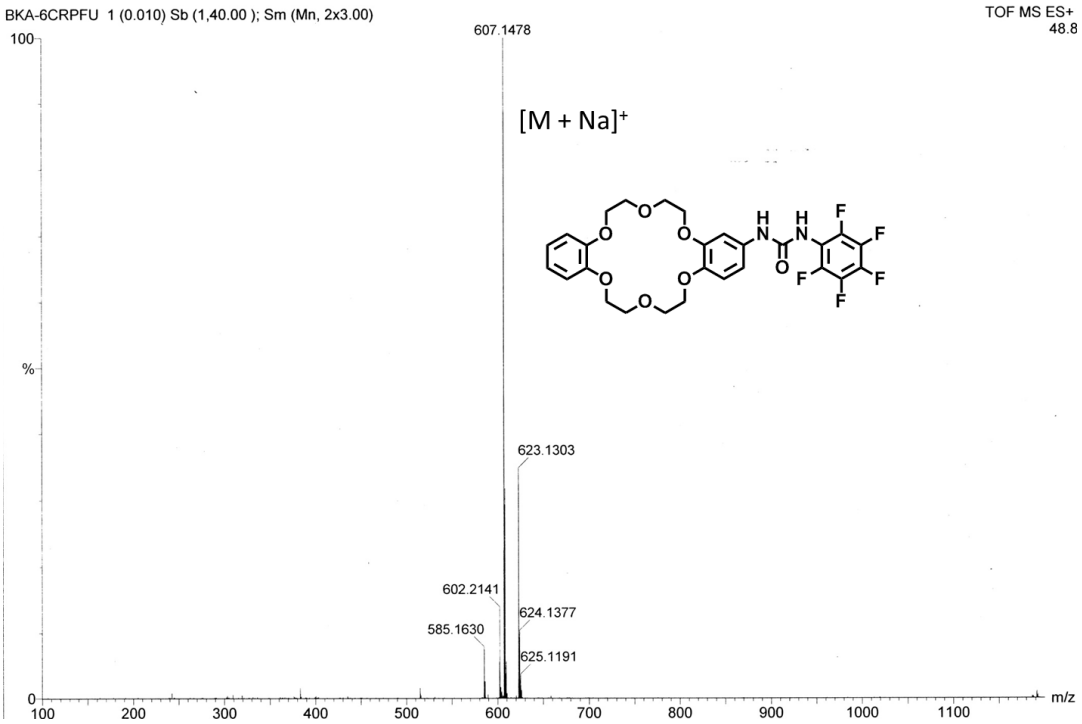


Figure S2 300 MHz ^{1}H-NMR spectrum of **L** in DMSO-d_6 at 25ºC.

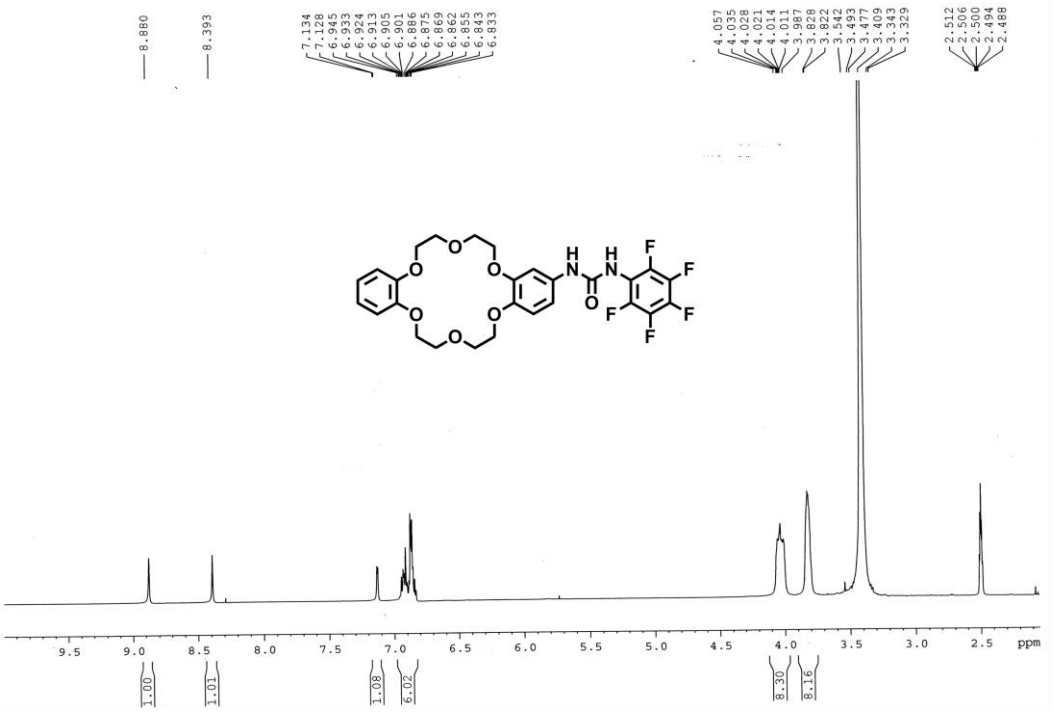


Figure S3 100 MHz ^{13}C-NMR spectrum of **L** in DMSO-d_6 at 25ºC.

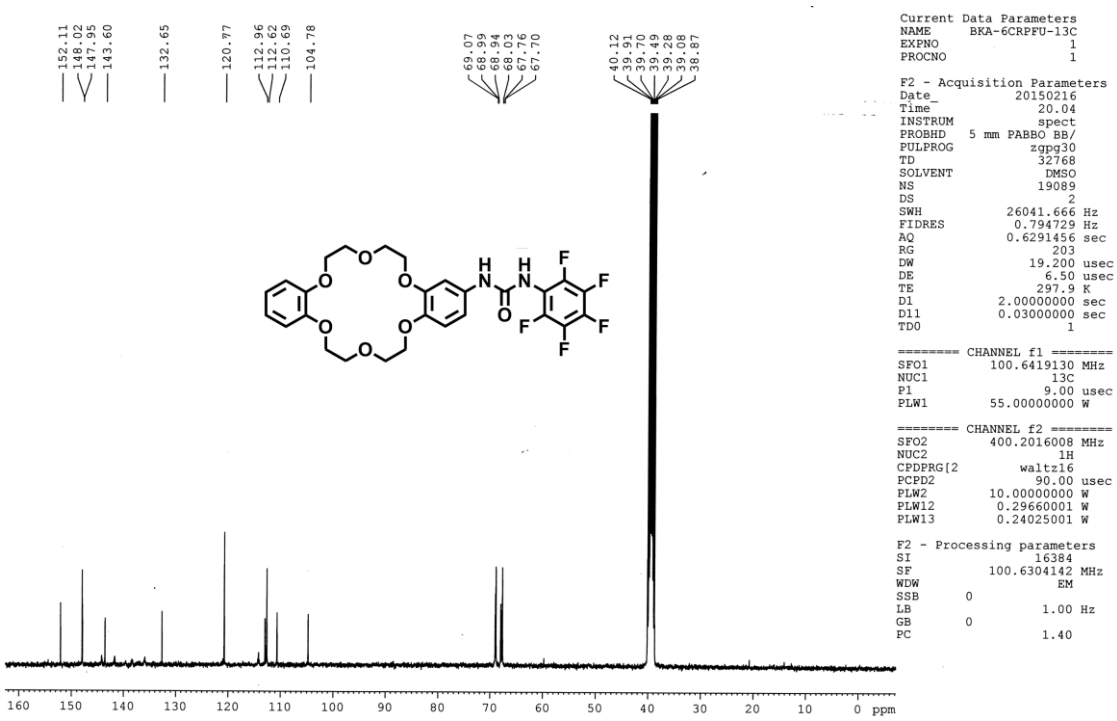


Figure S4 ESI-MS (-ve) spectrum of **L**.

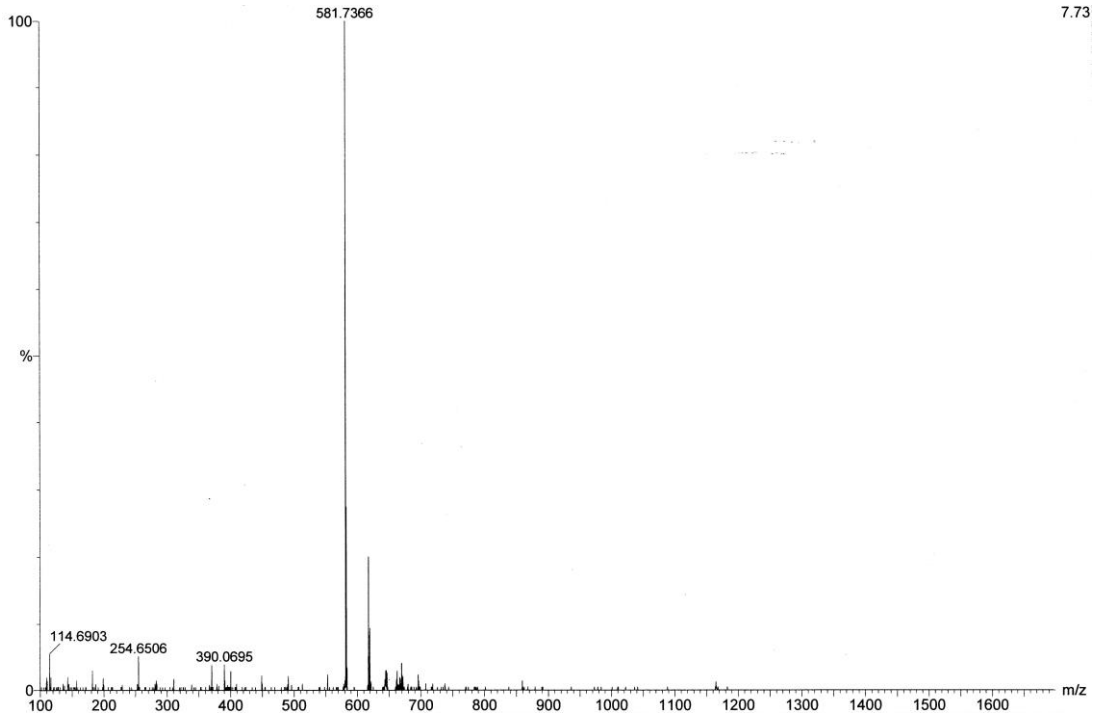


Figure S5 ESI-MS (-ve) spectrum of extracted mass obtained from the solid-liquid extraction of **L** with KCl.

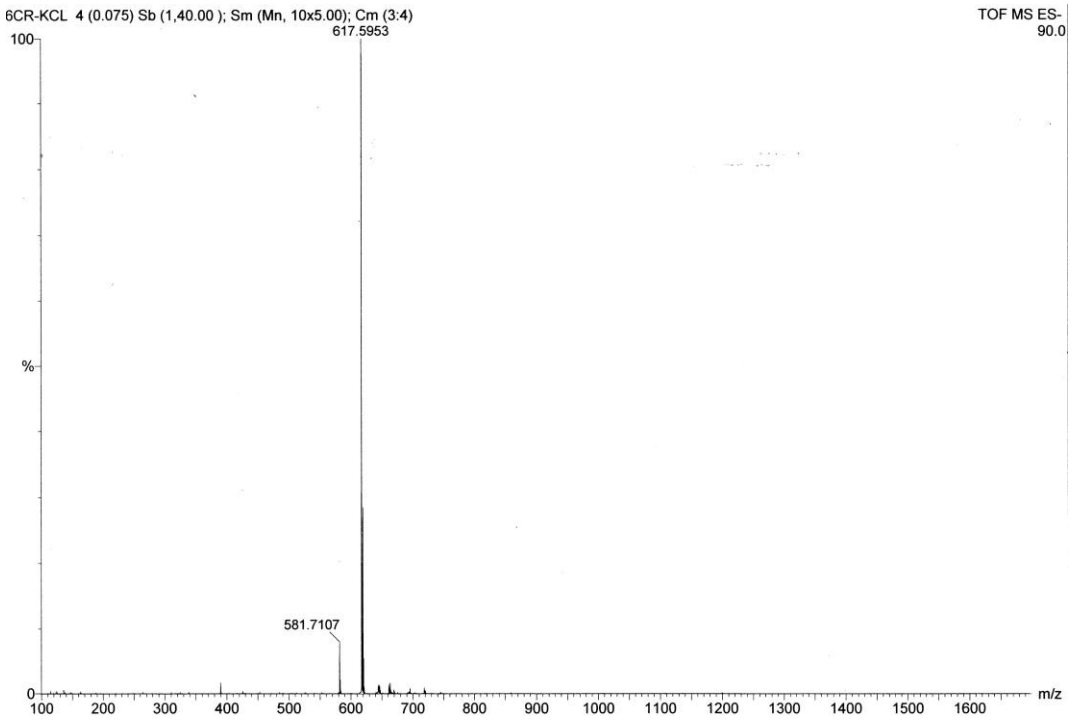


Figure S6 ESI-MS (-ve) spectrum of extracted mass obtained from the solid-liquid extraction of **L** with KBr.

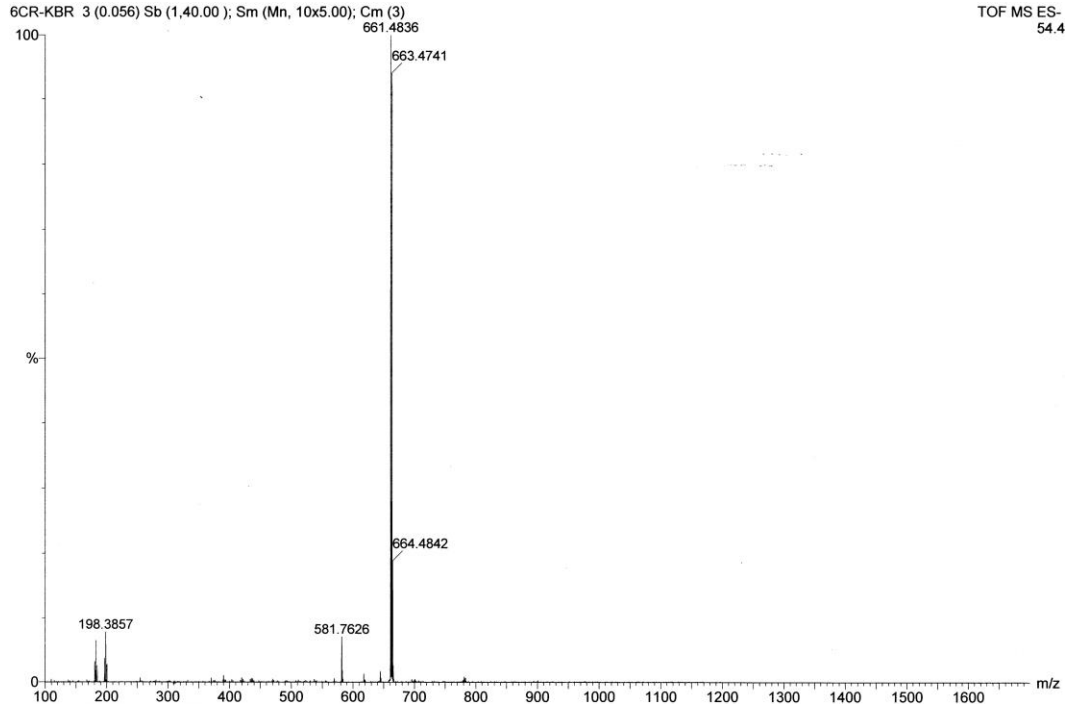


Figure S7 ESI-MS (-ve) spectrum of extracted mass obtained from the solid-liquid extraction of **L** with KNO_3.

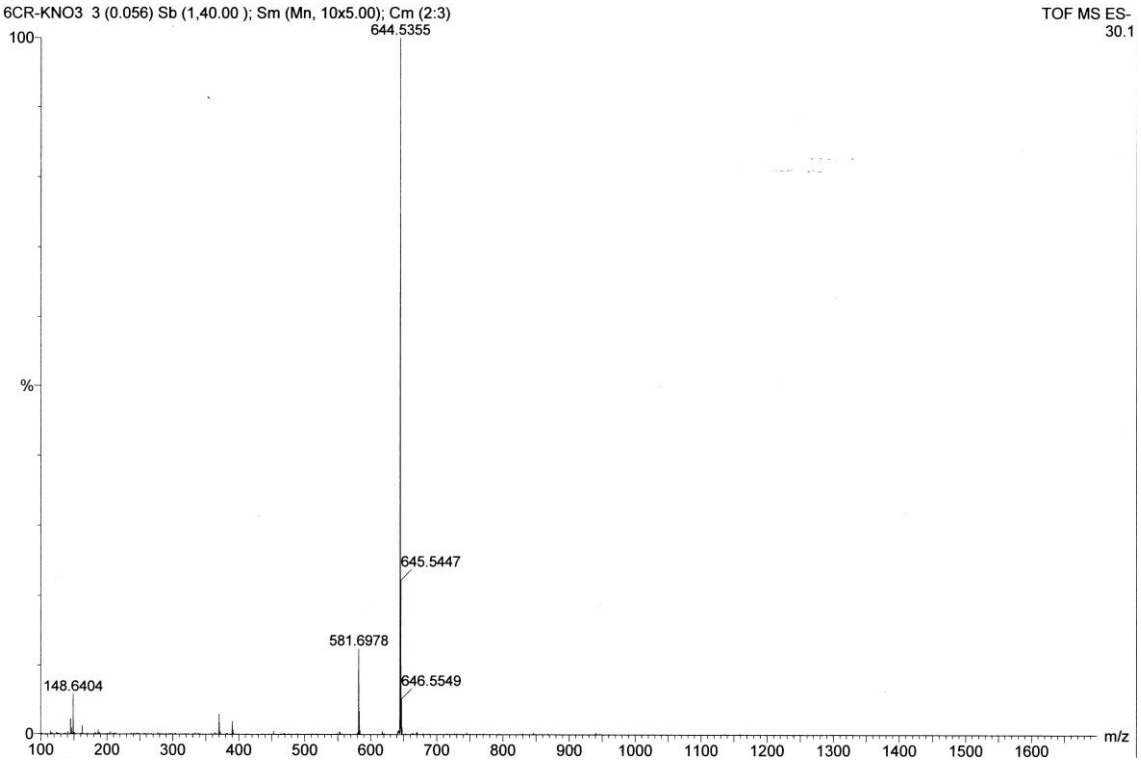


Figure S8 ESI-MS (-ve) spectrum of extracted mass obtained from the solid-liquid extraction of **L** with mixtures of KCl, KBr and KNO_3.

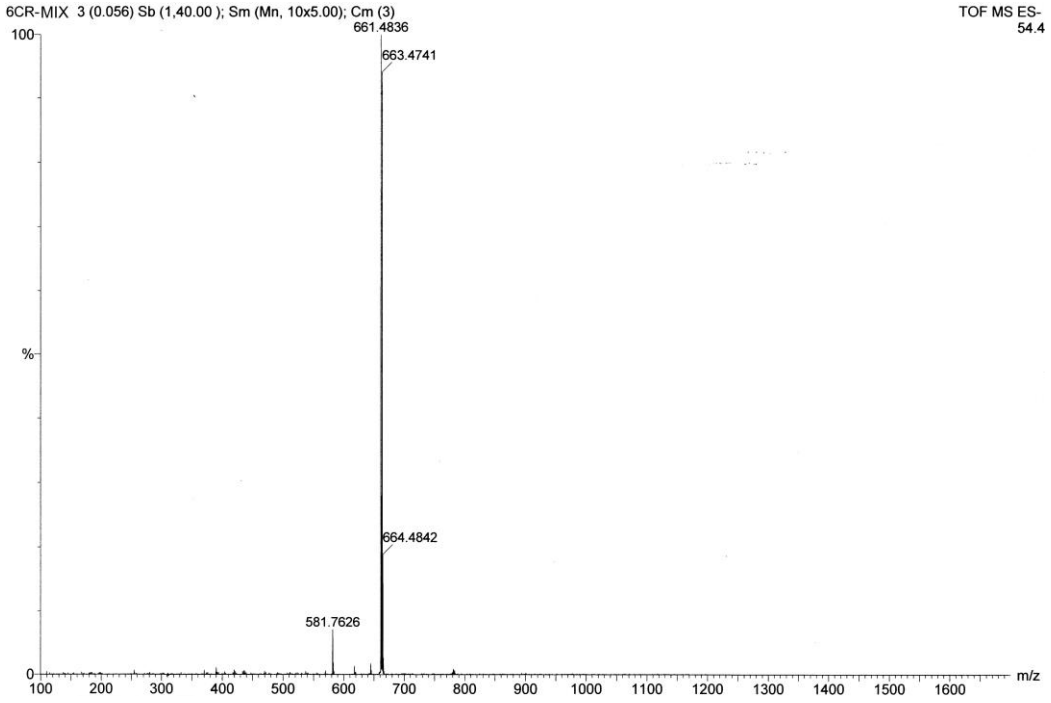


Figure S9 Comparative ^{1}H-NMR spectra of extracted mass obtained from the solid-liquid extraction of **L** with mixtures of K^{+} salts and ^{1}H-NMR spectra of extracted mass obtained from the solid-liquid extraction of **L** only with KBr in CD_3CN at 25ºC.

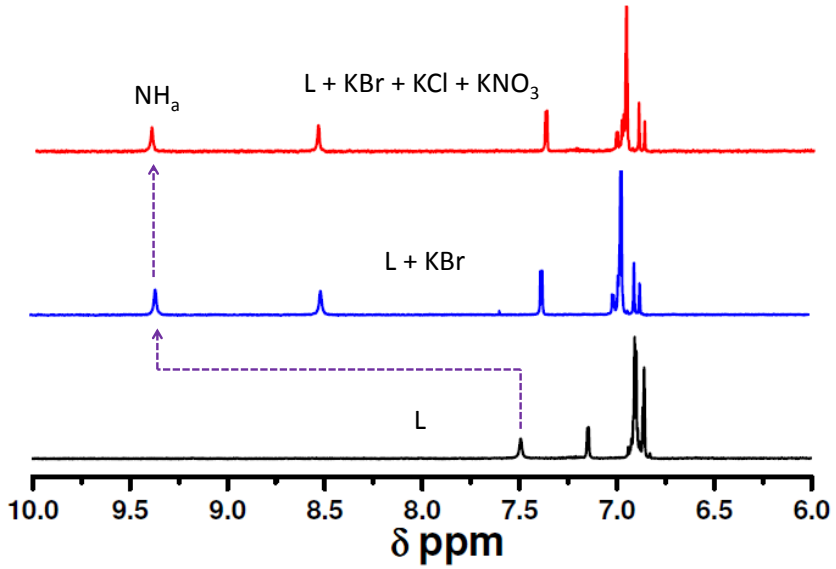
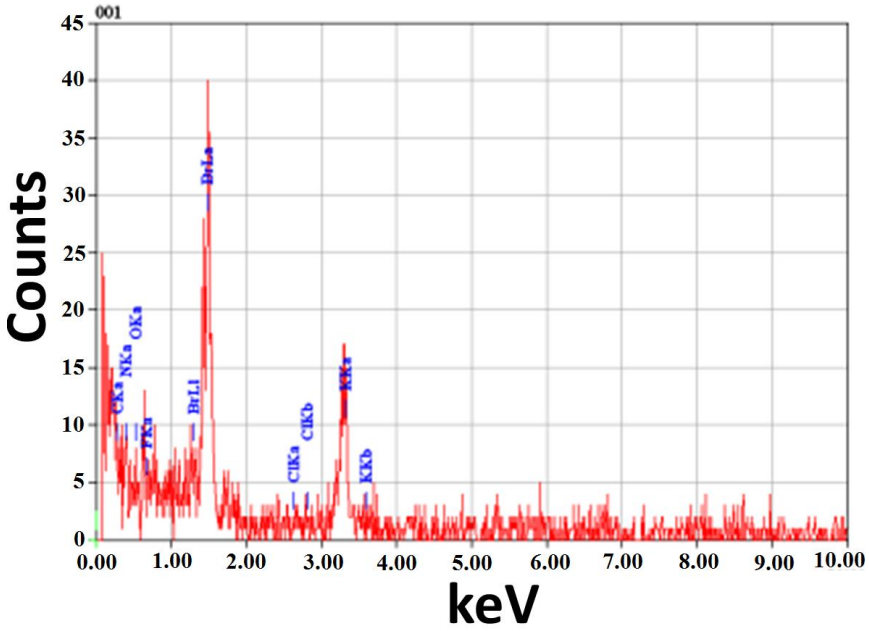


Figure S10 SEM-EDX experiments of of extracted mass obtained from the solid-liquid extraction of **L** with mixtures of KCl, KBr and KNO_3.



Ele...	Cl...	(keV)	mass%	Error%	At%
C	K				
N	K	0.392	42.50	2.15	59.32
O	K	0.525	24.21	2.76	29.58
F	K	0.677	0.91	1.77	0.94
Cl	K				
K	K	3.312	8.75	0.41	4.37
Br	L	1.480	23.63	0.74	5.78
Total			100.00		100.00

Figure S11 Qualitative ^{1}H-NMR spectrum of **L** in presence of 1:1 ratio of TBA-anuions in CD_3CN at 25ºC showing the chemical shifts of urea-NH_a proton.

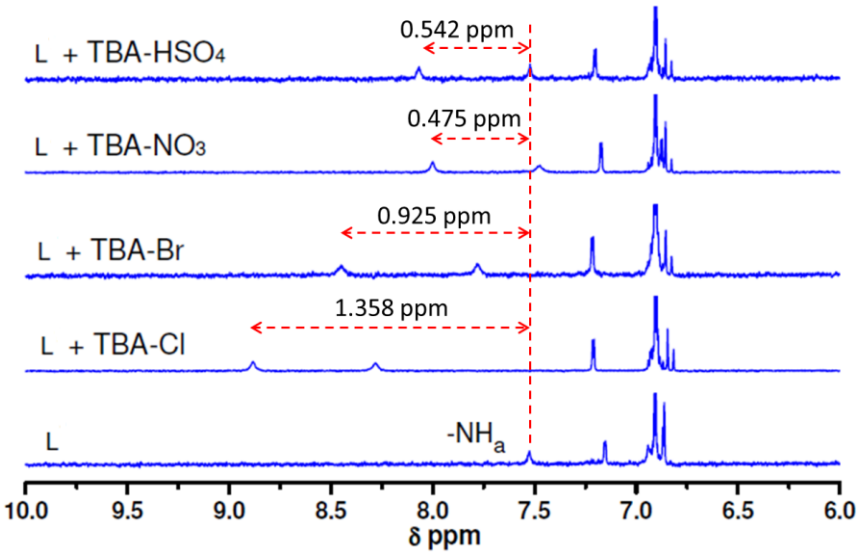
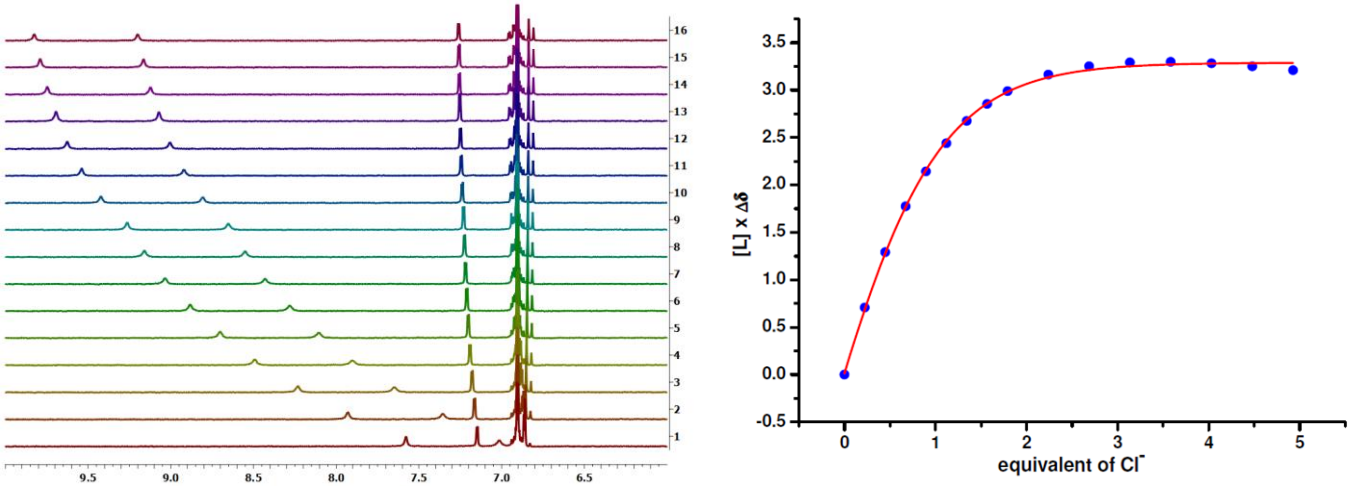
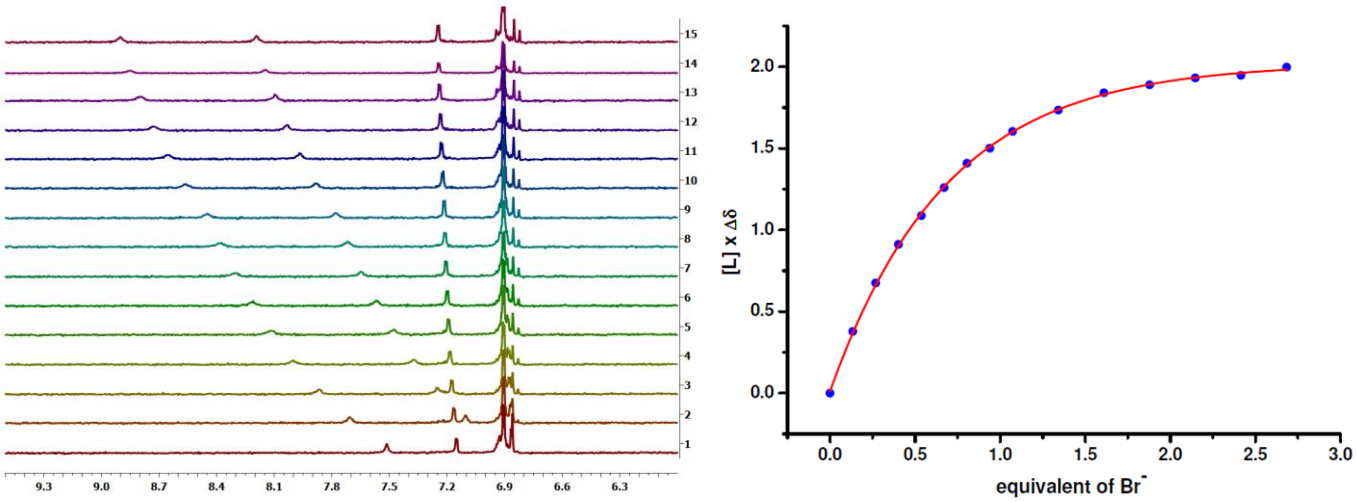


Figure S12 Plot of change in chemical shift of the urea-NH_a proton of **L** with increasing amounts of TBA-Cl in CD_3CN at 298 K.



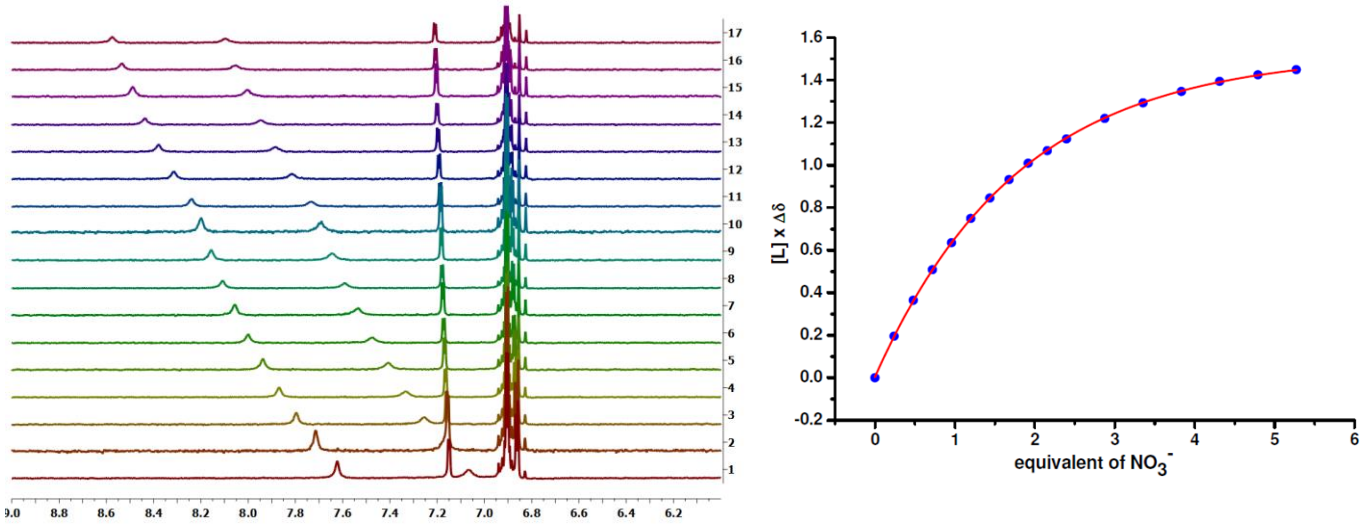
L: 2.0565 mmol; TBA-Cl: 23.0282 mmol.

Figure S13 Plot of change in chemical shift of the urea-NH_a proton of **L** with increasing amounts of TBA-Br in CD_3CN at 298 K.



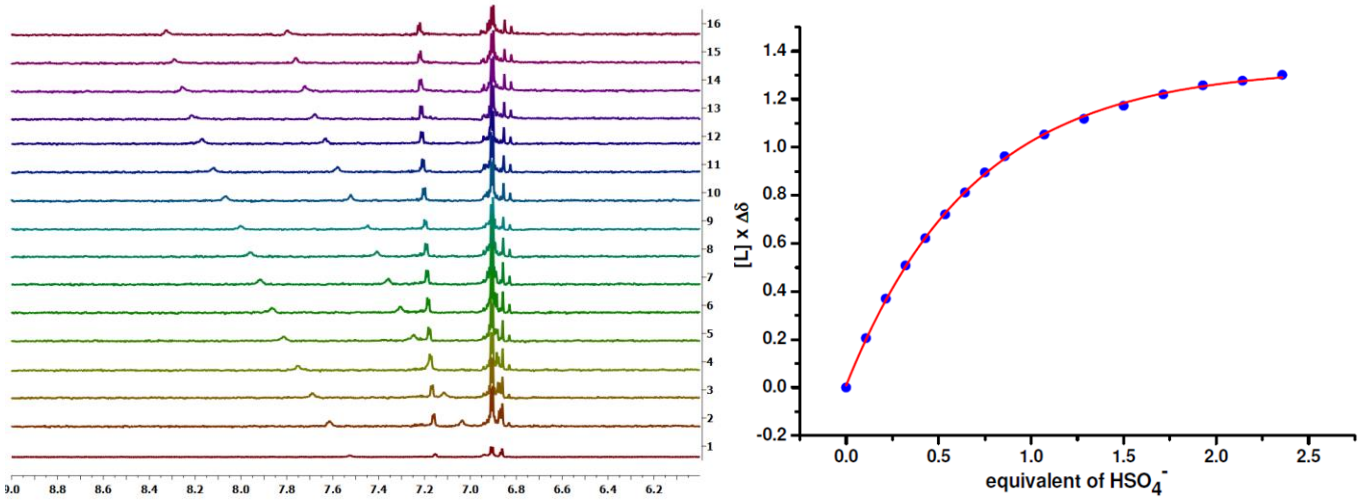
L: 1.9880 mmol; TBA-Br: 13.3387 mmol.

Figure S14 Plot of change in chemical shift of the urea-NH_a proton of **L** with increasing amounts of TBA-NO_3 in CD_3CN at 298 K.



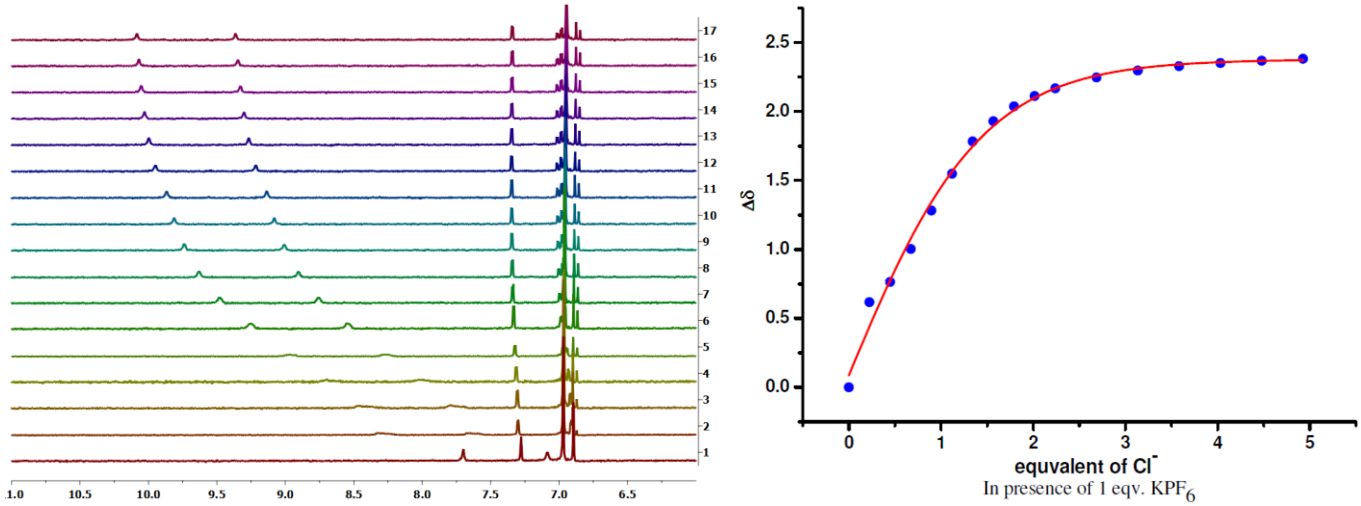
L: 2.1936 mmol; TBA-NO_3: 26.2752 mmol.

Figure S15 Plot of change in chemical shift of the urea-NH_a proton of **L** with increasing amounts of TBA-HSO_4 in CD_3CN at 298 K.



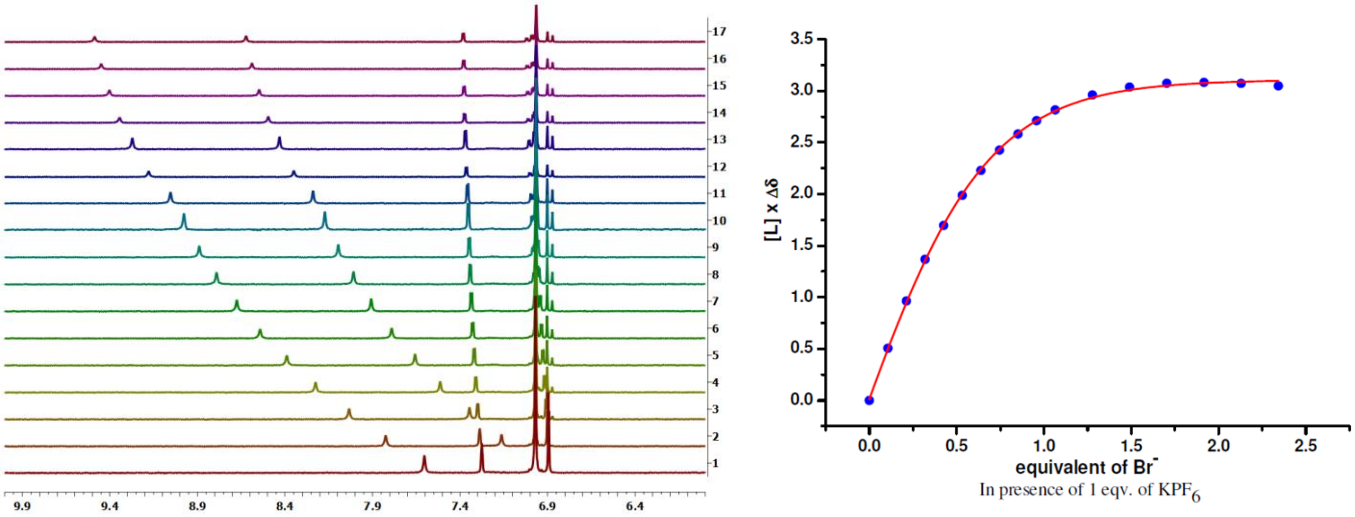
L: 2.3307 mmol; TBA-HSO_4: 12.4878 mmol.

Figure S16 Plot of change in chemical shift of the urea-NH_a proton of **L** with increasing amounts of TBA-Cl in presence of K^+ in CD_3CN at 298 K.



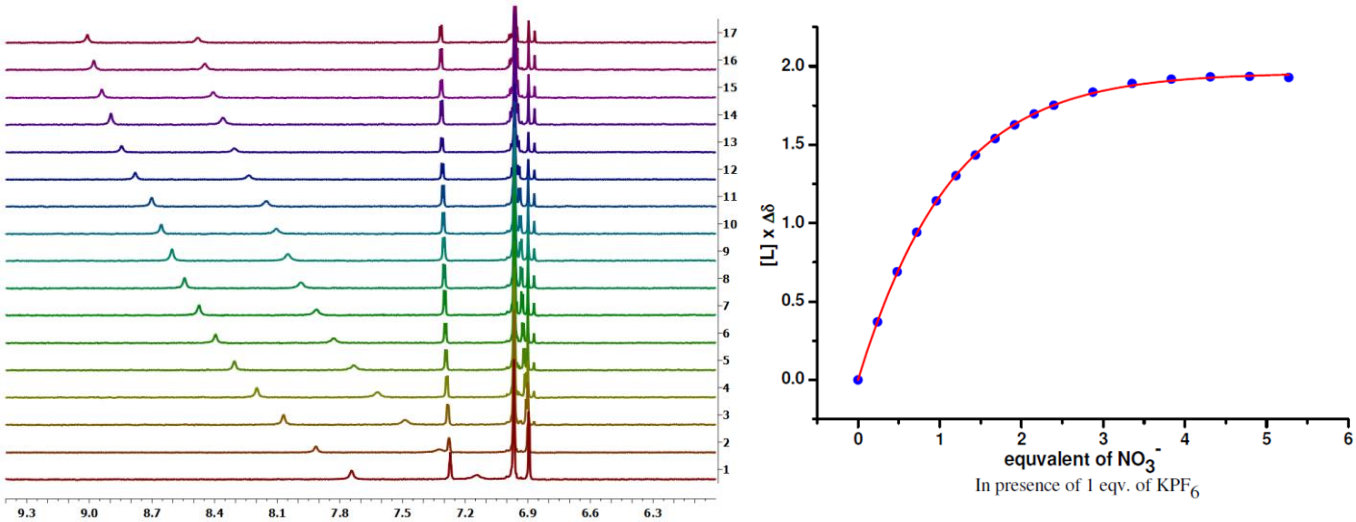
L: 2.0565 mmol; TBA-Cl: 23.0282 mmol.

Figure S17 Plot of change in chemical shift of the urea-NH_a proton of **L** with increasing amounts of TBA-Br in presence of K^+ in CD_3CN at 298 K.



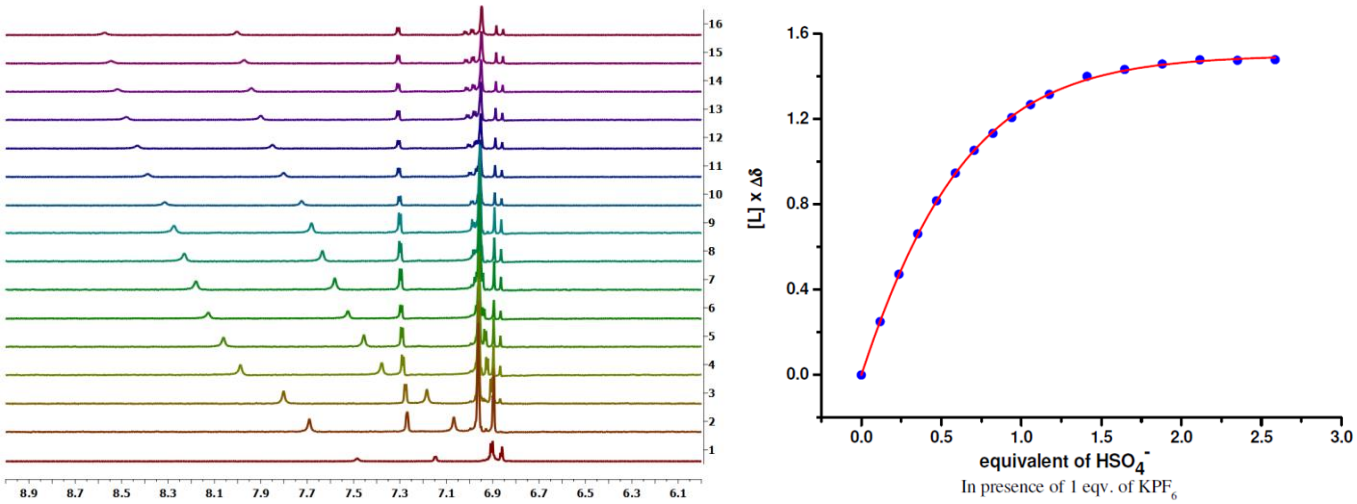
L: 2.3307 mmol; TBA-Br: 12.4081 mmol.

Figure S18 Plot of change in chemical shift of the urea-NH_a proton of **L** with gradual addition of TBA-NO_3 in presence of K^+ in CD_3CN at 298 K.



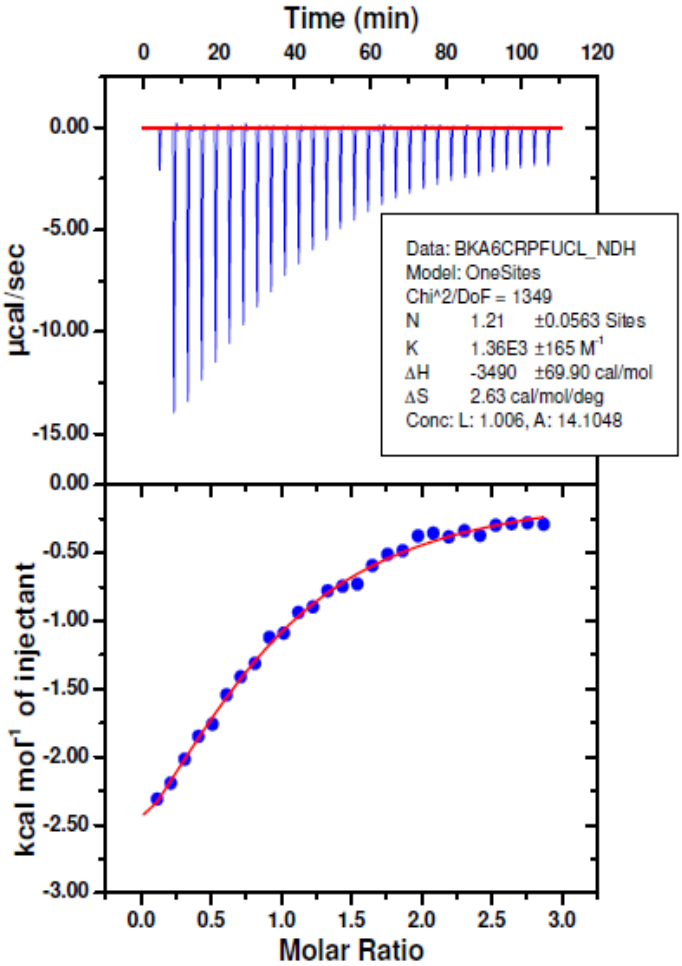
L: 2.1936 m.mol; TBA-NO_3: 26.2752 m.mol

Figure S19 Plot of change in chemical shift of the urea-NH_a proton of **L** with gradual addition of TBA-HSO_4 in presence of K^+ in CD_3CN at 298 K.



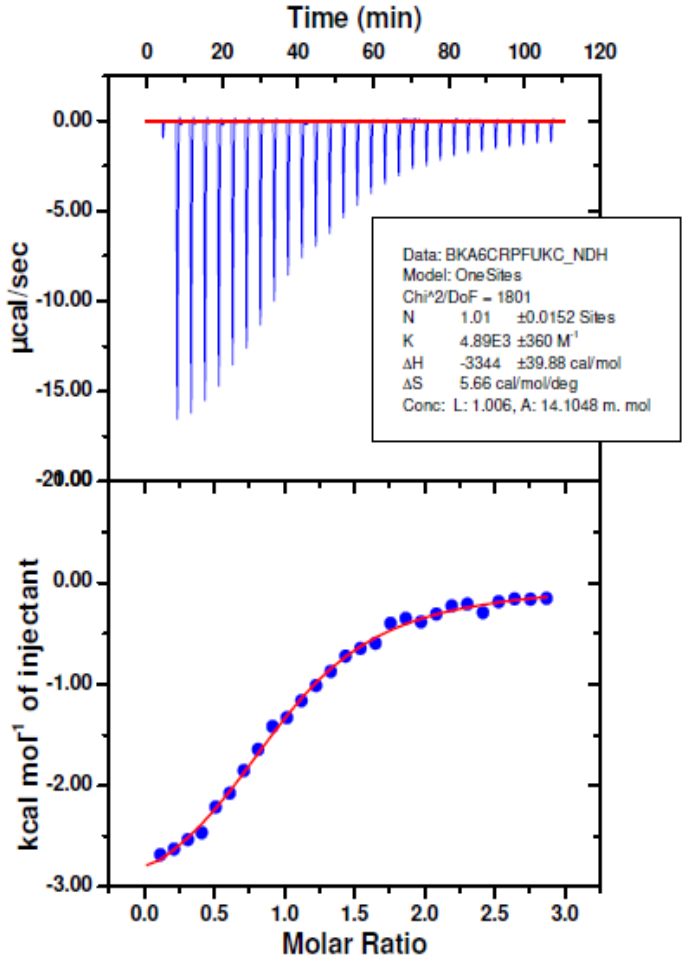
L: 2.1251 mmol; TBA-HSO_4: 12.4878 mmol.

Figure S20 ITC profile of Cl^- (14.1048 mM) binding to host **L** (1.006 mM) in dry CH_3CN at 298 K in absence of K^+.



The upper panel shows the heat pulses experimentally observed in each titration step. The lower panel reports the respective time integrals translating as the heat absorbed for each aliquot and its coherence to a 1:1 binding model.

Figure S21 ITC profile of Cl^- (14.1048 mM) binding to host **L** (1.006 mM) in dry CH_3CN at 298 K in presence of 1 equivalent of K^+.



The upper panel shows the heat pulses experimentally observed in each titration step. The lower panel reports the respective time integrals translating as the heat absorbed for each aliquot and its coherence to a 1:1 binding model.