Electronic Supplementary Information

Encapsulation of discrete cyclic halide water tetramer $[X_2(H_2O)_2]^{2-}$, X=Cl^-/Br^- within dimeric capsular assembly of tripodal amide receptor

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Experimental Section:

^{1}H and ^{13}C NMR spectra were recorded on a Varian FT-400 MHz spectrometer in DMSO−d_6 at 298 K. The IR spectra were recorded on a Perkin-Elmer-Spectrum One FT-IR spectrometer with KBr disks in the range 4000-450 cm^{-1}. All the tetrabutylammonium (TBA) salts used were purchased from Sigma-Aldrich, USA and were used as received. Solvents were purchased from Spectrochem Ltd., India. Chemical shifts for ^{1}H and ^{13}C NMR were reported in parts per million (ppm), calibrated to the residual solvent peak set, with coupling constants reported in Hertz (Hz). The thermal analyses of the polymorphs were performed by using an SDTA 851 e TGA thermal analyzer (*Mettler Toledo*) with a heating rate of $10^{o}C$ per min in a N_2 atmosphere. Elemental analyses were obtained from a Perkin-Elmer Series II Analyzer.

Crystallographic Refinement Details:

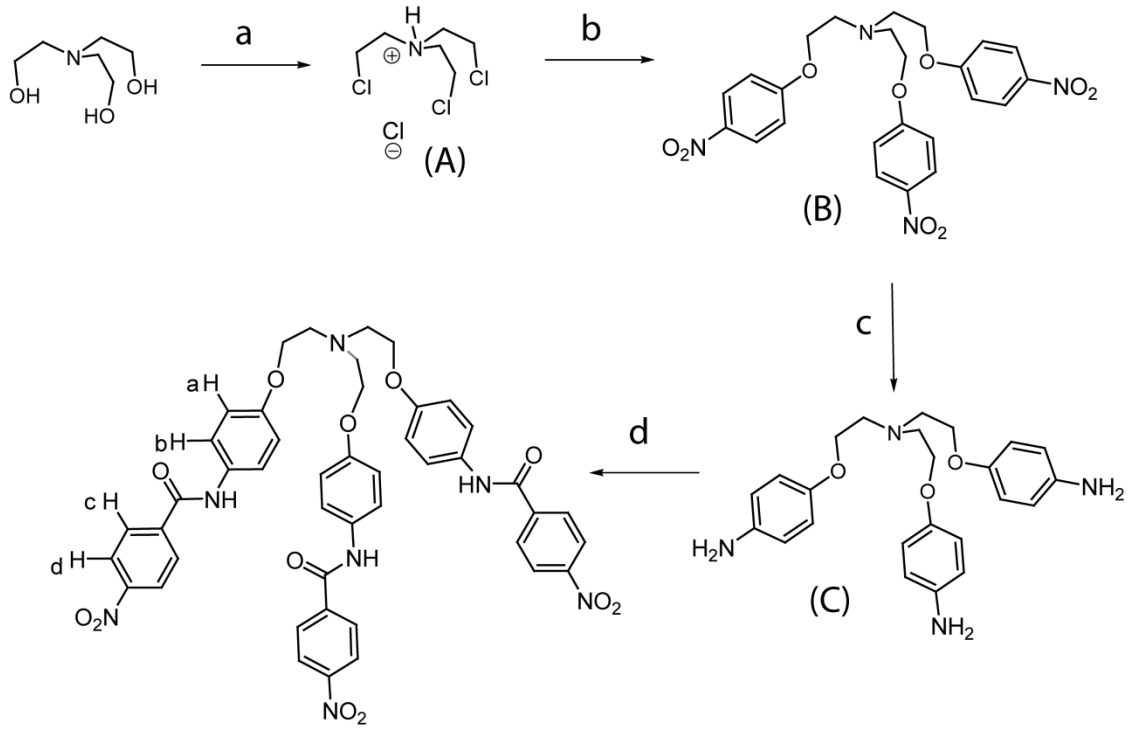
The crystallographic data and details of data collection for complexes **1, 2** and **3** are given in Table S1. In each case, a crystal of suitable size was selected from the mother liquor and immersed in silicone oil, then mounted on the tip of a glass fibre and cemented using epoxy resin. Intensity data for the crystals were collected Mo-Kα radiation (λ = 0.71073Å) at 298(2) K, with increasing ω (width of 0.3° per frame) at a scan speed of 6 s/ frame on a Bruker SMART APEX diffractometer equipped with CCD area detector. The data integration and reduction were processed with SAINT[1] software. An empirical absorption correction was applied to the collected reflections with SADABS.[2] The structures were solved by direct methods using SHELXTL[3] and were refined on F^2 by the full-matrix least-squares technique using the SHELXL-97 program package.[4] Graphics are generated using MERCURY 3.0.[5] In all cases, non-hydrogen atoms are treated anisotropically. Wherever possible, the hydrogen atoms are located on a difference Fourier map and refined. In other cases, the hydrogen atoms are geometrically fixed. PLATON/SQUEEZE[6] was performed to refine the host framework in **3** excluding the disordered solvent electron densities. These calculations amount to 73 electrons per molecule void and may be attributed to two disordered DMSO molecules, further supported by the ^{1}H NMR spectra of complex **3**.It is important to mention that the wR2 value of complex 3 is comparatively higher. The high wR2 value (33%) for complex **3** is due to poor data quality. The situation did not improve even after recrystallization and fresh data collection. However, the reported data is the best possible data set for complexe **3**.

NMR studies

^{1}H NMR titration studies were done to determine the binding constants of L for chloride anion in DMSO-d_6 at room temperature. Initial concentrations were $[ligand]_0$ = 10 mM, and $[anion]_0$ = 100 mM. Each titration was performed by 10–12 measurements at room temperature. The association constant K was calculated by fitting NH signals with a 1 : 1 binding model, using Benesi-Hildebrand (Hanna-Ashbaugh) procedure.[7-9]

The binding constants of the Cl^- with receptor L was calculated by plotting 1/ Δδ(change in chemical shift) against $1/[L]_0$ fits a linear relationship. The ratio for the intercept versus slope gives the association or binding constant (Ka) for the receptor–chloride complex.

Synthetic Scheme



(a) $SOCl_2$ CH_2Cl_2 (b) *(p)*-NO_2-C_6H_4OH, NaOH, EtOH, reflux, (c) Pd/C, N_2H_4,H_2O, EtOH reflux (d) *(p)*-NO_2-C_6H_4COCl, CH_2Cl_2, Et_3N, 3h stirring.

Synthesis of receptor L

Receptor **L** was synthesized from previously reported tris(2-chloroethyl)amine hydrochloride[10] (A) by SN_2 substitution with 4-nitro phenol in EtOH (Yield 65%) followed by reduction of nitro group yield corresponding triamine (C) (Yield 72%).[11] Subsequently, triamine (C) solution in CH_2Cl_2 was slowly added to a mixture of three equivalents of 4-nitrobenzoyl chloride in presence of triethylamine in dry CH_2Cl_2 and stirred for 3 hrs. The reaction mixture is filtered and the precipitate is washed with water and methanol to remove the triethylammonium chloride and dried under vacuum to yield the pale yellow solid of **L** (Yield = 83%).

L : MP :203-205 °C, ^{1}H NMR (400 MHz, DMSO−d_6) δ (ppm): 10.44(s, 3N–H), 8.32(*J* = 8 Hz d, 6H,), 8.15(*J* = 7.2 Hz d, 6H), 7.65(*J* = 7.6 Hzd, 6H), 6.93(*J* = 7.6 Hzd, 6H), 4.07(s(br), 6H) and 3.06(s(br), 6H) ^{13}C NMR (100 MHz, DMSO−d_6) δ (ppm): 163.64, 155.43, 149.27, 140.94, 132.04, 129.35, 123.74, 122.38, 114.78, 67.03 and 53.99. IR (KBr, cm^{-1}): 3326(N–H), 1345 (NO_2) and 1647(C=0) ESI mass spectrometry: calcd for 870 [M + H^+]; found 870 [M + H^+].

Chloride complex $[(LH)^+.Cl^-].H_2O$ (1) : chloride complex of the receptor was obtained by adding 0.5 mL of 37% hydrochloric acid (HCl) to a 5 mL dimethylformamide solution of **L** (200 mg, 0.23 mmol). After the addition of HCl, the solution was stirred for about 1 hr and was allowed to slowly evaporate at room temperature, which yielded yellow block shaped crystals suitable for XRD analysis within a week.

$[(LH)^+.Cl^-].H_2O$ (1): Yield = 65%, MP:186-188°C, Calc. for $C_{45}H_{42}ClN_7O_{13}$: C, 58.47; H, 4.58; N, 10.61; Found: C: 58.83, H: 4.74 N: 10.27, ^{1}H NMR (400 MHz, DMSO−d_6) δ (ppm): 10.54(s, 3N–H), 8.33(*J* = 7.2 Hz d, 6H), 8.17(*J* = 7.2 Hz d, 6H), 7.71(*J* = 8 Hz d, 6H), 7.00(*J* = 8 Hz d, 6H), 4.47(s(br), 6H) and 3.80(s(br), 6H) IR (KBr, cm^{-1}): 3383(N–H), 3274(O–H), 1345(NO_2) and 1670(C=0).

$[(LH)^+.Br^-].H_2O$ (2): Yield = 58%, MP:136-138°C, Calc.for $C_{45}H_{42}BrN_7O_{13}$: C, 55.79; H, 4.37; N, 10.12; Found: C: 55.95, H: 4.82 N: 9.94, ^{1}H NMR (400 MHz, DMSO−d_6) δ (ppm): 10.50(s, 3N–H), 8.34(*J* = 8.4 Hz d, 6H), 8.16(*J* = 8 Hz d, 6H), 7.72(*J* = 8.4 Hz d, 6H), 7.01(*J* = 8.8 Hz d, 6H), 4.45(s(br), 6H) and 3.82(s(br), 6H) IR (KBr, cm^{-1}): 3386(N–H), 3277(O–H), 1347(NO_2) and 1670(C=0).

[(LH)$^{+}$.I^{-}] (3): Yield = 56%, MP:165-166°C ^{1}H NMR (400 MHz, DMSO−d_6) δ (ppm): 10.48(s, 3N–H), 8.34(*J* = 7.6 Hz d, 6H), 8.15(*J* = 7.6 Hz d, 6H), 7.70(*J* = 7.2 Hz d, 6H), 7.00(*J* = 7.6 Hz d, 6H), 4.43(s(br), 6H),3.81(s(br), 6H) and 2.54 (DMSO solvent) IR (KBr, cm^{-1}): 3435(N–H), 3290(O–H), 1345(NO_2) and 1670(C=0).

Perchlorate complex[(LH)$^{+}$.(ClO_4)$^{-}$](4) : Perchlorate complex was obtained by adding 0.5 mL of 49% perchloric acid ($HClO_4$) to a 15 mL MeOH suspension of L (250 mg,). After the addition of acid, the suspension was stirred for about 3 hours at room temperature. The resulting solution was filtered and the residue was collected and dried in vacuum.

[(LH)$^{+}$.(ClO_4)$^{-}$](4): Yield = 88%, MP: 148-150°C,^{1}H NMR (400 MHz, DMSO−d_6) δ (ppm): 10.49(s, 3N–H), 8.35(*J* = 8 Hz d, 6H), 8.15(*J* = 7.6 Hz d, 6H), 7.70(*J* = 8 Hz d, 6H), 7.00(*J* = 8 Hz d, 6H), 4.44(s(br), 6H) and 3.82(s(br), 6H) IR (KBr, cm^{-1}): 3387(N–H), 1671(C=0).1345(NO_2) and 1100(ClO_4).

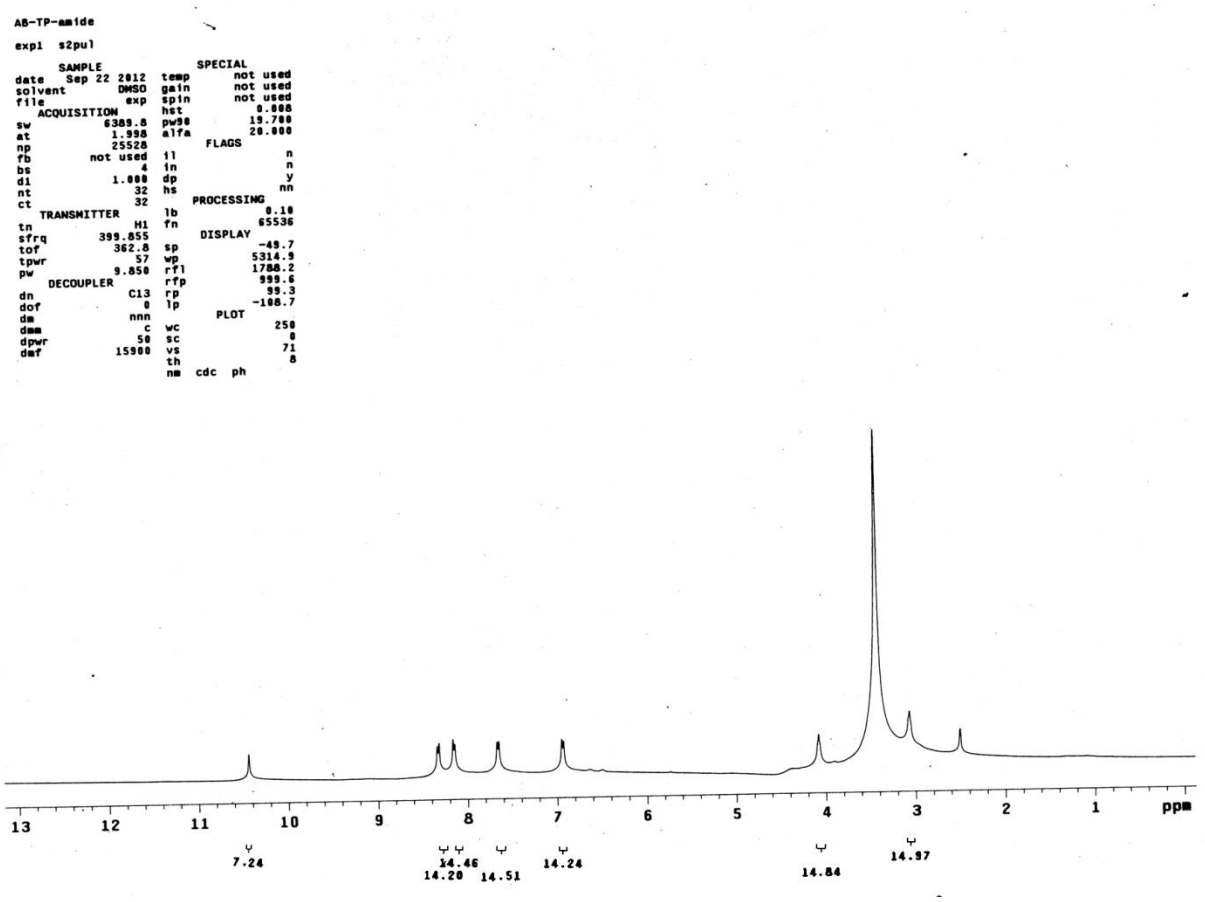


Fig.S1 ^{1}H NMR spectrum of **L** in DMSO-d_6 at 298 K.

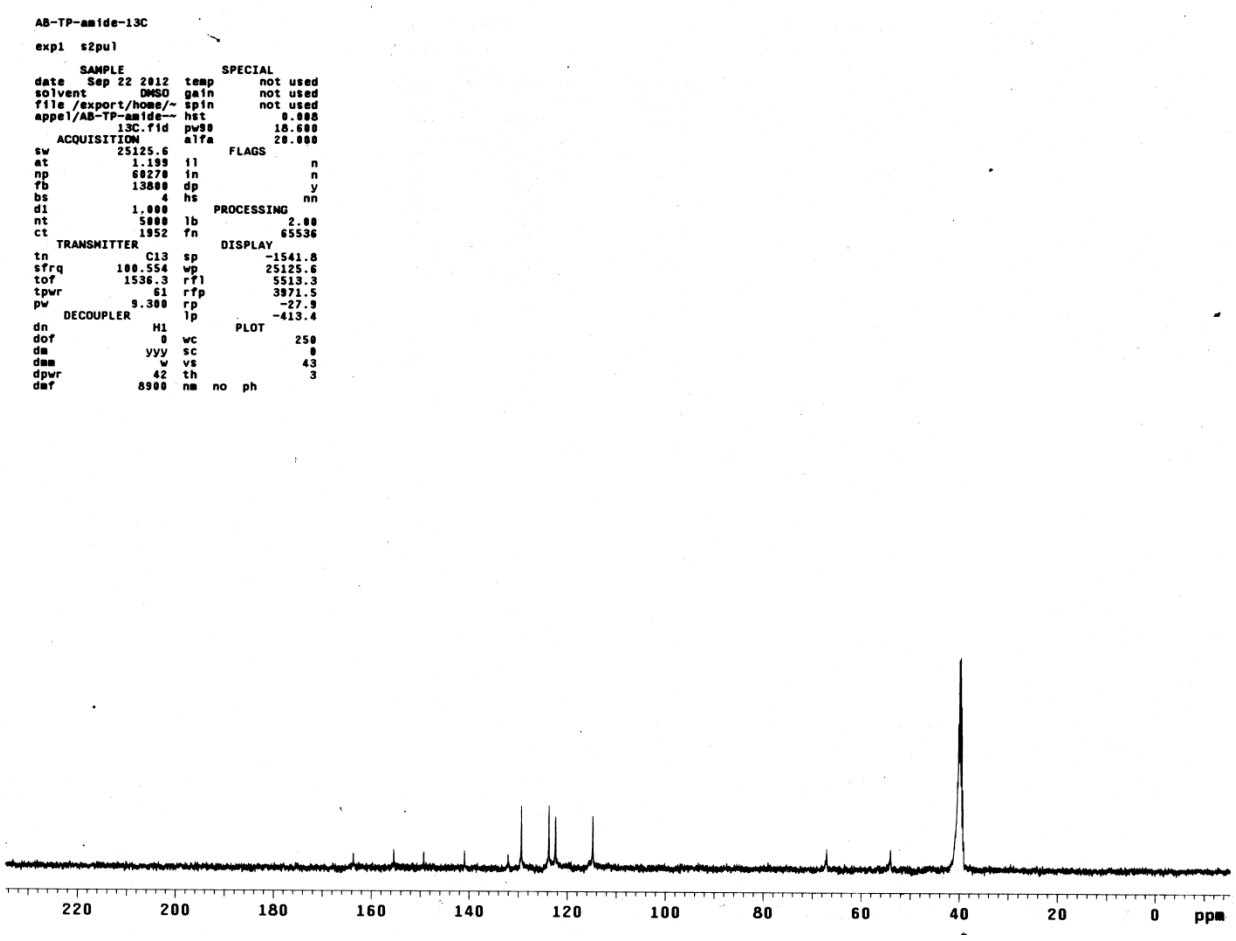


Fig. S2 ^{13}**C** NMR spectrum of **L** in DMSO-d_6 at 298 K.

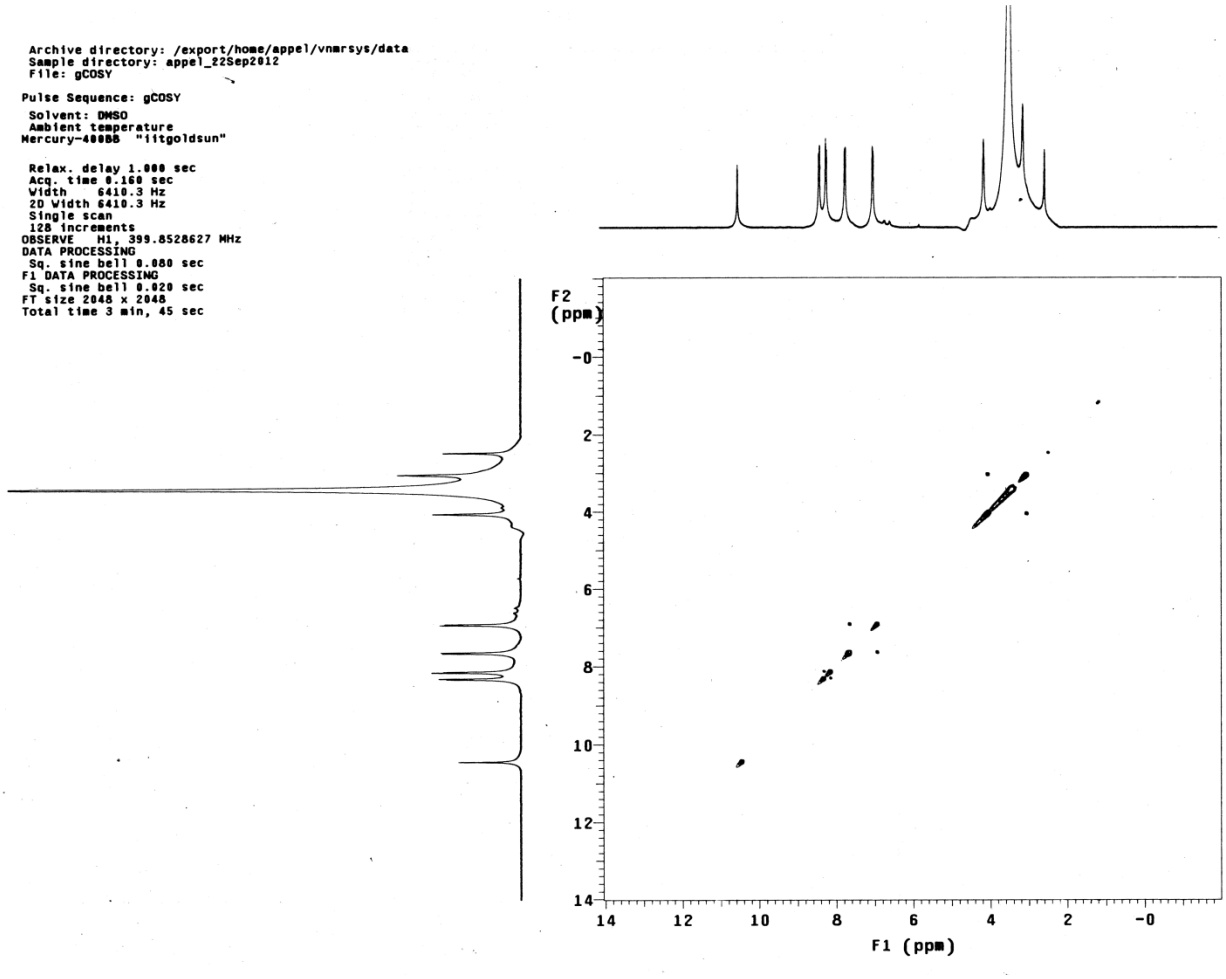


Fig.S3 COSY spectra of **L** in DMSO-d_6 at 298 K

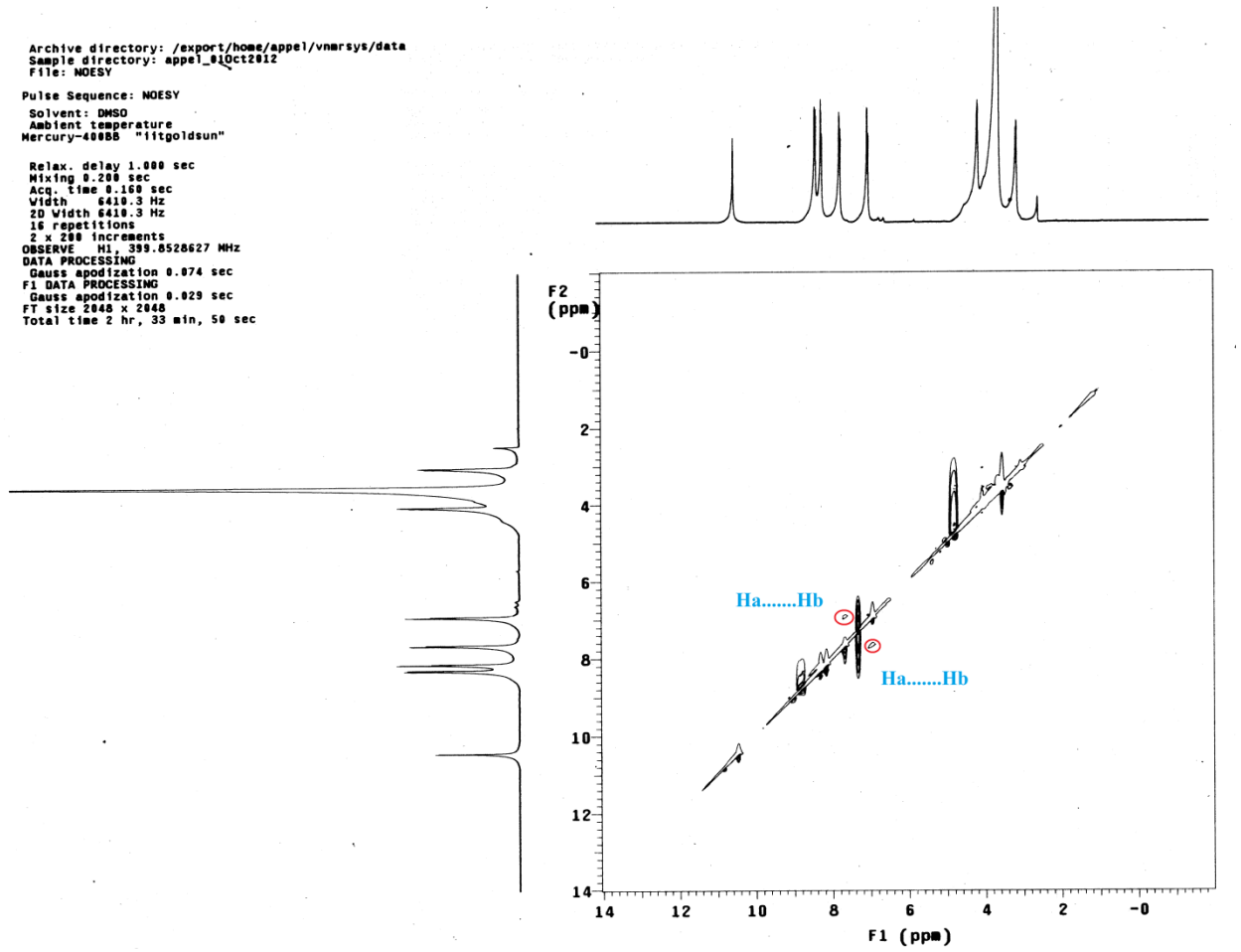


Fig.S4 NOESY spectra of **L** in DMSO-d_6 at 298 K

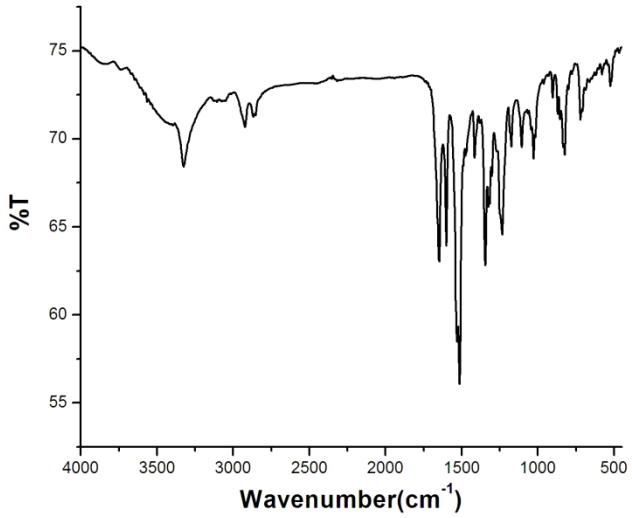


Fig.S5 FTIR spectrum of receptor **L.**

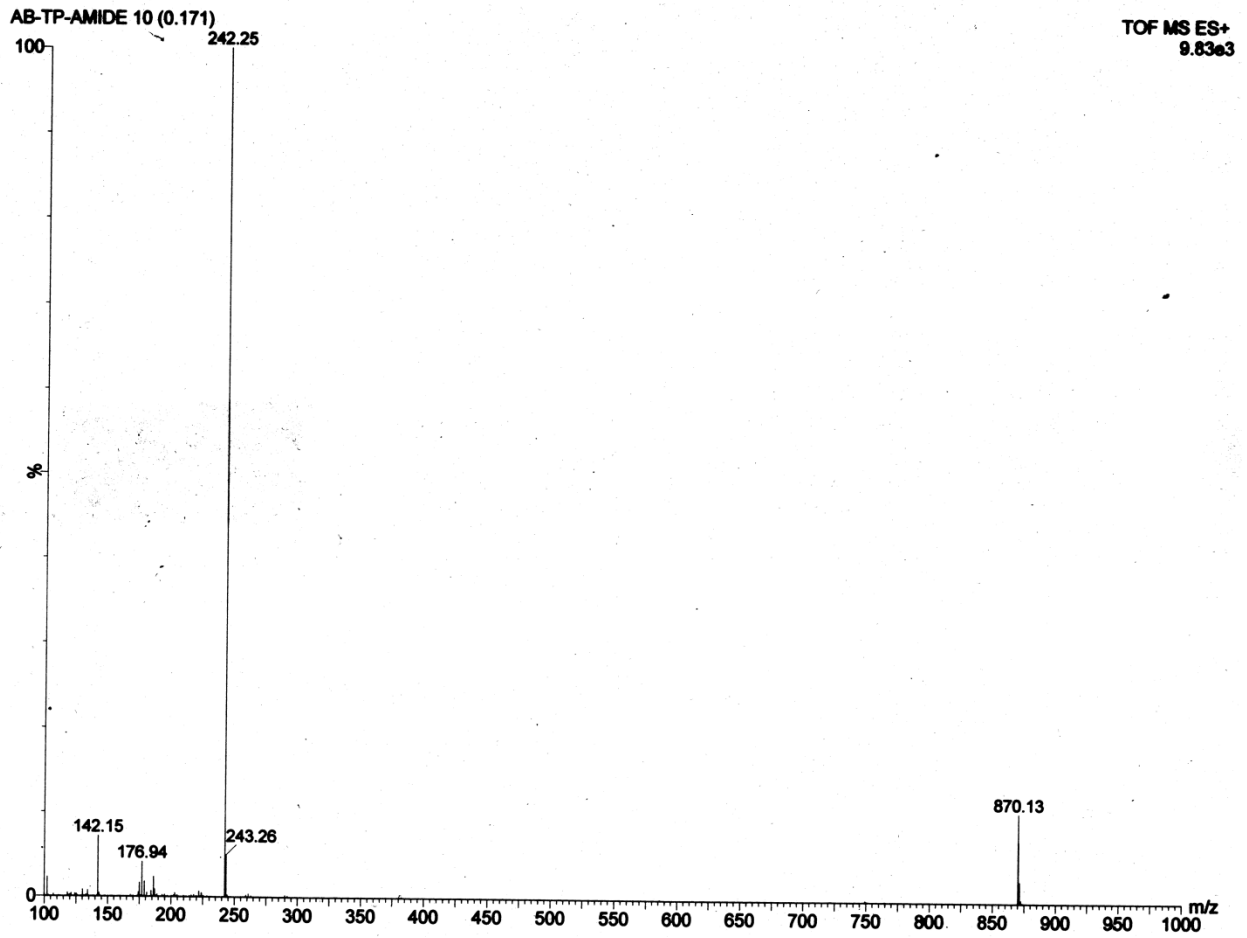


Fig.S6 ESI-Mass spectrum of receptor **L** in CH_3CN/ DMSO mixture.

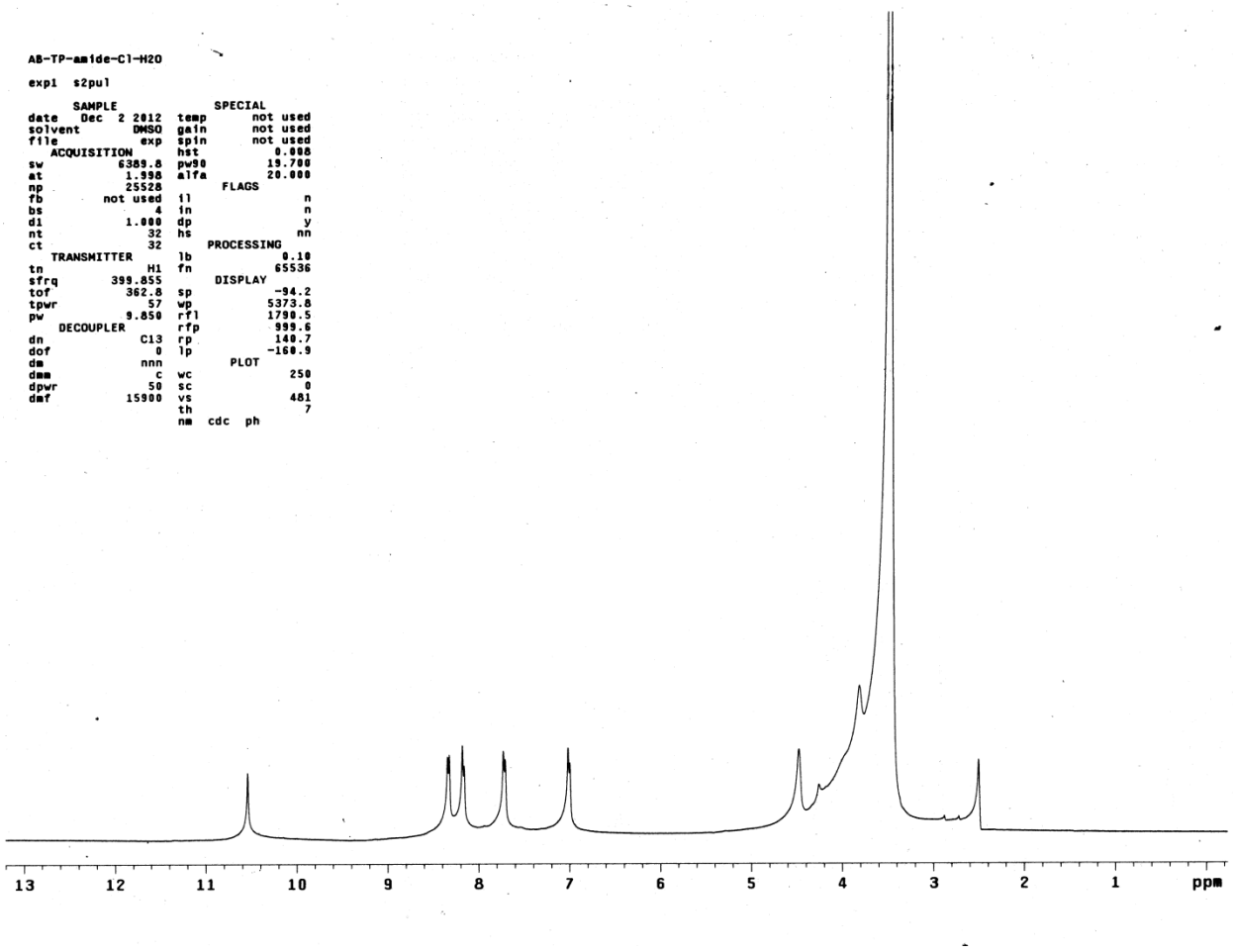


Fig.S7 ^{1}H NMR spectrum of complex **1** in DMSO-d_6 at 298 K.

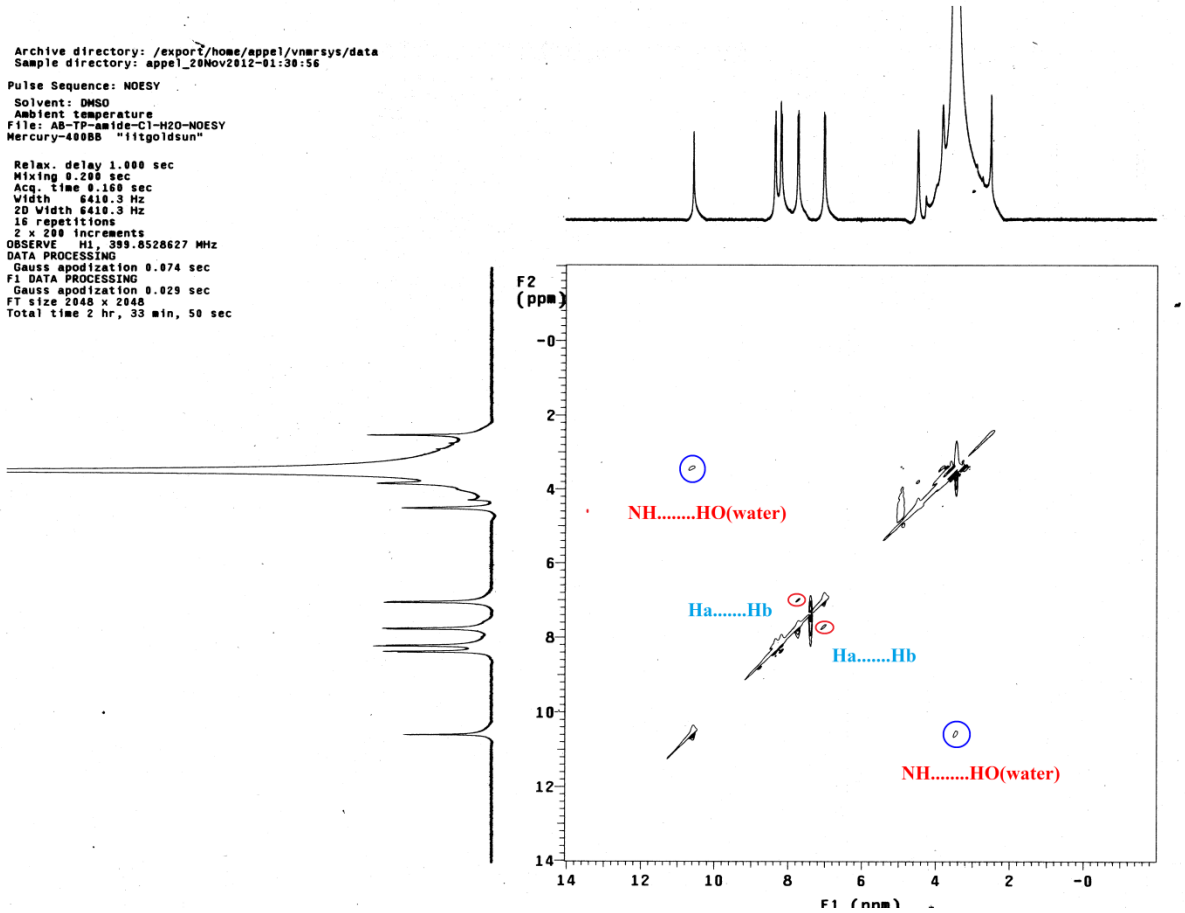


Fig.S8 NOESY spectra of complex **1** in DMSO-d*6* at 298 K

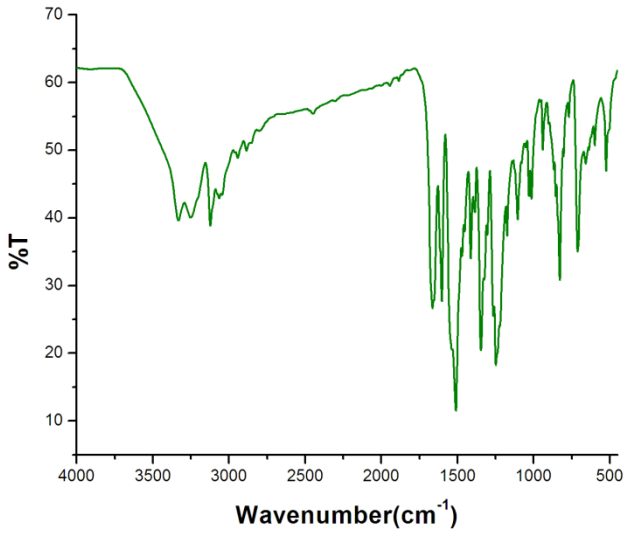


Fig. S9 FTIR spectrum of complex **1.**

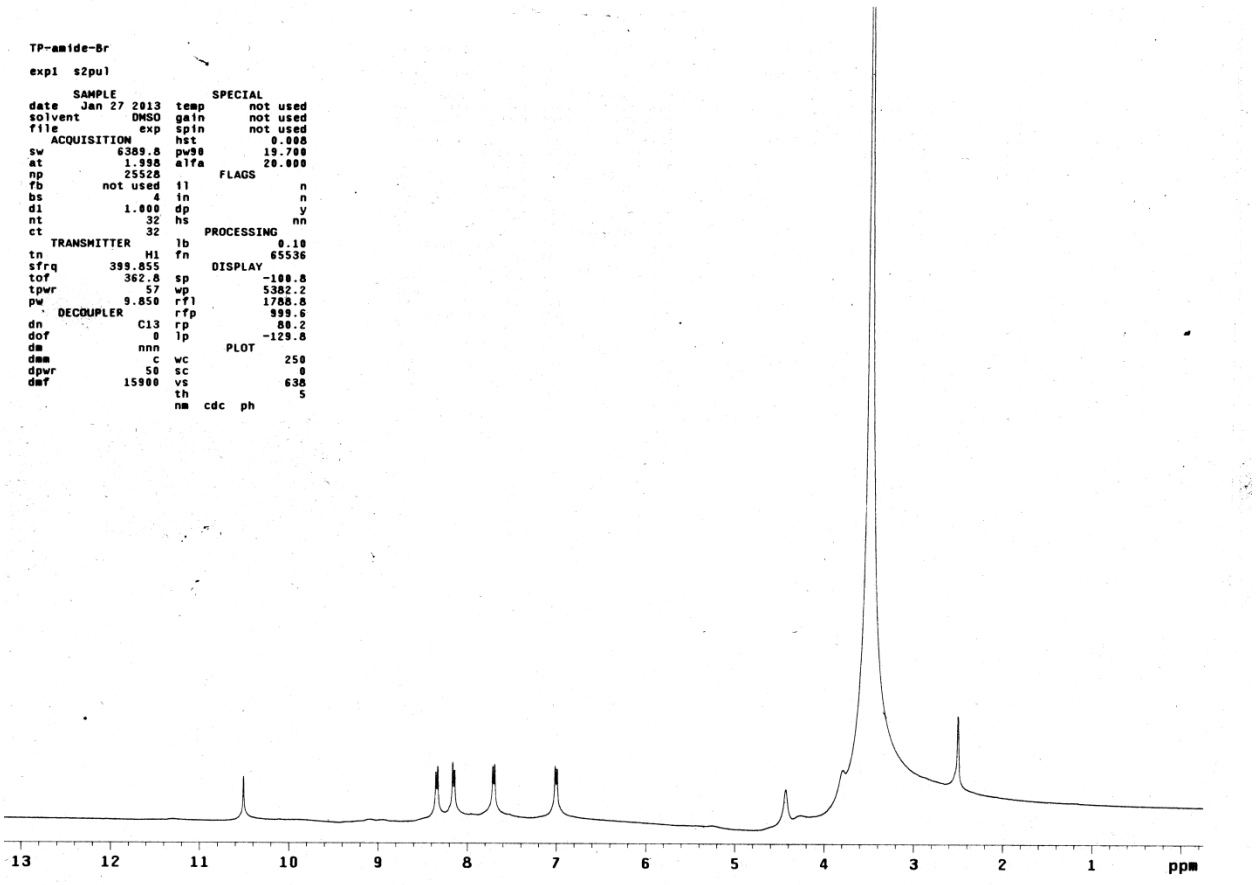


Fig. S10 ^{1}H NMR spectrum of complex **2** in DMSO-d_6 at 298 K.

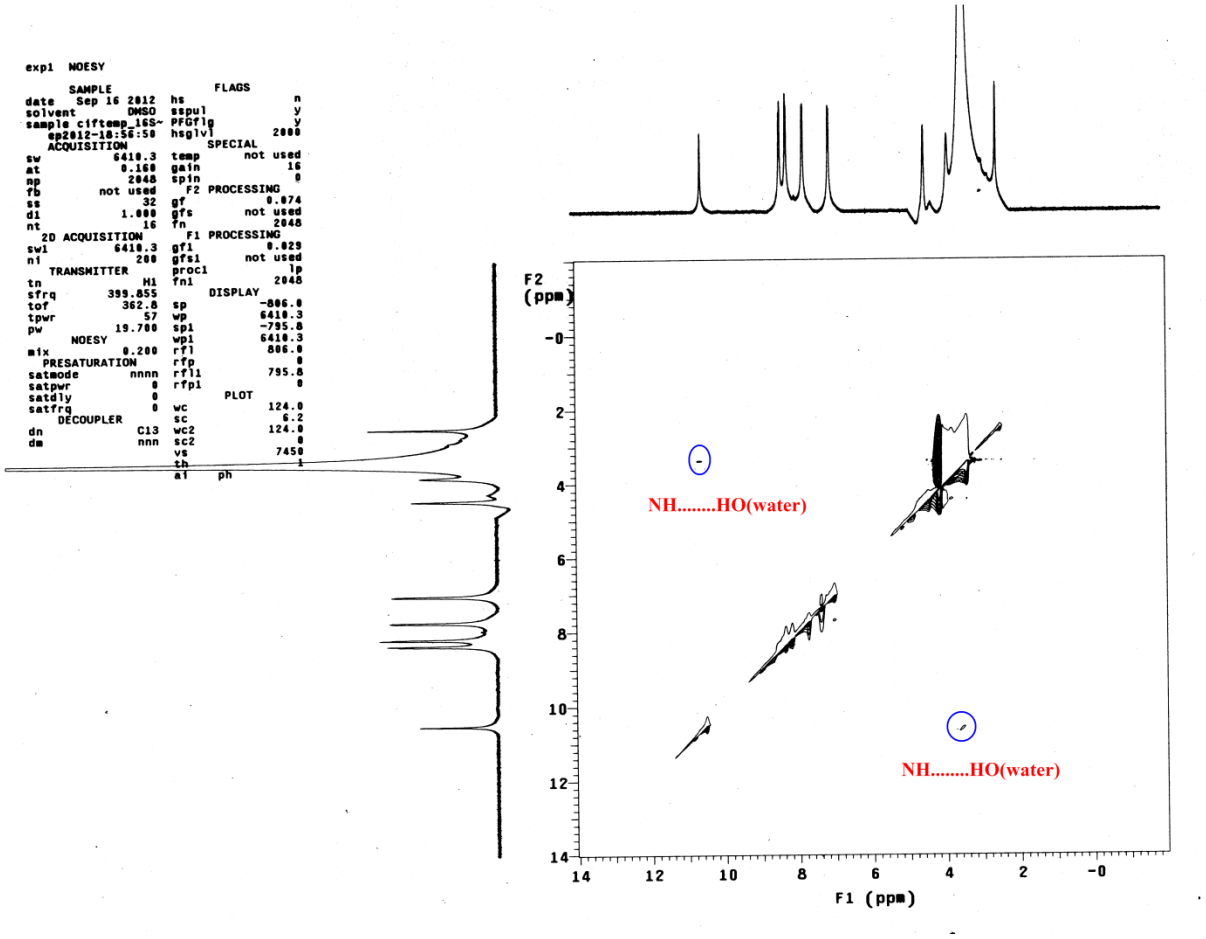


Fig. S11 NOESY spectrum of complex **2**in DMSO-d_6 at 298 K

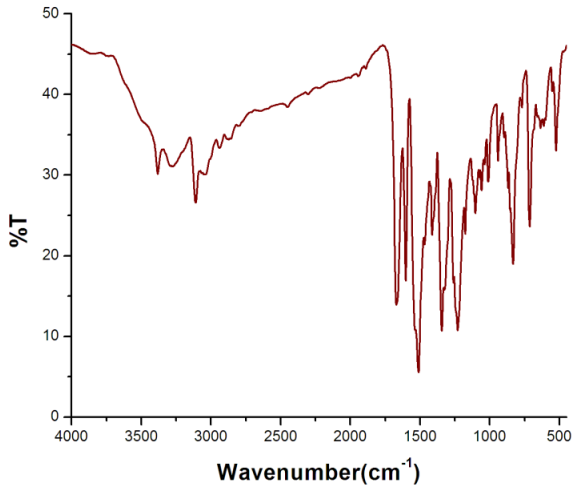


Fig. S12 FTIR spectrum of complex **2.**

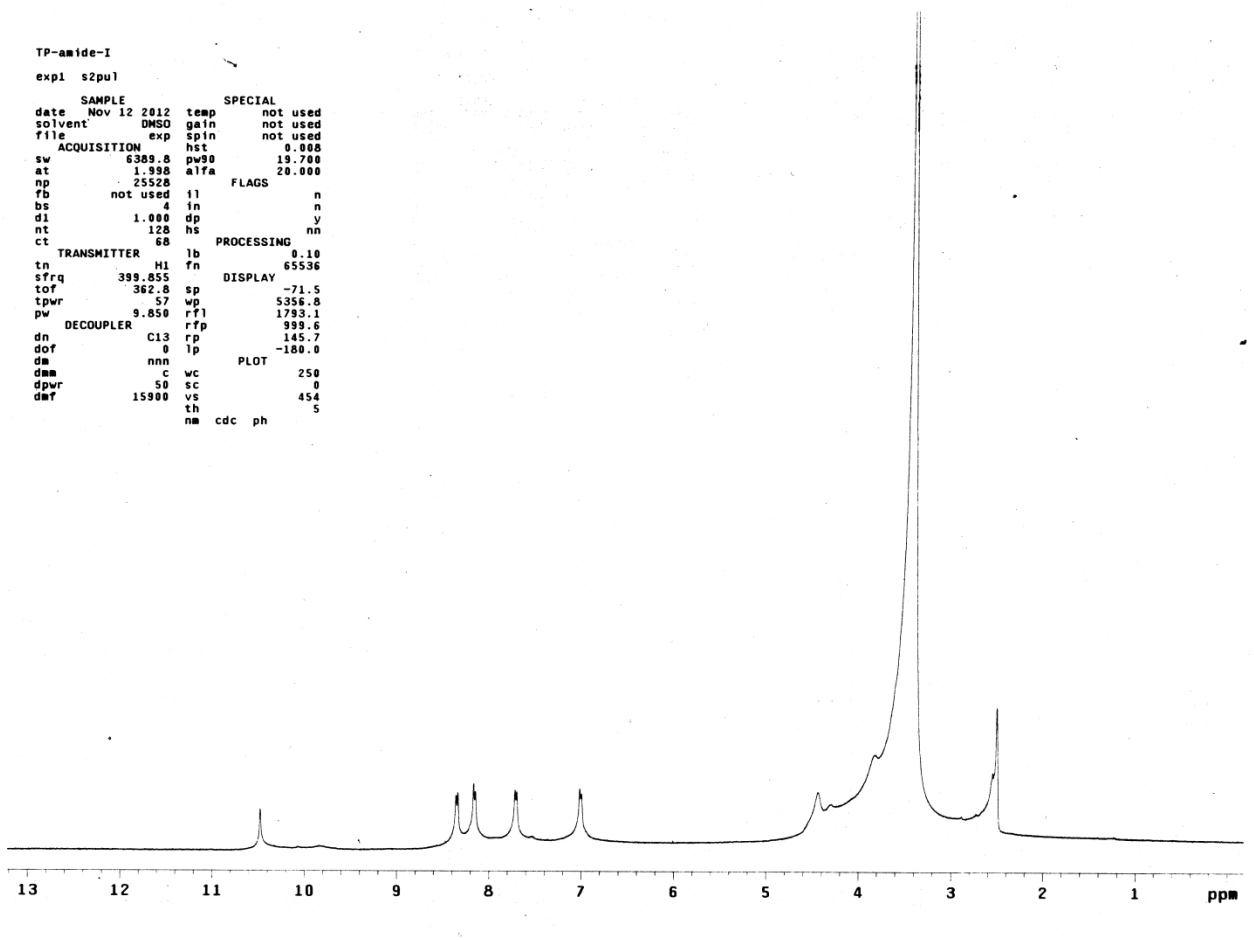


Fig. S13 ^{1}H NMR spectrum of complex **3** in DMSO-d$_6$ at 298 K.

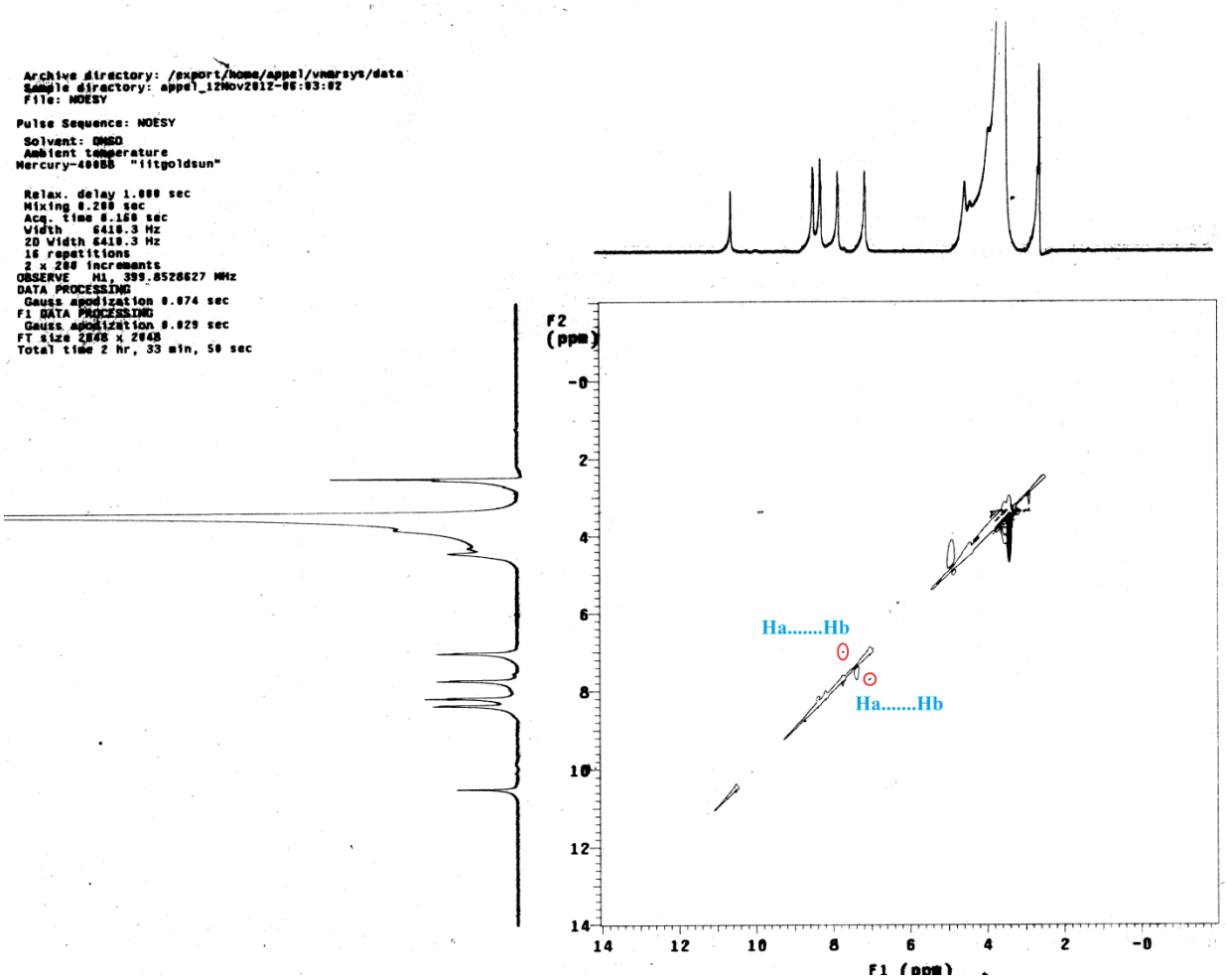


Fig. S14 NOESY spectra of complex **3** in DMSO-d_6 at 298 K.

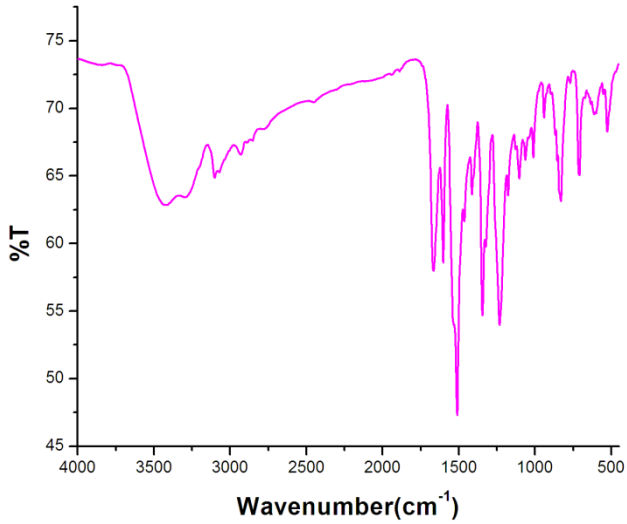


Fig. S15 FTIR spectrum of complex **3**

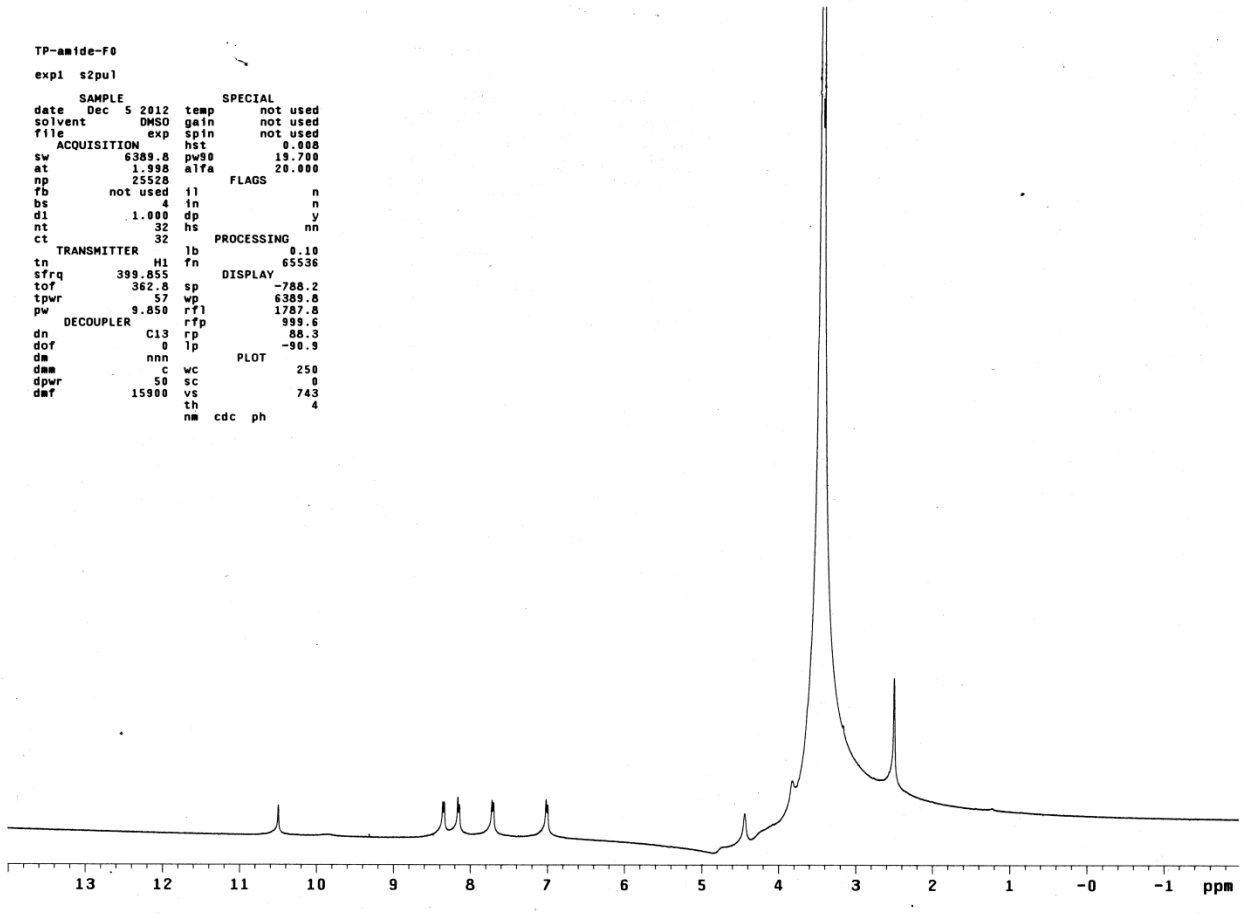


Fig. S16 ^{1}H NMR spectrum of **[(LH)$^{+}$.(ClO$_4$)$^{-}$]**(complex **4**) in DMSO-d$_6$ at 298 K.

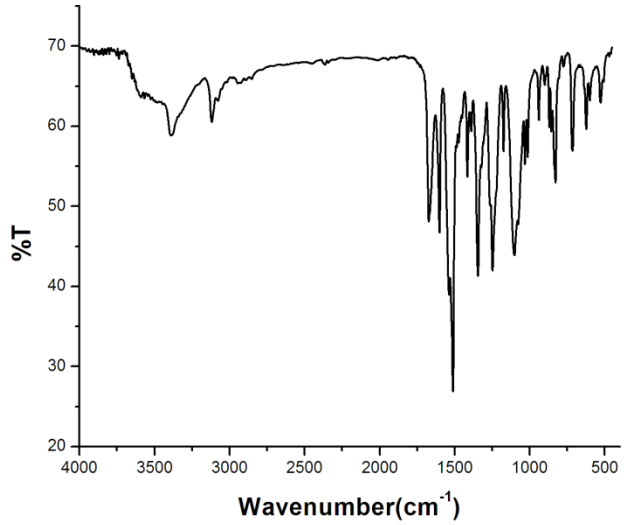


Fig. S17 FTIR spectrum of complex **4**

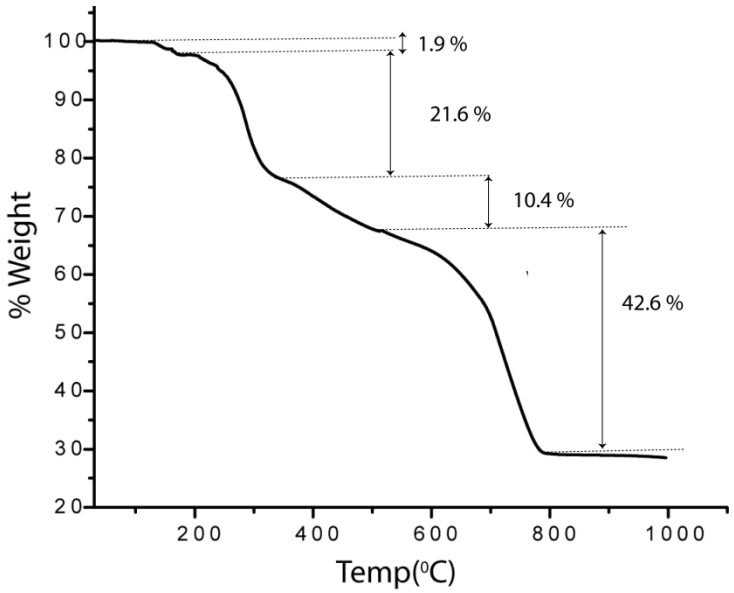


Fig.S18 Thermogravimetric analysis (TGA) curve of complex **1** at a heating rate of 10°C per min.

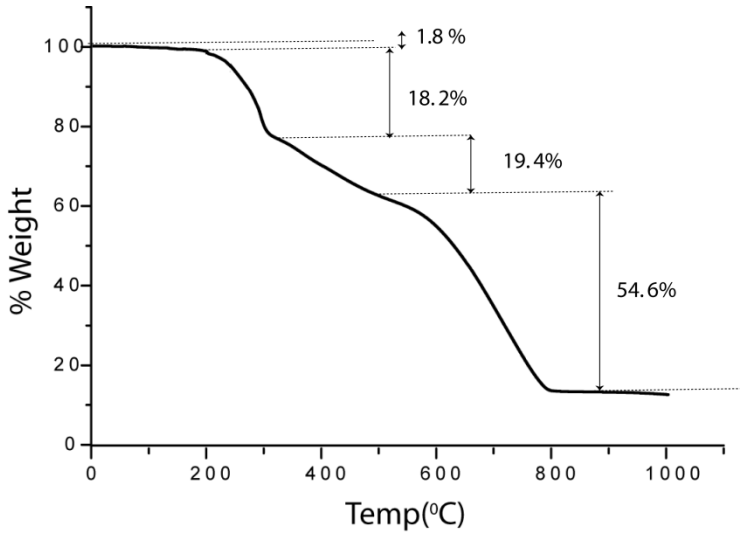


Fig.S19 Thermogravimetric analysis (TGA) curve of complex **2** at a heating rate of 10°C per min

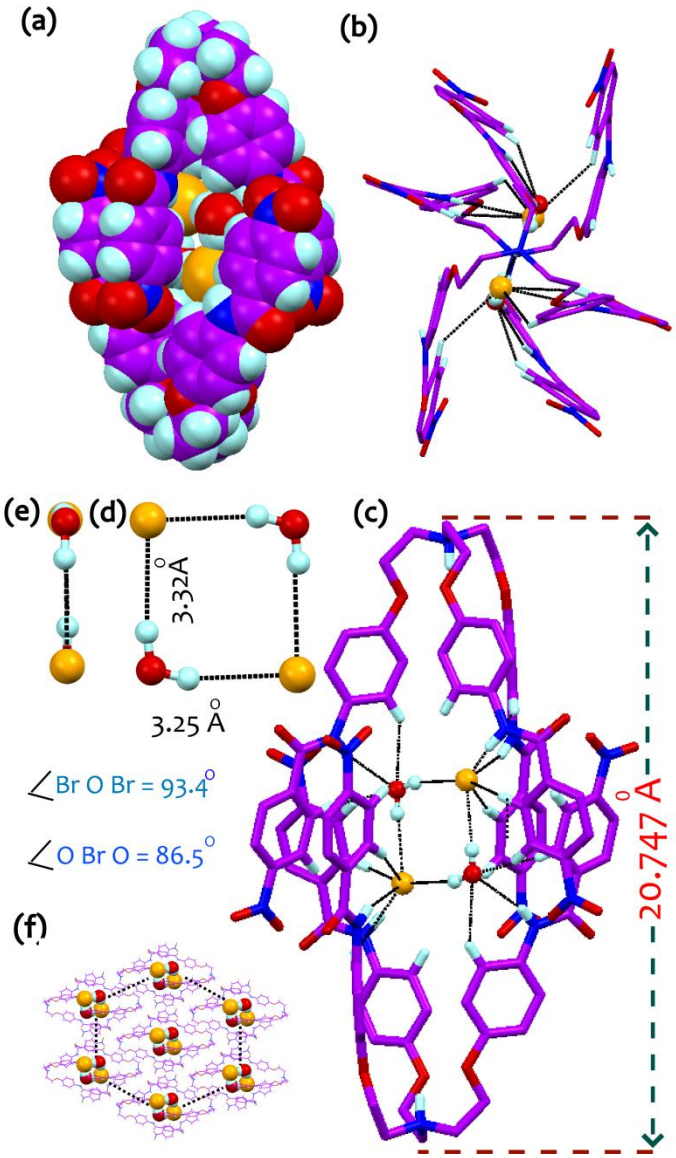


Fig.S20 (a) Space-filling representation depicting full encapsulation of the $[Br_2(H_2O)_2]^{2-}$ cluster inside the dimeric capsule-like assembly of protonated receptor **L**. (b) $[Br_2(H_2O)_2]^{2-}$ cluster encapsulation by the crystalline self-assembled capsule $\mathbf{LH^+}$, Two molecules of $\mathbf{LH^+}$, shown as stick models, and $[Br_2(H_2O)_2]^{2-}$ cluster is shown as a ball and stick model. (c) Showing the hydrogen bonding interactions of $[Br_2(H_2O)_2]^{2-}$ cluster with two $\mathbf{LH^+}$ unit. (d) Planer bromide water tetramer within crystalline self-assembled capsule $\mathbf{LH^+}$ (e) Side view showing the perfect planer nature of $[Br_2(H_2O)_2]^{2-}$.(f) Crystal packing of complex $\mathbf{[(LH)^+.Br^-].H_2O}$, as viewed down the crystallographic '*a*' axis.

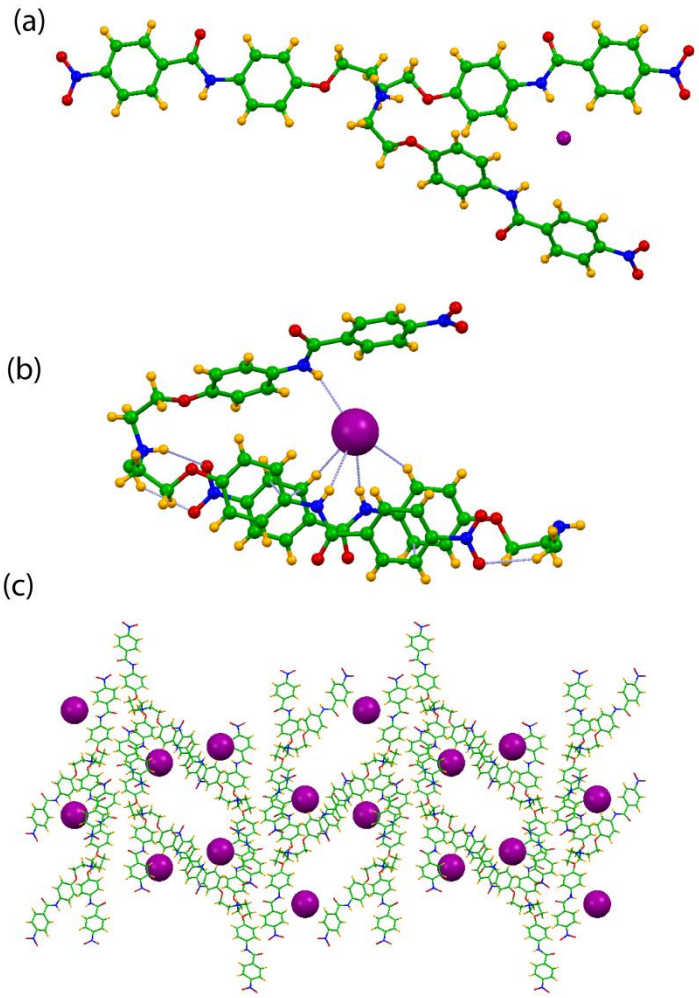


Fig.S21 (a) Ball and stick representation of molecular structure **[(LH)$^{+}$.I^{-}](3)**.(b) Hydrogen-bonding interactions of Iodide anions with **LH+** in complex **3**. (c) Crystal packing of complex **3**, as viewed down the crystallographic '*a*' axis.

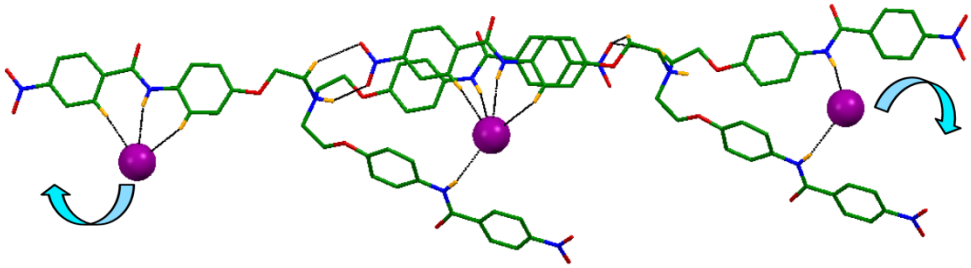


Fig. S22 Showing formation of polymeric aggregation upon iodide coordination.

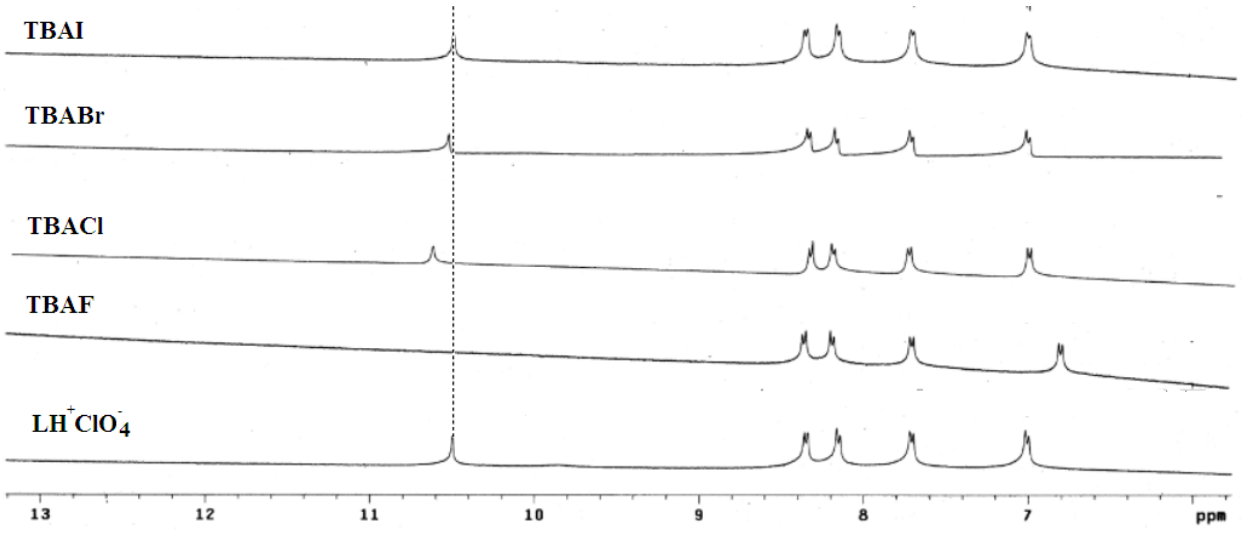


Fig. S23 ^{1}H NMR spectra (400 MHz, DMSO-d_6, 298 K) of complex **4** and change of amide NH resonance upon addition 10 equivalent of F^-, Cl^-, Br^-, and I^- as their tetrabutylammonium salts.

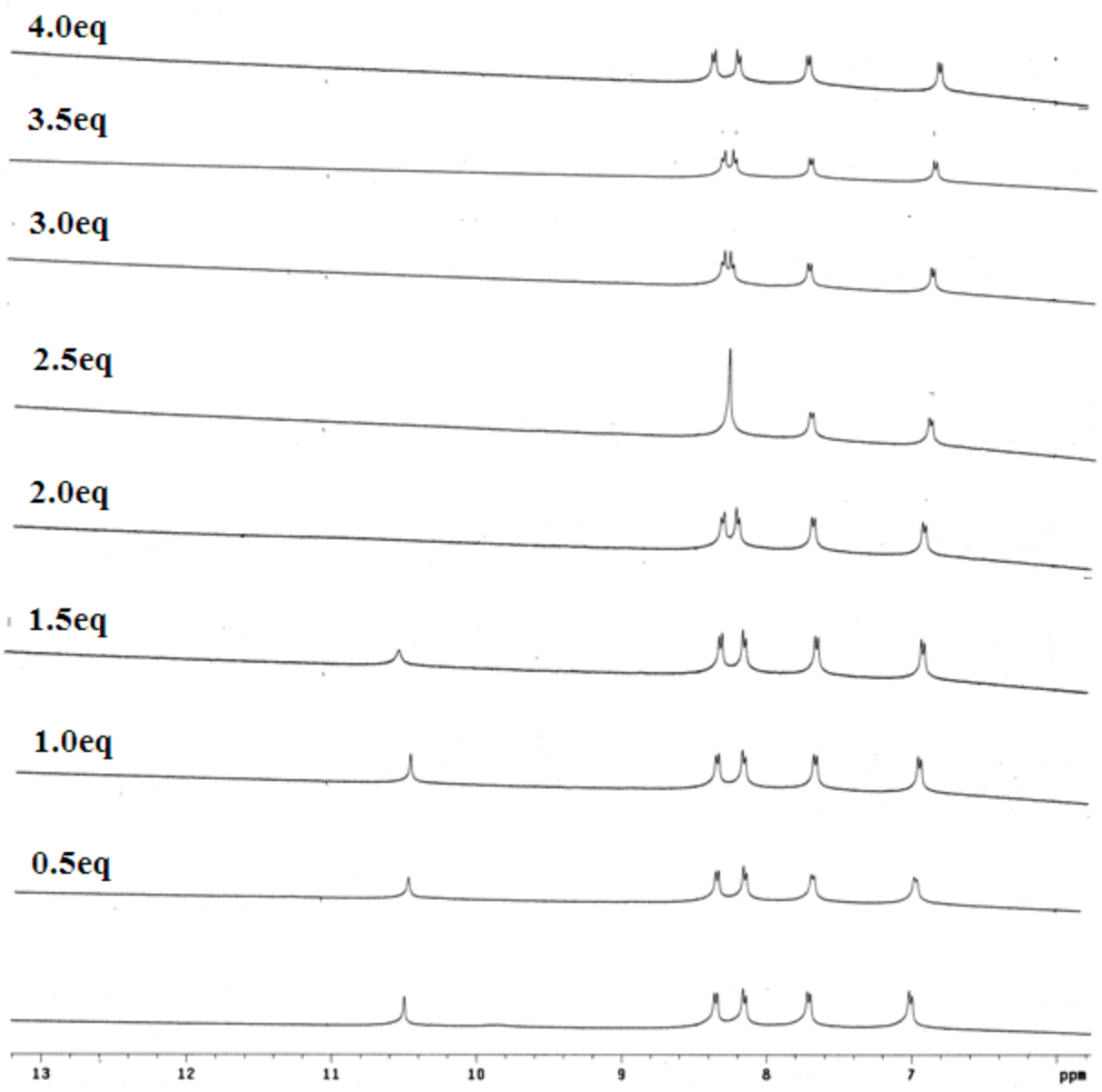


Fig.S24 Stack plot of the ^{1}H NMR spectra of perchlorate salt of receptor **L**(complex **4**) in the presence of increasing amounts of [*n*-Bu_4N^+]F^- recorded in DMSO-d_6 at 298 K.

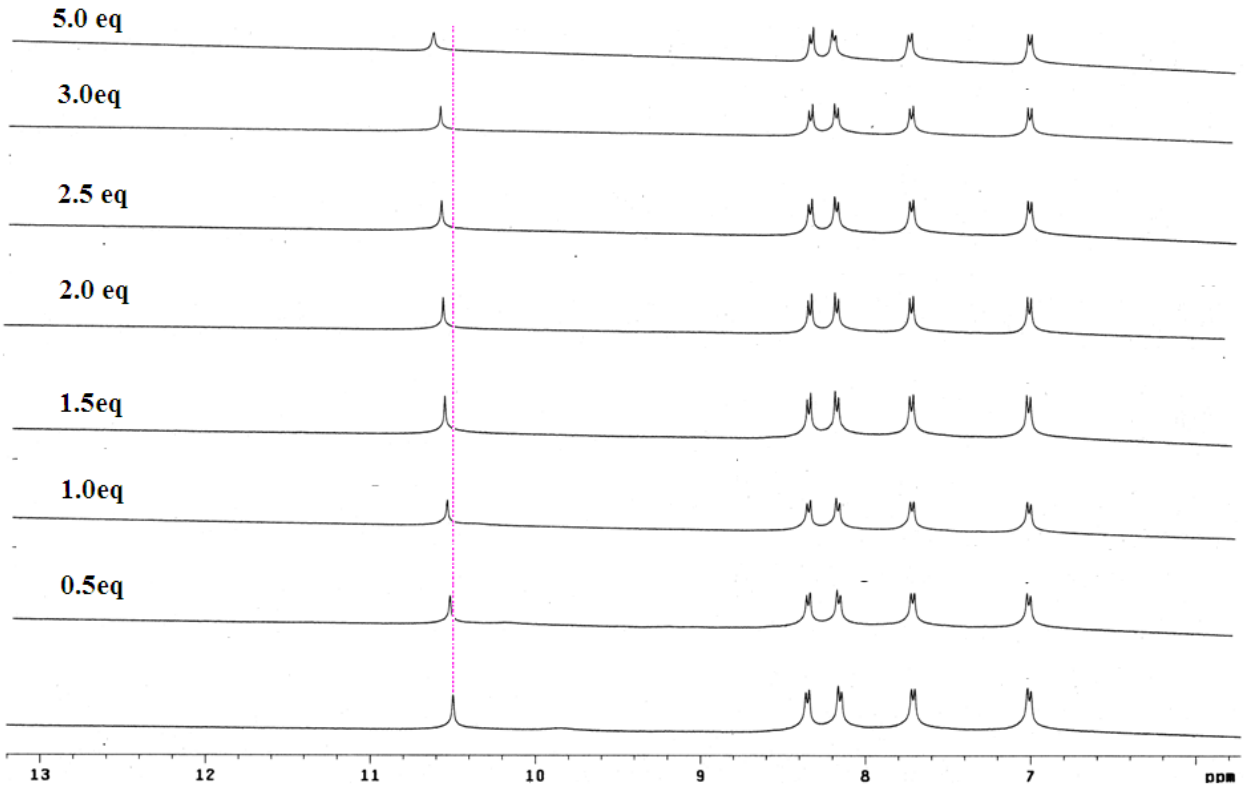


Fig.S25 Stack plot of the ^{1}H NMR spectra of perchlorate salt of receptor **L** in the presence of increasing amounts of [*n*-Bu_4N^+]Cl^- recorded in DMSO-d_6 at 298 K.

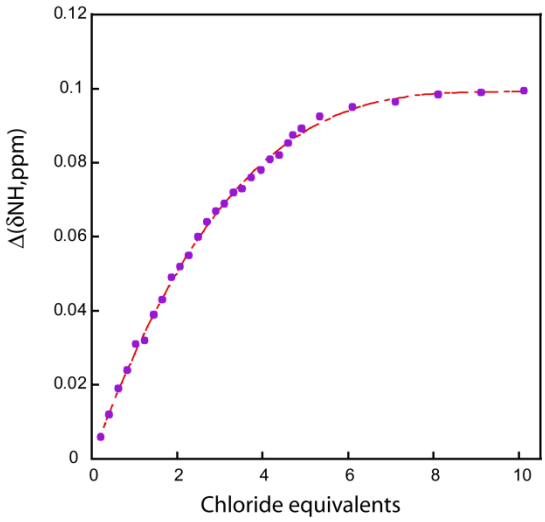


Fig. S26 ^{1}H NMR titration curves of $LH^+.ClO_4^-$ with Cl^- in DMSO-d_6 at RT. Net changes in the chemical shifts of amidic –NH is shown against the increasing amount of chloride anion.

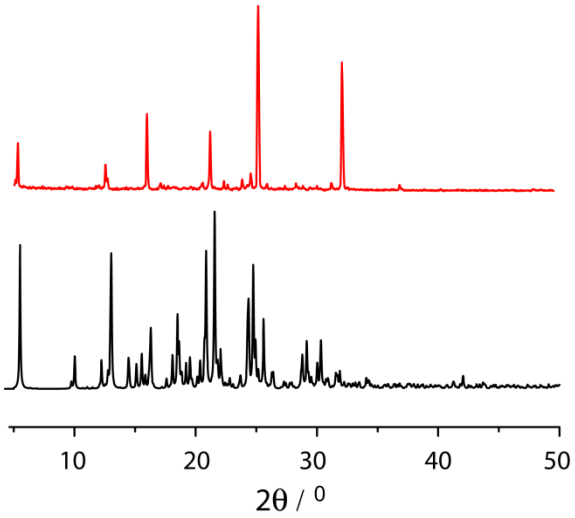


Fig. S27 Powder X-ray diffraction: simulated pattern from the single−crystal X-ray of complex **1** (black), experimental pattern from the crystalline solid of complex **1** (red),

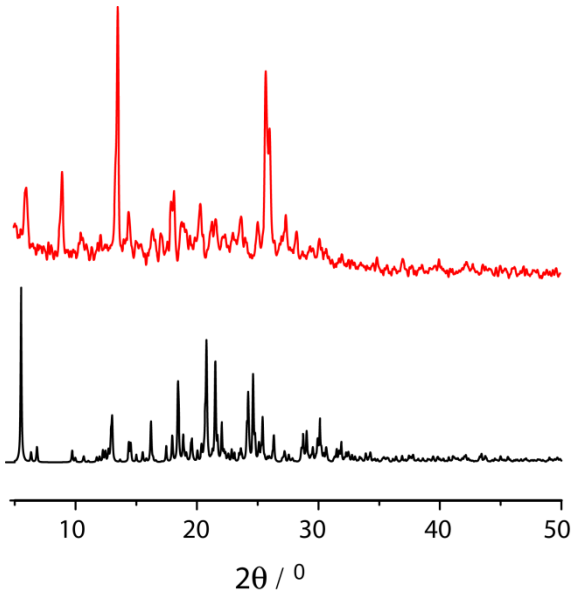


Fig. S28 Powder X-ray diffraction: simulated pattern from the single−crystal X-ray of complex **2** (black), experimental pattern from the crystalline solid of complex **2** (red),

Table S1. Crystal Parameters and Refinement Data

Compound	**Chloride-complex(1)**	**Bromide-complex(2)**	**Iodide-complex(3)**
formula	$C_{45}H_{42}ClN_7O_{13}$	$C_{45}H_{42}BrN_7O_{13}$	$C_{45}H_{40}IN_7O_{12}$
formula weight	924.31	968.76	997.74
crystal system	Triclinic	Triclinic	Monoclinic
space group	P-1	P-1	P 21/c
a (Å)	9.3971(5)	9.4231(11)	8.0650(5)
b (Å)	14.8204(7)	14.9240(12)	41.706(2)
c (Å)	17.5829(9)	17.6464(15)	15.0999(8)
α (deg)	69.237(3)	68.839(8)	90.00
β (deg)	75.363(3)	74.960(9)	97.283(6)
γ (deg)	83.377(3)	83.360(8)	90.00
V (Å)	2214.51(19)	2234.3(4)	5038.0(5)
Z	2	2	4
T (K)	298(2)	298(2)	298(2)
μ (cm^{-1})	0.161	0.992	0.699
dcal (g cm^{-3})	1.386	1.440	1.315
cryst dimens (mm^3)	0.28x0.25x0.22	0.31x0.27x0.24	0.26x0.24x0.21
no. of reflns collected	10812	11412	12947
no. of unique reflns	4793	4794	6479
no. of params	614	614	587
R1; wR2 ($I > 2\sigma(I)$)	0.0568, 0.1436	0.0830, 0.2079	0.1001, 0.2983
R(int)	0.0415	0.0770	0.0532
GOF (F^2)	0.861	0.988	1.120
CCDC NO.	922581	922582	922583

Table S2. Hydrogen bonding distances (Å) and Bond angles (º) in the complexes (**1-3**).

D—H····A	**H····A(Å)**	**D····A(Å)**	**<D−H….A(°)**
[$(LH)^+$.Cl^-]. H_2O(1)			
N6H····Cl1	2.51	3.330(3)	162.9(3)
C11H···· Cl1	2.76	3.544(4)	147.2(2)
C35H···· Cl1	2.88	3.567(3)	131.7(2)
C41H···· Cl1	2.81	3.684(3)	155.8(2)
O13HA···· Cl1	2.30	3.127(2)	162.3(1)
O13HB···· Cl1	2.32	3.177(2)	174.9(1)
C20H····O13	2.57	3.374(3)	145.0(2)
N4H····O13	2.07	2.92(1)	160.7(3)
C26H····O13	2.40	3.252(4)	152.2(2)
C12H····O13	2.71	3.551(4)	150.1(2)
[$(LH)^+$.Br^-]. H_2O (2)			
N6H····Br1	2.66	3.481(4)	159.9(3)
C11H···· Br1	2.76	3.638(7)	143.2(4)
C35H····Br1	2.98	3.669(5)	131.3(3)
C41H····Br1	2.88	3.789(5)	163.3(3)
O13HA····Br1	2.42	3.250(5)	164.4(3)
O13HB····Br1	2.48	3. 326 (4)	172.7(3)
C20H····O13	2.57	3.374(6)	144.5(2)
N4H····O13	2.23	3.058(6)	161.6(3)
C26H····O13	2.42	3.227(7)	145.1(4)
C12H····O13	2.81	3.634 (4)	148.0(4)
[$(LH)^+$.I^-](3)			
N2H····I1	3.08	3.795(5)	141.9(3)

N4H····I1	2.97	3.776(7)	155.2(4)
N6H····I1	3.11	3.919(5)	156.2(3)
C45H····I1	2.95	3.847(6)	161.9(3)
C37H····I1	3.15	3.978(6)	147.7(4)
N1H····O11	2.27	3.084(7)	148.0(3)
C31HA····O12	2.58	3.411(9)	143.6(4)

References.

1. SAINT and *XPREP*, 5.1 ed.; Siemens Industrial Automation Inc.: Madison, WI, 1995.Sheldrick,G. M.

2. *SADABS, empirical absorption Correction Program*; University of Göttingen: Göttingen, Germany, 1997.

3. G. M. Sheldrick, *SHELXTL Reference Manual:* V*ersion 5.1*; Bruker AXS: Madison, WI, 1997.

4. G. M. Sheldrick, *SHELXL-97: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

5. Mercury 2.3 Supplied with Cambridge Structural Database; CCDC: Cambridge, U.K., 20011-20012.

6. P. Van der Sluis and A. L. Spek, *Acta Crystallogr.*, 1990, A46, 194.

7. L. Fielding, *Tetrahedron* , 2000, **56**, 6151−6170

8. R. Mathur, E. D. Becker, R. B. Bradley and N. C. Li, *J. Phys. Chem.*, 1963, **67**, 2190.

9. M. W. Hanna and A. L. Ashbaugh, *J. Phys. Chem.*, 1964, **68**, 811−816.

10. S. K. Dey and G. Das, *Cryst. Growth Des.*, 2009, **10**, 750–760.

11. B. K. Dutta, C. Kar, A. Basu and G. Das, *Tetrahedron Lett*., 2013, **54**, 771–774.