Supporting Information

Trapped Inorganic Phosphate Dimer

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Experimental Section

Materials. Tris-(2-aminoethyl)amine, pentafluorophenyl isocyanate, tetrabutylammonium dihydrogenphosphate, tetrabutyammonium acetate, tetrabutyammonium nitrate, and tetrabutyammonium perchlorate were purchased from Sigma-Aldrich, USA and were used as received dichloromethane (DCM) purchased from S.D. Fine, India was distilled over anhydrous calcium hydride prior to use.

Physical Measurements. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 200 MHz and 75.47 MHz FT-NMR spectrometers instruments respectively. HRMS (ESI) measurements were carried out on Waters QTof-Micro instruments.

X-ray Crystallography. The crystallographic data and details of data collection for **L** and **1** are given in Table 1S and Table 4S respectively. In each case, a crystal of suitable size was selected from the mother liquor and immersed in paratone oil, then mounted on the tip of a glass fiber and cemented using epoxy resin. Intensity data for all three crystals were collected using Mo K_α (λ = 0.7107 Å) radiation on a Bruker SMART APEX diffractometer equipped with CCD area detector at 100K. The data integration and reduction were processed with SAINT[1a] software. An empirical absorption correction was applied to the collected reflections with SADABS[1b]. The structures were solved by direct methods using SHELXTL[2] and were refined on F^2 by the full-matrix least-squares technique using the SHELXL-97[3] program package. Graphics are generated using PLATON[4] and MERCURY 1.3.[5] In both cases the non-hydrogen atoms are refined anisotropically till the convergence. Hydrogen atoms attached to the amide nitrogens in both the compounds and the hydrogen atoms attached to the dihydrogenphosphate moiety of compound **1** were located from the difference Fourier map and refined isotropically. Rest of the hydrogen atoms in both of the compounds were stereochemically fixed at idealized positions.

(1) (a) SAINT and *XPREP*, 5.1 ed.; Siemens Industrial Automation Inc.: Madison, WI, 1995.Sheldrick, G. M. (b) *SADABS, empirical absorption Correction Program*; University of Göttingen: Göttingen, Germany, 1997.

(2) Sheldrick, G. M. *SHELXTL Reference Manual: Version 5.1*; Bruker AXS: Madison, WI, 1997.

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

(4) Spek, A. L. *PLATON-97*; University of Utrecht: Utrecht, The Netherlands, 1997.

(5) Mercury 1.3 Supplied with Cambridge Structural Database; CCDC: Cambridge, U.K., 2003-2004.

Synthesis

Synthesis of Compound **L:**

2.6 mL (20 mmol) of pentafluorophenyl isocyanate was dissolved in 25 mL of dry dichlorometahne (DCM) at room temperature in a 100 mL 2-neck round bottom flask equipped with a dropping funnel. Tris-(2-aminoethyl) amine (1.0 mL, 6.5 mmol) was dissolved in 25 mL of dry DCM and was added drop-wise with constant stirring. The resulting solution was stirred for another 1 h at room temperature in N_2 atmosphere. The colorless precipitate formed was filtered off and washed with DCM twice. The precipitate collected was dried in air. Yield of **L** is 98%. Single crystals of **L** suitable for X-ray analysis were isolated when we attempted complexation of bromide with **L** upon treating **L** with tetrabutylammonium bromide in dimethylforamide (DMF). Slow evaporation of above solution yielded colorless crystals of **L** after 3 days which were filtered off from the mother liquor. Isolated yield is 50%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.55 (t, 6H, NC*H*$_2$), 3.15 (t, 6H, NCH_2C*H*$_2$), 6.55 (s, 3H, NH_a), 8.352 (s, 3H, NH_b). ^{13}C NMR (75.47 MHz, DMSO-d_6): δ 38.914 (N*C*H_2), 54.528 (NCH_2*C*H_2), 115.737 (m of s, Ar, *C*C-F, J_{CCF} = 15Hz), 137.94 (m of d, Ar, *C*-F, J_{CF} = 247 Hz), 138.77 (m of d, Ar, *C*-F J_{CF} = 247 Hz), 143.62 (m of d, Ar, *C*-F, J_{CF} = 246 Hz), 155.36 (s, *C*=O). Positive ESI HRMS: m/z 774.5637 [**L**+H$^+$] 100%.

Synthesis of Complex **1**:

50 mg of **L** was dissolved in 5 mL DMF/MeCN (1:1 v/v, pH ~ 7.89) binary solvent in a 25 mL beaker. In to this solution 25 mg of n-$Bu_4N^+H_2PO_4^-$ was added in one shot and mixture was stirred for 5 min with a magnetic stirrer at room temperature. Resulting solution was filtered using a filter paper. Filtrate was allowed to evaporate under room temperature. Colorless crystals of the dihydrogenphosphate complex of **L**, [**L**(H_2PO_4)]·DMF (**1**), suitable for X-ray diffraction was obtained after a week. Isolated Yield of **1** is 60%. ^{1}H NMR (200 MHz, DMSO-d_6): δ 1.20 (t, 3H, $NCH_2CH_2CH_2C$*H*$_3$), 1.55 (m, 2H, NCH_2CH_2C*H*$_2CH_3$), 1.62 (m, 2H, NCH_2C*H*$_2CH_2CH_3$), 2.45 (s, 6H, NC*H*$_2$), 3.15 (s, 6H, NCH_2C*H*$_2$), 3.20 (m, 2H, NC*H*$_2CH_2CH_2CH_3$), 7.87 (br, 3H, NH_a), 9.43 (br, 3H, NH_b). Positive ESI HRMS: m/z 774.5637 [**L**+H$^+$].

^{1}H NMR studies. Binding constants were obtained by ^{1}H NMR (200 MHz Bruker) titrations of **L** with $[n\text{-Bu}]_4N^+A^-$ (A-: $H_2PO_4^-$, CH_3COO^-) in DMSO-d_6 at 25ºC. The initial concentration of **L** was 20 mM. Aliquots of anions were added from two different stock solutions 25 mM and 50 mM of anions (host : guest = up to 1:1, 25 mM stock solution was used, and above 1:1 ratio higher concentration anion was used). Tetramethylsilane (TMS) in DMSO-d_6 was used as an internal reference, and each titration was performed by 15 measurements at room temperature. All proton signals were referred to TMS. The association constants[6], *K*, were calculated by fitting the change in the N-H chemical shift with a 1:1 association model with non-linear least square analysis. The error limit in *K* was less than 10%. There were no detectable chemical shift of -NH in cases of NO_3^- and ClO_4^- guests indicate no host-guest complex formation.

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.

(6) Hynes, M. J. *J. Chem. Soc., Dalton Trans*. **1993**, 311-312.

Table 1S: Crystallographic Parameters for Ligand **L**

Crystal Data	**Ligand**
Empirical formula	$C_{27}H_{18}F_{15}N_7O_3$
FW	773.48
Crystal size (mm)	0.65X0.45X0.23
Crystal description	BLOCKS
Crystal system	Triclinc
Space group	P-1
a/Å	9.2984(10)
b/Å	13.3540(14)
c /Å	13.7161(14)
$\alpha/^0$	118.317(2)
$\beta/^0$	90.295(2)
$\gamma/^0$	96.329(2)
Volume / $Å^{-3}$	1487.0(3)
Z	2
$D_{calc.}/Mgm^{-3}$	1.728
F(000)	776
μ MoK_{α} (mm^{-1})	0.179
Temperature (K)	100(2)
2θ max (°)	28.29
Observed reflections [$I > 2\sigma(I)$]	6733, (R_{int} =0305)
Parameters refined	493
Goodness of fit	1.081
Final R_1 on observed data	0.0582
Final wR_2 on observe data	0.1215

Figure 1S: ORTEP diagram of **L** with atom numbering with 50% probability factor for the thermal ellipsoids.

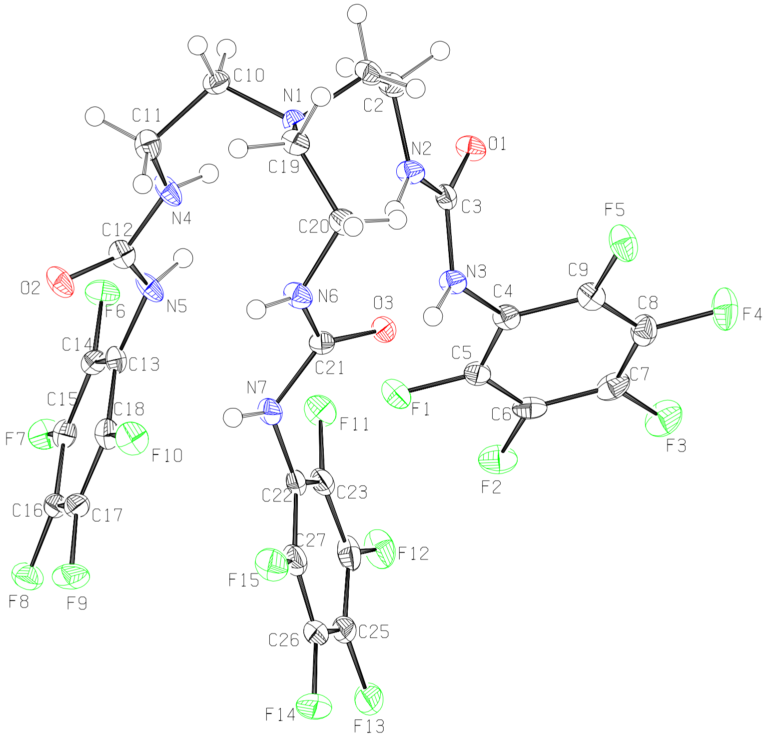
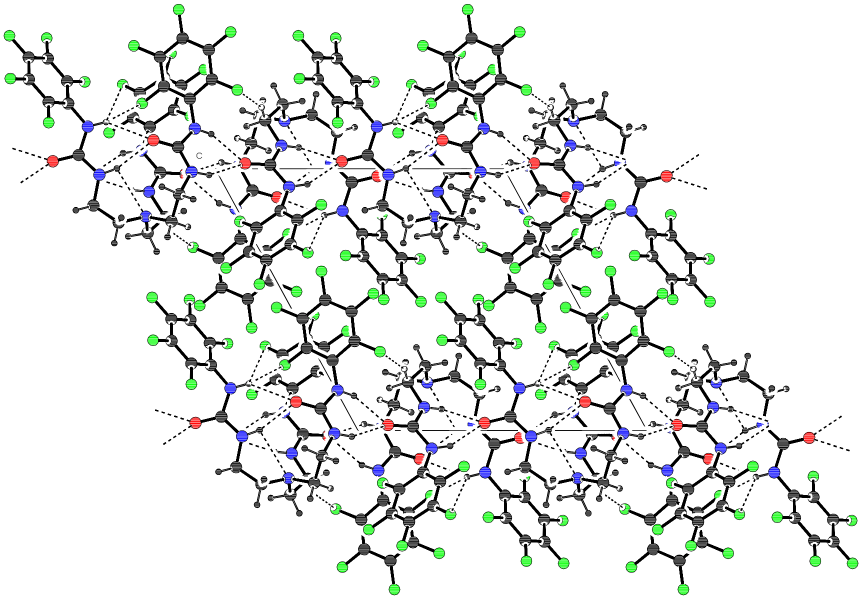


Figure 2S: Packing diagram of **L** viewed down a-axis showing the one dimensional hydrogen bonded layers of molecules in the bc-plane.



Packing diagram of **L** is viewed down a-axis depicting the various H-bonding interactions are shown in Figure 2S. As shown in the figure the alternate ligand moiety is oriented in opposite direction along b-axis and are involved various intermolecular hydrogen bonding interactions to form a layered network along bc-plane. Thus, Hydrogen atoms attached of the diamide nitrogens from all the strands are involved in intermolecular hydrogen bonding via N-H…O and and N-H…F interactions with the tethered urea oxygen of oppositely oriented tripodal ligands. Thus three N-H…O , two N-H…F and one C-H…F interaction between the methylene hydrogen H11B with F15 of the pentaflouro aryl ring is responsible for the generation of layared network arrangement in the packing mode.

Table 2S: Hydrogen bonding table for **L** with symmetry code

D-H···A	***d*(H···A), Å**	***d(*D···A), Å**	**<DHA deg**
N(2)-H(2C)•••O(3)^{1}	H(2C)•••O(3) = 2.18(4)	N(2)•••O(3) = 3.003(3)	N(2)-H(2C)•••O(3) = 162(3)
N(3)-H(3C)•••F(11)^{1}	H(3C)•••F(11) = 2.35(3)	N(3)•••F(11) = 3.027(3)	N(3)-H(3C)•••F(11) = 136(2)
N(3)-H(3C)•••F(7)^{2}	H(3C)•••F(7)= 2.47(3)	N(3)···F(7)= 3.015(3)	N(3)--H(3C) ..F(7) = 122(2)
N(3)-H(3C)•••O(3)^{1}	H(3C)•••O(3) = 2.44(3)	N(3)•••O(3) = 3.176(3)	N(3)-H(3C)•••O(3) = 144(2)
N(4)-H(4C)•••O(1)^{3}	H(4C)••• O(1) = 2.16(4)	N(4)••• O(1) = 2.888(3)	N(4)-H(4C)•••O(1) = 144(3)
N(5)-H(5C)•••O(1)^{3}	H(5C)•••O(1)= 2.03(4)	N(5)•••O(1)= 2.823(3)	N(5)-H(5C)•••O(1) = 153(2)
N(6)-H(6C)•••O(2)^{4}	H(6C)•••O(2) = 2.10(3)	N(6)•••O(2) = 2.871(3)	N(6)-H(6C)•••O(2) = 150(2)
N(7)-H(7C)•••O(2)^{4}	H(7C)•••O(2) = 2.07(3)	N(7)•••O(2) = 2.834(3)	N(7)-H(7C)•••O(2) = 158(2)
C(11) --H(11B) ···F(15)^{4}	H(11B)···F(15)= 2.50	C(11)···F(15)= 3.414(3)	C(11)-H(11B) ···F(15) = 157

1. x, y,z 2. 1+x,y,z 3. -x,1-y,-z 4. -x,2-y,-z

Table 3S: Different Non-bonding Interactions in **L**

C-F···F-C/Cg···F-C	***d* (F···F/Cg···F) in Å**	**< C-F···F/Cg···F-C in (deg)**
C(6)-F(2)···F(9)-C(17)^{1}	F(2)···F(9) = 2.753	C(17)-F(9)···F(2) = 158.12
C(25)-F(13)···F(1)-C(5)^{1}	F(13)···F(1) = 2.741	C(5)-F(1) ···F(13) = 159.40
Cg1···F(13)-C(25)^{1}	Cg1···F(13) = 3.027	Cg1···F(13)-C(25) = 128.12

symmetry code : 1. `-x,2-y,1-z`

Where Cg1 represents the centroid of C13-C18.

Figure 3S. ORTEP diagram of **1** with atom numbering with 40% probability factor for the thermal ellipsoids.

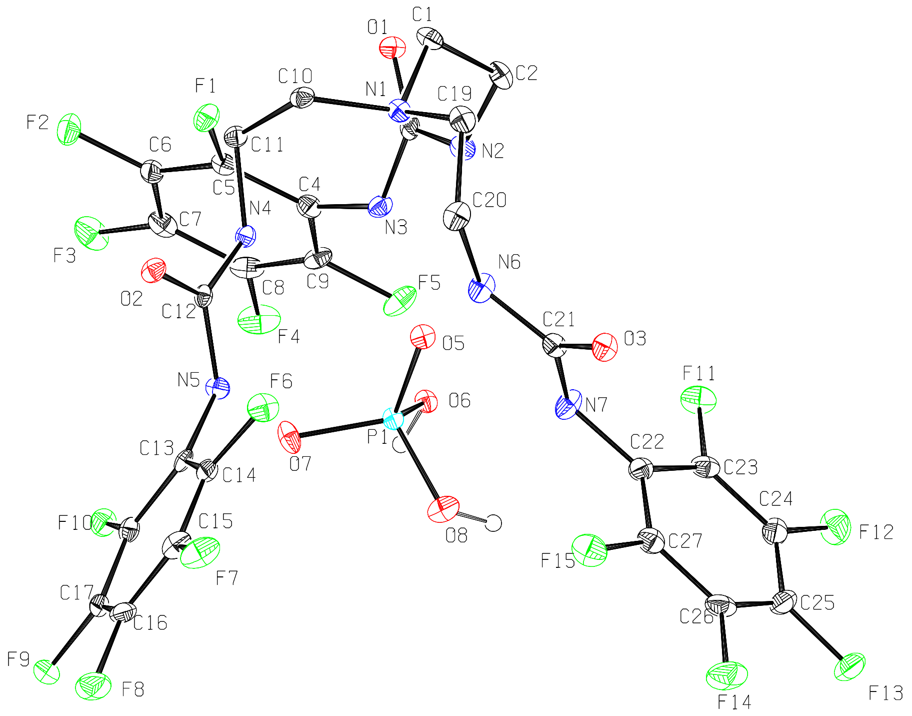


Table 4S: Crystallographic Parameters for Complex **1**

Crystal Data	**Complex 1**
Empirical formula	$C_{46}H_{63}F_{15}N_9O_3P_1$
FW	1186.02
Crystal size (mm)	0.35 x 0.24 x 0.22
Crystal description	PLATES
Crystal system	Triclinic
Space group	P-1
a/Å	13.3363(11)
b/Å	14.0385(11)
c /Å	15.5942(13)
$\alpha/^0$	99.391(2)
$\beta/^0$	95.841(2)
$\gamma/^0$	108.885(2)
Volume / $Å^{-3}$	2687.8(4)
Z	2
$D_{calc.}/Mgm^{-3}$	1.465
F(000)	1232
μ MoK_α (mm^{-1})	0.163
Temperature (K)	100(2)
2θ max	25
Observed reflections [$I > 2\ \sigma(I)$]	9400 [R(int) = 0.0411]
Parameters refined	750
Goodness of fit	1.117
Final R_1 on observed data	0.0640
Final wR_2 on observe data	0.1252

Table.5S: Hydrogen bonding table for the complex **1**.

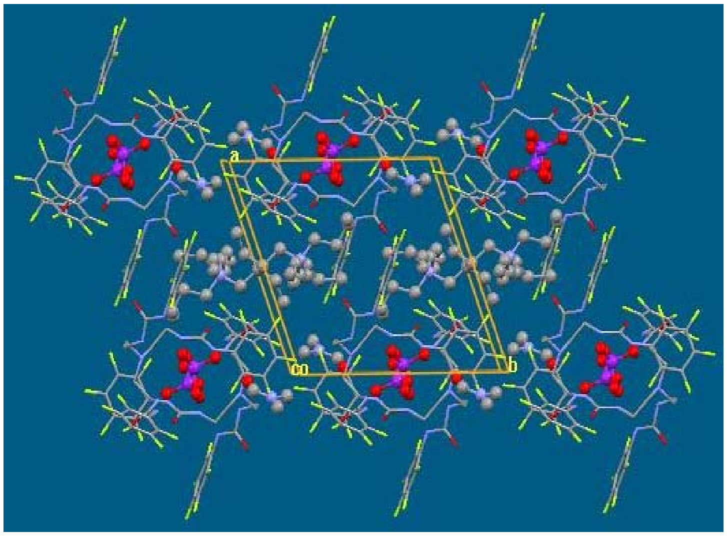
D-H ···A	***d*(H···A), Å**	***d(*D ···A), Å**	**<DHA °**
N(2)-H(2C)···O(5)^{1}	H(2C)···O(5) = 2.10(3)	N(2)···O(5) = 2.898(4)	N(2)-H(2C)···O(5) = 169(3)
N(3)-H(3C)···O(6)^{1}	H(3C)···O(6) = 2.03(4)	N(3)···O(6) = 2.893(3)	N(3) -H(3C)···O(6) = 160(3)
N(4)-H(4C)···O(5)^{1}	H(4C)···O(5) = 2.36(3)	N(4)···O(5) = 3.132(4)	N(4)-H(4C)···O(5) = 164(3)
N(5)-H(5C)···O(7)^{1}	H(5C)···O(7) = 1.95(4)	N(5)···O(7) = 2.753(4)	N(5)-H(5C)···O(7) = 172(3)
N(6)-H(6C)···O(5)^{1}	H(6C)···O(5) = 2.19(3)	N(6)···O(5) = 2.976(4)	N(6)-H(6C)···O(5) = 159(4)
O(6)-H(6D)···O(7)^{2}	H(6D)···O(7) = 1.67(3)	O(6)···O(7) = 2.563(3)	O(6)-H(6D)···O(7) = 177(3)
N(7)-H(7C)···O(5)^{1}	H(7C) ···O(5) = 2.16(4)	N(7)···O(5) = 2.966(3)	N(7)-H(7C)···O(5) =160(4)
N(7)-H(7C)···O(8)^{1}	H(7C)···O(8) = 2.59(3)	N(7)···O(8) = 3.202(4)	N(7)-H(7C)···O(8) = 131(3)
O(8) -H(8D) ···O(4)^{3}	H(8D) ···O(4)= 1.76(4)	O(8) ···O(4)= 2.576(4)	O(8) -H(8D) ···O(4)= 168(4)
C(28) -H(28A)···O(3)^{4}	H(28A) ···O(3)= 2.37	C(28)···O(3)=3.332(4)	C(28) -H(28A) ···O(3)= 172
C(29) -H(29B) ···O(2)^{1}	H(29B) ···O(2)= 2.55	C(29) ···O(2)=3.432(4)	C(29) -H(29B) ···O(2)= 151
C(32)-H(32B) ···O(1)^{5}	H(32B) ···O(1)= 2.53	C(32) ···O(1)=3.491(4)	C(32) -H(32B) ···O(1)= 173
C(37) -H(37A) ···O(3)^{4}	H(37A) ···O(3)= 2.52	C(37) ···O(3)=3.430(5)	C(37) -H(37A) ···O(3)= 155
C(40) -H(40A) ···O(2)^{1}	H(40A) ···O(2)= 2.31	C(40) ···O(2)=3.284(4)	C(40) -H(40A) ···O(2)= 179
1. x, y, z 2. -x,1-y,-z 3. -1+x,y,z 4. 1-x,1-y,1-z 5. 1+x,y,z			

Table 6S: Different Non-bonding Interactions in Complex **1**

C-F···F-C/Cg···F-C	***d* (F···F/Cg···F) Å**	**< C-F···F/ Cg···F-C deg**
C(18)-F(10)···F(5)-C(9)^{1}	F(10)···F(5) = 2.872	C(9)-F(5) ···F(10) = 163.76
Cg2···O(4)-C(46)*^{2}	Cg2···O(4) = 3.474	Cg2···O(4)-C(46) = 152.19
Cg3···O(8)-P(1)^{1}	Cg3···O(8) = 3.420	Cg3···O(8)-P(1) = 140.85
Cg4···F(3)-C(7)^{1}	Cg4···F(3) = 3.545	Cg4···F(3)-C(7) = 124.89
Symmetry code: 1. -x,1-y,-z 2. 1-x,1-y,-z		

Where Cg2, Cg3, and Cg4 represents the centroids of C4-C9 and C22-C27 respectively.
* with the shortest distance C23···O4 = 3.025 Å

Figure 4S: Packing diagram of **1** viewed down c-axis showing the arrangement of the dimeric anion encapsulated capsules along b-axis and the n-tetrabutyl ammonium cations between the adjacent layers of the anionic capsules.



Packing diagram of the compound viewed down c-axis is shown in Fig. 3S. As depicted in the Figure the dihydrogen phosphate dimers are wrapped by two tripodal moiety are oriented along with the DMF molecules are H-boned with the $[H_2PO_4]^-$ units form either end of the dimres and are oriented as a layer along along b-axis . The tert-butyl cations are occupied between the adjacent anionic layers; two tert-butyl cations molecules are surrounded by the four of the paired anionic capsules. Extensive strong C-H…O hydrogen bonding do exits between the amide oxygens of the tripodal moiety and the ethylenic and methyl hydrogens from different arms of the tert-butyl ammonium cation. These C-H…O interactions not only stabilize the cation between the four anionic tripodal capsules but also a bridge between the adjacent encapsulated anionic tripodal array along a-axis.

Figure 5S: Job plot for **L** with n-$Bu_4N^+H_2PO_4^-$ in DMSO-d_6 at 25ºC.

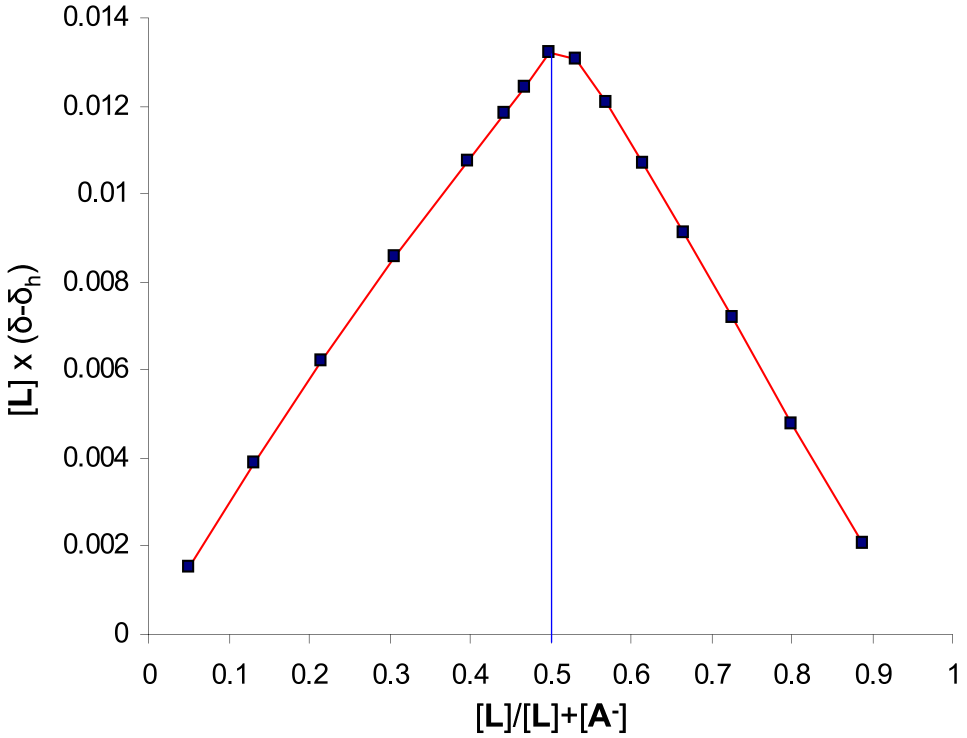


Figure 6S: Job plot for **L** with n-$Bu_4N^+CH_3COO^-$ in DMSO-d_6 at 25ºC.

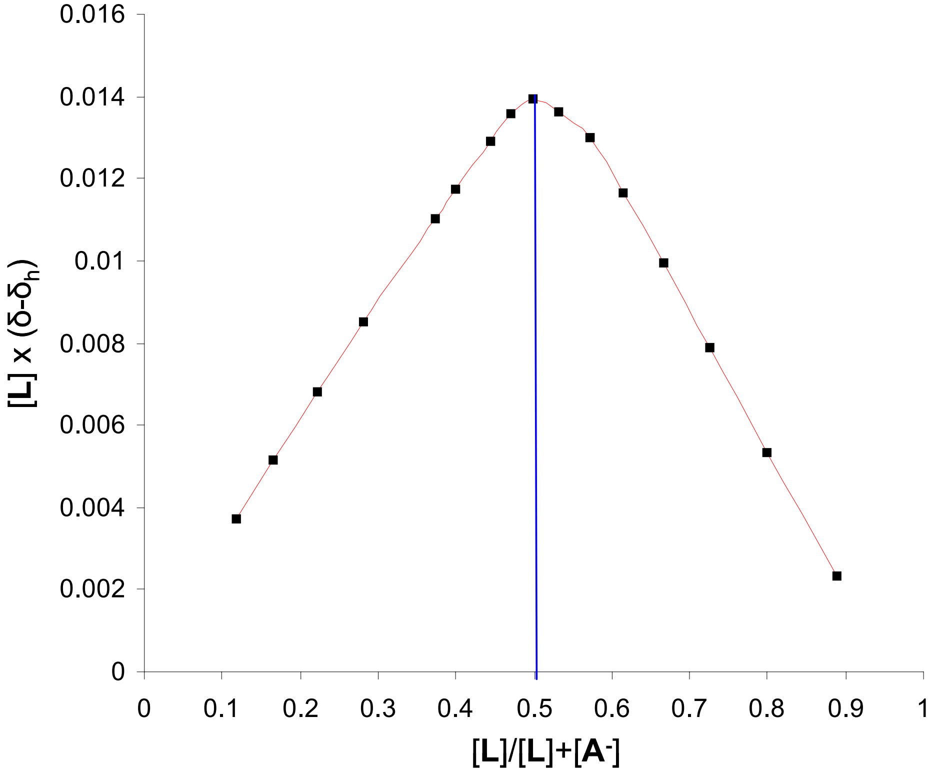


Figure 7S: Solution state ^{1}H-NMR Experiments of **L** in presence of different combination of anions.