Supporting Information

Unusual Recognition of (n-Bu₄N)₂SO₄ by a Cyanuric Acid based Host via Contact Ion-Pair Interactions

I. Ravikumar, and Pradyut Ghosh*

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, 2A & B Raja S. C. Mullick Road, Kolkata 700 032. India.

E-mail: icpg@iacs.res.in
Table of Contents

1. Materials and Methods      -4-
2. Scheme for synthesis of L     -5-
3. Synthesis and characterization of II   -5-
4. Synthesis and characterization of III  -6-
5. Synthesis and characterization of IV   -6-
6. Synthesis and characterization of receptor, L    -7-
7. Synthesis and characterization of complex 1    -7-
8. Figure 1S: $^1$H-NMR spectra of II     -8-
9. Figure 2S: $^{13}$C-NMR spectra of II     -9-
10. Figure 3S: DEPT-NMR spectra of II    -10-
11. Figure 4S: $^1$H-NMR spectra of IIa   -11-
12. Figure 5S: $^{13}$C-NMR spectra of IIa   -12-
13. Figure 6S: DEPT-NMR spectra of IIa    -13-
14. Figure 7S: HRMS spectra of IIa       -14-
15. Figure 8S: $^1$H-NMR spectra of III   -15-
16. Figure 9S: $^{13}$C-NMR spectra of III   -16-
17. Figure 10S: HRMS spectra of III     -17-
18. Figure 11S: HRMS spectra of IV      -18-
19. Figure 12S: $^1$H-NMR spectra of receptor, L -19-
20. Figure 13S: $^{19}$F-NMR spectra of receptor, L -20-
21. Figure 14S: ESI mass spectra of receptor, L -21-
22. Figure 15S: $^1$H-NMR spectra of complex, 1 -22-
23. Figure 16S: $^{13}$C-NMR spectra of complex, 1 -23-
24. Figure 17S: $^{19}$F-NMR spectra of complex, 1 -24-
25. Figure 18S: ESI mass spectra of complex, 1 -25-
26. Single crystal X-ray description    -26-
27. Table 1S: Crystallographic table for complex, 1 -27-
28. Figure 19S: ORTEP diagram for complex, 1 -28-
29. Table 2S: Hydrogen-bonding table for complex, 1
30. Diffusion Measurements
31. Figure 20S: DOSY-NMR spectra of $\text{(n-Bu}_4\text{N})_2\text{SO}_4$^2-
32. Figure 21S: DOSY-NMR spectra of receptor, L
33. Figure 22S: DOSY-NMR spectra of complex 1 at 298 K
34. Figure 23S: DOSY-NMR spectra of complex 1 at 313 K
35. Figure 24S: DOSY-NMR spectra of complex 1 at 333 K
36. Figure 25S: DOSY-NMR spectra of L in presence of TBAH$_2$PO$_4$
37. Figure 26S: DOSY-NMR spectra of L in presence of TBAC$_3$COO
38. Figure 27S: DOSY-NMR spectra of L in presence of TBANO$_3$
39. Figure 28S: DOSY-NMR spectra of L in presence of TBACl
40. Figure 29S: Partial $^1$H-NMR spectra of L with different anions
41. Figure 31S: Change in chemical shift of L upon addition of aliquots of $(n\text{-Bu}_4\text{N})_2\text{SO}_4$^2-
42. Figure 30S: Job’s plot of L with $(n\text{-Bu}_4\text{N})_2\text{SO}_4$^2- in DMSO-$d_6$
43. Figure 31S: Change in chemical shift of L upon addition of aliquots of $n\text{-Bu}_4\text{N}^+\text{H}_2\text{PO}_4$^-
44. Figure 32S: Job’s plot of L with $n\text{-Bu}_4\text{N}^+\text{H}_2\text{PO}_4$^ in DMSO-$d_6$
45. Figure 33S: Change in chemical shift of L upon addition of aliquots of $n\text{-Bu}_4\text{N}^+\text{CH}_3\text{COO}^-$
46. Figure 34S: Job’s plot of L with $n\text{-Bu}_4\text{N}^+\text{CH}_3\text{COO}^-$ in DMSO-$d_6$
47. Figure 35S: Change in chemical of L upon addition of aliquots of $n\text{-Bu}_4\text{N}^+$Cl
48. Figure 36S: Job’s plot of L with $n\text{-Bu}_4\text{N}^+$Cl in DMSO-$d_6$
1. Materials and Methods:

1,3,5-Tris(2-hydroxyethyl)-1,3,5-triazine-2,4,6-trione (I), pentafluorophenyl isocyanate, tetrabutylammonium salts of fluoride, chloride, bromide, iodide, nitrate, acetate, sulfate, dihydrogenphosphate, and perchlorate were purchased from Sigma-Aldrich, USA and were used as purchased without further purification. Dichloromethane (DCM), Tetrahydrofuran (THF), diethylether, ethylacetate, dimethylformamaide (DMF) and dimethylsulfoxide (DMSO) were purchased from Spectrochem Ltd., India. $^1$H-NMR (300 MHz) and $^{13}$C-NMR (75 MHz) spectra were recorded on a Bruker DPX 300 FT-NMR spectrometer. 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). 19F-NMR (500 MHz) were recorded on a Bruker AVII 500MHz spectrometer with trifluorotoluene as an external standard.
2. Scheme for synthesis of L

\[
\begin{align*}
&\text{I} \quad \text{II} \quad \text{III} \\
&\text{O} \quad \text{N} \quad \text{N} \quad \text{OH} \quad \text{TsO} \quad \text{N} \quad \text{O} \quad \text{N} \quad \text{OTs} \quad \text{N} \quad \text{N} \\
&\text{OH} \quad \text{N} \quad \text{N} \quad \text{OH} \quad \text{OTs} \quad \text{N} \quad \text{N} \\
&\text{L: R = -C}_6\text{F}_5
\end{align*}
\]

3. Synthesis of 1,3,5-Tris(2-tosylethyl)-1,3,5-triazine-2,4,6-trione (II):

2.0 g (7.6 mmol) of trialcohol was taken in a 250 ml two neck round bottom flask. It was suspended in 100 ml of dry THF and was cooled to 0°C by an ice bath. 3.0 ml of freshly distilled triethylamine was added to the reaction mixture. The reaction mixture was allowed to stir at 0°C for 30 min. 5.1 g (26.7 mmol) of tosyl chloride dissolved in 50 ml of dry THF was taken in a pressure equalizing funnel and added slowly for a period of 1-2 hrs to the reaction mixture at 0°C. The reaction mixture was allowed to stir at 0-5°C for 3 hrs and at RT for 2 days at nitrogen atmosphere. The precipitate so formed was filtered and washed with cold THF (5 ml x 5 times). The filtrate was evaporated to dryness under reduced pressure. The crude semi solid product obtained was dissolved in 100 ml of DCM. The organic layer was washed with 2 x 50 ml of water, 1 x 100 ml of 5% NaHCO₃ and again twice with 2 x 50 ml of water. The organic layer was collected and dried over sodium sulfate. The solvent was removed under vacuum to yield a semi solid mass. The product was kept in the freezer for overnight to obtain a colorless solid. The crude colorless solid was stirred with 100 ml of diethyl ether for 4 hrs and filtered off. The precipitate was washed several times with cold diethyl ether. The pure product was isolated as colorless solid in 66% yield by column chromatography (silica gel: CHCl₃ eluent). The ditosylate product was isolated by
column chromatography (silica gel: ethylacetate:CHCl$_3$ (1:4 v/v)) eluent. HRMS (ESI): 724.2229 [M+H$^+$] (100%). $^1$H NMR (300 MHz, CD$_3$CN): d 2.40 (s, 9H, Ar-CH$_3$), 3.94 (t, 6H, NCH$_2$, J = 5 Hz), 4.19 (t, 6H, NCH$_2$CH$_2$, J = 5 Hz), 7.38 (d, 6H, Ts-H, J = 8 Hz), 7.72 (d, 6H, Ts-H, J = 8 Hz). $^{13}$C NMR (75.47 MHz, CD$_3$CN): d 20.67 (Ts-CH$_3$), 41.41 (NCH$_2$CH$_2$), 66.66 (NCH$_2$CH$_2$), 127.71 (Ts-CH), 130.04 (Ts-CH), 132.44 (Ts-C), 145.65 (Ts-C), 148.29 (s, C=O).

4. Synthesis of 1,3,5-Tris(2-azidoethyl)-1,3,5-triazine-2,4,6-trione (III):

Tritosylate (1.0 g, 1.38 mmole) was dissolved in 20 ml of dry DMF. Sodium azide (0.36 g, 5.5 mmole) was added to the solution. The reaction mixture was stirred at 75°C for two days in nitrogen atmosphere. After two days of continuous stirring, the reaction mixture was cooled to room temperature and poured into ice cold water (600 ml). The aqueous solution was extracted with ethylacetate (150 ml) three times. The combined organic layers were washed with water and dried over anhydrous sodium sulfate. The solvent was removed under vacuum to give colorless semisolid. The crude product was re-dissolved in diethylether and covered with a parafilm. The beaker was kept in the refrigerator at 4°C. A crystal of triazole (2) was obtained upon slow evaporation at 4°C after three days. In 85% yield HRMS (ESI): 358.8098 [M+Na$^+$] (100%).$^1$H NMR (300 MHz, CDCl$_3$): d 3.58 (t, 6H, NCH$_2$, J = 3.6 Hz), 4.16 (t, 6H, NCH$_2$C$_2$, J = 3.6 Hz). $^{13}$C NMR (75.47 MHz, CDCl$_3$): d 41.79 (NCH$_2$C$_2$), 48.43 (NCH$_2$C$_2$), 148.69 (s, C=O).

5. Synthesis of 1,3,5-Tris(2-aminoethyl)-1,3,5-triazine-2,4,6-trione (IV):

400 mg (0.12 mmole) of triazole was dissolved in 50 ml of dry ethanol in a 200 ml flask. 200 mg of 10% Pd on activated charcoal was added. Hydrogenation was performed at RT in 60 psi of hydrogen pressure for 12 hrs. After this time, the Pd on charcoal was filtered through a filter paper and washed several times with ethanol. The filtrate was evaporated under reduced pressure to give a colorless oily mass. Acetonitrile (10 ml) was added to the semi solid and sonicated for few minutes. A colorless solid precipitates out. The precipitate was washed with CH$_3$CN and then with diethylether and finally dried in a dessicator to yield a colorless solid in 95% yield. HRMS (ESI): 259.0164 [M+H$^+$].$^1$H NMR (300 MHz, CD$_2$CN): d 2.71 (t, 6H, NCH$_2$, J = 6 Hz), 3.34 (t, 6H, NCH$_2$CH$_2$, J = 6 Hz), 5.42 (t, 6H, NH$_2$).

6. Synthesis of Compound L:

Triamine, (516 mg, 0.2 mmol) was taken in a 100 mL round bottomed flask, and dissolved in 50 mL of dry tetrahydrofuran (THF). The reaction mixture was allowed to stir at room temperature in nitrogen
atmosphere for 15 min for complete dissolution. 0.125 g (0.6 mmol) of 2,3,4,5,6-pentafluorophenyl isocyanate was dissolved in another 50 mL of dry THF and taken in a 100 mL pressure equalizing funnel. This solution was added dropwise for a period of 1 hour at constant stirring in room temperature. After the addition, the reaction mixture was allowed to stir at room temperature in nitrogen atmosphere for another 14 h. The white precipitate formed was filtered out, and washed three times with cold THF. The colorless solid was washed again with diethylether and to yield the required product as colorless solid (yield: 95%). ESI (–ve mode): 884.0 [M−H+](100%).

\[ ^{1}H\text{NMR (300 MHz, DMSO-d}_6\]: \delta 3.24 (t, 6H, NC\text{H}_2, J = 6 Hz), 3.81 (t, 6H, NCH\text{2C}_2H, J = 6 Hz), 6.55 (t, 3H, NH), 8.29 (s, 3H, NH).\]

\[ ^{13}C\text{NMR (75.47 MHz, DMSO-d}_6\]: \delta 38.40 (NC\text{H}_2), 53.68 (NCH\text{2C}_2H), 112.68 (m of s, Ar, CC-F, J_{CCF} = 15Hz), 137.87 (m of d, Ar, C-F, J_{CF} = 252 Hz), 142.20 (m of d, Ar, C-F, J_{CF} = 249 Hz), 157.88 (s, C=O).\]

\[ ^{19}F\text{NMR (500 MHz, CDCl}_3\]: \delta -164.94 (t, 2Ar-F, J_{F-F} = 23 Hz), -161.06 (t, Ar-F, J_{F-F} = 23 Hz), -147.25 (d, 2 Ar-F, J_{F-F} = 23 Hz).\]

Elemental analysis: Calculated: C-40.69, H-2.05, N-14.24 %, Experimental: C-40.77, H-2.05, N-14.30 %.

7. Synthesis of Complex 1:

83 mg (0.01 mmol) of L was dissolved in 10 ml of DMF and then 10.0 mg (0.03 mmol) of n-Bu_4N^+HSO_4^- was added to the above solution. Then the mixture was stirred at room temperature for 10 minutes. Then, the mixture was filtered and allowed to evaporate for crystallization. After a week, colorless crystals of complex [L(SO_4^2-):2 n-Bu_4N^+·DMF (1) suitable for X-ray diffraction studies were obtained in 85% yield. \(^{1}H\text{NMR (300 MHz, CDCl}_3\]: \delta 0.94 (m, 3H, NCH\text{2C}_2H\text{2CH}_3), 1.35 (m, 2H, NCH\text{2C}_2H\text{2CH}_3), 1.55 (m, 2H, NCH\text{2C}_2H\text{2CH}_3), 2.89 (d, 3H, NCH\text{3}), 2.97 (d, 3H, NCH\text{3}), 3.21 (m, 2H, NCH\text{2C}_2H\text{2CH}_3), 3.51 (m, 6H, NCH\text{2CH}_2), 4.11 (m, 6H, NCH\text{2CH}_2), 8.018 (br, 1H, NH) 8.66 (br, 3H, NH), 10.02 (br, 3H, NH). \(^{13}C\text{NMR (75.47 MHz, CDCl}_3\]: \delta 13.48 (NCH\text{2C}_2H\text{2CH}_3), 19.65 (NCH\text{2C}_2H\text{2CH}_3), 23.95 (NCH\text{2C}_2H\text{2CH}_3), 31.46 (NCH\text{3}), 36.52 (NCH\text{3}), 37.22 (NCH\text{2CH}_2), 42.05 (NCH\text{2CH}_2), 58.65 (NCH\text{2C}_2H\text{2CH}_3), 112.68 (m of s, Ar, CC-F, J_{CCF} = 15Hz), 137.87 (m of d, Ar, C-F, J_{CF} = 252 Hz), 142.20 (m of d, Ar, C-F J_{CF} = 252 Hz), 144.16 (m of d, Ar, C-F, J_{CF} = 249 Hz), 157.88 (s, C=O). \(^{19}F\text{NMR (500 MHz, CDCl}_3\]: \delta -165.26 (br, 2Ar-F), -158.48 (br, Ar-F), -145.38 (br, 2 Ar-F). Elemental analysis: calculated: C – 50.71%, H – 6.35%, N – 10.92% and experimental: C – 50.66%, H – 6.33%, N – 10.89%.
8. **Figure 1S.** $^1$H-NMR Spectra of II in CD$_3$CN at 25°C.
9. **Figure 2S.** $^{13}$C-NMR Spectra of II in CD$_3$CN at 25ºC.
10. **Figure 3S.** DEPT-NMR Spectra of II in CD$_3$CN at 25°C.
11. **Figure 4S.** $^1$H-NMR Spectra of IIa in CD$_3$CN at 25°C.
12. **Figure 5S.** $^{13}$C-NMR Spectra of IIa in CD$_3$CN at 25°C.
13. **Figure 6S.** DEPT-NMR Spectra of IIa in CD$_3$CN at 25ºC.
14. **Figure 7S.** HRMS Spectra of IIa.
15. **Figure 8S.** $^1$H-NMR Spectra of **III** in CDCl$_3$ at 25°C.
16. **Figure 9S.** $^{13}$C-NMR Spectra of III in CDCl$_3$ at 25ºC.
17. **Figure 10S.** HRMS Spectra of 1,3,5-Tris(2-azidoethyl)-1,3,5-triazine-2,4,6-trione III.
18. **Figure 11S.** HRMS Spectra of 1,3,5-Tris(2-aminoethyl)-1,3,5-triazine-2,4,6-trione IV.
19. **Figure 12S.** $^1$H-NMR Spectra of receptor, $L$ in DMSO-$d_6$ at 25°C.
20. **Figure 13S.** $^{19}$F-NMR Spectra of receptor, L in DMSO-$d_6$ at 25°C.
21. **Figure 14S**. ESI mass (negative mode) spectra of receptor, L.
22. **Figure 15S.** $^1$H-NMR Spectra of complex, 1 in DMSO-$d_6$ at 25°C.
23. **Figure 16S.** $^{13}$C-NMR Spectra of complex, 1 in DMSO-$d_6$ at 25°C.
24. **Figure 17S.** $^{19}$F-NMR Spectra of complex, 1 in DMSO-$d_6$ at 25°C.
25. **Figure 18S.** ESI mass (negative mode) spectra of complex, 1.
26. Single-crystal X-ray studies:

The crystallographic data and details of data collection and refinement for complex 1 is listed below. In the present case, a single crystal of suitable size was selected from the mother liquor and immersed in paratone oil and then mounted on the tip of a glass fibre and cemented using epoxy resin. Intensity data for this crystal was collected using MoKα (\(\lambda = 0.7107 \text{ Å}\)) radiation on a Bruker SMART APEX II diffractometer equipped with CCD area detector at 100 K. Reflections were measured from a hemisphere of data collected with each frame covering 0.5° in \(\theta\). The data integration, reduction and structure solutions/refinements were carried out using the software package of Bruker SMART APEX. Graphics were generated using PLATON 97\(^1\) and MERCURY 2.2.\(^2\) In complex 1, the non-hydrogen atoms were refined anisotropically until convergence. All the hydrogen atoms in this complex were geometrically fixed at idealized positions and refined isotropically.

Reference:


27. **Table 1S.** Crystallographic table for complex 1.

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<td>Temperature (K)</td>
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<tr>
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<td>Final R indices [F(^{2})&gt;2s]</td>
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<td>R indices (all data)</td>
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<td>Goodness-of-fit of F(^{2})</td>
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<tr>
<td>Largest and mean shift (su)</td>
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<td>Largest diff. peak and hole (e Å(^3))</td>
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28. **Figure 19S.** ORTEP diagram of complex 1 with 50% probability of thermal ellipsoids. Two TBA\(^+\) and DMF molecules in the asymmetric unit are omitted for clarity.
29. **Table 2S.** Hydrogen bonding interactions of encapsulated sulfate with the receptor L and tetrabutylammonium cations.

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<td>N4-H4···O9[^1]</td>
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<td>3.523(8)</td>
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30. Diffusion measurements:

All 2D-DOSY experiments were performed on a Bruker AVII 500 MHz spectrometer. Data analyses were performed using tools within TOPSPIN 2.1 software. Sample volumes were 500 µL and the concentration of the sample was 5 mM. Anions were added as their tetrabutylammonium salts. All the experiments were performed in DMSO-$d_6$ solvent. Diffusion coefficients and hydrodynamic radii are correlated theoretically by the Stokes-Einstein relation.

\[
D = \frac{kT}{6\pi \eta r_s} \Rightarrow r_s = \frac{kT}{6\pi \eta D}
\]

D is the diffusion coefficient; k is the Boltzmann constant ($1.3807 \times 10^{-23}$ m²Kgs⁻²K⁻¹); T is the temperature in Kelvin; \( \eta \) is the viscosity of the solution (DMSO 1.991 x 10⁻² gcm⁻¹s⁻¹); rs is the hydrodynamic radius of the molecular sphere.
31. **Figure 20S.** $^1$H-DOSY-NMR Spectra of $(n$-Bu$_4^+$)$_2$SO$_4$$_2^-$ in DMSO-$d_6$ at 298 K.
32. **Figure 21S.** $^1$H-DOSY-NMR Spectra of receptor, L in DMSO-$d_6$ at 298 K.
33. **Figure 22S.** $^1$H-DOSY-NMR Spectra of complex, 1 in DMSO-$d_6$ at 298 K.
34. **Figure 23S.** $^1$H-DOSY-NMR Spectra of complex, 1 in DMSO-$d_6$ at 313 K.
35. **Figure 24S.** $^1$H-DOSY-NMR Spectra of complex, 1 in DMSO-$d_6$ at 333 K.
36. **Figure 25S.** $^1$H-DOSY-NMR Spectra of receptor, L in the presence of $n$-Bu$_4$N$^+$H$_2$PO$_4^-$ in DMSO-$d_6$ at 298 K.
37. **Figure 26S.** $^1$H-DOSY-NMR Spectra of receptor, L in the presence of $n$-Bu$_4$N$^+$CH$_3$COO$^-$ in DMSO-$d_6$ at 298 K.
38. **Figure 27S.** $^1$H-DOSY-NMR Spectra of receptor, $L$ in the presence of $n$-Bu$_4$N$^+$NO$_3^-$ in DMSO-$d_6$ at 298 K.
39. **Figure 28S.** $^1$H-DOSY-NMR Spectra of receptor, \( L \) in the presence of \( n\)-Bu$_4$N$^+$Cl$^-$ in DMSO-$d_6$ at 298 K.
40. **Figure 29S.** Partial 1H-NMR spectra of L and downfield shift urea NH groups upon addition of different anions as tetrabutylammonium salts in DMSO-$d_6$ at 298 K.

The large downfield shift of the urea protons $\Delta \delta$ -NH$_c$ 1.47 and $\Delta \delta$ -NH$_d$ 1.73 ppm in the case of sulfate; $\Delta \delta$ -NH$_c$ 0.54 and $\Delta \delta$ -NH$_d$ 0.42 ppm for dihydrogen phosphate; $\Delta \delta$ -NH$_c$ 1.21 and $\Delta \delta$ -NH$_d$ 0.78 ppm for acetate; $\Delta \delta$ -NH$_c$ 0.21 and $\Delta \delta$ -NH$_d$ 0.09 ppm for chloride are observed. The addition of $n$-Bu$_4$N$^+$F$^-$ to the DMSO-$d_6$ solution of the receptor L showed the disappearance of both the urea $\Delta \delta$ -NH$_c$ and $\Delta \delta$ -NH$_d$ signals. This observation may be attributed to the deprotonation of acidic urea protons by more basic fluoride anions. This prohibited us to evaluate the association constant for L with this anion. There are no considerable changes in the chemical shift of the urea protons of L with Br$^-$, I$^-$, ClO$_4^-$ and NO$_3^-$ observed, suggesting energetically unfavorable interaction of L with these anions in solution.
41. **Figure 30S.** Plot of change in chemical shift of urea-NH groups of \( \textbf{L} \) with increasing amounts of \((n\text{-Bu}_4\text{N})_2\text{SO}_4^{2-}\) in DMSO-\(d_6\) at 25ºC.
42. **Figure 31S.** Job’s Plot of L with \((n\text{-Bu}_4\text{N})_2\text{SO}_4^{2-}\) in DMSO-\(d_6\) at 25ºC.
43. **Figure 32S.** Plot of change in chemical shift of urea -NH groups of L with increasing amounts of $n$-Bu$_4$N$^+$H$_2$PO$_4^-$ in DMSO-$d_6$ at 25°C.

$$
\begin{align*}
\Delta \delta & = 2.20911 \times 10^{-5} \\
R^2 & = 0.9959
\end{align*}
$$
44. **Figure 33S.** Job’s Plot of L with $n$-Bu$_4$N$^+$H$_2$PO$_4^-$ in DMSO-d$_6$ at 25ºC.
45. **Figure 34S.** Plot of change in chemical shift of urea -NH groups of L with increasing amounts of \( n\text{-Bu}_4\text{N}^+\text{CH}_3\text{COO}^- \) in DMSO-\( d_6 \) at 25\(^\circ\)C.
46. **Figure 35S.** Job’s Plot of \( L \) with \( n\text{-Bu}_4N^+\text{CH}_3\text{COO}^- \) in DMSO-\( d_6 \) at 25ºC.
47. **Figure 36S.** Plot of change in chemical shift of urea -NH groups of L with increasing amounts of $n$-Bu$_4$N$^+$Cl$^-$ in DMSO-$d_6$ at 25°C.

\[
\chi^2 = 1.11552 \times 10^{-6}
\]

\[
R^2 = 0.99904
\]
48. **Figure 37S.** Job’s Plot of L with $n$-Bu$_4$N$^+$Cl$^-$ in DMSO-d$_6$ at 25ºC.