Synthesis, Spectroscopic Evaluations and UV-Vis Titration Studies of New Symmetrical Amide Compounds Derived from *N*-6-[(4-pyridylmethylamino)carbonyl]-pyridine-2-carboxylic Acid Methyl Ester

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Abstract

In this study, 2 flexible and pre-organized tetraamide compounds derived from *N*-6-[(4-pyridylmethylamino)carbonyl]-pyridine-2-carboxylic acid methyl ester namely 1,2-bis[*N,N'*-6-(4-pyridylmethylamido)pyridyl-2-carboxyamido]pentane (L1) and 1,2-bis[*N,N'*-6-(4-pyridylmethylamido)pyridyl-2-carboxyamido]hexane (L2) have been successfully synthesized when reacted with diamines in 1:2 ratio. These new compounds were built from combination of 3 main components, as a trend requires for anion receptor which are (i) 2,6-pyridine dicarboxamide moieties as targeted anion binding host, (ii) amino methyl pyridine pendants arms as the flexible moieties and (iii) pentyl (-C_5H_{10}-) and hexyl (-C_6H_{12}-) unit as the spacer. Compounds L1-L2 were fully characterized by using elemental analyzer, Fourier transform infrared (FTIR) spectroscopy, gas chromatography-mass spectroscopy (GC-MS), ^{1}H, 2D NOESY and ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopies, and Ultraviolet-visible (UV-Vis) spectroscopies. In this study, anion titration methods were used to identify the affinity towards selected anions. The results showed that L1 (having a pentyl spacer) had the highest affinity towards phosphate anions as compared to L2, where the red shift changes were observed in the UV-vis spectrum at the amide region.

Keywords: Tetraamide, Symmetry, Conformation, Flexible, Anion, Pre-organized

Introduction

Anions play an important role in daily life, especially in biology, medicine, catalysis, industry and agriculture [1]. In reality, anions can have adverse effects on aquatic environment and human health when present beyond the normally acceptable range [2]. Anions are also found in nylon dyes, agricultural wastewater, industrial wastewater, electroplating, metal pickling and leather tanning. The conventional water treatment, such as resins and zeolite are known as efficient to separate anions with high valence, greater atomic weights, and small radii anions such as nitrate and sulphate. Several phosphate detection techniques, such as spectrophotometry, fluorometry and chromatography, are available. However, their time-consuming, labor-intensive and costly characteristics, dependence on skilled operators and hazardous chemicals, make them inappropriate for monitoring purposes [3,4]. Separation or isolation of large radii anions from water such as phosphate requires other suitable materials that are unavailable. Amide compounds have been commonly used as anion receptors either in discrete molecules or coordination polymers, due to the presence of the amide NH binding group [5-7].

Modification to the design of the anion receptors derived from amides normally involved the use of pre-organised amide structures and acidic functional groups to enhance the receptors capability to interact with anions. In a report by Martínez-Aguirre *et al.* [8], aminopyridine functional group was added to acidify the CH and NH bonds which made the receptor a better proton donor for hydrogen bonding. Therefore, in this study, 2 new tetraamide compounds namely, 1,2-bis[*N,N'*-6-(4-pyridylmethylamido)pyridyl-2-carboxyamido]pentane (L1) and 1,2-bis[*N,N'*-6-(4-pyridylmethylamido)pyridyl-2-carboxyamido]hexane (L2). **Figure 1** shows the designated structures of L1 and L2.

n=5 (L1), n=6 (L2)
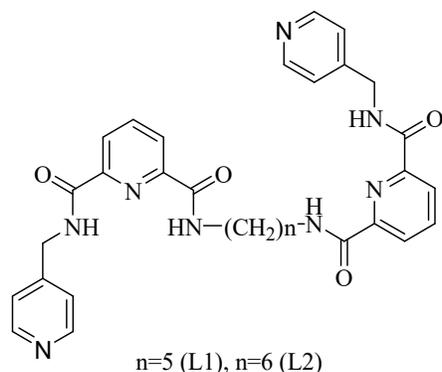
Figure 1 Structure of L1 and L2.

Materials and methods

The syntheses method of L1 and L2 were adapted from the literature study [9] with slight modifications. Further details on the syntheses are reported in the following sub-section. The materials used in this research involved 2,6-dimethylpyridine dicarboxylate, 4-aminomethylpyridine, dilute hydrochloric acid, sodium bicarbonate, sodium sulphate, pentane-1,5-diamine, hexane-1,6-diamine, tetrabutyl ammonium salts (chloride, bromide, nitrate, phosphate and hydrogen sulphate), methanol, toluene, dichloromethane and acetonitrile were used in this study, without further purification. Shimdazu ITRracer 100, Attenuated Total Reflection (ATR) was used for FTIR analysis and the spectrum was recorded in the range of 4,000 - 400 cm^{-1}. Nuclear Magnetic Resonance was recorded using Bruker Advance II 400 spectrometer. UV-Vis analysis was recorded using Spectrophotometer Shimadzu UV-1,800. CHNS Analyzer Flash EA 1112 was used to record CHN elements.

Synthesis of 1,2-bis[*N,N'*-6-(4-pyridylmethylamido)pyridyl-2-carboxyamido]pentane (L1)

N-6-[(4-Pyridylmethylamino)carbonyl]-pyridine-2-carboxylic acid methyl ester (1.01 g, 3.7 mmol) and pentane-1,5-diamine (0.22 mL, 1.9 mmol) were suspended in toluene (40 mL) and heated at reflux under inert atmosphere for 55 h. Thin layer chromatography (TLC) technique was used to monitor the reaction till completion. After the reflux process was completed, the solvent (toluene) was removed by using the rotary evaporator (55 °C at 70 mbar). The product was obtained as an aqueous liquid after removing the solvent. The aqueous liquid solidified on standing for 2 days to give L1 as sticky yellow precipitate (0.93 g, 53 %) Mp 109 - 111 °C. Selected IR bands (ATR, cm^{-1}): 3,278 (m), ν(N-H) str. (asym); 2,931 (m), ν(C-H) str; 1,651 (s), ν(C=O) str.; 1,527 (s), ν(N-H) bend,: 1,419 (m), ν(C-H) bend,: 1,373 (m), ν(C-N) str,: 1,002 (s), ν(C=C) (aromatic). ^{1}H NMR (400 MHz, DMSO-d_6); δ = 1.38 (2H, q, *J* = 6.8 Hz, H-1); 1.63 (2H, q, *J* = 7.2 Hz, H-2); 3.30 (2H, q, *J* = 6.8 Hz, H-3); 4.62 (2H, d, *J* = 6 Hz, H-9); 7.33 (2H, d, *J* = 6 Hz, H-10); 8.20 (3H, m, H-5, H-6, H-7); 8.50 (2H, d, *J* = 4.4 Hz, H-11); 9.33 (1H, t, *J* = 6.4 Hz, H-4) and 9.89 (1H, t, *J* = 6.4 Hz, H-8). ^{13}C (100MHz, DMSO-d_6) ppm: δ = 21.12 (CH$_2$); 24.12 (CH$_2$); 29.37 (CH$_2$); 41.47 (pyCH$_2$NH); 122.06, 128.29, 128.98, 139.64, 148.32, 148.97, 149.70 (C-py); 163.05 and 163.81 (C=O). Anal. Calc. for C$_{31}$H$_{32}$N$_8$O$_4$ (566.61 g/mol): C, 64.12 %; H, 5.55 %; N, 19.30 %. Found: C, 64.27 %; H, 5.61 %; N, 19.35 %.

Synthesis of 1,2-bis[*N,N'*-6-(4-pyridylmethylamido)pyridyl-2-carboxyamido]hexane (L2)

N-6-[(4-Pyridylmethylamino)carbonyl]-pyridine-2-carboxylic acid methyl ester (1.0 g, 3.7 mmol) and hexane-1,6-diamine (0.22 mL, 1.8 mmol) were suspended in toluene (40 mL) and heated at reflux under inert atmosphere for 55 h. Thin layer chromatography (TLC) technique was used to monitor the reaction till completion. After the reflux process was completed, the solvent (toluene) was removed by using the rotary evaporator (55 °C at 70 mbar). The product was obtained as an aqueous liquid after removing the solvent. The aqueous liquid solidified on standing for 2 days to give L2 as sticky yellow precipitate (1.03 g, 62 %) Mp 96 - 98 °C. Selected IR bands (ATR, cm^{-1}): 3,294 (m), ν(N-H) str. (asym); 2,920 (m), ν(C-H) (str); 1,654 (s), ν(C=O) str.; 1,531 (s), ν(N-H) bend,: 1,415 (s), ν(C-H) bend; 1,370 (m), ν(C-N) str; 1,002 (m), ν(C=C). ^{1}H NMR (400 MHz, DMSO-d_6); δ = 1.37 (2H, q, *J* = 8 Hz, H-1); 1.56 (2H, q, *J* = 4 Hz, H-2); 3.32 (2H, q, *J* = 6.4 Hz, H-3); 4.62 (2H, d, *J* = 6.4 Hz, H-9); 7.30 (2H, d, *J* = 6 Hz, H-10); 8.20 (3H, m, H-5, H-6, H-7); 8.49 (2H, d, *J* = 6 Hz, H-11); 9.34 (1H, t, *J* = 6.4 Hz, H-4) and 9.90 (1H, t, *J* = 6.4 Hz, H-8). ^{13}C (100 MHz, DMSO-d_6) ppm: δ = 21.15 (CH$_2$); 26.25 (CH$_2$); 29.56 (CH$_2$); 41.49 (pyCH$_2$NH);

122.09, 128.32, 129.01, 139.71, 148.34, 148.94, 149.70 (C-py); 163.08 and 163.84 (C=O). Anal. Calc. for $C_{32}H_{34}N_8O_4$ (594.66 g/mol): C, 64.63 %; H, 5.76 %; N, 18.84 %. Found: C, 64.42 %; H, 5.61 %; N, 18.67 %.

Results and discussion

The synthetic pathways for flexible tetraamide compounds L1 and L2 are shown in **Scheme 1**. Compound L1 and L2 were synthesized by reacting *N*-6-[(4-pyridylmethylamino)carbonyl]-pyridine-2-carboxylic acid methyl ester with pentane-1,5-diamine and hexane-1,6-diamine, in toluene, respectively. The mixture was heated at reflux until completion, and toluene was evaporated using a rotary evaporator, to yield a yellow oil in the range from 70 - 90 %, which solidified to a sticky yellowish solid after 2 days standing at room temperature. The synthesis of L1 and L2 is facile and straightforward, and the final product was washed with methanol and diethyl ether to remove the remaining unreacted precursor. Structures of L1 and L2 were confirmed using a combination of spectroscopic methods, such as Fourier transform infrared (FTIR), gas chromatography-mass spectroscopy (GC-MS), ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR), 2D NOESY, elemental analysis and ultraviolet-visible (UV-Vis) spectroscopy.
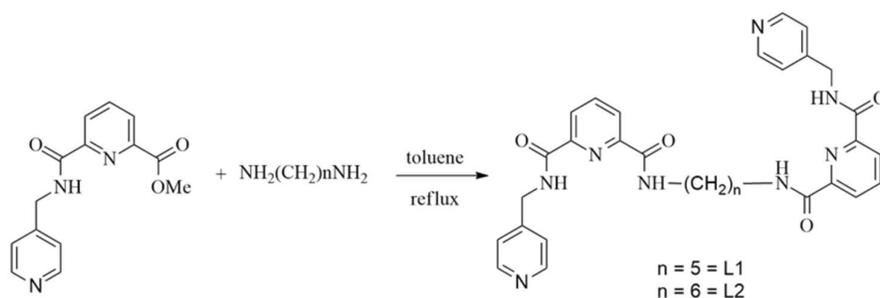

Scheme 1 Synthesis route of L1 and L2.

In the FTIR spectra of L1 and L2, several distinctive peaks representing ν(N-H) stretching, ν(C-H) stretching, ν(C=O), ν(N-H) bending, ν(C-H) bending, ν(C-N) stretching and ν(C=C) aromatic were observed at 3,278 - 3,294, 2,920 - 2,931, 1,651 - 1,654, 1,527 - 1,531, 1,415 - 1,419 and 1,002 cm^{-1}, respectively. From the FTIR spectra, the ν(N-H) stretching of L1 observed at 3,278 cm^{-1} displayed sharp band (**Figure 2**), while the ν(N-H) stretching of L2 has a broadening peak. The ν(C-H) stretching of L1 displays a weak signal peak at 2,925 cm^{-1} respective to the formation of sp^3 hybridization. Compound L2 shows the intense signal of ν(C-H) stretching at 2,920 cm^{-1}. The UV spectra of L1 and L2 showed broad absorption band at λ_{max} 222 - 226 and 275 nm which assigned were to $\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$ transitions. This corresponded to pyridine and C=O moieties, respectively.
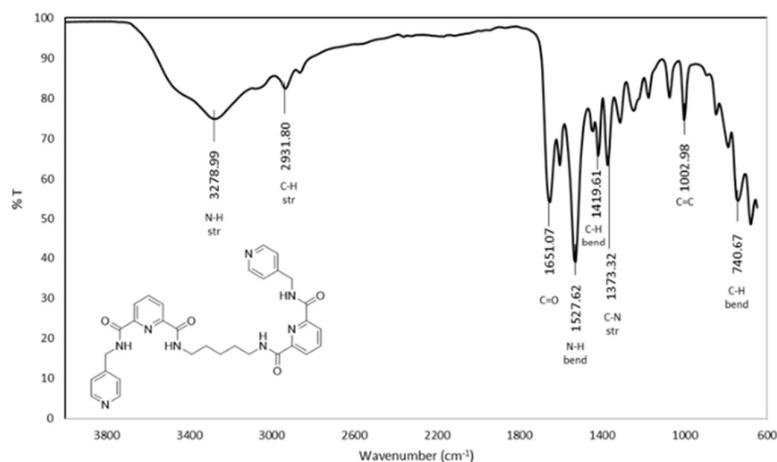
Figure 2 FTIR spectrum of L1.

In the mass spectra of L1 (**Figure 3**), the parent ion was indicated at 107 m/z which stands for half of the symmetrical species. Other fragments peak for *N*-(pyridin-4-ylmethyl)formamide (137 m/z), 6-formyl-*N*-(pyridin-4-ylmethyl)picolinamide (243 m/z) and *N,N*-methyl(pyridine-4-ylmethyl)pyridine-2,6-dicarboxamide (271 m/z) were also indicated. Compound L2 exhibits a significant molecular size and possesses a symmetrical state. As a consequence, the fragmentation of this molecule results in equal division of its fragments. This result can be observed at 295 m/z, indicating the cleavage of the molecule into 2 halves at the hexyl spacer. The ion with a 239 m/z is generated by the process of propan-1-amine elimination from the 295 m/z. Additional fragment peaks were observed for 2-amino-*N*-(pyridine-4-ylmethyl)penta-2,4-dienamide at 203 m/z, pyridine-4-ylmethanamine at 107 m/z and 4-methylpyridine at 93 m/z were indicated. As can be observed in the mass spectra, the molecular arrangements of L1 and L2 can be distinguished by fragments at 271 and 295 m/z, respectively. The fragment shows that molecules L1 and L2 produced 2 identical parts but with different numbers of carbons and hydrogens.

(a)

(b)
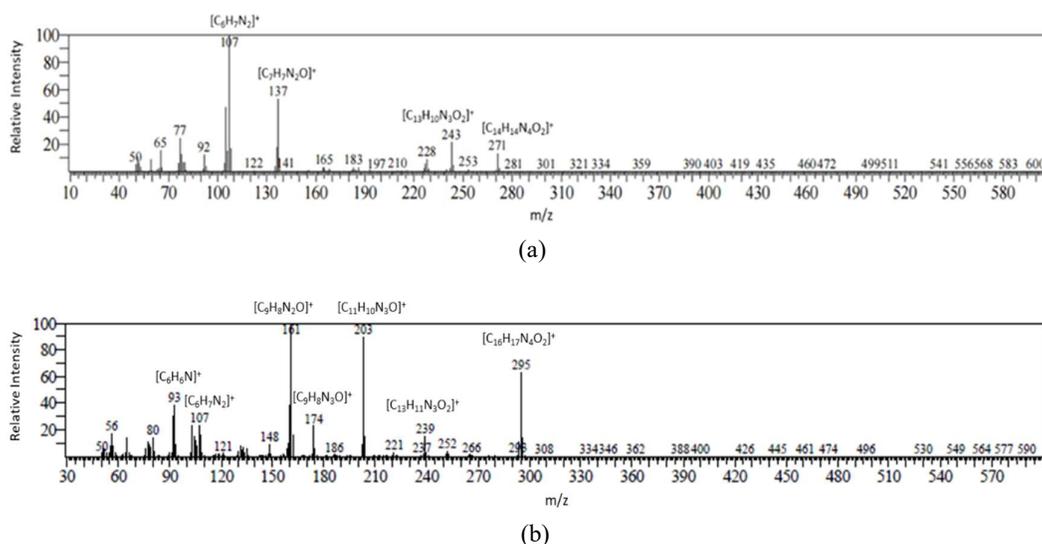
Figure 3 The GC-MS of (a) L1 and (b) L2 showing parent peak at 107 and 161 m/z, respectively.

^{1}H NMR spectra showed a common spectrum for symmetrical compounds as clearly indicated in **Figures 4** and **5**. Compounds L1 and L2, exhibited pentyl and hexyl spacer where protons signals at 1.38 - 3.30 and 1.37 - 3.32 ppm, were indicated, respectively. The chemical shifts for methylene pyridine protons (H-9) and pyridine pendant arms were observed at 4.62 and 7.33 - 8.50 ppm, respectively. In addition to this, 2 signature peaks representing NH amide (H-4) and -NH pyridine (H-8) was observed at 9.33 ppm and 9.89 ppm, respectively. ^{1}H NMR for L1 and L2 has been presented in **Table 1**. In ^{13}C NMR, 3 signals from L1 and L2, which included pentyl and hexyl spacers, both shifted up field area to 21.12 - 29.37 and 21.15 - 29.56 ppm. Clearly from the structure, compounds L1 and L2 have different quantity of CH_2 groups, however, in the spectra, the numerical carbon values are identical as evidence in **Figures 6** and **7**. The resonance signal of CH_2 attached to the pyridine was observed in the range 41.47 - 41.49 ppm for all compounds. Jakob *et al.* [10] stated that methylene (CH_2) resonance signals were within the anticipated range. C-aromatic pyridine signals were observed at 122.06 - 149.10 ppm. There were 2 carbonyl peaks (C=O) observed at a range of 163.05 - 163.81 ppm.

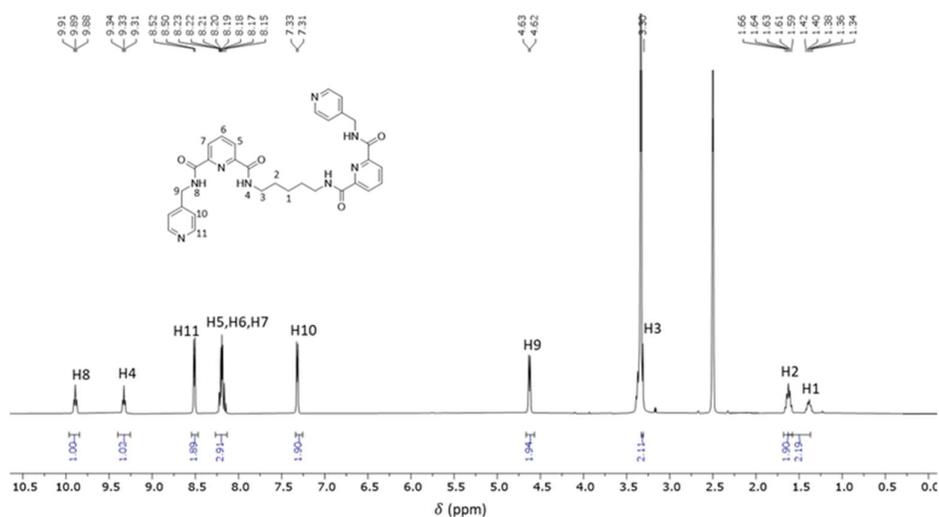**Figure 4** ^{1}H NMR spectrum of L1.

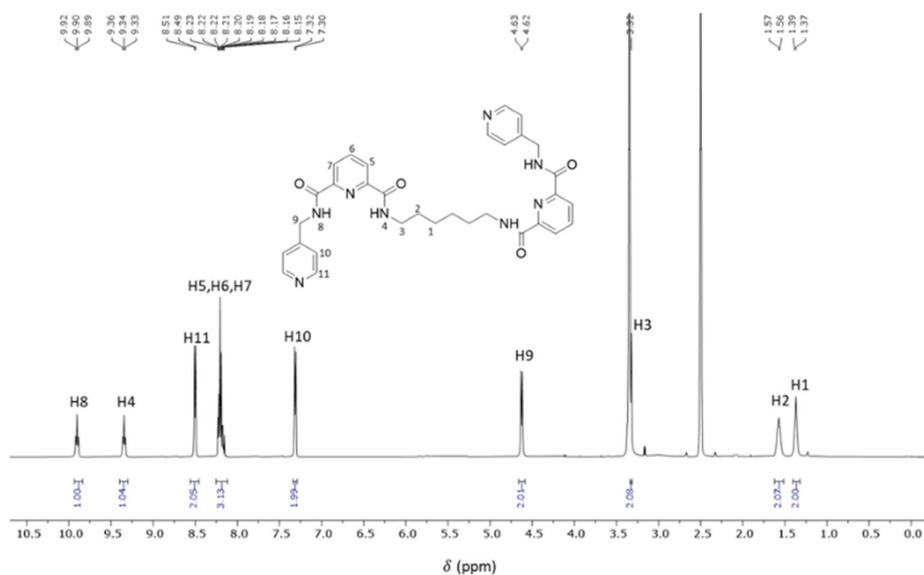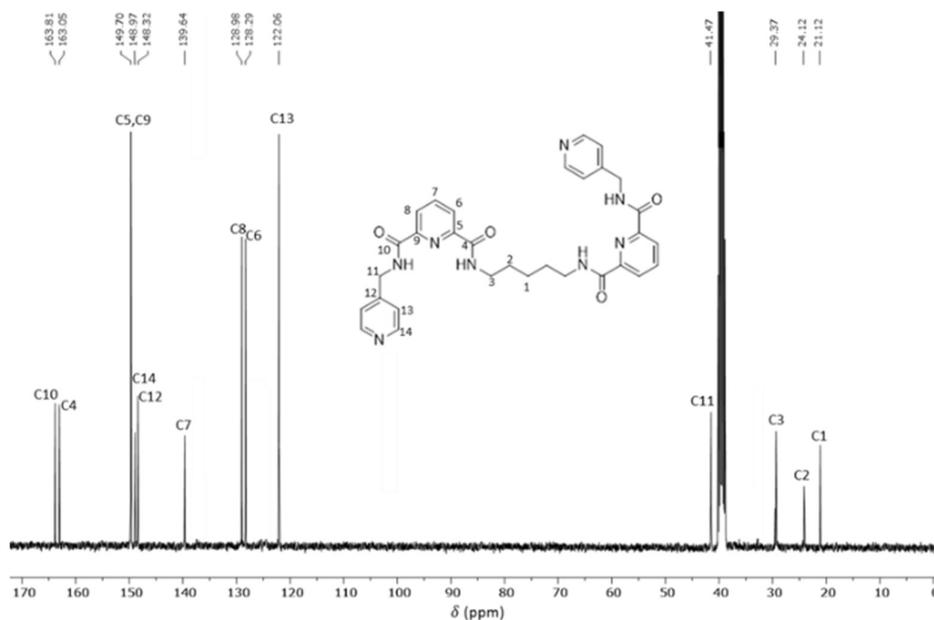**Figure 5** ^{1}H NMR spectrum of L2.

Table 1 ^{1}H NMR data compounds L1 and L2.

| Position	L1	L2
H1	1.38 (q, *J* = 6.8 Hz)	1.37 (d, *J* = 8 Hz)
H2	1.63 (q, *J* = 7.2 Hz)	1.56 (d, *J* = 4 Hz)
H3	3.30 (q, *J* = 6.8 Hz)	3.32 (q, *J* = 6.4 Hz)
H4	9.33 (t, *J* = 6.4 Hz)	9.34 (t, *J* = 6.4 Hz)
H5 - H7	8.20 (m)	8.20 (m)
H8	9.89 (t, *J* = 6.4 Hz)	9.90 (t, *J* = 6.4 Hz)
H9	4.62 (d, *J* = 6 Hz)	4.62 (d, *J* = 6.4 Hz)
H10	7.33 (d, *J* = 6 Hz)	7.30 (d, *J* = 6 Hz)
H11	8.50 (d, *J* = 4.4 Hz)	8.49 (d, *J* = 6 Hz)

Figure 6 ^{13}C NMR spectrum of L1.
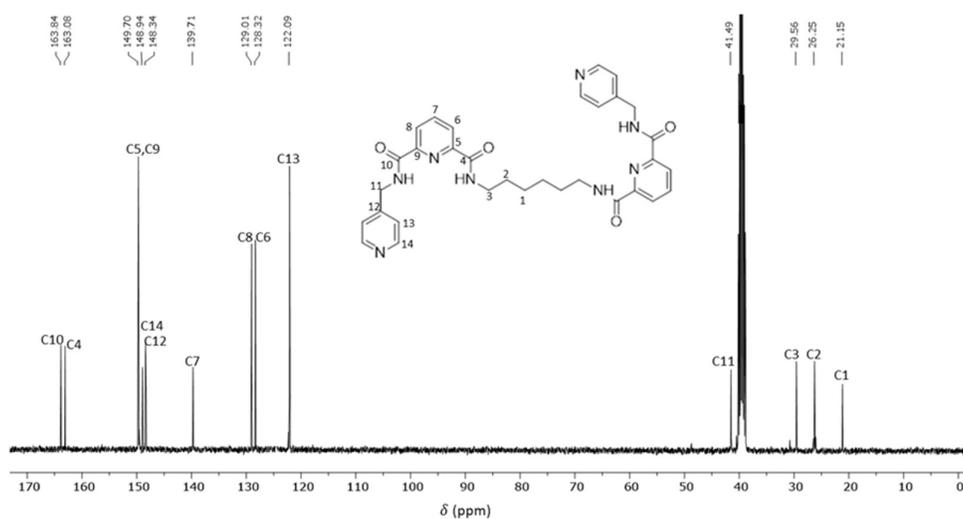
Figure 7 ^{13}C NMR spectrum of L2.

In this study, further investigation on the compounds structure was carried out by using NOESY analysis. In the NOESY spectrum for L1, a cross-peak correlation between H8 at 9.89 ppm with the peak for H10 at 7.33 ppm was indicated. A cross peak connecting H10 (7.33 ppm) with H5, H6 and H7 resonances at 8.20 ppm were determined. In similar for L1, the spectrum shows connecting resonances, such as H9 at 4.62 ppm, H8 at 9.89 ppm and H10 at 7.33 ppm. Resonance signal of H3 (at 3.30 ppm), which shows a cross-peak correlation with H10 (at 7.33 ppm) supports the interaction between the amide moieties. In similar to, the results obtained for L2 shows a cross-peak correlation between H3 with H8 and H10, as expected, due to the clefts of this moieties due to the flexible pendant pyridine arms (**Figure 8**).
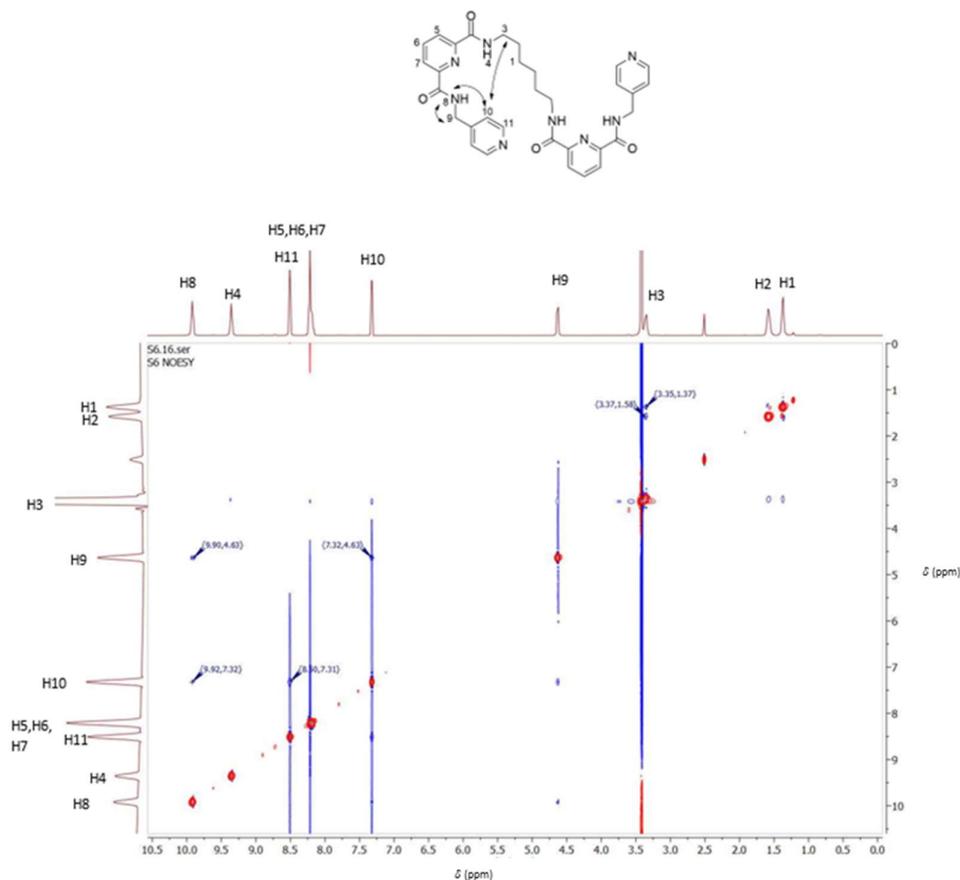
Figure 8 NOESY NMR spectrum of L2.

Anion titration studies

The compounds were examined using naked-eye colorimetric analysis to detect anions in acetonitrile. However, no alterations in color were noted either before or after adding the anions. There is no discernible alteration in color for chloride ions (Cl^-), bromide ions (Br^-), nitrate ions (NO_3^-), phosphate ions (PO_4^{3-}), and hydrogen sulfate ions (HSO_4^-) when added to these 2 new compounds. To the best of our knowledge, based on the preliminary screening analysis, L1 and L2 exhibit a relatively low fluorescence intensity, therefore UV-vis absorption spectroscopy technique is utilized in this preliminary study [11].

UV titration towards selected tetrabutylammonium salts (Br^-, Cl^-, NO_3^-, PO_4^{3-} and HSO_4^-) were further investigated. Two stock solutions were freshly prepared in acetonitrile; for compounds (10 mL, 3.33×10^{-5} M) and another for anions (10 mL, 2×10^{-5} M). In the titration experiment, an aliquot from stock solution of compounds was transferred into 5 separate volumetric flasks, each with a volume of 3 mL. Then, the anions were added in each volumetric flask in different volumes (10, 20, 30, 40 and 50 μL). After adding the anions, the final volume in each flask was adjusted to 10 mL by adding more acetonitrile solvent. This step ensured that the total volume in each flask is the same and consistent across all samples.

When tetrabutylammonium nitrate was titrated into a solution of L1 and L2, the absorption peak of pyridine immediately disappeared. This can be attributed to the cleavage of the conjugated π bond system causing the absorbance of the chromophore to disappear. According to Namashivaya *et al.* [12], nitrate exhibited a significant degree of selectivity, which was necessary for its functioning in an aqueous solution. **Figure 9(a)** depicts the spectra obtained these compounds were titrated with tetrabutylammonium chloride, whereby a blue shift change was observed, from 225 shifted to 221 nm. Similar blue shifts were found when the compounds were titrated with tetrabutylammonium hydrogen sulfate an tetrabutylammonium bromide (**Figures 9(b)** - **9(c)**). L2 has similar properties to L1 when undergoing titration with chloride and bromide ions, resulting in a blue shift from 224 to 222 and 217 nm, respectively. Chakraborty *et al.* [13] proposed that the blue-shifted band could be attributed to the internal charge transfer for deprotonating the -NH moiety at the 2,6-pyridine carboxamide or the hydrogen bonding interactions.

(a)

(b)

(c)
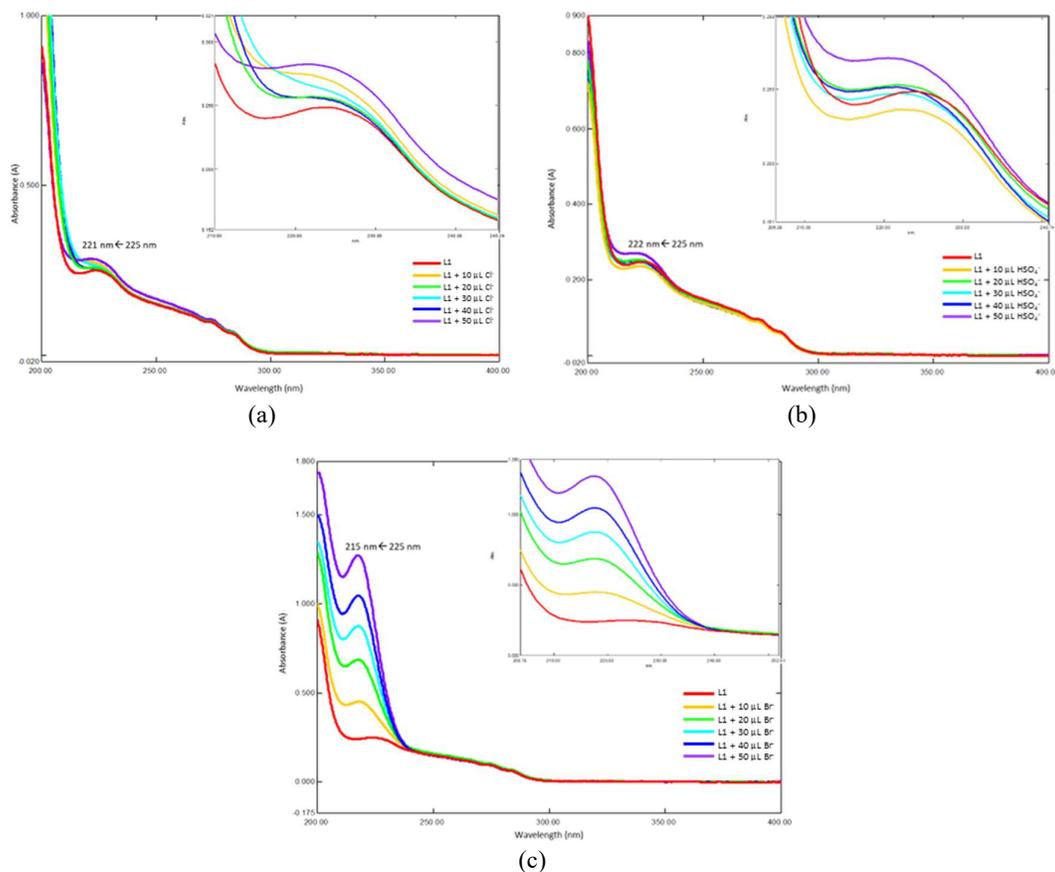
Figure 9 Titration spectra between L1 with (a) chloride, (b) sulfate and (c) bromide.

However, when L1 was titrated with tetrabutylammonium phosphate, a systematic decrease in the absorption band at pyridine was observed. This followed by a red-shift from 221 to 223 nm (**Figure 10**). Khansari *et al.* [14] proposed that the red shift and decreased in absorption band behaviours were attributed to the formation of a $[L(PO_4^{3-})]$ complex. The observed binding sequence based on ^{1}H NMR and UV-Vis titration shows the Hofmeister effect (phosphate (PO_4^{3-}) > sulfate (SO_4^{2-}) > chloride (Cl^-) > bromide (Br^-) > nitrate (NO_3^-)), which indicates that the primary factor governing binding is the relative basicity of anions. The compounds exhibit significant selectivity and align with the Hofmeister trend by showing a preference for binding phosphate anions. In contrast, L2 compound exhibits a blue shift from 224 to 223 nm when it is titrated with phosphate anions. L1 and L2 have different performance of anion titrations, where the strength of anion interaction decreases with an increase in the number of alkyl chain. According to a study conducted by Lopez-Martinez *et al.* [15], the length of the alkyl chain contributes to the steric effect. On the other hand, as the number of alkyl groups incorporated into the molecule increases, the available spatial volume for forming the covalent bond with the electrophile diminishes. Hence, with an increase in steric bulk such as L2, may experience hindrance in its ability to undergo specific reactions that allows the conformational changes in anion complex formation compared to L1.
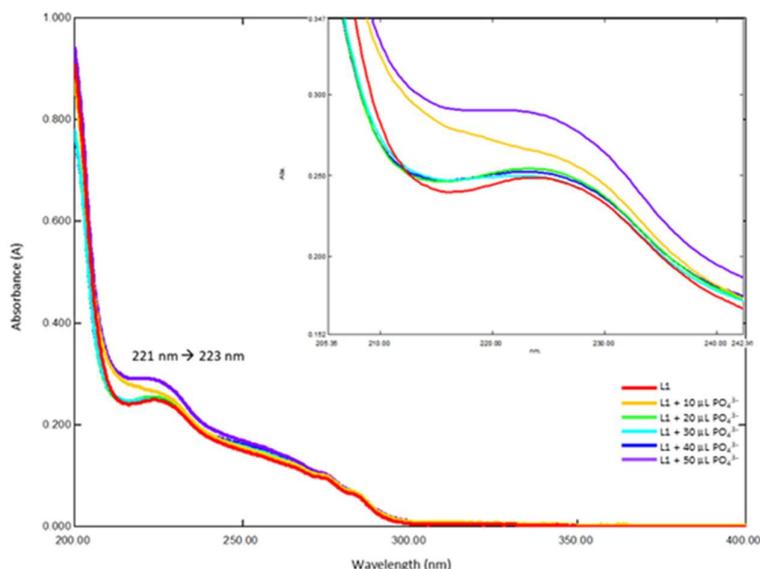
Figure 10 UV-vis titration spectrum when titrated with phosphate anions.

Conclusions

In summary, 2 new flexible and pre-organized tetraamide compounds containing carboxamide NH binding hosts which potentially designed as anion receptors have been successfully synthesized and characterized. UV-vis titration techniques were used to investigate the compound's interaction with anions. From the UV titration results, addition of anions (chloride, phosphate, hydrogen sulphate and bromide) provided significant absorbance changes, showing potential to bind with the studied anions except for nitrate. However, amongst all, ligand L1 (pentyl spacer) showed a high affinity towards phosphate anions as recommended by Hofmeister trend. This is also supported by L1 structure that has shorter alkyl spacer compared to L2 which attributes to less steric affects in the anion complex formation.

Acknowledgements

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