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Anion Titration Studies of Flexible Amide Ligands Bearing Propyl Spacer as Potential Anion Receptors for Dichromate

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Amide compounds are appealing organic ligands that can be further customized to produce a wide range of coordination polymers or metal-organic frameworks. Because of their crucial significance as anion receptors, they have also been a target used in the biological and chemical industries as potential materials for separation or chemical sensor. In this study, the addition of a propyl spacer to an amide ligand was utilized to increase flexibility, size of cavity, and potentiality of the molecules as anion receptors. Therefore, in this study, two flexible amide containing propyl spacer, namely 1,2-bis[*N,N'*-6-(3-pyridylmethylamido)pyridyl-2-carboxyamido] propane (L1), and 1,2-bis[*N,N'*-6-(4-pyridylmethylamido)pyridyl-2-carboxyamido]propane (L2), which were obtained from the reaction between *N*-6-[(3-pyridylmethylamino)carbonyl]-pyridine - 2-carboxylic acid methyl ester with 1,3-propylenediamine, respectively, were utilized. Combination of typical analytical and spectroscopy techniques such as Nuclear Magnetic Resonance (NMR), Fourier Transform Infrared (FTIR), and Ultraviolet-Visible (UV-Vis) were used to characterize these two isomers. Initial investigation on the potential of these compounds to act as anion receptors was carried out using anion titration techniques. The results obtained from this method showed that L1 and L2 have promising potential to interact with dichromate anions compared to nitrate and chloride.

Key words: Amide; dichromate; propyl; spacer; titration

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Anion pollution can be caused by fertiliser run-off, metallo-toxic anions, agricultural and industrial waste [1]. Even at sub-micromolar concentrations, anions in groundwater can be harmful to human health [2]. Chromate for example, has been classified as toxic anions. This anion has been widely used in industrial such as chromate salt production, electroplating, metal pickling, and leather tanning. Exposure to chromate can lead to the risk of respiratory tract cancer, effecting other internal organs such as gastrointestinal tract and lead to genetic of DNA damage [3]. It is a highly toxic carcinogen due to its strong oxidizing potential and high mobility across the cell membrane. Other anions are essential but the excess can bring harm. Abundant concentration of nitrate leads to low nitrogen-use efficiency and accelerates eutrophication of water [4]. Conventional methods such as flocculation and filtration are not suitable to separate this anion from water.

The term flexible ligand is used to describe the properties of a molecule that is incorporated with a functional group that has a flexible spacer or linker. The flexible ligand can adopt different conformations and low symmetry due to rotations between C-C single bonds, such as owned by alkyl chains [5]. As an advantage of this flexibility, the ligand bends and rotates when coordinating with a metal center or counter anion and it can fold on their own, which is used to block the anion pocket from anions encapsulation or solvent molecules. Aliphatic amine linker, for example, can form a large structure that can capture solvents or anions, and give rise to the formation of interpenetrating frameworks [6]. Therefore, flexible ligands are used to construct metal−organic framework systems with a flexible backbone, and this approach can reveal an adaptive ability of the "breath effect" in supramolecular interactions [7].

Instead of being prominently used as ligands, amide has been frequently employed as a neutral anion sensor due to its effective binding and capacity to establish hydrogen bonds with anions. Amide can recognize counter anion and the incoming molecule via hydrogen bonding interaction. Moreover, the N-H bond donor group can act effectively as a neutral anion receptor. The anion receptor interaction can generate π electron delocalization and the basic anion

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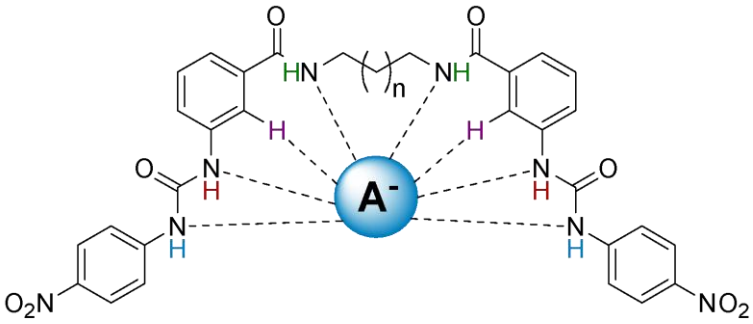


Figure 1. Chemical structure of oligomethylene bis(4-nitrophenylureylbenzamide) with anion binding [9]

can cause N-H deprotonation, which acts as the signal output [8]. For example, a study on oligomethylene bis(4-nitrophenylureylbenzamide) (Figure 1) shows that this molecule can act as bifunctional receptor, where the anions were interacted through weak hydrogen bonding at amide NH moieties [9].

Motivated by the interest in the recognition and detection of anions, many researches have been conducted with a focus on the non-covalent interaction between amide ligands and anions, which involved hydrogen bonds interaction [10,11]. Furthermore, the incorporation of ligands possessing hydrogen bond (H-bond) moieties has also become a strategy of the first choice to synthesis coordination frameworks capable of interactions with anions. Amides are the most extensively employed hydrogen bond donors in hydrogen-bonding receptors because of their ease of synthesis, albeit the presence of C=O hydrogen bond acceptor in these anion binding sites might be inconvenient due to aggregation effects. This inconvenience can be avoided by using pyrrole or imidazole as anion binding in the structures of anion receptors. Furthermore, the CH bond is polarized by the collective electronegativity of the three nitrogen atoms, which, when combined with the lone electron pairs on the nitrogen atoms, forms a massive 5D dipole oriented along with the CH bond.

They are interesting candidates for amide bond surrogates because the combination of intramolecular N−H···O hydrogen bonding and aromatic π-π stacking between the receptor's flexible arms results in a highly organized hydrogen-donating cavity [11]. The group of amide hydrogen bond donors was chosen for two reasons: they are often utilized to bind anions and they can be easily synthesized in large quantities in high yielding

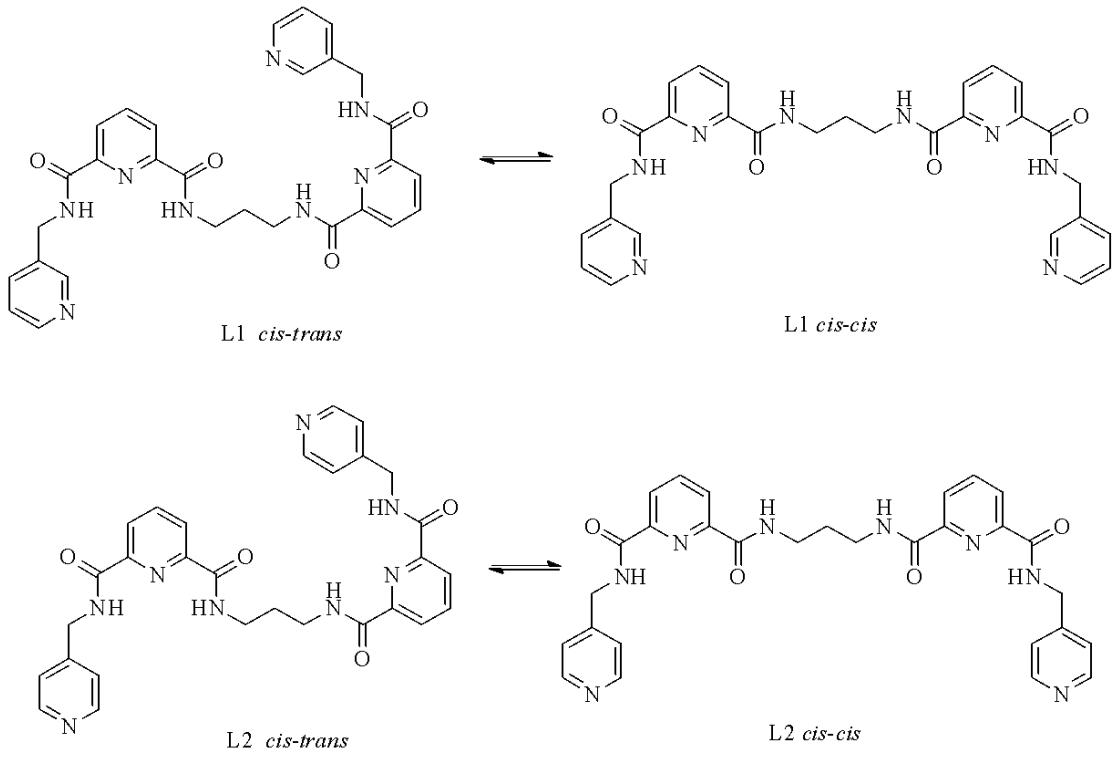


Figure 2. Structure of L1 and L2

processes [12]. As anion binding sites, amide ligands integrated with N-H amide and appeared to maintain their U-shaped structure in the solid-state [13]. The amide ligands were designed for anion binding, hence a pre-organized amide was used to direct the NH amide into the cavity of molecule. The anion can be confined in the amide cavity using this design, where interaction between the ligand and anion molecules occurs via weak hydrogen bonds.

Therefore, in this research, two isomers of flexible amide ligands, namely 1,2-bis[*N,N'*-6-(3-pyridylmethylamido)pyridyl-2-carboxyamido]propane (L1) and 1,2-bis[*N,N'*-6-(4-pyridylmethylamido) pyridyl-2-carboxyamido]propane (L2) (Figure 2) were synthesized. Both ligands contained two expanded pre-organized amide structures that were useful as anion pockets. The merging of linker groups gave different conformation options around the relationships, thus forming a different molecular geometry at the starting point in which supramolecular aggregated with different electronic couplings [14]. Propyl linkers can help to minimize adverse swelling close to the conjugated spine and to balance the conduction properties of a mixture of n-type in aqueous electrolytes [15]. Due to the independent torsional and well adaptation quality, the flexible ligands exhibited variable coordination modes. The flexible ligands can adopt different conformational arrangements to capture anion in varying size and shape. As shown in Figure 2, these ligands can be formed in two geometries, either in *cis-trans* conformation or *cis-cis* conformation. Previous study has investigated the conformation of flexible ligands via computational studies and crystal structure, where it was preferable to form *cis-trans* conformation in that influenced by intermolecular interaction with solvent molecules or anions due to the rotation at one of 2,6-pyridine dicarboxamide entity [10].

MATERIALS AND METHODS

These chemicals were used without further purification. The chemicals and solvents involved were 2,6-dimethylpyridine dicarboxylate, 3-aminomethylpyridine, 4-aminomethylpyridine, dilute hydrochloric acid, sodium bicarbonate, sodium sulphate, 1, 3 -propylenediamine, potassium dichromate, potassium chloride, potassium nitrate, methanol, toluene, dichloromethane, and acetonitrile. Compounds L1 and L2 were prepared using the literature procedures with several modifications [10] which are described as follows:

Synthesis of 1,2-bis[*N,N*'-6-(3-pyridylmethylamido) pyridyl-2-carboxyamido]propane (L1)

A suspension of *N*-6-[(3-pyridylmethylamino) carbonyl]-pyridine-2-carboxylic acid methyl ester (0.50 g, 1.8 mmol) and a slight excess of 1,3-propylenediamine (0.065 mL, 0.96 mmol) in toluene (40 mL) was heated at reflux for 36 h with nitrogen. The solvent was removed in vacuo to give a brown solid. The solid was purified by flash column chromatography on silica gel, eluting with 1:9 methanol–CH_2Cl_2, to give L1 as a cream solid (0.32 g, 62%). Mp 171–172 ℃. The analysis found the following: C, 61.80; H, 5.00; and N, 19.64. $C_{28}H_{30}N_8O_5$ required C, 61.03; H, 5.31; N 19.64. ^{1}H NMR (400 MHz) δ = 1.63 (2H, m, *CH*$_2$CH$_2$NH), 1.74 (2H, m, CH$_2$*CH*$_2$NH), 4.62 (2H, d, J = 6.45 Hz, pyCH$_2$*NH*), 7.34 (1H, m, H9), 7.72 (1H, d, J = 7.87, 4.80 Hz, H10), 8.27 (3H, m, H4, H5, H6), 8.45 (1H, m, H11), 8.58 (1H, m, H12), 9.48 (1H, t, NH), and 9.88 (1H, t, NH). ^{13}C NMR (75.1 MHz) δ =163.85, 163.21, 150.93, 148.83, 148.33, 147.77, 139.58, 138.22, 134.93, 134.79, 123.56, 122.79, 122.68, and 20.49. Selected IR bands (ATR, cm^{-1}) were as follows: 3287 (m), 1657 (s), 1524 (s), 1433 (m), 1312 (m), 1073 (m), and 999 (m).

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

A suspension of *N*-6-[(4-pyridylmethylamino) carbonyl]-pyridine-2-carboxylic acid methyl ester (0.50 g, 1.8 mmol) and a slight excess of 1,3-propylenediamine (0.065 mL, 0.96 mmol) in toluene (40 mL) was heated at reflux for 36 h with nitrogen. The solvent was removed in vacuo to give a brown solid. The solid was purified by flash column chromatography on silica gel, eluting with 1:9 methanol–CH_2Cl_2, to produce L2 as a cream solid (0.29 g, 55%). Mp 145–46 ℃. The analysis found the following: C, 59.28; H, 5.12; and N, 19.21. ($C_{29}H_{32}N_8O_6$) required C, 59.16; H, 5.49; N 19.04. ^{1}H (400 MHz) δ = 1.78 (4H, m, *CH*$_2$CH$_2$NH), 1.86 (4H, m, CH$_2$*CH*$_2$NH), 4.62 (4H, m, py*CH*$_2$NH), 7.32 (4H, m, H9), 8.22 (6H, m, H4, H5, H6), 8.50 (4H, m, pyH10), 9.53 (2H, m, CH$_2$CH$_2$*NH*) and 9.94 (2H, m, NH). ^{13}C (75.1 MHz; DMSO-d_6; Me$_4$Si) δ= 164.38, 163.70, 150.06, 149.10, 148.70, 148.32, 140.09, 124.90, 124.83, 122.44, 41.89, 36.92, and 30.28. Selected IR bands (ATR, cm^{-1}) were as follows: 3228 (m), 1658 (s), 1531 (s), 1415 (m), 1315 (m), 1072 (m), and 999 (m).

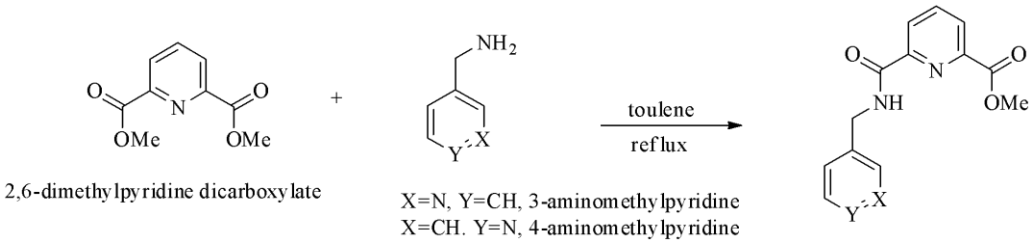
Anion Titration Study

Preparation of Stock Solutions

Stock solution of L1 and L2 (3.33 x 10^{-5} M) and stock solutions of anions (1.0 x 10^{-2} M) were prepared in acetonitrile.

Preparation of Working Standards Solution

3 mL of stock solution of ligands was transferred into five separate volumetric flasks (10 mL). Then, in each volumetric flask, 10 µL, 20 µL, 30 µL, 40 µL, and 50 µL was added. The mixture was marked up to 10 mL with acetonitrile to reach a concentration of 1.0 x 10^{-5} M for each standard.

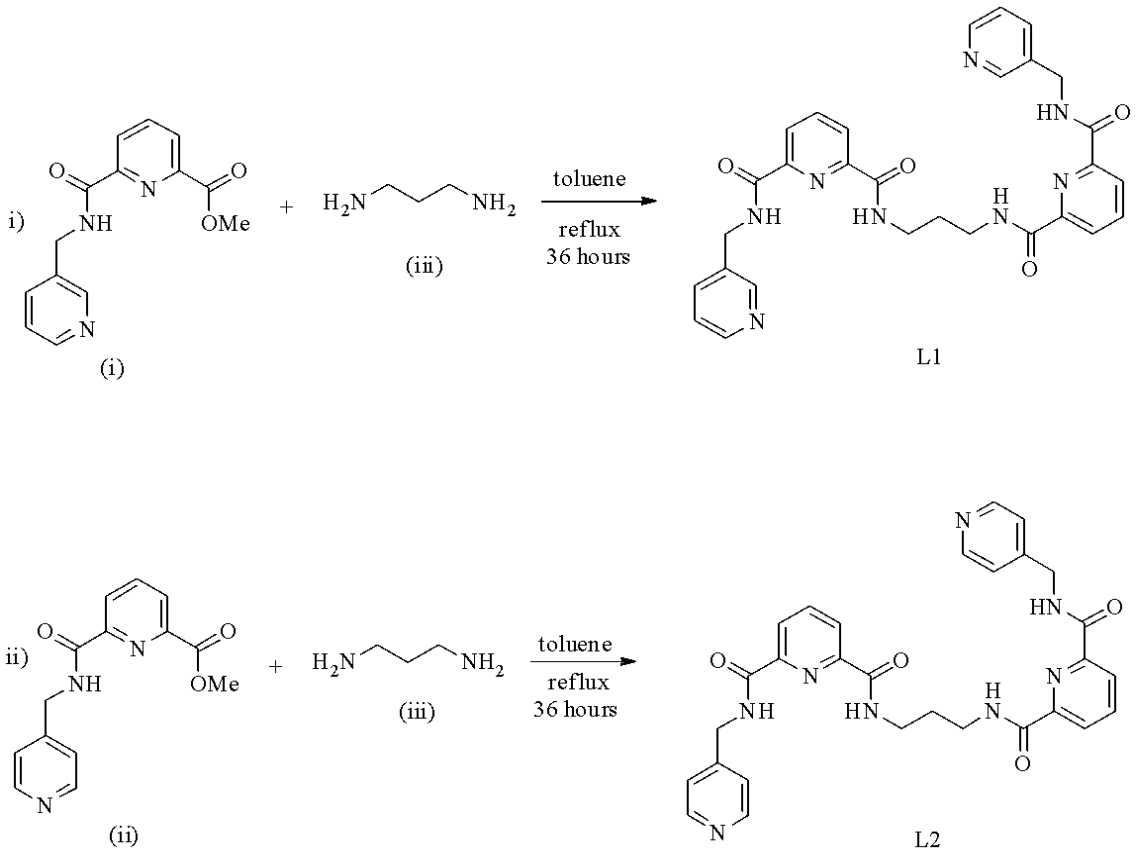


Scheme 1. Synthesis of *N*-6-[(*N*-pyridylmethylamino)carbonyl]-pyridine-2-carboxylic acid methyl ester

RESULTS AND DISCUSSION

This study draws attention to the synthesis of two flexible amide ligands of L1 and L2. The compounds of L1 and L2 were prepared based on the paper reported [10] by refluxing 1,3-propylenediamine with *N*-6-[(N-pyridylmethylamino)carbonyl]-pyridine-2-carboxylic acid methyl ester at a ratio of 1:2. To prepare these two compounds, methyl ester precursor, which was derived from 2,6-dimethyl pyridine dicarboxylate, was synthesized (Scheme 1). To synthesize the precursors, 1 mol of 2,6-dimethylpyridine dicarboxylate and 3-aminomethyl pyridine (or 4-aminomethylpyridine) were suspended in toluene, and underwent inert atmosphere to reflux. The reaction was monitored by thin-layer chromatography (TLC) until the reaction was completed. After completion, the toluene was removed by using a rotary evaporator. Then, the residue was dissolved in dichloromethane and washed with dilute hydrochloric acid before the dichloromethane layer was discarded. The aqueous extract was neutralized with sodium bicarbonate and extracted with dichloromethane, dried over sodium sulphate and the solvent was removed in vacuo.

Synthesis of L1 required reactions between *N*-6-[(3-pyridylmethylamino)carbonyl]-pyridine-2-carboxylic acid methyl ester (i) and 1,3-propylenediamine (iii) in toluene. The suspended mixture was heated at reflux under nitrogen for 36 hours. After the reaction was completed, toluene was removed by using a rotary evaporator to produce the compound as a brown solid. A similar result was obtained when *N*-6-[(4-pyridylmethylamino) carbonyl]-pyridine-2-carboxylic acid methyl ester (ii) reacted with 1,3-propylenediamine (iii). Scheme 2(i), and 2(ii) that showed synthetic route for the preparation of L1 and L2.



Scheme 2. Synthesis of L1 and L2

Typical analytical and spectroscopy techniques such as Nuclear Magnetic Resonance (NMR), Fourier Transform Infrared (FTIR), and Ultra-violet-Visible (UV-Vis) were used to analyze the produced compound. The existence of methyl, aromatic carbon, and amide resonance at δ_H 1.63-4.62 ppm, 7.32-8.58 ppm, and 9.48-9.94 ppm, respectively, were found by ^{1}H NMR spectroscopy. Meanwhile, the infrared analysis indicated the presence of three primary absorptions, which were $_{vstr}$(N-H), $_{\nu}$(C=O), and $_{\nu}$(C=N) with wavelengths of range 3228 -3287 cm^{-1}, 1657-1658 cm^{-1}, and 1312-1415 cm^{-1}, respectively. The FTIR and NMR spectra can be referred to the supplementary data file.

MS study of L1 and L2 showed that these molecules disassociated into few species (Figure 3). The fragmentation peaks for 4-methyl pyridine, *N*-(pyridin-4-ylmethyl)propionamide, *N*-(3-forma mido propyl)picolinamide and *N*-propyl-*N*-(pyri din-4-ylmethyl)pyridine-2,6-dicarboxamide were indicated at 93 m/z, 161 m/z, 203 m/z, and 295 m/z, respectively. Similar results were obtained for L1.

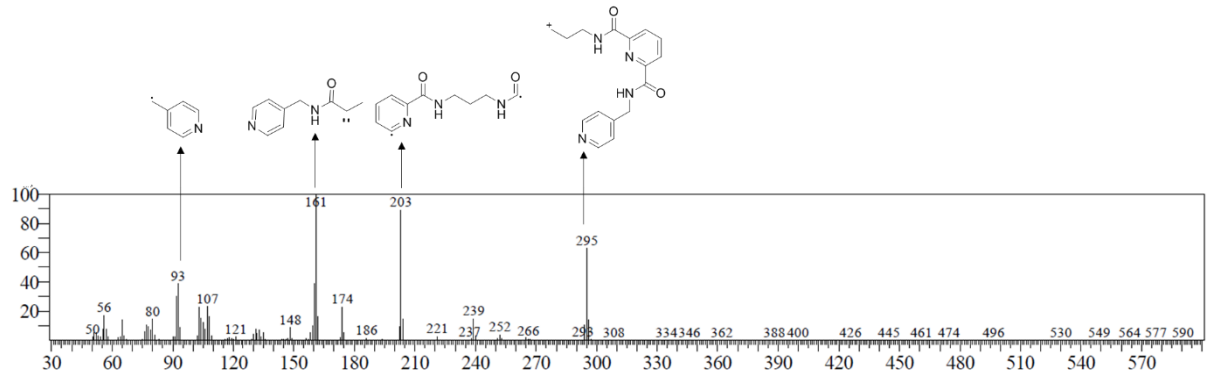
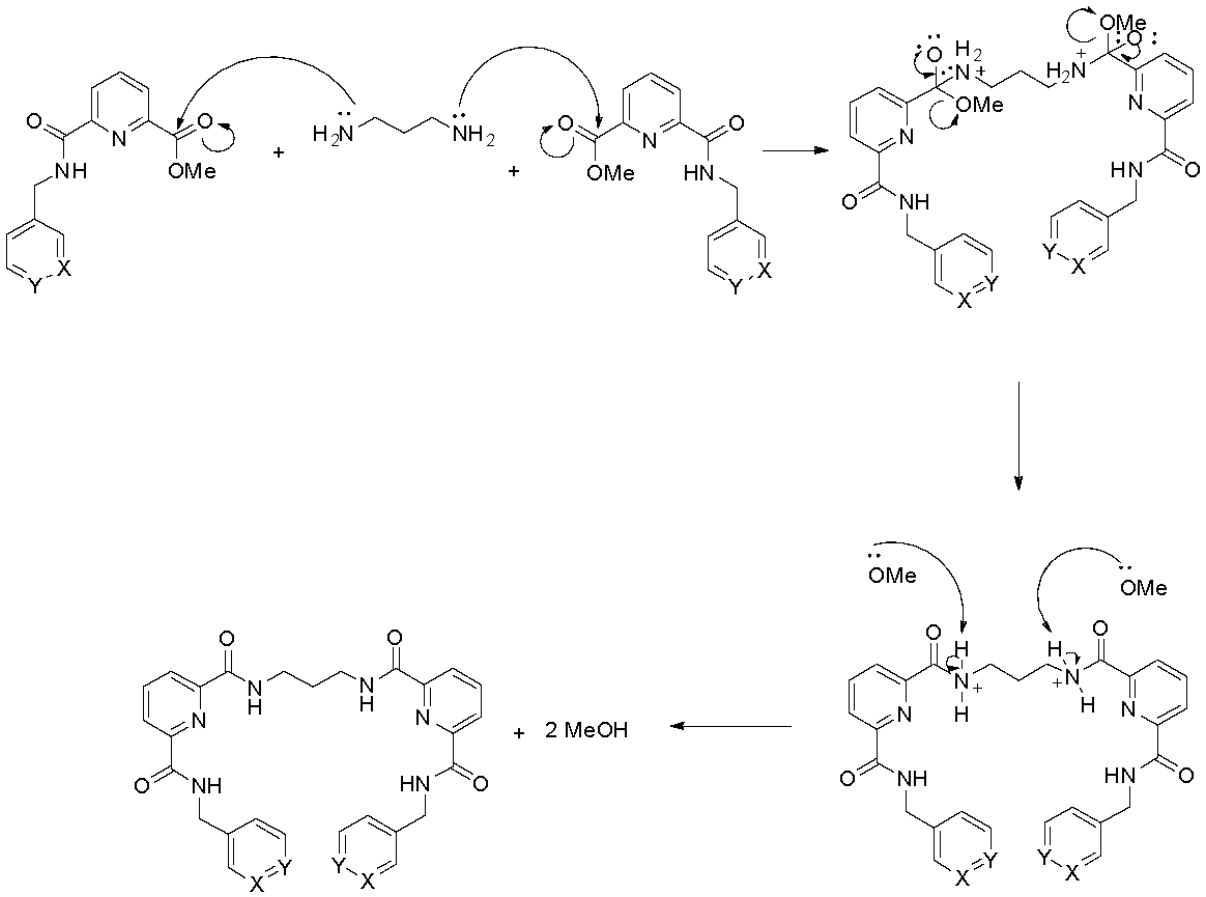


Figure 3. The GC-MS spectrum of L2



Scheme 3. Mechanisms formation of L1 and L2

As illustrated in Scheme 3, the mechanism for the formation of L1 and L2 was proposed. The reaction was initiated with the nucleophilic attack from the nitrogen atom on 1,3-propylenediamine towards the carbon carbonyl. The NH_2 group on 1,3-propylenediamine acted as a neutral nucleophile because it contained lone pair of electrons. It resulted in the formation of a sp^3 hybridized intermediate that has a negative charge on the oxygen atom. The lone pair from the oxygen atom reformed the π bond causing the methoxy group to depart the molecule. To be specific, the methoxy group is known as a good leaving group due to the p*K*a value being much weaker compared to amine.

According to UV spectra, the amide ligand had an absorption at λ_{max} 254 nm (n to π*) for the carbonyl group and 223 nm (π to π*) for the pyridine group. UV-Vis spectrum is a crucial tool to indicate the responses of a host with analyte. From the UV-Vis spectra of L1 and L2 (Figure 4), the presence of two absorption peaks that corresponded to the carbonyl and pyridine groups were determined. Based on the UV-vis spectrum of L1, the absorbance of the carbonyl group at max 254 nm that represented transition from n-π* and the pyridine group at λ_{max} 223 nm that indicated the transition from π to π* (carbonyl and pyridine groups) were found. This absorbance adopted molar absorption values of 14900 M^{-1} cm^{-1} and 25100 M^{-1} cm^{-1}, respectively. Similar absorbance reading for L2 is listed in Table 1.

As reported in previous study [11], the absorbance of analyte increases as the concentration of analyte is increased. Meanwhile, the ligand's absorbance was reduced due to the weakening of binding between the ligand (host) and the analyte that had occurred in the solution. This pattern suggested that the formation of a saturated anion-complex solution had occurred in the solution. Based on this situation, the anion titration study of L1 and L2 with three anions, which are chloride, nitrate and dichromate were carried out. Table 2 shows the volume of ligands and anions used for anion titration study.

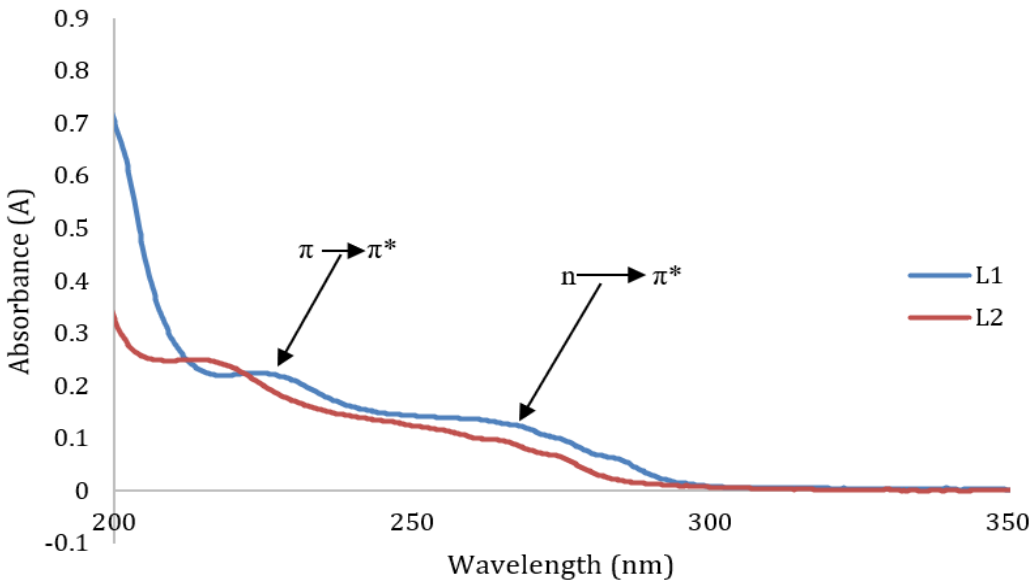


Figure 4. UV-Visible spectrum of L1

Table 1. UV-Visible data of L1 and L2

Compounds	$\pi \rightarrow \pi^*$ (nm)	$n \rightarrow \pi^*$ (nm)
L1	223	254
L2	224	255

→

Table 2. The volume used for anion titration study

Sample	Volume (µL)		Endpoint volume (10mL)	The concentration of anions in a 10 mL volumetric flask (M)
	Amide ligand	Anions		
1	3000	-	3mL ligand + 7 mL solvent	-
2	3000	10	3mL (ligand) + 10 µL (anion) + 6.99 mL solvent	1 x 10^{-5}
3	3000	20	3mL (ligand) + 20 µL (anion) + 6.98 mL solvent	2 x 10^{-5}
4	3000	30	3mL (ligand) + 30 µL (anion) + 6.98 mL (solvent)	3 x 10^{-5}
5	3000	40	3mL (ligand) + 40 µL (anion) + 6.97 mL (solvent)	4 x 10^{-5}
6	3000	50	3mL (ligand) + 50 µL (anion) + 6.95 mL (solvent)	5 x 10^{-5}

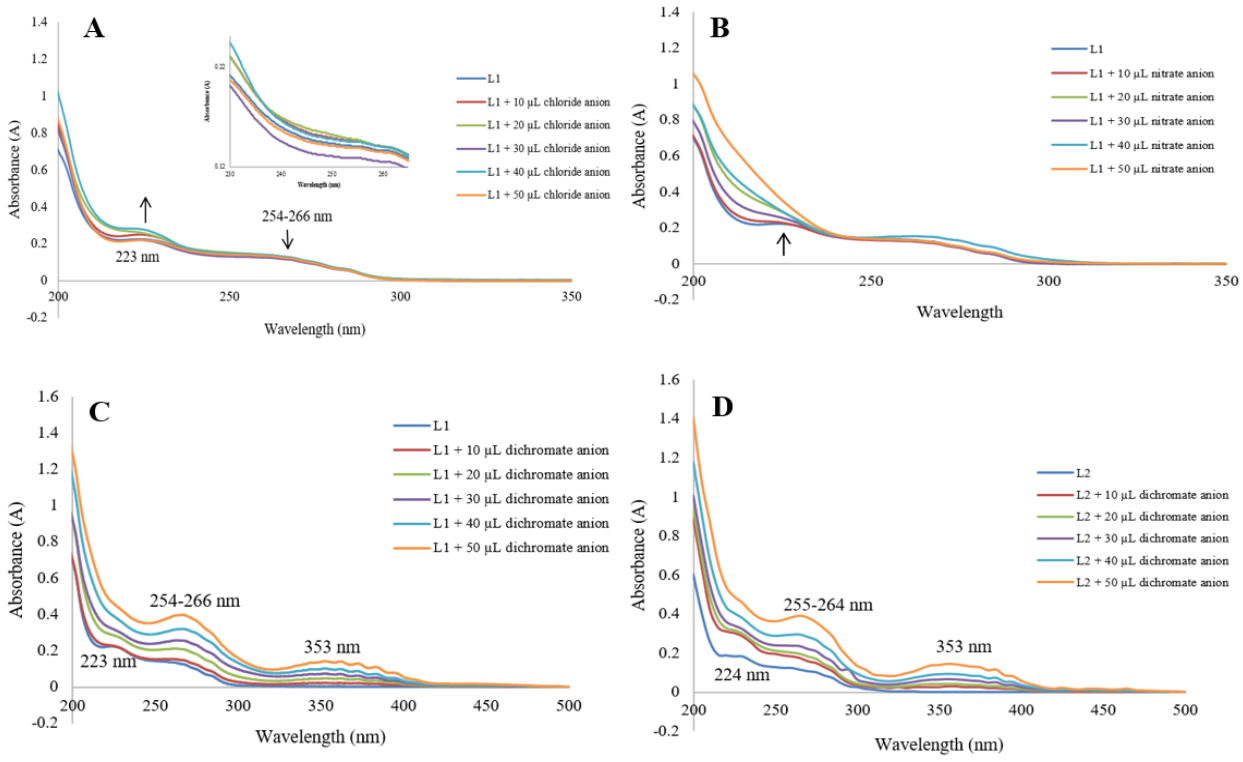


Figure 5. L1 with (a) chloride (b) nitrate (c) dichromate anions and (d) L2 with dichromate anions

However, the UV-Vis spectra of these three analytes gave different patterns of absorbance. The change in the absorbance of L1 at 223 nm and 254 nm due to the addition of anions, was not consistent. For instance, the absorbance of L1 at 223 nm was gradually increased and then dramatically decreased when high concentration of chloride (5 x 10^{-5} M) was titrated. In other observation, the interest peak of

absorbance at 254 nm underwent a consistent bathochromic shift to 266 nm when more chloride anions were added, indicating the interaction of the anions to the carbonyl moieties occurred, which was not within the amide NH moieties as expected (Figure 5 (a)). Similar inconsistent increasing peaks at 223 nm was also given by L1 and L2 when titrated with nitrate anions, but the absorbance peak at 254 nm disappeared when more nitrate was added (Figure 5(b)). As reported in a previous study, a low UV absorbance indicates two possibilities: (i) creation of a saturated anion complex, or (ii) weakening of anion-receptor interaction because the anion is highly concentrated.

The UV-Vis titration was continued with dichromate anions. Interestingly, the result showed consistent changes in the interest peaks at 223 nm and 254 nm, respectively. Firstly, there were overlapping peaks at 223 nm when the lowest concentration of dichromate anion was titrated with L1 and L2. After consistent addition of dichromate anion, a constant change in absorbance was indicated, showing potential weak binding through hydrogen bonding interactions [16]. For example, as shown in Figure 5 (c), as the concentration of dichromate anion was increased, the absorbance of dichromate anion at 353 nm also increased as expected. In return, the absorbance of the ligand at 223 nm gradually disappeared, indicating the presence of strong interaction or binding at the pyridine moieties as expected [13]. In addition, the carbonyl peak absorbance at 254 nm underwent gradual red shifts to 266 nm along with the addition of dichromate anions. Interestingly, the dichromate peaks at 353 nm were also seen in the spectrum. Titration with L2 also gave similar results as L1 (Figure 5 (d)).

CONCLUSION

In conclusion, L1 and L2 have been successfully synthesized and structurally characterized. The recognition of three anions, nitrate, chloride, and dichromate was studied by using UV-Vis titration. Based on the present work, the studies showed that L1 and L2 have potential to be used as receptors for dichromate compared to chloride and nitrate anions, based on the presence of strong interaction or binding at the pyridine moieties with dichromate anions. It is also showed from this study that the position of nitrogen atom at the pyridine group from the two isomers (meta and para) does not influence the interactions of the ligands with anions.

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SUPPLEMENTARY FILE

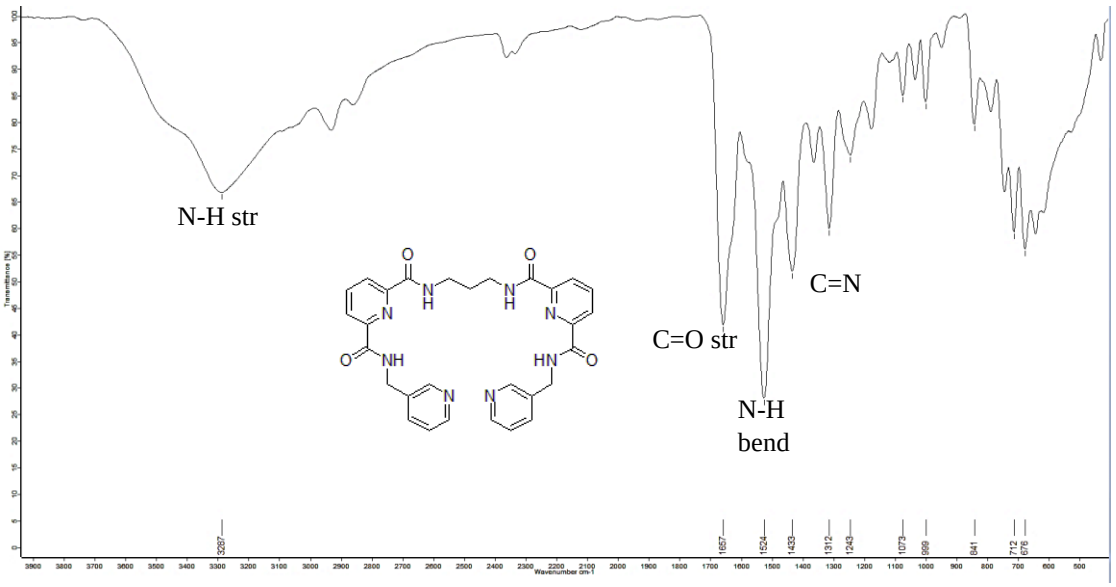

Figure S1. FTIR spectrum of L1

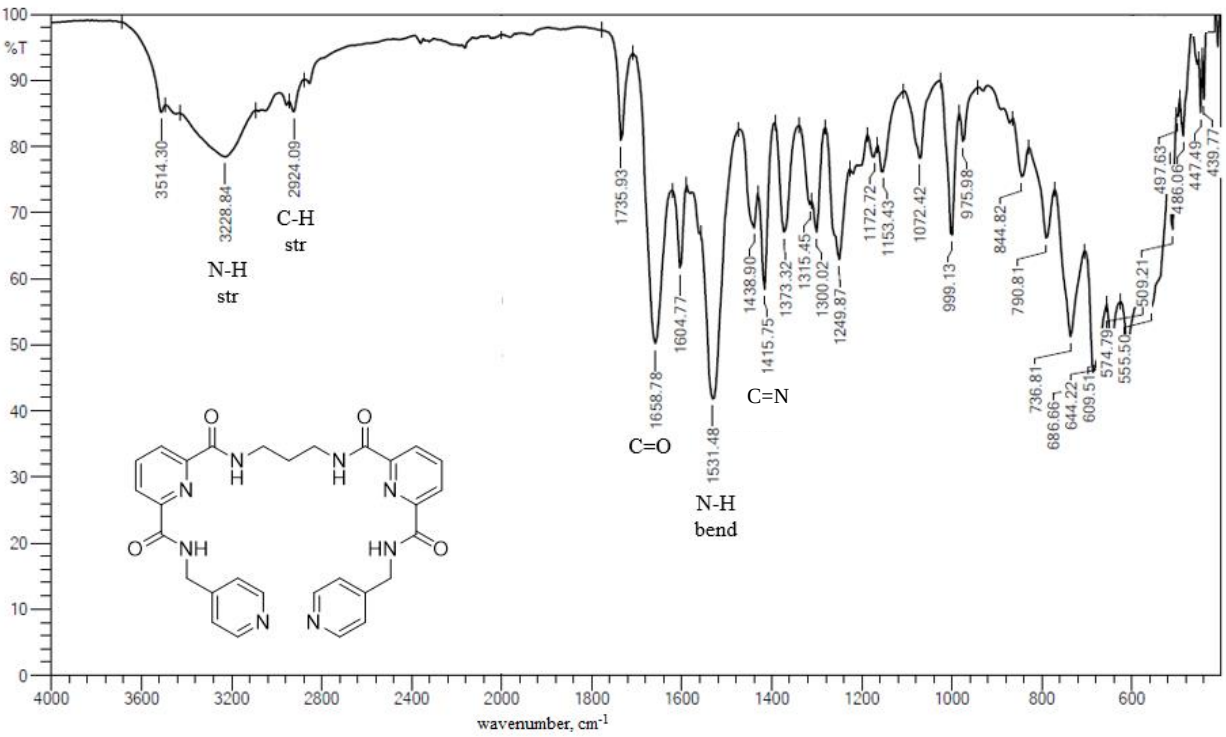

Figure S2. FTIR spectrum of L2

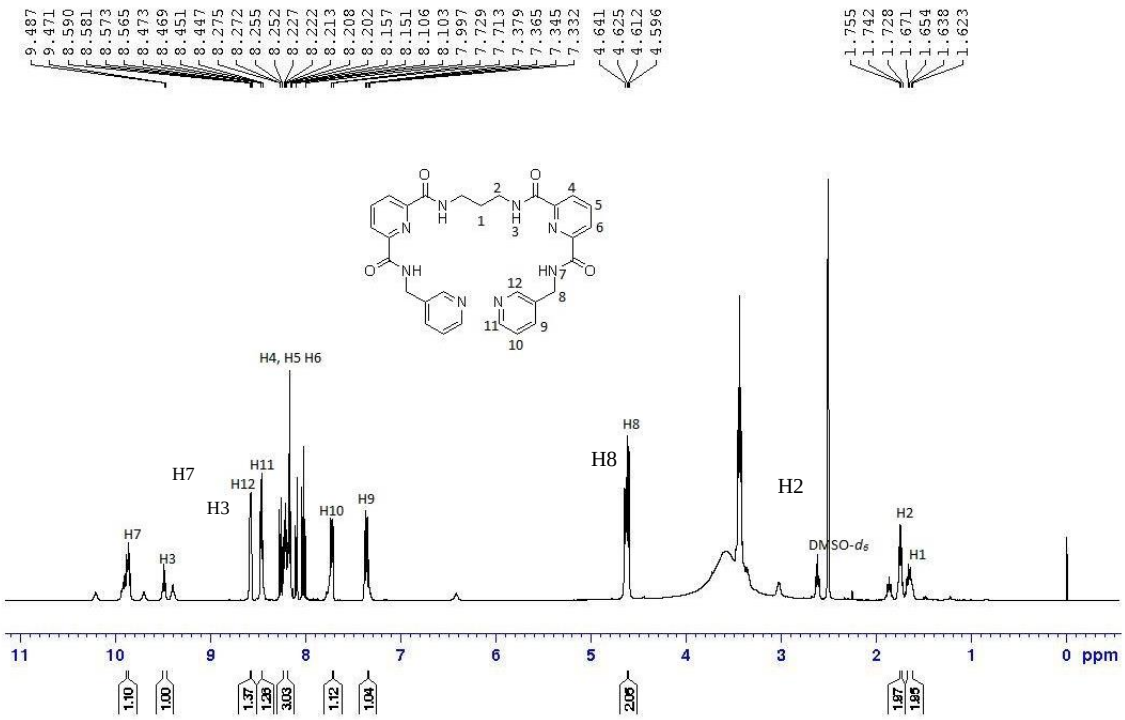

Figure S3. ^{1}H NMR spectrum of L1

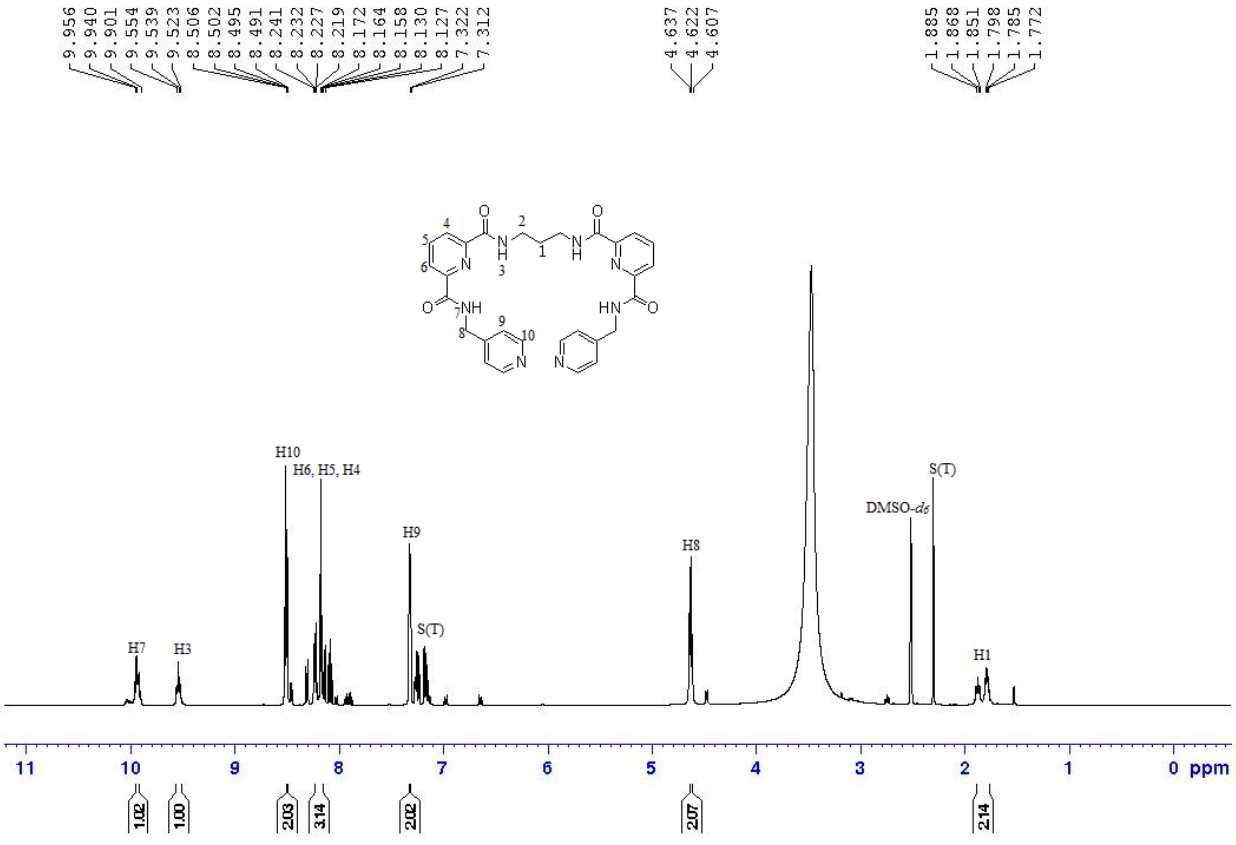

Figure S4. ^{1}H NMR spectrum of L2

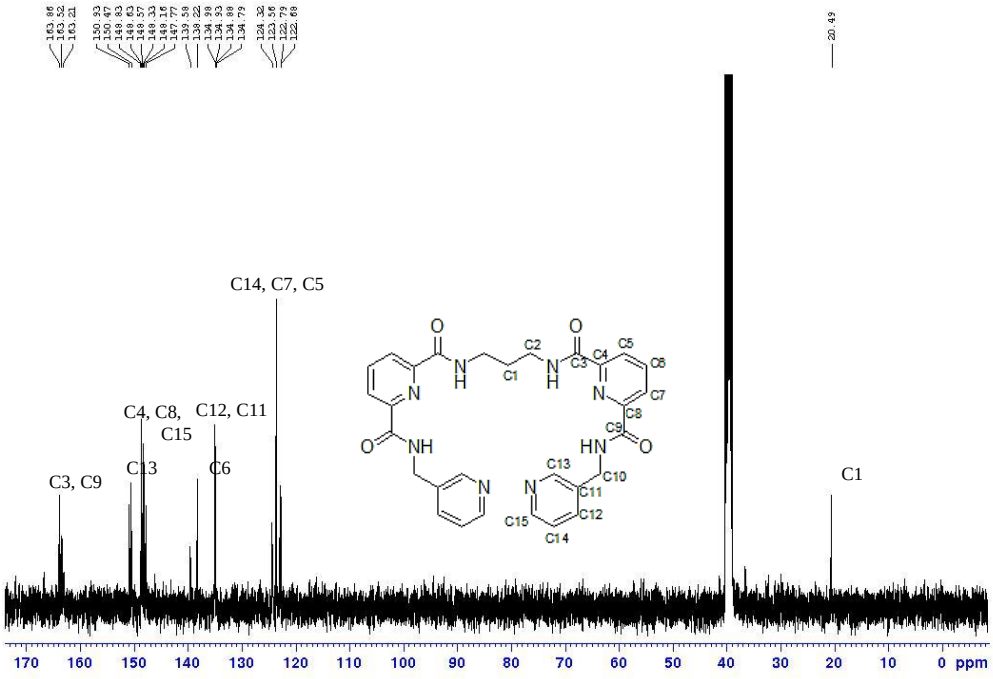

Figure S5. ^{13}C NMR spectrum of L1

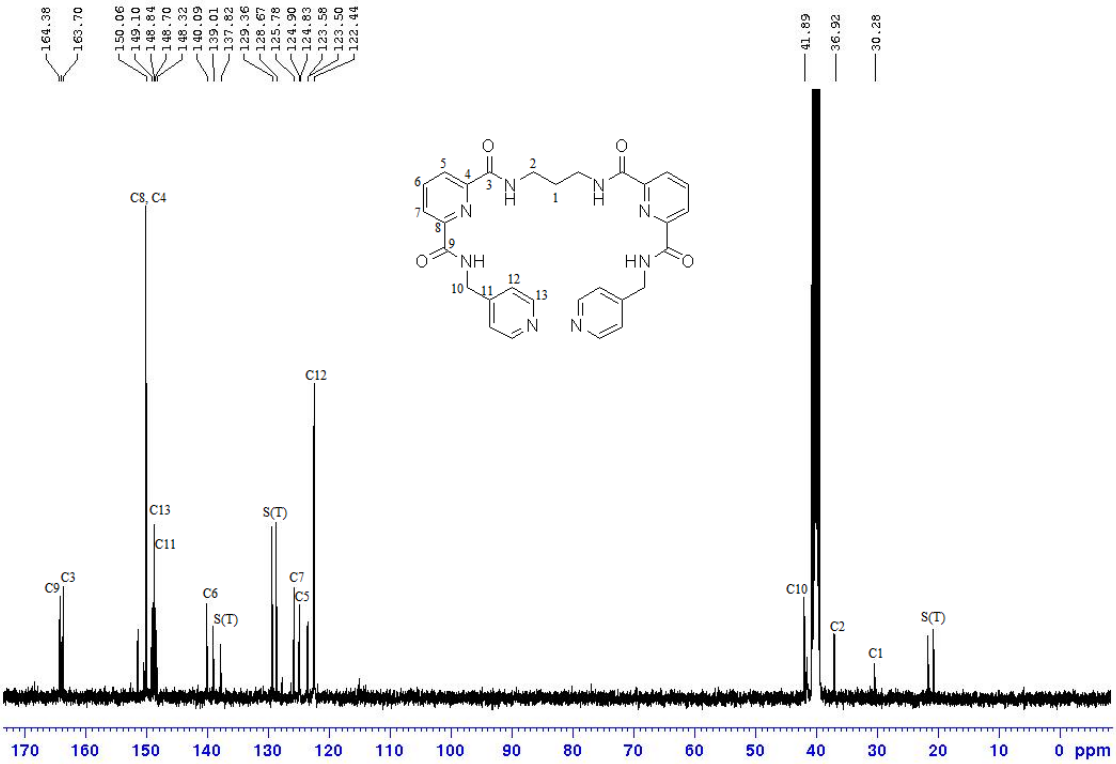

Figure S6. ^{13}C NMR spectrum of L2