

UV-Vis Spectroscopic Studies of Diamide Ligands as Potential Tools for Anion Sensor

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Abstract

This paper describes the results from ultraviolet (UV) spectroscopic studies of diamide ligands namely *N,N'*-2,6-bis(3-pyridylmethyl)pyridine dicarboxamide (L5) and *N,N'*-2,6-bis(4-pyridylmethyl)pyridine dicarboxamide (L6) towards chloride, nitrate and chromate anions in solution. The responses of the ligands towards anions are monitored by the changes of the absorbance in the UV spectra. The time interval experiments were conducted from 0 to 3 hours, resulted to the rise of the absorbance of the ligands. The change in the absorbance value is attributed to the increase of interaction between the ligands and anions that is proportional with time. In contrast to the ligands, the absorbance of anion is decreased showing the reduction of anion concentration in the solution. Rapid UV response indicates the sensitivity of these ligands towards anions which at the same time showing promising potential as sensitive anion sensor.

Keyword Anion binding, diamide, anion, anion sensor

INTRODUCTION

The field of anion coordination chemistry has undergone phenomenal growth in these recent years due to the impacts anions have in nature [1-3]. Fertilizer run-off, metallo-toxic anions and sulfate anions from agricultural and industrial waste for instance, can cause to water pollutant. The presence of anions in groundwater can be toxic to human health even at sub-micromolar concentration [4-5]. Thus, an efficient anion receptors that can selectively bind and separate wide range of anions from the water body is needed to overcome this problem. In recent years, utilization of novel supramolecular molecules as anion receptors has been widely explored. This includes the incorporation of supramolecular anion sensor such pyrrole, amide, guanidinium, imidazolium, urea and thiourea [6-7]. Among the approaches, amide has been widely used as neutral anion receptors due to its efficient binding its ability to form hydrogen bonding with anions. The hydrogen bonding can caused π electron delocalization and the basic anion can induced N-H deprotonation that serves as the signal output of the anion receptor interaction [8-9]. Example of anion binding interaction in a pre-organized anthracene-based amide [10] with anion cavity is showed in Figure 1.

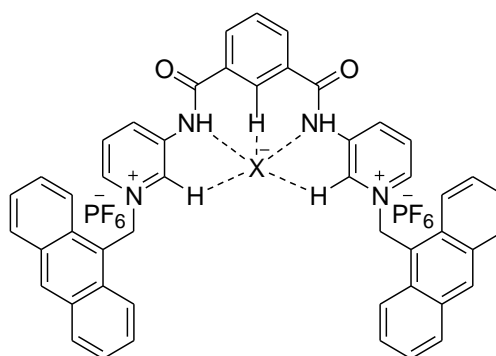


Figure 1 Example of anthracene-based bispyridinium amide receptor

In this structure, the anion (X^-) is interacted with the amide (NH) by weak hydrogen bonding. In similar to many of the anion receptor studies, our group have designed two potential anion receptors which derived

from amide, namely *N,N'*-2,6-bis(3-pyridylmethyl)pyridine dicarboxamide (L5) and *N,N'*-2,6-bis(4-pyridylmethyl)pyridine dicarboxamide (L6) [11]. These ligands were incorporated with NH amide as anion binding sites and appeared to maintain their U-shaped structure in the solid state. As mentioned above, ligands L5 and L6 were designed for anion binding therefore a pre-organized diamide was utilized to direct the NH amide into the cavity of the molecule (Figure 2).

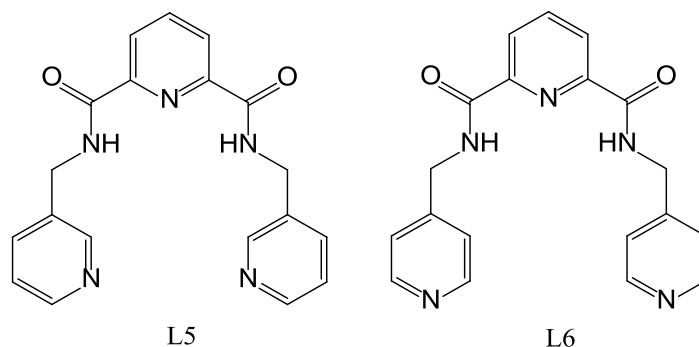


Figure 2 Molecular structure of L5 and L6

With this kind of design, the anion can be trapped in the amide cavity where interaction is expected to be occurred between the ligand and the anion molecules through weak hydrogen bond. In this study, the ligands were expected to form two conformation in the solution due to its flexibility at CH₂ spacer that existed in between amide and the pyridine (Figure 3). To further understand the behavior of this ligand towards selected anions particularly in solution, a method involving UV spectroscopy was carried out as describe in this paper.

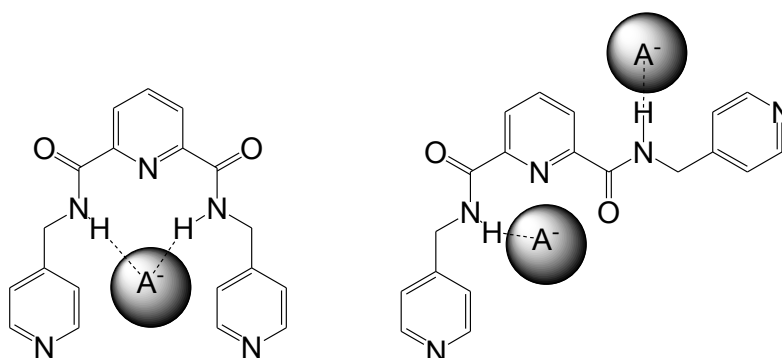


Figure 3 Two expected conformations that can be formed by L6 (anion = A)

MATERIALS AND METHODS

General methods

Unless otherwise stated, all chemicals were obtained from commercial sources and used as received. Ligands *N,N'*-2,6-bis(3-pyridylmethyl)pyridine dicarboxamide (L5) and *N,N'*-2,6-bis(4-pyridylmethyl)pyridine dicarboxamide (L6) were prepared according to methods described in the literature with slight modifications[11]. To prepare the ligands, 2,6-dimethylpyridine dicarboxylate (0.78 g, 4.00 mole) was combined with 3 or 4-aminomethylpyridine (1.12 mL, 0.0011 mole). The reaction mixture was heated at reflux for 24h. After the reaction is completed, toluene was removed by using rotary evaporation (111°C at 77mbar). The residue is obtained as oil and was dissolved in 100 mL of dichloromethane and washed with 50 mL of saturated sodium bicarbonate for two times to obtain the product. The product was dried over MgSO₄ and dichloromethane was removed by using rotary evaporation (55°C at 900mbar). The residue

after rotary evaporation was washed with 10 mL of diethyl ether for three times to produce pale yellow powder (0.7996g, 83.95%). The powder was collected through filtration and dried in dessicator. The synthesized ligands were characterized *via* typical spectroscopic methods such as Infrared (IR) and Nuclear Magnetic Resonance (NMR). IR spectra were recorded on Perkin Elmer 100 Fourier Transform Infrared (FT-IR) spectroscopy using KBr pellet. NMR spectra were recorded by using Bruker DRX-400MHz and UV-Vis spectrophotometer were recorded on Shimadzu UV-Vis 1601 series.

(Spectroscopic data for L5 and L6):

(Ligand L5): Found: C, 64.1; H, 5.6; N 20.39. $C_{19}H_{17}N_5O_2$ requires C, 65.7; H, 4.9; N 20.2%; max (KBr disk)/ cm^{-1} 3256, N-H str. (asym.); 1654, C=O str. and 1542, N-H *bend*; 1H (400 MHz; $CDCl_3$; Me_4Si) $\delta=4.64$ (4H, d, py CH_2NH), 7.37 (4H, d, H5'), 8.9.24 (1H, t, H4), 8.47 (4H, d, H2', H6'), 8.24 (2H, d, H3, H5), 9.89 (2H, t, NH) ppm; ^{13}C (100 MHz; $CDCl_3$; Me_4Si) 39.79, 123.55, 124.59, 138.41, 139.63, 148.17, 148.49 and 163.54 ppm. (Ligand L6): Found: C, 65.3; H, 5.7; N 19.39. $C_{19}H_{17}N_5O_2$ requires C, 65.7; H, 4.9; N 20.2%; max (KBr disk)/ cm^{-1} 3257, N-H str. (asym.); 1653, C=O str. and 1540, N-H *bend*; 1H (400 MHz; $CDCl_3$; Me_4Si) $\delta=4.57$ (4H, d, py CH_2NH), 7.1 (4H, d, H3', H5'), 8.05 (1H, t, H4), 8.34 (4H, d, H2', H6'), 8.39 (2H, d, H3, H5), 8.71 (2H, t, NH) ppm; ^{13}C (100 MHz; $CDCl_3$; Me_4Si) 42.27, 122.61, 125.70, 139.31, 148.57, 149.26 and 163.94 ppm.

Absorbance Study through Time Interval

In this experiment, three individual solution containing a mixture of ligand and anions in the concentration at range (2.5×10^{-5} M) concentration were prepared in 20 mL volumetric flask. Solution 1 contains a mixture of ligand (0.1735 mg) and tetraethylammonium chloride (0.0841 mg); Solution 2 contains a mixture of ligand (0.1735 mg) and tetraethylammonium nitrate (0.0842 mg); Solution 3 contains a mixture of ligand (0.1735 mg) with potassium dichromate (0.14 mg, 0.05 mmol). Each solutions were analyzed by UV-Vis spectrophotometry and the changes of the absorbance within the time interval (1 hour, 2 hours and 3 hours) were recorded.

Anion Titration Study

UV-Visible titration study was conducted by preparing two solutions in similar concentration mentioned above. Solution A was prepared by dissolving 0.1735 mg ligand in methanol. Solution B, which consists of combination of anion and ligand (called as anion host solution) was prepared in deionized water:methanol (50:50 ratio) and labeled as B1, B2 and B3. Solution B1 was prepared by dissolving ligand with tetraethylammonium chloride. Solution B2 and B3 was prepared in the similar manner solution B1 was prepared, but using tetraethylammonium nitrate (B2) and potassium chromate (B3), respectively. In this experiment, solution (A) was titrated with 0.1 mL, 0.2 mL, 0.4 mL, 0.6 mL and 0.7 mL of solution B1-B3. The changes of absorbance of the ligand in the UV spectra were recorded.

Anion competition study

In anion competition study, equimolar amounts of ligands (L5 and L6) were combined with anion mixtures containing potassium dichromate, tetraethylammonium nitrate and tetrabutylammonium chloride. The result for anion competition study was monitored using UV-Vis spectrophotometer and the changes in the absorbance of the UV spectra were recorded.

RESULTS AND DISCUSSION

In order to investigate the interactions between the ligands (host) and the anions (analyte), the UV spectra of the free ligands was analyzed as reference. The spectrum showed several common distinctive peaks assigned for carbonyl (C=O) and pyridine groups (aromatic) at 260 and 230 nm, respectively. Both peaks represents the $n \rightarrow \pi^*$ transition. The data obtained from UV-Vis analysis is summarized in Table 1.

Table 1 UV-Vis analysis for L5 and L6

Ligands	Chromophores	Transition	λ_{\max} (nm)	ϵ , L cm ⁻¹ M ⁻¹
L5	C=O	$n \rightarrow \pi^*$	260	5 200
L6		$n \rightarrow \pi^*$	260	10 400
L5	Pyridine	$n \rightarrow \pi^*$	230	6 000
L6		$n \rightarrow \pi^*$	230	11 600

Absorbance Study through Time Interval

The time interval study was conducted to investigate the strength of interaction between the ligands and anions proportional with time. For this experiment, ligand L5 and chromate was prepared in a mixture of methanol:deionized water and left to stand from 0 to 3 hours at room temperature. The freshly prepared solution was analyzed and the initial absorbance was recorded. The solution was analyzed by UV every one hour until the absorbance become constant. The results of the UV showed that the absorbance of the ligand (261 nm) is increased when the ligand is left in a long period with the chromate anion. This indicates that the strength of binding between ligand L5 and chromate anion is increased in proportional with time. Inversely, the absorbance of chromate (354 nm) in the solution is reduced from 0.0874 to 0.0868 showing the decreased of chromate concentration in the solution (Figure 4).

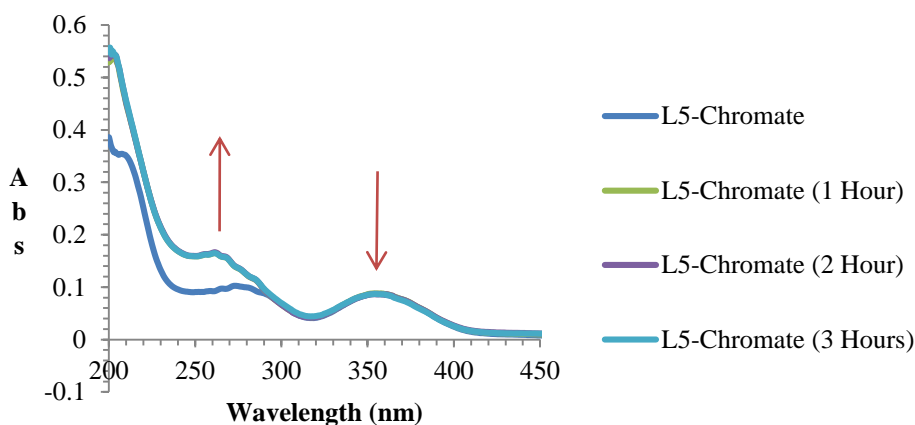


Figure 4 The UV spectrum showing of combination of Ligand L5 (peak at 261.5 nm) and chromate anion (peak at 354 nm)

This result is obtained as expected and is similar to the previous anion binding study [12]. The time interval study was continued by combining L5 with other anions, such as nitrate and similar result was obtained, in which the absorbance for the ligand is increased while the absorbance for nitrate anion is decreased. The UV study between the ligand and chloride anions gave negative absorbance. This indicates that the interaction between the ligand and anion does not occur. This might be due to the size of chloride anion that is large and might not fit with the ligand cavity. Moreover, the tendency of chloride in forming hydrogen bond with the host is also unfavorable, as reported by Kondo *et al.*, in his works [13]. At some point, chloride anions prefer to form salts rather than interacting with the ligand. This can be observed by the formation of white precipitate in the solution upon analysis. The absorbance pattern for ligand L6 is similar to ligand L5. Again, the absorbance for ligand L6 is increased and the absorbance for nitrate and chromate is decreased when the solution is left for long periods of time. In contrast to L5, the peaks occurred in the UV of ligand L6 has high absorbance and good separation thus indicates the absence of intra or molecular hydrogen bonding networks within the molecules or with the solvents (Figure 5 and Figure 6).

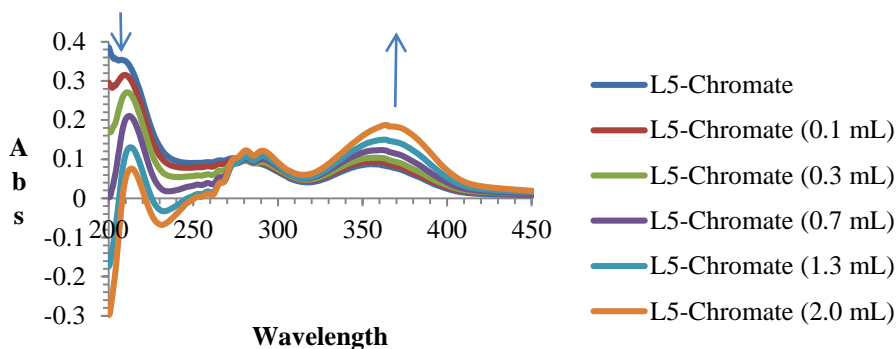


Figure 5 The UV-Vis spectrum for titration

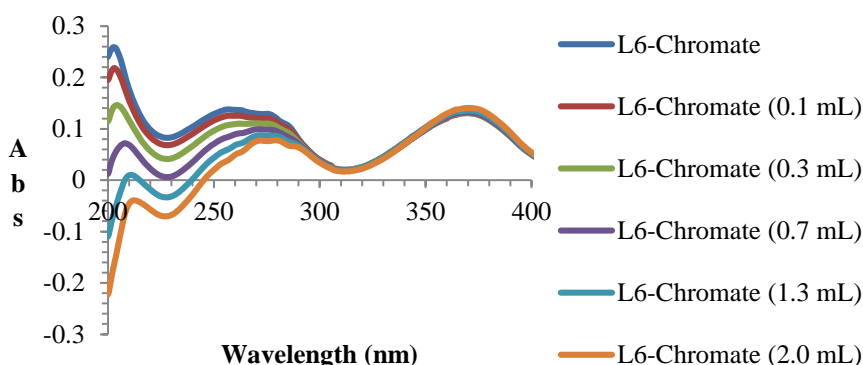


Figure 6 The UV-Vis spectrum for titration study of L6 with chromate

Chromate anion in other aspect has similar geometry structure with perchlorate, one of the most lipophilic anions (sitting high in the Hofmeister series between organic anions and iodide). Therefore based on the UV results, the ligands are expected to have high affinity towards chromates compared to nitrate and chloride [14].

Anion Titration Study

The anion titration study was conducted to determine the lowest concentration of ligand and anion that can be observed by UV. To conduct this analysis, a solution of ligand (A) was titrated with 0.1 mL, 0.3 mL, 0.7 mL, 1.3 mL and 2.0 mL anion-ligand mixed solution (B1, B2 and B3). The response from each titration is observed by UV. The UV spectrum in Figure 6 showed that, as the concentration of the chromate is increased, the absorbance for chromate is also increased. Meanwhile, the absorbance of the ligand at 230 and 260 nm are decreased resulting from the weakening of binding between the ligand and chromate which consistently developed in the solution. This kind of pattern has been reported by Bala and co-workers in 2013, that suggested the formation of saturated solution of anion-complex in solution has been reached [15]. The low absorbance of the solution detected by UV shows two possible conditions; (i) The formation of saturated anion complex and (ii) the weakening binding of anion with the receptor as the anion is too concentrated. This study has showed that the best results occurred at titration of 0.7 mL of chromate (approximately 6.75×10^{-5} M). This gave optimum absorbance for ligand at 0.0121 and chromate at 0.1871. Similar result was obtained for L6 when titrated with chromate. As the amount of chromate increases, the absorbance of chromate is also increasing. This study resulted to an optimum concentration of anion titration which is calculated as 6.75×10^{-5} M. In this experiment, the absorbance for ligand L5 and nitrate is slightly decreases from -0.0217 to -0.2205 and from 0.4248 to -0.1497, indicating the occurrence of complicated hydrogen bonds networks in the solution that weakening the interaction between the ligand and anion (Figure 7). This result is in contrast to ligand L6, where the absorbance of the ligand at 260 nm is decreased from 0.0356 A to -0.0632 A, and the absorbance for nitrate is increased from 0.5017 A to 0.9684 A (Figure 8). By adding only 0.1 mL of nitrate, the optimum concentration for nitrate anion for L6 detection is

obtained as 5.25×10^{-5} M.

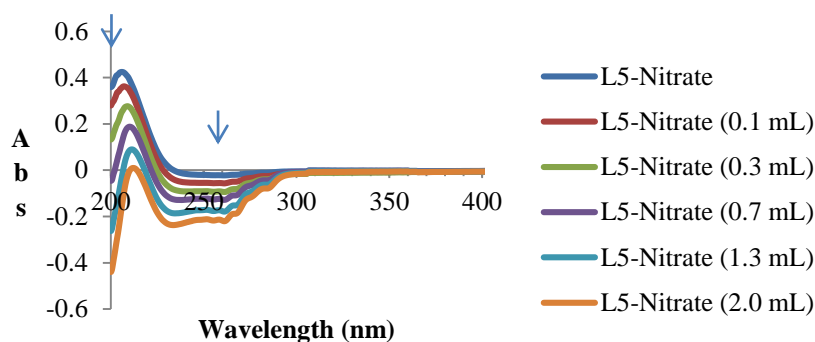


Figure 7 The UV-Vis spectrum for titration study of L5 with nitrate

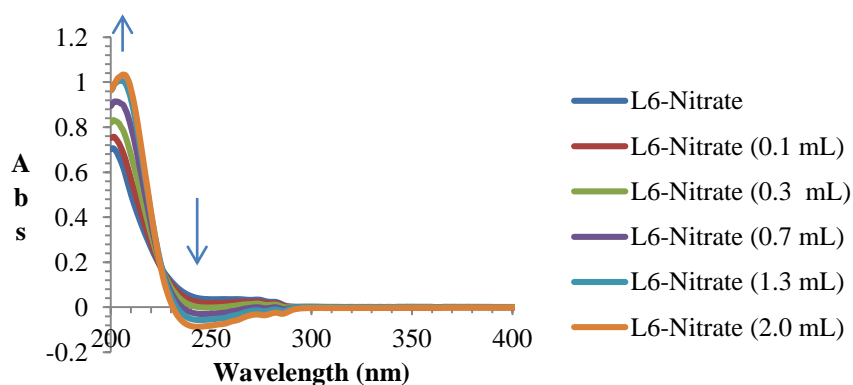


Figure 8 The UV-Vis spectrum for titration study of L6 with nitrate

Anion Competition Study

Anion competition study is attempted to investigate the preference of the ligands or the affinity of the ligands to bind anions in competitive condition. This study was carried out by mixing ligand (2.5×10^{-5} M) with the anions (chromate, nitrate and chloride) and the appearances of absorbance peaks were identified. Figure 9 shows the spectrum for L5+anions (red line) and L6+Anions (blue line).

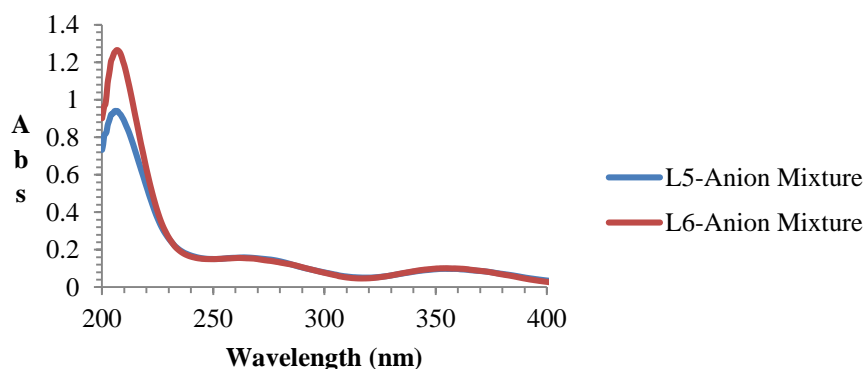


Figure 9 The UV-Vis spectrum resulted from anion competition study for ligands L5 and L6

The UV spectrum shows two absorbance peaks for chromate and nitrate at 354 nm and 206 nm. Based on the results, it can be concluded that both ligands L5 and L6 have high selectivity towards oxoanions nitrate and chromate where absorbance with chloride was not appeared. Both ligands showed similar response to chromate anions where the absorbance for both is almost identical (0.06 A at 354 nm). However, the absorbance for ligands which normally occurred at 230 nm is expected to be overlapped with the nitrate absorbance peak, thus caused to the broadening of the peak. Another ligand peak at 260 nm was also appeared to be broadening, which might be affected by the formation of anion complex.

CONCLUSION

In conclusion, L5 and L6 have high affinity and selectivity towards oxoanions such as chromate and nitrate. The interaction between the ligands and sphere anions such as chloride does not occurred due to the tendency of chloride anions to form salts rather than interacting with the ligands. The UV spectra also supports the formation of complicated hydrogen bond networks in the solution of L5-anions which somehow affects it efficiency in detecting or interacting with anions compared to L6.

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REFERENCES

- [1] Gale, P. A. (2000). Anion coordination and anion-directed assembly: highlights from 1997 and 1998. *Coordination Chemistry Reviews*. 199, 181-233.
- [2] Dong, Z.Y., Yang, Y., Zhang, L. F., Xue, Y.R., Feng, M. Y. & Gao, G. H. (2012). Ionic liquids containing the urea moiety for recognition of halides and complex anions. *Chinese Science Bulletin*. 57 (5), 473-478.
- [3] Ranjan, D. and Pradyut, G. (2014). Recent developments in anion induced capsular self-assemblies. *Chem. Commun.* 50, 10538-10554.
- [4] Cametti, M. and Rissanen, K. (2009). Recognition and sensing of fluoride. *Chem Commun.* 2809-2829.
- [5] Cametti, M. and Rissanen, K. (2013). Highlights on contemporary recognition and sensing of fluoride anion in solution and in the solid state. *Chem Soc. Rev.* 42, 2016-2038.
- [6] Gale, P.A., Sessler, J. L., Kral, V., Lynch, V. (1996). Calix[4]pyrroles: Old yet new anion binding agents." *J. Am. Chem. Soc.* 118, 5140-5141.
- [7] James, A. S. and Scott, G. W. (2006). Calix[4]pyrrole: Synthesis and anion-binding properties. An organic chemistry laboratory experiment. *J. Chem. Educ.* 83 (9), 1330-1332.
- [8] Kai, C. C., Shih, S. S., Maurie, O. O., Alistair, J. L. (2015). Anion recognition and sensing by transition-metal complexes with polarized N-H recognition motifs. *Coordination Chemistry Reviews*. 284, 111-123.
- [9] Qian, Y.C., Yuan M.H., Pei, S.Y., Wen, F.F., Yu, X., Jing, H. L. (2014). A new ferrocene-anthracene dye bearing amide and triazolium donors for dual-signaling sensing to anions. *Tetrahedron Letters*. 55, 248-251.
- [10] Ghosh, K., Sarkar, A. R., & Masanta, G. (2007). An anthracene based bispyridinium amide receptor for selective sensing of anions. *Tetrahedron Letters*. 48: 8725-8729.
- [11] Sumbly, C.J. and Hanton, L. R. (2009). Syntheses and studies of flexible amide ligands: a toolkit for studying metallo-supramolecular assemblies for anion binding. *Tetrahedron*. 65, 4681-4691
- [12] Shi, P.F., Zhao, B., Xiong, G., Hou, Y.L., Cheng, P. (2012). Fast capture and separation of, and luminescent probe for, pollutant chromate using a multi-functional cationic heterometal-organic framework. *Chem. Commun.* 48: 8231-8233.
- [13] Kondo, S., Nagamine, M., Karasawa, S., Ishihara, M., Unno, M. (2011). Anion recognition by 2,20-binaphthalene derivatives bearing urea and thiourea groups at 8- and 80-positions by UV-vis and fluorescence spectroscopies. *Tetrahedron*. 67, 943-950.
- [14] Harakuwe, A.H., Haddad, P. R., Thomas, R. (1999). The effect of butan-1-ol on the separation of inorganic anions using capillary zone electrophoresis with reversed electroosmotic flow. *Journal of Liquid Chromatography & Related Technologies*. 22 (5), 659-667.
- [15] Bala, R., Kashyap, M., Kaur, A., Golobič, A. (2013). A hexaureachromium(III) complex as a molecular receptor for oxoanions. *Journal of Molecular Structure*. 1031, 246-253.