Metal Ion Control the Selective Sensing of Oxalate Anion by Dinuclear Complexes under Indicator Displacement Strategy

Nattawat Chatphueak,1 Sarayut Watchasit2 and Chomchai Suksai1 *

1Department of Chemistry and Center for Innovation in Chemistry, Faculty of Science, Burapha University
2Nuclear Magnetic Resonance Spectroscopic Laboratory, Science Innovation Facility, Faculty of Science, Burapha University

Received : 12 November 2020
Revised : 15 December 2020
Accepted : 19 December 2020

บทคัดย่อ

ได้ทำการสังเคราะห์และพิสูจน์โครงสร้างของสารประกอบโคออร์ดิเนชันชนิดไดนิวเคลียร์ของคูเปอร์ (II) และสังกะสี (II) กับลิแกนด์ bis(dipicolylamine) ที่มี para-xylylene ทำหน้าที่เป็นสะพานเชื่อม bis(dipicolylamine) ทั้ง 2 หมู่ (CuL1 และ ZnL1) หลังจากนั้นสารประกอบทั้งสองชนิดมาใช้เป็นเรซิเดอร์สำหรับการตรวจวัดแอนไอออนโดยใช้อินดิเคเตอร์ bromopyrogallol red หรือ BPG เป็นอินดิเคเตอร์ที่ใช้สำหรับตรวจวัดในตัวทำละลายผสม 80/20 (%/v/v) ของอะซิทัวไตรลล์และ HEPES ความเข้มข้น 10 mM ที่ pH 7.0 จากการศึกษาพบว่าเมื่อเอนเซมบิล [CuL1•BPG] และ [ZnL1•BPG] พบว่ามีเพียงเอนเซมบิล [CuL1•BPG] เท่านั้นที่สามารถตรวจจับออกซัลแอนไอนิออนจากแอนไอนิออนชนิดต่าง ๆ ได้ โดยที่ออกซัลแอนไอนิออนคือ BPG ในรูปอิสระได้ จากผลการทดลองที่ได้มีการเตรียมเอนเซมบิล [CuL1•BPG] สำหรับการตรวจจับออกซัลแอนไอนิออนในช่วงของค่า pH ที่ 3 - 9 ทำให้สามารถตรวจจับออกซัลแอนไอนิออนได้ในช่วงของความเข้มข้นที่ 20 - 50 µM (R² = 0.995) และมีค่าขีดจุดกำลังในการตรวจจับตัวอย่างเหลาที่ 20 µM

คำสำคัญ : สารประกอบโคออร์ดิเนชันชนิดไดนิวเคลียร์ ; เทคนิคการถูกแทนที่ของอินดิเคเตอร์ ; ออกซัลแอนไอนิออน ; การเห็นสีด้วยตาเปล่า ; เอนเซมบิล
Abstract

Two dinuclear complexes of Cu(II) and Zn(II) with bis(dipicolylamine) linked by a para-xylylene bridge, CuL1 and ZnL1 have been synthesized and characterized. Both compounds are applied as metal-based indicator displacement assay (IDA) receptors for anions using bromopyrogallol red (BPG) as sensing indicators in 80/20 (% v/v) acetonitrile/water solution buffered with 10 mM HEPES at pH 7.0. After addition of various anions to the solution of [CuL1•BPG] and [ZnL1•BPG] ensemble, the results showed that only [CuL1•BPG] could discriminate oxalate from other anions obviously resulting in the color change from blue-violet of ensemble to magenta color of free BPG. This result indicates that the nature of metal ion plays a crucial role to control the selective sensing of oxalate in this work. The quantitative detection of oxalate by [CuL1•BPG] ensemble was ranged from 20 – 50 µM, and a correlation coefficient ($R^2$) = 0.995. The detection limit was 20 µM by the naked eye.

Keywords : dinuclear complex ; indicator displacement assay ; oxalate ; naked eye ; ensemble

*Corresponding author. E-mail : jomjai@buu.ac.th
Introduction

As one of the biological important anions, oxalate is naturally present in several foods and serves as a nutrient in the human body (Merusi et al., 2010). However, an excess consumption of oxalate is associated with the development of kidney stones (Ogawa & Miyazato, 2000), renal failure (Kasidas et al., 1986; Marengo & Rose, 2008) and pancreatic insufficiency (Cartery et al., 2011). Importantly, there is no enzyme in the human body to degrade oxalate. Therefore, oxalate is excreted by the kidney into the urine (Pundir et al., 1998). Normal levels of oxalate for a healthy human are 10-30 mg/24 h (100-300 µM) in urine and 0.8 – 2.50 µM in plasma (Pundir et al., 1998). Hence, it is increasingly important to develop highly selective and sensitive oxalate. To date, several quantification analytical methods for oxalate detection mostly involved complicated and expensive equipment such as enzymatic methods (Kalra & Pundir, 2004), HPLC (Honow et al., 2002), capillary electrophoresis (Munoz * Lopez, 2010; Nobilitt et al., 2009), gas chromatography (Li et al., 2008) and electrochemical methods (Rodriguez et al., 2012). Based on the current researches of anions detection, chemosensors for oxalate are more active in the field of detection because of their low price and visually detectable (Suksai & Tuntulani, 2003; Curriel et al., 2015). For example, Bhattacharya and co-workers have employed rhodamine complex with Cu(II) for quantification of oxalate in agricultural crops, drinking and human urine (Dey et al., 2018). Dungchai and co-workers have constructed paper-based colorimetric device for point-of-care monitoring oxalate in artificial urine sample (Worramongkona et al., 2018). Indicator displacement assay (IDAs) is an alternative strategy for chemosensors due to its conveniences for constructions the visual observation systems. The recognition unit and sensory unit interact by non-covalent interactions (Wiskur et al., 2001; Lavigne & Anslyn, 2006; Nguyen & Anslyn, 2006). Recently, colorimetric detection of oxalate by IDAs has been reported (Tang & Liu, 2010; Su et al., 2010; Hu & Feng, 2012; Rhaman et al., 2014; Tang et al., 2014; Inoue et al., 2018). Herein, in the continuation of our ongoing research on the construction of dinuclear complex of copper(II) or Zn(II) as meal based IDA receptors for anion (Watchasit et al., 2010; Watchasit et al., 2014), we reported the synthesis of homodinuclear complexes of Cu(II) and Zn(II) with bis(dipicolylamine) linked by a para-xylylene bridge, CuL1 and ZnL1, and investigated the sensing abilities of those two complexes as metal-based IDA receptors for oxalate and using bromopyrogallol red (BPG) as the sensing indicator in 80% acetonitrile aqueous solution buffered with 10 mM HEPES pH 7.0. We anticipated that the nature of meal ion center will lead to the discriminate sensing for oxalate from other anions and also interested dicarboxylates anions. Interestingly, we found that the dinuclear CuL1 complex is a suitable receptor for indicator displacement assay of oxalate. Moreover, the anion sensing abilities of the mononuclear complex CuL2 have also studied compared to the dinuclear complex CuL1. The structures of CuL1, ZnL1, CuL2 and BPG are shown in Figure 1.
Methods

1. Materials and methods

All chemicals were at least of analytical grade and used without further purification. Sterile water for injection was obtained from General Hospital Products Public Co., Ltd, (PathumThani, Thailand). All UV-vis absorption spectra were recorded using an Agilent 8453 UV-vis spectrophotometer. All complexes and indicator solutions were freshly prepared immediately before UV-vis experiments. $^1$H- and $^{13}$C-NMR spectra were carried out using Bruker AVANCE III HD 400 MHz Ultra Shield spectrometer. Dipicolylamine (DPA) was synthesized according to the previously published procedure (Watchasit et al., 2010).
2. Synthesis of \( \text{L1} \)

The mixture of 1,4-bis(bromomethyl)benzene (3.25 g, 12.32 mmol), bis(pyridin-2-ylmethyl)amine (5.86 g, 29.45 mmol), \( \text{Cs_2CO}_3 \) (9.58 g, 29.40 mmol) and KI (3.06 g, 18.43 mmol) in \( \text{CH}_2\text{CN} \) (150 mL) were dissolved in dry \( \text{CH}_2\text{CN} \). The reaction mixture was reflux under nitrogen atmosphere for 24 h. The dark precipitate was filtered. The filtrate was removed solvent under vacuum. The residual was redissolved in \( \text{CH}_2\text{Cl}_2 \) (100 mL) and washed with water (3 × 300 mL). The organic extracts were dried with anhydrous \( \text{Na}_2\text{SO}_4 \). After solvent removal, a dark oil of \( \text{L1} \) was obtained and then purified by column chromatography (silica gel, MeOH : \( \text{CH}_2\text{Cl}_2 = 2:8 \nu/\nu \)). The light yellow solid of \( \text{L1} \) was obtained (0.23 g, 2.36%) after recrystallization in acetone and water.

\(^1\text{H}-\text{NMR} \) (400 MHz, \( \text{CD}_3\text{CN} \), ppm): \( \delta \) 8.47-8.45 (m, 4H, \( \text{ArH} \)), 7.73-7.69 (m, 4H, \( \text{ArH} \)), 7.61 (s, 2H, \( \text{ArH} \)), 7.59 (s, 2H, \( \text{ArH} \)), 7.37 (s, 4H, \( \text{ArH} \)), 7.20-7.16 (m, 4H, \( \text{ArH} \)), 3.73 (s, 8H, \(-\text{CH}_2\text{-}\)), 3.63 (s, 4H, \(-\text{CH}_2\text{-}\)).

\(^{13}\text{C}-\text{NMR} \) (100 MHz, \( \text{CD}_3\text{CN} \), ppm): \( \delta \) 159.73, 148.78, 137.99, 136.43, 128.76, 122.77, 100.02, 59.66, 57.84.

HRMS ESI positive mode: 501.2785 [\( \text{L1}^+\text{H}^+ \)], 523.2606 [\( \text{L1}^+\text{Na}^+ \)].

3. Synthesis of \( \text{CuL1} \)

The water solution of \( \text{Cu(CIO}_3\text{)}_2\cdot\text{H}_2\text{O} \) (0.74 g, 2 mmol) was gradually added to acetonitrile solution suspension of \( \text{L1} \) (0.2 g, 0.40 mmol) and the color of solution changed to blue immediately. Then, the mixture was heated for 10 min. After cooling to room temperature, the blue solid precipitate was filtered and washed with \( \text{CH}_2\text{Cl}_2 \) to obtain \( \text{CuL1} \) (0.28 g, 68 % yield). HRMS ESI positive mode: 924.9718 [\( \text{CuL1}^+\text{3ClO}_3^+ \)].

4. Synthesis of \( \text{ZnL1} \)

The ethanol solution of \( \text{Zn(CIO}_3\text{)}_2\cdot\text{H}_2\text{O} \) (0.74 mg, 2 mmol) was added to the ethanol solution suspension of \( \text{L1} \) (0.2 g, 0.40 mmol) and then ether and hexane were added into the solution mixture, respectively. The white solid precipitate was filtered and washed with \( \text{CH}_2\text{Cl}_2 \) to obtain \( \text{ZnL1} \) (0.15 g, 40 % yield).

\(^1\text{H}-\text{NMR} \) (400 MHz, \( \text{CD}_3\text{CN} \), ppm): \( \delta \) 8.80 (d, \( J = 4.8 \text{ Hz} \), 4H, \( \text{ArH} \)), 8.24-8.19 (m, 4H, \( \text{ArH} \)), 7.77-7.69 (m, 8H, \( \text{ArH} \)), 7.37 (s, 4H, \( \text{ArH} \)), 4.32 (d, \( J = 16.0 \text{ Hz} \), 4H, \(-\text{CH}_2\text{-}\)), 3.90 (t, \( J = 16.4 \text{ Hz} \), 8H, \(-\text{CH}_2\text{-}\)).

\(^{13}\text{C}-\text{NMR} \) (100 MHz, \( \text{CD}_3\text{CN} \), ppm): \( \delta \) 154.49, 148.11, 141.99, 132.05, 131.91, 125.46, 125.27, 55.64, 55.02.

HRMS ESI positive mode: 928.9745 [\( \text{ZnL1}^+\text{3ClO}_3^+ \)].

5. Synthesis of \( \text{L2} \)

The mixture of (bromomethyl)benzene (1.86 g, 10.88 mmol), bis(pyridin-2-ylmethyl)amine (2.60 g, 13.07 mmol), \( \text{Cs}_2\text{CO}_3 \) (4.30 g, 13.20 mmol) and KI (2.74 g, 16.50 mmol) were dissolved in \( \text{CH}_2\text{CN} \) (150 mL). The reaction mixture was reflux under nitrogen atmosphere for 24 h. The dark precipitate was filtered. The filtrate was removed solvent under vacuum. The residual was redissolved in \( \text{CH}_2\text{Cl}_2 \) (100 mL) and washed with water (3 × 300 mL). The organic extracts were dried with anhydrous \( \text{Na}_2\text{SO}_4 \). After solvent removal, a dark oil of \( \text{L2} \) was obtained and then...
purified by column chromatography (silica gel, MeOH : CH₂Cl₂ = 1:9 v/v). The light yellow liquid of L₂ was obtained (1.34 g, 42.34%).

¹H-NMR (400 MHz, CD₃CN, ppm): δ 8.53 (t, J = 11.6 Hz, 2H, ArH), 7.70-7.60 (m, 4H, ArH), 7.42 (d, J = 7.2 Hz 2H, ArH), 7.35-7.13 60 (m, 5H, ArH), 3.82 (d, J = 3.6 Hz, 4H, -CH₂-), 3.70 (s, 4H, -CH₂-).

¹³C-NMR (100 MHz, CD₃CN, ppm): 159.69, 148.87, 138.90, 136.47, 128.83, 128.30, 127.06, 122.80, 121.97, 60.02, 58.52. HRMS ESI positive mode; 290.1753 [L₂+H⁺].

6. Synthesis of CuL₂

The ethanolic solution of Cu(ClO₄)₂.6H₂O (1.28 mg, 3.46 mmol) 10 mL was added to the ethanolic solution of L₂ (0.2 mg, 6.91 mmol) 10 mL. The reaction mixture was stirred at room temperature for 3 hours. Then, diethyl ether 100 mL was added to the blue solution and, stirred at room temperature for 30 min. The blue solid precipitate was filtered and washed with CH₂Cl₂ to obtain mononuclear CuL₂ (0.24 g, 63.02%).

HRMS ESI positive mode; 451.0449 [CuL₂ + 3ClO₄⁻]⁺

7. Screening for selective anion sensing

A stock solution of CuL₁, ZnL₁ and CuL₂ (20 µM) and BPG (400 µM) was prepared in 20% (v/v) water/acetonitrile solutions buffered at pH 7.0 with HEPES. A solution of BPG 400 µM (0.1 mL) in 20% (v/v) water/acetonitrile solutions buffered at pH 7.0 with HEPES was added into a solution of each complex of CuL₁, ZnL₁ and CuL₂ 20 µM (2 mL) in the same solvent system. Then, 10 equivalents of interested anions (1 mM) was then added to the as-prepared ensemble. The resulting mixtures were allowed to stand still for 5 min and subjected to UV-vis spectroscopic measurements. Photographs were taken by a digital camera (Canon EOS 7D with Tamron 17-50 mm F2.8 lens).

Results

1. Synthesis of L₁, CuL₁ and ZnL₁

Ligand L₁ was synthesized in one step reaction as shown in Scheme 1. The dipicolylamine was reacted with 1,4-bis(bromomethyl)benzene in refluxing acetonitrile using Cs₂CO₃ as base to yield L₁ in 30% yield. The HRMS spectrum of L₁ showed the parent peak at m/z at 501.2784 amu and 523.2066 amu assigned to the molecular ion of [L₁ + H⁺]⁺ and [L₁+ Na⁺], respectively (Figure S7, ESI).
Scheme 1. Synthesis procedure of L1

Addition of Cu(ClO₄)₂ or Zn(ClO₄)₂ to methanolic solutions of L1 gave CuL1 and ZnL1 in 68% and 40%, respectively. The HRMS spectrum of green solid of CuL1 showed the parent peak at m/z 924.9718 amu which is assigned to the molecular ion of the mononuclear complex of [CuL1+3(ClO₄)]⁺ species (Figure S8, ESI). For ZnL1, the parent peak at m/z 928.9745 amu corresponding to the molecular ion of the dinuclear complex [ZnL1+3(ClO₄)]⁺ was observed (Figure S9, ESI). All ¹H and ¹³C-NMR of L1, L2 and ZnL1 are shown in Figure S1-S6 in ESI.

2. Sensing abilities studies of CuL1 and ZnL1 with BPG ensemble towards anions

The addition of CuL1 or ZnL1 to BPG solution in 80% acetonitrile aqueous solution buffered with 10 mM HEPES pH 7.0 resulting in the color change from magenta color of free BPG to blue-violet color of ensemble suggested that those two complexes could form the colorimetric ensemble with BPG. Then, those two ensembles were treated with several interested anions in the same solvent system. As is evident from inspection of Figure 2, only ensemble formation between BPG and CuL1 showed the highly selective sensing toward oxalate anion in which only oxalate could change the color of the ensemble solution from blue-violet color to magenta color, Figure 2(a). In the case of ZnL1 ensemble with BPG, it was not only selective to oxalate anion but also several anions could turn the blue-violet color of ensemble to magenta color of free BPG for example PPi, TPP, AMP and ATP. This result might be expected that the binding affinity of BPG to ZnL1 was lower than that of CuL1.
Figure 2 Color changes of ensemble (a) CuL₁ (20 µM) and (b) ZnL₁ (20 µM) with indicator BPG (20 µM) after addition of various anions (12.5 equivalents). All experiments have been carried out in 80/20 (v/v) acetonitrile/water solution buffered with 10 mM HEPES at pH 7.0.

Next, the sensing abilities of [CuL₁•BPG] and [ZnL₁•BPG] have further studies by UV-visible spectrophotometry. Figure 3(a) showed that upon addition of various anions (12.5 equivalents) to the [CuL₁•BPG] ensemble solutions, only oxalate showed the bathochromic shift from concomitantly to the color of solution change from blue-violet to magenta of the unbound dye, whereas no noticeable absorption changes were observed upon addition of other anions. In contrast to [ZnL₁•BPG] ensemble, it was not only selective to oxalate but also other anions could alter the spectrum. These results suggested that [CuL₁•BPG] possessed a high selectivity towards oxalate anion over other common anions.

Figure 3 UV-vis spectra obtained by addition of various anions (10 equiv. of sodium salts) to an ensemble solution of (a) [CuL₁•BPG] and (b) [ZnL₁•BPG] (20 µM) in 80/20 (%v/v) acetonitrile/water solution buffered with 10 mM HEPES at pH 7.0.
3. Studies of ensemble formation constants between CuL1 and ZnL1 with BPG by UV-vis spectrophotometry

The ensemble formation constants of BPG with CuL1 and ZnL1 were determined by UV-vis titration experiments. The magenta color of free BPG was titrated with increasing amounts of each CuL1 and ZnL1 complex in 80% acetonitrile aqueous solution buffered with 10 mM HEPES pH 7.0. The absorption spectrum of free BPG exhibited an absorption band centered at 567 nm. Upon addition of CuL1 or ZnL1 to BPG solution, the absorbance at 567 nm decreased concomitantly to the bathochromic shift to 574 nm, with a significant visible color change from magenta to blue-violet color, Figure 4. The absorption at 574 nm reached saturation when 1.4 equivalent of CuL1 or ZnL1 was added. The stoichiometric ratios between BPG with CuL1 or ZnL1 were evaluated by Job’s plot analysis. The results suggested that the tertiary complexes between BPG with CuL1 or ZnL1 were formed with a 1:1 stoichiometry (Figure S10, ESI). Moreover, the ensemble formation constants (log $\beta$) of two ensembles have calculated using SPECFIT computer program (Binstead et al., 2000; Gampp et al., 1986; Gampp et al., 1985) and found to be 5.98 ± 0.26 and 5.20 ± 0.41 for [CuL1•BPG] and [ZnL1•BPG], respectively. It should be reminded that the ensemble formation constant of [CuL1•BPG] was higher than that of [ZnL1•BPG] as we expected and agreed well with Irving-Williams series.

![Figure 4](image-url) UV/vis spectra obtained by addition of (a) CuL1 (400 µM) and (b) ZnL1 (400 µM) to ensemble solution of BPG (20 µM) in 80/20 (% v/v) acetonitrile/water solution with 10 mM HEPES buffered at pH 7.0. (c) The color changes of BPG solution as a function of equivalents of CuL1 in 80/20 (% v/v) acetonitrile/water solution differed with 10 mM HEPES at pH 7.0: (1) BPG, (2) 0.1 eq., (3) 0.2 eq., (4) 0.3 eq., (5) 0.4 eq., (6) 0.5 eq., (7) 0.6 eq., (8) 0.7 eq., (9) 0.8 eq., (10) 0.9 eq., (11) 1.0 eq., (12) 1.1 eq., (13) 1.2 eq., (14) 1.3 eq. and (15) 1.4 eq. of CuL1.
4. Sensing studies of oxalate by [CuL1•BPG] ensemble under IDAs

The displacement of bound BPG by oxalate was studied by UV-vis spectrometry, Figure 5. Increasing oxalate concentration to an ensemble solution of [CuL1•BPG] caused an absorbance increase around 567 nm and an absorbance decrease around 574 nm (hypsochromic shift), with a color change from magenta to blue-violet, revealing that the BPG indicator was displaced from the cleft of CuL1 by the oxalate. The UV-vis spectrum at 567 nm was completely saturated at 12.5 equivalents of oxalate. The apparent competitive binding constant (log $\beta$) of [CuL1•2(oxalate)] was found to be 6.25 ± 0.38 using SPECFIT computer program. In addition, the formation of 1:2 complex species of [CuL1•2(oxalate)] could be confirm by HRMS that shown in Figure 5(b). The cluster of m/z at 928.9898 amu corresponding to the adduct species of [CuL1 + 2(oxalate) + ClO$_4^-$ + Na$^+$ + H$^+$] could be clearly observed. According to HRMS result, we expected that each oxalate anion acts as bidentate ligand coordinate to each Cu$^{2+}$ ions in CuL1 possessing the 1:2 complex cation of CuL1:2(oxalate). The proposed structure of the ternary complex of CuL1 and oxalate anion was shown in Figure 5(b).

![Figure 5](image_url)
According to mass spectrometry results, we concerned that the mononuclear complex CuL2 can be exploited as the M-IDA receptor for oxalate instead of CuL1. Therefore, we decided to synthesize ligand L2 and CuL2 complex and also investigated the sensing abilities of \([\text{CuL2•BPG}]\) ensemble towards the same series of anions and also in the same solvent system.

\[
\text{CuL2}
\]

\[\text{(ClO}_4\text{)}_2\]

**Figure 6** Color changes of ensemble \([\text{CuL2•BPG}]\) 20 µM after addition of various anions (5.0 equivalents). All experiments have been carried out in 80/20 (% v/v) acetonitrile/water solution buffered with 10 mM HEPES at pH 7.0.

Obviously, Figure 6 showed that the \([\text{CuL2•BPG}]\) ensemble could not be able to discriminate oxalate anion selectively because other anions, especially phosphate containing anions could change the purple color of ensemble to magenta color of free BPG. It could be expected that in \([\text{CuL2•BPG}]\) structure, BPG might be coordinated to Cu\(^{2+}\) ion in CuL2 complex in bidentate fashion. Therefore, several bidentate and polydentate ligands can replace the bound BPG from ensemble easily. Contrast to \([\text{CuL1•BPG}]\) ensemble, BPG acts as tetradentate ligand and coordinates to two Cu\(^{2+}\) ion in CuL1 more tightly. Therefore, the naked-eye sensing mechanism of oxalate by \([\text{CuL1•BPG}]\) ensemble under indicator displacement assay are shown in Scheme 2.
Scheme 2. Sensing mechanism of oxalate under IDAs by [CuL1·BPG] ensemble.

Discussion

To investigate sensing ability, [CuL1·BPG] ensemble can be utilized as a selective naked-eye sensor for oxalate against other anions, the competition experiments with oxalate and the other anions were conducted in 80% acetonitrile aqueous solution buffered with 10 mM HEPES pH 7.0, as shown in Figure 7. Compared to [CuL1·BPG] ensemble containing oxalate, no obvious changes in the absorbance at 574 nm were observed with the other anions. These results strongly recommend that the coexistence of other anions could not interfere the sensing of oxalate under displacement strategy. Therefore, [CuL1·BPG] ensemble exhibits the highest selectivity toward oxalate. The absorbance at 567 nm was plotted as a function of oxalate concentration and showed a good linear relationship between absorbance change and oxalate concentration in the range of 20 - 50 µM of oxalate with a linearly dependent coefficient, $R^2 = 0.995$. The detection limit of oxalate by naked eye was found at 20 µM.

Figure 7 Sensing of oxalate by [CuL1·BPG] ensemble in the presence of competitive anions (12.5 equiv.) in 80/20 (v/v) MeCN/H$_2$O solution buffered with 10 mM HEPES at pH 7. (1) = buffer, (2) = Pi, (3) = PPI, (4) = TPP, (5) = AMP, (6) = ADP, (7) = ATP, (8) = CN, (9) = ox, (10) = $SO_4^{2-}$, (11) = NO$_3^-$, (12) = $CO_3^{2-}$, (13) = HCO$_3^-$, (14) = AcO$, (15) = BzO$, (16) = SCN$, (17) = OH$, (18) = F$, (19) = Cl$, (20) = Br and (21) = I$.
Conclusion

In conclusion, we successfully synthesized two dinuclear complexes of Cu(II) and Zn(II) bearing dipicolylamine containing p-xylene scaffold, CuL1 and ZnL1, respectively. Both compounds have been investigated as IDA receptors for anions by using BPG as sensing indicator. We have found that only [CuL1•BPG] ensemble could discriminate oxalate anion from other common anions and dicarboxylate anions because oxalate anion could displace the bound BPG from ensemble cavity. In contrast to [ZnL1•BPG], several anions could replace the bound BPG from the ensemble structure. It could be implied that the binding constant of BPG with CuL1 is stronger than that of ZnL1. Therefore, in this work the nature of metal ion plays a crucial role to control the selective sensing for oxalate anion over other anions.

Supporting Information

Additional 1H and 13C NMR spectra of L1, ZnL1 and L2. Please contact corresponding author for detail of supporting information.

Acknowledgement

This work was partially supported by the Center of Excellence for Innovation in Chemistry (PERCH-CIC), Office of the Higher Education Commission, Ministry of Education. The authors acknowledge the technical support provided by Faculty of Science, Burapha University, Thailand.

References


