

Synthesis and Binding Properties of 1,3,5-Tris(2-arylthiomethyl)mesitylene: A Selective Ag (I) Ionophore

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Received November 22, 2007

The efficient synthesis of four mesitylene-based receptors **1-4** and their potentiometric response characteristics to alkali metal, alkaline earth metal, and transition metal ions, under various pH conditions are outlined. Receptor **1**-based electrode exhibited more sensitive response to Ag⁺ ion (49 mV/decade of range from 10⁻⁶ to 10⁻² M) than the **2**-based electrode (47 mV/decade of range from 3 × 10⁻⁵ to 10⁻² M), while the **3**- and **4**-based ones revealed sub-Nernstian below 40 mV/pAg⁺. All electrodes showed substantial responses to Ag⁺ ion under acidic condition, but there was almost nil-response to other transition metal ions (Fe²⁺, Co²⁺, Zn²⁺, Ni²⁺, Pb²⁺, Cd²⁺, Cu²⁺ and Hg²⁺). The association constant of receptor **1** toward Ag⁺ ion, measured by ¹H NMR titration, showed the largest value (200 M⁻¹) among the tested receptors. The results were interpreted with semi empirically-modeled structures.

Key Words : Tripodal receptor, Mesitylene, NMR titration, ISE, Silver ion selective

Introduction

Selective metal ion recognition by neutral receptors has attracted increasing interest in recent years because of their significant importance and potential applications in physiological, environmental, and supramolecular chemistry.¹ Silver (I) is one of the main transition metals used in electrical and electronic applications, photographic film industries and drugs. Due to their antibacterial properties, silver compounds have been used for dental and pharmaceutical purposes. Therefore, the design of Ag⁺-selective ionophores and the construction of ion-selective electrodes (ISEs) have attracted much attention regarding environmental and clinical analyses.^{2,3} Various ionophores including calix[4]arenes,⁴ crown ether derivatives,⁵ benzene-based tripodal derivatives,⁶ and steroidal tweezers⁷ have been used for the selective detection of Ag⁺ ions by introducing soft heteroatoms such as N and S, as an electron donor to metal cations. Rigid benzene-platforms have been widely used as building blocks for extended, well-defined molecular architecture and as a scaffold of synthetic receptors that show high selectivity toward cations, anions and organic molecules.^{8,9} Raymond *et al.* synthesized tripodal ionophores by attaching three catechol units to mesitylene and found that the binding constant of tris(catechol)mesitylene for Fe (III) is higher than that of the natural enderobactin.¹⁰ By incorporating heterocyclic units such as pyrazole, indole, and pyridine into a benzene motif, complexation studies with Pd (II),¹¹ Fe (II),¹² and Cu (I)¹³ have been performed.

Recently, we have designed new receptors that contain thiazole moieties.¹⁴ The ISEs based on solvent polymeric membranes (plasticized PVC) doped with these ionophores, exhibited large cation selectivity. To better understand the

cation recognition of these ionophores, we introduced benzothiazole,¹⁵ benzoxazole,¹⁶ pyridine, and pyrimidine units into a mesitylene-platform (compounds **1-4** in Scheme 1), and compared their binding properties to soft heavy metal ions. We described herein an efficient synthesis of four different mesitylene-based receptors **1-4** and their response characteristics to various mono- and divalent cations (alkali metal, alkaline earth metal, and transition metal ions). The cation binding characteristics of **1-4** are also investigated with PVC-based ISE membrane; their sensitivity and selectivity to various transition metal cations and alkali and alkaline earth metal cations were understood structurally in conjunction with solution NMR results.

Experimental Section

General. Melting points were measured on Thomas Hoover Melting point apparatus and are uncorrected. ¹H and ¹³C NMR spectra were recorded on a Varian Unity Spectrometer (¹H, 300 MHz; ¹³C, 75 MHz) in a CDCl₃ solution with TMS as an internal standard. ¹H NMR titrations were run at 45 mM concentrations, with aliquots of a 0.25 M (nBu)₄N⁺X⁻ salts solution added, on a Bruker AM-400 spectrometer. Elemental analyses were performed at the Center for Scientific Instruments, Kyungpook National University. Flash column chromatography was performed with Merck silica gel 60 (70-230 mesh) (Art 7734). All reactions were carried out under an atmosphere of argon. 2-Mercaptobenzothiazole, 2-mercaptobenzoxazole, 2-mercaptopyridine, 2-mercaptopyrimidine, and cesium carbonate were purchased from Aldrich Chemical Co and used without further purification. 1,3,5-Tris(bromomethyl)mesitylene was prepared according to the literature procedure.¹⁷

General procedure for the preparation of receptor. A mixture of 2-arylthiol (3.3 eq) and CsCO₃ (3.3 eq) in CH₃CN (30 mL) was refluxed for 1 h, and then 1,3,5-tris(bromomethyl)mesitylene (0.5 mmol, 1.0 eq) was added, and refluxed for 12 h. After the solvent was removed, it was extracted with dichloromethane, washed with brine, dried over anhydrous sodium sulfate, and concentrated. The residue was crystallized to yield product.

1,3,5-Tris(2'-benzothiazolylthiomethyl)-2,4,6-trimethylbenzene (1). This compound was obtained from 2-mercaptobenzothiazole as a white solid in a 85% yield, mp 197 °C (CHCl₃-hexane); ¹H NMR δ 8.05 (d, *J* = 7.5 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.49 (dd, *J* = 7.5, 8.0 Hz, 1H), 7.39 (dd, *J* = 7.5, 8.0 Hz, 1H), 4.76 (s, 2H, PhCH₂S), 2.51 (s, 3H, PhCH₃); ¹³C NMR δ 166.7, 153.0, 137.9, 135.1, 130.5, 126.2, 124.4, 121.5, 121.1, 34.2, 16.4. Anal. Calcd. For C₃₃H₂₇N₃S₆·H₂O: C, 58.63; H, 4.32; N, 6.22; S, 28.46. Found: C, 58.80; H, 4.11; N, 6.00; S, 28.59.

1,3,5-Tris(2'-benzoxazolylthiomethyl)-2,4,6-trimethylbenzene (2). This compound was obtained from 2-mercaptobenzoxazole as a white solid in a 85% yield, mp 193 °C (CH₂Cl₂-hexane); ¹H NMR δ 7.66 (d, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.28-7.33 (m, 2H), 4.74 (s, 2H, PhCH₂S), 2.61 (s, 3H, PhCH₃); ¹³C NMR δ 164.5, 151.9, 141.9, 138.2, 130.2, 124.4, 124.08, 118.5, 109.9, 32.9, 16.3. Anal. Calcd. For C₃₃H₂₇N₃O₃S₃: C, 65.00; H, 4.46; N, 6.89; S, 15.78. Found: C, 65.05; H, 4.52; N, 6.99; S, 16.17.

1,3,5-Tris(2'-pyridylthiomethyl)-2,4,6-trimethylbenzene (3). This compound was obtained from 2-mercaptopyridine as a white solid in a 84% yield, mp 171 °C (CH₂Cl₂-hexane); ¹H NMR δ 8.46 (d, *J* = 4.2 Hz, 1H), 7.47 (dd, *J* = 7.5, 7.8 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 6.98 (dd, *J* = 5.1, 6.9 Hz, 1H), 4.49 (s, 2H, PhCH₂S), 2.48 (s, 3H, PhCH₃); ¹³C NMR δ 159.9, 149.5, 136.8, 135.8, 131.4, 122.0, 119.3, 31.0, 16.2. Anal. Calcd. For C₂₇H₂₇N₃S₃: C, 66.22; H, 5.56; N, 8.58; S, 19.64. Found: C, 66.09; H, 5.64; N, 8.83; S, 19.62.

1,3,5-Tris(2'-pyrimidylthiomethyl)-2,4,6-trimethylbenzene (4). This compound was obtained from 2-mercaptopyrimidine as a white solid in a 94% yield, mp 206 °C (CH₂Cl₂-hexane); ¹H NMR δ 8.53 (d, *J* = 4.8 Hz, 2H), 6.97 (dd, *J* = 4.8, 4.8 Hz, 1H), 4.49 (s, 2H, PhCH₂S), 2.51 (s, 3H, PhCH₃); ¹³C NMR δ 172.9, 157.2, 137.2, 130.7, 116.4, 31.9, 16.2. Anal. Calcd. For C₂₄H₂₄N₆S₃: C, 58.51; H, 4.91; N, 17.06; S, 19.53. Found: C, 58.78; H, 5.02; N, 17.51; S, 19.60.

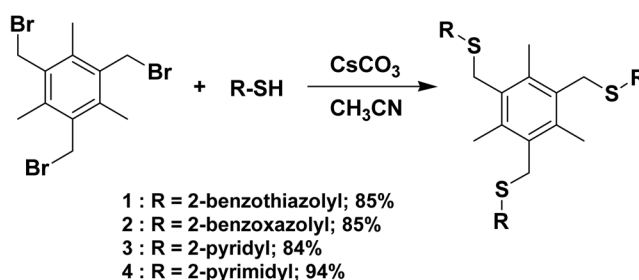
Preparation of electrodes and their potentiometric evaluation. Ion-selective membranes were prepared with 4 different ionophores (composition of membrane cocktails: 2 mg of ionophore 1-4, 66 mg of PVC and 132 mg of plasticizer [DOA]) in a THF (1.0 mL). The cocktail solutions were then poured into a glass ring (i.d. 22 mm) placed on a slide glass, and dried at room temperature for a day. After curing, 5.5 mm diameter disks were punched from the cast films and mounted in Phillips electrode bodies (IS-561; Glasblaserei Möller, Zürich, Switzerland). For all electrodes, 0.1 M of KCl was used as the internal reference electrolyte. All electrodes were presoaked in distilled water for 1 h

before use. Potential differences between the ISEs and the Orion sleeve-type double junction Ag/AgCl reference electrode (Model 90-02) were measured using a PC equipped with a high-impedance input 16-channel analog-to-digital converter (KOSENTECH, Inc. Busan, Korea). The dynamic response curves for transition metal were obtained by adding standard solutions to vary the concentration of each ionic species stepwise from 10⁻⁷ to 10⁻² M at 200 mL of a magnetically-stirred background electrolyte (0.01 M of magnesium acetate-HNO₃, pH 4.5) for every 100 s. The measurements for alkali, alkaline earth metal and ammonium ions were also conducted in neutral buffer solution (0.05 M of Tris-H₂SO₄, pH 7.4) to interference check. The potentials were measured every 100 s. The response of the electrodes to pH changes was tested by adding aliquots of a saturated sodium hydroxide solution to a solution of 11.4 mM of boric acid, 6.7 mM of citric acid, and 10.0 mM of NaH₂PO₄. All potentiometric measurements were carried out at room temperature. The selectivity coefficients were determined by using the matched potential method;^{18,19} the concentration of the primary ion that brings about the same response potential corresponding to 10⁻³ M interfering ion was determined and their activities have been compared. The detection limits of the electrodes were obtained from the calibration curves, as described in the reference.¹⁹

Results and Discussion

Synthesis and binding properties of 1,3,5-tris(2-arylthiomethyl)mesitylenes. The reaction of 1,3,5-tris(bromomethyl)mesitylene with 2-arylthiols in the presence of CsCO₃ provided corresponding mesitylene-based tripodal receptors 1-4 in good yields as depicted in Scheme 1. The crucial starting material, 1,3,5-tris(bromomethyl)mesitylene, was readily prepared by bromomethylation of mesitylene with HBr in acetic acid in a good yield.¹⁷ The structures of the obtained compounds were characterized by ¹H, ¹³C NMR, and elemental analyses. The ¹H NMR spectrum of 1 showed the expected four aromatic protons of benzothiazole at δ 8.05 (d, *J* = 7.5 Hz, H-5), 7.92 (d, *J* = 8.0 Hz, H-2), 7.49 (dd, *J* = 7.5, 8.0 Hz, H-4), and 7.39 (dd, *J* = 7.5, 8.0 Hz, H-3), methylene protons at δ 4.76 as singlet, and three methyl protons at δ 2.51.

The selective binding ability of receptor 1 toward silver (I) was determined initially by ¹H NMR study. As shown in Figure 1, the interaction between 1 and AgOTf in a DMSO-



Scheme 1

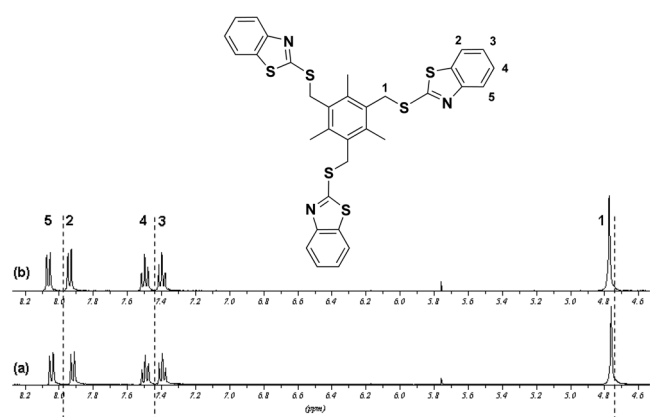


Figure 1. Partial ^1H NMR (400 MHz) spectra of (a) **1** (4.5×10^{-3} M) and (b) 1:1 mixture of **1** with AgOTf in $\text{DMSO-}d_6$ at 25°C .

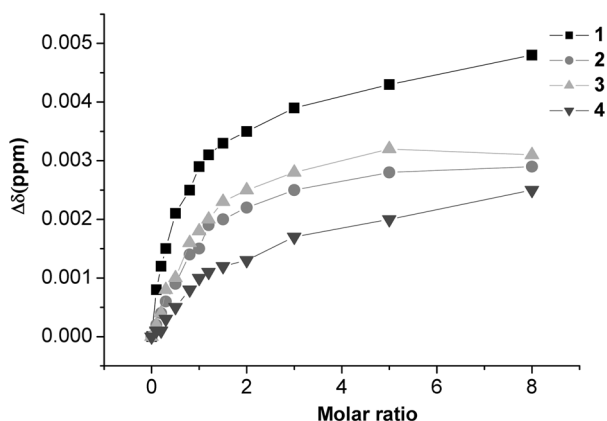


Figure 2. ^1H NMR titration curves of receptors with AgOTf in $\text{DMSO-}d_6$ at 25°C .

d_6 solution is obvious. When **1** was mixed with 1 equiv. of Ag^+ , the proton signals of methylene (H-1) and benzothiazole (H-2 and -5) in **1** moved to downfield in which the proton signal of H-2 clearly underwent downfield shift from δ 8.045 to 8.068, whereas the proton of H-1 underwent downfield shift from δ 4.761 to 4.772. These results implicate that cation binding take place in the core of tripodal receptor.

Binding studies of receptors **1-4** were performed by standard ^1H NMR titrations in the presence of AgOTf in a $\text{DMSO-}d_6$ solution as shown in Figure 2.²⁰ The association constants of receptors **1-4**, obtained by a nonlinear curve fitting EQ-NMR program,²¹ showed 200, 100, 75, 30 M^{-1} for the binding of Ag^+ , and are presented in Table 1. Receptor **1** showed the largest association constant among the tested receptors.

Evaluation of potentiometric properties. For a series of tris(arylthiomethyl)mesitylene shown in Scheme 1, we compared their potentiometric properties with plasticized PVC membranes. In general, the ISE membranes were prepared in standard way: adding 1 wt % of ion binding ligand compound into the mixture of 33 wt % PVC and 66 wt % plasticizer (DOA). Since commercial PVC normally contains anionic impurities such as carboxylic or sulfonic

Table 1. Association constants (M^{-1}) of receptors obtained from ^1H NMR titration^a

Receptor	1	2	3	4
K_a	200	100	75	30

^aDetermined in $\text{DMSO-}d_6$ at 25°C , $[\text{H}]_0 = 5 \times 10^{-3}$ M. Errors estimated to be $\leq 15\%$.

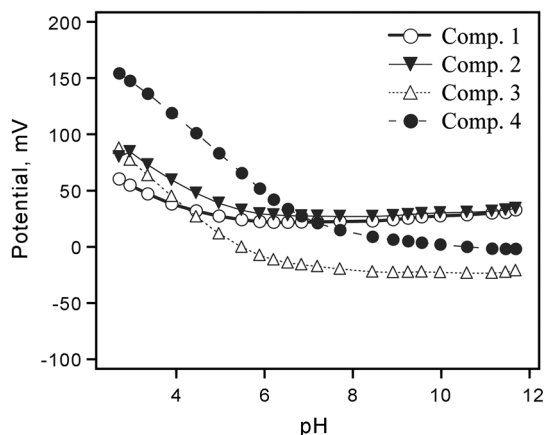


Figure 3. The pH responses of the **1**-, **2**-, **3**-, and **4**-based membrane electrodes to varying pH scales in universal buffer.

residues from industrial manufacturing process, no additional anionic sites were incorporated in the evaluation of newly synthesized ionophores. To focus on the structure-dependent selectivity and sensitivity relations of tripodal binding site, we tried to use the standard matrix compositions for all ionophores instead of carrying out an extensive matrix optimization study.

Figure 3 shows the response of the electrodes to pH changes varied by adding aliquots of a saturated hydroxide solution to a universal buffer at room temperature as described in Experimental section. The compound **4**-based electrode exhibited the most sensitive response in the pH 2.5-8.2 range. Other electrodes also showed some pH responses in acidic regions, but flattened sensitivity beyond pH 6. Since the pH responses of the **1**-, **2**-, **3**-, and **4**-based membrane electrodes are negligible near pH 8, we examined their responses to other cations near neutral and alkaline conditions. We measured the potentiometric responses of the compounds **1**-, **2**-, **3**-, and **4**-based membrane electrodes to various cations, *e.g.*, alkali metal, alkaline earth metal cations, and ammonium ion. All electrodes exhibited negligible responses to common physiological cations below 10^{-3} M, but as shown in Figure 4, increased responses to sodium, potassium and ammonium ions at high concentrations ($> 10^{-2}$ M) in 0.05 M tris-HCl (pH 7.4) were noted: the potential differences from 10^{-3} to 10^{-1} M were about 50-80 mV.

The potentiometric responses and properties of the ISEs are summarized in Table 2. Structurally similar compounds **1** (contains benzothiazole groups) and **2** (benzoxazole groups) showed nearly Nernstian response to silver ions, whereas other membranes based on the compounds containing pyri-

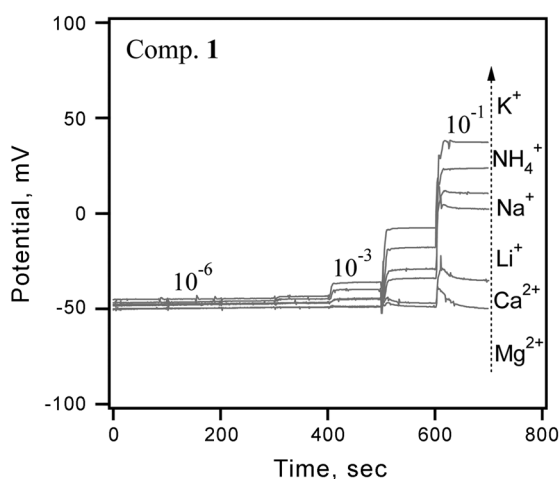


Figure 4. The potentiometric responses of the DOA-plasticized PVC membranes prepared with the tripodal benzothiazole (**1**) in 0.05 M tris- H_2SO_4 (pH 7.4). The same type of membranes prepared with benzoxazolyl (**2**), pyridyl (**3**), and pyrimidyl (**4**), containing 1,3,5-tris(2-arylthiomethyl)mesitylene moieties also exhibit similar negligible responses below 10^{-2} M.

Table 2. Potentiometric response properties of the **1**-, **2**-, **3**-, and **4**-based membrane electrodes

No.	Ionophore	Slope ^a (mV/dec)	Det. Limit ^b -log[Ag ⁺ /M]	Linear range (M)
1	Comp. 1	48.8	-6.4	1×10^{-6} to 1×10^{-2}
2	Comp. 2	47.1	-5.3	3×10^{-5} to 3×10^{-2}
3	Comp. 3	28.0	-6.6	1×10^{-6} to 1×10^{-2}
4	Comp. 4	NR ^c	-	-

^aSlopes from the linear range. ^bLogarithmic scale. ^cNR is negligible response.

dine and pyrimidine (compounds **3** and **4**) groups exhibited poor potentiometric properties. The dynamic response and calibration curves obtained from compounds **1**- and **2**-based ISEs (see Figure 5) manifest highly sensitive responses to Ag^+ ion from 10^{-6} to 10^{-2} M. In spite of the structural similarity between compound **1** and **2**, the compound **1**-based electrode exhibited more sensitive response to Ag^+ ion (49 mV/decade of range from 10^{-6} to 10^{-2} M) in a wider range than the compound **2**-based electrode (47 mV/decade of range from 3×10^{-5} to 10^{-2} M). While **1**- and **2**-based ISEs resulted in sub-Nernstian response to Ag^+ , they do not respond to other common transition metal ions, Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} tested in this experiment (negligible response up to 10^{-2} M) and their potentiometric properties are almost Ag^+ -specific. It is apparent that the compounds **1** and **2** are highly selective to silver but with relatively low binding constants as discussed below. The pyridine containing compound **3**-based ISE membrane also exhibited good sensitivity and low detection limit to silver ion. However, its response slope, 28 mV/decade, was much inferior to **1**- and **2**-based membranes. The pyrimidine containing compound **4**-based ISE membrane exhibited slight response to silver ions, but nil to all other transition

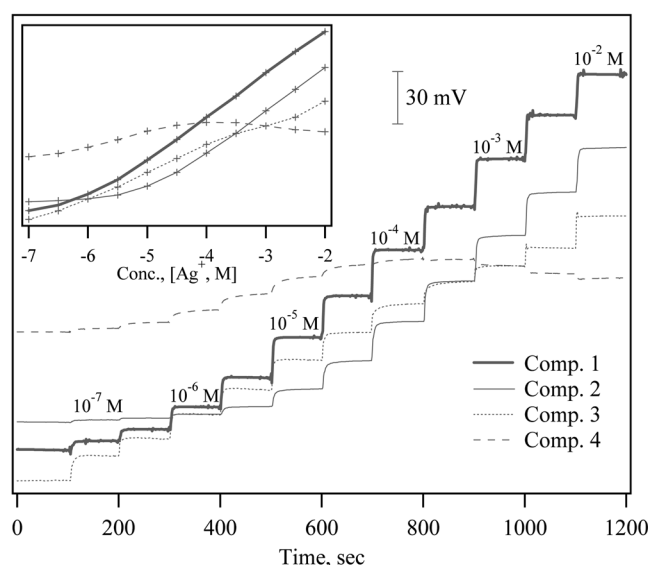


Figure 5. The potentiometric responses of the **1**-, **2**-, **3**-, and **4**-based membrane electrode to Ag^+ at 0.01 M magnesium acetate- HNO_3 (pH 4.5). The inset shows the calibration curves.

metal ions.

The potentiometric experimental results suggest that silver ion is primarily bound to the sulfur in tripodal groups and held tightly by the assistant binding groups. The benzothiazole moiety in compound **1** provides additional sulfur atoms to tightly hold the silver ion primarily bound to sulfur in linking tripod. The NMR results also corroborate with this interpretation. On the other hand, semi-empirical simulation study shows that the pocket size, about 5 Å, formed by tripodal group is larger than the van der Waals radii of silver ion (about 3 Å),²² suggesting a loose binding at the pore. It may explain a sub-Nernstian behavior of the compound **1**-based membrane. As indicated by the low slope, the benzoxazole group in compound **2** is less efficient in holding the silver ion in the pore.

The low sensitivity of **3**-based membrane indicates that the pendant pyridine group in tripodal moiety is not efficient in holding the silver ion, partly because of unfavorable binding angle toward the central ion held in the pore. The significantly reduced sensitivity of pyrimidine-based membrane **4** compared to that of pyridine-based membrane is not clearly understood although it is assumed that the sp^2 electron density at nitrogen in pyrimidine is less favorable for binding the metal cation than the pyridine.²³ Nonetheless, it is apparent that a sulfur containing moiety is more advantageous than that with nitrogen in designing the soft transition metal ion binding ligands. Another improvement may be made if the size of central pore can be controlled with flexible pendant groups around the periphery of benzene scaffold.

Acknowledgements. This work was supported by Kyungpook National University Research Fund, 2007. G. S. Cha also acknowledges the support from Kwangwoon University in 2006.

References

- (a) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; John Wiley & Sons Ltd.: 2000. (b) Kim, S. H.; Youn, N. J.; Park, J. Y.; Choi, M. G.; Chang, S.-K. *Bull. Korean Chem. Soc.* **2006**, *27*, 1553.
- Wygladacz, K.; Radu, A.; Xu, C.; Qin, Y.; Bakker, E. *Anal. Chem.* **2005**, *77*, 4706.
- Zhang, X.-B.; Han, Z.-X.; Fang, Z.-H.; Shen, G.-L.; Yu, R.-Q. *Anal. Chim. Acta* **2006**, *562*, 210.
- (a) Jeon, Y.-M.; Lim, T.-H.; Kim, J.-G.; Kim, J.-S.; Gong, M.-S. *Bull. Korean Chem. Soc.* **2007**, *28*, 816. (b) Higuchi, H.; Matsufuji, T.; Oshima, T.; Ohto, K.; Inoue, K.; Tsend-Ayush, T.; Gloe, K. *Chem. Lett.* **2005**, *34*, 80. (c) Morakot, N.; Tomapatanaget, B.; Ngeon-Tae, W.; Aeungmaitrepirom, W.; Tuntulani, T. *Supramol. Chem.* **2005**, *17*, 655. (d) Lu, J.; He, X.; Zeng, X.; Wan, Q.; Zhang, Z. *Talanta* **2003**, *59*, 553. (e) Zeng, X.; Weng, L.; Chen, L.; Xu, F.; Li, Q.; Leng, X.; He, X.; Zhang, Z. *Tetrahedron* **2002**, *58*, 2647. (f) Kim, Y. H.; Cha, N. R.; Chang, S.-K. *Tetrahedron Lett.* **2002**, *43*, 3883. (g) Chen, L.; Ju, H.; Zeng, X.; He, X.; Zhang, Z. *Anal. Chim. Acta* **2001**, *437*, 191. (h) Zeng, X.; Weng, L.; Chen, L.; Leng, X.; Ju, H.; Zhang, Z. *J. Chem. Soc. Perkin Trans. 2* **2001**, 545. (i) Xie, J.; Zheng, Q.-Y.; Zheng, Y.-S.; Chen, C.-F.; Huang, Z.-T. *J. Incl. Phenom.* **2001**, *40*, 125. (j) Chen, L.; Zeng, X.; Ju, H.; He, X.; Zhang, Z. *J. Microchem.* **2000**, *65*, 129.
- (a) Park, S. B.; Yoon, I.; Seo, J.; Kim, H. J.; Kim, J. S.; Lee, S. S. *Bull. Korean Chem. Soc.* **2006**, *27*, 713. (b) Goldcamp, M. J.; Ashley, K.; Edison, S. E.; Pretty, J.; Shumaker, J. *Electroanalysis* **2005**, *17*, 1015. (c) Isildak, I.; Yolcu, M.; Isildak, O.; Topal, G.; Horsgoren, H. *Microchim. Acta* **2004**, *144*, 177. (d) Su, C. C.; Chang, M. C.; Liu, L. L. K. *Anal. Chim. Acta* **2001**, *432*, 261. (e) Rutrack, K.; Koval'chuck, A.; Bricks, J. L.; Slominskii, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 6205. (f) Matsumoto, K.; Hashimoto, M.; Toda, M.; Tsukube, H. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2497.
- (a) Kim, H.-S.; Kim, D.-H.; Kim, K. S.; Choi, J.-H.; Choi, H. J.; Kim, S. H.; Shim, J. H.; Cha, G. S.; Nam, H. *Talanta* **2007**, *71*, 1986. (b) Hiraoka, S.; Yi, T.; Shiro, M.; Shinoya, M. *J. Am. Chem. Soc.* **2002**, *124*, 14510.
- (a) Kim, B. H.; Hong, H. P.; Cho, K. T.; On, J. H.; Jun, Y. M.; Jeong, I. S.; Cha, G. S.; Nam, H. *Talanta* **2005**, *66*, 794. (b) Shim, J. H.; Jeong, I. S.; Lee, M. H.; Hong, H. P.; On, J. H.; Kim, K. S.; Kim, H.-S.; Kim, B. H.; Cha, G. S.; Nam, H. *Talanta* **2004**, *63*, 61.
- Hennrich, G.; Anslyn, E. V. *Chem. Eur. J.* **2002**, *8*, 2219, references cited therein.
- Selected references: (a) Kim, J.; Raman, B.; Ahn, K. H. *J. Org. Chem.* **2006**, *71*, 38. (b) Turner, D. R.; Paterson, M. J.; Steed, J. W. *J. Org. Chem.* **2005**, *71*, 1598. (c) Seong, H. R.; Kim, D.-S.; Kim, S. G.; Choi, H.-J.; Ahn, K. H. *Tetrahedron Lett.* **2004**, *45*, 723. (d) Vacca, A.; Nativi, C.; Cacciarini, M.; Pergoli, R.; Roelens, S. *J. Am. Chem. Soc.* **2004**, *126*, 16456. (e) Choi, H. J.; Park, Y. S.; Yun, S. H.; Kim, H.-S.; Cho, C. S.; Ko, K.; Ahn, K. H. *Org. Lett.* **2002**, *4*, 795. (f) Hiraoka, S.; Yi, T.; Shiro, M.; Shinonoya, M. *J. Am. Chem. Soc.* **2002**, *124*, 14510. (g) Sasaki, S.; Citterio, D.; Ozawa, S.; Suzuki, K. *J. Chem. Soc., Perkin Trans. 2* **2001**, 2309.
- Stack, T. D. P.; Hou, Z.; Raymond, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 6466.
- Hartshorn, C. M.; Steel, P. J. *Chem. Commun.* **1997**, 541.
- (a) Holm, R. H.; Kennepohl, P.; Solomon, E. I. *Chem. Rev.* **1996**, *96*, 2239. (b) Stack, T. D. P.; Holm, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 2546.
- Walsdorff, C.; Saak, W.; Pohl, S. *J. Chem. Soc. Dalton Trans.* **1997**, 1857.
- (a) Choi, J. H.; Koh, Y. K.; Kwon, I.-C.; Kim, H.-S.; Park, H. J.; Kim, S. J.; Cha, G. S.; Nam, H. *Bull. Korean Chem. Soc.* **1999**, *20*, 581. (b) Kim, H.-S.; Park, H. J.; Oh, H. J.; Koh, Y. K.; Choi, J. H.; Lee, D.-H.; Cha, G. S.; Nam, H. *Anal. Chem.* **2000**, *72*, 4683. (c) Kim, H.-S.; Choi, J. H.; Koh, Y. K.; Choi, H.-J.; Park, H. J.; Cha, G. S.; Nam, H. *J. Inclusion Phenom.* **2001**, *40*, 265. (d) Kariuki, B. M.; Lee, S.-O.; Harris, K. D. M.; Kim, H.-S.; Do, K.-S.; Kim, K.-I. *Cryst. Growth & Design* **2002**, *2*, 309. (e) Kim, H.-S.; Do, K. S.; Kim, K. S.; Shim, J. H.; Cha, G. S.; Nam, H. *Bull. Korean Chem. Soc.* **2004**, *25*, 1465. (f) Kwon, O.-S.; Kim, H.-S. *Supramol. Chem.* **2007**, *19*, 277.
- Akhond, M.; Tashkhourian, J. *Bull. Korean Chem. Soc.* **2003**, *24*, 489.
- Akhond, M.; Ghaedi, M.; Tashkhourian, J. *Bull. Korean Chem. Soc.* **2005**, *26*, 882.
- van der Made, A. W.; van der Made, R. H. *J. Org. Chem.* **1993**, *58*, 1262.
- Gadzekpo, V. P. Y.; Christian, G. D. *Anal. Chim. Acta* **1984**, *164*, 279.
- (a) Buck, R. P.; Lindner, E. *Pure Appl. Chem.* **1994**, *66*, 2527. (b) Umezawa, Y.; Umezawa, K.; Sato, H. *Pure Appl. Chem.* **1995**, *67*, 507.
- Fielding, L. *Tetrahedron* **2000**, *56*, 6151.
- (a) Hynes, M. J. *J. Chem. Soc. Dalton Trans.* **1993**, 311. (b) Connors, K. A. *Binding Constants*; Wiley: New York, 1987.
- Reddy, P. J.; Ravichandran, V.; Chacko, K. K.; Weber, E.; Saenger, W. *Acta Cryst.* **1989**, *C45*, 1871.
- Gozzo, F. C.; Eberlin, M. N. *J. Org. Chem.* **1999**, *64*, 2188.