Chinese Chemical Letters Vol. 16, No. 6, pp 733-735, 2005
http://www.imm.ac.cn/journal/ccl.html

Efficient Amide Based Halogenide Anion Receptors

Hong Xing WU[1], Feng Hua LI[1], Hai LIN[2], Shou Rong ZHU[1], Hua Kuan LIN[1]*

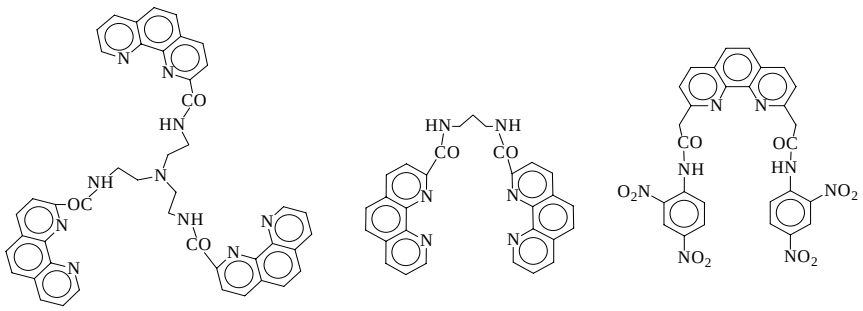
[1]Department of Chemistry, Nankai University, Tianjin 300071
[2]State Key Laboratory of Functional Polymer Materials for Absorption and Separation, Nankai University, Tianjin 300071

Abatract: In this paper, we present the synthesis and anion recognition properties of the amide based phenanthroline derivatives **1**, **2** and **3**. In all cases 1:1 receptor : anion complexes were observed. The receptors were found to be selective for fluoride and chloride respectively over other putative anionic guest species.

Keyword: Anion receptor, phenanthroline, spectroscopic titration.

Recently, supramolecular chemists have devoted considerable effort to developing systems to be capable of recognizing, sensing and transporting negatively charged species[1]. Some simple, water-soluble anions such as fluoride, chloride and phosphate play critical roles in many biological processes and a number of diseases associated with fluorosis or cystic fibrosis and are thus considered important targets in terms of receptor design[2, 3]. The amide NH groups of the receptor **1** and **2**, **3** could function as anion binding moieties while the phenanthroline rings might serve as a colorimetric receptor of any binding events.

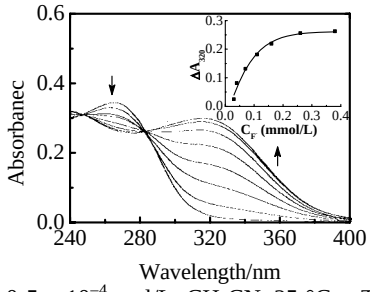
Figure 1 Structures of receptors of **1**, **2** and **3**



1 **2** **3**

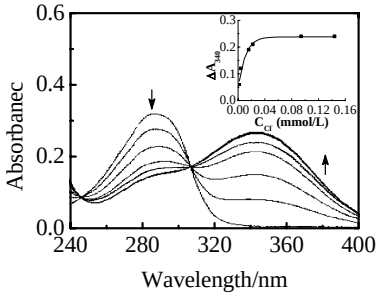
* E-mail: hklin@nankai.edu.cn

Figure 2 UV spectral changes of **1** upon the addition of fluoride anion



$C_{\mathbf{1}} = 1.0 \times 10^{-5}$ mol/L, $C_{TBAF} = 0\text{-}5 \times 10^{-4}$ mol/L, CH_3CN, 25 °C. The inset shows the fit of the experimental data to a 1:1 binding profile.

Figure 3 UV spectral changes of **3** upon the addition of chloride anion



$C_{\mathbf{3}} = 1.0 \times 10^{-5}$ mol/L, $C_{TBACl} = 0\text{-}5 \times 10^{-4}$ mol/L, CH_3CN, 25 °C. The inset shows the fit of the experimental data to a 1:1 binding profile.

Table 1 Binding constants (mol^{-1}) of **1-3**[a] with various anions[b] in CH_3CN

	1	**2**	**3**
F^-	13000	2800	ND[c]
Cl^-	940	750	72000
Br^-	210	90	8100
I^-	70	ND[c]	590

[a] All errors are ± 10% All binding constants are reported as the average of 2-4 trials.
[b] Anions used in this assay were in the form of their tetrabutylammonium (TBA) salts.
[c] ND = not determined.

The host molecules **1**, **2** and **3** were synthesized starting from tris(aminoethyl)amine, propylenediamine and 2,4-dinitroaniline by reaction with the appropriate acid chlorides[4-8]. Compounds **1-3** were isolated in 40-70% yields after recrystallization and were characterized by ^{1}H NMR, infrared spectroscopy, mass spectrometry and elemental analysis.

The receptors were required to contain electron withdrawing nitro substituents and/or electron poor phenanthroline rings that would render the amide N-H protons more acidic, thereby promoting the key anion-to-receptor interactions. In addition, the more recognition sites would increase the stability of the anion-receptor complex. In the case of receptors **1**, **2** and **3**, these electron poor/withdrawing effects were expected to take

place efficiently and lead to high binding affinities.

As a test of the above hypothesis, the fluoride, chloride, bromide and iodide anion binding properties of the receptors were studied by UV spectroscopy in CH_3CN using the tetra-*n*-butylammonium (TBA) salts of the anions in question. **Figure 2** shows the spectroscopic changes observed when receptor **1** is treated with increasing concentrations of TBAF. In this case, the peak at 265 nm decreased upon the addition of TBAF, a new peak at 320 nm appeared with saturation being observed after the addition of *ca.* 25 equiv. **Figure 3** shows the spectroscopic changes observed of receptor **3**. The peak at 285 nm decreased and a new peak at 340 nm appeared upon the addition of TBACl, with saturation of *ca.* 3 equiv in this case. From Job-plot analysis, these spectral changes are ascribed to the formation of 1:1 complex between the receptor and fluoride or chloride anion. Standard curve-fitting procedures were then used to derive binding constants[9]. The resulting values are collected in **Table 1**.

Receptor **1** displayed higher affinities (**Table 1**) for various anions than **2**, which is not really surprising, because the more recognition sites of **1** lead increase in the stability of anion-receptor complex. Besides, we also found that **1** and **2** are selective for the smaller fluoride anion over other putative anionic guest species. As to receptor **3**, its absorbance spectroscopy did not show an evident change upon the addition of TBAF, because that the size of fluoride anion is too small to coordinate with the two amide N-H groups simultaneously. But it displayed a very high affinity (**Table 1**) for chloride anion. Relative to **1** and **2**, the greater "success" for chloride and bromide of **3** is due to the greater electron deficiency of phenanthroline and the dinitro substitutes which lead increase of its hydrogen bond-donating character.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (No. 20371028) and the Natural Science of Tianjin(No. 023605811)

References

1. (a) B. Valeur, I. Leray, *Coord. Chem. Rev.*, **2000**, *205*, 3; (b) P. A. Gale, *Coord. Chem. Rev.*, **2000**, *199*, 181; (c) T. Jentsch, C. Opin. *Neurobiol.*, **1996**, *6*, 303.
2. J. M. Tomich, D. Wallace, K. Henderson, *et al.*, *Biophys. J.*, **1998**, *74*, 256.
3. D. P. Wallace, J. M. Tomich, T. Iwamoto, *et al.*, *Am. J. Physiol.*, **1997**, *272*, C1672.
4. R. Jairam, P. G. Potvin, *J. Org. Chem.*, **1992**, *57*, 4136.
5. Y. P. Khanna, E. M. Pearce, B. D. Forman, D. A. Bini, *J. Polym. Sci. Polym. Chem. Ed.*, **1981**, *19*, 2799.
6. Von K. Madeja, *J. Praket. Chem.*, **1962**, *17*, 97.
7. A. Harold, R. N. Goodwin, *Aust. J. Chem.*, **1967**, *20*(2), 217.
8. A. Moghimi, R. Alizadeh, A. Shokrollehi, *et al.*, *Inorg. Chem.*, **2003**, *42*, 1616.
9. A. K. Connors, *Binding Constants: The Measurement of Molecular Complex Stability*, Wiley-VCH, Neo York, **1987**.

Received 29 June, 2004