Bull. Korean Chem. Soc. 2009, Vol. 30, No. 12 3089
DOI 10.5012/bkcs.2009.30.12.3089

Fluorescent Anion Receptor of Tweezer-type: Using Pyrene Amide Unit with Cationic Pyridinium Skeleton

Byung Ju Ryu, Ah Leum Lee, Young Ju Lee,† and Kye Chun Nam*

Department of Chemistry, and Institute of Basic Science, Chonnam National University, Gwangju 500-757, Korea
**E-mail: kcnam@chonnam.ac.kr*
†Korea Basic Science Institute, Gwangju Center, Gwangju 500-757, Korea
Received September 17, 2009, Accepted October 14, 2009

Key Words: Anion sensor, Binding constant, Anion template

The synthesis of macrocyclic and acyclic compounds has been facilitated largely by the use of template methodology to their construction.[1] Since the structures of catenane and rotaxane are similar to DNA, they are drawing much attention in the study of biochemical structure. They can be utilized in the newly emerging field of controlling molecules in nano-scale such as molecular electronics, molecular mechanics and molecular self-assembly.[2] To date, most of these schemes depend on the use of neutral or cationic species to achieve the desired template effect, utilizing a variety of noncovalent forces such as metal-ligand coordination, hydrogen bonding, π-π stacking, and solvophobic interactions.[3] Stang,[4] Taujita,[5] Sauvage[6] have been actively developing catenane, rotaxane and pseudorotaxane using the coordination chemistry using Cu(II), Pb(II), and Fe(II) as templates as the simple ionophore has been developed from cation. The absence of anionic species as more general participants in this arena is often attributed to the relatively small ratio of charge to radius and sizable solvation energy as compared to cations.[7] However, there are a growing number of reports of anion templation accumulating in the literature, demonstrating the efficacy of such an approach. For the purpose of the development of molecular machine such as rotaxane and catenane, an anion receptor with pyrene unit in a simple cationic pyridinium skeleton was synthesized and its anion binding properties were investigated from fluorescence and ^{1}H NMR analysis.

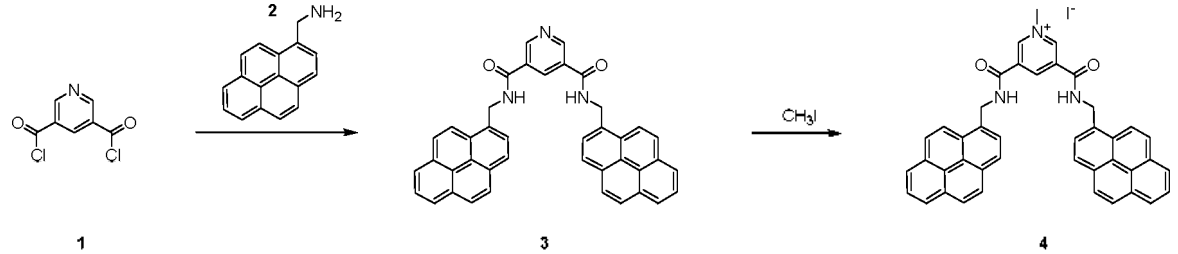
Results and Discussion

Target molecule **4** was synthesized by the methylation of **3** which was prepared from the reaction of **1** with 1-pyrenemethylamine as shown in Scheme 1 in high yield. The amide ligand structure was easily confirmed from the ^{1}H NMR spectrum such as a triplet at δ 9.82 ppm for two N-H proton, two singlets at δ 9.55 and 9.38 for three pyridine protons, a multiplets at δ 8.06 - 8.47 for eighteen pyrene protons, one doublet at δ 5.30 for four methylene protons, and one singlet at δ 4.40 for three methyl protons.

The fluorescent titration experiments were carried out in an acetonitrile solution. A receptor solution (1×10^{-6} M) was treated with the representative anions such as tetrabutylammonium (TBA) fluoride, chloride, bromide, iodide, dihydrogen phosphate, hydrogen sulfate, perchlorate, acetate and benzoate. Excited at 343 nm, **4** display fluorescence emission at 414 nm. When compound **4** formed a complex with various anions, fluorescence intensity was quenched at 414 nm. Decrease in fluorescence intensity in anions were observed: ($F^- > CH_3COO^- > C_6H_5COO^- > Cl^- > H_2PO_4^- > HSO_4^-$).

To understand the association between the receptor **4** and anions in detail, the ^{1}H -NMR titration method was employed in DMSO-d_6. A large downfield shift of NH protons and the slight shift of aromatic protons were observed upon the addition of TBA salts of fluoride, chloride, dihydrogen phosphate, benzoate and acetate to the receptor **4**. Particularly, the singlet peak of the amide NH signals shifted rapidly and it was used to determine the binding constants of receptor **4** and anions by the nonlinear curves fitting program Win EQ-NMR.[8] (Table 1). Due to the broadness of NH proton signal upon the addition of HSO_4^-, $H_2PO_4^-$ and F^-, the binding constants could not be determined in these cases.

As shown in Table 1, receptor **4** binds chloride anion strongly, which can be observed previously in the case of isophtalamide derivatives.[9] It could be explained by the subtle difference in the structure complementarity between receptor **4** and anions. The size of chloride anion fitted well with the cavity size of the receptor **4** while the sizes of other halide anions were not. In addition, in case of fluoride anion, the dramatic fluorescence



1 3 4

Scheme 1. Synthesis of fluorescent chemosensors **4**

Table 1. The association constants (K_a) of receptor **4** with anions in DMSO-d_6

Anion	F^-	Cl^-	Br^-	I^-	ClO_4^-	HSO_4^-	$C_6H_5COO^-$	CH_3COO^-	$H_2PO_4^-$
K_a(Error%)	[a]	5941(4)	[b]	[b]	[b]	[a]	3613(9)	1358(8)	[a]

[a]Due to the broadness of NH proton signal in ^{1}H NMR titration . the stability constant was not determined. [b]Very slightly shift of NH proton signal in ^{1}H NMR titration was observed.

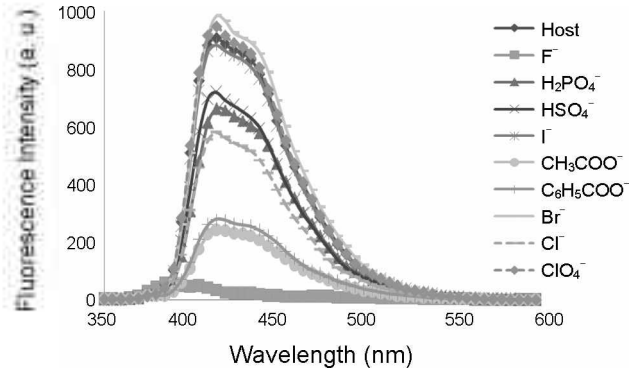


Figure 1. Emission spectra of **4** (1.0 μM) upon the addition of various anions to 1000 eq in acetonitrile. (The excitation wavelength is 343 nm and emission at 414 nm).

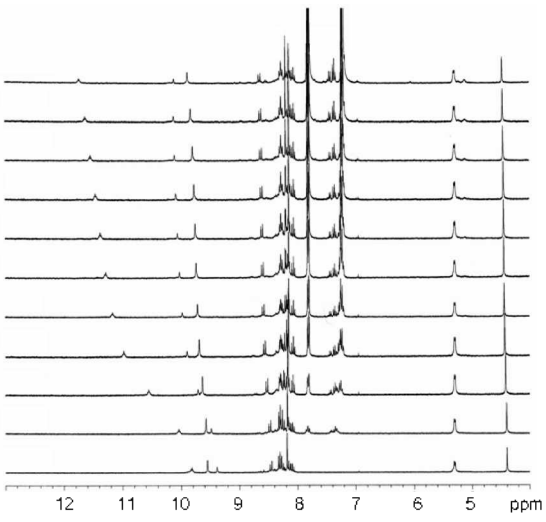


Figure 2. The partial ^{1}H NMR spectra of compound **4** (0.4 mM) in the presence of $TBA^+C_6H_5COO^-$ in DMSO-d_6. Numbers at the left side indicate the equivalent amounts of $C_6H_5COO^-$ added.

quenching was observed probably due to the deprotonation of NH proton from the relatively basic fluoride anion which resulted in the broadness of NH peak during the titration. The ^{1}H NMR experiment supported the deprotonation as observed in NMR as a new triplet at around 16 ppm, which corresponds to the formation of FHF^-.[10] It is also interesting feature that the binding constant of receptor **4** with benzoate is somewhat higher than in case of acetate anion, which could attribute the aromatic stacking interaction[11] between the pyrene unit of receptor **4** and phenyl unit of benzoate.

In conclusion, we have prepared a novel tweezer-type fluorescent anion receptor **4** based on pyrene amide and cationic pyridinium skeleton which shows the sensitivity to fluoride, chloride, acetate, and benzoate. The binding constant of receptor **4** with chloride is very high as compared to other anions, probably due to the size compatibility.

Experimental

***N,N'-Bis*(1-pyrenylmethyl)pyridine-3,5-dicarboxamide (3).** To a mixture of 9-aminomethylpyrene (0.268 g, 1 mmol) and triethylamine (0.5 mL) in dichloromethane (10 mL) was added 3,5-pyridinedicarbonyl dichloride (0.096 g, 0.47 mmol) solution in dichloromethane (10 mL). The mixture was stirred at room temperature for 2 h. The white precipitate was filtered off and washed with water and methanol to afford the 0.24 g of **3** (86%). ^{1}H NMR (DMSO-d_6, 300 MHz) δ 9.56 (t, 2H, NH, J = 5.7 Hz), 9.20 (s, 2H, -CHNCH-, pyridine), 8.748 (t, 1H, CH, J = 2.1 Hz, from pyridine), 8.05-8.50 (m, 18H, pyrene), 5.258 (d, 4H, 2-CH_2-pyrene, J = 5.7 Hz). ^{13}C NMR (DMSO-d_6, 300 MHz) δ 164.31, 150.625, 132.364, 130.762, 130.270, 130.171, 129.533, 128.137, 127.637, 127.355, 127.080, 126.840, 126.256, 125.279, 125.180, 124.722, 124.028, 123.898, 123.173, 41.536.

1-Methyl-3,5-*bis*(pyren-1-ylmethylcarbamoyl)pyridinium iodide (4). To a solution of *N,N'*-bis(1-pyrenylmethyl)pyridine-3,5-dicarboxamide **3** (0.24g, 0.40 mmol) in 1,1,2,2,-tetrachloromethane (20 mL), 5 mL of methyl iodide was added and refluxed for 48 hours. The precipitate was collected and washed with methanol (10 mL) to give 0.26 g of **4** (88%). ^{1}H NMR (DMSO-d_6, 300 MHz) δ 9.82 (t, 2H, NH, J = 5.4 Hz), 9.55 (s, 2H, -CHNCH-, from pyridine), 9.38 (br, t, 1H, CH, from pyridine), 8.06-8.47 (m, 18H, pyrene), 5.305 (d, 4H, 2-CH_2-pyrene, J = 5.4 Hz), 4.40 (s, 3H, -CH_3). ^{13}C NMR (DMSO-d_6, 300 MHz) δ 160.960, 147.240, 141.002, 132.887, 131.460, 130.747, 130.438, 130.239, 128.316, 127.828, 127.332, 127.259, 126.390, 125.466, 125.310, 124.726, 124.055, 123.837, 123.135, 48.446, 41.536. ESI MS(+) *m/z* (M^+-I^-): Calcd, 608.2338. Found, 608.2330.

Acknowledgments. This work was supported by Korea Research Foundation Grant (KRF-2007-001-C00165). NMR spectra were taken at the Korea Basic Science Institute, Gwangju, Korea.

References

1. (a) Raymo, F. M.; Stoddart, J. F. *Templated Organic Synthesis*; Wiley: Weinheim, Germany, 2000. (b) Hubin, T. J.; Busch, D. H. *Coord. Chem. Rev.* **2000**, *202*, 5.
2. (a) Collier, C. P.; Mattersteig, G.; Wong, E. W.; Luo, Y.; Beverly, K.; Sampaio, J.; Raymo, F. M.; Stoddart, J. F.; Heath, J. R. *Science* **2000**, *289*, 1172. (b) Jeppesen, J. O.; Perkins, J.; Becher, J.; Stoddart, J. F. *Angew. Chem. Int. Ed.* **2001**, *40*, 1216.
3. Leigh, D. A.; Lusby, P. J.; Teat, S. J.; Wilson, A. J.; Wong, J. K. *Angew. Chem. Int. Ed.* **2001**, *40*, 1538.
4. Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853.

5. (a) Fujita, M.; Fujita, N.; Ogura, K.; Yamaguchi, K. *Nature* **1999**, *400*, 52. (b) Hori, A.; Kumazawa, K.; Kusukawa, T.; Chand, D. K.; Fujita, M.; Sakamoto, S.; Yamaguchi, K. *Chem. Eur. J.* **2001**, *7*, 4142.
6. (a) Sauvage, J. P. *Acc. Chem. Res.* **1998**, *31*, 611. (b) Collin, J. P.; Heitz, V.; Bonnet, S.; Sauvage, J. P. *Inorg. Chem.* **2005**, *8*, 1063.
7. (a) *Supramolecular Chemistry of Anions*; Bianchi, A.; Bowman-James, K.; Garcia-Espana, E., Eds.; Wiley-VCH: New York, 1997. (b) Beer, P. D.; Gale, P. A. *Angew. Chem. Int. Ed.* **2001**, *40*, 486.
8. (a) Kavallieratos, K.; de Gala, S. R.; Austin, D. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 2325. (b) Kavallieratos, K.; Bertao, C. M.; Crabtree, R. H. *J. Org. Chem.* **1999**, *64*, 1675.
9. (a) Kim, J. S.; Quang, D. T. *Chem. Rev.* **2007**, *107*, 3780. (b) Leray, I.; Lefevre, J. P.; Delouis, J. F.; Delaire, J.; Valeur, B. *Chem. Eur. J.* **2001**, *7*, 4590.
10. Yeo, H. M.; Ryu, B. J.; Nam, K. C. *Org. Lett.* **2008**, *10*, 2931.
11. (a) Kim, J.; Raman, B.; Ahn, K. H. *J. Org. Chem.* **2006**, *71*, 38. (b) Hunter, C. A.; Lawson, K. R.; Perkin, J.; Urch, C. J. *J. Chem. Soc., Perkin Trans.* **2001**, *2*, 651. (c) Waters, M. L. *Current Opinion in Chemical Biology* **2002**, *6*, 736.