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A Simple Colorimetric and Fluorescent Anion Sensor Based on 4-Amino-1,8-naphthalimide: Synthesis and its Recognition Properties

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A neutral 4-amino-1,8-naphthalimide-based anion receptor 1 containing a thiourea binding site was synthesized by simple steps. Its recognition capabilities for various anions were investigated by UV–vis, fluorescence and ^{1}H NMR spectra, which showed that compound 1 could effectively and selectively recognize F^- and AcO^- over other anions (Cl^-, Br^-, I^-, NO_3^-, HSO_4^-, ClO_4^-). In particular, a moderate color change (from greenish yellow to bright yellow) and significant fluorescence quenching were synchronously observed upon addition of F^- or AcO^-. Nonlinear curve fitting and Job plot method established the formation of 1:1 hydrogen-bonding complex between compound 1 and the bound anions.

Keywords: Anion receptor; Colorimetric sensor; Fluorescence quenching; Hydrogen bonding

INTRODUCTION

The selective recognition and sensing of anions have been becoming a focus in the field of supramolecular chemistry due to their fundamental roles in biomedical, environmental and chemical process [1–3]. Hydrogen bonding (amide [4–6], sulfonamide [7,8], phenol [9], pyrrole [10–13], urea [14–16], thiourea [17–20]) is widely used for the design of neutral anion receptors considering their availability and controllable directionality. In this regard, nature has provided us with many excellent natural receptors for anions utilizing the hydrogen bonds [21]. The thiourea binding subunit is especially helpful in the design of neutral anion receptors because of its strong hydrogen-bond donor capability and easy synthesis [22].

Among all the types of anion receptors, colorimetric sensing is the most attractive one because of its capability of rapid detection of the anion without resorting to any expensive instruments [23–27]. On the other hand, fluorescent sensing is becoming increasing importance for chemical detection considering its simplicity and high sensitivity [28–31]. To the best of our knowledge, the examples of anion receptors simultaneously utilizing the above two sensing modes are still few [32,33]. The naphthalimide chromophore has obvious advantages over others due to its high photo-stability, strong absorption in the visible region and strong fluorescence emission in the green. Some anion receptors based on 4-hydrazine-1,8-naphthalimide have been developed, which could work as colorimetric sensors for anions [34,35]. In addition, some 4-amino-1,8-naphthalimide-based anion receptors also gave rise to drastic color changes upon interaction with F^-, which is due to the deprotonation of the 4-amino NH [36–39]. However, the absorption spectral changes of previously reported anion receptors based on 4-amino-1,8-naphthalimide were generally slight except for the special examples of fluoride-induced NH deprotonation. What interested us is to design some 4-amino-1,8-naphthalimide-based anion receptors, which could effectively recognize and sense the given anions by concurrent changes of UV–vis and fluorescence spectra. In this article, we report the synthesis and recognition properties of compound **1** based on 4-amino-1,8-naphthalimide [40,41]. The strong hydrogen-bond donor ability of aromatic thiourea and the flexible ethyl spacer expectedly utilize thiourea NH and 4-amino NH of naphthalimide

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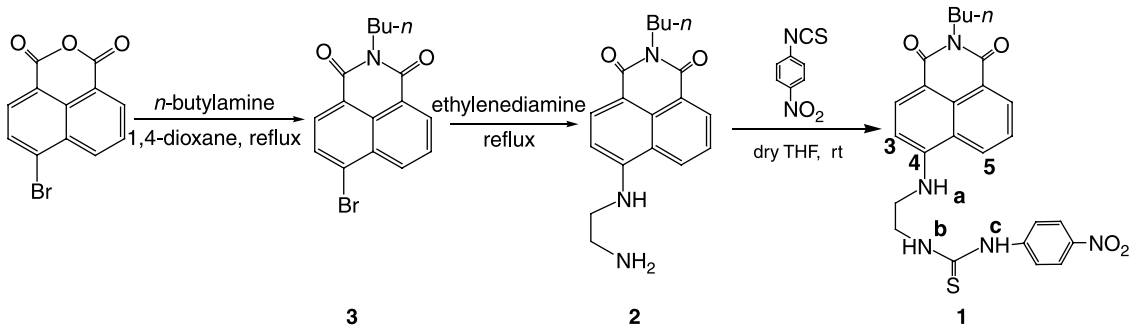


SCHEME 1 Synthesis of compound **1**.

while binding the anions, cooperatively, thereby leading to concurrent changes of absorption and fluorescence spectra of the naphthalimide chromophore. The anionic recognition properties of compound **1** were investigated by UV–vis absorption, fluorescence emission spectra and ^{1}H NMR spectroscopy.

RESULTS AND DISCUSSION

The structure of compound **1** was shown in Scheme 1. The synthesis of compound **1** was achieved in three steps by first reacting excess of *n*-butylamine with 4-bromo-1,8-naphthalic anhydride in refluxing 1,4-dioxane, which gave the imide **3** [42] as a white solid after aqueous work-up. Nucleophilic substitution was accomplished by refluxing excess of ethylenediamine with imide **3** to afford **2** [38] as a golden powder. The last step was finished in dry THF by reacting compound **2** with *p*-nitrophenylisothiocyanate at room temperature. The structure of compound **1** was established by ^{1}H NMR, IR, HRMS and elemental analysis.

Absorption and Fluorescence Spectra

The absorption and fluorescence spectra were recorded from a solution of compound **1** in the absence or presence of the anions. In each case the anion was used as its tetrabutylammonium salt.

The interactions of compound **1** with various anions were firstly investigated by UV–vis titration spectra. Figure 1 demonstrated the absorption spectral changes of compound **1** (1.0×10^{-5} M in DMSO) after addition of increasing amount of F^-. Two characteristic absorption peaks of compound **1** underwent significant changes during the recognition process, i.e., the peak at 364 nm (attributed to ICT of *p*-nitrophenyl moiety) was

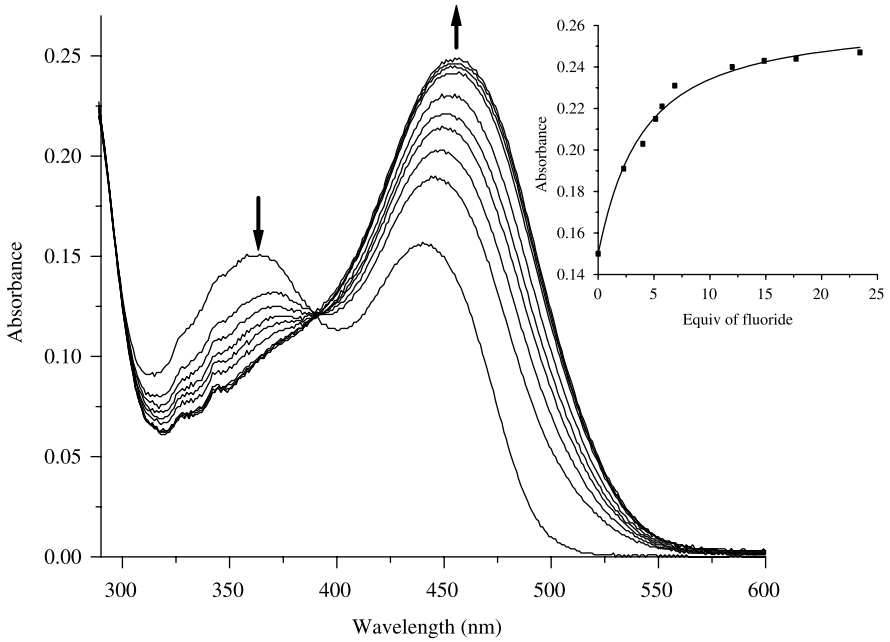


FIGURE 1 The UV–vis titration spectra of compound **1** (1.0×10^{-5} M in DMSO) after addition of increasing amount of F^-. The inset is the nonlinear curve fitting of absorbance at 449 nm as a function of equivalent of F^-. Equivalent of F^-: 0, 2.29, 4.00, 5.14, 5.71, 6.86, 12.00, 14.86, 17.71, 23.43.

gradually decreased, whilst the peak at 440 nm (attributed to ICT of naphthalimide moiety) was progressively increased, concomitant with a moderate red shift of 10 nm. The concurrent changes of two absorption peaks implied that 4-amino NH of naphthalimide and thiourea NH were synchronously involved in F^- binding. In addition, a distinct isosbestic point at 390 nm was observed, suggesting the coexistence of the two species, i.e., compound **1** and **1**·F^-. It was noticeable that a moderate color change was seen after addition of 10.0 equivalent of F^-. The color of the solution changed from greenish yellow to bright yellow, which was visible to the naked eye. The appearance of bright yellow was due to a gradual enhancement of the absorption peak at 450 nm. The relatively small red shift of λ_{max} (ca. 10 nm) and moderate color change may suggest that the F^- binding was dominated by hydrogen bonding interaction. Addition of some protic solvent (such as methanol) to the titrated solution could restore the color of the solution to greenish yellow, indicating that the protic solvent destroyed the complexation between compound **1** and F^-, which confirmed that the interaction between compound **1** and F^- was hydrogen bond in essence [43–46]. Excess of F^- often caused the deprotonation of 4-amino NH of naphthalimide fragment, leading to drastic color change and great spectral changes [36–39]. When 70.0 equiv of F^- was added to compound **1** (1.0×10^{-5} M in DMSO), an orange red solution was seen along with the appearance of new absorption peaks at 340 nm and 500 nm as shown in Figs. 2 and 3. The same results were obtained on titration of compound **1** using $Bu_4N^+OH^-$, which confirmed deprotonation of 4-amino NH at high concentration of F^-. After deprotonation, the drastic increase of the charge density on the amino nitrogen caused the large change of the push–pull character of the ICT, leading to great spectral and color changes. Addition of AcO^- to the solution of compound **1** also induced the similar color change as that of F^- (from greenish yellow to bright yellow). However, no appearance of the band at 500 nm and development of the orange–red color were observed, even after addition of a huge excess of the AcO^- (beyond 100.0 equiv). In contrast, there were no notable absorption spectral changes and color changes of compound **1** after addition of Cl^-, Br^-, I^-, NO_3^-, HSO_4^-, ClO_4^-. Figure 4 showed the absorption spectral changes of compound **1** after addition of various anions, from which a good selectivity of compound **1** toward F^- and AcO^- over other anions was clearly seen.

FIGURE 3 The color change of compound **1** (1.0×10^{-5} M in DMSO) after addition of different amounts of F^-. From left to right: free, +25.0 equiv, +45.0 equiv, +70.0 equiv, + OH^-.

Fluorescence has been extensively used to investigate the interaction of the receptor-substrate due to its high detection limit and simplicity. Figure 5 demonstrated fluorescence changes of compound **1** after addition of various anions. Addition of anions such as Cl^-, Br^-, I^-, NO_3^-, HSO_4^- and ClO_4^- to

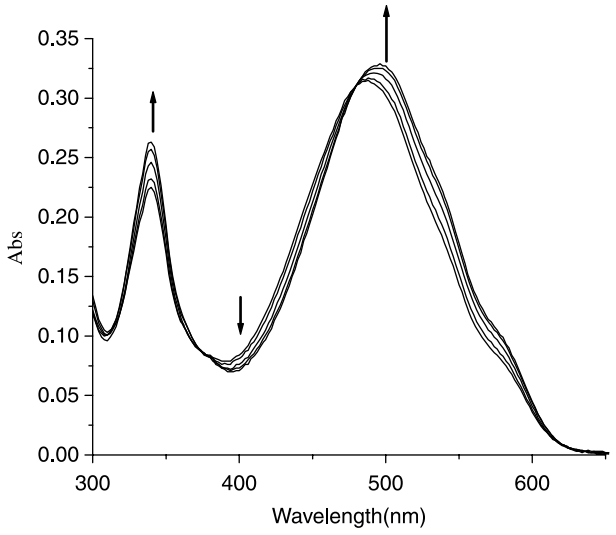


FIGURE 2 The UV–vis spectral changes of compound **1** (1.0×10^{-5} M in DMSO) after deprotonation of 4-amino NH of naphthalimide. (Equiv of F^-: 70.0, 90.0, 115.0, 140.0, 160.0, 180.0).

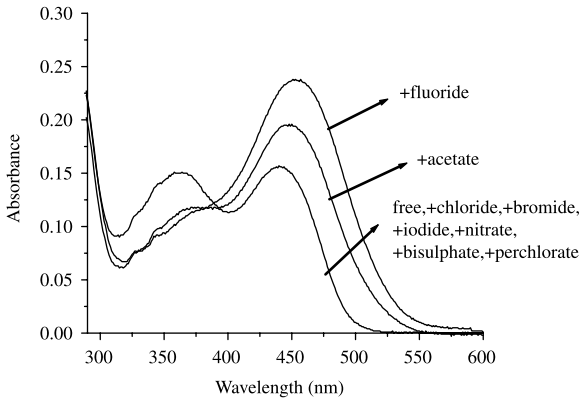


FIGURE 4 The absorption spectral changes of compound **1** (1.0×10^{-5} M in DMSO) after addition of 8.0 equivalent of various anions.

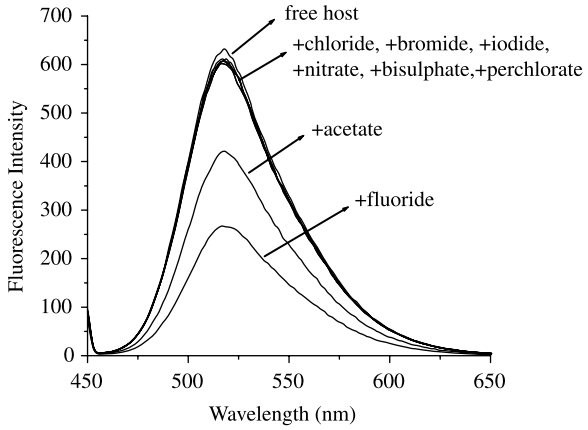


FIGURE 5 The fluorescence changes of compound **1** (0.50×10^{-5} M in DMSO) after addition of various anions (Equiv of anions: 8.0; excitation wavelength: 444 nm).

compound **1** in DMSO only caused very slight fluorescence changes, however, considerable fluorescence quenching was observed for F^- and AcO^- under the same condition.

When excited at 444 nm, compound **1** gave the maximum emission centered at 518 nm. Figure 6 showed a family of fluorescent titration spectra of the compound **1** after addition of various amount of F^-. The fluorescence emission was progressively decreased, while the concentration of F^- was gradually increased. After addition of 35.0 equiv of F^-, the fluorescence emission was quenched by 81%. Under the same conditions, the fluorescence quenching by AcO^- was 55%. The bound anion heightened the reduction potential of the thiourea moiety, thus made the process of PET (from electron-rich thiourea subunit to the excited state of naphthalimide subunit) much easier, resulting in the significant fluorescence quenching.

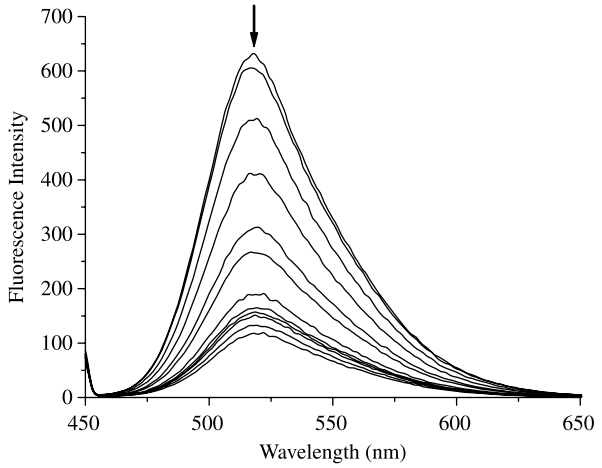


FIGURE 6 A family of fluorescent titration spectra of the compound **1** (0.50×10^{-5} M in DMSO) after addition of various amount of F^-. (Equiv of F^-: 0, 4.57, 5.14, 5.71, 6.86, 8.00, 10.29, 12.57, 14.86, 17.14, 22.59, 34.86; excitation wavelength at 444 nm).

Because compound **1** had many binding sites, Job plot experiment was conducted to determine the complex ratio [47]. Figure 7 demonstrated the Job plot of compound **1** and F^- (with a total concentration of 2.0×10^{-5} M). While the mole fraction of F^- was 0.50, the absorbance of the hydrogen bonding complex reached a maximum, indicating the formation of 1:1 complex between compound **1** and F^-.

^{1}H NMR Study

^{1}H NMR technology is widely utilized to disclose the nature of interaction between receptor and substrate [48,49]. While 1.0 equivalent of F^- was added to the solution of compound **1** in DMSO-d_6, the signals of 4-amino NH proton (H_a) and thiourea protons (H_b, H_c) were, respectively shifted from 7.80 to 8.01 ppm, 7.90 to 9.14 ppm and 10.29 to 10.90 ppm. After another one equivalent of F^- was added, the signal of H_a further downfield shifted from 8.01 to 9.04 ppm along with a great broadening, and the thiourea NH signals completely disappeared. During the titration process, the proton at position 5 of the naphthalimide experienced a downfield shift of 0.10 ppm due to the effect of electronstatic polarization exerted by the F^-. In contrast, the other protons of the naphthalimide ring underwent an upfield shift (<0.15 ppm) due to the effect of through bond propagation. There was no appearance of a triplet at 16.0 ppm attributed to HF_2^- even after addition of 3.0 equivalent of F^-, indicating that the deprotonation event did not occur at low concentration of F^- [50]. The significant changes of chemical shifts attributed to 4-amino NH and thiourea NH showed that multiple hydrogen bonding interactions were responsible for the binding of F^-. Based on the above results, we proposed a possible binding mode between compound **1** and F^- as described in Scheme 2. This arrangement has been proposed for related compounds binding to $H_2PO_4^-$ [38,39], but this is the first instance where F^- was bound in such a manner.

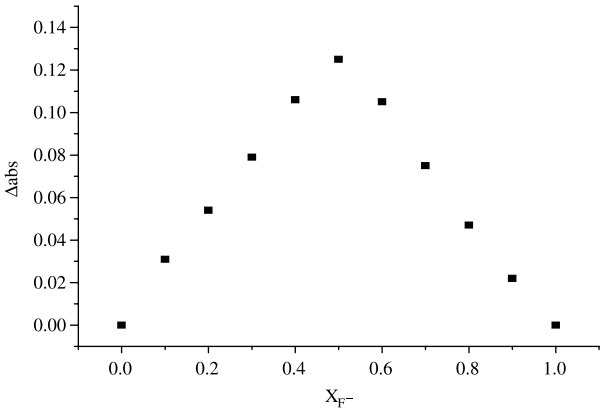
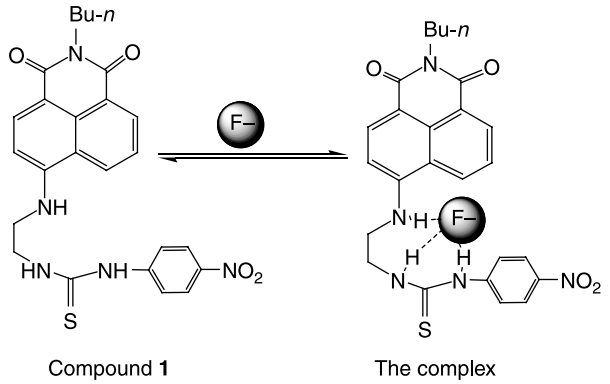


FIGURE 7 The Job plot of compound **1** and F^- with a total concentration of 2.0×10^{-5} M.



SCHEME 2 The possible binding mode between compound **1** and F^-.

Determination of the Binding Constant of the Complex

The following equation could be utilized to determine the binding constant for a 1:1 stoichiometric complex formed between the host and guest anion [51,52]:

$$A = A_0 + (A_{lim} - A_0)/2A_0\{(C_H + C_G + 1/k) - [(C_H + C_G + 1/k)^2 - 4C_HC_G]^{1/2}\}$$

Where A represents the absorbance in the presence of anion, A_0 represents the absorbance in the absence of anion, C_H and C_G represents the corresponding concentrations of the host and anion guest, k represents the binding constant. The binding constant and correlation coefficient (R) obtained by a nonlinear curve fitting of A versus C_G and C_H were listed in Table I. The data showed that compound **1** had a good affinity and selectivity toward F^- and AcO^- over the other anions, and the selectivity order was: $F^- > AcO^- \gg Cl^-$, Br^-, I^-, NO_3^-, HSO_4^- and ClO_4^-, which is due to the intrinsic strong basicity of F^- and AcO^-. All the correlation coefficients (R) obtained were larger than 0.99, which also showed the formation of 1:1 stoichiometric complex between compound **1** and the bound anions.

TABLE I Binding constants (k) and correlation coefficient (R) of receptor **1** with anions

Anion†	k (M^{-1})‡	Correlation coefficient (R)
F^-	$(3.03 \pm 0.37) \times 10^4$	0.9945
AcO^-	$(1.47 \pm 0.22) \times 10^4$	0.9904
Cl^-, Br^-, I^-,	ND¶	
NO_3^-, HSO_4^-, ClO_4^-	ND	

† The anions were used as their tetrabutylammonium salts. ‡ The data were obtained from UV–vis titration in DMSO. All error values were obtained from the results of nonlinear curve fitting. ¶ ND = The spectral change was too small to determine the binding constant accurately.

CONCLUSION

In summary, a neutral 4-amino-1,8-naphthalimide-based anion receptor **1** was synthesized by simple steps in a high yield. Receptor **1** could form 1:1 complexes with the bound anions by multiple hydrogen-bonding interactions, synchronously involving the naphthalimide 4-amino NH and thiourea NH. Moreover, receptor **1** had a good affinity and selectivity toward F^- and AcO^- over the other anions. Importantly, we could monitor the recognition process by fluorescence changes along with the color change, enabling receptor **1** as a dual responsive chemosensor for the detection of F^- and AcO^-.

EXPERIMENTAL

Materials and Methods

IR spectra were measured on a Nicolet 670 FT-IR spectrophotometer. ^1H NMR spectra were obtained in DMSO-d_6 on a Varian Mercury VX-300 MHz spectrometer. High resolution mass spectra (MALDI-TOF) were determined on QSTAR spectrometer. Elemental analysis was determined with a Finnigan FLASH 1112 SERIES instrument. UV–vis spectra were measured on TU-1900 spectrometer. Fluorescence spectra were determined on a Schimadzu RF-5301 luminescence spectrometer. THF was dried and distilled from CaH_2. All other commercially available reagents were directly used without further purification. Compound **3** [42] and **2** [38] were prepared according to the previously reported literature.

Synthesis of Compound 1

p-Nitrophenylisothiocyanate (18 mg, 0.1 mmol) was added to a THF (20 mL) solution of compound **2** (31 mg, 0.1 mmol), the resulted mixture was stirred at room temperature overnight. After evaporation of solvent, the residue was subjected to column chromatography using $CHCl_3$/MeOH (20/1, v/v) as eluent. Compound **1** was recrystallized by THF/petroleum ether with a good yield (85%, 42.0 mg). ^1H NMR (300 MHz, DMSO-d_6): 0.93 (t, 3H, $J = 7.2$ Hz, CH_3), 1.31–1.39 (m, 2H, CH_2), 1.58–1.63 (m, 2H, CH_2), 3.62–3.69 (m, 2H, CH_2), 3.82–3.90 (m, 2H, CH_2), 4.04 (t, 2H, $J = 7.2$ Hz, CH_2), 7.01 (d, 1H, $J = 8.1$ Hz, Ar-H), 7.76 (d, 2H, $J = 8.7$ Hz, Ar-H), 7.80 (s, 1H, 4-NH), 7.90 (br, 1H, NHCS), 8.18 (d, 2H, $J = 8.7$ Hz, Ar-H), 8.31 (d, 1H, $J = 8.7$ Hz, Ar-H), 8.46–8.49 (m, 2H, Ar-H), 8.73 (d, 1H, $J = 8.1$ Hz, Ar-H), 10.29 (br, 1H, NHCS); IR (KBr pellets, cm^{-1}) 3339, 1546, 1331, 1303, 750; HRMS (MALDI-TOF) Calcd for $C_{25}H_{25}N_5O_4SH^+$: 492.1700; found:

492.1702; Anal. Calcd. for $C_{25}H_{25}N_5O_4S$: C, 61.08; H, 5.13; N, 14.25; S, 6.52; Found: C, 61.25; H, 5.02; N, 14.30; S, 6.80.

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References

[1] Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609.
[2] Beer, P. D.; Gale, P. A. *Angew. Chem. Int. Ed.* **2001**, *40*, 486.
[3] Beer, P. D.; Hayes, E. J. *Coord. Chem. Rev.* **2003**, *240*, 167.
[4] Kang, J. M.; Jo, J. H.; In, S. J. *Tetrahedron Lett.* **2004**, *45*, 5225.
[5] Szumna, A.; Jurczak, J. *Eur. J. Org. Chem.* **2001**, *21*, 4031.
[6] Kang, J. M.; Kim, J. H. *Tetrahedron Lett.* **2005**, *46*, 1759.
[7] Starnes, S. D.; Arungundram, S.; Saunders, C. H. *Tetrahedron Lett.* **2002**, *43*, 7785.
[8] Hettche, F.; Hoffmann, R. W. *New J. Chem.* **2003**, *27*, 172.
[9] Davis, A. P.; Perry, J. J.; Warham, R. S. *Tetrahedron Lett.* **1998**, *39*, 4569.
[10] Black, C. B.; Andrioletti, B.; Try, A. C.; Ruiperez, C.; Sessler, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 10438.
[11] Sessler, J. L.; Maeda, H.; Mizuno, T.; Lynch, V. M.; Furuta, H. *Chem. Commun.* **2002**, 862.
[12] Sessler, J. L.; Pantos, G. D.; Katayev, E.; Lynch, V. M. *Org. Lett.* **2003**, *5*, 4141.
[13] Aldakov, D.; Anzenbacher, P., Jr. *Chem. Commun.* **2003**, 1394.
[14] Jagessar, R. C.; Shang, M.; Scheidt, W. R.; Burns, D. H. *J. Am. Chem. Soc.* **1998**, *120*, 11684.
[15] Esteban-Gómez, D.; Fabbrizzi, L.; Licchelli, M. *J. Org. Chem.* **2005**, *70*, 5717.
[16] Cho, E. J.; Moon, J. W.; Ko, S. W.; Lee, J. Y.; Kim, S. K.; Yoon, J.; Nam, K. C. *J. Am. Chem. Soc.* **2003**, *125*, 12376.
[17] Gunnlaugsson, T.; Davis, A. P.; O'Brien, J. E.; Glynn, M. *Org. Lett.* **2002**, *4*, 2449.
[18] Kondo, S. I.; Nagamine, M.; Yano, Y. *Tetrahedron Lett.* **2003**, *44*, 8801.
[19] Vázquez, M.; Fabbrizzi, L.; Taglietti, A.; Pedrido, R. M.; González-Noya, A. M.; Bermejo, M. R. *Angew. Chem. Int. Ed.* **2004**, *43*, 1962.
[20] Land, E. J.; Ramsden, C. A.; Riley, P. A. *Tetrahedron* **2006**, *62*, 4844.
[21] Bianchi, A.; Bowman, J. K.; Garcia-Espana, E. *Supramolecular Chemistry of Anions*; Wiley-VCH: New York, 1997.
[22] Kim, Y. J.; Kwak, H.; Lee, S. J.; Lee, J. S.; Kwon, H. J.; Nam, S. H.; Lee, K.; Kim, C. *Tetrahedron* **2006**, *62*, 9635.
[23] Yen, Y. P.; Ho, K. W. *Tetrahedron Lett.* **2006**, *47*, 1193.
[24] Ghosh, T.; Maiya, B. G.; Samanta, A. *Dalton Trans.* **2006**, 795.
[25] Wu, C. Y.; Chen, M. S.; Lin, C. A.; Lin, S. C.; Sun, S. S. *Chem. Eur. J.* **2006**, *12*, 2263.
[26] Winstanley, K. J.; Sayer, A. M.; Smith, D. K. *Org. Biomol. Chem.* **2006**, *4*, 1760.
[27] Jun, E. J.; Swamy, K. M. K.; Bang, H.; Kim, S. J.; Yoon, J. *Tetrahedron Lett.* **2006**, *47*, 3103.
[28] Maeda, H.; Ito, Y. *Inorg. Chem.* **2006**, *45*, 8205.
[29] Schazmann, B.; Alhashimy, N.; Diamond, D. *J. Am. Chem. Soc.* **2006**, *128*, 8607.
[30] Kim, S. K.; Singh, N. J.; Kwon, J.; Hwang, I. -C.; Park, S. J.; Kim, K. S.; Yoon, J. *Tetrahedron* **2006**, *62*, 6065.
[31] Hu, H. Y.; Chen, C. F. *Tetrahedron Lett.* **2006**, *47*, 175.
[32] Ghosh, K.; Adhikari, S. *Tetrahedron Lett.* **2006**, *47*, 8165.
[33] Zhou, L. L.; Sun, H.; Li, H. P.; Wang, H.; Zhang, X. H.; Wu, S. K.; Lee, S. T. *Org. Lett.* **2004**, *6*, 1071.
[34] Gunnlaugsson, T.; Kruger, P. E.; Jensen, P.; Tiemey, J.; Ali, H. D. P.; Hussey, G. M. *J. Org. Chem.* **2005**, *70*, 10875.
[35] Liu, B.; Tian, H. *Chem. Lett.* **2005**, *34*, 686.
[36] Gunnlaugsson, T.; Kruger, P. E.; Jensen, P.; Pfeffer, F. M.; Hussey, G. M. *Tetrahedron Lett.* **2003**, *44*, 8909.
[37] Gunnlaugsson, T.; Kruger, P. E.; Lee, T. C.; Parkesh, R.; Pfeffer, F. M.; Hussey, G. M. *Tetrahedron Lett.* **2003**, *44*, 6575.
[38] Pfeffer, F. M.; Buschgens, A. M.; Barnett, N. W.; Gunnlaugsson, T.; Kruger, P. E. *Tetrahedron Lett.* **2005**, *46*, 6579.
[39] Pfeffer, F. M.; Seter, M.; Lewcenko, N.; Barnett, N. W. *Tetrahedron Lett.* **2006**, *47*, 5241.
[40] For naphthalimide-based anion receptors, see: Gunnlaugsson, T.; Glynn, M.; Tocci, G. M.; Kruger, P. E.; Pfeffer, F. M. *Coord. Chem. Rev.* **2006**, *250*, 3094.
[41] During the period of the preparation of our manuscript, an analogous compound (*p*-CF_3 substitution instead of *p*-NO_2) was prepared by Gunnlaugsson. The related article has not been published until now, and the structure of this analogous compound was mentioned in Ref [40].
[42] Gan, J. A.; Tian, H.; Wang, Z. H.; Chen, K. C.; Hill, J.; Lane, P. A.; Rahn, M. D.; Fox, A. M.; Bradley, D. D. C. *J. Organometal. Chem.* **2002**, *645*, 168.
[43] Wu, J. L.; He, Y. B.; Wei, L. H.; Liu, S. Y.; Meng, L. Z.; Hu, L. *Supramol. Chem.* **2004**, *16*, 353.
[44] Wu, F. Y.; Li, Z.; Wen, Z. C.; Zhou, N.; Zhao, Y. F.; Jiang, Y. B. *Org. Lett.* **2002**, *4*, 3203.
[45] Liu, S. Y.; He, Y. B.; Wu, J. L.; Wei, L. H.; Qin, H. J.; Meng, L. Z.; Hu, L. *Org. Biomol. Chem.* **2004**, *2*, 1582.
[46] Zhang, X.; Guo, L.; Wu, F. Y.; Jiang, Y. B. *Org. Lett.* **2003**, *5*, 2667.
[47] Nishizawa, S.; Kato, R.; Hayashita, T.; Teramae, N. *Anal. Sci.* **1998**, *14*, 595.
[48] Nishiyabu, R.; Palacios, M. A.; Dehaen, W.; Anzenbacher, P., Jr. *J. Am. Chem. Soc.* **2006**, *128*, 11496.
[49] Kondo, S. I.; Harada, T.; Tanaka, R.; Unno, M. *Org. Lett.* **2006**, *8*, 4621.
[50] Shenderovich, I. G.; Tolstoy, P. M.; Golubev, N. S.; Smirnov, S. N.; Denisov, G. S.; Limbach, H. -H. *J. Am. Chem. Soc.* **2003**, *125*, 11710.
[51] Bourson, J.; Pouget, J.; Valeur, B. *J. Phys. Chem.* **1993**, *97*, 4552.
[52] Valeur, B.; Pouget, J.; Bourson, J.; Kaschke, M.; Ernsting, N. P. *J. Phys. Chem.* **1992**, *96*, 6545.