J Incl Phenom Macrocycl Chem (2011) 69:57–61
DOI 10.1007/s10847-010-9813-5

ORIGINAL ARTICLE

A new colorimetric anion sensor which have both a fat brown RR dye and a nitrophenyl group as signaling group

Jin Joo Park · Jongmin Kang

Received: 1 April 2010 / Accepted: 27 May 2010 / Published online: 11 June 2010

Abstract A new colorimetric anion sensor **1** has been synthesized based on both Fat brown RR dye and a nitrophenyl group. This new receptor **1** could recognize the presence of fluoride and acetate ion selectively by the change of color of solution.

Keywords Anion receptor · Colorimetric receptor · Hydrogen bonding · Naked eye detector

The rational design and synthesis of efficient receptors to selectively recognize biologically and environmentally important anion species is an attractive field of supramolecular chemistry [1–7]. Both fluorogenic [8–15] and chromogenic [16–25] anion receptors have attracted a considerable amount of attention due to the simplicity in recording their optical responses upon forming complexes with anions.

For sensing approach, anion recognition site is usually coupled to the reporting groups, which binding process is transduced into a signaling event. The interaction with anion typically stabilizes the excited state of chromophore and induces red shift of the charge transfer absorption band, thus providing an efficient way for qualitative and quantitative evaluation of anion activity in solution [26]. In addition, they can be often easily synthesized from commercially available reagents even by a single step procedure [27–29]. We have also reported on novel colorimetric receptors containing a nitrophenyl group as chromogenic signaling subunit and urea as binding sites, which were selective for fluoride or acetate ion [30, 31].

J. J. Park · J. Kang (✉)
Department of Chemistry, Sejong University, Seoul 143-747, Korea
e-mail: kangjm@sejong.ac.kr

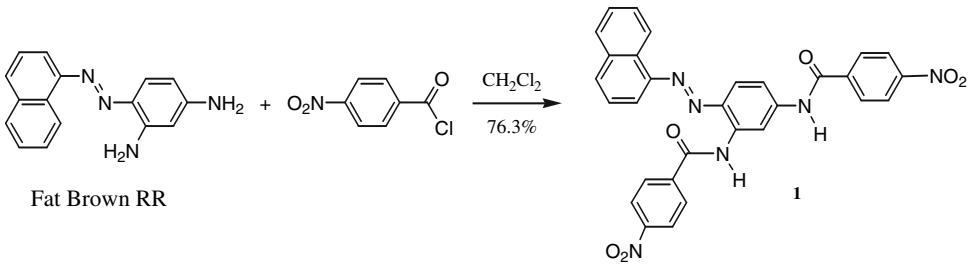
As a part of our efforts to develop more efficient anion receptors, we planned to design a new colorimetric anion sensor **1** utilizing both Fat brown RR dye and nitrophenyl group as chromogenic signaling sites and amide moiety as binding sites. The receptor **1** was found to be an efficient detector for fluoride ion by the change of UV–vis, ^{1}H NMR spectra and the naked-eye observation. Receptors **1** was synthesized using the one step reaction of Fat Brown RR and 4-nitrobenzoyl chloride in 76.3% yield (Scheme 1).[1]

The receptor **1** displayed strong absorption bands at 412 nm in DMSO. Figure 1a shows the family of spectra obtained over the course of the titration of the solution **1** with tetrabutylammonium fluoride in DMSO. As tetrabutylammonium fluoride was added to the 40 μM solution of **1**, the intensity of absorption spectrum decreased at 337 nm and increased at 412 nm and the clear isosbestic point appears at 371 nm. This result suggests that a typical hydrogen bonding complex forms between the receptor **1** and the fluoride ion as the basicity of anion is insufficient to induce deprotonation of receptor at this fluoride concentration. However, when an excess of fluoride ions was added, a new intense absorption band developed at 531 nm, which is attributed to the deprotonated receptor [32].

In addition, spectra showed a new isosbestic point at 444 nm (Fig. 1b). The presence of the sharp isosbestic point at 444 nm indicates that only two species were

[1] To a solution of 200 mg (0.76 mmol) of Fat Brown RR in 10 mL of dichloromethane was added 420 mg (2.26 mmol) of 4-nitrobenzoyl chloride and the mixture was stirred overnight at room temperature. The solvent was evaporated from the reaction mixture. Washing the remained solid with acetone gave 326 mg of red solid in 76.3% yield. ^{1}H NMR (DMSO-d_6) 11.0 (d, J = 8.0, 2H), 8.9 (d, J = 9.0, 1H), 8.8 (s, 1H), 8.4 (m, 4H), 8.3 (q, J = 8.5, 4H), 8.1 (d, J = 8.0, 1H), 8.0 (m, 2H), 7.9 (m, 2H), 7.7 (m, 3H) LRMS (ES) calculated for $C_{30}H_{20}N_6O_6$, 560.52; found for 560.57.

Scheme 1 The synthetic scheme for the anion receptor **1**



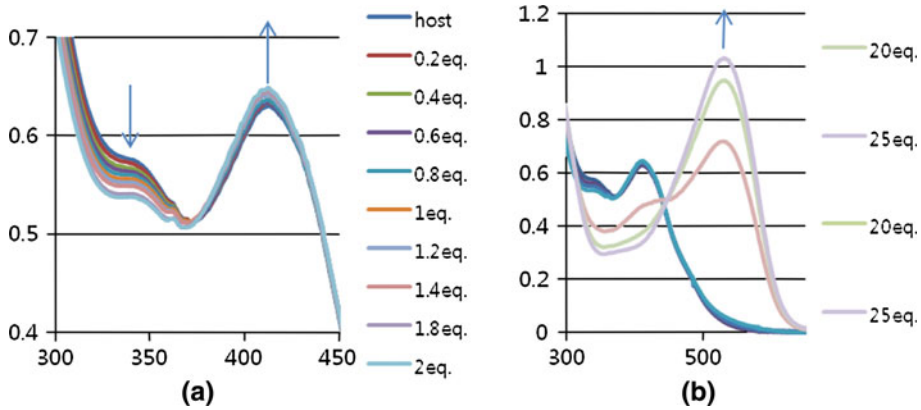


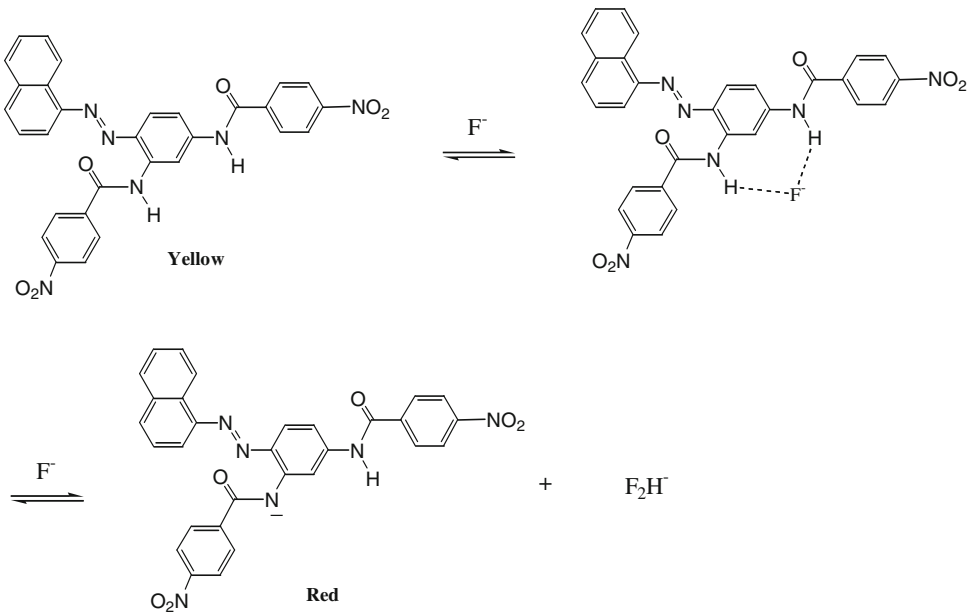
Fig. 1 Family of spectra recorded over the course of titration of 40 μM DMSO solution of the receptor **1** with a standard solution tetrabutylammonium fluoride **a** 0–2 equivalents of fluoride ions added **b** 0–25 equivalents of fluoride ions added

present at equilibrium over the course of the titration experiment. Therefore, fluoride ion initially forms the hydrogen bonded complex, but with high excess of added anions, the deprotonation occurs with formation of the hydrogen bonded anion dimer F_2H^- (Fig. 2) [33]. The deprotonated receptor **1** can be seen clearly when the solution of the receptor **1** is titrated with tetrabutylammonium hydroxide (Fig. 3). Like in the case of excess fluoride ions with the receptor **1**, absorption band at 531 nm developed again.

Assuming 1:1 stoichiometry, a Benesi–Hildebrand plot [34] by use of change in the 412 and 531 nm gave association constant and equilibrium constant for deprotonation respectively. From the experiments, the receptor **1** showed association constant 1.8×10^4 and equilibrium constant 8.3×10^2 for fluoride.

The binding phenomenon could be confirmed by a ^1H NMR titration in DMSO-d_6 (Fig. 4). As the amide N–H hydrogen peak became invisible upon addition of fluoride ion, one of the aromatic signals located next to amide

Fig. 2 The interaction of receptor **1** and fluoride



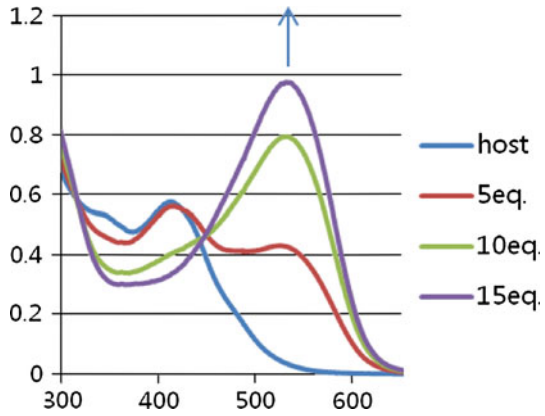


Fig. 3 Family of spectra recorded over the course of titration of 40 μM DMSO solution of the receptor **1** with a standard solution tetrabutylammonium hydroxide

(8.40 ppm) was used for titration. For the receptor **1**, this aromatic signal moved from 8.40 to 8.31 ppm until 1.5 equivalents of fluoride ion was added. In fact, two effects are expected as a result of hydrogen bond formation between the amide subunit and the anion. (i) A through-bond propagation increases electron density in the phenyl ring, which causes a shielding effect and promotes an upfield shift (ii) A through-space effect increases a polarization of C–H bonds, which causes deshielding and promotes a downfield shift. In this case, the through-bond propagation dominates, and an upfield shift is observed for the all of aromatic peaks. Analysis of chemical shift utilizing EQNMR [35] gave association constant 1.9×10^4, which is similar value obtained from UV–vis titration.

With acetate, same phenomenon was observed. In UV–vis titration, until 7 equivalents of acetate was added, only hydrogen bonded complex forms (Fig. 5a). With excess acetate, the deprotonation occurs again (Fig. 5b). The association constant and the equilibrium constant were calculated as 8.5×10^3 and 2.7×10^2 respectively. In a ^{1}H NMR titration in DMSO-d_6, the amide N–H hydrogen peak became invisible upon addition of acetate ion and aromatic signal at 8.40 ppm moved to 8.37 ppm and the saturation occurred at 2.1 equivalents of acetate ions. The association constant was calculated as 9.0×10^3, which is also similar value obtained from UV–vis titration.

We also investigated association constants of other anions. Among the anions investigated benzoate showed only discrete hydrogen-bonded complex. Even with excess benzoate ions, UV–vis spectra did not show any spectrum result from deprotonation. Benzoate is not basic enough to deprotonate the amide N–H hydrogen of the receptor **1** at any concentration in DMSO. The association constant was calculated as 1.5×10^3. Other anions such as chloride, bromide, iodide, perchlorate, hydrogensulfate, nitrate did not bind to the receptor **1** in DMSO at all.

Figure 6 shows the color change of the solutions of the receptor **1** upon additions of various anions in DMSO. It can be seen that the color changed from yellow to red in the presence of fluoride and acetate with naked eye. Other anions did not induce any color changes even with excess amounts. Probably, as we can see from the NMR titration with fluoride ion, deprotonation of the receptor **1** by the fluoride and acetate induces the change of the color.

In summary, we developed a new chromogenic anion receptor **1** with utilizing Fat Brown RR and nitrophenyl group as signaling group. The receptor **1** binds anions via hydrogen bonds with a selectivity of $F^- > CH_3CO_2^- > C_6H_5CO_2^-$ and proved to be an efficient naked-eye detector for the fluoride and acetate ion.

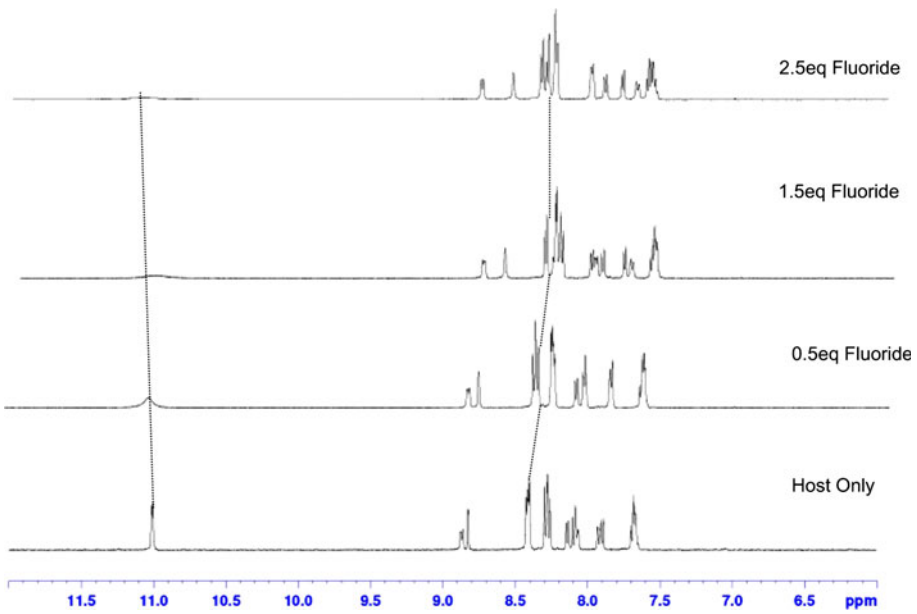


Fig. 4 ^{1}H NMR spectra of 2 mM solution of **1** with increased amounts of tetrabutylammonium fluoride in DMSO-d_6

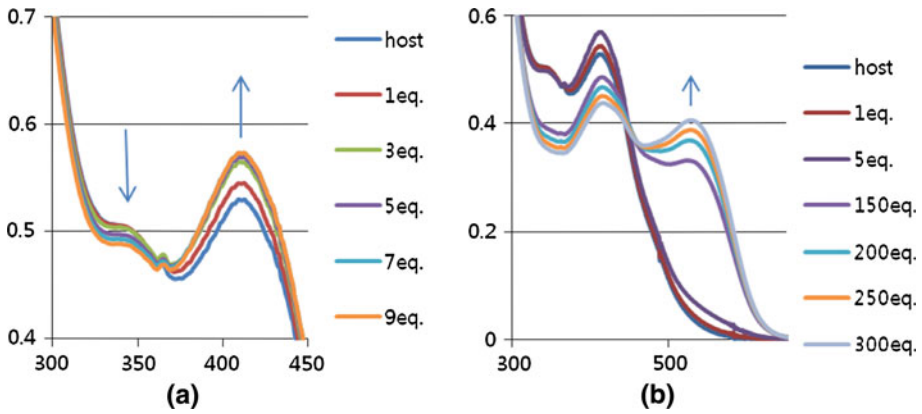


Fig. 5 Family of spectra recorded over the course of titration of 40 μM DMSO solution of the receptor **1** with a standard solution tetrabutylammonium acetate **a** 0–7 equivalents of acetate ions added **b** 0–300 equivalents of fluoride ions added

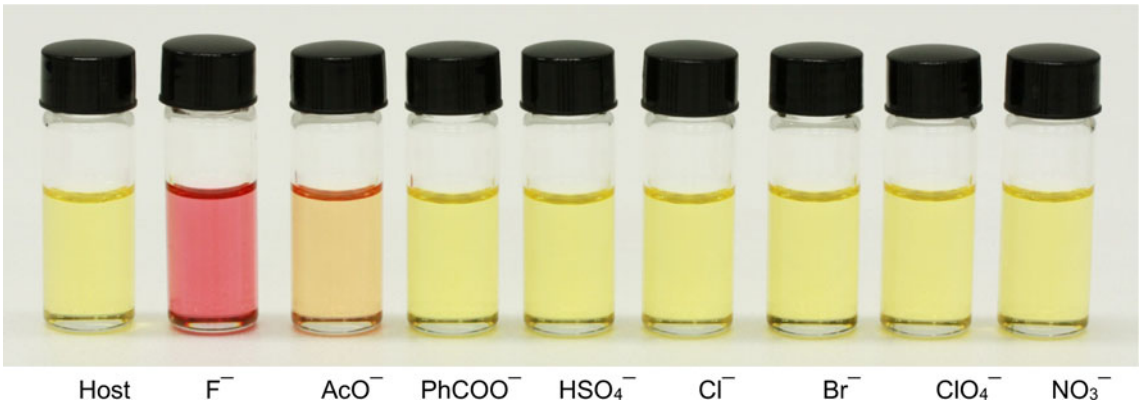


Fig. 6 The color changes of the receptor **1** when 40 μM solution of the receptor was treated with 20 equivalents of various anions in DMSO

References

1. Bianchi, A., Bowman-James, K., Garcia-Espana, E.: Supramolecular Chemistry of Anions. Wiley-VCH, New York (1997)
2. Schmidtchen, F.P., Berger, M.: Artificial organic host molecules for anions. Chem. Rev. **97**, 1609–1646 (1997)
3. Beer, P.D., Gale, P.A.: Anion recognition and sensing: the state of the art and future perspectives. Angew. Chem. Int. Ed. **40**, 486–516 (2001)
4. Sessler, J.L., Davis, J.M.: Sapphyrins: versatile anion binding agents. Acc. Chem. Res. **34**, 989–997 (2001)
5. Chellappan, K., Singh, N.J., Hwang, I.-C., Lee, J.W., Kim, K.S.: Calix[4]imidazolium[2]pyridine as an anion receptor. Angew. Chem. Int. Ed. **44**, 2899–2903 (2005)
6. Yoon, J., Kim, S.K., Singh, N.J., Kim, K.S.: Imidazolium receptors for the recognition of anions. Chem. Soc. Rev. **35**, 355–360 (2006)
7. Best, M.D., Tobey, S.L., Anslyn, E.V.: Abiotic guanidinium containing receptors for anionic species. Coord. Chem. Rev. **240**, 3–15 (2003)
8. de Silva, A.P., Gunaratne, H.Q.N., Gunnlaugsson, T., Huxley, A.J.M., McCoy, C.P., Rademacher, J.T., Rice, T.E.: Signaling recognition events with fluorescent sensors and switches. Chem. Rev. **97**, 1515–1566 (1997)
9. Martínez-Máñez, R., Sancenon, F.: Fluorogenic and chromogenic chemosensors and reagents for anions. Chem. Rev. **103**, 4419–4476 (2003)
10. Kwon, J.Y., Singh, N.J., Kim, N.H., Kim, S.K., Kim, K.S., Yoon, J.: Fluorescent GTP-sensing in aqueous solution of physiological pH. J. Am. Chem. Soc. **126**, 8892–8893 (2004)
11. Martínez-Máñez, R., Sancenon, F.: New advances in fluorogenic anion chemosensors. J. Fluoresc. **15**, 267–285 (2005)
12. Cho, E.J., Moon, J.W., Ko, S.W., Lee, J.Y., Kim, S.K., Yoon, J., Nam, K.C.: A new fluoride selective fluorescent as well as chromogenic chemosensor containing a naphthalene urea derivative. J. Am. Chem. Soc. **125**, 12376–12377 (2003)
13. Chmielewski, M.J., Charon, M., Jurczak, J.: 1,8-Diamino-3,6-dichlorocarbazole: a promising building block for anion receptors. Org. Lett. **6**, 3501–3504 (2004)
14. Curiel, D., Cowley, A., Beer, P.D.: Indolocarbazoles: a new family of anion sensors. Chem. Commun. 236–238 (2005)
15. Piatek, P., Lynch, V.M., Sessler, J.L.: Calix[4]pyrrole[2]carbazole: a new kind of expanded calixpyrrole. J. Am. Chem. Soc. **126**, 16073–16076 (2004)
16. Susaki, C., Tuntulani, T.: Chromogenic anion sensors. Chem. Soc. Rev. **32**, 192–202 (2003)
17. Yamamura, S.S., Wade, M.A.: Direct spectrophotometric fluoride determination. Anal. Chem. **34**, 1308–1312 (1962)
18. Kubo, Y., Maeda, S., Tokita, S., Kubo, M.: Colorimetric chiral recognition by a molecular sensor. Nature **382**, 522–524 (1996)
19. Kinoshita, T.: Visualization of molecular length of α,ω-diamines and temperature by a receptor based on phenolphthalein and crown ether. J. Am. Chem. Soc. **121**, 3807–3808 (1999)
20. Lavigne, J.J., Anslyn, E.V.: Teaching old indicators new tricks: a colorimetric chemosensing ensemble for tartrate/malate in beverages. Angew. Chem. Int. Ed. **38**, 3666–3669 (1999)
21. Miyaji, H., Sato, W., Sessler, J.L.: Naked-eye detection of anions in dichloromethane: colorimetric anion sensors based on calix[4]pyrrole. Angew. Chem. Int. Ed. **39**, 1777–1780 (2000)

22. Sancenon, F., Descalzo, A.B., Martínez-Máñez, R., Miranda, M.A., Soto, J.: A colorimetric ATP sensor based on 1,3,5-triarylpent-2-en-1,5-diones. Angew. Chem. Int. Ed. **40**, 2640–2643 (2001)
23. Nishiyabu, R., Anzenbacher Jr, P.: Sensing of antipyretic carboxylates by simple chromogenic calix[4]pyrroles. J. Am. Chem. Soc. **127**, 8270–8271 (2005)
24. Miyaji, H., Sessler, J.L.: Off-the-shelf colorimetric anion sensors. Angew. Chem. Int. Ed. **40**, 154–157 (2001)
25. Metzger, A., Anslyn, E.V.: A chemosensor for citrate in beverages. Angew. Chem. Int. Ed. **37**, 649–652 (1998)
26. Suksai, C., Tuntulani, T.: Chromogenic anion sensors. Chem. Soc. Rev. **32**, 192–203 (2003)
27. Kang, S.O., Linares, J.M., Powell, D., VanderVelde, D., Bowman-James, K.: New polyamide cryptand for anion binding. J. Am. Chem. Soc. **125**, 10152–10153 (2003)
28. Kondo, S.-I., Hiraoka, Y., Kurumatani, N., Yano, Y.: Selective recognition of dihydrogen phosphate by receptors bearing pyridyl moieties as hydrogen bond acceptors. Chem. Commun. 1720–1723 (2005)
29. Xie, H., Yi, S., Wu, S.: Study on host–guest complexation of anions based on tri-podal naphthylthiourea derivatives. J. Chem. Soc., Perkin Trans. **2**, 2751–2754 (1999)
30. Kim, H., Kang, J.: Anion receptors with 2-imidazolidone molecular scaffold. Bull. Korean Chem. Soc. **28**(9), 1531–1534 (2007)
31. Lee, S.-K., Kang, J.: Urea receptors which have both a fat brown RR and a nitrophenyl group as a signaling group. Bull. Korean Chem. Soc. **30**(12), 3031–3033 (2009)
32. Pérez-Casas, C., Yatsimirsky, A.K.: Detailing hydrogen bonding and deprotonation equilibria between anions and urea/thiourea derivatives. J. Org. Chem. **73**, 2275–2284 (2008)
33. Amendola, V., Esteban-Gomez, D., Fabbrizzi, L., Licchelli, M.: What anions do to N−H-containing receptors. Acc. Chem. Res. **39**, 343–353 (2006)
34. Benesi, H., Hildebrand, H.: A spectrophotometric investigation of the interaction of iodine with aromatic hydrocarbons. J. Am. Chem. Soc. **71**, 2703–2707 (1949)
35. Hynes, M.J.: EQNMR: a computer program for the calculation of stability constants from nuclear magnetic resonance chemical shift data. J. Chem. Soc., Dalton Trans. 311–312 (1993)