

An optical and electrochemical anion sensor of F⁻ investigated by UV–vis, ¹H NMR and cyclic voltammetry

Jianwei Li · Hai Lin · Ping Jiang · Huakuan Lin

Received: 25 February 2008 / Accepted: 1 May 2008 / Published online: 3 June 2008
© Springer Science+Business Media B.V. 2008

Abstract A new anion receptor: 1,1'-di-(2'',4''-di-nitrophenylhydrazino- β -carbonyl)-ferrocene (**1**) based on ferrocene has been designed and synthesized as a highly colorimetric and electrochemical sensitive sensor for F⁻. The binding mode with F⁻ was further investigated by UV–vis titration and ¹H NMR titration experiments. In addition, the cyclic voltammetry (CV) was performed to discuss the electrochemical sensing for F⁻.

Keywords Anion recognition · Electrochemical sensing · Fluoride · Ferrocene · Naked-eye detection

Introduction

Since anions are ubiquitous and play important roles in many biological and chemical systems, there is an increasing interest in the design and development of receptors that selectively recognize and sense specific anions through visible, electrochemical, and optical feedback [1, 2]. Among the range of biologically important anions, fluoride is of particular interest owing to its serious effects in the human body [3, 4]. And then, it is significant

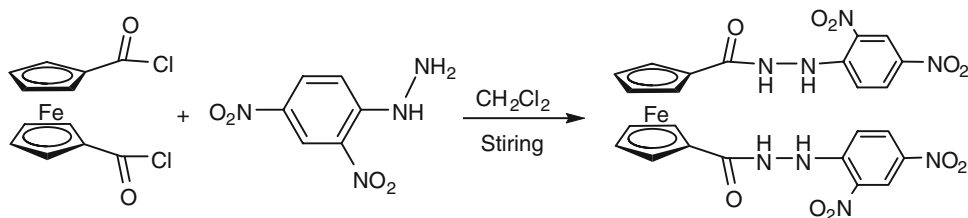
to design and synthesize the sensitive receptors for fluoride. Cheng et al. [5] showed that the pyrrole- and cystine-based cyclopeptido-mimetics were able to bind fluoride and acetate ions well in CH₃CN. Also, strategy based on hard acid-hard base interaction has been developed for sensing fluoride anion with boronic derivatives of ferrocene, which was reported by Shinkai et al. [6]. Very recently, Shiraiishi et al. [7] discovered that a commercially-available 'unmodified' fluorescein behaved as a fluorescent chemosensor for fluoride ions.

Even though these receptors for fluoride ions have been reported, there are few reports on the receptors based on the formation of molecular architectures which contain redox, chromogenic, or fluorogenic groups that are covalently or noncovalently linked to the receptor moiety [8–10]. The ferrocene moiety has been studied extensively in the redox-responsive anion receptors, for it offers the possibility to modulate the anion-receptor interactions according to the redox state; e.g. electrostatic interactions can be switched on by the oxidation of ferrocene to ferricinium [11]. In addition, the 2,4-dinitrophenylhydrazine has been successfully inducted into anion receptors as chromogenic group and binding unit [12, 13].

From this perspective, we designed and synthesized the receptor by combining the redox activity of the ferrocene moiety with 2,4-dinitrophenylhydrazine derivative (Scheme 1). The investigation of the receptor presented that it is an excellent sensor for F⁻. In particular, the receptor displayed highly selective UV–vis spectra changes with F⁻ among the various anions. Furthermore, the nature of the interaction between the receptor and the F⁻ was investigated by ¹H NMR titration experiments. Additionally, the cyclic voltammetry experiments bestowed a consistent result as UV–vis investigation, which should be with interest for future applications in F⁻ sensors.

J. Li · P. Jiang · H. Lin (✉)
Department of Chemistry, Nankai University,
Tianjin 300071, China
e-mail: hklin@nankai.edu.cn

H. Lin
Education Ministry Key Laboratory of Functional Polymer
Materials, Nankai University, Tianjin 300071, China

Scheme 1 The synthetic route of the receptors **1**

Experimental section

Reagents and instruments

Most of the starting materials were obtained commercially and all reagents and solvents used were of analytical grade. All anions, in the form of tetrabutylammonium salts, were purchased from Sigma-Aldrich Chemical Co., stored in a desiccator under vacuum containing self-indicating silica, and used without any further purification. Dimethyl sulfoxide (DMSO) was distilled in vacuo after dried with CaSO_4 . Tetra-*n*-butylammonium salts (such as $(n\text{-C}_4\text{H}_9)_4\text{NF}$, $(n\text{-C}_4\text{H}_9)_4\text{NCl}$, $(n\text{-C}_4\text{H}_9)_4\text{NBr}$, $(n\text{-C}_4\text{H}_9)_4\text{NI}$, $(n\text{-C}_4\text{H}_9)_4\text{NAcO}$, and $(n\text{-C}_4\text{H}_9)_4\text{NH}_2\text{PO}_4$) were dried for 24 h in vacuum with P_2O_5 at 333 K before use. C, H, N elemental analysis were made on an elementar vario EL.

General methods

^1H NMR spectra were recorded on a Varian UNITY Plus-400 MHz Spectrometer. ESI-MS was performed with a Mariner apparatus. UV–vis Spectroscopy titrations were made on a Shimadzu UV2450 Spectrophotometer at 298.2 ± 0.1 K. A series of DMSO solutions having same host concentration and different anion concentrations were prepared, respectively. The affinity constants K_s were obtained by the determination of absorption of the series of solutions and analysis of obtained absorption values with non-linear least square calculation method for data fitting. Electrochemical measurements were performed using a CH-Instruments-430 potentiostat interfaced with Pentium PC. A platinum wire was used as an auxiliary electrode, an Ag/AgCl reference electrode was used and the working electrode was a glassy carbon electrode (diameter = 3.8 mm). NaClO_4 (0.1 mol L^{-1}) was present as the supporting electrolyte. The scan rate was 100 mV s^{-1} .

Synthesis of 1,1'-di-(2'',4''-dinophenylhydrazinocarbonyl)-ferrocene (**1**) [14]

A solution of 1,1'-ferrocenyldicarbonyl dichloride (0.78 g, 2.50 mmol) in CH_2Cl_2 (30 mL) was added slowly at 0°C to a solution of 2,4-dinitrophenylhydrazine (0.99 g, 5.00 mmol) and pyridine (0.4 mL, 5.00 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for 12 h, the

formed precipitate was filtered off and washed five times with CH_2Cl_2 (30 mL). This procedure yielded 1.08 g (68%) of pure product after drying in vacuo. ^1H NMR (400 MHz; DMSO-d_6 ; Me_4Si) 10.5 (2H, s, CONH), 10.1 (2H, s, NH), 8.9 (2H, d, Ph), 8.3 (2H, dd, Ph), 7.4 (2H, m, Ph), 5.1 (4H, s, Fc), 4.6 (4H, s, Fc) Elemental analysis: Calc. for $\text{C}_{24}\text{H}_{18}\text{FeN}_8\text{O}_{10}$: C, 45.43; H, 2.84; N, 17.67; Found: C, 45.32; H, 2.97; N, 17.69. ESI-MS (m/z): 634.53(M + H, calcd. 634).

Results and discussion

UV–vis anion titration studies

Firstly, visual inspection of solution of **1** after addition of varies tetrabutylammonium (TBA) anions showed a dramatic change, from brown to red, in the case of fluoride (F^-) suggesting strong binding, whereas the addition of acetate (AcO^-), dihydrogenphosphate (H_2PO_4^-), chloride (Cl^-), bromine (Br^-) or iodine (I^-) resulted slight change in color (Fig. 1), which meant that the 'naked-eye' detection was provided. We believe that this is the outcome of conjunct operation from the difference in sizes of binding sites and the direct result of basicity of anions.

Then, the anion-binding properties in quantitative analysis were carried out by UV–vis titration of the receptor in dry DMSO solution using standard tetrabutylammonium salts of AcO^- , F^- , H_2PO_4^- , Cl^- , Br^- and I^- at 298.2 ± 0.1 K. As shown in Fig. 2, the solution of **1** (1.0×10^{-5} M) has the original absorption peaks at 345 and 496 nm, which due to the nitrophenylhydrazone. Significantly, the absorption peaks at 345 nm were decreasing, whereas the absorption peaks at 496 nm were increasing by



Fig. 1 Color changes of **1** (5.0×10^{-5} M) upon addition of 3 equiv. of different anions in DMSO at 298 K (from left to right: **1** only, **1**+ AcO^- , **1**+ F^- , **1**+ H_2PO_4^- , **1**+ Cl^- , **1**+ Br^- , **1**+ I^-)

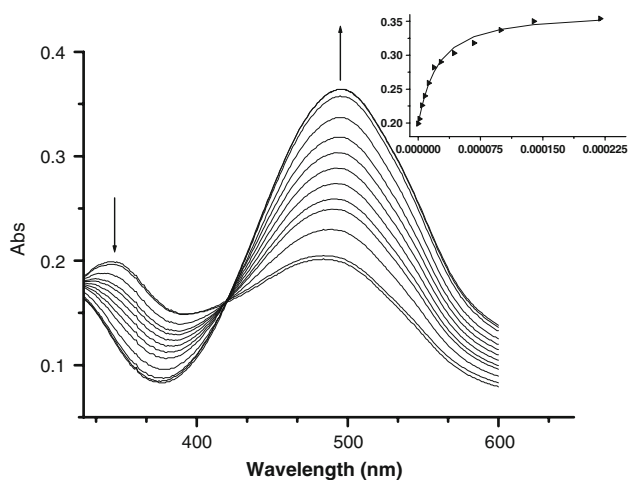


Fig. 2 Family of spectra taken in the course of the titration of a 1.0×10^{-5} M solution of **1** with a standard solution of F^- at 298.2 ± 0.1 K

F^- titration, accompanying the formation of an isosbestic point at 420 nm. As the corresponding results of visual inspection, the addition of AcO^- and $H_2PO_4^-$ led to similar spectral changes but the changes were slight. However, as the Cl^- , Br^- and I^- were titrated into **1**, the spectra hardly change even the anions were excessive.

Continuous variation method was used to determine the stoichiometric ratios of the receptors to the fluoride anion guest. In Fig. 3, job plot [15, 16] of **1** and F^- in DMSO shows the maximum at a molar fraction of 0.5. This result indicates that **1** binds fluoride anion guest with a 1:1 ratio. Moreover, similar results can also be obtained for other anions (AcO^- and $H_2PO_4^-$).

For a complex of 1:1 stoichiometry, the relation in Eq. 1 could be derived easily, where X is the absorption intensity, and C_H or C_G is the concentration of the host or the anion guest correspondingly [17].

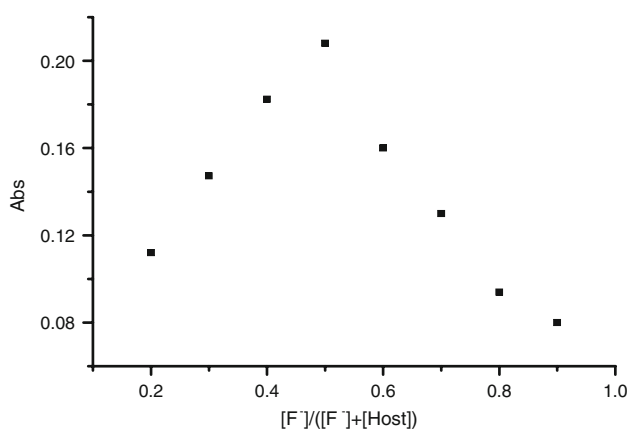


Fig. 3 A Job plot for complexation of receptor **1** with F^- determined by UV-vis in DMSO at 298.2 ± 0.1 K, $[1] + [F^-] = 2.0 \times 10^{-5}$ M

Table 1 The affinity constants of receptor **1** with anions at 298.2 ± 0.1 K in DMSO

Anion	AcO^-	F^-	$H_2PO_4^-$	Cl^-	Br^-	I^-
$\lg K_{ass}^a$ (M^{-1})	3.70 ± 0.17	4.77 ± 0.18	3.46 ± 0.12	ND ^b	ND ^b	ND ^b

^a All errors below 10%

^b ND = cannot be determined

$$X = X_0 + (X_{lim} - X_0) \left\{ C_H + C_G + 1/K_{ass} - \left[(C_H + C_G + 1/K_{ass})^2 - 4 C_H C_G \right]^{1/2} \right\} / 2 C_H \quad (1)$$

The affinity constants of receptor **1** for anionic species are calculated and listed in the Table 1.

As a validation to the qualitative and quantitative analysis, UV-vis changes (Fig. 4) of **1** operated in DMSO (1.0×10^{-5} M) after the addition of 0.5 equiv of anions provided a more convinced evidence that **1** was an excellent sensor for F^- .

Obviously, the recognition function of **1** is selective for F^- . The reason may be that receptor **1** has the cavity that is proper to F^- , spherical anion geometrically, which can match the receptors better than trigonal and tetrahedral anions. Further more, F^- is an atom anion, which means that it can form a five-membered chelate ring with the carbonylhydrazine derivatives that is steadier than seven-membered chelate ring formed by AcO^- or $H_2PO_4^-$. Finally, the ability of F^- binding H is much stronger than Cl^- , Br^- and I^- .

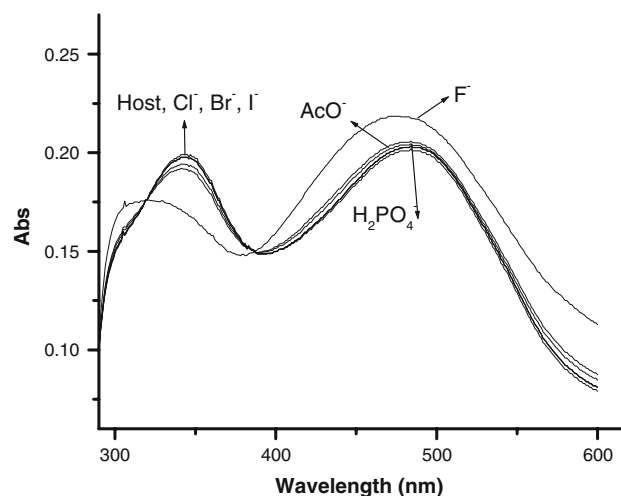


Fig. 4 UV-vis changes of **1** operated in DMSO (1.0×10^{-5} M) after the addition of 0.5 equiv of anions

¹H NMR anion titration studies

Proton NMR titration experiments were conducted to further investigate the interaction of **1** with F⁻ in DMSO-d₆. It was noticed in Fig. 5 that original signals of carbonylhydrazine -NH_a and -NH_b (marked in Scheme 2) protons appearing respectively at 10.5 and 10.1 ppm broadened and amalgamated as only one wider peak at 10.8 ppm with 0.6 equiv. F⁻. Interestingly, the wider peak

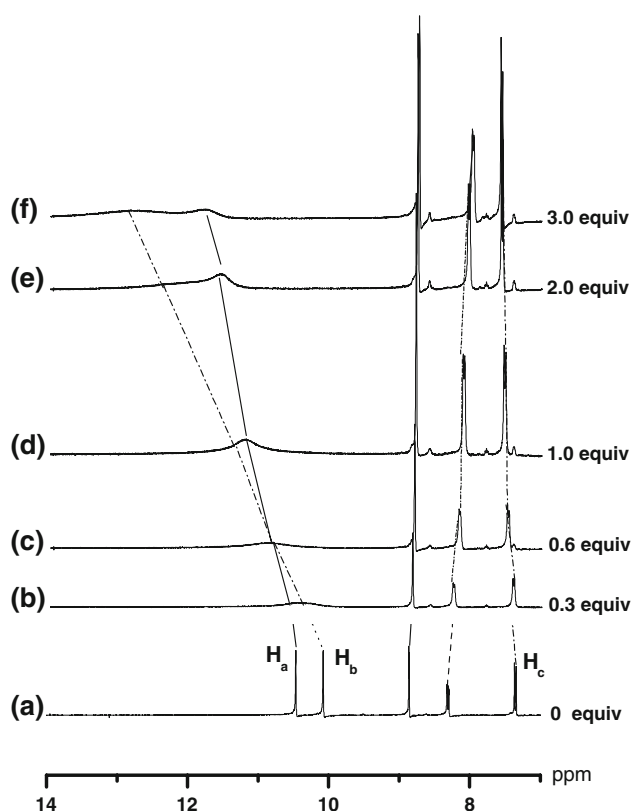


Fig. 5 N-H ¹H NMR (400 MHz) spectra of **1** in DMSO-d₆ (a) the absence and the presence of (b) 0.3, (c) 0.6, (d) 1.0, (e) 2.0, (f) 3.0 equiv of F⁻

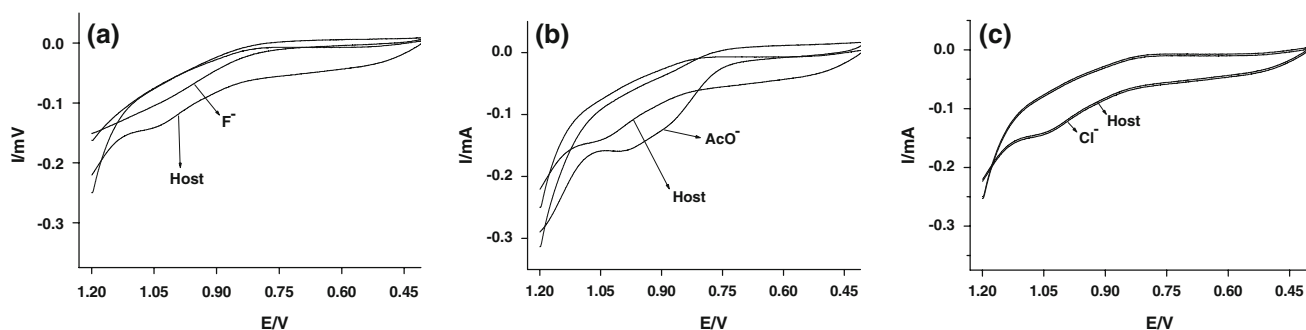
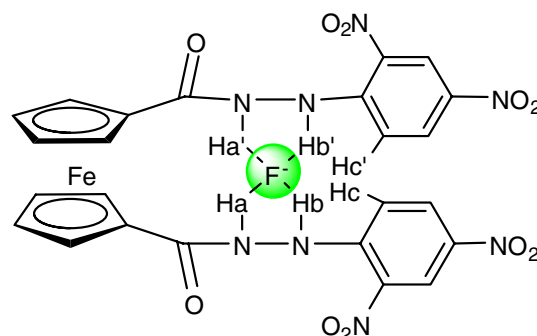


Fig. 6 (a) CVs of receptor **1** operated in acetonitrile (2.0×10^{-3} M) after the addition of 3 equiv of F⁻; (b) CVs of receptor **1** operated in acetonitrile (2.0×10^{-3} M) after the addition of 3 equiv of AcO⁻; (c)

reverted into two peaks upon the addition of 1 equiv. F⁻. When 3 equiv. F⁻ were titrated, -NH_a and -NH_b moved to downfield about $\Delta\delta = 1.0$ and 2.5 ppm, respectively. This suggests that F⁻ is being combined with the receptor **1** by hydrogen bondings. Similarly, the -H_c also shifted downfield for reason that the C-H bonds in proximity to the hydrogen bonds were polarized through ring effects, and then, partial positive charge on protons was created. On the other hand, the else aromatic protons had upfield shifts due to the NH-anion hydrogen bonds formation which increased the electron density of the phenyl ring. Above all, these results corroborated that the complex had been formed between the receptor **1** and F⁻. Correspondingly, the proposed binding mode of **1** and F⁻ was given in Scheme 2.

Electrochemical sensing studies

In order to evaluate the electrochemical sensing of the receptor **1** with the feature that the incorporation of a redox center proximate to the anion-binding site, the chemical behavior of the sensor has been performed by cyclic voltammetry (CV) in acetonitrile containing 0.1 M NaClO₄ as supporting electrolyte.



Scheme 2 The proposed binding mode of **1** and F⁻

CVs of receptor **1** operated in acetonitrile (2.0×10^{-3} M) after the addition of 3 equiv of Cl⁻

Table 2 Electrochemical response of receptor **1** to anionic guests

Anion	AcO ⁻	F ⁻	H ₂ PO ₄ ⁻	Cl ⁻	Br ⁻	I ⁻
$\Delta E_{pa,1}^a$ (mV)	71	157	87	- ^b	- ^b	- ^b

^a Anode shift of the oxidation wave of receptor **1** with 3 equiv of anionic guest added in DMSO solution, solution were 2.0×10^{-3} M in receptor, temperature = 298 K, $\Delta E_{pa,1} = E_{pa,1} - E_{pa,1+anion}$

^b Too small to determined

As shown in Fig. 6, the receptor is irreversibly oxidized during the course of the experiment, which is indicative of an EC mechanism [17]: strong product adsorption on the electrode surface that exhibits an adsorption peak before the normal diffusion peak in the CV scans. The electrochemical response of **1** upon addition of 3 equiv Cl⁻ show identical CV compared to that of the free receptor, indicating that the presence of this anion has little effects on its electrochemical response. In contrast, the addition of the same concentrations of F⁻, AcO⁻ and H₂PO₄⁻ caused a significant electrochemical response that the oxidation wave moves to more negative potentials, whereas F⁻ behaved the best stirringly among the three with the $\Delta E_{pa,1} = 157$ mV (see Table 2). All these results present that the anions have been coordinated to the -NH protons close to the ferrocene group facilitates its oxidation redox process.

Conclusion

In summary, we have investigated a novel anion colorimetric and electrochemical receptor by UV-vis, proton NMR and CV. Considering it is selective for F⁻ optically and electrochemically, it is expected to have a potential application sensor for F⁻.

Acknowledgments This work was supported by the projects 20371028, 20671052 from the National Natural Science Foundation of China.

References

- 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)

- Martinez, M.R., Sancenon, F.: Fluorogenic and chromogenic chemosensors and reagents for anions. *Chem. Rev.* **103**, 4419–4476 (2003)
- Yun, S., Ihm, H., Kim, H.G., Lee, C.W., Indrajit, B., Oh, K.S., Gong, Y.J., Lee, J.W., Yoon, J., Lee, H.C., Kim, K.S.: Molecular recognition of fluoride anion: benzene-based tripodal imidazolium receptor. *J. Org. Chem.* **68**, 2467–2470 (2003)
- Kim, S.K., Yoon, J.: A new fluorescent PET chemosensor for fluoride ions. *Chem. Commun.* 770–771 (1995)
- Zhang, Y.H., Yin, Zh.M., He, J.Q., Cheng, J.P.: Effective receptors for fluoride and acetate ions: synthesis and binding study of pyrrole- and cystine-based cyclopeptido-mimetics. *Tetrahedron Lett.* **48**, 6039–6043 (2007)
- Yamamoto, H., Ori, A., Ueda, K., Dusemund, C., Shinkai, S.: Selective fluoride recognition with ferroceneboronic acid. *J. Chem. Soc. Chem. Commun.* 333–334 (1995)
- Zhang, X., Shiraishi, Y., Hirai, T.: Unmodified fluorescein as a fluorescent chemosensor for fluoride ion detection. *Tetrahedron Lett.* **48**, 8803–8806 (2007)
- Buda, M., Ion, A., Moutet, J.C., Eric, S.A., Ziessel, R.: Electrochemical response to anions by neutral ferrocenyl receptors containing 2,2'-bipyridyl arms. *J. Electroanal. Chem.* **469**, 132–138 (1999)
- Savage, D., Alley, S.R., Gallagher, J.F., Goel, A., Kelly, P.N., Kenny, P.T.M.: The synthesis and structural characterization of novel N-meta-ferrocenyl benzoyl dipeptide esters. *Inorg. Chem. Commun.* **9**, 152–155 (2006)
- Goel, A., Brennan, N., Brady, N., Kenny, P.T.M.: Electrochemical recognition of anions by 1,1-N,N-ferrocenylbisamino acid esters. *Biosens. Bioelectron.* **22**, 2047–2050 (2007)
- Reynes, O., Maillard, F., Moutet, J.C., Royal, G., Eric, S.A., Stanciu, G., Dutasta, J.P., Gosse, I., Mulatier, J.C.: Complexation and electrochemical sensing of anions by amide-substituted ferrocenyl ligands. *J. Organomet. Chem.* **637–639**, 356–363 (2001)
- Wang, Y.H., Lin, H., Shao, J., Cai, Z.Sh., Lin, H.K.: A phenylhydrazone-based indole receptor for sensing acetate. *Talanta* **74**, 1122–1125 (2008)
- Shao, J., Lin, H., Yu, M., Cai, Z.Sh., Lin, H.K.: Study on acetate ion recognition and sensing in aqueous media using a novel and simple colorimetric sensor and its analytical application. *Talanta* **75**, 551–555 (2008)
- Hartering, C.G., Nazarov, A.A., Arion, V., Giester, G., Kuznetsov, M.L., Galanski, M., Keppler, B.K.: 1,1'-Bis(oxazolin-2-yl)ferrocenes: an investigation of their complexation behavior toward $[Pd(\eta^3\text{-allyl})Cl]_2$. *Eur. J. Inorg. Chem.* (2005) 1589–1600
- Liu, Y., Han, B.H., Zhang, H.Y.: *Curr. Org. Chem.* **8**, 35–46 (2004)
- Liu, Y., You, C.C., Zhang, H.Y.: *Supramolecular Chemistry*. Nankai University Press, Tianjin (2001)
- Connors, K.A.: *Binding Constants*, 1st edn. Wiley, New York (1987)
- Southampton Electrochemistry Group: *Instrumental Methods in Electrochemistry*. Ellis Horwood, Chichester (1985)