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Synthesis and anion recognition properties of pyrrole-bearing acyclic receptors

Yanhua Zhang,[a] Zhenming Yin,[a,b,*] Zucheng Li,[c] Jiaqi He[a] and Jin-Pei Cheng[a,*]

[a]*Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China*
[b]*College of Chemistry and Life Science, Tianjin Normal University, Tianjin 300074, China*
[c]*Center for Theoretical and Computational Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China*

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Abstract—A new series of acyclic anion receptors (**1**–**4**) based on methyl 5-(aminomethyl)-1*H*-pyrrole-2-carboxylate were designed and synthesized. The anion recognition properties of these receptors were examined by ^{1}H NMR spectroscopy and rationalized by density functional theoretical calculation. Receptor **1** displays the highest affinity and selectivity for anionic guests mainly due to the intramolecular hydrogen bonds and rigid molecular geometry.

1. Introduction

Molecular recognition for biologically important anions is currently an expanding area in the field of supramolecular chemistry.[1] Accordingly, development of synthetic receptors with high binding affinity and selectivity for anionic guests is an important goal for researchers. Recent reports in the area of anion recognition have produced a variety of neutral acyclic anion receptors based on pyrrole or amide group because these systems are simple to synthesize and have remarkable anion binding properties. Crabtree et al. developed some simple amide-bearing systems, which formed very strong complexes with halides and acetate in organic solution.[2] Gale et al. showed that 2,5-diamidopyrrole could be a new motif for the construction of anion receptors with interesting binding and self-assembly properties.[3] They also demonstrated that a series of bis-amido dipyrrolylmethanes showed special binding preference for oxo-anions even in aqueous media.[4] We have previously found that the *o*-phenylenediamide-bearing pyrrole receptor has a good fluoride binding ability in DMSO.[5] Considering that methyl 5-(aminomethyl)-1*H*-pyrrole-2-carboxylate may also be able to serve as an effective anion binding motif by virtue of its pyrrole-NH and a potential amide for H-bonding with the N-residing electron pairs, we in this work explored the ability of this versatile fragment as effective anion binding site. Herein, a series of new acyclic receptors (**1**–**4**) based on this building block were designed and synthesized for their far-ranging application in anion recognition. The ^{1}H NMR study revealed that these receptors formed 1:1 complexes with anionic guests in polar solvent. Particularly, receptor **1** was found to be the most effective receptor to bind with anions, especially with the small fluoride ion with respect to the other three species.

2. Results and discussion

2.1. Synthesis

The synthesis of receptors **1**–**4** is summarized in Scheme 1. Catalytic hydrogenation of oxime **5**[6] with Pd/C in the presence of hydrochloric acid yielded the raw material, methyl 5-(aminomethyl)-1*H*-pyrrole-2-carboxylate (**6**), which was then *N*-protected with di-*tert*-butyl-dicarbonate (Boc_2O) under basic conditions and followed by saponification to afford compound **7**. Compounds **1** and **2** were synthesized, respectively, by the reactions of 2,6-pyridine dicarboxylic chloride and isophthaloyl dichloride with 2 equiv of compound **6** in the presence of triethylamine, and then recrystallized from methanol. Compounds **3** and **4** were obtained by direct condensation of 2 equiv of compound **7** with 2,6-diaminopyridine or *m*-phenylenediamine in dry dichloromethane using *N*,*N*′-dicyclohexylcarbodiimide (DCC) as coupling reagent in the presence of triethylamine and a catalytic amount of 4-dimethylaminopyridine (DMAP). Both **3** and **4** were purified by column chromatography.

2.2. ^{1}H NMR studies

The recognition properties of the receptors **1**–**4** with a variety of anionic guests in DMSO-d_6 were monitored by ^{1}H NMR

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* Corresponding authors. E-mail addresses: hsxyyzm@mail.tjnu.edu.cn; chengjp@nankai.edu.cn

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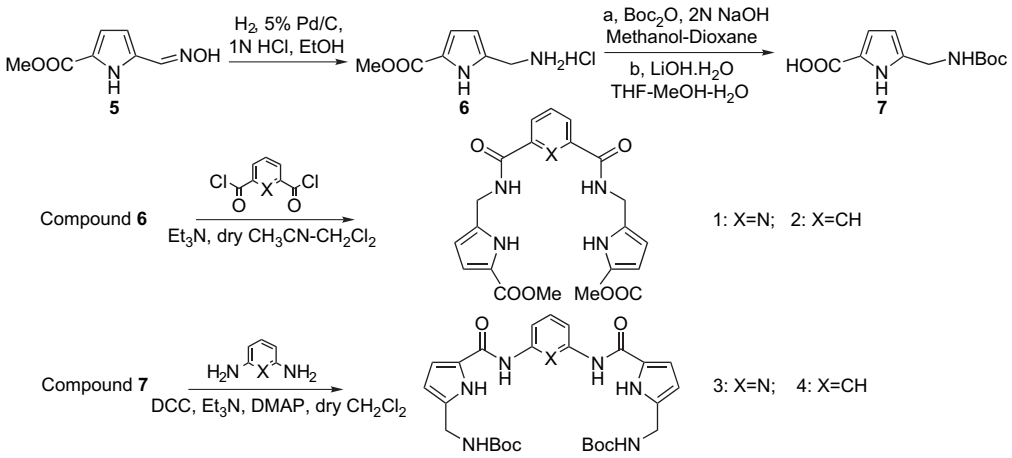

Scheme 1. General synthetic routes to target compounds **1**–**4**.

titration at room temperature. Addition of the tetrabutylammonium salts ($[n\text{-Bu}]_4N^+A^-$; A^-=F^-, $H_2PO_4^-$, AcO^-, Cl^-, and HSO_4^-) into DMSO-d_6 solution of receptors **1** and **2** led to downfield shifts of pyrrole-NH and amide-NH signals. This indicated that all the four NHs from the two clefts of receptors **1** and **2** have participated in complexing with the anionic guests through hydrogen bonding. The titration curves of receptor **1** with anions are shown in Figure 1. When small aliquots of fluoride was added, the NH signals shifted downfield dramatically with the peaks broadened, indicating that receptor **1** bound fluoride anion very effectively and there should be formed a strong H-bonded complex between **1** and F^-. However, the signals became sharp after 1 equiv of fluoride was added, and this may be explained by considering that the fluoride ion bound all NH donors very efficiently during complex formation so as to prevent exchanges of the NH protons with the solvent.[7] On the other hand, it was observed that upon addition of dihydrogen phosphate ion or acetate ion to the DMSO-d_6 solution of receptor **1**, the ^{1}H NMR signals of pyrrole-NH and amide-NH of **1** also shifted downfield significantly but with less extent than fluoride did. This was probably due to their basicity and the differences in their sizes and shapes. In the cases of chloride or hydrogen sulfate ions, only slightly downfield shift of the NH signals was observed when anions were added. This may be resulted from the much larger size, lower basicity, and weaker hydrogen bond acceptor abilities of these two anionic guests.[8]

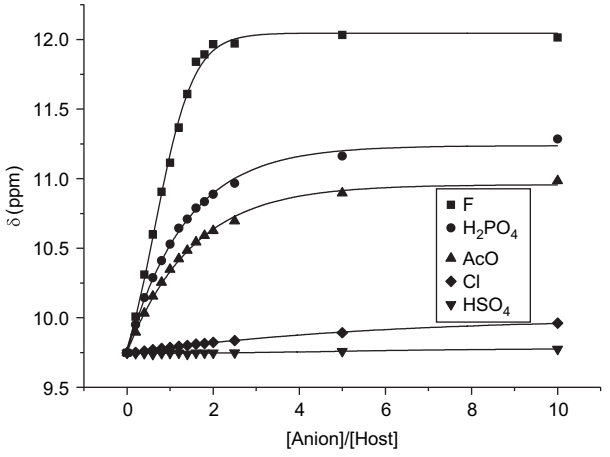

Figure 1. ^{1}H NMR titration curves for amide-NH of receptor **1** with F^-, $H_2PO_4^-$, AcO^-, Cl^-, and HSO_4^-. Anions added as their tetrabutylammonium (TBA) salts.

As for receptors **3** and **4**, when anions were added into the DMSO-d_6 solution of these receptors, the signals of pyrrole-NH and amide-NH from the amidopyrrole moieties shifted downfield and became broad, and at meanwhile, no obvious changes for the two *tert*-butyloxy-carbonyl (Boc) amide protons were observed. This reveals that the hydrogen bonding interactions only take place between the anion and the protons from the two amidopyrrole subunits rather than from the Boc amide, which is likely due to the bulky size of the Boc group.

According to the chemical shifts of the amide-NH protons, all receptors show the 1:1 type binding model with anions. Association constants for receptors **1**–**4** with anionic guests were calculated by nonlinear least-square analysis following the standard procedure.[8,9] The results are summarized in Table 1. The data in Table 1 revealed that the pyridyl-bridged receptor **1** has higher anion binding ability than the phenyl-bridged receptor **2**. This can be ascribed to the intramolecular hydrogen bonding interactions between the two amide protons and the pyridine nitrogen, which helps to pre-organize the rigid U-shape cleft of receptor **1**.[10] A similar situation may also be applied to induce a greater anion binding

Table 1. Association constants[a] of receptors with various anions[b] determined by ^{1}H NMR titrations in DMSO-d_6 at 298 K

Anions	Association constants K_{ass} (M^{-1})			
	1	**2**	**3**	**4**
F^-	1266	138	102	73
$H_2PO_4^-$	448	459	147	129
AcO^-	380	262	74	75
Cl^-	75	75	65	52
HSO_4^-	21	<10	<10	[c]

[a] All errors were estimated to be less than 15%.
[b] Anions added as their tetrabutylammonium (TBA) salts.
[c] No significant shift.

ability for receptor **3** than receptor **4**. On the other hand, the acidity of NH proton should be another factor to influence anion recognition. As can be seen from the ^{1}H NMR spectra, the signals of pyrrole-NH and amide-NH of receptor **1** (9.75, 11.84) were much more downfield compared to those of receptor **2** (8.95, 11.74). Similar tendency was observed for **3** (9.97, 11.48) versus **4** (9.76, 11.29). Table 1 also demonstrated that receptors **3** and **4** show considerably less anion affinity with respect to **1** and **2**. This is primarily due to the two bulky Boc groups present in the two receptors, which limit the models to adopt the desired U-shape conformation.

Furthermore, compared with the results in our earlier study on neutral pyrrole-amide receptor[5] *(320 M^{-1} for F^-, 100 M^{-1} for $H_2PO_4^-$, determined by proton NMR titrations in DMSO-d_6)*, receptor **1** here is a much better anion receptor. This may be attributed to the pre-organized conformation in the latter case that offers all the four H-bond donors to more tightly and efficiently complex with anions in solution. Receptor **1** is also observed to have higher fluoride binding ability than phenyl 2,5-diamidopyrrole derivatives[3a] and the stable 5,5′-dicarboxamido-dipyrrolylmethane derivatives[4b] reported in literature *(measured under slightly different experimental conditions)*. However, the binding ability of **1** for oxo-anions such as dihydrogen phosphate is not as good as above cases. This may be explained in terms of the different complexation geometries of 2,6-pyridine diamide and 2,5-pyrrole diamide.[11] Such differences in geometry and conformation can lead to distinct changes in binding affinity for anions.

2.3. Density functional theoretical calculation

In order to further understand the nature of receptor–anion interaction, the geometries of receptors **1** and **2** were optimized at the B3LYP/6-31G* level using GAUSSIAN 03 program.[12] However, the optimized geometries of **3** and **4** were not obtained perhaps due to the large volume of the Boc groups that make the potential surfaces too flat and make the desired geometries difficult to locate. As can be seen from Figure 2, the 2,6-dicarbamoyl moiety on receptor **1** is planar, a well-established framework resulted from the two intramolecular hydrogen bonds, and the two NHs form a convergent binding structure. The N–H···N hydrogen bond

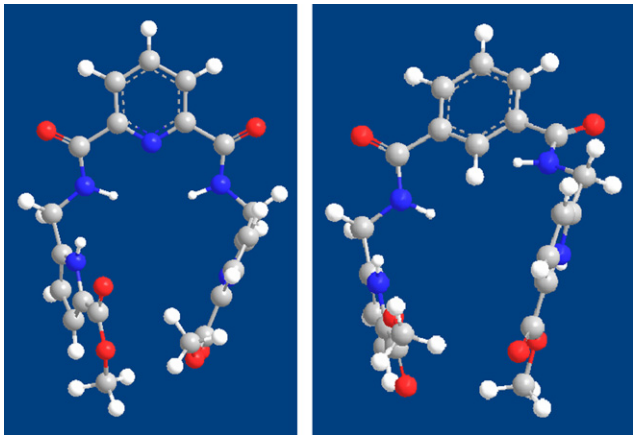

Figure 2. Optimized geometries of the free receptors **1** (left) and **2** (right) at B3LYP/6-31G* level.

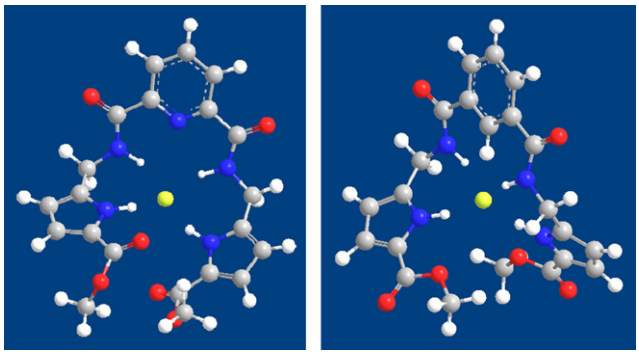

Figure 3. Optimized geometries of $\mathbf{1}\cdot\mathbf{F}^-$ (left) and $\mathbf{2}\cdot\mathbf{F}^-$ (right) complexes at B3LYP/6-31G* level.

distances are 2.254 and 2.228 Å. As for receptor **2**, however, one N–H points up but the other points down with respective to the phenyl group due to the repulsion between the amide N–H groups and phenyl C–H group. This is consistent with the ^{1}H NMR result that receptor **1** has better pre-organized geometries than receptor **2**. The geometry of $\mathbf{1}\cdot\mathbf{F}^-$ and $\mathbf{2}\cdot\mathbf{F}^-$ complexes has also been optimized. As shown in Figure 3, in $\mathbf{1}\cdot\mathbf{F}^-$ complex, all N–H groups form convergent geometry to allow hydrogen bonding with fluoride tightly and efficiently. This is also in agreement with the ^{1}H NMR result that all the four NHs of **1** participated in anion recognition. In $\mathbf{2}\cdot\mathbf{F}^-$ complex, compared with the free receptor **2**, the N–H···F$^-$ hydrogen bonds forced all N–Hs of the receptor to point inside the cavity. Consequently, all N–H groups and the phenyl C–H of **2** have been involved in binding with fluoride.

3. Conclusion

In summary, we have developed a new series of pyrrole-based acyclic anion receptors. The experimental results indicated that these receptors formed 1:1 complexes with anionic guests by multi-hydrogen-bonding interactions. Interestingly, receptor **1** turns out to be a very good anion receptor with remarkably high preference in binding with fluoride ion in polar solvent. This is not of any surprise because the possession of a higher degree of preorganization provides better geometry for binding with anion of suitable size. The results also demonstrated that methyl 5-(aminomethyl)-1*H*-pyrrole-2-carboxylate is an excellent building block to be used in the design of anion receptors.

4. Experimental

4.1. General

^{1}H NMR spectra were recorded in DMSO-d_6 and $CDCl_3$, with TMS as the internal standard, on a BRUKER AC-P 300 MHz instrument. ^{13}C NMR spectra were recorded on VARIAN MERCURY PLUS 100 MHz spectrometer. Mass spectra were recorded with an AEIMS-50/PS 30 mass spectrometer or IonSpec/7.0T FT mass spectrometer. Acetonitrile was refluxed and distilled from alkaline $KMnO_4$, followed by fractional distillation from phosphorous pentoxide. Dichloromethane was distilled from calcium hydride.

All other commercially available reagents were used without further purification.

4.2. Procedure for the synthesis of compounds

4.2.1. Methyl 5-(aminomethyl)-1*H*-pyrrole-2-carboxylate 6. HCl (2 M, 1.5 mL, 3 mmol) and Pd/C (5%, 120 mg) were added into a solution of oxime **5** (504 mg, 3 mmol) in ethanol (80 mL). The resulting suspension was flushed with N_2 to vent oxygen, and then hydrogenated under an H_2-filled balloon. The reaction mixture was stirred at room temperature for 2 h. The reaction mixture was filtered and the solvent was evaporated to give pale solid (572 mg, quant.). ^{1}H NMR (300 MHz, DMSO-d_6, TMS): δ 3.77 (s, 3H, CH_3), 4.01 (s, 2H, CH_2), 6.29–6.31 (m, 1H, 3-C_4H_2N), 6.76–6.78 (m, 1H, 4-C_4H_2N), 8.34 (s, 3H, NH_3^+), 11.96 (s, 1H, pyrrole-NH).

4.2.2. Compound 7. A solution of Boc_2O (523 mg, 2.4 mmol) in methanol/dioxane (2/1, 10 mL) and a solution of NaOH (320 mg, 8 mmol) in water (2 M, 4 mL) were added dropwise into a well-stirred solution of compound **6** (381 mg, 2 mmol) in methanol/dioxane (2/1, 100 mL). The reaction mixture was stirred continuously until TLC showed the consumption of all starting materials at room temperature (usually 2 h). The reaction mixture was filtered to remove the precipitate and the filtrate was concentrated in vacuo. Then, it was poured into water (100 mL) and extracted with ethyl acetate (30 mL×3). The combined organic phases were dried over Na_2SO_4. The solvent was removed via vacuum distillation and the residue was purified by column chromatography with ethyl acetate and chloroform (10/1) to afford the *N*-protecting compound (463 mg, 91%) as pale yellow solid. ^{1}H NMR (300 MHz, DMSO-d_6, TMS): δ 1.39 (s, 9H, Boc-H), δ 3.74 (s, 3H, CH_3), 4.10 (d, 2H, J=5.4 Hz, CH_2), 5.97–5.99 (m, 1H, 3-C_4H_2N), 6.68–6.70 (m, 1H, 4-C_4H_2N), 7.20 (t, 1H, NH), 11.62 (s, 1H, pyrrole-NH).

The intermediate (1017 mg, 4 mmol) was dissolved in THF/MeOH/H_2O (3/1/1, 20 mL), and $LiOH\cdot H_2O$ (504 mg, 12 mmol) was added into this solution. After being stirred at room temperature for 12 h, the reaction mixture was acidified to pH 5 with citric acid (2 M), the solvent was evaporated, and the residue was then poured into water (50 mL), which was extracted with ethyl acetate (30 mL×3). The organic layer was washed with water, dried over anhydrous Na_2SO_4, and concentrated in vacuo to afford product **7** (898 mg, 93.6%) as pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.47 (s, 9H, Boc-H), 4.29 (d, 2H, J=5.4 Hz, CH_2), 6.08–6.10 (m, 1H, 3-C_4H_2N), 6.90–6.92 (m, 1H, 4-C_4H_2N), 9.98 (s, 1H, NH), 10.35 (s, 1H, pyrrole-NH); MS (ESI): m/z 239.12 $[M-H]^-$.

4.2.3. Compound 1. A well-stirred solution of compound **6** (381 mg, 2 mmol) and triethylamine (0.63 mL, 4.5 mmol) in dry acetonitrile/dichloromethane (1/1, 100 mL) was cooled to −5 °C in an ice–salt bath. A solution of 2,6-pyridine dicarboxylic chloride (204 mg, 1 mmol) in dichloromethane (50 mL) was added dropwise into this mixture. The reaction mixture was allowed to warm up to room temperature and stirred for 12 h. The solution was evaporated in vacuo. The residue was dissolved in ethyl acetate and the solution was washed sequentially with 15 mL of 5% HCl, saturated brine, 5% $NaHCO_3$, saturated brine, and H_2O. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was recrystallized from methanol solution to give compound **1** (298 mg, 68%) as pale yellow acicular crystals. Mp: 220–221 °C; ^{1}H NMR (300 MHz, DMSO-d_6, TMS): δ 3.74 (s, 6H, CH_3), 4.57 (d, 4H, J=3 Hz, CH_2), 6.02–6.04 (m, 2H, 3-C_4H_2N), 6.70–6.72 (m, 2H, 4-C_4H_2N), 8.16–8.26 (m, 3H, pyridine-CH), 9.75 (t, 2H, NH), 11.84 (s, 2H, pyrrole-NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 36.3, 51.7, 108.6, 116.2, 121.4, 125.3, 136.5, 140.3, 149.2, 161.4, 164.1; HRMS (ESI) calcd for $C_{21}H_{21}N_5O_6$ $[M+Na]^+$: 462.1384, found: 462.1389.

4.2.4. Compound 2. Compound **2** was obtained as yellow crystals (250 mg, 57%) from isophthaloyl dichloride and compound **6** by a procedure similar to that employed in the synthesis of **1**. Mp: 138.5–139.5 °C; ^{1}H NMR (300 MHz, DMSO-d_6, TMS): δ 3.74 (s, 6H, CH_3), 4.48 (d, 4H, J=5.4 Hz, CH_2), 6.06–6.08 (m, 2H, 3-C_4H_2N), 6.70–6.73 (m, 2H, 4-C_4H_2N), 7.58 (t, 1H, ArH), 8.02–8.00 (m, 2H, ArH), 8.35 (s, 1H, ArH), 8.95 (t, 2H, NH), 11.74 (s, 2H, pyrrole-NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 36.6, 51.6, 108.8, 116.1, 121.4, 126.9, 129.2, 130.7, 135.0, 136.5, 161.4, 166.6; HRMS (ESI) calcd for $C_{22}H_{22}N_4O_6$ $[M+Na]^+$: 461.1432, found: 461.1424.

4.2.5. Compound 3. A solution of Boc-protected compound **7** (480 mg, 2 mmol) in dry dichloromethane (100 mL) was added to a solution of 2,6-diaminopyridine (109 mg, 1 mmol), triethylamine (0.28 mL, 2 mmol), and catalytic quantity of DMAP in dry dichloromethane (100 mL), and the solution was cooled to −5 °C in an ice–salt bath. A solution of DCC (412.7 mg, 2 mmol) in dry dichloromethane (50 mL) was dripped into this ice-cold solution. The reaction mixture was allowed to warm up to room temperature and stirred for 12 h. Then, the solution was washed sequentially with 5% HCl, saturated brine, 5% $NaHCO_3$, saturated brine, and H_2O. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography with ethyl acetate and chloroform (1/2) to afford target product **3** (149 mg, 27%). Mp: 160–161 °C; ^{1}H NMR (300 MHz, DMSO-d_6, TMS): δ 1.39 (s, 18H, Boc-H), 4.12 (s, 4H, CH_2), 6.00 (d, 2H, J=3.6 Hz, 3-C_4H_2N), 7.06 (d, 2H, J=1.0 Hz, 4-C_4H_2N), 7.21 (t, 2H, NH), 7.79–7.82 (m, 3H, pyridine-CH), 9.97 (s, 2H, NH), 11.48 (s, 2H, pyrrole-NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 28.9, 37.3, 78.7, 108.0, 110.1, 113.3, 125.0, 136.5, 140.4, 151.17, 156.3, 159.5; HRMS (ESI) calcd for $C_{27}H_{35}N_7O_6$ $[M+H]^+$: 554.2722, found: 554.2715.

4.2.6. Compound 4. Compound **4** was obtained as pale yellow solid (188 mg, 34%) from *m*-phenylenediamine and compound **7** by a procedure similar to that employed in the synthesis of **3**. Mp>250 °C; ^{1}H NMR (300 MHz, DMSO-d_6, TMS): δ 1.40 (s, 18H, Boc-H), 4.13 (s, 4H, CH_2), 6.00 (d, 2H, J=3.6 Hz, 3-C_4H_2N), 7.01 (d, 2H, J=3.6 Hz, 4-C_4H_2N), 7.19–7.44 (m, 4H, ArH), 8.13 (t, 2H, NH), 9.76 (s, 2H, NH), 11.29 (s, 2H, pyrrole-NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 28.9, 37.3, 78.7, 107.7, 112.3, 112.5, 115.6, 125.8, 129.19, 135.8, 140.0, 156.3, 159.6; HRMS (ESI) calcd for $C_{28}H_{36}N_6O_6$ $[M+Na]^+$: 575.2589, found: 575.2593.

4.3. Binding titration

In a typical anion titration experiment,[8,13] titrations were run at 5 mM of receptor, aliquots of a solution of 0.5 M [*n*-Bu]$_4$N$^+$A$^-$ (tetrabutylammonium fluoride, acetate, dihydrogen phosphate, chloride, and hydrogen sulfate) in DMSO-d_6 were added to 0.5 mL solution of the receptor. Fourteen aliquots were added corresponding to 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2, 2.5, 5, and 10 equiv of anion. The chemical shifts of the amide-NH and pyrrole-NH protons on the receptor were monitored as they moved downfield with the addition of anions. For 1:1 stoichiometric complexes, the association constants between receptors and anions were calculated by nonlinear least-square procedure.[8,9]

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.05.054.

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