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SHORT COMMUNICATION

Rational Design of Novel Benzimidazole-Based Sensor Molecules that Display Positive and Negative Fluorescence Responses to Anions

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Abstract Two novel and neutral benzimidazole derivatives-based anion receptors bearing a 1,10-phenanthroline fluorophore, *N*,*N*′-di-(2′-benzimidazolyl-methylene)-1, 10-phenanthroline-2,9-diamide (1) and *N*,*N*′-di-[2′-(benzimidazolyl-2′-) ethyl-]-1,10-phenanthroline-2,9-diamide (2), which exhibited turn-on and turn-off fluorescence responses to various anions, were rationally designed and synthesized and their fluorescent response toward anions was investigated in DMSO solution. In the process of anions binding, there were two different fluorescent responses in presence of anions: a quenching of the fluorescence emission for F^- and AcO^- and an enhancement of the fluorescence emission for Cl^-, Br^- and I^-. Two different luminescent mechanisms of the receptors 1 and 2 resulting from various anions were exploited to rationalize quenching and enhancement of the fluorescence emission: a photo-induced electronic transfer mechanism (PET) and the increase of the rigidity of the host molecules, respectively. In particular, chloride could be recognized selectively from the anions tested according to changes of fluorescence spectrum.

Keywords Anion receptor · Fluorescence · Turn-on · PET · Supramolecuar chemistry

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Introduction

More and more attentions have been paid to the design and synthesis of the receptors that selectively recognize specific anions such as fluoride [1], carboxylate [2], iodide [3], and phosphate [4, 5] as anions are ubiquitous throughout biological systems and play crucial roles in the areas of medicinal, catalysis, biochemistry, and environmental chemistry [6]. For example, the carboxylate anions exhibit specific biochemical behaviors in the enzymes and antibodies and are also critical components of numerous metabolic processes [7]. In particular, Cl^- which has relatively high extracellular concentrations is essential to human health and is transported across cell membranes by various Cl^- proteins, often in conjunction with cation transportation [8]. Due to the large ionic radius low charge density and low hydrogen bonding ability, chloride is difficult to be sensed. Therefore, development of receptors that can recognize chloride selectively is strongly desired.

In general, the anion binding event can be transduced into observable signals: color changes, redox potential changes, UV-vis spectral changes and so on [9]. While the fluorescent response has gained more considerable attentions and in particular, fluorescence enhancement "switch on" rather than quenching "switch off" upon recognition is advantageous in terms of the detection limit, of which the signal-to-noise ratio is specific for a certain host–guest supramolecular ensemble, because the latter often indicates a counterproductive effect in terms of specificity and sensitivity [10]. Commonly, the design of fluorescent chemosensors is mainly based on photoinduced electron/energy transfer (PET) [11], metal-ligand charge transfer (MLCT) [12], intramolecular charge transfer (ICT) [13], excimer/exciplex formation [14], guest-induced changes in the rigidity of the host molecules [15–18] and so on.

Among these mechanism, PET process would induce fluorescence quenching and the rigidity of the host molecules would result in fluorescence enhancement. Consequently, we assumed that such two mechanisms acted simultaneously in single receptor for binding of different guests, which would improve the selectivity of host molecule for anions. However, to the best of our knowledge, such receptors were quite rare in the literature.

A successful approach to obtain such anions receptors is that functional groups such as amide, urea/thiourea, –OH as well as pyrrole are covalently or noncovalently linked to fluorescent groups [19–22]. Nevertheless, it should be noted that the fluorescent probes/chemosensors with N–H of benzimidazole as binding sites are quite limited, although it has been documented previously [3, 23–25]. Bearing these in mind, we designed and synthesized two novel anion receptors with flexible structure: *N*,*N*′-di-(2′-benzimidazolyl-methylene)-1,10-phenanthroline-2,9-diamide (1) and *N*,*N*′-di-[2′-(benzimidazolyl-2′-) ethyl-]-1,10-phenanthroline-2,9-diamide (2), which were obtained by introducing benzimidazole derivatives (binding sites) into 1,10-phenanthroline group (fluorophore). Just as expected, receptors 1 and 2 showed unique luminescence property: fluorescence quenching for F^- and AcO^- ions and fluorescence enhancement for Cl^-, Br^- and I^- ions. The anion recognition via hydrogen-bonding interactions can be easily monitored by the changes of fluorescent intensity induced by anion-complex-action. In addition, a feature of binding mode is described on basis of the ^1H NMR titration experiments.

Experimental

Apparatus

^1H NMR spectra were obtained on a Varian UNITY Plus-400 MHz Spectrometer using tetramethylsilane (TMS) as an internal standard. ESI-MS was performed with a MARINER apparatus. C, H, N elemental analyses were made on an elementar vario EL. Fluorescent spectra were recorded on a Shimadzu RF-5301PC Spectrophotometer at 298.2±0.1 K and the width of the slits used is 5 nm.

Chemicals

All reagents for synthesis obtained commercially were used without further purification. In the titration experiments, all the anions were added in the form of tetra-*n*-butylammonium (TBA) salts, which were purchased from Sigma-Aldrich Chemical, stored in a vacuum desiccator containing self-indicating silica and dried fully before using. DMSO was dried with CaH_2 and then distilled in reduced pressure.

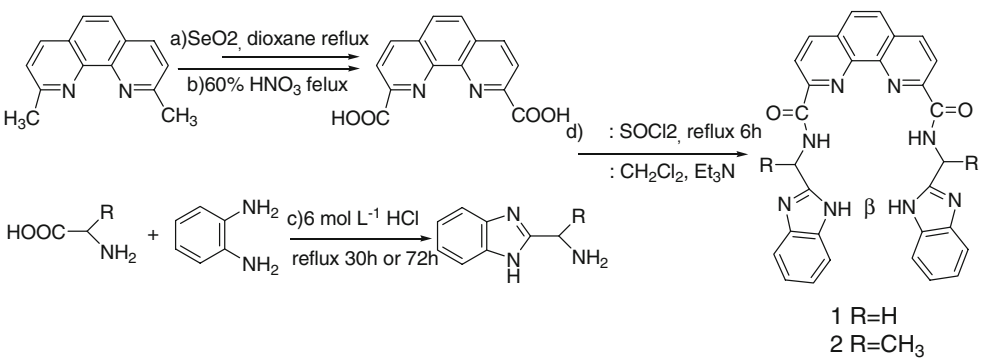
General method

All titration experiments were carried out at 298 K. The stock solutions of compounds1 and 2 were prepared in DMSO with a concentration of 2.0×10^{-4} mol l^{-1} for each and stored in the dry atmosphere. This solution was used for all spectroscopic studies after appropriate dilution. Solutions of 1.0×10^{-2} M tetrabutyl ammonium (TBA) salts of the respective anions were prepared in dried and distilled DMSO and were stored under a dry atmosphere. Then, the mixture of 0.5 ml solution of the receptor 1 and given amount of anions was diluted with DMSO to 5 ml, whose Fluorescent spectra were tested immediately. And excitation wavelength (λ=368 nm) was exploited. Then affinity constants of receptor 1 for anionic species were determined by non-linear fitting analyses of the titration curves according to the equation described by Valeur. The fluorescence quantum yields, ϕ_f, were estimated using the integrated emission intensity of fluorescein (0.85) in 0.1 M NaOH aq.as a standard *via*

$$\phi_f = \phi_f^{'}\left(I_{sample}/I_{std}\right)\left(A_{std}/A_{sample}\right)\left(\eta^2_{sample}/\eta^2_{std}\right)$$

where $\phi_f^{'}$ is the quantum yield for the fluorescein (0.85) in 0.1 M NaOH aq. used as a standard; I_{sample} and I_{std} are the integrated emission intensities; A_{sample} and A_{std} are the absorbances at the excitation wavelength, and η^2_{sample} and η^2_{std} are the respective refractive indices.

Scheme 1 Synthesis of the receptors 1and 2



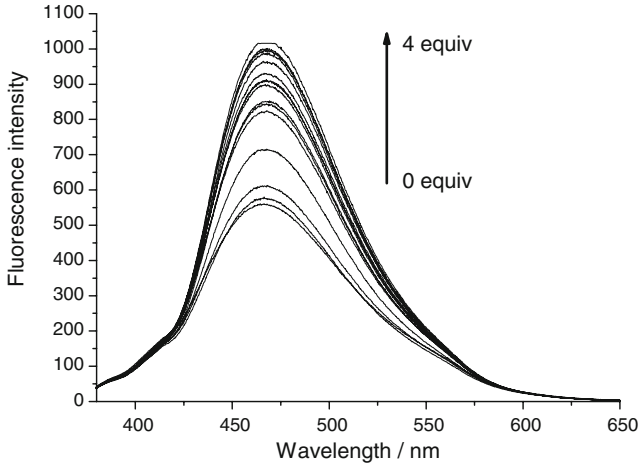


Fig. 1 Fluorescence spectra (excitation at 368 nm) of the receptor 1 (2×10^{-5} mol l^{-1}) in the presence and absence of chloride ion

^{1}H NMR titration experiments were carried out in the DMSO-d_6 solution (TMS as an internal standard). A 5.0×10^{-3} M solution of the compound 1 in DMSO-d_6 was prepared. Then, the increased amount of anions (1.0 M in DMSO-d_6) was added to the solution above-mentioned and ^{1}H NMR of the host-guest system was tested.

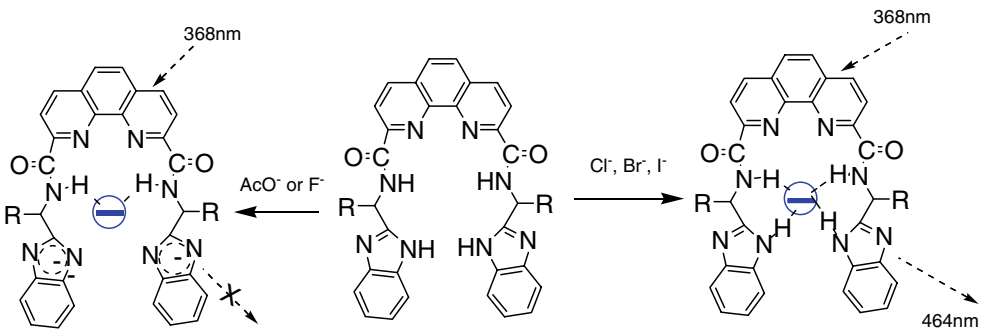
Synthesis of the receptor 1and 2

The receptors 1 and 2 were prepared according to Scheme 1. To 1,10-phenanthroline-2,9-dicarboxylic acid (1.1 g, 4 mmol), whose synthesis was shown in the Supporting Information, was added distilled thionyl chloride (25 ml) and the mixture solution was refluxed for 6 h. Then, the solution was concentrated to dryness under reduced pressure. The slight yellow residue was dissolved in 25 ml dry CH_2Cl_2 followed by addition of a catalytic amount of triethylamine. The relevant benzimidazole derivatives (8.1 mmol), whose synthesis was shown in the Supporting Information, were added slowly to the above-mentioned cold mixture solution, stirred for 3 days at room temperature, poured into saturated sodium bicarbonate solution, filtered and washed with water (3×5 ml) to give pure solid 1 and 2 after crystallization from DMF. *N*,*N*′-di-(2′-benzimidazolyl-methylene)-1,10-phenanthroline-2,9-diamide (1). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ=12.34 (s, 2H, NH), 9.97 (s, 2H, NH), 8.73 (d, J=8.2 Hz, 2H, phen-H), 8.46 (d, J=8.0 Hz, 2H, phen-H), 8.22 (s, 2H, phen-H), 7.53 (d, J=8.0 Hz, 2H, phenyl-H), 7.41 (d, J=8.0 Hz, 2H, phenyl-H), 7.07 (m, 4H, phenyl-H), 4.84 (d, J=8.4 Hz, 4H, CH_2); ESI-mass: m/z 527.15 $(M+H)^+$; Elemental analysis calcd for $C_{30}H_{22}N_8O_2\cdot2H_2O$: C,64.06%, H, 4.63%, N, 19.93%. Found: C, 64.45%, H, 4.43%, N, 20.33%. *N*,*N*′-di-[2′-(benzimidazolyl-2′-) ethyl-]-1,10-phenanthroline-2,9-diamide (2). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ= 12.37 (s, 2H, NH), 9.69 (s, 2H, NH), 8.77 (d, J=8.2 Hz, 2H, phen-H), 8.47 (d, J=8.0 Hz, 2H, phen-H), 8.22 (s, 2H, phen-H), 7.52 (d, J=8.0 Hz, 2H, phenyl-H), 7.43 (d, J=8.0 Hz, 2H, phenyl-H), 7.12 (m, 4H, phenyl-H), 5.48 (m, 2H, CH), 2.35 (m, 6H, CH_3); ESI-mass: m/z 555.25 $(M+H)^+$; Elemental analysis calcd for $C_{32}H_{26}N_8O_2\cdot2H_2O$: C, 65.08%, H, 5.08%, N, 18.98%.Found: C, 65.17%, H, 4.83%, N, 18.93%.

Results and discussion

Firstly, the anion binding ability of 1 and 2 was investigated using fluorescence titration experiments. The receptor 1 displayed weak fluorescence emission (ϕ_f=0.09, excitation at λ=368 nm) in DMSO as shown in Fig. 1. The emission of the receptor 1 (2×10^{-5} mol l^{-1}) was increased in intensity (ϕ_f=0.16 when 4 equiv. Cl^- ion was added) as the concentration of tetrabutylammonium chloride was increased, which indicated that an association between the receptor 1 and Cl^-. The mechanism for this enhancement of emission was via an increase of the rigidity of the host molecules upon binding anions, which was quite limited to be used in anion recognition. The enhancing process was proposed as following; before the recognition process, the benzimidazole moieties of the host molecular 1 could rotate freely. However, after addition of Cl^- ion, and the formation of the hydrogen bonding interactions between Cl^- and N–H of 1, there was an increase in the rigidity of the receptor 1 and the rotation of the groups was restrict

Scheme 2 The proposed binding mode in solution



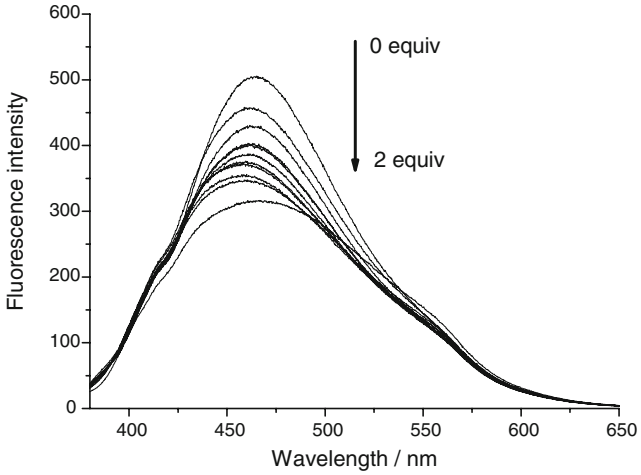


Fig. 2 Fluorescence spectra (excitation at 368 nm) of the receptor 1 (2×10^{-5} mol l^{-1}) in the presence and absence of fluoride ion

markedly (see Scheme 2). Thus, a large increase in emission intensity was obtained because of inhibiting vibrational and rotational relaxation modes of nonradiative decay [15–18]. Addition of Br^- and I^- ions resulted in similar changes in the fluorescent spectrum with Cl^- ion (see Electronic supplementary material).

However, interestingly, the intensity of the emission spectrum of 1 decreased upon addition of AcO^- and F^- (see Fig. 2), which demonstrated that there was different recognition process with Cl^- ion. We proposed that addition of AcO^- and F^- resulted in the deprotonation of N–H_β of benzimidazole group, which made the benzimidazole groups rotate freely and anions bond had no effect on the rigidity of the receptor 1. In addition, no significant spectral changes in absorption spectra were observed, confirming that fluorescence quenching of the receptor 1 took place via a photoinduced electron transfer (PET) mechanism [11,12]. It was clear that in a system where a fluorophore and a binding site were separated, anion binding to N–H hydrogens caused an increase in reduction potential of N–H bonds, making the electron transfer more feasible. Accordingly, fluorescence quenching (φ_f=0.06 when 2 equiv. F^- ions were added) was observed during fluorescence titration experiments just as Fig. 2 showed. Noteworthily, addition of Cl^- resulted in absolutely different changes in the fluorescence spectrum with addition of AcO^- and F^-. Although Cl^- ion could not be differentiate selectively from AcO^- and F^- ions by virtue of association constants, Cl^- ion could be recognized selectively and easily from other anions according to the changes of spectrum.

The interactions between various anions and the receptor 2 were investigated under the same conditions as the receptor 1. The receptor 2 experienced similar spectral changes with the receptor 1 upon interaction with anions tested (see supporting Information). However, the host 2 bore electron-donating substituent: $-CH_3$, which reduced the overall electrostatic attraction of the receptor while it allowed the increase of the electron density of 2 and the reduction in the acidity of the hydrogen-bond donors. Therefore, the hydrogen-bonding interactions between the receptor 2 and anions above-mentioned were less than the receptor 1, but its selectivity for specific anion was improved remarkably (see Table 1).

Table 1 Affinity constants (K_a mol l^{-1}) of the receptors 1 and 2 with anions in DMSO at 298.2±0.1 K

Anions[a]	1	2
F^-	8.49 (±0.12)×10^4	2.80(±0.05)×10^4
Cl^-	8.56 (±0.8)×10^3	<100
Br^-	368±45	ND[b]
I^-	140±10	ND
AcO^-	3.26 (±0.065)×10^4	–[c]
$H_2PO_4^-$	ND	ND

[a] All the anions were added in the form of tetra-n-butylammonium (TBA) salts.
[b] The affinity constants could not be determined due to slight spectral changes.
[c] The spectral changes were not suitable for accurate measurement of the K_a value.

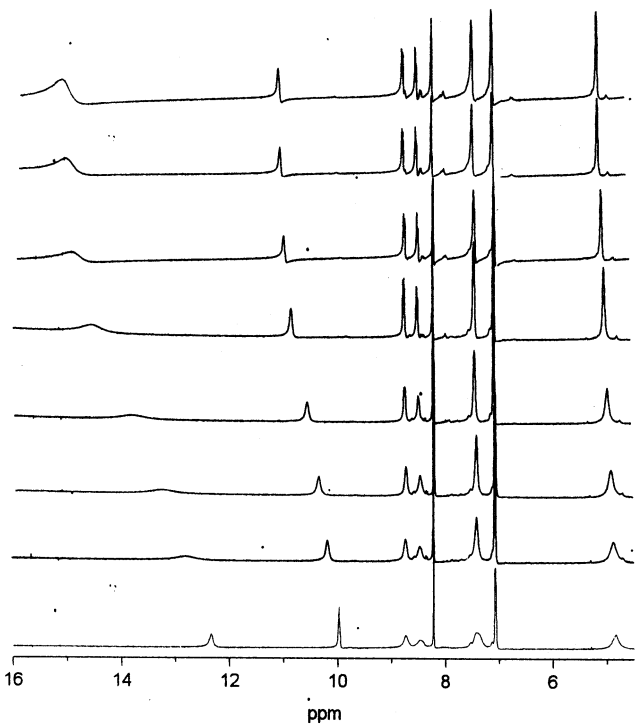


Fig. 3 Plot of ^{1}H NMR spectra of receptor 1 (5×10^{-3} mol l^{-1}) on addition of F^- in DMSO-d_6 (from *bottom to top*: 0, 0.5, 1, 2, 5, 10, 20, 50 equiv., respectively)

Affinity constants of the receptors for anionic species, which were shown in Table 1, were determined by non-linear fitting analyses of the titration curves according to the Eq. 1, 1:1 host–guest complexation [26]

$$I = I_0 + (I_{\lim} - I_0) \left\{ c_H + c_G + 1/K_a - \left[(c_H + c_G + 1/K_a)^2 - 4c_H c_G \right]^{1/2} \right\} \Big/ 2c_H \quad (1)$$

Where, c_G and c_H were the concentration of guest and host, respectively and I was the intensity of emission at certain concentration of host and guest. I_0 was the intensity of fluorescence emission of host only and I_{lim} was the maximum intensity of fluorescence of host when gust was added. K_a is the affinity constant of host–guest complexation. Obviously shown in Table 1, the receptors 1 and 2 could bind F^- ion stronger than the other anions tested. It became clear early on that the selectivity for special anions can be rationalized on the basis of the guest basicity and shape complementarity between the host and the anionic guests. In particular, multiple hydrogen-bonding interactions are necessary in high-affinity anion binding sites [27]. As expected from the basicity of anions, F^- gave a stronger complex than other anions tested. However, acetate ion was a plane and triangular and might be the fittest for four hydrogen atoms on binding sites of the receptor among the anions tested and form multitopic hydrogen-bonding interactions with the receptors. In addition, the flexible framework of the receptors was more compatible to the size of Cl^- than to the size of other anions such as Br^- and I^-. So the receptors could strongly encapsulate Cl^- according to its size.

Secondly, to further shed light on the nature of the interactions between the anions and the receptor 1 or 2, ^1H NMR titrations were carried out in DMSO-d_6. To examine the spectroscopic features in detail, two effects [28], which would be expected to result from the deprotonation of one N–H fragment, should be considered: (1) through-bond effects, which increase the electron density of the phenyl ring and promote an upfield shifts, and (2) through-space effects, which polarize C-H bond in proximity to hydrogen bond, create the partial positive charge on the proton and cause a downfield shifts. The series of ^1H NMR spectra of receptor 1 (5×10^{-3} mol l^{-1}) upon addition of increasing amounts of tetrabutylamminiun fluoride (0–50 equiv.) in DMSO-d_6 were shown in Fig. 3. As the concentration of fluoride salt was increased, the signal of amide (H_α) shifted downfield dramatically but the signal of N–H_β of benzimidazole group first shifted downfield, broadened, finally disappeared and a new proton signal appeared at 16 ppm, which could be the signal of the FHF^- complex [29]. All the results observed indicated that there were two steps in the ^1H NMR titration: (1) in the first step, the fluoride ion exhibited a hydrogen-bonding interaction with 1, and (2) in the second step, the deprotonation of N–H_β of benzimidazole group took place. In addition, the results of ^1H NMR titration also further corroborated the above supposition of the interactions between the host and fluoride or acetate ion during fluorescence titrations. The results observed from ^1H NMR titration of the receptor 1 with F^- and ^1H NMR titration of the receptor 2 with F^- or AcO^- were similar with the results above-mentioned (see Electronic supplementary material). As mentioned above, the proposed binding mode in solution was shown in Scheme 2.

Conclusion

In conclusion, two neutral fluorescent anion receptors based upon benzimidazole moieties were designed and synthesized. On account of different basicity of anions, there were two dissimilar recognition mechanisms, which induced fluorescence quenching and fluorescence enhancement, respectively, during fluorescence titration experiments. Such spectral behaviors required two factors for binding sites of the receptors 1 and 2: (1) appropriate acidity of N–H groups; (2) conformationally flexible molecule structure. This finding is expected to provide the basis for a new design strategy for fluorescent anion sensors. The design strategy and unique photophysical properties of the sensors would help to extend the development of fluorescent sensors for biologically important anions. And therefore, the receptors 1 and 2 would act as selective sensors for chloride by virtue of changes of fluorescence spectrum.

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