LETTER

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Conformational switching fluorescent chemosensor for chloride anion†

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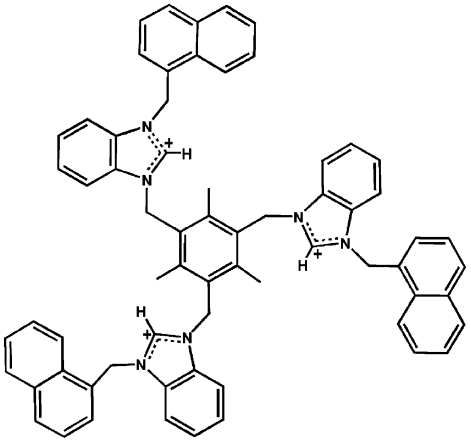
A new fluorescent "off–on" signaling chemical sensor with high selectivity for chloride anion through a guest-induced conformational switching process was achieved by using a positively charged tripodal receptor with naphthyl groups attached to the benzoimidazolium arms.

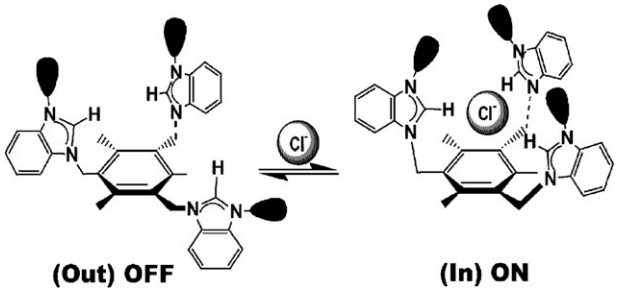
Introduction

Due to the many possible applications in analytical chemistry and biomedical research, considerable attention has been focused on the design of receptors that have the ability to selectively bind and sense anions through an optical response.[1–3] The mechanisms used in the signaling process for anion sensing are generally photo-induced electron transfer (PET),[4,5] metal-to-ligand charge transfer (MLCT),[6] excimer/exiplex and intramolecular charge transfer (ICT)[7,8] *etc*. Much less explored is the concept of the conformational switching process in which the guest-induced binding results in a marked change in host geometry that in turn, influences signal intensity.[8–10] In this paper, we report a new "off–on" signaling chemical sensor **1** for halide anions by incorporating the naphthalene ring into the preorganized benzene-based tripodal receptor with arms comprising benzoimidazolium hydrogen bonding moieties (Scheme 1). The new type of charged hydrogen binding between the halide anion and the benzoimidazolium is very intriguing in comparison with many other types of hydrogen bonding,[11,12] and provides the possibility to moderate the host geometry by placing the binding sites in a suitable location.



Scheme 1

The host falls into the category of the fluorophore–spacer–receptor model and could act as a simple PET sensor. The presence of more than one naphthyl group allows the excited naphthyl unit to associate with the ground state of a second fluorophore to produce an intramolecular excimer through the anion-bonding induced conformational changes (Scheme 2). In the presence of a specific anion conformational template, the hydrogen bonds between the arms and the anion induce the tripodal receptor to display a cone conformation with all three positive charged arms orientated in the same direction (in) and to bring the three naphthalene lumophores into close proximity with one another, leading to excimer fluorescence ("on" state). In the absence of the conformation template anion, the electrostatic interactions between the benzoimidazolium groups destabilize the cone conformation of the podand and lead to the spread out conformation (out), in which the three naphthyl lumophores are separated from each other and no excimer fluorescence will be observed ("off" state).



Scheme 2

Compounds **1** · 3Br was synthesized by reacting 1-(1-naphthylmethyl)-1-benzoimidazole with 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene in $CHCl_3$, and identified by ^{1}H NMR and ESI-MS spectral evidence as well as elemental analyses (see ESI†). Upon addition of chloride anion to the solution of the compound **1** · 3BPh$_4$, a large downfield shift was observed for the hydrogen atoms attached to the electron-deficient C-2 carbon atoms in the benzoimidazolium group of the host, suggesting the existence of CH^+-anion charged hydrogen bonds. ^{1}H NMR titration curves (Fig. 1) with the chloride or bromide anion indicated the formation of a 1 : 1 complex. The additional Job plot analyses gave the association constants as 3.9×10^3 and 2.4×10^2 M^{-1}, with free energies of 4.90 and 3.25 kcal mol^{-1} for chloride and bromide anions, respectively. Addition of I^- to a DMSO-d$_6$ solution of the host **1** · 3BPh$_4$

† Electronic supplementary information (ESI) available: ^{1}H NMR spectra of the host **1** · 3BPh$_4$, the compound **1** · 3Br and **1** · 3BPh$_4$ containing 1.0 equivalents of chloride. See http://www.rsc.org/suppdata/nj/b5/b500252d/

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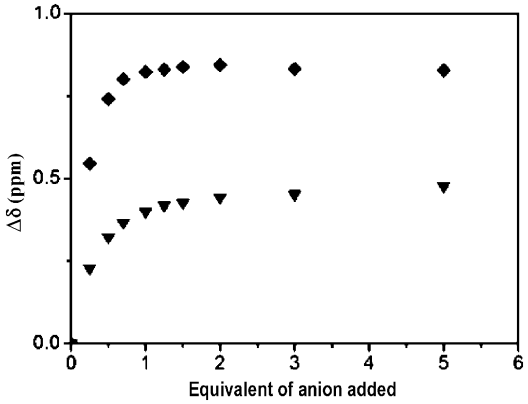

Fig. 1 ^{1}H NMR titration curves of host **1** with chloride (◆) and bromide (▼) anion. $\Delta\delta$ is the chemical shift difference of the C-2 proton of the benzoimidazolium moieties.

did not result in a significant chemical shift of the protons. The marked selectivity sequence ($Cl^- > Br^- > I^-$) was consistent with the size match of the anions for the host conical cavity and negative charge density consideration.[13]

The compound **1** · 3BPh$_4$ exhibited a structureless broad fluorescence band with emission maximum around 340 nm, and very weak excimer fluorescence in the region of 400–700 nm (Fig. 2), indicating that the host adopted the spread out conformation with the three lumophore naphthyl rings away from each other and no excimer emission was triggered (''off'' state). Upon the addition of chloride anion, the fluorescence intensity of the structureless band did not change significantly, but the intensity of the excimer fluorescence was dramatically enhanced. The excimer emission intensity reached a plateau at a molar ratio of host to chloride anion of about 1 : 1 with the association constant calculated as 4.1×10^3 M^{-1}.

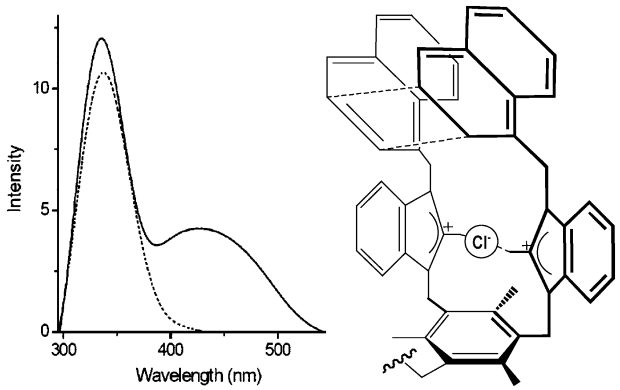

Fig. 2 Emission spectra of **1** · 3BPh$_4$ (1×10^{-4} M) (dotted line) and upon addition 1.0 equiv of chloride anion (solid line) in DMSO excited at 295 nm (left) and the potential $2\pi + 2\pi$ cycloaddition of the naphthyl rings within the anion templated cone conformation (3-up) under the UV–Vis irradiation (right).

Meanwhile, UV spectral changes on the naphthyl rings were not observed, indicative that the three lumophore rings did not interact with each other significantly in the ground state. Furthermore, the fluorescent intensity at 450 nm was observed to increase markedly over time. This result suggested the more fluorescent species is being formed in solution.[10a,14] It was possible that this species resulted from the $2\pi + 2\pi$ cycloaddition of the two naphthyl rings within the anion templated cone conformation (3-up) under the UV–Vis irradiation (Fig. 2). The related $4\pi + 4\pi$ cycloaddition of two anthracene units has been observed in tripodal aminopyridinium derived anion-binding hosts and the fluorescence intensity of the control compounds was also increased.[10a] In the presence of bromide and iodide anions, the excimer fluorescence intensities were only changed weakly, and the response was too small to permit determination of the association constant. Subsequently, the fluorescent response of the host **1** · 3BPh$_4$ was found to show unique selectivity for chloride anion responding in the ''off–on'' manner due to the conformational change. Further investigation on the $2\pi + 2\pi$ cycloaddition and the selectivity for chloride is ongoing.

Anion binding induced conformational switching luminescence sensing has been reported for a tripodal aminopyridinium-based host and exhibited efficient recognition for halide anion;[10a] the emission is reduced at least 30% on the addition of chloride anion and 50% for the iodide anion tripodal aminopyridinium-based host.[10a] A tripodal fluorescence receptor with pyrene or other aromatic units as reporter has also been reported in which anion-induced conformation changes bring about the intramolecular interaction of pyrene rings to show a new band at around 500 nm.[15] The receptor exhibited good selectivity for the phosphate both in the association constant and the emission intensity, however, the presence of other guests also induced significant excimer emission. In the tripodal fluorescence receptor reported here, the very directional $(CH)^+\cdots$anion hydrogen bonding meant that the excimer emission is only observed in the prescence of the chloride anion.

In a summary, a simple modular approach has been described to an tripodal cation displaying a marked anion chelate effect and special fluorescent response in an ''off–on'' manner through anion induced conformational change. The benzene-based tripodal receptor with arms comprising benzoimidazolium hydrogen bonding moieties is promising for the development of a luminescence sensor for chloride anion.

Experimental

General methods

^{1}H NMR spectroscopic measurements were recorded on a Bruker AM-500 NMR spectrometer, using TMS (SiMe$_4$) as an internal reference at room temperature. ^{1}H NMR titration was recorded on a Bruker AM-500 NMR spectrometer using DMSO-d$_6$ solution (8×10^{-3} M). Fluorescence spectra were recorded on an AMINCO Bowman Series 2 Luminescence Spectrometer. The fluorescence titration was recorded on an AMINCO Bowman Series 2 Luminescence Spectrometer in DMSO solution (1×10^{-4} M). UV–Vis spectra were recorded on a UV-3100 spectrometer in DMSO solution (5×10^{-5} M). Electrospray Mass Spectra (ESI-MS) spectral measurements were recorded on a LCQ System (Finngan MAT, USA) with CH_3OH as the mobile phase.

Synthesis

1 · 3Br. 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene (1.0 g, 2.5 mmol) and 1-(1-naphthylmethyl)-1-benzoimidazole (1.94 g, 7.50 mmol) were dissolved in $CHCl_3$ (80 mL) and stirred at reflux for 15 h. During this time, a white precipitate formed. The product was filtered off and washed with $CHCl_3$ to give the desired product as a white powder (1.90 g, 65%). Compound **1** · 3Br, Anal. Calcd. (%) for $C_{66}H_{57}N_6Br_3 \cdot 3H_2O$: C, 64.6; H, 5.2; N, 6.8. Found: C, 64.2; H, 5.1; N, 6.9%. EI-MS: m/z = 507.0 $[\mathbf{1} \cdot Br^-]^{2+}$, 1091.8 $[\mathbf{1} \cdot 2Br^-]^+$. ^{1}H NMR (500 MHz, DMSO-d$_6$, TMS): δ = 10.49 (s, 3H, benzimidazole), 8.38 (d, 3H, ArH), 7.96 (d, 6H, ArH), 7.87 (d, 3H, ArH), 7.79 (t, 3H, ArH), 7.74 (d, 3H, ArH), 7.65 (t, 3H, ArH), 7.52 (t, 3H, ArH), 7.41 (t, 3H, ArH), 7.27 (t, 3H, ArH), 7.02 (d 3H, ArH), 6.26 (s, 6H, CH_2), 5.99(s, 6H, CH_2), 2.47 (s, 9H, CH_3).

1 · 3BPh4. A solution of the mixture of **1** · 3Br (1.0 g, 0.86 mmol) and NaB(C$_6$H$_5$)$_4$ (0.88 g, 2.6 mmol) was stirred at room

temperature for 6 h. The white precipitated formed was was filtered, washed with methanol and diethyl ether, and dried *in vacuo*. Yield 1.5 g, 93%. Anal. Calcd. (%) for $C_{138}H_{117}N_6B_3$: C, 87.6; H, 6.2; N, 4.4. Found: C, 87.3; H, 6.1; N 4.5%. EI-MS: $m/z = 311.1$, $\mathbf{1}^{3+}$, 626.1 $[\mathbf{1} \cdot B(C_6H_5)_4^-]^{2+}$. ^{1}H NMR (500 MHz, DMSO-d_6, TMS): $\delta =$ 10.05 (s, 3H, benzimidazole), 8.27 (d, 3H, ArH), 7.97 (q, 6H, ArH), 7.89 (d, 3H, ArH), 7.78 (q, 6H, ArH), 7.65 (t, 3H, ArH), 7.57 (t, 3H, ArH), 7.48 (t, 3H, ArH), 7.30 (t, 3H, ArH), 7.18 (s, 24H, ArH), 7.08 (d, 3H, ArH), 6.92 (t, 24H, ArH), 6.79 (d, 12H, ArH), 6.20 (s, 6H, CH_2), 5.95 (s, 6H, CH_2), 2.45 (s, 9H, CH_3).

Acknowledgements

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