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A ratiometric fluorescent probe for fluoride ion based on naphthoimidazolium receptor†

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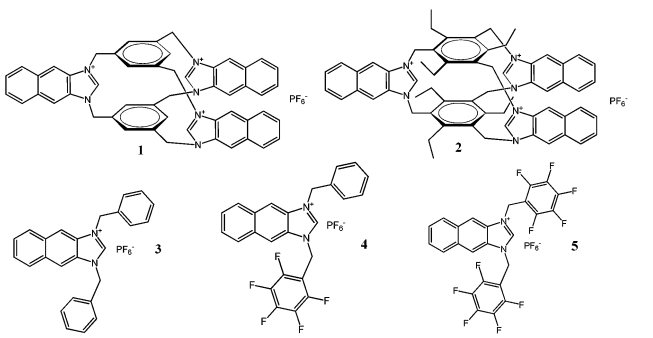
Three imidazolium derivatives **3–5** were designed and synthesized, in which naphthaimidazolium group acted as both fluorophore and anion receptor. Compound **3** exhibited high selectivity for F^- in CH_3CN solution over all the other anions and acted as a ratiometric fluorescent probe for F^- with an enhanced blue-shift in emission. However, the fluorescence of compound **4** and **5** displayed a quenched blue-shift in emission with fluoride ion and could be quenched by some other tested anions, where the degree of quenching depended on the characteristic of the anions. More importantly, only compound **3** could detect F^- in DMSO–water (95 : 5, v/v) aqueous solution ratiometrically. Based on the analysis of the results of ^{1}H-NMR and ^{19}F-NMR, it was deduced that compound **3** bound with F^- mainly by the force of hydrogen bonding, while compound **4** and **5** coordinated with F^- through electrostatic interaction.

Introduction

Fluorine is an essential trace element which is often added to toothpaste and drinking water because of its pivotal role in the prevention of dental problems and treatment of osteoporosis. However, excessive fluoride causes skeletal fluorosis and osteosarcoma.[1] Therefore, development of detection methods for fluoride ion has received great attention. Many fluorescent probes toward fluoride ion sensing have been reported in recent years. Fluoride ion is the smallest radius unary anion with high electron-negativity. According to this feature, a lot of F^- receptors have been designed based on different recognition mechanism, including hydrogen bonding,[2–4] deprotonation,[5–7] electrostatic interaction,[2,8] specific reaction with fluoride ion,[9–12] special structure such as ring and cage,[13–15] and anion–π interactions.[16–19] Many receptors have been reported combining with multiple function units.[7–9] Imidazolium is a useful functional group in F^- detecting because it is able to form a special C–H···X hydrogen bonding through the 2-positon H atom. This type of hydrogen bonding can be functioned as the $(C–H)^+\cdots X^-$ type because the charge–charge electrostatic interaction dominates.[20,21] Although many imidazolium salts for F^- detecting have been reported so far, a lot of them are lack of effective signal output, which is detected by NMR or electrochemistry methods.[13,15] In addition, a number of fluorescent probes have been designed with fluorescence quenching signals,[2,4,8] which is not propitious to quantitative detection.

In the previous work,[11,19,21] naphthaimidazolium group was utilized as the signal source for the detection system, and also as an anion binding receptor. As shown in Scheme 1, the cage compounds **1** and **2** contained three naphthaimidazolium groups inserted between two substituted benzene rings.[21] With the addition of 1 equiv. of F^-, a strongly increased fluorescent emission of compound **2** centered at 385 nm appeared at the expense of 474 nm. However, the addition of fluoride quenched the fluorescence of compound **1**. ^{19}F and ^{1}H NMR spectroscopy, fluorescence emission and theoretical calculations results showed that three $(C–H)^+\cdots F^-$-type ionic hydrogen bonds formed and from this, the anion–π interaction between the two electron-rich alkylbenzene rings and the fluoride ion existed in compound **2**. For compound **1**, the electrostatic interaction between the imidazolium and fluoride anion dominated in the recognition process.[21]



Scheme 1 Structures of compounds **1–5**.

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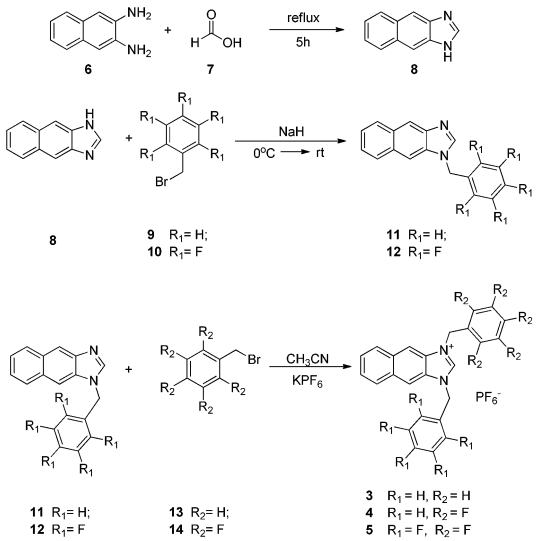


Scheme 2 Synthesis of compounds **3–5**.

In this study, a two benzyl naphthaimidazolium salts (compound **3**), an approximate "half open structure" of compound **1**, was designed and synthesized to further study the mechanism. By the change of the substitutions in the 1,3-position of imidazole, another two reference compounds **4** and **5**, with one or two electropositive pentafluoro-substituted benzyl groups, were synthesized. (Scheme 2).

Experimental

All chemicals were analytical pure and used without further purification. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AV-400 spectrometer (TMS as an internal standard). Mass spectrometry data were obtained with a HP1100LC/MSD and MALDI micro MX mass spectrometer. Fluorescence measurements were carried out on a JASCO FP-6500 fluorescence spectrophotometer. Absorption spectra were collected on a Hewlett-Packard HP-8453 UV-Vis spectrophotometer.

Synthesis of compound 8

Under N_2 gas, 2,3-diaminonaphthalene (1.0 g, 6.3 mmol) was dissolved in 10 mL formic acid. The solution was heated to reflux and kept for 5 h. After cooling to room temperature, the mixture was concentrated to remove formic acid. The residue was treated with 30 mL boiling water to dissolve, refluxed for 0.5 h with some activated charcoal, and then filtered while hot and added stronger ammonia water to the filtrate dropwise until the product precipitated completely. The grey white precipitate was collected by filtration and then dried in a vacuum oven to give **8** (0.75 g, yield: 71%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.20 (s, 1H), 8.09 (s, 2H), 7.95 (d, $J = 3.0$ Hz, 2H), 7.41 (d, $J = 3.1$ Hz, 2H), 3.10 (s, 1H). MS (ES API$^+$): m/z $[C_{11}H_8N_2 + H]^+$ calcd 169.19, found: 169.1.

Synthesis of compound 11

Under N_2 gas, **8** (0.22 g, 1.3 mmol) was dissolved in 15 mL THF and NaH (petroleum ether 60%, 0.065 g, 1.6 mmol) was added under ice bath. The mixture was stirred for 0.5 h, and benzyl bromide (0.18 mL, 1.5 mmol) in THF (5 mL) was added dropwise. Then the mixture was kept for 2 h under ambient temperature, and water (25 mL) was added to finish the reaction. Multiple extraction with CH_2Cl_2 combined with drying by $MgSO_4$. The filtrate was concentrated and purified by flash column chromatography (CH_2Cl_2–CH_3OH, 100 : 1, $R_f = 0.5$) to obtain the compound **11** (0.26 g, yield: 75%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 8.32 (s, 1H), 8.12 (s, 1H), 8.01 (d, $J = 5.9$ Hz, 1H), 7.87 (d, $J = 5.9$ Hz, 1H), 7.68 (s, 1H), 7.40 (d, $J = 5.0$ Hz, 2H), 7.34 (d, $J = 7.8$ Hz, 3H), 7.23 (d, $J = 6.4$ Hz, 2H), 5.43 (s, 2H), 1.55–1.53 (m, 1H). MS (ES API$^+$) m/z $[C_{18}H_{14}N_2 + H]^+$ calcd 259.3, found: 259.2.

Synthesis of compound 12

Starting from compound **8** (0.20 g, 1.2 mmol) and penta-fluorobenzyl bromide (0.21 mL, 1.4 mmol), compound **12** was prepared according to the same procedure of compound **11** and was purified by flash column chromatography (CH_2Cl_2–CH_3OH, 100 : 1, $R_f = 0.4$) (0.28 g, yield: 68%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 8.32 (s, 1H), 8.12 (s, 1H), 8.01 (d, $J = 5.9$ Hz, 1H), 7.87 (d, $J = 5.9$ Hz, 1H), 7.68 (s, 1H), 7.40 (d, $J = 5.0$ Hz, 2H), 7.34 (d, $J = 7.8$ Hz, 3H), 7.27–7.17 (m, 2H), 5.43 (s, 2H), 1.31 (t, $J = 231.6$ Hz, 1H). MS (ES API$^+$) m/z $[C_{18}H_9N_2 + H]^+$ calcd 349.3, found: 349.1.

Synthesis of compound 3

Under N_2 gas, benzyl bromide (55 μL, 0.47 mmol) was added to the solution of compound **11** (0.10 g, 0.39 mmol) in 15 mL dioxane, which was heated to reflux and kept for 24 h. After cooling to room temperature, the yellowish precipitate was collected by filtration and then washed with some cold CH_2Cl_2 to give the bromated. Then it was dissolved in DMF, and dropped saturated KPF_6 aqueous solution to precipitate the product **3**, which was purified by flash column chromatography (CH_2Cl_2–CH_3OH, 20 : 1, $R_f = 0.4$) to give light gray white powder (0.11 g, yield: 60%). **3**: ^{1}H NMR (400 MHz, CD_3CN, δ ppm) 9.19 (s, 1H), 8.31 (s, 2H), 8.10 (dd, $J = 6.4$, 3.3 Hz, 2H), 7.64 (dd, $J = 6.5$, 3.2 Hz, 2H), 7.52 (dd, $J = 7.8$, 1.5 Hz, 4H), 7.46 (m, $J = 7.2$ Hz, 6H), 5.70 (s, 4H). ^{13}C NMR (100 MHz, CD_3CN, δ ppm) 147.24, 134.37, 131.38, 130.64, 129.50, 129.22, 128.83, 128.71, 127.26, 111.90, 50.61. HRMS (TOF LD$^+$) m/z $[C_{25}H_{21}N_2^+]$ calcd 349.1699, found: 349.1728.

Synthesis of compound 4 and 5

Starting from compound **12** (0.20 g, 0.57 mmol), compound **4** (0.21 g, yield: 64%) and **5** (0.20 g, yield: 59%) were obtained according to the synthetic procedure of **3**.

Compound 4. ^{1}H NMR (400 MHz, CD_3CN, δ ppm) 9.30 (s, 1H), 8.36 (s, 1H), 8.32 (s, 1H), 8.22–8.17 (m, 1H), 8.13–8.08 (m, 1H), 7.71–7.64 (m, 2H), 7.52 (dd, $J = 7.7$, 1.6 Hz, 2H), 7.47 (dd, $J = 10.4$, 5.1 Hz, 3H), 5.83 (s, 2H), 5.72 (s, 2H). ^{13}C NMR (100 MHz, CD_3CN, δ ppm) 146.57, 133.56, 132.65, 132.54, 131.08, 30.26,

129.47, 129.37, 129.18, 128.36, 128.32, 118.27, 112.71, 111.81, 111.79, 111.77, 52.13, 39.59. HRMS (TOF LD$^+$) m/z [$C_{25}H_{16}F_{11}N_2^+$] calcd 439.1228, found: 439.1198.

Compound 5. ^{1}H NMR (400 MHz, CD_3CN, δ ppm) 9.40 (s, 1H), 8.35 (s, 2H), 8.21 (dd, J = 5.9, 2.9 Hz, 2H), 7.70 (dd, J = 6.3, 2.8 Hz, 2H), 5.85 (s, 4H). ^{13}C NMR (100 MHz, CD_3CN, δ ppm) 148.13, 147.08, 145.69, 137.67, 132.64, 130.68, 129.39, 128.50, 112.01, 107.79, 39.83. HRMS (TOF LD$^+$) m/z [$C_{25}H_{21}N_2^+$] calcd 529.0757, found: 529.0752.

Results and discussion

The selectivity of **3–5** for fluoride ion detection was first investigated through UV-Vis spectra by adding various anions (F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$ and HSO_4^- as n-Bu_4N^+ salts; NO_3^- as sodium salt) to the solution of compound **3–5** in CH_3CN (Fig. S1†). The free compounds **3–5** displayed a similar absorption band peaked at 325 nm due to the absorption of naphthalene part. Upon addition of 5 equiv. of F^-, the absorption peak of compound **3–5** approximately shifted to 347 nm (Fig. 1 and S1†), which indicated the strong interactions between compound **3–5** and F^- in stationary state. With addition of 5 equiv. of other anions (Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, NO_3^-, and HSO_4^-), the UV-Vis spectra of compound **3** exhibited little change, whereas the absorption spectra of compound **4** and **5** showed different levels of redshift on the addition of 5 equiv. of AcO^- and $H_2PO_4^-$.

The UV-Vis titration experiments were performed in CH_3CN solution to investigate the behaviour of compound **3–5** upon progressive addition of F^-, as shown in Fig. 1. When F^- (0–40 equiv.) was progressively added to a solution of **3**, a decrease of 325 nm was observed with the appearance of a red-shifted and increased absorption centered at 347 nm.

It suggested the hydrogen bond formed between compound **3** and F^- reduced the transfer energy of excited stated charge to redshift the absorption spectra. As for compound **5**, the first 4 equiv. F^- induced the similar UV-Vis response compared to compound **3**, but more F^- addition (4–40 equiv.) decreased the intensity at 347 nm while a new absorption at 360 nm appeared (Fig. S2†). Compound **4** displayed the same responses as compound **5** when F^- was added gradually. It showed that compound **4** and **5** may experience two steps of complexation with F^-.

The fluorescence emission spectroscopy and titration experiments were displayed in Fig. S3† and 2, respectively. The emission spectrum of free **3** displays a broad band with a maximum at 438 nm when it was excited at 331 nm. When F^- was added progressively to a solution of **3**, a significant increasing fluorescent emission in the 373 nm was observed at the expense of the fluorescent emission centered at 438 nm, which behaved differently from compound **1**. A clear iso-emission point appeared at 407 nm, and no obvious changes were observed with the addition of other anions. Hence, **3** is a ratiometric fluorescent probe for F^-, and the dependence of the ratio of the emission intensities at 373 and 438 nm (I_{373}/I_{438}) on the concentration of F^- was shown in the inset of Fig. 2(a). Naphthoimidazolium is a donor–acceptor system and can

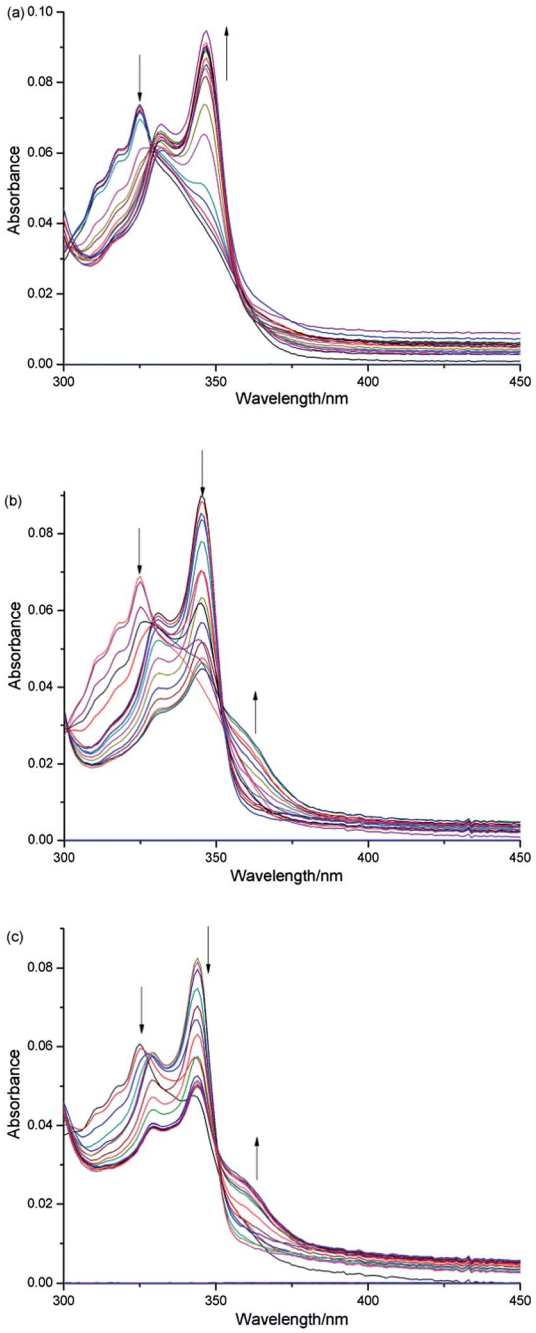


Fig. 1 Changes in UV-Vis spectra of compound **3–5** (10 μM) upon the addition of 0–40 equiv. of F^- in CH_3CN. (a) Compound **3**, (b) compound **4** and (c) compound **5**.

undergo internal charge transfer (ICT) from naphthalene to imidazolium upon excitation by light, with imidazolium acting as an acceptor. When F^- bonds with imidazolium, the electron-withdrawing ability of imidazolium would be weakened and an anion-induced blueshift in emission would occur.[19]

As for compound **4** and **5**, a strong fluorescence quenching were observed with the addition of F^-, and the fluorescence decreased to the minimum with about 4 equiv. Adding more F^- induced a low fluorescence recovery peaked at 396 nm, which was in accordance with the UV-Vis titration results of

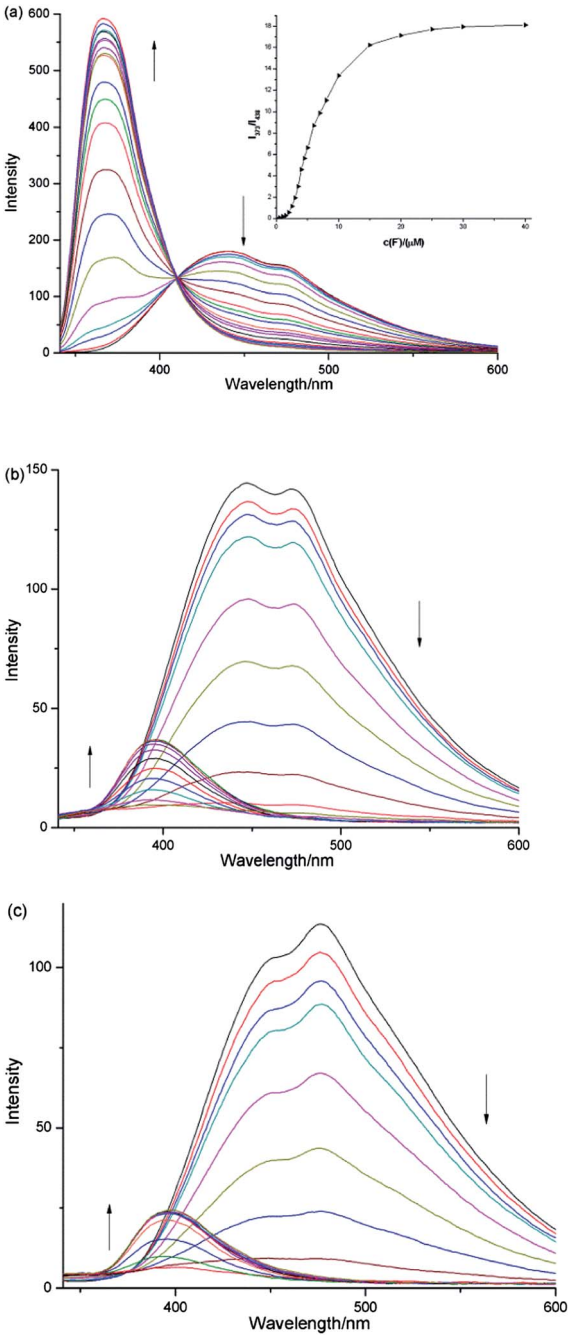


Fig. 2 Fluorescence titration spectra of **3–5** (a–c) in the presence of different amounts of F^- (0–40 equiv.) in CH_3CN. [**3**] = [**4**] = [**5**] = 10 μM, λ_{ex} = 331 nm. Inset: ratiometric calibration curve I_{373}/I_{438} of compound **3** as a function of the F^- concentration.

compound **4** and **5**. Adding of AcO^- and $H_2PO_4^-$ caused little emission changes between **4** and **5**, and negligible changes occurred before and after adding of other anions. The fluorescence responses of compounds **4** and **5** were quenched by F^- while compound **3** behaved as a selective fluorescence increased probe for F^-. Based on the former work,[11,18] we preliminarily concluded that most amount of F^- approached compounds **4** and **5** from the direction close to the naphthoimidazolium part under the force of static electricity for the steric hindrance of the pentafluoro benzyl group, which induced a PET effect from F^- to naphthalene to quench the fluorescence, and then small fluorescence recovered until a comparable stable hydrogen bond formed after more than 4 equiv. F^- addition. While **3** was attacked by F^- from the direction of imidazolium–C_2–H more easily for the less hindrance, which would not quench the fluorescence.

To understand the interaction of compound **3–5** with F^-, ^1H NMR and ^{19}F NMR tests were carried out in CD_3CN and the results are shown in Fig. 3, 4 and S4.† As shown in Fig. 3(a), when 1 equiv. of F^- was added to the solution of **3**, the peak of imidazole–C_2–H shifted downfield (δ = 9.19 to 9.50 ppm), which indicates a hydrogen bond was formed between the proton and F^-. Upon the addition of $F^- \geq 2$ equiv., the signal of imidazole–C_2–H of compound **3** disappeared, which might be due to the partial deprotonation of imidazole–C–H and/or the formation of imidazole–C_2–F complex.[19] The aromatic hydrogen almost shifted highfield due to the electrostatic interaction between compound and anion. In the corresponding ^{19}F NMR of compound **3** as shown in Fig. 3(b), the resonance of PF_6^- appeared as a doublet at δ = 72 and 74 ppm. The sharp singlet at δ = 152 ppm may result from C_2–H–F^-, and the signal increased

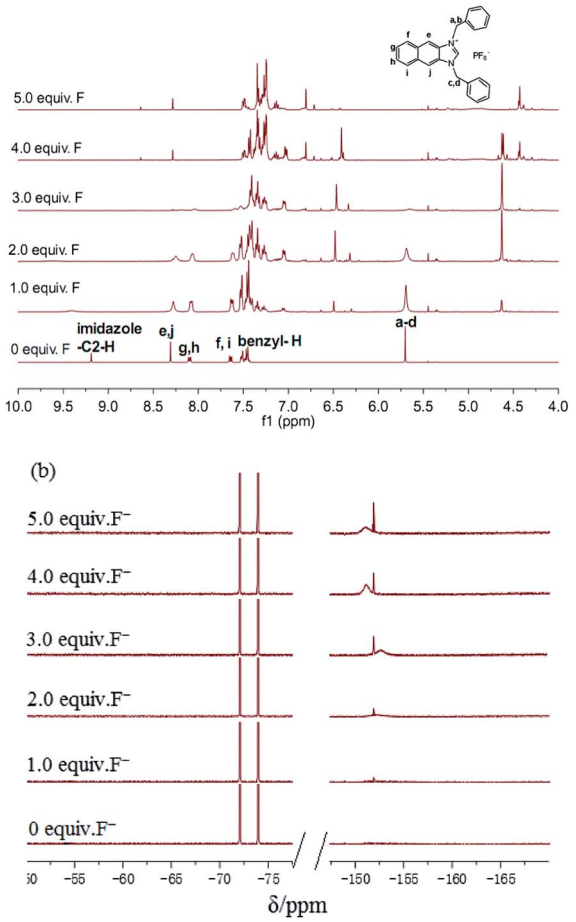


Fig. 3 ^1H NMR (a) and ^{19}F NMR (b) spectra of **3** with fluoride in CD_3CN at room temperature. [**3**] = 2×10^{-2} mol L^{-1}.

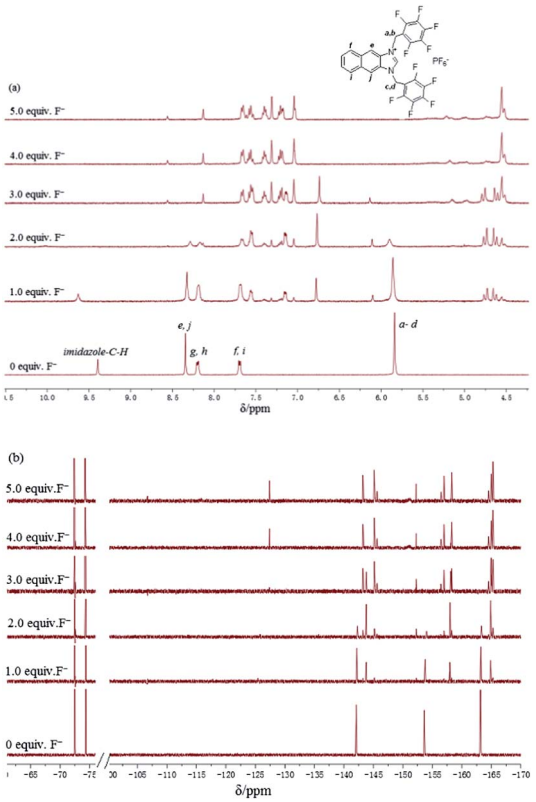


Fig. 4 ^{1}H NMR (a) and ^{19}F NMR (b) spectra of **5** with fluoride in CD_3CN at room temperature. [**5**] = 1×10^{-2} mol L^{-1}.

with the amount of F^-. As for compound **4** and **5**, although different responses observed in UV-Vis and fluorescence emission, the ^{1}H NMR and ^{19}F NMR results displayed the similar trends as compound **3**: the signal of imidazole–C_2–H disappeared with the progressive addition of F^-, meanwhile the aromatic hydrogen shifted highfield and the sharp singlet at δ = 152 ppm in ^{19}F NMR increased with the amount of F^-. These results indicated that interaction of hydrogen bond and electrostatic force also existed in compound **4** and **5**. The sharp singlet appeared at near δ 125 ppm corresponds to the free F^- which appeared in the ^{19}F NMR results of compound **4** and **5**. Besides, a board singlet at about 150 ppm was almost due to the formation of C_2–F bond,[19,22] and the MALDI-TOF mass spectra (Fig. 5, S5 and S6†) were examined to prove the mechanism. For

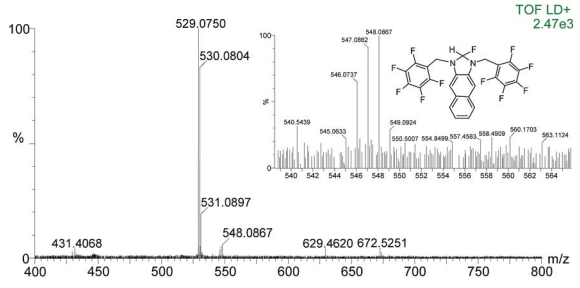
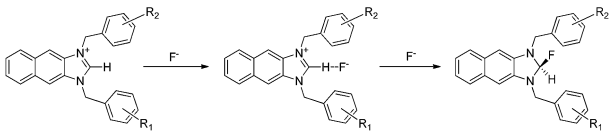


Fig. 5 MALDI-TOF (LD^+) spectrum of compound **5** with 5 equiv. F^- addition.



Scheme 3 Proposed recognition process that occurred when excess F^- was added to compounds **3–5**.

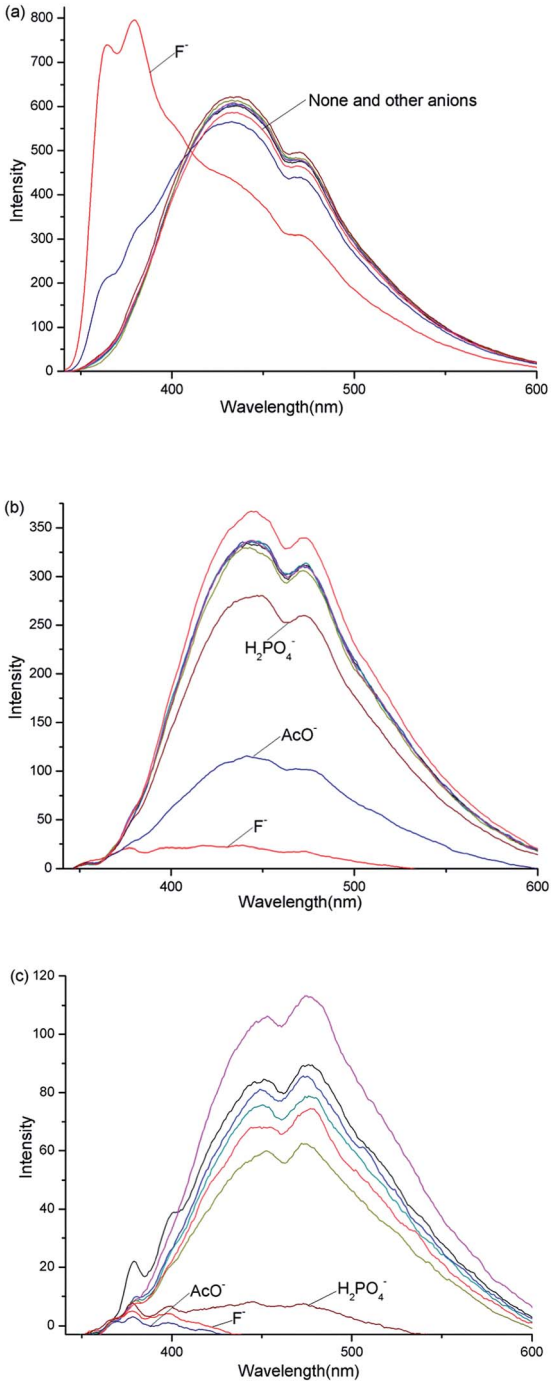


Fig. 6 Fluorescence responses of **3** (a), **4** (b) and **5** (c) to various anions (50 μM) in DMSO–water (95 : 5, v/v). [**3**] = [**4**] = [**5**] = 10 μM, λ_{ex} = 331 nm.

example, the peak at m/z 529.07 was assigned to M^+ of compound **5**, and the peak at m/z 548 was fluorine adduct of **5** as shown in the inset of Fig. 5. Similar results were observed for compound **3** and **4** (see Fig. S5 and S6†). In addition, the aromatic fluorine of compound **4** and **5** shifted highfield which may result from the interaction between F^- and the pentafluoro-benzyl groups, such as anion–π interaction for the positive quadrupole moment in the pentafluoro-substituted benzyl groups.

Based on the above discussion, we know that compound **3–5** bound with F^- by hydrogen bond and electrostatic force, and excess F^- induced deprotonation and addition (Scheme 3).

In addition, the F^- binding ability of compound **3–5** in aqueous solution was examined by the fluorescence responses in the presence of F^- in DMSO–water (95 : 5, v/v). Fig. 6 shows the fluorescence emission of compound **3–5** with 5 equiv. of various anions. It should be noticed that compound **3** behaved similarly in DMSO–water (95 : 5, v/v) as in CH_3CN, while only quenched fluorescence responses of **4** and **5** were observed. These results indicated that compound **3** showed the potential application of detecting F^- in aqueous solution.

Conclusion

In summary, we have designed and synthesized three naphthaimidazolium derived compound **3–5** based on the previous work which interacted with F^- by hydrogen bonding and electrostatic force. Combined with the results of UV-Vis spectra, fluorescence emission spectra, ^1H and ^{19}F NMR titration experiments, it was deduced that compound **3–5** reacted with F^- mostly by the force of hydrogen bond and the electrostatic force, but gave different fluorescence responses by the different attacking modes due to various steric hindrance. In particular, compound **3** coordinated with F^- resulted in a blue-shifted increase of fluorescence intensity. Most importantly, compound **3** behaved similarly in DMSO–water (95 : 5, v/v) as in CH_3CN, which indicated the potential application of detecting F^- in aqueous solution.

Acknowledgements

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