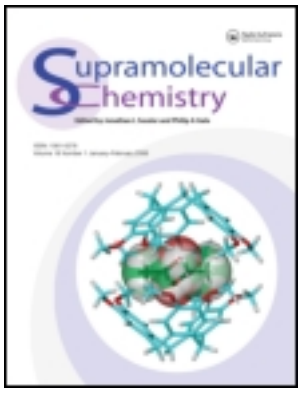

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Anion recognition by 2,2′-binaphthalene bearing imidazolium groups in MeCN

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A novel anion receptor **1b** based on 2,2′-binaphthalene bearing two imidazolium groups was prepared. UV–vis spectra of **1b** showed a marked hypochromic shift at 310 nm upon the addition of anions because of the restriction of the rotation around the single bond connecting two naphthyl moieties by cooperative anion binding with two imidazolium moieties. The order of the spectral changes and the association constants was $AcO^- > (EtO)_2PO_2^- \approx Cl^- > Br^-$. However, fluorescence changes upon the addition of these anions showed characteristics depending on the anions added. ^{1}H NMR titration revealed that hydrogen bonds were formed by six C—H groups to recognise the anions.

Keywords: 2,2′-binaphthalene; imidazolium; anion recognition; fluorescence spectroscopy; UV–vis spectroscopy

Introduction

Anion recognition is an emerging area in host–guest chemistry because of its wide range of applications in medicinal and environmental chemistry (*1*). Therefore, considerable attention has been devoted in the last two decades to the design and preparation of artificial receptors for anionic species. Recently, polarised C—H groups such as cationic imidazoliums (*2*, *3*), pyridiniums (*4*) and neutral triazoles (*5*) have been used as anion recognition sites. In particular, 1,3-disubstituted imidazolium groups are useful as anion binding sites by forming a $(C—H)^+\cdots X^-$ hydrogen bond with a concomitant electrostatic interaction between C(2)—H of the imidazolium ring and the target anion. From the pioneering works by Alcalde (*6*) and Sato's groups (*7*), imidazolium-based receptors have been widely accepted as anion recognition sites. Various artificial receptors bearing imidazolium moieties have been evaluated. Fluorescent and UV–vis spectroscopic detections of analytes are of low cost and are effective methods (*8*). Therefore, fluororeceptors (*9*) and chromoreceptors (*10*) bearing imidazolium groups have been widely developed. Nevertheless, few receptors show both fluorescent and UV–vis spectral changes by interaction with anions. Beer and co-workers reported UV–vis and fluorescence sensing of anions by the zinc metalloporphyrin receptor bearing both four amides and four imidazolium groups. However, the role of the imidazolium moieties remains unclear because of the variety of recognition sites including the amides and the Lewis acidic zinc centre (*11*). Yu et al. reported UV–vis and fluorescent changes by imidazolium-functionalised BINOL upon addition of AcO^- and F^- (*12*). Mashraqui et al. (*13*) reported that the naphthalimide-based receptor directly connecting an imidazolium group shows UV–vis and fluorescence sensing for targeting the fluoride anion. More recently, You and Lan's group reported that 1,1′-binaphthyl-based imidazolium receptors were evaluated for selective and chiral recognition of tryptophan (*14*). A more elaborated receptor bearing imidazolium moieties showing large UV–vis and fluorescence changes upon the addition of appropriate anions is needed.

Recently, we designed 2,2′-binaphthalene-based receptors bearing recognition sites at 8- and 8′-positions for anionic (*15*) and cationic species (*16*). The receptors show not only fluorescence changes but also UV–vis spectral changes upon the addition of appropriate guest species. In the absence of any guest molecule, two naphthyl moieties freely rotate. Furthermore, two energetically stable conformers, *transoid* and *cisoid*, come to equilibrium as depicted in Scheme 1. During the recognition process, cooperative interactions of the two recognition sites with one guest molecule provide restriction of the rotation of the single bond connecting two naphthyl moieties. This conformational restriction induces a characteristic diminishment of UV–vis absorbance at 310 nm by a predominant formation of the *cisoid* conformer. Moreover, the 2,2′-binaphthyl moiety shows strong fluorescence properties as observed for the anthracene moiety. Therefore, a fluorescence detection of guest species is expected. In the present work, we designed and synthesised receptor **1** based on 2,2′-binaphathalene bearing imidazolium groups as a novel receptor that can use both a fluororeceptor and chromoreceptor for anions.

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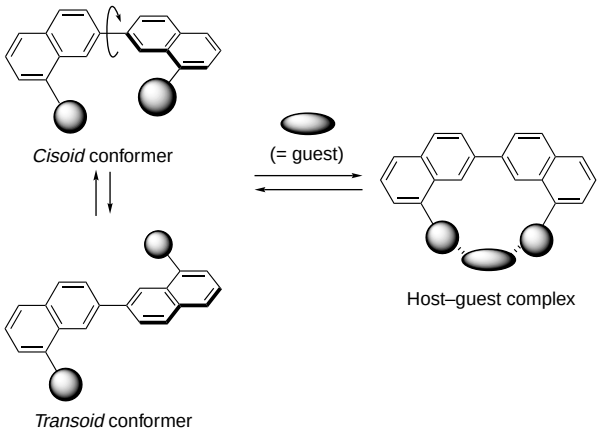


Scheme 1. 2,2′-Binaphthalene-based receptor.

Results and discussion

Synthesis

A useful intermediate, 8,8′-dibromomethyl-2,2′-binapthalene (**2**), was prepared from chlorobenzene in seven steps, as reported previously (*16*). Scheme 2 shows that **2** was allowed to react with 1-butylimidazole in reflux in acetonitrile to give bisimidazolium salt **1a**. Anion exchange of **1a** with PF_6^- gave receptor **1b** in good yield, as pale yellow solids and the structure of **1b** was fully characterised by NMR, electrospray ionisation mass spectroscopy (ESI-MS) and FAB-HR-MS.

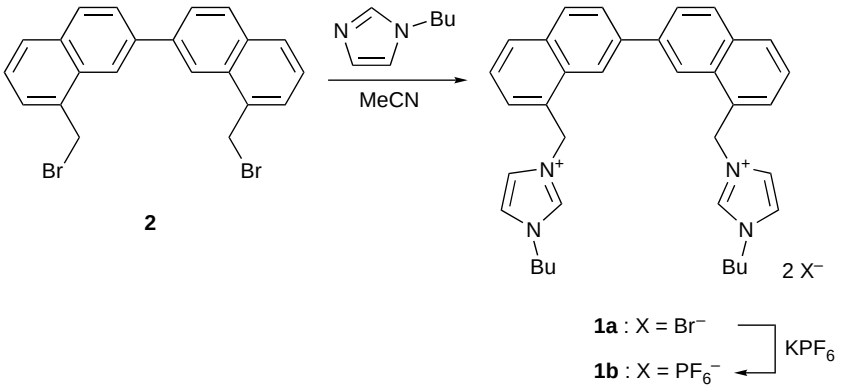
ESI-MS study

ESI-MS provides useful information about a host–guest complex and supramolecular chemistry in solution (*17*). ESI-MS of **1b** and the presence of anions were recorded in MeCN and the result is presented in Figure 1. In all cases, strong peaks corresponding to $[\mathbf{1b}\text{-}2(PF_6) - H]^+$ and $[\mathbf{1b}\text{-}(PF_6)]^+$ were observed. In the presence of AcO^- and $(EtO)_2PO_2^-$, the corresponding **1b** anion complexes cannot be observed, perhaps because of the strong basicity of these anions to form $[\mathbf{1b}\text{-}2(PF_6) - H]^+$ in the gas phase. However, clear peaks corresponding to the anion complex are in good agreement of isotope patterns in the presence of less basic anions, Cl^- and Br^-. It is noteworthy that no peak of **1b** was observed in the negative ion mode of ESI-MS in the absence and the presence of anions because of the divalent positive charge of the receptor **1b**. The results indicate clearly that the stable **1b** anion complexes can be formed in both the solution and gas phases.

UV–vis titrations

Binding studies were performed using UV–vis, fluorescence and NMR titration methods with anions (as their tetrabutylammonium salts to minimise the effect of cation). Figure 2 shows that the absorption band at 312 nm of **1b**, which is assigned to the $\pi-\pi^*$ transition of the 2,2′-binaphthyl moiety, was diminished and showed a small bathochromic shift upon the addition of AcO^- through isosbestic points at 332 and 290 nm in MeCN, indicating the existence of two states of 1:1 complex. By the addition of other anions such as $(EtO)_2PO_2^-$, Cl^- and Br^-, similar but lower spectral changes were observed. The spectral changes at 307 nm upon the addition of various anions were depicted in Figure 3 and the order of the spectral changes is $AcO^- > (EtO)_2PO_2^- \approx Cl^- > Br^-$. The titration curves clearly suggest a 1:1 stoichiometry, and the association constants of **1b** for anions were calculated using non-linear curve fitting of the spectral titrations. They are presented in Table 1.

Decreased absorption at around 310 nm of 2,2′-binaphthalene is assigned to be a shift from *cisoid–transoid* equilibrium towards a *cisoid*-preferred equilibrium by the restriction of the free rotation around the single bond between two naphthyl moieties to form a



Scheme 2. Synthesis of **1**.

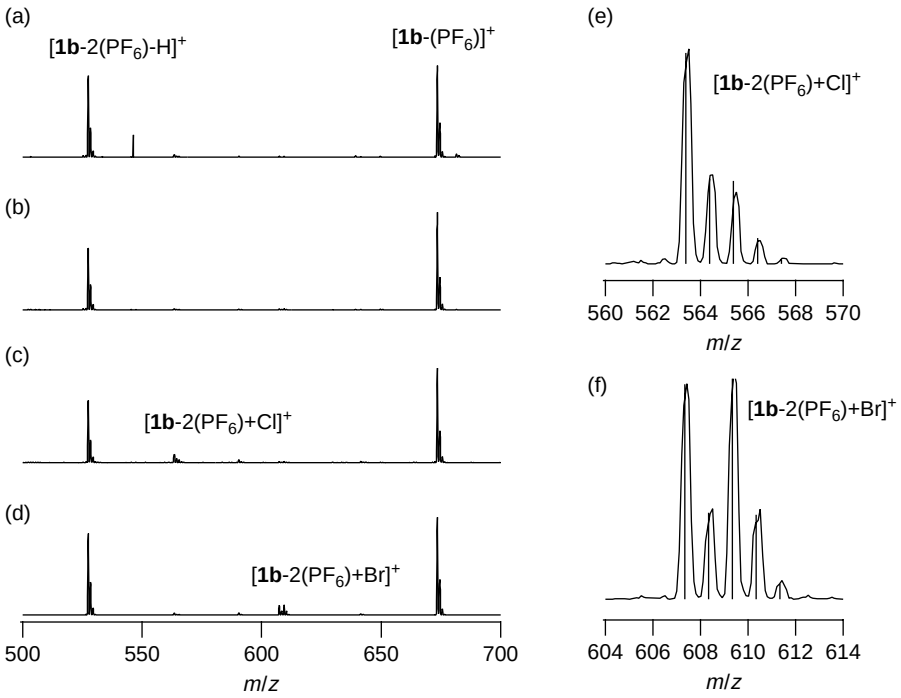


Figure 1. Positive ion mode of ESI-MS of **1b** in the presence of 1 equiv. of AcO^- (a), $(EtO)_2PO_2^-$ (b), Cl^- (c) and Br^- (d). Observed and calculated (bars) isotope patterns of $[\mathbf{1b}\text{-}2(PF_6) + Cl]^+$ and $[\mathbf{1b}\text{-}2(PF_6) + Br]^+$ are shown in (e) and (f), respectively.

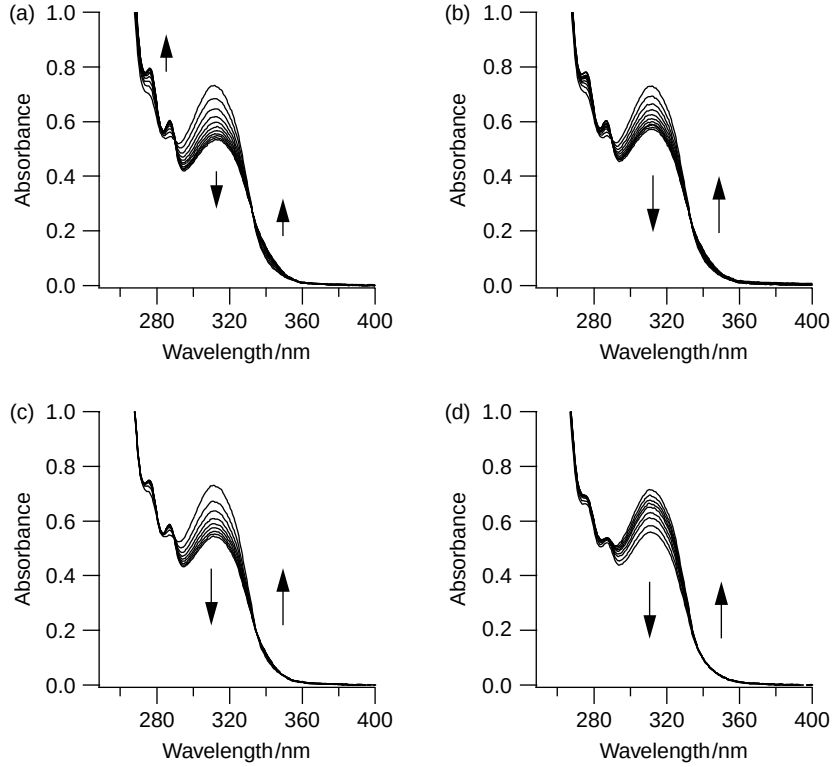


Figure 2. UV–vis spectral changes of **1b** upon the addition of AcO^- (a), $(EtO)_2PO_2^-$ (b), Cl^- (c) and Br^- (d) in MeCN at 298 K. $[\mathbf{1b}] = 3.33 \times 10^{-5}$ mol dm^{-3}.

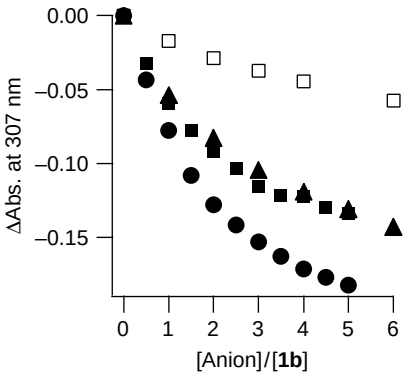


Figure 3. The plot of change in the absorbance at 307 nm of **1b** upon the addition of AcO^- (●), $(EtO)_2PO_2^-$ (■), Cl^- (▲) and Br^- (□) in MeCN at 298 K. [**1b**] = 3.33×10^{-5} mol dm^{-3}.

Table 1. The association constants of **1b** in MeCN.

	K_{11} (mol^{-1} dm^3)	
Anion	UV–vis[a]	Fluorescence[b]
AcO^-	$2.25 \pm 0.01 \times 10^4$	$2.42 \pm 0.18 \times 10^4$
$H_2PO_4^-$	ND[c]	ND[c]
$(EtO)_2PO_2^-$	$1.78 \pm 0.08 \times 10^4$	$5.83 \pm 0.84 \times 10^3$
Cl^-	$1.26 \pm 0.22 \times 10^4$	$1.53 \pm 0.05 \times 10^4$
Br^-	$3.36 \pm 0.01 \times 10^3$	$3.10 \pm 0.01 \times 10^3$

[a] Determined at 298 K. [**1b**] = 3.33×10^{-5} mol dm^{-3}.
[b] Determined at 293 K. [**1b**] = 2.00×10^{-5} mol dm^{-3}.
[c] Precipitates were formed during the titration experiments.

host–guest complex by cooperative binding of two recognition sites at 8- and 8′-positions, as previously reported (*15*, *16*).

Recently, Yoon and co-workers reported that bisimidazolium receptors showed high $H_2PO_4^-$ selectivity over other anions (*9k*). However, results showed that precipitations were formed by the addition of $H_2PO_4^-$ into a solution of **1b** in MeCN. Therefore, the interaction between receptor **1b** and $H_2PO_4^-$ was confirmed, but the association constant could not be evaluated. The association constants of dimethylimidazolium-based receptors for Cl^- and Br^- were reported to be 78 and 59 mol^{-1} dm^3 in MeCN-d_3, respectively (*7*). Comparison between the values and our results ($K_{11} = 1.26 \pm 0.22 \times 10^4$ and $3.36 \pm 0.01 \times 10^3$ mol^{-1} dm^3 for Cl^- and Br^-, respectively) strongly suggests that the two imidazolium groups of **1b** cooperatively associate a target anion in MeCN.

Fluorescence studies

A well-resolved fluorescence spectrum ($\lambda_{em} = 362$ and 380 nm) of **1b** is visible in MeCN excited at 290 nm, which is an isosbestic point during titration of **1b** with AcO^- in MeCN, as portrayed in Figure 4. The fluorescence intensity of **1b** gradually decreased after addition of AcO^- in MeCN with no spectral shift that could be attributed to the photoinduced electron transfer mechanism (*9h*, *9k*). It is particularly interesting that addition of other anions showed that characteristic changes of the fluorescence depend on the anions. When $(EtO)_2PO_2^-$ was added to a solution of **1b**, the fluorescence was gradually enhanced. The addition of Cl^- decreased the intensity of the peak at 362 nm and increased the intensity of the peak at 380 nm. Finally, addition of Br^- caused a large decrease in the intensity, which might be attributable to dynamic quenching as is visible for acridinium and quinolinium salts such as lucigenin (*18*) and SPQ (*19*). The addition of $H_2PO_4^-$ also prevents fluorescence titrations because of the formation of precipitates, as observed in the UV–vis titration. Figure 5 portrays fluorescence changes of **1b** at 380 nm. The association constants of **1b** for anions can be determined by non-linear curve fitting of the spectral titrations as described above and as presented in Table 1. The determined values show fairly good agreement with values determined by UV–vis spectral titrations. A difference in the association constants of $(EtO)_2PO_2^-$ on UV–vis and fluorescence spectral titrations might be attributable to small fluorescence changes of **1b** upon the addition of $(EtO)_2PO_2^-$. It is noteworthy that these anions are distinguishable by the combination of UV–vis and fluorescence spectral titrations.

NMR studies

To explore the event of binding the receptor with anions, ^{1}H NMR titration experiments were conducted. In MeCN-d_3, C(2)—H protons of imidazolium groups in free receptor **1b** are observed at 8.49 ppm. The C(2)—H protons displayed a significant downfield shift upon the addition of AcO^- ($\Delta\delta_\infty = 2.35$ ppm) and Cl^- ($\Delta\delta_\infty = 1.62$ ppm) as shown in Figures 6 and 7, respectively, indicating strong hydrogen bond formation of C(2)—H of imidazolium and anions, and the equilibrium on complexation is faster than NMR time scale. Scheme 3 shows $\Delta\delta_\infty$ of each proton of **1b** upon the addition of AcO^- and Cl^-. Interestingly, 1- and 1′-CH of the binaphthyl moiety showed a downfield shift ($\Delta\delta_\infty = 0.35$ ppm for AcO^- and 0.40 ppm for Cl^-), and methylene CH between the imidazolium and binaphthyl group also showed a larger downfield shift ($\Delta\delta_\infty = 0.37$ ppm for AcO^- and 0.60 ppm for Cl^-). These results strongly suggest that the anions such as AcO^- and Cl^- are hydrogen bonded by the six CH groups: imidazolium C(2)—H, aryl CH and alkyl CH_2 groups, as shown in Scheme 3. The association constants of **1b** were determined as 2.02×10^3 and 3.67×10^3 mol^{-1} dm^3 for AcO^- and Cl^-, respectively, by ^{1}H NMR titrations. The observed smaller values compared to those determined by UV–vis and fluorescence spectroscopies might be attributable to the increase in the polarity of MeCN

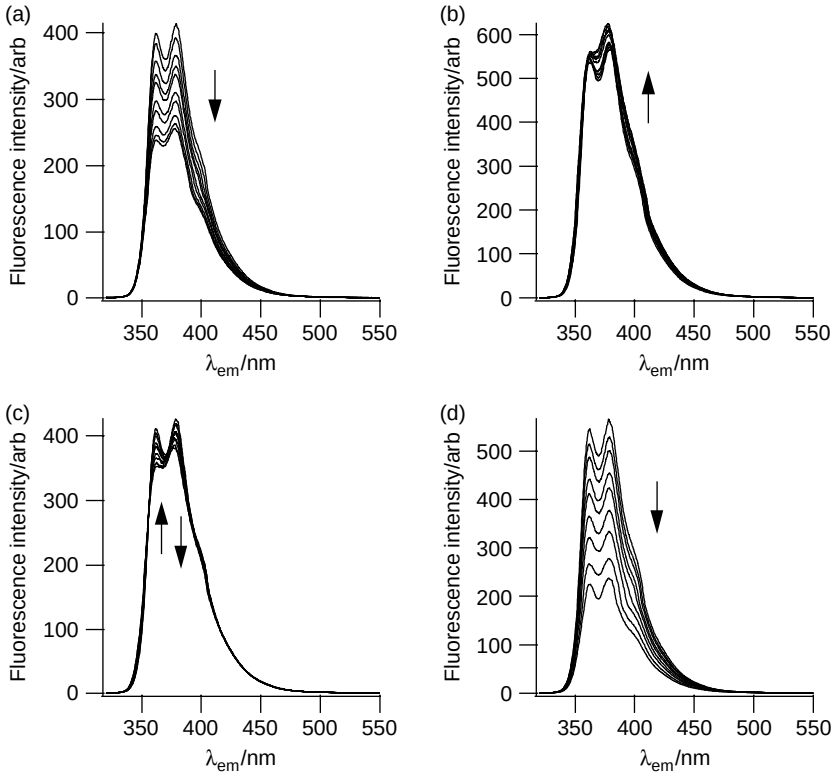


Figure 4. Fluorescence spectral changes of **1b** upon the addition of AcO^- (a), $(EtO)_2PO_2^-$ (b), Cl^- (c) and Br^- (d) in MeCN at 298 K. [**1b**] = 2.0×10^{-5} mol dm^{-3} and λ_{ex} = 290 nm.

solution by the concentrated solution of the ionic receptor molecules in the NMR experiment.

Conclusions

Herein, we have presented a novel anion receptor **1** based on 2,2′-binaphthalene bearing two imidazolium groups. The receptor showed characteristic UV–vis and fluorescence spectral changes upon the addition of anions. In

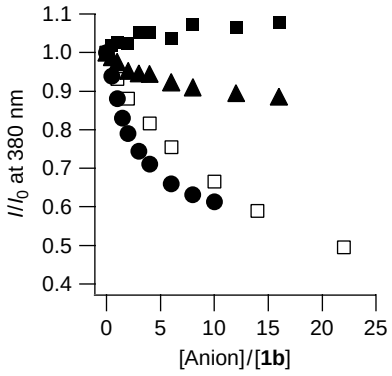


Figure 5. The plot of change in the relative fluorescence intensity at 380 nm of **1b** upon the addition of AcO^- (●), $(EtO)_2PO_2^-$ (■), Cl^- (▲) and Br^- (□) in MeCN at 298 K. [**1b**] = 2.0×10^{-5} mol dm^{-3} and λ_{ex} = 290 nm.

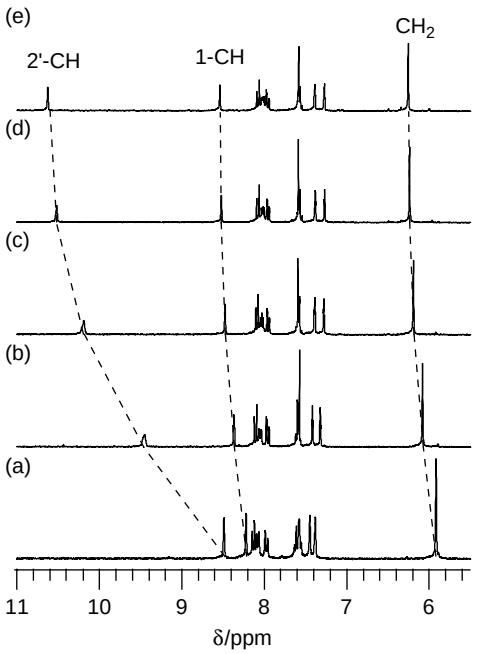


Figure 6. 300 MHz ^{1}H NMR spectra of **1b** in the absence (a) and the presence of 0.5 (b), 1.0 (c), 1.5 (d) and 2.0 (e) equiv. of AcO^- in MeCN-d_3.

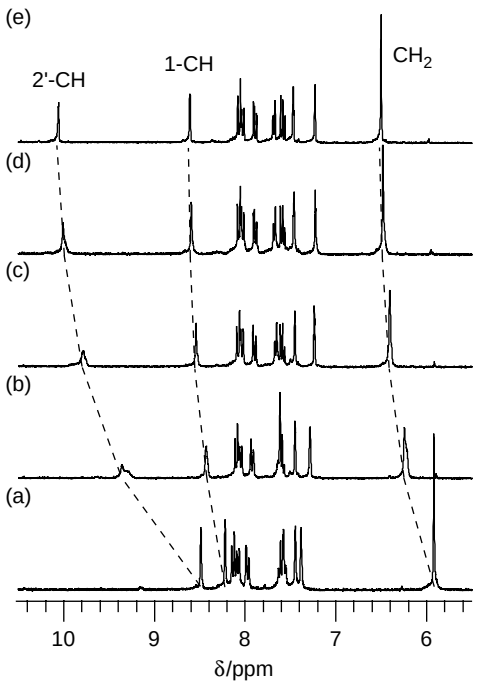


Figure 7. 300 MHz ^{1}H NMR spectra of **1b** in the absence (a) and the presence of 0.5 (b), 1.0 (c), 1.5 (d) and 2.0 (e) equiv. of Cl^- in MeCN-d_3.

particular, fluorescence changes were greatly influenced by the added anions. Results of ^{1}H NMR titration revealed that anions are recognisable by the formation of hydrogen bonds from six C—H groups of receptor **1**. Further studies to improve the selectivity of the receptor by introduction of additional recognition sites are in progress at our laboratory.

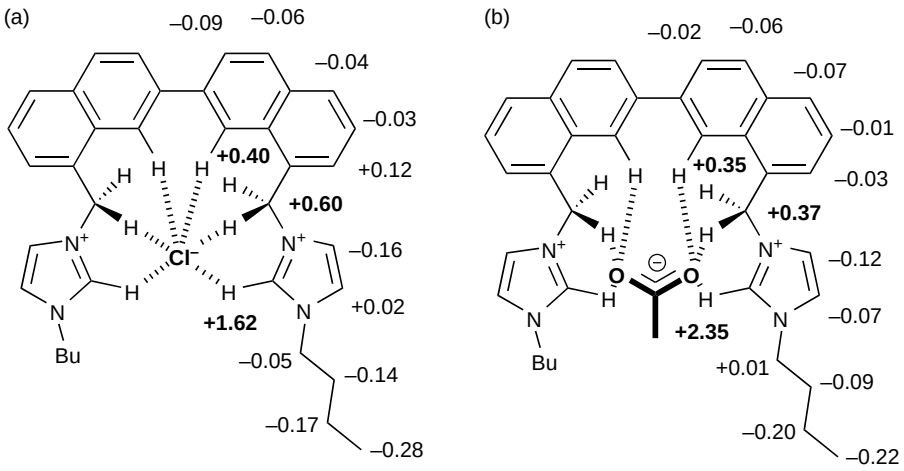
Experimental

Material and methods

All reagents used were of analytical grade. UV–vis spectra were recorded on a Shimadzu UV-2500PC spectrometer with a thermal regulator (±0.5°C). NMR spectra were measured on JEOL AL300 and JEOL ECA500 spectrometers. ESI-MS were recorded on an Applied Biosystems/MDS-Sciex API-100 spectrometer. The HR-MS were recorded on a JEOL JMX-SX 102 mass spectrometer. FT-IR spectra were recorded on Shimadzu FTIR-8400S spectrometer. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrometer. Melting points were determined using a Yanagimoto micro melting point apparatus and are uncorrected. 1-Butylimidazole (*20*) and 8,8′-bis(bromomethyl)-2,2′-binaphthalene were prepared using procedures reported in the literatures (*16*).

Synthesis of 8,8′-bis(3-butyl-imidazolylmethyl)-2,2′-binaphthalene bis(hexafluorophosphate) (1)

A mixture of 8,8′-bis(bromomethyl)-2,2′-binaphthalene (440 mg, 1.0 mmol) and 1-butylimidozole (256 mg, 2.0 mmol) in acetonitrile (15 ml) was refluxed under argon atmosphere for 2 days. The mixture was evaporated under reduced pressure. Into the solution of the residue in MeCN, a solution KPF_6 (368 mg, 2 equiv.) in MeCN was added, and the mixture was stirred for 1 h. The mixture was evaporated under reduced pressure. Then, water was added to the mixture. The precipitate was washed with water and dried *in vacuo* to give the product as a pale yellow solid (725 mg, 89%). Mp 84–86°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.29 (s, 2H, Im 2-CH), 8.42 (s, 2H, 1- and 1′-CH), 8.19 (d, 2H, $J = 8.4$ Hz, 4- and 4′-CH), 8.12 (d, 2H, $J = 8.4$ Hz, 3- and 3′-CH), 8.09 (d, 2H,



Scheme 3. The chemical shift changes of **1b** upon the addition of Cl^- (a) and AcO^- (b) in MeCN-d_3.

$J = 7.5$ Hz, 5- and 5′-CH), 7.85 (s, 2H, Im CH), 7.83 (s, 2H, Im CH), 7.62 (dd, 2H, $J_1 = 7.0$ Hz, $J_2 = 7.5$ Hz, 6- and 6′-CH), 7.53 (d, 2H, $J = 7.0$ Hz, 7- and 7′-CH), 6.08 (s, 4H, CH_2), 4.15 (t, 4H, $J = 7.1$ Hz, CH_2), 1.71 (quint, 4H, $J = 7.4$ Hz, CH_2), 1.13 (t, 4H, $J = 7.4$ Hz, CH_2), 0.76 (t, 6H, $J = 7.4$ Hz, CH_3). ^{13}C NMR (125 MHz, DMSO-d_6): δ 138.2, 136.4, 132.9, 130.7, 130.5, 129.7, 129.4, 128.1, 126.0, 126.1, 126.0, 122.9, 122.8, 120.9, 49.9, 48.7, 31.2, 18.7, 13.1. IR (KBr), 557, 841, 1155, 1564, 2876, 2935, 2964 and 3161 cm^{-1}. ESI-MS: calcd for [**1b**-$(PF_6)]^+$ 673.289. Found 673.3. HR-MS (FAB): calcd for [**1b**-$(PF_6)]^+$ 673.2889. Found 673.2911.

UV–vis and fluorescence titrations

All experiments were conducted in MeCN. In a typical titration experiment, aliquots of a stock solution of anions (as tetrabutylammonium salts) were added to a solution of receptor **1b** (3.33×10^{-5} and 2.00×10^{-5} mol dm^{-3} for UV–vis and fluorescence titrations, respectively) in MeCN and spectra were recorded successively. All data were used for the calculation of the association constants with the non-linear curve fitting method to the 1:1 binding isotherm.

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