Colorimetric 'naked-eye' and fluorescent sensors for anions based on amidourea functionalised 1,8-naphthalimide structures: anion recognition *via* either deprotonation or hydrogen bonding in DMSO

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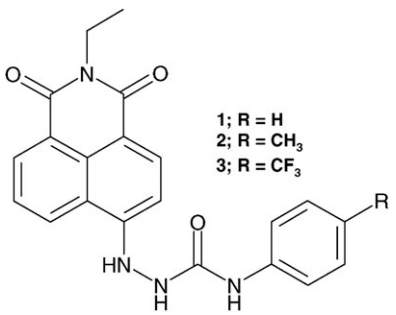
The synthesis and the spectroscopic studies of three new amidourea-based sensors for anions, **1–3**, are described. These are based on the use of 4-hydrazine-1,8-naphthalimides which upon reaction with isocyanates give rise to the formation of the desired amidoureas. **1–3** absorb strongly in the visible region, due to the internal charge transfer excited state character of the naphthalimide moieties. Large colorimetric changes were observed upon the addition of various anions such as acetate, dihydrogenphosphate and fluoride to **1–3** in DMSO, and are brought about through either hydrogen bonding to, or deprotonation of, the amidourea. These changes were clearly visible to the naked eye, changing from yellow/green to purple, and were reversed upon addition of protic solvents. Moreover, each of the three anions gave rise to unique changes in the structure of the absorption spectra which can be considered as being a 'fingerprint' identity for each of them. The fluorescence emission spectra were also affected upon anion binding, being significantly red shifted upon excitation. Non-linear regression analysis of the ground and excited state changes showed the anions were recognized in either 1 : 1 or 2 : 1 stoichiometry, and that the aryl-urea substituents govern the sensitivity of the binding; which in the case of acetate was in the order of **3** > **1** > **2**. The anion recognition was also monitored by ^{1}H NMR spectroscopy in DMSO-d_6.

Introduction

Anion recognition and sensing has become a fast growing field of research in the last few years.[1,2] In particular the study of anion sensing using fluorescent or colorimetric sensors has been actively studied.[3,4] In the latter, anion recognition gives rise to changes in the absorption spectra with associated colour changes.[5,6] The use of charge neutral anion receptors such as imidazoles,[7,8] pyrroles,[9] calixpyrroles,[10] amides,[11,12] cabamides,[13] phenols,[14] ureas,[15,16] thioureas[17,18] and amidoureas[19–21] to achieve such sensing has been demonstrated. For these receptors, the anion is recognized through hydrogen bonding or by deprotonation[22,23] of labile protons by the basic anions (such as fluoride) in organic solvents. Such sensors can also operate within supporting matrices[24] or polymers as recently demonstrated by Anzenbacher[25] or by simply absorbing anion sensors onto cellulose, or filter paper.[26] The recognition moiety often forms part of a chromophore possessing a *push–pull* character based on electron-donor–acceptors,[27] which often make them non or weakly luminescent. We have been active in developing sensors for anions.[28,29] Herein we present three new anion sensors **1–3**, based on the 4-amino-1,8-naphthalimide[30] structure, which has an internal charge transfer excited state, and which has been extensively used for sensing cations such as Na^+, K^+[31] and transition metal ions.[32] We[15a] and others[19–21,33] have previously shown that such amidoureas are particularly effective hydrogen bonding donors capable of anion recognition. Indeed, by simply changing the 4-amino moiety for a hydrazine and reacting the 'free amine' with isocyanates gave the desirable 4-amidourea-1,8-napthalimide based sensors. By incorporating electron withdrawing substituents such as CF_3, as part of the amidourea moiety we were also able to 'tune' both the selectivity and sensitivity of the anion recognition.[34,35] These anion sensors were all strongly coloured, absorbing in the visible region with a λ_{max} of 450 nm, and we demonstrate that the ICT fluorescence of **1–3** is significantly modulated upon excitation of the ICT band, as well as upon excitation of the newly formed long wavelength absorption band at 540 nm, which gives rise to long wavelength emission. These colour changes were clearly visible to the naked eye even at low concentrations.



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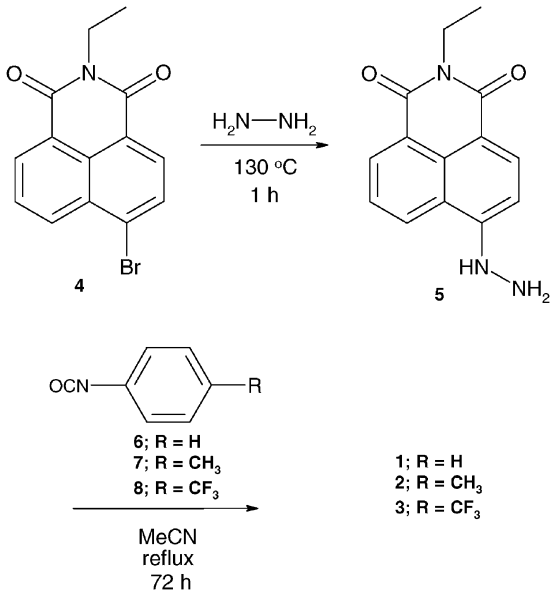

Scheme 1 Synthesis of anion sensors **1–3**.

Results and discussion

Synthesis and characterisation

The three anion sensors differ only in the nature of the 'urea' part of their receptors. Where **1** is a simple aryl urea, **2** has an electron donating substituent making the receptor more electron rich whilst **3**, in contrast, has a strongly electron withdrawing substituent, making its urea protons better hydrogen bonding donors.[34] It was hoped that these simple structural differences could be used to fine-tune the sensitivity of the anion binding.

The synthesis of **1–3** is shown in Scheme 1. 6-Bromo-2-ethyl-benzo[*de*]isoquinoline-1,3-dione **4** was formed in 89% yield using a literature procedure[6] from the corresponding 4-bromo-1,8-naphthalic anhydride, which was then reacted with hydrazine monohydrate at 130 °C for one hour.[6] Upon cooling to room temperature, the solution was added to H_2O, which gave a yellow precipitate which was collected and washed with H_2O, giving **5** in 95% yield. Finally, the anion sensors **1–3** were formed by reacting **5** with phenyl isocyanate (**6**), *para*-tolyl isocyanate (**7**) and 4-trifluoromethylphenyl isocyanate (**8**), respectively, under reflux in anhydrous MeCN. This gave rise to the formation of precipitates after *ca.* 30 min, which were collected and purified by washing with hot CH_2Cl_2 : MeOH (1 : 4) solvent mixture. This gave **1–3** in 41, 52 and 45% yields, respectively, with no further purification needed. All the compounds were fully characterised (see Experimental); by, for instance, their characteristic urea protons as observed in the ^{1}H NMR spectrum (400 MHz, DMSO-d_6). For instance, for **3**, the characteristic resonances for the urea protons were observed in the ^{1}H NMR (400 MHz, DMSO-d_6) at 9.64 and 9.45 ppm, respectively (Fig. 1). The 4-amino proton occurred at 8.90 ppm, and the five naphthalimide protons as well as the two resonances for the aryl urea based receptors were all clearly visible. All the compounds were highly coloured and gave rise to strong green fluorescence typical for such naphthalimide derivatives.

Ground state investigations of anion recognition

The anion sensors **1–3** are soluble in a variety of solvents such as EtOH, DMSO, CH_3CN and 50 : 50 H_2O–EtOH mixtures. However, preliminary studies of these amidourea sensors showed that they were only able to successfully bind anions in aprotic solvents.† Therefore, anion recognition of **1–3** was carried out in DMSO at room temperature. In DMSO their extinction coefficients were determined to be 14 586, 14 507 and 13 748 M^{-1} cm^{-1}, respectively, for the ICT transition, which for **3** had a λ_{max} at 420 nm. Upon the addition of acetate (AcO^-), dihydrogenphosphate ($H_2PO_4^-$) or fluoride (F^-) to **3**, the 420 nm band decreased in intensity in response to each anion (Fig. 2 for AcO^-). Indeed, binding of AcO^- also gave rise to the concomitant formation of two new absorption bands, one at longer wavelength (*ca.* 569 nm) and one at shorter wavelength (*ca.* 360 nm). These changes were also accompanied by the formation of two clear isosbestic points at 385 and 470 nm, respectively. The ICT band was significantly reduced in absorbance after the titration, appearing as a broad shoulder at *ca.* 430 nm. These overall changes are consistent with anion binding, through hydrogen bonding at the amidourea moiety, which enhances the ICT character of the chromophore by placing a highly electron rich moiety adjacent to the donating amine. This gives rise to a stronger 'push–pull' effect and consequently, shifts the long wavelength absorption towards the red. This feature was characteristic of all the anion titrations carried out on **1–3**.

Further analysis of these spectral changes (Fig. 2) clearly shows that the long wavelength absorption band has the appearance of 'fine structure', while the short wavelength absorption increased in intensity to *ca.* 80% of the band for the free (unbound) sensor at 420 nm. Similar features were also observed for the titrations against **1** or **2**. For **1** a λ_{max} at 415 nm was recorded for the free sensor and upon titration with AcO^- two new bands arose centred at 353 and 556 nm, respectively, with associated isosbestic points at 384 and 464 nm, respectively. Similarly for **2**, a λ_{max} at 419 nm was observed for the free sensor whilst after titration with AcO^- two new bands appeared centred at 353 and 558 nm, respectively. Again, two clear isosbestic points were observed at 382 and 466 nm, respectively. The reversibility of this sensing action was also confirmed by adding a polar protic solvent (EtOH) to the above sample. This fully reversed the changes seen in the absorption spectra in Fig. 2. Such changes were not seen in the thiourea analogue of **1**,[6] which allowed for the sensing of AcO^- in aqueous media.

When titrations were carried out on **3** using either $H_2PO_4^-$ or F^-, similar overall results were observed as seen in Fig. 3 and Fig. 4, respectively. However, the absorption spectra of each displayed some subtle differences from that observed for the titration with AcO^-. In the case of $H_2PO_4^-$, the formation of a long wavelength absorption band at 565 nm was accompanied by the formation of a short wavelength absorption band at 353 nm and two isosbestic points at 356 and 459 nm, respectively. However, the latter of these was shifted slightly to

† This is in contrast to their thioureaamido analogues that we have also investigated and shown to sense anions in both organic and aqueous solutions (see ref. 6).

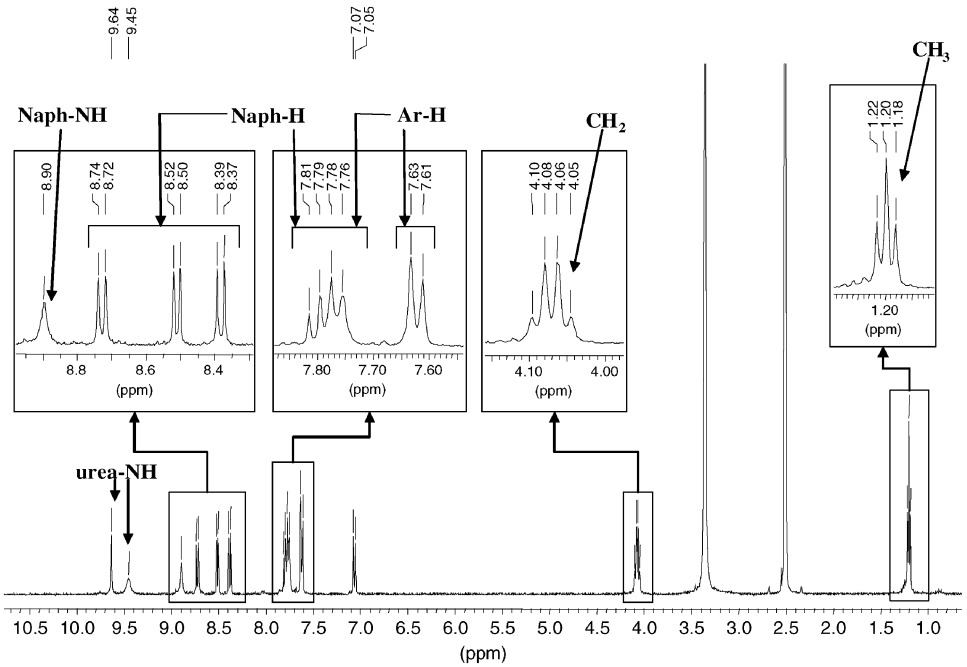

Fig. 1 ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **3** with assignments.

the red at high anion concentration. We also noted that the short wavelength absorption band was not as 'broad' as that seen for AcO^- in Fig. 2, and that the long wavelength absorption band was slightly more structured. Again, we assign these changes to the recognition of the anion at the amidourea moiety, occurring through hydrogen bonding.

These differences were even more pronounced for F^- where 'collapse' of the λ_{max} band at 420 nm was initially replaced by the formation of a shoulder similar to that observed for both AcO^- and $H_2PO_4^-$ above, and eventually by an absorption band centred at *ca.* 419 nm. Moreover, the long wavelength absorption was more structured than that seen for either AcO^- or $H_2PO_4^-$, with significantly sharper 'tailing off' towards the red, and a λ_{max} at 559 nm. Furthermore, looking at the ratio between the 559 nm and the short wavelength 353 nm transitions, yields an almost 1 : 1 ratio between these two wavelengths, whereas in Fig. 2 and Fig. 3, the short wavelength band was *ca.* 50% and 40% stronger than the long wavelength absorptions, for AcO^- and $H_2PO_4^-$, respectively.

Upon carrying out anion titrations on **1** and **2**, similar behaviour was observed for each anion–sensor combination. The changes in the absorption spectra for **1** upon titration with AcO^- are shown in Fig. 5 and subtly demonstrate a difference to the absorption spectra of **3**. Hence, we propose that these changes are due to the direct interaction of the anion with the receptors in a specific and unique manner, and not due to one common mechanism such as deprotonation of the thiourea protons, as such mechanism would have lead to the formation of the same 'product' for all of these anions, and hence an identical absorption spectrum. These titrations were also carried out on **1–3** using ether Cl^- or Br^-, but these titrations did not lead to measurable changes in the absorption spectra.

By plotting the growth of the new long wavelength band of these colorimetric sensors as a function of −log [anion],

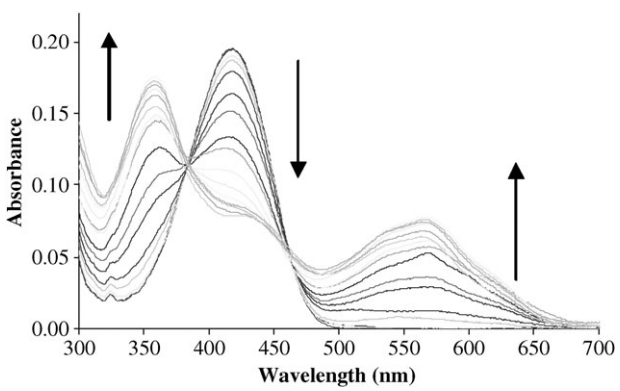

Fig. 2 The changes observed in the absorption spectrum of urea **3** (1.5×10^{-5} M) upon addition of AcO^- (0 M → 3×10^{-3} M) in DMSO.

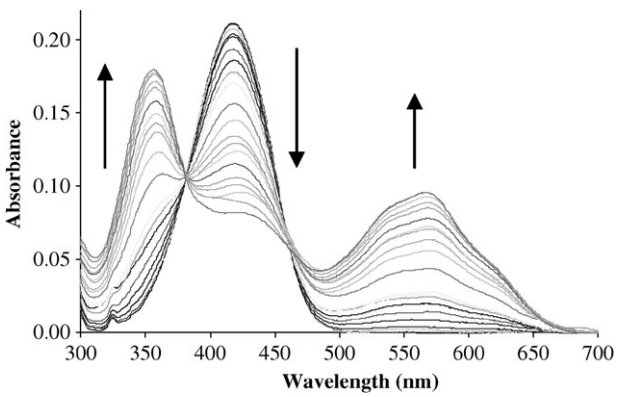

Fig. 3 The changes observed in the absorption spectrum of urea **3** (1.5×10^{-5} M) upon addition of $H_2PO_4^-$ in DMSO at 25 °C (0 M → 3×10^{-3} M).

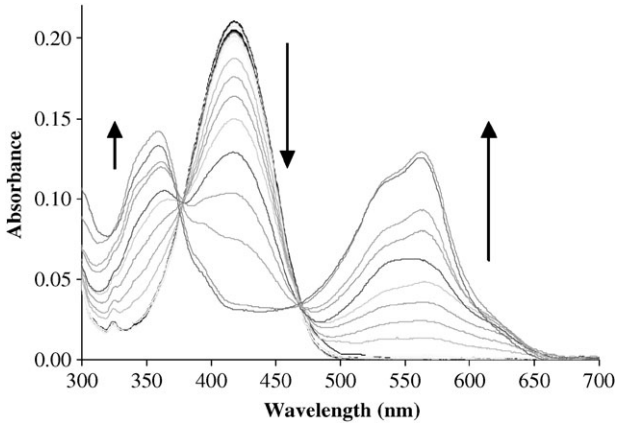

Fig. 4 Changes observed in the absorption spectrum of urea **3** (1.5×10^{-5} M) upon addition of F^- in DMSO at 25 °C (0 M → 3×10^{-3} M).

sigmoidal binding curves were observed, which changed over approximately two log units for both AcO^- and $H_2PO_4^-$, which is indicative of 1 : 1 binding. This stoichiometry was also confirmed by fitting the changes in the long wavelength band using the nonlinear regression analysis program SPECFIT. Using a number of different binding models with host-to-guest stoichiometries such as 1 : 1, 1 : 2 and 1 : 3, gave log β values as shown in Table 1. However, only the 1 : 1 binding gave good fits to the experimental data. In contrast to these results it was not possible to accurately calculate the log β values for F^- binding, as the resulting log β values carried significant errors. This is most likely due to the nature of the binding interactions of F^- with the amidourea protons. For AcO^- and $H_2PO_4^-$ the sensing is due to hydrogen bonding interactions between the anion and the amidourea protons, however for F^-, initial hydrogen bonding interaction is most likely followed by the formation of the ion pair complex (bifluoride ion) HF_2^-, because of the ability of this anion to deprotonate acidic moieties. Similar deprotonation events have been demonstrated previously by our own group as well as those of Gale,[19,23] Fabbrizzi[18] and Pfeffer.[7,16]

Colorimetic responses: naked eye detection of anions

As is clear from the above ground state changes, the absorption spectra of **1–3** were dramatically affected upon interaction with AcO^-, $H_2PO_4^-$ or F^-, and each one of these anions gives rise to unique change in the structure of the absorption spectra. However, the 'colour' changes seen in the absorption spectra were also clearly visible to the naked eye as demonstrated in Fig. 6, which shows the chromogenic response of **3** (1×10^{-3} M) in DMSO upon the addition of these anions (1 eq.). In general, the colour change was from a bright fluorescent colour to blue or deep purple. However, in the case of F^-, the purple colour change was only observed at low guest concentrations, as at high concentrations the initial colour changed, *via* purple, to pale orange. This may be ascribed to the deprotonation of the N–H protons of the urea/thiourea moiety of the sensor, resulting in the formation of the HF_2^-. No colour change was seen in the presence of either Cl^- or Br^-.

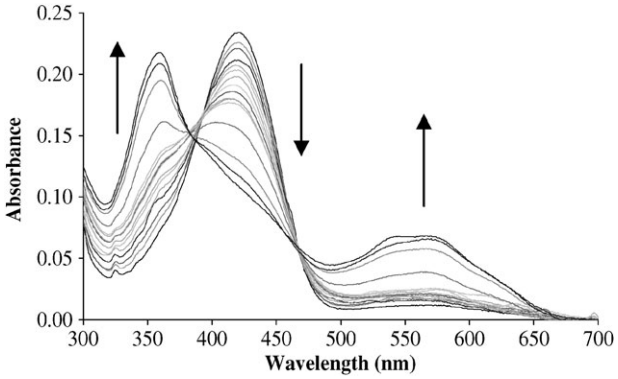

Fig. 5 The changes observed in the absorption spectrum of urea **1** (1.5×10^{-5} M) upon addition of AcO^- (0 M → 3×10^{-3} M) in DMSO.

Excited state spectroscopic investigation of anion recognition

In parallel with the absorption binding experiments discussed above, the changes in the fluorescence emission spectra of **1–3** were also monitored in DMSO upon anion sensing. The changes in the fluorescence emission of **1** upon excitation λ_{max} at 420 nm, is shown in Fig. 7. The emission spectrum of the free sensor gave rise to the formation of a broad band with a maximum intensity at 520 nm upon excitation of the ICT band at 420 nm. Following titration with AcO^- fluorescence quenching was observed for this band and the emission was significantly "*switched off*". However, it is clear from Fig. 7 that the λ_{Fmax} was also shifted to a longer wavelength. When the changes in emission intensity at the 520 nm band are plotted as a function of $-\log [AcO^-]$ (Fig. 7, insert) a sigmoidal profile results, indicative of 1 : 1 binding between the anion and the sensor. From these changes, we estimated the binding constant log β to be ~ 5.0 (± 0.2), which correlates well with that observed in the ground state (Table 1). The emission spectra was also monitored by exciting at the two isosbestic points shown in Fig. 1, as well as at the anion induced long wavelength absorption band. Upon excitation of the isosbestic point at 360 nm, similar changes were observed, with λ_{max} at 510 nm. However, here the emission was fully quenched, or fully "switched off", with concomitant formation of a new weakly emitting band at longer wavelength centred at *ca.* 625 nm. On the other hand, when exciting at the 470 nm isosbestic point, an emission band with λ_{max} at 545 nm was observed that tailed into the 760 nm region. This emission was much less modulated upon titration with AcO^-, with only

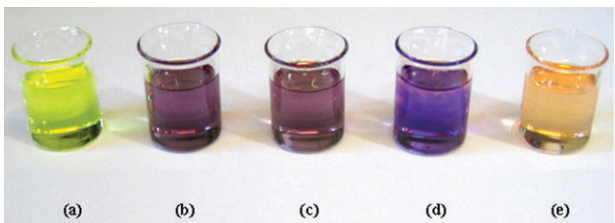

Fig. 6 Chromogenic response of solutions of sensor **3** (1×10^{-3} M) upon interaction with various anions: (a) Free host **3**; (b) **3** + 1 eq. AcO^-; (c) **3** + 1 eq. $H_2PO_4^-$; (d) **3** + 1 eq. F^-; (e) **3** + F^- (excess).

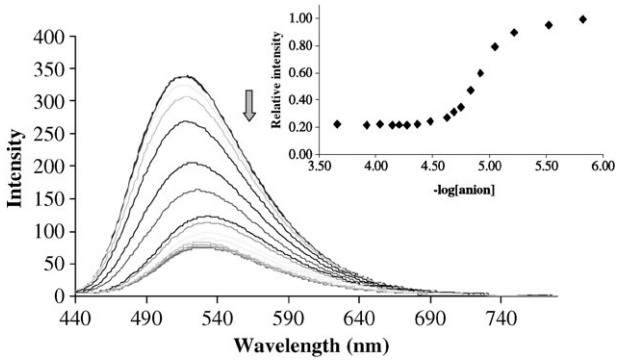

Fig. 7 Changes observed (quenching) in the fluorescence of **1** (1.5×10^{-5} M) upon addition of AcO^- in DMSO at 25 °C (excited at 420 nm; 0 M → 3×10^{-3} M). Insert: the changes at 520 nm as a function of −log [AcO^-]. See Fig. 5 for the corresponding ground state changes.

ca. 15% changes being observed in the emission intensity. This long wavelength emission was also clearly observed when exciting at the newly formed band at 569 nm, where a λ_{max} was observed at *ca.* 610 nm, with a smaller shoulder at 690 nm, which was enhanced upon increasing the concentration of AcO^-. Both **2** and **3** also gave rise to long wavelength emission bands upon excitation at the ICT bands and at their isosbestic points, which was again modulated upon titration with AcO^- in a similar manner to that described above.

These titrations were also carried out using $H_2PO_4^-$ and F^-. The changes in the fluorescence emission of **1** (upon excitation λ_{max} at 420 nm) following the addition of $H_2PO_4^-$, are shown in Fig. 8. However, in contrast to the behaviour noted for AcO^-, initially only a slight quenching of the fluorescence emission by these anions was observed. These changes were however, followed by a significant "*switching on*" effect (after the addition *ca.* 50 equivalents of the anion) which also gave rise to a red shift from a maximum intensity at 520 nm to 530 nm, Fig. 8. Similarly, the effect of the addition of either $H_2PO_4^-$ or F^- following excitation at 360 nm gave rise to an initial decrease in the fluorescence emission (λ_{max} 510 nm) by *ca.* 25%, followed by an increase in the same band with the appearance of two new bands at 440 and 615 nm, respectively, Fig. 9 shows these changes for **1** in the presence of F^-. Similar behaviour was also observed for **2** and **3** when titrated with $H_2PO_4^-$ or F^-.

One rationale for these changes is that the hydrazine proton directly attached to the 4-position of the naphthalimide ring is also involved in the binding of these anions. In the case of $H_2PO_4^-$ it may be due to hydrogen-bonding interactions with this moiety as demonstrated by Pfeffer *et al.* for related

Table 1 Stability constants (log β) obtained from fitting the changes in the absorption spectra of **1–3** using the nonlinear regression analysis program SPECFIT and fitting the data to 1 : 1 binding[a]

Sensor	AcO^-	$H_2PO_4^-$	F^-[b]
1	4.19 ± 0.03	2.86 ± 0.04	—
2	3.99 ± 0.06	—[b]	—
3	4.26 ± 0.06	3.49 ± 0.02	—

[a] All measured in DMSO. [b] The binding profile was too complicated to allow for accurate determination of log β.

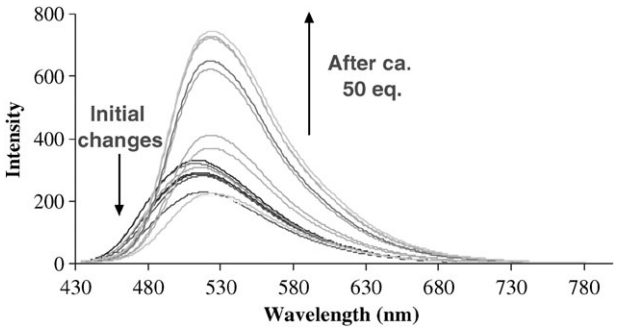

Fig. 8 Changes observed in the fluorescence of **1** (1.5×10^{-5} M) upon addition of $H_2PO_4^-$ in DMSO at 25 °C (excited at 420 nm; 0 M → 3×10^{-3} M.

systems, which, in our case could result in full proton transfer.[16] In the case of F^- it is possible that initially the ion is bound through hydrogen bonding to the urea moiety, followed by either the binding of a second F^- at the 4-amino moiety or, by deprotonation of a urea NH, or the 4-amino moiety protons, in either case to yield HF_2^-. We have recently demonstrated that such deprotonation occurs for similar 4-amino-1,8-naphthlimides at high concentrations of F^- will deprotonate the most acidic proton to form HF_2^-. The changes shown in Fig. 9, suggest that such deprotonation is probably occurring here. Analysis of the emission spectra by plotting the changes at 440, 510 and 615 nm, respectively, as a function of −log [F^-], clearly revealed the complexity of the anion recognition–deprotonation process for both $H_2PO_4^-$ or F^-, supporting our explanation. Unfortunately, we were unable to determine accurate binding constants from these changes by fitting the emission changes by using the nonlinear regression analysis program SPECFIT.

^{1}H NMR spectroscopic investigation of anion recognition

Having established above that anion recognition was either through 'pure' hydrogen bonding interactions, or as a combination of hydrogen bonding and/or deprotonation, we carried out detailed ^{1}H NMR spectroscopic titrations on **1–3** in DMSO-d_6 using 1.0×10^{-2} M of the above anions at 25 °C.

The naked eye effect discussed above was also quite striking in these studies due to the relatively high concentration of the sensors, and the yellow to purple colour change began to occur immediately after the addition of 0.1 equivalent of anion. The naphthalimide protons of these sensors were primarily monitored as the chemical shifts of the NH protons of the urea moiety broadened significantly early on in the titration. Nevertheless, it was also possible to observe the changes in the chemical shift of the 4-amino-naphthamide proton in **1** and **2**, while that of sensor **3** became too broad to monitor upon anion interaction, most likely due to the electron-withdrawing effect of the 4-(trifluoromethyl)-phenyl substituents which would be expected to increase in the acidity of the urea N–H protons.

Fig. 10 and Fig. 11 show the changes observed in the ^{1}H NMR spectrum of **3** upon the addition of AcO^- and F^-, respectively. The data obtained from these titrations was plotted as the cumulative changes in chemical shift ($\Delta\delta$) against the equivalents of anion added and the resulting plots

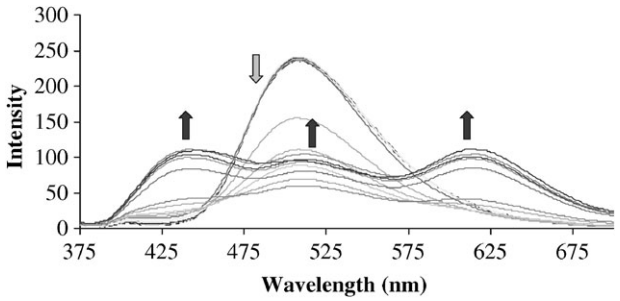

Fig. 9 Changes observed in the fluorescence of **1** (1.5×10^{-5} M) upon addition of F^- ($0 \rightarrow 3 \times 10^{-3}$ M) in DMSO upon excitation at 360 nm; light grey arrow: first significant change; dark grey arrow: second significant change).

were analysed using WinEQN MR. As can be seen from Fig. 10, the amide protons disappeared after *ca.* 0.1 equivalent of the anion, consequently it should be noted that since the changes were comparably small in magnitude, hence carried larger errors. For all the three sensors, the binding curves obtained for their complex formation with AcO^- reached a plateau after *ca.* one equivalent, indicating a 1 : 1 host : guest stoichiometry. This supports our finding from the ground and the excited state measurements discussed above that the binding is solely due to hydrogen bonding. On the other hand, the binding of either $H_2PO_4^-$ required the addition of two equivalents of the anion in order for the binding process to reach completion. In the case of F^-, Fig. 11, the deprotonation process was clearly visible, with the formation of the characteristic triplet for the formation of HF_2^-, at *ca.* 16 ppm. There are many reports of a 1 : 2 host : guest stoichiometry for F^- binding, mostly due to such anion induced protonation. However, there are to the best of our knowledge no known cases of the binding of two equivalents of $H_2PO_4^-$ to such a simple mono-urea (or thiourea) receptor. We were however, unable to determine the binding constant for this second interaction accurately (*cf.* Table 2), which supports that

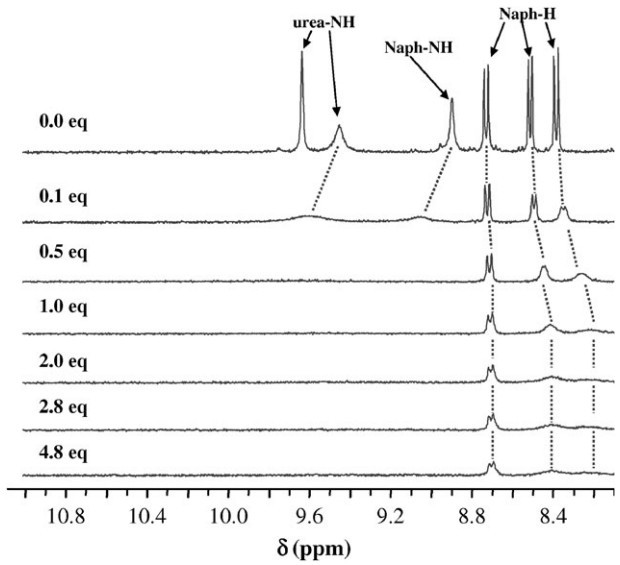

Fig. 10 Stack plot of ^{1}H NMR spectra of **3** (1×10^{-2} M) upon addition of AcO^- in DMSO-d_6 at 25 °C.

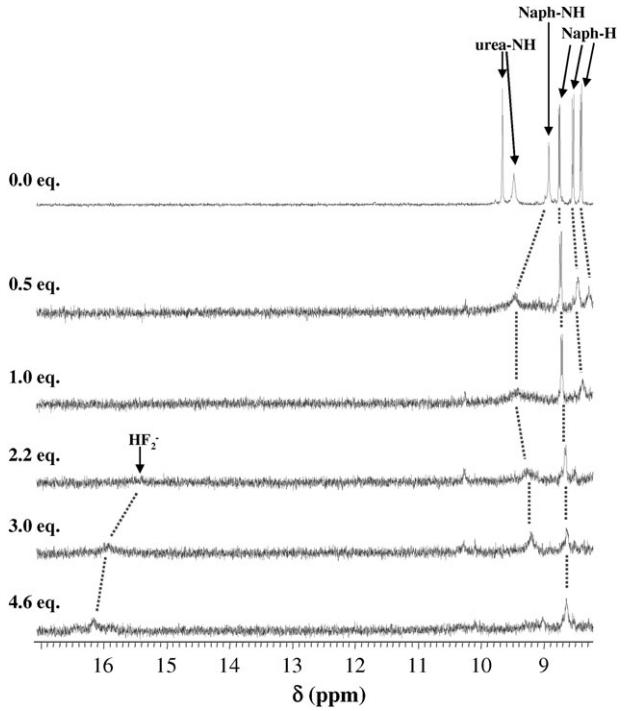

Fig. 11 Stack plot of ^{1}H NMR spectra of **3** (1×10^{-2} M) upon addition of F^- in DMSO-d_6 at 25 °C. (Note: The chemical shifts were greatly perturbed; hence, the ^{1}H NMR spectra had to be magnified significantly after the first addition of F^-.)

theory. The binding constants (log β) for the binding of **1–3** (determined by the WinEQN MR program) are listed in Table 2. On all occasions a good fit was observed. Unfortunately, we were unable to determined binding constants for F^- due to the deprotonation of the urea N–H. However, the results demonstrate the same trend as observed for the ground state changes, and highlight the effect the substituents has on the anion affinity for these sensors.

Conclusions

A family of colorimetric sensors based on the use of 4-amino-1,8-napthlimide as a chromophore (fluorophore) were developed for the sensing of anions through hydrogen bonding with a few steps synthesis. All the three sensors showed significant changes in the absorption spectra upon binding to anions such as AcO^-, $H_2PO_4^-$ and F^- in DMSO, where the ICT band of the naphthalimide moiety was shifted to longer wavelength, and a new band was formed at shorter wavelengths and with the formation of several isosbestic points. These changes were fully reversible upon addition of a polar protic solvent. Only minor changes were seen for Cl^- and Br^-. The sensitivity of the anion binding could also be tuned by changing the nature of the aryl urea moiety. Importantly, unique differences were seen in the fine structure of the resulting absorption bands as a consequence of the AcO^-, $H_2PO_4^-$ and F^- binding, which can be considered as being a 'fingerprint' identity for each of these anions. Moreover, the anion binding and the changes seen in the absorption spectra were also clearly visible to the naked eye.

Table 2 Stability constants (log β) obtained from fitting the changes in the ^{1}H NMR spectra of **1–3** upon titration with various anions[a]

Sensor	AcO^-	$H_2PO_4^-$	F^-[b]
1	3.58	2.21[c]	—
2	2.85	—[a]	—
3	3.75	2.33[c]	—

[a] All measured in DMSO-d_6. [b] The binding process is too complicated for analysis by WinEQN MR.. [c] For the 1 : 1 binding mode. Estimated error: 10%

The fluorescence of these sensors was also modulated upon anion recognition, where the ICT band was either quenched or shifted to longer wavelengths. From these changes we were able to determine binding constants which showed that AcO^- was bound more strongly than $H_2PO_4^-$ and that the binding of F^- was most likely due to initial hydrogen bonding to the anion receptor followed by deprotonation and the formation of HF_2^-. The formation of this species in solution was also confirmed by ^{1}H NMR measurements; which demonstrated that AcO^- was recognised through 'pure' hydrogen bonding. In contrast, the changes observed upon binding of $H_2PO_4^-$ and F^- to **1–3** suggest that the initial recognition is more likely due to initial hydrogen bonding interactions, followed by full or partial deprotonation. Hence, we conclude that if the anion is basic enough in the solvent media deprotonation will occur on the most acidic protons of the sensors. However, since the absorption spectrum does not give rise to identical spectra at the endpoint, it strongly suggests that each of AcO^-, $H_2PO_4^-$ and F^- binds to **1–3** in a unique manner, which can be potentially used to aid in the distinction of these anions. We are currently investigating these and related systems as anion sensors for real time monitoring and sensing of anions in competitive media.

Experimental

Starting materials were obtained from Sigma Aldrich and Fluka. Solvents used were HPLC grade unless otherwise stated. ^{1}H NMR spectra were recorded at 400 MHz using a Bruker Spectrospin DPX-400, with chemical shifts expressed in parts per million (ppm or δ) downfield from the standard. ^{13}C NMR spectra were recorded at 100 MHz using a Bruker Spectrospin DPX-400 instrument. Infrared spectra were recorded on a Mattson Genesis II FTIR spectrophotometer equipped with a Gateway 2000 4DX2-66 workstation. Mass spectroscopy was carried out using HPLC grade solvents. Electrospray Mass spectra were recorded on a Micromass LCT spectrometer. The system was controlled by MassLynx 3.5 on a Compaq Deskpro workstation. UV-Vis spectroscopic analysis was carried out on a Varian Cary 100 UV-Vis spectrophotometer. Luminescence measurements were carried out on Varian Carey Eclipse spectrophotometer.

6-Bromo-2-ethyl-benzo[*de*]isoquinoline-1,3-dione (4)

4-Bromo-1,8-naphthalic anhydride (2.00 g, 7.2 mmol) and ethylamine (70% solution in water) (0.69 mL, 8.66 mmol) were refluxed in 1,4-dioxane (100 mL) for 7 h. The solution was then poured into water. A precipitate is formed, which was collected by filtration, washed with water and dried to yield **4** as a cream-coloured solid (1.96 g, 89%). m.p. 160–162 °C (lit., 163 °C); calculated for $C_{14}H_{10}NO_2Br$: C, 55.3; H, 3.3; N, 4.6%; found: C, 55.2; H, 3.3; N, 4.7%.

2-Ethyl-6-hydrazino-benzo[*de*]isoquinoline-1,3-dione (5)

Hydrazine monohydrate (excess) was added to **4** (0.20 g, 0.66 mmol). The neat reaction mixture was heated at 130 °C and left stirring for 1 h. It was then poured into water, forming a precipitate, which was collected by filtration, washed with water and dried to yield **5** as a yellow solid (0.16 g, 95%). m.p. 255–257 °C; HRMS (MeOH, ES^+): calculated for $C_{14}H_{14}N_3O_2$: 256.1086 $(M + H)^+$; found: 256.1077; δ_H (400 MHz, $(CD_3)_2SO$) 9.13 (1H, br s, Naph-N*H*), 8.61 (1H, d, J = 8.5 Hz, Naph-*H7*), 8.41 (1H, d, J = 7.0 Hz, Naph-*H5*), 8.28 (1H, d, J = 7.5 Hz, Naph-*H2*), 7.64 (1H, dd, J = 7.8 Hz, 8.0 Hz, Naph-*H6*), 7.24 (1H, d, J = 8.6 Hz, Naph-*H3*), 4.69 (2H, d, J = 10.6 Hz, Naph-NH-*NH*$_2$), 4.05 (2H, q, J = 7.0 Hz, *CH*$_2$), 1.18 (3H, t, J = 7.0 Hz, *CH*$_3$); δ_C (100 MHz, $(CD_3)_2SO$) 163.6, 162.7, 153.2, 134.2, 130.5, 128.2, 127.3, 124.1, 121.7, 118.4, 107.4, 104.0, 34.2, 13.3; IR (KBr) υ_{max} (cm^{-1}) 3450, 3366, 3316, 1672, 1636, 1614, 1578, 1540, 1439, 1389, 1366, 1346, 1310, 1251, 1114, 1069, 950, 772.

General synthesis of 1–3

The appropriate isocyanate (1.1 eq.) was added to the amine and this reaction mixture was stirred with heating at reflux for 3 days in dry CH_3CN. A precipitate formed, which was collected and washed with CH_3CN. The solid was then dried, yielding a yellow solid. Purification of the crude products was carried out by hot filtration using a mixture of DCM : MeOH (1 : 4).

2-Ethyl-6-[(phenylcarbamoyl)hydrazino]benzo[*de*]iso-quinoline-1,3-dione (1)

1 was synthesised according to above procedure using **5** (0.21 g, 0.82 mmol) and phenyl isocyanate **6** (0.11 g, 0.90 mmol) in dry MeCN (30 mL). The desired product was obtained as a dark yellow solid (0.12 g, 41%). m.p. 252–254 °C; calculated for $C_{21}H_{18}N_4O_3{\cdot}(H_2O)$: C, 64.3; H, 5.1; N, 14.3%; found: C, 64.0; H, 4.5; N, 14.5%; δ_H (400 MHz, $(CD_3)_2SO$) 9.60 (1H, br s, urea-N*H*), 9.03 (1H, br s, urea-N*H*), 8.73 (1H, d, J = 8.8 Hz, Naph-*H7*), 8.67 (1H, br s, Naph-N*H*), 8.50 (1H, d, J = 7.0 Hz, Naph-*H5*), 8.37 (1H, d, J = 7.9 Hz, Naph-*H2*), 7.78 (1H, t, J = 7.9 Hz, Naph-*H6*), 7.51 (2H, d, J = 7.9 Hz, Ar-*H2*, Ar-*H6*), 7.26 (2H, t, J = 7.4 Hz, Ar-*H3*, Ar-*H5*), 7.05 (1H, d, J = 8.8 Hz, Naph-*H3*), 6.97 (1H, t, J = 7.0 Hz, Ar-*H4*), 4.07 (2H, q, J = 6.7 Hz, C*H*$_2$), 1.20 (3H, t, J = 7.0 Hz, C*H*$_3$); δ_C (100 MHz, $(CD_3)_2SO$) 163.4, 162.7, 155.8, 152.6, 151.3, 139.7, 139.6, 133.7, 130.7, 128.8, 128.6, 124.8, 122.1, 121.8, 119.0, 118.1, 110.7, 105.1, 34.4, 13.3; IR (KBr) υ_{max} (cm^{-1}) 3285, 1641, 1545, 1498, 1444, 1388, 1369, 1349, 1239, 1141, 1066, 914, 876, 839, 773, 742, 691.

2-Ethyl-6-[(*para*-tolylcarbamoyl)hydrazino]-benzo[*de*]iso-quinoline-1,3-dione (2)

2 was synthesised according to above procedure using **5** (0.20, 0.78 mmol) and *para*-tolyl isocyanate **7** (0.11 g, 0.86 mmol) in

dry MeCN (30 mL). The desired product was obtained as a dark yellow solid (0.16 g, 51%). m.p. decomposed at 310 °C; calculated for $C_{22}H_{20}N_4O_3 \cdot 1/2H_2O$: C, 66.5; H, 5.3; N, 14.1%; found: C, 66.5; H, 5.0; N, 13.5%; δ_H (400 MHz, $(CD_3)_2SO$) 9.59 (1H, br s, urea-N*H*), 8.92 (1H, br s, urea-N*H*), 8.73 (1H, d, J = 7.9 Hz, Naph-*H7*), 8.61 (1H, br s, Naph-N*H*), 8.50 (1H, d, J = 7.0 Hz, Naph-*H5*), 8.37 (1H, d, J = 7.9 Hz, Naph-*H2*), 7.78 (1H, t, J = 7.9 Hz, Naph-*H6*), 7.39 (2H, d, J = 8.8 Hz, Ar-*H2*, Ar-*H6*), 7.05 (3H, m, Ar-*H3*, Ar-*H5*, Naph-*H3*), 4.07 (2H, q, J = 7.0 Hz, CH_2), 2.23 (3H, s, Ar-CH_3), 1.20 (3H, t, J = 7.0 Hz, CH_3); δ_C (100 MHz, $(CD_3)_2SO$) 163.5, 162.8, 151.4, 136.9, 133.8, 130.9, 130.8, 129.2, 129.0, 125.8, 124.8, 121.9, 119.1, 110.6, 105.1, 34.4, 20.3, 13.3; IR (KBr) υ_{max} (cm^{-1}) 3295, 1641, 1580, 1543, 1434, 1390, 1370, 1350, 1310, 1243, 1143, 1066, 917, 877, 832, 774, 757.

2-Ethyl-6-[(4-trifluoromethylphenylcarbamoyl)hydrazino]-benzo[*de*]iso-quinoline-1,3-dione (3)

3 was synthesised according to above procedure using **5** (0.20 g, 0.80 mmol) and 4-trifluoromethyl-phenyl isocyanate **8** (0.16 g, 0.88 mmol) in dry MeCN (30 mL). The desired product was obtained as a dark yellow solid (0.15 g, 45%). m.p. decomposed at 250 °C; calculated for $C_{22}H_{17}N_4F_3O_3 \cdot H_2O$: C, 57.4; H, 4.2; N, 12.2%; found: C, 57.7; H, 3.8; N, 12.0%; δ_H (400 MHz, $(CD_3)_2SO$) 9.64 (1H, br s, urea-N*H*), 9.45 (1H, br s, urea-N*H*), 8.90 (1H, br s, Naph-N*H*), 8.73 (1H, d, J = 7.9 Hz, Naph-*H7*), 8.51 (1H, d, J = 7.9 Hz, Naph-*H5*), 8.38 (1H, d, J = 8.8 Hz, Naph-*H2*), 7.78 (3H, m, Ar-*H3*, Ar-*H5*, Naph-*H6*), 7.62 (2H, d, J = 8.8 Hz, Ar-*H2*, Ar-*H6*), 7.06 (1H, d, J = 7.0 Hz, Naph-*H3*), 4.07 (2H, q, J = 6.7 Hz, CH_2), 1.20 (3H, t, J = 7.0 Hz, CH_3); δ_C (100 MHz, $(CD_3)_2SO$) 163.4, 162.7, 155.5, 151.1, 149.7, 143.4, 133.7, 130.8, 128.9, 125.8, 124.9, 123.2, 121.9, 120.7, 118.6, 113.0, 110.9, 105.1, 34.4, 13.3; δ_F (376 MHz, $(CD_3)_2SO$) −58.59 (Ar-CF_3); IR (KBr) υ_{max} (cm^{-1}) 3317, 1641, 1548, 1434, 1389, 1371, 1327, 1234, 1162, 1111, 1066, 1016, 916, 875, 841, 773, 756, 705.

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