A quinolinium-derived turn-off fluorescent anion sensor†

Adam N. Swinburne,[a] Martin J. Paterson,[b] Andrew Beeby*[a] and Jonathan W. Steed*[a]

Received 23rd September 2009, Accepted 18th November 2009
First published as an Advance Article on the web 4th January 2010
DOI: 10.1039/b919821k

A quinolinium-derived anion sensor has been synthesised which shows a turn-off fluorescence response in the presence of anions, with selectivity for acetate. The compound exhibits complex anion binding comprising of a host dimer, 2 : 1 and 1 : 1 host : guest species. Fluorescent quenching is due to both dynamic and static processes with charge transfer being the dominant mechanism.

Introduction

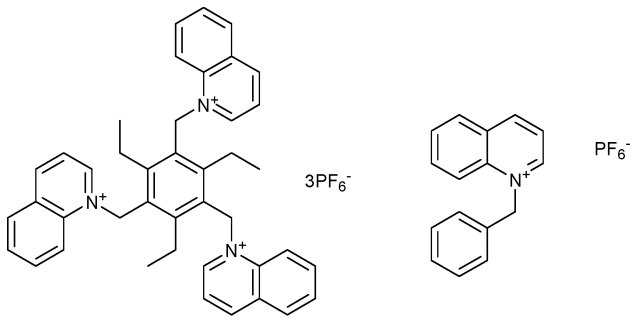
The design of receptors capable of selectively binding and sensing anions is challenging and is a current area of active research.[1–4] We[5–9] and others[10–13] have used receptors derived from a hexa-substituted triethyl benzene scaffold as a means of creating conformationally flexible anion hosts exhibiting some degree of preorganisation. These hosts have proved effective anion receptors with the addition of redox active (ferrocenyl)[14] or luminescent (anthracenyl,[5] pyrenyl[9]) reporter groups allowing electrochemical or 'turn on' fluorescent sensing. Several recent examples of turn-off PET sensors for biologically relevant anions have also been reported.[15–19]

The use of quinolinium salts as anion sensors has been investigated due to their ease of synthesis, their water solubility and their known fluorescent quenching by anions.[20–23] Many studies have focused on halide detection, particularly chloride. Chloride is an anion of great importance in biological chemistry, as a component of extra-cellular fluids, in environmental science as well as consumer products and industrial processes.[20]

The quinolinium based sensors reported to date are invariably sensors based on dynamic quenching processes with no specific anion recognition built-in.[20] To our knowledge there have been no quinolinium based sensors derived from preorganised anion receptors capable of binding and discriminating between anions. We now report a receptor based on quinolinium functionalities that acts as both binding and 'turn off' fluorescent sensing unit appended to a hexa-substituted benzene core.

Synthesis

The synthesis of compound **1** (Scheme 1) involves the reaction of quinoline with 1,3,5-tribromomethyl-2,4,6-triethylbenzene in a manner analogous to related pyridinium-based receptors.[5] The reaction time required is considerably longer than for the pyridinium compounds (*ca.* 48 h as opposed to 6 h) and reflects the added steric hindrance found in the quinolinium derivative. The (unoptimised) isolated yield is also lower (24%) compared to 92% for the pyridinium analogue. However, the low yield might be due in part to the repeated recrystallisation required to remove the incompletely reacted two arm substituted product. The control compound **2** has also been prepared in an analogous manner. This lacks the preorganised, multiply charged binding cavity found in compound **1** and allows a comparison to be made between preorganised multivalent[24] and non-preorganised, single binding site quinolinium based anion sensors.



Scheme 1 Compounds **1** and **2**.

The structure of compound **2** was confirmed by single crystal X-ray structural determination (Fig. 1). The crystal packing exhibits π–π stacking of the aryl rings, with a plane to plane distance of 3.616(3) Å. The crystal also shows quinolinium to quinolinium π–π stacking with a plane to plane distance of 3.413(2) Å.

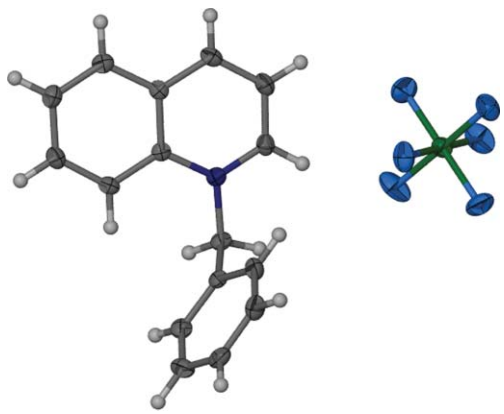


Fig. 1 Molecular structure of compound **2**.

[a]*Department of Chemistry, Durham University, South Road, Durham, UK DH1 3LE. E-mail: jon.steed@durham.ac.uk; Fax: +44 191 384 4737; Tel: +44 191 334 2085*
[b]*School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, UK EH14 4AS*

† Electronic supplementary information (ESI) available: Fig. S1–S8. CCDC reference number 755341. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b919821k

Solution state binding properties

The solution state binding properties of compound **1** were investigated using ^{1}H NMR spectroscopic titration in CD_3CN solvent with a number of anion guests. The binding isotherms are shown in Fig. 2.

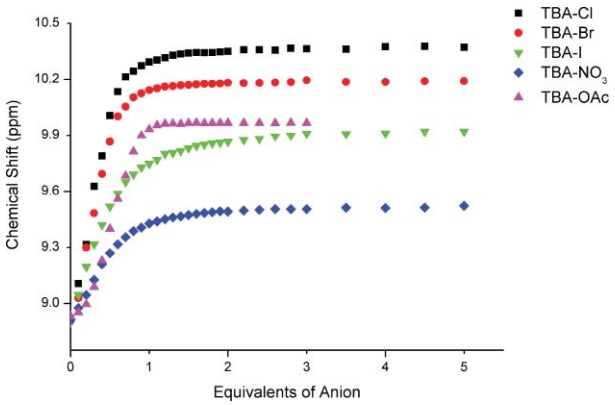


Fig. 2 Binding isotherms for the *ortho*-quinolinium proton of compound **1** with various anions in acetonitrile-d_3. Precipitation occurred after 3 equivalents of acetate.

Significant chemical shift changes in the resonances assigned to the protons *ortho* and *meta* to the quinolinium nitrogen atom were observed, with very small shifts for the other signals. In all cases, inflections in the isotherms occur before the addition of one equivalent of anion, suggesting more a complicated series of binding equilibria than a 1 : 1 host : guest stoichiometry.

In order to determine the appropriate binding model a Job plot with TBA-I was determined (Fig. 3). Iodide was chosen due to the high solubility of the host–iodide complex. The data points appear skewed further to the right hand side of the plot than might be expected for a 1 : 1 host : guest stoichiometry. A 2 : 1 host : guest stoichiometry would give rise to a maximum at a mole fraction of 0.66, whereas a 1 : 1 host : guest stoichiometry would give a maximum at 0.5 mole fraction. It is possible that both of these species coexist resulting in an intermediate value between the two.

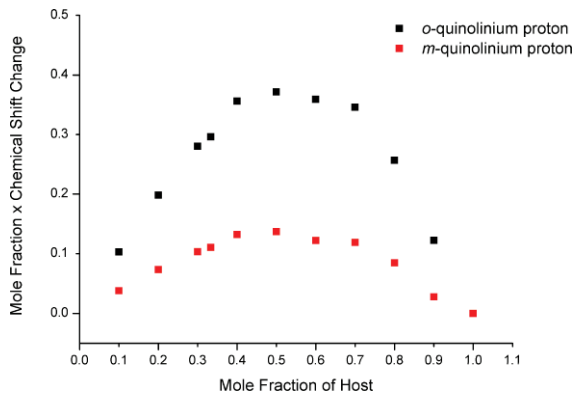


Fig. 3 Job plot for compound **1** with TBA-I.

The presence of a host dimer can be established *via* a dilution study on the host as the PF_6^- salt (Fig. 4). The host shows modest chemical shift changes as a function of concentration however a value of log K_{20} = 1.57(7) fits the data well. This

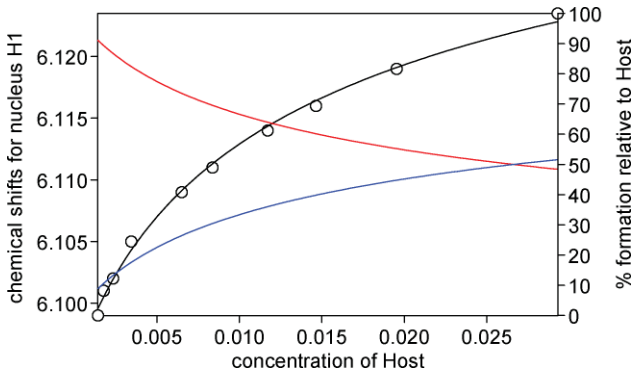


Fig. 4 ^{1}H NMR dilution study for **1**. The CH_2-quinolinium proton is followed.

dimerisation constant was included into the stoichiometry model incorporating both 1 : 1 and 2 : 1 host : anion complexes, to give an improved fit to the complexation data. The binding constants thus determined for compound **1** for various anions are summarised in Table 1 as determined by non-linear least squares fitting using HypNMR 2006.[25] DOSY NMR experiments were attempted to further confirm the presence of a host dimer. However as the dimer also forms in the presence of anions other than PF_6^- this technique was not able to distinguish a change in diffusion coefficient within the experimental error.

Bromide was found to bind the strongest, with chloride having a similar affinity. Iodide is bound significantly less strongly than the other anions tested. Interestingly, the compound shows strong binding to nitrate, with binding constants in the same region as those to chloride. Binding constants could not be refined for acetate in this solvent due to very strong binding. A ^{1}H NMR spectroscopic titration of compound **1** with acetate in DMSO-d_6 (a more competitive solvent) was carried out, unfortunately small chemical shift changes were observed (*ca.* 0.2 ppm) for which a binding constant could not be determined.

The ^{1}H NMR spectrum of compound **2** was also recorded with the addition of 1, 2 and 3 equivalents of TBA-Cl. The major change is a shift of the peak at 9.17 ppm by up to 0.3 ppm, accompanied by broadening and is in contrast to compound **1** in which a change of approximately 1.5 ppm is observed. All other chemical shift

Table 1 Binding constants determined by ^{1}H NMR spectroscopic titrations

Anion	Stoichiometry (H–G)	Log β_{HG} **1**
Host Dimer	2 : 0	1.57(7)
Cl^-	1 : 1	4.54(5)
	2 : 1	8.01(8)
Br^-	1 : 1	4.75(5)
	2 : 1	8.10(7)
I^-	1 : 1	3.391(1)
	2 : 1	6.120(8)
NO_3^-	1 : 1	4.55(2)
	2 : 1	8.18(3)
$CH_3CO_2^-$	[a]	
$H_2PO_4^-$	[b]	
HSO_4^-	[b]	

[a] Binding constant too large to be determined by this method. [b] Precipitate.

changes for compound **2** are less than 0.1 ppm. This experiment implies that there is a markedly weaker interaction between anions and **2** compared to the preorganised, multidentate compound **1**.

DFT calculations were used to further understand the binding mode of compound **1**. The complex geometry was optimised using a B3LYP/4-31G basis set on the host with the hydrogen atoms proximal to the anion augmented with additional s and p diffuse functions and a B3LYP/6-311+G* basis set on chloride and B3LYP/6-31+G* on acetate.

The optimised 1 : 1 host : guest complex of **1** with chloride is shown in Fig. 5. The complex shows C_{3v} symmetry with hydrogen bonding to the chloride by *o*- and *m*-quinolinium hydrogen atoms. The hydrogen bonding pattern suggested by the calculation matches the pattern of contact induced chemical shift changes observed using ^{1}H NMR spectroscopic titrations in solution. Acetate also binds strongly to the host. The non-spherical shape of the acetate means the optimised geometry consists of each acetate oxygen atom hydrogen bonded to two quinolinium arms.

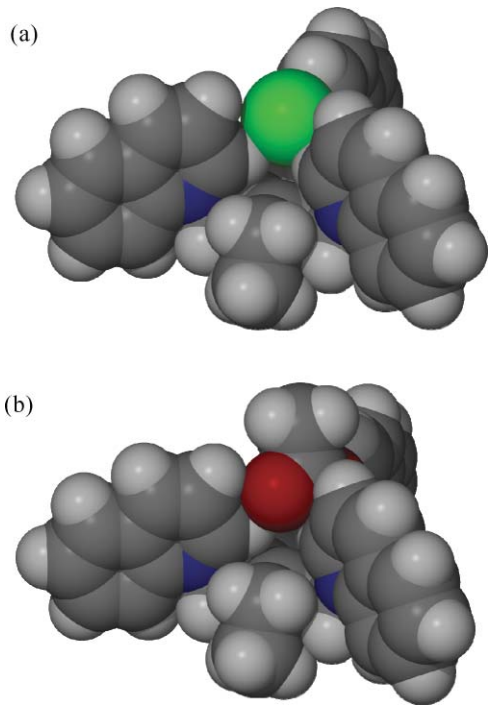


Fig. 5 DFT optimised geometries for (a) **1** with chloride and (b) **1** with acetate.

The binding equilibrium suggested by ^{1}H NMR titration data suggests a 2 : 1 host : guest complex. DFT calculations were used to further test the feasibility of this complex. Fig. 6 shows the optimised geometry for the 2 : 1 host : chloride complex. The chloride is equidistant between the two cations and sits higher in the binding cavity than is observed for the 1 : 1 complex. At low basis sets the complex falls apart and is only stable using higher basis sets. This suggests that the interactions in the complex are weak, as would be expected given the electrostatic repulsion between the two hosts and the measured association may have a significant solvophobic component.

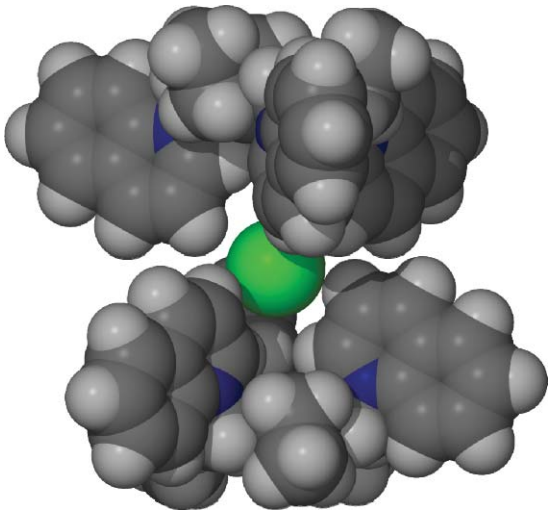


Fig. 6 DFT optimised geometry for the 2 : 1 host : guest structure of **1** with chloride.

Photophysical properties

The absorbance and excitation spectra of **1** as the hexafluorophosphate salt are shown in Fig. 7. Both spectra show the same λ_{max} of 317 nm (typical for a compound of this type) and the same overall band shape.[20,26,27] A broad featureless emission band is observed with a tail reaching to approximately 550 nm and a Stokes shift of 90 nm.

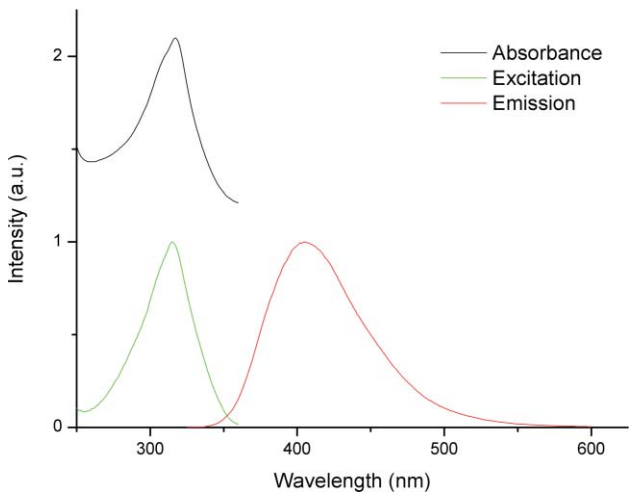


Fig. 7 Photophysical properties of compound **1**. λ_{ex} = 317 nm. λ_{em} = 408 nm.

The fluorescent properties of compound **2**, used as a standard, were also investigated. The band shapes and λ_{max} of the absorbance, excitation and emission spectra, are identical to that of compound **1**.

The photoluminescent quantum yield (PLQY) of compounds **1** and **2** was calculated *via* an integration sphere methodology[28] to give a PLQY of 0.21 for compound **1** and a markedly lower value of 0.09 for compound **2**. Table 2 collates the important photophysical data of compound **1** and **2**. The effect of the addition of anions on the fluorescent emission of compound **1** was investigated using fluorescent spectroscopic titrations. Solutions of

Table 2 Summary of the photophysical properties of **1** and **2**

	Compound	
	1	**2**
Absorbance λ_{max}/nm	317	317
Excitation λ_{max}/nm	317	317
Emission λ_{max}/nm	408	408
PLQY	0.21	0.09
Lifetime	17.7	5.1
ns	2.26	1.84
$E_{1/2}$	–0.79	–0.84
V *vs.* SCE		

2.33×10^{-6} mol dm^{-3} of host were titrated against the TBA-salts of chloride, bromide, iodide, nitrate and acetate. Fig. 8 shows the quenching of the fluorescence emission observed with the addition of acetate.

This quenching is significant and can be observed with the naked eye, Fig. 9.

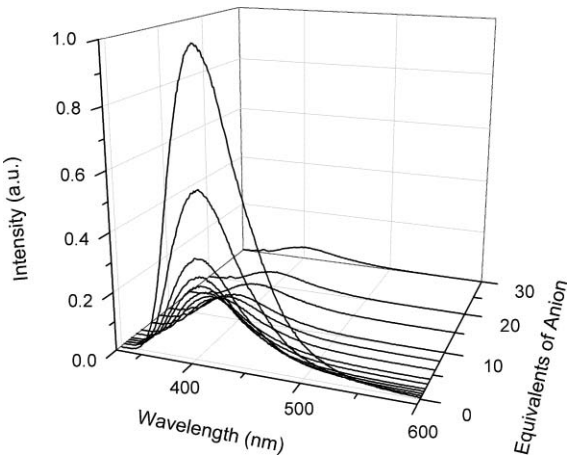


Fig. 8 Fluorescence quenching of **1** upon addition of acetate.

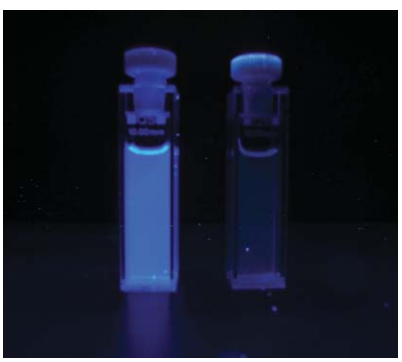


Fig. 9 Compound **1** (1×10^{-4} mol dm^{-3}) in the absence of acetate (left) and the presence of excess acetate.

Stern–Volmer plots were created for the various anions titrated and have been corrected for dilution effects (Fig. 10). Due to the complex nature of the binding equilibrium it is not possible to fit the data using standard Stern–Volmer equations although

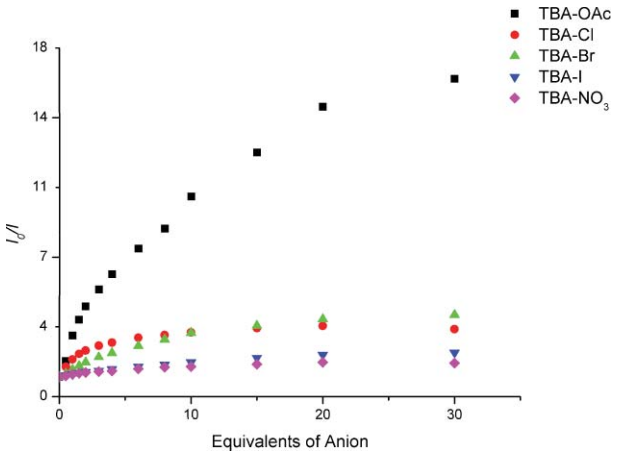


Fig. 10 Stern–Volmer plot for compound **1** with various anions.

the data are still useful in a qualitative sense. For ease of interpretation the number of equivalents of guest rather than quencher concentration is used for the *x*-axis. As can be seen from Fig. 10, acetate is by far the best quencher at virtually all equivalents of guest, and it can therefore be concluded that the receptor is selective for acetate and discriminates this anion. This also corresponds well to the strong binding of acetate by **1** shown by ^{1}H NMR. Interestingly, chloride is also a very good quencher, showing equal or better quenching than the heavier atom bromide (especially at low equivalents). Iodide on the other hand is much worse at quenching the fluorescence. This is the opposite selectivity observed for related published quinolinium based systems containing one fluorophore, which are dominated by the electron transfer properties of the anion in water.[29] A dynamic quenching mechanism has been suggested for these compounds that does not involve specific complex formation.[20] Thus the present preorganised anion receptor is apparently altering the ability of the quinolinium to discriminate particular anions by means of its fluorescence emission by specific binding effects, with strongly bound anions such as chloride quenching more than iodide.

The control compound **2** also shows quenching of its fluorescence upon addition of anions. A linear trend with anion concentration is observed in most cases. Table 3 contains the calculated K_{sv} values. Comparison of the K_{sv} values to the literature for similar systems shows compound **2** has much less variation in the K_{sv} than has previously been observed, although water was used in previous work instead of acetonitrile.[20,26,27,30] This may be explained by binding processes supported by NMR evidence (*vida supra*). This observation along with the use of a less viscous solvent may, in part, explain the observations.[29] Importantly, compound **1** shows significantly higher quenching and greater discrimination of anions than compound **2**.

Table 3 Stern–Volmer data for compound **2**

Anion	K_{sv}/M^{-1}
Chloride	570 ± 50
Bromide	490 ± 40
Iodide	410 ± 40
Nitrate	600 ± 40
Acetate	Non-linear

Typically Stern–Volmer plots are linear for static or dynamic quenching, showing deviation if mixtures of the two mechanisms are operating.[18,20] The Stern–Volmer plot for acetate quenching of **1** shows two principal regions—significant quenching up to 2 equivalents of anion followed by a shallower region which eventually begins to curve. Since the binding affinity is high, complexation is likely to be essentially complete after the addition of only a few equivalents of guest and hence the continued quenching up to a 30 fold excess of anion suggests that a collisional quenching mechanism is also operating.

UV-vis spectroscopic titrations were used to investigate the effect of anion on the absorbance bands of compounds **1** and **2** as a means of distinguishing the quenching mechanisms. Fig. 11 shows the UV absorbance spectrum of compound **1** with a λ_{max} of 317 nm in the absence of guest and in the presence of 10 equivalents of TBA-Cl with negligible dilution effects. It can be seen that there is an increase in the overall intensity of the band and a small shift in the λ_{max} (*ca.* 2 nm), suggesting the formation of a host–guest complex and static quenching, consistent with the ^{1}H NMR spectroscopic experiments (*vida infra*). The same experiment was also performed on compound **2** there is an overall decrease in the band intensity and no significant λ_{max} change, consistent with dilution effects only and dynamic quenching.

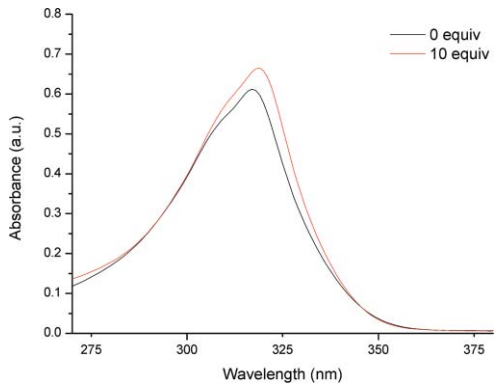


Fig. 11 Absorbance band of compound **1** in the absence and presence of 10 equivalents of TBA-Cl.

A dilution study was also conducted on the host compound in the absence of guest and is shown in Fig. 12. The data shows a distinct non-linear trend and deviates from the Beer–Lambert law. The control compound **2** however shows a linear relationship

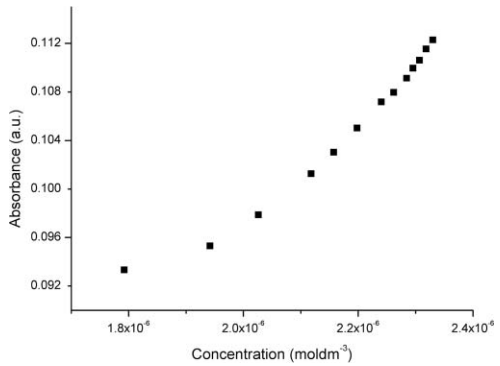


Fig. 12 UV-vis dilution study of compound **1**.

between concentration and absorbance. This provides further evidence for the formation of a host dimer for **1**.

A further method of distinguishing static from dynamic quenching is to investigate how the fluorescent lifetime of a species varies with added anion. The emission from compound **1** and **2** shows a bi-exponential decay, possibly suggesting complex emissive decay processes. Similar behaviour has been observed for related systems and is attributed to nanosecond solvent relaxation processes.[31–33] The fluorescent lifetimes of compound **1** were monitored at a range of anion concentrations for a range of anions. Fig. 13 shows the logarithmic plot of the decay of the fluorescence at various equivalents of chloride. The decay becomes steeper, consistent with shorter lifetimes, and less linear as chloride concentration increases. In all cases a decrease in the excited state lifetime is observed and suggests that both static and dynamic processes contribute to the quenching of the fluorescence of compound **1**.

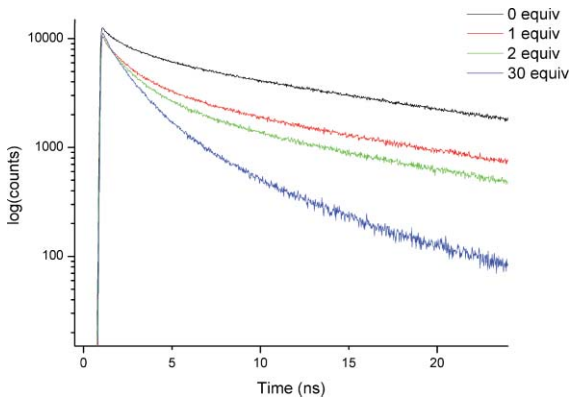


Fig. 13 Logarithmic plot of the fluorescence decay of compound **1** at several different equivalents of TBA-Cl.

Similar experiments conducted on compound **2** also showed a general decrease in the excited state lifetime of the compound in the presence of anion. It seems likely that as with compound **1** there is a mixture of dynamic and collisional quenching occurring for this system. The ^{1}H NMR data suggests static quenching may also play a role in the quenching of compound **2**.

Both compounds exhibit dynamic and collision quenching. However for compound **1** the ^{1}H NMR, UV-vis and fluorescence spectroscopic titrations suggest static quenching is the dominant process. Compound **2** on the other hand appears to be dominated by dynamic quenching.

There are several possible quenching mechanisms for quinolinium based sensors including electron transfer from the anion,[34-36] charge-transfer complex or exciplex formation,[37,38] or heavy atom quenching.[39] Jayaraman *et al.*[29] have shown that the log k_q is linearly proportional to the indicated excited state reduction potential of the quinolinium species and the free energy change for charge transfer. In addition the quenching rate decreases with increasing anion oxidation potential for dynamically quenched systems in water. They conclude therefore that the quenching mechanism is *via* a dynamic excited state charge transfer process.

Whilst a full scale mechanistic study for compounds **1** and **2** has not been undertaken, insights into the mechanism can be gained *via* simple experiments. An estimate of the excited state reduction potential (known as the indicated excited state reduction potential)

for compound **1** and **2** can be calculated by $E_{red} + E_{0,0}$ where E_{red} is the reduction potential and $E_{0,0}$ is the singlet excitation energy. The reduction potential can be obtained by cyclic voltammetry (see Table 2). Both compounds **1** and **2** have the same singlet excitation energy of 3.90 eV and therefore give an indicated excited state reduction potential of 3.11 V and 3.06 V for compound **1** and **2**, respectively. This is exactly in line with that observed for methyl quinolinium.[29] Given the very similar excited state reduction potentials for compounds **1** and **2** to that of methyl quinolinium, which is known to be quenched by charge transfer processes, it is logical to assume that this mechanism also occurs for compounds **1** and **2**. However further experiments would be required to confirm this.

Compound **1** is also water soluble and has the potential to act as an anion sensor in aqueous media. Unfortunately ^{1}H NMR titrations in water showed very small changes in all proton chemical shifts, suggesting the solvent is too competitive for **1** to bind anions effectively. In addition, there is negligible quenching by anions over that of dilution effects. Polar aprotic solvents such as DMSO also proved too competitive for effective anion binding.

Conclusions

It has been shown that a tripodal anion receptor with quinolinium arms providing charge assisted hydrogen bonding functionality, binds anions strongly with complicated speciation consisting of an unbound host, a host dimer, and both 1 : 1 and 2 : 1 host : guest complexes. The fluorescence of the quinolinium groups can be used as an anion sensing reporter, with quenching occurring in the presence of anions. Crucially the preorganised, tripodal receptor, **1** exhibits a different quenching selectivity to simple quinolinium derivatives. A mixture of static and dynamic quenching was observed, with selectivity for acetate. In the case of the preorganised compound **1** static quenching dominates, however for compound **2** dynamic quenching dominates. The mechanism of quenching has provisionally been assigned as *via* the formation of a charge transfer complex.

Experimental

Instrumentation

All NMR spectra were performed on a Varian Mercury-400 (400 MHz for ^{1}H), Varian Inova-500 machine (500 MHz for ^{1}H, 126 Hz for ^{13}C) or a Varian DD-700 (700 MHz for ^{1}H, 176 MHz for ^{13}C) and were referenced to residual solvent. Electrospray (ES) mass spectroscopy was recorded on a Thermo-Finnigan LTQ instrument, whilst Matrix Assisted Laser Desorption Ionisation (MALDI) experiments were recorded on an ABI Voyager-DC STR. Fourier transform infrared spectra were recorded with a Perkin Elmer Spectrum 100 ATR instrument (Perkin-Elmer, Norwalk, Ct., USA). For each spectrum, 64 scans were conducted over a spectral range of 4000 to 600 cm^{-1} with a resolution of 4 cm^{-1}. The analysis was carried out with the Spectrum Express 1.01 software. Elemental analysis was performed using an Exeter Analytical inc. CE-400 Elemental Analyser. Commercial reagents were used as supplied, without further purification. 1,3,5-Tri(bromomethyl)-2,4,6-triethylbenzene was prepared as previously reported.[40]

General procedure for ^{1}H NMR spectroscopic titrations

All chemical shifts are reported in ppm relative to residual solvent. A solution of the host species of known concentration typically 0.5–1.5 mM, was made up in an NMR tube using the appropriate deuterated solvent (0.5 ml). Solutions of the anions, as TBA salts (1 ml) were made ten times the concentration of the host solution. The guest solution was typically added in 10 µl aliquots, representing 0.1 equivalents of the guest with respect to the host. Larger aliquots were used in some cases where no inflection of the trace was evident. Spectra were recorded after each addition and the trace was followed simultaneously. Results were analysed using the curve-fitting program HypNMR 2006.[25]

General procedure for UV-vis spectroscopic titrations

UV-vis titration were carried out using a Perkin-Elmer Lambda 35. A solution of typical concentration 1×10^{-4} mol dm^{-3} of host was made in a volumetric flask. A 3 ml sample of host solution of concentration of 2.33×10^{-6} mol dm^{-3} for **1** and 1×10^{-5} mol dm^{-3} for **2** were prepared by dilution of the stock solution. Guest solutions were prepared such that 300 µl of guest solution corresponds to 10 equivalents of host. Solutions were prepared using acetonitrile as solvent.

Fluorescence spectroscopy

Emission and excitation spectra were obtained using a Jobin-Yvon Horiba Fluorolog 3-22 Tau-3 spectrofluorimeter with a right angle illumination method and were corrected for the spectral response of the instrument.

Fluorescence spectroscopic titrations were carried out using the equipment described above. A solution of concentration 1×10^{-4} mol dm^{-3} of host was made in a volumetric flask. A 3 ml sample of host solution of typical concentration 2.33×10^{-6} mol dm^{-3} for **1** and 1×10^{-5} mol dm^{-3} for **2** were prepared by dilution of the stock solution. Guest solutions were prepared such that 300 µl of guest solution corresponds to 10 equivalents of host. Solutions were prepared using acetonitrile as solvent.

Photoluminescent quantum yields were calculated using either a Jobin-Yvon Horiba Fluorolog 3-22 Tau-3 spectrofluorimeter with a right angle illumination method and an integration sphere, following the integration sphere method of Beeby *et al.*[28]

Lifetimes were obtained *via* the time-correlated single-photon counting technique. The method described by Beeby *et al.*[41] was used. Samples were excited using the third harmonic of mode-locked cavity dumped Ti-sapphire laser. The emission was collected at 90° to the source of excitation and the emission wavelength selected by a monochromator (Jobin Yvon Triax 190). Fluorescence detection was obtained using a single photon avalanche diode (ID-Quantique ID-100) that was linked to a time-to-amplitude converter (Ortec 567) and a pulse height analyser, PHA, (E.G. & G. Trump Card and Maestro for Windows v 5.10). Fluorescence decays were recorded to a minimum of 10 000 counts in the peak channel of the PHA with a record length of 1000 channels. The decay and IRF data were transferred to PC for analysis in Microsoft Excel *via* the method of iterative reconvolution and nonlinear least squares fitting.

General procedure for cyclic voltammetry experiments

Cyclic voltammetry was carried out on a Chi Instruments Model 420 Electrochemical Analyser using two Pt wire counter electrodes and a 2 mm Pt working electrode or a 3 mm glassy carbon working electrode. The ferrocene/ferrocinium redox couple was used as an internal reference. $E_{1/2}$ values are reported *vs.* SCE (Fc = 0.4 V with $TBAPF_6$ in MeCN).[42] A 0.1 mol dm^{-3} solution of $TBAPF_6$ in dry MeCN was used as electrolyte. Solutions were degassed by bubbling through N_2 and the cell was kept under positive pressure of N_2 at all times.

Synthesis of 1

1,3,5-Tri(bromomethyl)-2,4,6-triethylbenzene (0.50 g, 1.13 mmol) and quinoline (0.51 g, 3.97 mmol) were dissolved in dry DCM and heated at reflux for 24 h. The solvent was evaporated and 50 ml of methanol was added to the residue. Ten equivalents of NH_4PF_6 were added and the product was precipitated as the PF_6^- salt. Yield = 0.28 g, 0.27 mmol, 24%. m.p. 210–222 °C; ^{1}H NMR (CD_3CN, 700 MHz) δ = 9.18 (3H, d, J = 8.7 Hz, ArH), 8.77 (3H, d, J = 7.8 Hz, ArH), 8.74 (3H, d, J = 6.0 Hz, ArH), 8.47 (3H, d, J = 7.8 Hz, ArH), 8.40 (3H, t, J = 7.8 Hz, ArH), 8.13 (3H, t, J = 7.8 Hz, ArH), 8.1 (3H, dd, J = 8.7 and 6.0, ArH), 6.13 (6H, s, CH_2-N^+), 2.43 (6H, br q, CH_2CH_3), 1.16 (9H, br t, CH_2CH_3); ^{13}C-{^{1}H} NMR (CD_3CN, 176 MHz) δ = 151.9, 148.5, 145.8, 139.3, 136.6, 131.3, 130.9, 130.6, 127.9, 122.5, 118.7, 54.0, 24.1, 14.6; ν/cm^{-1} 3096 (C–H), 2972 (C–H), 1625 (Ar C=C), 1591 (Ar C=C), 1524 (Ar C=C), 1377, 1229, 987, 817. Found: C, 45.39; H, 4.44; N, 3.74. Calc. for $C_{42}H_{42}F_{18}N_3P_3 \cdot 5H_2O$: C, 45.29; H, 4.71; N, 3.77%. Mass spectrometry could not be obtained for this compound.

Synthesis of 2

Quinoline (0.50 g, 3.9 mmol) was dissolved in dichloromethane (60 ml). Benzyl bromide was added (3.31 g, 19.1 mmol, 5 eq) and the solution refluxed for 24 h. The solvent was removed *in vacuo* resulting in a white powder. The powder was washed with diethyl ether then dissolved in methanol. Excess (1.50 g) NH_4PF_6 was added and a white powder precipitated out of solution slowly. The powder was isolated by filtration, washed with diethyl ether and dried under ambient conditions. m.p. 140–146 °C; ^{1}H NMR (CD_3CN, 700 MHz) δ = 9.17 (2H, m, ArH), 8.39 (1H, d, J = 8.5 Hz, ArH), 8.34 (1H, d, J = 9.6 Hz ArH), 8.16 (1H, m, ArH), 8.08 (1H, dd, J = 9.0, 6.4 Hz, ArH), 7.99 (1H, d, J = 7.3 Hz, ArH), 7.43 (3H, m, ArH), 7.31 (2H, m, ArH), 6.17 (2H, s, CH_2-N^+); ^{13}C-{^{1}H} NMR (CD_3CN, 176 MHz) δ = 150.4, 149.6, 139.4, 137.2, 133.7, 132.0, 131.5, 131.4, 130.4, 130.4, 128.7, 123.2, 119.9, 62.0; m/z (ES^+) 220.1 [M – PF_6]$^+$; ν/cm^{-1} 3097 (C–H), 1627 (Ar C=C), 1590 (Ar C=C), 1528 (Ar C=C), 1456, 1379, 1361, 1045, 817. Found: C, 51.65; H, 3.85; N, 3.91. Calc for $C_{16}H_{14}F_6NP \cdot 0.3H_2O$: C, 51.85; H, 3.97; N, 3.78%.

Acknowledgements

We are grateful to the EPSRC and Durham University for funding, the Heriot-Watt University Information and Computing Services for use of the Heriot-Watt high performance cluster service.

References

1 J. L. Sessler, P. A. Gale and W.-S. Cho, *Anion Receptor Chemistry*, Royal Society of Chemistry, Cambridge, 2006.
2 C. Caltagirone and P. A. Gale, *Chem. Soc. Rev.*, 2009, **38**, 520.
3 P. A. Gale, *Coord. Chem. Rev.*, 2006, **250**, 2917, preface to the special issue and subsequent reviews.
4 T. Gunnlaugsson, M. Glynn, G. M. Tocci, P. E. Kruger and F. M. Pfeffer, *Coord. Chem. Rev.*, 2006, **250**, 3094.
5 K. J. Wallace, W. J. Belcher, D. R. Turner, K. F. Syed and J. W. Steed, *J. Am. Chem. Soc.*, 2003, **125**, 9699.
6 D. R. Turner, M. J. Paterson and J. W. Steed, *J. Org. Chem.*, 2006, **71**, 1598.
7 S. J. Dickson, E. V. B. Wallace, A. N. Swinburne, M. J. Paterson, Gareth. O. Lloyd, A. Beeby and J. W. Steed, *New J. Chem.*, 2008, **32**, 786.
8 A. Barnard, S. J. Dickson, M. J. Paterson, A. M. Todd and J. W. Steed, *Org. Biomol. Chem.*, 2008, **7**, 1554.
9 M. H. Filby, S. J. Dickson, N. Zaccheroni, L. Prodi, S. Bonacchi, M. Montalti, C. Chiorboli, M. J. Paterson, T. D. Humphries and J. W. Steed, *J. Am. Chem. Soc.*, 2009, **130**, 4105.
10 V. Amendola, M. Boiocchi, L. Fabbrizzi and A. Palchetti, *Chem.–Eur. J.*, 2005, **11**, 5648.
11 H. Ihm, S. Yun, H. G. Kim, J. K. Kim and K. S. Kim, *Org. Lett.*, 2002, **4**, 2897.
12 Y. Bai, B. G. Zhang, J. Xu, C. Y. Duan, D. B. Dang, D. J. Liu and Q. J. Meng, *New J. Chem.*, 2005, **29**, 777.
13 Y. Bai, B.-G. Zhang, C. Y. Duan, D.-B. Dang and Q.-J. Meng, *New J. Chem.*, 2006, **30**, 266.
14 J. Zhang, A. M. Bond, J. Belcher, K. J. Wallace and J. W. Steed, *J. Phys. Chem. B*, 2003, **107**, 5777.
15 W. X. Liu and Y. B. Jiang, *Org. Biomol. Chem.*, 2007, **5**, 1771.
16 C. M. G. Dos Santos, T. McCabe and T. Gunnlaugsson, *Tetrahedron Lett.*, 2007, **48**, 3135.
17 R. M. Duke and T. Gunnlaugsson, *Tetrahedron Lett.*, 2007, **48**, 8043.
18 C. M. G. Dos Santos, M. Glynn, T. McCabe, J. S. S. De Melo, H. D. Burrows and T. Gunnlaugsson, *Supramol. Chem.*, 2008, **20**, 407.
19 E. B. Veale, G. M. Tocci, F. M. Pfeffer, P. E. Kruger and T. Gunnlaugsson, *Org. Biomol. Chem.*, 2009, **7**, 3447.
20 C. D. Geddes, *Meas. Sci. Technol.*, 2001, **12**, R53.
21 C. D. Geddes, *J. Photochem. Photobiol., A*, 2000, **137**, 145.
22 M. S. Mehata and H. B. Tripathi, *J. Lumin.*, 2002, **99**, 47.
23 O. van den Berg, W. F. Jager and S. J. Picken, *J. Org. Chem.*, 2006, **71**, 2666.
24 L. Baldini, A. Casnati, F. Sansone and R. Ungaro, *Chem. Soc. Rev.*, 2007, **36**, 254.
25 P. Gans, *HypNMR 2006*, University of Leeds, Leeds.
26 C. D. Geddes and P. Douglas, *J. Appl. Polym. Sci.*, 2000, **76**, 603.
27 R. Krapf, N. P. Illsley, H. C. Tseng and A. S. Verkman, *Biophys. J.*, 1988, **53**, A196.
28 L. Porres, A. Holland, L. O. Palsson, A. P. Monkman, C. Kemp and A. Beeby, *J. Fluoresc.*, 2006, **16**, 267.
29 S. Jayaraman and A. S. Verkman, *Biophys. Chem.*, 2000, **85**, 49.
30 C. D. Geddes, K. Apperson, J. Karolin and D. J. S. Birch, *Dyes Pigm.*, 2001, **48**, 227.
31 C. D. Geddes, K. Apperson and D. J. S. Birch, *Dyes Pigm.*, 2000, **44**, 69.
32 S. G. Schulman, R. M. Threatte, A. C. Capomaccia and W. L. Paul, *J. Pharm. Sci.*, 1974, **63**, 876.
33 D. Pant, H. B. Tripathi and D. D. Pant, *J. Lumin.*, 1992, **51**, 223.
34 J. Najbar and M. Mac, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 1523.
35 H. Shizuka, M. Nakamura and T. Morita, *J. Phys. Chem.*, 1980, **84**, 989.
36 H. Shizuka, T. Saito and T. Morita, *Chem. Phys. Lett.*, 1978, **56**, 519.
37 K. A. Abdullah and T. J. Kemp, *J. Photochem.*, 1985, **28**, 61.
38 A. R. Watkins, *J. Phys. Chem.*, 1973, **77**, 1207.
39 J. Bendig, S. Helm and D. Kreysig, *Chem. Phys. Lett.*, 1978, **54**, 466.
40 K. J. Wallace, R. Hanes, E. Anslyn, J. Morey, K. V. Kilway and J. Siegel, *Synthesis*, 2005, 2080.
41 A. Beeby, S. FitzGerald and C. F. Stanley, *Photochem. Photobiol.*, 2001, **74**, 566.
42 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877.

