Optical–structural correlation in a novel quinoxaline-based anion sensor

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Protonation of 2,3-dipyridin-2-ylquinoxaline **1** results in a significant change in the conformation of the molecule as revealed by ^{1}H NMR and optical spectroscopies and by single crystal X-ray diffraction studies performed upon the product, 2-(3-pyridin-2-ylquinoxalin-2-yl)pyridinium hexafluorophosphate, **2**. A further consequence of protonation is that the electronic properties of **2** are altered in such a way as to produce a luminescent compound, the luminescence of which is quenched by a variety of biologically and commercially relevant anions.

There is considerable current interest in the development of molecular and supramolecular systems which have the ability to identify and signal the presence of negatively charged ions.[1] The motivation behind such studies is the recognition that anions enjoy an important role in biology, medicine and the environment.[2] There exists a wide variety of systems which are capable of behaving as anion sensors, and a number of excellent reviews of the topic are available.[3–5] We are particularly interested in sensors which do not utilise a metal centre in anion binding, and recently there have been several reports of anion sensors of this kind.[6–8] Metal-free anion sensors typically utilise hydrogen bonding and electrostatic interactions to bind anions, and many varieties exist based on chemical archetypes including amides, ureas, pyrroles, ammonium macrocycles, guanidinium and pyridinium moieties.[2,5] The latter type of functionality consists of positively charged groups which are capable of forming hydrogen bonds to anions through quaternised NH groups in addition to utilising coulombic interactions between the charged receptors and guest anions.[7] The use of hydrogen bonding is essential to the majority of anion receptors, and in neutral systems such as amides and ureas, it is the 'acidic' amide protons which act as hydrogen-bond donors. Macrocyclic systems such as those based upon amide-derivatised calix-[4]arenes[9] and hetero-calixarenes[10] have also been employed as anion sensing devices because their cavities may be 'tuned'.[11] They may be used in ion selective electrode (ISE) systems,[12] yielding a colourimetric response to anion recognition,[13] or act as luminescent anion sensors.[14] Indeed, luminescent signalling of anion recognition has been achieved using a variety of chemical units including naphthalene, anthracene, pyrene and quinoxaline derivatives which operate by either quenching of luminescence or conversely by suppression of photoinduced electron transfer (PET) and enhancement of luminescence upon anion association.[15] Sensors based on anion-induced changes in luminescence properties are particularly attractive because of their potential for high selectivity at low substrate concentrations.[7] Additionally, such sensors are of great utility because of their relative ease of use as compared with more established methods for anion detection.[16] Advantageous properties for such sensors include selectivity for the target substrate, an ability to both absorb and emit within the visible region (*i.e.* $\lambda > 350$ nm)[7] and an ability to function in the presence of water or in a solvent in which water is miscible.

We found that all of these criteria were met by the pyridinium salt of 2,3-dipyridin-2-ylquinoxaline, **1**: 2-(3-pyridin-2-ylquinoxalin-2-yl)pyridinium, **2**. Our studies with this compound developed from our interest in coordination complexes which incorporate **1** as a ligand,[17–19] where the topological and electronic properties[20] of the molecule make it particularly useful as a bridging motif. Indeed, the electronic properties of **1** are well established and it is known to be an electron-accepting ligand which may be readily reduced by alkali metals in solution, yielding stable radical anion salts.[21] Conversely, it has been shown that the pyridyl nitrogen atoms of **1** can enter into a charge-transfer complex with diatomic iodine by acting as a Lewis base through an $n \rightarrow \sigma^*$ interaction.[22] The spectroscopic properties of quinoxaline based chromophores are also particularly attractive because this moiety may be readily functionalised, allowing facile steric and electronic 'tuning' of the back-bone to be made.[16] Nevertheless, whilst extensive photo- and physico-chemical studies have been performed upon **1** and its compounds, we are unaware of such studies having included **2**. We address this shortfall here and in addition to reporting the synthesis, solution and solid-state structural characterisation of **2**, we present its full optical characterisation, including its luminescence behaviour in the presence of a variety of biologically and commercially relevant anions.

Experimental

All reagents used were obtained from commercial sources and were used as received. ^{1}H NMR spectra were recorded on a Bruker DPX-400 spectrometer using CD_3CN with TMS as an internal standard. IR spectra were recorded as KBr pellets on a Perkin Elmer Paragon 1000 FT-IR spectrometer. Electrospray mass spectra (ESMS) were recorded on a Micromass LCT electrospray mass spectrometer. UV–Visible absorption spectra were recorded on a Unicam UV4 spectrometer, typically as 10^{-4} M solutions in 1 cm quartz cuvettes. Elemental analyses were carried out at the Microanalytical Laboratory, University College Dublin. Luminescence spectra were recorded on a Perkin Elmer LS50B luminescence spectrometer. 2,3-Dipyridin-2-ylquinoxaline, **1**, was prepared by the literature method[23] without significant modification.

2-(3-Pyridin-2-ylquinoxalin-2-yl)pyridinium hexafluorophosphate, 2

2,3-Dipyridin-2-ylquinoxaline (284 mg, 1 mmol) was slowly dissolved with stirring and gentle heating in 1.0 M HCl (8 ml). To this solution was added a saturated aqueous solution of

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Table 1 Single crystal diffraction parameters for compound **2**

	2
Chemical formula	$C_{18}H_{13}N_4PF_6$
Formula weight	430.29
Crystal system	Monoclinic
Space group	$P2_1/c$
μ(Mo-Kα)/cm^{-1}	0.228
a/Å	9.009(1)
b/Å	20.526(3)
c/Å	9.623(1)
α/°	90
β/°	92.156(3)
γ/°	90
V/Å^3	1778.3(4)
Z	4
T/K	153(2)
R_{int}	0.100
R, $wR2$ [$I > 2\sigma(I)$]	0.0526, 0.1096
R, $wR2$ (all data)	0.1090, 0.1317
Reflections:	
collected	18549
independent	4135

NH_4PF_6 in dropwise fashion until all precipitation had ceased. The suspension was then cooled to 4 °C for 2 h. After this time, the colourless precipitate was removed by filtration and washed with water. Recrystallisation from acetonitrile and diethyl ether gave a colourless crystalline solid (378 mg, 88%). Found: C, 49.99; H, 2.97; N, 12.86%. $C_{18}H_{13}N_4PF_6$ requires C, 50.24; H, 3.05; N, 13.02%. λ_{max}/nm (MeCN) 337 (ε/M^{-1} cm^{-1} 7830), 284 (26500) and 250 (19590). δ_H (CD_3CN, 400 MHz): 7.87 (t, 2H, J = 6.88 Hz), 7.99 (dd, 2H, J = 2.96, 5.55 Hz), 8.17 (m, 2H), 8.37 (t, 2H, J = 7.84 Hz), 8.43 (d, 2H, J = 7.84 Hz), 8.76 (d, 2H, J = 4.88 Hz), 15.45 (s, 1H). ν_{max}/cm^{-1} (KBr) 840 ($\nu(PF_6)$). ESMS (MeCN): m/z 285.07 $(M - PF_6)^+$.

Crystallographic measurements on 2

The single crystal X-ray diffraction experiment (Table 1) was carried out on a Bruker SMART diffractometer. A crystal was mounted onto the diffractometer under dinitrogen at *ca.* 120 K. An empirical absorption correction was applied using SADABS. Structure solution and refinement used SHELXTL Version 5.1 (Sheldrick, 1998).[24] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located from a Fourier difference map and were subject to full refinement. CCDC reference number 159689. See http://www.rsc.org/suppdata/p2/b1/b102023o/ for crystallographic files in cif or other electronic format.

Anion affinity studies

Assessments of anion affinities for **2** were deduced by observing the extent to which the luminescence intensity of the sensor was quenched at its maximum at 454 nm by the addition of solutions of each anion according to eqn. (1),[25] where F refers to the

$$F/F_o = (1 + (k_f/k_s)K[L])/(1 + K[L]) \quad (1)$$

fluorescence intensity at any given anion concentration, F_o is the fluorescence intensity of the receptor alone, k_f is the proportionality constant of the association complex, k_s is the proportionality constant of the substrate and K is the anion association constant. A typical experiment involved addition of 5 μL aliquots of a solution of the anion in question (of concentration 0.01 to 1.0 M depending on the degree of quenching efficiency) to a 1.4×10^{-4} M solution of the sensor **2**. All experiments were carried out in HPLC grade acetonitrile (Lab-Scan Analytical Sciences), although it was noted that the addition of stoichiometric quantities of water had no effect on the luminescence intensity of **2**. All anions were used as their tetrabutylammonium salts.

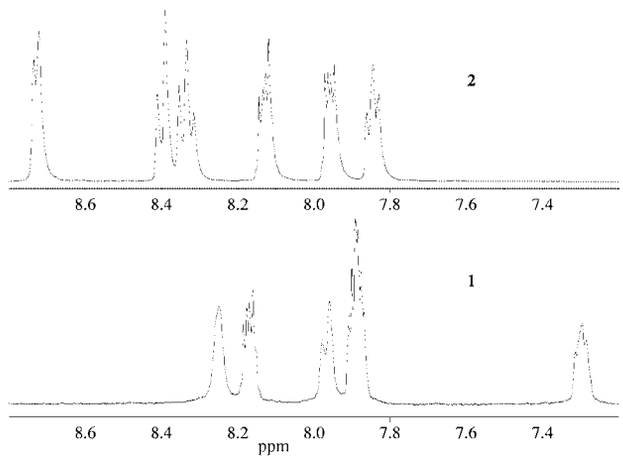


Fig. 1 Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) of **1** and **2**.

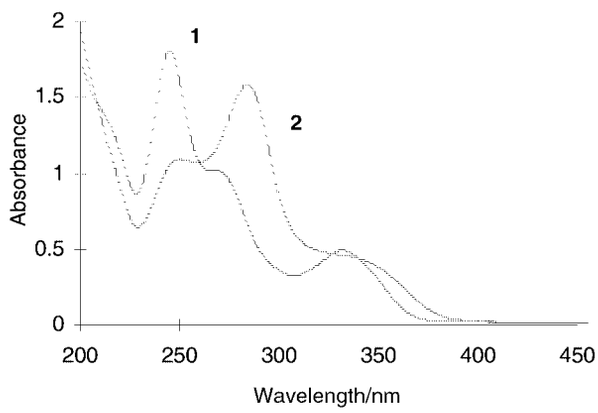
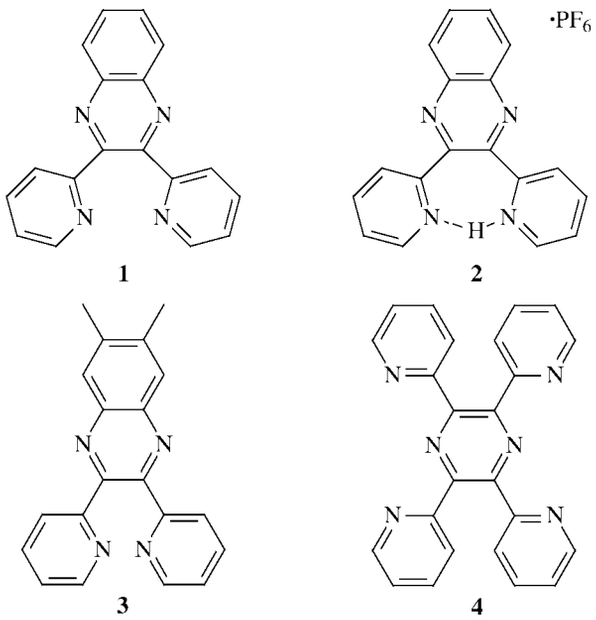


Fig. 2 Absorption spectra of **1** and **2** in acetonitrile solution.

Results and discussion

Before considering the structural and physical properties of **2**, it is instructive to first investigate the attributes of the parent compound 2,3-dipyridin-2-ylquinoxaline, **1**. This well-known molecule was prepared by the straightforward condensation of 1,2-phenylenediamine with 2,2′-pyridil.† [23] The free base consists of two pyridyl rings attached *ortho* to one another on the quinoxaline moiety. In CD_3CN the ^{1}H NMR spectrum of **1** indicates that the compound is symmetrical about its C_2 axis, in that only four signals corresponding to pyridyl protons and one broad AA′BB′ signal corresponding to the quinoxaline protons are observed (Fig. 1). The optical properties of **1** in acetonitrile (Fig. 2) are unremarkable, with absorbance at 332 nm (ε = 13000 M^{-1} cm^{-1}), 268 nm (27000 M^{-1} cm^{-1}) and 246 nm (40300 M^{-1} cm^{-1}), and extremely weak luminescence at 405 nm ($\varphi = 1.2 \times 10^{-4}$ upon excitation at 332 nm). Protonation yields **2**. Whilst microanalysis, infrared and mass spectra were consistent with the formation of a protonated salt, ^{1}H NMR spectroscopy (Fig. 1) verified that, in fact, the pyridinium salt had been produced, as only four pyridyl signals were observed, indicating that **2** is symmetrical about its C_2 axis in solution. The splitting pattern of the quinoxaline ring protons also attests to this symmetry. This may not have been expected and, indeed, is contrary to that found for the semi-perchlorate salt of 2,3-dipyridin-2-yl-6,7-dimethylquinoxaline, **3**, which is protonated on the quinoxaline rather than the pyridyl nitrogen atom.[26] In the case of **2**, however, the presence of the NH proton at 15.45 ppm in the ^{1}H NMR spectrum, coupled with the obvious symmetry of the molecule, suggests that the proton may be part of a strong intramolecular N^+–H ··· N hydrogen bond.

† The IUPAC name for 2,2′-pyridil is di-2-pyridylglyoxal.



The optical properties of **2** differ quite markedly from those of **1**,[27] such that the compound now is strongly luminescent in solution. The absorption spectrum of **2** in acetonitrile also shows significant changes, with the absorption band at 337 nm not appearing to have changed significantly, contrasting with the bands which were observed at 246 and 268 nm in **1** which appear to have been red-shifted to 250 and 284 nm in **2** (Fig. 2). As a corollary of this change, the emission band of **2** is also red-shifted to 454 nm with the intensity of the emission being increased significantly ($\varphi = 8.0 \times 10^{-4}$ and $\tau = 0.13$ ns upon excitation at 332 nm). Such changes in wavelength are consistent with a lowering in the energy gap between the HOMO and the LUMO of the molecule upon protonation, whilst the increase in intensity of the emission band indicates that a change has occurred within the molecule which allows it to function more efficiently as a chromophore. Such a change could be explained if the conjugation within the molecule were extended so that the quinoxaline and perhaps the pyridyl rings were involved in electron delocalisation. Steric crowding would clearly prevent **2** from adopting a strictly planar conformation and yet it appears that conjugation throughout the molecule has been increased. We determined to elucidate the structure of **2** as its hexafluorophosphate salt, in the hope that these novel properties could be explained and perhaps exploited to yield a potential anion sensor. Such hopes were based on the knowledge of the solid state structures of doubly protonated tetra(2-pyridyl)pyrazine,[28] **4**, and of the protonated **3**,[29] where it has been shown by the application of NMR and X-ray diffraction studies that a dramatic distortion of the molecular backbone takes place upon protonation. To discern the degree of coplanarity of the pyridyl rings with the quinoxaline moiety of **2**, and therefore gain insight into the electron delocalisation that may be possible, a single crystal X-ray diffraction study was undertaken.

Crystal structure of 2

The atomic numbering scheme and atom connectivity for **2** are shown in Fig. 3. In itself there is nothing unusual or remarkable about the structure of **2**, as the bond lengths and angles are as expected for a quinoxaline-based ring system, Table 2. More specifically though, the structure of **2** shows remarkable differences to that of its parent free base, **1**, previously described by the group of Brewer,[30] and whose more salient features are compared here. Firstly, the angle of the pyridyl rings to each other has dropped markedly to 32.0(1)° (*cf.* **1**, 62.1(1)°), and a substantial decrease in the torsion angle between the carbon–

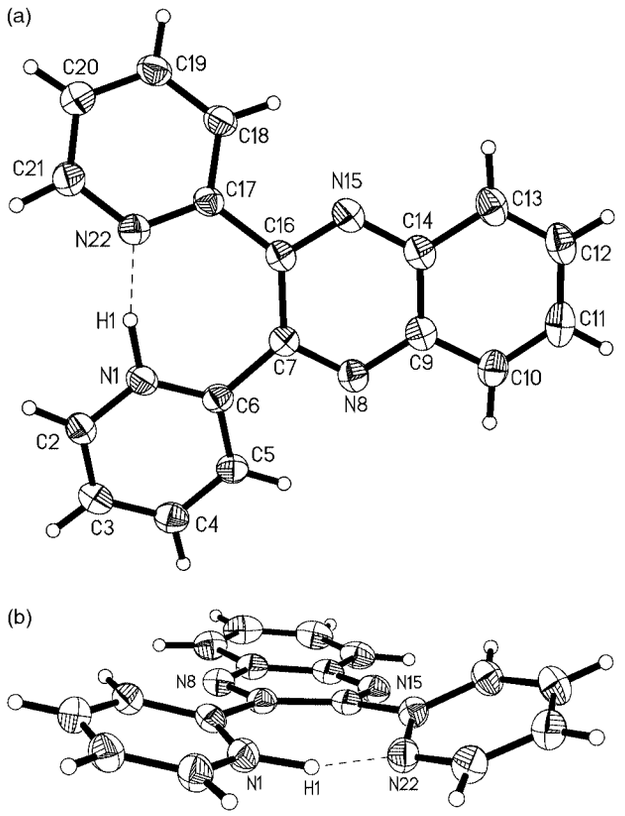


Fig. 3 a) Molecular structure and atomic numbering scheme for **2**. b) Side-view of **2** showing extended planarity. Thermal ellipsoids are shown at the 50% level. Hexafluorophosphate anion omitted for clarity.

Table 2 Selected bond lengths (Å) and angles (°) for **2**

N(1)–C(6)	1.339(3)	C(3)–C(4)–C(5)	120.1(3)
N(1)–C(2)	1.346(3)	C(4)–C(5)–C(6)	119.7(3)
C(2)–C(3)	1.366(4)	N(1)–C(6)–C(5)	118.7(2)
C(3)–C(4)	1.375(4)	N(1)–C(6)–C(7)	120.5(2)
C(4)–C(5)	1.383(4)	C(5)–C(6)–C(7)	120.9(2)
C(5)–C(6)	1.386(4)	N(8)–C(7)–C(16)	119.9(2)
C(6)–C(7)	1.501(4)	N(8)–C(7)–C(6)	111.0(2)
C(7)–N(8)	1.324(3)	C(16)–C(7)–C(6)	129.1(2)
C(7)–C(16)	1.460(4)	C(7)–N(8)–C(9)	119.8(2)
N(8)–C(9)	1.359(3)	N(8)–C(9)–C(14)	120.1(2)
C(9)–C(14)	1.410(4)	N(15)–C(14)–C(9)	120.1(2)
C(14)–N(15)	1.358(3)	C(16)–N(15)–C(14)	120.2(2)
N(15)–C(16)	1.317(3)	N(15)–C(16)–C(7)	119.7(2)
C(16)–C(17)	1.503(4)	N(15)–C(16)–C(17)	111.0(2)
C(17)–N(22)	1.335(3)	C(7)–C(16)–C(17)	129.1(2)
C(17)–C(18)	1.398(4)	N(22)–C(17)–C(18)	120.8(2)
C(18)–C(19)	1.383(4)	N(22)–C(17)–C(16)	120.8(2)
C(19)–C(20)	1.372(4)	C(18)–C(17)–C(16)	118.5(2)
C(20)–C(21)	1.370(4)	C(19)–C(18)–C(17)	118.6(3)
C(21)–N(22)	1.344(3)	C(20)–C(19)–C(18)	120.0(3)
C(6)–N(1)–C(2)	122.2(2)	C(21)–C(20)–C(19)	118.6(3)
N(1)–C(2)–C(3)	120.7(3)	N(22)–C(21)–C(20)	122.2(3)
C(2)–C(3)–C(4)	118.6(3)	C(17)–N(22)–C(21)	119.8(2)

carbon bonds connecting the pyridine rings to the pyrazine ring of the quinoxaline moiety (C(6)–C(7)–C(16)–C(17)) to 7.3(1)° (*cf.* 30.3(2)° in **1**) is evident. Secondly, the angles subtended by the pyridyl ring mean planes, (N(1)–C(2)–C(3)–C(4)–C(5)–C(6)) and (C(17)–C(18)–C(19)–C(20)–C(21)–N(22)), to the quinoxaline ring mean plane, (C(7)–N(8)–C(9)–C(14)–N(15)–C(16)), have also fallen significantly to 11.2(1)° and 25.2(1)° (*cf.* 31.7(2)° and 46.6(2)° in **1**). There is also a reduction in the degree of distortion of the pyrazine ring from planarity, which in the current instance is only removed from it by 3.5(1)° (*cf.* 8.4(1)° in **1**). As a consequence of these differences the structure of **2** is considerably flattened with respect to that of **1**.

Table 3 Anion affinity constants (K_a) for compound **2** as determined by luminescence quenching (λ_{max}(ex) = 332 nm, λ_{max}(em) = 454 nm). All errors are ± 10%. Affinity constants are reported as the average of 4 determinations

Anion	K_a /M^{-1}
$H_2PO_4^-$	21500
PF_6^-	20
F^-	19400
Cl^-	13400
Br^-	530
I^-	140

Optical–structural correlation in 2

Such flattening in **2** would be expected to have a noticeable effect upon electronic communication within the molecule, by increasing the amount of electron density delocalisation that is possible. This quite remarkable structural outcome offers a credible explanation for the optical properties of **2**, as the flattened disposition of the molecule as a whole and the quinoxaline moiety in particular allow for extended conjugation throughout the molecule, thus changing radically its properties as a chromophore. Similar flattening of related compounds has been reported in the literature, most notably with the tetrafluoroborate salt of protonated **3**[29] and the doubly protonated bis(tetraphenylborate) salt of **4**.[28] In the latter case a yellow colour is produced upon anion exchange of chloride for the poor hydrogen bond acceptor anion tetraphenylborate. The colouration was shown to be due to the flattened conformation produced by the formation of intramolecular N^+–H···N hydrogen bridges. In the former case an N^+–H···N intramolecular hydrogen bond was found to link the nitrogen atoms of neighbouring pyridyl groups, resulting in changes to the overall topology of the molecule analogous to that in **2**. Indeed, in both compounds the formation of the intramolecular hydrogen bond 'forces' the molecules to readjust their bond lengths and angles, primarily within the quinoxaline plane. Sessler and co-workers have also postulated similar effects to be responsible for the quenching of quinoxaline-based luminescence within related dipyrrolylquinoxaline species.[16]

Evaluation of 2 as an anion sensor

Pyridinium moieties may act as receptors for anions both by virtue of their charged nature and as CH and NH hydrogen bond donors. The conformation adopted by **2** offers an opportunity to exploit the molecule as an anion sensor, as the molecule is in a disposition that favours interaction between the quinoxaline chromophore and an anionic substrate.

The effect of anionic species on the intensity of luminescence of sensor **2** in acetonitrile solution was examined by the method outlined in the Experimental section. The anions tested were iodide, bromide, chloride, fluoride, dihydrogenphosphate and as a control experiment, hexafluorophosphate. These anions, studied as their tetrabutylammonium (TBA) salts, were chosen both because of their biological relevance and because of their commercial or environmental importance. The results of these investigations are presented in Table 3. Among the halide ions, fluoride gave the strongest response[16] (Fig. 4), with the emission intensity at 454 nm being only 50% of the initial value at an anion concentration of 5.0×10^{-5} M. Chloride also quenched the emission of **2** effectively, with the intensity measuring only 34% of the original at an anion concentration of 1.0×10^{-4} M. However, bromide and iodide gave only relatively weak responses in terms of luminescence quenching, hence it appears that as ionic radius of the halide increases, the ability to quench the luminescence of **2** diminishes.[31] These results rule out a 'heavy atom' quenching mechanism. Of the non-spherical anions, hexafluorophosphate gave a very weak response indeed, indicating that the anion is weakly associating as

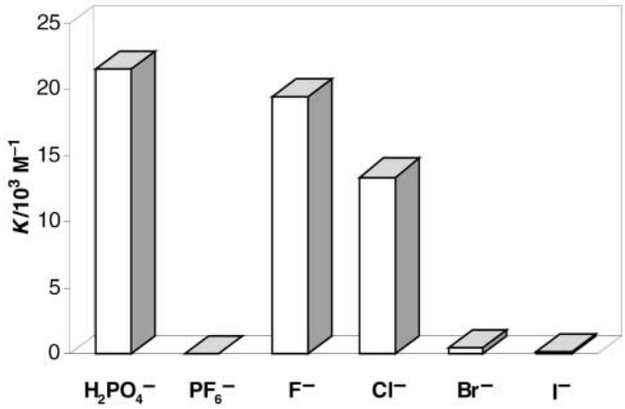


Fig. 4 Graphical representation of variation of association constant of **2** with anion species in acetonitrile solution.

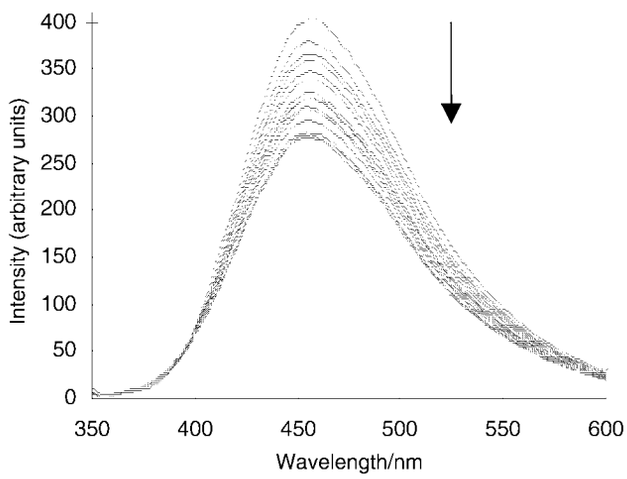


Fig. 5 Luminescence spectra for titration of 5 μL aliquots of 0.0033 M $NBu_4H_2PO_4$ with a 1.44×10^{-4} M solution of sensor **2**.

regards the receptor, and consequently vindicates the use of hexafluorophosphate as a counterion for the cationic receptor **2**. Dihydrogenphosphate gave a very strong response (Fig. 5), with luminescence intensity at 454 nm being equal to 60% of the initial value at an anion concentration of 3.5×10^{-5} M. This result was greatly encouraging as it demonstrated that this biologically relevant anion shows a strong ability to interact with the sensor **2**. The overall order for binding affinity was determined to be: $H_2PO_4^- \cong F^- > Cl^- >> Br^- > I^- > PF_6^-$. At low concentrations the quenching effects produced by all anions were modelled adequately by eqn. (1), indicating that dynamic quenching was the dominant process.[32] Indeed, for iodide, bromide, chloride and dihydrogenphosphate there were no significant deviations from this behaviour in the concentration ranges measured. Conversely, fluoride appeared to show deviations from this behaviour above a concentration of 5×10^{-5} M. When data above this concentration were fitted to a Perrin plot,[33] a good agreement was observed, indicating that static quenching is a possibility at high fluoride concentrations. It is possible, however, that simple (1 : 1) binding may not be the dominant condition between fluoride and receptor **2** or that ionic strength effects may be important at such concentrations.[31] In addition, deprotonation of the receptor was observed at very high anion concentrations when chloride, fluoride and dihydrogenphosphate anions were introduced as substrates for **2**. The product of the deprotonation reaction in each case was the parent free base of the receptor, **1**, as evidenced both by absorption and luminescence spectroscopy. Thus, compound **2** is an effective anion sensor that shows a degree of selectivity for dihydrogenphosphate, chloride and fluoride over the heavier halogen ions.

In an effort to further improve the versatility of **2** as an anion

sensor, we determined to investigate salts other than the hexafluorophosphate in an attempt to obtain a more water soluble compound. The chloride form of **2** may be isolated either by anion exchange from the hexafluorophosphate salt or by direct synthesis from the parent free base **1**. Whilst this compound displays much improved water solubility compared with that of the analogous hexafluorophosphate salt, it was noted that the emission intensity at 454 nm was much diminished and that a significant emission band at 405 nm had appeared. This indicated that in aqueous solution the chloride form of **2** would be of considerably less utility as an anion sensor, both because of the diminished intensity of emission and because an equilibrium between the protonated and free base forms exists in solution. This was an unfortunate result given the tolerance of **2** to the addition of stoichiometric quantities of water in acetonitrile solution.

Conclusion

Protonation of the well-known compound 2,3-dipyridin-2-ylquinoxaline, **1**, followed by anion exchange, gives 2-(3-pyridin-2-ylquinoxalin-2-yl)pyridinium hexafluorophosphate **2**, in high yield. This compound displays significantly different optical properties to that of its parent free base; most notably it is intensely luminescent in acetonitrile solution under air-equilibrated conditions. This change in optical properties is caused by a radical alteration to the structure of the molecule, which persists both in solution and in the solid state. Compound **2** contains an N^+–H···N intramolecular hydrogen bond which forces the molecule as a whole to adopt a flattened and hence better conjugated structure, which performs strongly as a chromophore. A consequence of this structure is that the pyridinium receptor units are held in an orientation that encourages interaction between the chromophore and bound anions. In the case of fluoride and dihydrogenphosphate and to a lesser extent chloride, experiments indicated a high degree of quenching at relatively low anion concentrations, thus it is clear that compound **2** has the potential to operate as an efficient anion sensor. In addition, the sensor displayed a degree of selectivity, as it was relatively insensitive to the addition of bromide, iodide and hexafluorophosphate.

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