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A ditopic fluorescent sensor for potassium fluoride†

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The addition of potassium fluoride 'switches on' the fluorescence of sensors 1 and 2 while potassium chloride and bromide cause no fluorescence change; the fluorescence can be 'switched off' by removing the potassium cation from the benzocrown ether receptors of sensors 1 and 2 through the addition of [2.2.2]-cryptand and restored by the addition of the potassium cation as potassium chloride.

The simultaneous binding of cationic and anionic guests as an ion pair by heteroditopic receptors is an expanding area of molecular recognition.[1–7] Synthetic fluorescent sensors for anions and cations are well known,[8–10] however, there are few systems capable of selectively reporting ion pair binding by absorption[11,12] or fluorescence.[13–15]

Simultaneous complexation of cations and anions has been observed previously in a boronate crown ether.[16] This type of receptor molecule is a heteroditopic host for fluoride and metal ions. The boron atom which is a 'hard acid' strongly interacts with the fluoride anion which is a 'hard base'. When boronic acid binds to fluoride the sp^2 hybridised trigonal boron atom becomes sp^3 hybridised.[17] The potassium ion is held by a combination of the crown ether and electrostatic interactions with the fluoride ion.

We have been involved in the development of fluorescent sensors[18–20] and colorimetric sensors[21] for fluoride based on the strong interaction between fluoride and boron.

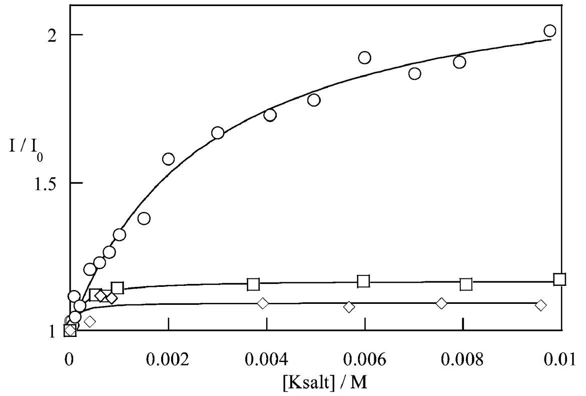
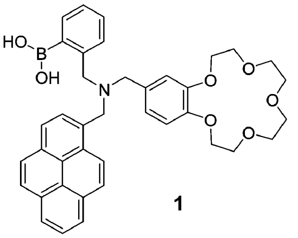


Fig. 1 Relative fluorescence intensity of sensor **1** (5×10^{-7} M) *versus* KF (○), KCl (□) and KBr (◇) at 25 °C in methanol; λ_{ex} = 343 nm, λ_{em} = 397 nm.

With this research we set out to use our knowledge of boron based receptors in combination with the known cation binding properties of crown ethers to develop a fluorescent AND logic system[22] capable of selectively reporting the presence of ion pairs of potassium fluoride. Our goal is to design a system where cation and anion binding are achieved independently yet the combination of both recognition events is required in order to generate a signal. Towards that goal we prepared sensors **1**‡ and **2** and model systems **3**, **4** and **5**.



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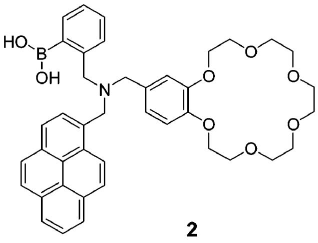

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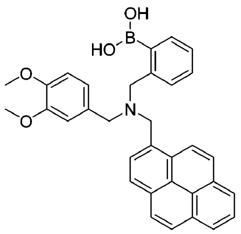

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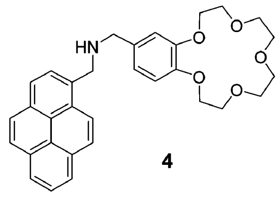

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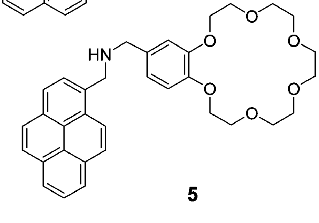

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The intensity of the fluorescence emission (I_F) of sensors **1** and **2** and model compounds **3**, **4** and **5** in methanol solution were measured at different concentrations of potassium fluoride, chloride and bromide salts. The titration curves for sensor **1** with the salts are shown in Fig. 1.

Binding of potassium fluoride enhanced the fluorescence of sensors **1** and **2**, containing both binding units: benzocrown ether and boronic acid. Addition of chloride and bromide salts did not cause any change in the fluorescence intensity. Also sensors lacking the boronic acid unit binding units (compounds **4** and **5**) did not change fluorescence on addition of potassium fluoride.

The observed fluorescence enhancement factor (EF) at a potassium concentration of 6 mM for sensor **1** was 1.77 and for sensor **2** was 1.60. The fluorescence enhancement for model compound **3** with 6 mM potassium fluoride was only 1.07. Model compound **3** can bind fluoride but cation binding is weak.

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† Electronic supplementary information (ESI) available: Details of computational methods employed in the analysis of sensors **1**, **2** and **3**. Titration curves for **1**, **2** and **3** with KF and selected synthetic data for **2** and **3**. See http://www.rsc.org/suppdata/cc/b4/b415522j/
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Model systems **4** and **5** both displayed a decrease in fluorescence of 0.88 and 0.93 with 6 mM potassium fluoride respectively.

The fluorescence enhancements and formation constants of the complexes formed between the sensors and potassium fluoride were analysed using two independent computational methods: using OPIUM[23] at a fixed wavelength and using HYPERQUAD[24] over a range of wavelengths. For a general model to analyse the titrations, formation of [KSensor], [SensorF] and [KSensorF] need to be considered. However, for **3** only [SensorF] can form and the titration is a simple 1 : 1 binding isotherm. The value of *K* determined for [SensorF] with **3** is much lower than the expected [KSensor] for **1** and **2**.[25] Therefore, we consider two stepwise equilibria to dominate the titrations of **1** and **2** (see below). The logarithm of stability constants of sensors **1** and **2** and model compound **3** are shown in Table 1. From Table 1 it is clear that the fluoride affinity for sensors **1**, **2** and **3** is not affected by the strength of the potassium ion binding. Also, the observed potassium ion binding constants reflect those of the parent crown ethers.[25]

$$[\mathrm{K}]+[\mathrm{Sensor}] \overset{K_1}{\rightleftharpoons} [\mathrm{KSensor}]$$

$$[\mathrm{KSensor}]+[F] \overset{K_2}{\rightleftharpoons} [\mathrm{KsensorF}]$$

The results presented so far illustrate that for the system to show significant signal enhancement a crown ether unit is required, since sensor **3** displays only modest fluorescence enhancement. It is also clear that the boronic acid unit is also required since sensors **4** and **5** do not display fluorescence enhancement. Futhermore, both potassium and fluoride are required to ‘switch on’ the fluorescence of sensors **1** and **2** since potassium chloride and bromide cause no fluorescence change.

Having demonstrated that it is possible to turn on the fluorescence of sensors **1** and **2** using ion pairs of potassium and fluoride, we decided to probe what would occur if we selectively removed one of the inputs from the system. This was achieved by the addition of [2.2.2]-cryptand to solutions of sensors **1** and **2** containing 6 mM of potassium fluoride. [2.2.2]-Cryptand has a much higher binding constant (log *K*) in methanol with potassium (10.6)[25] than 15-crown-5 (3.43)[25] or 18-crown-6 (6.08)[25] Since the sensors require both potassium and fluoride to be switched on, the sensor should not work when the potassium is encapsulated by the [2.2.2]-cryptand. The results obtained for the addition of potassium fluoride followed by the addition of [2.2.2]-cryptand are shown in Table 2. Since we have previously shown that addition of potassium chloride does not in itself affect the fluorescence of sensors **1** and **2**, we added excess potassium chloride to the system, effectively giving the crown ether back the potassium. As predicted this addition of potassium (as potassium chloride) restored the fluorescence, and switched the signal back on (Table 2).

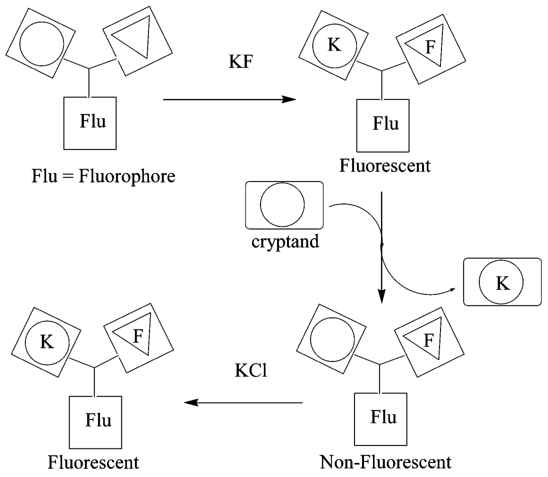
Table 1 Logarithm of stability constants *K* for sensors **1**, **2** and **3**

Sensor	K^+ log K_1	F^- log K_2
1	4.0 ± 0.5	2.5 ± 0.5
2	4.7 ± 0.2	2.4 ± 0.2
3	—[a]	2.7 ± 1.1

[a] Does not form a stable complex with potassium or potassium fluoride.

Table 2 Average fluorescence enhancement factors (EF) for sensors **1** and **2** with added potassium fluoride, [2.2.2]-cryptand and potassium chloride

Sensor	Additives (6mM)	EF
1	KF	1.76 ± 0.07
	[2.2.2]-Cryptand	1.07 ± 0.08
	KCl	1.64 ± 0.20
2	KF	1.61 ± 0.02
	[2.2.2]-Cryptand	1.01 ± 0.03
	KCl	1.57 ± 0.02



Scheme 1 Observed fluorescence behaviour of sensors **1** and **2**.

When just potassium, is bound to the crown ether the system is non-fluorescent (potassium chloride, potassium bromide). When just the boronic acid is bound to fluoride, the system is non-fluorescent (potassium fluoride and [2.2.2]-cryptand). Fluorescence is only observed when both potassium and fluoride are bound to the sensors (potassium fluoride). These observations are outlined in Scheme 1. The equilibria illustrated are those that apply in aprotic solvents. Studies are ongoing on similar systems that would function over a range of pH in predominantly aqueous solution.

In conclusion sensors **1** and **2** behave like an AND logic gate having potassium and fluoride as ionic inputs and fluorescence enhancement as output. The system simultaneously recognizes an anion and a cation. This specificity in signal enhancement demonstrates a key design principle that will guide the design of ditopic sensors of greater practical utility.

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Notes and references

‡ Selected data for **1**: mp 122 °C (dec.); $\nu_{max}(\mathrm{CHCl_3})/\mathrm{cm^{-1}}$ 1371 s (B–O), 1140 s (B–C); δ_H(400 MHz; $CDCl_3$; Me_4Si) 3.53–3.76 (12H, m, 6 × CH_2), 3.88 (4H, s, 2 × CH_2), 4.00 (2H, s, NCH_2–$C_6H_4B(OH)_2$), 4.07 (2H, s, NCH_2–benzocrown), 4.25 (2H, s, pyrene–CH_2N), 6.74–6.78 (3H, m, 3 × benzocrownC*H*), 7.31–7.41 (4H, m, 4 × $C_6H_4(OH)_2$), 7.92–8.18 (9H, m, 9 × pyrene-C*H*); δ_C(100 MHz; $CDCl_3$; Me_4Si) 55.2 (NCH_2–$C_6H_4B(OH)_2$), 58.1 (pyrene–CH_2N), 62.0 (NCH_2–benzocrown), 68.5,

68.9, 69.2, 69.5, 70.3, 70.4, 70.8, 71.0 (CH_2), 113.5, 114.9, 122.6, 122.9, 124.4, 124.5, 124.6, 125.0, 125.0, 125.7, 127.2, 127.3, 127.7, 128.9, 129.8, 130.2, 130.5, 130.8, 131.0, 131.3, 133.8, 136.5, 141.3, 148.3, 148.9 (Ar); *m*/*z* (ES^+) 646 (100%, $[M + H]^+$); (HRMS: found 646.2973, $[M + H]^+$. $C_{39}H_{41}BNO_7$ requires 646.2976).

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