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Salt (LiF) Regulated Fluorescence Switching

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A supramolecular host-guest complex stimulated by lithium cation and fluoride anion, functioning as reliable fluorescence "Off-On-Off" switching system has been developed. Nonfluorescent, receptor-bound fluorophore is exclusively displaced by second guest, fluoride anion to release the fluorophore that becomes highly fluorescent in guest concentration dependent way. Again, this process is completely reversed upon exposure to Li^+. The entire process is an excellent model for fluorescence-based logic system.

Introduction

The development of stimuli-controlled supramolecular logic devices is a challenging task since they require molecular systems that provide a differential recognition for various substrates. Molecular logic, in which initiation of event is followed by recognition, has been demonstrated with various systems including rotaxanes,[1] molecular grid[2] and basic logic devices.[3] However, it is seldom that the input-output signal is completely controlled by inorganic salt. In recent years, anions, particularly inorganic ones are gaining increasing attention for their pivotal role in medicine, biology[4] and environmental science.[5] Consequently, enormous efforts have been devoted to designing and synthesizing chemosensors so as to achieve selective recognition and sensing of anions. Among the anions of biological interest, fluoride anion (F^-) has attracted special attention due to its potential toxicity in various living systems, especially humans.[6] Although much progress has been made in the area of F^- recognition and sensing, there are only few easy-to-use chemosensors that operate with high sensitivity. Indeed, it remains a considerable challenge to produce receptors that convert a given binding event into a readable signal, particularly the one that translates the recognition event into an increasing easy-to-monitor fluorescence intensity.[7] One simple and seemingly attractive approach to producing such a sensor for the fluoride anion involves the use of an "Indicator Displacement Assay" (IDA). This approach, pioneered by Anslyn and co-workers[8] can be modified to allow "Turn-On" detection via the use of appropriately chosen fluorophores or chromophores. The Fluorescence-IDA (F-IDA) approach has been recognized lately as more sensitive method for sensing anions even in biological systems.[9] In fact, many fluorescent indicators combined with various macrocyclic receptors have been successfully applied along these lines.[10] However, a viable F^- sensor based on the F-IDA approach has yet to be described. In an early work by Gale, Twyman, and Sessler, calix[4]pyrrole, a tetrapyrrolic macrocycle with a well-recognized ability to bind certain anions in organic media, was exploited for fluoride anion detection using a simple colorimetric IDA.[11] However, this system requires the use of excess indicator and thus displayed low sensitivity. This issue led us to target an F^- sensor that would display a sensitive "Turn-On" fluorescence upon exposure to fluoride anion. Although there are a few reports that describe a fluorescence-based anion sensors in so-called "Turn-Off" fashion,[12] to the best of our knowledge, no calix[4]pyrrole-based receptors that display a fluorescence "Turn-On" response to F^- have been reported. Here, we report a simple-to-construct, calix[4]pyrrole-based, "Turn-On" F-IDA sensor that facilitates detection of F^- with unprecedently high sensitivity and selectivity. At the same time, this fluorescence "Turn-On" behavior can be completely reversed (into "Turn-Off) upon exposure to lithium cation (Li^+). This fluorescence "Off-On" process can be modulated repeatedly by Li^+ and F^- without diminished fluorescence intensity. The present system thus functions as a novel molecular On/Off switch whose function is regulated via the choice of added anions and cation. Such ion-switched systems are rare, but beginning to attract on account of some very recent attention.[13]

Results and Discussion

Our system consists of a modified calix[4]pyrrole bearing *cis*-4-fluorophenyl pickets (**1**) as the receptor and 2-oxo-4-(trifluoromethyl)-2*H*-chromen-7-olate ($\mathbf{2}^-$) as a highly fluorescent indicator (Scheme 1). When the highly fluores-

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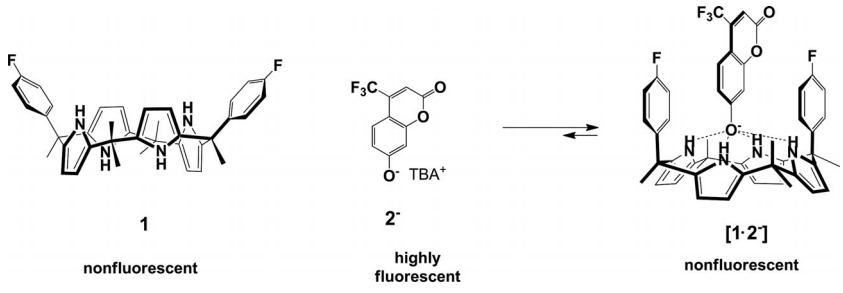
cent chromenolate anion **2**$^-$ was bound to the calix[4]pyrrole cavity through hydrogen donding, it became completely nonfluorescent presumably as the result of photo-induced electron transfer (PET) from calix[4]pyrrole to bound **2**$^-$. Direct interaction between *p*-fluoro moieties of calix[4]pyrrole and chromenolate could be a contributing factor for the quenching. If the binding affinity of an analyte anion is comparable with **2**$^-$, then the bound **2**$^-$ can be displaced by the analyte anion that will eventually result in recovering the original fluorescence of **2**$^-$. To exploit this supramolecular displacement event for more useful analyte anion detection, the relative binding affinities of **2**$^-$ and the anionic analyte would have to be appropriately tuned; specifically, the chromenolate anion would need to have sufficient affinity with **1**, but still display an affinity that was slightly lower than that of analyte anion. Gratifyingly, these expectations were realized as described further below. The identity of the receptor **1** was verified by standard spectroscopic methods as well as by single-crystal X-ray crystallography (SI). The electron withdrawing *p*-fluorophenyl groups present in **1** are expected to create a suitable binding cavity and contribute for enhanced binding affinity.[14] Proton NMR titration indicated that calix[4]pyrrole **1** forms stable complex with chromenolate **2**$^-$ with a receptor/guest stoichiometry of 1:1 (SI). As shown in Figure 1, when highly fluorescent solution of chromenolate **2**$^-$ was titrated with receptor **1** in acetonitrile, receptor-dependent quenching of the fluorescence was observed (Figure 1, a) due to the formation of a strong receptor-indicator complex [**1**·**2**$^-$]. When, the complex [**1**·**2**$^-$] was titrated with F$^-$, complete recovery of fluorescence was observed (Figure 1, b) indicating that the binding affinity of fluoride anion with receptor **1** is stronger than that of with **2**$^-$. The complete recovery of the original spectral features (1000-fold increase) is ascribed to the F$^-$-driven displacement of the chromenolate **2**$^-$ from the calix[4]pyrrole binding site via the formation of a competitive receptor-fluoride complex [**1**·**F**$^-$]. The fluorescence enhancement was found to be linear at low F$^-$ concentrations (0–100 nM, Figure S14). The detection limit of 2.3 ppb was calculated; such a detection limit represents a dramatic improvement in sensitivity relative to the prior reported system.[8] Consistent with fluorescence studies, the formation of receptor-indicator complex [**1**·**2**$^-$] was initially verified by a blue shift of the λ_{max} from 433 nm to 390 nm observed in UV/Vis spectroscopic studies. Addition of F$^-$ into complex [**1**·**2**$^-$] produced a red-shifted absorption spectrum (390 nm → 433 nm), which is consistent with that of free **2**$^-$. These events were further supported by structural analysis obtained from single-crystal X-ray crystallography (SI) for [**1**·**F**$^-$] complex. Unfortunately, attempted growing crystal of complex [**1**·**2**$^-$] was not successful.

In order to verifiy the selectivity towards F$^-$, we exposed [**1**·**2**$^-$] complex to the other anions including Cl$^-$, Br$^-$, I$^-$, CN$^-$, SCN$^-$, AcO$^-$, NO_3^-, $PhCO_2^-$, PF_6^-, $HP_2O_7^{3-}$, HSO_4^-,



Scheme 1. Formation of strong supramolecular complex between calix[4]pyrrole (**1**) and chromenolate anion [**2**$^-$, as tetrabutylammonium (TBA) salt].

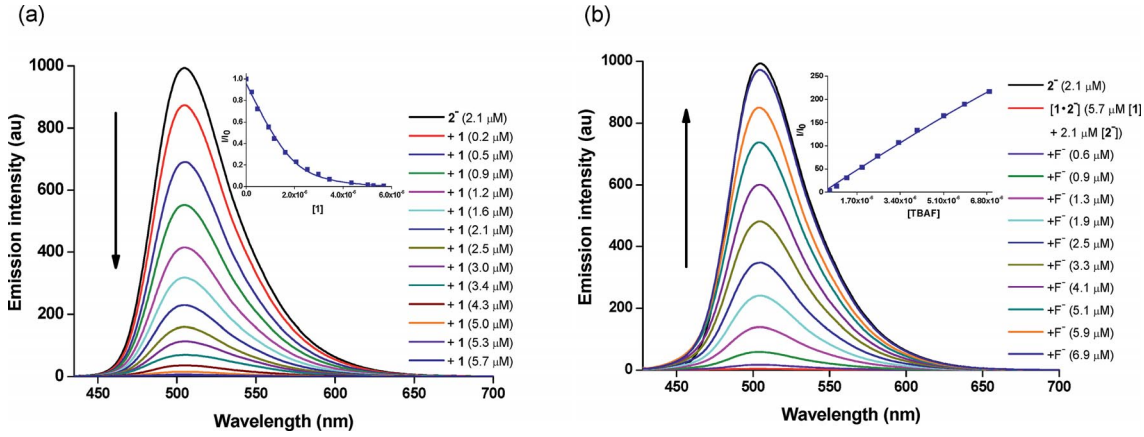


Figure 1. (a) Fluorescence quenching of fluorescent indicator **2**$^-$ (2.1 μM) upon titration with host **1** in acetonitrile at λ_{ex} = 410 nm; inset shows Stern–Volmer plot of the fluorescence quenching ($K_{SV} = 4.78 \times 10^6$). (b) Recovery of fluorescence upon titration with F$^-$ (as its tetrabutyl ammonium salt) in acetonitrile at λ_{ex} = 410 nm, [**1**] = 5.7 μM, [**2**$^-$] = 2.1 μM; inset shows a plot of I/I_0 vs. TBAF concentration.

and $H_2PO_4^-$. No detectable changes either in fluorescence or absorbance were observed, suggesting that the displacement of receptor-bound indicator $\mathbf{2}^-$ is only possible by fluoride anion. Moreover, when complex [**1**·**2**$^-$] was exposed to a mixture of anions containing Cl^-, Br^-, NO_3^- and AcO^-, no appreciable changes in fluorescence was observed, but a strong fluorescence emission appeared when the mixture was loaded with F^-, indicating that [**1**·**2**$^-$] complex is highly specific towards F^- even in the presence of mixture of anions.

To explore counter cation effects on this sensing process, we tested the effect of metal ion to the fluorescence changes. Surprisingly, addition of Li^+ (as its perchlorate salt) to the highly fluorescent mixture of [**1**·**F**$^-$] and [**2**$^-$] resulted in complete quenching of the fluorescence which was analogous to what was seen in the case of mixing of receptor **1** with $\mathbf{2}^-$. This result can be rationalized by the disappearance of the host-bound fluoride anion complex (i.e., [**1**·**F**$^-$]) and the appearance of host-bound chromenolate complex [**1**·**2**$^-$] as the result of re-displacement of bound F^- by chromenolate $\mathbf{2}^-$ (Figure 2). Decomplexation of F^- from receptor **1** by Li^+ is ascribed to the stronger ion-pairing interaction between F^- and Li^+ which suggests that the current host-indicator complex can be considered as a molecular "On-Off" switching system controlled by inorganic salts (F^- and Li^+) (Scheme 2). In agreement, the red-shifted absorption spectrum corresponding to mixture of [**1**·**F**$^-$] and [**2**$^-$] was again moved back to original spectrum pertaining to [**1**·**2**$^-$] upon addition of Li^+ (SI). It is important to note here that the solubility of LiF in acetonitrile has been found to be 90 μM.[15] Since we have used considerably smaller amounts of F^- and Li^+ [6.9 μM F^-, 8.6 μM Li^+ for fluorescence titration (Figure 2) and, 40 μM F^-, 47.6 μM Li^+ for UV/Vis titration (Figure S17)], we did not see LiF getting precipitated out from the solution. ^{1}H NMR titration studies conducted in CD_3CN further corroborated this entire switching process. For example, the pyrrole *N*-*H* signal of free host **1** was shifted from δ = 7.80 ppm to 11.43 ppm upon addition of 1.04 equiv. of chromenolate anion $\mathbf{2}^-$ indicating the 1:1 stoichiometric association of receptor **1** with $\mathbf{2}^-$. When F^- (as its tetrabutyl ammonium salt) was added into the solution of complex [**1**·**2**$^-$], on the other hand, the *N*-*H* signal was shifted further downfield, i.e, from δ = 11.43 ppm to 12.56 ppm, indicating displacement of $\mathbf{2}^-$ by $\mathbf{F}^-$ to form the new complex [**1**·**F**$^-$]. Then, the reformation of complex [**1**·**2**$^-$] was achieved upon addition of Li^+ into the mixture of [**1**·**F**$^-$] and $\mathbf{2}^-$. It is important to note here that during the titration of **1** or [**1**·**2**$^-$] with F^-, the *N*-*H* signals were shifted downfield with a doublet splitting but not broadening at all, thus, virtually ruling out the possibility of deprotonation (SI). No significant spectral changes were observed in the ^{1}H NMR spectrum upon addition of other anions other than fluoride to the complex [**1**·**2**$^-$] (SI). Fortuitously, all these observations were in good agreement with the absorption and fluorescence results noted above.

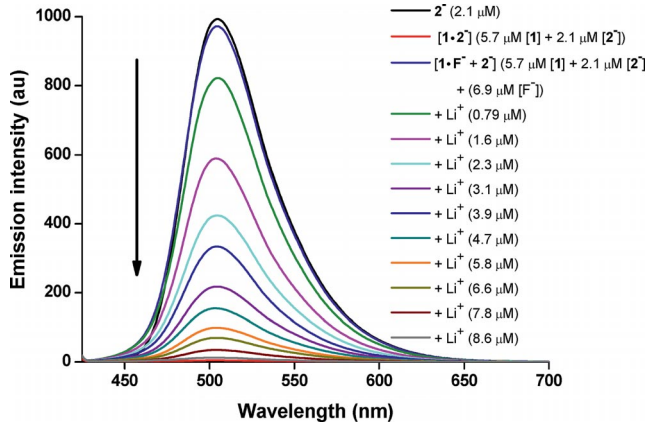
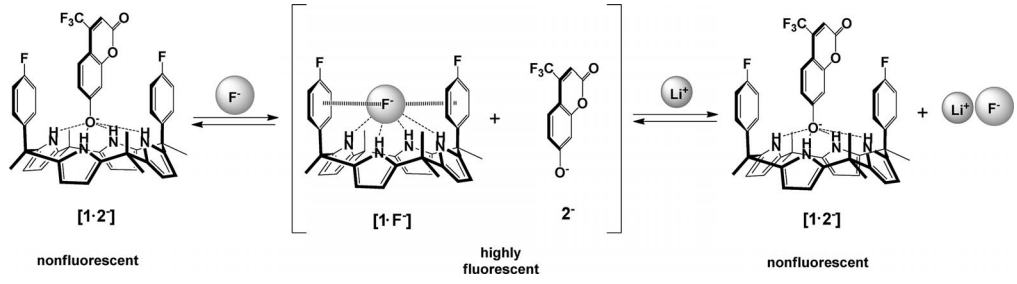


Figure 2. Quenching of fluorescence emission of the solution containing [**1**·**F**$^-$ + $\mathbf{2}^-$] upon titration with Li^+ (as its ClO_4^- salt) in acetonitrile. [**1**] = 5.7 μM, [$\mathbf{2}^-$] = 2.1 μM, [TBAF] = 6.9 μM; λ_{ex} = 410 nm.

In order to determine the energetics associated with the formation of [**1**·**2**$^-$] and [**1**·**F**$^-$], Isothermal Titration Calorimetry (ITC) and UV/Vis spectroscopic measurements were performed. The obtained binding isotherm for the binding of receptor **1** with $\mathbf{2}^-$ and **1** with F^- displayed clean exothermic 1:1 stoichiometric binding for the formation of either [**1**·**2**$^-$] or [**1**·**F**$^-$]. As anticipated, the affinity constant for the formation of [**1**·**F**$^-$] ($K = 5.96 \times 10^6$ M^{-1}) was slightly larger than that of the formation of [**1**·**2**$^-$] ($K = 4.69 \times 10^6$ M^{-1}), providing a basis for the observed preference for the formation of [**1**·**F**$^-$]. The receptor **1** displayed a much larger binding affinity with $\mathbf{2}^-$ than does simple *meso*-octamethyl calix[4]pyrrole ($K = 6.66 \times 10^4$ M^{-1}). This is in agreement with design expectations and serves to confirm that receptor **1** is superior receptor as far as the anionic guests involved in the present study are concerened.



Scheme 2. Schematic representation of reversible fluorescence "Off-On-Off" switching of supramolecular complex [**1**·**2**$^-$] by F^- and Li^+.

Since nonfluorescent solutions of complex [**1**·**2**$^-$] become highly fluorescent on addition of stoichiometric quantities of the fluoride anion and complete quenching of the fluorescence is possible upon addition of lithium ion, the current system could be a good model for molecular logic controlled by specific cation and anion. Indeed, the fluorescence can be completely switched "On" and "Off" via reversible displacement (Figure 3). The cycle can be repeated over many times starting with chromenolate **2**$^-$ followed by addition of receptor **1** to form nonfluorescent complex [**1**·**2**$^-$] without loss of fluorescence intensity. Addition of F^- to the solution of the complex fully reinstates the original fluorescence and subsequent addition of Li^+ results in a complete quenching of the fluorescence once again. The response time of this On/Off operation is instantaneous with the emission intensity of the "On" state remaining virtually the same across repeated cycles.

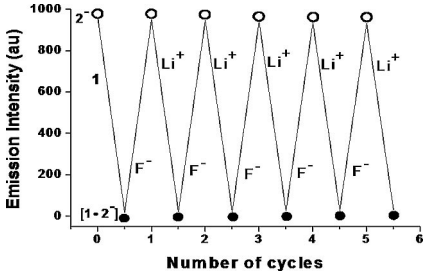


Figure 3. Repeated memory cycles starting with chromenolate **2**$^-$, adding receptor **1** (to form the nonfluorescent complex [**1**·**2**$^-$]), followed by the addition of first F^- and then Li^+ in CH_3CN. The response time is instantaneous and the emission intensity in the "On" state remains virtually the same with repeated cycles. Note that the emission intensity change is about 1000 fold. (λ_{ex} = 410 nm). [**2**$^-$] = 2.1 μM.

Conclusions

In summary, we have developed a new calix[4]pyrrole based fluorescent "Turn-On" chemosensor displaying remarkable sensitivity and selectivity towards F^-. The "Turn-On" mechanism is based on the displacement of fluorescent indicator from indicator–calix[4]pyrrole complex upon addition of F^- to form a strong [**1**·**F**$^-$] complex that results in a full reinstatement of the original indicator fluorescence. The receptor-bound fluoride anion can be easily displaced by treatment with Li^+ resulting in reformation of the indicator complex and a complete quenching of the fluorescence. This switchable "Off-On" operation was completely reversible and could be carried out through many repeated memory cycles. We expect that the current "Turn-On" and "Turn-Off" ion-mediated events would provide useful insights into the design and development of more selective chemosensors and could lead to the development of molecular scale information storage devices.

Experimental Section

General: ^1H NMR spectra were recorded on a 400 and 300 MHz Bruker NMR spectrometer using TMS as the internal standard. Chemical shifts are reported in parts per million (ppm). When peak multiplicities are given, the following abbreviations are used: s, singlet; br. s, broad singlet; d, doublet; t, triplet; m, multiplet. ^{13}C NMR spectra were proton decoupled and recorded on a 100 MHz Bruker spectrometer using TMS as the internal standard. Fluorescence spectra were recorded using LS-55B (Perkin–Elmer) model spectrometer. Pyrrole was distilled at atmospheric pressure from CaH_2. All other chemicals and solvents were purchased from commercial sources and were used as such, unless otherwise mentioned. Column chromatography was performed over silica gel (Merck, 230–400 mesh). All titrations (UV/Vis, fluorescence and ITC) were performed using HPLC grade CH_3CN purchased from Aldrich.

Synthetic Procedures

Tetrabutylammonium 2-Oxo-4-(trifluoromethyl)-2*H*-chromen-7-olate (2$^-$): Commercially available 7-hydroxy-4-(trifluoromethyl)coumarin **2** (0.1 g, 0.43 mmol) in MeOH (10 mL) was added into a solution of tetrabutylammonium hydroxide (0.17 g, 0.65 mmol) in MeOH (10 mL) at room temperature. After addition was complete, stirring continued at room temperature for 30 min. The solvent was then removed in vacuo and the residue triturated with Et_2O afforded the tetrabutylammonium salt of coumarin **2**$^-$ as a yellow powder that was dried under high vacuum and gave satisfactory spectroscopic data; yield 0.15 g (73%). ^1H NMR (300 MHz, CD_3CN): δ = 7.25 (d, J = 2.0 Hz, 1 H, coumarin-H), 6.37 (d, J = 2.0 Hz, 1 H, coumarin-H), 6.12 (s, 1 H, coumarin-H), 5.94 (s, 1 H, coumarin-H), 3.10–2.99 (m, 8 H, CH_2), 1.64–1.54 (m, 8 H, CH_2), 1.38–1.33 (m, 8 H, CH_2), 0.96 (t, J = 7.18 Hz, 12 H, CH_3) ppm. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.32 (d, J = 2.0 Hz, 1 H, coumarin-H), 6.50 (d, J = 2.0 Hz, 1 H, coumarin-H), 6.35 (s, 1 H, coumarin-H), 5.98 (s, 1 H, coumarin-H), 3.15–3.11 (m, 8 H, CH_2), 1.58–1.54 (m, 8 H, CH_2), 1.40–1.45 (m, 8 H, CH_2), 0.97 (t, J = 7.32 Hz, 12 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.4. 158.8, 142.4, 142.1, 125.6, 123.9, 121.2, 120.1, 104.8, 58.7, 23.9, 19.7, 13.6 ppm. $C_{26}H_{40}F_3NO_3$·0.6 H_2O: calcd. C 64.73, H 8.61, N 2.90; found C 64.90, H 8.48, N 2.73.

5-(4-Fluorophenyl)-5-methyldipyrromethane (3): To the mixture of commercially available 4-fluoroacetophenone (2.0 mL, 16.48 mmol) and pyrrole (11.4 mL, 164.80 mmol) kept under argon atmosphere at 0 °C, trifluoroacetic acid (1.2 mL, 16.51 mmol) was added dropwise. After addition was complete, stirring continued at 0 °C to 25 °C for 12 h. The reaction mixture was quenched by adding aqueous NaOH (0.1 N, 50 mL) and extracted with CH_2Cl_2 (50 mL × 2). The organic layer was dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure to afford the crude reaction mixture, which was purified by silica gel column chromatography (hexane/EtOAc = 9.5:0.5) to afford pure product **3** as a white solid; yield 2.76 g (66%). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.71 (br. s, 4 H, pyrrole-NH), 7.07–7.02 (m, 2 H, Ar-H), 6.96–6.90 (m, 2 H, Ar-H), 6.63–6.62 (m, 2 H, pyrrole-H), 6.17–6.14 (m, 2 H, pyrrole-H), 5.94–5.92 (m, 2 H, pyrrole-H), 2.00 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.2, 160.8, 143.6, 143.6, 137.7, 129.5, 129.5, 117.6, 115.3, 115.1, 108.7, 106.9, 44.7, 29.4 ppm. MALDI-MS Calcd. for $C_{16}H_{15}FN_2$ 254.12, found 255.03 (M + 1).

5,15-(4-Fluorophenyl)-5,10,10,15,20,20-hexamethylcalix[4]pyrrole (1): To the solution of compound **3** (1.5 g, 5.90 mmol) in acetone (300 mL) was added $BF_3{\cdot}OEt_2$ (1.5 mL, 11.80 mmol) and the mixture stirred for 12 h at room temperature. The reaction mixture was quenched upon addition of triethylamine (3.5 mL, 25.36 mmol). Excess acetone was removed under reduced pressure and the mixture was combined with water and extracted with CH_2Cl_2 (100 mL × 2). The organic layer was dried with anhydrous Na_2SO_4

and the solvent was removed in vacuo. Column chromatography on silica afforded a clear separation of two isomers. The first minor fraction containing *trans* isomer (0.10 g, 3%) was collected in 9.7:0.3 hexane/EtOAc mixture. While the second major fraction containing the required *cis* isomer **1** was collected as a white solid in 9.4:0.6 hexane/EtOAc mixture; yield 0.73 g (21%). ^{1}H NMR (300 MHz, CD_3CN) δ = 7.81 (br. s, 4 H, pyrrole-NH), 6.97–6.90 (m, 8 H, Ar-H), 5.86–5.84 (m, 4 H, pyrrole-H), 5.62–5.60 (m, 4 H, pyrrole-H), 1.64 (s, 6 H, CH_3), 1.56 (s, 6 H, CH_3), 1.49 (s, 6 H, CH_3) ppm. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20 (br. s, 4 H, pyrrole-NH), 6.95–6.87 (m, 8 H, Ar-H), 5.94–5.92 (m, 4 H, pyrrole-H), 5.62–5.60 (m, 4 H, pyrrole-H), 1.87 (s, 6 H, CH_3), 1.61 (s, 6 H, CH_3), 1.53 (s, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.6, 160.2, 143.7, 143.7, 138.5, 136.4, 129.0, 128.9, 114.4, 114.2, 106.0, 103.3, 44.2, 35.1, 30.1, 27.9, 27.9 ppm. MALDI-MS Calcd. for $C_{38}H_{38}F_2N_4$ 588.31, found 589.21 (M + 1).

Supporting Information (see footnote on the first page of this article): Synthetic schemes, copies of NMR spectra, single-crystal X-ray structures and spectroscopic data to support fluoride sensing behaviour. The crystal data for the structural refinement of **1** and [**1**·F^-] are also provided.

CCDC-820611 (for **1**) and -820612 (for [**1**·F^-]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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