Available online at www.sciencedirect.com

ScienceDirect

Tetrahedron Letters 48 (2007) 3135–3139

Tetrahedron Letters

Selective fluorescent sensing of chloride

Cidália M. G. dos Santos, Thomas McCabe and Thorfinnur Gunnlaugsson*

School of Chemistry, Centre for Synthesis and Chemical Biology, Trinity College Dublin, Dublin 2, Ireland

Received 20 February 2007; revised 27 February 2007; accepted 8 March 2007
Available online 13 March 2007

Abstract—The urea functionalised phenanthroline sensor **1**, which was characterised by several methods, including X-ray crystallography, gives rise to large changes in the fluorescence emission spectra upon interaction with several anions such as acetate, phosphate, fluoride and chloride in CH_3CN. However, only in the presence of Cl^- was the emission enhanced, as for the other ions photoinduced electron transfer (PET) quenching was observed. Fitting these fluorescence changes, using non-linear regression analysis, showed that these anions bind to **1** in 1:1 (anion:sensor) stoichiometry, with the exception of Cl^-, which was shown to give rise to 1:1 as well as 1:2 binding, as a result of coordination of the chloride to two equivalents of **1**.

The recognition and sensing of anions has become a very topical area of research in the field of supramolecular chemistry.[1–3] Anions play a major function in the environment, industry and importantly, in biology where phosphate, carbonate and chloride are the most commonly found. In particular, Cl^- which has relatively high extracellular concentrations, is essential to human health and is transported across cell membranes by various Cl^- proteins, often in conjunction with cation transportation.[4] Due to its spherical structure and relative large ionic radius, Cl^- recognition is not trivial, and often requires the use of structurally complex hosts, such as those developed by Davis[5] and Smith.[6] Nature often transports Cl^- in the form of ion pairs and non-peptide based natural transporters are known such as the prodigiosins, which can transport HCl.[7] A few examples of such transport mimics have recently been published by Sessler et al. and by Gale and co-workers respectively.[8,9] These examples demonstrate the feasibility of the use of small and hence, structurally simple molecules for such recognition. We are interested in the recognition and sensing of anions[3,10] using either lanthanide based coordination complexes,[11] or charge neutral receptors such as ureas,[12] thioureas[13] and amidoureas.[14] For these latter examples, the detection of ions such as AcO^-, $H_2PO_4{}^-$, pyrophosphate and F^- has been demonstrated selectively over many other anions such as Cl^-, Br^- and I^-. However, in recent work, where we focused our efforts on the development of heteroditopic receptors, we synthesised the 1,10-phenanthroline (*phen*) based urea ligand **1** (of which the X-ray crystal structure is shown in Fig. 1),[15] and investigated the effect that anion coordination had on the photophysical properties of the *phen* structure. Interestingly, we discovered that while **1** could strongly bind to a series of anions in CH_3CN solution, the sensing of Cl^- by **1** was particularly interesting being both strong and achieved by the formation of a 2:1 self-assembly complex between **1** and Cl^-. This is, to the best of our knowledge, the first example of a simple charge neutral fluorescent sensor which demonstrates both strong and good selectivity for Cl^-.[16]

The synthesis of **1** was achieved in a few high yielding steps as shown in Scheme 1. The first step involved reduction of commercially available 5-nitro-1,10-phenanthroline, **2**, in refluxing ethanol solution, under argon, using hydrazine monohydrate (N_2H_4) and 10% Pd/C catalyst. A yellow solid was obtained after filtration and removal of the solvent under reduced pressure. This solid was washed twice with diethyl ether to produce **3** as a pale yellow solid in 92% yield. This was then

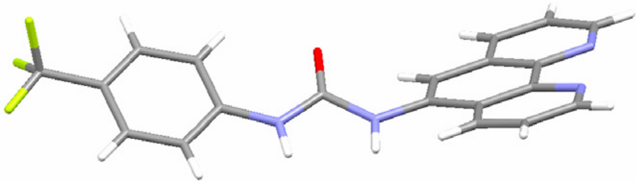
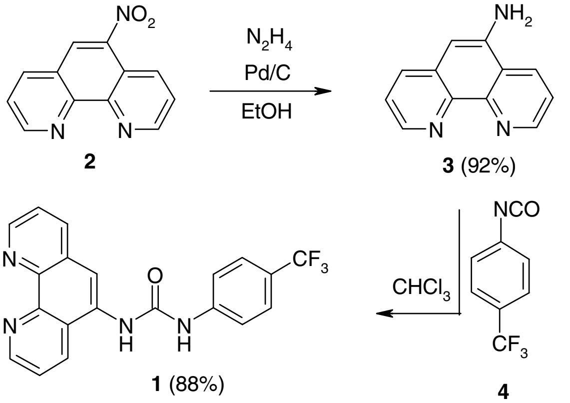


Figure 1. The X-ray crystal structure of **1**.

---

* Corresponding author. Tel.: +353 1 896 3459; fax: +353 1 671 2826; e-mail: gunnlaut@tcd.ie

0040-4039/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2007.03.061



Scheme 1. The synthesis of **1**.

reacted with trifluoro-*p*-tolyl isocyanate, **4**, in $CHCl_3$ at room temperature, under an inert atmosphere to yield an off white precipitate, which was filtered and washed with cold $CHCl_3$. This gave an off-white solid which was recrystallised from hot MeOH to yield the desired receptor **1** as a crystalline solid in 88% yield.[17] The ^1H NMR spectrum (400 MHz, DMSO-d_6) showed the presence of the two urea N–H singlets at 9.55 and 9.12 ppm, respectively, as well as the expected set of doublets for the phenyl aromatic protons. The ^{13}C NMR (100 MHz, DMSO-d_6) of **1** showed all the expected 18 signals, with the urea carbonyl quaternary resonance appearing at 152.87 ppm.

The X-ray crystal structure of **1** is presented in Figure 1, and shows that the urea moiety is coplanar with the trifluoro-*p*-tolyl group (torsion angle of −0.26°), while being significantly shifted out of the plane of the *phen* moiety (torsion angle of −35°).[15] The two urea N···H bond lengths were found to be identical at 0.860 Å. As is clear from the crystal structure, the two urea protons are ideally situated for directional hydrogen bonding interactions with anions that can participate in linear interactions such as AcO^-, $H_2PO_4^-$ and F^-. We were unable to produce suitable crystals of **1** in the presence of anions for X-ray crystal structure analysis.

The ability of **1** to sense various anions was evaluated in CH_3CN using the anions as their tetrabutylammonium salts (TBA^+). The absorption spectrum of **1**, in the absence of anions, exhibited a band centred at 266 nm ($\log\varepsilon = 4.50$), assigned to the π–π^* transition of the *phen* moiety and a broad shoulder centred at around 320 nm ($\log\varepsilon = 3.85$), which was assigned to the n–π^* transitions. When exciting the sample at both of these wavelengths, a broad emission band was observed with λ_{max} at 422 nm. Thus both absorptions were assigned to the *phen* chromophore. Significant changes were observed in the absorption spectra upon titration of **1** with anions such as AcO^- and $H_2PO_4^-$ and interestingly, also for Cl^-.[18] These responses, clearly signify changes in the ground state of the sensor upon hydrogen bonding to these anions as demonstrated for Cl^- in Figure 2. The sensing of Cl^- is unusual as it is typically not observed for such simple urea or amidourea based receptors. As seen in Figure 2, an increase was observed in both the 266 nm and 320 nm transitions upon increasing the concentration of Cl^-, but no other spectral shifts, or the formation of isosbestic points, were observed. For both AcO^- and $H_2PO_4^-$ similar changes were observed, where the absorption was enhanced by ca. 20–30%. However, more structural changes were observed in the absorption spectra in the case of F^-, where the 266 nm band was shifted to 270 nm, while the 320 nm band was shifted to 325 nm, with the formation of concomitant isosbestic points. These changes demonstrate the ability of F^- to (i) bind to the urea moiety, and (ii) potentially deprotonate the urea moiety.[19] In contrast to these results, minor changes were observed for Br^- at very high anion concentrations.

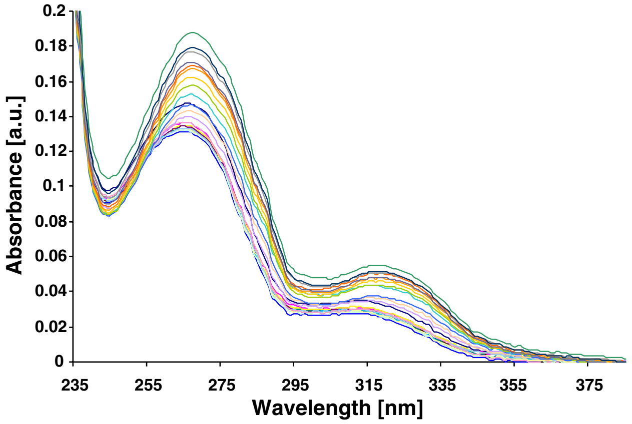


Figure 2. The changes in the absorption spectra of **1** (4.8 μM) upon gradual addition of Cl^- (0–17.50 mM) in MeCN.

The fluorescence emission spectra were also monitored upon addition of anions following excitation at both the 265 nm and 320 nm transitions. Upon addition of AcO^-, $H_2PO_4^-$ and F^-, the fluorescence emission was considerably quenched (98%, 94%, and 93%, respectively), or '*switched off*', as shown in Figure 3 for the changes observed with AcO^-. This clearly demonstrates the ability of **1** to function as a luminescent '*on–off*' switch for these anions. It is worth pointing out that no other spectral changes occurred in the fluorescence

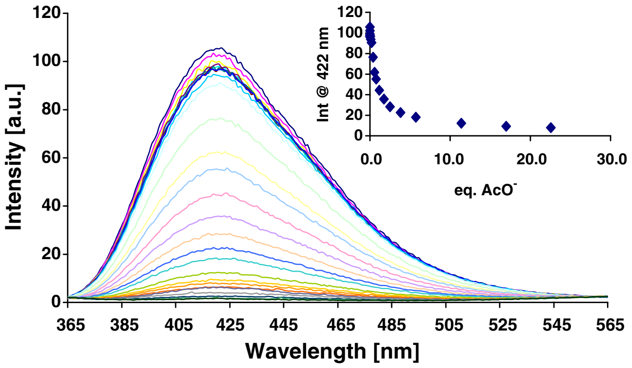


Figure 3. The changes in emission intensity of **1** (4.8 μM) upon gradual addition of AcO^- ($[AcO^-] = 0$–1.53 mM), in MeCN upon excitation at 265 nm. Inset: The changes in the emission intensity at 422 nm as a function of AcO^- equivalents.

emission spectra, that is, no shifts in $\lambda_{\max}$ or the formation of long wavelength emitting species were observed. Hence, we propose that upon anion recognition, the urea moiety is twisted out of the plane of the *phen* fluorophore which gives rise to the slight enhancement in the $\pi\rightarrow\pi$ nature of the fluorophore (as seen in the absorption spectra). At the same time, electron transfer quenching of the *phen* excited state, from the electron rich anion receptor, is activated, causing the emission to ‘*switch off*’. Hence, this can be considered as being an anion modulated photoinduced electron transfer (PET) quenching, even though no formal covalent spacer separates the fluorophore from the urea receptor.[12,20] From these changes, binding constants of $\log\beta_{11} = 5.19$ ($\pm$0.03) and $\log\beta_{11} = 4.35$ ($\pm$0.06) were observed for **AcO$^-$·1** and **H$_2$PO$_4$$^-$·1**, respectively, using the nonlinear least-squares fitting programme SPECFIT. These values indicate strong binding of **1** for these anions in CH$_3$CN. The fact that AcO$^-$ is bound more strongly than H$_2$PO$_4$$^-$ reflects the ability of this anion to bind to the receptor in a more linear ‘Y’ shape hydrogen bonding manner. Hence, on all occasions the best fit for the above changes was observed for the 1:1 binding stoichiometry. The changes in the emission intensity of **1** upon titration with F$^-$ were, however, best fitted to 2:1 binding (anion:sensor) interactions. This is in agreement with the findings from the absorption data, where a two-step equilibrium was observed. These can be viewed as involving the initial interaction of the anion with **1** through hydrogen bonding to give the **F$^-$·1** complex, followed by binding and subsequent deprotonation by the second F$^-$ to give bifluoride HF$_2$$^-$, in a manner previously postulated by ourselves and Gale et al.[19,21] From these changes $\log\beta_{11} = 4.75$ ($\pm$0.26) and $\log\beta_{21} = 4.73$ ($\pm$0.21) values were determined for **F$^-$·1** and **F$^-_2$·1** (the formation of HF$_2$$^-$), respectively. As in the ground state investigation above, titrations using Br$^-$ did not give rise to any significant luminescent quenching except at high concentrations, which could be due to a heavy atom effect rather than binding of this anion to the receptor.

However, the most interesting results were observed for the fluorescence titration of **1** with Cl$^-$, Figure 4. Here the quenching of the singlet excited state was not observed as in the above cases, but a fluorescence enhancement. Here, the *phen* emission was enhanced by ca. 45%, with a concomitant shift towards longer wavelengths ($\lambda_{\max}$ 422 nm → 428 nm), with the formation of an iso-emissive point at 399 nm. This is the first time that we have observed such luminescent behaviour for such structurally simple receptors. Furthermore, it is clear that these changes are of a different nature to those observed for the AcO$^-$ or H$_2$PO$_4$$^-$ titrations above, and thus cannot be assigned to an enhancement in PET quenching. We therefore propose that upon recognition of Cl$^-$, the aforementioned anion induced twisting of the urea moiety (from the *phen* ligand) is minor and the spherical anion reduces the effect of the PET quenching from the trifluoro-*p*-tolyl group to the *phen* fluorophore, by ‘blocking’ the pathway of the electron transfer. Such ‘intervening media’ has been proposed to influence energy transfer quenching in several electron-donor-acceptor systems, such as in those developed by Shimidzu et al.[22] where a cation was employed, and in supramolecular systems designed to mimic the nature of the electron transfer in the photosynthetic reaction centre.[23]

Plotting the changes at 422 nm as a function of $-\log[\mathrm{Cl}^-]$ gave rise to changes occurring over ca. 4 logarithmic units, indicating more than a simple 1:1 binding process. By fitting the changes observed in Figure 4 for 1:1 type complex formation, **Cl$^-$·1**, a binding constant of $\log\beta_{11} = 3.84$ ($\pm$0.14) was determined. While this shows that **1** has high affinity for Cl$^-$, we and others, have demonstrated that usually such simple urea based receptors do not bind to large spherical anions[3] but rather through multiple binding interactions.[4,24] Consequently, we considered an alternative binding mode for **1**, where two sensors self-assemble around the anion to give a **Cl$^-$·1$_2$** complex. Fitting the above changes to such stoichiometry, gave a strong binding constant of $\log\beta_{12} = 5.94$ ($\pm$0.16). Analysis of the speciation distribution diagram, shown in Figure 5, clearly shows that the initial addition of Cl$^-$ gives rise to the formation of a self-assembly (blue line) of two molecules of **1** and Cl$^-$, and that up to 27% of the species in solution

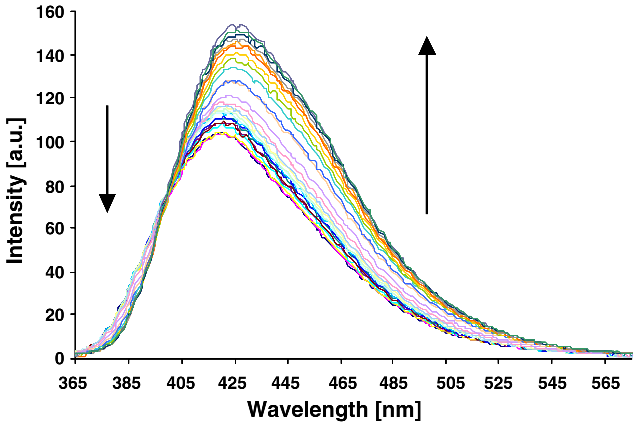


Figure 4. Changes in the emission spectra of **1** (4.8 μM) upon titration with Cl$^-$ (0–17.50 mM) in MeCN, upon excitation at 265 nm.

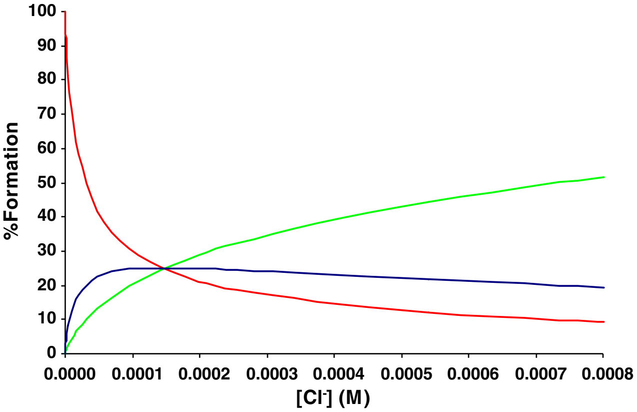


Figure 5. The speciation distribution plot for the binding of **1** (4.8 μM) to Cl$^-$: —— = **1**; —— = **Cl$^-$·1**; —— = **Cl$^-$·1$_2$**. Only part of the concentration range is shown.

from $[\mathrm{Cl}^-] = 0 \rightarrow 0.8$ mM is in the form of the $\mathbf{Cl^- \cdot 1_2}$ complex. However, the formation of the 1:1 complex begins to dominate after 0.2 mM (green line), eventually being the most stable species in solution.[25,26] With the aim of demonstrating the selectivity of **1** for Cl^-, the luminescence of **1** was recorded in the presence of one equivalent of AcO^-, which quenched the fluorescence. However, upon addition of increased concentrations of Cl^-, the emission was restored, giving rise to a red shifted emission, as observed in Figure 4. These results demonstrate that Cl^- can be sensed selectively by **1**, through (a) the formation of a self-assembly, and (b) by the fact that only for Cl^- was the fluorescence of **1** increased, while being quenched by other competitive ions such as AcO^-, $\mathrm{H_2PO_4}^-$ and F^-.

In summary, we have developed **1** as a selective fluorescence sensor for Cl^-. While only minor changes were observed in the absorption spectra of **1** upon anion recognition, the fluorescence emission spectra were dramatically affected. Nevertheless, only for the sensing of Cl^- was the fluorescence of **1** enhanced. For other competitive ions the emission was either quenched or not modulated. We are currently evaluating the anion binding of **1** in the presence of both transition and lanthanide ions.

Acknowledgements

We would like to thank TCD and IRCSET for financial support, Dr. John E. O'Brien for assisting with NMR and Dr. Sally E. Plush and Dr. Susan Quinn for their help. We particularly would like to thank Dr. Joseph P. Leonard for his assistance at the start of this investigation.

References and notes

1. Sessler, J. L.; Gale, P. A.; Cho, W. S., *Anion Receptor Chemistry*; Royal Society of Chemistry: Cambridge, UK, 2006; Steed, J. W. *Chem. Commun.* **2006**, 2637; Gale, P. A. *Acc. Chem. Res.* **2006**, *39*, 465; Martínez-Máñez, R.; Sancenón, F. *Chem. Rev.* **2003**, *103*, 4419; Suksai, C.; Tuntulani, T. *Chem. Soc. Rev.* **2003**, *32*, 192.
2. Wu, F. Y.; Li, Z.; Guo, L.; Wang, X.; Lin, M. H.; Zhao, Y. F.; Jiang, Y. B. *Org. Biomol. Chem.* **2006**, *4*, 624; Ghosh, K.; Adhikari, S. *Tetrahedron Lett.* **2006**, *47*, 8165; Evans, L. S.; Gale, P. A.; Light, M. E.; Quesada, R. *Chem. Commun.* **2006**, 965; Pfeffer, F. M.; Seter, M.; Lewcenko, N.; Barnett, N. W. *Tetrahedron Lett.* **2006**, *47*, 5251; Jun, E. J.; Swamy, K. M. K.; Bang, H.; Kim, S. J.; Yoon, J. Y. *Tetrahedron Lett.* **2006**, *47*, 3103; Liu, B.; Tian, H. *Chem. Lett.* **2005**, *34*, 686; Wel, L. H.; He, Y. B.; Wu, J. L.; Wu, X. J.; Meng, L.; Yang, X. *Supramol. Chem.* **2004**, *16*, 561.
3. Gunnlaugsson, T.; Glynn, M.; Tocci (née Hussey), G. M.; Kruger, P. E.; Pfeffer, F. M. *Coord. Chem. Rev.* **2006**, *250*, 3094.
4. Davis, A. P.; Sheppard, D. N.; Smith, B. D. *Chem. Soc. Rev.* **2007**, *36*, 348.
5. Davis, A. P.; Joos, J. B. *Coord. Chem. Rev.* **2003**, *240*, 143; Boon, J. M.; Smith, B. D. *Curr. Opin. Chem. Biol.* **2002**, *6*, 749.
6. McNally, B. A.; Koulov, A. V.; Smith, B. D.; Joos, J.-B.; Davis, A. P. *Chem. Commun.* **2005**, 1087.
7. Ohkuma, S.; Sato, T.; Okamoto, M.; Matsuya, H.; Arai, K.; Kataoka, T.; Nagai, K.; Wasserman, H. H. *Biochemistry* **1998**, *334*, 731.
8. Sessler, J. L.; Elleer, L. R.; Cho, W. S.; Nicolaou, S.; Aguilar, A.; Lee, J. T.; Lynch, V. M.; Magda, D. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 5989.
9. Gale, P. A.; Light, M. E.; McNally, B.; Navakhun, K.; Sliwinski, K. E.; Smith, B. D. *Chem. Commun.* **2005**, 3773.
10. Gunnlaugsson, T.; Ali, H. D. P.; Glynn, M.; Kruger, P. E.; Hussey, G. M.; Pfeffer, F. M.; dos Santos, C. M. G.; Tierney, J. *J. Fluoresc.* **2005**, *15*, 287.
11. Leonard, J. P.; dos Santos, C. M. G.; Plush, S. P.; McCabe, T.; Gunnlaugsson, T. *Chem. Commun.* **2007**, 129; Harte, A. J.; Jensen, P.; Plush, S. E.; Kruger, P. E.; Gunnlaugsson, T. *Inorg. Chem.* **2006**, *45*, 9465; Gunnlaugsson, T.; Leonard, J. P. *Chem. Commun.* **2005**, 3114; Gunnlaugsson, T.; Leonard, J. P. *J. Fluoresc.* **2005**, *15*, 585; Harte, A. J.; Leonard, J. P.; Nieuwenhuyzen, M. *Supramol. Chem.* **2003**, *15*, 505; Gunnlaugsson, T.; Harte, A. J.; Leonard, J. P.; Nieuwenhuyzen, M. *Chem. Commun.* **2002**, 2134.
12. Pfeffer, F. M.; Buschgens, A. M.; Barnett, N. W.; Gunnlaugsson, T.; Kruger, P. E. *Tetrahedron Lett.* **2005**, *46*, 6579; Gunnlaugsson, T.; Davis, A. P.; O'Brien, J. E.; Glynn, M. *Org. Biomol. Chem.* **2005**, *3*, 48; Pfeffer, F. M.; Gunnlaugsson, T.; Jensen, P.; Kruger, P. E. *Org. Lett.* **2005**, *7*, 5375; Gunnlaugsson, T.; Davis, A. P.; O'Brien, J. E.; Glynn, M. *Org. Lett.* **2002**, *4*, 2449; Gunnlaugsson, T.; Davis, A. P.; Hussey, G. M.; Tierney, J.; Glynn, M. *Org. Biomol. Chem.* **2004**, *2*, 1856; Gunnlaugsson, T.; Davis, A. P.; Glynn, M. *Chem. Commun.* **2001**, 2556.
13. dos Santos, C. M. G.; Glynn, M.; McCabe, T.; Seixas de Melo, J. S. Burrows, H. D.; Gunnlaugsson, T. *Supramol. Chem.*, **2007**, *19*, in press.
14. Quinlan, E.; Matthews, S. E.; Gunnlaugsson, T. *Tetrahedron Lett.* **2006**, *47*, 9333; Gunnlaugsson, T.; Kruger, P. E.; Jensen, P.; Tierney, J.; Ali, H. D. P.; Hussey, G. M. *J. Org. Chem.* **2005**, *70*, 10875.
15. The data were collected on a Bruker Smart Apex Diffractometer*. The crystal was mounted on a 0.35 mm quartz fibre and immediately placed on the goniometer head in a 150 K N2 gas stream. The data were acquired using Smart Version 5.625 software in multi-run mode and 2400 frames in total, at 0.3° per frame, were collected. Data integration and reduction was carried out using Bruker Saint+ Version 6.45 software and corrected for absorption and polarization effects using Sadabs Version 2.10 software. Space group determination, structure solution and refinement were obtained using Bruker Shelxtl Ver. 6.14 software. *SMART Software Reference Manual, version 5.625, Bruker Analytical X-ray Systems Inc., Madison, WI, 2001. Sheldrick, G. M. SHELXTL, An Integrated System for Data Collection, Processing, Structure Solution and Refinement, Bruker Analytical X-ray Systems Inc., Madison, WI, 2001. *Crystal data*: $\mathrm{C_{80}H_{52}F_{12}N_{16}O_4}$, Monoclinic, space group $P21/c$, $a = 13.1965(14)$, $b = 11.8685(12)$, $c = 11.0189(11)(17)$ Å, $\beta = 91.320(2)°$, $U = 1725.4(3)$ Å^3, $T = 150$ K, μ (Mo-Kα) $= 0.117$ mm^{-1}, $Z = 4$, a total of 13251 reflections were measured for $4 < 2\Theta < 57$ and 3031 unique reflections were used in the refinement, [R(int) = 0.0288], the final parameters were $wR2 = 0.1693$ and $R1 = 0.0648$ [$I > 2\sigma(I)$]. CCDC 637076.
16. We have previously demonstrated the sensing of such halides using heavy atom affect quenching: Gunnlaugsson, T.; Bichell, B.; Nolan, C. *Tetrahedron* **2004**, *60*, 5799; Chloride has also been elegantly detected by NMR using catechols: Smith, D. K. *Org. Biomol. Chem.* **2003**, *1*, 3874; and recently by using accridone fluorescence sensing:

Blázquez, M. T.; Muñiz, F. M.; Sáez, S.; Simón, L. M.; Alonso, Á.; Raposo, C.; Lithgow, A.; Alcázar, V.; Morán, J. R. *Heterocycles* **2006**, *69*, 73.

17. Sensor **1** was obtained as an off-white solid in 88% yield (1.38 g). Mp decomposes above 290 °C; Calculated for $C_{20}H_{14}N_4OF_3$ [M+H] $m/z = 383.1120$. Found $m/z = 383.1107$. ^{1}H NMR(400 MHz, DMSO-d_6) δ_H: 9.55 (br s, 1H, NH), 9.16 (d, 1H, PhenCH, $J = 4$ Hz), 9.12 (br s, 1H, NH), 9.00 (d, 1H, PhenCH, $J = 4.04$ Hz), 8.65 (d, 1H, PhenCH, $J = 8.52$ Hz), 8.43 (d, 1H, PhenCH, $J = 8.04$ Hz), 8.39 (s, 1H, PhenCH), 7.89 (dd, 1H, PhenCH, $J = 8.52$ Hz), 7.72 (m, 5H, PhenCH + ArCH); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 152.87, 149.87, 148.74, 145.89, 143.34, 143.13, 135.61, 132.08, 130.44, 128.50, 126.25, 126.22, 123.77, 123.68, 122.95, 122.21, 118.01, 116.07; ^{19}F NMR (376 MHz, DMSO-d_6): -60.58 (CF_3).
18. Chloride has recently been used as a template for the formation of anion pseudocyrptands and directed self-assemblies: Nabeshima, T.; Masubuchi, S.; Taguchi, N.; Akina, S.; Saiki, T.; Sato, S. *Tetrahedron Lett.* **2007**, *48*, 1595; Goetz, S.; Kruger, P. E. *Dalton Trans.* **2006**, 1277; Beer, P. D.; Sambrook, M. R.; Curiel, D. *Chem. Commun.* **2006**, 2105; Keegan, J.; Kruger, P. E.; Nieuwenhuyzen, M.; O'Brien, J.; Martin, N. *Chem. Commun.* **2001**, 2192.
19. Gunnlaugsson, T.; Kruger, P. E.; Lee, T. C.; Parkesh, R.; Pfeffer, F. M.; Hussey, G. M. *Tetrahedron Lett.* **2003**, *44*, 6575; Gunnlaugsson, T.; Kruger, P. E.; Jensen, P.; Pfeffer, F. M.; Hussey, G. M. *Tetrahedron Lett.* **2003**, *44*, 8909.
20. It is possible that the anion sensing also contributes to the formation of a twisted internal charge transfer (TICT) excited state in **1**. de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T. *Tetrahedron Lett.* **1998**, *39*, 5077; Letard, J.-F.; Lapouyade, R.; Retting, W. *Pure Appl. Chem.* **1993**, *65*, 1705.
21. Evans, L. S.; Gale, P. A.; Light, M. E.; Quesada, R. *New J. Chem.* **2006**, *30*, 1019; Camiolo, S.; Gale, P.; Hursthouse, M. B.; Light, M. E. *Org. Biomol. Chem.* **2003**, *1*, 741.
22. Iyoda, T.; Morimoto, M.; Kawasaki, N.; Shimidzu, T. *J. Chem. Soc., Chem. Commun.* **1991**, 1480.
23. de Silva, A. P.; Rice, T. E. *Chem. Commun.* **1999**, 163; Harriman, A.; Heitz, V.; Sauvage, S.-P. *J. Phys. Chem.* **1993**, *97*, 5940.
24. Davis, A. P. *Coord. Chem. Rev.* **2006**, *250*, 2939; Schazmann, B.; Alhashimy, N.; Diamond, D. *J. Am. Chem. Soc.* **2006**, *128*, 8606; Bai, Y.; Zhang, B.-G.; Xu, J.; Duan, C.-Y.; Dang, D.-B.; Liu, D.-L.; Meng, Q.-J. *New J. Chem.* **2005**, *29*, 777.
25. Without X-ray crystallographic data for the $\mathbf{Cl^-\cdot 1_2}$ complex it is difficult to predict its structure. However, we propose that the two sensors hydrogen bond to the anion in a head-to-tail fashion, where the two *phen* moieties would be facing away from each other. See also Ref. 26.
26. During the course of our work, a ditopic receptor was found to bind Cl^- upon addition of Cu(I) in a semi-helical fashion: Amendola, V.; Boiocchi, M.; Colasson, B.; Fabbrizzi, L. *Inorg. Chem.* **2006**, *45*, 6138.