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# Selective Recognition of Fluoride Anion Using a $Li^+$–Metallacrown Complex

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Holger Piotrowski, and Kay Severin*

With the final goal of constructing specific chemosensors for fluoride anions, considerable efforts have been put into the synthesis of compounds that are able to bind fluoride ions with high affinity and selectivity. The receptors described include organic macrocycles with convergent H-bond donor groups and compounds containing Lewis acidic boron, silicon, or tin atoms.[1, 2] Here we report a conceptually new fluoride receptor, the basic principle of which is shown in Figure 1. A lithium ion, which serves as a binding site, is coordinated inside a three-dimensional host compound. The accessibility of the $Li^+$ center is controlled by the steric requirements of the host: the small fluoride anion is able to enter the cavity whereas larger anions are efficiently blocked. Since the radius of the fluoride ion is significantly shorter than that of most other anions,[1b] a highly specific receptor is obtained.

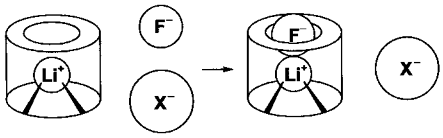

Figure 1. Schematic representation of a selective fluoride receptor with a $Li^+$ ion binding site.

The utilization of the hard acid $Li^+$ ion for the binding of the hard base $F^-$ appears to be very attractive, but so far $Li^+$-based fluoride receptors have not been described. In fact, there is not even structural data available on complexes containing molecular LiF,[3, 4] although numerous examples of other alkali metal halide complexes are known. The difficulty of stabilizing molecular LiF arises from its very high lattice energy which makes crystalline LiF a thermodynamic trap.[4b]

Recently, we have described the synthesis of trimeric organometallic complexes of the general formula $[L_nM(C_5H_3NO_2)]_3$ ($L_nM$ = arene-Ru or Cp*Rh; Cp* = $C_5Me_5$).[5] These analogues of [12]crown-3[6] were shown to bind alkali metal halides with remarkable affinity and selectivity. In an extension of this work we have investigated the reaction of $[\{Cp^*IrCl_2\}_2]$ with 3-hydroxy-2-pyridone in the presence of base. As in the cases with the analogous ruthenium and rhodium complexes, a trimeric complex $[Cp^*Ir(C_5H_3NO_2)]_3$ (**1**) was obtained. The metallamacrocycle was characterized by NMR spectroscopy ($^1H$, $^{13}C$), elemental analysis, and single-crystal X-ray analysis (Figure 2).[7] A pseudo-$C_3$-symmetric geometry is observed in the solid state, with dianionic pyridonate ligands bridging the $Cp^*Ir^{III}$ frag-

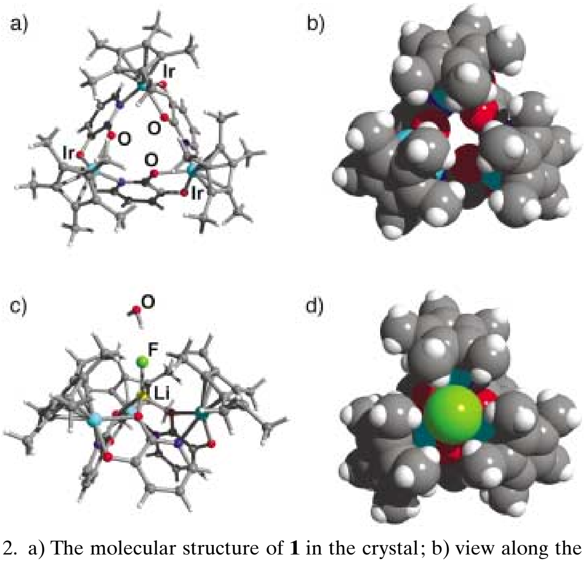

Figure 2. a) The molecular structure of **1** in the crystal; b) view along the pseudo-$C_3$ axis of **1** highlighting the sterically shielded binding site (space filling representation); c) the molecular structure of **1**·LiF in the crystal; d) view along the pseudo-$C_3$ axis of **1**·LiF. Four very short CH ⋯ F contacts are observed (the water molecule is omitted in the space filling representation).

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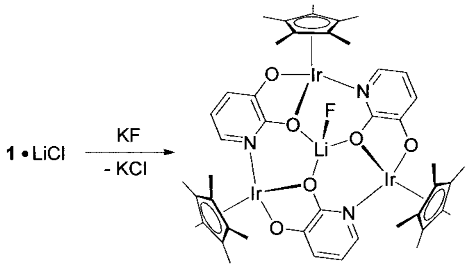
ments. Three oxygen donor atoms are positioned in a cavity that is well shielded by the Cp* ligands.

Although the molecular structure of **1** in the crystal is similar to that of the corresponding rhodium complex $[Cp^*Rh(C_5H_3NO_2)]_3$ (**2**),[5b] the host–guest properties were found to be strikingly different. If **2** is dissolved in $CD_3CN$ saturated with LiCl, the adduct **2**·LiCl is obtained in quantitative yield in less than eight minutes as evidenced by $^1H$ NMR spectroscopy. For the iridium complex **1**, on the other hand, the complexation of LiCl takes more than one hour. The half-life was determined to be 19 minutes with a pseudo first-order rate constant of $k = 5.8 \times 10^{-4}\,s^{-1}$. Compared to other $Li^+$ ionophores, this is a remarkably slow reaction.[8] The small association rate constant indicated that the binding site of receptor **1** is very rigid and sterically shielded. These characteristics prompted us to investigate the possibility of using **1** for the construction of a fluoride ion sensor as schematically depicted in Figure 1.

First, we have examined whether the metallacrown **1** can be used to stabilize molecular LiF. The molecule has to be prepared in situ because of the very low solubility of LiF. Therefore, we have synthesized the adduct **1**·LiCl, which was subsequently treated with an excess of KF in a mixture of benzene and $CH_3OH$ (140:1). We were able to isolate the complex **1**·LiF in analytically pure form by crystallization from benzene/pentane (Scheme 1).



Scheme 1. Synthesis of **1**·LiF by anion exchange.

The successful Cl–F anion exchange was evident from the NMR spectroscopic data: the $^7Li$ NMR spectrum of **1**·LiF shows a doublet resulting from coupling to the adjacent fluoride ion, while the $^{19}F$ NMR spectrum displays a quartet resulting from coupling to a $^7Li$ center (Figure 3). The $^{19}F$-$^7Li$ coupling constant of 101 Hz is larger than those found for other compounds with Li···F contacts.[9]

In the crystal, the LiF complex shows a triangular geometry similar to that of the free receptor **1** (Figure 2).[7] The presence of the guest molecule results in a slightly expanded macrocycle with an average Ir···Ir distance of 5.43 Å (**1**: 5.37 Å). The lithium ion is coordinated to the three O atoms inside the cavity (Li–O = 1.97, 2.00, and 2.02 Å) with the fourth coordination site being occupied by the fluoride ion. The Li–F distance is of special interest: with 1.755(11) Å it is significantly shorter than that found for crystalline LiF (2.009 Å).[10] The difference can be attributed, at least partially, to the reduced coordination numbers of the $Li^+$ as well as of the $F^-$ ion. The compound $[Li(THF)_2P(SiFtBu_2)_2]$, for example, with a fourfold coordinate $Li^+$ ion shows a Li–F bond length of 1.843(15) Å.[11]

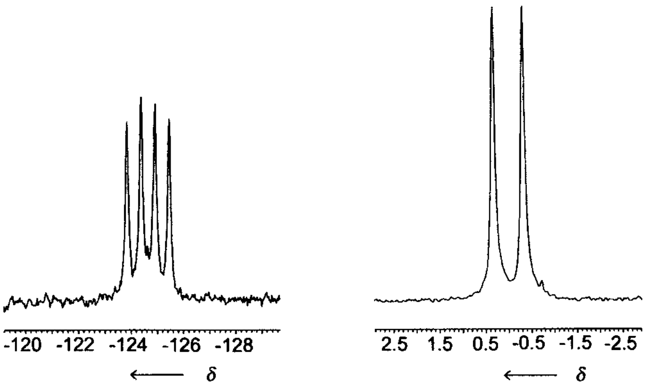


Figure 3. $^{19}F$ (left) and $^7Li$ NMR (right) spectra of complex **1**·LiF ($C_6D_6$).

The fluoride ion is positioned at the opening of the cavity. As a result, four very short CH···F contacts between the Cp* ligands and the $F^-$ ion can be observed (CH···F = 2.15–2.28 Å). This very tight encapsulation of the fluoride ion is expected to contribute to the overall stability of the host–guest complex.[12] Furthermore, the fluoride ion is bound through a hydrogen bond to a water molecule (F···O = 2.640(7) Å).

After having established that the macrocycle **1** is able to complex LiF, we have investigated whether lithium salts of **1** can be employed for the selective recognition of a fluoride anion. For this purpose we have synthesized the adduct **1**·$LiBF_4$. The X-ray structural analysis revealed that in the solid state the salt is likewise bound as an ion pair with an almost linear $Li(\mu\text{-}F)BF_3$ fluoro bridge (172.9(7)°).[7] The Li–F bond length of 1.957(16) Å is significantly longer than that found for **1**·LiF and that calculated for $[(H_2O)_3Li(\mu\text{-}F)BF_3]$ (1.768 Å).[4a] The adduct shows, once again, a pseudo-$C_3$ molecular symmetry with short CH···F contacts ranging from 2.27 to 2.49 Å. NMR data indicate that in solution ($CDCl_3$:$CD_3CN$, 2:1) the weekly bound $BF_4^-$ ion is not coordinated to the lithium ion: even at low temperatures coupling between $^7Li$ and $^{19}F$ centers cannot be observed. Furthermore, the $^1H$ and $^7Li$ NMR spectra of **1**·LiCl and **1**·$LiBF_4$ are identical, which suggests that in both cases the ion-separated, solvated complex [**1**·$Li^+(Solv.)_x$] (Solv. = solvent) is present. If 0.5 equivalents of $NBu_4F$ are added to a solution of **1**·$LiBF_4$, signals of the ion-paired complex **1**·LiF are immediately observed by $^{19}F$ and $^7Li$ NMR spectroscopy. The clearly distinguishable signals of **1**·LiF appear in the $^1H$ NMR spectrum. These experiments showed that the cationic complex [**1**·$Li^+(Solv.)_x$], generated by dissolving **1**·$LiBF_4$ in a mixture of $CDCl_3$ and $CD_3CN$, acts as a high-affinity receptor for fluoride anions. In contrast to the complexation of the lithium cation by the free receptor **1**, the coordination of the fluoride anion to [**1**·$Li^+(Solv.)_x$] is very fast.

To test the selectivity of the receptor we have performed competition experiments with **1**·$LiBF_4$, $NBu_4X$ ($X^- = Cl^-$, $Br^-$, $I^-$, $NO_3^-$), and $NBu_4F\cdot 3H_2O$ (receptor:$X^-$:$F^-$ = 1:100:2). In spite of the large excess of the competing anion ($X^-$), the exclusive formation of **1**·LiF was determined by

NMR spectroscopy ($^1$H, $^7$Li) in all cases.[13] Given that the yield of **1**·LiF is at least 97 %, the fluoride/X$^-$ selectivity must be higher than $1.6 \times 10^3$.[14]

A receptor with high affinity and selectivity is a prerequisite for potential applications in fluoride sensing. However, the possibility to transduce the binding event into some kind of signal output is likewise of central importance. In this respect, electrochemical responses are especially suited.[15] When a solution of the complex **1**·LiBF$_4$ in CHCl$_3$:CH$_3$CN (2:1) was investigated by differential pulse voltammetry, the peak potential for the first oxidation of the redox-responsive host was observed at 890 (±3) mV (against Ag/AgCl).[16] The complex was significantly easier to oxidize ($\Delta E = -203$ mV) when five equivalents of NBu$_4$F were added, presumably because the electron-withdrawing character of the ion-paired LiF guest is smaller than that of the solvated lithium ion (Table 1). In agreement with the NMR studies, only small changes were observed upon addition of Cl$^-$, Br$^-$, NO$_3$$^-$, HSO$_4$$^-$, or ClO$_4$$^-$ salts ($\Delta E < 24$ mV). Similar results were obtained in solutions containing methanol (CDCl$_3$:CD$_3$CN:CH$_3$OH = 4:2:1). This result is in contrast to many other fluoride receptors which cannot be used in protic solvents.[1, 2] It should be pointed out that all electrochemical investigations were carried out in 0.1 M NBu$_4$BF$_4$ as a supporting electrolyte. Apparently, the very large excess of BF$_4$$^-$ ions (BF$_4$$^-$:F$^-$ = 140:1) does not interfere with the selective detection of fluoride ions.

Table 1. Absolute difference of the peak potential for the first oxidation of **1**·LiBF$_4$ (0.36 mM) after addition of five equivalents of NBu$_4$X.[a]

| X$^-$ | $\Delta E$ [mV] solvent A | $\Delta E$ [mV] solvent B |
|---|---|---|
| F$^-$ | 203 | 191 |
| Cl$^-$ | 24 | < 20[b] |
| Br$^-$ | 6 | < 20[b] |
| NO$_3$$^-$ | 24 | 18 |
| HSO$_4$$^-$ | 12 | 0 |
| ClO$_4$$^-$ | 6 | 0 |

[a] Determined by differential pulse voltammetry. Solvent A: CHCl$_3$:CH$_3$CN (2:1;), solvent B: CHCl$_3$:CH$_3$CN:CH$_3$OH (4:2:1). [b] The peak appears as a shoulder.

In summary, we have shown that the organometallic metallacrown complex **1** can act as a receptor for LiF. To the best of our knowledge, the resulting adduct **1**·LiF represents the first structurally characterized complex of molecular LiF. The unique situation of LiF inside the macrocyclic host is reflected by the very short Li–F distance and the large $^{19}$F-$^7$Li NMR coupling constant, unparalleled by other compounds with Li···F contacts. On the basis of these results, we have constructed a highly selective chemosensor that allows the detection of fluoride anions by electrochemical means, even in protic solvents.

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anisotropically defined. H atoms were placed in calculated positions using the riding model. CCDC-175844 (**1**), CCDC-175845 (**1**·LiF), and CCDC-175846 (**1**·$\mathrm{LiBF_4}$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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# Cyclo[8]pyrrole: A Simple-to-Make Expanded Porphyrin with No Meso Bridges[**]

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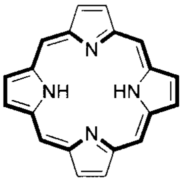
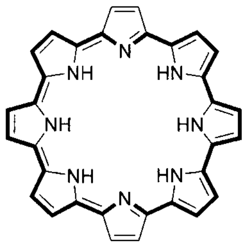
*Dedicated to Professor James P. Collman*
*on the occasion of his 70th birthday*

Porphyrin (for example, **1**), a tetrapyrrolic macrocycle, is the active component of many naturally occurring pigments and has been known and studied for centuries; its biological importance can hardly be overestimated.[1] In spite of this ubiquity, it was only in 1966 that the first expanded porphyrin analogue, sapphyrin, was reported,[2] and it has only been in recent years that the area of expanded porphyrin research has begun to attract attention as its own rapidly evolving field.[3–5] One of the unexpected surprises to emerge from this work is the finding that large expanded porphyrins (those containing eight or more pyrrole rings) are often not flat but rather adopt "figure-eight" and other twisted conformations in spite of being highly conjugated.[6–11] It thus remains a challenge at present to produce large aromatic expanded porphyrins that display the classic disklike structure of simple porphyrins.[12–15]



**1**



**2**

One structure that might allow this elusive goal to be met is cyclo[8]pyrrole (**2**; [30]octaphyrin(0.0.0.0.0.0.0.0)). This target can be derived, at least in theory, by replacing all four meso-carbon bridges with four additional pyrrolic rings. If it is produced in this way, cyclo[8]pyrrole would possess an extended 30-π-electron periphery that, in analogy to the 18-π-electron system of porphyrin, would be aromatic in a Huckel ($4n+2$) π-electron sense (compare **1** and **2**).

A retrosynthetic analysis of **2** leads to the consideration that it could be "split up" by disconnection of one or more of the $\alpha$–$\alpha'$ bonds between the individual pyrrolic subunits, which means it could be prepared (at least in principle) from linear oligopyrrolic fragments, such as a linear octipyrrolic unit, two quaterpyrrolic units, four bipyrrolic units, or ultimately eight

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