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Authors: Sinchan Maji and Debaprasad Mandal

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Perfluoroalkylated Calix[4]pyrrole: Fluoride Ion Extraction from Aqueous Medium

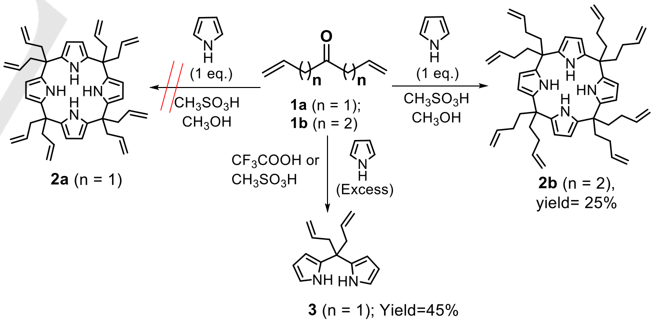
Sinchan Maji and Debaprasad Mandal*

Abstract: Octaalkenyl calix[4]pyrrole ($CH_2{=}CH(CH_2)_2)_8C4P$) is highly useful for post functionalization towards design of different calix[4]pyrrole with desired functionality. Functionalization with perfluoroalkyl chains [$CF_3(CF_2)_n$; R_{fn}] gives perfluoroalkyl calix[4]pyrroles ($R_{fn}(CH_2)_4)_8C4P$; n=6, 8), having >60% fluorine content which creates hydrophobic environment inside the calix[4]pyrrole cavity and recognizes fluoride and chloride ion from solution as well as solid. Fluoride ion is extracted efficiently from aqueous CsF and TBAF solutions by ($R_{f6}(CH_2)_4)_8C4P$ as droplets. Fluorous chain generates hydrophobic environment which destroys the hydration shell associated with anion and separates out fluoride ion as droplets from aqueous medium. Further fluoride ion competitively replaces chloride ion from ($R_{f6}(CH_2)_4)_8C4P$ cavity.

Anion specific recognition, extraction and transportation play a key role in several chemical and biological processes.[1] Selective recognition and extraction of anions particularly the charge-dense small anions like fluoride, sulfate which are highly hydrophilic, and residing far down of Hofmeister series[2] is often challenging owing to their high hydration energy. Anion receptors with a variety of hydrogen bond donors like urea, pyrrole and indole based systems have been developed for specific interactions where calix[4]pyrrole has proved to be highly effective and a novel anion receptor.[3] Calix[4]pyrroles are extensively used as neutral receptors for sensing, extraction and transportation of anions, ion-pairs, electron rich compounds[4] and biomolecules[5]. Octamethyl calix[4]pyrrole binds effectively with small anions like F^- and Cl^- owing to its small cavity size in non-aqueous solvents.[6] Modification of calix[4]pyrrole cavity is essential to recognize these anions from aqueous phase. Other particular guests are accommodated often by modulation of cavity with specific functionalities by substitution at *meso*-position or β-pyrrole position of calix[4]pyrrole.[7,8] However, the modifications are often cumbersome and offer poor yield due to formation of unwanted oligomeric products. An easily available common *meso*-substituted calix[4]pyrrole would be of great importance to achieve various customized structure for specific interactions with different guest molecules. Substitution of alkyl chains with terminal double bond at the *meso*-position of calix[4]pyrrole as tolerable functionality would be a common precursor for various modifications, where post functionalization of the terminal double bonds will aid in synthesizing different calix[4]pyrrole with tunable cavity for specific interaction with different guest molecules. For example, the incorporation of perfluoroalkyl groups [$CF_3(CF_2)_{n-1}$ abbreviated R_{fn}] at the terminal double bond would create hydrophobic environment inside the calix[4]pyrrole cavity due to highly hydrophobic nature of perfluoroalkyl chains. Hofmeister biased anions like fluoride ion remains highly solvated in aqueous solution having very high hydration energy. Once the hydrated F^- interacts via hydrogen bonding in the calix cavity, the hydration shell is destroyed by the hydrophobic environment of perfluoroalkyl chains (R_{fn}). Now the interaction between calix-NH and F^- completely depends on charge density of anion without the hydration shell and overcomes the Hofmeister biasness.

Fluoride ion, owing to its significance in biology and environmental pollution, has been one of most popular target for recognition and sensing studies.[9] While most neutral receptors recognize fluoride ion from tetrabutylammonium fluoride (TBAF) salt in organic solvents, only a few can detect fluoride ion from TBAF, KF or CsF in aqueous solutions or extracted it from water where F^- received least preference among several anions due to its high hydration energy.[7d,10]

Here, we have shown the synthesis of *meso*-substituted octaalkenyl calix[4]pyrrole and dipyrromethane derivative followed by further substitution of their terminal double bonds with perfluoroalkyl groups. These perfluoroalkylated calix[4]pyrrole receptors recognize fluoride ion selectively from solution as well as solids.



Scheme 1. Synthesis of octaalkenylcalix[4]pyrrole **2b** and dipyrromethane **3**

We have synthesized octa(but-3-en-1-yl)calix[4]pyrrole **2b** with 25% yield as shown in Scheme 1. However, the homologous compound **2a** with one methylene spacer at *meso*-position could not be synthesized in several attempts (Scheme 1). When equimolar **1a** and pyrrole were reacted by varying solvents and acid catalysts, in each case unreacted ketone was recovered and a black polymeric pyrrole was obtained. Further, **1a** was converted to dipyrromethane **3** with large excess of pyrrole (1:10) where pyrrole acted as both reactant as well as solvent. It was assumed that dimer formation is facile due to its flexibility whereas ketone **1a** was unable to coordinate with pyrrole to give

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[a] Sinchan Maji, Dr. Debaprasad Mandal
Department of Chemistry
Indian Institute of Technology Ropar
Nangal Road, Punjab 140001, India
E-mail: dmandal@iitrpr.ac.in

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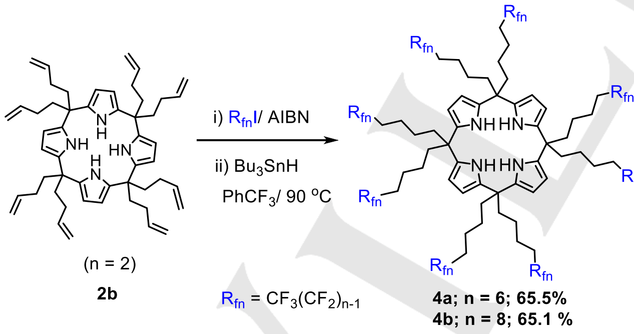
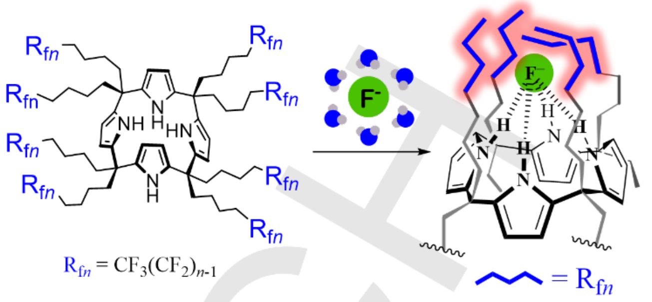
2a due to either steric or electronic effect or both. Whereas, analogous 4-heptanone easily forms octapropylcalix[4]pyrrole (**5**) with pyrrole over 30% yield (Scheme S3, SI). Dimer **3** was obtained as 45% yield after purification by column chromatography. Calix[4]pyrrole **2b**, and **3** were characterized by ^{1}H, ^{13}C NMR and HRMS. Single crystals of **2b** obtained from slow evaporation of DCM/MeOH mixture (v/v 10/1) was also analyzed by single crystal X-ray measurement. The crystal structure shows that calix[4]pyrrole **2b** possess a C_2 symmetry and two plane of symmetry (C_{2v} point group) (Figure S1, SI). The pyrrole rings adopt 1, 3-alternate conformations and alkenyl groups at *meso*-positions are directed outward from the calixpyrrole cavity. The crystal structure does not show any intermolecular interaction in the solid state.

Terminal double bonds of octaalkenyl calix[4]pyrrole **2b** and dimer **3** can easily be functionalized with the addition of phosphine, amine, hydroxyl, borane and perfluoroalkyl group. The addition of eight perfluoroalkyl groups (perfluorohexyl, R_{f6} and perfluorooctyl, R_{f8}) to these double bonds of **2b** give perfluoroalkyl calix[4]pyrrole **4a** and **4b** according to Scheme 2 as light yellow solids with 65% yield. **4a** and **4b** were characterized by ^{1}H, ^{19}F NMR and HRMS, wherein ^{1}H NMR shows doublets for β-pyrrole CH at 5.93 ppm and a broad singlet for pyrrole NH at 7.0 ppm (Figure S5, S9, SI) suggesting 1,3-alternate conformation in $CDCl_3$ like other calix[4]pyrrole.[11] **4a** and **4b** both are soluble in $PhCF_3$, $C_6F_5CF_3$, chloroform, THF, and ether but are insoluble in methanol, water, acetonitrile, and DMSO. Both fluorous calix[4]pyrroles behave very similar except **4b** is more fluorophilic due to more fluorine content than **4a**. Perfluorohexyl calix[4]pyrrole **4a** forms needle shape crystals upon slow evaporation from ethyl acetate/hexane mixture (v/v 1:9). However, single crystal X-ray data could not be solved due to poor data, probably due to long fluorine chains.

Perfluoroalkyl calix[4]pyrroles (fluorine content ≥60 wt%) are highly hydrophobic due to large hydrophobic surface of perfluoroalkyl chains and low polarizability of fluorine compared to hydrogen.[12]



Scheme 2. Synthesis of perfluoroalkyl calix[4]pyrroles **4a** and **4b**



Scheme 3. Fluoride ion inside the hydrophobic cavity of **4a** after destroying the hydration shell.

Presence of perfluoroalkyl chain at *meso*-position of **4a** creates hydrophobic environment which is helpful for extraction of anions from aqueous medium since kosmotropic anions have an affinity for hydrophobic concavity.[13] **4a** undergoes conformational change to attain cone conformation when interacts with an acceptor anion. At the same time, the anion bound cone conformer calix core will rearrange the *meso* perfluoroalkyl chains which make the calix[4]pyrrole cavity hydrophobic as shown in Scheme 3. Subsequently, the solvated anion coordinated with pyrrole NH would release the water molecules of hydration shell from hydrophobic environment and overcomes Hofmeister bias in anion extraction process.

Dimer **3** is an important precursor to achieve different calix[4]pyrrole derivatives from the reaction with different ketones.[14] For example, tetramer **6** and **7** were synthesized from the reaction of **3** with acetone and 4-hydroxy-2-butanone respectively (Scheme S4, SI). Calix[4]pyrroles **6** and **7** were characterized by ^{1}H, ^{13}C NMR and HRMS. Compound **6** is a mixture of two isomers, however, we didn't observe them in ^{1}H NMR. Further, **3** was reacted with benzyl phosphine, to form 3° phosphine bridged dimer **9** as a major product and 2° phosphine attached with dimer **8** as minor product (Scheme S4, SI).

In a preliminary study anion binding affinity of **4a** was analyzed with tetraalkylammonium halide by ^{1}H and ^{19}F NMR titration in $CDCl_3$ and in THF-d_8. Since **4a** is insoluble in most of the polar solvents, we have analyzed the binding affinity by solid-liquid extraction of different tetramethylammonium (TMA) salts. It was observed that $CDCl_3$ solution of **4a** can extract F^- and Cl^- from excess solid TMAF.4H_2O and TMACl salts respectively. In case of TMAF, ^{1}H NMR showed a clear shift in NH protons from 6.99 ppm to 12.33-12.43 ppm and β-pyrrole CH protons were shifted upfield from 5.93 ppm to 5.52 ppm on binding with F^- as shown in Figure 1. Further the interaction of fluoride with NH protons of calix showed splitting into doublet at room temperature due to coupling between bound fluoride anion and pyrrole-NH protons. The extraction of TMAF was also supported from the peak at 3.22 ppm correspond to the protons of $[TMA]^+$. The ^{19}F NMR spectrum of perfluorohexyl calix[4]pyrrole-TMAF complex showed appearance of a new peak at –93.69 ppm (multiplet) which indicates fluoride anion bound with pyrrole NH of host calix[4]pyrrole and coupling between them (Figure S17, SI). Similarly, on addition of excess solid TMACl to host solution, pyrrole NH proton was shifted to 11.18 ppm and β-CH peaks were shifted to 5.51 ppm (Figure 1). Cl^- shows a weaker binding and the binding is only partial as observed in ^1H NMR, one part of NH and β-CH protons were shifted while other part remained at the same position. However, other TMA salts (Br^-, I^-, NO_3^- and HSO_4^-) do not show any interaction according to NMR studies. More importantly, solid CsF showed small binding in $CDCl_3$ as evidenced from the shift of NH protons and β-CH in ^1H NMR (Figure S18, SI).

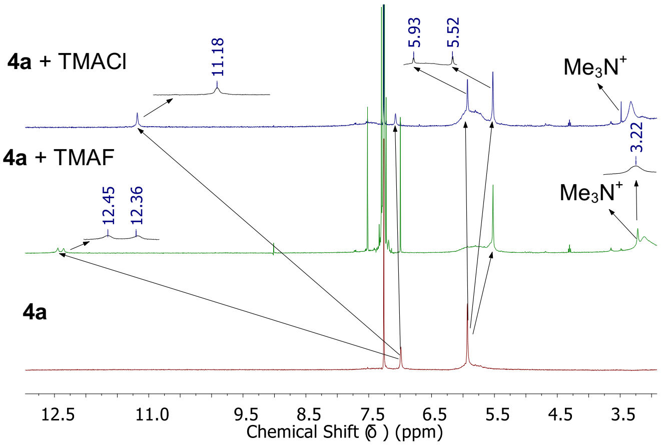


Figure 1. Changes in ^1H NMR of **4a** in $CDCl_3$ upon addition of quantities of solid TMAF and TMACl

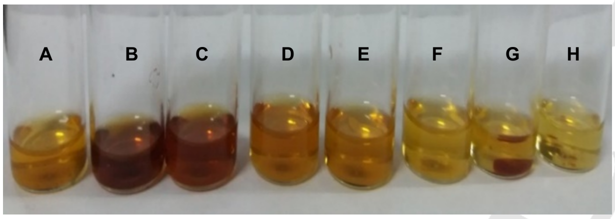


Figure 2a. Colours of THF solutions (A) **4a** (B) **4a** + TBAF.3H_2O (C) **4a** + Aliquat 336 (D) **4a** + TBABr (E) **4a** + TBAI (F) **4a** + $TBAHSO_4$ (G) **4a** + TMAF in MeOH (H) **4a** + TMACl in MeOH

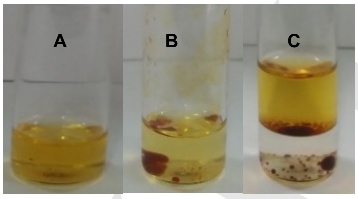


Figure 2b. (A) **4a** in THF; droplets from (B) **4a** in THF + TBAF in H_2O (C) **4a** in THF + CsF in H_2O

Moreover, when TBAF was added to a THF solution of **4a** the colour changed from yellow to deep wine-red (Figure 2a) possibly due to the pyrrole-F complex formation in polar aprotic solvents which is now possible for naked eye detection. Similarly, Aliquat 336 (Cl^- source) gives a very slow colour change over more than 2 h. Similarly, in UV-vis study appearance of a new peak at 375 nm for F^- and Cl^- complex of **4a** was observed in THF (Figure S15, SI). It was further confirmed by NMR study where upon addition of TBAF, pyrrole NH undergoes downfield shift to 12.50 ppm and β-pyrrole proton was shifted upfield to 5.44 ppm in THF-d_8 (Figure 3). Upon successive addition of TBAF to **4a** in THF-d_8 during NMR titration, both free calix 4a, (pyrrole NH, 9.40 ppm and β-pyrrole CH 5.87 ppm) and fluoride bound complex **4a**-F^- (pyrrole NH-F (12.50 ppm and β-pyrrole CH 5.87 ppm) were present together and no intermediate peak of partial binding could be observed indicating a fast complexation kinetics between **4a** and fluoride ion (Figure S19, SI). Screening of other anions for **4a** in THF didn't give any colorimetric response except F^- and Cl^- (Figure 2a) or change in the NMR. It is interesting that **4a**-F^- complex was protected within the fluorous cavity even in the presence of water. Upon addition of D_2O (30 mol% of host) to the NMR solution no change was observed both in pyrrole NH as well as β-pyrrole CH peak positions. On further addition of large excess of D_2O only exchange of NH peak took place whereas β-CH peak shifted only slightly downfield due to the dilution effect (Figure S20, SI). Further, when aqueous solution of TBAF was added to the THF solution of **4a**, droplets were formed and settled at the bottom (Figure 2b), as **4a** extracts and separates out F^- from water in the form of droplets. The isolated droplets gave dark violet colour when dried and the ^1H NMR in THF-d_8 showed ^1H and ^{19}F NMR similar to **4a**-TBAF complex (Figure 3 and S22, SI). It was interesting to note that the remaining solution after separation of droplets showed only excess of TBAF and a negligible trace of the host in ^1H NMR (Figure S23, SI). This ensures that maximum amount of host separates out as droplets by extracting F^- from aqueous TBAF solution. In a separate experiment when excess **4a** in THF-d_8 was stirred with TBAF/D_2O solution, no TBAF traces could be detected in the remaining D_2O solution confirms complete extraction of F^-. To understand the extraction ability, **4a** was treated with aqueous CsF where perfluoro calix[4]pyrrole **4a** isolates F^- as droplets (Figure 2b). After encapsulation of fluoride ion from the aqueous interface, the complex becomes insoluble either in THF or water, therefore host-guest complex separates out as droplets from water-THF solvent mixture. These results suggest that **4a** is capable of extracting fluoride ion exclusively from their aqueous solutions. Association constant (K_a) of fluoride ion with **4a** was obtained as 1.24×10^5 M^{-1} using Cram's extraction method with 65.7% extraction yield of fluoride ion.[15] Since the alkyl chains also exert hydrophobicity, a similar binding studied of TBAF with octapropylcalix[4]pyrrole **5** was performed in chloroform and in THF-H_2O mixture. According to β-pyrrole shift in ^1H NMR, a weak binding of fluoride with **5** was detected in $CDCl_3$ with excess of TBAF which releases F^- upon addition of D_2O and the β-pyrrole peaks return to its previous position (Figure S24 SI). Further, when aqueous TBAF solution was added to a THF solution of **5**, no droplets formation or any changes was observed in ^1H NMR. From these experiments it was clear that the hydrophobicity of perfluoroalkyl group in calix[4]pyrroles helps extraction of fluoride ion from aqueous medium overcoming Hofmeister bias rather than long chain alkyl groups.

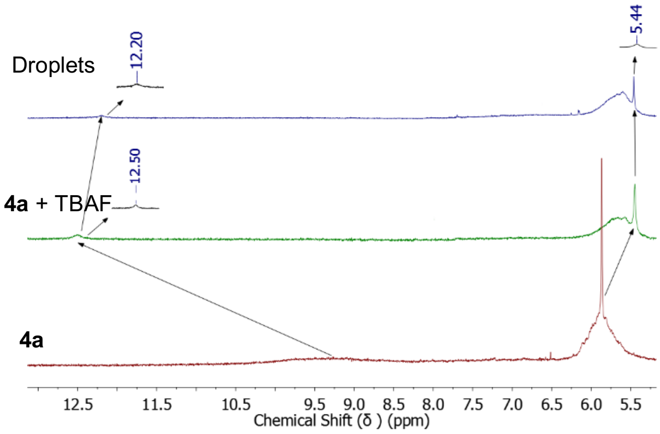


Figure 3. Comparative ^{1}H NMR in THF-d_8 of host **4a**, **4a**-F^- complex and extracted fluoride (droplets) by **4a** from water

In order to understand the comparative binding affinity of F^- and Cl^- with the host, equimolar quantities (4.50 equiv.) of both anions were added to $CDCl_3$ solution of **4a** and NMR was taken. The pyrrole NH peak appears at 12.33-12.43 ppm and the β-CH peaks was shifted to higher fields and appears at 5.52 ppm, but no peak corresponding to 11.18 ppm was observed (Figure S25, SI). This clearly indicates the formation of $((R_{f6}(CH_2)_4)_8)$calix-F^- complex rather than chloride bound complex. To get further insight, both anions were added sequentially in different equivalence. Initially addition of 1.0 equiv. of TMACl (solid) to host showed a peak at 11.18 ppm corresponding to Cl^- ions bound with pyrrole NH protons. On successive addition of TMAF (0.5 equiv on 1st addition and 1.0 equiv. on 2nd addition), the NH peak corresponding to bind Cl^- decreased and a new peak appeared at 12.33-12.43 ppm gradually. On further addition of TMAF, Cl^- from cavity was completely replaced by F^- (Figure S26, SI). However, further addition of excess TMACl to the resulting solution showed no change in NMR which indicates that F^- ion can replace bound Cl^- ion from host whereas Cl^- is not able to remove bound F^- anion. Therefore perfluorohexyl calix[4]pyrrole is a better fluoride anion receptor than chloride. Fluoride anion binding capability of the perfluorocalix[4]pyrrole receptor was also confirmed from ^{19}F NMR. Competitive anion binding studies were also done with TMABr, TBAI, $TMANO_3$ and $TBAHSO_4$ but the corresponding anions of these salt did not show any binding with host perfluorohexyl calix[4]pyrrole.

In conclusion we have synthesized terminal double bond substituted *meso*-octaalkenyl calix[4]pyrrole and dialkenyl dipyrromethane as common useful precursors in good yield for further functionalization for designing different calix[4]pyrrole with desired functionality. The terminal double bonds were easily functionalized with perfluoroalkyl chains and phosphine and they can be further extended to borane, hydroxyl functionalization and polymerization for different applications. The dipyrromethane derivative is an important precursor for the synthesis of various unsymmetrical calix pyrroles. Highly hydrophobic perfluoroalkyl substituted calix[4]pyrrole recognizes hydrated F^- and Cl^- anion from solid as well as from aqueous solution overcoming Hofmeister bias with colorimetric detection. Fluoride ion was extracted efficiently and isolated from aqueous CsF and TBAF by $((R_{f6}(CH_2)_4)_8$C4P) exclusively as droplets.

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Keywords: perfluoroalkyl • calix[4]pyrrole • fluoride ion• anion recognition • Hofmeister bias

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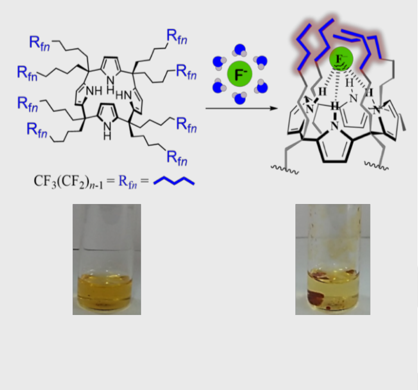
Entry for the Table of Contents

COMMUNICATION

Fluoride anion extraction from water: Perfluoroalkyl substituted calix[4]pyrroles entrap the fluoride ion in its hydrophobic cavity and separates out as droplets from aqueous solution by destroying the hydration shell and overcome the Hofmeister bias.



*Sinchan Maji and Debaprasad Mandal**

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Perfluoroalkylated Calix[4]pyrrole: Fluoride Ion Extraction from Aqueous Medium