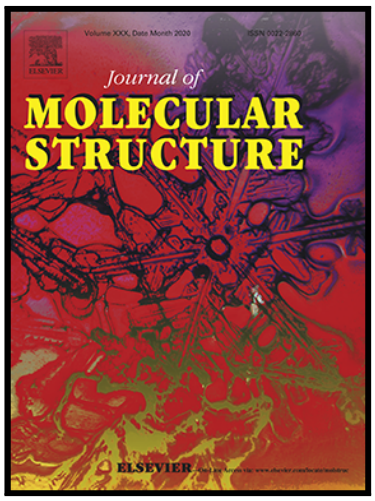


Carbazole diester strapped calix[4]pyrrole: synthesis, anion binding and self assembly based on ion pair recognition

Ashoke Kumar Patra , Dibakar Halder , Anik Roy , Somenath Kundu , Maidul Hossain , Rajat Saha , Indrajit Saha

PII: S0022-2860(23)01300-5
DOI: https://doi.org/10.1016/j.molstruc.2023.136210
Reference: MOLSTR 136210

To appear in: *Journal of Molecular Structure*

Received date: 5 April 2023
Revised date: 11 July 2023
Accepted date: 13 July 2023

Please cite this article as: Ashoke Kumar Patra , Dibakar Halder , Anik Roy , Somenath Kundu , Maidul Hossain , Rajat Saha , Indrajit Saha , Carbazole diester strapped calix[4]pyrrole: synthesis, anion binding and self assembly based on ion pair recognition, *Journal of Molecular Structure* (2023), doi: https://doi.org/10.1016/j.molstruc.2023.136210

Highlights

- A new carbazole strapped calix[4]pyrrole **1** has been synthesized for anion binding.
- Receptor **1** showed enhanced halide binding than parent octamethyl calix[4]pyrrole.
- Different linear supramolecular assemblies were constructed by ion pair binding.
- Solid state structure of ion pair complex of CsI with strapped calix[4]pyrrole **1**.
- Extraction of CsF and CsCl salts under solid-to-liquid extraction condition.

Carbazole diester strapped calix[4]pyrrole: synthesis, anion binding and self assembly based on ion pair recognition

Ashoke Kumar Patra[a], Dibakar Halder[a], Anik Roy[a], Somenath Kundu[b], Maidul Hossain[b,*], Rajat Saha[c,*], Indrajit Saha[a,*]

[a]Department of Chemistry, Ramakrishna Mission Residential College (Autonomous), Narendrapur, Kolkata, 700103, India

E-mail: indra_ku@yahoo.co.in

[b]Department of Chemistry, Vidyasagar University, Midnapore, 721102, India

Email: hossainm@mail.vidyasagar.ac.in

[c]Department of Chemistry, Kazi Nazrul University, Asansol, 713340, India

E-mail: rajat.saha@knu.ac.in

[*]Corresponding author.

Abstract

A new carbazole strapped calix[4]pyrrole **1** has been synthesized and ion binding properties was investigated using ^{1}H NMR, isothermal titration calorimetry and single crystal X-ray diffraction analyses. Compared to the parent octamethyl calix[4]pyrrole **2**, receptor **1** showed enhanced binding towards halide anions. Solid state structural analysis revealed that receptor **1** is capable of binding various halide salts showing different binding modes depending on the bound ion pairs. Interestingly, complexes of tetrabutyammonium (TBA^{+}), tetraethylammonium (TEA^{+}) and tetramethyl ammonium (TMA^{+}) salts of chloride anion displayed three distinctly different binding geometries in the solid state. As a result, the linear supramolecular polymers seen in the crystal lattices are also dramatically different for these three chloride complexes of **1**. Combination of ^{1}H NMR and solid state studies revealed that binding of anion in one condition do not translates to another completely. Receptor **1** also found to form 1/1 complexes with CsCl, CsBr and CsI salts and 1D coordination polymer chains are stabilized in the solid state. Overall, construction of four different 1D linear chains are described for chloride anion based on ion-pair recognition. In addition, the solid state structure of ion-pair complex with CsI salt is unprecedented in the calix[4]pyrrole chemistry. Moreover, under solid-to-liquid extraction condition, receptor **1** is able to solubilise CsF and CsCl ion-pairs in chloroform in which these salts are otherwise insoluble.

Key words

calix[4]pyrrole; halide binding; ion pair binding; coordination polymer; supramolecular polymer

Introduction

In recent years, enormous effort has been invested in the design and synthesis of artificial anion receptors and myriad of charged and neutral anion receptors have been reported.[1-2] This is because anions are ubiquitous in nature and plays critical roles in variety of biological, environmental and chemical processes.[1] Among the various electroneutral anion receptors calix[4]pyrrole and related macrocycles have found extensive applications in diverse areas including recognition, extraction, transport, sensing and self assembly.[3-8]

To date, numerous calix[4]pyrrole derivatives have been synthesized by functionalizing the parent octamethyl calix[4]pyrrole at either β-pyrrolic positions or *meso*-positions to modulate anion selectivity and affinity.[3-8] Among the these strategies, single side strapping, first reported by Lee et al in 2002, displayed superior affinity and anion selectivity and many strapped systems have been synthesized over the last 20 years or so.[9, 4e] Simple strapped calix[4]pyrroles bearing auxiliary hydrogen bonding donors on the strap was found to be an effective way to tune the anion affinity of calix[4]pyrroles. In most cases, these receptors showed improved affinities for halide anions, especially for larger halides, which is ascribed to the size complementarities between the host and the halide anion in question. Specifically, the smaller fluoride anion forms stronger hydrogen bonds with calix[4]pyrrole subunit than do the other halides and with increase in size of the cavity distances between fluoride anion and hydrogen bond donors on the strap increases. This results in weaker hydrogen bonding interaction between fluoride anion and the auxiliary hydrogen bond donors present in the strap. Naturally, the larger halides can form stronger hydrogen bonds with strapping subunit than does the fluoride anion. However, chloride over fluoride selectivity was achieved in only few instances.[5a, 10]

Anion bound cone conformation of calix[4]pyrrole core also provide a π-electron rich bowl-shaped cavity suitable to accommodate charge diffuse cations such as cesium, thalium, tetraalkylammonium, tetraalkylphosphonium, imidazolium etc.[11] Thus, calix[4]pyrroles could also act as ion-pair receptors. Several strapped calix[4]pyrroles having additional cation binding sites (such as crown ether, calix[4]arene, hemispherand etc) on the strap have been reported for the recognition of various ion pairs.[4e] Ion pair complexation by some of these strapped calix[4]pyrroles are also shown to offer an opportunity to create new self-assembled structures that can be controlled by selection of ion pairs and crystallization conditions.[12] In this regard, ion pair binding and self –assembly studies with simple strapped system is underexplored. Recently, Sessler et al. showed simple strapped systems bearing additional

pyrrole moiety on the strap over-perform the parent octamethyl calix[4]pyrrole in capturing cesium halide salts in solution and solid state structures of the complexes with CsF, CsCl and CsBr were also reported.[13] However, both the parent octamethyl calix[4]pyrrole and pyrrole strapped calix[4]pyrrole were unable to form stable complex with CsI in solid state. This was ascribed to the very weak hydrogen bonding interactions between iodide anion and calix[4]pyrroles. It is worthy to mention that solid state structure of CsI salt with calix[4]pyrrole is not reported yet and still remains as challenge.

Based on these findings, we became interested in designing and investigating anion binding and ion pair recognition induced self-assembly properties of simple strapped systems. Herein, we wish to report the syntheses and ion binding properties of a new strapped calix[4]pyrrole **1** bearing a carbazole moiety in the strap. The receptor **1** is expected to show improved binding towards larger halides due its large cavity size as well the presence of additional hydrogen bond donors on the carbazole strap. As detailed below, the receptor **1** exhibited enhanced affinities for larger halides, especially for bromide and iodide anion, compared to parent octamethyl calix[4]pyrrole **2**. In addition, the receptor **1** showed dramatic changes in the ion pair binding modes depending on the combination of bound anion and cation in solid state. Specifically, three different ion pair complexation modes were seen in the chloride complexes of **1** depending on the bound tetraalkyl ammonium cations (TMA^+, TEA^+ or TBA^+ cations) in the solid state. Consequently, dramatically different linear supramolecular polymers were stabilized in the crystal lattices of these three complexes. Receptor **1** also formed ion pair complexes with cesium halide salts and complexes of CsCl, CsBr and CsI salts are found to be stabilized as linear 1D coordination polymers in solid state. Moreover, under solid-liquid extraction condition, the receptor **1** is capable of extracting both the CsF and CsCl salts into $CDCl_3$ solution with high efficiency.

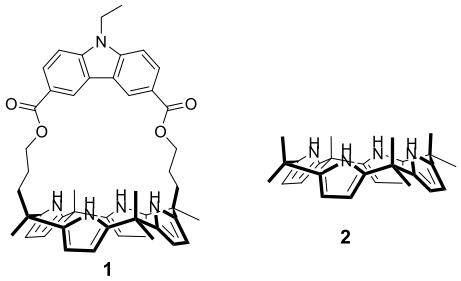
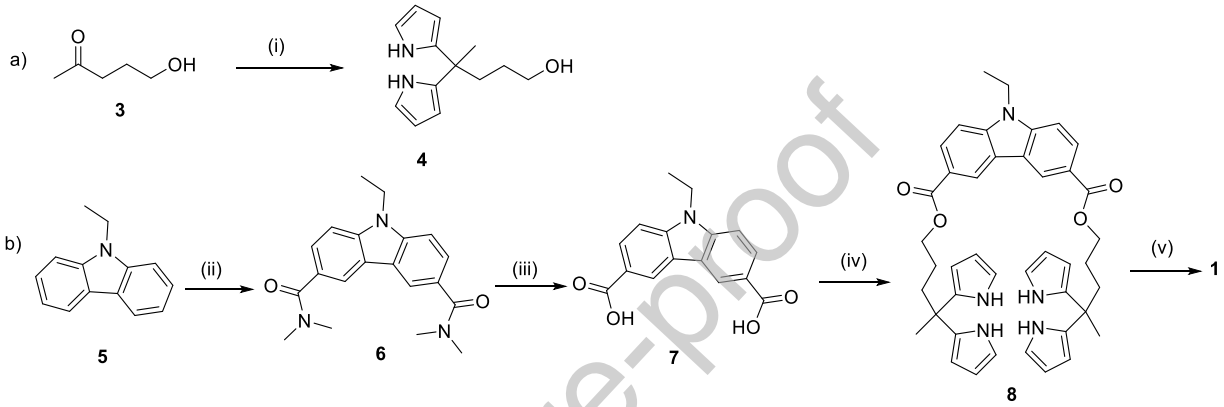


Figure 1. Molecular structures of receptor **1** and octamethyl calix[4]pyrrole **2**.

Results and Discussion

The synthesis of receptor **1** was outlined in the scheme **1**. At first, compound **4** was synthesized by acid catalyzed condensation of 5-hydroxy-2-pentanone **3** and pyrrole in the

presence of trifluoroacetic acid.[9] On the other hand, Friedel-Crafts reaction of 9-ethyl carbazole **5** with N,N-dimethyl carbamoyl chloride using anhydrous $AlCl_3$ in dichloroethane afforded the diamide **6**, which on base-catalyzed hydrolysis using ethanolic NaOH followed acidification yielded the dicarboxylic acid **7**.[14] Compound **7** was then coupled with **4** using EDC.HCl/ HOBt,/ DIPEA in DMF to give bisdipyrromethane derivative **8**. Acid-catalyzed condensation of **8** with acetone in the presence of BF_3•$(OEt)_2$ gave the desired strapped calix[4]pyrrole **1** in 8% yield. Structure of **1** was confirmed by means of conventional spectroscopic technique (ESI).



Scheme 1. Reagents and conditions: a) i) pyrrole, trifluoracetic acid, 0 °C to room temperature, 20 min. 35%; b) ii) N,N-dimethyl carbamoyl chloride, anhydrous $AlCl_3$, dichloroethane, reflux, 24 h, 82%; iii) NaOH, EtOH, reflux, 14 h, 90%; iv) **4**, EDC.HCl, HOBt, DIPEA, DMF; 58% v) Acetone, $BF_3(OEt)_2$, high dilution condition, room temperature, 8%.

Structure of receptor **1** was further confirmed by single crystal X-ray diffraction analysis. Single crystals suitable for X-ray diffraction analysis were grown from the slow evaporation of saturated solution of **1** in CH_3CN/MeOH (4:1, v/v). Analysis of the diffracted X-ray data revealed that the calix[4]pyrrole subunit adopt a 1, 2-alternate conformation and the carbazole strap remain almost perpendicular (slightly offset) to the mean plane of the calix[4]pyrrole core. As shown Figure 2, two methanol molecules are directly hydrogen bonded to the calix[4]pyrrole subunit - one sits within cavity defined by calix[4]pyrrole and carbazole strap, while the other one interacts from the opposite side, each forming two NH---O hydrogen bonds with NHs of calix[4]pyrrole with N---O distances ranging from 2.996 – 3.080 Å. The methanol molecule bound within the strap also hydrogen bonded to third molecule of methanol which in turn hydrogen bonded to the carbonyl oxygen of another molecule of **1**. The corresponding O---O distances were found to be 2.761 and 2.774 Å, respectively. An acetonitrile molecule is also found to be co-crystallized within the crystal lattice resulting in overall crystal composition **1**•$(CH_3OH)_3$•CH_3CN.

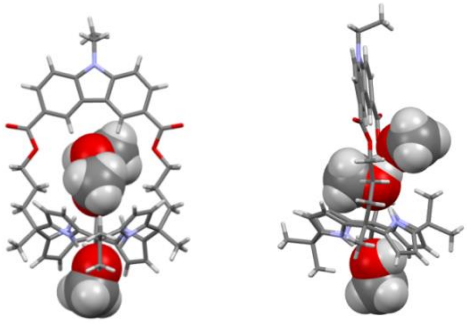


Figure 2. Two different views of single crystal X-ray structure of **1**•$(CH_3OH)_3$•CH_3CN. Acetonitrile molecule was not shown for clarity.

Initial evidence that receptor **1** binds halide anion was came from the analysis of the single crystal structures of its complexes with fluoride, chloride and bromide anions as their tetraalkyl ammonium salts. Attempted crystal growth with TBAF or TEAF was proved to be unsuccessful in our hands. However, slow evaporation of $CHCl_3$/CH_3OH (4:1, v/v) solution of **1** in the presence of TMAF afforded diffraction-grade single crystals of **1**•TMAF complexes. Structural analysis of the resulting crystals revealed the formation of 1/1 complex, wherein the anion was found to sit within the cavity of **1** by forming four hydrogen bonds with the pyrrolic NH's of the calix[4]pyrrole core with N---F^- distances of 2.797 - 2.846 Å (Figure 3). Additionally, the fluoride anion also interacted with the protons on the *meso*-methyl (C_{ml}) carbons and *meso*-methylene (C_{ml}) carbons of propyl subunits of the strap, presumably via CH---F^- hydrogen bonding interactions as characterized by C_{ml}---F^- and C_{me}---F^- distances of 3.599 – 3.639 and 3.720 – 3.801 Å, respectively. The distances between the inner CH protons of carbazole (ArCH) and the bound fluoride anion was found to be 4.364 and 4.429 Å (ArC---F^- distances ranges from 5.285 – 5.338 Å, respectively), indicating the absence of hydrogen bonding interactions between these protons and fluoride anion in solid state. Thus, the fluoride anion was stabilised inside the cavity of **1** via eight-point hydrogen bonds in the solid-state. The calix[4]pyrrole core adopted a cone-like conformation and the propyl subunits fold in same direction at *meso*-methylene carbon resulting a bent-type geometry, as seen in the most cases.[4e] The tetramethylammonium cations are nestled within the bowl-shaped π-electron rich cavities of calix[4]pyrrole, presumably via cation-π and CH-π interactions. The TMA^+ cations also interacts directly with fluoride anion bound to another molecule of **1**, presumably via CH---F^- hydrogen bonding and charge-charge interactions. This results in the formation of linear supramolecular polymer in which the carbazole subunits are found to be pointed in the same direction (Figure 3).

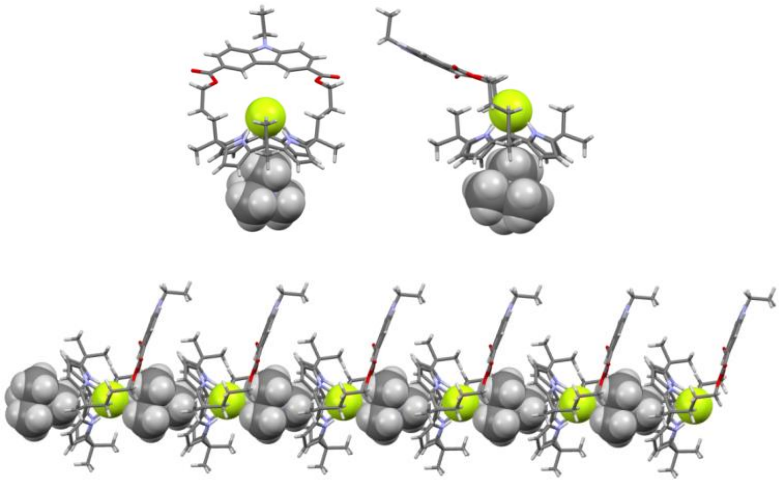


Figure 3. Two different views of single crystal X-ray structure of **1**•TMAF•$CHCl_3$ (upper traces) and partial view of the linear supramolecular polymer seen in the crystal lattice (lower trace). Chloroform molecules were not shown for clarity.

In analogy to what was seen with TMAF, receptor **1** also formed 1/1 complexes with TBACl and TMACl salts in the solid state. However, the binding modes of these 1/1 complexes differ significantly (Figure 4). Single crystals of both the complexes were grown by slow evaporation of $CHCl_3/CH_3OH$ (4:1, v/v) solution of **1** containing corresponding tetraalkyl ammonium chloride salts. Structural refinement revealed that in both the complexes the calix[4]pyrrole core adopted cone-like conformation and the chloride anion is bound to NHs of calix[4]pyrrole through four NH---Cl^- hydrogen bonds with N---Cl^- distances of 3.327 - 3.403 and 3.307 - 3.389 Å for **1**•TBACl and **1**•TMACl complexes, respectively. In addition, the chloride anion also formed four CH---Cl^- hydrogen bonds with the protons on the *meso*-methyl and *meso*-methylene carbons. The corresponding C_{ml}---Cl^- and C_{me}---Cl^- distances were estimated to be 3.740 – 3.803 and 3.925 – 3.959 Å for **1**•TBACl complex and, 3.780-3.916 and 3.783 - 3.820 Å for **1**•TMACl complex, respectively. The inner aromatic protons of carbazole subunit also interact with chloride anion via ArCH---Cl^- type hydrogen bonding interactions as characterized by ArC---Cl^- distances of 3.769 - 4.053 and 3.879 – 4.116 Å for **1**•TBACl and **1**•TMACl complexes, respectively. Thus, in both the complexes chloride anion is stabilized inside the cavity of **1** via ten-point hydrogen bonding interactions. This stands in contrast to the eight-point hydrogen bonding interactions seen in the case of **1**•TMAF complex. Again, unlike the bent-type conformation of the propyl subunits in **1**•TMAF complex, the propyl subunits move in opposite direction at *meso*-methylene carbon and adopted a twisted conformation in both the **1**•TMACl and **1**•TBACl complexes. The dispositions of the carbazole subunits in these two complexes are significantly different. While in the **1**•TBACl complex the carbazole subunit found to remain almost orthogonal

(slightly tilted) to the mean plane of calix[4]pyrrole core containing four N-atoms, in **1**•TMACl complex it is found to be significantly tilted from the orthogonal orientation.

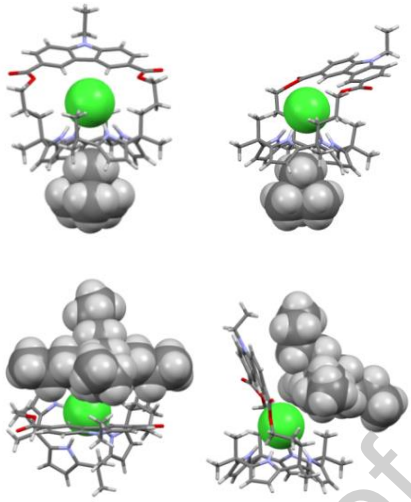


Figure 4. Two different views of single crystal X-ray structures of **1**•TMACl•CH_3OH (upper traces) and **1**•TBACl•$CHCl_3$ (lower traces). Solvent molecules were not shown for clarity.

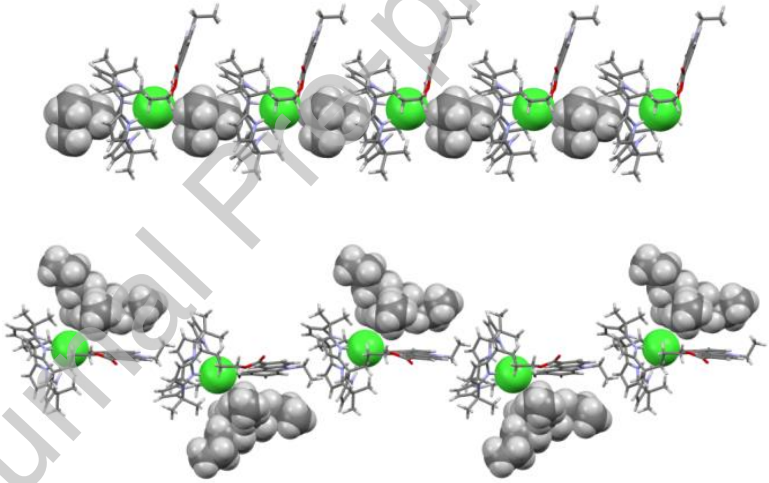


Figure 5. Partial view of the linear supramolecular polymer seen in the crystal lattice of **1**•TMACl•CH_3OH (upper trace)and **1**•TBACl•$CHCl_3$ (lower trace). Solvent molecules were not shown for clarity.

In the **1**•TMACl complex, the TMA^+ cations are complexed within the π-electron rich bowl of the calix[4]pyrrole subunit through electrostatic cation-π and CH---π interactions. The TMA^+ cation also interacts directly with the Cl^- anion bound to another molecule of **1** resulting in the formation of linear supramolecular polymer in which carbazole subunits point in same direction – analogous to that seen in the case of TMAF complex (Figure 5). In contrast, the π-electron rich bowl-shaped cavities of calix[4]pyrroles are not bound to the TBA^+ counter cations in **1**•TBACl complex, rather it was found to be occupied by the pendent N-ethyl group of the carbazole subunit of another molecule of **1**, presumably via

CH---π interactions (Figure 5). In this case, the TBA^+ cation is found to interact directly with the bound chloride anion and the carbazole subunit of the same receptor leading to the formation of contact ion pair complex, presumably stabilized by CH---Cl^-, CH---O, CH---π, cation-π interactions along with charge-charge interactions. Therefore, in the resulting supramolecular chain, the TBA^+ counter cations do not acts as linker of repeat unit rather it interacts with the supramolecular polymeric chain from outside and occupies alternate sides of the strap.

In contrast, analysis of the crystals obtained by layering methanolic solution of TEACl over $CHCl_3$ solution of **1** revealed the formation of 2/2 complex (Figure 6). In the resulting complex, propyl subunits adopt twisted conformation and the carbazole subunit resides almost perpendicular to the mean plane of the calix[4]pyrrole subunit containing four N-atoms. The chloride anion is bound within the cavity of **1** via ten-point hydrogen bonding interactions including four NH---Cl, two CH_{ml}---Cl^-, two CH_{me}---Cl^- and two ArCH---Cl^- interactions. The corresponding N---Cl^-, C_{ml}---Cl^-, C_{me}---Cl^- and ArC---Cl^- distances were found to vary from 3.314 – 3.353, 3.813 – 3.828, 3.819 - 3.939 and 3.814 – 3.946 Å, respectively.

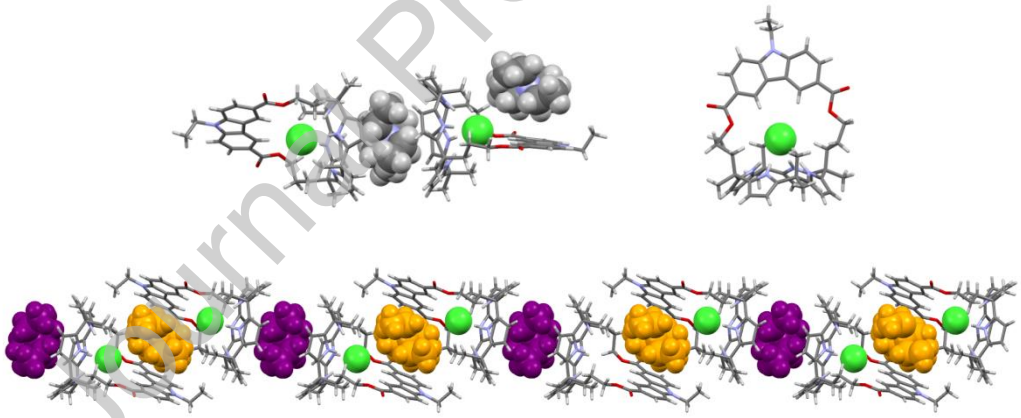


Figure 6. Single crystal X-ray structure of $\mathbf{1}_2$•$(TEACl)_2$ (upper left trace) and chloride binding mode of receptor **1** (upper right trace). Partial view of the linear supramolecular polymer chain seen in the crystal lattice (lower trace). Co-crystallized water molecules are not shown for clarity.

Interestingly, two different binding modes were seen for TEA^+ counter cations. One disordered TEA^+ cation is found to be complexed within the π-electron rich 'bowls' of two calix[4]pyrrole subunits of two different molecules of **1**, presumably via cation-π and CH---π interactions. The other TEA^+ cation interacts directly with two chloride anions that are bound to the cavities of two different receptors. This TEA^+ cation is also sandwiched between the

carbazole subunits of these two receptors, presumably via cation-π and CH---π interactions. Thus, the 2/2 complex **1**$_2$•(TEACl)$_2$ could be considered as a hybrid of a contact ion pair and a receptor-shared ion pair complexes. As a result, as shown in Figure 6, a linear supramolecular polymer chain is stabilized in solid state. Thus, TMACl, TEACl and TBACl complexes of **1** are stabilized as linear supramolecular polymers in the solid state but the repeat units of the these supramolecular polymers are distinctly different.

Attempts to grow single crystals of bromide complexes of **1** using TBA^+ and TEA^+ as counter cations were unsuccessful in our hands. However, single crystals suitable for X-ray diffraction analysis were obtained by layering methanolic solution of TMABr over $CHCl_3$ solution of **1**. X-ray diffraction analysis revealed the formation of 1/1 complex in which the bromide anion is bound within the cavity of **1** involving ten-point hydrogen bonds and the propyl subunits adopt twisted conformation (Figure 7). As expected, the N---Br^- distances for four NH---Br^- interactions were found to be slightly larger (ranges from 3.429 – 3.540 Å) as compared to the corresponding chloride complexes. In this case, the C_{ml}---Br^-, C_{me}---Br^- and ArC---Br^- contacts for CH_{ml}---Br^-, CH_{me}---Br^- and ArCH---Br^- hydrogen bonding interactions were found to range from 3.853 – 4.003, 3.847 – 3.869 and 3.873 – 4.051 Å respectively. Again, a linear supramolecular polymer is stabilized in solid state, wherein the TMA^+ cations bound within the π-electron rich cavities of calix[4]pyrrole subunit interacts with Br^- anion bound to another molecule of **1**.

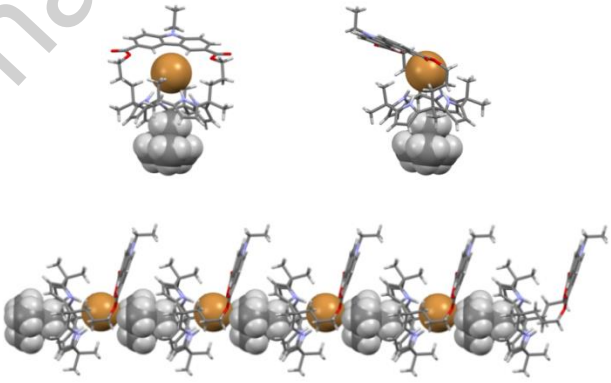


Figure 7. Two different views of single crystal X-ray structure of **1**•TMABr•CH_3OH (upper traces) and partial view of the linear supramolecular polymer seen in the crystal lattice (lower trace).

Preliminary evidence for the ability of receptor **1** to complex halide anions in solution came from the ^{1}H NMR spectroscopic studies carried out in CD_3CN. In anion-free state, the NH protons and the inner ArCHs of receptor **1** resonate as singlet at 8.44 and 8.83 ppm, respectively. As shown in Figure 8, upon addition less than 1.0 equivalent amount of TBAF

to the CD_3CN solution of **1** result in the appearance of two distinct sets proton signals corresponding to the anion free and fluoride bound receptor **1**. The presence of proton signals corresponding to both anion-free **1** and its complex is consistent with the slow complexation-decomplexation kinetics of the complex on ^1H NMR time scale at room temperature. The NH resonance shifted to 13.05 ppm ($\Delta\ \delta$ = 4.61 ppm) and appeared as doublet. The appearance of doublet is ascribed to the coupling of bound fluoride with N-H protons (J_{HF} = 40.5 Hz). The inner carbazole protons (ArCHs) shifted to 9.15 ppm, while the positions of other protons on carbazole remained almost unaltered. In addition, methylene protons adjacent to the alkoxy oxygen (-OCH_2-) of ester functions were shifted slightly to the downfield region from 3.86 to 3.97 ppm. The *meso*-methyl protons (CH_{ml}) and *meso*-methylene (CH_{me}) protons also shifted to downfield direction slightly. The pyrrolic *β*-CHs, originally resonating at 5.87 and 5.83 ppm, underwent upfield shift and appeared at 5.57 and 5.54 ppm, as expected. The changes in the ^1H NMR spectrum were essentially complete upon addition of ca. 1.0 equivalent of TBAF. These observations support the suggestion that the receptor **1** forms strong 1/1 complex with fluoride anion in CD_3CN solution, wherein calix[4]pyrrole core adopts cone like conformation and the anion is stabilized within the cavity of **1** through multiple CH---F^- type hydrogen bonding interactions with the strap along with strong hydrogen bonding interactions with the NHs of calix[4]pyrrole. Notably, the participation of ArCHs and -OCH_2- protons in hydrogen bonding interaction with fluoride anion in solution stands in contrast to the solid state structure of **1**•TAMF complex where these protons are seen to stay beyond the hydrogen bonding contacts with the bound fluoride anion. In fact, in all the complexes of halide anions the -OCH_2- protons do not form hydrogen bonds with the bound anion in the solid state but do form hydrogen bonds with the bound anion in solution as inferred from ^1H NMR studies (*vide infra*).

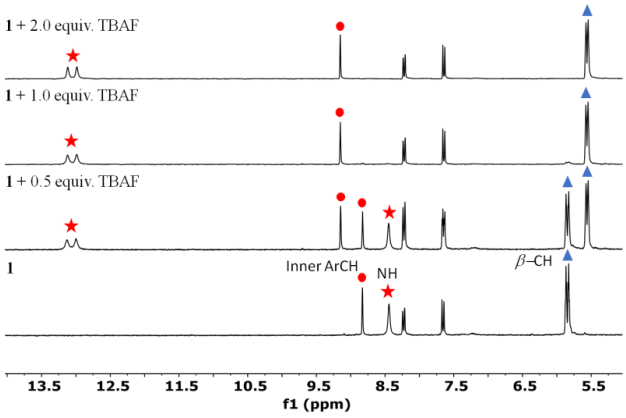


Figure 8. Partial ^1H NMR spectra recorded during the titration of receptor **1** with TBAF in CD_3CN.

In analogy to what was seen upon addition fluoride anion, similar trends in the changes in the protons signals of **1** were noticed during addition of chloride or bromide anion (as their TBA^+ salts) suggesting the formation of 1/1 complexes that are in slow equilibrium with anion-free form of **1** (Figures S2-S5). As expected, in the presence of chloride or bromide anion, the resonance corresponding to the pyrrolic NHs underwent smaller downfield shifts compared to that observed for fluoride anion and appeared as singlet at 11.30 and 10.88 ppm, respectively (Figure 9). However, resonances corresponding to ArCHs and $–OCH_2$- protons were found to experience larger downfield shifts in the presence of chloride or bromide anion as compared to those observed for fluoride anion. Specifically, ArCHs, and $–OCH_2$- proton signals are shifted to 9.71 and 4.18 ppm in the presence of chloride anion and, 9.89 and 4.27 ppm in the presence of bromide anion, respectively. These observations are consistent with the notion that both the chloride and bromide anions formed shorter hydrogen bonds with the strapping subunit than does the fluoride anion, while the fluoride anion forms shorter hydrogen bonds with the calix[4]pyrrole subunit than does the chloride or bromide anion. The cavity generated by calix[4]pyrrole and carbazole incorporated strapping subunit is quite large for fluoride anion. Consequently, the fluoride anion, tightly bound with NHs of the calix[4]pyrrole core, resides away from the inner CHs of the strapping subunit due its smaller size. On the other hands, the larger halides fits well within the cavity of **1** and are able to interact with inner CHs of the strapping unit more strongly. Such conclusion is also consistent with the metric parameters observed for ArCH---anion (anion = F^-, Cl^- and Br^-) interactions for fluoride, chloride and bromide complexes of **1** in solid-states.

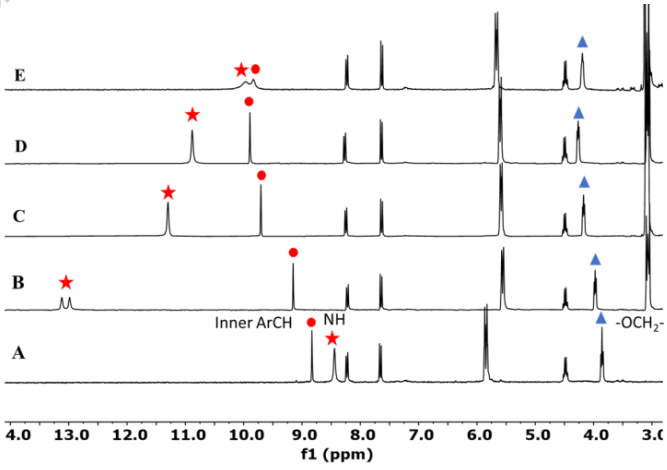


Figure 9. Partial ^1H NMR of A) **1**; B) **1** + ca. 2.0 equivalents TBAF; C) **1** + ca. 3.0 equivalents TBACl; D) **1** + ca. 2.0 equivalents TBABr; E) **1** + ca. 6.0 equivalents TBAI in CD_3CN.

In contrast to what were seen upon addition of fluoride, chloride and bromide anions, addition of iodide (as TBA^+ salt) to the CD_3CN solution of **1** result in gradual shift of the key proton signals (Figure S7). For example, resonances corresponding to the NHs and ArCHs were broadened and gradually shifted to 9.97 and 9.84 ppm upon addition of ca. 6.0 equivalent of iodide anion, respectively (Figure 9). This observation indicates the fast complexation-decomplexation kinetics (on ^1H NMR time scale and at room temperature) between **1** and **1**•I^- complex and iodide anion interacts much weakly than do the other halides. An association constant value of K_a = 183 M^{-1} was determined by non linear least square fitting of the chemical shift changes of NH protons against iodide concentration to 1/1 binding model.[15]

Since the ^1H NMR studies with fluoride, chloride and bromide anions showed the presence of slow complexation-decomplexation kinetics on ^1H NMR time scale, binding affinities of receptor **1** towards these anions were estimated by isothermal titration calorimetry (ITC) carried out in CH_3CN (Figures S8-S10). Each ITC titration experiments were repeated three times and the average association constant values and thermodynamic parameters are summarized in Table 1. Receptor **1** displayed similar association constant values for fluoride and chloride anions (marginally higher for chloride). This may be ascribed to the larger size of the chloride anion, which ensured better fitting of the anion inside the cavity of **1**. Chloride anion formed weaker hydrogen bonds with the NHs of calix[4]pyrrole but stronger hydrogen bonds with the protons on the strap. In contrast, the stronger hydrogen bonding interaction between calix[4]pyrrole subunit and smaller fluoride anion shifts fluoride anion away from the inner carbazole CHs leading to the weaker CH---F^- hydrogen bonding interactions with the protons on the strap. The combined effects of these two interactions results in similar association constant values for fluoride and chloride anions. Receptor **1** also displayed moderate affinity for bromide anion with K_a values of 9.48×10^4 M^{-1}. It is also evident from the Table 1 that binding of fluoride anion is benefited from large entropic factor while the binding of chloride and bromide anions are entirely driven by enthalpy.[16] The larger enthalpic terms for the interactions of **1** with chloride and bromide anions are presumably due to better fitting of these anions within the hydrogen bonding cavity of **1** resulting larger overall hydrogen bond energy. Moreover, the association constant values of **1** toward bromide and iodide anions are found to be higher than most of the other similar strapped calix[4]pyrroles reported to date (Table S4).

Table 1. Binding constants (K_a, M^{-1}) and thermodynamic parameters for the interaction of receptor **1** with various halides (as their TBA^+ salts) measured by ^1H NMR titrations or isothermal titration calorimetry at 298K carried out in CD_3CN or CH_3CN. Affinity values for receptor **2** are also cited.

Anions	Receptor **1**				K_a for **2**
	K_a	ΔG kcal/mol	Δ H kcal/mol	TΔS kcal/mol	
Fluoride	$(6.94 \pm 0.30) \times 10^{5}$[a]	-7.969 ± 0.026	-5.650 ± 0.107	2.319 ± 0.105	> 100000[c,d]
Chloride	$(7.35 \pm 0.36) \times 10^{5}$[a]	-8.002 ± 0.029	-8.04 ± 0.14	-0.094 ± 0.009	1.08×10^{5}[a,e]
Bromide	$(9.86 \pm 1.22) \times 10^{4}$[a]	-6.810 ± 0.071	-7.844 ± 0.060	-1.033 ± 0.044	3.6×10^{3}[a,e]
Iodide	(183 ± 33)[b]	-[f]	-[f]	-[f]	12.6[b,e]

[a]measured by ITC analyses; [b]measured by ^1HNMR titration carried out in CD_3CN; [c]measured by ^1H NMR titration carried out in CD_3CN containing 0.5% D_2O; [d]value from ref. 3c; [e]values from ref. 3d; [f] not available.

The observed variations in binding modes of **1** during the complexation of TBA^+, TEA^+ and TMA^+ cations (as chloride salts) in solid state tempted us to investigate the cesium halide binding properties. Analysis of the single crystals of **1** obtained in the presence of cesium halide salts revealed that the receptor **1** is also able to form stable complexes with CsCl, CsBr and CsI in solid state. In analogy to what were seen in the cases of **1**•TMACl, **1**•TEACl, **1**•TBACl and **1**•TMABr complexes, the propyl subunits of **1** adopt a twisted conformation in all these cesium halide ion-pair complexes. Diffraction-grade single crystals of the CsCl complex were obtained by layering methanolic solution of CsCl over the CH_3CN/ $CHCl_3$ solution of receptor **1**. Structural analysis of the resulting complex exposed that calix[4]pyrrole subunit adopt cone-like conformation and the chloride anion formed four NH---Cl^- hydrogen bonds with N---Cl^- distances of 3.352 – 3.368 Å. One proton from each of the *meso*-methyl and *meso*-methylene carbons also formed CH---Cl type hydrogen bonds as characterized by C_{ml}---Cl^- and C_{me}---Cl^- distances of 3.855 – 3.887 and 3.834 - 3845 Å, respectively. In addition, the two inner carbazole CHs also form ArCH---Cl^- hydrogen bonds with ArC---Cl^- distances of 3.868 – 3.939 Å. The Cs^+ ion was bound to the π-electron rich bowl of calix[4]pyrrole via cation-π interactions. The distances between the centroids of the pyrrole rings and Cs^+ ion were found to vary from 3.302 to 3.602 Å. Further, the Cs^+ ion is also coordinated to one of the alkoxy oxygen atom of another molecule of **1** as well as Cl^- ion bound to it with Cs^+---O and Cs^+---Cl^- distances of 3.296 and 3.597 Å, respectively. As shown in Figure 10, such intermolecular Cs^+---O and Cs^+---Cl^- interactions lead to the stabilization of 1-D coordination polymeric chain in solid state. In contrast to what were seen in the cases of linear supramolecular polymer formed between **1** and tetramethyl ammonium halides, the carbazole subunits are point in opposite direction resulting in a zig-zag type arrangement in the 1-D coordination polymers of CsCl, CsBr and CsI complexes (*vide infra*).

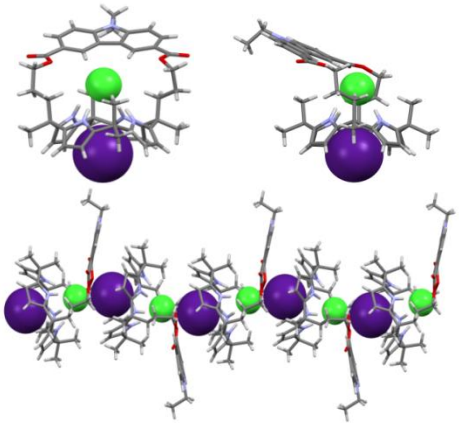


Figure 10: Top: two different views of the single crystal X-ray diffraction structure of **1**•CsCl complex (upper traces) and partial view of the 1-D coordination polymer chain seen in the crystal lattice (lower trace).

Single crystals of CsBr complex of **1** were also grown by layering methanolic solution of CsBr over the CH_3CN/ $CHCl_3$ solution of receptor **1**. The resulting crystal structure revealed the formation of 1/1 stoichiometric complex and a linear 1-D coordination polymer is stabilized in the solid state- analogous to that observed for **1**•CsCl complex (Figure 11). The Br^- anion is also found to bind within the cavity of **1** via ten-point hydrogen bonding interactions. The corresponding N---Br^-, C_{mi}---Br^-, C_{me}---Br^- and ArC---Br^- distances were found to range from 3.474 – 3.556, 3.950 – 3.989, 3.896 – 3.989 and 3.893 - 3.983 respectively. Again, the Cs^+ ion is bound within concave cavity of calix[4]pyrrole via cation-π interaction and linear 1D coordination polymer is stabilised in the solid state presumably stabilized via Cs^+---O and Cs^+---Br^- interaction between Cs^+ ion with one of the alkoxy oxygen of another molecule of **1** and Br^- bound to it with distances of 3.360 and 3.652 Å, respectively. The distances between Cs^+ and centroids of pyrrole rings are found range from 3.364 – 3.511 Å.

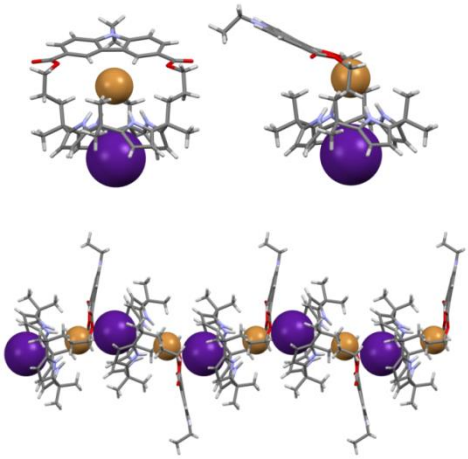


Figure 11. Two different views of single crystal X-ray structure of **1**•CsBr•CH_3OH complex (upper traces) and partial view of the linear supramolecular polymer seen in the crystal lattice (lower trace).

Delightfully, when methanolic solution of CsI was layered over the $CH_3CN/CHCl_3$ solution of receptor **1**, single crystals of **1**•CsI complex were obtained. X-ray diffraction analysis of the resulting crystals revealed that the strapped calix[4]pyrrole **1** holds I^- anion inside its cavity through the formation of ten-point hydrogen bonds including four NH---I and two CH_{ml}---I^-, two CH_{me}---I^- and two ArCH---I^- hydrogen bonds (Figure 12). The corresponding N---I^-, C_{ml}---I^-, C_{me}---I^- and ArC---I^- distances are found to range from 3.581 – 3.752, 4.002 – 4.153, 3.938 - 3.971 and 3.953 – 4.008, respectively. Again, the Cs^+ ion found to sit within the bowl-shaped concave cavity of calix[4]pyrrole via cation-π interaction. The distances between centroids of pyrrole rings and Cs^+ ion were found to range from 3.396 – 3.430 Å. The bound Cs^+ ion found to be in close contact with one of the alkoxy oxygen atom of another molecule of **1** and I^- ion bound to it. The corresponding Cs^+---O and Cs^+---I^- distances are 3.411 and 3.708 Å, respectively. As a result, 1D linear coordination polymer is stabilized in solid state- analogous to that seen for **1**•CsCl and **1**•CsBr complexes.

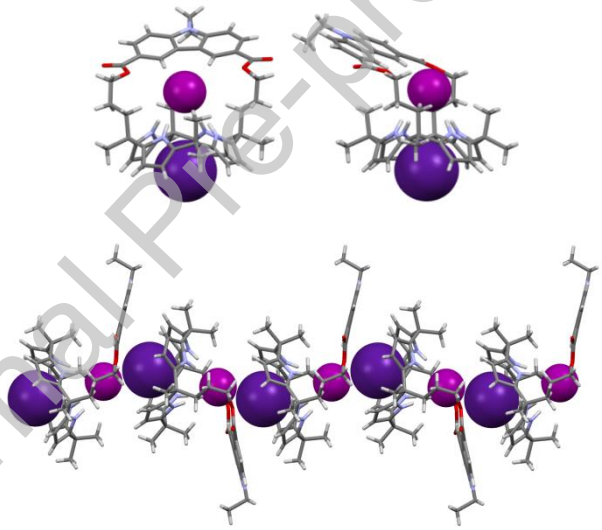


Figure 12. Two different views of single crystal X-ray structure of **1**•CsI complex (upper traces) and partial view of the linear supramolecular polymer seen in the crystal lattice (lower trace).

The formation of cesium halide ion-pair complexes in solution was investigated by recording the ^1H NMR spectra of **1** in the presence of ca. 10 equivalent amounts of cesium halide salts in $CDCl_3/CH_3OH$ (4:1, v/v) mixture solvent (Figure 13). In the presence of ca. 10 equivalents of CsF dramatic changes in the chemical shifts of **1** was observed. The singlet corresponding to the pyrrolic NHs at 8.74 ppm, shifted to 12.22 ppm ($\Delta\delta$ = 3.48 ppm) and appeared as a doublet (J_{HF} = 37.5 Hz). The ArCH protons originally appearing at 8.54 ppm were shifted to 9.20 ppm. Positions of other protons on the carbazole ring remain almost unchanged before and after addition of CsF. The β-pyrrolic protons originally resonating as

multiplet centred at 5.84 ppm (from 5.83-5.85 ppm) was shifted to upfield region and appeared at 5.58 ppm (from 5.56-5.60 ppm), consistent with the binding induced conformational change of the calix[4]pyrrole core to cone conformation. Significant downfield shift of the NH protons (δ = 11.48, $\Delta\delta$ = 2.74 ppm) was also noticed in the presence of ca. 10 equivalent of CsCl along with up field shift of β-pyrrolic protons. The resonance corresponding to inner carbazole ring protons was shifted to lower field direction and appeared at 9.68 ppm, while insignificant or no change in chemical shift positions of other carbazole ring protons was noticed. Similar changes in the proton signals of receptor **1** were also noticed upon addition of ca. 10 equivalent of CsBr. In this case, the NH and ArCH protons were shifted to 10.99 and 9.71 ppm, respectively. Immediate precipitation upon the addition of ca. 10.0 equivalent of CsI precluded the detection of **1**•CsI complex in solution.

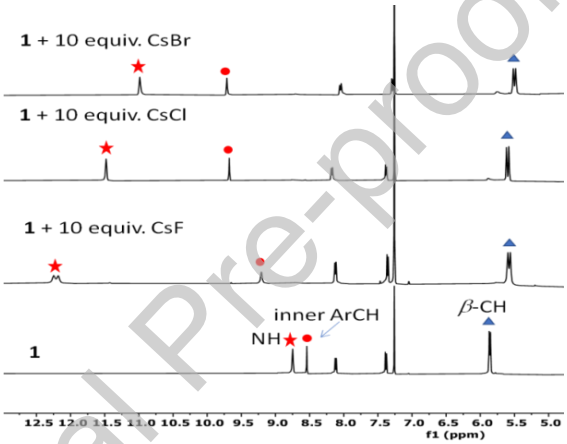


Figure 13. Partial ^{1}H NMR of **1** in absence and presence of ca. 10.0 equivalent amounts of CsF, CsCl and CsBr in $CDCl_3/CH_3OH$ (9/1, v/v).

Inspired by the strong interaction between receptor **1** and CsF and CsCl salts in solution, we have carried out solid-liquid extraction experiments using **1** and CsF or CsCl salts. Chloroform was chosen as liquid phase as these salts are insoluble in this solvent. $CDCl_3$ solution of **1** was first sonicated for 1 hour in the presence of ca. 10 equivalents of CsF and then ^{1}H NMR of the soluble portion was recorded (Figure 14). Analysis of the resulting ^{1}H NMR spectra revealed that almost all the available calix[4]pyrrole **1** formed ion-pair complex with CsF (extraction efficiency ~ 99%). Interestingly, similar solid-to-solution extraction experiment between **1** and CsCl also revealed that most of the available receptor **1** formed ion-pair complex with CsCl (Figure 14). Based on these findings we suggest that receptor **1** is capable of extracting CsF and CsCl under solid liquid extraction condition. Extraction experiment using CsBr under similar condition resulted partial extraction of CsBr salts in to $CDCl_3$ solution (Figure S13).

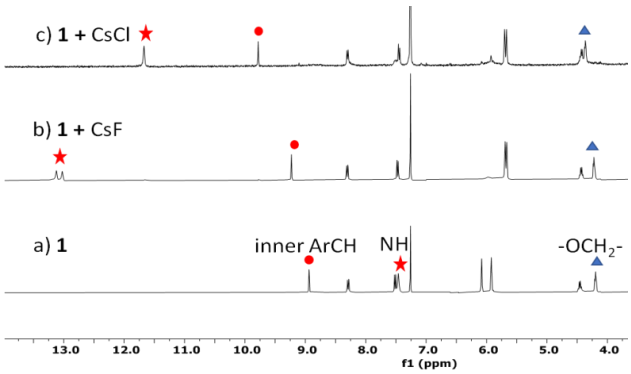


Figure 14. Partial ^{1}H NMR spectra of **1** recorded at room temperature in $CDCl_3$ a) before, and after the addition of b) CsF and c) CsCl followed by sonication 1 for hour.

Conclusion

In conclusion, a new carbazole diester strapped calix[4]pyrrole **1** has been synthesized and characterized using conventional spectroscopic techniques as well as single crystal X-ray diffraction analysis. Combination ^{1}H NMR titration and isothermal titration calorimetry carried out in acetonitrile revealed that the receptor **1** possesses higher affinities for halides, compared to the parent octamethyl calix[4]pyrrole. Ion-pair complexation modes of receptor **1** with various halides salts were also investigated in the solid state. Solid state structural analysis of the complex of receptor **1** with TMAF revealed the formation of 1/1 complex, wherein the fluoride anion is bound to the calix[4]pyrrole core and resides away from the inner CHs of carbazole aromatic protons, clearly indicating the absence of any hydrogen bonding interaction between them. However, ^{1}H NMR studies in CD_3CN revealed the presence of hydrogen bonding interaction between inner CHs of carbazole and fluoride anion. On other hand, larger halides form hydrogen bonds with inner CHs of carbazole and NHs of calix[4]pyrrole simultaneously in both solid and solution phase. It was also revealed by ^{1}H NMR studies that the -OCH_2- protons of the ester functions also participate in anion binding in solution, while these protons remain non interacting in the solid state. These findings led us to suggest that anion complexation modes in condition do not necessarily replicate to another completely. Interestingly, single crystal X-ray diffraction analysis disclosed dramatic differences in the binding modes of **1** with TMACl, TEACl and TBACl salts. Both the TMACl and TBACl formed 1/1 complexes with receptor **1**. In **1**•TMACl complex, the TMA^+ is bound to the π-electron rich bowl of the calix[4]pyrrole. In contrast, in **1**•TBACl complex the pendant ethyl group of the carbazole subunit occupy the π-electron rich bowl of calix[4]pyrrole and TBA^+ cation directly interact with the bound chloride anion forming a contact ion pair complex. On the other hand, receptor **1** formed 2/2 complex with TEACl, wherein two distinct binding modes for TEA^+ cations were seen. As a result, three distinctly

different linear supramolecular chains for **1**•TMACl, $\mathbf{1}_2$•$(TEACl)_2$ and **1**•TBACl complexes were formed in the crystal lattice. Importantly, the enhanced affinity of **1** towards iodide anion results in the stabilization of **1**•CsI complex in solid state. Ion pair complexes of CsCl, CsBr and CsI salts are stabilized as similar linear 1D-coordination polymer. Overall, four different 1D linear chains are produced for chloride complexes of **1** depending on the bound counter cations. Taken in concert, the present study serves to illustrate that in addition to modulating affinity and selectivity for halide anions, the simple calix[4]pyrrole could also be used to create new self-assembled structures based on ion pair recognition. Unravelling the underlying principles will allow to get better control over ion recognition and self-assembly.

Authors contributions

A.K.P.: Conceptualization, Investigation, Methodology, Formal analysis, Data curation. M.H., D.H., A.R. and S.K.., R.S.: Data curation, formal analysis. I.S.: Conceptualization, Resources, Supervision. All authors contributed in Writing –review & editing.

Supplementary materials: Experimental details, X-ray data, Spectroscopic data, and ITC analyses. CCDC 2254181, 2254184, 2254188, 2254189, 2254190, 2254191, 2254192, 2254193 and 2254195 contain the supplementary crystallographic data for this paper.

Acknowledgements

I.S. thanks SERB (EEQ/2019/000372), Government of India for Financial support. A.K.P. thanks SERB, D.H. thanks, SVMCM, Govt. of West Bengal and A.R. thanks CSIR, New Delhi for fellowships. Support of Dr. Prasanta Ghosh, Ramakrishna Mission Residential College for X-ray crystallography is acknowledged.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. a) J. L. Sessler, P. A. Gale and W.-S. Cho, Anion Receptor Chemistry, J. F. StoddartRoyal Society of Chemistry, Cambridge, 2006; b) J. M. Lehn Supramolecular Chemistry, VCH Press, Weinheim, Germany, 1995; c) A. Bianchi , K. Bowman-James and E. García-España, Supramolecular Chemistry of Anions, Willey, New York, 1997; d) K. Bowman-James, A. Bianchi and E. García-España, Anion Coordination Chemistry, Wiley-VCH, Weinheim, 2011.
2. a) R. Martínez-Máñez and F. Sancenán, *Chem. Rev.*, 2003, **103**, 4419 —4476; b) P. A. Gale, N. Busschaert, C. J. E. Haynes, L. E. Karagiannidis and I. L. Kirby, *Chem. Soc. Rev.*, 2014, **43**, 205 —241; c) M. Wenzel, J. R. Hiscock and P. A. Gale, *Chem. Soc. Rev.*, 2012, **41**, 480 —520; d) P. A. Gale, *Chem. Soc. Rev*., 2010, **39**, 3746 —3771; e) C. Caltagirone and P. A. Gale, *Chem. Soc. Rev*., 2009, **38**, 520 —563; f) P. A. Gale and G. Caltagirone, *Chem. Soc. Rev*., 2015, **44**, 4212 —4227; g) S. O. Kang , R. A. Begum and K. Bowman-James, *Angew. Chem., Int. Ed.*, 2006, **45**, 7882 -7894; h) S. O. Kang, J. M. Llinares, V. W. Day and K. Bowman-James, *Chem. Soc. Rev.*, 2010, **39**, 3980 —4003; i) L. Chen, S. N. Berry, X. Wu, E. N. W. Howe and P. A. Gale, *Chem*, 2020, **6**, 61 —141; j) Y. Hu, S. Long, H. Fu, Y. She, Z. Xu and J. Yoon *Chem. Soc. Rev*. 2021, **50**, 589-618; k) L. K. Macreadie, A. M. Gilchrist, D. A. McNaughton, W. G. Ryder, M. Fares and P. A. Gale, *Chem*, 2022, **8**, 46 -118.
3. a) P. A. Gale, J. L. Sessler, V. Kral and V. Lynch, *J. Am. Chem. Soc.*, 1996, **118**, 5140–5141; b) J. L. Sessler, D. E. Gross, W.-S. Cho, V. M. Lynch, F. P. Schmidtchen, G. W. Bates, M. E. Light and P. A. Gale, *J. Am. Chem. Soc.*, 2006, **128**, 12281–12288; c) P. Anzenbacher, Jr., A. C. Try, H. Miyaji, K. Jursikova, V. M. Lynch, M.Marquez and J. L. Sessler, *J. Am. Chem. Soc.*, 2000, **122**, 10268-10272; d) L. Adriaenssens, G. Gil-Ramirez, A. Frontera, D. Quiñonero, E. C. Escudero-Adan, and P. Ballester, *J. Am. Chem. Soc.*, 2014, **136**, 3208–3218.
4. a) C.-H. Lee, H. Miyaji, D. W. Yoon and J. L. Sessler, *Chem. Commun*., 2008, 24–34; b) I. Saha, J. T. Lee and C.-H. Lee, *Eur. J. Org. Chem.*, 2015, 3859–3885; c) Q. He, G. I. Vargas-Zuniga, S. H. Kim, S. K. Kim and J. L. Sessler, *Chem. Rev.*, 2019, **119**, 9753–9835; d) I. A. Rather, S. A. Wagay, M. S. Hasnain and R. Ali, *RSC Adv*., 2019, **9**, 38309-38344; e) S. Peng, Q. He, G. I. Vargas-Zúñiga, L. Qin, I. Hwang, S. K. Kim, N. J. Heo, C.-H. Lee, R. Dutta and J. L. Sessler, *Chem. Soc.Rev*., 2020, **49**, 865-907; f) Z. Lai, T. Zhao, J. L. Sessler and Q. He, *Coord. Chem. Rev.*, 2020, **425**, 213528; g) J. H. Oh, B. P. Hay, V. M. Lynch, H. Li, J. L. Sessler and S. K. Kim, *J. Am. Chem. Soc.*, 2022, **144**, 16996–17009; h) D. S. Kim and J. L. Sessler, *Chem. Soc. Rev***.**, 2015, **44**, 532-546.
5. a) S. K. Kim, J. Lee, N. J. Williams, V. M. Lynch, B. P. Hay, B. A. Moyer and J. L. Sessler, *J. Am. Chem. Soc.*, 2014, **136**, 15079–15085; b) H. Wang, L. O. Jones, I. Hwang, M. J. Allen, D. Tao, V. M. Lynch, B.D. Freeman, N. M. Khashab, G. C. Schatz, Z. A. Page and J. L. Sessler, *J. Am. Chem. Soc.*, 2021, **143**, 20403–20410; c) Q. Zhang, Y. Zhou, M. Ahmed, N. M. Khashab, W. Han, H. Wang, Z. A. Page, and J. L. Sessler, *J. Mater. Chem. A*, 2022, **10**, 15297-15308.

6. a) P. A. Gale, C. C. Tong, C. J. E. Haynes, O. Adeosun, D. E. Gross, E. Karnas, E. M. Sedenberg, R. Quesada and J. L. Sessler, *J. Am. Chem. Soc.*, 2010, **132**, 3240–3241; b) M. Yano, C. C. Tong, M. E. Light, F. P. Schmidtchen and P. A. Gale, *Org. Biomol. Chem.*, 2010, **8**, 4356−4363; c) I-W. Park, J. Yoo, B. Kim, S. Adhikari, S. K. Kim, Y. Yeon, C. J. E. Haynes, J. L. Sutton, C. C. Tong, V. M. Lynch, J.L. Sessler, P. A. Gale and C.-H. Lee, *Chem. Eur. J.*, 2012, **18**, 2514-2523; d) S.-K Ko, S. K. Kim, A. Share, V. M. Lynch, J. Park, W. Namkung, W. V. Rossom, N. Busschaert, P. A. Gale, J. L. Sessler and I. Shin, *Nature Chem*, 2014, **6**, 885–892; e) J. Yang, G. Yu, J. L. Sessler, I. Shin, P. A. Gale and F. Huang, *Chem*, 2021, **7**, 3256–3291; f) S.-H. Park, I. Hwang, D. A. McNaughton, A. J. Kinross, E. N.W. Howe, Q. He, S. Xiong, M. D. Kilde, V. M. Lynch, P. A. Gale, J. L. Sessler and I. Shin, *Chem*, 2021, **7**, 3325–3339; e) I. B. Toumia, M. Ponassi, P. Barboro, E. Iervasi, G. C. Vargas, B. Banelli, S. Fiordoro, L. C. Ghedira, F. H. Kohnke, A. Izzotti and C. Rosano, *Invest New Drugs*, 2022,**40**, 1185–1193.
7. a) P. A. Gale, L. J. Twyman, C. I. Handlin and J. L. Sessler, *Chem. Commun*., 1999, 1851-1852; b) J. Yoo, M.-S. Kim, S.-J. Hong, J. L. Sessler and C.-H. Lee, *J. Org. Chem.*, 2009, **74**, 1065–1069; c) S. Bähring, H. D. Root, J. L. Sessler and J. O. Jeppesen, *Org. Biomol. Chem.*, 2019, **17**, 2594-2613; d) P. Sokkalingam, J. Yoo, H. Hwang, P. H. Lee, Y. M. Jung and C.-H. Lee, *Eur. J. Org. Chem.*, 2011, 2911–2915; e) P. Sokkalingam, D. S. Kim, H. Hwang, J. L. Sessler and C.-H. Lee, *Chem. Sci*., 2012, **3**, 1819-1824; f) E. Mulugeta, Q. He, D. Sareen, S.-J. Hong, J. H. Oh, V. M. Lynch, J. L. Sessler, S. K. Kim and C.-H. Lee, *Chem*, 2017, **3**, 1-13.
8. a) D. S. Kim and J. L. Sessler, *Chem. Soc. Rev.*, 2015, **44**, 532-546; b) J. S. Park and J. L. Sessler, *Acc. Chem. Res.*, 2018, **10**, 2400–2410; c) I. A. Rather, R. Ali and A. Ali, *Org. Chem. Front.*, 2022, **9**, 6416-6440; d) Q. Zhang, Y. Zhou, M. Ahmed, N. M. Khashab, W. Han, H. Wang, Z. A. Page and J. L. Sessler, *J. Mater. Chem. A*, 2022, **10**, 15297-15308; e) P. Ballester and G. Gil-Ramirez, *PNAS*, 2009, **106**, 10455-10459; b) P. Ballester, *Isr. J. Chem*., 2011, **51**, 710–724; f) L. Adriaenssens and P. Ballester *Chem. Soc. Rev.*, 2013, **42**, 3261-3277; g) N. Kiriyama, M. Ebihara, T. Udagawa and H. Miyaji, *RSC Adv.*, 2016, **6**, 19794–19796; h) T. Hirao, D. S. Kim, X. Chi, V. M. Lynch, K. Ohara, J. S. Park, K. Yamaguchi and J. L. Sessler, *Nat Commun*, 2018, **9**, 823.
9. D.-W. Yoon, H. Hwang and C.-H. Lee, *Angew. Chem. Int. Ed.*, 2002, **41**, 1757-1759.
10. a) R. Samanta, S. P. Mohanta, S. Chaudhury, P. K. Panda and A. Narahari, *Inorganica Chimica Acta*, 2011, **372**, 281-285; b) R. Samanta, S. P. Mohanta, S.Ghanta and P. K. Panda, *RSC. Adv.*, 2012, **2**, 7974-7977.
11. a) R. Custelcean , L. H. Delmau , B. A. Moyer , J. L. Sessler , W.-S. Cho, D. Gross, G. W. Bates, S. J. Brooks, M. E. Light and P. A. Gale, *Angew. Chem., Int. Ed.*, 2005, **44**, 2537 —2542; b) J. L. Sessler, D. E. Gross, W.-S. Cho, V. M. Lynch, F. P. Schmidtchen, G. W. Bates, M. E. Light and P. A. Gale, *J. Am. Chem. Soc.*, 2006, **128**, 12281 —12288; c) S. K. Kim and J. L. Sessler, *Acc. Chem. Res.*, 2014, **47**, 2525 — 2536; d) H. Zhai, S. Xiong, S. Peng, W. Sheng, G. Xu, J. L. Sessler and Q. He, *Org. Lett.*, 2021, **23**, 2638 —2642.

12. S. K. Kim, H. G.Lee,G. I. Vargas-Zungia, V. M. Lynch, C. Kim and J. L. Sessler *Chem. Eur. J.*, 2014, **20**, 11750-11759.
13. J. H. Yang, V. M. Lynch, J. L. Sessler and S. K. Kim, *Supramol. Chem.,* 2019, **31**, 203−210.
14. H.-P. Shi, Y. Cheng, W.-J. Jing, J.-B. Chao, L. Fang, X. Q. Dong and C. Dong, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 2010, **75**, 525-532.
15. Association constant (K_a) was evaluated using BindFit v5.0, available from https://app.supramolecular.org/bindfit/.
16. a) R. Dutta, S. Samala, H. Jo, K. M. Ok and C.-H. Lee**,** *J. Org. Chem.*, 2019, **84**, 11, 6851–6857; b) R. Dutta, D. Firmansyah, J. Kim, H. Jo, K. M. Ok, and C.-H. Lee, *Chem. Commun.*, 2018,**54**, 7936-7939.

Graphical abstract