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Dipyridinocalixcrown/diiodoperfluorocarbon binary host systems for CsI: structural studies and fluorous phase extraction of caesium

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Abstract—A mixture of *partial cone* 2,4-bis[(2-pyridylmethyl)oxy]-(1,3)-*p*-*tert*-butylcalix[4]crown-6, hexadecafluoro-1,8-diiodooctane and CsI in EtOH produces a crystalline 'supramolecular salt'. In the solid state the caesium ion of the 'supercation' is encapsulated inside the cavity created by the crown ether loop, the picolyl and the inverted phenyl moieties, while the two iodide ions of the 'superanion' form a discrete five-component aggregate held together by co-existing hydrogen and halogen bonds. Similar calix/CsI/iodofluorocarbon adducts are shown to exist also in solution. In a prototypical study, a combination of this calixcrown and liquid octafluoro-1,4-diiodobutane acts as an effective 'binary host' system for the selective extraction of CsI from aqueous to fluorous phase.

1. Introduction

Self-assembly processes commonly profit from a well-recognized set of weak intermolecular noncovalent forces, the most frequently used being hydrogen bonding, metal coordination, π–π stacking, and van der Waals attraction.[1] Halogen bonding (XB) has recently been added as a further option for the construction and control of ordered supramolecular architectures.[2] XB typically takes place between a species bearing a halogen atom as an electrophilic site (XB donor) and a suitable neutral or anionic electron density donor (XB acceptor), in a manner parallel to hydrogen bonding.[2a] The building blocks that are employed generally bear bromo- or iodoperfluoroalkyl and -aryl moieties,[3] iodoalkynes[4] or iodoarenes[5] as XB donors, and halide anions[6] or compounds possessing a Lewis-basic heteroatom (nitrogen,[7] oxygen,[8] sulfur[9]) as XB acceptors. When choosing halide anions as XB acceptors, the ion-pairing effect—inherent to halide salts—reduces their electron donor effectiveness because of the diminished electron density. In order to circumvent this drawback, it is a common practise to resort to 'naked' halide anions, generated for instance by confinement of metal counterions in the interior of a suitable receptor.[2a]

The XB formation between naked iodide anions and iodoperfluoroalkanes affords $I^{-}\cdots$iodoperfluoroalkane 'superanions', which show a remarkable fluorophilicity owing to the perfluorinated ponytail appended to the iodide ion.[10] Once the anions become fluorophilic, the respective countercations are drawn into perfluorinated solvents. If salt extraction in these media is pursued, a tight binding of the perfluoroalkyl ponytail is advantageous and iodide salts should be used. In keeping with the high polarizability and nucleophilicity of iodide anions, $I^{-}\cdots$iodoperfluoroalkane superanion formation is favoured over that of similar supramolecular species generated with chloride or bromide anions.[2] For instance, as a result of potassium cryptation by Kryptofix® 2.2.2,[10] KI becomes highly soluble in fluorous media.[11]

Keywords: Calixcrowns; Caesium extraction; Fluorous medium; Halogen bonding; Perfluorocarbons; Supramolecular salts.

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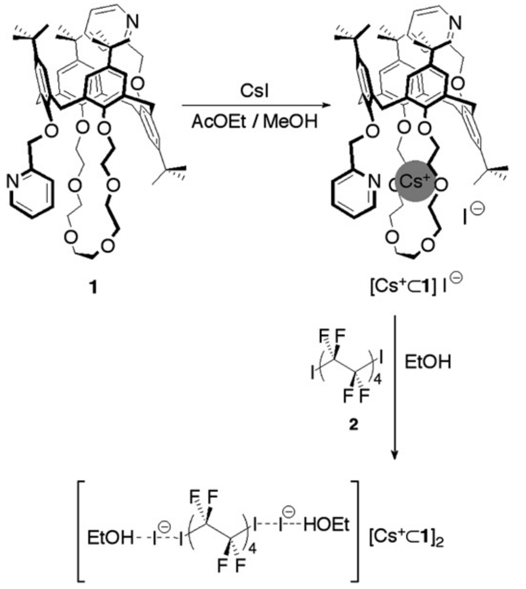
The usefulness of fluorous media originates from their exceptional chemical and thermal inertness and from their poor miscibility in both water and most organic solvents. These unique properties make them attractive as solvents and as a result they are currently being used in several research fields ranging from synthetic methodologies[12] to separation techniques.[13] We thus wondered if the caesium cation, a long-lived radioactive waste component, could be selectively extracted as an iodide salt, provided the caesium cation is selectively encapsulated by an appropriate receptor and the iodide anion is involved in $\mathrm{I}^-\cdots$iodoperfluoroalkane superanion formation.

With this in mind, we turned our attention to calixarenes, which are known to be well suited to play the role of selective cation sequestering agents, on account of the availability of an assortment of derivatives that can tightly accommodate the different sizes of alkali and alkali-earth metal ions.[14] As far as caesium ions are concerned, consolidated[15] and more recent[16] examples of effective calixarene based receptors are reported in the literature where a crown-6 loop or bis-crown loops play a key role in metal ion segregation. We had shown by ESI-MS competitive complexation experiments with mixtures of alkali metal iodides that *partial cone* 2,4-bis[(2-pyridylmethyl)oxy]-(1,3)-*p*-*tert*-butylcalix[4]crown-6 **1**[17] is highly selective for caesium ions.[17] We thus tested the above-mentioned hypothesis by investigating the ability of calixarene **1** to work as a potential segregating agent of Cs^+ ions when admixed with CsI. Naked I^- anions were formed, which could trigger the self-assembly process with diiodoperfluoroalkane modules. Hexadecafluoro-1,8-diiodooctane **2** was chosen as a potential bidentate XB donor and the production of multi-component supramolecular arrays was finally observed. The structural aspects of the hybrid supramolecular salt thus formed were investigated in the solid state and in solution. The concept that these hybrid supramolecular salts can be used in the selective extraction of CsI in fluorous media was experimentally proven.

2. Results and discussion

We have previously reported on the formation of hybrid supramolecular assemblies from equimolar quantities of *cone* 1,3-bis[(2-pyridylmethyl)oxy]-*p*-*tert*-butylcalix[4]crown-5, potassium iodide and diiodoperfluorocarbons.[18] Upon crystallization, these mixtures produced crystalline supramolecular salts where the K^+ ion is embedded in the ionophoric pocket created by the heteroatoms at the lower rim of the calixarene skeleton and the iodide ions behave as bidentate XB acceptors and form infinite fluorous polyanionic chains as a result of an XB directed self-assembly process. Similar behaviour was shown by *p*-*tert*-butylcalix[4]arenetetra-*N*,*N*-diethylacetamide, BaI_2 and diiodoperfluorooctane mixtures. Here again, the calixarene modules segregate the Ba^{2+} ions and yield naked iodide ions, which in turn assemble with the diiodoperfluorocarbon chains to form homochiral halogen-bonded double helices.[19]

The stepwise procedure illustrated in Scheme 1 was used to obtain solid adducts suitable for single crystal X-ray analyses in order to get detailed information on the structure of the self-assembled adduct **1**/CsI/**2**. Calixcrown **1** was crystallized in the presence of CsI from an AcOEt/MeOH solution to afford crystals of $[\mathrm{Cs}^+\subset\mathbf{1}]\mathrm{I}^-$, which were subsequently dissolved in EtOH and allowed to crystallize in the presence of **2**. Slow evaporation of the solvent afforded pale yellow crystals of the **1**/CsI/**2** adduct, which was shown by X-ray analysis to exist as a hybrid supramolecular salt consisting of the charge-separated supercation $[\mathrm{Cs}^+\subset\mathbf{1}]$ and superanion $[\mathrm{EtOH}\cdots\mathrm{I}^-\cdots\mathrm{I}\text{-}(\mathrm{CF}_2)_8\text{-}\mathrm{I}\cdots\mathrm{I}^-\cdots\mathrm{HOEt}]$ components.



Scheme 1. Stepwise assembly of the hybrid supramolecular salt $[\mathrm{Cs}^+\subset\mathbf{1}]_2[\mathbf{2}\cdot2\mathrm{I}^-\cdot2\mathrm{EtOH}]$.

Calixcrown **1** adopts the expected *partial cone* conformation and acts as a remarkable caesium sequestering agent (Fig. 1). The six crown ether oxygen atoms lie approximately on the same plane (Fig. 1a,b) and are coordinated to the caesium ion, the Cs···O distances being in the range 2.984–3.473 Å. Caesium is additionally coordinated by the inverted aryl group on one side of the crown ether loop, and by the oxypicolyl group on the other side. The inverted aryl group lies nearly parallel to the crown ether loop, the aryl centroid being at 3.252(2) Å from the caesium ion (cation–π interaction). On the other hand, the oxypicolyl Cs···O and Cs···N distances were found to be 3.359(2) and 3.236(2) Å, respectively. The optimization of the Cs···N interaction is achieved through an O–C–C–N torsion angle of 105.1(3)°, while the

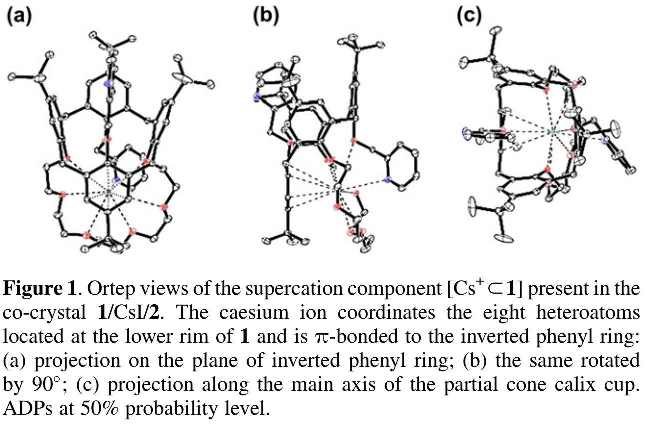


Figure 1. Ortep views of the supercation component $[\mathrm{Cs}^+\subset\mathbf{1}]$ present in the co-crystal **1**/CsI/**2**. The caesium ion coordinates the eight heteroatoms located at the lower rim of **1** and is π-bonded to the inverted phenyl ring: (a) projection on the plane of inverted phenyl ring; (b) the same rotated by 90°; (c) projection along the main axis of the partial cone calix cup. ADPs at 50% probability level.

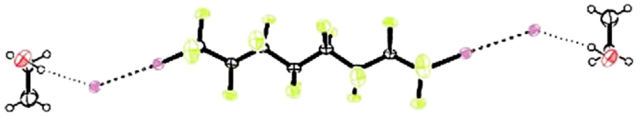


Figure 2. Ortep plot of the supramolecular anion component [$\mathbf{2}\cdot 2I^-\cdot(EtOH)_2$], viewed along the twofold axis. ADPs at 50% probability level, H atoms not to scale.

corresponding torsion for the picolyl group tethered to the inverted phenol residue is 176.1(2)°. Clearly, this latter group is strongly included into the calixarene cavity generated by the three remaining aryl rings (Fig. 1).

In the presence of iodoperfluoroalkanes, naked iodide anions usually act as bidentate[11] or tridentate ligands[10,20] and form 1D or 2D polyanions. The trimer where a central 1,2-diiodoperfluoroethane is halogen bonded at either end to two iodide anions is, to the best of our knowledge, the only reported case where the iodide is monodentate.[20] In the **1**/CsI/**2** adduct, the supramolecular anion consists of a discrete C_2 symmetric assembly of diiodoperfluorooctane **2** bonded to two iodine anions, which are, in turn, hydrogen bonded to the hydroxyl group of two ethanol molecules (Fig. 2). The $I^-\cdots OH–CH_2$ and $I^-\cdots I–CF_2$ interaction distances are 3.533(3) and 3.321(1) Å, respectively. For the sake of comparison, the mean $I^-\cdots O$ distance in 136 $I^-\cdots OH–R$ hydrogen bonds ($I^-\cdots H$ distance below the sum of van der Waals radii) is 3.508 Å (CCDC data bank, version 5.27, November 2005) and the mean $I^-\cdots I$ distance in 104 $I^-\cdots I–C$ anions ($I^-\cdots I$ distance below the sum of van der Waals radii) is 3.531 Å. The short $I^-\cdots I–C$ interaction observed in **1**/CsI/**2** adduct is consistent with the ability of iodoperfluorocarbons to work as strong XB donors.

In the **1**/CsI/**2** adduct, both the hydrocarbon and the fluorocarbon chains are nicely ordered. This is quite unusual for perfluoroalkyl chains, and so we took advantage of this fortuitous event to perform a detailed analysis of the perfluorooctene chain of **2**, which can be viewed as a possible model segment of the polytetrafluoroethylene polymer chain. Revealing the conformation of perfluoroalkyl chains is of paramount importance to the understanding of the helical structure of perfluorinated polymers, this structure being responsible for the very rich phase behaviour of these relatively simple polymers. The carbon chain of **2** adopts a distorted *all-trans* conformation; the torsion angles along the $I–C_1\cdots C_8–I$ chain have the same sign and vary between 159.2(2) and 169.3(2)° (mean 166.4°). A helical conformation results (Fig. 3) with a total $I–C_1\cdots C_8–I$ torsion of 85.0(3)°. These values are smaller than those shown by module **2** in the nicely ordered assembly formed with Kryptofix® 2.2 (the mean value for the single torsion angle along the $I–C_1\cdots C_8–I$ chain is 169.9° and the total $I–C_1\cdots C_8–I$ torsion is 109.3(6)°).[21] This difference may be related to the different packing constraints on the perfluoroalkyl chain conformations, constraints probably being greater in the Kryptofix® 2.2/**2** adduct (where diiodoperfluorooctane is locked in a 1D infinite chain formed via N⋯I halogen bondings) than in the **1**/CsI/**2** adduct (where diiodoperfluorooctane forms discrete systems). The **1**/CsI/**2** adduct was thus considered more reliable than Kryptofix® 2.2/**2** assembly in the attempt to obtain valuable information on the polytetrafluoroethylene conformation. Assuming that module **2** adopts, in the **1**/CsI/**2** adduct, the torsion typical for the polytetrafluoroethylene polymer, the polytetrafluoroethylene helix may approximately possess a pitch of about $360/(180-166.4)\approx 27$ carbon bonds. This value fits nicely with literature data.[22]

Figure 3. Mercury stick representation of the $I-C_1\cdots C_8-I$ chain of **2**, viewed along $C_1\cdots C_8$. A more pronounced helicity in the **1**/CsI/**2** adduct (present work, right) than in the Kryptofix® 2.2/**2** adduct (Ref. 21, left) is apparent.

Apart from the above-described interactions involving the caesium cation and iodide anion, the packing of the **1**/CsI/**2** co-crystals does not present any other special features, the only other interaction worth mentioning being a weak hydrogen bond between couples of centrosymmetric picoline moieties not engaged in caesium coordination ($N\cdots H_{benzyl}[1-x,1-y,1-z]$ 2.51 Å).

Consistent with previous findings,[18–20] the present study confirms the exceptional ability of naked iodide anions, derived from cryptated inorganic salts, to prevail over other XB acceptors (e.g., the nitrogen atoms of picolyl moieties). Moreover, the composition and structure of the supramolecular anion [$EtOH\cdots I^-\cdots I–(CF_2)_8–I\cdots I^-\cdots HOEt$] are particularly promising with respect to our aim of extracting caesium ions from aqueous into fluorous phase. The coexistence of halogen ($I\cdots I^-$) and hydrogen ($I^-\cdots HO$) bondings[23] in the **1**/CsI/**2** co-crystal isolated from ethanol solutions indicates that the $I\cdots I^-$ interaction is strong enough to survive in protic solvents despite the efficiency of the latter as anion coordinating agents.[24] ^{19}F NMR experiments unequivocally confirm the existence in protic media of $I^-\cdots$iodoperfluoroalkane XB. On addition of $[Cs^+\subset \mathbf{1}]I^-$ to a chloroform/methanol solution of **2** the signal of the $–CF_2I$ group undergoes a high field shift ($\Delta\delta$=+1.48 ppm) typical of XB formation.[10,25]

Since XB effectively competes with hydrogen bonding in iodide anion coordination, the possibility of appending an iodoperfluoroalkane ponytail to an iodide anion in aqueous media and thus of extracting the iodide salt in fluorous media is confirmed. In other words, the solid state structure of the supramolecular salt **1**/CsI/**2** and the ^{19}F NMR experiments described above forcefully suggest that a combination of calixcrown **1** and diiodoperfluorocarbons might function as a ‘dual[26] (or binary[27]) host’ system in the complexation of caesium iodide. More specifically, they would seem to be able to simultaneously and synergically complex both cation and anion.

To verify this hypothesis, solid 1,8-diiodoperfluorooctane **2** (mp 73–77 °C) was replaced by a variety of liquid (di)iodoperfluorocarbons in the hope of having them play the double role of XB donor and fluorous phase extracting agents. Iodoperfluorobenzene, 1-iodoperfluorohexane, 1-iodoperfluorooctane and 1,4-diiodoperfluorobutane **3** were all screened

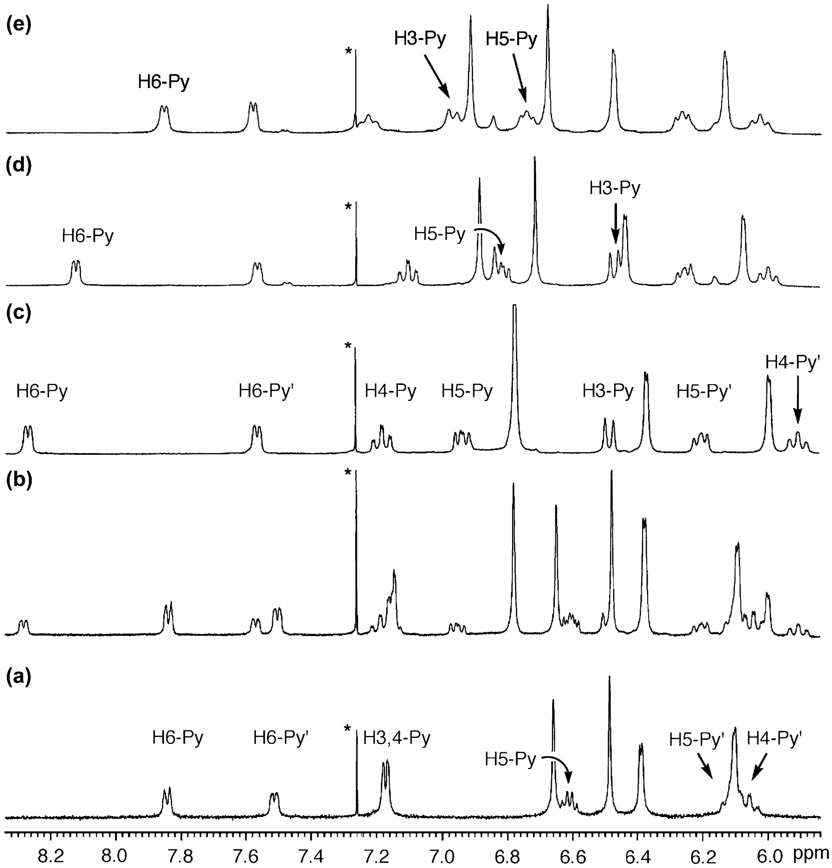
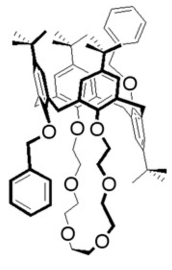


Figure 4. Partial ^{1}H NMR spectrum (300 MHz, 10 mM in $I(CF_2CF_2)_2I$, 25 °C) of **1** (a), and spectral changes after extraction from aqueous CsI (1.0 equiv) (b), or addition of an excess of solid CsI (c), or addition of an excess of solid KI (d), or addition of an excess of solid NaI (e). An asterisk denotes the residual peak due to the presence of $CDCl_3$ inside the coaxial insert of the NMR tube.

to test their ability to solubilize **1** and extract CsI from aqueous solutions.[28] 1,4-Diiodoperfluorobutane **3** (mp −9 °C) was eventually chosen as the most promising candidate to this end.[29]

Calixcrown **1** is sufficiently soluble in **3**, and addition of an excess of solid CsI to a 10 mM solution of **1** in **3** resulted, after sonication, in the intake of the salt in the fluorous phase, with quantitative saturation of the cationic receptor (i.e., $Cs^+ \subset \mathbf{1}$). Complexation is slow on the NMR time scale, and spectra recorded in neat **3** (locking was obtained by means of a tube fitted with a coaxial insert containing $CDCl_3$) show significant complexation induced shifts (CIS) for all the signals of the calixcrown **1** after the addition of the salt. A scrutiny of the low-field region of the spectra, shown in Figure 4, reveals that the CIS experienced by the aromatic protons of the supercation $Cs^+ \subset \mathbf{1}$ are consistent with the coordination geometry found in the solid state. The hydrogen atoms of the pyridine ring involved in the complexation of Cs^+ (henceforth notations Py and Py′ will refer to the pyridine ring *syn* or *anti* to the crown ether moiety, respectively) experience small to significant downfield shifts relative to uncomplexed **1** (H4–Py, $\Delta\delta$=+0.01 ppm; H5–Py, $\Delta\delta$=+0.33 ppm; H6–Py, $\Delta\delta$=+0.43 ppm). A notable exception is represented by H3–Py proton, which displays an opposite trend undergoing a strong upfield shift (H3–Py, $\Delta\delta$=−0.69 ppm). This results from *trans* to *gauche* reorientation[30] of the O and N heteroatoms of the OCH_2Py group after complexation, occurring through the rotation of the Py group around the O–*C*–*C*–N axis, which brings the H3–Py proton under the shielding region of the juxtaposed phenol ring. On the other hand, most of the protons of the Py′ group attached to the inverted phenol residue experience substantial upfield shifts (H3–Py′, $\Delta\delta$=−0.35 ppm; H4–Py′, $\Delta\delta$=−0.15 ppm; H5–Py′ $\Delta\delta$=−0.41 ppm) because of a deeper inclusion of the *exo*-orientated *N*-heterocyclic moiety inside the hydrophobic calixarene cavity.

Extraction experiments were carried out by mixing together (1 h at 25 °C) an aqueous 2 mM CsI solution (2.5 mL) with a 10 mM solution of **1** in 1,4-diiodoperfluorobutane (0.5 mL), and the distribution coefficient for caesium ions (D_{Cs}=$[Cs^+]_{fluorous}/[Cs^+]_{aqueous}$) was then determined by analysis of both phases. Direct integration of the ^{1}H NMR signals (e.g., H6–Py, CH_2Py′, ^{t}Bu) of free and complexed receptor **1** in fluorous phase **3** (Fig. 4b) provided a D_{Cs} value of 2.7. This value was confirmed by ion-exchange chromatographic analysis on the aqueous solution. The superior efficiency of calixcrown **1**—as a caesium extractant in fluorous phase—with respect to the model *partial cone* dibenzyloxy-*p*-*tert*-butylcalix[4]crown-6 conformer **4**[31] (D_{Cs}=0.8), devoid of the ring nitrogen donor atoms, suggests that the heteroatoms on the two picolyl moieties play an active role both in facilitating cation complexation and in enhancing the fluorophilicity of the formed supercation via likely N···I[32] interactions with the Py′ moiety.



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Although the D_{Cs} in **3** is not particularly high,[33] the selectivity shown by our receptor in this fluorous phase is noteworthy. Both ionophore **1** and XB donor **3** have to be simultaneously present for CsI extraction to take place. Under our standard extraction conditions (see Section 4), neither a 10 mM $CHCl_3$ solution of calixcrown **1** nor the same chloroform solution in combination with 10 equiv of **3** was able to extract CsI from water. Similarly, treatment of an aqueous caesium iodide solution with just **3** (0.5 mL), revealed (^1H NMR)[34] no Cs^+ uptake. The three experiments taken together demonstrate the synergic action of **1** and **3** and the importance of the latter as the extracting phase. Calixcrown **1** and 1,4-diiodoperfluorobutane **3** proved to be selective for both the cation and anion. In a control experiment where $CsNO_3$ was the target salt, no extraction of Cs^+ into the fluorous phase was detected, consistent with the poor ability of the nitrate anion to work as an XB acceptor.[10] However, after addition of sodium iodide (1 equiv) to the aqueous phase, only caesium transfer (as CsI) was observed. Furthermore, under our standard extraction conditions neither sodium nor potassium ions (added as iodide salts) were appreciably extracted into the fluorous phase. The concentration of both ions was found to be below detection level by NMR and ion-exchange chromatography. It should be noted, however, that sonication of fluorous solutions of **1** in **3** in the presence of an excess of solid KI or NaI resulted in a quantitative uptake of the salts in the fluorous phase (see Fig. 4, traces in d and e, respectively). It is likely that the **1/3** binary system is not able to overcome the solvation/desolvation energy barriers of sodium and potassium ions and as a result no extraction from aqueous solution is observed. Our NMR data show that in analogy with the larger caesium ion, complexation of sodium and potassium cations is slow on the NMR time scale. Although $Na^+\subset$**1**, $K^+\subset$**1** and $Cs^+\subset$**1** supercations exhibit similar ^1H NMR spectral patterns (e.g., H3–, H5– and H6–Py) their chemical shifts are quite different, allowing the direct identification of a given encapsulated cation to be made.

3. Conclusions

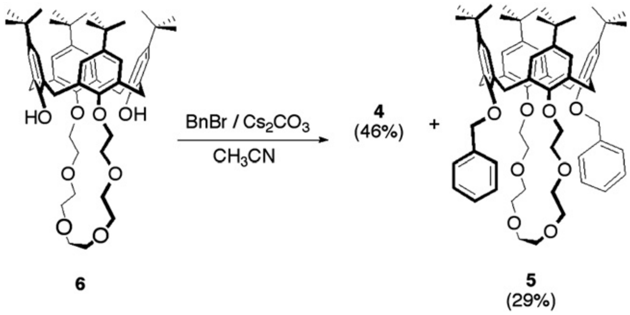
Inorganic, organic and perfluorinated derivatives usually display a low affinity for each other. In this paper, we have shown how judicious design of the specific derivatives enables a nice complementarity. Specifically, the self-assembly of hybrid supramolecular salts compounded of CsI, calixarenes and iodoperfluoroalkanes can be induced, both in the solid state and in solution, by harnessing a set of noncovalent forces. In the solid state, the caesium ion is nested in the crown loop of the receptor, and shielded by a picolyl unit and a phenol ring involved in cation–π interactions. The iodide anion, on the other hand, assembles into discrete aggregates held together by the concomitant action of hydrogen bonding (ethanol–iodide) and XB (diiodoperfluorocarbon–iodide). Single crystal X-ray analysis and ^{19}F as well as ^1H NMR techniques show that the iodide anion is a strong XB acceptor. It prevails over other neutral XB acceptor sites and the $I^-\cdots$iodoperfluoroalkane XB also occurs in protic solvents. XB has thus been used to force the selective uptake of caesium iodide into a fluorous phase by exploiting the fluorophilicity induced by the perfluoroalkyl chain appended to the iodide anion. The novelty of this approach is the caesium removal/transfer from aqueous to fluorous phase. Since fluorous media are orthogonal to both water and organic solvents, our findings may represent the starting point for the development of a selective caesium salt extraction methodology from radioactive wastes based on the synergic action of cation and anion coordination (by convenient ionophores and iodoperfluorocarbons). Perfluorinated derivatives are endowed with exceptionally high chemical and thermal stabilities and so fluorous phase extraction might represent a particularly attractive option for aggressive wastes.

4. Experimental

4.1. General

Melting points were determined on a Kofler melting point apparatus and are uncorrected. Unless otherwise stated, ^1H (300 MHz) and ^{19}F (282 MHz) NMR spectra were obtained at 25 °C in neat 1,1,2,2,3,3,4,4-octafluoro-1,4-diiodobutane (**3**) (using $CDCl_3$ as the locking solvent) or in $CDCl_3$/CD_3OD, 9:1 (using $CFCl_3$ as an internal standard), respectively. FTIR spectra were recorded as KBr pellets on a Nicolet Nexus FTIR spectrophotometer equipped with the Smart Endurance system (UATR). All solvents and chemicals were of reagent grade and were used without further purification. Calixcrowns **1**[17] and **6**[35] were prepared according to literature procedures.

4.2. Benzylation of (1,3)-*p*-*tert*-butylcalix[4]crown-6 6



A stirred mixture of **6** (100 mg, 0.119 mmol), benzyl bromide (81 mg, 0.474 mmol) and Cs_2CO_3 (155 mg, 0.474 mmol) in dry acetonitrile (20 mL) was refluxed for 18 h under N_2. Evaporation of the solvent left a residue, which was acidified with 1 M HCl and extracted with

CH$_2$Cl$_2$ (2×20 mL). The combined organic extracts were washed with water and dried (MgSO$_4$). Concentration to dryness gave a residue, which upon column chromatography (SiO$_2$, eluent *n*-hexane/AcOEt, 6:1, v/v) gave dibenzylated *partial cone* **4** (56 mg, 46%) and *cone* **5** (36 mg, 29%) conformers in that order. When K$_2$CO$_3$ was used in place of Cs$_2$CO$_3$, the reaction produced only *cone* **5**.

4.2.1. *Partial cone*: 2,4-bis-benzyloxy-(1,3)-*p-tert*-butylcalix[4]crown-6 4. Mp 191–193 °C (CH$_2$Cl$_2$/MeOH). ^{1}H NMR (CDCl$_3$) δ 0.67, 1.27, 1.39 (3×s, ratio 1:2:1, 36H, C(CH$_3$)$_3$), 2.35 (s, 2H, OCH_2Ph′), 2.99, 4.29 (AX, J=12.5 Hz, 4H, ArCH_2Ar), 3.24–3.31 (m, 2H, OCH$_2$CH$_2$O), 3.5–3.9 (m, 22H, OCH$_2$CH$_2$O and ArCH_2Ar), 4.85 (s, 2H, OCH_2Ph), 6.04 (d, J=6.9 Hz, 2H, H2–Ph′), 6.67 (s, 2H, ArH), 6.88 (t, J=7.2 Hz, 2H, H3-Ph′), 6.94 (t, J=7.1 Hz, 1H, H4–Ph′), 7.00, 7.15 (2×d, J=2.4 Hz, ratio 1:1, ArH), 7.18 (s, 2H, ArH), 7.23–7.33 (m, 5H, Ph) ppm; ^{13}C NMR (CDCl$_3$) δ 30.6, 31.5 (×3) [q, C(CH$_3$)$_3$], 30.8, 38.1 (t, ArCH$_2$Ar), 33.5, 34.0, 34.1 (×2) [s, C(CH$_3$)$_3$], 69.1, 70.2, 70.7, 71.1, 71.6 (t, OCH$_2$CH$_2$O), 70.3 (t, OCH$_2$Ph′), 77.7 (t, OCH$_2$Ph), 124.7 (×2), 125.6 (×2), 126.2 (×2), 126.3 (×2), 126.4, 127.0 (d, Ph and Ph′), 127.2, 127.8, 128.2, 130.1 (d, ArH), 132.7, 133.3, 133.5, 136.8 (s, *ortho*-ArH), 137.2, 139.0 (s, *ipso*-Ph′ and *ipso*-Ph), 144.2, 144.7, 145.6 (×2) (s, *para*-ArH), 151.5, 154.1 (×2), 154.5 (s, *ipso*-ArH) ppm; FAB$^+$ MS, *m/z* 1031 (MH$^+$). Anal. Calcd for C$_{68}$H$_{86}$O$_8$: C, 79.19; H, 8.40. Found: C, 79.44; H, 8.21.

4.2.2. *Cone*: 2,4-bis-benzyloxy-(1,3)-*p-tert*-butylcalix[4]-crown-6 5. Mp 204–207 °C (CHCl$_3$/MeOH). ^{1}H NMR (CDCl$_3$) δ 0.83, 1.34 (2×s, ratio 1:1, 36H, C(CH$_3$)$_3$), 3.05, 4.33 (AX, J=12.6 Hz, 8H, ArCH_2Ar), 3.39, 3.60 (2×t, J=5.2 Hz, ratio 1:1, 8H, OCH$_2$CH$_2$O), 3.65 (s, 4H, OCH$_2$CH$_2$O), 3.88, 4.09 (2×dd, J=9.5, 6.0 Hz, ratio 1:1, 8H, OCH$_2$CH$_2$O), 4.74 (s, 4H, OCH_2Ph), 6.44, 7.10 (2×s, 8H, ArH), 7.35–7.48 (m, 10H, PhH) ppm; ^{13}C NMR (CDCl$_3$) δ 31.0 (t, ArCH$_2$Ar), 31.1, 31.7 [q, C(CH$_3$)$_3$], 33.6, 34.1 [s, C(CH$_3$)$_3$], 69.4, 70.4, 70.6, 71.1, 72.0 (t, OCH$_2$CH$_2$O), 78.1 (t, OCH$_2$Ph), 124.5, 125.5, 128.0, 128.4, 129.6 (d, *meta*-ArH and Ph), 131.7, 135.4 (s, *ortho*-ArH), 137.7 (s, *ipso*-Ph), 144.3, 145.1 (s, *para*-ArH), 151.9, 154.6 (s, *ipso*-ArH) ppm; FAB$^+$ MS, *m/z* 1031 (MH$^+$). Anal. Calcd for C$_{68}$H$_{86}$O$_8$: C, 79.19; H, 8.40. Found: C, 79.37; H, 8.52.

4.3. Procedure for the formation of the hybrid supramolecular salt 1/CsI/2

A solution of calixcrown **1** (90 mg, 0.087 mmol) in AcOEt (4 mL) was mixed with a solution of CsI (22.7 mg, 0.087 mmol) in MeOH (1 mL). After stirring at room temperature for 2 h, the solvents were allowed to evaporate and [Cs$^+$$\subset$**1**]I$^-$ (98 mg) was filtered as yellowish crystals after 48 h, mp 210–212 °C (AcOEt/MeOH); FTIR (KBr/ν/cm^{-1}, selected bands): 2952, 2869, 1591, 1479, 1362, 1203, 1115, 1050, 956. An ethanol solution of [Cs$^+$$\subset$**1**]I$^-$ (42 mg, 0.032 mmol) and diiodoperfluorooctane **2** (21 mg, 0.032 mmol) in a clear borosilicate vial was allowed to evaporate at room temperature when closed in a wide-mouth brown vial containing Vaseline oil. After 24 h, the hybrid supramolecular salt **1**/CsI/**2** (58 mg) was isolated as yellowish crystals, mp 256–258 °C (EtOH). FTIR (KBr/ν/cm^{-1}, selected bands): 3036, 2962, 2931, 2905, 1481, 1211, 1190, 1151, 1114, 1050, 629.

4.4. ^{1}H NMR studies

4.4.1. *Partial cone*: 2,4-bis[(2-pyridylmethyl)oxy]-(1,3)-*p-tert*-butylcalix[4]crown-6 1. ^{1}H NMR δ 0.33, 0.67, 0.94 (3×s, ratio 2:1:1, 36H, C(CH$_3$)$_3$), 2.51, 3.76 (AX, J=12.1 Hz, 4H, ArCH_2Ar), 2.75–2.83 (m, 2H, OCH$_2$CH$_2$O), 2.87–3.03 (m, 4H, OCH$_2$CH$_2$O), 3.09 (pseudo s, 8H, OCH$_2$CH$_2$O), 3.22–3.33 (m, 6H, OCH$_2$CH$_2$O), 3.34, 3.43 (ABq, J=17.3 Hz, 4H, ArCH_2Ar), 3.61 (s, 2H, OCH_2Py′), 4.07 (d, J=7.5 Hz, 1H, H3–Py′), 4.60 (s, 2H, OCH_2Py), 6.05 (td, J=7.5, 1.8 Hz, 1H, H4–Py′), 6.10 (d, J=2.0 Hz, 2H, ArH), 6.11 (m, 1H, H5–Py′), 6.39 (d, J=2.0 Hz, 2H, ArH), 6.49 (s, 2H, ArH), 6.61 (m, 1H, H5–Py), 6.66 (s, 2H, ArH), 7.17 (m, 2H, H3–Py, H4–Py), 7.51 (d, J=4.4 Hz, 1H, H6–Py′), 7.84 (d, J=4.8 Hz, 1H, H6–Py) ppm.

4.4.2. *Inclusion complex*: [Cs$^+$$\subset$1]I$^-$. Mp 210–212 °C (AcOEt/MeOH); FTIR (KBr/ν/cm^{-1}, selected bands) 2952, 2869, 1591, 1479, 1362, 1203, 1115, 1050, 956; ^{1}H NMR δ 0.12, 0.90, 0.98 (3×s, ratio 2:1:1, 36H, C(CH$_3$)$_3$), 2.67, 3.52 (AX, J=12.5 Hz, 4H, ArCH_2Ar), 3.10–3.36 (m, 20H, OCH$_2$CH$_2$O, overlapping to part of an AB system, 2H, ArCH_2Ar), 3.51 (part of an AB system, J=17.0 Hz, 2H, ArCH_2Ar), 3.72 (d, J=7.8 Hz, 1H, H3–Py′), 3.80 (s, 2H, OCH_2Py′), 4.52 (s, 2H, OCH_2Py), 5.90 (td, J=7.8, 1.5 Hz, 1H, H4–Py′), 5.99 (d, J=2.3 Hz, 2H, ArH), 6.20 (dd, J=6.3, 5.6 Hz, 1H, H5–Py′), 6.37 (d, J=2.3 Hz, 2H, ArH), 6.48 (d, J=7.7 Hz, 1H, H3–Py), 6.78 (s, 4H, ArH), 6.94 (dd, J=7.4, 5.1 Hz, 1H, H5–Py), 7.18 (td, J=7.6, 1.7 Hz, 1H, H4–Py), 7.56 (d, J=4.6 Hz, 1H, H6–Py′), 8.28 (d, J=4.0 Hz, 1H, H6–Py) ppm.

4.4.3. *Inclusion complex*: [K$^+$$\subset$1]I$^-$. ^{1}H NMR δ 0.14, 0.84, 1.01 (3×s, ratio 2:1:1, 36H, C(CH$_3$)$_3$), 2.59, 3.58 (AX, J=12.4 Hz, 4H, ArCH_2Ar), 3.08–3.42 (m, 20H, OCH$_2$CH$_2$O, overlapping to part of an AB system, 2H, ArCH_2Ar), 3.50 (part of an AB system, J=16.1 Hz, 2H, ArCH_2Ar), 3.80 (d, J=8.1 Hz, 1H, H3–Py′), 3.91 (s, 2H, OCH_2Py′), 4.56 (s, 2H, OCH_2Py), 5.94 (td, J=7.4, 1.3 Hz, 1H, H4–Py′), 6.02 (d, J=2.1 Hz, 2H, ArH), 6.21 (dd, J=7.5, 5.3 Hz, 1H, H5–Py′), 6.40 (d, J=2.0 Hz, 2H, ArH), 6.44 (d, J=7.9 Hz, 1H, H3–Py), 6.69 (s, 2H, ArH), 6.79 (dd, J=6.3, 4.4 Hz, 1H, H5–Py), 6.87 (s, 2H, ArH), 7.09 (td, J=7.8, 1.8 Hz, 1H, H4–Py), 7.57 (d, J=4.3 Hz, 1H, H6–Py′), 8.16 (d, J=4.0 Hz, 1H, H6–Py) ppm.

4.4.4. *Inclusion complex*: [Na$^+$$\subset$1]I$^-$. ^{1}H NMR δ 0.17, 0.82, 1.02 (3×s, ratio 2:1:1, 36H, C(CH$_3$)$_3$), 2.59 (part of an AX system, J=12.4 Hz, 2H, ArCH_2Ar), 2.89–3.70 (overlapping m, 26H, OCH$_2$CH$_2$O and ArCH_2Ar), 3.79 (d, J=8.0 Hz, 1H, H3–Py′), 3.98 (s, 2H, OCH_2Py′), 4.74 (s, 2H, OCH_2Py), 5.98 (br t, J=7.8 Hz, 1H, H4–Py′), 6.08 (d, J=2.2 Hz, 2H, ArH), 6.23 (dd, J=6.9, 5.7 Hz, 1H, H5–Py′), 6.44 (d, J=2.2 Hz, 2H, ArH), 6.65 (s, 2H, ArH), 6.72 (dd, J=7.7, 4.6 Hz, 1H, H5–Py), 6.90 (s, 2H, ArH), 6.97 (d, J=7.4 Hz, 1H, H3–Py), 7.23 (br t, J=7.1 Hz, 1H, H4–Py), 7.59 (d, J=4.9 Hz, 1H, H6–Py′), 7.87 (d, J=3.8 Hz, 1H, H6–Py) ppm.

4.5. Crystal structure determination of 1/CsI/2

Single crystal X-ray diffraction measurements were performed on a Bruker APEX CCD diffractometer, graphite monochromator, Mo Kα radiation (λ=0.71073 Å, T=90 K (Oxford low temperature device)). $(C_{66}H_{84}CsN_2O_8)^+I^-\cdot 0.5(C_8F_{16}I_2)\cdot C_2H_6O$, M_r=1666.17, monoclinic, space group $C2/c$, a=36.105(5), b=16.924(2), c=23.645(3) Å, β=97.41(2)°, V=14,327(3) Å^3, Z=8, D_c=1.545 g cm^{-3}, μ(Mo Kα)=1.456 mm^{-1}, 100,489 collected data ($2\theta<60.14°$), 20,929 unique [14,087 with $I_o>2\sigma(I_o)$], R_{ave}=0.0363. The structure was solved by direct methods (*SIR*2002),[36] and refined by full-matrix least-squares (SHELXL-97);[37] final disagreement factors for all (observed) reflections: $R_w(F^2)$=0.0885(0.0791), R=0.0736(0.0385); residues $-0.75<\Delta\rho<1.28$ eÅ^{-3}. All crystallographic data (excluding structural factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC 631592. Copies of the data can be obtained free of charge on application to CCDC, 2 Union Road, Cambridge CB2 1EZ, UK; e-mail: deposit@ccdc.cam.ac.uk.

4.6. ^{19}F NMR studies

Solid $[Cs^+\subset\mathbf{1}]I^-$ (0.012 mmol) was added to 0.5 mL of a 4.8×10^{-2} M solution of 1,8-diiodoperfluorooctane **2** in $CDCl_3/CD_3OD$ (9:1) and the sample was then sonicated for 10 min at room temperature. Halogen bonding induced shifts on the $-CF_2I$ group ($\Delta\delta$=+1.48 ppm), resulting from $[Cs^+\subset\mathbf{1}]I^-$ addition, were determined as $\Delta\delta = \delta_2 - \delta_{\{2+[Cs^+\subset 1]I^-\}}$.

4.7. Extraction experiments

Aqueous solutions were prepared using ultrapure water (conductivity<0.1 µS) sonicated for 30 min. To avoid picoline nitrogen protonation, all fluorous solvents (octafluoro-1,4-diiodobutane, tridecafluoro-1-iodohexane, heptadecafluoro-1-iodooctane, iodopentafluorobenzene) were treated with a 10% NaOH aqueous solution and then passed through neutral alumina prior to use. Liquid–liquid extraction experiments were performed in duplicate according to the following procedure: 2.5 mL of a 2 mM aqueous solution of each salt (NaI, KI, CsI and $CsNO_3$) and 0.5 mL of 10 mM solution of calixcrown (**1** or **4**) were shaken in a stoppered glass vial for 1 h at 25 °C. The equilibrated sample was centrifuged for 5 min prior to analysis. Metal ion concentration was determined for both phases (aqueous and fluorous or organic) and from these values the distribution coefficient ($D_M=[M^+]_{\text{fluorous or organic}}/[M^+]_{\text{aqueous}}$) was calculated after appropriate dilution. Metal cation (Na^+, K^+, Cs^+) concentration in the aqueous phase was determined by ion-exchange chromatography, using an apparatus equipped with a Dionex GP40 gradient pump and a mod. REV D0602 conductometric detector coupled with a CSRS-II self-regenerant suppressor. Analyses were performed under isocratic conditions using 25 mM methansulfonic acid as the eluent (flow rate=1.0 mL/min) at T=25 °C on an IonPac CS12A cation-exchange column fitted with an IonPac CG12A guard column. Cation determination in the fluorous phase was carried out by direct ^{1}H NMR analysis of the peak intensity ratio of free and complexed probe resonances (e.g., H6–Py, C*H*$_2$Py$'$, ^{t}Bu). Spectra were recorded at 25±1 °C.

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33. Caesium ion distribution coefficients may vary considerably ($<10^2$–$>10^2$) depending on the receptor/solvent system and the presence of additives/modifiers employed for the extraction. Besides the cases cited in Refs. 15 and 16, other examples of effective Cs$^+$ extraction from H_2O into organic solvents or ionic liquids have involved the use of calix[4]arene-bis-crown ethers (D_{Cs} up to 35, see: Engle, N. L.; Bonnesen, P. V.; Tomkins, B. A.; Haverlock, T. J.; Moyer, B. A. *Solvent Extr. Ion Exch.* **2004**, *22*, 611–636) or *N*-alkyl-aza-18-crown-6 (D_{Cs} up to 30, see: Luo, H.; Dai, S.; Bonnesen, P. V. *Anal. Chem.* **2004**, *76*, 2773–2779), respectively. In addition, D_{Cs}s in the range of 100 have been reported in the presence of bis-(*tert*-butylbenzo)-21-crown-7 and lipophilic anions (see: McDowell, W. J.; Case, G. N.; McDonough, J. A.; Bartsch, R. A. *Anal. Chem.* **1992**, *64*, 3013–3017).
34. No signals accounting for the presence of $Cs^+\subset 1$ were detected in the ^{1}H NMR spectrum of **3** after addition of **1** (1 equiv).
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