Supramolecular Chemistry

Hybrid Calixarene/Inorganic Salt/Diiodoperfluorocarbon Supramolecular Assemblies

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1,3-Bis(α-picolyloxy)-*p-tert*-butylcalix[4]crown-5 in the cone conformation (2), 1,8-diiodoperfluorooctane or 1,6-diiodoperfluorohexane, and potassium iodide ternary mixtures undergo in solution self-sorting and afford crystalline "supramolecular salts". These hybrid materials consist of supercation $[K^+ \subset 2]$ and superanion $[I-(CF_2)_n-I \cdots I^- \cdots I-(CF_2)_n-I \cdots I^- \cdots]$ ($n = 6,8$) components. In the supercations the potassium ion is embedded in the ionophoric pocket created by the heteroatoms present at the lower rim. In the superanions the iodide ions form infinite fluorous polyanionic chains as a result of a self-assembly process which relies on halogen bonding. Both cation encapsulation and anion-perfluorocarbon halogen bonding were detected in solution by ^1H and ^{19}F NMR, and in the gas phase by ESI MS.

Keywords: Calixarenes; Halogen bonding; Perfluorocarbons; Supramolecular salts; X-ray

INTRODUCTION

Progress in supramolecular chemistry has closely followed the ability of researchers first to understand and then to exploit and control noncovalent interactions at a molecular level. Over the years, noncovalent synthesis of high-order supramolecular architectures has mostly relied on hydrogen bonding, $\pi-\pi$, and van der Waals interactions to connect molecules with complementary (stereo)electronic and topological features [1–3].

Unlike these well-established noncovalent forces, halogen bonding [4–7] has only recently attracted attention as an additional and powerful tool for promoting self-assembly processes. This interaction takes place between appropriate pairs of molecules bearing a halogen atom working as electron-acceptor site (Lewis acids, halogen bonding donors) and a lone-pair possessing atom working as electron-donor site (Lewis bases, halogen bonding acceptors). A variety of halogen-containing organic molecules (e.g. bromo/iodo-perfluoroalkanes and arenes [8–10], iodoalkynes [11,12], and iodoarenes [13]) and different types of heteroatom-possessing (nitrogen [14], oxygen [15], and sulfur [16]) compounds as well as halide anions [17,18] are thus currently being employed as complementary modules for the construction of supramolecular architectures via halogen bonding.

The strength of halogen bonding depends both on the electron deficiency present at the donor site and on the electron density residing on the acceptor site [19]. As a consequence of this, halogen-bonding-driven self-assembly processes involving anionic acceptors (e.g. halides) are adversely affected by ion-pairing effects, which inevitably reduce the electron density, particularly when metal halides in organic media are used. We have, however, successfully resorted to 'naked' anions, generated via confinement of the countercation inside the cavity of an appropriate receptor, to enhance the electron donating properties of iodide anions. Despite the low reciprocal affinity of the components, this approach effectively promoted the self-assembly of hydrocarbon/inorganic salt/perfluorocarbon (cryptand K.2.2.2, KI and BaI_2, $I-(CF_2)_n-I$) ternary mixtures into multi-component supramolecular architectures [20,21].

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Aiming to acquire a deeper understanding of this type of supermolecule and eventually gain control over their formation (crystal engineering) we have now turned our attention to calixarenes [22–24], as a class of more versatile cation sequestrating agents. In recent years, these synthetic macrocycles have played a prominent role in the development of supramolecular chemistry and calixcrowns [25], in particular, are among the most effective size-selective 'metal' ion receptors known to date. Sulfonatocalixarenes have been used to produce, in the presence of transition [26] and alkali [27,28] metal ions, supercation and superanion assemblies, while picoline-containing analogues [29] have been shown to interact with perfluoroarenes, via halogen bonding.

In this paper we report on the formation of two hybrid supermolecules, obtained from calixarene/KI/diiodoperfluoroalkane ternary mixtures. We also describe the structural features of the adducts both in solution and in the solid state.

RESULTS AND DISCUSSION

Investigations on the self-assembly properties of calixarenes, perfluorocarbons, and inorganic salts were carried out by using 2,4-bis[(2-pyridylmethyl)oxy]-(1,3)-*p-tert*-butylcalix[4]crown-5 in the cone conformation (**2**) [30] as prototype cation segregating agent, KI as iodide source, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-hexadecafluoro-1,8-diiodooctane (**3a**) and 1,1,2,2,3,3,4,4,5,5,6,6-dodecafluoro-1,6-diiodohexane (**3b**) as bidentate halogen bonding donors.

2
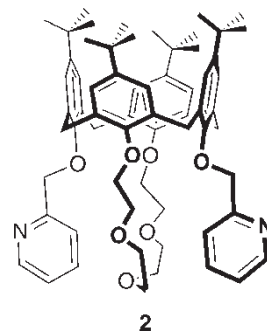
Earlier UV and potentiometric titration experiments had shown that calixcrown **2** efficiently binds ($\log\beta \cong 4.8$, in CH_3OH) potassium ions (added as thiocyanate salt) [30]. In addition, ^{1}H NMR studies (in $CDCl_3/CD_3OD$, 1:1) had also revealed that K^+ ion complexation is slow on the NMR time scale and takes place at the lower rim of **2**. It was expected that this cation binding mode would provide naked iodide ions, from inorganic salts (e.g. KI), which in turn, by acting as powerful electron-donor species, would be able to promote self-assembly of the diiodoperfluorocarbon modules via networks of halogen bonding. Preliminary ^{1}H NMR investigation of the interaction between **2** and increasing amounts of KI confirmed the formation of a 1:1 $K^+ \subset$ **2** inclusion complex (Fig. 1).

Potassium complexation affects all the proton chemical shifts of **2**, in particular those of the oxyethylene and picolyloxymethylene groups, as well as those of the picolyl (Py) ring (H3- and H6-Py) which move up or downfield with complexation induced shifts (CIS) in the range 0.3–0.7 ppm.
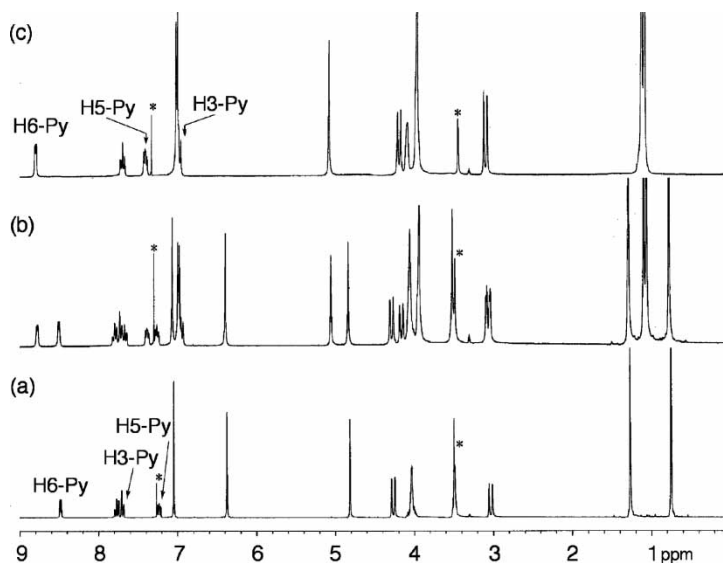
FIGURE 1   The ^{1}H NMR spectrum (300 MHz, $CDCl_3/CD_3OD$ 9:1, v/v, 293 K) of **2** (a), and spectral changes upon addition of 0.5 (b) and 1.0 equiv (c) of KI. The doubling of all signals in trace (b) shows that the exchange between the free calixarene **2** and the $K^+ \subset$ **2** complex is slow on the NMR timescale. The large CIS values observed in trace (c) for H3- and H6-Py provide evidence for K^+/Py interactions (*Residual solvent peak).

The shifts of the latter heteroaromatic protons suggest that the *anti* orientation adopted by the picolyl nitrogen in the free receptor evolves to a *syn* orientation upon K^+ binding. Potassium ions are therefore believed to be encapsulated into the ionophoric cavity defined by the phenoxy and crown ether oxygen atoms, and bis-capped by the two picolyl nitrogens, for a total of nine binding sites.

Upon addition of 1.0 equiv. of 1,8-diiodoperfluoro-octane **3a** to an equimolar solution of **2** and KI (5.0×10^{-2} M; in $CDCl_3$), no spectral changes were detected in the ^1H NMR spectrum. In contrast, the ^{19}F NMR spectrum of this solution showed an upfield shift of the $-CF_2I$ signals of **3a** ($\Delta\delta = 3.76$ ppm, from $\delta = -59.57$ to $\delta = -63.33$ ppm), with respect to neat **3a**, considered of diagnostic value in revealing the formation of strong halogen bondings [31,32]. Identical ^1H and ^{19}F NMR spectra were obtained when the **2**/KI/**3a** ternary mixture was directly dissolved (extensive sonication was necessary) in $CDCl_3$. This series of experiments rules out the alternate two-species self-assembly pathway leading to one-dimensional infinite chains of **2** and **3a**

(Scheme 1), which in principle might have happened if the two diametrically opposite picolyl nitrogen atoms of **2** had acted as halogen bonding acceptors [33] towards the halogen bonding donor **3a**. Most importantly, these findings show that $I^-\cdots I$ prevails over $N\cdots I$ halogen bonding.

To gain a more precise insight into the supra-molecular behaviour of the **2**/KI/**3a** ternary mixture, and in particular on the fate of the iodide anion (released after $K^+ \subset \mathbf{2}$ formation) upon exposure to diiodoperfluorocarbon **3a**, calixcrown **2** was crystallized from a methanol solution of potassium iodide and the solid complex formed $[K^+ \subset \mathbf{2}]I^-$ was then dissolved in absolute ethanol and allowed to recrystallize in the presence of **3a** (1.0 equiv.). Slow evaporation of the solvent from this mixture afforded pale yellow single-crystals of **1a** which were suitable for X-ray analysis. In the solid state, the **2**/KI/**3a** ternary mixture forms the hybrid "supramolecular salt" [34] **1a**, consistent with the presence of supercation $[K^+ \subset \mathbf{2}]$ and superanion $[I-(CF_2)_8-I\cdots I^-\cdots I-(CF_2)_8-I\cdots I^-\cdots]$ components (Scheme 2).
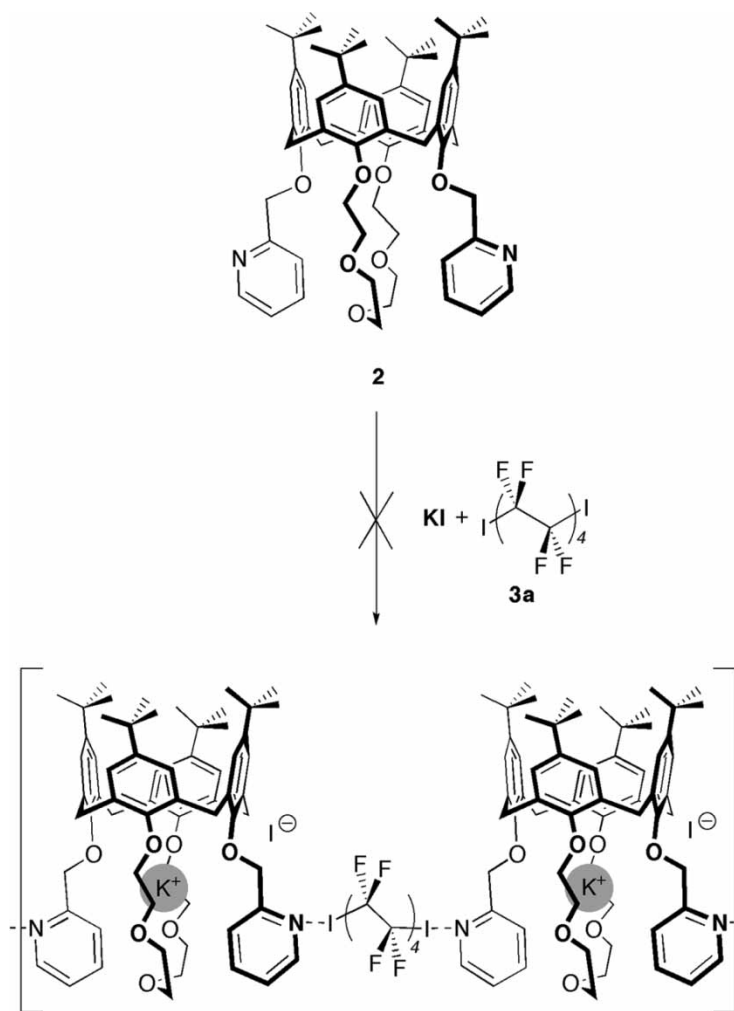
SCHEME 1   Unobserved self-assembly mode of **2** and **3a** ($N\cdots I$ halogen bonding is not formed).
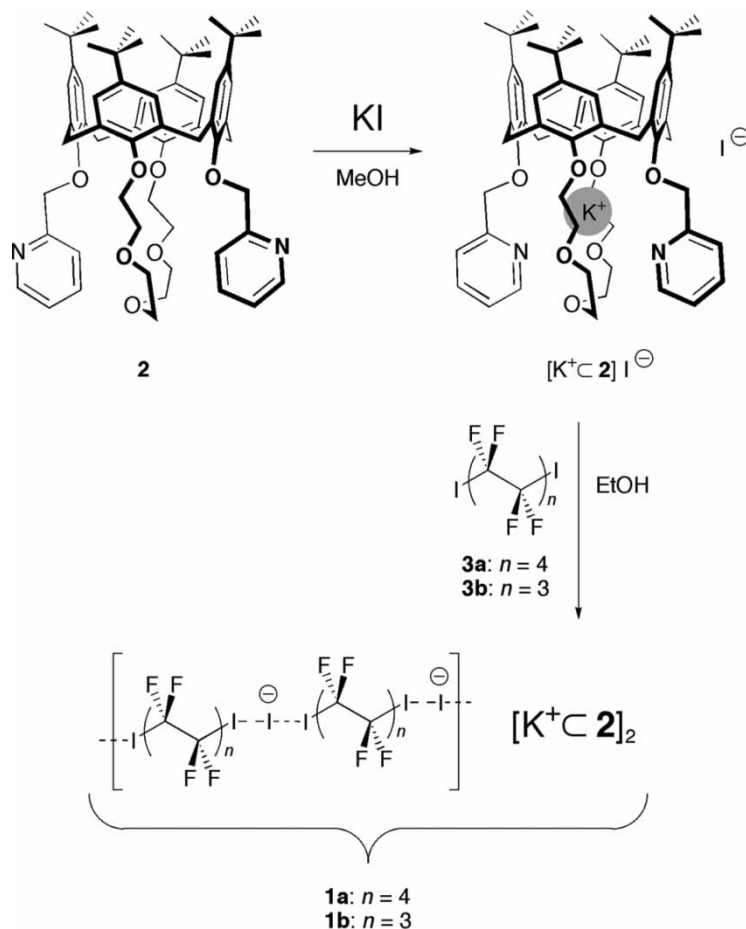
SCHEME 2   Observed self-assembly of the hybrid "supramolecular salts" **1a** and **1b**.

Overall, the packing of co-crystal **1a** is heavily influenced by the steric bulkiness of the calixcrown modules (Fig. 2). Each of these units shows van der Waals contacts with two polyether chains, a *tert*-butyl group and the pyridine ring not involved in potassium complexation (see below) belonging to four other molecules related to the first by a centre of symmetry.

The calixcrown modules act as cation sequestrating agents and, in so doing, adopt a cone conformation wherein distortion is less pronounced than that observed in the free receptor
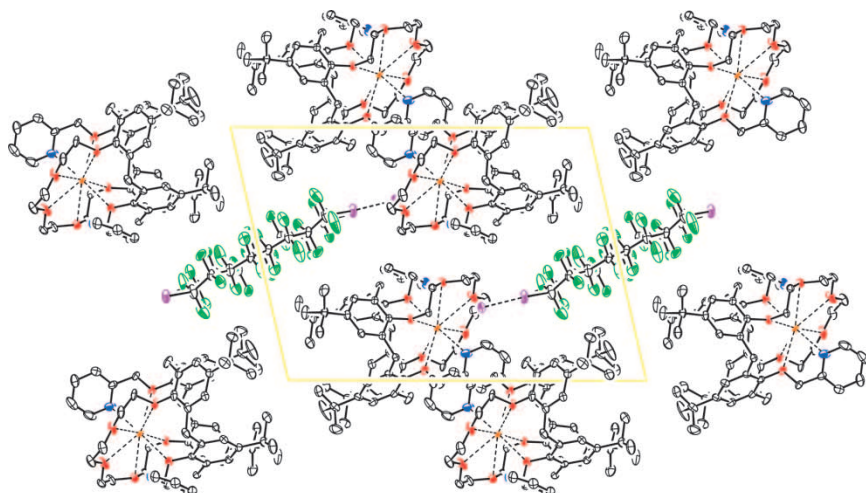
FIGURE 2   Crystal packing of the hybrid "supramolecular salt" $[K^+ \subset \mathbf{2}]$ $[I-(CF_2)_8-I\cdots I^-\cdots I-(CF_2)_8-I\cdots I^-\cdots]$ **1a**, co-crystallized from the **2/KI/3a** ternary mixture, viewed down the *a* axis. Colors are as follows: carbon, black; nitrogen, blue; oxygen, red; iodine, purple; fluorine, green; potassium, orange.
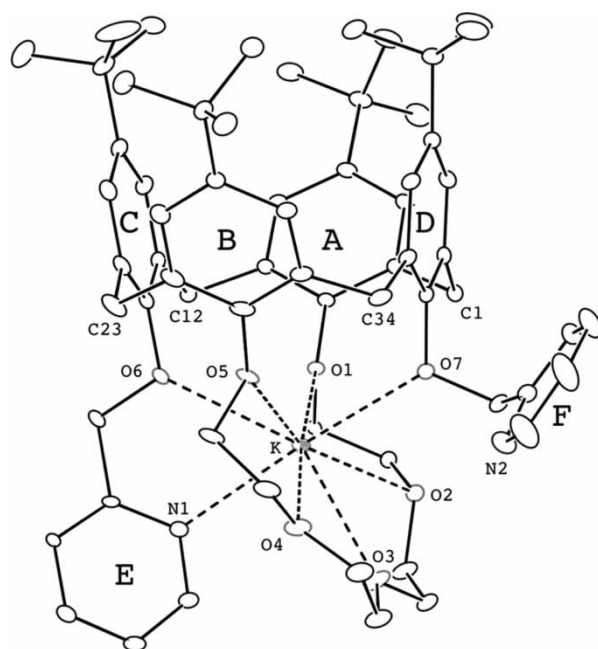
FIGURE 3 Ortep view of the supercation component $K^+ \subset \mathbf{2}$ present in the co-crystal **1a**, showing the potassium ion coordinated by eight out of the nine heteroatoms (N2 being the exception) located at the lower rim of **2**.

FIGURE 4 View along the *a* axis of the superanion components present in the co-crystal **1a**, showing the halogen bonded infinite zig-zag chains formed by **3a** and iodide ions. Only one of the two conformers of the disordered perfluroalkane molecules is reported. Colors are as follows: carbon, black; iodine, purple; fluorine, green. Halogen bondings are represented as dashed lines. The supercation components have been omitted for the sake of clarity.

[30]. The interplanar angles between the aryl rings A and B (which are linked by the polyether bridge) and aryl rings C and D (bearing the picolyl pendant groups) are 67.3(1) and 13.1(1)°, respectively (Fig. 3). The four linking methylene carbon atoms (C1, C12, C23 and C34) are coplanar to within 0.03(1) Å. The calixarene cavity is empty and supercation formation takes place via encapsulation of the potassium ion inside the ionophoric pocket created by the heteroatoms present at the lower rim. Four phenoxy, three ethereal oxygen and one picolyl nitrogen atoms (O1, O6, O5, O7, O2, O3, O4, and N1, respectively) coordinate K^+ and shield it from the surrounding environment and from its counteranion. The $O \cdots K^+$ distances range between 2.614(1) and 3.106(2) Å, while the $N \cdots K^+$ distance measures 3.010(5) Å. The potassium ion lies 0.285(2) Å out of the mean plane containing the oxygen atoms (O1, O2, O3, O4, and O5) of the polyoxyethylene moiety, in the direction of the N1 atom.

The spaces left empty by the crystal packing of the supercation are filled with halogen bonded infinite chains of superanion components where 1,8-diiodoperfluorooctane modules and iodide ions alternate. The structure of this polyanion is rather complex. Two independent molecules (A and B) of **3a** are located over two distinct crystallographic centres of symmetry. The A molecules show a TGTGT [35] conformation. The type B molecules, being disordered, have been split into two equally-populated
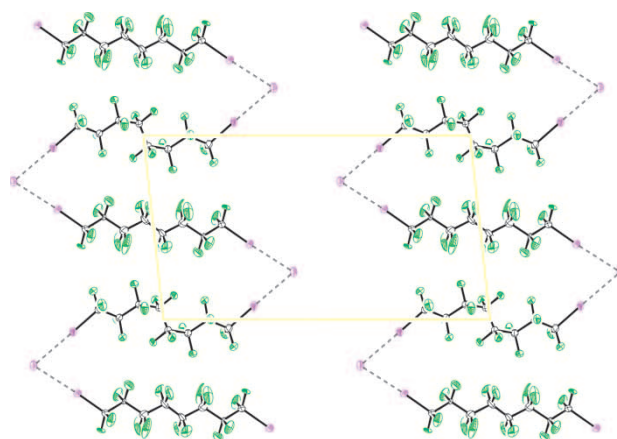
entities (designated B1 and B2), both of which adopt a nearly *all-trans* conformation. The iodide ions and the diiodoperfluorocarbon modules behave as bidentate halogen bonding acceptors and donors respectively, and self-assemble into infinite zig-zag chains according to the $\cdots A \cdots I^- \cdots B1(B2) \cdots I^- \cdots A \cdots I^-$ alternating sequence. The mean angle and length of the $I \cdots I^- \cdots I$ bondings are 74.4° and 3.359 Å. The distance values are approximately 20% shorter than the sum of the van der Waals radii of an iodine atom (1.98 Å) and an iodide ion (2.20 Å) [36] and are therefore consistent with rather strong halogen bonding. The fluorocarbon superanions segregate in the crystal lattice into pleated strings, to minimize contact with the hydrocarbon supercation $K^+ \subset \mathbf{2}$ (Fig. 4).

The formation of these zig-zag chains suggests that the rather dense packing of the supercation components and possibly the length of the perfluoroalkane prevent the iodide anion from behaving as a tridentate halogen bonding donor (as in the case of the K.2.2.2/KI/**3a** ternary mixture) [20] and even hamper the growth of straight fluorous polyanionic chains. To verify this hypothesis and try to correct this sterical mismatch, $[K^+ \subset \mathbf{2}]I^-$ was crystallized from ethanol in the presence of the shorter 1,6-diiodoperfluorohexane **3b**, in place of **3a**, to afford pale yellow crystals of **1b** (Scheme 2). A rapid screening of a $CHCl_3/CH_3OH$ (2:1) solution of **1b** by electrospray ionization mass spectroscopy (ESI MS) [37], both in the positive and negative ion mode, confirmed the formation of $K^+ \subset \mathbf{2}$ as well as $I-(CF_2)_6-I \cdots I^-$ assemblies ($m/z = 1027.8$ and 680.4, respectively, see Fig. 5).

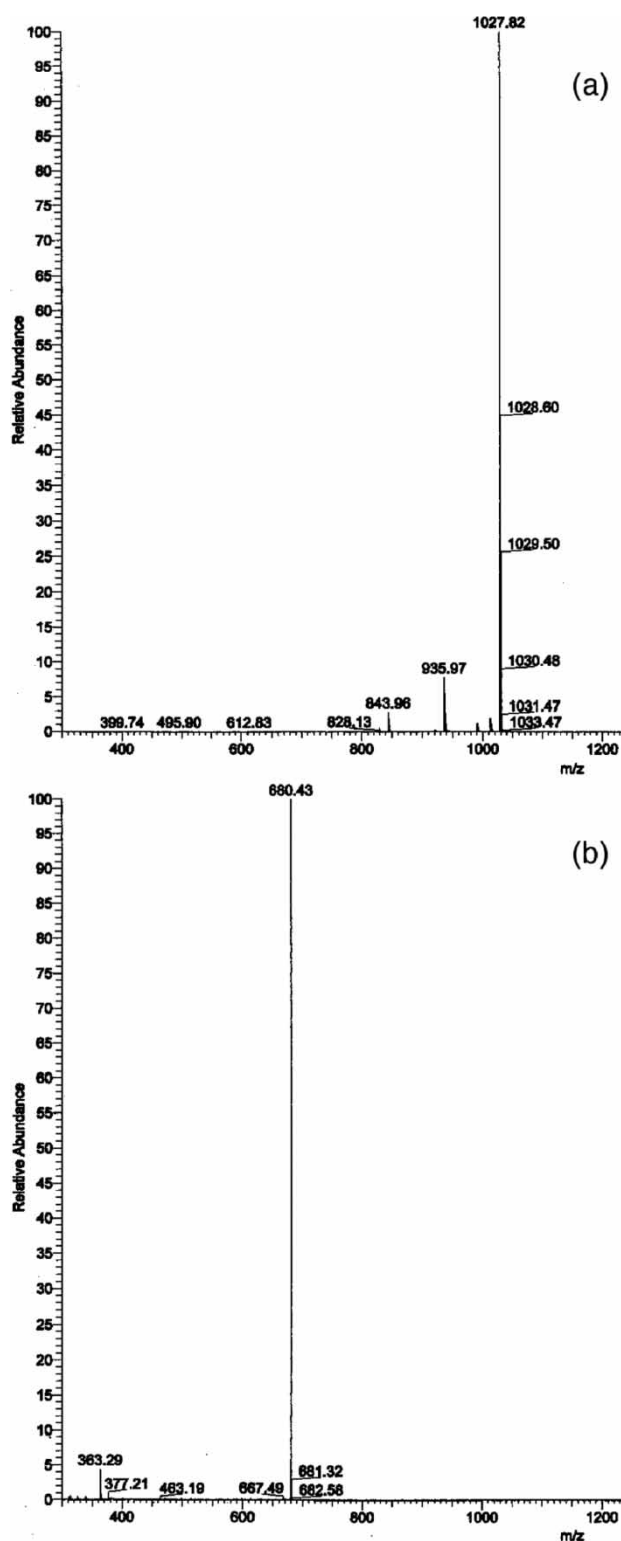Unlike **1a**, X-ray data of **1b** could not be collected at very low temperature. Consequently, while the

FIGURE 5   (a) Positive-ion ESI MS spectrum for the $K^+ \subset 2$ supercation. (b) Negative-ion ESI MS spectrum for the $I{-}(CF_2)_6{-}I\cdots I^-$ superanion.

structural features of **1b** were unambiguously determined, the data quality was poor. In **1b**, the calixcrown **2** behaves once again as an effective cation sequestrating agent, embedding the potassium ions at the lower rim (Fig. 6).

In this case, however, both nitrogen atoms present on the two picolyl pendants weakly bind the K^+ ion and the calixcrown module adopts an approximate C_2 symmetry. The four bridging methylene carbon atoms (C1, C12, C23 and C34) are essentially coplanar to within 0.064(3) Å. The two aryl rings linked by the polyoxyethylene chain (A and B) and the remaining two holding the picolyl groups (C and D) form interplanar angles of 27.3(2) and 60.7(2)°, respectively. The potassium ion is encapsulated at the lower rim, surrounded by a nine coordinate heteroatom cage. The $N\cdots K^+$ distances are 3.327(5)–3.648(15) and 3.622(10)–3.841(16) (for the two models used for refining the disordered structure), while the $O\cdots K^+$ distances range between 2.615(3) and 2.855(4) Å. The potassium ion lies 0.027(2) Å to the mean plane containing O2, O3, O4, O5, and O6 polyethereal oxygens. As shown in Fig. 7, the supercations form layers perpendicular to b, with the insertion of carbon tetrachloride solvent molecules.

The molecules of diiodoperfluorohexane **3b** show an *all-trans* conformation. In the co-crystal **1b**, both **3b** and iodide anions behave as bidentate modules and the halogen bonding driven self-assembly of the two modules produces infinite chains of fluorous polyiodide anions. These chains develop parallel to the direction $(10\bar{1})$ and the $I\cdots I^-$ distances are 3.355(2) and 3.360(2) Å. The $I\cdots I^-\cdots I$ angle is 153.09(5)°, therefore, in contrast to **1a**, the infinite chains in **1b** are linear. The chains of the superanion are dispersed throughout the supercation matrix and have no contact with each other. Fig. 8 shows two of them, lying around the plane at $y = 0.25$.

CONCLUSIONS

In conclusion, our findings show how a subtle interplay of non-covalent interactions overcomes the low affinity that perfluorocarbons have for both calixarenes and inorganic salts. Self-sorting and self-assembly of the ternary mixture occur and supramolecular architectures are formed. Confinement of the cation inside an appropriately chosen receptor, and anion-driven self-assembly of electron-poor perfluoroalkanes are the two processes that, by acting in concert, determine the formation of supercation and superanion structures. As far as the superanion is concerned, both in **1a** and **1b** the halogen bonding donor and acceptor consistently behave as bidentate species. Differences in the length of the diiodoperfluoroalkanes **3a** and **3b**, produce crystalline structures with different shapes (pleated vs straight chains in **1a** and **1b**, respectively). Minor variations on the binding mode of the cation to the calixarene receptor also occur as one and two picolyl nitrogens interact with the metal ions (in **1a** and **1b**, respectively).
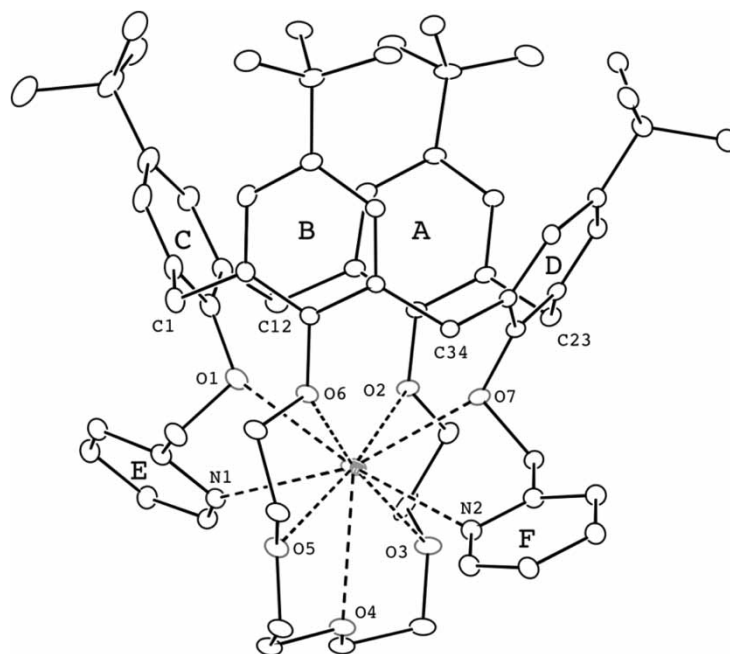
FIGURE 6 Ortep view of the supercation component $K^+ \subset 2$ present in the co-crystal **1b**. The potassium ion is coordinated by all the phenoxy and ethereal oxygen atoms and in addition is bis-capped by the two picolyl nitrogen atoms.

Consistent with previous finding [20,21], the present study confirms the exceptional ability of naked iodide anions, derived from inorganic salts, to prevail over other halogen bonding acceptors (e.g. nitrogen atoms of picolyl moieties).

FIGURE 7 Section around $y = 0.0$ of the crystal packing of the supercation $K^+ \subset 2$ and carbon tetrachloride present in the co-crystal **1b**, view along the b axis. Colours are as follows: carbon, black; nitrogen, blue; oxygen, red; potassium, orange; chlorine, green. For the sake of clarity, only a part of the disordered supercation components is shown.

Investigations on the properties of these hybrid materials and the synthesis of new ones, employing calixarenes with different cation selectivity, are currently in progress.

EXPERIMENTAL

General Methods

Melting points were determined on a Kofler melting point apparatus and are uncorrected. Unless otherwise stated, the ^{1}H (300 MHz) and ^{19}F (282 MHz) NMR spectra were obtained at 293 K in CDCl$_3$/CD$_3$OD (9:1, v/v), using TMS and CFCl$_3$ as internal standards. FT-IR spectra were recorded as KBr pellets on a Nicolet Nexus FT-IR spectrophotometer equipped with the Smart Endurance system (UATR). ESI mass spectra were acquired on a Finnigan LCQ DECA ThermoQuest mass spectrometer as CHCl$_3$/CH$_3$OH (2:1; $\sim 10^{-7}$ M). All solvents and chemicals were reagent grade and were used without further purification. Calixcrown **2** was prepared according to a reported procedure [30].

Procedure for the Formation of the Hybrid Supramolecular Salts

Co-crystals **1a** and **1b** were both grown in a sealed chamber by slow diffusion, at room temperature, of CCl$_4$ vapors into an uncapped clear borosilicate glass vial, containing an absolute ethanol solution of $[K^+ \subset 2]I^-$ and diiodoperfluoroalkanes **3a** or **3b** in equimolar amounts. Solid $[K^+ \subset 2]I^-$ was crystal-

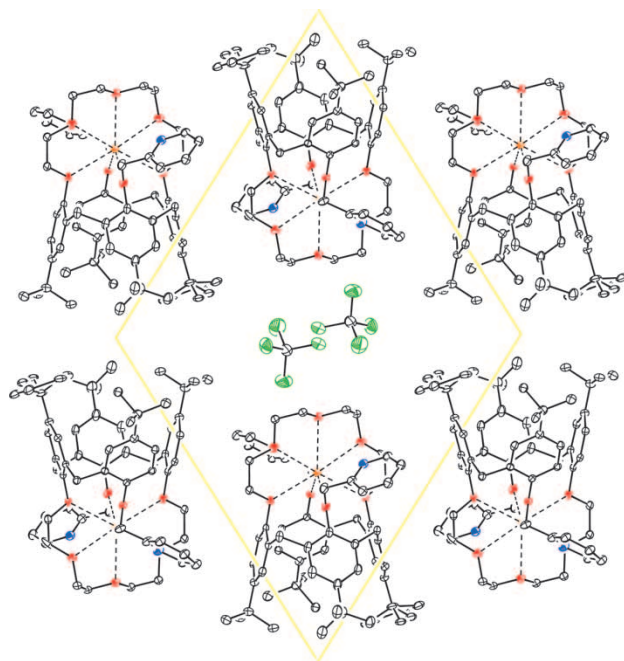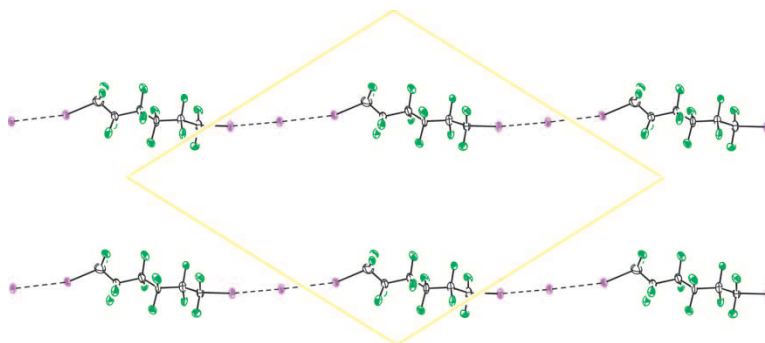FIGURE 8 Projection along the *b* axis of two chains of the superanion components present in the co-crystal **1b**, lying near the crystallographic plane at *y* = 0.25. Colours are as follows: carbon, black; fluorine, green; iodine, purple. Halogen bonds are represented as dashed lines. The supercation components have been omitted for the sake of clarity.

lized from a 1:1 mixture of calixcrown **2** and KI in CH$_3$OH.

Inclusion Complex [K$^+$ ⊂ 2]I$^-$

Mp (CH$_3$OH) 254–262 °C; FT-IR (selected bands) 2961, 2926, 2868, 1592, 1479, 1190, 1124, 1097, 869, 774 cm^{-1}; ^{1}H NMR δ 1.08, 1.11 [s, 18 H each, C(CH$_3$)$_3$], 3.09, 4.19 (AX, *J* = 12.4 Hz, 8 H, ArCH$_2$Ar), 3.96, 4.09 (pseudo-s, ratio 3:1, 16 H, OCH$_2$CH$_2$O), 5.08 (s, 4 H, OCH$_2$Py), 6.97 (d, *J* = 7.6 Hz, 2 H, H3-Py), 7.00, 7.02 (s, 4 H each, ArH), 7.41 (ddd, *J* = 7.2, 5.0, 1.1 Hz, 2 H, H5-Py), 7.69 (td, *J* = 7.8, 1.7 Hz, 2 H, H4-Py), 8.80 (d, *J* = 4.3 Hz, 2 H, H6-Py) ppm.

Co-crystal 1a

Mp (EtOH) 192–198° C; FT-IR (selected bands) 3065, 2962, 2870, 1480, 1363, 1192, 1151, 1121, 1055, 960, 869, 768, 643, 542 cm^{-1}; ^{19}F NMR δ − 122.12 (br s, −CF$_2$CF$_2$CF$_2$CF$_2$I), − 121.31 (br s, −CF$_2$CF$_2$-CF$_2$I), − 113.58 (br s, −CF$_2$CF$_2$I), − 60.46 (t, *J* = 14.3 Hz, −CF$_2$I) ppm.

Co-crystal 1b

Mp (EtOH) 182–188 °C; FT-IR (selected bands) 2964, 2870, 1592, 1480, 1362, 1299, 1208, 1145, 960, 870, 790, 636, 553 cm^{-1}; ^{19}F NMR δ − 121.34 (br s, −CF$_2$CF$_2$CF$_2$I), − 113.56 (m, −CF$_2$CF$_2$I), − 60.31 (br s, −CF$_2$I) ppm.

Crystal Structure Determinations

Single-crystal x-ray diffraction measurements were performed on a Bruker APEX CCD area detector diffractometer, graphite monochromator, Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by SIR-92 [38] and refined by full-matrix least-squares on F^2, using SHELXL-97 [39]. Hydrogen atoms were introduced in calculated positions and not refined. All crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC 279022 and 279021, for **1a** and **1b** respectively. 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

Crystal Structure of 1a

C$_{64}$H$_{80}$N$_2$O$_7$K$^+$·I$^-$·C$_8$F$_{16}$I$_2$, M$_r$ = 1809.18, triclinic, space group *P*1̄, *a* = 12.0590(9), *b* = 15.7424(12), *c* = 21.209(2) Å, α = 101.930(8), β = 93.223(7), γ = 102.506(8)°, *V* = 3824.3(5) Å^3, *Z* = 2, *D$_c$* = 1.571 g cm^{-3}, μ(Mo-Kα) = 1.371 mm^{-1}. Data were collected at *T* = 90 K, because at room temperature the mean intensity of the reflections vanished at very low values of 2θ. 61610 Reflections were collected up to 2θ = 60.0°; 22188 unique [18042 with *I$_o$* > 2σ(*I$_o$*)], *R*$_{ave}$ = 0.0274. Final disagreement factors for all (observed) reflections: $R_w(F^2)$ = 0.0953(0.0915) and *R* = 0.0445(0.0350), goodness-of-fit = 1.083, 1244 parameters, 1487 restraints. The structure is partially disordered. The two picolyl moieties, the polyether chain and one of the two independent 1,8-diiodoperfluorooctane molecules (excluding the terminal iodine atoms), were split into two models that were refined with variable populations. The final population ratio found was 0.639(2)/0.361. The refinement was carried out with restraints both on ADPs and geometric parameters.

Crystal Structure of 1b

C$_{64}$H$_{80}$N$_2$O$_7$K$^+$·I$^-$·C$_6$F$_{12}$I$_2$·CCl$_4$, M$_r$ = 1862.97, monoclinic, space group *P*2$_1$/*n*, *a* = 19.147(3), *b* = 24.836(4), *c* = 19.343(3) Å, α = 116.20(2)°, *V* = 8253 (2) Å^3, *Z* = 4, *D$_c$* = 1.499 g cm^{-3}, μ(Mo-Kα) = 1.391 mm^{-1}. The diffraction pattern was poor because of the molecular disorder. Any attempts to lower the crystal temperature caused a phase transition with twinning, apparently below 233 K. Data were then collected at 243 K. 125868 Reflections were collected up to

$2\theta = 52.16°$; 16312 unique [9446 with $I_o > 2\sigma(I_o)$], $R_{ave} = 0.0421$. Final disagreement factors for all (observed) reflections: $R_w(F^2) = 0.1425(0.1282)$ and $R = 0.0763(0.0454)$, goodness-of-fit = 0.971, 1389 parameters, 2340 restraints. In spite of the low quality of the data, the complex structure was clearly understood. The structure consists of $K^+ \subset$ calix[4]crown-5 supercations, fluorous polyiodide superanions (composed of 1,6-diiodoperfluorohexane molecules linked to iodide ions via halogen bonding), and carbon tetrachloride solvent molecules. All these elements were placed in a general position. The structure is largely disordered, the CCl_4 molecules, all the *t*-butyl groups, and most of the atoms of both the polyether chain and the picolyl moieties were split into two models. Different refinement protocols were attempted but, in the end, only the population factor of the polyether chain was refined and converged to the ratio 0.55(2)/0.45 for the two conformations. A value of 0.5 was assigned to all the other split atoms.

Acknowledgements

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