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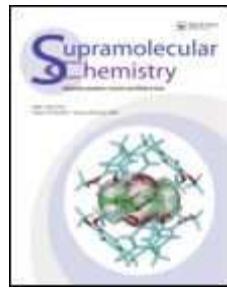
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assemblies**

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Keywords:	Anion coordination, Calixarenes, Comb-like copolymer, Halogen bonding, X-ray



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16 **Self-assembly of ternary mixtures composed of
17 cation segregating agent/inorganic halide (penta-
18 *tert*-butyl-
19 pentakis(ethoxycarbonylmethoxy)calix[5]arene
20 (1)/NaI or 4,7,13,16,21,24-hexaoxa-1,10-
21 diazabicyclo[8.8.8]hexacosane (4)/BaI₂) and
22 diiodoperfluorocarbon (1,8-diiodoperfluoroctane
23 (2)) produces crystalline supramolecular salts 3
24 and 5, respectively, whose structural
25 characteristics in the solid state have been
26 elucidated by single-crystal X-ray analyses.
27 Encapsulation of alkali or alkali-earth metal ions
28 inside the complexing pocket of the appropriate
29 receptor generates naked iodide anions, which
30 effectively drive the self-assembly of
diiodoperfluoroctane 2 into halogen-bonded
supramolecular anions with a comb-like
copolymer structure.**

31 Keywords: Anion coordination; Calixarenes; Comb-like
32 copolymer; Halogen bonding; X-ray

33 **1. INTRODUCTION**

34 Cation coordination chemistry has contributed to
35 major advances in and benefited by major
36 contributions from several areas of chemistry
37 spanning both fundamental studies (*e.g.* aggregation,
38 recognition, and self-assembly processes) and
39 application-oriented investigations (*e.g.* phase
40 transfer catalysis, waste-water cleaning, light
41 emitting devices) [1]. The toolbox of modules to
42 design and implement cation coordination is quite
43 rich and allows for specific strategies tailored to fit
44 the substrate cation and the targeted function.

45 Anion coordination is a much less developed area
46 [2]. While moderately good information is available
47 on the construction of discrete adducts through *endo*-

recognition of anions [3], the understanding of *exo* recognition phenomena involving anions is still in its infancy [4], and a tremendous difference exists between the ability to self-assemble infinite networks by using cations as compared to anions as templating agents.

Halogen bonding (XB) is a non-covalent interaction in which halogens act as electron acceptors (Lewis acids, XB donors) [5]. For a given halogen site, the higher the electron density on the electron donor partner (Lewis base, XB acceptor), the stronger the resulting XB [6]. Anions (*e.g.* iodides and bromides) usually give rise to stronger XBs than neutral electron donors [4h] (*e.g.* the nitrogen atoms of amine and pyridine moieties or the oxygen atoms of ether and carbonyl functionalities) and it has already been reported that both discrete adducts and infinite networks can be formed when polydentate XB donors are used [7]. Interestingly, with a given XB donor (*e.g.* 1,8-diiodoperfluoroctane and 1,2-diiodotetrafluoroethane) iodide ions can work as mono-, bi-, or tridentate XB acceptors and as a result trimeric adducts [8], 1D [4b, 4i, 9], 2D [4a, 4c, 7a, 10], or 3D [4c, 7a, 11] networks can be formed.

Halides are spherical anions and the nature of the associated cation affects their coordination valency when involved in XB formation. The size and shape of the cation influence its distance from the anion and consequently the tendency of the anion to work as electron donor (namely its coordination number and sphere) [12]. Moreover, cation size and shape also influence the geometry and the metrics of the crystal packing and thus affect the size and shape of the space potentially available for the supramolecular anion. Indeed, we have shown how the topology of the overall crystal packing can be designed in detail when the mutual fit between cation and anion is conveniently controlled [4a, 8a, 9a].

Two classes of selective cation sequestering agents will be presented in this paper, the calix[5]arene **1** and the cryptand K.2.2.2 **4**. Their ability to tightly accommodate alkali and alkali-earth metal ions of different sizes is well known [13], but the fate of the counterion freed upon complexation has scarcely been investigated. We will report here on the formation of the hybrid supermolecule **3** obtained from calixarene/NaI/diiodoperfluoroctane ternary mixtures and on its structural properties in the solid state. The structural features of the supramolecular anion formed upon anion-templated assembly of diiodoperfluoroctane **2** will be described and compared with the supramolecular anion present in the hybrid supermolecule **5**, where the anion and the diiodoperfluorocarbon modules are the same but the metal cation and its sequestering agent are different (Ba²⁺ and K.2.2.2, respectively).

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RESULTS AND DISCUSSION

2.1 Penta-*tert*-butyl-pentakis(ethoxycarbonylmethoxy)calix[5]arene/NaI/1,8-diiodoperfluorooctane assembly

The self-assembly of ternary adducts compounded of calixarenes, perfluorocarbons, and inorganic salts was carried out by using penta-*tert*-butyl-pentakis(ethoxycarbonylmethoxy)calix[5]arene (**1**) [14], NaI, and 1,8-diiodoperfluorooctane (**2**). Diiodooctane **2** has already been proven to act as an efficient XB donor towards iodide anions [15]. Calixarene **1**, on the other hand, is known to be an effective ionophore [14] and a selective carrier of sodium cations through liquid membranes [16]. The use of **1** was then expected to provide, upon sodium iodide exposure, “naked” iodide anions readily available for XB formation.

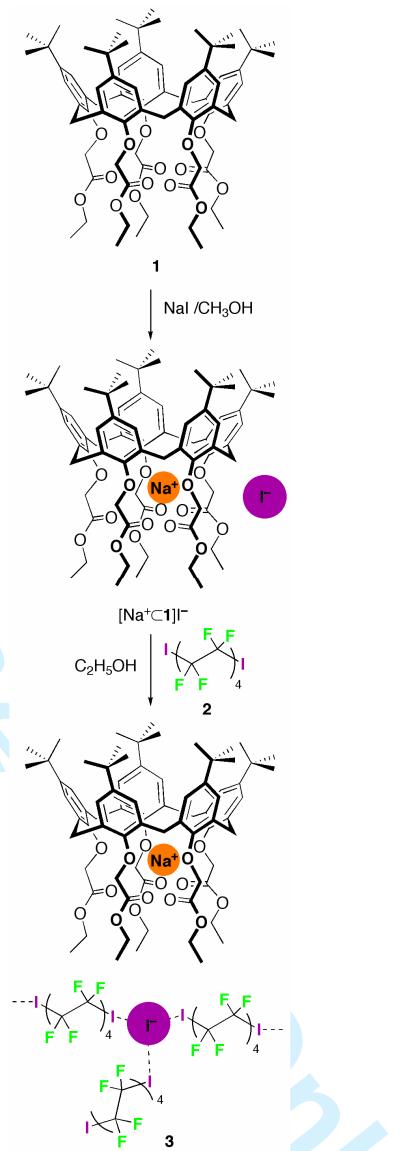
The $[\text{Na}^+ \subset \mathbf{1}]^-$ complex was obtained as a white powder upon evaporation of a methanol solution of equimolar amounts of **1** and NaI. The formation of the supramolecular cation $[\text{Na}^+ \subset \mathbf{1}]$ featuring a Na^+ ion embedded in the ionophoric pocket created by the ethereal and carbonyl oxygen atoms at the lower rim of the calixarene was confirmed by ^1H NMR and ESI-MS spectral data [17].

X-ray quality single crystals of the ternary system **3** were obtained by slow evaporation of an ethanolic solution of $[\text{Na}^+ \subset \mathbf{1}]^-$ in the presence of **2** (see Experimental section for details). Variation of the $[\text{Na}^+ \subset \mathbf{1}]^- : \mathbf{2}$ ratio in the 1:1 to 1:2 interval had no effect on the isolation of the final adduct **3**. The stepwise assembly of **3** is illustrated in Scheme 1.

Single crystal X-ray analysis of **3** has revealed the structural details of the system. The $[\text{Na}^+ \subset \mathbf{1}]^-$ to **2** ratio is 1:2 and iodide anions are involved in the formation of three XBs. This is consistent with a remarkable electron donor ability of the iodide anion, derived from a particularly effective ion pair dissociation. Calix[4]arene derivatives have already been used to sequestrate potassium, cesium and barium cations and generate naked iodide anions to be involved in halogen bonding-driven self-assembly. The adduct **3** is the first example of a supramolecular salt exploiting NaI as the iodide ion source and a preorganized cone calix[5]arene derivative as a segregating agent. It appears that $[\text{Na}^+ \subset \mathbf{1}]^-$ can be considered a valuable alternative to previous XB acceptors based on calix[4]arene/alkali metal iodide adducts. The elucidation of the structure of the supercation component arising from a sodium

calix[5]arene pentaester complex in the co-crystals of **3** is unprecedented in the literature.

In the solid state the complex adopts a distorted cone conformation, quite similar to the one found for the free host **1** [14] and the sodium complex of a structurally related calix[5]arene pentaketone [18].



Scheme 1. Stepwise assembly of the supramolecular salt **3** (**1**/NaI/**2**, 1:1:2 ratio).

One of the five *tert*-butylphenyl residues (ring E) is leaning towards the interior of the upper rim hydrophobic calixarene cavity, while the other four are pointing outwards. The tilt angles of the aromatic rings to the mean plane of the bridging methylenes are 136.68, 107.95, 102.79, 137.03, and 61.66° for rings A to E, respectively. The relatively small Na⁺ ion is surrounded by a seven coordinated oxygen cage composed of two phenolic oxygens, four ester carbonyl oxygen atoms and a water molecule. It lies off-center from the lower rim ionophoric cage because the outward-oriented pendant group of the self-inclined ring is not involved in the complexation. The Na⁺...O distances are in the range of 2.326–2.918 Å (Figure 1).

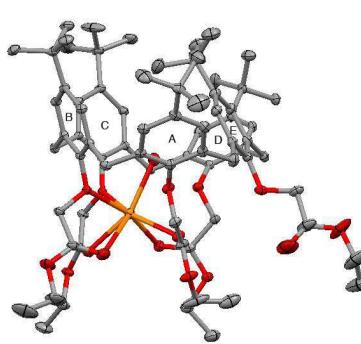


Figure 1. Side view of the supercation component $[\text{Na}^+ \cdot \mathbf{1}]$ present in the co-crystal **3**. ADPs at 50% probability level. Colors are as follows: carbon, gray; oxygen, red and sodium, orange. Here and in all other Figures, only one conformation of the disordered groups is drawn; hydrogen atoms are omitted for clarity.

The phenolic rings in the calixarene structure are quite rigid since they have to comply with the conformational requirements dictated by the ion complexation. By contrast, the pendants bonded to the phenolic oxygens potentially display great mobility and can assume a large variety of conformations. In the supercation $[\text{Na}^+ \cdot \mathbf{1}]$ two of the ethoxycarbonylmethoxy chains are doubly bonded and two are singly bonded to the sodium. Despite the fact that data were collected at 90 K, the pendants show some conformational disorder, one of the chains being refined in two conformations with population factor ratio 0.672/0.328.

The supramolecular cations $[\text{Na}^+ \cdot \mathbf{1}]$ loosely interact with each other in the crystal packing as they are separated by halogen bonded perfluorinated supramolecular anions having the structure of comb-like copolymers (Figure 2). Iodide anions act as tridentate electron donors towards the iodine atoms

of diiodoperfluorooctane **2**, the latter working as either bidentate or monodentate electron acceptor(s). The bidentate diiodoperfluorooctane molecules interconnect the iodide anions, leading to the formation of unlimited chains; the monodentate diiodoperfluorooctane modules are also appended to the iodide anions, forming the teeth of the halogen-bonded comb-like copolymer. The angles around the iodide anions are 78.42(2), 76.73(3) and 145.14(1)^o for $\text{I}^3 \cdots \text{I}^5 \cdots \text{I}^2$, $\text{I}^3 \cdots \text{I}^5 \cdots \text{I}^1$ ($i=x,1+y,z$) and $\text{I}^2 \cdots \text{I}^5 \cdots \text{I}^1$, respectively. The XB lengths are 3.373(2), 3.402(1) and 3.424(1) Å for $\text{I}^5 \cdots \text{I}^3$, $\text{I}^5 \cdots \text{I}^1$ and $\text{I}^5 \cdots \text{I}^2$, in that order. These distances are very short (in the ternary adduct $[\text{K}^+ \subset \text{K}.2.2.2] \{ [\text{I}-(\text{CF}_2)_8-\text{I}]_2\Gamma \}$ where the iodide anions are tridentate, the $\text{I} \cdots \text{I}^-$ distances are 3.474 Å) and indicate strong interactions, once again consistent with a high degree of ion pair dissociation.

In general, the difluoromethylene groups of halogen-bonded α,ω -diiodoperfluoroalkanes show some disorder, while the iodine atoms, pinned by the XB, are ordered. This is also the case in the $[\text{Na}^+ \subset \mathbf{1}] \{ [\text{I}-(\text{CF}_2)_8-\text{I}]_2\Gamma \}$ supramolecular assembly **3**, where most of the carbon and fluorine atoms of the monodentate diiodooctane modules, and some of the carbon and fluorine atoms of the bidentate diiodooctane modules, were split over two locations with occupancy 0.5 in order to model the disorder. Interestingly, the terminal iodines of the teeth, which are not involved in any XBs, also show some disorder.

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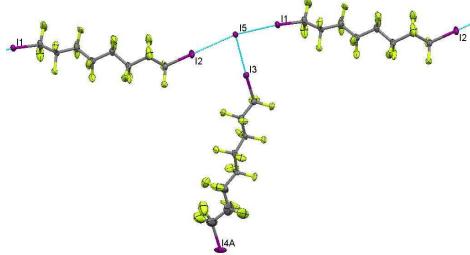


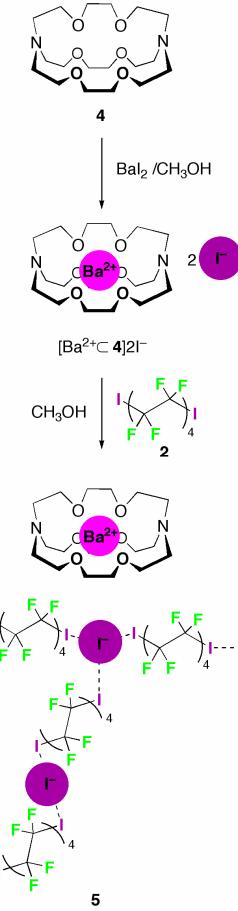
Figure 2. The superanion $\{[\text{I}-(\text{CF}_2)_8-\text{I}]_2\Gamma\}$ present in the co-crystal **3**. ADPs at 50 % probability level. Colors are as follows: carbon, gray; fluorine, green and iodine, purple.

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2.2. 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane/BaI₂/1,8-diiodoperfluorooctane assembly

For the purpose of comparison, adduct **5** compounded of 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (K.2.2.2) **4**, BaI₂, and diiodoperfluorooctane **2** was also investigated. Crystallization of a methanol solution of **4** and BaI₂ afforded the solid cryptate [Ba²⁺⊂**4**]2I⁻. Single crystals suitable for X-ray analysis of the three-component system [Ba²⁺⊂**4**]{[I-(CF₂)₈-I]₃2I⁻} **5** (Scheme 2) were isolated by evaporation of a methanol solution of [Ba²⁺⊂**4**]2I⁻ in the presence of **2** (see Experimental section for details).



Scheme 2. Stepwise assembly of the supramolecular assembly **5** (4/BaI₂/2, 1:1:3 ratio).

X-ray analysis shows that barium cations are, as expected, embedded in the K.2.2.2 core (Figure 3, top) and the coordination sphere is saturated by two additional molecules of methanol. The supramolecular and halogen-bonded anions are seen as comb-like copolymers structurally similar to those observed in **3**, the greatest difference being the size of the teeth, which are longer in **5** than in **3** (Figure 3, bottom). Table 1 reports lengths and angles of XBs in the comb-like superanions of **5** where both diiodoperfluorooctane molecules, the XB donor modules, and the iodide anions, the XB acceptor modules, show two different binding modes.

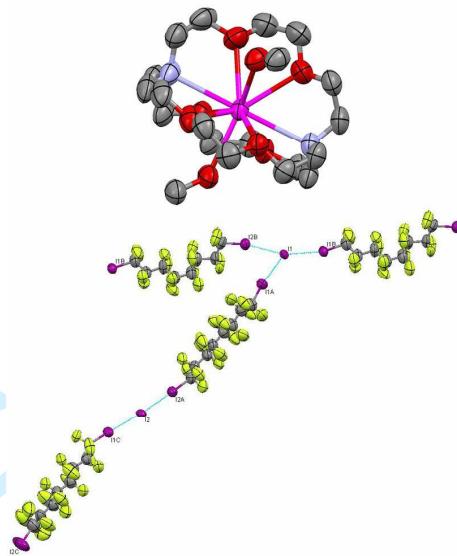


Figure 3. The supercation [Ba²⁺⊂**4**] and the superanion {[I-(CF₂)₈-I]₃2I⁻} components (top and bottom, respectively) present in the co-crystal **5**. ADPs at 50% level. Color codes: carbon, gray; oxygen, red; barium, pink; nitrogen, light blue; fluorine, green and iodine, purple.

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Table 1. XB lengths and angles of the superanion components of **5**.

Distance (Å)			
I1-IIA	3.584(4)	I1A-II-IIB	126.96(13)
I1-IIB	3.531(5)	I1A-II-2B ⁱ	70.30(11)
I1-2B ⁱ	3.603(5)	I1B-II-2B ⁱ	160.93(11)
I2-I2A ⁱⁱ	3.464(4)	I2A ⁱⁱ -I2-IIC	174.51(16)
I2-IIC	3.442(4)		

ⁱ(x,y,1+z); ⁱⁱ(-1+x,y,-1+z)

The iodide I1 is tridentate and forms the unlimited chains of the copolymer on binding two diiodoperfluorooctane molecules (specifically, on binding I1B and translated I2B(x,y,1+z)). These two diiodoperfluorooctane molecules are bidentate and

adopt a *ttgtt* [19] conformation along their carbon backbone. It also binds a third diiodoperfluorooctane molecule which is bidentate, adopts a distorted all *trans* conformation, and forms the teeth of the comb-like copolymer. These teeth are further elongated through the I₂···I₂A(-1+x,y,-1+z) and I₂···I₁C XB_s involving the iodide anion I₂, which is bidentate, and another diiodoperfluorooctane molecule, which is in turn monodentate. As previously seen in the case of **3**, here too the terminal monodentate diiodoperfluorooctane molecule shows some degree of disorder at its end.

Fluoroalkane derivatives have a low affinity for hydrocarbon derivatives [20] and thus it is not surprising that the supramolecular fluorous anions and hydrocarbon cations are segregated from each other and give rise to adjacent layers which alternate in the crystal of the two supramolecular assemblies **3** and **5** (Figure 4).

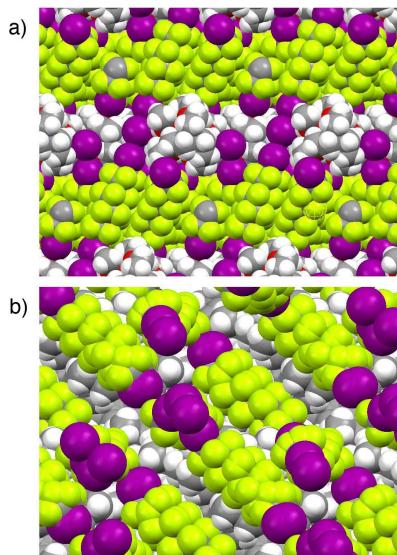


Figure 4. Space-filling representation of the different types of segregation present in the co-crystals, **5** (a) projection parallel to the hydrocarbon/perfluorocarbon layers and **3** (b) projection nearly parallel to the teeth. Colors are as follows: carbon, gray; hydrogen, white; oxygen, red; fluorine, green, and iodide, purple.

A similar behavior has already been observed in several other perfluorocarbon/hydrocarbon hybrid systems [21]. Interestingly, segregation is much less pronounced in **3** (Figure 4b), probably partly as a consequence of the lower content of fluoroalkyl groups which in turn results from the lower content of iodide ions required to counterbalance a mono- vs a

double-charged cation of the original salt (Na^+ in **3** vs Ba^{2+} in **5**).

3 CONCLUSIONS

We have demonstrated that cation segregating agents **1** and **4** generate naked iodide anions which effectively drive the self-assembly of diiodoperfluorooctane **2** into halogen-bonded supramolecular anions with a comb-like structure, a hitherto unreported topology.

It had been previously reported how –on using metal cations and cation coordinating agents different from those employed here– naked iodide anions were generated which worked either as mono-, bi-, or tridentate XB acceptors and assembled diiodoperfluorooctane **2** into three component adducts wherein the supramolecular anion was a discrete system, an infinite chain, or a (6,3)-network, respectively [7–10]. The three-component adduct **5** is the first structure wherein iodide anions with different coordination numbers coexist in the same crystal. Specifically, iodide anions act as both bi- and tridentate XB acceptors. X-ray data show that differences in supercation size and shape ($[\text{Na}^+ \subset \mathbf{1}]$ and $[\text{Ba}^{2+} \subset \mathbf{4}]$) produce halogen-bonded comb-like copolymers with different metrics and crystal packing. $[\text{Na}^+ \subset \mathbf{1}]$ creates a dense hydrocarbon packing in **3**, while in **5** the greater content of perfluoroalkane residues promotes a more pronounced segregation of the hydrocarbon and perfluorocarbon layers.

The results reported here suggest that the cation coordinating agent plays two interrelated roles in allowing metal iodides to assemble iodoperfluorocarbons into supramolecular anions with complex topologies. The primary role is to form a naked iodide anion, namely to allow it to act as an XB acceptor. The key parameter in this case is its effectiveness in sequestering the cation. The secondary role is to tune the induced XB acceptor ability of the anion and in this case the key parameter is the size and shape of the supramolecular counterion. When effectively naked, iodide anions are rather chameleonic XB acceptors [7–10]. The number and geometry of the XB_s they form and the topology of the resulting supramolecular anion is heavily influenced by the restraints that the inherent packing preferences of the cation impose on the overall crystal packing. Further studies are underway to verify whether the XB acceptor ability of other naked halide anions (e.g. bromide anions) is similarly sensitive to cation nature, size, and shape.

1 2 4. EXPERIMENTAL

3 4.1 General Methods

5 Melting points were determined on a Kofler melting
 6 point apparatus and are uncorrected. ^1H and ^{19}F NMR
 7 spectra (300 and 282 MHz, respectively) were
 8 obtained at 293 K, using TMS and CFCl_3 as internal
 9 standards. FT-IR spectra were recorded as KBr
 10 pellets on a Nicolet Nexus FT-IR spectrophotometer
 11 equipped with the Smart Endurance system (UATR).
 12 All solvents and chemicals were reagent grade and
 13 were used without further purification. Calixarene **1**
 14 was prepared according to a reported procedure
 15 [14b].

16 Procedure for the formation of the hybrid 17 supermolecular salts

18 **1/Nal/2 (3).** Solid $[\text{Na}^+ \subset \text{I}]^-$ was crystallized from a
 19 1:1 mixture of pentaester **1** and NaI in methanol. Co-
 20 crystal **3** was grown in an uncapped clear borosilicate
 21 glass vial, placed inside a sealed chamber partially
 22 filled with vaseline oil, by slow evaporation at room
 23 temperature, from an absolute ethanol solution of
 24 $[\text{Na}^+ \subset \text{I}]^-$ and **2** in equimolar amounts.

25 **4/BaI₂/2 (5).** In a similar way, co-crystals **5** were
 26 obtained by slow evaporation, at room temperature,
 27 of a methanol solution containing equimolar amounts
 28 of $[\text{Ba}^{2+} \subset \text{I}]^-$ and **2**.

29 Inclusion complex $[\text{Na}^+ \subset \text{I}]^-$

30 Mp 146–156 °C (CH_3OH); FT-IR (selected bands)
 31 2963, 2875, 1747, 1480, 1385, 1238, 1191, 1129, and
 32 1069 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.04 (s, 45 H,
 33 $\text{C}(\text{CH}_3)_3$), 1.34 (t, $J = 7.1$ Hz, 15 H, CH_2CH_3), 3.35
 34 and 4.36 (AX, $J = 13.9$ Hz, 10 H, ArCH_2Ar), 4.28 (q,
 35 $J = 7.1$ Hz, 10 H, CH_2CH_3), 4.50 (s, 10 H, OCH_2),
 36 and 6.96 (s, 10 H, ArH) ppm.

37 Co-crystal 3

38 Mp 199–200 °C ($\text{C}_2\text{H}_5\text{OH}$); FT-IR 2964, 2907, 2871,
 39 1748, 1481, 1215, 1072, 633, and 545 cm^{-1} . The ^1H
 40 NMR spectrum of **3** is superimposable to that of
 41 $[\text{Na}^+ \subset \text{I}]^-$. ^{19}F NMR (CD_3OD) δ -123.45 (4 F,
 42 $\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$), -122.68 (4 F, $-\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$), -114.90 (4 F, $-\text{CF}_2\text{CF}_2\text{I}$) and -61.52 (4 F, $-\text{CF}_2\text{I}$)
 43 ppm.

44 Inclusion complex $[\text{Ba}^{2+} \subset \text{I}]^-$

45 Mp 290–292 °C (CH_3OH); FT-IR 3510, 2886, 2844,
 46 2049, 1607, 1475, 1356, 1255, 1124, 952, and 928
 47 cm^{-1} ; ^1H NMR (CD_3OD) δ 2.55–2.59 (m, 12 H,

OCH₂CH₂N), 3.57–3.59 (m, 12 H, OCH₂CH₂N), and
 3.62 (s, 12 H, OCH₂CH₂O) ppm.

Co-crystal 5

Mp 165–170 °C (CH_3OH); FT-IR 3453, 2886, 2831,
 1629, 1214, 1154, 1106, and 953 cm^{-1} ; ^1H NMR
 (CD_3OD) δ 2.56–2.60 (m, 12 H, OCH₂CH₂N), 3.55–
 3.59 (m, 12 H, OCH₂CH₂N), and 3.64 (s, 12 H,
 OCH₂CH₂O) ppm; ^{19}F NMR (CD_3OD) δ -122.13 (4
 F, $\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$), -121.33 (4 F, $-\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$), -113.76 (4 F, $-\text{CF}_2\text{CF}_2\text{I}$), and -62.39 (4 F, $-\text{CF}_2\text{I}$)
 ppm.

4.2 Crystal Structure Determinations

Single-crystal X-ray diffraction measurements were
 performed on a Bruker APEX CCD area detector
 diffractometer, graphite monochromator, Mo-K α
 radiation ($\lambda=0.71073\text{\AA}$). The structures were solved
 by SIR2002 [22] and refined by full-matrix least-
 squares on F^2 , using SHELXL-97 [23]. 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 697160 and 237537 for **3**
 and **5**, 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

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Crystal Structure of 3

$\text{C}_{91}\text{H}_{102}\text{F}_{32}\text{I}_5\text{NaO}_{16}$, Mr=2733.33, triclinic, space
 group P-1, $a=16.555(2)$, $b=18.865(2)$, $c=21.391(2)$
 \AA , $\alpha=96.55(2)$, $\beta=112.05(2)$, $\gamma=113.97(2)^\circ$,
 $V=5370.4(10)\text{\AA}^3$, $Z=2$, $p=1.680\text{ g cm}^{-3}$, $\mu(\text{Mo}-K\alpha)=$
 1.566 mm^{-1} . Data were collected at $T=90\text{ K}$, because
 at room temperature the mean intensity of the
 reflections vanished at very low values of 20. 188801
 reflections were collected up to $2\theta = 72.41$; 49938
 unique [40459 with $I_0 < 2\sigma(I_0)$], $R_{\text{ave}} = 0.0428$. Final
 disagreement factors for all (observed) reflections:
 $Rw(F^2) = 0.1580(0.1489)$ and $R = 0.0841(0.0677)$,
 goodness-of-fit = 1.093, 1528 parameters, 529
 restraints. In spite of the low temperature of data
 collection, both the perfluorinated molecules were
 partially disordered and were refined with some
 restraints on geometry and ADP parameters; the
 same was true for an ethoxycarbonyl pendant of **1**.
 Other ethoxycarbonyl and *tert*-butyl pendants of **1**
 showed large ADPs but it was impossible to split
 these groups into two models because of very large
 correlation parameters.

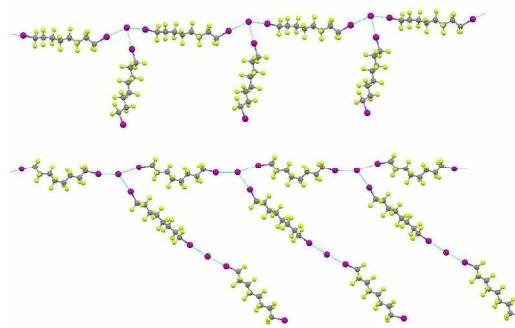
1
2 Crystal Structure of 5
3

4 C₄₄H₄₄Ba₄₈I₈N₂O₈, Mr=2793.35, triclinic, space
5 group P-1, a=13.068(3), b=17.900(4), c= 19.064(4)
6 Å, α =109.88(2), β =96.18(3), γ =94.75(3)°,
7 V=4135.1(18) Å³, Z=2, ρ =2.243 g cm⁻³, μ (Mo-K α) =
8 3.618 mm⁻¹, room temperature. 56251 reflections
9 were collected up to 2σ =55.10; 19054 unique 11321
10 with $I_0 < 2 \sigma(I_0)$, R_{ave} = 0.0426. Final disagreement
11 factors for all (observed) reflections: $Rw(F^2)$ =
12 0.1081(0.1015) and R = 0.0640(0.0371), goodness-
13 of-fit = 0.946, 1389 parameters, 3978 restraints. Two
14 of the three perfluorinated molecules were
15 completely disordered and refined with restraints
16 both on geometric parameters and ADPs.

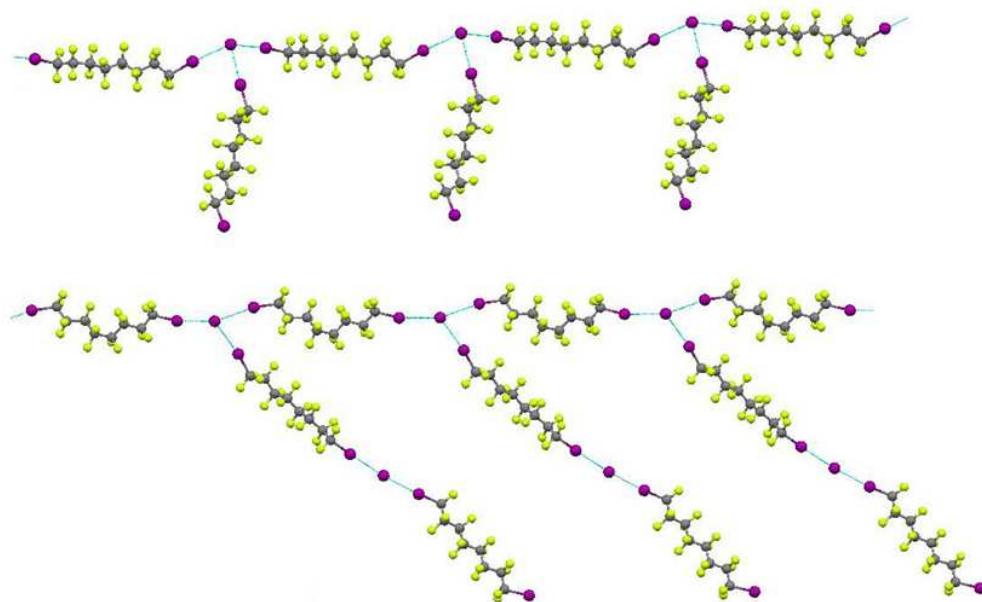
17 5. REFERENCES
18

- [1] Eryazici, I.; Moorefield, C. N.; Newkome, G. R. *Chem. Rev.* **2008**, *108*, 1834–1895; Fromm, K. M. *Coord. Chem. Rev.* **2008**, *252*, 856; Mao, J.-G. *Coord. Chem. Rev.* **2007**, *251*, 1493–1520; Kruppa, M.; König, B. *Chem. Rev.* **2006**, *106*, 3520–3560; Morohashi, N.; Narumi, F.; Iki, N.; Hattori, T.; Miyano, S. *Chem. Rev.* **2006**, *106*, 5291–5316; Baleizão, C.; Garcia, H. *Chem. Rev.* **2006**, *106*, 3987–4043; Zilberman, I.; Maimon, E.; Cohen, H.; Meyerstein, D. *Chem. Rev.* **2005**, *105*, 2609–2625; Alessio, E. *Chem. Rev.* **2004**, *104*, 4203–4242; Gokel, G. W.; Matthew Leevy, W.; Weber, M. E. *Chem. Rev.* **2004**, *104*, 2723–2750; Lane, B. S.; Burgess, K. *Chem. Rev.* **2003**, *103*, 2457–2473; Gorden, A. E. V.; Xu, J.; Raymond, K. N. *Chem. Rev.* **2003**, *103*, 4207–4282; Gokel, G. W.; Mukhopadhyay, A. *Chem. Soc. Rev.* **2001**, *30*, 274–286; Atwood, J. L.; Barbour, L. J.; Hardie, M. J.; Raston, C. L. *Coord. Chem. Rev.* **2001**, *222*, 3–32; Dixon, I. M.; Collin, J.-P.; Sauvage, J.-P.; Flamigni, L.; Encinaa, S.; Barigelli, F. *Chem. Soc. Rev.* **2000**, *29*, 385–391.
[2] Sessler, J. L.; Gale, P. A.; Cho, W. S. *Anion Receptor Chemistry*; Royal Society of Chemistry: Cambridge, U.K., 2006; Bianchi, A.; Bowman-James, K.; García-España E. *Supramolecular chemistry of anions*; Wiley-VCH: New York, 1996.
[3] Misra, R.; Chandrashekhar, T. K. *Acc. Chem. Res.* **2008**, *41*, 265–279; Lankshear, M. D.; Beer, P. D. *Acc. Chem. Res.* **2007**, *40*, 657–668; Filby, M. H.; Steed, J. W. *Coord. Chem. Rev.* **2006**, *250*, 3200–3218; García-España, E.; Díaz, P.; Linares, J. M.; Bianchi, A. *Coord. Chem. Rev.* **2006**, *250*, 2952–2986; Davis, A. P. *Coord. Chem. Rev.* **2006**, *250*, 2939–2951; Anzenbacher, P.; Nishiyabu, R.; Palacios, M. A. *Coord. Chem. Rev.* **2006**, *250*, 2929–2938; Gale, P. A. *Acc. Chem. Res.* **2006**, *39*, 465–475; Amendola, V.; Esteban-Gómez, D.; Fabbri, L.; Licchelli, M. *Acc. Chem. Res.* **2006**, *39*, 343–353; Chandrashekhar, T. K.; Venkatraman, S. *Acc. Chem. Res.* **2003**, *36*, 676–691; Sessler, J. L.; Davis, J. M. *Acc. Chem. Res.* **2001**, *34*, 989–997.
[4] (a) Metrangolo, P.; Meyer, F.; Pilati, T.; Resnati, G.; Terraneo G. *Chem. Commun.* **2008**, 1635–1637; (b) Casnati, A.; Liantonio, R.; Metrangolo, P.; Resnati, G.; Ungaro, R.; Uguzzoli, F. *Angew. Chem. Int. Ed.* **2006**, *45*, 1915–1918; (c) Liantonio, R.; Metrangolo, P.; Meyer, F.; Pilati, T.; Navarrini, W.; Resnati, G. *Chem. Commun.* **2006**, 1819–1821; (d) Gimeno, N.; Vilar, R. *Coord. Chem. Rev.* **2006**, *250*, 3161–3189; (e) Gale, P. A.; Quesada, R. *Coord. Chem. Rev.* **2006**, *250*, 3219–3244; (f) Lankshear, M. D.; Beer, P. D. *Coord. Chem. Rev.* **2006**, *250*, 3142–3160; (g) Wichtmann, K.; Antonioli, B.; Söhnle, T.; Wenzel, M.; Gloe, K.; Gloe, K.; Price, J. R.; Lindoy, L. F.; Blake, A. J.; Schröder, M. *Coord. Chem. Rev.* **2006**, *250*, 2987–3003; (h) Liantonio, R.; Metrangolo, P.; Pilati, T.; Resnati, G. *Cryst. Growth & Des.* **2003**, *3*, 355–361; (i) Farina, A.; Meille, S. V.; Messina, M. T.; Metrangolo, P.; Resnati, G. *Angew. Chem. Int. Ed.* **1999**, *38*, 2433–2436.
[5] Metrangolo, P.; Meyer, F.; Pilati, T.; Resnati, G.; Terraneo, G. *Angew. Chem. Int. Ed.* **2008**, *47*, 6114–6127; Metrangolo, P.; Resnati, G.; Pilati, T.; Liantonio, R.; Meyer, F. *J. Polymer Chem. A* **2007**, *45*, 1–15; Metrangolo, P.; Pilati, T.; Resnati, G. *CrystEngComm.* **2006**, *8*, 946–947; Metrangolo, P.; Neukirch, H.; Pilati, T.; Resnati, G. *Acc. Chem. Res.* **2005**, *38*, 386–395; Metrangolo, P.; Pilati, T.; Resnati, G.; Stevenazzi, A. *Current Opinion Coll. Interface Sc.* **2003**, *8*, 215–222; Metrangolo, P.; Resnati, G. *Chem. Eur. J.* **2001**, *7*, 2511–2519.
[6] Metrangolo, P.; Panzeri, W.; Recupero, F.; Resnati, G. *J. Fluorine Chem.* **2002**, *114*, 27–33; Messina, M. T.; Metrangolo, P.; Panzeri, W.; Ragg, E.; Resnati, G. *Tetrahedron Lett.* **1998**, *39*, 9069–9072.
[7] (a) Lindeman, S. V.; Hecht, J.; Kochi, J. K. *J. Am. Chem. Soc.* **2003**, *125*, 11597–11606; (b) Bock, H.; Holl, S. Z. *Naturforsch., B: Chem. Sci.* **2001**, *56*, 152–154; (c) Lohr, H.-G.; Engel, A.; Josel, H.-P.; Vogtle, F.; Schuh, W.; Puff, H. J. *Org. Chem.* **1984**, *49*, 1621–1627.
[8] (a) Gattuso, G.; Pappalardo, A.; Parisi, M. F.; Pisagatti, I.; Crea, F.; Liantonio, R.; Metrangolo, P.; Navarrini, W.; Resnati, G.; Pilati, T.; Pappalardo, S. *Tetrahedron* **2007**, *63*, 4951–4958; (b) Fox, B. D.; Liantonio, R.; Metrangolo, P.; Pilati, T.; Resnati, G. *J. Fluorine Chem.* **2004**, *125*, 271–281.
[9] (a) Gattuso, G.; Liantonio, R.; Metrangolo, P.; Meyer, F.; Resnati, G.; Pappalardo, A.; Parisi, M. F.; Pilati, T.; Pisagatti, I.; Resnati, G. *Supramol. Chem.* **2006**, *18*, 235–243; (b) Caronna, T.; Liantonio, R.; Logothetis, T. A.; Metrangolo, P.; Pilati, T.; Resnati, G. *J. Am. Chem. Soc.* **2004**, *126*, 4500–4501.
[10] Rosokha, S. V.; Neretin, I. S.; Rosokha, T. Y.; Hecht, J.; Kochi, J. K. *Heterroat. Chem.* **2006**, *17*, 449–459; Logothetis, T. A.; Meyer, F.; Metrangolo, P.; Pilati, T.; Resnati, G. *New J. Chem.* **2004**, *28*, 760–763; Yamamoto, H. M.; Maeda, R.; Yamaura, J.-I.; Kato, R. *J. Mater. Chem.* **2001**, *11*, 1034–1041.
[11] Nakamoto, T.; Wang, Q.; Miyazaki, Y.; Sorai, M. *Polyhedron* **2002**, *21*, 1299–1304.
[12] Bowman-James, K. *Acc. Chem. Res.* **2005**, *38*, 671–678.
[13] Gutsche, C. D. *Calixarenes Revised*; Stoddart, J. F., Ed.; Monographs in Supramolecular Chemistry; The Royal Society of Chemistry: London, UK, 1998; Vicenç, J.; Böhmer, V. *Calixarenes: A Versatile Class of Macrocyclic Compounds*; Eds.; Kluwer: Dordrecht, 1991; Gutsche, C. D. *Calixarenes*; Stoddart, J. F., Ed.; Monographs in Supramolecular Chemistry; The Royal Society of Chemistry: Cambridge, 1989; Vol. 1.
[14] (a) Danil de Namor, A. F.; Zegarra-Fernandez, K. *J. Phys. Chem. B* **2007**, *111*, 7321–7330; (b) Barrett, G.; McKervey, M. A.; Malone, J. F.; Walker, A.; Arnaud-Neu, F.; Guerra, L.

- 1
2
3 Schwing-Weill, M.-J.; Gutsche, C. D.; Stewart, D. R. *J. Chem.*
4 *Soc., Perkin Trans. 2* **1993**, 1475–1479.
5 [15] Metrangolo, P.; Meyer, F.; Pilati, T.; Proserpio, D. M.;
6 Resnati, G. *Chem. Eur. J.* **2007**, *13*, 5765–5772; Neukirch, H.;
7 Guido, E.; Liantonio, R.; Metrangolo, P.; Pilati, T.; Resnati,
8 G. *Chem. Commun.* **2005**, 1534–1535; Metrangolo, P.; Pilati,
9 T.; Resnati, G.; Stevenazzi, A. *Chem. Commun.* **2004**, 1492–
10 1493; Bertani, R.; Metrangolo, P.; Moiana, A.; Perez, E.;
11 Pilati, T.; Resnati, G.; Rico-Lattes, I.; Sassi, A. *Adv. Materials*
12 **2002**, *14*, 1197–1201.
13 [16] Arnaud-Neu, F.; Fanni, S.; Guerra, L.; McGregor, W.; Ziat,
14 K.; Schwing-Weill, M.-J.; Barrett, G.; McKervey, M. A.;
15 Marrs, D.; Malone, J. F.; Walker, A.; Seward, E. M. *J. Chem.*
16 *Soc., Perkin Trans. 2* **1995**, 113–118.
17 [17] Upon addition of NaI (1 equiv.) to a CDCl₃ (5.0 mM) of **1**, the
18 aromatic and ethereal OCH₂ signals underwent a 0.11 and
19 0.10 ppm downfield complexation induced shift, respectively.
20 Similarly, positive ESI-MS analysis of a 10 mM
21 CHCl₃/CH₃OH solution of **1**:NaI (1:1) showed a peak at *m/z* =
22 1263.7, consistent with the formation of a [1-Na]⁺ complex.
23 [18] Bell, S. E. J.; Browne, J. K.; McKee, V.; McKervey, M. A.;
24 Malone, J. F.; O'Leary, M.; Walker, A. *J. Org. Chem.* **1998**,
25 63, 489–501.
26 [19] *t* and *g* stand for *trans* and *gauche*, respectively.
27 [20] Smart, B. E. In *Organofluorine Chemistry: Principles and*
28 *Commercial Applications*; Banks, R. E., Smart, B. E., Tatlow,
29 J. C., Eds.; Plenum Press: New York, 1994; Dorset, D. L.
30 *Macromolecules* **1990**, *23*, 894–901; Hildebrand, J.; Cochran,
31 D. R. F. *J. Am. Chem. Soc.* **1949**, *71*, 22–25.
32 [21] Amati, M.; Lelj, F.; Liantonio, R.; Metrangolo, P.; Luzzati, S.;
33 Pilati, T.; Resnati, G. *J. Fluorine Chem.* **2004**, *125*, 629–640;
34 Liantonio, R.; Metrangolo, P.; Pilati, T.; Resnati, G.;
35 Stevenazzi, A. *Cryst. Growth & Des.* **2003**, *3*, 799–803;
36 Navarrini, W.; Messina, M. T.; Metrangolo, P.; Pilati, T.;
37 Resnati, G. *New J. Chem.* **2000**, *24*, 777–780; Cardillo, P.;
38 Corradi, E.; Lunghi, A.; Meille, S. V.; Messina, M. T.;
39 Metrangolo, P.; Resnati, G. *Tetrahedron* **2000**, *56*, 5535–
40 5550; Corradi, E.; Meille, S. V.; Messina, M. T.; Metrangolo,
41 P.; Resnati, G. *Tetrahedron Lett.* **1999**, *40*, 7519–7523.
42 [22] Burla, M. C.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.;
43 Giacovazzo, C.; Polidori G.; Spagna, R. *J. Appl. Cryst.* **2003**,
44 *36*, 1103.
45 [23] Sheldrick, G. M. *SHELXTL 6*; Bruker AXS Inc., Madison,
46 Wisconsin, USA, 2001.
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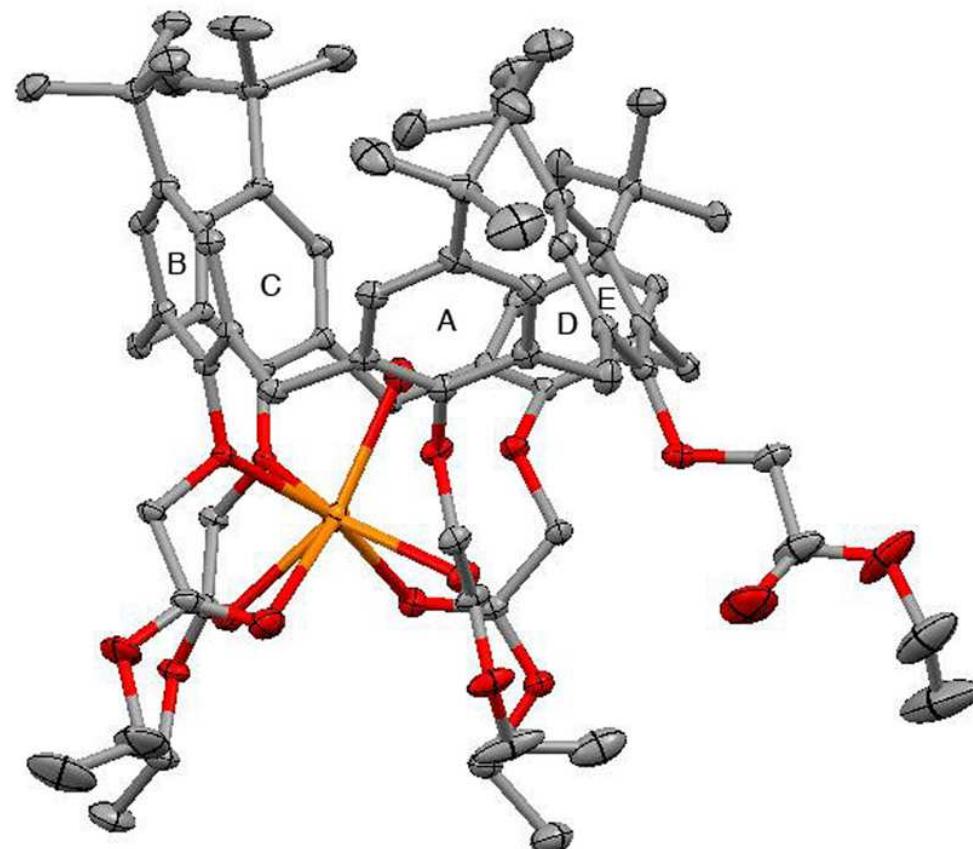


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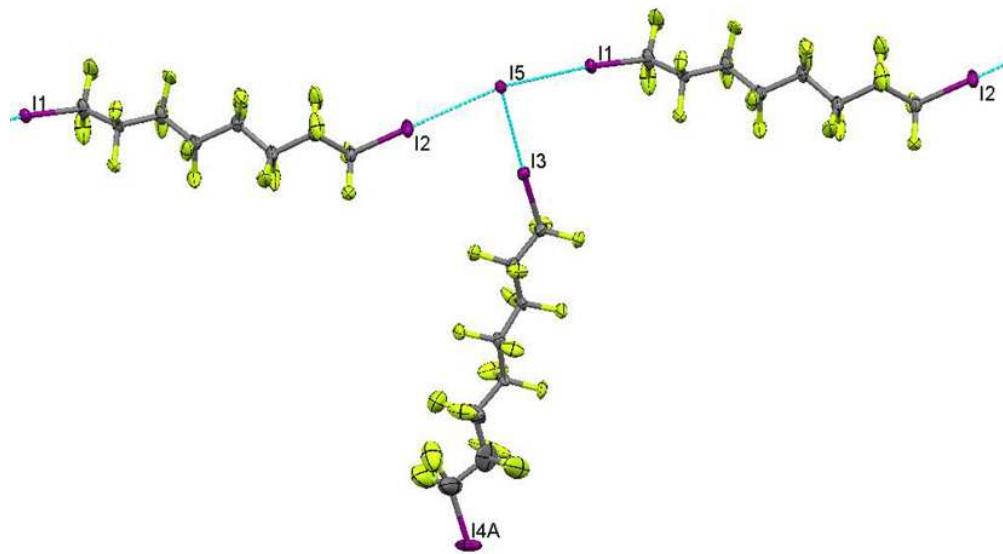
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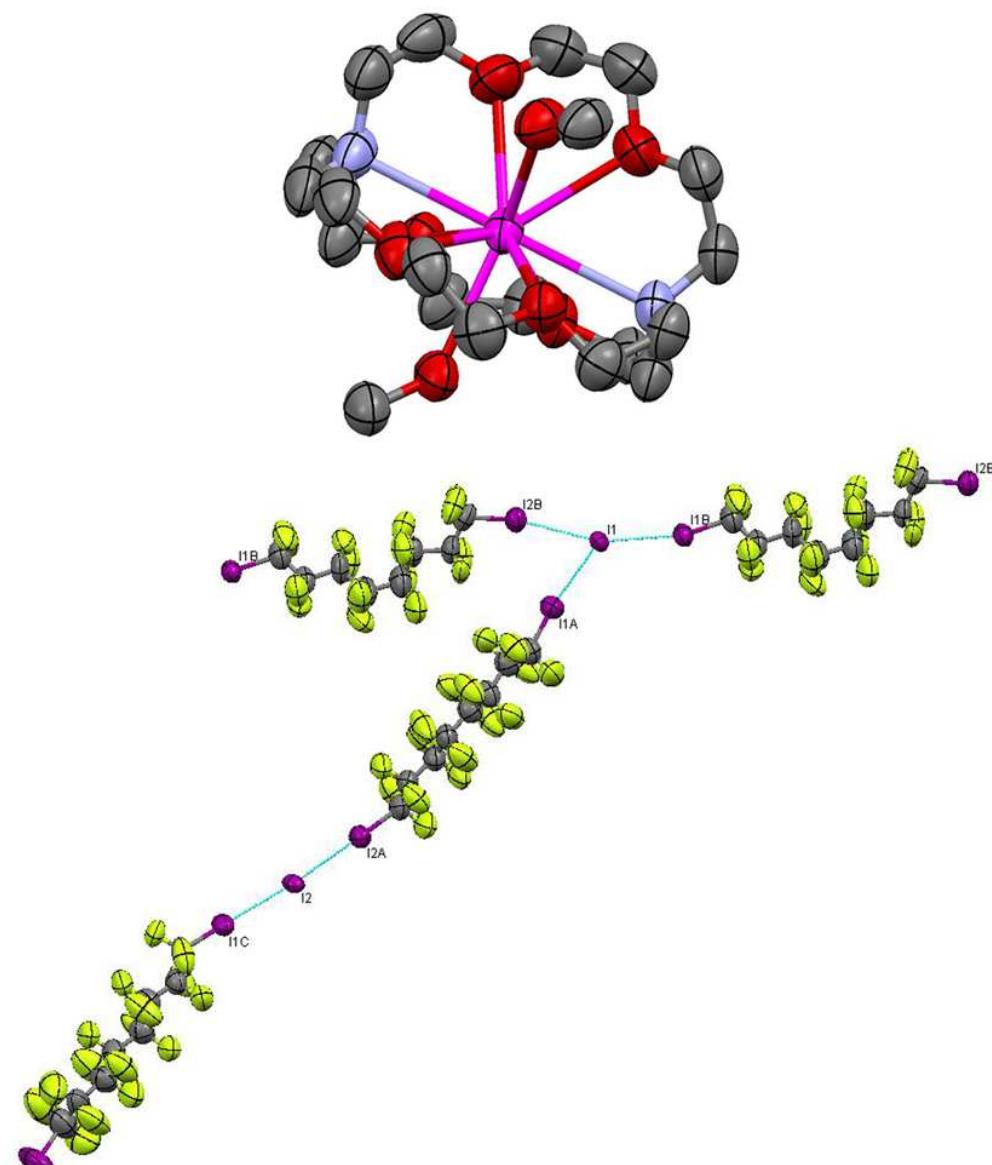


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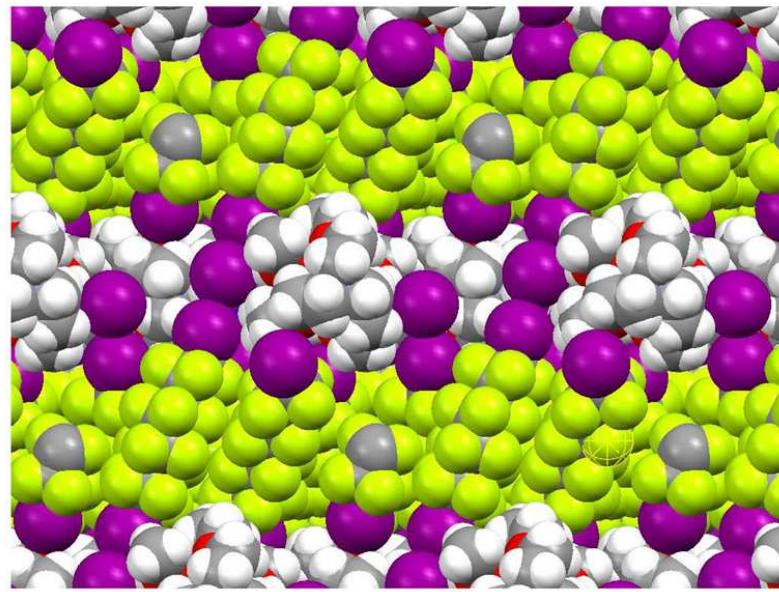


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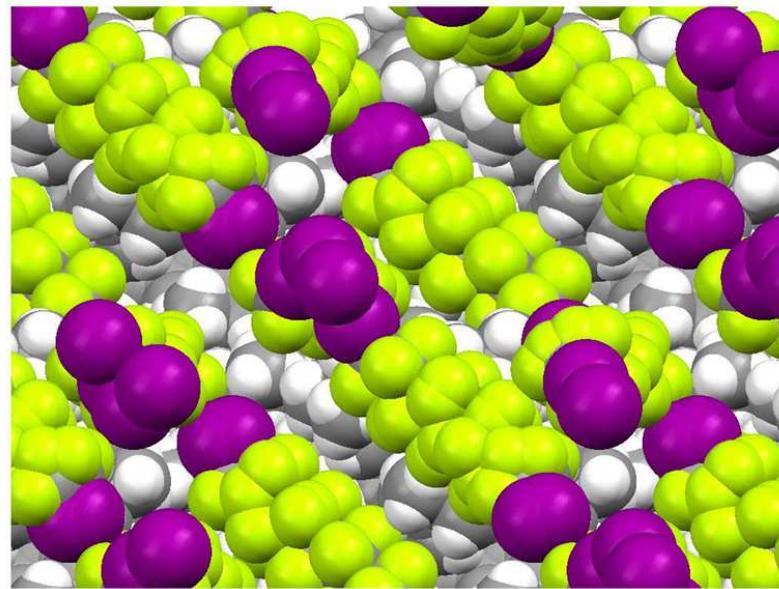


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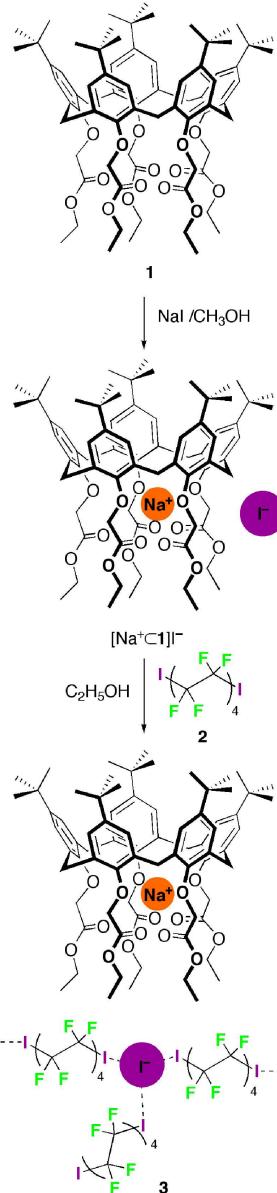
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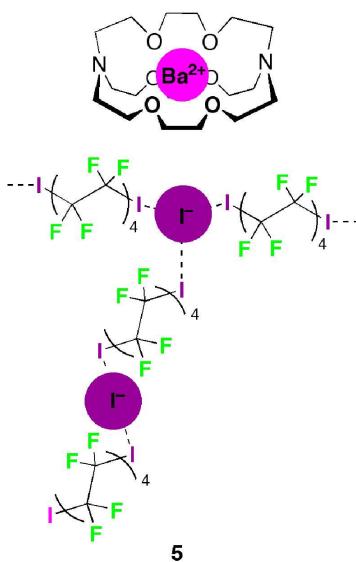
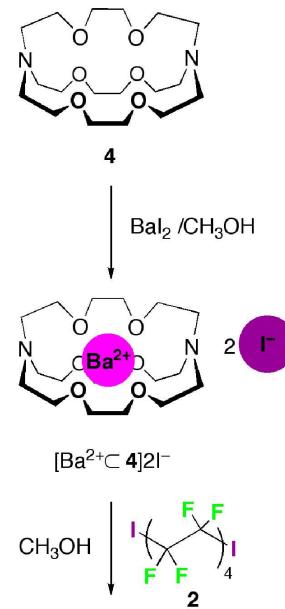
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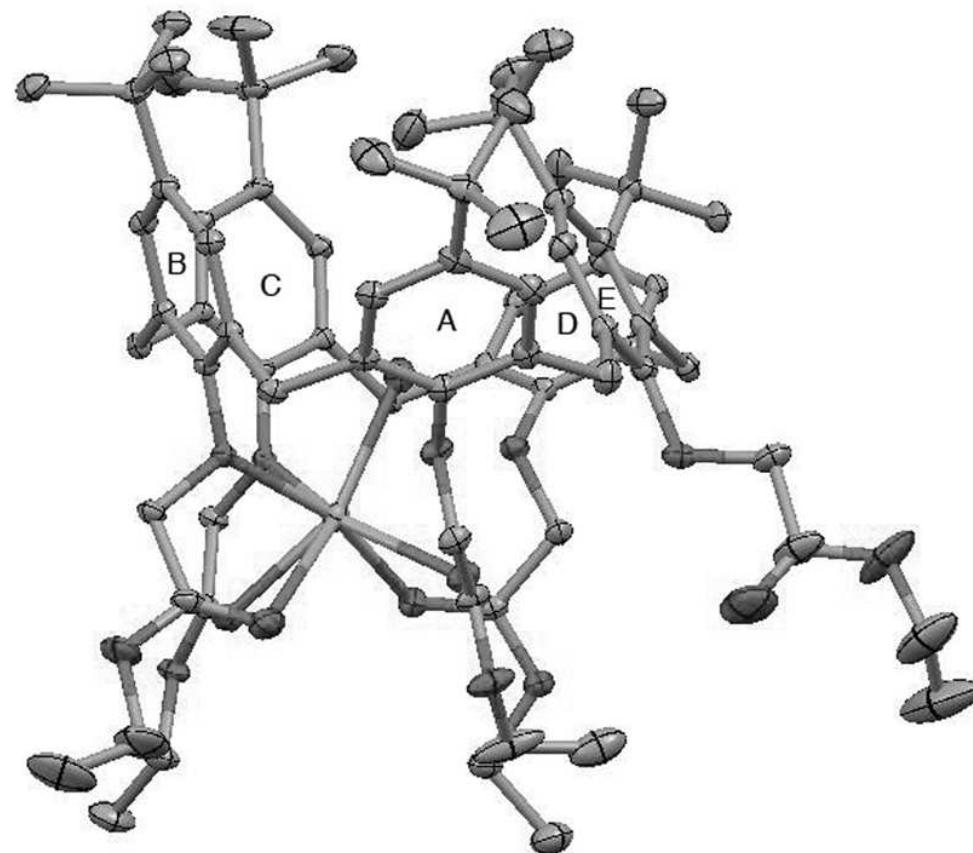


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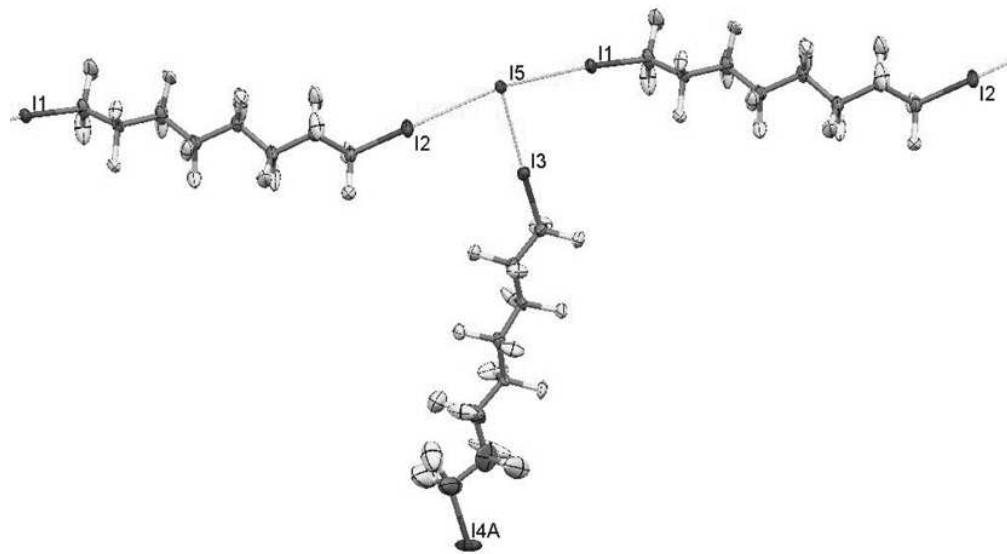
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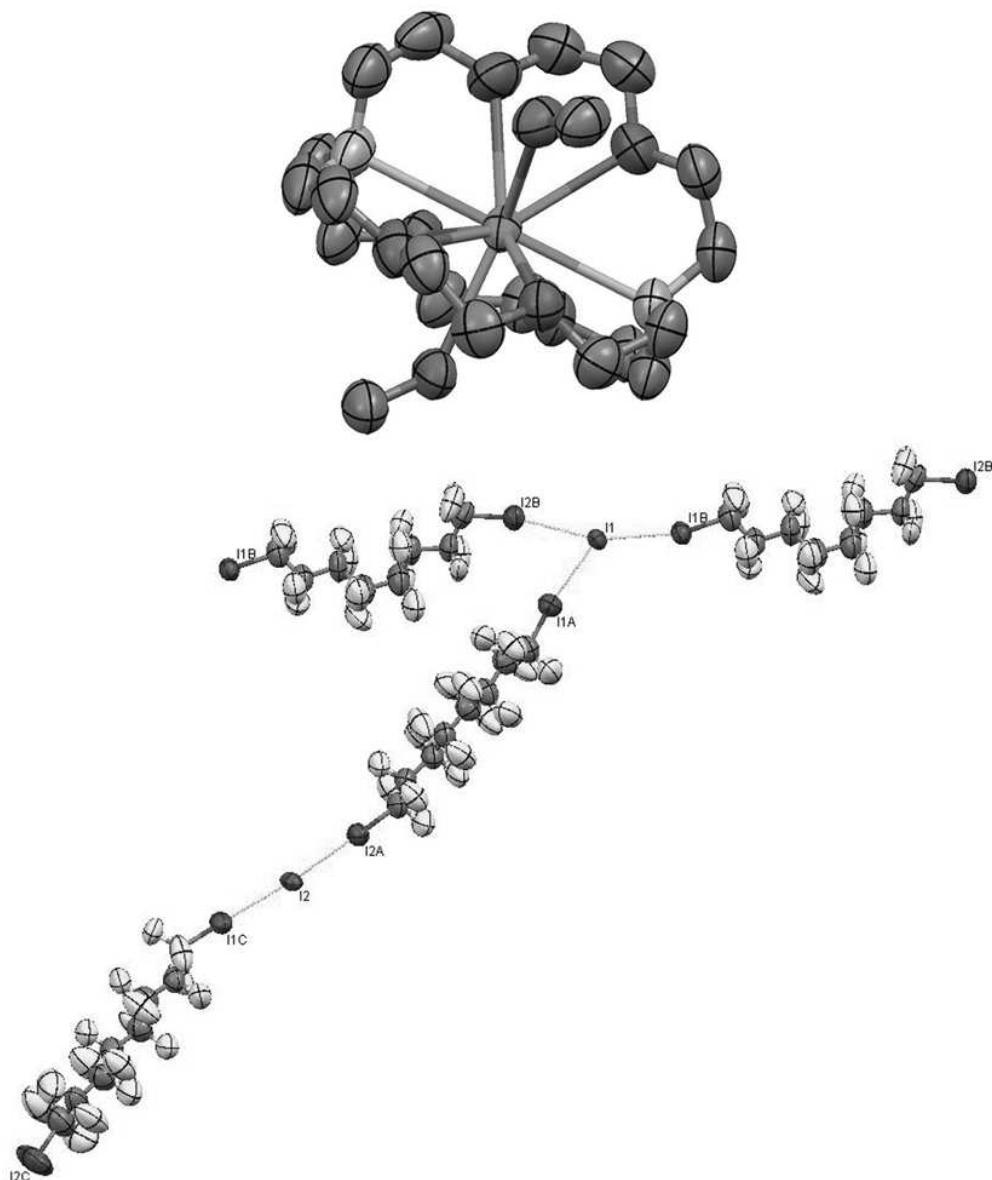


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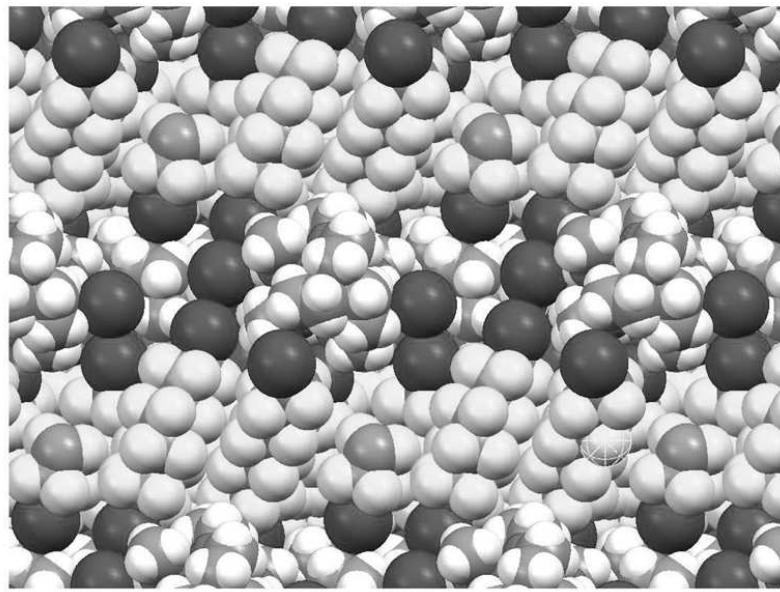


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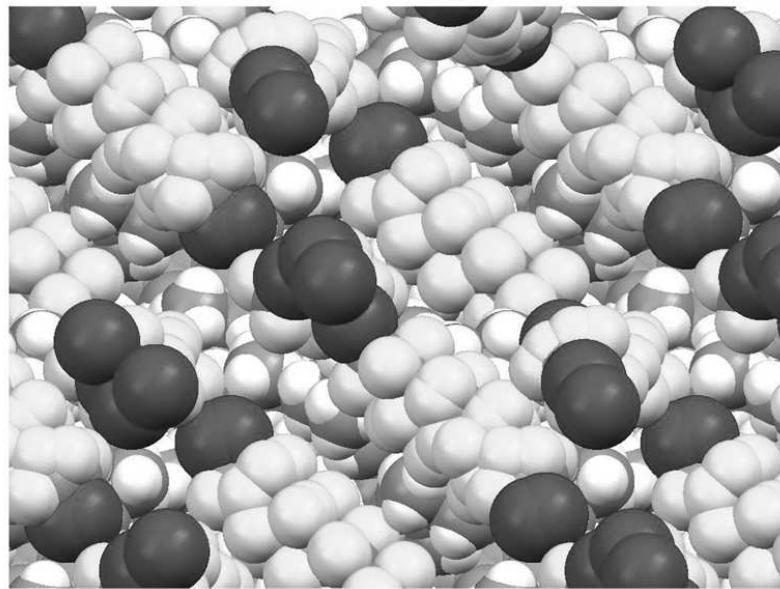


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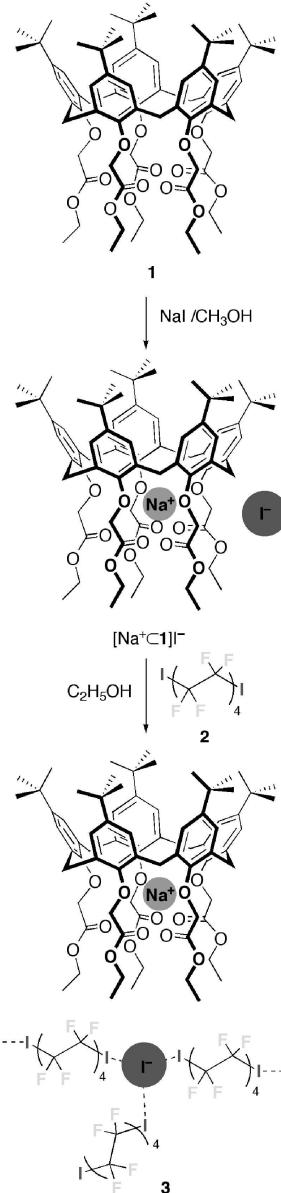
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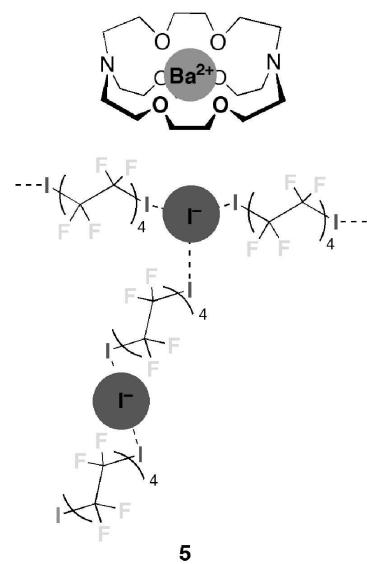
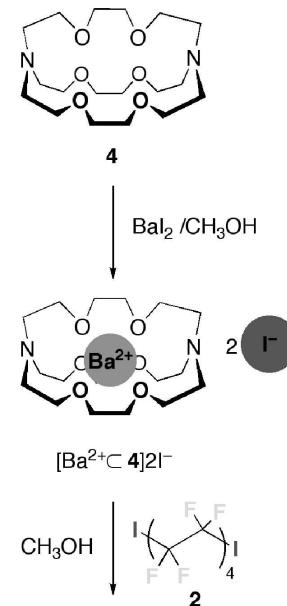
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