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Polyfluorinated hydroxy and carboxy benzenes as a new type of H-donors for selfassembly with 18-crown-6 ether: synthesis, supramolecular structure and stability of co-crystals

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Graphical abstract



Highlights

- Co-crystallization of hydroxy/carboxy polyfluoroarenes with 18-crown-6 was studied.
- Co-crystals structure is based on the water-mediated H-bond [C(O)]O-H...O(H)-H...O_{cr}.
- $\pi_{\rm F}$ - $\pi_{\rm F}$ Stacking is the second structure-forming synthon in the 1D assemblies.
- Supramolecular parameters and fusion enthalpies of co-crystals were determined.
- Water-induced co-crystallization behavior was rationalized using DFT calculations.

Abstract

Potential of polyfluoroaromatic compounds containing OH, COOH, and mixed H-donor functions as co-formers in co-crystallization with 18-crown-6 ether was explored. Pentafluorophenol, 1,3- and 1,4-dihydroxytetrafluorobenzenes and pentafluorobenzoic acid form with 18-crown-6 hydrated co-crystals containing one water molecule per H-donor group upon contact of the solutions with atmospheric moisture; pentafluorophenol gives a co-crystal with double the amount of water in aqueous EtOH. Aminotetrafluorobenzyl alcohol and aminotetrafluorobenzoic acid are capable of forming anhydrous 1:1 and 2:1 co-crystals with 18-crown-6. In the crystalline hydrates, co-formers molecules are connected via water-mediated synthon [C(O)]O-H^{...}O(H)-H^{...}O_{cr}. According to quantum chemical calculations, the participation of each water linker molecule in H-bonding increases the stability of the supramolecular structure by about 100 kJ mol⁻¹. Associates of bifunctional arenes exhibit Hbonded 1D assembly as an only structure-determining motif; molecules of monofunctional arenes in the co-crystals are bound via $\pi_{\rm F}$... $\pi_{\rm F}$ stacking to give the H-bonded/ π -stacked 1D assembly. The calculated π -stacking energy depends on the nature of the H-donor function (NH₂, OH, COOH), decreasing with a decrease in the molecule dipole moment.

Keywords: Hydroxy and carboxy polyfluorobenzenes; Crown ether; Molecular co-crystals; Supramolecular architecture; Water-mediated H-bonds; X-ray diffraction analysis

1. Introduction

Crystal supramolecular associates formed via non-covalent interactions are of considerable interest due to their potential applications in optoelectronics, nonlinear optics, electric conductivity, magnetism, gas storage, catalysis, pharmaceutics, drug delivery tools, etc. [1-11]. Construction of multi-component crystals (supramolecular associates), as opposed to homocrystals, provides novel structures and integrated functionalities, which cannot be realized by each building block alone. Crystal engineering uses a combination of directional interactions of the molecules to form the required supramolecular architecture of the crystal and to achieve the desired properties. Therefore, the study on the relationships between the supramolecular structure, properties of co-crystals, and chemical structure of co-formers is of both fundamental and practical importance.

In the design of organic co-crystals, the strongest and widely used directional interactions are hydrogen bonds [12-17]. For this reason, molecules comprising hydroxyl, carboxyl, and amino groups are reliable H-donor co-formers in crystal engineering. In turn, suitable acceptors for self-assembling of the H-bonded architectures are macrocyclic ethers. In particular, 18crown-6 is a common component of organic supramolecular frameworks and functional materials. Numerous works [18-22] report on ternary complexes of anilinium salts with 18crown-6 formed via H-bond +N-H···Ocr; these co-crystals exhibit the temperature-dependent reversible order/disorder-type molecular motions in solids which induce appearance of magnetic anomaly, pyroelectricity, SHG response, etc. Binary co-crystals of neutral amino compounds with 18-crown-6 were employed to design certain supramolecular architectures [23-27]; some of them were used as models for active pharmaceutical ingredients [28, 29]. In the series of the 1:1 associates of polyfluorinated arylenediamines with 18-crown-6 that are H-bonded 1D assemblies, a linear correlation between the co-crystal fusion enthalpy and the supramolecular unit length was revealed [23], which underlies the selective co-crystallization (the molecular recognition). This finding was used in practice for the preparation of high-purity polyfluoroaromatic diamines [30-31], which can serves as monomers in the synthesis of polyimides for optic and optoelectronic applications (see, for example, [32]). Incorporation of 18-crown-6 into the crystal matrix of polyhalogenated (get)arylamines is accompanied by a change in the amine fluorescent properties caused by the rearrangement of molecular packing [33, 34]. Some elements of the arylamine structure can be used as design tools for controlling molecular packing in the homocrystal and co-crystal and, thereby, for the purposeful modification of its properties [34]. Self-assembly of sterically rigidified trigonal triphenols and their carboxyl analogues with 18-crown-6 [35-37] was exploited for the development of functional organic materials like organic networks with a controlled pore diameter for guest inclusion. Solvent-mediated co-crystallization of 18-crown-6 with 5-nitroisophthalic acid

induces an acentric crystal packed structures capable of exhibiting a significant optical nonlinearity [38].

In contrast to the polyfluoroaromatic amines, self-assembly of polyfluorinated phenols, alcohols, and carboxylic acids with 18-crown-6 was not reported [39], although there are various data on using such compounds in other fields of supramolecular chemistry. Supramolecular assemblies in homo- and co-crystals of fluorinated hydroxy and carboxy compounds are considered as low-molar-mass synthetic analogues of biological systems; their study serves to reveal the balance between hydrogen and halogen bonding, to search for control tools of enzyme-substrate recognition, to develop new possibilities for the modification of biologically important structures including peptides and oligonucleotides (see [40-42] and Refs therein). There are also some examples of using these compounds to engineer unique donor-acceptor organic materials [43], shearing and elastic crystals [44].

The purposes of the present work are to investigate the potentialities of polyfluoroaromatic compounds containing hydroxyl, carboxyl, and mixed proton donor functions (OH+NH₂, COOH+NH₂) as co-formers in the co-crystallization with 18-crown-6, to study in detail their supramolecular architecture, types and energy of the structure-supporting interactions, to determine the thermal stability and structure reproducibility. Similar co-crystals based on polyfluoroaromatic amines [23, 33] were used as comparison objects.

2. Results and discussion

2.1. Supramolecular structure of co-crystals

As the compounds of this research, we used 18-crown-6 (**cr**) and pentafluorophenol (**A**), pentafluorobenzoic acid (**B**), 1,3-dihydroxytetrafluorobenzene (**C**), 1,4-dihydroxytetrafluorobenzene (**D**), 4-aminotetrafluorobenzyl alcohol (**E**), and 4-aminotetrafluorobenzoic acid (**F**) (Fig. 1). Pentafluorophenylethanol was also tested as H-donor co-former, but its associate with 18-crown-6 was shown to have a melting point below 0 °C, which limits the possibility of studying the co-crystal structure and properties.

2.1.1. Associates of monofunctional arenes

It was found that monofunctional derivatives, i.e. phenol **A** and acid **B**, unlike polyfluoroaromatic amines [23, 26, 33, 34], form no co-crystals with **cr** in anhydrous solvents (*t*-BuOMe, CCl₄, benzene, *n*-hexane). Slow growth of co-crystals begins only in an open vessel, when the co-formers solution comes in contact with atmospheric moisture. Under these conditions, crystalline precipitates are formed, which are ternary compounds **2A**·**cr**·2H₂O and **2B**·**cr**·2H₂O (according to XRD); the exact data for each compound are given in Section 4.3. The identity of the chemical composition and phase structure of the precipitates and single crystals prepared for the XRD analysis was monitored by matching experimental PXRD and simulated patterns (see Figs. S1-S4 for the above and below-mentioned samples), as well as by DSC method (Section 2.3). Co-crystals have the reproducible melting points which differ from those of the co-formers that testifies to the formation of crystal associates as individual compounds.



Fig. 1. Structures of polyfluoroaromatic co-formers and 18-crown-6.

The crystallographic data on the synthesized co-crystals and parameters of their structure refinements are given in Table S1. Fig. 2 presents the view of the co-crystal fragments. Supramolecular structure of the both co-crystals $2A \cdot cr \cdot 2H_2O$ and $2B \cdot cr \cdot 2H_2O$ comprises water-mediated H-bonds [C(O)]O-H···O(H)-H···O_{cr}: **cr** molecule is connected to the OH groups of **A** molecules and COOH groups of **B** molecules through water molecules located on either side of the crown ether plane. According to CSD [39], participation of water or small molecule proton donor solvents (MeOH, EtOH) in the formation of H-bonded networks is typical of the associates of 18-crown-6 with neutral non-fluorinated compounds containing phenol or carboxyl function (see, for example, [35-37, 45-49]). Adjacent oxygen atoms in the **cr** molecule are prone to form two H-bonds with bifunctional donors such as NH₂ group [23-29, 33, 34, 49, 50]. When a guest molecule contains only one donor atom capable of H-bonding, the water molecule serves as a simple bifunctional donor to link the host and guest molecules [37, 46, 49]. It can be assumed that incorporation of water balances the ratio of H-bond donors/acceptors [51]. Table S2 presents parameters of the water-mediated H-bonds in the co-crystals.



Fig. 2. Structures of the co-crystal fragments and individual arenes showing the atom labelling scheme: **2A**·**cr**·2H₂O (a); **2A**·**cr**·4H₂O (b); **2B**·**cr**·2H₂O (c); **C**·**cr**·2H₂O (d); **D**·**cr**·2H₂O (e); **E**·**cr** (f); **F**·**cr**·H₂O (g); **2F**·**cr** (h); **E** (i); **F** (j). Displacement of ellipsoids is drawn at a probability level of 50%. Hydrogen atoms in the **cr** molecules are omitted for clarity. In the disordered structures (d, f, h), see Section 4.1, one variant is shown.

Molecules of pentafluorobenzoic acid **B** in its co-crystal are bound via π -stacking ($\pi_F \cdots \pi_F$) which is the second structure-forming interaction. Thus, supramolecular structure of **2B**·cr·2H₂O corresponds to the H-bonded/ π -stacked 1D assembly (rod, chain) (Fig. 3c) and in

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whole is similar to the structure of polyhalogenated (het)arylamines and 18-crown-6 co-crystals [33, 34]. Centroids of the six oxygen atoms in the **cr** molecules form the rod axis directed along a crystallographic axis. Table 1 presents supramolecular characteristics of the 1D assembly, Table 2 – parameters of π -electron interactions between arene molecules. Note that the slope of the components to the axis in adjacent rods of 2**B**·cr·2H₂O is characterized by angles α and 180– α ; accordingly, the direction of these rods is designated as a and -a.

Crystal packing in 2A·cr·2H₂O is based on the same intermolecular interactions, but there are two symmetry-independent trimers in the crystallographic cell and, accordingly, the cocrystal comprises two types of the 1D assemblies, denoted 1 and 2, with slightly differing parameters (Tables 1 and 2, Fig. 3a). Just as in the 2B·cr·2H₂O co-crystal, the slope of the components in these rods is characterized by angles α and 180– α . The main difference between 1 and 2 rods lies in the arrangement and interaction of pentafluorophenol A molecules: in the 1 type rod, A molecules form centrosymmetrical pairs with a parallel displaced stack geometry; in the 2 type rod, two crystallographically independent A molecules adopt a non-parallel stack geometry with the dihedral angle of 6°, interplane and intercentroid distances being longer than in the first pair. The relatively large horizontal displacement of A molecules in stacked pairs enables the interaction of electronegative fluorine atoms with the electropositive center of the perfluorinated ring, i.e. C-F^{\dots} π_F contact in addition to π -stacking. In **2B**·cr·2H₂O co-crystal, C- $F^{...}\pi_F$ contacts occur between **B** molecules which are located at an angle of 21° and belong to the adjacent 1D assemblies. These interactions form layers of parallel rods in the crystal (Table 1, Fig. S5). In **2A**·cr·2H₂O co-crystal, layers can be selected according to the minimal distance between the rod axes; recurrent rod sequence in the layer is (1, 2, -2, -1, -2, 2), where -1 and -2 indicate the rods in which the components are located at the angles 180- α . (Table 1, Fig. S6).

It should be noted that many hydroxy compounds and pentafluorophenol in particular are prone to polymorphism, expressed in the presence of multiple molecules in the asymmetric unit and appearance of large unit cells, as well as to incorporation of solvent in the structure (see, for example, [52, 53]). In accordance with this, we found that co-crystallization of phenol **A** with **cr** in aqueous EtOH gives a co-crystal with double the amount of water **2A**·**cr**·4H₂O. The 1D assembly unit in this co-crystal contains two-water-mediated H-bonds (Table S2). Topology of the H-bonded network has the following features: one water molecule forms H-bonds with three molecules – with phenol **A** as H-bond acceptor, with **cr** and second water molecule as H-bond donor; second water molecule interacts only with water and **cr** molecules (Fig. 3b). Inside the rod, phenol **A** molecules are connected by π -stacking and C-F^{...} π_F contacts; in addition, C-F^{...} π_F interactions between adjacent rods form layers in the co-crystal (Tables 1 and 2, Fig. S5).



Fig. 3. Molecular packing in the co-crystals $2\mathbf{A}\cdot\mathbf{cr}\cdot 2\mathbf{H}_2\mathbf{O}$ (a), $2\mathbf{A}\cdot\mathbf{cr}\cdot 4\mathbf{H}_2\mathbf{O}$ (b), and $2\mathbf{B}\cdot\mathbf{cr}\cdot 2\mathbf{H}_2\mathbf{O}$ (c), top view on the rods.

Associate	Direction of the rod $axis^a$	Number of the molecules in the unit	Length of the rod unit, $l_{\rm U}({\rm \AA})$	Slope of the molecule planes to the rod axis $(deg)^a$		Layer parameters	
			-	Arene	cr	Direction	Distance between rods axis
2A·cr·2H ₂ O	$a (-a)^{b}$	5	13.07	46	56	<i>a</i> , $c + 1/3b^b$	7.95
				12, 17 ^c	51		
2A·cr·4H ₂ O	b-c	7	16.05	3	34	<i>b-c, a</i>	7.22
2B·cr·2H ₂ O	a (-a)	5	15.18	45	50	<i>a</i> , <i>b</i> + <i>c</i>	7.79
C·cr·2H ₂ O	a+c	4	11.15	12	57	<i>a+c</i> , <i>a-c</i>	6.92
D·cr·2H ₂ O	а-с	4	11.02	19	56	<i>a-c</i> , <i>a</i> + <i>c</i>	6.89
E·cr	а-с	2	9.44	14	74	<i>a-c, a+c</i>	7.33
F·cr·H ₂ O	b	3	11.51	15	67	<i>b</i> , <i>a</i> - <i>c</i>	6.91
2F·cr	<i>c</i> + <i>1</i> /2 <i>a</i>	3	18.19	7	69	c+1/2a, a- 1/2c	5.37

Table 1Parameters of the crystal packing in the associates.

^{*a*} In co-crystals **2A·cr·2H₂O** and **2B·cr·2H₂O** the slope angles of the components are α in the rods directed along *a* and 180- α in the rods directed along -*a*.

^b There are two types of the rods differing in the supramolecular parameters: the upper line relates to the 1 type rod and the lower line relates to the 2 type rod; recurrent rod sequence in the layer is (1, 2, -2, -1, -2, 2), where -1 and -2 indicate the rods in which the components are located at the angles 180- α . ^c Dihedral angle is 6°.

Table 2

Parameters of π -electron interactions between arene molecules in the associates.

Associate	$C_g \cdots C_g$	C _g …plane	C-F C _g distance ^{<i>a</i>} (Å)	F…plane
	distance ^{<i>a</i>} (A)	distance ^{<i>a</i>} (A)		distance (Å)
$2\mathbf{A} \cdot \mathbf{cr} \cdot 2\mathbf{H}_2\mathbf{O}^b$	3.53	3.36	3.71	3.36
	3.88	3.61, 3.46 ^{<i>c</i>}	3.67, 3.88, 3.93	3.51, 3.64, 3.67
2A·cr·4H ₂ O	3.74	3.53	$3.83, 3.89^d$	$3.53, 3.69^d$
2B·cr·2H ₂ O	3.68	3.66	3.60^{d}	3.31^{d}
2F·cr	3.79 ^e	3.42 ^e		

^{*a*} C_g is the centre of gravity of the aromatic ring.

^b There are given data on the two types of the rods, see Table 1.

^{*c*} Dihedral angle is 6° .

^{*d*}C-F^{...} π contact between molecules in adjacent rods.

^{*e*}Aromatic molecules inside the rod are connected via H-bonded dicarboxylic synthon; π -stacking is realized between molecules in adjacent rods.

2.1.2. Associates of bifunctional arenes

It is natural that dihydroxy derivatives C and D also give no co-crystals with cr in anhydrous solvents (t-BuOMe, CCl₄, benzene, n-hexane), and upon contact of the co-formers solution with atmospheric moisture, crystalline hydrates C·cr·2H₂O and D·cr·2H₂O are formed. The supramolecular structure of both associates is based on the water-bridged H-bonded motif (Table S2, Fig. 4a,b). The fact that C molecule has C_{2h} symmetry and is disordered in a ratio of 50:50, does not affect the supramolecular parameters. We have previously shown (see [23] and references herein) that the supramolecular architecture of co-crystals of polyfluorinated arylenediamine with **cr** is determined by the location of the amino groups: in the 1D assemblies of para-isomers, components are arranged in a pairwise parallel manner, in the 1D assemblies of *meta*-isomers – in a zigzag manner relative to the rod axis. However, the supramolecular characteristics of the associates of both *meta*- and *para*-dihydroxy arenes C and D are quite close and practically unaffected by the mutual arrangement of the proton donor functions (Table 1): the mass centers of the co-former molecules lie on the rod axis, their planes are arranged in pairwise parallel manner, macrocycles are slopped to the rod axis at angles of 56 and 57° and aromatic ring planes – at angles of 12 and 19°. Thus, the structure of rods in $C \cdot cr \cdot 2H_2O$ and **D**·cr·2H₂O is similar to the structure of *para*-arylenediamines associates, that is, the watermediated H-bond in the ternary co-crystals eliminates the influence of the co-formers isomerism and ensures the supramolecular isomerism of the 1D assemblies.



Fig. 4. Molecular packing in the co-crystals $C \cdot cr \cdot 2H_2O$ (a, without orientational disorder), **D** $\cdot cr \cdot 2H_2O$ (b), and **E** $\cdot cr$ (c, without orientational disorder), top view on the rods.

2.1.3. Associates of arenes with mixed proton donor functions

According to CSD [39], crystal associates of alcohols with 18-crown-6, in contrast to the associates of phenols, contain no water. Overall crystal packing effects in these adducts appears to allow alcohol OH groups to form H-bonds with crown oxygen atoms without a mediator. In the associates of monoalcohols, one **cr** molecule can be connected via four H-bonds with four alcohol molecules, two on either side of the macrocycle plane [46], but dialcohols can form 1:1 H-bonded co-crystals [54, 55]. Aminobenzyl alcohol **E** contains two functional groups of different nature, i.e. NH₂ and CH₂OH, capable of acting as H-bond donors relative to **cr**; accordingly, co-crystallization of **E** with **cr** easily occurs under any conditions to give a co-crystal **E cr**, which is built without water molecules even when the solution contacts with atmospheric moisture. Characteristics of the structure-forming H-bonds are presented in Table S2, supramolecular parameters of the H-bonded 1D assembly – in Table 1. The rod components are arranged in a pairwise parallel manner, the aromatic molecule being disordered in a ratio of 50:50 (Fig. 4c shows a fragment of the rod without orientational disorder). It should be noted that this feature is peculiar only to the co-crystal **E cr**, whereas in the **E** homocrystal, there is no disorder in the H-bonded network (see ESI, Fig. S7 and crystal packing description).

Bifunctional arene \mathbf{F} containing carboxyl and amino groups co-crystallizes with \mathbf{cr} in an open vessel, i.e. upon contact of the solution with atmospheric moisture to form crystalline

hydrate **F**•**cr**•H₂O. Supramolecular structure of the associate corresponds to the 1D assembly based on the two types of H-bonds (Fig. 5a): N-H···O_{cr} typical of arylamine associates [23-29, 33, 34, 49] and water-mediated bond C(O)O-H···O(H)-H···O_{cr} typical of carboxylic acid associates [36, 38, 49]. Characteristics of the structure-forming H-bonds are presented in Table S2, supramolecular parameters of the 1D assembly – in Table 1.

However, aromatic carboxylic acids are known [25, 41, 56, 57] to assemble in crystals through the formation of the cyclic dicarboxylic motif (Fig. 5c) and such carboxy-dimer relates to the widespread robust synthons in crystal engineering [13-17]. In the presence of an alternative H-bond donor, this synthon competes with other strong H-bonds, as is realized, for example, in polymorphs of aminobenzoic acid (**aba**) [58]. Thus, in the polymorph α , molecules form cyclic carboxy-dimers which are interconnected through N-H...O=C contacts, but in the polymorph β , there are no carboxy-dimers and all molecules are linked via carboxy-amino headto-tail H-bonds. Molecular packing in the homocrystal of polyfluorinated acid F is similar to that in α polymorph of the non-fluorinated **aba** (see ESI, Fig. S8 and crystal packing description), that is, **F** is also prone to form the cyclic carboxy-dimer. Indeed, under anhydrous conditions, cocrystallization of F and cr yields a 2:1 associate 2F·cr, and this result is independent on the coformers ratio in the growth solution (2:1 or 1:1). In this co-crystal, pairs of F molecules form cyclic carboxy-dimers which get connected with **cr** molecules via N-H...O_{cr} contact to generate H-bonded 1D assembly (Tables 1 and S2). Thus, the incorporation of crown-ether into the matrix of aminobenzoic acid F in anhydrous solvents results in the replacement of the N-H···O=C and N-H...F bonds for the N-H...Ocr bond, while the cyclic carboxy-dimer is retained; however, in the presence of water, the water-mediated bond C(O)O-H···O(H)-H···O_{cr} is preferred. It should be noted that the 2:1 co-crystal of non-fluorinated aba with cr [25] is arranged in a similar manner as 2F·cr. In addition to H-bonds, in the 2F·cr co-crystal, π -stacking is realized between F molecules belonging to adjacent 1D assemblies (Table 2), which are thereby combined into 2D supramolecular structure (Fig. 5b). In the 1:1 co-crystals of bifunctional compounds C, D, E, and F, there are no interactions between H-bonded 1D assemblies; therefore, layers can be selected according to the minimal distance between the rod axes (Table 1, Figs. S9a-d).



Fig. 5. Molecular packing in the co-crystals $\mathbf{F} \cdot \mathbf{cr} \cdot 2H_2O(\mathbf{a})$ and $\mathbf{2F} \cdot \mathbf{cr}(\mathbf{b})$, top view; cyclic dicarboxylic motif (c).

2.1.4. Co-formers geometry in the co-crystals

Intermolecular interactions in the homo- and co-crystals of polyfluorinated benzoic acids **B** and **F**, as well as of **aba** [25, 59, 60], affect the molecules geometry (Table 3). Cyclic carboxydimers exhibit varying degree of orientational disorder in the crystal lattice: according to the C=O and C-OH bond lengths, the disorder is greater in the associates **2F·cr** and **2aba·cr** (up to the full in **2F·cr**), and less in the homocrystals **B**, **F**, and **aba**(α). Rotation angle of the carboxyl group relative to the benzene ring depends on both the crystal packing and nature of substituents in the molecule. The cyclic dicarboxylic motif reduces the rotation angle in the crystals **B**, **F**, **aba**(α), **2F·cr**, **2aba·cr** as compared to the H-bond C(O)O-H···O_{cr} or C(O)O-H···N in the crystals **2B·cr**·2H₂O, **F·cr**·H₂O, **aba**(β). For both types of the crystal packing, *para*-NH₂ group in **F** and **aba** molecules significantly reduces the rotation angle as compared to *para*-fluorine atom in **B** molecule. This is apparently due to an increase in the conjugation of COOH group with a ring containing the donor substituent, which also manifests itself in a decrease of C–COOH bond length in a series of crystals **B**, **F**, **aba** (except for β polymorph). The influence of four electron acceptor fluorine atoms in the **F** molecule, which are able to partially compensate for the donor effect of NH₂ group and, therefore, to reduce the rotation angle, is implemented only in the crystal containing no cyclic motif (cf. **F·cr·H**₂O and **aba**(β)).

Table 3

Geometry of the carboxylic groups in the crystals of different benzoic acids.

Code	Cyclic dimer	Bond lengths	Rotation angle			
		С=О	C–OH	O–H	C–COOH	relative to the
						benzene ring (deg)
2B·cr·2H ₂ O	no	1.196(3)	1.305(3)	0.99(3)	1.508(3)	42
B [57]	yes	1.2282(2)	1.2777(2)	0.99	1.4987(2)	29
F·cr·H ₂ O	no	1.172(4)	1.296(4)	0.82	1.487(3)	19
2F·cr	yes	1.252(3)	1.252(3)	0.81(9)	1.476(6)	0
F	yes	1.236(2)	1.274(3)	0.97(4)	1.480(2)	2
2aba·cr ^{<i>a</i>} [25]	yes	1.267(4)	1.285(4)	1.12(6)	1.463(4)	2
aba (α) [60]	yes	1.236(3)	1.316(3)	0.95	1.455(4)	2
aba (β) [59]	no	1.219(3)	1.312(3)	-	1.505(4)	11

^a Co-crystal **2aba·cr** packs with six symmetry-independent **aba** molecules in the asymmetric unit; the table shows data for one of them having middle parameters.

The **cr** molecule in the associate $\mathbf{F} \cdot \mathbf{cr} \cdot \mathbf{H}_2 O$ has no symmetry. In the associates $\mathbf{C} \cdot \mathbf{cr} \cdot 2\mathbf{H}_2 O$ and $\mathbf{2F} \cdot \mathbf{cr}$, symmetry of the **cr** molecules is C_{2h} (rotation axis pass through the middle of the bonds C5-C5 and C8-C8, respectively). In the rest of associates, **cr** molecules have the C_i symmetry. The conformation of the **cr** molecules in the co-crystals under consideration is close to the classical crown 3(TGT,T–GT) except the conformation 3(TGT)3(T-GT) in **2F** \cdot **cr** co-crystal, where T stands for *trans*- and G stands for *gauche*-conformations of the C-C and C-O fragments.

2.2. Computational study of intermolecular interactions

To estimate and compare the efficiency of supramolecular synthons, we explored the associates $2A \cdot cr \cdot 2H_2O$, $2A \cdot cr \cdot 4H_2O$, $2B \cdot cr \cdot 2H_2O$, $E \cdot cr$, $F \cdot cr \cdot H_2O$, and $2F \cdot cr$ by quantum chemical calculations. These selected examples cover all the observed types of intermolecular interactions. The calculated values of the interaction energies are presented in Table 4. These data show that the energy of the $O-H \cdots O_{cr}$ H-bond formed by the alcohol OH group in $E \cdot cr$ differs insignificantly from the energies of similar bonds $N-H \cdots O_{cr}$ formed by the amino groups,

both in the associates of **E** and **F** compounds and in the previously studied associate of pentafluoroaniline **2pfa·cr** [33]. In contrast, the energy of water-mediated H-bonds in the associates of phenol **2A·cr**·2H₂O, benzoic acid **2B·cr**·2H₂O, and aminobenzoic acid **F·cr**·H₂O is approximately doubled, and it is three times higher in the **2A·cr**·4H₂O associate. Thus, the participation of one water molecule in the H-bonding increases its total energy by ~100 kJ mol⁻¹. The binding energy in the cyclic carboxy-dimer of the associate **2F·cr** is about half that the energy of the water-mediated H-bond C(O)O-H···O(H)-H···O_{cr}; this appears to cause the preferred formation of **F·cr**·H₂O in the presence of even small amounts of water (upon contact of the solution with atmospheric moisture).

Table 4

Associate	H-	π-stacking		
	D	n	ΔE	-
2A·cr· 4H ₂ O	0	2	299.6	22.4
2A·cr· 2H ₂ O	0	1	222.2 / 202.0 / 188.1 ^a	20.2 / 17.8 ^a
2B·cr· 2H ₂ O	0	1	231.0	7.7
2pfa·cr [33]	Ν	0	100.6	28.9
E·cr	0	0	104.4	
	Ν	0	74.9	
F·cr·H ₂ O	0	1	191.0	
	Ν	0	115.7	
$2\mathbf{F}\cdot\mathbf{cr}^b$	Ν	0	96.6	29.6

Interaction energies in the associates (kJ mol⁻¹ per interacting molecules).

^a Different types of the interactions (Tables 1, 2, S2).

^b Energy of H-bonding in the cyclic carboxy-dimer is 100.3 kJ mol⁻¹.

The π -stacking energy of phenol **A** molecules is somewhat lower than that of **pfa** molecules, and the π -stacking energy of benzoic acid **B** molecules is ~ 3 times less than these values (Table 4), despite the fact that supramolecular parameters of the stacked dimers do not differ much (Table 2). In all three cases, π -stacking is implemented in the anti-parallel displaced geometry (Fig. 3), which is mainly driven by the electrostatic interactions. A significant part of the overall π -interaction energy is known to be provided by dispersion interactions, but in systems with nonzero dipole moment, there can be an equally important electrostatic contribution [61-63]. Indeed, in the series of compounds **pfa**, **A**, **B**, there are symbate changes in the dipole moment (2.95, 2.54 [64], 1.70 D [56], respectively) and the π -stacking energy. A high value of the π -stacking energy of the aminobenzoic acid **F** molecules appears to be due to the fact that two *para*-substituents in this compound have opposite electronic effects and provide a large dipole moment of the molecule.

2.3. Thermal analysis of co-crystals

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The crystal associates were investigated using the differential scanning calorimetry (DSC) to determine the homogeneity and temperature stability of the crystal phase, as well as the ability of supramolecular structure to regenerate from melt. The onset temperatures of the phase transition (T_{onset}) and the specific enthalpies of fusion (ΔH_W) were determined, and the molar enthalpies of fusion (per unit of the rod, ΔH_U) were calculated (Table 5). DSC curves of the co-crystals except **F**·**cr**·H₂O exhibit a single endothermic peak of the crystal-to-liquid phase transition (Figs. 6a-c, S10-S14). It should be emphasized that the T_{onset} and ΔH_W values of the asprepared co-crystals and single crystals used in the XRD study are the same.



Fig. 6. DSC curves of the co-crystals, the first (black) and subsequent (red, green) heating runs: **2A**·**cr**·2H₂O (a); **2B**·**cr**·2H₂O (b), C·**cr**·2H₂O (c).

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Co-crystal ^a	$T_{\text{onset}}^{b}(\mathbf{C})$		$\Delta H_{\mathrm{W}}^{c,d} (\mathrm{J g}^{-1})$		$\Delta H_{\rm U}^{d,e}$ (kJ g-unit ⁻¹)		
	from solution	from melt	from solution	from melt	from solution	from melt	
2A·cr ·2H ₂ O	70	69	110	116	73	77	
2A·cr ·4H ₂ O	74	73	174	176	122	124	
2B·cr·2H ₂ O	84	78	146	101	106	73	
C·cr·2H ₂ O	93	92	182	212	88	102	
D·cr ·2H ₂ O	103	97	185	140	89	67	
E∙cr	112	111	183	182	84	84	
2F·cr	173	166	152	125	104	86	

 Table 5

 DSC data on the co-crystals

^{*a*} Data on the **F**·**cr**·H₂O were not determined because of partial heat destruction of the co-crystal.

^{*b*} T_{onset} is the melting onset.

^{*c*} $\Delta H_{\rm W}$ is the specific melting enthalpy.

^{*d*} Determination accuracy is $\pm 2\%$.

 $^{e}\Delta H_{\rm U}$ is the melting enthalpy calculated on the weight of unit.

Thermal characteristics of the co-crystals $2A \cdot cr \cdot 2H_2O$, $2A \cdot cr \cdot 4H_2O$, $C \cdot cr \cdot 2H_2O$, and $E \cdot cr$ are fully reproduced in the melting-crystallization cycle that testifies to (*i*) the regeneration of the crystal structure and (*ii*) the uniformity in the structure of co-crystals formed from melts and

solutions. Thermocycling of $\mathbf{C}\cdot\mathbf{cr}\cdot 2\mathrm{H}_2\mathrm{O}$ leads to a noticeable increase in the ΔH_W value (up to 15%) in the second melt (Table 5). Comparison of the PXRD patterns of the $\mathbf{C}\cdot\mathbf{cr}\cdot 2\mathrm{H}_2\mathrm{O}$ samples formed from solution and from melt indicates their similarity (Fig. S2); in turn, this suggests similarity of the crystal packing. Therefore, the noted differences in ΔH_W at thermocycling seem to be caused by normalization or quenching of the sample without any change in the crystal structure. In contrast to $\mathbf{C}\cdot\mathbf{cr}\cdot 2\mathrm{H}_2\mathrm{O}$, associate of isomeric *para*-dihydroxy benzene $\mathbf{D}\cdot\mathbf{cr}\cdot 2\mathrm{H}_2\mathrm{O}$ incompletely regenerate its structure when crystallizing the melt (Fig. S11): ΔH_W in the second melt is ~ 75% of the original. A similar behavior is peculiar to the associates of both arenes containing the carboxyl group $2\mathbf{B}\cdot\mathbf{cr}\cdot 2\mathrm{H}_2\mathrm{O}$ and $2\mathbf{F}\cdot\mathbf{cr}$ (Figs. 6b and S13). It is possible that a controlled mode of slow cooling is required to completely regenerate the structure of these co-crystals from the melt.

DSC curve of $\mathbf{F}\cdot\mathbf{cr}\cdot\mathbf{H}_2\mathbf{O}$ has two phase transitions with close thermal effects (Fig. S14), which are reproduced in the second melting, but the heat capacity of the sample becomes higher. Matching the experimental PXRD and simulated from the single crystal XRD data patterns (Fig. S3) testifies to the uniformity of the chemical composition and crystal structure of the sample, so the additional thermal anomaly can not be explained by the presence of an impurity phase. Comparison of these data with visual effects, i.e. changing the crystal appearance when a sample is heated below the melting point, indicates the possibility of solid-phase transitions with partial destruction of the co-crystal. After cooling the melt, the crystal structure of $\mathbf{F}\cdot\mathbf{cr}\cdot\mathbf{H}_2\mathbf{O}$ seems to regenerate incompletely and a partially degraded sample has a higher heat capacity because of increasing the degrees of freedom of the molecules.

When comparing ΔH_U of the co-crystals (Table 5), we can observe some dependence of these values on the nature of substituents in the polyfluoroarenes. The range of fusion enthalpies of the associates of phenols **A**, **C**, **D** and alcohol **E** lies below than that of the associates of carboxylic acids **B** and **F** (ΔH_U 73-89 *vs* 104-106 kJ g-unit⁻¹). Only ΔH_U of the co-crystal with double the amount of water **2A**·**cr**·4H₂O deviates noticeably upward (122 kJ g-unit⁻¹). It should be noted that quantum chemical calculations of the interaction energies in the co-crystals are consistent with this trend, at least for structurally similar H-bonded/ π -stacked associates (Section 2.2). According to Table 4, in the series of **2A**·**cr**·2H₂O, **2B**·**cr**·2H₂O, **2A**·**cr**·4H₂O co-crystals, there is an increase of interaction energies, which is mostly determined by the H-bonding energies.

It is noteworthy that the associates of isomeric *meta*- and *para*-dihydroxybenzenes **C** and **D** have close ΔH_U values, and this fact contrasts with the difference in ΔH_U values of the associates of isomeric *meta*- and *para*-diaminoarenes [23]. The work [23] reported a correlation between the architecture of H-bonded 1D assemblies in the co-crystals of *meta*- and *para*-diamino derivatives of perfluorobenzene and perfluoronaphthalene and their fusion enthalpy: the *para*-diamine associates composed of pairwise parallel assemblies with a shorter unit length have a greater ΔH_U , and *meta*-diamine associates composed of zigzag like assemblies with a longer unit length have a lesser ΔH_U . Unlike this, in the co-crystals of isomeric dihydroxybenzenes **C** and **D**, the water-mediated H-bond eliminates the effect of co-formers' isomerism on both supramolecular (Section 2.1) and thermal characteristics (Table 5).

3. Conclusion

In this work we report the crystal associates prepared from 18-crown-6 and polyfluoroaromatic compounds containing hydroxyl, carboxyl, and mixed proton donor functions, their supramolecular architecture, types and energy of the structure-forming synthons.

We have found that unlike polyfluoroaromatic amines [23, 33, 34], phenols **A**, **C**, **D** and carboxylic acid **B** form no co-crystals with **cr** in anhydrous conditions; only when the co-formers solution comes in contact with atmospheric moisture, they form ternary compounds $2\mathbf{A}\cdot\mathbf{cr}\cdot2\mathbf{H}_2\mathbf{O}$, $2\mathbf{B}\cdot\mathbf{cr}\cdot2\mathbf{H}_2\mathbf{O}$, $\mathbf{C}\cdot\mathbf{cr}\cdot2\mathbf{H}_2\mathbf{O}$, $\mathbf{D}\cdot\mathbf{cr}\cdot2\mathbf{H}_2\mathbf{O}$. Moreover, phenol **A** can give a co-crystal with double the amount of water $2\mathbf{A}\cdot\mathbf{cr}\cdot4\mathbf{H}_2\mathbf{O}$ in aqueous EtOH. Co-crystallization of aminobenzyl alcohol **E** with **cr** easily occurs under any conditions to give a co-crystal **E**\cdot**cr**, which is built without water molecules. Aminobenzoic acid **F** is capable of forming a co-crystal **2F**\cdot**cr**, but in the presence of moisture, crystalline hydrate **F**\cdot**cr**\cdot $\mathbf{H}_2\mathbf{O}$ is predominantly formed. Thus, the presence of water in the growth solution in some cases can serve as a tool to control the composition and structure of the crystalline phase.

In the crystalline hydrates, molecules of the aromatic co-formers **A**, **B**, **C**, **D**, **F** are connected with **cr** via water-mediated synthons [C(O)]O-H···O(H)-H···O_{cr}; in phenol **A** cocrystal, this synthon can involve two water molecules. According to quantum chemical calculations, the participation of each water linker molecule in H-bonding increases the stability of the supramolecular structure by about 100 kJ mol⁻¹. The alcohol OH group in **E** molecule forms H-bond without a mediator, i.e. O-H···O_{cr}. Pairs of acid molecules in **2F·cr** are connected via cyclic carboxy-dimer. In addition, **E** and **F** molecules participate in the second type of Hbonds, i.e. N-H···O_{cr} synthon typical of amines. The calculated energies of the O–H···O_{cr} and cyclic dicarboxylic synthons are comparable with the energy of N–H···O_{cr} synthon.

Associates of bifunctional arenes C·cr·2H₂O, D·cr·2H₂O, E·cr, and F·cr·H₂O exhibit Hbonded 1D assembly as an only structure-determining motif. Molecules of monofunctional arenes in the co-crystals 2A·cr·2H₂O, 2A·cr·4H₂O, and 2B·cr·2H₂O are bound via $\pi_{\rm F}^{...}\pi_{\rm F}$ stacking which is the second structure-forming interaction; their supramolecular structure corresponds to the H-bonded/ π -stacked 1D assembly. Calculation of the interaction energies reveals the H-bonding to be the primary binding force in these crystals; the contribution of π stacking is less important and depends on the nature of the H-donor function. In the pairs of C₆F₅X molecules when X=NH₂, OH, COOH, there observes a decrease in the π -stacking energy, which is symbate to a decrease in the dipole moment. In the 2F·cr co-crystal, π -stacking is realized between F molecules belonging to the adjacent H-bonded 1D assemblies thus connecting them into 2D supramolecular structure.

The presented features of self-assembly of co-crystals of H-donor polyfluoroarenes with a macrocyclic receptor as well as estimation of the comparative efficiency of molecular recognition motifs can assist in engineering high-performance donor-acceptor materials and in creating expedient tools for the modification of biologically important systems.

4. Experimental

4.1. Measurements

¹H and ¹⁹F NMR spectra were recorded on a Bruker AV-300 spectrometer using residual protons of the deuterated solvent and C₆F₆ ($\delta = -163$ ppm from CCl₃F) as internal standards; δ are given in ppm relative to TMS and CCl₃F, *J* are given in Hz. In the spectra of some samples, the intensities of signals of the protons in carboxylic or phenolic groups and water are reduced due to intense exchange processes, or signals are not observed. To determine the co-formers' ratio in the co-crystals using NMR spectroscopy, 4,4'-dimetoxyoctafluorobiphenyl was used as an internal standard. FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer in the ATR mode. Melting points were determined on an Apotec RS instrument.

Single crystal X-ray diffraction study of co-crystals and individual polyfluoroarene crystals was performed on a Bruker Kappa Apex II diffractometer equipped with a twodimensional CCD-detector using ω , φ scanning. Absorption correction was applied using the SADABS program. The structures were solved by the direct method and refined by full-matrix least-squares method in an anisotropic approximation (except H atoms) using the SHELXL-97 programs [65]. Positions of hydrogen atoms of amino groups were found from difference map and refined isotropically, the rest hydrogen atoms were located geometrically and refined in the riding model. The aminobenzyl alcohol molecule in **E**·cr is located on the center of symmetry and disordered with 0.5:0.5 ratio. Polyfluoroarenes C and F molecules in the co-crystals C·cr·2H₂O and 2F·cr have the C_{2h} and C_s symmetry, respectively, and are disordered with 0.5:0.5 ratio. The intermolecular interactions were analyzed using PLATON [66] and MERCURY programs [67]. Processing and solving of the data was carried out within several crystal systems of different spatial groups using a complex of programs Bruker Apex2 (2012) and SIR2004. The twinning options offered by the program cell_now did not lead to a decrease in the R-factor. Powder X-ray diffraction study was performed on a Bruker Kappa Apex II diffractometer.

The intermolecular interaction energies were explored by quantum chemical calculations using the DFT (M06-2X/TZV) method with GAMESS software. Point energy calculations were made using the crystal coordinates of non-hydrogen atoms. The coordinates of hydrogen atoms were normalized with MERCURY program.

Thermal analysis was performed with a differential scanning calorimeter NETZSCH DSC 204 F1 Phoenix. DSC measurements were carried out by heat flow measurement method at a constant cooling/heating rate in 25 ml min⁻¹ Ar flux. Powdered samples of precipitates or single crystals with a mass 3-12 mg were distributed uniformly over the bottom, carefully tamped and cold sealed in aluminum crucibles. The baseline signal obtained by heating two empty crucibles was subtracted from the experimental results of samples. Netzsch Proteus Analysis software was used to determine DSC peak areas and transition temperatures values. The transition temperatures were defined from the resulting heat flow as intersections of the peak onset with the corresponding baseline. The peak area determination was performed by integrating the area between the measurement curve and the integral tangential baseline. The sensitivity of the sample carrier sensors and temperature scale graduation were calibrated by melting and crystal-to-crystal transition measurements of standard samples (cyclohexane, adamantane, Hg, Ga, naphthalene, benzoic acid, KNO₃, In, Sn) [68]. *4.2. Materials*

The following commercial products were used without further purification: anhydrous NH₃, 18-crown-6 (**cr**), pentafluorophenol (**A**), pentafluorobenzyl alcohol, pentafluorobezoic acid (**B**), 1,3-dihydroxy-2,4,5,6-tetrafluorobenzene (**C**), 1,4-dihydroxy-2,3,5,6-tetrafluorobenzene (**D**). Solvents *n*-hexane, EtOH, *t*-BuOMe, CCl₄, and benzene were distilled over a drying agent. 4-Amino-2,3,5,6-tetrafluorobenzyl alcohol (**E**) was synthesized by means of aminodefluorination of pentafluorobenzyl alcohol in anhydrous ammonia at 100 °C by analogy with the procedure [39], mp 97-98 °C (cf. [69] mp 96-98 °C), CCDC 1995841. 4-Amino-2,3,5,6-tetrafluorobenzoic acid (**F**) was synthesized using the procedure [70], mp 182-184 °C (cf. [70] mp 181-181.5 °C), CCDC 1995842.

Single crystals of the arenes were grown by crystallization from the appropriate solvent: **E** from benzene+n-hexane mixture (2:1), **F** from benzene.

4.3. Preparation of associates of arenes and 18-crown-6 ether

A solution of 18-crown-6 (0.9 mmol) in a convenient solvent (10 mL) heated to 60 °C was added in small portions to a stirred solution of arene (1.0 or 2.0 mmol) in the same solvent (10 mL) at the same temperature. The mixture was slowly cooled to ambient temperature (~20 °C) and was kept at 5 °C for 12-24 h. The fine-crystalline precipitate formed was filtered off and dried in air to a constant weight. If necessary, single crystals of the associate suitable for X-ray diffraction studies were obtained by spontaneous evaporation of a solvent in various conditions. The identity of the chemical and phase structures of the precipitate and single crystals was monitored using PXRD (Figs. S1-S4), NMR and DSC methods.

Associate of pentafluorophenol and 18-crown-6, 2:1, dihydrate, 2(C₆HF₅O)*C₁₂H₂₄O₆*2H₂O (**2A·cr·**2H₂O) was obtained from benzene, *n*-hexane in an open vessel, yield 45%, mp 69–70 °C. IR, v/cm⁻¹: 3520, 3456 (O–H); 2920, 2895 (C_{al}–H); 2681, 2611, 2517 (O–H); 1639 (C_{ar}-C_{ar}); 1537, 1514, 1475, 1389, 1352, 1252; 1101 (C_{al}–O); 1014, 982, 958, 839. ¹H NMR (acetone-d₆) δ : 3.10 (br.s, H₂O), 3.58 (br.s, 24H, CH₂), 10.25 (br.s, OH). ¹⁹F NMR (acetone-d₆), δ : -161.6 (m, 2F, F-2, F-6), -165.3 (m, 2F, F-3, F-5), -171.8 (tt, 1F, *J*_{FF}=6, *J*_{FF}=22,

F-4). CCDC: 1995834

Associate of pentafluorophenol and 18-crown-6, 2:1, tetrahydrate, 2(C₆HF₅O)*C₁₂H₂₄O₆*4H₂O (**2A·cr**·4H₂O) was obtained from EtOH+H₂O mixture (4:1), yield 68%, mp 73–75 °C. IR, v/cm⁻¹: 3489, 3458, 3379, 3198 (O–H); 2922, 2888 (C_{al}–H); 2578, 2470 (O–H); 1649 (C_{ar}-C_{ar}); 1536, 1512, 1477, 1381, 1354, 1254; 1099 (C_{al}–O); 1016, 987, 956, 839. ¹H NMR (acetone-d₆) δ : 3.58 (br.s, 24H, CH₂). ¹⁹F NMR (acetone-d₆), δ : -161.6 (m, 2F, F-2, F-6), -165.3 (m, 2F, F-3, F-5), -171.8 (tt, 1F, J_{FF}=6, J_{FF}=22, F-4). CCDC: 1995833

Associate of pentafluorobenzoic acid and 18-crown-6, 2:1, dihydrate, 2(C₇HF₅O₂)*C₁₂H₂₄O₆*2H₂O (**2B·cr·**2H₂O) was obtained from *t*-BuOMe, CCl₄+*n*-hexane mixture (1:1), benzene+*n*-hexane mixture (1:1) in an open vessel, yield 77%, mp 79–82 °C. IR, v/cm⁻¹: 3421 (O–H); 2918 (C_{at}–H); 3000-2100 (O–H); 1890; 1716 (C=O); 1649 (C_{ar}-C_{ar}); 1524, 1491, 1321, 1240; 1093 (C_{at}–O); 997, 957, 837, 721. ¹H NMR (acetone-d₆) δ : 3.58 (br.s, 24H, CH₂). ¹⁹F NMR (acetone-d₆), δ : -139.4 (m, 2F, F-2, F-6), -150.8 (tt, 1F, *J*_{FF}=6, *J*_{FF}=22, F-4), -161.7 (m, 2F, F-3, F-5). CCDC: 1995835

Associate of 1,3-dihydroxy-2,4,5,6-tetrafluorobenzene and 18-crown-6, 1:1, dihydrate, $C_6H_2F_4O_2*C_{12}H_{24}O_6*2H_2O$ (**C**·**cr**·2H₂O) was obtained from *t*-BuOMe in an open vessel, yield 60%, mp 84–91 °C. IR, v/cm⁻¹: 3549, 3452 (O–H); 2920, 2883 (C_{al}–H); 2871, 2600, 2532 (O–H); 1631 (C_{ar}-C_{ar}); 1551, 1512, 1473, 1429, 1377, 1250; 1099 (C_{al}–O); 993, 979, 957, 839. ¹H NMR (acetone-d₆) δ : 2.93 (br.s, H₂O), 3.58 (br.s, 24H, CH₂), 9.31 (br.s, 1H, OH). ¹⁹F NMR (acetone-d₆), δ : -161.1 (d, 1F, *J*_{FF}=5, F-2), -167.9 (dt, 1F, *J*_{FF}=5, *J*_{FF}=21, F-5), -170.0 (d, 2F, *J*_{FF}=21, F-4, F-6). CCDC: 1995836

Associate of 1,4-dihydroxy-2,3,5,6-tetrafluorobenzene and 18-crown-6, 1:1, dihydrate, C₆H₂F₄O₂*C₁₂H₂₄O₆*2H₂O (**D**·cr·2H₂O) was obtained from *t*-BuOMe+*n*-hexane mixture (1:1) in an open vessel, yield 60%, mp 97–102 °C. IR, v/cm⁻¹: 3533, 3458 (O–H); 2920, 2885 (C_{al}–H); 2677, 2586 (O–H); 1633 (C_{ar}-C_{ar}); 1552, 1504, 1470, 1400, 1352, 1250; 1101 (C_{al}–O); 1018, 957, 839. ¹H NMR (acetone-d₆) δ : 3.14 (br.s, H₂O), 3.58 (br.s, 24H, CH₂), 9.38 (br.s, OH). ¹⁹F NMR (acetone-d₆), δ : -164.1 (s). CCDC: 1995837

Associate of 4-amino-2,3,5,6-tetrafluorobenzyl alcohol and 18-crown-6, 1:1, C₇H₅F₄NO*C₁₂H₂₄O₆ (**E**·**cr**) was obtained from *t*-BuOMe in a closed or open vessel, yield 86%, mp 111–112.6 °C. IR, v/cm⁻¹: 3471, 3435, 3346, 3226 (O–H, N–H); 2920, 2885 (C_{al}–H); 1668 (C_{ar}-C_{ar}); 1525, 1495, 1471, 1431, 1350, 1288, 1250; 1105 (C_{al}–O); 1020, 958, 887, 839. ¹H NMR (acetone-d₆) δ : 3.58 (br.s, 24H, CH₂), 4.27 (br.s, 1H, OH), 4.60 (s, 2H, CH₂), 5.37 (br.s, 2H, NH₂). ¹⁹F NMR (acetone-d₆), δ : -148.5 (m, 2F, F-2, F-6), -162.8 (m, 2F, F-3, F-5). CCDC: 1995838

Associate of 4-amino-2,3,5,6-tetrafluorobenzoic acid and 18-crown-6, 1:1, hydrate, C₇H₃F₄NO₂*C₁₂H₂₄O₆*H₂O (**F·cr·**H₂O) was obtained from *t*-BuOMe in an open vessel, yield 85%, mp 115-120 °C (decompos). IR, v/cm⁻¹: 3500, 3471, 3410, 3325, 3221 (O–H, N–H); 2885 (C_{at}–H); 3000-2400 (O–H); 1705 (C=O); 1649 (C_{ar}-C_{ar}); 1541, 1496, 1473, 1352, 1309, 1250; 1101 (C_{at}–O); 957, 943, 841, 714. ¹H NMR (acetone-d₆) δ : 3.58 (br.s, 24H, CH₂), 6.05 (br.s, 2H, NH₂). ¹⁹F NMR (acetone-d₆), δ : -141.6 (m, 2F, F-2, F-6), -162.7 (m, 2F, F-3, F-5). CCDC: 1995839

Associate of 4-amino-2,3,5,6-tetrafluorobenzoic acid and 18-crown-6, 2:1, 2(C₇H₃F₄NO₂)*C₁₂H₂₄O₆ (2**F**·**cr**) was obtained from benzene or its mixture with CCl₄ in a closed vessel (component ratios in the growth solution are 1:1 or 2:1), yield 95%, mp 172-173 °C. IR, v/cm⁻¹: 3394, 3317, 3205 (N–H); 2881 (C_{at}–H); 3000-2400 (O–H); 1686 (C=O); 1643 (C_{ar}-C_{ar}); 1542, 1496, 1417, 1352, 1309, 1250; 1099 (C_{at}–O); 943, 841, 723. ¹H NMR (acetone-d₆) δ : 3.58 (br.s, 24H, CH₂), 6.05 (br.s, 2H, NH₂). ¹⁹F NMR (acetone-d₆), δ : -141.6 (m, 2F, F-2, F-6), -162.7 (m, 2F, F-3, F-5). CCDC: 1995840

Conflicts of Interest

There are no conflicts to declare.

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Supplementary data

X-ray crystallographic information files (CIF), Cambridge Crystallographic Data Centre, CCDC ID: 1995833, 1995834, 1995835, 1995836, 1995837, 1995838, 1995839, 1995840, 1995841, 1995842.

Supplementary material related to this article can be found, in the online version, at https://doi.org/

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