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Structural and Compositional Study by SFM of the Crystal Surfaces of Halogen-Bonded Hybrid Materials Containing Long-Chain Perfluorocarbons

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Halogen bonding (XB) has demonstrated to be an effective tool for inducing the self-assembly of halo-perfluorocarbons (PFCs) with hydrocarbons and/or inorganic salts and obtain new hybrid, crystalline materials containing long-chain PFCs [1]. Here, we report the first examination of the surface of these crystals through Scanning Force Microscopy (SFM) techniques providing a new insight into their unusual structures. Our attention was focused on the ternary supramolecular complex **5** given by 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-hexadecafluoro-1,8-diiodooctane (**4**) with the cryptate Kryptofix[®] 222 c KI **3** (formed by 4,7,13,16,21-24-hexaoxa-1,10-diazabicyclo[8,8,8]-hexacosane **1** and potassium iodide **2**). The ternary system **5** crystallizes with trigonal symmetry in the P $\bar{3}$ space group and forms large hexagonal or triangular thin plates having their largest faces perpendicular to the *c* crystallographic axis.

SFM techniques enabled obtaining useful structural and surface compositional informations [2]. In particular, we exploited the ability of surface potential (SP) microscopy to detect changes in chemical composition by measuring the potential V_s on a surface. Alternating large "dark" and narrow "bright" regions were observed (Figure 1) having low and high V_s values, respectively, with a strict correlation between the alternating terraces in the topography image and equipotential regions. Assuming thermodynamic control, the relative areas covered by the specific crystal faces are inversely proportional to their relative surface energies, which depend on the exposed molecular functionalities. As a consequence, PFC module **4** is expected covering the largest surface of the crystal, corresponding to the dark terraces.

In order to further investigate the crystallographic (001) surface, with a single-module composition, and the [001] zone of **5**, which is expected to exhibit a two-modules composition, Force Spectroscopy (FS) was performed. Figure 2 shows different Force-distance curves. The violet and red curves, collected on the "dark regions" of the (001) surface, are identical and reproducible in different scans/points, suggesting a homogeneous molecular composition. Moreover, the large adhesion forces observed are those expected for hydrophobic surfaces (as fluorinated ones). Low adhesion forces were instead observed after leaving the crystal under high vacuum conditions, a result that we ascribe to the removal of the 1,8-diiodoperfluorooctane module **4** from the (001) surface. On the other hand, force curves acquired on the [001] zone (green and blue) are strongly surface-point dependent with curves gradually switching from high to low adhesion, consistently with a surface exposing both modules (alternating **3** and **4**) with the tip probing the local forces at the approach point.

In conclusion, SFM techniques were employed to obtain structural and surface compositional informations. The fundamental (001) surface, which is the largest in the crystal **5**, was found to consist of large and narrow terraces, which expose the single PFC module **4**, and the cryptate **3**, respectively with the PFC module **4** covering the largest area.

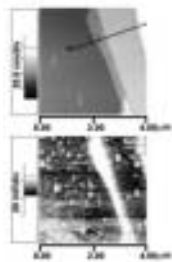


Figure 1.

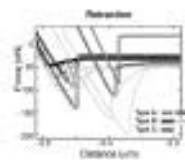


Figure 2.

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Analysis of solid conductors by means of Voronoi-Dirichlet partition

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Voronoi-Dirichlet partition of crystal space was used to model the sites of alkali ions and to analyze the paths of their migration in the crystal structures of Na_{1+x}Zr₂Si_xP_{3-x}O₁₂ (NASICON), Li₃M₂P₃O₁₂ (LIPHOS), Li₄SiO₄ (LISICON), and other 3D framework alkali superionic materials. The notions 'cavity', 'channel', 'migration path', and their geometrical properties are given in terms of the Voronoi-Dirichlet partition. Namely, the elementary (smallest) voids and the channels between them coincide with vertices and edges of atomic Voronoi-Dirichlet polyhedra. The criteria are proposed to select significant cavities and migration channels, which are based on averaged parameters of Voronoi-Dirichlet polyhedra for alkali atoms. A general algorithm is developed to investigate the crystal structure of a superionic material; the algorithm is implemented in the automatized system of crystallochemical analysis TOPOS. A friendly interface of TOPOS is easy to analyze solid conductors of any complexity by any crystal chemist even without special grounding. The proposed method allows one to determine precisely the most probable sites of charge carriers and to predict conductive properties of a substance at the conditions of X-ray experiment. A fair correspondence is found between the results of theoretical forecasting and experimental data on crystal structures and conductivity of various phases of alkali solid conductors. In particular, the method gives a proper qualitative prediction of existence, dimensionality, and directions of the migration paths in NASICON, LIPHOS, and other known superionic materials.

The main advantages of the proposed method over the traditional 'geometrical' approaches [1, 2] are its independence of any system of ionic radii, and use of 'topological' criteria for determining the channel network: this network coincides with the edge net of a Voronoi-Dirichlet partition. Let us emphasize that the algorithm and the principles of the analysis are independent of the nature of superionic material: there are no essential obstacles to apply them in the investigations of anionic solid conductors, molecular sieves, or molecular substances. The method is implemented into an automatized computer program that allows one to search for perspective solid conductors within large groups of inorganic compounds.

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