Anisotropy of Chemical Bonding in Semifluorinated Graphite C$_2$F Revealed with the Angle-Resolved X-Ray Absorption Spectroscopy

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Supporting Information

Supplementary Figures

Figure S1. XRD pattern of initial HOPG (a), fluorinated HOPG keeping in a cell under the Br$_2$ vapors (b), and fluorinated HOPG dried in nitrogen flow (c). The measurements were performed using a DRON-SEIFERT-RM4 powder diffractometer (Cu Kα radiation). The distance between the adjacent intercalate layers in Br$_2$–C$_2$F compounds was determined from the position of (002) reflection.

Figure S2. Raman spectrum of the fluorinated HOPG measured at the excitation of 514.5 nm.
**Figure S3.** XPS F 1s spectrum (a) and Br 3d spectrum (b) of the fluorinated HOPG. The spectra were measured using a monochromatized Al Kα radiation with the energy of 1486.7 eV. The Br 3d spectrum was fitted by two 3d_{5/2}–3d_{3/2} spin-orbit doublets with intensity ratio 2:1.

**Figure S4.** CK-edge NEXAFS spectra simulated for two C$_2$F models with isolated double bonds and different mutual orientation of four fluorine atoms in a hexagon. In the top model, C–F bonds are directed “up”, “down”, “up”, “down”, in the bottom models they are directed “up”, “up”, “down”, “down”. The bare carbon atoms are shown by white spheres, variation in color (blue or yellow) corresponds to the change of fluorine atom orientation relative to the graphene plane. The spectra have the same set of the peaks and the change in fluorine atoms orientation results in little change of some peaks in relative position (the peak around 274 eV) and relative intensity (the peak around 279.6 eV).
Figure S5. Fragment of fluorinated graphene where the fluorinated chains are separated by one-hexagon thick ribbon. The total energy of this fragment calculated at the B3LYP/6-31G level is ~0.15 eV higher than that of the model 1, where the fluorinated chains are separated by one-atom thick ribbon.

**Calculation of the theoretical curves corresponding to the behavior of the relative intensity of graphite π* resonance on the incidence angle θ of radiation**

The mutual orientation of graphite crystallites in the sample is characterized by a certain angular distribution. We can assume that this angular distribution is described by a normal law with zero mean:

\[
\rho(\Theta, w) = A \cdot \exp\left(-\frac{(\Theta / w)^2}{2}\right) \cdot \ln(2),
\]

where \( A \) is a normalizing factor. For a given half-width \( w \), the function \( \rho(\Theta, w) \) defines number of graphene sheets whose normal vectors are situated on a cone surface with an apical angle of \( 2\Theta \). The corresponding angular dependence of the intensity of the NEXAFS spectrum can be written as:

\[
I(\theta, w) = \int_0^{\pi/2} (I_{\pi}(\Theta, \theta) + I_{\pi}(\Theta, \theta)) \cdot \rho(\Theta, w) \cdot \sin \Theta d\Theta,
\]

where \( \sin \Theta \) is a weighting factor.

Figure S6 represents the dependence of the NEXAFS spectrum intensity on the incidence angle \( \theta \) of the polarized radiation calculated for various average angular deviations of graphene sheets from a sample surface.
Figure S6. Angular behavior of the relative intensity of π* resonance of graphite calculated for different Gaussian distribution $w$ of the graphene sheets in a sample.