Unraveling Structural Models of Graphite Fluorides by Density Functional Theory Calculations

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Supporting Information

S.1 Atomic configurations of C_2F ($CF_{0.5}$) crystal structure considered in this work

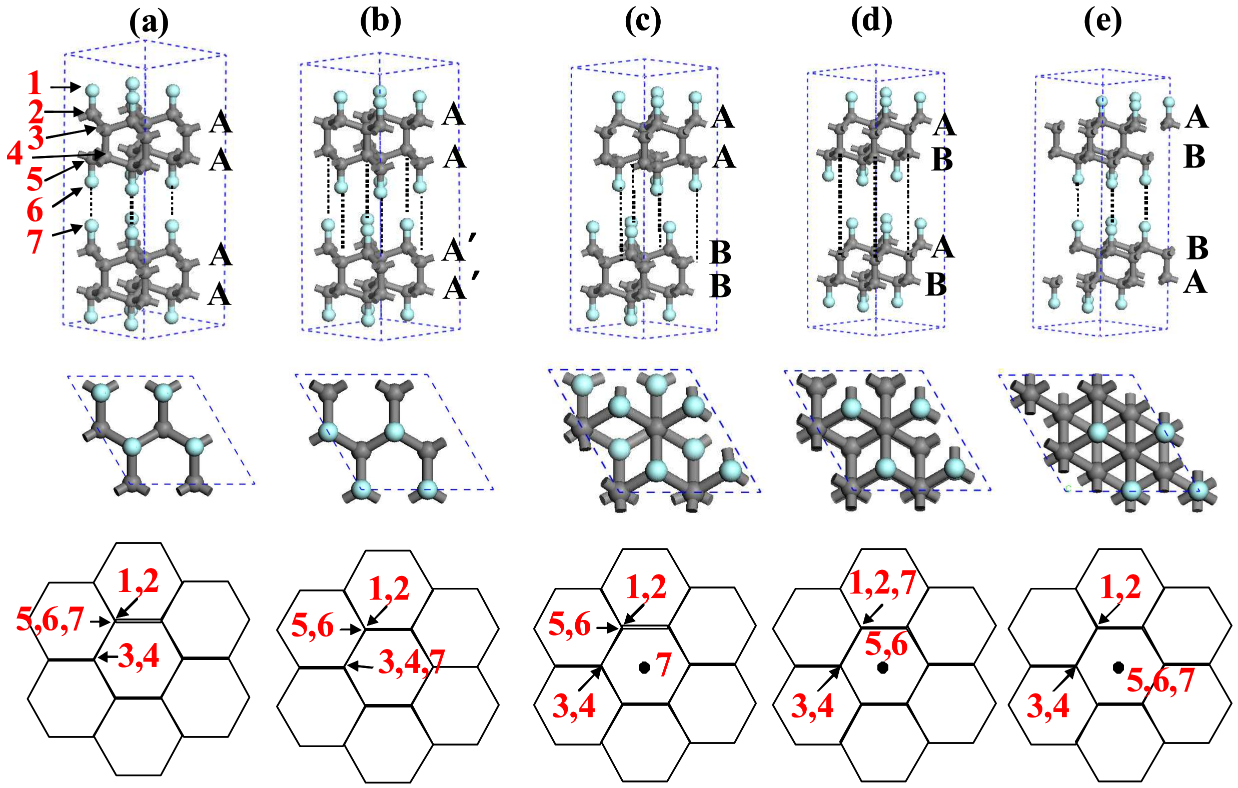


Figure S1. Atomic configurations of C_2F($CF_{0.5}$) crystal structures shown in Fig. 3(a)-(e). The first column indicates the overview of each structure, the second is top view, and the third is the schematic picture of atomic configuration. Here gray and cyan are carbon and fluorine, respectively. Also, the numbers of 1, 6, and 7 means fluorine atoms and 2-5 carbon atoms.

S2 Difference between original Kita model and new Kita model

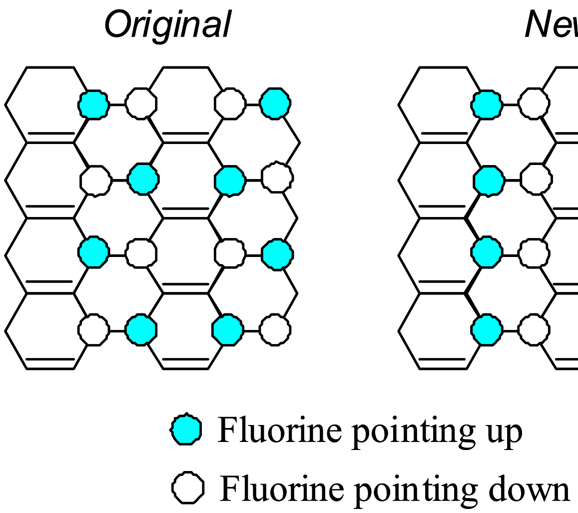
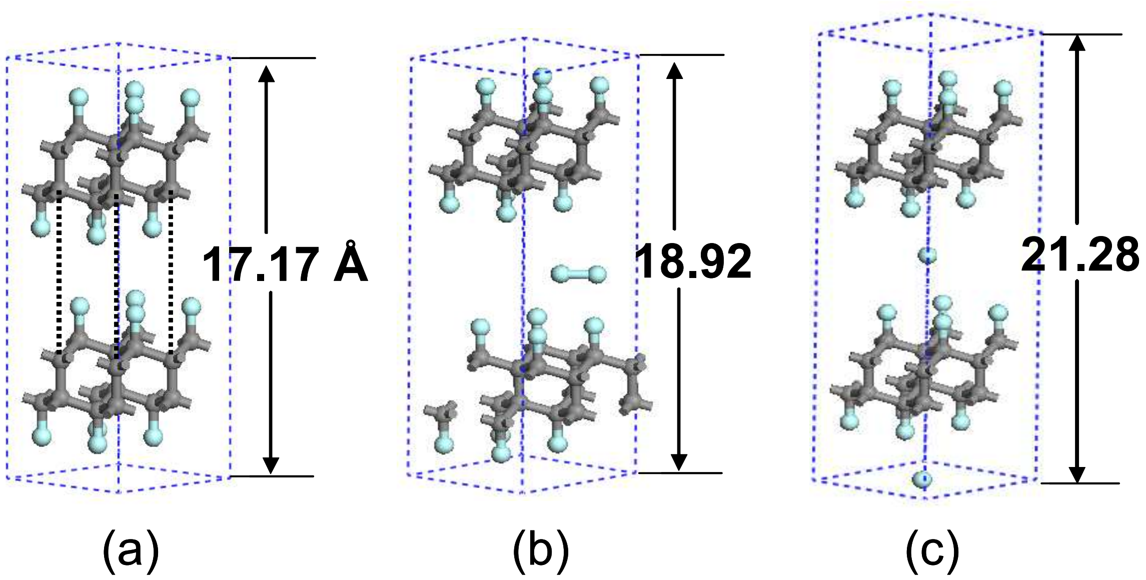


Figure S2. Original model proposed by Kita et al.9e and new Kita-like model (Fig. 6e). The models differ in the way fluorine line up perpendicular to the double bonds. In the original model, the fluorines line in an alternating fashion (up and down), while in the new Kita-like modle all of the up and down fluorines line up together in rows. Lining up in an alternating fashion created large distortions in the carbon-carbon bonds, causing high heat of formation and incompatible layer stackings. On the other hand, the new model is a regular periodic structure.

S.3 DFT result on structural change of C_2F ($CF_{0.5}$) crystal with further fluorination



(a) (b) (c)

Figure S3. DFT results on structural change of C_2F ($CF_{0.5}$) crystal (Fig. S1(d)) as proposed by Touhara et al.[7] with further fluorination. (a) pure C_2F, (b) C_2F after adding a F_2 molecule, and (c) C_2F after adding two F atoms. These structures show the end-points of the DFT-energy minimization and indicate that no C-C bond cleavage takes place and fluorine remains in the interlayer-space.

S.4 DFT result on C-C dissociation in reported C_2F ($CF_{0.5}$) structure

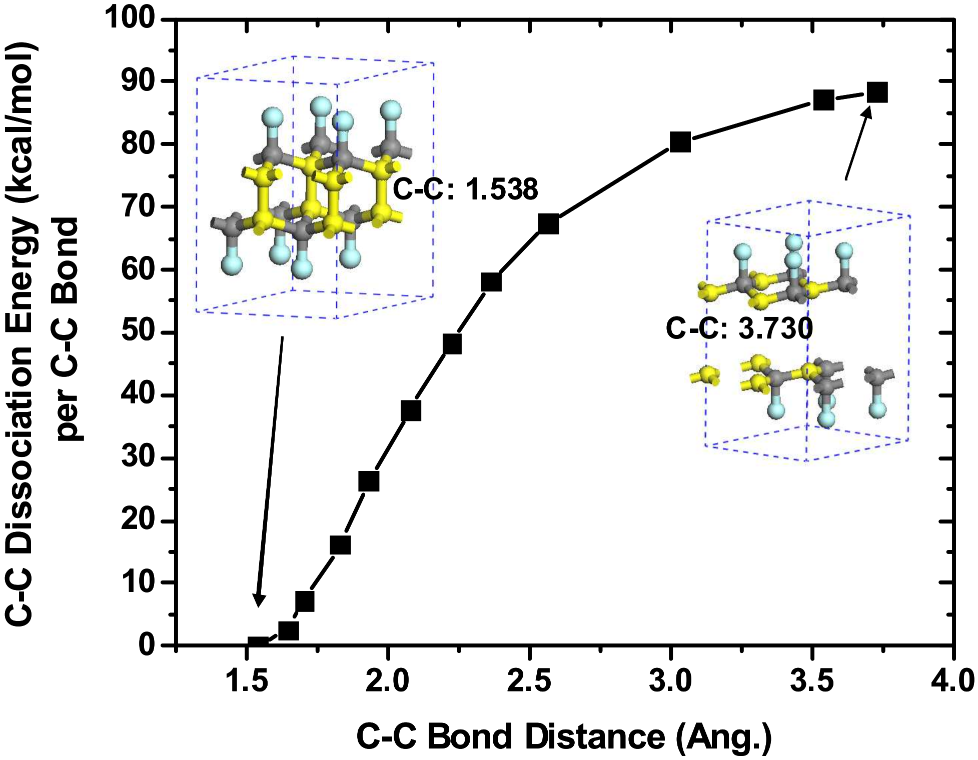


Figure S4. DFT results on C-C bond dissociation of C_2F ($CF_{0.5}$) crystal (Fig. S1(d)) as proposed by Touhara et al.[7] During geometry optimization process, carbon atoms (yellow) with C-C carbon bonds are fixed, however all of others are fully optimized. And because of calculation cost, only two graphene layers were considered.

S.5 Formation mechanisms of graphite fluorides by direct F_2 molecules

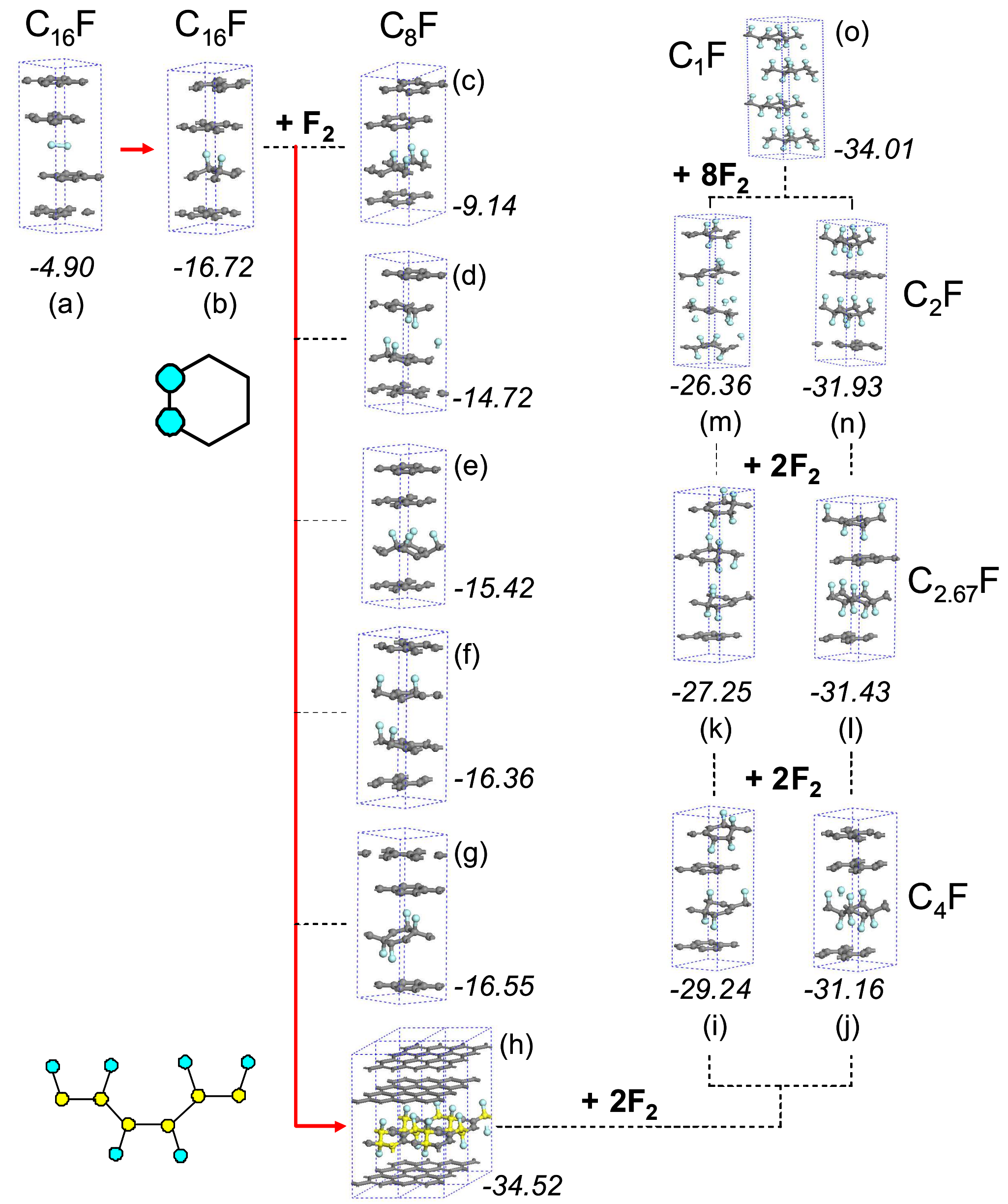


Figure S5A. The formation mechanism of graphite fluorides by the ortho configuration of fluorine. The numbers underneath the structures indicate their heat of formation (in kcal/mol) relative to pure graphite and a F_2 molecule, calculated by DFT. Here the final product is Fig. (h) of C_8F.

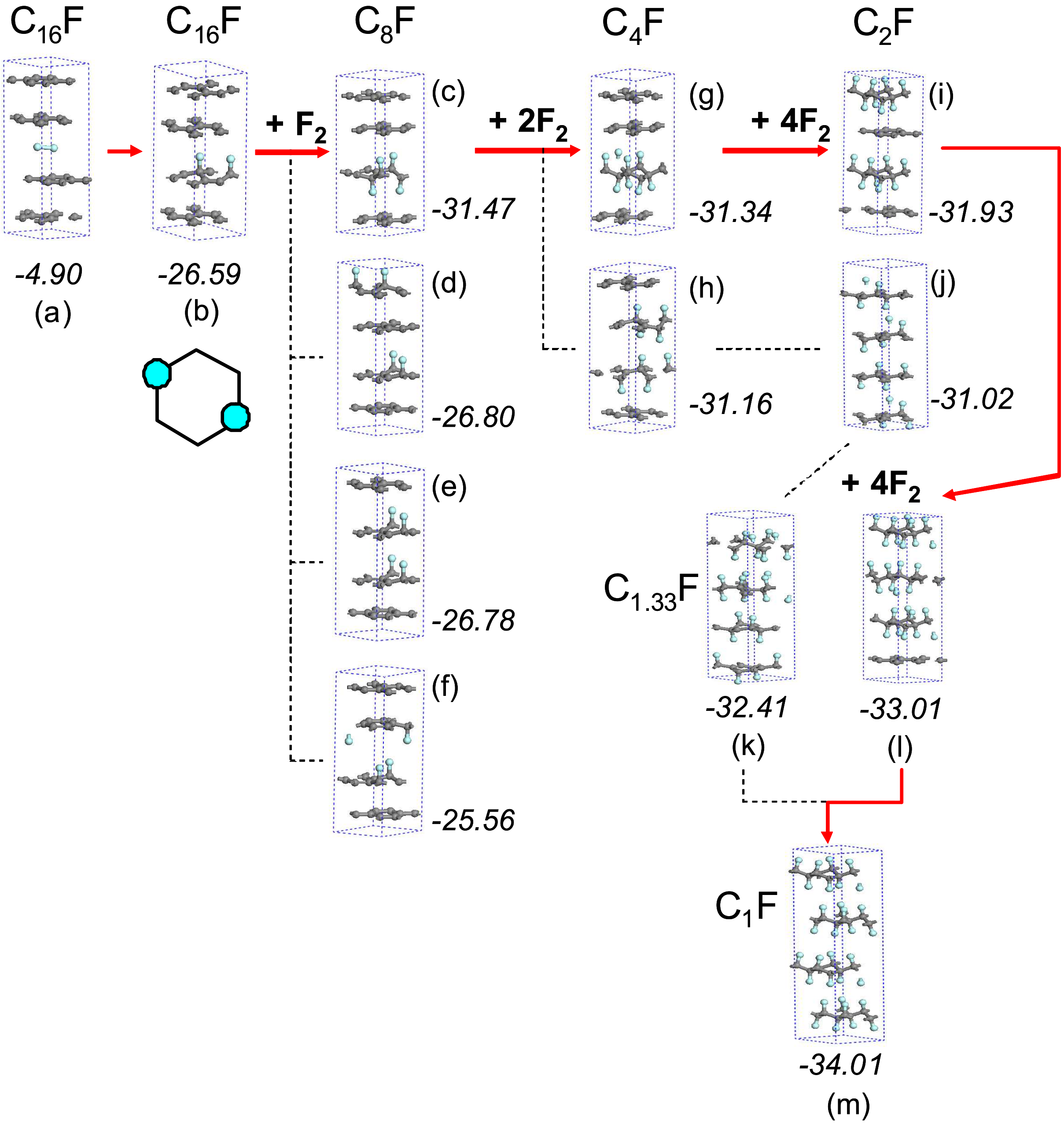


Figure S5B. The formation mechanism of graphite fluorides by the para configuration of fluorine. The numbers underneath the structures indicate their heat of formation (in kcal/mol) relative to pure graphite and a F_2 molecule, calculated by DFT. Here the final product is Fig. (m) of boat-type C_1F, and Fig. (j) is same to a model suggested by Kita et al.[9c]