# Reactivity of Fluorographene: A Facile Way toward Graphene Derivatives

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S *Supporting Information*

ABSTRACT: Fluorographene (FG) is a two-dimensional graphene derivative with promising application potential; however, its reactivity is not understood. We have systematically explored its reactivity in vacuum and polar environments. The C−F bond dissociation energies for homo- and heterolytic cleavage are above 100 kcal/mol, but the barrier of S_N2 substitution is significantly lower. For example, the experimentally determined activation barrier of the FG reaction with NaOH in acetone equals 14 ± 5 kcal/mol. The considerable reactivity of FG indicates that it is a viable precursor for the synthesis of graphene derivatives and cannot be regarded as a chemical counterpart of Teflon.
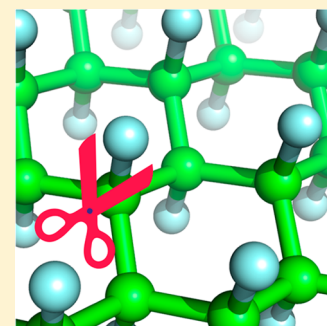
Halogenated graphenes are versatile 2D materials whose physical/chemical properties give them a wide range of potential applications[1,2] in fields such as (opto)electronics[3−5] and biomedicine.[6,7] Their practical potential is enhanced by the fact that their properties can be tuned by adjusting their degree of halogenation,[8,9] substitution patterns,[10,11] and the identity of their halogen components,[12] as well as by incorporating them into layered heterostructures.[13−15] Fluorographene (FG, C_1F_1), a prominent member of the halogenated graphene family, can be prepared by fluorinating graphene[16] or chemical/mechanical exfoliation of graphite fluoride.[3,17,18] FG is an insulator with a direct band gap of 7−8 eV[19,20] and has been regarded as a two-dimensional counterpart of polytetrafluoroethylene (more commonly known as Teflon),[17] which is widely used as a chemically inert and thermally stable nonadhesive surface coating.[21] This idea is supported by the rather high thermal stability of FG, which starts to decompose above 300 °C[17,22] and is converted into low-molecular-weight volatile compounds (C_xF_y) at temperatures above ∼500 °C.[16]

While the thermal decomposition of FG has been studied, little is known about its chemistry. The C−F bond is generally very strong, with a typical bond dissociation energy (BDE) of 108−130 kcal/mol.[23,24] Consequently, C−F bonds are usually rather unreactive,[21,24] which may explain the assumption that FG would be chemically inert. Surprisingly, however, it was shown that FG can be converted into graphene under rather mild conditions (150 °C, polar solvent) by reaction with KI.[18] The transient formation of C−I bonds was confirmed during this reaction. It may be that the C−F bond of FG has a semi-ionic character,[19,25] which could explain its unusually facile cleavage. Regardless of the underlying reason, this finding indicates that FG might undergo diverse substitution reactions,

making it a potentially valuable precursor for the preparation of other graphene derivatives. A very recent paper describing preparation of thiofluorographene from FG supports this idea.[26]

To shed light on the chemistry of FG, we investigated its reactivity using computational methods that have been shown to provide reliable information on the electronic structures of related materials,[13,27−29] their reactivity,[30,31] and their intermolecular interactions.[32,33] Several reaction scenarios were considered including radical decomposition, S_N1 and S_N2 nucleophilic substitution reactions, and elimination reactions. In addition, we explored the reactivity of FG at surface and edge sites (Figure 1), both in vacuum and in aqueous solution. We also analyzed the coverage dependence of the radical C−F bond cleavage reaction. Finally, as an example of high FG
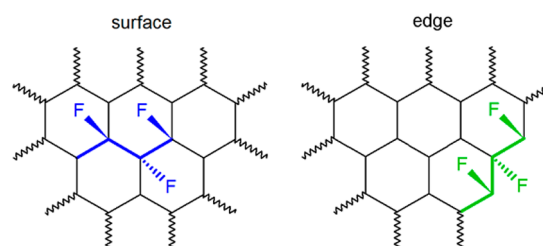

Figure 1. Finite FG surface models examined in this work, showing the surface and edge sites with the corresponding labels. The remaining F atoms are omitted for clarity.
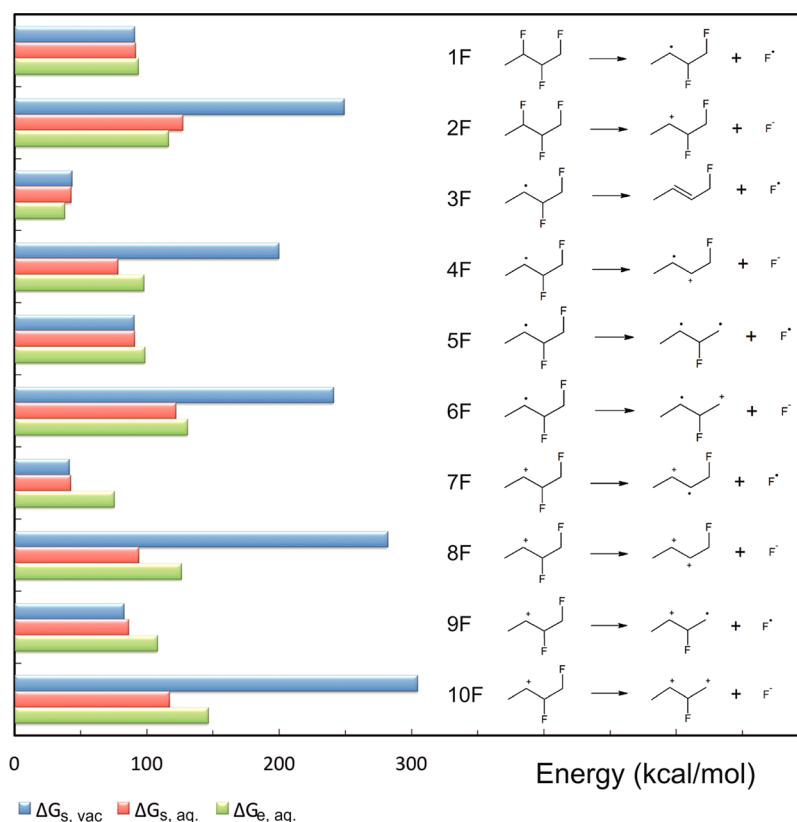
Figure 2. Reaction (bond dissociation) Gibbs free energies ΔG (at RT) for various FG defluorination pathways involving surface (ΔG_s) and edge (ΔG_e) sites in water (aq.) and vacuum (vac), in kcal/mol (see Table S1 in the Supporting Information for further details).

reactivity, we experimentally proved that FG reacts with NaOH in acetone (at ambient temperature), losing fluorine atoms. The apparent activation barrier of this reaction was found to be 14 ± 5 kcal/mol. Overall, our results explain the apparent susceptibility of FG to nucleophilic substitution, indicating that the S_N2 reaction mechanism is the kinetically preferred channel both in vacuum and in water. The results pave the way to the preparation of new graphene derivatives using FG as a versatile precursor.

The calculated BDEs and room temperature (RT) bond dissociation Gibbs free energies (BDGs) for the radical and S_N1 decompositions of FG are reported in Table S1 (Supporting Information) and Figure 2. The BDE of the C−F bond at the surface site (1F, Table S1, Supporting Information) was 104.7 kcal/mol in vacuum and 105.5 kcal/mol in water. The corresponding value for the edge site was 1.8 kcal/mol higher due to the presence of another fluorine atom bound to the same carbon atom.[21] The BDGs were lower (by 14 kcal/mol) than the corresponding BDEs because entropy favors the formation of dissociated states. After an initial homolytic C−F bond cleavage, the removal of a second surface fluorine atom from a carbon atom adjacent to the empty site with an unpaired electron (3F, Table S1, Supporting Information) became more energetically favorable; the BDE and BDG for the second C−F bond were both around 53 kcal/mol. This process, which results in the overall elimination of F_2 and the formation of a new carbon−carbon double bond, is even more favorable (by around 5 kcal/mol) at edge sites. The overall change in Gibbs free energy for the elimination reaction ($C_nF_n \rightarrow C_nF_{n-2} + F_2$) was 158.5 kcal/mol; for comparative purposes, the ΔE and ΔG values for the homolytic dissociation of F_2 ($F_2 \rightarrow F + F$) in

water at RT are 43.3 and 35.8 kcal/mol, respectively. These findings indicate that the removal of the first fluorine atom is the reaction-limiting step and that the elimination reaction is endothermic under ambient conditions. The high and positive Gibbs energy change of the elimination reaction explains the high stability of FG under ambient conditions.
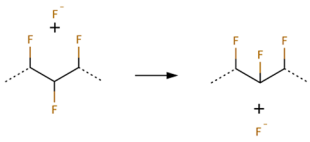
The homolytic dissociation of a surface C−F bond is much more favorable for the fluorine atoms that lie immediately next to the fluorine vacant site, and their removal via the radical pathway leads to a covalent bond formation. The strength of the C−F bond for the fluorine atoms at the second-nearest-neighbor site is not significantly affected (5F, Table S1, Supporting Information). These results imply that defluorination of FG may hardly proceed homogeneously over the entire surface, but rather, it more likely proceeds locally in the vicinity of defects.

The influence of the surface C/F ratio on the C−F BDE was analyzed using the periodic model (cf. the Supporting Information). Table 1 indicates that FG with a stoichiometry of C_1F_1 has the strongest C−F bond; the C−F BDE declined

Table 1. Distances between the C and F Atoms d(C−F), Energies Required to Remove a Neutral F Atom from Fluorinated Graphenes (BDE), and Deformation Energies (DE) as a Function of the Fluorine Coverage

stoichiometry	d(C−F) Å	BDE kcal/mol	DE kcal/mol
CF	1.38	112.3	26.1
C_2F	1.42	80.5	25.3
C_4F	1.46	76.2	22.8
$C_{32}F$	1.57	49.6	26.2

Table 2. S_N2 Reaction Relative Energies ΔE (kcal/mol) and Gibbs Free Energies ΔG (at RT, in Parentheses) with Respect to the Reactants (Infinitely Separated F^- and FG) in Water and Vacuum[b]

		R(vdw)	TS[a]	P(vdw)	P
Water	ΔE	−0.9	40.0	25.4	56.6
	ΔG	5.9	48.1	34.0	56.3
Vacuum	ΔE	−14.9	3.1	−21.8	57.0
	ΔG	−11.1	10.4	−13.7	56.8

[a]$\Delta E^{\ddagger}_{wat} = 40.9$, $\Delta E^{\ddagger}_{vac.} = 18.0$, $\Delta G^{\ddagger}_{wat} = 48.1$, $\Delta G^{\ddagger}_{vac.} = 21.1$ kcal/mol [b]R(vdw): van der Waals reactant; TS: transition state; P(vdw): van der Waals product; P: final product.

systematically (from 112 to 50 kcal/mol) as the fluorine content of the material fell. The energy required to restore the sp² hybridization of the FG carbon atoms clearly decreased with the F coverage because the presence of fluorinated sp³ carbon atoms caused local strain and disrupted the π-conjugation of graphene. As the deformation energy is almost constant for all fluorinated graphenes ranging from 23 to 26 kcal/mol, the disruption of π-conjugation seems to be responsible for the systematically decreasing BDE with the fluorine content. This finding is qualitatively consistent with the experimental observation of spontaneous fluorine atom loss from lightly fluorinated graphenes under ambient conditions[8,34] and our experimental results (cf. below). We note that similarly low BDEs have been reported for C−F bonds in low-coverage fluorinated graphene[35] and fluorinated carbon nanotubes.[36]

The energy required for the heterolytic S_N1 dissociation of a surface C−F bond with the release of a fluoride ion (2F, Figure 2) was twice as high as that required for homolytic dissociation in vacuum, and 40% greater than that required in water (1F, Figure 2). Heterolytic dissociation at the edge site was ~12 kcal/mol more favorable than that at the surface sites but still less favorable than the radical pathway. It should be noted that release of a second surface fluorine atom (see 4F, 6F, 8F, and 10F in Figure 2) from FG with a defect (a missing F atom or F anion) was energetically less demanding than the S_N1 cleavage of a C−F bond in unperturbed FG (2F, Figure 2). In vacuum, only reactions starting from neutral FG were cheaper (4F and 6F). Clearly, an additional positive charge is strongly disfavored (8F and 10F), contrary to the solvent environment able to accommodate and stabilize it (on the surface). On the other hand, at the edge, a second C−F bond cleavage was energetically more demanding than the first bond cleavage in all cases (6F, 8F, and 10F, Figure 2) except one (4F, Figure 2).

The energetics of the S_N2 reaction of FG with a nucleophilic fluoride anion are presented in Table 2. In vacuum, the activation free energy barrier amounted to 21.5 kcal/mol, and the reaction product was thermodynamically disfavored by 56.8 kcal/mol due to the buckling of the surface. In the polar water environment, the barrier increased to 48.1 kcal/mol, which is as expected for mechanisms of this sort.[37] These data clearly indicate that FG is kinetically susceptible to nucleophilic attack via the S_N2 mechanism, especially in nonpolar environments. In accord with this conclusion, experimental results have shown that the kinetics of FG reaction with KI is solvent-dependent.[18]

Our tests on FG with a stoichiometry of $C_{16}F$ indicated that low-coverage FGs are likely to be even more susceptible to S_N2 substitution. In a polar solvent, the presence of the F^- nucleophile induced the spontaneous removal of the opposite-side F atom from the low-coverage FG and in vacuum; the free energy barrier of the S_N2 reaction was only ~1 kcal/mol. Both reactant and product states are thus easily accessible; therefore, the products of the reaction are determined entirely by thermodynamic factors.

We experimentally verified the predicted susceptibility of FG for the substitution reaction with NaOH. We prepared FG colloid in acetone and monitored the reaction with NaOH (Supporting Information). At ambient conditions, the opalescent FG colloid changed its original color to gray–brown (Figures 3A and B), which allowed us to monitor the course of reaction by UV/vis spectroscopy. The reaction with NaOH was accompanied by a loss of fluorine atoms (Figure 3B). The X-ray photoelectron and Raman spectra suggest that the final product corresponds to graphene oxide (Figure 3C and Supporting Information). The activation free energy of the reaction, which was derived from the Eyring plot (Figure 3D), equaled to 14 ± 5 kcal/mol. The experimental value was lower than the theoretically predicted barrier of this reaction ($\Delta G^{\ddagger}_{acetone} = 31$ kcal/mol), which indicates that the calculated barriers represent an upper-bound limit for the reactivity, while real FG can be more reactive due to the presence of defects and irregularities. Any case, FG behaves as a substrate susceptible to nucleophilic attack rather than an inert unreactive Teflon-like material. Practical consequences of this finding include use of FG as a precursor for new graphene derivatives with an unforeseen potential in 2D chemistry.

We have analyzed the reactivity of FG and fluorinated graphenes and evaluated several mechanisms for the cleavage of their C−F bonds. The energies required for homo- and heterolytic cleavage of the C−F bond were rather high, amounting to more than 100 kcal/mol. However, the energy required for homolytic cleavage declined significantly as the fluorine content decreased in nonstoichiometrically fluorinated graphenes (C_xF_y). This may explain the experimentally observed spontaneous loss of fluorine atoms from lightly fluorinated graphene derivatives. FG was susceptible to S_N2 nucleophilic attack, which we proved also experimentally. This suggests that FG is a useful precursor material for the preparation of other graphene derivatives and may enable further investigations into the chemistry of carbon-based 2D
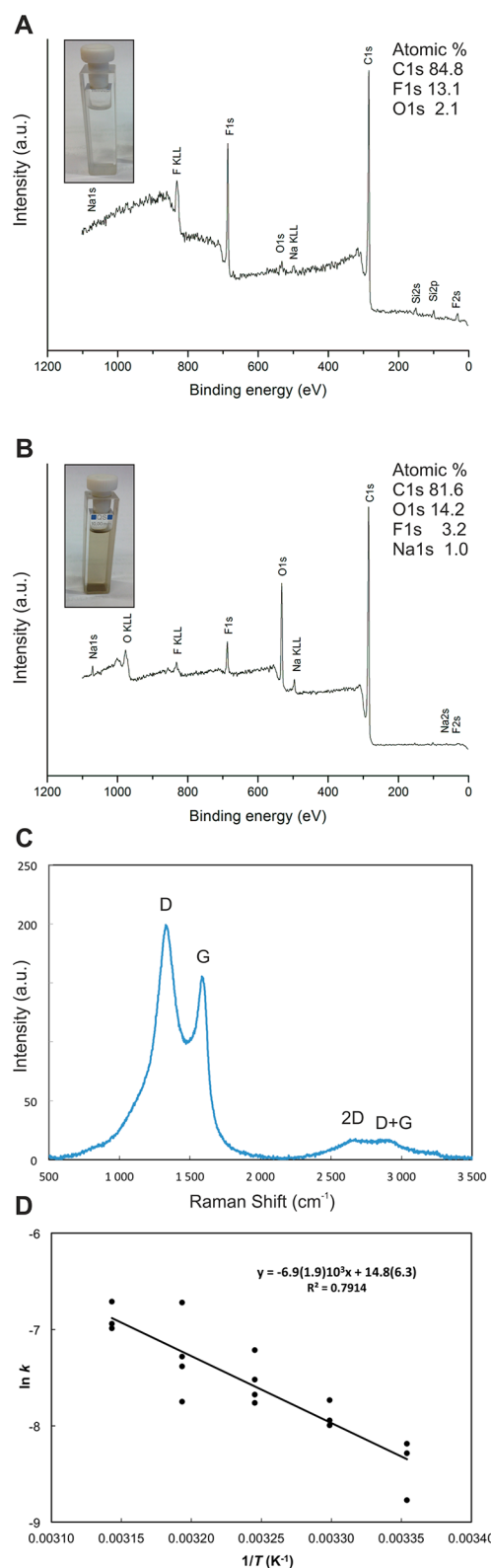
materials. Finally, the predicted reactivity of FG suggests that it cannot be regarded as a 2D equivalent of Teflon.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of the preparation of the fluorographene colloid, kinetic measurements, material characterizations by SEM, EDS, TEM, SAED, XPS, and Raman, and computational methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Karlický, F.; Datta, K. K. R.; Otyepka, M.; Zbořil, R. Halogenated Graphenes: Rapidly Growing Family of Graphene Derivatives. *ACS Nano* **2013**, *7*, 6434−6464.

(2) Georgakilas, V.; Otyepka, M.; Bourlinos, A. B.; Chandra, V.; Kim, N.; Kemp, K. C.; Hobza, P.; Zbořil, R.; Kim, K. S. Functionalization of Graphene: Covalent and Non-Covalent Approaches, Derivatives and Applications. *Chem. Rev.* **2012**, *112*, 6156−6214.

(3) Withers, F.; Dubois, M.; Savchenko, A. K. Electron Properties of Fluorinated Single-Layer Graphene Transistors. *Phys. Rev. B* **2010**, *82*, 073403.

(4) Wang, L.; Xie, X.; Zhang, W.; Zhang, J.; Zhu, M.; Guo, Y.; Chen, P.; Liu, M.; Yu, G. Tuning the Light Response of Organic Field-Effect Transistors Using Fluorographene Nanosheets as an Interface Modification Layer. *J. Mater. Chem. C* **2014**, *2*, 6484−6490.

(5) Ho, K.-I.; Huang, C.-H.; Liao, J.-H.; Zhang, W.; Li, L.-J.; Lai, C.-S.; Su, C.-Y. Fluorinated Graphene as High Performance Dielectric Materials and the Applications for Graphene Nanoelectronics. *Sci. Rep.* **2014**, *4*, 5893.

(6) Wang, Y.; Lee, W. C.; Manga, K. K.; Ang, P. K.; Lu, J.; Liu, Y. P.; Lim, T. C.; Loh, K. P. Fluorinated Graphene for Promoting Neuro-Induction of Stem Cells. *Adv. Mater.* **2012**, *24*, 4285−4290.

(7) Goenka, S.; Sant, V.; Sant, S. Graphene-Based Nanomaterials for Drug Delivery and Tissue Engineering. *J. Controlled Release* **2014**, *173*, 75−88.

(8) Stine, R.; Lee, W.-K.; Whitener, K. E.; Robinson, J. T.; Sheehan, P. E. Chemical Stability of Graphene Fluoride Produced by Exposure to XeF₂. *Nano Lett.* **2013**, *13*, 4311−4316.

(9) Kashtiban, R. J.; Dyson, M. A.; Nair, R. R.; Zan, R.; Wong, S. L.; Ramasse, Q.; Geim, A. K.; Bangert, U.; Sloan, J. Atomically Resolved Imaging of Highly Ordered Alternating Fluorinated Graphene. *Nat. Commun.* **2014**, *5*, 4902.

(10) Withers, F.; Bointon, T. H.; Dubois, M.; Russo, S.; Craciun, M. F. Nanopatterning of Fluorinated Graphene by Electron Beam Irradiation. *Nano Lett.* **2011**, *11*, 3912−3916.

(11) Lee, W. H.; Suk, J. W.; Chou, H.; Lee, J.; Hao, Y.; Wu, Y.; Piner, R.; Akinwande, D.; Kim, K. S.; Ruoff, R. S. Selective-Area Fluorination of Graphene with Fluoropolymer and Laser Irradiation. *Nano Lett.* **2012**, *12*, 2374−2378.

(12) Karlický, F.; Zbořil, R.; Otyepka, M. Band Gaps and Structural Properties of Graphene Halides and Their Derivates: A Hybrid Functional Study with Localized Orbital Basis Sets. *J. Chem. Phys.* **2012**, *137*, 034709.

Figure 3. (A) XPS spectrum of FG colloid (inset). (B) Loss of fluorine atoms from FG after reaction with NaOH and a change in the color (inset). The Raman spectrum of the product in (C) corresponds to graphene oxide. The Eyring plot in (D) shows the logarithm of experimentally measured rate constants (ln k) of the FG reaction with NaOH in acetone versus $1/T$. The activation free energy barrier is equal to 14 ± 5 kcal/mol, presented as the mean and tolerance interval at $\alpha = 0.05$.

(13) Li, Y.; Li, F.; Chen, Z. Graphane/Fluorographene Bilayer: Considerable C−H···F−C Hydrogen Bonding and Effective Band Structure Engineering. *J. Am. Chem. Soc.* **2012**, *134*, 11269−11275.

(14) Lin, X.; Xu, Y.; Hakro, A. A.; Hasan, T.; Hao, R.; Zhang, B.; Chen, H. Ab Initio Optical Study of Graphene on Hexagonal Boron Nitride and Fluorographene Substrates. *J. Mater. Chem. C* **2013**, *1*, 1618−1627.

(15) Geim, A. K.; Grigorieva, I. V. Van der Waals Heterostructures. *Nature* **2013**, *499*, 419−425.

(16) Robinson, J. T.; Burgess, J. S.; Junkermeier, C. E.; Badescu, S. C.; Reinecke, T. L.; Perkins, F. K.; Zalalutdniov, M. K.; Baldwin, J. W.; Culbertson, J. C.; Sheehan, P. E.; Snow, E. S. Properties of Fluorinated Graphene Films. *Nano Lett.* **2010**, *10*, 3001−3005.

(17) Nair, R. R.; Ren, W.; Jalil, R.; Riaz, I.; Kravets, V. G.; Britnell, L.; Blake, P.; Schedin, F.; Mayorov, A. S.; Yuan, S.; et al. Fluorographene: A Two-Dimensional Counterpart of Teflon. *Small* **2010**, *6*, 2877−2884.

(18) Zbořil, R.; Karlický, F.; Bourlinos, A. B.; Steriotis, T. A.; Stubos, A. K.; Georgakilas, V.; Šafářová, K.; Jančík, D.; Trapalis, C.; Otyepka, M. Graphene Fluoride: A Stable Stoichiometric Graphene Derivative and Its Chemical Conversion to Graphene. *Small* **2010**, *6*, 2885−2891.

(19) Karlický, F.; Otyepka, M. Band Gaps and Optical Spectra of Chlorographene, Fluorographene and Graphane from G0W0, GW0 and GW Calculations on Top of PBE and HSE06 Orbitals. *J. Chem. Theory Comput.* **2013**, *9*, 4155−4164.

(20) Karlický, F.; Otyepka, M. Band Gaps and Optical Spectra from Single- and Double-Layer Fluorographene to Graphite Fluoride: Many-Body Effects and Excitonic States. *Ann. Phys.* **2014**, *526*, 408−414.

(21) Lemal, D. M. Perspective on Fluorocarbon Chemistry. *J. Org. Chem.* **2004**, *69*, 1−11.

(22) Sun, C.; Feng, Y.; Li, Y.; Qin, C.; Zhang, Q.; Feng, W. Solvothermally Exfoliated Fluorographene for High-Performance Lithium Primary Batteries. *Nanoscale* **2014**, *6*, 2634−2641.

(23) Smart, B. E. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: Deerfield Beach, FL, 1986; Vol. 3, p 141.

(24) Sandford, G. Perfluoroalkanes. *Tetrahedron* **2003**, *59*, 437−454.

(25) Sato, Y.; Itoh, K.; Hagiwara, R.; Fukunaga, T.; Ito, Y. On the So-Called "Semi-Ionic" C−F Bond Character in Fluorine−GIC. *Carbon* **2004**, *42*, 3243−3249.

(26) Urbanová, V.; Holá, K.; Bourlinos, A. B.; Čépe, K.; Pumera, M.; Karlický, F.; Otyepka, M.; Zbořil, R. Thiofluorographene−Hydrophilic Graphene Derivative with Semiconducting and Genosensing Properties. *Adv. Mater.* **2015**, DOI: 10.1002/adma.201500094.

(27) Boukhvalov, D. W.; Katsnelson, M. I. Modeling of Graphite Oxide. *J. Am. Chem. Soc.* **2008**, *130*, 10697−10701.

(28) Hossain, M. Z.; Johns, J. E.; Bevan, K. H.; Karmel, J. H.; Liang, Y. T. Chemically Homogeneous and Thermally Reversible Oxidation of Epitaxial Graphene. *Nat. Chem.* **2012**, *4*, 305−309.

(29) Lazar, P.; Zbořil, R.; Pumera, M.; Otyepka, M. Chemical Nature of Boron and Nitrogen Dopant Atoms in Graphene Strongly Influences Its Electronic Properties. *Phys. Chem. Chem. Phys.* **2014**, *16*, 14231−14235.

(30) Cao, Y.; Osuna, S.; Liang, Y.; Haddon, R. C.; Houk, K. N. Diels−Alder Reactions of Graphene: Computational Predictions of Products and Sites of Reaction. *J. Am. Chem. Soc.* **2013**, *135*, 17643−17649.

(31) Cao, Y.; Liang, Y.; Zhang, L.; Osuna, S.; Hoyt, A.-L. M.; Briseno, A. L.; Haddon, R. C. K.; Houk, N. Why Bistetracenes Are Much Less Reactive than Pentacenes in Diels−Alder Reactions with Fullerenes. *J. Am. Chem. Soc.* **2014**, *136*, 10743−10751.

(32) Lazar, P.; Karlický, F.; Jurečka, P.; Kocman, M.; Otyepková, E.; Šafářová, K.; Otyepka, M. Adsorption of Small Organic Molecules on Graphene. *J. Am. Chem. Soc.* **2013**, *135*, 6372−6377.

(33) Cho, Y.; Cho, W. J.; Youn, I. S.; Lee, G.; Singh, N. J.; Kim, K. S. Density Functional Theory Based Study of Molecular Interactions, Recognition, Engineering, and Quantum Transport in π Molecular Systems. *Acc. Chem. Res.* **2014**, *47*, 3321−3330.

(34) Worsley, K. A.; Ramesh, P.; Mandal, S. K.; Niyogi, S.; Itkis, M. E.; Haddon, R. C. Soluble Graphene Derived from Graphite Fluoride. *Chem. Phys. Lett.* **2007**, *445*, 51−56.

(35) Sahin, H.; Topsakal, M.; Ciraci, S. Structures of Fluorinated Graphene and Their Signatures. *Phys. Rev. B* **2011**, *83*, 115432.

(36) Bettinger, H. F.; Kudin, K. N.; Scuseria, G. E. Thermochemistry of Fluorinated Single Wall Carbon Nanotubes. *J. Am. Chem. Soc.* **2001**, *123*, 12849−12856.

(37) Von Shaik, S. S.; Schlegel, H. B.; Wolfe, S. *Theoretical Aspects of Physical Organic Chemistry: The S_N2 Mechanism*; Wiley: New York, 1992.