SUSNANO
SUSTAINABLE NANOSENSORS

Summer School

Sustainable nanosensors for water pollution detection

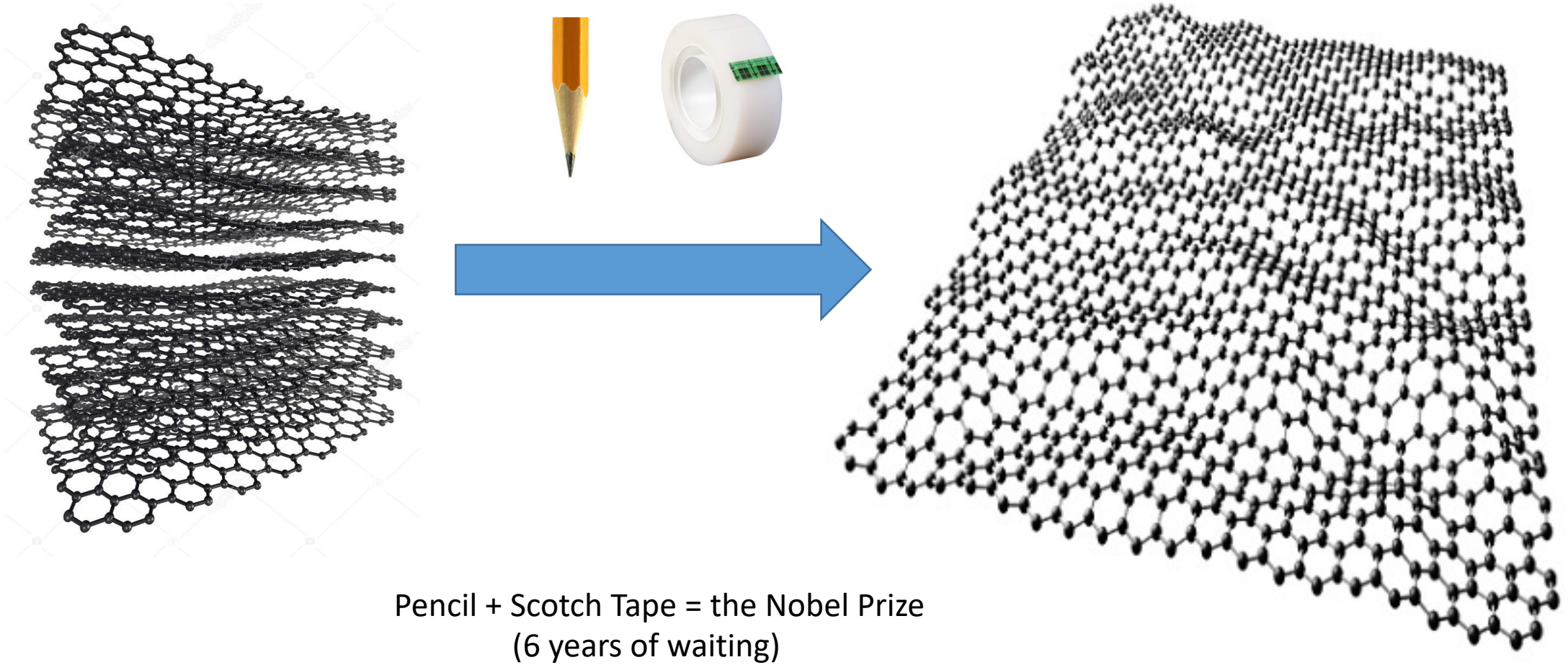
Tirana, March 23-25

Graphene derivatives based on fluorographene chemistry

by Michal Otyepka

Funded by the
European Union

Graphene



Pencil + Scotch Tape = the Nobel Prize
(6 years of waiting)

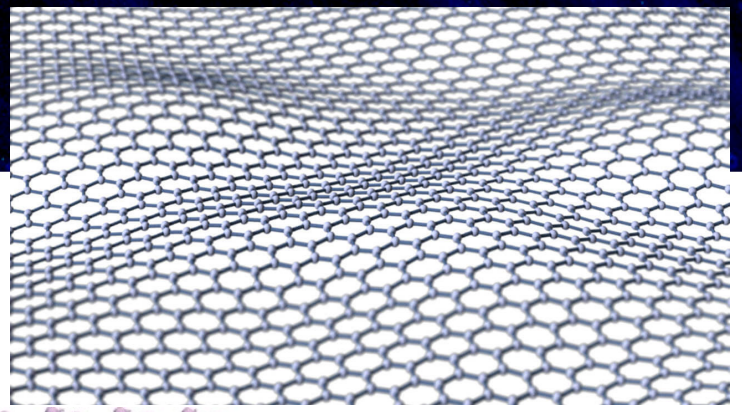
Graphene 2D material, which should not exist

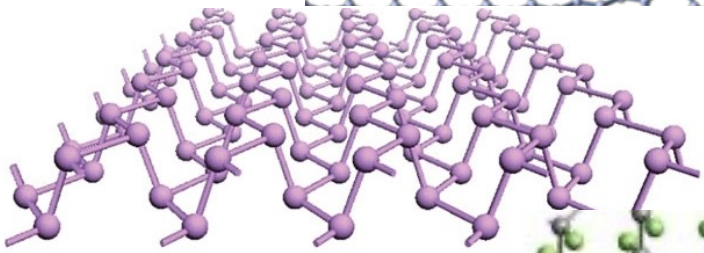
- *”More than 70 years ago, Landau and Peierls argued **that strictly two-dimensional (2D) crystals were thermodynamically unstable and could not exist**11,12. Their theory pointed out that a divergent contribution of thermal fluctuations in low-dimensional crystal lattices should lead to such displacements of atoms that they become comparable to interatomic distances at any finite temperature13. The argument was later extended by Mermin14 and is strongly supported by a whole omnibus of experimental observations. Indeed, the melting temperature of thin films rapidly decreases with decreasing thickness, and they become unstable (segregate into islands or decompose) at a thickness of, typically, dozens of atomic layers15,16. For this reason, atomic monolayers have so far been known only as an integral part of larger 3D structures, usually grown epitaxially on top of monocrystals with matching crystal lattices15,16. Without such a 3D base, 2D materials were presumed not to exist until 2004, when the common wisdom was flaunted by the experimental discovery of graphene7 and other free-standing 2D atomic crystals (for example, single-layer boron nitride and half-layer BSCCO)8. These crystals could be obtained on top of non-crystalline substrates8-10, in liquid suspension7,17 and as suspended membranes18.”*

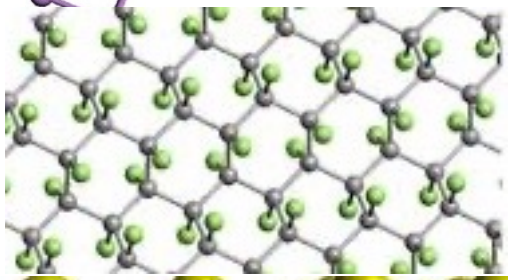
taken from … Nature Mat. 6, 183–191, 2007

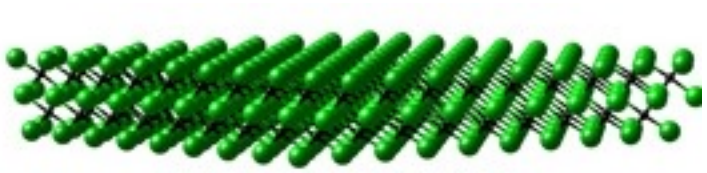
2D Materials

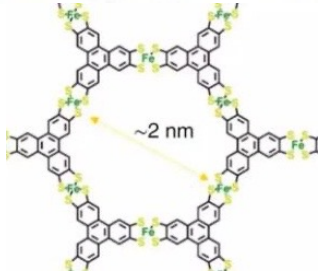
- Graphene - 2004 by Novoselov and Geim
- Wide family of 2D materials
  - One element
    - graphene (C), phosphorene (P) …
  - More elements
    - graphene derivatives – graphane (C_xH_x), fluorographene (C_xF_x), graphene oxide
    - graphene analogs – hBN
    - G-C_3N_4
    - MXenes (Ti_3C_2 …)
    - transition metal chalcogenides (MoS_2 …)
    - transition metal oxides and hydroxides (TiO_2, …
    - 2D zeolites
    - 2D MOFs, COFs











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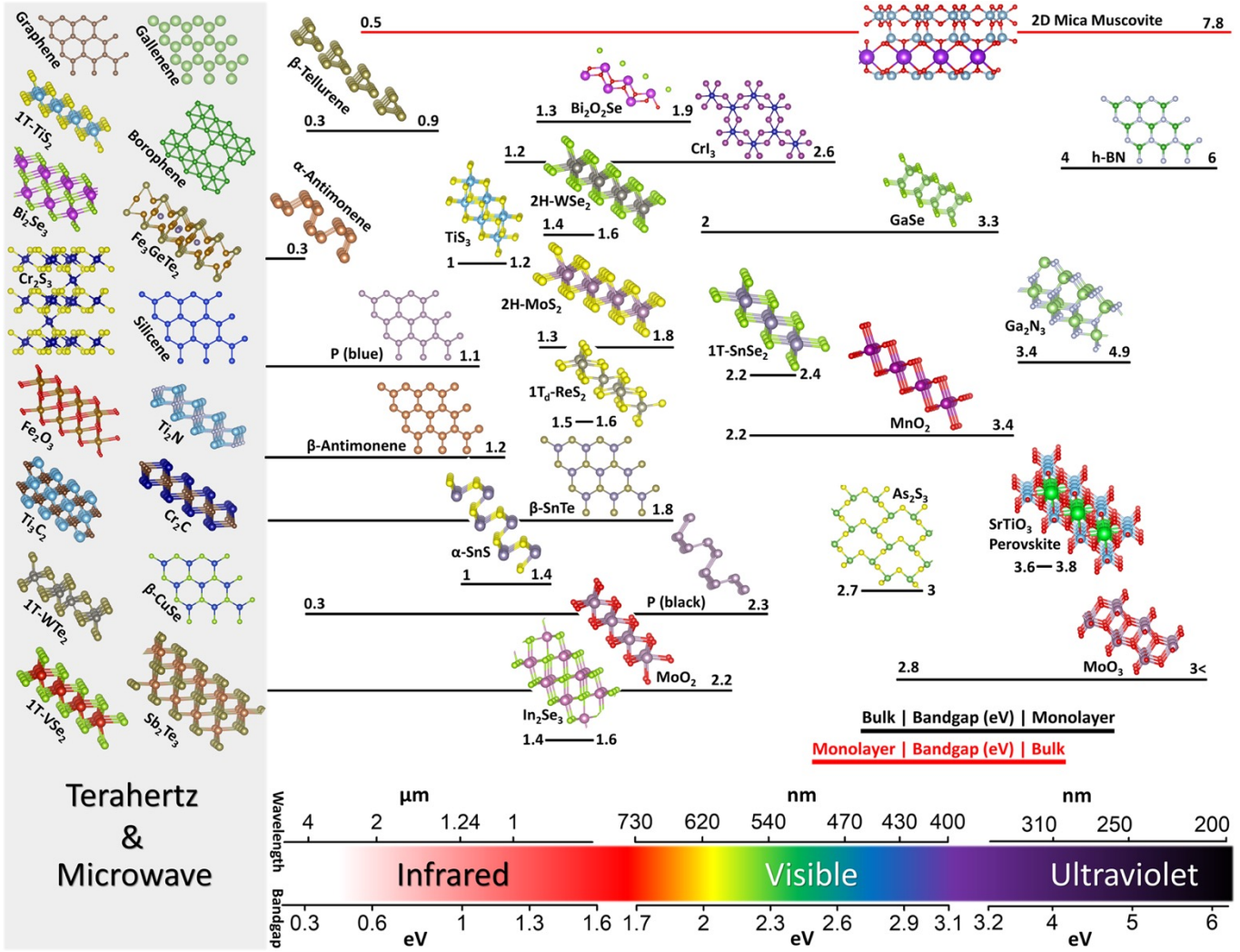
Band-gaps of 2D Materials



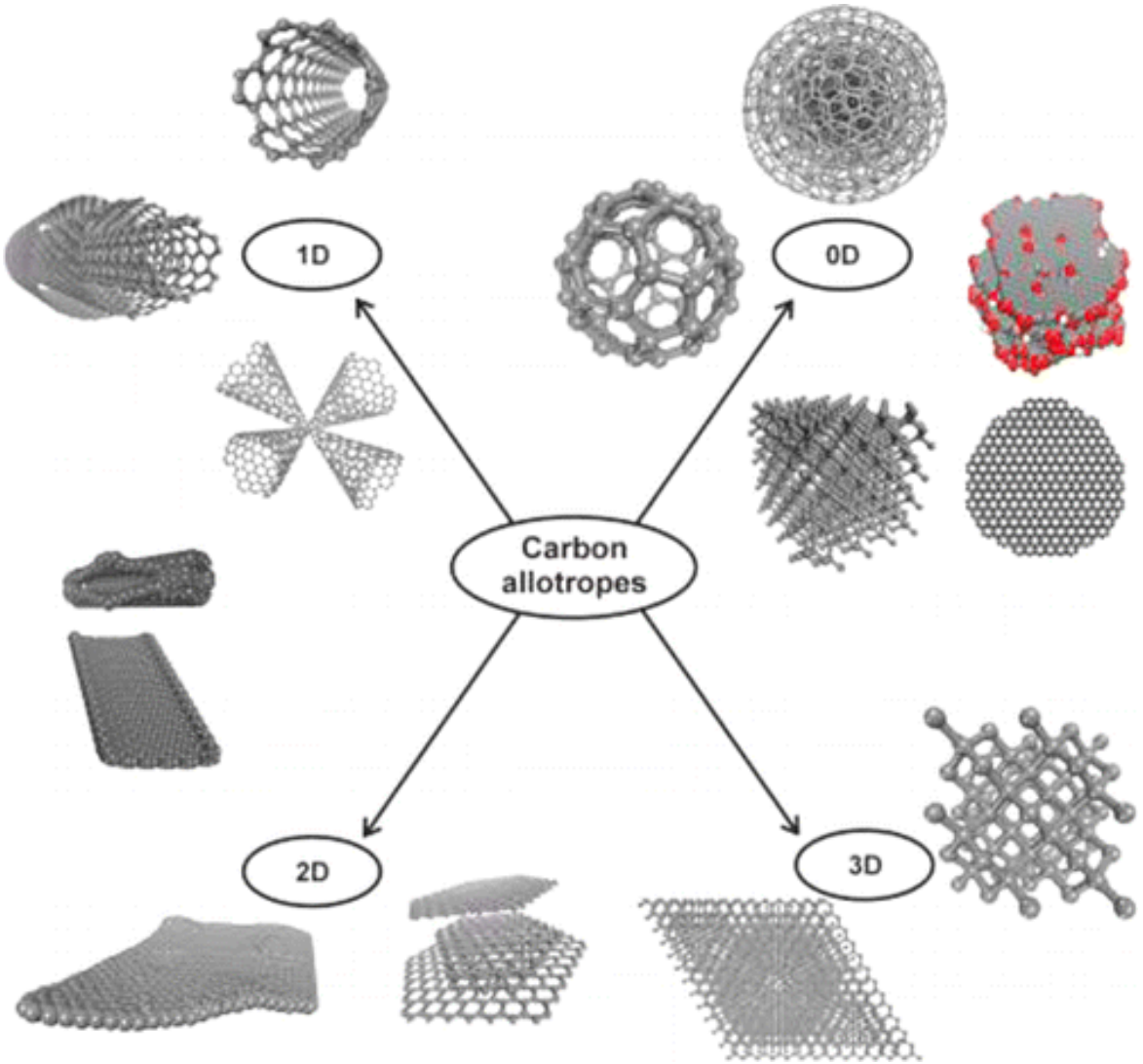
2D materials are chosen for their experimental significance and demonstration, with depictions of a perspective view of their crystal structures. Arrangement is in accordance with their bandgap, guided by the bottom wavelength/bandgap scale, whereas the bar beneath each structure indicates bandgap range from bulk to monolayer. Typically, the bulk bandgap is smaller than that of its monolayer (black bars), but there are exceptions (red bars). 2D materials on the far left, indicated by a gray box, are zero or near-zero bandgap, metallic, or semimetallic.

npj 2D Materials and Applications 4, 29 (2020)

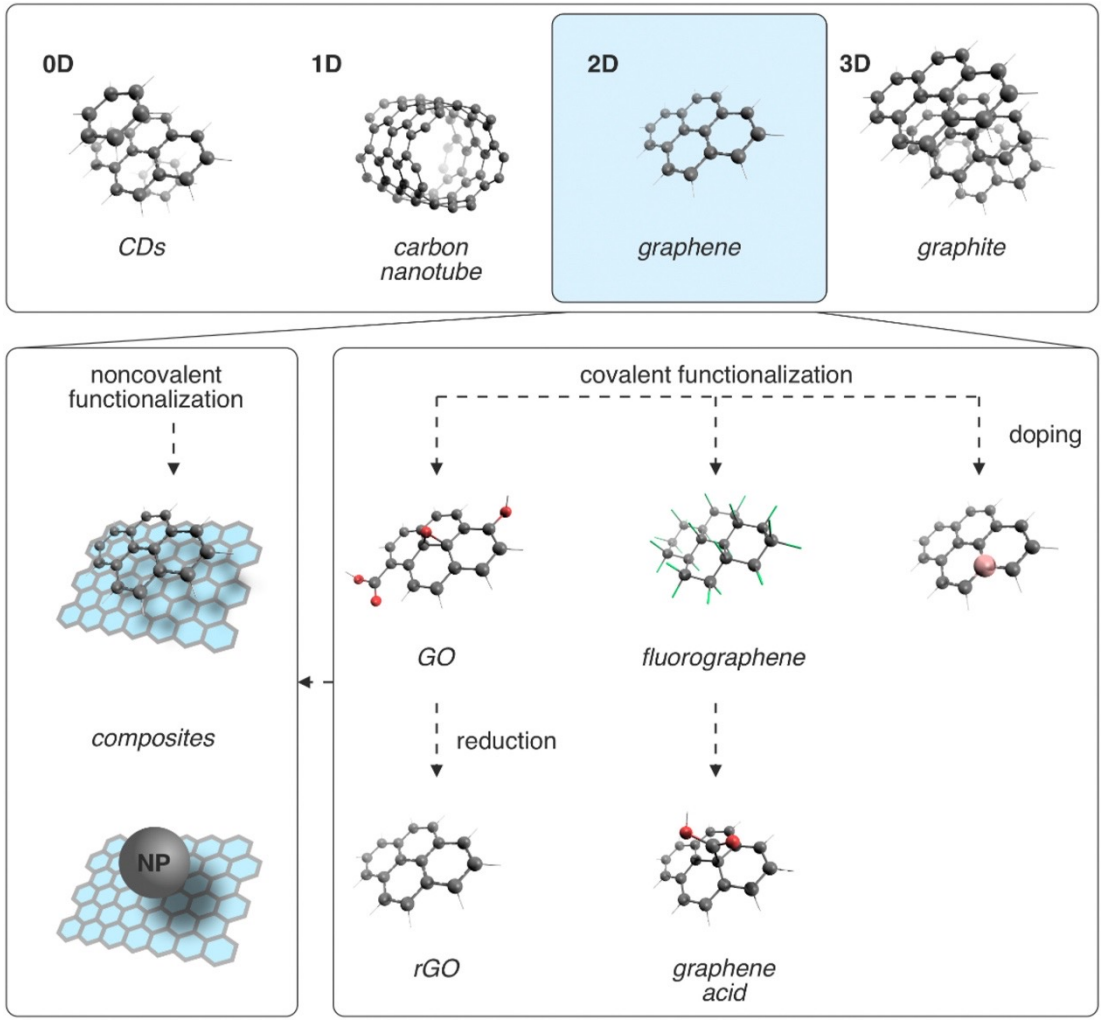
Carbon nanoallotropes

(i) 0D carbon nanostructures such as fullerenes, OLC structures, C-dots, and nanodiamonds, (ii) 1D nanoallotropes such as CNTs, carbon nanofibers, and SWNHs (although the latter are organized into 3D aggregates), and (iii) 2D nanoallotropes such as graphene, graphene nanoribbons, and few-layer graphenes

Chem. Rev. 2015, 115, 11, 4744–4822



Graphene functionalization



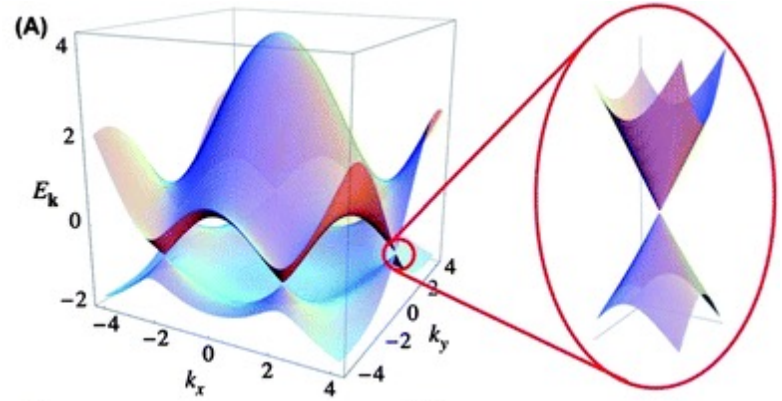
An overview of noncovalent and covalent graphene functionalization. CDs stands for carbon dots, GO graphene oxide, rGO reduced GO, and NP nanoparticle.

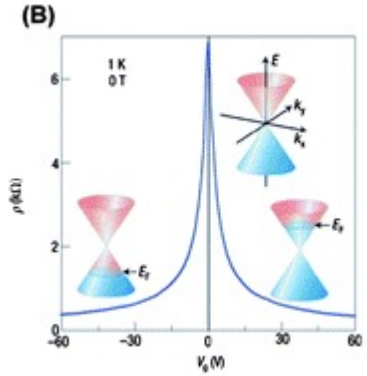
Biosens. Bioelectron., 166, 112436, 2020

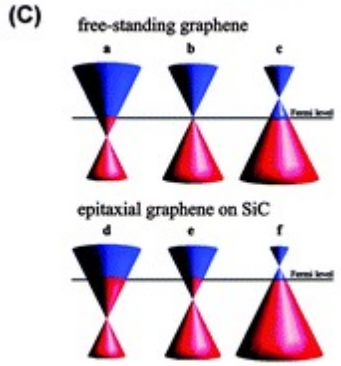
Georgakilas V, Otyepka M, Bourlinos AB, Chandra V, Kim N, Kemp KC, Hobza P, Zbořil R, Kim KS: Functionalization of Graphene: Covalent and Non-Covalent Approaches, Derivatives and Applications. *Chem. Rev., 112(11), 6156-6214, 2012*.

Noncovalent functionalization

Nature Materials 6, 652, 2007

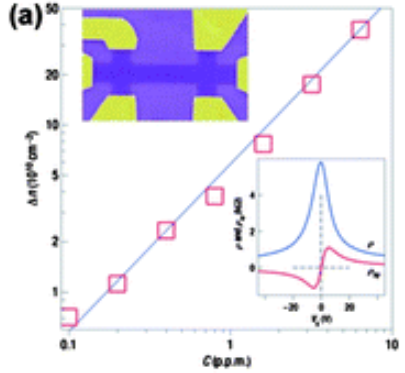


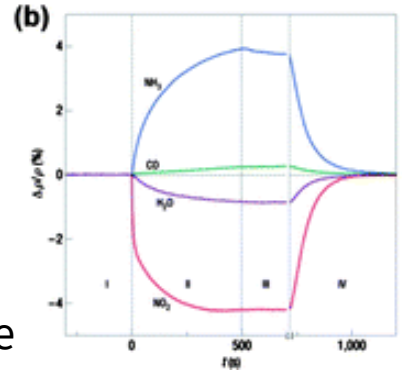


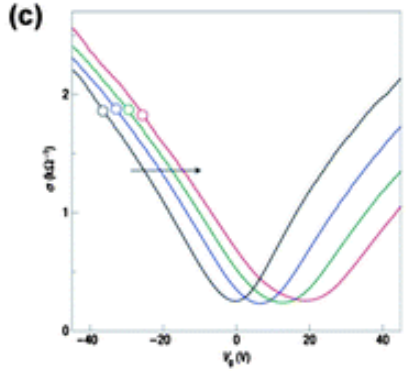


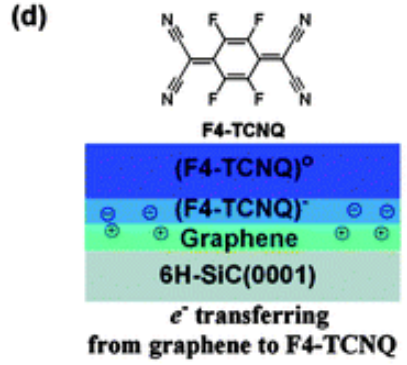
p-type

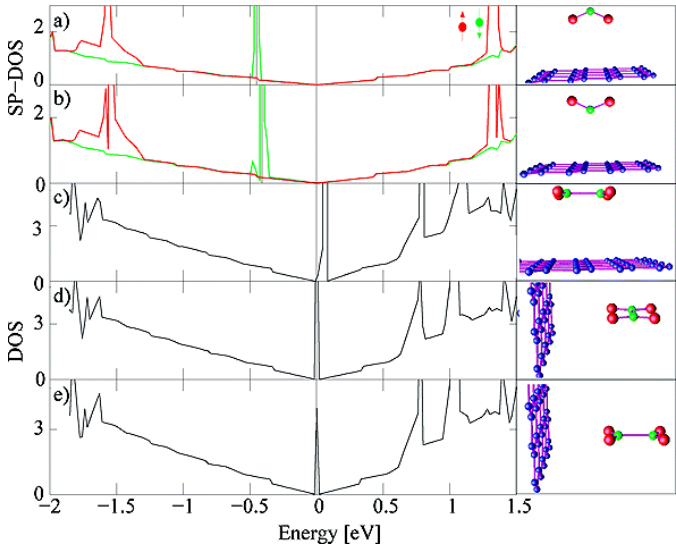
n-type











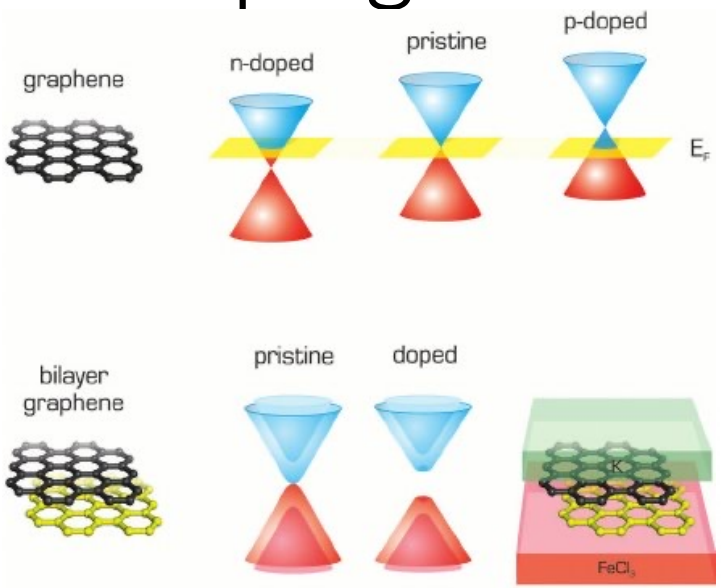
Nano Lett. 2008, 8, 1, 173

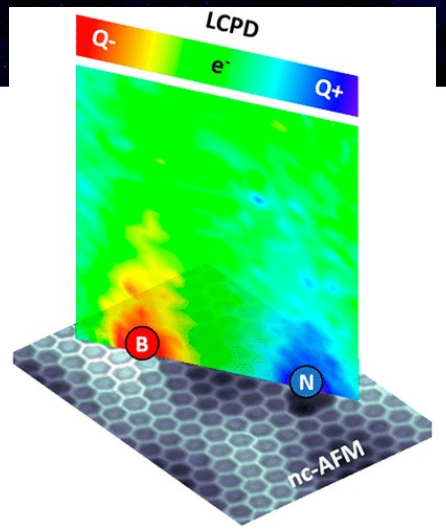
(A) Band structure of graphene and zoom-in of the energy bands close to the Dirac points. (B) Ambipolar electric field effect in single-layer graphene. (C) Position of the Dirac point and FL as a function of doping. The upper panel is n-type doped, pristine and p-type doped free standing graphene (a-c). The lower panel is n-type doped, pristine and p-type doped epitaxial graphene grown on silicon carbide (SiC) (d to f).

Concentration, $\triangle n$, of induced charge carriers in single-layer graphene exposed to different concentrations, C, of NO_2. (b) Changes in resistivity, ρ, at zero B caused by graphene's exposure to various gases diluted in concentration to 1 ppm. The positive (negative) sign of changes is chosen here to indicate electron (hole) doping. (c) Constant mobility of charge carriers in graphene with increasing chemical doping. The parallel shift implies a negligible scattering effect of the charged impurities induced by chemical doping.

J. Mater. Chem., 2011, 21, 3335 (+ refs therein)

Doping





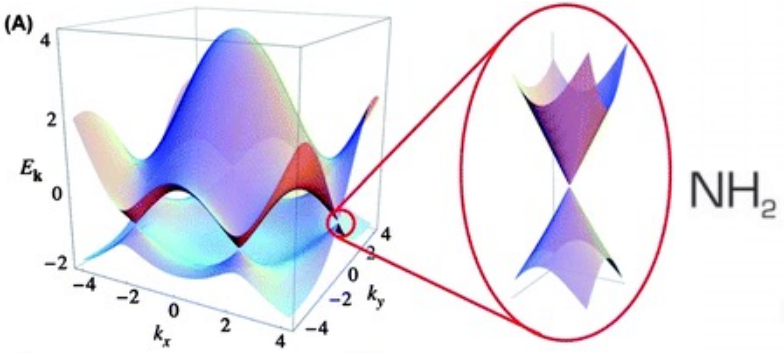
local potential difference (LCPD) measured above the dopant atoms

ACS Sustainable Chem. Eng. 2020, 8, 8, 3437

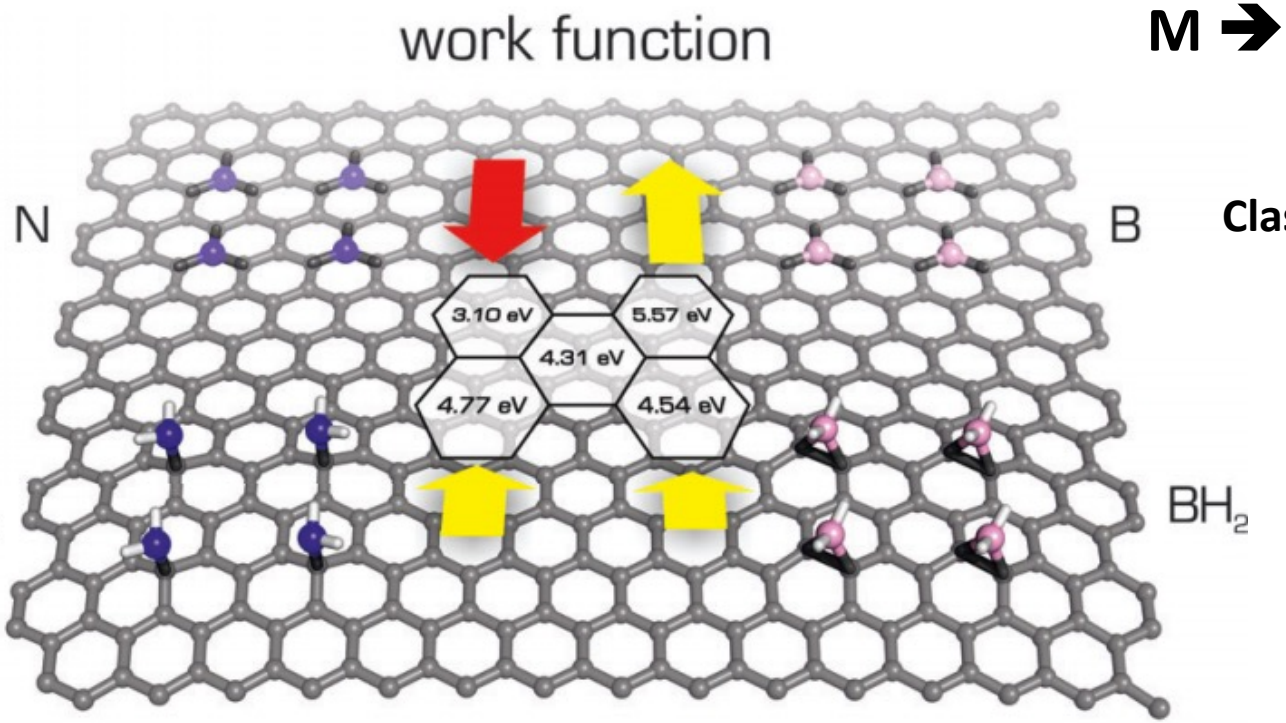
$$G + XH_x$$

$$W_f$$

$$M \rightarrow M^+ + e^-$$



J. Mater. Chem., 2011, 21, 3335



Classical n/p doping

Smaller effect but the same trend for N/B

PCCP, 16, 14231, 2014

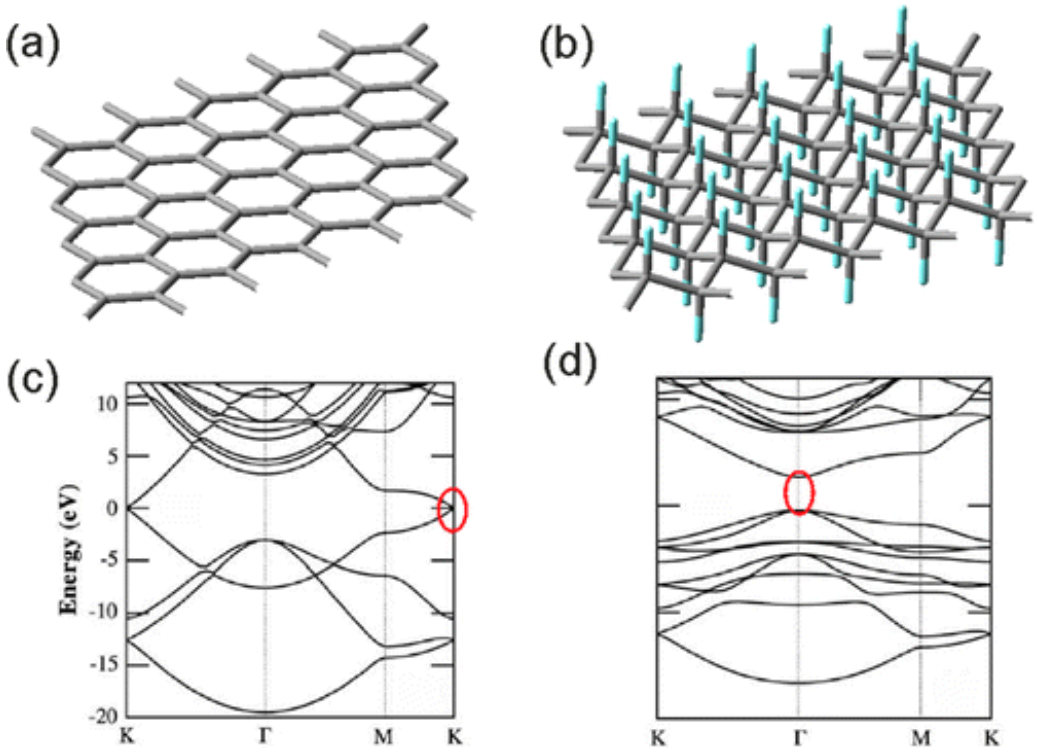
Graphene functionalization

- 2007 – Graphane and Graphene fluoride predicted
  - Sofo JO et al. PRB 75, 153401 (2007)
- 2009 – Graphane synthesized
  - Elias DC et al. Science, 323, 610 (2009)
- 2010 – Fluorographene/G. fluoride prepared
  - Fluorination of graphene
    - Robinson JT et al. Nano Letters 10, 3001 (2010)
    - Cheng SH et al. PRB 81, 205435 (2010)
  - Mechanical exfoliation of graphite fluoride
    - Nair RR et al. Small 6, 2877 (2010)
  - Chemical exfoliation of graphite fluoride
    - Zbořil R et al. Small 6, 2885 (2010)

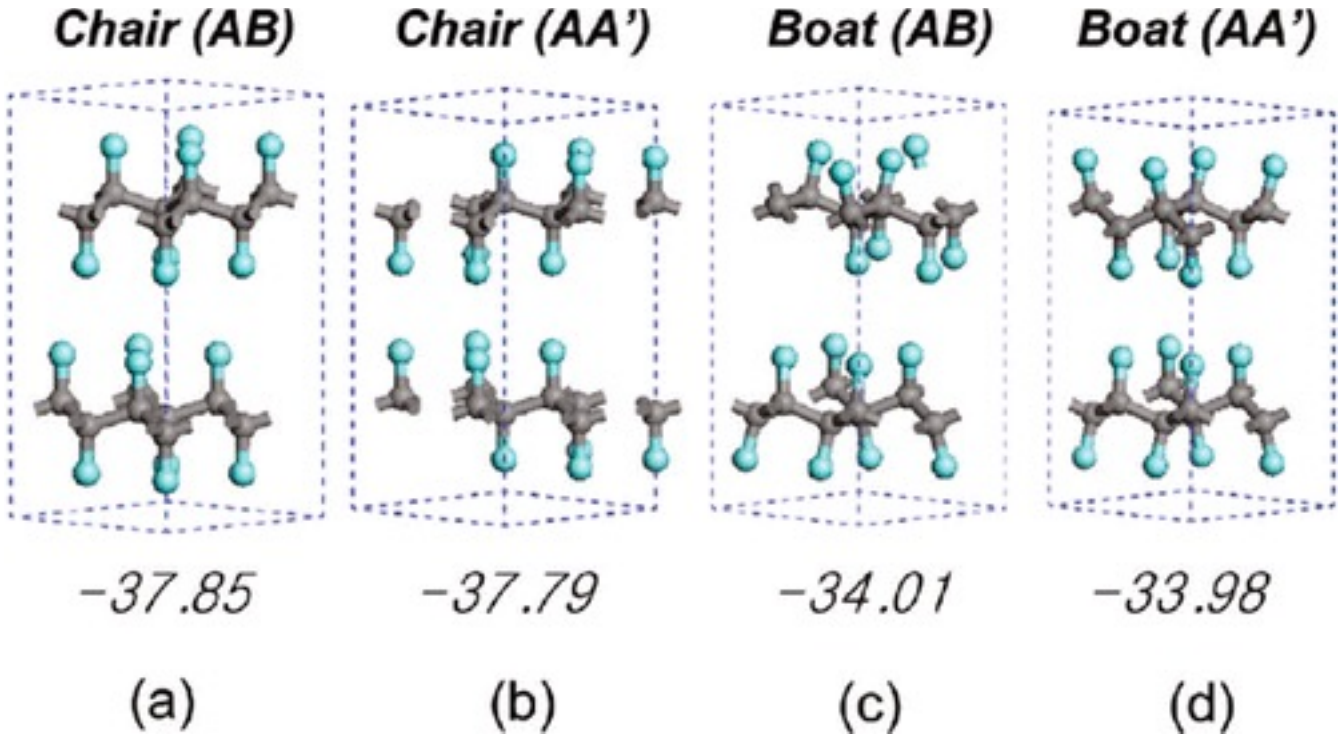
Phys. Rev. B, 75, 153401 (2007)

Graphene functionalization

sp^2 carbons to sp^3, decrease in conductivity
depends on the element, DF, topography/arrangement, …



ACS Nano 2013, 7, 8, 6434



Chem. Mater. 2010, 22, 2142

Graphene functionalization

sp^2 carbons to sp^3, decrease in conductivity
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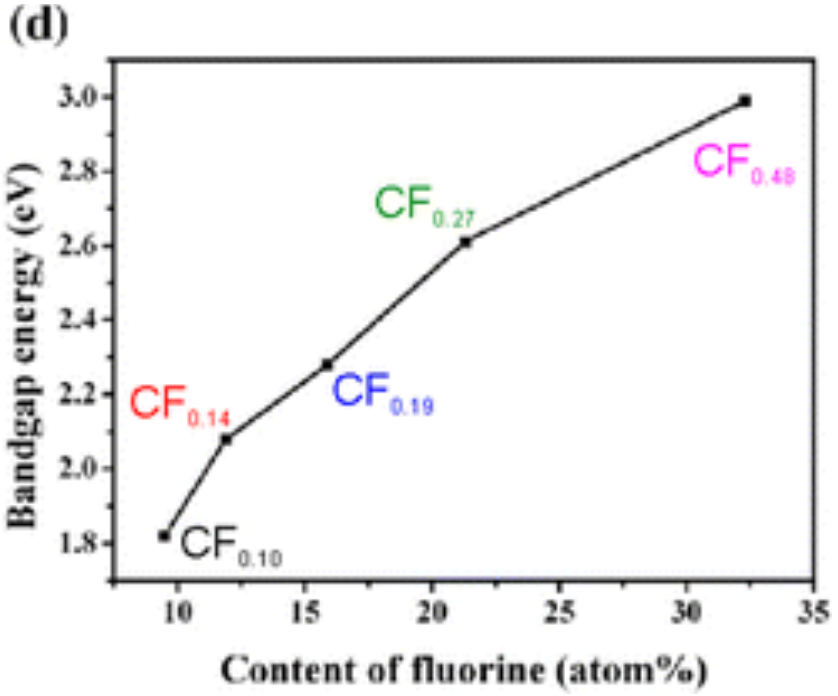
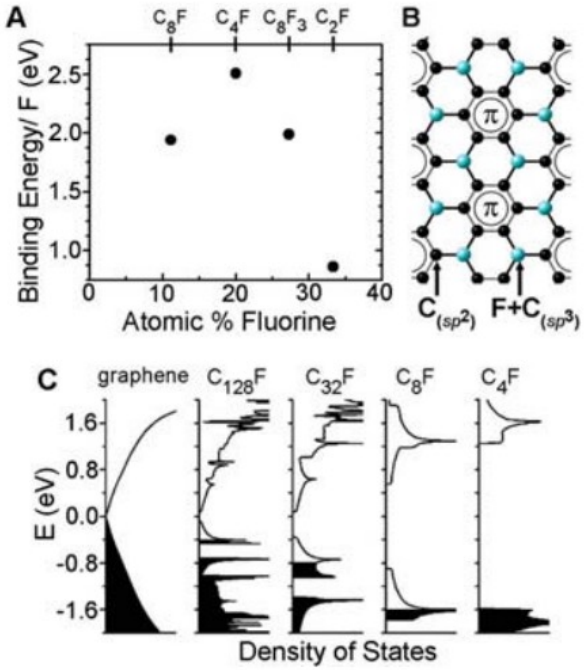
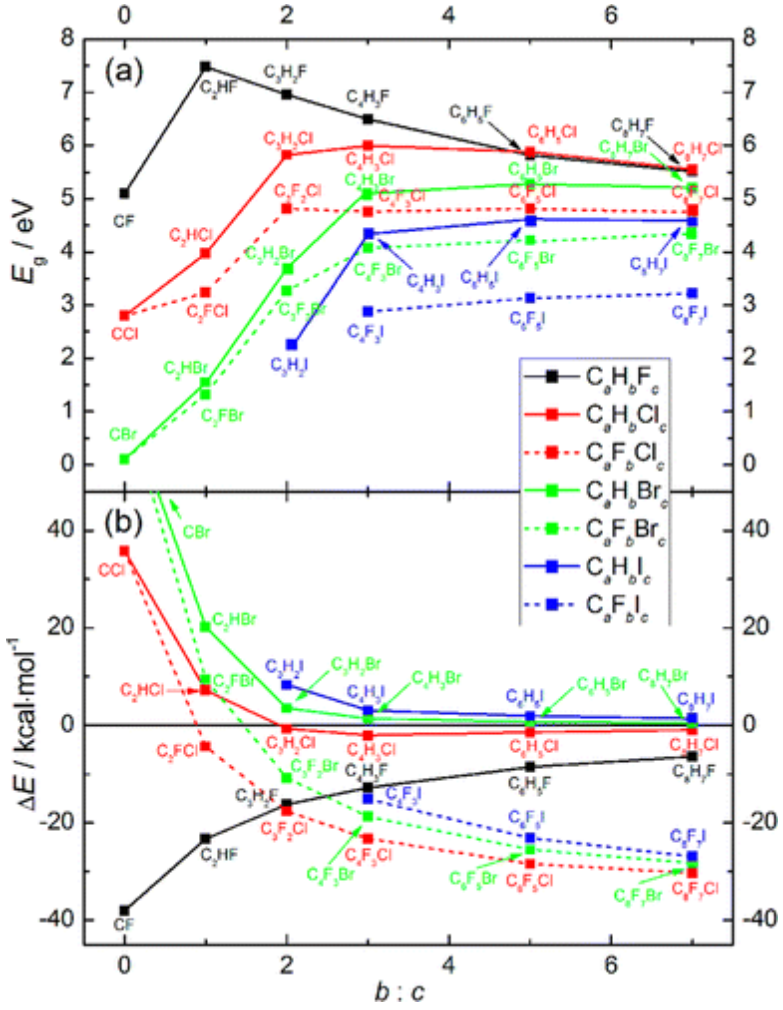


Carbon 2012, 50, 5403



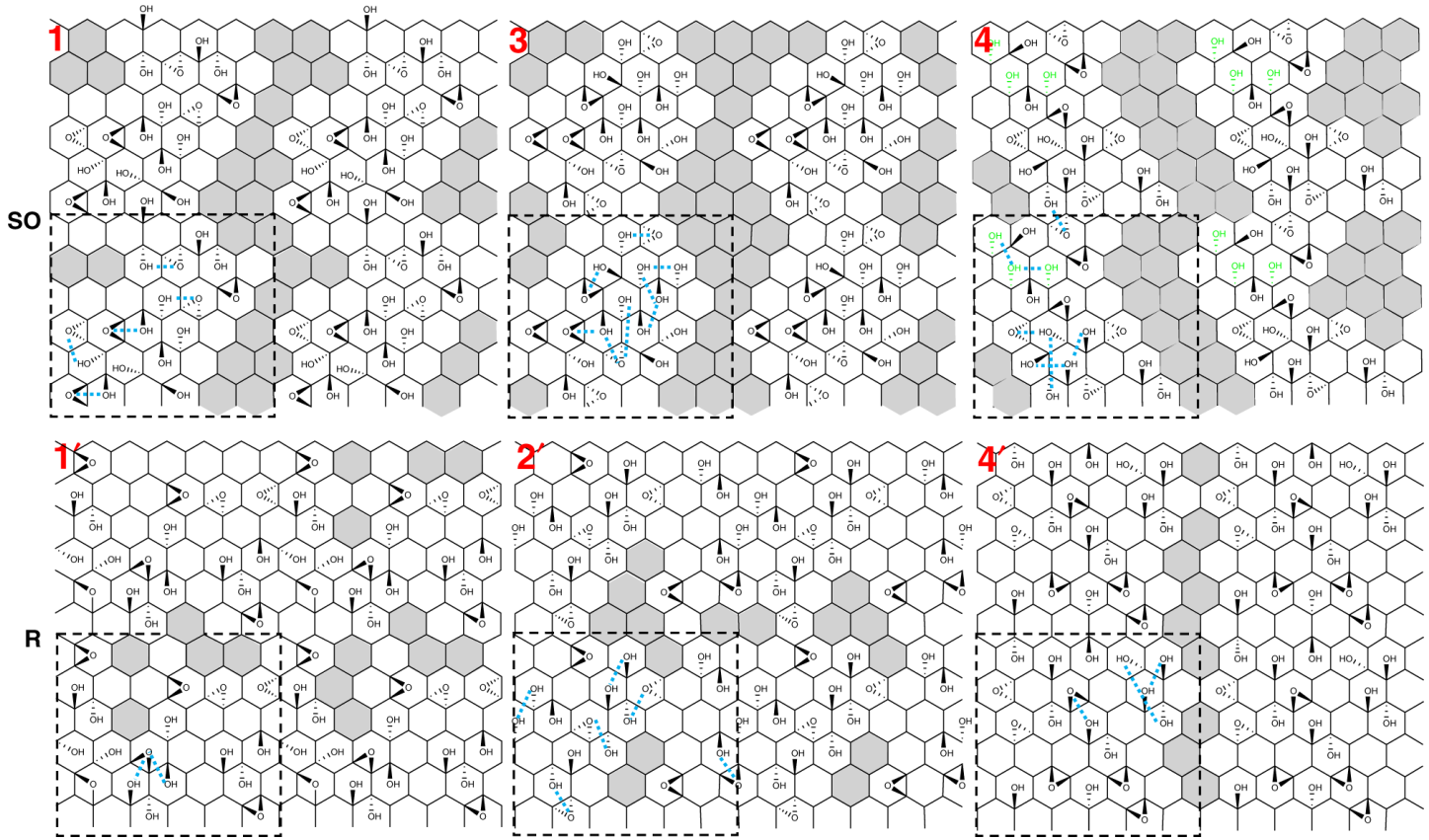
Nano Lett. 2010, 10, 3001



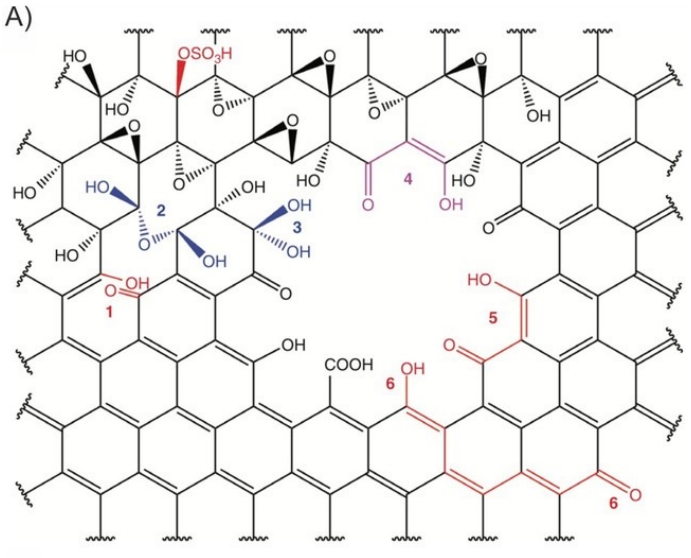
J. Chem. Phys. 2012, 137, 034709

Graphene oxide

- Prepared by oxidation of graphene/graphite + exfoliation, hydrophilic material, but non-conductive
- Chemically very complex material



Nature Communications 11, 1566 (2020)



ChemNanoMat 4, 3, 224, 2018

Graphene derivatives

- Noncovalent
  - Affecting properties of both graphene/adsorbate
  - Can be used for detection …
- Covalent
  - Significant effect on properties – band gap opening
    - Depend on element, degree of functionalization and topography

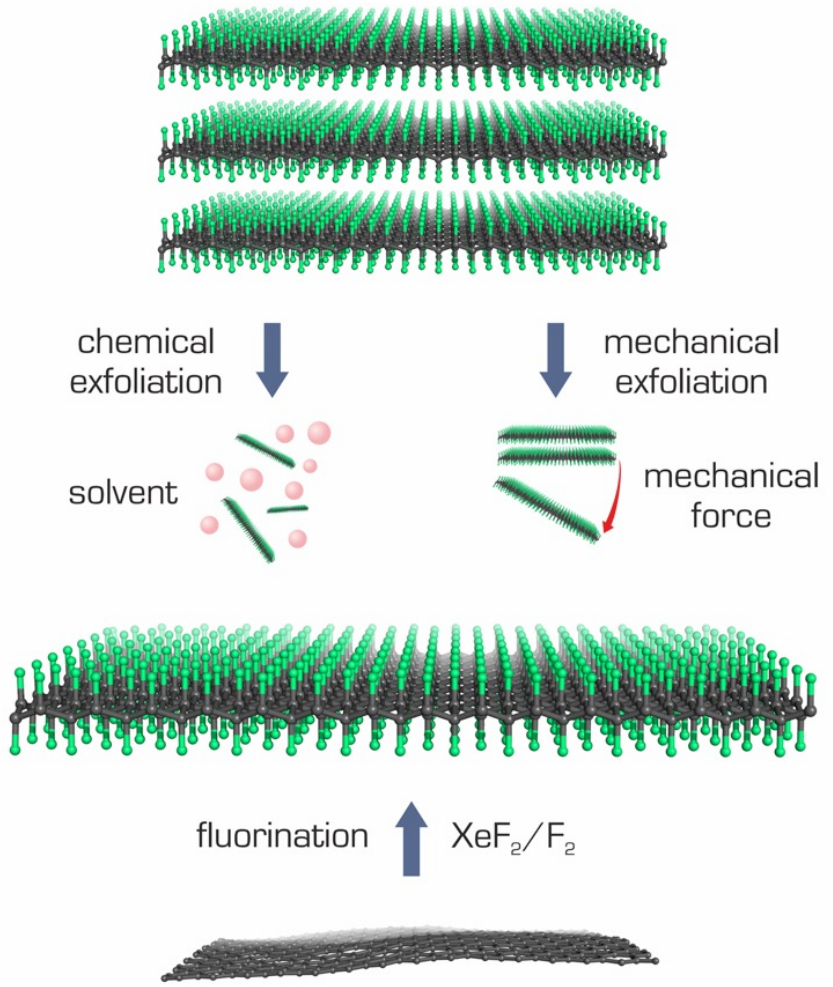
Fluorograhene

Discovered in 2010

Mechanical exfoliation of graphite fluoride
Nair RR *et al.* Small 6, 2877 (2010)

Chemical exfoliation of graphite fluoride
Zbořil R *et al.* Small 6, 2885 (2010)

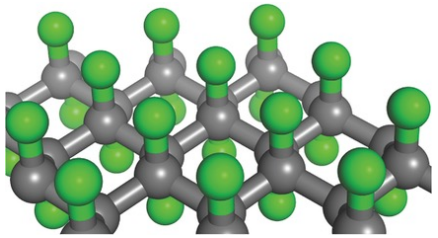
Fluorination of graphene
Robinson JT *et al.* Nano Letters 10, 3001 (2010)
Cheng SH *et al.* PRB 81, 205435 (2010)

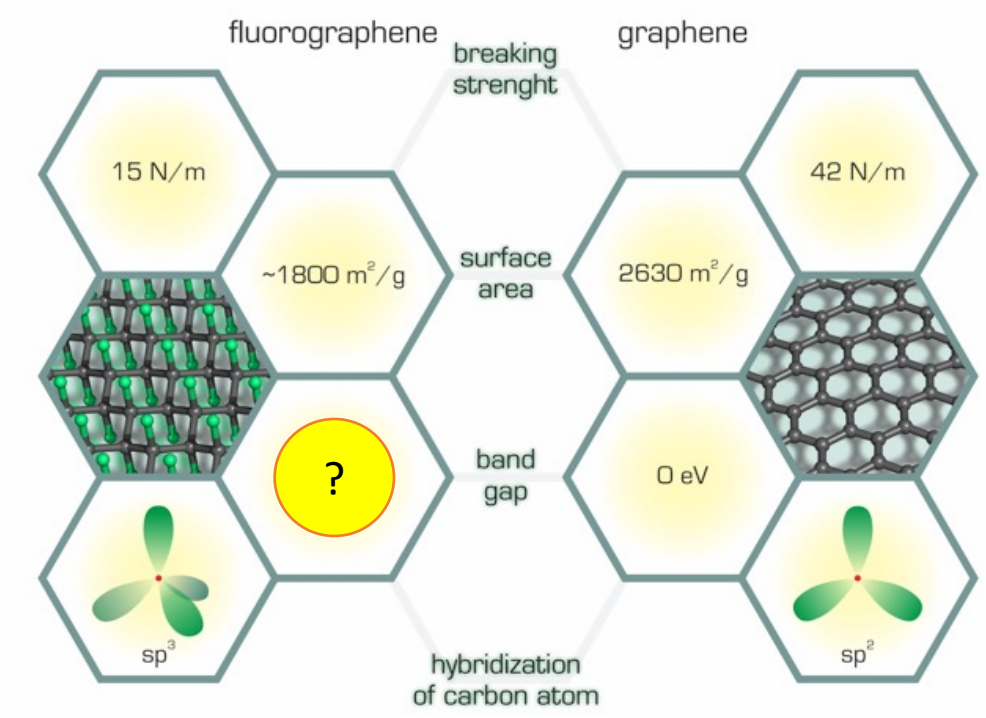


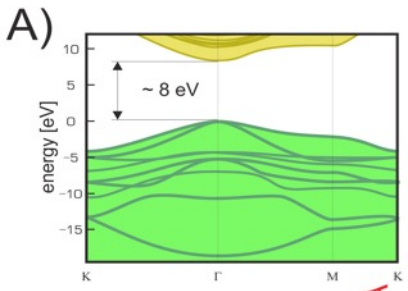
ACS Nano 7, 6434, 2013
Appl. Mater. Today, 9, 60, 2017

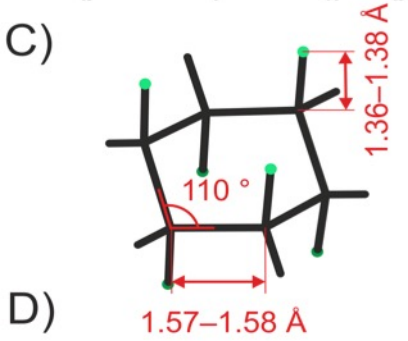
Properties of Fluorographene

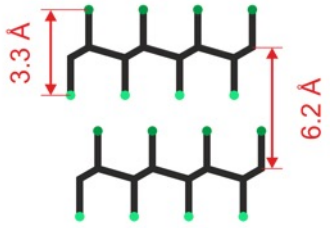
$C_1F_{1(1.1)}$

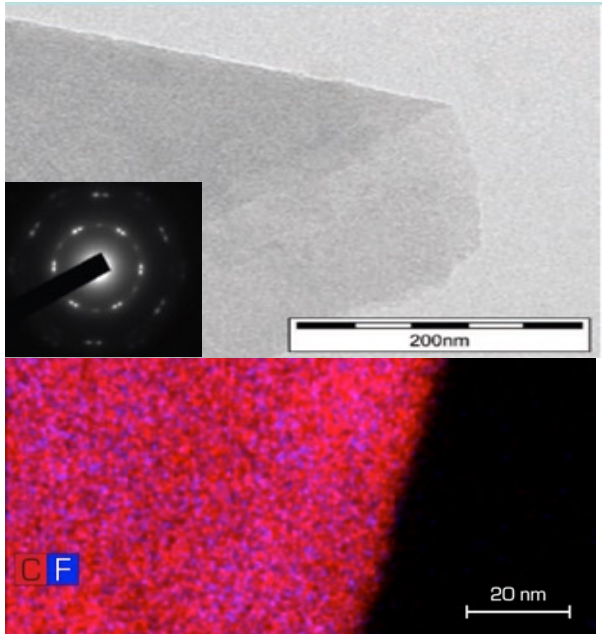


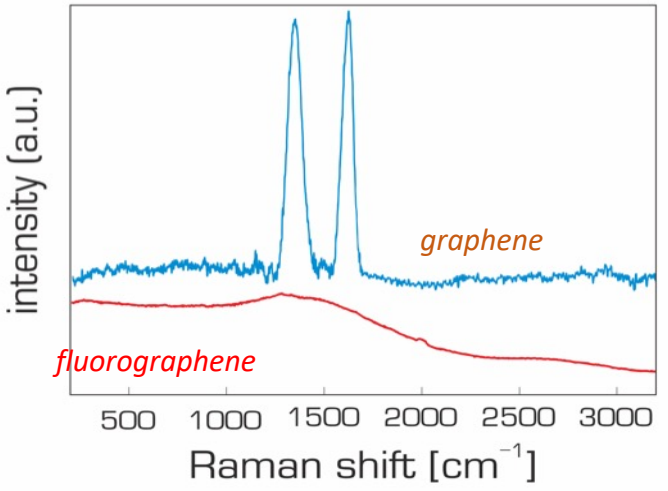












ACS Nano 7, 6434, 2013

Appl. Mater. Today, 9, 60, 2017

CATRIN
Czech Advanced Technology Research Institute

Fluorographene is Reactive

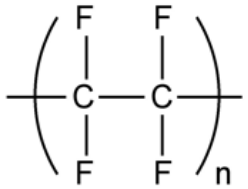
Fluorinated graphene

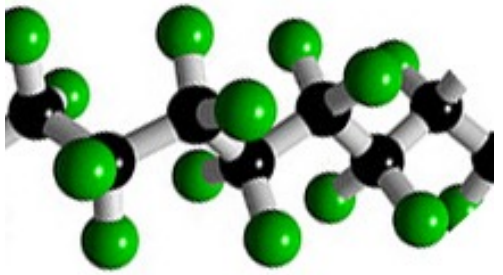
Fluorographene: A Two-Dimensional Counterpart of Teflon

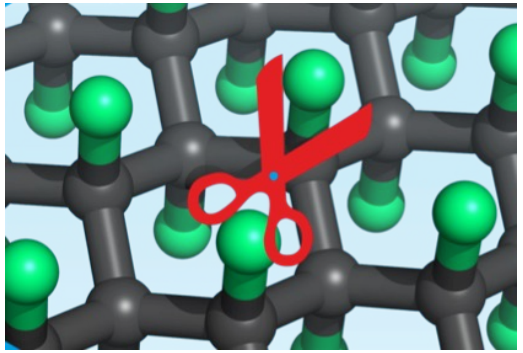
Rahul R. Nair, Wencai Ren, Rashid Jalil, Ibtsam Riaz, Vasyl G. Kravets, Liam Britnell, Peter Blake, Fredrik Schedin, Alexander S. Mayorov, Shengjun Yuan, Mikhail I. Katsnelson, Hui-Ming Cheng, Wlodek Strupinski, Lyubov G. Bulusheva, Alexander V. Okotrub, Irina V. Grigorieva, Alexander N. Grigorenko, Kostya S. Novoselov,* and Andre K. Geim**

A stoichiometric derivative of graphene with a fluorine atom attached to each carbon is reported. Raman, optical, structural, micromechanical, and transport studies show that the material is qualitatively different from the known graphene-based nonstoichiometric derivatives. Fluorographene is a high-quality insulator (resistivity > 10^2 Ω) with an optical gap of 3 eV. It inherits the mechanical strength of graphene, exhibiting a Young's modulus of 100 N m^{-1} and sustaining strains of 15%. Fluorographene is inert and stable up to 400 °C even in air, similar to Teflon.

Nair et al., Small 6, 2878, 2010







Graphene

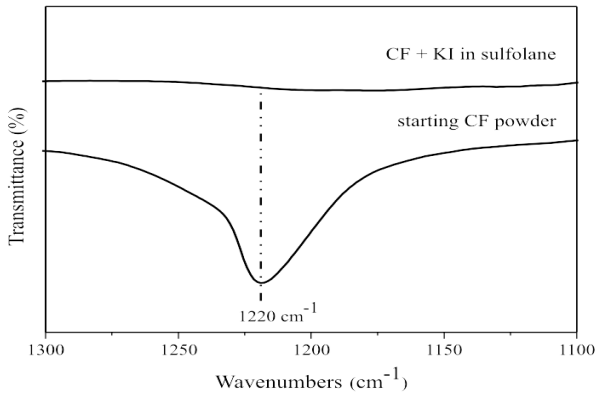
Graphene Fluoride: A Stable Stoichiometric Graphene Derivative and its Chemical Conversion to Graphene

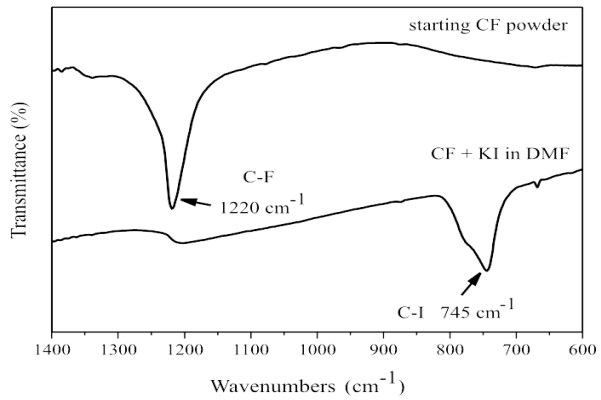
Radek Zbořil, František Karlický, Athanasios B. Bourlinos, Theodore A. Steriotis, Athanasios K. Stubos, Vasilios Georgakilas, Klára Šafářová, Dalibor Jančík, Christos Trapalis, and Michal Otyepka**

Stoichoimetric graphene fluoride monolayers are obtained in a single step by the liquid-phase exfoliation of graphite fluoride with sulfolane. Comparative quantum-mechanical calculations reveal that graphene fluoride is the most thermodynamically stable of five studied hypothetical graphene derivatives; graphane, graphene fluoride, bromide, chloride, and iodide. The graphene fluoride is transformed into graphene via graphene iodide, a spontaneously decomposing intermediate. The calculated bandgaps of graphene halides vary from zero for graphene bromide to 3.1 eV for graphene fluoride. It is possible to design the electronic properties of such two-dimensional crystals.

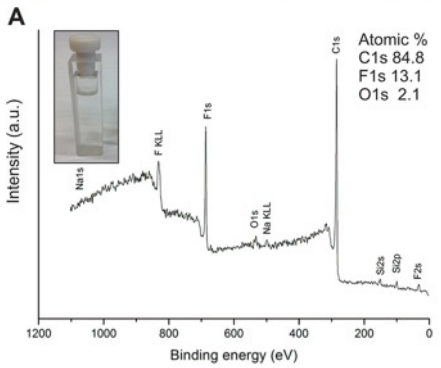
Zbořil et al., Small 6, 2885, 2010

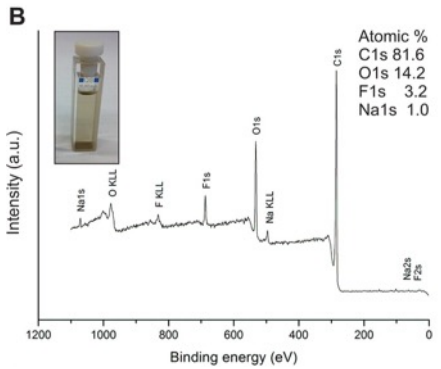
$$CF + KI \rightarrow KF + [CI]\ ;\ [CI] \rightarrow C + \tfrac{1}{2} I_2 \quad (180^\circ\ C)$$



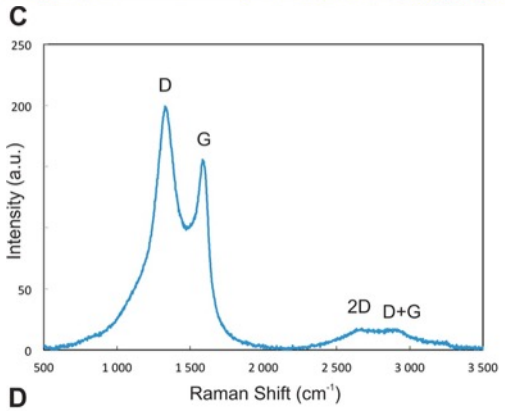


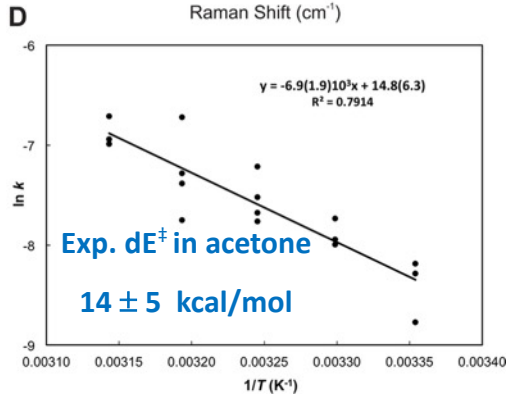
Fluorographene Reactivity

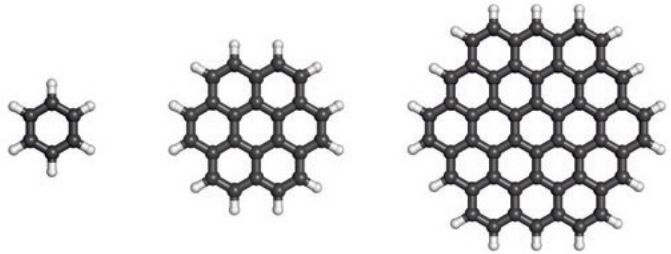


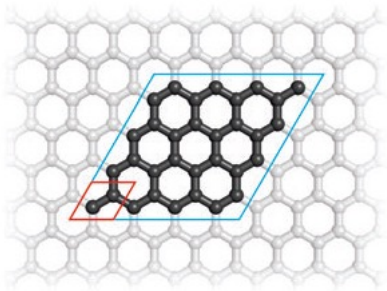


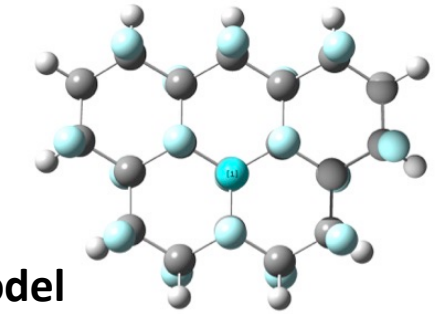
NaOH











Finite size model

C-F → C• + F•

S_{rad} dE‡ = 109 kcal/mol

C-F → C+ + F-

S_N1 dE‡ > 200 kcal/mol

S_N2 dE‡ = 18 kcal/mol

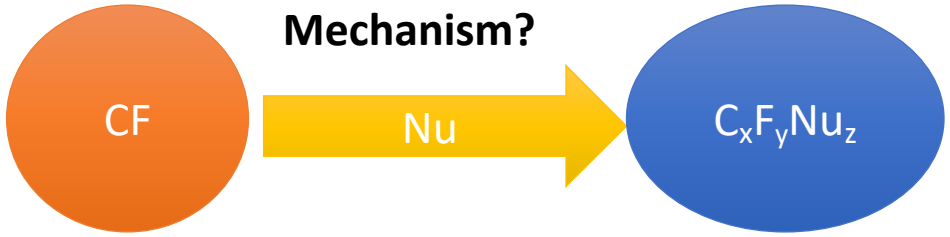
ωB97xD/6-311G(d,p)//B97D/6-311G(d,p)

PBC

C-F → C• + F•

S_{rad} dE‡ = 112 kcal/mol

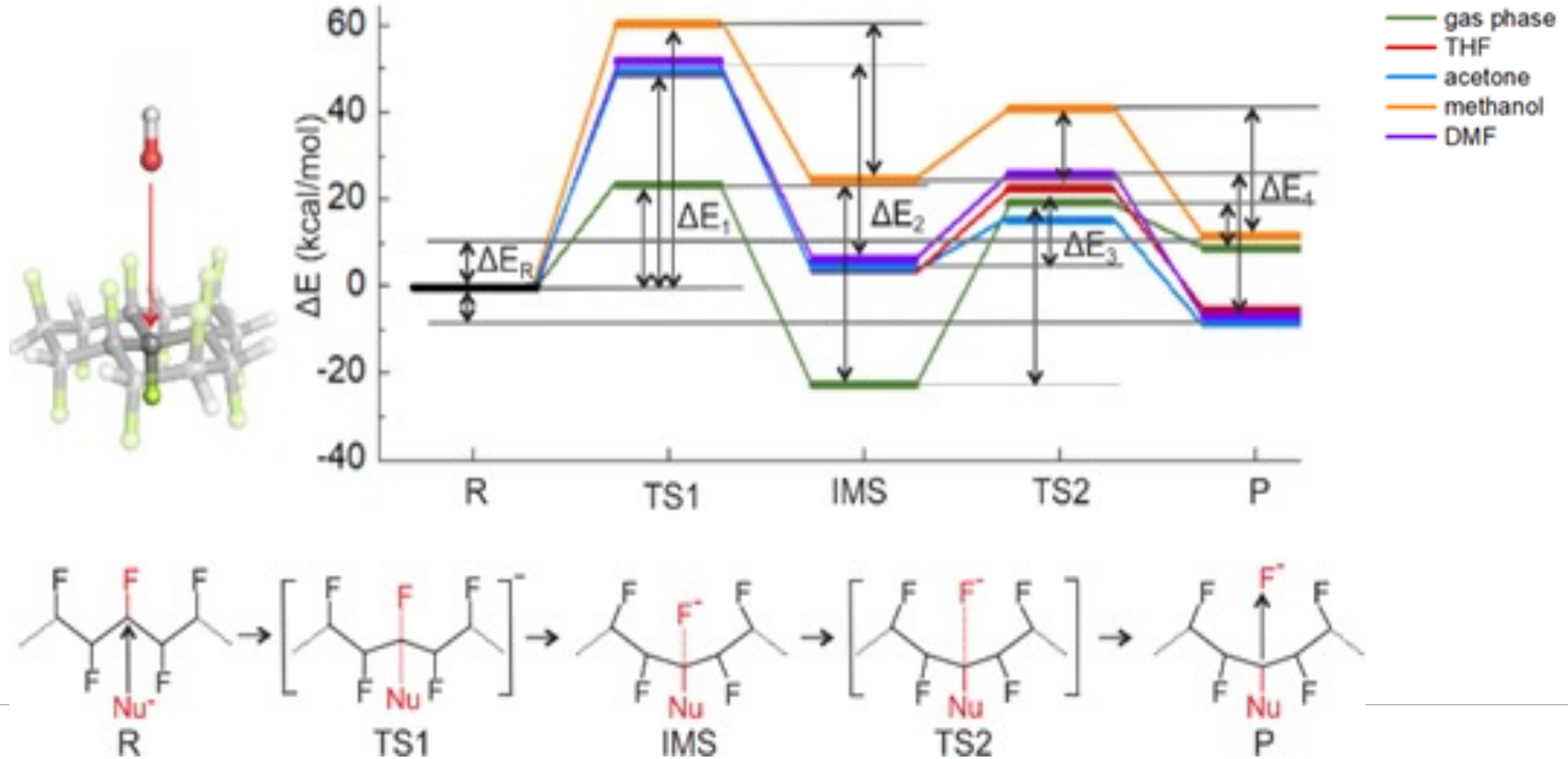
Mechanism?



J. Phys. Chem. Lett. 6, 1430, 2015

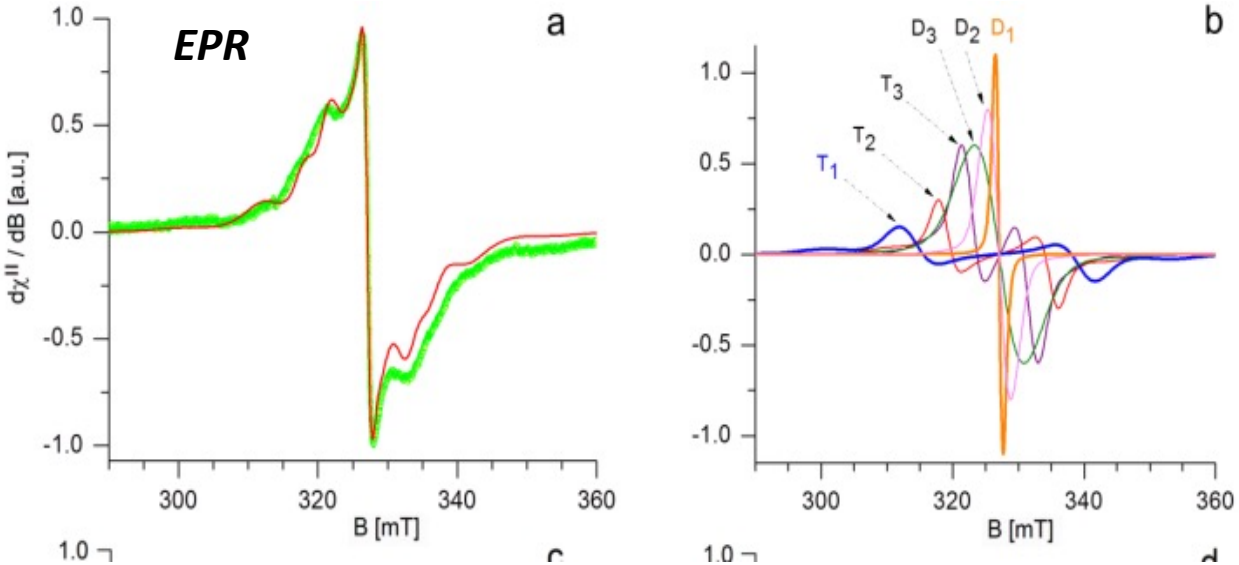
Fluorographene Reactivity

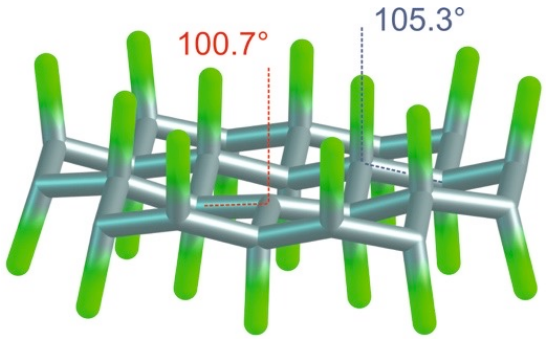
Reaction profiles of the S_N2 reaction of FG with OH^- in gas phase and different solvents



ωB97XD/6-311+G(d,p)/SMD

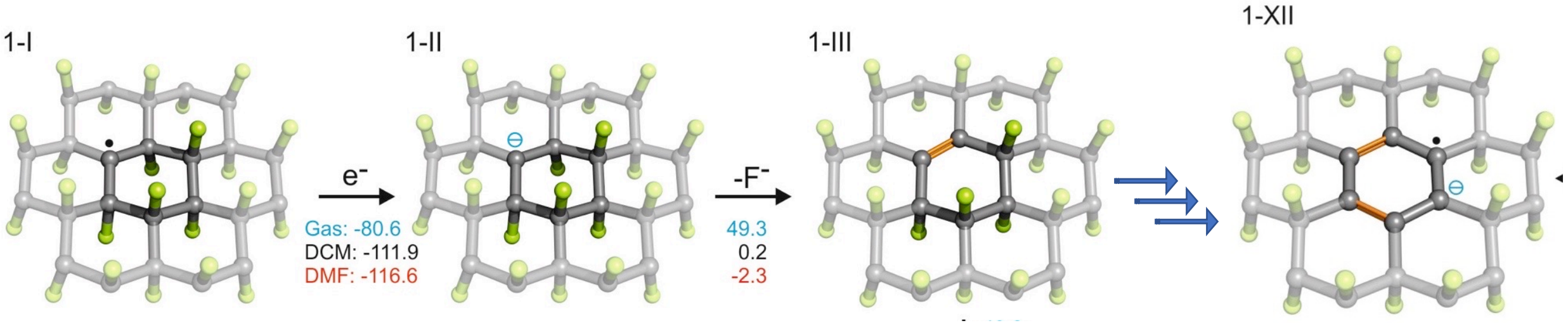
Fluorographene Chemistry is Triggered by Defects





Some like it hot (1959)

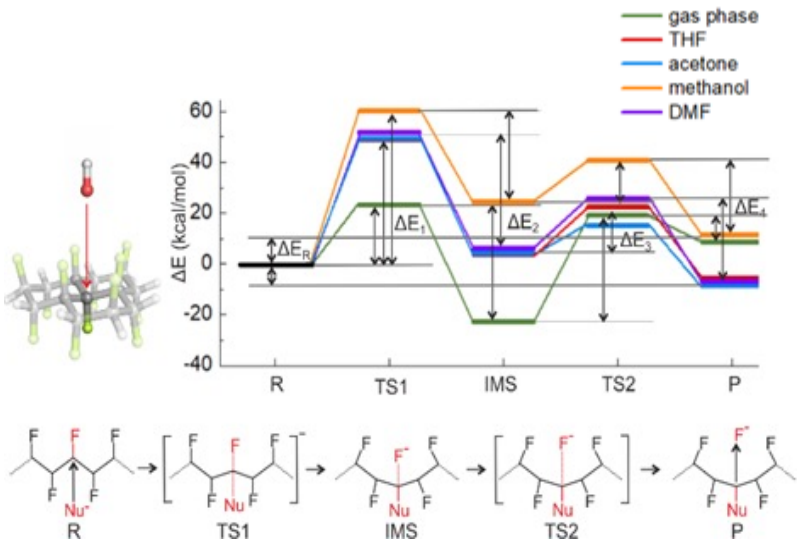
1 defect per ~1000 C, 5 x 5 nm²



Nanoscale 10, 4696, 2018

Defects are Elphiles

Nu attack on pristine FG

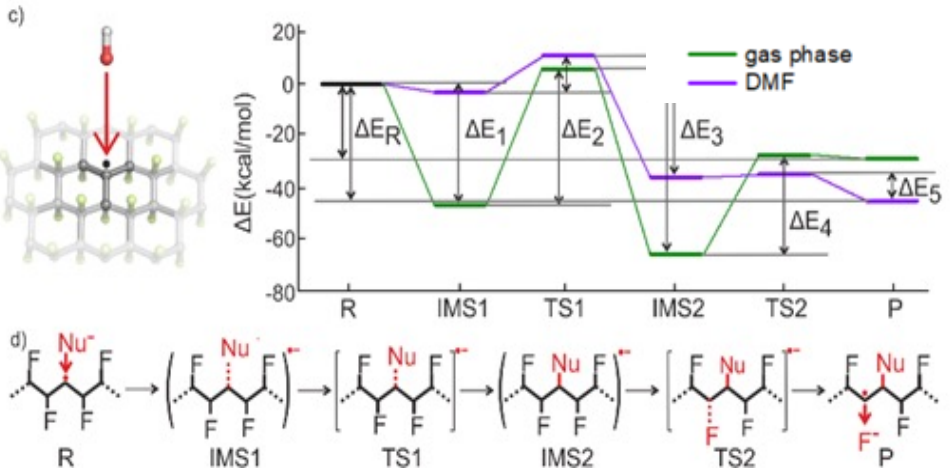


Reaction profiles of the S_N2 reaction of FG with OH^- in gas phase and different solvents

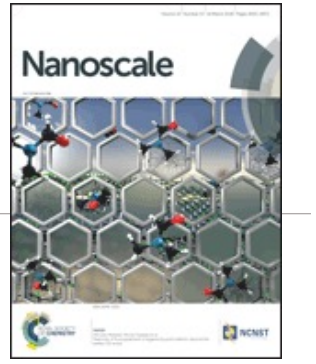
Exp. barrier in acetone is 14 ± 5 kcal/mol*

**J. Phys. Chem. Lett. 6, 1430, 2015*

Nu attack on a FG radical site



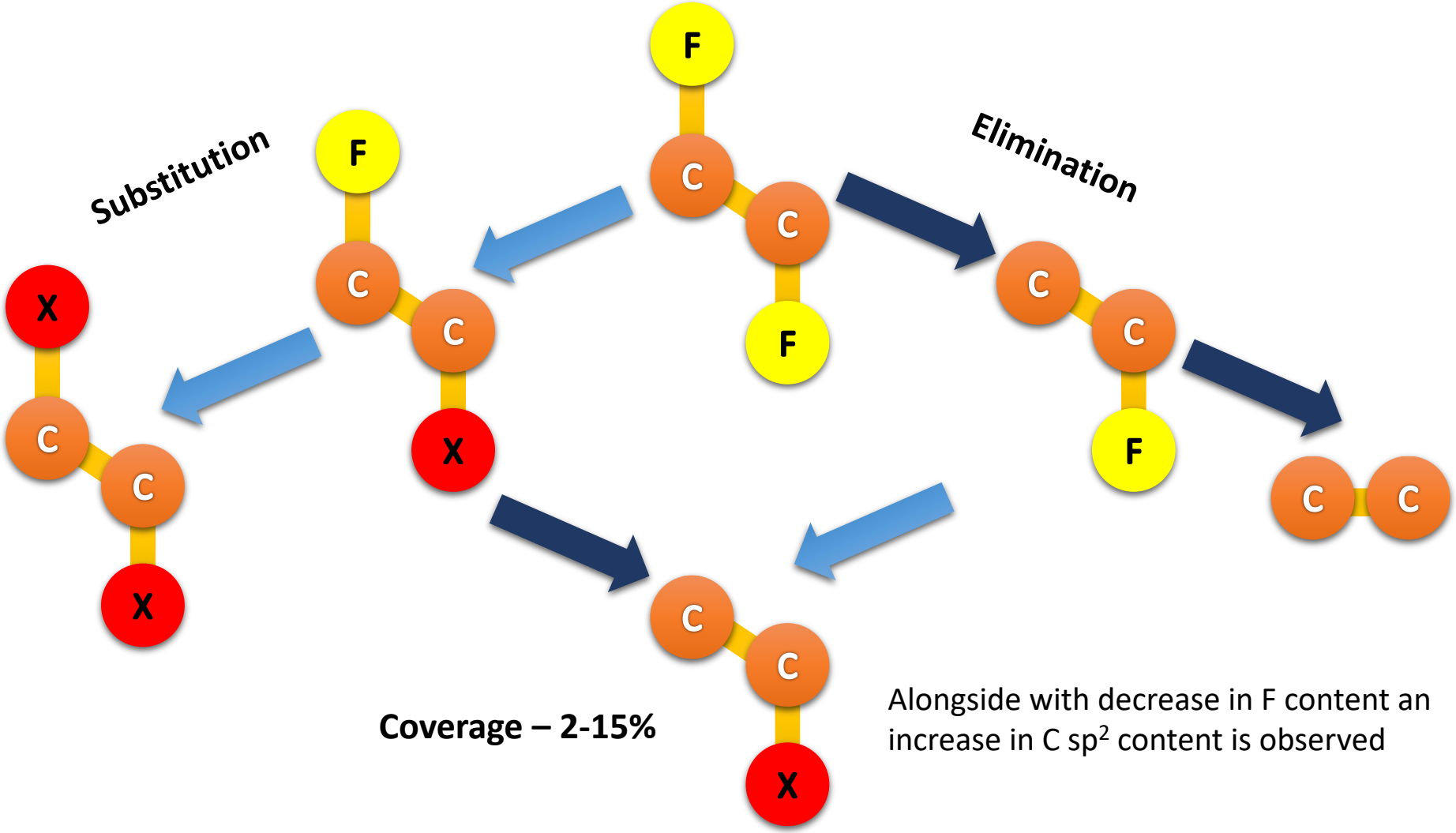
Reaction profiles for Nu attack of OH^- on a FG radical site, followed by release of F^-.



- 70.4 kcal/mol

J. Phys. Chem. Lett. 9, 3580, 2018

Fluorographene Reactivity



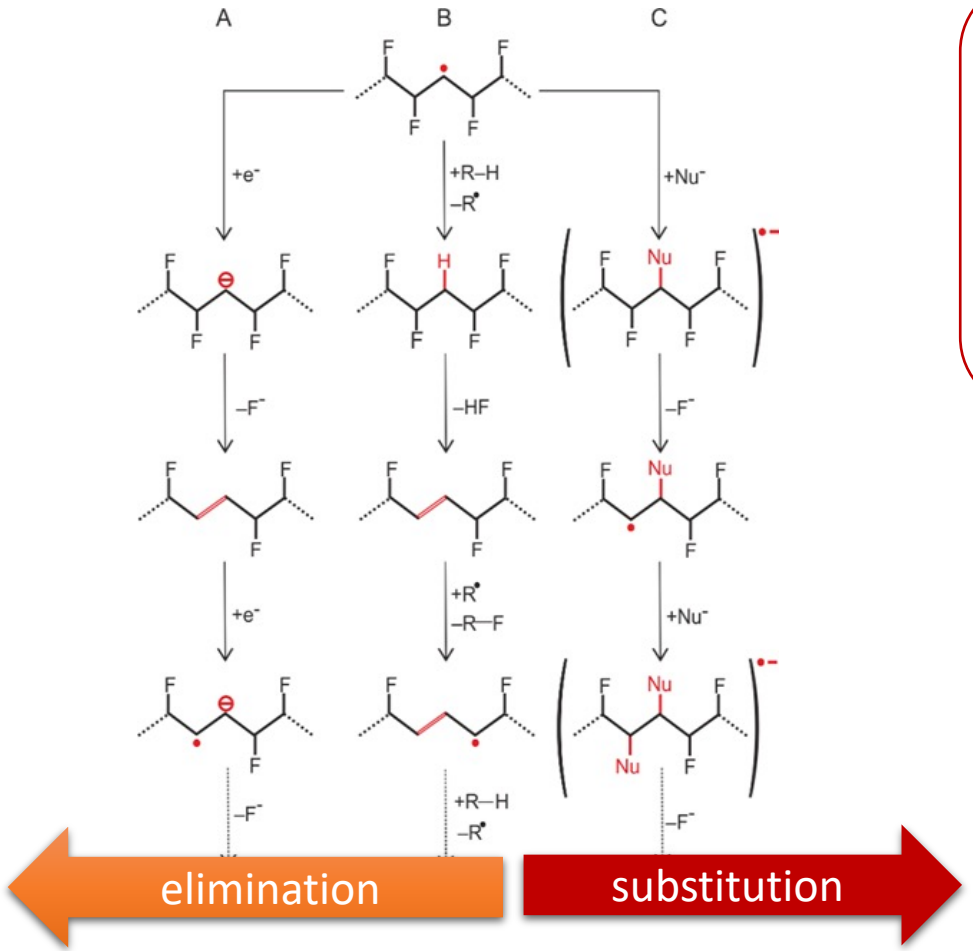
Alongside with decrease in F content an increase in C sp^2 content is observed

Reductive defluorination occurs simultaneously with substitution

Appl. Mater. Today, 9, 60, 2017
Nanoscale, 10, 4696, 2018

Reaction Channels

Possible reaction pathways



Different thermodynamics

Different kinetics

Different solvent effects

Possibility to control reduction and substitution by changing reaction time, temperature, solvent

Defluorination and nucleophilic substitution starting on FG radical centers. A. Electron transfer. B. Hydrogen transfer. C. Nucleophilic attack

J. Phys. Chem. Lett. 9, 3580, 2018

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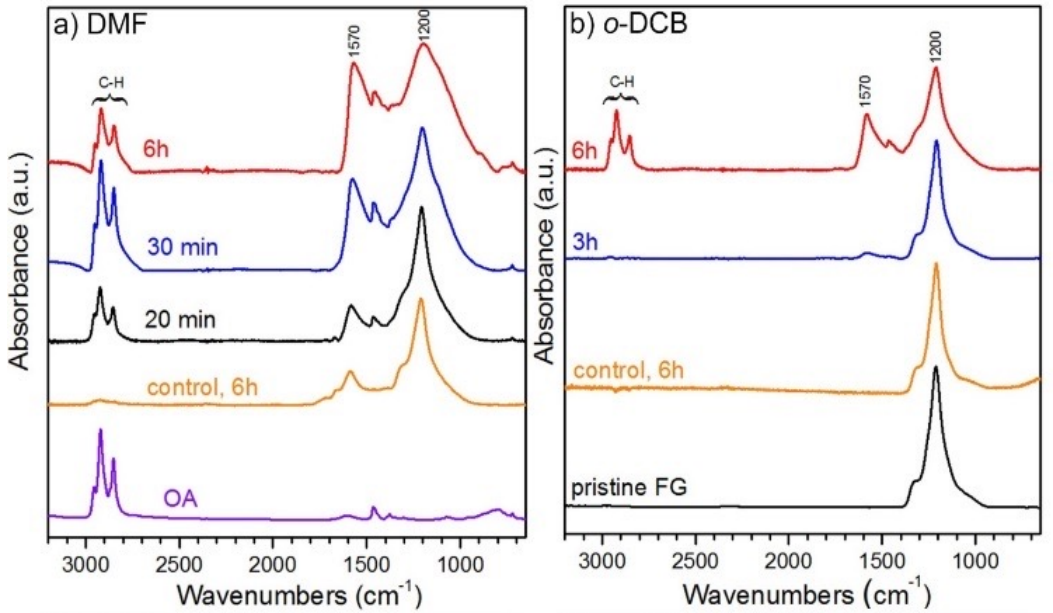
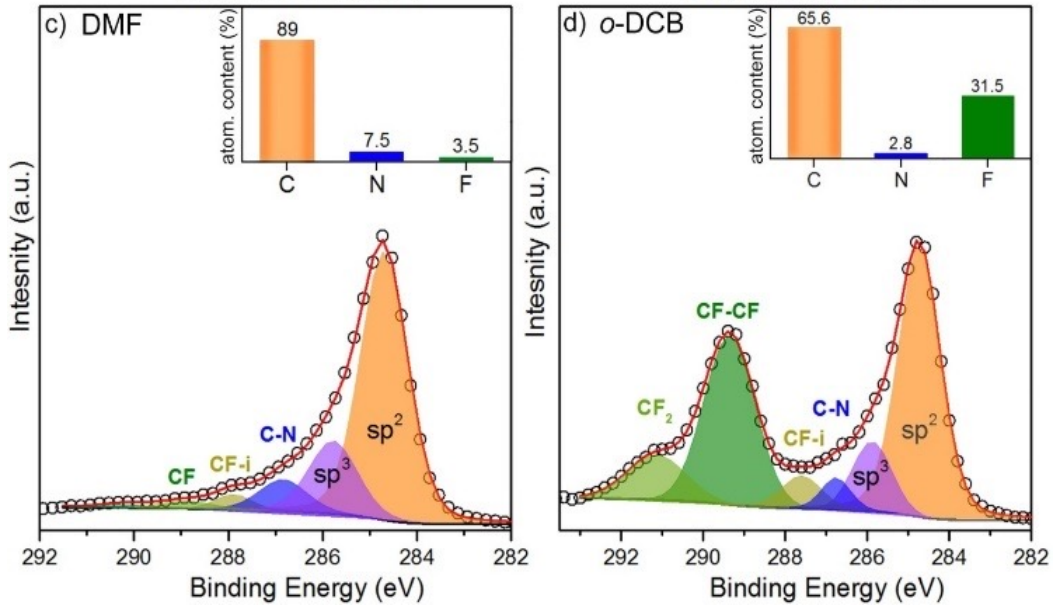
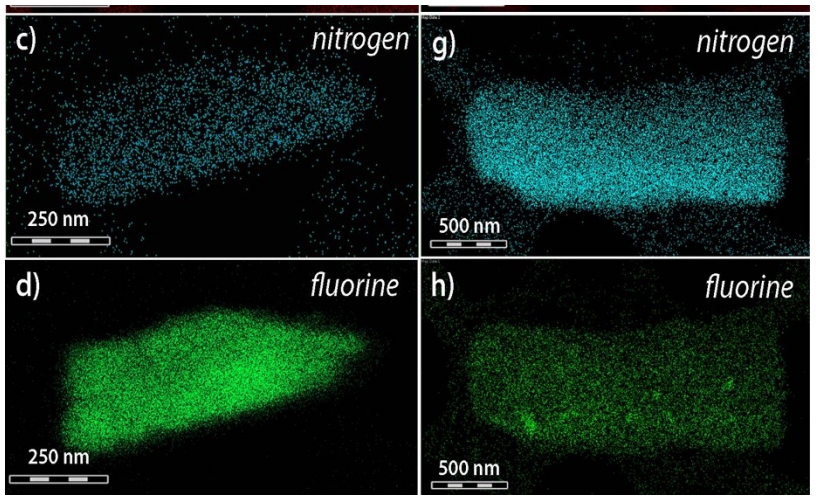
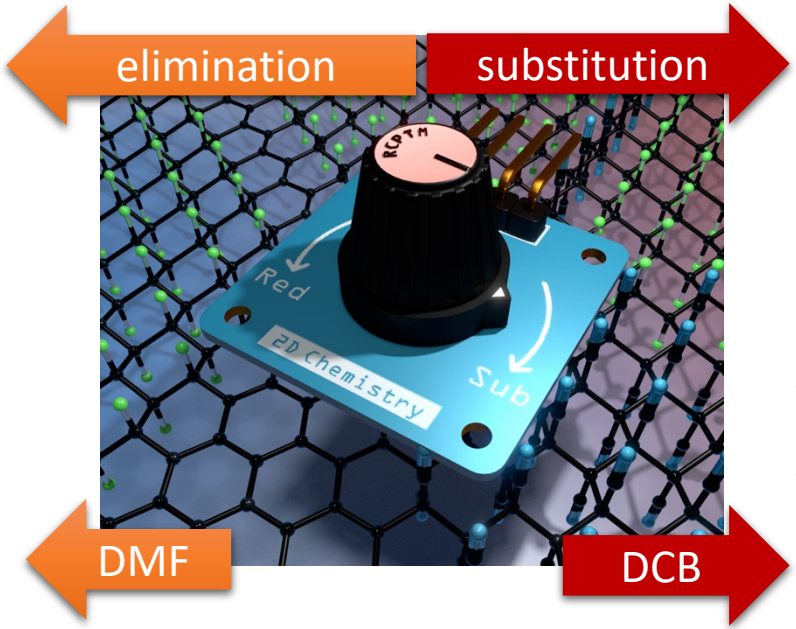
Reaction Control by Solvent





FG + Octylamine





J. Phys. Chem. Lett. 9, 3580, 2018

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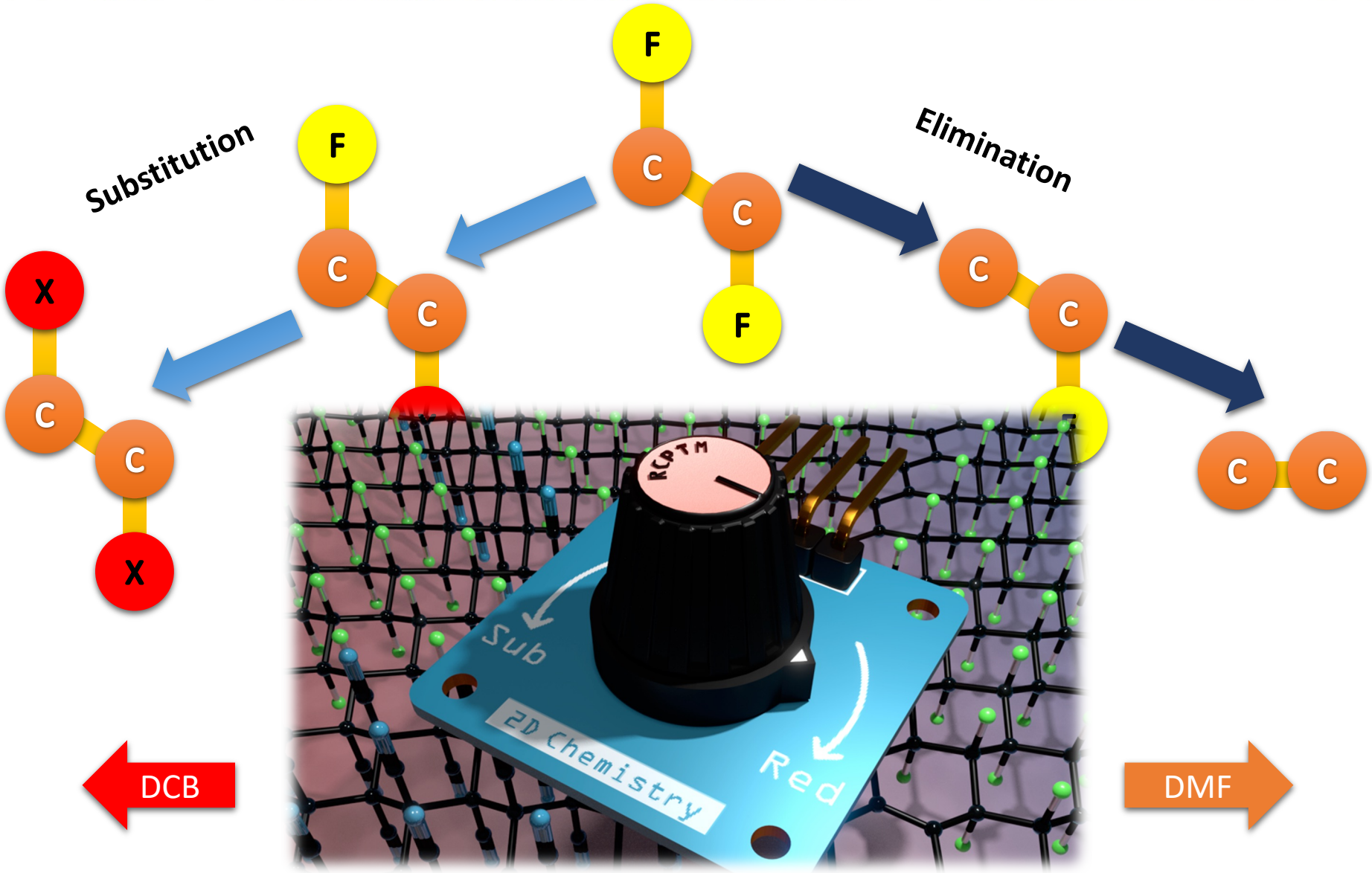
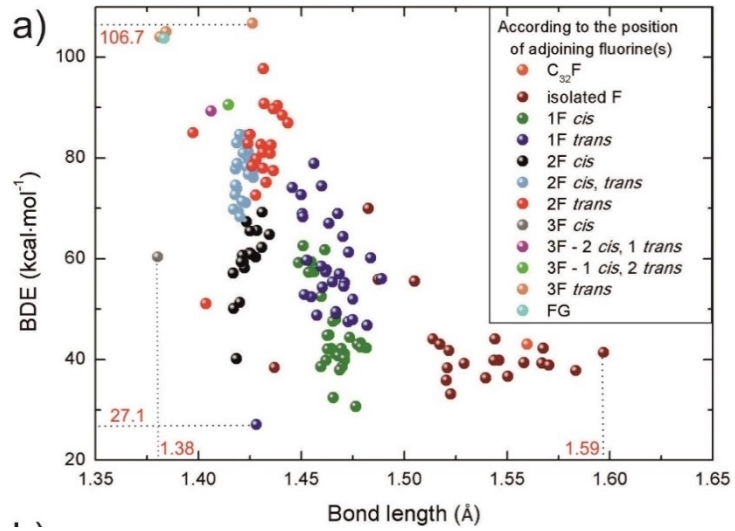
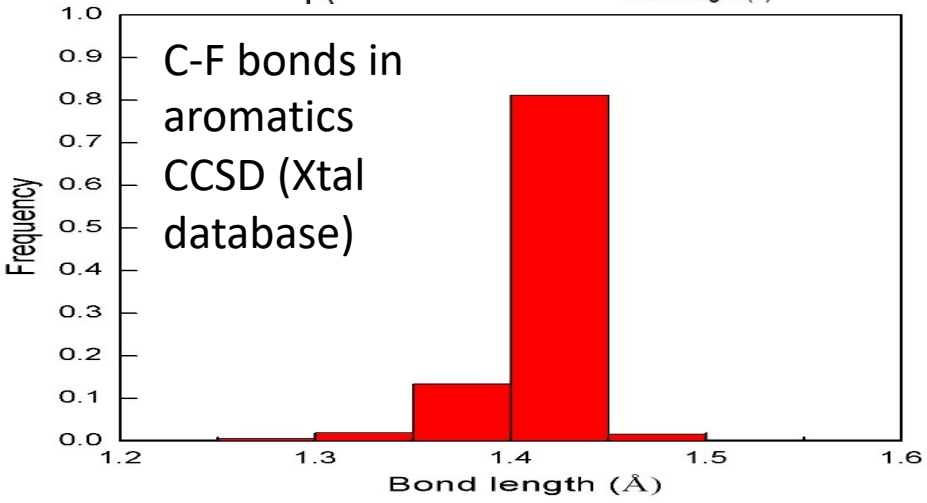
Reaction Control



J. Phys. Chem. Lett. 9, 3580, 2018

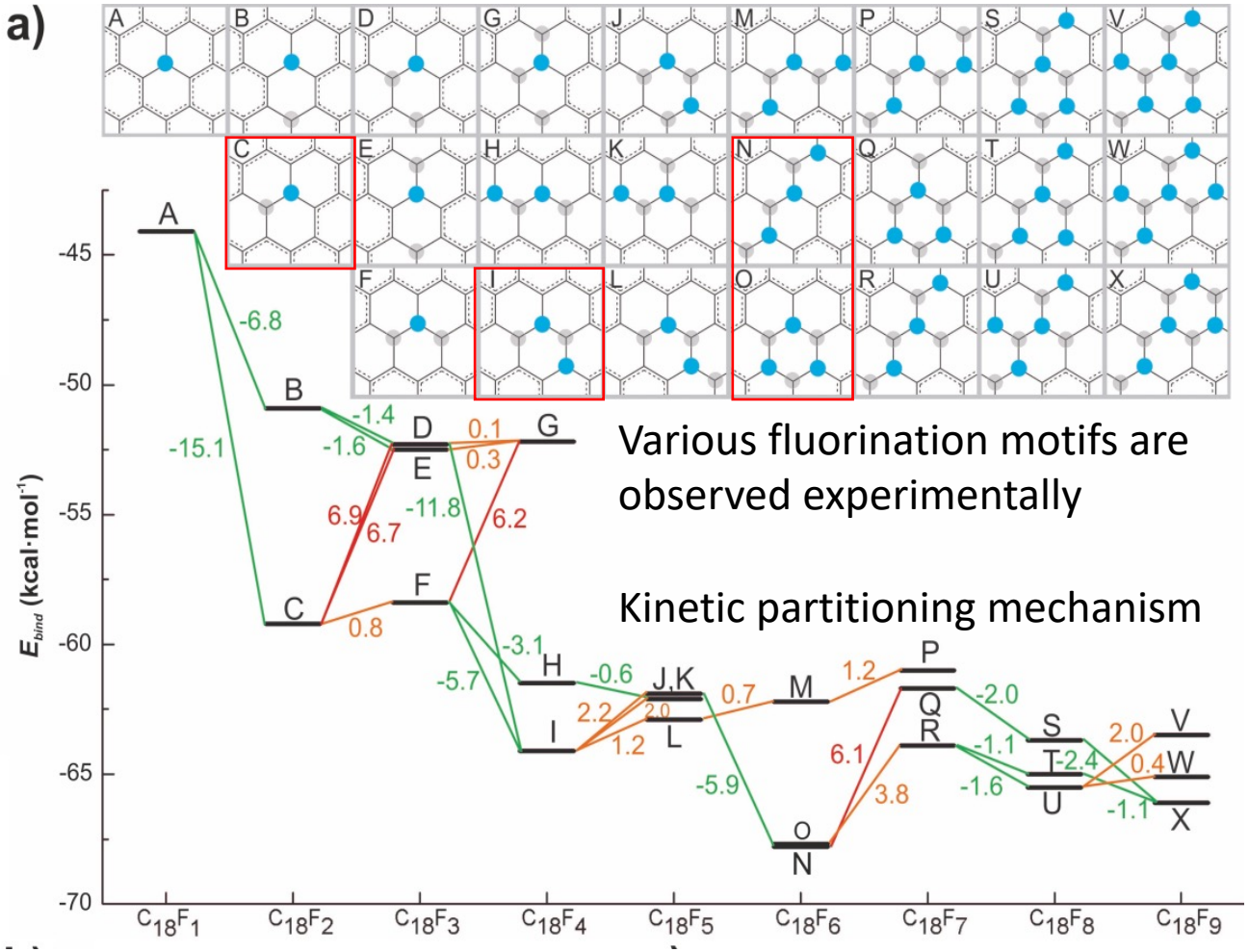
Complexity of C-F Bonding in C_xF_y





IMPORTANT FOR FLUORINATION C → C_xF_y

Compact clusters are preferred



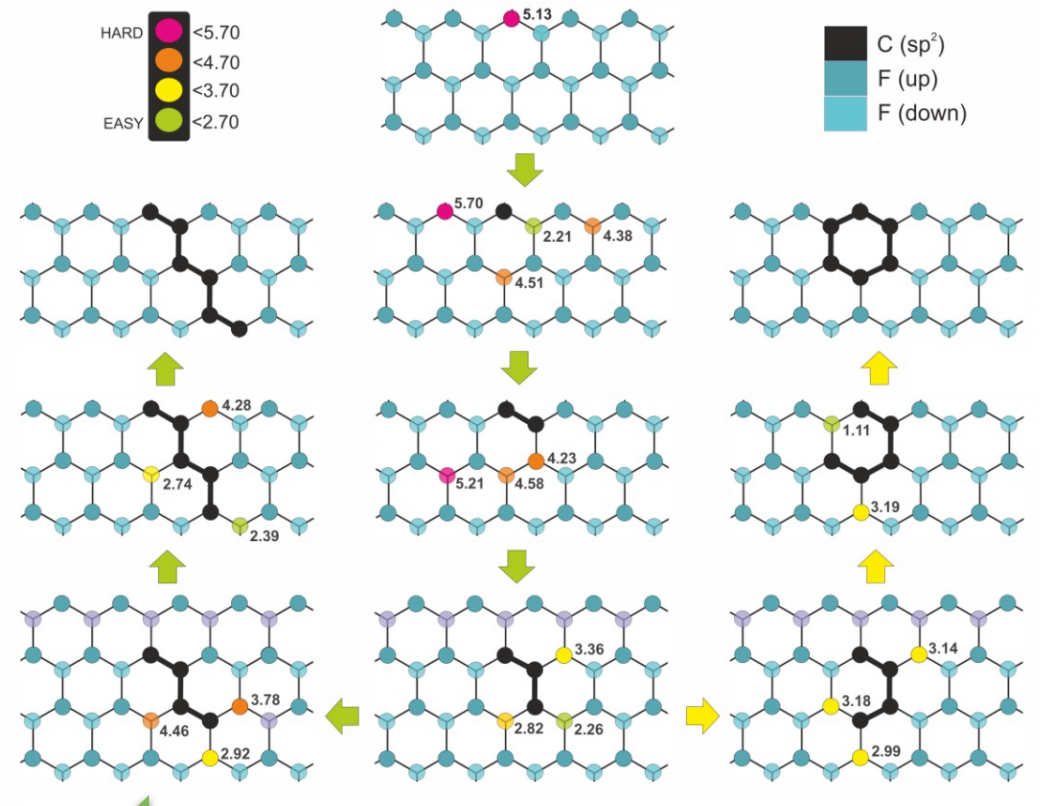
Various fluorination motifs are observed experimentally

Kinetic partitioning mechanism

J. Phys. Chem. C 123 (45), 27896, 2019

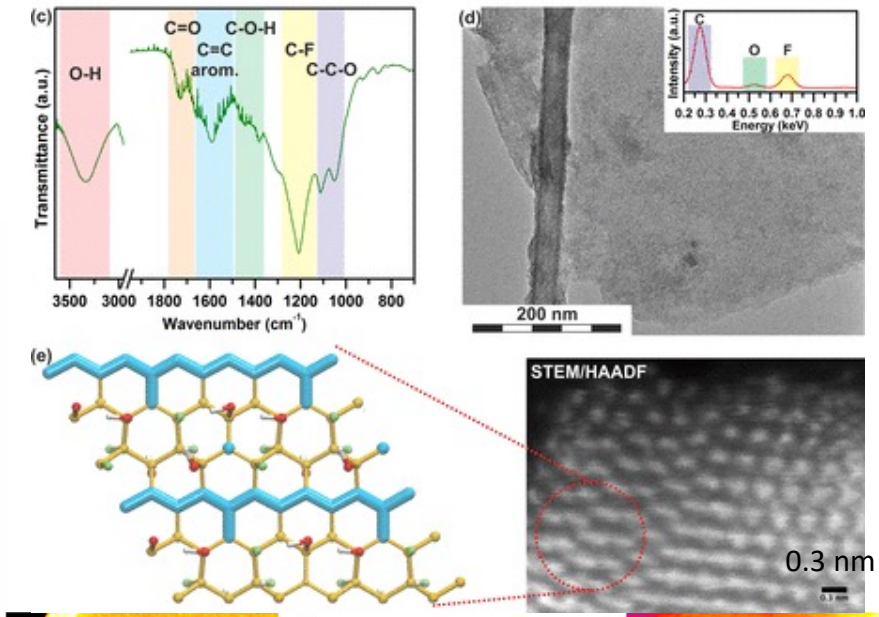
Directionality of Defluorination

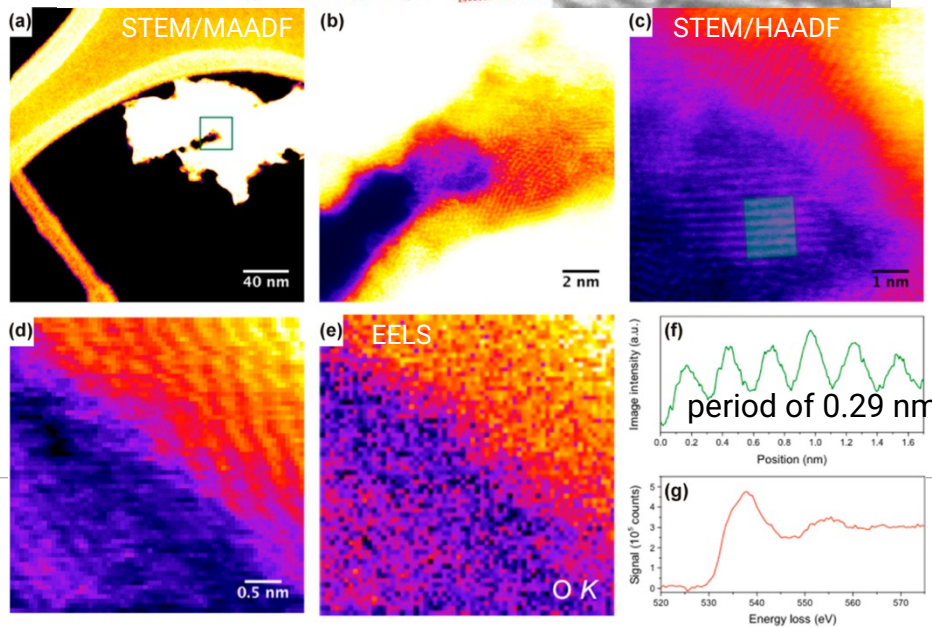
IMPORTANT FOR DEFLUORINATION

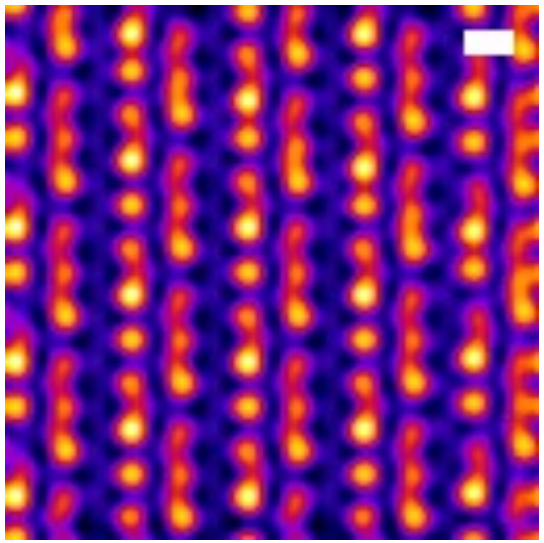


favored

Zig-zag sp^2 lines inside sp^3 matrix are preferred







↔ 0.29 nm

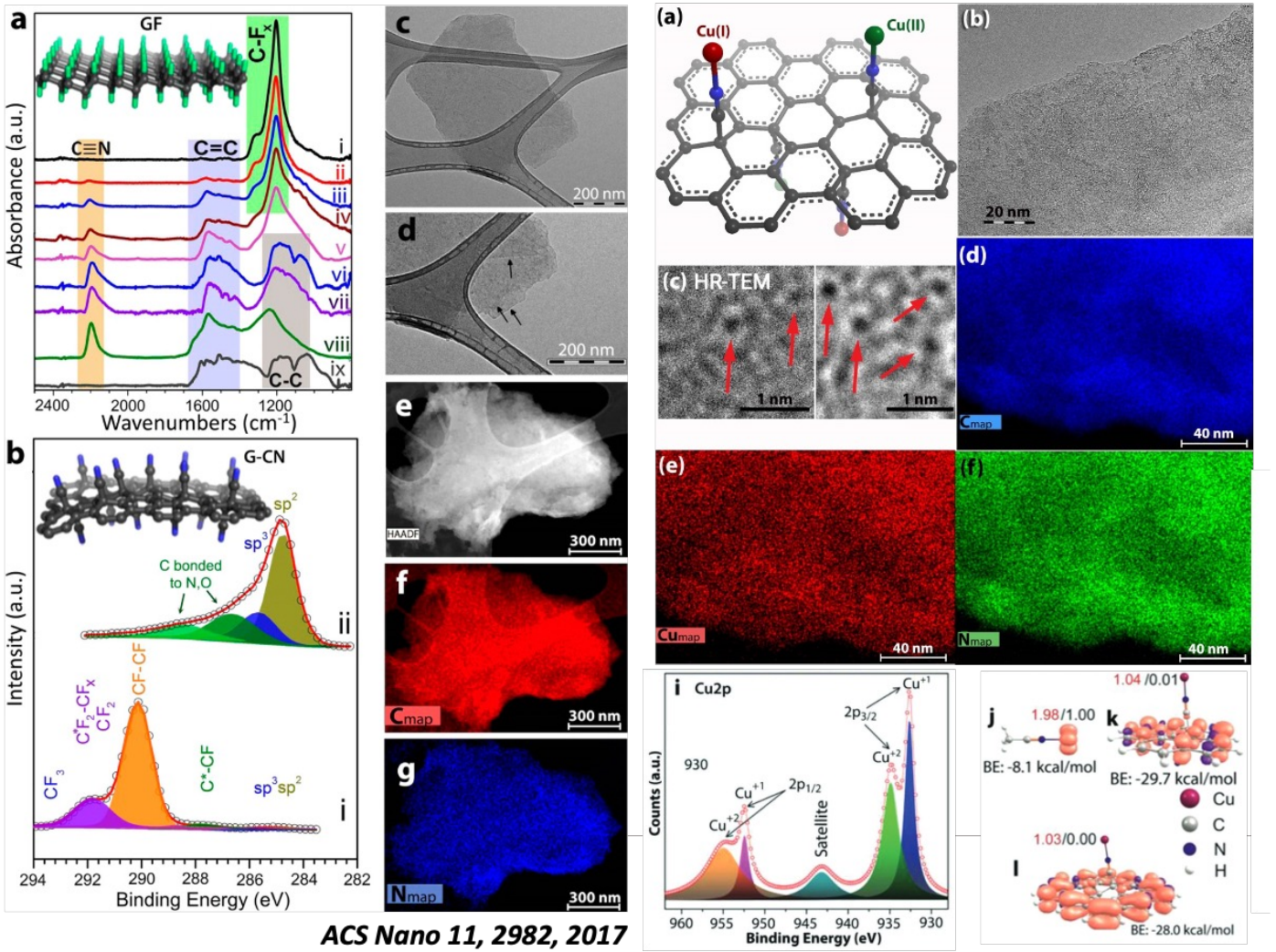
MODEL $C_{18}F_5(OH)_4$

LEADS TO RT MAGNETIC ORDERING (talk by P. Blonski)

ACS Nano 12, 12847, 2018

Cyanographene a 2D-ligand

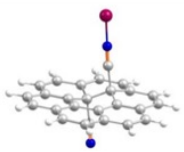
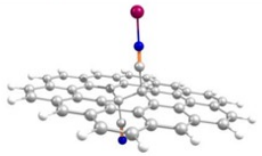
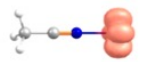
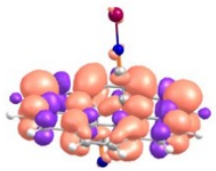
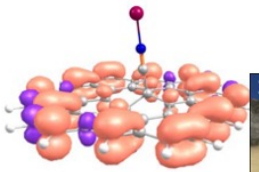
FG + NaCN → G-CN



ACS Nano 11, 2982, 2017

Cyanographene a 2D-ligand

Table S2. The binding of Cu(II) cations to G-CN in various solvents. The structures, selected bond lengths (Å), binding energies (kcal mol^{-1}), spin density plots (contour value: 0.001), atomic spin, and natural charge densities (a.u.) on the copper atom of model R-CN-Cu(II) systems were computed at the U-B3LYP/6-31+G(d)/SMD level of theory. The structures were obtained via constrained geometry optimizations at the same level of theory (see text for details on the constraints).

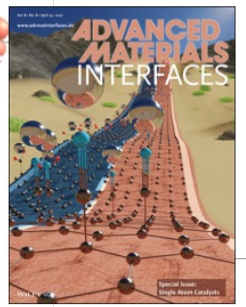
Model	ACN-Cu(II)	Corronene-2CN-Cu(II)	Cyc14-2CN-Cu(II)
Structure			
R_{C-N}/R_{N-Cu}			
Water	1.157/2.108	1.159/1.867	1.159/1.863
PAM	1.156/2.090	1.157/1.871	1.158/1.872
BAM	1.157/2.071	1.157/1.873	1.158/1.875
Binding energy			
Water	−8.1	−29.7 (−28.7)[a]	−28.0
PAM	−17.7	−56.5 (−55.7)	−59.5
BAM	−28.7	−87.6 (−86.8)	−92.8
Spin density			
Spin density on Cu			
Water	1.00	0.01	0.00
PAM	0.72	0.00	0.00
BAM	0.68	0.00	0.00
Charge density on Cu			
Water	1.96 (1.68)[b]	1.04 (0.74)	1.03 (0.77)
PAM	1.67 (1.31)	1.02 (0.72)	1.01 (0.78)
BAM	1.63 (1.28)	1.01 (0.71)	1.00 (0.74)

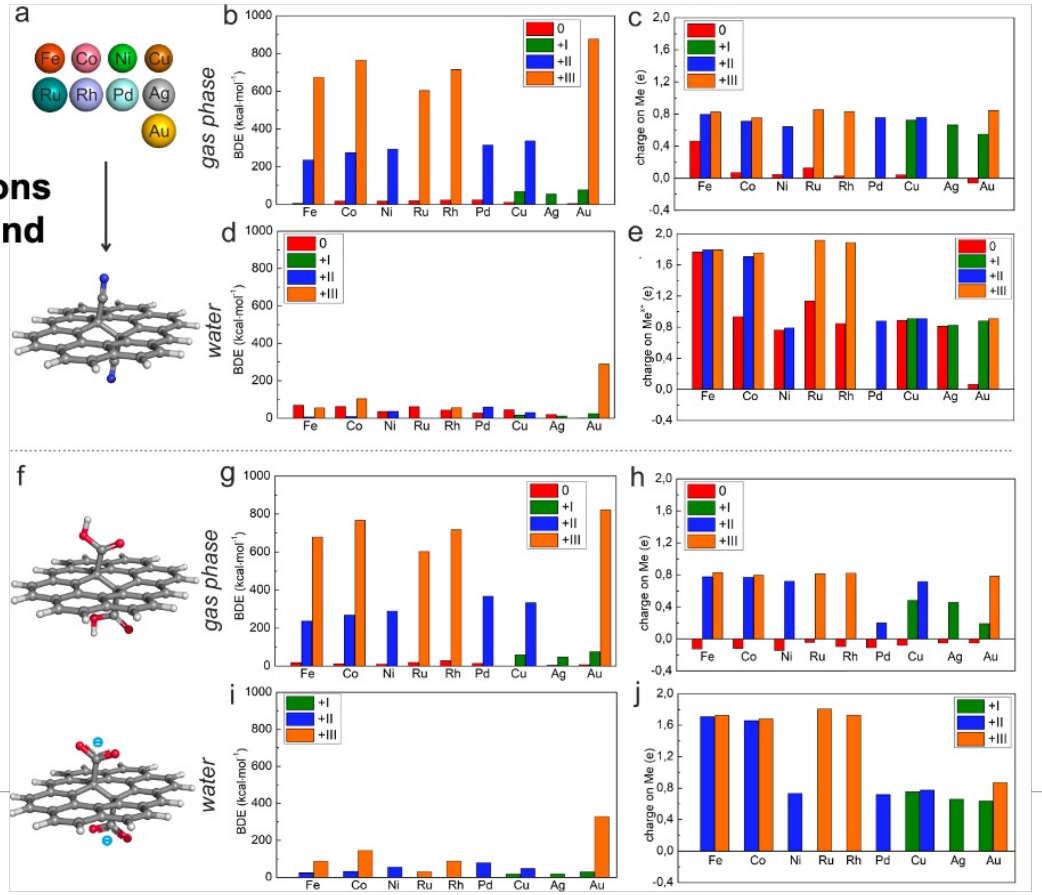
[a]The values in parentheses were obtained from the RO-B3LYP calculations.
[b]The values in parentheses were determined via Mulliken population analysis.

Adv. Mater. 31(17), 1900323, 2019

- **Strong binding – reduced charge/spin density on Cu(II), charge transfer facilitates reduction**

Other elements/ions can be bound





Adv. Mater. Interface, 8(8), 2001392, 2020

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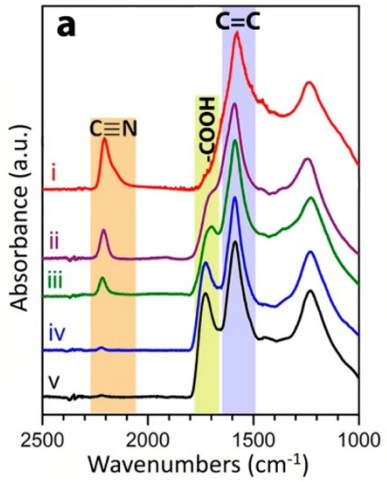
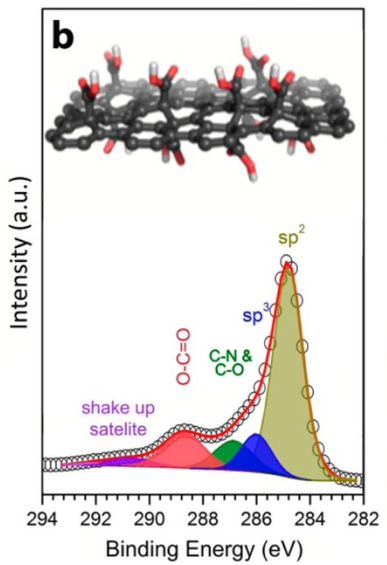
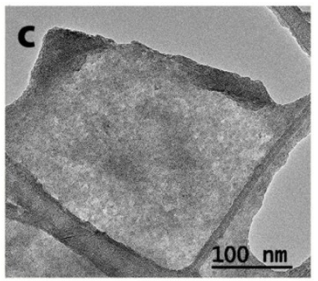
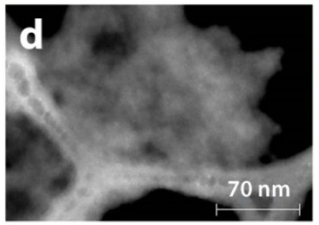
G-CN + HNO_3 → G-COOH

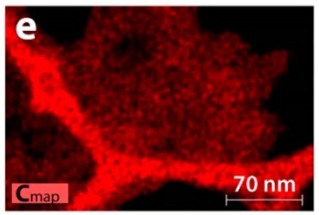
Cyanographene to Graphene Acid

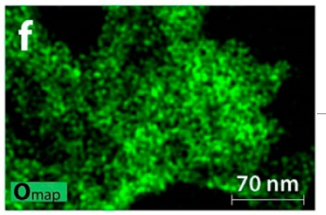


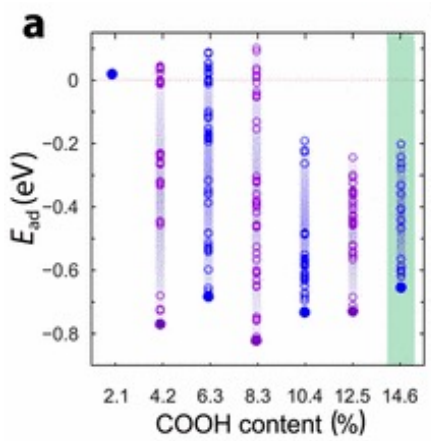


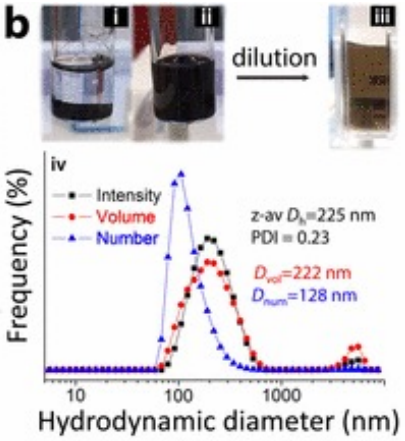


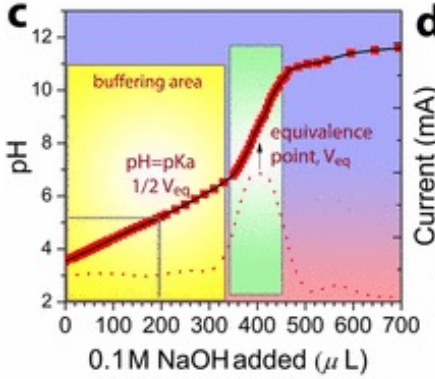


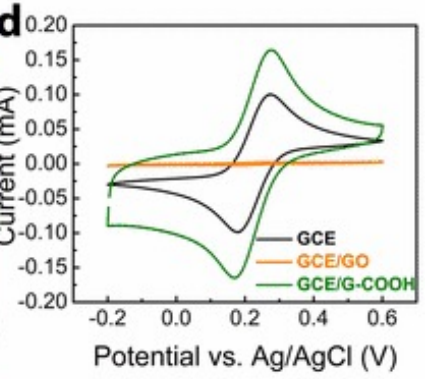


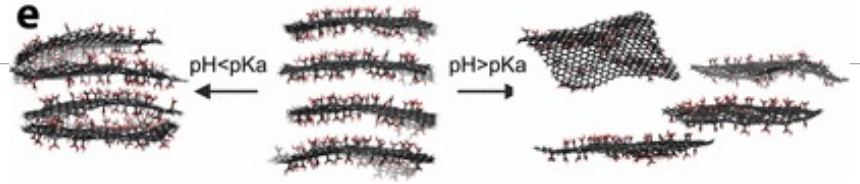




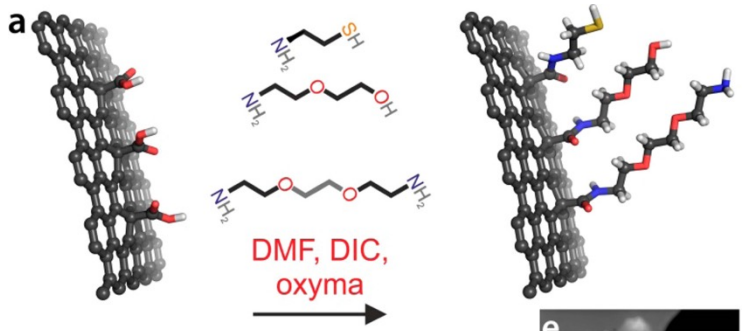


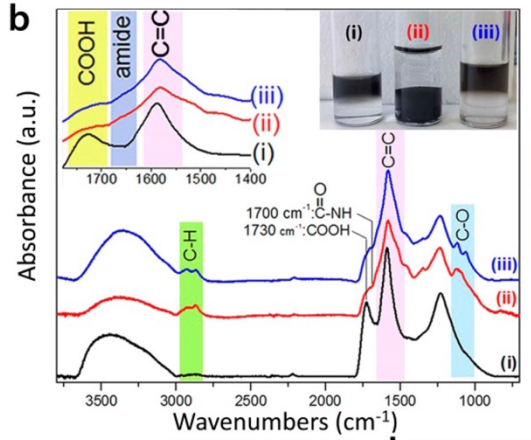


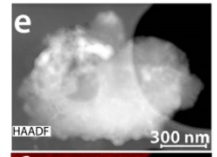


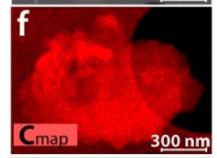


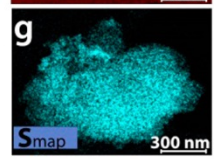
G-COOH + NH_2-R

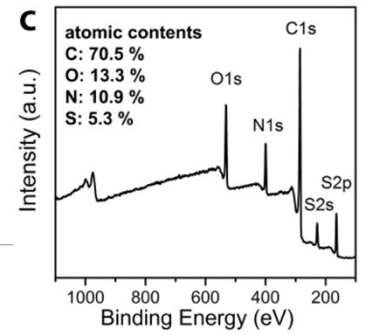


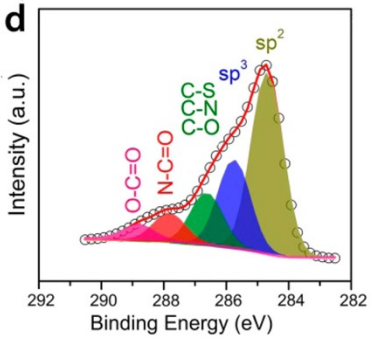












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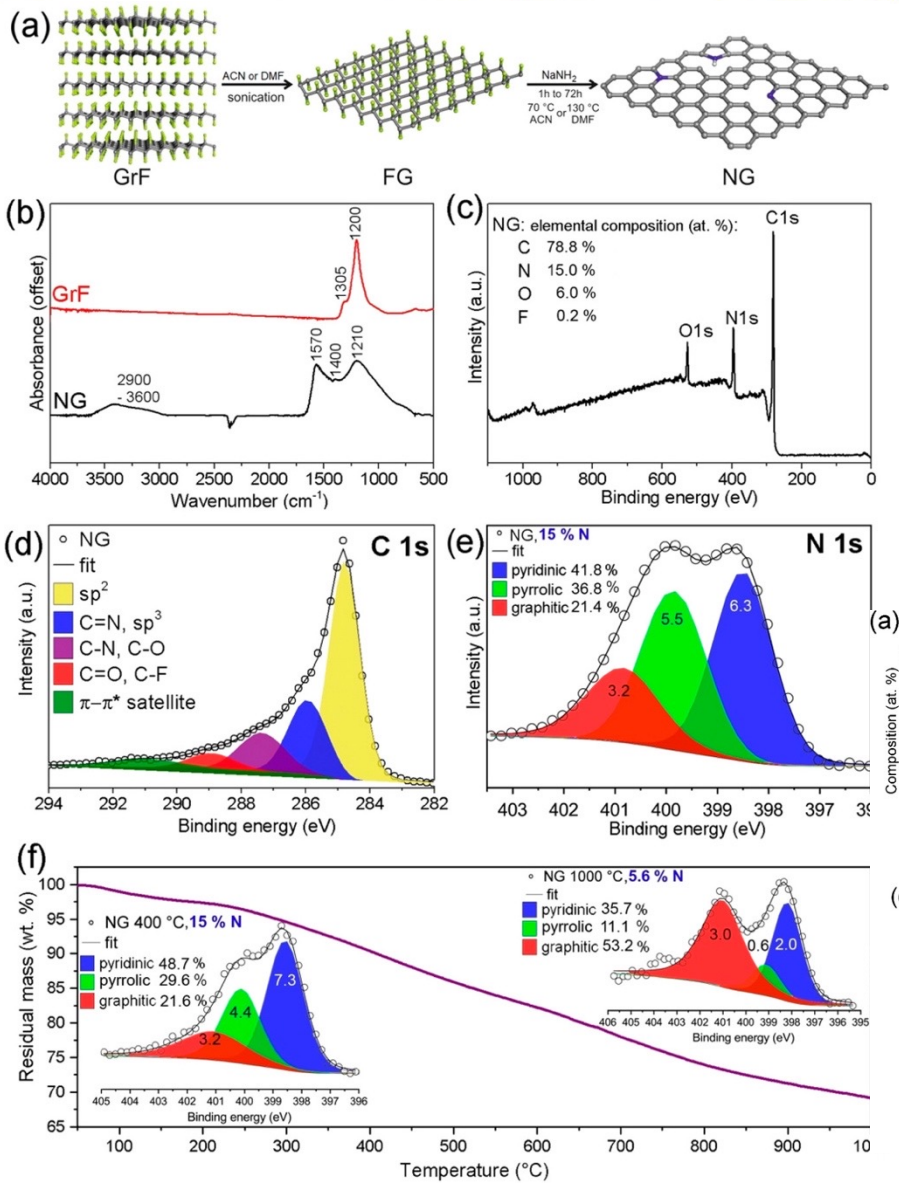

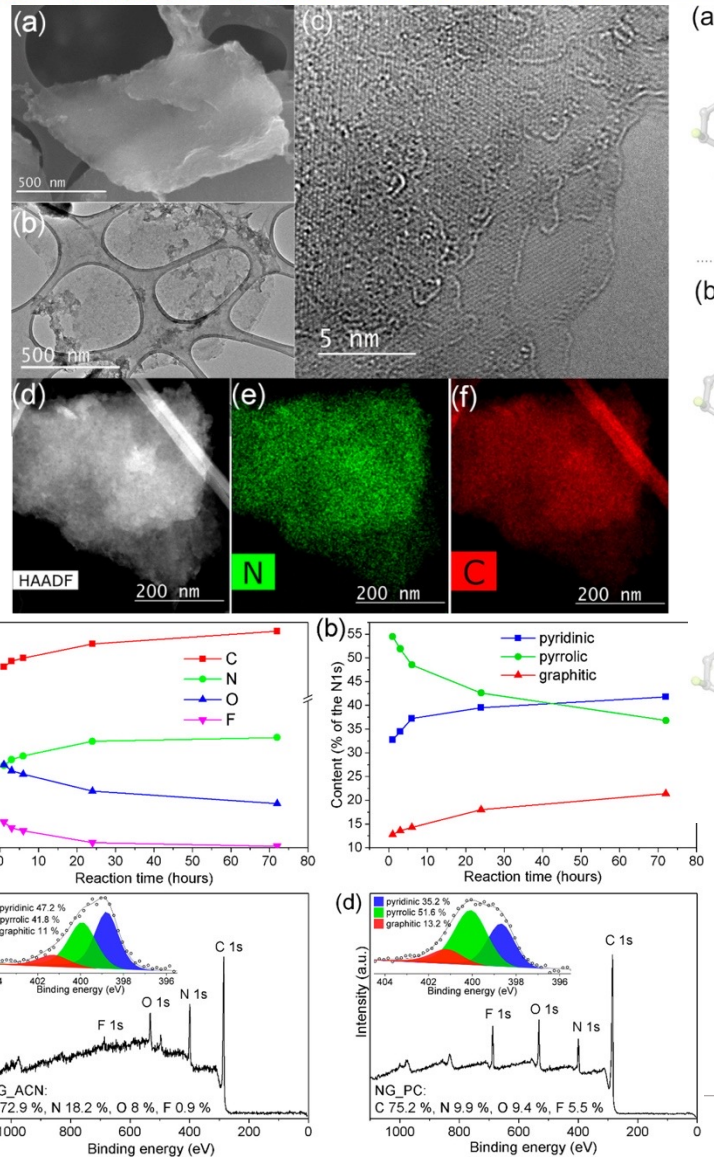

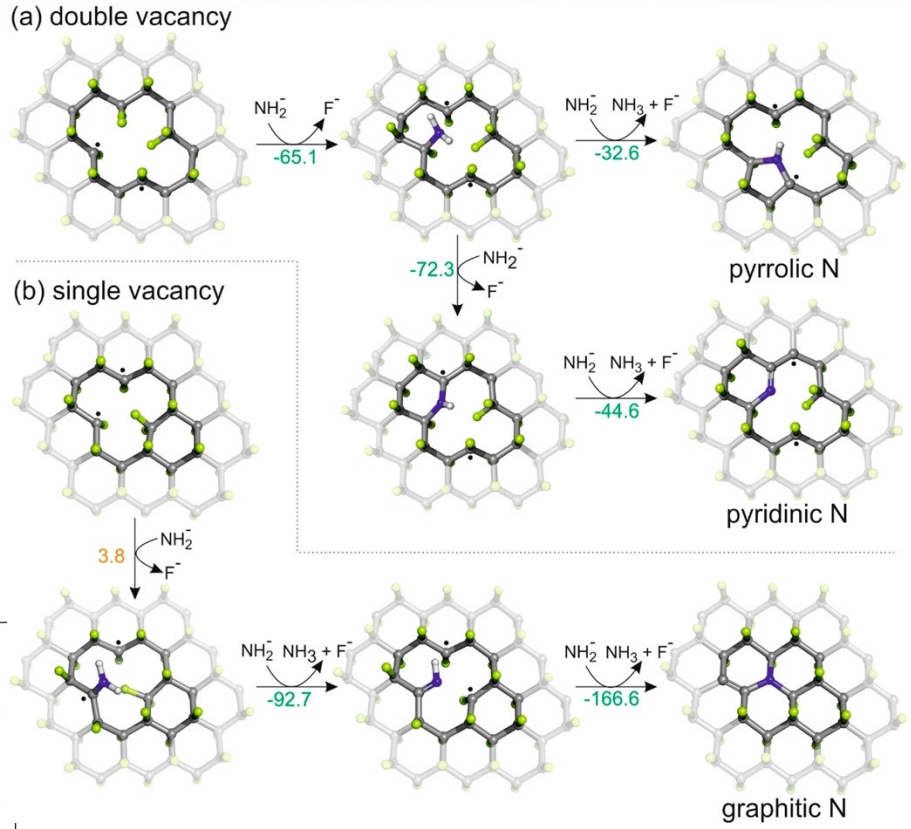

ACS Sustainable Chem. Eng., 8, 4764, 2020

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Fluorograhene reacts at mild conditions

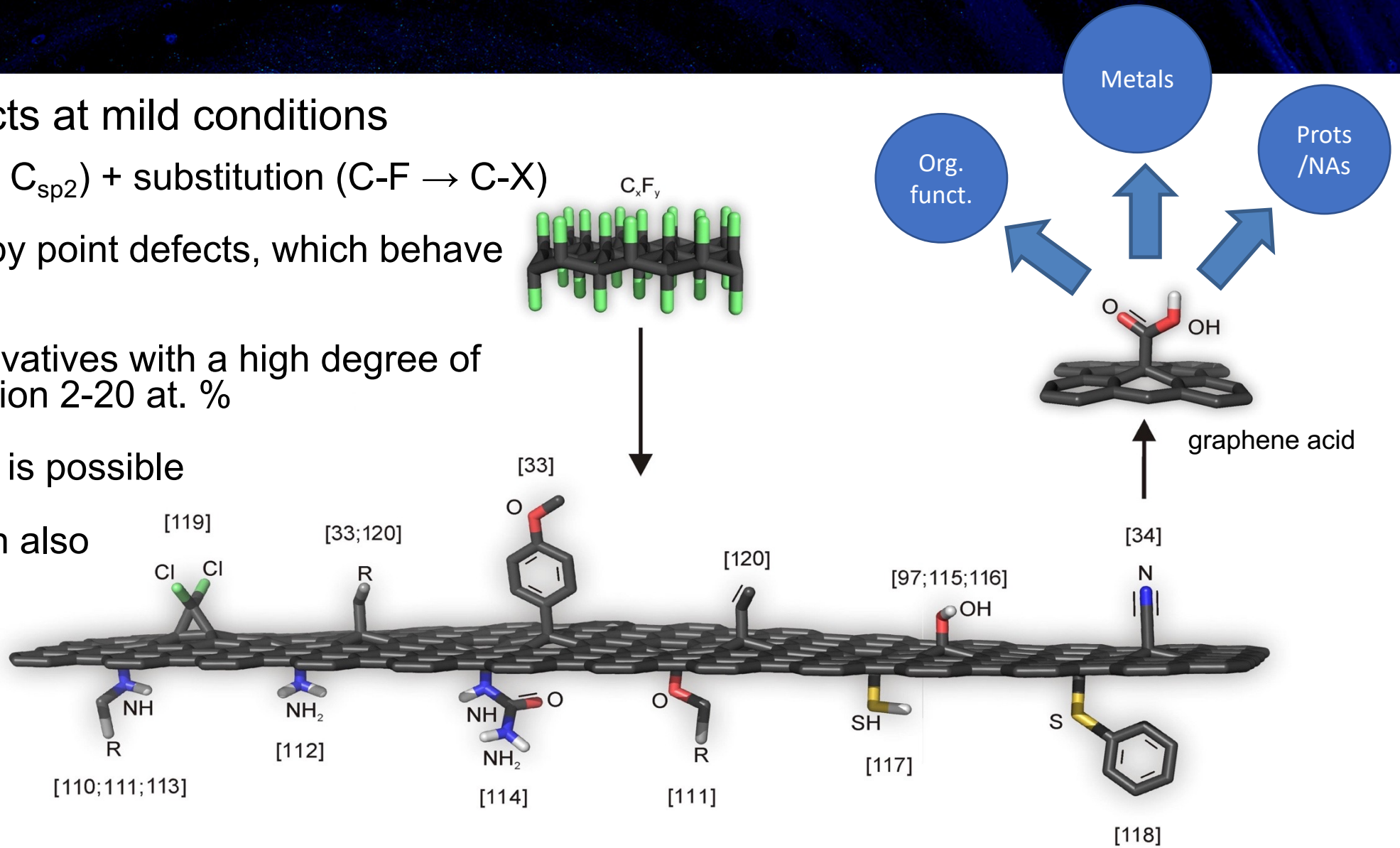
elimination (C_{sp3}-F → C_{sp2}) + substitution (C-F → C-X)

reaction is triggered by point defects, which behave like el-philes

lead to graphene derivatives with a high degree of surface functionalization 2-20 at. %

dual functionalization is possible

doped graphenes can also be prepared



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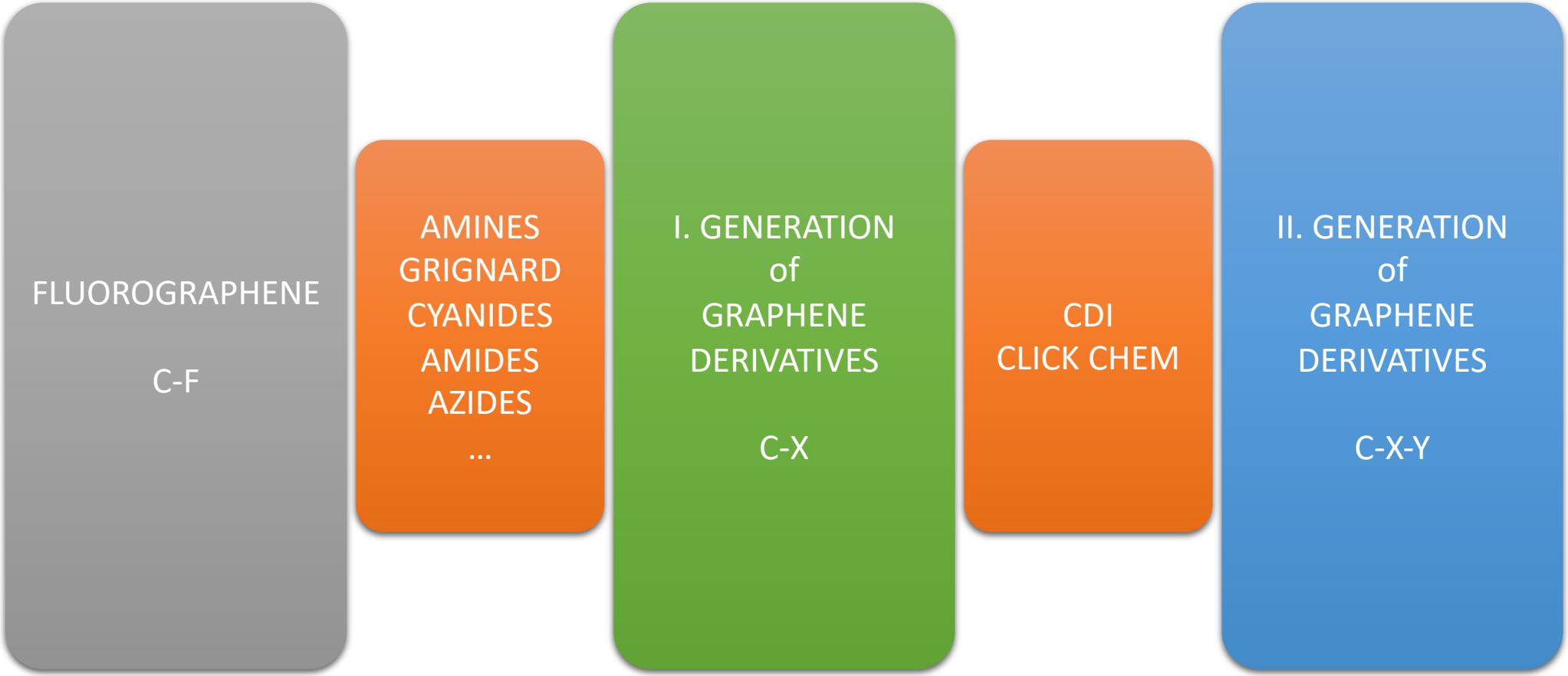
[refs therein]

Graphene derivatives based on fluorographene chemistry



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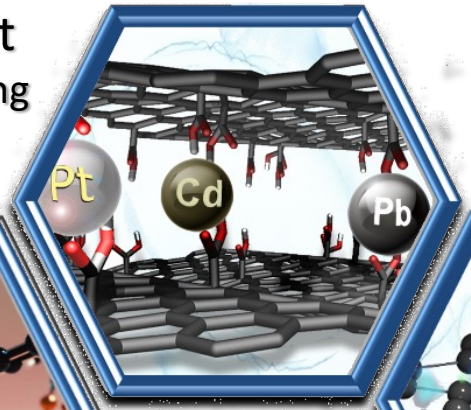
Fluorographene derivatives are useful for many applications

Environment
Detox-monitoring

ACS Nano **2021**, 15, 3349
Small **2022**, 18, 2201003



Spin control
Magnetism

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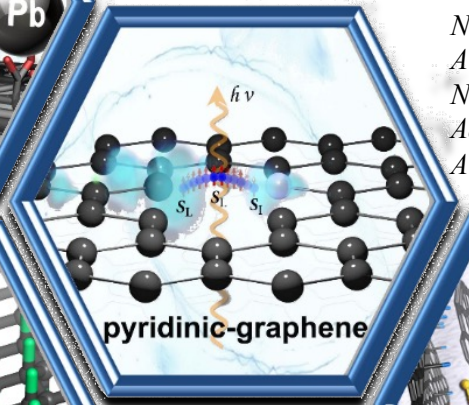

Catalysis

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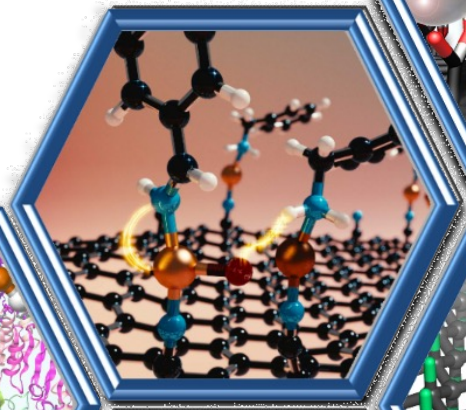
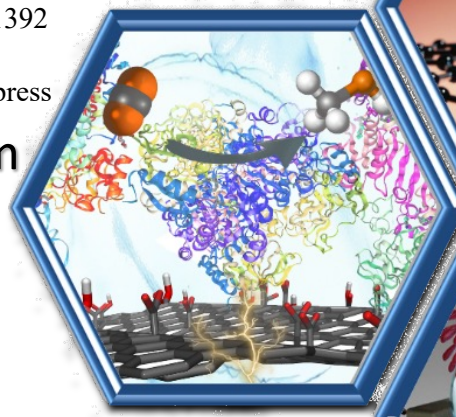
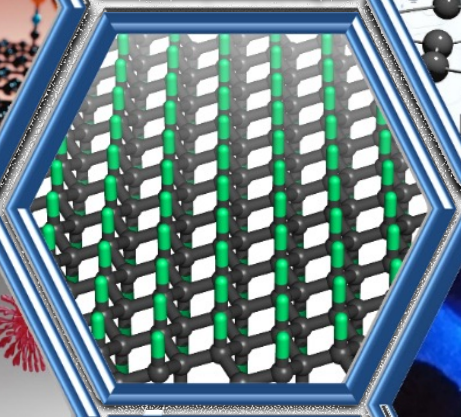
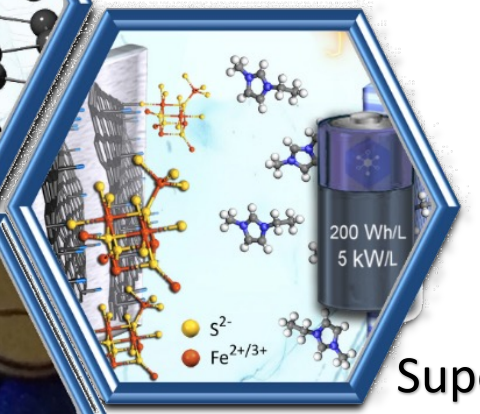


Single Atom Catalysis







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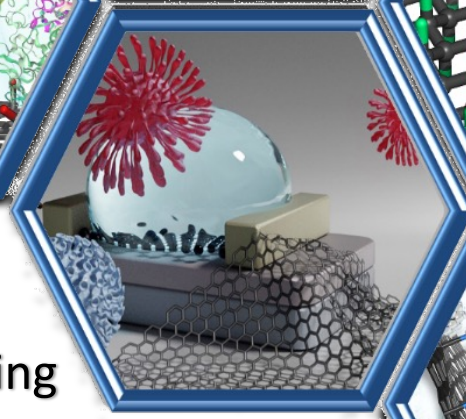

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Nano-bio interface

Antibacterial mat.; *Adv. Sci.* **2021**, 2003090

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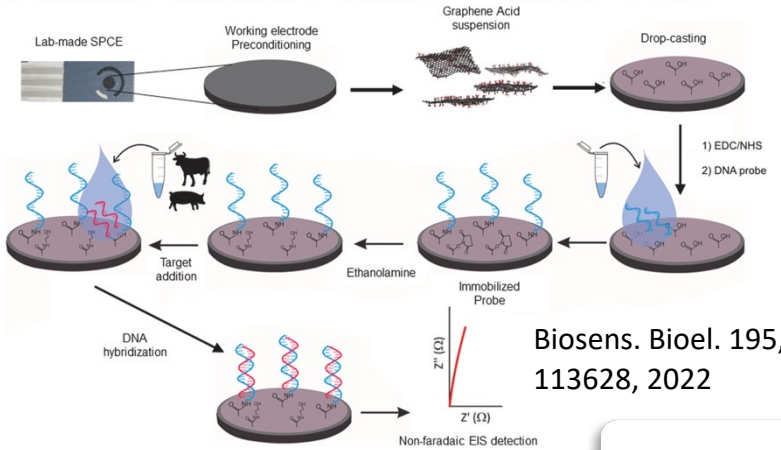

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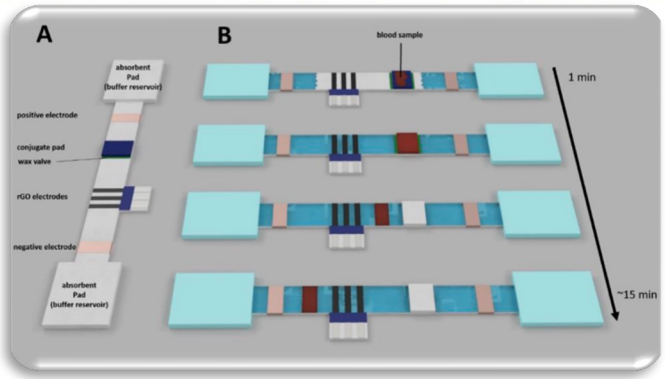
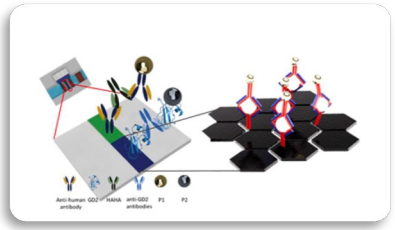
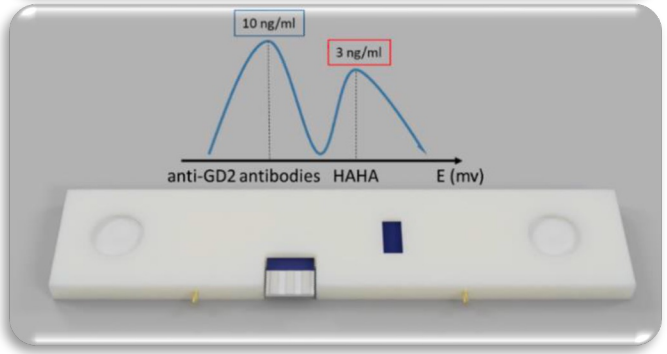






- Active sensing material
- Meet adulteration
- EuroNanoMed III (2022-25)

  GLEBioassay: a multiplexed point of care (PoC) nanobiosensing platform to monitor the efficacy of the naxitamab-based immunotherapy in neuroblastoma

- ATB sensing via PoC

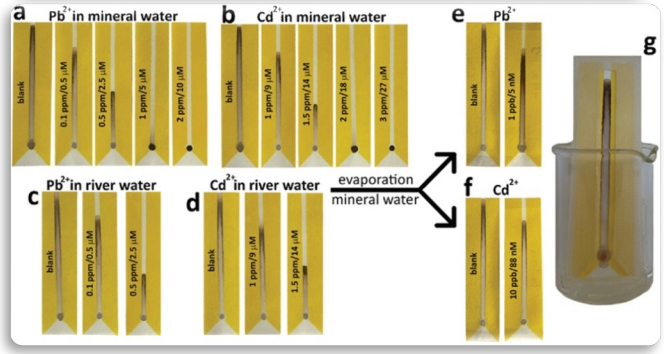
Palacký University Olomouc

ICN2 Institut Català de Nanociència i Nanotecnologia

Arben Merkoçi

SJD Sant Joan de Déu Institut de Recerca

nehir BİYOTEKNOLOJİ



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European Research Council

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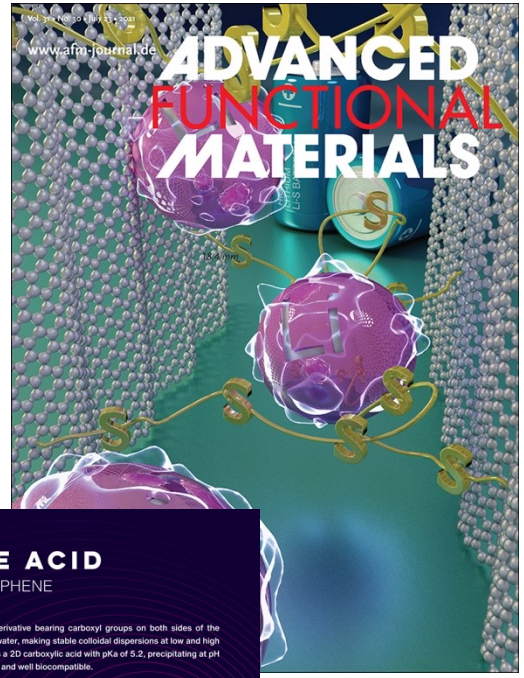

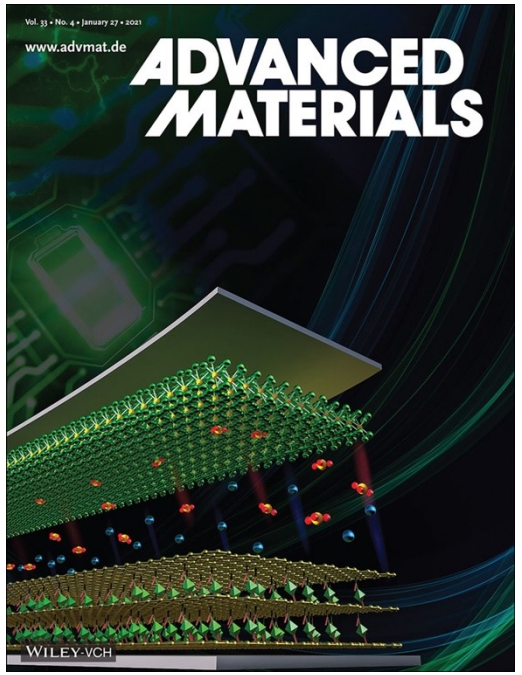

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