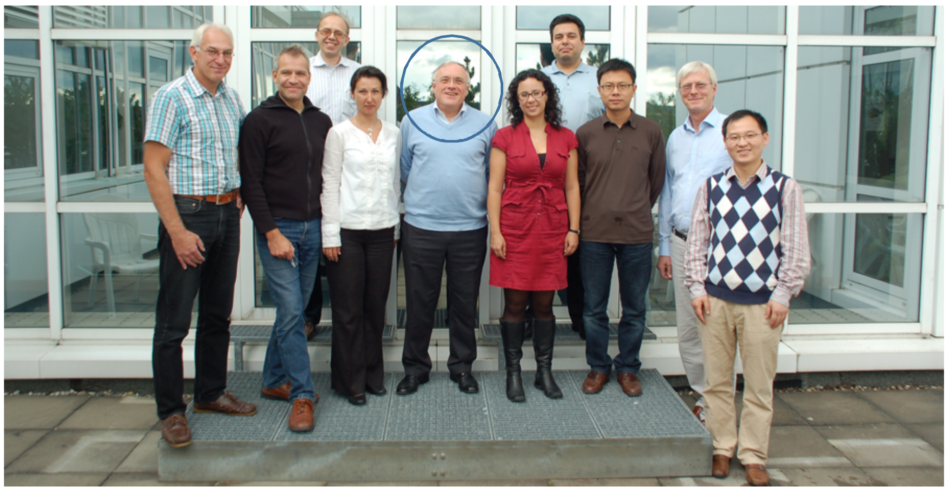
Career Review

(Klaus Mullen)

06/10/2015

Ki-Young Yoon

Prof. Klaus Müllen



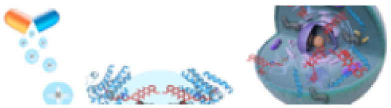
at Max Planck Institute

for Polymer Research, Germany

- Born in 1947
- Ph.D. in 1971 at Univeristy of Basel
- Post Doc. at ETH Zurich
- Independent career (1979-Present)
- Director at MPIP (1989-Present)
- JACS associate editor (2006-Present)

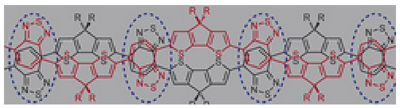
>1700 papers, H index=117

Research Interests



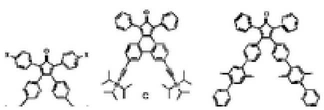
Biomaterials

Dr. Kalina Peneva



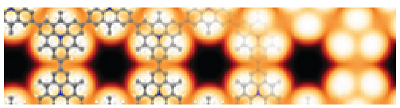
Conjugated Polymers

Prof. Dr. Martin Baumgarten



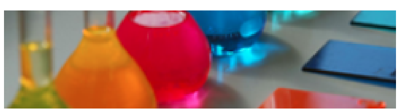
Dendritic Materials

Prof. Dr. Martin Baumgarten



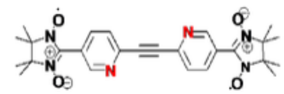
Graphite Group

Prof. Dr. Xinliang Feng / Dr. Manfred Wagner



High Performance Rylene Dyes

Dr. Long Chen



High Spin Organics

Prof. Dr. Martin Baumgarten

Mass Spectrometry

Dr. Hans Joachim Räder

NMR Spectroscopy

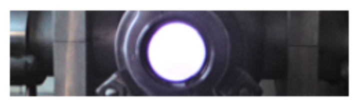
Dr. Manfred Wagner

Polymerisation Procedures

Dr. Markus Klapper

Material Science

Dr. Wojciech Pisula



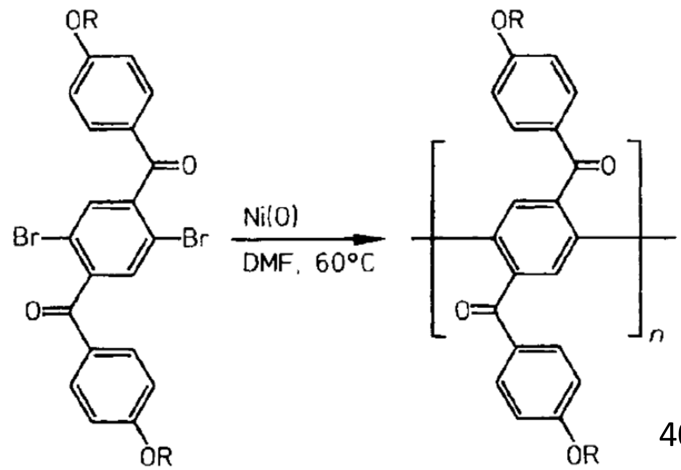
Inorganic-Organic Hybrid Systems

PD Dr. Hermann Sachdev

Mullen's webpage
http://www.mpip-mainz.mpg.de/17142/Research

Graphene nanoribbon

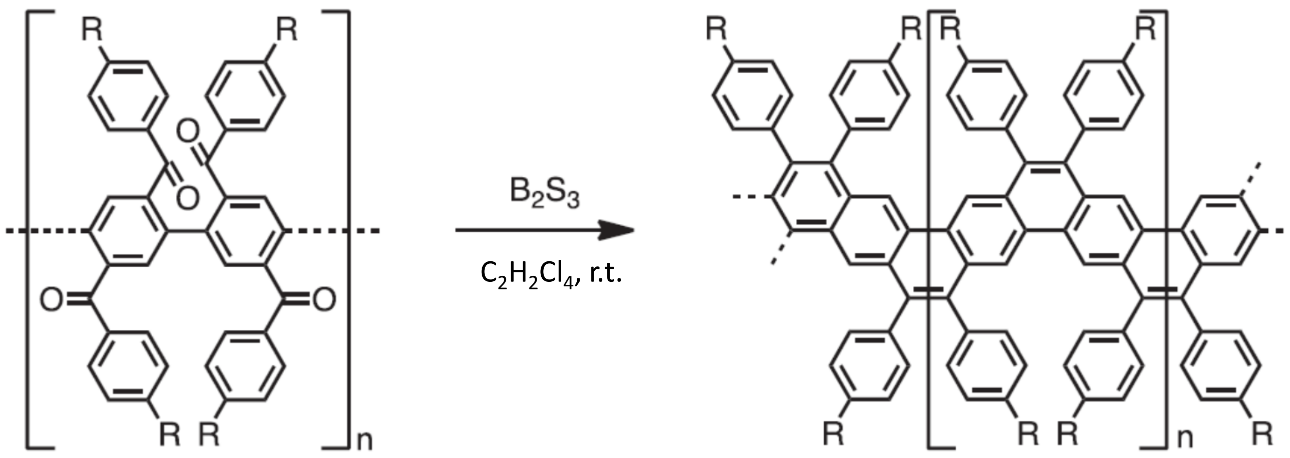
In 1993



4000 Da (PDI=1.37)

Yamamoto polymerization,
followed by carbonyl olefination

They hadn't realized
this was a graphene nanoribbon



1
R = $OC_{10}H_{21}$

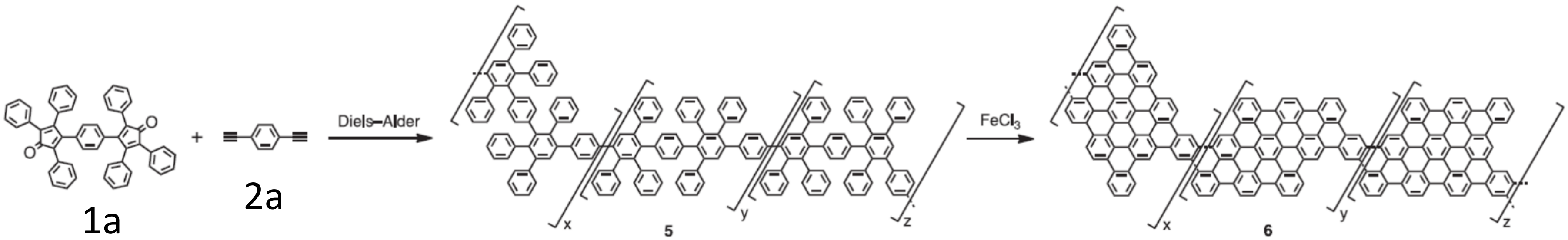
B_2S_3 was form In situ
from the mixture of BCl_3 with tricyclohexyltin sulfide

2

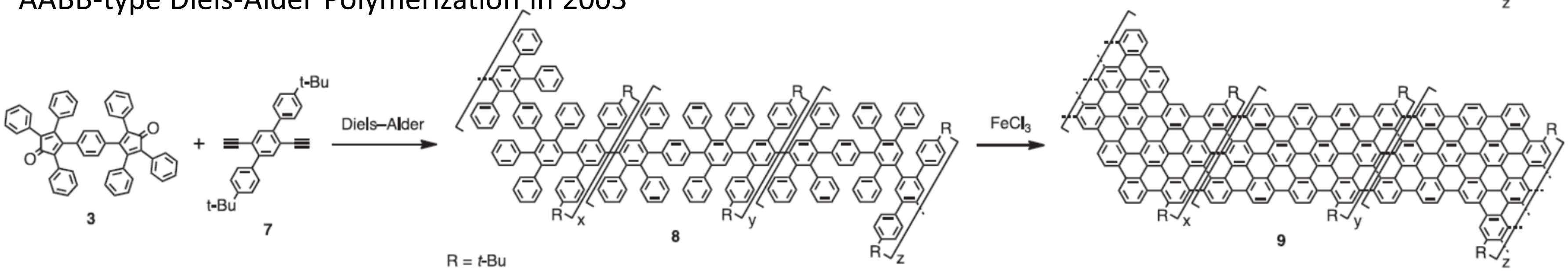
Macromol. Rapid. Commmun. **1993**, *14*, 217.

Graphene Nanoribbons (Solution Synthesis)

AABB-type Diels-Alder Polymerization in 2000 “Graphite ribbon”



AABB-type Diels-Alder Polymerization in 2003



M_n=6200 (PDI=1.9) – M_n=30100 (PDI=4.0)

Table 1. Reaction Conditions and Characterization of the Polymers (3a) Prepared by the Diels−Alder Polycondensation between 1,4-Bis(2,4,5-triphenylcyclopentadienone-3yl)benzene (1a) and 1,4-Diethynylbenzene (2a)

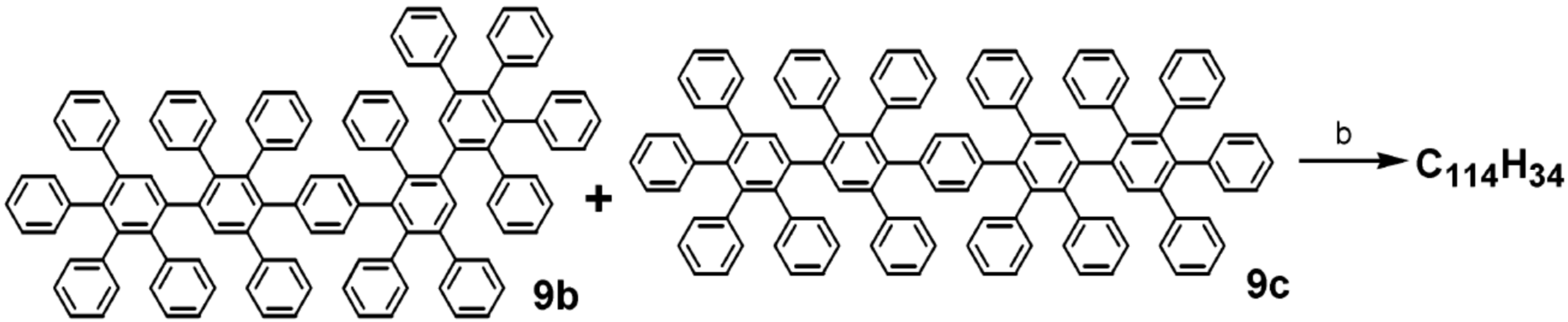
runs	concn of **1a** and **2a** [mol/L]	time of reaction [h]	yield [%]	$M_w \times 10^{-3\,a}$ [g mol^{-1}] (SEC)	$M_n \times 10^{-3\,a}$ [g mol^{-1}] (SEC)	M_w/M_n	MALDI-TOF (detected species)
a	0.3	18	92	12.3	6.2	1.9	16mer
b	0.3	30	94	17.4	8.6	2.0	18mer
c	0.5	18	91	32.2	14.1	2.3	18mer
d	0.5	30	92	40.6	16.8	2.5	*b*
e	0.5	48	94	51.5	19.7	2.7	*b*
f	0.7	48	93	101.4	26.6	3.9	*b*
g	0.7	72	94	121.6	30.1	4.0	*b*

[a] Determined with polystyrene as standard. [b] Measurements were not performed.

Higher monomer concentration
Longer reaction time
=> Higher MW

Macromolecules **2000**, *33*, 3525
Macromolecules **2003**, *36*, 7082

How to characterize the polymers after Scholl oxidation



(a) Ph_2O, reflux; (b) $FeCl_3$, CH_2Cl_2, CH_3NO_2, 20 h.

MALDI

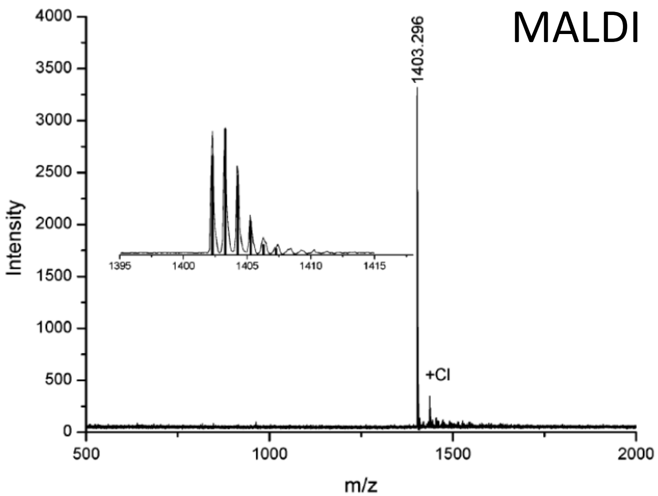


Figure 1. MALDI MS spectrum for $C_{114}H_{34}$: calculated, 1403.54; found, 1403.30 (100%). Isotope distribution is in good agreement with the simulated results (black bar). In addition, some chloronation took place during the cyclodehydrogenation with Lewis acid iron(III) chloride.

UV

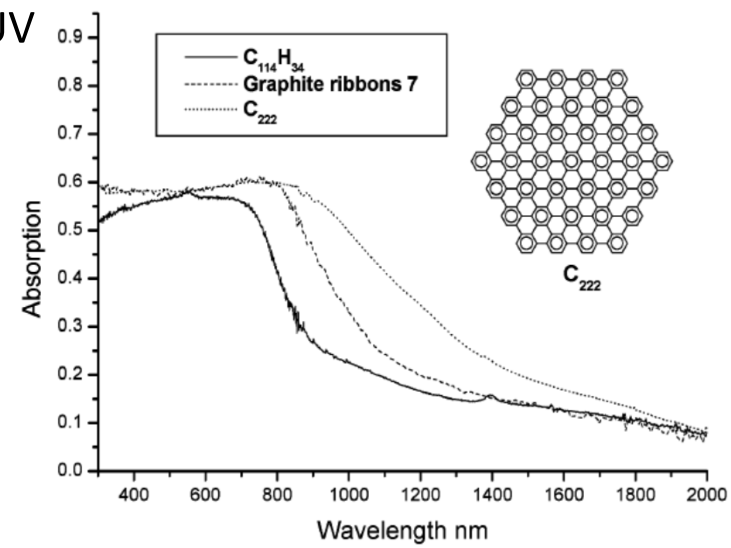


Figure 2. Solid-state UV−vis spectrum of graphite ribbon **7**, **C114H34**, and **C222**.

Macromolecules **2003**, *36*, 7082

How to characterize the polymers after Scholl oxidation

IR

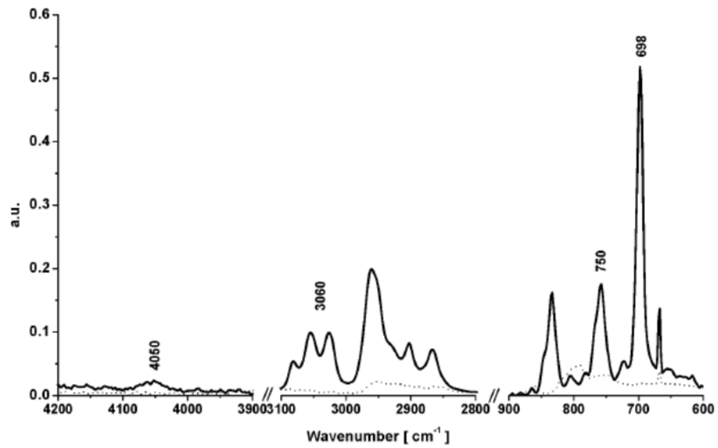


Figure 3. Infrared spectra of branched polyphenylene precursor **6** (solid line) and graphite ribbon **7** (dot line).

Raman

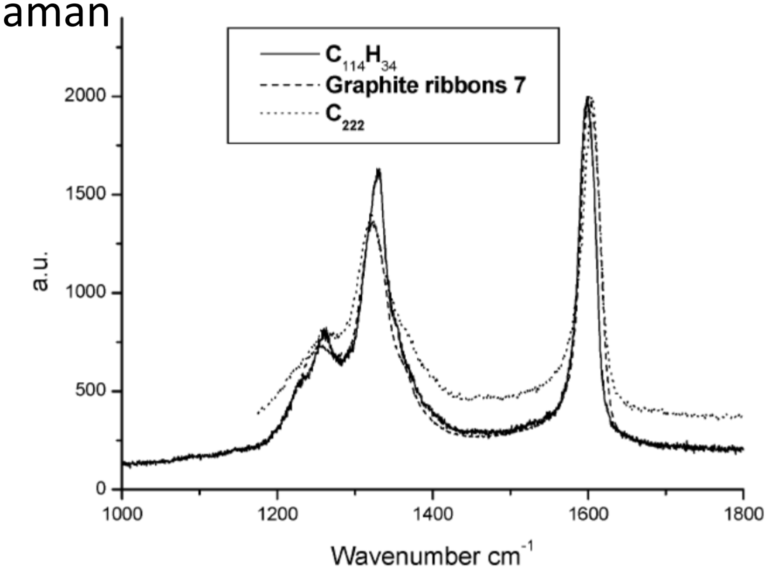


Figure 4. Raman spectra of graphite ribbon **7**, **C114H34**, and **C222**.

Disappearance of
monosubstituted benzene peaks
& “free” rotated benzene peak

Existence of
G band (~1600 cm^{-1}) & D band (~1300 cm^{-1})

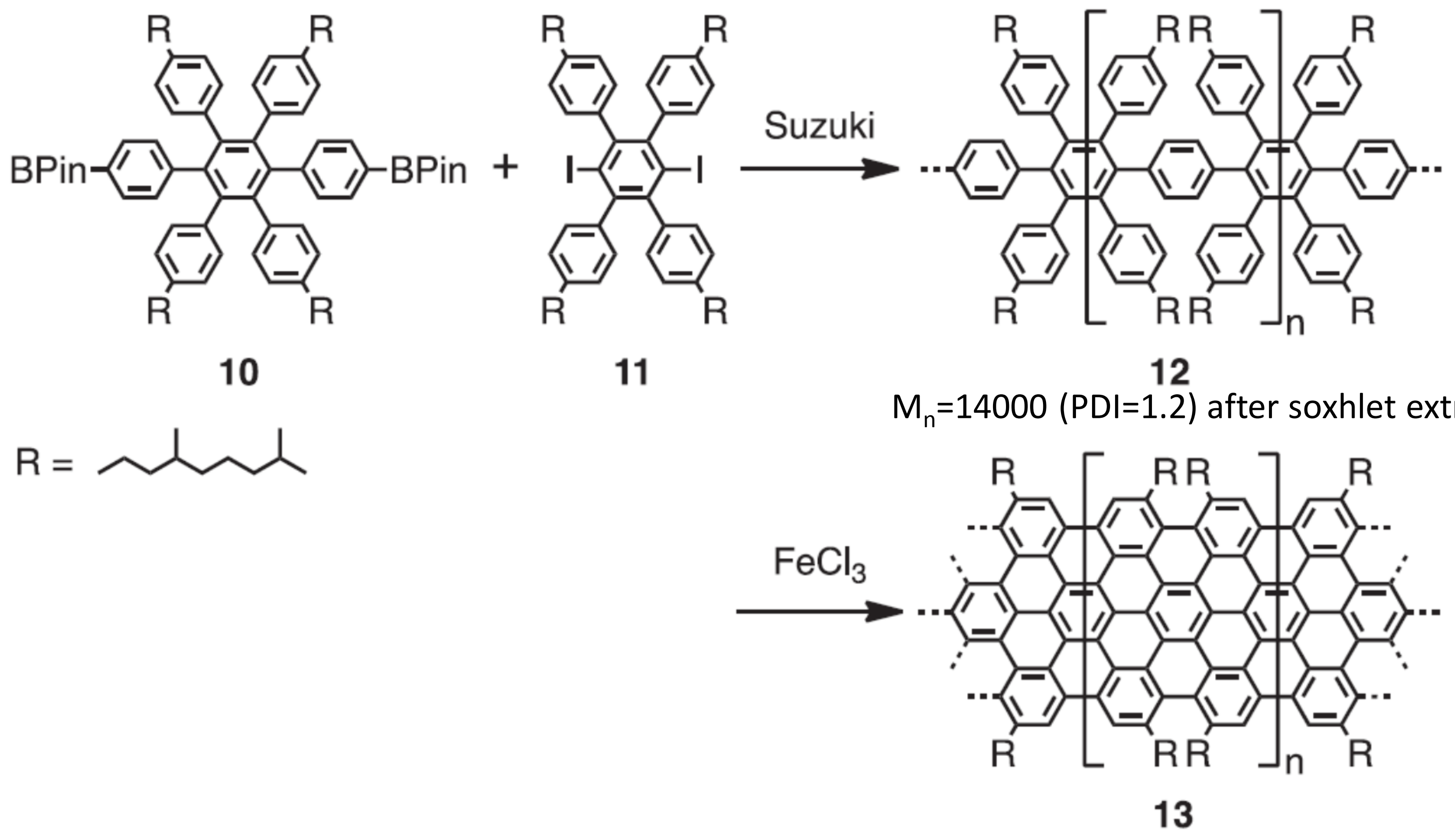
+ Microscopic analyses

Macromolecules **2003**, *36*, 7082

Graphene Nanoribbons (Solution Synthesis)

AABB-type Suzuki Polymerization in 2008

"Graphene Nanoribbon"



M_n=14000 (PDI=1.2) after soxhlet extraction

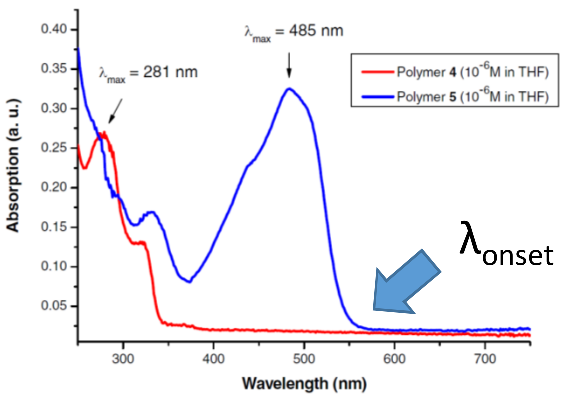
N=9 GNR

Only up to 12 nm GNR

JACS **2008**, *130,* 4216

Graphene Nanoribbons (Solution Synthesis)

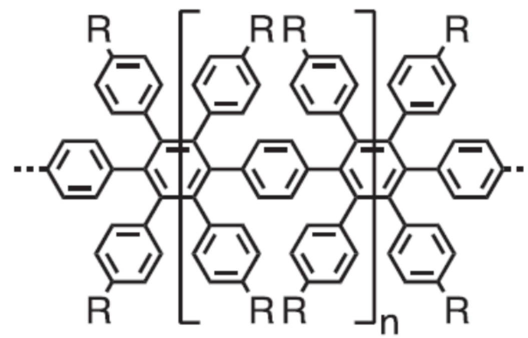
AABB-type Suzuki Polymerization in 2008



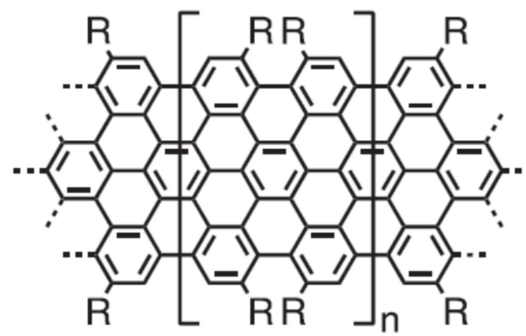
λ_{onset}=~550 nm

2.3 eV
Too large bandgap
(if infinite length, 1 eV)

Tip : 1240/ λ_{onset}= Bandgap (eV)



12



13

N=9 GNR

Only up to 12 nm GNR

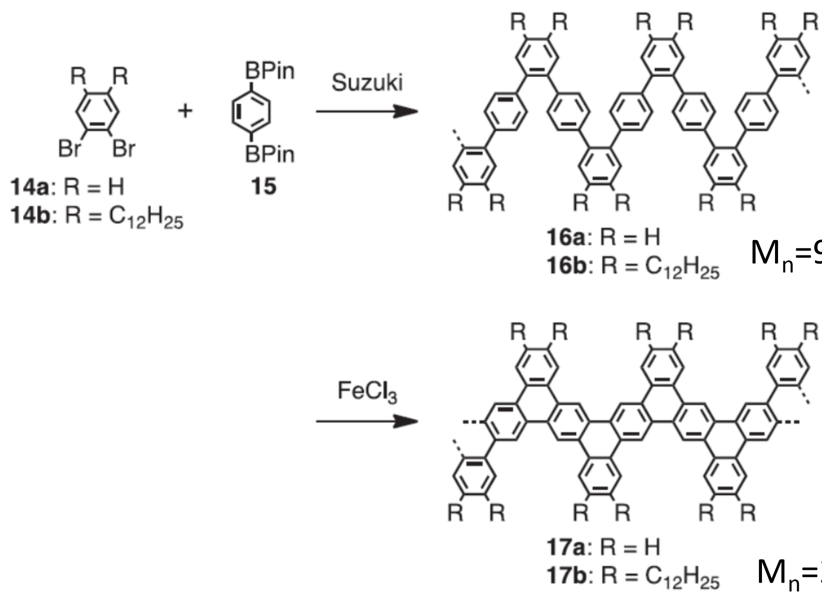
The low efficiency of polymerization was presumably

i) High steric hindrance
ii) Limited solubility due to rigid PPP backbone

JACS **2008**, *130*, 4216

Graphene Nanoribbons (Solution Synthesis)

AABB-type Suzuki Polymerization in 2011



M_n=9900 (PDI=1.4)

M_n=20000

Q3

Less steric hindrance,
Better solubility (Flexible polymer)
- 40 mg/mL in DCM, THF, Toluene

No bandgap information

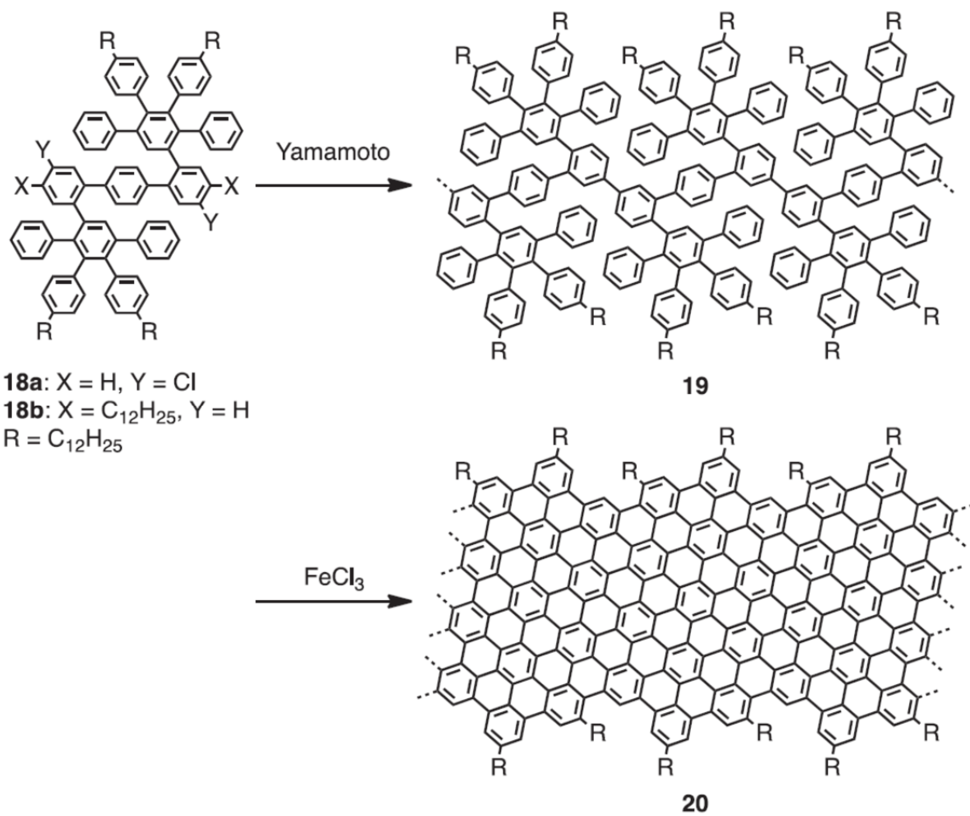
25 nm for GNR
(no evidence)

A paper that the main script doesn't match with SI.

ACIE. **2011**, *50*, 2540

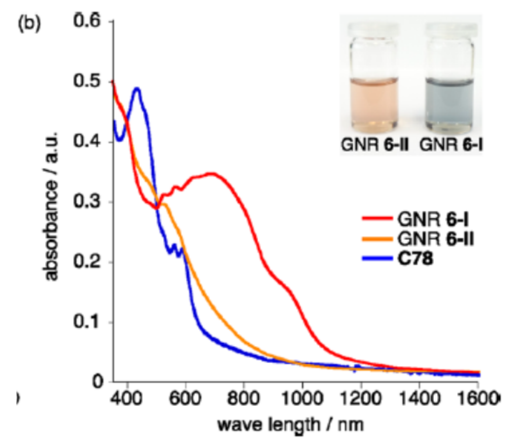
Graphene Nanoribbons (Solution Synthesis)

AA-type Yamamoto Polymerization in 2012



From polymer with M_n=13000 (PDI=2.2), (by prep GPC)

High MW part, M_n=44000 (PDI=1.2)
Low MW part, M_n=6700 (PDI=1.1)



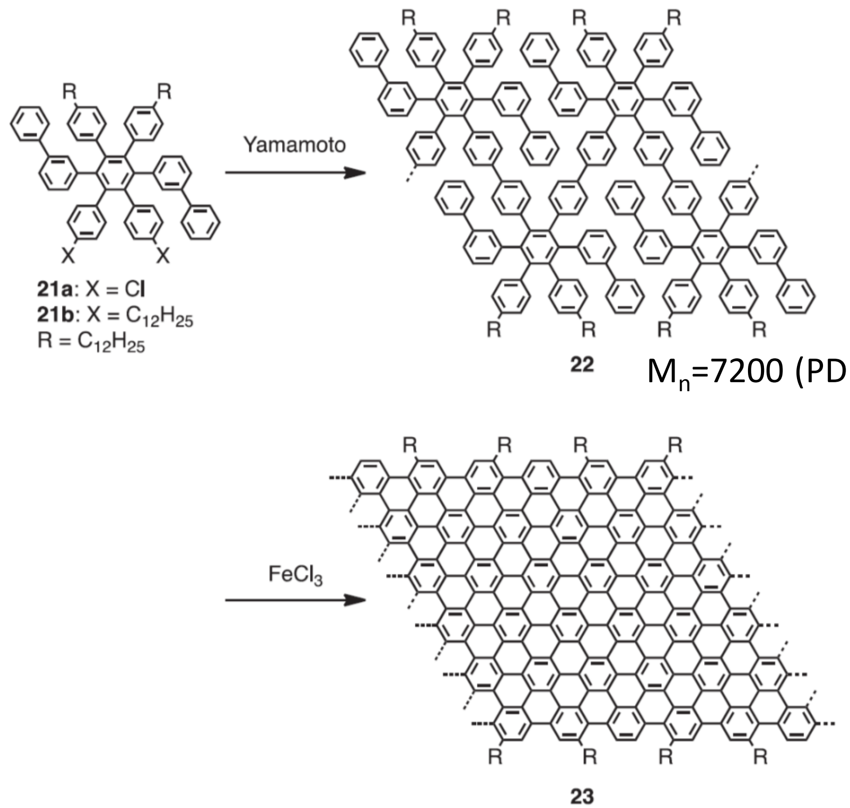
20-30 nm length based on M_n & Bandgap
(No microscopic data)

No problem of stoichiometric inbalance
, which AABB-type polymerization always has.

JACS. **2012**, *134,* 18169

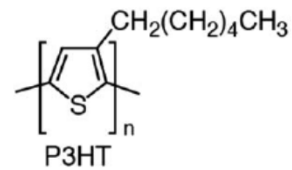
Graphene Nanoribbons (Solution Synthesis)

AA-type Yamamoto Polymerization in 2014



M_n=7200 (PDI=1.4)

OFET device (with P3HT)

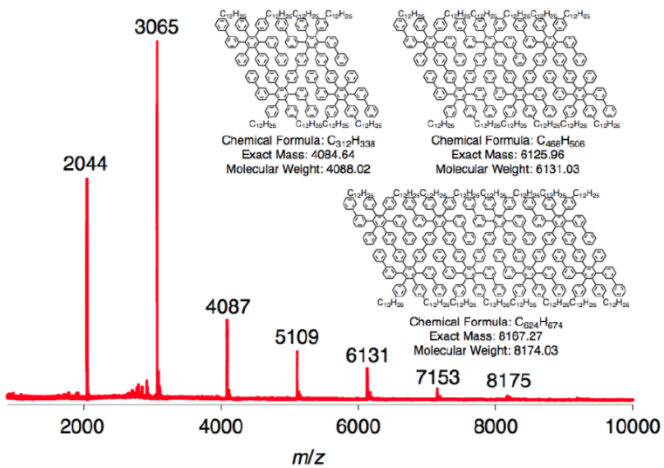


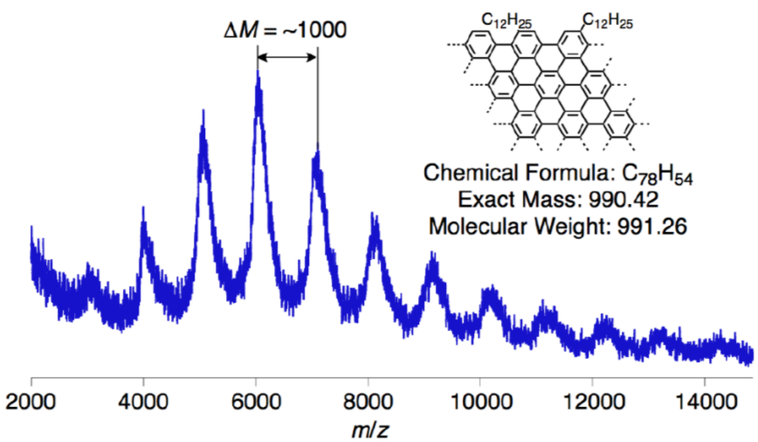
Optical bandgap=~1.6 eV => **Q1**

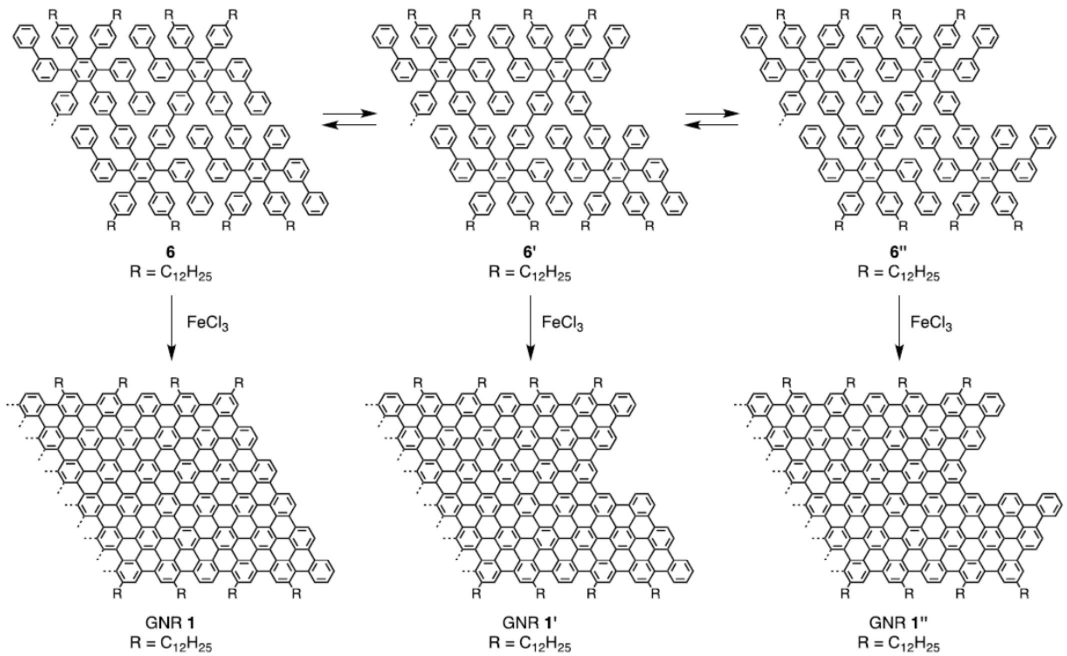
Nanoscale. **2014**, *6,* 6301

Graphene Nanoribbons (Solution Synthesis)

AA-type Yamamoto Polymerization in 2014





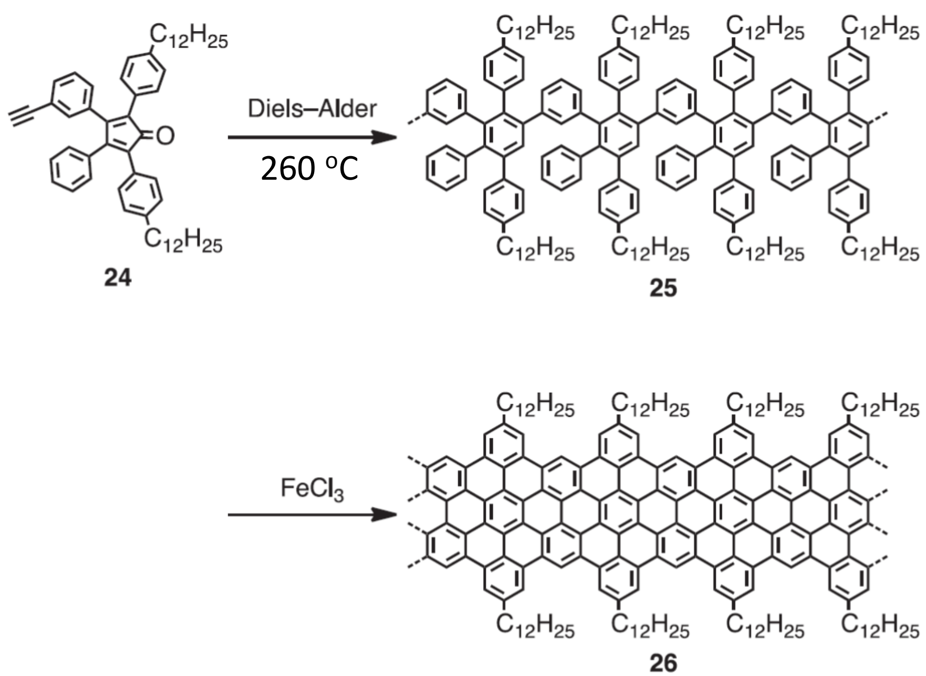


Very broad mass spec

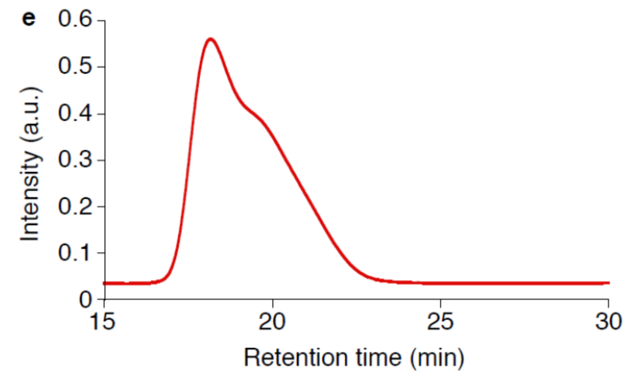
Nanoscale. **2014**, *6,* 6301

Graphene Nanoribbons (Solution Synthesis)

AB-type Diels-Alder Polymerization in 2014

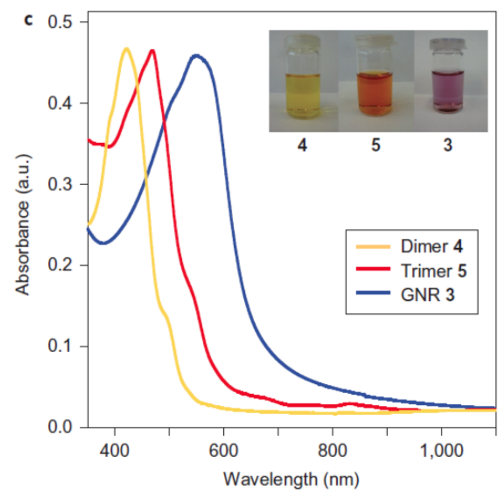


GPC trace



M_n=340,000 (PDI=1.9) after fractionation.

UV/vis



Bandgap
=1.88 eV

Nat. Chem. **2014**, *6,* 126

Graphene Nanoribbons (Solution Synthesis)

AB-type Diels-Alder Polymerization in 2014

Entry	Solvent	C (mM)	T (h)	$M_{w,PPP}$–$M_{w,PS}$ (kgmol^{-1})	$M_{n,PPP}$–$M_{n,PS}$ (kgmol^{-1})	PDI_{PPP}–PDI_{PS}
1	Ph_2O	36.6	25	14–24	6.1–7.9	2.3–3.0
2	Ph_2O	228	28	73–150	19–27	3.8–5.6
2'	—	—	—	100–220	65–120	1.5–1.8
3	Ph_2O	1410	20	220–530	29–41	7.6–13
3'	—	—	—	270–640	160–340	1.7–1.9
4	melt	—	1.5	150–350	29–41	5.2–8.5
4'	—	—	—	150–380	69–120	2.2–3.1
5	melt	—	5.0	250–620	32–45	7.8–14

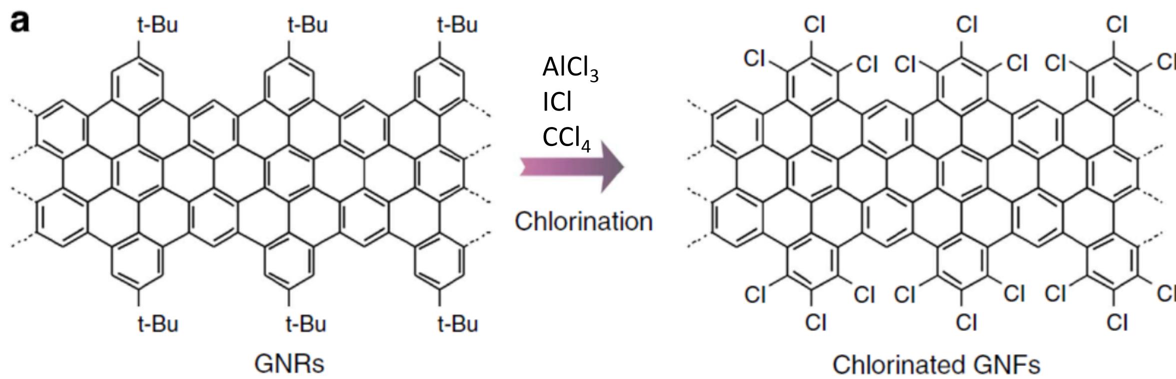
Although purified, M_n is very high

After fractionation by prep GPC

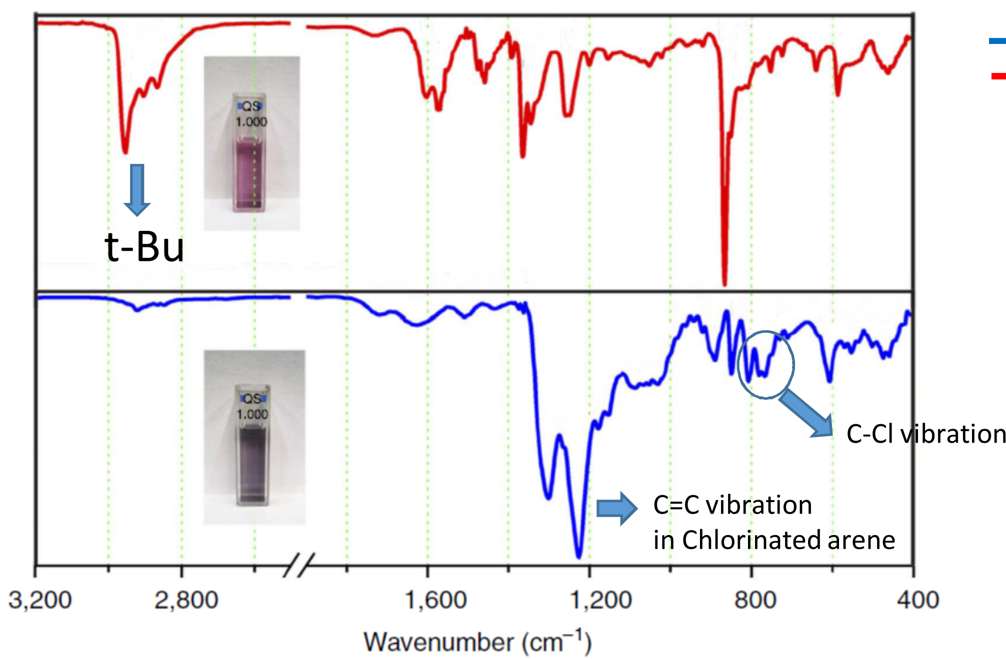
Nat. Chem. **2014**, *6,* 126

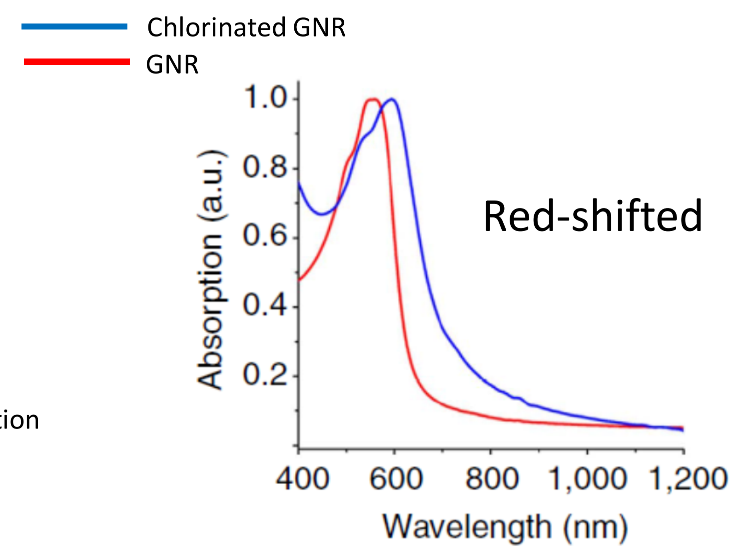
Graphene Nanoribbons (Solution Synthesis)

Chlorination of GNR reported in NChem2014



Solubility increases
0.05 mg/mL
in NMR or trichlorobenzene





Nat. Commun. **2013**, *4*, 2646

Graphene Nanoribbons (Solution Synthesis)

Conductivity from GNR of NChem2014

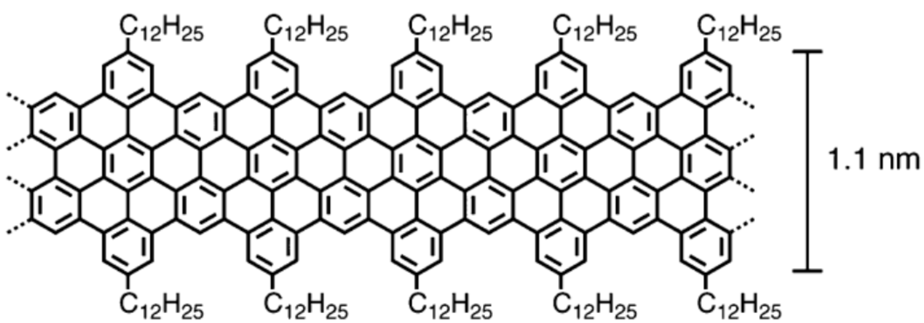


Figure 1. Chemical structure of the GNRs investigated. Quantum confinement in the lateral dimension induces a bandgap of 1.88 eV.

Mobility itself is good
Quantum Yield is low

Table 1. Fit Parameters from the Probe Frequency-Dependent GNR Data and CNT Conductivity Fitted to the Drude−Smith Model, eq 1[a]

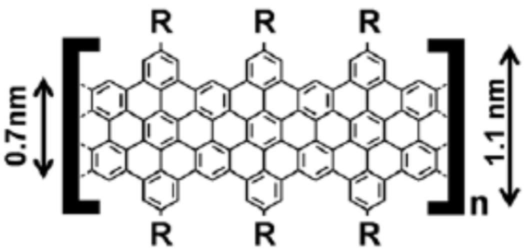
	c	τ (fs)	QY (%)
GNR dispersion	−0.92 ± 0.01	30 ± 3	3 ± 1
GNR film	−0.79 ± 0.07	35 ± 20	4 ± 3
CNTs in gel	−0.90 ± 0.02	170 ± 50	15 ± 10
CNT film	−0.72 ± 0.05	150 ± 15	27 ± 10

Our findings of longer scattering times and higher free carrier generation quantum efficiency in CNTs as compared to GNRs suggest that CNT-based (opto)-electronic devices will likely be more efficient than GNR-based ones.

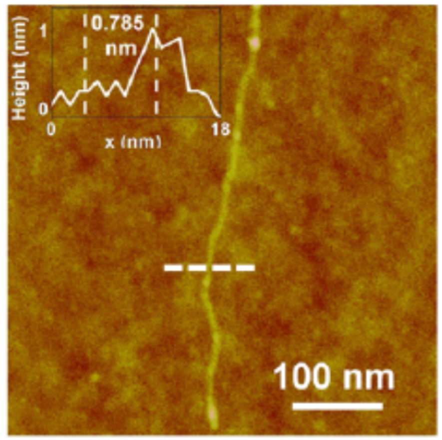
Nano Lett. **2013**, *13*, 5925

Graphene Nanoribbons (Solution Synthesis)

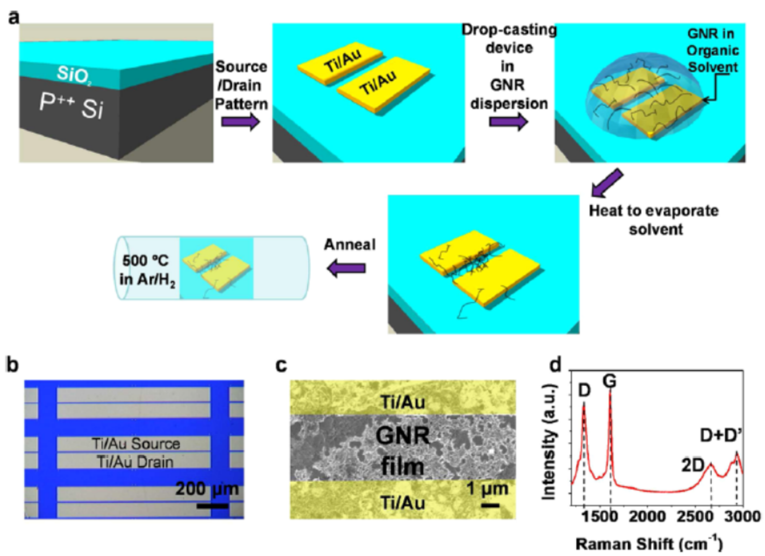
Single-GNR-based device : NO_2 sensing



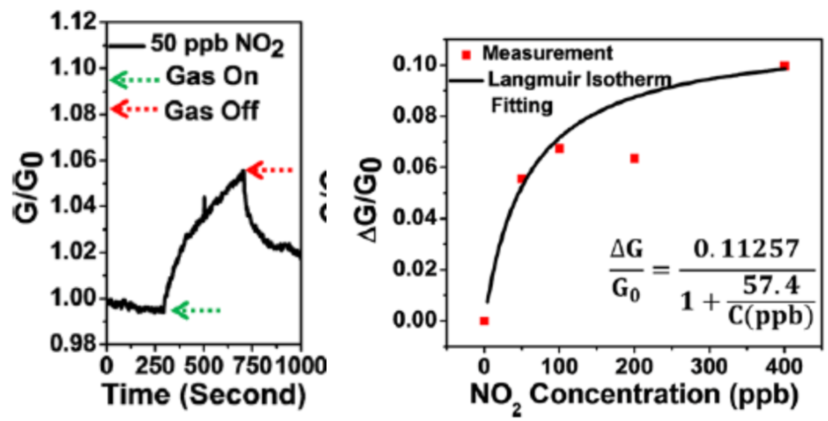
1a: R = $C_{12}H_{25}$
1b: R = *t*-Bu



500 nm length



Conductance (G)
increases by electron extraction from NO_2

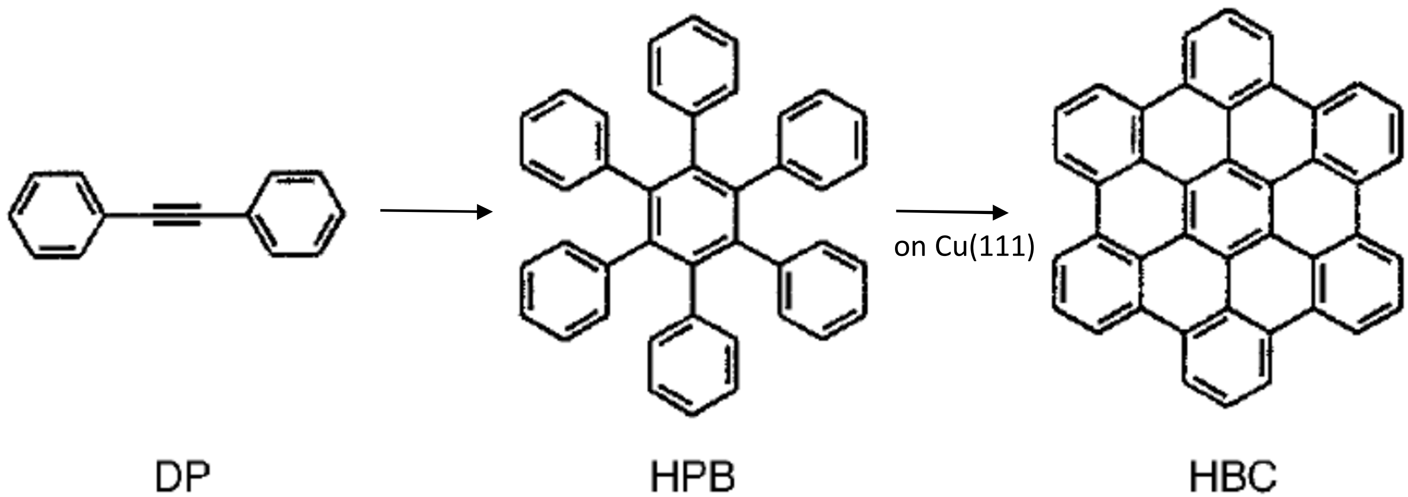


$$\frac{\Delta G}{G_0} = \frac{0.11257}{1 + \frac{57.4}{C(ppb)}}$$

JACS **2014**, *136*, 7555

Graphene Nanoribbons (Surface Synthesis)

Surface-assisted synthesis in 1999.

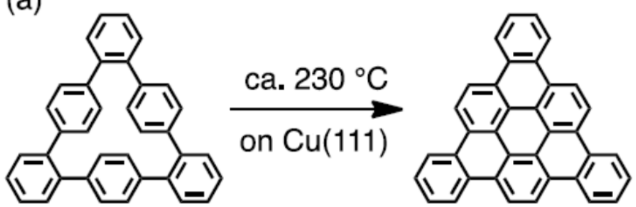


ACIE. **1999**,*38*, 3748

Graphene Nanoribbons (Surface Synthesis)

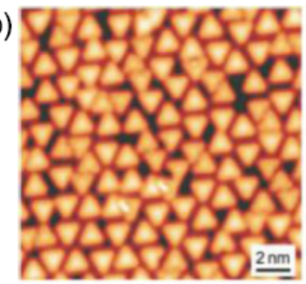
Surface-assisted synthesis in 2010 with Fasel group.

(a)

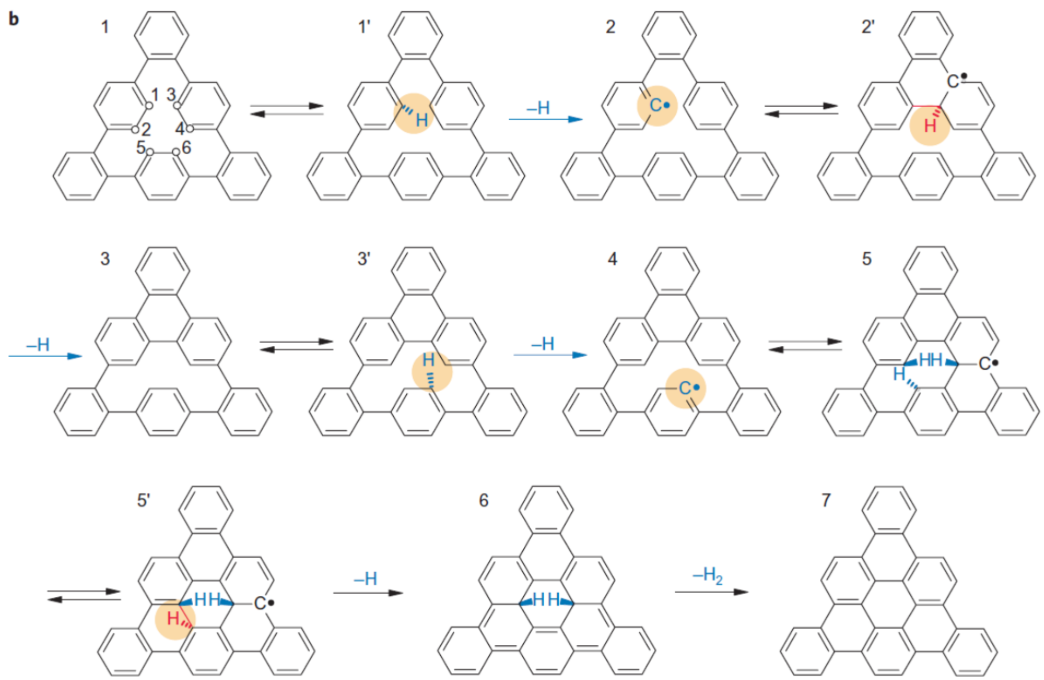


27 28

(b)



Surface-assisted cyclodehydrogenation



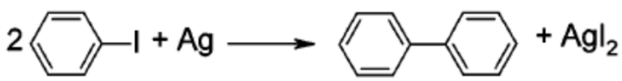
Based on STM imaging & Ab initio simulation

Nat. Chem. **2011**, *3,* 61

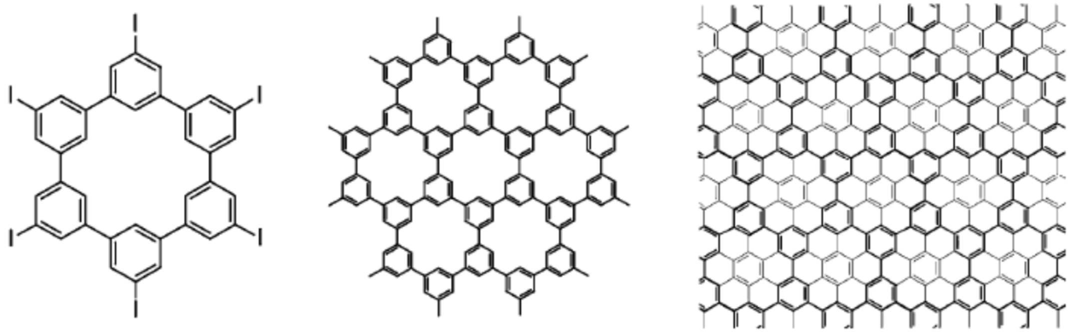
Graphene Nanoribbons (Surface Synthesis)

Surface-assisted synthesis in 2009 with Fasel group.

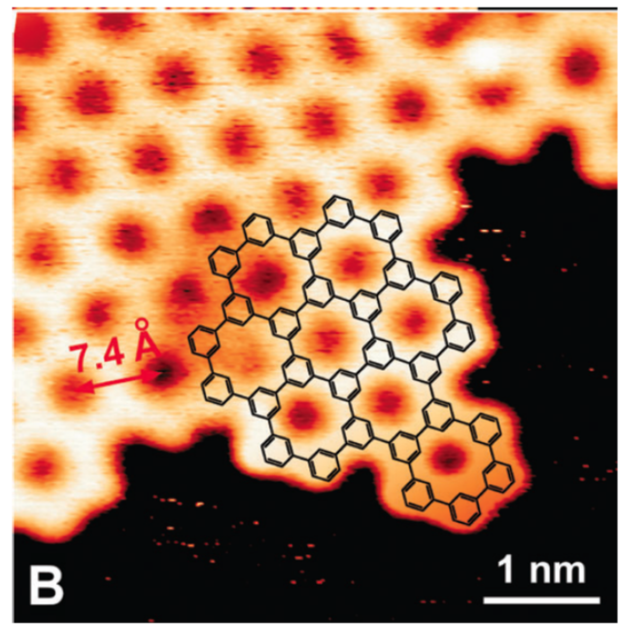
On Ag(111) surface at 200 °C



A On-surface coupling of aryl halide



B C D

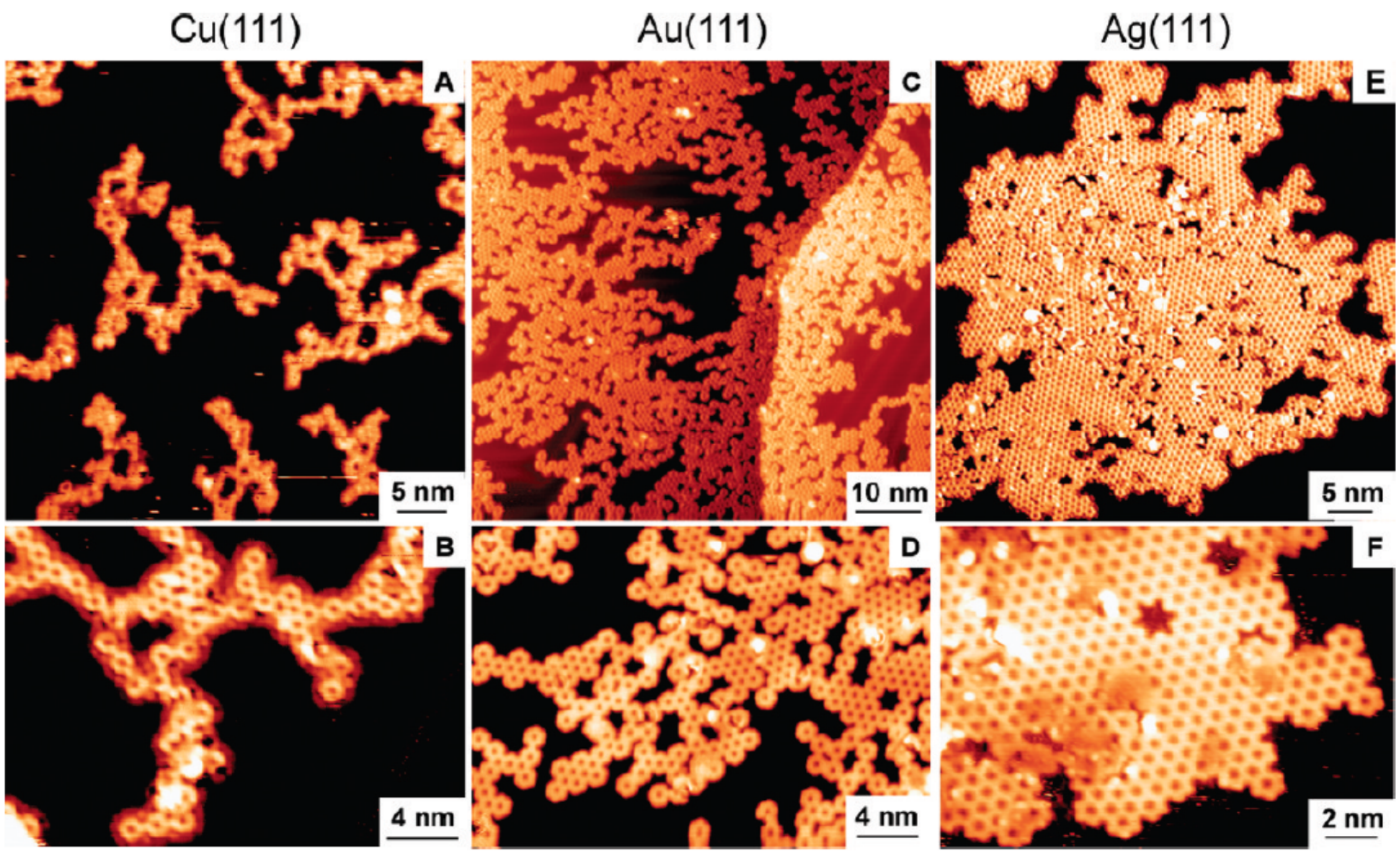


Radical formation on surface, and then radical polymerization

Chem. Commun. **2009***,* 6919

Graphene Nanoribbons (Surface Synthesis)

Surface-assisted synthesis in 2010 with Fasel group.

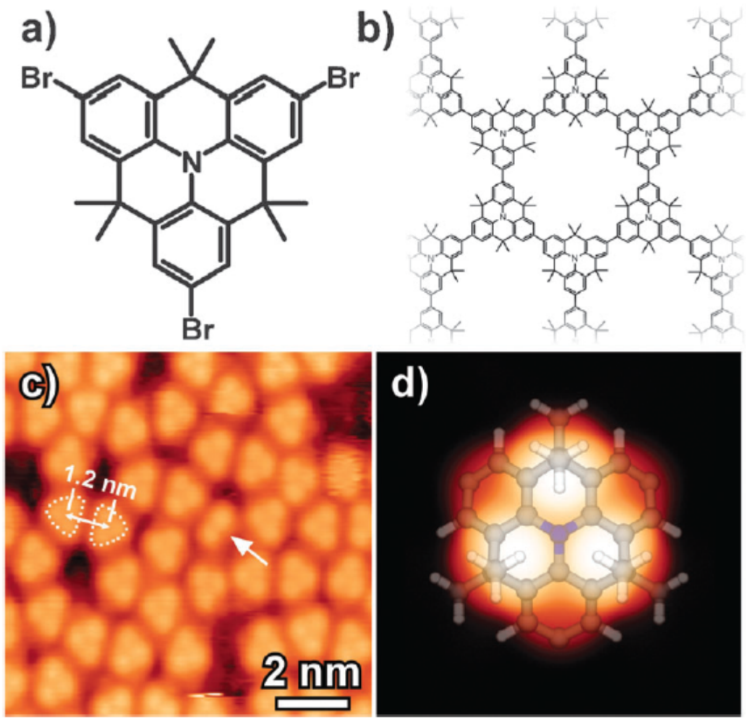


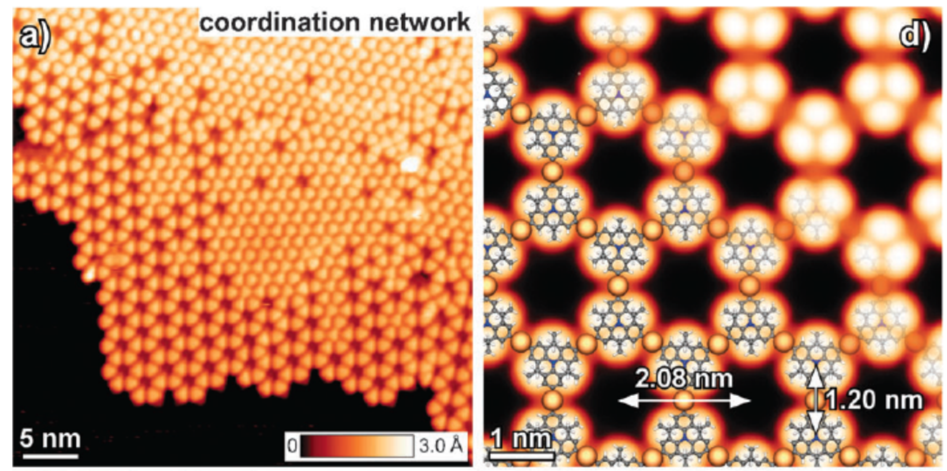
The choice of surface plays a crucial role,
Mainly because of the balance between diffusion and intermolecular coupling

JACS. **2010***, 132,* 16669

Graphene Nanoribbons (Surface Synthesis)

Surface-assisted synthesis in 2010 with Fasel group.



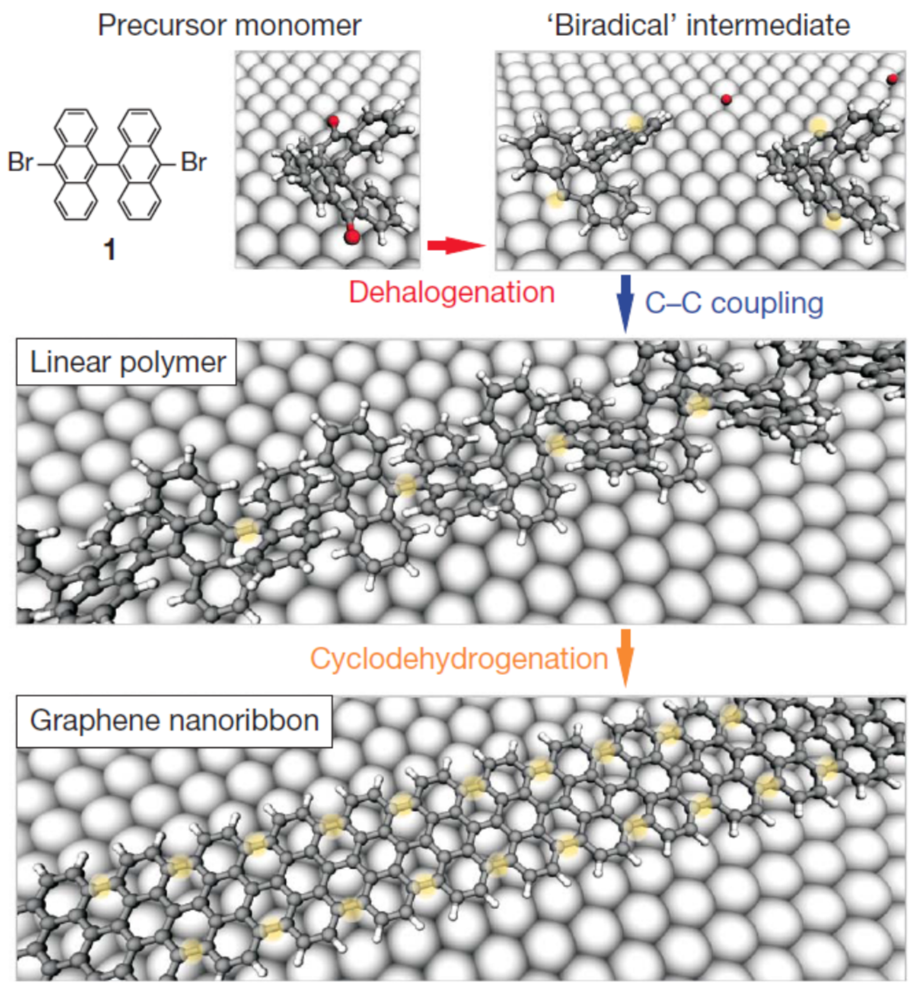


N-doped version

Chem. Commun. **2011**, *47*, 6919

Graphene Nanoribbons (Surface Synthesis)

Surface-assisted synthesis of graphene nanoribbon in 2010.



Typical procedure

i) Vacuum sublimation
of dihalogenated monomers onto a metal surface

ii) Biradical monomer formation
by thermal cleavage on surface

iii) Radical polymerization
of the surface-stabilized biradical intermediates

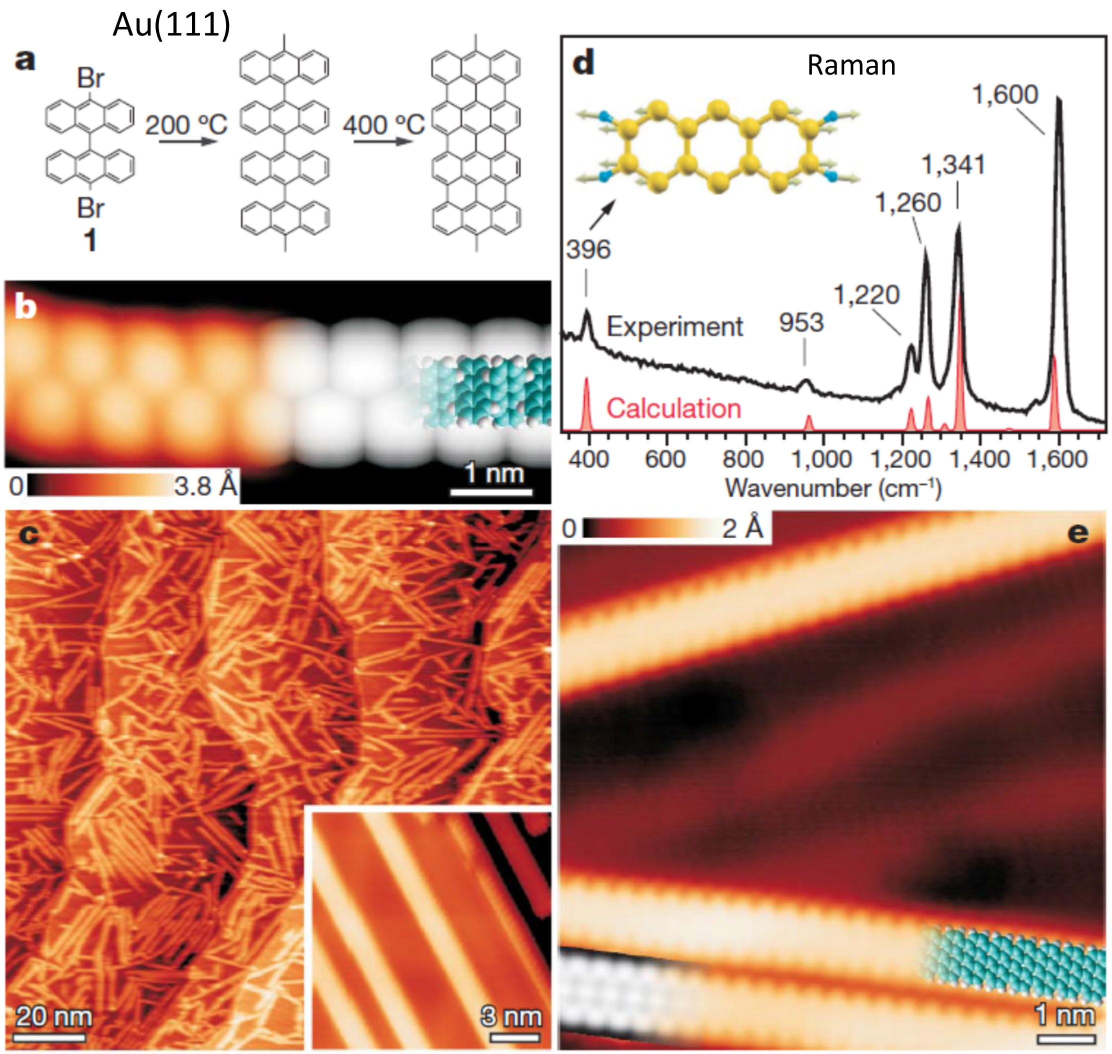
iv) Surface-assisted cyclodehydrogenation
by annealing at a higher temperature.

Advantage
- no worries about solubility
- in situ STM monitoring

Nature **2010**, *466*, 470

Graphene Nanoribbons (Surface Synthesis)

Surface-assisted synthesis of graphene nanoribbon in 2010.

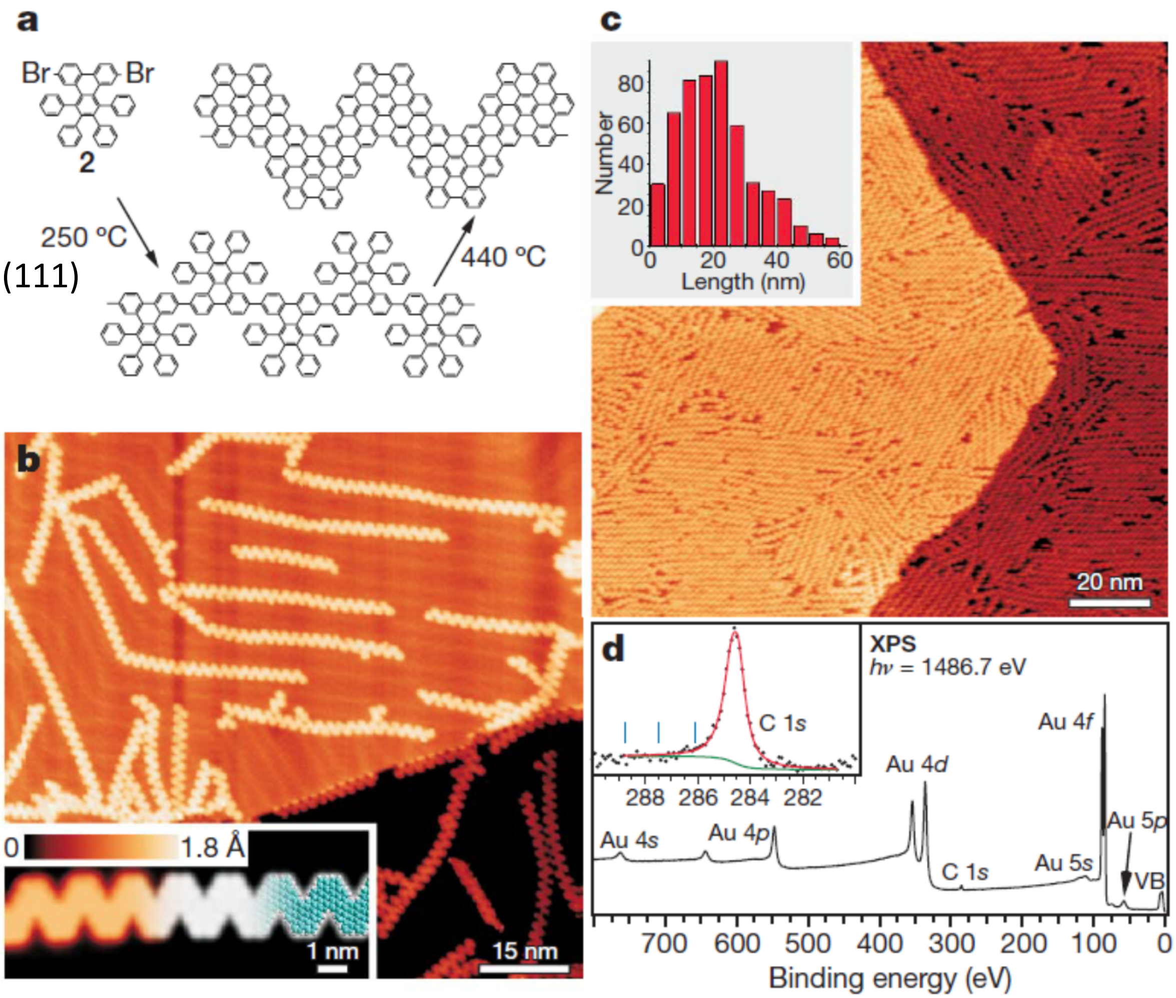


Atomically precious
and very long GNR

Nature **2010**, *466*, 470

Graphene Nanoribbons (Surface Synthesis)

Surface-assisted synthesis of graphene nanoribbon in 2010.



Au(111)

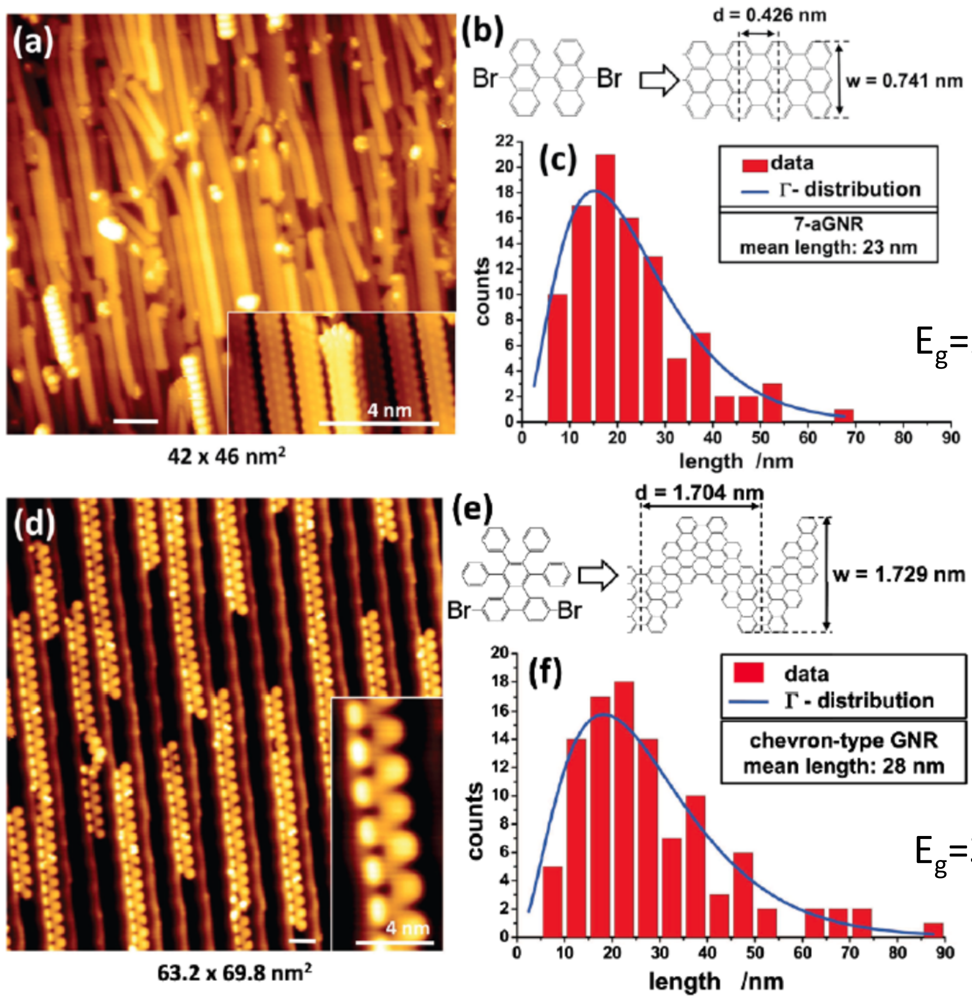
Chevron-type GNR

Chemically pure

Nature **2010**, *466*, 470

Graphene Nanoribbons (Surface Synthesis)

Surface-assisted synthesis of graphene nanoribbon in 2012.



On Au(788) surface,

Spatially aligned GNRs

E_g=2.8 eV on Au(788),
2.3 eV on Au(111)

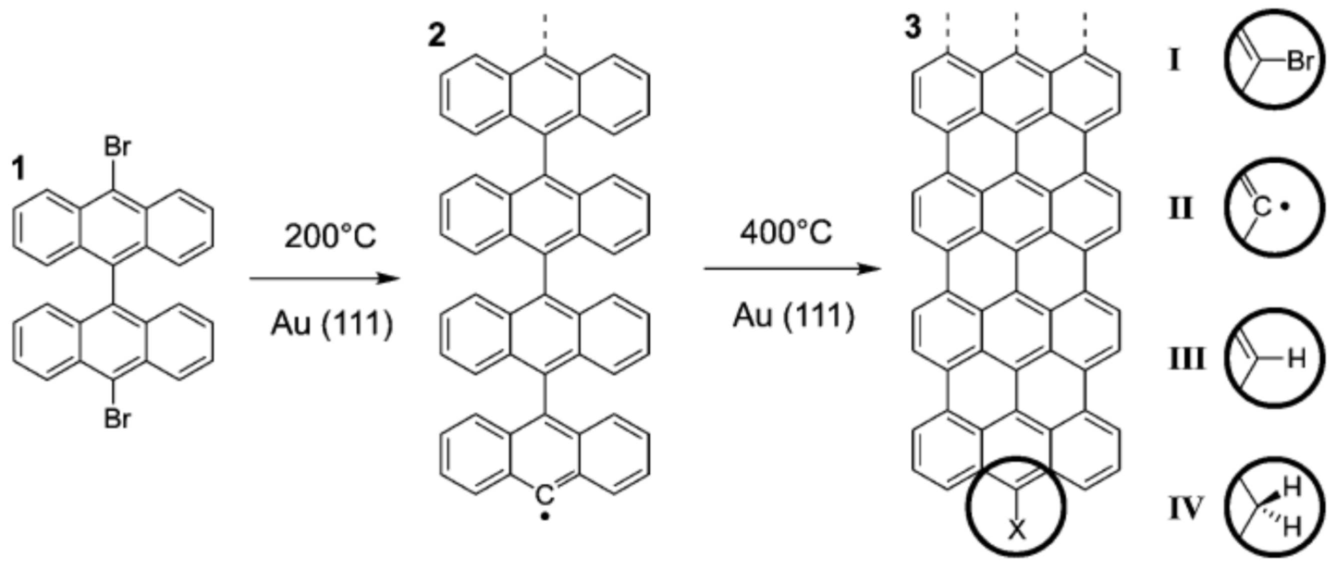
E_g=3.1 eV

Phys. Rev. Lett. **2012**, *108,* 216801

Graphene Nanoribbons (Surface Synthesis)

Termination factor of Surface-assisted GNR synthesis in 2013.

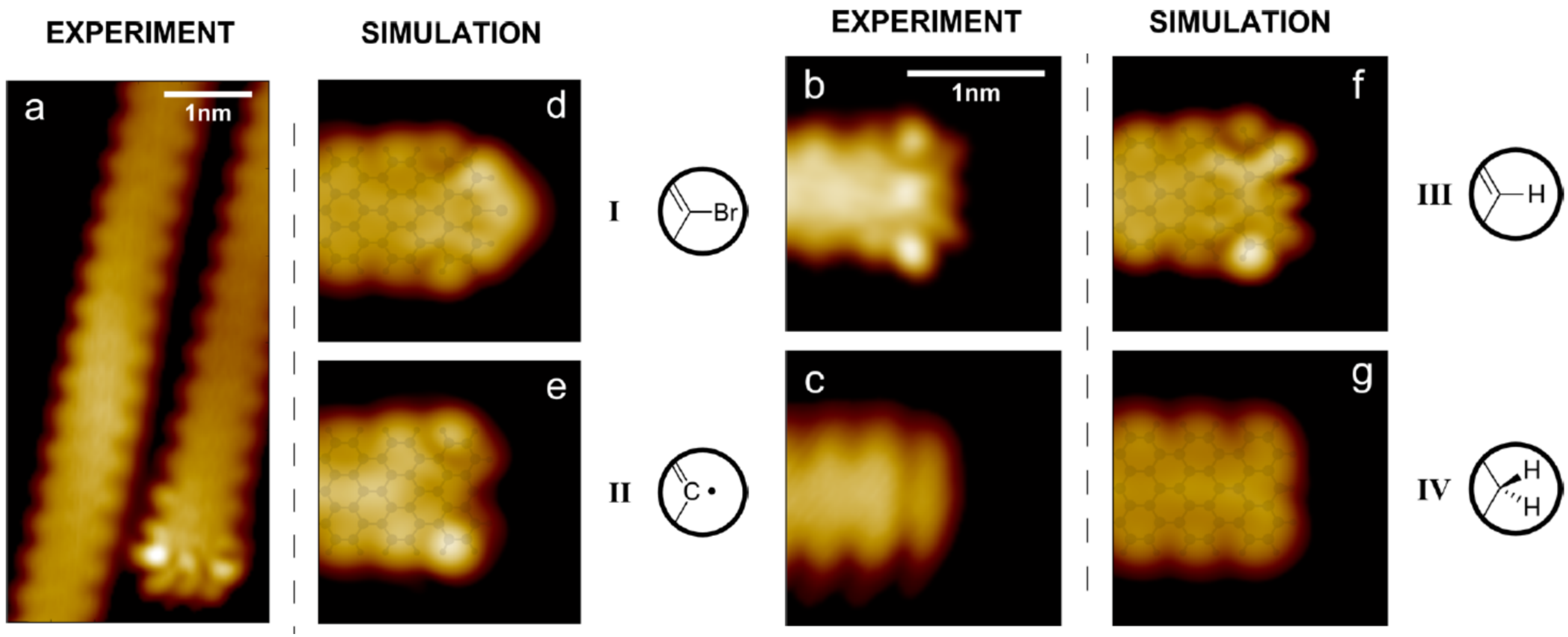
Scheme 1. On-Surface Synthesis of 7-AGNRs with Plausible Terminations I–IV



JACS. **2013**, *132,* 16669

Graphene Nanoribbons (Surface Synthesis)

Termination factor of Surface-assisted GNR synthesis in 2013.



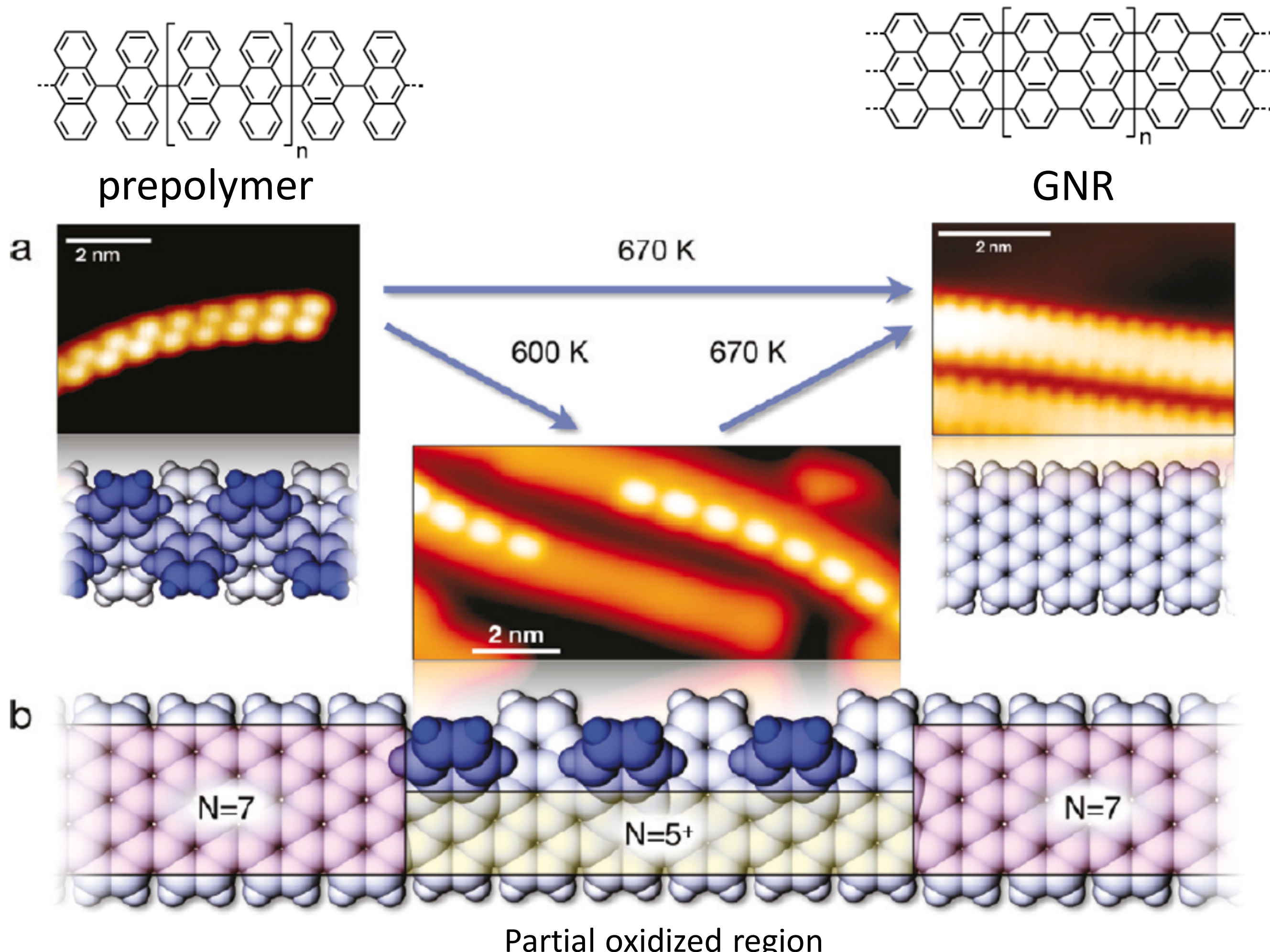
Polymer growth is terminated by the passivation of the radicals with hydrogen

=> Suppressing the spontaneous generation of hydrogen during the radical polymerization step is crucial

JACS. **2013**, *132,* 16669

Graphene Nanoribbons (Surface Synthesis)

Intraribbon heterojunction formation in 2012.

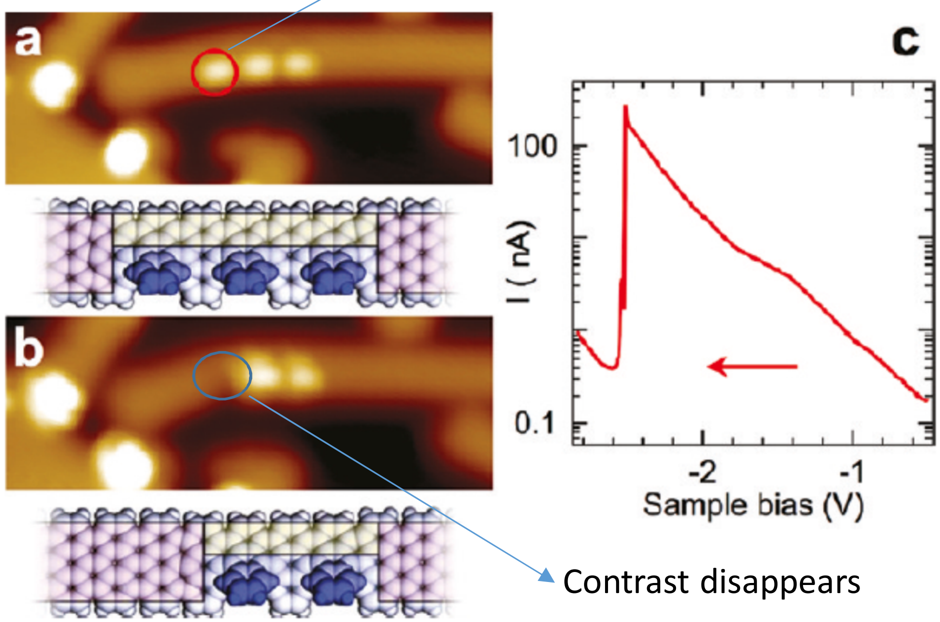


ACS Nano **2012**, *6*, 2020

Graphene Nanoribbons (Surface Synthesis)

Intraribbon heterojunction formation in 2012.

STM tip here, and apply the larger voltage



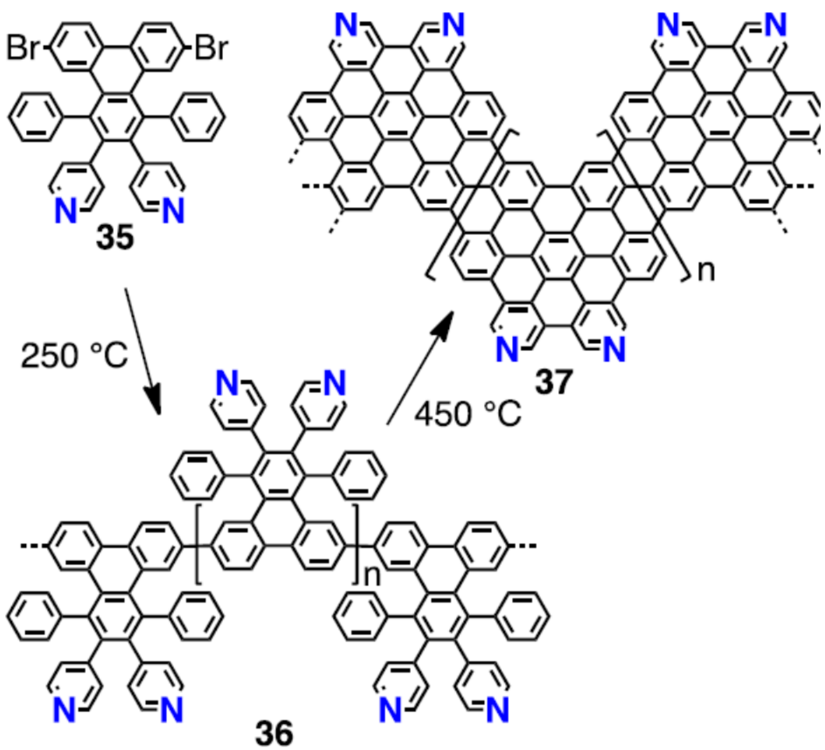
Contrast disappears

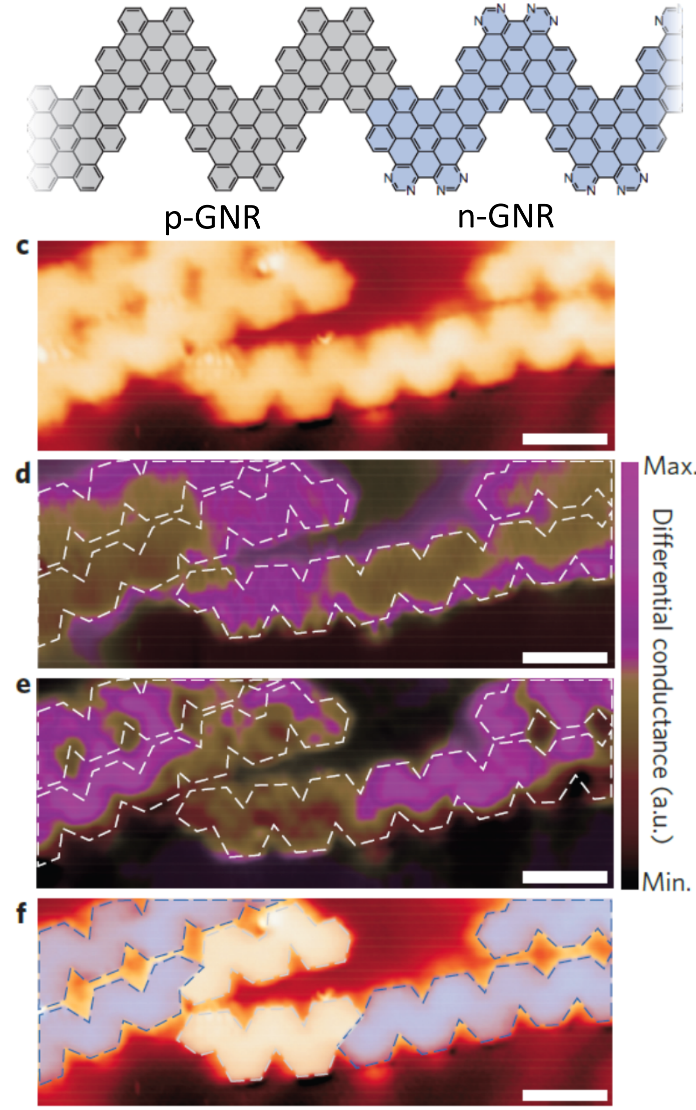
STM Tip-induced dehydrogenation
(electron-stimulated cyclodehydrogenation)

ACS Nano **2012**, *6,* 2020

Graphene Nanoribbons (Surface Synthesis)

Graphene nanoribbon heterojunction in 2014.



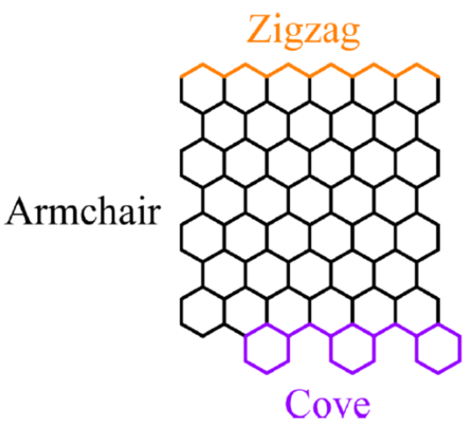


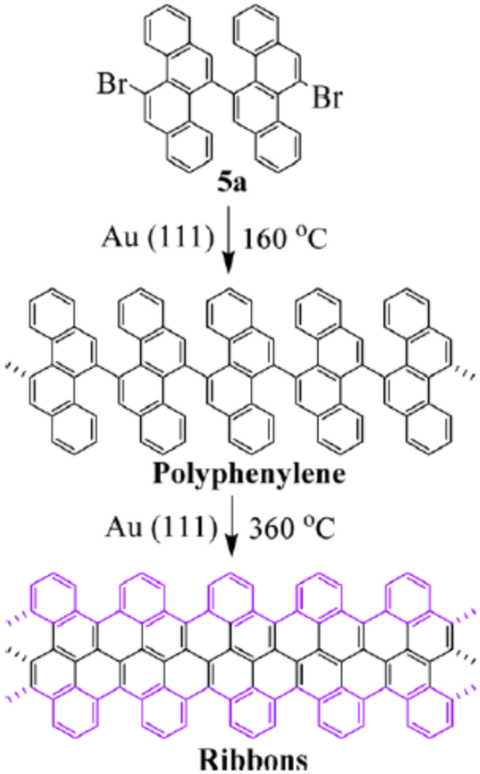
Nat. Nanotech. **2014**, *9,* 896
Appl. Phys. Lett. **2014**, *105*, 023101

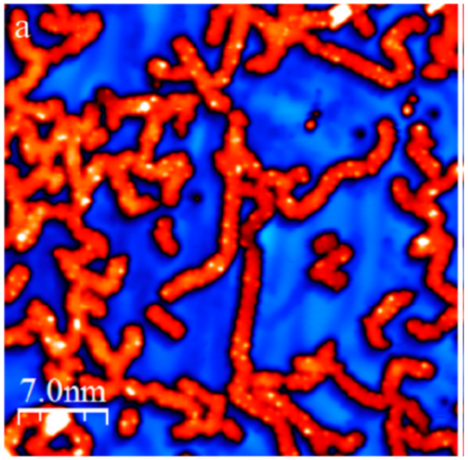
Graphene Nanoribbons (Surface Synthesis)

Cove edge GNR in 2015.

Scheme 1. Edge Structure of Graphene







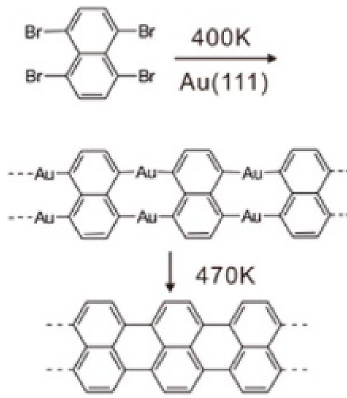
No empirical data about optical/electrochemical properties

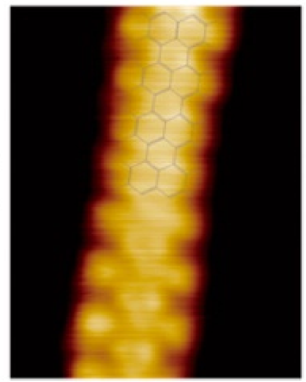
JACS. **2015**, *137*, 6097

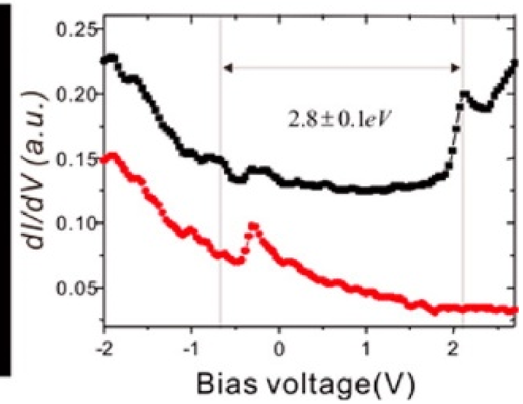
Graphene Nanoribbons (Surface Synthesis)

N=3p+2 GNR in 2015.

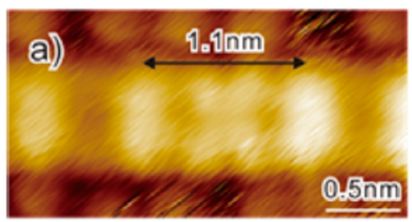
Three subfamilies of GNR
N=3p
N=3p+1
N=3p+2 -> rare

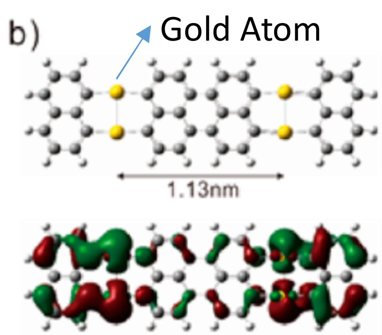






N=5 GNR





Not direct radical coupling,

Au directly involved C-C coupling.

JACS. **2015**, *137*, 4022

Thank you

1. UV/vis absorption spectroscopy is one of the nice methods to calculate bandgap between valence band (or HOMO) and conduction band (or LUMO). If we obtain a UV/vis spectrum, we can easily calculate the bandgap of material by using the simple equation, bandgap (eV) =1240/λ_{onset} (nm).

When the optical bandgap is known as 1.6 eV, what is the expected UV/vis spectrum?

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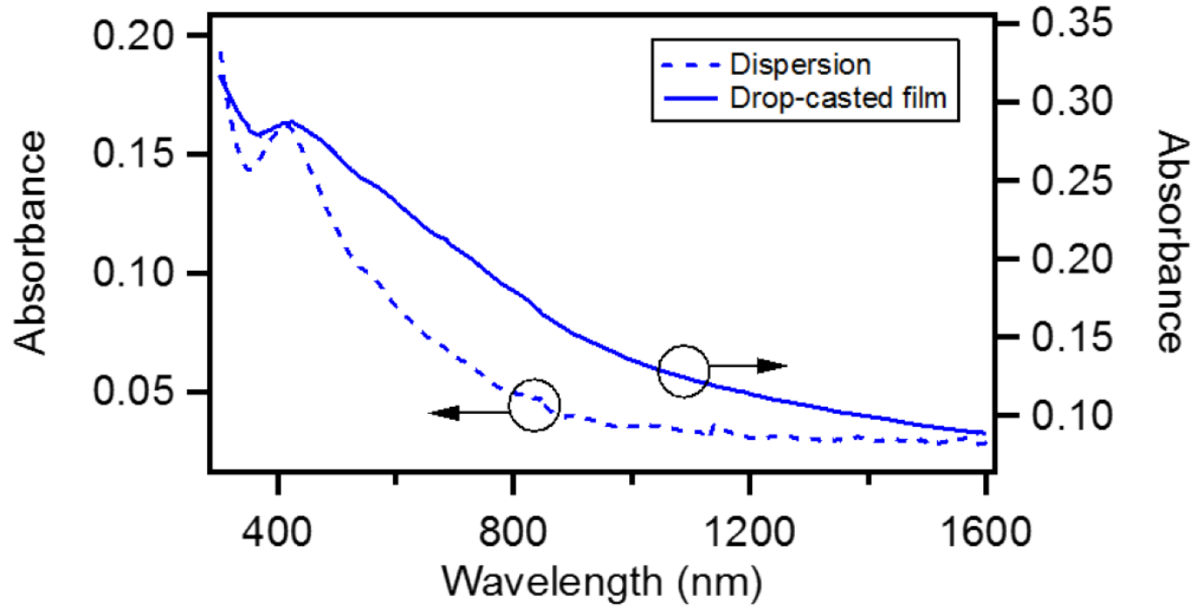
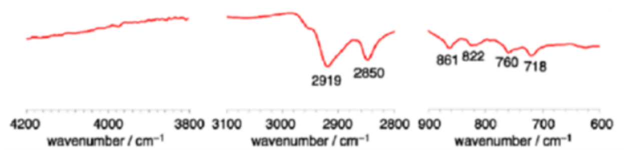
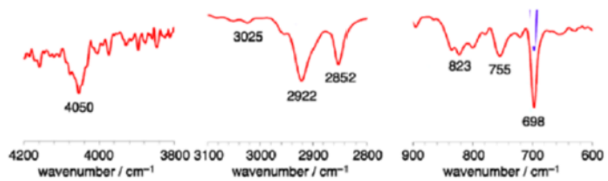
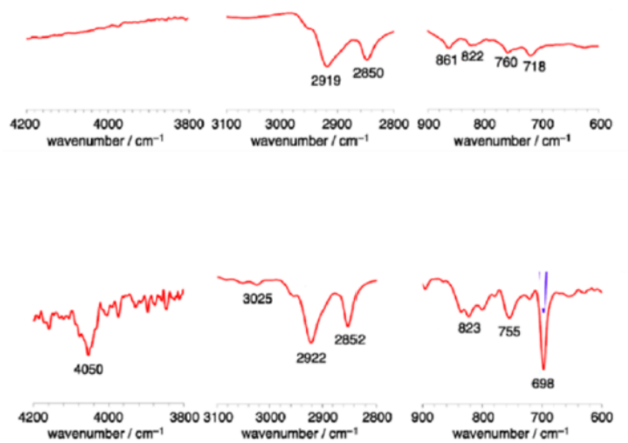






When we make graphene nanoribbons in a bottom-up approach, IR absorption spectroscopy is one of the good tools to determine whether cyclodehydrogenation is successful or not. Which one is the spectrum of polymers before cyclodehydrogenation, and which one is the spectrum of polymers after cyclodehydrogenation? Why?



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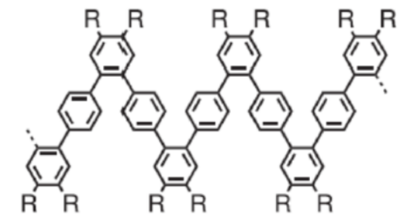
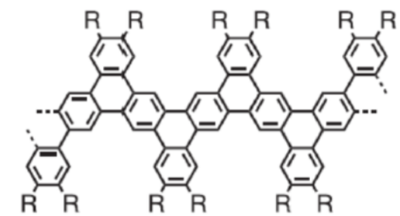
Upper : after cyclodehydrogenation

Lower : before cyclodehydrogenation

3. GPC gives us a relative average molecular weight of the polymer compared to the standard polymer (usually polystryrene). Different size of polymer has different retention time on GPC trace, so we can calculate MW using the calibration curve of polystryrene. However, retention time actually depends on not the real size of polymers but the **hydrodynamic size** of polymers (size of solvated polymer including solvent). Usually more flexible polymers tend to have smaller hydrodynamic volume because they are likely to be a random-coil state (like noodles). With these in mind, explain the huge difference of GPC MWs (9900 Da vs. 20000 Da) from the polymers **16b** and **17b**



16a: R = H
16b: R = $C_{12}H_{25}$



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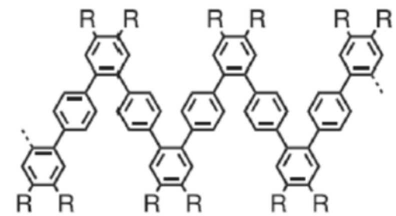

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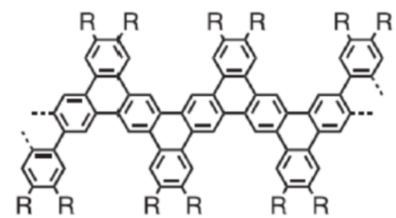


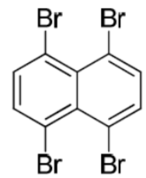
17a: R = H
17b: R = $C_{12}H_{25}$

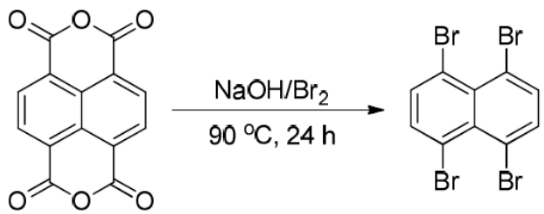
17b is much more rigid than 16b

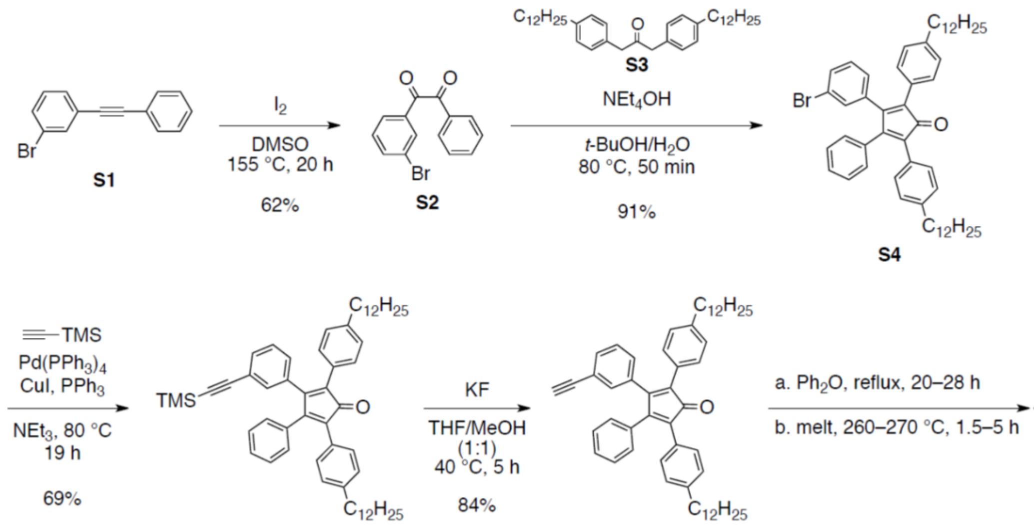
⟹ Hydrodynamic volumn of 17b is much larger than that of 16b

⟹ Retention time of 17b is much shorter than that of 16b

⟹ GPC shows much higher MW for 17b than 16b


Br
Br
Br
Br


NaOH/Br2
90 °C, 24 h


S1
I2
DMSO
155 °C, 20 h
62%
S2
S3
NEt4OH
t-BuOH/H2O
80 °C, 50 min
91%
S4
Pd(PPh3)4
CuI, PPh3
NEt3, 80 °C
19 h
69%
KF
THF/MeOH
(1:1)
40 °C, 5 h
84%
a. Ph2O, reflux, 20–28 h
b. melt, 260–270 °C, 1.5–5 h