Total Organic Synthesis and Characterization of Graphene Nanoribbons

Gang Li

Seminar in Dong group

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Content

- History of Graphene
- Synthesis and Characterization and Properties of Graphene
- Conceptual Approaches to synthesize Graphene Ribbons from alkynes functionality
- The other examples

History of Graphene

- In 1859, Benjamin Collins Brodie was aware of the highly lamellar structure of thermally reduced graphite oxide;
- In 1916, the structure of graphite was solved;
- In 1947, the theory of graphene was first explored by P. R. Wallace;
- In 1948, the earliest TEM images of few-layer graphite were published by G. Ruess and F. Vogt; Later, single graphene layers were also observed directly by electron microscopy;
- in 2004, Andre Geim and Kostya Novoselov at University of Manchester extracted single-atom-thick crystallites from bulk graphite. Geim and Novoselov received several awards for their pioneering research on graphene, notably the 2010 Nobel Prize in Physics.

http://en.wikipedia.org/wiki/Graphene

Progress in Materials Science **2011,***56*, 1178–1271

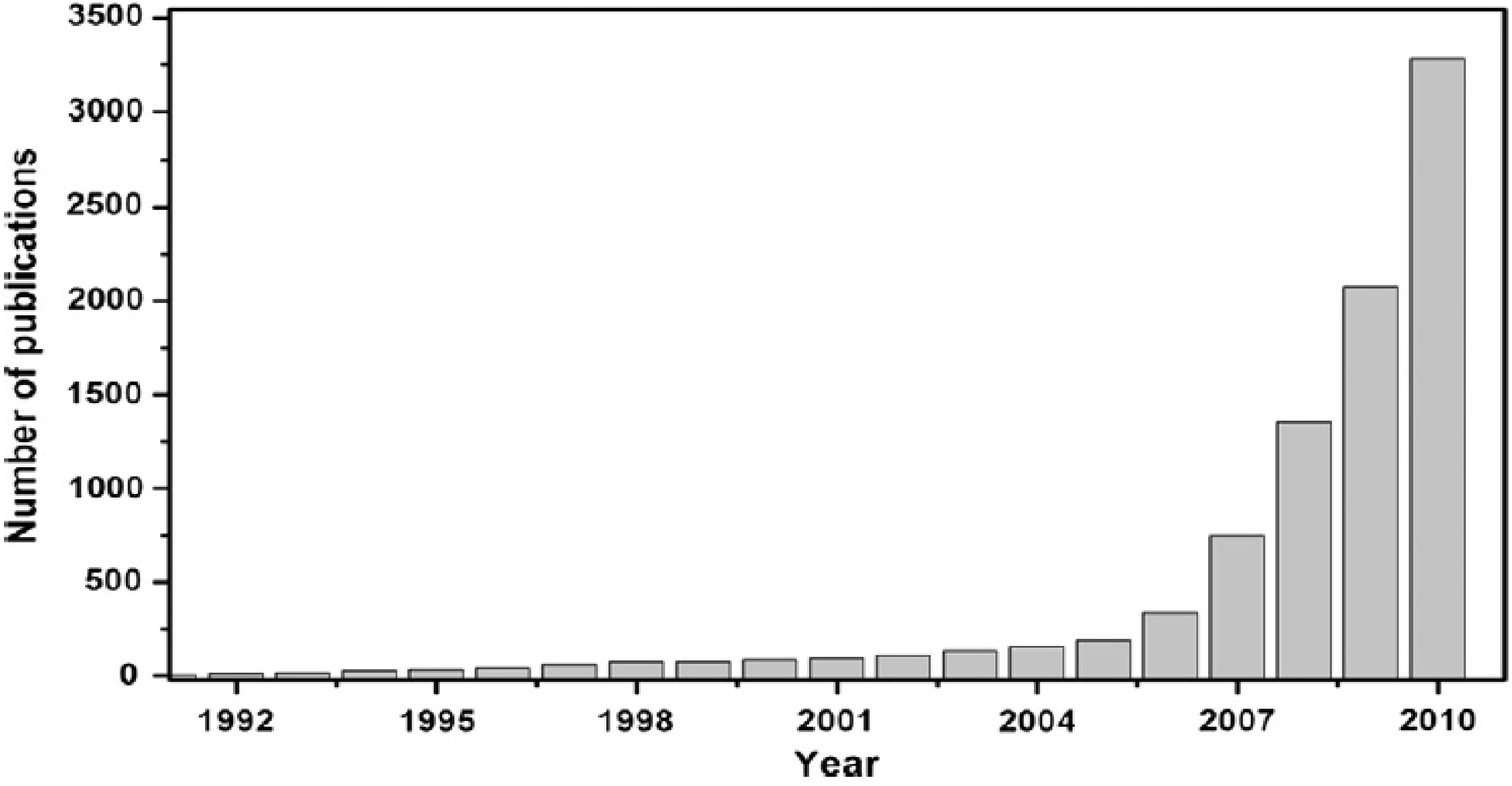


Fig. 2.1. Number of publications on graphene in past 20 years.

According to ISI Web of Knowledge, the number of publications on graphene increases dramatically after 2004.

Progress in Materials Science **2011,***56*, 1178–1271

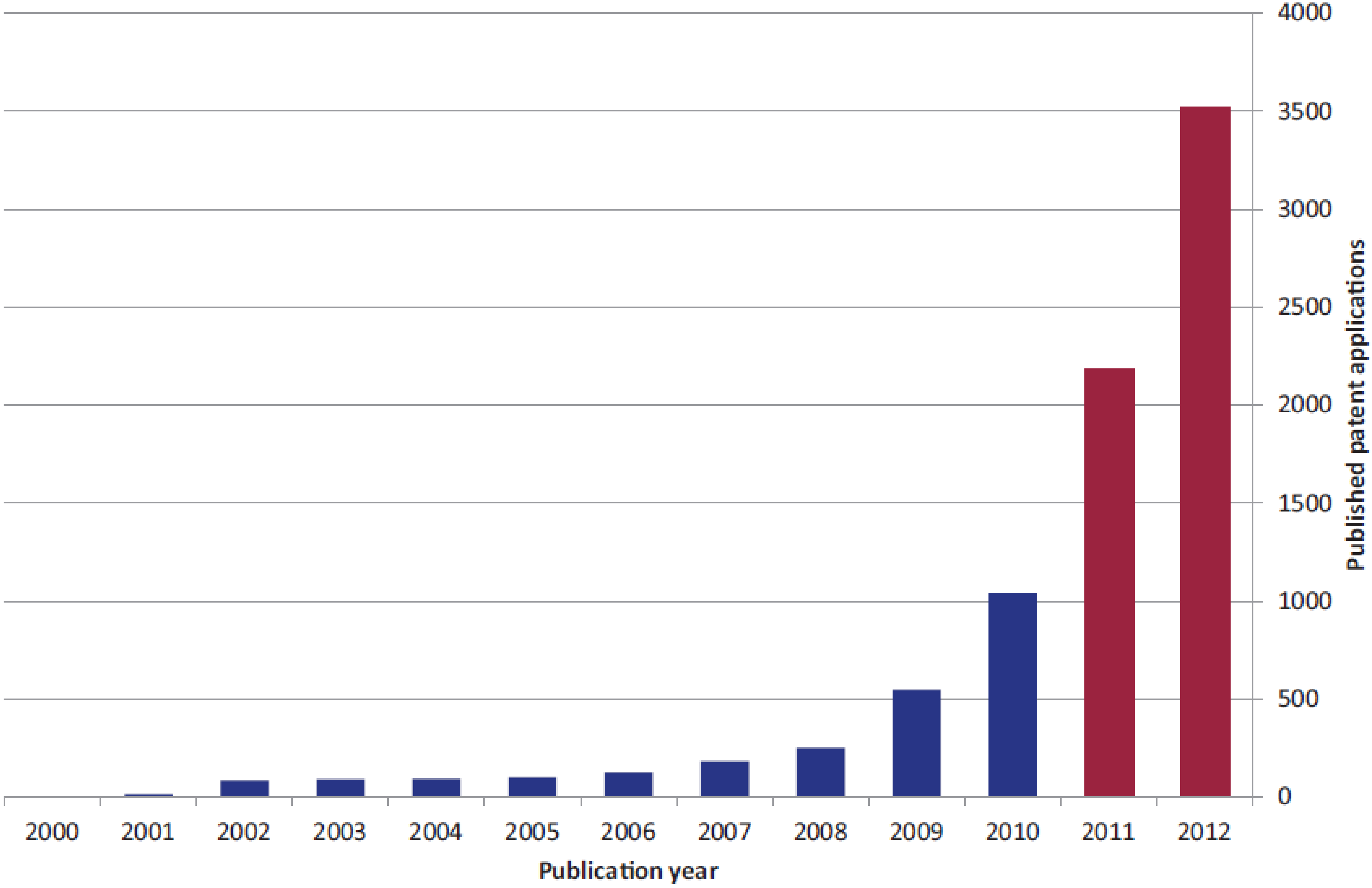


Figure 1: Worldwide patent publications by publication year

Synthesis of Graphene

Two distinct strategies have been established to synthesize graphene: exfoliating graphite to graphene(top-down) and building up graphene from molecular building blocks (bottom-up)

Synthetic pathways:

- Liquid-Phase Exfoliation
- Chemical vapor deposition
- Chemically derived graphene
- **Organic synthesis of graphene**

Angew. Chem. Int. Ed. **2012**, *51*, 7640 – 7654

Progress in Materials Science **2011,***56*, 1178–1271

Graphene: Characterization and properties

Characterization:

- IR, Raman spectroscopy, Atomic force microscopy (AFM), Scanning electron microscopy (SEM) ,Transmission electron microscopy (TEM), Scanning tunneling microscopy (STM), Fluorescence quenching technique

Progress in Materials Science **2011,***56*, 1178–1271

Graphene: properties and Applications

Properties:

In the past few years many fascinating properties were discovered through the investigation of pristine graphene:

- **high charge mobility with 2.3% absorption of visible light;**
- **Thermal conductivity (3000W/Mk);**
- **Highest strength(130GPa);**
- **The highest theoretical specific area(2600m^2/g);**
- **Half integer quantum hall effect even at room temperature.**

Its potential applications include single molecule gas detection, transparent conducting electrodes, composites and energy storage devices

Progress in Materials Science **2011,***56*, 1178–1271

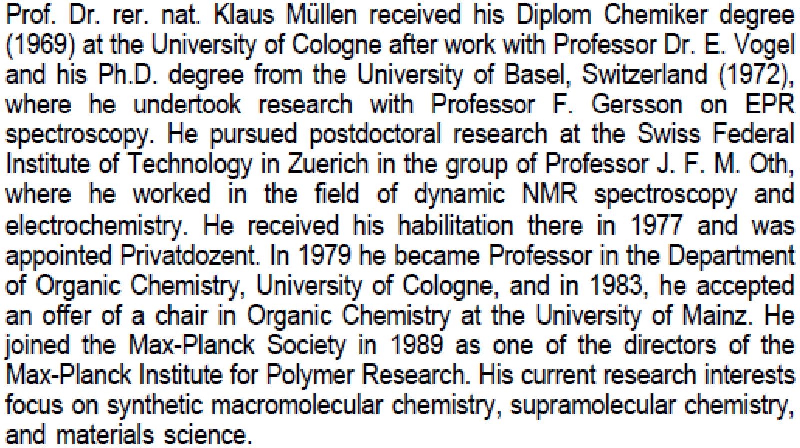
Totally Organic Synthesis

Total synthesis of graphene-like polyacyclic hydrocarbons (PAHS) has been explored for decades

Main player in organic synthesis of graphene is Prof. Klaus Mullen in Germany;

Advantages: synthesis versatility and the capability of grafting aliphatic chains to improve solubility

Main challenge lies in preserving dispensability and a planar geometry for large PAHs.



Prof. Dr. rer. nat. Klaus Müllen received his Diplom Chemiker degree (1969) at the University of Cologne after work with Professor Dr. E. Vogel and his Ph.D. degree from the University of Basel, Switzerland (1972), where he undertook research with Professor F. Gersson on EPR spectroscopy. He pursued postdoctoral research at the Swiss Federal Institute of Technology in Zuerich in the group of Professor J. F. M. Oth, where he worked in the field of dynamic NMR spectroscopy and electrochemistry. He received his habilitation there in 1977 and was appointed Privatdozent. In 1979 he became Professor in the Department of Organic Chemistry, University of Cologne, and in 1983, he accepted an offer of a chair in Organic Chemistry at the University of Mainz. He joined the Max-Planck Society in 1989 as one of the directors of the Max-Planck Institute for Polymer Research. His current research interests focus on synthetic macromolecular chemistry, supramolecular chemistry, and materials science.

Chem. Rev. **2007**, *107*, 718–747

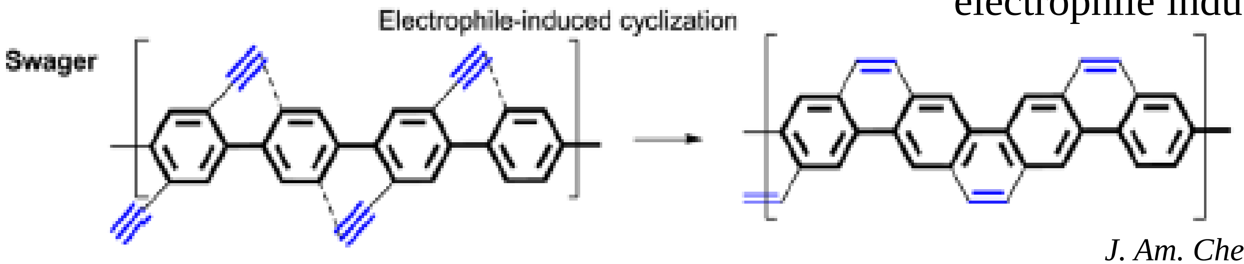
Progress in Materials Science **2011,***56*, 1178–1271

Conceptual Approaches to synthesize Graphene Ribbons from Alkynes functionality

Center is assembled via cross-coupling: Alkynes are used to make the side rings

electrophile induced alkyne cyclization

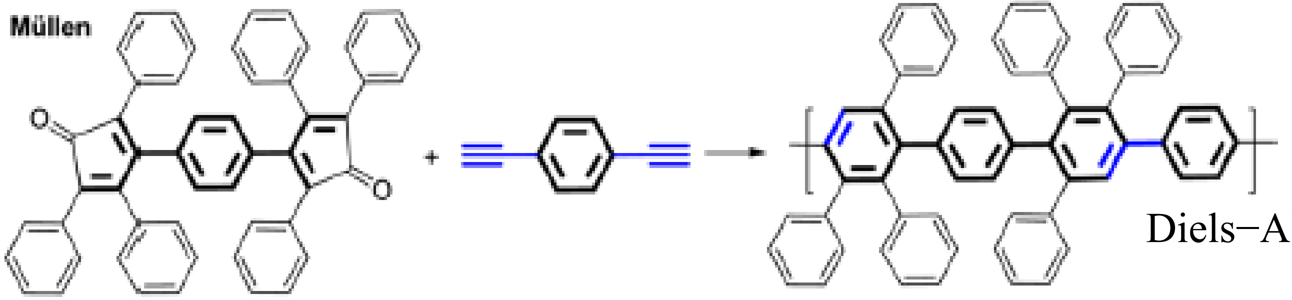
1.



J. Am. Chem. Soc. ***1997, 119, 4578-4593***

Center is assembled via Diels-Alder reactions: Alkynes are partially incorporated in the center

2.

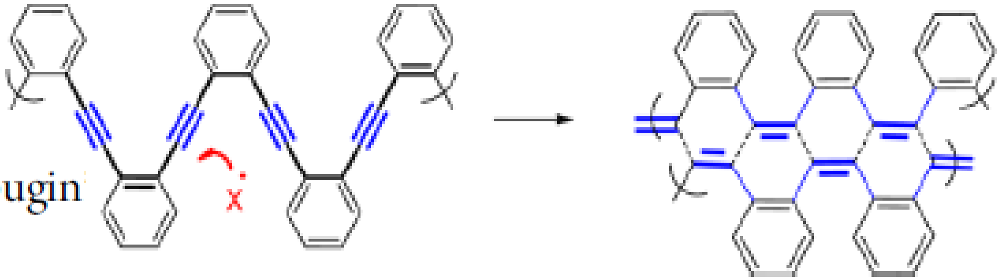


Diels−Alder polymerization

Macromolecules ***2003, 36, 7082-7089***

Central rings are assembled via alkyne cyclizations: All central atoms are derived from alkynes

3.



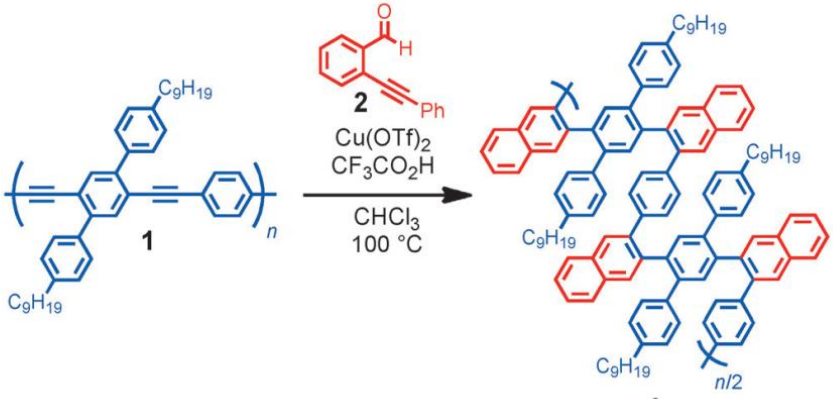
Igor V. Alabugin

radical polymerization

J. Am. Chem. Soc. 2012, 134, 9609−9614

4. the benzannulation–cyclodehydrogenation approach

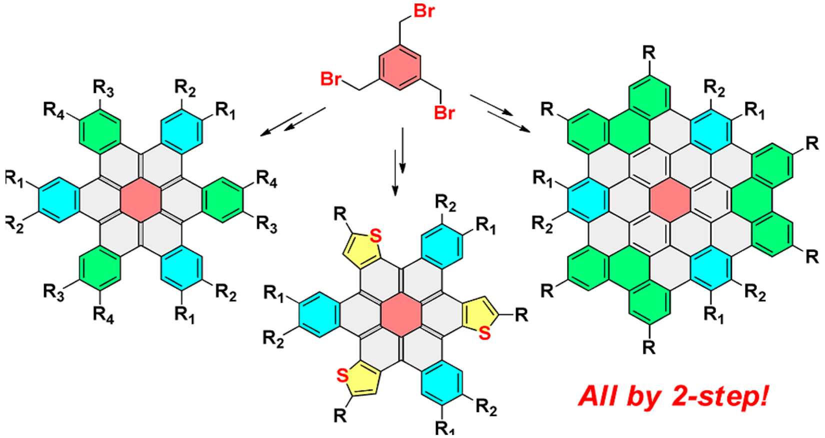
William R. Dichtel



Angew. Chem. Int. Ed. **2012**, *51*, 12051 – 12054

5. the covalent self-sorting assembly (CSA) strategy

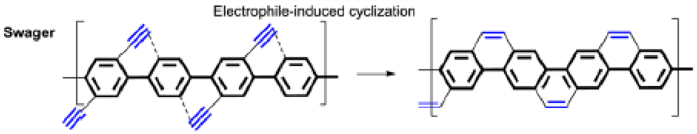
Junfa Wei



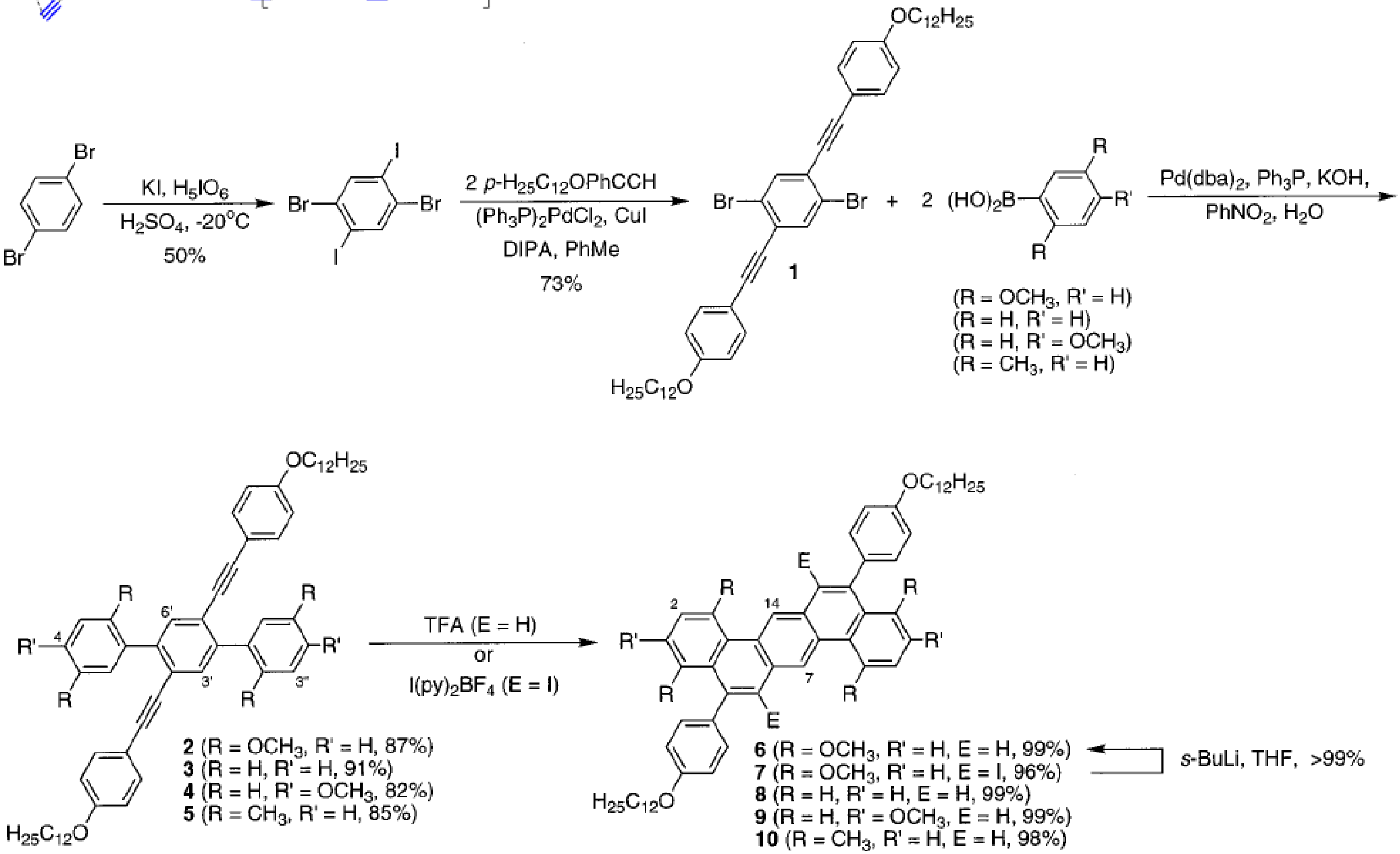
All by 2-step!

dx.doi.org/10.1021/ja413018f | J. Am. Chem. Soc. XXXX, XXX, XXX−XXX

Directed Electrophilic Cyclizations: Efficient Methodology for the Synthesis of Fused Polycyclic Aromatics



Timothy M. Swager



(R = OCH_3, R' = H)
(R = H, R' = H)
(R = H, R' = OCH_3)
(R = CH_3, R' = H)

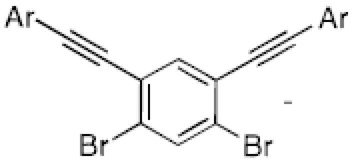
2 (R = OCH_3, R' = H, 87%)
3 (R = H, R' = H, 91%)
4 (R = H, R' = OCH_3, 82%)
5 (R = CH_3, R' = H, 85%)

6 (R = OCH_3, R' = H, E = H, 99%)
7 (R = OCH_3, R' = H, E = I, 96%)
8 (R = H, R' = H, E = H, 99%)
9 (R = H, R' = OCH_3, E = H, 99%)
10 (R = CH_3, R' = H, E = H, 98%)

Strong electrophiles such as TFA and iodonium tetrafluoroborate.

J. Am. Chem. Soc. **1997**, *119*, 4578−4593

Phenyl migration by a phenonium ion.



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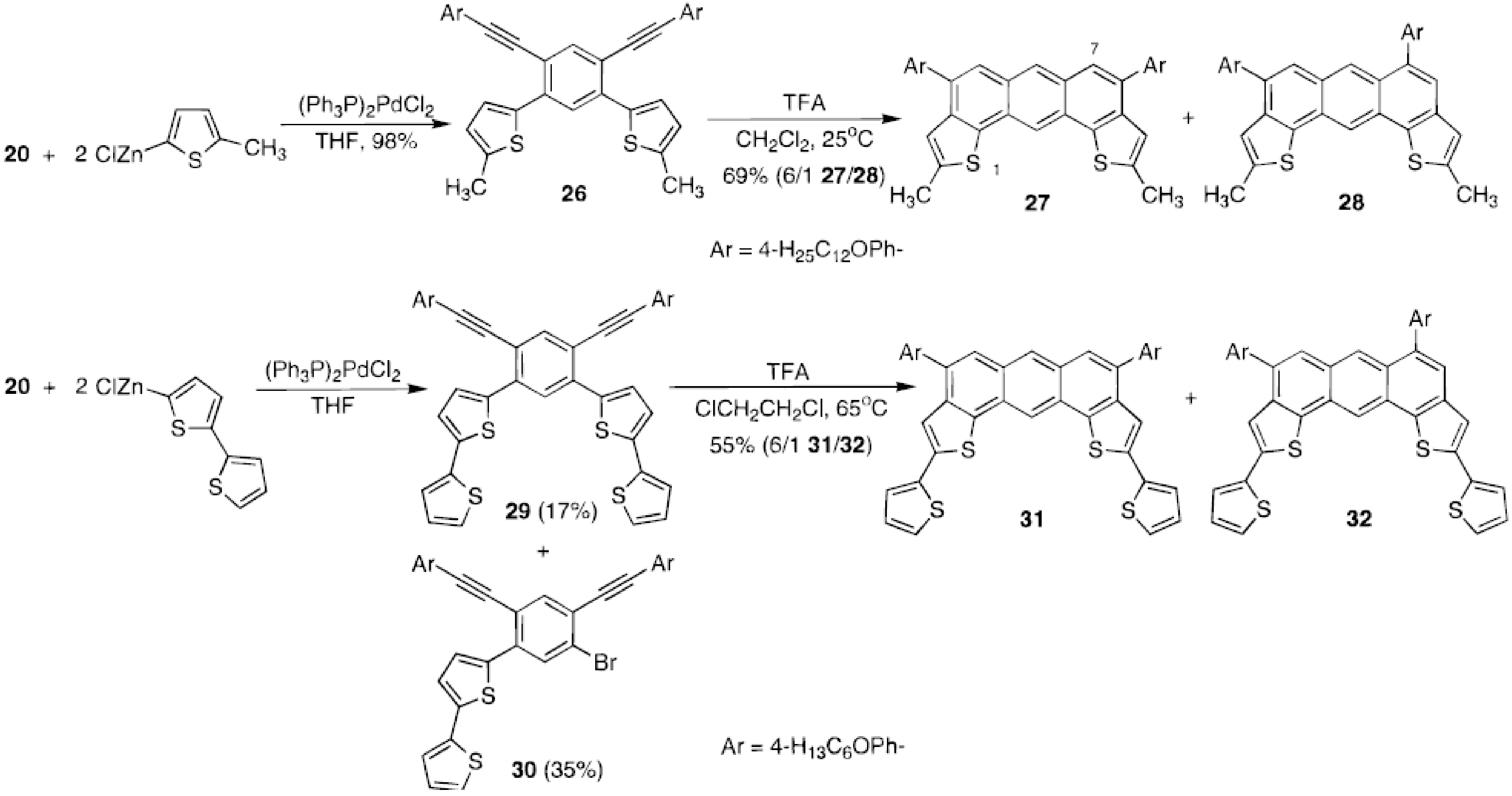


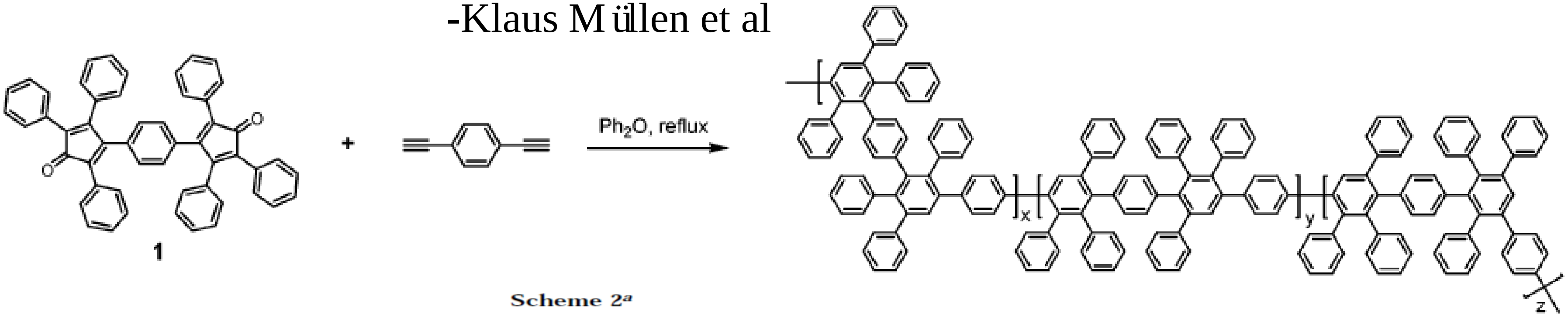
Ar = 4-$H_{25}C_{12}OPh$-

Ar = 4-$H_{13}C_6OPh$-

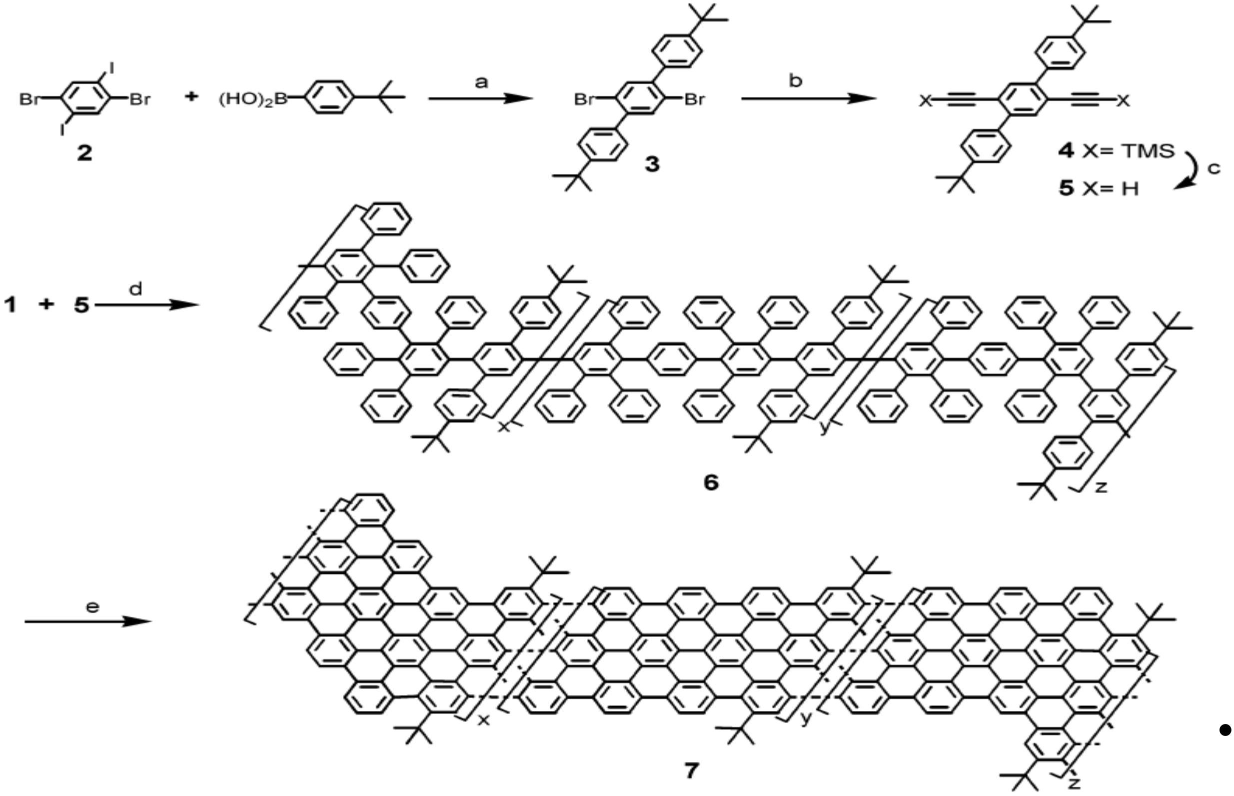
J. Am. Chem. Soc. **1997,** *119,* 4578−4593

From Branched Polyphenylenes to graphite Ribbons

-Klaus Müllen et al



Scheme 2^a



- Three-block polymer Due to rotation about phenyl single bond

- Diels−Alder polymerization

ey: (a) $Pd(PPh_3)_4$, K_2CO_3, toluene, 95 °C, 92%; (b) trimethylsilyl acetylene, $Pd(PPh_3)_4$, CuI, piperidine, 80 °C, 89%; (c) K_2CO_3, anol/dichloromethane, 92%; (d) Ph_2O, refluxing, 88%; (e) $FeCl_3$, nitromethane/dichloromethane, 24 h.

Macromolecules **2003, 36, 7082-7089**

Characterization of Graphene Ribbons

- Insolubility of polymer limited structure elucidation
- The electronic and vibrational properties were probed by Solid-state UV-vis, FTIR and raman spectroscopy.

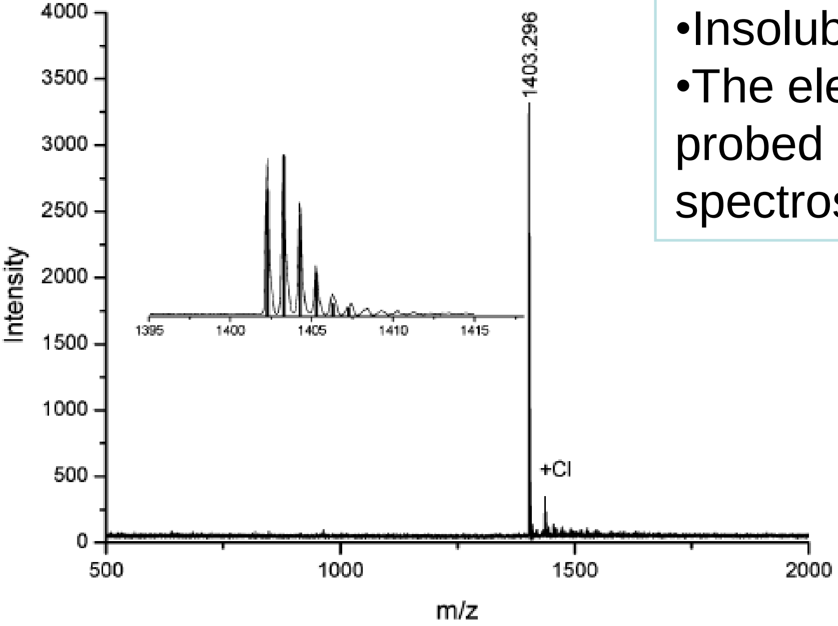


Figure 1. MALDI MS spectrum for $C_{114}H_{34}$: calculated, 1403.54; found, 1403.30 (100%). Isotope distribution is in good agreement with the simulated results (black bar). In addition, some chloronation took place during the cyclodehydrogenation with Lewis acid iron(III) chloride.

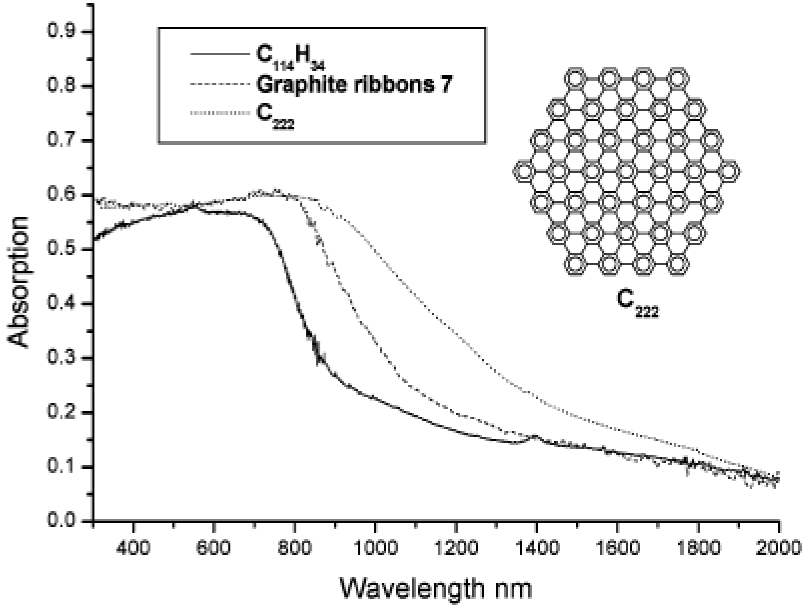


Figure 2. Solid-state UV−vis spectrum of graphite ribbon **7**, **C114H34**, and **C222**.

- A wide and unstructured absorption band covering the visible range of the electronic spectrum (*ìmax 800 nm) is observed, confirming the highly extended conjugated framework.*

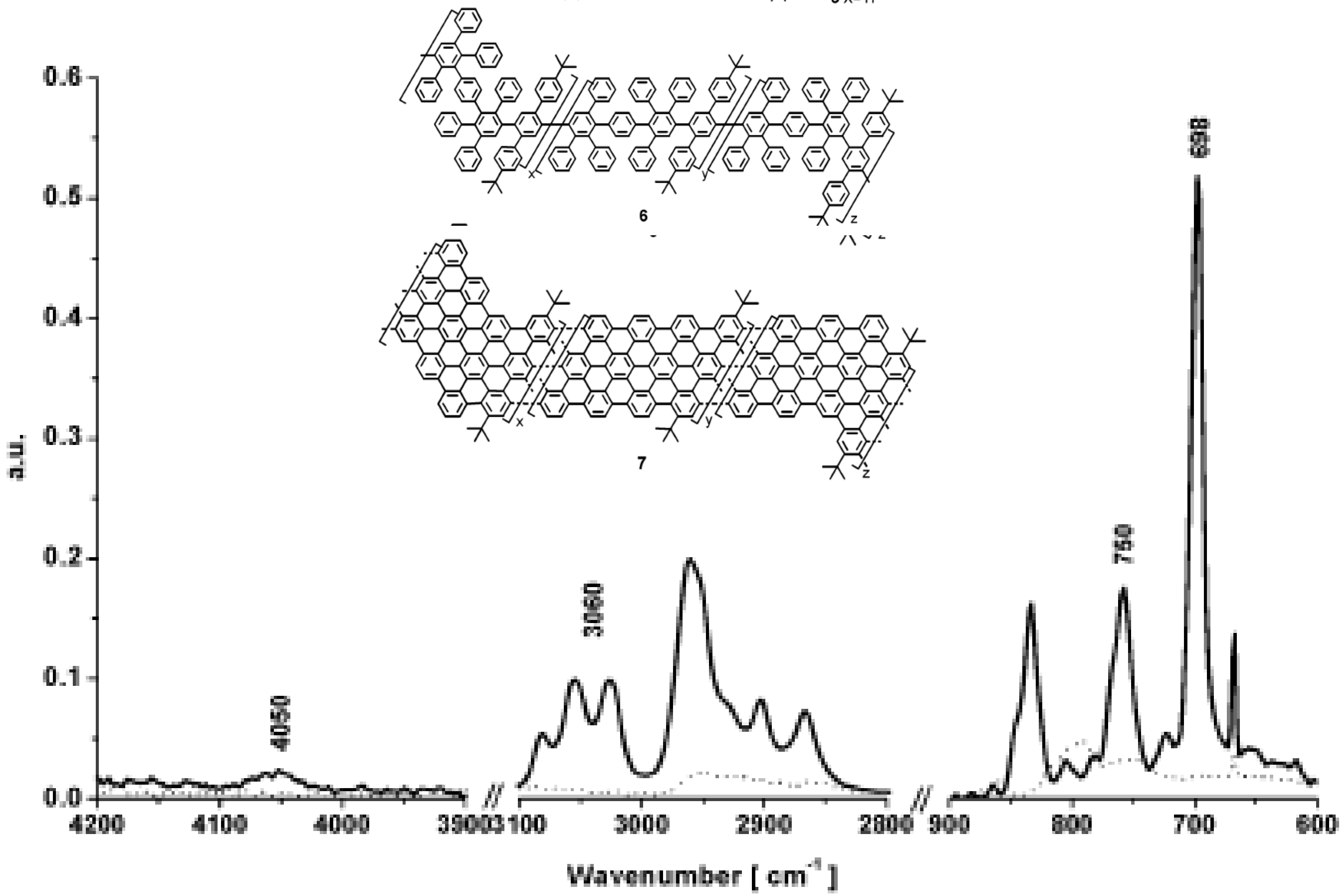


Figure 3. Infrared spectra of branched polyphenylene precursor **6** (solid line) and graphite ribbon **7** (dot line).

Monosubstituted benzene rings (at 698, 750, and around 3060 cm-1) and the combination peak at 4050 cm-1 in precursor 6 have disappeared in the spectrum of GNR 7

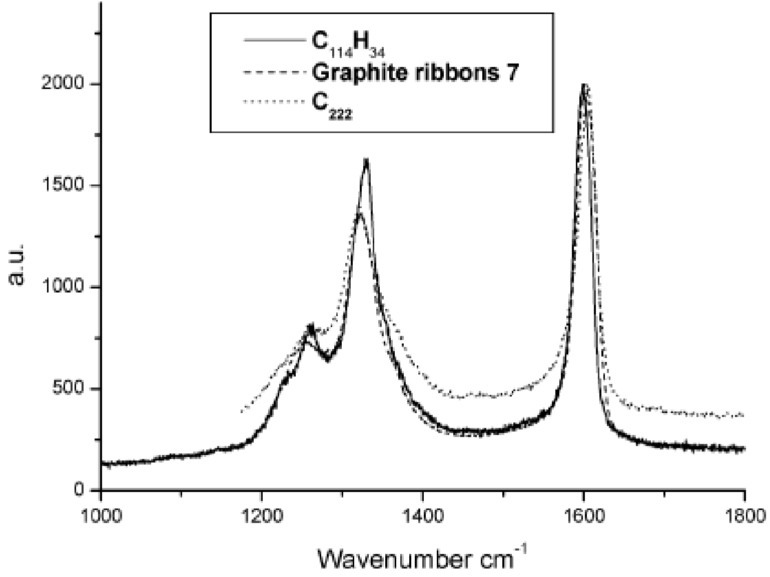


Figure 4. Raman spectra of graphite ribbon **7**, **C114H34**, and **C222**.

Raman spectrum of the material is similar to that of the reported GNR with two strong bands (at 1603 and 1322 cm-1), corresponding to the G and D bands of graphite

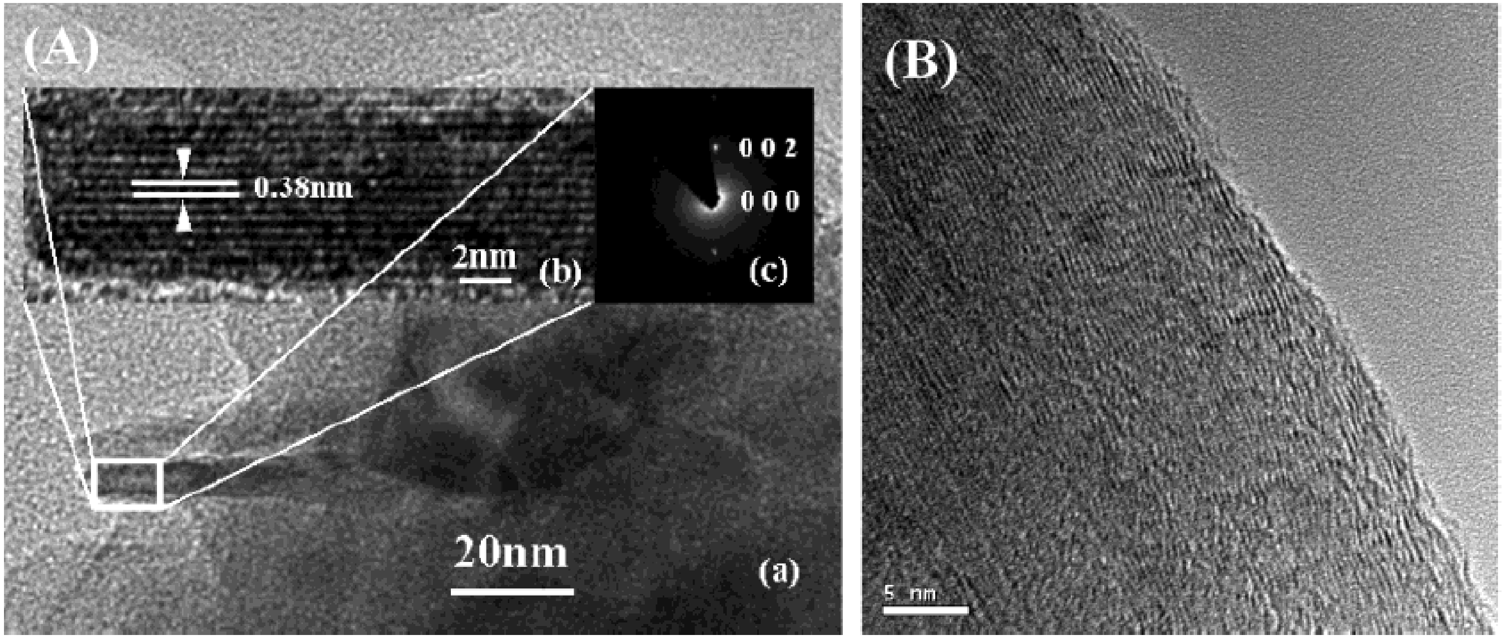
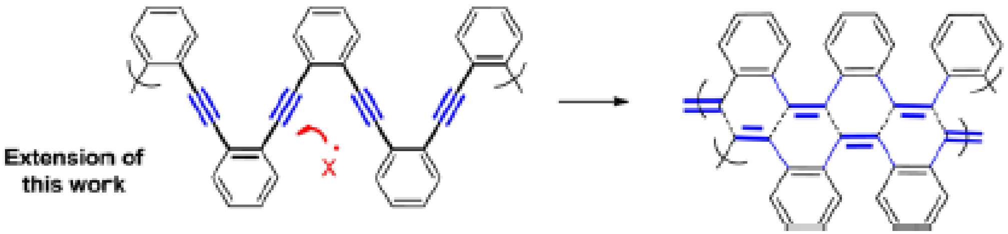


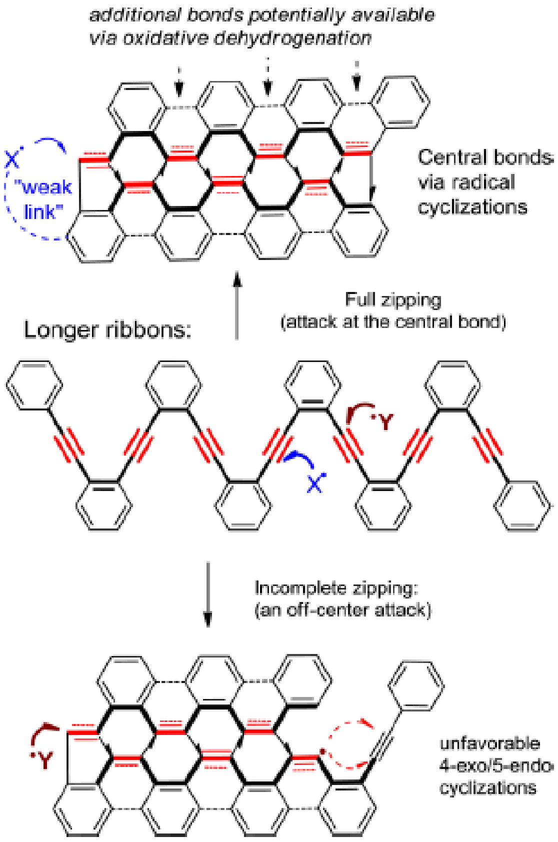
Figure 5. (A) (a) TEM images of the graphite ribbon samples **7**, where an ordered graphite layer structure is marked by a square; (b) high-resolution image (HRTEM) of marked area exhibiting a layer distance of 3.8 Å; (c) selected area electron diffraction (SAED) pattern from marked area showing 002 reflections. (B) Another extended highly ordered graphite layer structure.

Polyaromatic Ribbons from Oligo-Alkynes via Selective RadicalCascade: Stitching Aromatic Rings with Polyacetylene Bridges

Igor V. Alabugin

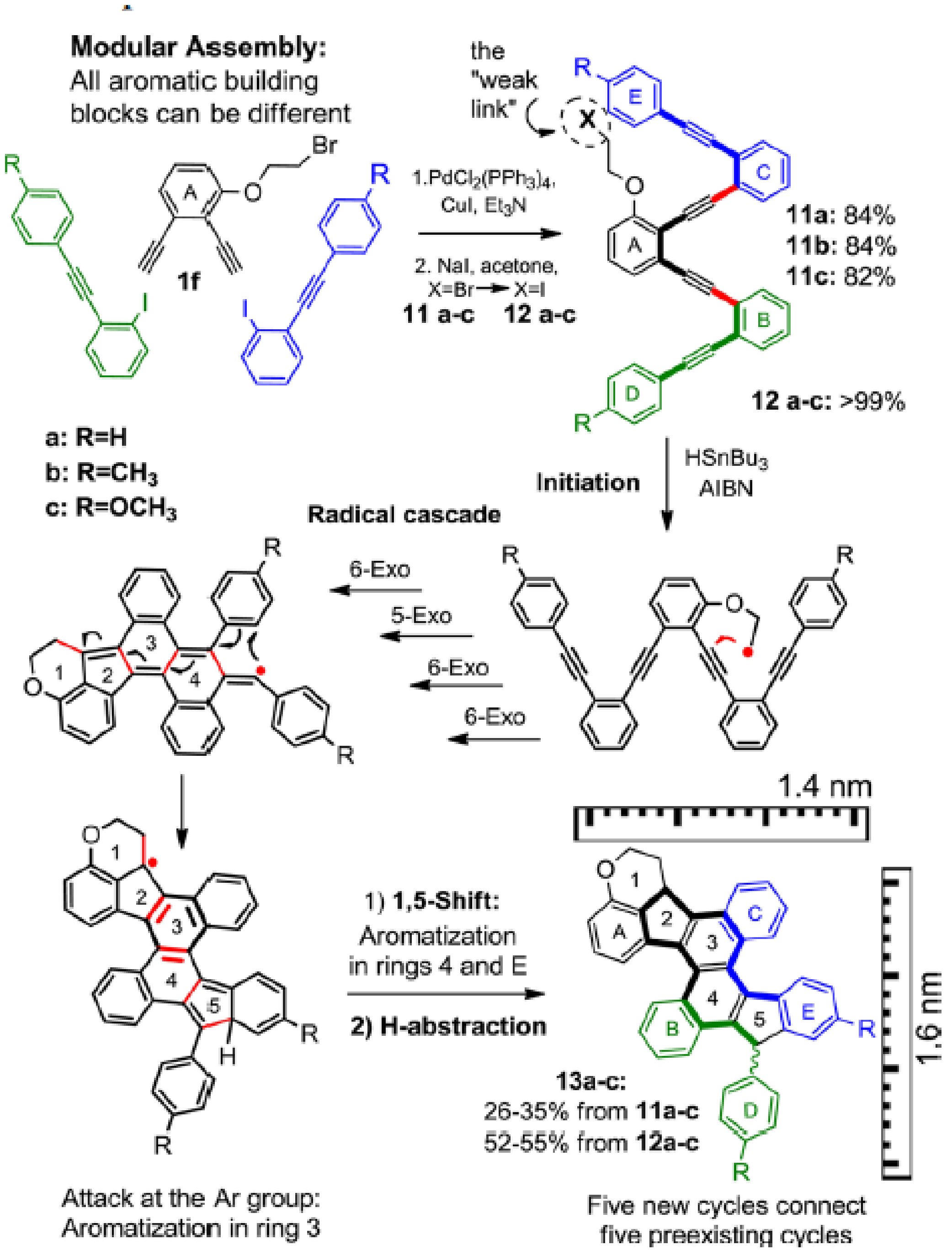
Central rings are assembled via alkyne cyclizations: All central atoms are derived from alkynes





Scheme 2. Proposed Extension of the Alkyne Radical Cascade towards Longer Graphene Ribbons and Importance of Selective Radical Attack at the Central Alkyne

J. Am. Chem. Soc. 2012, 134, 9609−9614



Modular Assembly:
All aromatic building blocks can be different

Attack at the Ar group:
Aromatization in ring 3

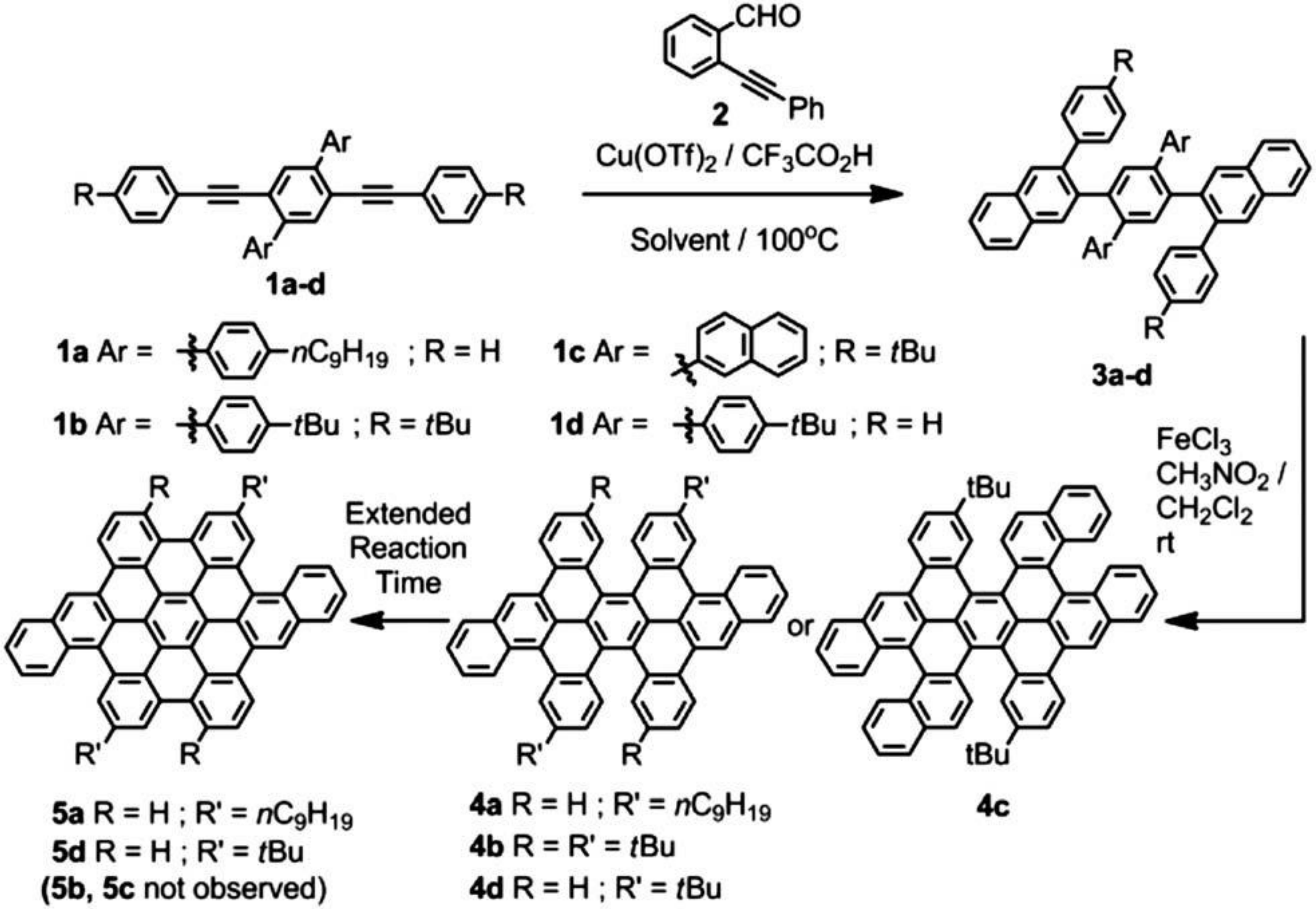
13a-c:
26-35% from **11a-c**
52-55% from **12a-c**

Five new cycles connect five preexisting cycles

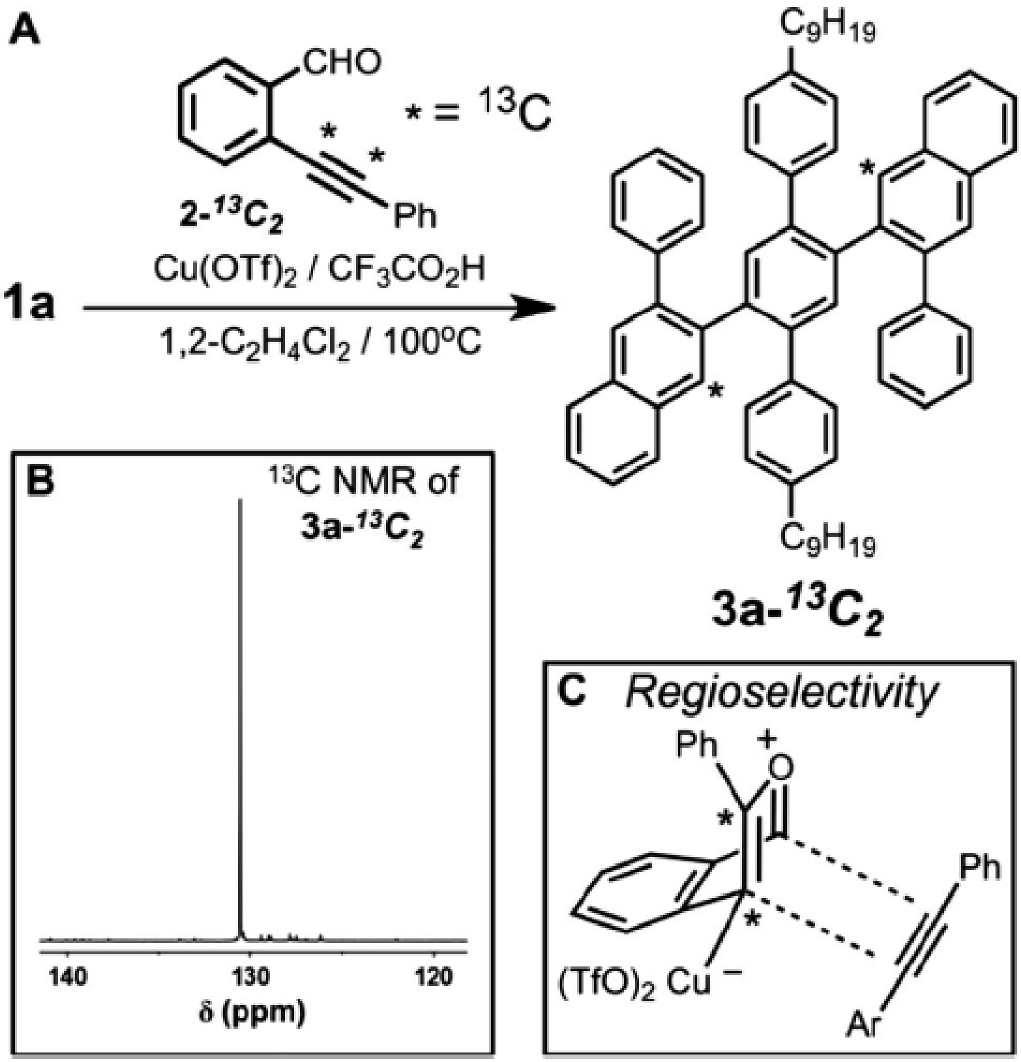
J. Am. Chem. Soc. 2012, 134, 9609−9614

Poly(phenylene ethynylene)s Benzannulation-cyclodehydrogenation approach

William R. Dichtel



Chem. Sci., 2013,**4**, 3973-3978



Benzannulation reaction was run with isotopically labelled benzaldehyde. As determined by ^{13}C NMR spectroscopy, the resulting benzannulated product contained one isotopic label per reactive site,

Poly(phenylene ethynylene)s Benzannulation-cyclodehydrogenation approach

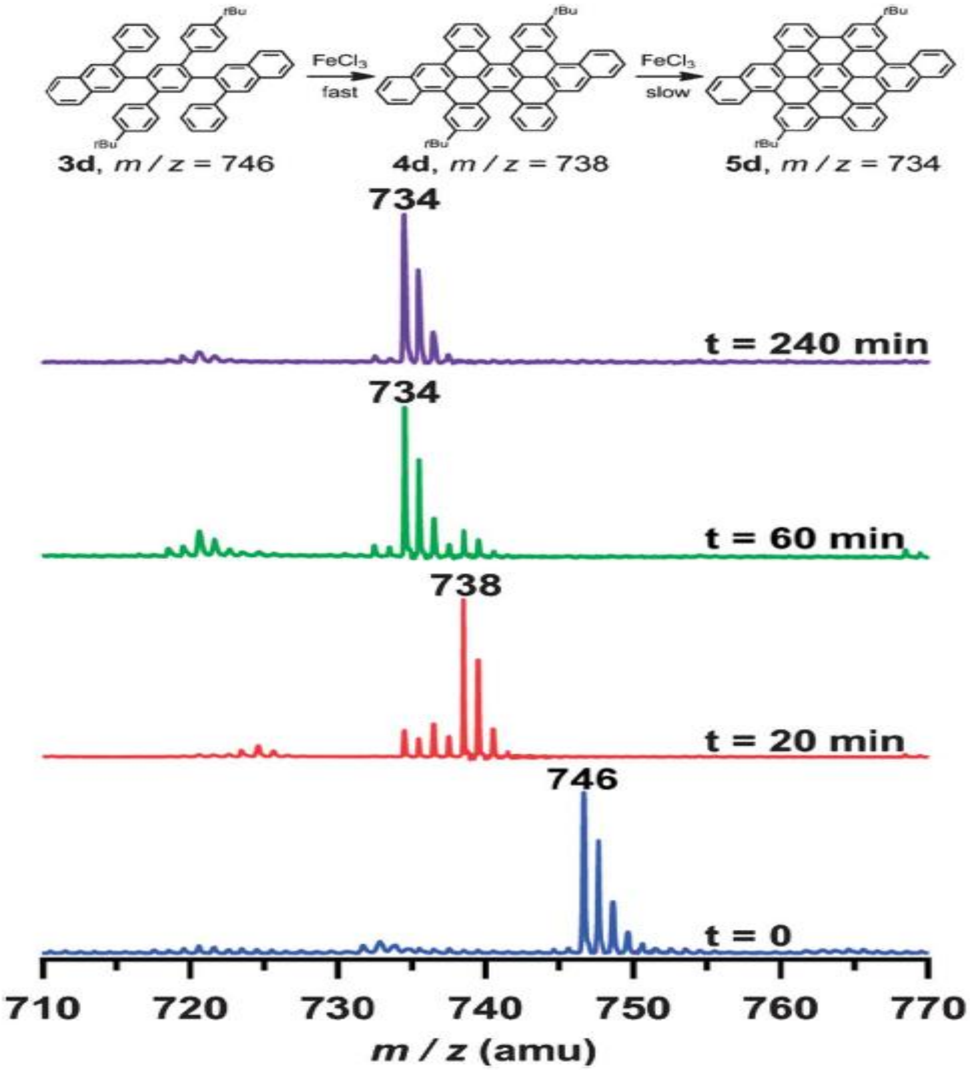
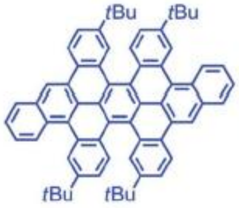


Fig. 5 MALDI-TOF MS spectra taken of the oxidation of **3d** as a function of reaction time. Four carbon–carbon bonds are formed in fewer than 20 minutes, while full oxidation occurs after longer reaction times.

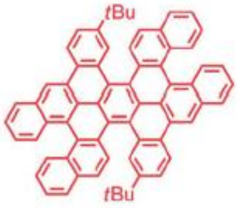
Chem. Sci. **2013**, *4*, 3973-3978

Poly(phenylene ethynylene)s Benzannulation-cyclodehydrogenation approach

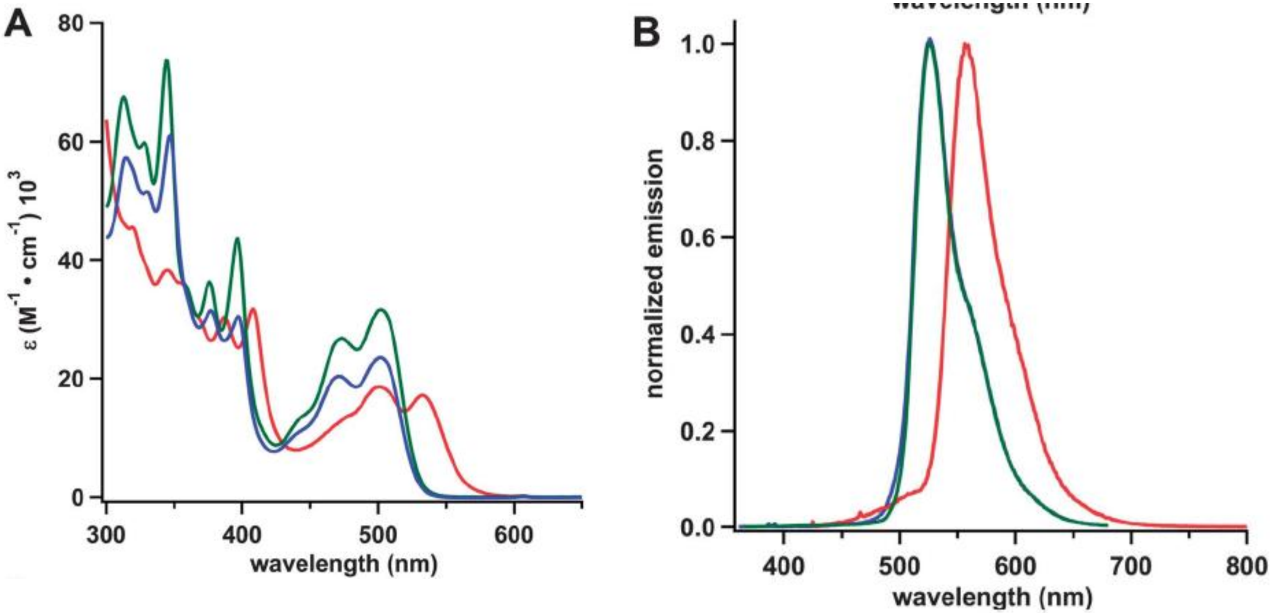
4a



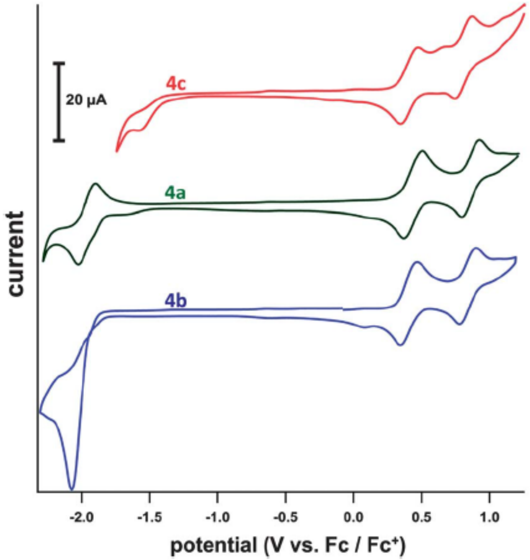
4b



4c



. 7 (A) UV/vis and (B) fluorescence spectra of contorted compounds **4a–c**.

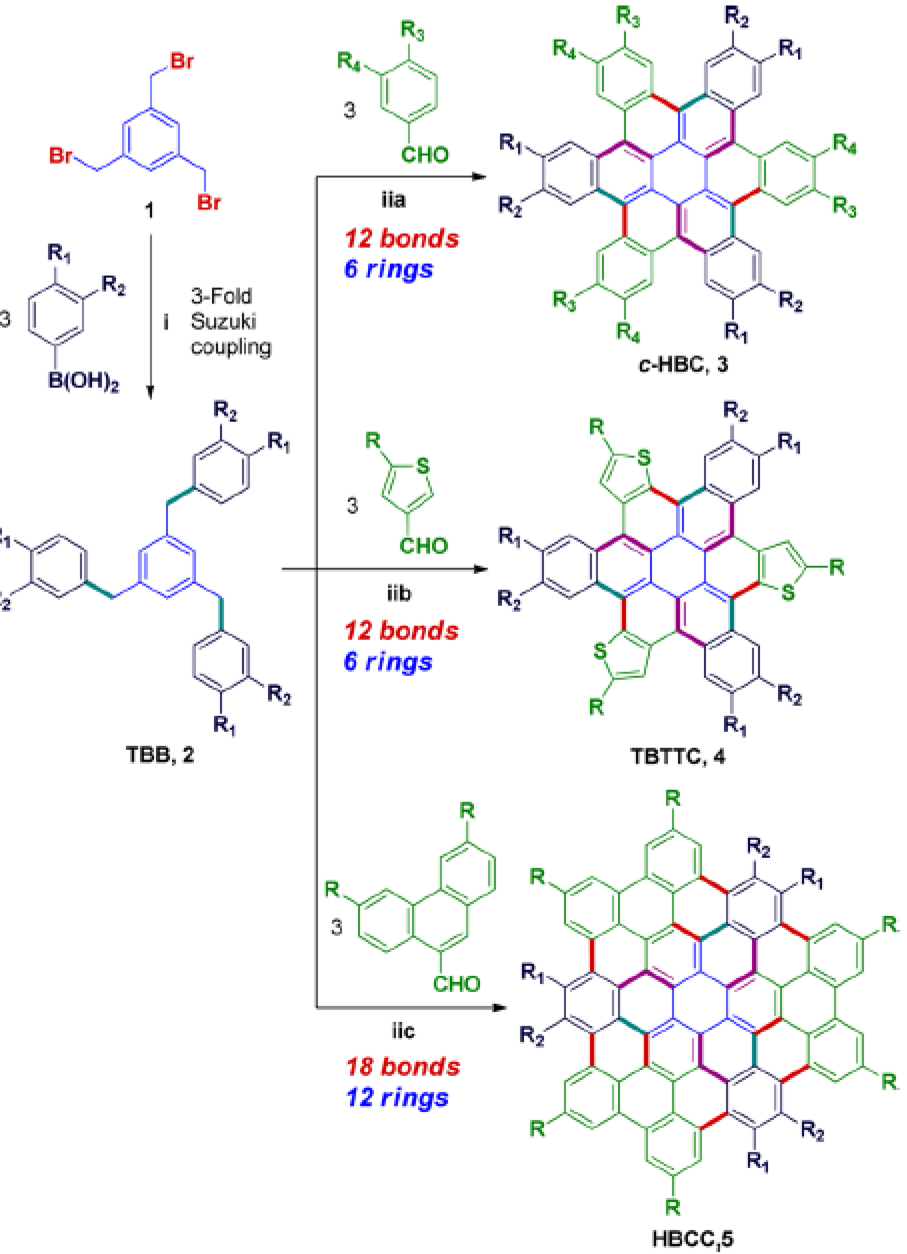


Cyclic voltammetry (0.1 M Bu_4NPF_6 in CH_2Cl_2; Pt button electrode) of **4a–c**.

1. Compounds 4a-c show similar absorbance and fluorescence properties
2. The similar oxidation potentials of each compound, along with the shift in the reduction potential of 4c relative to 4a and 4b suggest that the extended conjugation of 4c lowers its LUMO energy, making it a better electron acceptor.

Chem. Sci., 2013,**4**, 3973-3978

Facile Bottom-Up Synthesis of Coronene-based 3-Fold Symmetrical and Highly Substituted Nanographenes from Simple Aromatics



Interesting :

- $FeCl_3$ as catalyst/oxidant and acetic anhydride as dehydrator in a DCM/CH_3NO_2 solution at room temperature
- a total of 12 C−C bonds and 6 benzene rings are constructed in a single step
- four 3-fold transformations take place in tandem, that is, Friedel−Crafts hydroarylation and intramolecular alkylation, dehydrogenative aromatization and intramolecular Scholl reaction

[a] Conditions: (i) $PdCl_2$, Na_2CO_3, Me_2CO/H_2O, rt 12 h, then 37-38 °C, 3 d, 64−83%; (ii) 10 mol % $FeCl_3$, Ac_2O, CH_2Cl_2, $MeNO_2$, Ar, rt; then excess $FeCl_3$. The newly formed bonds are highlighted in colored bold.

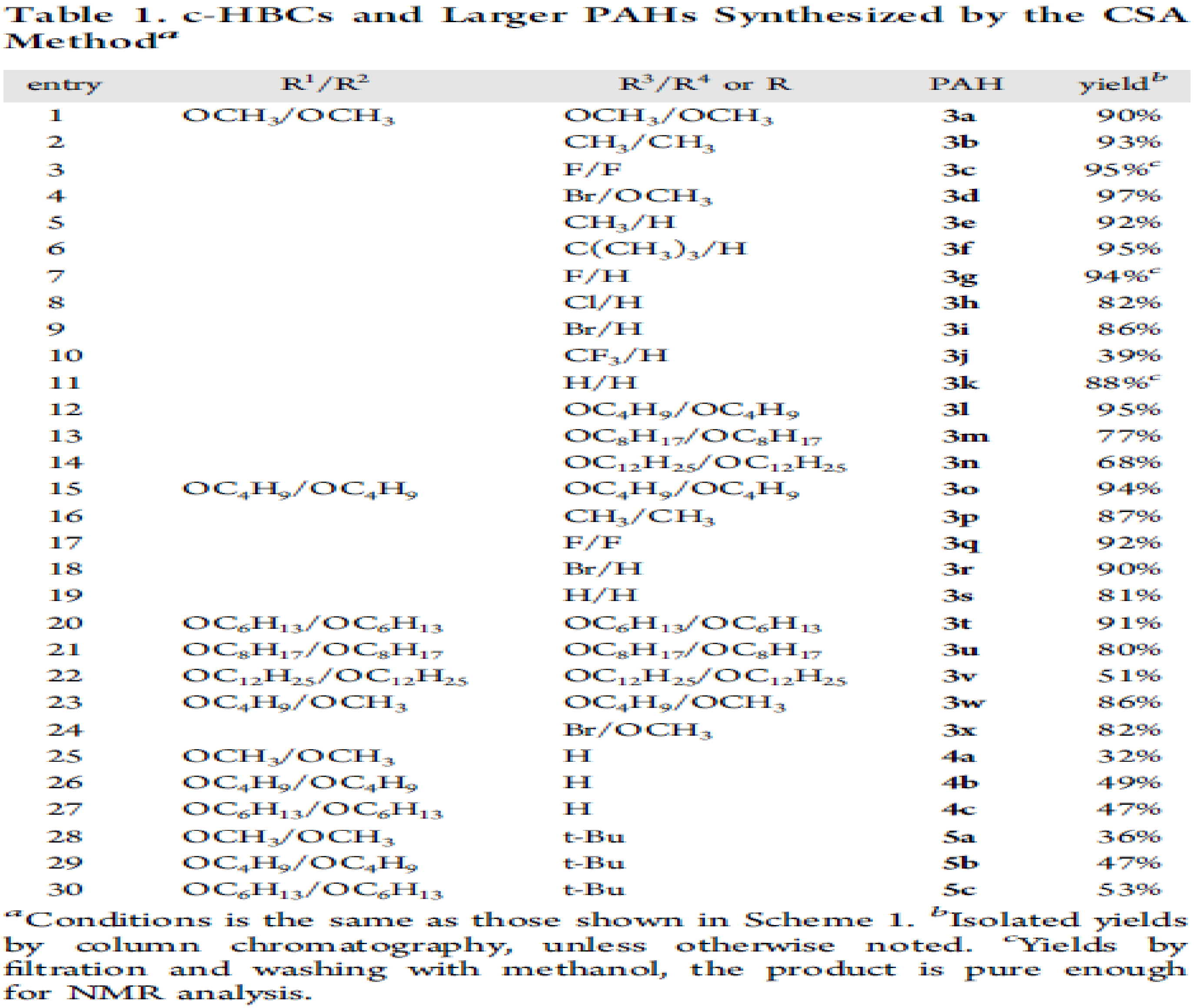


Table 1. c-HBCs and Larger PAHs Synthesized by the CSA Method[a]

entry	R^1/R^2	R^3/R^4 or R	PAH	yield[b]
1	OCH_3/OCH_3	OCH_3/OCH_3	3a	90%
2		CH_3/CH_3	3b	93%
3		F/F	3c	95%[c]
4		Br/OCH_3	3d	97%
5		CH_3/H	3e	92%
6		$C(CH_3)_3/H$	3f	95%
7		F/H	3g	94%[c]
8		Cl/H	3h	82%
9		Br/H	3i	86%
10		CF_3/H	3j	39%
11		H/H	3k	88%[c]
12		OC_4H_9/OC_4H_9	3l	95%
13		OC_8H_{17}/OC_8H_{17}	3m	77%
14		$OC_{12}H_{25}/OC_{12}H_{25}$	3n	68%
15	OC_4H_9/OC_4H_9	OC_4H_9/OC_4H_9	3o	94%
16		CH_3/CH_3	3p	87%
17		F/F	3q	92%
18		Br/H	3r	90%
19		H/H	3s	81%
20	OC_6H_{13}/OC_6H_{13}	OC_6H_{13}/OC_6H_{13}	3t	91%
21	OC_8H_{17}/OC_8H_{17}	OC_8H_{17}/OC_8H_{17}	3u	80%
22	$OC_{12}H_{25}/OC_{12}H_{25}$	$OC_{12}H_{25}/OC_{12}H_{25}$	3v	51%
23	OC_4H_9/OCH_3	OC_4H_9/OCH_3	3w	86%
24		Br/OCH_3	3x	82%
25	OCH_3/OCH_3	H	4a	32%
26	OC_4H_9/OC_4H_9	H	4b	49%
27	OC_6H_{13}/OC_6H_{13}	H	4c	47%
28	OCH_3/OCH_3	t-Bu	5a	36%
29	OC_4H_9/OC_4H_9	t-Bu	5b	47%
30	OC_6H_{13}/OC_6H_{13}	t-Bu	5c	53%

[a] Conditions is the same as those shown in Scheme 1. [b] Isolated yields by column chromatography, unless otherwise noted. [c] Yields by filtration and washing with methanol, the product is pure enough for NMR analysis.

Most reaction show high yields. Electron-rich aromatic aldehyde are favorable to give the c-HBCs; while electron-poor ones hinder the assemble reaction

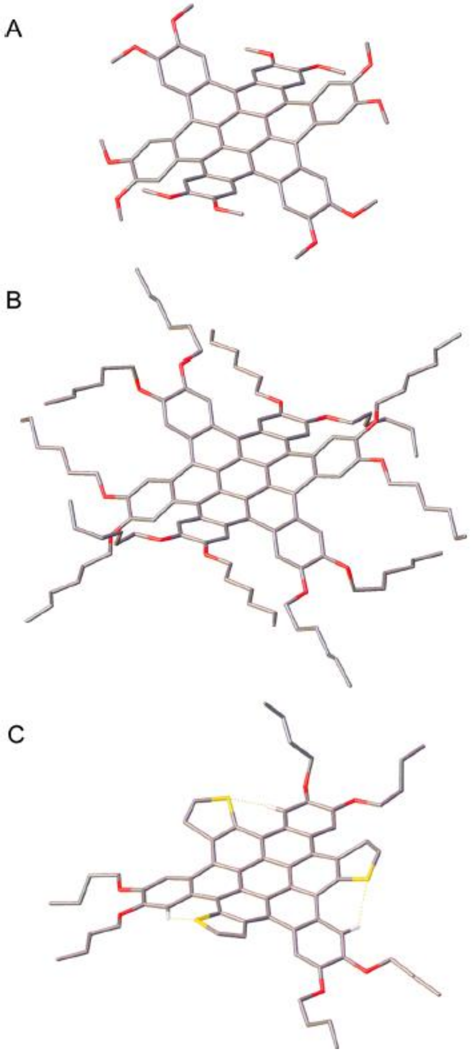


Figure 1. X-ray molecular structures of *c*-HBCs (A) **3a** and (B) **3t** and (C) TBTTC **4b** (**3a** and **3t** was measured at room temperature while **4b** at 105 K. Hydrogen atoms are omitted for clarity; oxygen is depicted in red and sulfur in yellow).

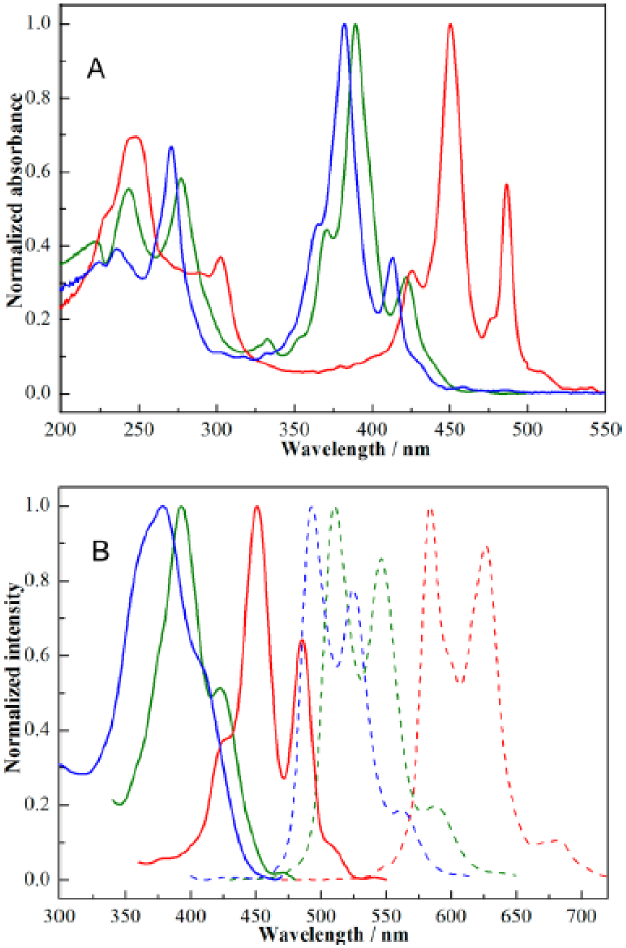
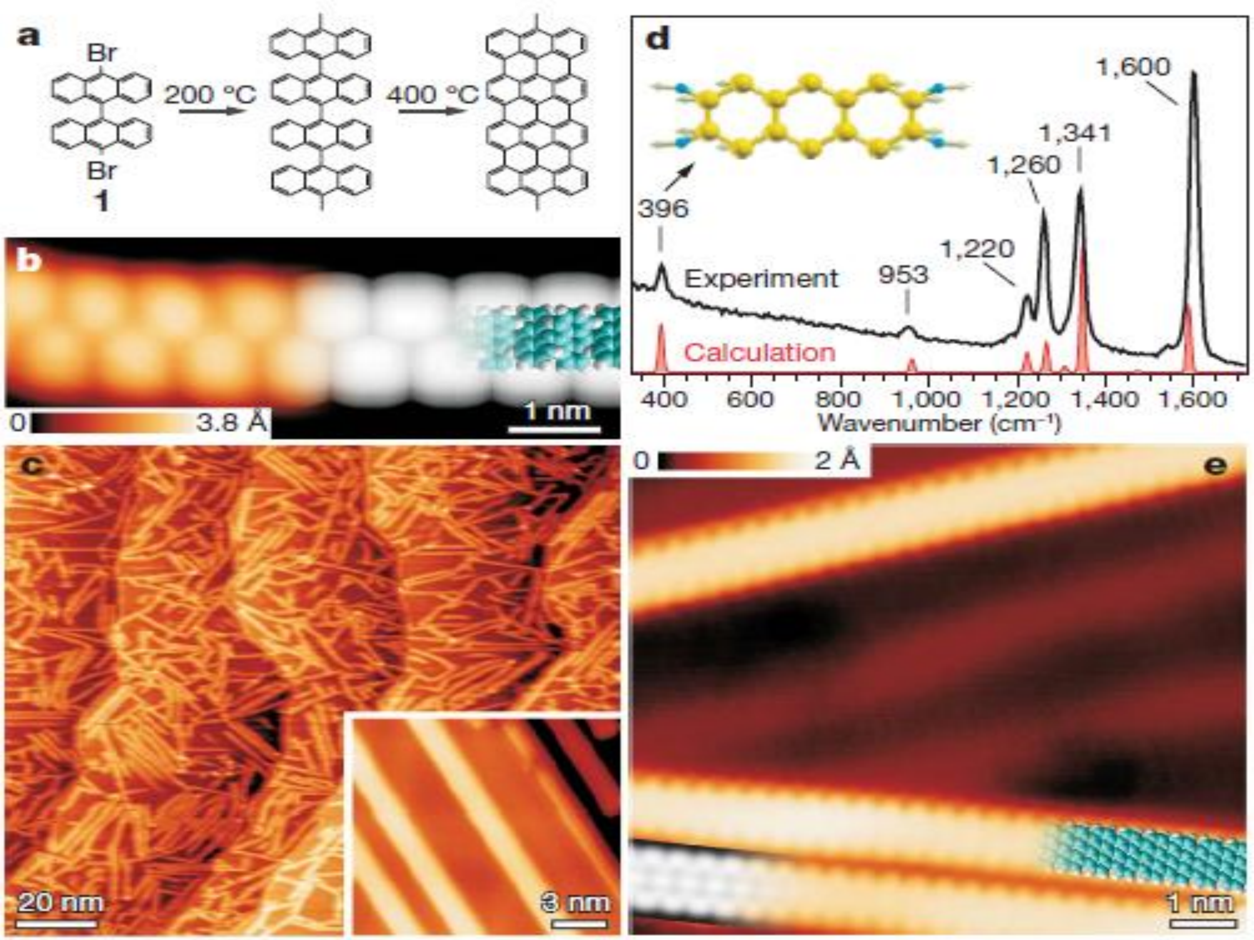


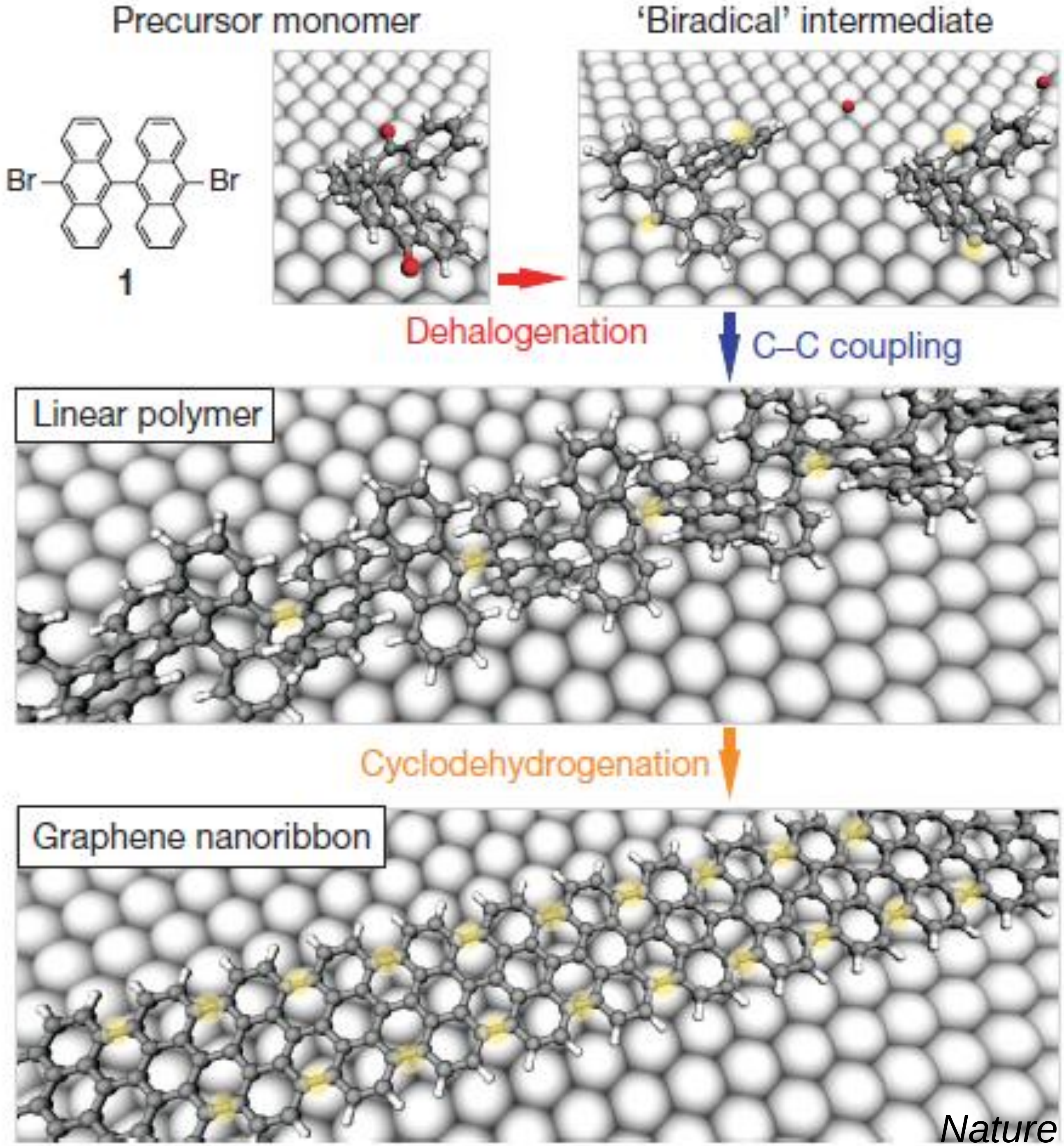
Figure 3. Normalized spectra of *c*-HBC **3a** (green) and TBTTC **4b** (blue) and HBCC **5c** (red profile). A: UV−visible spectra (4.00 μM for **3a** and **4b**; 2.00 μM for **5c**; all in DCM); B: emission and excitation (dashed line) spectra (rt., 0.40 μM in DCM).

Several interesting examples



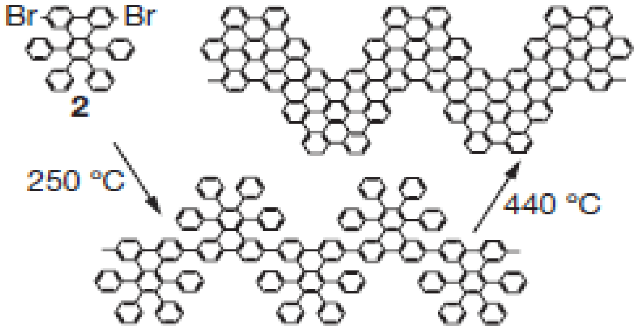
besides the D and G peaks and several other peaks appearing due to the finite width and low symmetry of the ribbons, the spectrum shows the width-specific radial-breathing-like mode as a sharp peak at 396cm-1

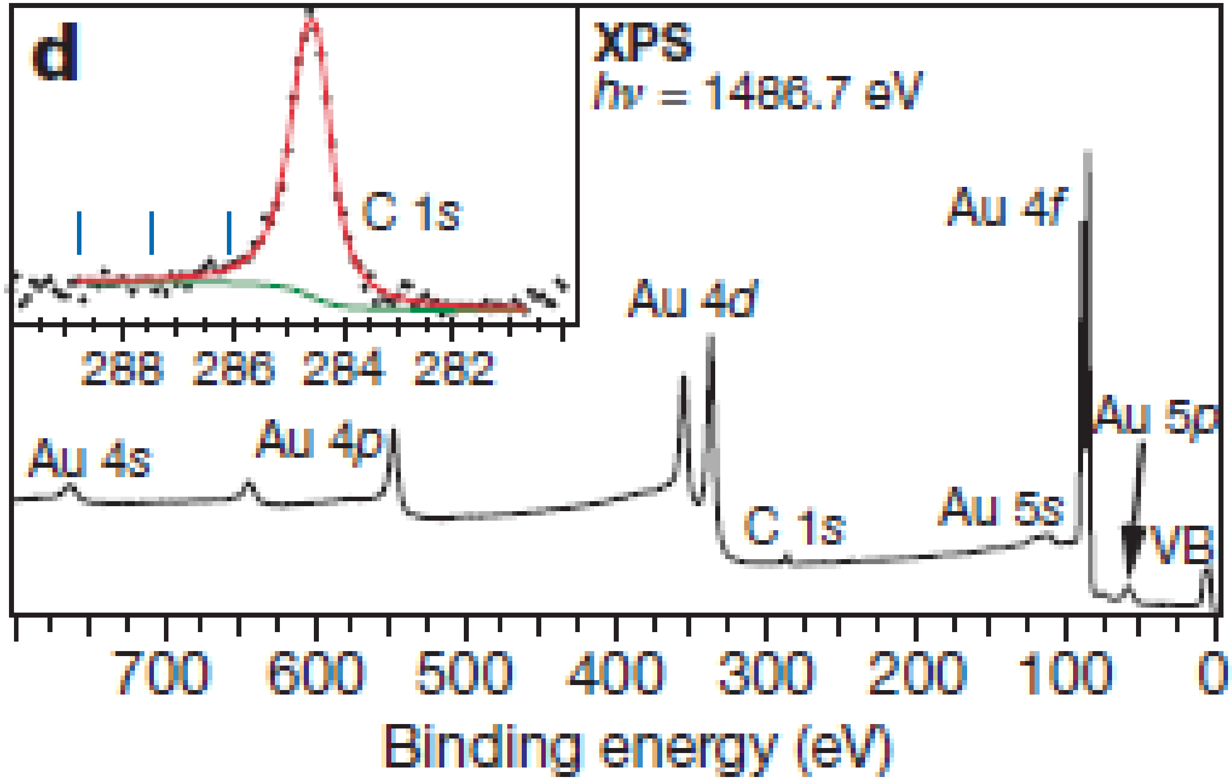
Nature **2010,** *460*, 470



Nature **2010,** *460*, 470

Chevron-type GNR



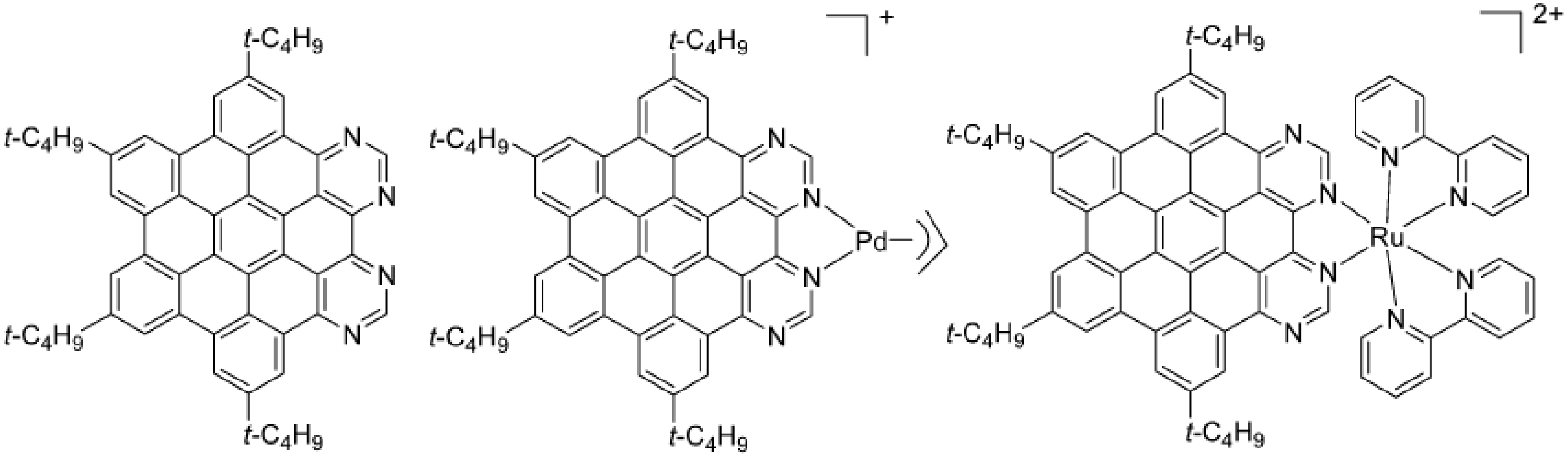


the C1s peak consists of a single sharp component at 284.5 eV binding energy characteristic of sp2 bonded carbon. There are no signs of carbon in other chemical environments (blue bars)

Nature **2010**, *460*, 470

Complexed Nitrogen Heterosuperbenzene: The Coordinating Properties of a Remarkable Ligand

----Sylvia M. Draper et al



56 **57** **58**

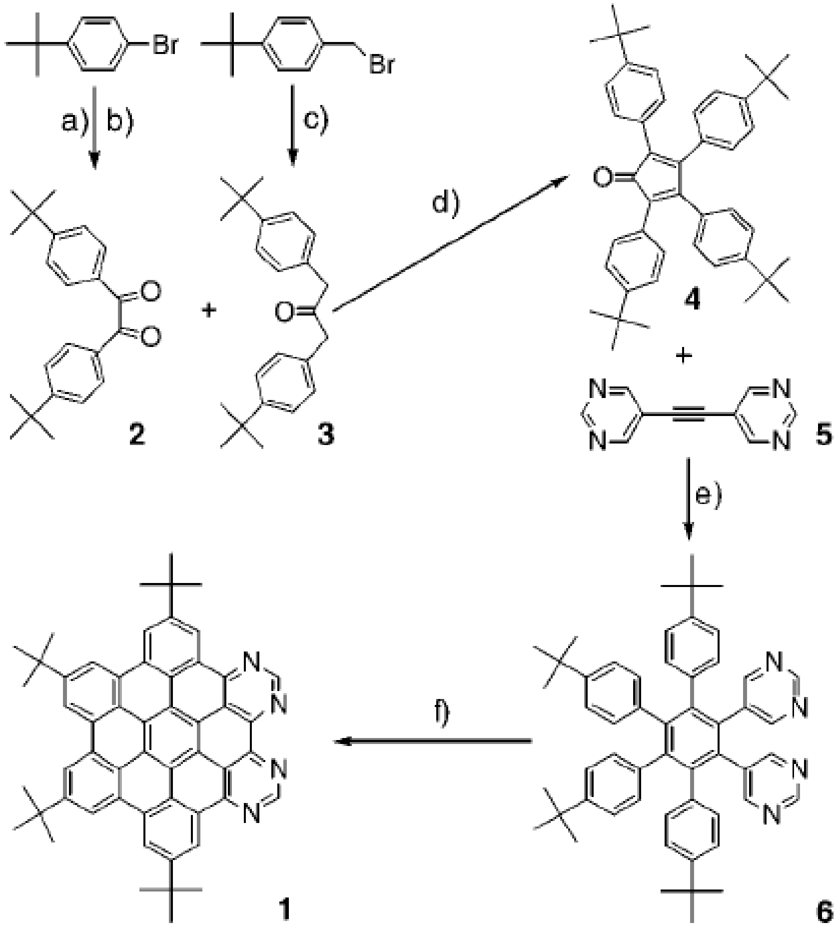
Figure 14. Nitrogen-containing HBC and its metal complexes.

The only reported example of graphene nanoribbons with coordinate metal

Chem. Rev. **2007**, *107*, 718–747 **J. AM. CHEM. SOC. 2002**, *124*, 3486−3487 **J. AM. CHEM. SOC. 2004**, *126*, 8694−8701

Complexed Nitrogen Heterosuperbenzene: The Coordinating Properties of a Remarkable Ligand

Scheme 1. The Systematic Synthesis of **1**[a]

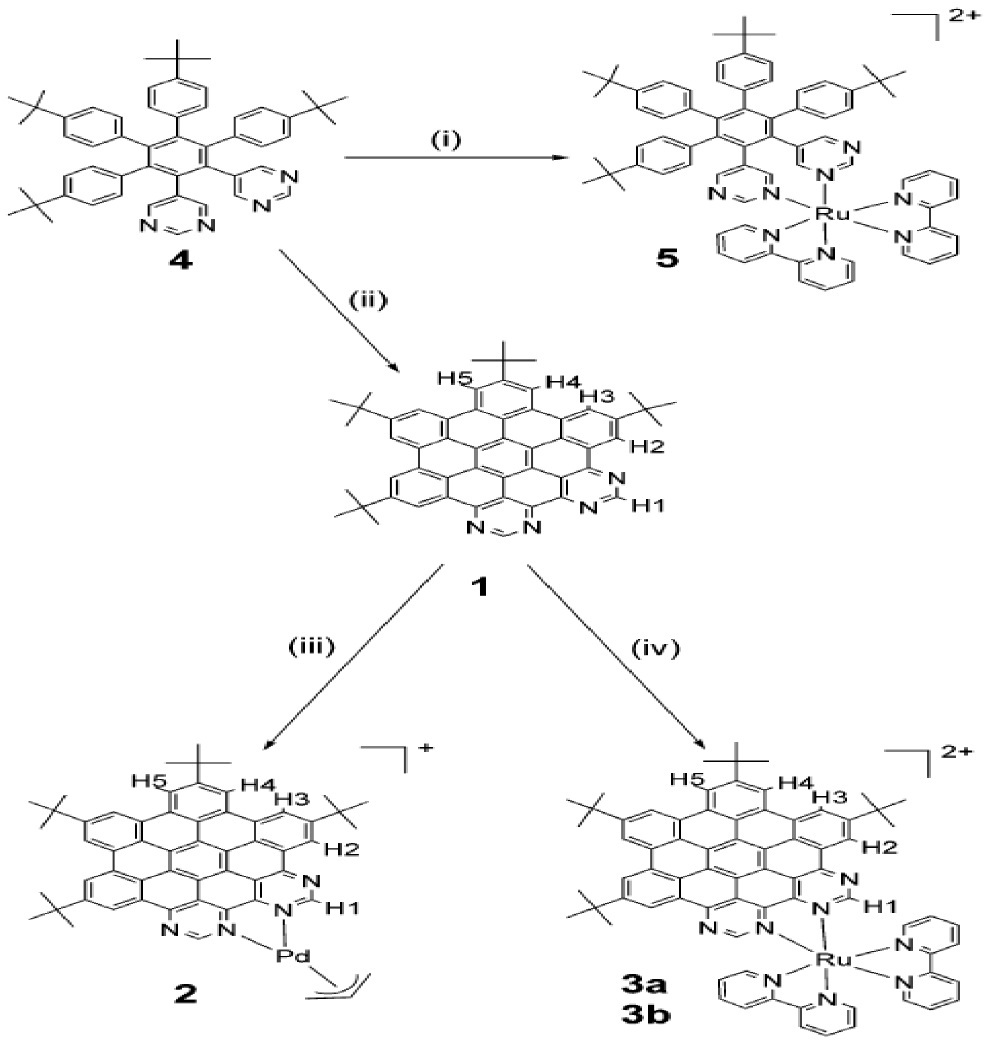


[a] Conditions: (a) BuLi, THF, −78 °C; (b) DMPD, THF, −78 °C, 70%;[4] (c) $Ca(OH)_2$, $Bu_4N^+HSO_4^-$, $Fe(CO)_5$, 1:1 CH_2Cl_2/H_2O, room temperature, 5 h; 65%;[5] (d) KOH, EtOH, 3 h, 65%;[6] (e) Ph_2O, melt, 1 h, 81%; (f) $AlCl_3$, $CuCl_2$, CS_2, 72 h, room temperature, 49%.

J. AM. CHEM. SOC. 2002, *124*, 3486−3487

The presence of N atoms increased its overall electron-accepting properties by comparison to the full-C analogue

J. AM. CHEM. SOC. 2004, *126*, 8694−8701



[a] Reaction conditions: (i) $[Ru(bpy)_2(CH_3COCH_3)_2]^{2+}$, argon, 391 K, 72 h, n-butanol; (ii) ref 1; (iii) $[Pd(\eta^3\text{-}C_3H_5)(CH_3CN)_2](NO_3)$, argon, room temperature, 12 h, toluene/acetonitrile; (iv) $[Ru(bpy)_2Cl_2]$ or $[Ru(d_8\text{-}bpy)_2Cl_2]$, argon, 400 K, 20 h, diethylene glycol ethyl ether.

the authors reported complex formation of this graphene ligand with Pd(II) and Ru(II) metal salts. As a result of complexation, the strong green emission of ligand was quenched in the complexes. The Pd(II) coordination in complex 2 caused a red shift in the low-energy absorptions. The Ru(II) coordination complex was a “black” metal-ligand charge transfer (MLCT) absorber and a near-IR emitter

J. AM. CHEM. SOC. 2004, *126*, 8694−8701

Tetracyanoquaterrylene and Tetracyanohexarylenequinodimethanes with Tunable Ground States and Strong Near-Infrared Absorption**

-----Jishan Wu

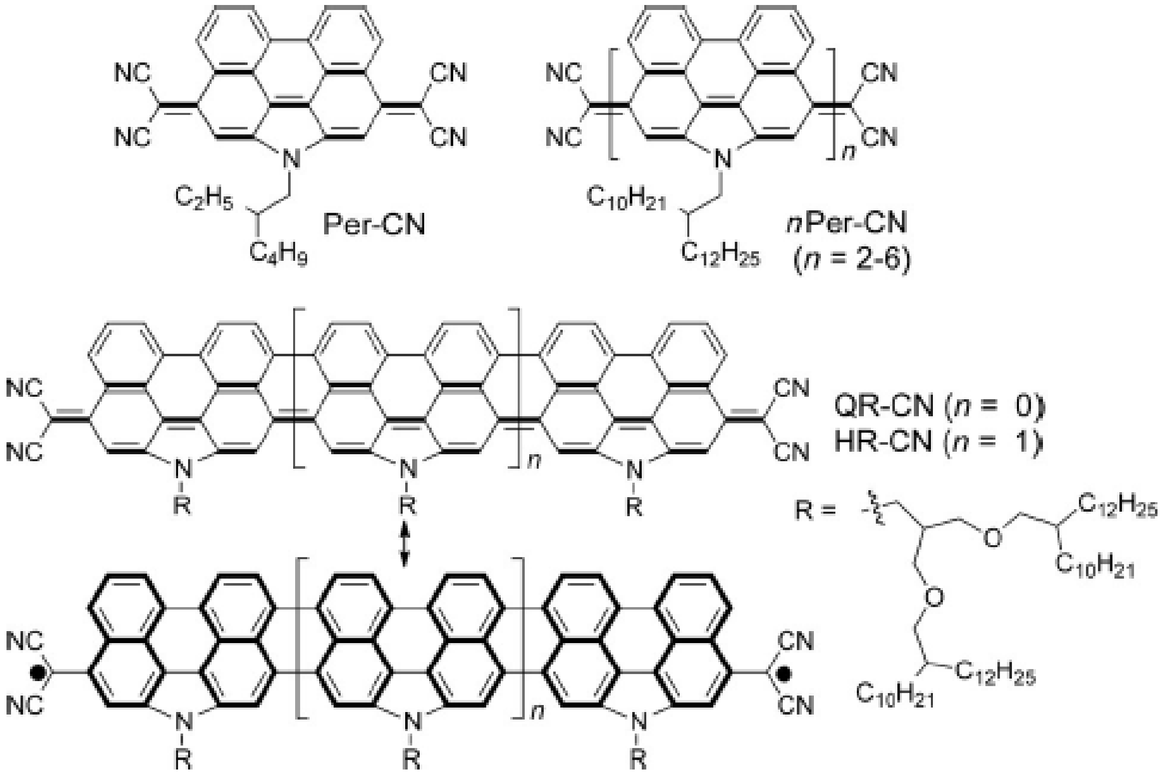
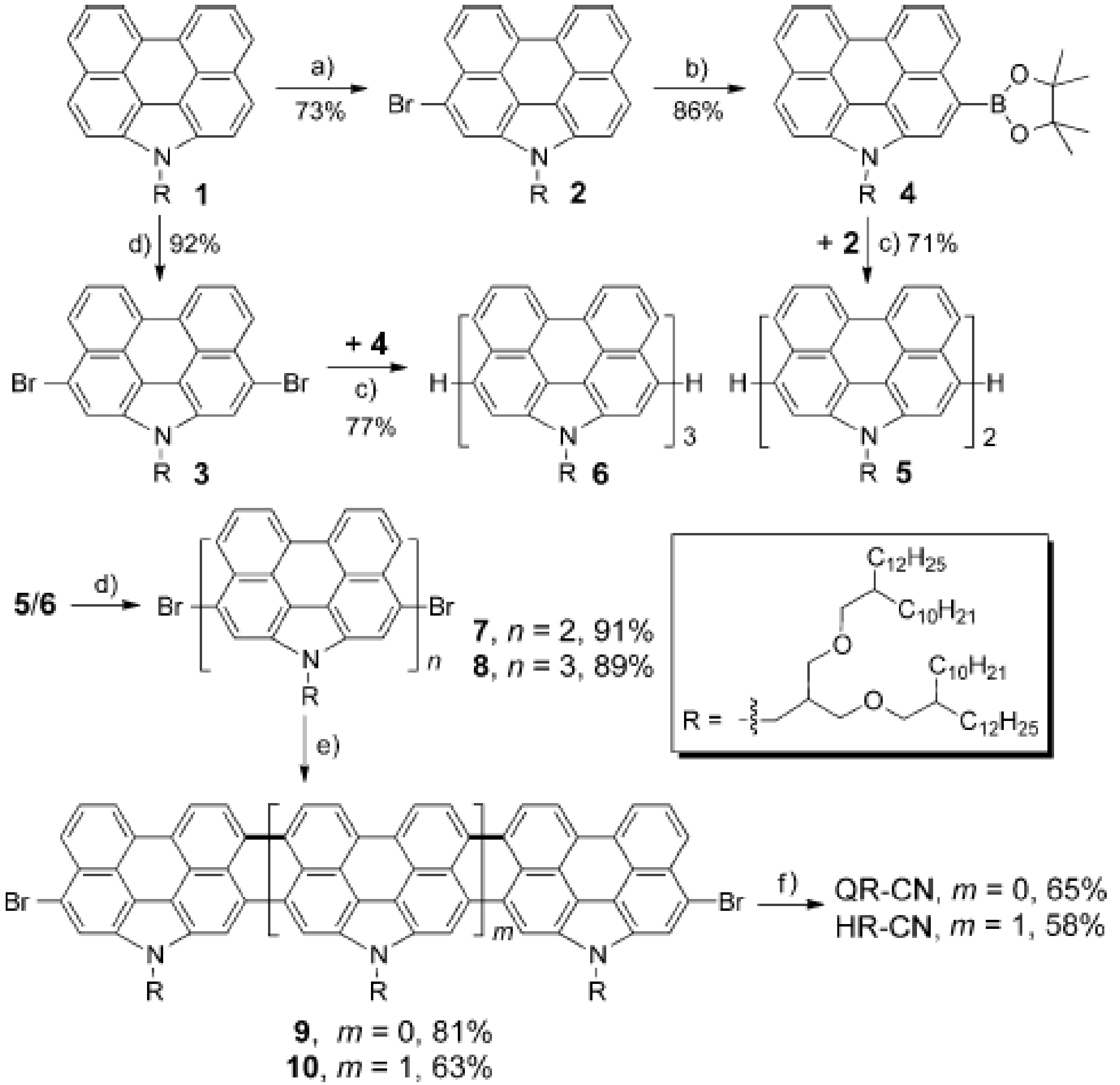


Figure 1. Chemical structures of Per-CN, *n*Per-CN, QR-CN, and the two resonance structures of HR-CN.

Angew. Chem. Int. Ed. **2013**, *52*, 8561–8565



Scheme 1. Reagents and conditions: a) NBS (1 equiv), CH_2Cl_2, 0 °C; b) pinacolborane, [$PdCl_2(PPh_3)_2$], 1,2-dichloroethane/Et_3N, 90 °C; c) [$Pd(PPh_3)_4$], Cs_2CO_3, toluene/DMF, 90 °C; d) NBS (2 equiv), CH_2Cl_2/DMF, 0–25 °C; e) DDQ/Sc(OTf)$_3$, toluene, reflux; f) i) malononitrile, NaH, [$Pd(PPh_3)_2Cl_2$], reflux; ii) HCl (2 M), 0–5 °C.

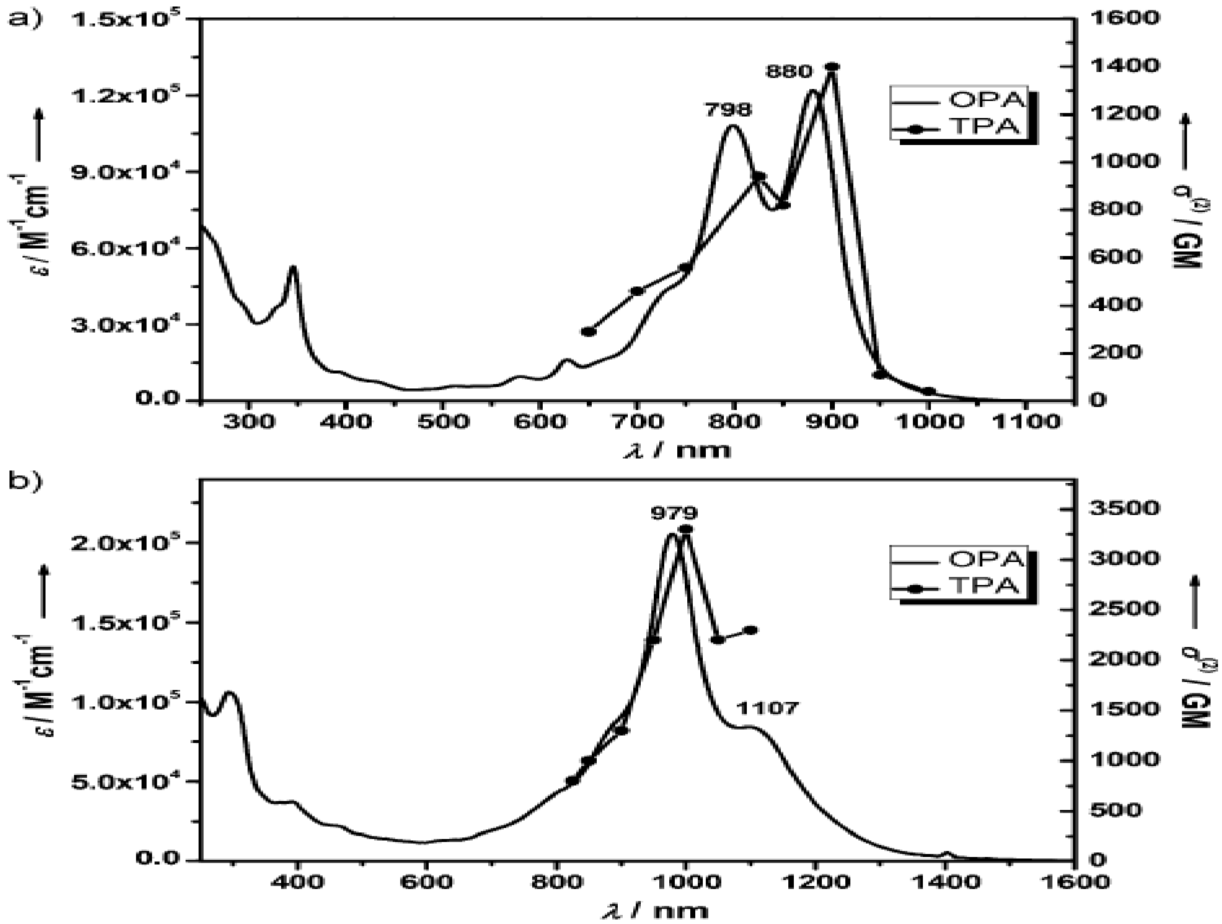


Figure 3. OPA spectra (left vertical axis) and TPA spectra (right vertical axis) of (a) QR-CN and (b) HR-CN in toluene. TPA spectra are plotted at $\lambda_{ex}/2$.

OPA------
One-photo absorption

TPA-----
Two-photo absorption

QR-CN and HR-CN showed very strong OPA and TPA response in the NIR range owing to the extended p-conjugation as well as the appropriate singlet biradical character

Thank you for your attention!