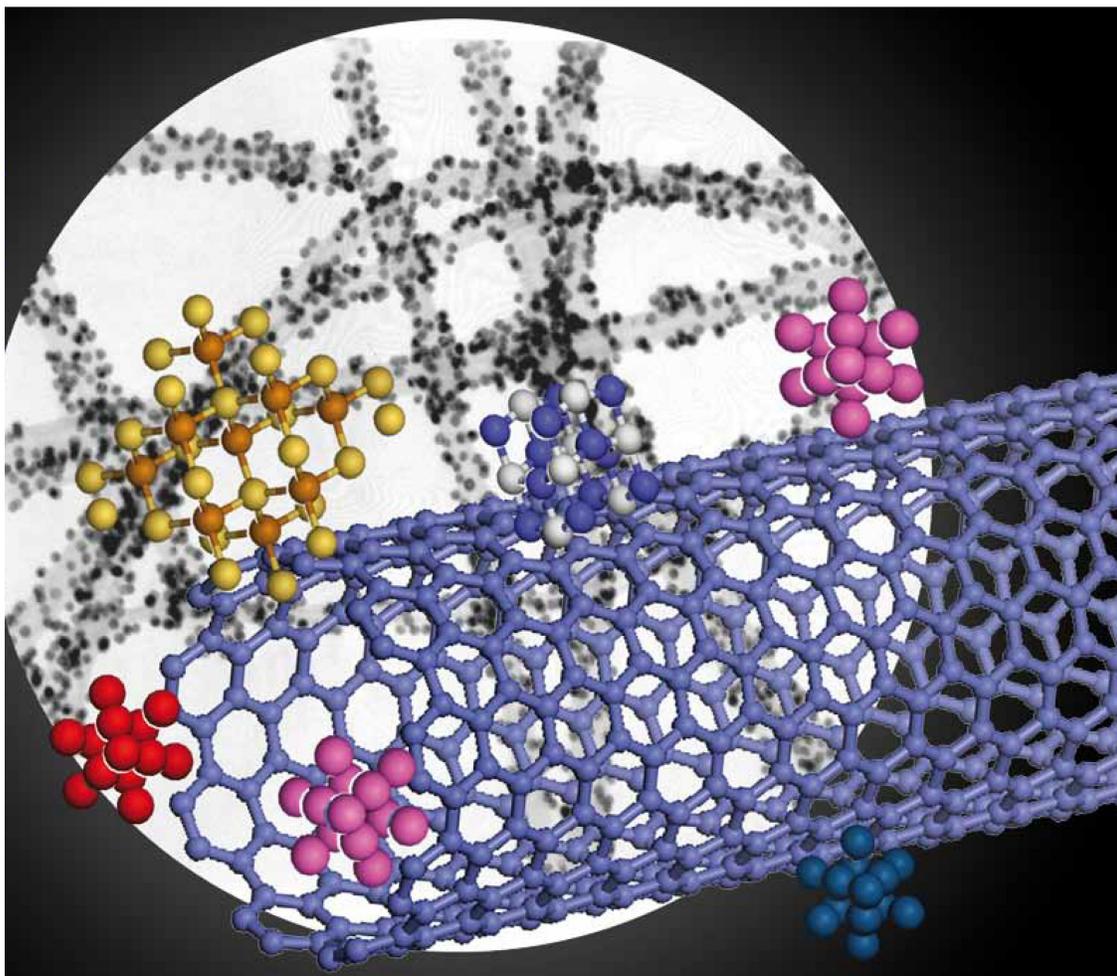# Chemical Approach for Carbon Nanotubes
~Recent progress in Organic Synthesis~

Chem. Soc. Rev. **2009**, *38*, 1076

1. Introduction: What is "Carbon Nanotube" ?

参考文献:
齋藤弥八、坂東俊治 「 カーボンナノチューブの基礎」 1998、コロナ社
齋藤理一郎、篠原久典 「 カーボンナノチューブの基礎と応用」 2004、培風館
Terrones M. *Annu. Rev. Mater.Res.* **2003**, *33,* 419

1-1. Identification
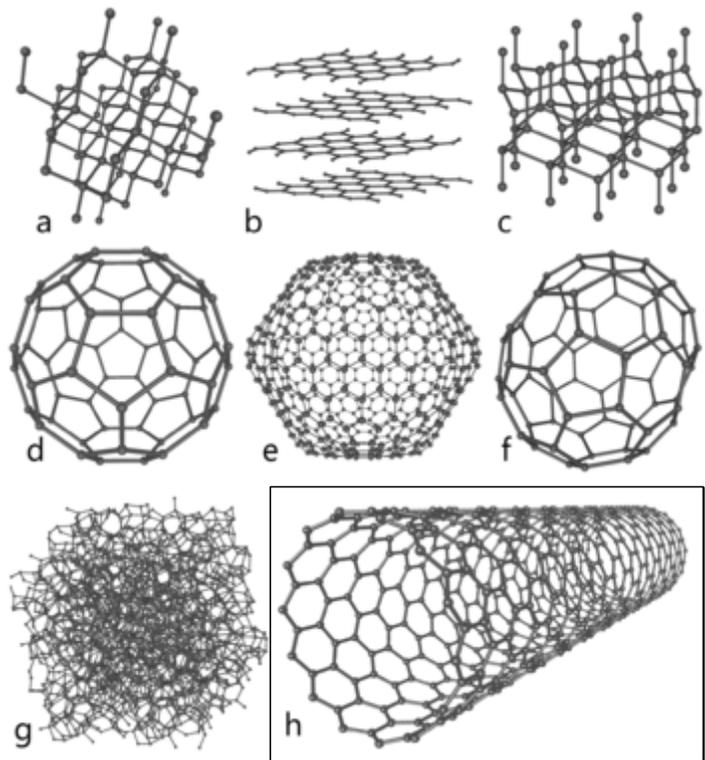
Carbon Nanotube (CN):
One of the allotropes of Carbon with a nano-scale cyrindrical structure of a graphene sheet.
First discovered in 1991 by Dr. Iijima (NEC corporation)   Iijima S. *Nature* **1991**, *354*, 56

cf. Graphene sheet: a 1-atom-thick sheet of graphite (network of sp^2-hybridized carbons)
first generated by Dr. Geim and Dr. Novoselov. (2010 Novel prize in physics)

Dr. Sumio Iijima
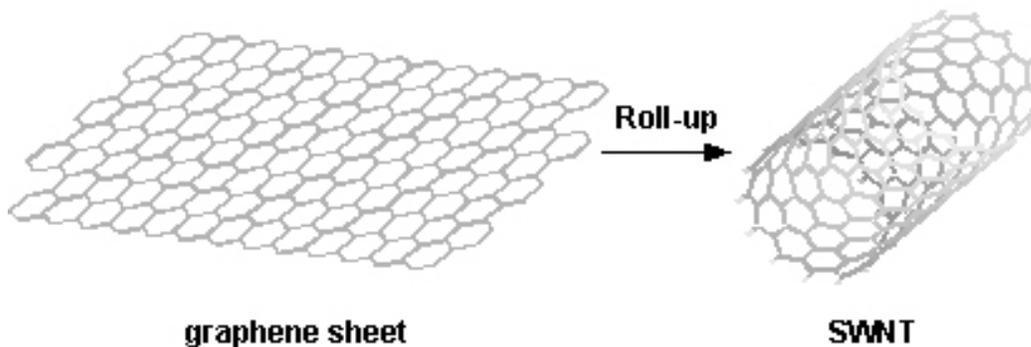http://www.nec.co.jp/rd/innovative/cnt/top.html

Some allotropes of carbon:
a) diamond; b) graphite; c) lonsdaleite;
d-f) fullerenes (C_{60}, C_{540}, C_{70});
g) amorphous carbon; h) **carbon nanotube**

http://schools-wikipedia.org/wp/c/Carbon.htm

graphene sheet   Roll-up →   SWNT
(Single-Wall Carbon Nanotube)
http://www.nanotech-now.com/nanotube-buckyball-sites.htm

History of discovery:

  Fullerene, another allotrope of carbon, was first found in 1985, and around 1990-1991 was developed the large-scale synthesis by using arc discharge method.

  Although in those days many researchers were interested only in fullerene synthesis, Dr. Iijima paid attention to sediment left on cathode after fullerene formation.

  Analyzing it by electron microscope, he discovered the first multi-walled carbon nanotubes (MWNTs).

Structural diversity:
(1) Wall number

  Single-walled nanotube (SWNT): Rolled single graphene sheet
  Diameter = 0.5~5 nm (*cf.* fullerene ~0.7nm)
  Length = *ca.* 1μm (max.~18.5cm *Nano Lett.* **2009**, *9*, 3137)
  Simpler electrical property than MWNTs
  Multi-walled nanotube (MWNT):   Rolled multiple number of graphene sheets
  Diameter = 4~50 nm, Length >10μm
  Stronger materials than SWNTs

(a) (b) 5nm (c) (d) 5nm 5nm
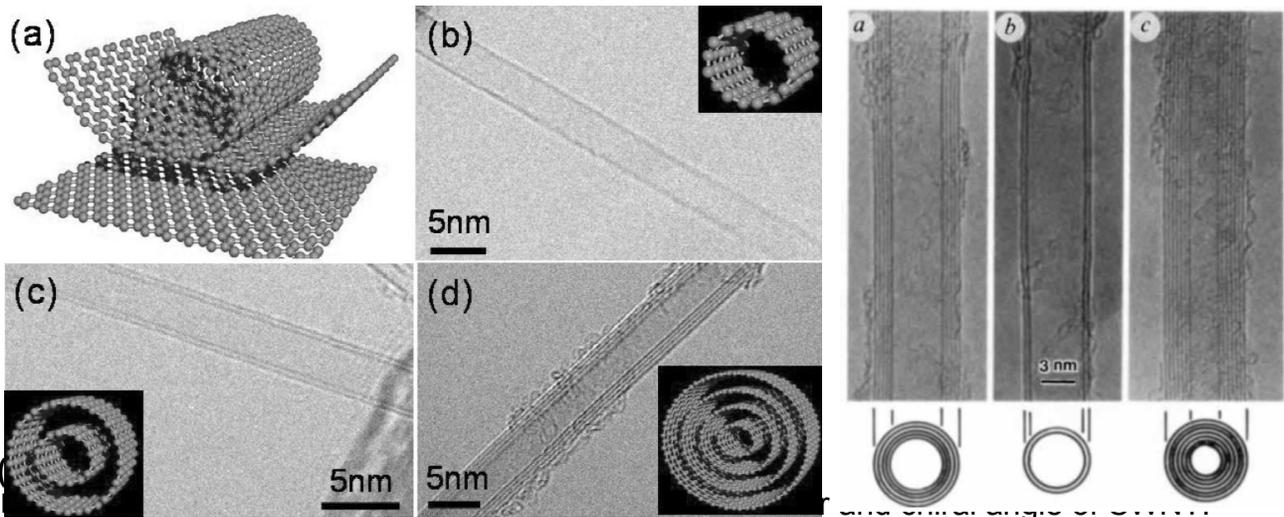
Pure. Appl. Chem. **2006**, *76*, 1703   Iijima S. *Nature* **1991**, *354*, 56
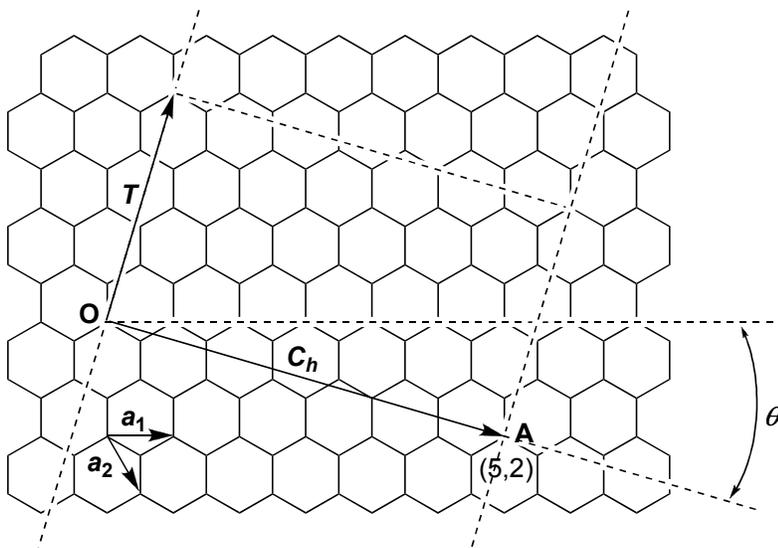
O = A in the rolled structure
a_1, a_2: elementary vector
C_h: chiral vector (= $\overrightarrow{OA}$ = na_1 + ma_2 = (n,m))
T: lattice vector (= tube direction)
d: diameter of tube, θ: chiral angle
a_{c-c}: distance between nearest carbon atoms

$$d = \frac{\sqrt{3}a_{c-c}\sqrt{n^2 + nm + m^2}}{\pi}$$

$$\theta = \tan^{-1}\left(-\frac{\sqrt{3}m}{2n + m}\right) \ (|\theta| \leq \frac{\pi}{6})$$

In this case,
C_h = $5a_1$ + $2a_2$ = (5,2)

There are **3 kinds of classification** in the structure of SWNTs.

O → (8,0)

a_1

a_2

(6,4)

(5,5)

graphene sheet

Roll-up

**a** **b** **c**

armchair **zigzag** **chiral**
$C_h = (5,5)$ $C_h = (8,0)$ $C_h = (6,4)$
n = m **m = 0** **the other case**
$(\theta = \pi/6)$ $(\theta = 0)$ $(0 < |\theta| < \pi/6)$
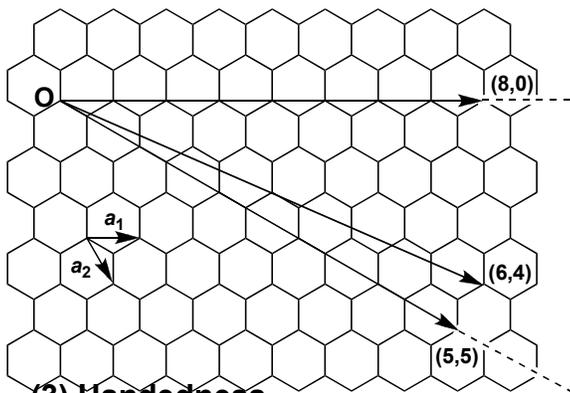
(3) Handedness
 = direction of helicity (positive or ne
In the case of chiral SWNTs, two kinds of I

(4) "Cap"
The terminal of tubes is often closed by a I
Each cap has six 5-membered rings that a
By using proper methods (*e.g.* oxidation), the cap can be removed and "open (end) nanotubes" can be
obtained which have carboxylic groups on terminal instead of fullerene caps.
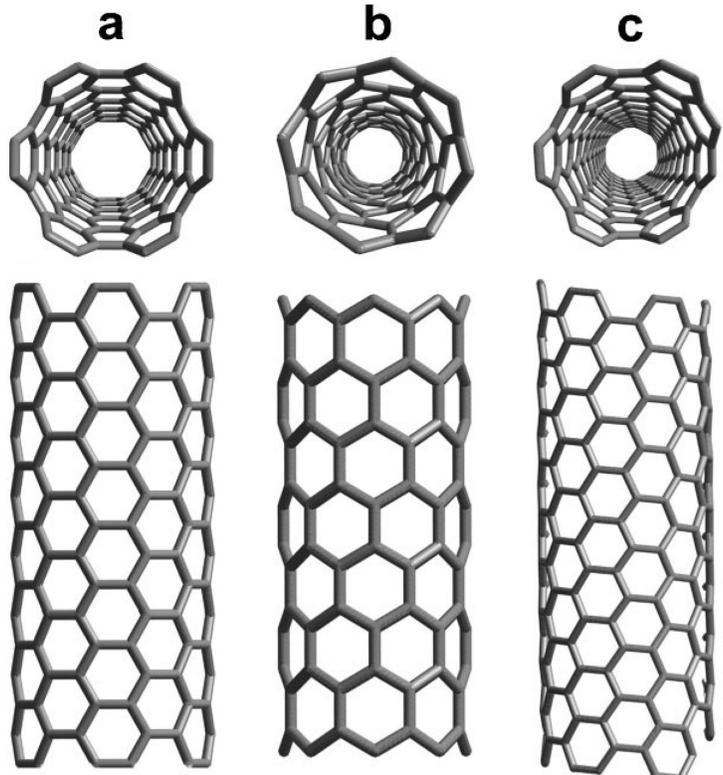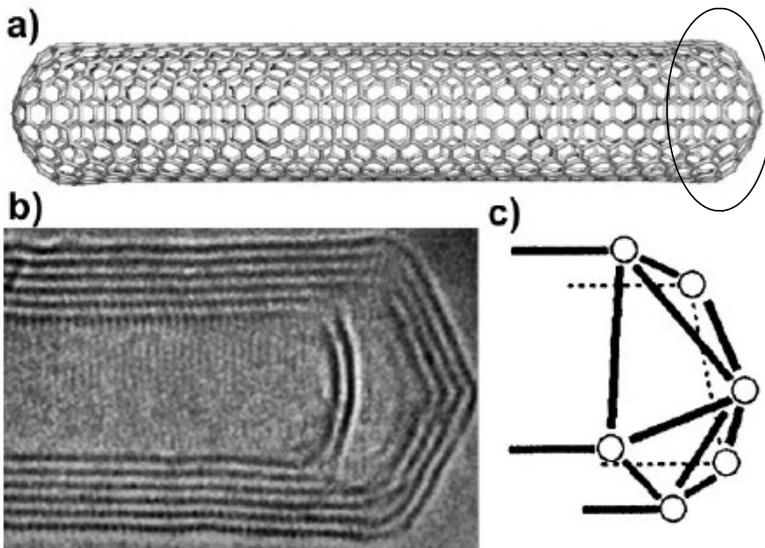
a) Model of a capped SWNT
b) HRTEM image of a capped MWNT
c) Model of closed MWNT indicating the
 location of six pentagons
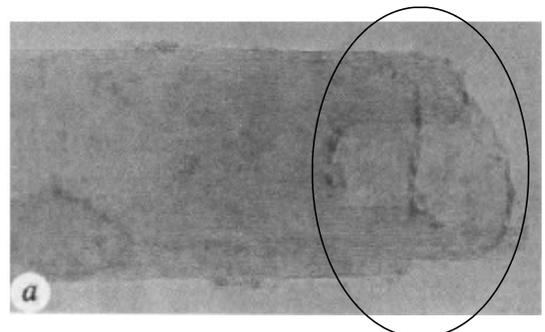
Uncapped MWNT
Iijima S. *et al. Nature* **1993**, *362*, 522

4

1-2. Physical properties and applications

(1) Electrical property
Carbon nanotube can become **both metal and semi-conductor !**

About "metal (metallic conductor)" and "semiconductor"

Metallic conductor: No band gap between valence band and conduction one.
The more the temp increases, the lower the conductivity becomes.
Semiconductor: Possesing a smaller band gap.
The more the temp increases, the higher the conductivity becomes.
Insulator: Possesing a bigger band gap. Electrons are forced to stay in valence band.

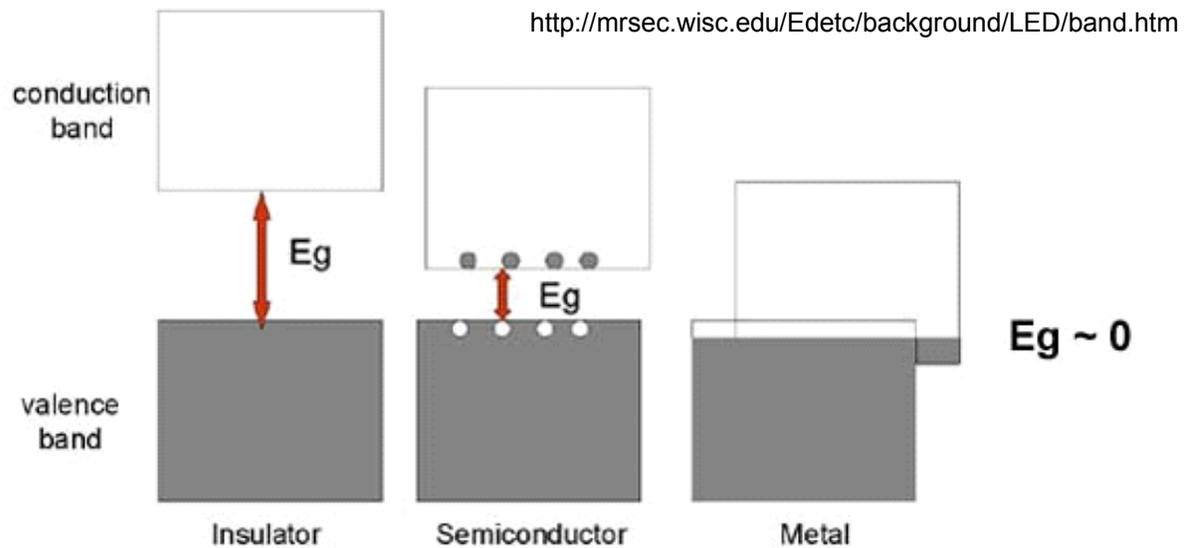http://mrsec.wisc.edu/Edetc/background/LED/band.htm

Graphene itself is known as a **zero-gap semiconductor** due to the lack of band gap.
On the other hand, as the quantum conditions appear due to rolling the graphene sheet,
the band gap of CN becomes different from graphene.

quantum condition:
$C_h \cdot k = 2\pi q$ (k = wavenumber, q = integer)

$\Rightarrow$
$n - m = 3q$: **metal**
$n - m \neq 3q$: **semi-conductor**

⊙ : metal ● : semiconductor
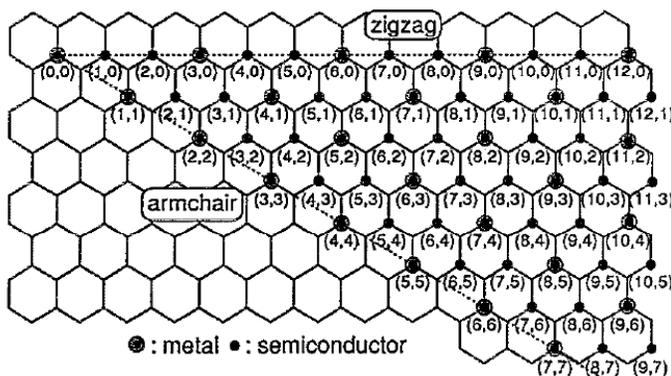
Saito R. *et al. Appl. Phys. Lett.* **1992**, *60*, 2204
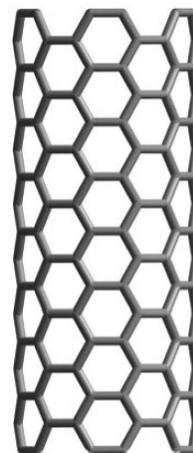
armchair
C_h = (5,5)
⬇
metal

zigzag
C_h = (8,0)
⬇
metal or semiconductor
(In this case, both are semiconductor)

chiral
C_h = (6,4)
⬇

(2) Strength

Current density: 1000 times larger than copper (~ 4×10^9 A/cm^2)
Science **2001**, *292*, 2462
Electrical conductivity: larger than copper (in the case of metallic CN) $\Rightarrow$ **Next generation LSI instead of silicon-based IC**
Thermal conductivity: 7-8 times larger than silver (3000 W/m/K)

Tensile strength: almost same as diamond (~63 GPa for MWNTs) $\Rightarrow$ **Tough materials (Rope for space elevator ?)**
Science **2000**, *287*, 637

(3) Large surface area (2000 m^2/g if opened)

Aspect ratio (length-to-width) : ~ 10 million
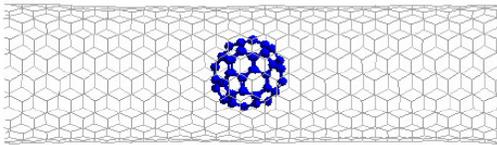Opened SWNT can become clathrate holding small molecules inside. $\Rightarrow$ **Strage of gas molecules Gas sensor**
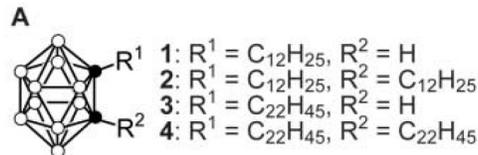
To dope new elements or to absorb other molecules inside,
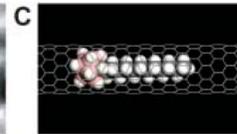physical property of materials can surprisingly change. $\Rightarrow$ **Development of new materials**

Carbon peapod
(C$_{60}$ @ [10,10]SWNT)

Nanotechnology **2006,** *17,* 5691

A

1: R^1 = C$_{12}$H$_{25}$, R^2 = H
2: R^1 = C$_{12}$H$_{25}$, R^2 = C$_{12}$H$_{25}$
3: R^1 = C$_{22}$H$_{45}$, R^2 = H
4: R^1 = C$_{22}$H$_{45}$, R^2 = C$_{22}$H$_{45}$

○BH ●C

B C
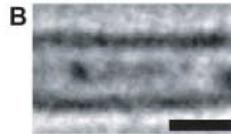
Carborane as a guest molecule

Nakamura E. *et al. Science* **2007**, *316*, 853
See also: Dr. Morimoto's Lit. Semi. (2007.8.1)

(4) Field emission

Electrons are easily emissed from pentagons of CN cap
by putting in an electric field. $\Rightarrow$ **Field emission display**

(5) Poor solubility

Capped CNs are not soluble for most solvents
due to the large molecular weight.

It was known the commercially available
green tea "伊右衛門 濃いめ" can dissolve
SWNTs, probably due to containing
catechin. *Chem. Lett.* **2007**, *36*, 1140

C$_{60}$ fullerene   [7,7]SWNT
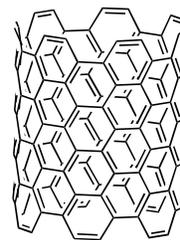
Mw: 720   >10^7
Solubility: good   bad

"伊右衛門 濃いめ"
(Suntory)

As carbon nanotubes possess a lot of interesting properties and corresponding uses,
required features of each purpose are so various.
ex. gas strage...large-scale, large surface area
LSI...large-scale, chirality control (metallic or semiconducting)

$\Rightarrow$ Both **large-scale synthesis** and **selective synthesis** are important.

1-3. Difficulties in conventional syntheses

Conventional synthetic methods: Ref. http://www.nedo.go.jp/
Bertozzi C. R. *et al. Chem. Phys. Lett*. **2010**, *494*, 1

(1) Arc discharge synthesis (First discovery of CNs in 1991)

While a current is passed between two graphitic electrodes under inert atmosphere,
some graphites vaporize and condense on the cathode as CNs.

(2) Laser ablation

A pulsed lasar is used to vaporize a graphite/catalyst target generating CNs on the walls of the reactor.
Yield and selectivity (purity) are better, but costly and not useful for large-scale production

(3) Chemical vapor deposition (CVD)

A metal catalyst particle is deposited on a substrate and placed into a high temperature furnace.
A carbon gas source (*e.g.* CH_4, C_2H_2) is then passed, resulting in growth of CNs on the substrate.
Useful for large-scale production. Several advanced methods are available.
  cf. High pressure carbon monooxide method (HiPCO)
    Super growth CVD method: Highly pure SWNTs   Hata K., Iijima S. *et al. Science* **2004**, *306*, 1362
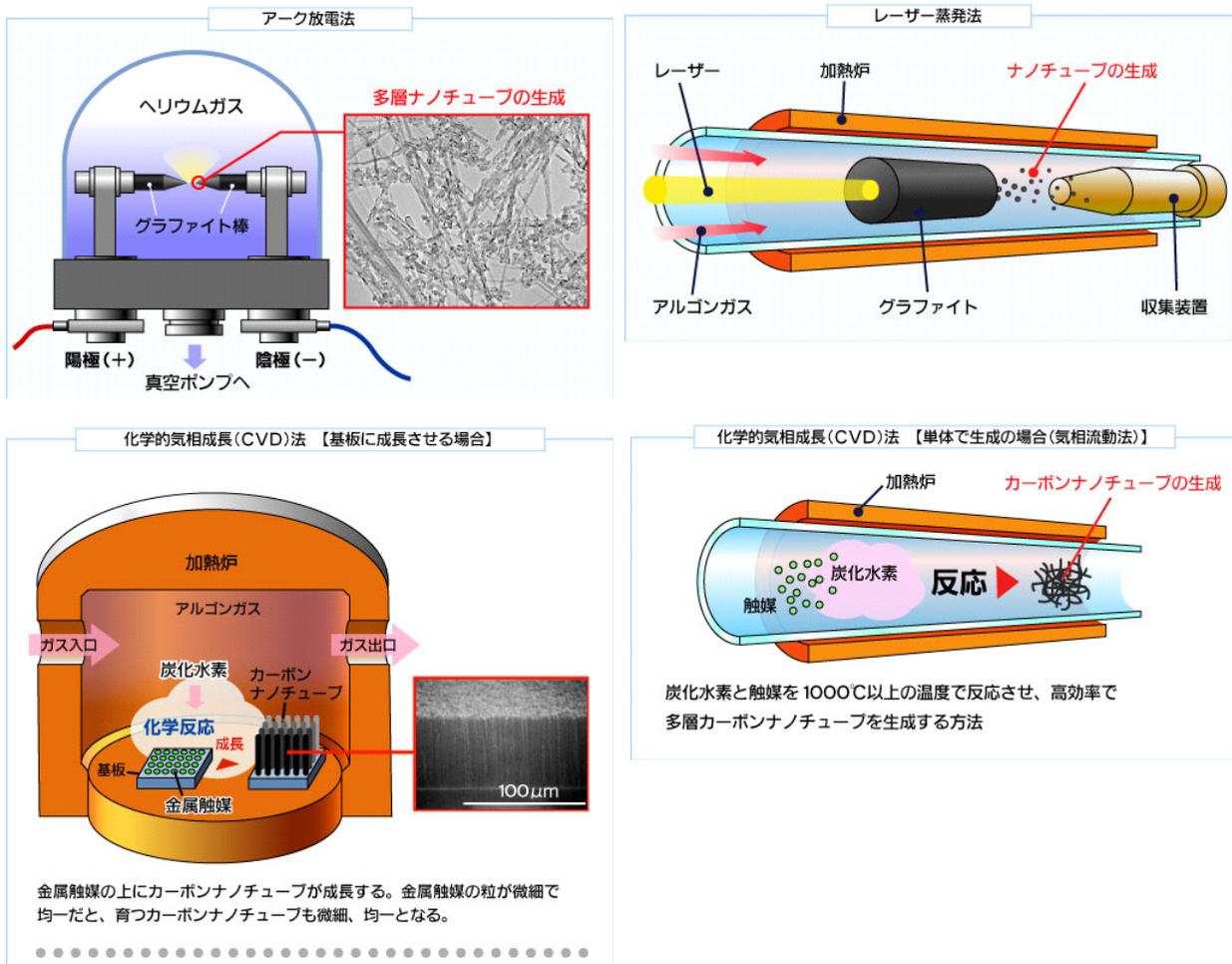
Some advanced methods can produce enough "pure" CNs to utilize for several industrial purposes.
For example, ratio of metallic/semiconducting can be controled as 90:10 ~ 5:95.
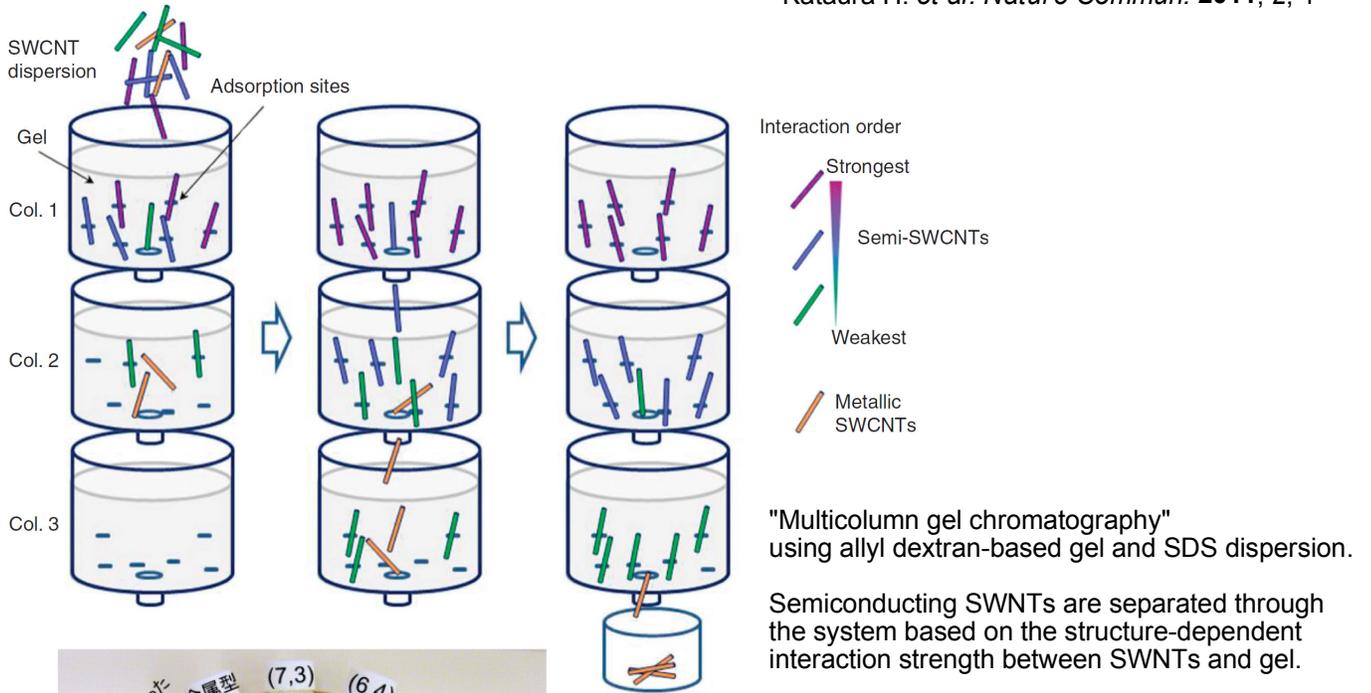(*Science* **2009**, *326*, 116; *Nano Lett.* **2008**, *8*, 2682)

But these methods **cannot control the chirality** completely (produced "pure" CNs are always mixture), although
many applications (conductive films, transistors, nanosensors, chemical research *etc.*) require chirality-pure CNs.
It is unclear how to extend these empirical results to chirality-selective synthesis of CNs.

Conventional purification methods:

Unfortunately, CNs are not dissolved in most solvents due to their large molecular weight.
So it is expected to be difficult to apply general chromatographical purification methods.

Recently, large-scale **single chirality separation of SWNTs** by using simple gel was reported.

Kataura H. *et al. Nature Commun.* **2011**, *2*, 1

"Multicolumn gel chromatography"
using allyl dextran-based gel and SDS dispersion.

Semiconducting SWNTs are separated through the system based on the structure-dependent interaction strength between SWNTs and gel.

13 kinds of semiconducting SWNT were separated in 39~94% purity.

Each SWNT was determined by analyzing its specific wavelength (for excitation/emission).

http://www.aist.go.jp/aist_j/press_release/pr2011/pr20110511/pr20110511.html

But generally, purification is an **inefficient** and **stressful** process,
and so ideally it is the best to produce the chirality-pure CNs **without purification steps**.
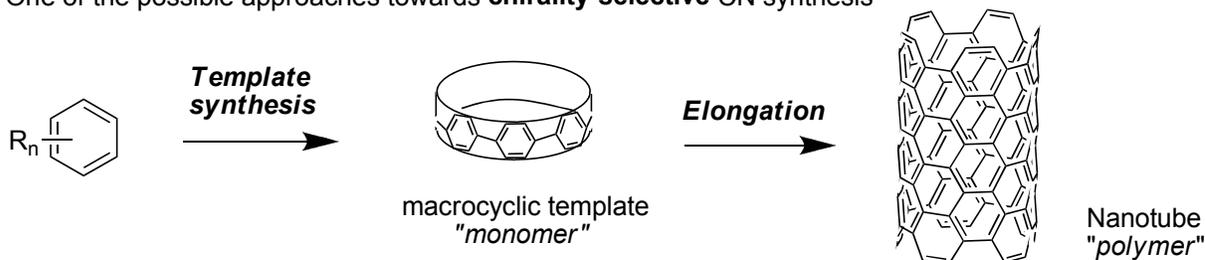
⟹ **New strategy for chirality-selective CN synthesis is highly required today.**

2. Organic synthesis approach

2-1. About "Bottom-up template synthesis"

~ One of the possible approaches towards **chirality-selective** CN synthesis

Advantages of organic synthesis approach:
(1) Strategy is more reliable because it's based on mechanistically well-understood reactions.
(2) Lower temperature (~200°C) can be applied than current methods (>1000°C).
(3) Structural diversification should be possible. (*e.g.* Regioselective doping of other elements)
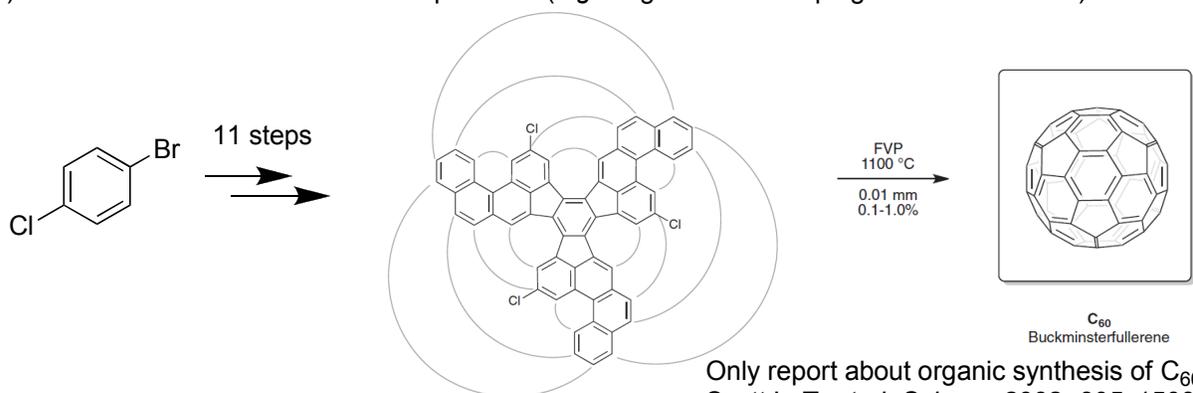
Only report about organic synthesis of C_{60}
Scott L. T. *et al. Science* **2002**, *295*, 1500

There has been **NO REPORT** about organic synthesis of carbon nanotubes.

Candidates for "templates"

Sidewall segments of an armchair carbon nanotube

Vögtle belt
(pyrene type)
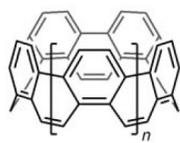
cyclophenacene
(phenanthrene type)
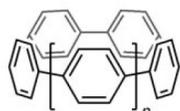
cycloparaphenylene
(benzene type)
[*n*]-CPP
"carbon nanohoop"

Sidewall segment of a zigzag carbon nanotube
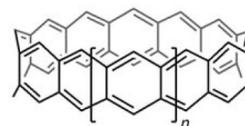
cyclacene

Main theme of this chapter
Bertozzi (2008)
Itami (2009, 2010, 2011)
Yamago (2010, 2011)

Prof. Carolyn R. Bertozzi
University of California, Berkeley

Prof. Kenichiro Itami
Nagoya University

Prof. Shigeru Yamago
Kyoto University

Difficulty in CPP synthesis: Strain energy caused by aryl ring closure

cyclization
(−XY)
55 kcal mol^{-1}
- - - - - →

polymerization

A

1

[12]CPP:
48.1 (kcal/mol)

Figure 4. Correlation of strain energies of [*n*]CPP and [*n*]CPPA versus the diameters of the rings.

[*n*]CPP

[*n*]CPPA

Itami K. *et al. ACIE* **2009**, *48*, 6112

Itami K. *et al. Org. Lett.* **2010**, *12*, 2262

Key point: **How to overcome such a big strain energy**

2-2. Synthesis of CPP ~ Prof. Bertozzi's work

The first report of CPP synthesis Bertozzi C. R. *et al. J. Am. Chem. Soc.* **2008**, *130*, 17646

3

1) ^{n}BuLi, THF
2) benzoquinone

1) NaH, THF
2) MeI

4: R = I (34%)

1) ^{n}BuLi, THF
2) ^{i}PrOBPin

5: R = BPin
(82%)

4 + 5

Pd(PPh$_3$)$_4$, Cs$_2$CO$_3$

toluene/MeOH (10:1)
80°C

6, m = 2, 2%
7, m = 3, 10%
8, m = 5, 10%

Unexpected homocoupling of **5**

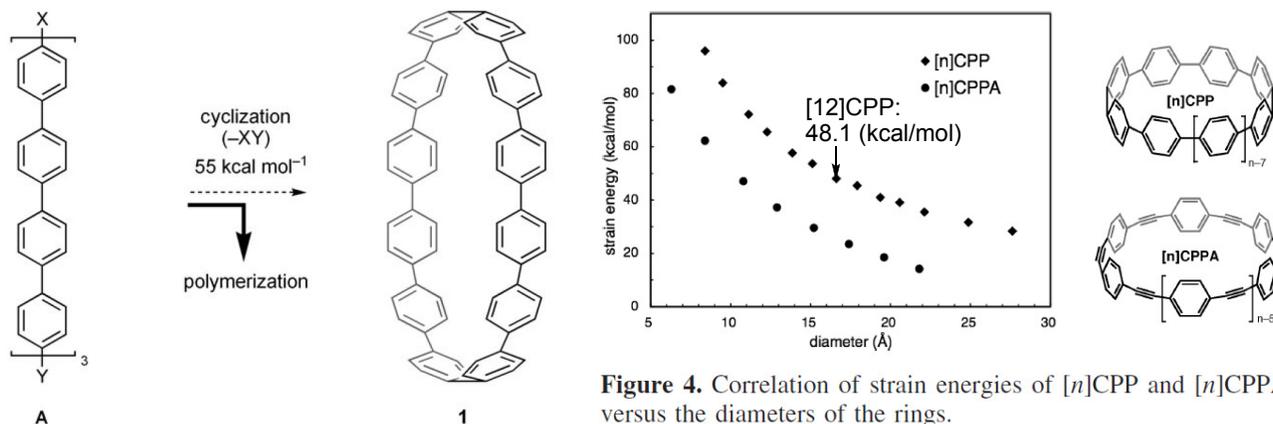To Introduce some **sp^3-carbons** as cyclohexa-1,4-diene moieties, strain energy of aryl ring decreases.

6, 7, or 8

Li$^+$ [naphthalene]$^{\bullet-}$

THF, -78°C

12

e$^-$

13

[9]CPP: **9**, n = 5, 43%
[12]CPP: **10**, n = 8, 52%
[18]CPP: **11**, n = 14, 36%
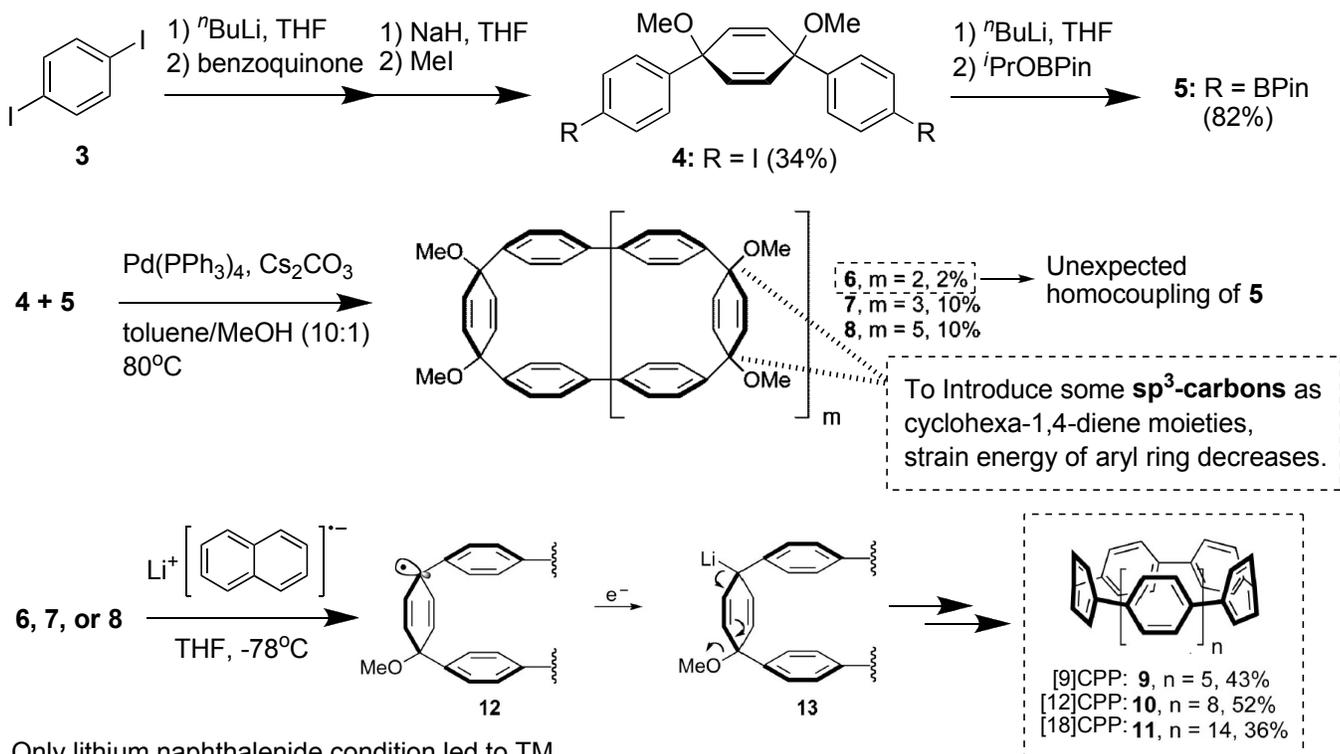
Only lithium naphthalenide condition led to TM.
(Nucleophilic hydride source, Tin(II), and low-valent titanium didn't give good result.)
Structures were determined by ^{1}H-NMR, ^{13}C-NMR, IR, and MALDI-TOF-MS.

Summary of Bertozzi's work
First report of CPP synthesis (0.2 ~ 1.4% overall yield for 5 steps)
Introduced sp^3-carbons to decrease the strain energy
Macrocyclization step is not so satisfying (low yield, no selectivity).

2-3. Synthesis of CPP ~ Prof. Itami's work

(1) Selective synthesis of [12]CPP   Itami K. *et al. Angew. Chem. Int. Ed.* **2009**, *48*, 6112

Itami's strategy

Linear oligoarenes (**A**) cannot be cyclized due to the big strain energy (~55 kcal/mol).

By introducing **cyclohexane moieties**, strain energy decreases to **5 kcal/mol !**
→ Cyclization occurs more easily.

cis-**2** (48%)
(*cis/trans*=81/19)

MOMCl, *i*Pr₂NEt, CH₂Cl₂

3 (98%)

(BPin)₂, PdCl₂(dppf), KOAc, DMSO

4 (81%)

3 + **4**
(10eq.)

PdCl₂(dppf) (0.1 eq.)
NaOH (5 eq.),
H₂O (16 eq.),

1,4-dioxane (8mM)
60°C, 24 h

trimer **6** (81%)

cyclic tetramer **7** (Not obtained)

Despite the screening of conditions, their first target (cyclic tetramer **7**) was not obtained in one pot.

trimer 6

4 (1.4 eq.)

Pd(OAc)$_2$ (0.2 eq.)
X-Phos (0.2 eq.)
NaOH (5 eq.)
H$_2$O (26 eq.)

1,4-dioxane (2mM)
80°C, 24 h

cyclic tetramer 7 (51%)

p-TsOH

m-xylene
150°C, μw

[12]CPP (62%)

X-Phos

2 mM is the best concentration.
No other cyclic oligomer was obtained !

By introducing MOM group to only one monomer,
the purification of **6** and **7** was greatly simplified.

Cascade sequence;
1) MOM deprotection
2) eight-fold dehydration
3) oxidation (aromatization)

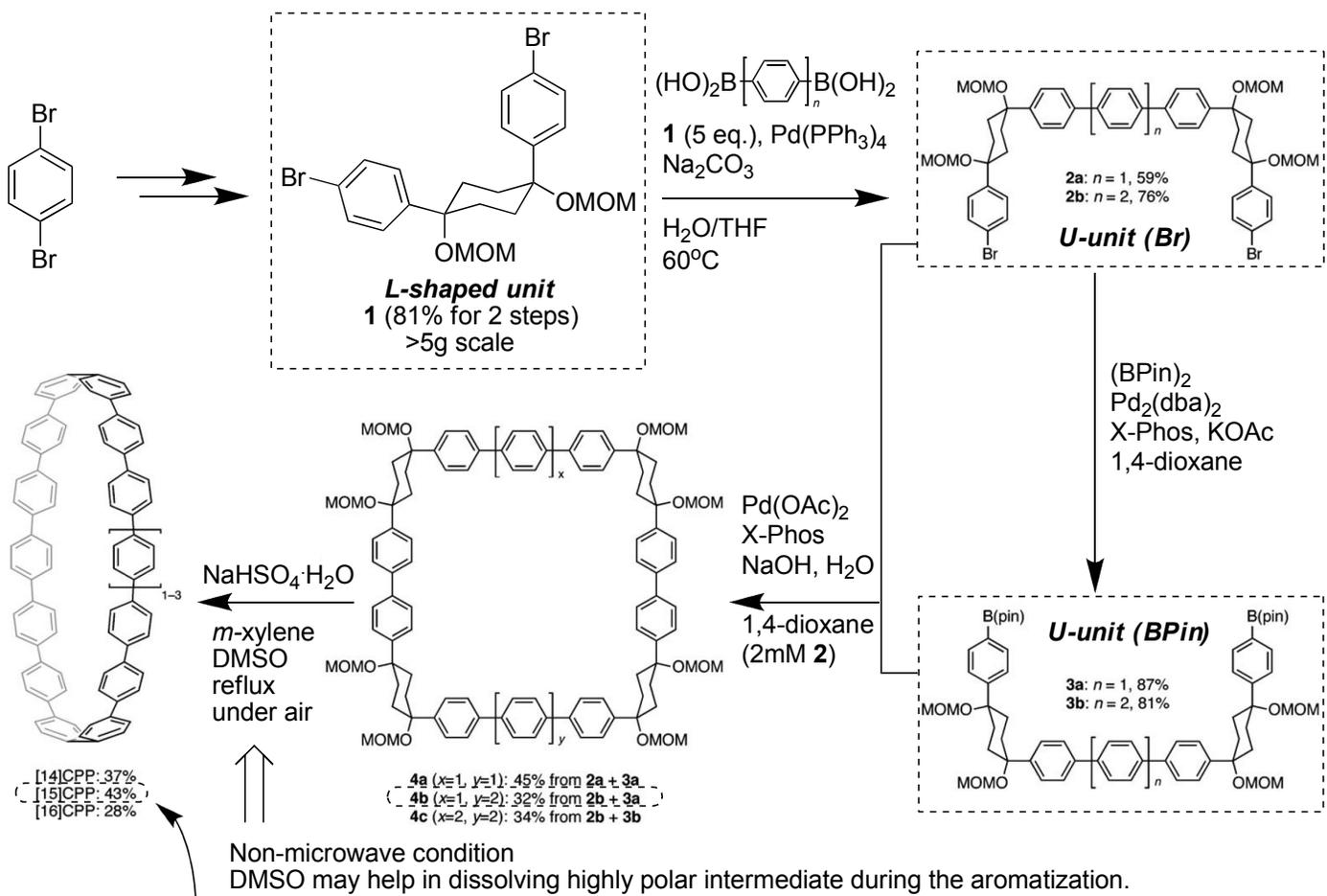## (2) Selective synthesis of [14], [15], [16]CPP   Itami K. *et al. Angew. Chem. Int. Ed.* **2010**, *49*, 10202

New strategy

(1) Synthesis of several U-shaped units (≒ trimer)

(2) Cross-coupling between two U-shaped units

U-Shaped Units

aromatization

[12]CPP
[previous work]

[14]CPP
[this work]

[15]CPP
[this work]

[16]CPP
[this work]

Advantages of this strategy:

(1) **Odd-numbered CPP** can be designed
by using different U-shape units.

(2) It can be a **uniform synthetic strategy** for
[n]CPP (n ≧ 14), as the ring number of
U-shaped units can be easily increased.

L-shaped unit
1 (81% for 2 steps)
>5g scale

$(HO)_2B$—⬡$_n$—$B(OH)_2$
1 (5 eq.), $Pd(PPh_3)_4$
Na_2CO_3

H_2O/THF
60°C

U-unit (Br)
2a: $n = 1$, 59%
2b: $n = 2$, 76%

$(BPin)_2$
$Pd_2(dba)_2$
X-Phos, KOAc
1,4-dioxane

U-unit (BPin)
3a: $n = 1$, 87%
3b: $n = 2$, 81%

$Pd(OAc)_2$
X-Phos
$NaOH$, H_2O
1,4-dioxane
(2mM **2**)

4a ($x=1$, $y=1$): 45% from **2a** + **3a**
4b ($x=1$, $y=2$): 32% from **2b** + **3a**
4c ($x=2$, $y=2$): 34% from **2b** + **3b**

$NaHSO_4 \cdot H_2O$

m-xylene
DMSO
reflux
under air

[14]CPP: 37%
[15]CPP: 43%
[16]CPP: 28%

Non-microwave condition
DMSO may help in dissolving highly polar intermediate during the aromatization.

First selective synthesis of odd-numbered CPP

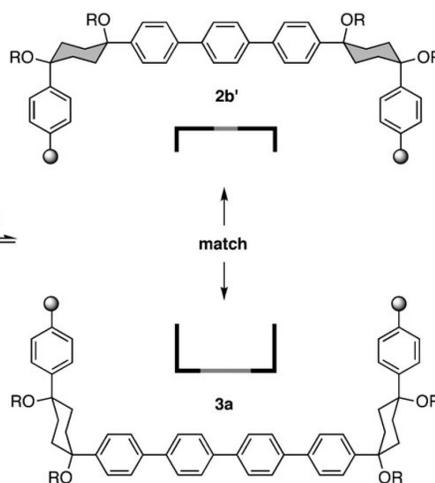Why does hetero-size coupling occur ?

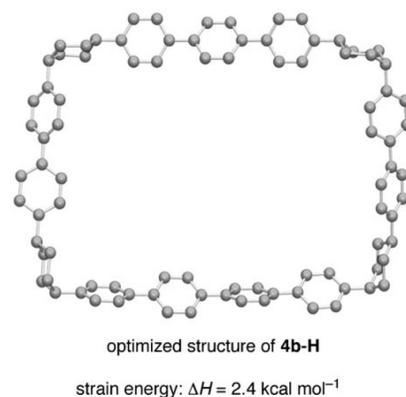"Arch widths" of U-shaped units are different.

⟶ Coupling does not occur.
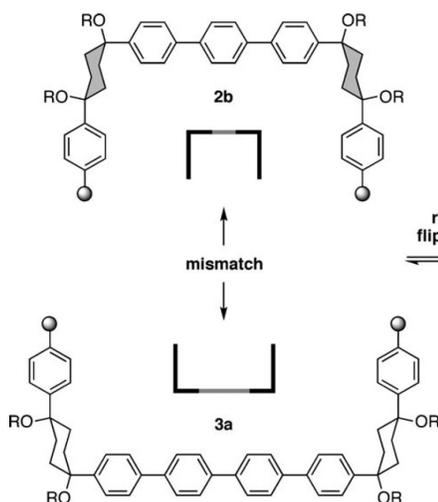
After chair-flipping of one unit,
"arch widths" of two units **nicely match**.

⟶ **"Hetero-size" coupling** does occur !

DFT calculation of **4b** implies the optimized structure matches well with the chair-flipped model.

2b

ring flipping

2b'

mismatch

match

3a

3a

optimized structure of **4b-H**

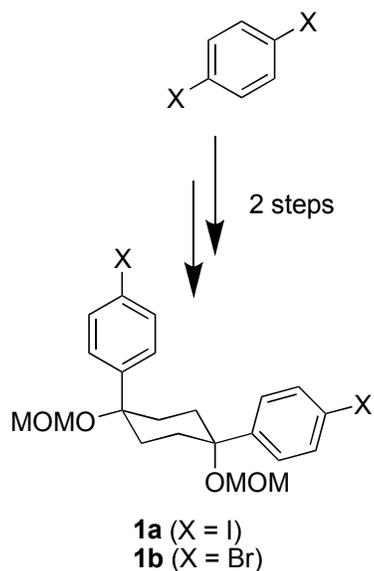strain energy: $\Delta H = 2.4$ kcal mol^{-1}

(3) Concise synthesis of [12]CPP — Itami K. *et al. Angew. Chem. Int. Ed.* **2011**, *50*, 3244

Problems of previous method: (1) Need of 2 monomers
(2) Stepwise macrocyclization
(3) Use of expensive Pd catalyst
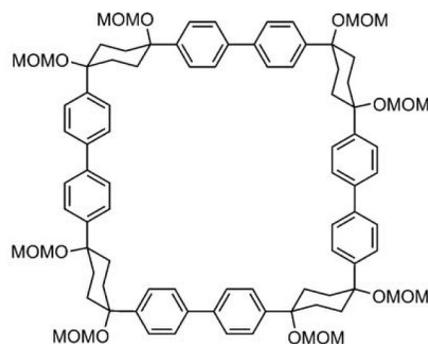(4) Low yield (4-10% overall)

As a solution →

(1) Need of **single monomer**
(2) **1-step** macrocyclization
(3) Use of **Ni** instead of Pd
(4) Higher overall yield

(Nickel mediated biaryl coupling: Too complex mechanism is proposed.
Kochi J. K. *et al. J. Am. Chem. Soc.* **1979**, *101*, 7547)

2 steps

1a (X = I)
1b (X = Br)

*1-step cyclization
from single monomer*

Ni(cod)$_2$ (2.0 eq.)
2,2'-bipyridyl (0.5 eq.)
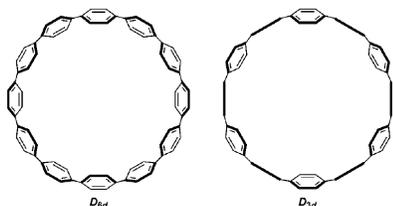COD (only for **1a**, 1.7 eq.)
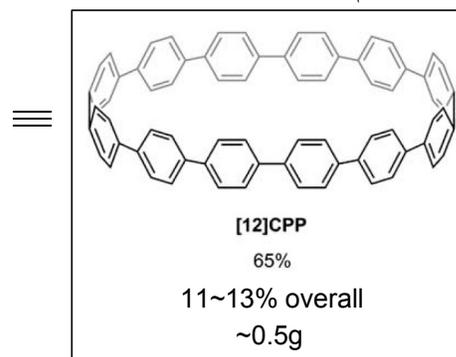
THF (16 mM), 60°C

>5g **2**
27% (from **1a**)
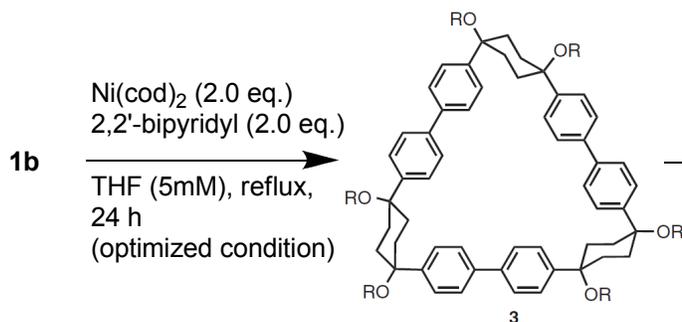22% (from **1b**)

NaHSO$_4$·H$_2$O
m-xylene/DMSO
reflux under air

**First X-ray crystal structure
of [12]CPP·(Cy)$_2$**
from CHCl$_3$/cyclohexane

D_{6d} D_{3d}

This x-ray structure is closer to D_{3d} form which has higher energy
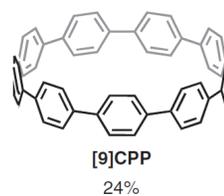(by 3.7 kcal/mol) than most stable D_{6d} form, indicated by DFT calculation.

≡

[12]CPP
65%
11~13% overall
~0.5g

In the macrocyclization step, cyclic trimer (**3**) was also obtained, which can be transformed to [9]CPP.

Itami K. *et al. Chem. Lett.* **2011**, *40*, 423

1b

Ni(cod)$_2$ (2.0 eq.)
2,2'-bipyridyl (2.0 eq.)

THF (5mM), reflux,
24 h
(optimized condition)
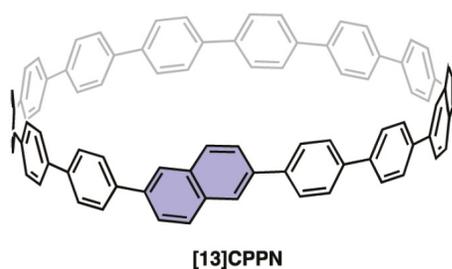
R = MOM
3 (32%), **2** (23%)

[9]CPP
24%

**X-ray crystal structure
of [9]CPP·(thf)$_2$**

14
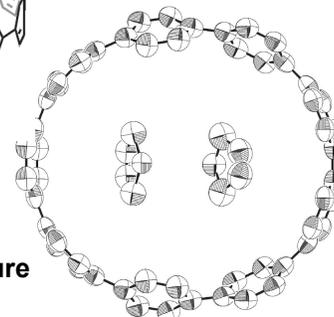
(4) Synthesis of [13]CPPN

Itami K. *et al. Org. Lett.* **2011**, *13*, 2480

[13]CPPN

CPPN is a **potential template of an [*n+2, n+1*]SWNT** (chiral CN).
They supposed their synthetic methodology of CPP can be applied to CPPN synthesis.

Shortest Sidewall Segments of Armchair and Chiral Carbon Nanotube Structures

Ar	shortest ring	carbon nanotube structure
none	[*n*]Cycloparaphenylene ([*n*]CPP)	armchair carbon nanotube ([*n,n*]SWNT)
	Cyclo[*n*]paraphenylene-2,6-naphthylene ([*n*]CPPN)	chiral carbon nanotube ([*n+2,n+1*]SWNT)
	Cyclo[*n*]paraphenylene-2,6-anthrylene ([*n*]CPPA)	chiral carbon nanotube ([*n+3,n+1*]SWNT)
	Cyclo[*n*]paraphenylene-2,8-tetracenylene ([*n*]CPPT)	chiral carbon nanotube ([*n+4,n+1*]SWNT)

[15,14]SWNT   *Top view of [15,14]SWNT*

According to DFT calculation, racemization energy of [13]CPPN is only 8.4 kcal/mol.
In order to achieve enantioselective synthesis of CPPN, new strategies must be required to avoid racemization.
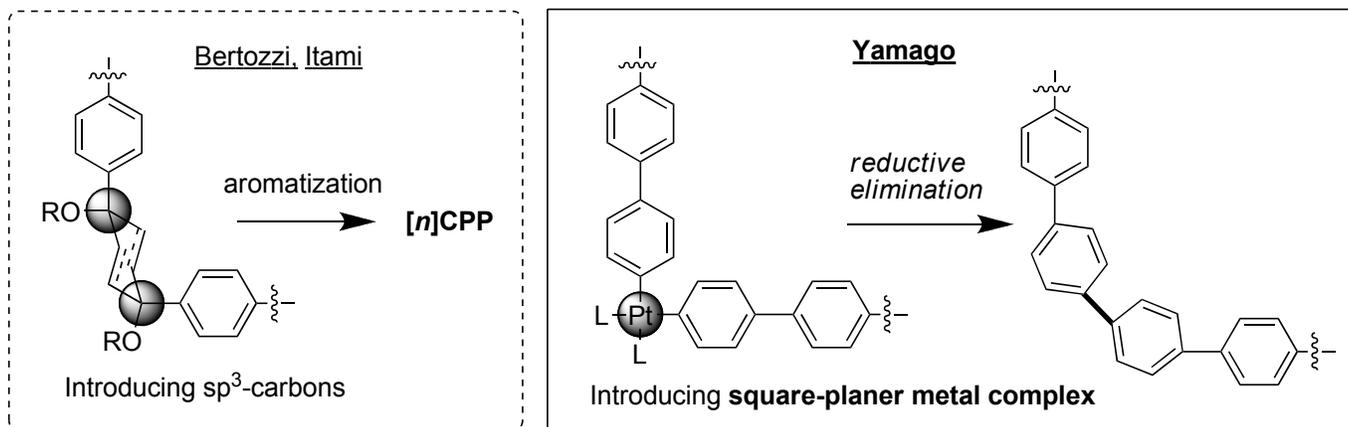
Summary of Itami's work
4~13% overall yield. Introducing **sp³-carbons** like Bertozzi's case
Selective synthesis for *n* = 12, **uniform strategy** for *n* ≧ 14 (14, 15, 16 were reported)
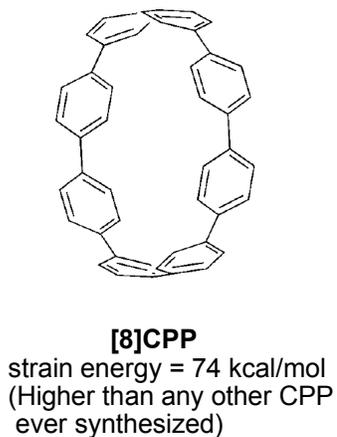Catalytic Pd or stoichiometric Ni (only for *n* =12)
Crystal structure of [12] and [9]CPP
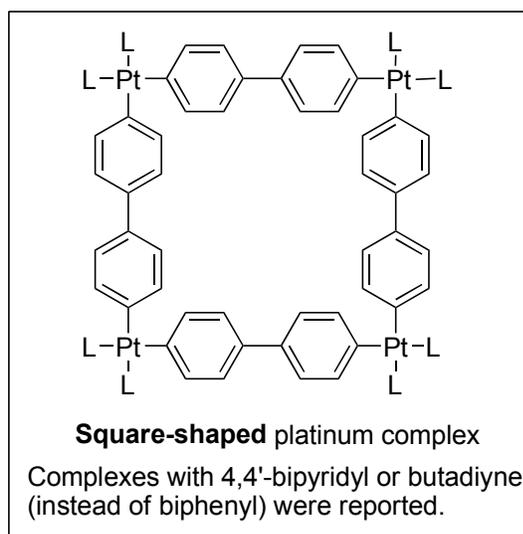
2-4. Synthesis of CPP ~ Prof. Yamago's work

Bertozzi, Itami

RO

aromatization → [*n*]CPP

RO

Introducing sp³-carbons

Yamago

reductive elimination

L−Pt L

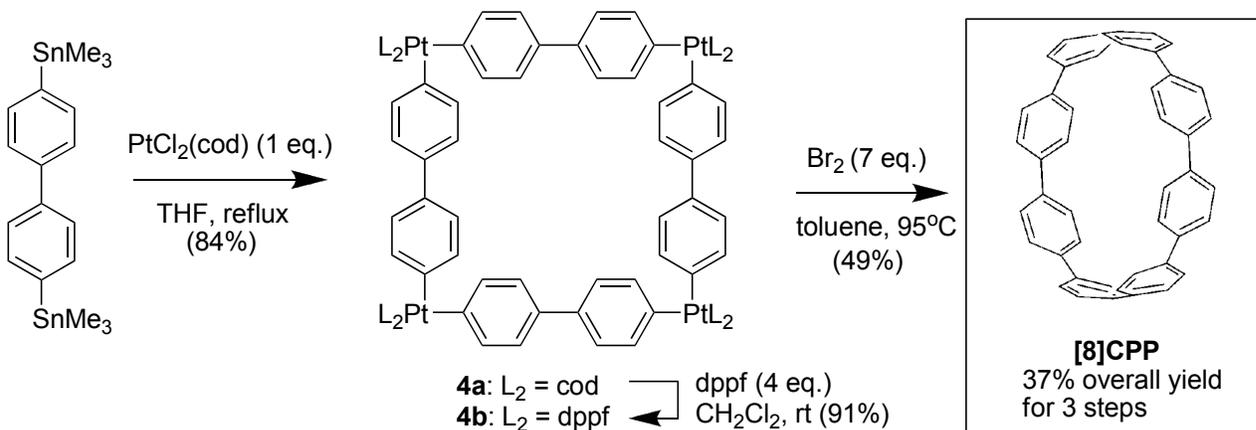Introducing **square-planer metal complex**

(1) Synthesis of [8], [12]CPP

Yamago S. *et al. Angew. Chem. Int. Ed.* **2010**, *49*, 757
Yamago S. *et al. J. Am. Chem. Soc.* **2011**, *133*, 8354

[8]CPP
strain energy = 74 kcal/mol
(Higher than any other CPP
ever synthesized)

reductive elimination ⟹

L−Pt Pt−L

L−Pt Pt−L

Square-shaped platinum complex

Complexes with 4,4'-bipyridyl or butadiyne
(instead of biphenyl) were reported.

Same strategy has already been utilized for [*n*]cyclothiophenes synthesis.
(But cyclothiophenes are almost planer molecules)   *Chem. Commun.* **2003**, *948*

SnMe₃

SnMe₃

PtCl₂(cod) (1 eq.)
→
THF, reflux
(84%)

L₂Pt PtL₂

L₂Pt PtL₂

4a: L₂ = cod ⎤ dppf (4 eq.)
4b: L₂ = dppf ⎦ CH₂Cl₂, rt (91%)

Br₂ (7 eq.)
→
toluene, 95°C
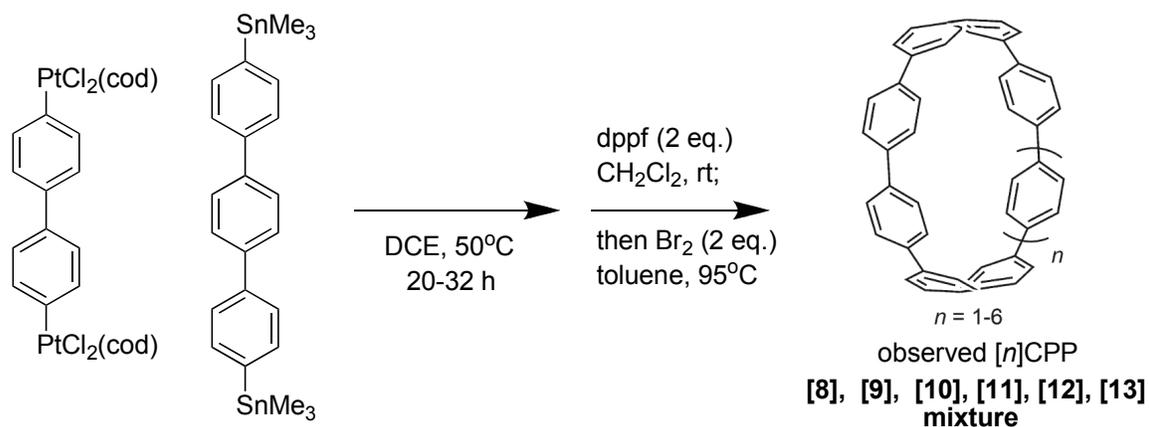(49%)

[8]CPP
37% overall yield
for 3 steps

Ligand effect: dppe, dppp, and xantphos gave only <2% [8]CPP,
even though the corresponding platinum phosphine complexes were obtained.
Reductive elimination: addition of iodine, triphenyl phosphine or additive-free condition didn't lead to good result.
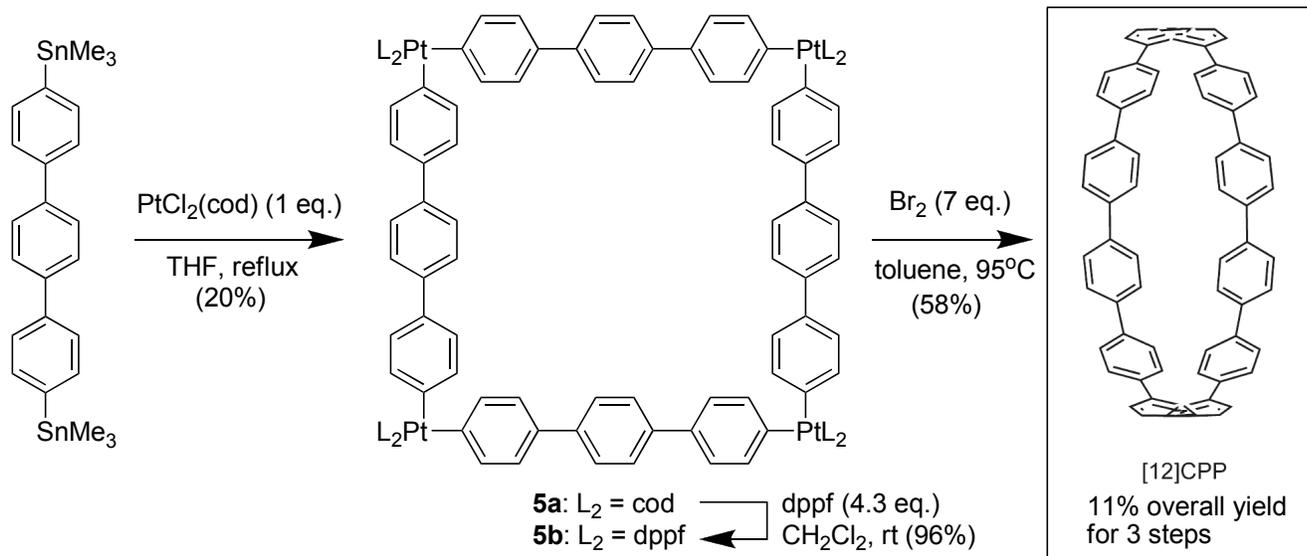
(2) Random synthesis of [*n*]CPP (*n* = 8 ~ 13)

They first expected the selective synthesis of [10]CPP, but as a result mixture of six [*n*]CPPs were obtained. This must be because the equilibrium during transmetallation and/or ligand exchange reaction.

Summary of Yamago's work
~ 37% overall yield (**highest**) for 3 steps (**shortest**)
Using **square-planer metal complex** to reduce the strain effect
Selective synthesis for only **[4*m*]CPP** (*m* = 2, 3 are reported.)
**Smallest numbered [*n*]CPP** synthesis ([8]CPP)

2-5. Elongation ~ Diels-Alder strategy

Bertozzi C. R. *et al. Chem. Phys. Lett.* **2010**, *494*, 1
Scott L. T. *et al. Polycycl. Aromat. Comp.* **2010**, *30*, 247

template   elonged template
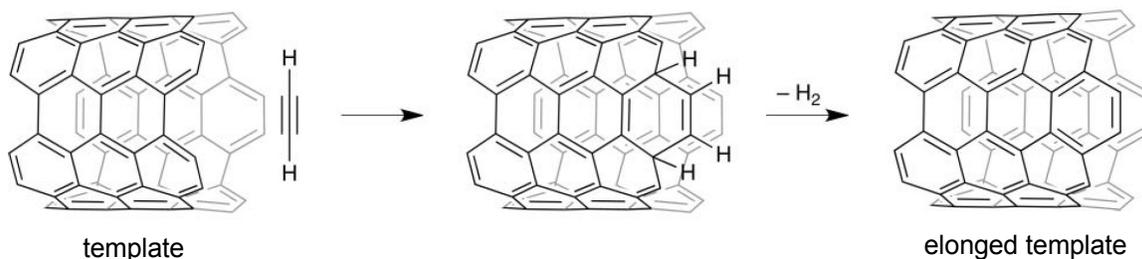
As additional carbon sources, acetylene (or its derivative) is used.
Repetitive 2-step cascade (bay region Diels-Alder and dehydrogenation) will lead to armchair (or chiral) CNs.

Advantages: [*n*]CPP or its derivatives are possible candidates of this substrate.
1 mg of a template grown to 1 mm long CNs would produce over 1 ton of CNs.
Ideally, no oxidant is required for dehydrogenation step because it's highly exothermic.
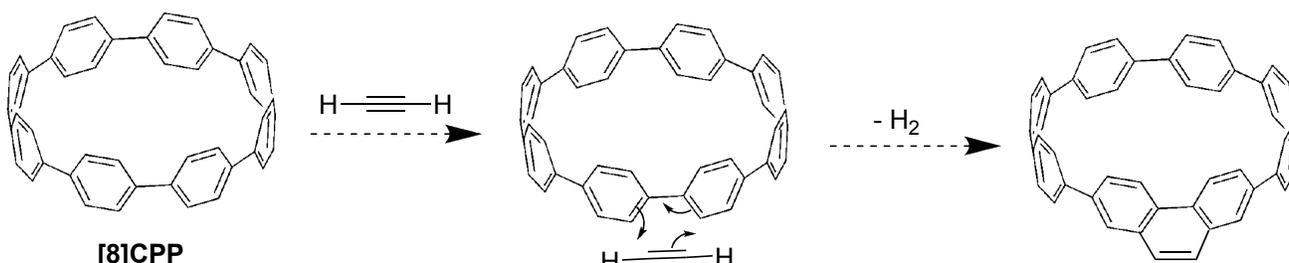
[8]CPP
Disadvantages: Zigzag nanotubes cannot be constructed.
Both acetylene and poryarene are not so reactive for Diels-Alder reaction.
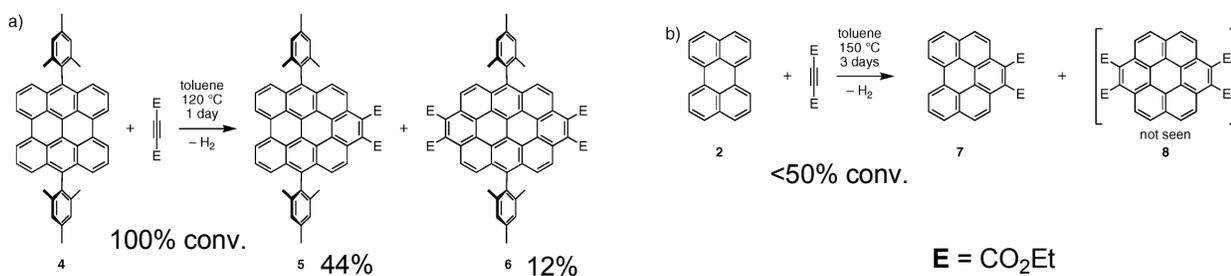
Reactivity of polyarenes   Scott L. T. *et al. J. Am. Chem. Soc.* **2009**, *131*, 16006
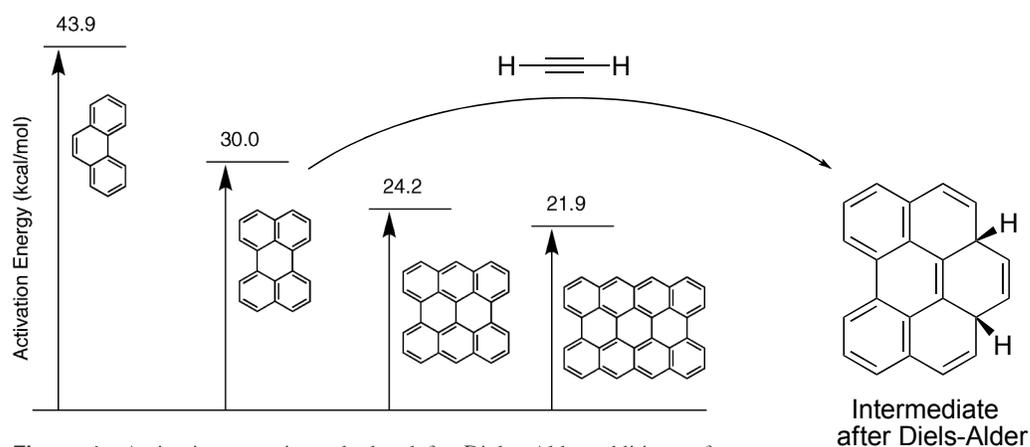
Figure 1. Activation energies calculated for Diels−Alder additions of acetylene to aromatic hydrocarbon bay regions (B3LYP/6-31G*).

They expected the [4+2] reactivity of polyarenes are related to **how low the activation energy is**.
As the number of benzene rings is increased, aromaticity is not so decreased even in the intermediate.

a)

toluene
120 °C
1 day
− H₂

4 100% conv.

5 44%   **6** 12%

b)

toluene
150 °C
3 days
− H₂

2 <50% conv.

7   +   [not seen **8**]

E = CO₂Et
Mesityl group is introduced both
to avoid the internal cycloaddition
and to increase the solubility.

It is confirmed **4** is much reactive
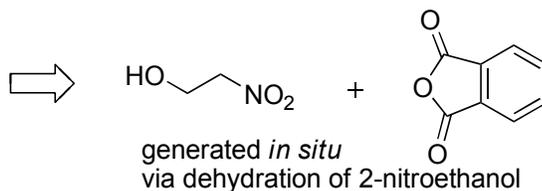for bay region Diels-Alder than **2**.

EtO₂C══CO₂Et

toluene, 100 °C, 22 h
− H₂

CO₂Et
CO₂Et

+   recovered
unchanged
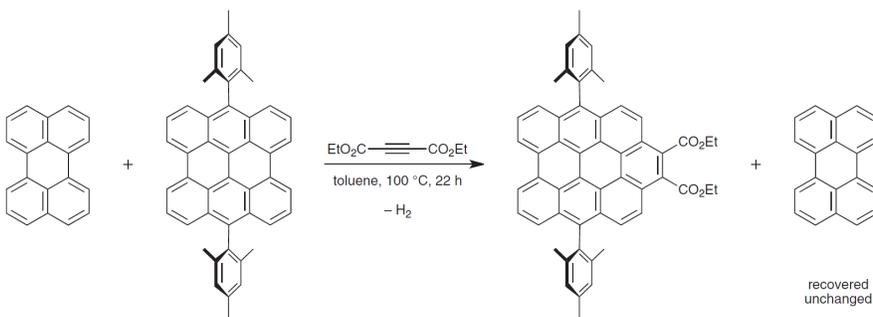
Promising example using nitroethylene   Scott L. T. *et al. Angew. Chem. Int. Ed.* **2010**, *49*, 6626
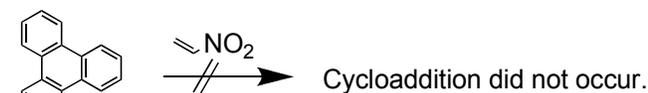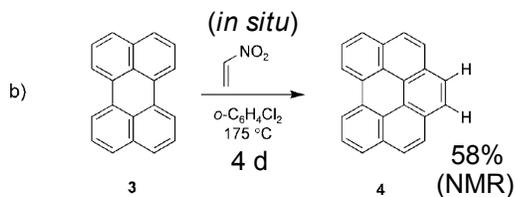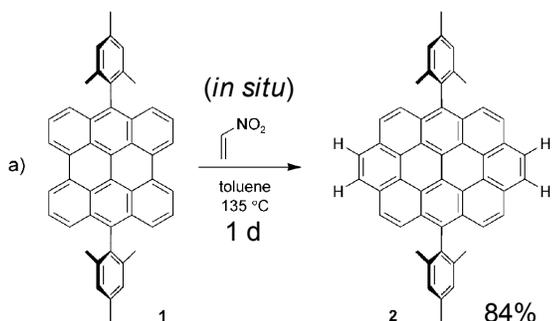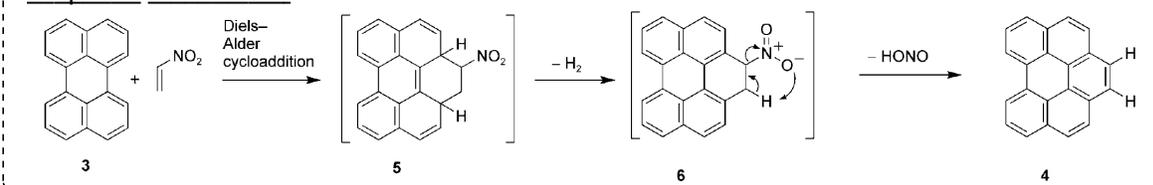
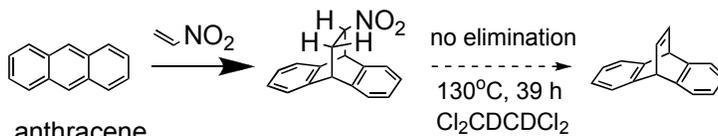In order to achieve cycloaddition/rearomatization sequence...

H──≡──H   Poorly reactive   EtO₂C──≡──CO₂Et   Reactive but need decarboxylation

nitroethylene
Reactive dienophile
"masked acetylene"

⇒   HO⌒NO₂   +   phthalic anhydride

generated *in situ*
via dehydration of 2-nitroethanol

Proposed mechanism:

Diels–
Alder
cycloaddition

3   NO₂ →   **5**   − H₂ →   **6**   − HONO →   **4**

a)

(*in situ*)
⌒NO₂

toluene
135 °C
1 d

1   **2** 84%

b)

(*in situ*)
⌒NO₂

o-C₆H₄Cl₂
175 °C
4 d

3   **4** 58% (NMR)

triphenylene   ⇝NO₂ ╱╱→   Cycloaddition did not occur.

Reactivity: **1** > **3** > triphenylene

anthracene   ⇝NO₂ →   (adduct)   no elimination
130 °C, 39 h
Cl₂CDCDCl₂

HONO elimination requires nitrogroup on benzylic position.

The auther says,
"Diels-Alder cycloadditions of CPP are expected to be **difficult**"
due to the strain effect and electronic consideration.

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3. __Summary__

Introduction __~__ __suffering__ __problems:__
  Carbon nanotubes have a lot of interesting potentials such as unique electrical and physical properties.
  Numerous kinds of industrial applications are being developed today.
  A problematic point lies in the absence of methodology to obtain chirality-pure carbon nanotubes,
and "bottom-up" organic synthesis approach may become one of the solutions for this point.

Template __synthesis:__
  Three groups have reported the synthesis of cycloparaphenylene (CPP).
  They utilized either introduction of sp^3-carbons or square-planer metal complex as an intermediate,
in order to reduce the strain energy.
  They could synthesize [n]CPP ($n \geqq 8$), but there has been no success for much smaller CPP synthesis.
  Perhaps, different methodologies should be prefered for narrower carbon nanotube synthesis.

Elongation __methods:__
  Diels-Alder strategy seems to be promissing, but no successful data were obtained in the case of cycloarene.
  Problems lie in poor reactivity and strain effect of CPP.
  Higher consideration must be required to achieve the great goal of carbon nanotube synthesis.