Ultimate goal of π-extended molecules is application for **nano devices**

1. efficient electronic interactions between individual segments
2. efficient energy transfer
3. uniform molecular structure (uniform property)
4. robust and stable structure
5. easy to process (solubility, toxicity, reactivity)
6. mass production

**Moore's law** – the number of transistors in a dense integrated circuit doubles approximately every two years.

**Hückel system**

- Planar?
- Planar?

**π molecules = Flat**

- aromatic
- nonaromatic
- reverse in Möbius system

- nonaromatic
- antiaromatic

- Will not cover...

- corrole
- corrin (GM; Tian, 2016)
- Phthalocyanine
- BODIPY
- supramolecules

- catenane (GM; Ishibara, 2010)
- rotaxane
- polymer
- multi wall nanotubes
- carbon nanohorn
- fullerene isomers
- oligothiophene

Harold Kroto passed away 30 Apr. 2016

1996
Harold Walter Kroto
Richard Errett Smalley
Robert Floyd Curl

2010
Andre Konstantin Geim
Konstantin Sergeevich Novoselov
Chemistry of \( \pi \)-extended Molecules

Rothemund Synthesis
1. cat. HCOOH
2. Chloranil
~10% yield after 2-3 column

\[ \text{Porphyrin} \]


\[ \text{selected examples of hetero-porphyrins} \]


JACS. 1936, 58, 625.

\[ \text{OPRD. 2003, 7, 799.} \]

\[ \text{MeLi} \]

\[ \text{Cu(OAc)}_2 \]

\[ \text{NiCl}_2, \text{PPh}_3 \]

\[ \text{Mes} \]

\[ \text{Zn} \]

\[ \text{X} = \text{Cl} \]

\[ \text{Mes} \]

\[ \text{PPh}_3 \]

\[ \text{ACIE. 2012, 51, 8542.} \]

\[ \text{Inorg. Chem. 2002, 51, 12879.} \]

\[ \text{Chem. Eur. J. 2012, 18, 16129.} \]

\[ \text{me} \]

\[ \text{16\pi} \]

\[ \text{Me} \]

\[ \text{1.47 ppm} \]

\[ \text{1.57 ppm} \]

\[ \text{X} = \text{Br} \]

\[ \text{NiCl}_2, \text{PPh}_3 \]

\[ \text{Zn} \]

\[ \text{X} = \text{Cl} \]

\[ \text{Na}_2\text{S•9H}_2\text{O} \]

\[ \text{PPh}_3 \]

\[ \text{ACIE. 2012, 51, 8542.} \]

\[ \text{Inorg. Chem. 2002, 51, 12879.} \]

\[ \text{Chem. Eur. J. 2012, 18, 16129.} \]

\[ \text{nonaromatic} \]

\[ \text{aromatic} \]

\[ \text{taking advantage of antiaromaticity} \]

\[ \text{TMS} \]

\[ \text{Mel} \]

\[ \text{TMS} \]

\[ \text{TMS} \]

\[ \text{H} \]

\[ \text{O} \]

\[ \text{1. Li; H}_2\text{SiCl}_2 \]

\[ \text{2. CHBr}_3 \]

\[ \text{K}_{\text{C}_8} \]

\[ \text{Ni(II)-norcorrole} \]

toluene, rt, 30 min 97% ✓ norcorrole (antiaram) x porphyrin (arm)

\[ \text{JACS. 1999, 121, 9722.} \]

\[ \text{Li, Na} \]

\[ \text{THF} \]

\[ \text{82%} \]

\[ \text{Ni/OAc}_2 \]

\[ \text{OPRD. 2003, 7, 799.} \]

\[ \text{Me} \]

\[ \text{Bu} \]

\[ \text{JACS. 2004, 126, 9993.} \]

\[ \text{ACIE. 2014, 53, 1506.} \]

\[ \text{H} \]

\[ \text{Ar} \]

\[ \text{Ar} \]

\[ \text{Ar} \]

\[ \text{Ar} \]

\[ \text{Ar} \]

\[ \text{Ar} \]

\[ \text{C}_{65536}\text{H}_{3970}\text{N}_{4096}\text{Zn}_{1024} (M = 1,061,658) \]

non detectable by MALDI-TOF


\[ \text{MeLi} \]

\[ \text{TMS} \]

\[ \text{Si} \]

\[ \text{TMS} \]

\[ \text{TMS} \]

\[ \text{TMS} \]

\[ \text{Ar} \]

\[ \text{Ar} \]

\[ \text{Ar} \]

\[ \text{Ar} \]

\[ \text{Ar} \]

\[ \text{12} \]

\[ \text{Science 2001, 293, 79.} \]

\[ \text{J. Phys. Chem. A, 2003, 107, 8792.} \]

\[ \text{X} \]

\[ \text{Si} \]

\[ \text{TMS} \]

\[ \text{TMS} \]

\[ \text{TMS} \]

\[ \text{TMS} \]

\[ \text{TMS} \]

\[ \text{TMS} \]

\[ \text{TMS} \]

\[ \text{TMS} \]

\[ \text{Ar} \]

\[ \text{Ar} \]

\[ \text{Ar} \]

\[ \text{Ar} \]

\[ \text{z} \]

\[ \text{12} \]

\[ \text{Science 2001, 293, 79.} \]

\[ \text{J. Phys. Chem. A, 2003, 107, 8792.} \]
highly twisted and fully conjugated system; *JACS*, 2015, 137, 142


**Möbius aromaticity:** *TL*, 1964, 29, 1923.

Möbius strip
- A surface with only one side and only one boundary.

Möbius product

Planar Möbius aromaticity; *Nat. Commun.*, 2014, 5, 3265

breaking aromaticity; *JACS*, 1975, 97, 6175.

**Möbius anti-aromaticity (30π)** stable @rt
*ACIE*. 2010, 49, 4950.

**Möbius aromatic (28π)** stable w/o metal @rt
*JACS*. 2009, 131, 7240.

**Planar Möbius aromaticity;**


**Möbius anti-aromatic (30π)** stable @rt
*ACIE*. 2010, 49, 4950.

**Möbius aromatic (28π)** stable w/o metal @rt
*JACS*. 2009, 131, 7240.
Chemistry of π-extended Molecules

Yuzuru Kanda

0D carbon material: Fullerene
– the largest particle possessing wave-particle duality
  total synthesis (7) of C_{60}; Science 2002, 295, 1500.

Name reactions in fullerene
– Bingel reaction
  \[
  C_{60} + \text{EtO} \rightarrow C_{60}
  \]
– Prato reaction
  \[
  C_{60} + \text{Ar}
  \]


– retro [2+2+2]
  \[
  C_{60} \rightarrow \text{Ar}
  \]

Baran lab Group Meeting
5/7/16

NMNO

H_{2}O

H_{2}O

H_{2}O

120 °C
90-95%
36 h
9,000 atm quant

X-ray was taken as
(Ni-porphyrin)_{2}H_{2}O@C_{60}
recent example; 2H_{2}O@C_{70}

kg-scale synthesis of corannulene; OPRD, 2012, 16, 664.
Chemistry of \(\pi\)-extended Molecules

Yuzuru Kanda

bent aromatics: \([n.n']\)Paracyclophane

to close the ring...

RCM
McMurry
Ramberg-Bäcklund
Wittig

1. \((\text{MeO})_2\text{CHBF}_4\)
2. KO\text{tBu}

1. \((\text{MeO})_2\text{CHBF}_4\)
2. KO\text{tBu}; DDQ

the smallest model for CNT

JOC. 2003, 68, 2089.

interesting reactivity of cyclophane

shorter N-C bond

through-bond interaction

not yet made!!!
(calc. predicted impossible)

cyclophane closure in total synthesis

TBAF, MS 3 Å;
Ac\text{O}, Et\text{3N}, DMAP

[2.2]\Paracyclophane as a chiral auxiliary; JOC. 1991, 56, 5672.

fijiolide A

JACS, 2015, 137, 11278

inverse electron demand D.A.
N,N-diethylniline

Rawal's intermediate
8 steps (15.8%)  

closure in total synthesis

45% for 3 steps

DMSO, 85°C

single atropisomer

JACS. 2002, 124, 583.

No isolated atropisomer

33% octahedrane

[5-5-3-5-5-5-5-3-5-5] fused ring system

Rawal's intermediate
8 steps (15.8%)  

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JACS. 2002, 124, 583.

No isolated atropisomer

33% octahedrane

[5-5-3-5-5-5-5-3-5-5] fused ring system

Rawal's intermediate
8 steps (15.8%)  

1. tBuLi; MgBr$_2$•Et$_2$O; PPh$_2$(O)Cl$
2. Br, triglyme, 230 °C

1/1 = S.M. + desired


1D carbon material: Carbon nanotube (SWNT)

1. Et$_3$SiCl, Et$_3$N
2. TBAF

> 99%ee


Kinetic resolution of peroxides;

Inseparable

Chiral boronic acid containing cyclopropane: *JACS*. 2003, 125, 7198.

approach towards the synthesis of uniform CNTs
1. armchair CNT

- Bertozzi's strategy; JACS. 2008, 130, 17646.
  - Ar-I
  - Pd(PPh₃)₄
  - Cs₂CO₃
  - toluene/MeOH
  - nBuLi (PrO)Bpin
  - LiNaph
  - e⁻

- Includes at least one homo coupling separable by column

- m = 2, 2%
m = 3, 10%
m = 5, 10%

- m = 4, 43%
m = 7, 52%
m = 13, 36%

1.². Itami's strategy; ACIE. 2011, 50, 3244.

- MOMO
  - Ni(cod)₂
  - bpy
  - NaHSO₄, air
  - m-xylene
  - DMSO
  - 65%
  - 6 isomers

- PPh₃
  - 94%

1.³. Yamago's strategy; ACIE. 2010, 49, 757.

- SnMe₃
  - PtCl₂(cod)
  - 57%
  - 3 steps
  - 13% yield

- SnMe₃
  - L₂Pt
  - L = cod
  - 91%

- SnMe₃
  - L₂Pt
  - L = dppf
  - 25% yield

- SnMe₃
  - L₂Pt
  - L = cod
  - 91%

- SnMe₃
  - L₂Pt
  - L = dppf
  - 25% yield

- SnMe₃
  - L₂Pt
  - L = cod
  - 91%

- SnMe₃
  - L₂Pt
  - L = dppf
  - 25% yield

smaller ring size
=> narrower HOMO-LUMO gap
[5]CPP has smaller gap than OPP

small ring-size CPPs exhibits strong polyene like character

- CPP

2. chiral CNT; Nat. Commun. 2011, 2:492

- X
  - Br
  - X = Bpin

- Miyaura borylation
  - 91%

- [5]CPP
  - has smaller gap than OPP
  - small ring-size CPPs exhibits strong polyene like character

3. zigzag CNT: ???

- [8]CPP
  - 1. NaNO₂
  - HCl
  - 2. H₂SO₄
  - 49%
  - 3 steps
  - 25% yield

- [5]CPP
  - Y39,000/ 20 mg

- [12]CPP
  - $1209.00/ 10 mg

- cycloacene
  - (not yet made!!!)

- JACs. 2011, 133, 8354.
Yuzuru Kanda

Chemistry of \( \pi \)-extended Molecules

Graphene, 2D molecules

Helicenes: the first helicene was synthesized by R. Weitzenbock in 1918

Chiral resolution; JACS. 1955, 77, 3420. JACS. 1956, 78, 4765.

(dearomatized to increase reactivity)


synthetic application JACS. 2010, 132, 4536.

3D carbon material: diamond, carbon nanohorn, junction of CNTs etc...

Stella BPM 37093
80,000 times heavier than the earth

nano-particle fluorescent
low toxicity
high stability

ND support synthesis:

other examples

pushing the synthetic limit... ACIE, 2005, 44, 6348.