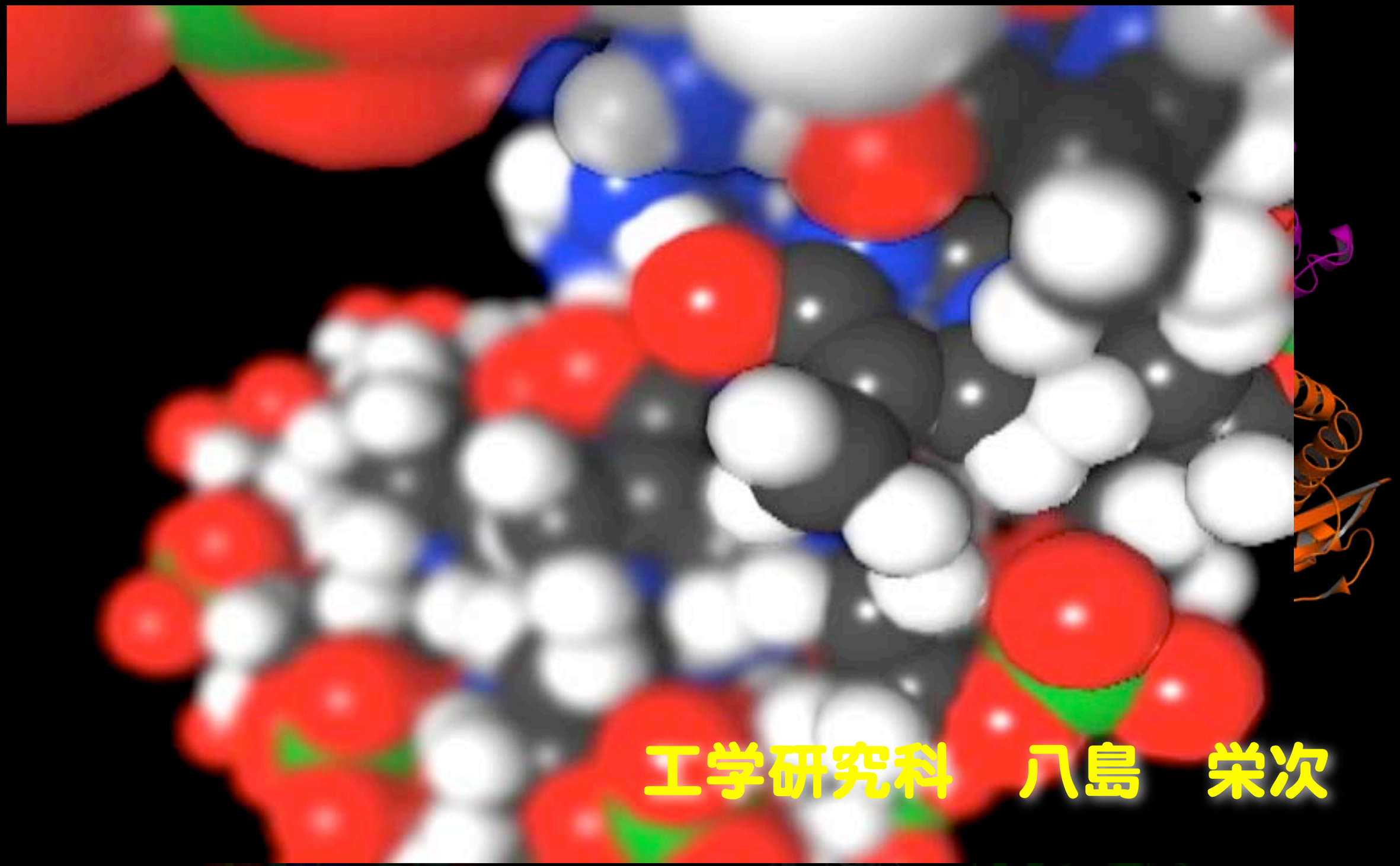
DNAは何故右巻きか？　化学からのアプローチ

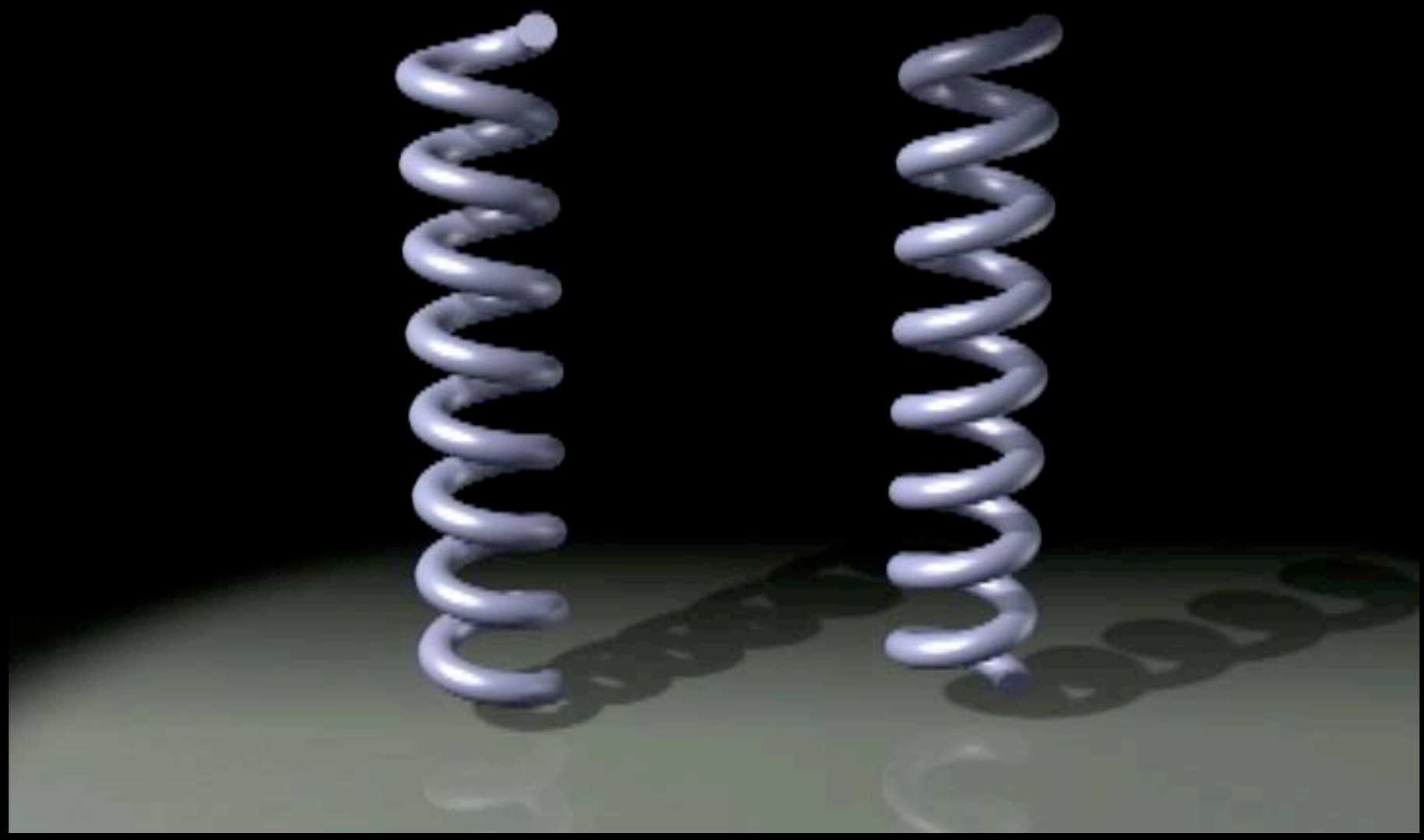


工学研究科　八島　栄次

Watson & Crick 1953

Pauling 1951

右巻きと左巻き：キラルな分子（鏡像体）

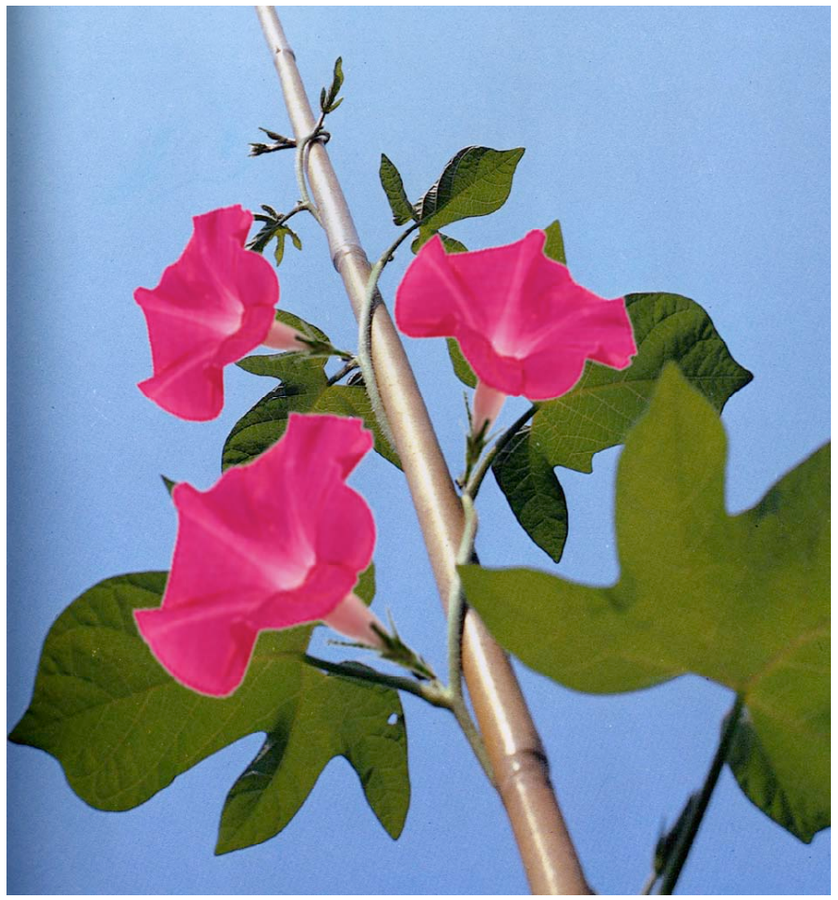


Right-handed Left-handed Right-handed Helix

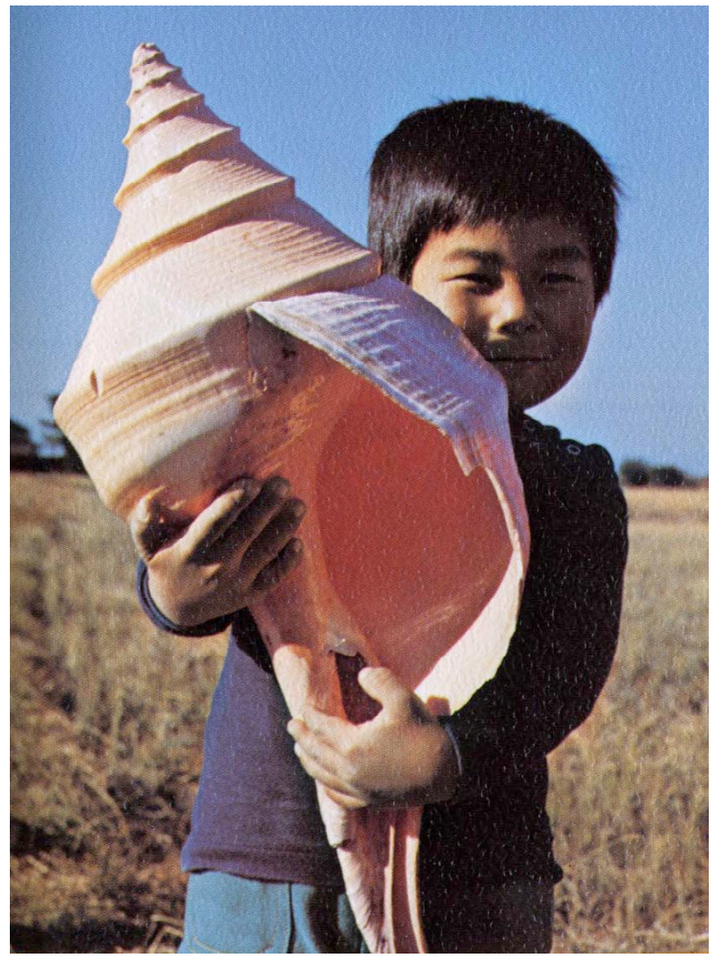
自然界にある”らせん”

Lady’s tresses (Right & Left)

ネジバナ



Morning glory (Right-handed)

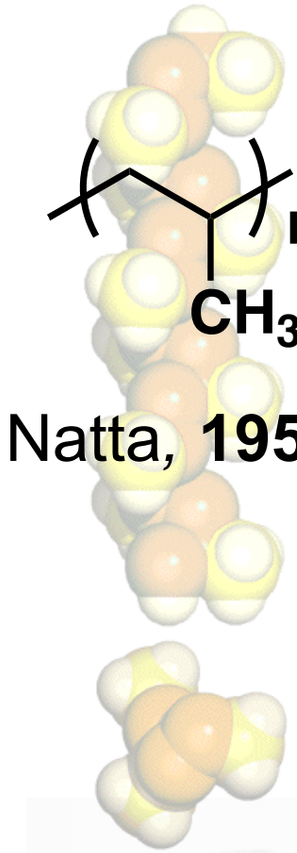


Big sea shell (Right > Left)

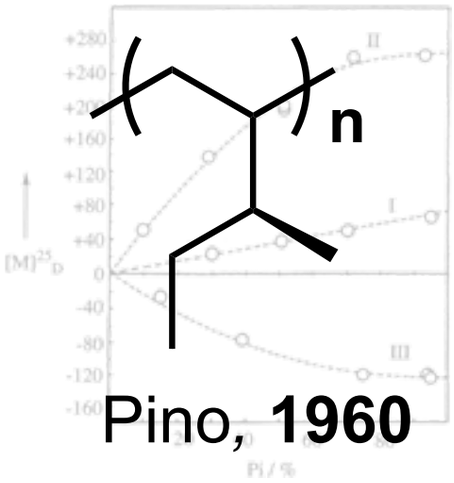
Snails (Right > Left)

講談社　パノラマ図鑑-アサガオ-
朝日新聞社　草木花-歳時記
あかね書房　科学のアルバム-海の貝-

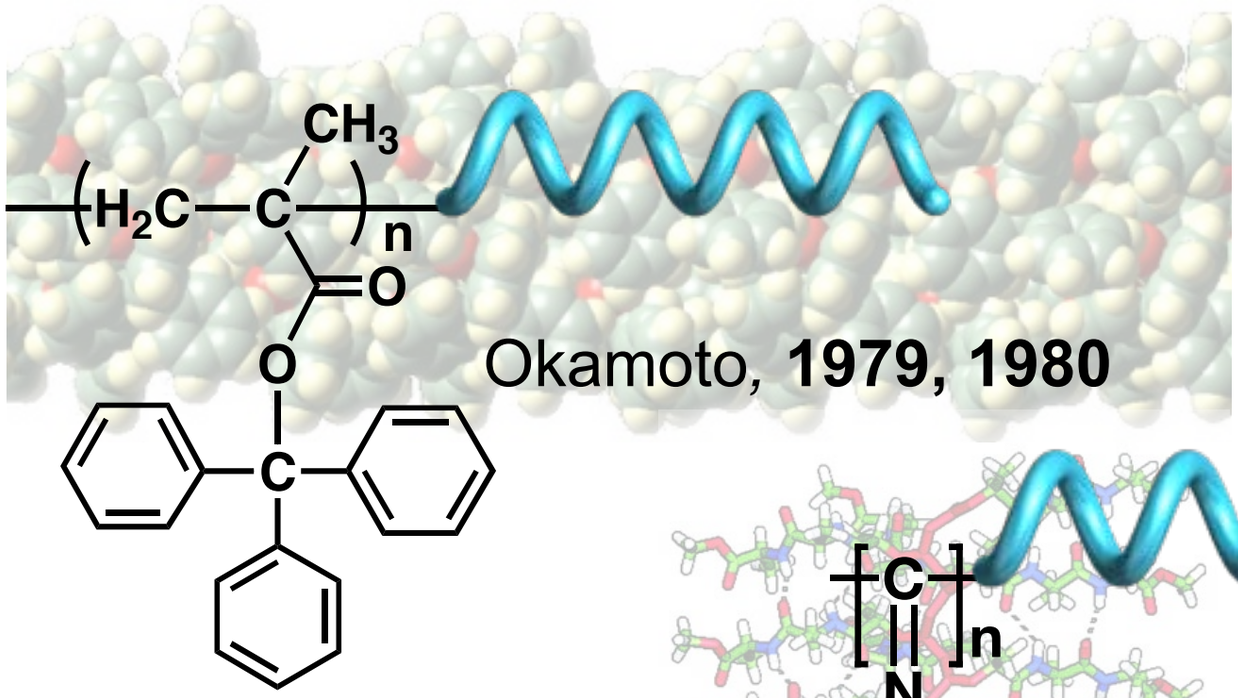
Background of Helical Polymers



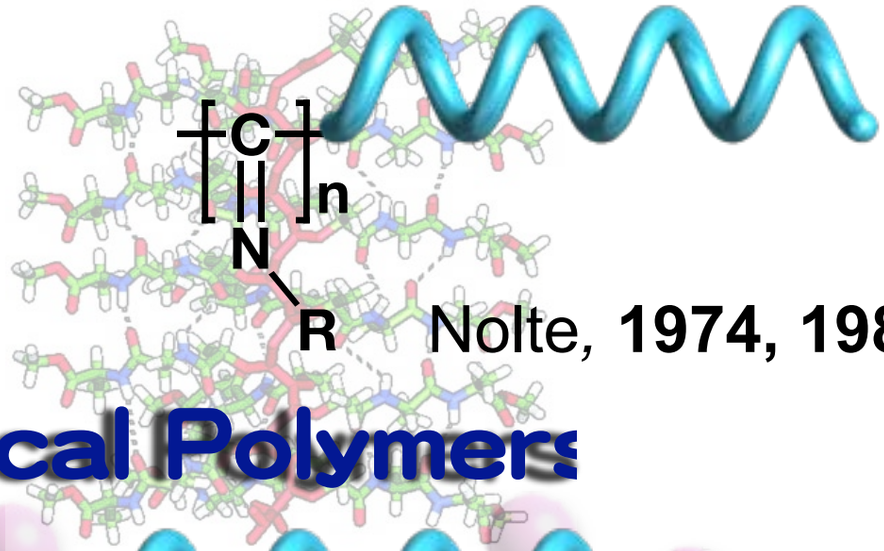
Natta, **1955**



Pino, **1960**

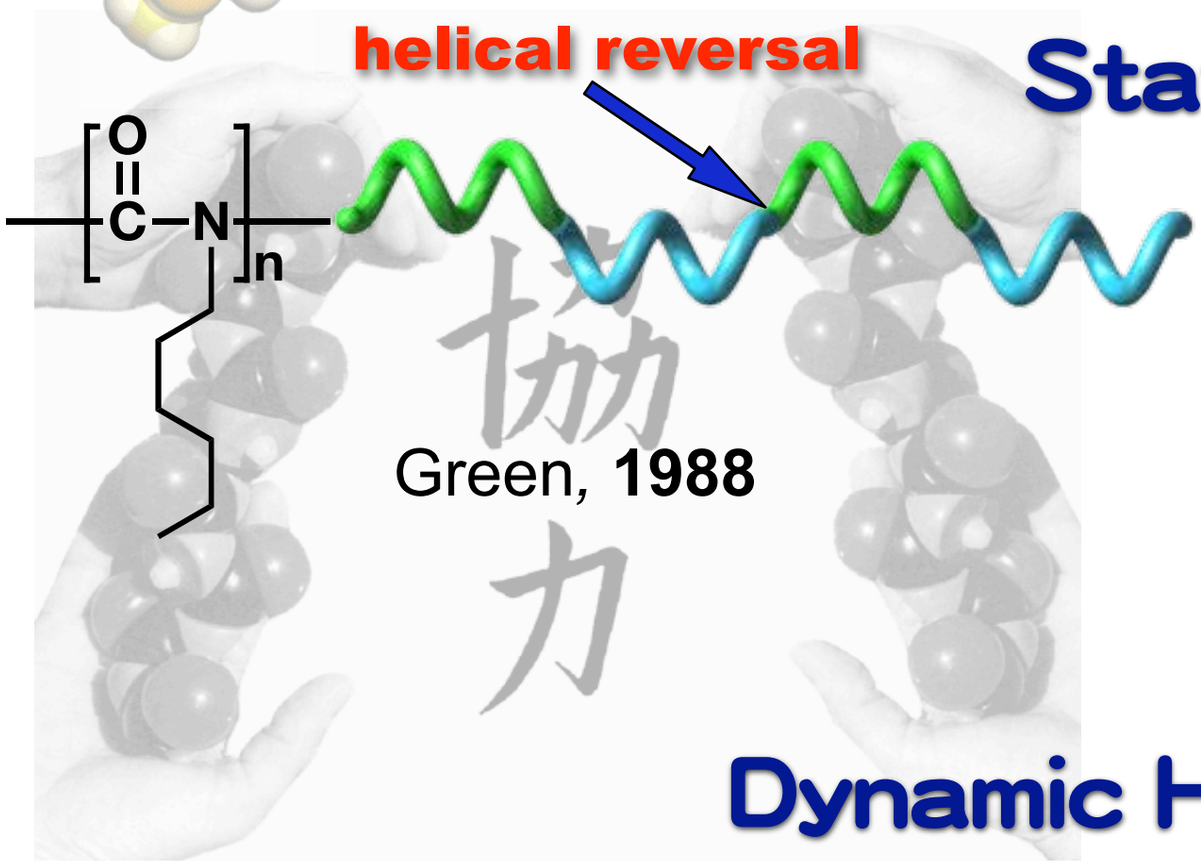


Okamoto, **1979, 1980**

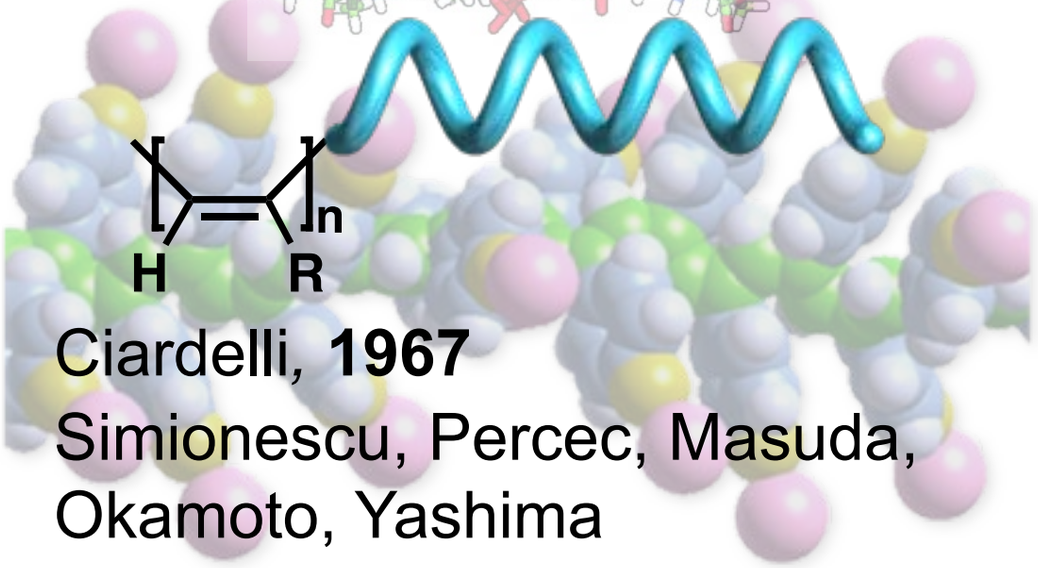


Nolte, **1974, 1986**

Static Helical Polymers



Green, **1988**

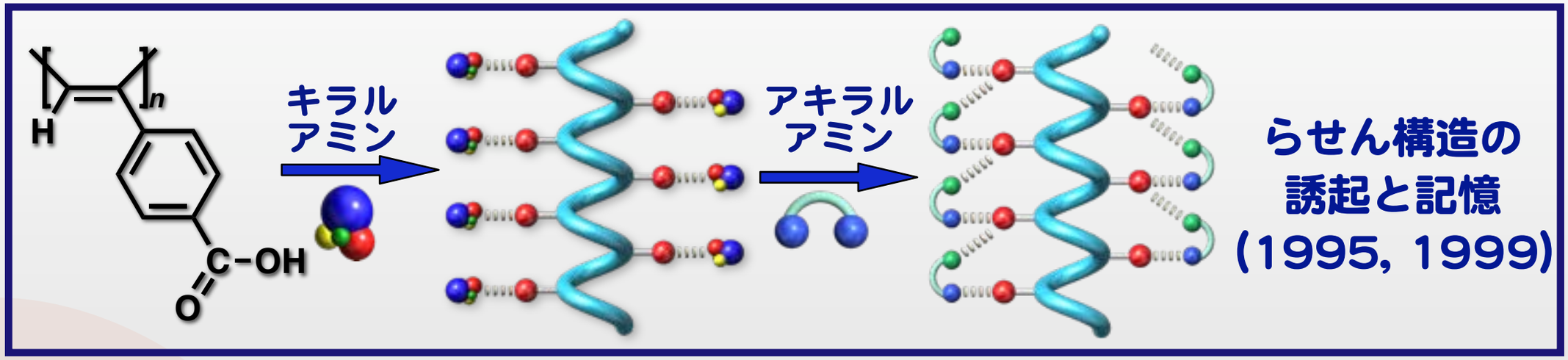


Ciardelli, **1967**

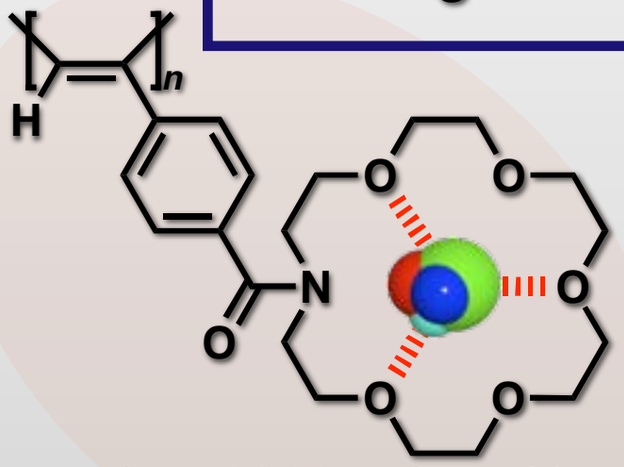
Simionescu, Percec, Masuda, Okamoto, Yashima

Dynamic Helical Polymers

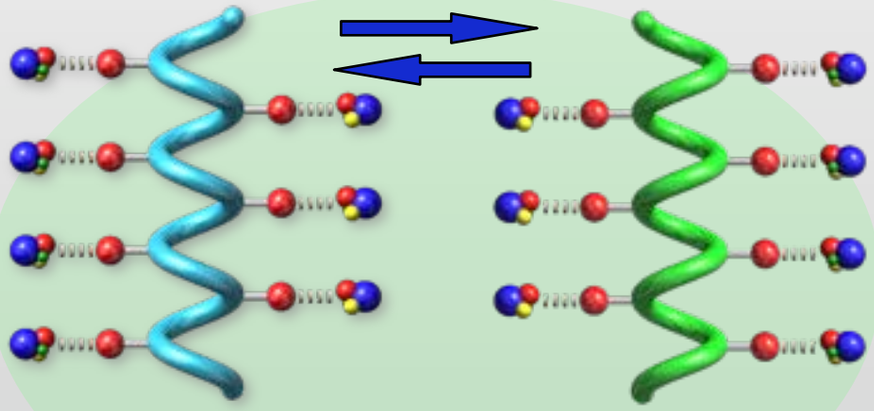
らせん構造の制御と機能の開拓



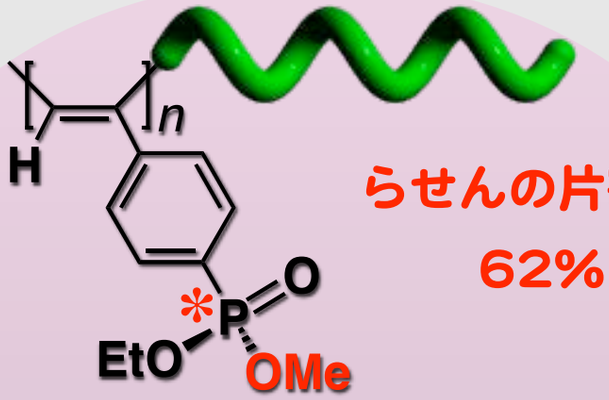
らせん構造の
誘起と記憶
(1995, 1999)



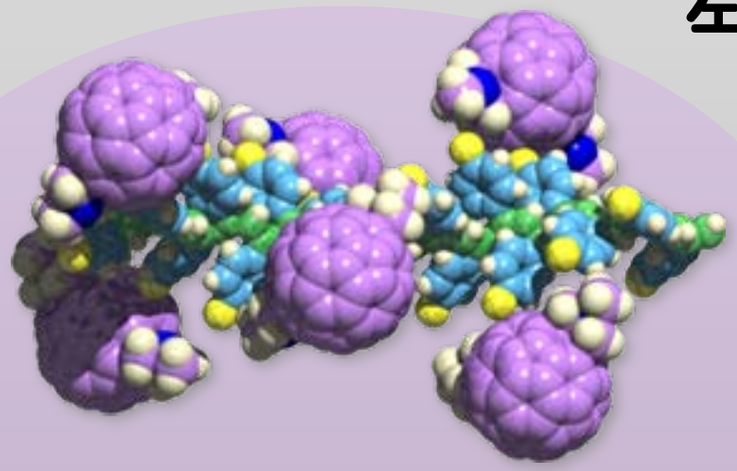
キラリティセンサー
(2003)



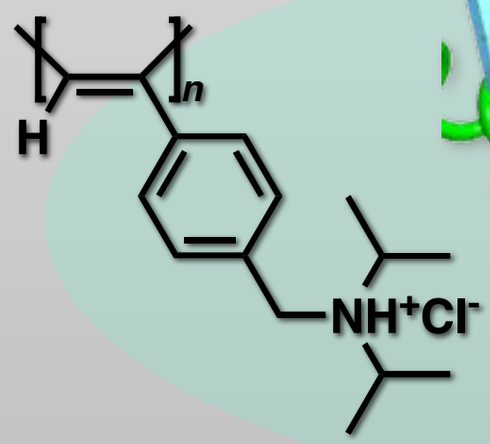
らせん反転を利用した
左右のらせんの記憶 (2005)



らせん構造の保存 (2005)

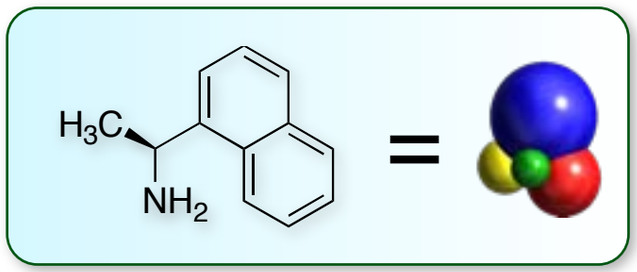


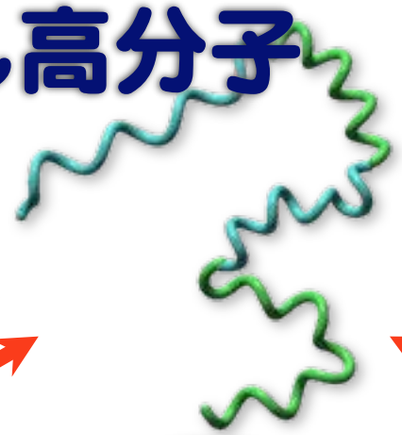
C_{60}のらせん状配列 (2004)

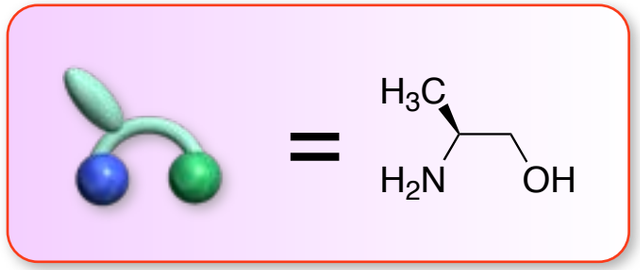


色素のらせん状配列制御と記憶
(2006, 2007)

■ 記憶力を有するらせん高分子

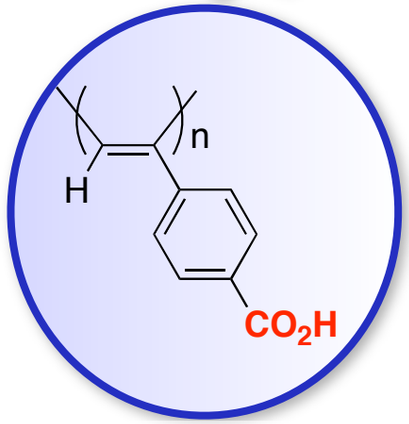


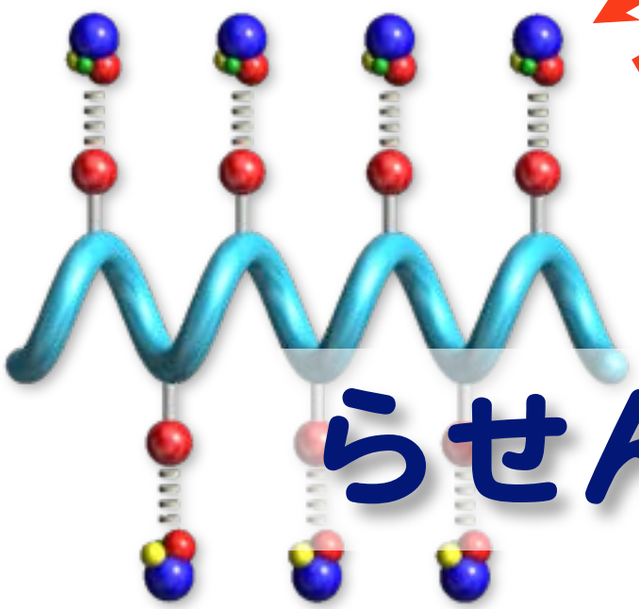


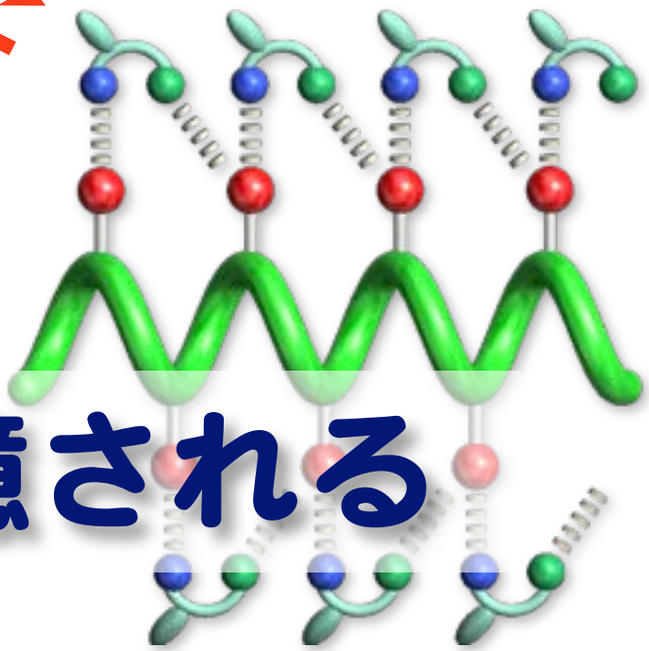


CF_3CO_2H

CF_3CO_2H



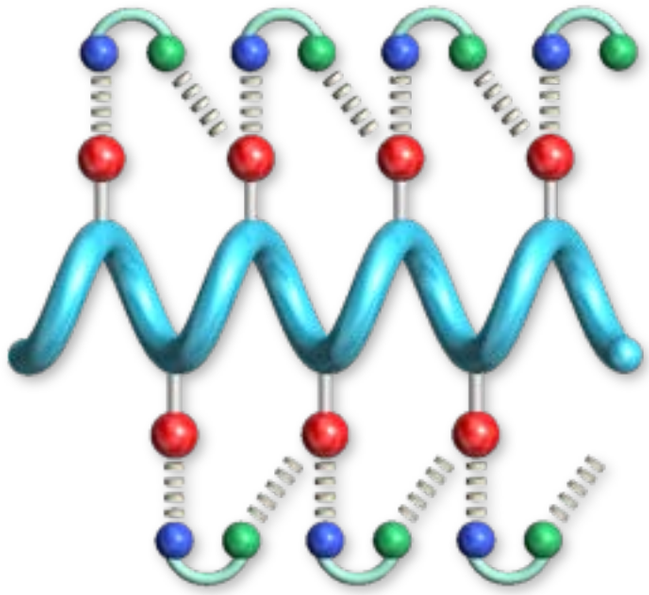


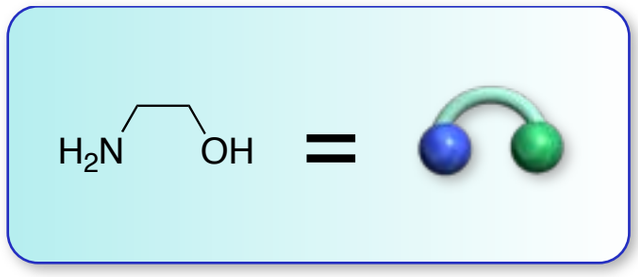


らせんはほどけず、記憶される

左巻き誘起らせん

右巻き誘起らせん





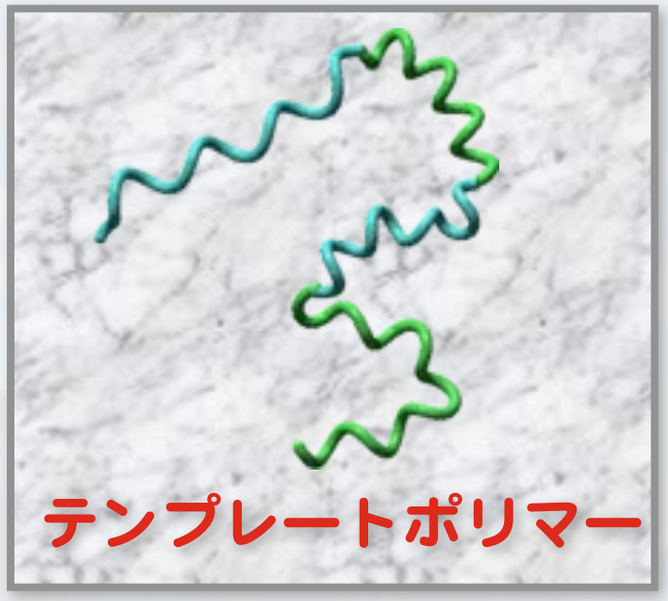
アキラルなアミノアルコール

らせん構造の記憶

JACS, 1995, 1997

Nature, 1999

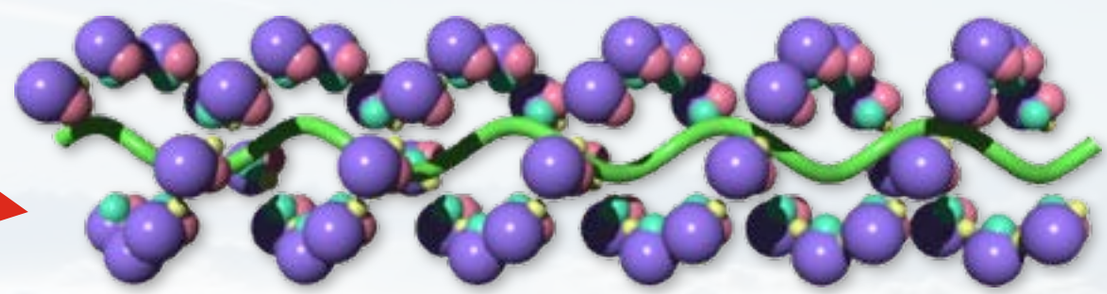
らせん誘起と記憶の展開



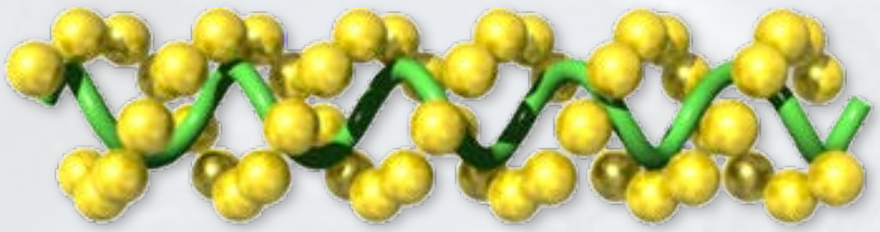
酵素

酵素をらせん状に配列する

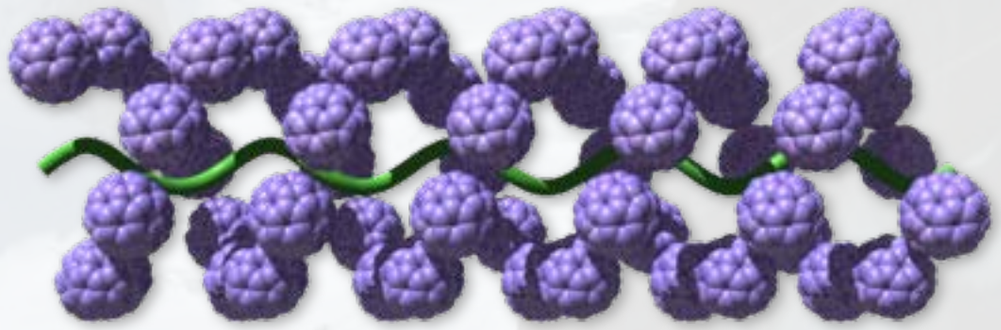
光学活性体



らせん誘起



らせん構造の記憶

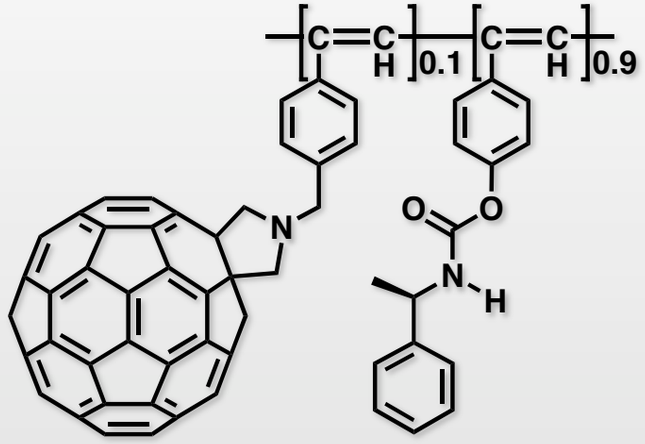


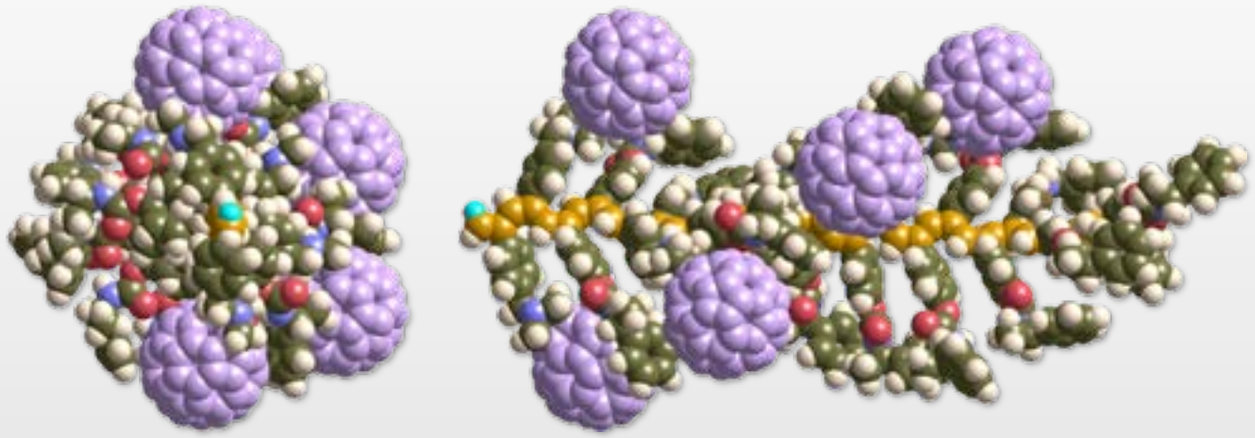
金属をらせん状に配列する

フラーレンをらせん状に配列する

Helical Arrays of Fullerenes

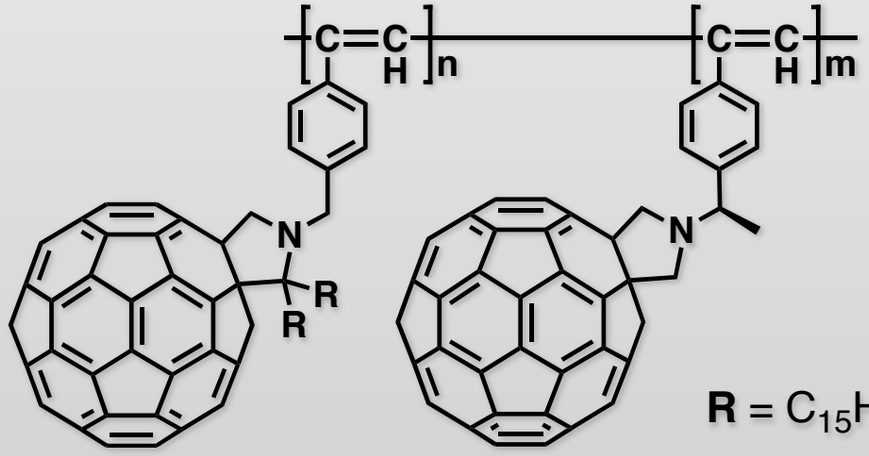
Copolymerization 1



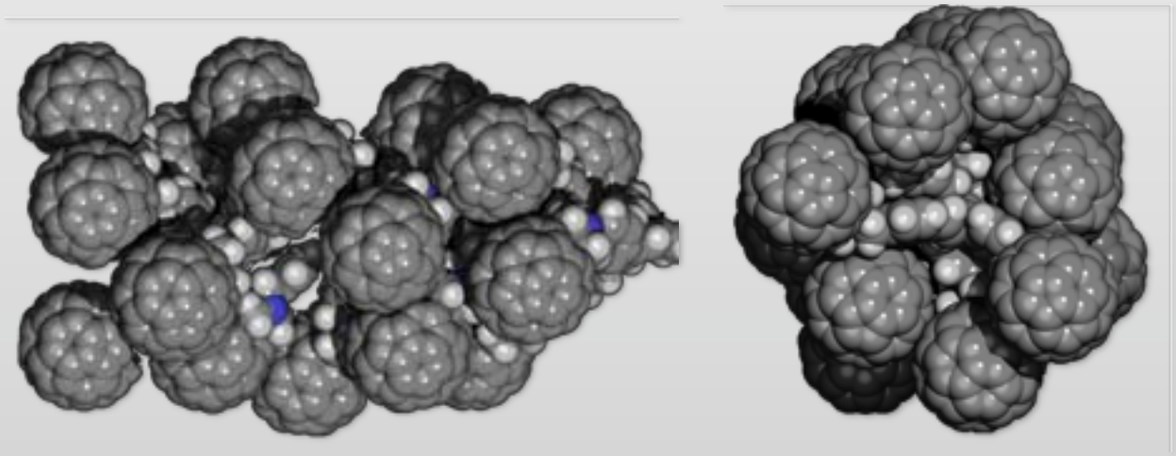


Angew. Chem. Int. Ed. **2002**; *Chem. Eur. J*. **2005**

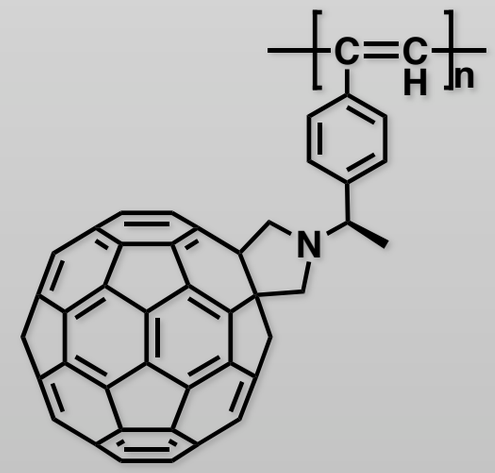
Copolymerization 2

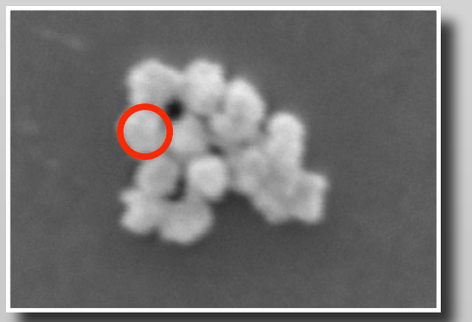


$\mathbf{R} = C_{15}H_{31}$

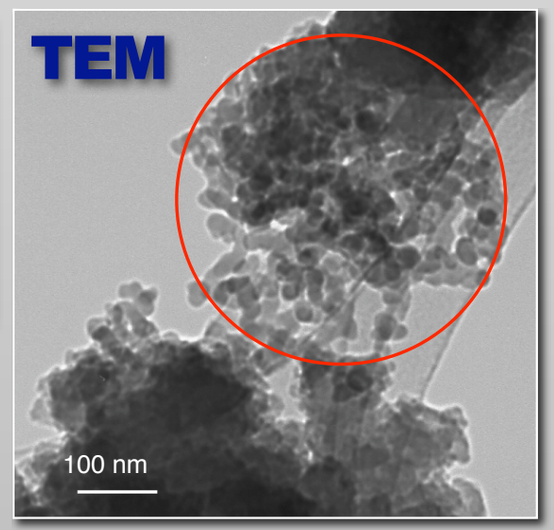


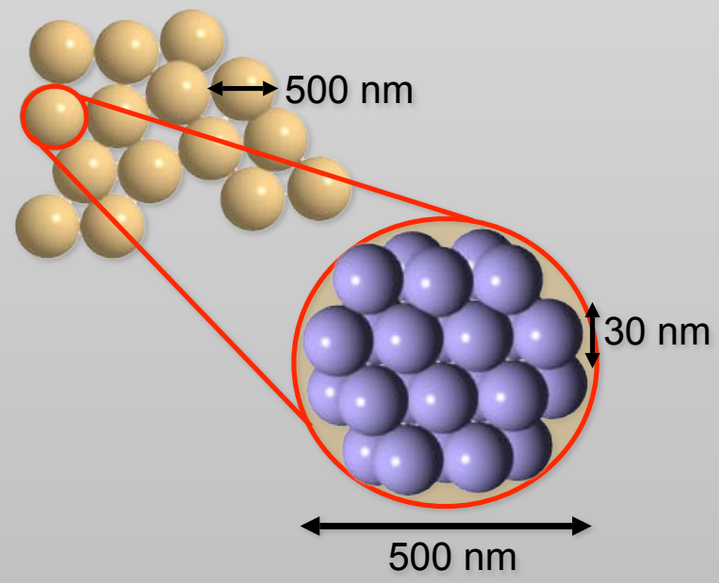
Macromolecules **2007**



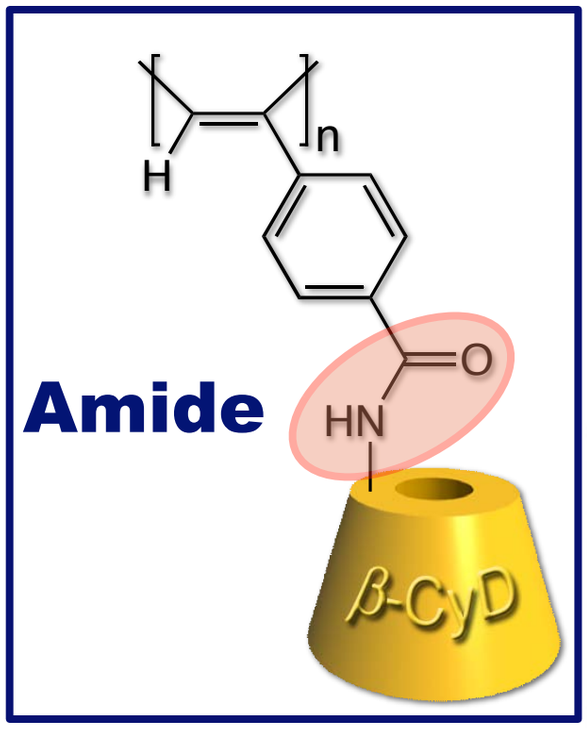


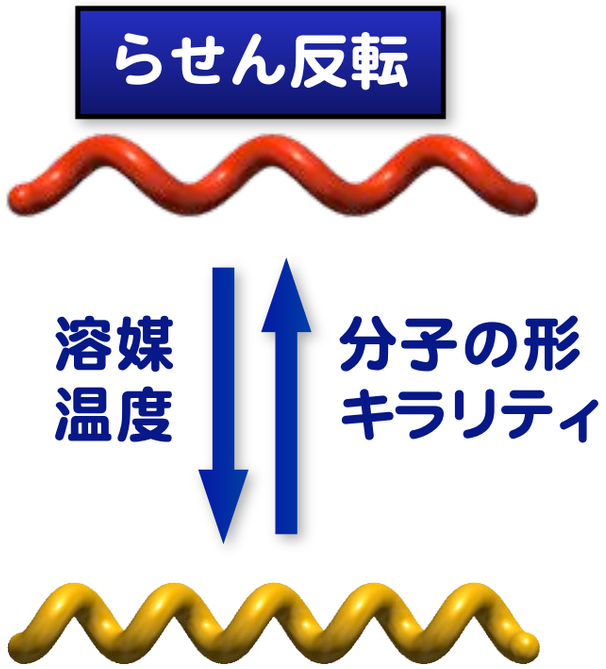
SEM

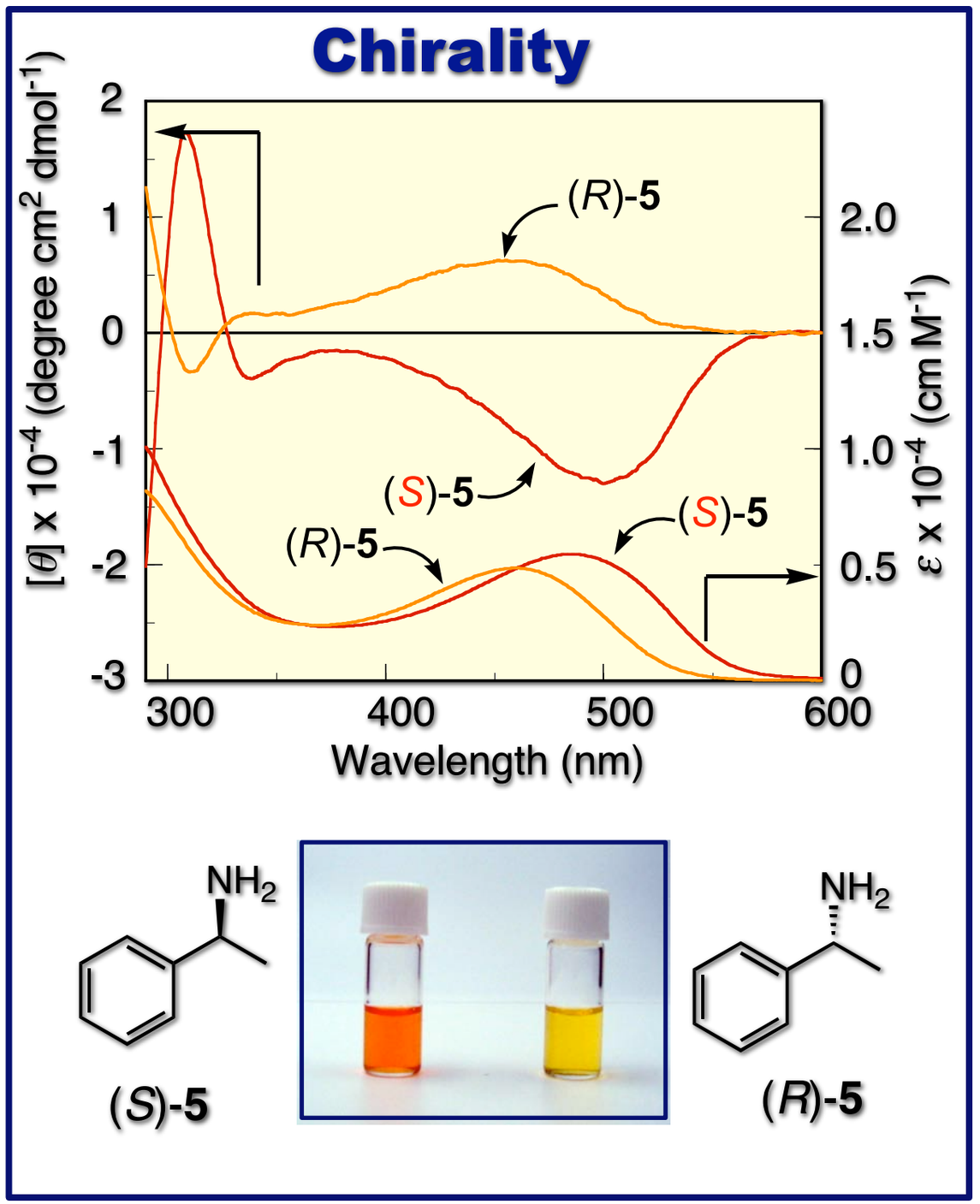


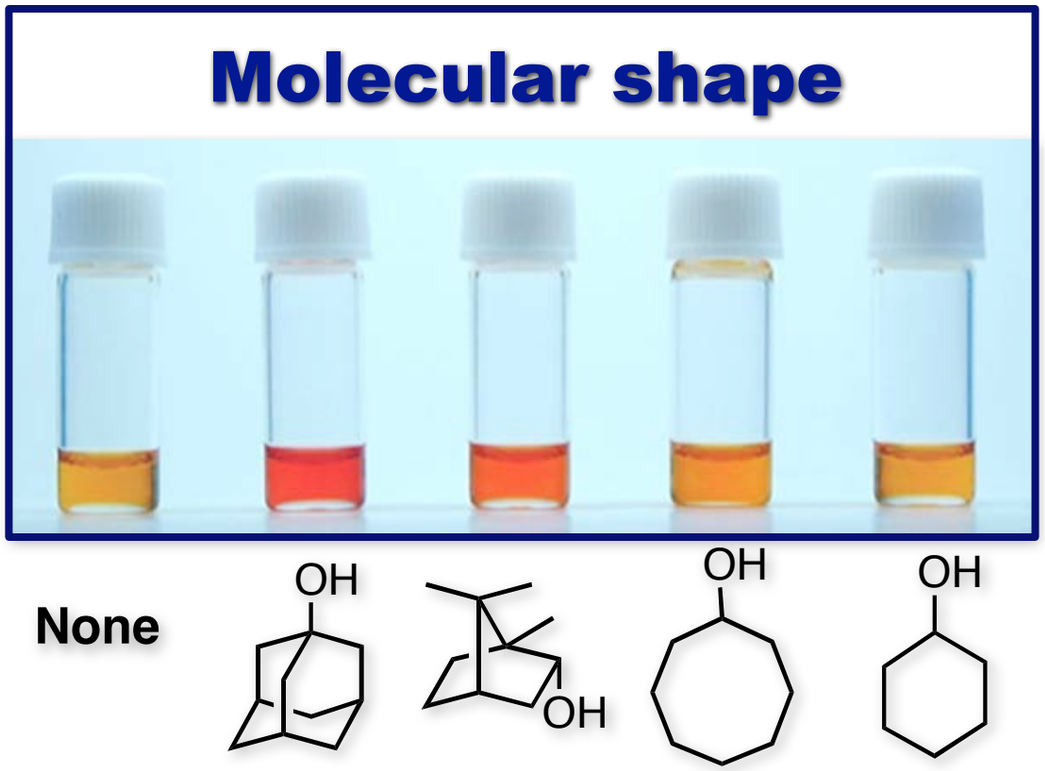


らせん反転を利用した分子・キラル識別





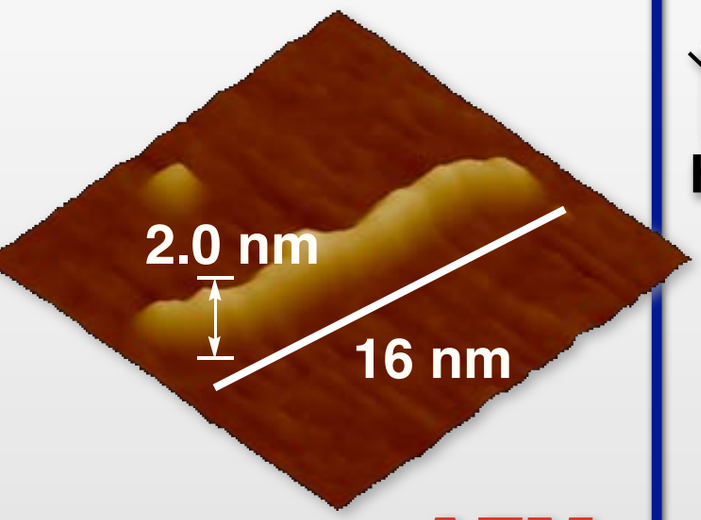




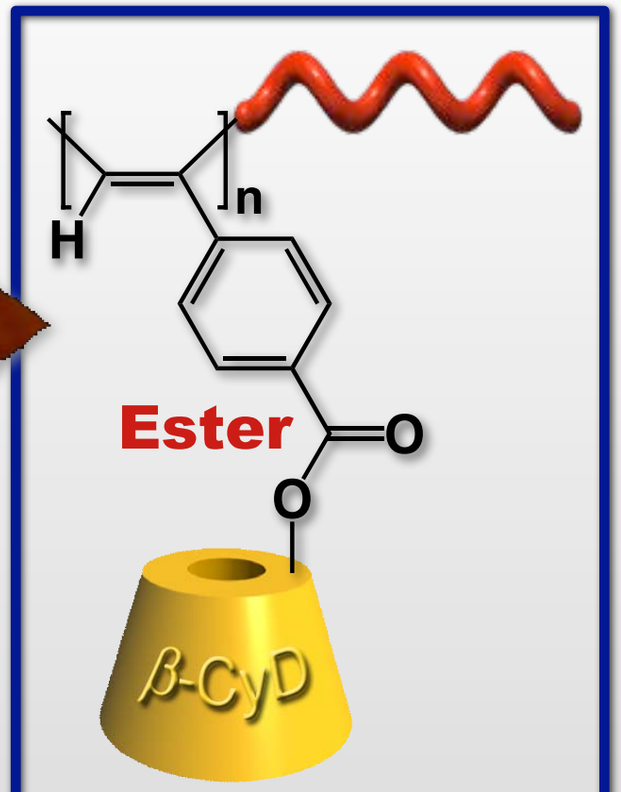
JACS, **2006**, *128*, 7639

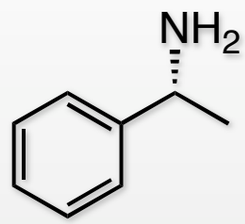
■ 色の変化を伴うらせん反転を利用して分子・キラル識別を実現

巨大ならせん高分子集合体



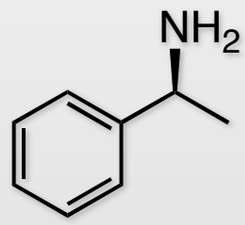
AFM



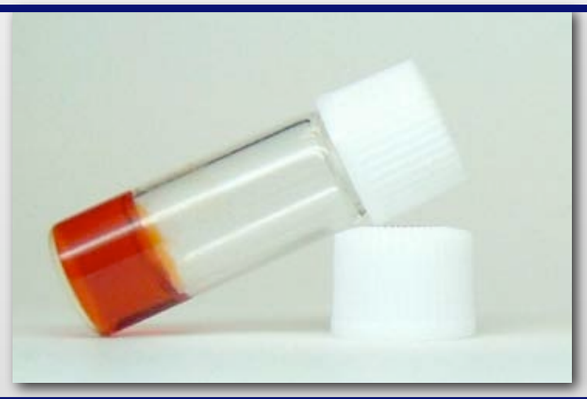


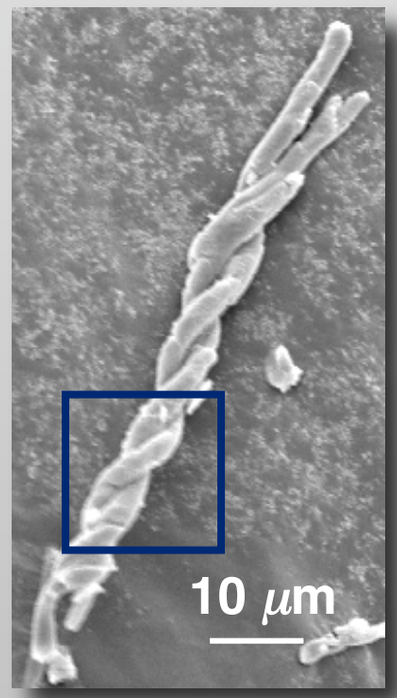
(*R*)-**5**

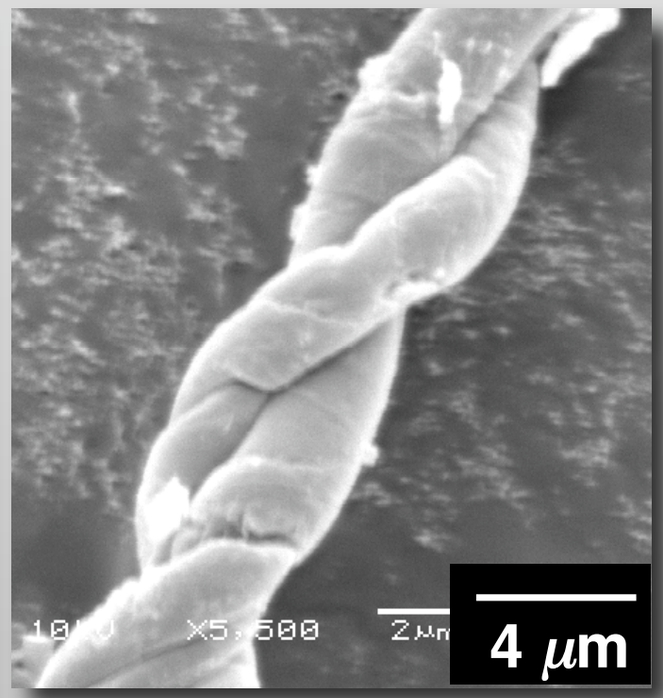
DMSO / H_2O
(4 / 6)

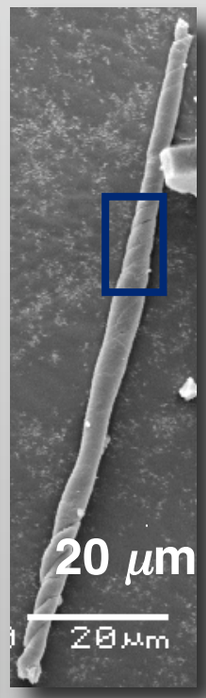


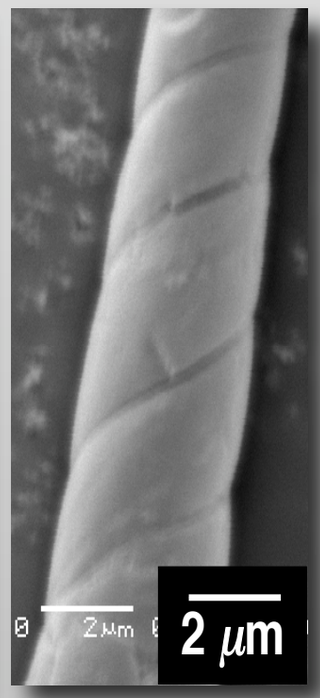
(*S*)-**5**

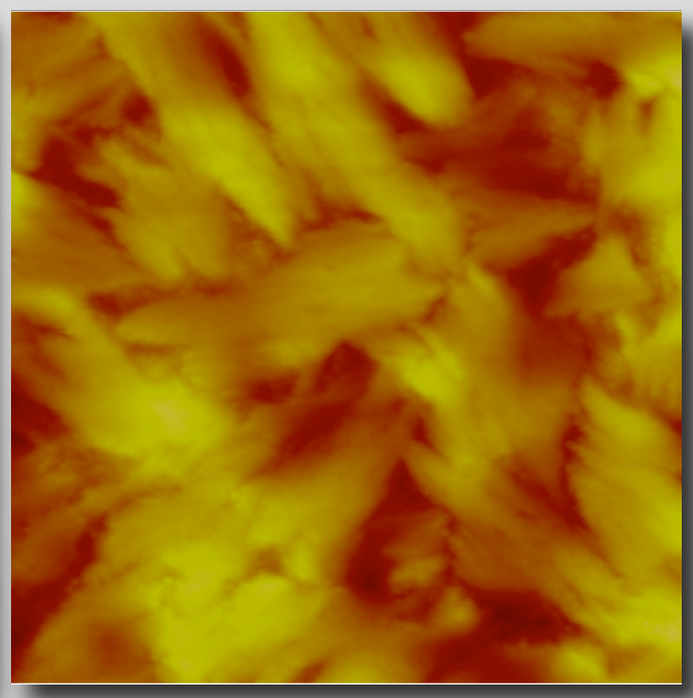










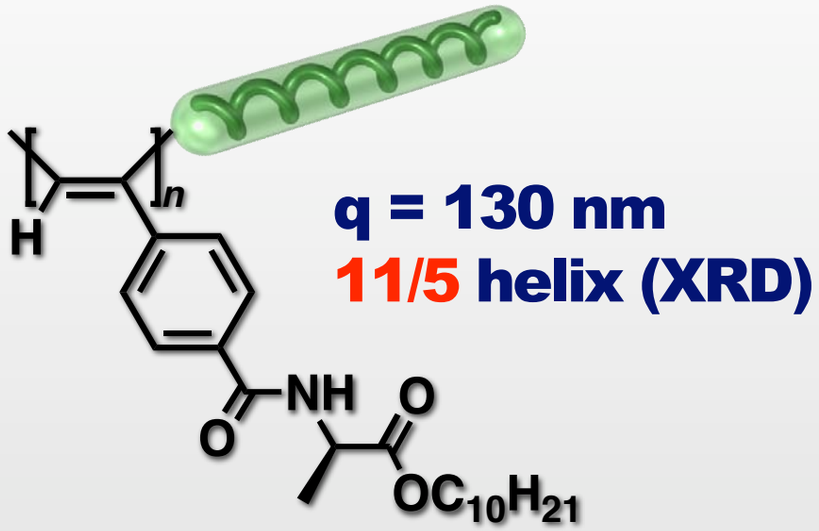


■ (S)体との相互作用によって、巨大ならせん状集合体が生成

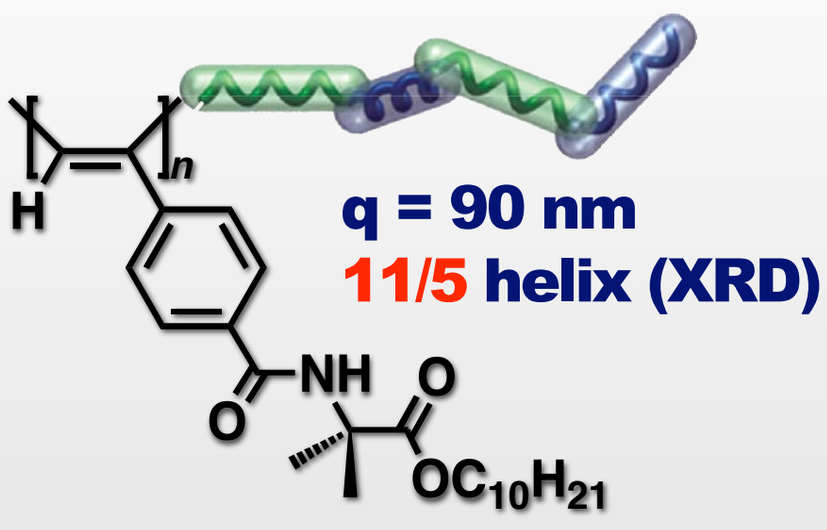
K. Maeda, *submitted.*

顕微鏡を使って
らせんを直接観る

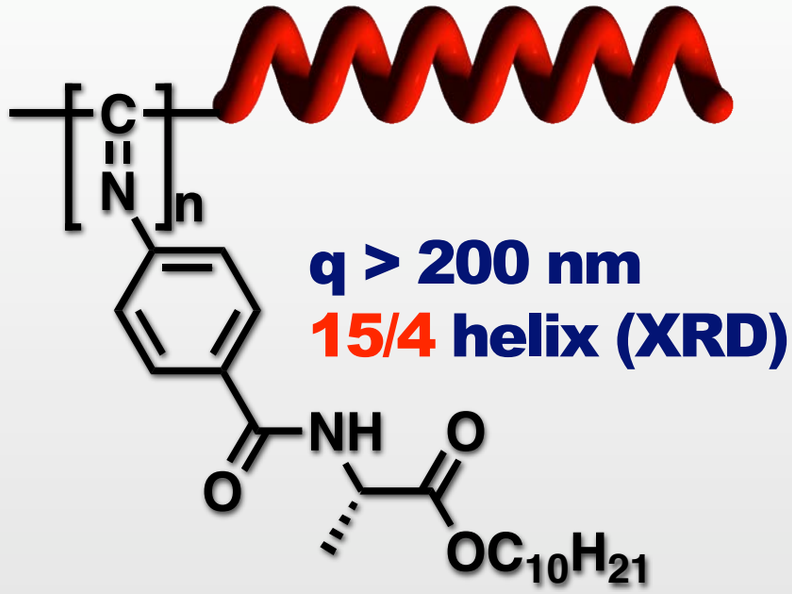
■ らせんを直接観る



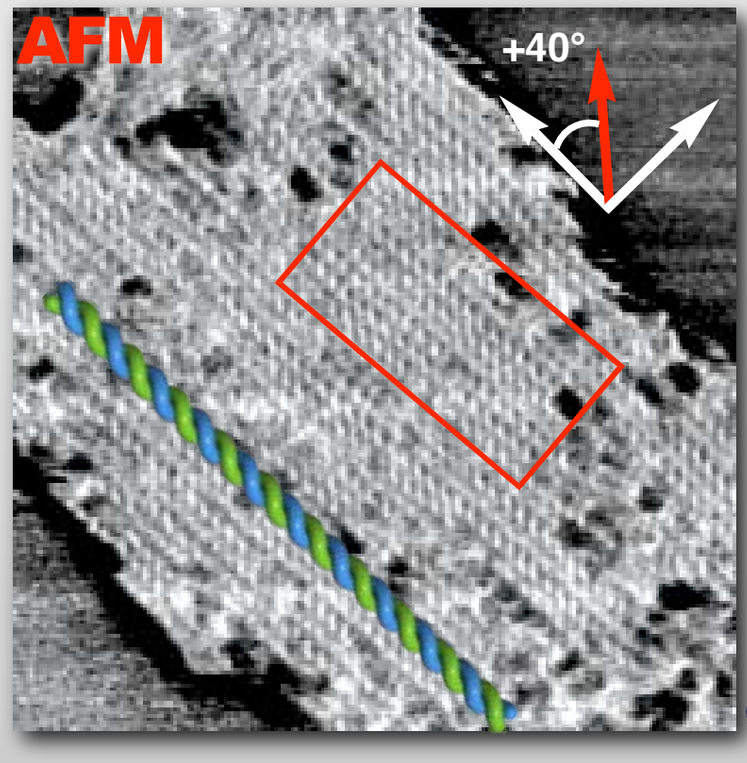
q = 130 nm
11/5 helix (XRD)

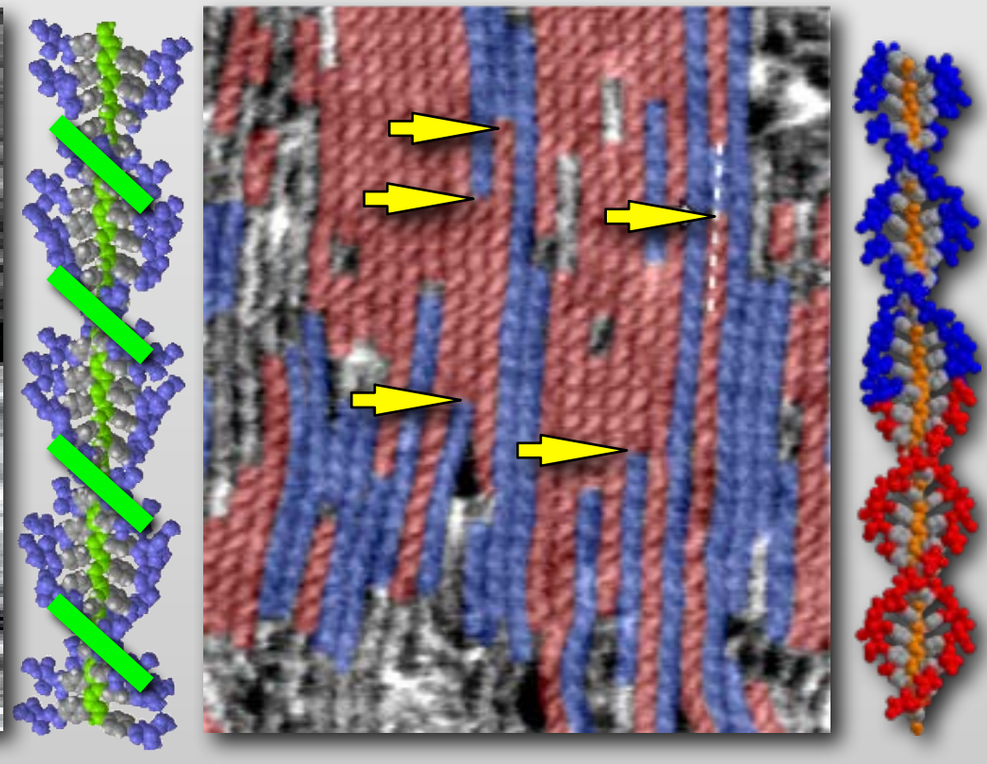


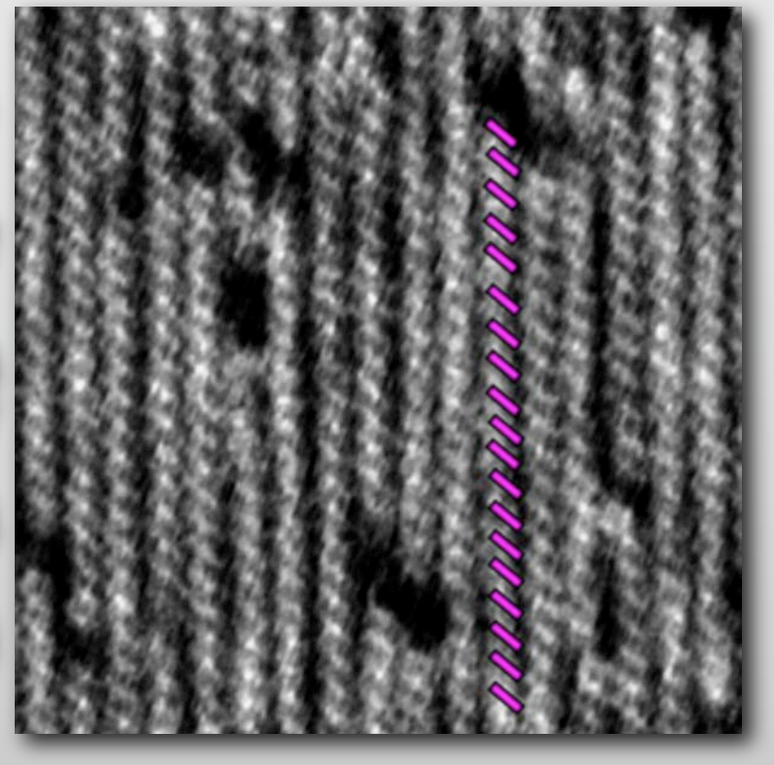
q = 90 nm
11/5 helix (XRD)



q > 200 nm
15/4 helix (XRD)







Right-handed: pitch= 2.33 nm

pitch= 2.3 nm

98% Left-handed: pitch= 1.28 nm

Angew. Chem. Int. Ed. **2006**, *45,* 1245;

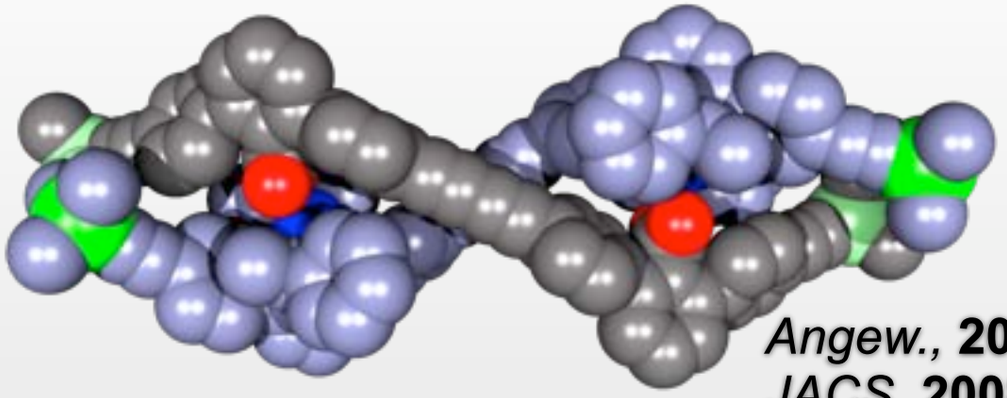
JACS, **2006**, *128,* 5650

Angew. Chem. Int. Ed. **2006**, *46,* 7606

JACS, **2006**, *128,* 708
JACS, **2008**, *130,* 229
JACS, **2009**, *131,* 6708

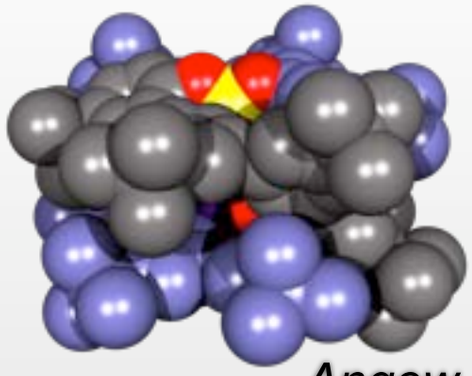
二重らせんを作る

ERATO PJ &
Nagoya Univ.



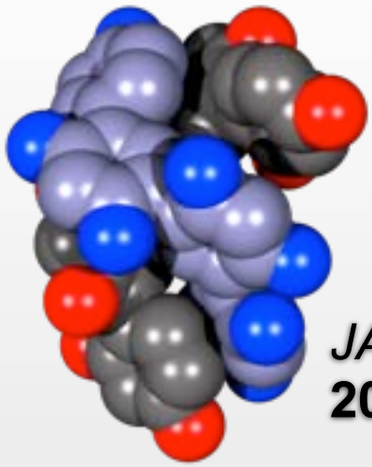
Angew., **2005**
JACS, **2008**

Complementary Double Helix*



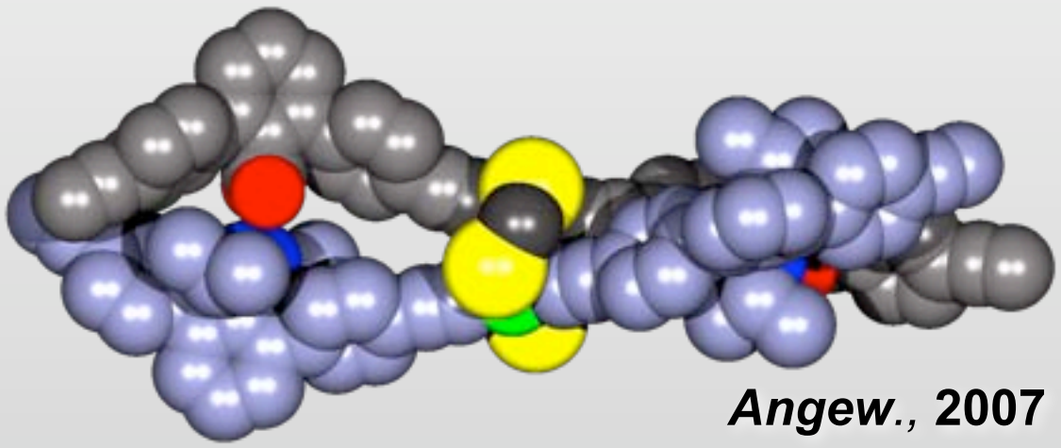
Angew., **2006**

Double Boron-Helicate*



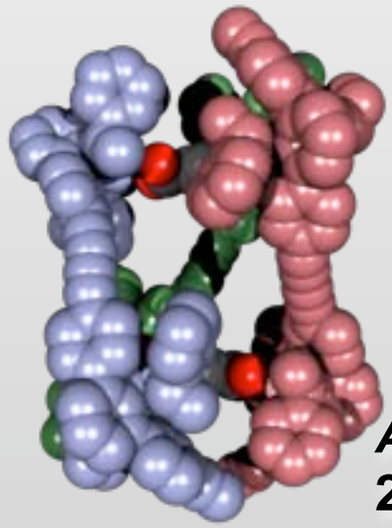
JACS,
2006, 2009

Water-Soluble Double Helix*



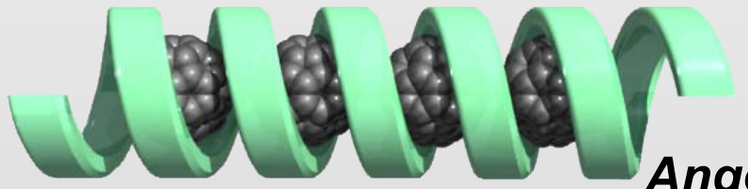
Angew., **2007**

Complementary Double Helix with Catalytic Activity*



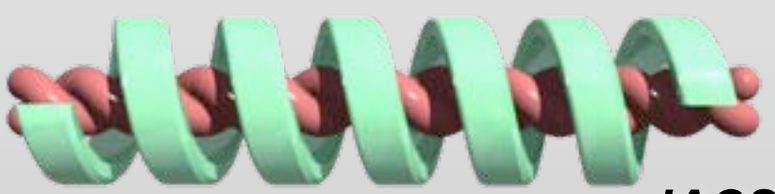
Angew.,
2007

Cylindrical Triple Helix*



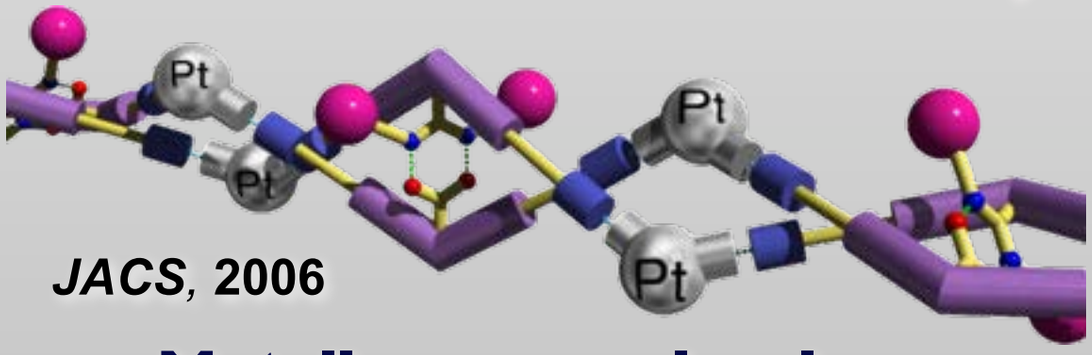
Angew.,
2008

st-PMMA-C_{60}*



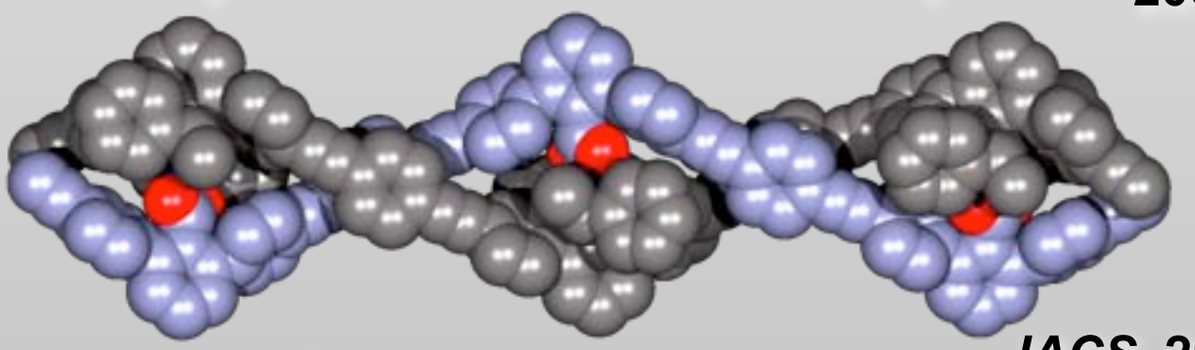
JACS,
2008

Stereocomplex*



JACS, **2006**

Metallosupramolecular Complementary Double Helix*



JACS, **2008**

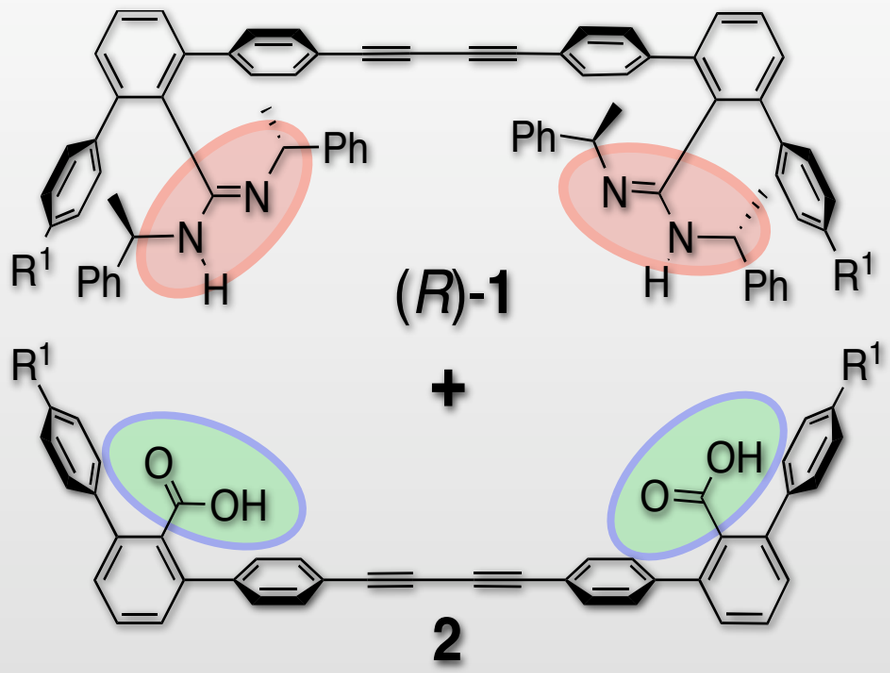
Complementary Double Helical Polymer*

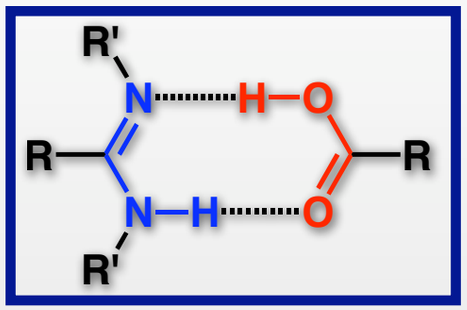
***Optically active forms are available.**

■ 二重らせんを作る・見る

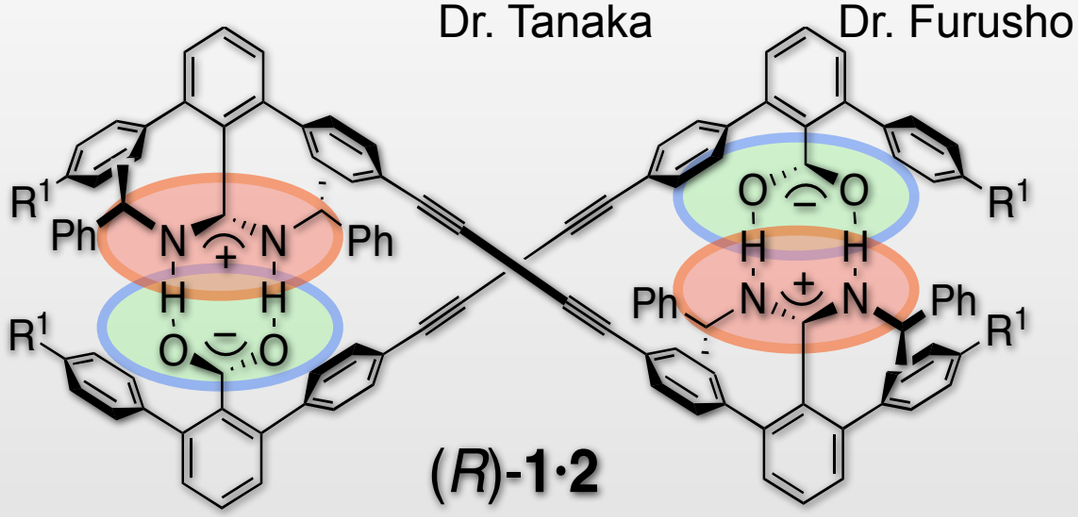
Dr. Tanaka

Dr. Furusho

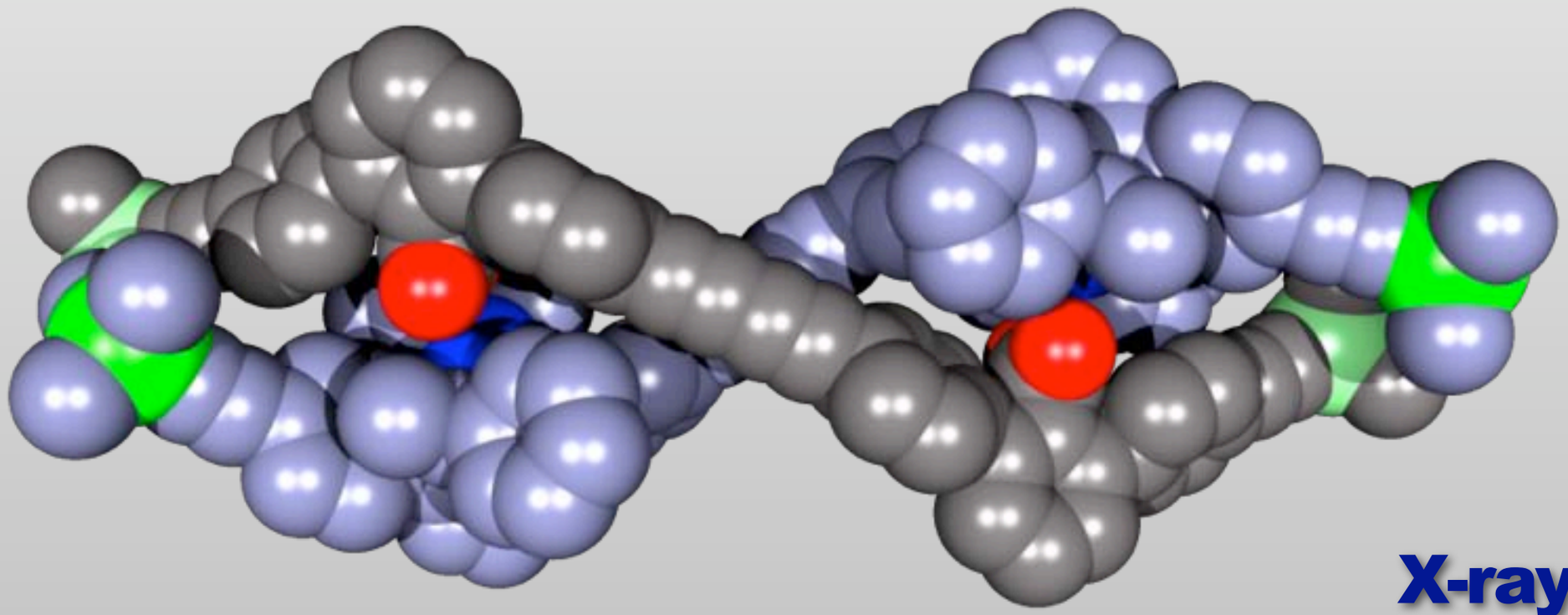




Salt Bridge



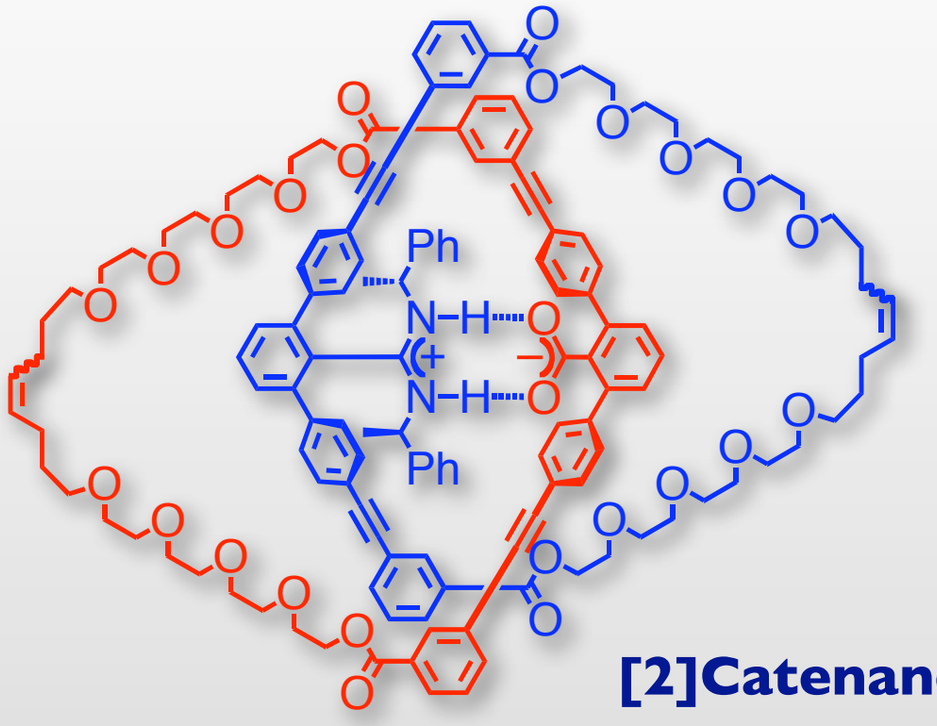
R^1 = 2-TMS-ethynyl



X-ray

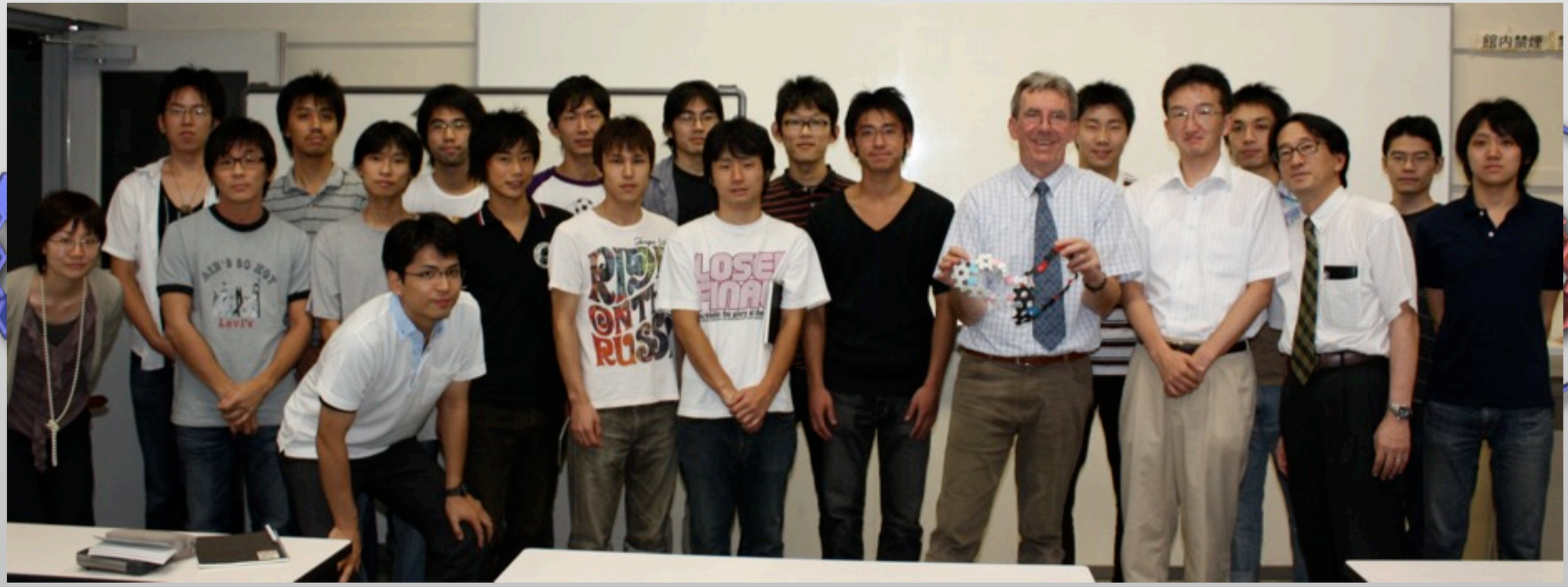
Tanaka, Katagiri, Furusho, *Angew. Chem., Int. Ed.* **2005**, *44*, 3867.

Double-Helix: Catenanes



[2]Catenane

Jean-Pierre Sauvage
(Université Louis Pasteur)

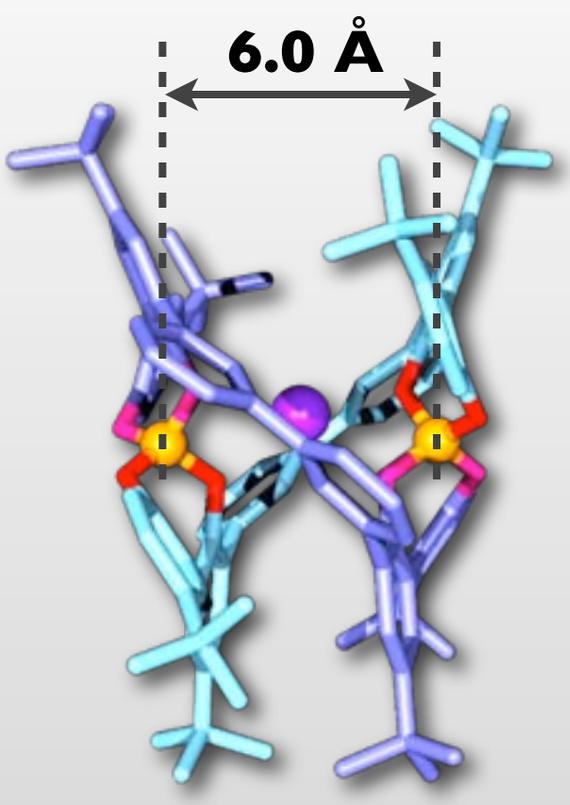


1a

2

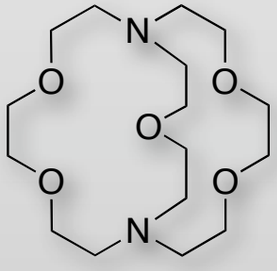
伸縮自在のらせん分子

Structures of Boron Helicates : $2_{BNaB}^{-}\cdot X^{+}$ and $2_{BB}^{2-}\cdot 2X^{+}$

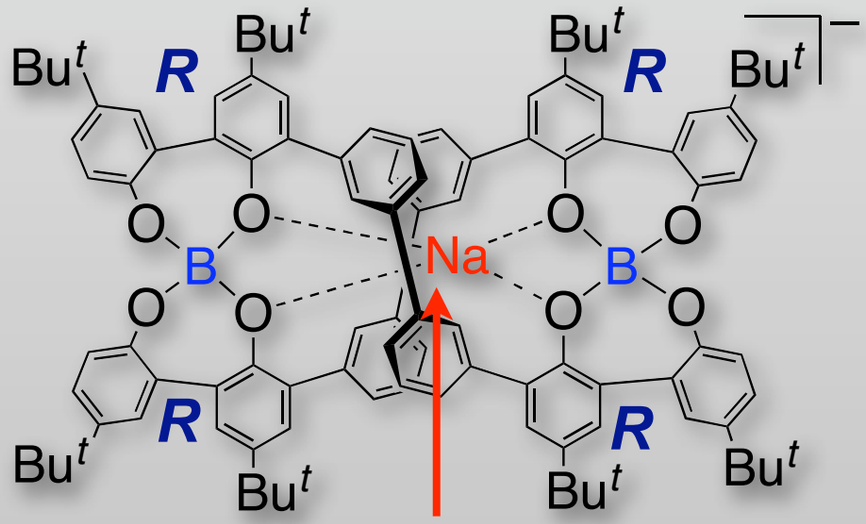


221 ⇌ $Na^{+}\subset$ 221

PF_6^{-} / $NaPF_6$

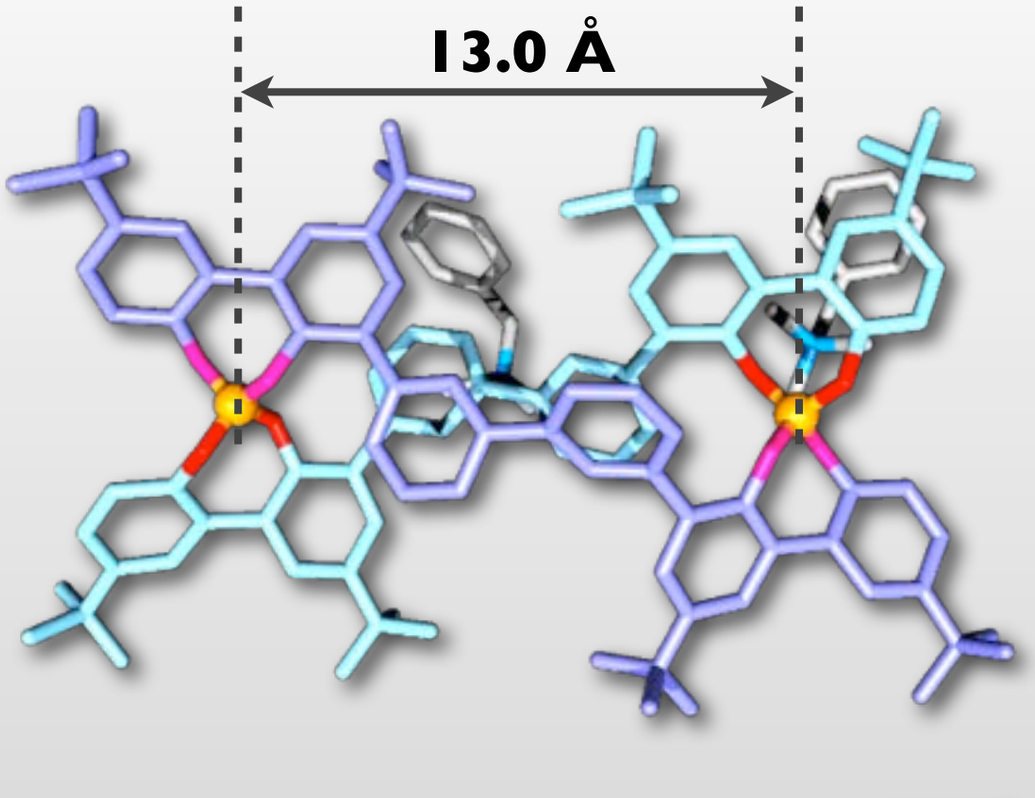


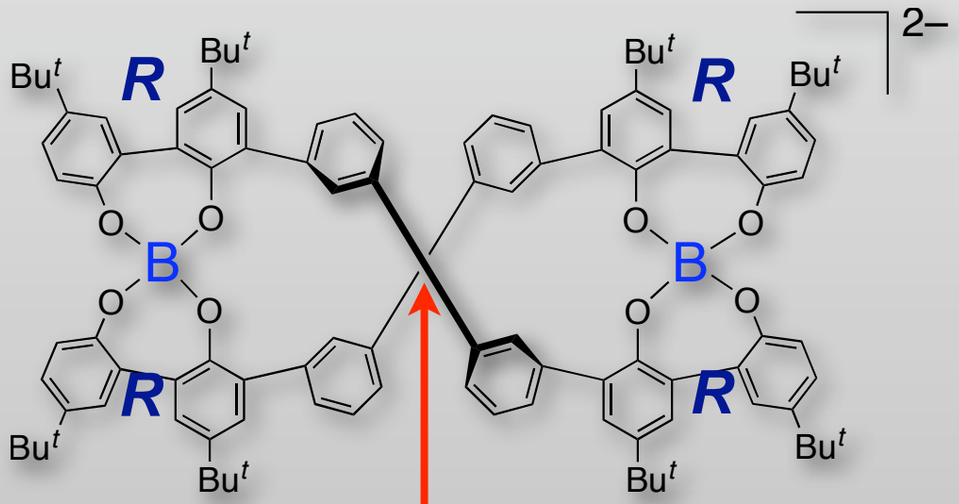
cryptand [221]



Na cation

2_{BNaB}^{-}

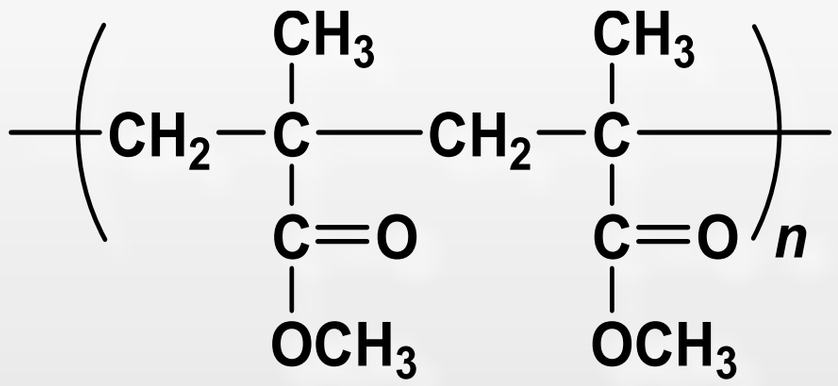




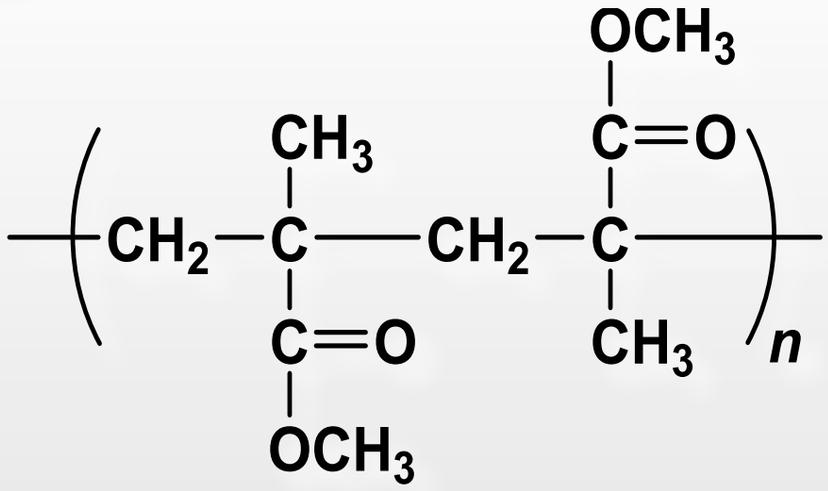
No Na cation inside

2_{BB}^{-}

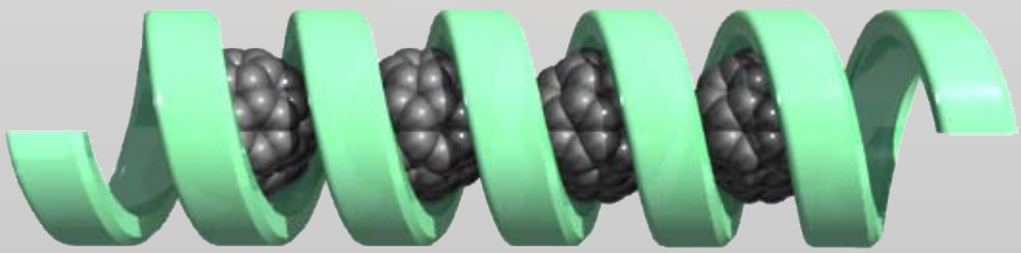
プラスチックから「らせん」を作る



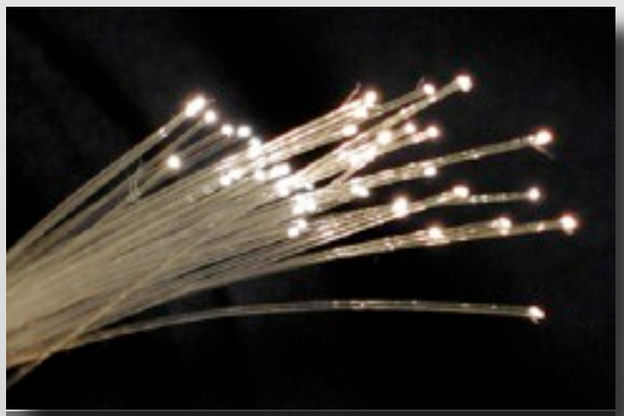
Isotactic PMMA

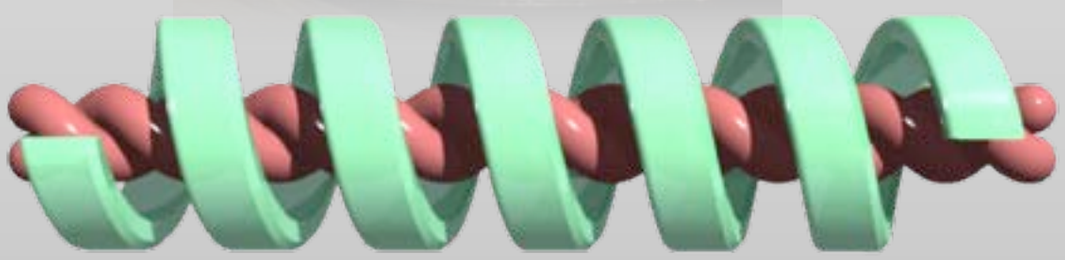


Syndiotactic PMMA



C_{60}-Encapsulated st-PMMA*





Stereocomplex*

化学の力で二重らせんを作る
ー　らせんを究める　ー

本研究室では、DNAやタンパク質など生体高分子の最も基本的ならせん構造に着目し、その形の制御とはたらきの発現を純粋に化学的手法（有機化学、超分子化学、高分子化学）にのっとり研究している。目指すらせんは生体が有する「分子認識能」や「触媒機能」・「複製（コピー）」機能を合わせもつ人工二重らせん！

挑戦 !!