

銅触媒による有機ホウ素化合物の新合成法と  
メカノ応答性をもつ発光性金錯体の開発

北海道大学大学院工学研究院 伊藤 肇

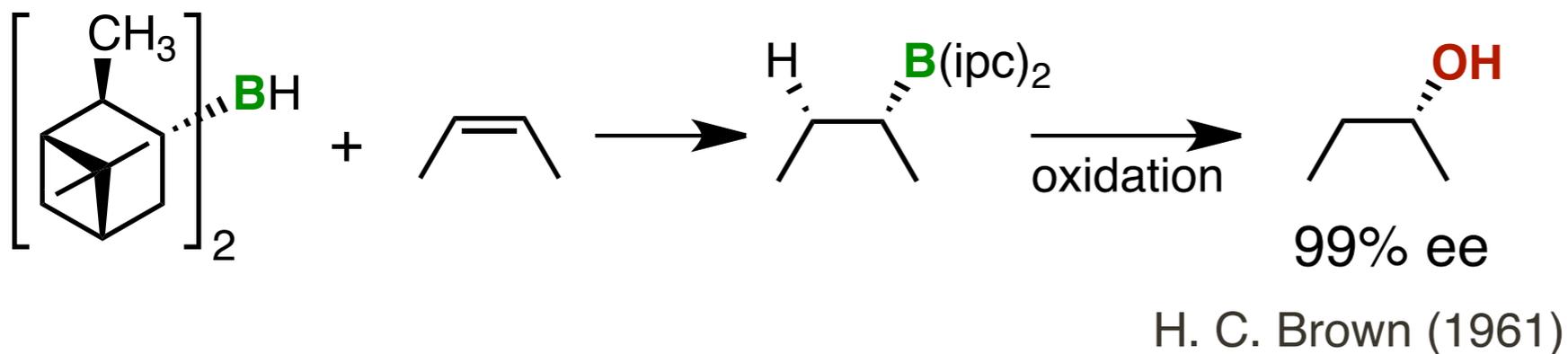
## 1. 銅触媒によるホウ素化反応：発見と展開

## 2. メカノ応答性をもつ発光性金錯体

**本日の講演資料: 4/1 HPで公開 検索「有機元素」**

# おもな有機ホウ素化合物と合成反応

■ H. C. Brown: 有機ホウ素化合物が優れた合成反応剤であることを見いだした。



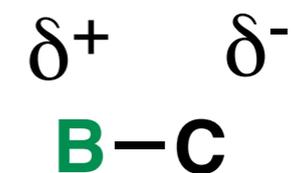
H. C. Brown (1912-2004)  
photo: Purdue Univ.

■ ホウ素は他の金属に比べて電気陰性度が大きい

	電気陰性度 (炭素：2.5)	M-C結合の イオン性
ホウ素	2.0	6%
Mg	1.2	34%

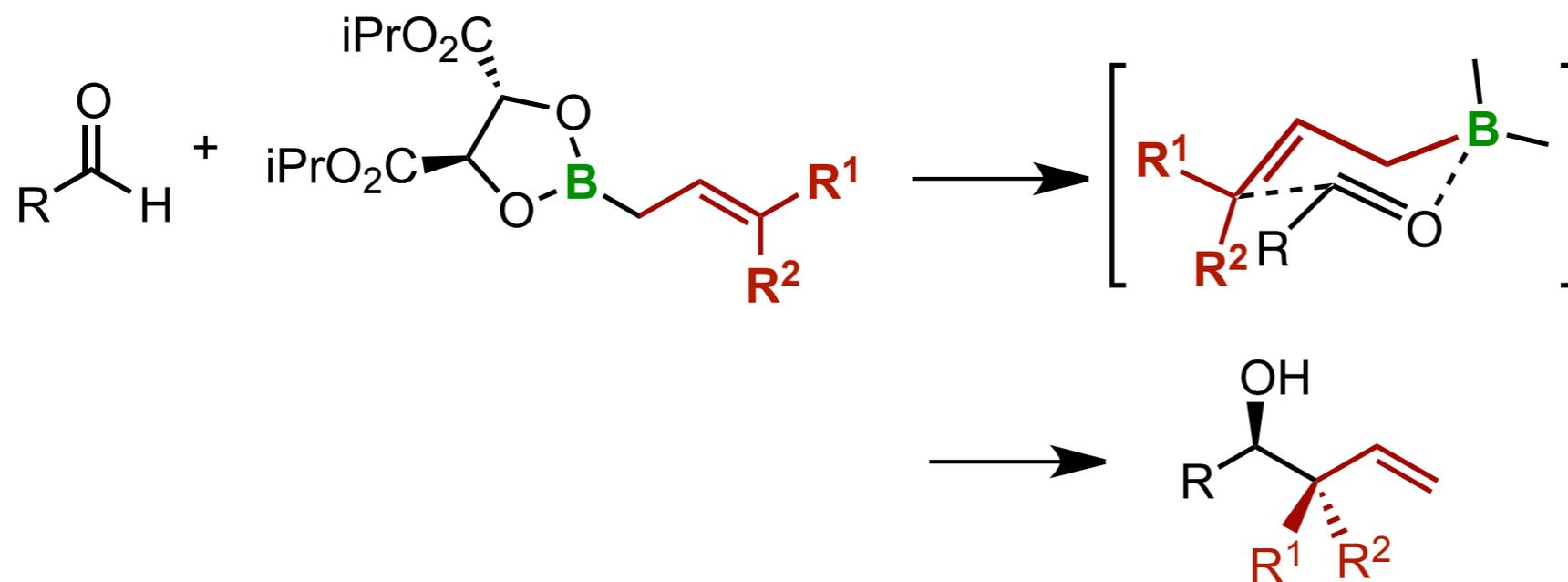
小 ← 電気陰性度 → 大

■ 有機ホウ素反応剤は高い**安定性**（保存性）  
と**反応性**と**選択性**、**官能基許容性**を兼ね備えている



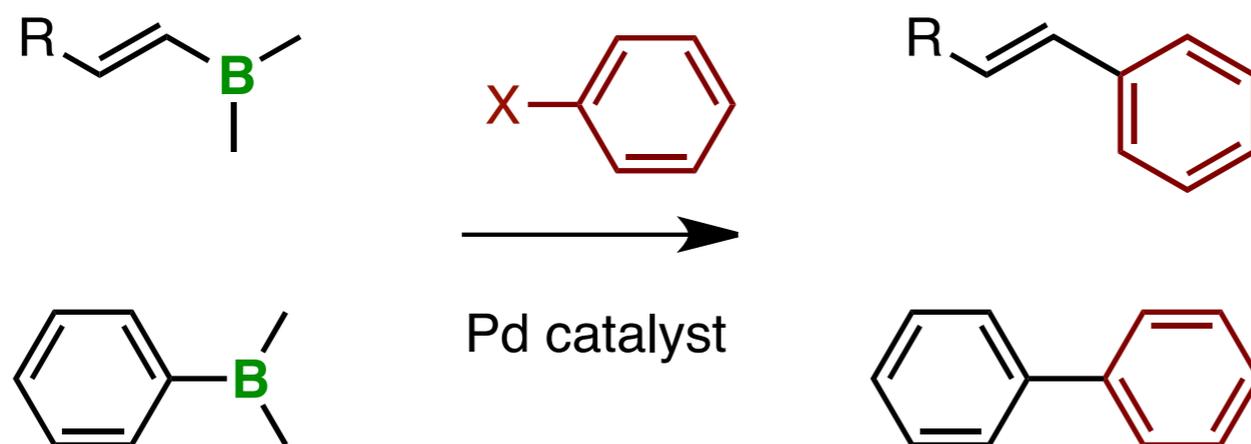
# 炭素-炭素結合形成：究極兵器

## ■ Roush アリル化 (1985～)



William R. Roush  
photo: Wikipedia

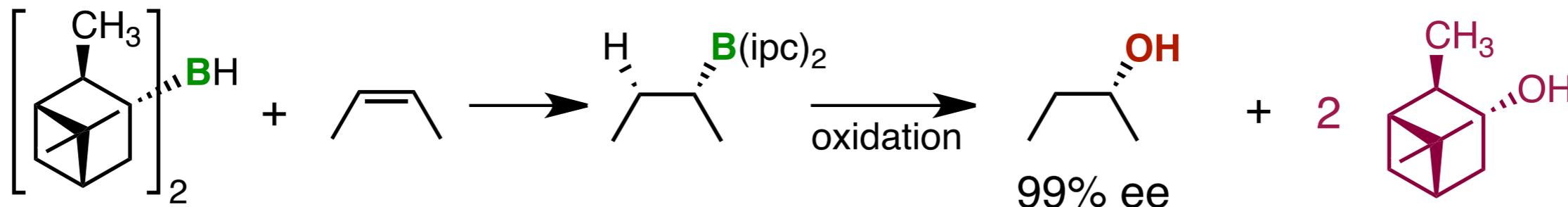
## ■ Suzuki-Miyaura クロスカップリング (1979～)



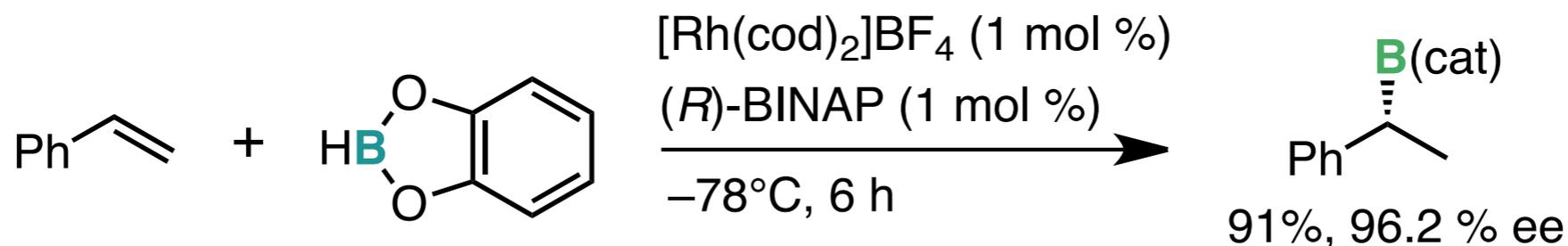
Akira Suzuki

# しかし、光学活性有機ホウ素化合物の**合成**は課題あり

## ■ 不斉ホウ素化合物を用いるヒドロホウ素化: **化学量論量の不斉源**

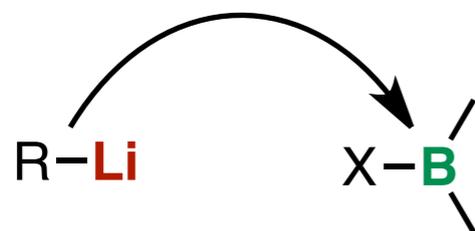


## ■ 触媒的不斉ホウ素化: **限定的**



Hayashi, T.; Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3426.

## ■ 炭素求核剤: **官能基許容性にも問題**

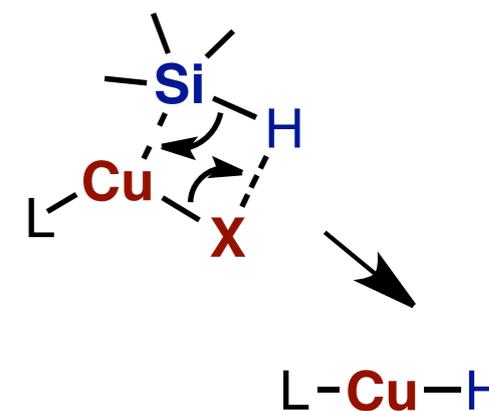
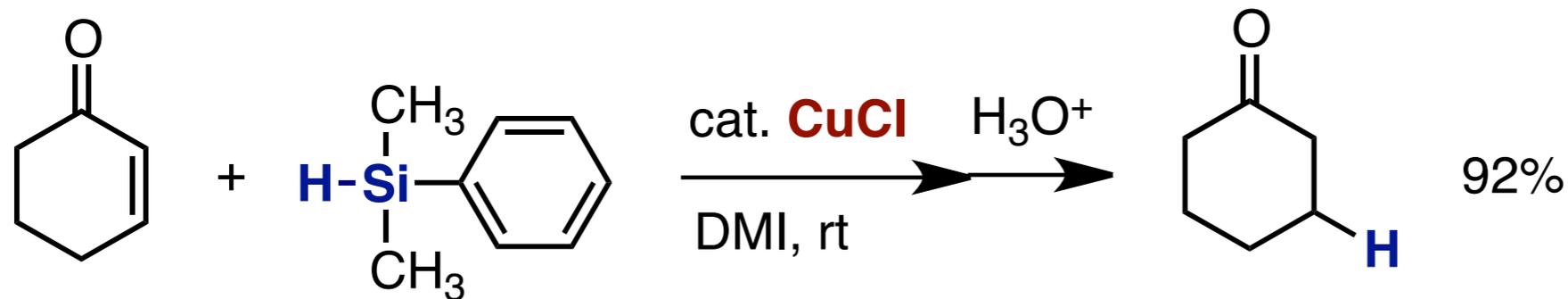


触媒的不斉合成  
官能基許容性

を満たすような  
合成方法の確立  
が課題であった。

# ケイ素-銅触媒反応系の発見 (1997~)

## ■ 銅触媒による1,4-還元 初めての例

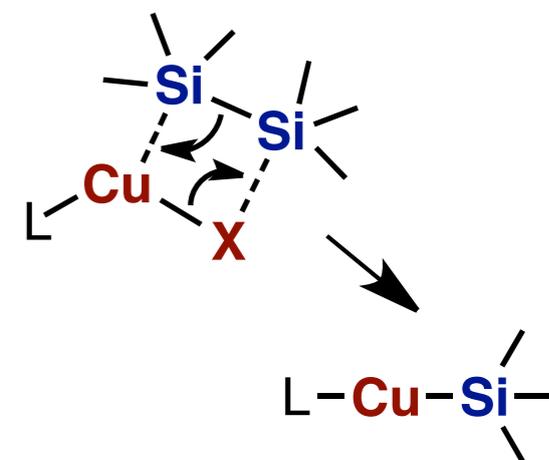
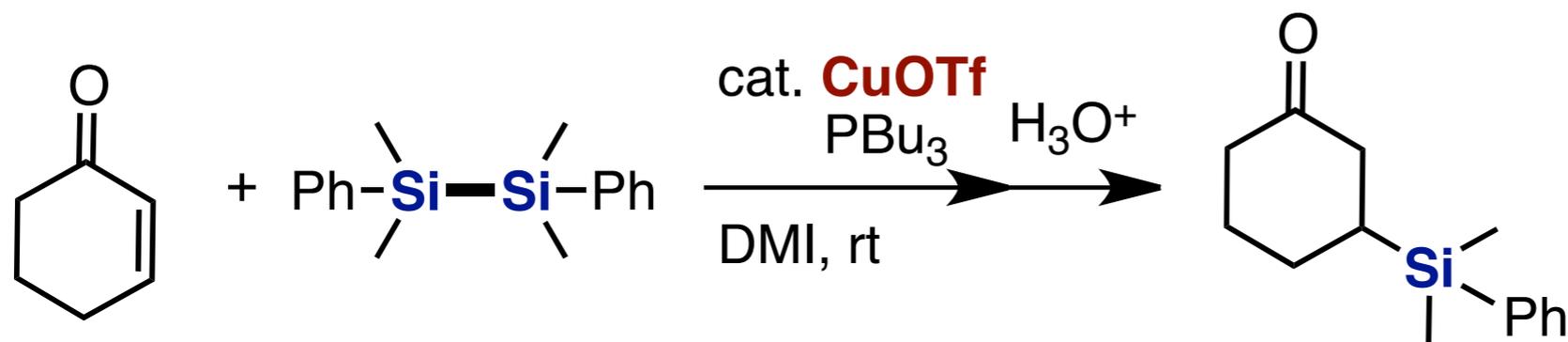


**CuCl / DMI / R<sub>3</sub>SiH:**

Ito, H.; Ishizuka, T.; Arimoto, K.; Miura, K.; Hosomi, A. *Tetrahedron Lett.* **1997**, 38, 8887.

**FCu(PPh<sub>3</sub>) / R<sub>3</sub>SiH:** Mori, A.; Fujita, A.; Nishihara, Y.; Hiyama, T. *Chem. Commun.* **1997**, 2159.

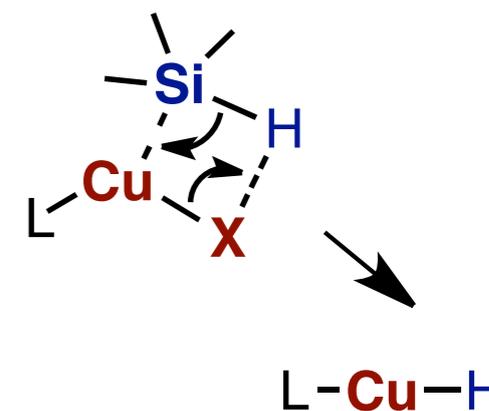
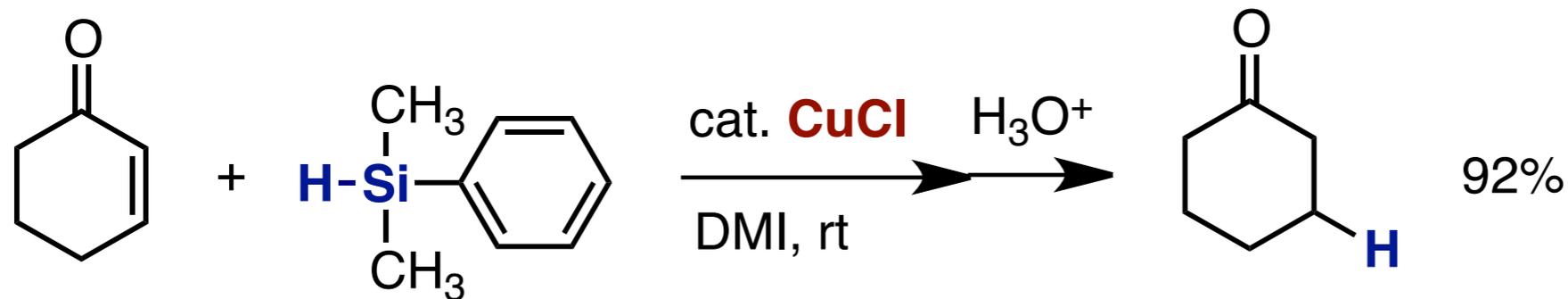
## ■ 銅触媒によるジシランの活性化、共役付加 初めての例



Ito, H.; Ishizuka, T.; Tateiwa, J.; Sonoda, M.; Hosomi, A. *J. Am. Chem. Soc.* **1998**, 120, 11196.

# ケイ素-銅触媒反応系の発見 (1997~)

## ■ 銅触媒による1,4-還元 初めての例

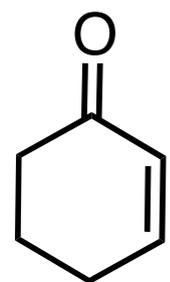


**CuCl / DMI / R<sub>3</sub>SiH:**

Ito, H.; Ishizuka, T.; Arimoto, K.; Miura, K.; Hosomi, A. *Tetrahedron Lett.* **1997**, 38, 8887.

**FCu(PPh<sub>3</sub>) / R<sub>3</sub>SiH:** Mori, A.; Fujita, A.; Nishihara, Y.; Hiyama, T. *Chem. Commun.* **1997**, 2159.

## ■ 銅触媒によるジシランの活性化、共役付加 初めての例



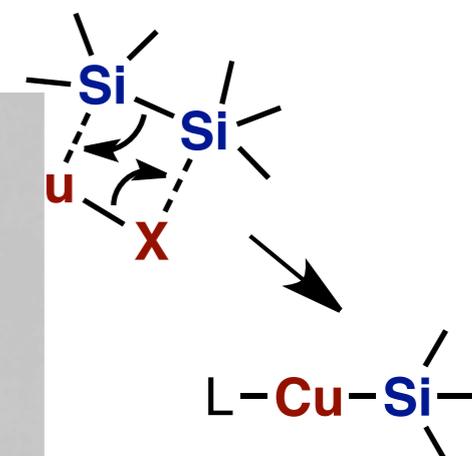
+



Ito, H.; Ishizuka, T.



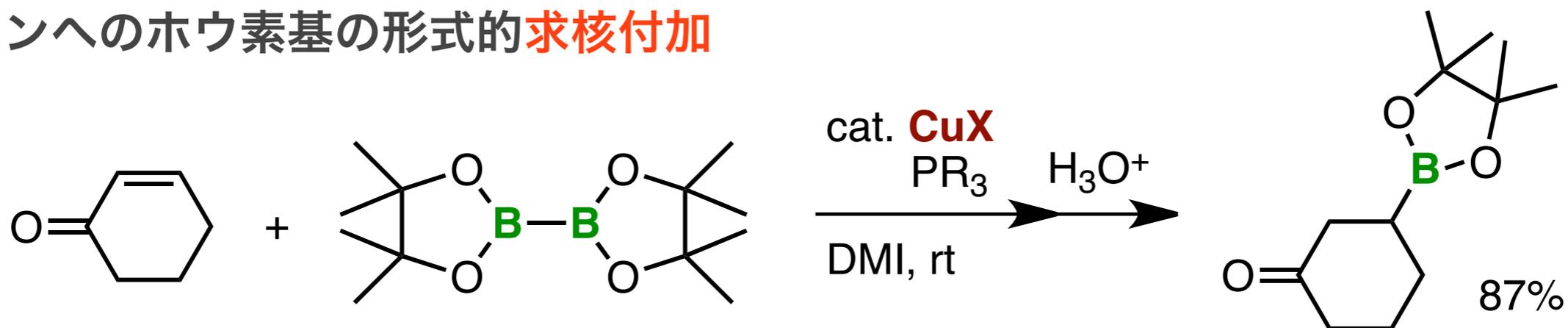
*J. Am. Chem. Soc.* **1997**, 119, 11196.



*J. Am. Chem. Soc.* **1997**, 119, 11196.

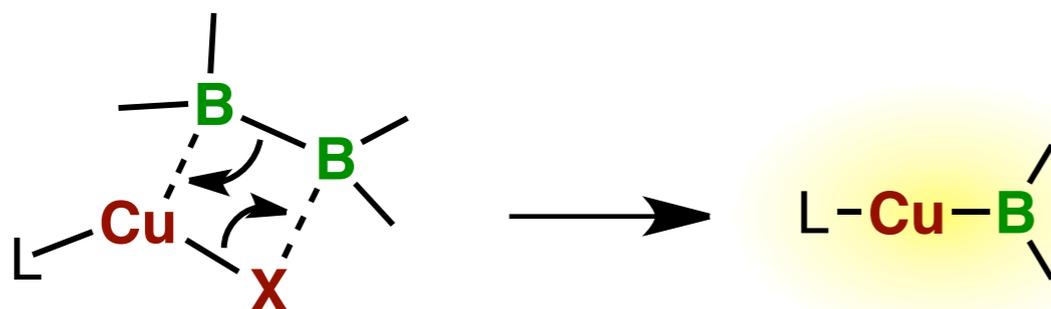
# ホウ素-銅触媒反応系の発見 (2000年)

## ■エノンへのホウ素基の形式的求核付加



**CuX/PR<sub>3</sub>**: Ito, H.; Yamanaka, H.; Tateiwa, J.; Hosomi, A. *Tetrahedron Lett.* **2000**, 41, 6821.

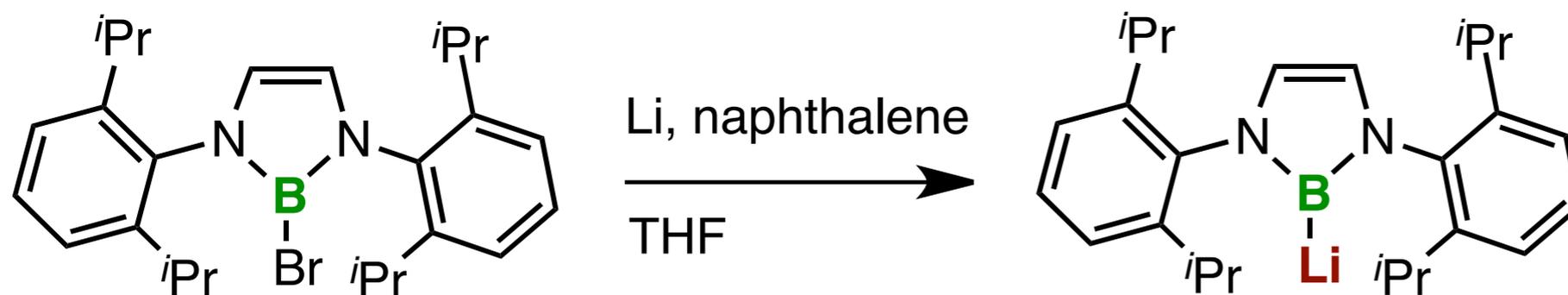
**CuCl/KOAc**: Takahashi, K.; Ishiyama, T.; Miyaura, N. *Chem. Lett.* **2000**, 982.



## ホウ素-銅触媒活性種

- ・求核的な反応特性
- ・選択性のコントロールが可能

## ■ホウ素アニオンは合成が困難であった。

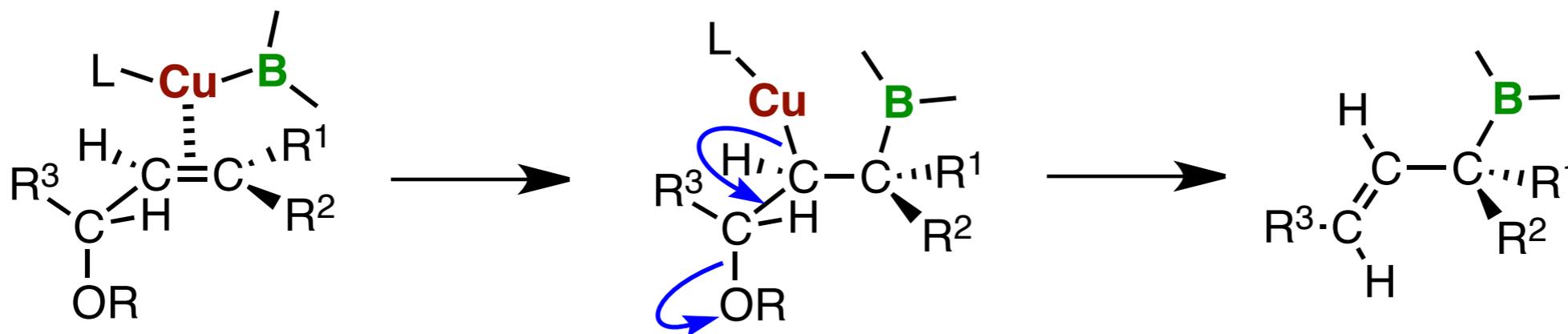
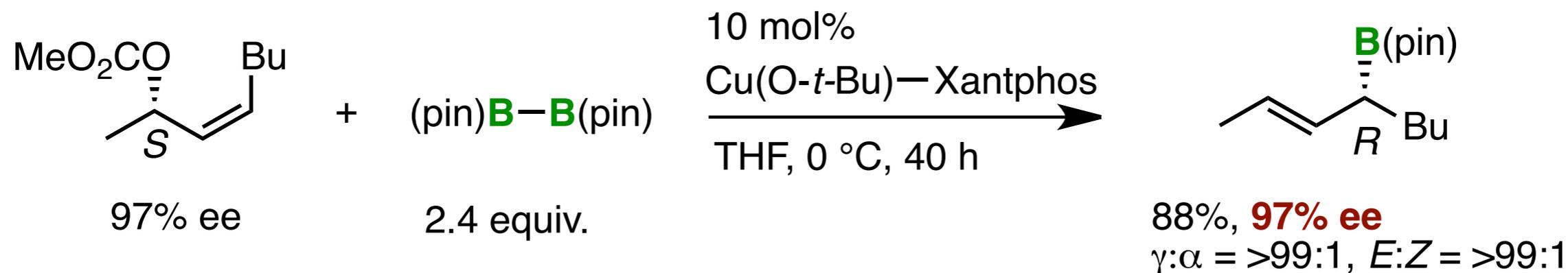


Segawa, Y.; Yamashita, M.; Nozaki, K. *Science* **2006**, 314, 113.

**銅触媒/ジボロン**  
を用いた有機ホウ  
素化合物の合成法  
を詳しく検討

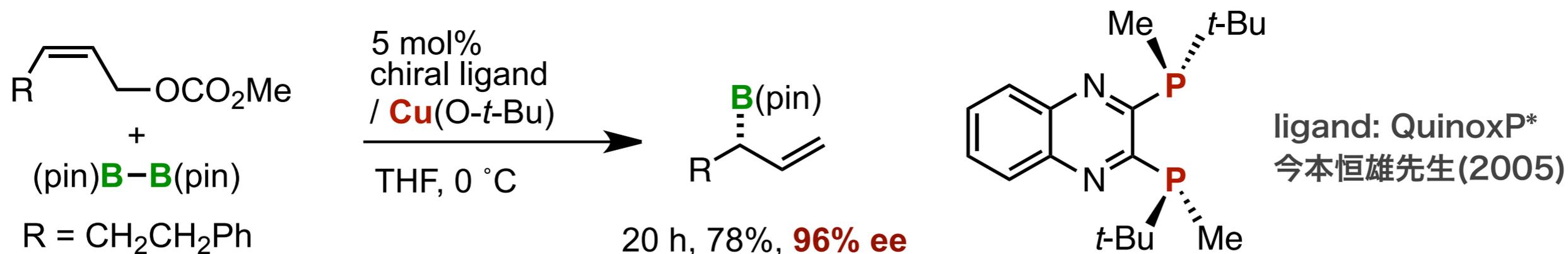
# アリル位ホウ素置換反応の開発 (2005年~)

## ■ S<sub>N</sub>2' 型反応により、さまざまなアリルホウ素化合物が合成可能



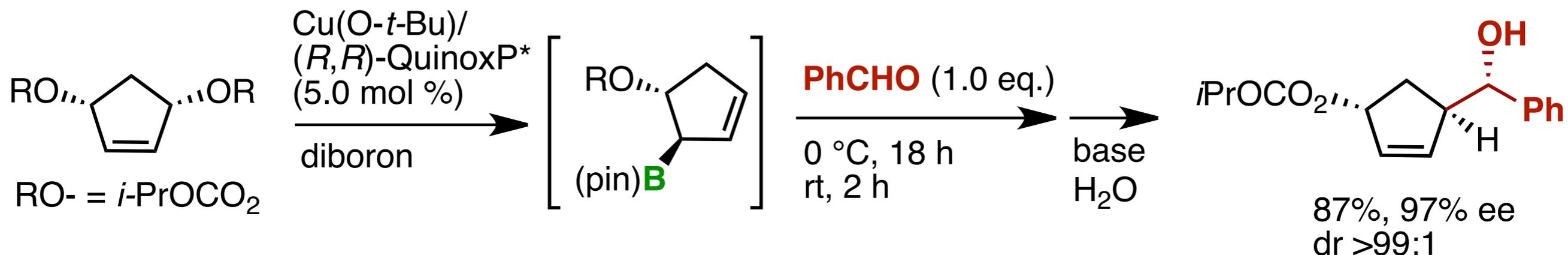
Ito, H.; Kawakami, C.; Sawamura, M. *J. Am. Chem. Soc.* **2005**, *127*, 16034.

## ■ アリルホウ素化合物の触媒的不斉合成に初めて成功

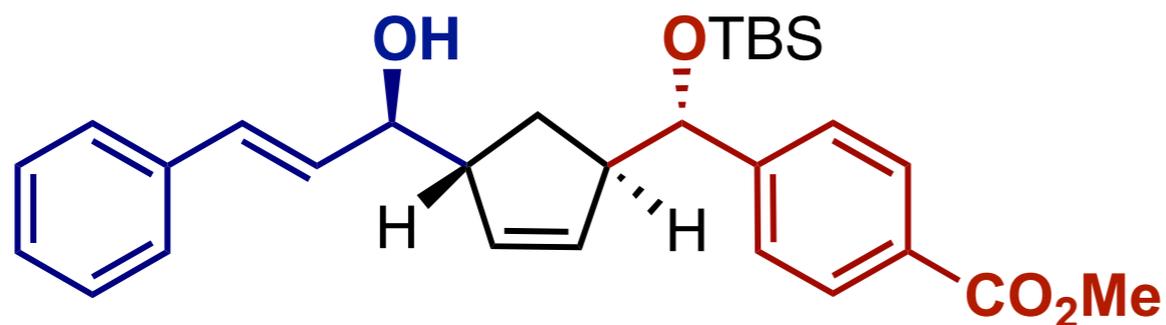


Ito, H.; Ito, S.; Sasaki, Y.; Matsuura, K.; Sawamura, M. *J. Am. Chem. Soc.* **2007**, *129*, 14856.

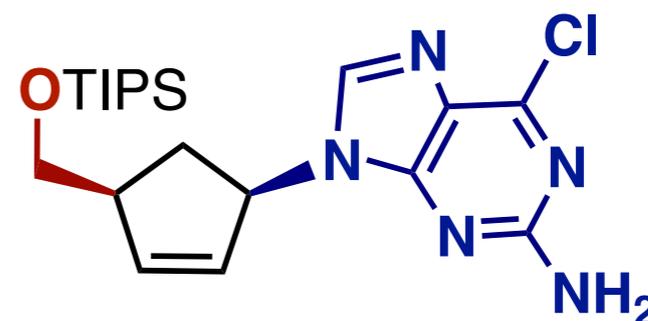
# メソ化合物の非対称化・アレニルホウ素合成



Ito, H.; Okura, T.; Matsuura, K.; Sawamura, M. *Angew. Chem., Int. Ed.* **2010**, 49, 560.

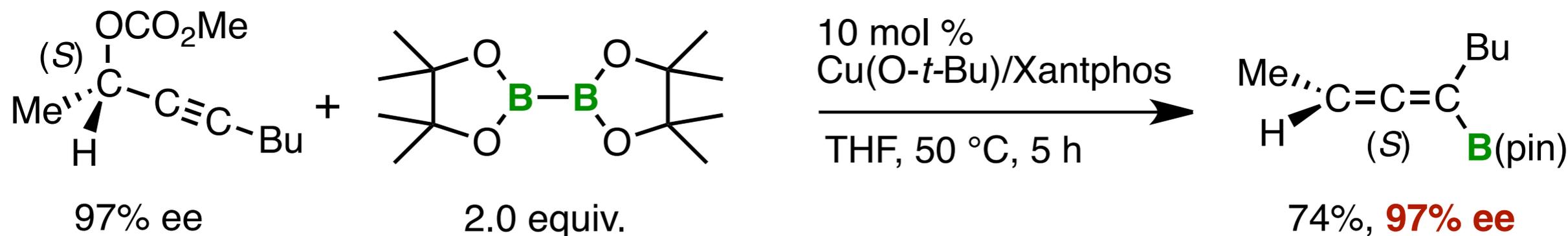


97% ee, >98% ds  
 複雑な構造の迅速不斉合成



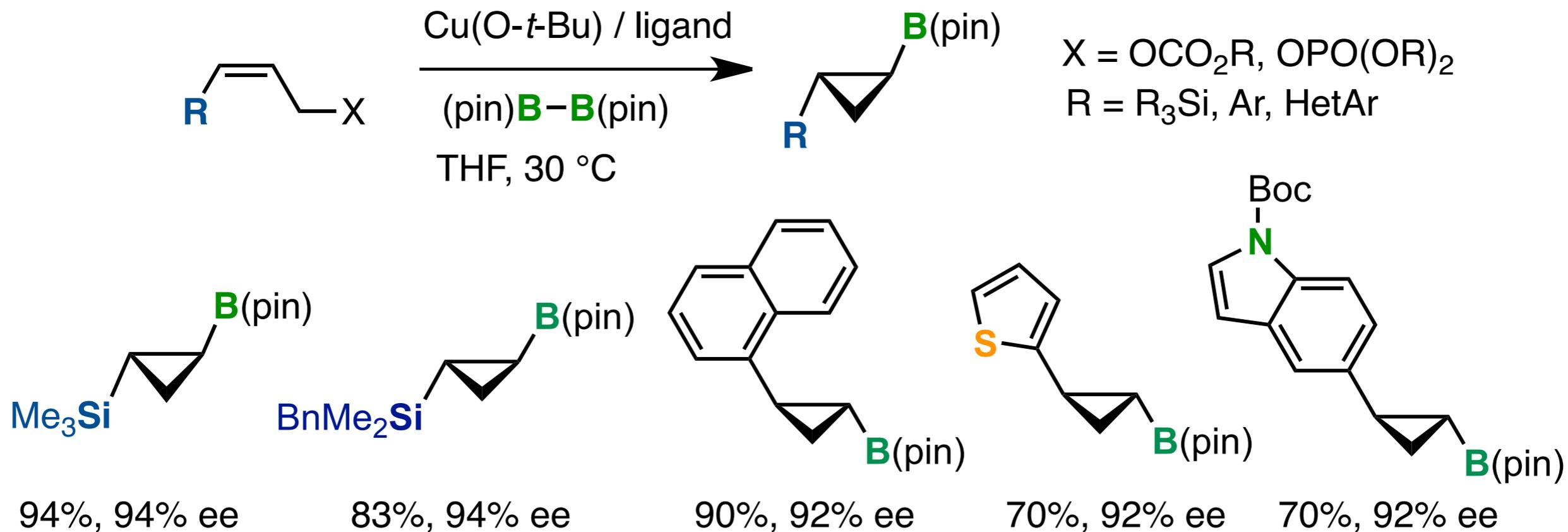
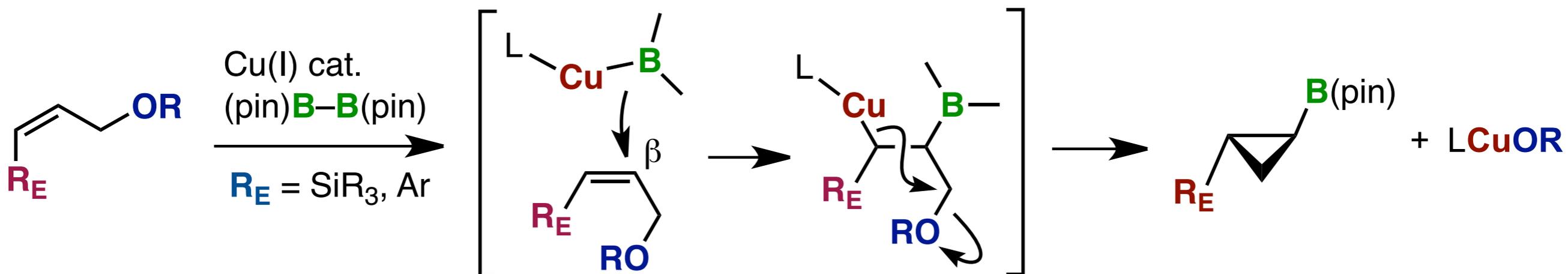
抗ウイルス剤前駆体

## ■ 高い光学純度を持つアレニルホウ素化合物の合成に始めて成功



Ito, H.; Sasaki, Y.; Sawamura, M., *J. Am. Chem. Soc.* **2008**, 130, 15774.

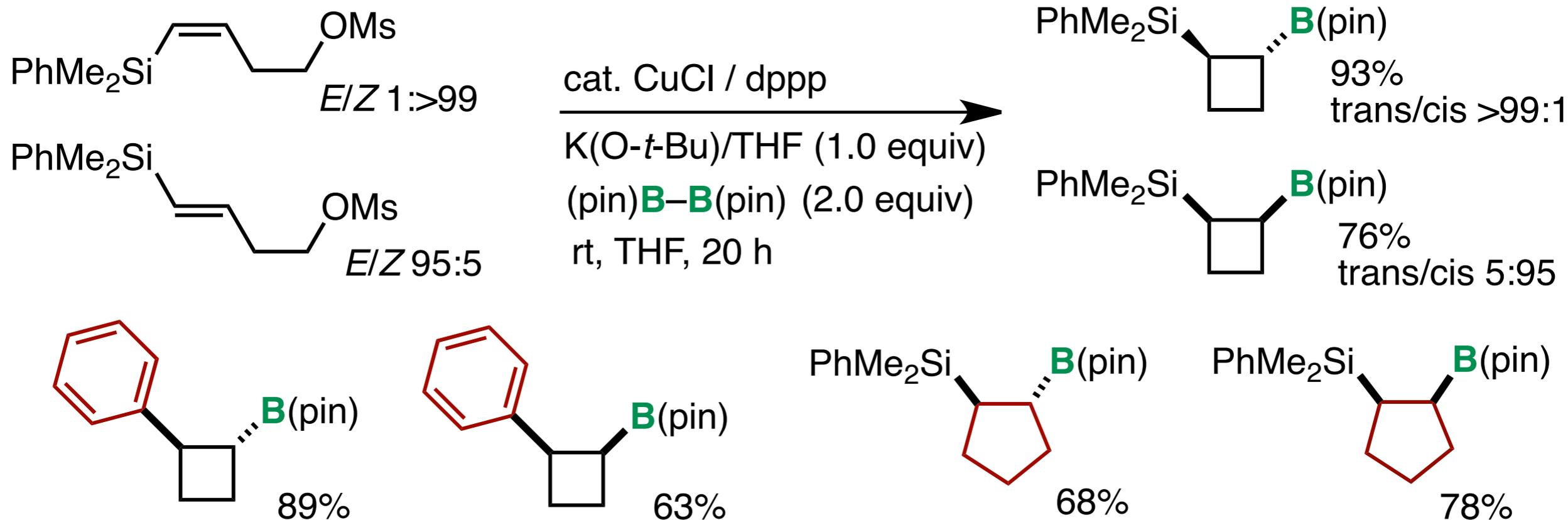
# 不斉環化ホウ素化反応の開発



**Ito, H.**; Kosaka, Y.; Nonoyama, K.; Sasaki, Y.; Sawamura, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7424.  
 Zhong, C.; Kunii, S.; Kosaka, Y.; Sawamura, M.; **Ito, H.** *J. Am. Chem. Soc.* **2010**, *132*, 11440.

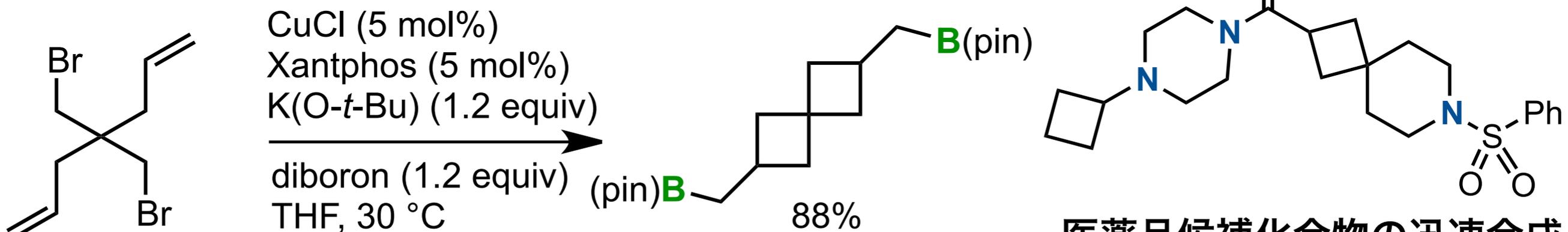
# さまざまな選択的環化ホウ素化への展開

## ■ 四員環・五員環化合物も立体選択的に合成可能



Ito, H.; Toyoda, T.; Sawamura, M. *J. Am. Chem. Soc.*, **2010**, *132*, 5990.

## ■ アルケニルハライドの環化

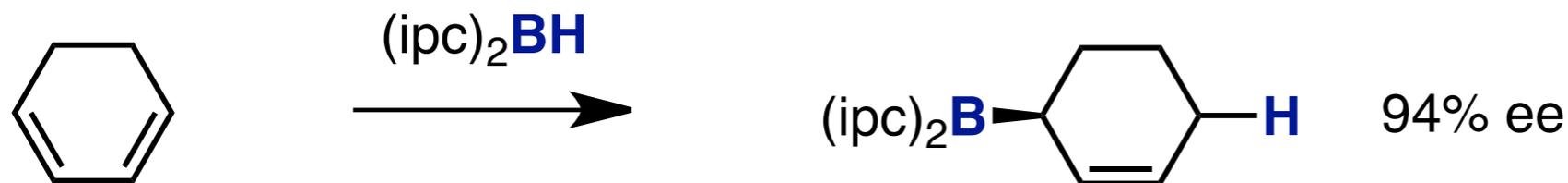


Kubota, K.; Yamamoto, E.; Ito, H. *J. Am. Chem. Soc.* **2013**, *135*, 2635.

医薬品候補化合物の迅速合成  
*Histamine H3 Receptor Ligand*

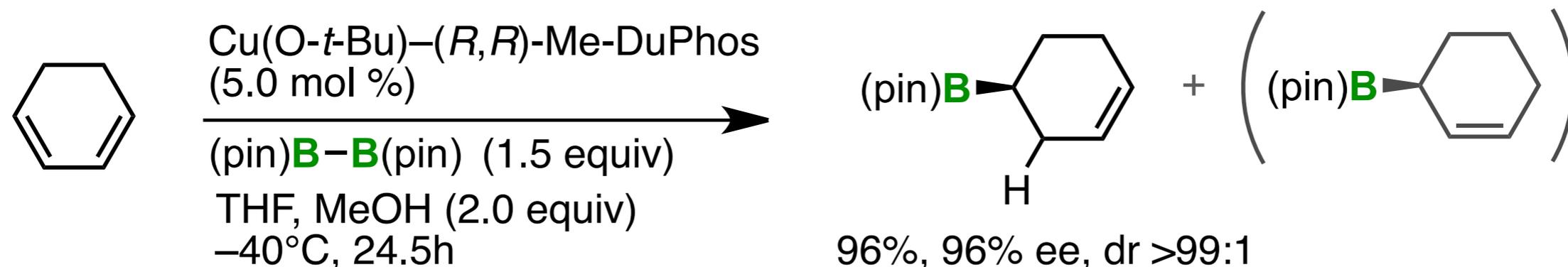
# 不斉ヒドロ (プロト) ホウ素化反応の開発

【背景】 1,3-ジエンでは、1,4-ヒドロホウ素化のみ報告例あり



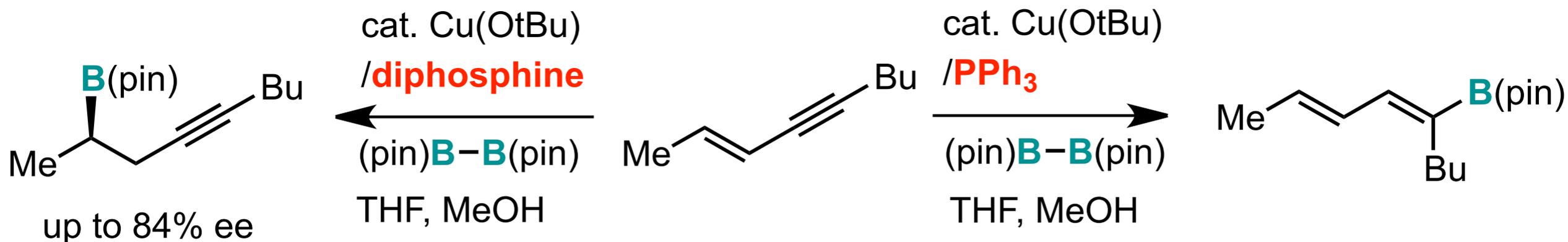
Brown, H. C.; Jadhav, P. K.; Bhat, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 2564.

## ■ 触媒的1,2-不斉ヒドロホウ素化に初めて成功



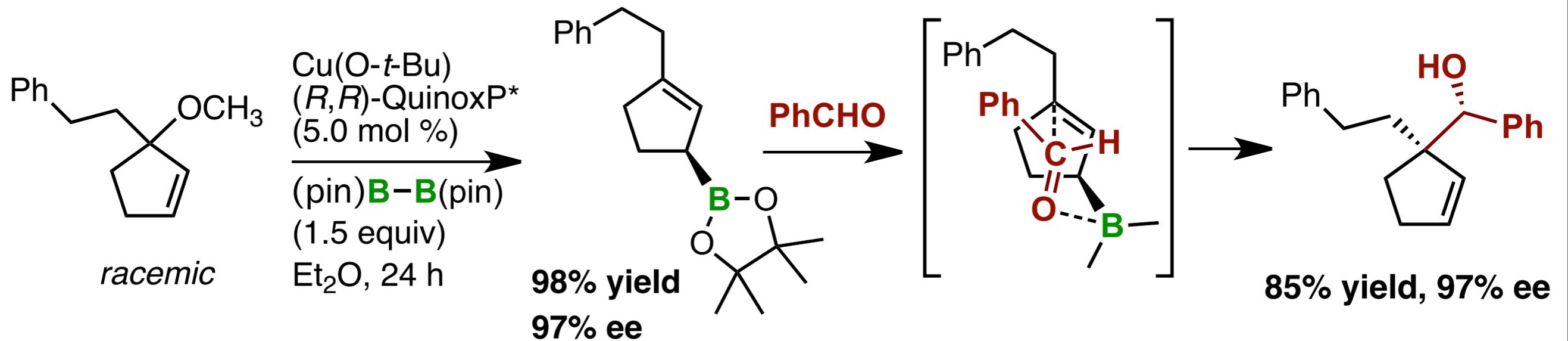
Sasaki, Y.; Zhong, C.; Sawamura, M.; Ito, H. *J. Am. Chem. Soc.* **2010**, *132*, 1226.

## ■ 1,3-enyne の選択的ヒドロホウ素化を実現した



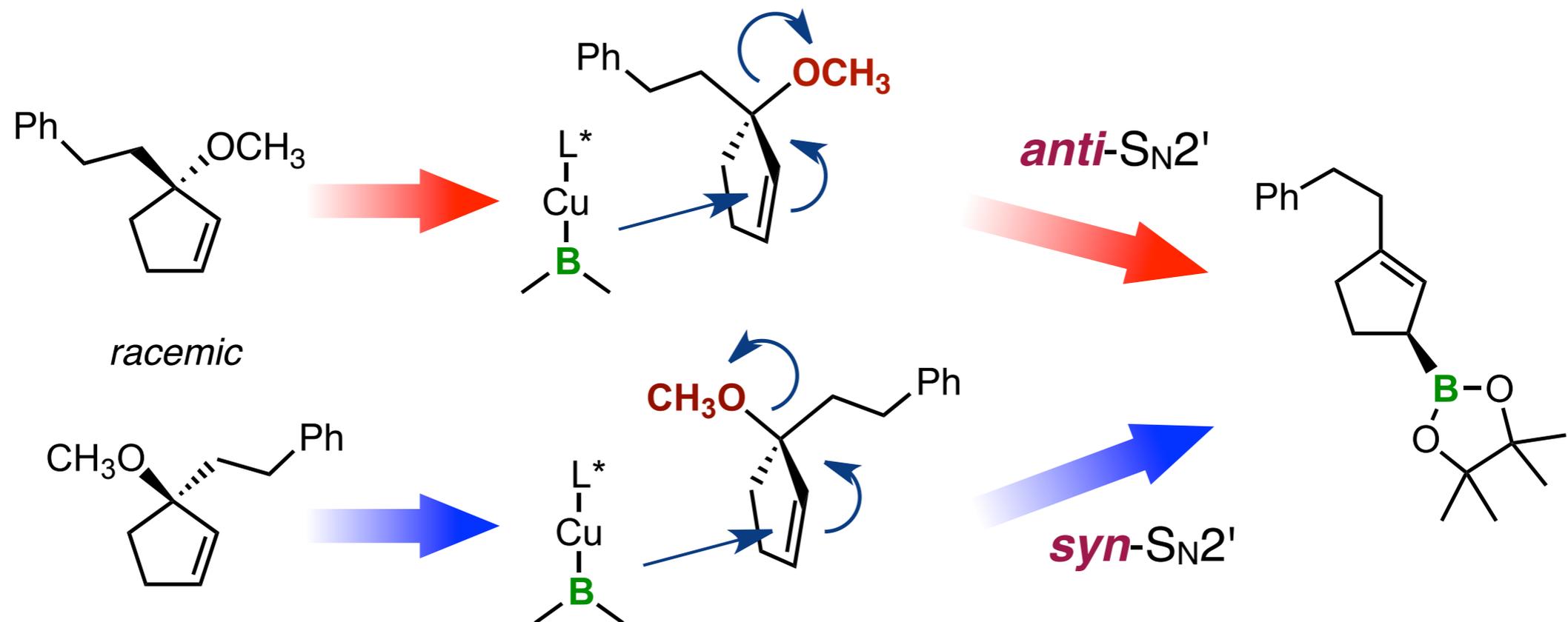
Sasaki, Y.; Horita, Y.; Zhong, C.; Sawamura, M.; Ito, H. *Angew. Chem., Int. Edit.* **2011**, *50*, 2778.

# 直接エナンチオ収束反応：人工触媒で初の発見

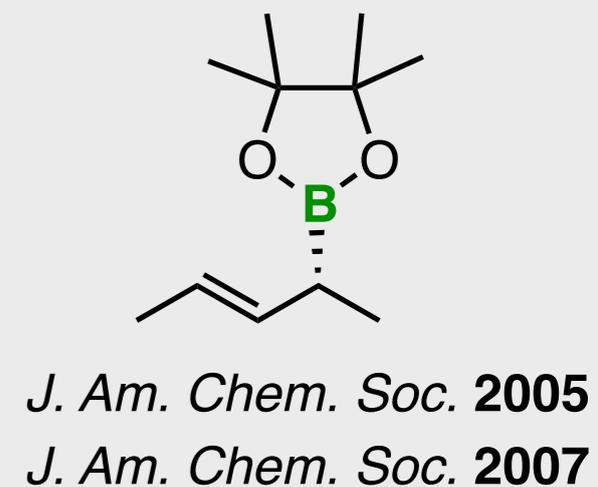
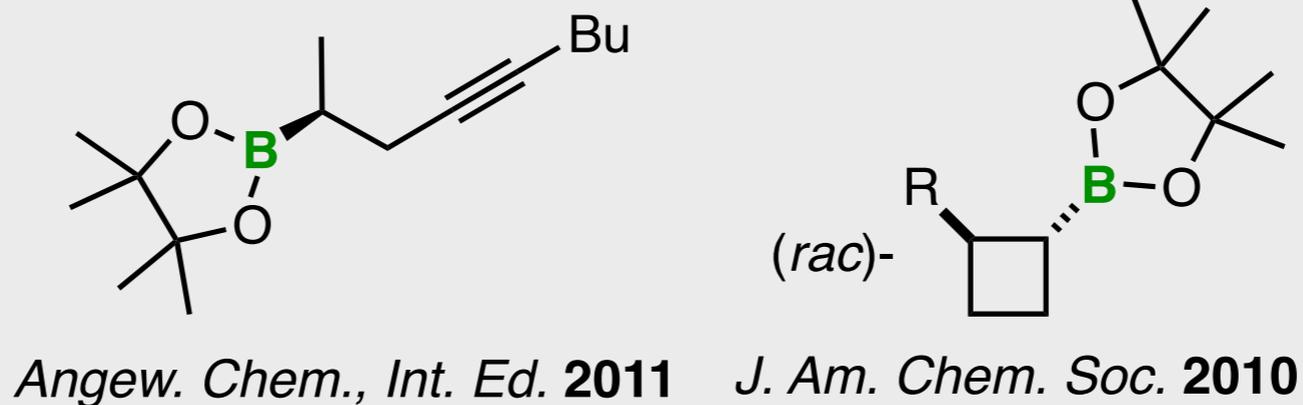
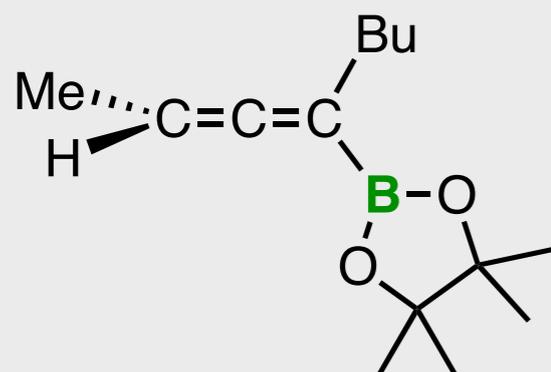


Ito, H; Kunii, S; Sawamura, M. *Nature Chemistry*, 2010, 2, 972.

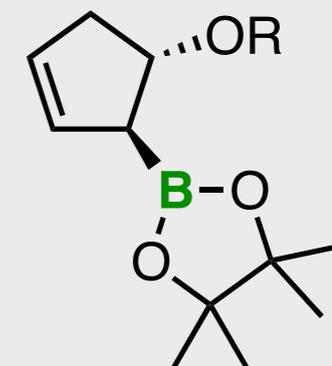
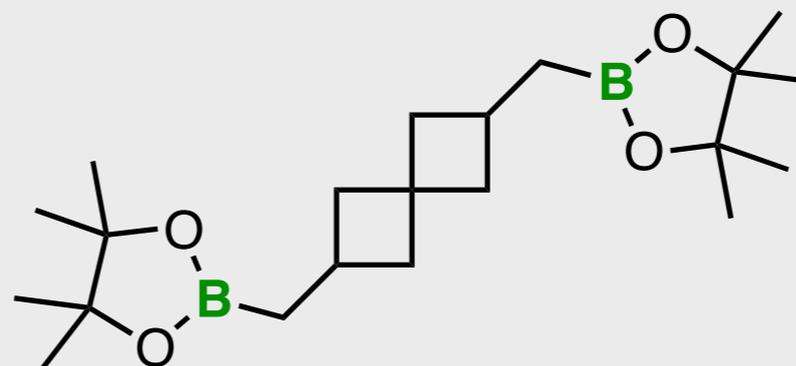
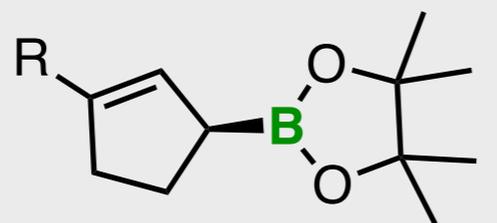
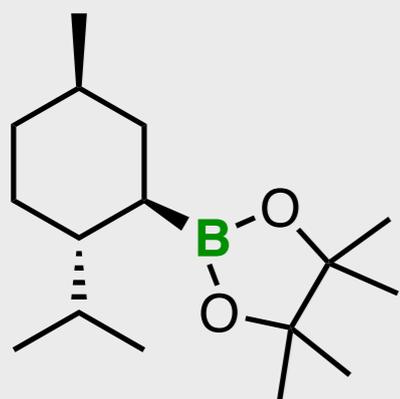
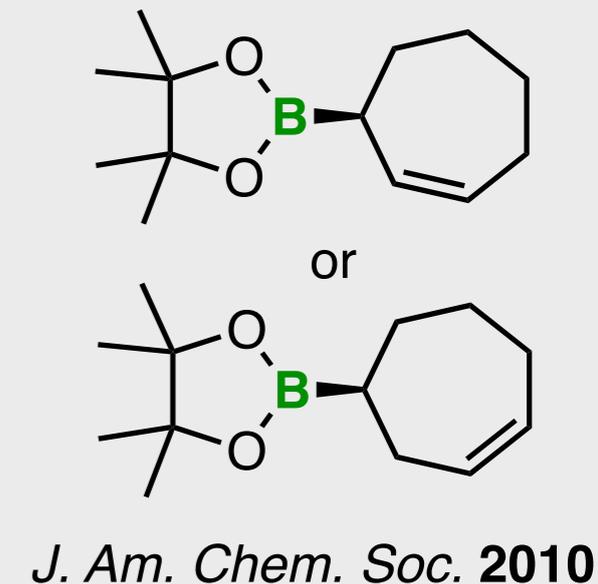
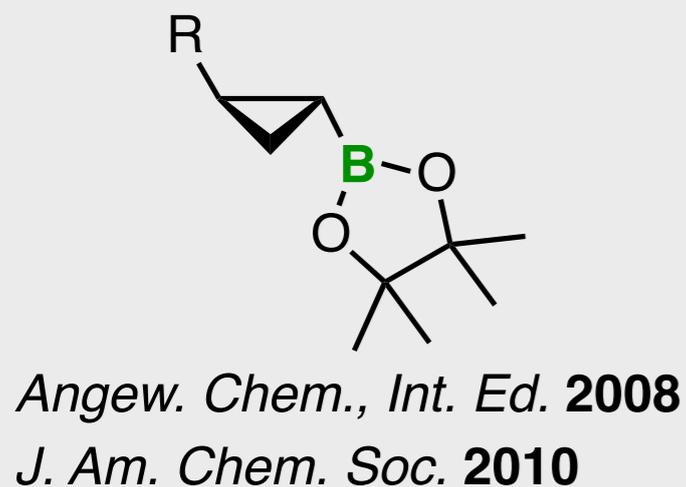
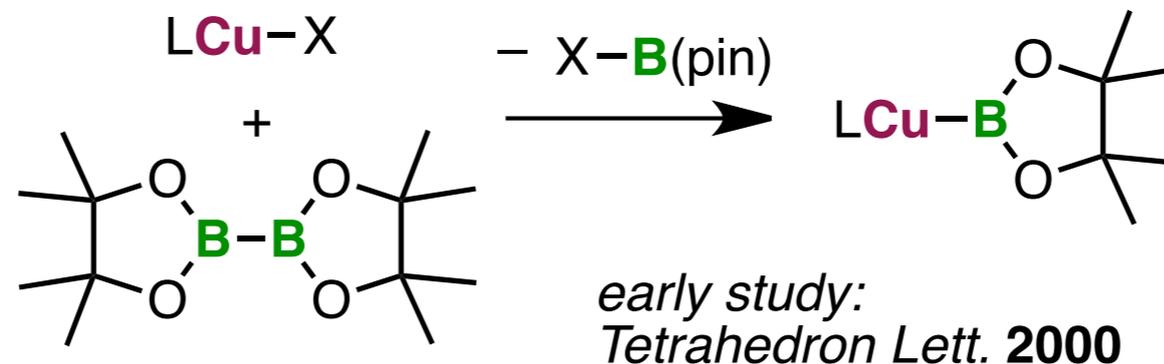
## ■ 一つの不斉触媒が二つのエナンチオ選択的反応を進行させる



# 過去に合成できなかった有機ホウ素化合物の新合成方法

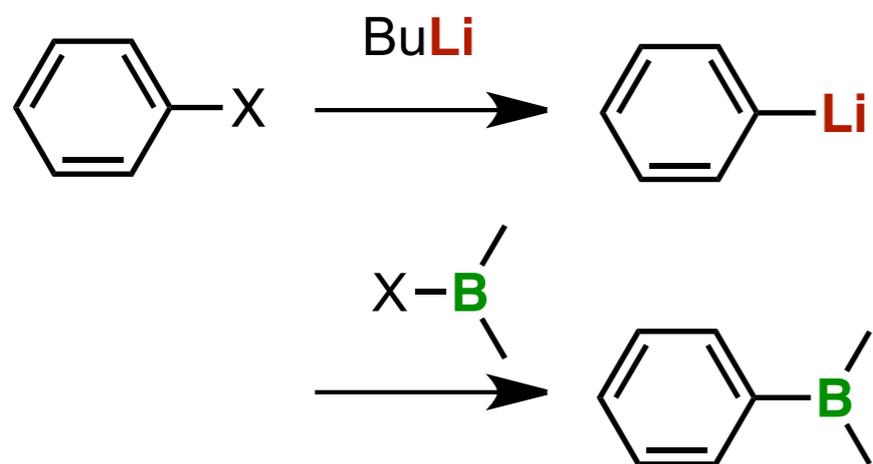


■ ホウ素-銅触媒活性種を用いた  
ホウ素化反応を世界で初めて開発した。



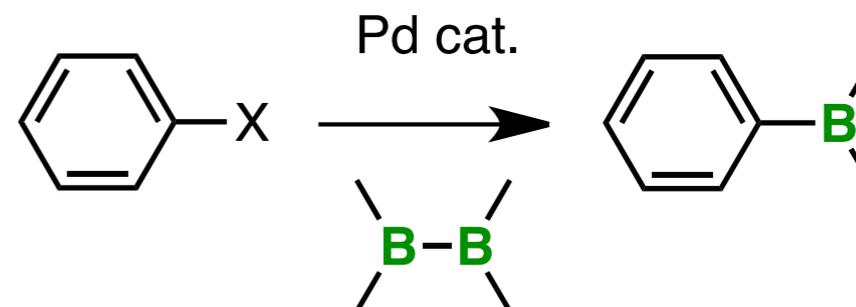
# 最近の新しい研究 (銅触媒以外)

## ■ アリールホウ素化合物の古典的合成



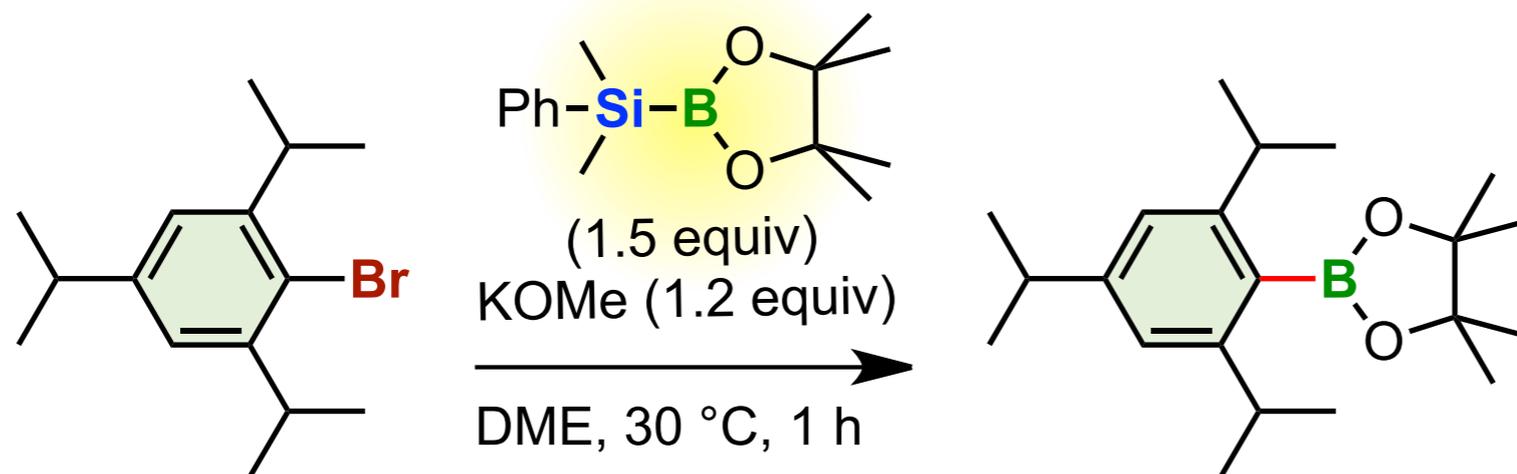
官能基許容性に問題あり

## ■ 宮浦パラジウム触媒法



パラジウム触媒の残存  
立体障害に弱い

## ■ シリルボラン/塩基法 遷移金属フリーのホウ素化



92% yield

Yamamoto, E.; Izumi, K.; Horita, Y.; Ito, H. *J. Am. Chem. Soc.* **2012**, *134*, 19997.

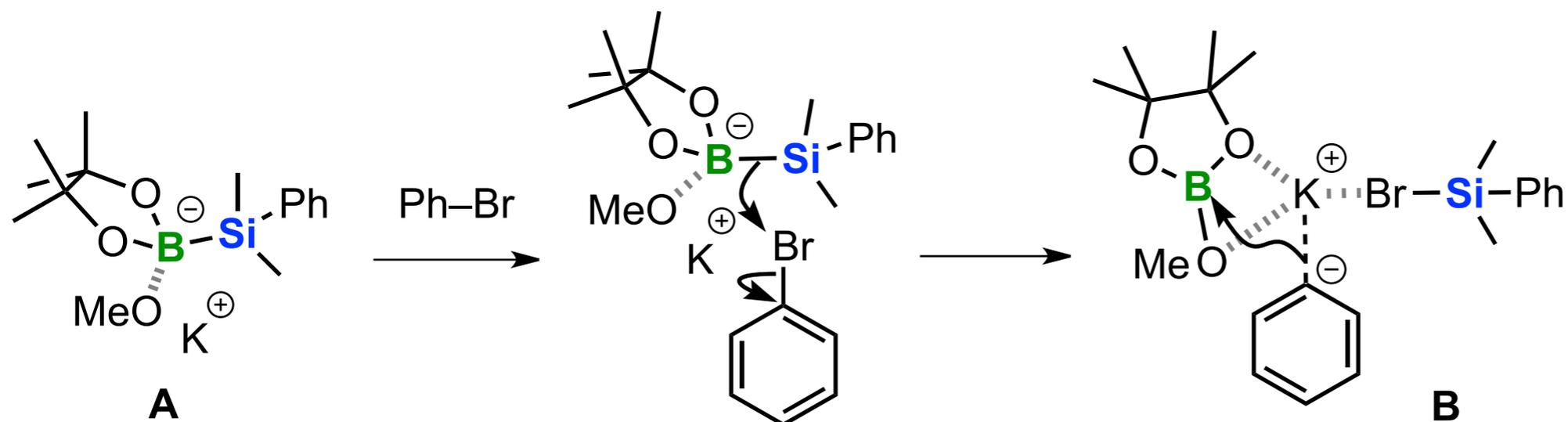


山本英治博士

堀田優子 泉 清孝

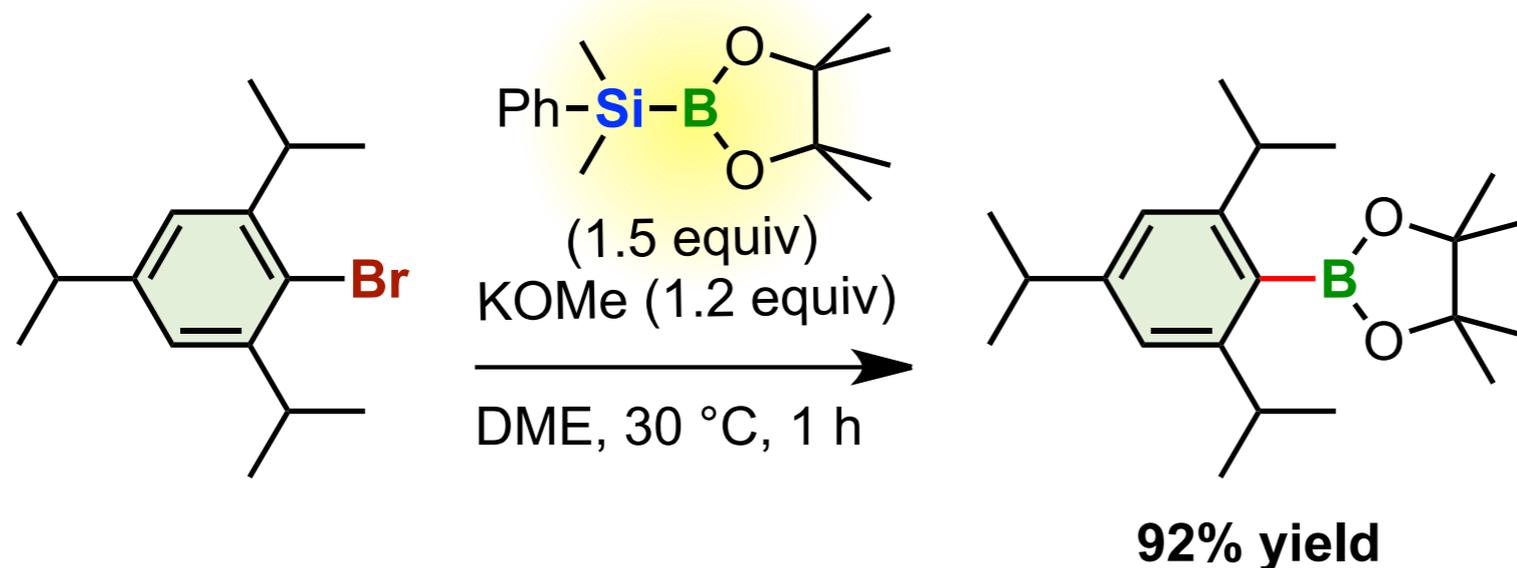
# 最近の新しい研究 (銅触媒以外)

## ■ AFIR/DFT 法による反応機構の研究: Ar基のホウ素への求核攻撃



北海道大学  
武次徹也 教授  
前田理 准教授  
植松遼平 君  
との共同研究

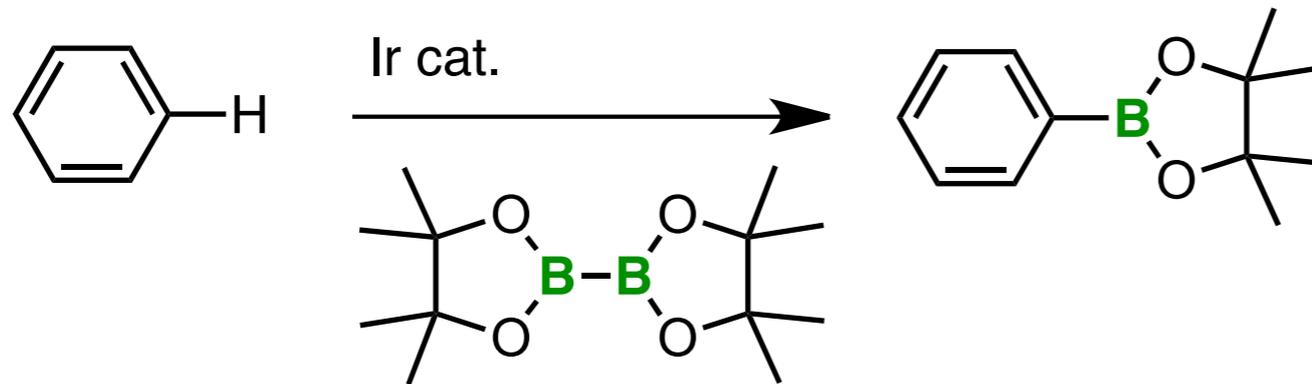
## ■ シリルボラン / 塩基法 遷移金属フリーのホウ素化



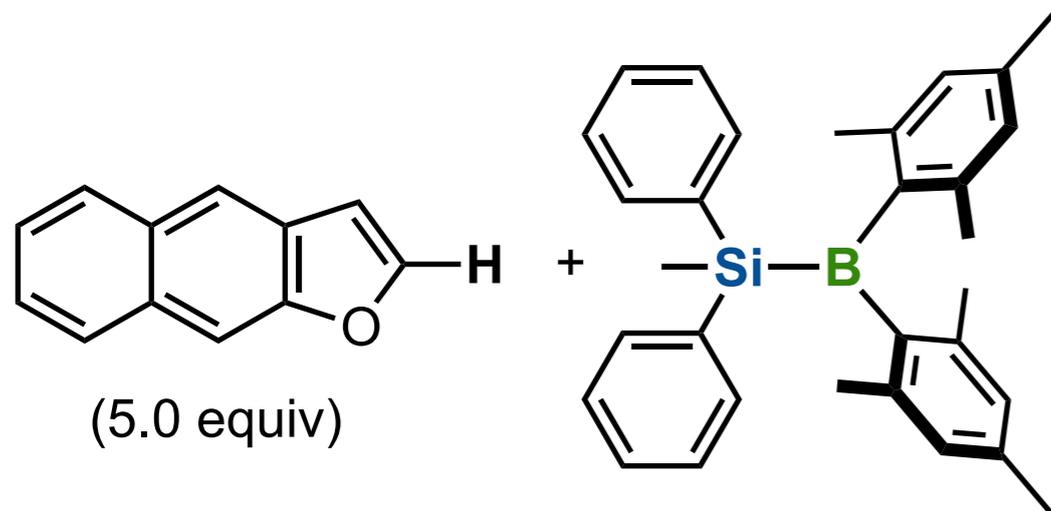
Yamamoto, E.; Izumi, K.; Horita, Y.; Ito, H. *J. Am. Chem. Soc.* **2012**, *134*, 19997.

# 最近の新しい研究 (銅触媒以外)

## ■ アリールホウ素化合物の合成：石山一宮浦ホウ素化



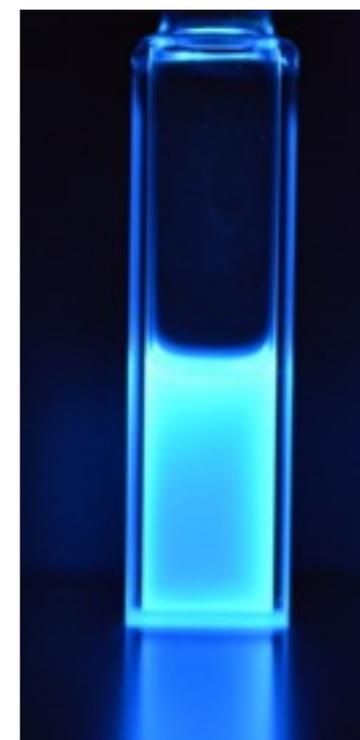
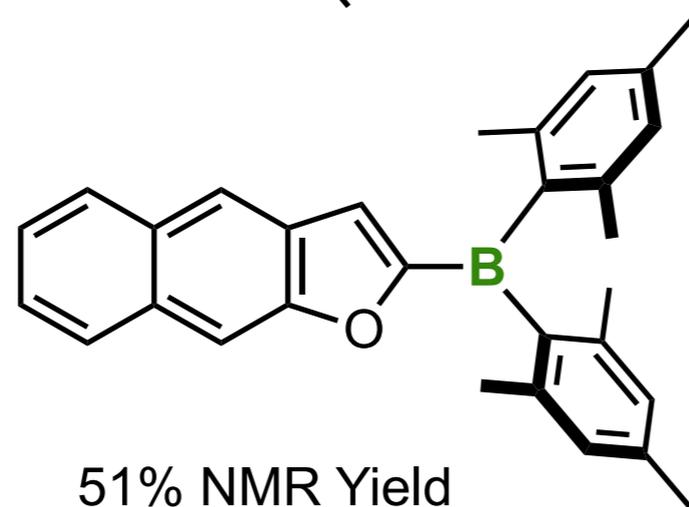
石山竜生准教授



## ■ CH活性化による 直接トリアリールボラン合成

catalyst:  
[IrCl(coe)<sub>2</sub>]<sub>2</sub>  
IMesCl  
K(O-*t*-Bu)

Dioxane  
100 °C, 48 h



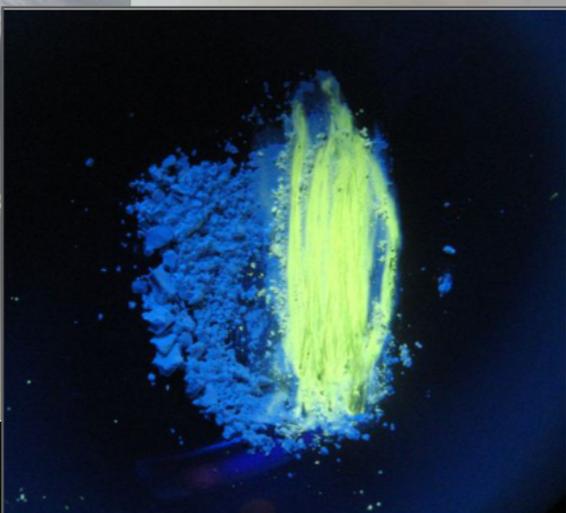
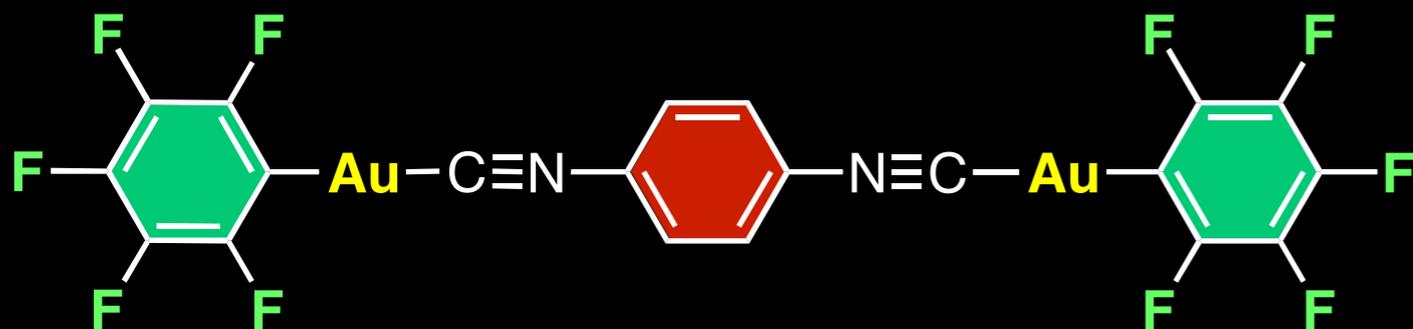
佐々木郁夫博士

詳細は明日  
28日 **2B4-12**

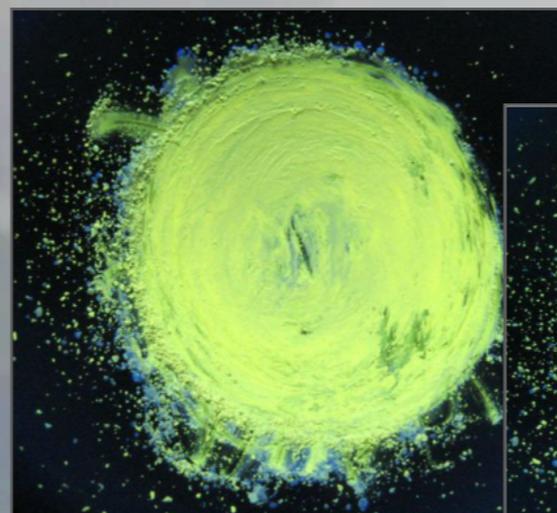
## 1. 銅触媒によるホウ素化反応：発見と展開

## 2. メカノ応答性をもつ発光性金錯体

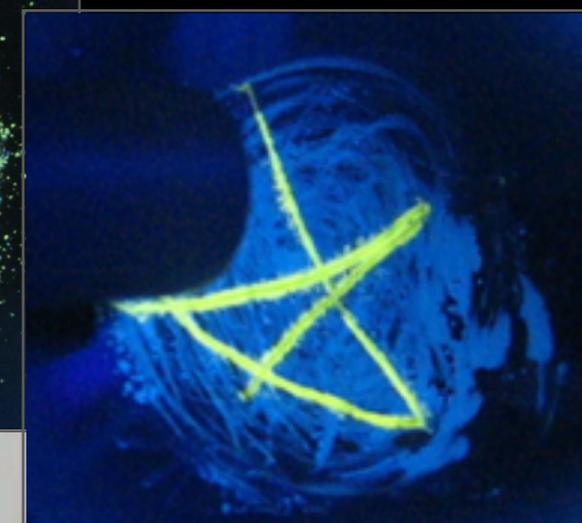
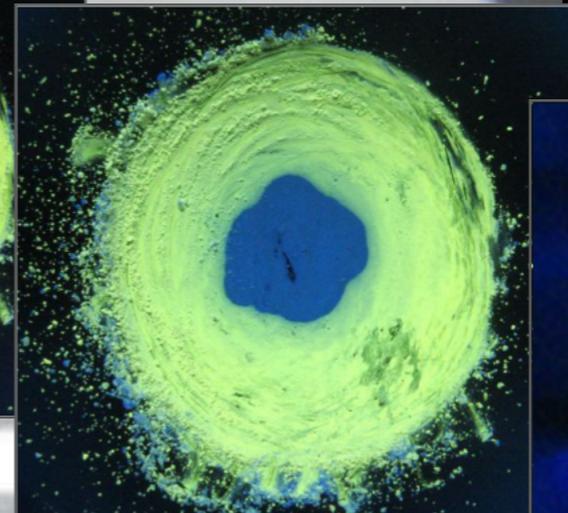
# 発光性メカノクロミズム



UV (365 nm)



UV (365 nm)



✓ 機械的刺激を与えた分  
発光色が変化

✓ 溶媒添加により  
もとにもどる

# 多数のジャーナルで紹介された



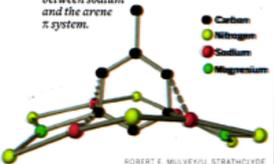
## SCIENCE & TECHNOLOGY CONCENTRATES

### 'SEWING MACHINE' MANIPULATES DNA MOLECULE

This ain't your grandmother's sewing machine. Using a single DNA molecule as a thread, researchers in Japan designed microhooks and microbobbins to form a "sewing machine" to manipulate DNA. Chromosomal DNA molecules are used in hybridization, protein binding, and epigenetics experiments. Because a chromosomal DNA double helix is only 2 nm in diameter, with a length ranging from millimeters to centimeters, the molecule easily breaks from hydrodynamic shear. To prevent this breakage, the research team, led by Kyobei Terao at Kyoto University, designed microscopic tools to move and direct the DNA (*Lab Chip*, DOI: 10.1039/b803753a). The tools, created via photolithography, consist of a Z-shaped microhook to catch the DNA and a microbobbin, around which the DNA is wrapped. Using laser methods to manipulate the microtools, Terao and colleagues captured and separated pairs of DNA helices with the microhook. Terao's group also wrapped and unwrapped the DNA from two microbobbins. These tools, the researchers say, will allow the use of large DNA molecules in genetics studies and biochemical assays.

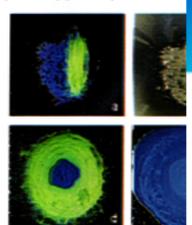
### ADDING METALS TO TOLUENE

Mixed-metal reagents can be tuned to selectively create metal-carbon bonds in toluene at 2,5 or 3,5 positions, depending on the identity of an alkyl component, says a group of researchers led by Robert E. Mulvey of the University of Strathclyde, in Scotland (*Angew. Chem. Int. Ed.*, DOI: 10.1002/anie.200801158). The Toluene can be selectively dimetalated at the 3,5 ring position. Dashed lines indicate interactions between sodium and the arene π system.



### GOLD COMPLEX CHANGES COLOR REVERSIBLY

Gentle grinding of a new Au(I) complex in solid form changes its luminescence behavior, Japanese researchers report. The color change in the compound as it goes from blue to yellow is reversible. The fully ground powder (c) drops of dichloromethane (d). Powder turned completely blue by solvent (e) reverts to yellow after the solvent evaporates and the solid is again ground with a pestle (f). Chemists Hajime Ito, Masaya Sawamura, and colleagues at Hokkaido University, in Sapporo, detected no change after 20 cycles of blue-to-yellow conversion (1,4-diisocyanobenzene) complex (*J. Am. Chem. Soc.*, DOI: 10.1021/ja8019356). X-ray and IR studies suggest that the stable crystalline blue phase into an amorphous coordination of the isocyanide ligands to the gold could be used in recording and sensing devices.



See a video of the reversible photochromism at [www.cen-online.org](http://www.cen-online.org).



### Mechanochromism: Gold crush

When Naoya Oshima gently pressed the powder of a newly developed gold(I) compound between two microscope slides in order to measure its emission spectrum, he noticed a change in its luminescence properties. The subsequent investigation of this effect by the team from Hokkaido University<sup>1</sup> showed subtle changes in molecular arrangement to be the origin of this mechanochromism.

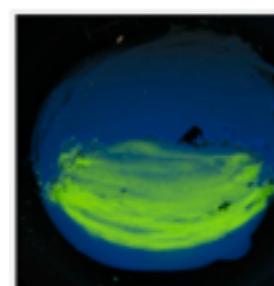


Fig. 1 | Photograph showing the color change of a gold(I) compound under UV light illumination. The part of powder that was crushed shows yellow luminescence, contrasting with the blue luminescence from the original compound.

There are not many reports on luminescence mechanochromism—the luminescent color change of a compound as a result of mechanical grinding. Under visible light the gold(I) compound [(C6F5Au)<sub>2</sub>(μ-1,4-Diisocyanobenzene)] appears no different, and has a grey-yellowish appearance. However, under UV irradiation the compound shows blue luminescence that shifts to yellow when the material is gently crushed (Fig. 1). The change in color is fully reversible through the addition of a solvent. Once the solvent evaporates, the color change can be reintroduced through mechanical grinding.

Mechanochromism in another gold(I) compound has been previously observed, but changes in color occurred through a chemical reaction, while in present experiments the origin is a more subtle interaction within the molecules of the solid compound. "The color change in our gold(I) compound is induced by changes in molecular arrangement, where weak bonds between gold atoms form," says Masaya Sawamura, leader of the project.

Upon gentle grinding, the so-called aurophilic interaction between the gold atoms leads to a change in the intermolecular attraction that alters their bonding structure. This in turn causes shifts in the molecule's electronic states and subsequent changes in their emission characteristics. The aurophilic interaction is broken again through the addition of a solvent. As the interaction is very weak, the process leads to no further modifications of the molecules and therefore is reversible.

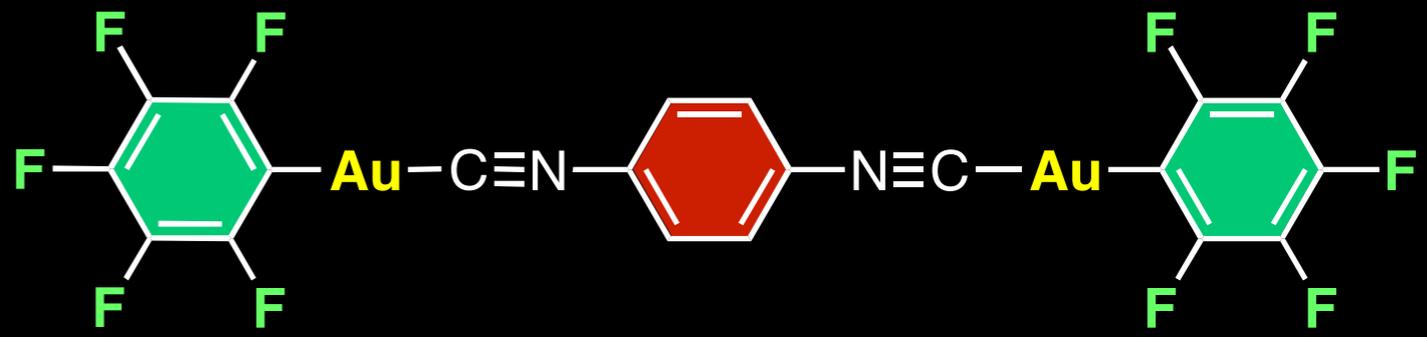
These findings have fundamental implications. "The observation that mechanical stimuli can change the intermolecular interactions is a powerful concept that could be used to design new materials with controllable emission properties," says Sawamura. For example, mechanochromic materials with different colors could be designed, or even compounds where the color change is the result of a chemical reaction.



C&EN  
JULY 17, 2008

Nature Asia Materials  
Oct 10, 2008

N. Oshima T. Saito



### EDITORS' CHOICE

EDITED BY GILBERT CHIN AND JAKE YESTON

#### VIROLOGY Modeling Microbicides

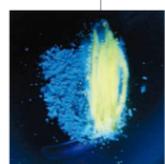
Phase III clinical trials are underway to test the efficacy of antiretroviral (ARV)-based microbicides in preventing HIV transmission. However, the risk that ARVs may be absorbed systemically and promote the evolution of drug-resistant viral strains if used by HIV-positive women remains poorly characterized.

Wilson *et al.* have modeled the effects of ARV-based microbicides on disease dynamics, either as part of a clinical trial or as a widespread public health intervention, in order to compare drugs with a high versus low potential risk for generating resistance. They find that a clinical trial will be unable to distinguish between high- and low-risk microbicides if HIV-positive participants are excluded on the basis of monthly tests for seroconversion (as planned for the upcoming dapivirine trial), given that resistance is expected to take at least 6 months on average to develop. If a high-risk microbicide is used as a public health intervention, the model predicts that the ratio of the number of prevented infections to the number of acquired resistant cases (the benefit-to-cost ratio) may not be much greater than 1. The ratio will be worse for women than for men, given that new cases of resistance will emerge in women initially and that drug-resistant strains have lower transmission efficiency than wild-type HIV. These results highlight the importance of collecting additional data on the resistance risks of new ARV-based microbicides before they are approved for popular use. — NM\*

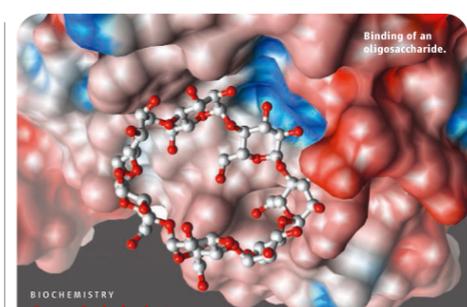
*Proc. Natl. Acad. Sci. U.S.A.* **105**, 9835 (2008). \*Nilah Monnier is a summer intern in Science's editorial department.

#### CHEMISTRY Blue, Yellow, and Gold

Mechanochromic compounds, which undergo a change in color or luminescence when solid samples are crushed or ground, can serve as detectors of mechanical action, but examples of such compounds are rare. Ito *et al.* synthesized a compound in which two C<sub>6</sub>F<sub>5</sub>Au groups are linked by a para-C≡C-H<sub>2</sub>NC ligand, and found that its photoluminescence changes from blue to yellow after grinding. Like other such compounds, its original luminescent state is restored upon dissolution and recrystallization, and this process could be repeated for 20 cycles without any decrease in luminescence. Structural and spectroscopic studies indicate that the long-lived blue emission in the crystal is intramolecular in origin and phosphorescent (a localized intraligand π-π\* transition), whereas the yellow emission appears to arise from an amorphous phase characterized by aurophilic interactions: intermolecular interactions between gold atoms. — PDS



*J. Am. Chem. Soc.* **130**, 10.1021/ja8019356 (2008).



#### BIOCHEMISTRY Curvy Carbohydrates

The global abundance of carbohydrate-based biopolymers and the prevalence of them in our diets support within the human gut a fascinating microbial ecosystem. Its role, from our point of view, is to degrade dietary polysaccharides; the flux through these pathways contributes as much as 10% of our daily calorie intake. One of the inhabitants of the human intestine is *Bacteroides*, and its starch utilization system (Sus) contains a number of regulatory and metabolic genes.

Koropatkin *et al.* have determined the structure of the outer membrane protein SusD on its own and with linear and cyclic oligosaccharides bound. They find that the side chains of aromatic residues of SusD align to offer a curved surface that complements the helical conformation of maltoheptaose as well as the curvatures of α- and β-cyclodextrins (composed of six and seven glucose units, respectively). The multivalent, low-affinity interaction may facilitate hydrolysis of longer polysaccharides by the neighboring amylase SusG or the loading of oligosaccharides into the outer membrane importer SusC. — GJC

*Structure* **16**, 1105 (2008).

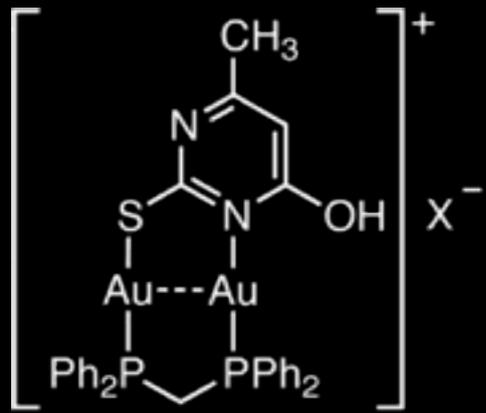
#### APPLIED PHYSICS Unscintillating Conversation

Air-to-air and air-to-ground communication are generally carried out with radiofrequency transmitters and receivers. By comparison, optical-based communication systems offer a number of advantages, including higher bandwidth and the capacity to communicate information at higher rates, bundled with low weight, compact size, low power requirements, and the added security of a direct line-of-sight communication channel. However, the air turbulence that makes stars twinkle or scintillate at a detector presents a substantial problem for airborne optical communication. Unchecked, such turbulence will introduce a large amount of error into a communication channel. As an alternative to the relatively large adaptive

Science July 25, 2008

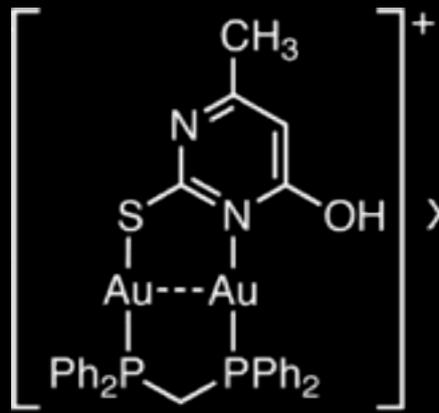
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# 発光性メカノ(ピエゾ)クロミズム: 研究の広がり

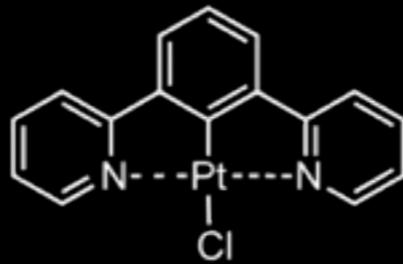


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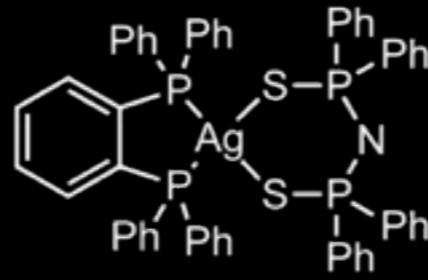
# 発光性メカノ(ピエゾ)クロミズム: 研究の広がり



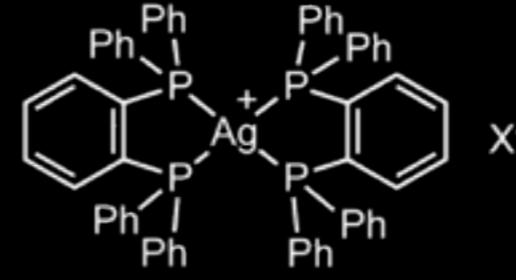
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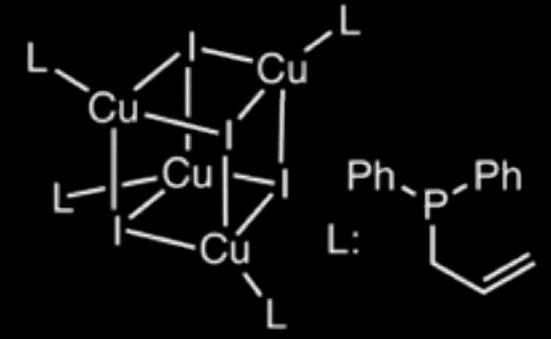
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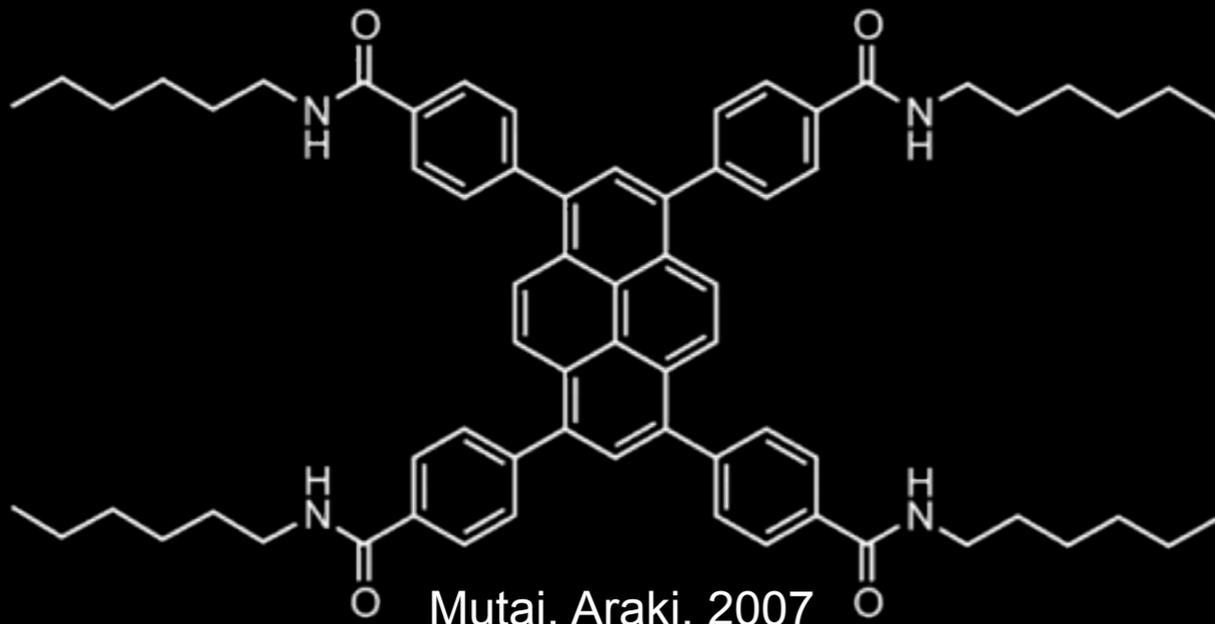
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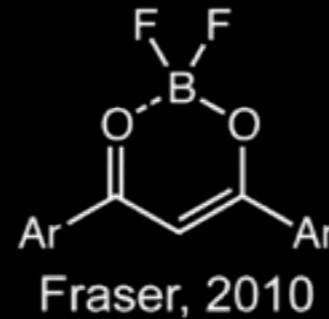
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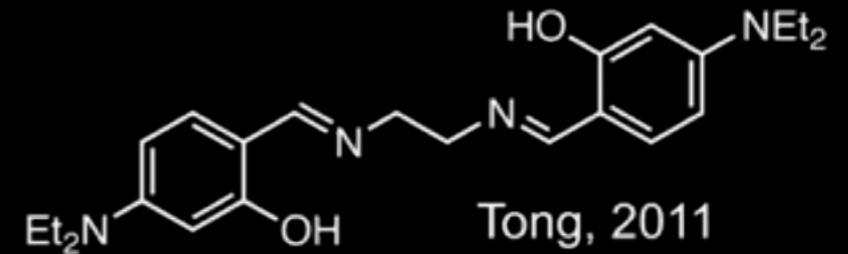
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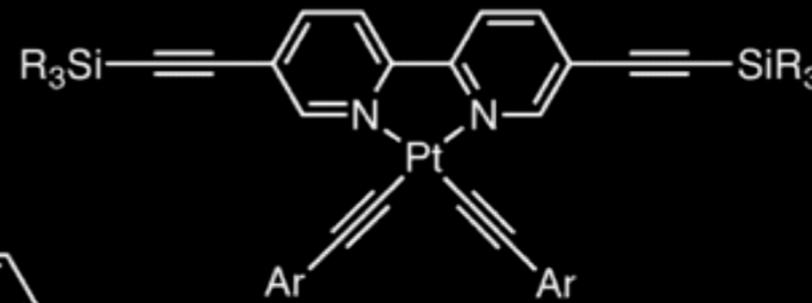
Mutai, Araki, 2007



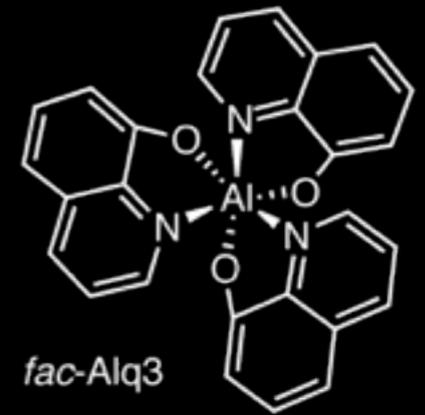
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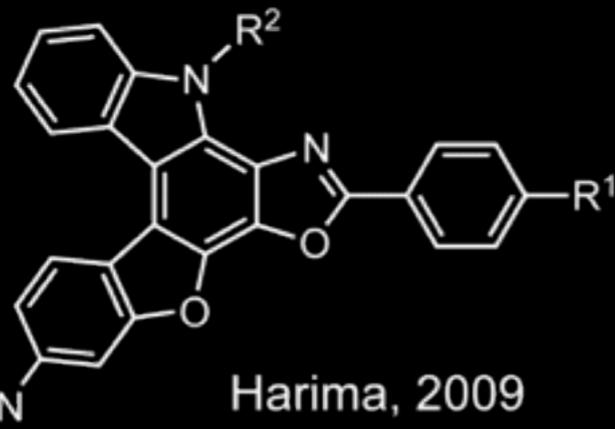
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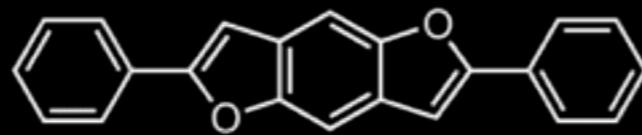
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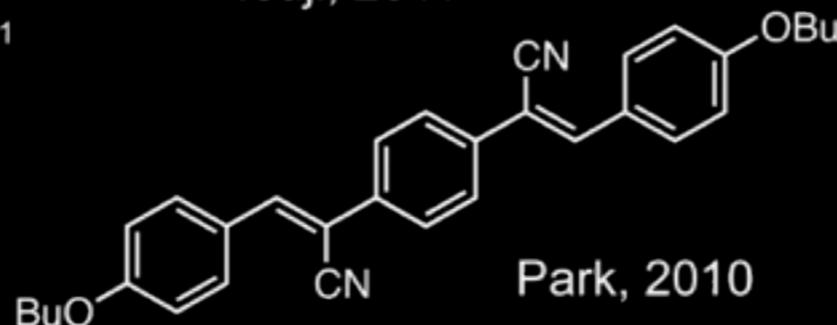
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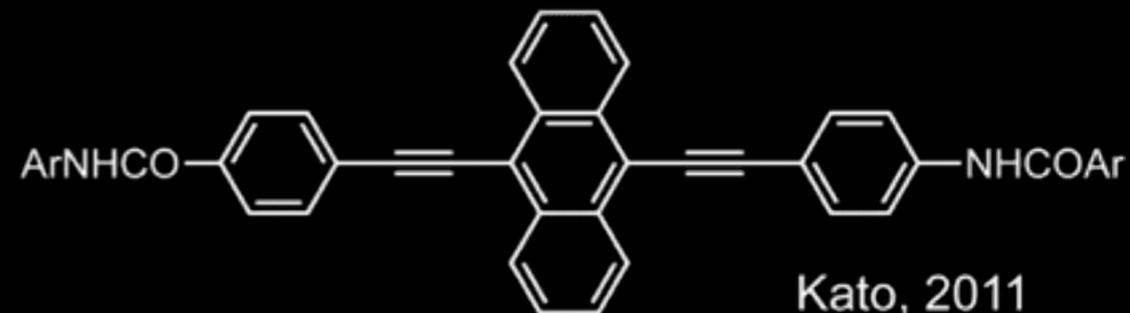
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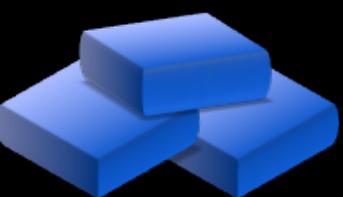
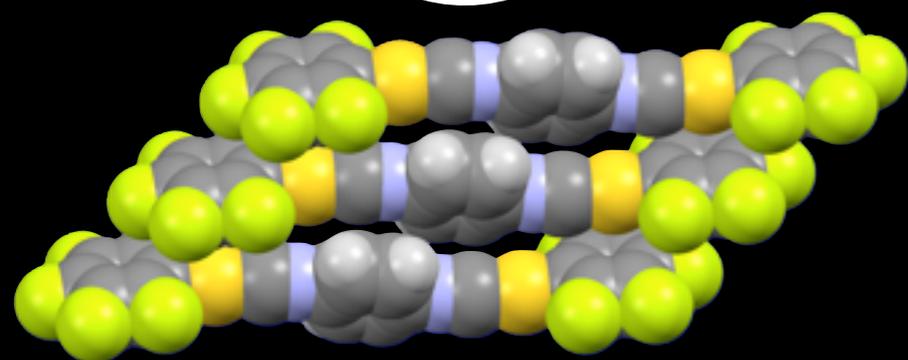
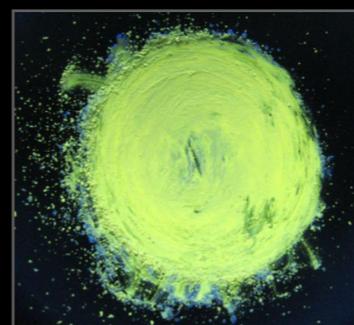


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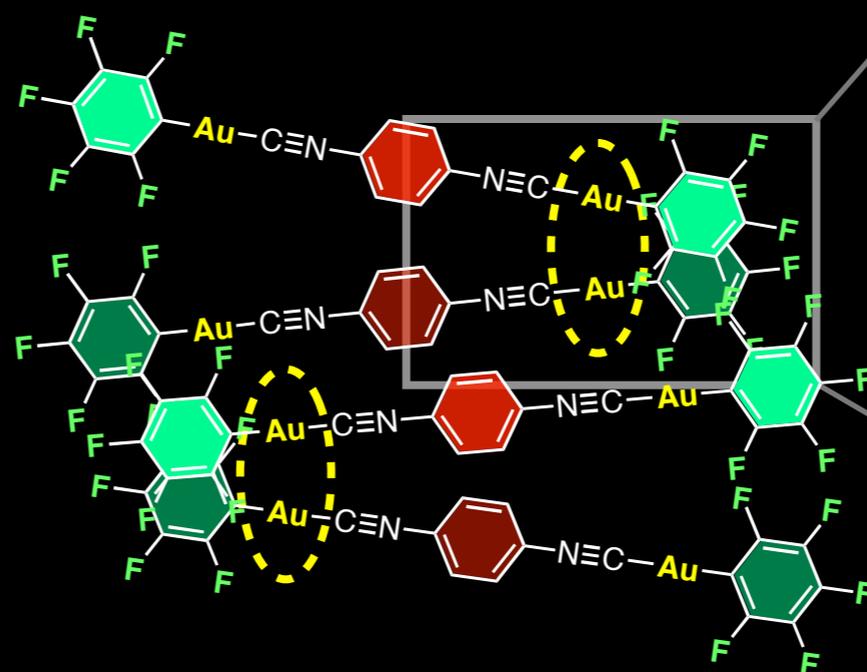


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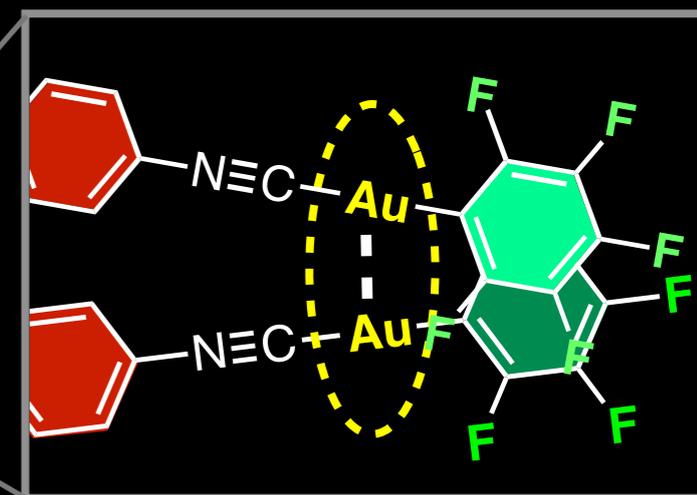
**Grinding**



**Micro Crystallines**  
(Single crystal XRD)



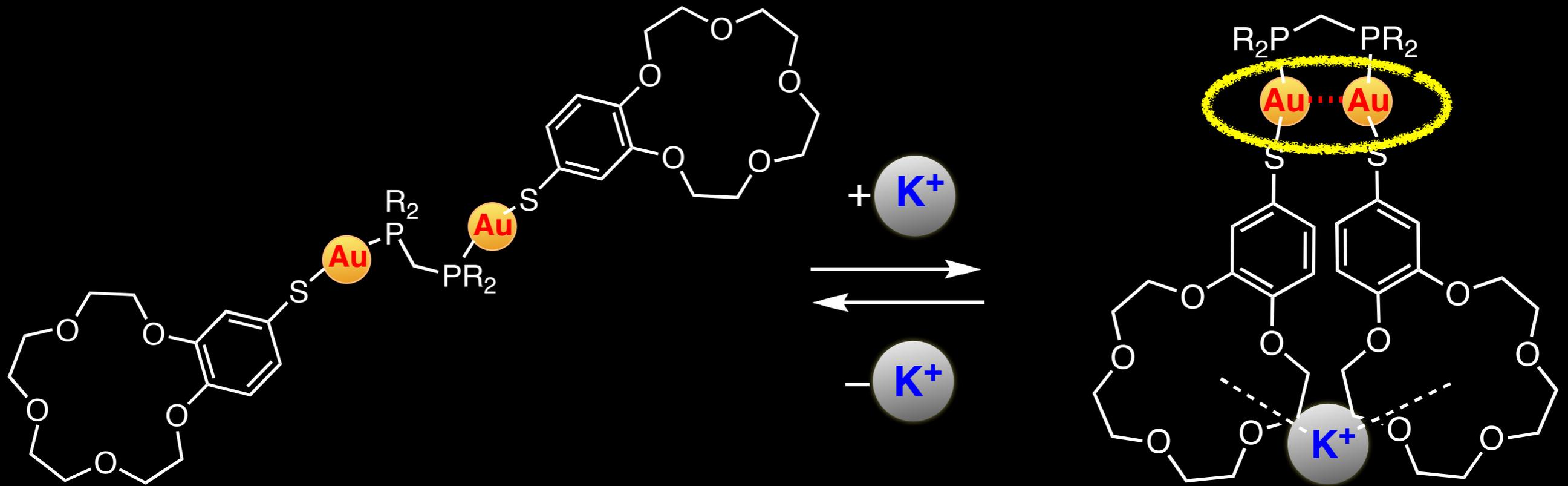
**Amorphous**  
(Powder XRD)



**Aurophilic Interactions**

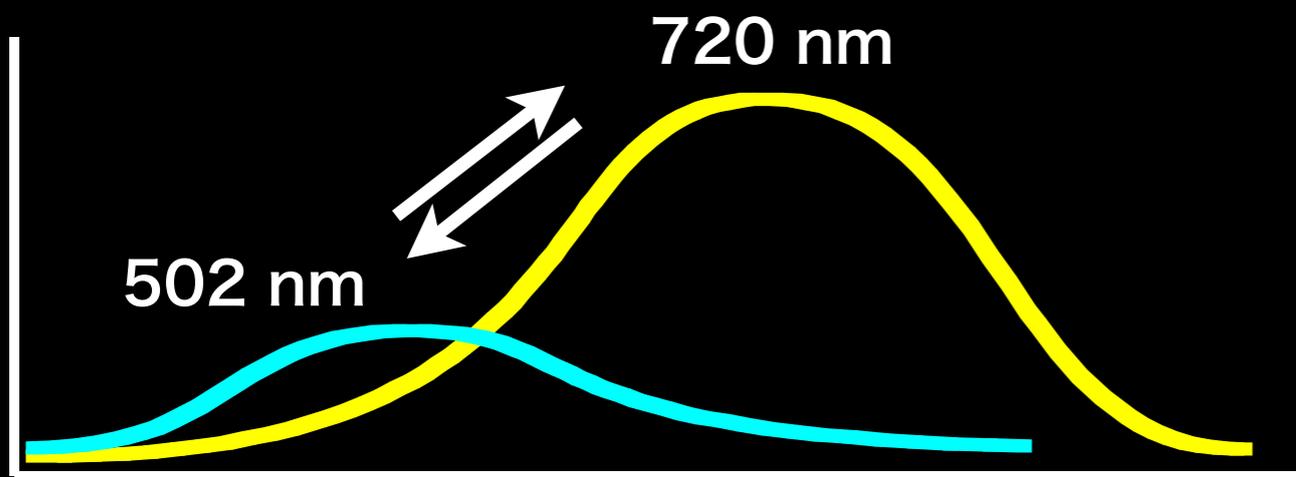
# 金錯体のAurophilicity と発光特性

金原子間距離 < 3.5 Å

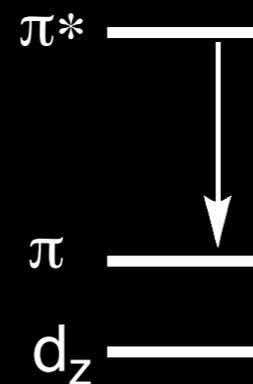


Yam, V. W. W.; Li, C. K.; Chan, C. L. *Angew. Chem. Int. Edit.* **1998**, *37*, 2857–2859.

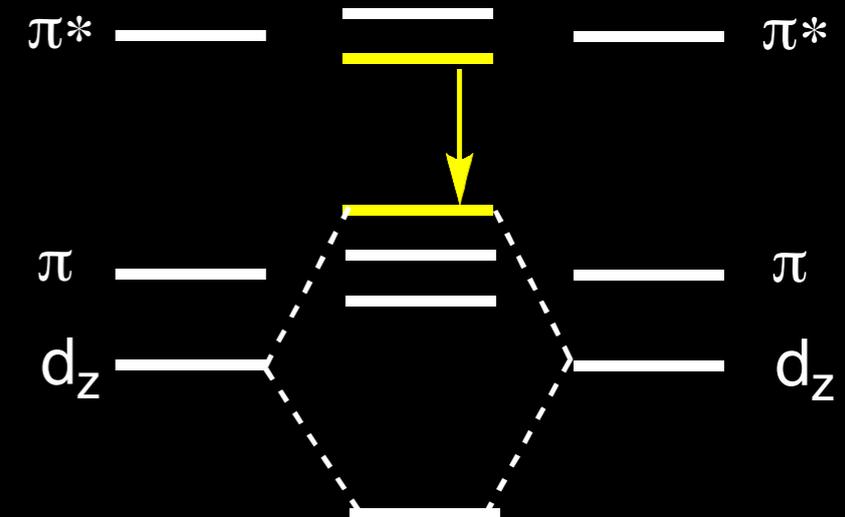
水素結合程度の強さ  
長波長シフトと発光増大



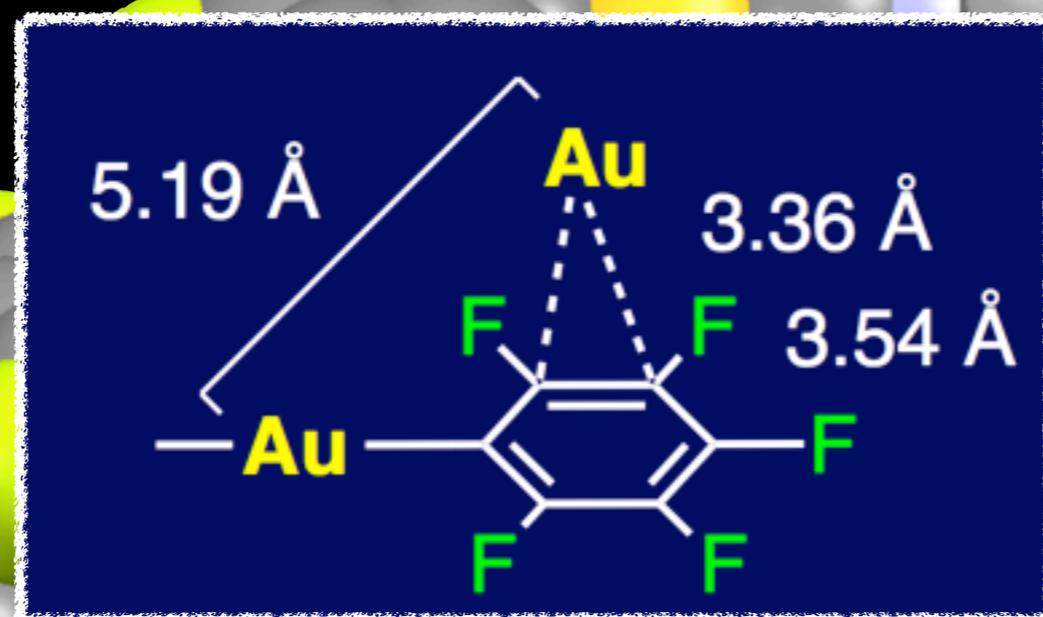
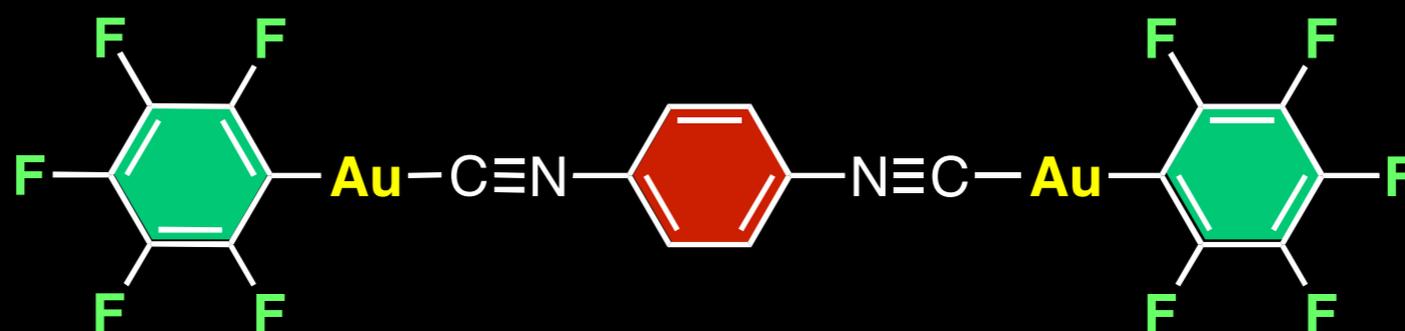
$\pi - \pi^*$



MMLCT



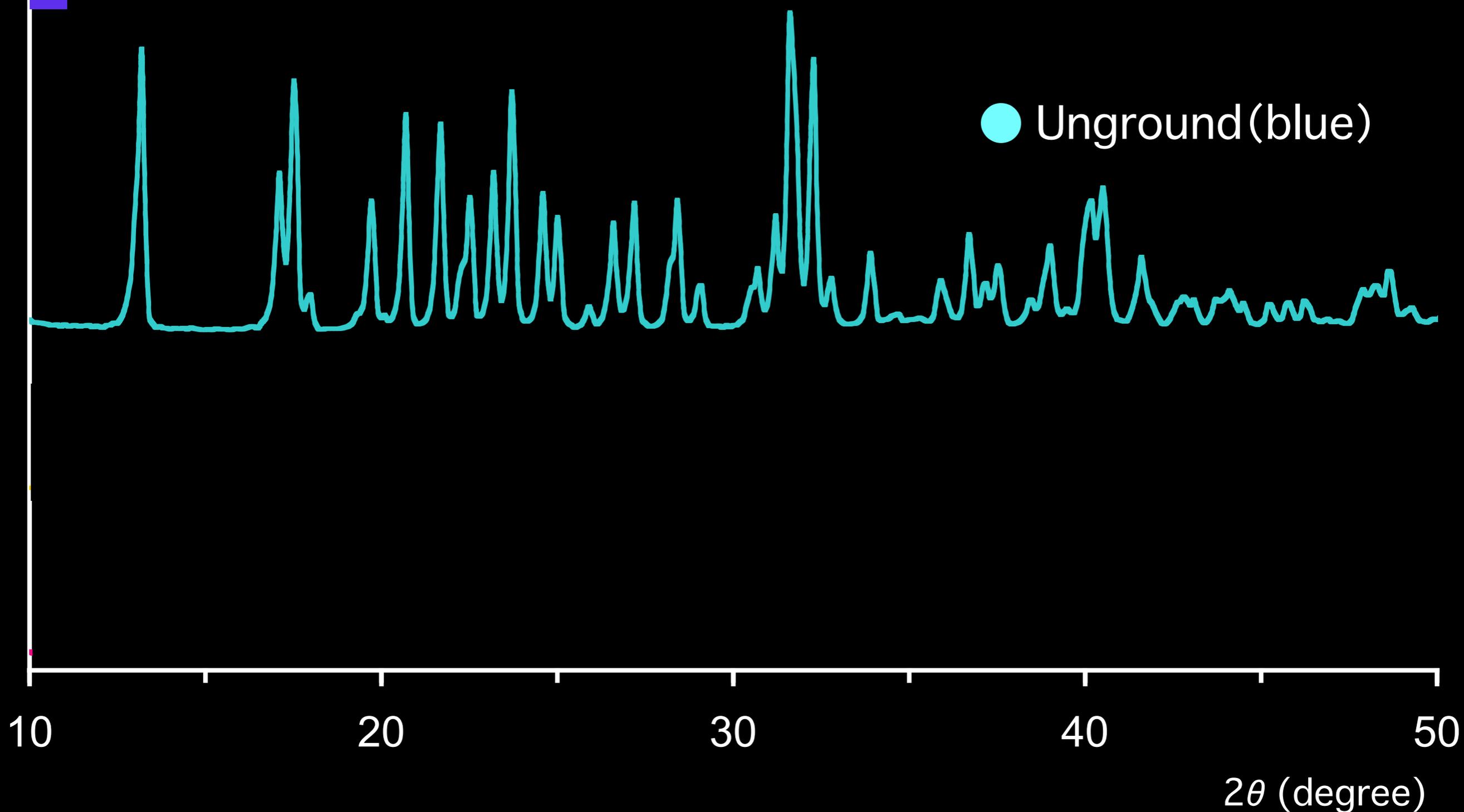
# 青色発光状態での結晶構造



$P21/c$  (No. 14),  $a=5.190(2)$  Å,  $b=17.154(6)$  Å,  
 $c=10.861(4)$  Å,  $\beta=90.83(3)^\circ$ ,  $R=0.0355$ ,  
 $R_w=0.0976$ ,  $\text{GOF}=1.007$ .

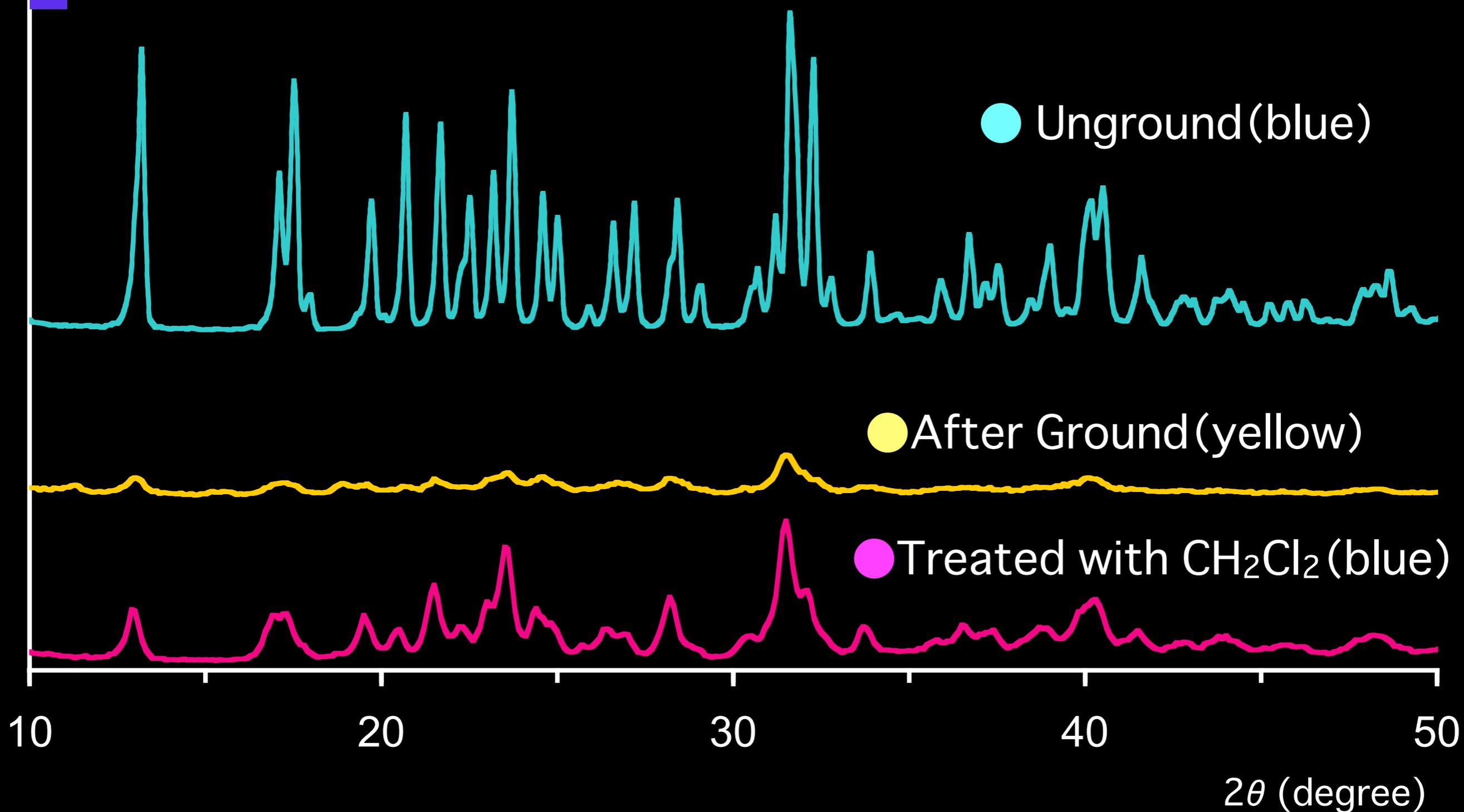
displaced  $\pi$ - $\pi$  interactions  
 $\pi$ -Au interactions

# 様々な状態でのPXRD測定



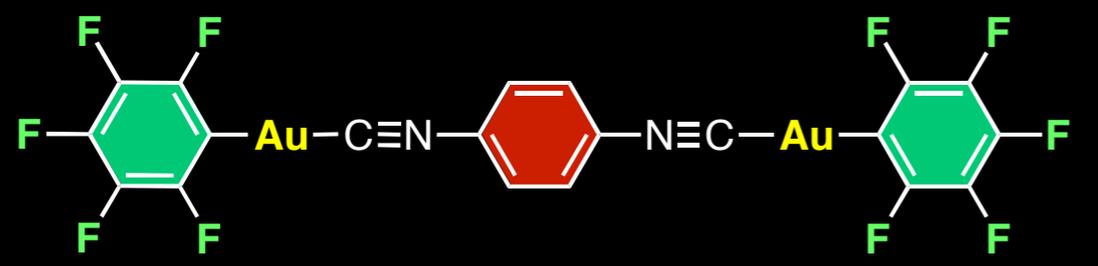
- すりつぶす (半日!) → アモルファスが見える
- CH<sub>2</sub>Cl<sub>2</sub> 処理 → 再結晶により安定な青色結晶へもどる

# 様々な状態でのPXRD測定

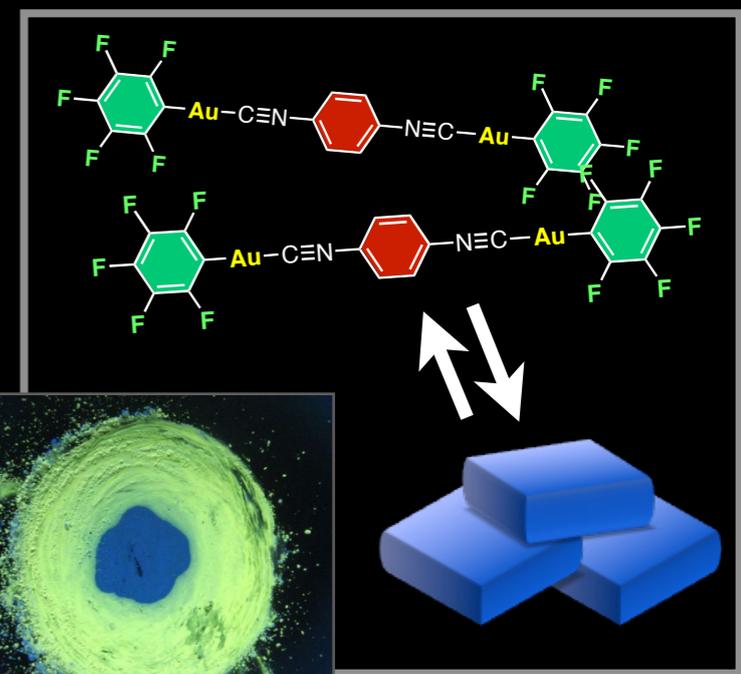


● すりつぶす (半日!) → アモルファスが見える

● CH<sub>2</sub>Cl<sub>2</sub> 処理 → 再結晶により安定な青色結晶へもどる

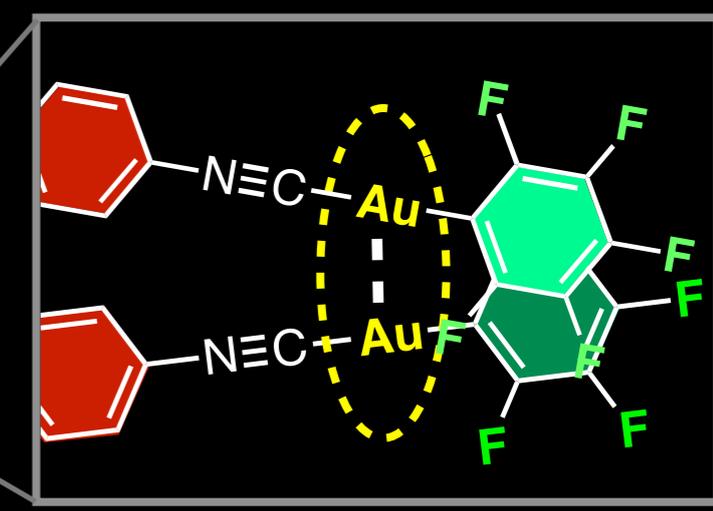
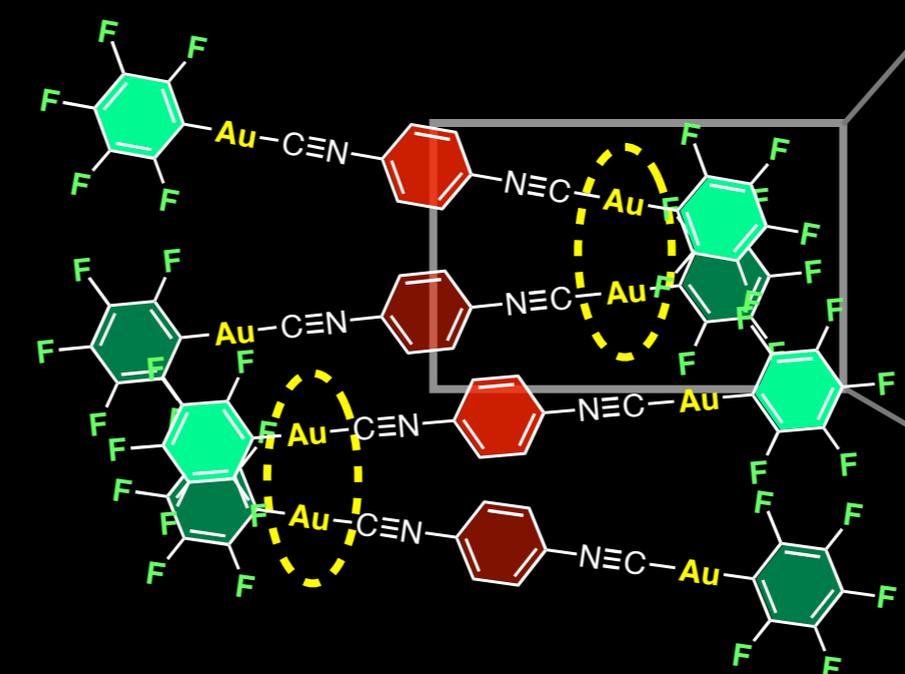
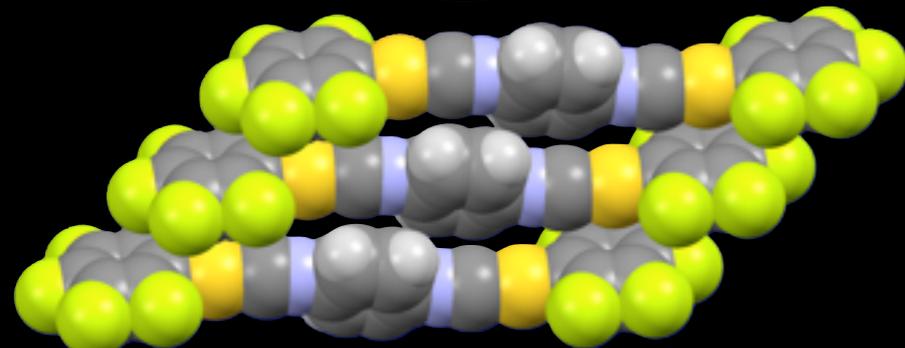
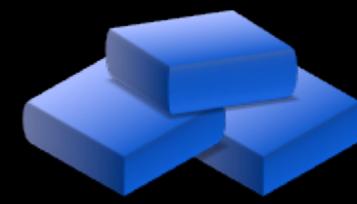
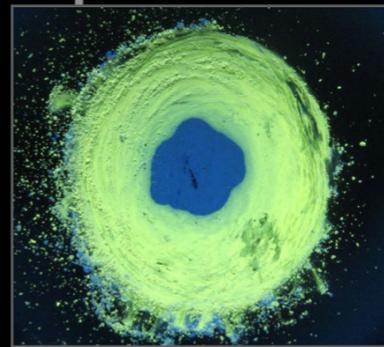
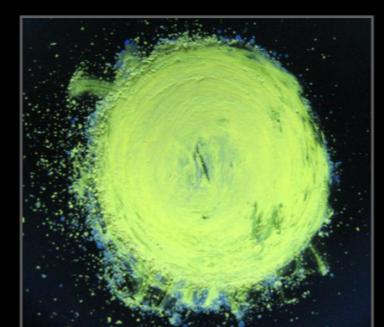


溶媒添加

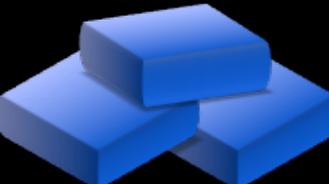


再結晶

Grinding



**Aurophilic Interactions**



micro crystallines  
(Single crystal XRD)

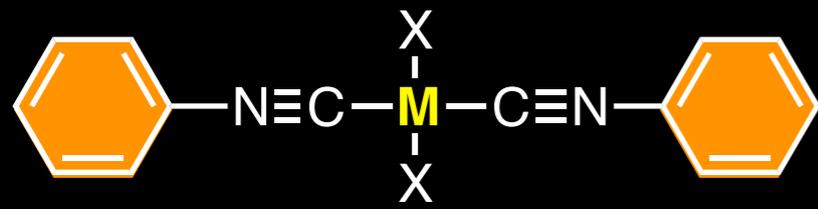


amorphous  
(Powder XRD)

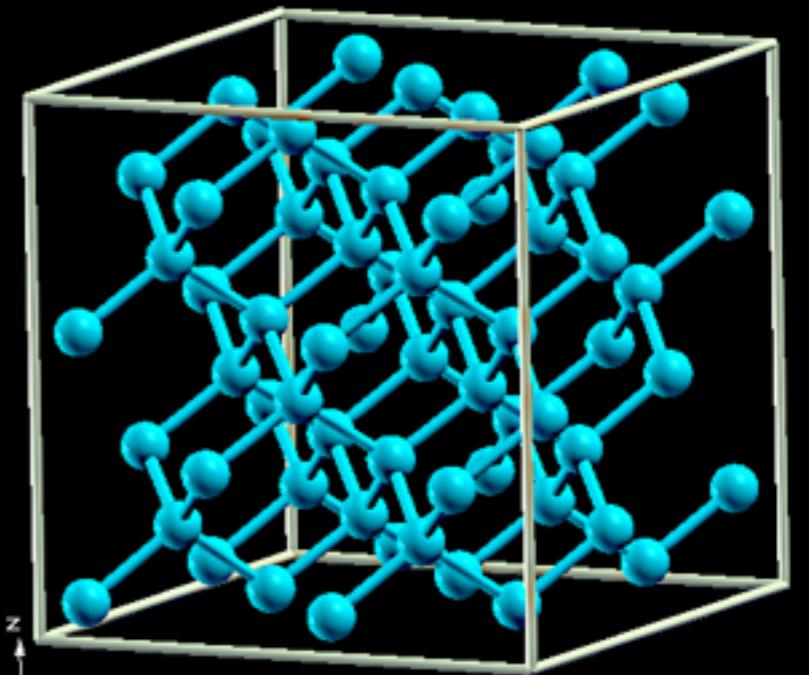
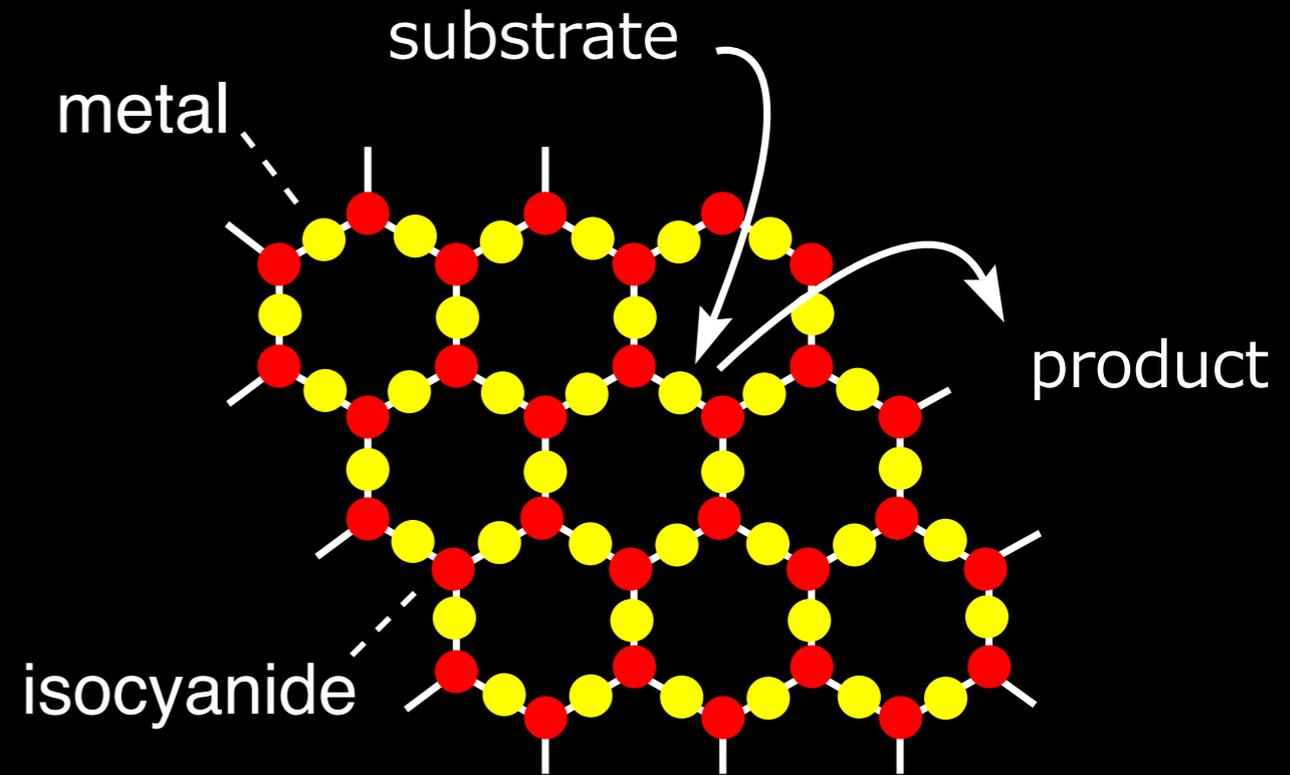
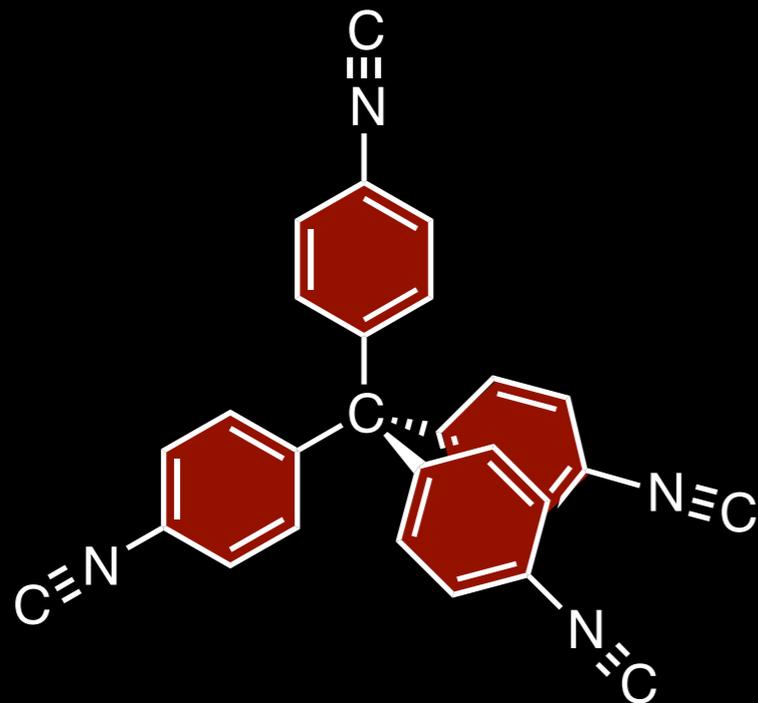
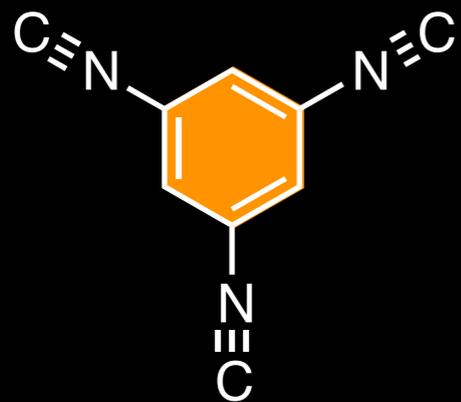
**MMLCT  
red shift**

# 研究のいきさつ：MOF触媒 (2003年ころ)

N. Oshima



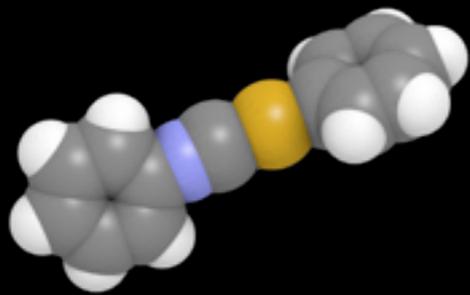
M = Pd, Pt; X = I



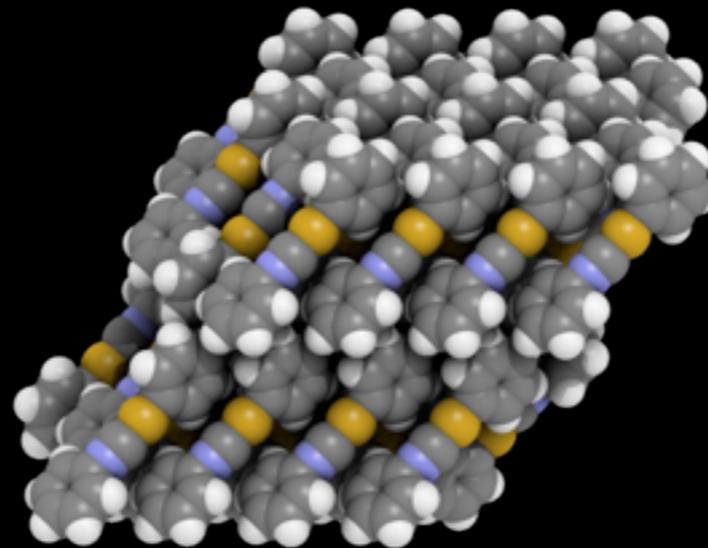
# 分子と結晶(バルク)をつなぐ？



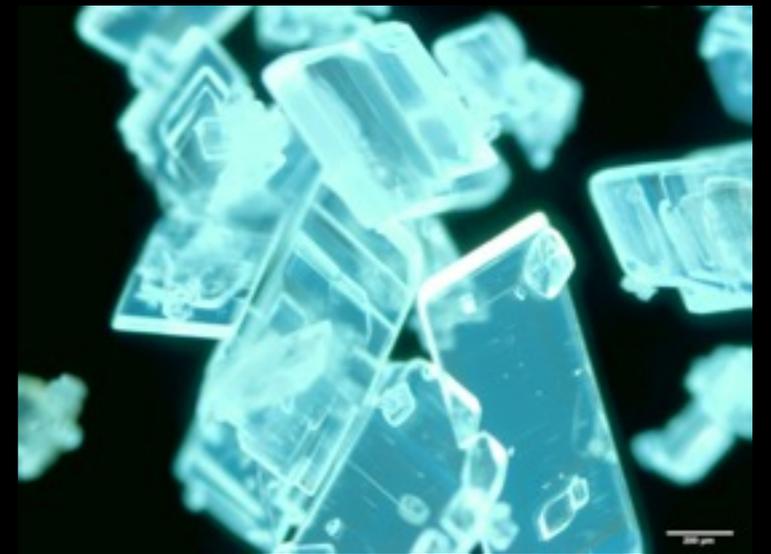
機械的刺激



分子

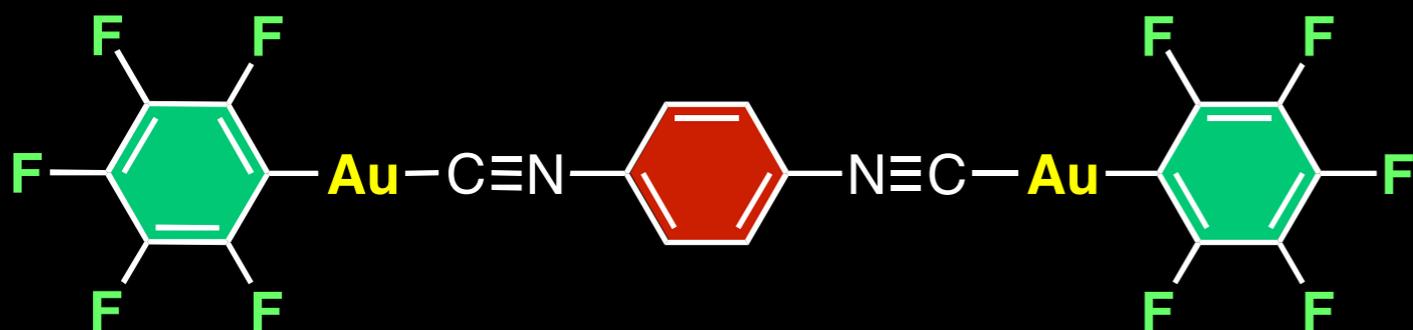


複数分子の集積

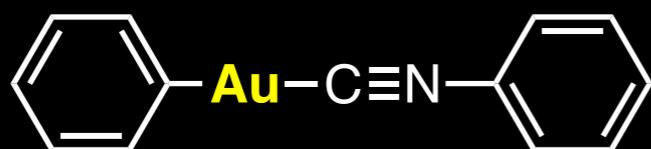


結晶

# 構造をシンプルにしてみるとどうなるか？



偶然の発見  
錯体触媒開発の副産物



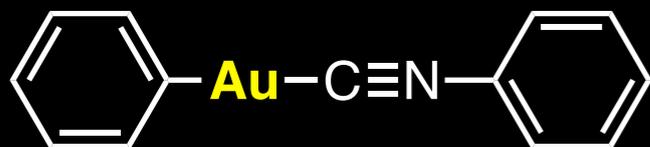
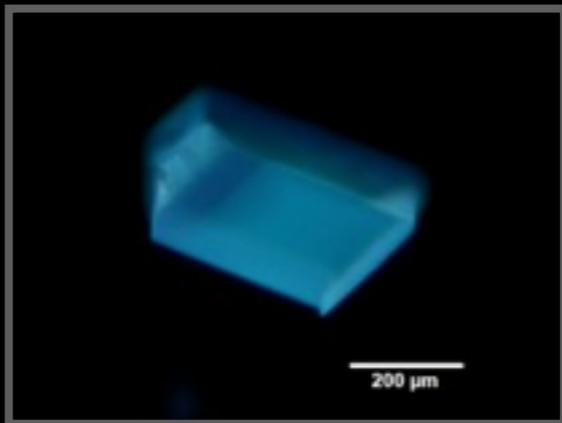
シンプル化  
による要素絞り込み

結晶において未知の挙動  
機械的刺激による単結晶-単結晶相転移  
(**分子ドミノ**) をしめす



室本麻衣

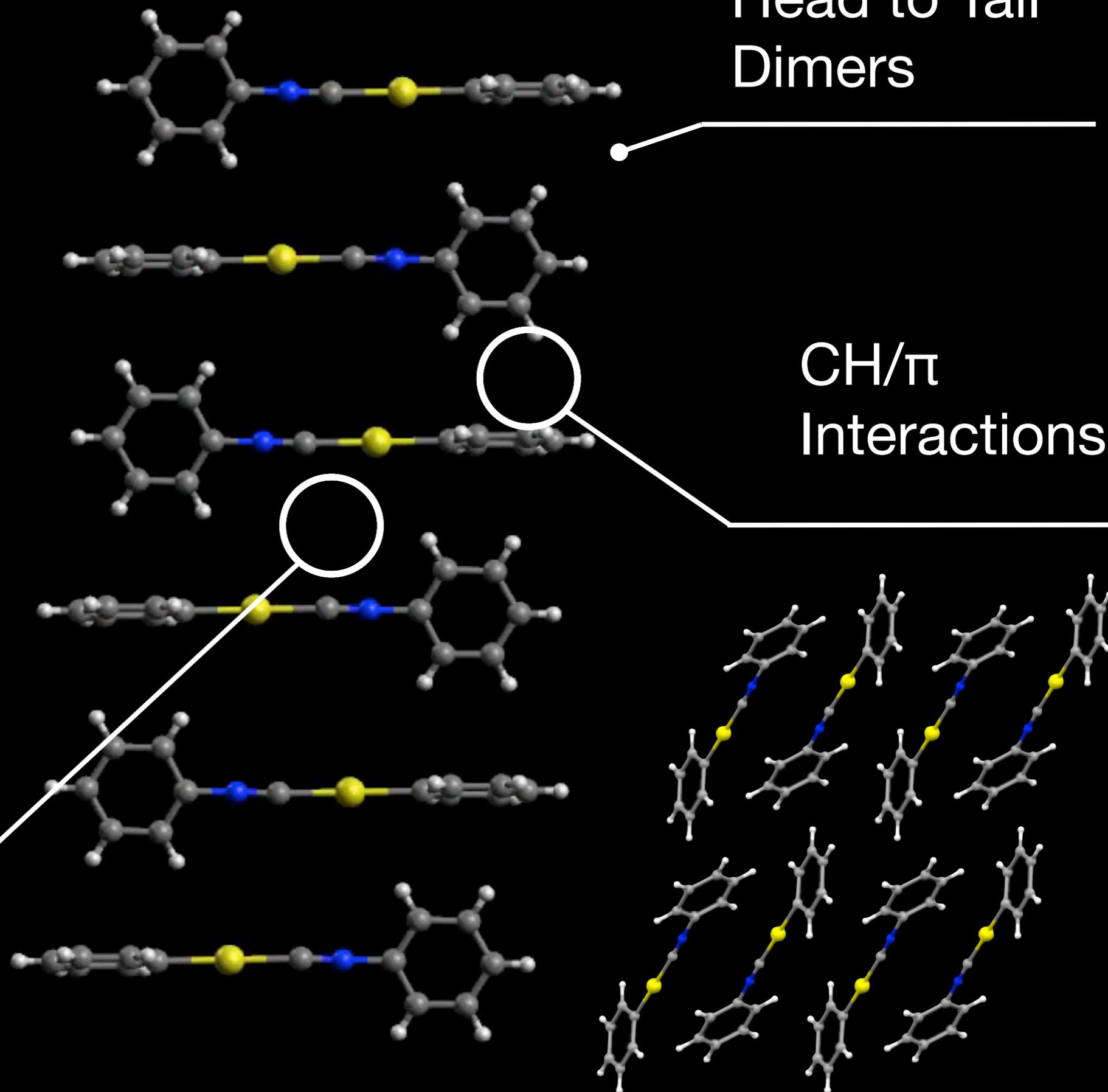
関朋宏  
特任助教



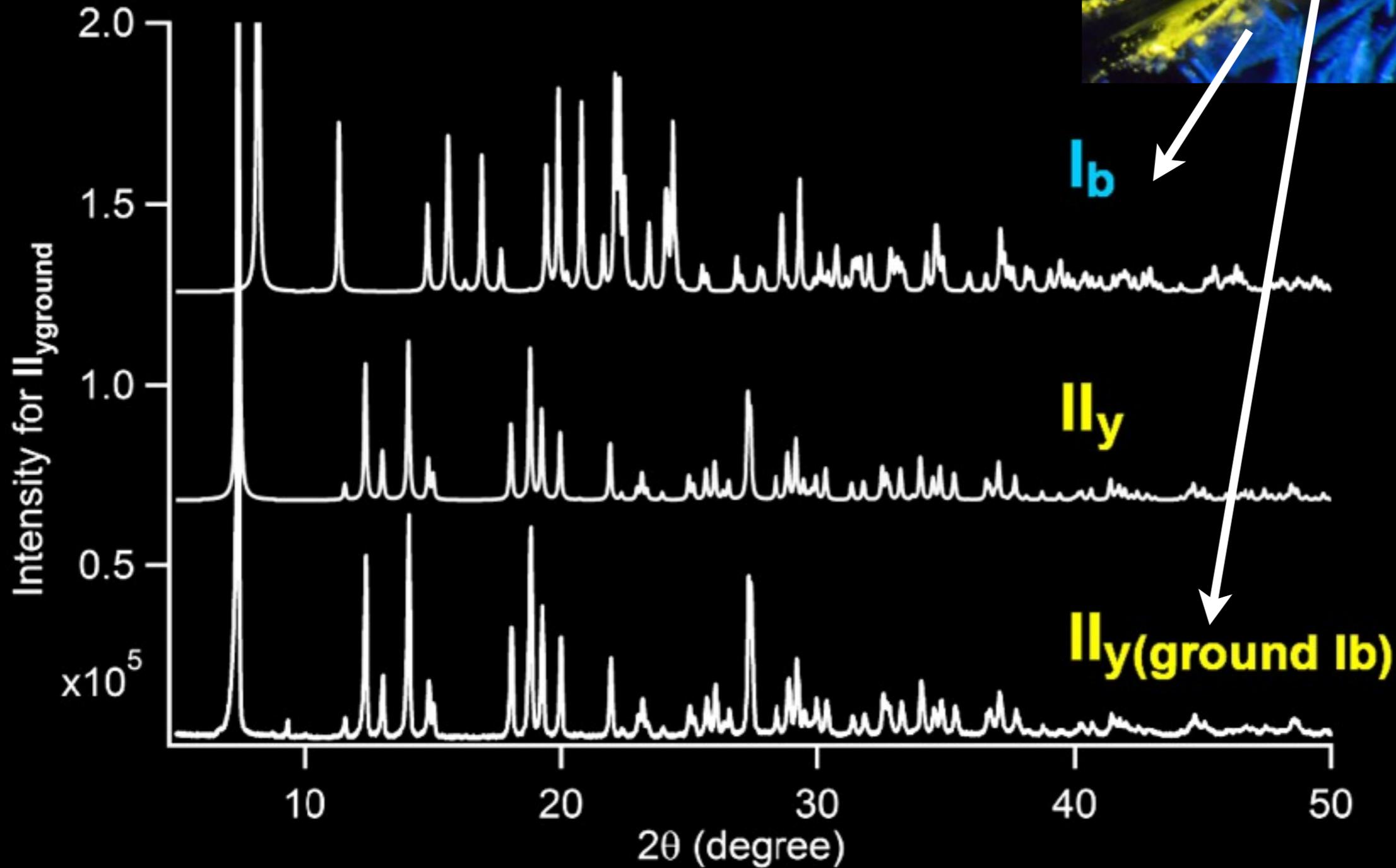
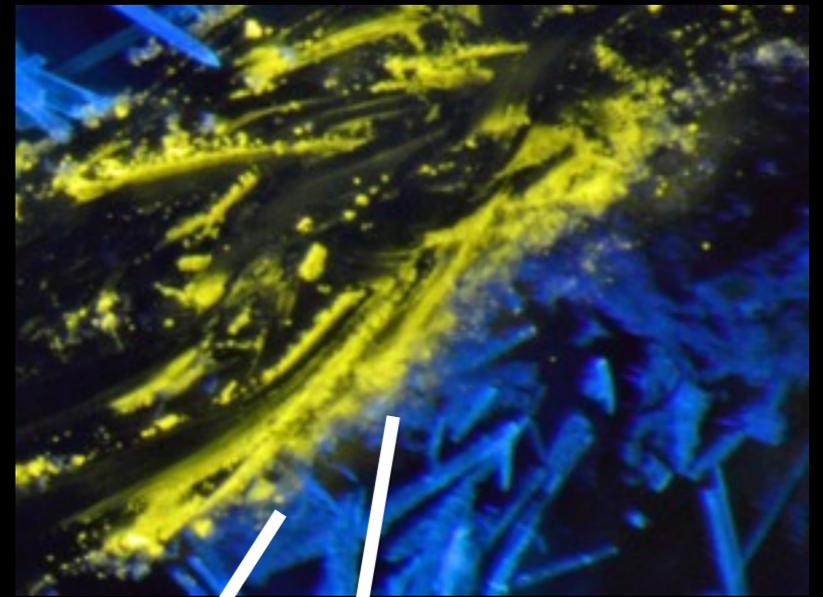
triclinic, P-1 (#2)  
Z = 2  
 $R_1 = 0.0326$   
 $wR_2 = 0.0819$   
GOF = 1.056

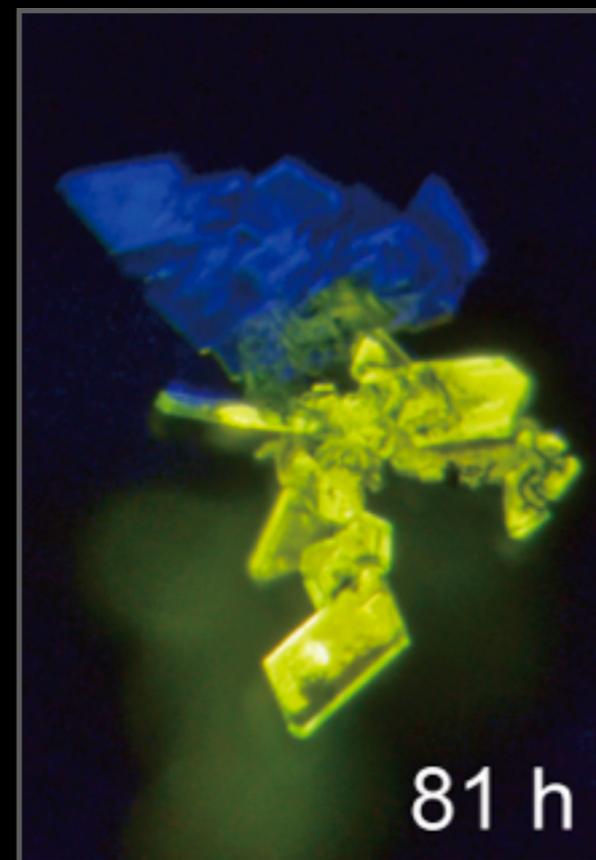
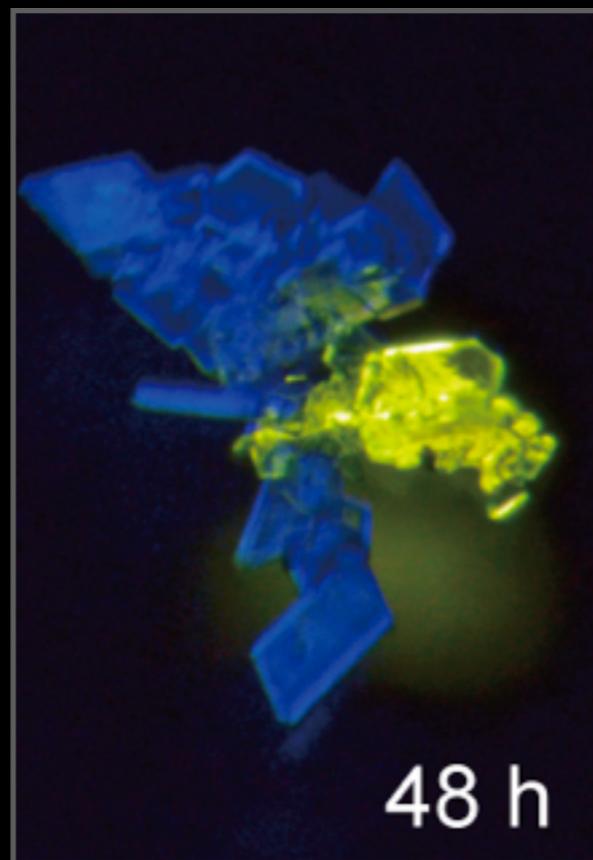
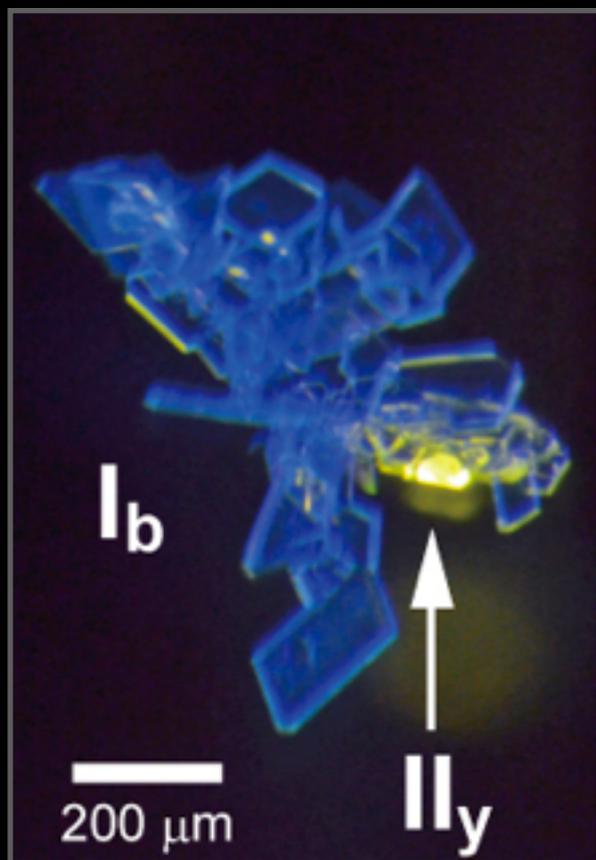
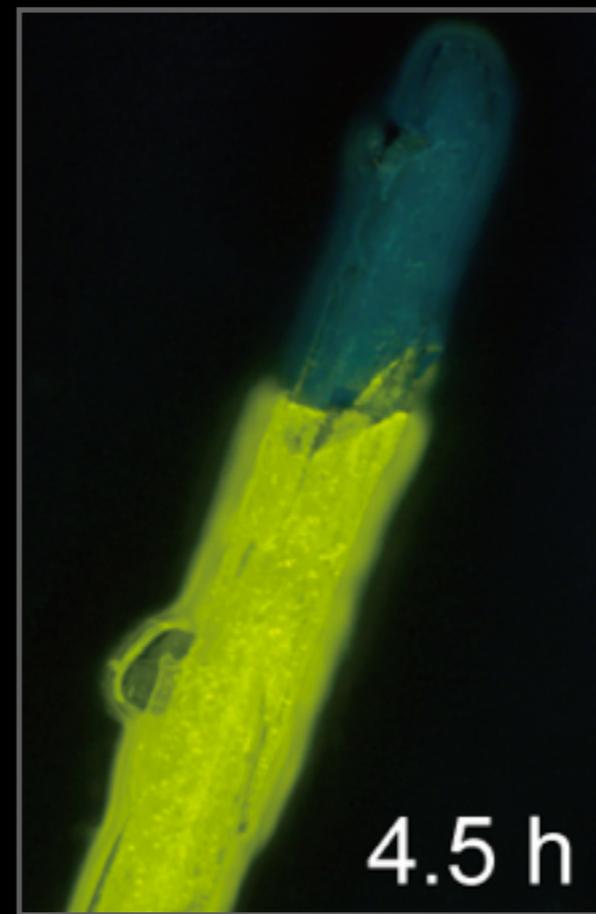
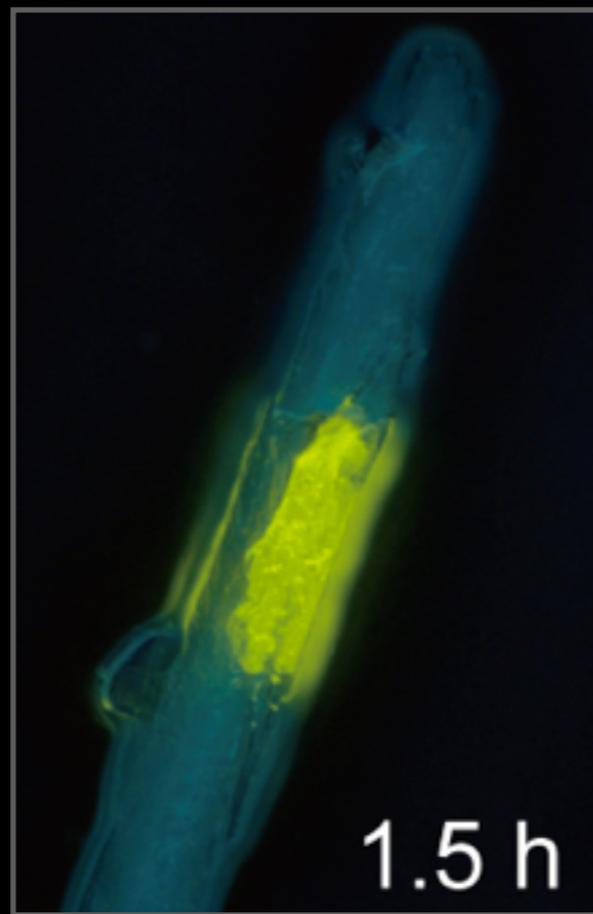
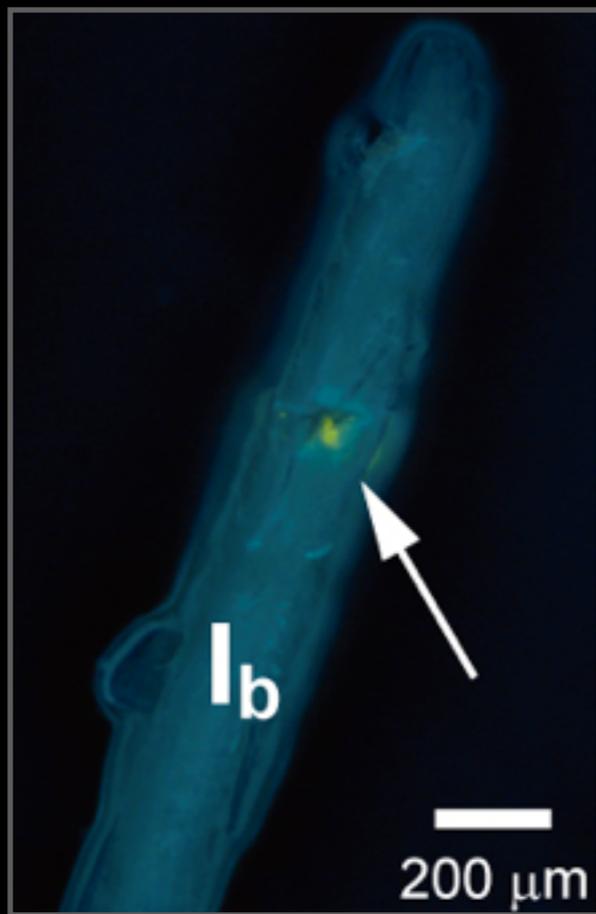
No Au-Au  
Interactions

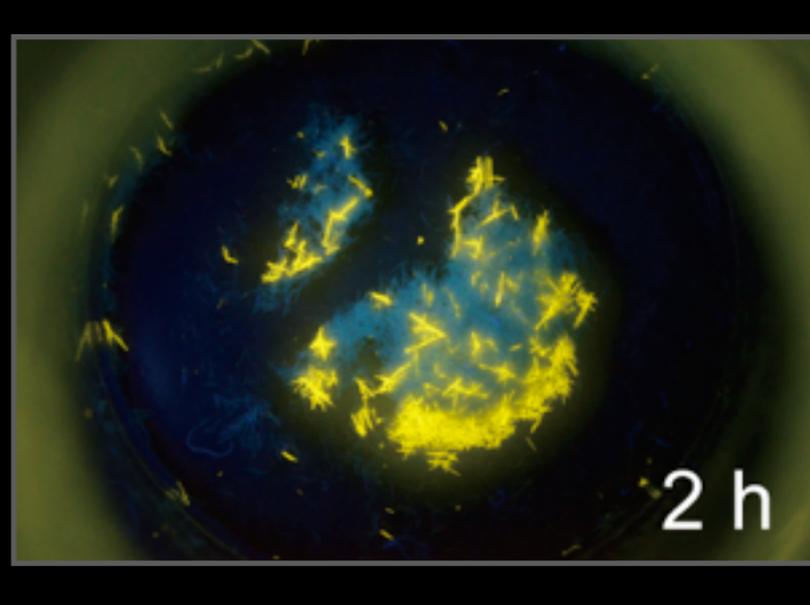
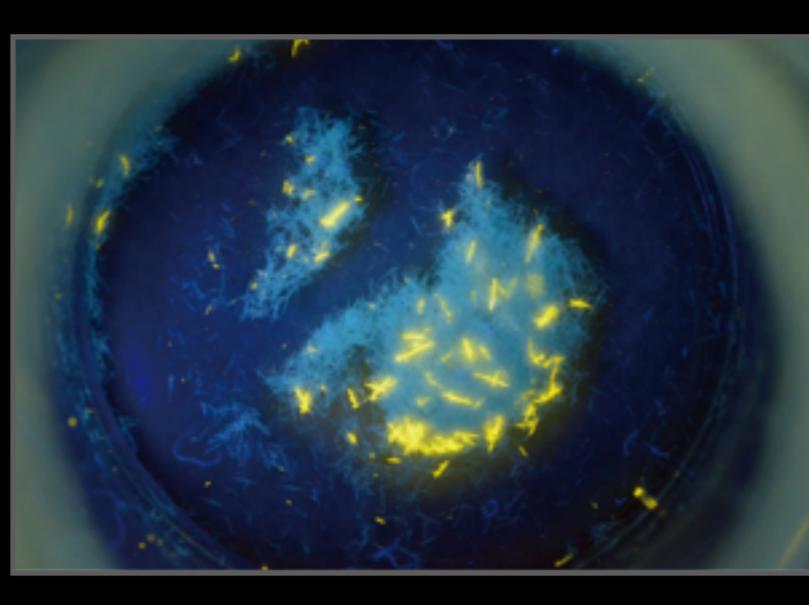
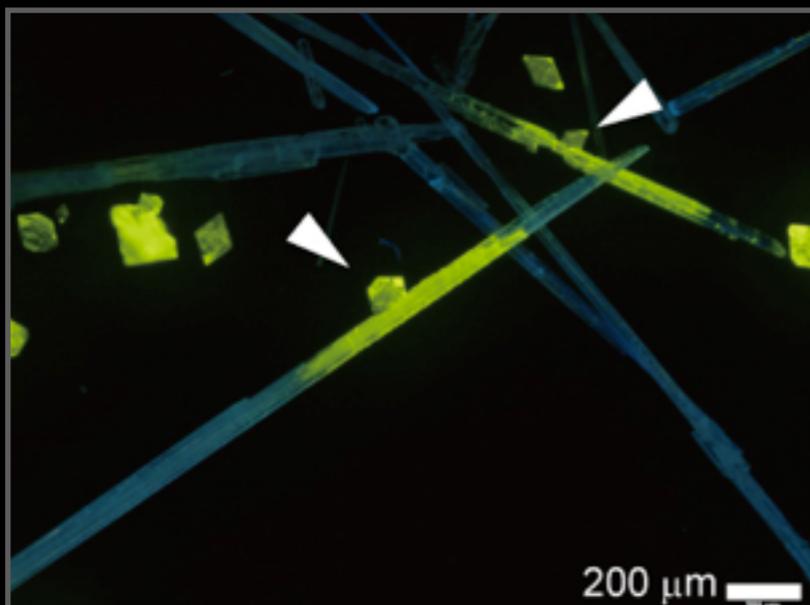
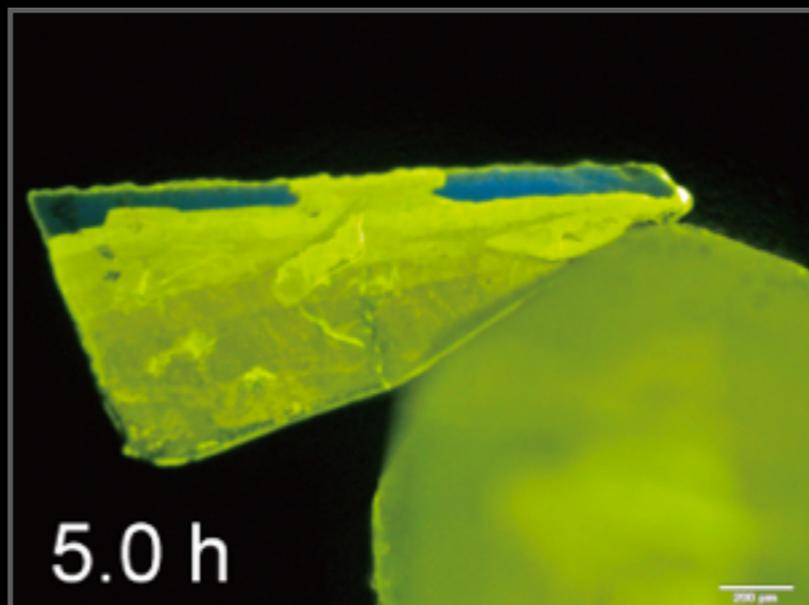
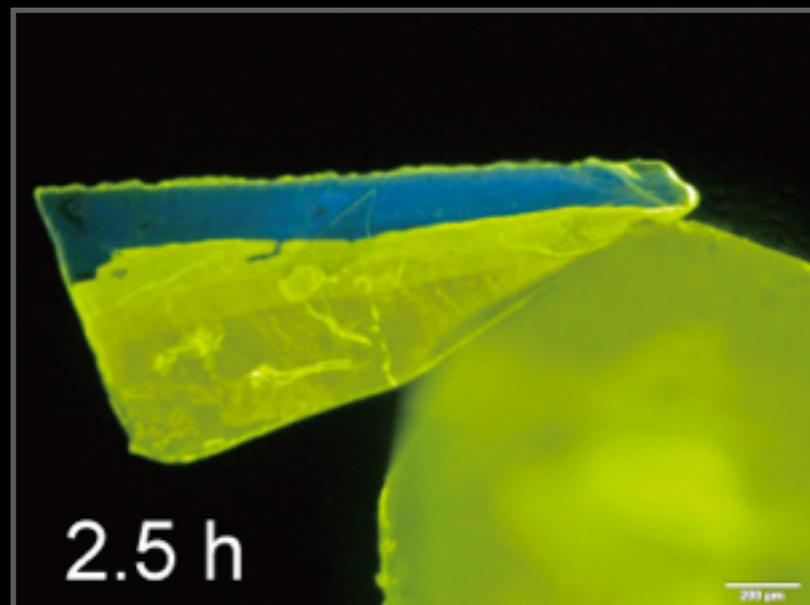
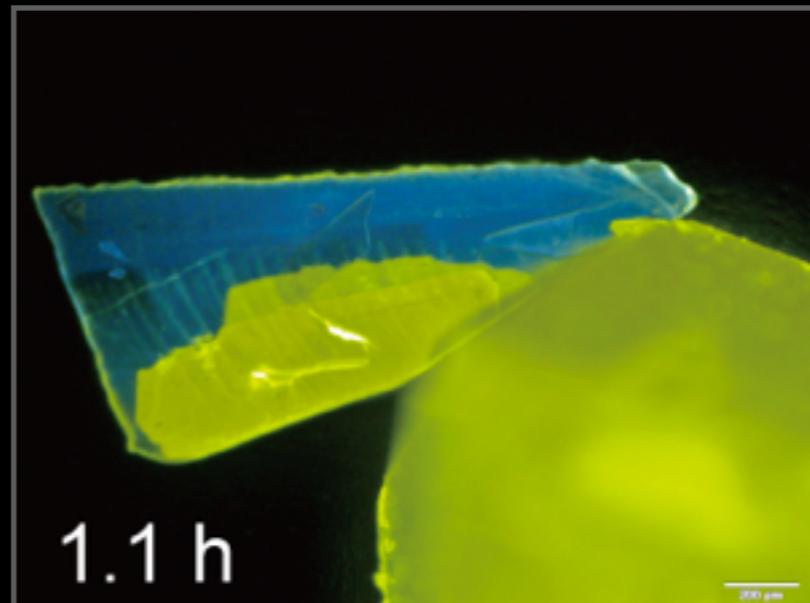
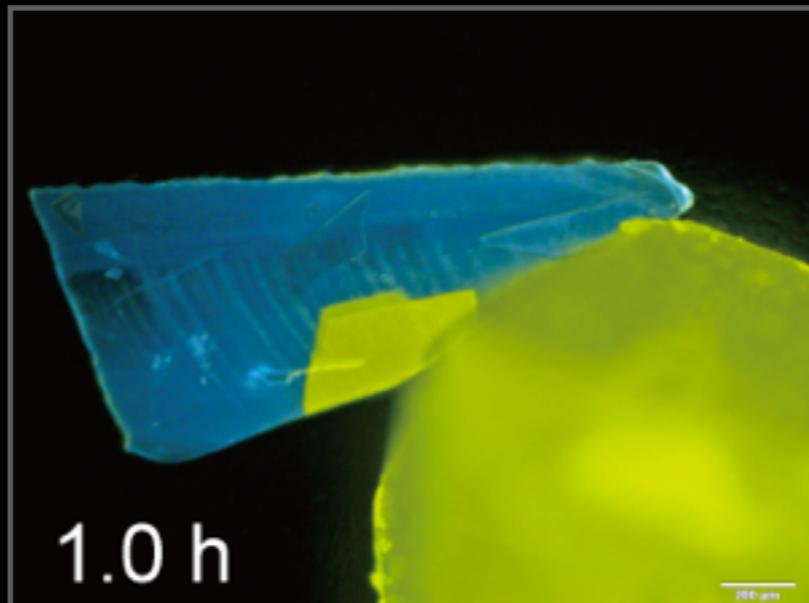
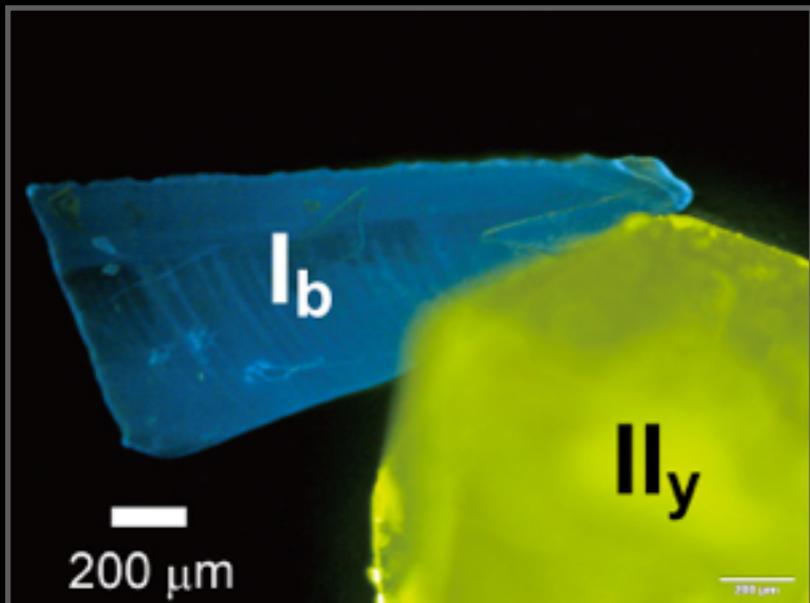
Au-Au  
: 5.733 Å  
(> 3.5 Å)

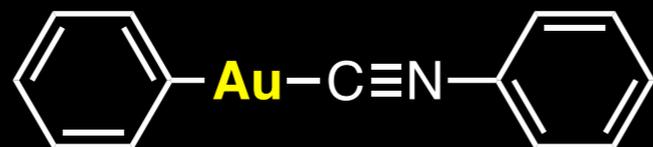
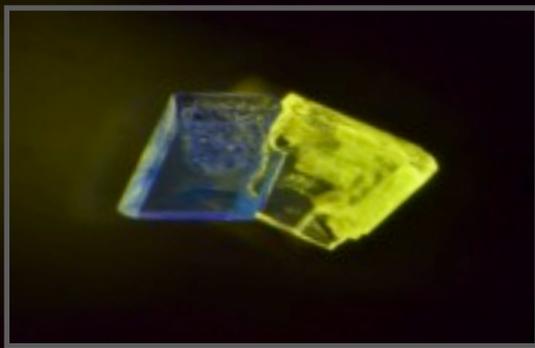


# PXRDは結晶相転移をしめた







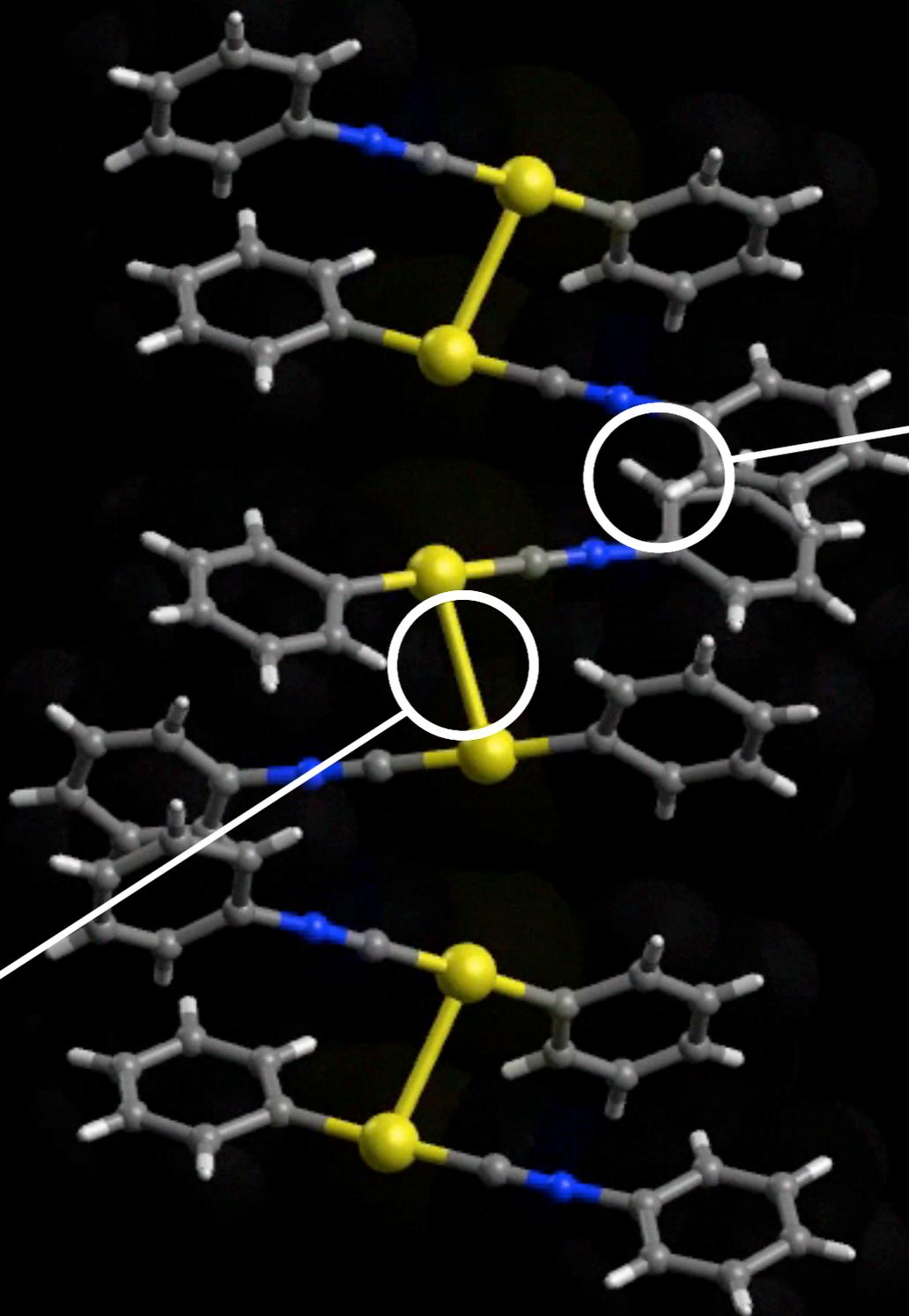


# Single Crystal to Single Crystal Transformation

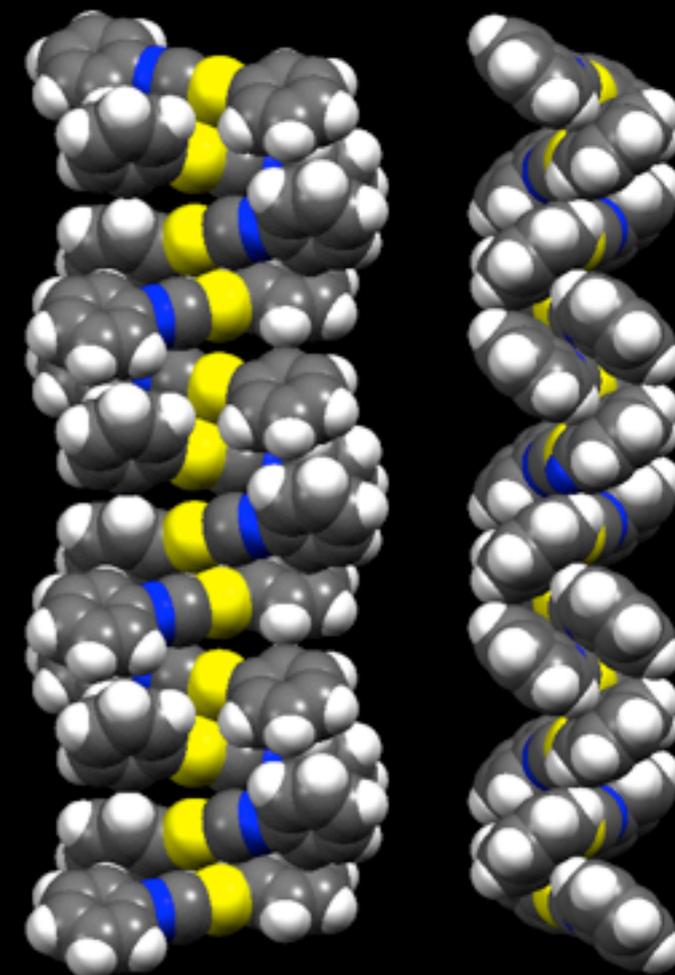
tetragonal, I-42d  
(#122)  
Z = 16  
 $R_1 = 0.0883$   
 $wR_2 = 0.2174$   
GOF = 1.316

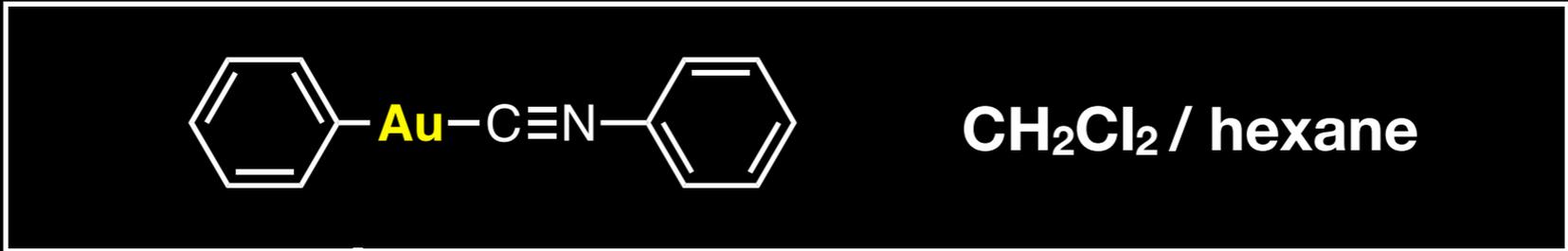
**Strong  
Au-Au  
Interactions**

3.161 Å  
( $< 3.5$  Å)



$\pi$ - $\pi$  (NC)  
Interactions



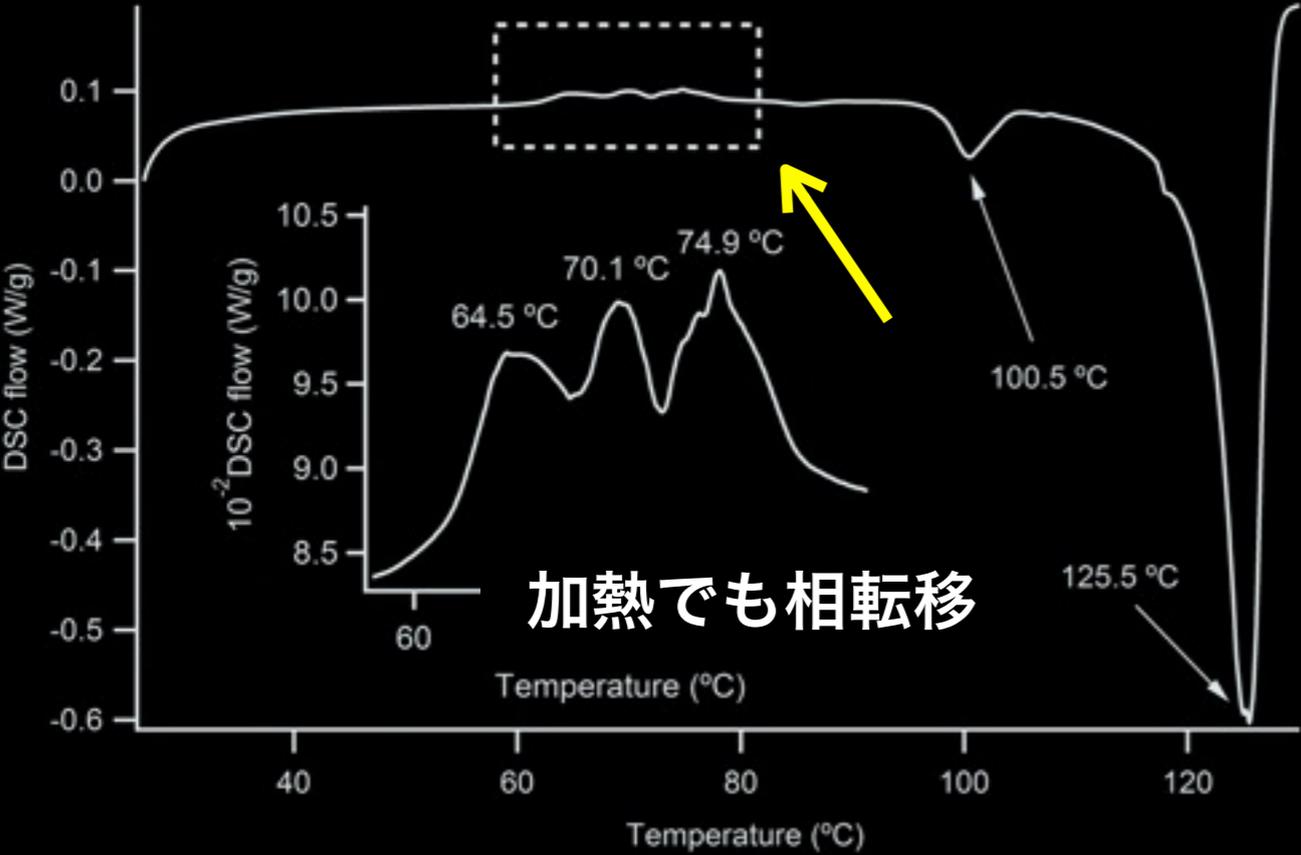
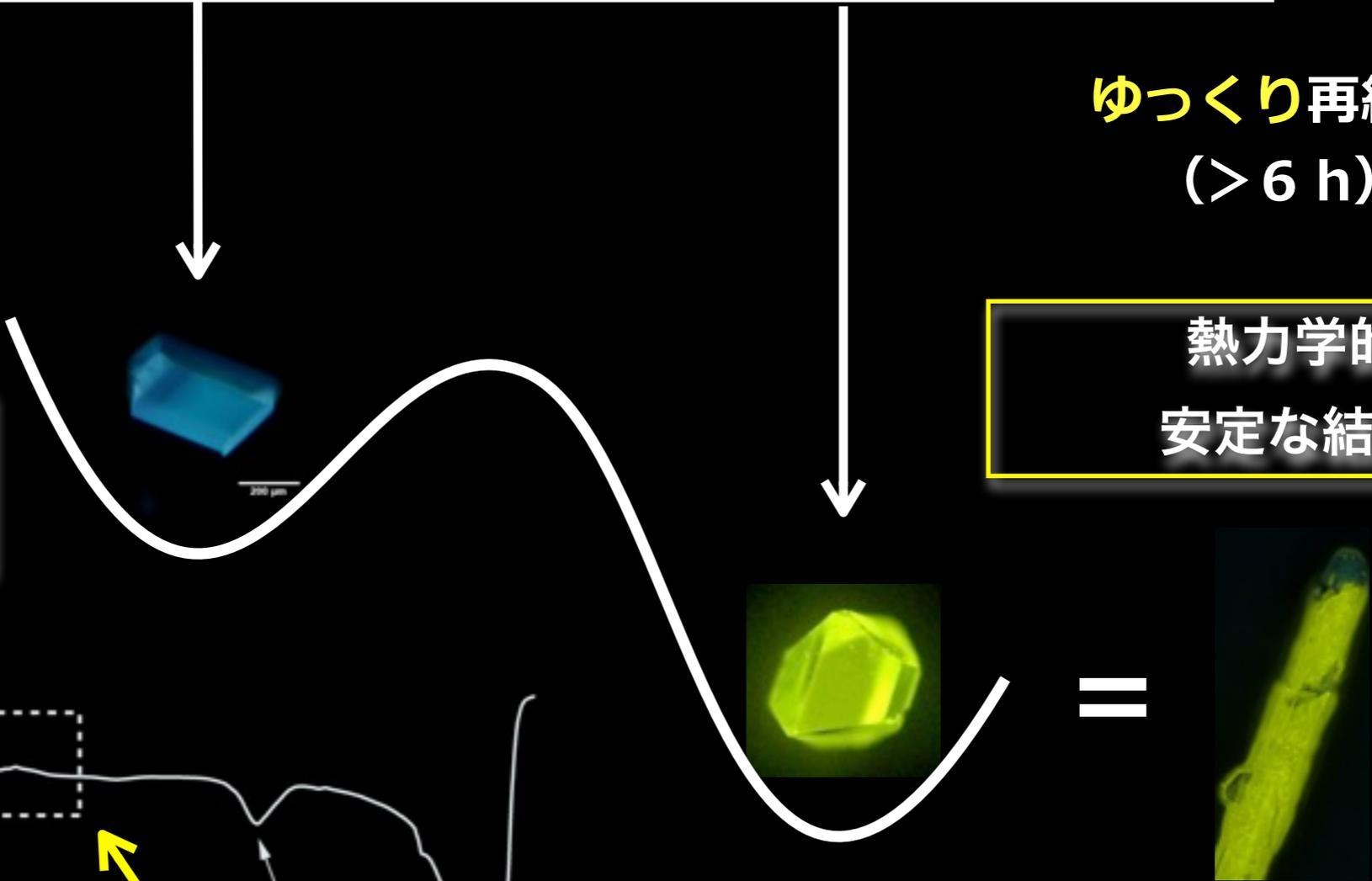


**すばやく再結晶**  
( < 5 min )

**ゆっくり再結晶**  
( > 6 h )

速度論的  
準安定結晶

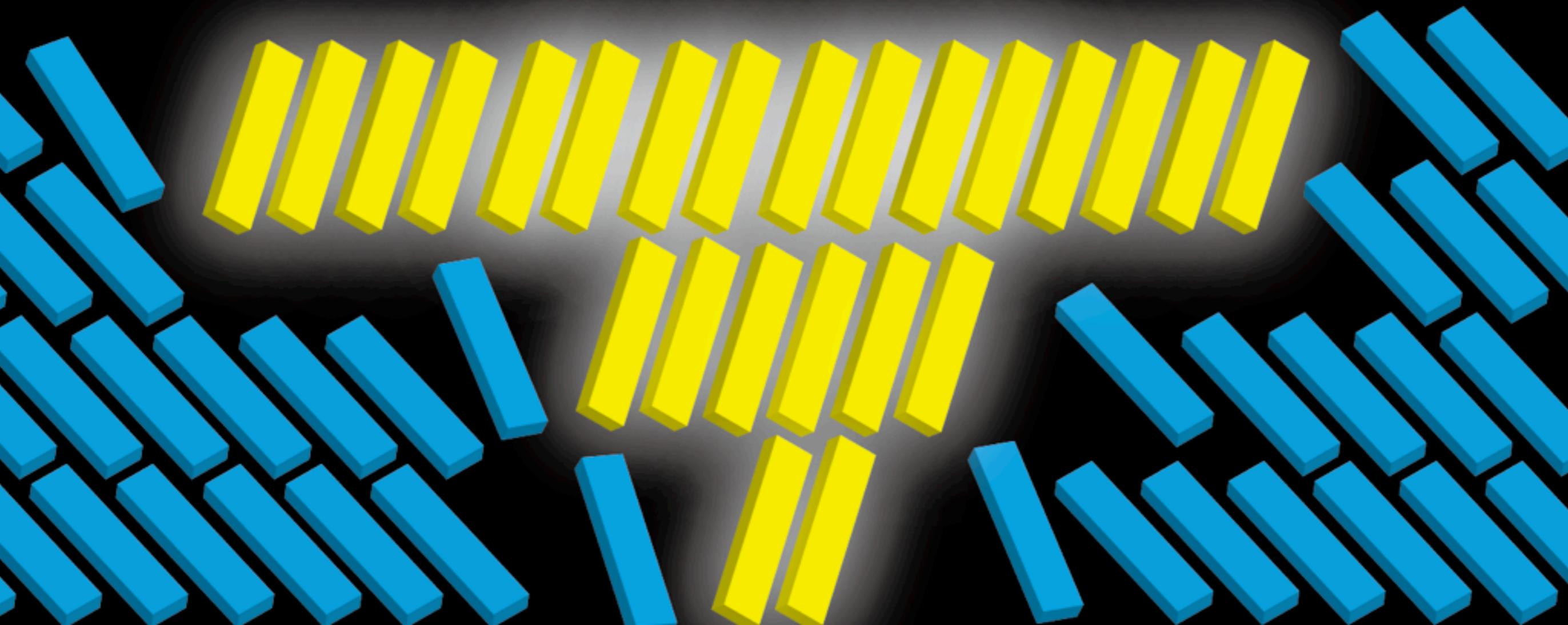
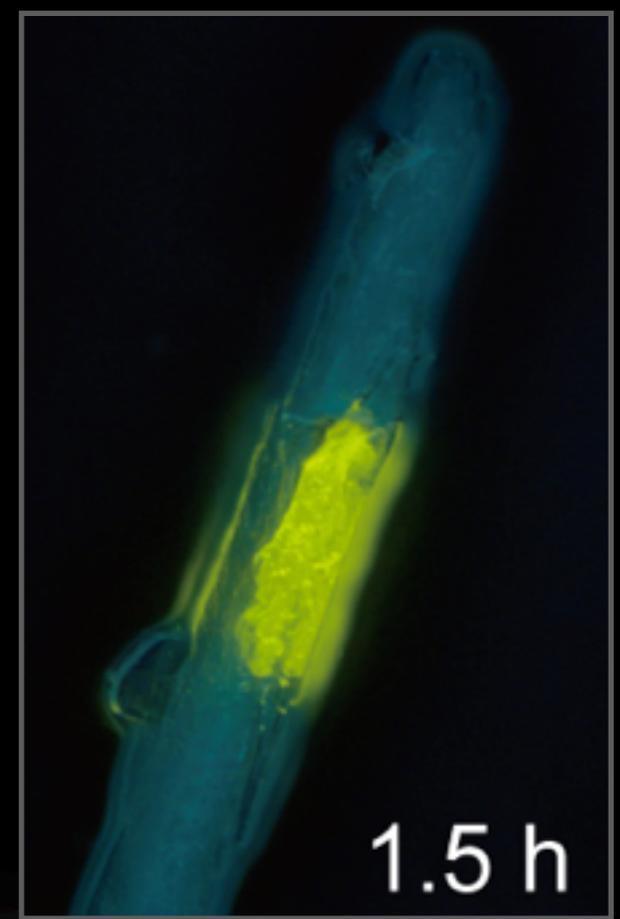
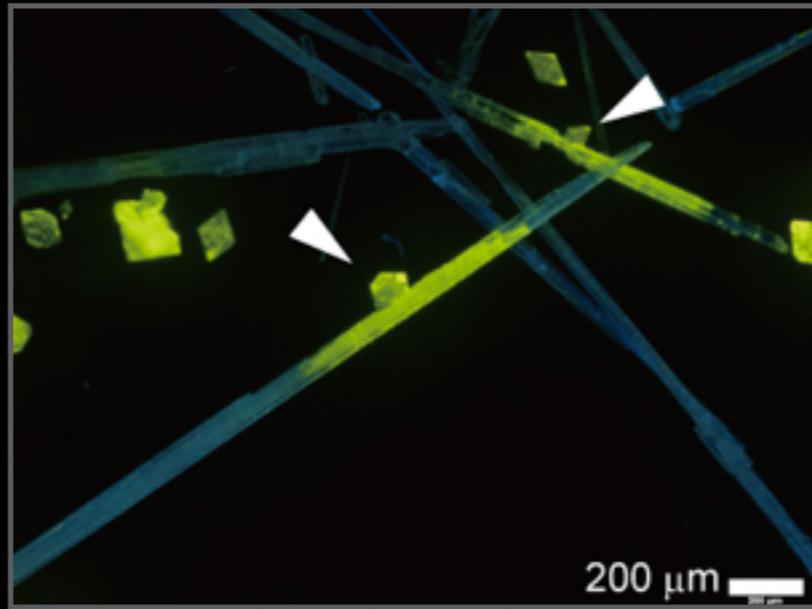
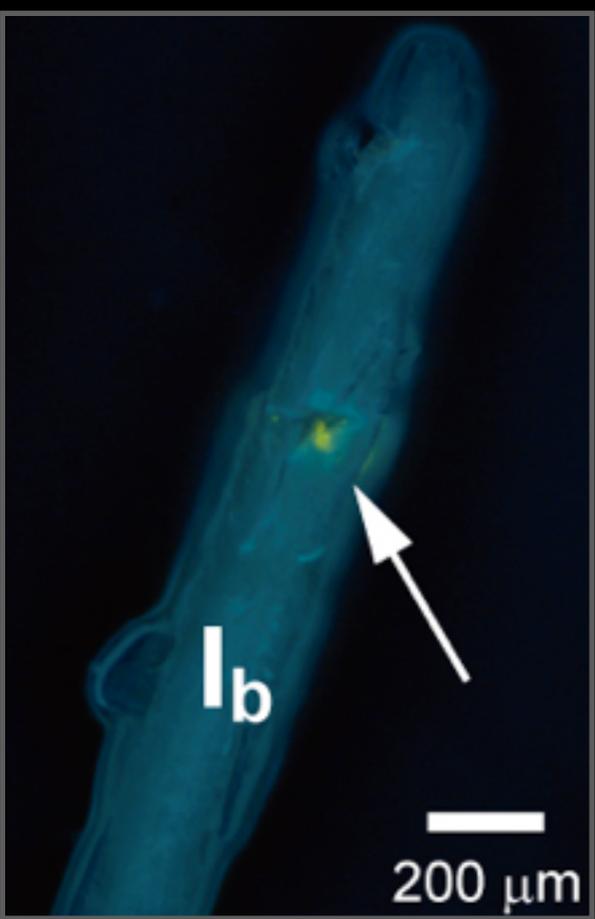
熱力学的  
安定な結晶



溶液から得た結晶と  
相転移から得た結晶はおなじ

Ostwaldの段階則  
(1897)

# 分子ドミノ

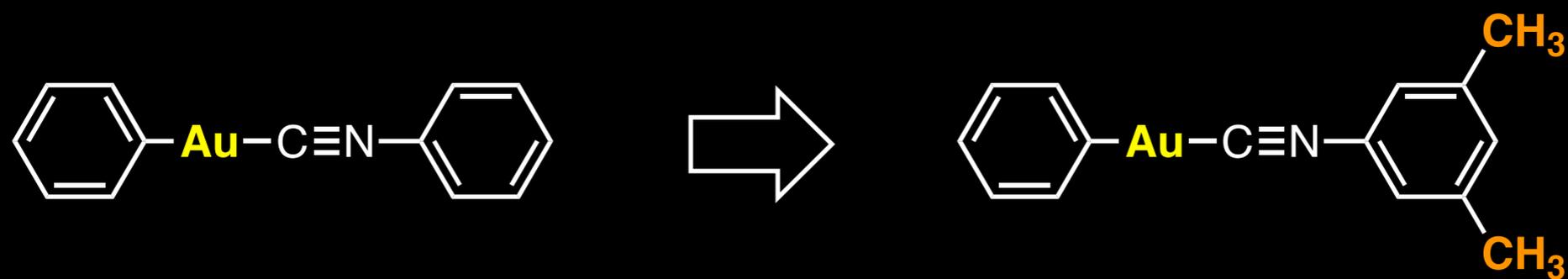


# シンプルにして付け足す：相互作用逆転型SCSC

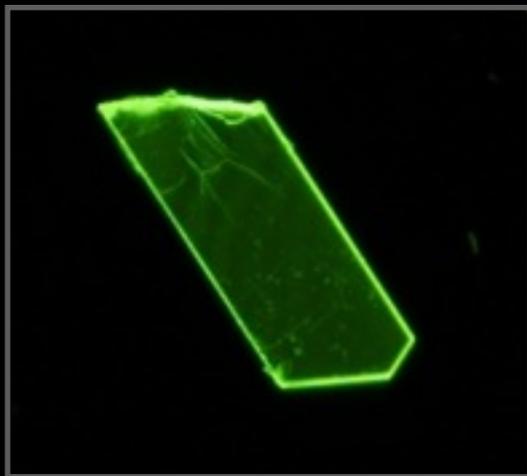


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特任助教

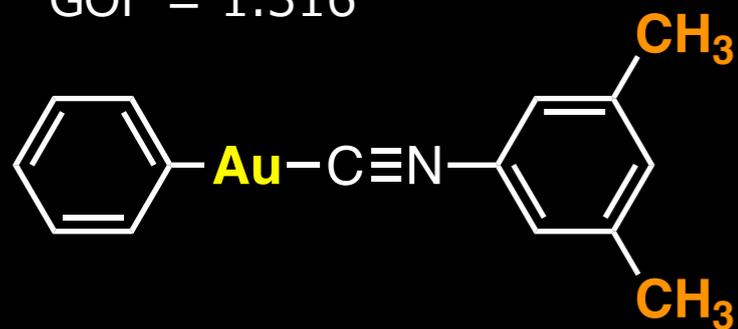
櫻田健太



Seki, T.; Sakurada, K.; Ito, H. *Angew. Chem., Int. Ed.*, 2013,52, 12828-12832, **VIP paper**



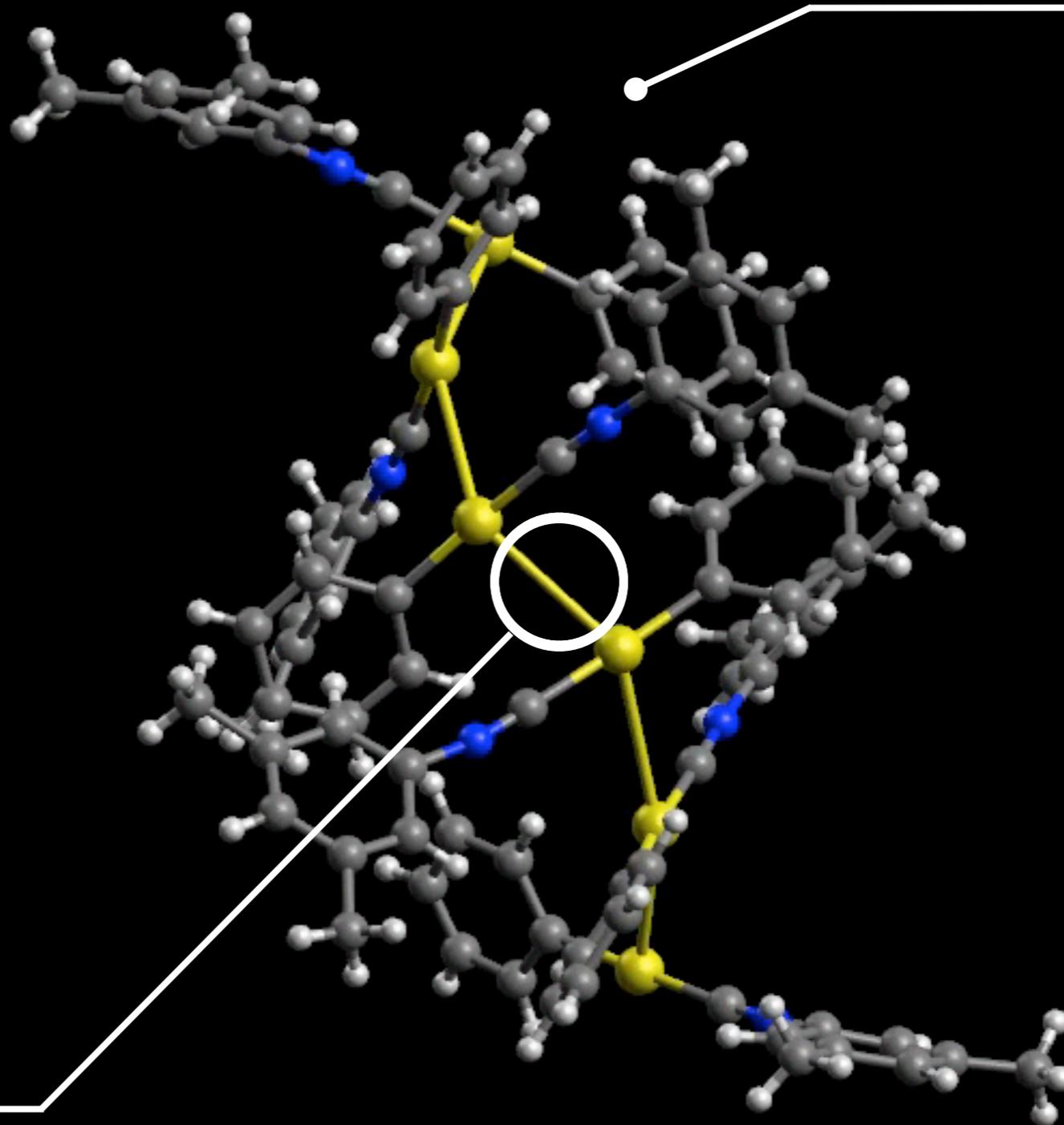
tetragonal, I-42d  
(#122)  
Z = 16  
 $R_1 = 0.0883$   
 $wR_2 = 0.2174$   
GOF = 1.316

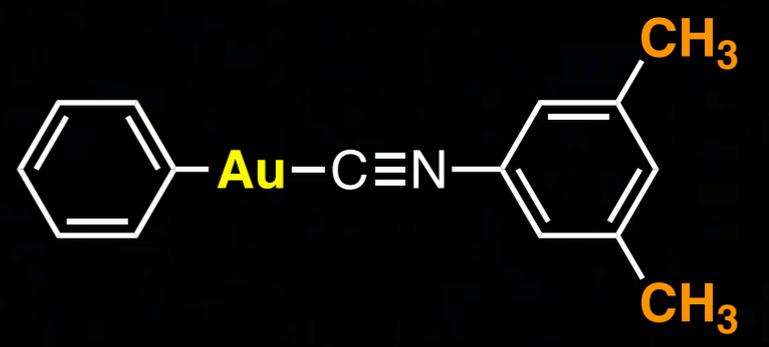
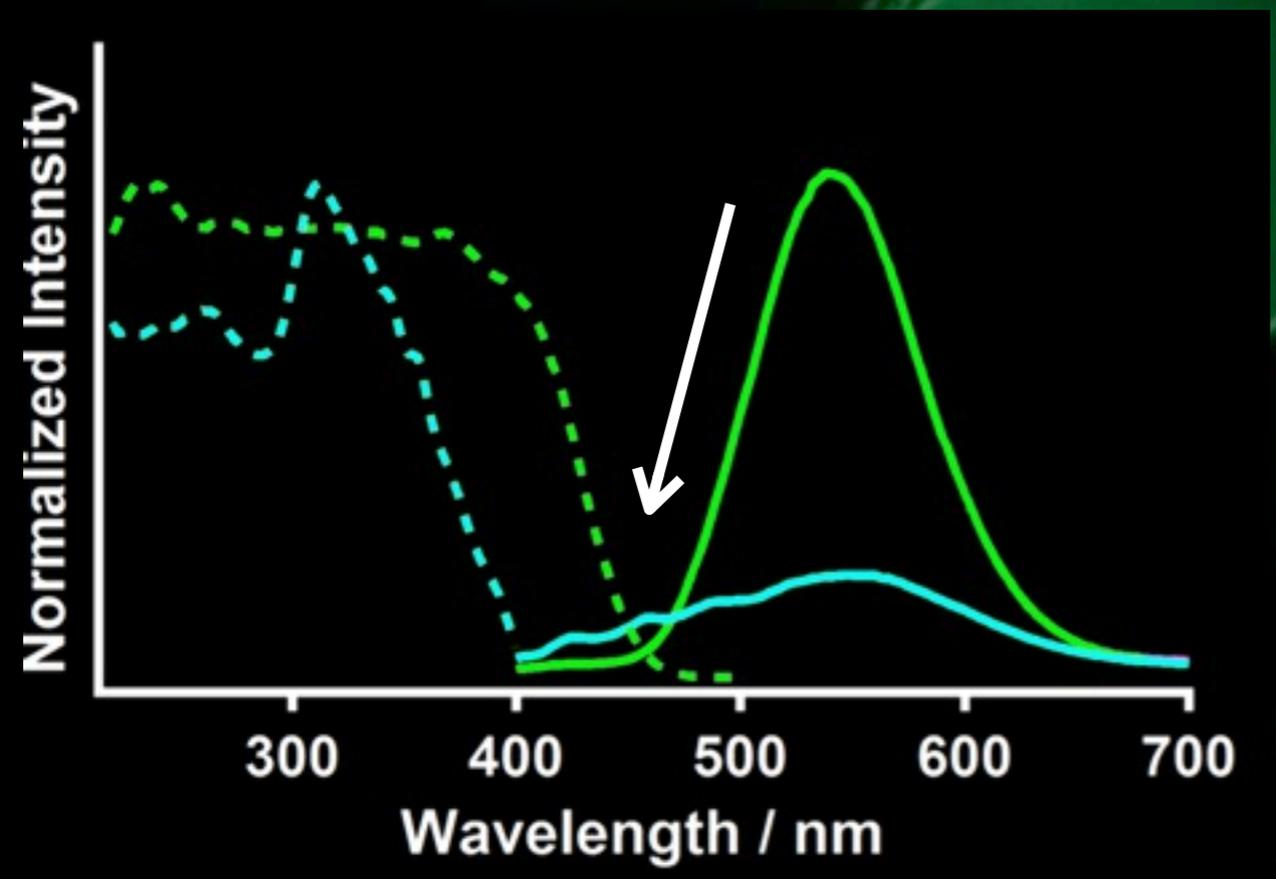
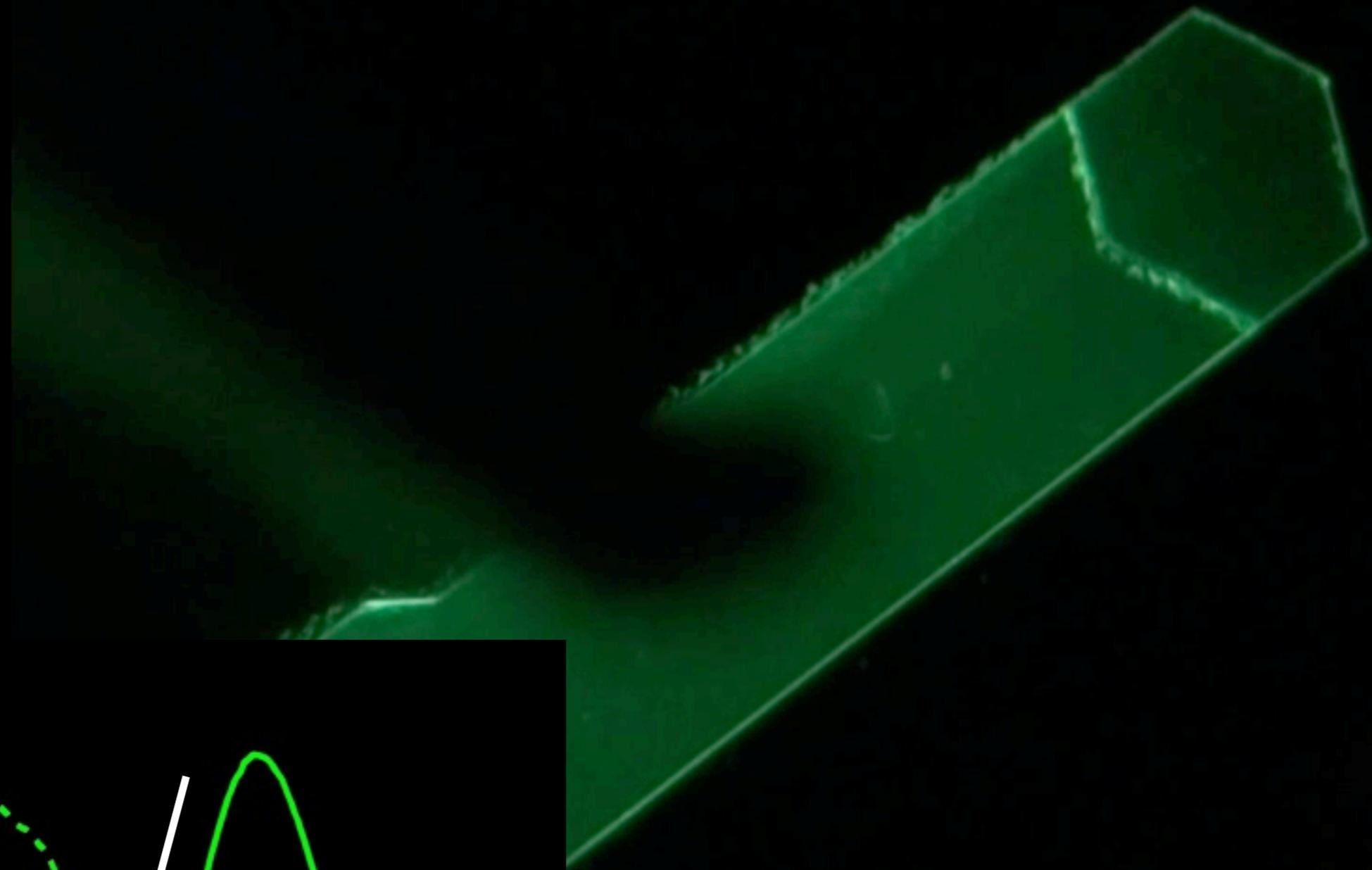


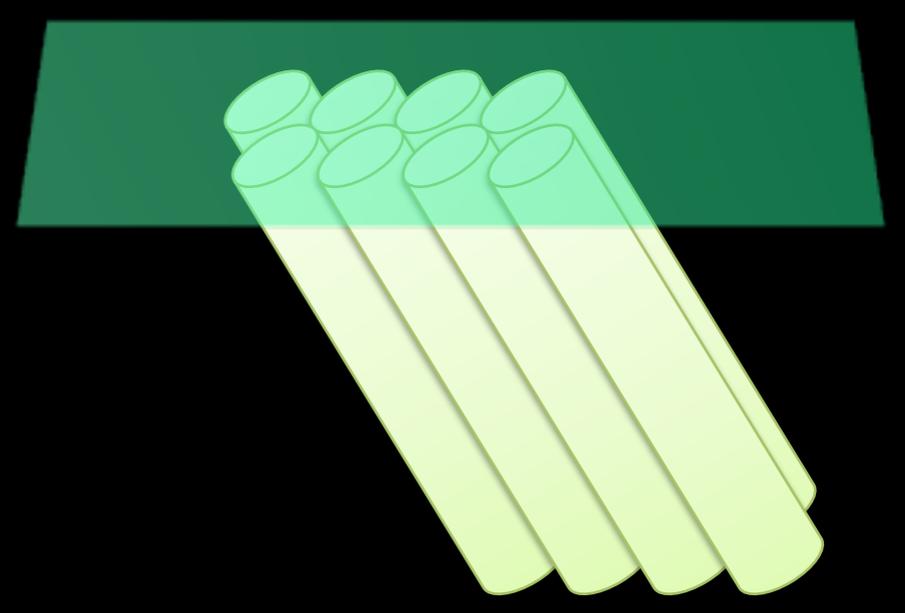
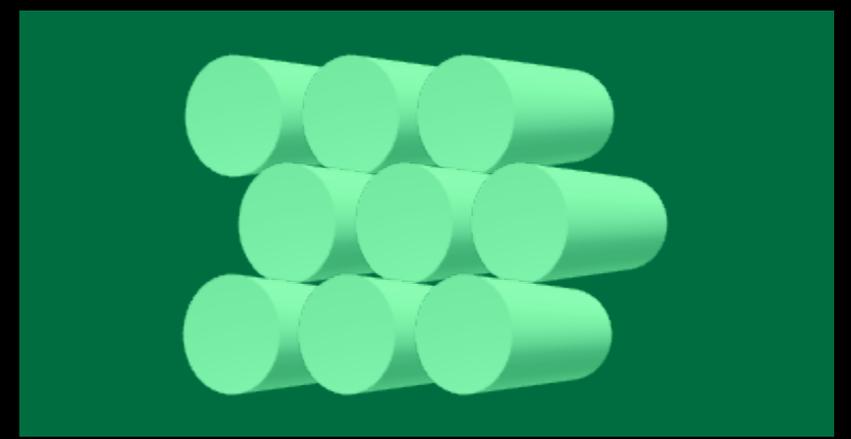
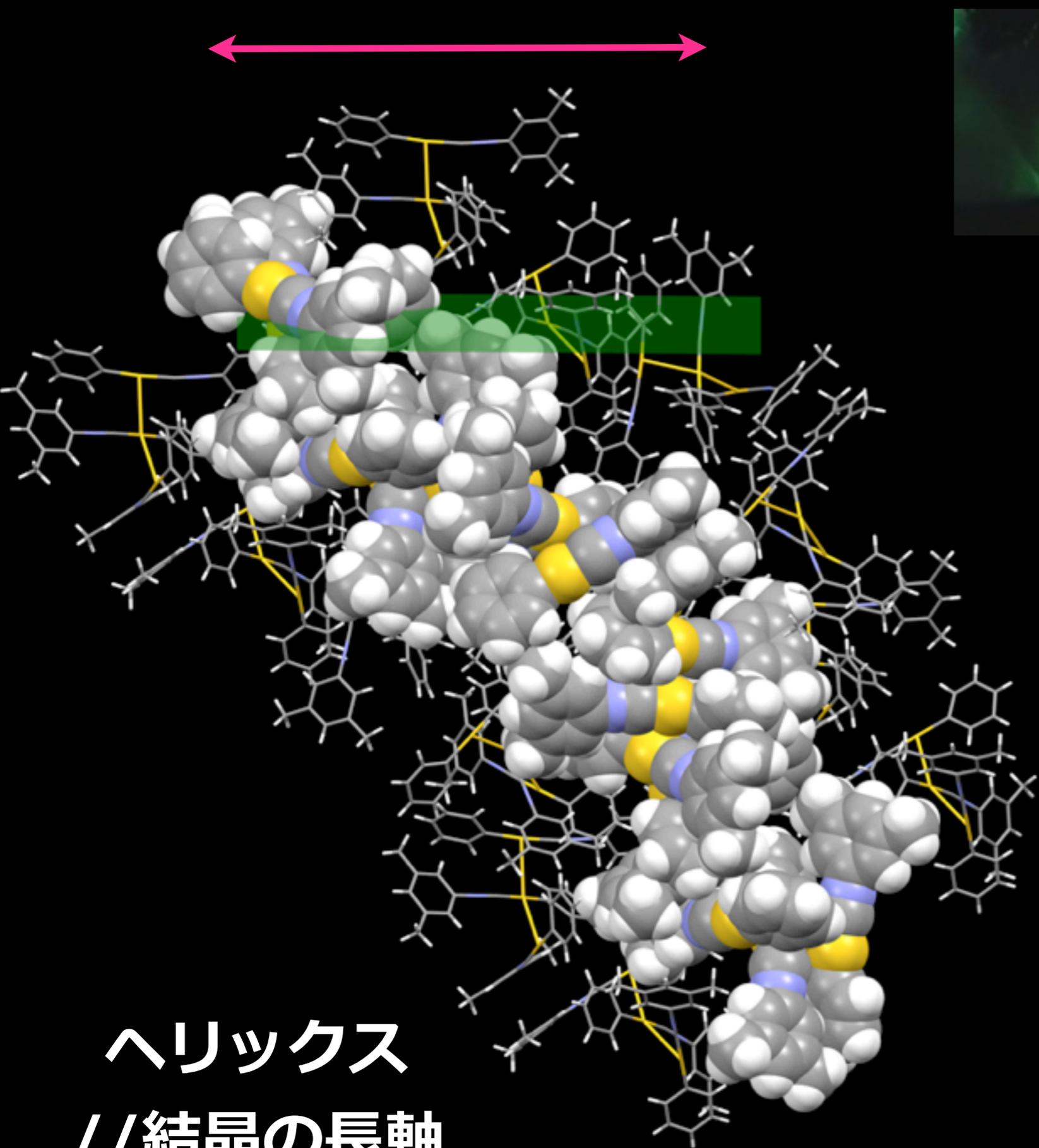
**Strong Au-Au  
Interactions**

Au-Au:  
3.135-3.304 Å (< 3.5 Å)

Hexameric  
Aggregation



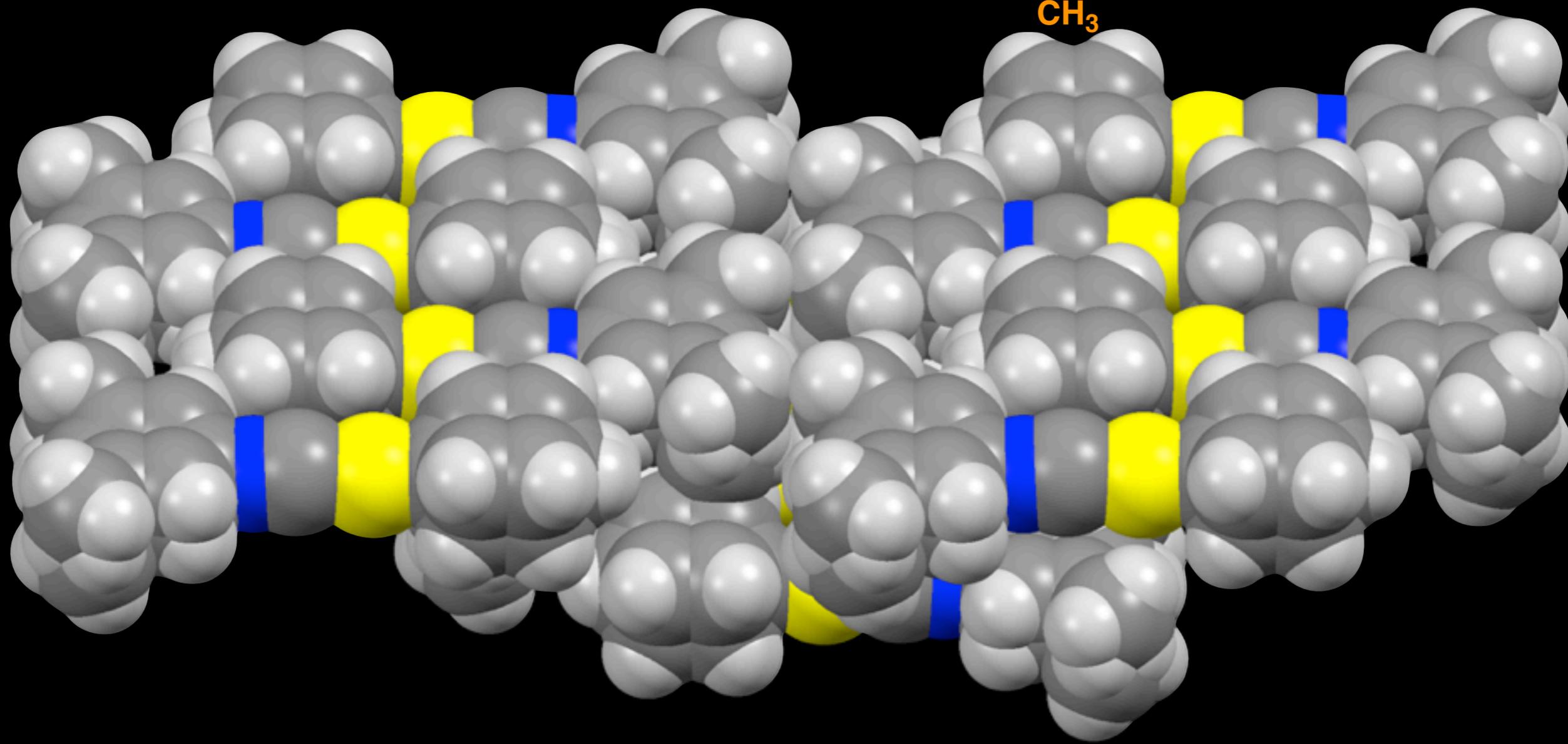
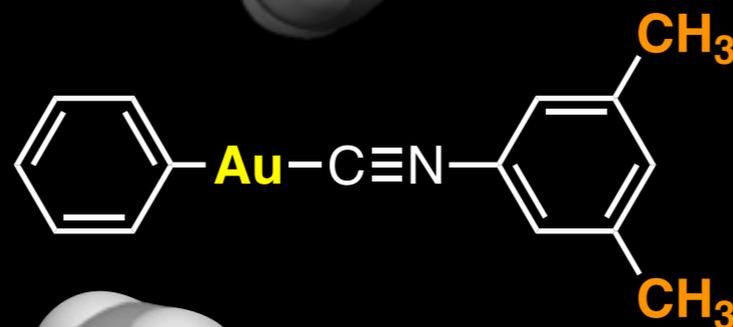
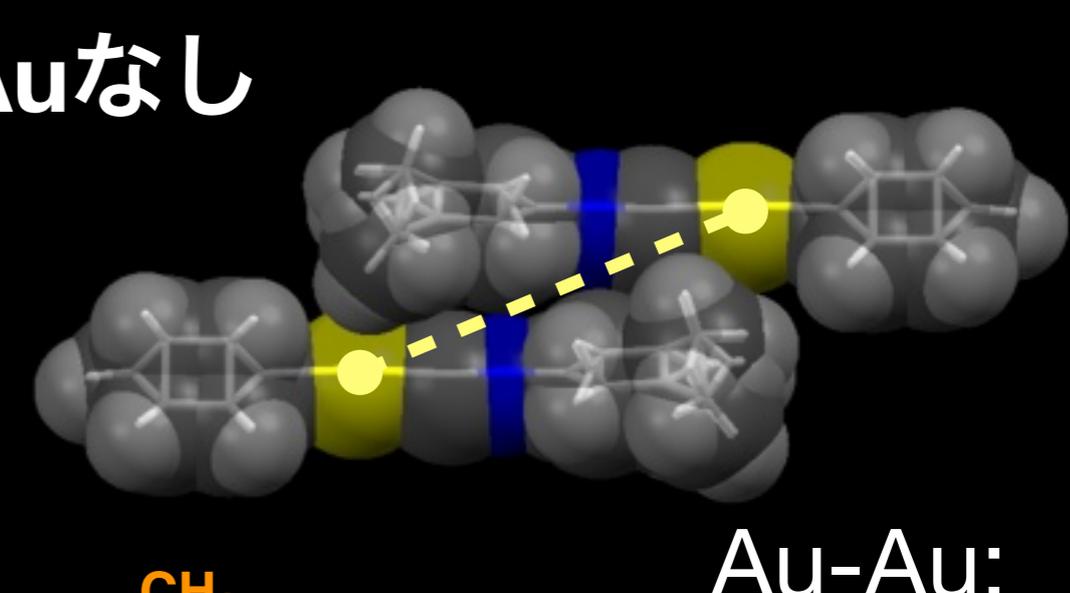
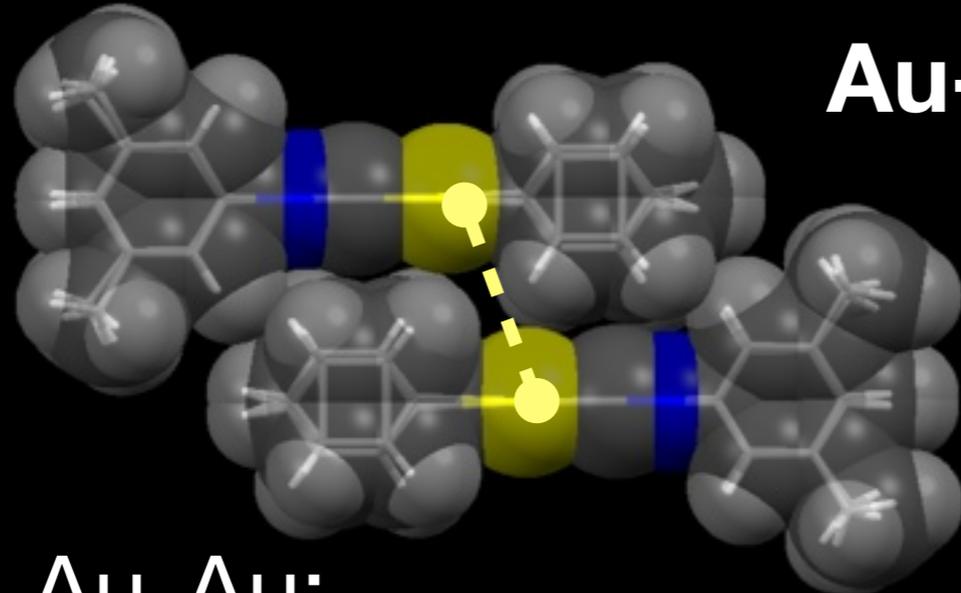


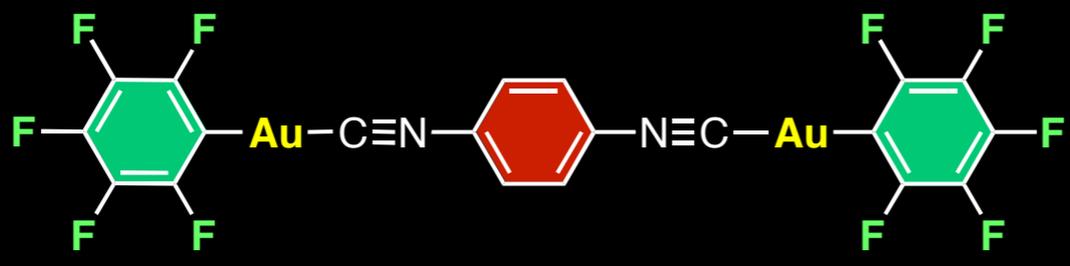


ヘリックス  
// 結晶の長軸



I-centered,  $Ima2$   
 $Z = 4$   
 $R_1 = 0.0883$   
 $wR_2 = 0.2174$   
 $GOF = 1.316$





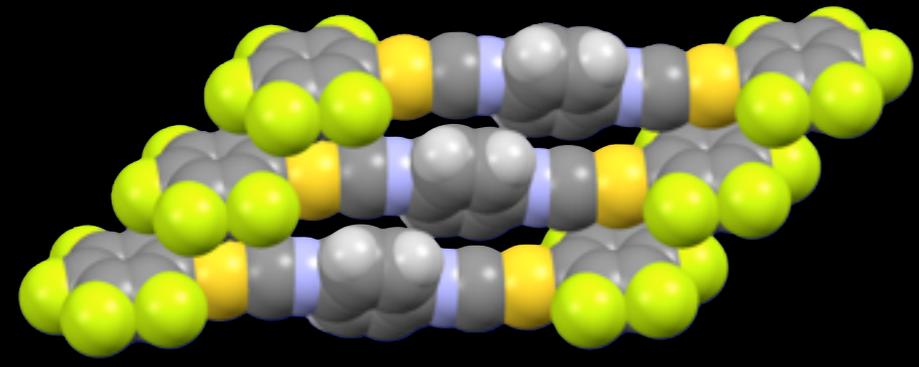
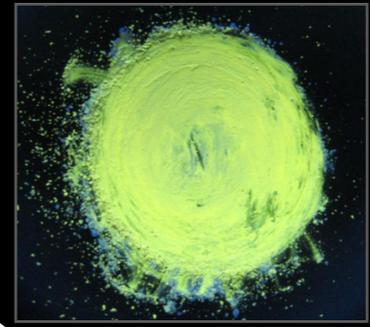
溶媒添加

再結晶

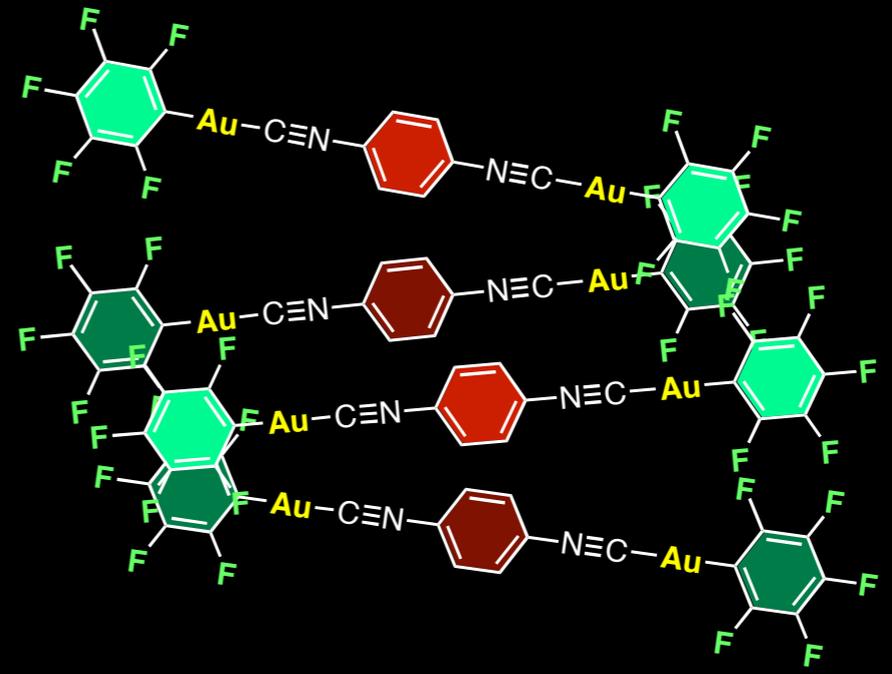
Grinding

準安定な  
アモルファス

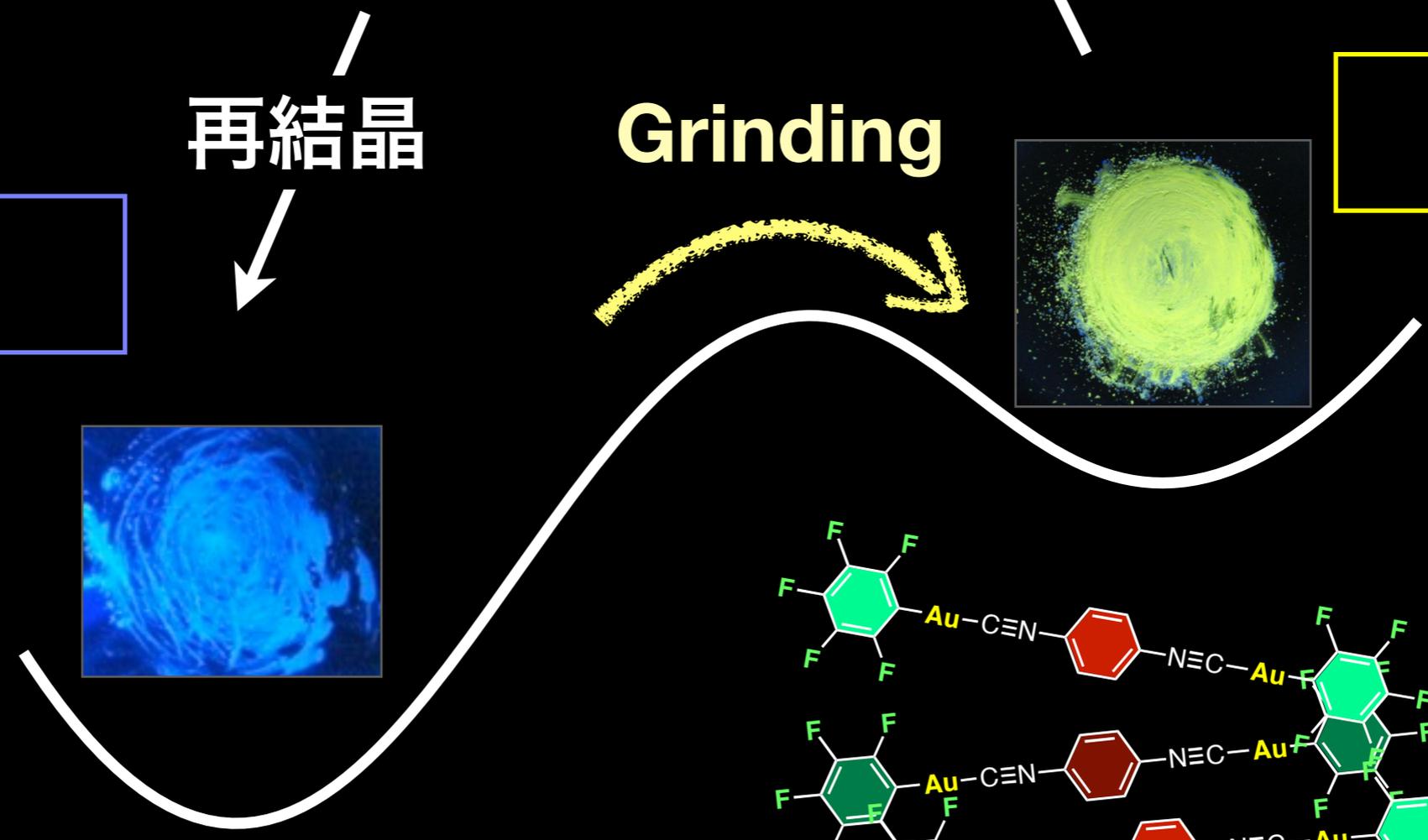
熱力学的に  
安定な結晶



Au/π 相互作用



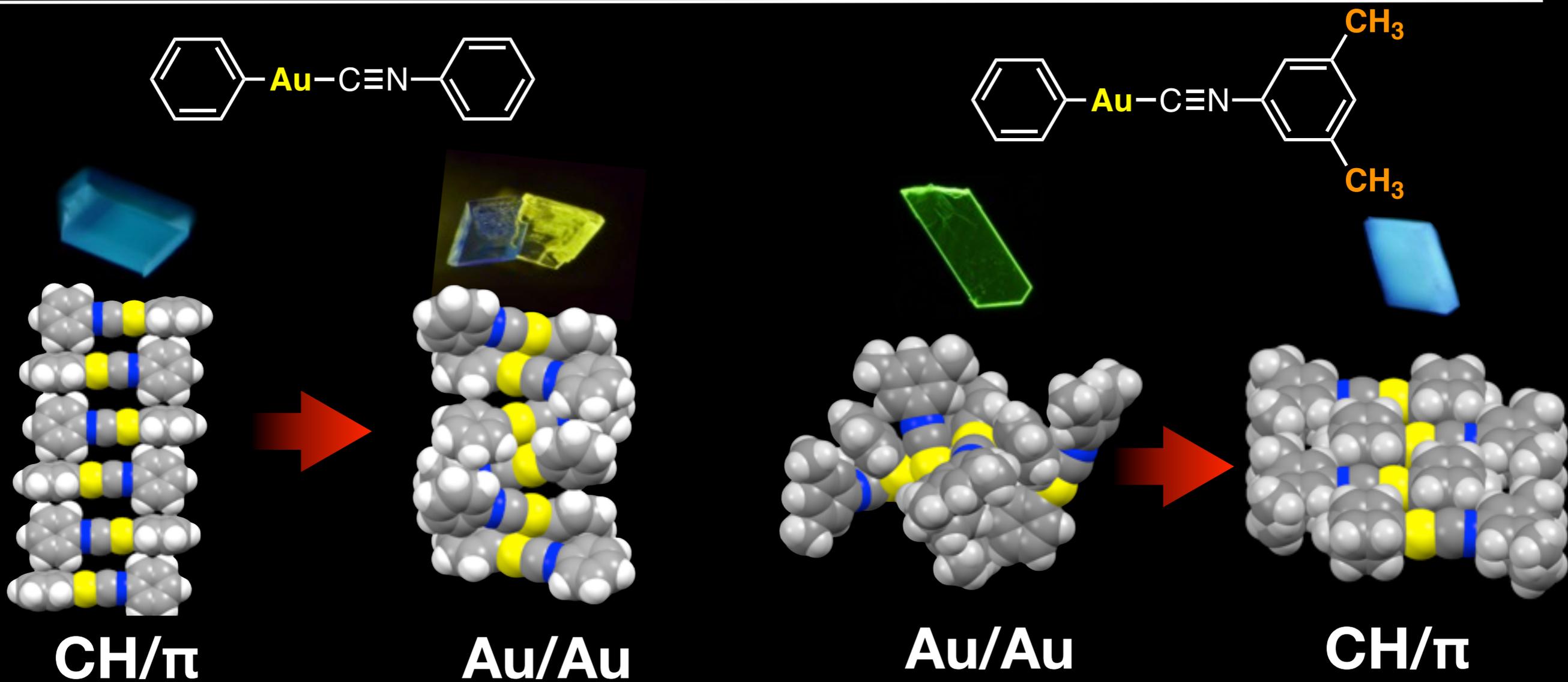
Au/Au 相互作用



分子ドミノ

速度論的  
準安定結晶

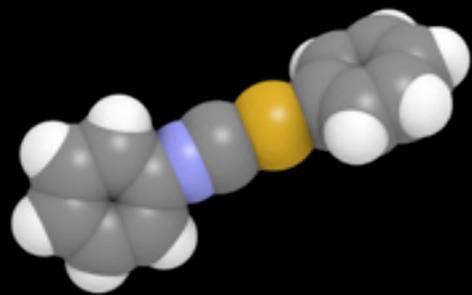
熱力学的に  
安定な結晶



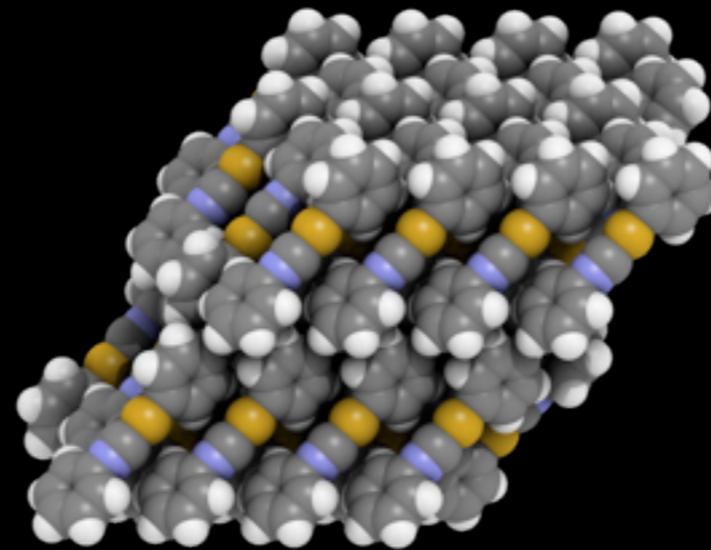
# 分子と結晶(バルク)をつなぐヒント



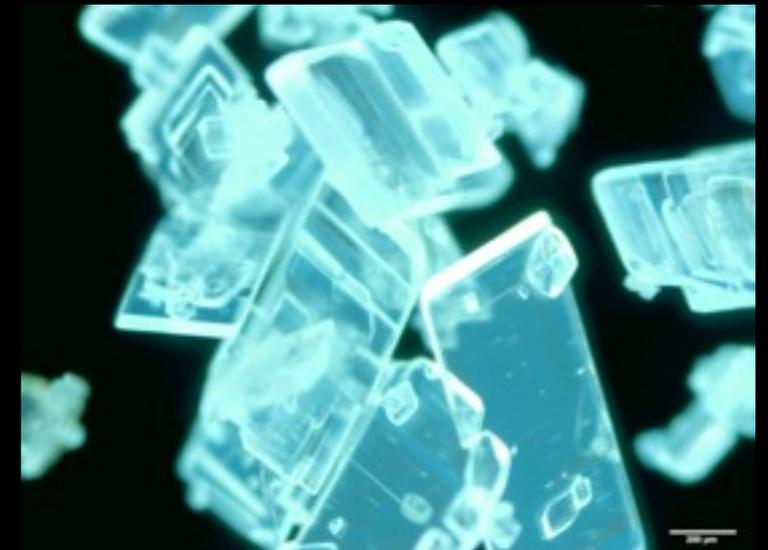
機械的刺激



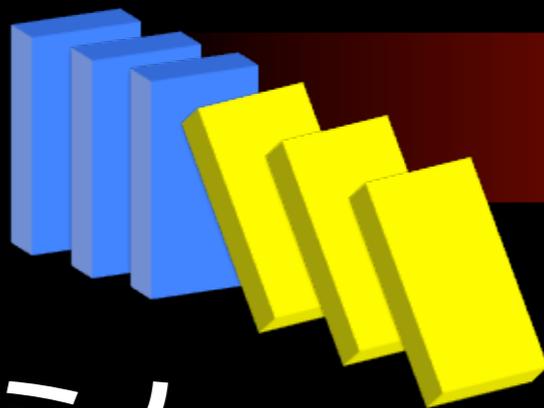
分子



複数分子の集積



結晶



分子ドミノ



# ごく最近の研究についての紹介

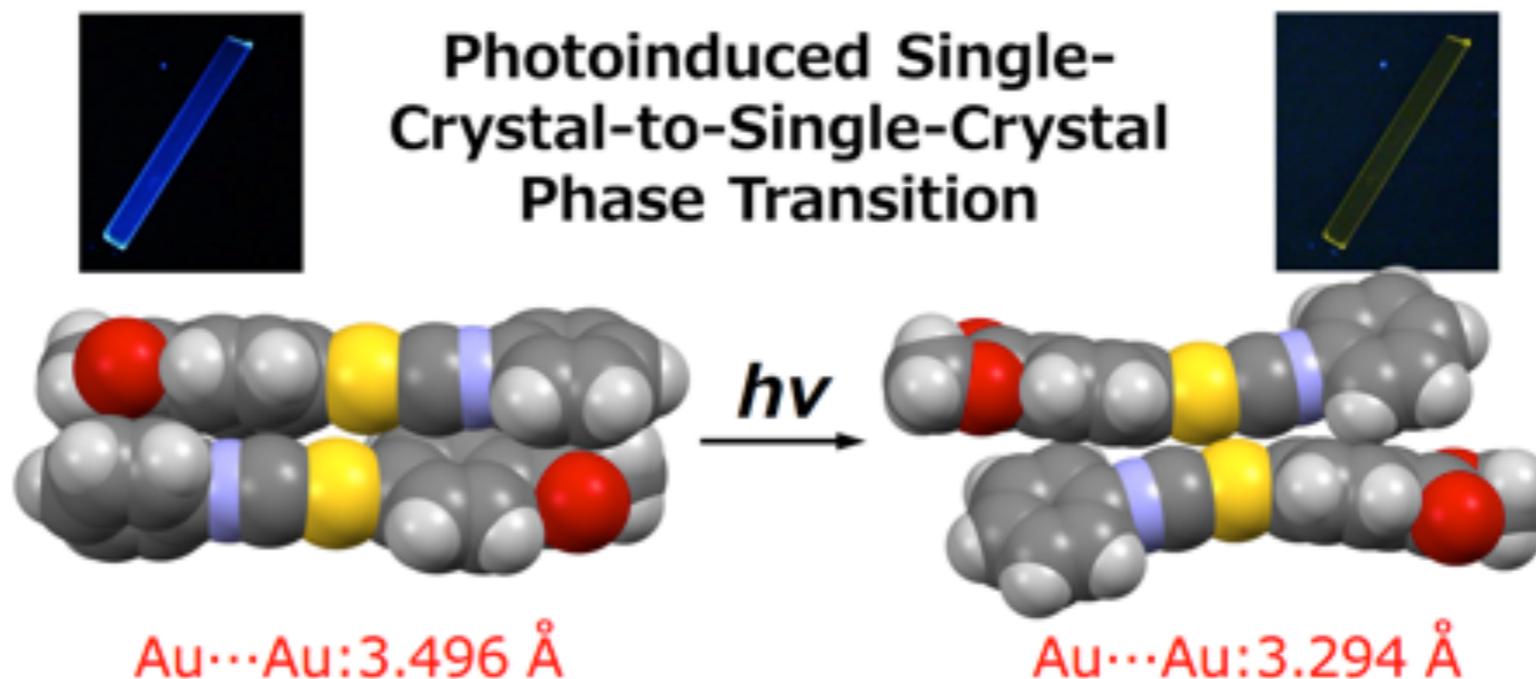
## 4F1-28



関朋宏  
特任助教

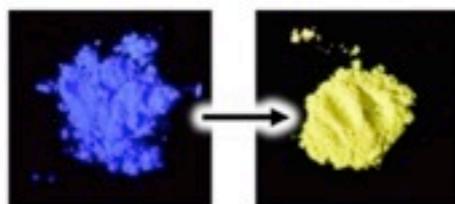
櫻田健太

### ■ 光照射によるAu-Au結合増強を伴うSCSC

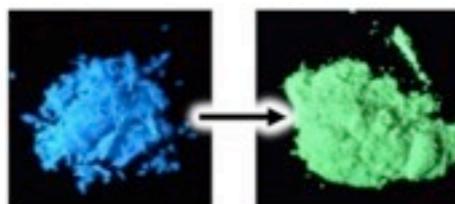


### ■ 金イソシアニド錯体合成スクリーニング

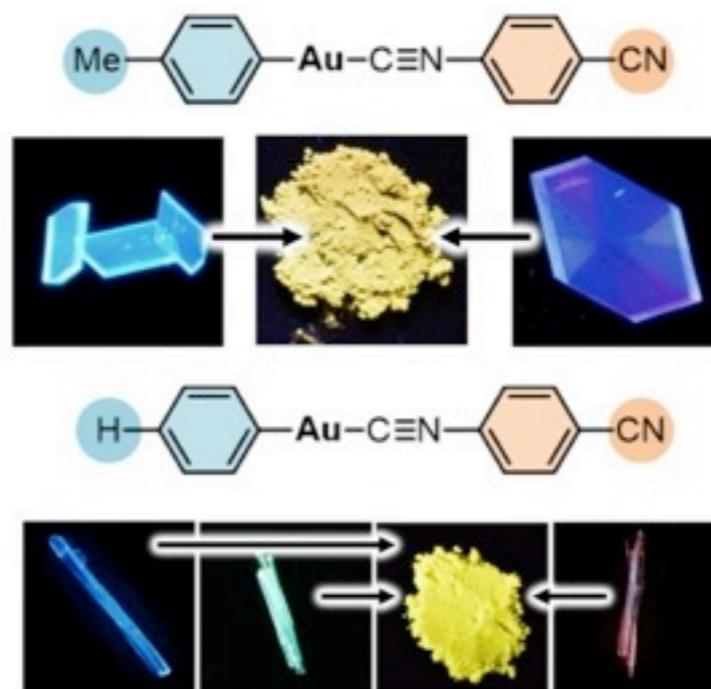
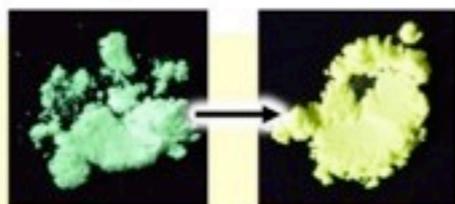
Type I  
 $R^1 = CF_3$   
 $R^2 = CF_3$



Type II  
 $R^1 = CF_3$   
 $R^2 = OMe$



Type III  
 $R^1 = CN$   
 $R^2 = CN$



## 4F1-29



関朋宏  
特任助教

高松雄輝

**1. 銅触媒によるホウ素化反応：発見と展開**

**2. メカノ応答性をもつ発光性金錯体**

**3.  $1 + 2 =$ メカノ反応 (最先端次世代)**

# ご協力いただいた先生方への謝辞

## 1. 銅触媒によるホウ素化反応：発見と展開

### 北海道大学

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鈴木 孝紀 教授

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今本 恒雄 千葉大学名誉教授

前田 理 准教授

谷野 圭司 教授

## 2. メカノ応答性をもつ発光性金錯体

### 北海道大学

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分島 亮 准教授

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佐々木 陽一 名誉教授

加藤 昌子 教授

柘植 清志 教授

(現富山大学)

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小西 克明 教授

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関 修平 教授 (大阪大学)

オラフカートハウス教授

(千歳科技大)

# 北海道大学総合化学院とリーディングプログラム

## 北海道大学大学院

### 総合化学院

#### 理学院 化学専攻

#### 工学院 応用化学

> 120名

武次 徹也 教授  
前田 理 准教授  
小林 正人 助教  
村越 敬 教授  
池田 勝佳 准教授  
保田 諭 講師  
魚崎 浩平 客員教授  
野口 秀典 客員准教授  
喜多村 昇 教授  
諸角 達也 助教  
作田 絵里 助教  
稲辺 保 教授  
原田 潤 准教授  
高橋 幸裕 助教  
武田 定 教授  
丸田 悟朗 助教  
景山 義之 助教  
加藤 昌子 教授  
小林 厚志 講師  
吉田 将己 助教  
日夏 幸雄 教授  
分島 亮 准教授  
土井 貴弘 助教  
吉川 信一 教授  
本橋 輝樹 准教授  
鱒淵 友治 助教  
忠永 清治 教授

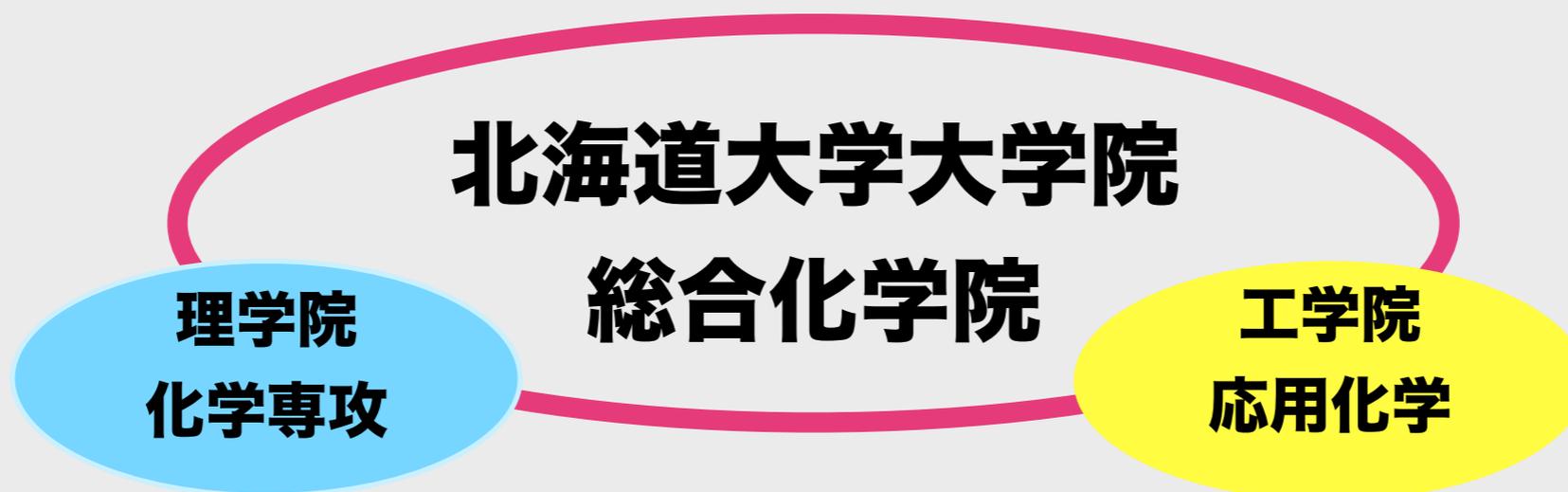
樋口 幹雄 准教授  
室町 英治 客員教授  
山浦 一成 客員教授  
原 正治 教授  
仙北 久典 准教授  
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黒野 暢仁 助教  
伊藤 肇 教授  
石山 竜生 准教授  
山本 靖典 特任准教授  
関 朋宏 特任助教  
鈴木 孝紀 教授  
原 憲秀 准教授  
上遠野 亮 助教  
澤村 正也 教授  
大宮 寛久 准教授  
岩井 智弘 助教  
及川 英秋 教授  
大栗 博毅 准教授  
南 篤志 助教  
谷野 圭持 教授  
鈴木 孝洋 准教授  
吉村 文彦 助教  
福岡 淳 教授  
原 賢二 准教授

小林 広和 助教  
中野 環 教授  
小山 靖人 准教授  
長谷川 淳也 教授  
中山 哲 准教授  
荒井 正彦 教授  
下川部 雅英 教授  
藤田 進一郎 講師  
岩佐 信弘 助教  
坪内 直人 准教授  
熊谷 治夫 助教  
増田 隆夫 教授  
多湖 輝興 准教授  
中坂 佑太 助教  
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青木 芳尚 准教授  
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打越 哲郎 客員教授

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加藤 一実 客員教授  
佐々木 毅 客員教授  
安住 和久 教授  
小泉 均 准教授  
田地川 浩人 助教  
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中西 貴之 助教  
葉 金花 客員教授  
加古 哲也 客員准教授  
居城 邦治 教授  
新倉 謙一 准教授  
松尾 保孝 准教授  
三友 秀之 助教  
佐田 和己 教授  
角五 彰 准教授  
小門 憲太 助教  
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陳 友根 特任助教  
佐藤 敏文 教授  
田島 健次 准教授  
坂口 和靖 教授  
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昆 俊亮 助教  
高木 睦 教授  
恵良田 知樹 准教授  
藤原 政司 助教  
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高畑 信也 助教  
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松本 謙一郎 准教授  
平尾 一郎 客員教授  
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# 北海道大学総合化学院とリーディングプログラム



北海道大学  
物質科学フロンティアを開拓する  
Ambitiousリーダー育成プログラム

博士課程教育：異分野交流・独立ラボ・海外研修  
M1からD3まで経済支援



新拠点：フロンティア科学  
研究棟（鈴木章先生記念）

# 謝辞

石山竜生

山本靖典

石塚 智子

川上 千佳

小坂 由紀

伊藤 慎一郎

大島 直哉

齋藤 智久

松浦 耕

野々山 浩輔

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竹ノ内 雄太

泉 清孝

小島 遼人

櫻田 健太

岩本 紘明

浮海 智

## ¥研究資金¥

科学研究費補助金

基盤研究(B)

特定領域研究(元素相乗系の化学)

挑戦的萌芽研究

JST さきがけ(物質と光作用)

最先端・次世代研究開発プログラム

**本日の講演資料: 4/1 HPで公開 検索「有機元素」**