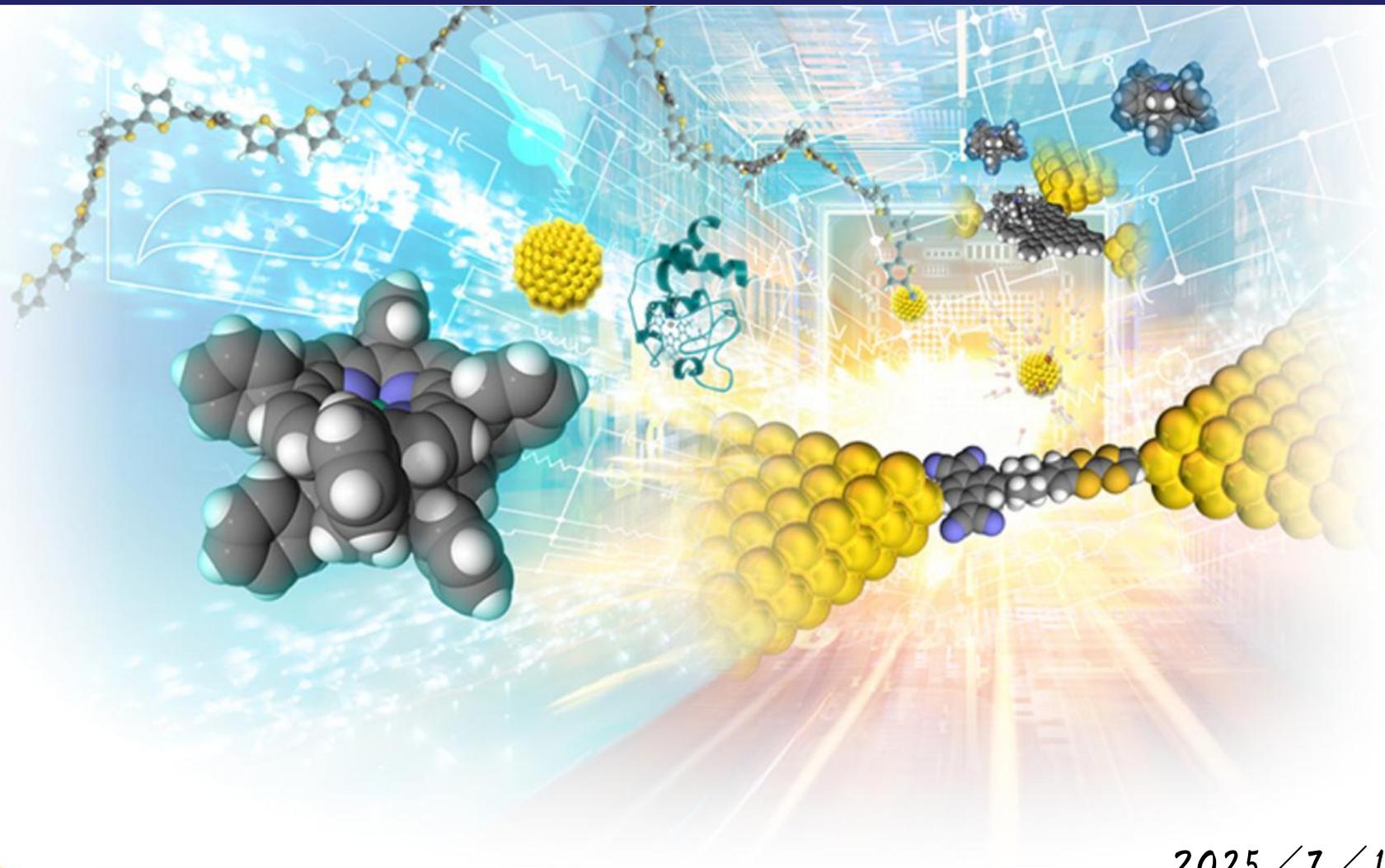


# 機能性高分子ワイヤの合成を基軸とする高分子デバイスの作製



2025/7/14

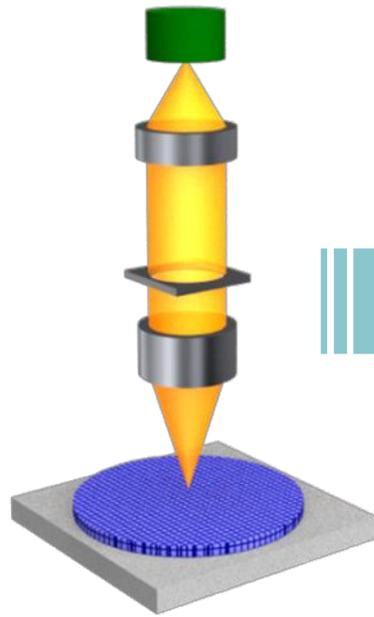


東京大学  
THE UNIVERSITY OF TOKYO

公益財団法人 矢崎科学技術振興記念財団 第2回発表会

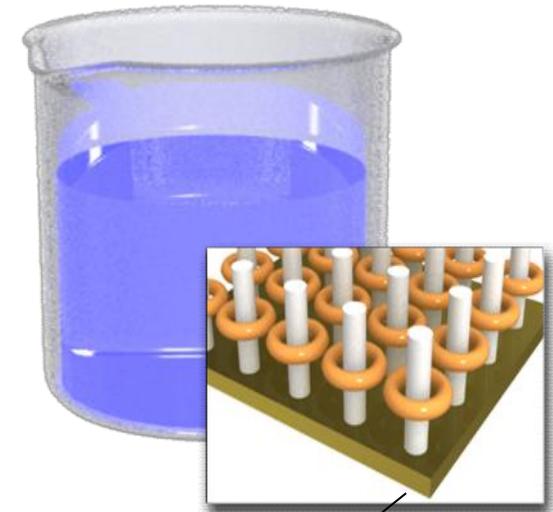
東京大学 大学院総合文化研究科・教授 / 寺尾 潤

# 集積回路の微細加工技術



フォトリソグラフィーなどの  
**トップダウン**的手法が中心

シリコンから有機分子テクノロジーへ

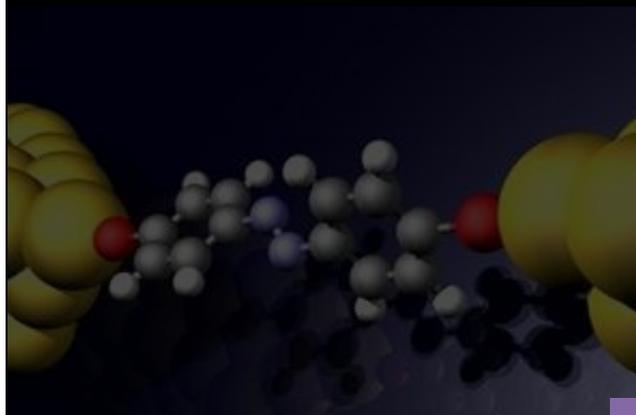


有機分子

自己組織化などの  
**ボトムアップ**的手法が中心

1. 大幅な製造コストの削減
2. 大幅な製造過程での省エネ効果
3. 超低消費電力のデバイスの作成

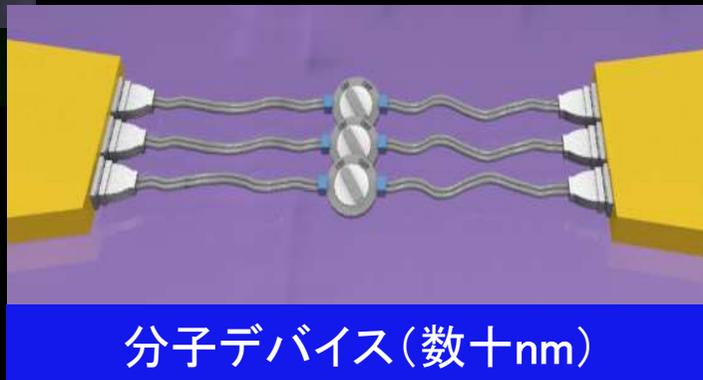
# 合成化学的手法による分子デバイスの作製



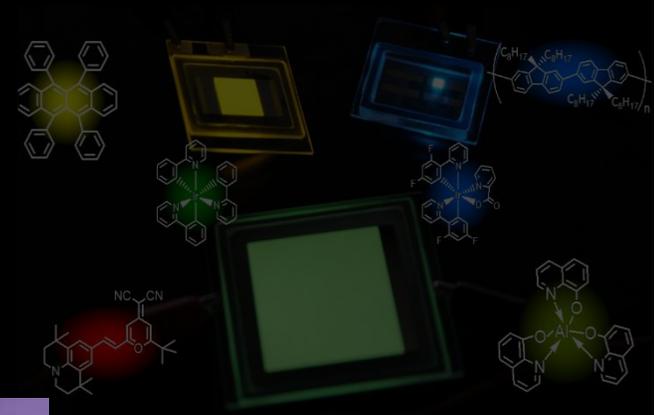
単分子エレクトロニクス (Å)

基礎研究段階

ブレイクジャンクション



分子デバイス (数十nm)



有機エレクトロニクス ( $\mu m$ )

実用的なデバイスが製品化

固定電極

# 着想の経緯

学研電子ブロック  
EX-SYSTEM





# 着想の経緯

学研電子ブロック  
EX-SYSTEM



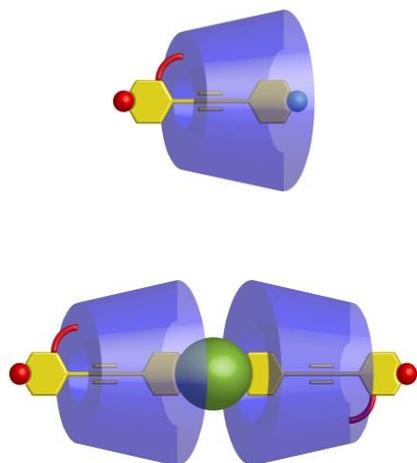
電子ブロック



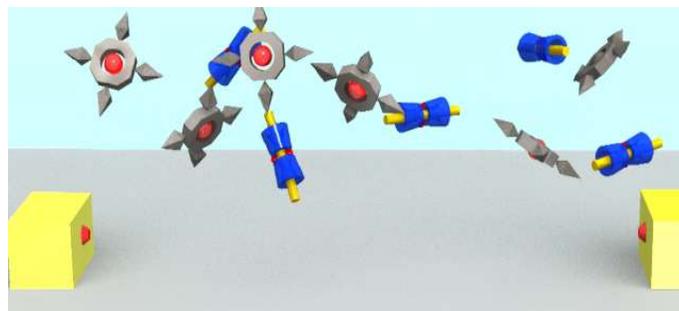
選んで目で見て配線



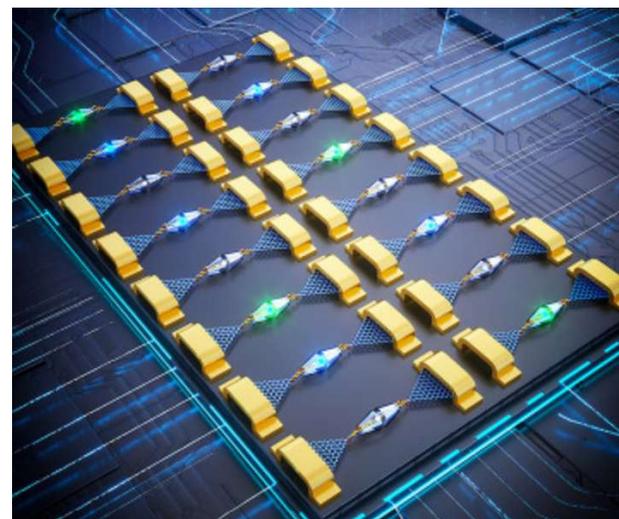
電子回路(電子デバイス)



被覆共役分子(分子ブロック)



選択的合成による分子配線



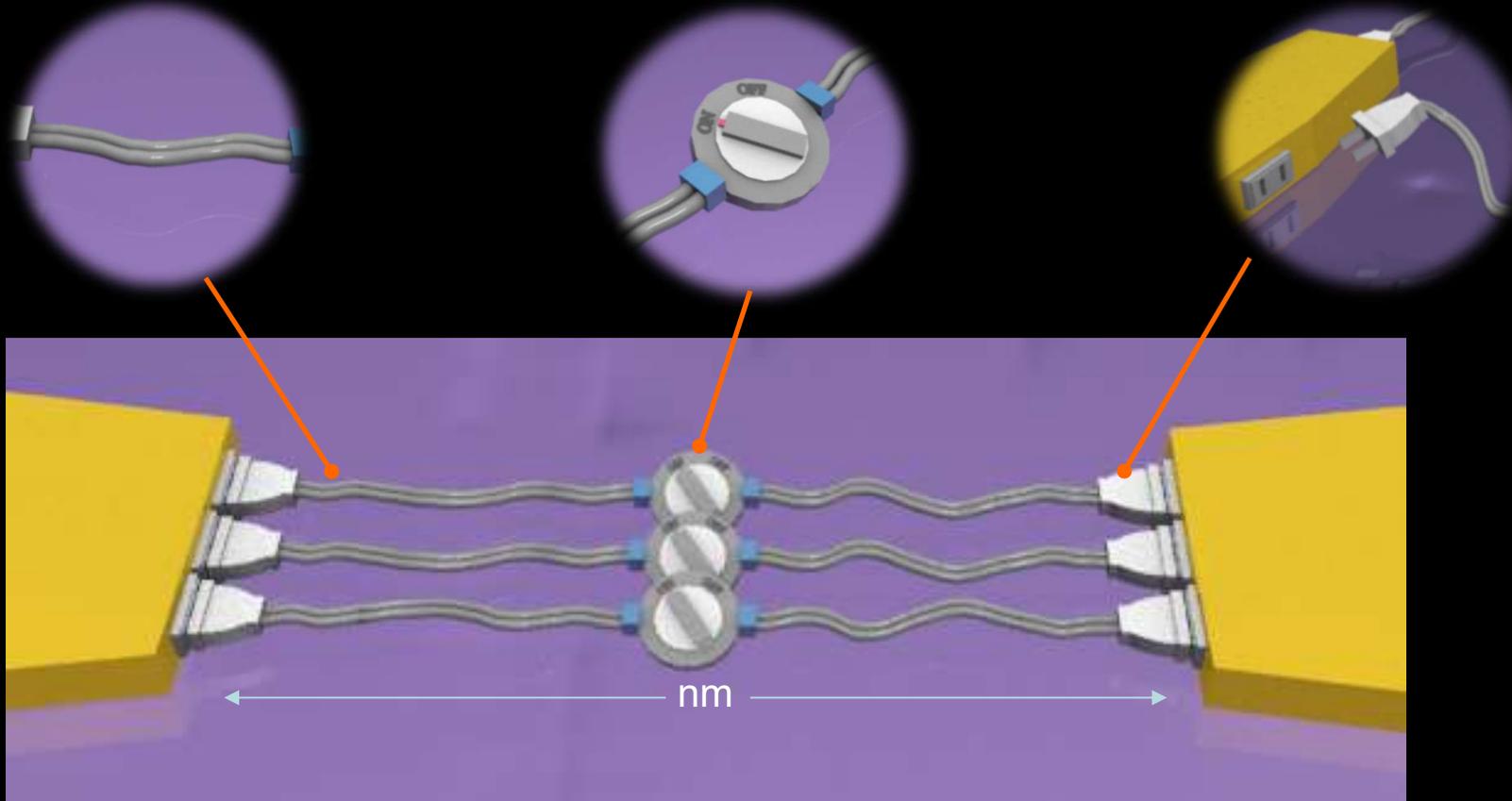
分子回路(電子デバイス)

# 研究戦略

1. 被覆型分子ワイヤの合成

2. 外部刺激応答性部位の導入

3. プラグ分子の導入

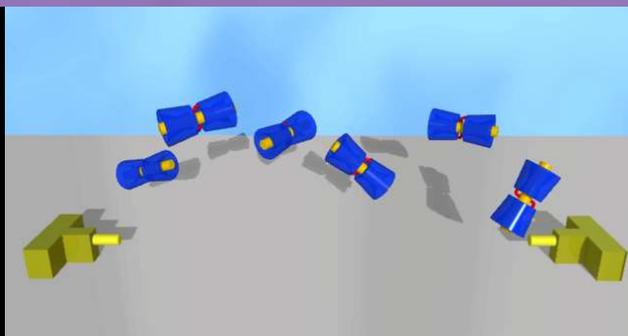
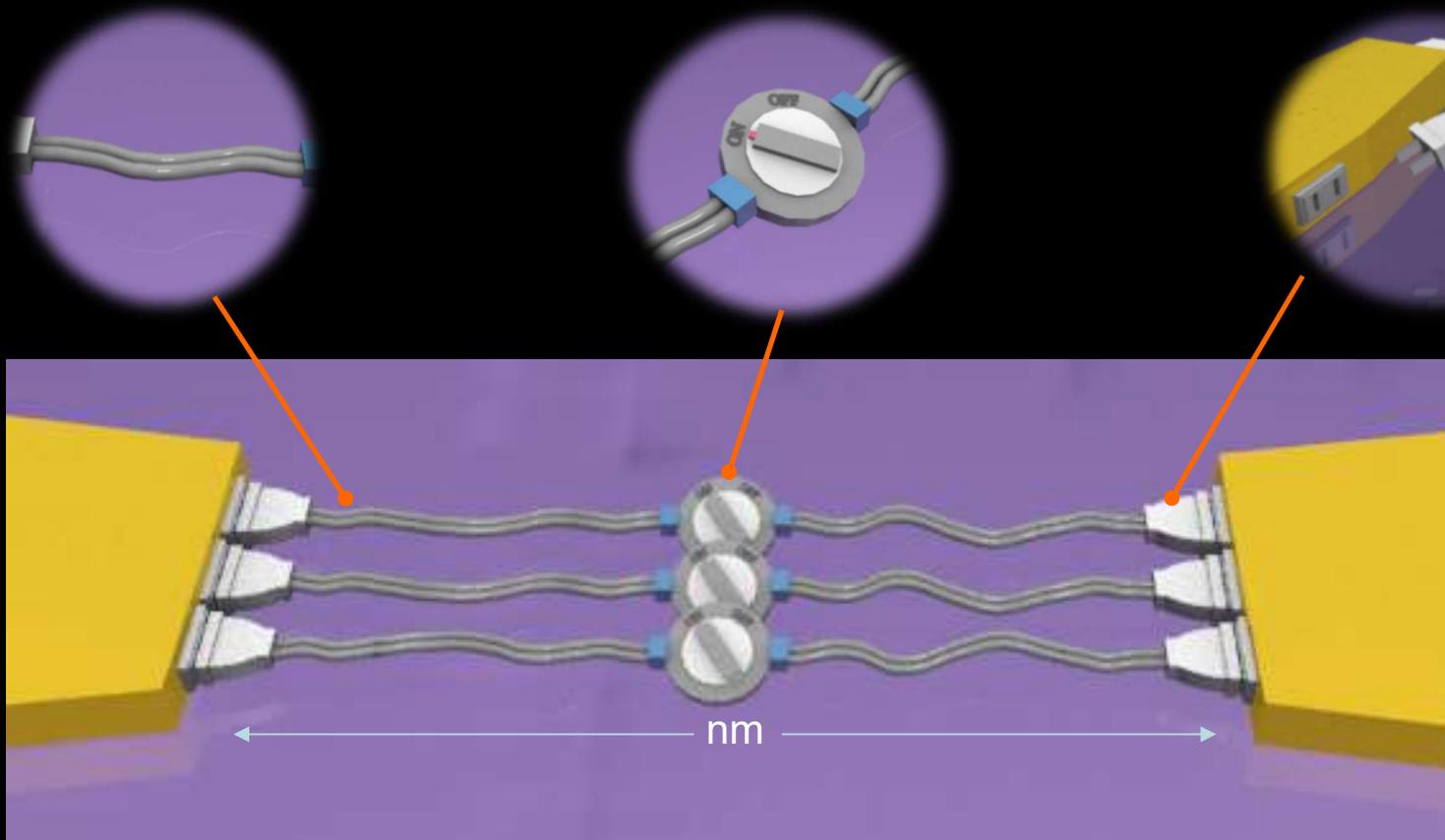


# 研究戦略

1. 被覆型分子ワイヤの合成

2. 外部刺激応答性部位の導入

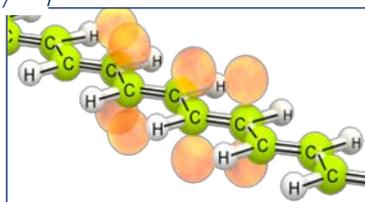
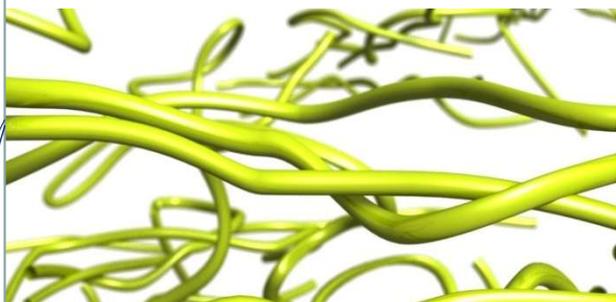
3. プラグ分子の導入



4. ビルドアップ型分子配線法の開発

# 被覆型分子ワイヤ

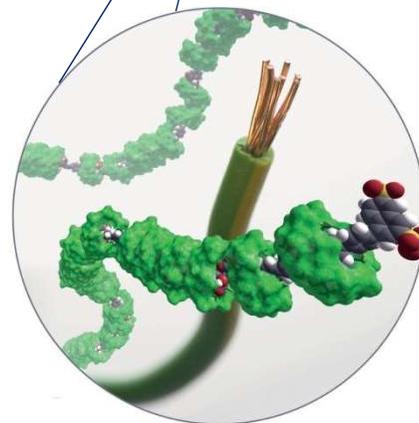
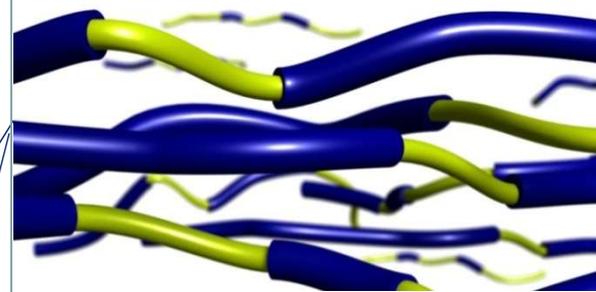
共役高分子



導電性・移動度 (中)  
蛍光性 (低)  
溶解性 (中)  
安定性・耐久性 (低)

被覆

被覆型分子ワイヤ

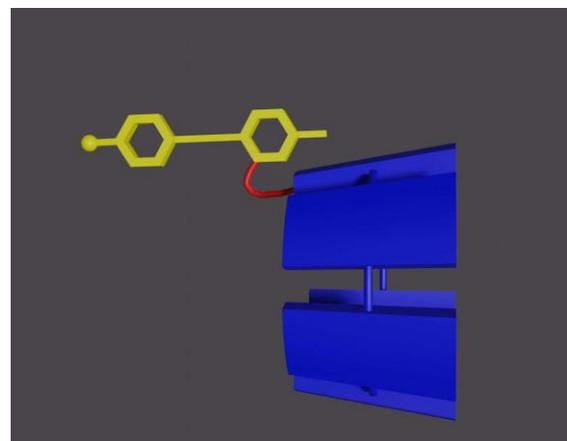
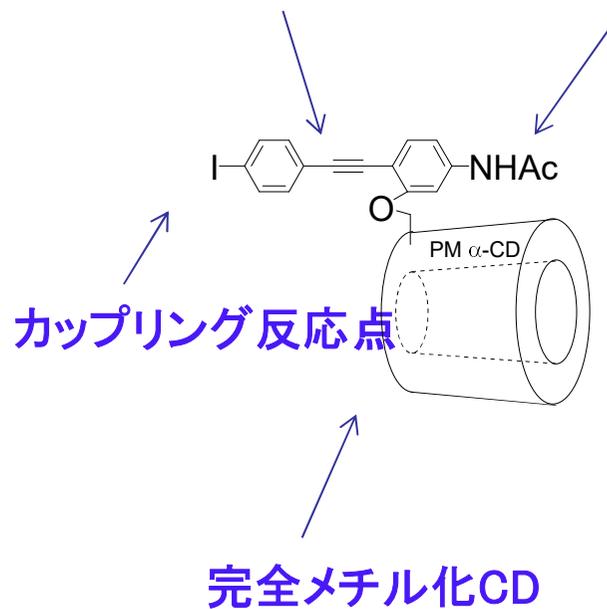


導電性・移動度 (高)  
蛍光性 (高)  
溶解性 (高)  
安定性・耐久性 (高)

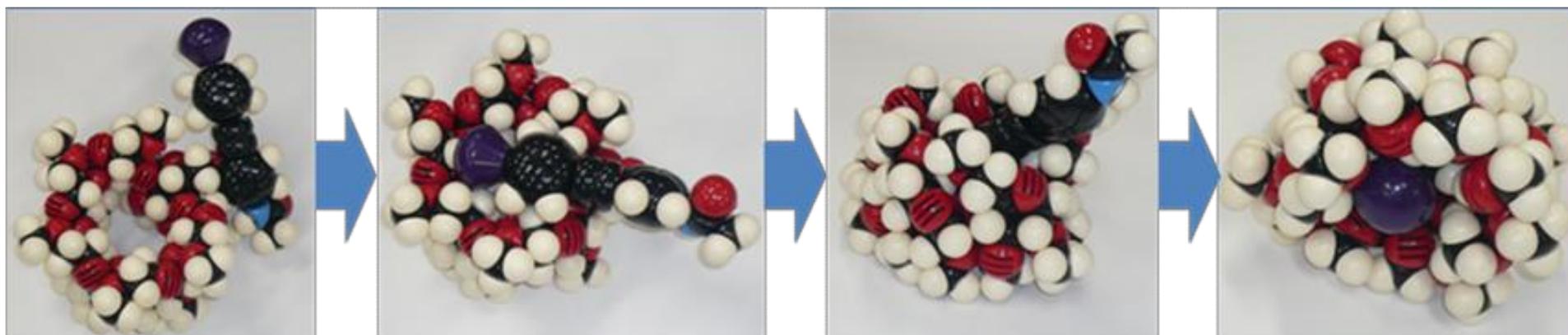
# 分子内自己包接

$\pi$ -共役ゲスト

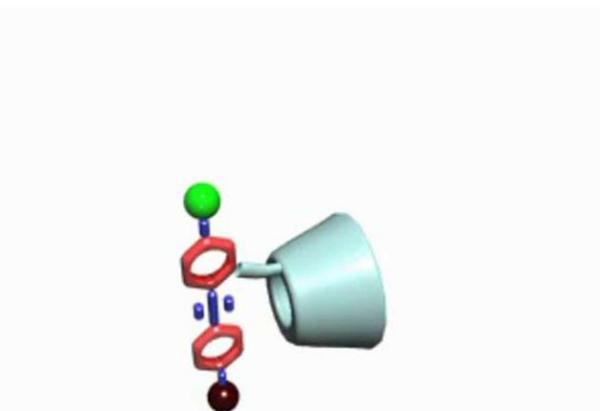
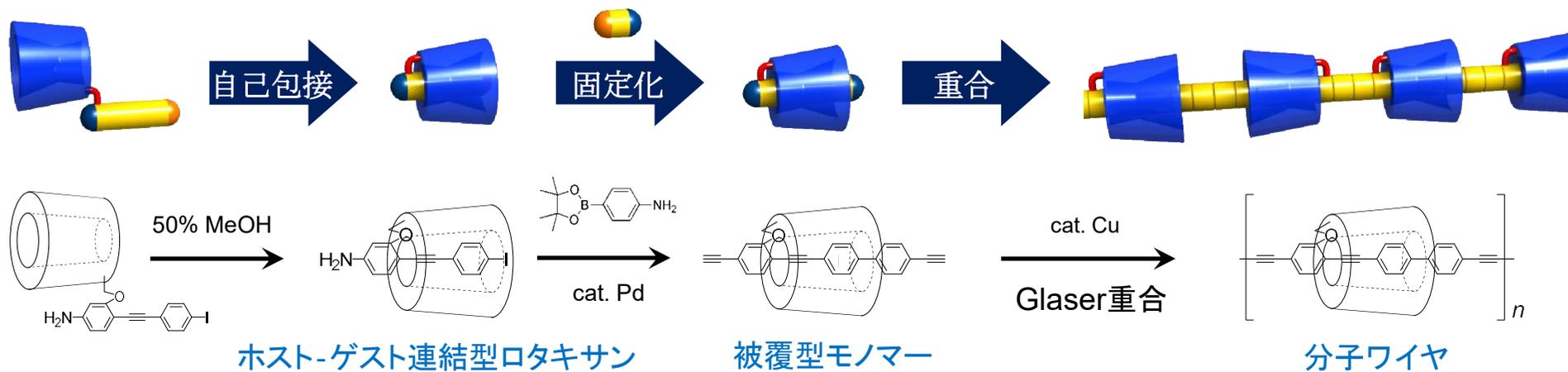
官能基変換部位



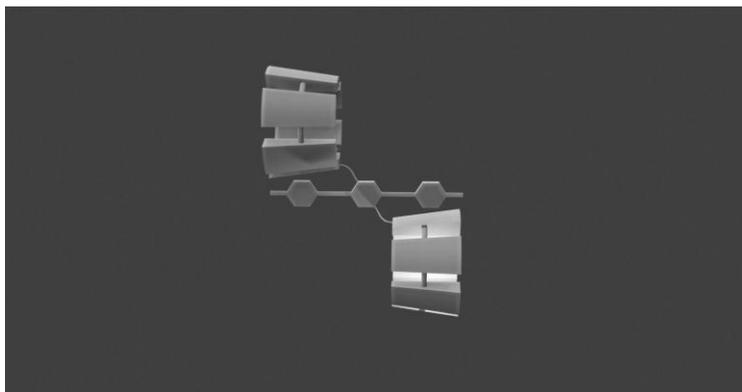
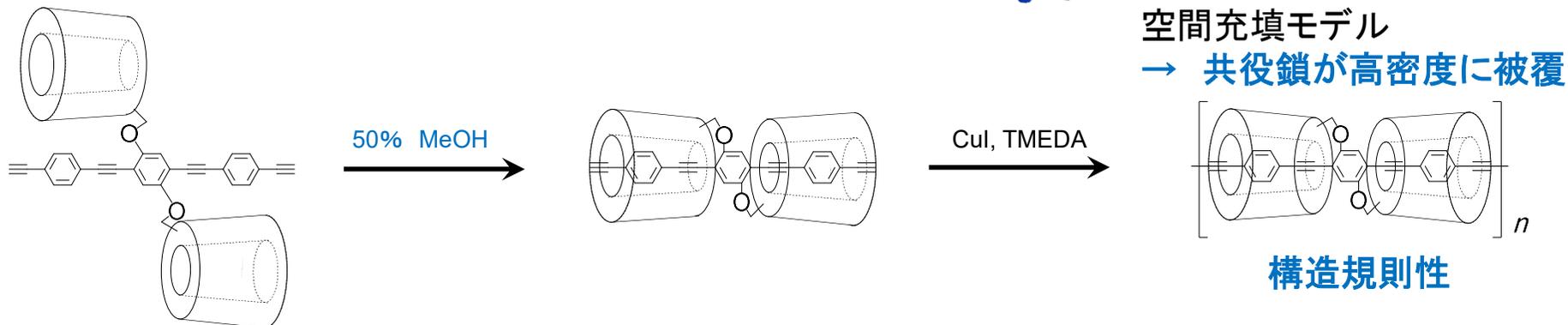
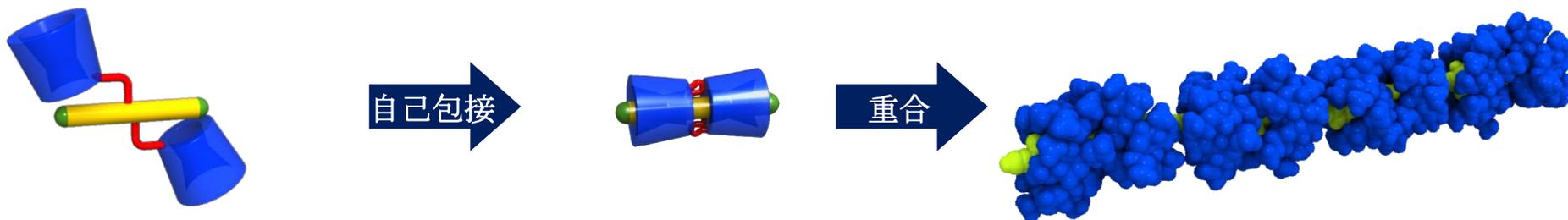
*Angew. Chem. Int. Ed.*, 2024, 63, e202414307.



# 高伝導性分子ワイヤの合成

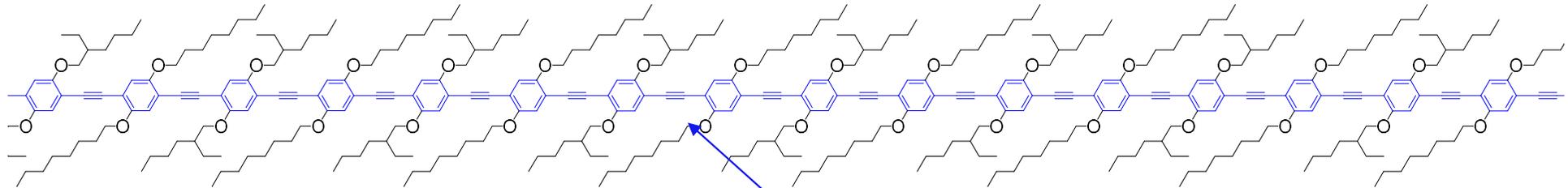


# 高被覆分子ワイヤの合成



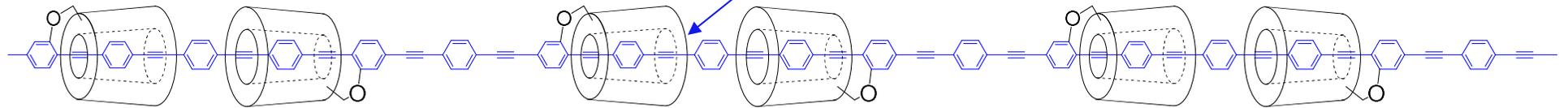
# 環状被覆効果： 固体中における電荷移動度 (TRMC法)

側鎖修飾型分子ワイヤ



$$\mu = 0.0022 \text{ cm}^2/\text{Vs}$$

環状被覆型分子ワイヤ



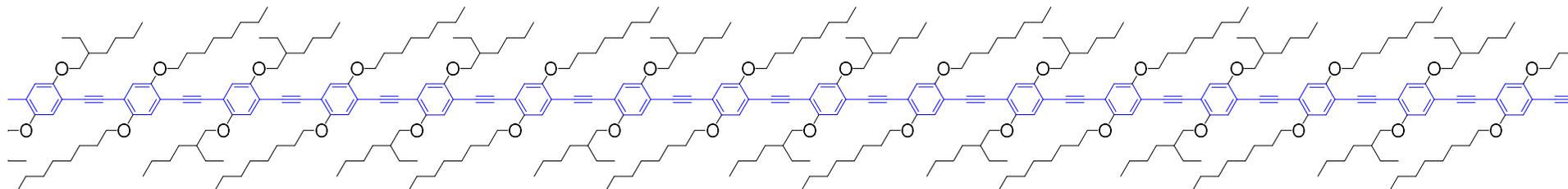
$$\mu = 0.71 \text{ cm}^2/\text{Vs}$$

ポリフェニレンエチニレン

三次元的被覆により主鎖の剛直性/一次元性が向上

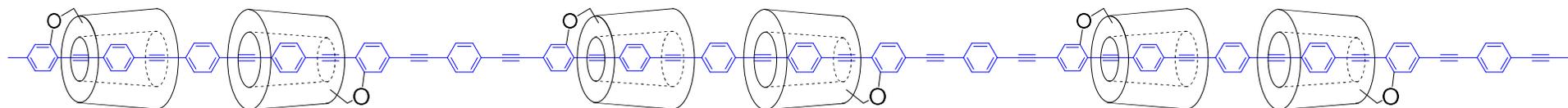
# ジグザグ型被覆分子ワイヤ

## 側鎖修飾型分子ワイヤ



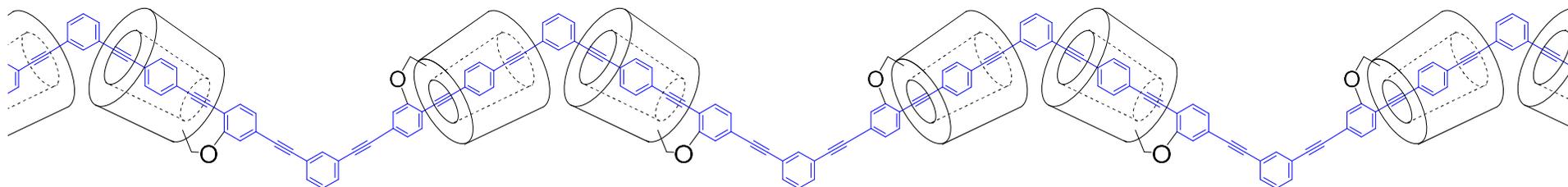
$$\mu = 0.0022 \text{ cm}^2/\text{Vs}$$

## 環状被覆型分子ワイヤ



$$\mu = 0.71 \text{ cm}^2/\text{Vs}$$

## ジグザグ型被覆分子ワイヤ



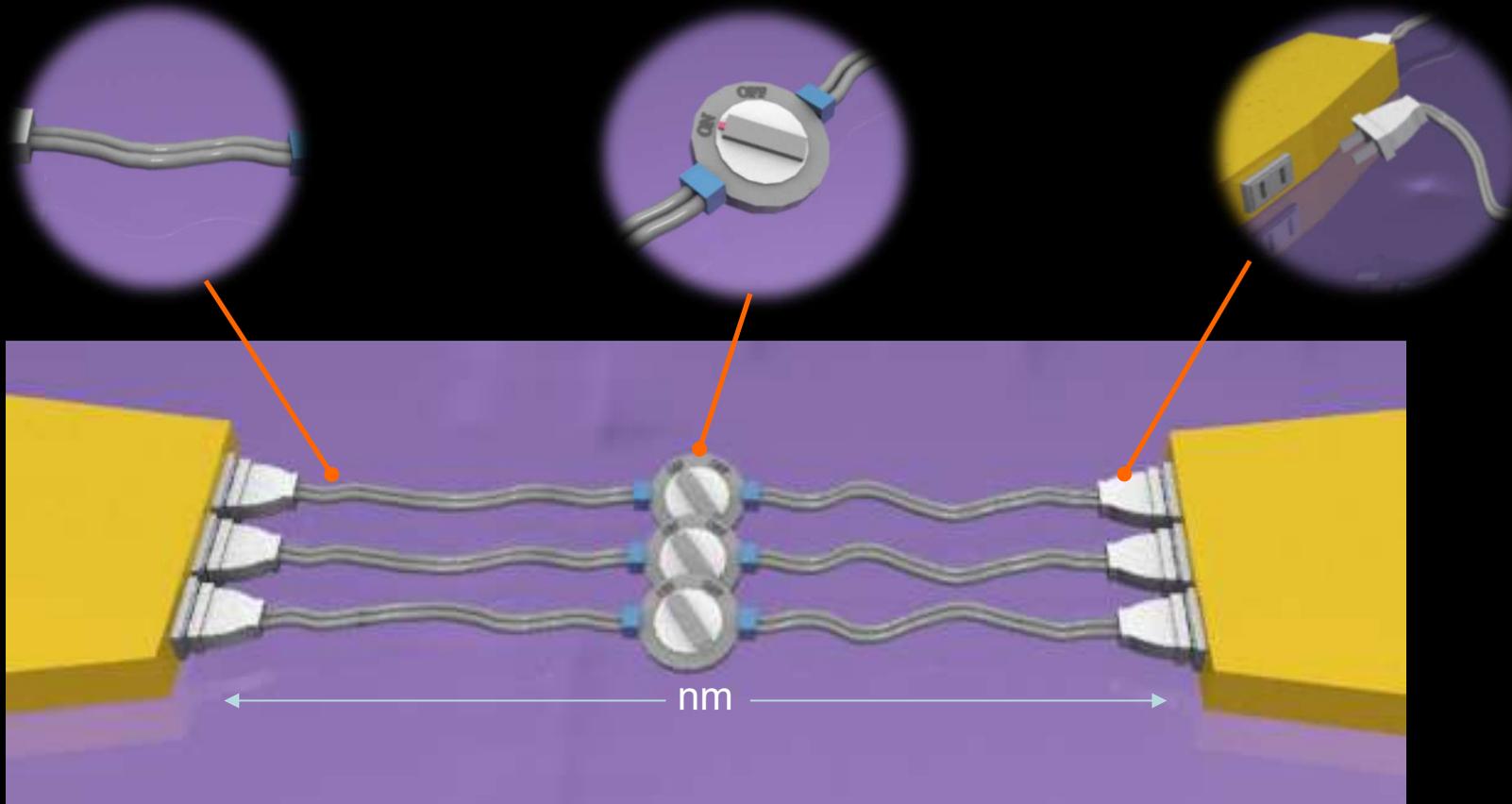
$$\mu = 2.1 \text{ cm}^2/\text{Vs}$$

メタ位で接合 (規則的な分子軌道の局在化)

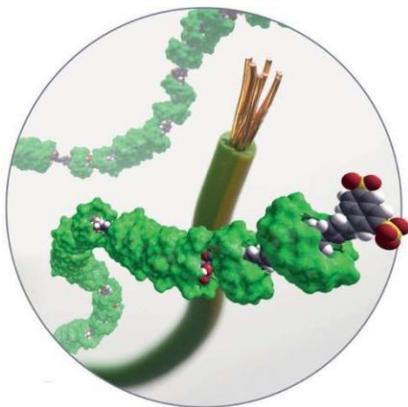
*Nat. Commun.* 2013, 4, 1691

# 研究戦略

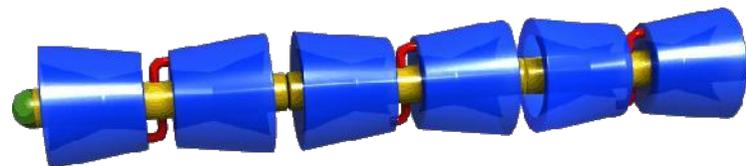
1. 被覆型分子ワイヤの合成
2. 外部刺激応答性部位の導入
3. 界面制御分子の導入



# 被覆型分子ワイヤの合成



単なる無機配線材料の模倣



- ・剛直性(直線性)
- ・固体発光性
- ・電荷輸送性

Reviews:

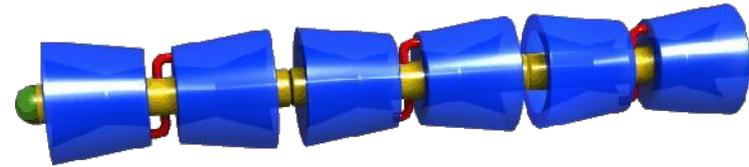
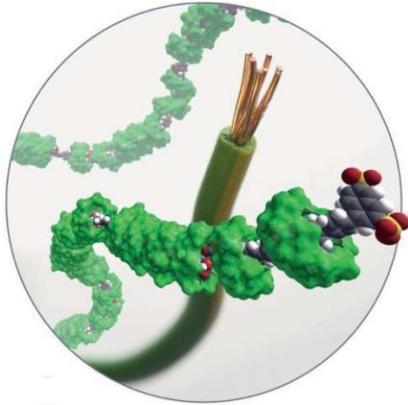
*Poly. Chem.*, **2011**, 2, 2444

*Chem. Rec.*, **2011**, 11, 269

*J. Incl. Phenom. Macrocycl. Chem.*, **2014**, 80, 165

*J. Synth. Org. Chem. Jpn.*, **2015**, 73, 1007

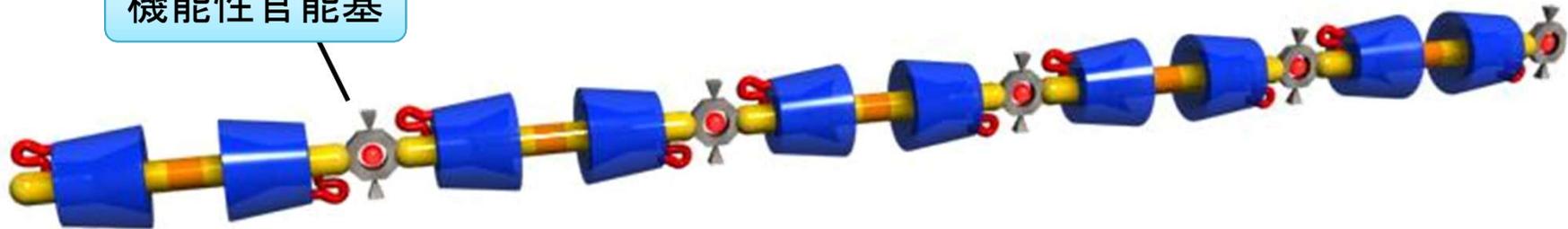
# 機能性分子ワイヤの合成



- ・剛直性(直線性)
- ・固体発光性
- ・電荷輸送性
- ・機能性



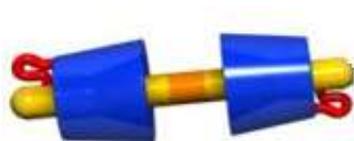
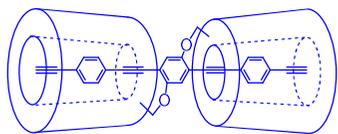
機能性官能基



機能性分子ワイヤ

# 被覆型機能性分子ワイヤの合成

## 被覆共役モノマー

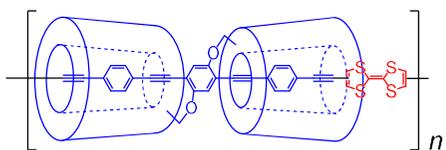
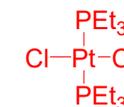
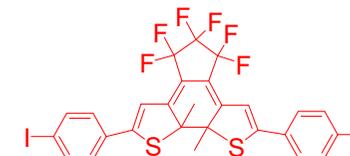
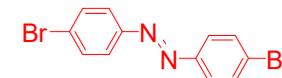
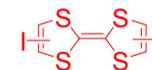


+

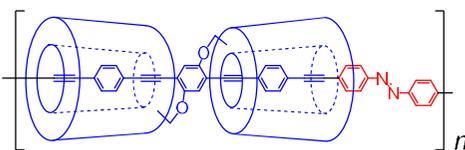


共重合反応

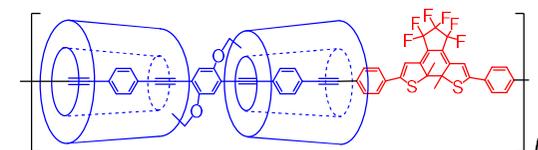
## 機能性モノマー



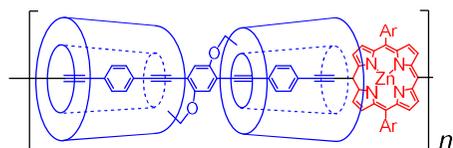
*Chem. Commun.* **2014**, 50, 658



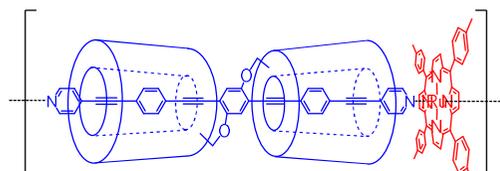
*J. Incl. Phenom. Macrocycl. Chem.* **2014**, 80, 165



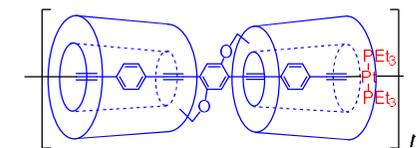
*Chem. Commun.* **2014**, 50, 658  
*Beilstein J. Org. Chem.* **2014**, 10, 2800



*Bull. Chem. Soc. Jpn.* **2014**, 87, 871

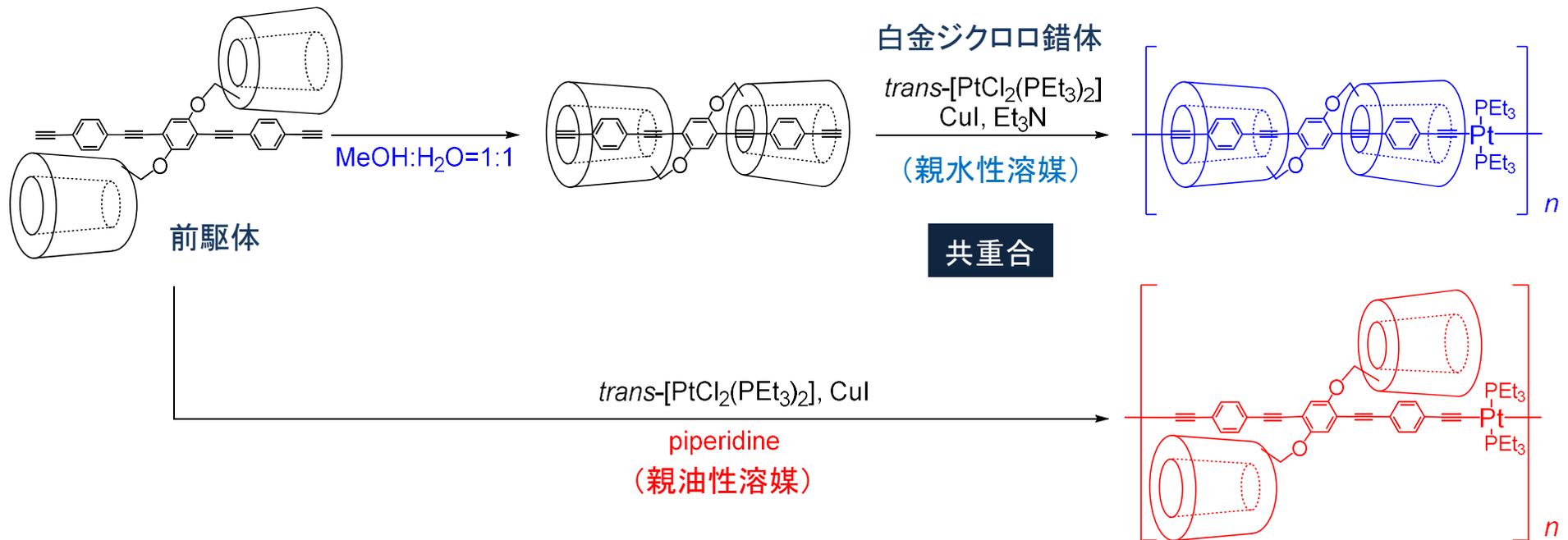


*Chem. Lett.* **2014**, 43, 1289  
*J. Am. Chem. Soc.* **2014**, 136, 1742  
*Tetrahedron Lett.* **2014**, 55, 4035



*J. Am. Chem. Soc.* **2014**, 136, 14714

# 被覆型・非被覆型メタロワイヤの選択的合成

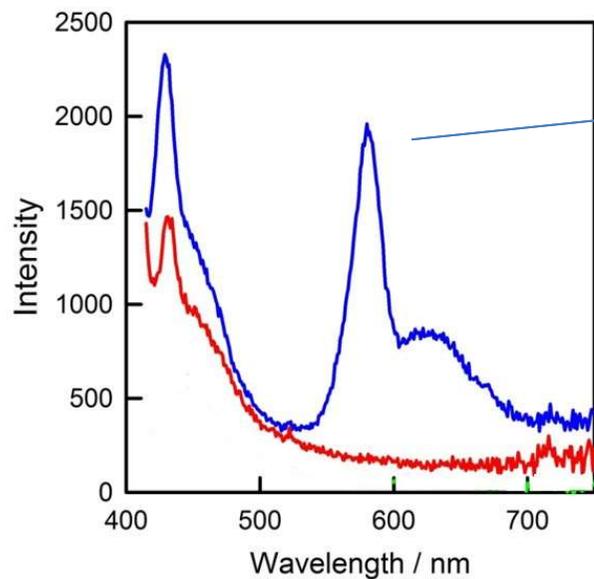


*J. Am. Chem. Soc.*, **2014**, *136*, 14714.

# 固体燐光分子ワイヤの合成



*J. Am. Chem. Soc.*, **2014**, *136*, 14714.

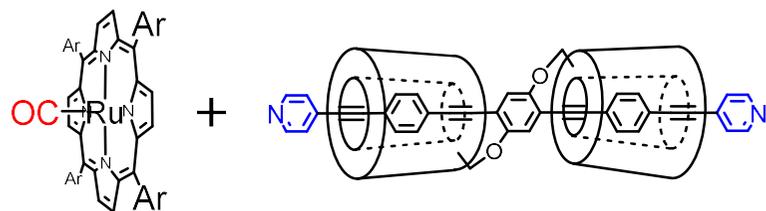


固体燐光発光の発現

環状被覆

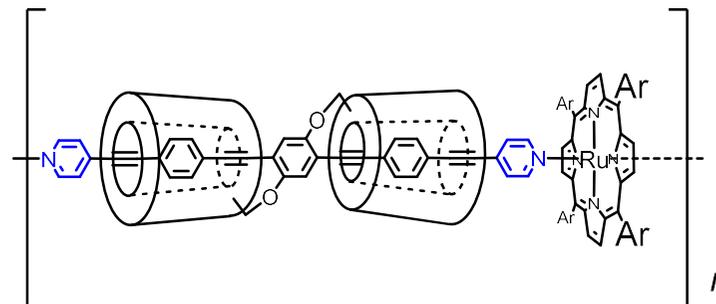
- ・分子間相互作用が抑制
- ・熱ゆらぎによる分子内失活が抑制

# 異なる外部刺激によるモノマー/ポリマー相互変換を実現



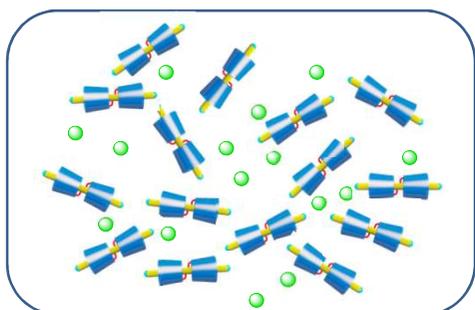
RuへのCO配位

1 atm CO gas  
分解



被覆型メタロワイヤ

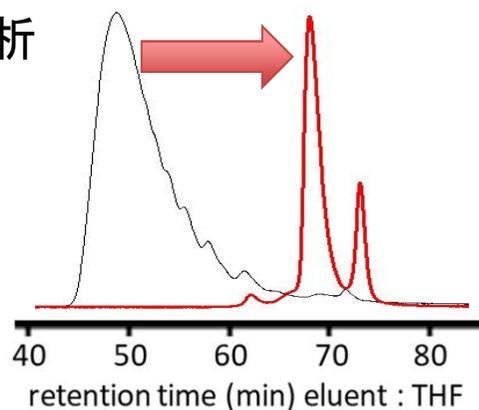
*J. Am. Chem. Soc.* **2014**, *136*, 1742



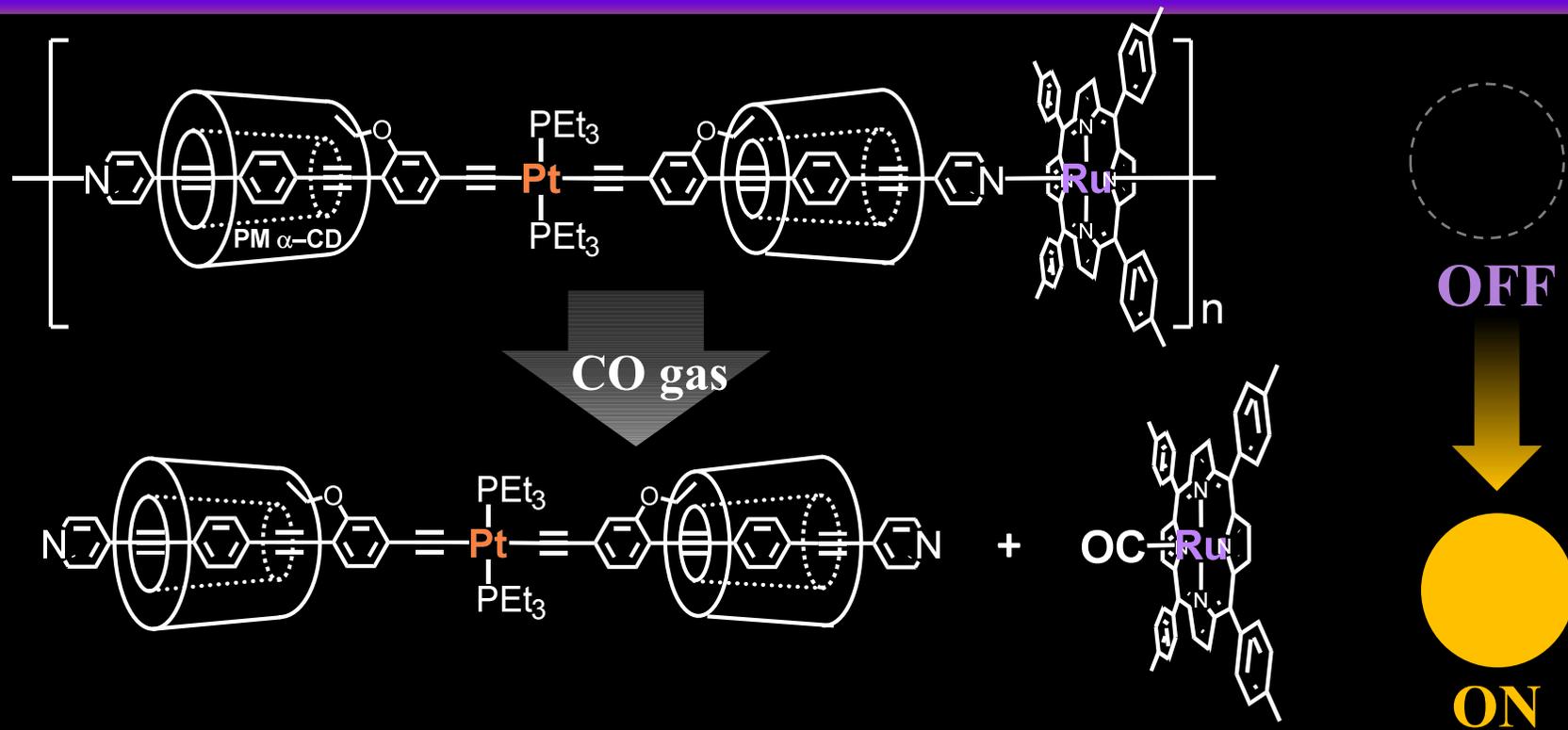
モノマー

自己修復材料  
COセンサ材料

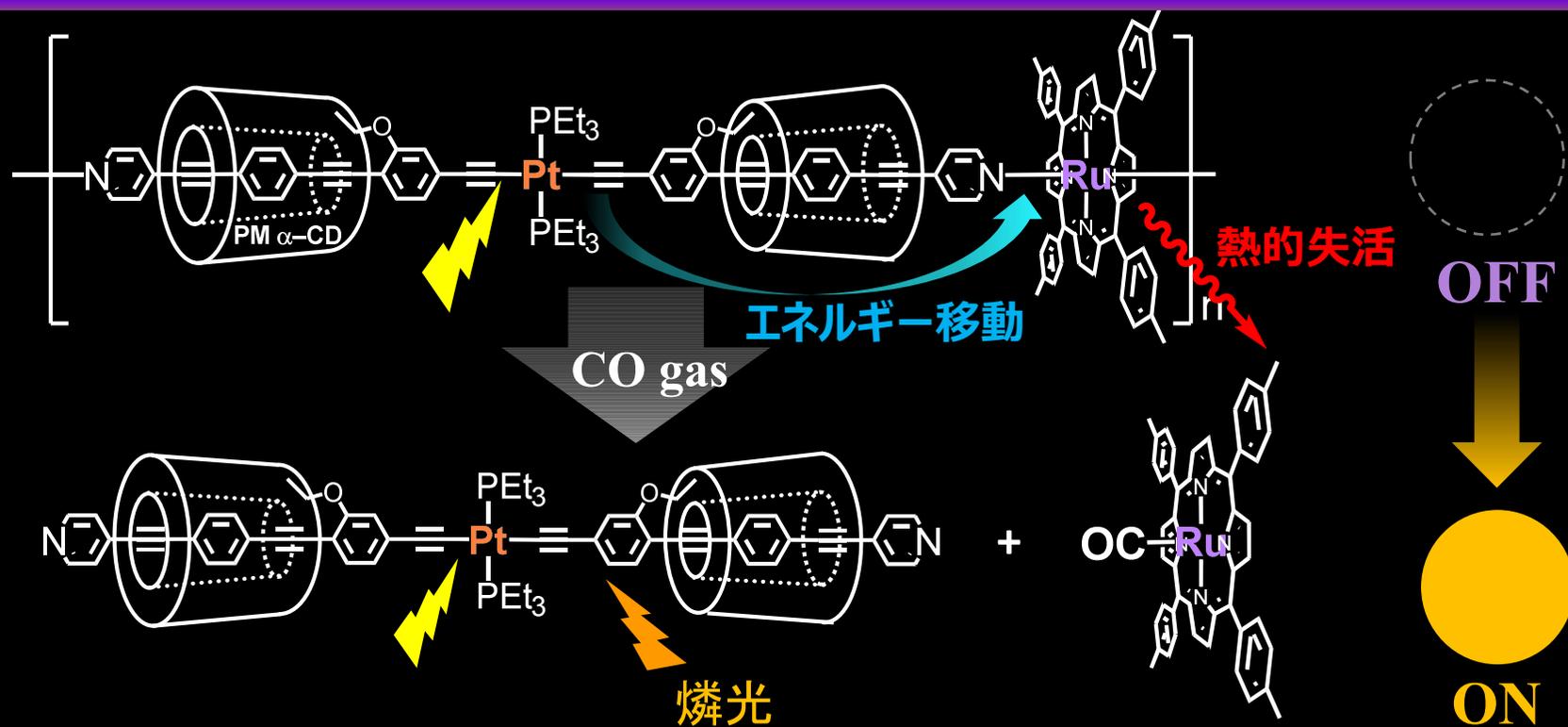
SEC分析



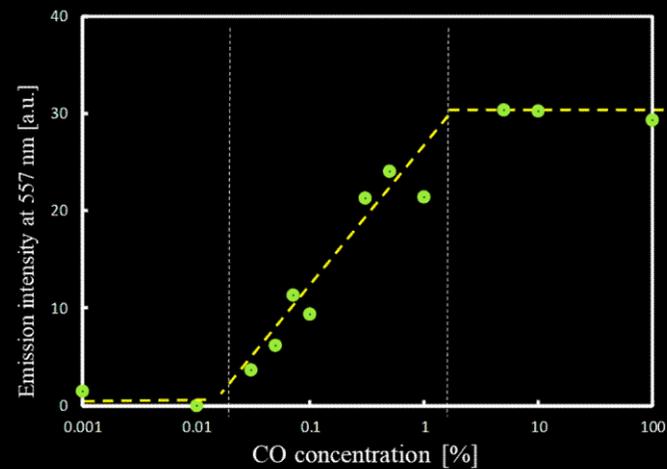
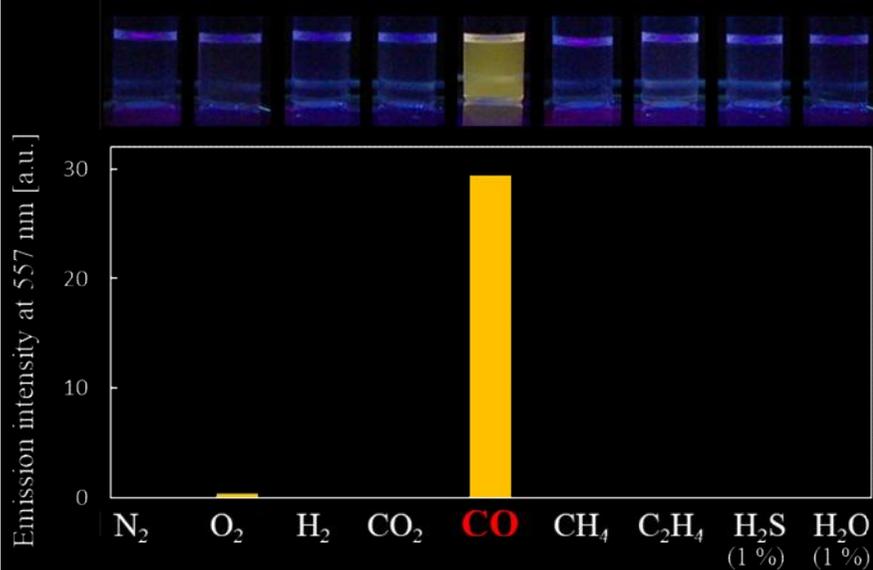
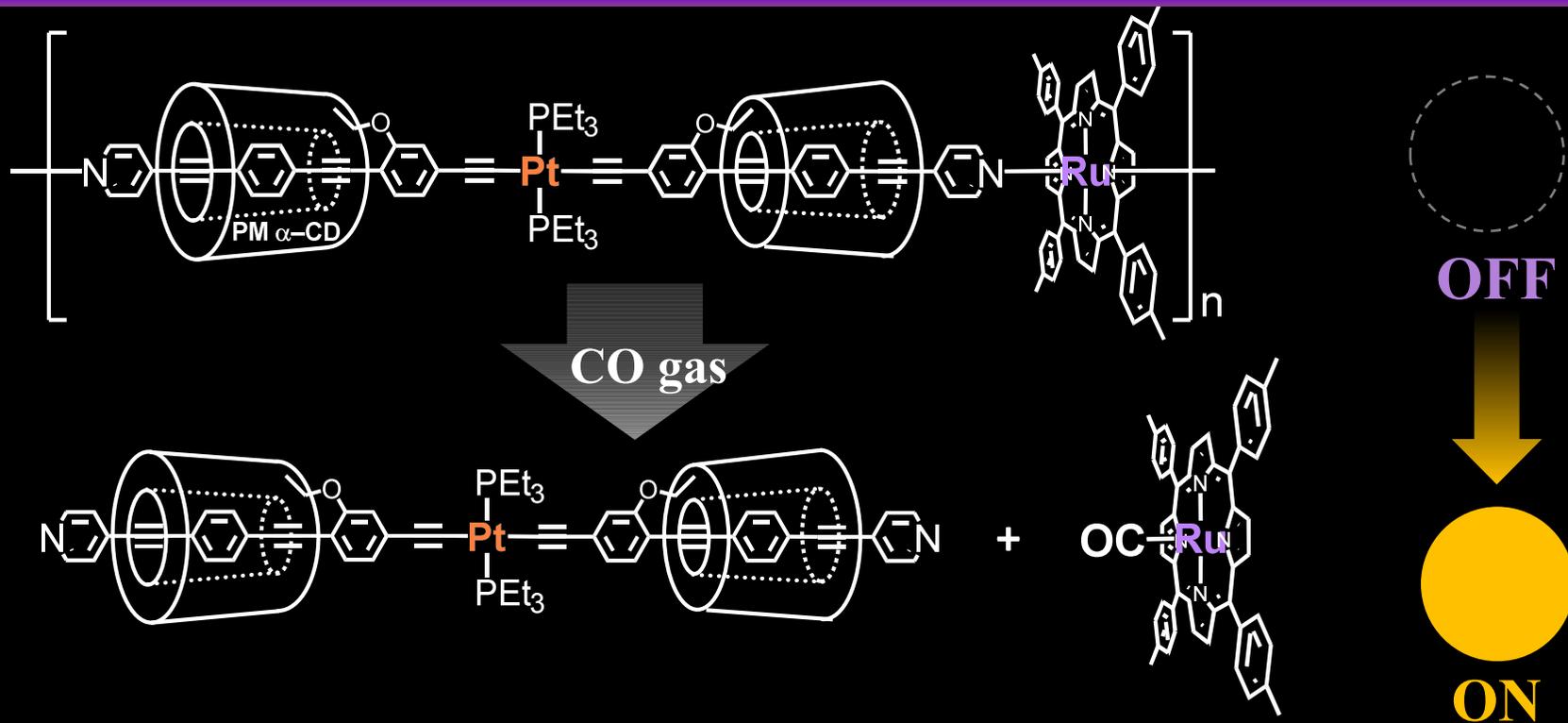
# 視認しやすい視覚変化を利用するセンサ材料の開発



# 視認しやすい視覚変化を利用するセンサ材料の開発



# 2つの閾値を持つシグモイド型応答性

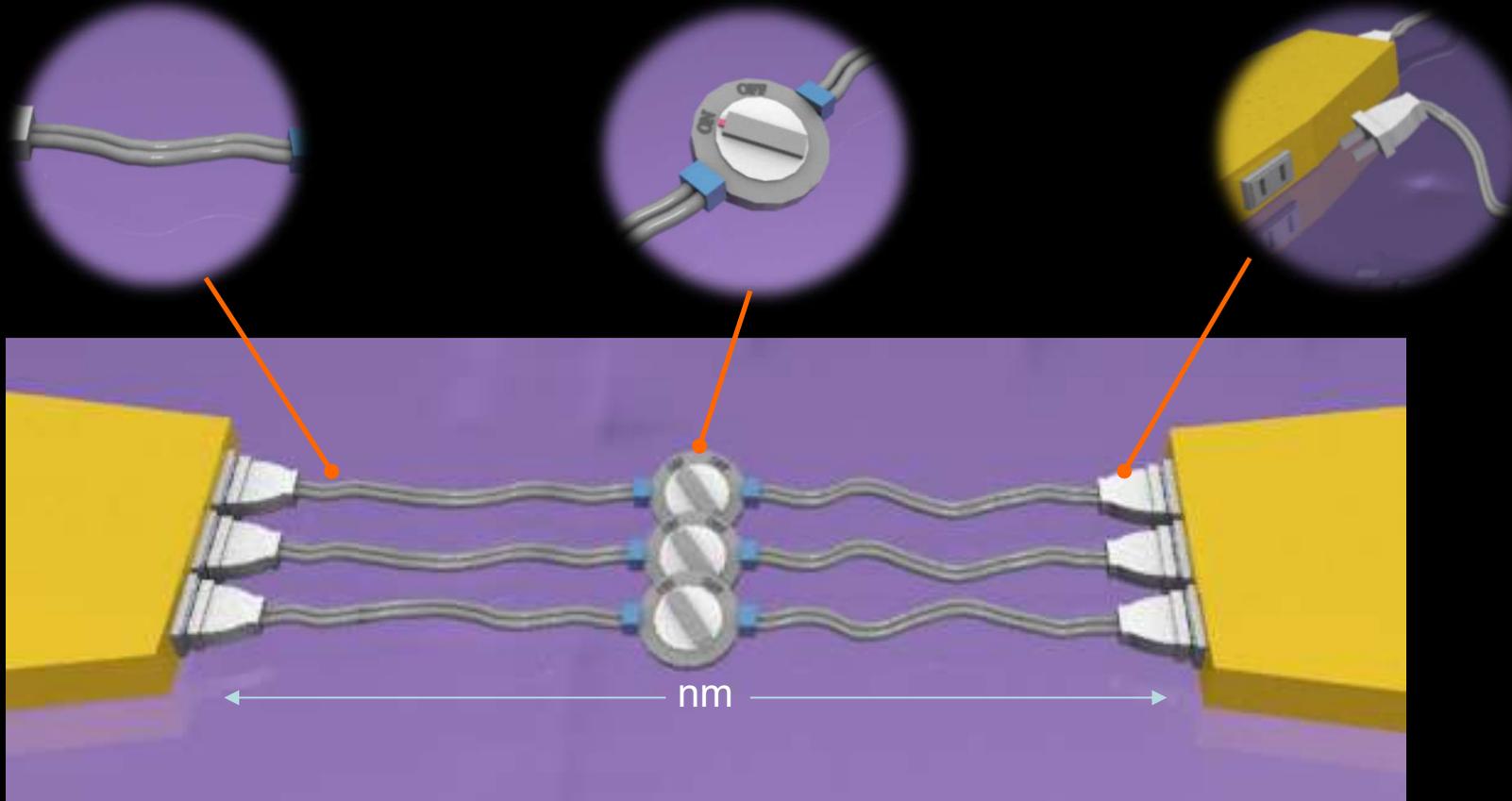


# 研究戦略

1. 被覆型分子ワイヤの合成

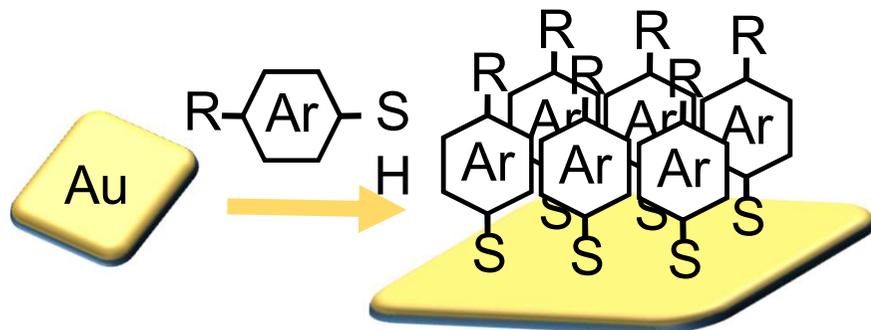
2. 外部刺激応答性部位の導入

3. プラグ分子の導入



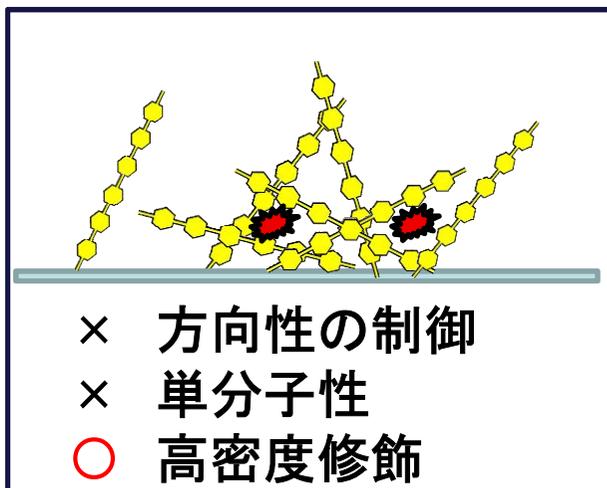
# 界面への $\pi$ 共役プラグ分子の導入

## Self Assembled Monolayer (SAM)



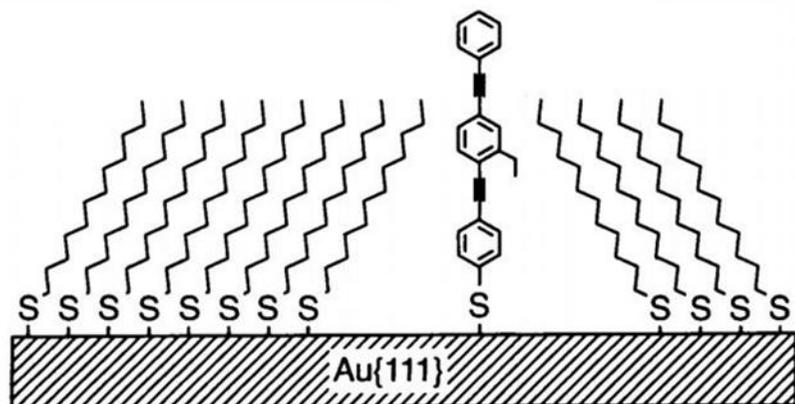
Tour, J. M.; Jones II, L.; Pearson, D. L.; Lamba, J. J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parikh, A. N.; Atre, S. *J. Am. Chem. Soc.* **1995**, *117*, 9529.

## 共役分子の基板修飾における課題



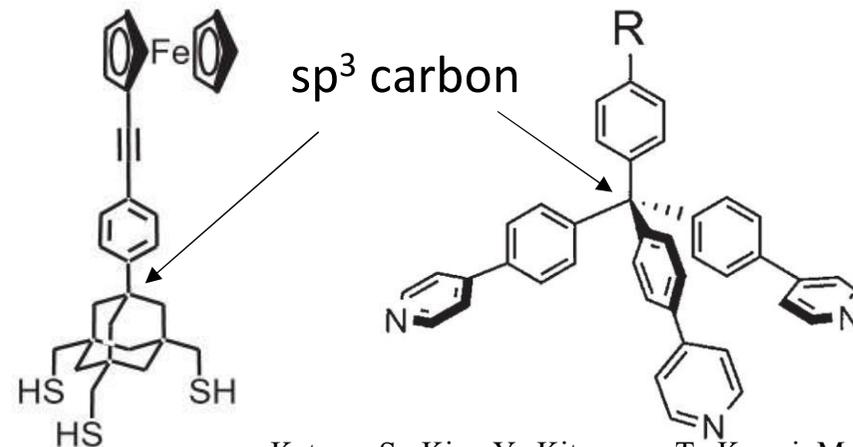
# 界面へのπ共役プラグ分子の導入

## 混合単層膜



Bumm, L. A.; Arnold, J. J.; Cygan, M. T.;  
Dunbar, T. T.; Burgin, T. P.; Jones II, L.; Allara, D. L.;  
Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705.

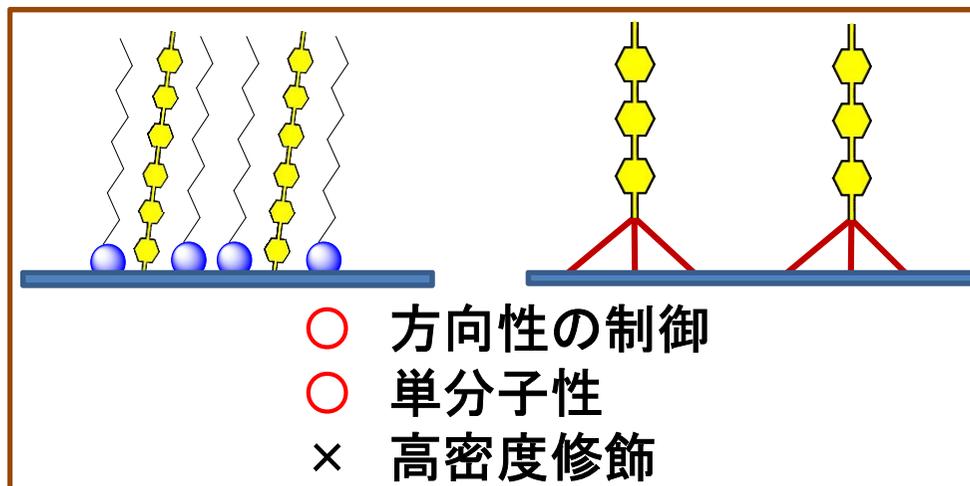
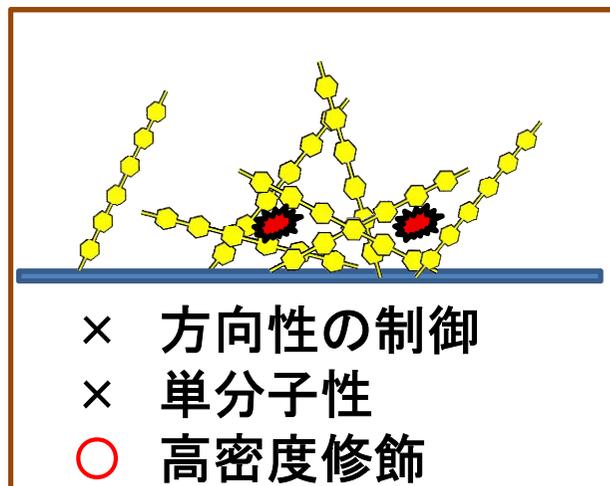
## 多脚アンカー分子



Katano, S.; Kim, Y.; Kitagawa, T.; Kawai, M.  
*Jpn. J. Appl. Phys.* **2008**, *47*, 6156.

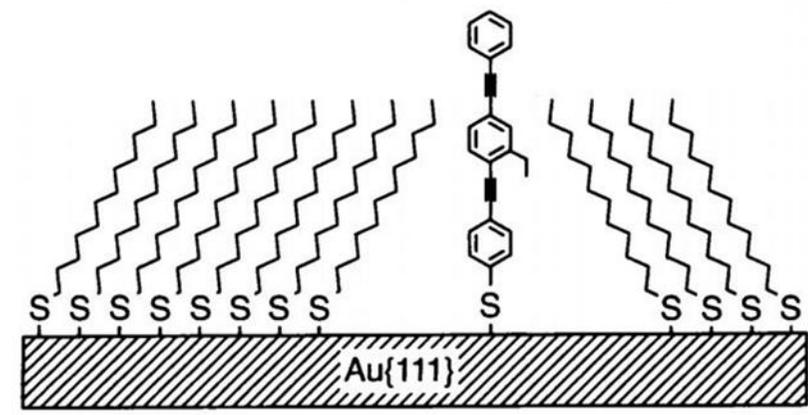
Ie, Y.; Hirose, T.; Nakamura, H.; Kiguchi, M.; Takagi, N.;  
Kawai, M.; Aso, Y. *J. Am. Chem. Soc.* **2011**, *133*, 3014.

## 共役分子の基板修飾における課題



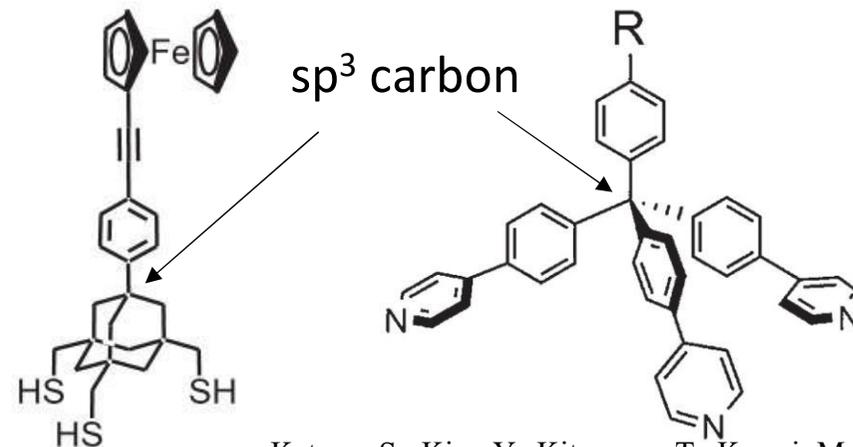
# 界面へのπ共役プラグ分子の導入

## 混合単層膜



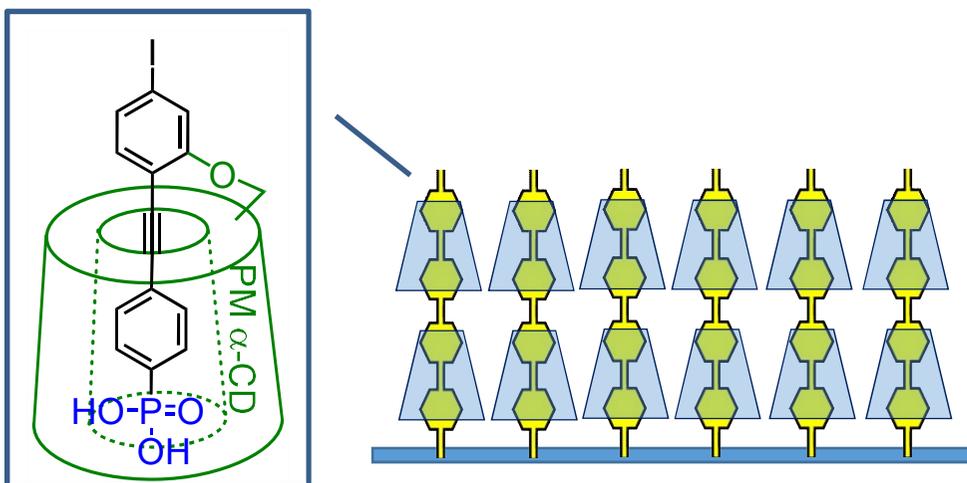
Bumm, L. A.; Arnold, J. J.; Cygan, M. T.;  
Dunbar, T. T.; Burgin, T. P.; Jones II, L.; Allara, D. L.;  
Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705.

## 多脚アンカー分子



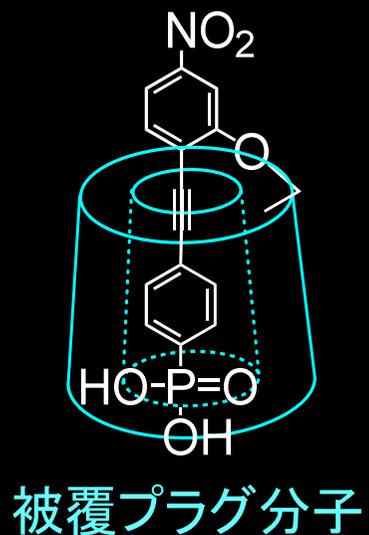
Katano, S.; Kim, Y.; Kitagawa, T.; Kawai, M.  
*Jpn. J. Appl. Phys.* **2008**, *47*, 6156.

Ie, Y.; Hirose, T.; Nakamura, H.; Kiguchi, M.; Takagi, N.;  
Kawai, M.; Aso, Y. *J. Am. Chem. Soc.* **2011**, *133*, 3014.



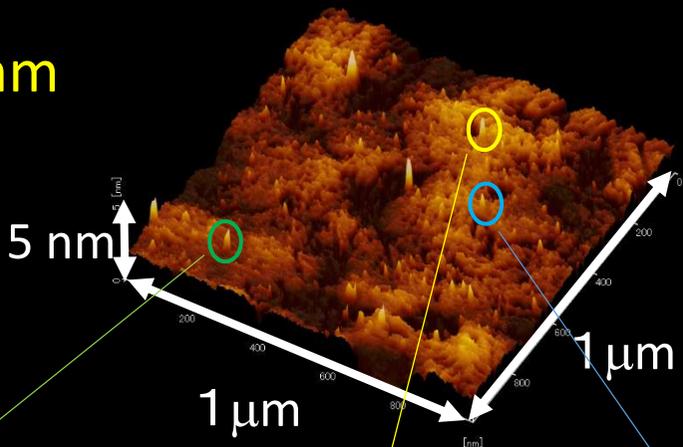
- 方向性 ○
- 単分子性 ○
- 高密度修飾 ○
- 機能性ユニットの導入 ○

# AFMによる表面形状観察

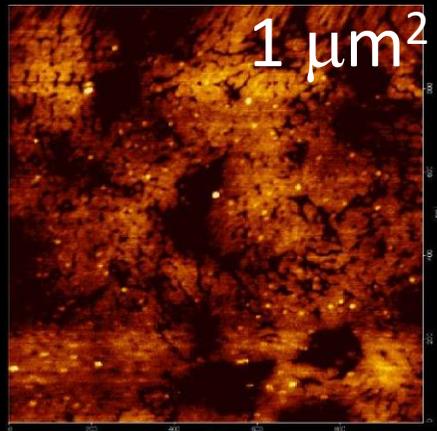


1.7 nm

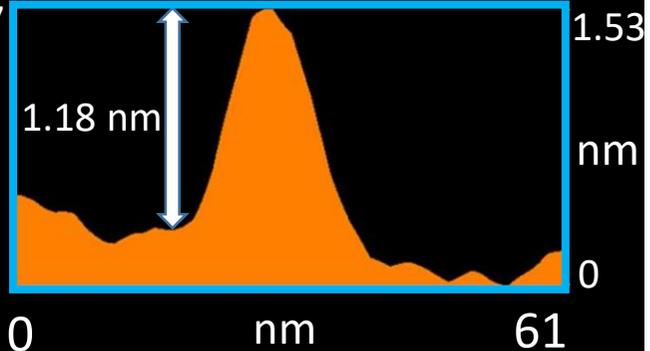
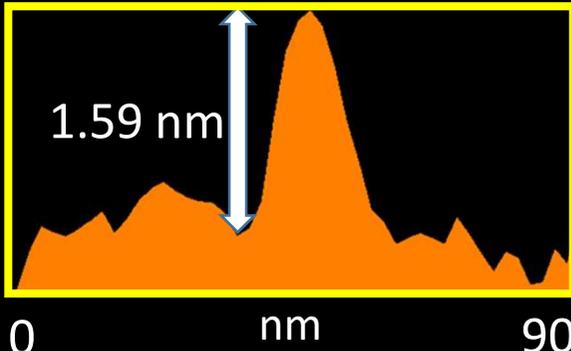
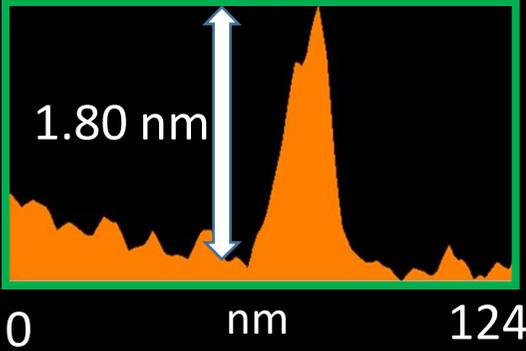
AFM Image(3D)



AFM Image(2D)



孤立



Solvent: MeOH 500 μM

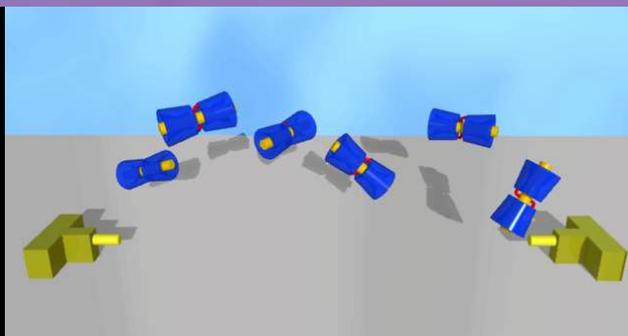
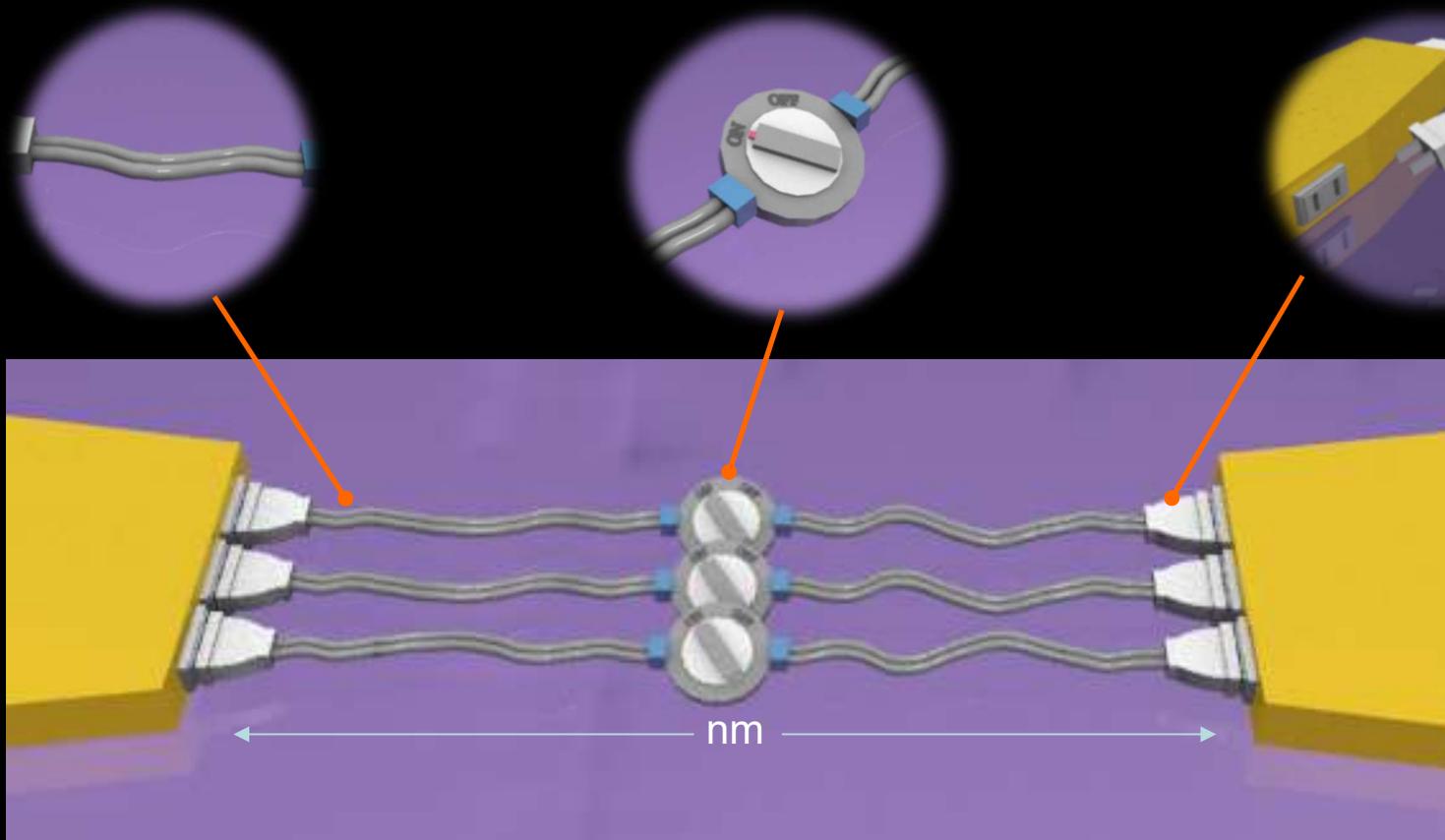


# 研究戦略

1. 被覆型分子ワイヤの合成

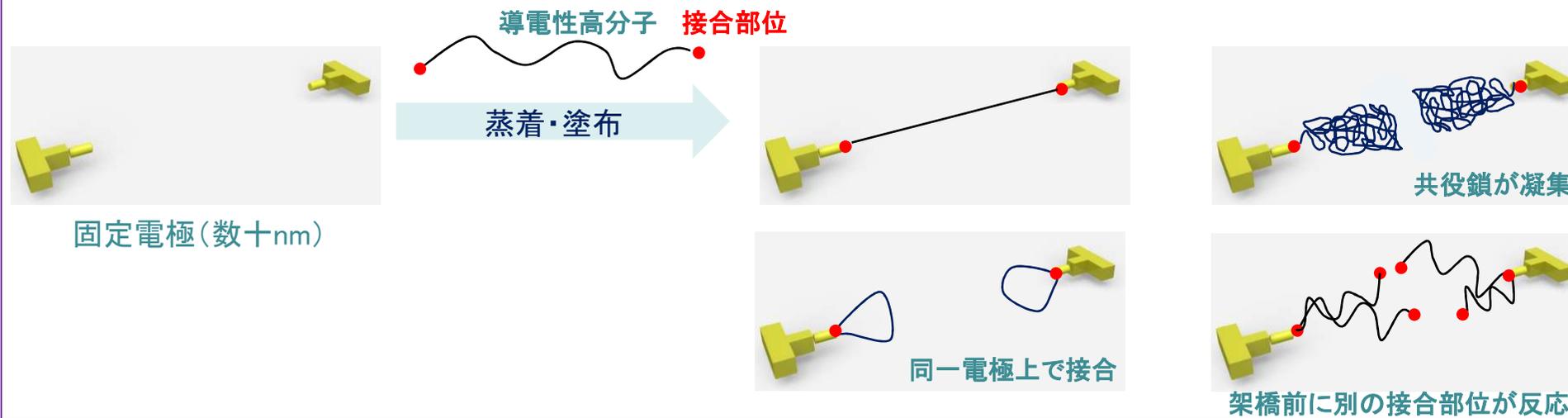
2. 外部刺激応答性部位の導入

3. プラグ分子の導入



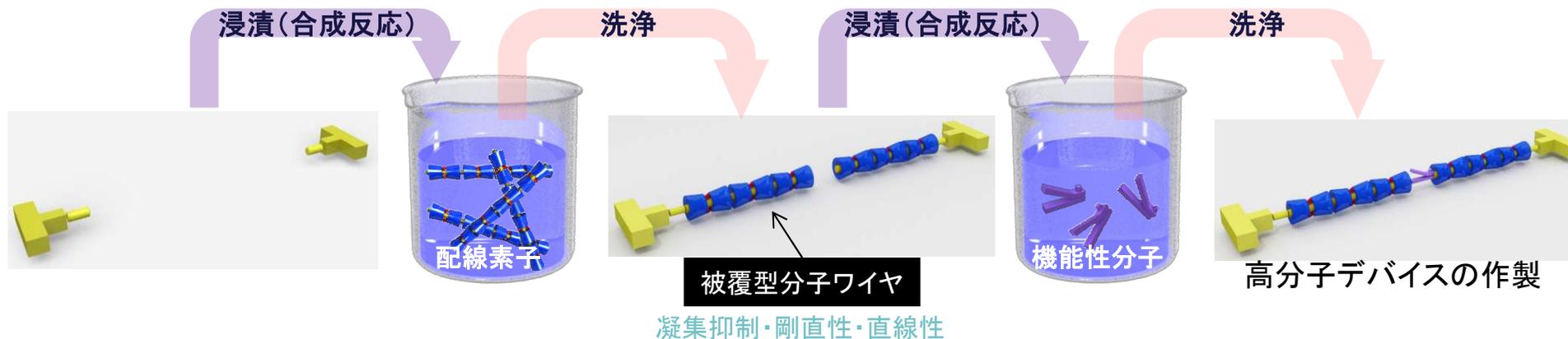
4. ビルドアップ型分子配線法の開発

# ナノ電極間への高分子配線: 数十nm



効率的な高分子配線法の確立

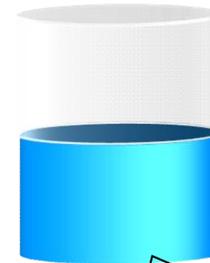
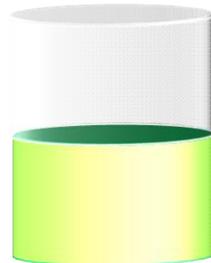
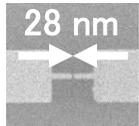
ナノ電極の両端から逐次的な伸張反応によるビルドアップ型の高分子配線



# ビルドアップ型高分子配線の開発に成功

逐次的クロスカップリング反応

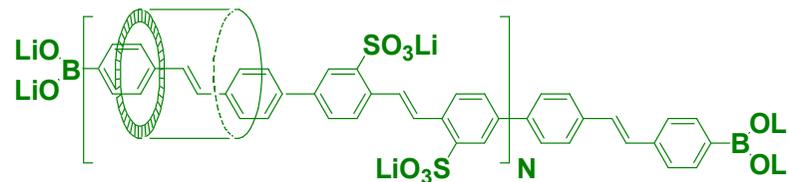
ナノ電極  
(電子線描画法)



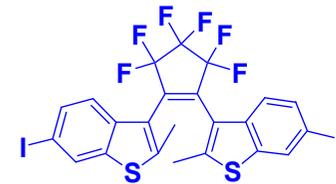
接合分子



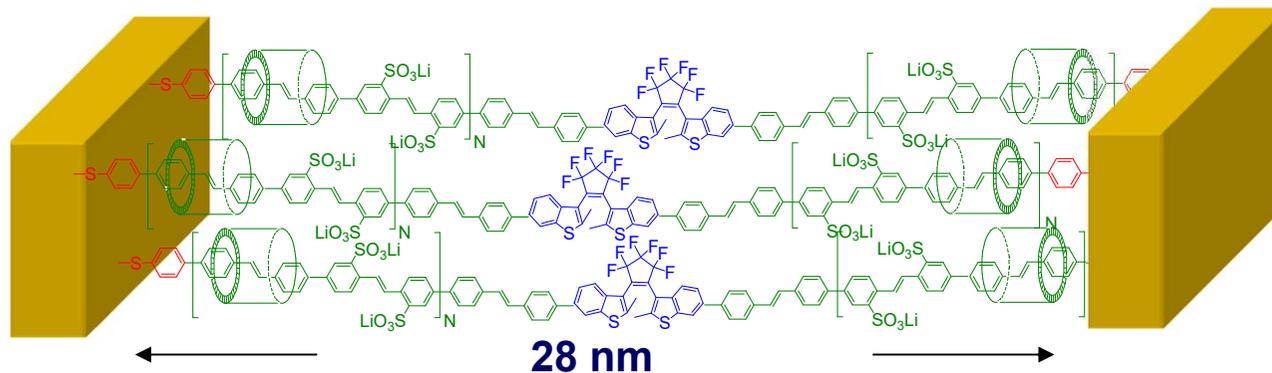
被覆型分子ワイヤ



機能性分子



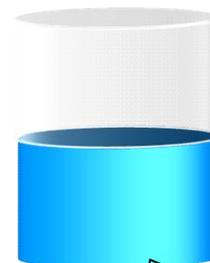
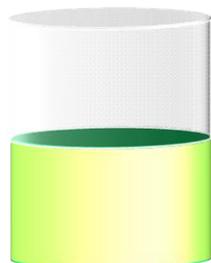
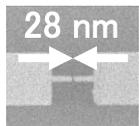
高分子デバイスの作製に初めて成功



Taniguchi, M.; Terao, J. et al. *J. Am. Chem. Soc.* **2006**, *128*, 15062

# ビルドアップ型高分子配線

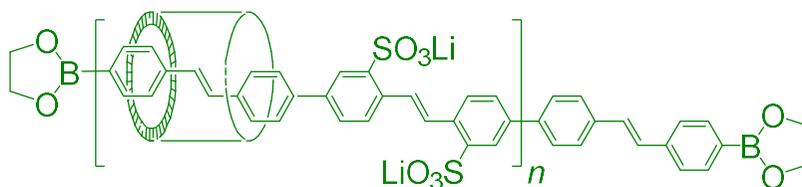
ナノ電極  
(電子線描画法)



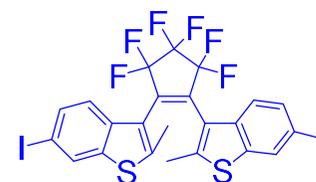
接合分子



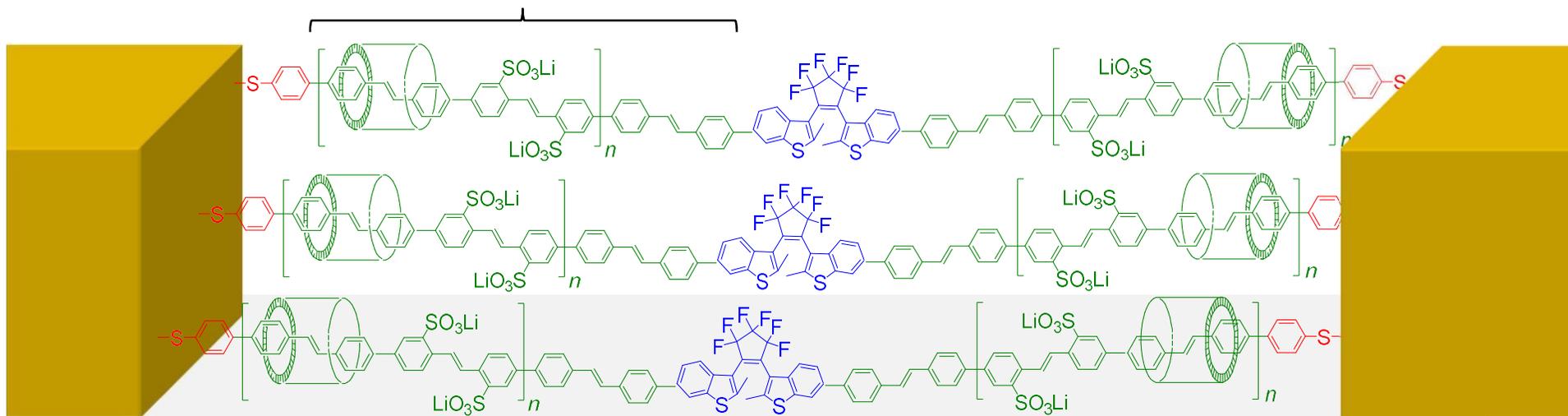
被覆型分子ワイヤ



機能性分子

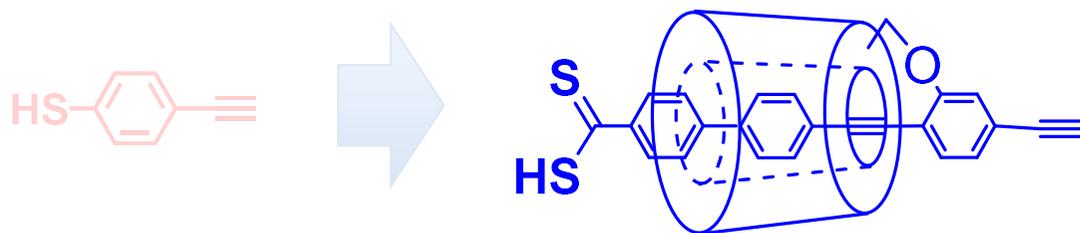


電極間距離の半分の長さの被覆型分子ワイヤを合成することが必要 → 合成が困難

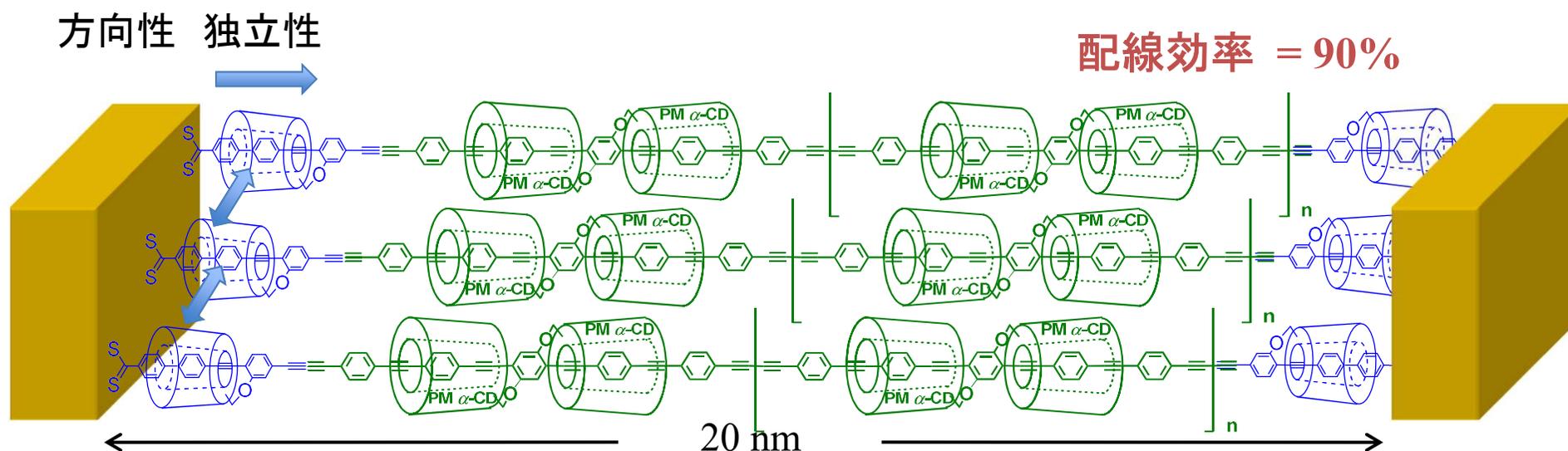


配線効率: <1% (従来法: 蒸着) → 30% (本手法: ビルドアップ配線)

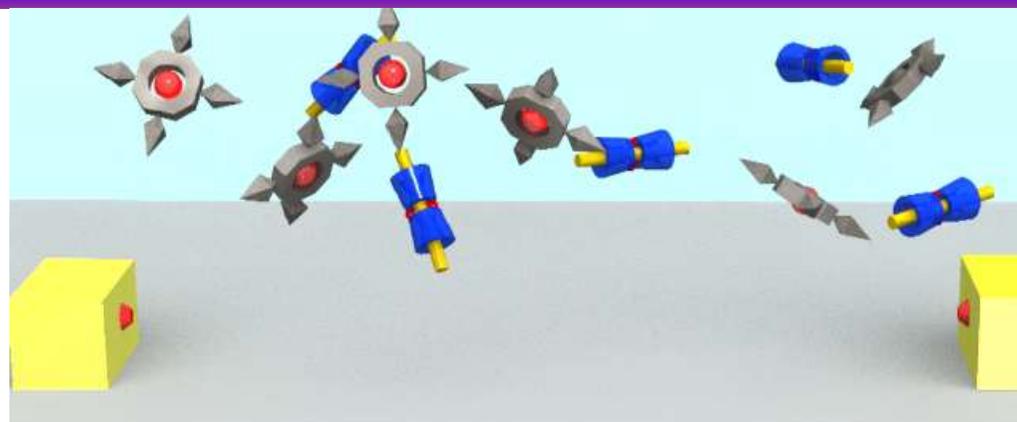
# プラグ分子の被覆効果



ロタキサン型プラグ分子



# 配位重合による分子配線



被覆型プラグ分子

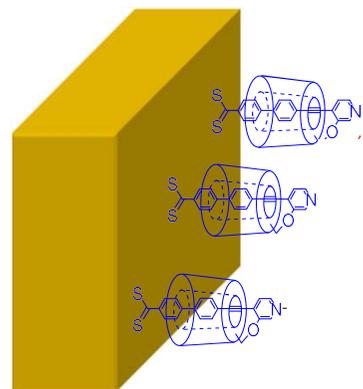
ナノ電極



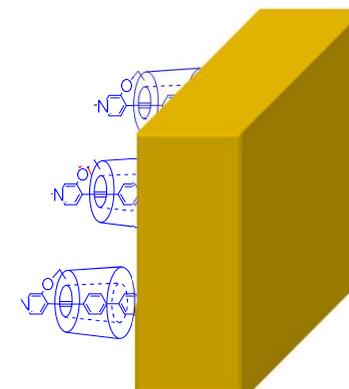
洗浄



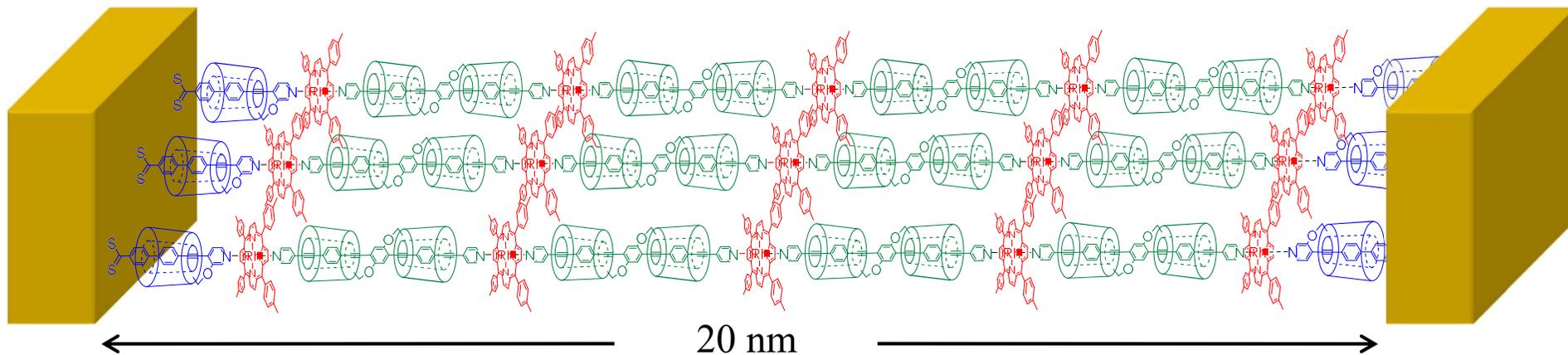
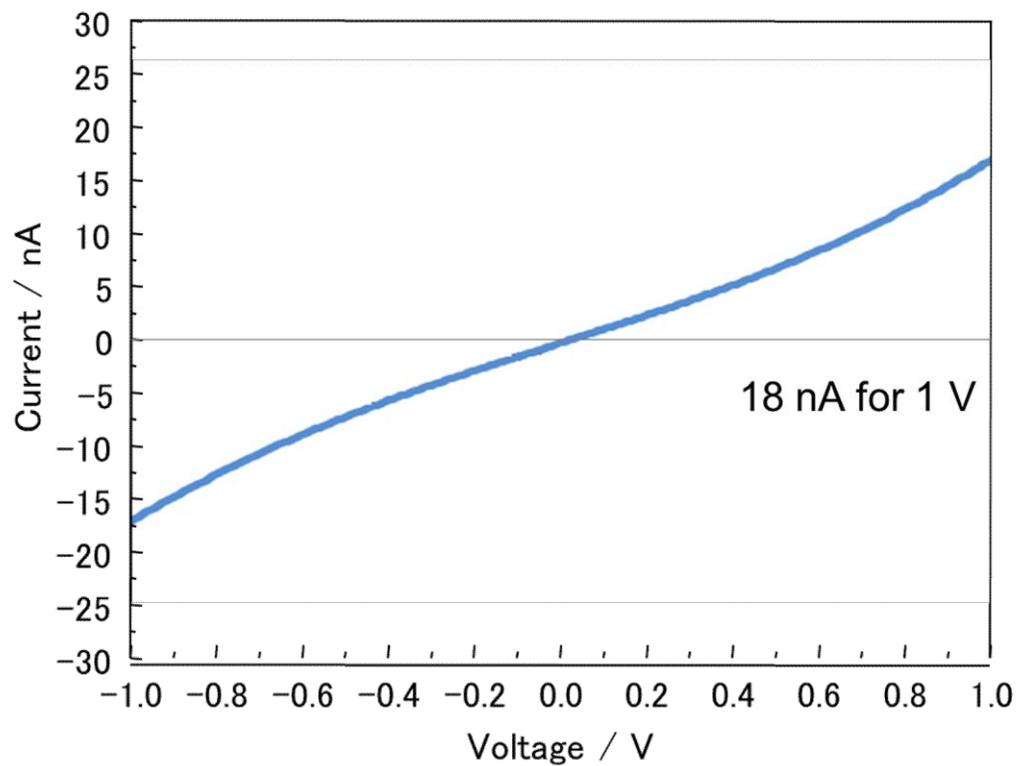
洗浄



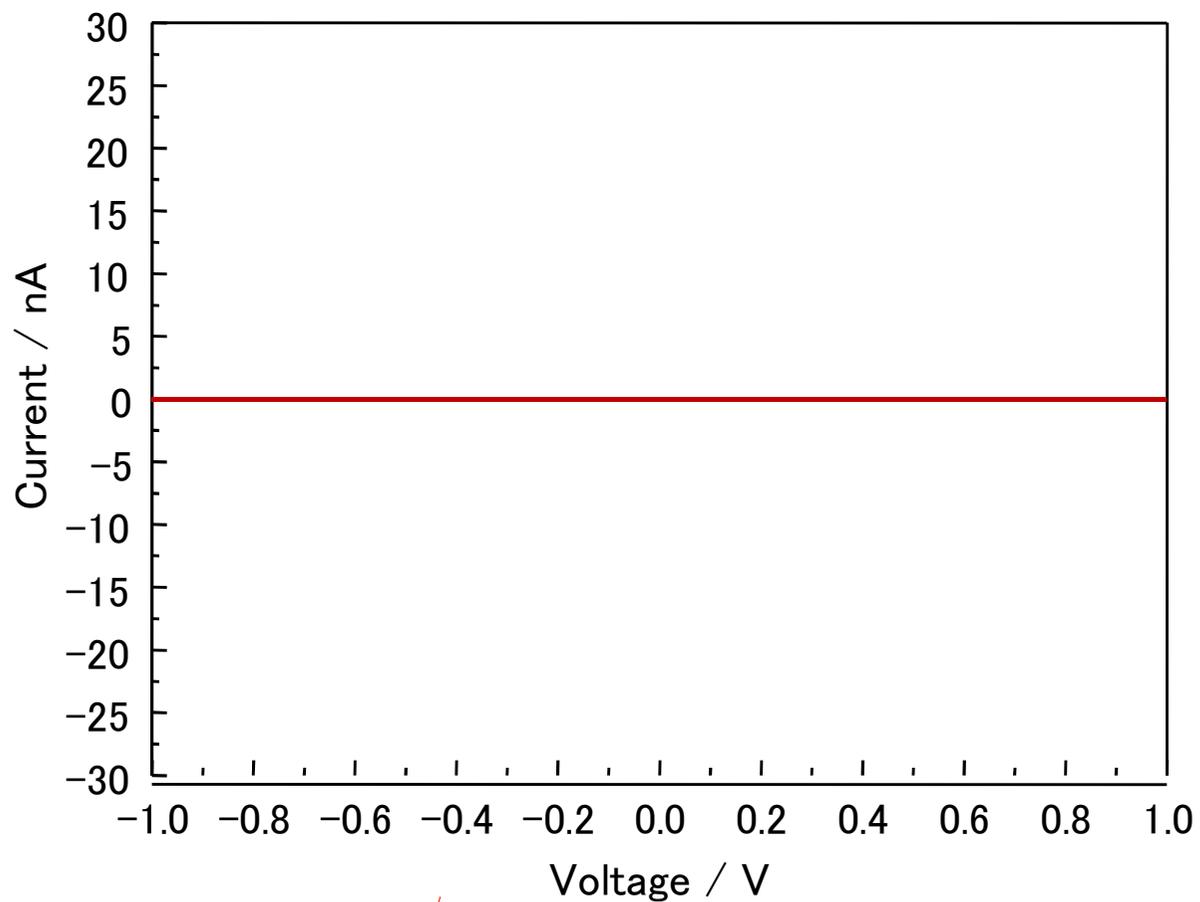
20 nm



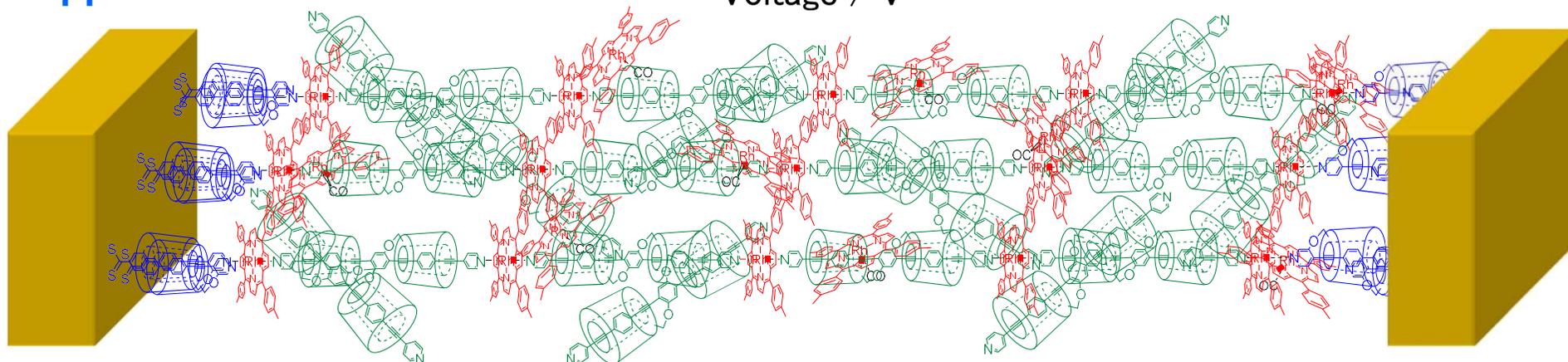
# 窒素下における伝導度測定



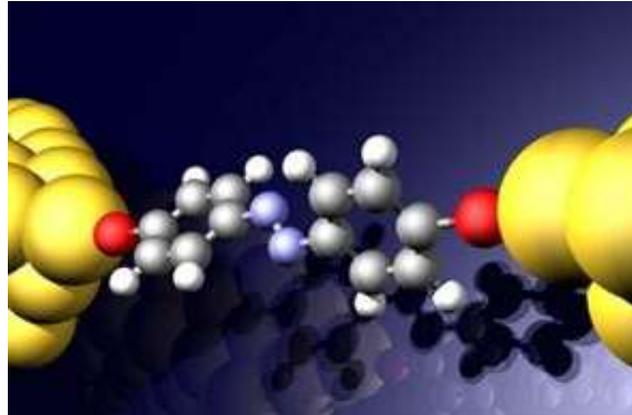
# 一酸化炭素下における伝導度測定



10 ppm CO



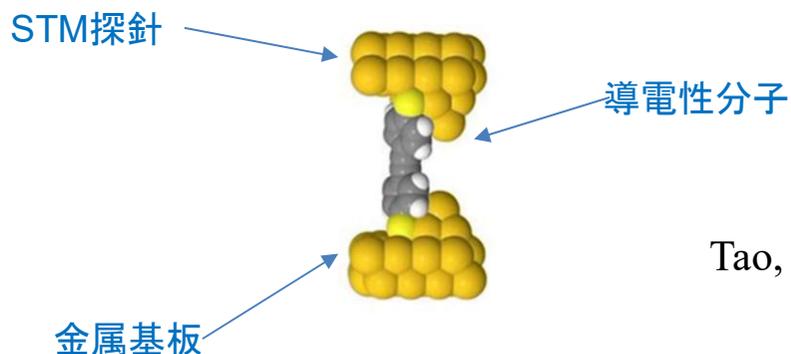
# 最近の研究成果について



分子エレクトロニクス(Å)

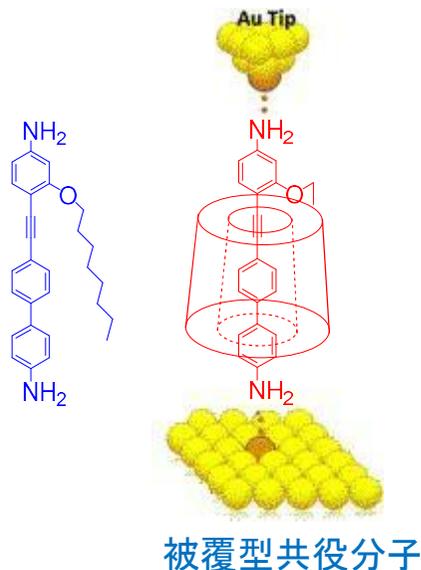
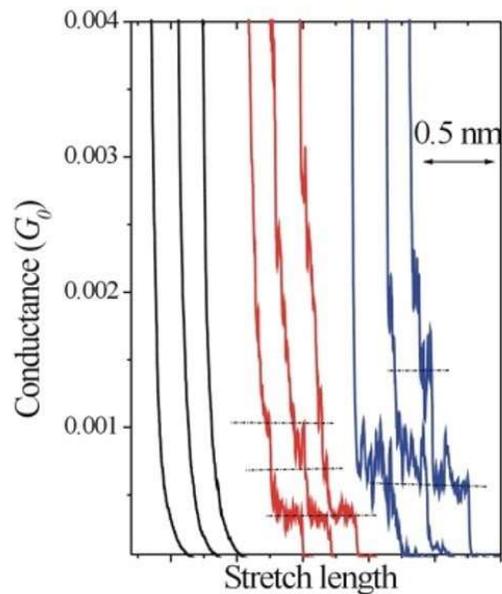
# ブレイクジャンクション法: Å ~ 数nm

ブレイクジャンクション法: Å から数nmスケールの単分子の導電性評価法



Tao, N. J. et al. *Science* **2003**, *301*, 1221

## 単分子伝導度測定



共役鎖の被覆により分子間相互作用が抑制

安定したコンダクションプラトーが観測

正確な単分子伝導度の測定が可能

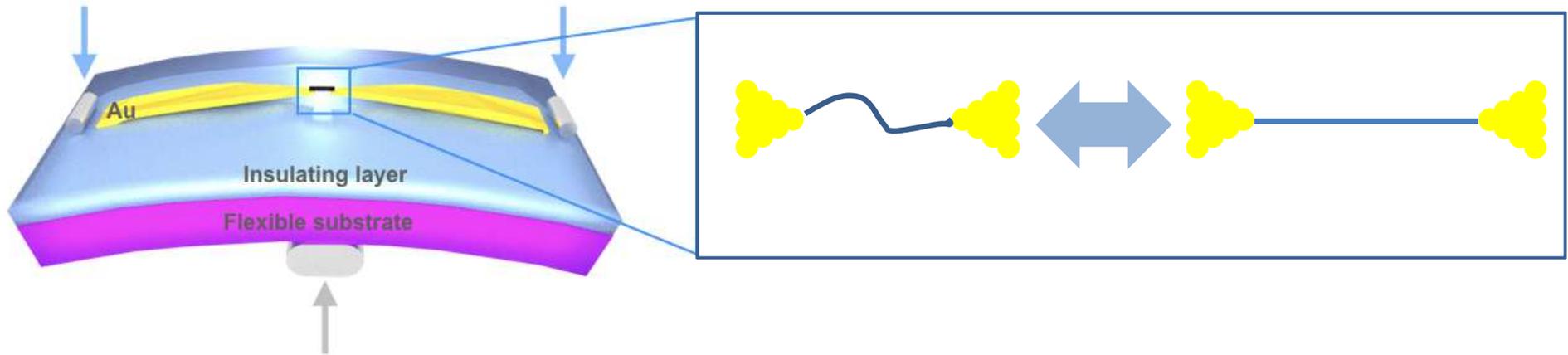
Kiguchi, M.; Terao, J. et al. *Small*, **2012**, *8*, 726

Terao, J.; Kiguchi, M. et al. *J. Am. Chem. Soc.* **2014**, *136*, 1742

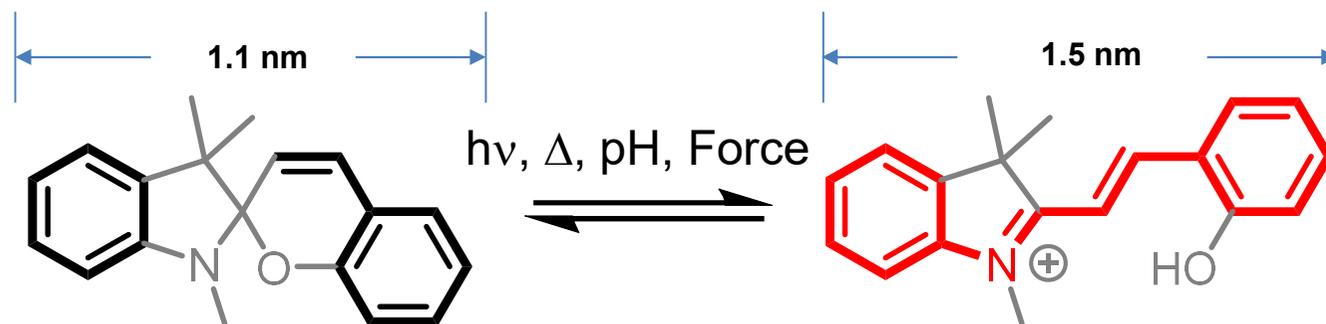
Kiguchi, M.; Terao, J. et al. *J. Phys. Chem. C*, **2015**, *119*, 19452

# 単分子の力学刺激による新物性発現

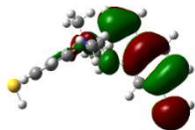
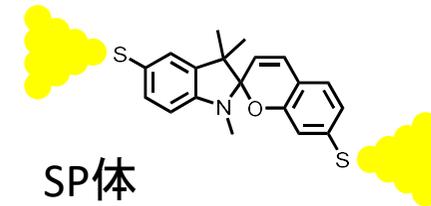
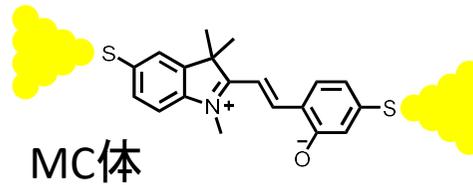
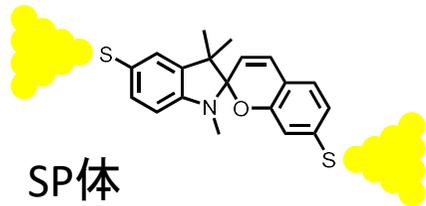
ピコメートルスケールで電極間距離を伸縮



Mechanically controllable break junction  
**MCBJ法**



# 単分子の力学刺激による導電性変化



HOMO



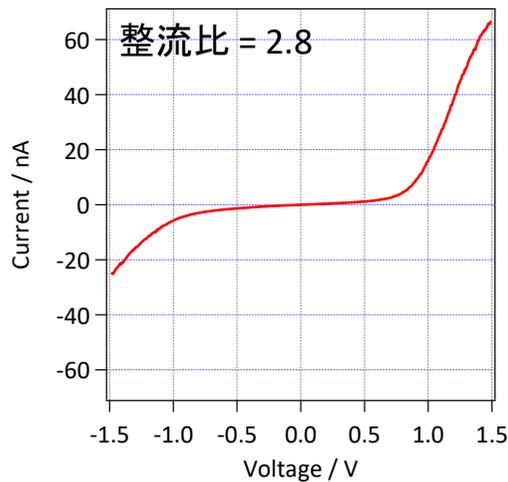
HOMO-1



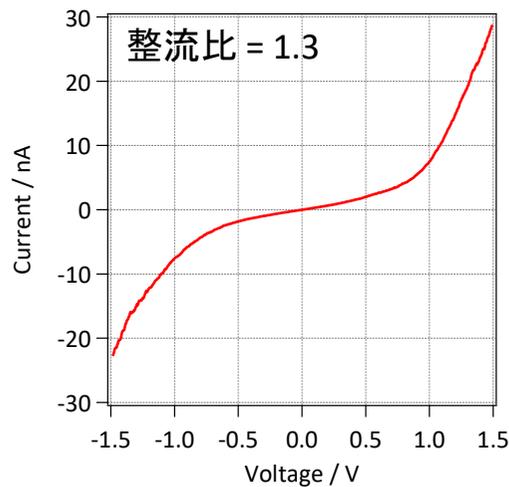
HOMO

スピロ炭素を境にHOMO・HOMO-1が分断  
→ 整流性が発現

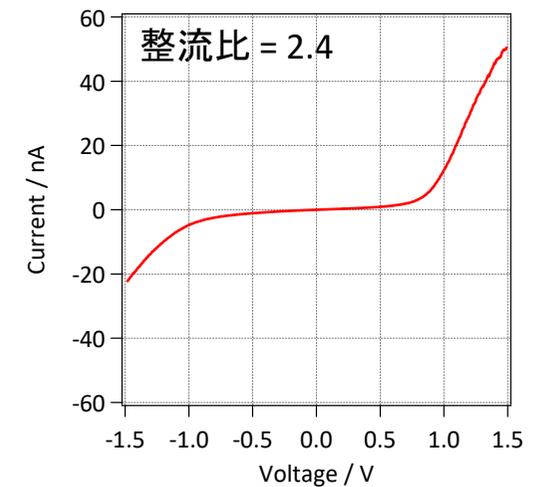
分子軌道が分子全体に拡張  
→ 対象なI-V特性



$$2.5 \times 10^{-5} G_0$$



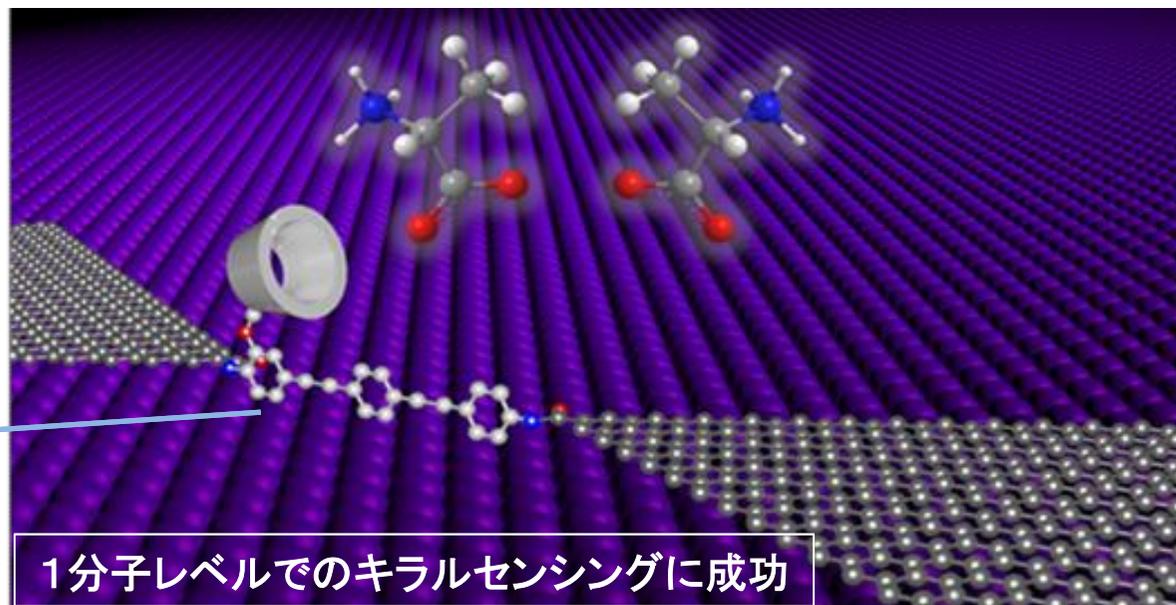
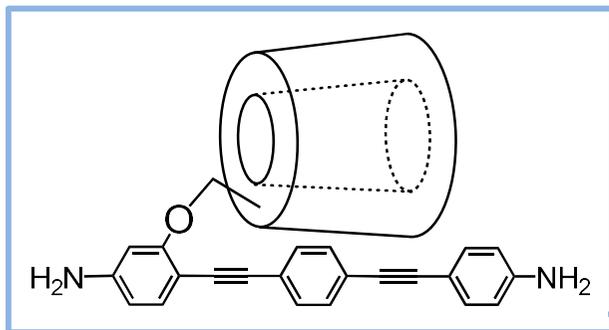
$$4.2 \times 10^{-5} G_0$$



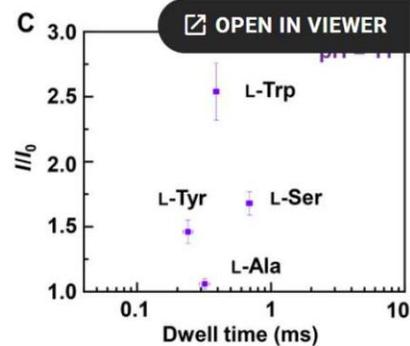
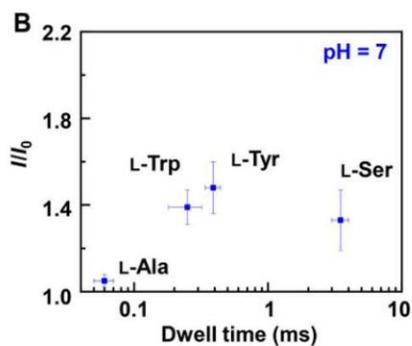
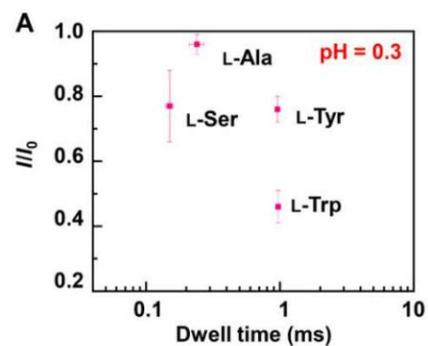
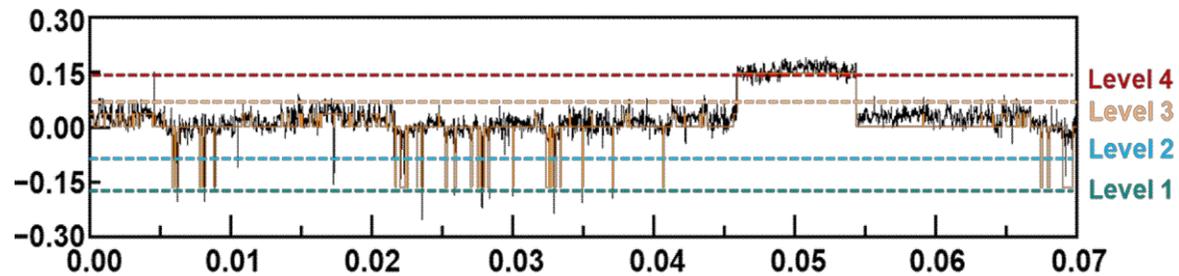
$$1.9 \times 10^{-5} G_0$$

0.2 Vにおけるコンダクタンス値:

*Nanoscale*, 2020, 12, 7527



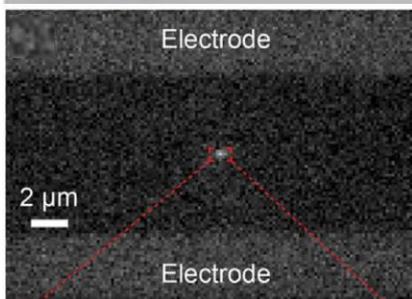
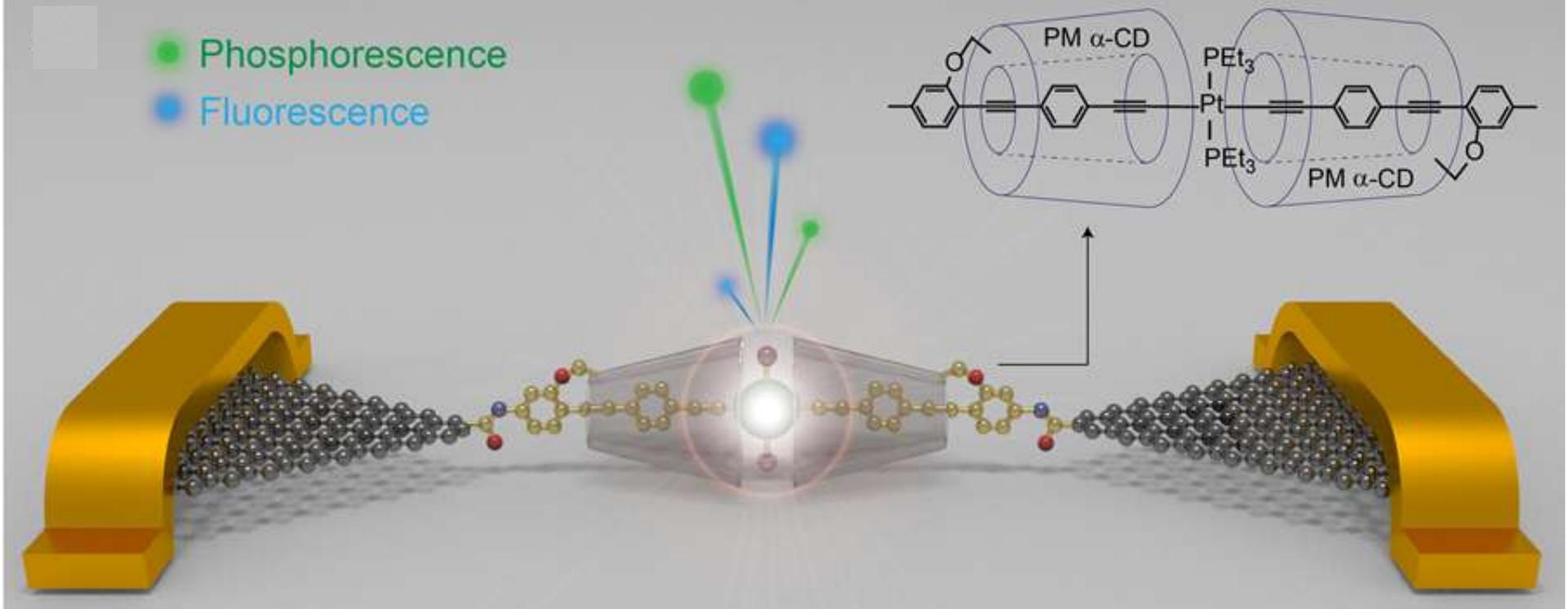
1分子レベルでのキラルセンシングに成功



*Small Methods*, 2019, 12, 1900464.  
*Science Advance*, 2021, 7, abe4365.

# 燐光・蛍光スイッチングデバイス

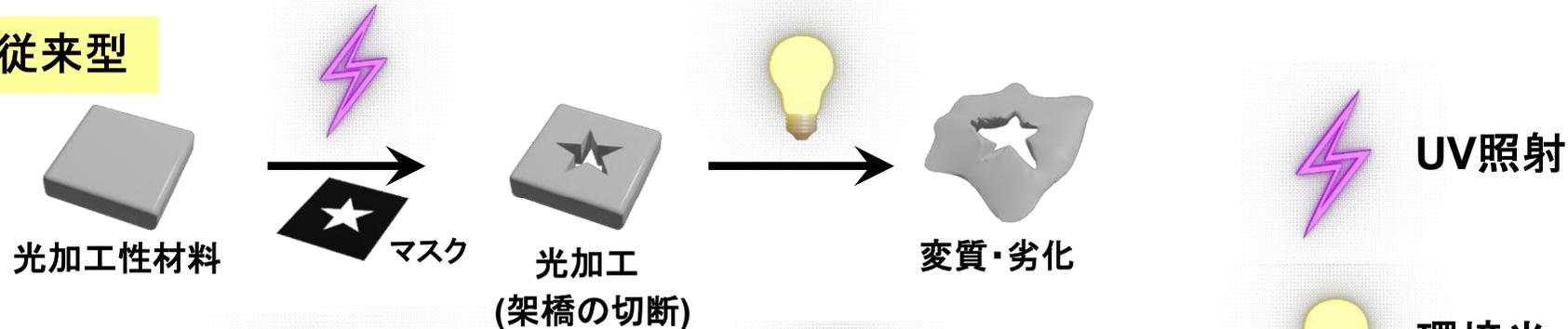
● Phosphorescence  
● Fluorescence



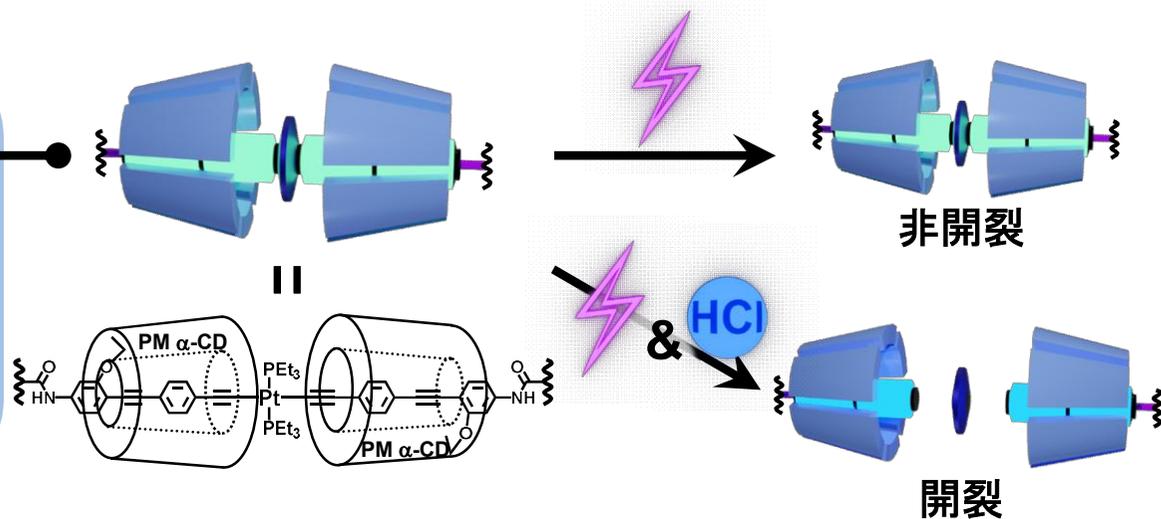
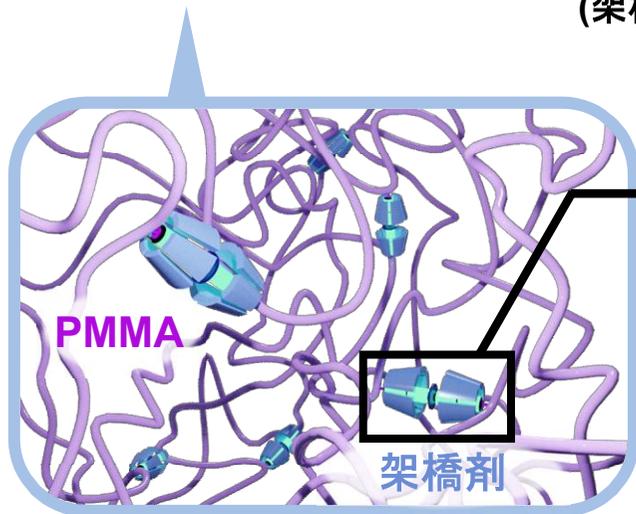
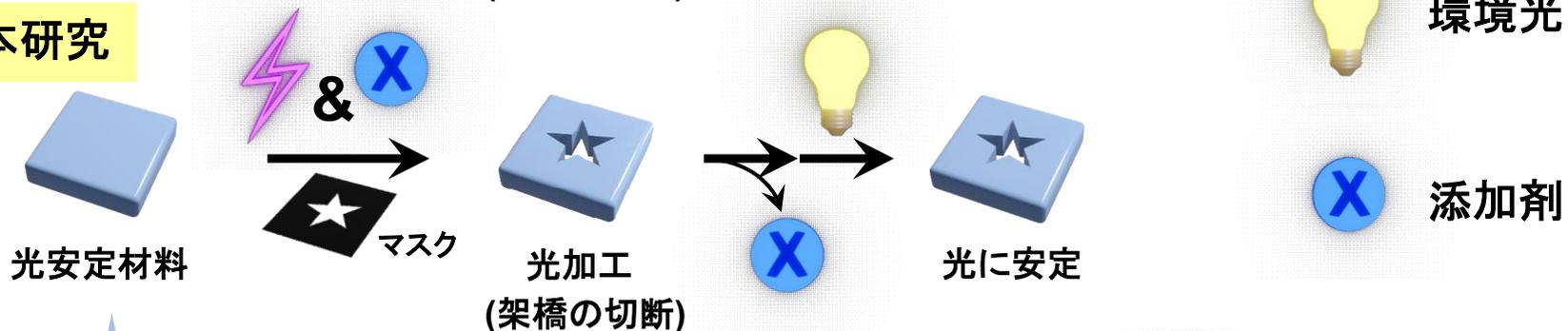
1分子レベルでの燐光蛍光スイッチに成功

# 光加工材料の問題点

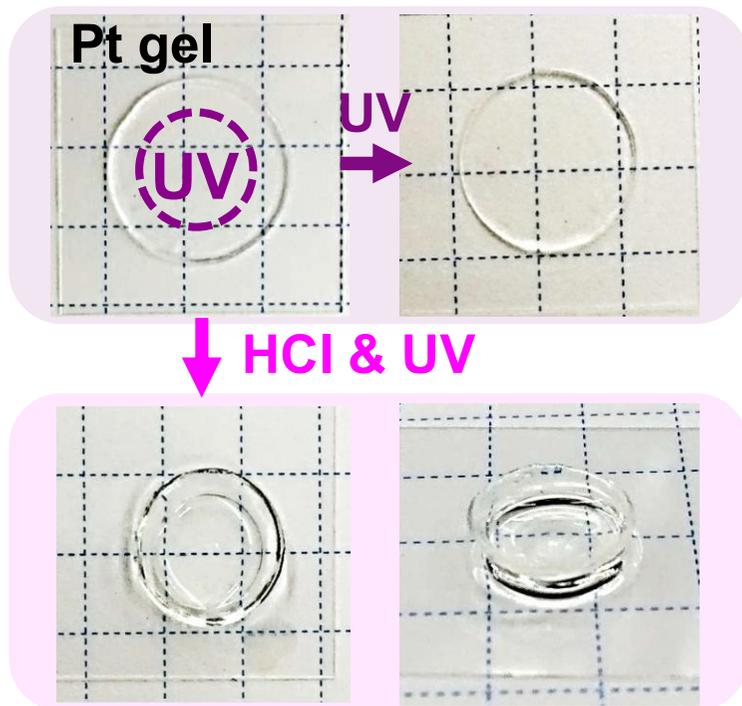
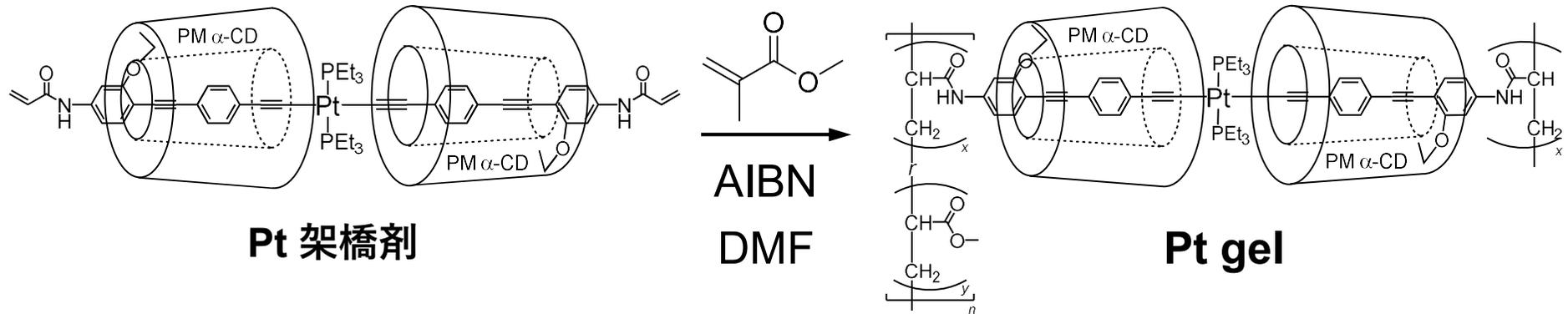
従来型



本研究



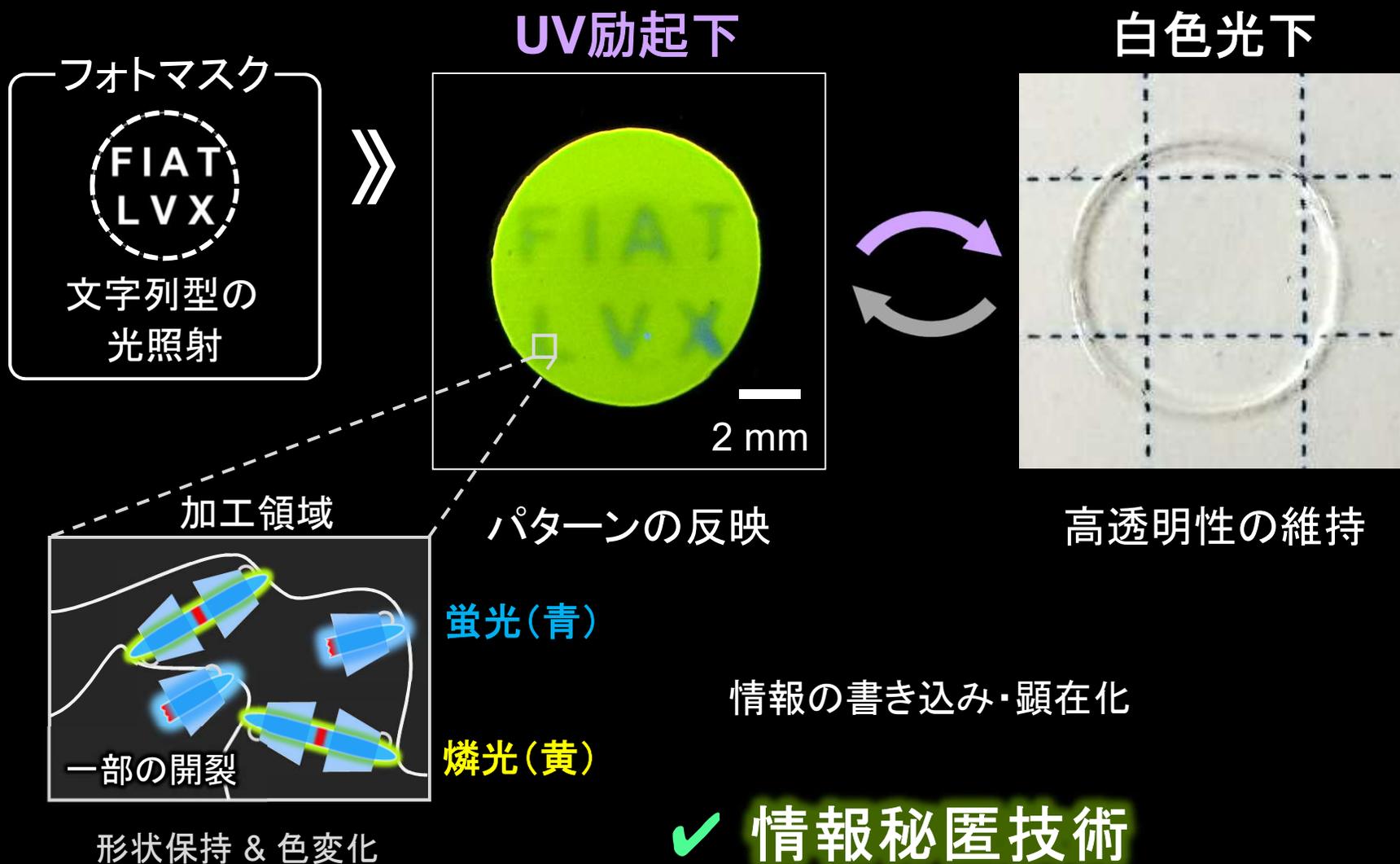
# 酸添加による光安定材料の光加工



✓ 光に安定かつ光加工可能

*Adv. Funct. Mater.*, **2022**, 32, 2205855.

光による印字加工



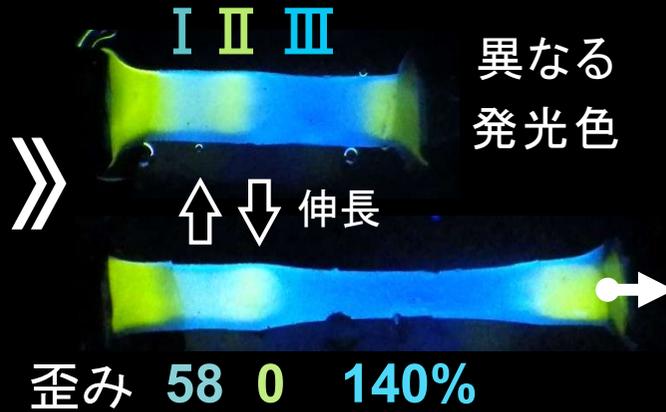
## 弾性率分布のイメージング

異なる弾性率領域の作製

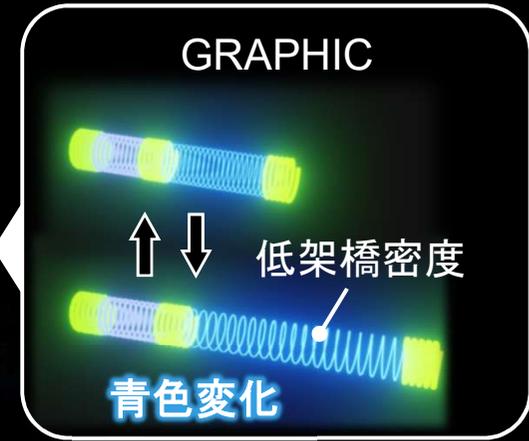


UV light (with HCl) 3 10 min

時間: III > I > II (未加工)

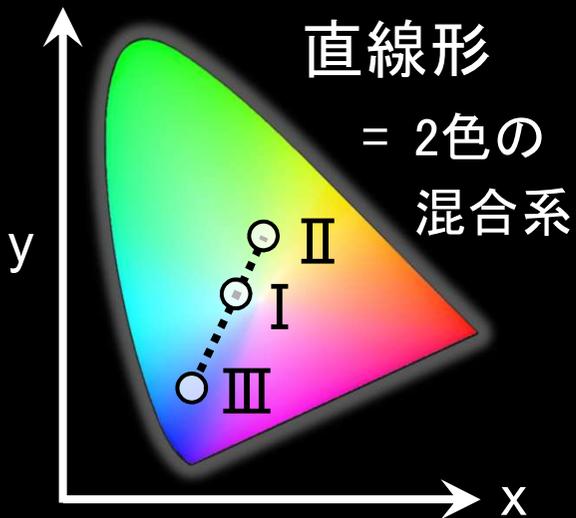


異なる弾性率



✓ 架橋密度の可視化

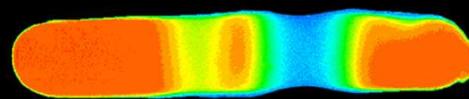
## CIE色度図



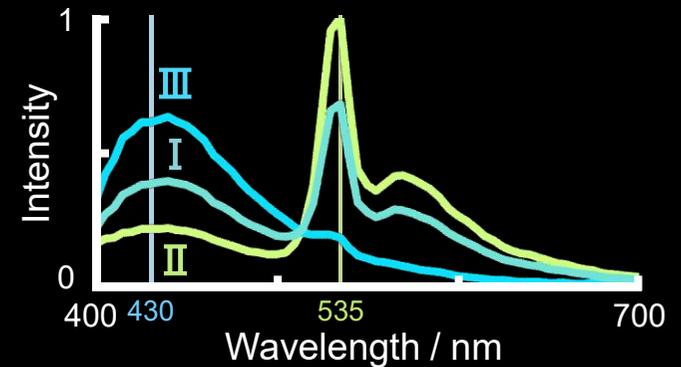
## ハイパースペクトルカメラ → 全ピクセルのスペクトル

$I_{535}$   $I_{430}$

Contrast map

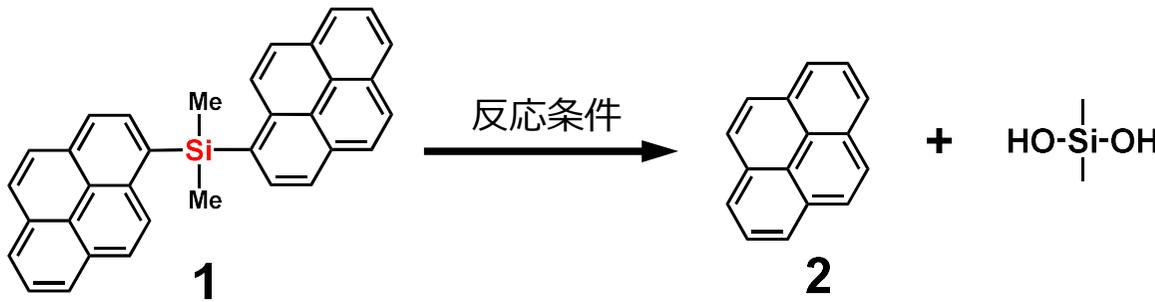


$I_{430} / I_{535} : III > I > II$

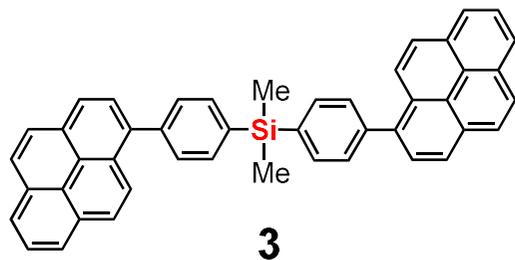


✓ 分解の進行と対応した発光色変化

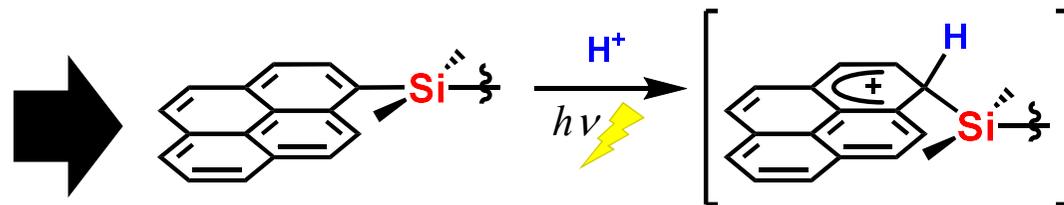
# ケイ素化合物における光・酸協働分解の実証



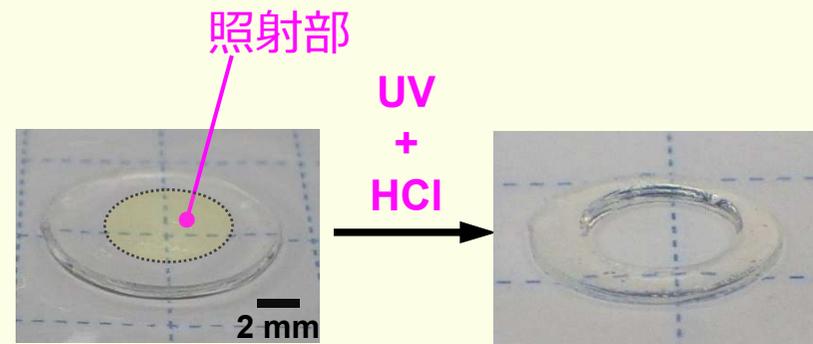
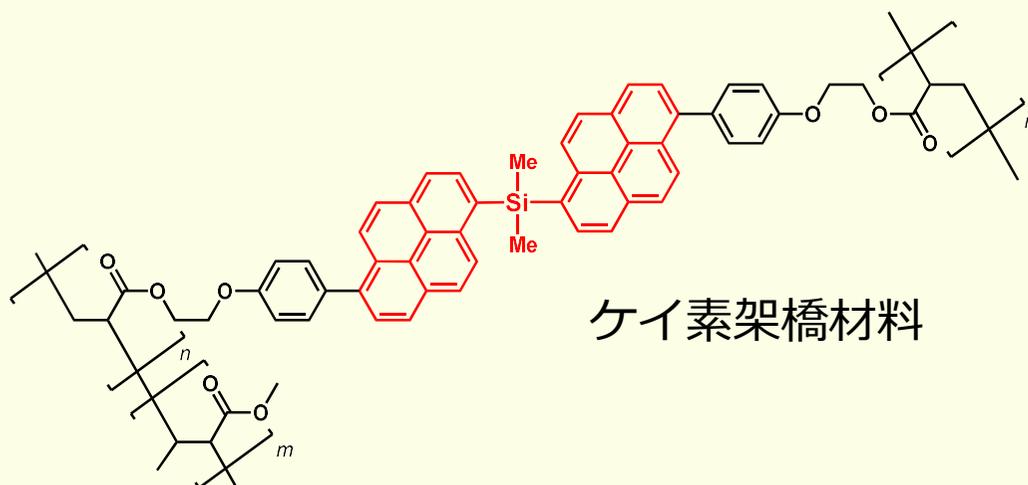
反応条件	GC Yield of 2
HCl+UV	75%
HCl	< 1%
UV	< 1%



協働反応性を発現せず



光誘起Wheland中間体形成を示唆



*Adv. Mater.*, **2025**, 37, 202412544.

# 謝辞

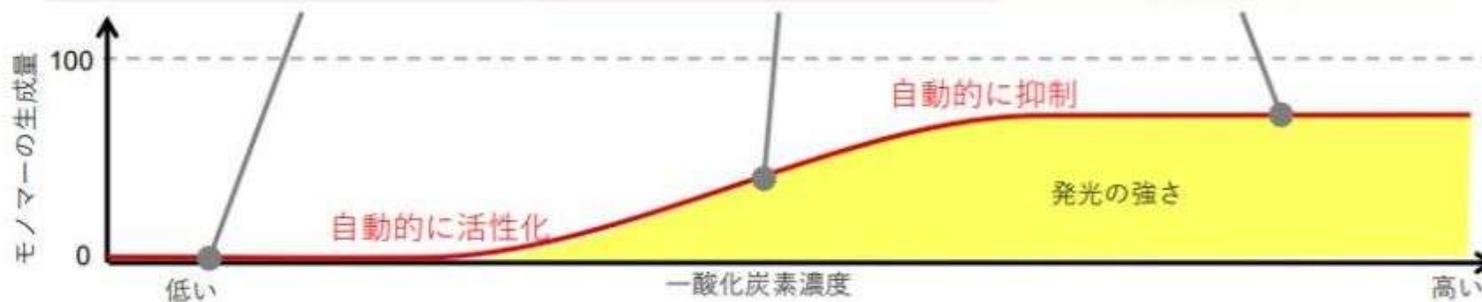
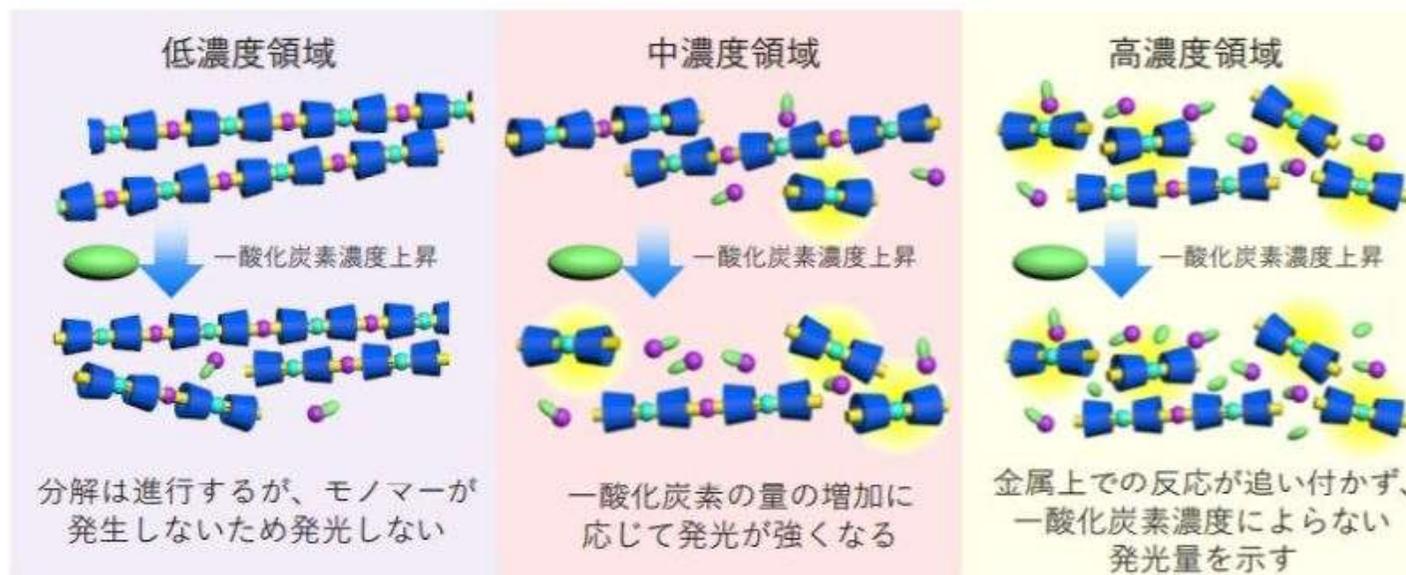
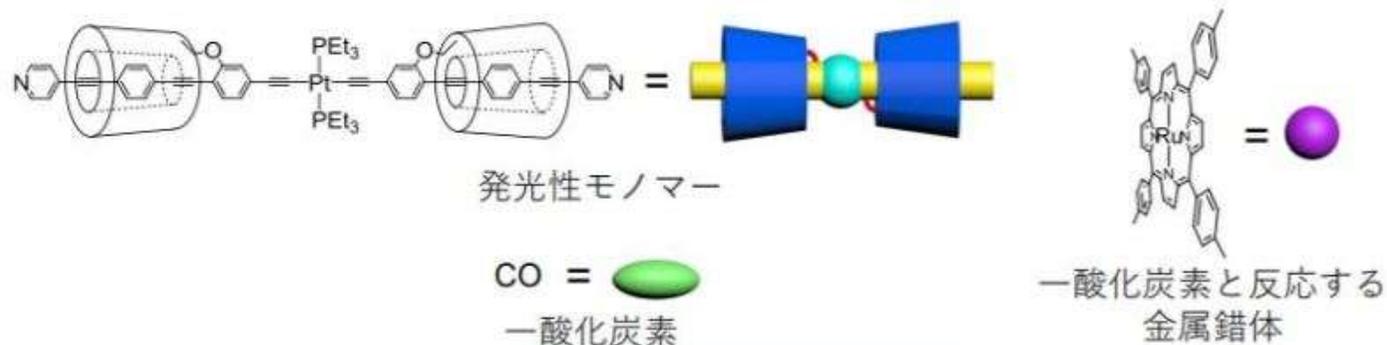


2016年度 矢崎科学技術記念財団 一般研究助成

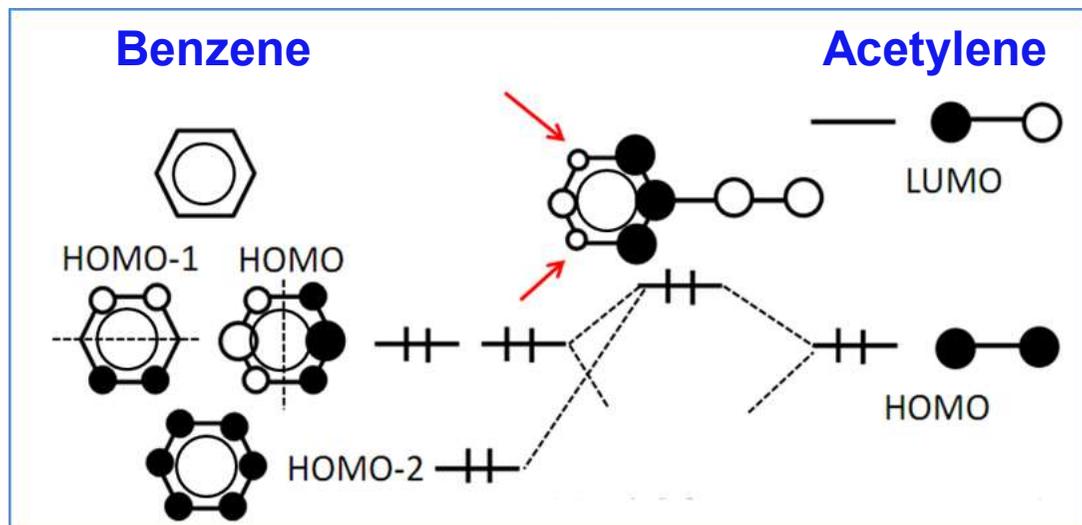
2022年度 矢崎科学技術記念財団 学術賞 功績賞



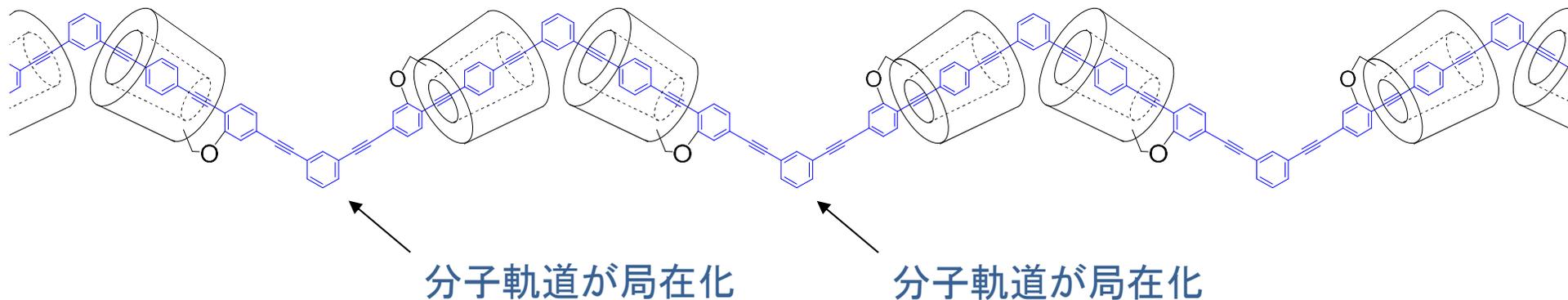
# 2つの閾値を持つシグモイド型応答性



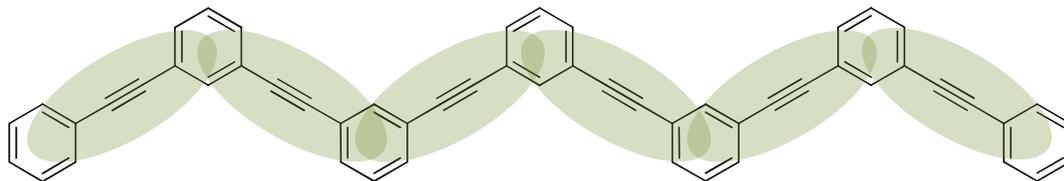
軌道係数が極端に小さい(メタ位)



ジグザグ型被覆分子ワイヤ



## ジグザグ型ポリフェニレンエチニレン



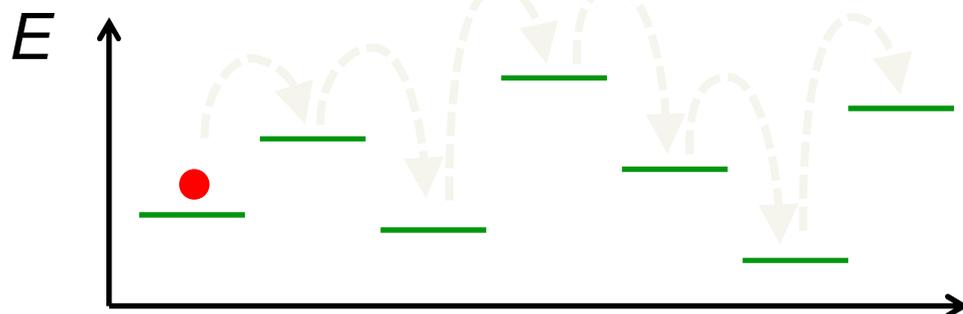
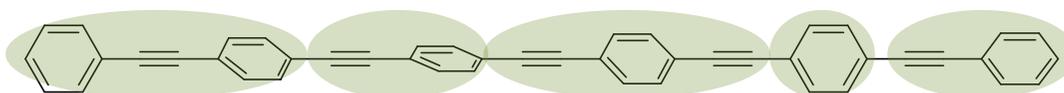
メタ接合部で規則的に局在化した軌道が形成



軌道エネルギー準位が同程度

→ 効率的なホッピング伝導

## 直線型ポリフェニレンエチニレン



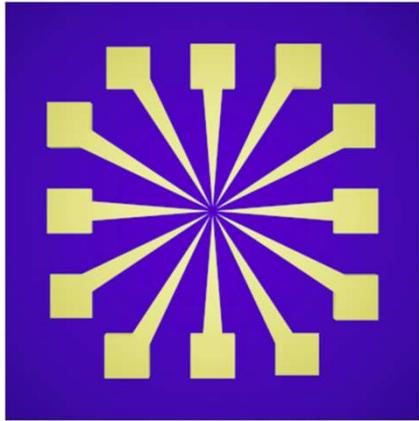
主鎖のランダムなねじれにより不規則に局在化した軌道が形成



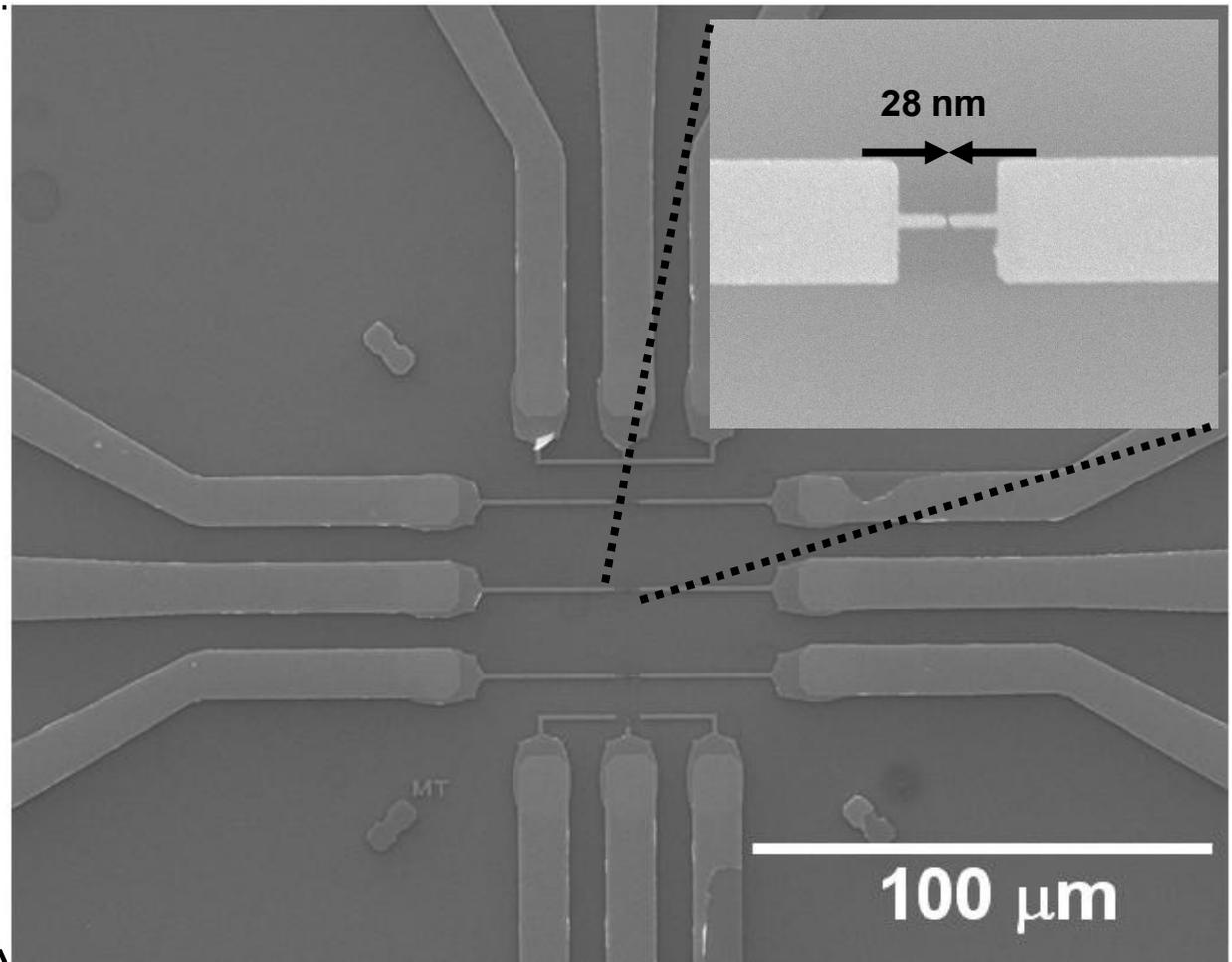
軌道エネルギー準位が広く分布

→ 非効率的なホッピング伝導

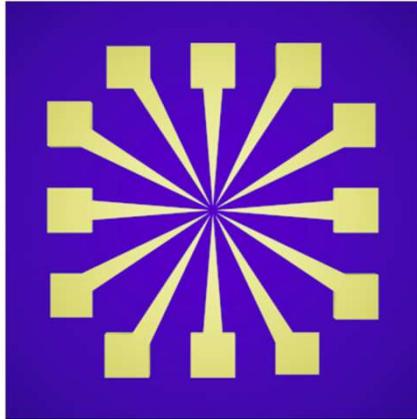
# ナノメートルのギャップを有する金電極（電子線描画法）



ナノ電極:  $\text{SiO}_2/\text{Au}/\text{Ti}$



# ナノメートルのギャップを有する金電極（電子線描画法）



# Step 1 : ナノ電極表面にクロスカップリング反応点を導入

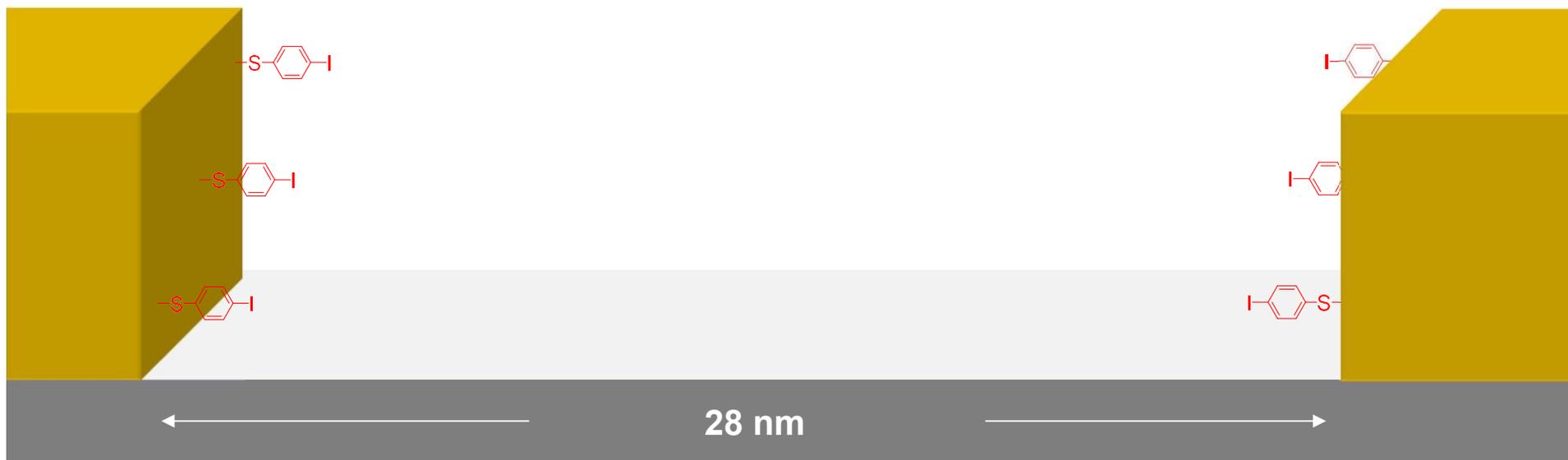
ナノ電極



接合分子



20 mM MeOH



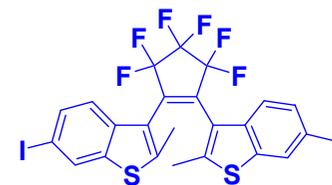


# Step 3: 機能性分子の導入

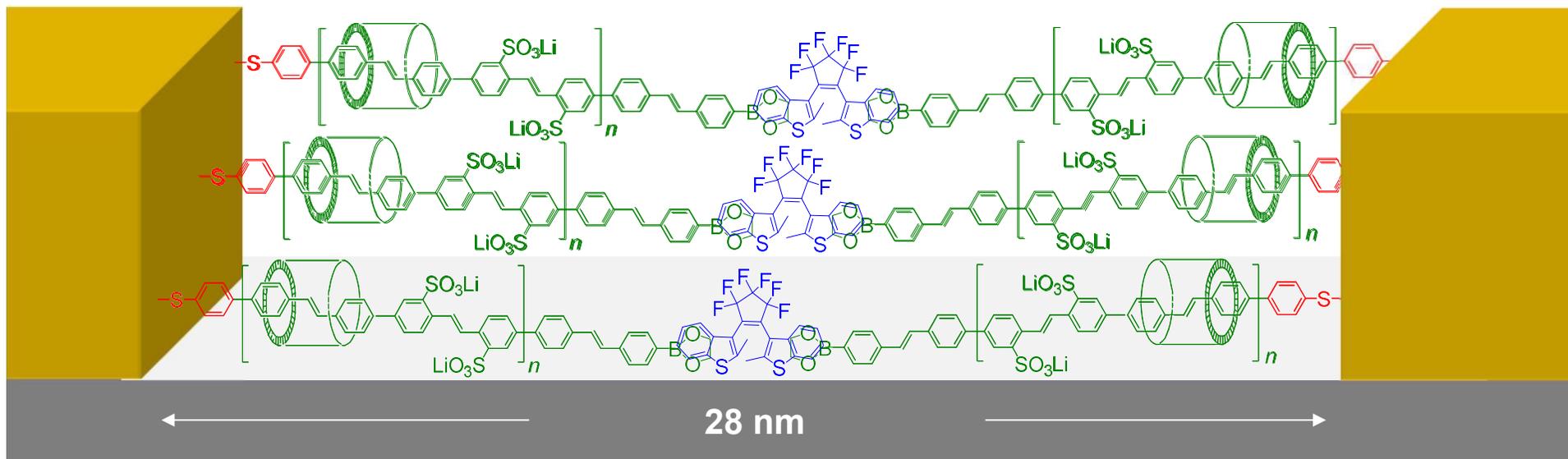


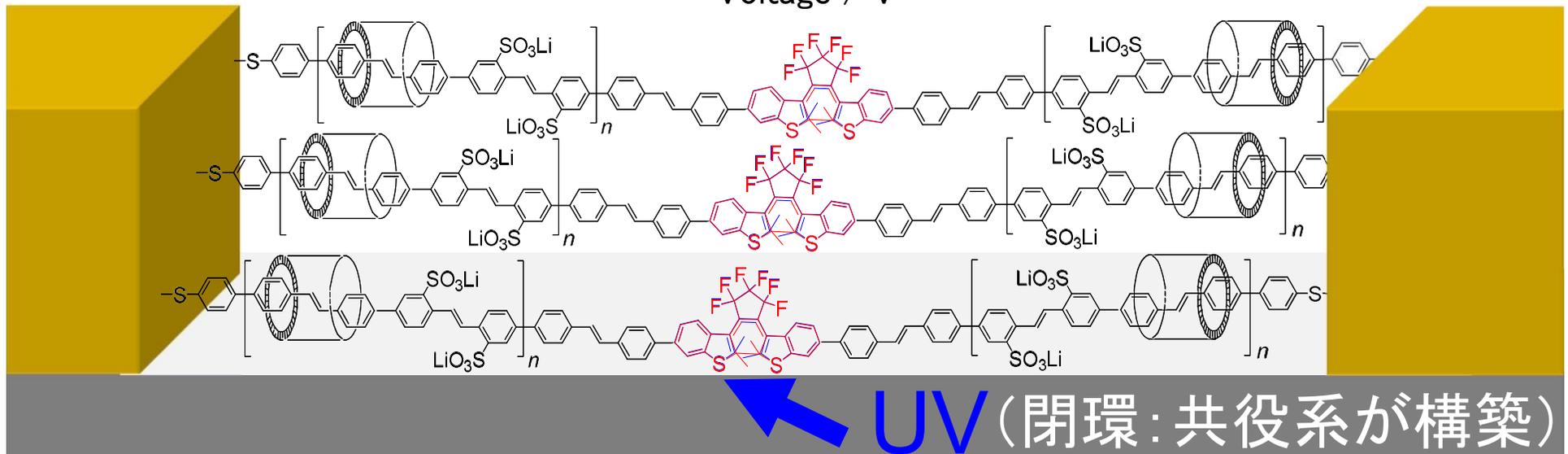
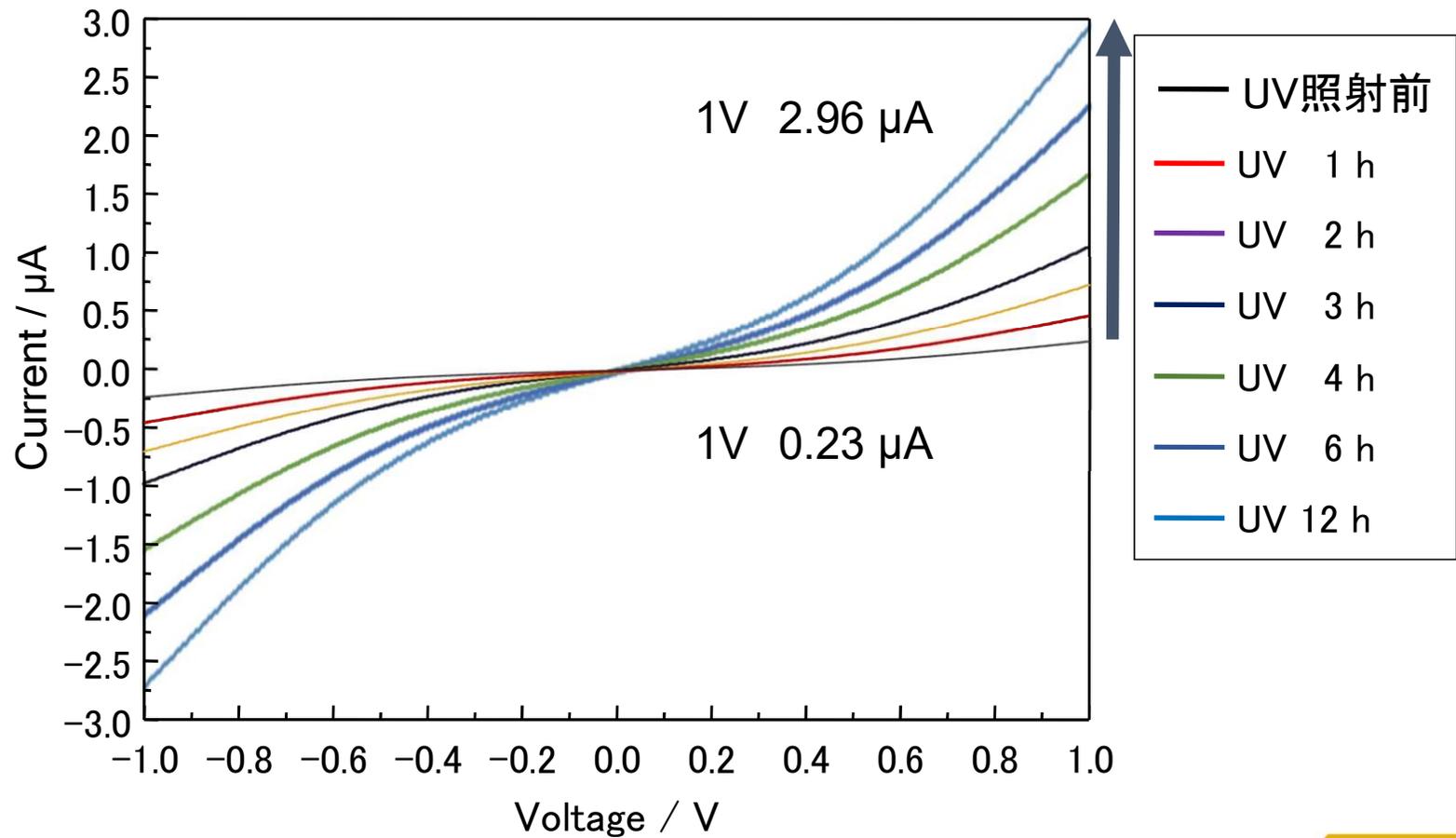
高分子デバイス

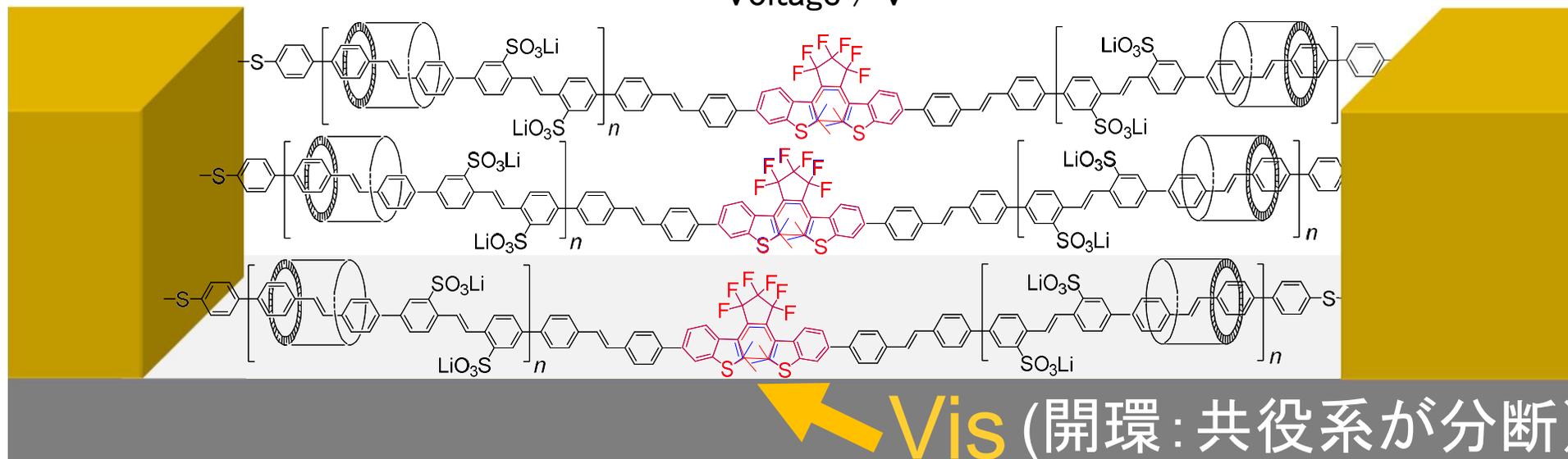
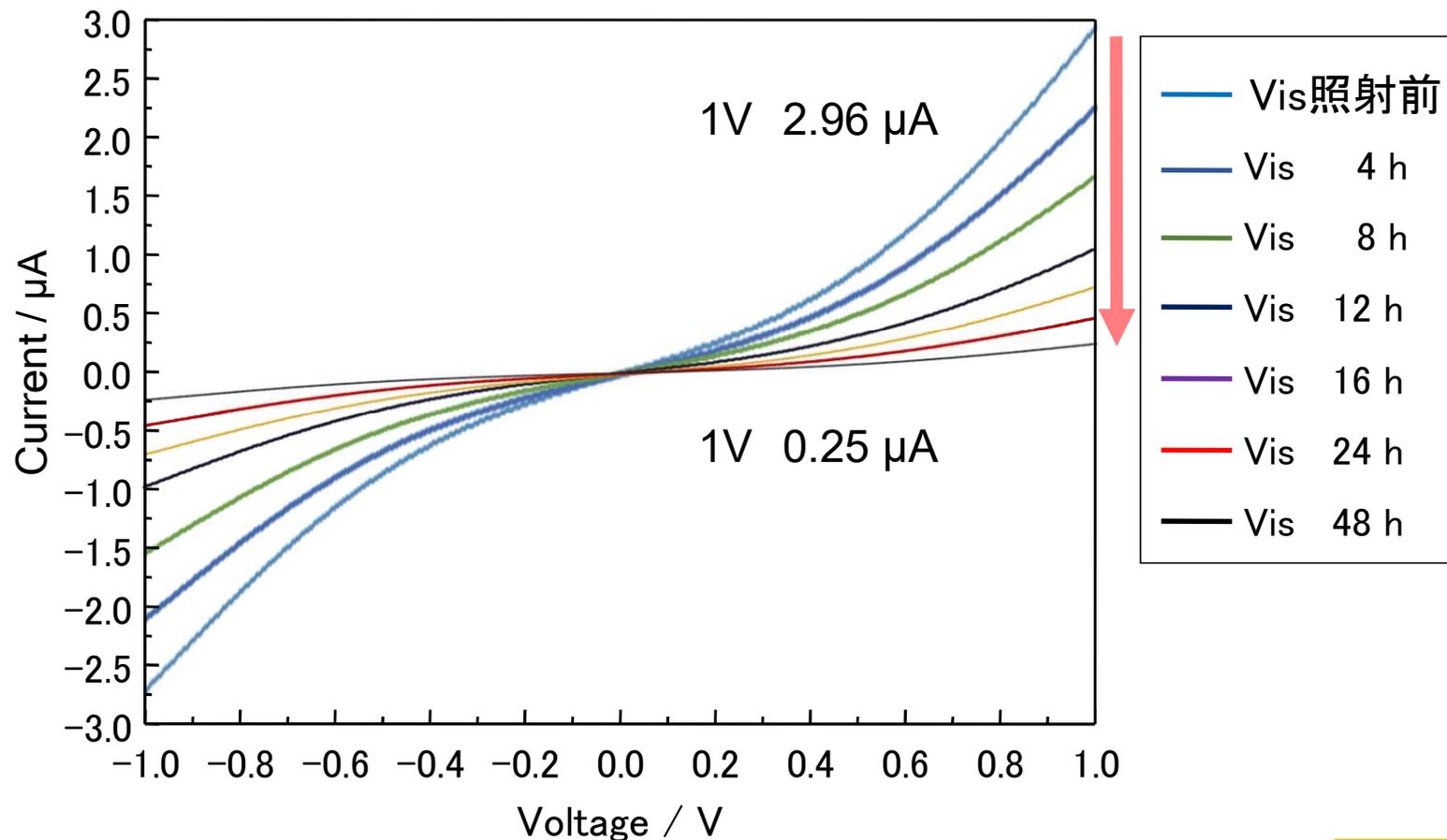
機能性分子



cat.  $\text{Pd}(\text{PPh}_3)_4, \text{K}_2\text{CO}_3$

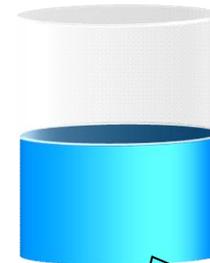
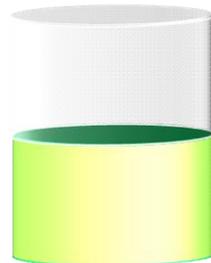
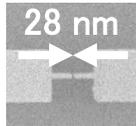






# ビルドアップ型高分子配線の開発

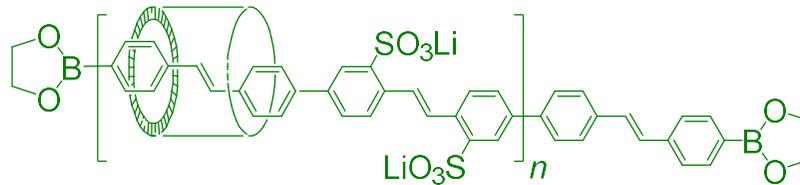
ナノ電極  
(電子線描画法)



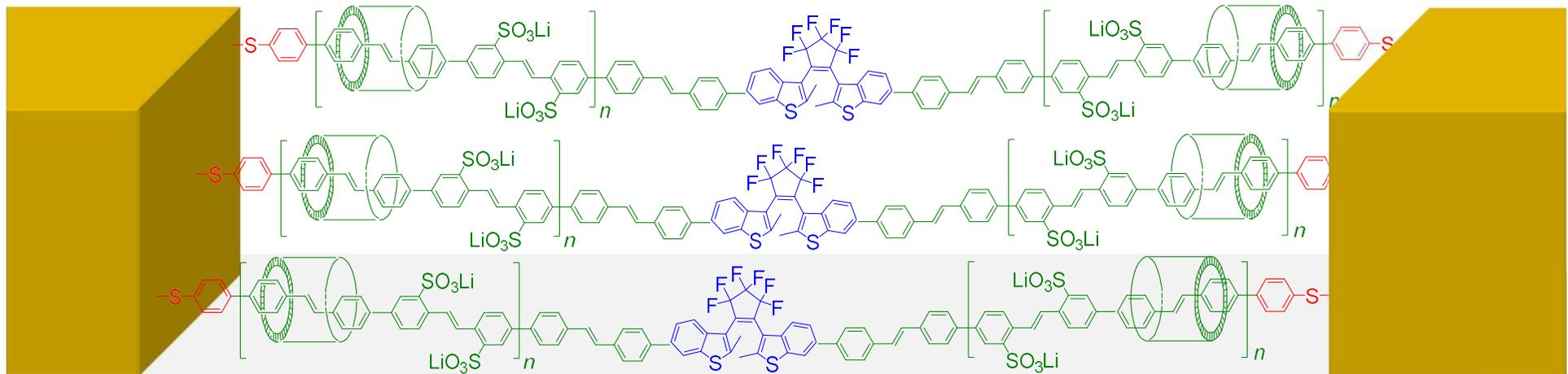
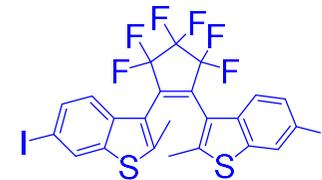
接合分子



被覆型分子ワイヤ

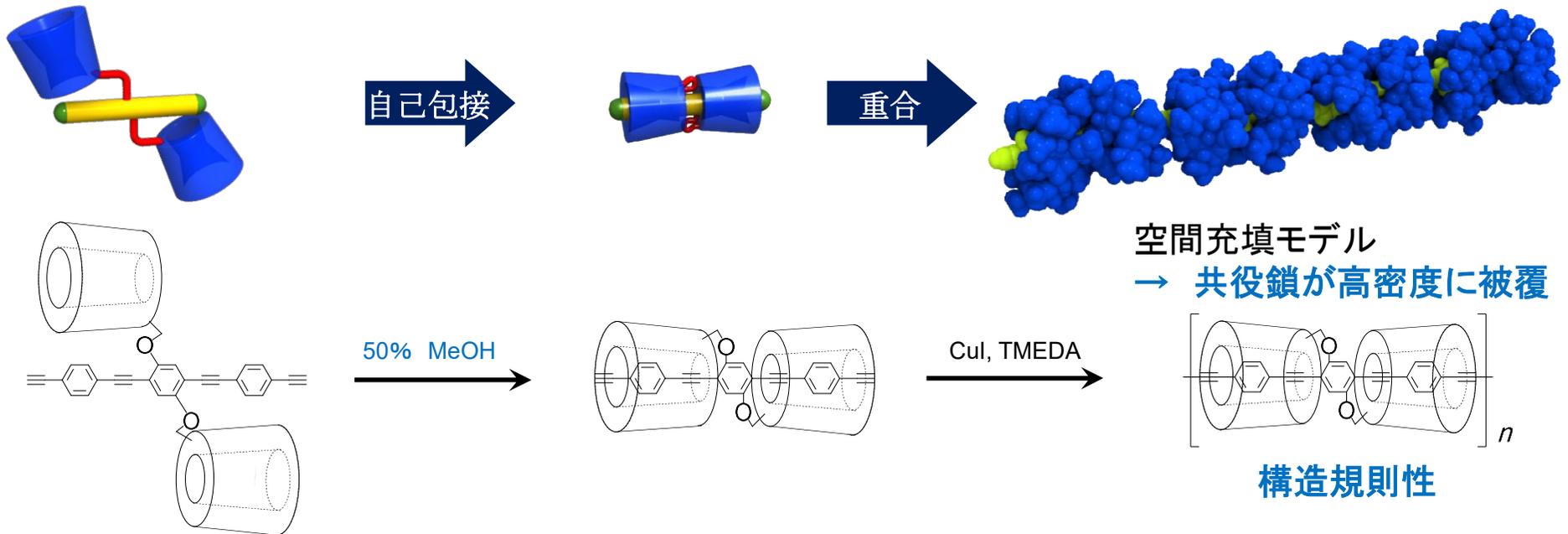


機能性分子



ナノスケール光スイッチデバイスの作製に成功

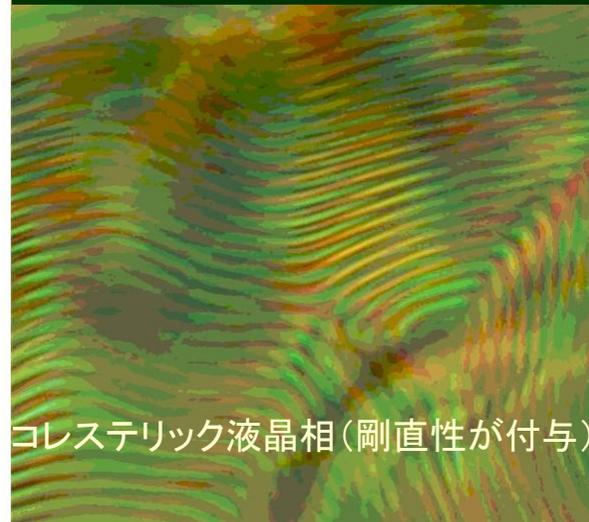
# 高被覆分子ワイヤの機能



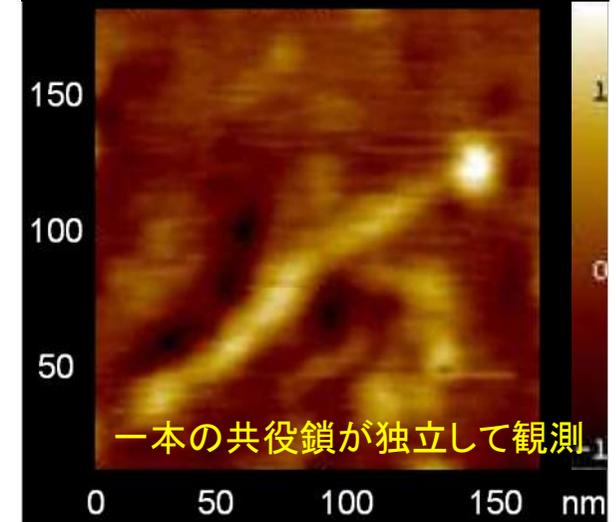
固体蛍光発光



偏光顕微鏡測定

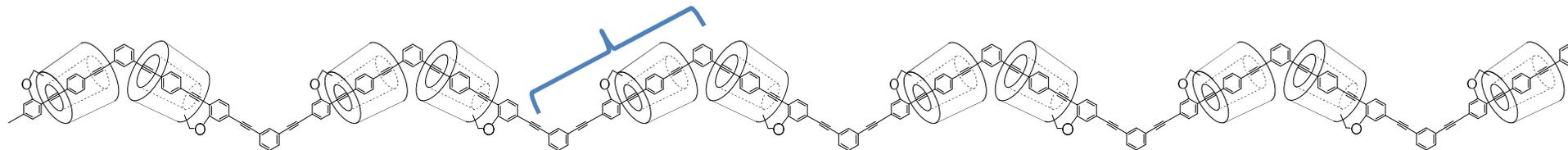


原子間力顕微鏡 (AFM) 測定



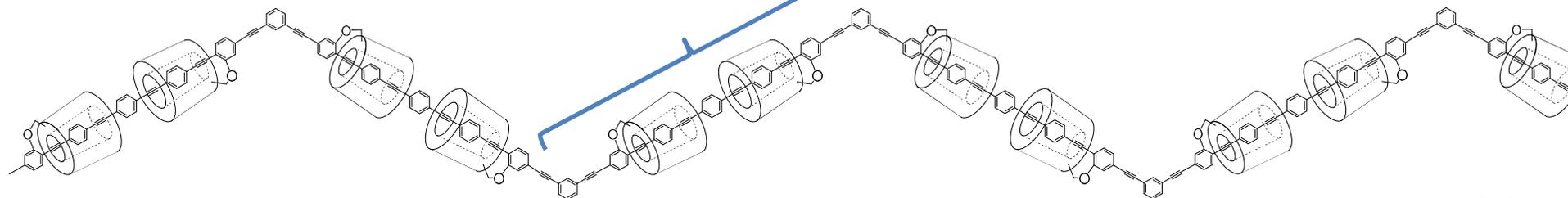
# メタ接合間距離の伸張による分子内電荷移動度の向上

PE units = 3



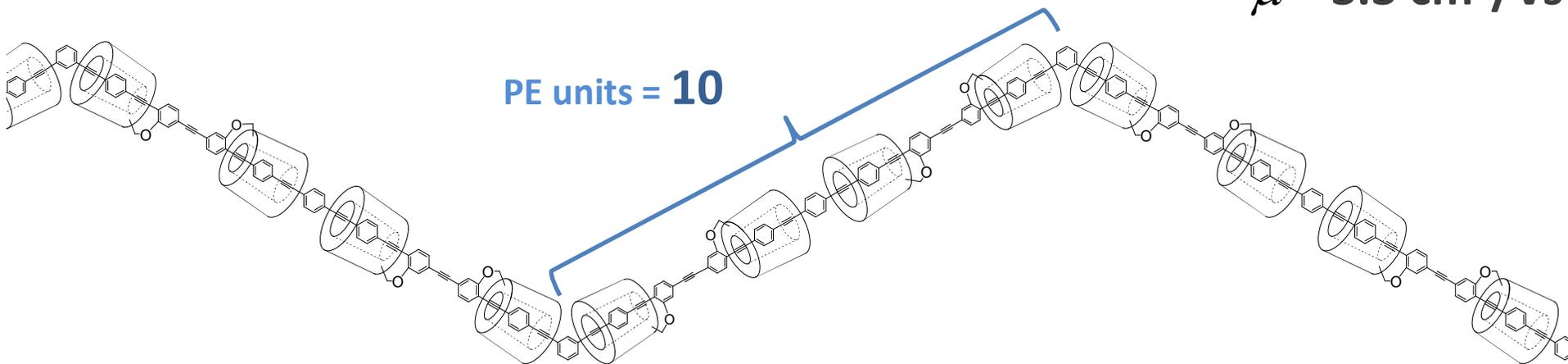
$\mu = 2.1 \text{ cm}^2/\text{Vs}$

PE units = 6



$\mu = 3.3 \text{ cm}^2/\text{Vs}$

PE units = 10



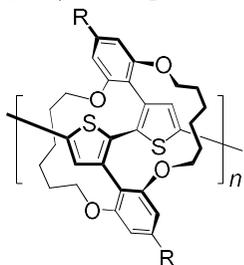
$\mu = 8.5 \text{ cm}^2/\text{Vs}$

# ホッピング伝導の上限値に迫る分子内電荷移動度を達成

アモルファスシリコン

$$\mu = 0.2 - 1.0 \text{ cm}^2/\text{Vs}$$

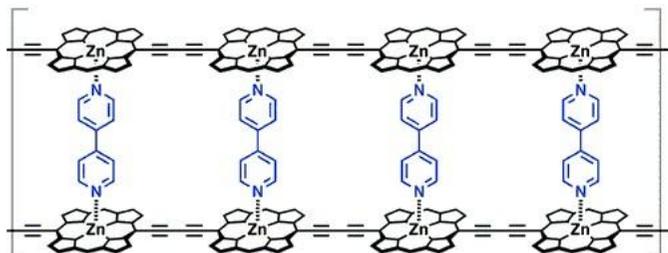
被覆型ポリチオフェン



$$\mu = 0.90 \text{ cm}^2/\text{Vs}$$

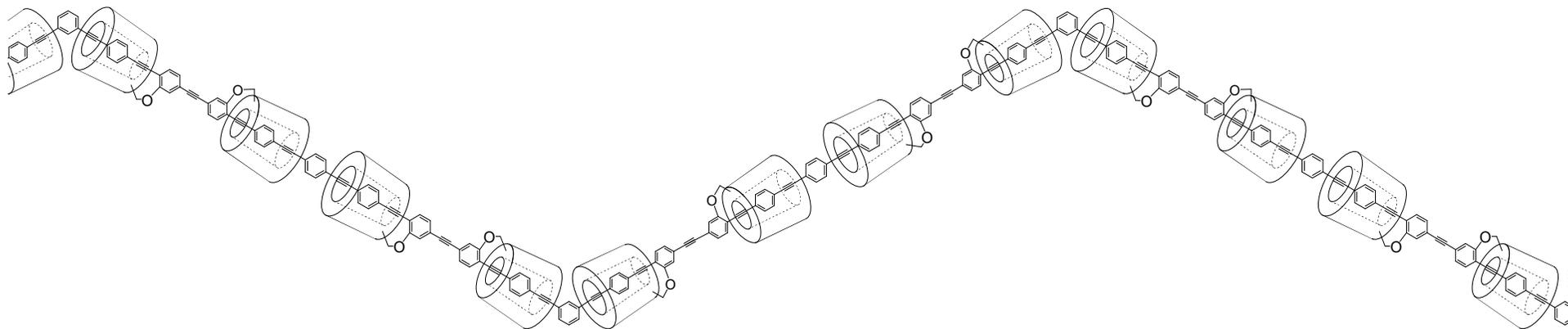
Sugiyasu, K.; Takeuchi, M. et al. *J. Am. Chem. Soc.* **2010**, *132*, 14754

ラダー型ポルフィリンポリマー



$$\mu = 0.91 \text{ cm}^2/\text{Vs}$$

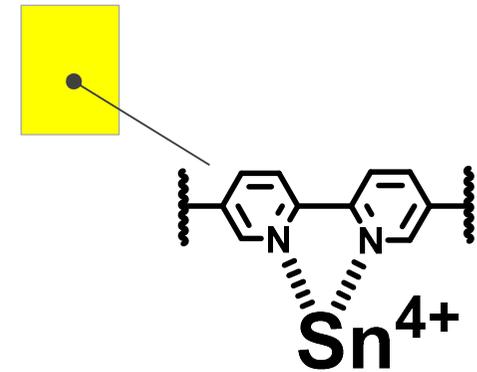
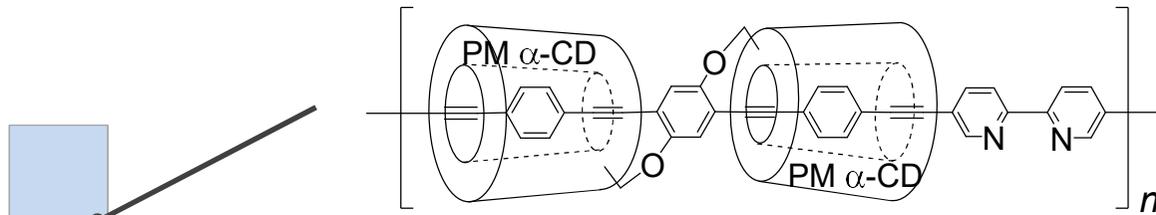
Siebbeles, L. D. A.; Anderson, H. L. et al. *J. Am. Chem. Soc.* **2007**, *129*, 13370



$$\mu = 8.5 \text{ cm}^2/\text{Vs}$$

*Nat. Commun.* **2013**, *4*, 1691

# 蛍光色変化による金属イオンセンサ



The films viewed under 365 nm UV.



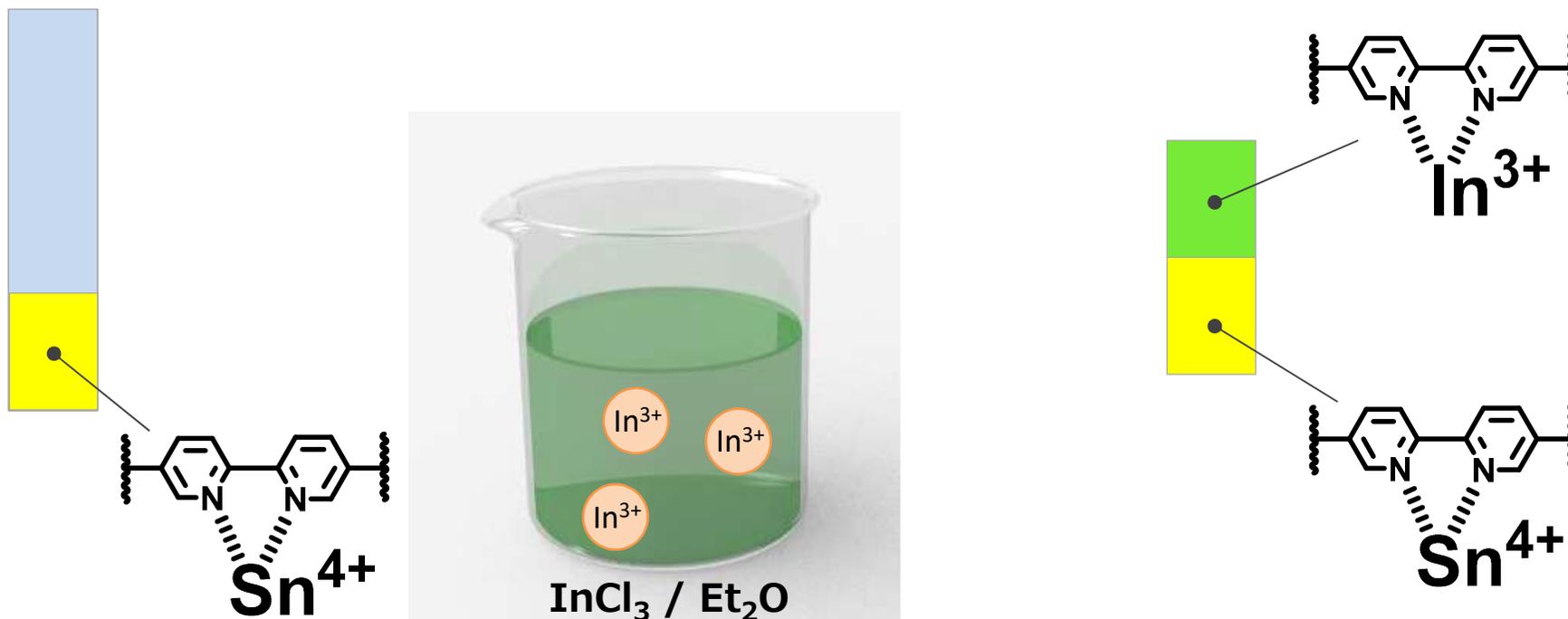
P1

$\text{SnCl}_4$

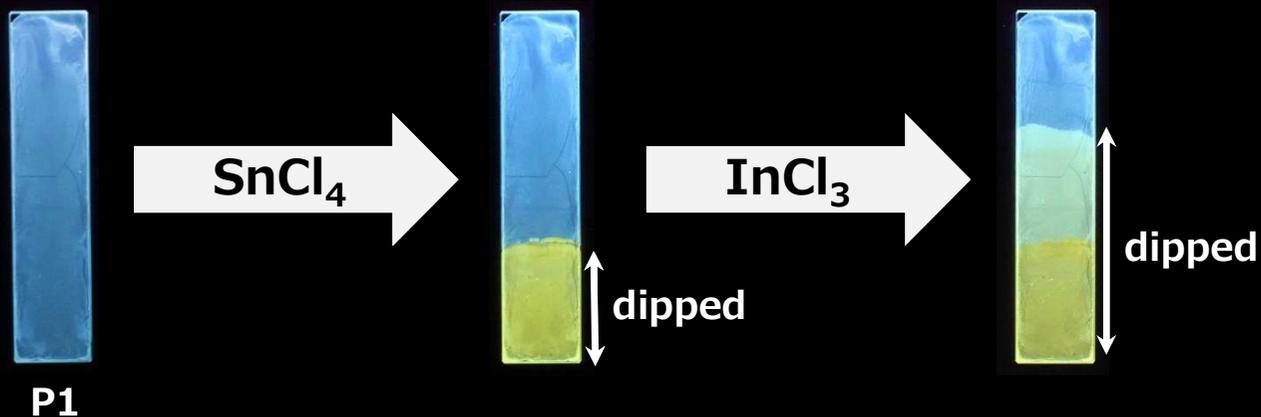


dipped

# 蛍光色変化による金属イオンセンサ



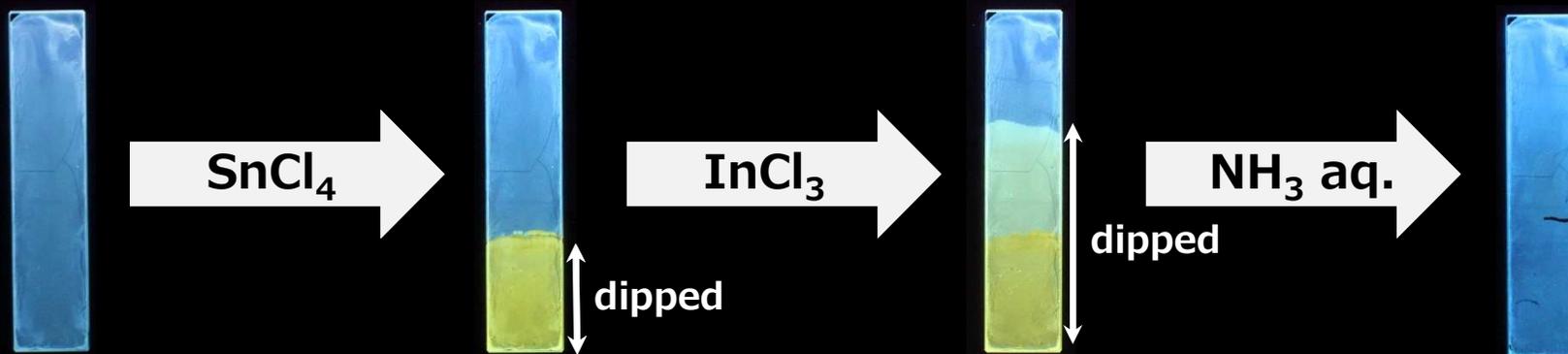
The films viewed under 365 nm UV.



# 蛍光色変化による金属イオンセンサ



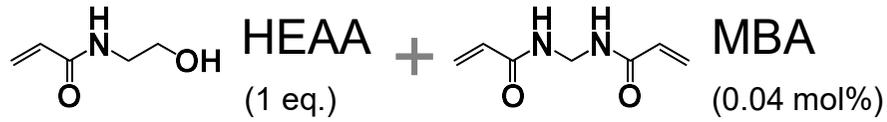
The films viewed under 365 nm UV.



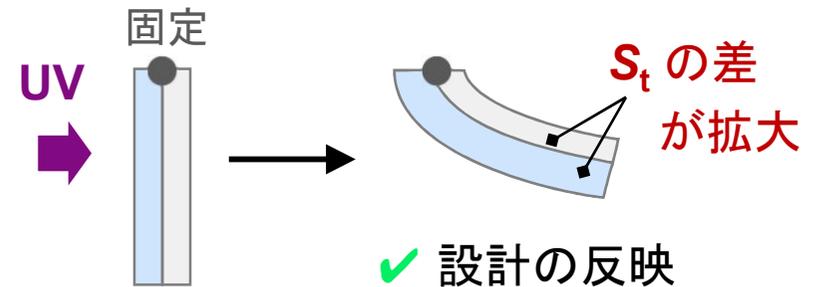
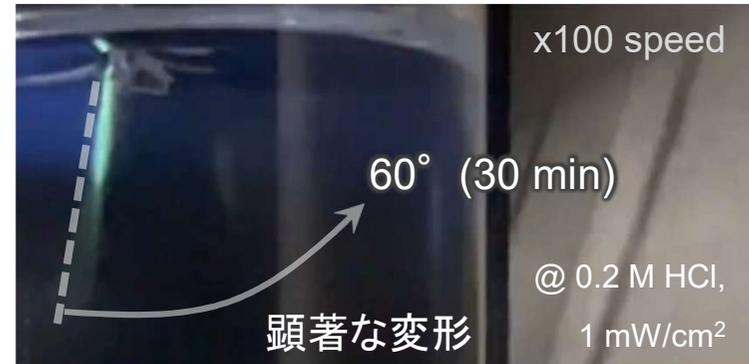
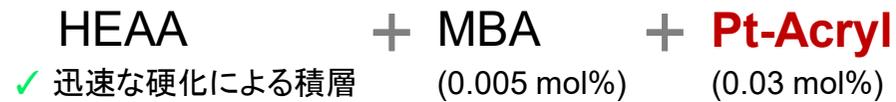
P1

# 膨潤現象の応用: 光造形

## 設計: 積層型ゲル

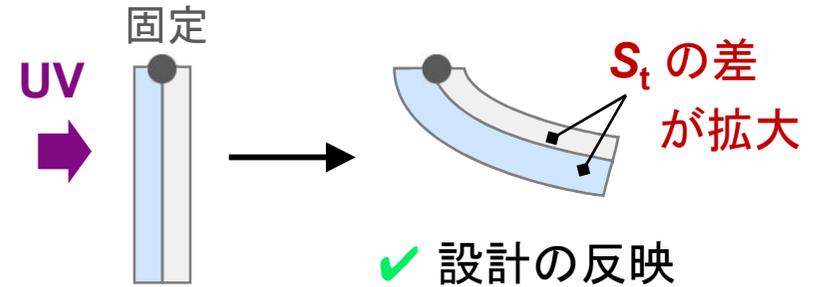
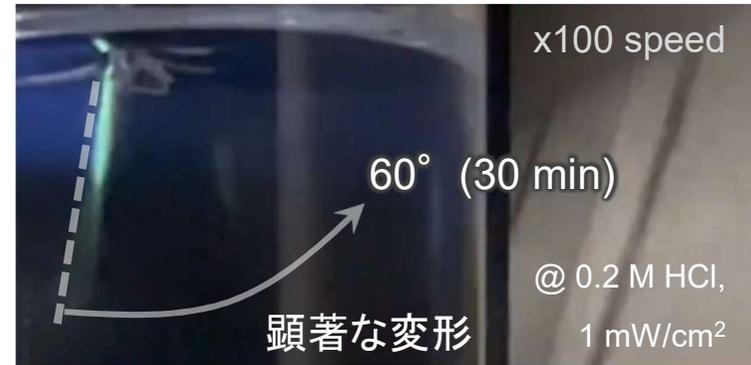
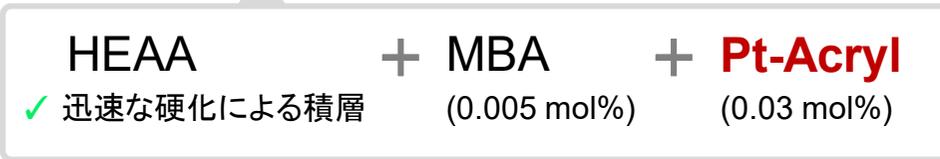
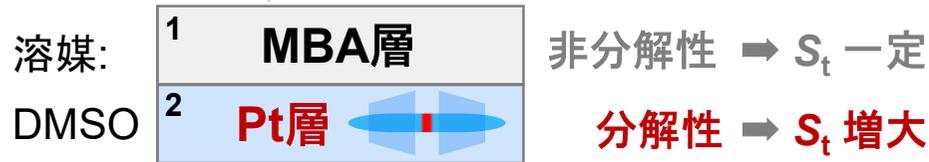
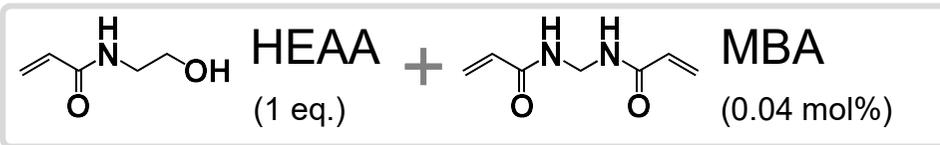


溶媒: 1 **MBA層** 非分解性  $\rightarrow S_t$  一定  
DMSO 2 **Pt層** 分解性  $\rightarrow S_t$  増大

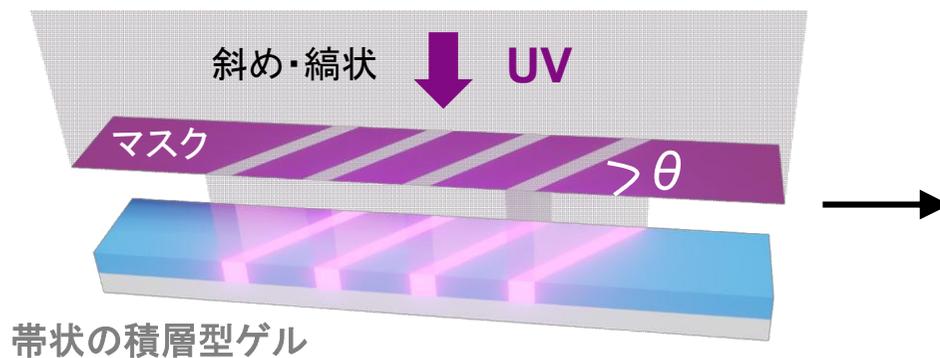


# 膨潤現象の応用: 光造形

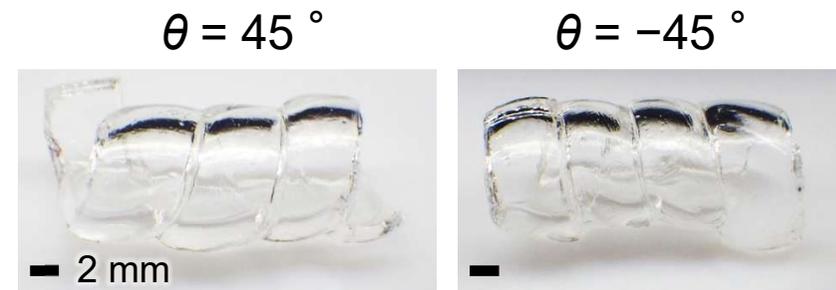
## 設計: 積層型ゲル



## 光パターニング



斜め折りと同様の効果



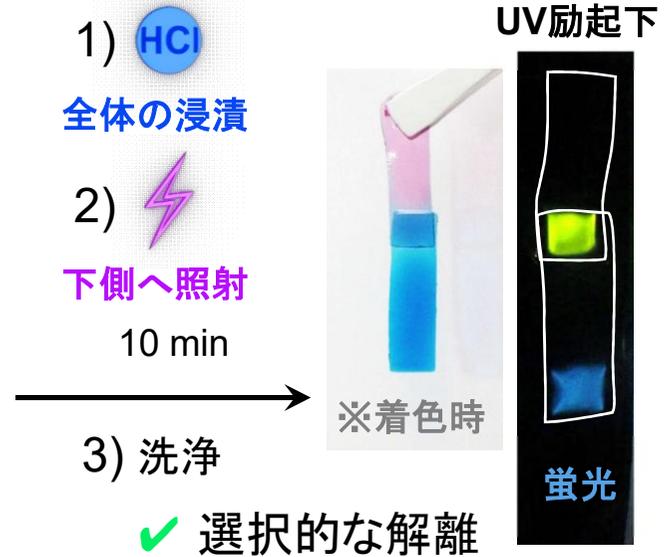
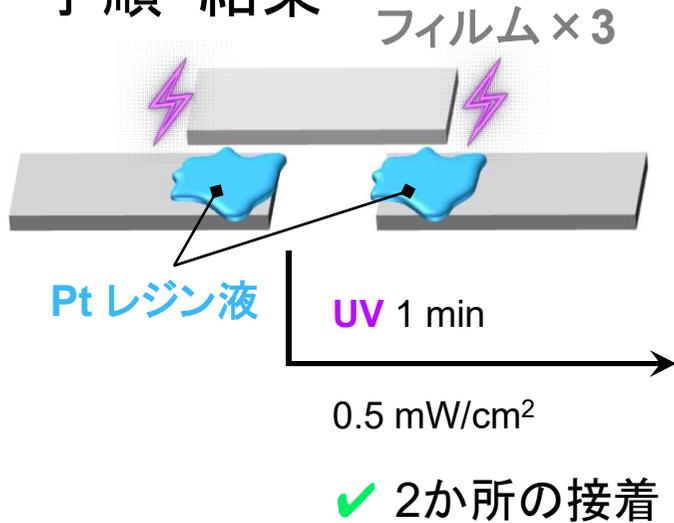
左巻き螺旋

右巻き螺旋

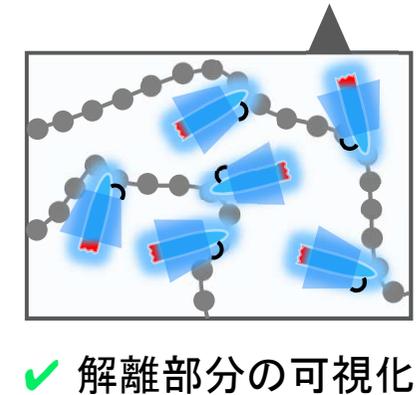
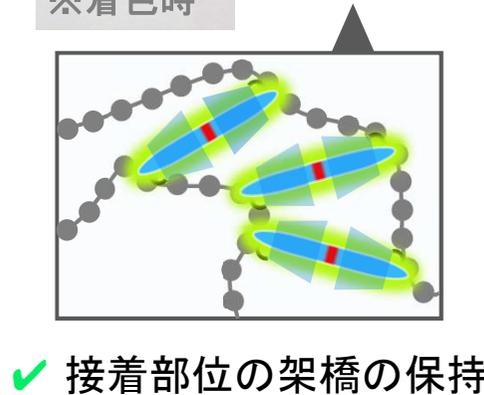
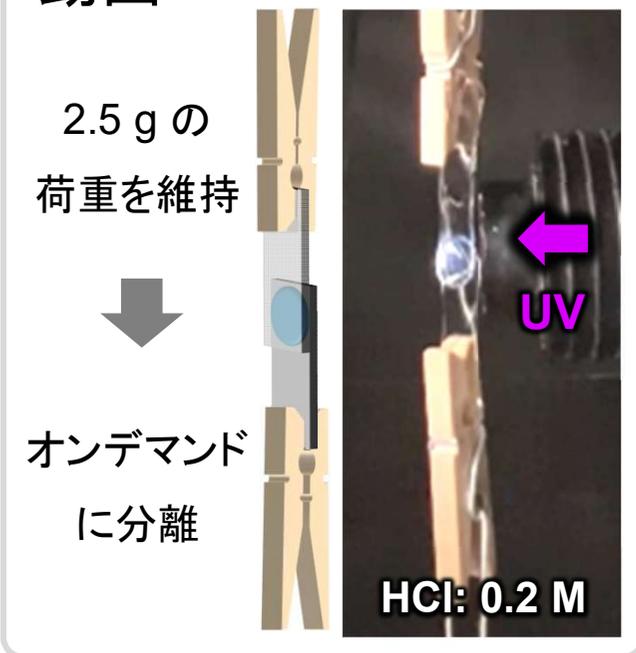
✓ 光の局所性を利用した形状制御

# 光分解による接着箇所的光解離

手順・結果



動画



✓ 光安定性と光分解性の両立に基づく  
光接着性・光解離性