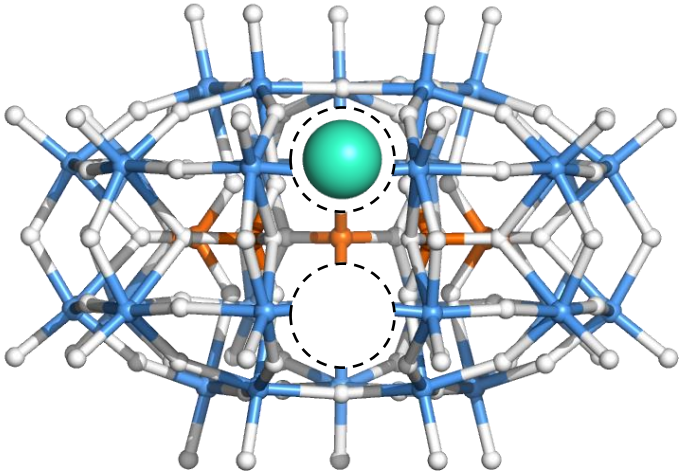
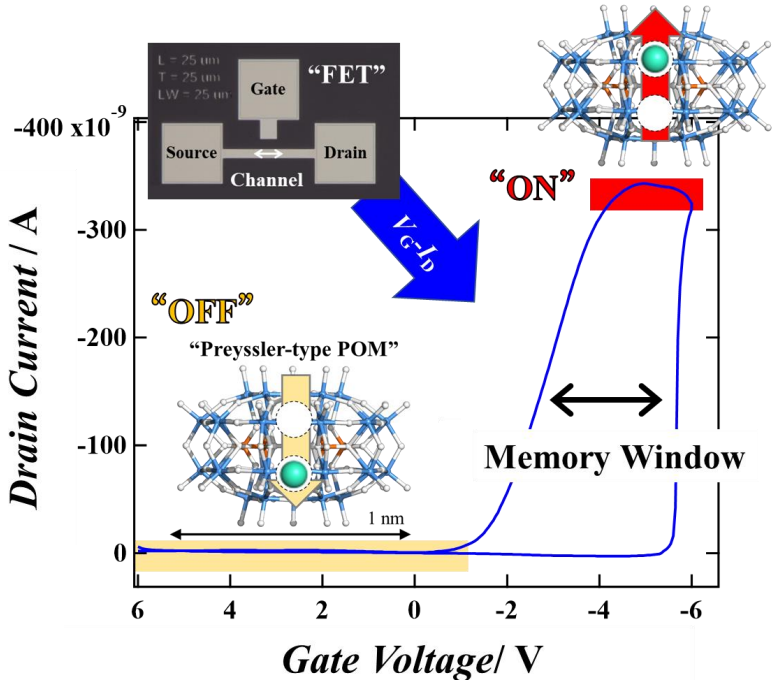
# 単分子で情報を記録する
# 単分子誘電体によるメモリ開発






藤林　将（宇部高専）

# Contents

1. Background and Motivation of our Study

2. Physical Properties and Mechanism of SME

3. Fabrication of Non-Volatile Memory

    1. Lateral-type FET

    2. Stacked-type FET

4. Conclusion

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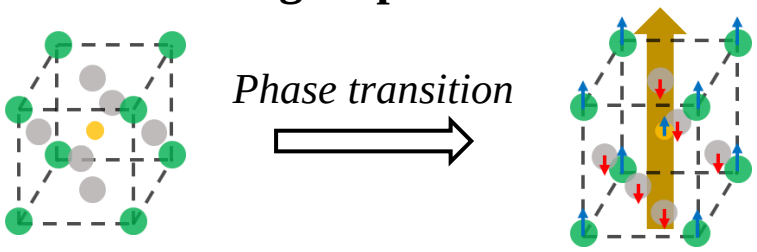
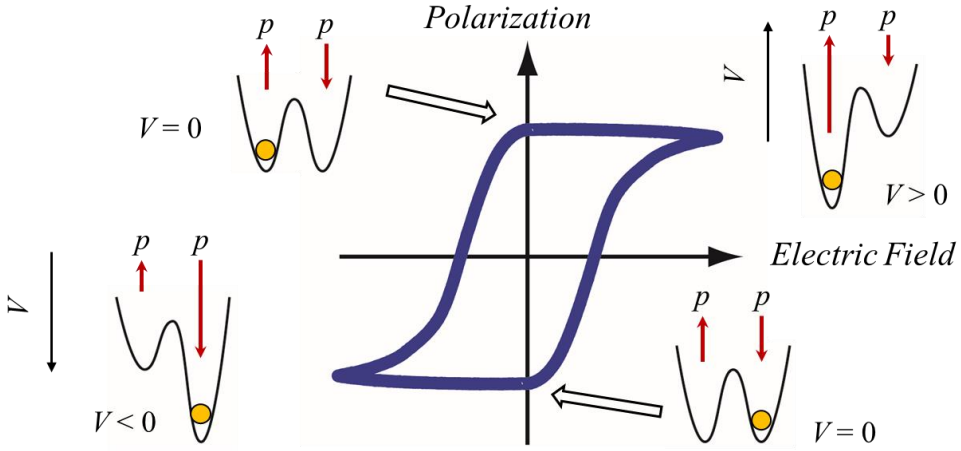
# Ferroelectric Materials and Memory Application

## Ferroelectric Materials

- ☑ Long-range ordering of dipole moments
- ☑ Positive interaction between the neighbor dipole

➔ **Large dipole moments**



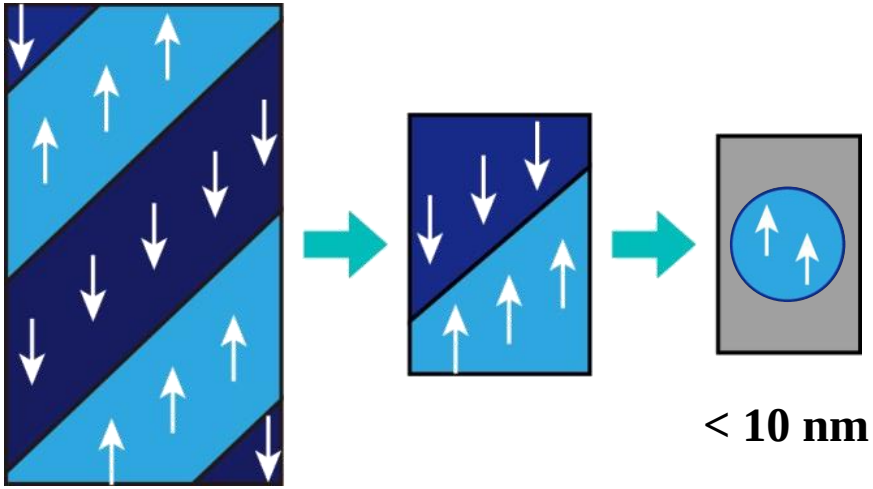

## Strong Point of Ferroelectric-based memory

**Rapid polarization Reversal**
→ Rapid response

**Non-volatile**
→ Low power consumption

**Spontaneous Polarization**
→ Long retention time

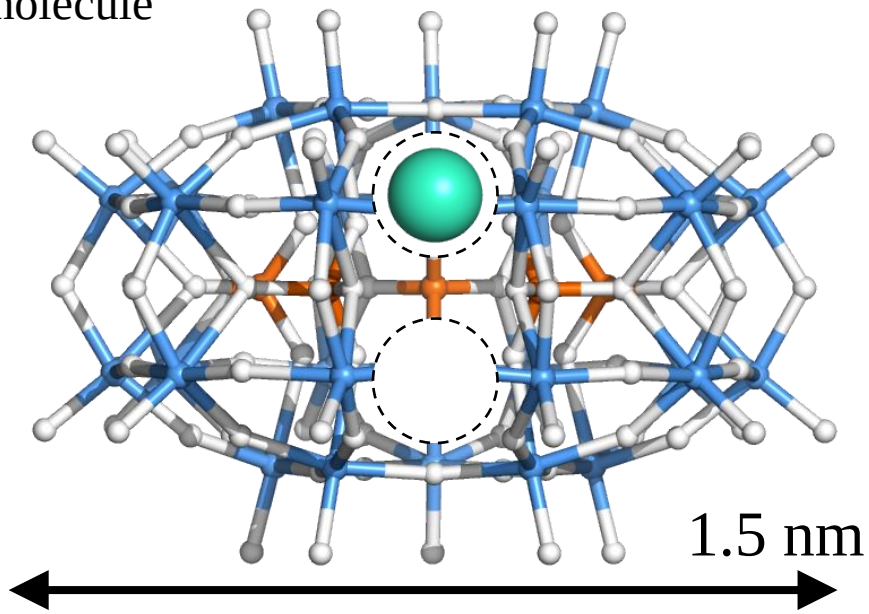
**Disadvantage of size limitation**
✖ High density memory



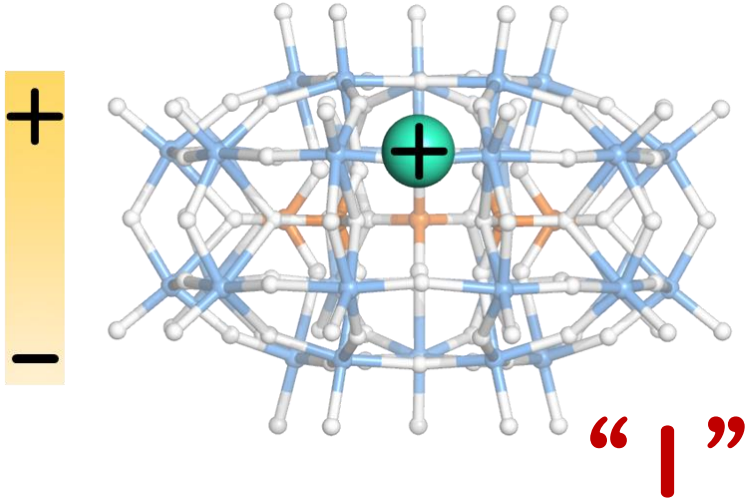
# Preyssler-type Polyoxometalate

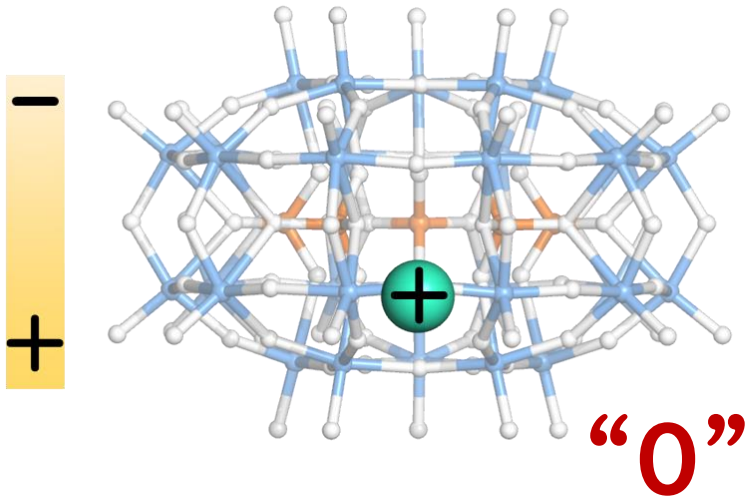
## Preyssler-type Polyoxometalate（POM）

- Cage-like molecular structure
- Anionic metal oxide molecule
- Clathrate molecule ($Tb^{3+}$)
- Two stable metal ionic sites within single molecule

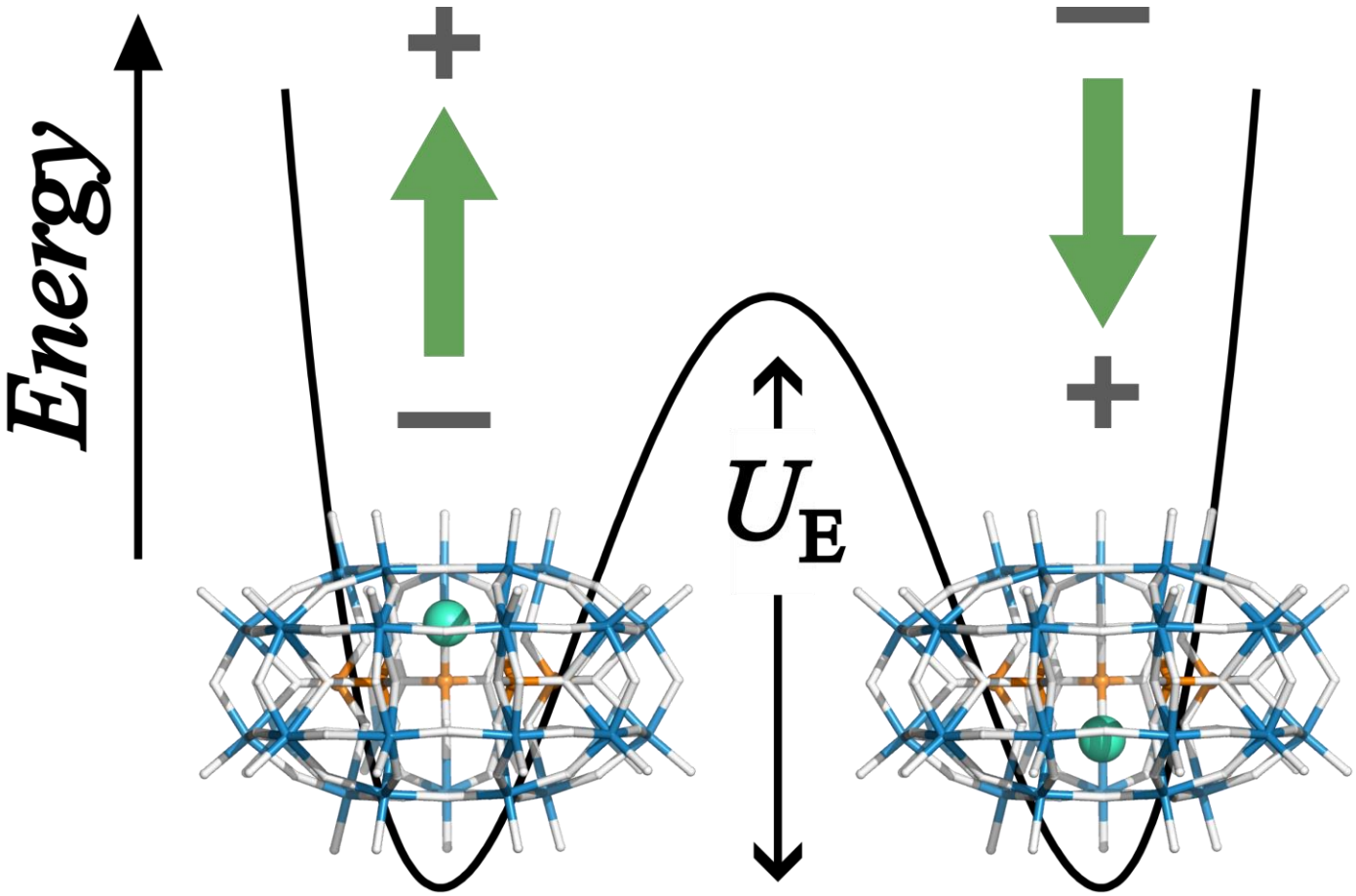



$[Tb^{3+}\subset P_5W_{30}O_{110}]^{12-}$



# Packing Structure of Preyssler-type POM




**Breakthrough the size limitation by Single Molecule**

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# Synthesis and sample preparation

$Na_2WO_4 \cdot 2H_2O$ dissolved in $H_2O$

| ← +85% $H_3PO_4$

(Hydrothermal reaction)

↓

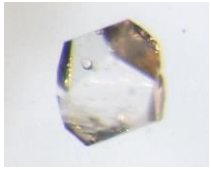
$K_{12.5}Na_{1.5}[Na^+ \subset P_5W_{30}O_{110}] \cdot 15H_2O$

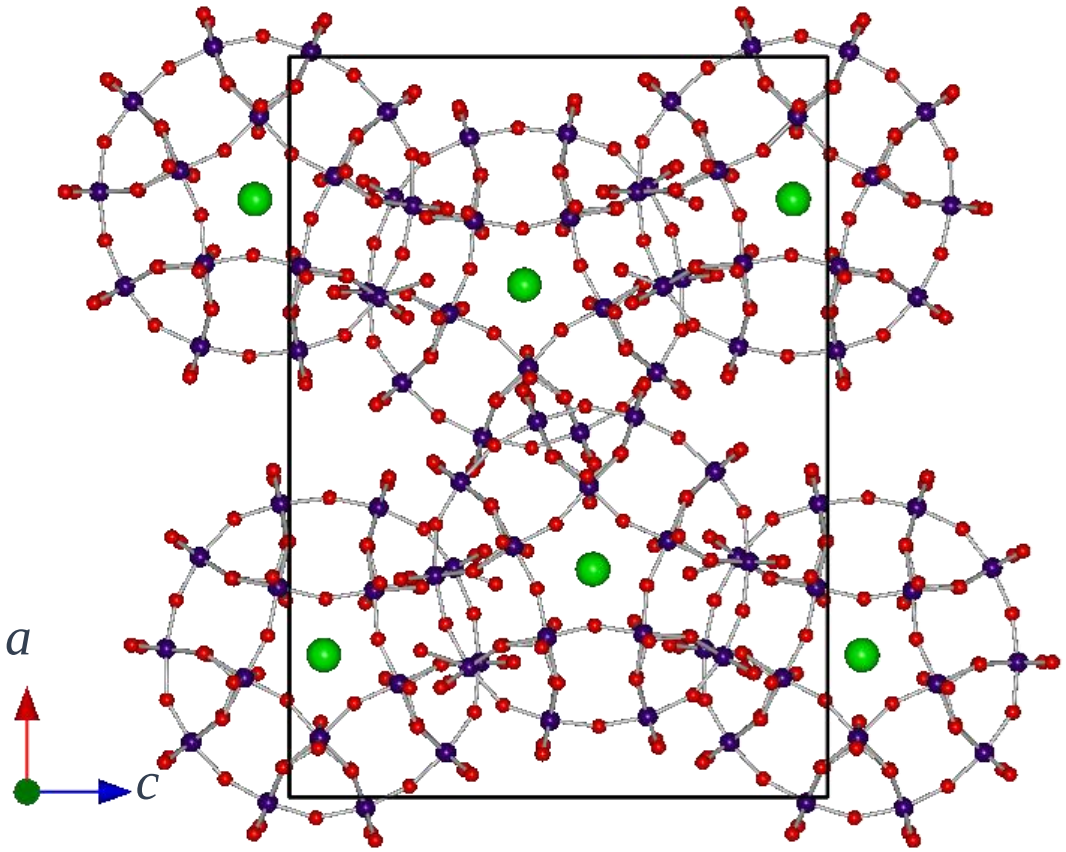
| ← +$Tb(NO_3)_3 \cdot nH_2O$

(Hydrothermal reaction)

↓

**$K_{12}[Tb^{3+} \subset P_5W_{30}O_{110}] \cdot xH_2O$**



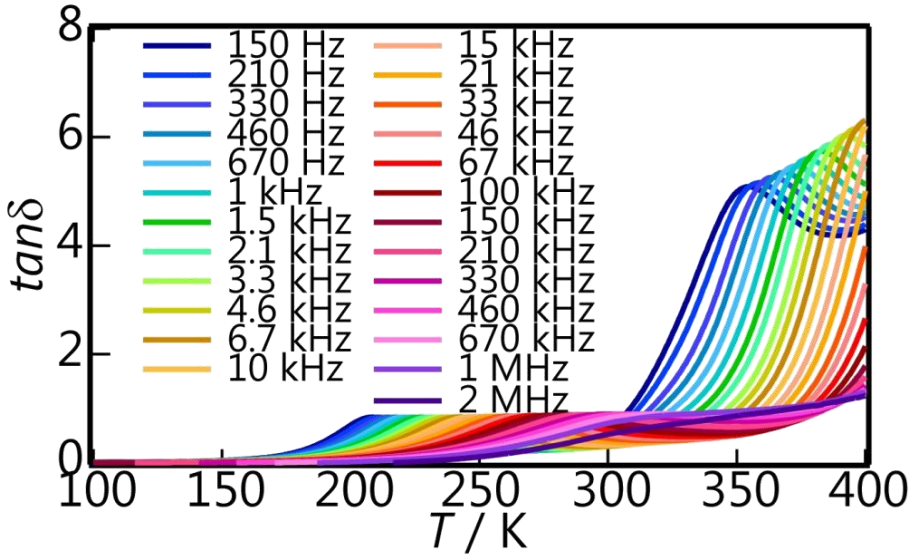


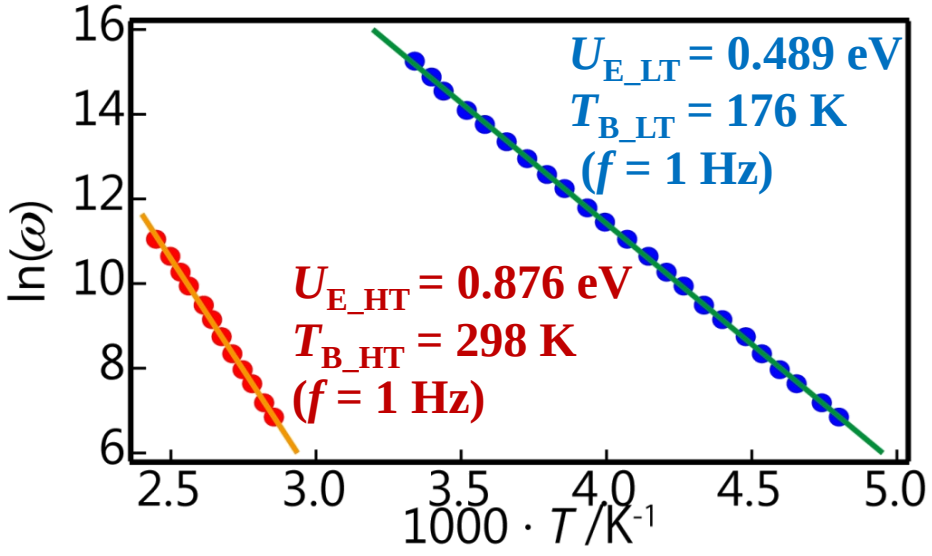

@ 173 K, Orthorhombic ***Pnma***

$a$ = 28.693(2), $b$ = 21.5210(16), $c$ = 20.8469(15) Å,

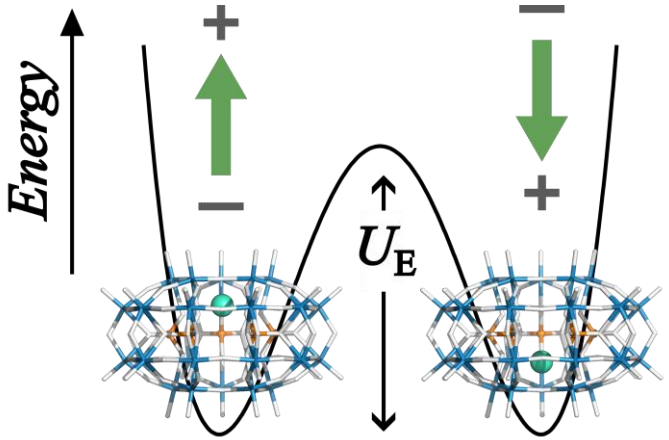
$V$ = 12873 Å$^3$, $Z$ = 4

# Dielectric properties of Preyssler-type POM




- No first-order phase transition
- Two kinds of frequency dispersed dielectric relaxation




| | Energy barrier | Blocking temperature |
|---|---|---|
| HT | 0.876 eV | 298 K |
| LT | 0.489 eV | 176 K |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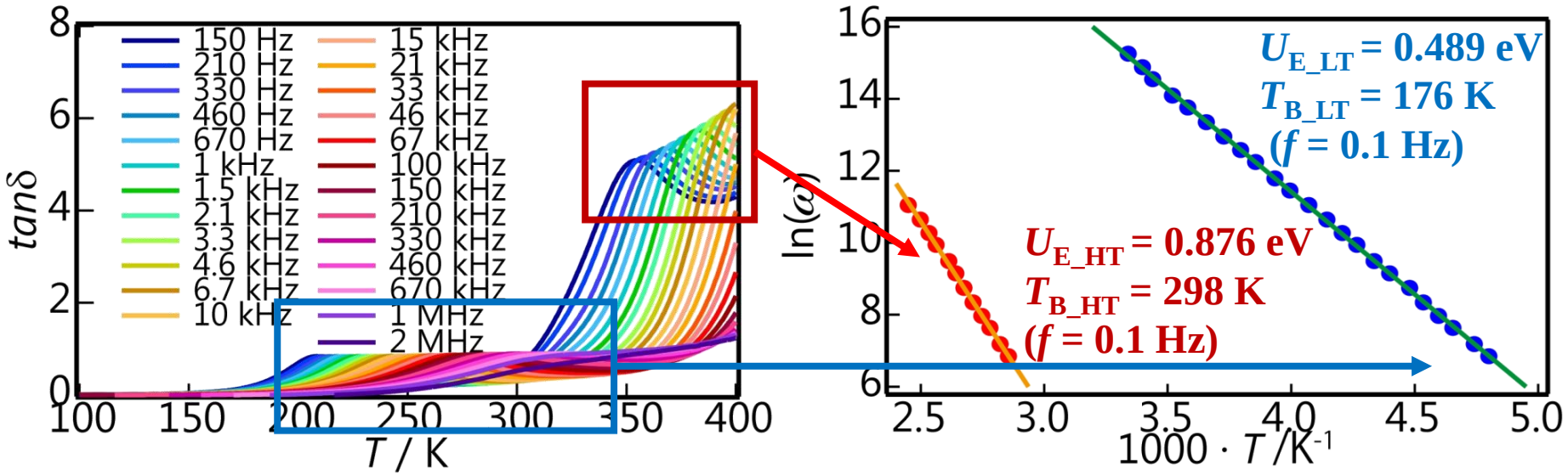
# Dielectric properties of Preyssler-type POM

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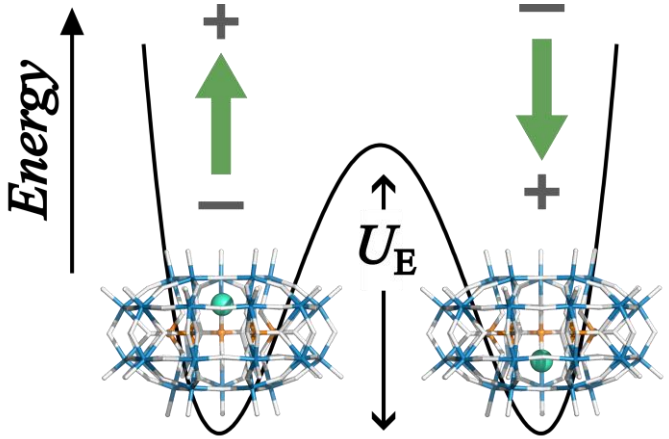


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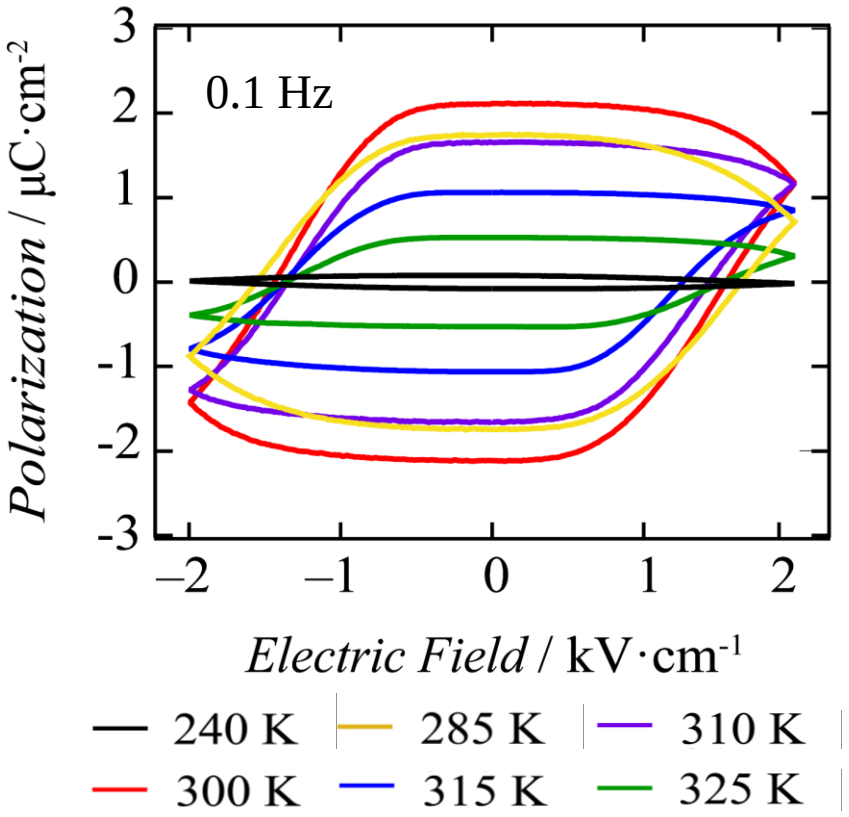
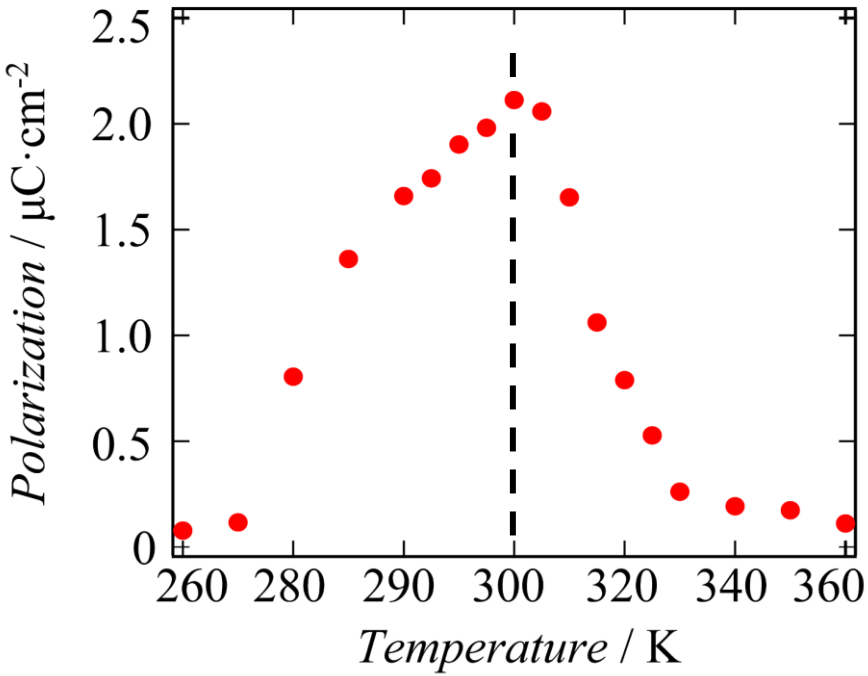


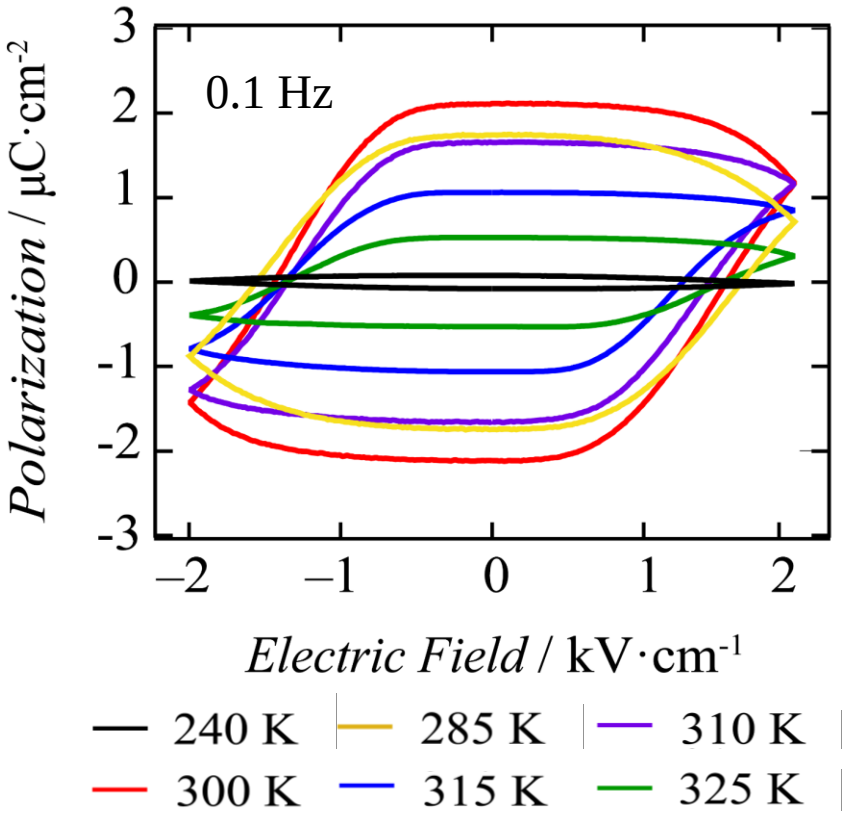



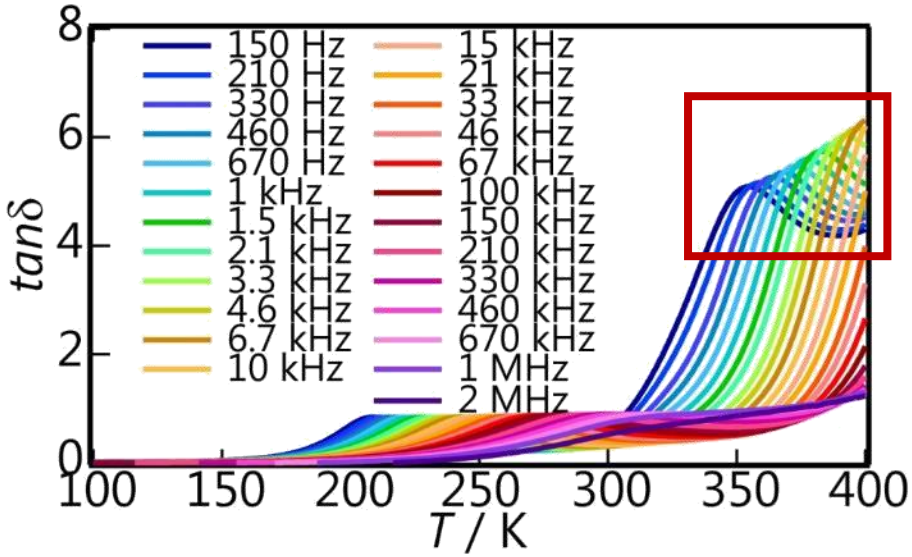

◆ Ferroelectric-like behaviors without long-range ordering of dipole moments

$P_{max}$ → 2.1 μC·cm$^{-2}$ at 300 K

**The terbium-ion movement** ⇨ **The high-temperature relaxation process**

# Dielectric properties of Preyssler-type POM

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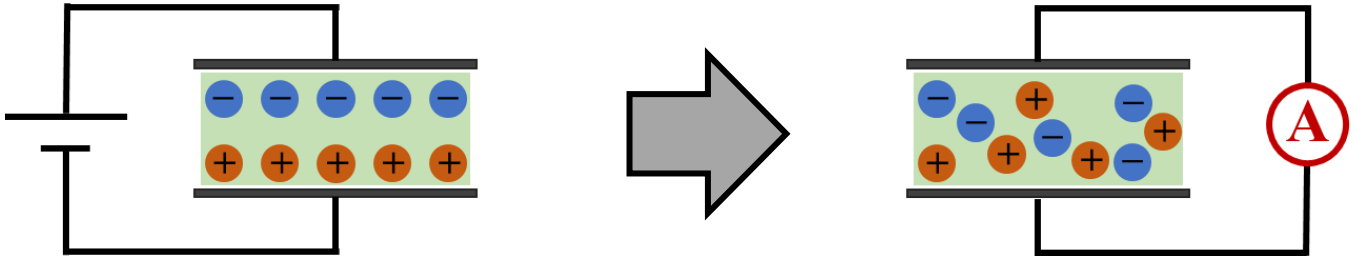
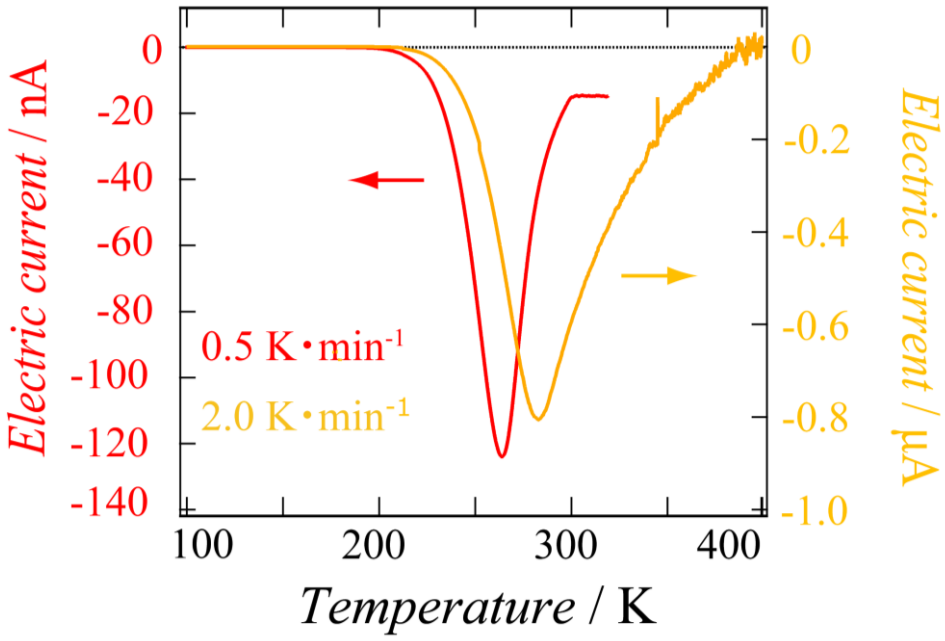
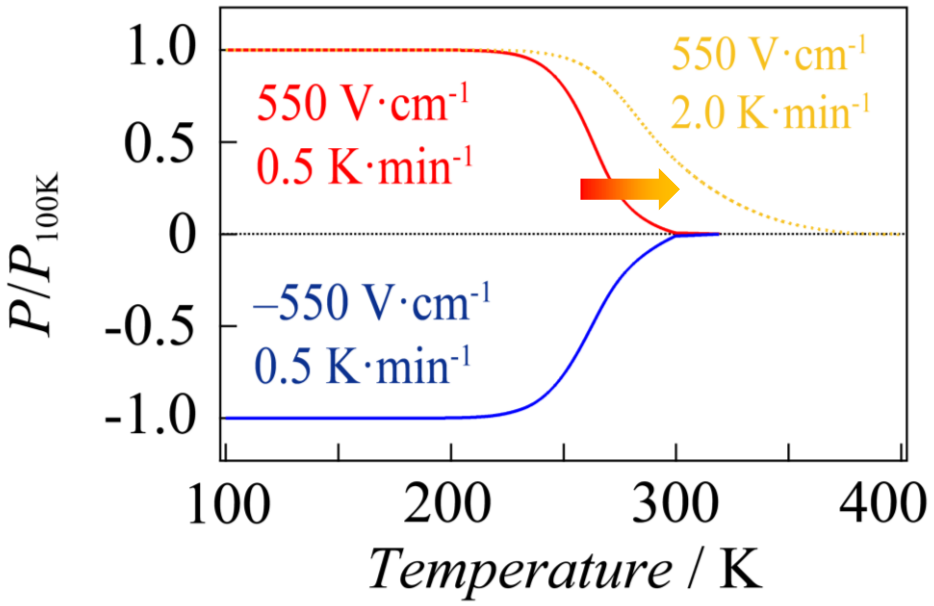
**The terbium-ion movement ⇨ The high-temperature relaxation process**

# Pyroelectric current behaviors




Heating rate: 0.5 and 2.0 K·min$^{-1}$



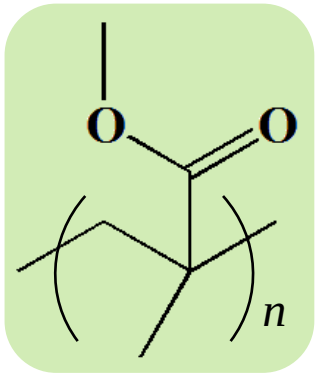

**Ferroelectric-like behavior originates from an individual POM molecule**

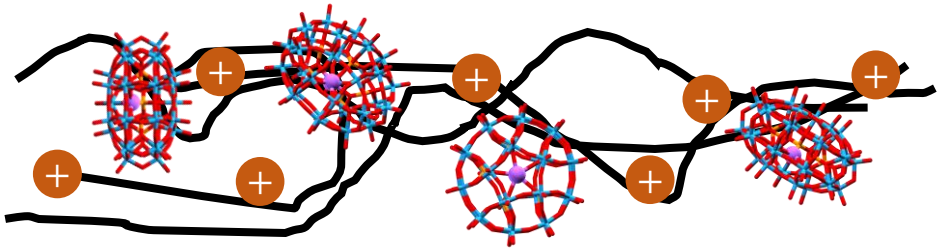
# P-E character of Polymer sample

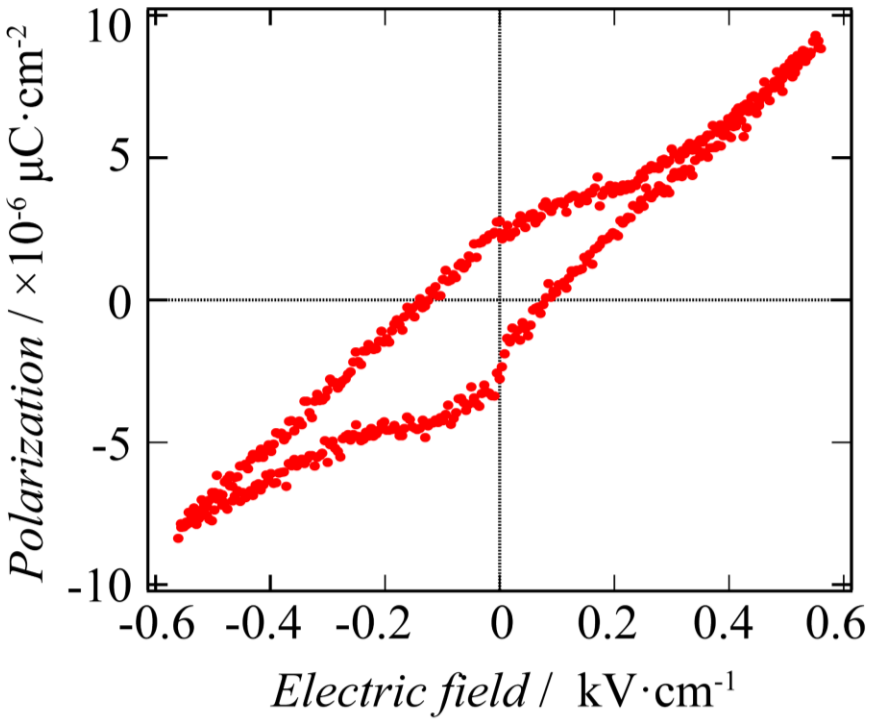
Polymethyl methacrylate
(PMMA)

+

$\{Tb^{3+} \subset P_5W_{30}\}$






Spontaneous polarization were originated from discreate POM cluster.

Single-molecule ➔ Ferroelectric-like behaviors

**Single-Molecule Electret (SME)**

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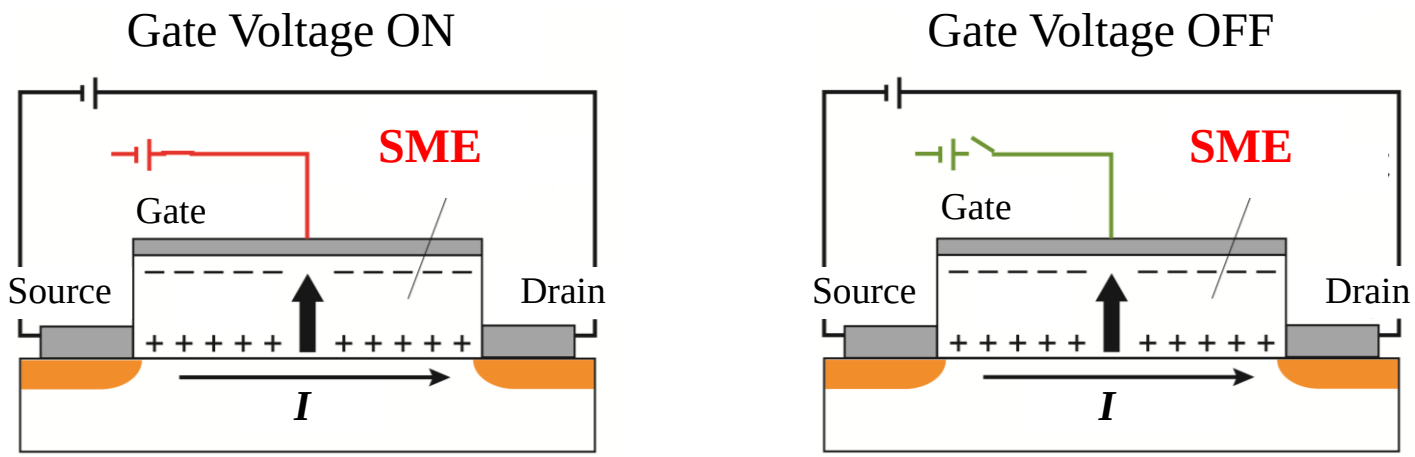
# Purpose – application of memory devices -

## Field effect transistor embedded with SME



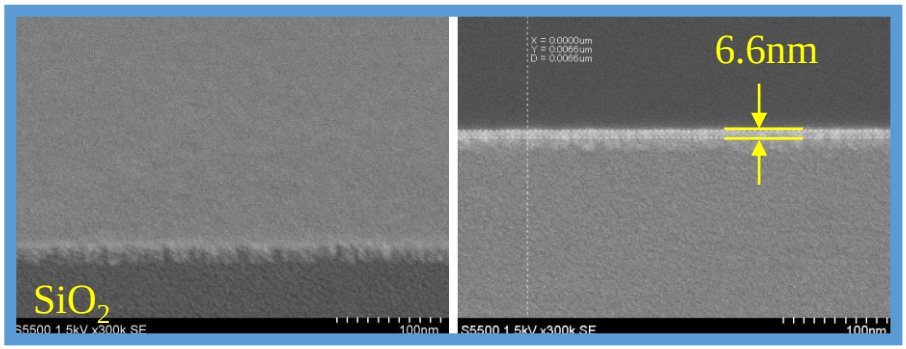

Gate insulator: SME (Preyssler-type polyoxometalate) thin film

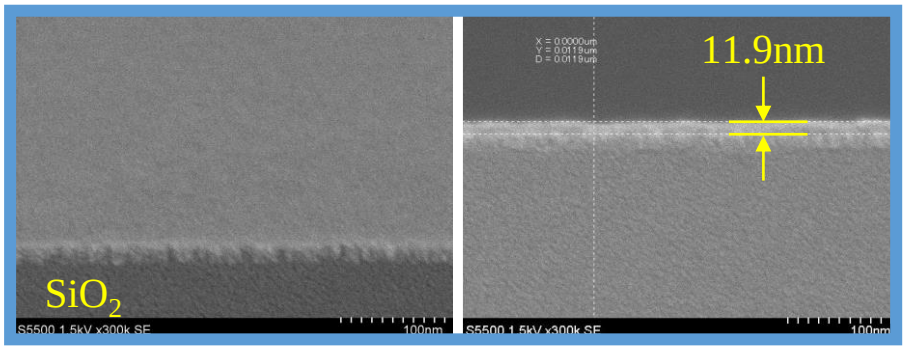
**POM-FET**

- Fabrication of memory devices
- Evaluation of $V_{GS}$-$I_{DS}$ characteres

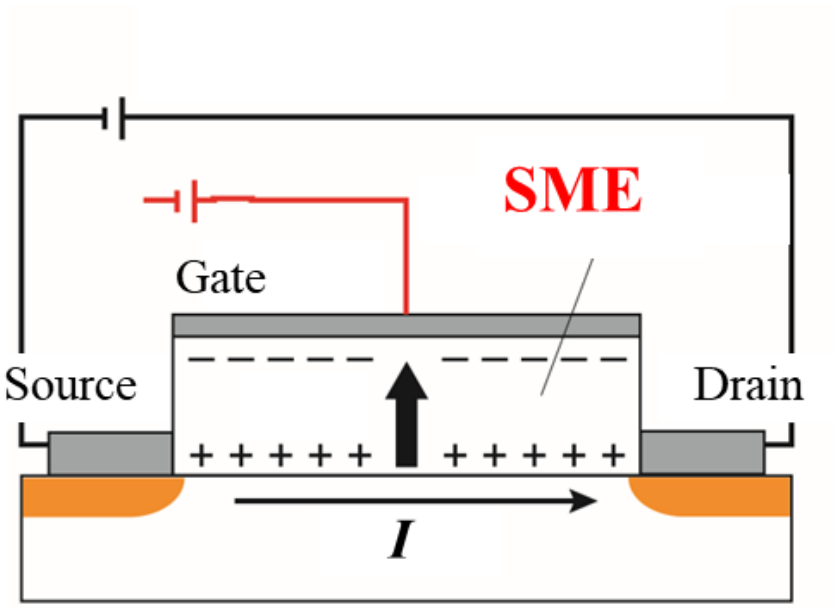
# Toward “Social Implementation”

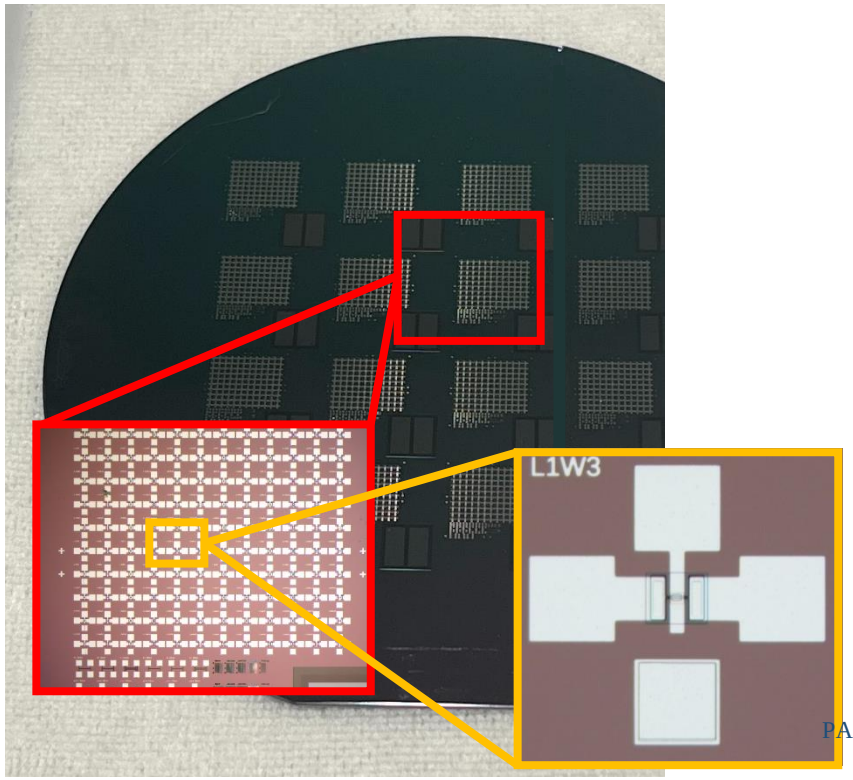
- SEM image of Spin coated POM films




- Stacked type FET



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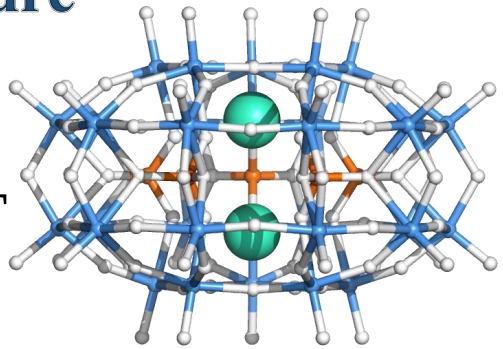
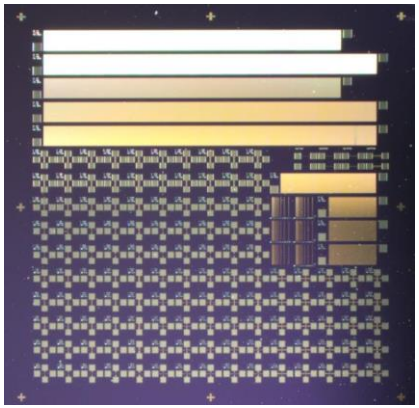
# Fabrication of Single-Molecule Electret Memory Devices based on Fe-FET Architecture



1. Observation of transistor properties of lateral-type FET
→ SME was worked as gate insulator!

2. Observation of memory window related to polarization switching in SME
→ Evidence of memory properties of SME!



3. Keeping wide MW until high temperature region
→ Possibility of practical application!

4. Successfully fabricated normal type FET with 10% quality

5. 20 sec retention time at least

**Achieved initial research toward the practical application of SME**

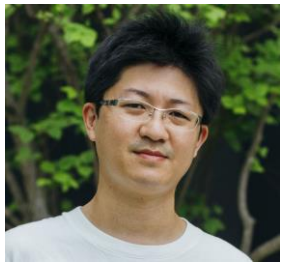
# Startup company ~Material Gate~

広島大学発 認定ベンチャー 88社目

MATERIAL GATE

～ 素材の力で未来を創る ～

*Since Jun 19th, 2023*



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CEO（代表取締役）

**Sadafumi Nishihara**

Chief Scientific Officer（最高科学責任者）

**Masaru Fujibayashi**

Technical Manager（技術主幹）

# Startup company ~Material Gate~

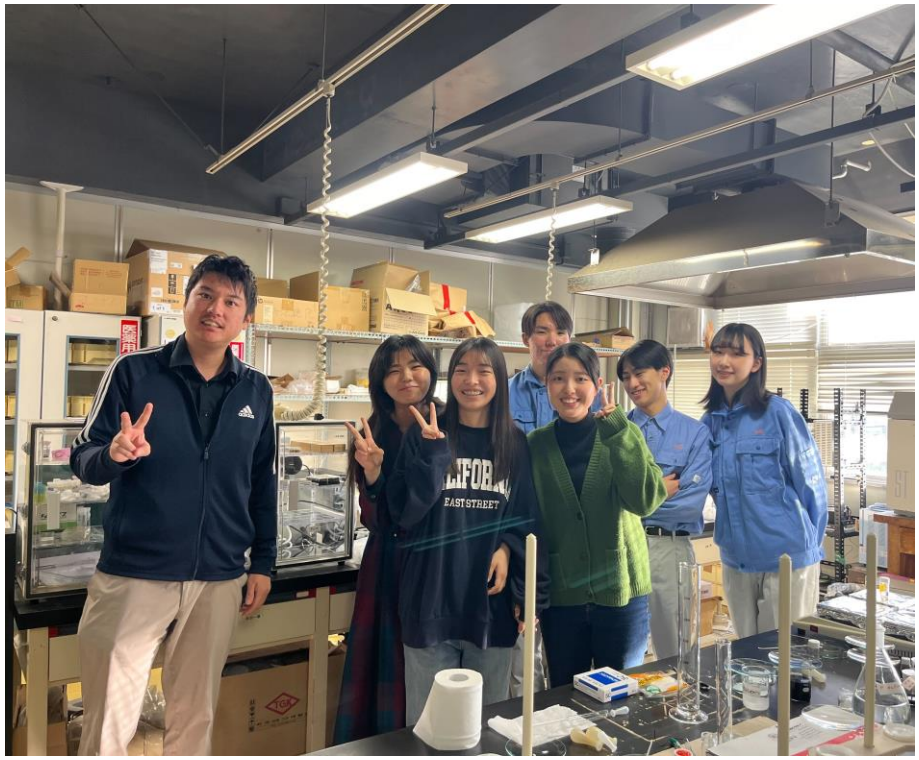
# Mission｜企業理念

## 素材の力で未来を創る

## Creating the future with the potential of materials

# Acknowledgement

Fujibayashi Lab in Ube NIT



Prof. Nishihara and Inoue's group
(Hiroshima University)

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ご清聴ありがとうございました