Resistance Switch in a Minimal-Fullerene devices

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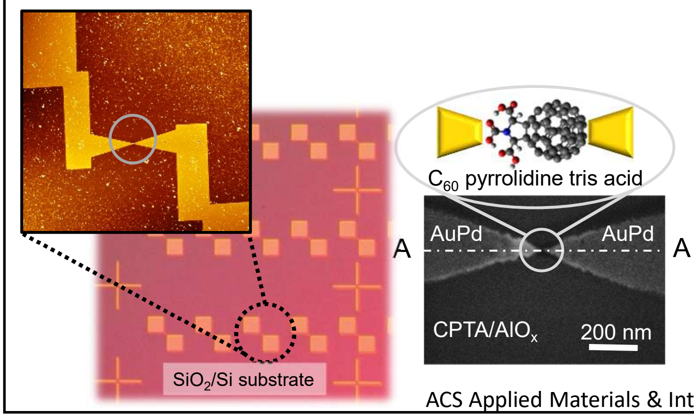
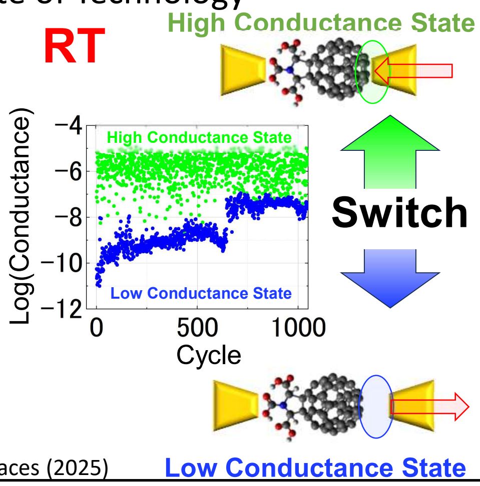




ACS Applied Materials & Interfaces (2025)

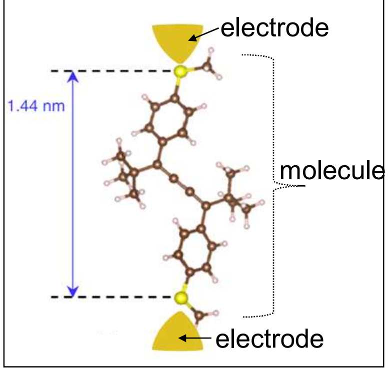
INTRODUCTION

Single molecule devices with electrodes

Single molecule device: examples and issues

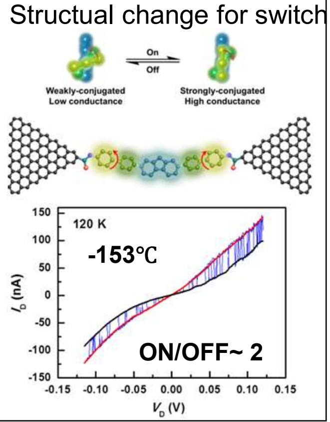
Single molecule with electrodes [1]

Device structure



Switching [2]

Structual change for switch



Issues

- Poor electric switching effect
- Operation at low-temp. only
- Extremely low-yield fabrication

No solution

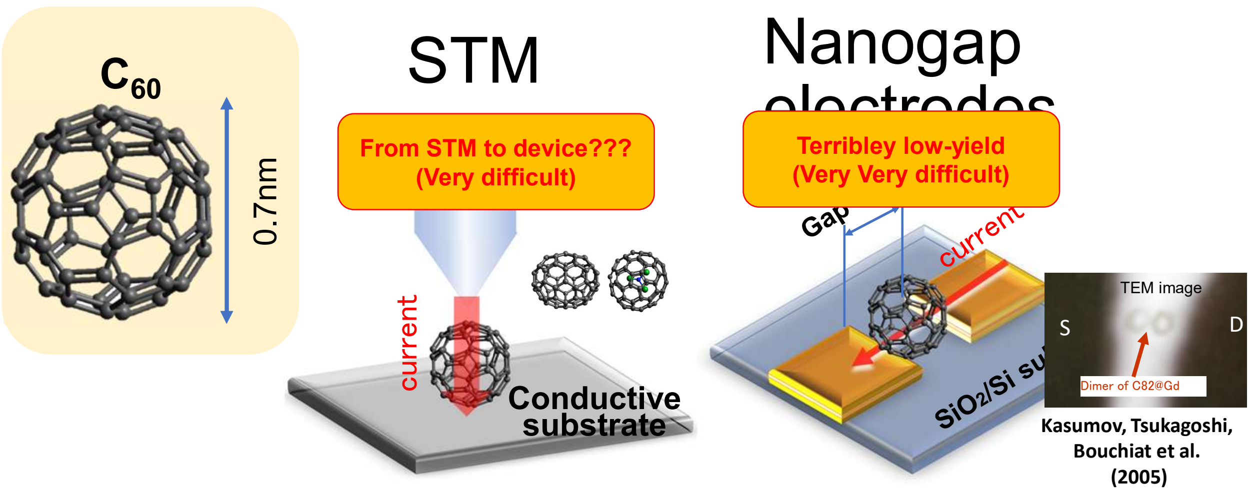
[1] Zang. Y. *et al*,. Directing isomerization reactions of cumulenes with electric fields. *Nat. Commun*. **2019**, 10, 4482.
[2] Ednubd. L. *et al*,. Detecting Mechanochemical Atropisomerization within an STM Break Junction. *J. Am. Chem. Soc*. **2018**, 140, 710−718.

INTRODUCTION

3

Possible approach to 0D-material

Example of fullerene transport



Over view of this talk

New scheme: Asymmetric molecule+Electro/Field migration

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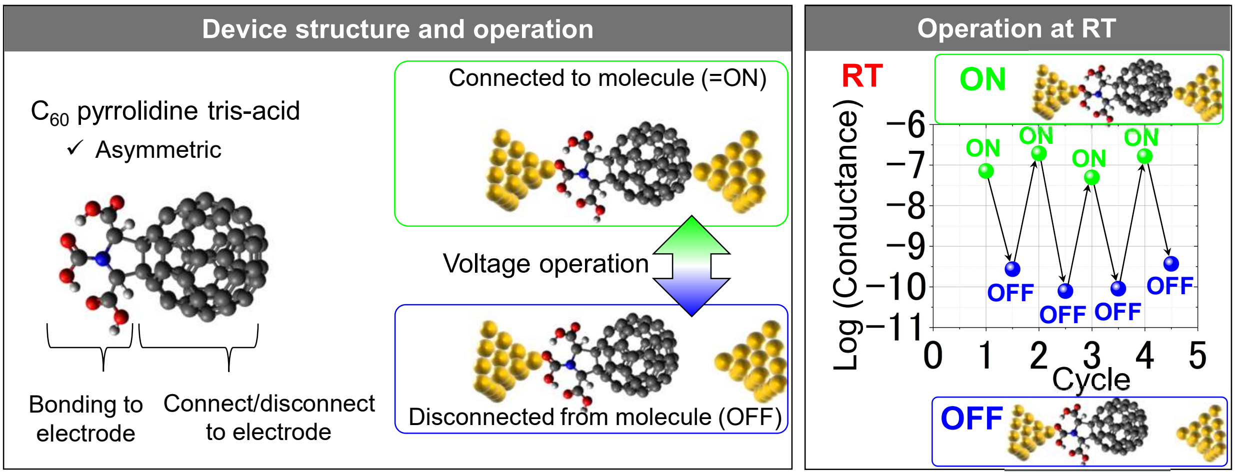
- Asymmetric molecule: **C_{60} pyrrolidine tris-acid (CPTA)** was **spin-coated**.
- **Electro-migration & Field-migration for gap resistance modulation** was applied.

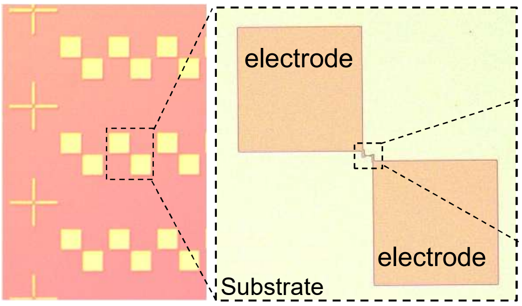


Device fabrication & structure

Electron beam lithography + spin coating

Electron lithography

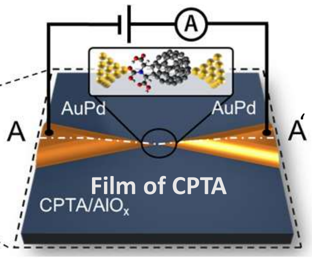
✓ Electron beam lithography

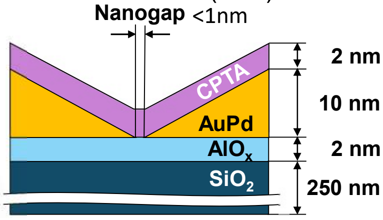


Nanogap by electromigration

CPTA film was spin-coated using CPTA solution

✓ Possible to extend "multiple device circuit"





Gap length estimation: Simmon's model [9]

$$I = A\frac{e}{2\pi h\Delta s^2}\left\{\left(\phi-\frac{eV}{2}\right)exp\left[-\frac{4\pi\Delta s}{h}(2m)^{1/2}\left(\phi-\frac{eV}{2}\right)^{1/2}\right] - \left(\phi+\frac{eV}{2}\right)exp\left[-\frac{4\pi\Delta s}{h}(2m)^{1/2}\left(\phi+\frac{eV}{2}\right)^{1/2}\right]\right\}$$

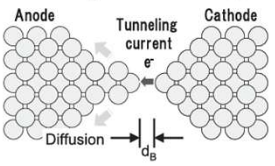
[9] Simmons, J. G. Generalized Formula for the Electric Tunnel Effect between Similar Electrodes Separated by a Thin Insulating Film. *J. Appl. Phys.* **1963**, 34 (6), 1793–1803.

Operation scheme：Electro-migration & Field-migration

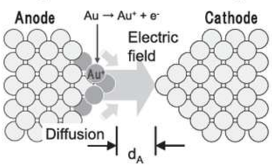
Gap opening: **Electro-migration**
Gap close: **Field-Migration**

Gap-length modification[3]

Electro-migration
～gap opening～
"Low-to-high resistance change"

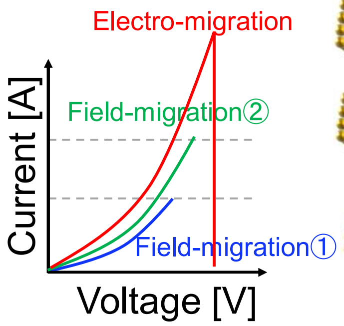


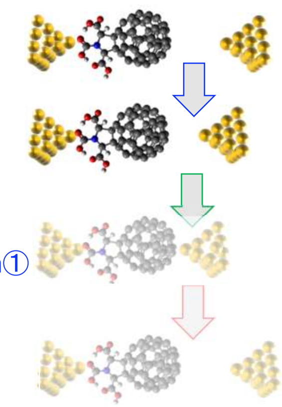
Field-migration
～gap closing～
"High-to-low resistance change"



Gap-length control by electric field

Source-Drain voltage to nanogap





[3] Naitoh. Y. *et al*,. Single-Molecular Bridging in Static Metal Nanogap Electrodes Using Migrations of Metal Atoms. *J. Phys. Chem. C* **2020**, *124*, 25, 14007–14015

Step1 : Analysis of conductance (with comparison of C_{60})

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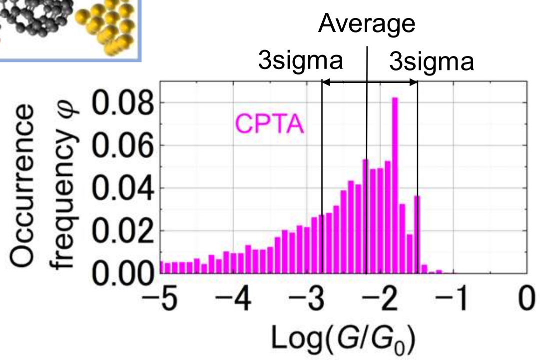
Average of CPTA conductance

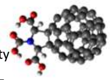
CPTA

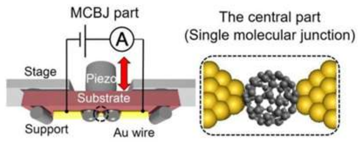
Histogram



Comparison with C_{60}

	Conductance
CPTA (this result)	***5.1*±0.6 mG_0** (standard measurement uncertainty from 1317 data)
C_{60} [4] *break-junction with single C60	3 - 5 mG_0





[4] K.Yasuraoka *et al*,. Surface-Enhanced Raman Scattering Stimulated by Strong Metal−Molecule Interactions in a C_{60} Single-Molecule Junction. *ACS Appl. Mater. Interfaces* **2021**, 13, 43, 51602–51607

One (or two) molecule is conducting in the film

Step2 : Single Level Tunneling Transport Model (SLTT) for CPTA conductance

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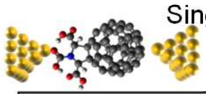


Single Level Tunneling Transport Model (SLTT) **[5] :**
from *I−V* characteristics, inherent energy level can be estimated.

Single Level Tunneling Transport Model (SLTT) [5]

$$I(V)=\frac{8e}{h}\frac{\Gamma_L\Gamma_R}{\Gamma_L+\Gamma_R}\left\{\tan^{-1}\left(\frac{\frac{\Gamma_R}{\Gamma_L+\Gamma_R}eV-\varepsilon_0}{\Gamma_L+\Gamma_R}\right)+\tan^{-1}\left(\frac{\frac{\Gamma_L}{\Gamma_L+\Gamma_R}eV+\varepsilon_0}{\Gamma_L+\Gamma_R}\right)\right\}$$

e : elementary charge

h: Planck constant

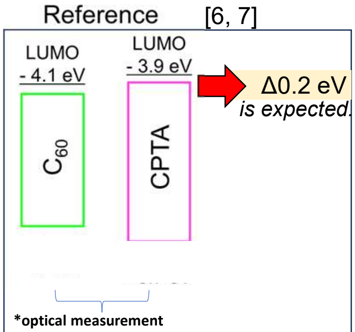
Γ : coupling strength

($\Gamma = \Gamma_L + \Gamma_R$)

ε_0 : energy difference between metal Fermi energy and molecule resonant state

$\varepsilon 0$(energy difference between metal Fermi energy and molecule resonant state) should be estimated.

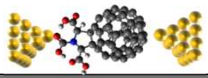
Reference [6, 7]



※ LUMO
Lowest unoccupied molecular orbital

[5] Isshiki. Y. *et al*,. Fluctuation in Interface and Electronic Structure of Single-Molecule Junctions Investigated by Current versus Bias Voltage Characteristics. *J. Am. Chem. Soc.* **2018**, 140, 3760−3767
[6] Arabnejad, S. et al,. Effect of Nuclear Motion on Charge Transport in Fullerenes: A Combined Density Functional Tight Binding—Density Functional Theory Investigation. *Front. Energy Res.*, **2019**, 29, 7, 1–7.
[7] Zijiang, Y. SnO_2-C_{60} Pyrrolidine Tris-Acid (CPTA) as the Electron Transport Layer for Highly Efficient and Stable Planar Sn-Based Perovskite Solar Cells. *J. Mater. Chem. A* **2020**, 8, 44, 23607–23616.

Step2：SLTT fitting on CPTA junction

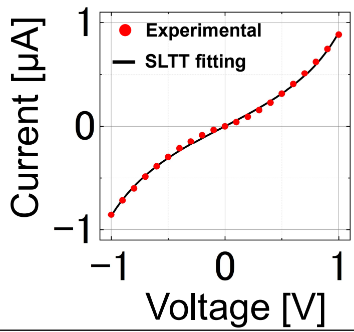


I–V characteristic can be fitted by

Single Level Tunneling Transport Model (SLTT) [5]

SLTT fitting

I-V of CPTA with 5.1 mG_0



	conductance
CPTA	**5.1 ± 0.3 mG_0**
C_{60} [4]	3～5 mG_0

Obtained parameter

CPTA vs C_{60}

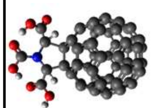
	CPTA (standard measurement uncertainty from **100 data**)	C_{60} [5] (*break-junction with single C60)
ε_0	**0.82 ± 0.02 eV**	**0.60 ± 0.03 eV**

$\Delta\varepsilon_0$ ~0.2 eV

ε_0 : **energy difference between metal Fermi energy and molecule resonant state**

[4] Yasuraoka. *et al*,. Surface-Enhanced Raman Scattering Stimulated by Strong Metal−Molecule Interactions in a C_{60} Single-Molecule Junction. *ACS Appl. Mater. Interfaces* **2021**, 13, 43, 51602–51607
[5] Isshiki. Y. *et al*,. Fluctuation in Interface and Electronic Structure of Single-Molecule Junctions Investigated by Current versus Bias Voltage Characteristics. *J. Am. Chem. Soc.* **2018**, 140, 3760−3767

Step3：Rectification due to asymmetric structure

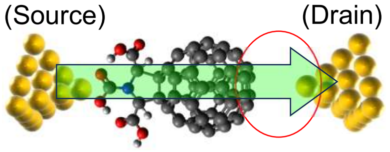


CPTA on Source (=cathode) of on Drain (=anode) for rectification “ *I(+V)/I(-V)*”

Assumption: CPTA on left electrode

Positive bias voltage

Left (Source) Right (Drain)



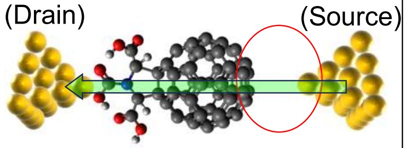
CPTA on Source (=cathode)
→work-function: lowered
→electron emission increases

⇩

Larger current

Negative bias voltage

Left (Drain) Right (Source)

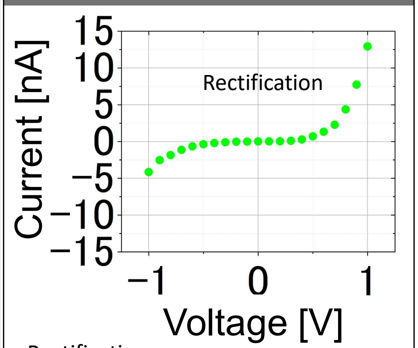


Metallic surface
→work-function: no change
→electron emission is suppressed

⇩

No current assist

Asymmetric I–V



Rectification ⇨ CPTA on Source electrode!

Step4：Fowler-Nordheim analysis for barrier height

Fowler-Nordheim analysis ⇒ tunnel barrier information

Fowler-Nordheim (FN) [10]

$$\mathrm{Ln}\left(\frac{I}{V^2}\right) \propto -\frac{4d\sqrt{2m_e\phi^3}}{3he}\left(\frac{1}{V}\right)$$

e : elementary charge

h: Planck constant

m: effective mass of a charge carrier

d: barrier thickness

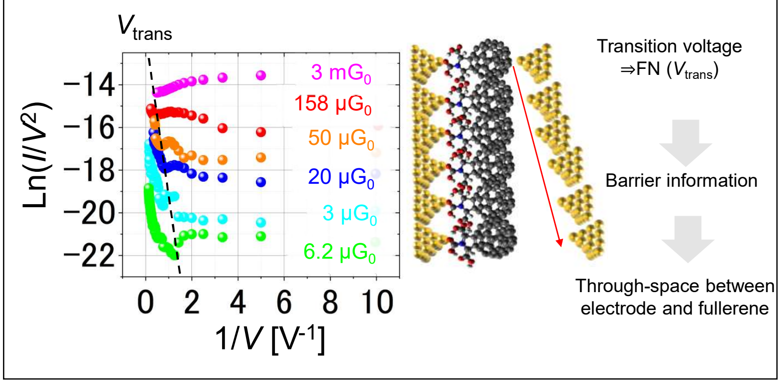
Φ: barrier height

Plot of "I/V ^{2} vs 1/V"

⇒ **FN tunneling**

indicating tunneling space

FN plot



※ PES : PhotoEmission Spectroscopy

[10] Chen, J. *et al*,. Quantifying Transition Voltage Spectroscopy of Molecular Junctions: Ab Initio Calculations. *Phys. Rev. B* **2010**, 82 (12), No. 121412.

Step4：Transition Voltage Spectroscopy (TVS) [10]

Using Fowler-Nordheim plot (V_{trans}), **junction symmetry can be visualized**

TVS analysis [10]

TVS [10]

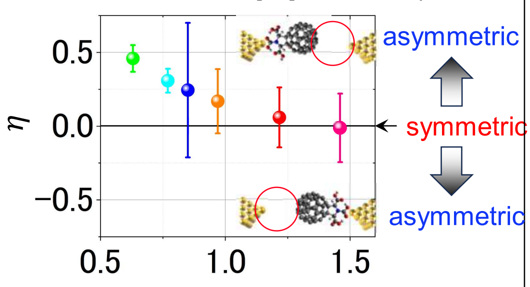
$$\eta = \frac{\varepsilon - 0.85 \times V_{trans}}{2.3 \times V_{trans}}$$

ε : energy difference between contact Fermi energy and molecule resonant energy (=**PES**)

η : asymmetric parameter
$(-0.5 \leq \eta \leq +0.5)$
$\eta = 0$: *symmetric*

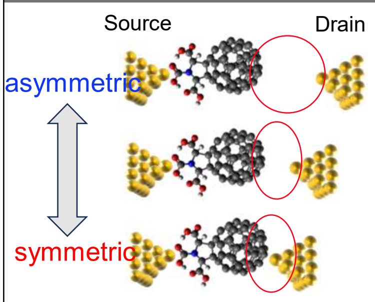
η vs V_{trans}

Based on PES ε [10], estimate η



Low conductive V_{trans} [V] High conductive

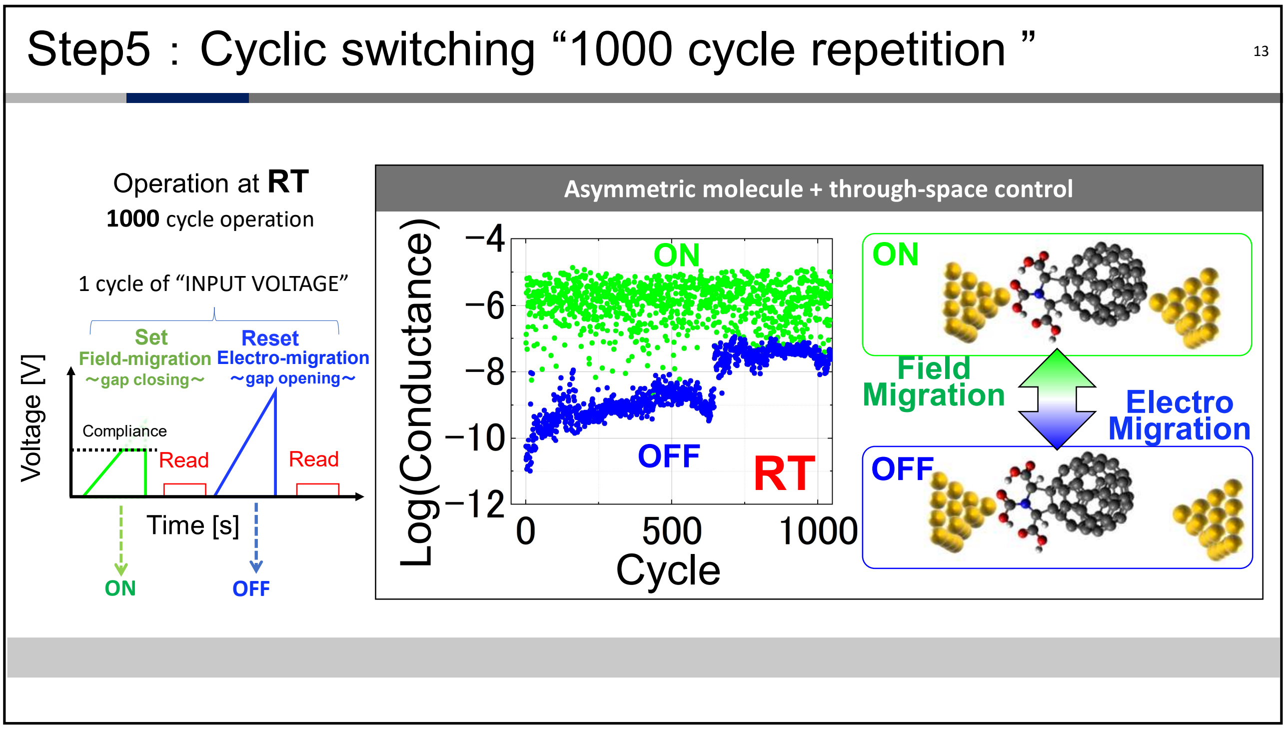
Junction modification



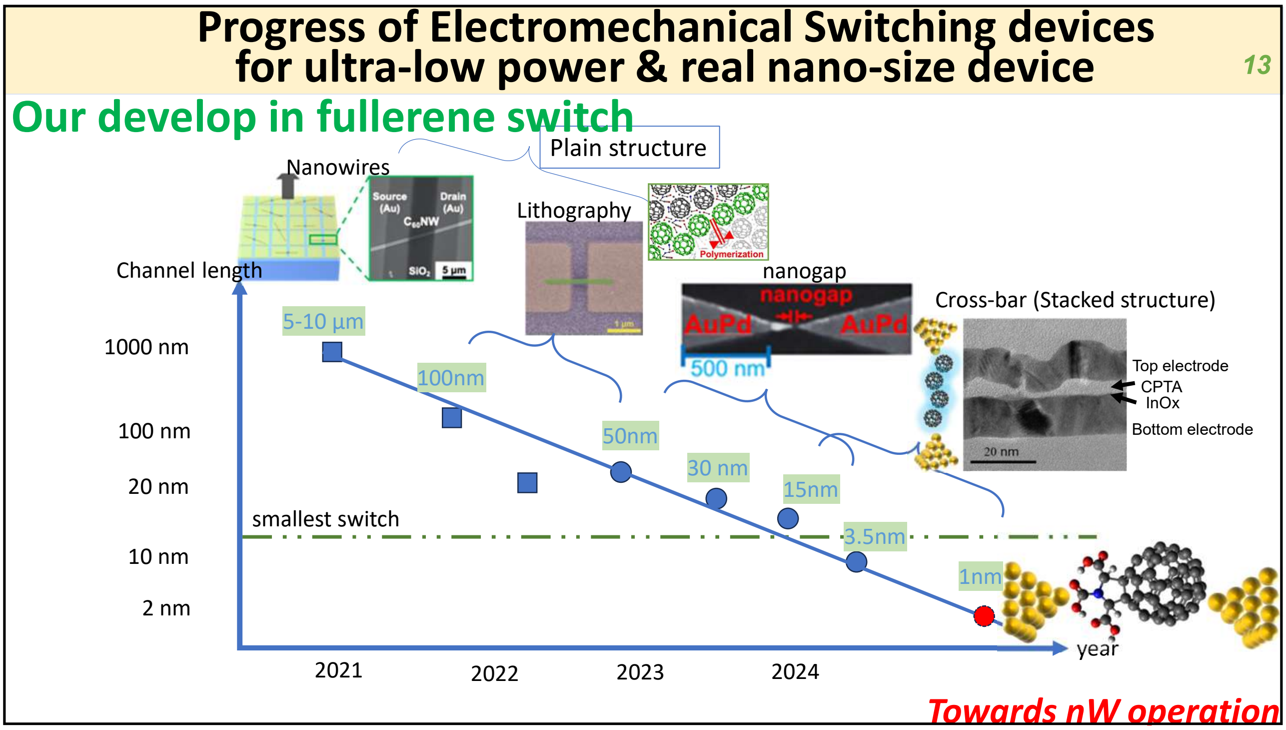
✓ V_{trans} indicates the junction structure
⇒structural change

※ PES : Photo Emission Spectroscopy 光電子分光法

[10] Markussen, T. *et al*,. Improving Transition Voltage Spectroscopy of Molecular Junctions. Phys. Rev. B 2011, 83 (15), No. 155407.



Step5：Cyclic switching “1000 cycle repetition ”
13
Operation at RT
1000 cycle operation
1 cycle of “INPUT VOLTAGE”
Set
Field-migration
~gap closing~
Reset
Electro-migration
~gap opening~
Voltage [V]
Compliance
Read
Read
Time [s]
ON
OFF
Asymmetric molecule + through-space control
Log(Conductance)
−4
−6
−8
−10
−12
0
500
1000
Cycle
ON
OFF
RT
ON
Field Migration
Electro Migration
OFF



Progress of Electromechanical Switching devices
for ultra-low power & real nano-size device
13
Our develop in fullerene switch
Plain structure
Nanowires
Lithography
Polymerization
nanogap
AuPd
AuPd
500 nm
Cross-bar (Stacked structure)
Top electrode
CPTA
InOx
Bottom electrode
20 nm
Channel length
1000 nm
100 nm
20 nm
10 nm
2 nm
5-10 µm
100nm
50nm
30 nm
15nm
3.5nm
1nm
smallest switch
2021
2022
2023
2024
year
Towards nW operation