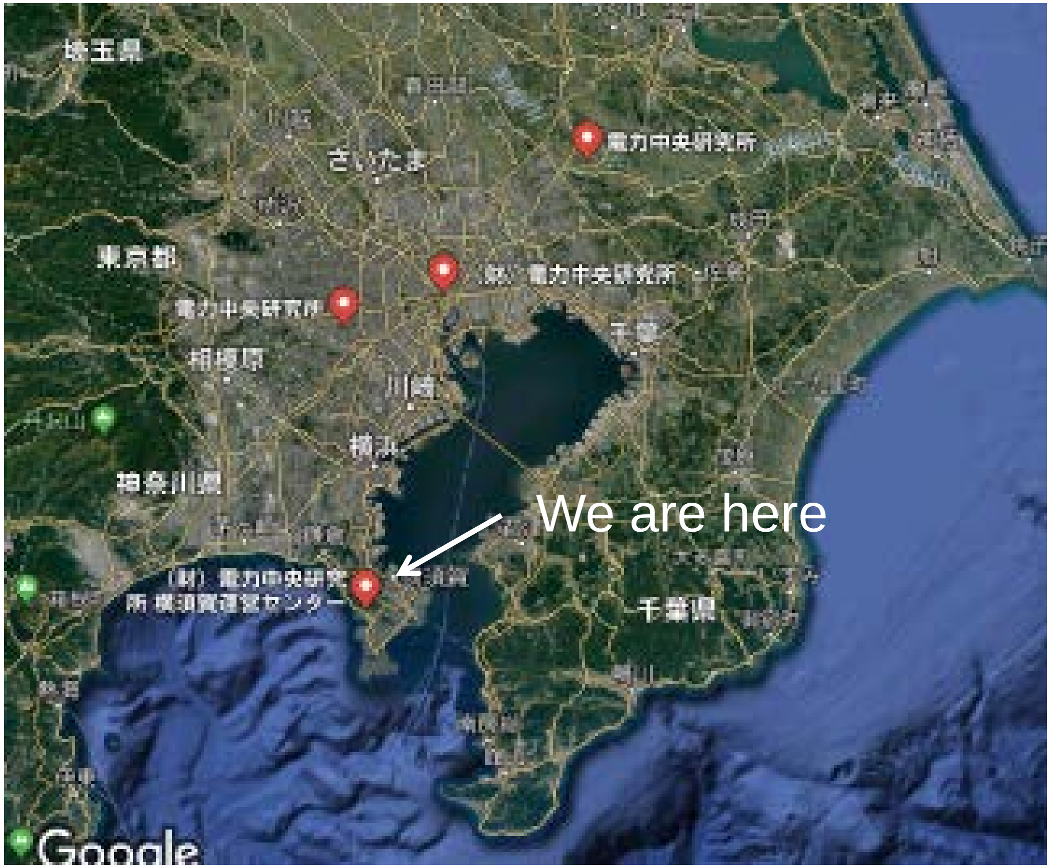
Development of iontronics

Central Research Institute of Electric Power Industry (CRIEPI)
Institute Néel, CNRS and Université Grenoble Alpes

Shimpei Ono

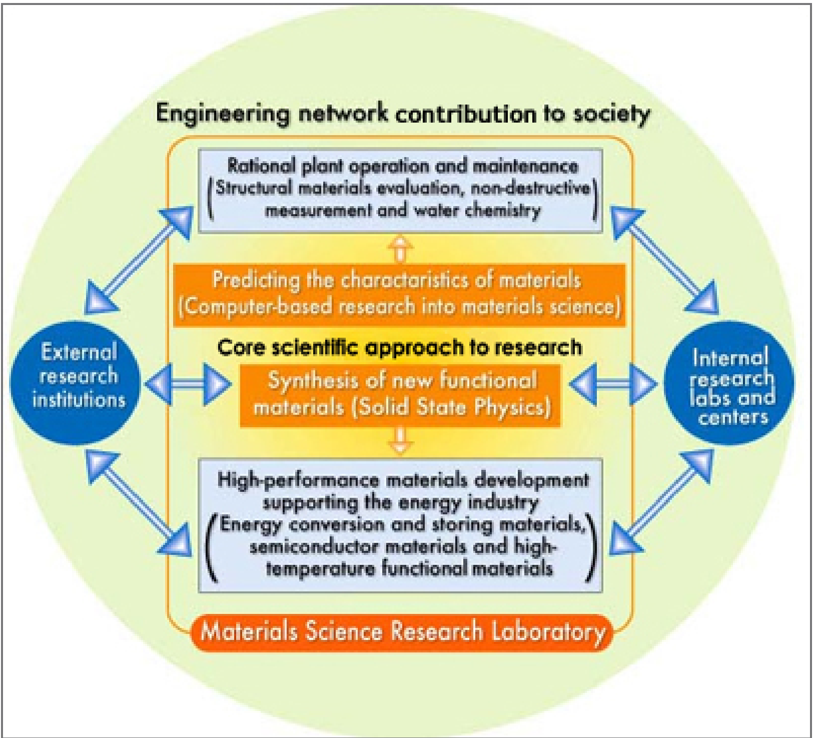
Where is CRIEPI?

- Central Research Institute of Electric Power Industry



Yokosuka Area

Nuclear Technology Research Lab.
Energy Innovation Center
Energy Engineering Research Lab.
System Engineering Research Lab.
Electric Power Engineering Lab.
High Power Testing Lab.
Material Science Research Lab.



Main research:
Structural Materials
Electrochemistry
Electric Materials

What is iontronics?

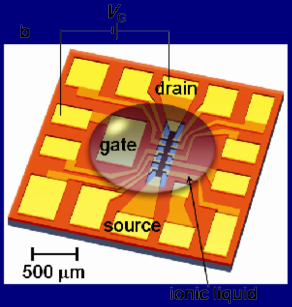
Electronics using salt

batteries

Capacitors

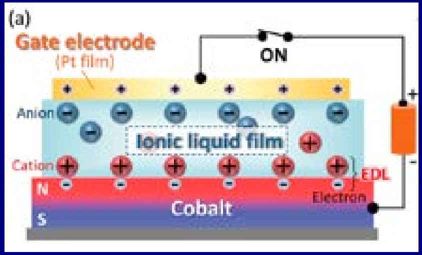
New tool and new applications

Electric states



Field-effect transistors

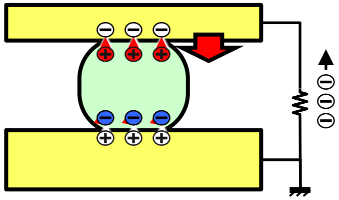
Magnetism



Spintronics

New applications

Light-emitting electrochemical cell



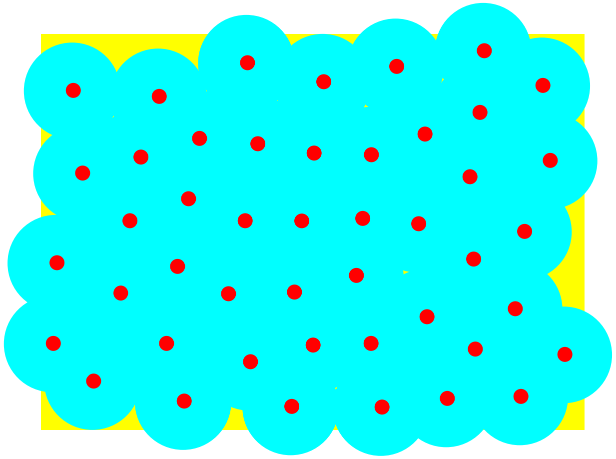
Energy Harvester

Introduction

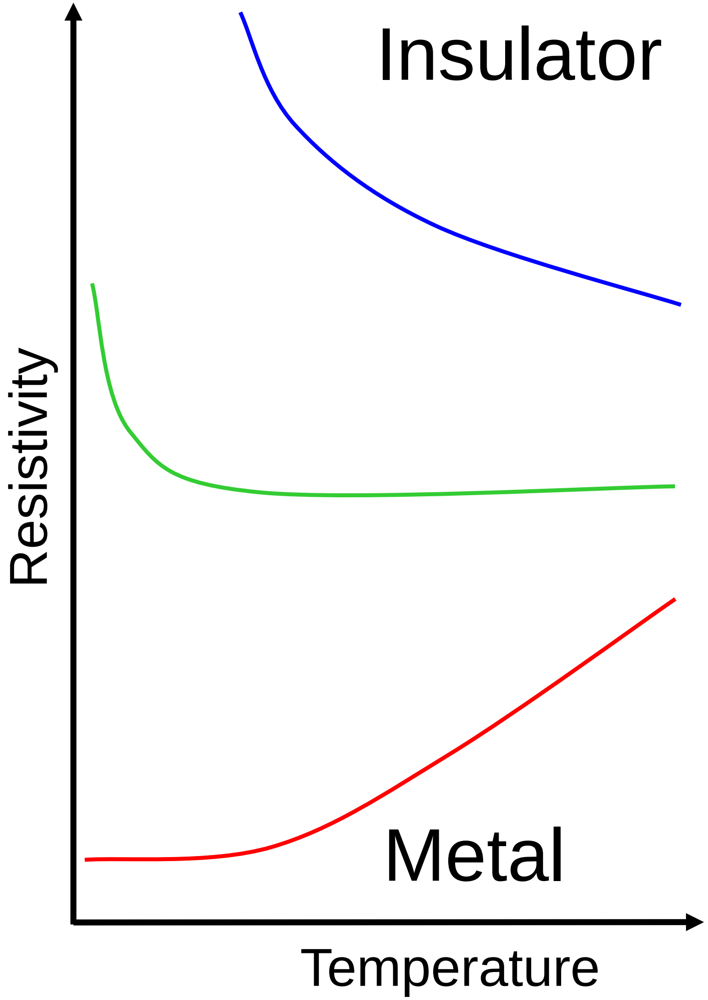
Carrier density is a key parameter not only physics but also applications

Most common method

1) Substitutional chemical doping



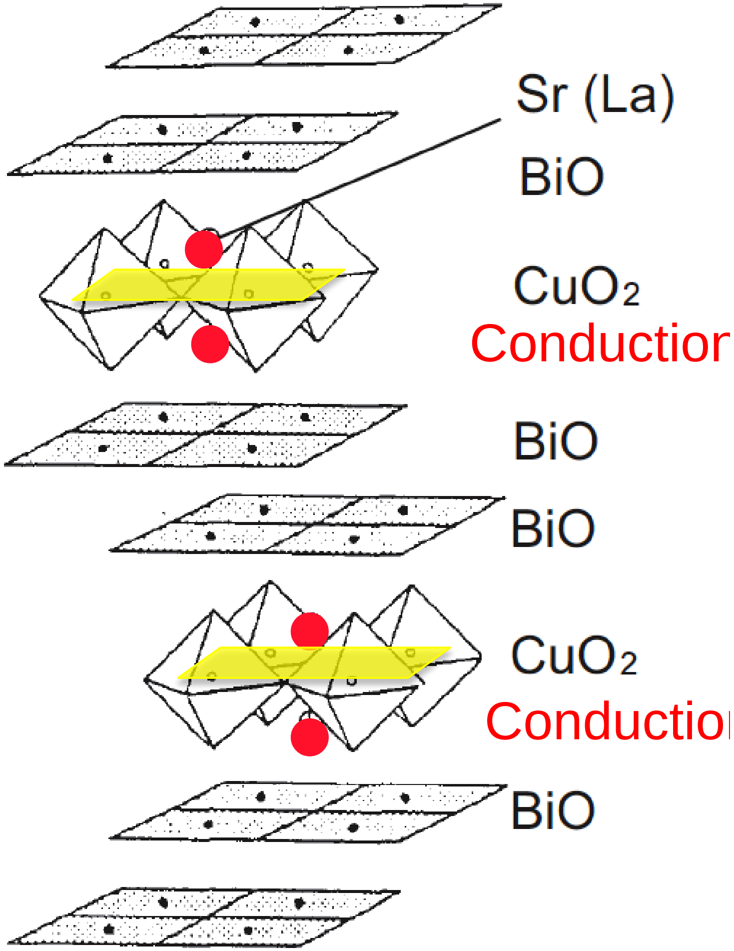
Metal

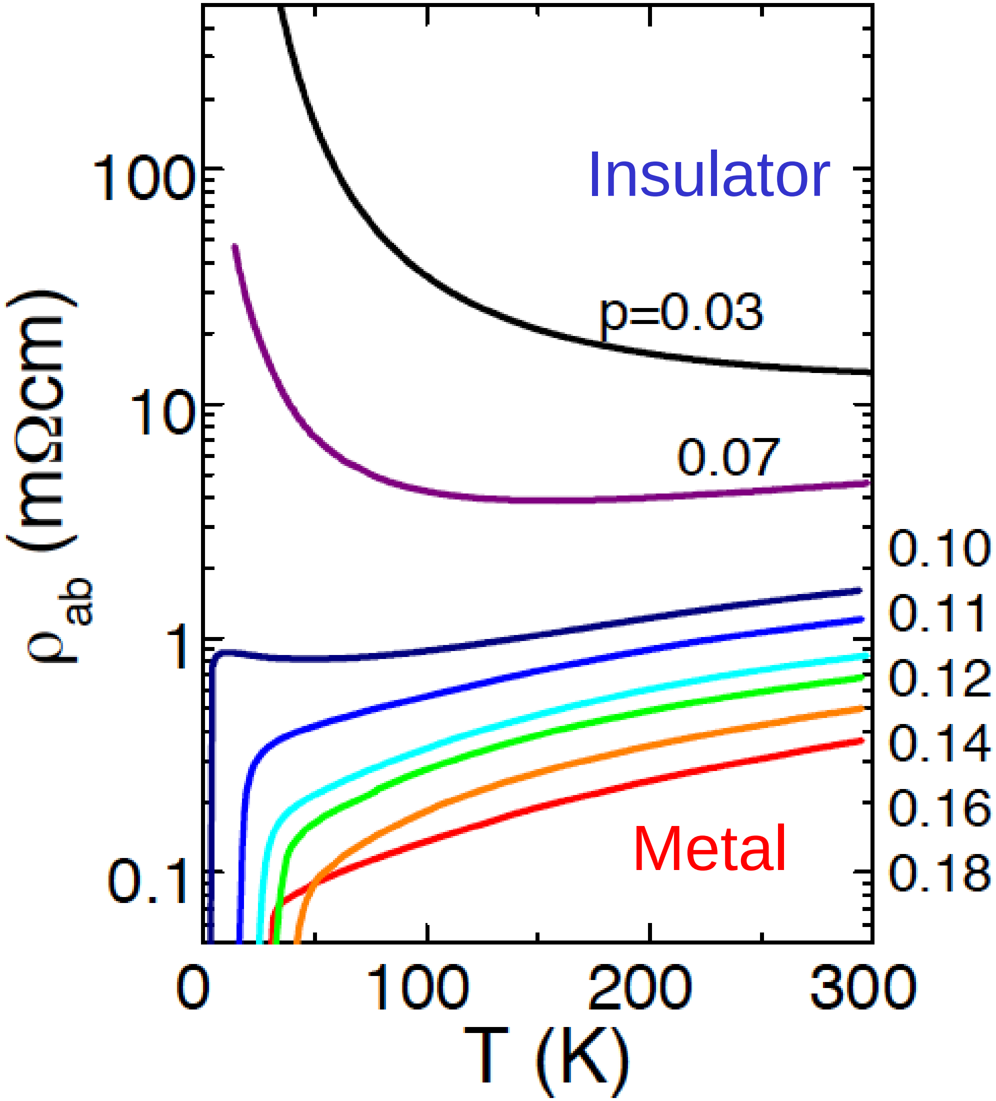


Chemical doping

Substitution of donor or acceptor

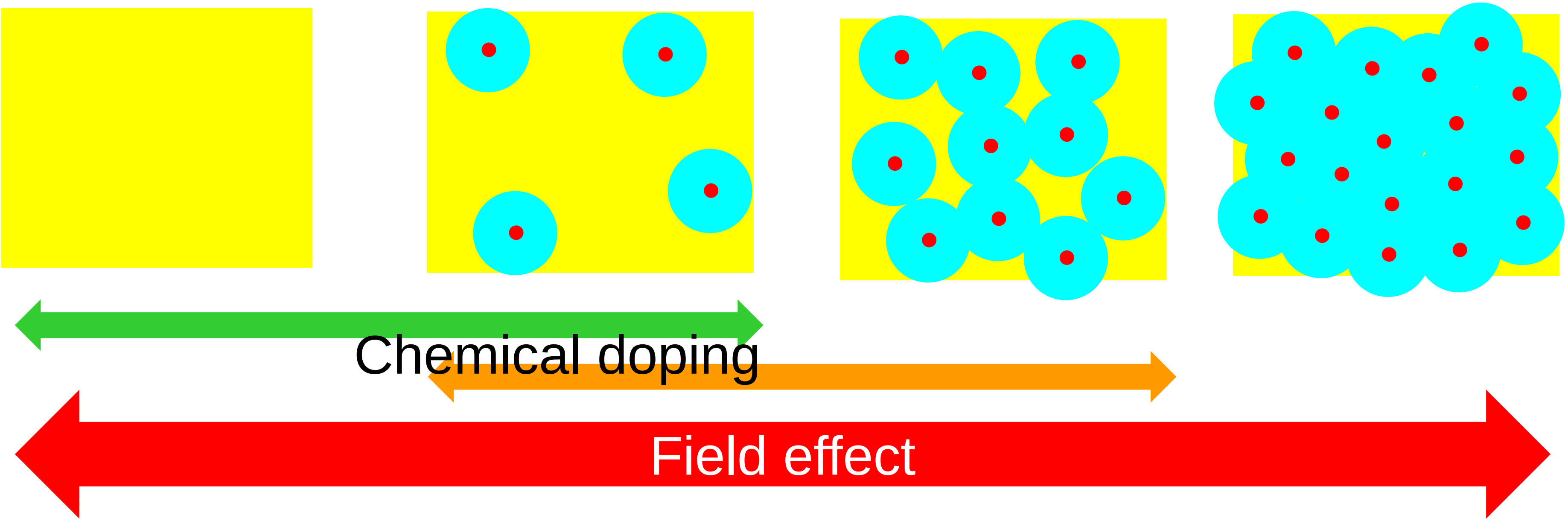
Ex) High-Tc cupurates





S. Ono *et al.*, PRB **67**, 104512 (2003)

Limitation of Chemical doping



Semiconductor/Insulator

Metal

Chemical doping

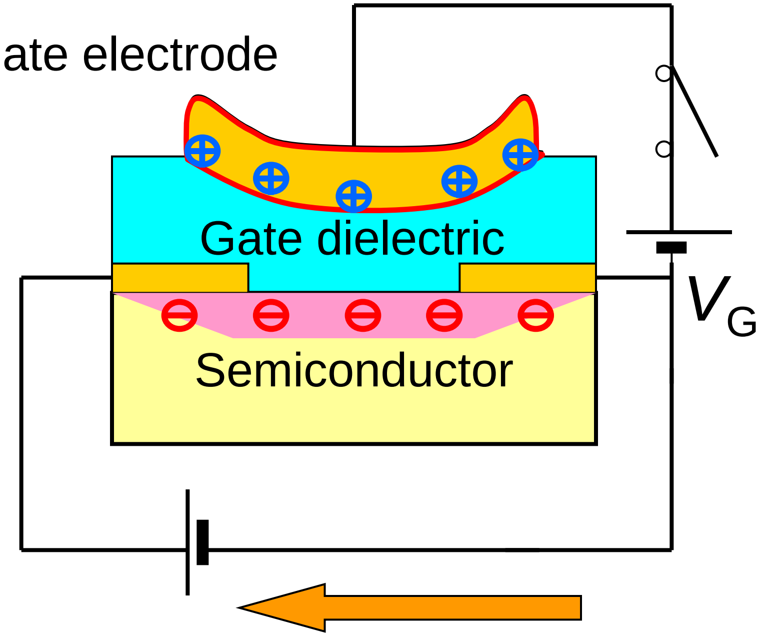
Field effect

Difficult to modify wide range of doping.

Not only carrier density but also structure disorder

Let’s change carrier density with field effect!!

Electric-field effect

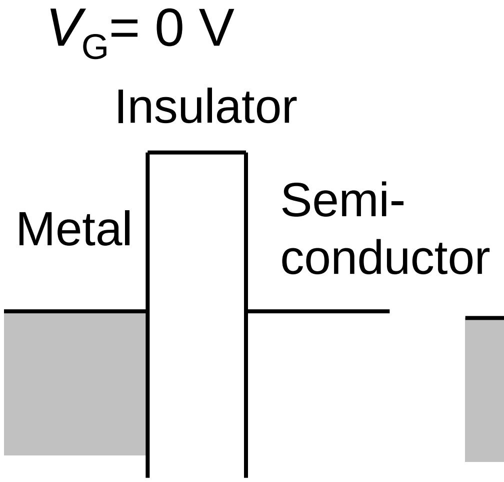

Gate electrode

Gate dielectric

Semiconductor

V_G

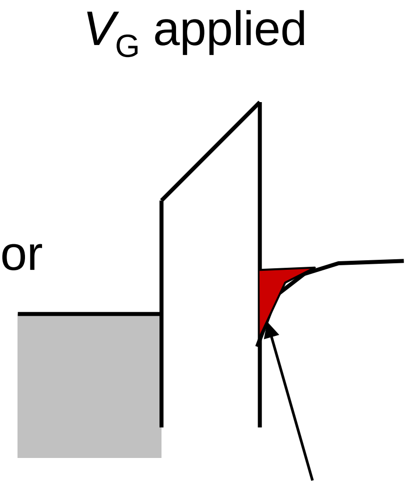
Current flow


V_G= 0 V

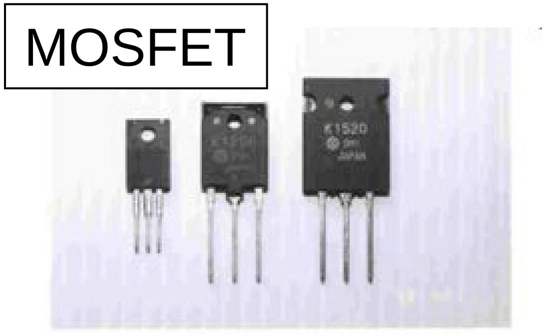
Insulator

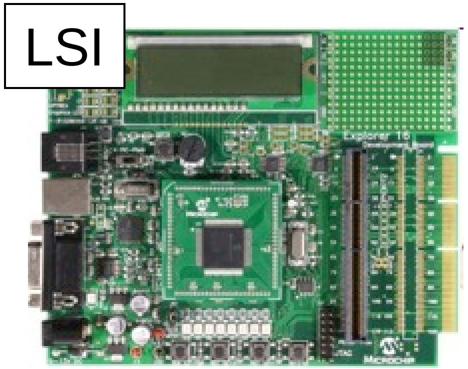
Metal

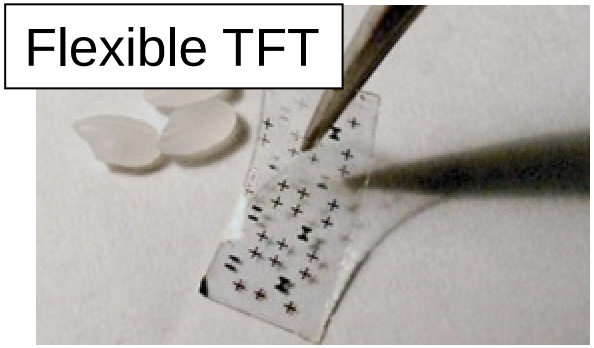
Semi-
conductor


V_G applied

Charge accumulation
=mobile charge carriers

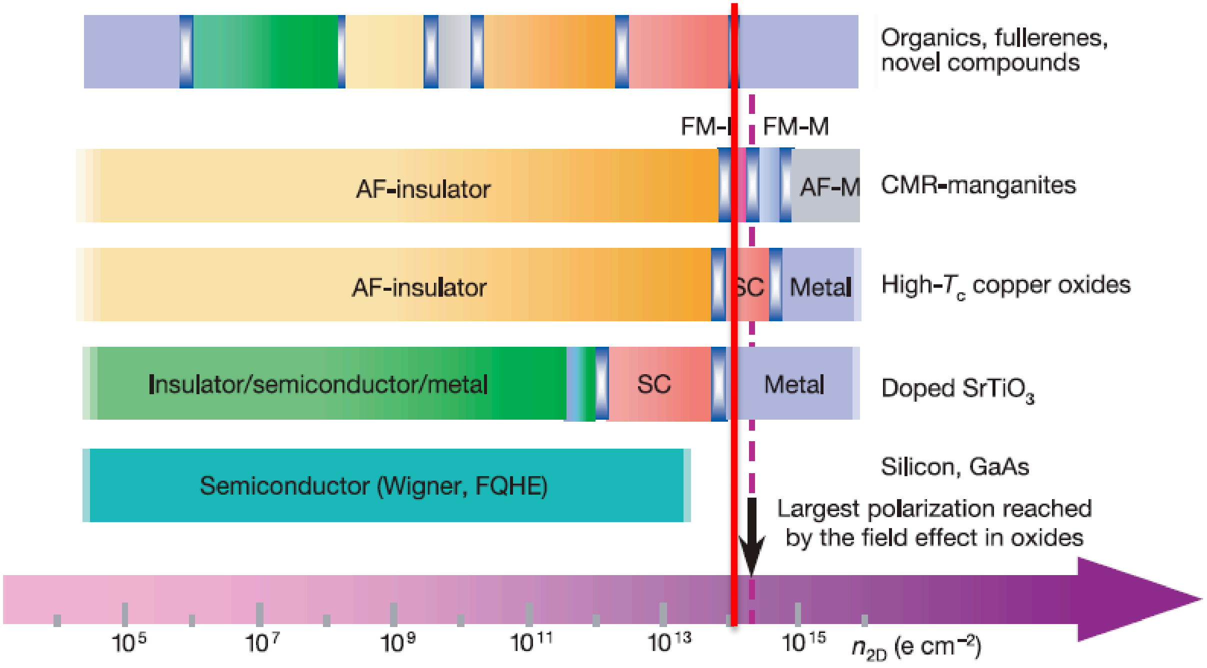

MOSFET

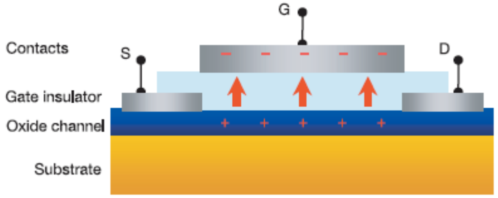

LSI


Flexible TFT

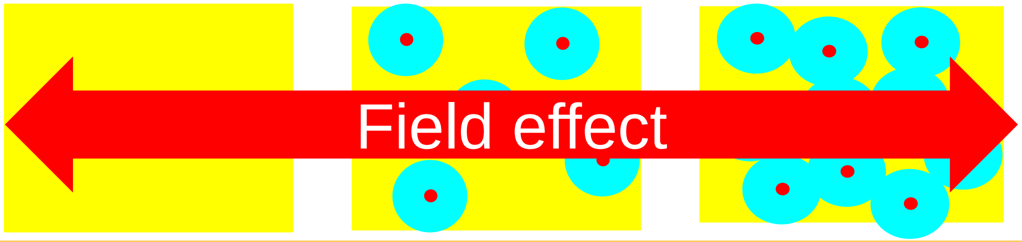
Electric field effect

2 Dimensional physics



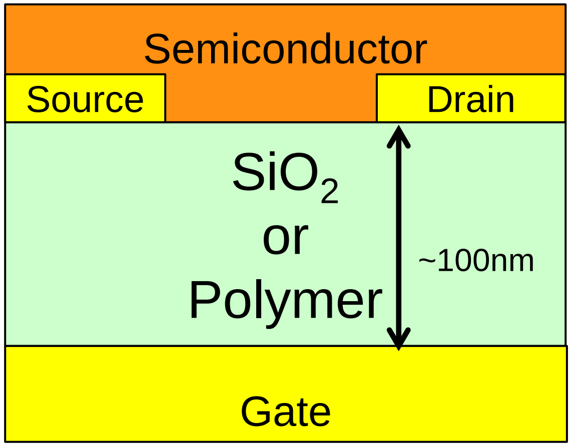


C. H. Ahn et al,
Nature **424** 1015 (2003)



To reach the stage of rich physics
We need to modulate carrier density at least 10^{14} cm^{-2}

Why we need electrolyte gating?

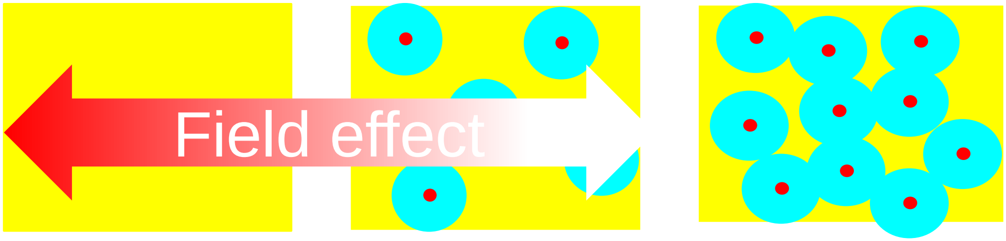


$$Q = C_i V$$

$$C_i = \frac{\epsilon \epsilon_0}{d}$$

To modify wide range

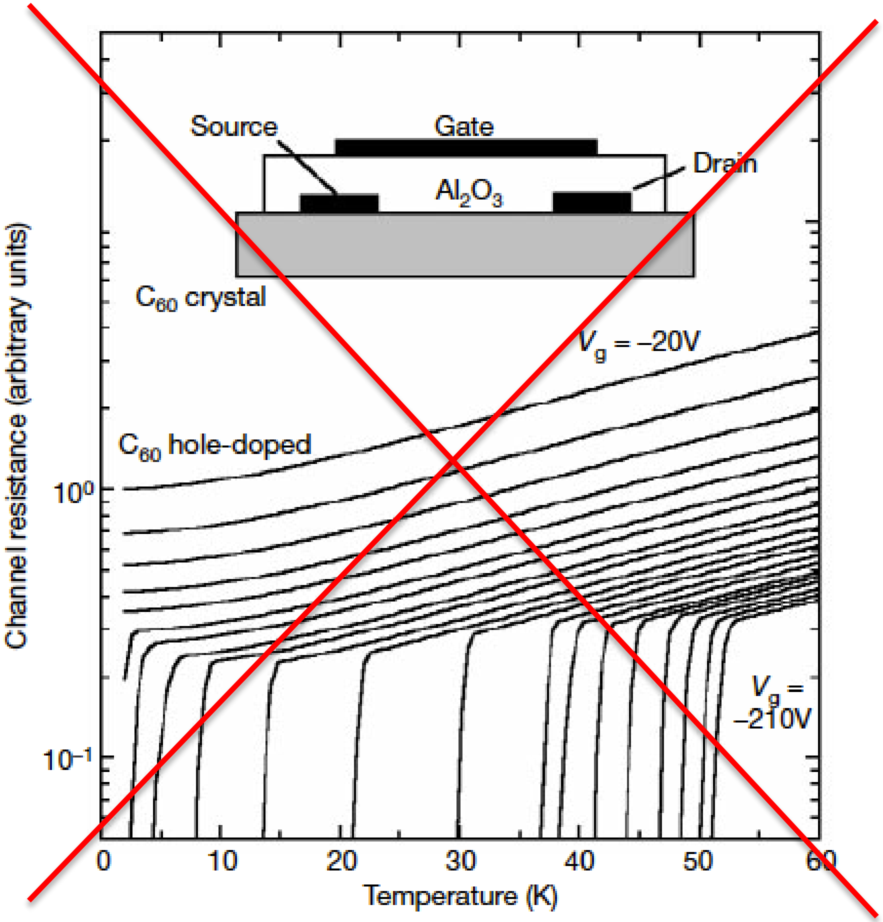
1） Thin gate insulator
2） Dielectric breakdown
3） High-k materials



Ex) SiO_2 (200nm)
5 MV/cm, ε = 3.9 (SiO_2)
C = 1.7×10^{-8} F/cm
Q = **$1.1\times10^{13}/cm^2$**

Still difficult to modify carrier density for a wide range

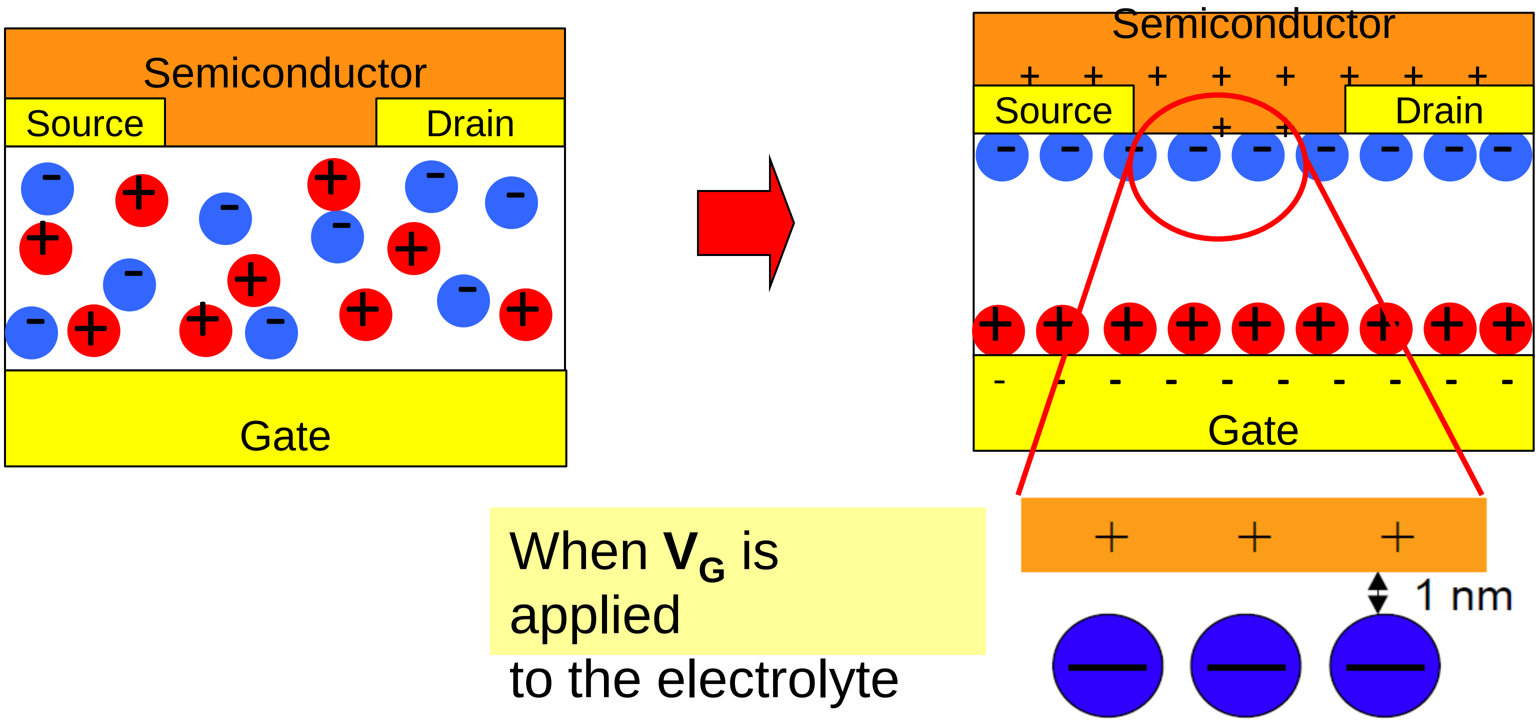
Fake experiments were done!!!



J. Schön *et al.*, (2000)

To overcome the limitations
Let’s use electrolyte

Why we use electrolytes?



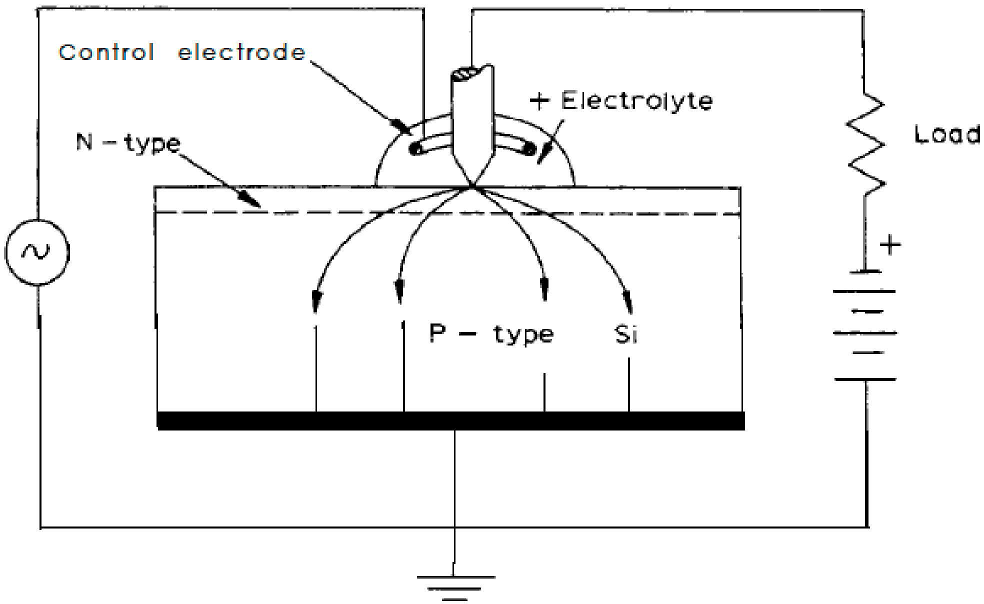
When $\mathbf{V_G}$ is applied
to the electrolyte

Electric double layers (EDLs) are formed after the ionic redistribution

Gate electric field is confined only to the EDL with **1nm**
Ex.) V_G = 3 V, Electric field at EDL **E_G ~ 30 MV/cm**

High-density carrier up to 10^{15} cm^{-2}
are induced at the surface!!

History of electrolyte gating

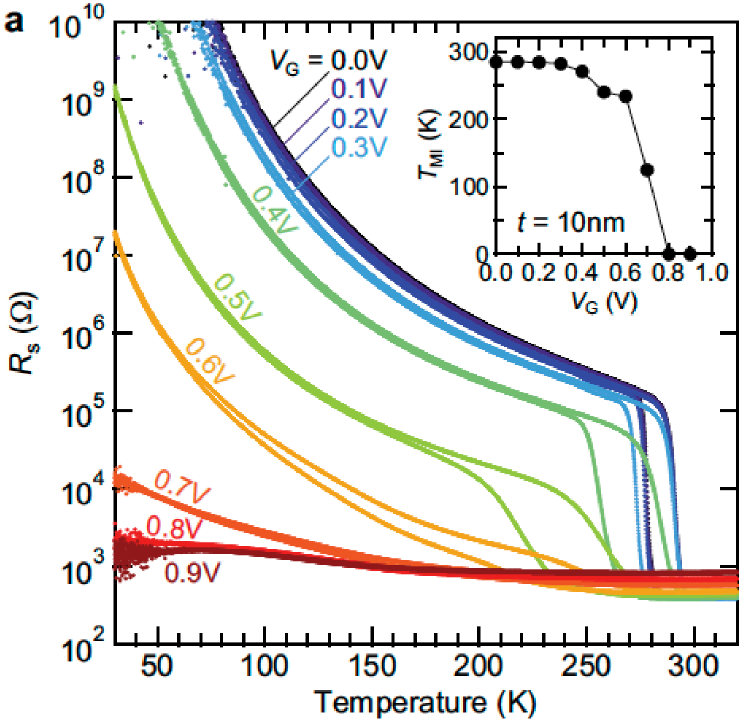


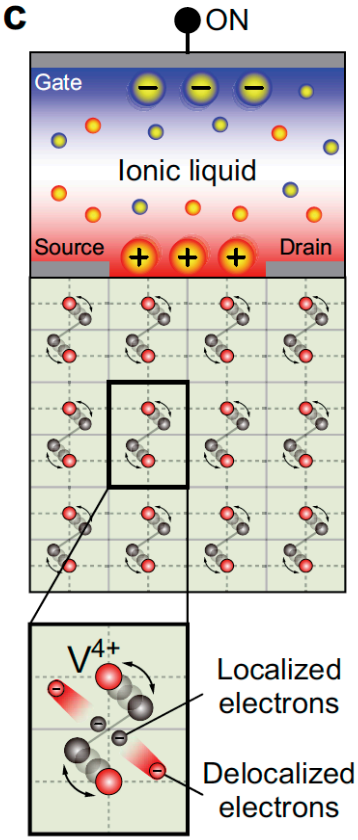
John Bardeen Nobel Lecture (1956)

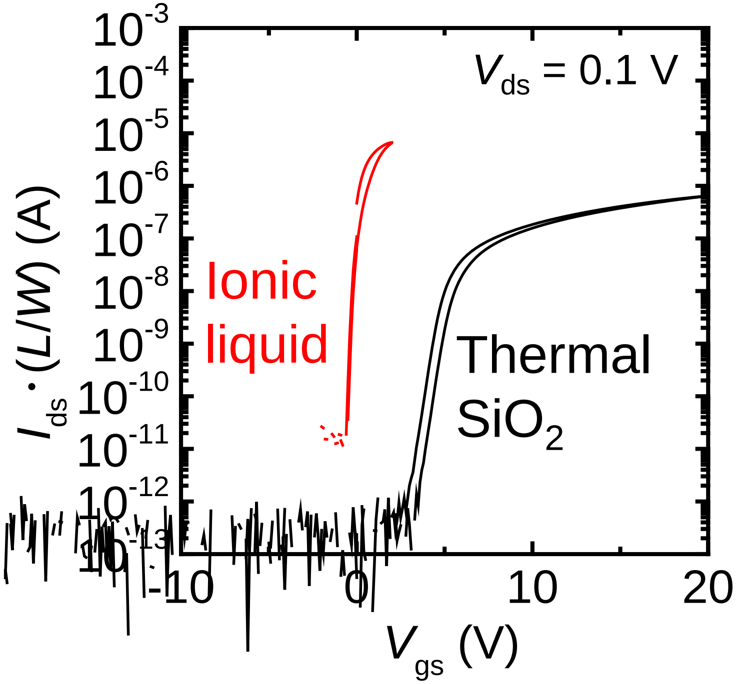
John Bardeen

First transistor was using **electrolyte** instead of solid gate dielectrics!!

New tools to study solid state physics!!







VO_2 thin film

M. Nakano, S. Ono *et al.*, Nature (2012).

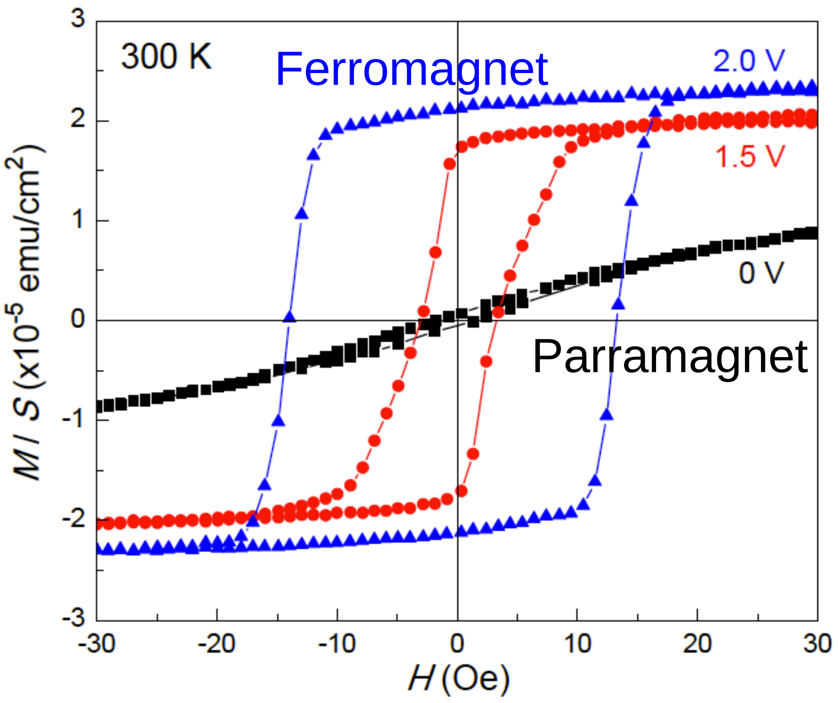
InGaZnO thin film

M. Fuji, S. Ono *et al.*, Scientific Rep. (2015).

Emergence of 3D metallic ground state!!

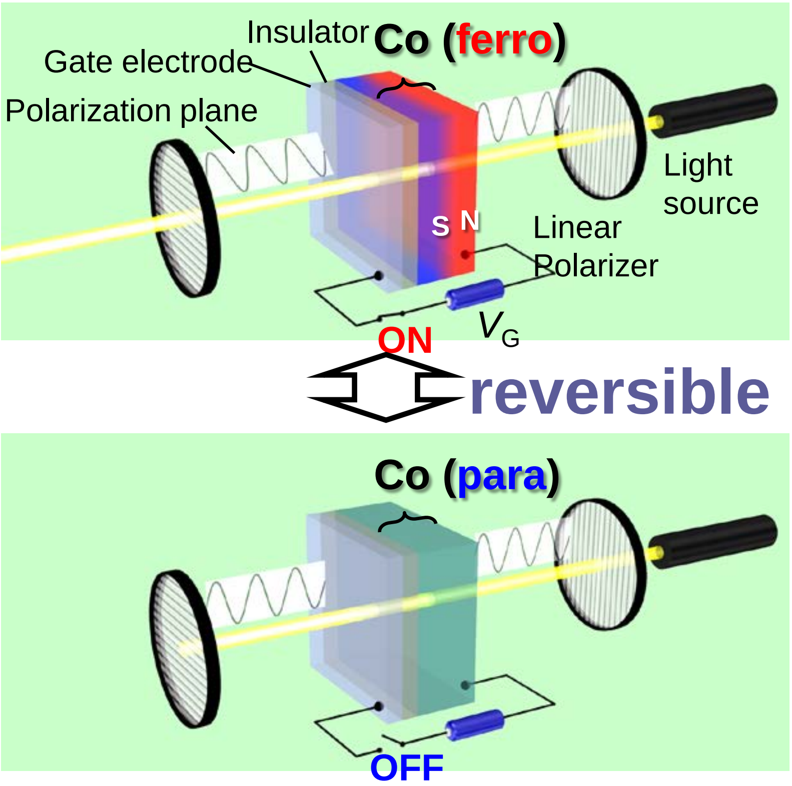
Low voltage operation !!

New tools to study solid state physics!!



Co thin film

K. Shimamura, D. Chiba, S. Ono *et al.*,
APL **100** 122402 (2012).



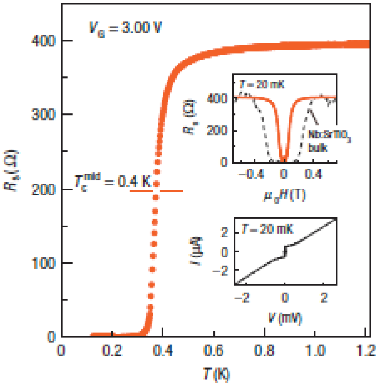
Co thin film

Y. Hibino, S. Ono *et al.*,
APEX (2017).

Electric-field induced ferromagnetic transition

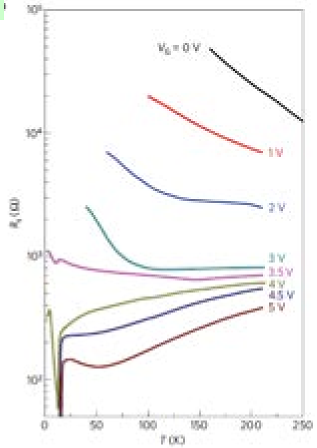
Electric-field induced superconductivity

$SrTiO_3$



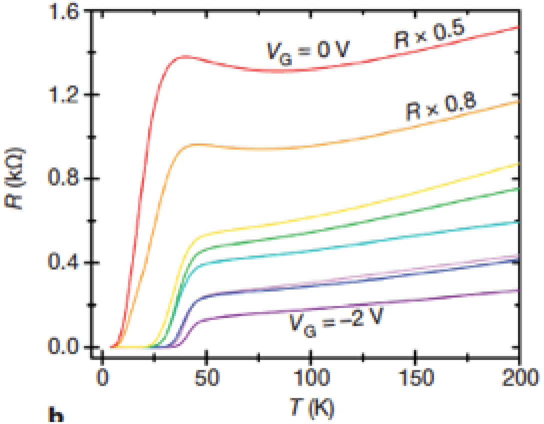
K. Ueno *et al*.,
Nature Mat. **7** 855 (2008).

ZrNCl



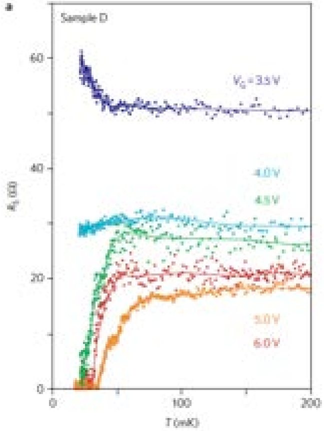
J.T. Ye *et al*.,
Nature Mat. **9** 125 (2009).

$La_{2-x}Sr_xCuO_4$ thin film



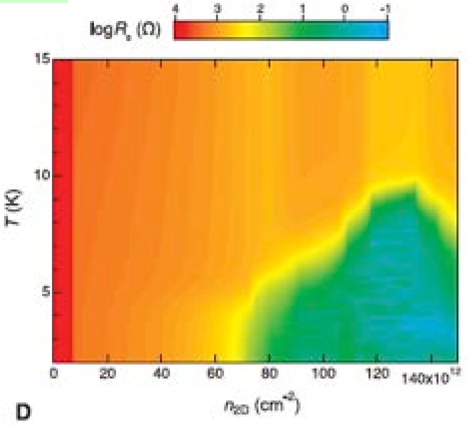
A.T. Bollinger *et al*.,
Nature **472** 458 (2011).

$KTaO_3$



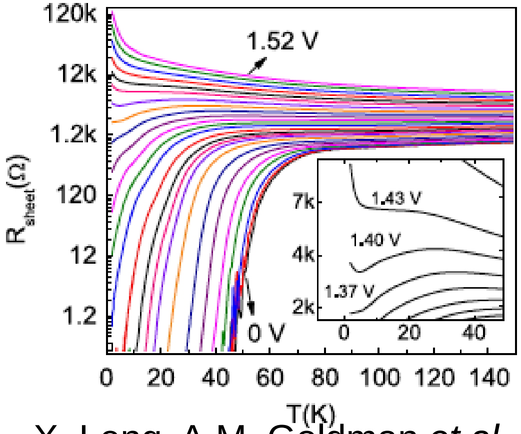
K. Ueno *et al*.,
Nature Nanotech. **6** 408 (2011).

MoS_2



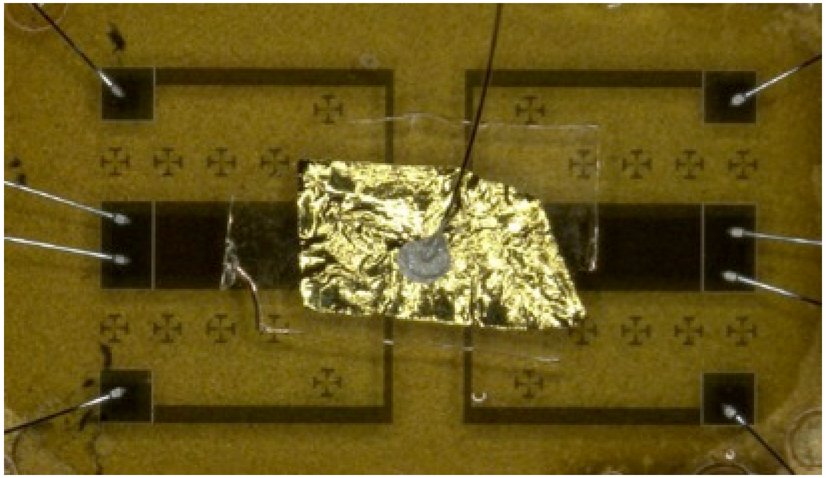
J.T. Ye *et al*.,
Science **388** 1193 (2012).

$YBa_2Cu_3O_{7-x}$ thin film

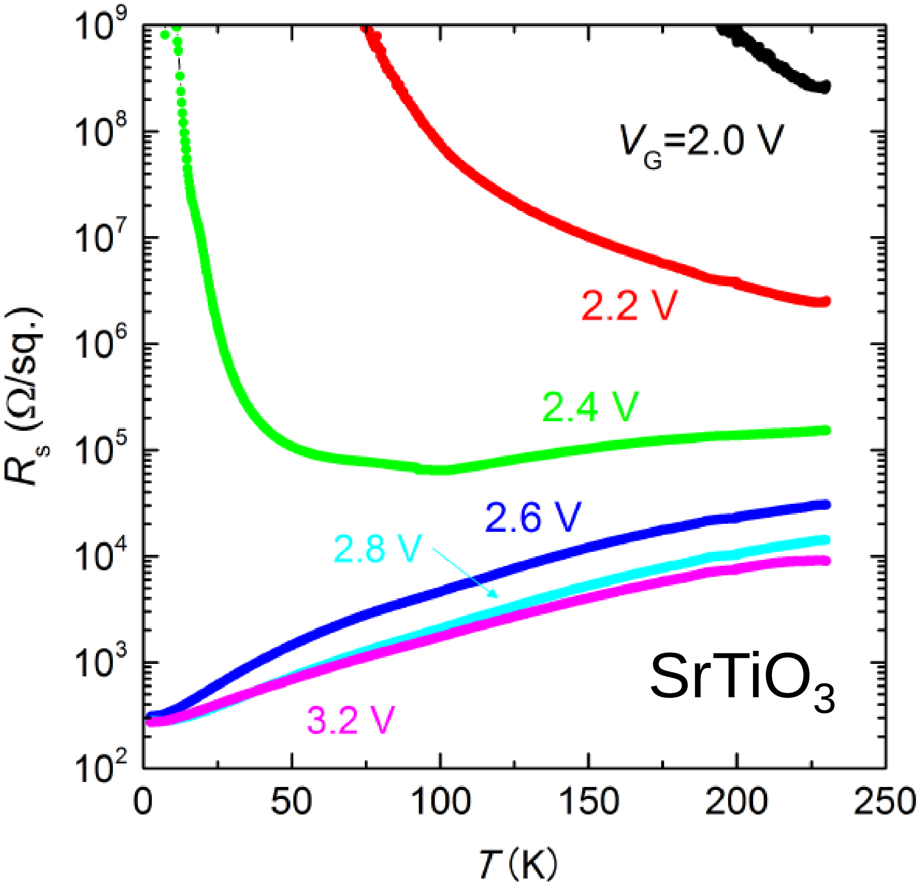


X. Leng, A.M. Goldman *et al*.,
PRL **107** 027001 (2011).

Cut & stick methods



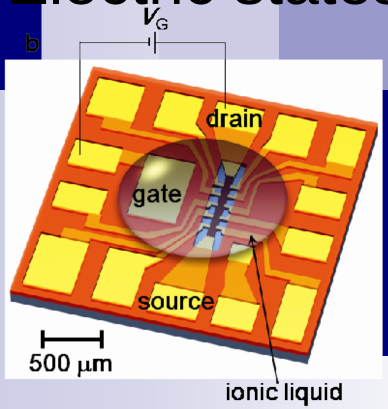
Solid electrolyte with ILs
(Polymer : ILs = 1:1)



What we can do?

Electric-field control using electrolyte gating

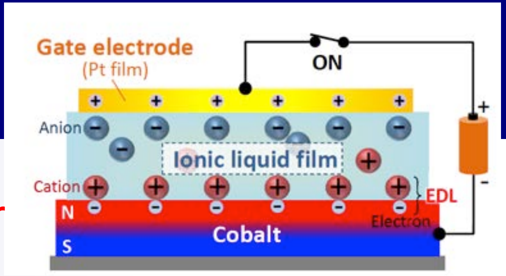
Electric states



Field effect transistor

OFETs,
NdNiO$_3$, VO$_2$,
Pr$_{1-x}$Sr$_x$MnO$_3$,
Diamond, Si, GaN,
CNTs, InGaZnO

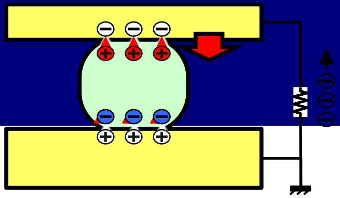
Magnetism



Spintronics
(Co, Fe, Ni,
(Ga, Mn)As)

Energy conversion

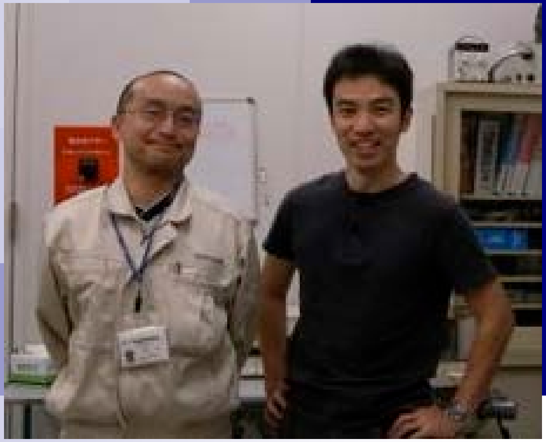
Light-emitting
electrochemical cell



Energy Harvester

New tool and new applications

How to choose the optimal ionic liquids
Case for OFETs

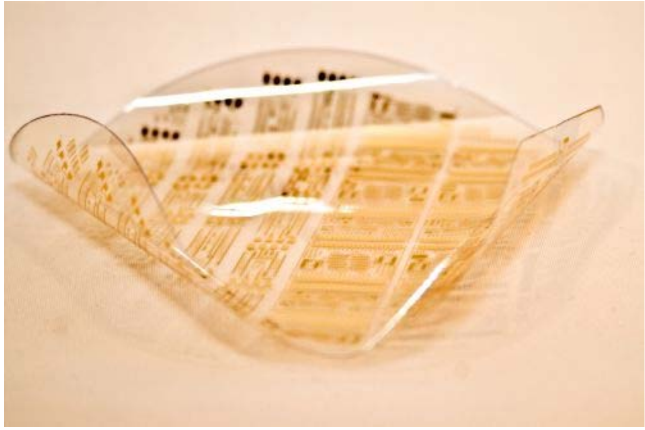


CRIEPI
Mr. Kazumoto Miwa
Dr. Shiro Seki
Dr. Roger Hausermann
Dr. Shimpei Ono

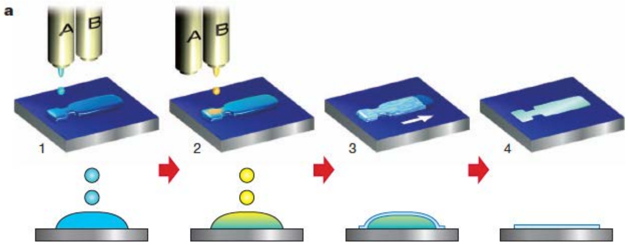
S. Ono *et al.*,
APL 108 063301 (2016).

Introduction

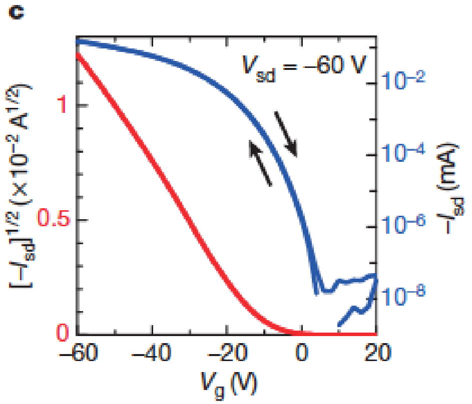
Organic field-effect transistors (OFETs)



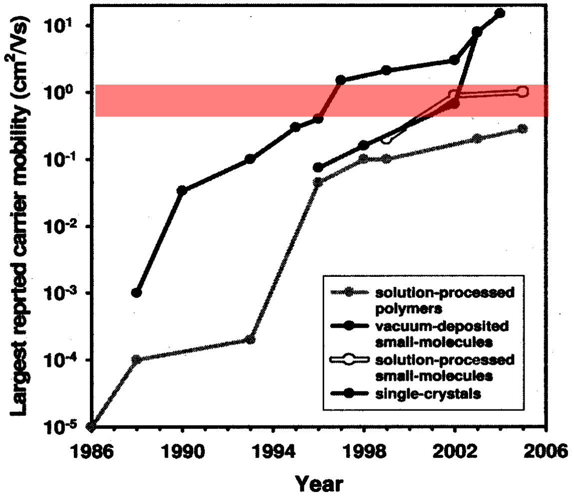
The **mobility** exceed more than **～30 cm^2/Vs**



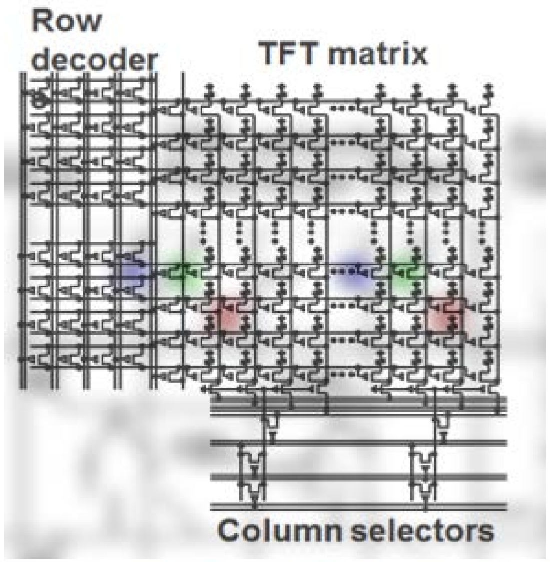
C_8-BTBT
$\mu \sim 30\ cm^2/Vs$

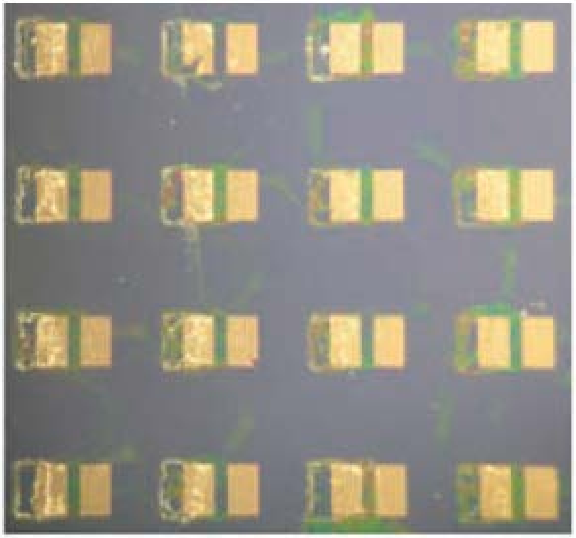


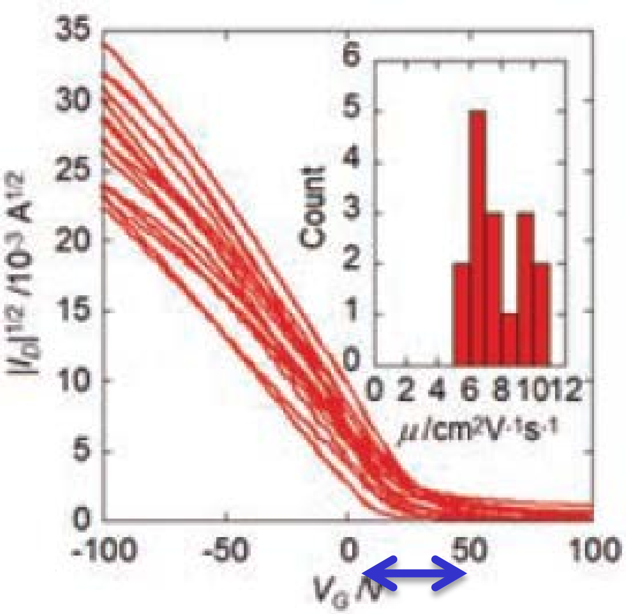
H. Minemawari, T. Hasegawa et al.,
Nature 475 364 (2011)



What is necessary for real application?





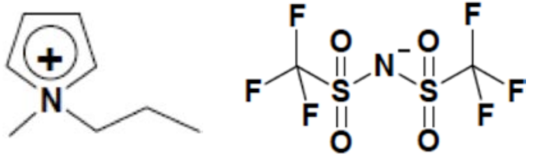


K. Nakayama et al.,
Adv. Mat. (2011)

Large thershold voltage fluctuation

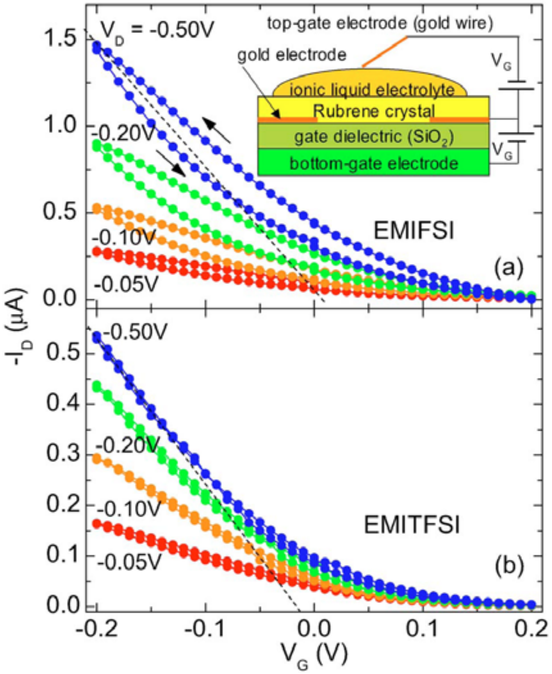
Serious technological challenge to operate OFETs with low voltages

Ionic liquids gating

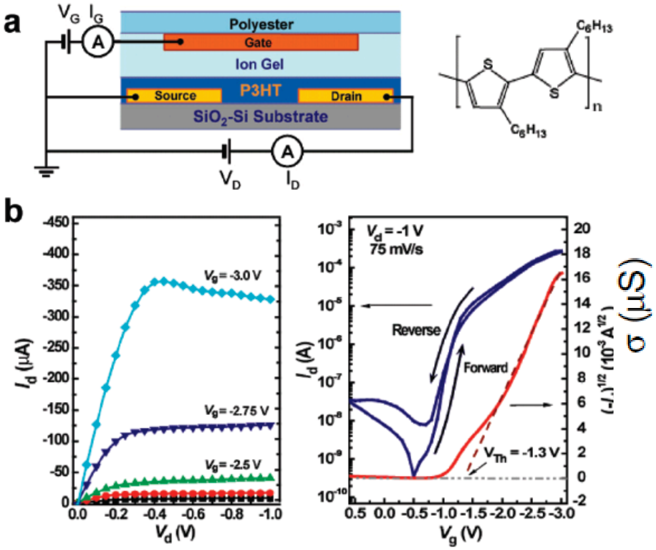


Electrolyte : Ionic liquids

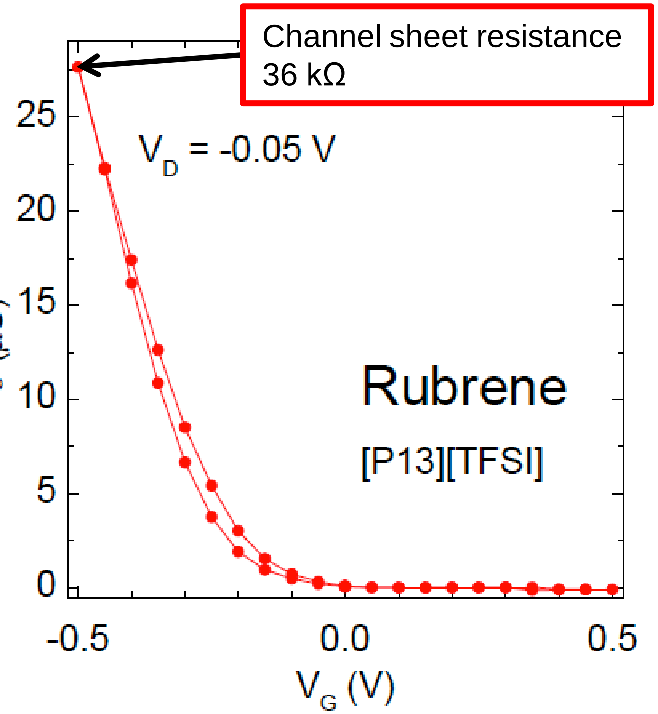
OFETs



S. Ono et al.,
APL **92**, 103313 (2008).
APL **94** 063301 (2009).



J. Lee, C.D. Frisbie *et al.*,
JACS **129**, 4532 (2007).



Channel sheet resistance
36 kΩ

SO et al., APL **94**, 063301 (2009).,
SO et al., APL **108**, 063301 (2016).

The advantage of ILs electrolyte
1) Better matching in ILs/semiconductors
2) Less damage to interface

Now, most of research are done with ionic liquids

What is the optimal ionic liquids for OFETs?

There are more than 2000 combinations available.

What is the key parameter?

1) Capacitance
2) Electrochemical windows
3) Hydrophobicity
4) Chemical stability

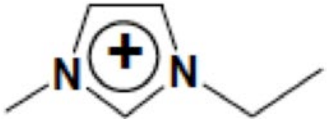
Both determine total charge accumulated at interface

Especially for n-type organic Semiconductor as well as inorganic materials

Various capacitance of ionic liquids

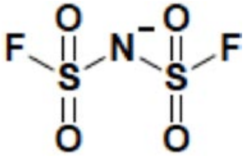
Imidazolium family

Cation

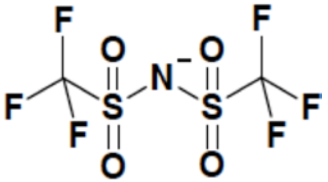


[emim]

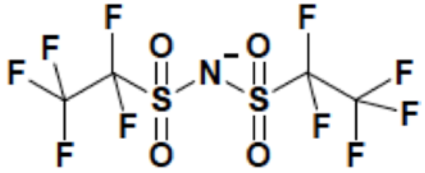
Anion



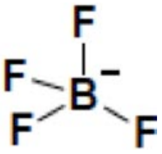
[FSI]



[TFSI]



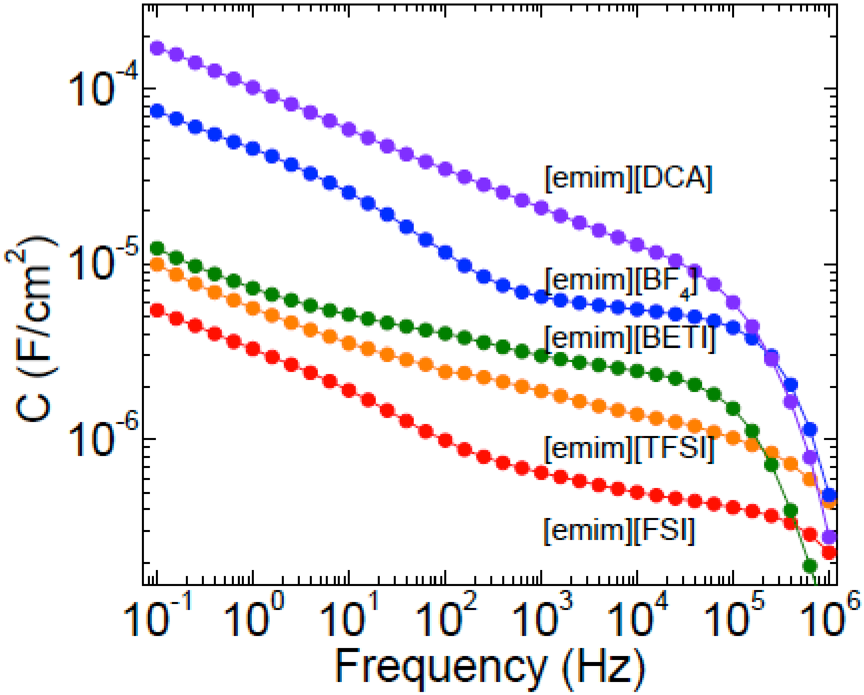
[BETI]



[BF_4]

$N\equiv C-\overset{-}{N}-C\equiv N$

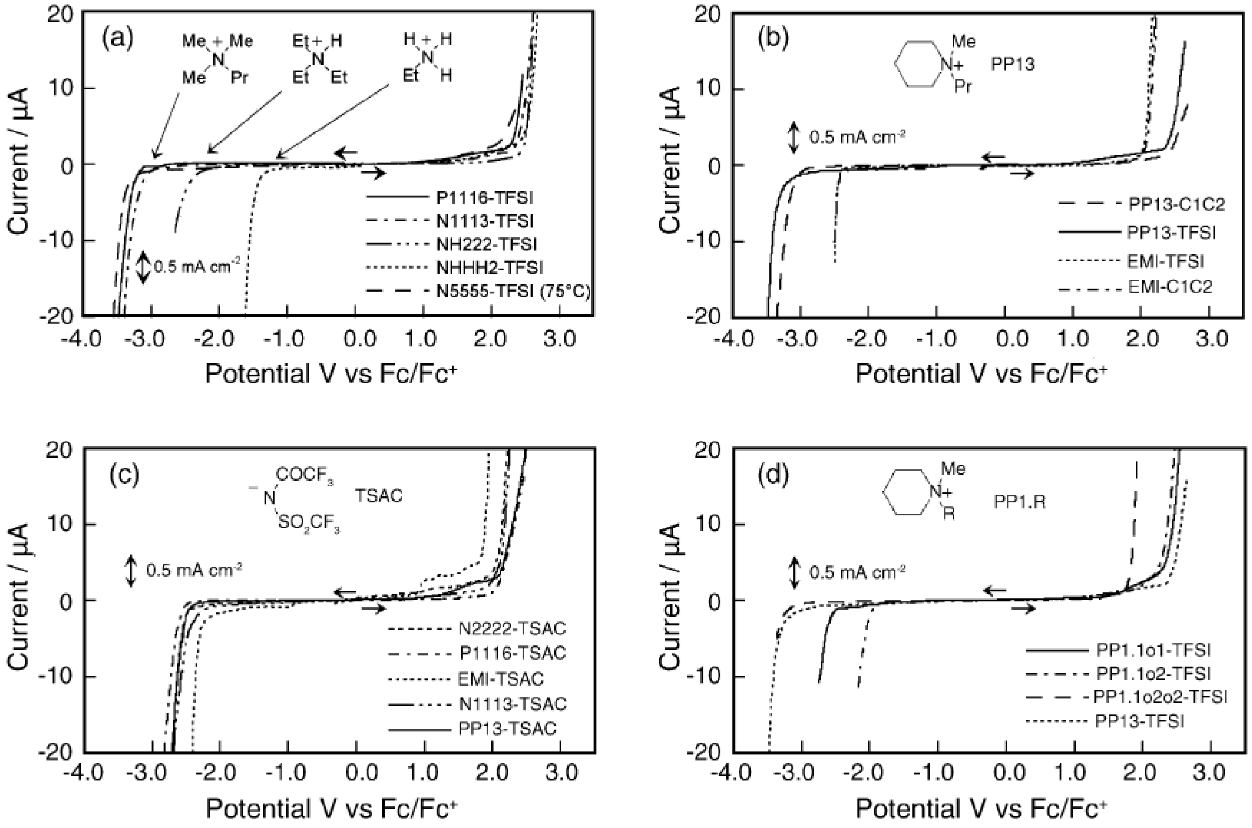
[DCA]



170 μF/cm^2 for [emim][DCA]
~**5.1 x 10^{14}/cm^2** at V_G = 1.0 V

By changing combinations, capacitance changes 2~3 orders

Electrochemical window



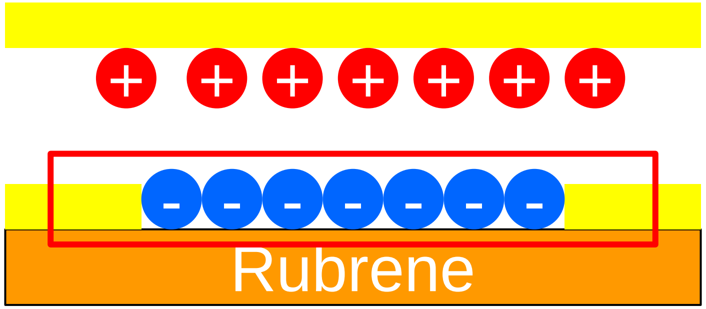
H. Matsumoto et al.,
J. Power Source
(2005)

Electrochemical window limit the maximum voltage we can apply to the ionic liquids

IL with large capacitance & wider chemical windows is preferable?

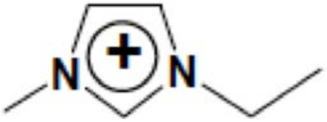
What is the optimal ionic liquids for OFETs?

Effect of anion for p-type semiconductor



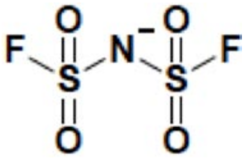
High-density carrier doping with ionic liquids

Cation

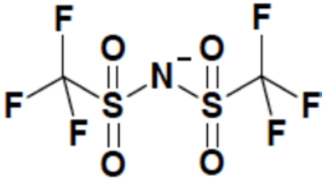


[emim]

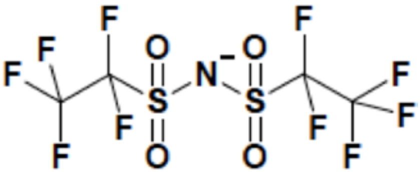
Anion



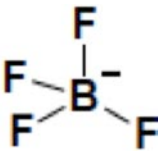
[FSI]



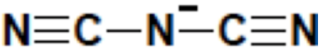
[TFSI]



[BETI]



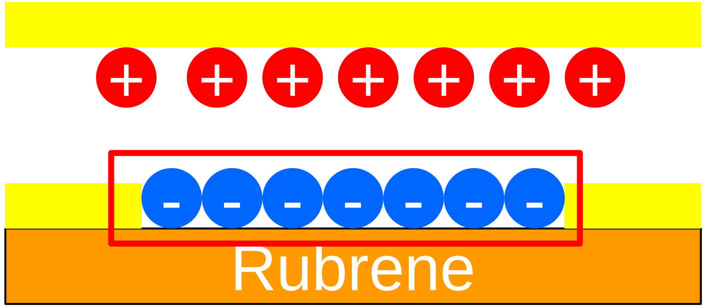
$[BF_4]$



$N{\equiv}C{-}N^{-}{-}C{\equiv}N$

[DCA]

Try to see the effect of anion which is in adjacent to ruburene

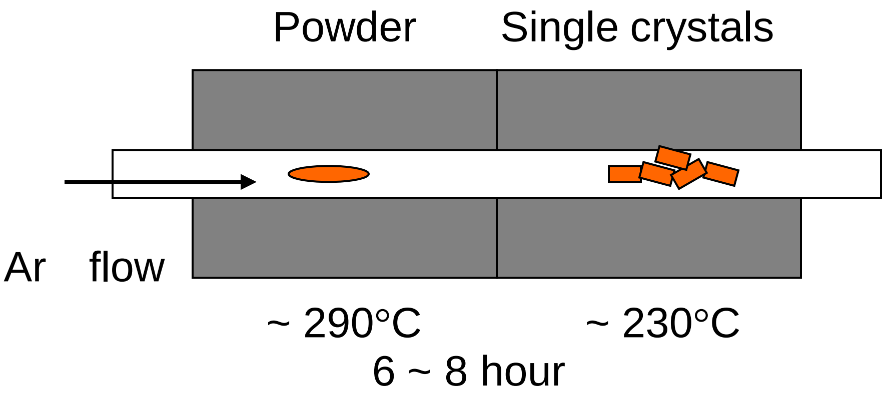


Anion is in adjacent to Rubrene

Is there any change?
Stronger effect?

Structure of OFETs

Physical Vapor Transport


Powder

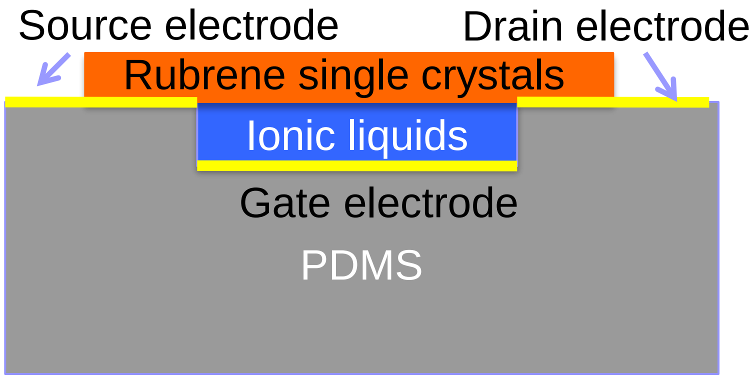
Single crystals

Ar flow

~ 290°C

~ 230°C

6 ~ 8 hour


Source electrode

Drain electrode

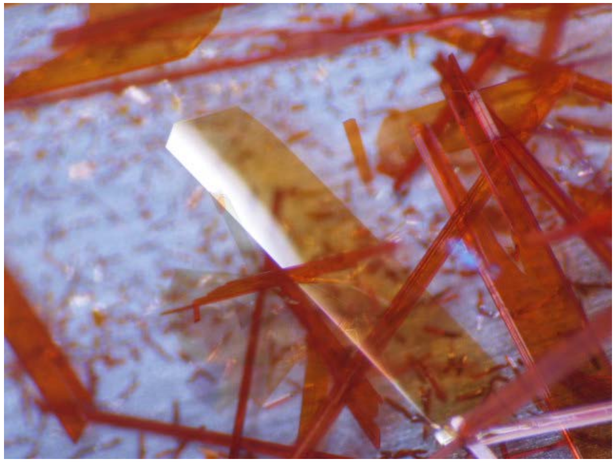
Rubrene single crystals

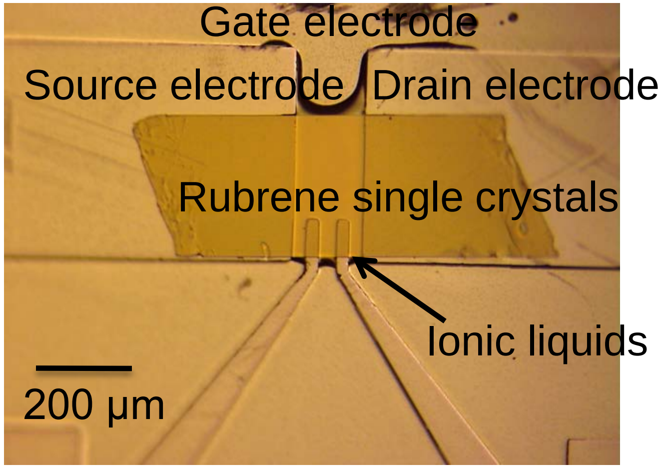
Ionic liquids

Gate electrode

PDMS

Rubrene single crystals




Gate electrode

Source electrode

Drain electrode

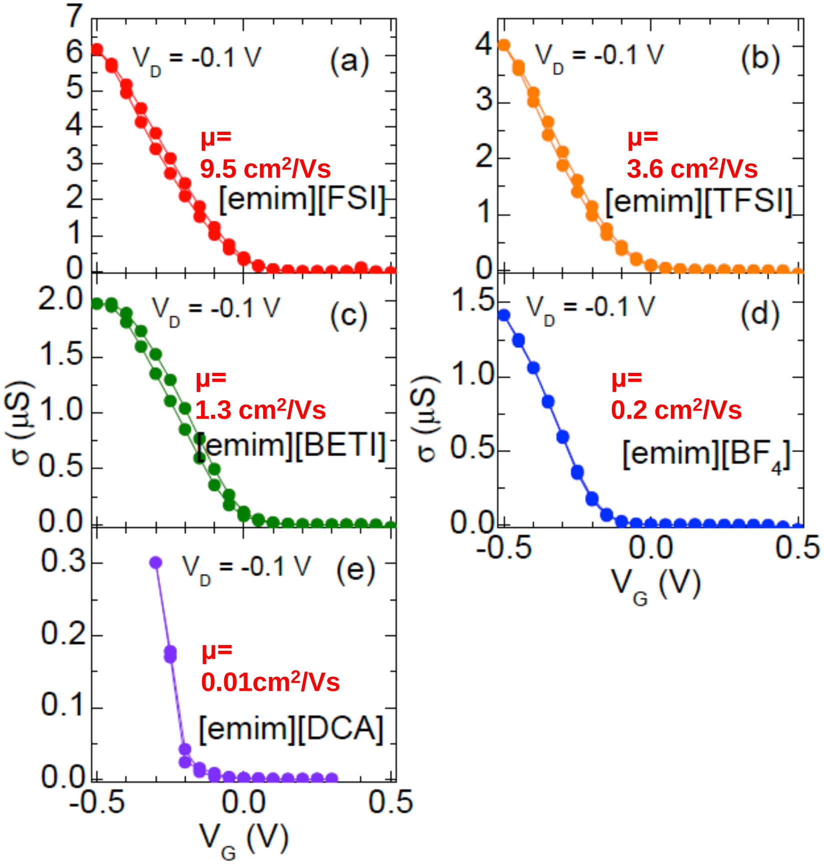
Rubrene single crystals

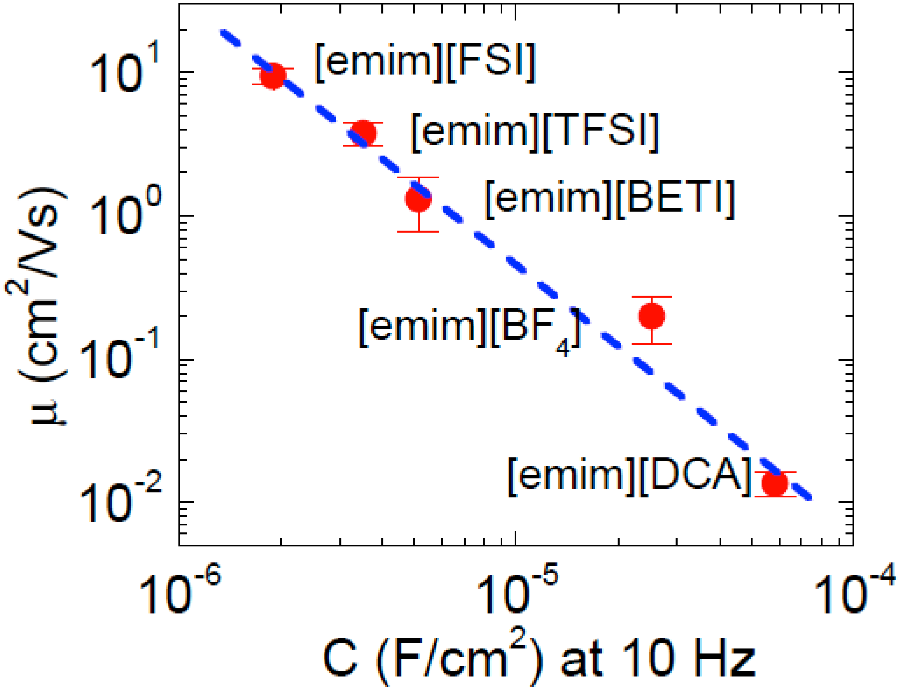
Ionic liquids

200 μm

Which ionic liquids is best so far?

Rubrene



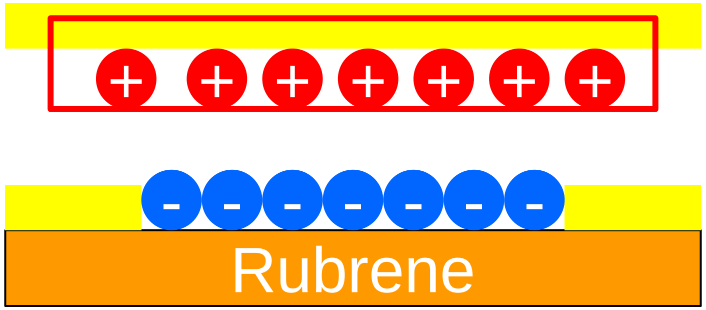


Lower capacitance IL is better to achieve higher mobility

S. Ono *et al.*, APL **94** 063301 (2009).

There is clear correlation between capacitance of IL and mobility of p-type semiconductor

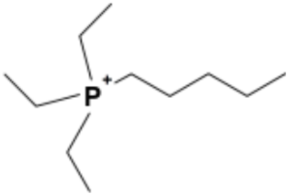
What is the optimal ionic liquids for OFETs?
Effect of cation for p-type semiconductor



Is there any change?
No effect?

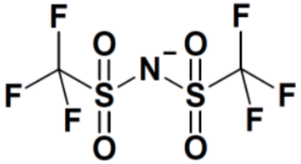
Let’s fix the anion and change cation!!

Cation

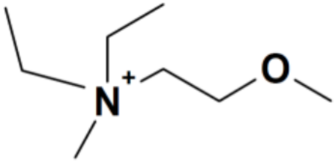


[TEPP]

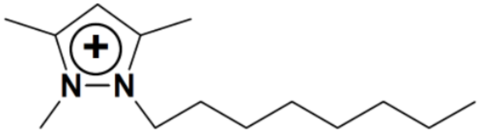
Anion



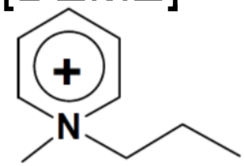
[TFSI]



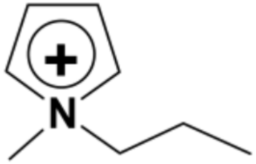
[DEME]



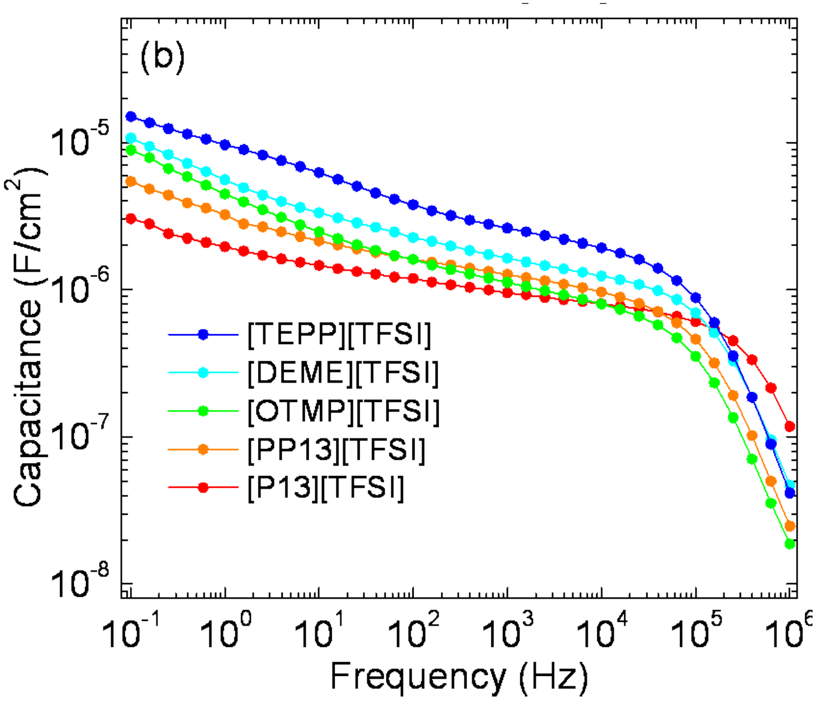
[OTMP]



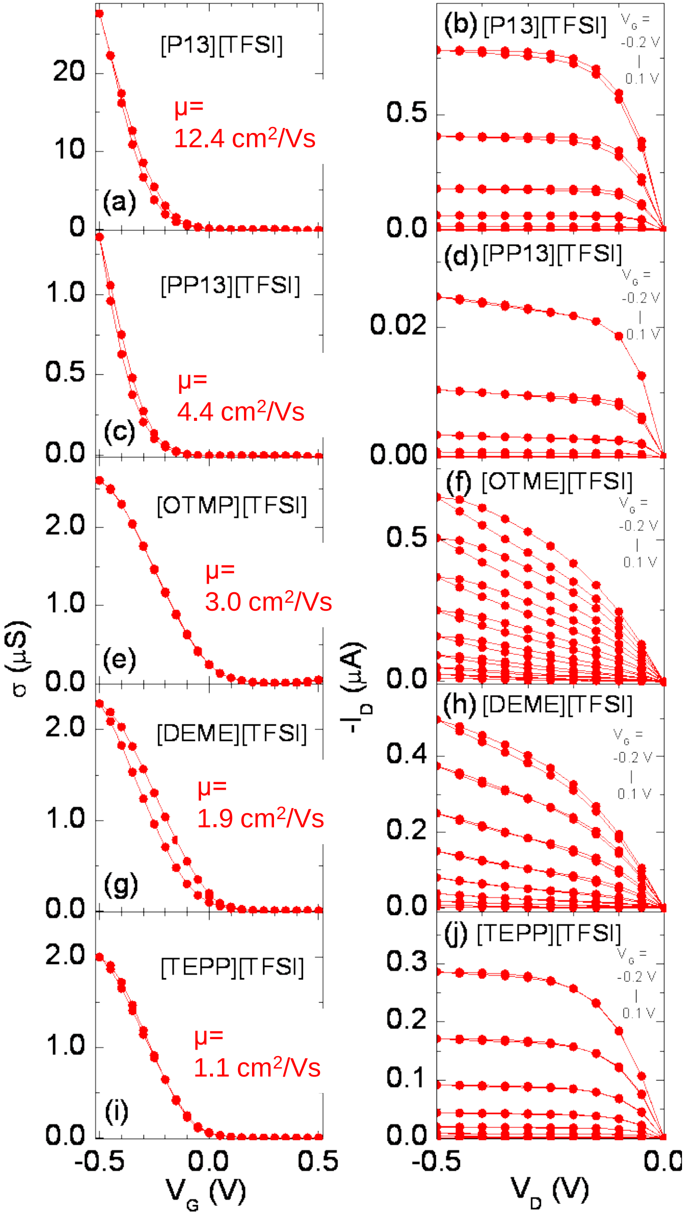
[PP13]



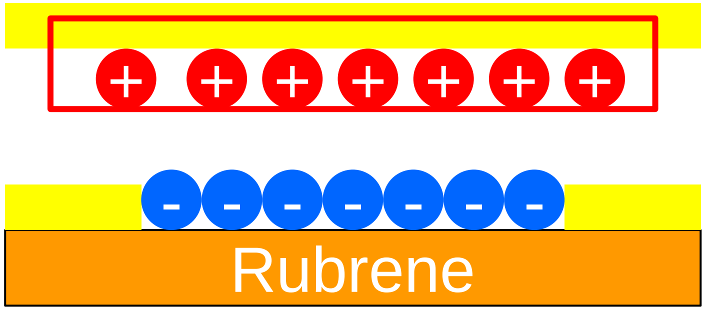
[P13]



Effect of ILs for p-type semiconductor

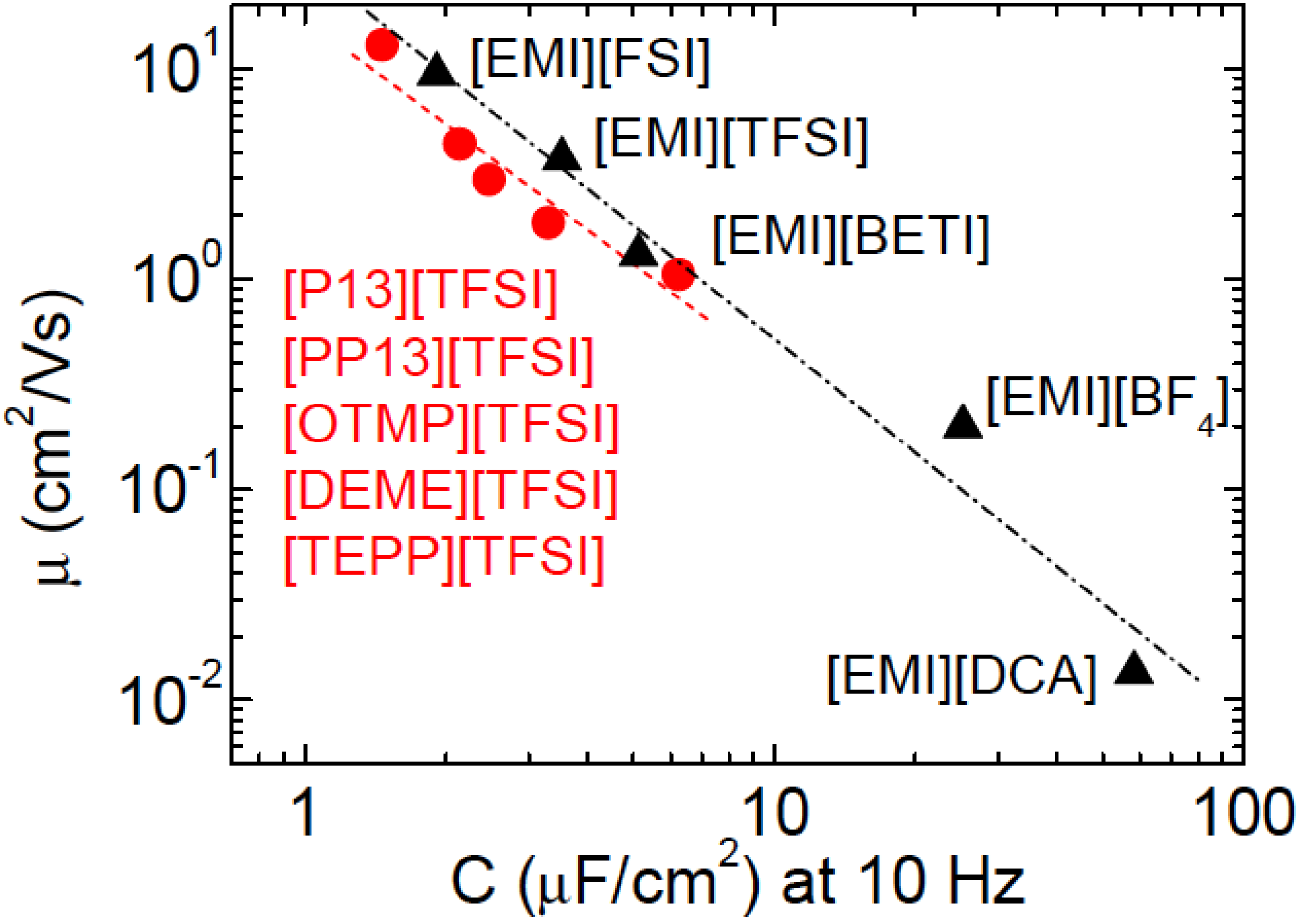


P-type semiconductor:
Rubrene single crystals



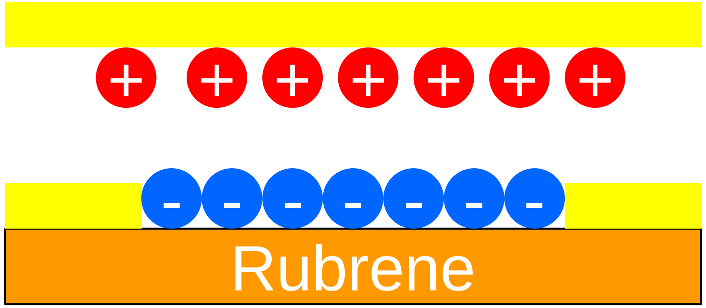
Even changing cation which is not adjacent to rubrene, the mobility of p-type semiconductor change.

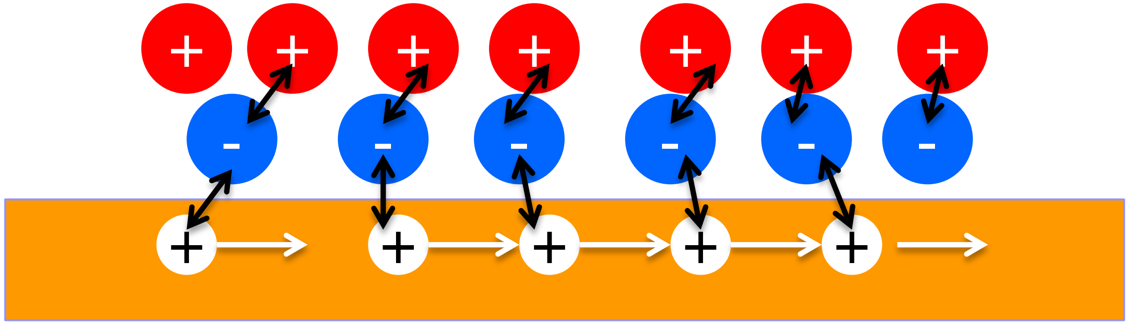
Discussion



For rubrene single crystals, relation between μ and capacitance does not depend on whether only the anions or only the cation are exchanged.

Why it happened?

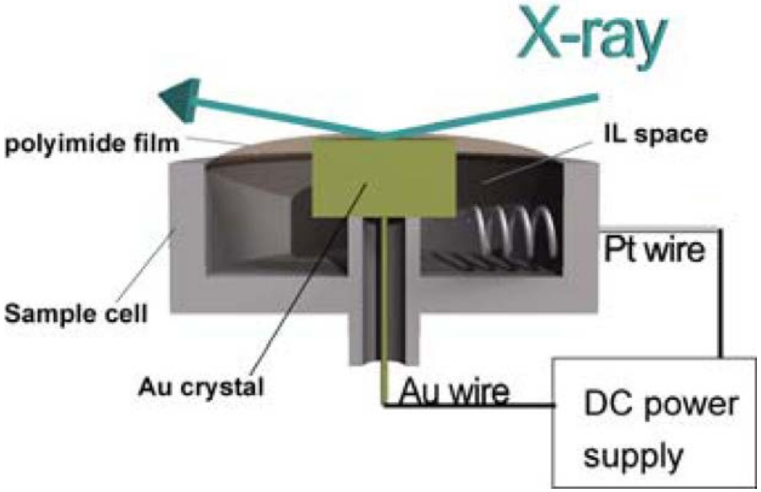




Ions next to the channel couple not only with the charge carrier at the interface, but also with counter ion in next layers.

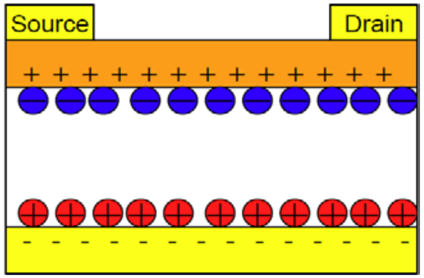
Mobility depends on the total capacitance of EDL which is produced by collective polarization of cation and anion

X-ray reflectivity experments



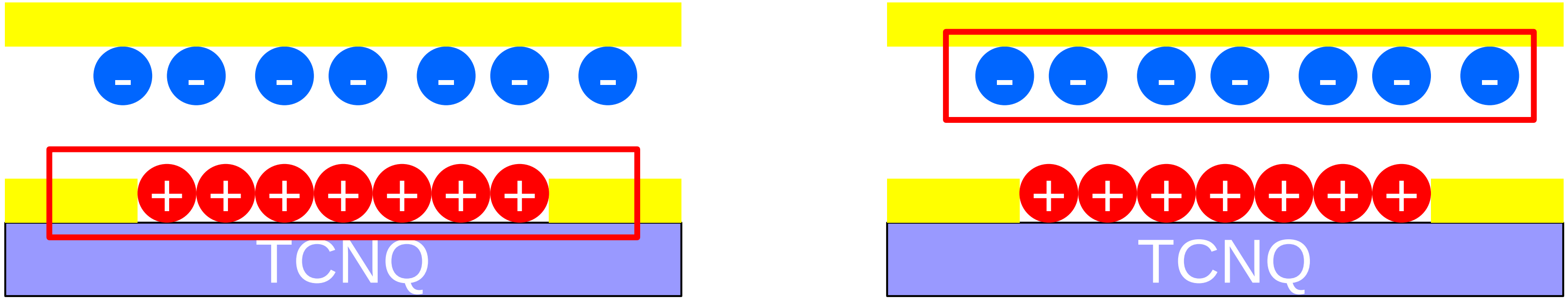
R. Yamamoto *et al.*, APL (2012).

The multiple layers of cations and anions are formed when gate voltage is applied.

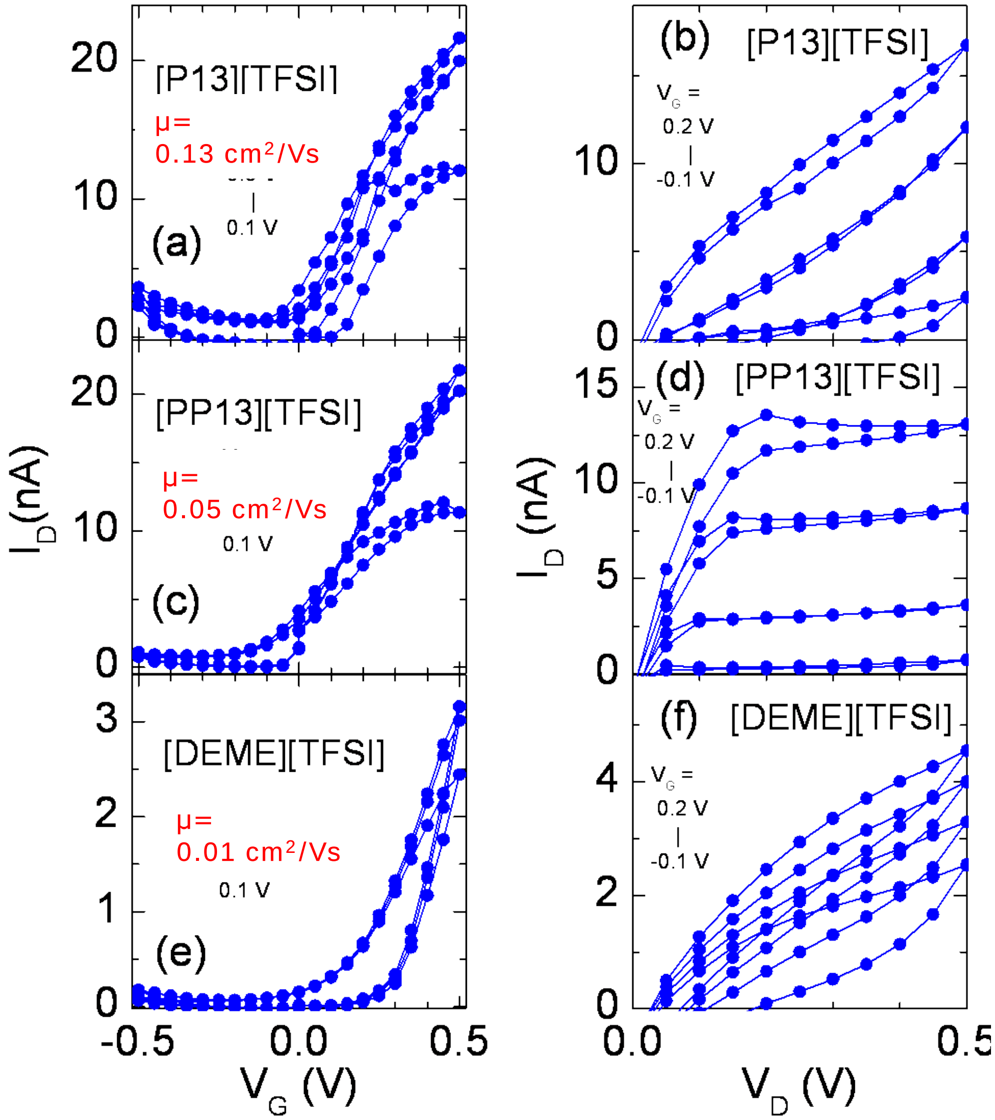


This picture is only applicable with diluted ionic liquids.
EDL with ILs is not at all simple.

What is the optimal ionic liquids for OFETs?
What is the case for n-type semiconductors?



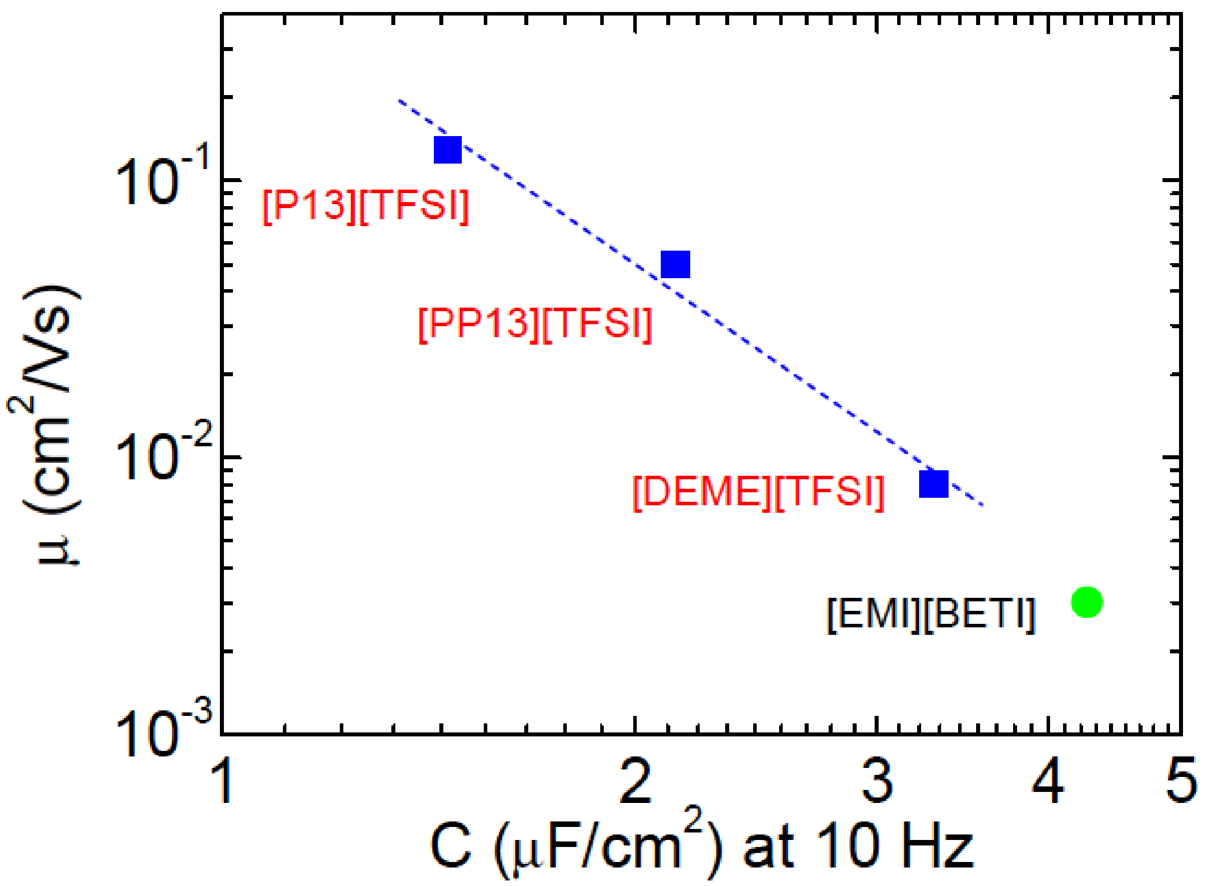
Effect of ILs for n-type semiconductor



n-type semiconductor: 7,7,8,8-tetracyanoquinodimethane (TCNQ) single crystals

The mobility strongly depends on the choice of Ils, not ion species at the semiconductor/IL interface.

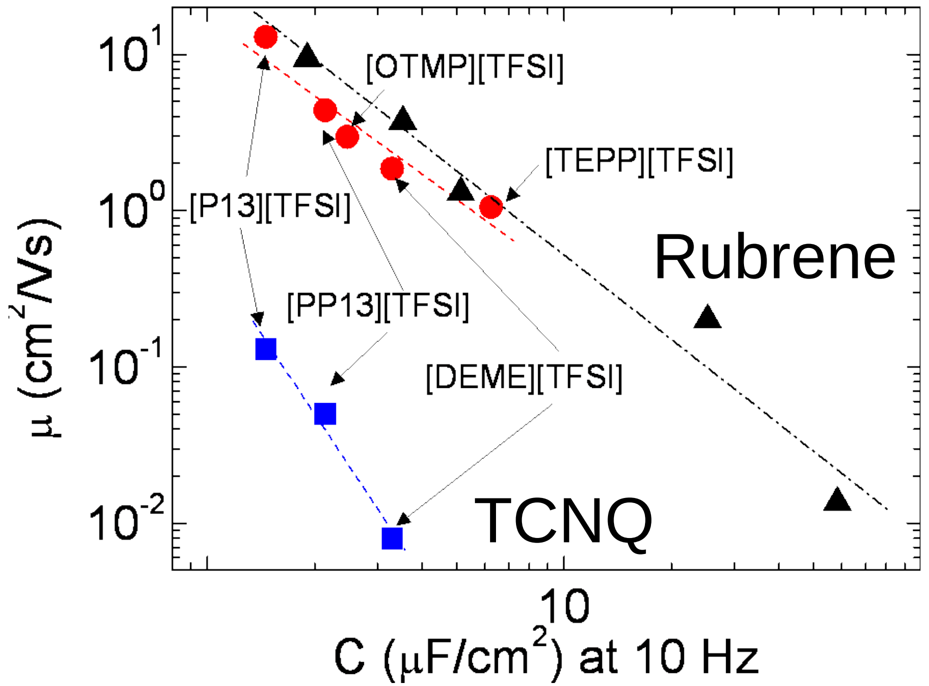
Discussion



Same trend is observed for n-type semiconductors

Lower capacitance IL is better to achieve higher mobility

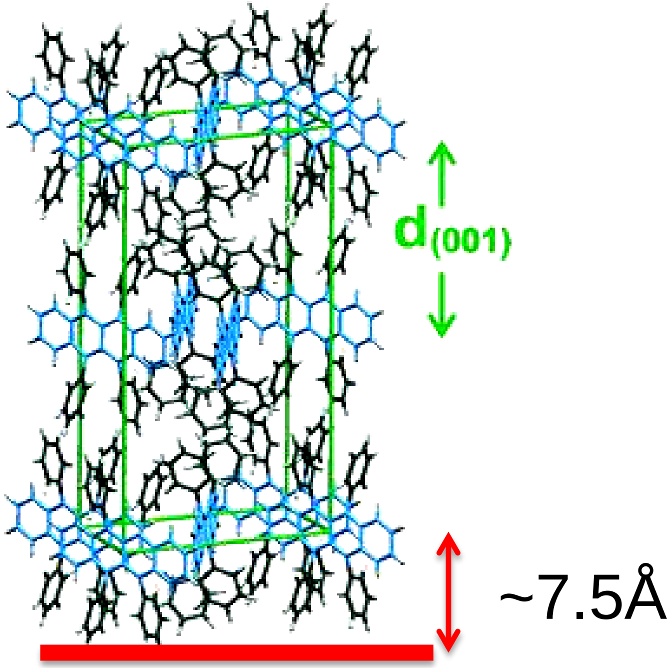
Discussion

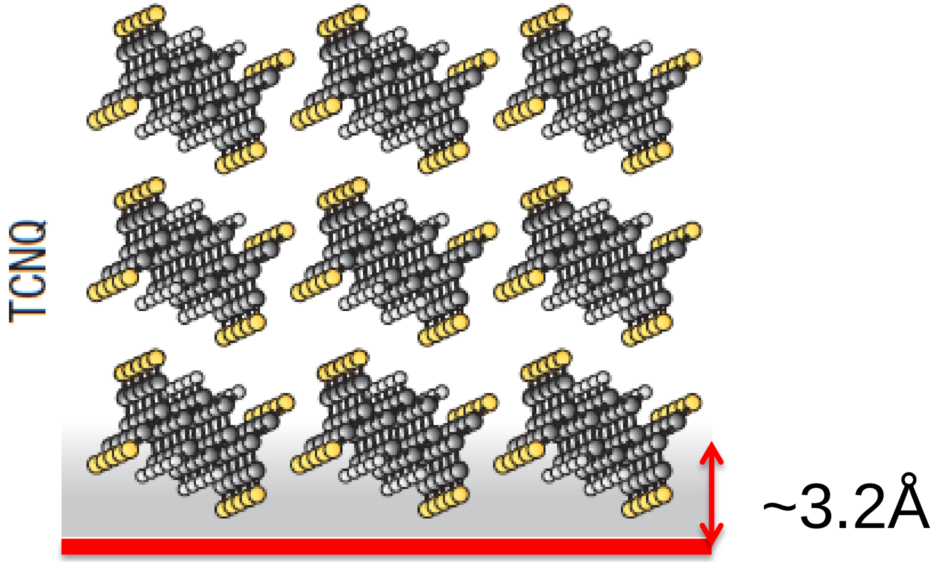


２） Slope of TCNQ is steeper than that of rubrene.

(Ruberne: -1.5, TCNQ: -3.4)

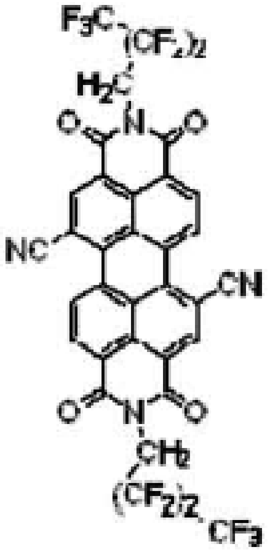
Why slope is different?

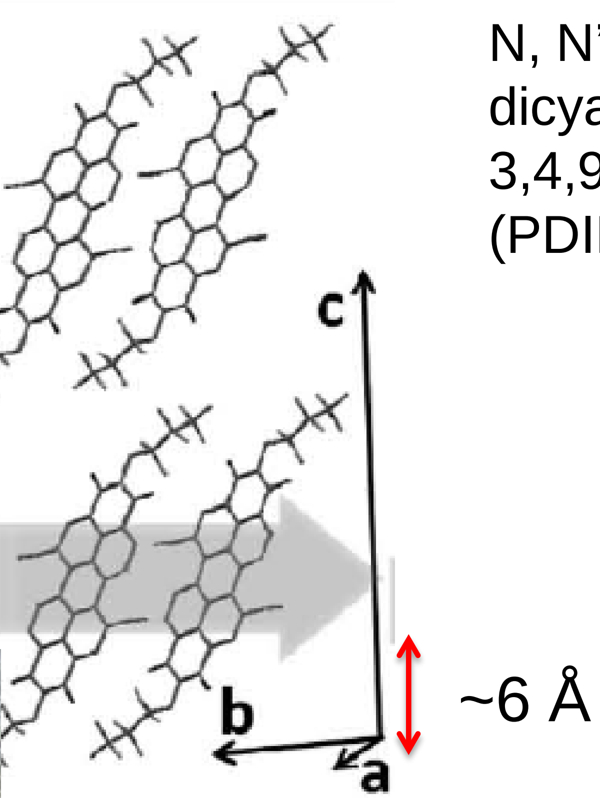




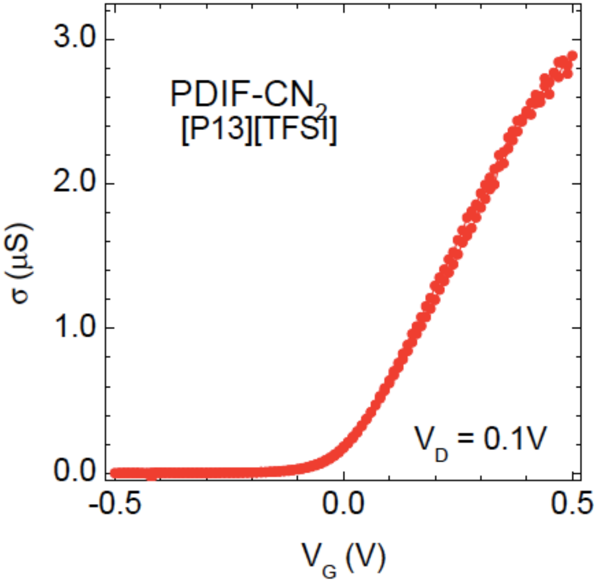
In TCNQ single crystal, π-conjugated layer is close to the interface
Electric polarization of gate dielectric has larger effect than that of rubrene single crystals.

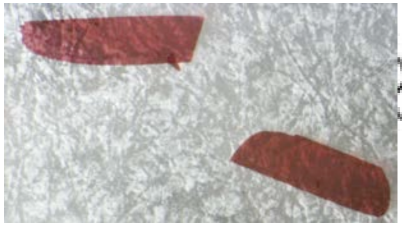
To further increase mobility (n-type)





N, N’-bis(n-alkyl)-(1,7 and 1,6)-dicyanoperylene-3,4,9,10-bis(dicarboximide)s (PDIF-CN2) single crystals

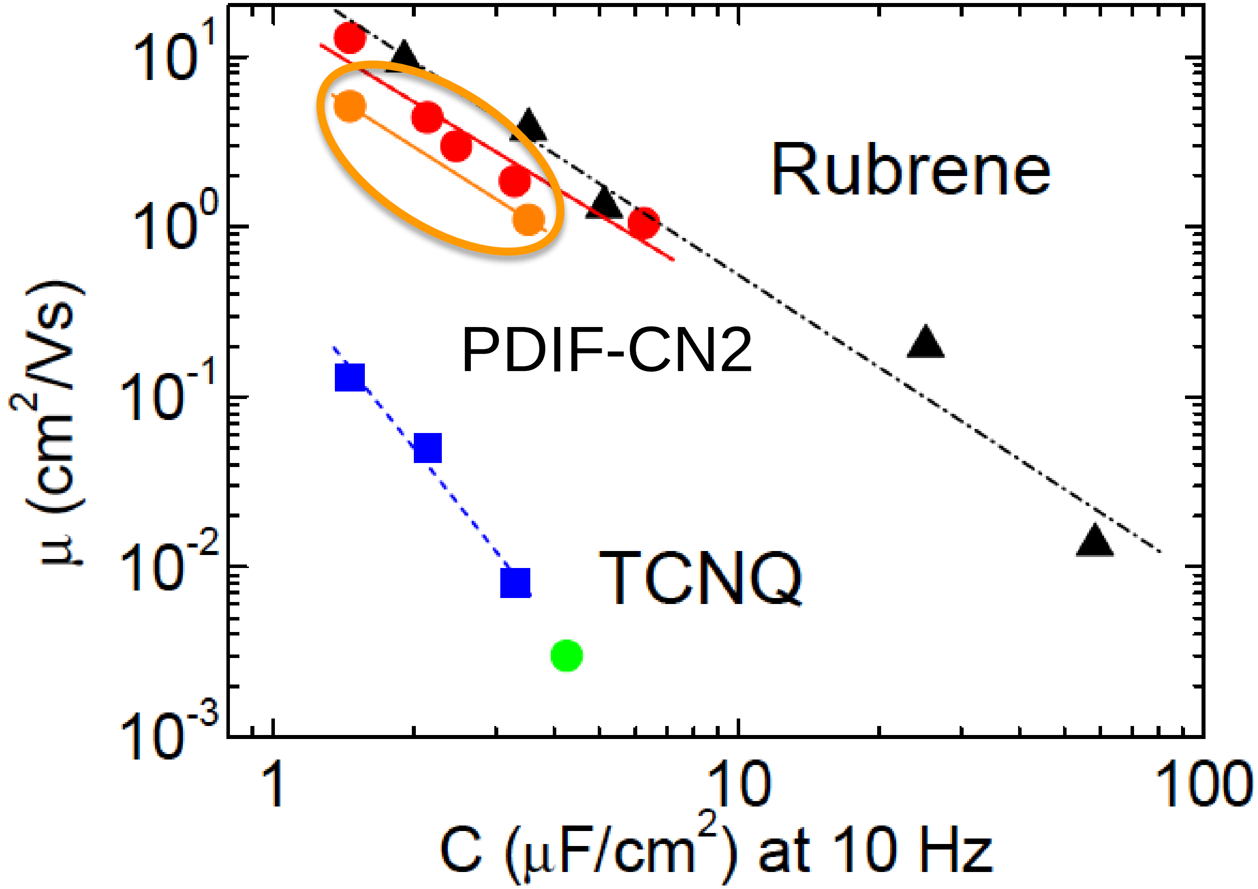




π-conjugated perylene layer is sandwiched with long fluorocarbon chain

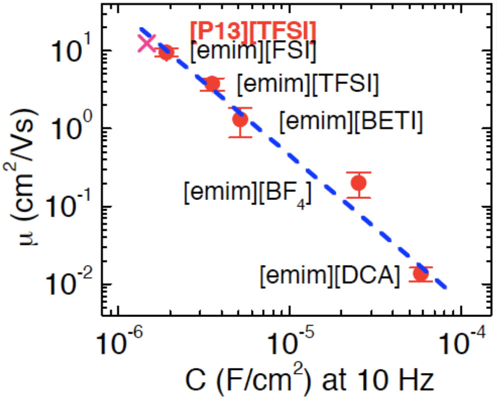
PDIF-CN$_2$ (n-type)
μ_{4T} = 5.1 cm^2/Vs
σ^T = 6.1 μS/V

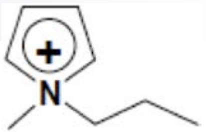
Discussion



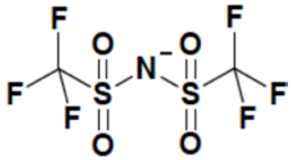
Indeed PDIF-CN2 show similar slope as Rubrene single crystals

Best performance of OFETs with ionic liquids



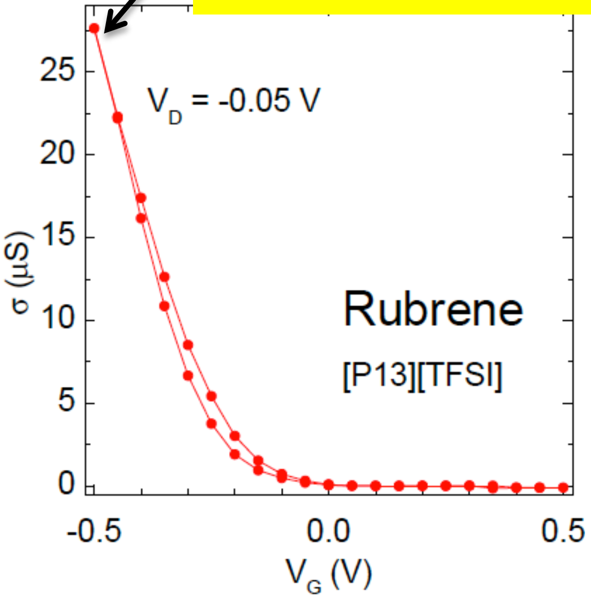


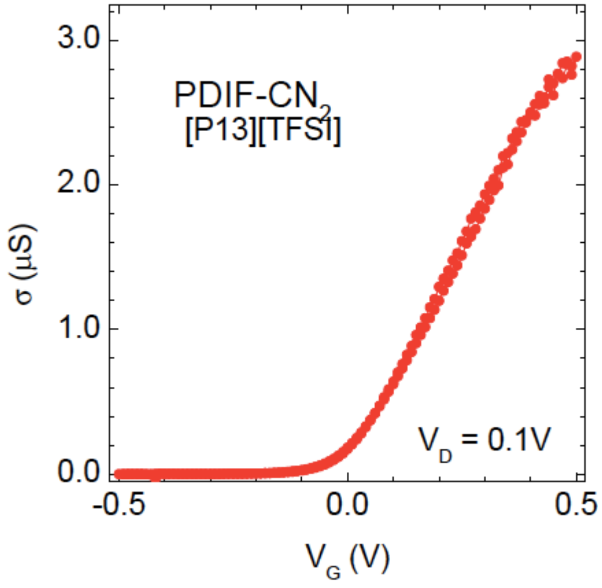
[P13]



[TFSI]

Channel sheet resistance 36 kΩ



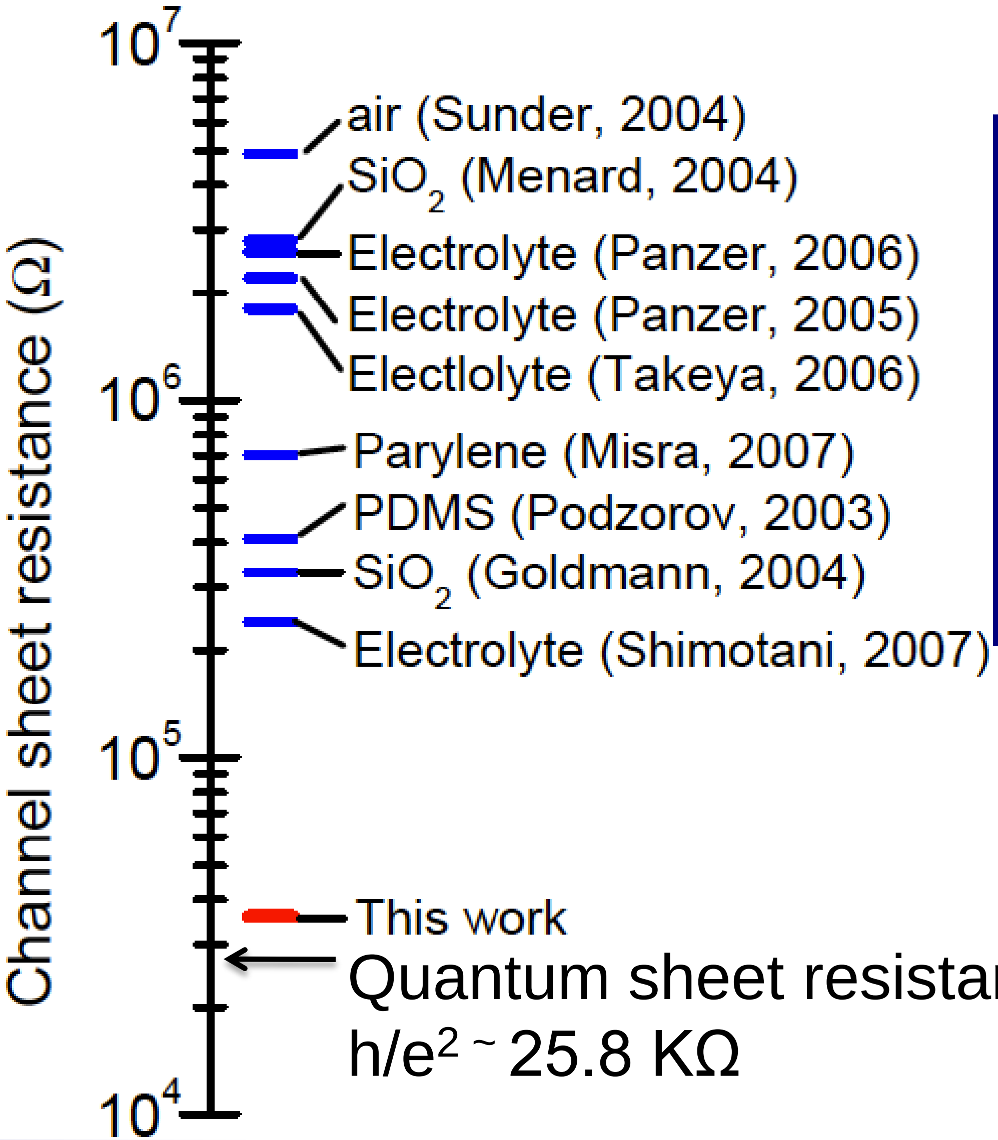


Rubrene (p-type)
μ_{4T} = **12.4 cm²/Vs**
σ^T = **60.3 μS/V**

PDIF-CN$_2$ (n-type)
μ_{4T} = **5.1 cm²/Vs**
σ^T = **6.1 μS/V**

S. Ono *et al.*, APL **97** 143307 (2010).

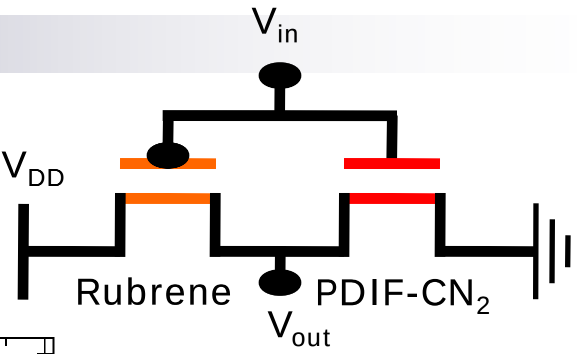
Where are we now ?

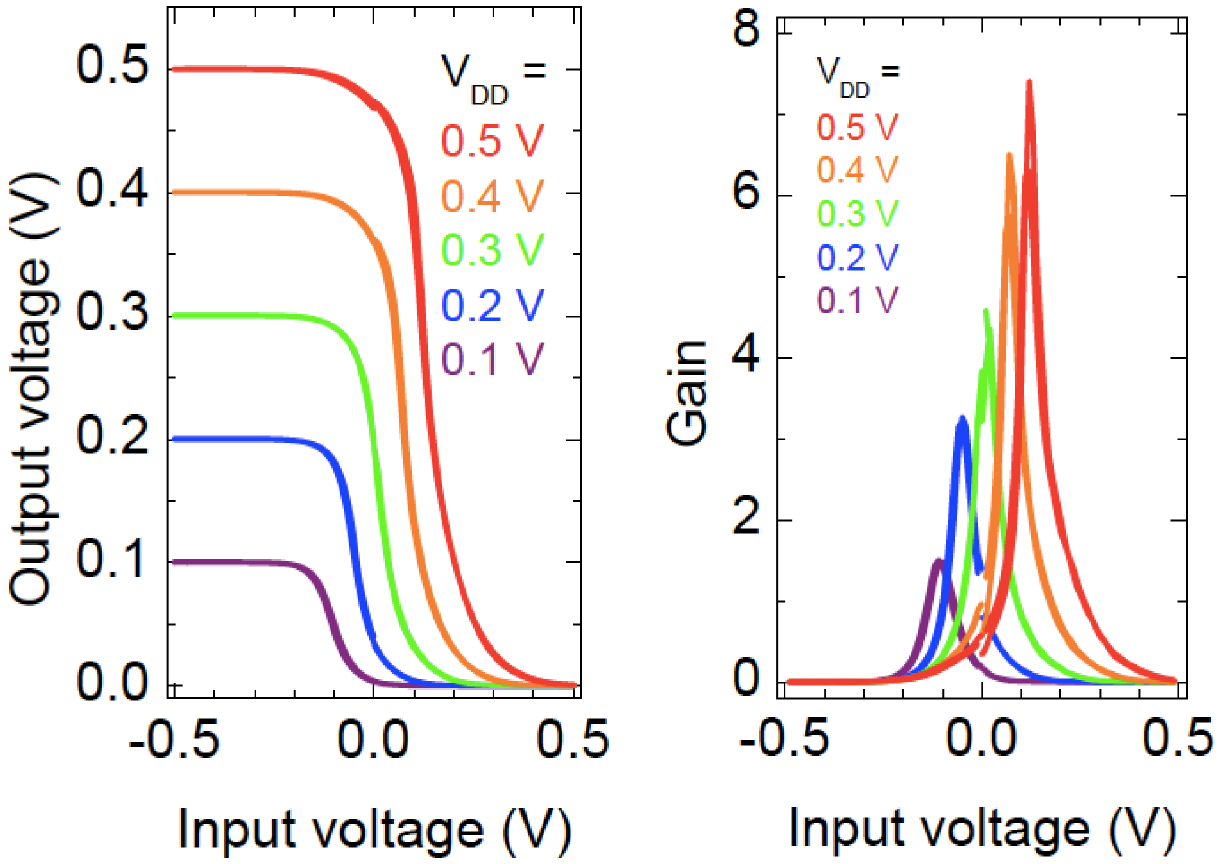


Quantum sheet resistance

$h/e^2 \sim 25.8$ KΩ

Complementary inverter





(0.1 V/s)

Large voltage gain (dV_{out}/dV_{in} ~ 7) is obtained with very small voltages

All inverter show remarkably small hysteresis

Summary

We investigate OFETs with various ionic liquids as gate dielectric.

We found that

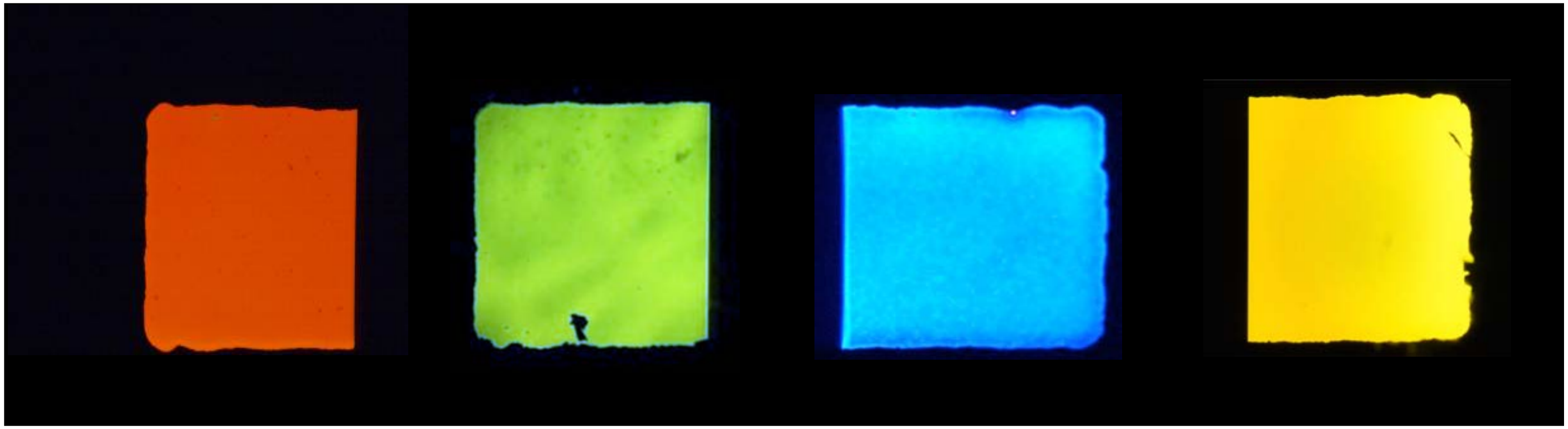
1) Mobility of both p-type and n-type OFETs increases with decreasing total capacitance of ILs, however does not depend on the ion species at the interface.

2) The coupling between mobile carrier and ILs is the key parameter for efficient carrier transport.

2 key factors

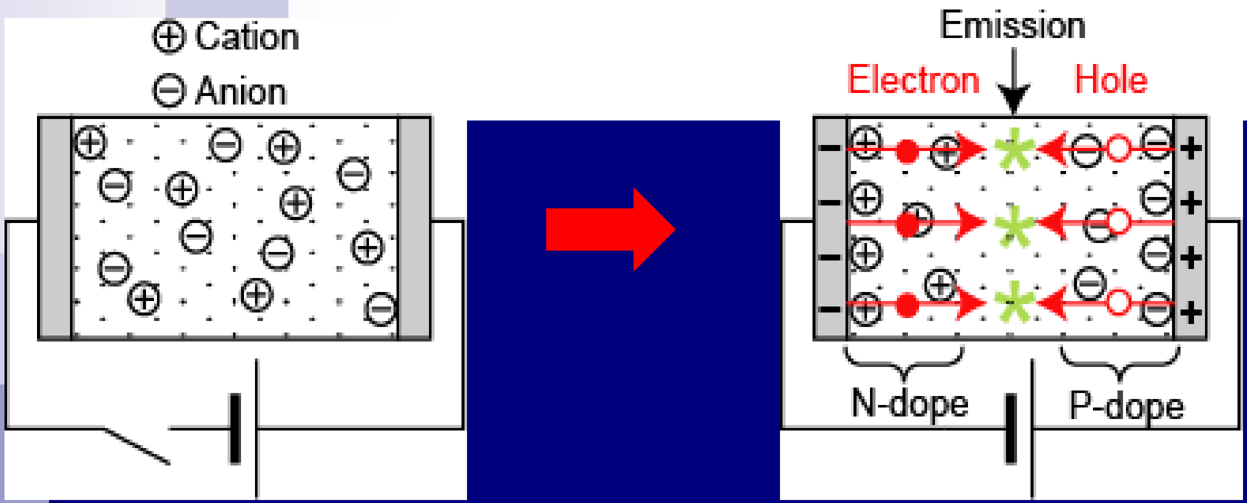
1) Increasing the distance between the π-core and interface
2) Weaken the interaction between ILs and charge carrier.

Light-emitting electrochemical cell with ionic liquids



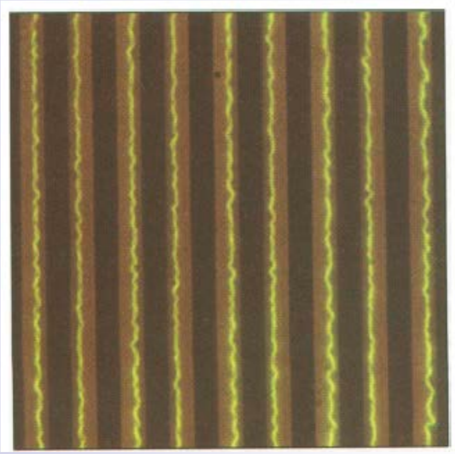
Nagoya Univ.
Prof. T. Sakanoue, Prof. T. Takenobu
CRIEPI
K. Miwa, Dr. M. Mongilo, L. Legrand, O. Badgot, M. Gaillard
Dr. D. Bragga and SO

Mechanism of LEC



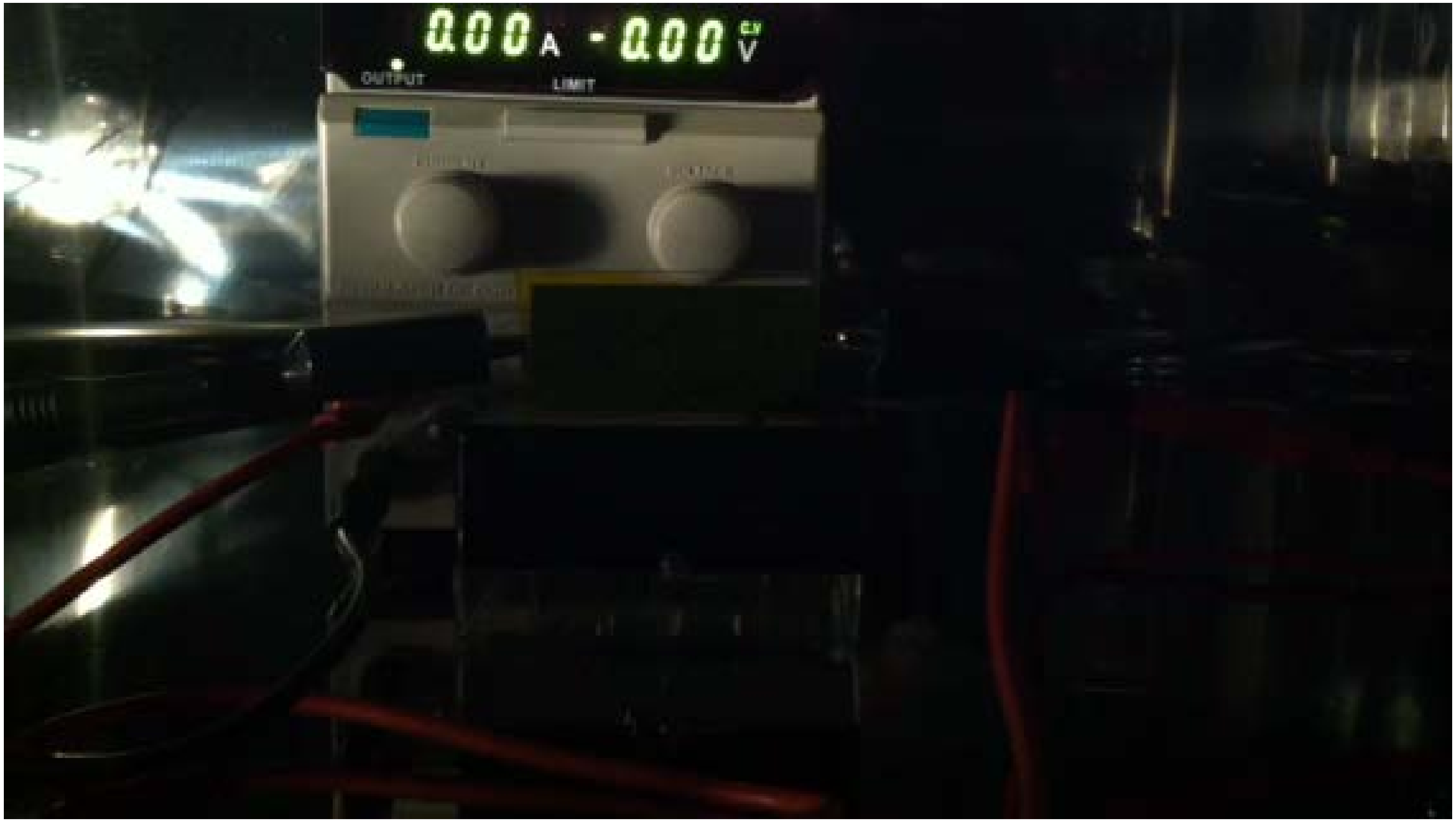
Self assembled P-N junction

Easy fabrication of devices



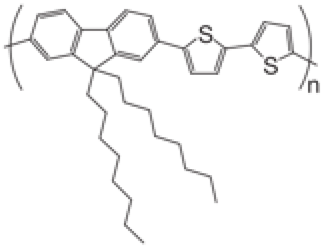
Q. Pai, A.J. Heeger et al., Science (1996)

Light-emitting electrochemical cell



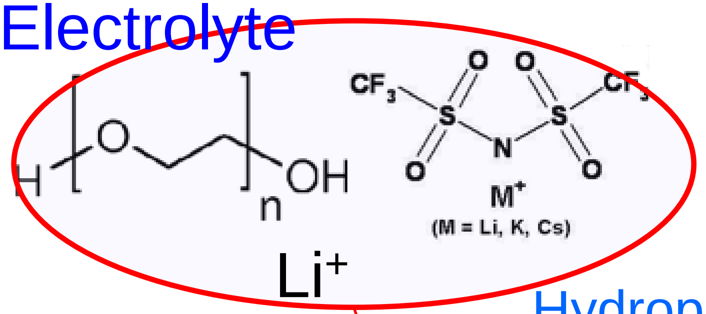
Why ionic liquids?

Fluorescent polymer (F8T2)



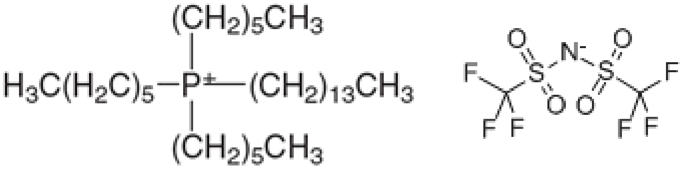
Hydrophobic

Electrolyte

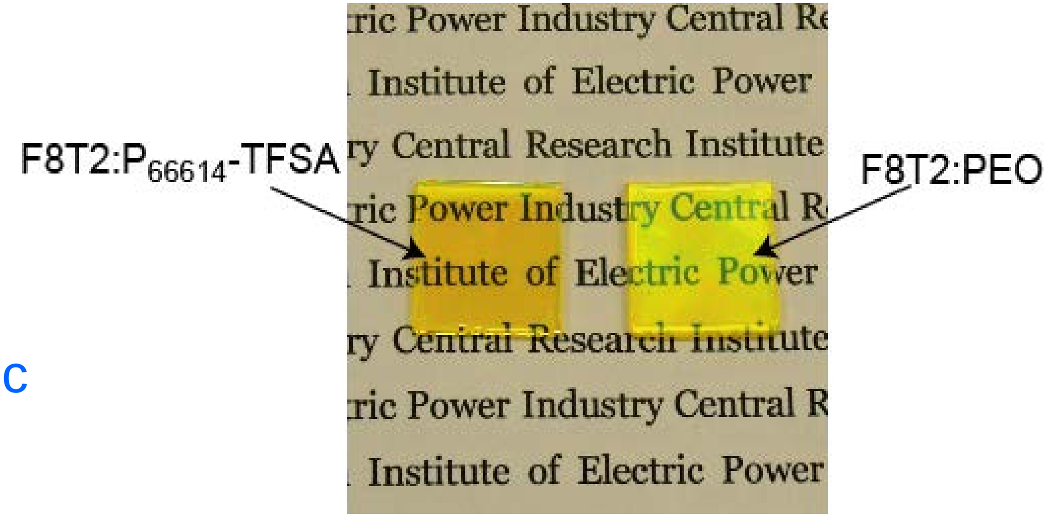


Hydrophilic

Ionic liquid; [P66614][TFSA]



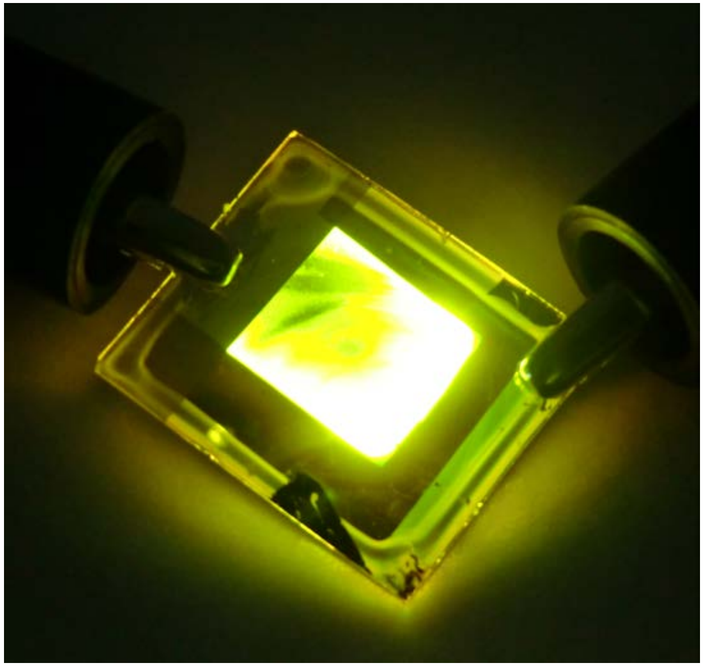
Hydrophobic

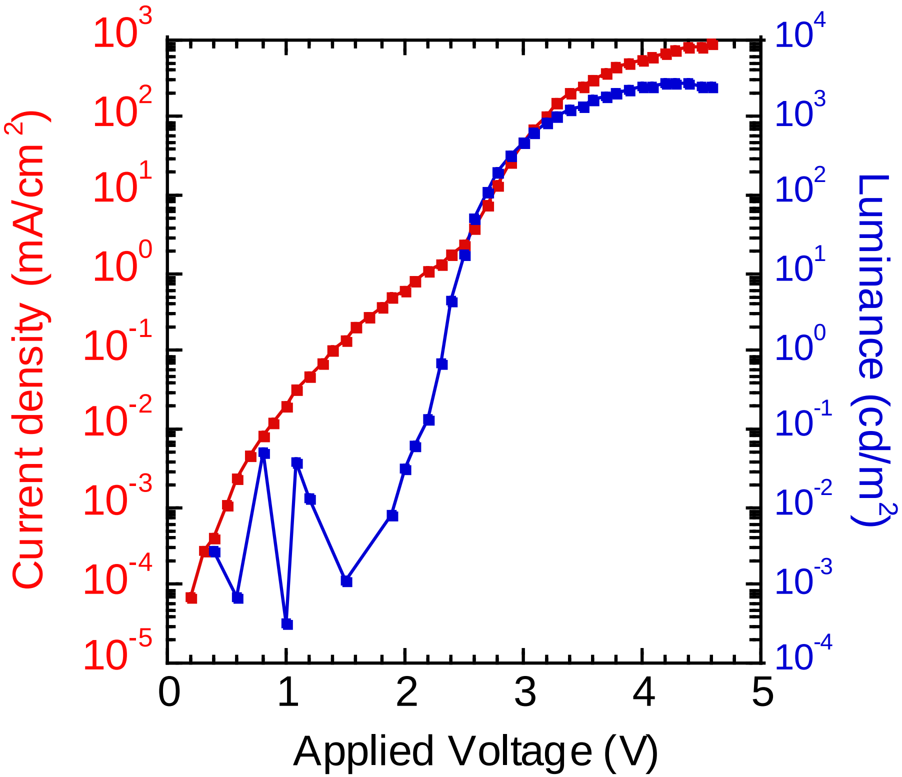


Thin film by spin coating
F8T2 : [P66614][TFSA] = 10:1

T. Sakanoue, S. Ono *et al.*,
APL **100** 263301 (2012).

Low voltage operation



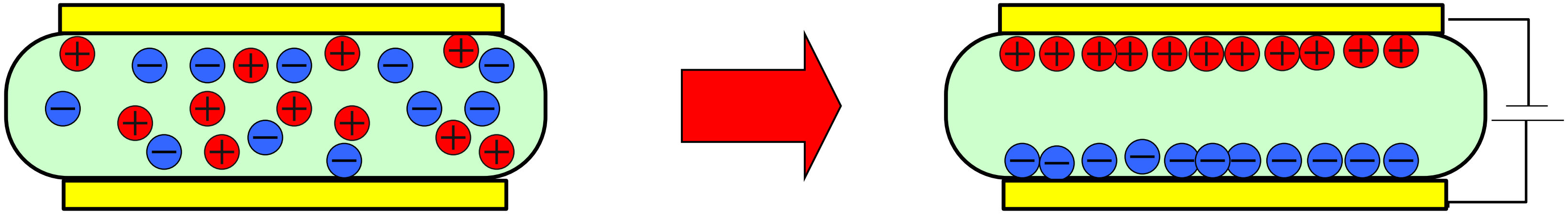


1.5 V is enough to obtain light.
Light emission up to 3000 cd/m^2!!!

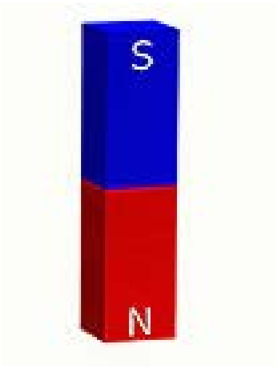
What is the next generation of iontronics?
Electric double layer electret

New electronics with fixed electric double layer

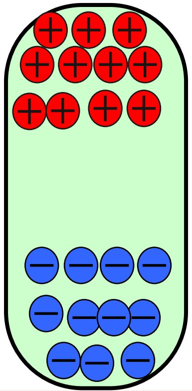
What is Electric double layer Electret?



Chemically connect ionic liquids and polymer after formation of electric double layer



Magnet

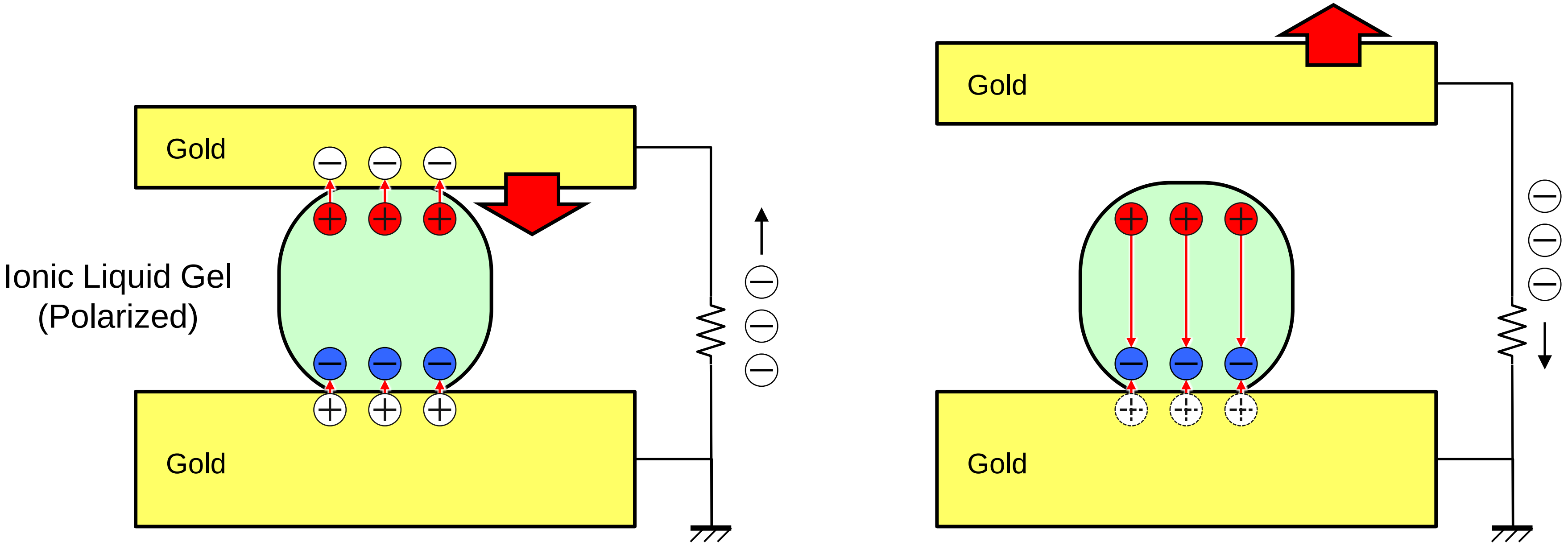


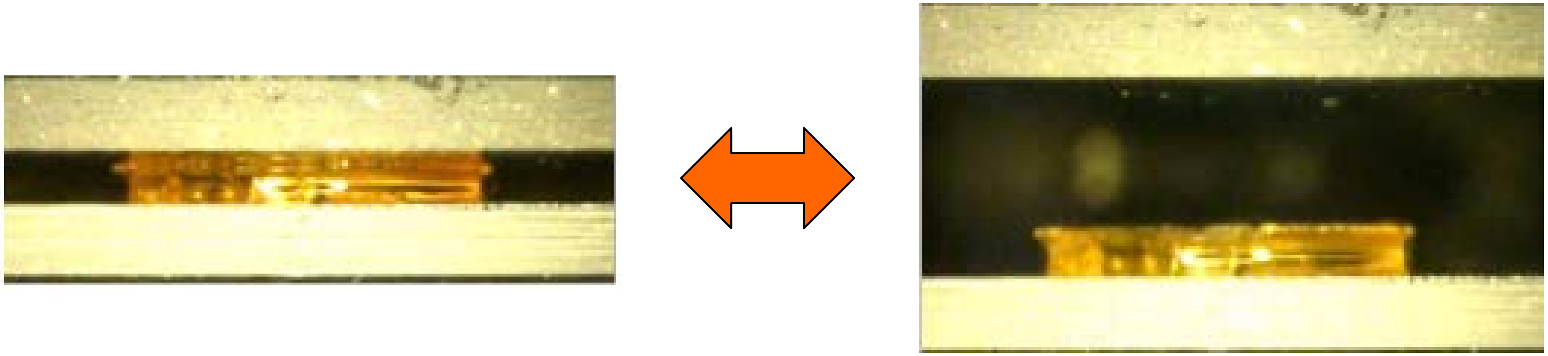
Electret

Instead of spin,
we fix dipole charges
To form electric double layer electret

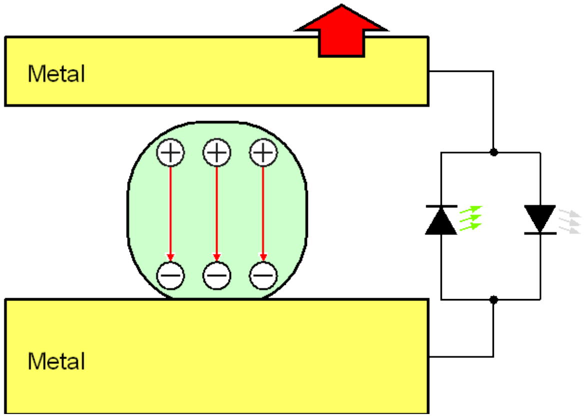
99 % of ions are fixed inside polymer networks

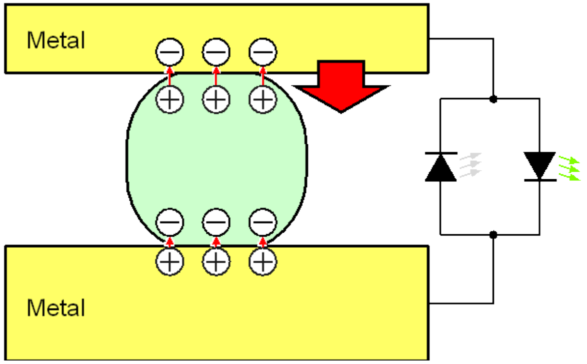
Energy harvester with Electric double layer electret





Demonstration





Output voltage above 2 V

Best performance so far

- Up to 1.2 mW/cm^2
- Output voltage as high as 2 V

Summary

- New type of energy harvester with electric double layer electrets is proposed

1) New concept of electric double layer electret
2) Generate current without external bias voltage
3) Large output power as high as 1.2 mW/cm^2 is obtained from low frequency vibrations

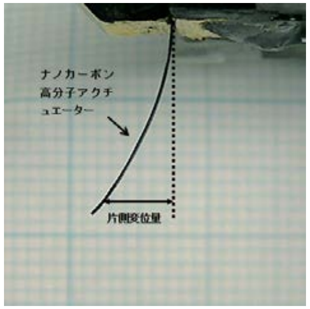
This work is partly supported by JST, NEDO

Summary

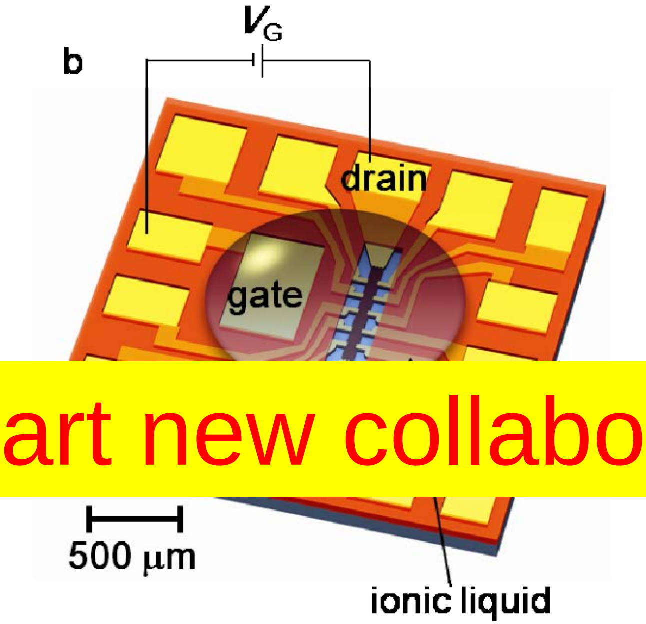
We can control almost all physical properties with ILs!!

The IL gating can be a promising technology to realize:

1) High-density carrier doping (up to 10^{15} cm^{-2})
2) Electric-field control of Metal-to-insulator transition
3) Electric-field control of Magnetism
4) New application (LEC, actuator)
5) New type of energy harvester



This technique can be applicable not only applications, but also new tool to study solid-state physics.



Let’s start new collaborations