About OMICS Group

OMICS Group International is an amalgamation of Open Access publications and worldwide international science conferences and events. Established in the year 2007 with the sole aim of making the information on Sciences and technology 'Open Access', OMICS Group publishes 400 online open access scholarly journals in all aspects of Science, Engineering, Management and Technology journals. OMICS Group has been instrumental in taking the knowledge on Science & technology to the doorsteps of ordinary men and women. Research Scholars, Students, Libraries, Educational Institutions, Research centers and the industry are main stakeholders that benefitted greatly from this knowledge dissemination. OMICS Group also organizes 300 International conferences annually across the globe, where knowledge transfer takes place through debates, round table discussions, poster presentations, workshops, symposia and exhibitions.

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OMICS Group International is a pioneer and leading science event organizer, which publishes around 400 open access journals and conducts over 300 Medical, Clinical, Engineering, Life Sciences, Phrama scientific conferences all over the globe annually with the support of more than 1000 scientific associations and 30,000 editorial board members and 3.5 million followers to its credit.

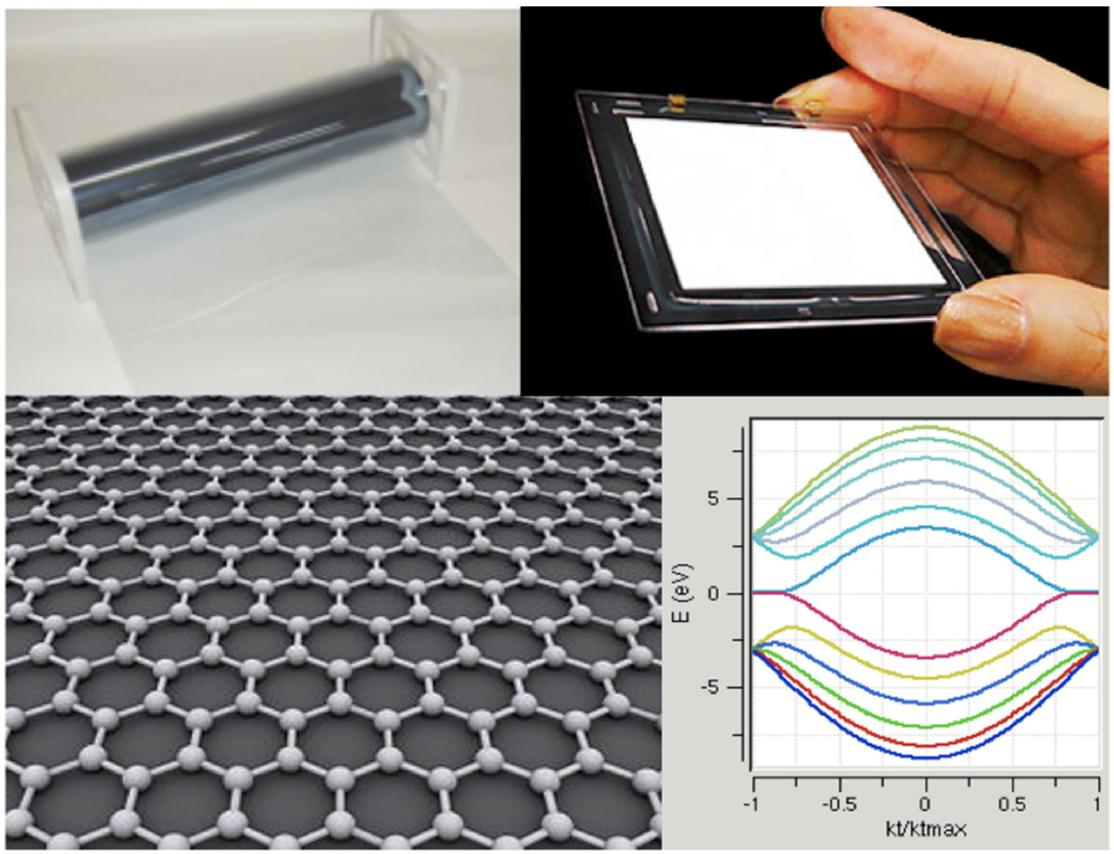
OMICS Group has organized 500 conferences, workshops and national symposiums across the major cities including San Francisco, Las Vegas, San Antonio, Omaha, Orlando, Raleigh, Santa Clara, Chicago, Philadelphia, Baltimore, United Kingdom, Valencia, Dubai, Beijing, Hyderabad, Bengaluru and Mumbai.

Molecular design and electronic properties of new doping system: Pure organic TTF-based salt-bridged crystals

Yuka Kobayashi
National Institute for Materials Science (NIMS), Tsukuba, Japan
Collaborators: Dr. T. Terauchi (NIMS), Dr. S. Sumi (NIMS), Dr. Y. Matsushita (NIMS)

Why organic ?

Light, Flexible, Eco-friendly

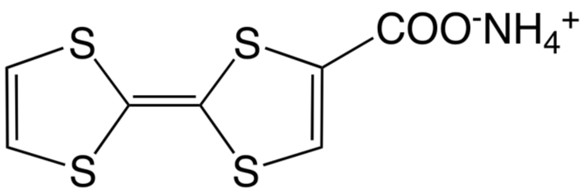


Unique physical properties

Carrier generation in pure organic compounds

No external components

Defect-induction doping



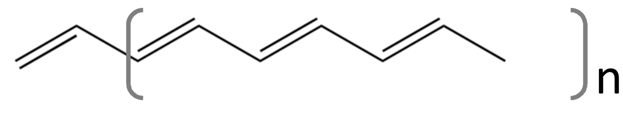
Semiconductor σ_{rt} = 10^{-4} S/cm

Kobayashi Y., Yoshioka M., Saigo K., Hashizume D., Ogura T.
J. Am. Chem. Soc. **2009**, *131*, 9995-10003.

No external dopant
No electrochemical oxidation

Addition of components

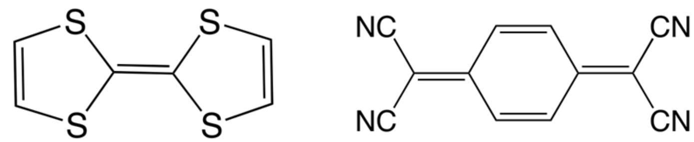
Conducting polymer



Polyacetylene with X_2

Shirakawa, H.; McDiarmid, A.; Heeger, A.
Chem. Comm. **1977**.

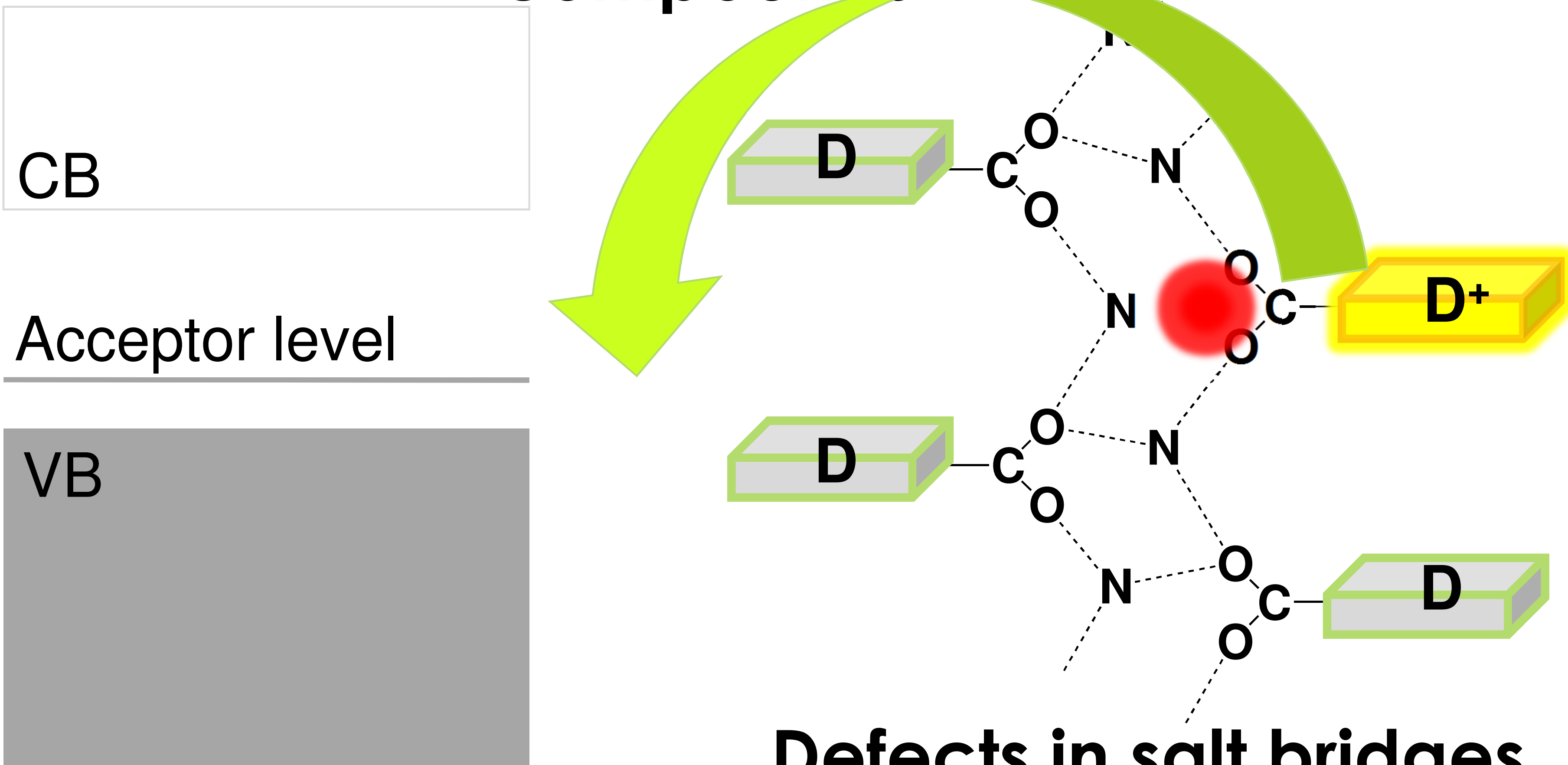
Charge transfer (CT) complex



TTF-TCNQ

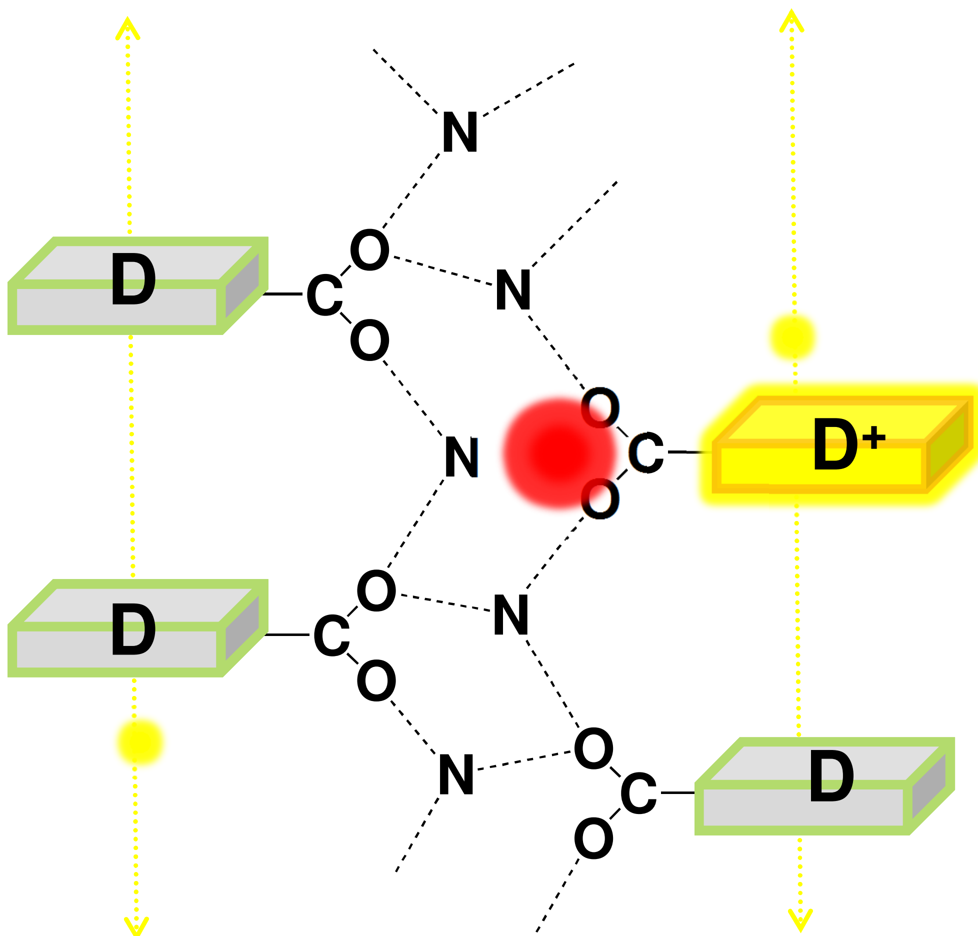
Mulliken, R. S. *J. Am. Chem. Soc*. **1952**.

New strategy for doping in pure organic compounds

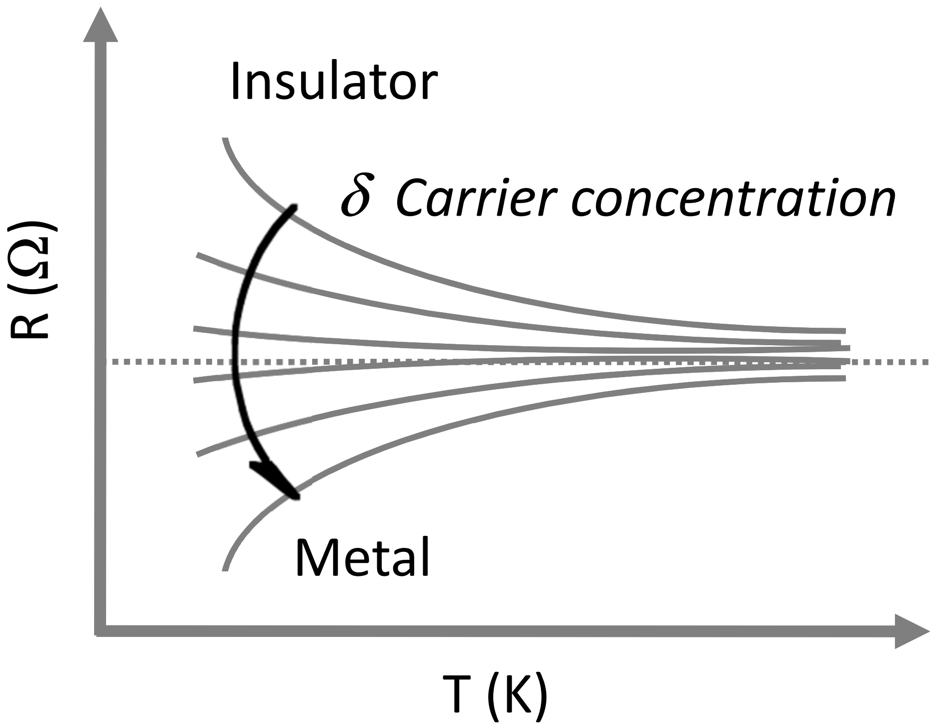


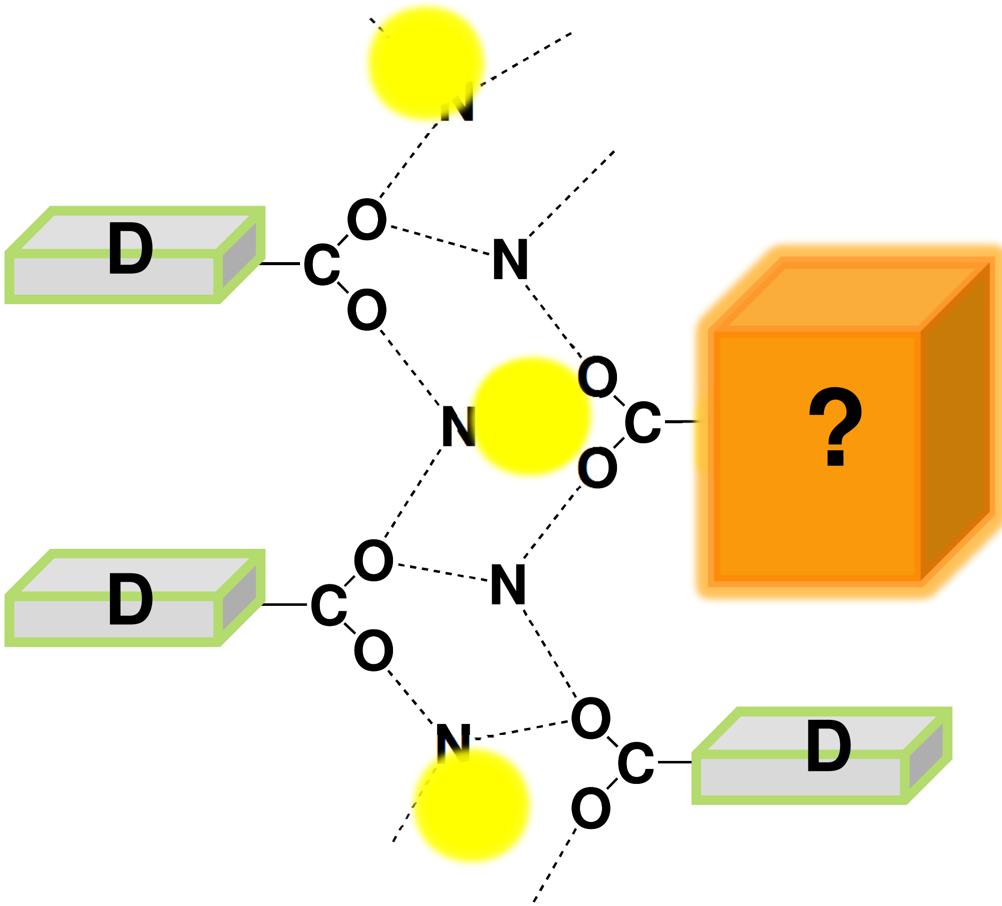
Defects in salt bridges

1: Mobile dopant via proton transport



2: Conductivity Control by Molecular Design





Contents

- Defect-induction doping utilizing salt bridges
- Electronic properties of a new doping system

  1. Thermopower (Effect of mobile dopant)

  2. Metalization (Effect of molecular design)

Defect-induction doping

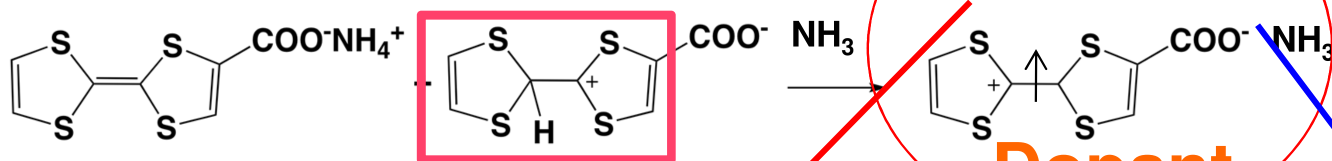
Solution

Cf. Protonation of TTF
M. Giffard et al.
Adv. Mater. **1994**, *6*, 298

Kobayashi, Y. et al. JACS **2009**

TTFCOO$^-$NH$_4^+$

TTF$^{\bullet+}$COO$^-$NH$_3$

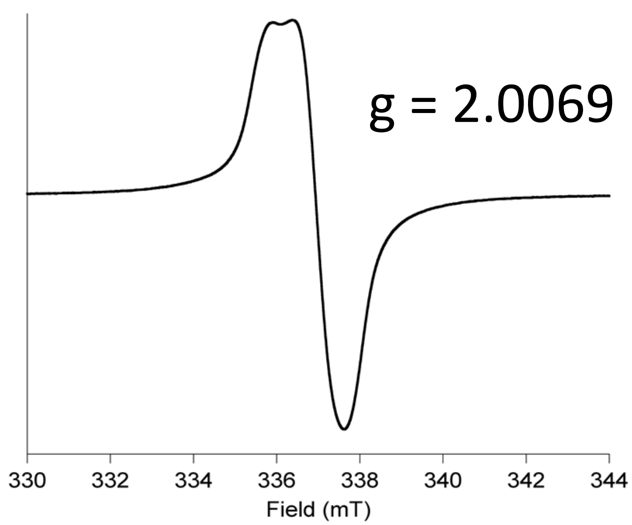


^{1}H NMR, ESI-TOF-MS *^{1}H NMR, ESI-TOF-MS*

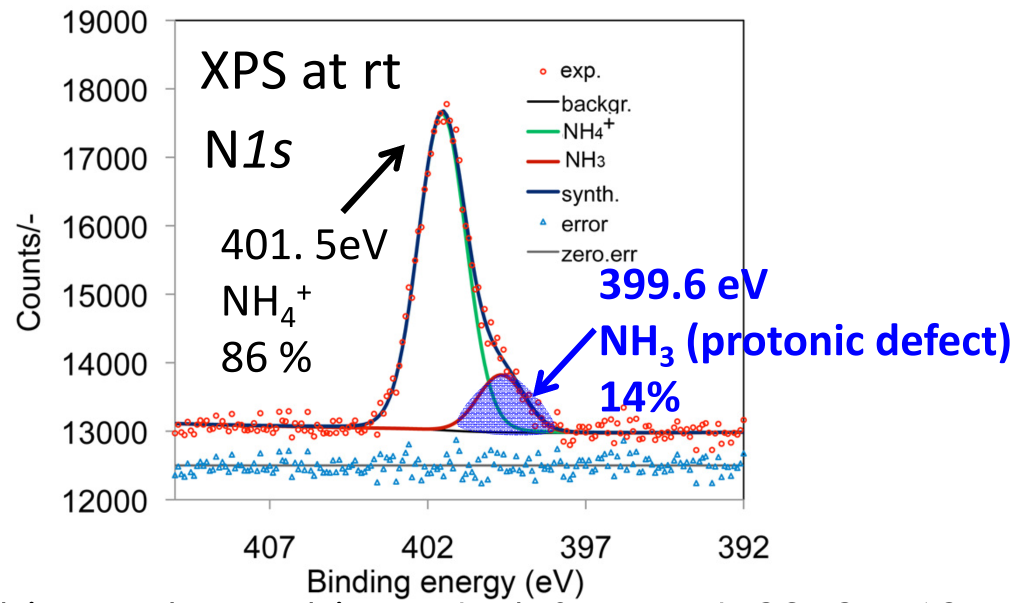
Solid

TTF$^{\bullet+}$COO$^-$: 16 %

ESR at rt



Protonic defect: 14 %



Terauchi, T. Kobayashi, Y. et al. Syn.Met. **2012**, *162*, 531

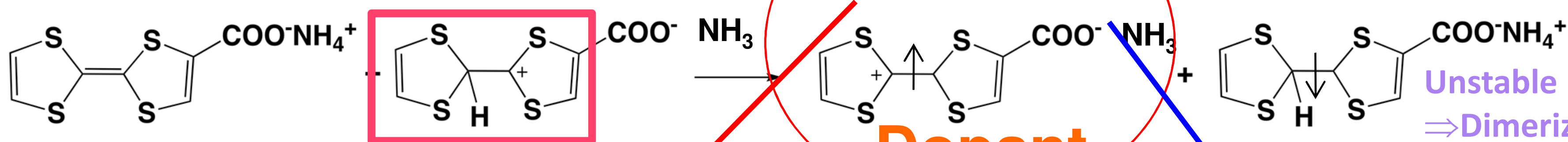
Defect-induction doping

Solution

Cf. Protonation of TTF
M. Giffard et al.
Adv. Mater. **1994**, *6*, 298

Kobayashi, Y. et al. JACS **2009**

$TTFCOO^{-}NH_4^{+}$



Dopant

Unstable byproduct
⇒Dimerization

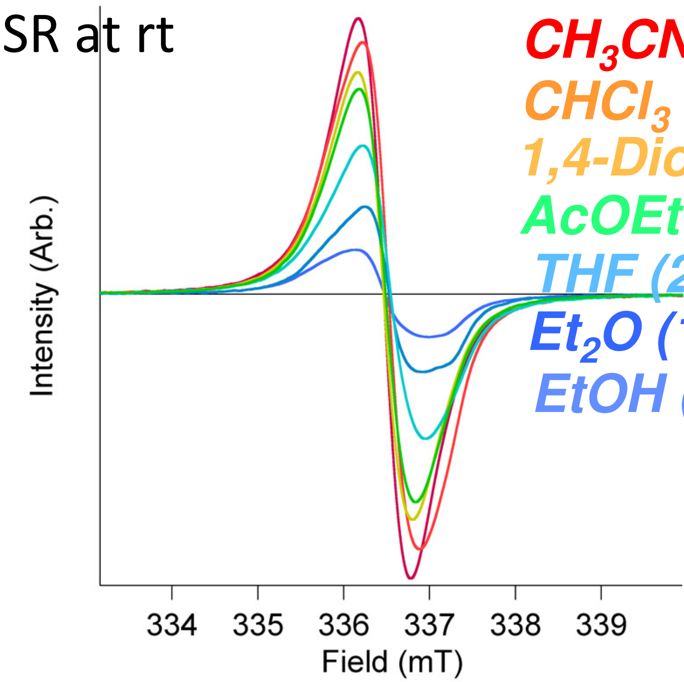
¹H NMR, ESI-TOF-MS

¹H NMR, ESI-TOF-MS

Solid

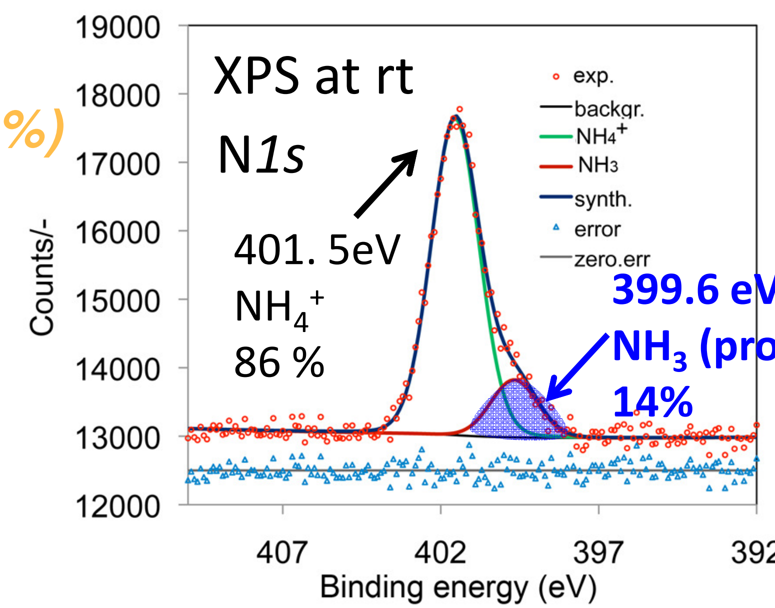
$TTF^{\bullet+}COO^{-}$: 9-33 %

ESR at rt



CH_3CN (33%)
$CHCl_3$ (33%)
1,4-Dioxane (29%)
AcOEt (27%)
THF (24%)
Et_2O (16%)
EtOH (9%)

Protonic defect: 14 %



Terauchi, T. Kobayashi, Y. et al. Syn.Met. **2012**, *162*, 53

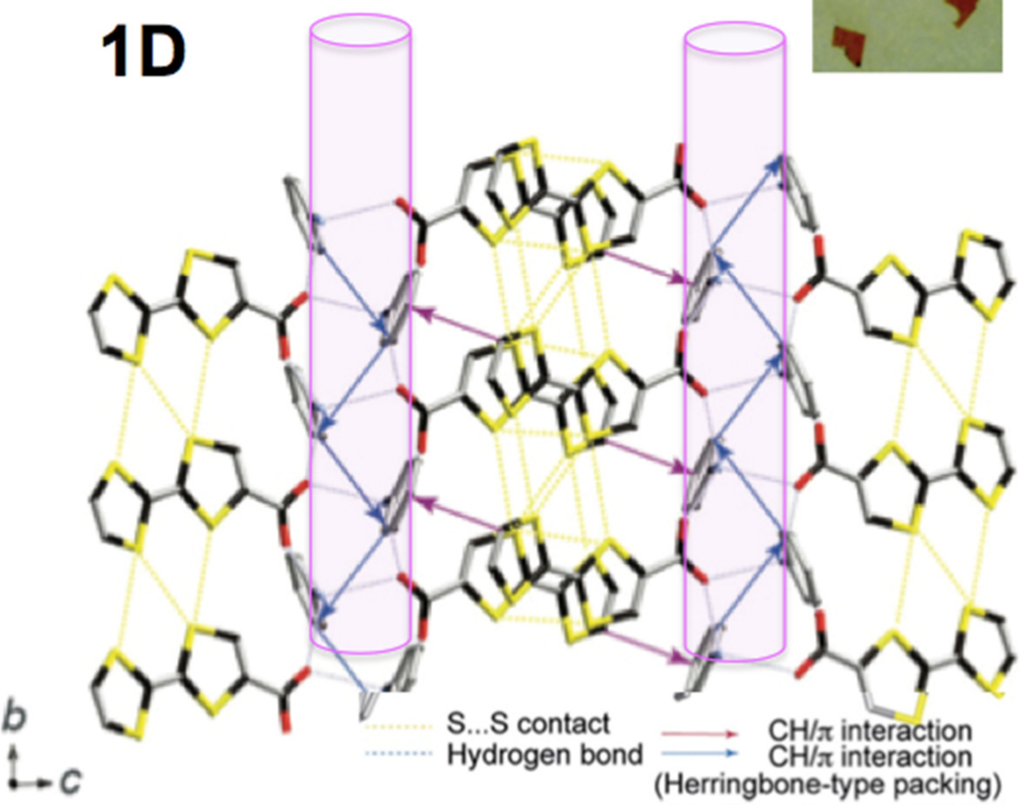
1D and 2D salt-bridged conductor, $TTFCOONH_3X$

$TTFCOONH_3Ph$

$[TTFCOONH_3Ph)_{1-x}(TTFCOONH_2Ph)_x]$

X = 0.25 (XPS evaluation)

1D



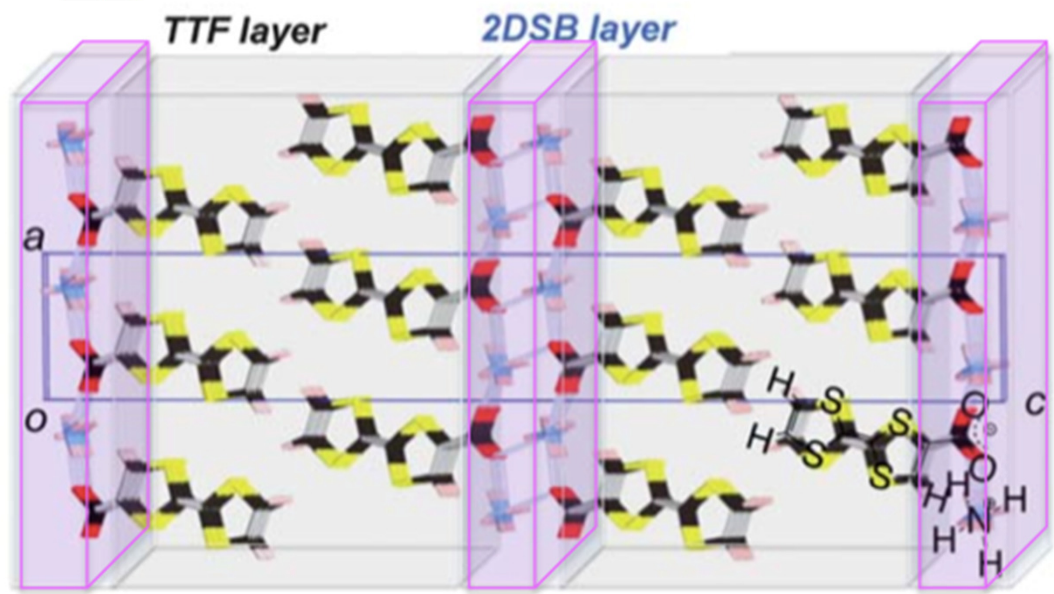
Dalton trans. **2013**

$TTFCOONH_4$

$[TTFCOONH_4)_{1-x}(TTFCOONH_3)_x]$

X = 0.16 (XPS evaluation)

2D



JMCA **2013**

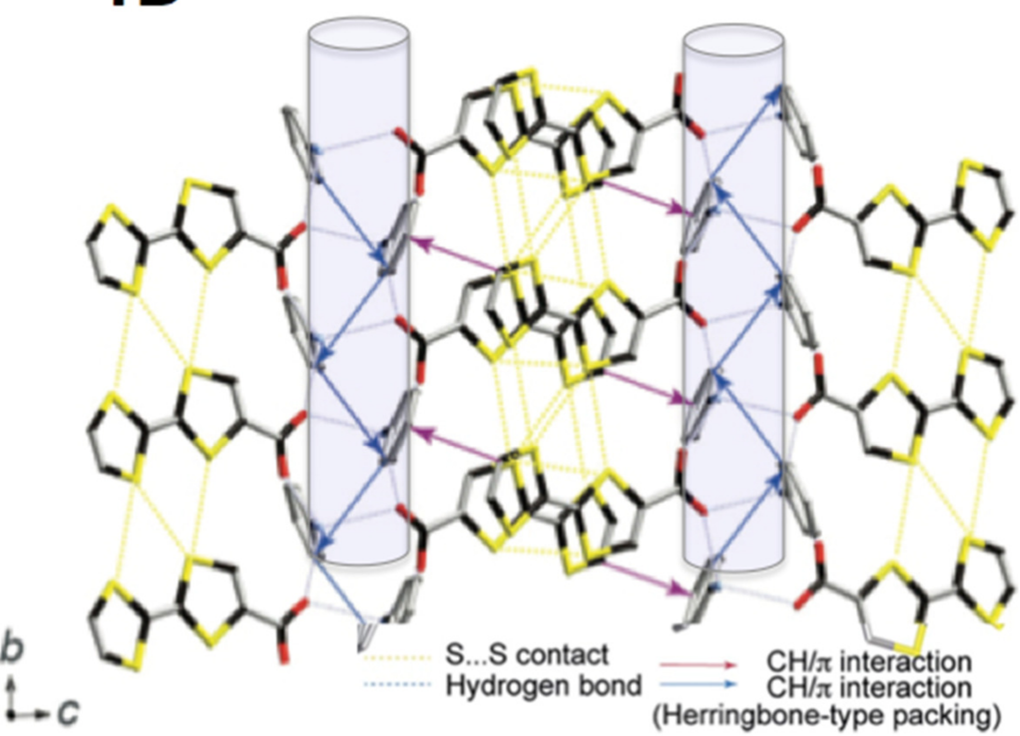
Isotope Substitution of Salt Bridge

TTFCOOND$_3$Ph
[TTFCOOND$_3$Ph)$_{1-x}$(TTFCOOND$_2$Ph)$_x$]
X = 0.20 (XPS evaluation)

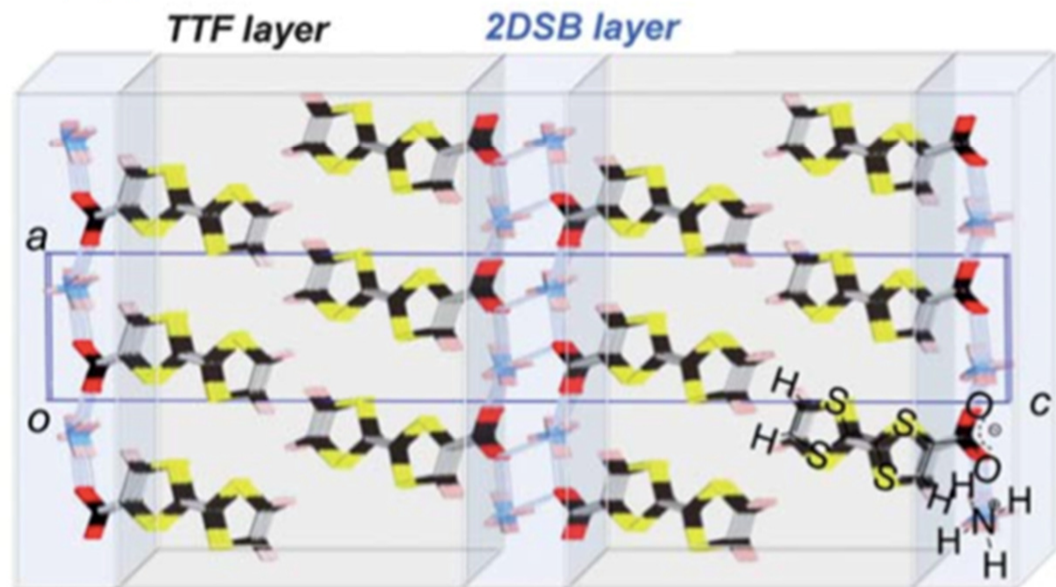
TTFCOOND$_4$
[TTFCOOND$_4$)$_{1-x}$(TTFCOOND$_3$)$_x$]
X = 0.13 (XPS evaluation)

Very similar chemical characteristics

1D



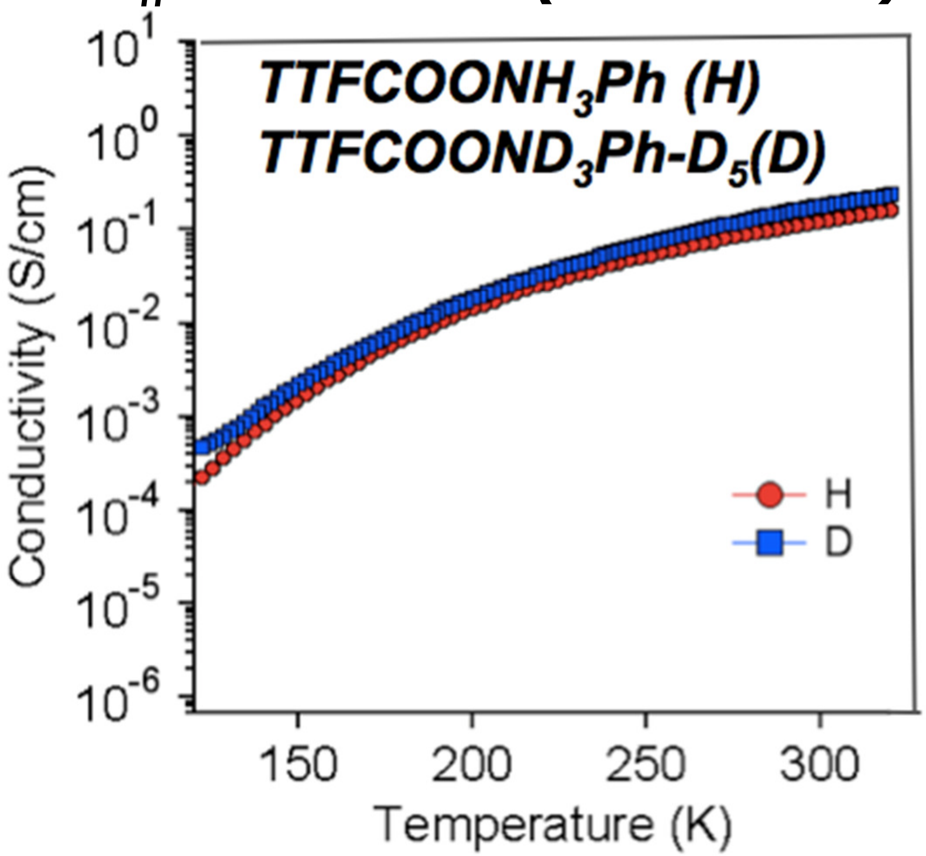
2D



Isotope Effect in DC conductivity

1D

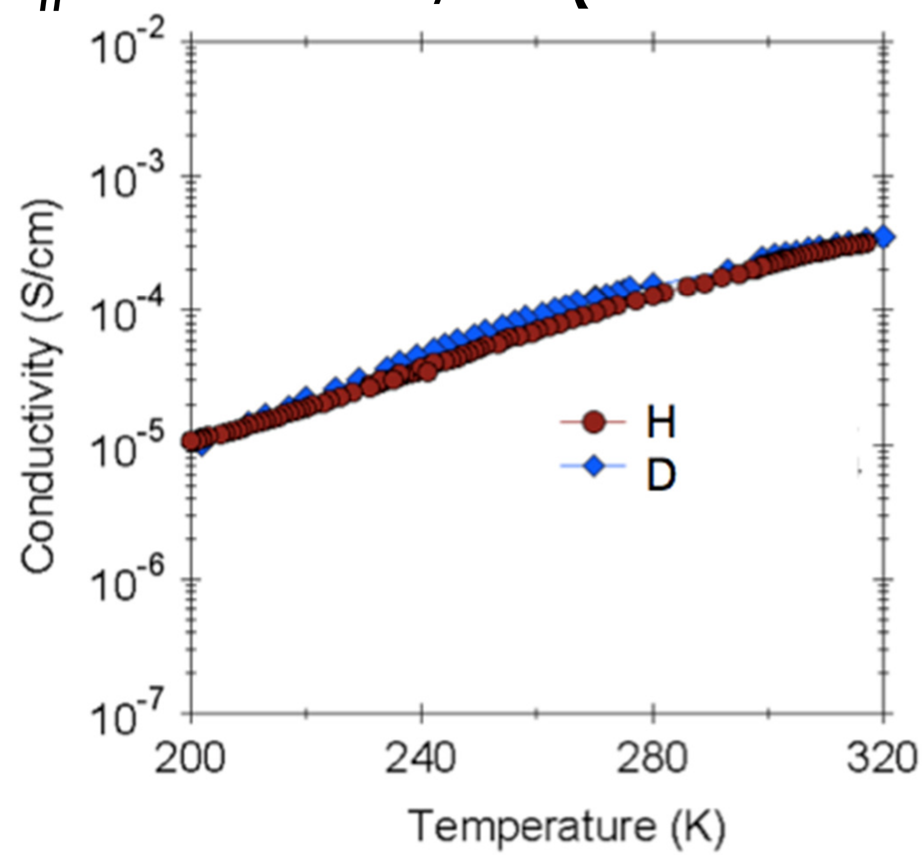
H: σ_{rt} ***= 0.16 S/cm (Ea = 0.11 eV)***
D: σ_{rt} ***= 0.18 S/cm (Ea = 0.10eV)***



Solid State Comm. **2013** *Dalton Trans.* **2013**

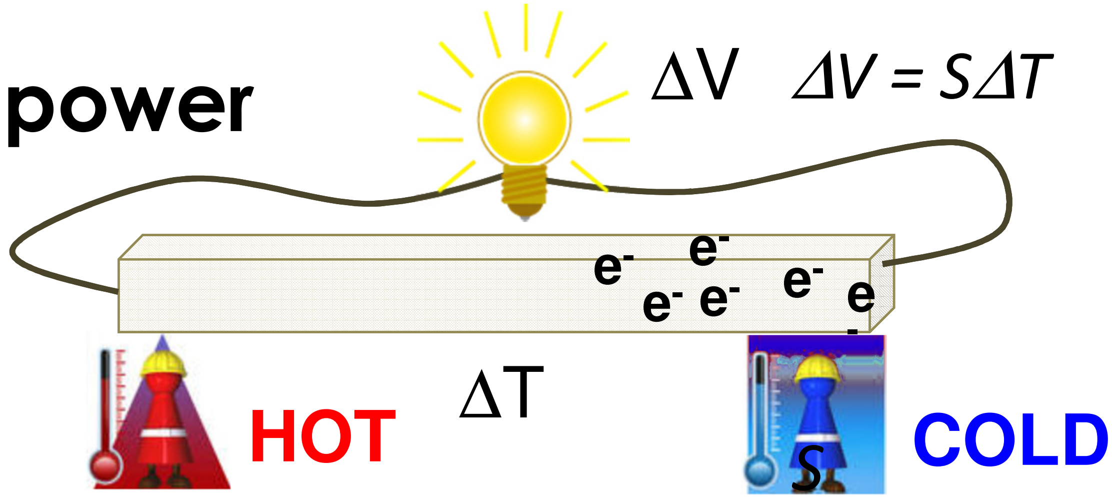
2D

H: σ_{rt} ***= 2.0 x 10***$^{-4}$ ***S/cm (Ea = 0.16 eV)***
D: σ_{rt} ***= 5.5 x 10***$^{-4}$ ***S/cm (Ea = 0.19 eV)***



JACS **2009**

Isotope effect in thermopower



Thermopower at rt

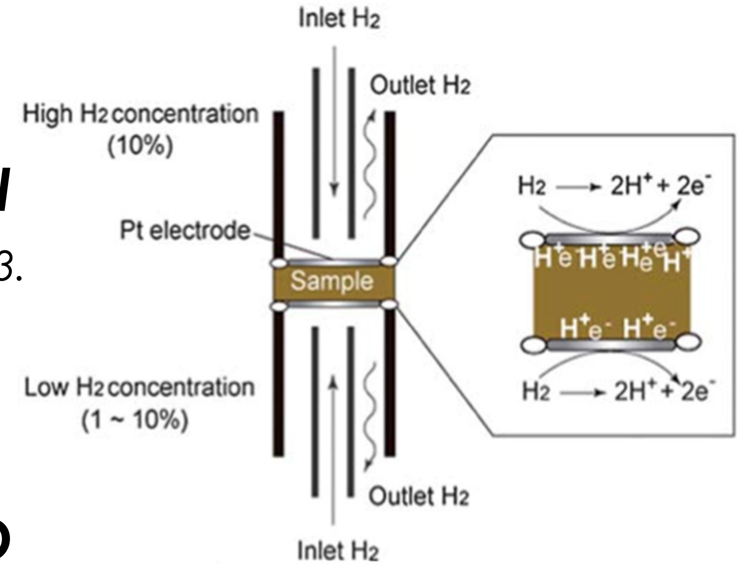
	1D S (μV/K) (rt)	2D S (μV/K) (rt)
H	**102**	**260**
D	**48**	**130**

Euro. JIC, **2014.** *J.Mater.Chem. A*, **2013.**

Isotope Effect in Proton Transport

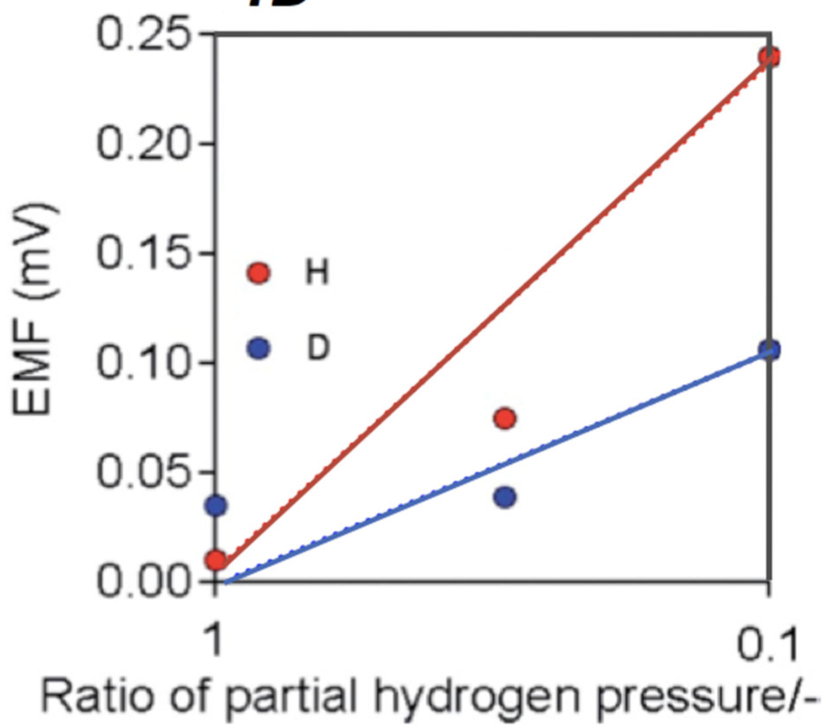
Hydrogen concentration cell

Iwahara, H. Solid State Ionics,1988, 28, 573.

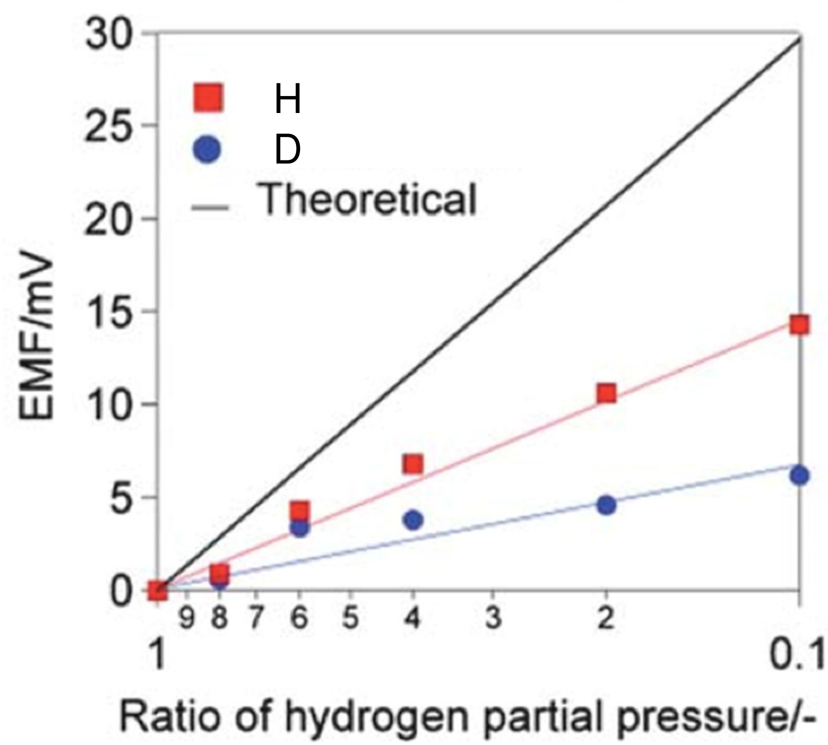


Proton transport ability at rt under anhydrous condition

1D



2D

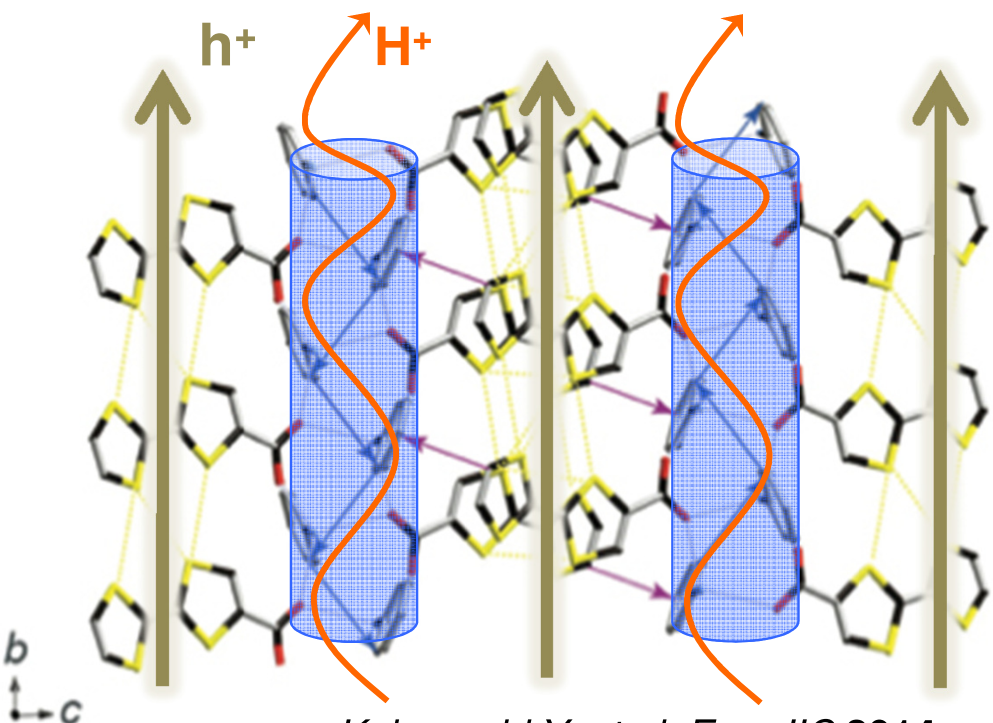


Role of mobile proton in thermopower

***TTFCOONH$_3$Ph** (1D system)*

Thermopower **H/D = 2.15**

Proton transport **H/D = 2.18**

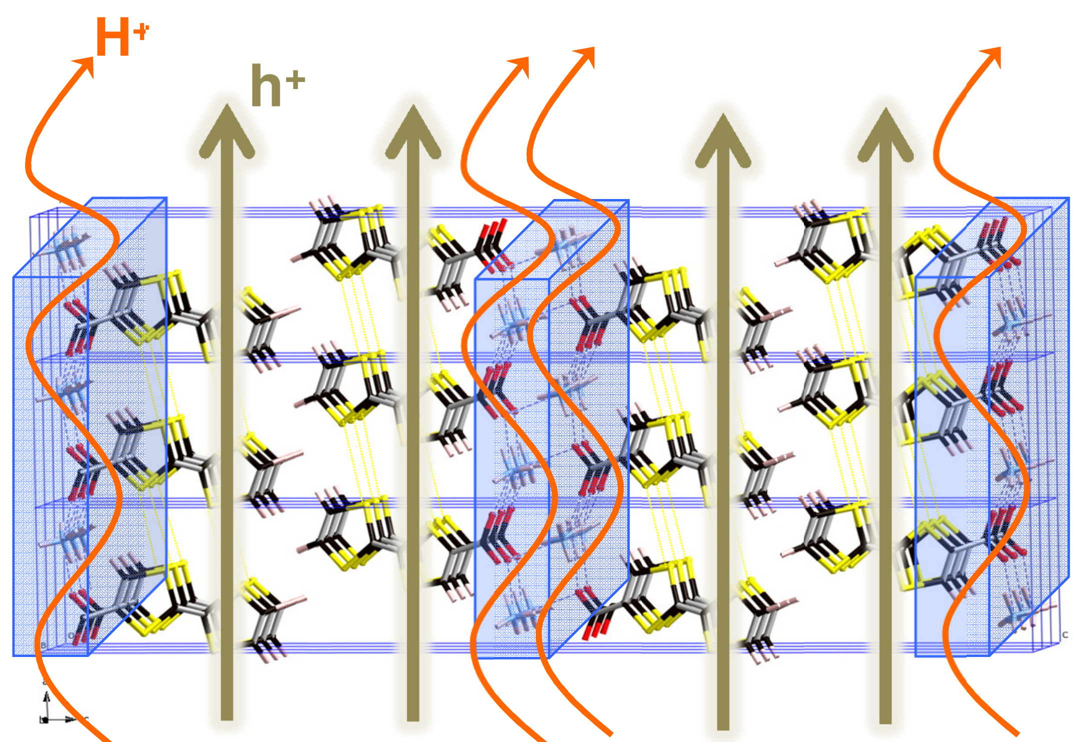


Kobayashi Y. et al. EuroJIC **2014**

***TTFCOONH$_4$** (2D system)*

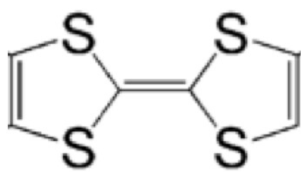
Thermopower **H/D = 2.41**

Proton transport (**H/D = 2.18**



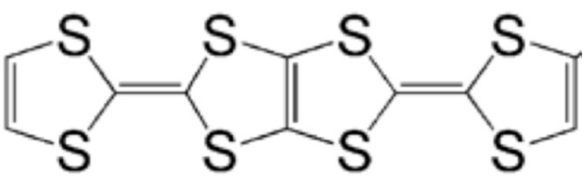
Kobayashi Y. et al. J. Mater. Chem. A **2013**

Molecular design for increasing conductivity

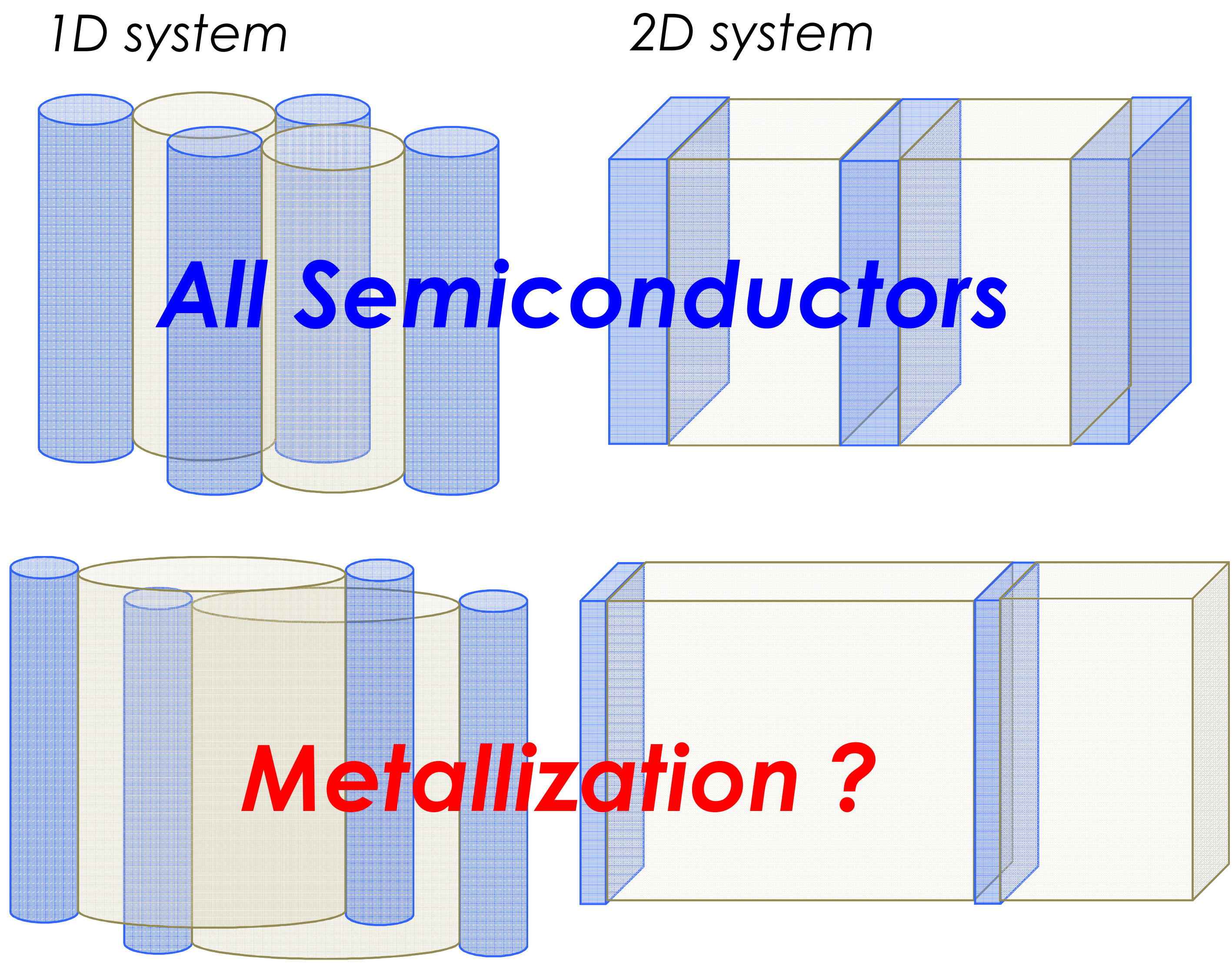


TTF

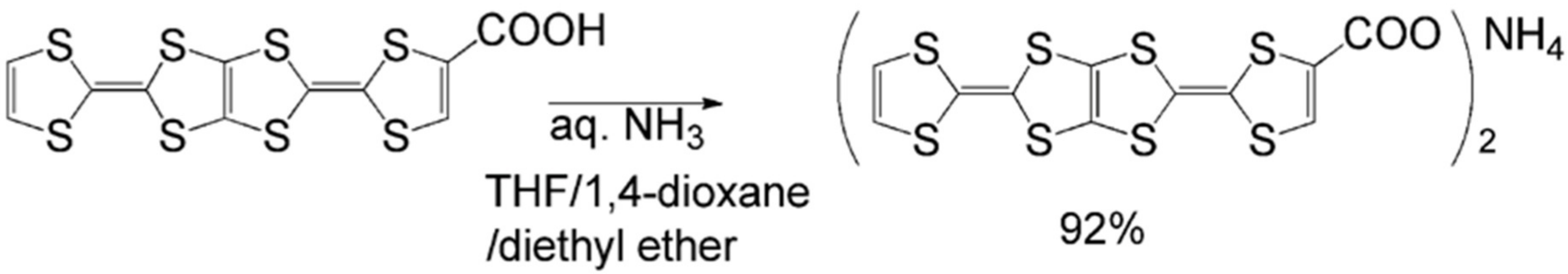
Extension of π-conjugate part



Tetrathiapentalene (TTP)



Molecular design for metallization



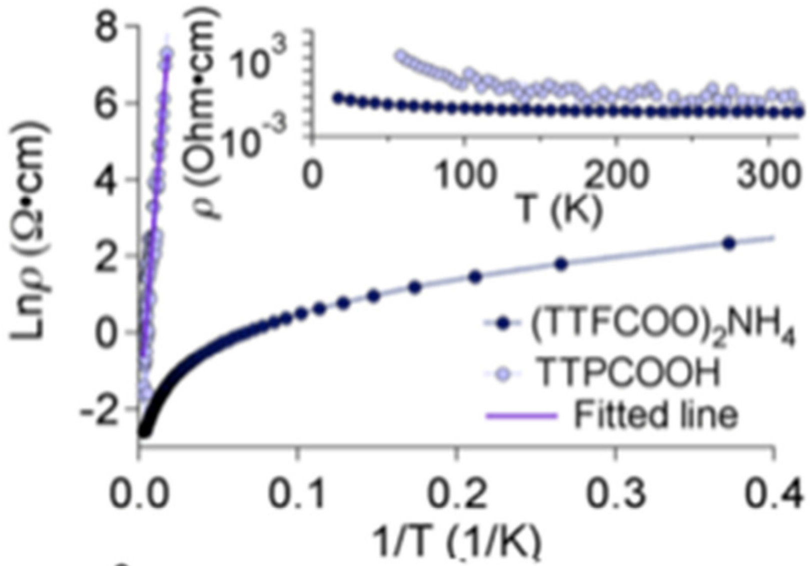
TTPCOOH

$[(TTPCOO^{-})_2NH_4^{+}]_{1-x}[(TTP^{\bullet +}COO^{-})_2NH_3]_x$

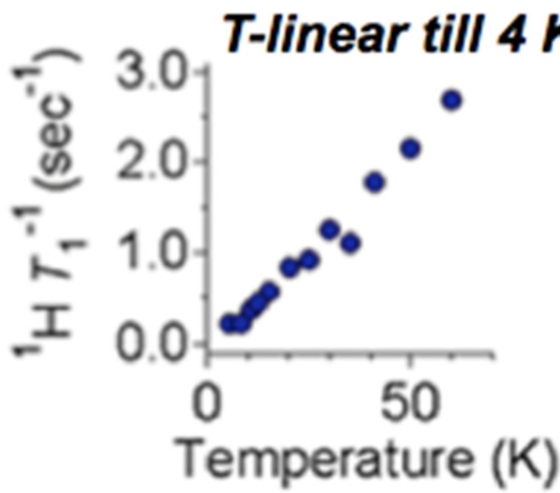
$\equiv (TTPCOO)_2NH_4$

Molecular metal prepared by defect induction

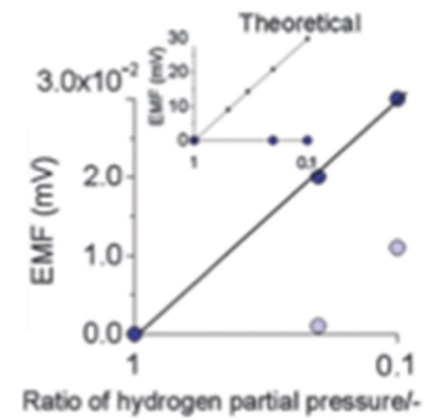
High conductivity, 13 S/cm at rt



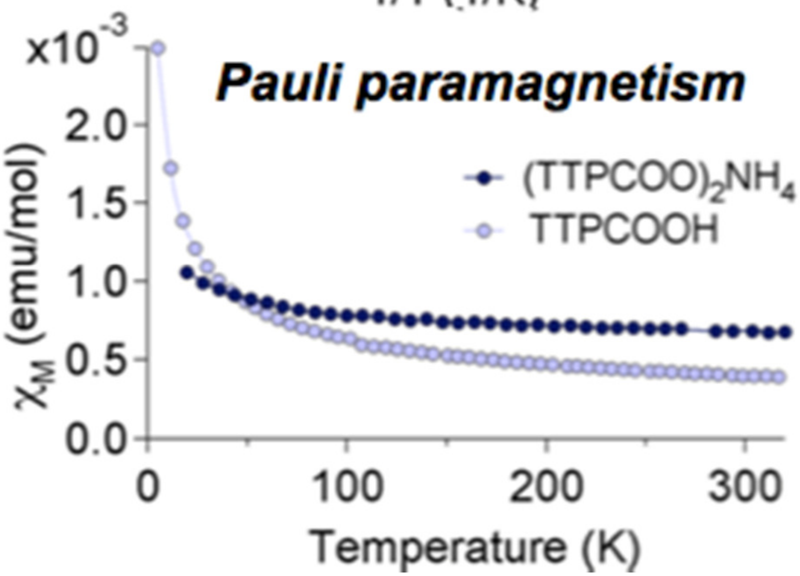
Solid state ¹H NMR



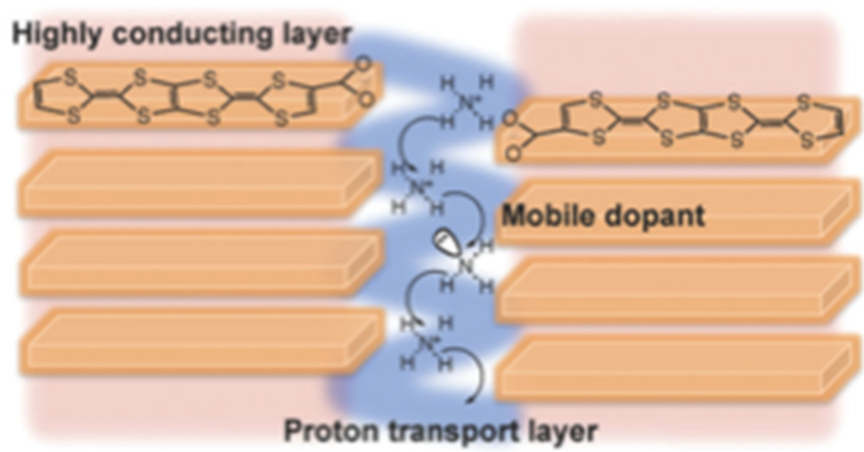
Proton transport

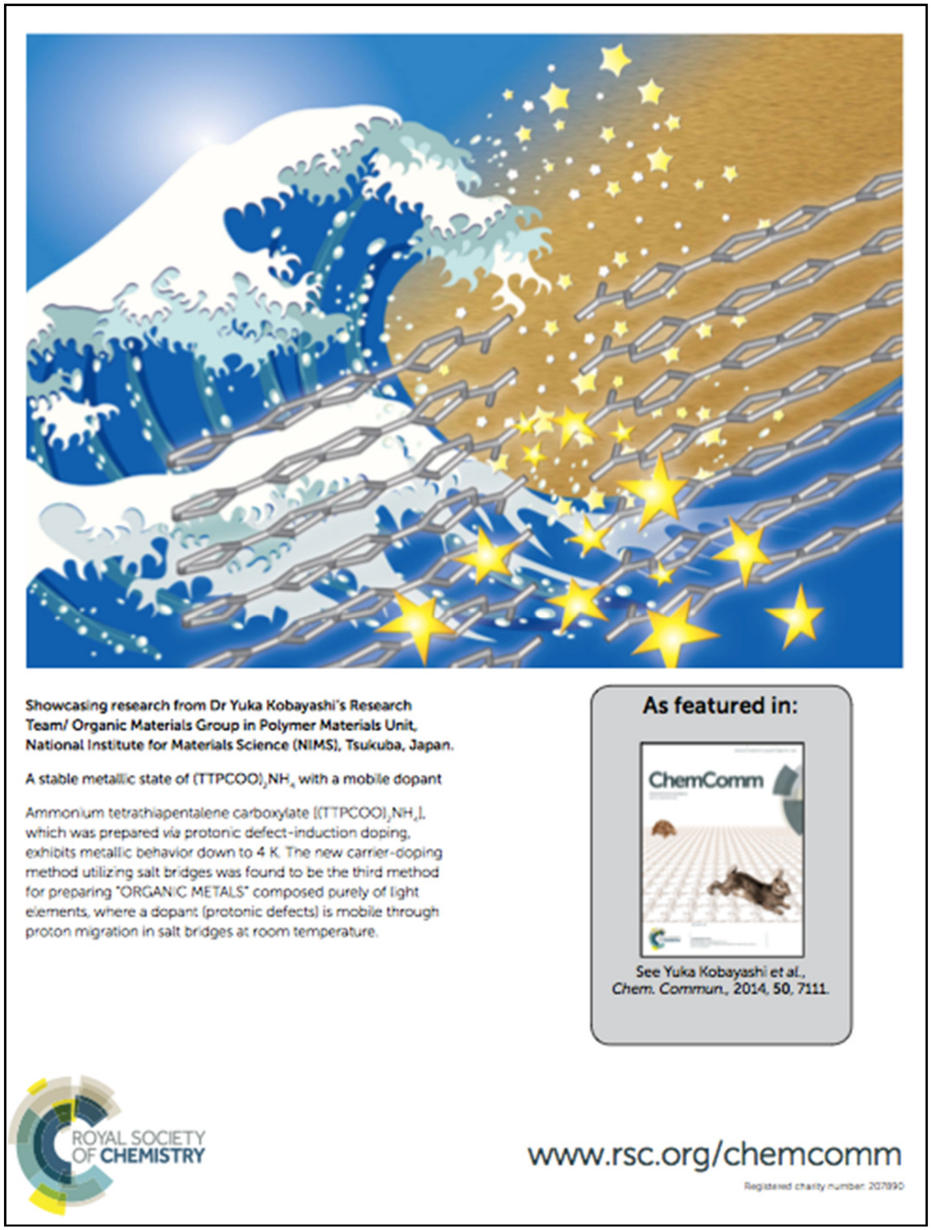


Mobile dopant



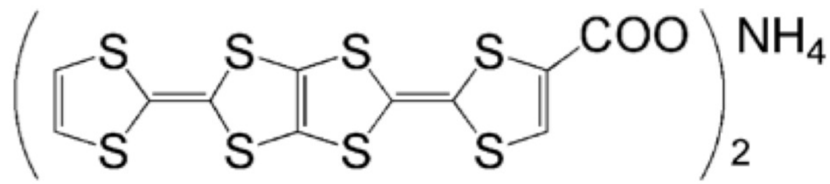
Schematic image for the molecular metal





A stable metallic state of $(TTPCOO)_2NH_4$ with a mobile dopant

A third method for preparing " pure organic metals "

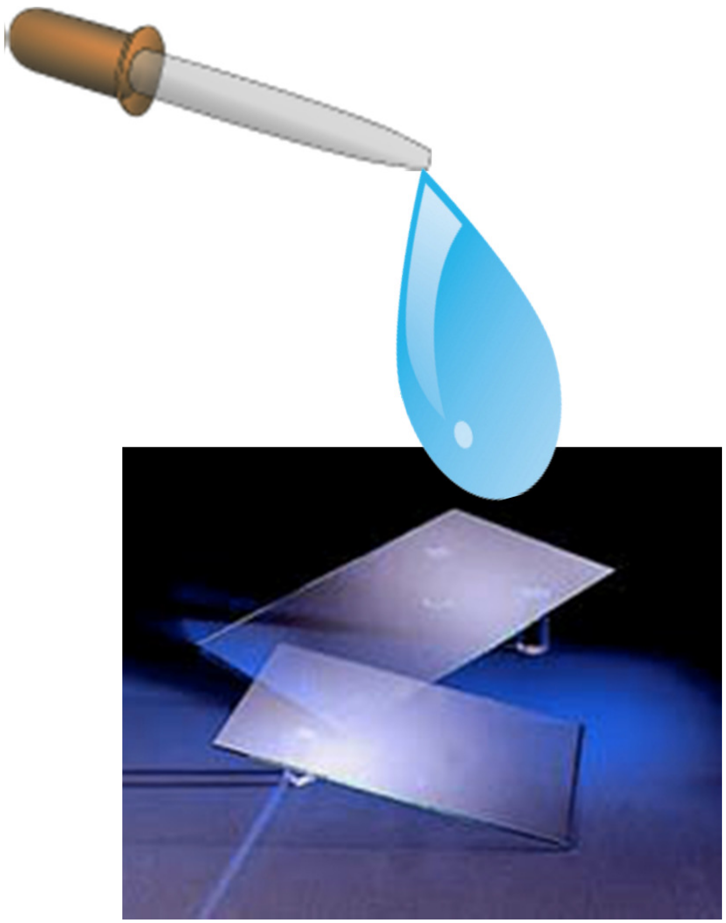


- No external dopant
- No electrochemical oxidation

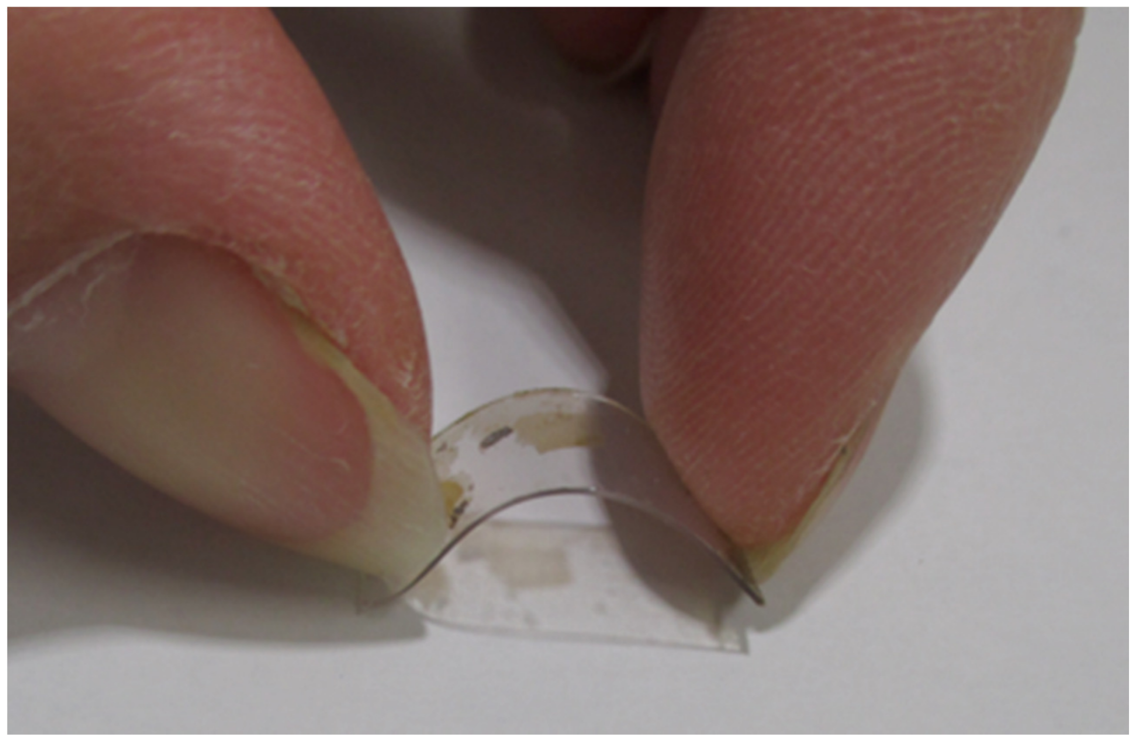
T. Terauchi, S. Sumi, Y. Kobayashi,
T. Nakamura, K. Furukawa, Y. Misaki

Chem. Comm. ***2014****, 50, 7111.*
Highlighted in the backcover picture.

Potential to apply for printed electronics



Organic transparent electrode



Summary

Effect of mobile proton in thermopower

Metallization of doped salt-bridge system by defect induction

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Nagoya Univ.

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