About OMICS Group

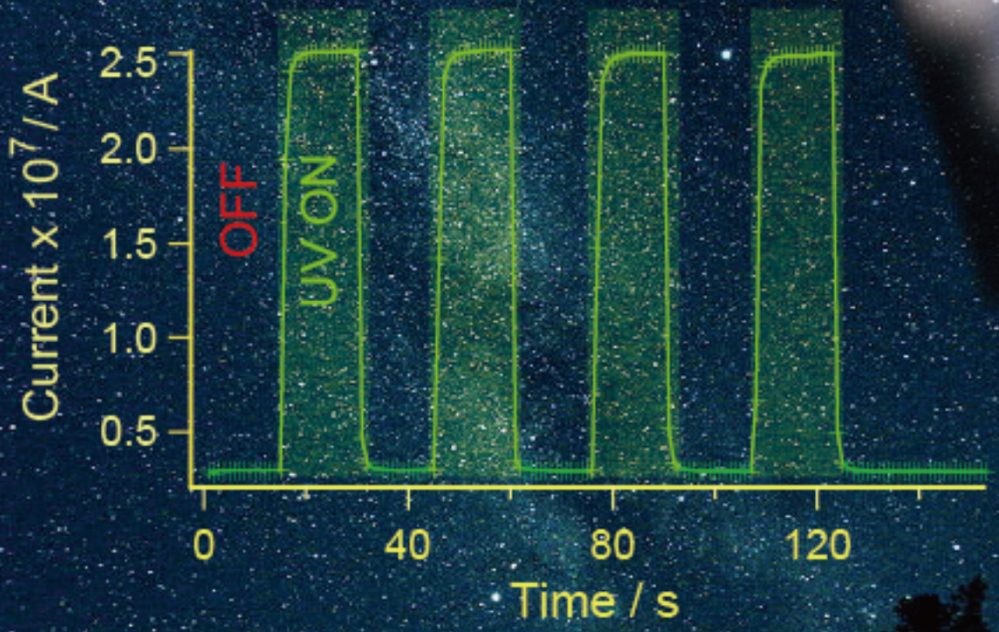
OMICS Group International is an amalgamation of Open Access publications and worldwide international science conferences and events. Established in the year 2007 with the sole aim of making the information on Sciences and technology 'Open Access', OMICS Group publishes 400 online open access scholarly 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.

About OMICS Group Conferences

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.

Giant Photoconductivity in Organic Materials by UV Irradiation



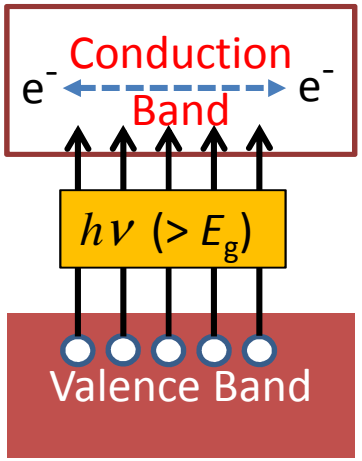
Toshio Naito

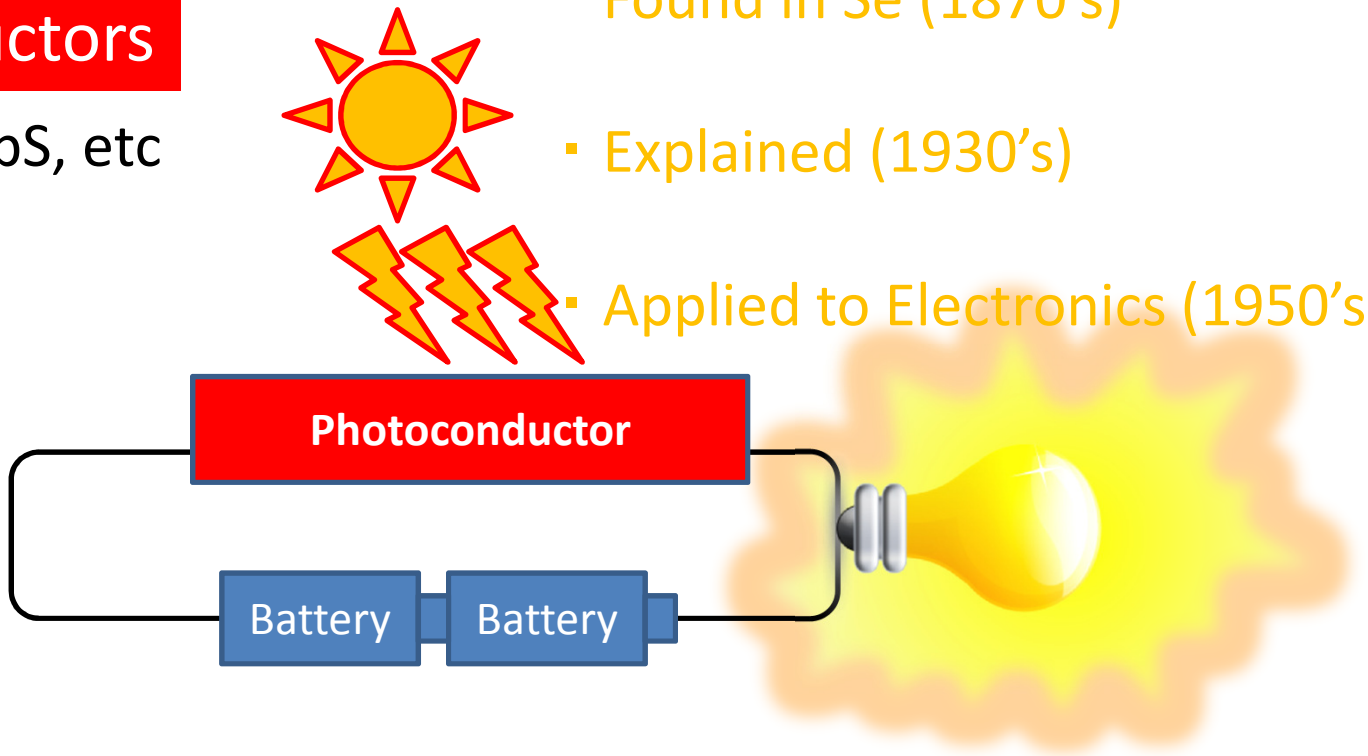
Ehime University

Photoconductors

ex. CdS, PbS, etc

- Found in Se (1870's)
- Explained (1930's)
- Applied to Electronics (1950's)





Applied to ex.) Laser Printer, Photocopy, Solar Cell, Sensor, CMOS, etc

various imaging & sensor devices

⇓ New (additional) Functions

Information / Communication Technology

Purpose

New PCs with additional functions*

*
- Wavelength-selectivity of response
- Different responses to different wavelengths
- Photo-magnetic-conductors

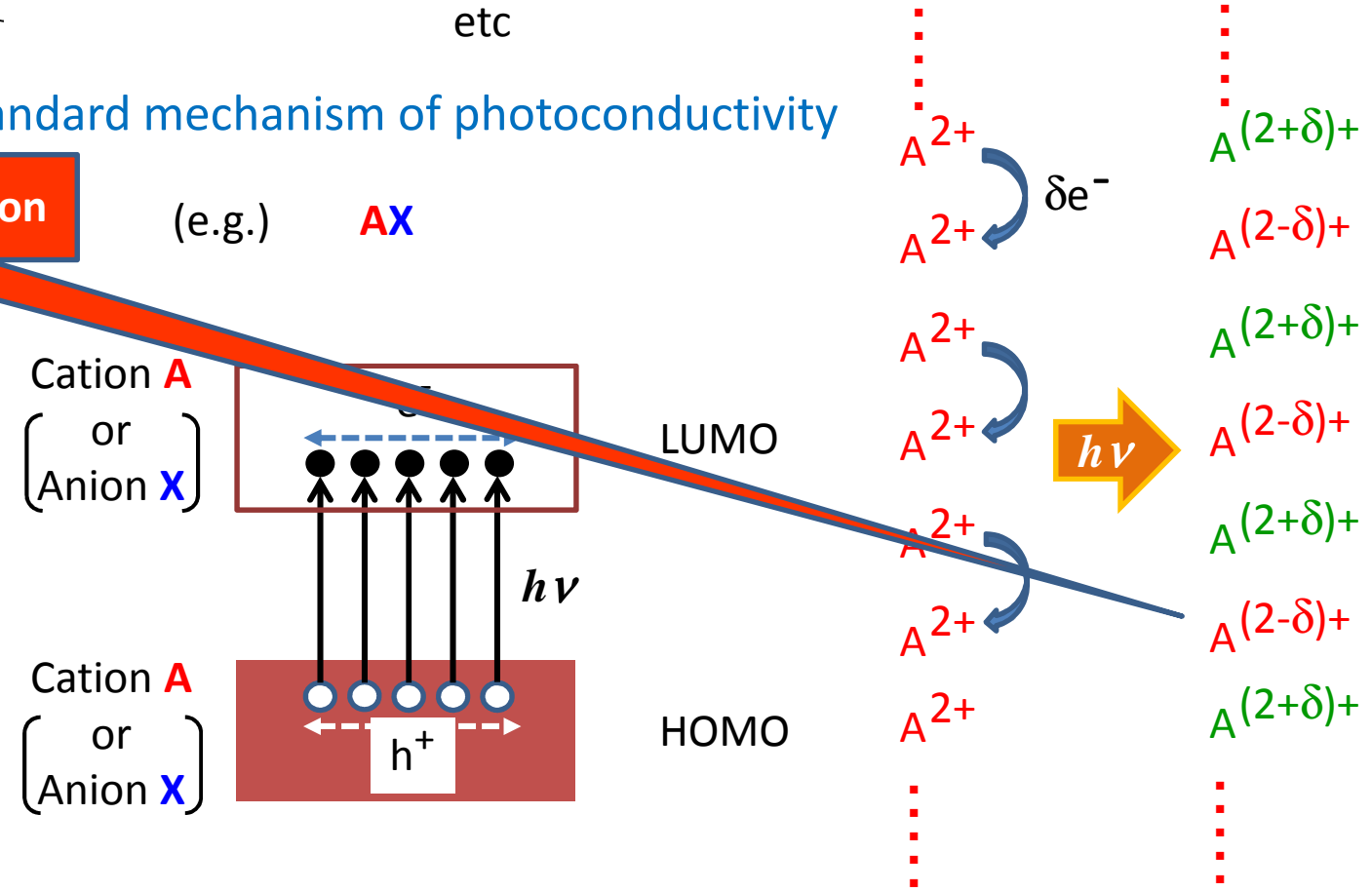
etc

→ **New Mechanism**

Standard mechanism of photoconductivity

Charge disproportionation

(e.g.) **AX**

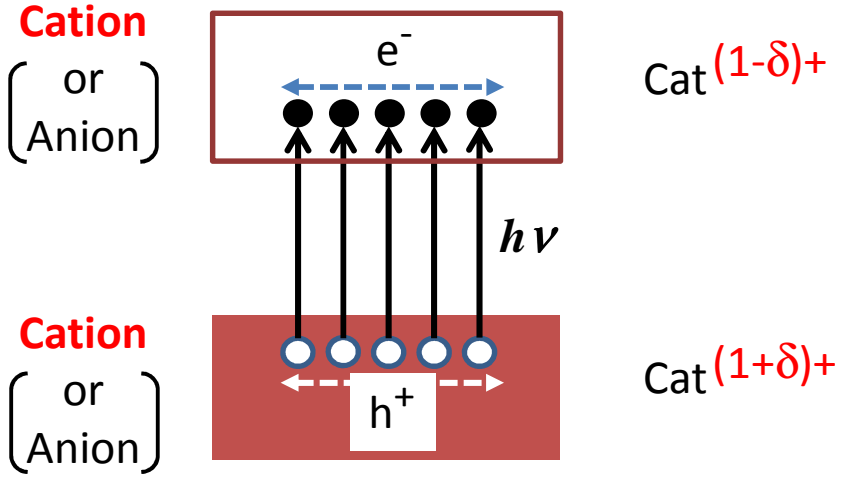


Our strategy

Merits

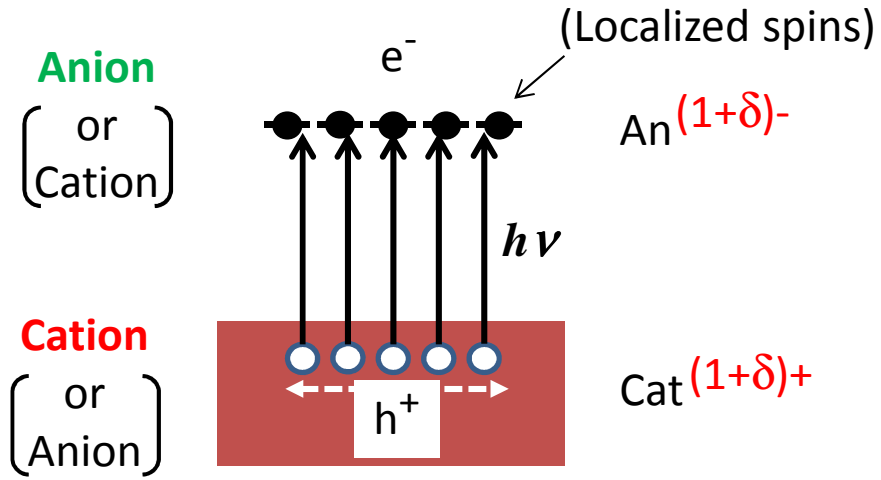
NO disproportionation
(for high conductivity)

Standard mechanism



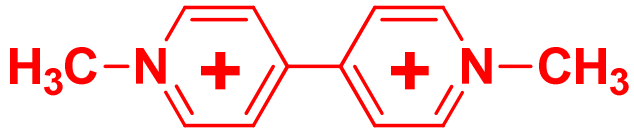
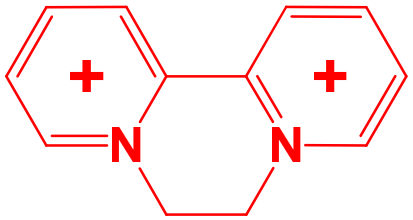
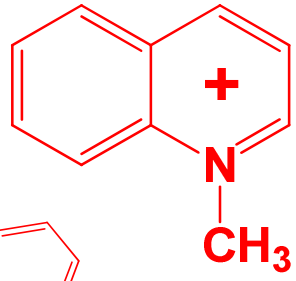
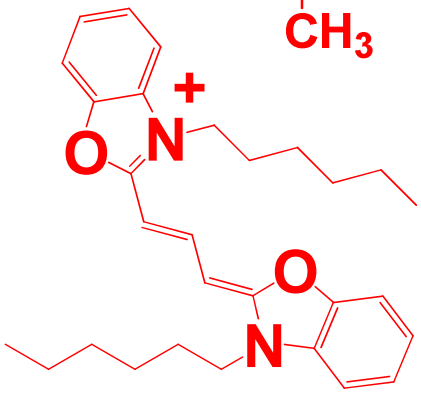
A-A or C-C Charge Transfer (CT)

Proposed (New) mechanism



C-A Charge Transfer (CT)

$C[Ni(dmit)_2]_X$

Abbre.	C (= Cations)	X	ref
MV		2 (α–, β–)	*Adv. Mater.*, 6153 (2012)
BPY		2, 6	*JACS* 18656 (2012)
NMQ		1 (α–, β–)	*Eur. J. Inorg. Chem.* (2014)
DiCC		1 (α–, β–)	*Chem. Lett.* 1119 (2014)

$[Ni(dmit)_2]^-$ salts

Conductivity Ratio (R_C)

Carrier Doping

$(A^- \xrightarrow{\delta e^-} C^+ \rightarrow A^{(1-\delta)-} \quad C^{(1-\delta)+})$

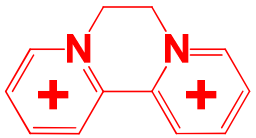
Charge Disproportionation

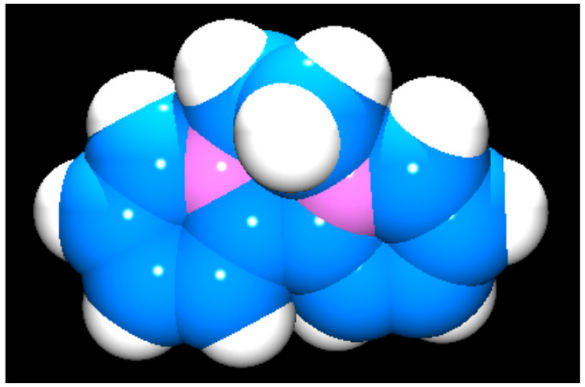
$(A^- \xrightarrow{\delta e^-} A^- \rightarrow A^{(1-\delta)-} \quad A^{(1+\delta)-})$

	C-A CT	A-A CT	(Almost) No CT
Cations	MV BPY	NMQ	DiCC $(n\text{-}C_4H_9)_4N$ $Ru(bpy)_3$ ....
R_C	10-1000	40-880	< 2-3

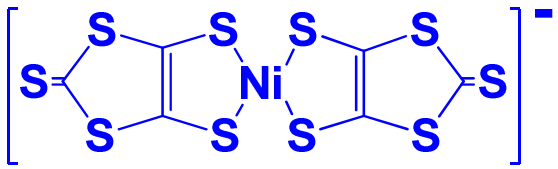
C-A CT

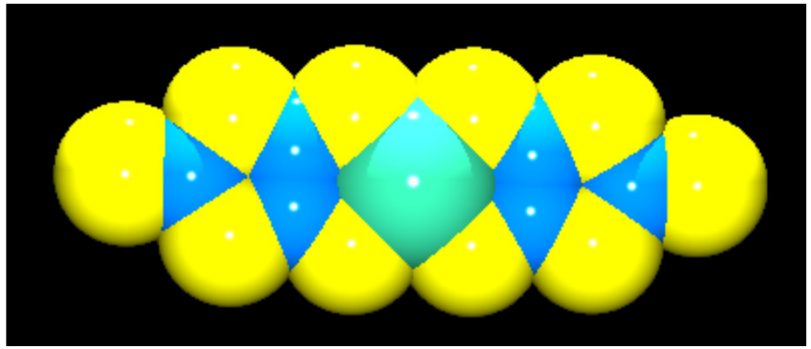
BPY^{2+}



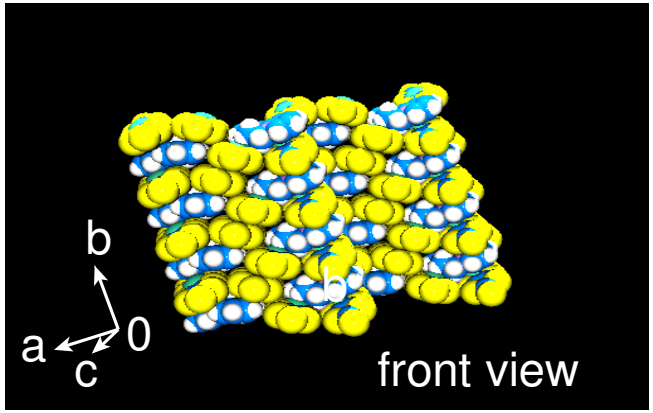


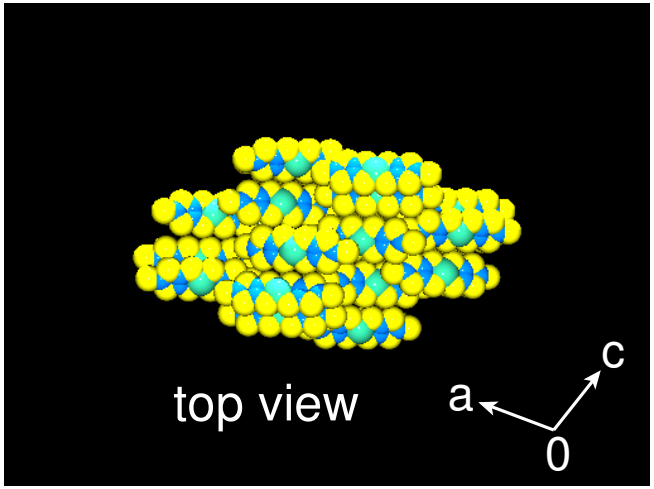
$[Ni(dmit)_2]^-$





$[Ni(dmit)_2]^-$ = conduction





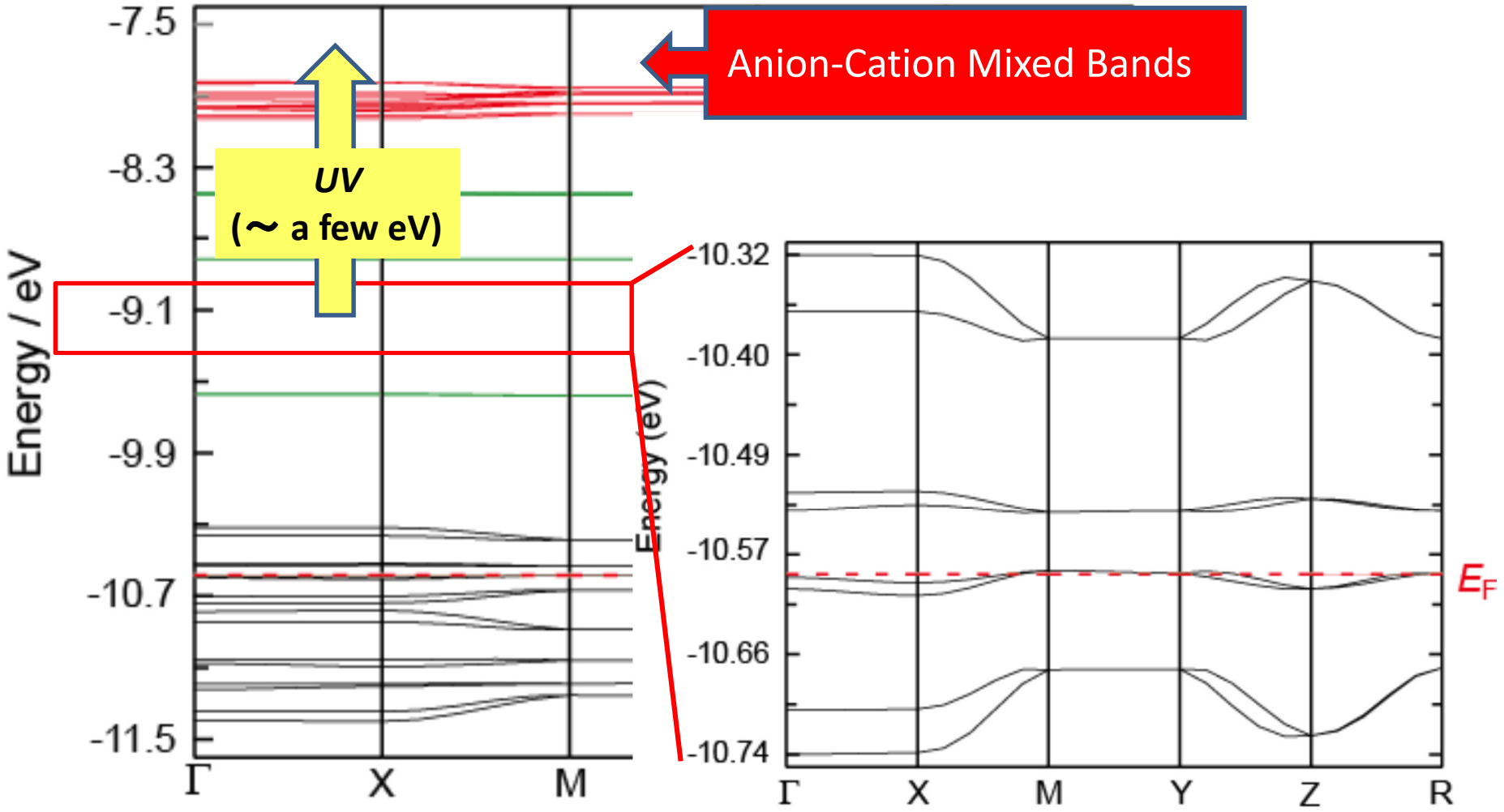
$BPY[Ni(dmit)_2]_2$ Band Calculation（Extended Hückel Method）

Red（16 bands）;

（e.g.）～37% $[Ni(dmit)_2]^-$

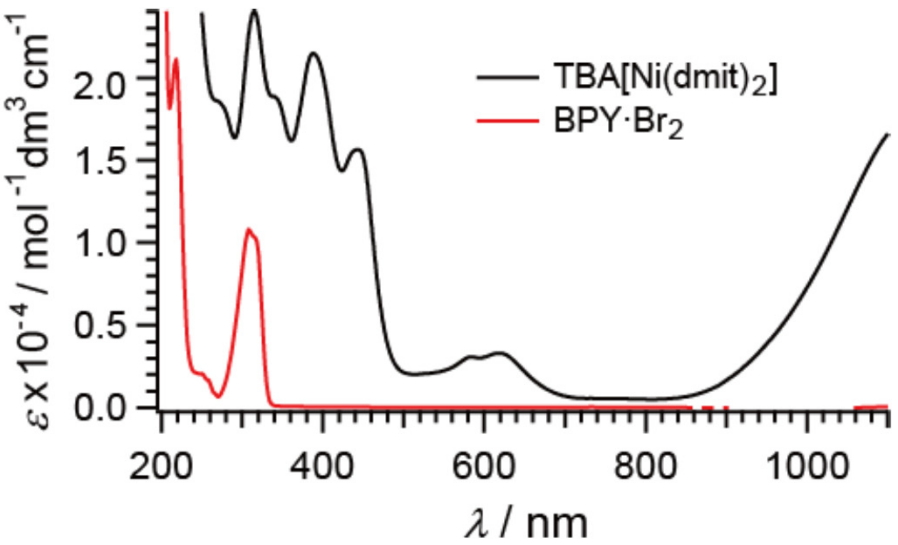
Green; ～100% BPY^{2+}

Black; ～100% $[Ni(dmit)_2]^-$

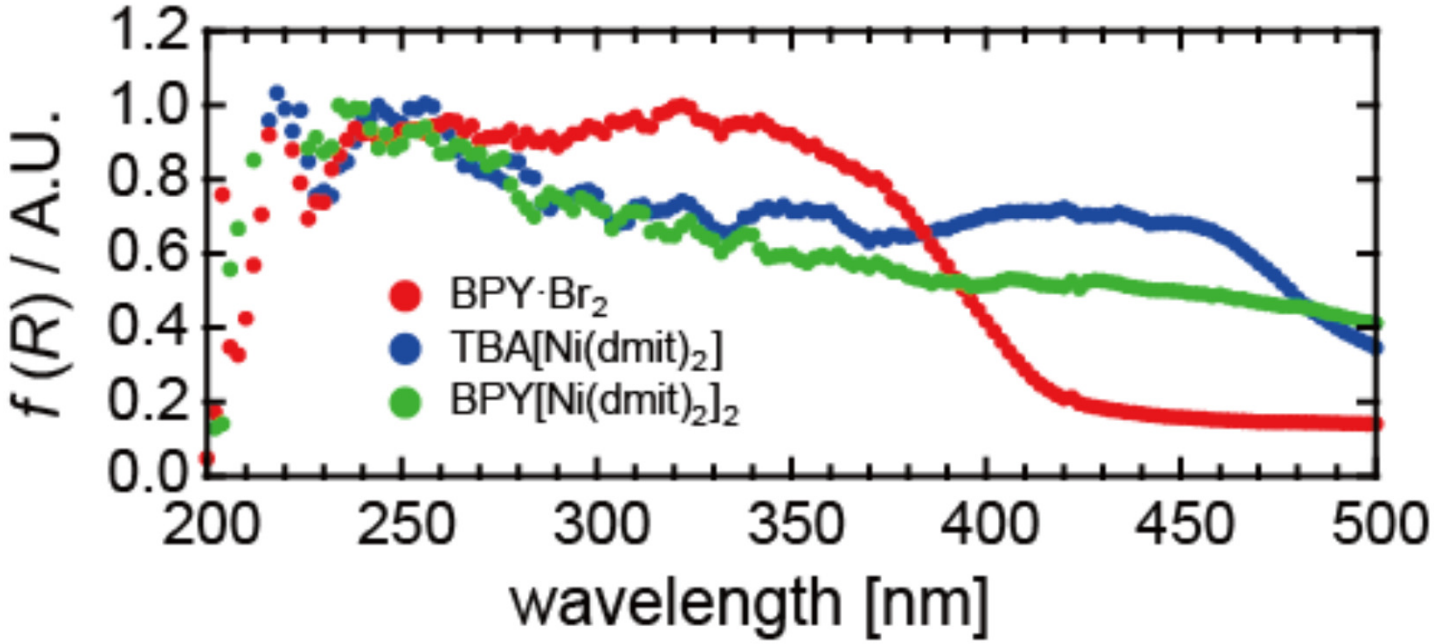


$BPY[Ni(dmit)_2]_2$ Solid State & Solution Spectra

Solution
（Absorption）



Solid State
（Diffuse
Reflection）



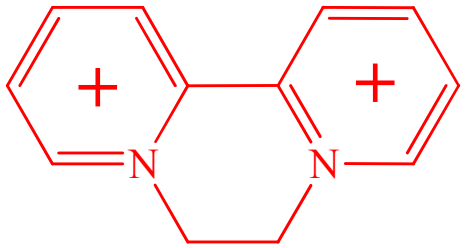
$A[Ni(dmit)_2]_2$

(A = BPY, MV)

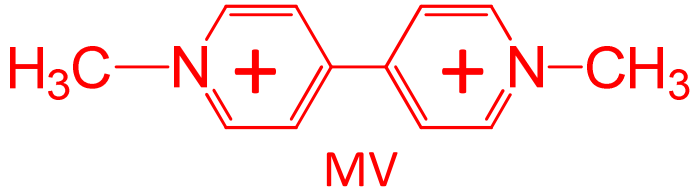
Conduction （Single Crystal）

Ground state = insulating

（dark）



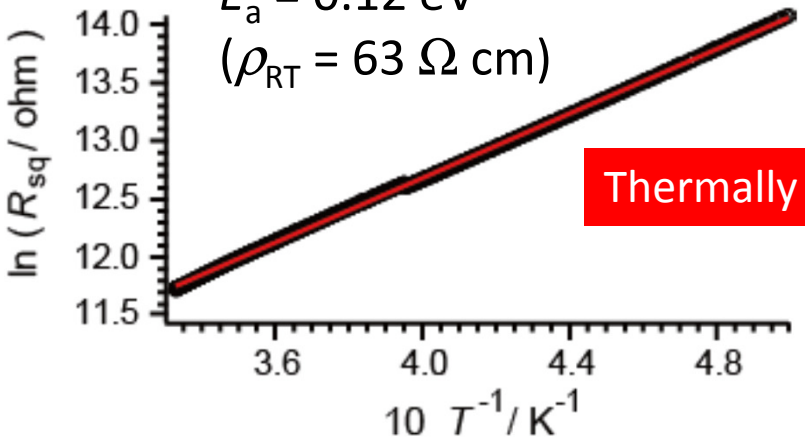
BPY



MV

E_a = 0.12 eV

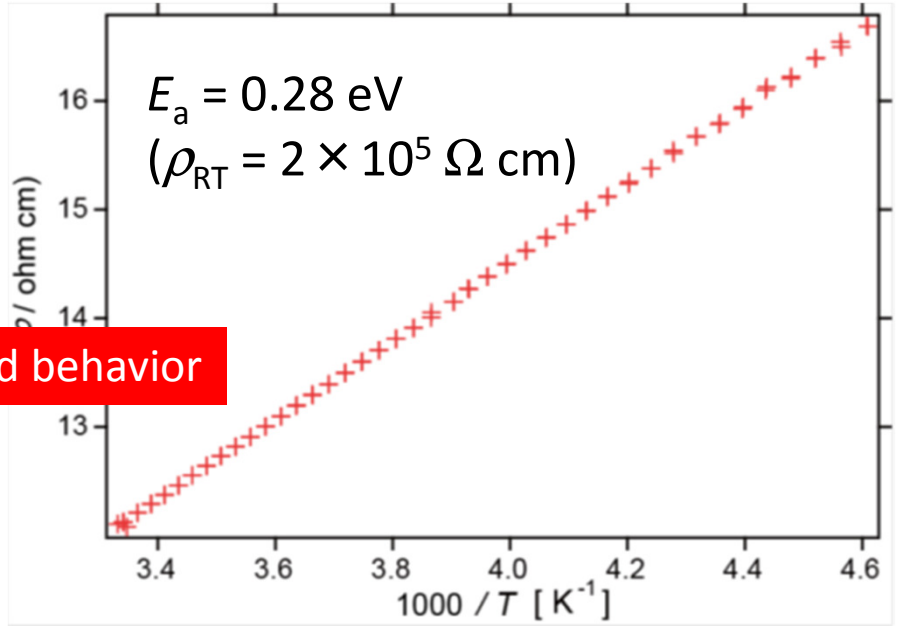
(ρ_{RT} = 63 Ω cm)



Thermally activated behavior

E_a = 0.28 eV

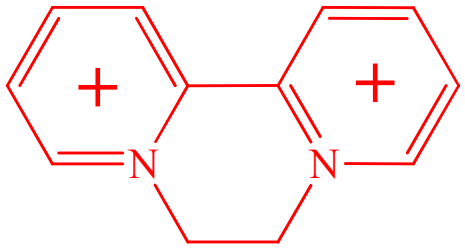
(ρ_{RT} = 2 × 10^5 Ω cm)



$A[Ni(dmit)_2]_2$ Conduction
(A = BPY, MV) （Single Crystal）

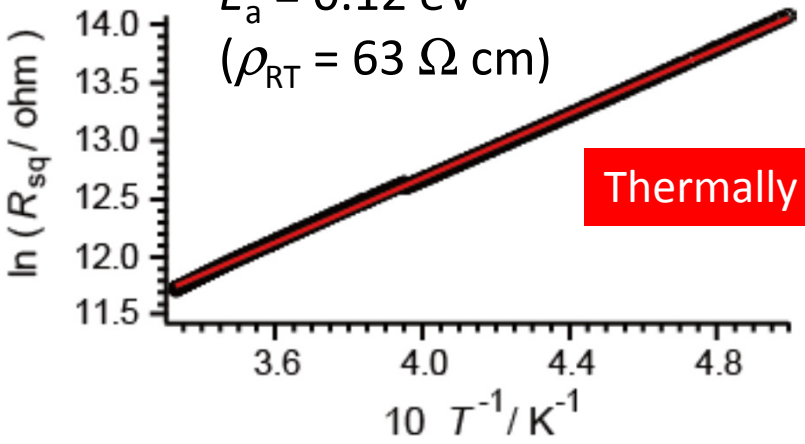
Ground state = insulating

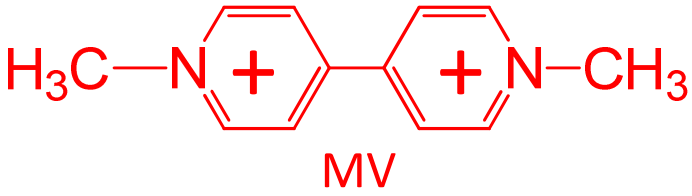
（dark）



BPY

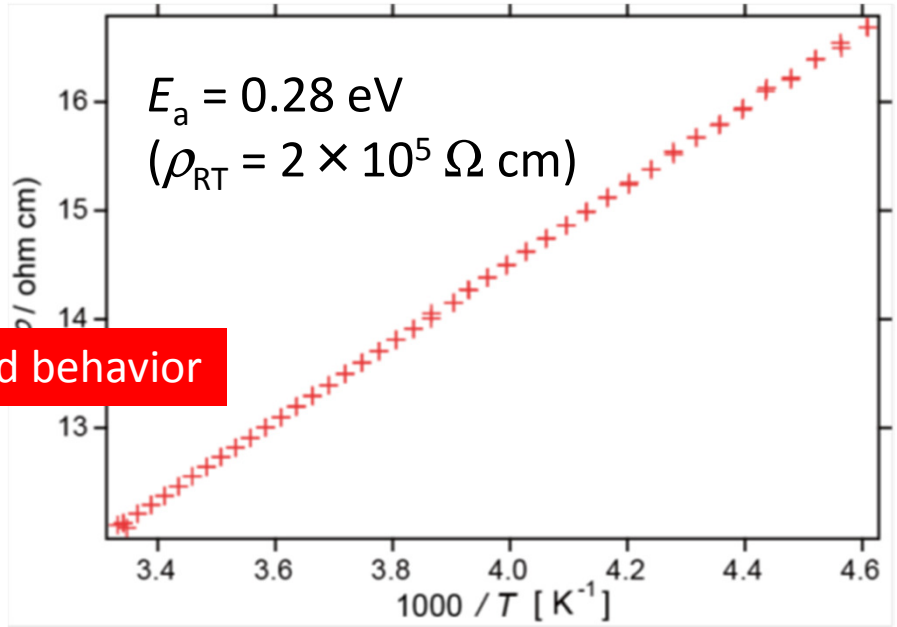
E_a = 0.12 eV
(ρ_{RT} = 63 Ω cm)





MV

E_a = 0.28 eV
(ρ_{RT} = 2 × 10^5 Ω cm)



Thermally activated behavior

E_g (cond) = 0.24 eV
cf. E_g (band) ~ 0.06 eV

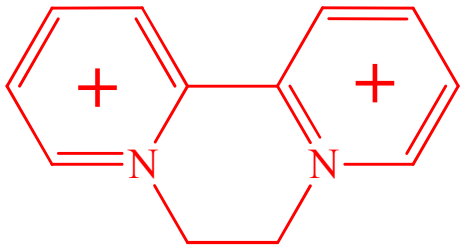
E_g (cond) = 0.56 eV
cf. E_g (band) ~ 0.05 eV

$A[Ni(dmit)_2]_2$

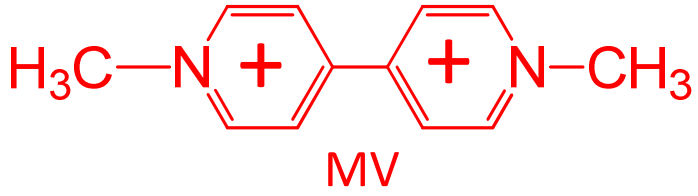
(A = BPY, MV)

Mag. Susceptibility （Polycrystal）

Ground state = diamagnetic (non-magnetic)

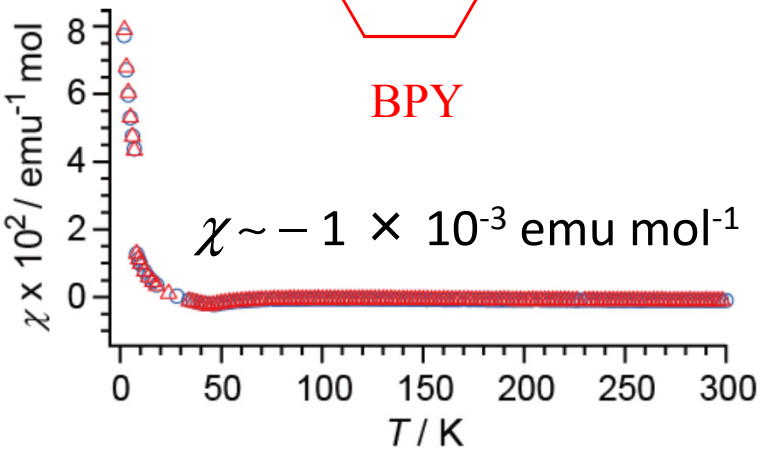


BPY

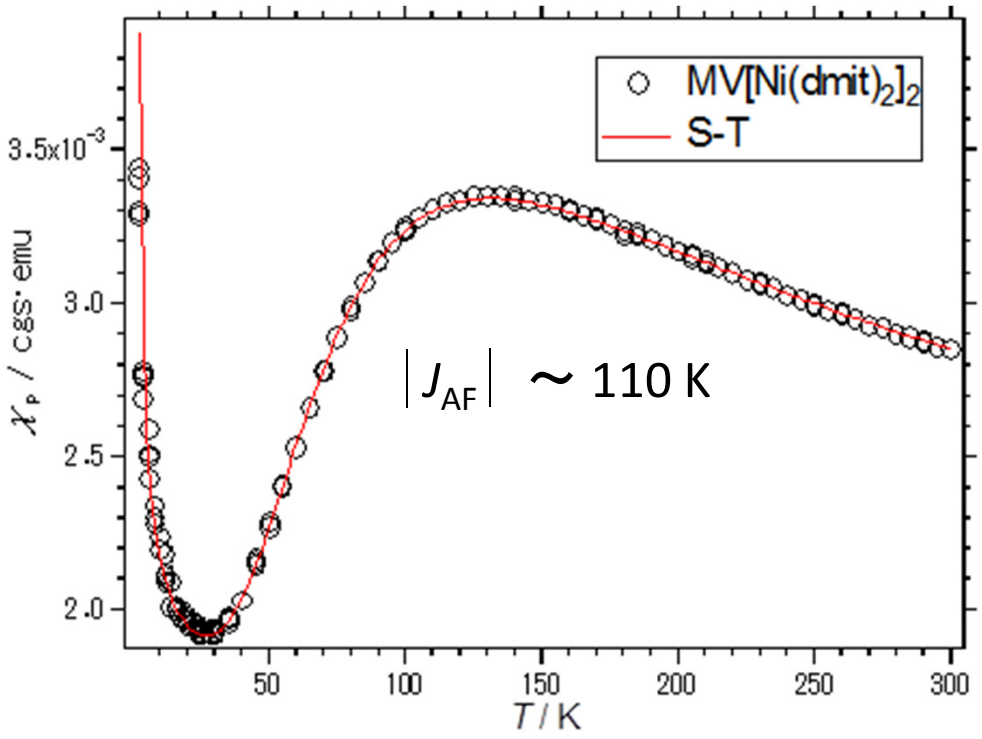


MV

dark



$\chi \sim -1 \times 10^{-3}$ emu mol^{-1}

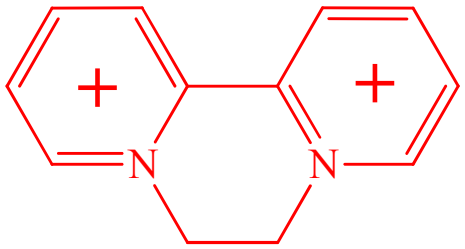


$|J_{AF}| \sim 110$ K

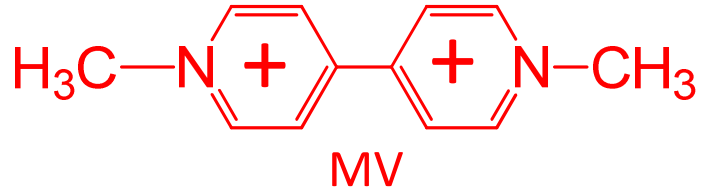
$A[Ni(dmit)_2]_2$ Mag. Susceptibility （Polycrystal）

(A = BPY, MV)

Ground state = diamagnetic (non-magnetic)

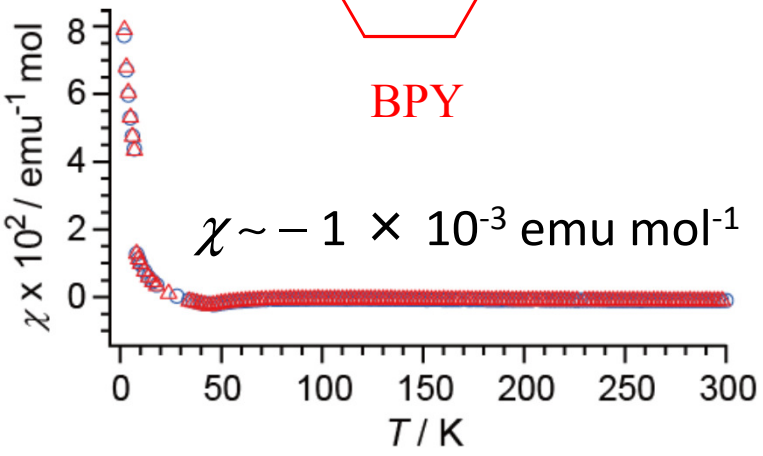


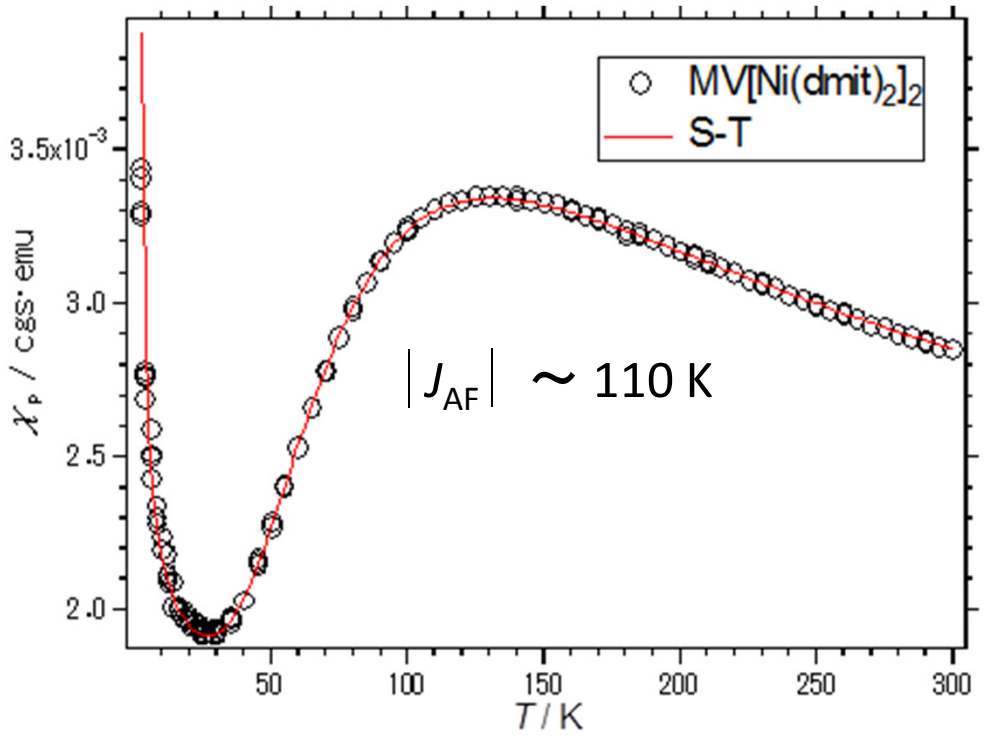
BPY



MV

dark





(e.g.) MV E_g (cond) = 0.56 eV

E_g (mag) ~ 0.02 eV

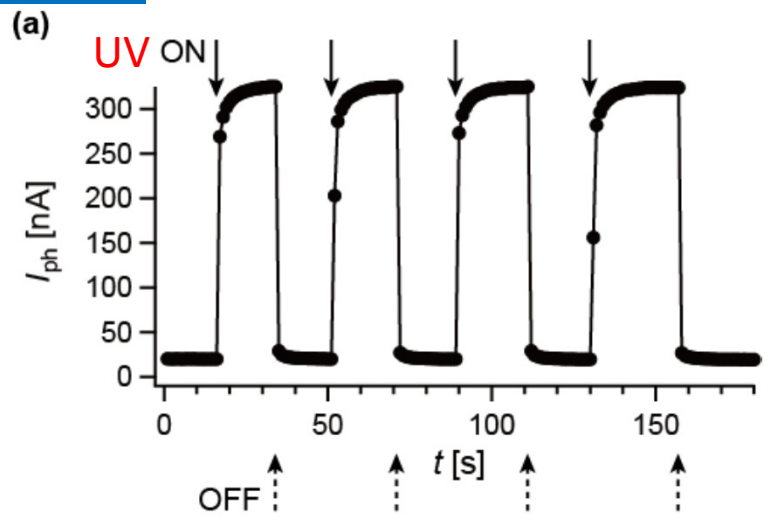
E_g (band) ~ 0.05 eV

$A[Ni(dmit)_2]_2$; photoconductivity

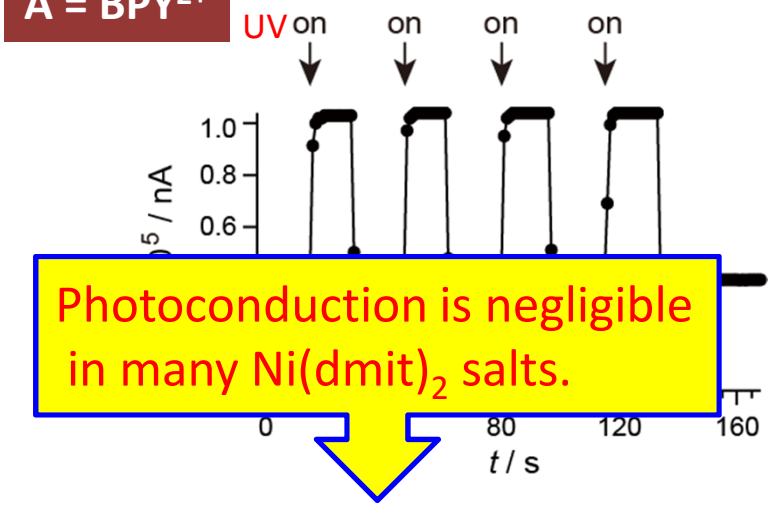
（Single Crystal）

（375 nm, 11.6 mW cm^{-2} , 300 K, in vacuo）

A = MV^{2+}

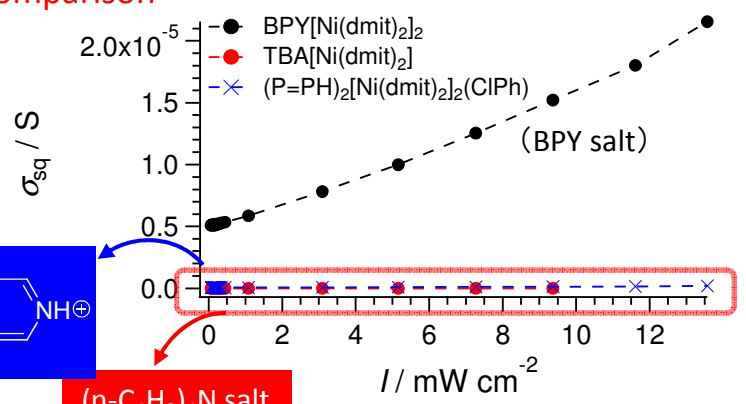


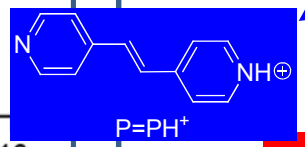
A = BPY^{2+}



Photoconduction is negligible in many $Ni(dmit)_2$ salts.

Comparison



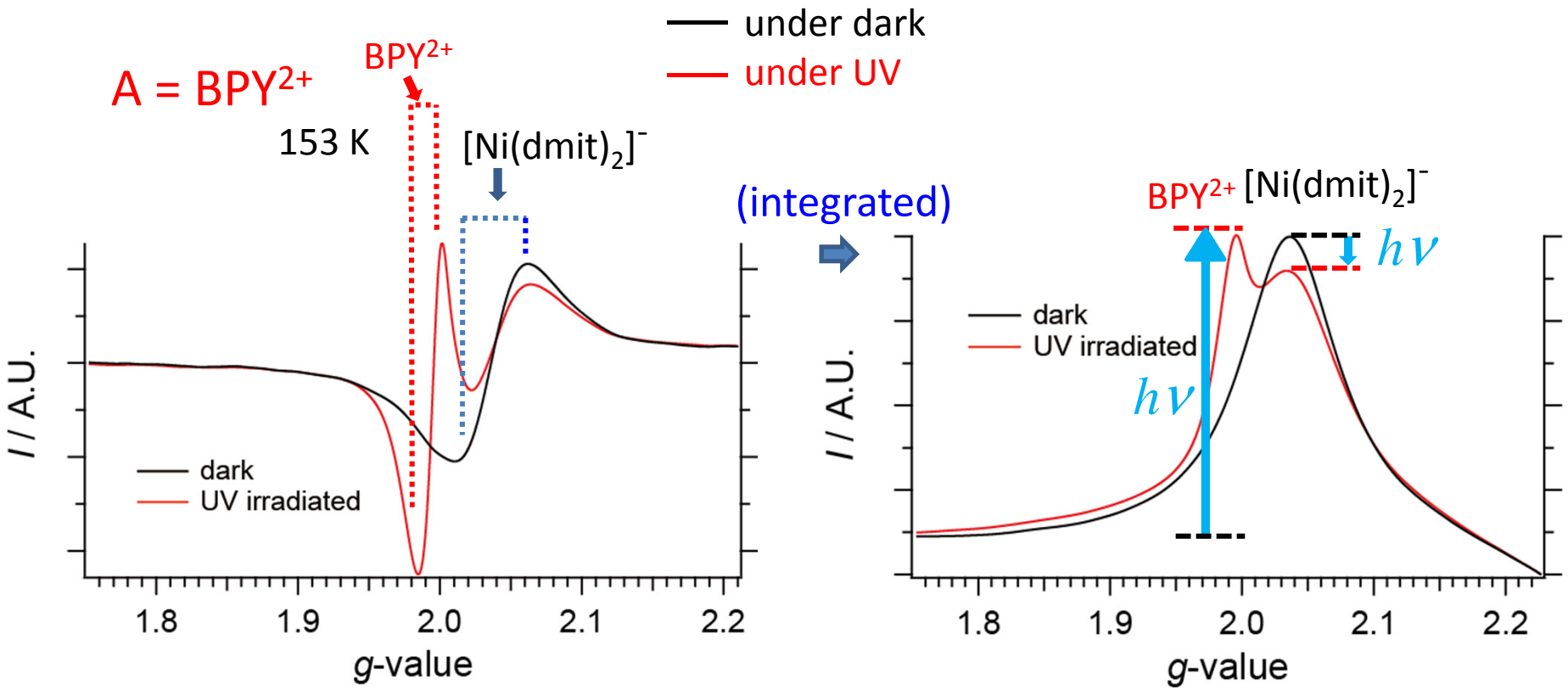


$(n\text{-}C_4H_9)_4N$ salt

~ 10^{-10} S

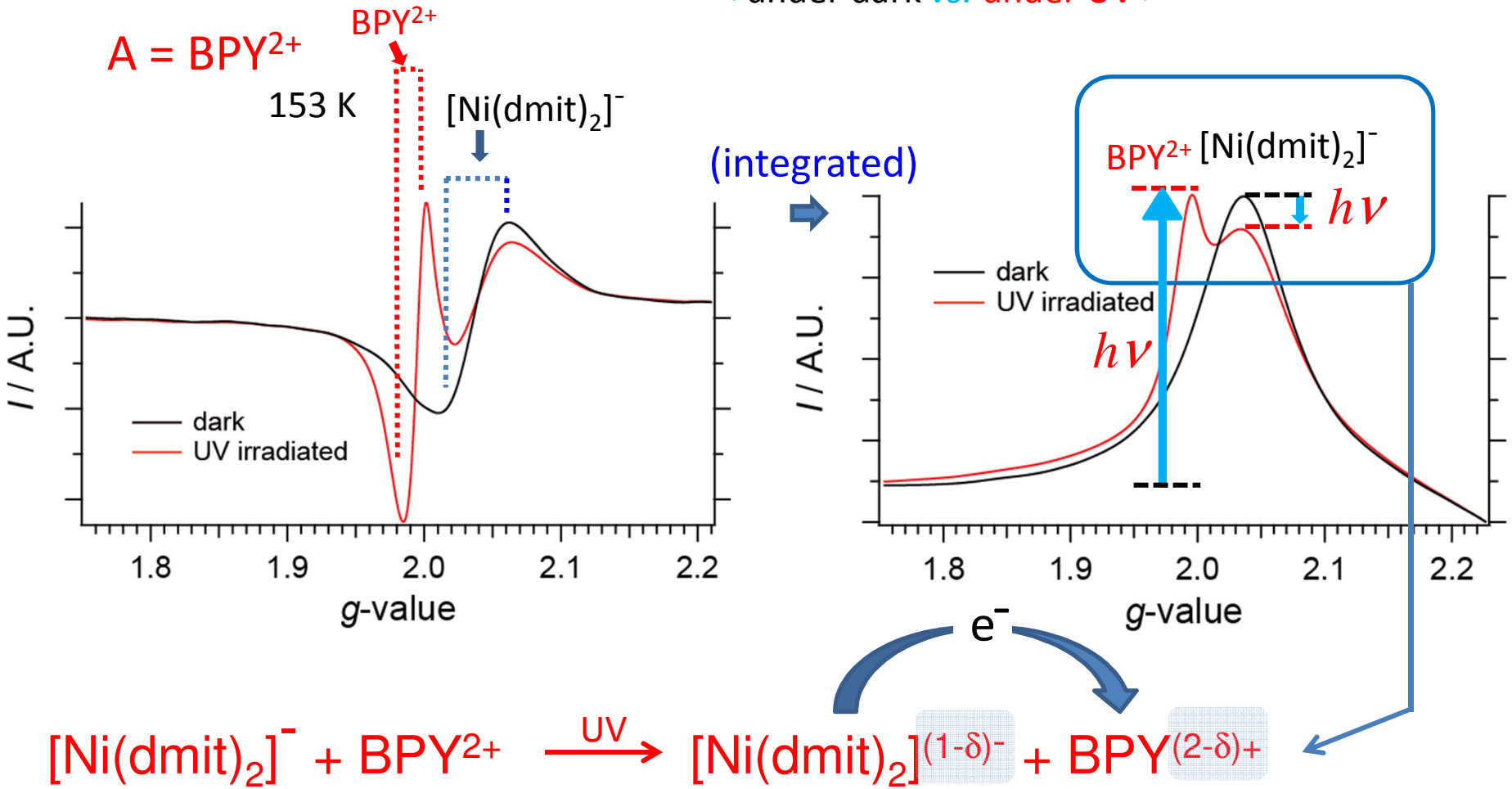
($\sigma_{ph}/\sigma_{dark} \leq 2$)

$A[Ni(dmit)_2]_2$ ESR （single crystal, $H \perp [010]$ ）



$A[Ni(dmit)_2]_2$ ESR （single crystal, $H \perp [010]$ ）

< under dark *vs.* under UV >



$$[Ni(dmit)_2]^- + BPY^{2+} \xrightarrow{UV} [Ni(dmit)_2]^{(1-\delta)-} + BPY^{(2-\delta)+}$$

$\delta \cong 0.1$ (Consistent with band calc. & UV spectra)

$A[Ni(dmit)_2]_2$; photoconductivity – I- & T-dependences

（Single Crystal）（375 nm, in vauo）

C-A CT type salts

New Features in Photoconduction σ

(1) $\sigma = \sigma_{dark} + aI + bI^2$ (I : light intensity)

(2) Wavelength selectivity (Responsive ONLY to ～250-450 nm)

C-A CT bands

Photoconduction mechanism is different from the known mechanism

$[Ni(dmit)_2]^-$ salts

Conductivity Ratio (R_C)

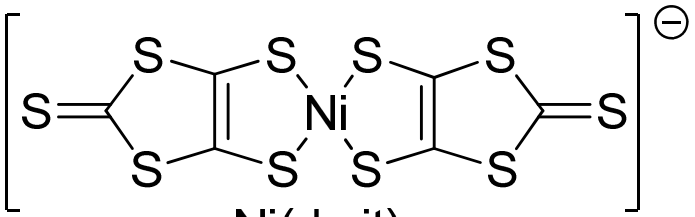
$$\equiv \frac{\text{Photoconductivity } (\sigma_{ph})}{\text{Dark conductivity } (\sigma_{dark})}$$

	C-A CT	A-A CT	(Almost) No CT
Cations	MV BPY	NMQ	DiCC $(n\text{-}C_4H_9)_4N$ $Ru(bpy)_3$ ....
R_C	10-1000	40-880 (RT) (200 K)	< 2-3

A-A CT-based PC

(A = Anion, C = Cation)

(A)



$Ni(dmit)_2$

NMQ (C)

$NMQ[Ni(dmit)_2]$*

Unique PC

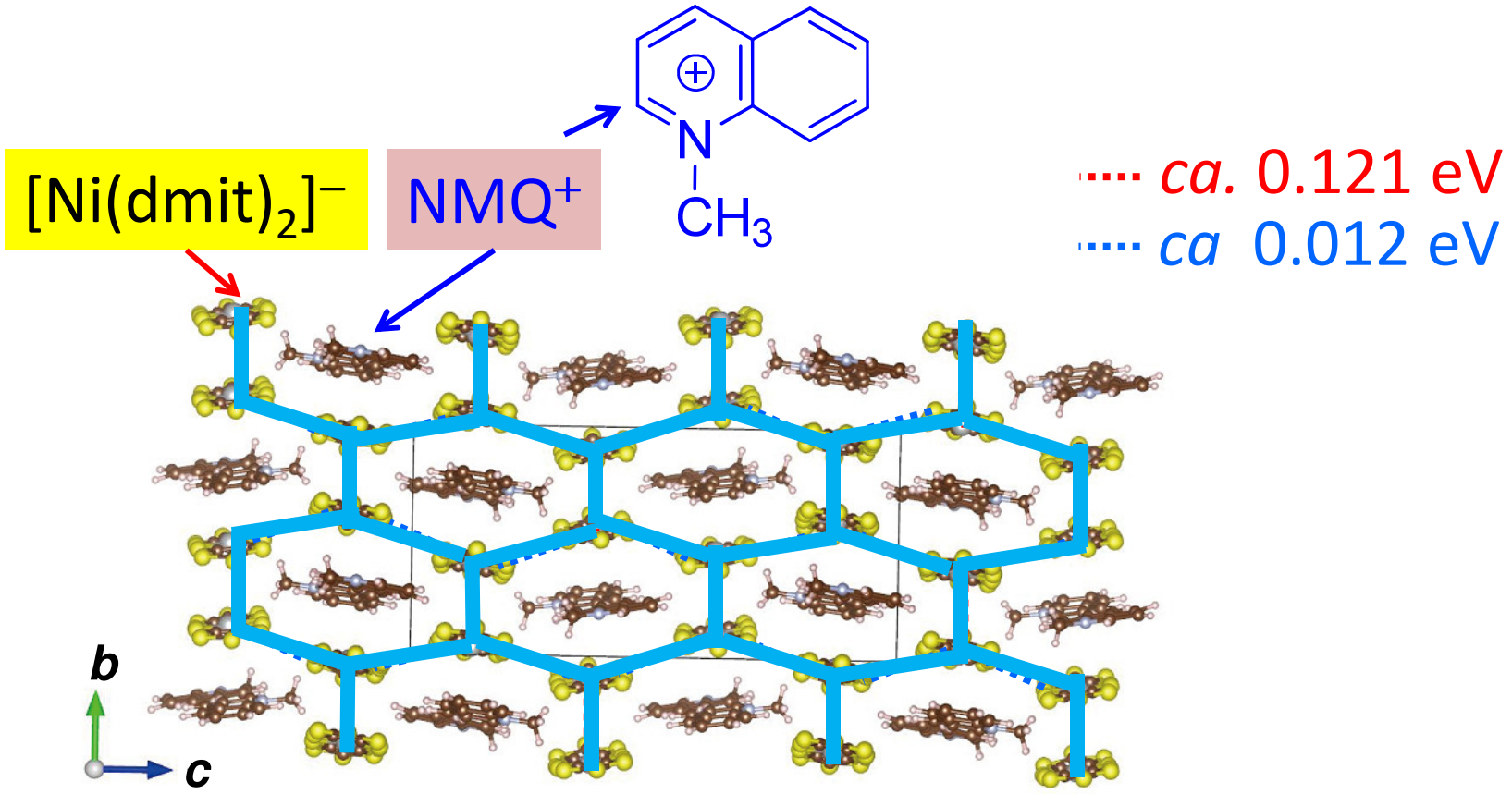
unusually

- Sharp wavelength-selectivity (Only ~ 375 nm)
- Large $\sigma_{UV} / \sigma_{dark}$ (eg. ~ 40 @300 K, ~ 880 @200 K)

* (in regard to synthesis, crystal structure, and dark conductivity)

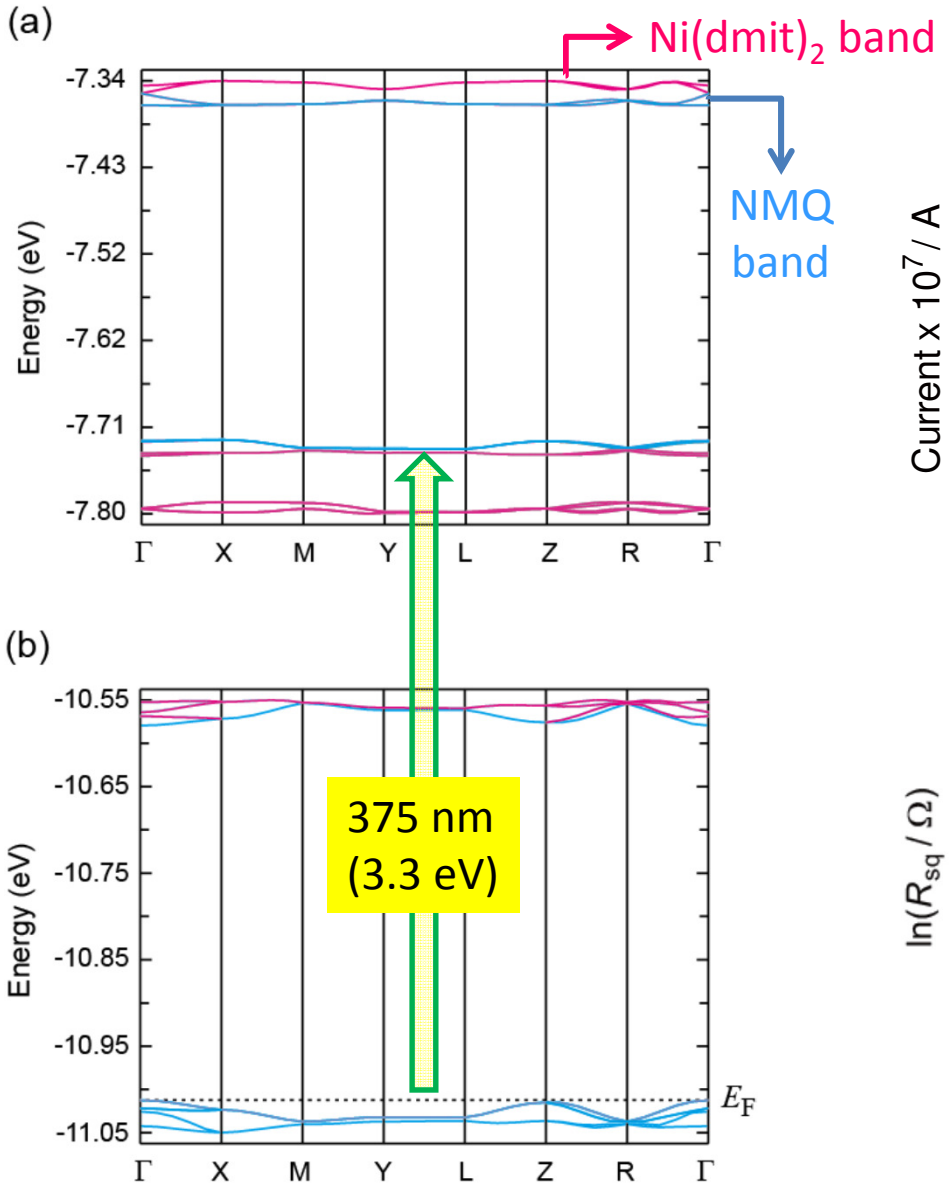
J. P. Cornelissen, et al. *Inorg. Chim. Acta* **1991**, 185, 97-102.

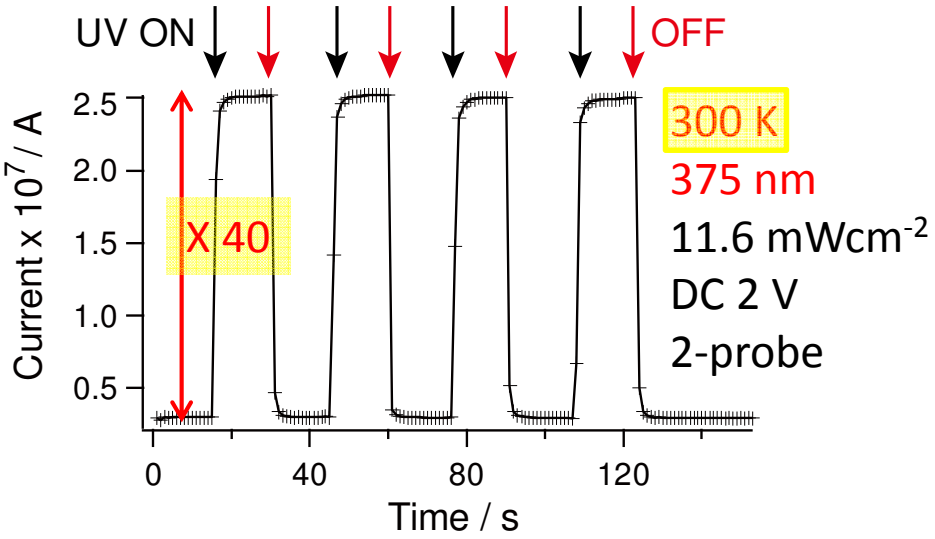
Crystal Structure

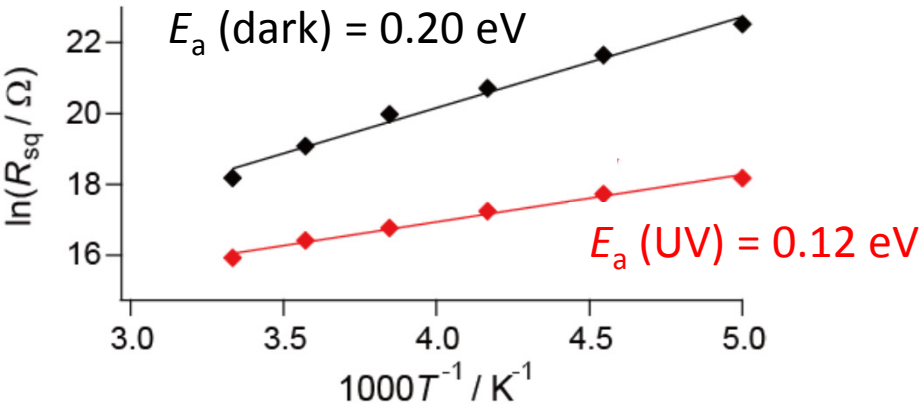


Negligible C-A interactions

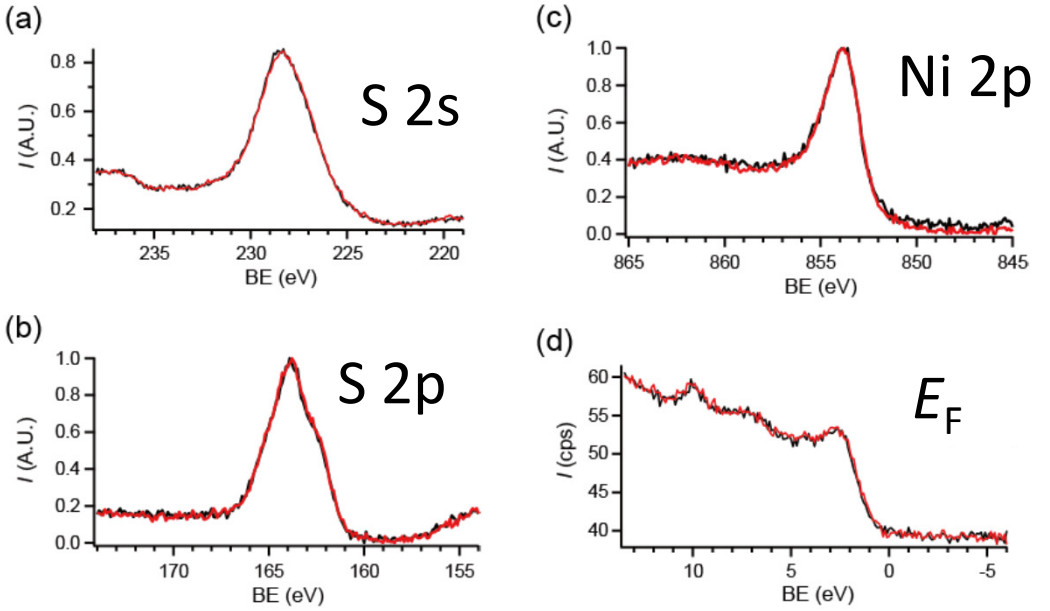
Band Structure & Conductivity

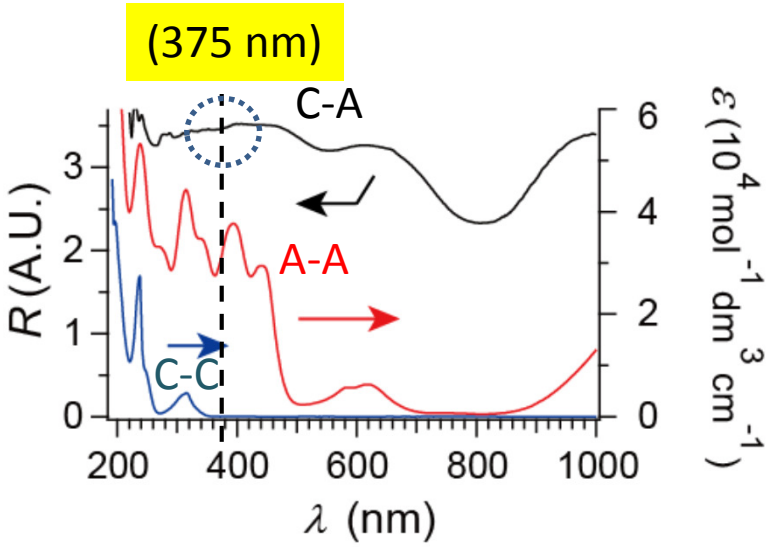






XPS & UV-Vis-NIR Spectra





Under UV-irradiation (375 nm)

Under dark

XPS (Ni, S, E_F) do NOT change (under dark and UV)

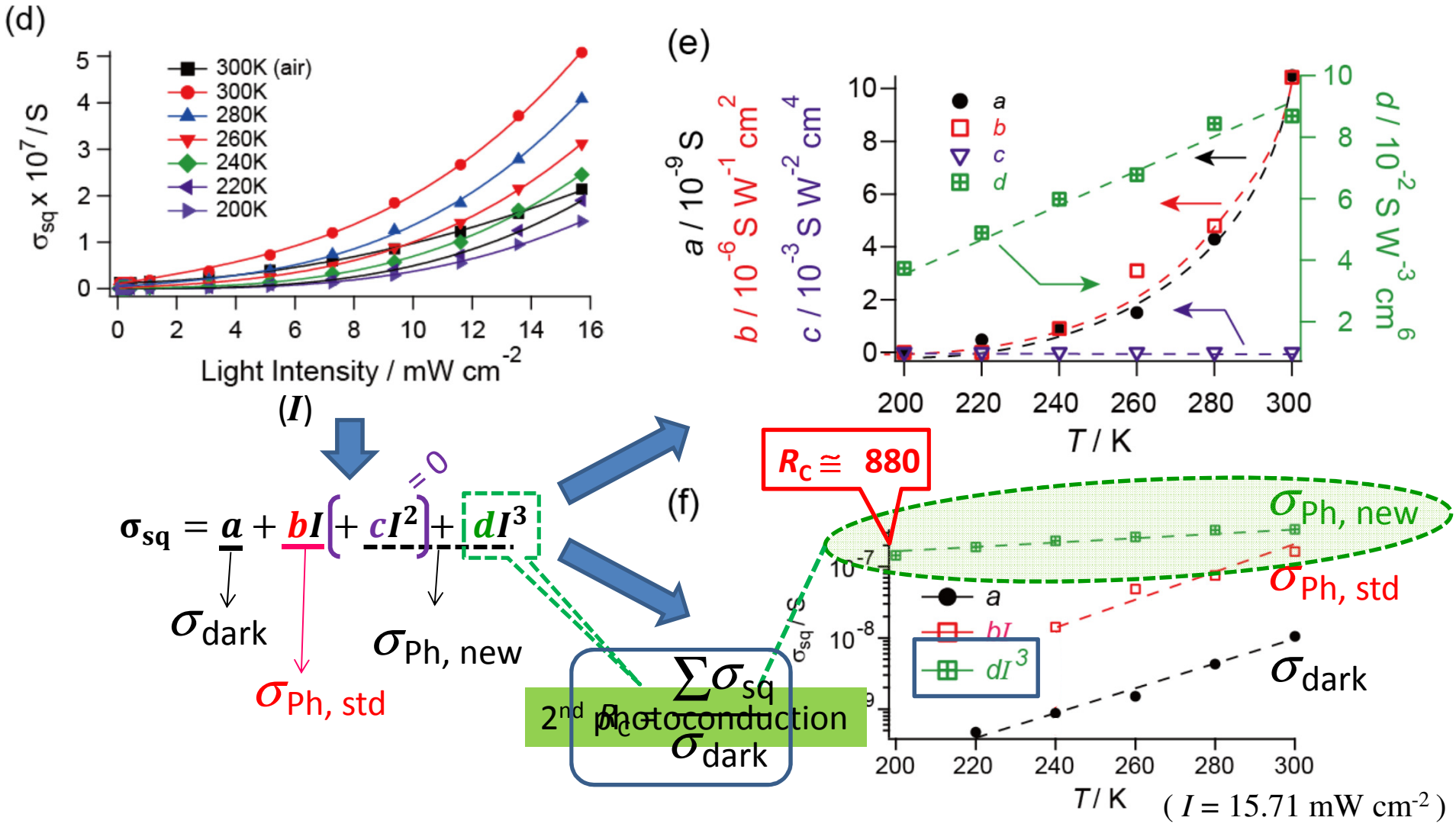
NMQ[Ni(dmit)$_2$] (powder)

$(C_4H_9)_4N[Ni(dmit)_2]$ (in CH_3CN)

NMQ·I (in CH_3CN)

CT between A-A (not C-A or C-C)

New contribution in PC

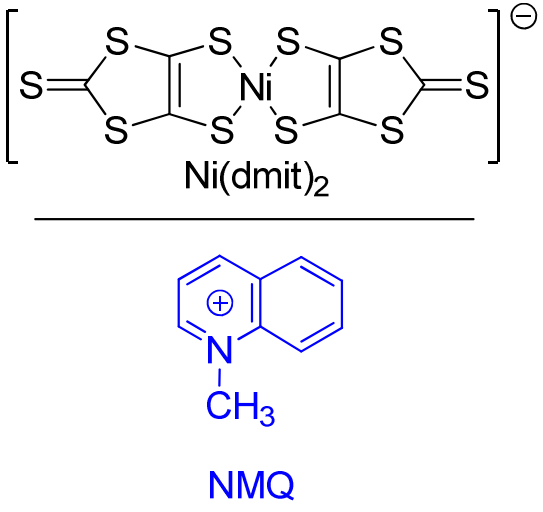


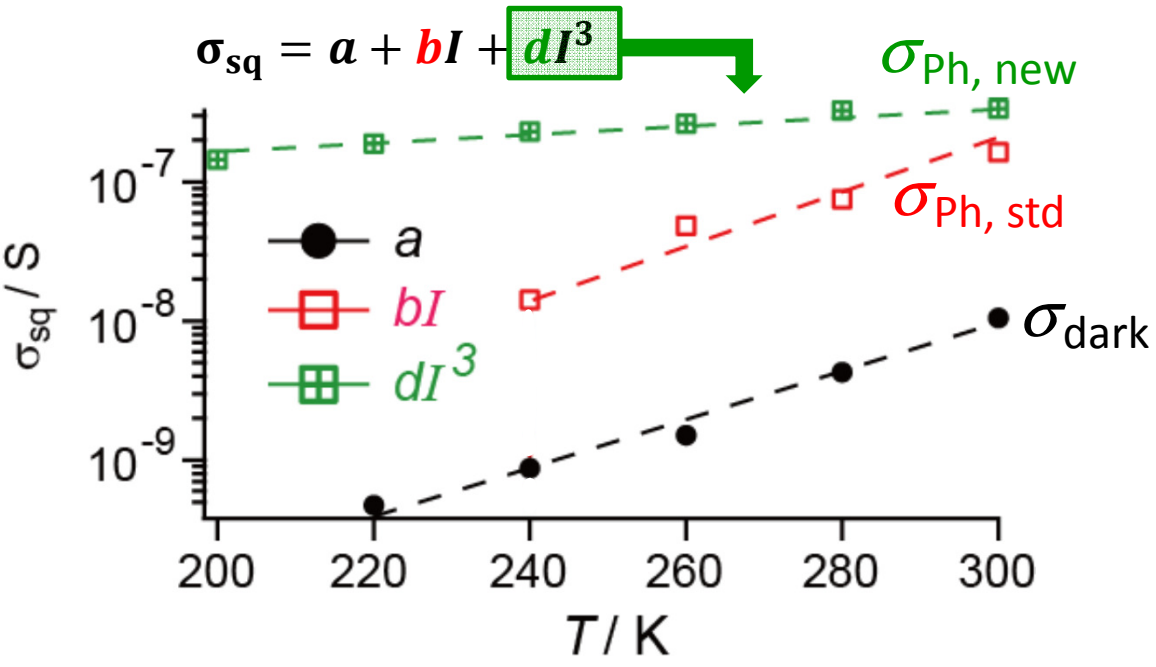
Summary; A-A CT

On the verge (or in the middle) of melting of charge-ordered state?

Remains to be clarified

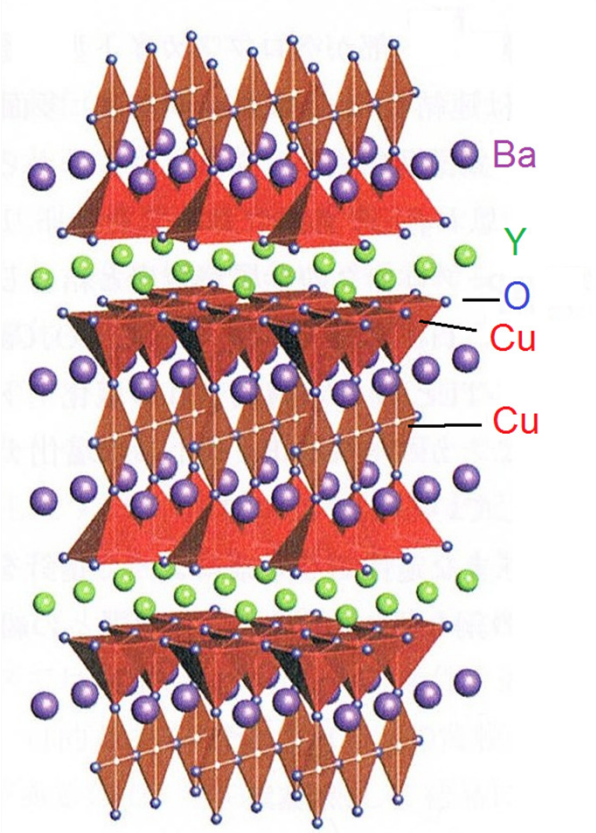
Coexistence of three kinds of (photo)conduction



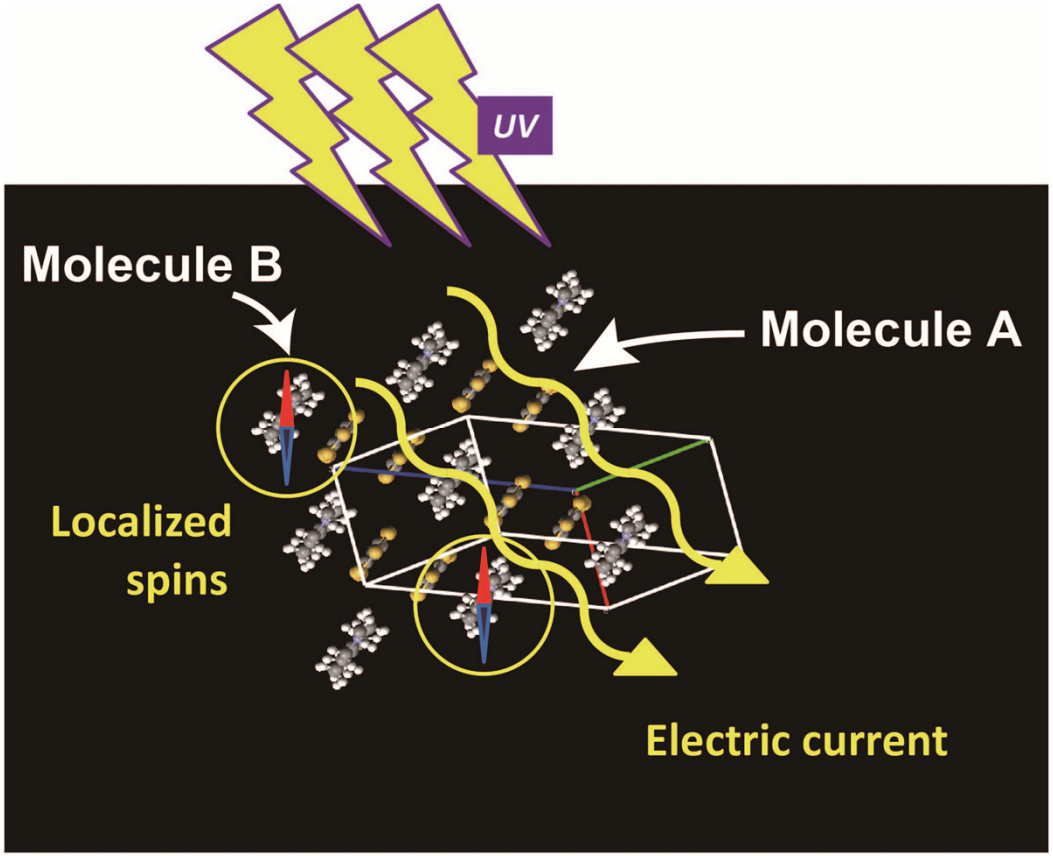


Optical Doping

$YBa_2Cu_3O_{7-\delta}$ (T_C = 90 K)



$MV[Ni(dmit)_2]_2$



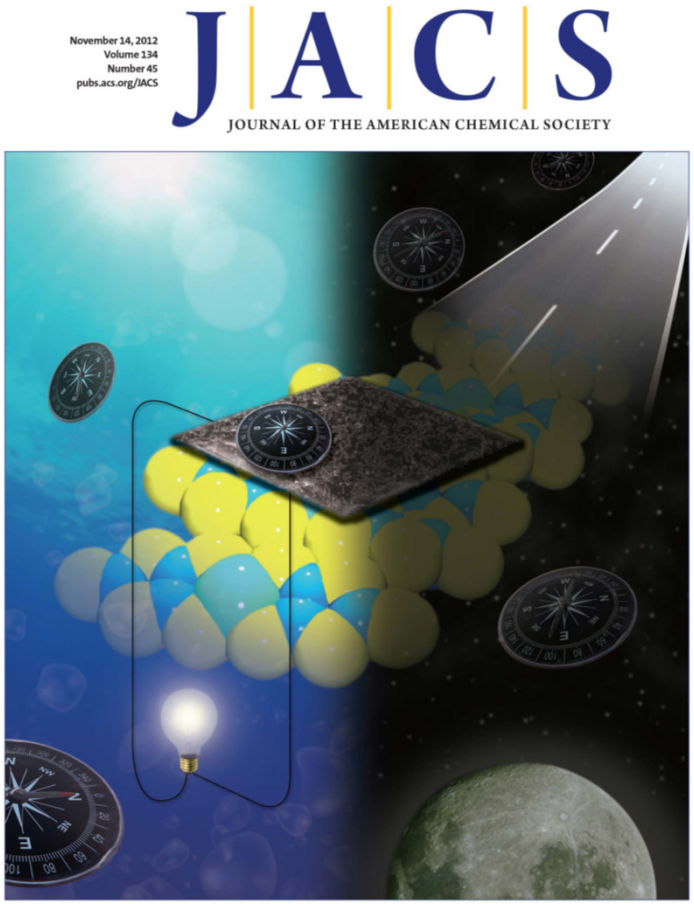
Chemical doping → Metastable State

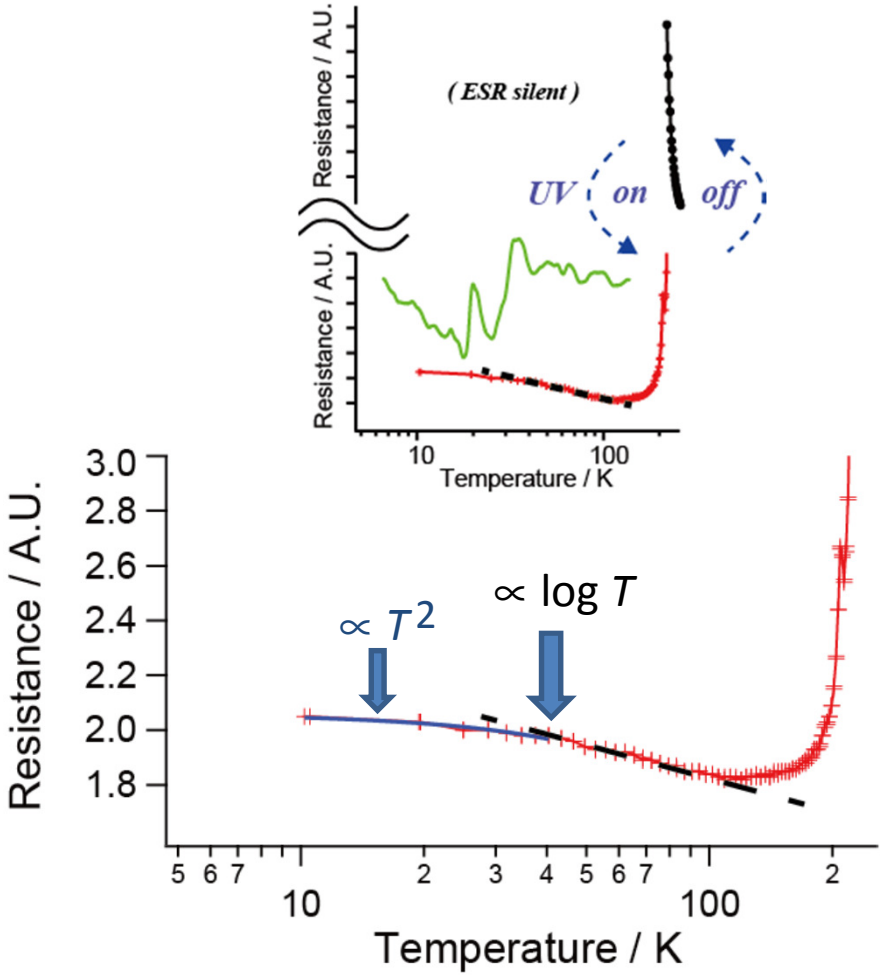
（930 ℃、5 h） → Oxygen deficiency（irrev.）

Irradiation → Photoexcited State

→ CT trans.（rev.）

PHOTOMAGNETIC CONDUCTORS





(Possible Kondo Effect under UV)

T. Naito *et al*, *Adv. Mater.*, **24** (46), 6153-6157 (2012)

T. Naito *et al*, *J. Am. Chem. Soc.*, **134**(45), 18656-18666 (2012)

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★ Collaborators

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Mr. T. Takano, Dr. Y. Takahashi, Prof. T. Inabe (Hokkaido University)

Profs. S. Nishihara & K. Inoue (Hiroshima University)

Profs. K. Furukawa* & T. Nakamura (IMS) (*present Niigata Univ.)

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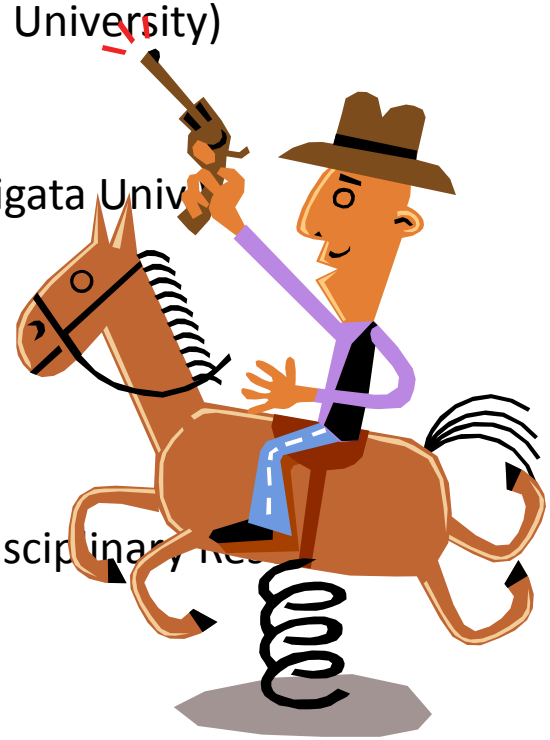
Japan Securities Scholorship
Ehime Univ. GP
Ehime Univ. Grant for Interdisciplinary Re

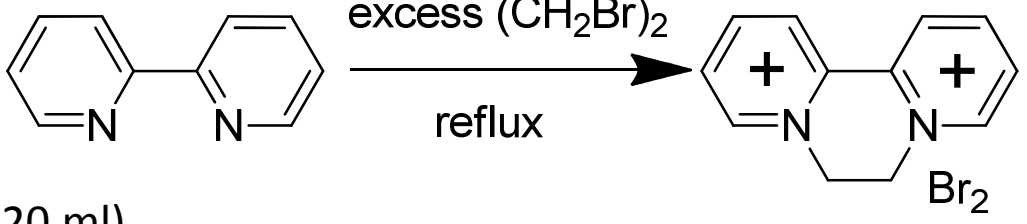
Thank you



Synthesis（Crystallization）

$A[Ni(dmit)_2]_X$

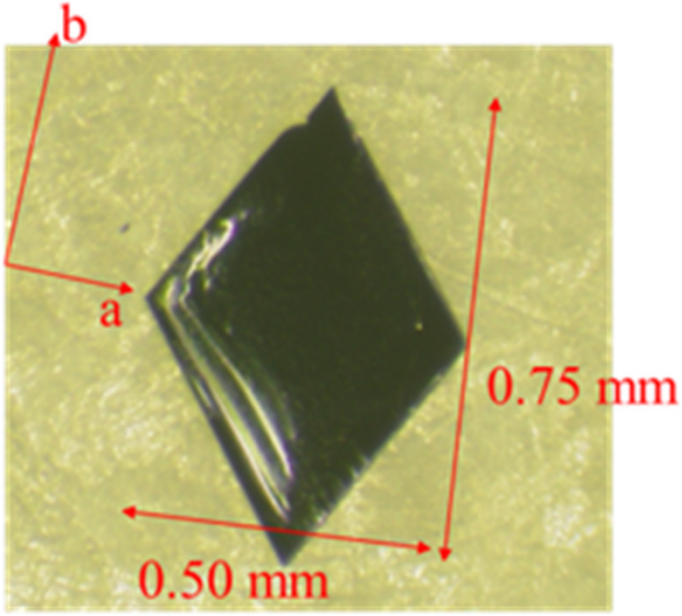
Step 1



Step 2

$(n\text{-}C_4H_9)_4N[Ni(dmit)_2]$ (10 mg) / CH_3CN (20 ml)

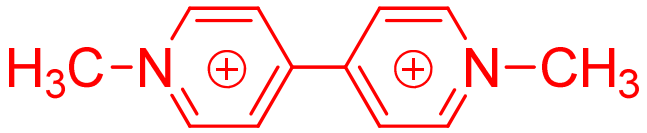
$BPY{\cdot}Br_2$
(10 mg) / CH_3CN (20 ml)



thickness : ~20 μm

Single crystal of $MV[Ni(dmit)_2]_2$

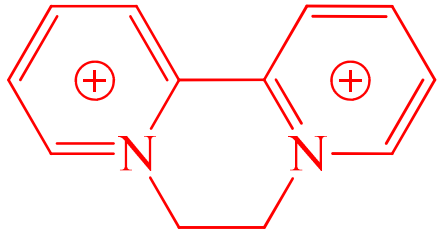
A X



2

(MV^{2+})

T. Naito *et al*, *Adv. Mater*. **24**, 6153 (2012)

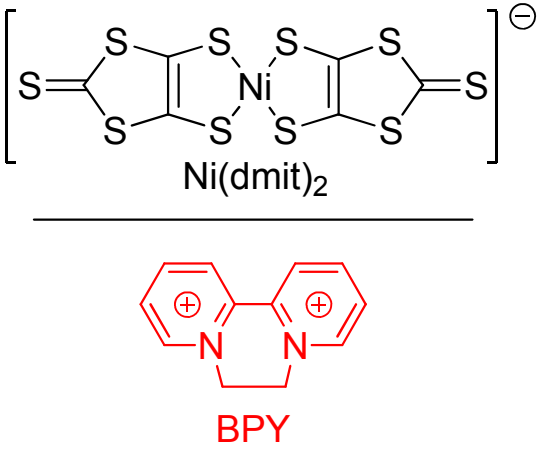


2, 6

(BPY^{2+})

Naito *et al.*, *J. Am. Chem. Soc.* **134**, 18656 (2012)

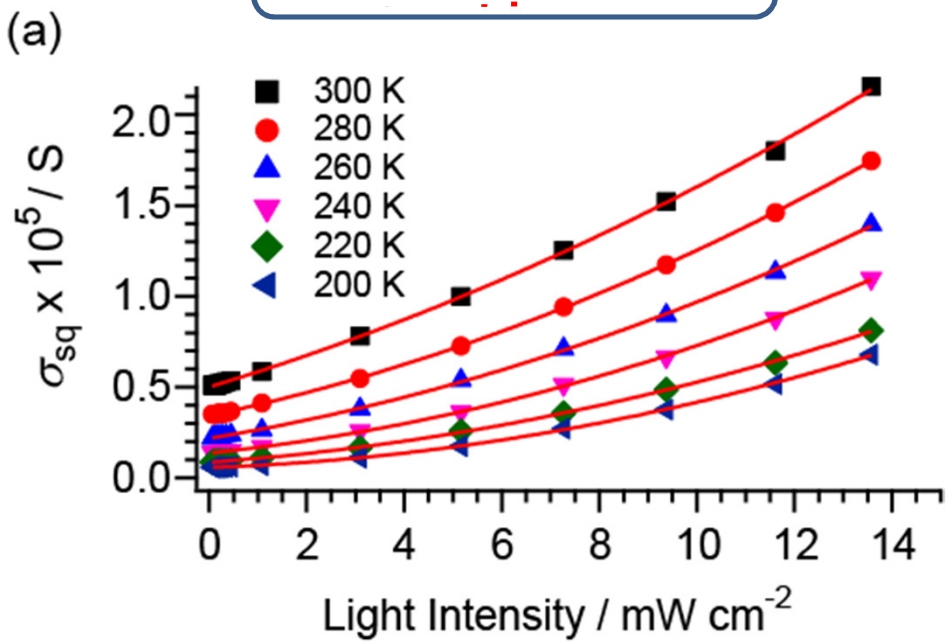
Case 1; D-A CT (3)



< ESR under dark vs. under UV >

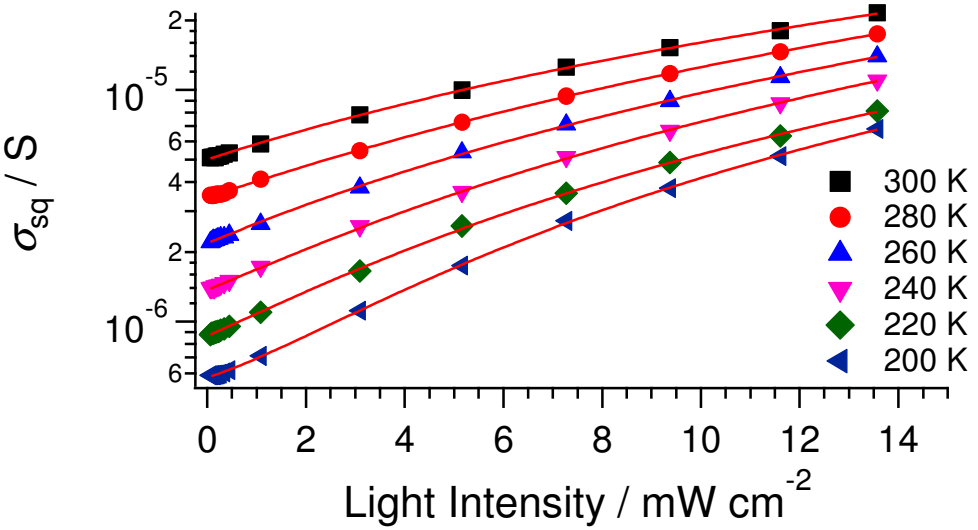
New Features for PC

Non-linear behavior



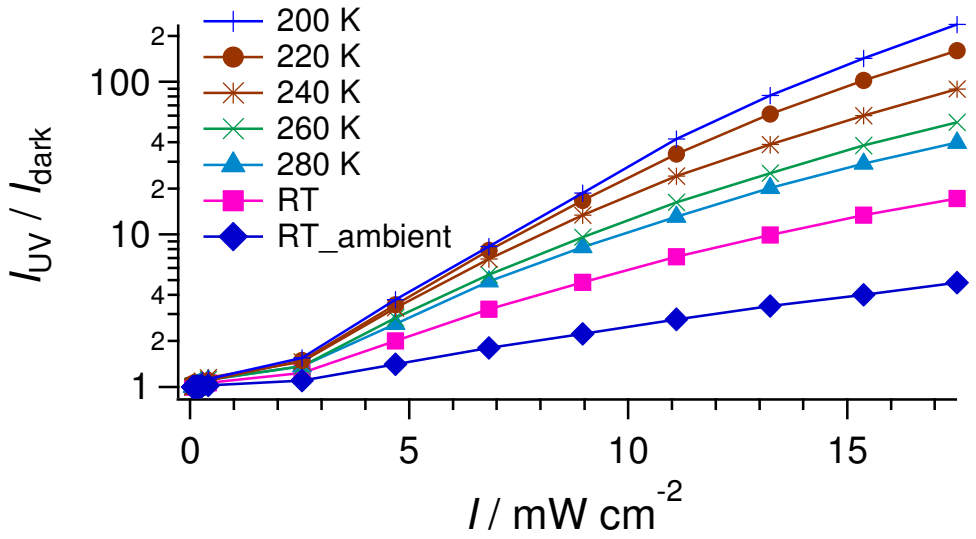
375 nm

T. Naito *et al*, *J. Am. Chem. Soc.*, **134**(45), 18656-18666 (2012)



BPY

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}$$

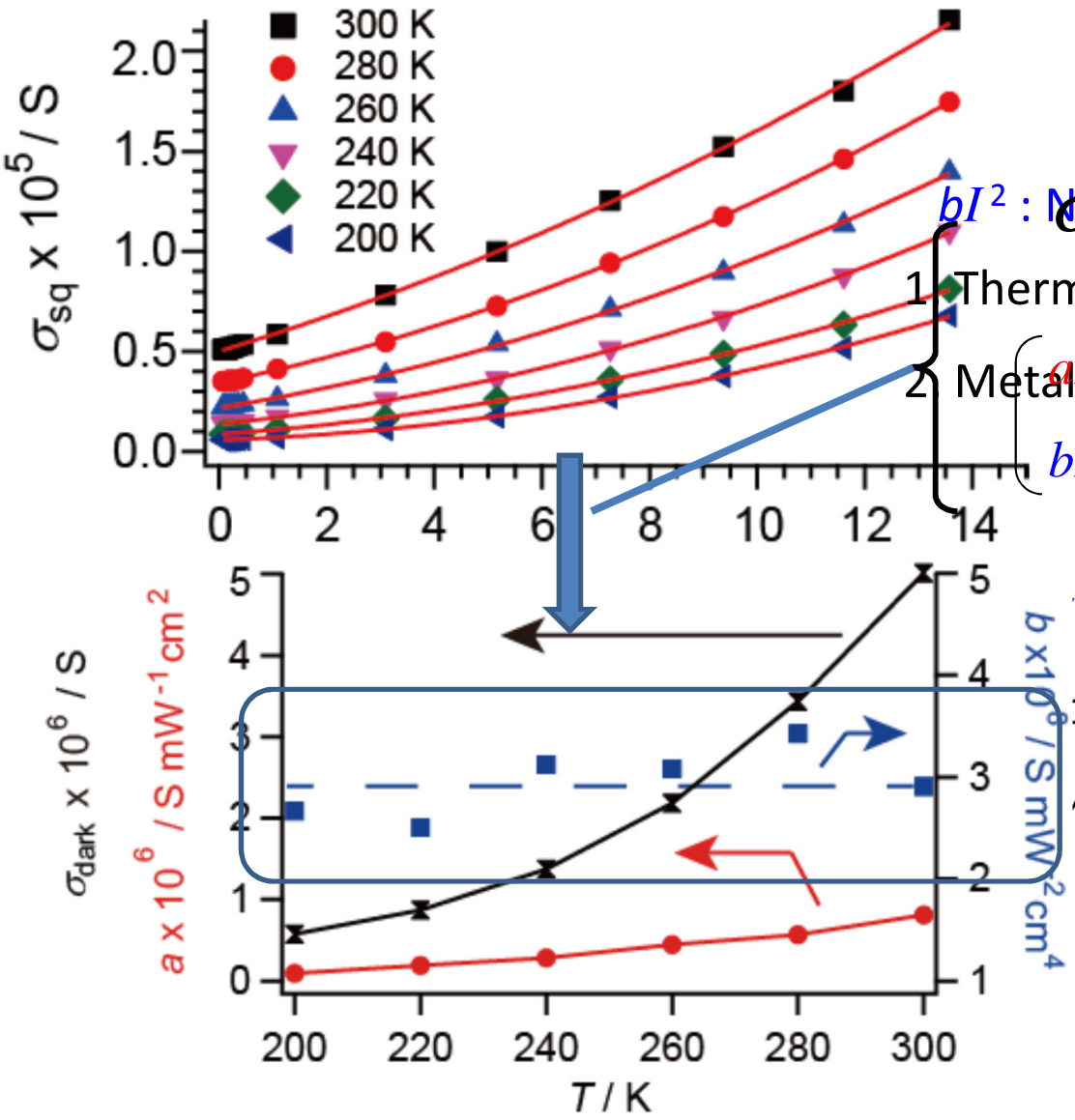


MV

A[Ni(dmit)$_2$]$_2$; photoconductivity – I- & T-dependences

A = BPY

（Single Crystal）（375 nm, in vauo）



$\sigma_{sq} = \sigma_{dark} + aI + bI^2$

bI^2 : Nearly T-independent

1 Thermally *inaccessible* to the dark states

2 Metallic conduction

aI : known/standard mechanism

bI^2 : a new mechanism

: Non-linear dependence on I

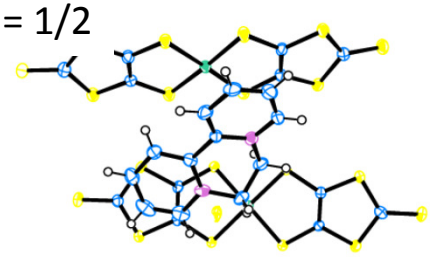
portance of coo rative effect*

s. Soc. Jpn. **2004**, *73*, 2868-2878.

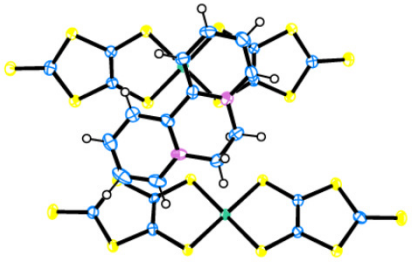
2+ 1-

$BPY[Ni(dmit)_2]_2$

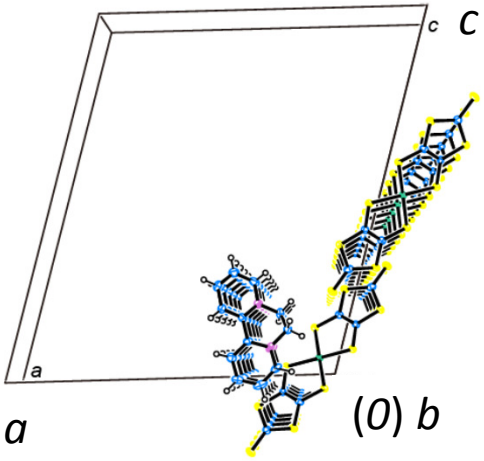
$S = 0$ $S = 1/2$



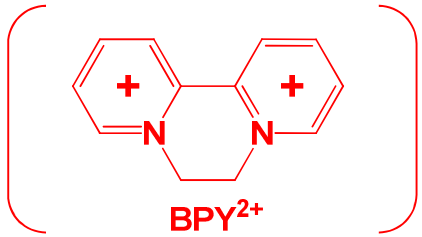
top view (1)

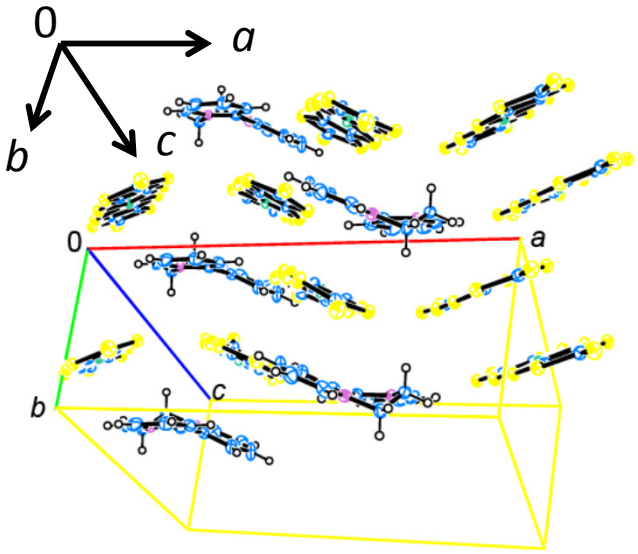


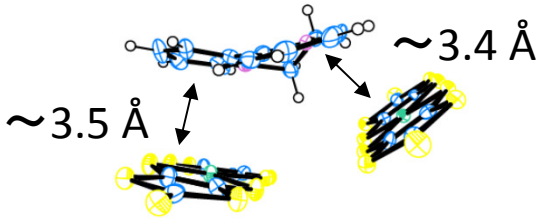
top view (2)



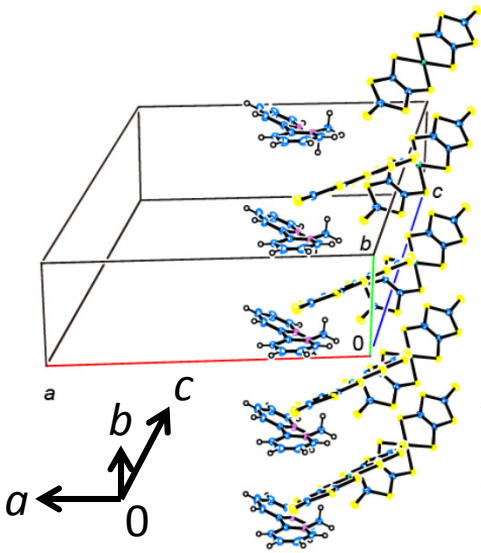
top view







side view



side view

Monoclinic, $P2_1/c$ (#14) (MV)

a = 20.856(5) Å (11.4125(9) Å)

b = 7.466(2) Å β = 105.585(4)°

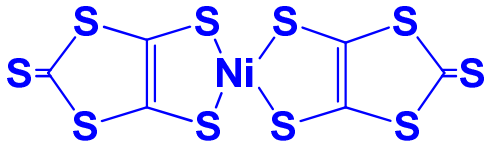
c = 24.162(7) Å

V = 3624(2) Å^3 (1882.7(3) Å^3)

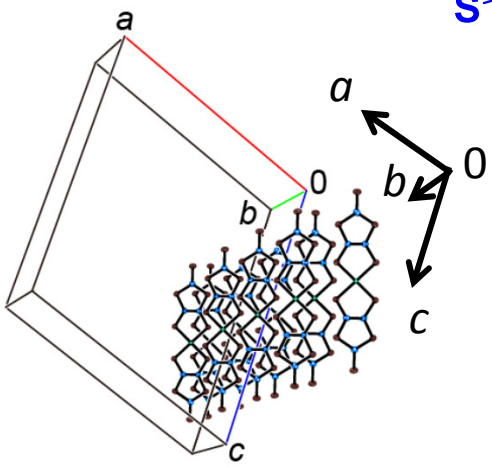
Z = 4 (Z = 2)

JACS, 18656 (2012)

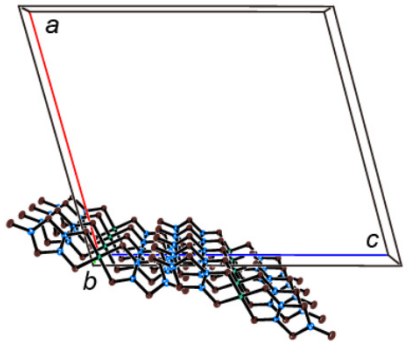
BPY[Ni(dmit)$_2$]$_2$

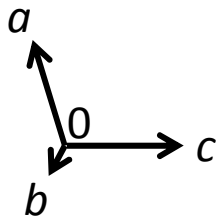


[Ni(dmit)$_2$]

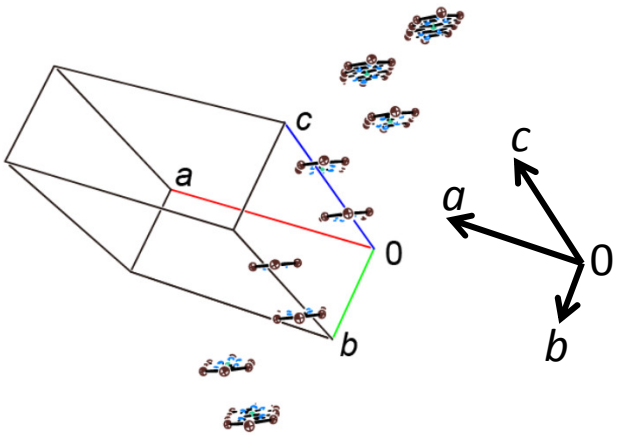


top view

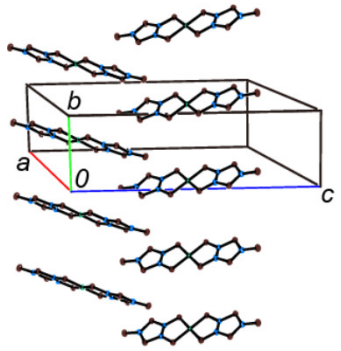


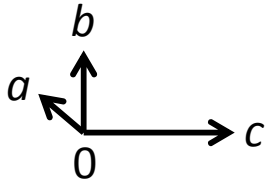


top view



side view

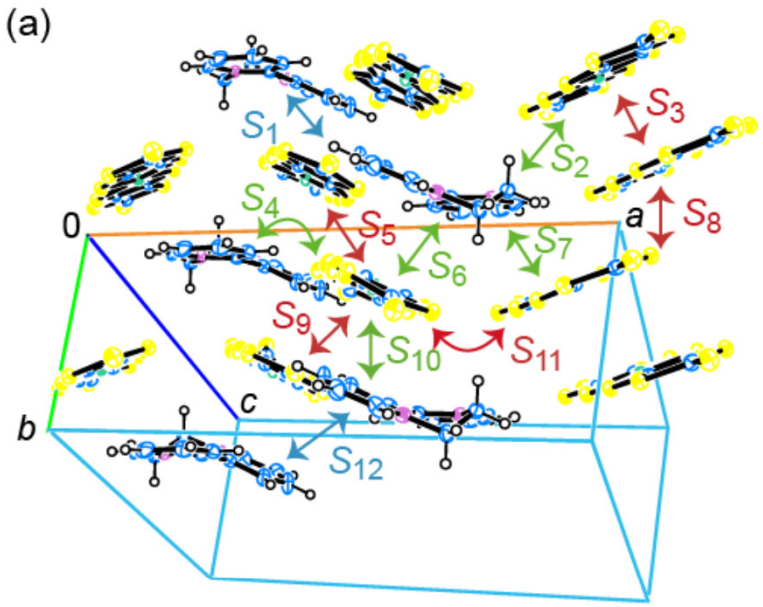


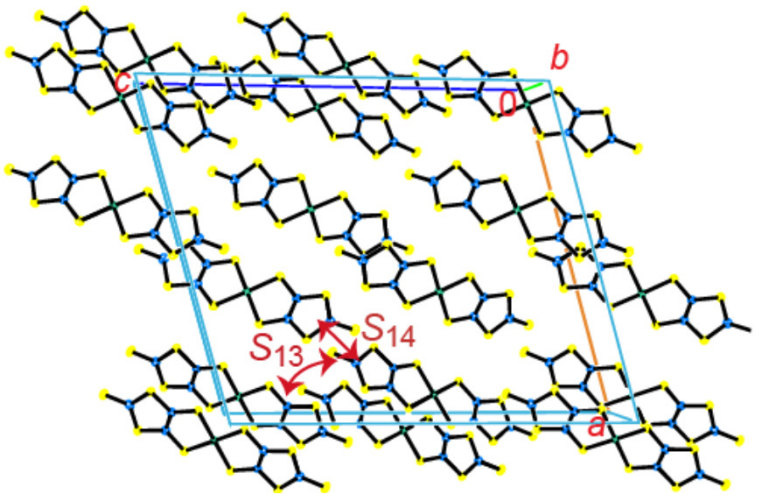


side view

JACS, 18656 (2012)

BPY[Ni(dmit)$_2$]$_2$ Intermolecular Interactions（Extended Hückel Method）





Ni(dmit)$_2$-Ni(dmit)$_2$

$S_3 \sim 0.015$

$S_9 \sim -0.004$

$S_5, S_8 \sim 0.002$

$S_{11}, S_{13}, S_{14} \leq 0.001$

BPY-Ni(dmit)$_2$

$S_2, S_6 \sim 0.001$

$S_7 \sim 0.002$

$S_{10} \sim 0.009$

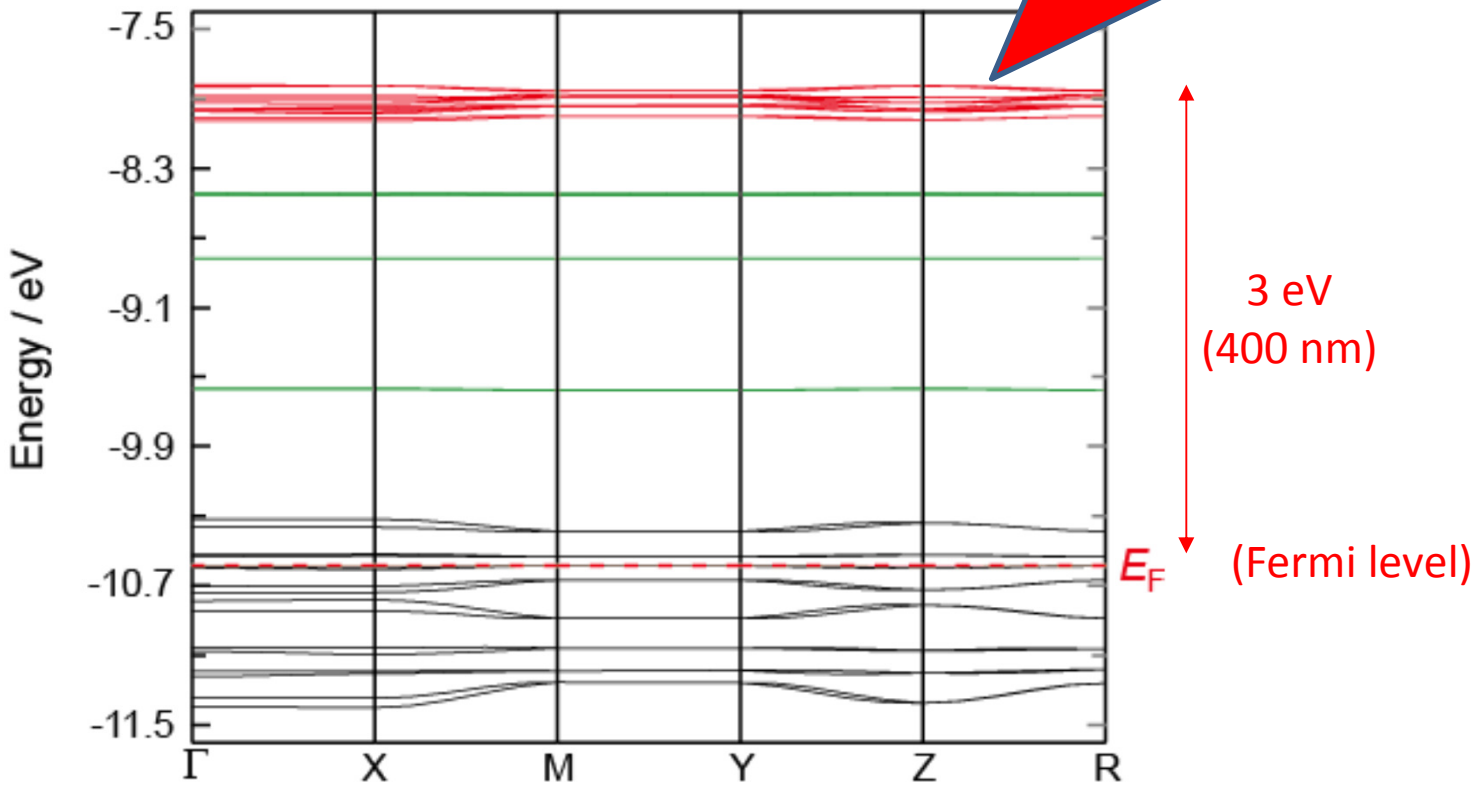
$BPY[Ni(dmit)_2]_2$ Band Calculation（Extended Hückel Method）

Red：(e.g.)～37% $Ni(dmit)_2$

Green：～100% BPY

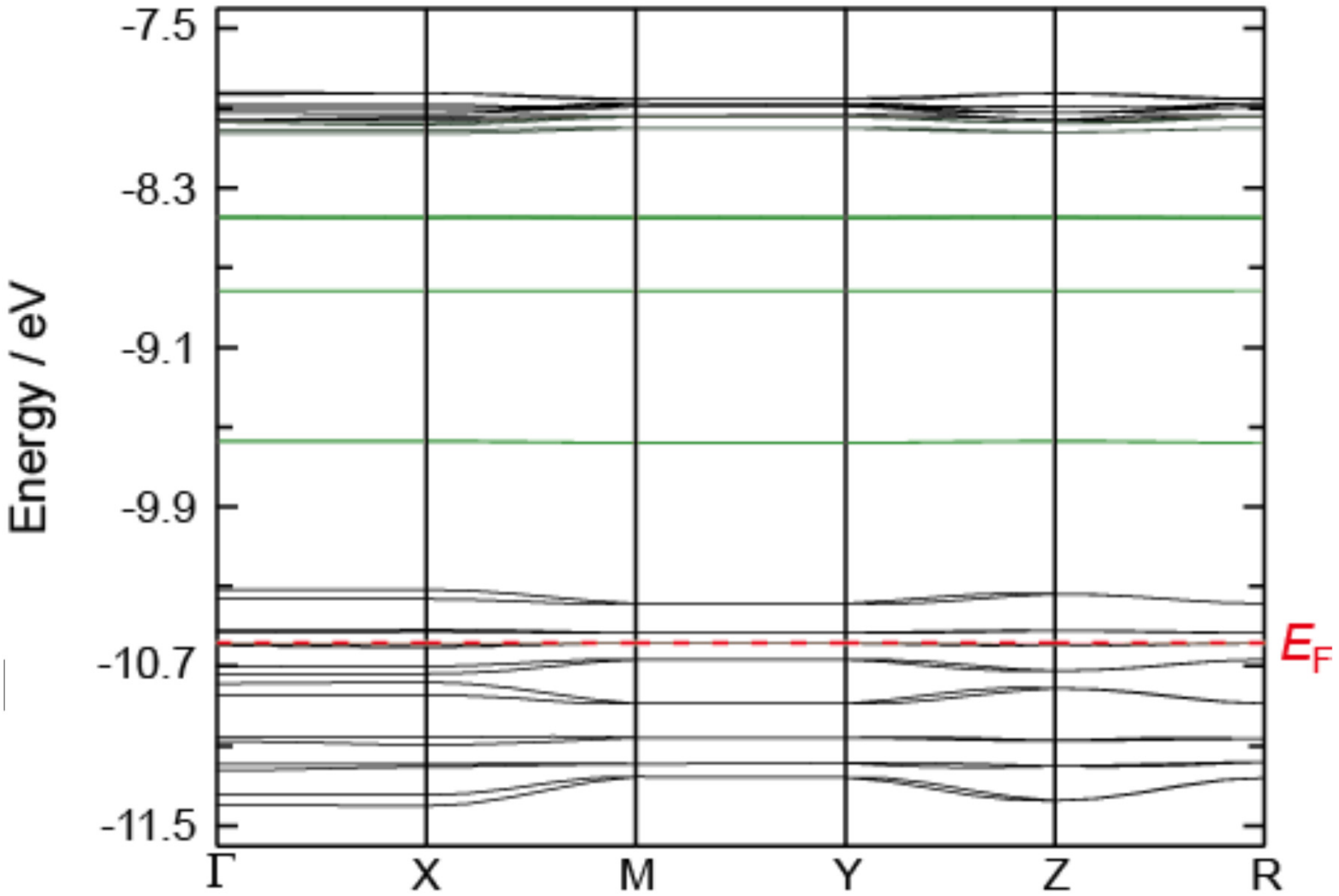
Black：～100% $Ni(dmit)_2$

Feat. 1) Anion-Cation Mixed Bands



JACS, 18656 (2012)

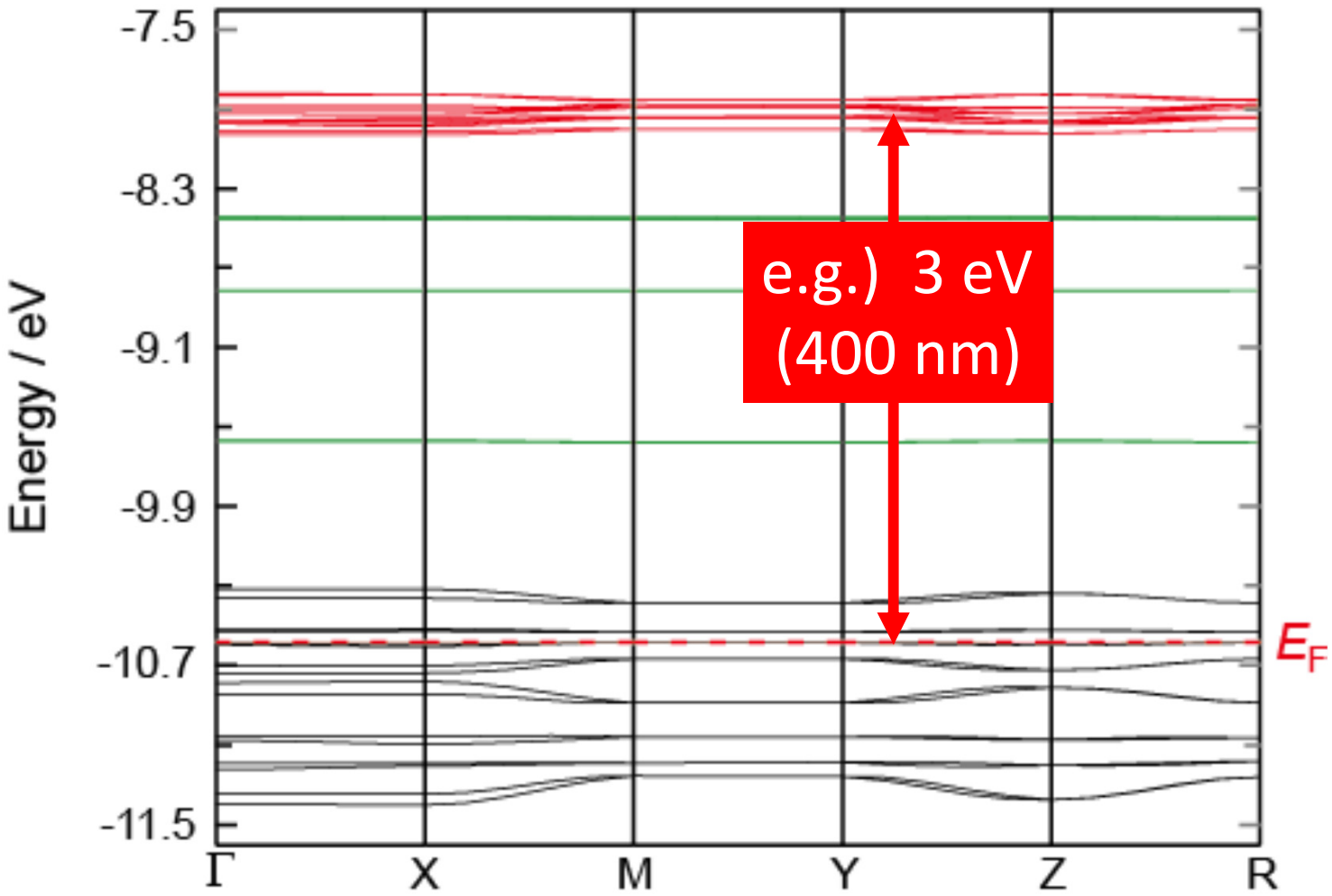
$BPY[Ni(dmit)_2]_2$ Band Structure（ Calc. Extended Hückel Method ）



$BPY[Ni(dmit)_2]_2$ Band Structure（ Calc. Extended Hückel Method ）

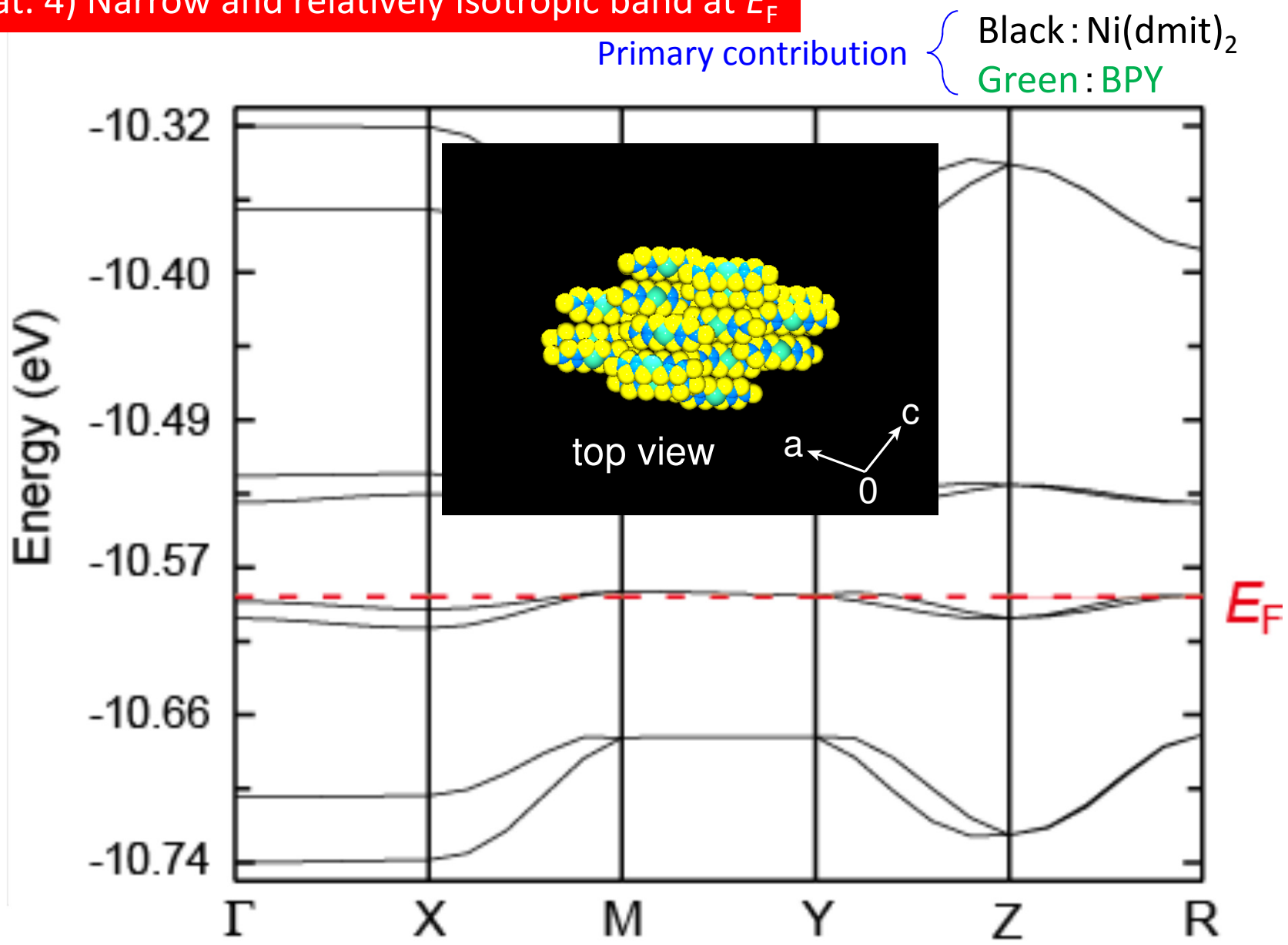
Feat. 3) CT ∈ UV region (~ a few eV)

Primary contribution { Black : $Ni(dmit)_2$ / Green : BPY



BP

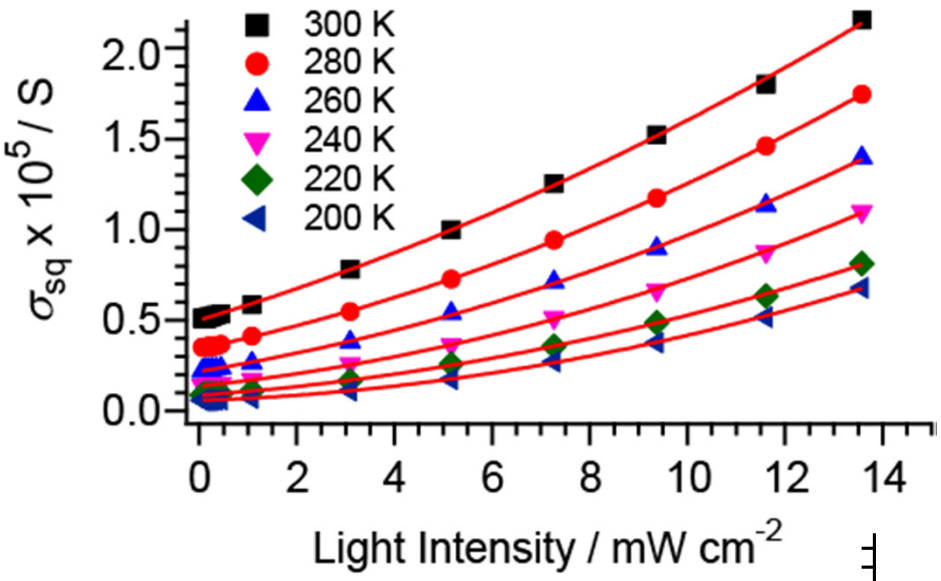
Feat. 4) Narrow and relatively isotropic band at E_F



A[Ni(dmit)$_2$]$_2$; photoconductivity – I- & T-dependences

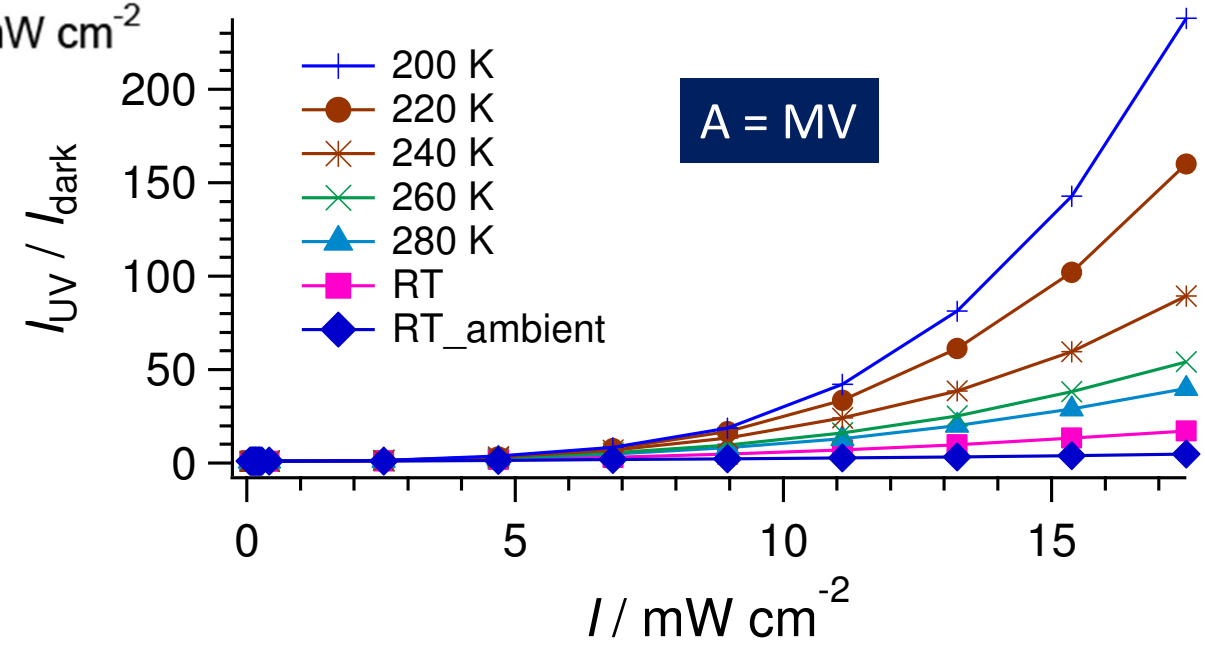
（Single Crystal）（375 nm, in vauo）

A = BPY



Non-linear

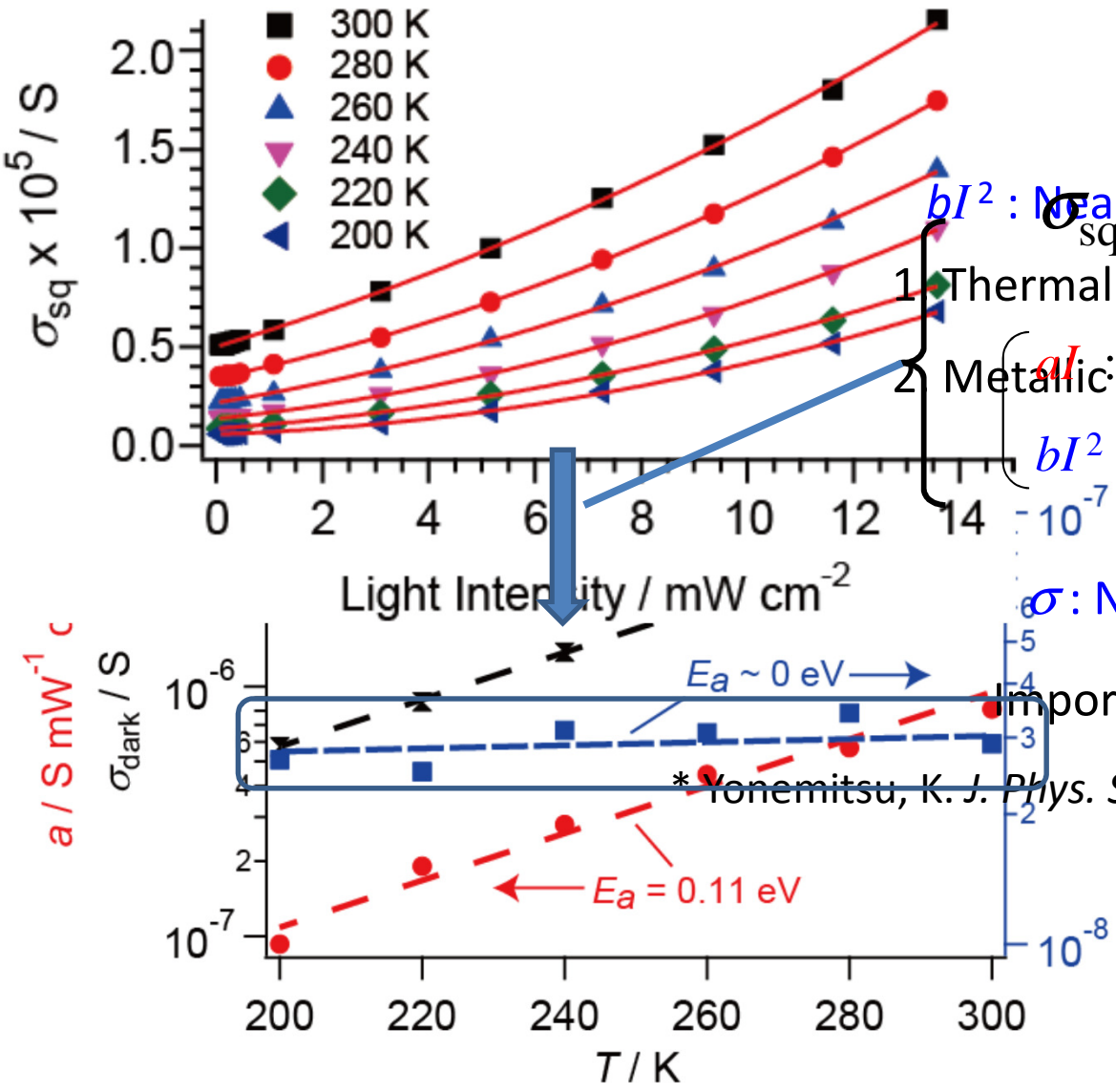
A = MV



A[Ni(dmit)$_2$]$_2$; photoconductivity – I- & T-dependences

A = BPY

（Single Crystal）（375 nm, in vauo）



$\sigma_{sq} = \sigma_{dark} + aI + bI^2$

1 Thermally *inaccessible* to the dark states

2 Metallic conduction

aI : known/standard mechanism

bI^2 : a new mechanism

bI^2 : Nearly T-independent

σ : Non-linear dependence on I

Importance of cooperative effect*

* Yonemitsu, K. *J. Phys. Soc. Jpn.* **2004**, *73*, 2868-2878.

Photoconductivity – I-dependence (General behavior)

Pentacene （Single Crystal）

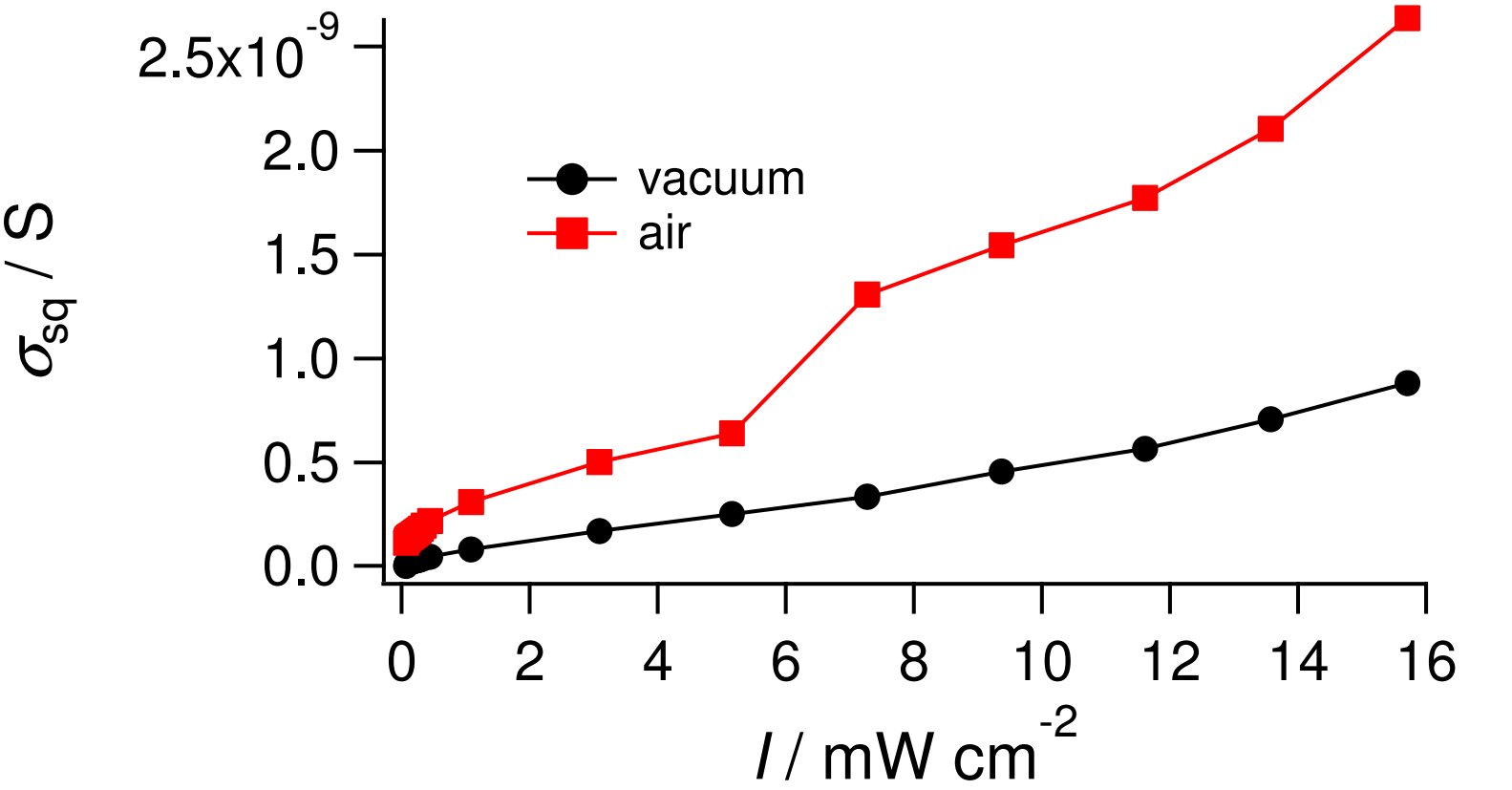
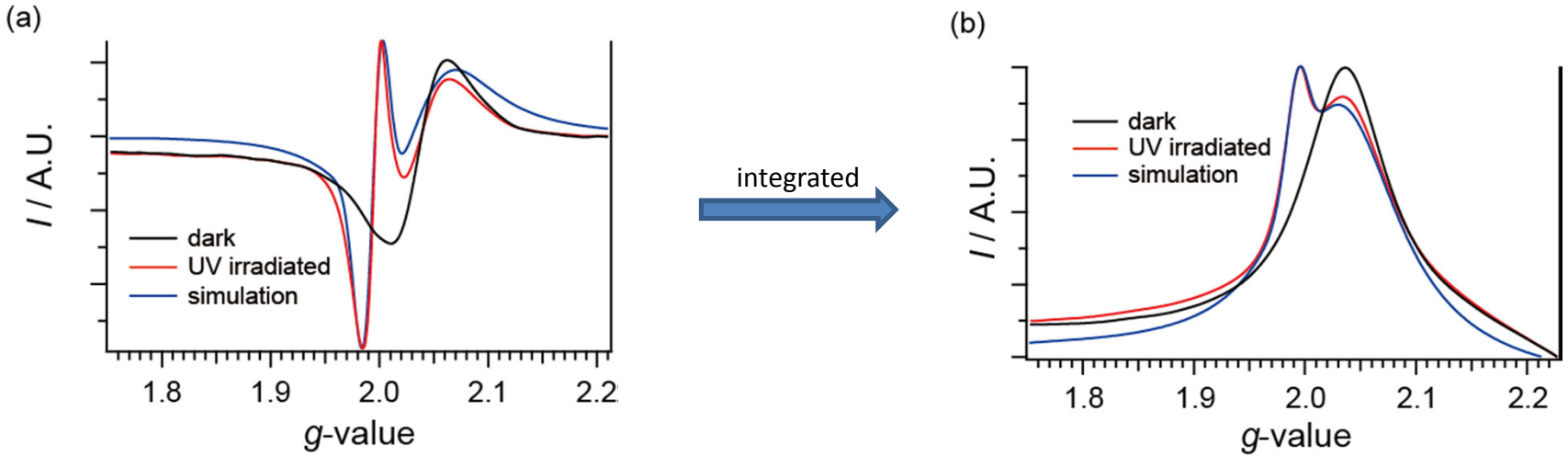
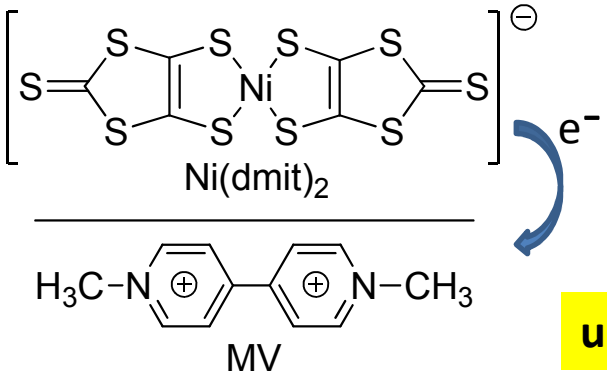


Table S3. ESR simulation parameters for BPY[Ni(dmit)$_2$]$_2$ (measured on the single crystal with H // [010] at 153 K).

Spin #	1 (on Ni(dmit)$_2$)	2 (on BPY)
Relative Intensity	110	4.0
Nuclear Spin I	1/2 (^{1}H)	1 (^{15}N)
Electron Spin S	1/2	1/2
g_x	2.035	1.988
g_y	2.020	1.992
g_z	2.040	2.001
A_x [mT]	2.50	1.30
A_y [mT]	3.50	0.50
A_z [mT]	6.00	0.50
Γ_x [mT]	12.5	2.50
Γ_y [mT]	8.50	2.50
Γ_z [mT]	9.20	2.50
Gaussian/Lorenzian	0/100	100/0



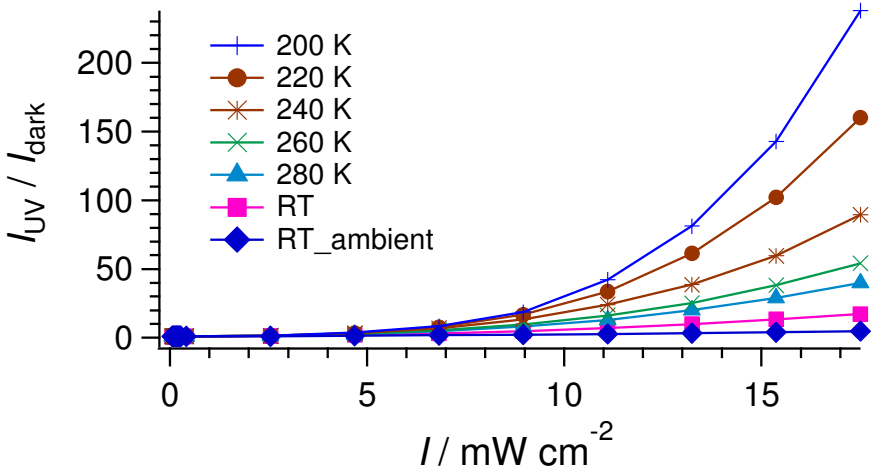
Our previous work; C-A CT

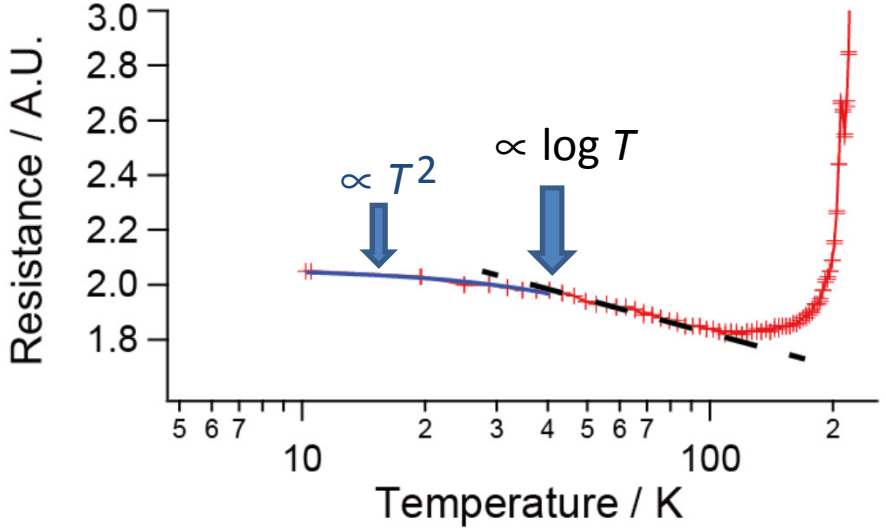


New Features for PC

Metallic conduction
(Possible) Kondo Effect
Non-linear dependence on ***I***

under continuous UV irradiation 375 nm





T. Naito *et al*, *Adv. Mater.*, **24** (46), 6153-6157 (2012)

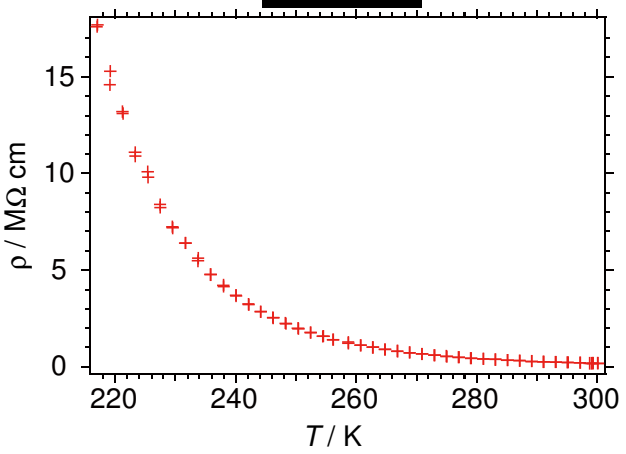
cf. T. Naito *et al*, *J. Am. Chem. Soc.*, **134**(45), 18656-18666 (2012)

$MV[Ni(dmit)_2]_2$

T-dependence of *R*（single crystal）

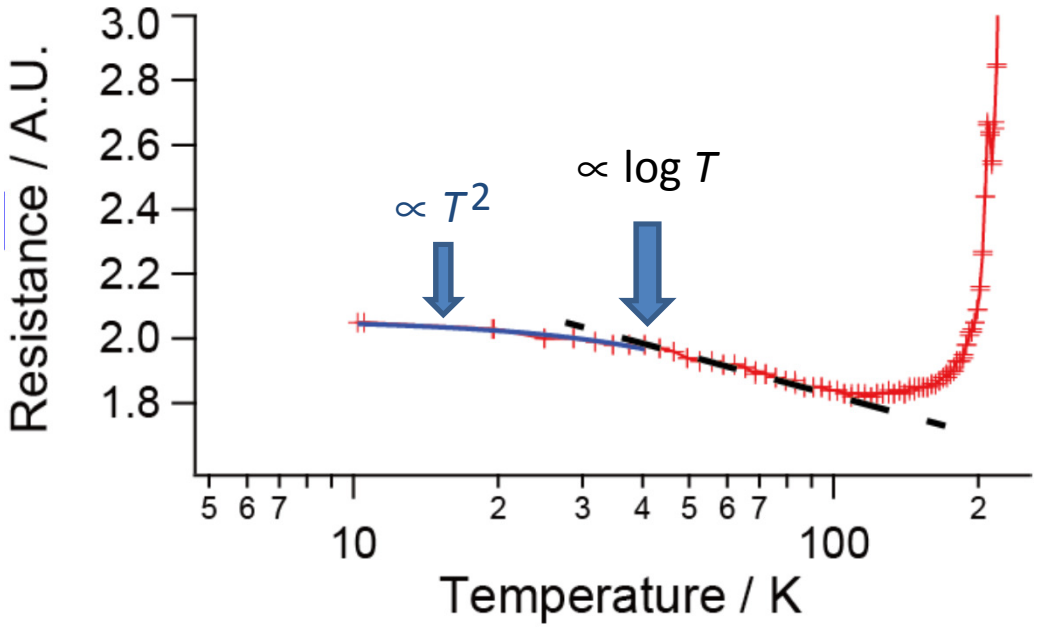
Evidence for Interaction between carriers and localized spins

dark



Semiconducting

under continuous UV irradiation



$[Ni(dmit)_2]^- \xrightarrow{UV} [Ni(dmit)_2]^{0.98-}$

(Estimated from band calc. & UV spectra)

Kondo Effect

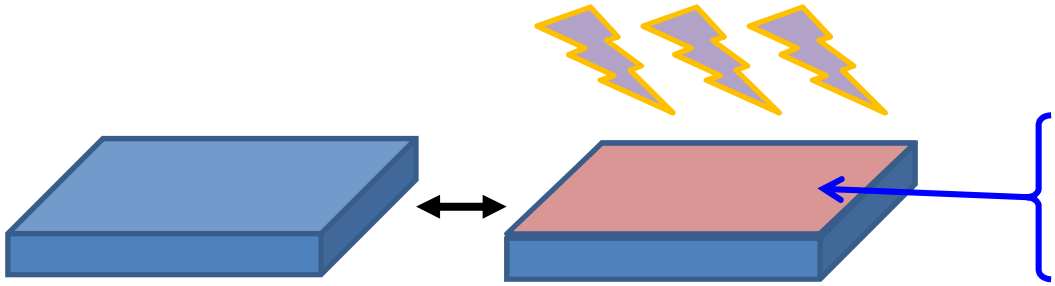
Metallic electronic system

(unpaired electrons for Conduction)

INTERACTION

Localized spin system

(unpaired electrons for Magnetism)



Dilute localized spin system (on MV)

Carriers (on $Ni(dmit)_2$)

D-A 相互作用で混じったバンド （各寄与がバンド毎に異なる）

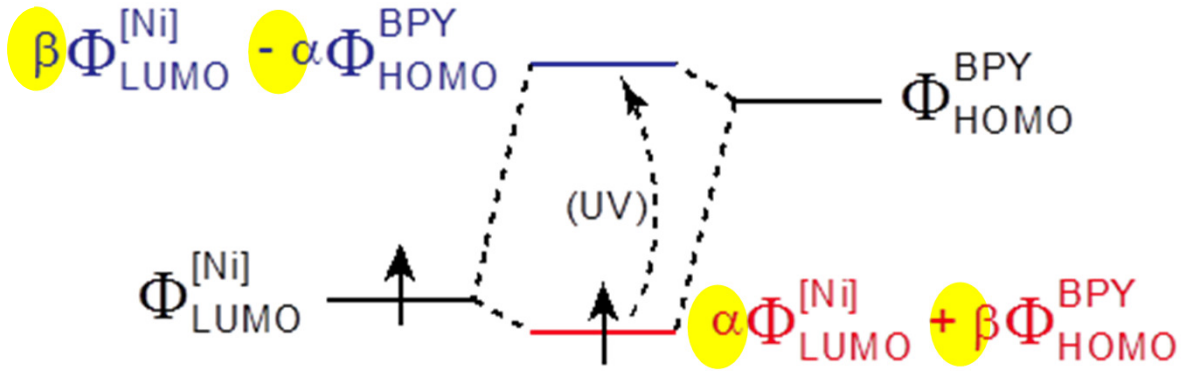
（例）

ドナー（D）分子

$[Ni(dmit)_2]^-$ ([Ni])

アクセプター（A）分子

BPY^{2+} (BPY)

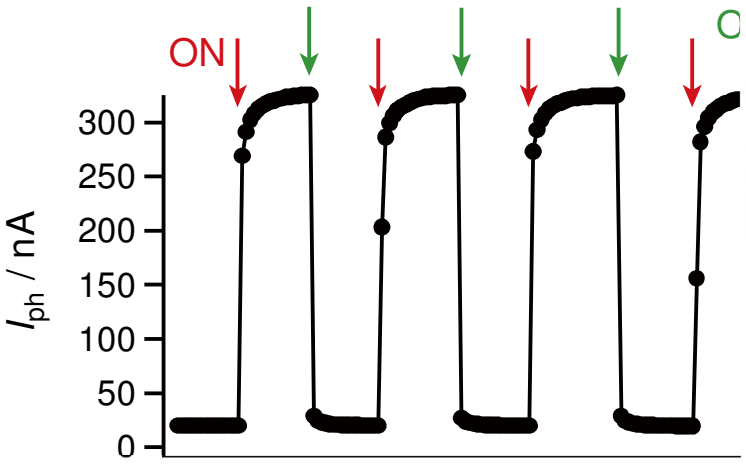


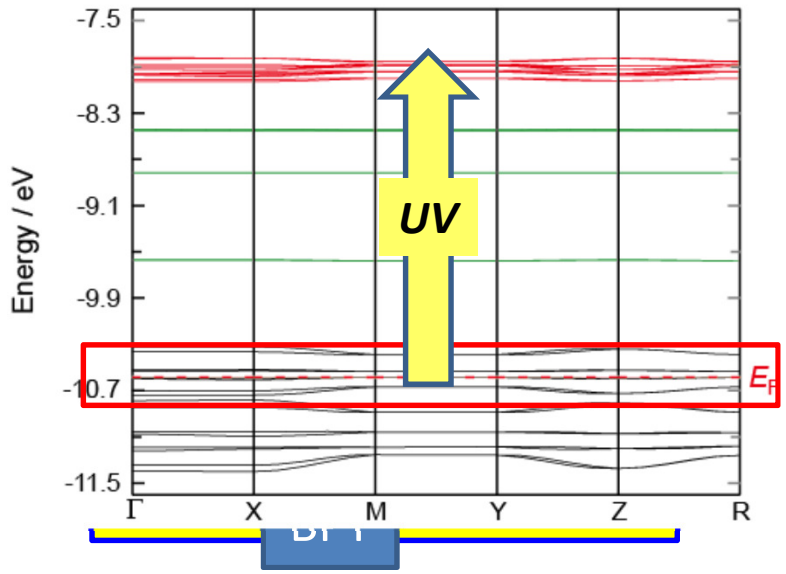
$$\delta = \frac{|\alpha^2 - \beta^2|}{\alpha^2 + \beta^2} \times f$$

$$[Ni(dmit)_2]^{-} \rightarrow [Ni(dmit)_2]^{(1-\delta)-}$$

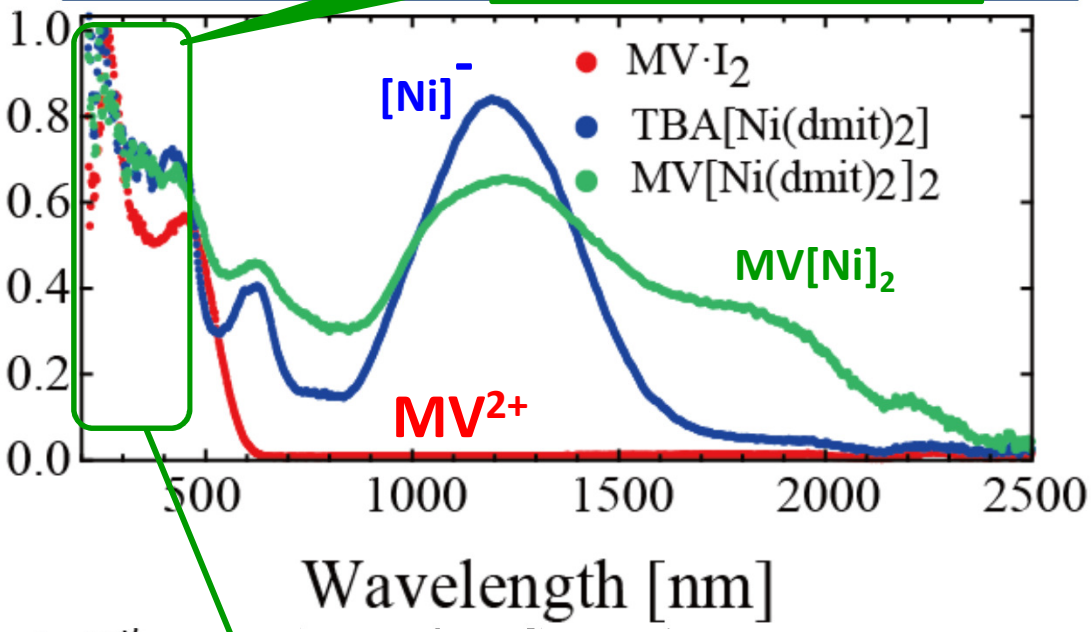
$A[Ni(dmit)_2]_2$（A = MV, BPY）; 光応答（単結晶）

光電流 (300 K, 375 nm, 11.6 mW

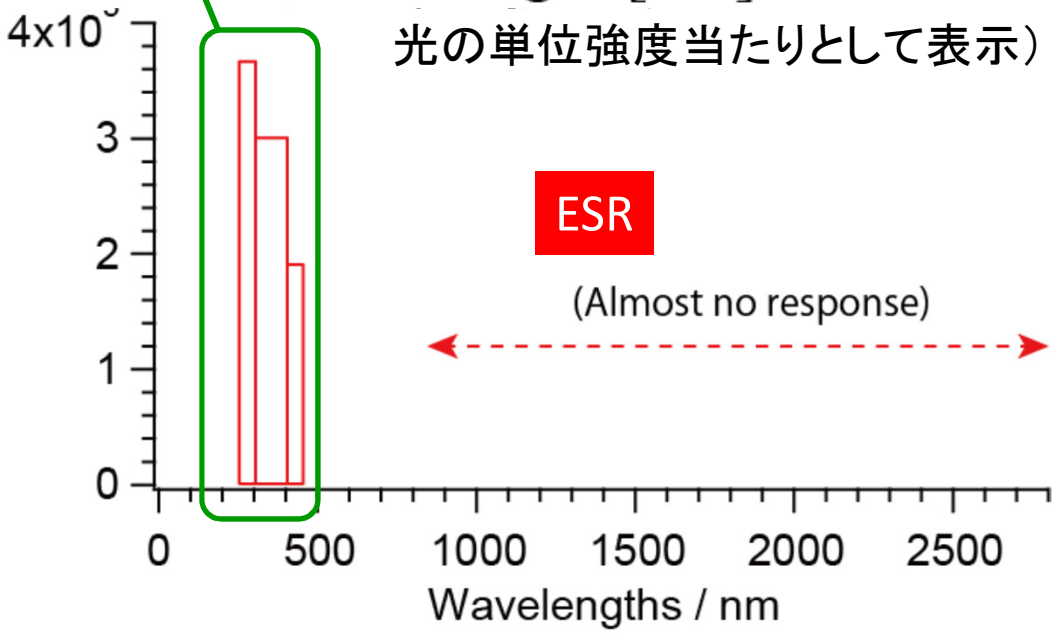




$MV^{2+} \xleftarrow{e^-} [Ni(dmit)_2]^-$



光の単位強度当たりとして表示）



ESR

(Almost no response)

$A[Ni(dmit)_2]_2$ (A = BPY, MV) Summary & Conclusion

Crystal Structure 3D closely packed $[Ni(dmit)_2]^-$ accommodating

photochemical redox active BPY^{2+} / MV^{2+}

Electronic Structure Isotropic

Strongly correlated (Narrow bands around E_F)

strong $Ni(dmit)_2$—cation interaction

Electronic Properties

Dark semiconducting & diamagnetic

UV irradiated Unpaired electrons on both of cation & $Ni(dmit)_2$

(cation ≈ Loc. Spins, $Ni(dmit)_2$ ≈ Carriers)

cf. Kondo effect (MV salt)

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