Spin transport and relaxation mechanism in disordered organic film

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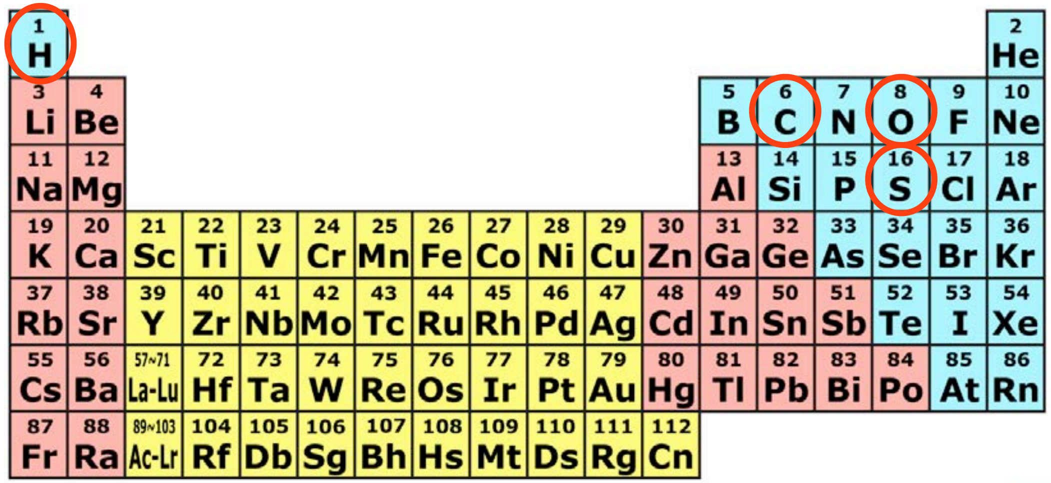
Organic spintronics

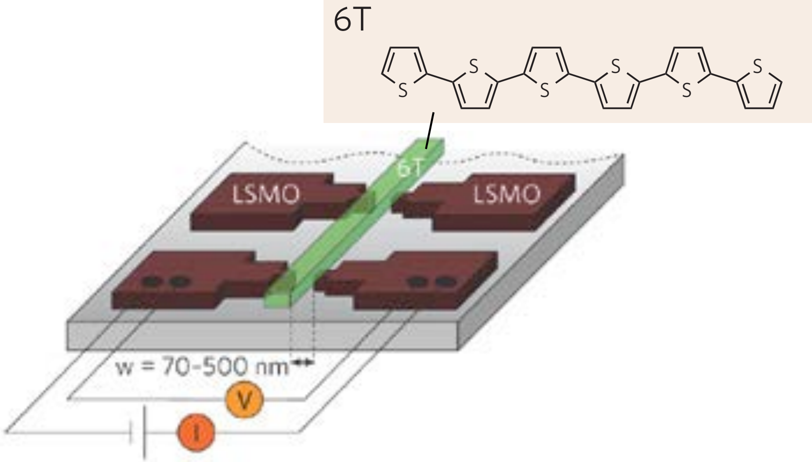
- Organic semiconductors consist of relatively light elements.(For example, C, H, O, S, ...)



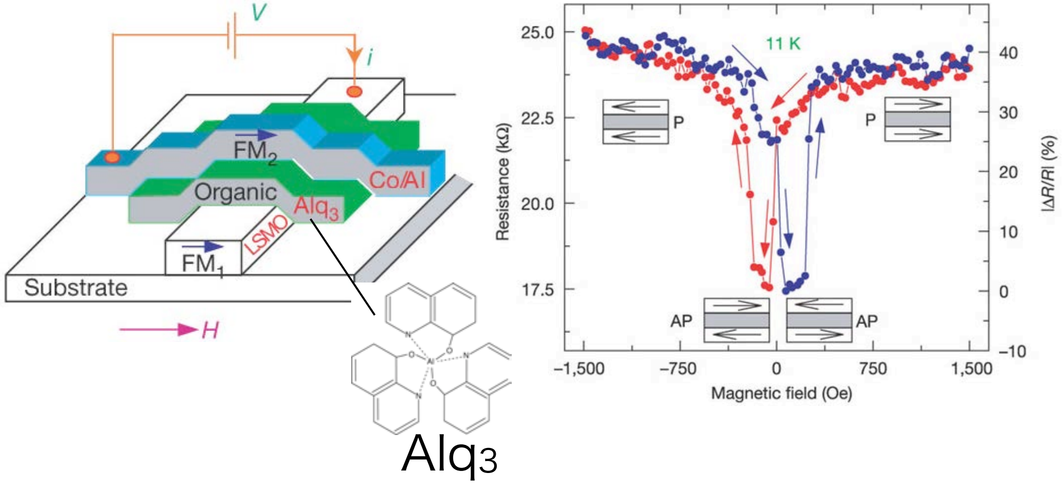
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57~71 La-Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89~103 Ac-Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn						

Small spin-orbit interaction

Long spin lifetime & diffusion length

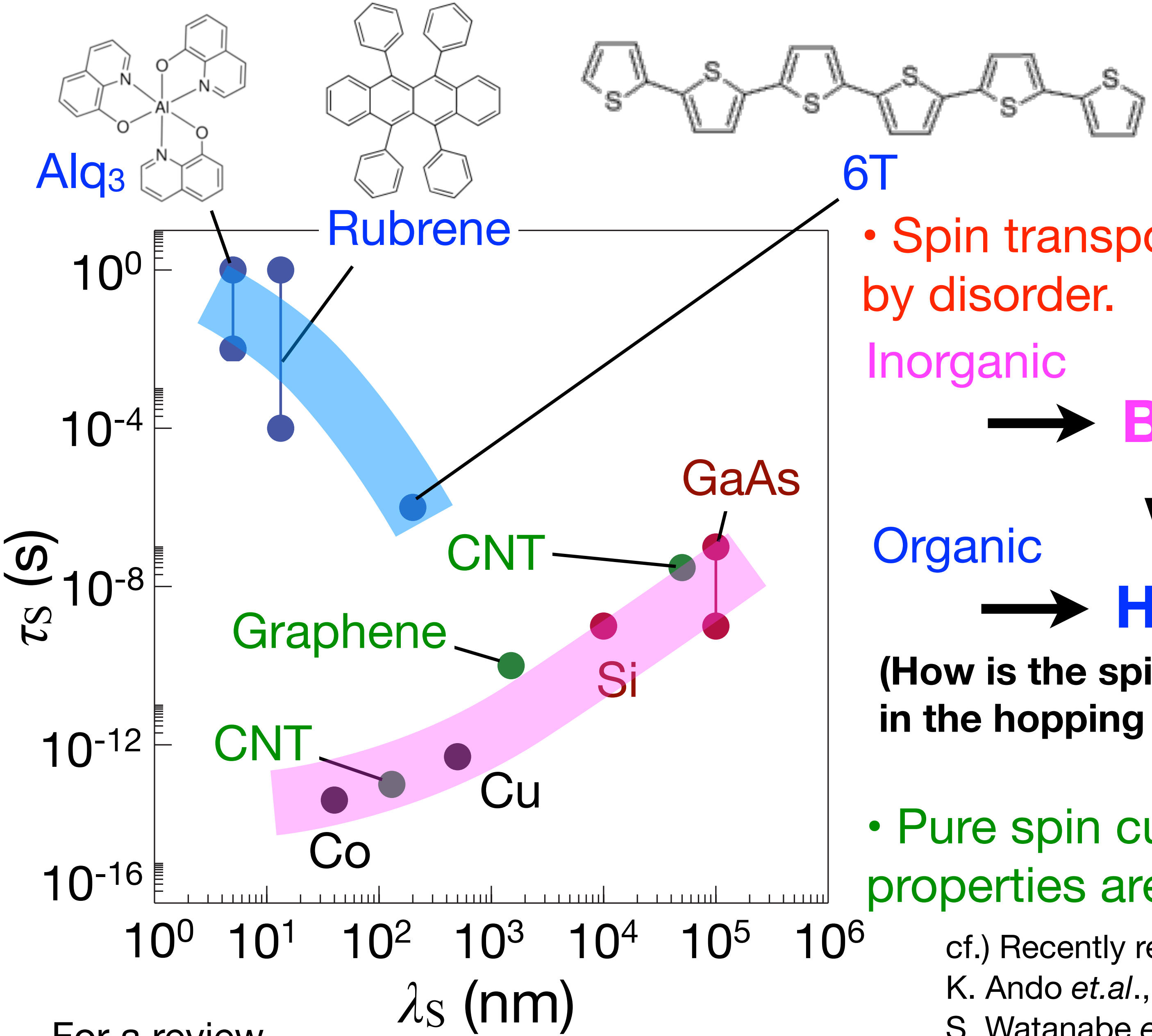


V. Dediu et al., Solid State Commun. **122** (2002) 181.



Xiong, Z. H., Wu, D., Vardeny, Z. V. & Shi, J. Nature **427**, 821 (2004).

Organic spintronics



- Spin transport is strongly limited by disorder.

Inorganic

→ **Band transport**

vs

Organic

→ **Hopping transport**

(How is the spin relaxation mechanism in the hopping regime?)

- Pure spin current transport properties are not fully understood.

For a review,
G. Szulczewski, *et.al*., Nature Mat, **8** (2009) 693.

cf.) Recently reported works,
K. Ando *et.al*., Nature Mat. **12** (2013) 622.
S. Watanabe *et. al*., Nature Phys. **10** (2014) 308.

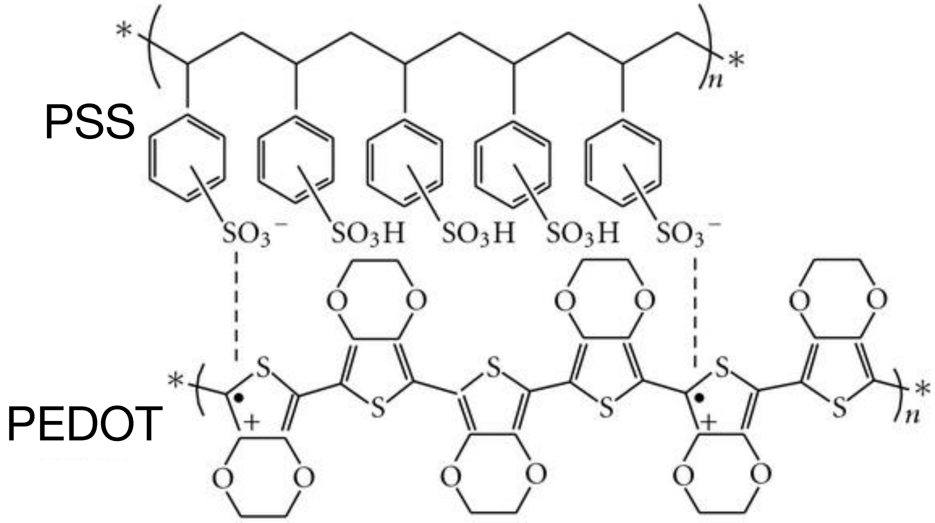
Motivation

- Comprehensive study of **pure spin transport** mechanism in organic semiconductors with **strong disorder**

- Experimental investigation of characteristic spin-transport parameters

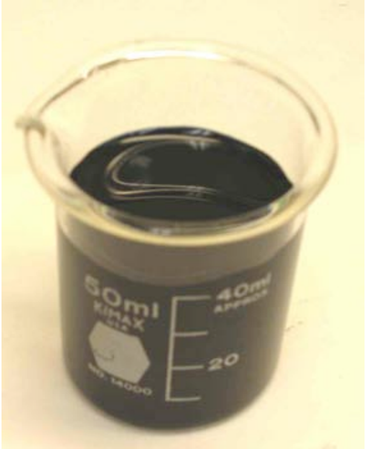
$$\underbrace{\lambda_S}_{\text{Spin pumping \& inverse spin Hall effect}} = \sqrt{\underbrace{D_S}_{\text{Charge transport}} \times \underbrace{\tau_S}_{\text{ESR (Electron spin resonance)}}}$$

Conducting polymer PEDOT:PSS

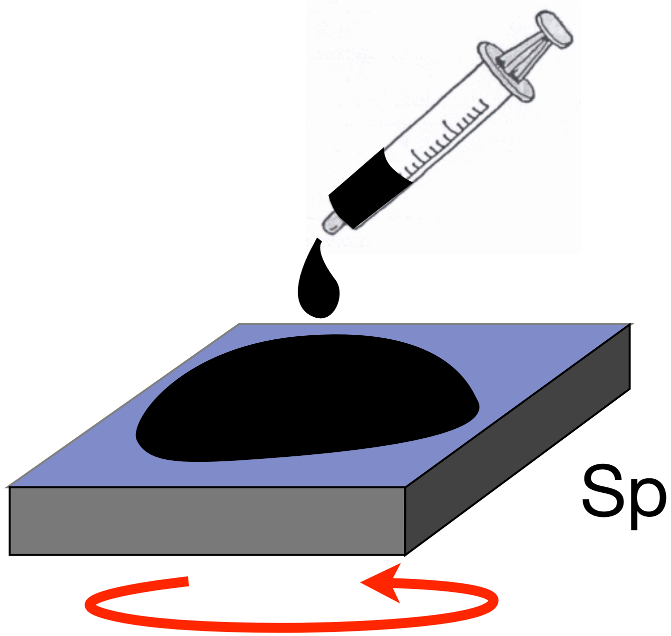


PEDOT is doped with PSS.

- Dopant density:
~10^{20}-10^{21} /cm^3
- Carrier: Hole of PEDOT
- Resistivity
~1 Ωcm (in-plane)
~10^3 Ωcm (out-of-plane)



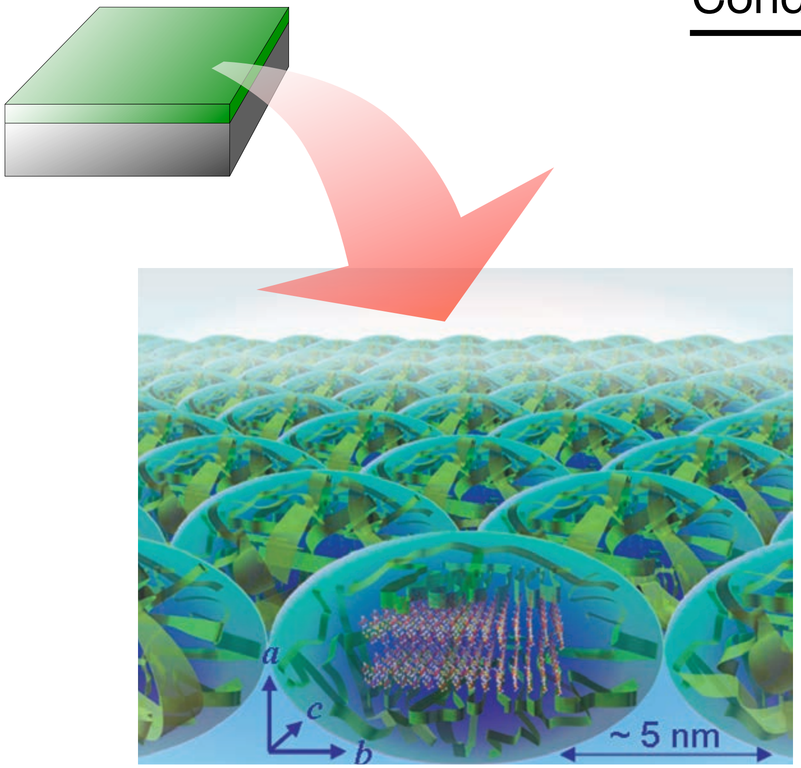
Water-based solution of PEDOT: PSS



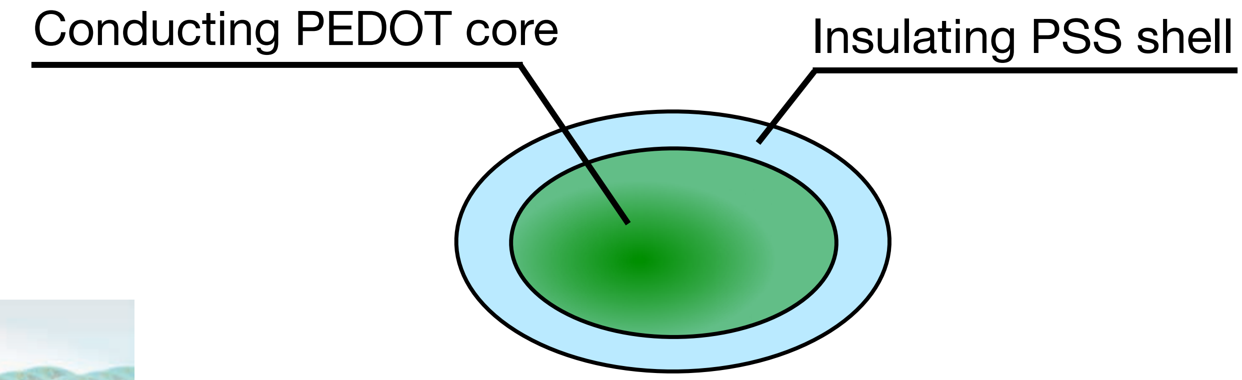
Spin coating

Conducting polymer PEDOT:PSS

- Nano-scale core-shell structure of PEDOT:PSS

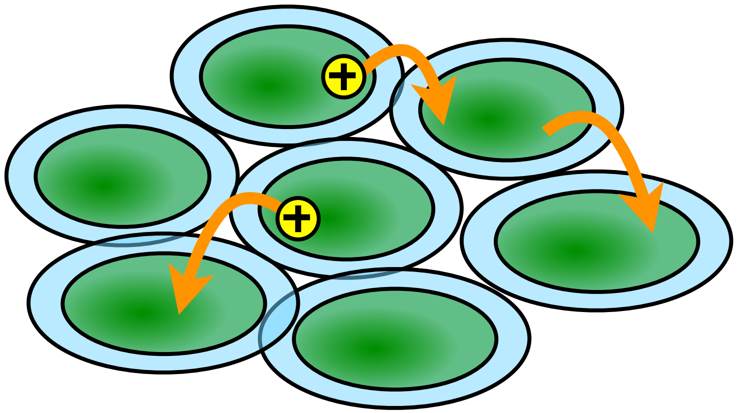


T. Takano *et.al*., Macromolecules 45 (2012) 3859.



Conducting PEDOT core

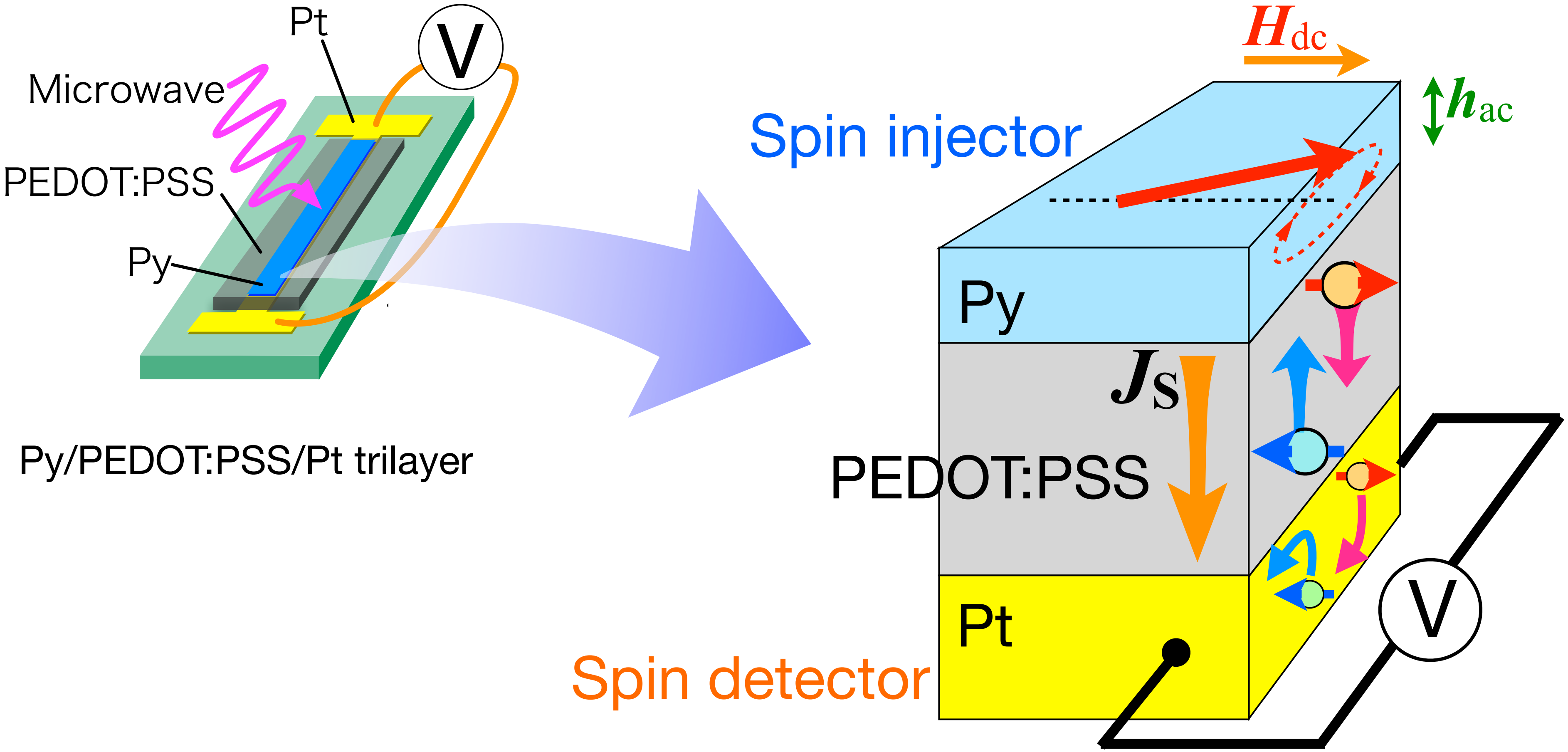
Insulating PSS shell



Highly doped OSC with strong disorder

Spin pumping & ISHE measurement in Py/PEDOT:PSS/Pt trilayers

S. Mizukami, *et.al.*, PRB **66**, 104413 (2002).
E. Saitoh, *et.al.*, APL **88**, 182509 (2006).

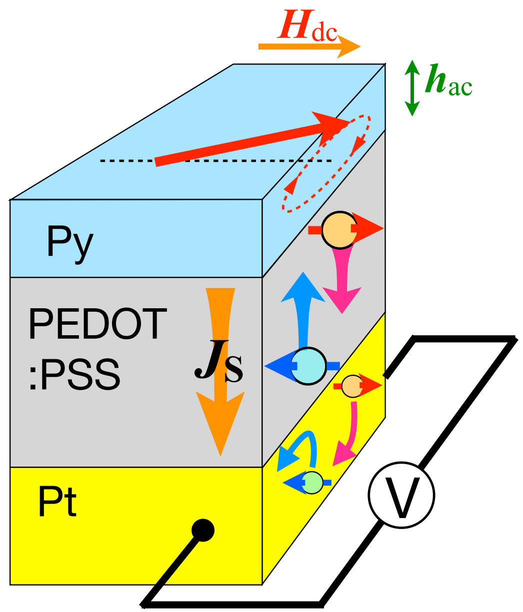


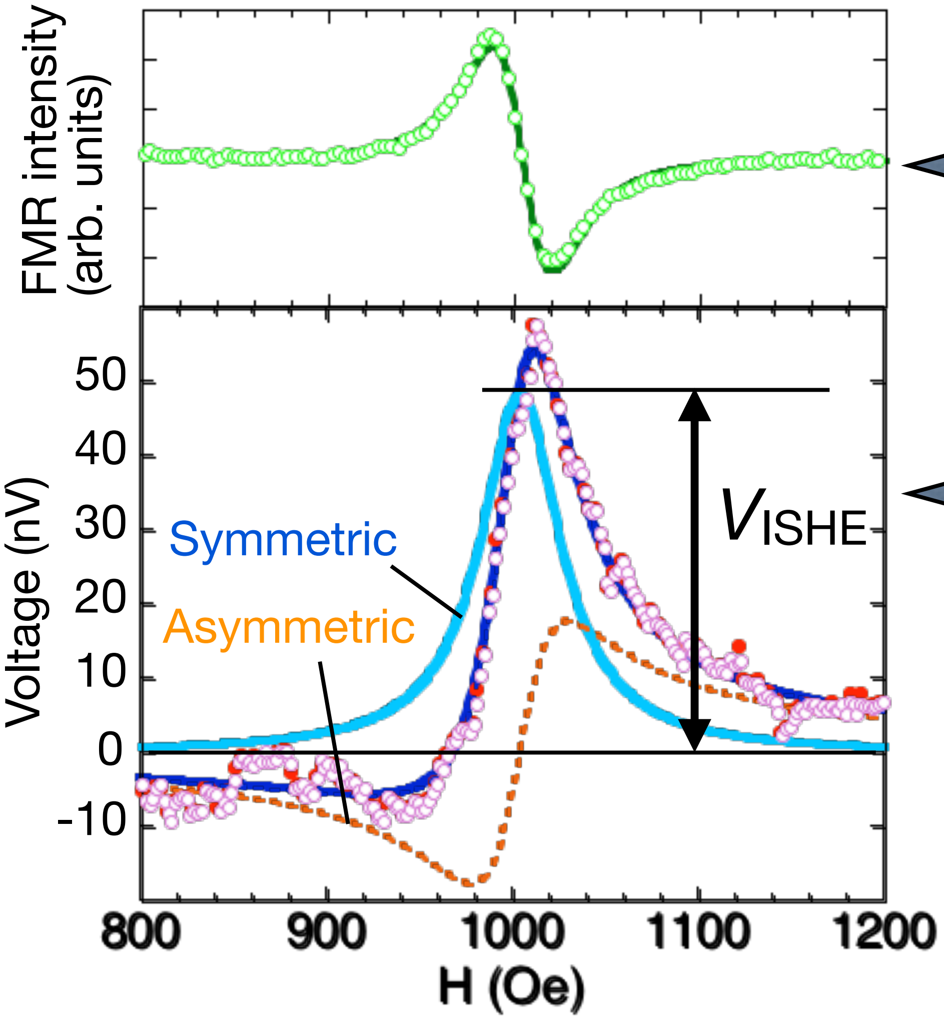
Py/PEDOT:PSS/Pt trilayer

The pure spin current through the PEDOT:PSS is detected as a voltage signal at the Pt layer.

Spin pumping & ISHE measurement in Py/PEDOT:PSS/Pt trilayers

PEDOT:PSS: 60nm
f = 9.5 GHz



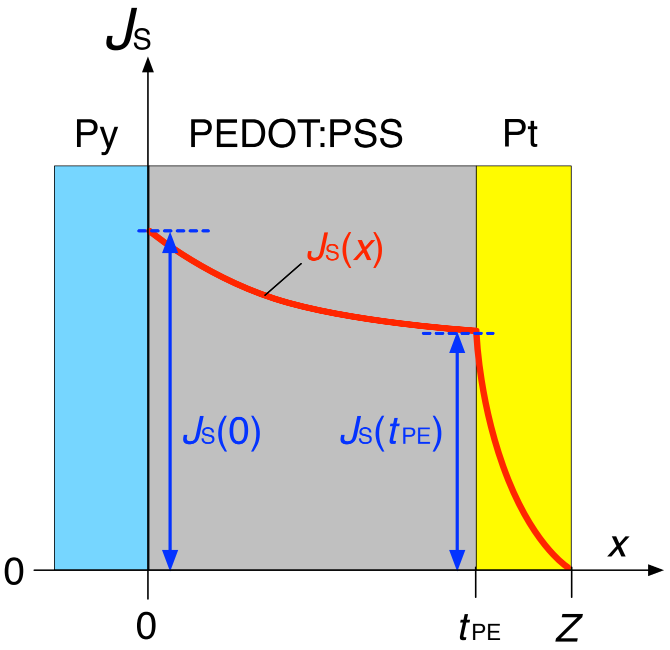


FMR

Voltage

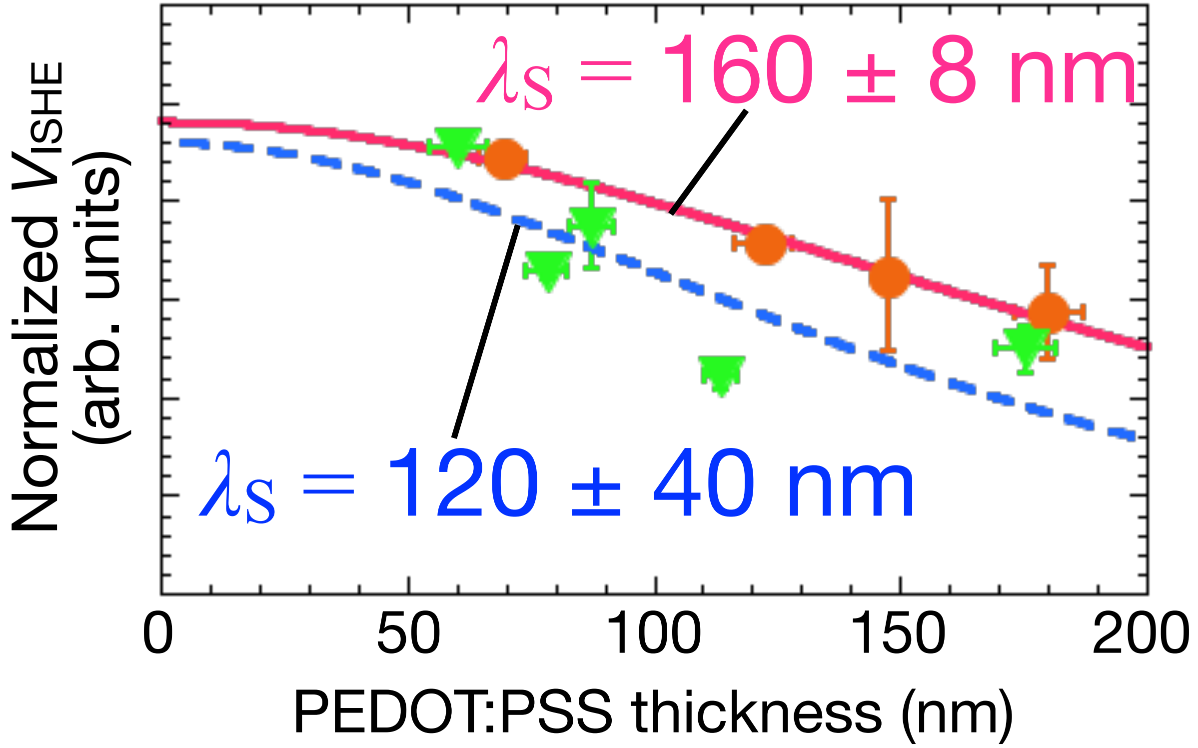
Symmetric contribution of the voltage signal → **Inverse spin Hall voltage**

PEDOT:PSS thickness dependence of V_{ISHE}



- 1D diffusion equation for trilayer

Spin absorption by the Pt layer is considered.



$$V_{\text{ISHE}} \propto J_S(t_{PE}) \approx J_S(0)\exp(\frac{t_{PE}}{\lambda_{PE}})[1\text{-}\tanh(\frac{t_{PE}}{\lambda_{PE}})]$$

Spin diffusion length of PEDOT:PSS = 140 ± 20 nm

Comprehensive study of spin transport

$$\underline{\underline{\lambda_S}} = \sqrt{\underline{\underline{D_S}} \times \underline{\underline{\tau_S}}}$$

Spin pumping

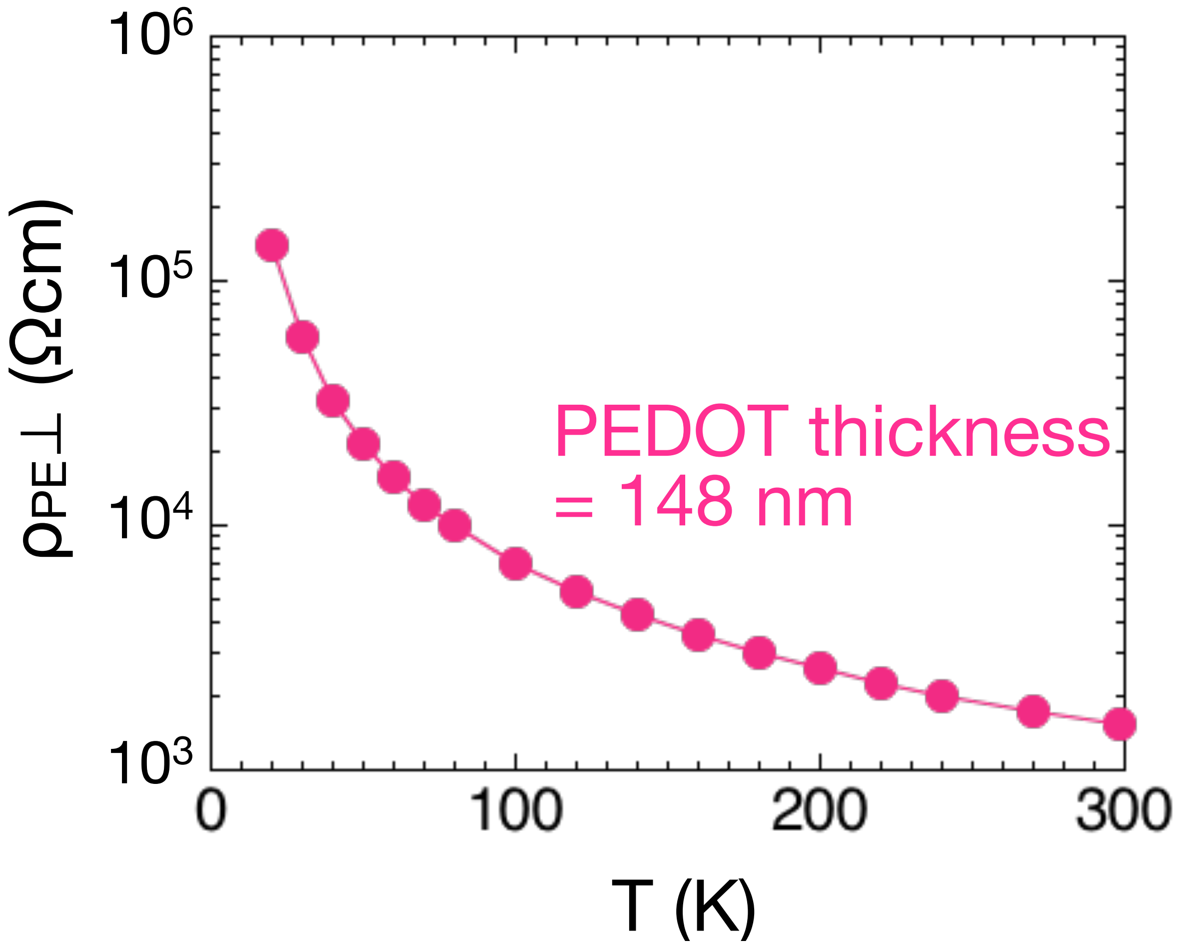
$\lambda_S = 140$ nm

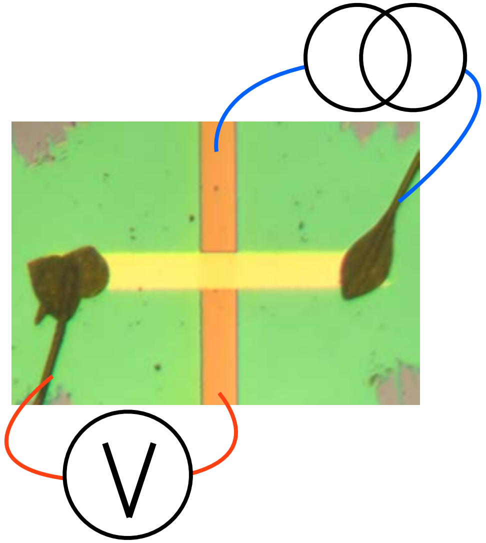
Charge transport

ESR

(Electron spin resonance)

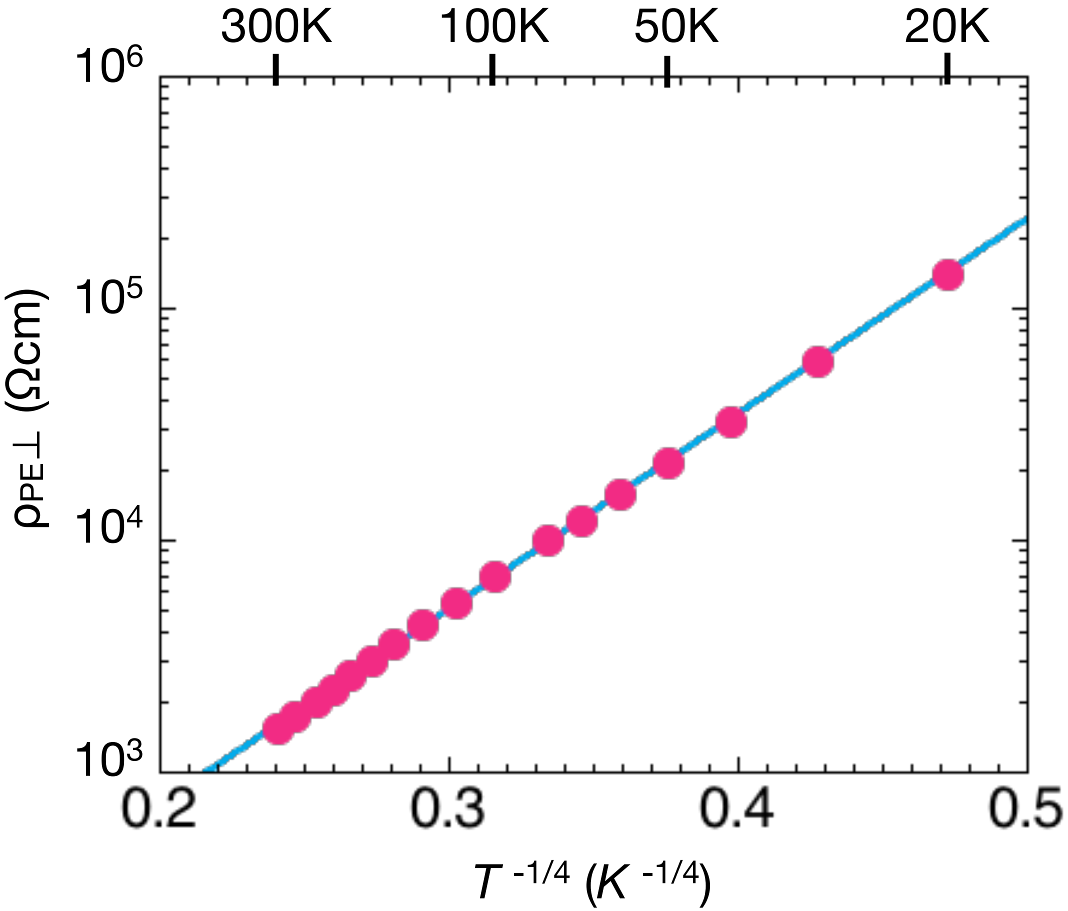
Charge transport measurement

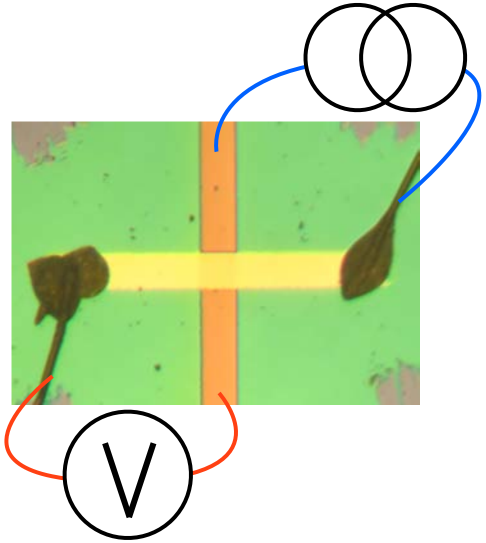




Insulating behavior below room temperature

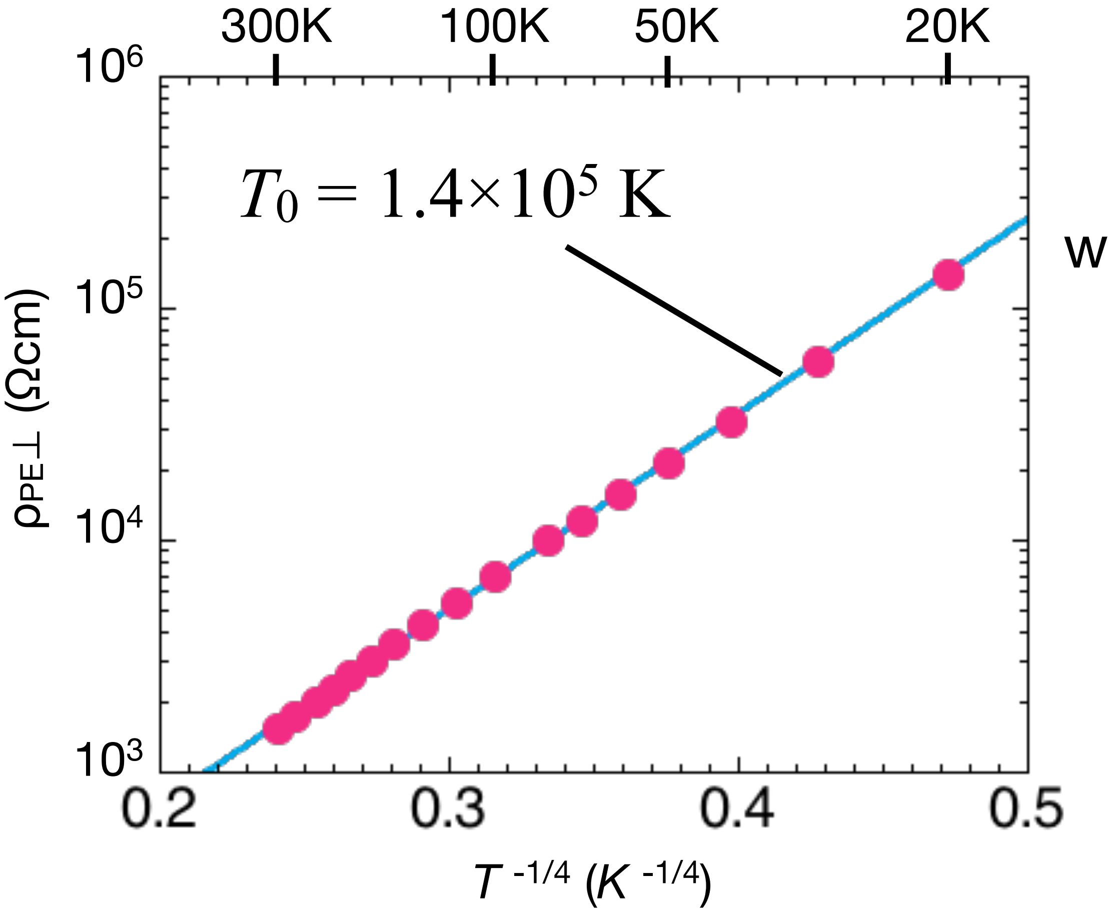
Charge transport measurement





- Almost linear with $T^{-1/4}$

Charge transport measurement



- Almost linear with $T^{-1/4}$

$$\rho_{PE}^{\perp} \propto \exp\left[\frac{T_0}{T}\right]^{1/4}$$

with characteristic temperature

$$T_0 = \frac{\beta}{k_B N(E_F)\xi^3}$$

β : numerical factor (18.1 for 3D-VRH)

$N(E_F)$: DOS at E_F

ξ: localization length

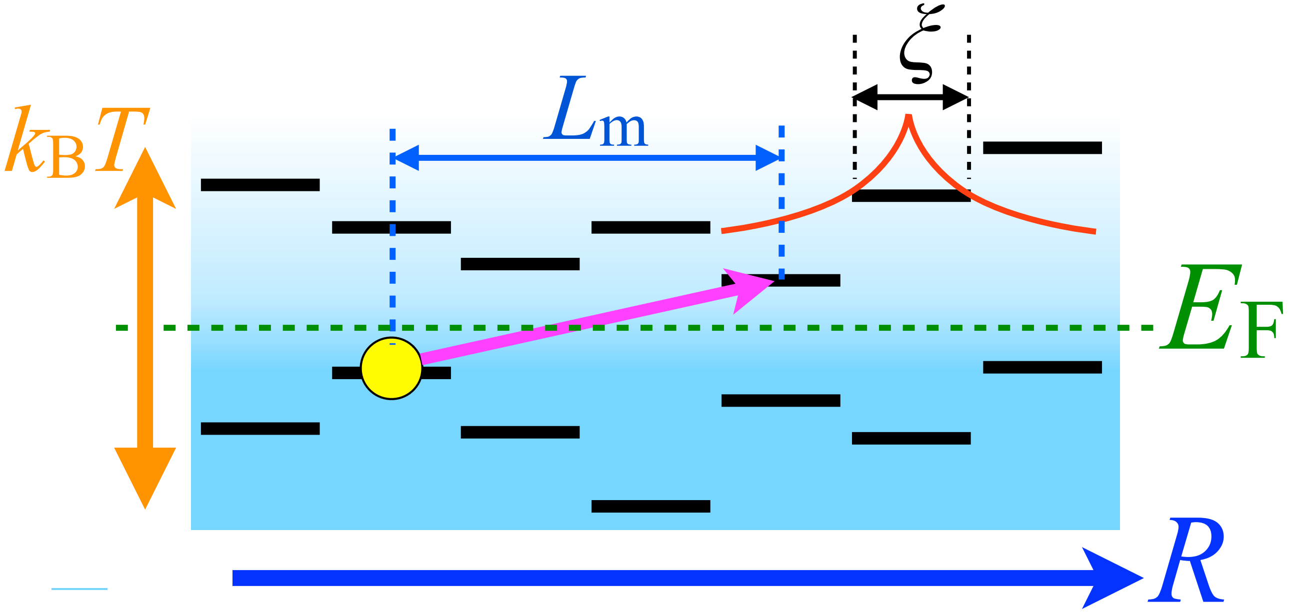
Variable range hopping (VRH) conduction

Einstein relation for VRH conduction

- Electron transport is dominated by tunneling process between metallic localized states.
- Hopping probability (∝conductivity) is proportional to the $N(E_\mathrm{F})$ of the localized states.

$$\sigma = e^2 N(E_\mathrm{F}) D_\mathrm{S}$$

G. Paasch, *et. al.*, Synth. Met. 132 (2002) 97.



Einstein relation for VRH conduction

- Electron transport is dominated by tunneling process between metallic localized states.
- Hopping probability (∝conductivity) is proportional to the $N(E_\mathrm{F})$ of the localized states.

cf) $D_\mathrm{S} \approx 2\times10^{2}\ \mathrm{cm^2/s}$
for pure Cu and Ag

$$N(E_\mathrm{F}) \approx 1\times10^{18}\ [\mathrm{eV^{-1}cm^{-3}}]$$

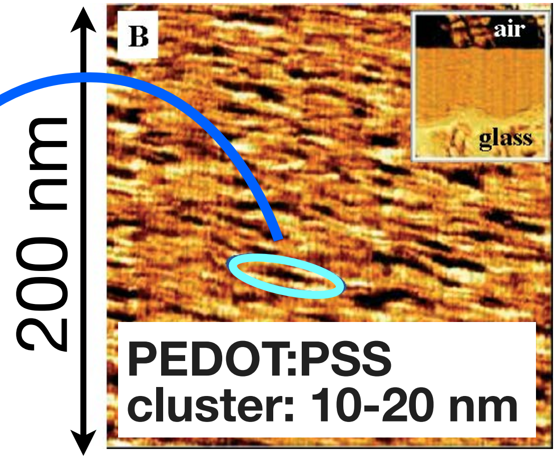
$$\sigma = e^2 N(E_\mathrm{F}) D_\mathrm{S} \longrightarrow D_\mathrm{S} = 7\times10^{-3}\ \mathrm{cm^2/s}$$

- Characteristic temperature of hopping conduction

$$\underbrace{T_0}_{1.4\times10^{5}\ \mathrm{K}} = \frac{18.1}{k_\mathrm{B}\,\underbrace{N(E_\mathrm{F})}_{\Downarrow}\,\underbrace{\xi^3}_{\approx 10\ \mathrm{nm}}}$$

$$\mathbf{N(E_\mathrm{F}) \approx 1\times10^{18}\ [eV^{-1}cm^{-3}]}$$

Cross section AFM



PEDOT:PSS cluster: 10-20 nm

A.M. Nerdes et. al., Adv. Mater. (2007), 19, 1196.

Comprehensive study of spin transport

$$\underline{\underline{\lambda_\mathrm{S}}} = \sqrt{\underline{\underline{D_\mathrm{S}}} \times \underline{\underline{\tau_\mathrm{S}}}}$$

Spin pumping

$\lambda_\mathrm{S} = 140\ \mathrm{nm}$

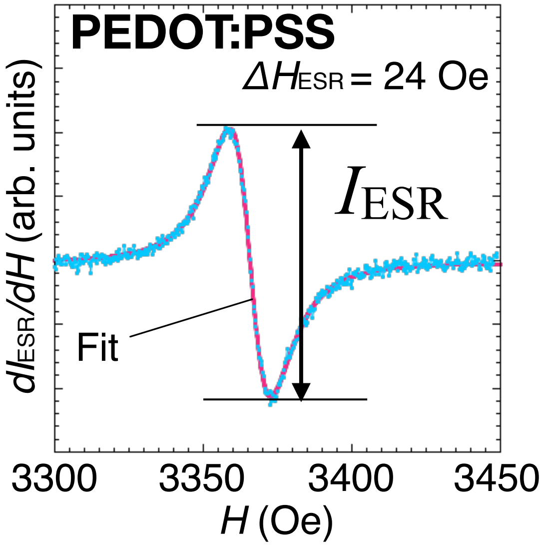
ESR

(Electron spin resonance)

Charge transport

$D_\mathrm{S} = 7\times10^{-3}\ \mathrm{cm^2/s}$

ESR experiment of PEDOT:PSS film

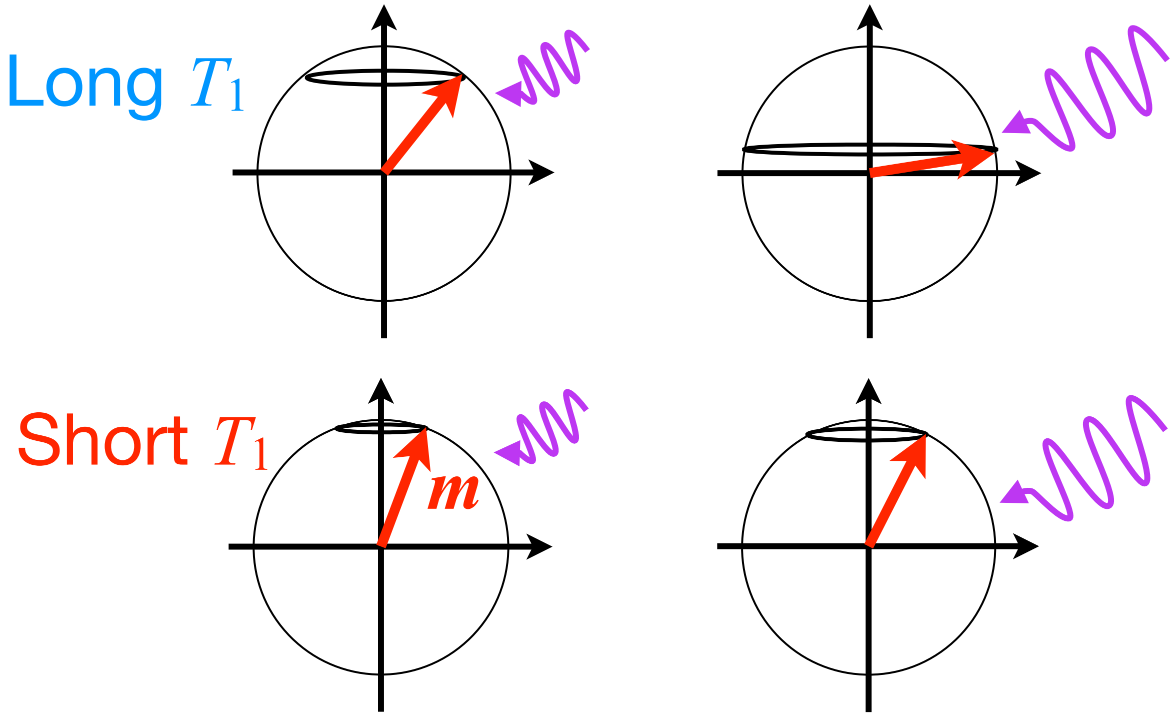


Spin lifetime for dc spin current

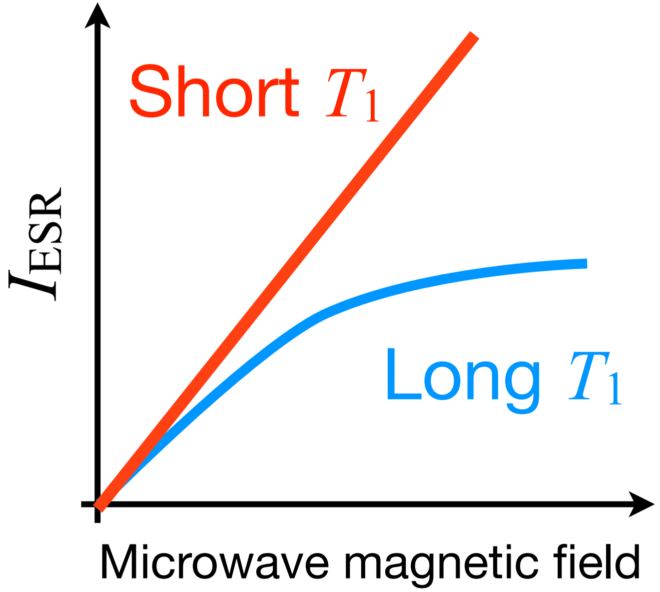
Longitudinal spin relaxation time T_1

- Microwave strength dependence of ESR intensity

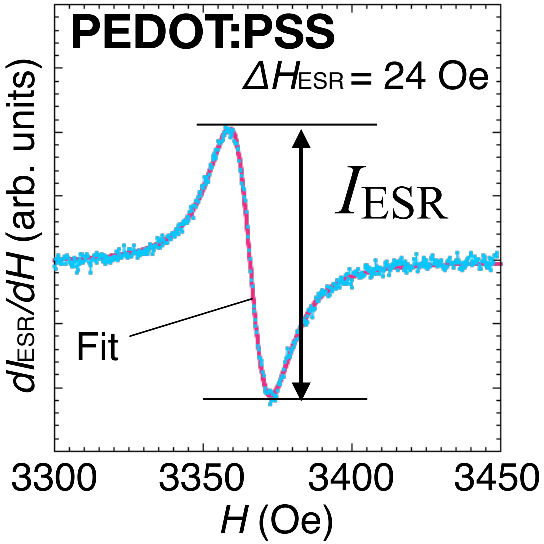
$$\frac{\partial m_z}{\partial t} = \gamma[\boldsymbol{m}\times\boldsymbol{H}]_z + \frac{m_0 - m_z}{T_1}$$



$I_{ESR} \propto m_z$



ESR experiment of PEDOT:PSS film



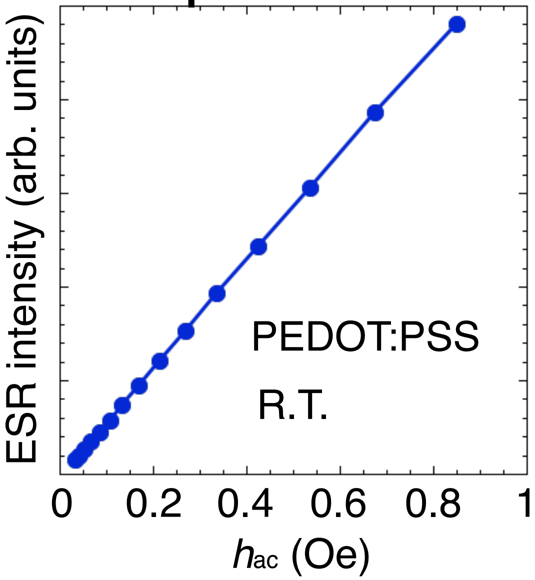
Spin lifetime for dc spin current

Longitudinal spin relaxation time T_1

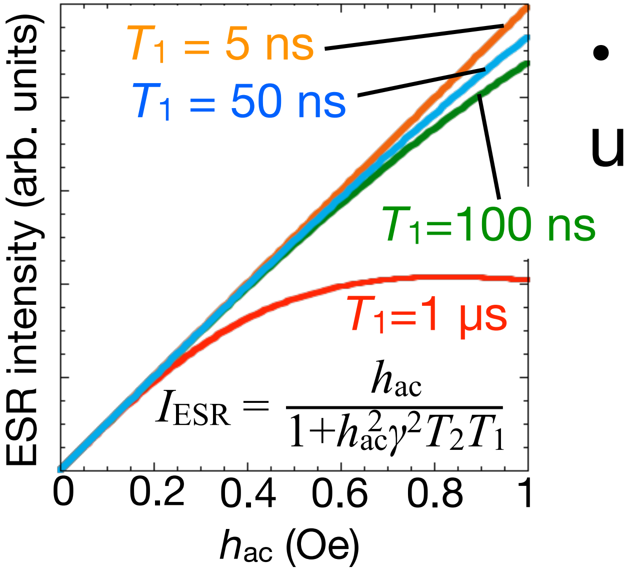
- Microwave strength dependence of ESR intensity

$$\frac{\partial m_z}{\partial t} = \gamma[\boldsymbol{m}\times\boldsymbol{H}]_z + \frac{m_0 - m_z}{T_1}$$

Experiment



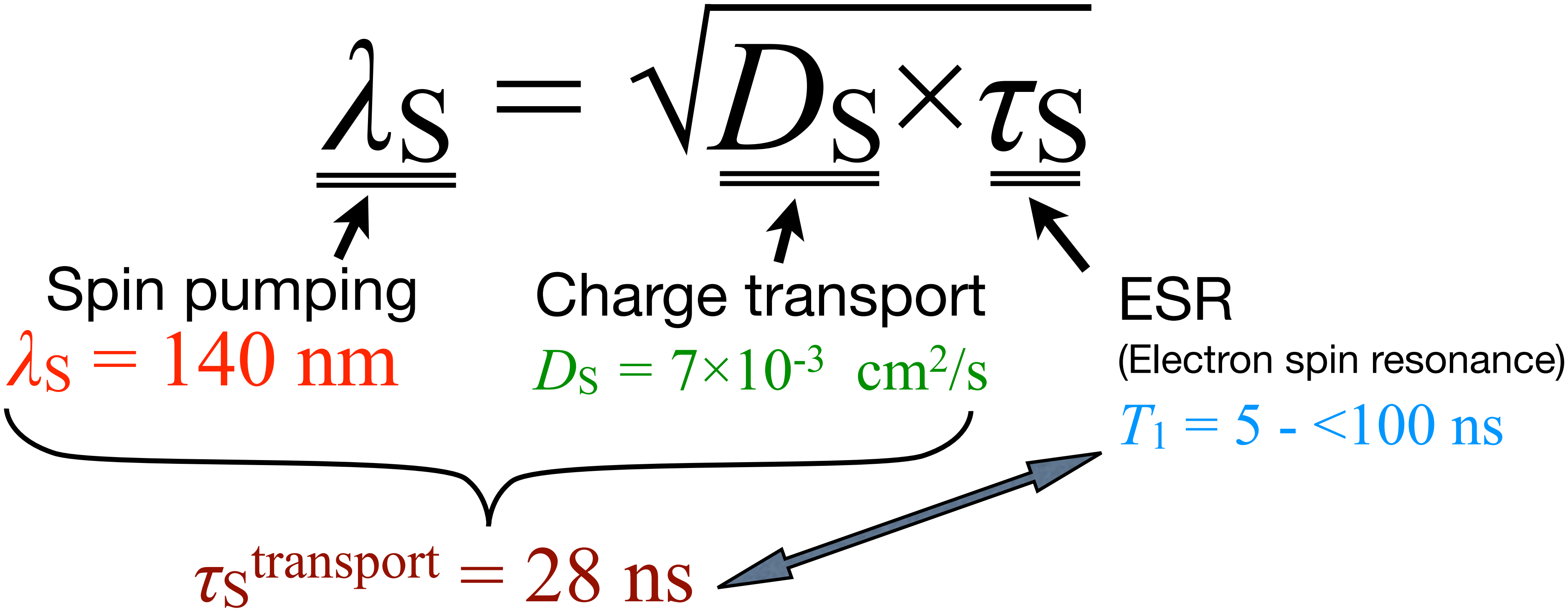
Simulation



- I_{ESR} does not saturate up to the highest h_{ac}.

T_1 = 5 - <100 ns

Comprehensive study of spin transport



$$\underline{\underline{\lambda_S}} = \sqrt{\underline{\underline{D_S}} \times \underline{\underline{\tau_S}}}$$

Spin pumping

$\lambda_S = 140$ nm

Charge transport

$D_S = 7\times10^{-3}$ cm^2/s

ESR

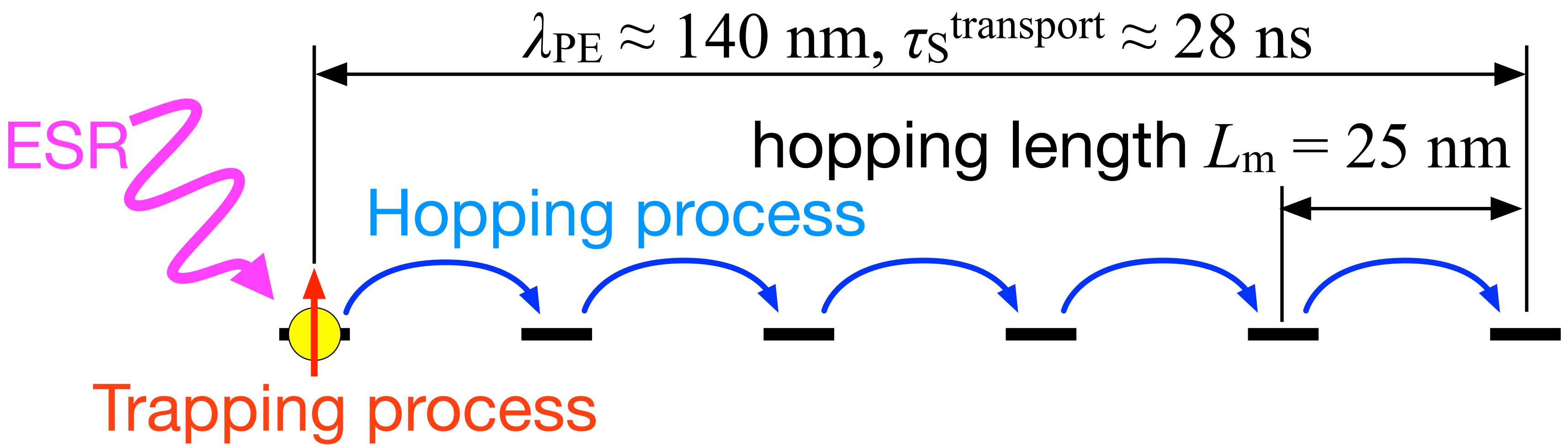
(Electron spin resonance)

$T_1 = 5$ - <100 ns

$\tau_S^{\mathrm{transport}} = 28$ ns

How is the relation between $\tau_S^{\mathrm{transport}}$ and T_1 ?.

Comparison between $\tau_S^{\text{transport}}$ and T_1



$\lambda_{PE} \approx 140$ nm, $\tau_S^{\text{transport}} \approx 28$ ns

hopping length $L_m = 25$ nm

ESR

Hopping process

Trapping process

$\tau_S^{\text{transport}}$:
trap and hopping process

$$1/\tau_S^{\text{transport}} = 1/\tau_S^{\text{hop}} + 1/\tau_S^{\text{trap}}$$

T_1: trapping state only

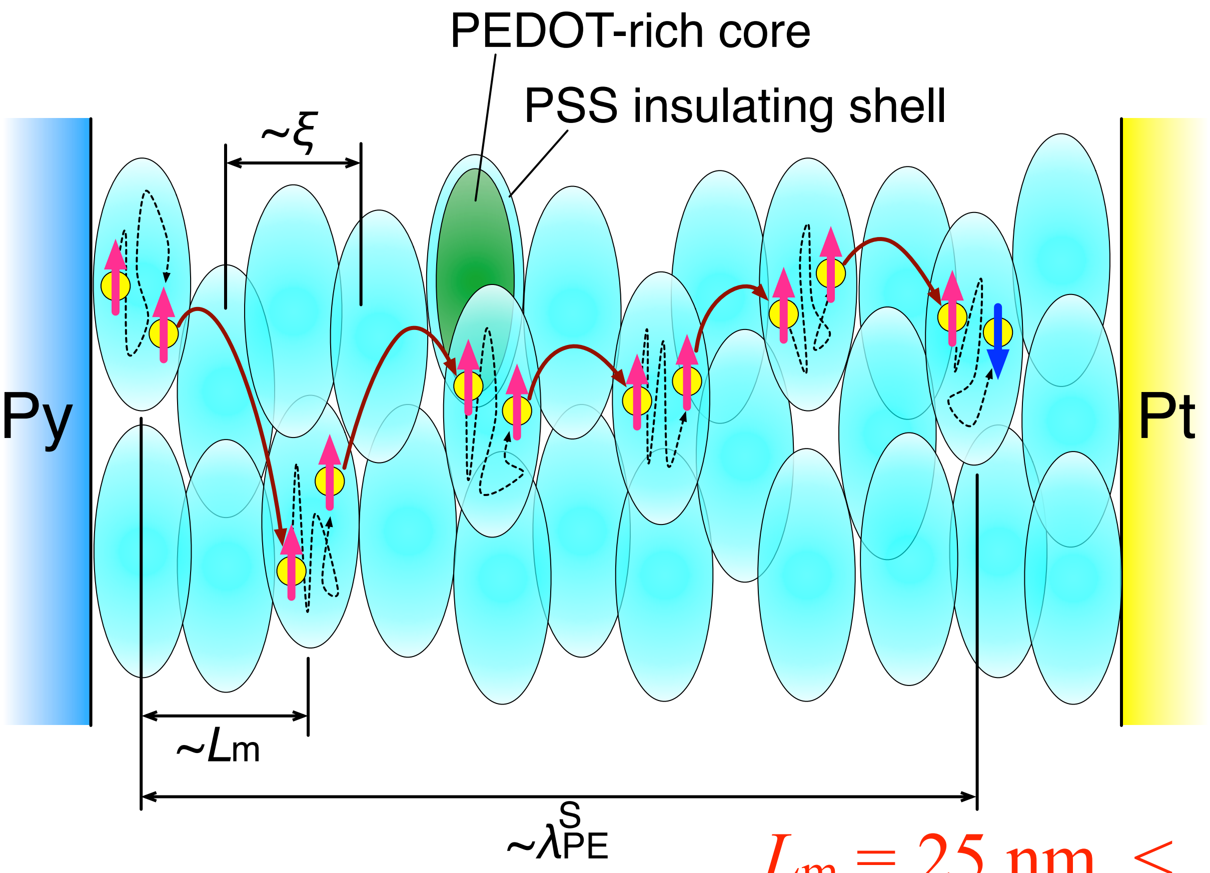
$$1/T_1 \approx 1/\tau_S^{\text{trap}}$$

$$\boxed{1/\tau_S^{\text{transport}} \approx 1/\tau_S^{\text{hop}} + 1/T_1}$$

Now, $1/\tau_S^{\text{transport}} \approx 1/T_1 \Longrightarrow 1/\tau_S^{\text{hop}} \ll 1/\tau_S^{\text{trap}}$

Spin relaxation mostly occurs in the trapping process.

Spin transport and relaxation mechanism in PEDOT:PSS



$L_\mathrm{m} = 25\ \mathrm{nm}\ <\ \lambda_\mathrm{S} = 140\ \mathrm{nm}$

- Spin angular momentum is almost preserved in the hopping event.
- Spin relaxation mostly occurs in the trapping process.

M. Kimata, *et. al*., PRB accepted.

Summary

- Comprehensive study of spin transport in highly doped disordered polymer film PEDOT:PSS was performed.

$$\underline{\underline{\lambda_S}} = \sqrt{\underline{\underline{D_S}} \times \underline{\underline{\tau_S}}}$$

Spin pumping

$\lambda_S = 140\ \mathrm{nm}$

Charge transport

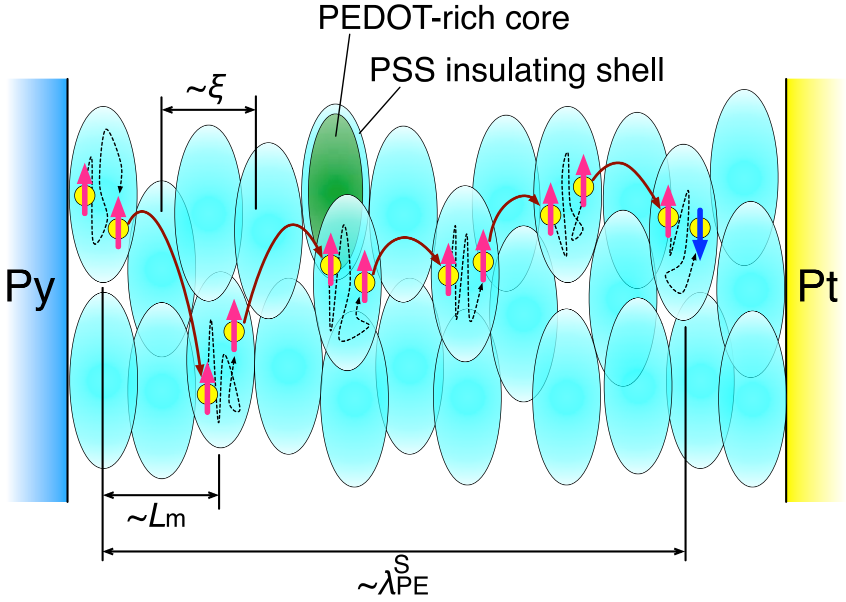
$D_S = 7\times10^{-3}\ \mathrm{cm^2/s}$

ESR

$T_1 = 5 - <100\ \mathrm{ns}$

$\tau_S^{\mathrm{transport}} = 28\ \mathrm{ns}$

$\tau_S^{\mathrm{transport}} \approx T_1$



- **Spin relaxation mostly occurs in the trapping process.**

- **Spin angular momentum is almost preserved in the hopping event.**

M. Kimata, *et. al*., PRB accepted.