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НАЦІОНАЛЬНА АКАДЕМІЯ НАУК УКРАЇНИ 1918

Функція густини локалізованих станів в аморфних органічних напівпровідниках для OLED застосувань: експеримент і теорія

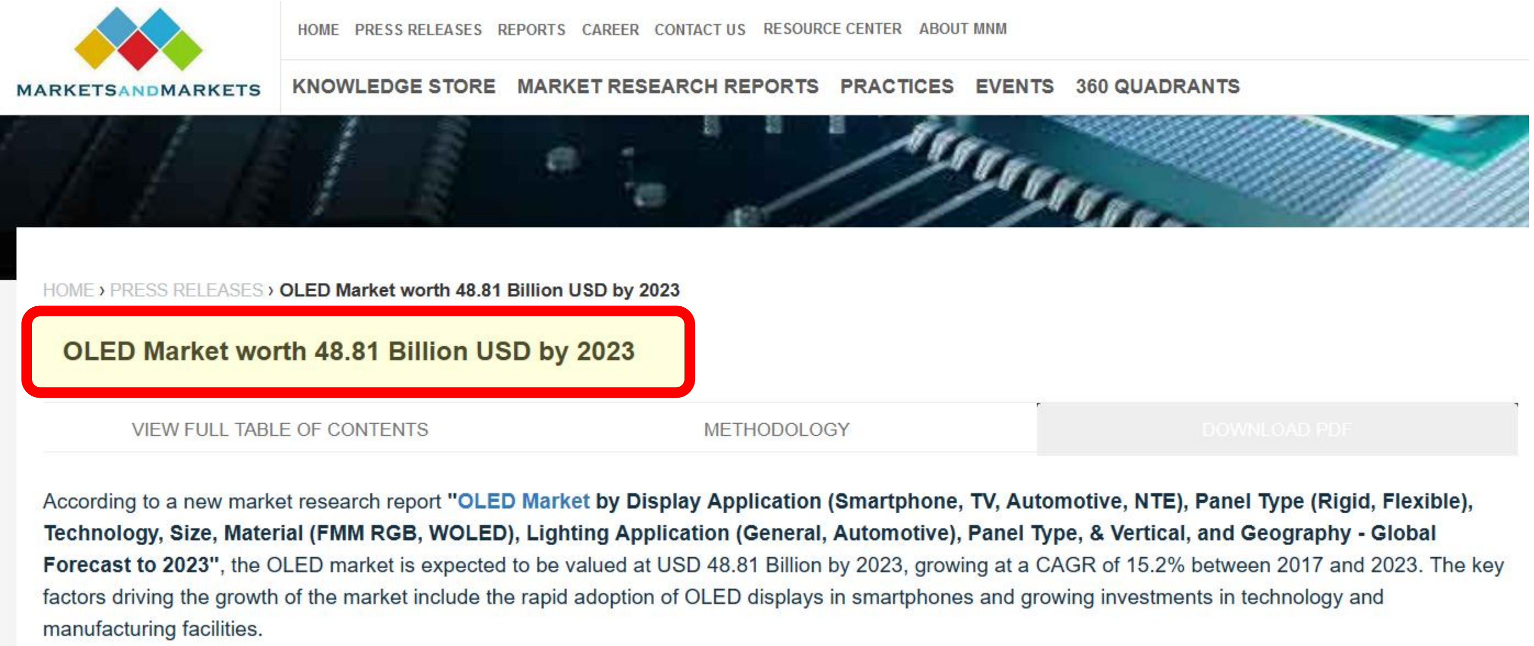
А. Станкевіч[1], О. Вахнін[1], **А. Кадащук[1]**, І. І. Фіщук[2], D. Andrienko[3]

[1] Інститут фізики НАН України, [2] Інститут ядерних досліджень НАН України,
[3] Max Planck Institute for Polymer Research, 55128 Mainz, Germany

European Commission

TADF life

Organic semiconductors for OLED applications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OLED Market worth 48.81 Billion USD by 2023

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According to a new market research report **"OLED Market by Display Application (Smartphone, TV, Automotive, NTE), Panel Type (Rigid, Flexible), Technology, Size, Material (FMM RGB, WOLED), Lighting Application (General, Automotive), Panel Type, & Vertical, and Geography - Global Forecast to 2023"**, the OLED market is expected to be valued at USD 48.81 Billion by 2023, growing at a CAGR of 15.2% between 2017 and 2023. The key factors driving the growth of the market include the rapid adoption of OLED displays in smartphones and growing investments in technology and manufacturing facilities.

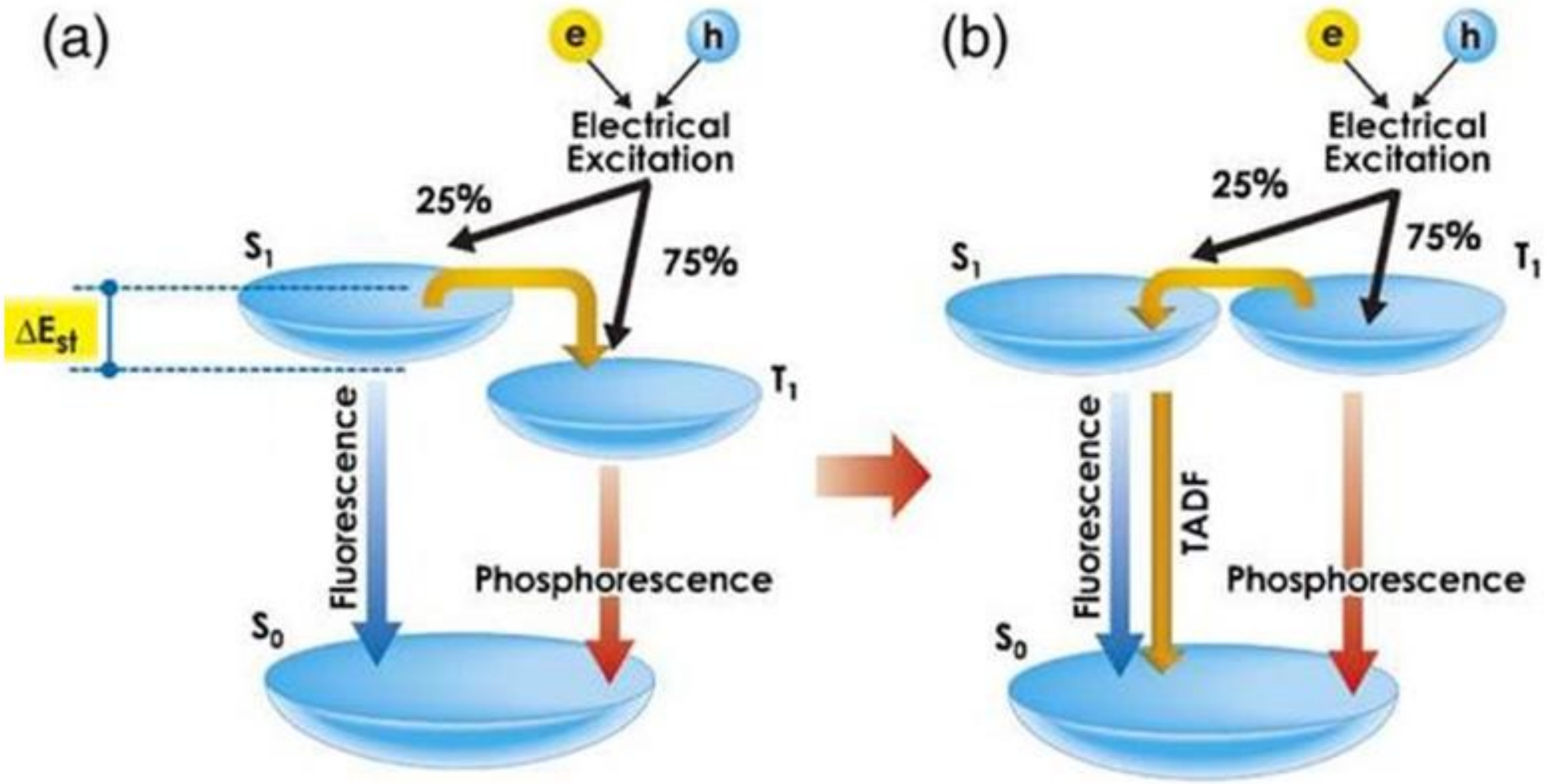
AMOLED Displays (Samsung)

OLED TVs are commercially available since 2013

LG 55-inch rollable TVs

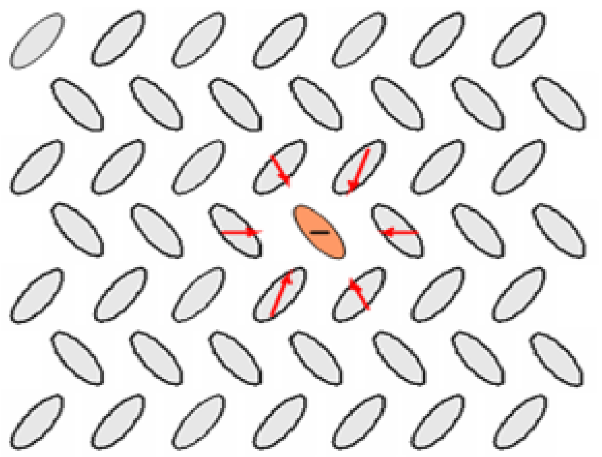
LG OLED lighting panels

Principle of TADF emission

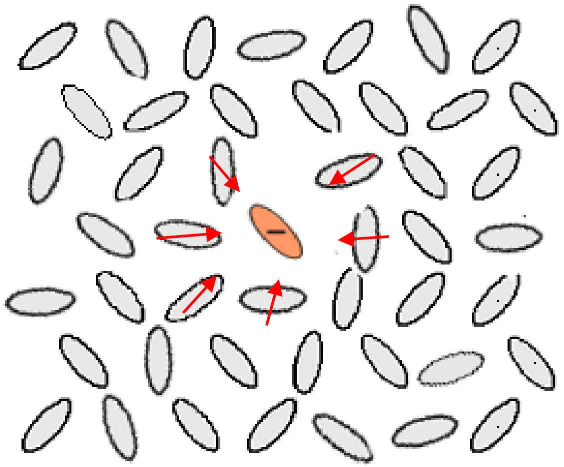


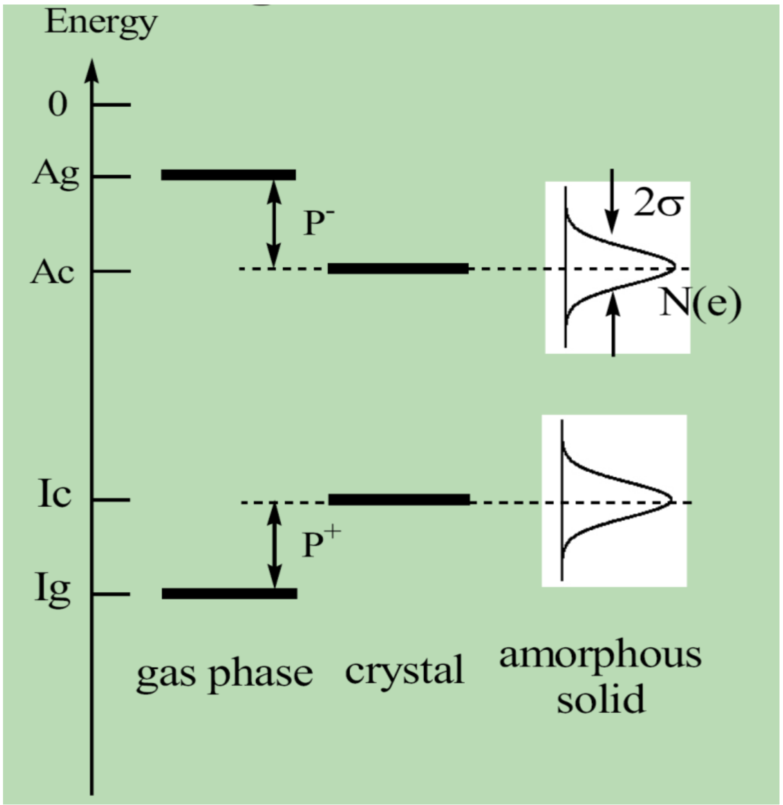
Density-of-States (DOS) distribution in amorphous organic semiconductors

Molecular crystal



Amorphous film





$$P_{id} = \frac{e^2}{2(4\pi\varepsilon_o)^2}\sum_j \frac{\overrightarrow{r_{ij,\beta}}\,\alpha_{\beta\gamma}\,\overrightarrow{r_{ij,\gamma}}}{r_{ij}^6}$$

$$\mu \propto \exp\left(-(\sigma/kT)^2\right)$$

Positional disorder gives rise to energy disorder

E. A. Silinsh and V. Capek, *Organic Molecular Crystals: Interaction, Localization, and Transport Phenomena* (API Press, 1994).

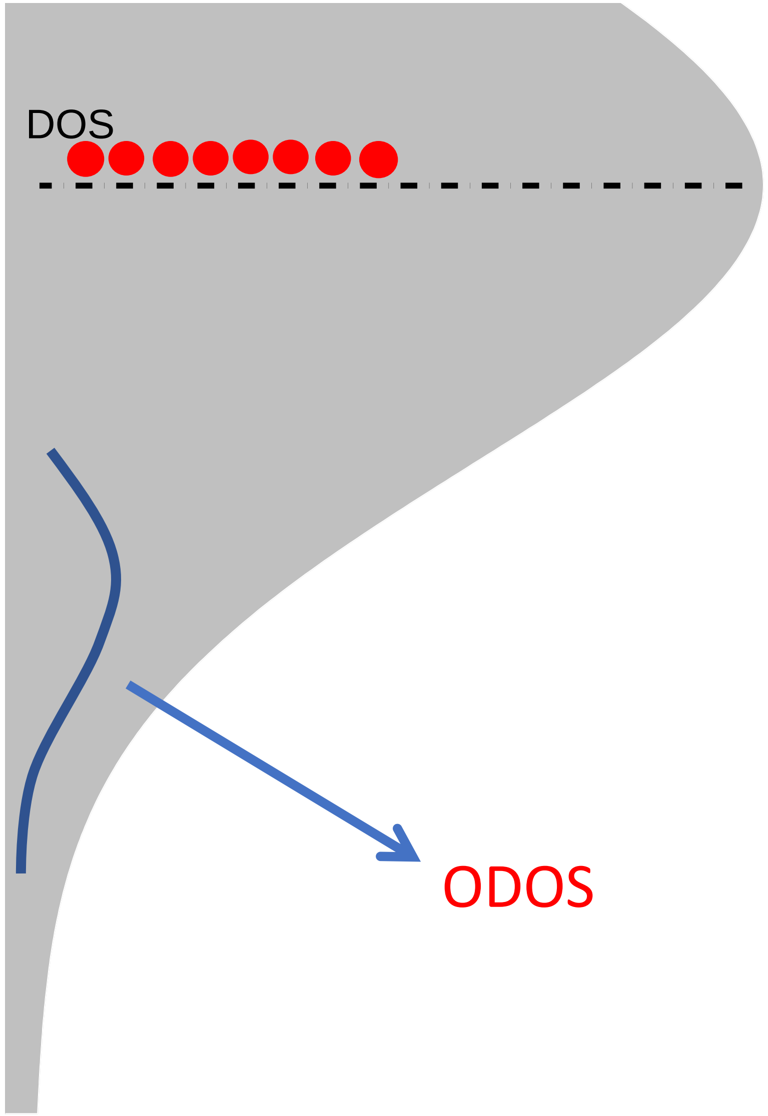
Determination of the Density-of-States (DOS) in organic materials is not a trivial task!

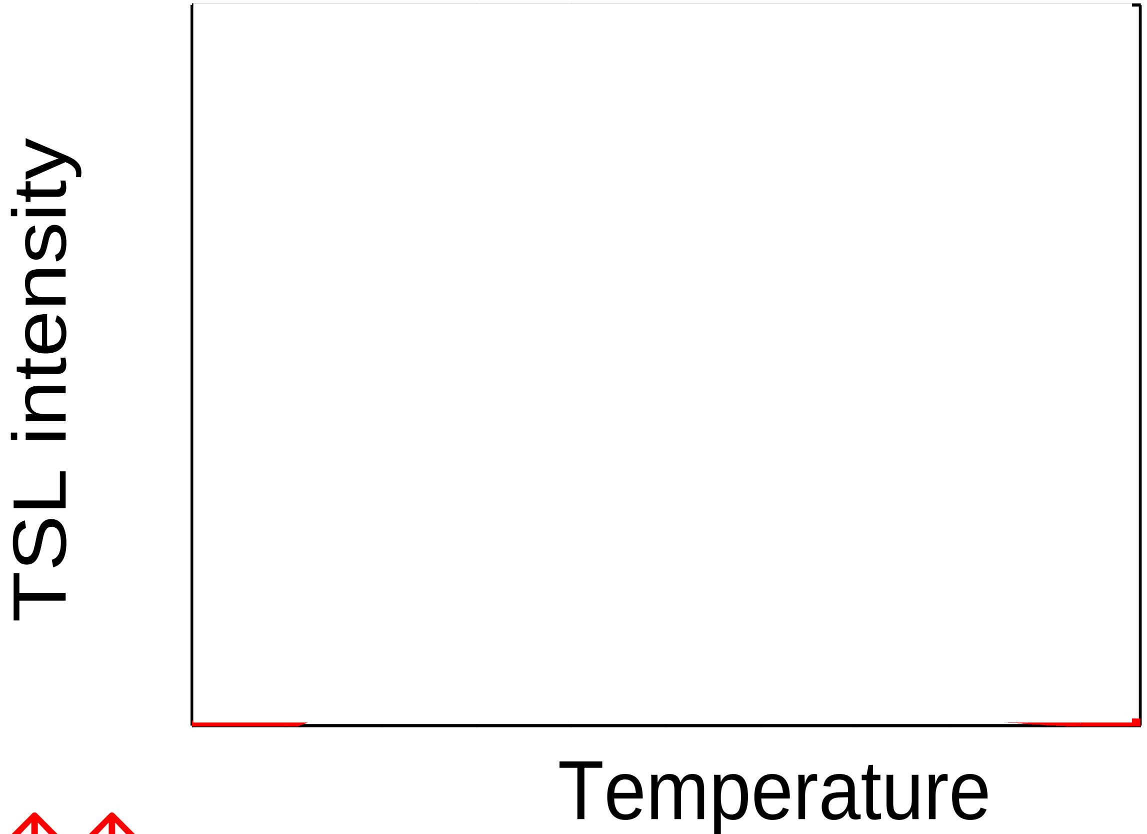
Experimental methods used so far for DOS probing

- Ultraviolet photoelectron spectroscopy (UPS)
- Inverse photoemission spectroscopy (IPS)
- Kelvin probe force microscopy (KPFM)
- Electrochemically gated transistor approach
- Temperature-dependent space-charge-limited-current
- **Thermally stimulated luminescence (TSL)**

Our experimental method:
Thermally-Stimulated Luminescence (TSL)

Principle of thermoluminescence (TSL)





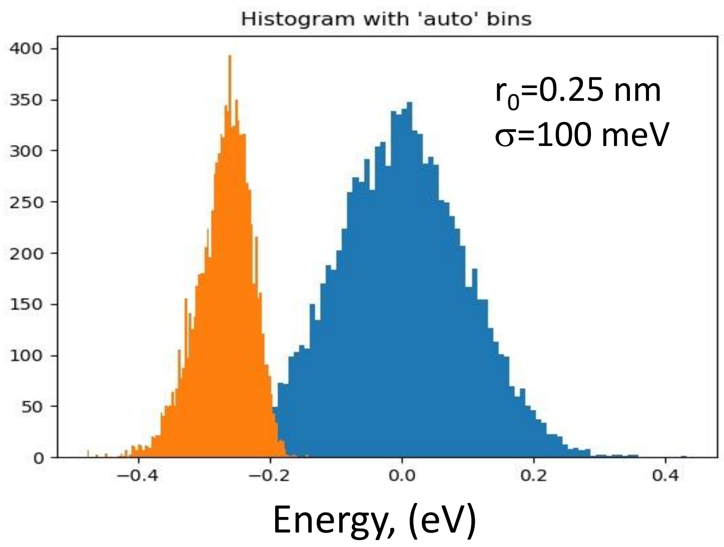
Heating↑↑

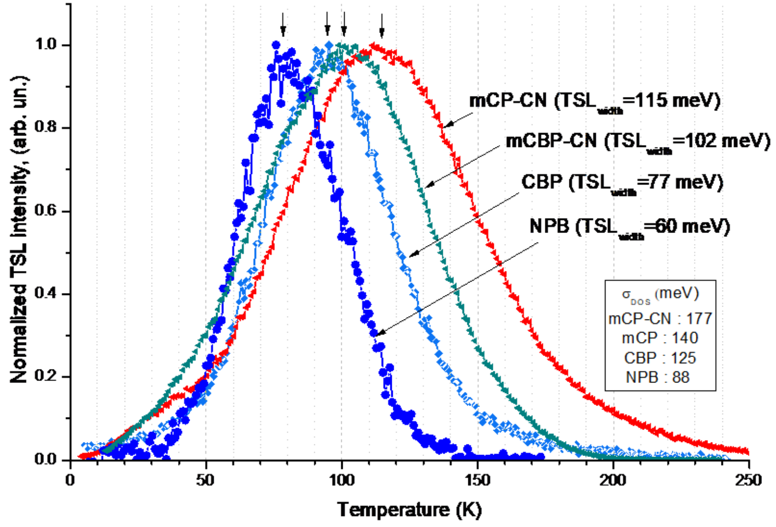
Only downward hopping!!!

$$g(E)=\frac{N_t}{\sqrt{2\pi}\sigma}\exp\left(-\frac{E^2}{2\sigma^2}\right)$$

Arkhipov, V. I., et al. *Chem. Physics* 266.1 (2001): 97-108.

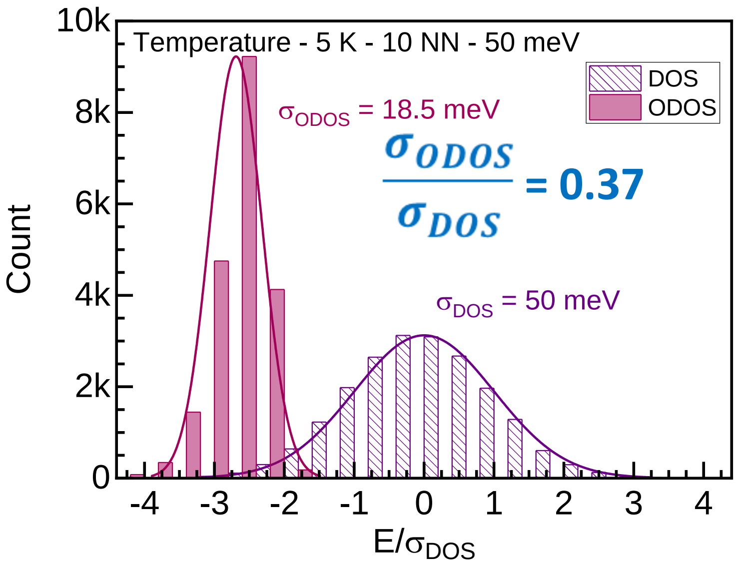
Monte-Carlo simulations vs. experiment

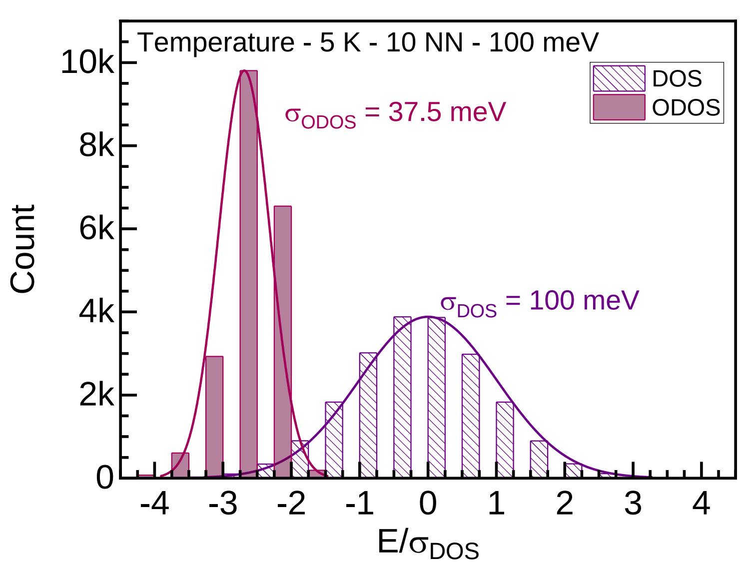


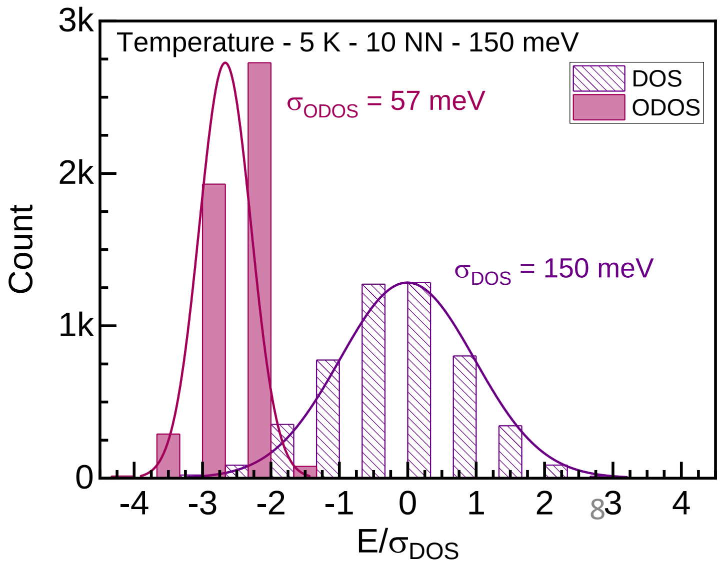


TSL experiment for different materials

MC-simulations of occupational DOS at 5K for different energy disorder

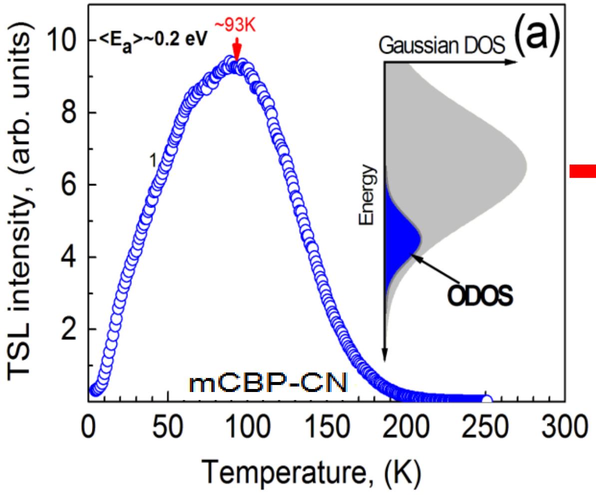




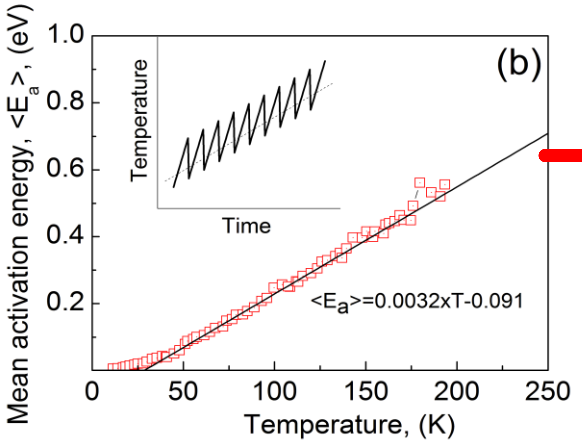


Example of DOS determination in mCBP-CN by TSL technique

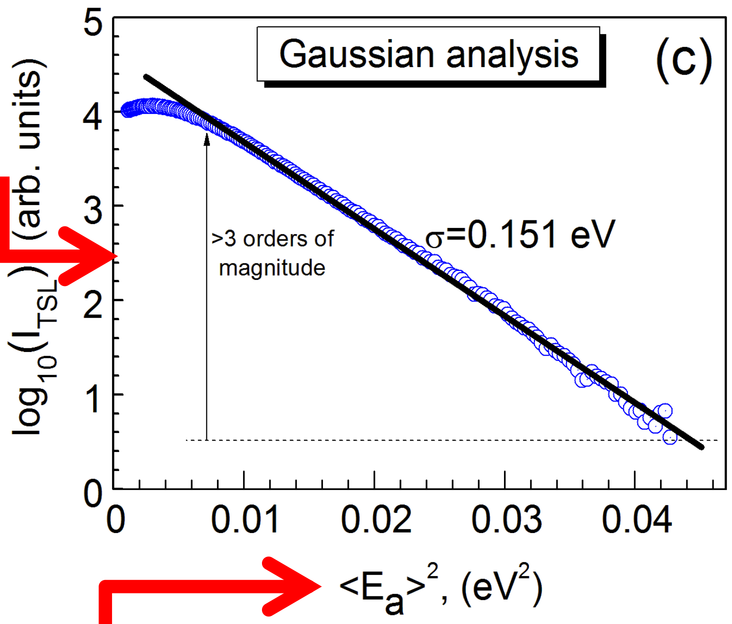
TSL curve measured for mCBP-CN



Activation energies by fractional TSL

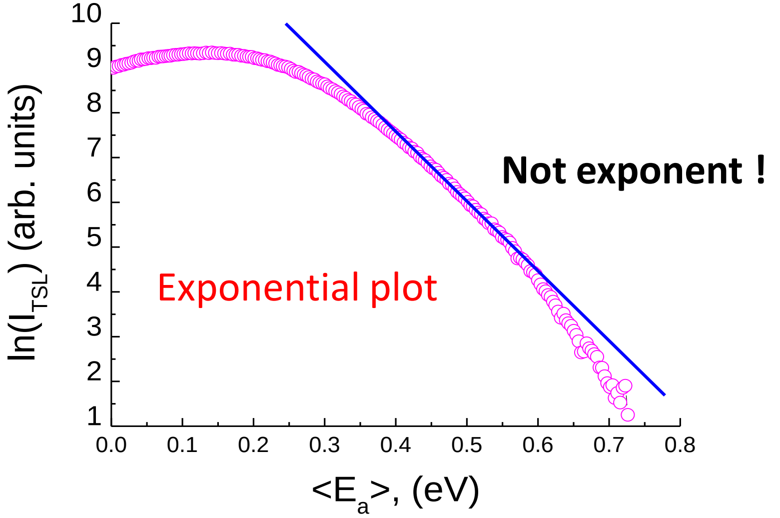


Gaussian analysis of TSL

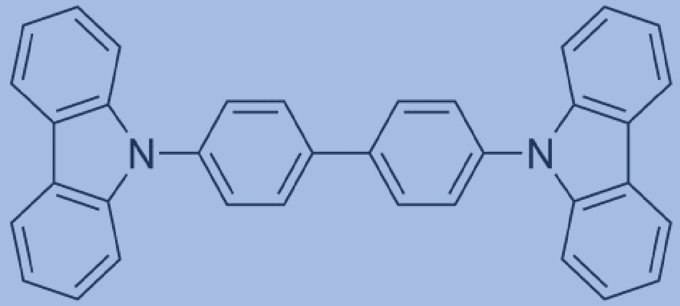


Converting T scale to E_a scale

Exponential analysis of TSL

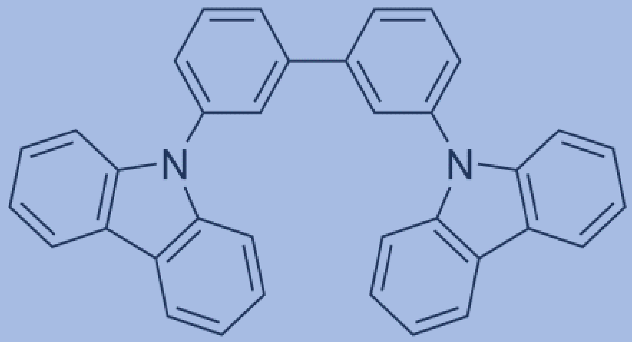


Two dipole series



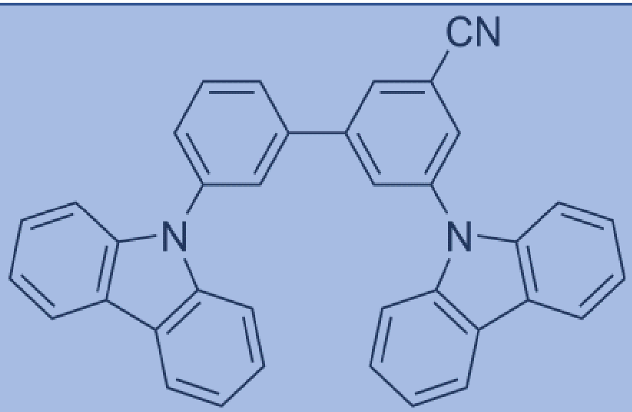
CBP

0 D



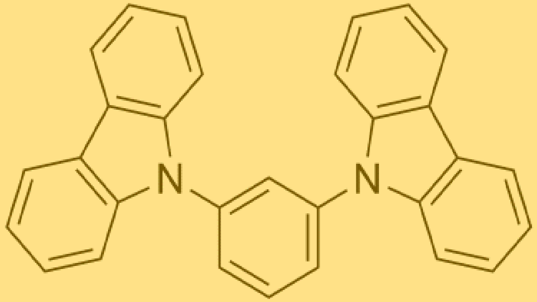
mCBP

2.15 D



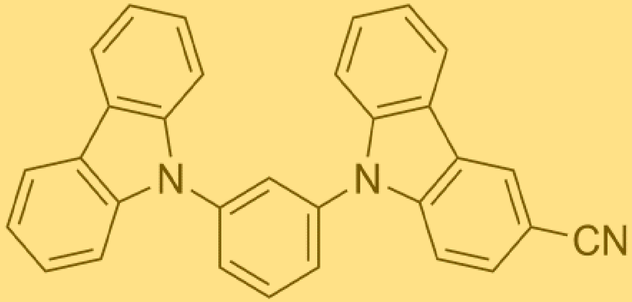
mCBP-CN

4.6 D



mCP

1.35 D



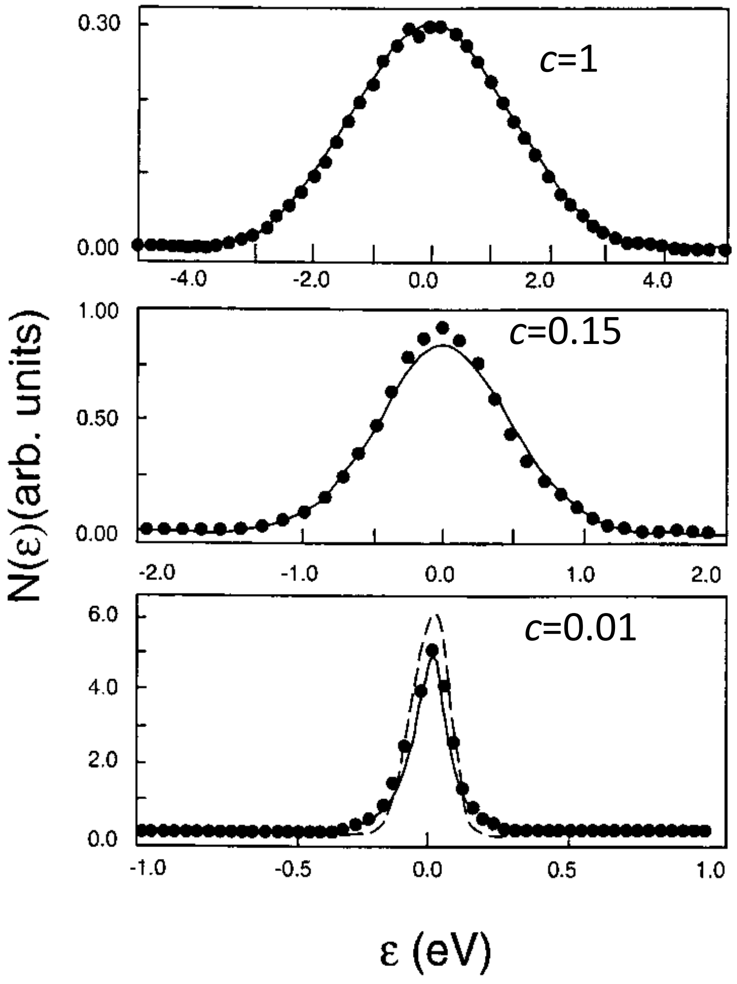
mCP-CN

6 D

Static dipole moments increase energy disorder

Dipole moment=6 D

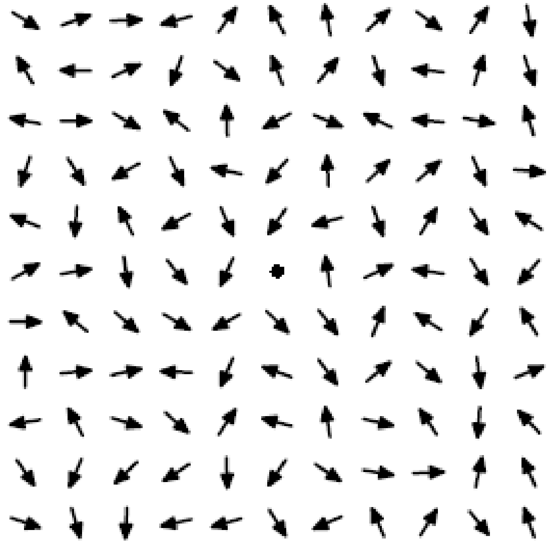
Dipole moment ↑ → ↑ σ energy Disorder paeamete



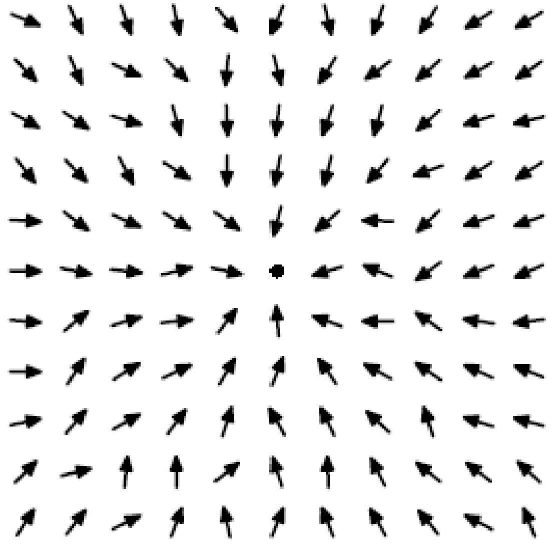
$$\sigma=\sqrt{\sigma_{dip}^{2}+\sigma_{vd}^{2}}$$

$$\sigma_D=\frac{3.06\, c^{2/3}}{a^{2}\epsilon} D$$

Stochastic cluster



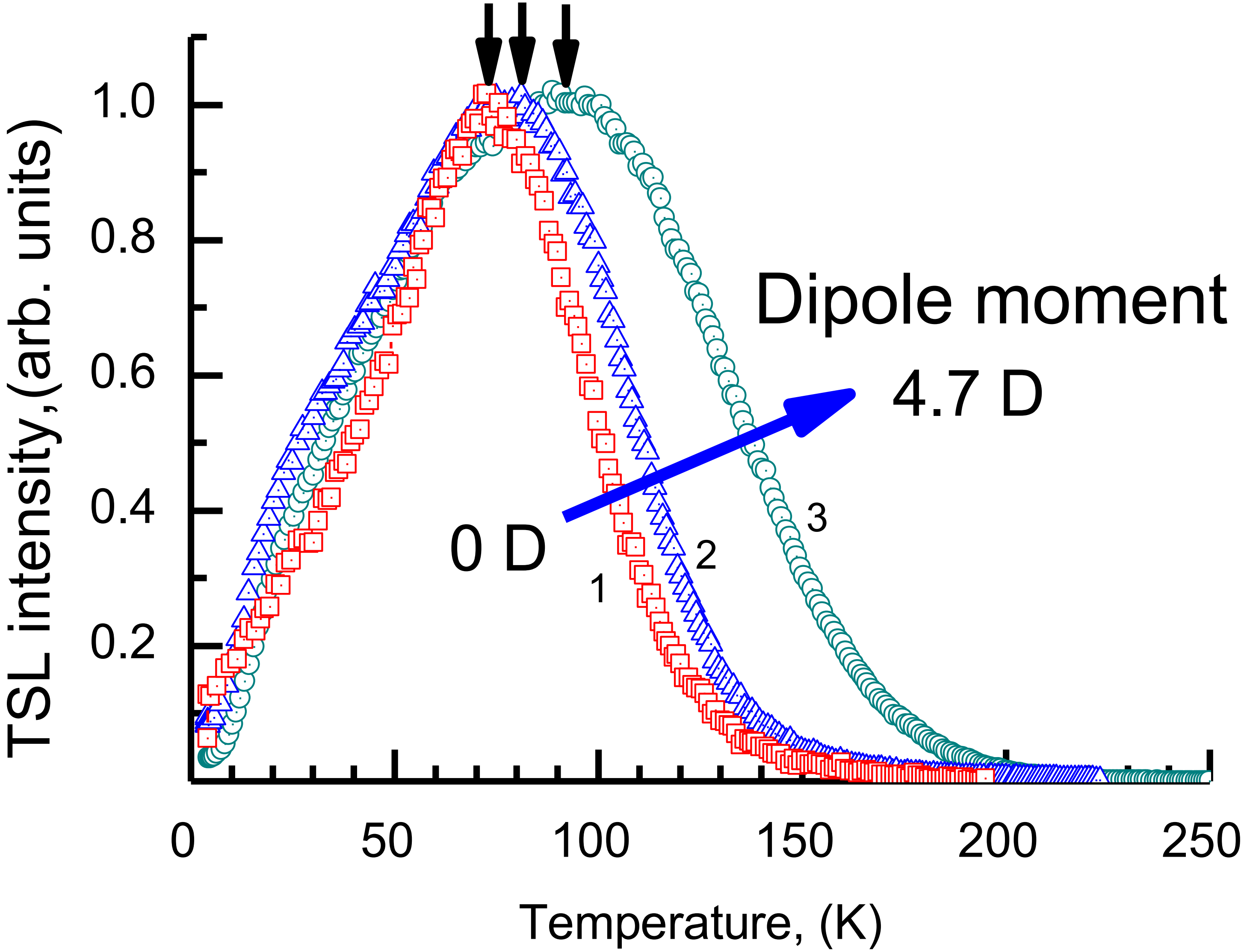
(a)



(b)

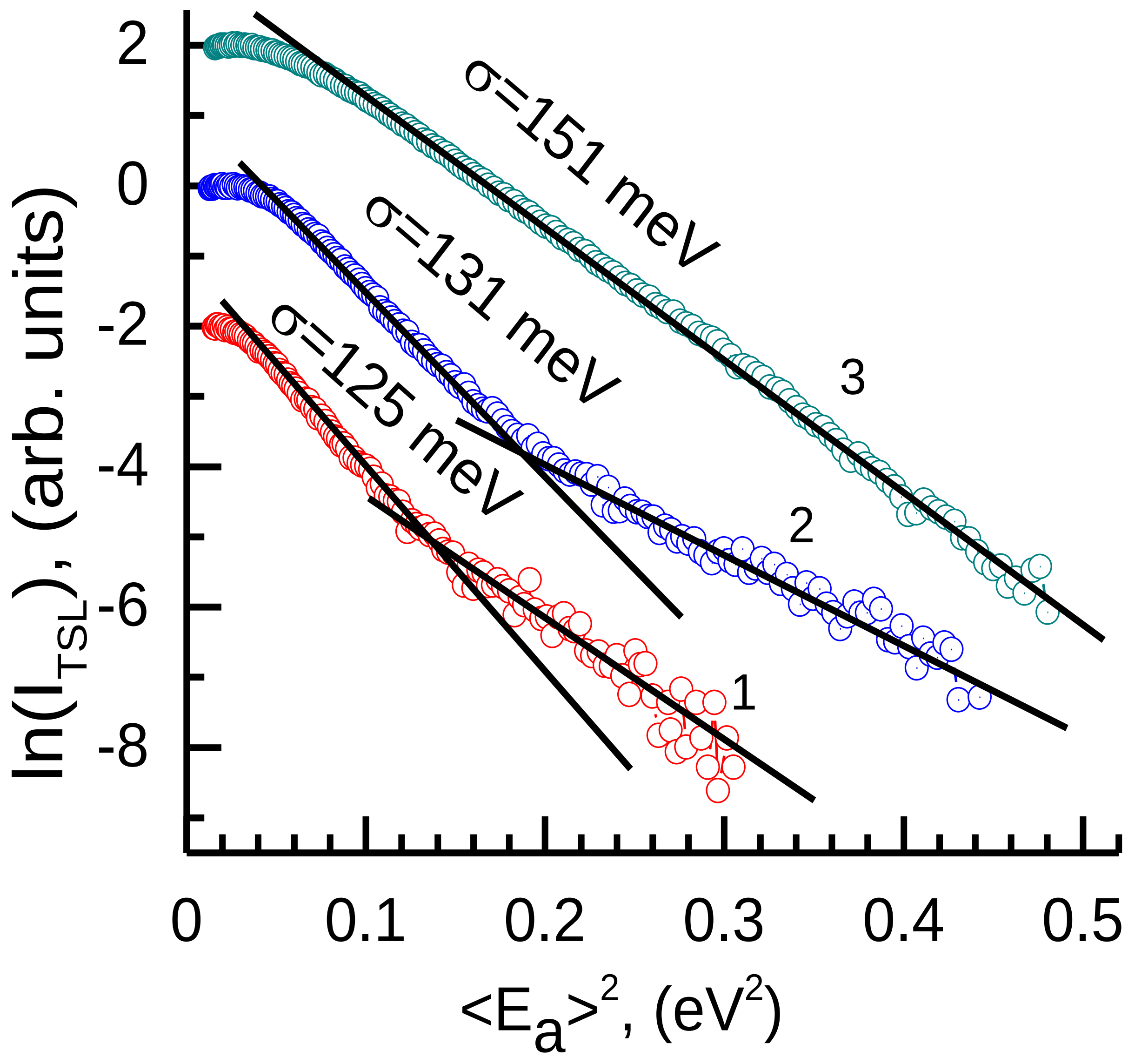
H. Bässler. *et al.* *J.Chem.Phys.* **99**. 8136 (1993)

TSL of CBP, mCBP, mCBP-CN



Material	**Dipole**
1) CBP	0 D
2) mCBP	2.4 D
3) mCBP-CN	4.7 D

ODOS of CBP, mCBP, mCBP-CN

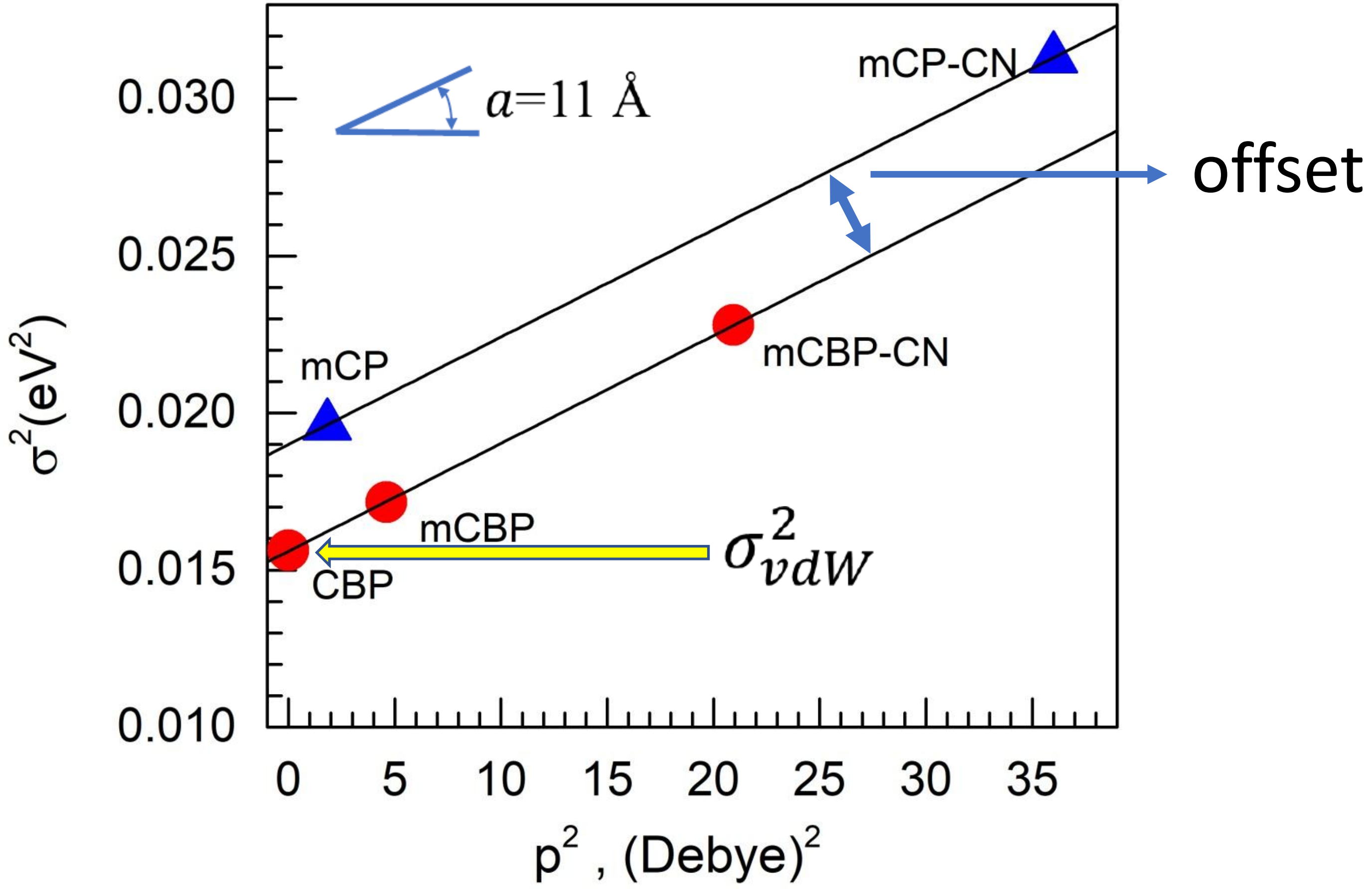


Material	Dipole
1) CBP	**0.8 D**
2) mCBP	**2.4 D**
3) mCBP-CN	**4.7 D**

Dipolar disorder effect

$$\sigma^2 = \sigma^2_{dip} + \sigma^2_{vdW} \qquad \sigma_D = \frac{3.06\, c^{2/3}}{a^2 \epsilon} D \quad \Rightarrow \quad \sigma^2 \sim D^2$$

$if\ \sigma^2_{vdW} = const$

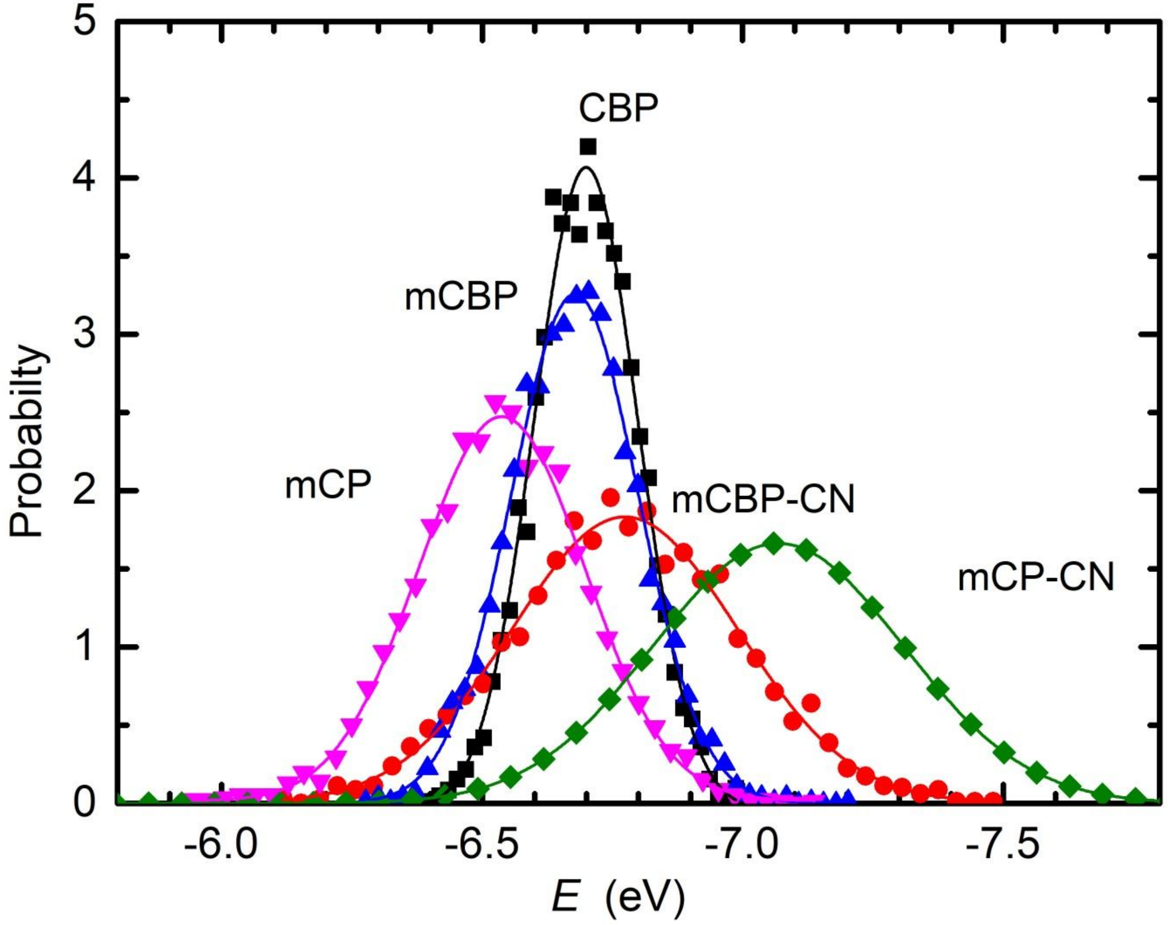


- $\sigma^2 \sim D^2$ **linear dependence for the same materials family**
- **The dependences *are offset* for two material series**
- **Intrinsically larger σ_{vdW} component in CP- derivatives**

A. Stankevych et al. (*Phys. Rev. Applied*, 2020)

Computed DOS distributions

The same trend for σ change as in TSL measurements



Simulations done by Andrienko group at MPIP (Mainz)

Material	Dipole moment p (D)	$\alpha_{neutr.}$ (Bohr³)	α_{cation} (Bohr³)	DOS width (from TSL) σ (eV)	DOS width (simulations) σ (eV)
CBP	0.04*	670	3200	0.125	0.10
mCBP	2.15*	600	3000	0.131	0.12
mCBP-CN	4.6*	600	3000	0.151	0.20
mCP	1.35*	450	1500	0.140	0.16
mCP-CN	6*	540	1500	0.177	0.24

Smaller $\alpha_{neutr.}$ and α_{cation} polarizability in mCP leads to weaker screening of electrostatic disorder, that results in larger σ!

Висновки

- Розроблена методика прямого визначення функції густини станів та параметру енергетичного безпорядку в полярних органічних напівпровідниках
- Встановлено, що основний вклад в енергетичний безпорядок вносить електростатична взаємодія зарядів із молекулярними диполями
- Вперше показано, що індукційна взаємодія призводить до зменшення безпорядку за рахунок ефектів екранування
- Експериментальні результати добре узгоджуються із даними молекуляроно-динамічного моделювання для досліджуваних аморфних органічних напівпровідників

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"Density of States of OLED Hosts from Thermally Stimulated Luminescence", Stankevych, A, Vakhnin A., Andrienko D, Paterson L, Fishchuk I. I, Bässler H, Köhler A, Kadashchuk A. (accepted in ***Physical Review Applied*** (2021).

Дякую за увагу!