ESMolNa European School on Molecular Nanoscience

ESAM European School on Advanced Materials

Electrical Characterization of Conductive Covalent- and Metal-Organic and Frameworks by Time Resolved THz Spectroscopy

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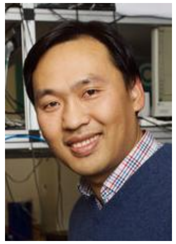
Acknowledgements

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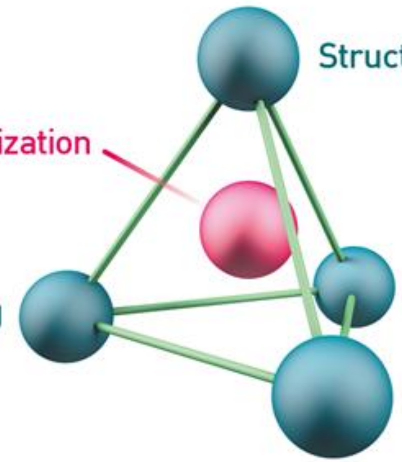
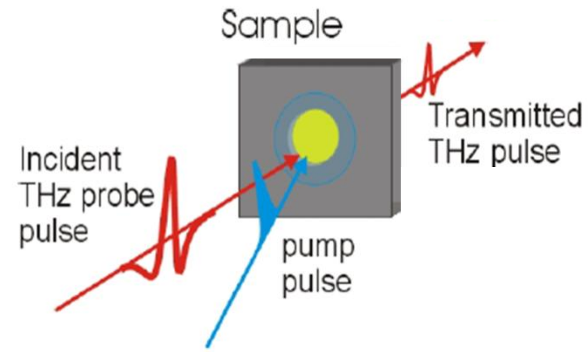
What we do?



We aim establishing neat correlations between structure, processing, properties and functionality in **semiconductors and their hetero-structures**, with a focus on **carrier dynamics and charge transport**. Our main tool is **time resolved THz spectroscopy**.

time-resolved terahertz spectroscopy



Charge transport in metal- and covalent-organic frameworks

Time resolved THz Spectroscopy: a non-contact electrical probe at the nanoscale with sub-ps resolution

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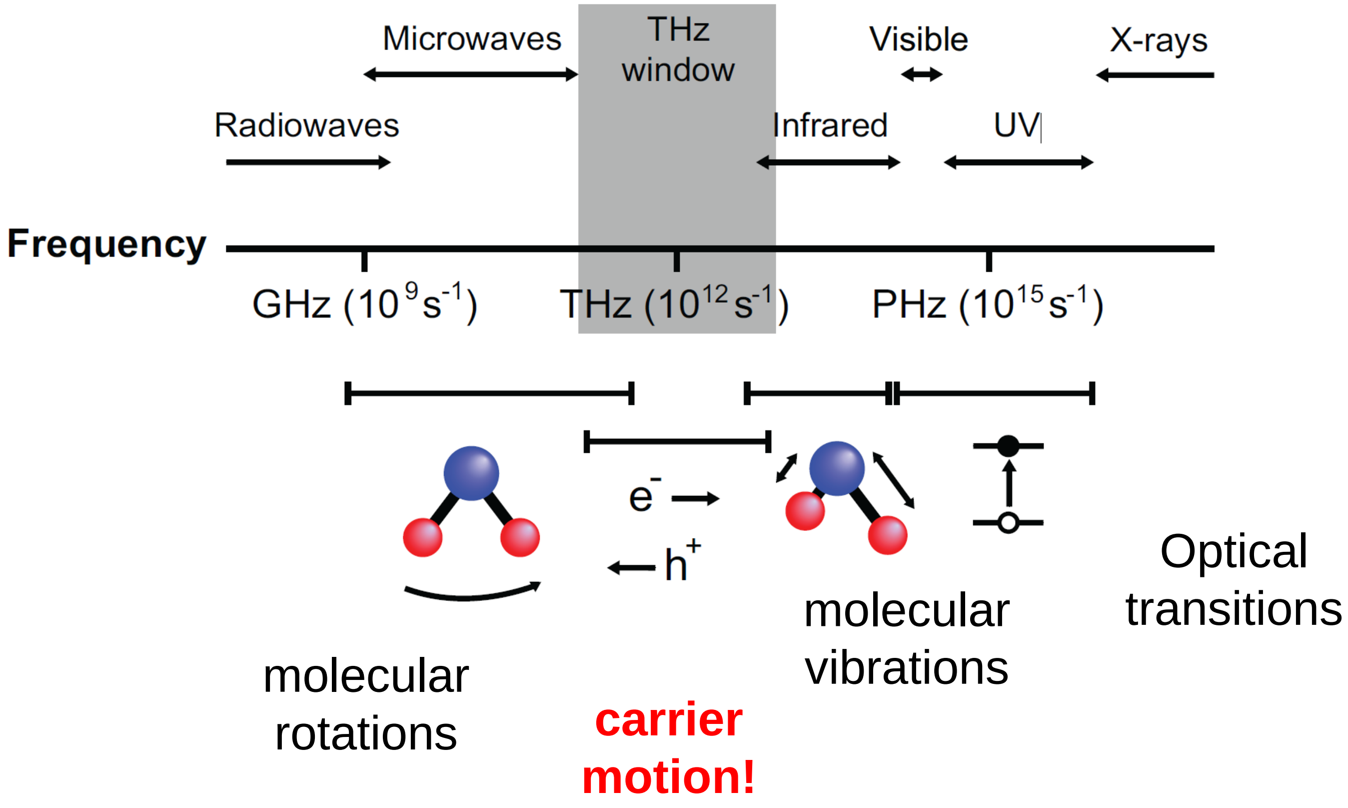
Frequency	$f = 1$ THz $= 10^{12}$ Hz
Oscillation period	$T = 1/f = 1$ ps
Wavelength	$cT = \lambda = 300\ \mu m$
Wavenumbers	$1/\lambda = 33\ cm^{-1}$
Photon energy	$h\omega = 4$ meV



we can measure carrier motion (conductivity) with THz light!

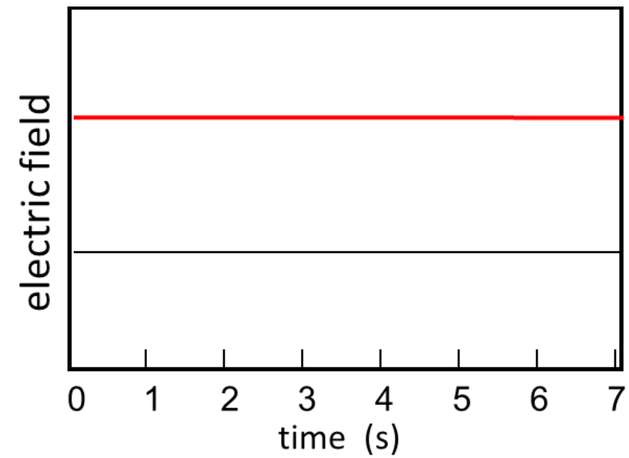
But… why and how?


E. Muybridge, “The horse in motion” (1878).

To “capture” horse motion:

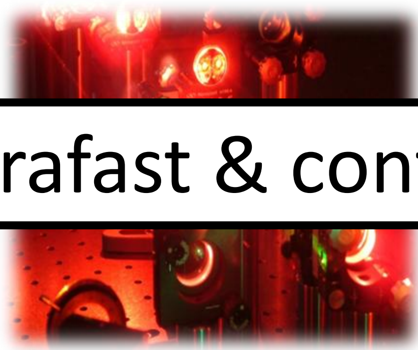
1 photo per milisecond (10^{-3}s).

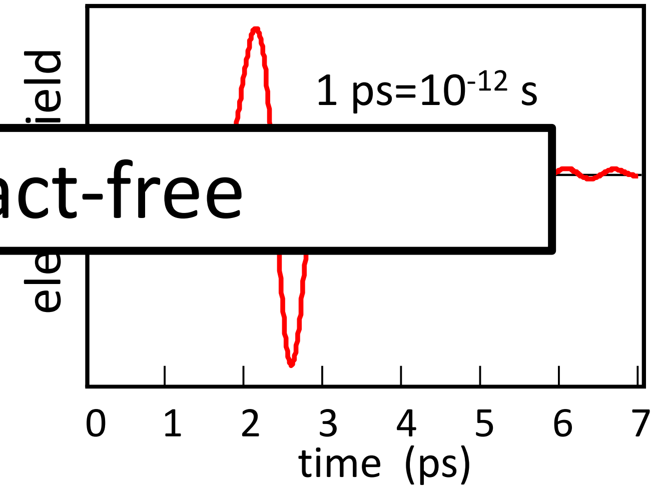
Instead of this:



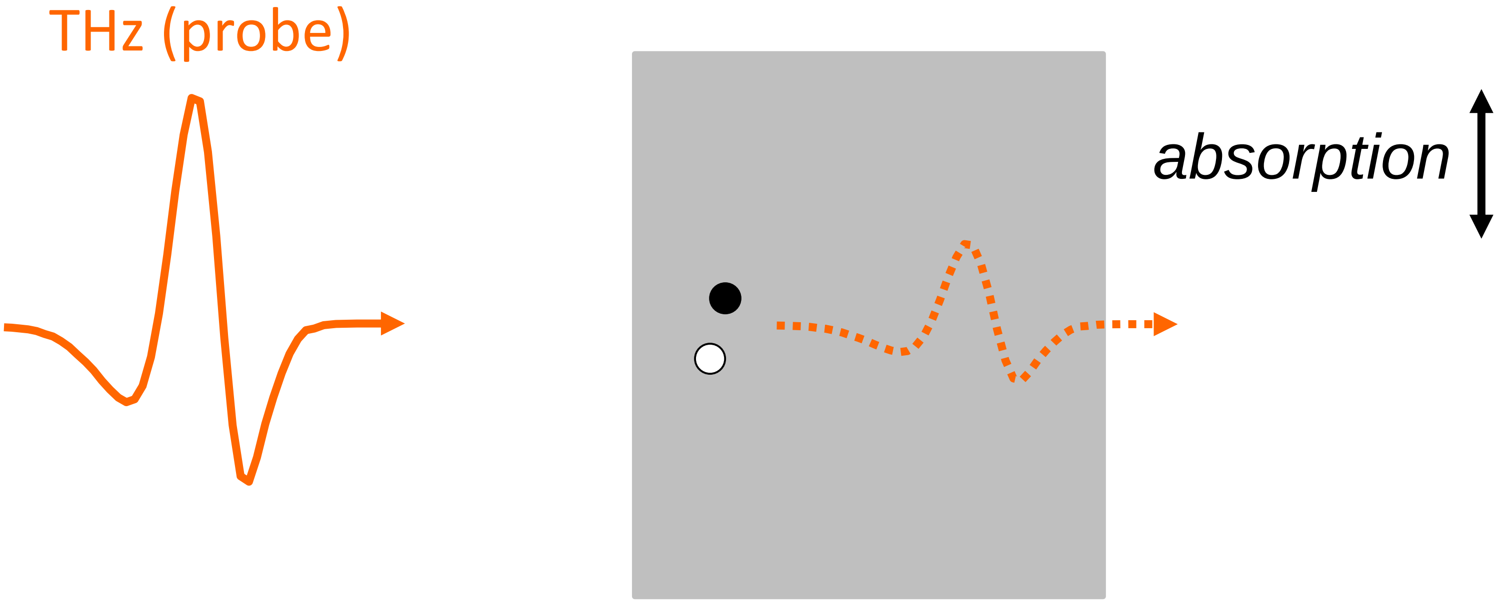
use

Ultrafast & contact-free





Terahertz (THz) spectroscopy

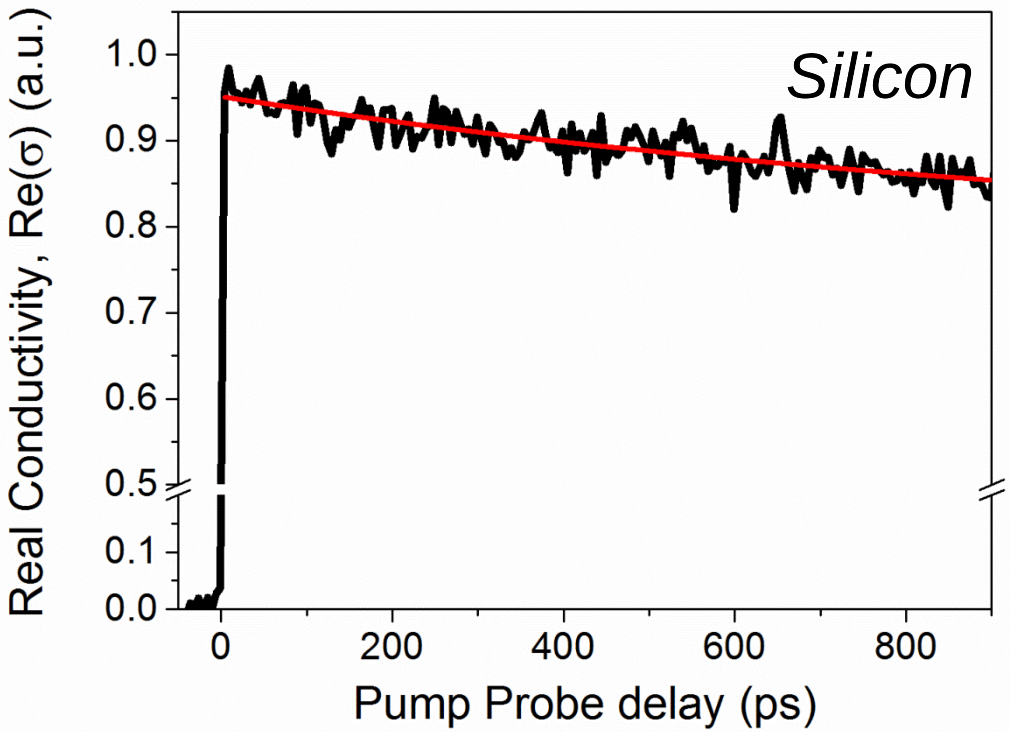


Absorption ~ Re(σ) = e·N·μ

N = number of carriers

μ = sample's mobility

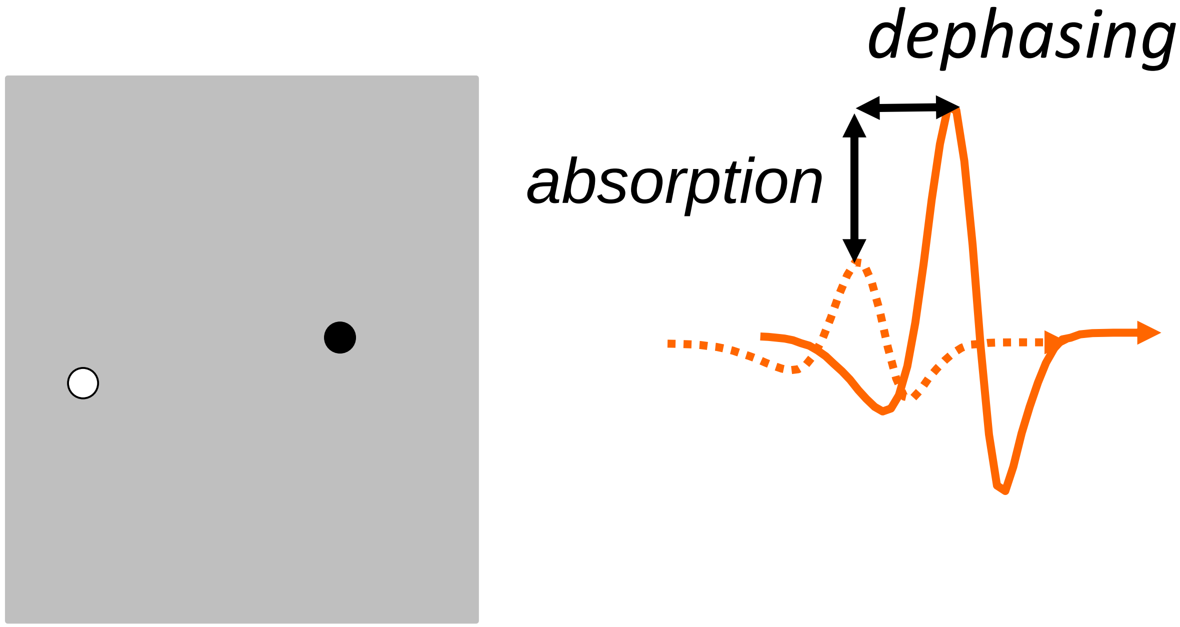
Absorption vs time after excitation ~ Re[σ](t) = e·*N(t)*·μ



$N(t) = N_{h\nu} \cdot exp(-k \cdot t)$

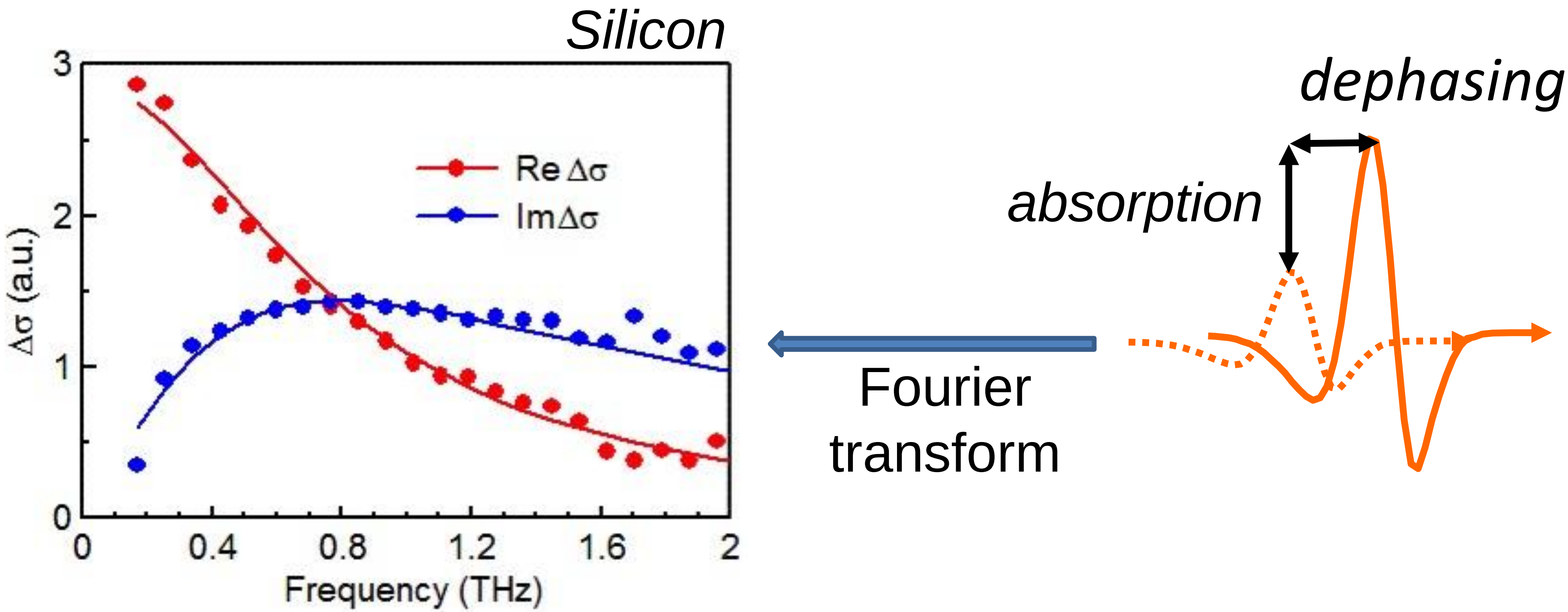
$N_{h\nu}$ ~ number photons

k ~ rate constant



Absorption ~ Re(σ) = e·N·μ

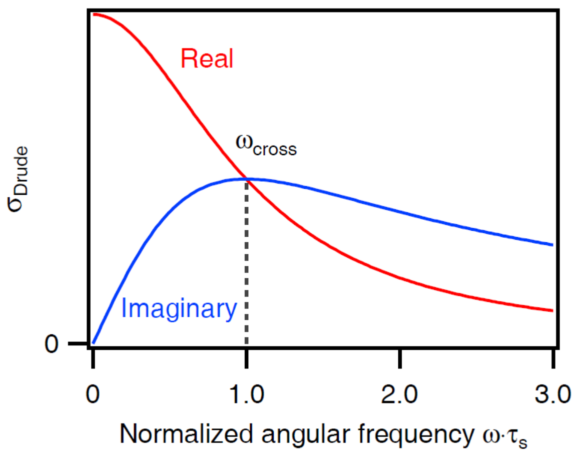
Dephasing ~ Im(σ)



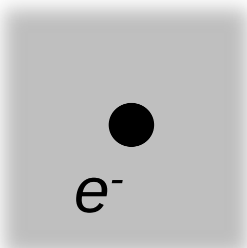
Conductivity ~ $\sigma(\omega) = e \cdot N(t_0) \cdot \mu(\omega)$

$\mu(\omega)$ is the frequency resolved mobility in the sample and is informative of the nature of the carriers!

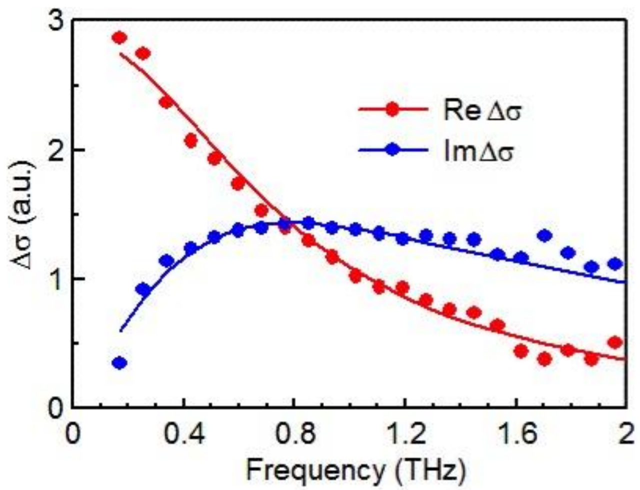
Drude Model



free carriers



Silicon

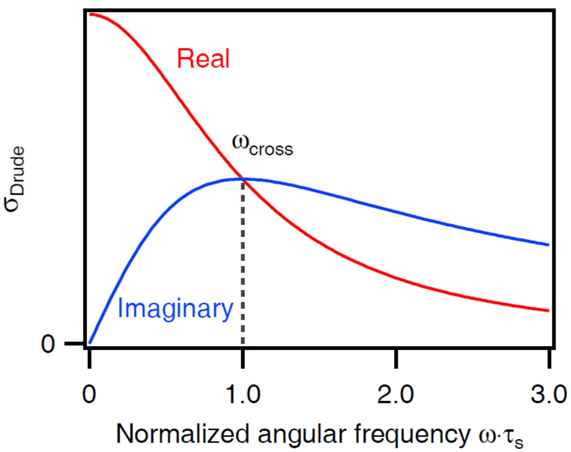


$$\sigma(\omega) = \frac{i\varepsilon_0\omega_p^2}{\omega + i\gamma} \qquad \gamma = \frac{1}{\tau} \qquad \omega_p^2 = \frac{Ne^2}{\varepsilon_0 m}$$

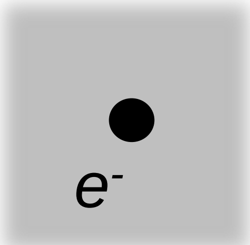
Scattering time, τ → $\mu(\omega)$

Plasma frequency $\omega_p{}^2$ → *N*

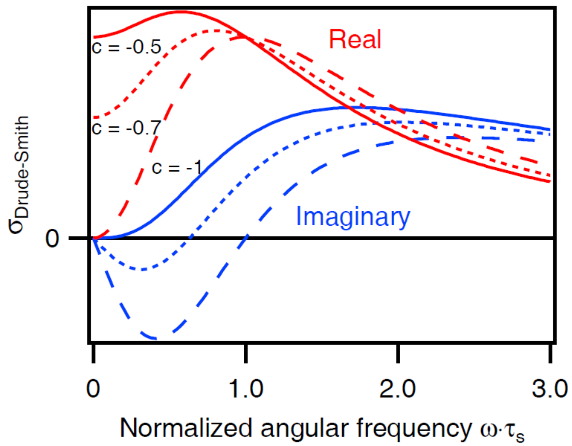
Drude Model



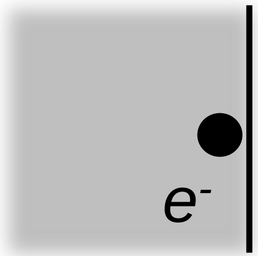
free carriers



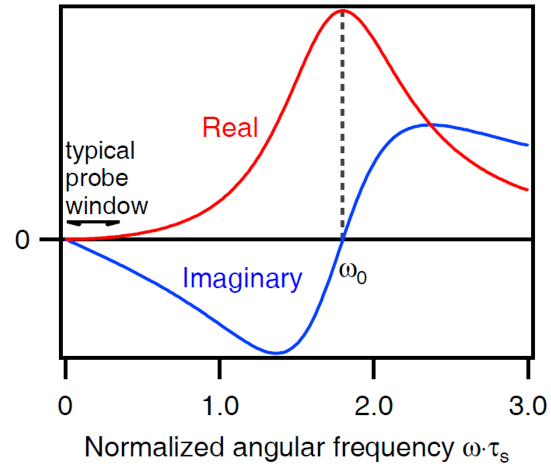
Drude-Smith Model



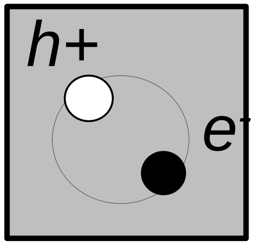
free carriers + backscattering



Lorentz Model

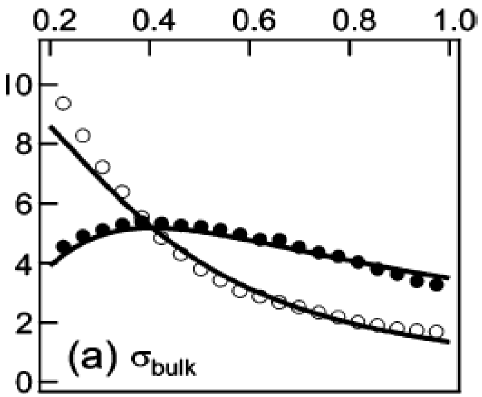


excitons

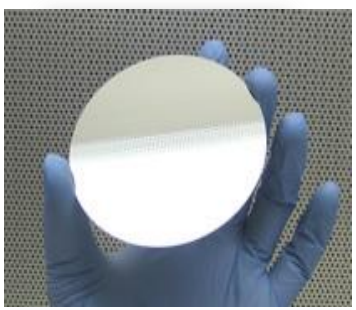


Increasing charge localization

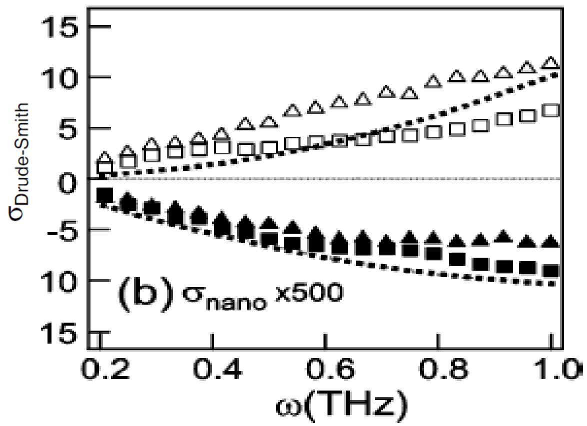
Drude Model



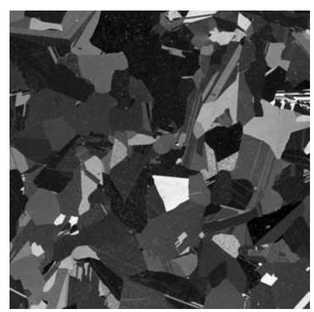
free carriers



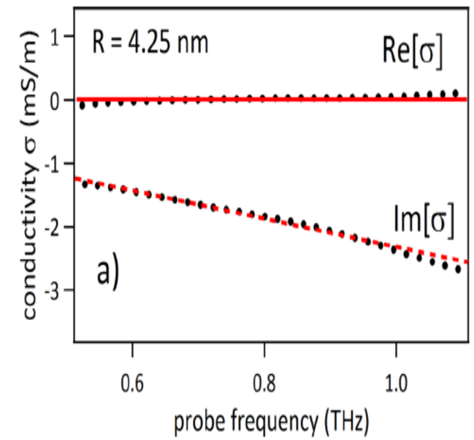
Drude-Smith Model



free carriers + backscattering



Lorentz Model



excitons

Increasing charge localization

- *THz spectroscopy allows for measuring sample's conductivity (ultrafast and contact free).*

$$\text{Conductivity} \sim \sigma(\omega) = e\cdot N\cdot \mu(\omega)$$

- *We can interrogate the fate of photo-generated carriers by monitoring the time evolution of carrier density,* N(t).

$$N(t)=N_{h\nu} \cdot \exp(-k\cdot t) \quad \text{where } 1/k \text{ is carrier lifetime}$$

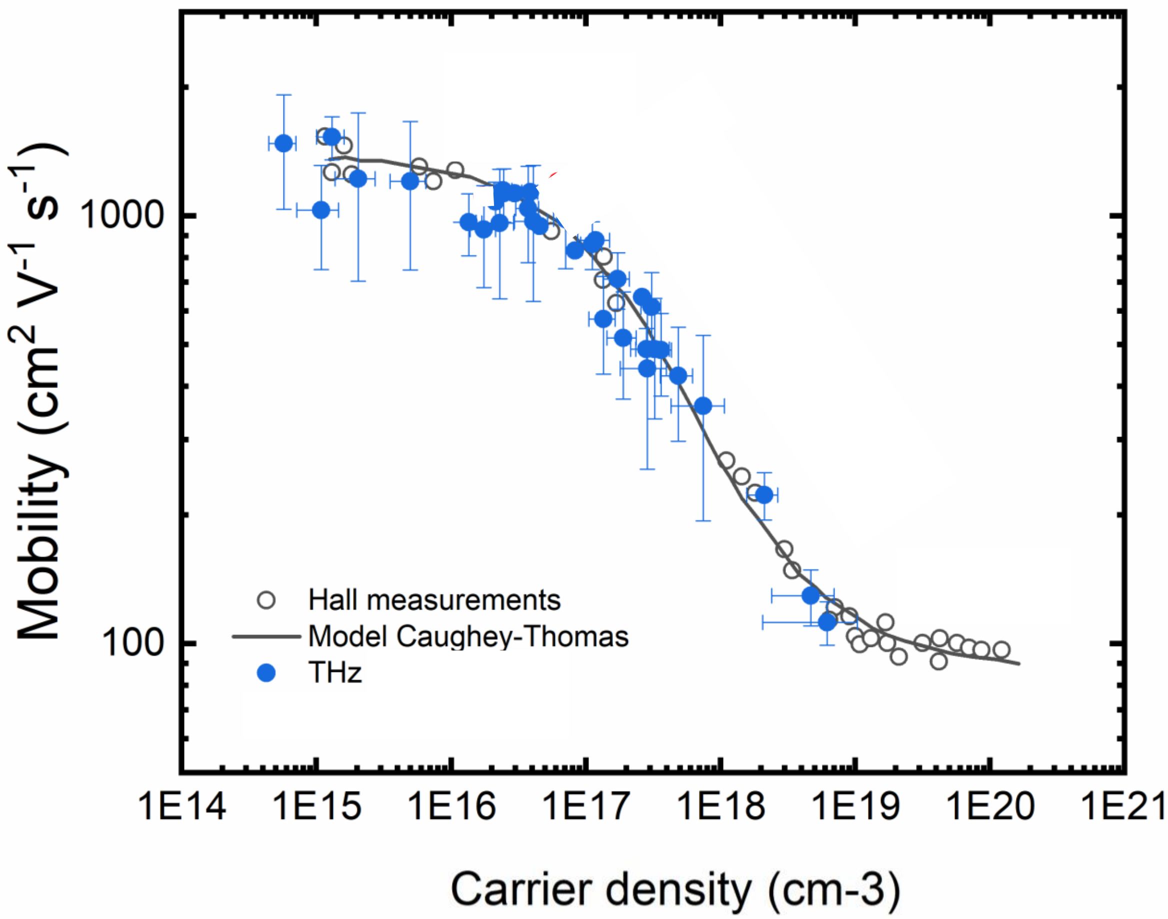
- *We can interrogate the nature of photo-generated carriers via modelling the frequency resolved conductivity (i.e. mobility).*

Modelling $\mu(\omega)$ → carrier *scattering time* τ_r

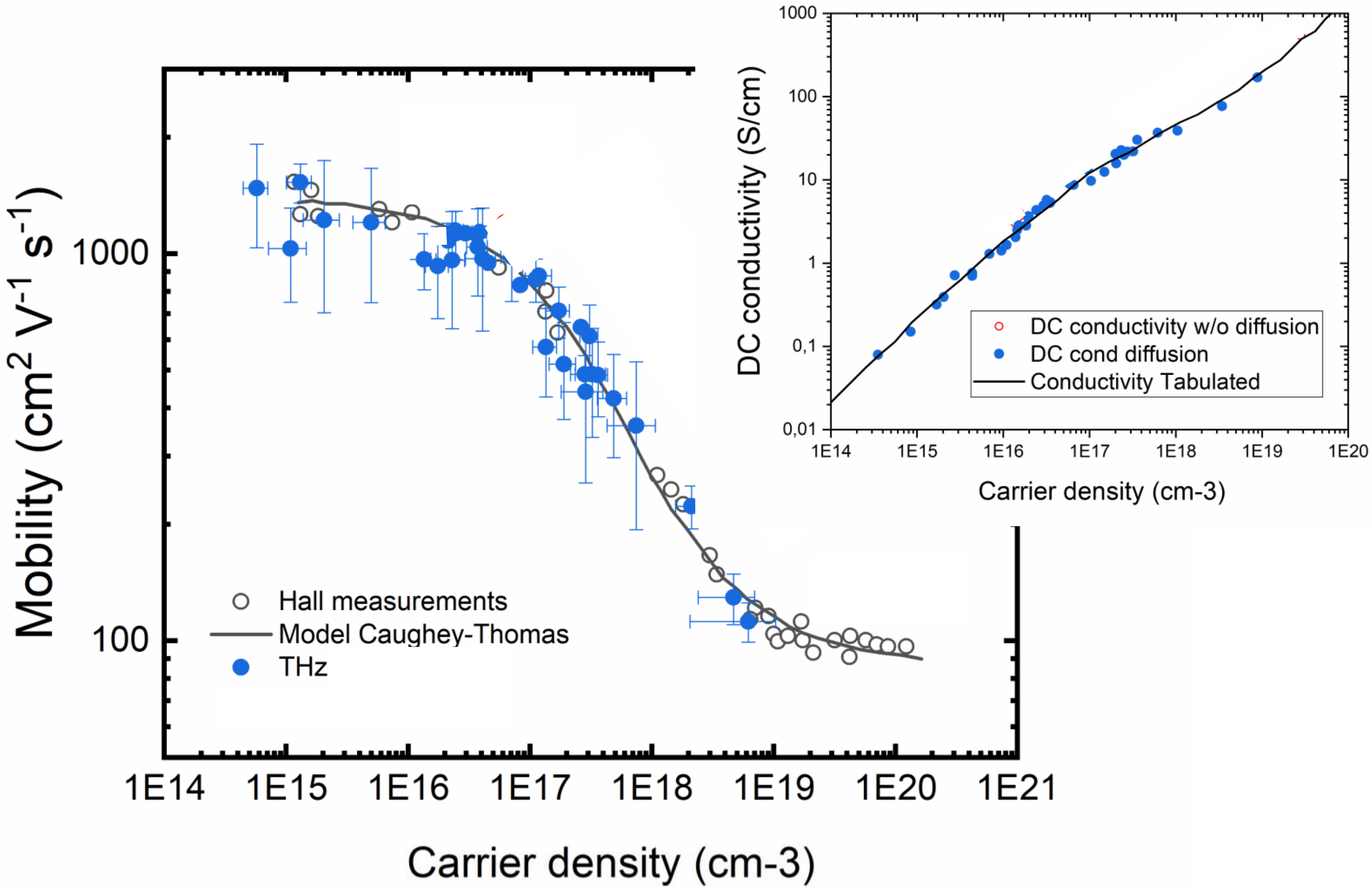
Piece of advice…

“Theories come and go, but good data remains forever”

Mary Leakey

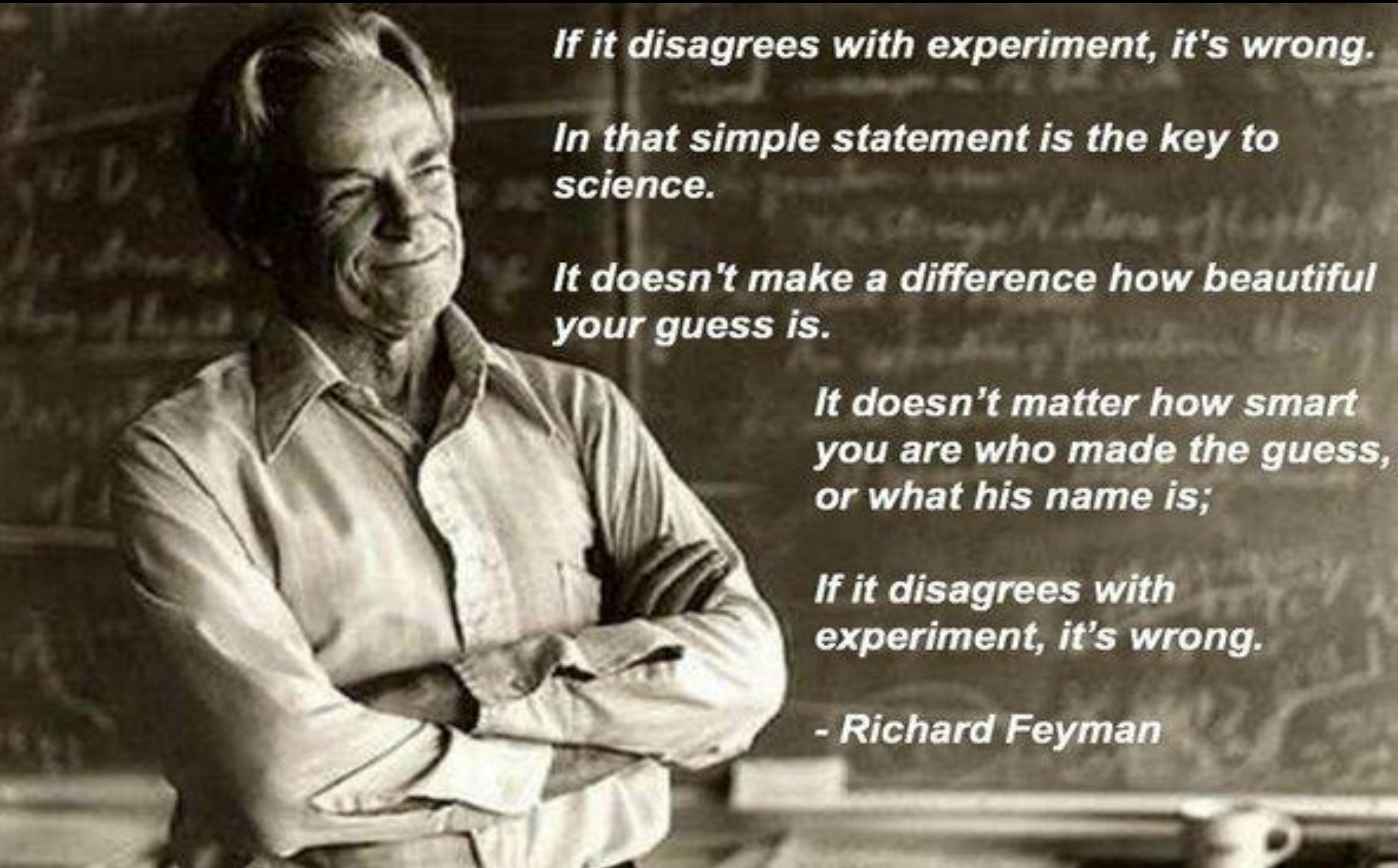


Phys. Rev. B 107, 085204 (2023)



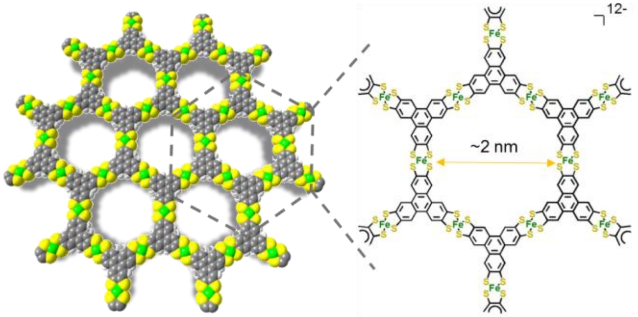
Phys. Rev. B 107, 085204 (2023)

Piece of advice…



time-resolved terahertz spectroscopy

Charge transport in metal- and covalent-organic frameworks



High-mobility band-like charge transport in a semiconducting 2D metal-organic framework

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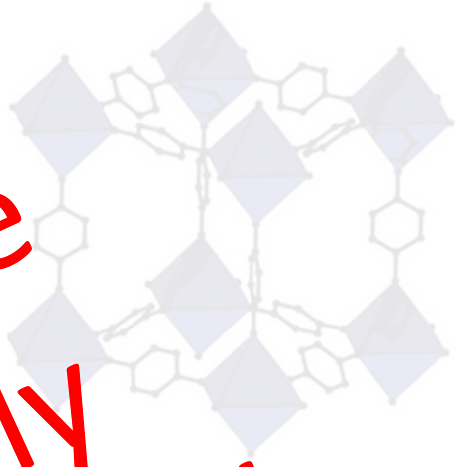
Nature Materials 2018

Cubic Space Division
Escher (1954)



MOF-5
Yaghi (1999)

Metal ions (or clusters) coordinated by organic ligands to form 1D, 2D and 3D crystalline materials:

- Countless combinations of building units (>100000 MOFs).
- Permanent crystalline porous structure (high surface area).
- Tunable functionality (gas storage and separation; catalysts and sensors; biomedical;…). opto-electronics?,…)

MOFs are generally insulating ☹!

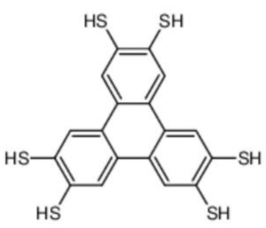
Target: High Conductivity!

$$\sigma = q \cdot N \cdot \mu$$

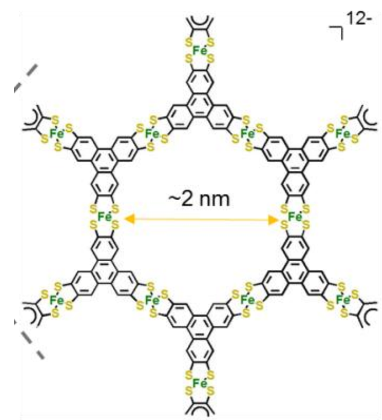
Enable high charge carrier densities via doping from metal ions (e.g. d^6 $Fe^{II/III}$) and/or organic ligands (e.g. radicals)

Enable high charge carrier mobilities via strong overlap between MOF building blocks orbitals.

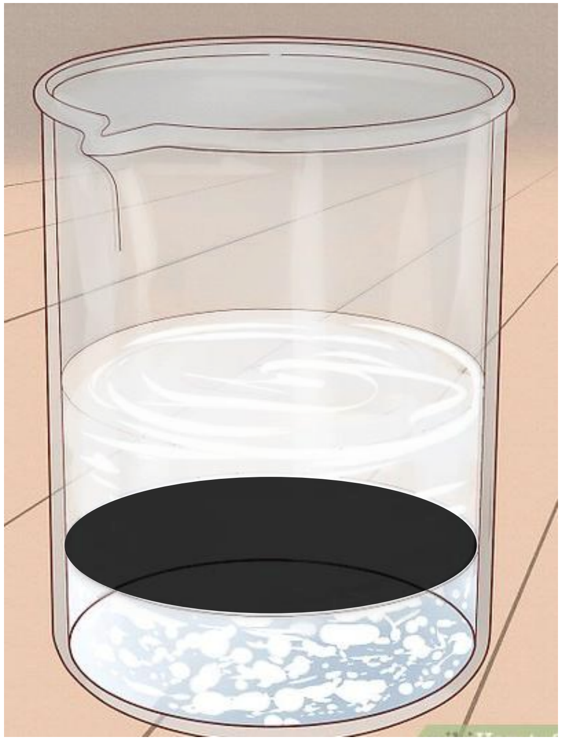
Develop an iron based fully π-d conjugated 2D MOF



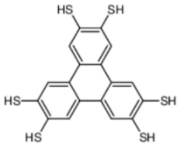
+ Fe(III) =



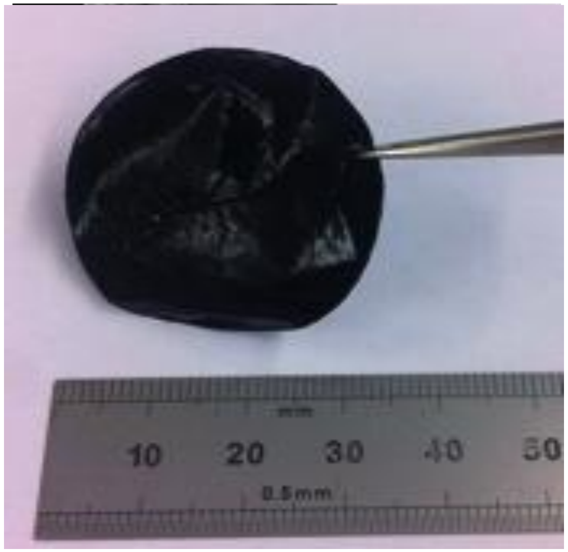
$Fe(III)_3(THT)_2(NH_4)_3$



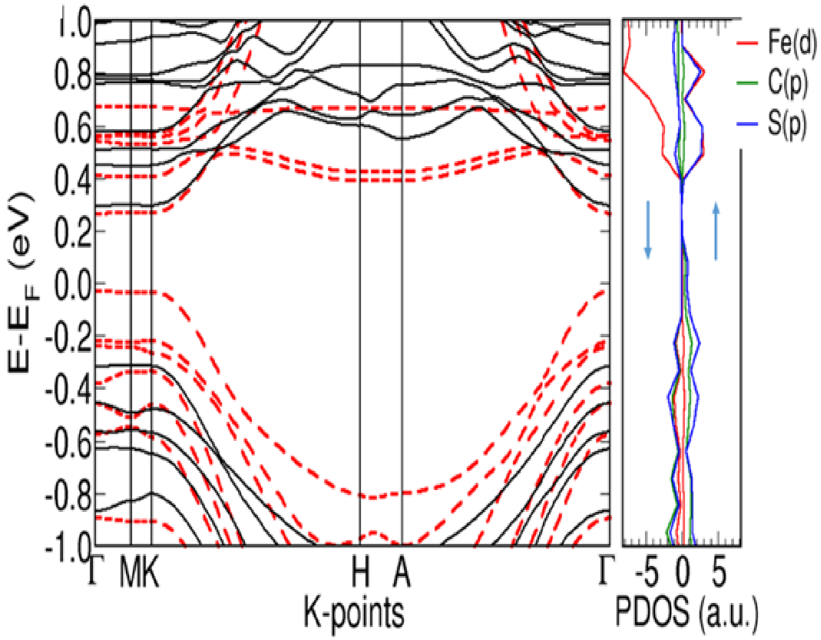
Water + $Fe(acac)_2$

Chloroform + 

Self-standing films

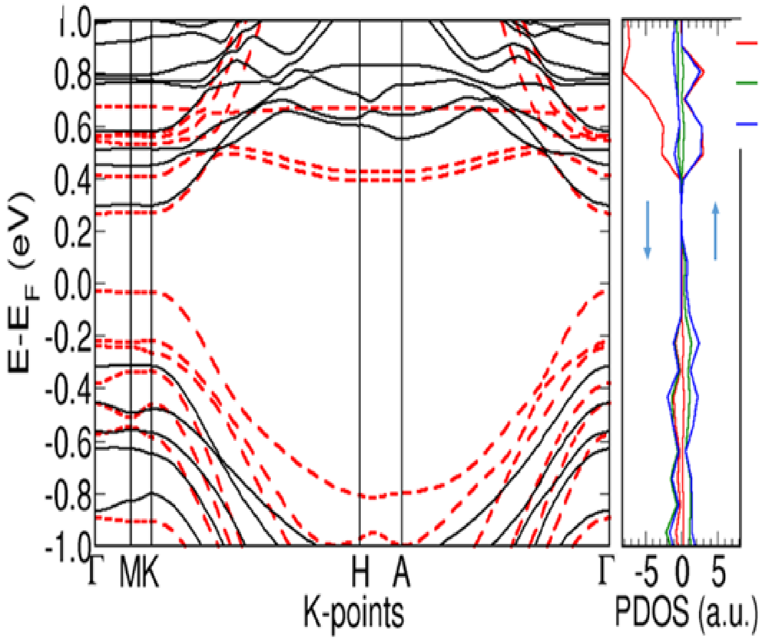


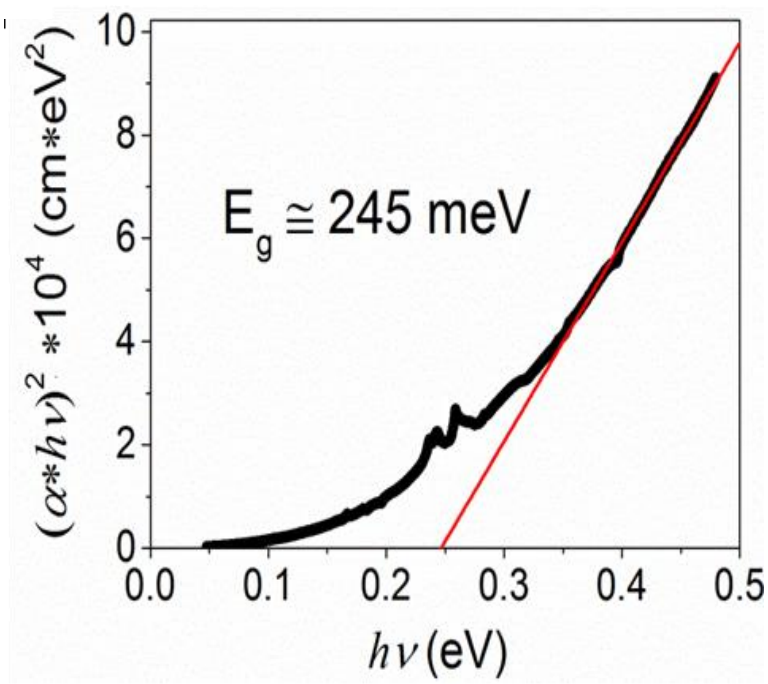
Semiconducting



Strong hybridation between metal and organic building blocks

Semiconducting



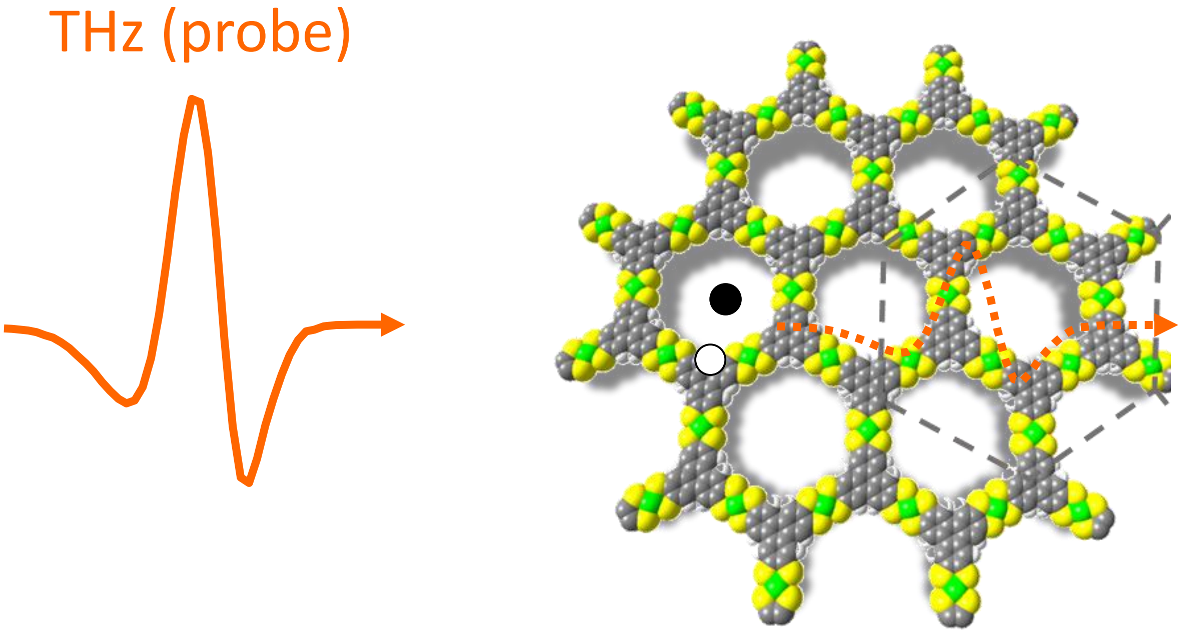


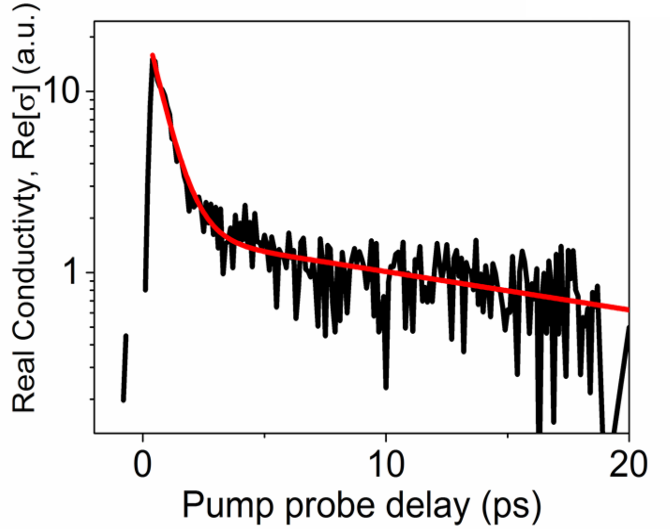
0.25eV direct bandgap

Time resolved THz spectroscopy

Quantify photoconductivity with ps time-resolution

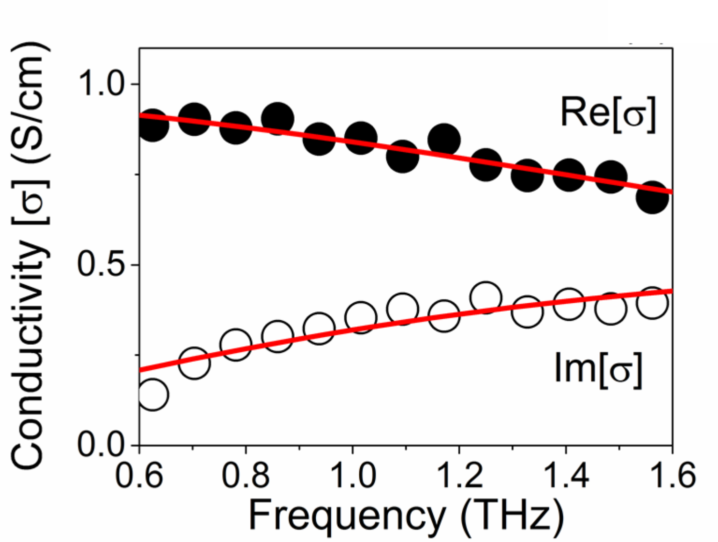
Contact free technique


THz (probe)



Fast photoconductivity relaxation

Re[σ](t) = q·N(t)·μ

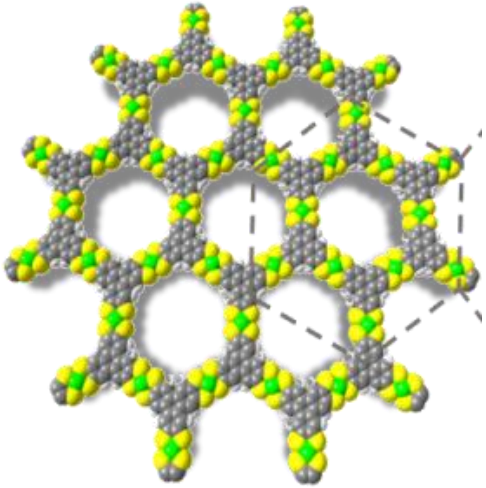


Drude response at the peak conductivity!

band-like transport in 2D MOFs!!!

$\mu = 220 cm^2/Vs$

We resolve band like transport in semiconducting 2D $Fe_3(THT)_2$ MOF.

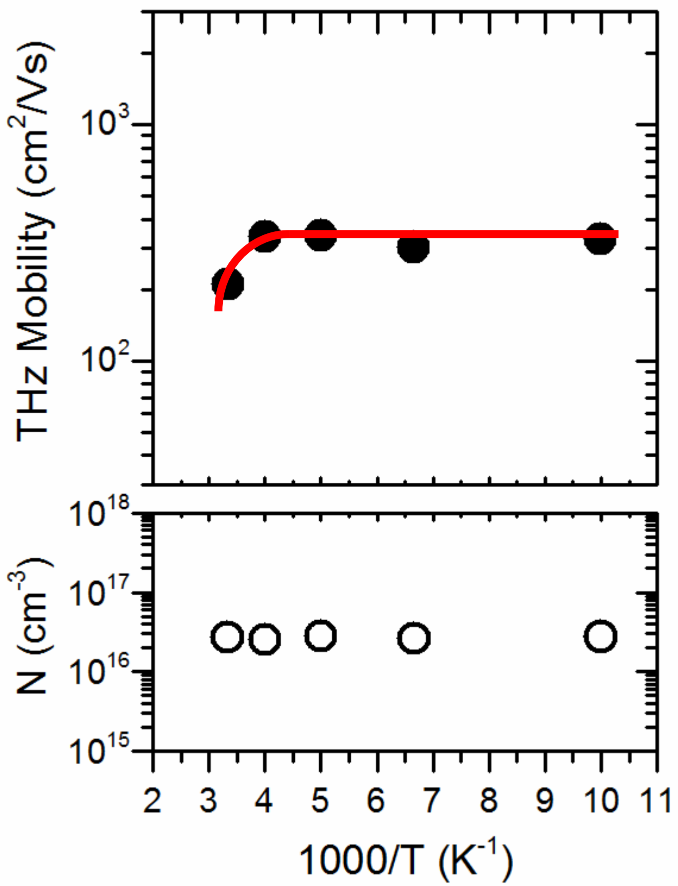


Can we improve the 220 cm^2/Vs mobility?

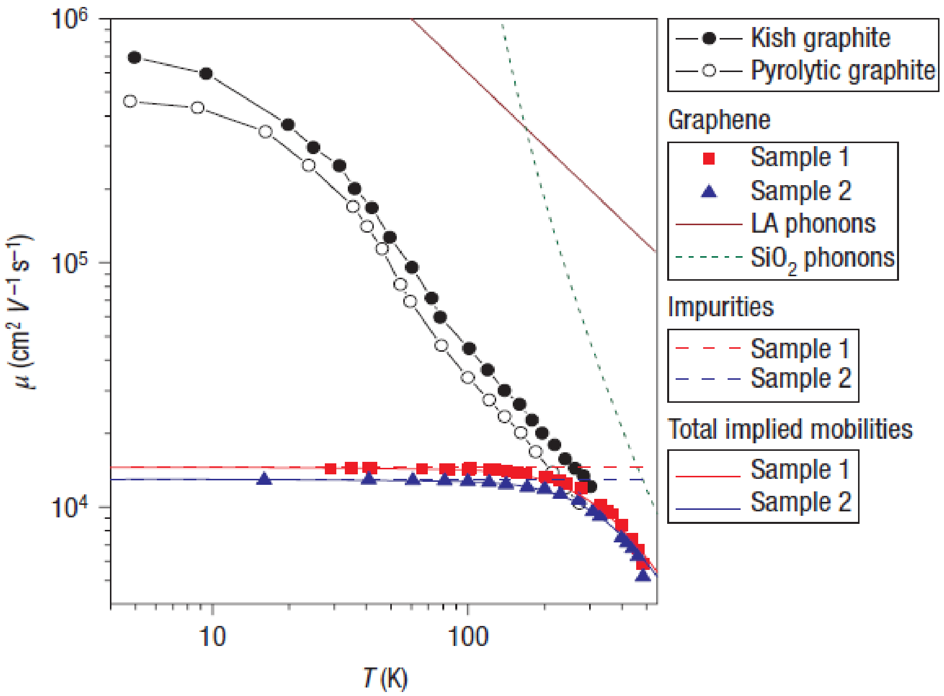
First identify scattering mechanisms limiting mobility, how?

Analyze the temperature dependence.

2D MOF

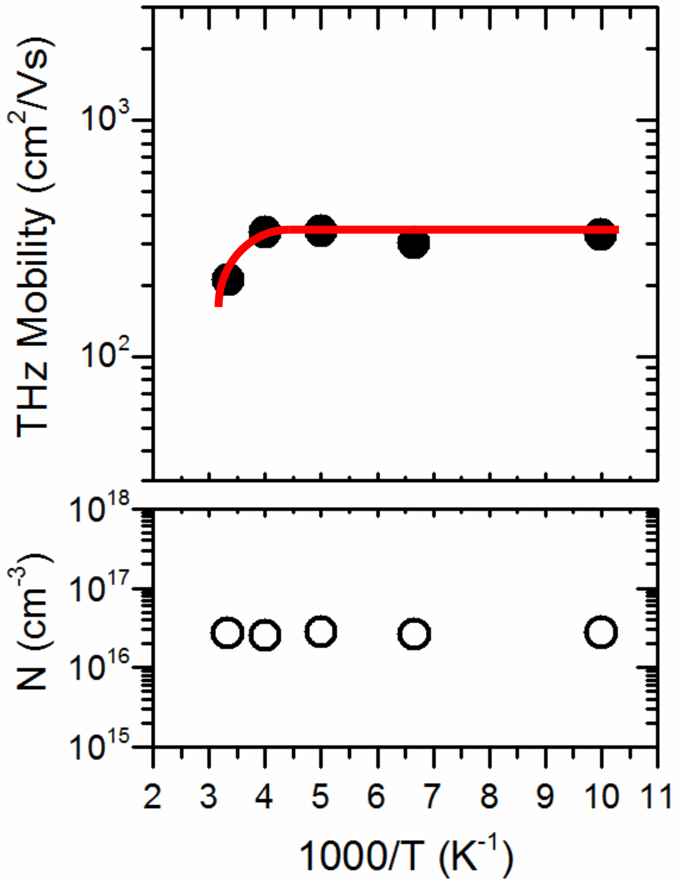


Graphene

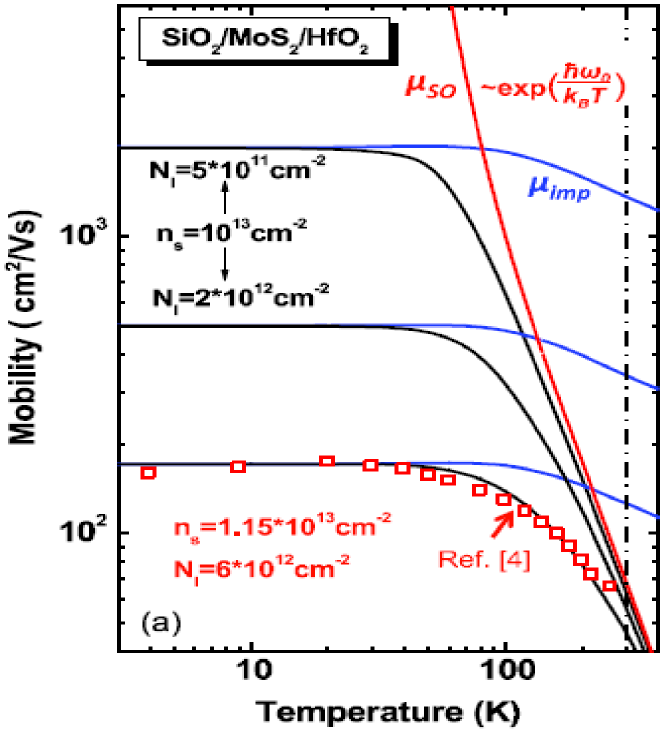


Nat. Nanotech. 3, 206 - 209 (2008)

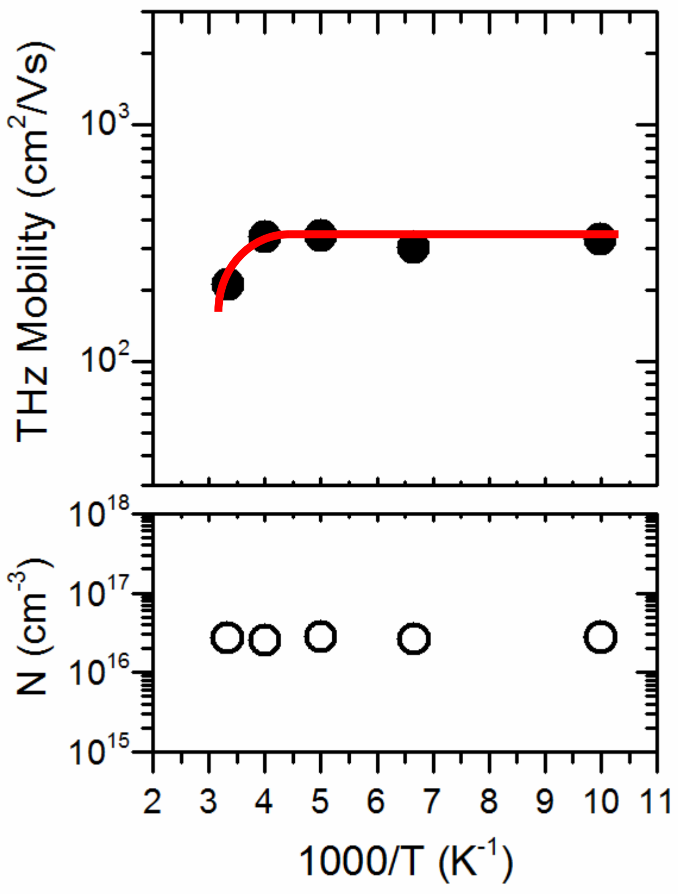
2D MOF



2D MoS_2



Phys. Rev. X 4, 011043 (2014)

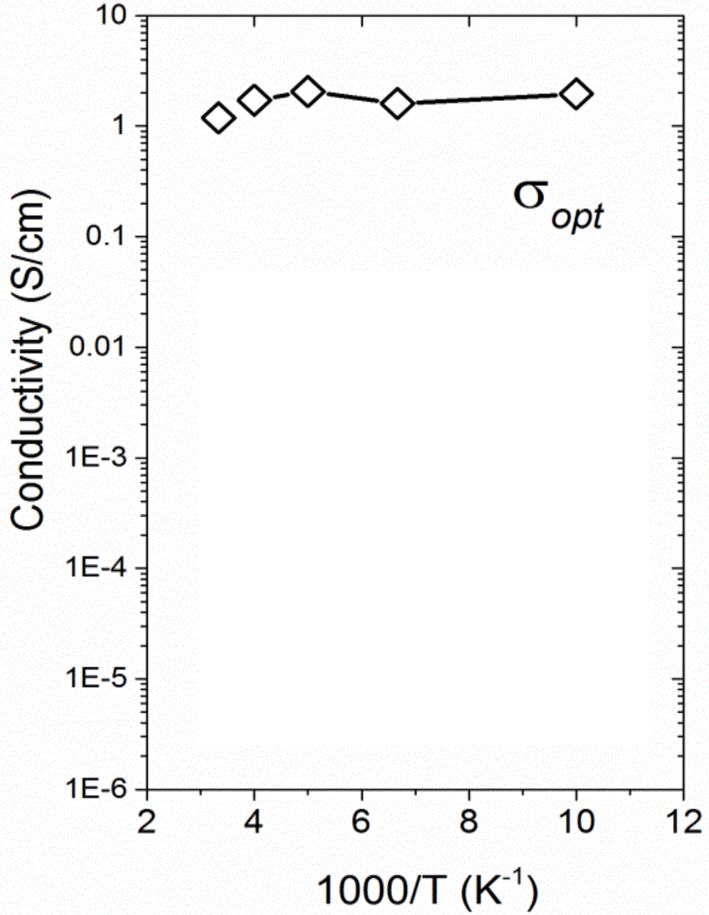


300-250K – phonon scattering.

>250K impurity scattering (heavy doping).

Doping engineering could boost mobilities values.

Comparing conductivities inferred optically and electrically



$$\sigma(\omega) = e \cdot N \cdot \mu(\omega)$$

Optical σ probed locally (nm's)

Mobility constant with T.

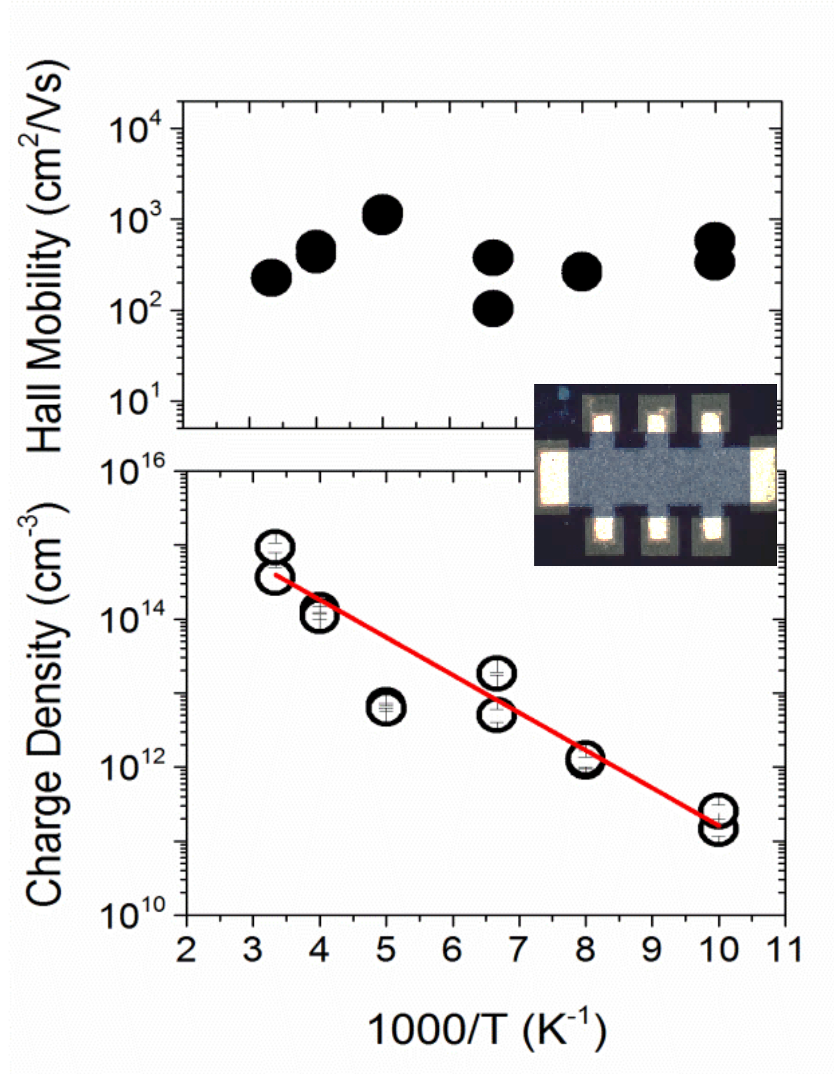
Carrier density fixed by #photons.

Hall Effect Measurements on 2D MOF

Hall (DC) mobility barely affected by temperature.

Temperature dependence of the electrical σ is dominated by intrinsic thermal population of carriers.

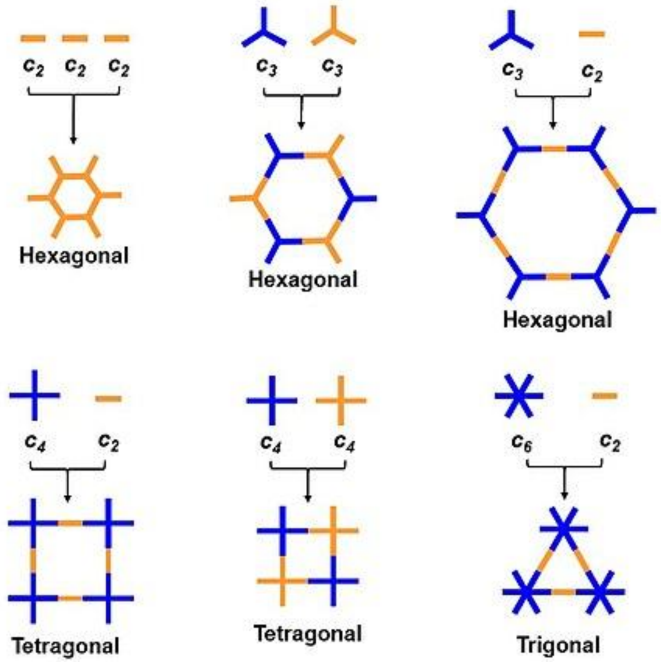
$N_i \propto exp(-E_g/2k_bT)$; E_g = 250meV



- *High-mobility band-like transport demonstrated in a semiconducting 2D metal organic framework (opened the path for MOF based opto-electronics).*

- *2D $Fe_3(THT)_2$ MOF samples display room temperature mobilities up to 220cm^2/Vs. Further improvements in mobilities are possible via doping and phonon engineering.*

What about covalent organic frameworks?



Exceptionally high charge mobility in phthalocyanine-based poly(benzimidazobenzophenanthroline)-ladder-type two-dimensional conjugated polymers

Mingchao Wang[1,10], Shuai Fu[2,10], Petko St. Petkov[3], Yubin Fu[1,4], Zhitao Zhang[5], Yannan Liu[1,4], Ji Ma[1,4], Guangbo Chen[1], Sai Manoj Gali[6], Lei Gao[2], Yang Lu[1,4], Silvia Paasch[1], Haixia Zhong[1], Hans-Peter Steinrück[7], Enrique Cánovas[2,8], Eike Brunner[1], David Beljonne[6], Mischa Bonn[2], Hai I. Wang[2]*, Renhao Dong[1,9]*, Xinliang Feng[1,4]*

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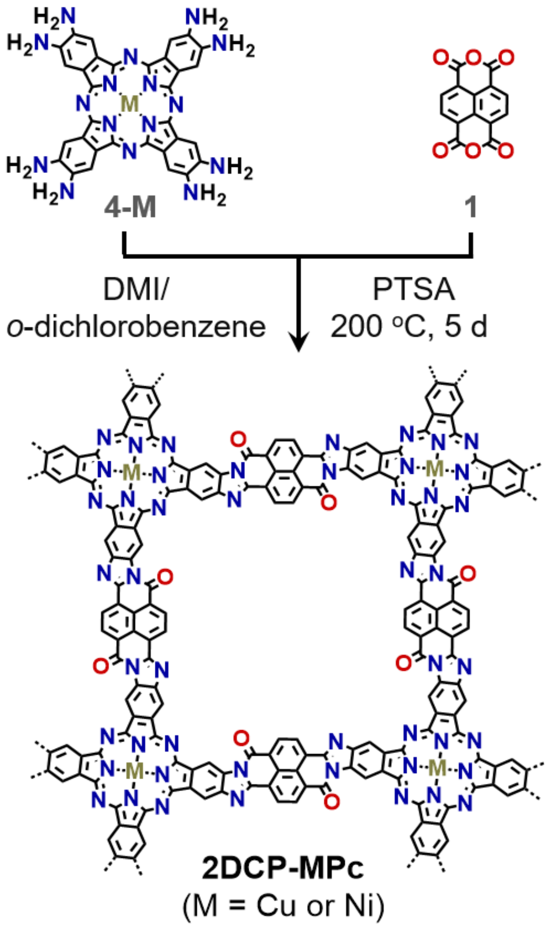
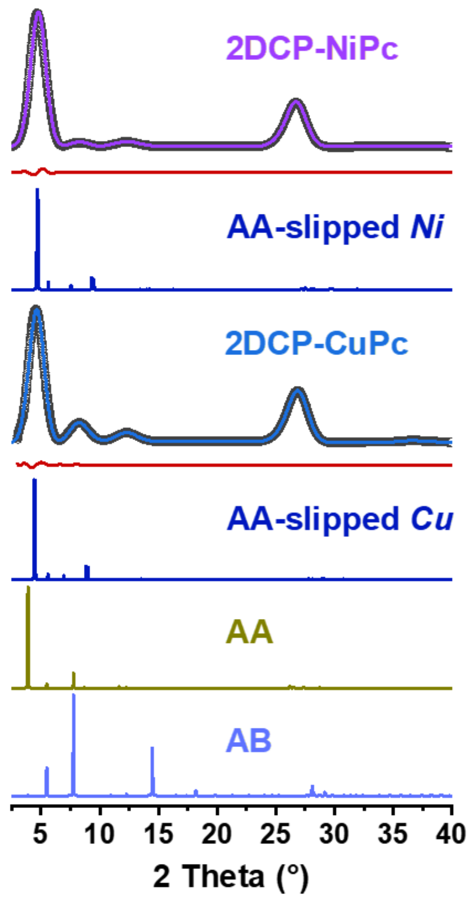
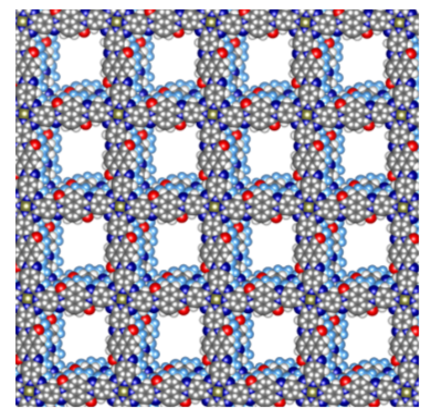
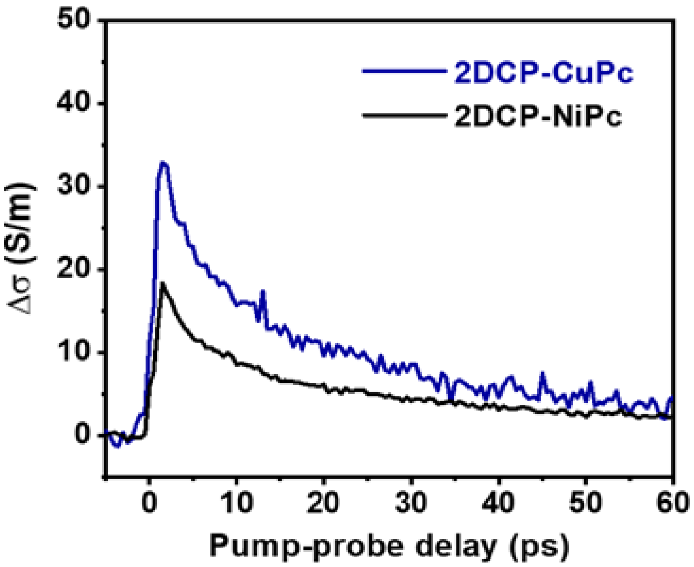
Phthalocyanine-based BBL-ladder-type COFs



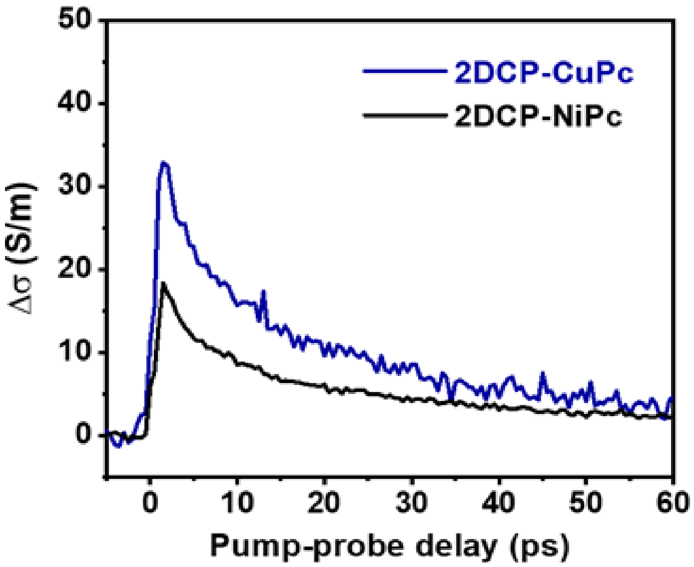






Fast photoconductivity relaxation

$$\mathrm{Re}(\sigma) = q \cdot (n \cdot \mu)$$

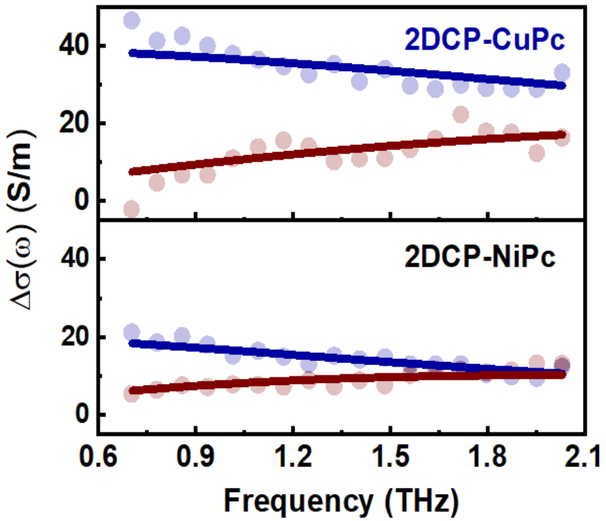


Fast photoconductivity relaxation

$$\mathrm{Re}(\sigma) = q\cdot(n\cdot\mu)$$

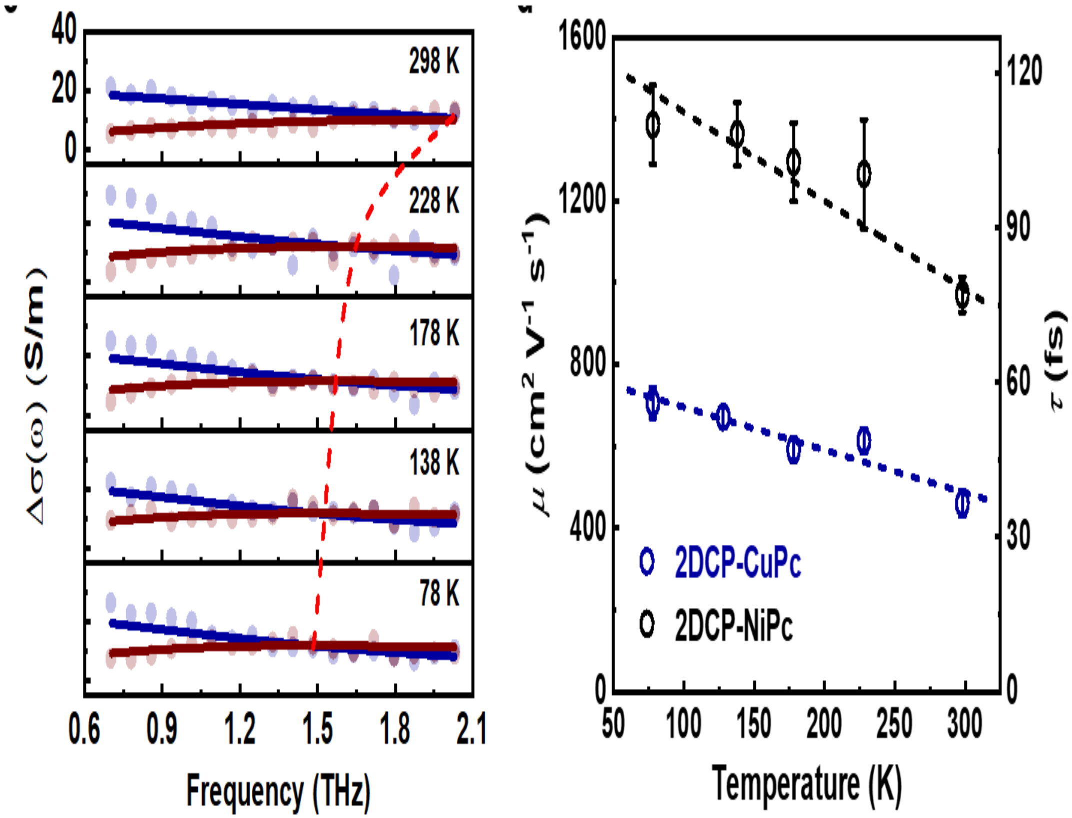
Drude responses at the peak conductivity!

High-mobility band-like transport in 2D COFs!



$\mu = 460\text{cm}^2/\text{Vs}$

$\mu = 970\ \text{cm}^2/\text{Vs}$



300-250K – phonon scattering.

>250K impurity scattering (heavy doping).

Doping engineering could boost mobilities values.

- *High-mobility band-like transport demonstrated in semiconducting 2D covalent organic frameworks.*

- *Analyzed 2D-COF samples display bandgaps of 1.3eV and world record room temperature mobilities up to 970cm^2/Vs (figures commensurate with Silicon but adding porosity and chemical tailorability)*

2D MOF and 2D COF semiconducting samples provide record-high mobilities up to 220 and 970 cm^2/Vs respectively.

These figures parallel those found in inorganic semiconductors, but on porous and highly tailorable materials.

Further improvements are possible by developing single crystalline samples and by defect engineering.

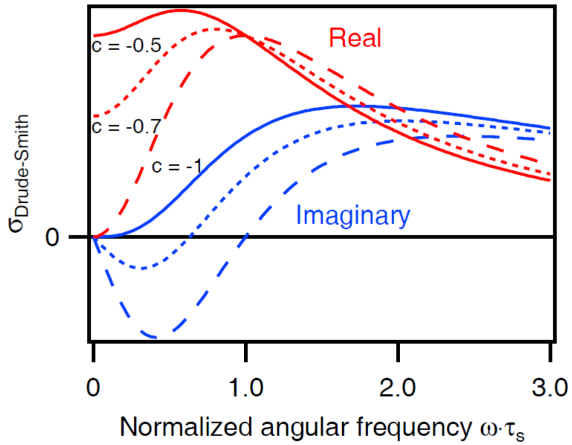
Piece of advice…

"The first principle is that you must not fool yourself—and you are the easiest person to fool."

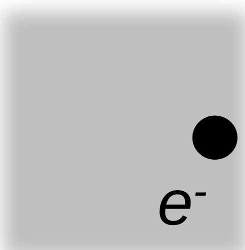
—Richard Feynman

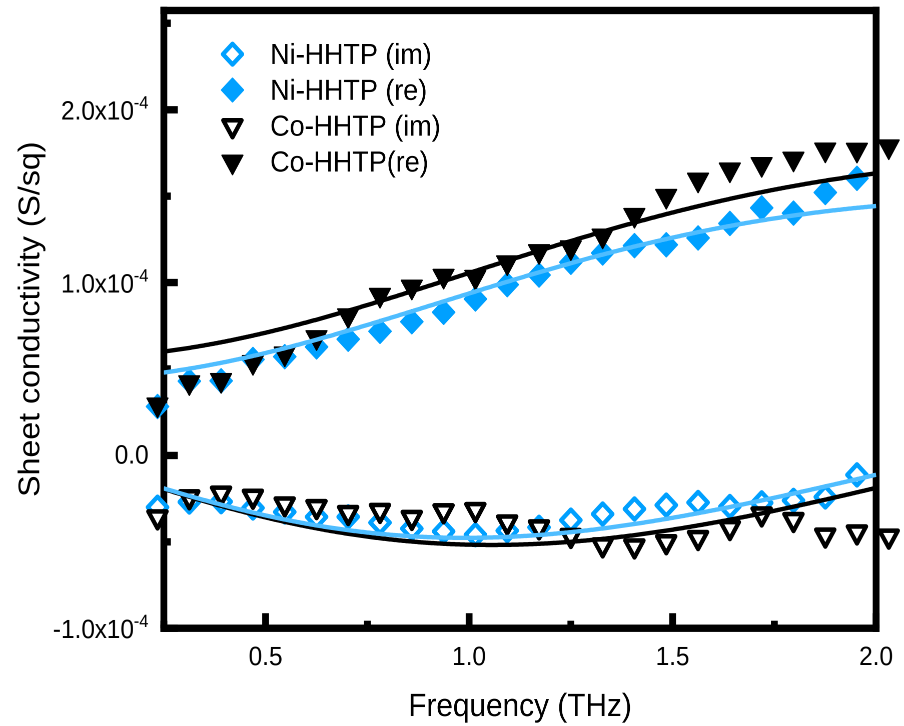
$(Cu,Co)_3$-$HHTP_2$

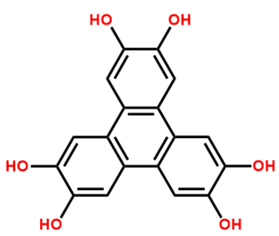
Drude-Smith Model



free carriers + backscattering



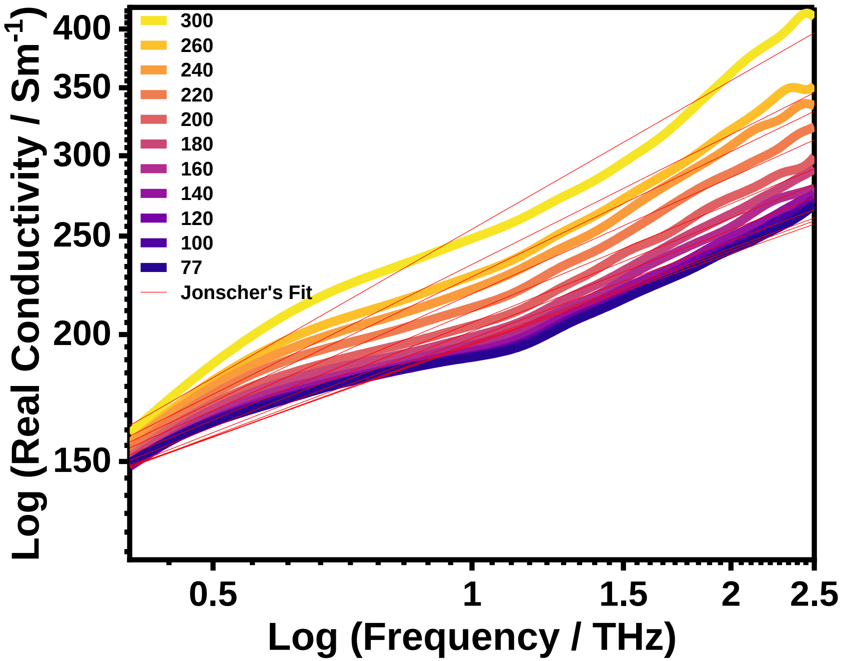


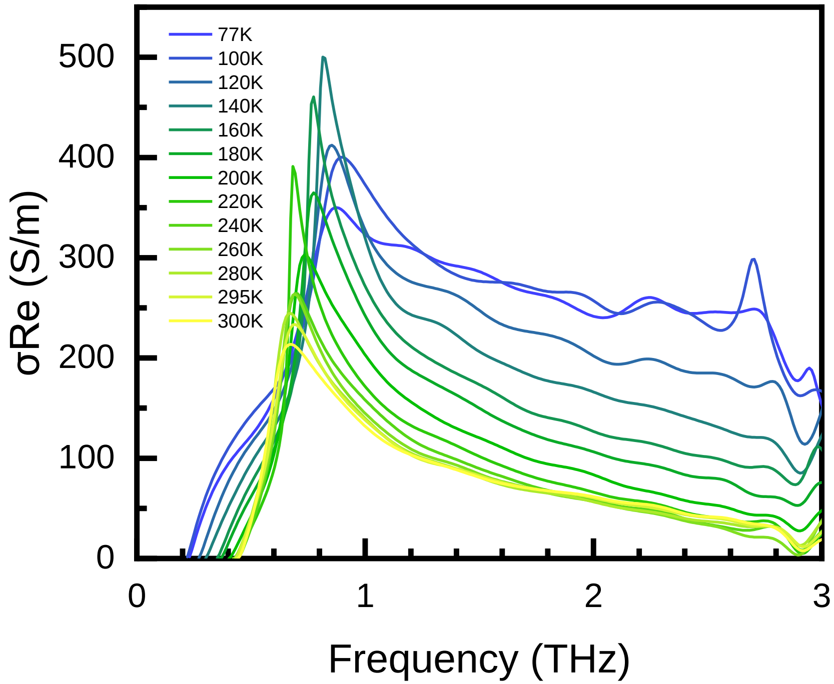


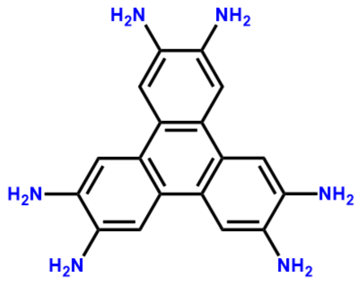
HHTP

Different metal center….
But same mobility,
"doping", backscattering…

Ni_3-HITP$_2$







HITP

Same sample, different local "exotic" responses…

Nice, but… a lot to be done yet.

THE GOOD: Drude-like band-like transport high mobility/conductivity demonstrated for metallic and semiconducting samples.

THE BAD: sample reproducibility (even within same sample/group), degradation/oxidation, large single crystals not available….

THE UGLY: Library of materials expanding, sample´s all surface, “doping” seems perturbative, little known about role of defects, short-lived charge carriers, DFT support limited to pristine samples….