ESMolNa
European School on Molecular Nanoscience

Electrical Characterization of Molecular Systems by Time Resolved THz Spectroscopy

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Prof. Enrique Cánovas

Research interests: Nanotechnology, Photovoltaics, Photocatalysis, Carrier Dynamics, THz spectroscopy

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Max Planck for Polymer Research
Mainz, Germany

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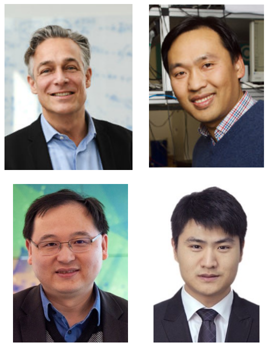
Acknowledgements



Prof. Mischa Bonn and Prof. Hai Wang
Max Planck Institute for Polymer Research

Prof. Xinliang Feng and Prof. Renhao Dong
Technical University of Dresden
Max Planck Institute of Microstructure Physics

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Acknowledgements

Nanostructured PV group @ IMDEA Nano

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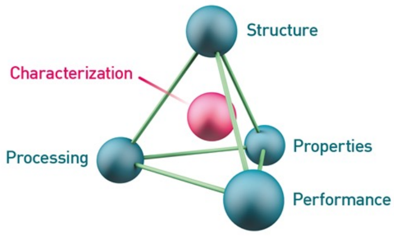
What we do?



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**.

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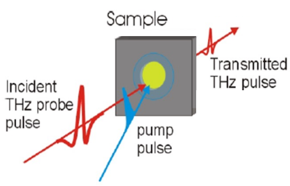
Summary of my talk

time-resolved terahertz spectroscopy



Electron transfer at quantum dot-bridge-metal oxide interfaces

Charge transport in metal organic frameworks

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

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Terahertz radiation

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

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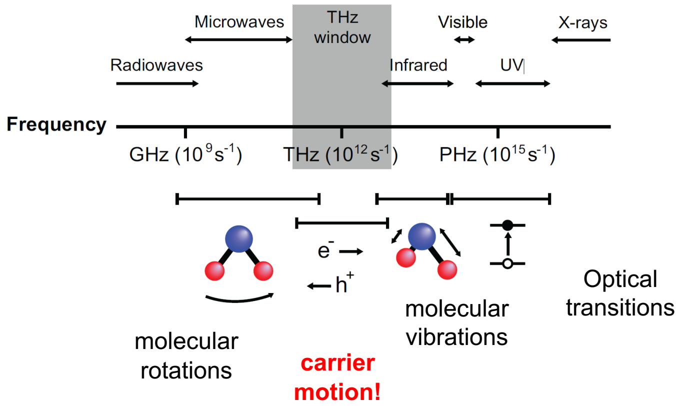
Terahertz (THz) frequencies



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

But… why and how?

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Why THz radiation allows measuring carrier motion?

E. Muybridge, "The horse in motion" (1878).

To "capture" horse motion:

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

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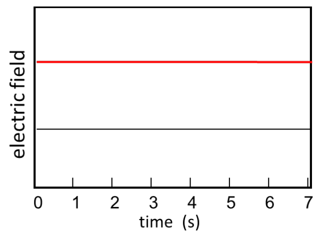
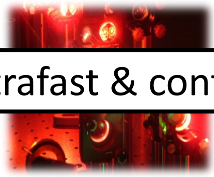
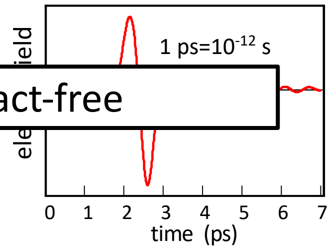
How do we measure conductivity by THz radiation?

Instead of this:



use **Ultrafast & contact-free**





Terahertz (THz) spectroscopy

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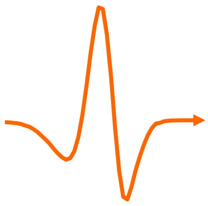
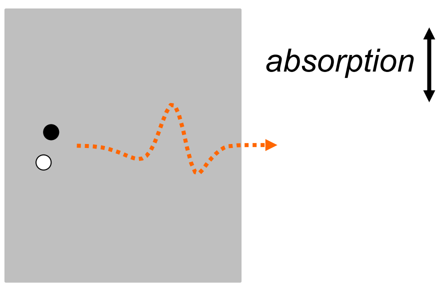
THz time domain spectroscopy THz-TDS

THz (probe)





Absorption ~ $\mathrm{Re}(\sigma) = e \cdot N \cdot \mu$
N = number of carriers
μ = sample's mobility

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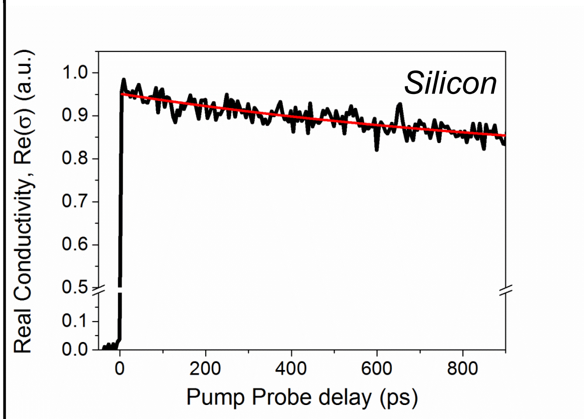
Carrier dynamics: interrogating the fate of electrons

Absorption vs time after excitation ~ $Re[\sigma](t) = e \cdot N(t) \cdot \mu$

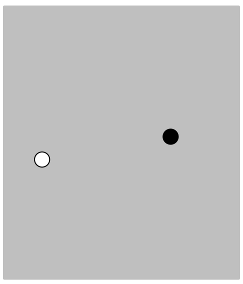


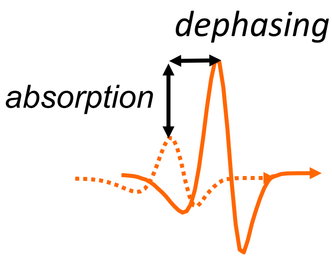
$N(t) = N_{h\nu} \cdot \exp(-k \cdot t)$

$N_{h\nu}$ ~ number photons

k ~ rate constant

THz time domain spectroscopy THz-TDS

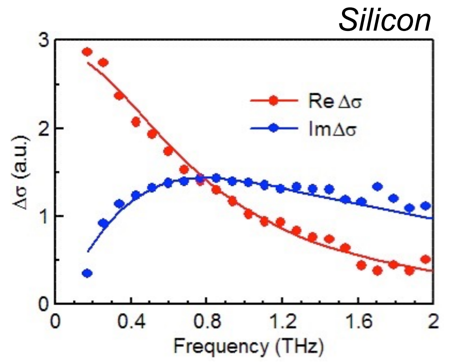


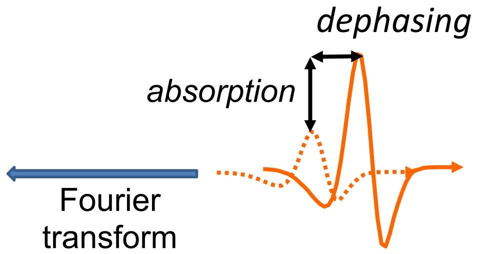


Absorption ~ $Re(\sigma) = e \cdot N \cdot \mu$

Dephasing ~ $Im(\sigma)$

Interrogating the nature of charge carriers





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!

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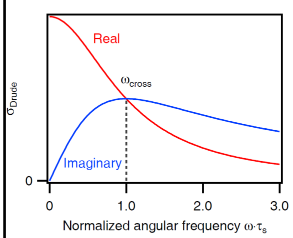
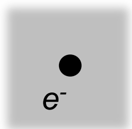
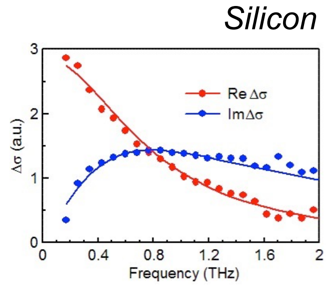
Conductivity for free carriers (the Drude Model)

Drude Model



free carriers





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

Scattering time, τ → $\mu(\omega)$

Plasma frequency ω_p^2 → N

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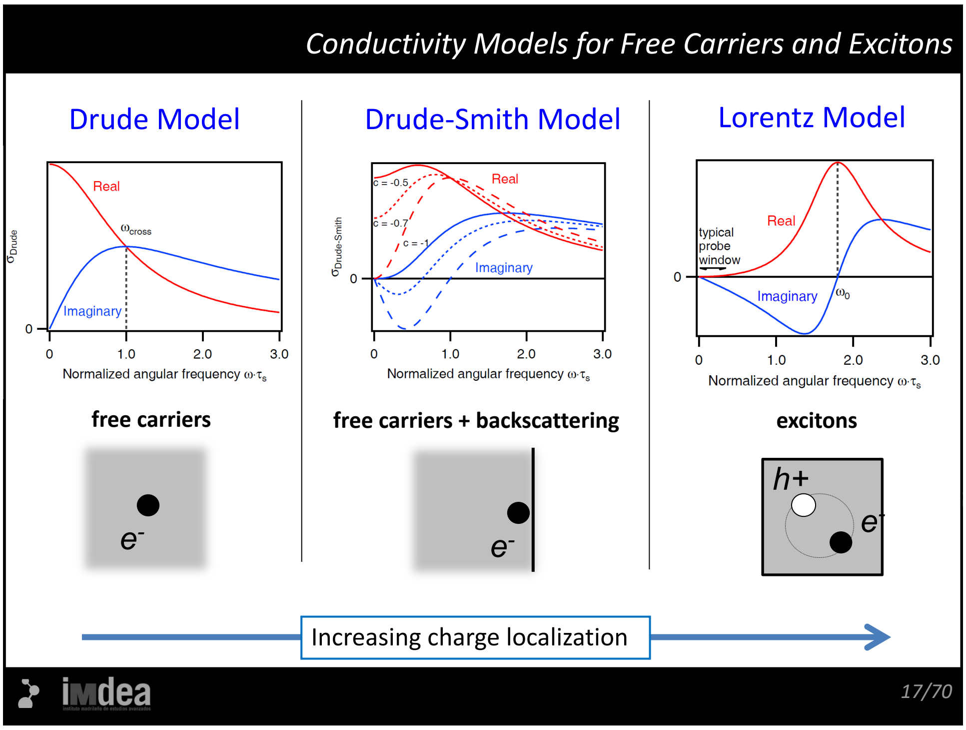
Conductivity Models for Free Carriers and Excitons
Drude Model
Drude-Smith Model
Lorentz Model
Real
Imaginary
ωcross
c = -0.5
c = -0.7
c = -1
typical probe window
ω0
Normalized angular frequency ω·τs
free carriers
free carriers + backscattering
excitons
e-
h+
Increasing charge localization
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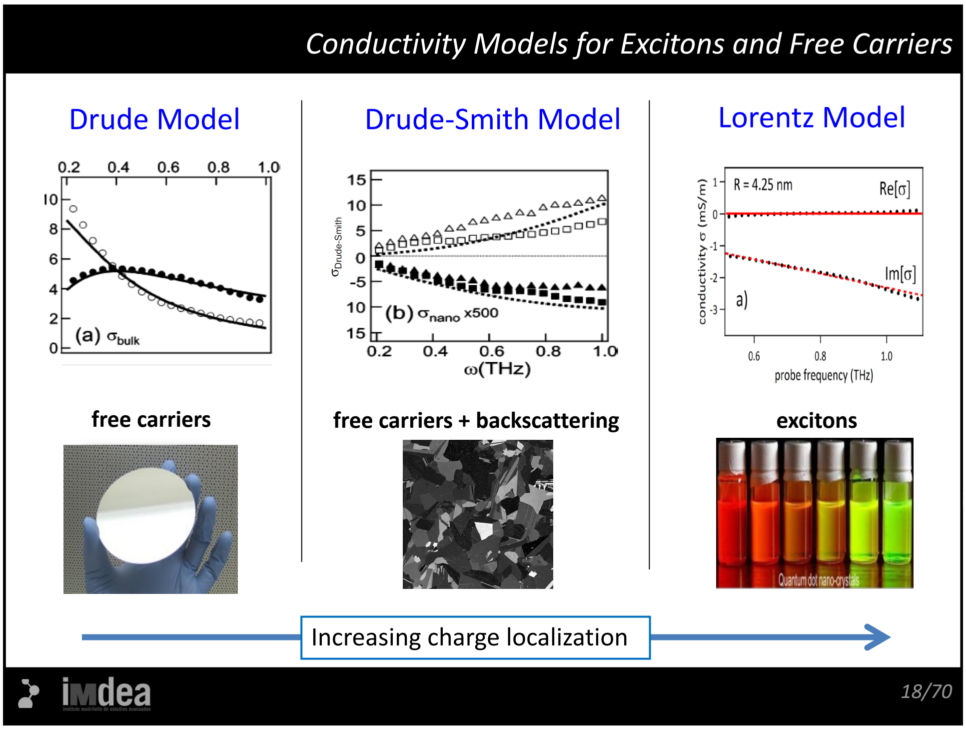
Conductivity Models for Excitons and Free Carriers
Drude Model
Drude-Smith Model
Lorentz Model
(a) σbulk
(b) σnano x500
ω(THz)
R = 4.25 nm
Re[σ]
Im[σ]
a)
conductivity σ (mS/m)
probe frequency (THz)
free carriers
free carriers + backscattering
excitons
Quantum dot nano-crystals
Increasing charge localization
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Message to take home

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

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

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

$N(t)=N_{h\nu} \cdot \exp(-k \cdot t)$ where 1/k 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

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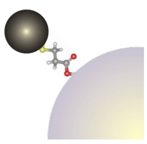
Summary of my talk

time-resolved terahertz spectroscopy



Electron transfer at quantum dot-bridge-metal oxide interfaces

Charge transport in metal organic frameworks

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Electron transfer at Quantum Dot-bridge-Metal Oxide Interfaces

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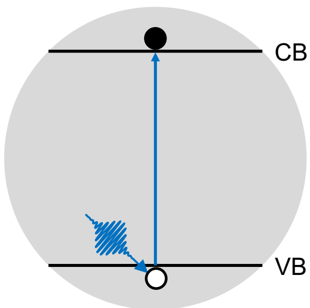
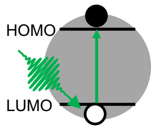
Why the QD-bridge-oxide system?



Metal oxides are good photocatalyst but poor light absorbers

Why the QD-bridge-oxide system?



Quantum dots are tunable strong absorbers

QD size

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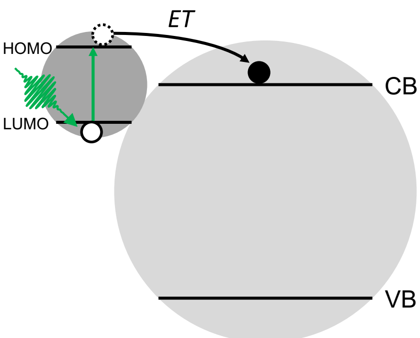
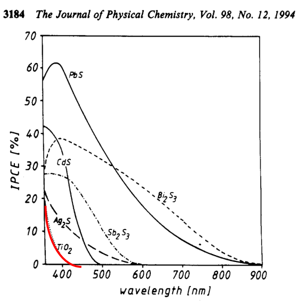
Why the QD-bridge-oxide system?



Sensitization with QDs bypass poor oxide light absorption…



…if electron transfer is efficient!

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Optical Pump-THz Probe

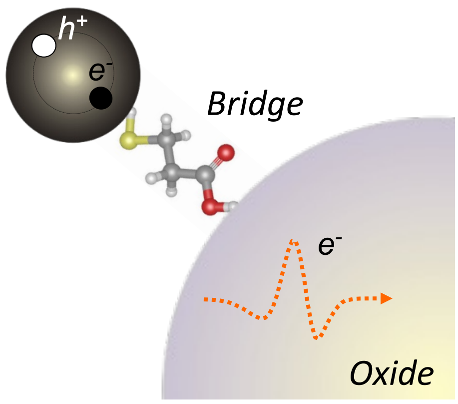
Optical pump-THz probe:

Quantify photoconductivity with ps time-resolution

Contact free technique

Optical Pump-THz Probe

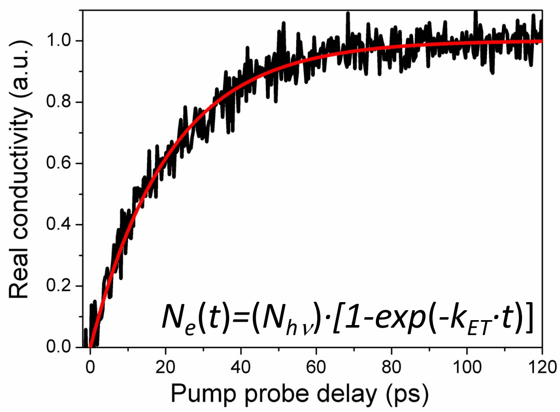
Quantum Dot



$Re[\sigma] \sim N_e$

The THz probe is only sensitive to free carriers!

Optical Pump-THz Probe



Electron transfer rates and efficiencies can be resolved unambiguously!

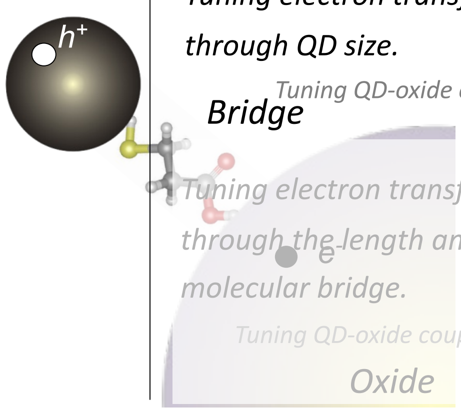
Photoinduced electron transfer in QD-bridge-oxide systems

Quantum Dot

Tuning electron transfer rates through QD size.

Tuning QD-oxide energetics

Bridge

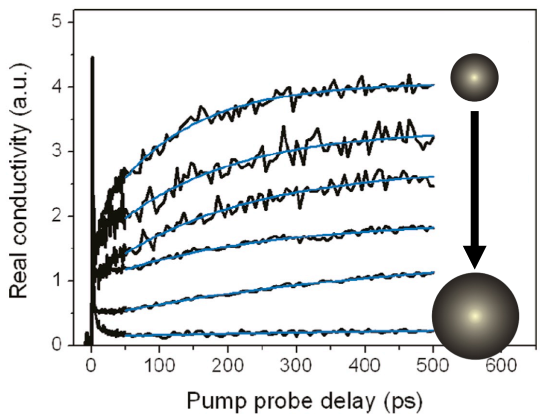


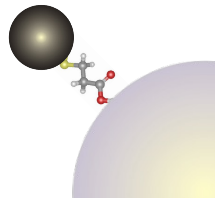
Tuning electron transfer rates through the length and nature of molecular bridge.

Tuning QD-oxide coupling strength

Oxide

Tuning donor-acceptor energetics by QD size

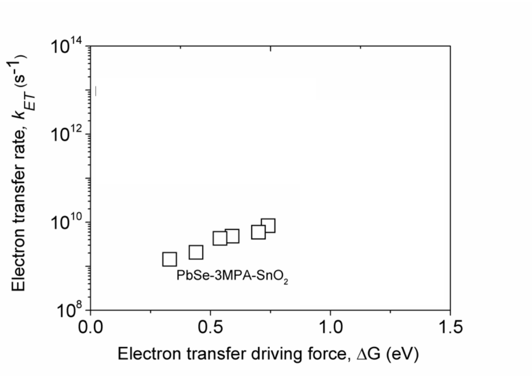


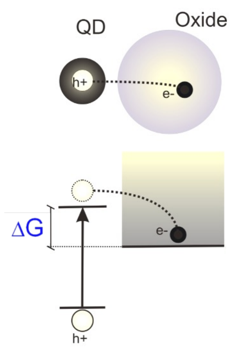


Nano Lett. 11(12), 5234 (2011).

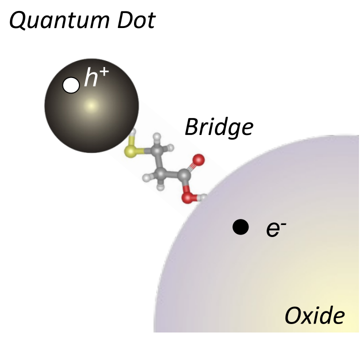
Tuning donor-acceptor energetics by QD size

ET rate is faster for bigger donor-acceptor energy difference (ΔG)





Nano Lett. 11(12), 5234 (2011).



Tuning electron transfer rates through QD size.

Tuning QD-oxide energetics

Tuning electron transfer rates through the length and nature of molecular bridge.

Tuning QD-oxide coupling strength

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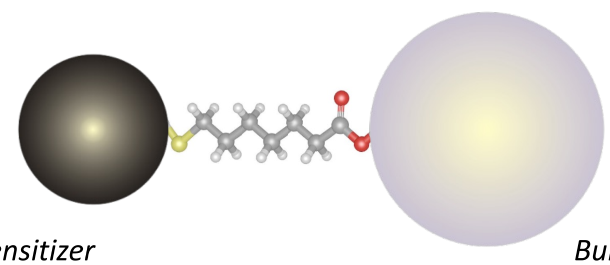
Tuning donor-acceptor coupling strength

Tuning molecular bridge length

HS-$[CH_2]_n$-COOH



QD sensitizer (donor)

Bulk oxide (acceptor)

Nano Lett., 13 (11), 5311 (2013).

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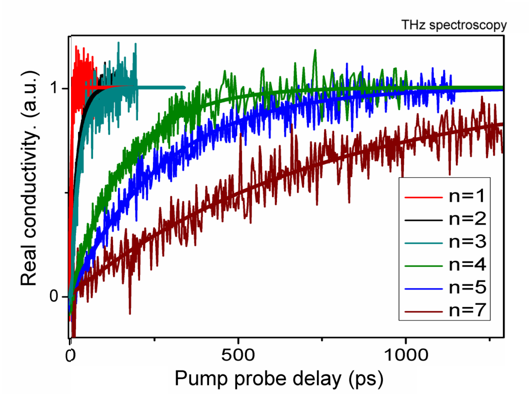
Tuning donor-acceptor coupling strength

Tuning molecular bridge length

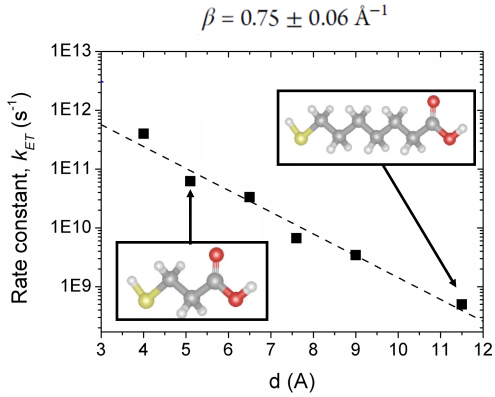
HS-[CH_2]$_n$-COOH

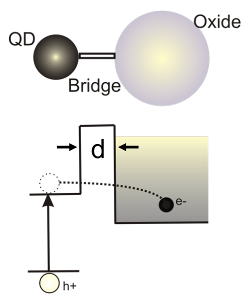


Nano Lett., 13 (11), 5311 (2013).

Tuning donor-acceptor coupling strength

$\beta = 0.75 \pm 0.06$ Å^{-1}



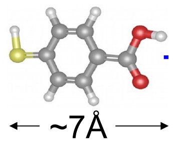


$$k_{ET}(d) = k_{ET}(0)\ \exp[-\beta d]$$

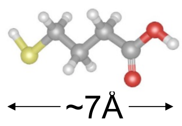
Nano Lett., 13 (11), 5311 (2013).

Tuning donor-acceptor coupling strength

Aromatic



vs. aliphatic



Nano Lett., 13 (11), 5311 (2013).

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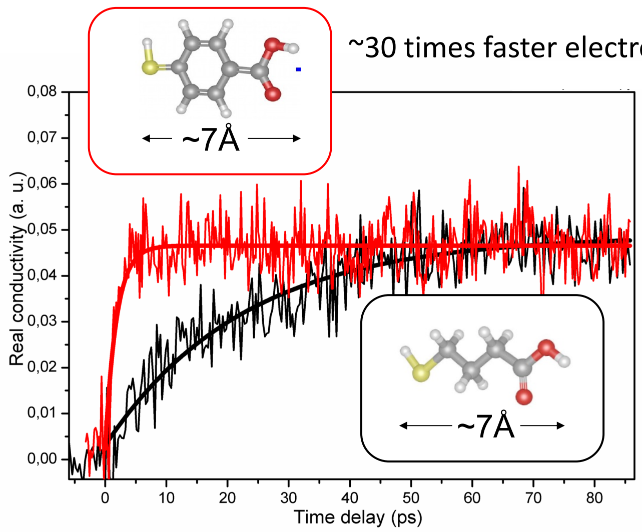
Tuning donor-acceptor coupling strength

~30 times faster electron transfer!



Nano Lett., 13 (11), 5311 (2013).

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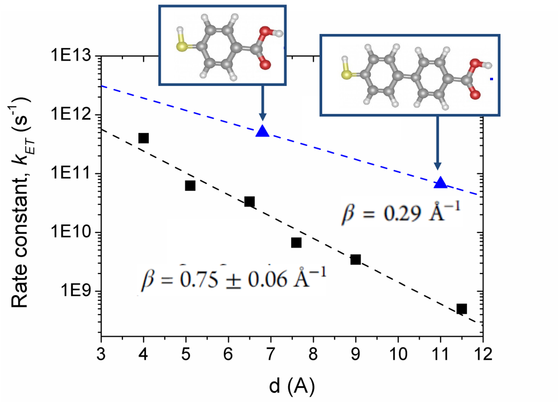
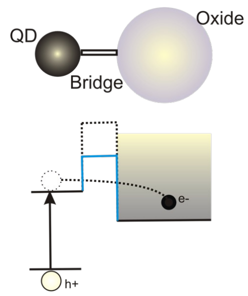
Tuning donor-acceptor coupling strength

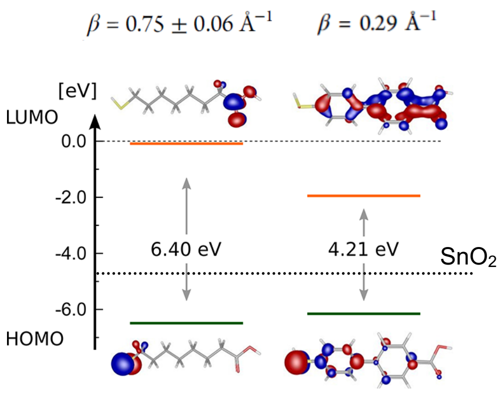




$$k_{ET}(d) = k_{ET}(0)\ \exp[-\beta d]$$

Nano Lett., 13 (11), 5311 (2013).

Tuning donor-acceptor coupling strength



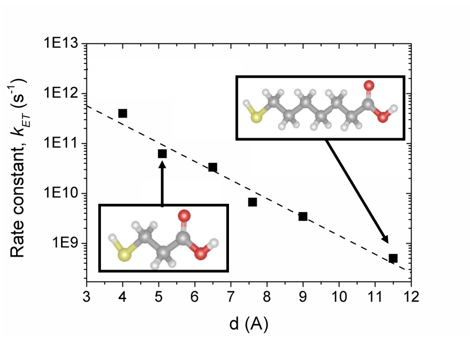
$$k_{et} = k_{tunn} = k_0 \exp(-\beta d_{DA})$$

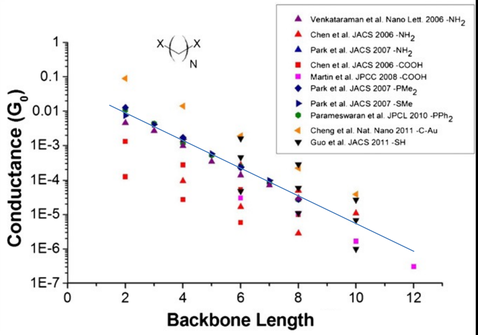
$$\beta = -(2/a)\ln(H_{BB}/\Delta E_{DB})$$

Analogy to STM single molecular conductance measurements

Nano Lett., 13 (11), 5311 (2013).

K_{ET} correlation with STM single molecular conductance





Nano Lett., 13 (11), 5311 (2013).

Semicond. Sci. Technol. **29** (2014) 054007

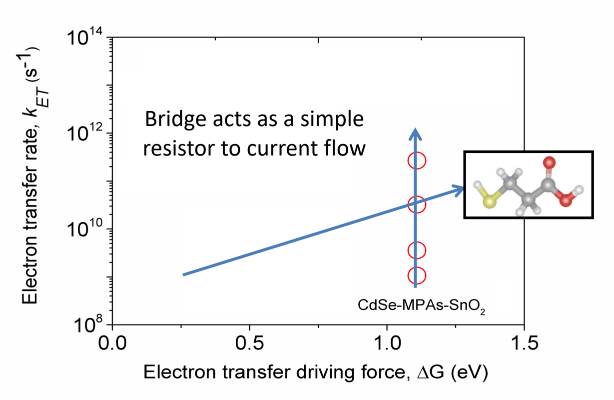
$K_{D\rightarrow A}(d)=K_{D\rightarrow A}(0)\ exp(-\beta\ d)$

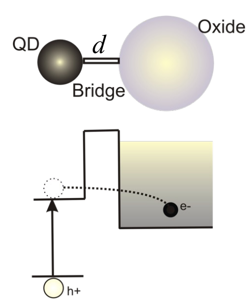
$\beta = 0.75 \pm 0.06$ Å^{-1}

$g(d)=g(0)\ exp(-\beta\ d)$

$\beta = 0.75$ Å^{-1}

The tunneling nature of K_{ET}: Ohm's law





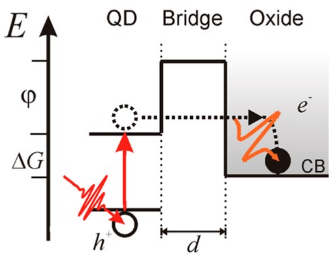
$$g \approx \frac{e^2}{\Gamma_D \Gamma_A F} k_{D\rightarrow A} \qquad G = \frac{I}{V} \qquad g(V) = 2e^2/h \sum_{ij} T_{ij}(E, V)$$

Science 300, 1387 (2011)

Electron transfer in QD-bridge-oxide systems /// Summary

Electron transfer in QD-bridge-oxides is mediated by tunneling.

The bridge acts as a simple resistor for current flow.



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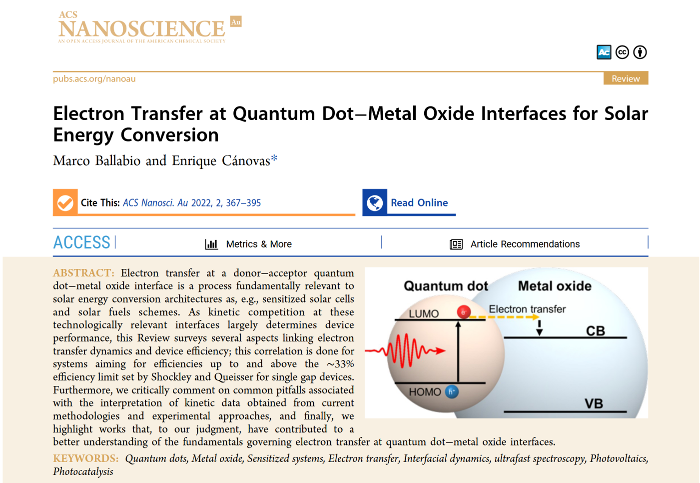
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Review

Electron Transfer at Quantum Dot−Metal Oxide Interfaces for Solar Energy Conversion

Marco Ballabio and Enrique Cánovas*

Cite This: ACS Nanosci. Au 2022, 2, 367−395

ABSTRACT: Electron transfer at a donor−acceptor quantum dot−metal oxide interface is a process fundamentally relevant to solar energy conversion architectures as, e.g., sensitized solar cells and solar fuels schemes. As kinetic competition at these technologically relevant interfaces largely determines device performance, this Review surveys several aspects linking electron transfer dynamics and device efficiency; this correlation is done for systems aiming for efficiencies up to and above the ~33% efficiency limit set by Shockley and Queisser for single gap devices. Furthermore, we critically comment on common pitfalls associated with the interpretation of kinetic data obtained from current methodologies and experimental approaches, and finally, we highlight works that, to our judgment, have contributed to a better understanding of the fundamentals governing electron transfer at quantum dot−metal oxide interfaces.

KEYWORDS: *Quantum dots, Metal oxide, Sensitized systems, Electron transfer, Interfacial dynamics, ultrafast spectroscopy, Photovoltaics, Photocatalysis*

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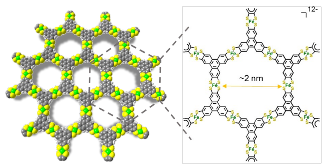
Summary of my talk

time-resolved terahertz spectroscopy

Electron transfer at quantum dot-bridge-metal oxide interfaces

Charge transport in metal organic frameworks



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

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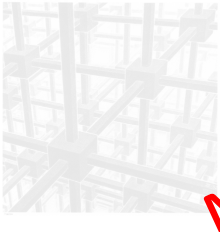
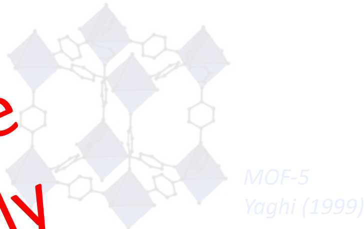
Metal Organic Frameworks (MOFs)





MOFs are generally insulating ☹!

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?,...)

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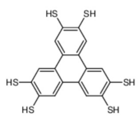
Development of Conductive Metal Organic Frameworks

Target: High Conductivity!
$\sigma = q \cdot N \cdot \mu$

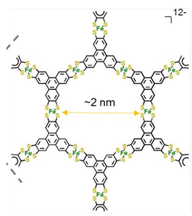
Enable high charge carrier densities via doping from metal ions (e.g. d^6 $Fe^{II/III}$) and/or organic ligands (e.g. radicals)

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) =



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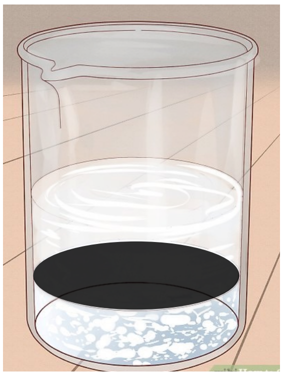
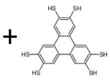
$Fe(III)_3(THT)_2(NH_4)_3$



Water + $Fe(acac)_2$

Chloroform + 

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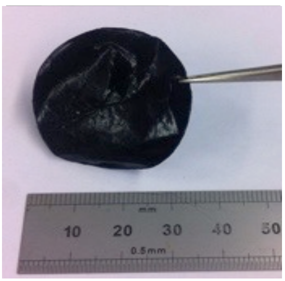
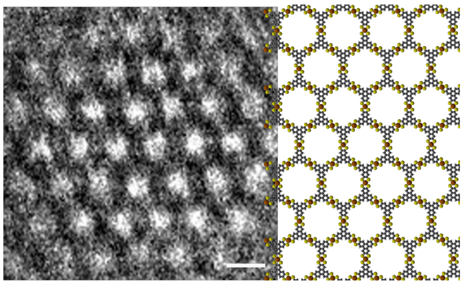
$Fe(III)_3(THT)_2(NH_4)_3$

Self-standing films





Crystalline with hexagonal structure
Surface area – 526m^2/g

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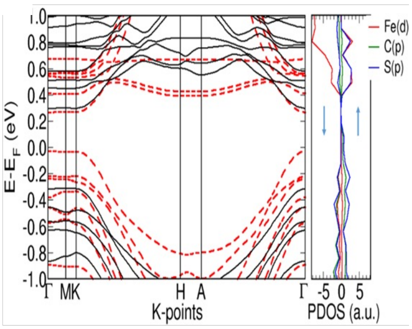
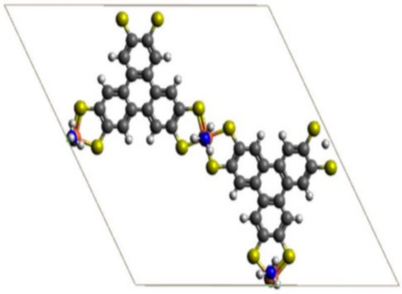
$Fe(III)_3(THT)_2(NH_4)_3$

Semiconducting





Strong hybridation between metal and organic building blocks

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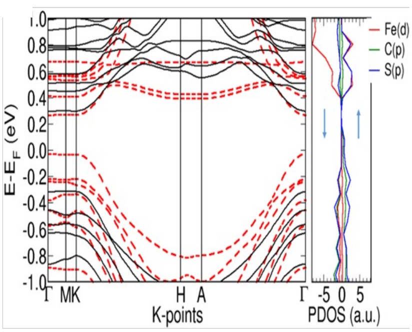
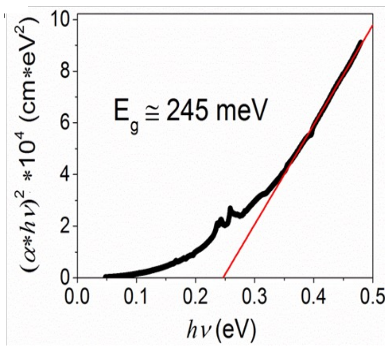
$Fe(III)_3(THT)_2(NH_4)_3$

Semiconducting





0.25eV direct bandgap

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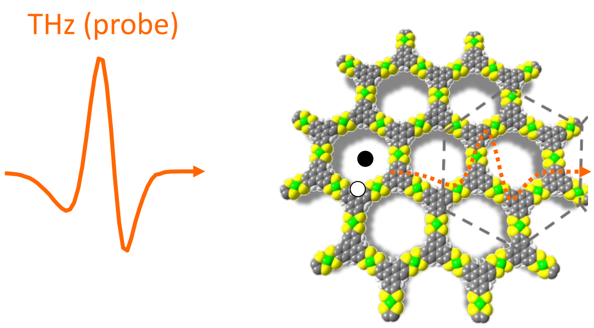
Time resolved THz spectroscopy

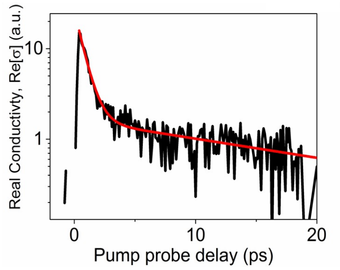
Time resolved THz spectroscopy

Quantify photoconductivity with ps time-resolution

Contact free technique

Time resolved THz spectroscopy





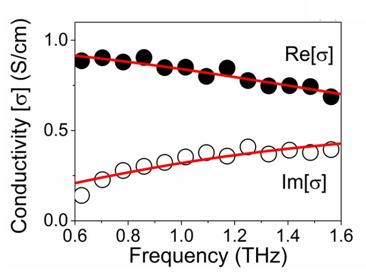
Fast photoconductivity relaxation

$Re[\sigma](t) = q \cdot N(t) \cdot \mu$

Drude response at the peak conductivity!

band-like transport in 2D MOFs!!!

μ=220cm^2/Vs



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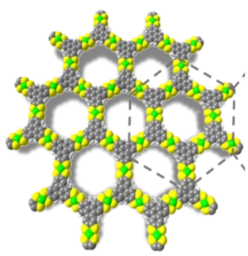
We resolve band like transport in semiconducting 2D $Fe_3(THT)_2$ MOF.



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

First identify scattering mechanisms limiting mobility, how?

Analyze the temperature dependence.

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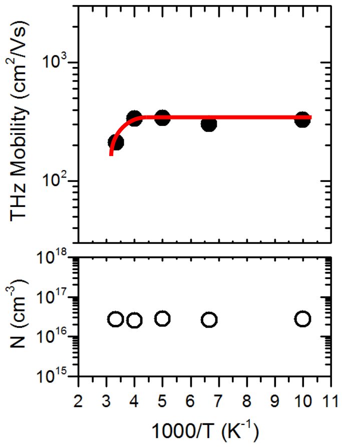
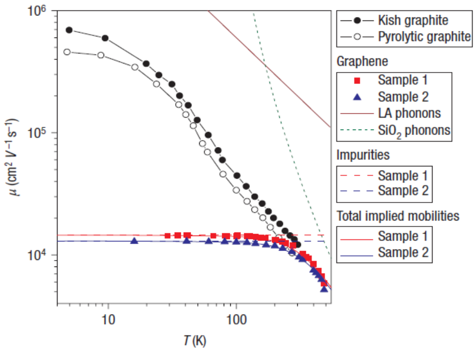
2D MOF

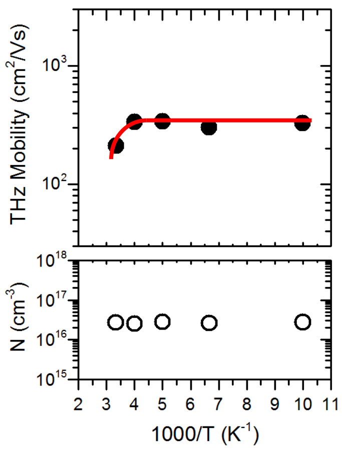


Graphene

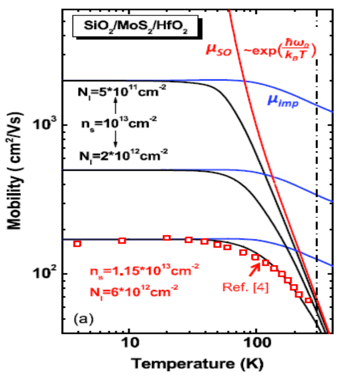


Nat. Nanotech. 3, 206 - 209 (2008)

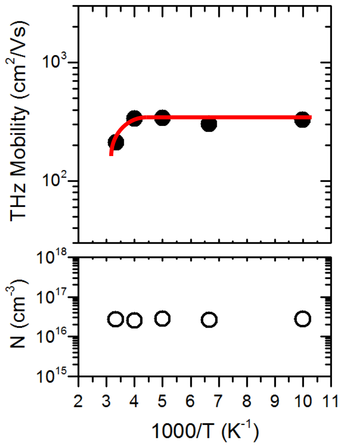
2D MOF



2D MoS_2



Phys. Rev. X 4, 011043 (2014)



300-250K – phonon scattering.

>250K impurity scattering (heavy doping).

Doping engineering could boost mobilities values.

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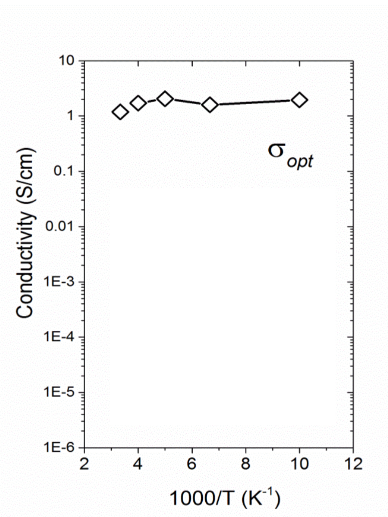
Comparing conductivities inferred optically and electrically

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



Optical σ probed locally (nm's)

Mobility constant with T.

Carrier density fixed by #photons.

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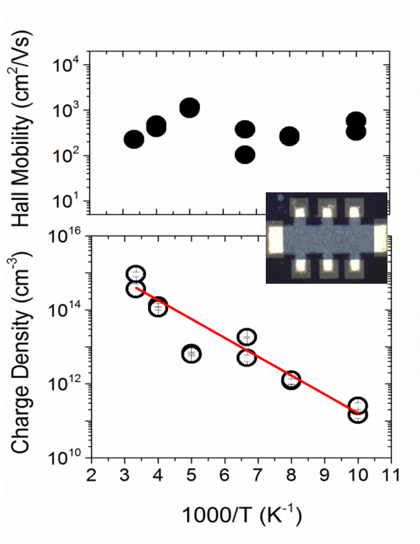
Hall Effect Measurements on 2D MOF

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



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Message to take home

- *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 220cm²/Vs. Further improvements in mobilities are possible via doping and phonon engineering.*

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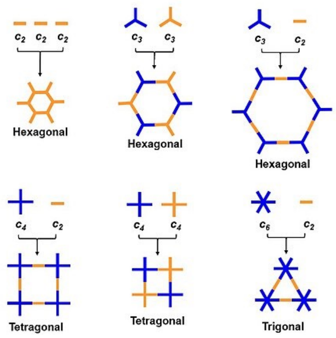
What about covalent organic frameworks?



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Record mobility in 2D COFs

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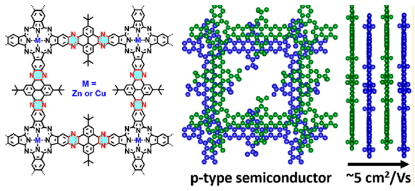
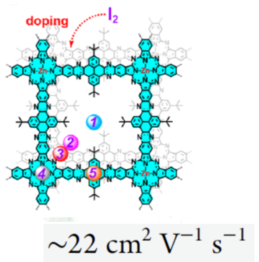
Cite This: J. Am. Chem. Soc. 2019, 141, 16810–16816 pubs.acs.org/JACS

Unveiling Electronic Properties in Metal–Phthalocyanine-Based Pyrazine-Linked Conjugated Two-Dimensional Covalent Organic Frameworks

Mingchao Wang,[†] Marco Ballabio,[‡] Mao Wang,[§] Hung-Hsuan Lin,[†] Bishnu P. Biswal,[†] Xiaocang Han,[⊥] Silvia Paasch,[†] Eike Brunner,[†] Pan Liu,[⊥] Mingwei Chen,[⊥,#] Mischa Bonn,[‡] Thomas Heine,[†,∥] Shengqiang Zhou,[§] Enrique Cánovas,[*,‡,%] Renhao Dong,[*,†] and Xinliang Feng[*,†]





JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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High-Mobility Semiconducting Two-Dimensional Conjugated Covalent Organic Frameworks with *p*-Type Doping

Mingchao Wang,[⊥] Mao Wang,[⊥] Hung-Hsuan Lin,[⊥] Marco Ballabio, Haixia Zhong, Mischa Bonn, Shengqiang Zhou, Thomas Heine, Enrique Cánovas,[*] Renhao Dong,[*] and Xinliang Feng[*]

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Article

Outstanding Charge Mobility by Band Transport in Two-Dimensional Semiconducting Covalent Organic Frameworks

Shuai Fu,# Enquan Jin,# Hiroki Hanayama, Wenhao Zheng, Heng Zhang, Lucia Di Virgilio, Matthew A. Addicoat, Markus Mezger, Akimitsu Narita, Mischa Bonn,* Klaus Müllen,* and Hai I. Wang*

Cite This: J. Am. Chem. Soc. 2022, 144, 7489–7496
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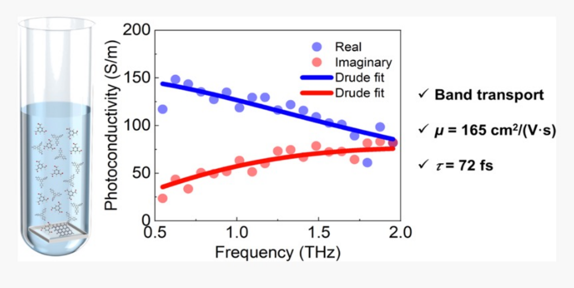

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highlight

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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[2]Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
[3]Faculty of Chemistry and Pharmacy, University of Sofia, 1164 Sofia, Bulgaria
[4]Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany
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[8]Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA Nanociencia), Faraday 9, 28049 Madrid, Spain.
[9]Key Laboratory of Colloid and Interface Chemistry of the Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, 250100 Jinan, China

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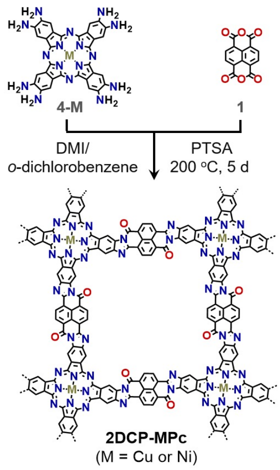
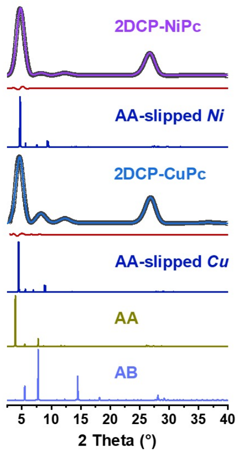
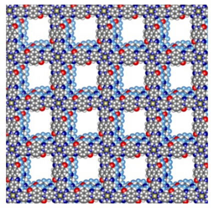
Phthalocyanine-based BBL-ladder-type 2DCP-MPcs







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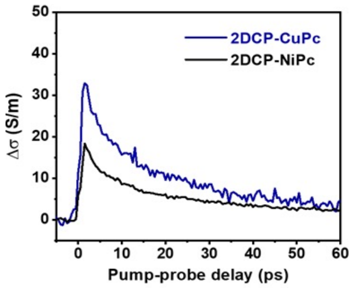

Fast photoconductivity relaxation

$$Re(\sigma) = q \cdot (n \cdot \mu)$$

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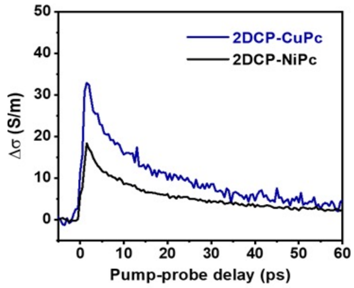
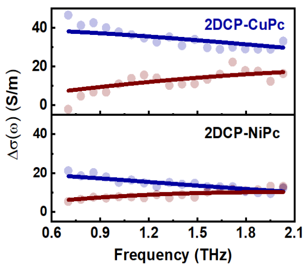


Fast photoconductivity relaxation

Re(σ) = q·(n·μ)

Drude responses at the peak conductivity!

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



μ = 460cm²/Vs

μ = 970 cm²/Vs

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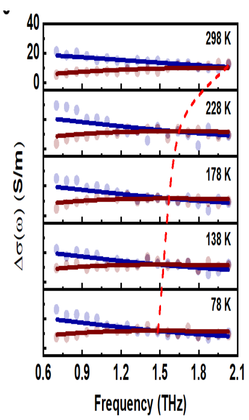

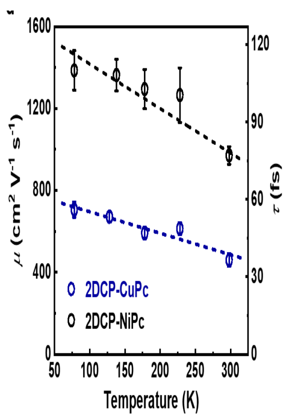

300-250K – phonon scattering.

>250K impurity scattering (heavy doping).

Doping engineering could boost mobilities values.

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Message to take home 2

- *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)*

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Concluding remarks

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.

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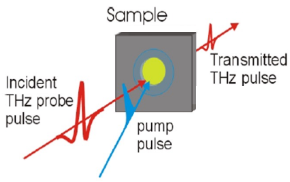
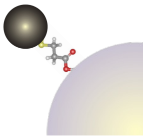
Thank you for your attention!

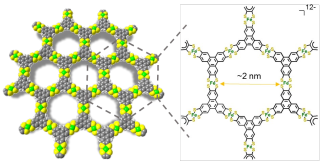
time-resolved terahertz spectroscopy





Electron transfer at quantum dot-bridge-metal oxide interfaces

Charge transport in metal organic frameworks



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