Optical Differential Reflectance Spectroscopy of Ultrathin Epitaxial Organic Films

Torsten Fritz and Roman Forker

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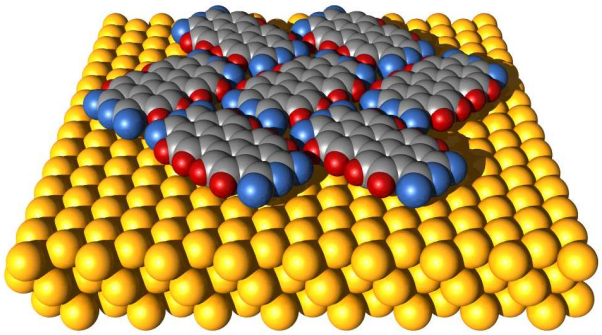

WS10-ETOLDs, Valencia

June 2, 2010

www. www.organics.uni-jena.de

Outline

1. Motivation
2. Differential Reflectance Spectroscopy (DRS)
3. Case I: From Single Molecule to Crystal
4. Case II: Function Follows Form
5. Case III: Charged Molecules on Metals
6. Summary

Motivation

Advantages of *in situ* optical spectroscopy on molecular films:

- **Organic molecules have large absorption coefficient: $\alpha \approx 10^7$ cm^{-1}**
  (cmp.: Si: $\alpha \approx 10^3$ cm^{-1})
- **Extremely sensitive, down to ~0.1 ML of aromatic molecules**

$\Rightarrow$ ***Substrate-film-interface can be probed***

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- **Optical properties depend sensitively on molecular arrangement:**

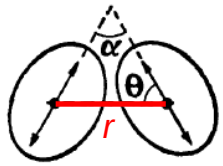
  - Lateral vs. vertical packing (anisotropy)

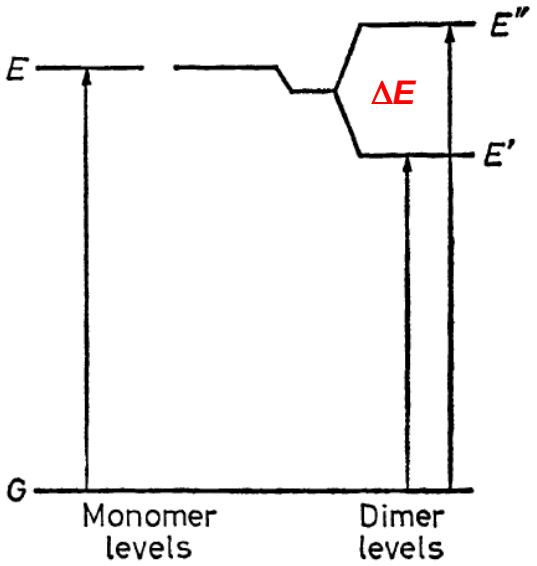
$$\Delta E = \frac{2|\vec{\mu}|^2}{r^3}\left(\cos(\alpha) - 3\cos^2(\vartheta)\right)$$

Δ*E* = exciton splitting energy

  - Effects of physical "chain length"
    (exciton delocalization and confinement)
  - Charge transfer (molecular ions)

⇒ ***Structural information can be deduced***





[M. Kasha et al., *Pure Appl. Chem.* 11, 371 (1965).]

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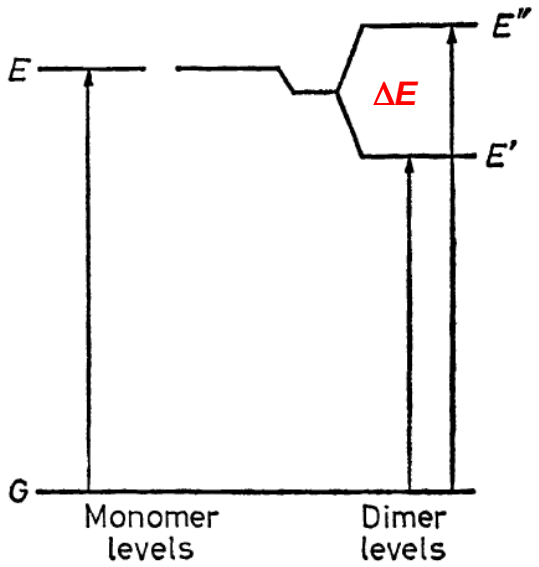

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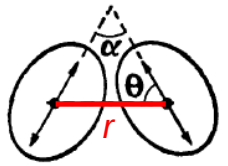


  ⇒ ***Structural information can be deduced***

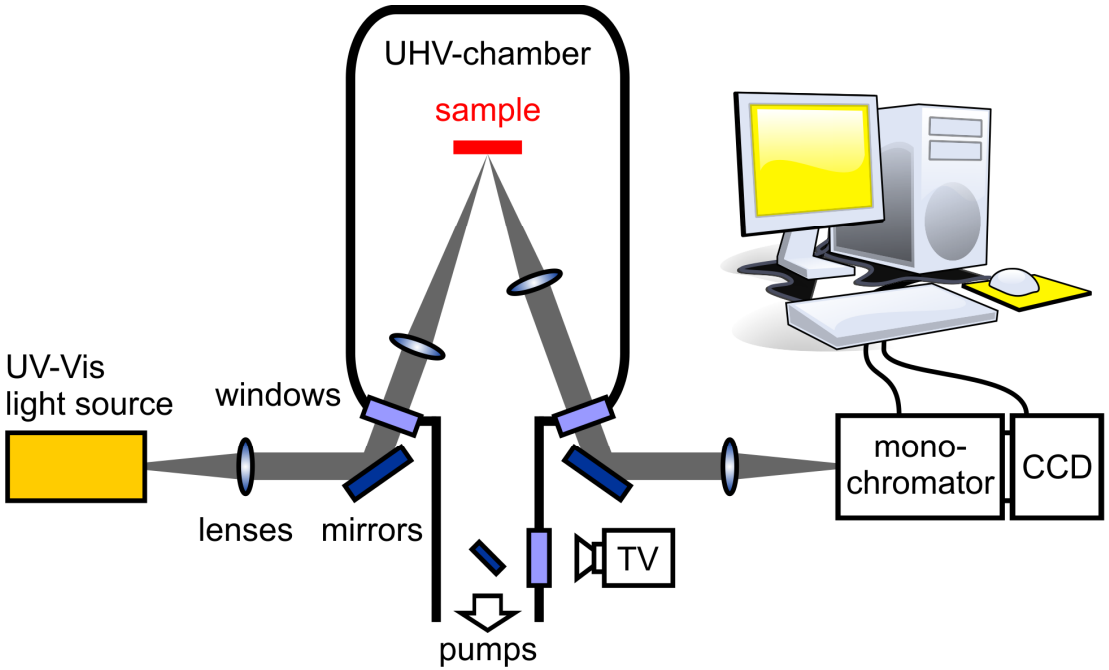
- **Non-destructive**

[M. Kasha et al., *Pure Appl. Chem.* 11, 371 (1965).]

Differential Reflectance Spectroscopy (DRS)

$$\mathrm{DRS}(E,d) = \frac{R(E,d) - R(E,0)}{R(E,0)}$$

***d* = film thickness (sub-ML to several MLs)**



Growth of molecular films:

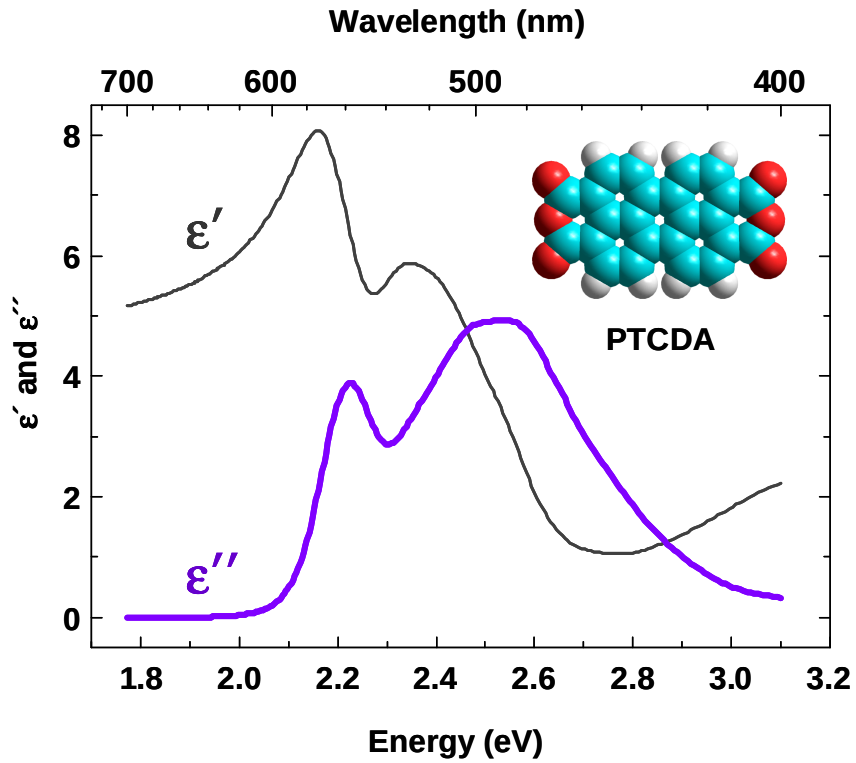
- Base pressure ≈ mid 10^{-10} mbar
- Deposition in UHV at ≈ 300 .. 500 ℃
- Rate: 0.1 .. 1 ML/min
- Substrates at room temperature

[H. Proehl et al., *Phys. Rev. B* 71, 165207 (2005).]
[R. Forker et al., *PCCP* 11, 2142 (2009).]

Differential Reflectance Spectroscopy (DRS)

Optical properties of molecules shall be described by energy-dependent dielectric function:

$$\hat{\varepsilon}_{film}(E) = \varepsilon'_{film}(E) - i \cdot \varepsilon''_{film}(E)$$



[A. B. Djurišić et al., *Opt. Commun.* 183, 123 (2000).]

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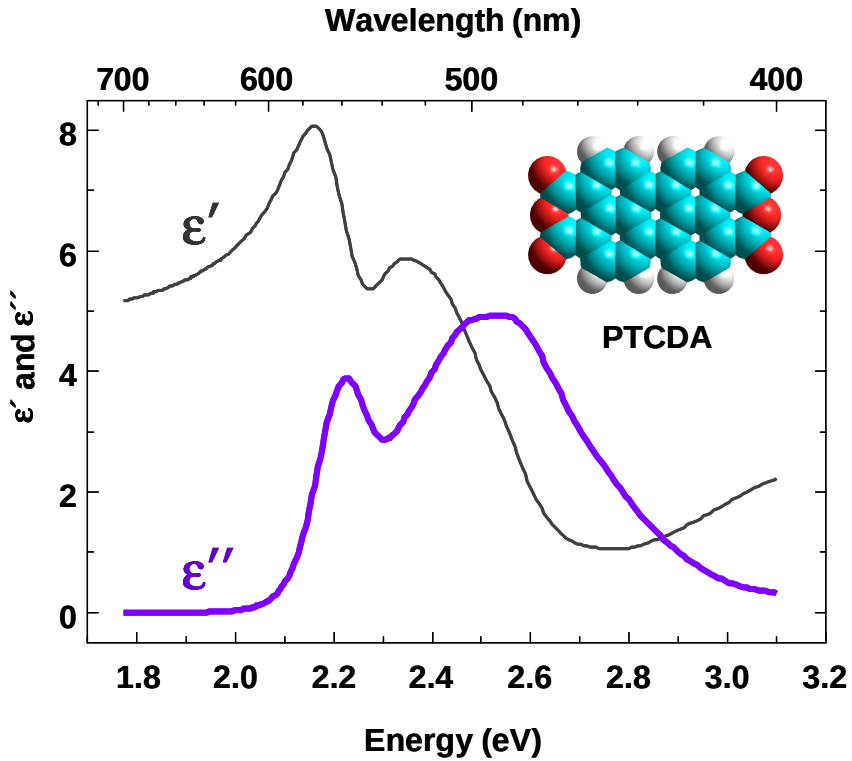

How are DRS and dielectric function related???

[A. B. Djurišić et al., *Opt. Commun.* 183, 123 (2000).]

Differential Reflectance Spectroscopy (DRS)

$$\mathrm{DRS}(E,d) = \frac{R(E,d) - R(E,0)}{R(E,0)}$$

McIntyre-approximation for ultrathin films ($d \ll \lambda$):

$$\mathrm{DRS} \approx -\frac{8\pi d}{\lambda} \cdot \left[A \cdot \varepsilon''_{film} + B \cdot \left(\varepsilon'_{film} - 1 \right) \right] \quad \Rightarrow \quad \varepsilon''_{film} \approx -\frac{\lambda}{8\pi d} \cdot \frac{\mathrm{DRS}}{A} - \frac{B}{A} \cdot \left(\varepsilon'_{film} - 1 \right)$$

- ***A*** and ***B*** depend solely on substrate's properties

[J.D.E. McIntyre et al., *Surf. Sci.* 24, 417 (1971).]

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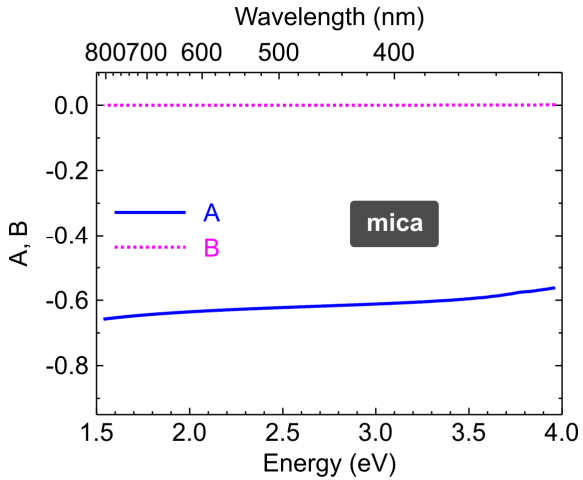
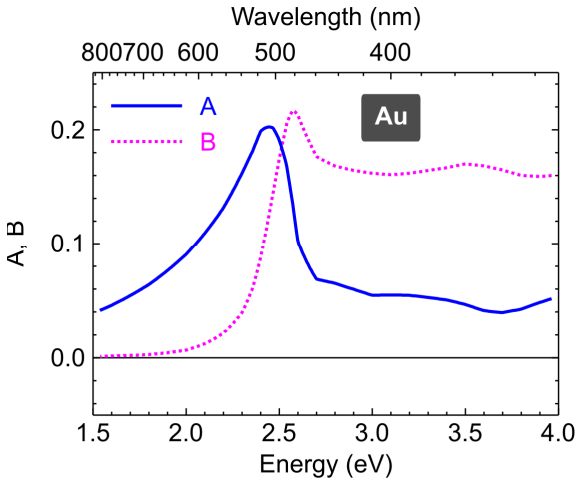
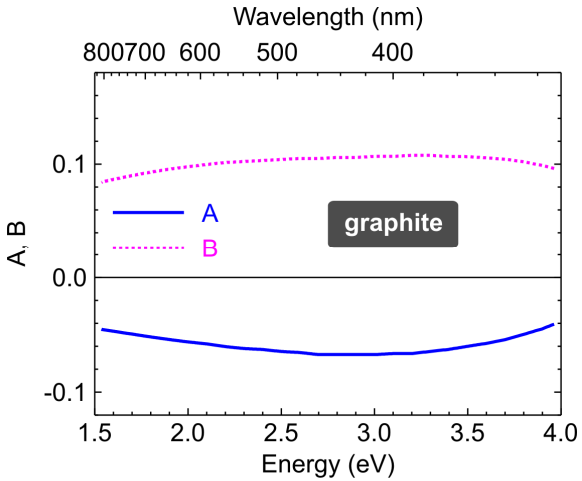


B ≈ 0
A ≠ 0



B ≈ 0 for low energies only
A ≠ 0



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- on **transparent substrates** and some metals (low *E*) : $B \approx 0$ → $\varepsilon''_{film} \approx -\frac{\lambda}{8\pi d} \cdot \frac{\mathrm{DRS}}{A}$

[R. Nitsche et al., *Phys. Rev. B* 70, 195432 (2004).]

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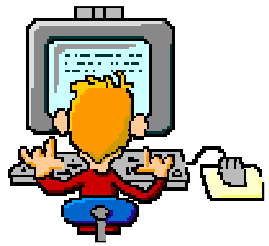
- on **non-transparent substrates**: numerical calculation required! → $\mathrm{DRS} \xrightarrow{\text{numerical extraction}} \varepsilon'_{film}$ *and* ε''_{film}

  - model-free Kramers-Kronig consistent algorithm
  - no approximations made in thin film equations
  - generally valid for all kinds of substrates



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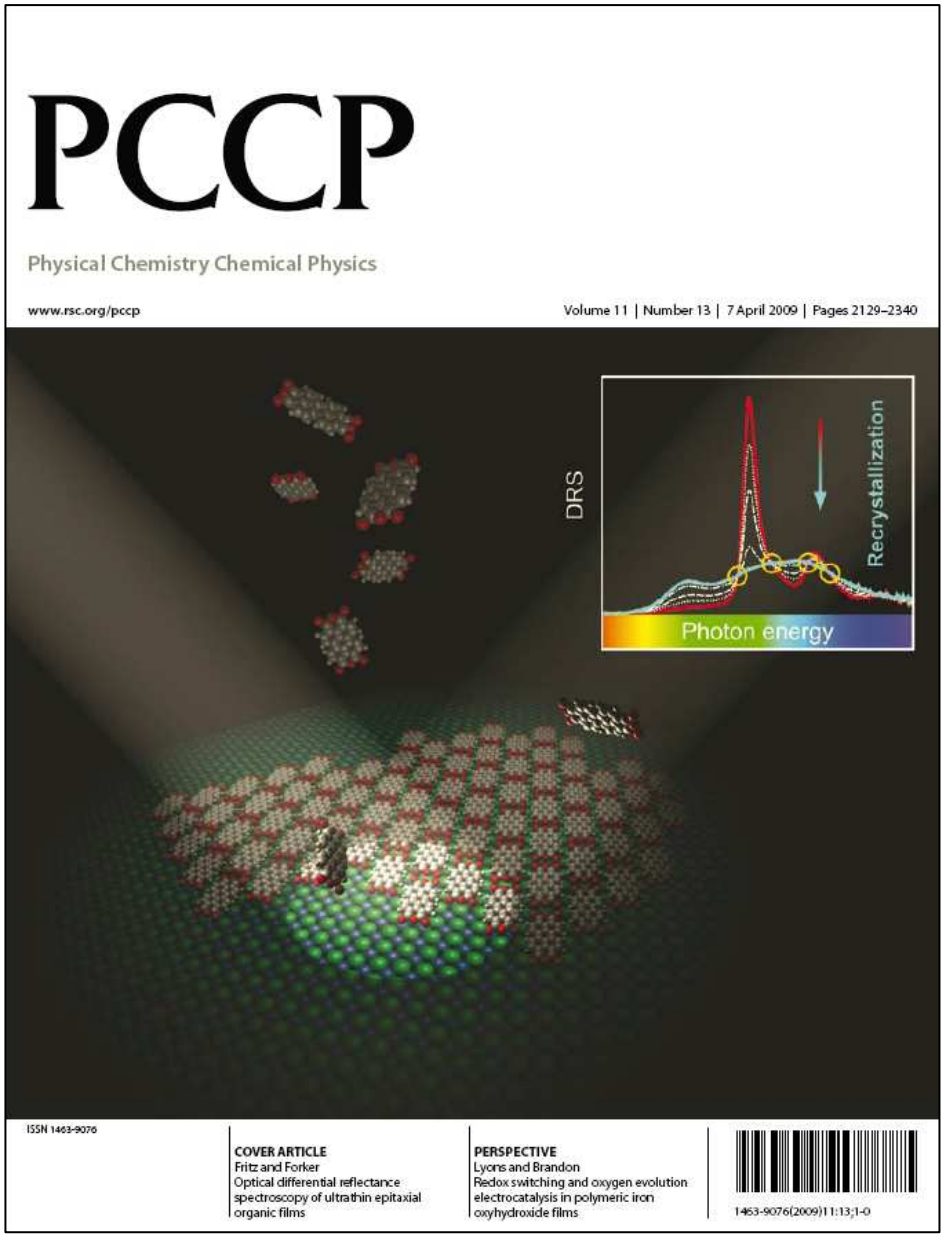
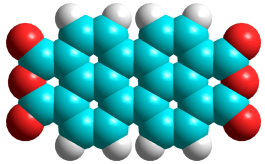


Further Details: Review-Article

Roman Forker und Torsten Fritz, *Phys. Chem. Chem. Phys.* 11, 2142–2155 (2009).

3. Case I: From Single Molecule to Crystal

PTCDA on Mica



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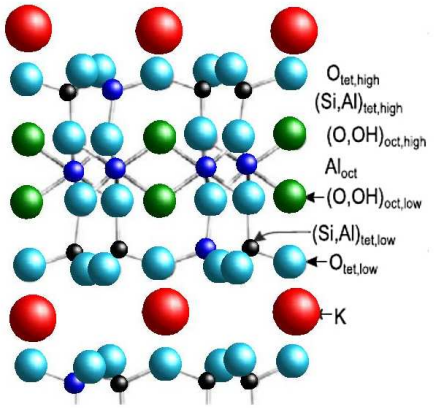
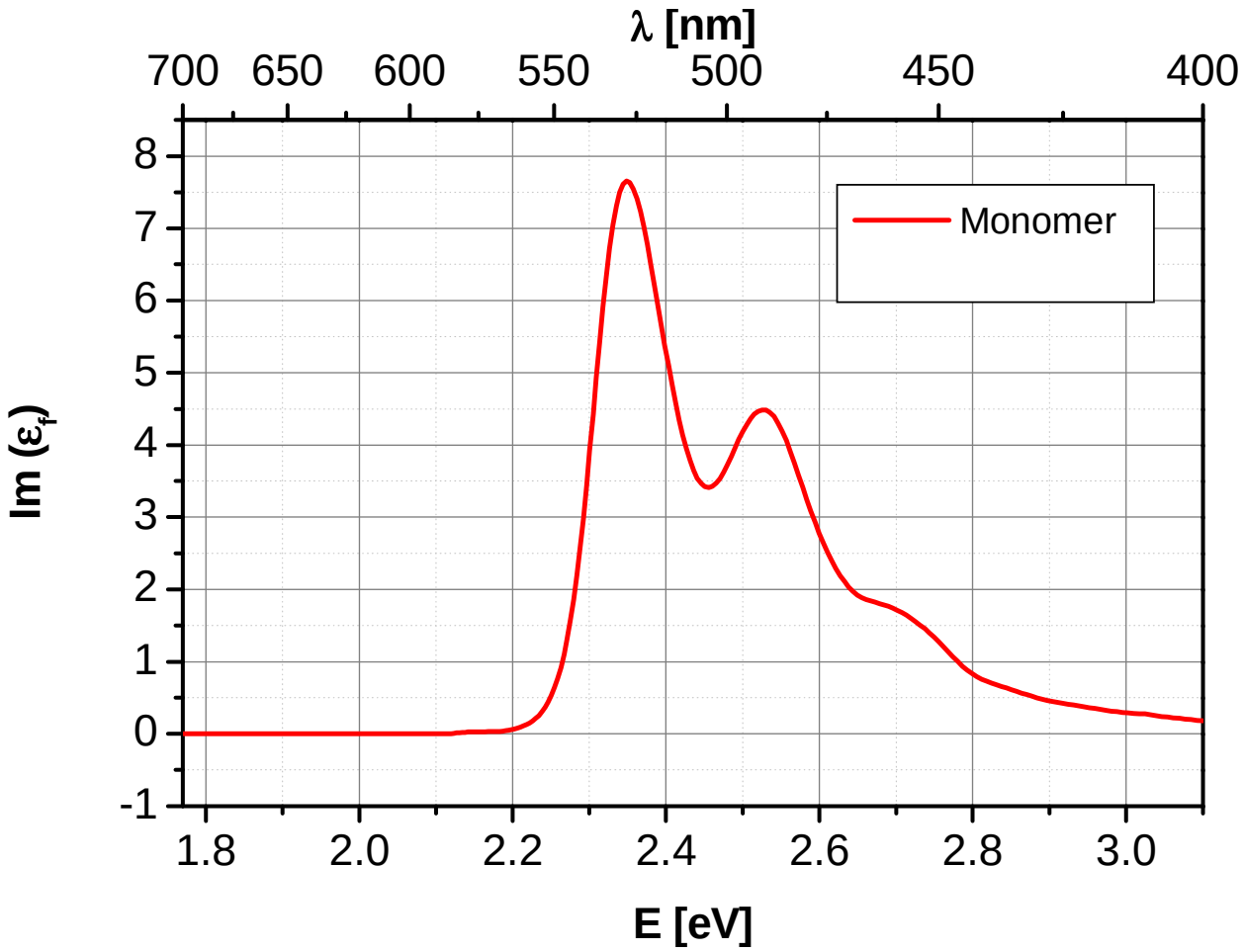


What is the Problem to be Solved?



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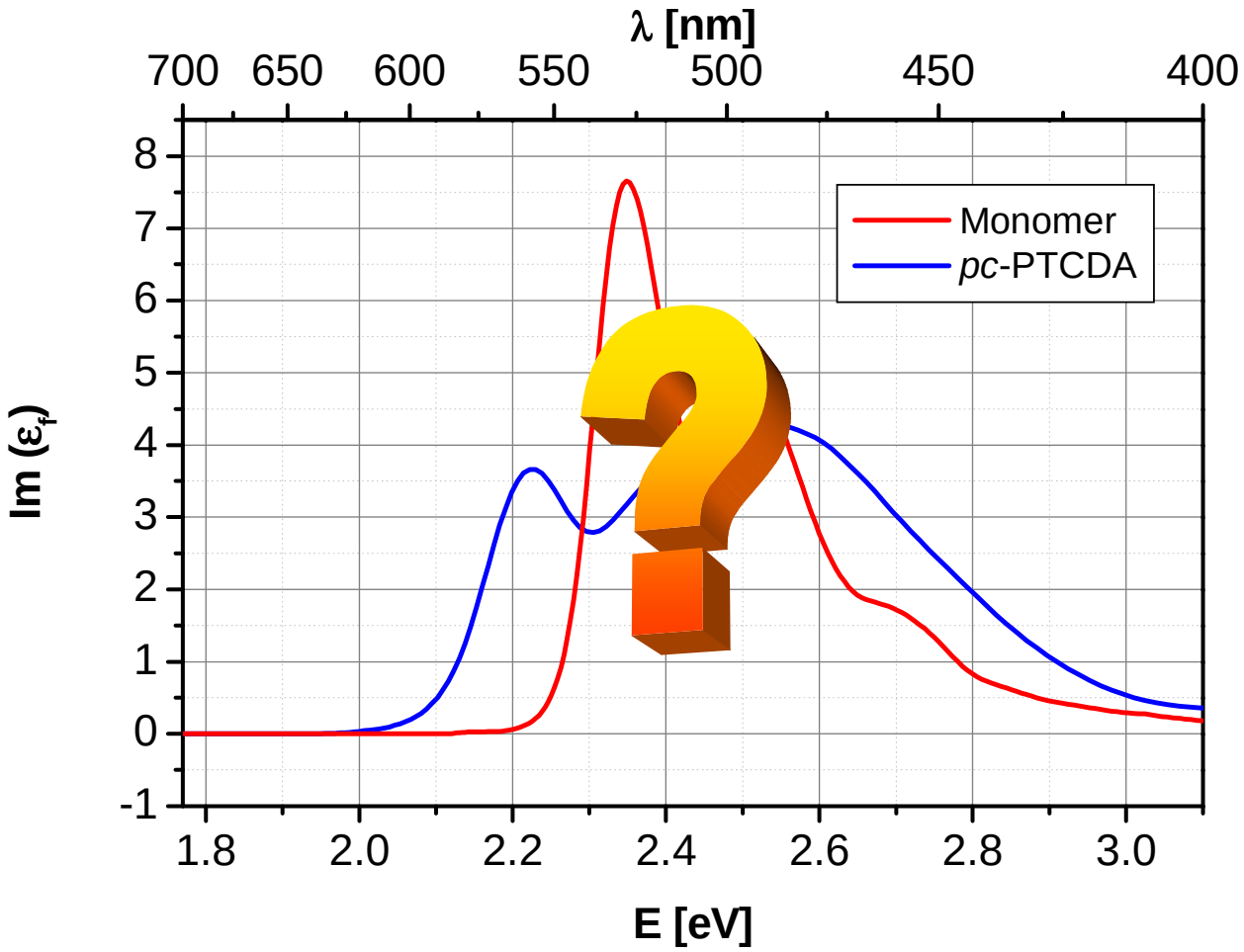
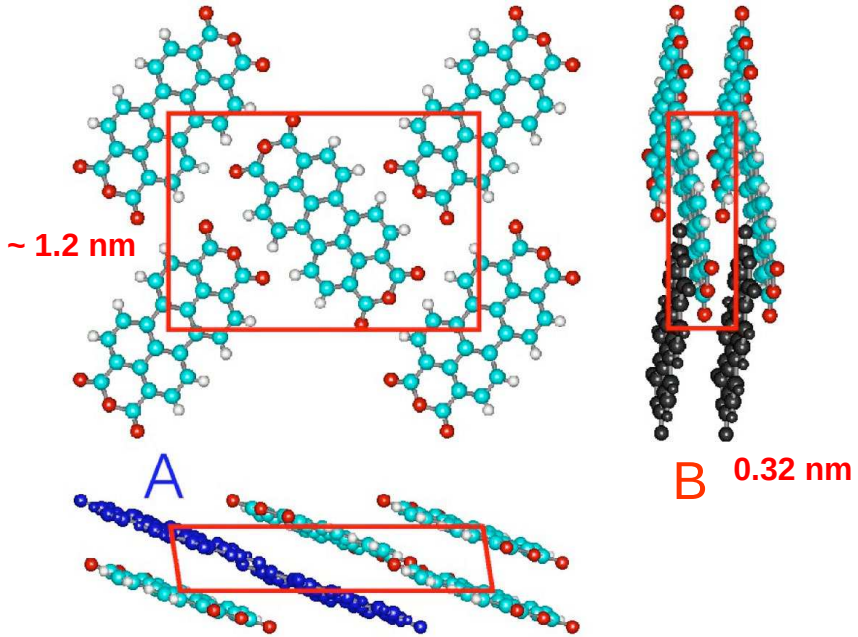


PTCDA is a quasi-1-dimensional Material

Why would one expect thickness depending properties?

Crystal Structure of PTCDA:



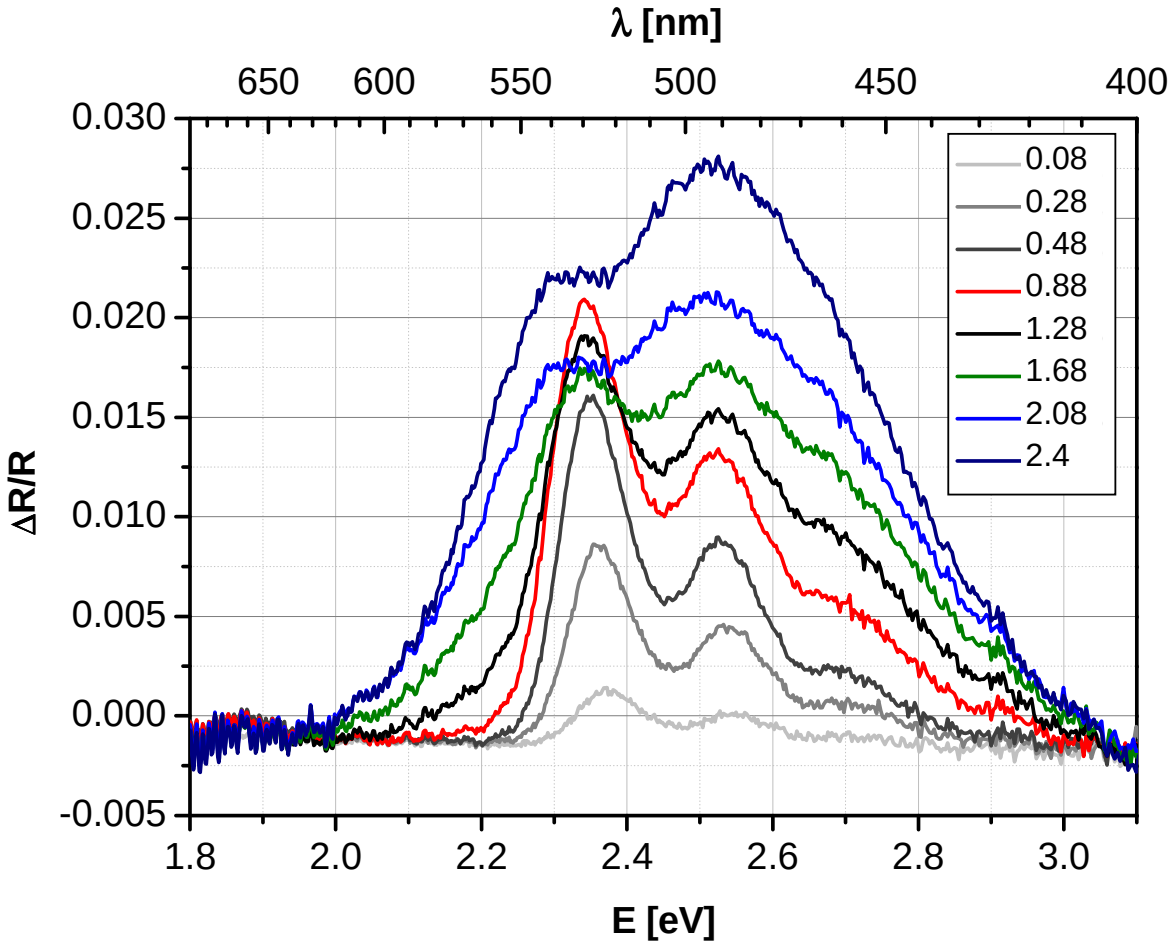
Two different dimers exist: A and B, but interaction in B very strong and in A very weak

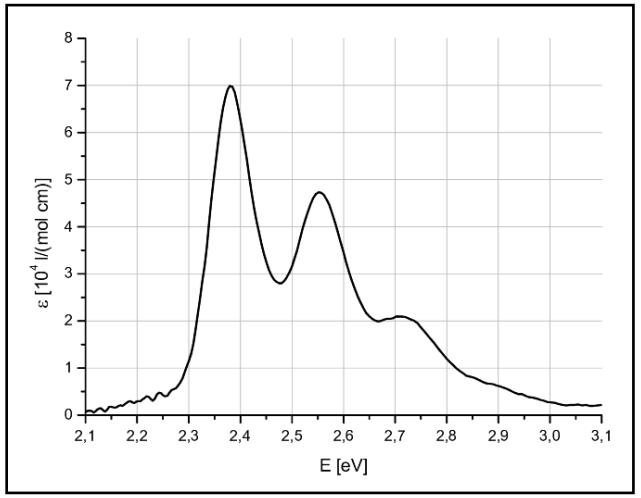
⇒ 3D-crystals behave like 1D-crystals, *and:*

⇒ Monomer should become visible for $d \rightarrow 1$ ML !

PTCDA on Mica

Monomer-Dimer-Transition





PTCDA in DMSO

[H. Pröhl, R. Nitsche, T. Dienel and TF, *PRL* 93, 097403 (2004).]

PTCDA on Mica

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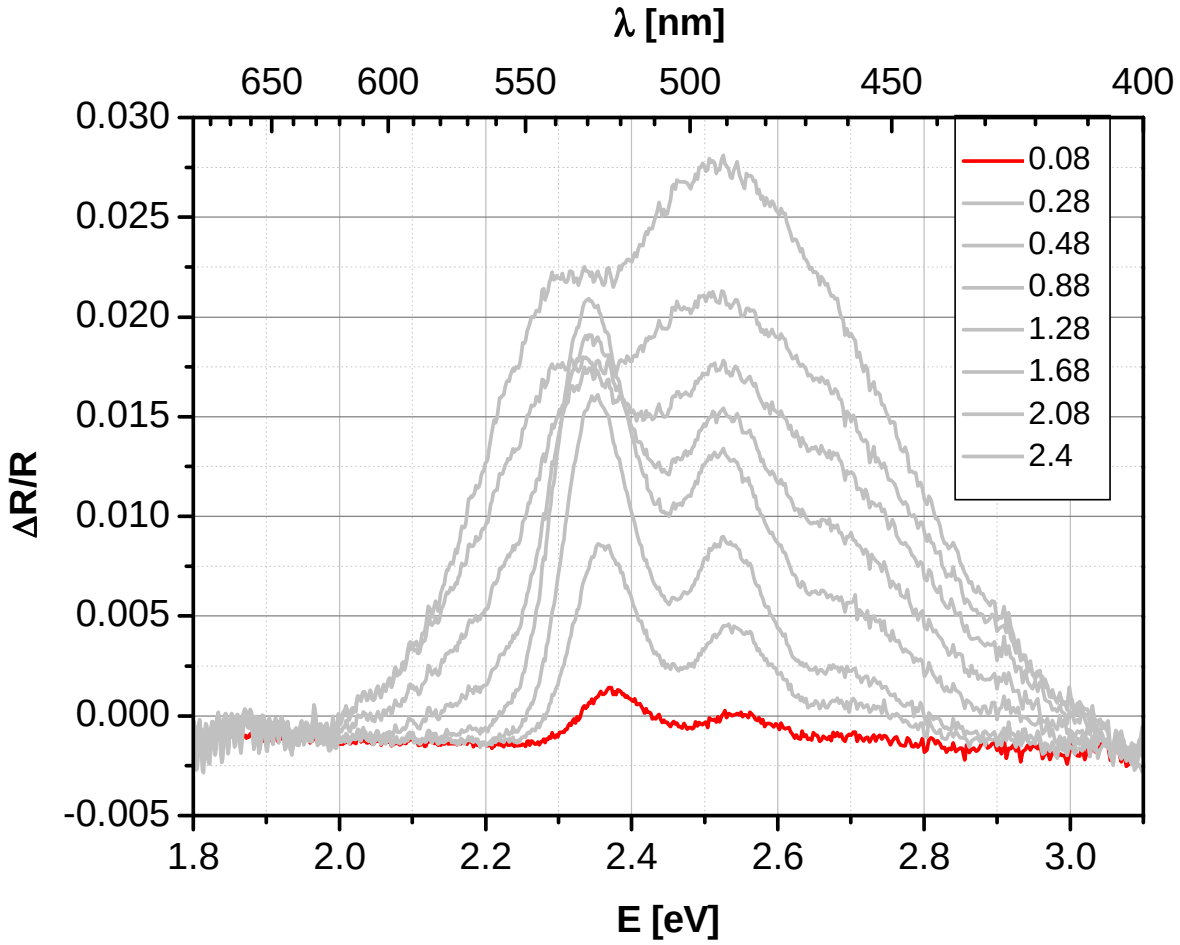

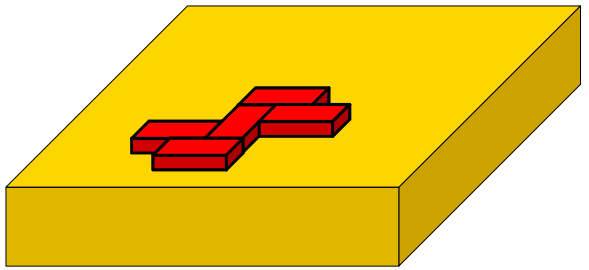

DRS = 0.1α(E)

[H. Pröhl, R. Nitsche, T. Dienel and TF, *PRL* 93, 097403 (2004).]

PTCDA on Mica

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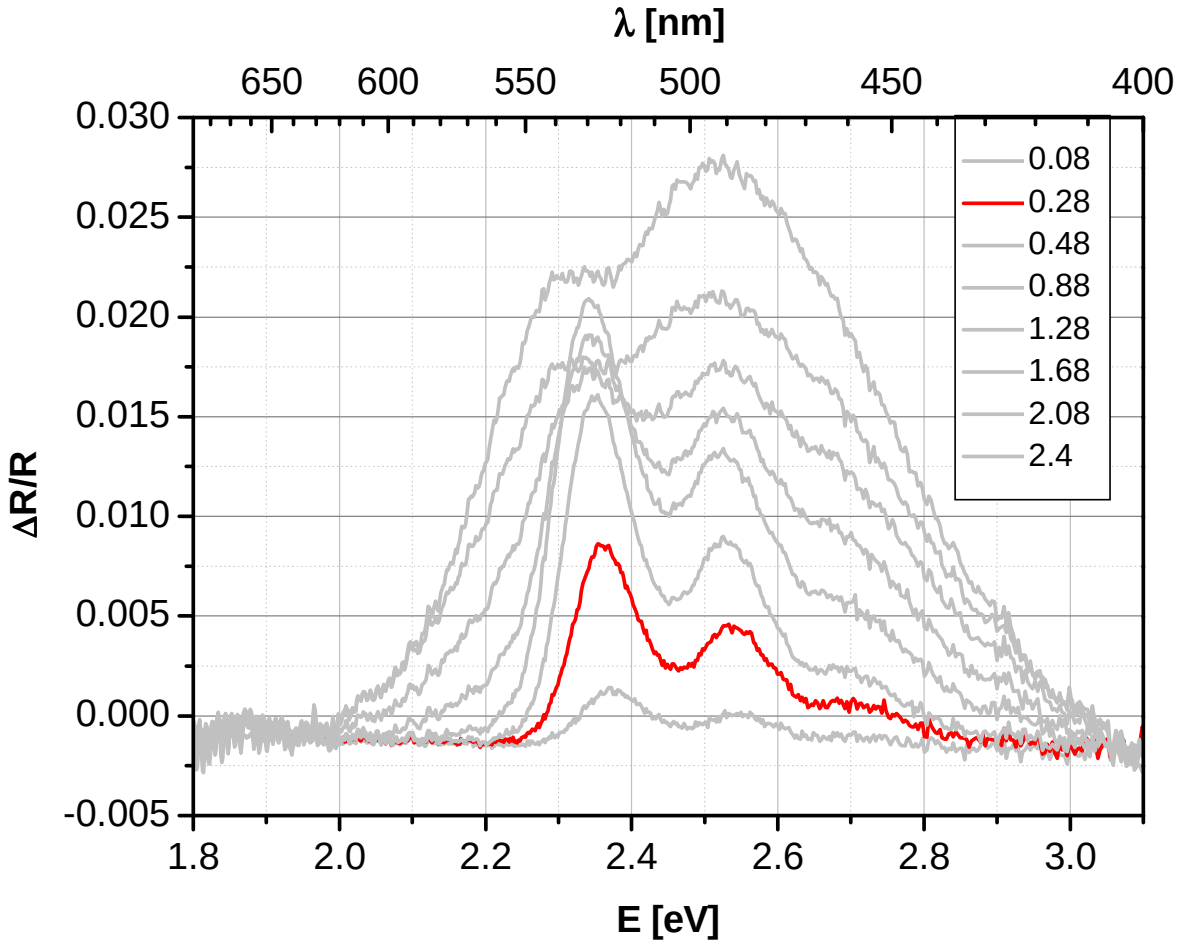

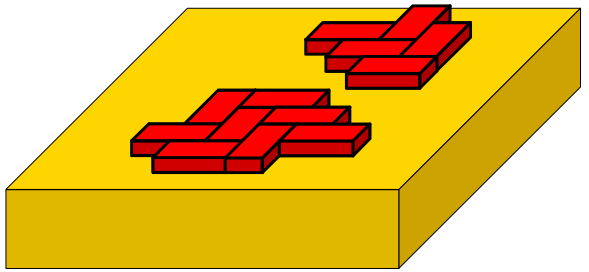

DRS = 0.3α(E)

[H. Pröhl, R. Nitsche, T. Dienel and TF, *PRL* 93, 097403 (2004).]

PTCDA on Mica

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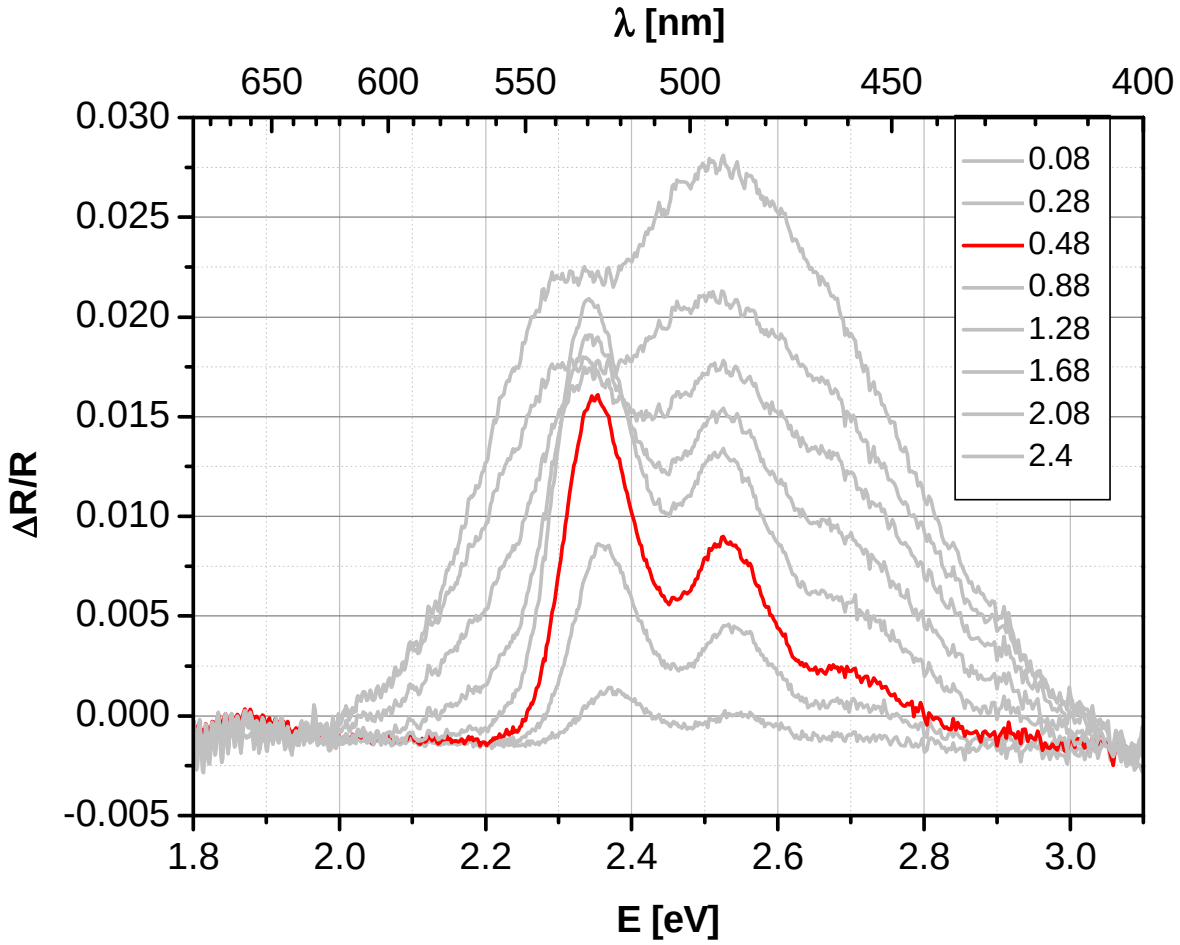

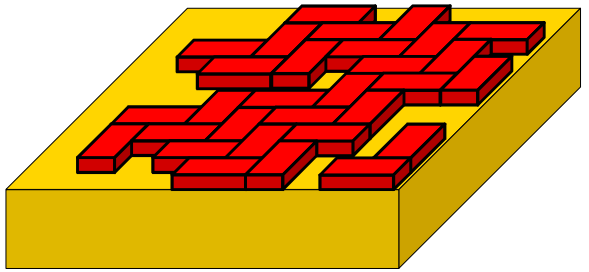

DRS = 0.5α(E)

[H. Pröhl, R. Nitsche, T. Dienel and TF, *PRL* 93, 097403 (2004).]

PTCDA on Mica

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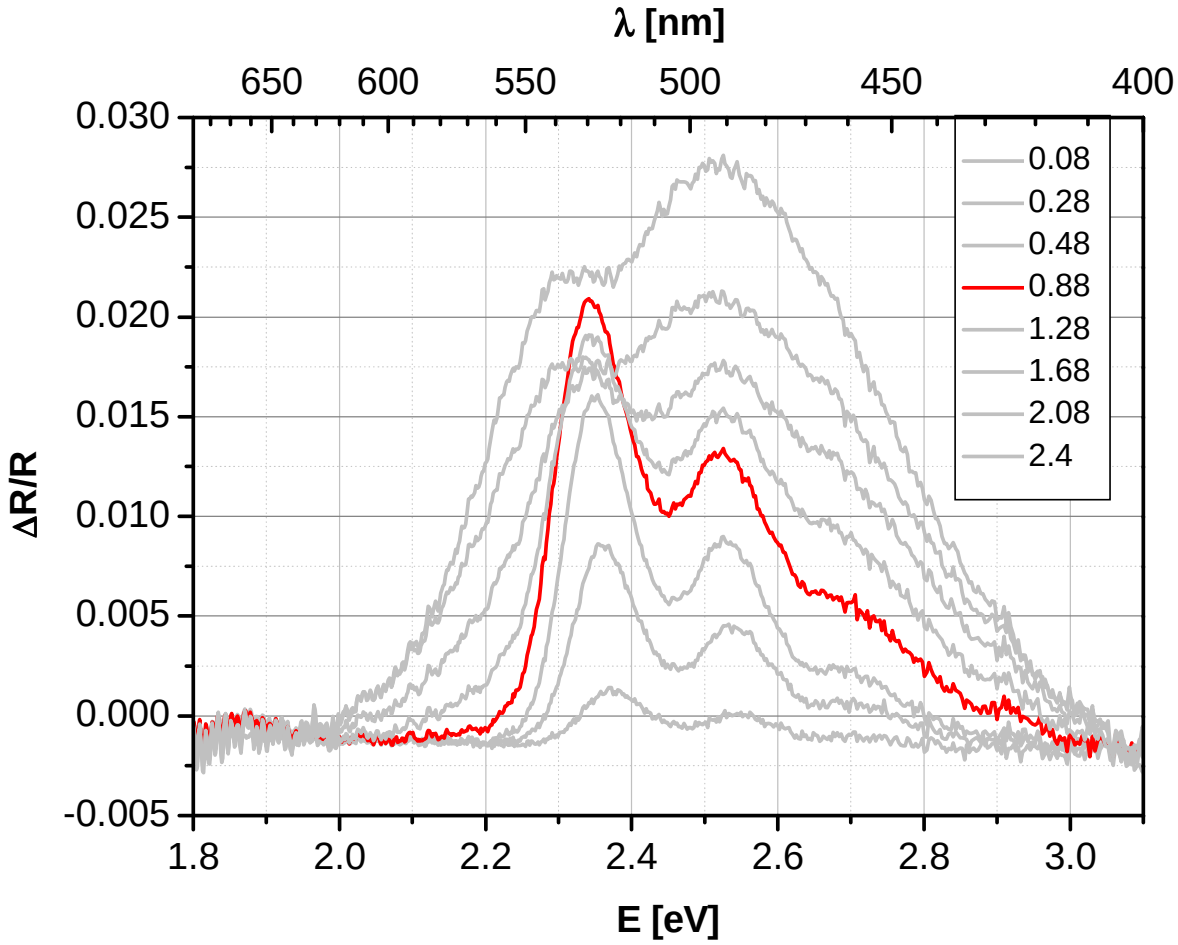

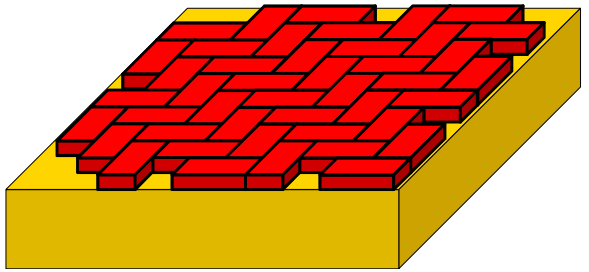

DRS = 0.9α(E) + 0β(E)

[H. Pröhl, R. Nitsche, T. Dienel and TF, *PRL* 93, 097403 (2004).]

PTCDA on Mica

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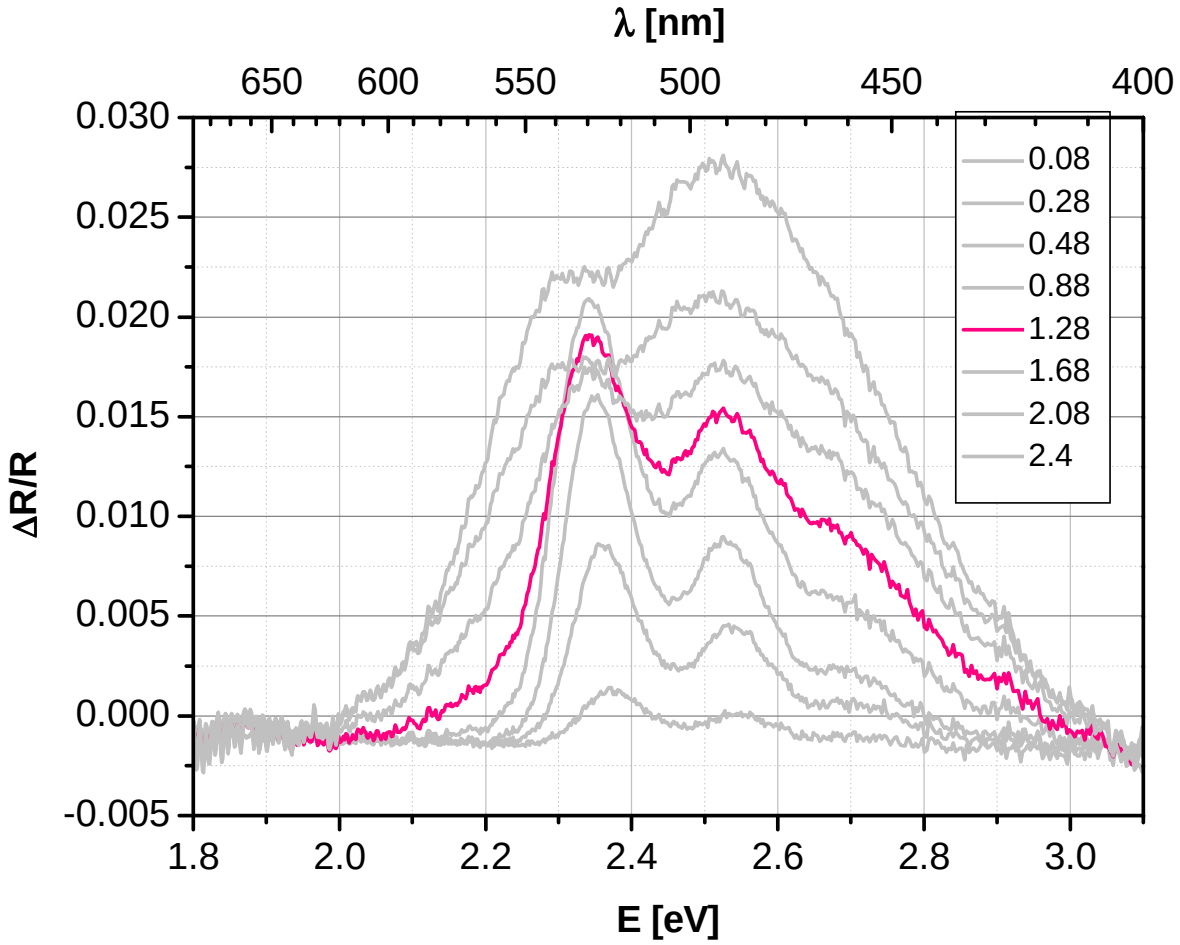

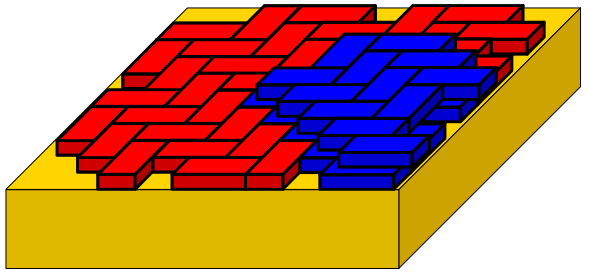

DRS = 0.7α(E) + 0.3β(E)

[H. Pröhl, R. Nitsche, T. Dienel and TF, *PRL* 93, 097403 (2004).]

PTCDA on Mica

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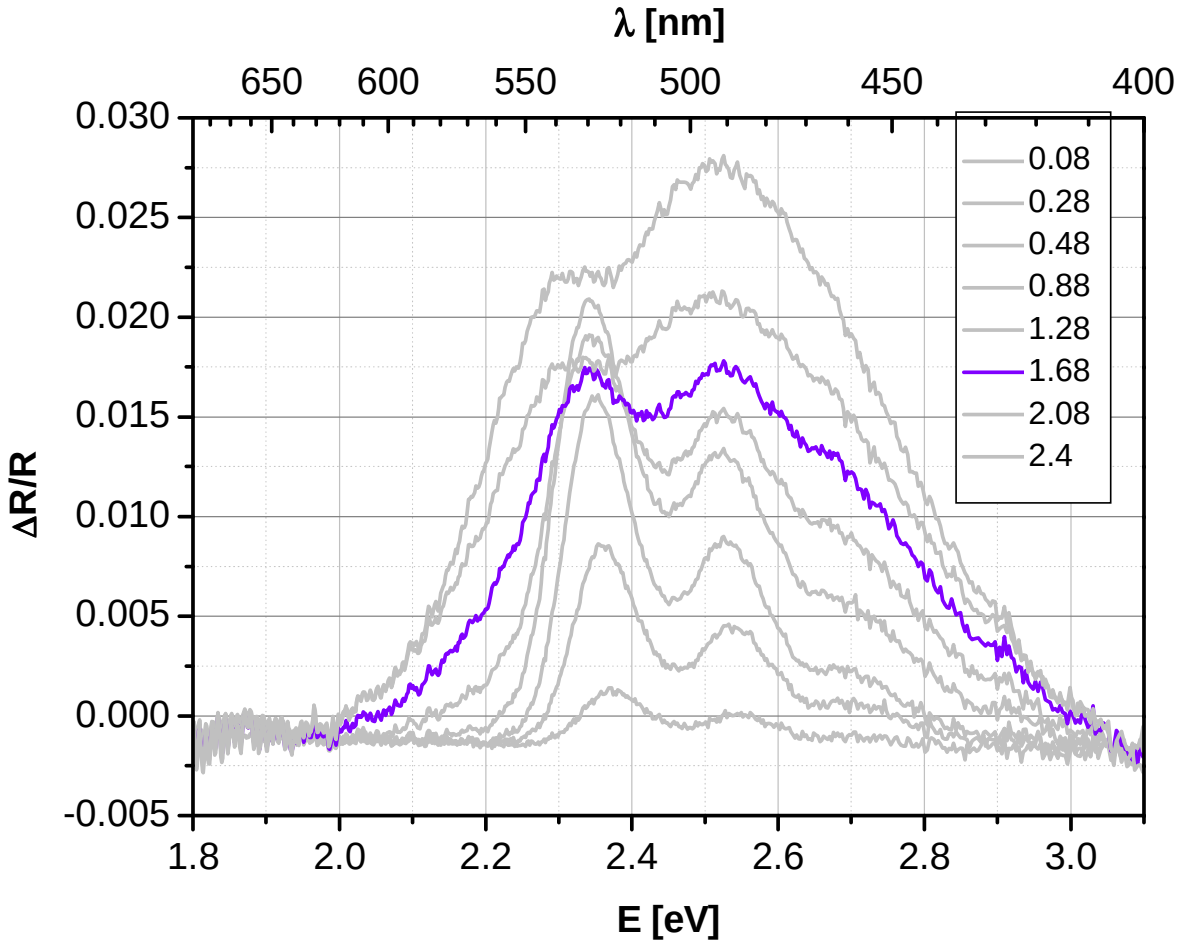
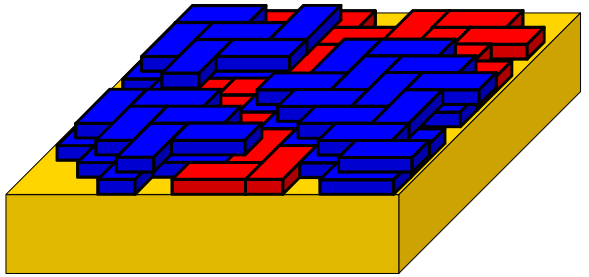


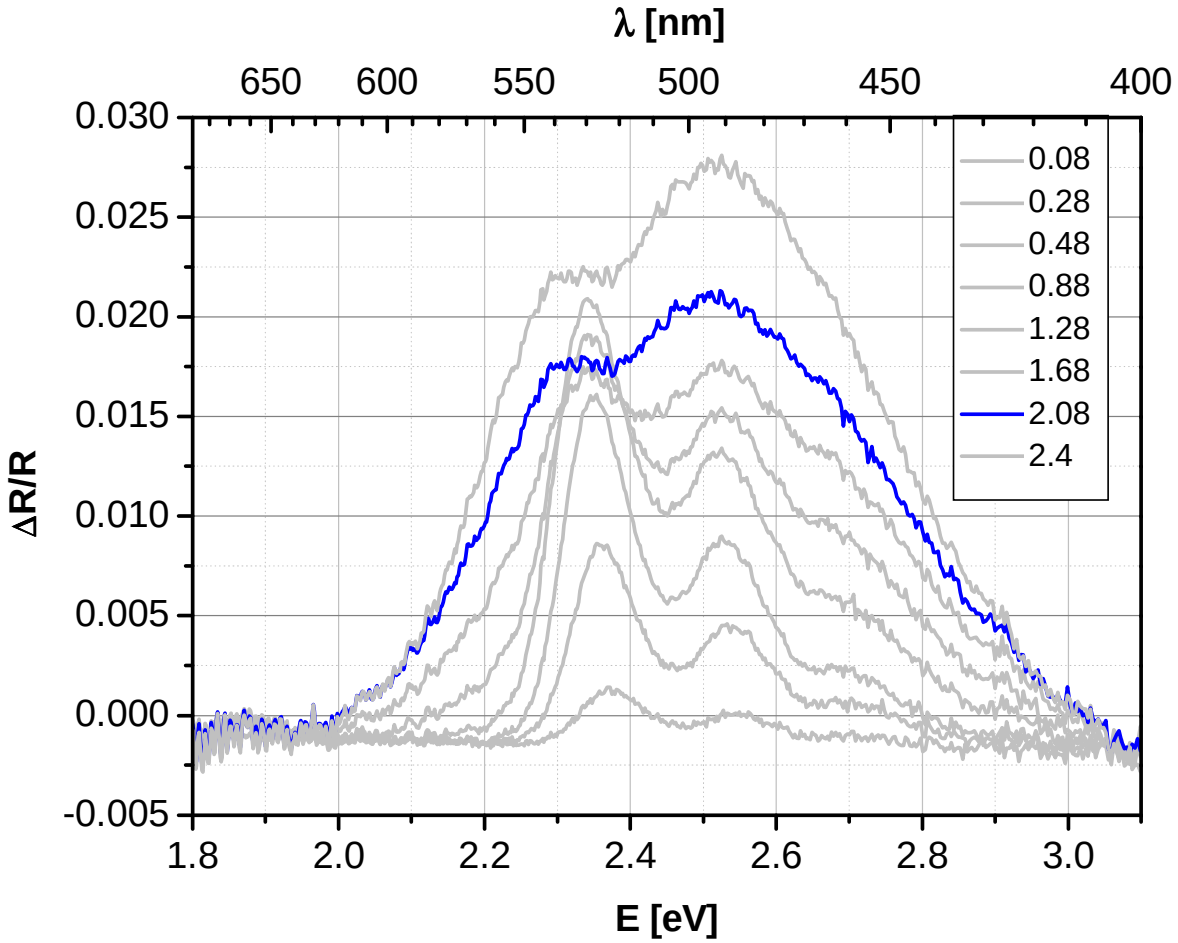


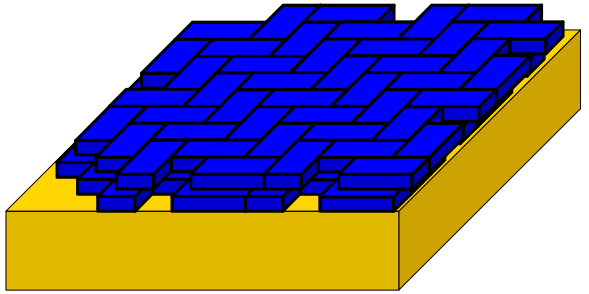
DRS = 0.3α(E) + 0.7β(E)

[H. Pröhl, R. Nitsche, T. Dienel and TF, *PRL* 93, 097403 (2004).]

PTCDA on Mica

Monomer-Dimer-Transition





DRS ~ 0α(E) + 1β(E)

[H. Pröhl, R. Nitsche, T. Dienel and TF, *PRL* 93, 097403 (2004).]

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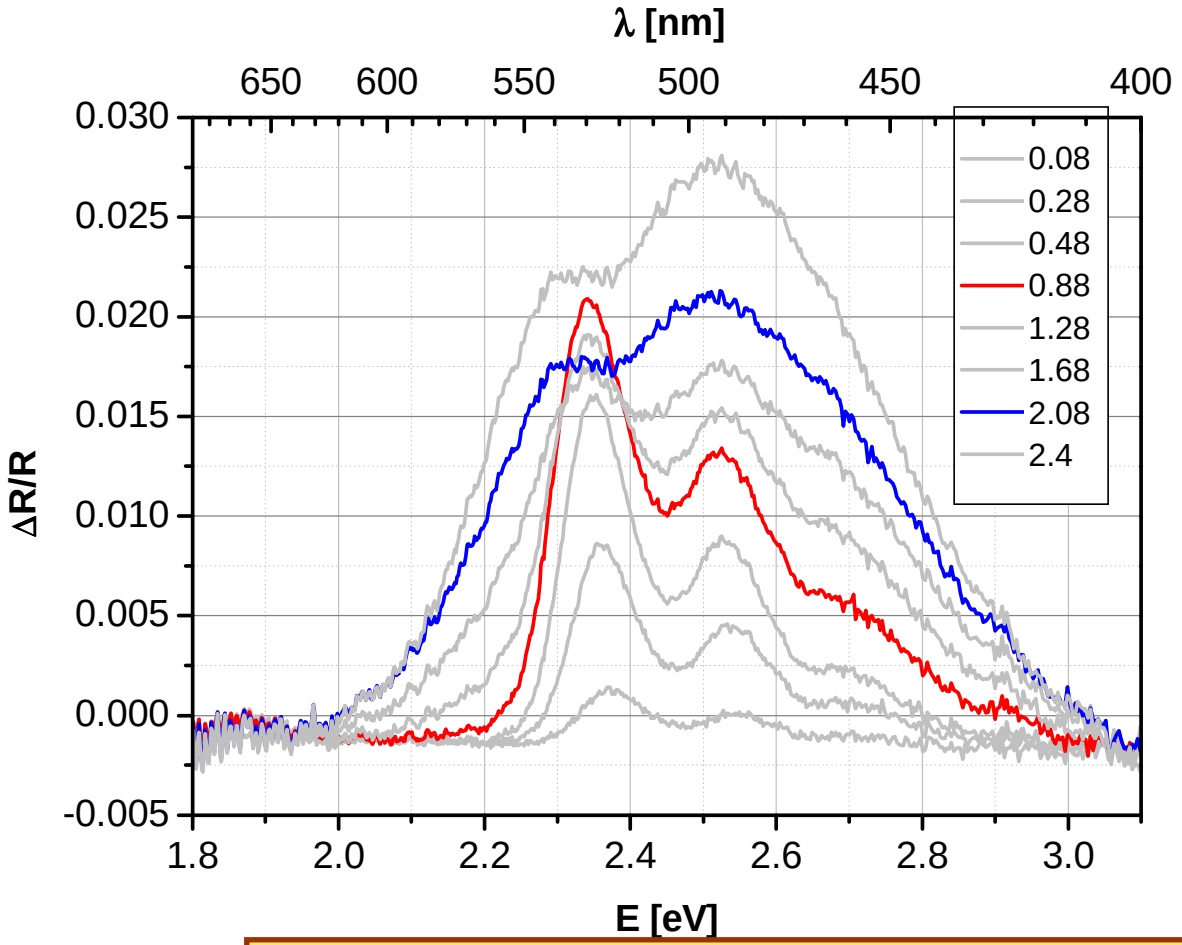
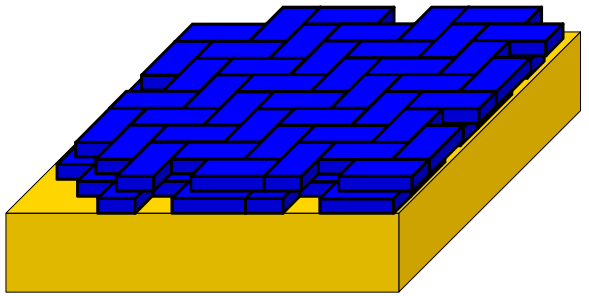




DRS ~ 0α(E) + 1β(E)

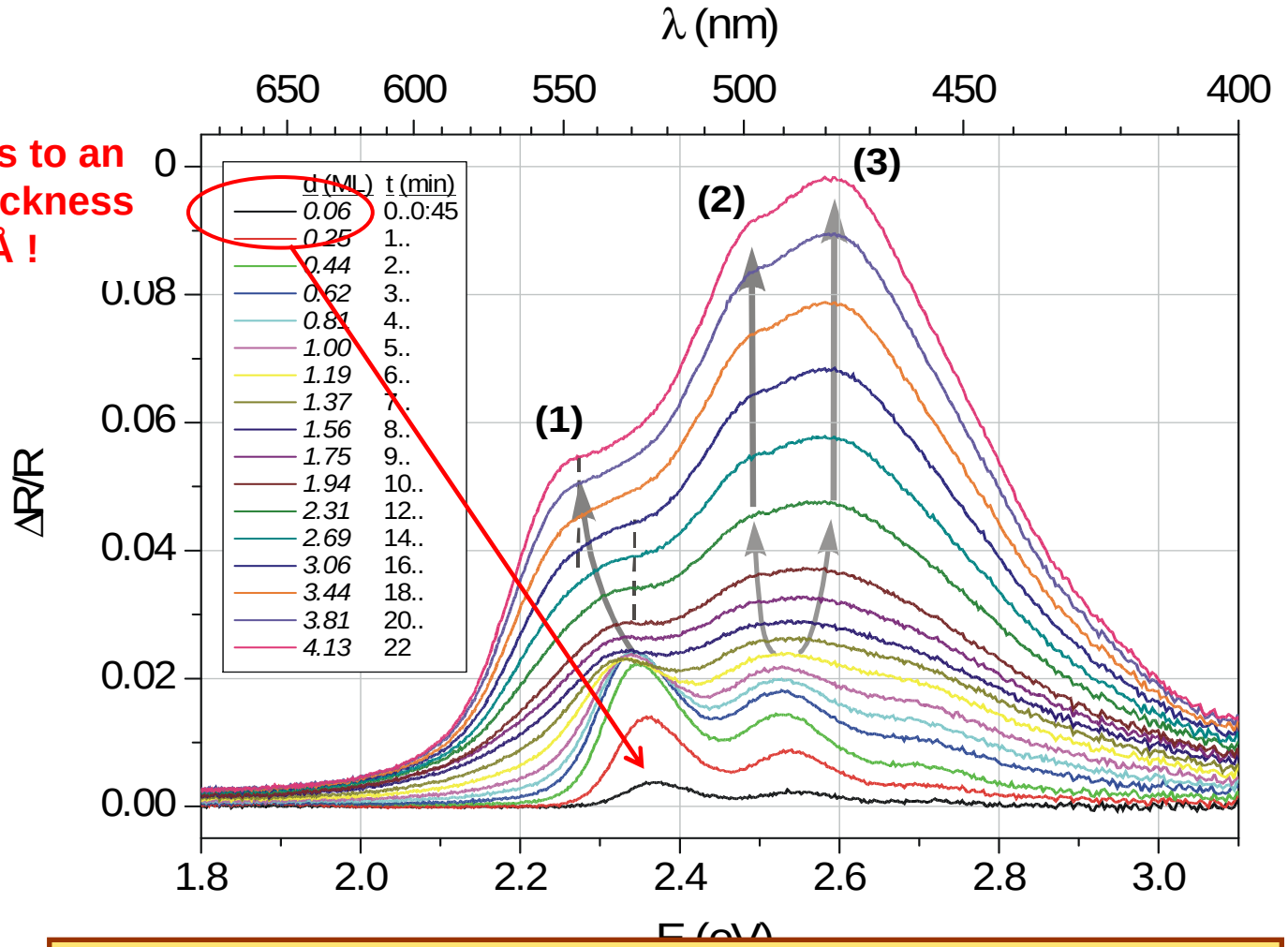
➔ **Different behavior of monomers and dimers, due to strong optical interaction in the stack**

[H. Pröhl, R. Nitsche, T. Dienel and TF, *PRL* 93, 097403 (2004).]

PTCDA on Mica

Monomer-Oligomer-Transition

corresponds to an effective thickness of only 0.2 Å !



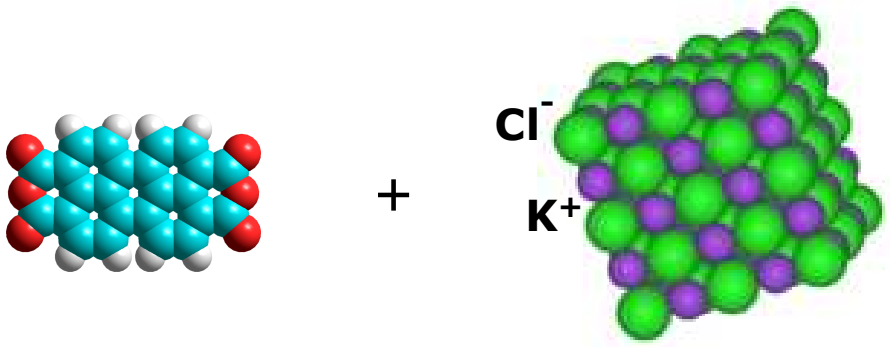
➔ **Smooth transition from dimer to infinite chain**

➔ **Spectral changes accomplished at ~4 ML**

[H. Pröhl, R. Nitsche, T. Dienel and TF, *PRL* 93, 097403 (2004).]

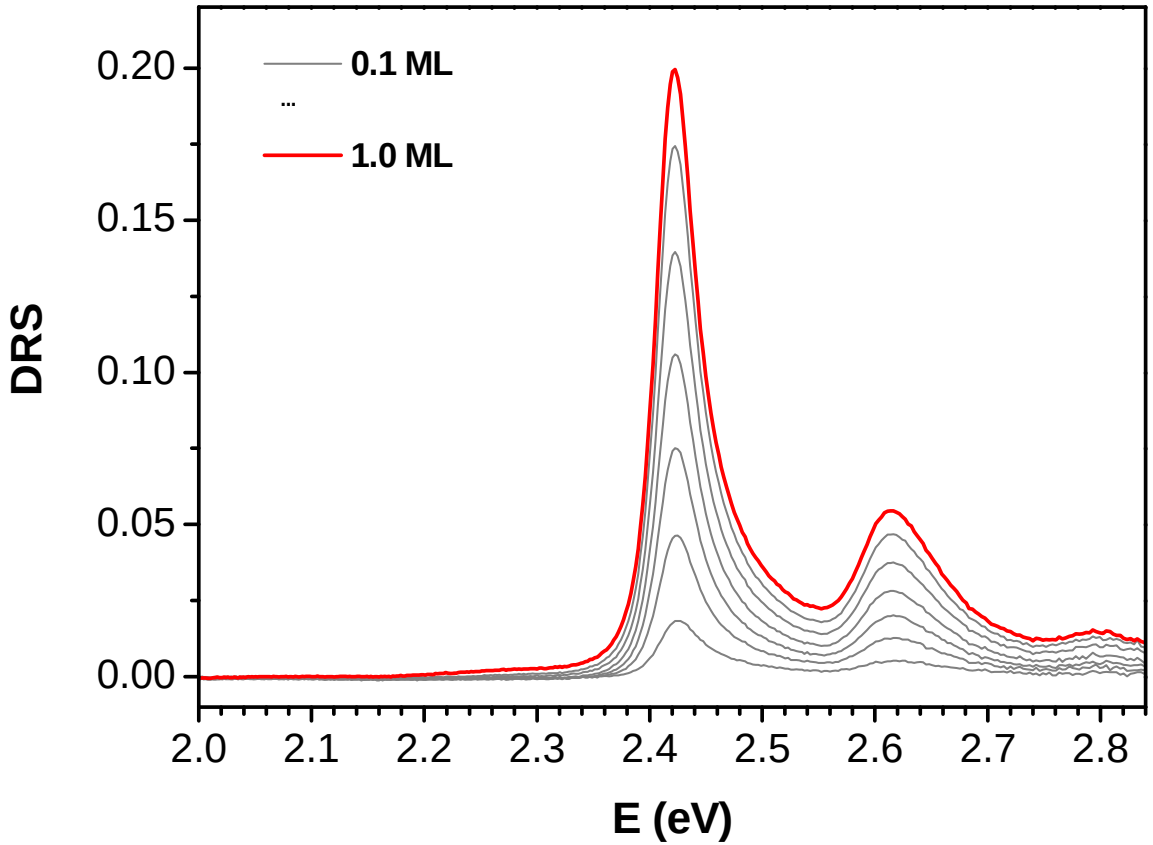
4. Case II: Function Follows Form

PTCDA on KCl(100)



PTCDA on KCl

DRS

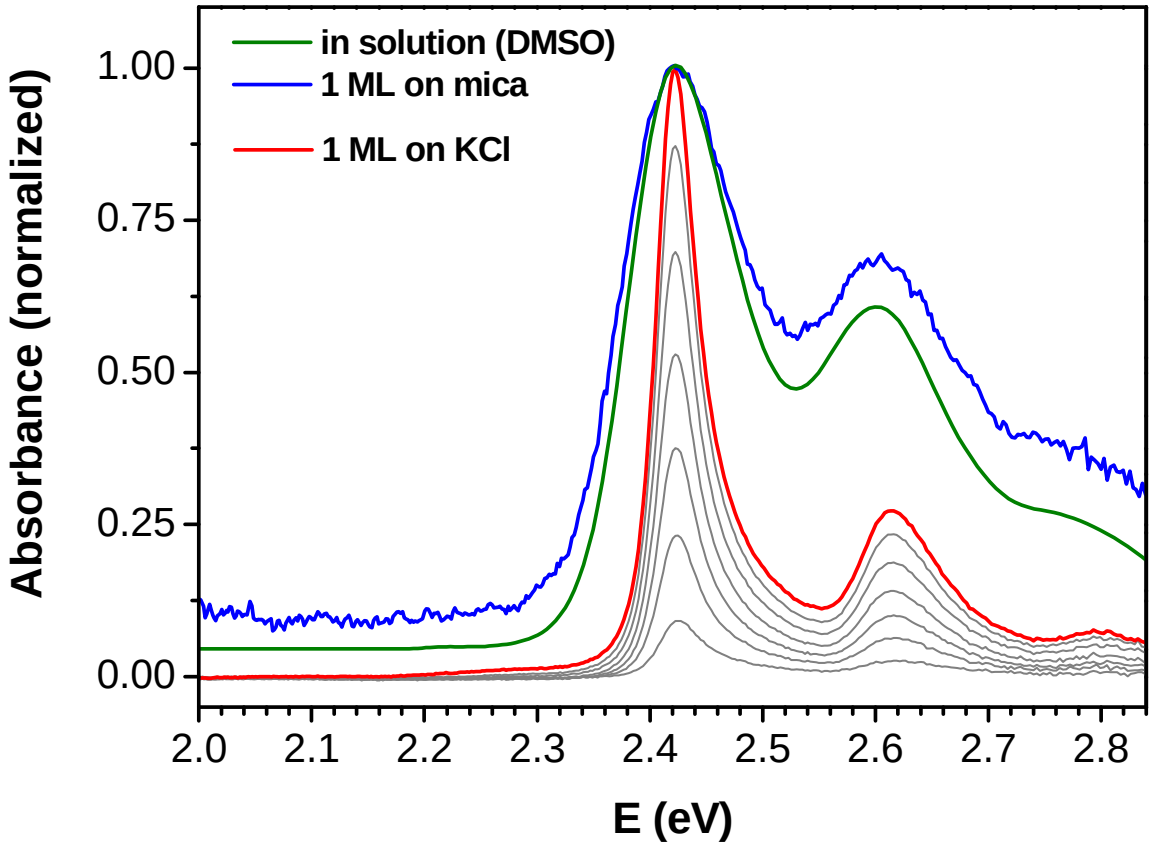


- **Monomer spectra for *d* < 1ML**

[T. Dienel, C. Loppacher, S. Mannsfeld, R. Forker and TF, *Adv. Mat.* 20, 959 (2008).]

PTCDA

Absorption



- **Monomer spectra for *d* < 1ML**
- **Extremely narrow bands in comparison to solution and on mica**

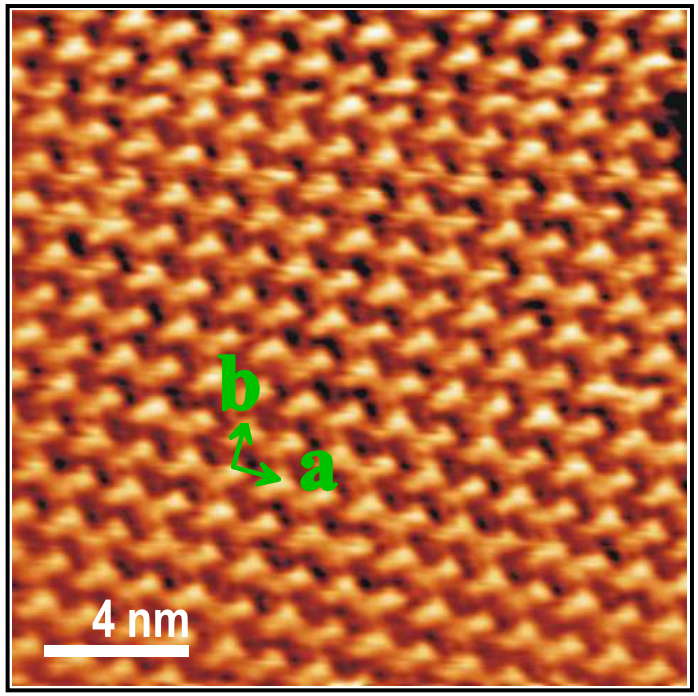
➔ **Strongly reduced inhomogeneous broadening**
➔ **Hints towards special layer structure**

[T. Dienel, C. Loppacher, S. Mannsfeld, R. Forker and TF, *Adv. Mat.* 20, 959 (2008).]

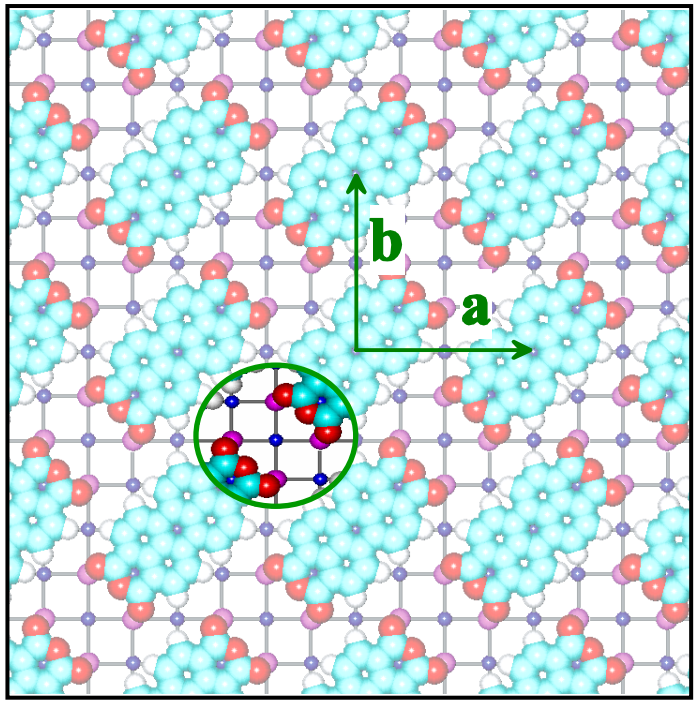
PTCDA on KCl

AFM

Low temperature NC-AFM (Chr. Loppacher):



PTCDA on KCl(100)



Model

➔ **Commensurate structure causes similar environment on atomic level for every molecule**

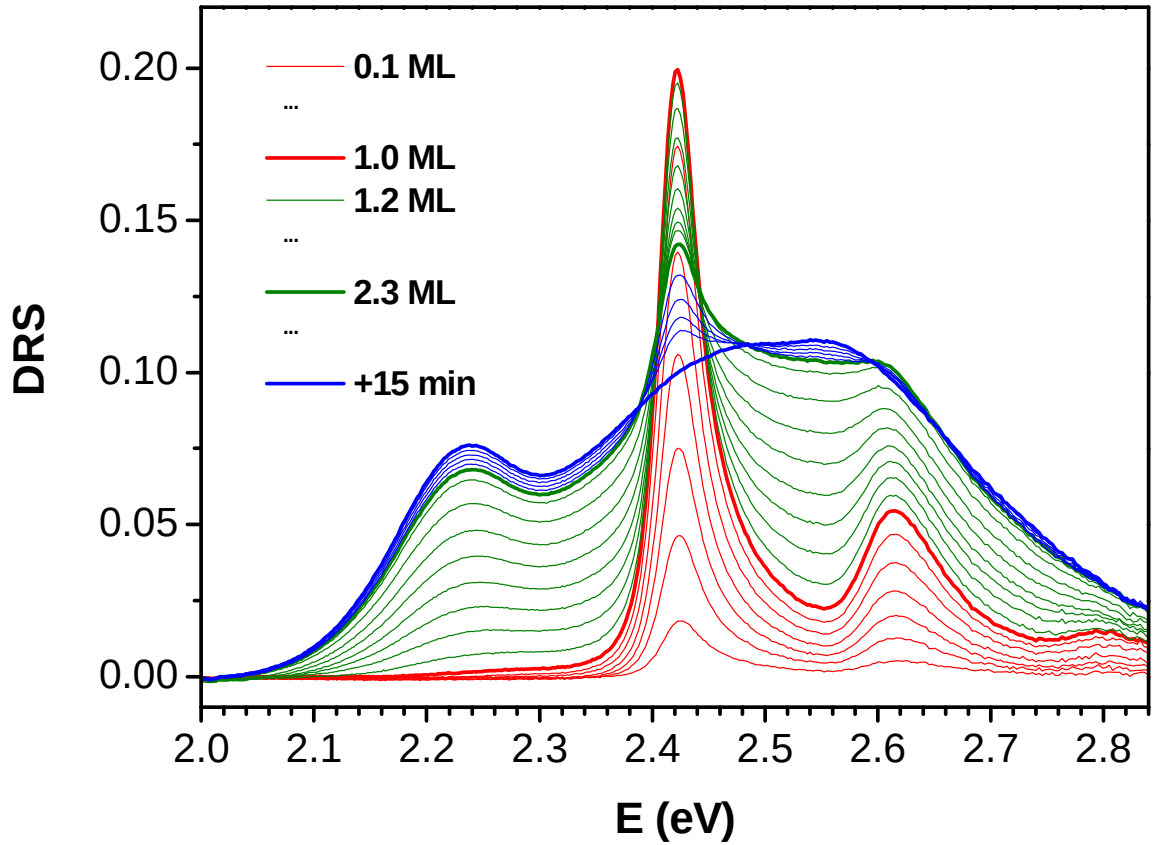
➔ **Reason why inhomogeneous broadening is strongly reduced**

[T. Dienel, C. Loppacher, S. Mannsfeld, R. Forker and TF, *Adv. Mat.* 20, 959 (2008).]

PTCDA on KCl

DRS

Increasing coverage to more than 1 ML renders structure instable:



- **Spectra become very broad**
- **Further ageing leads to spectrum similar to *pc* 3D-crystals**

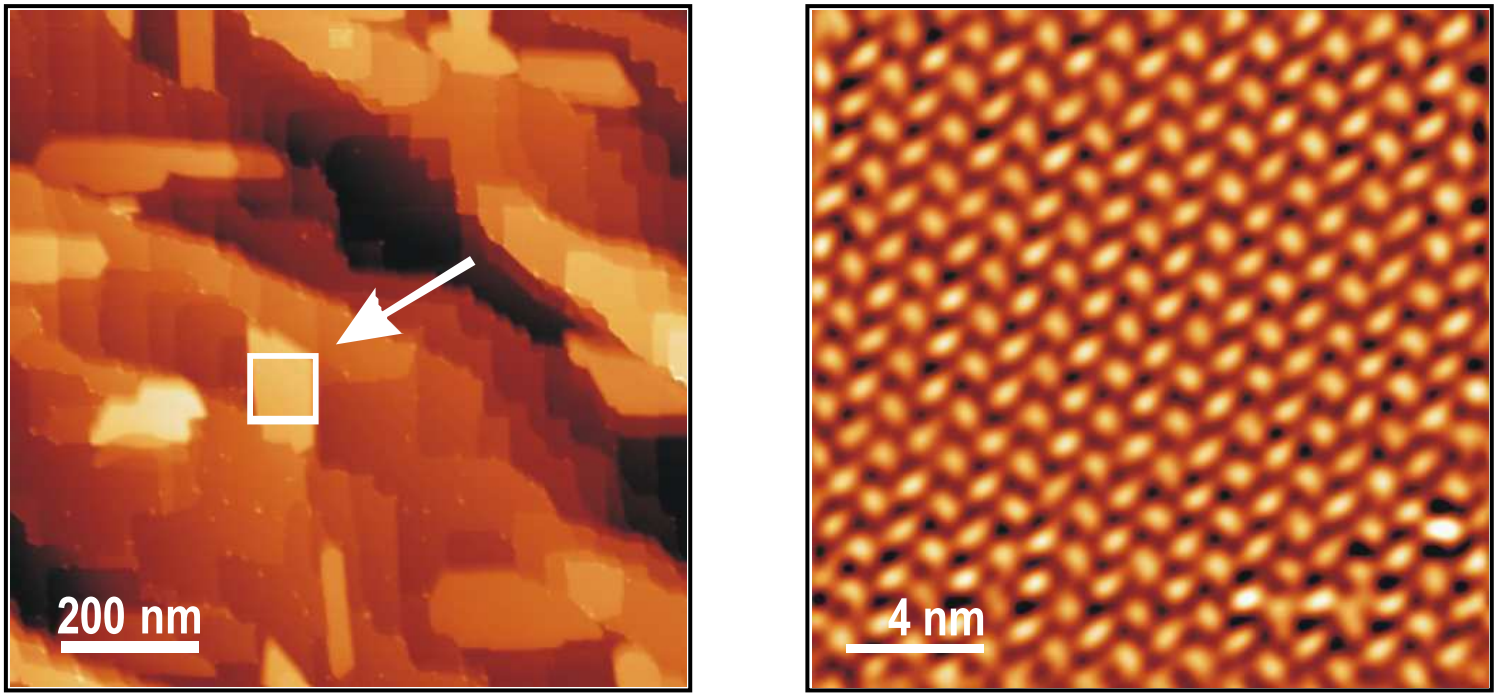
➔ **Spectroscopy tells us: recrystallization!**

[T. Dienel, C. Loppacher, S. Mannsfeld, R. Forker and TF, *Adv. Mat.* 20, 959 (2008).]

PTCDA on KCl

AFM

Low temperature NC-AFM (Chr. Loppacher):



2.5 ML PTCDA on KCl(100)

- ➔ **As the substrate's influence is already lost in the 2nd layer, layer has recrystallized into bulk structure**
- ➔ **Optical properties depend strongly on physical layer structure**

[T. Dienel, C. Loppacher, S. Mannsfeld, R. Forker and TF, *Adv. Mat.* 20, 959 (2008).]

PTCDA on KCl

Potential Energy Calculation

Recrystallization can be fully understood by potential energy calculations:

Calculated potential energy as function of layer number for PTCDA on KCl(100)

Values are given per molecule

Phase	Layer number	E_{inter} (kcal/mol)	E_{intra} (kcal/mol)	E_{total} (kcal/mol)
SQ	1.	-37.17	-4.62	-41.79
SQ	2.	-32.30	-4.62	-36.92
HB	1.	-22.74	-11.74	-34.48
HB	2.	-38.70	-11.74	-50.44
HB	3.	-40.26	-11.74	-52.00

[T. Dienel, C. Loppacher, S. Mannsfeld, R. Forker and TF, *Adv. Mat.* 20, 959 (2008).]

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HB	**1.**	**-22.74**	**-11.74**	**-34.48**
HB	2.	-38.70	-11.74	-50.44
HB	3.	-40.26	-11.74	-52.00

- **1st layer: square-phase (SQ) energetically superior to herringbone-phase (HB)**

[T. Dienel, C. Loppacher, S. Mannsfeld, R. Forker and TF, *Adv. Mat.* 20, 959 (2008).]

PTCDA on KCl

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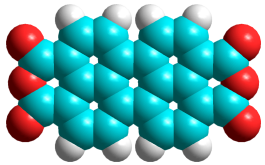
HB	1.	-22.74	-11.74	-34.48
HB	**2.**	**-38.70**	**-11.74**	**-50.44**
HB	3.	-40.26	-11.74	-52.00

➔ **Structures in organic-inorganic heteroepitaxie are determined by a delicate balance between substrate-molecule-interaction and molecule-molecule-interaction**

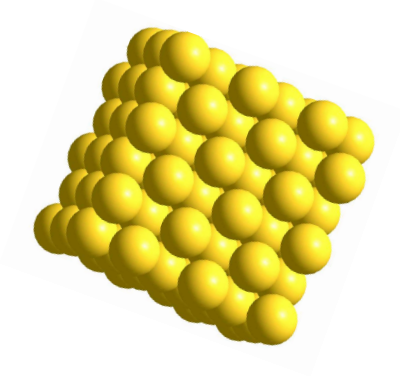
[T. Dienel, C. Loppacher, S. Mannsfeld, R. Forker and TF, *Adv. Mat.* 20, 959 (2008).]

5. Case III: Charged Molecules on Metals

PTCDA on Au(111) & *pc*-Al

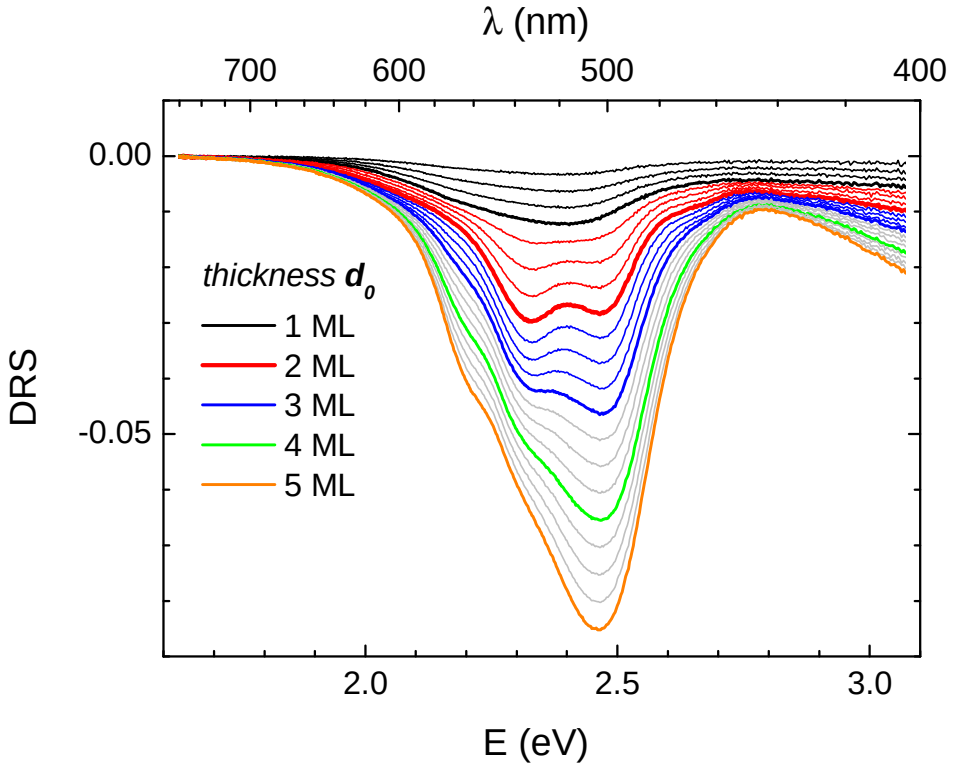


+



PTCDA on Au(111)

DRS



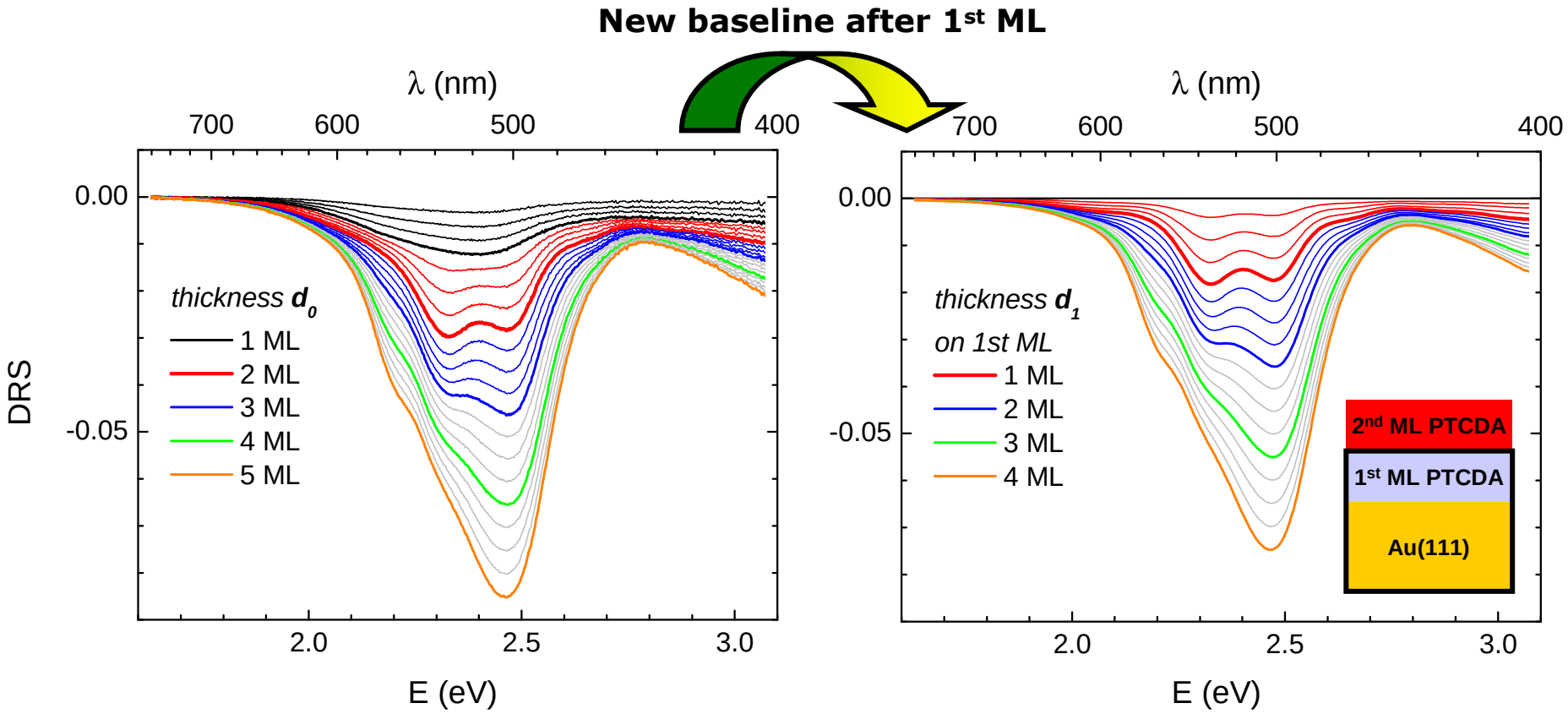
Distinct spectral development observed:

- **1st ML: Very broad spectra → coupling to Au!**
- **2nd ML: Two peaks resolvable**
- **3rd ML and thicker: Double-feature diminishes**

[R. Forker, C. Golnik, G. Pizzi, T. Dienel and TF, *Org. Electr.* 10, 1448 (2009).]

PTCDA on Au(111)

DRS



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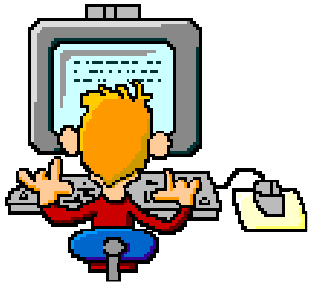
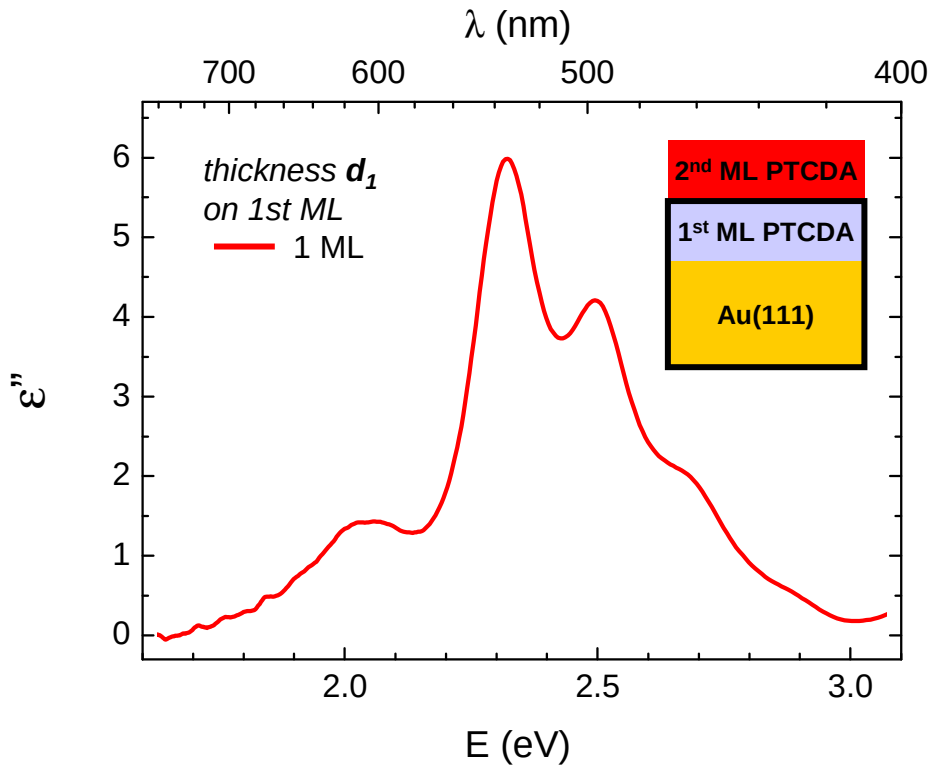
[R. Forker, C. Golnik, G. Pizzi, T. Dienel and TF, *Org.*



Calculation of dielectric function

PTCDA on Au(111)

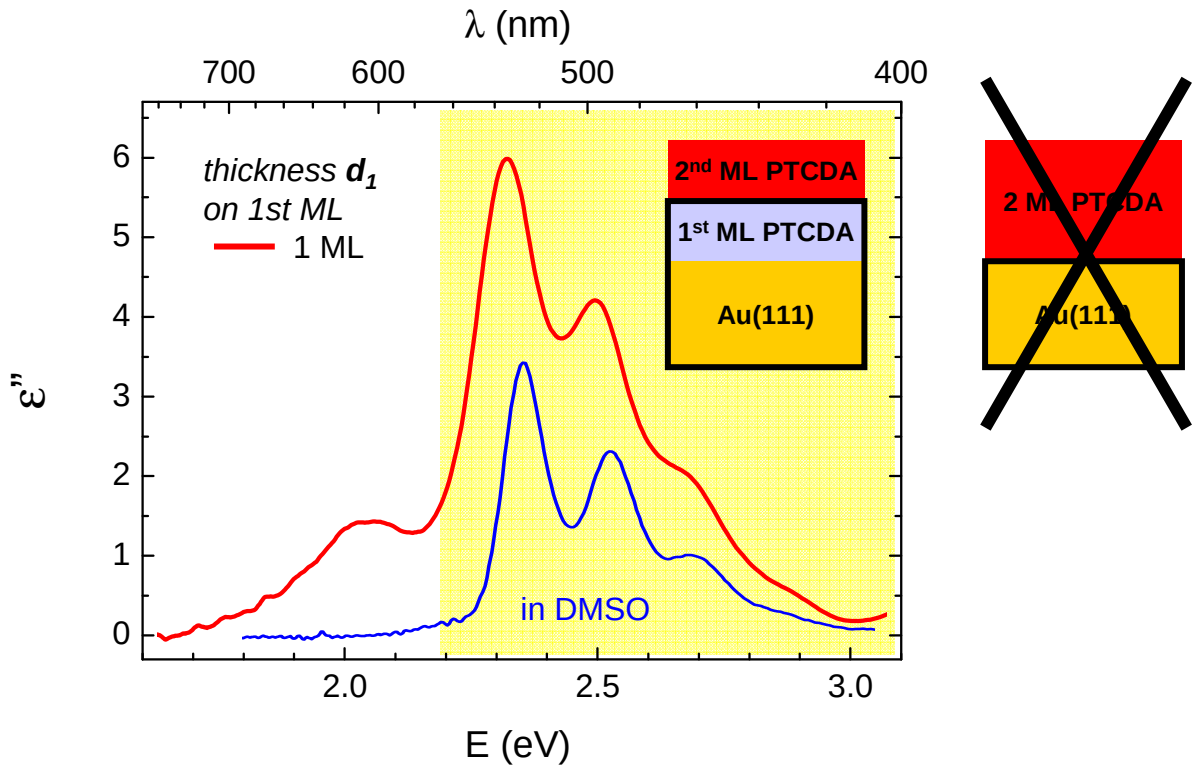
ε''



[R. Forker, C. Golnik, G. Pizzi, T. Dienel and TF, *Org. Electr.* 10, 1448 (2009).]

PTCDA on Au(111)

ε''



→ **Clear monomeric signature for E > 2.2 eV (neutral PTCDA)**

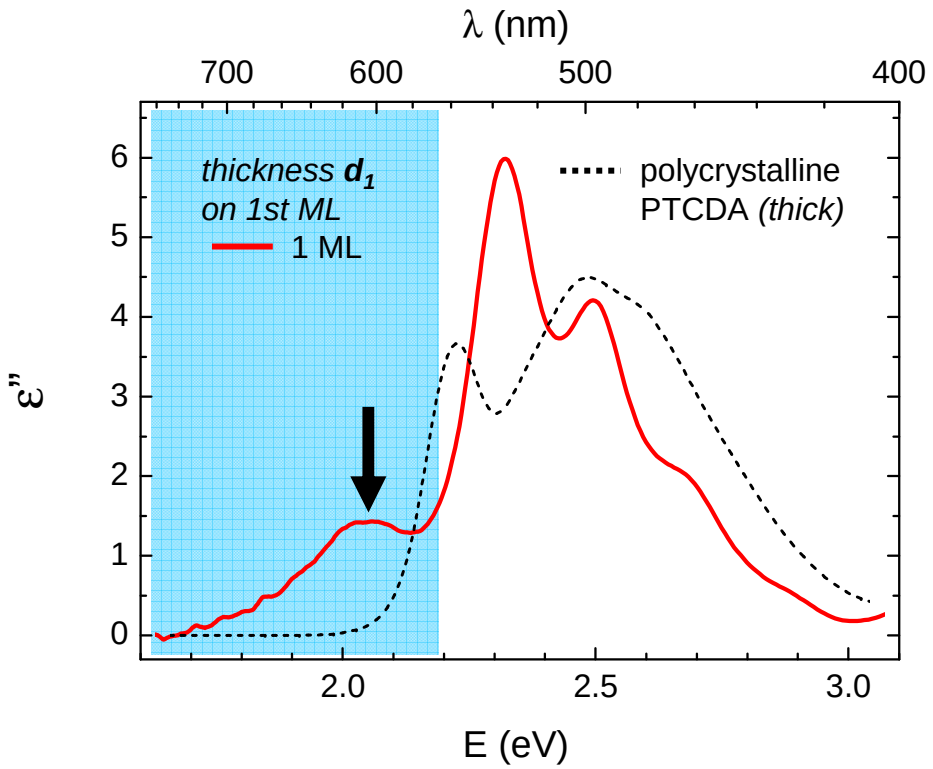
→ **No physical dimerization with the 1st ML of PTCDA !!!**

→ **Decoupling of 2nd ML is justification of 2-layer-approach**

[R. Forker, C. Golnik, G. Pizzi, T. Dienel and TF, *Org. Electr.* 10, 1448 (2009).]

PTCDA on Au(111)

ε''



→ Clear monomeric signature for E > 2.2 eV (neutral PTCDA)

→ No physical dimerization with the 1st ML of PTCDA !!!

→ Decoupling of 2nd ML is justification of 2-layer-approach

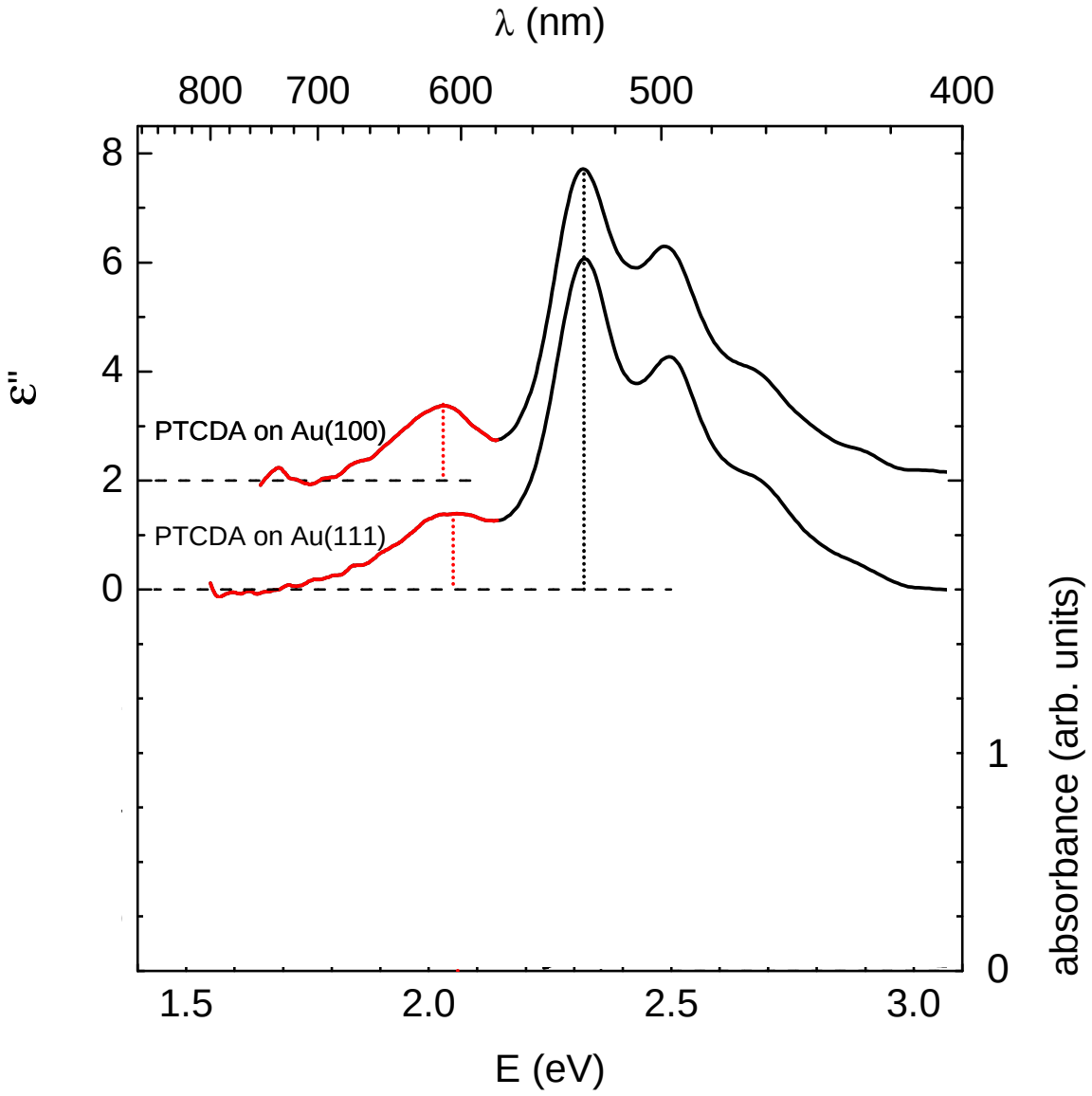
→ **New feature @ 2.05 eV which is no aggregation effect**

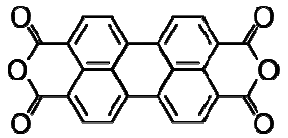
→ **Assignment to PTCDA radical cations ($PTCDA^{\bullet+}$)**

[R. Forker, C. Golnik, G. Pizzi, T. Dienel and TF, *Org. Electr.* 10, 1448 (2009).]

PTCDA on Au(111)

cmp. to solvent spectra





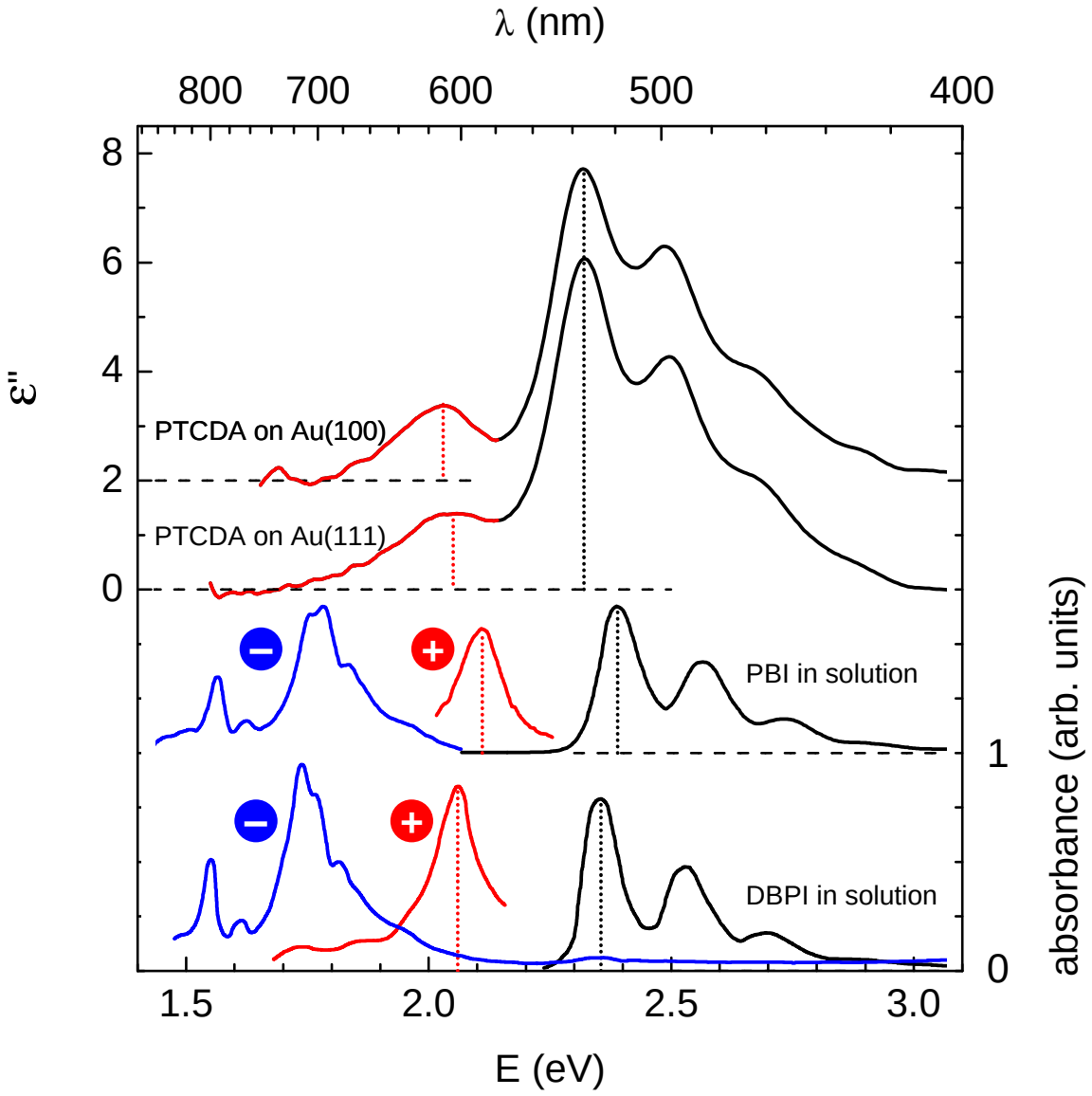
PTCDA

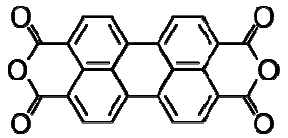
rather poor solubility

[R. Forker, C. Golnik, G. Pizzi, T. Dienel and TF, *Org. Electr.* 10, 1448 (2009).]

PTCDA on Au(111)

cmp. to solvent spectra





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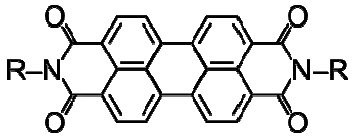
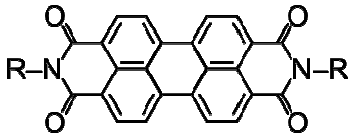


PBI

(R = 1-hexylheptyl)



DBPI

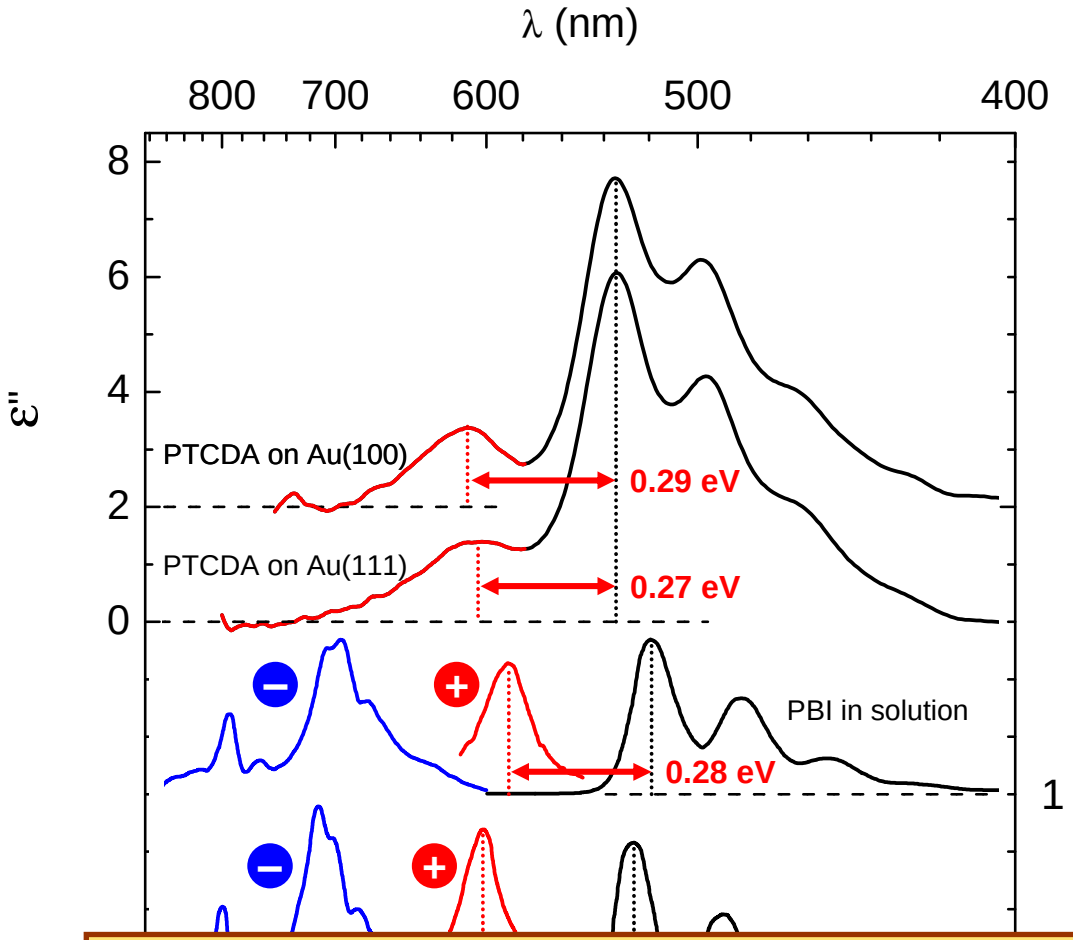
(R = 2,5-di-*tert*-butylphenyl)

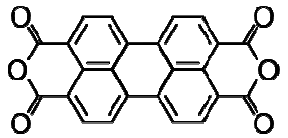
[T. Kircher *et al.*, PCCP 1, 3987 (1999).]
[W.E. Ford *et al.*, JPC 93, 6692 (1989).]

[R. Forker, C. Golnik, G. Pizzi, T. Dienel and TF, *Org. Electr.* 10, 1448 (2009).]

PTCDA on Au(111)

cmp. to solvent spectra





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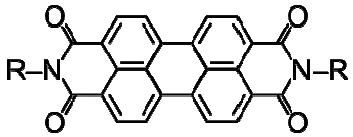
rather poor solubility



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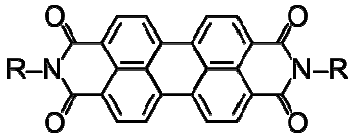


DBPI

(R = 2,5-di-*tert*-butylphenyl)

➔ **First direct observation of charge transfer from a molecule to a metal**

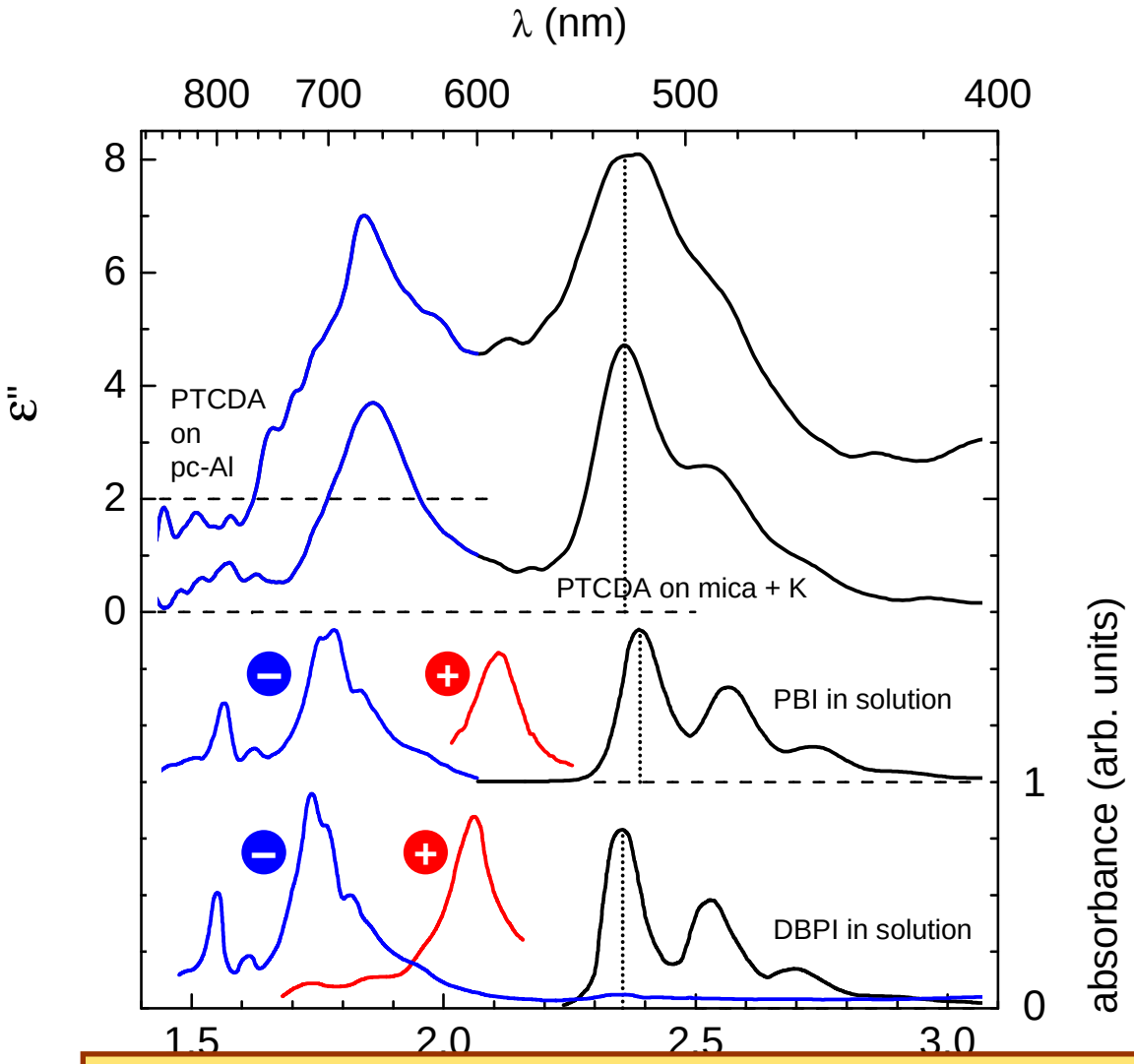
➔ **But how about other metals?**

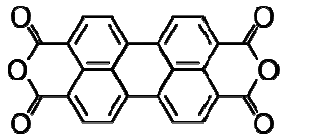
99).]
89).]

[R. Forker, C. Golnik, G. Pizzi, T. Dienel and TF, *Org. Electr.* 10, 1448 (2009).]

PTCDA on *pc*-Al

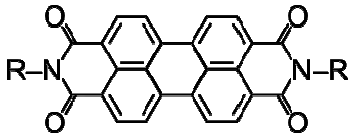
cmp. to solvent spectra





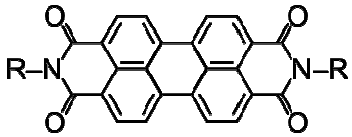
PTCDA

rather poor solubility



PBI

(R = 1-hexylheptyl)



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[T. Kircher *et al.*, PCCP 1, 3987 (1999).]
[W.E. Ford *et al.*, JPC 93, 6692 (1989).]

➔ **Occurrence of charged PTCDA depends on the metal**
➔ **Reason is differently oriented surface dipole**

[R. Forker, C. Gollnik, G. Pizzi, T. Dienel and TF, *Org. Electr.* 10, 1448 (2009).]

6. Summary

- ★ By DRS the optical properties of ultrathin films can be measured reliably and with an excellent SNR
- ★ DRS reflects directly changes in the physical structure of ultra thin films
- ★ On inert substrates (i.e. mica): molecules show monomeric behavior
- ★ On metals: first layer hybridizes with the metal; no distinct spectral features in 1st ML
- ★ Depending on the sign of the surface dipole, charging may be observed

Acknowledgment

Co-workers:

Dr.Roman Forker
Dr. Stefan Mannsfeld
Dr. Holger Pröhl
Dr. Thomas Dienel
Dr. Robert Nitsche
Dr. Michael Törker

Christian Wagner
Rainer Jacob
Andreas Krause
Giovanni Pizzi

TU Dresden, IAPP (head: Prof. Dr. Karl Leo)

$$$:

DFG, DAAD, Leibniz-Price Karl Leo

THE END