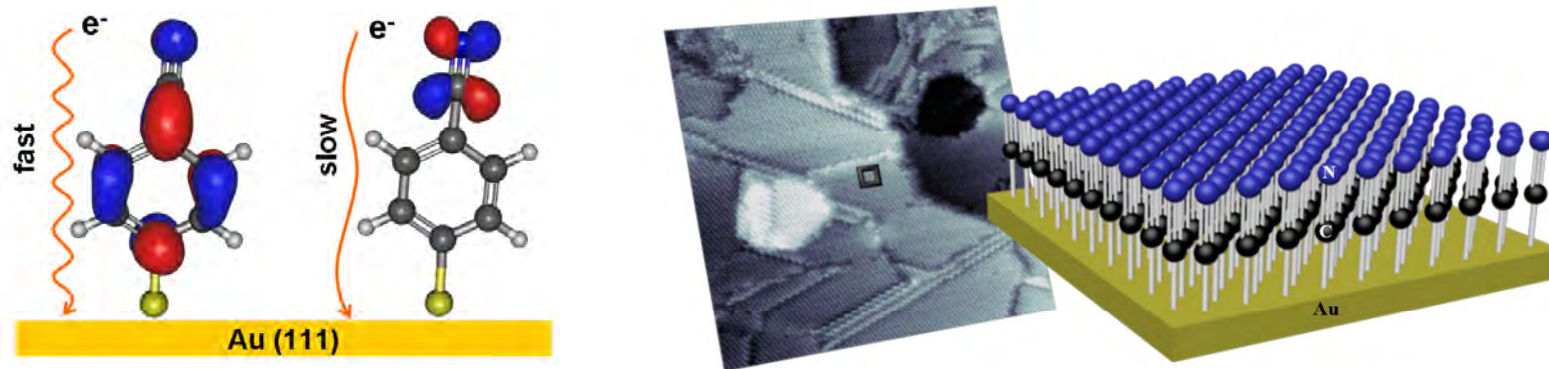


# Dynamics of electron transfer in monomolecular films

Michael Zharnikov

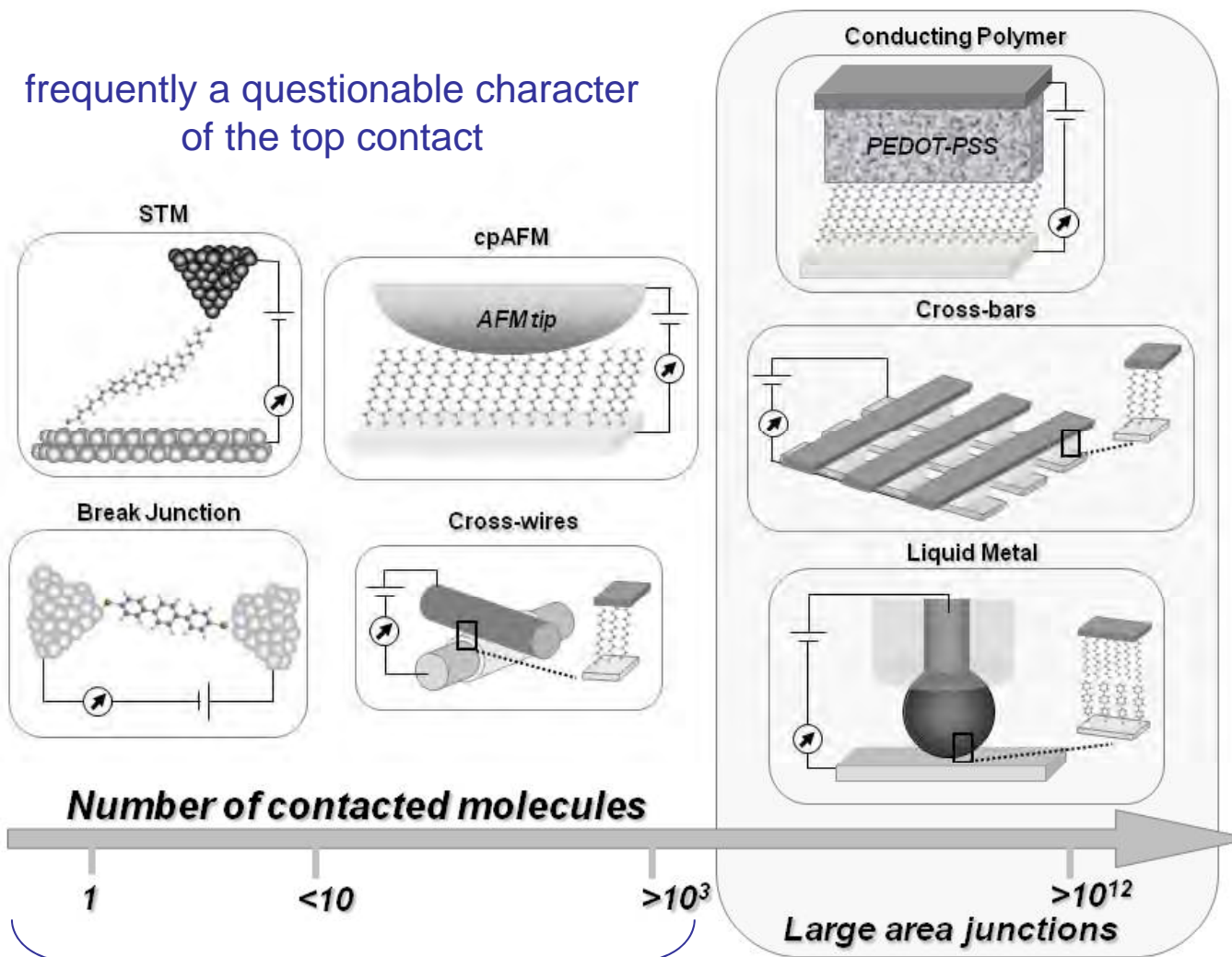
*Applied Physical Chemistry, Heidelberg University, Germany*



SPICE workshop “Molecular Electro-Opto-Spintronics”  
Mainz; October 17, 2019

# There are a variety of approaches to study static electric transport properties of molecules

frequently a questionable character  
of the top contact



is frequently not precisely known

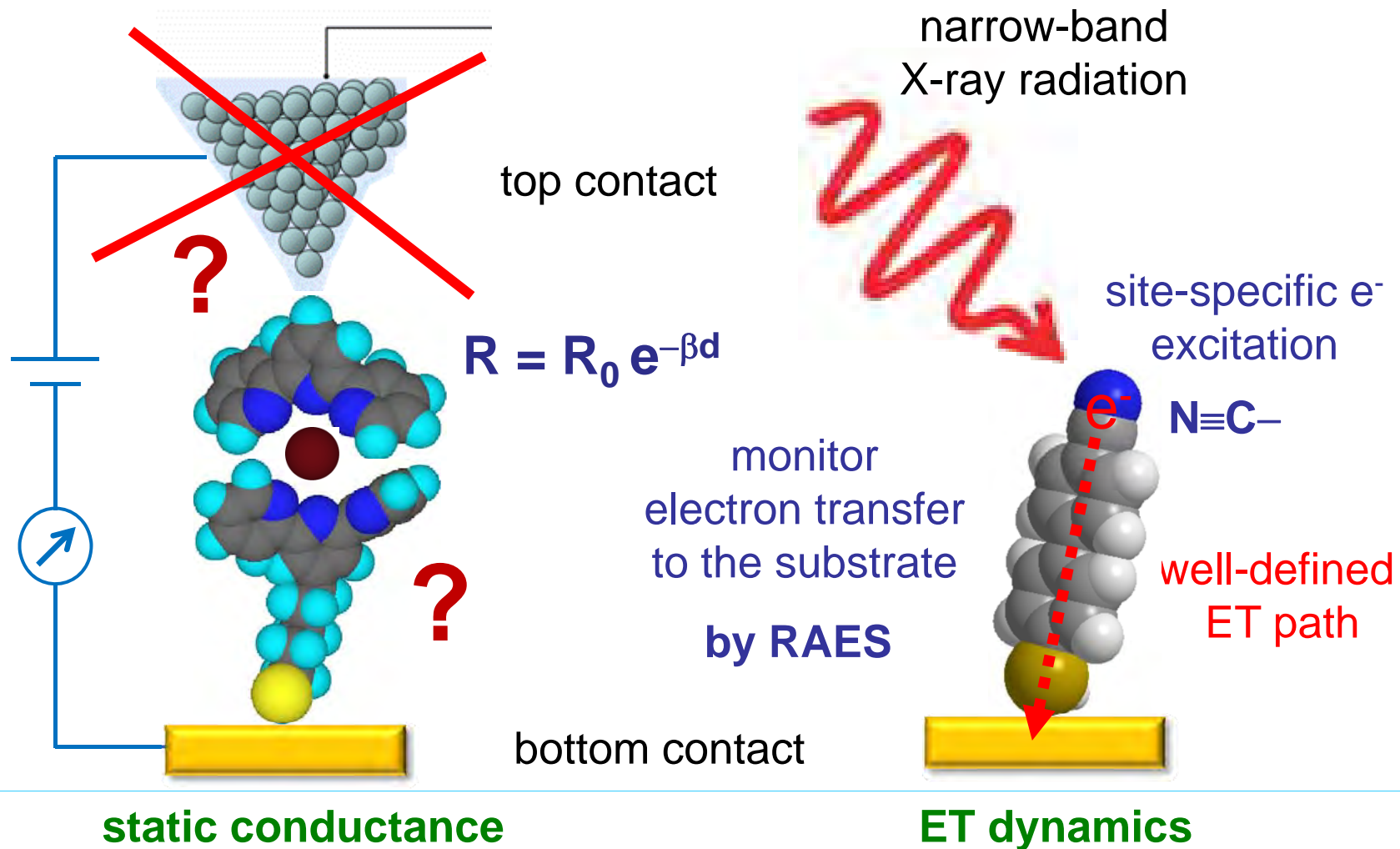
M. A. Rampi *et al.*, in *Top Curr Chem* (2011)

**An alternative approach:**

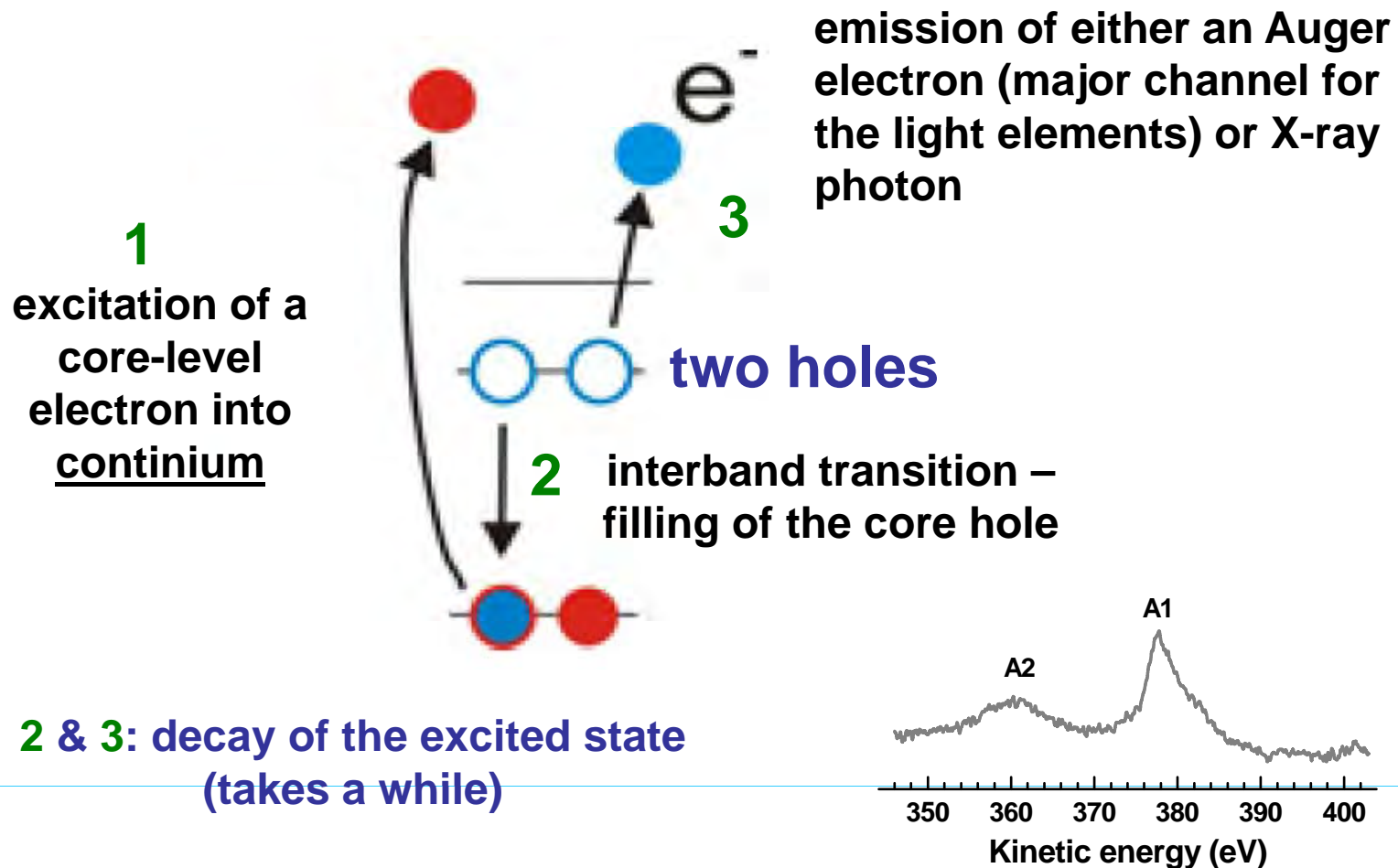
**Dynamics of the charge transfer  
through the molecular framework**

- a look at the same properties from a different perspective
- time-scale of Molecular Electronics

# Experiment: X-ray photon as the top contact & resonant Auger electron spectroscopy as a tool

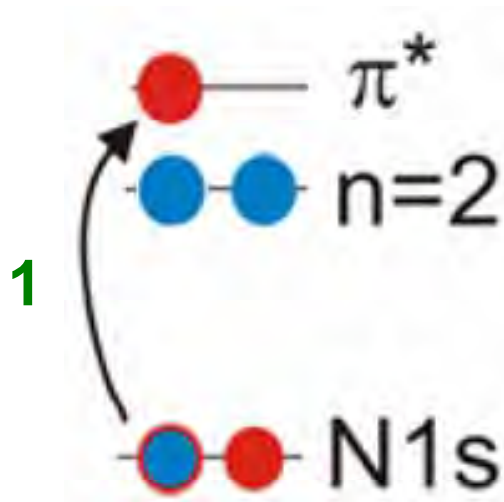


# Non-resonant (textbook) Auger electron spectroscopy



# Resonant Auger electron spectroscopy (RAES)

A suitable functional group (**nitrile** in our case) is required



excitation of  
a core-level electron  
into a bound state  
associated with  
a specific functional group

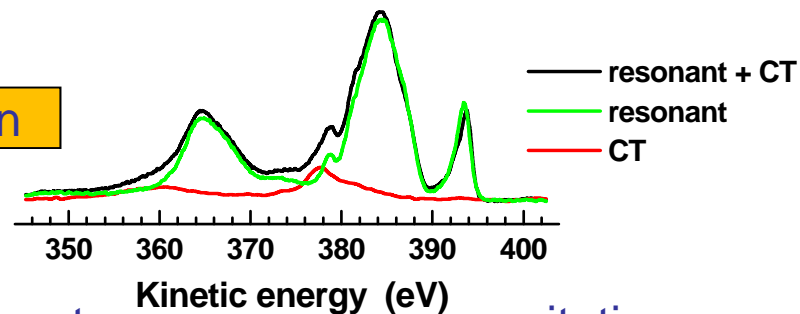
followed by the decay of the excited state  
which can occur by different ways

**narrow bandwidth X-rays:** the individual steps, viz. excitation and de-excitation, should be considered as parts of a one-step process

# RAES: decay channels & ET probability

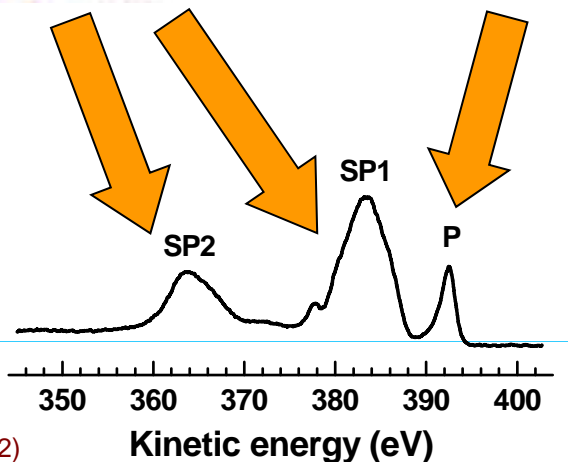
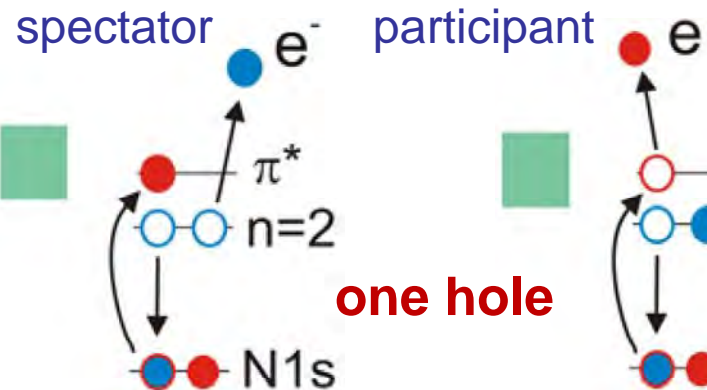
$P_{ET}$

spectrum decomposition



resonant

excitation



see e.g. Brühwiler et al., *Rev. Mod. Phys.* **74**, 703 (2002)

## Access to the femtosecond time domain

$$\tau_{ET} = \tau_{core} (1 - P_{ET}) / P_{ET}$$

“core hole clock“



$$\tau_{core} (\text{N1s}) = 6.4 \text{ fs}$$

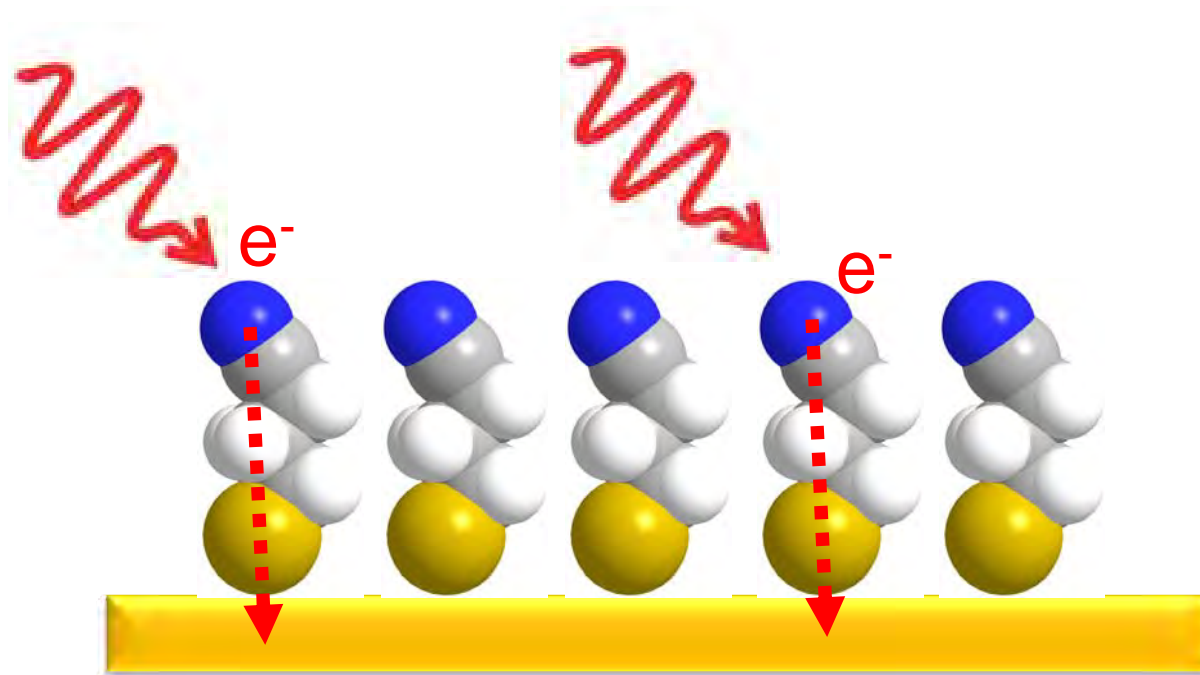
B. Kempgens *et al.* *J. Phys. B* **29**, 5389 (1996)

- access to the sub-fs and fs time domains
- $0.5 < \tau_{ET} < 120\text{-}150 \text{ fs}$

defined by a reliable spectra decomposition

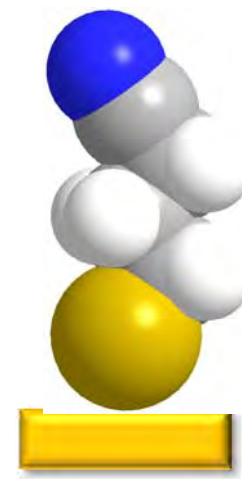
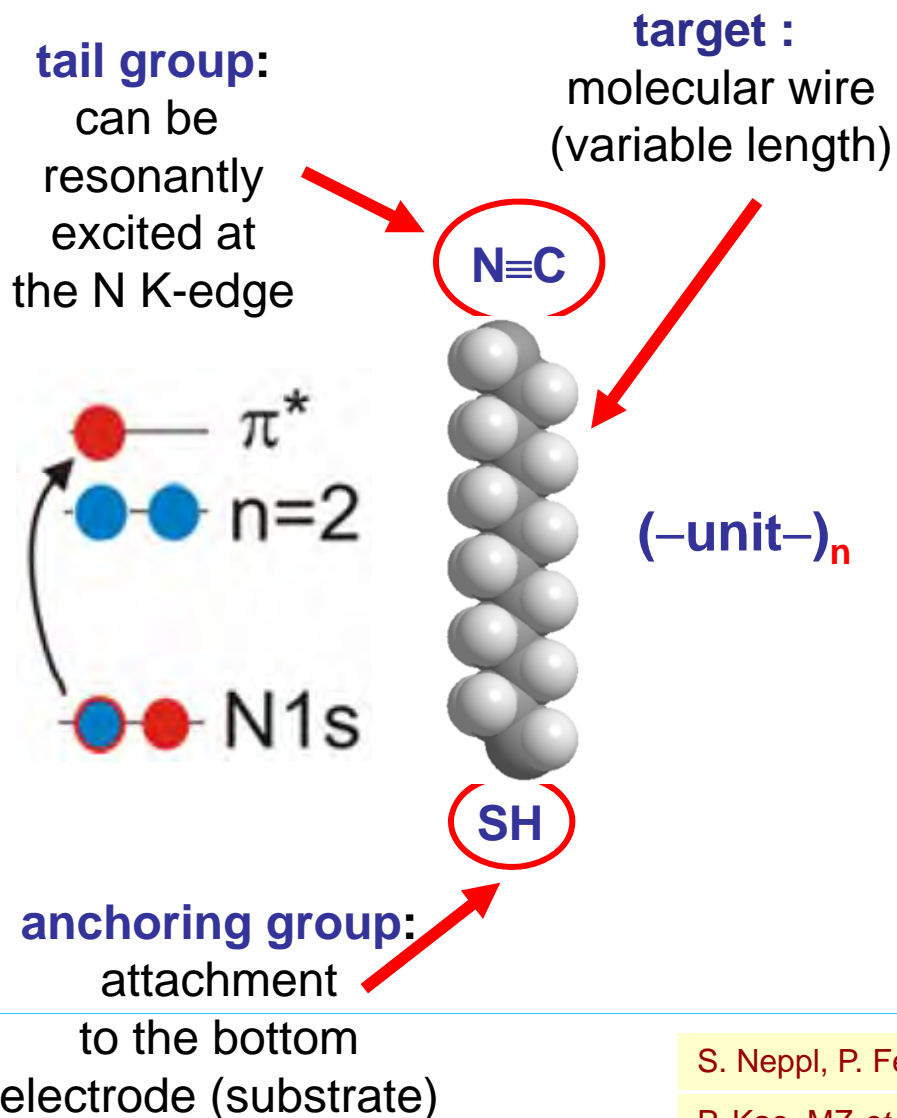


## The process involves individual molecules within a 2D assembly



- the number of the involved molecules (1) is precisely known
- RAES spectrum is an average over the assembly

# A basic system: alkyl chain (mol. wire): nitrile-substituted alkanethiolate SAMs on Au(111)



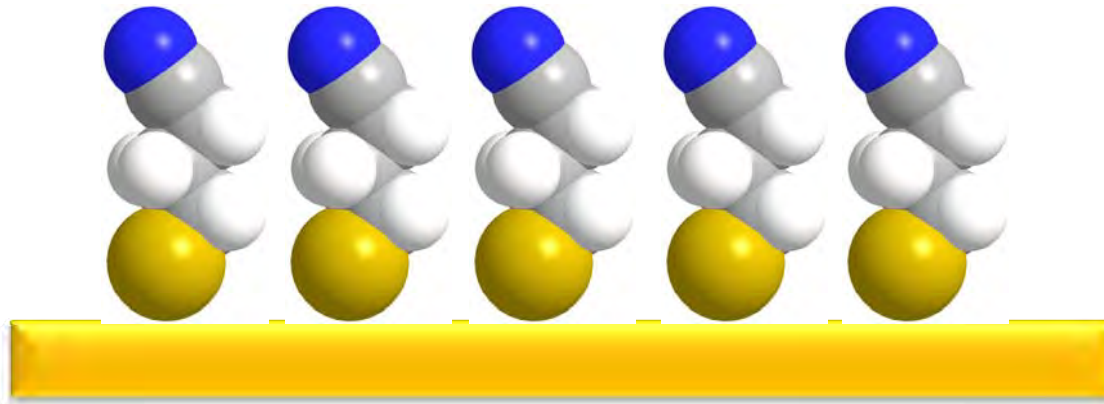
$(CH_2)_n$  chain:  $n = 2 - 4$  &  $16$

the films should survive  
exposure to ambient

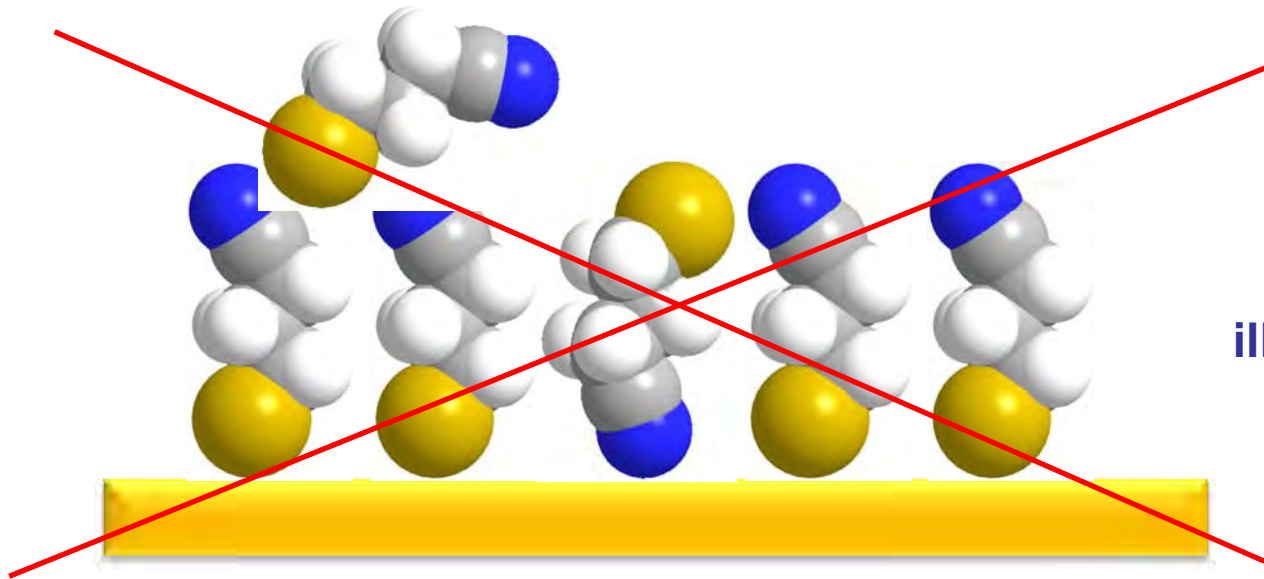
S. Neppel, P. Feulner, MZ *et al.*, *Chem. Phys. Lett.* **447**, 227 (2007)

P. Kao, MZ *et al.*, *J. Phys. Chem. C* **114**, 13766 (2010)

## An important requirement: well-defined films



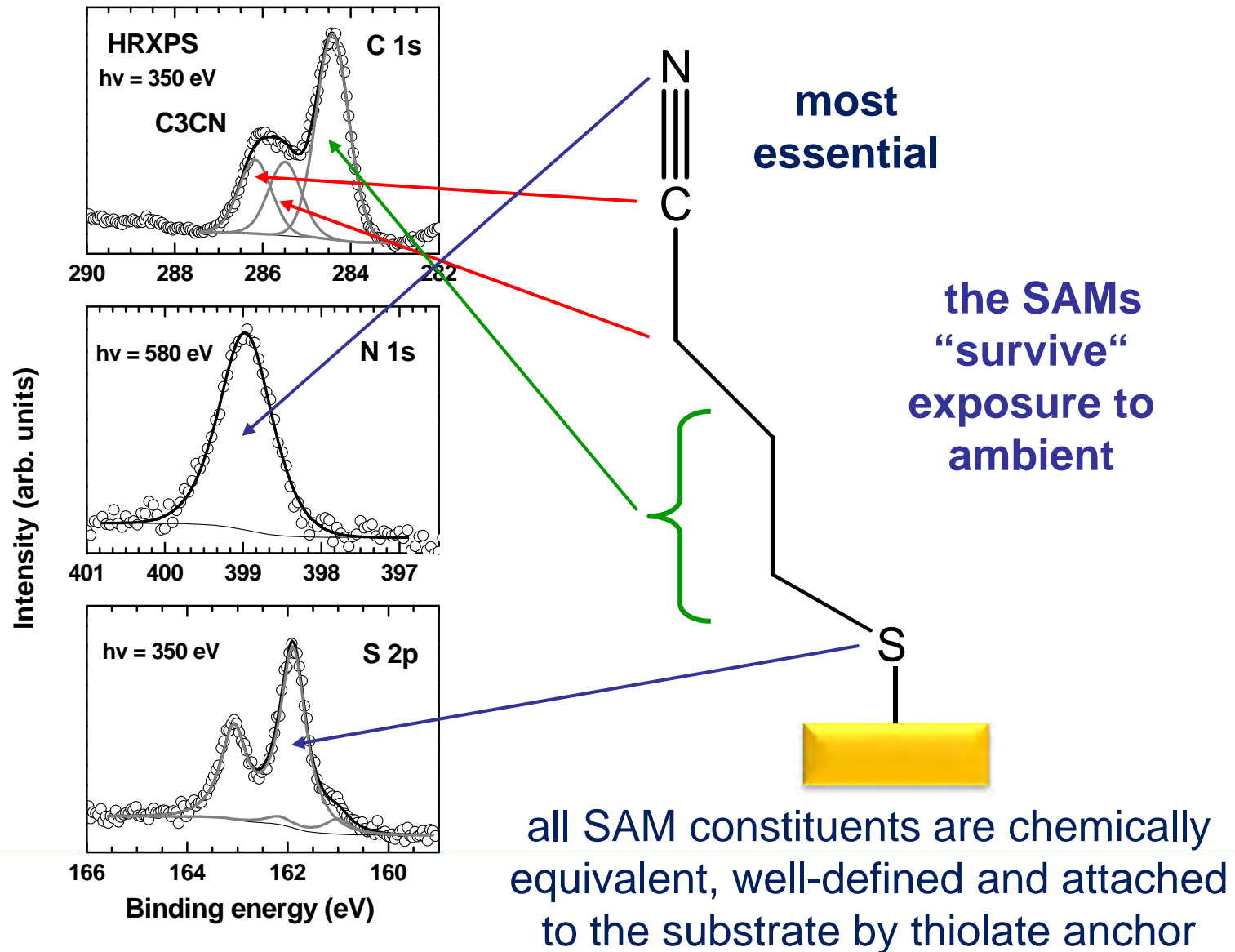
chemical  
integrity &  
homogeneity



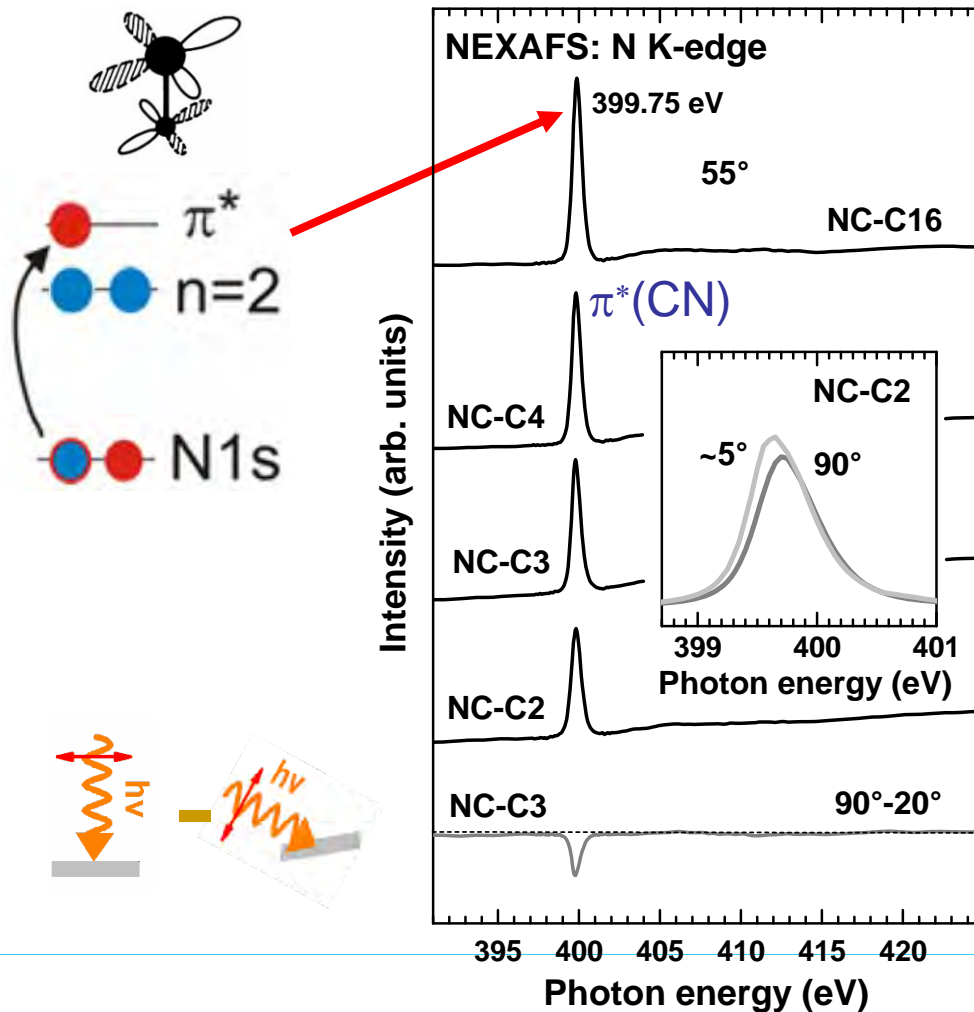
heterogeneity,  
ill-defined character

a detailed proof by advanced X-ray spectroscopy

# Identity and integrity of the SAMs: HRXPS



# Integrity and orientational order in the NC SAMs: X-ray absorption spectroscopy at the N K-edge



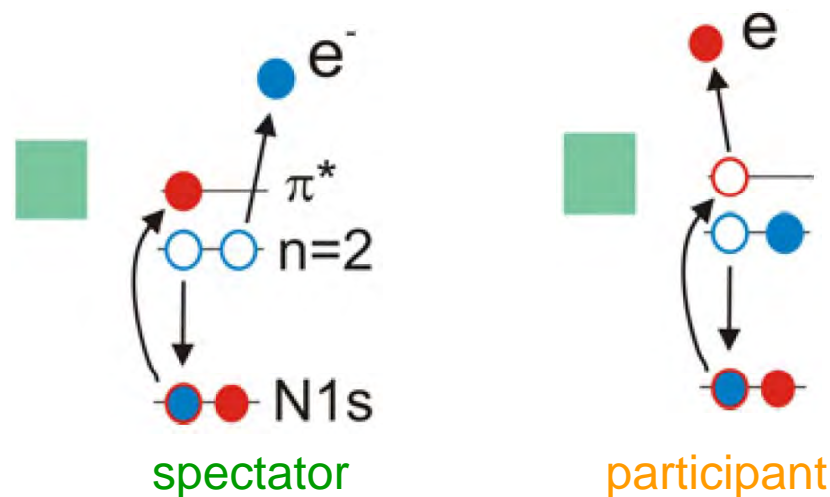
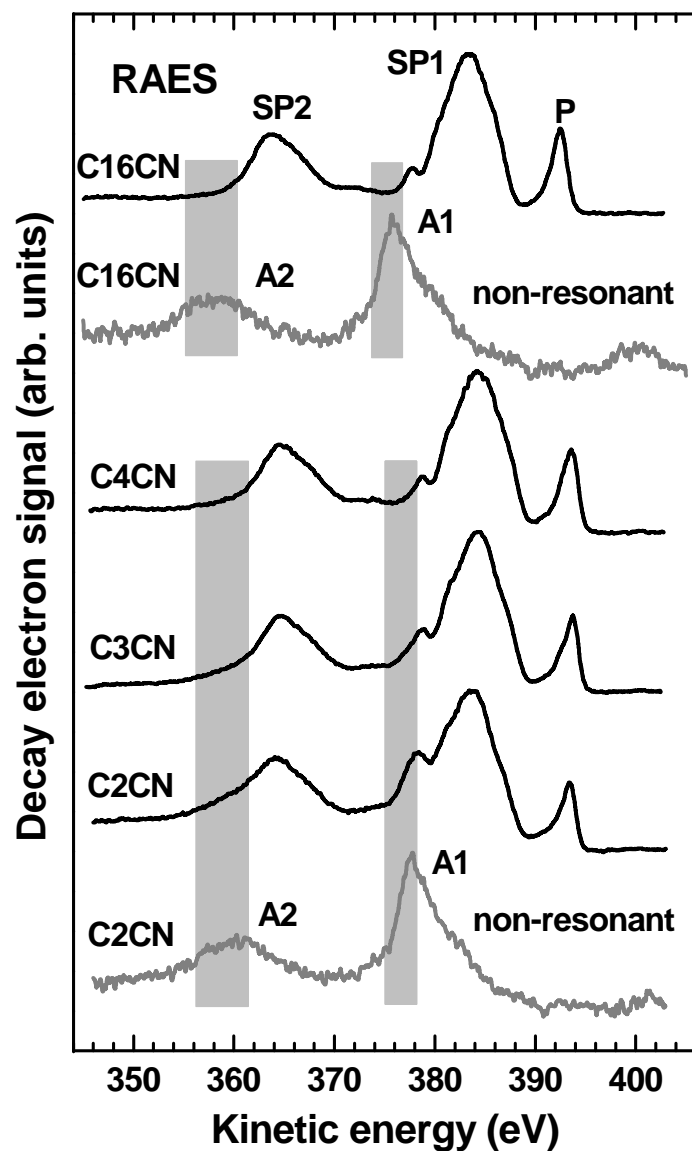
The degenerated  $\pi(\text{C}\equiv\text{N}^*)$  orbital, is used for the resonant excitation:  
 $\text{N}1s \rightarrow \pi(\text{C}\equiv\text{N}^*)$

No contamination

The energy of the  $\pi^*(\text{CN})$  resonance does not depend on the chain length

← CN groups are strongly inclined (as expected)

# RAES - $[N1s]\pi^*(C\equiv N)$ - spectra of the alkyl-based films

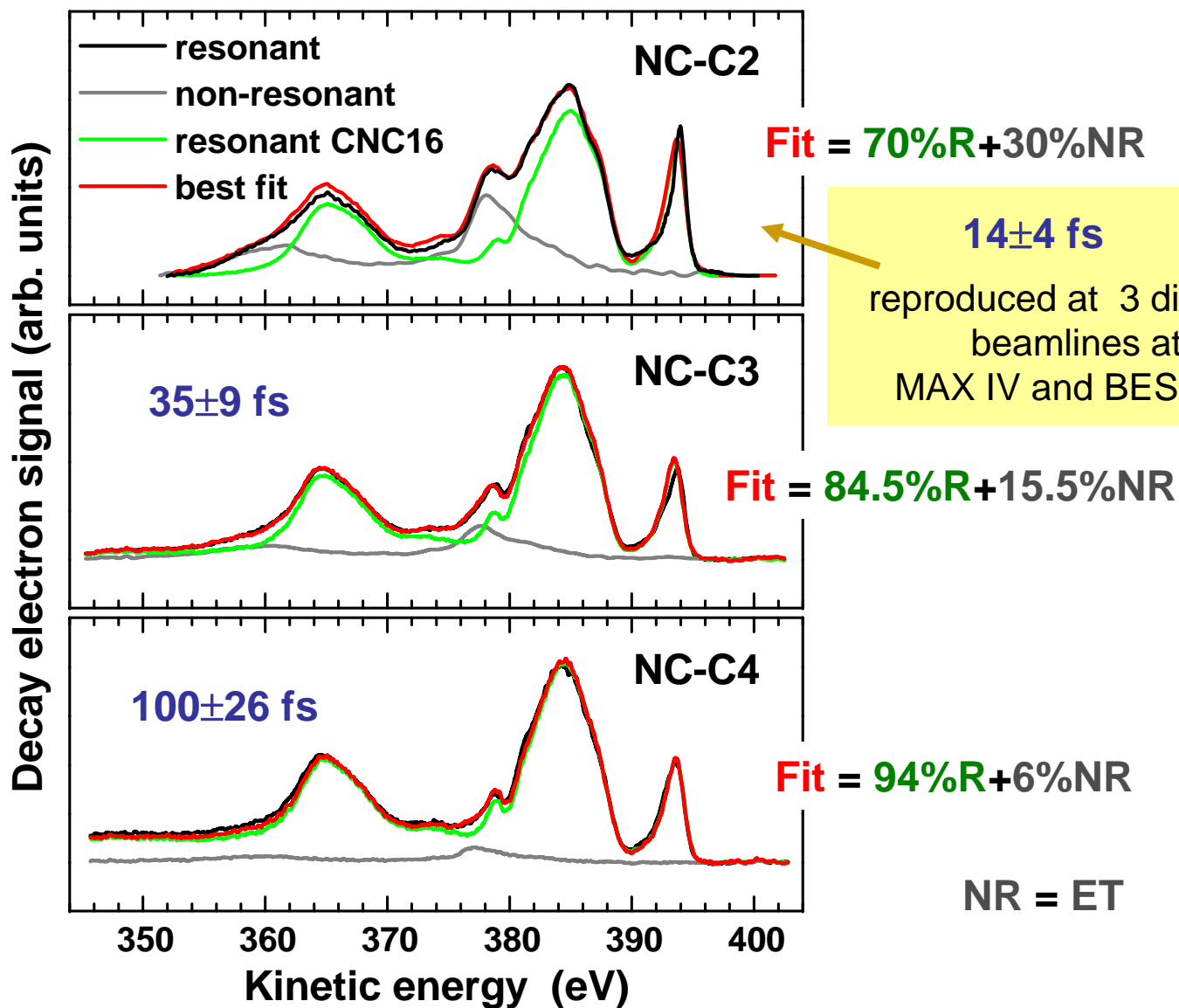
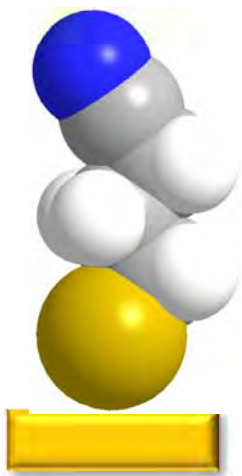


**SP1:** double holes in outer valence orbitals  
**SP2:** holes in outer and inner valence orbitals

■ - the ranges where the non-resonant (ET) contributions can be expected

- no trace of ET in the RAES spectra of NC-C16
- clear trace of ET in the RAES spectra of NC-C2, NC-C3, & NC-C4
- ET weight decreases with increasing  $n$

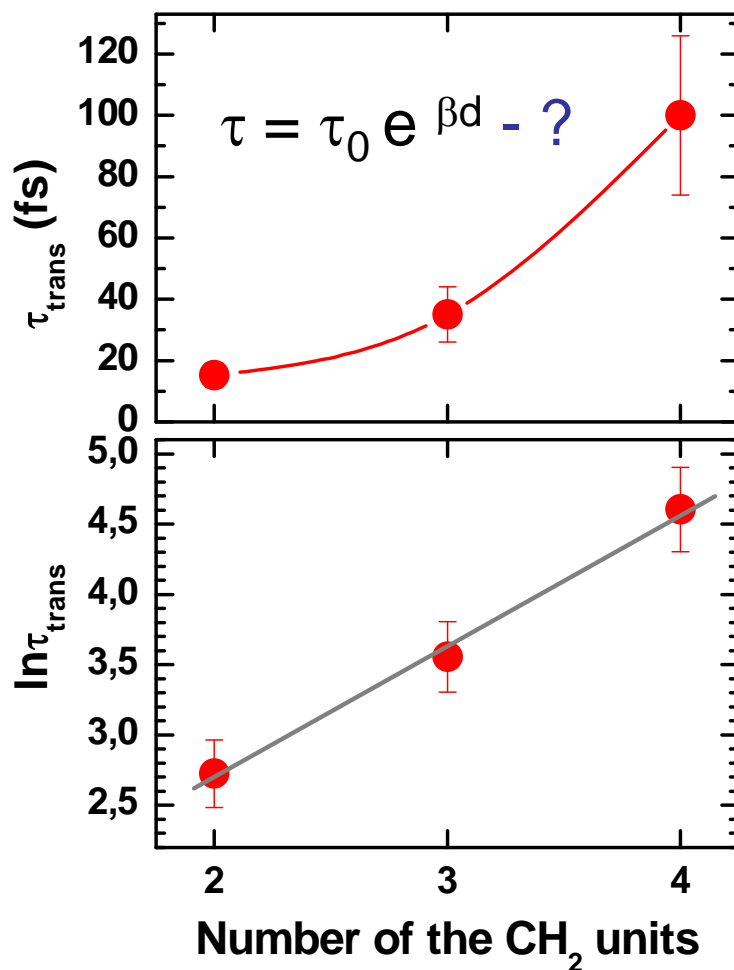
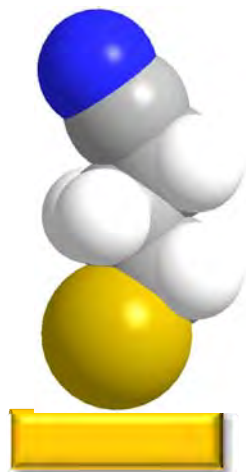
# Decomposition of the $[N1s]\pi^*(C\equiv N)$ RAES spectra



$14 \pm 4$  fs  
reproduced at 3 different  
beamlines at  
MAX IV and BESSY II

# Charge transfer time for alkyl-based systems

$$\tau_{ET} = \tau_{core} (1 - P_{ET}) / P_{ET}$$



$\tau = \tau_0 e^{\beta d}$  - analogous to the static conductance

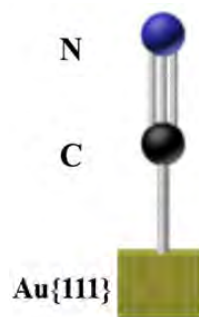
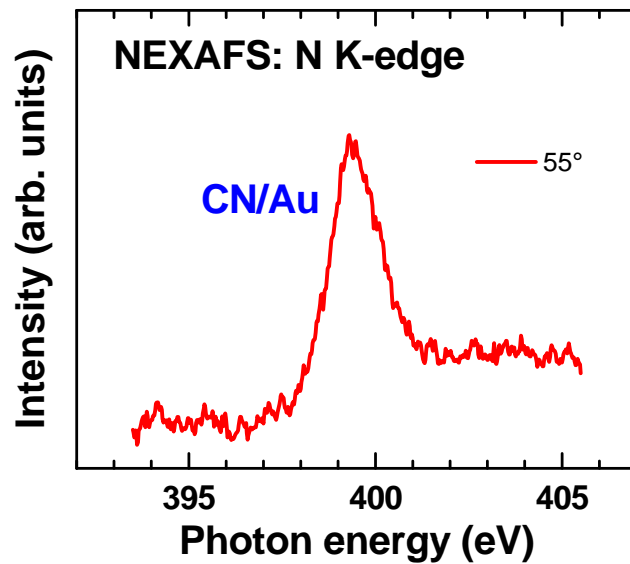
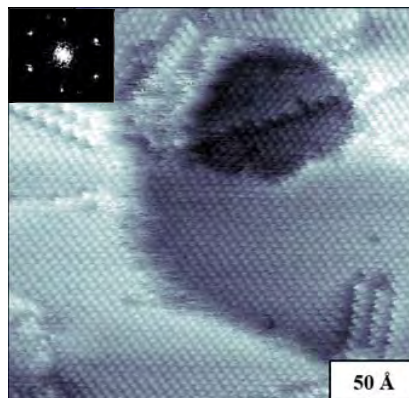
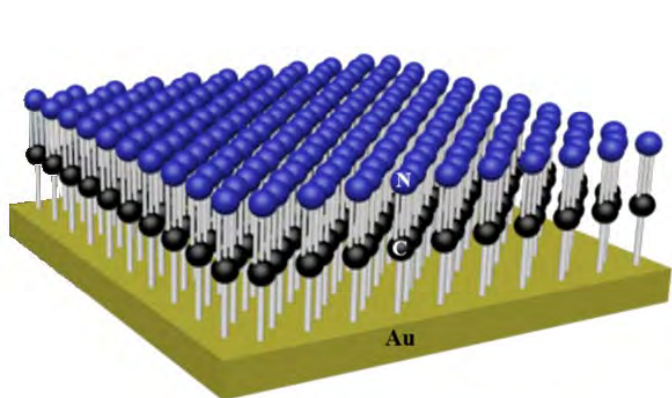
$\beta = 0.93$  per CH<sub>2</sub> = 0.72 Å<sup>-1</sup>  
- nearly identical to the static conductance value

$\ln \tau_0 = 0.83 \Rightarrow$   
 $\tau_0 = \tau(\text{C-S-Au}) = 2.3$  fs  
- high conductance

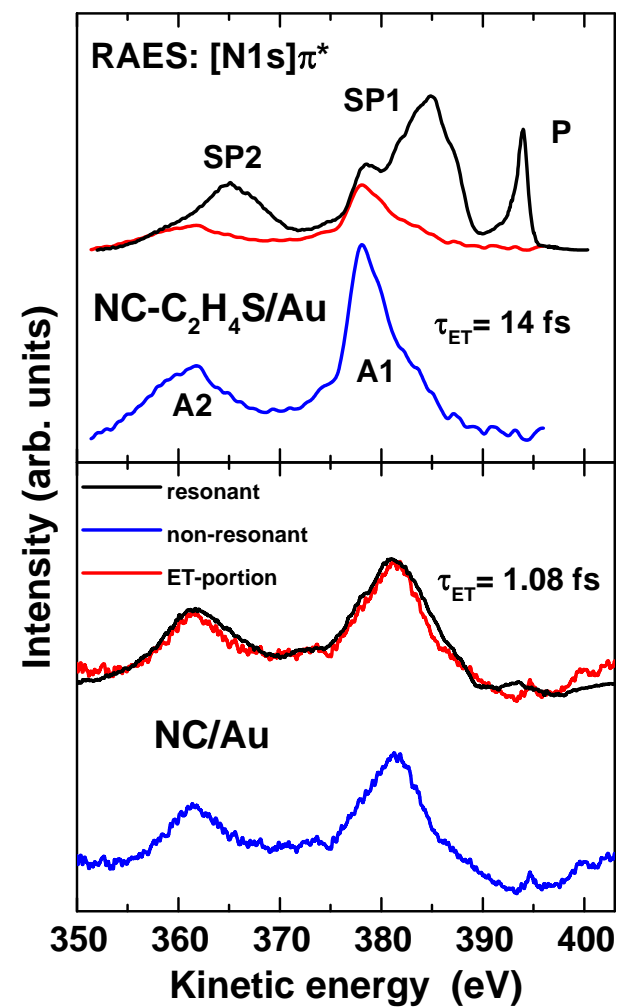
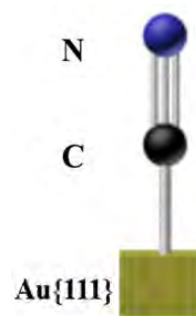
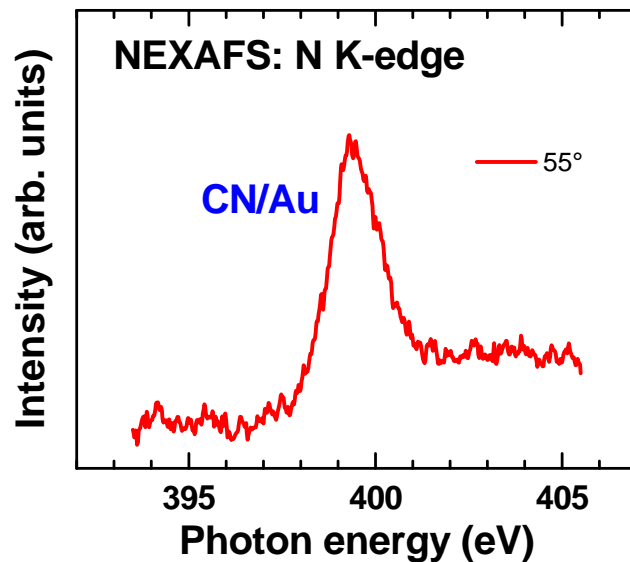
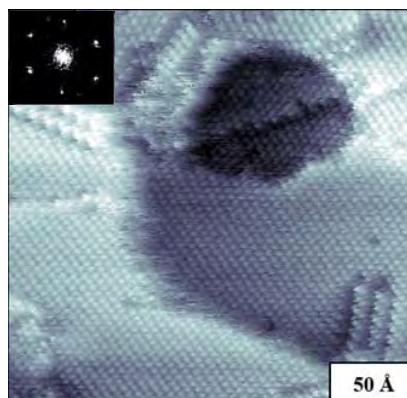
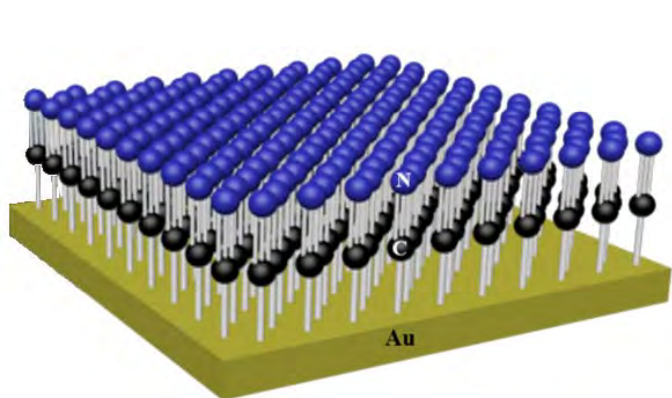
long ET time even for the short chain - important implications for molecular electronics & photoelectron spectroscopy



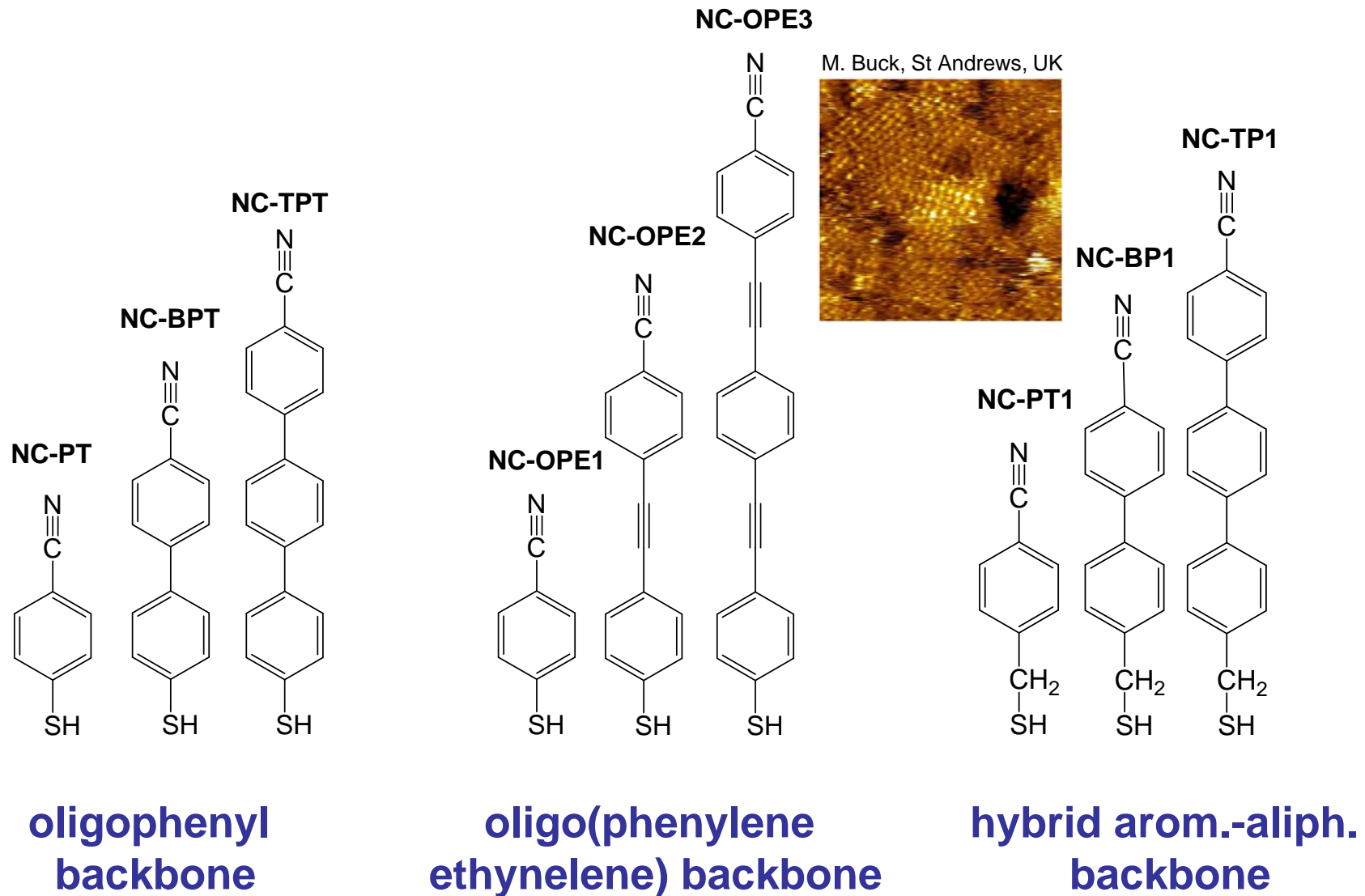
# An ultimate check of the approach: ultrafast electron transfer to the substrate



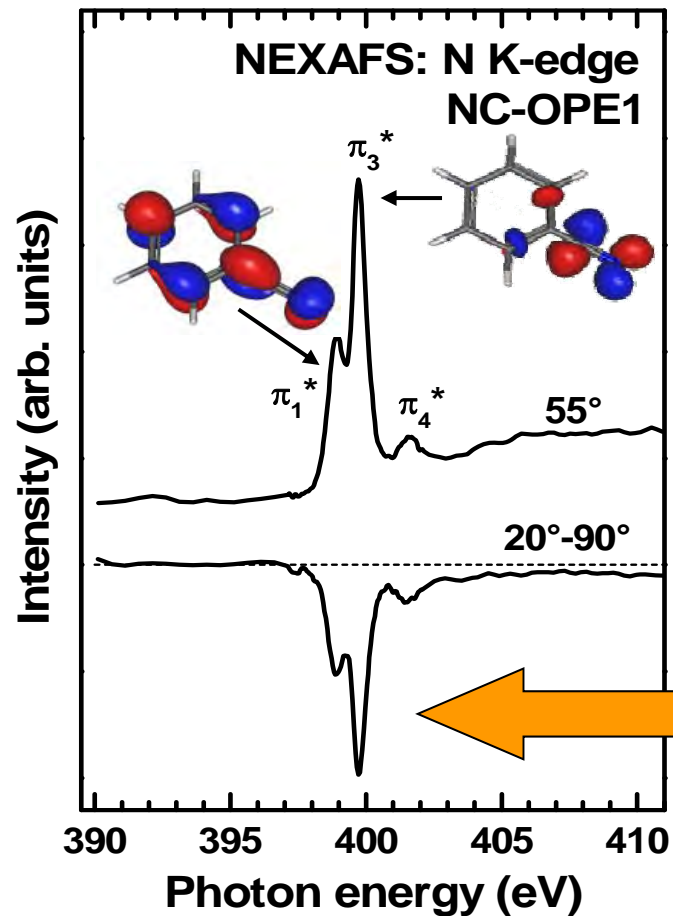
# An ultimate check of the approach: ultrafast electron transfer to the substrate



# Charge transfer dynamics in conjugated molecular wires



# Splitting of the $\pi^*(\text{N}\equiv\text{C})$ resonance into two components which can be selectively addressed by NEXAFS & RAES



the degeneration of the  $\pi^*(\text{C}\equiv\text{N})$  orbital is lifted

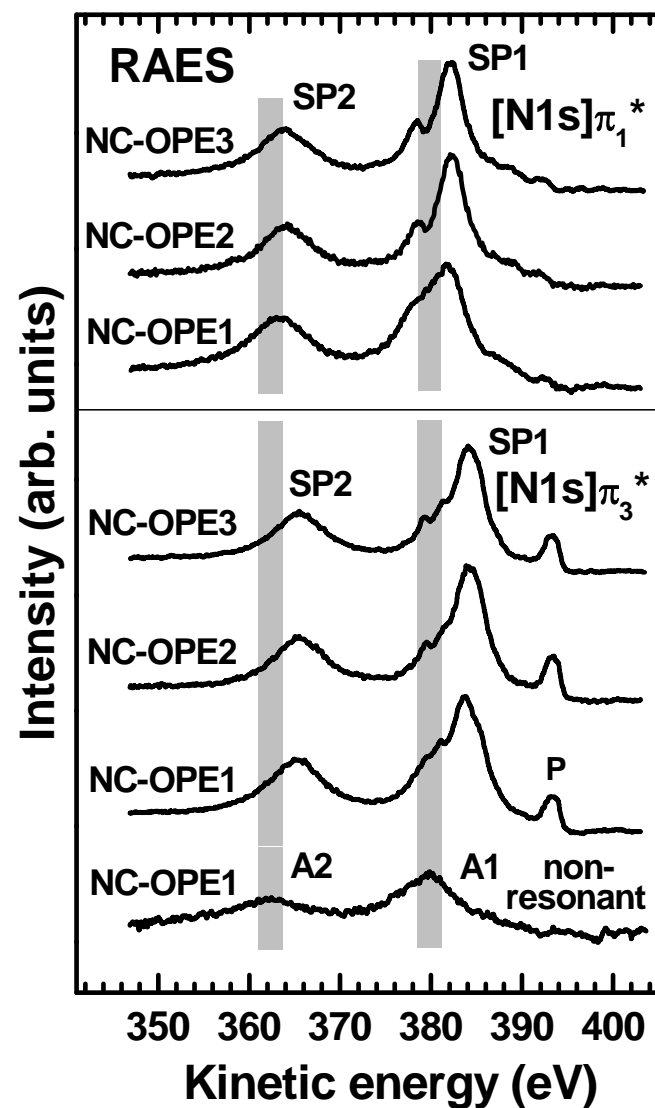
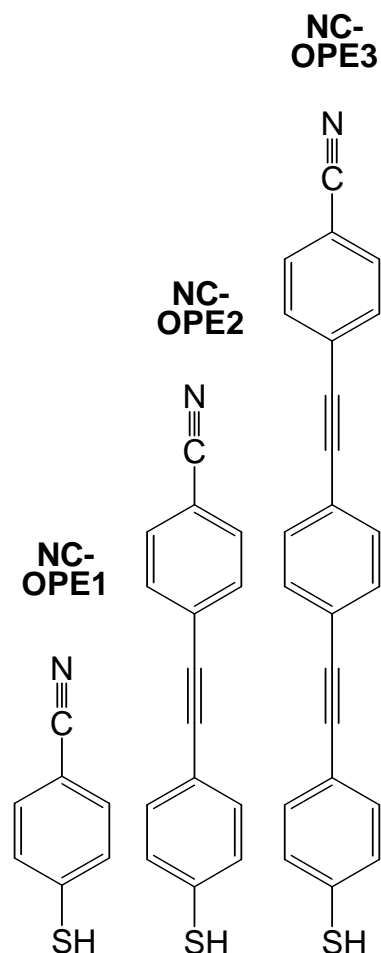
- $\pi_1^*$  is conjugated with the  $\pi^*$  system of the ring
- $\pi_3^*$  is localized at the CN group

good agreement with the previous calculations and gas phase data for benzonitrile

an upright orientation of the nitrile group

# Molecular-orbital-selective RAES spectra

(OPE, representative for the OPh and OPh1 series as well)



■ - the ranges where the non-resonant contributions can be expected

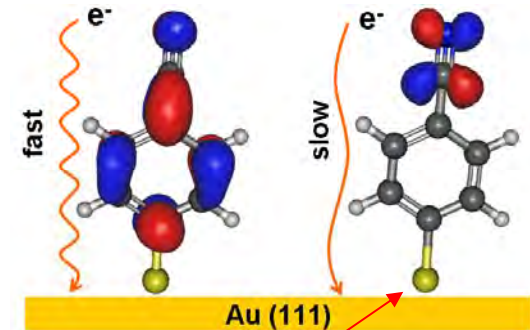
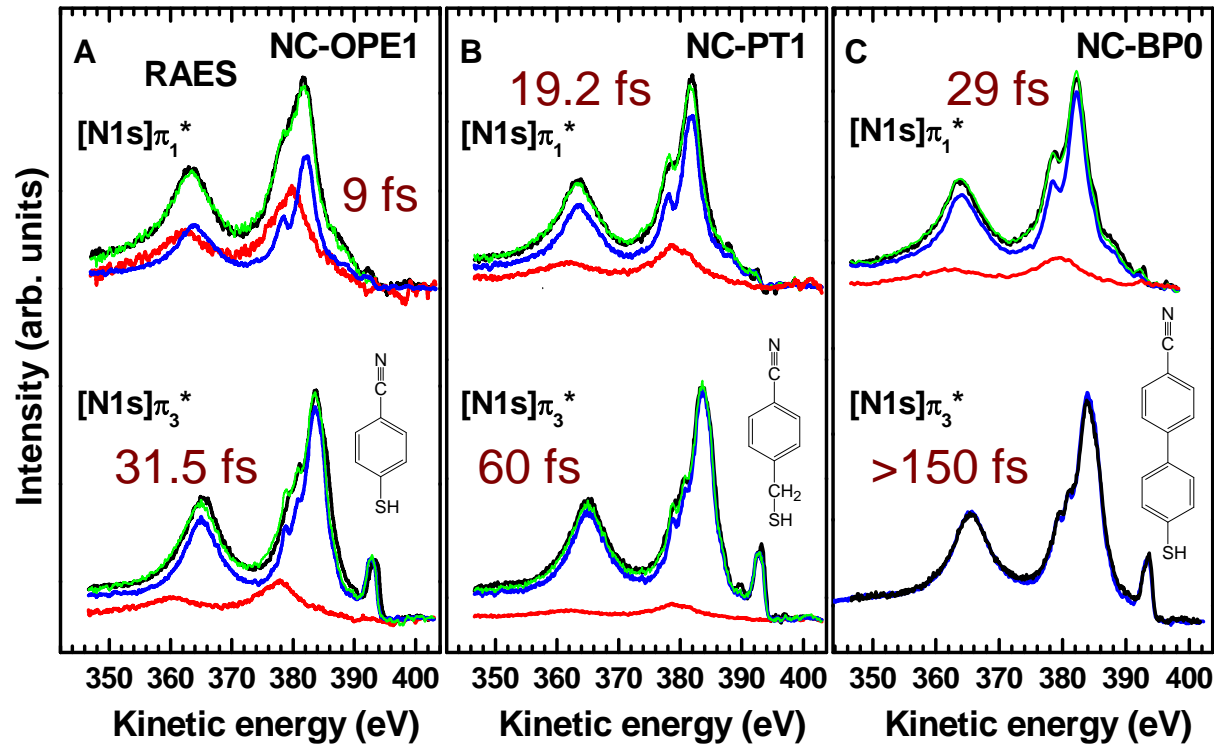
Disappearance of the P feature in the  $\pi_1^*$  case – an interesting side effect

No traces of ET in the RAES spectra of NC-OPE3 & NC-OPE2

These spectra are almost identical

Clear trace of ET in the RAES spectra of NC-OPE1 (as well as NC-PT1 and NC-BPT)

# Orbital-dependent ET dynamics – an particular advantage of the approach

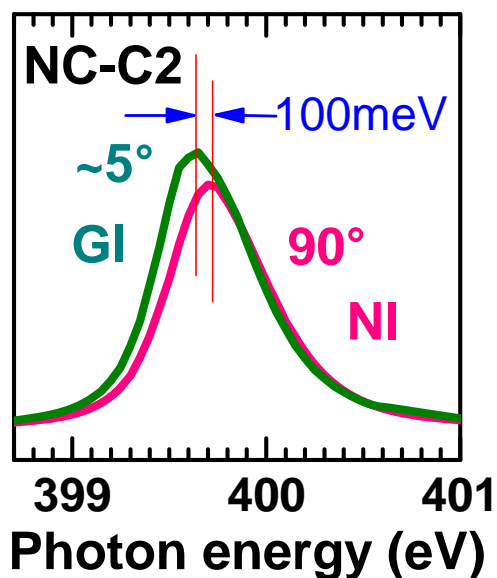


$$\tau_{\text{C-S-Au}} = 2.8 \text{ fs}$$

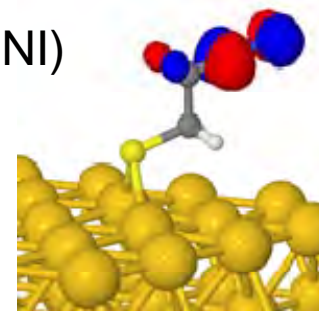
Oligophenyl wire:  $\beta(\text{conjugated}) = 0.28 \text{ \AA}^{-1}$   
 $\beta(\text{non-conjugated}) = 0.55 \text{ \AA}^{-1}$  close to the static value

The efficiency and rate of ET in molecular wires can be controlled by resonant injection of the charge carriers into specific MOs.

# Going back to the alkyl chain: looking at the degenerated $[N1s]\pi^*$ resonance in detail

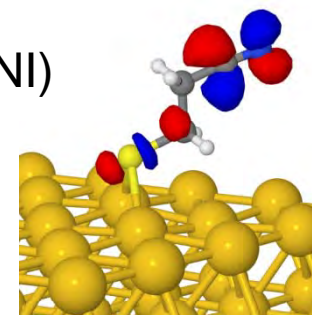


Normal incidence (NI)



$\pi_2^*$

Grazing incidence (NI)



$\pi_1^*$

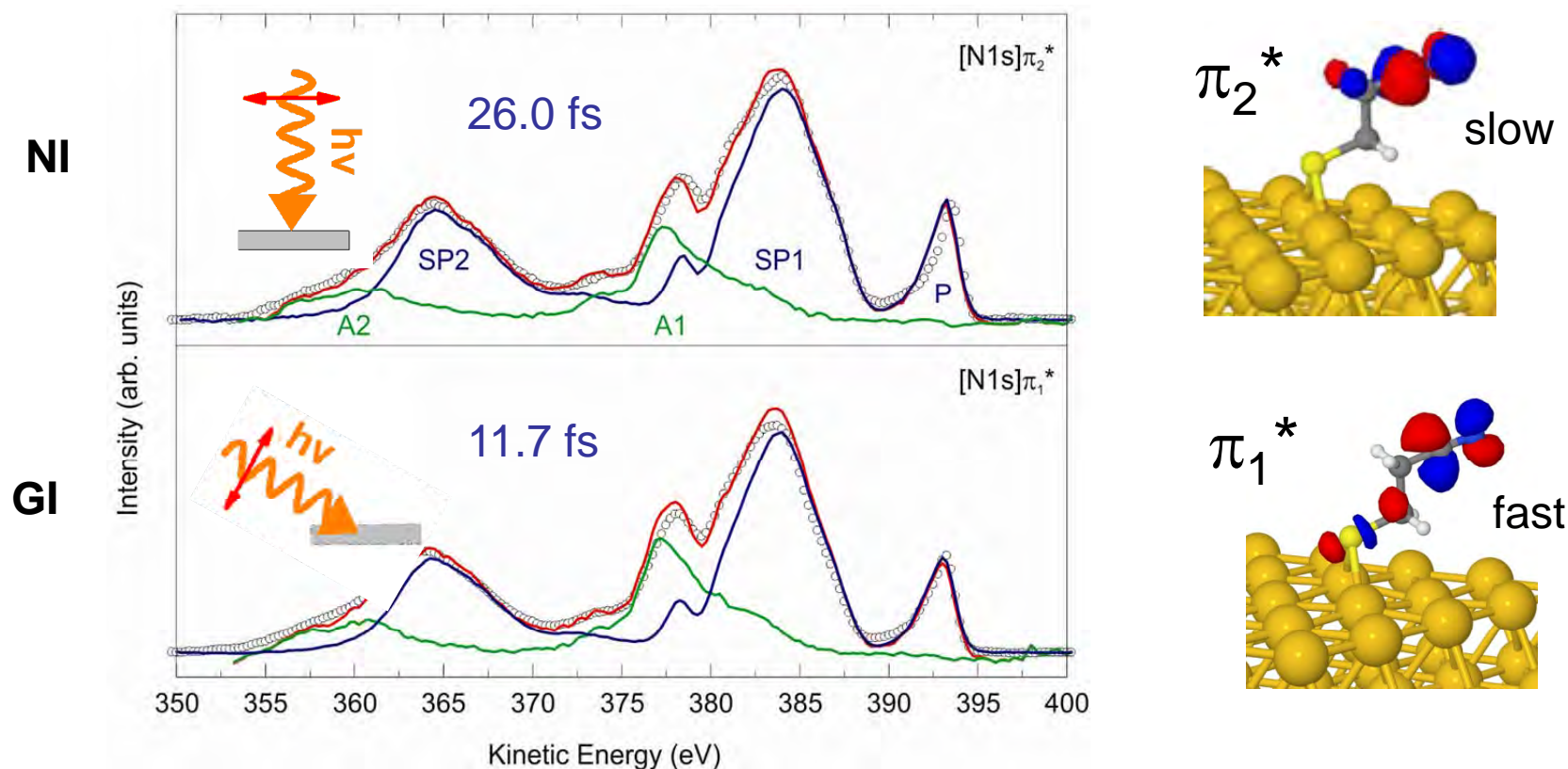
S. Neppl, P. Feulner, MZ *et al.*, *Chem. Phys. Lett.* **447**, 227 (2007)

F. Blobner, P. Feulner, M. Thoss, MZ *et al.*,  
*J. Phys. Chem. Lett.* **3**, 436 (2012)

The degeneration is lifted to some extent but the energy separation between the  $\pi_1^*$  and  $\pi_2^*$  orbitals is ~100 meV only which is too small to address them selectively by the energy selection.

Can it be done by exploiting symmetry selection rules?

# Exploiting symmetry selection rules rather than the photon energy tuning



The observed difference in  $\tau_{ET}$  is related to the different extension of the  $\pi_1^*$  and  $\pi_2^*$  orbitals onto the alkane backbone and the anchoring sulfur atom.

The efficiency and rate of CT in molecular wires can be controlled by resonant injection of the charge carriers into specific MOs.



# Acene backbone

Conflicting and hardly explainable results for the static conductance:

$$\beta = 0.51 \text{ \AA}^{-1} \text{ (thiols \& isocyanides)}$$

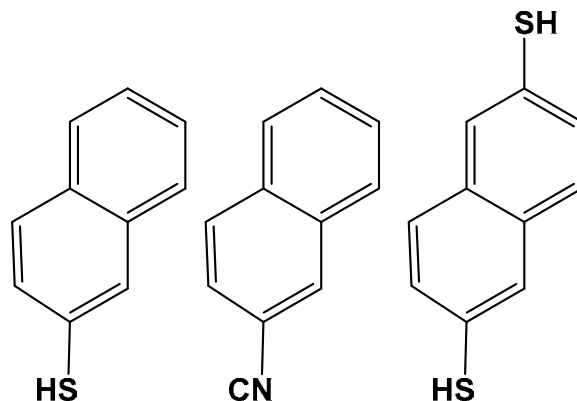
B. S. Kim, C. D. Frisbie, *et al.*, JACS 128, 4970 (2006)

$$\beta = 0.5 \text{ \AA}^{-1} \text{ (thiols)}$$

$$\beta = 0.2 \text{ \AA}^{-1} \text{ (dithiols)}$$

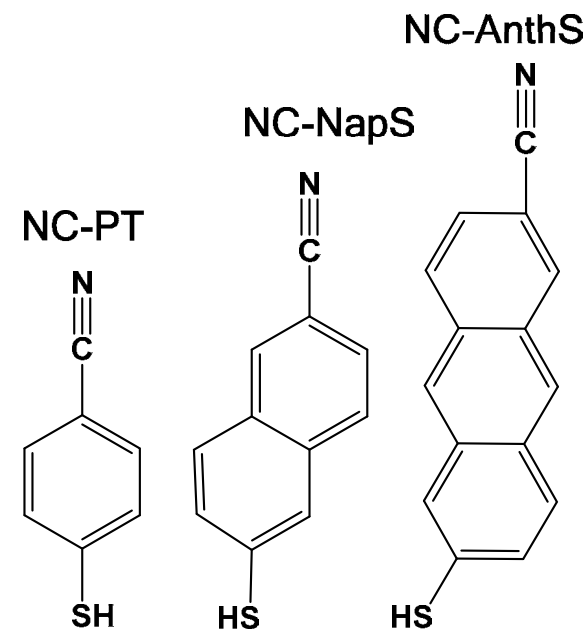
B. S. Kim, C. D. Frisbie, *et al.*, JACS 133, 19864 (2011)

is  $\beta$  affected by the coupling to the top electrode?



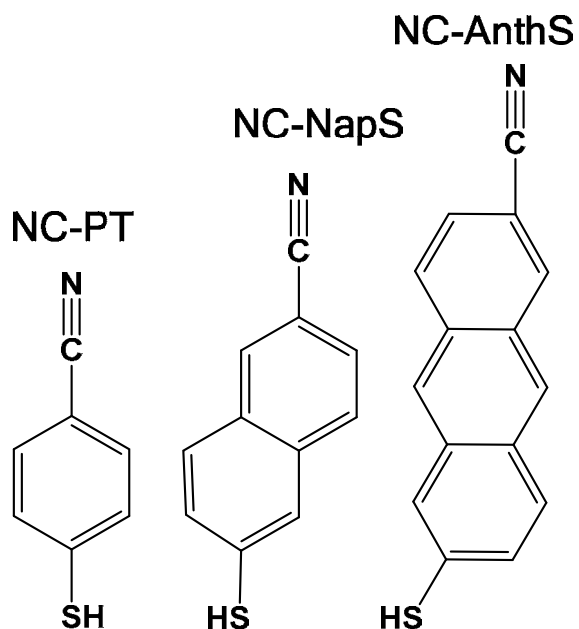
$$J = J_0 e^{-\beta d}$$

can be proved with our approach:

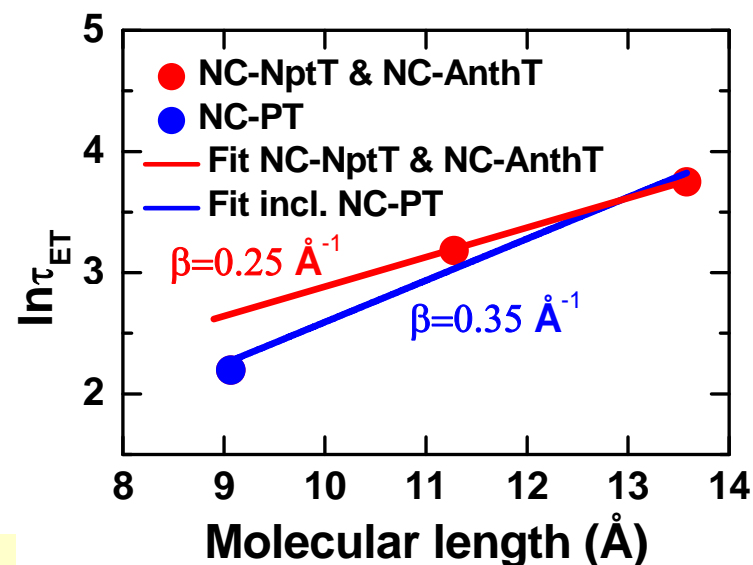
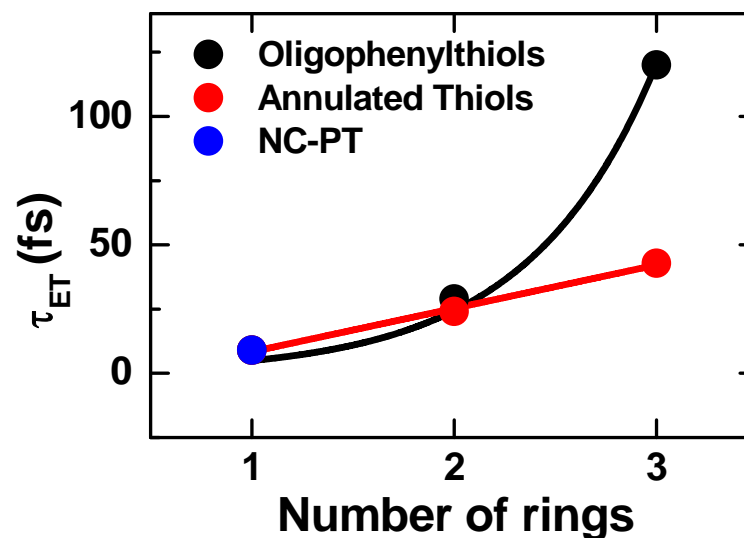


ideal coupling to the "top electrode" (photon)

# The smaller $\beta$ value suits better in the ET dynamics case – the effect of the coupling is verified

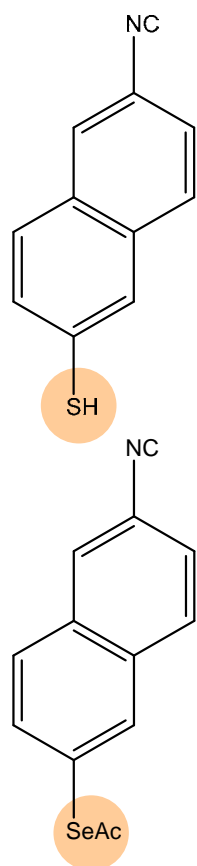


NC-PT can be hardly considered as a true member of the acene series

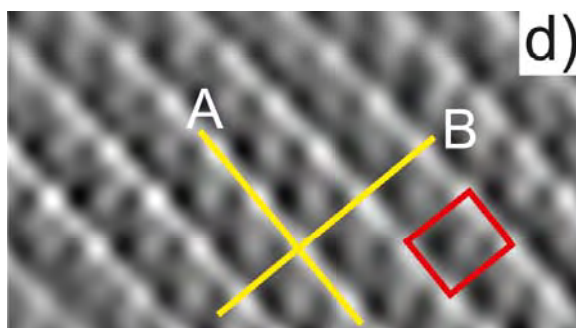
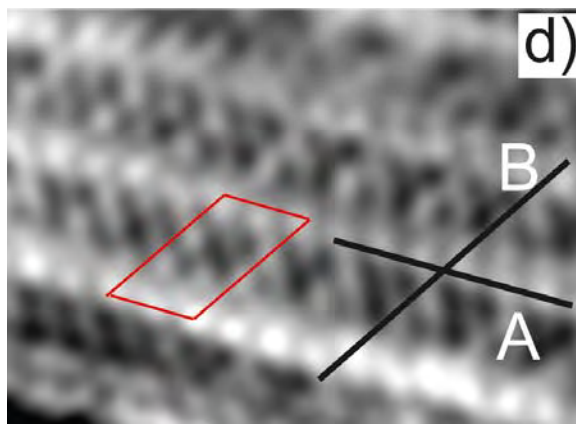


# Se as an alternative to S: a better anchor for ME?

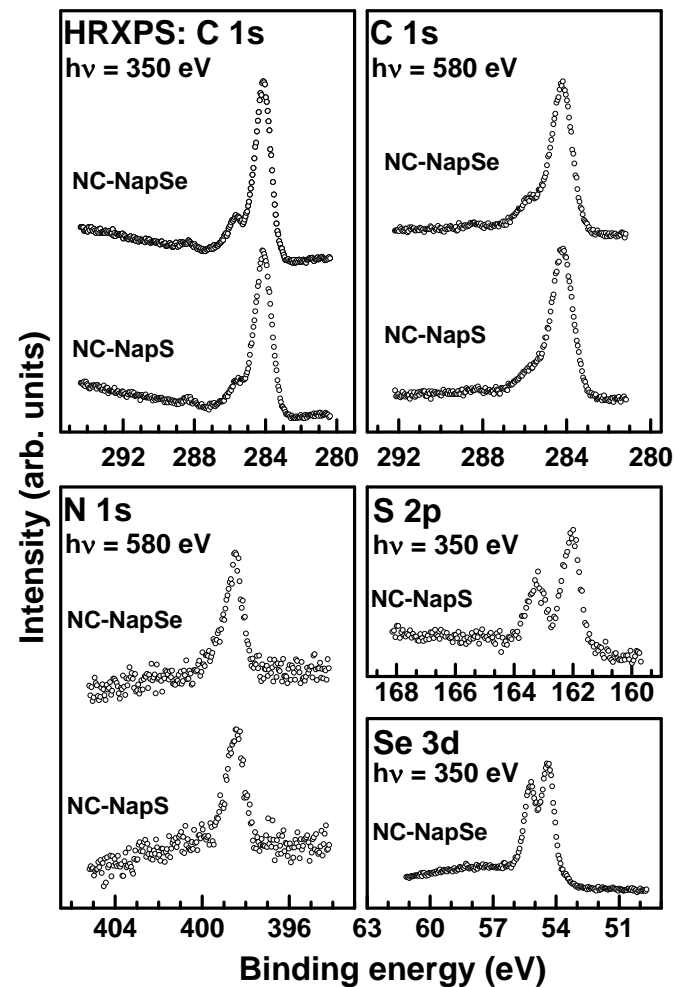
Literature: controversial statements (poorly defined systems, differences between the S- & Se-based films, contact problems?)



well-defined systems

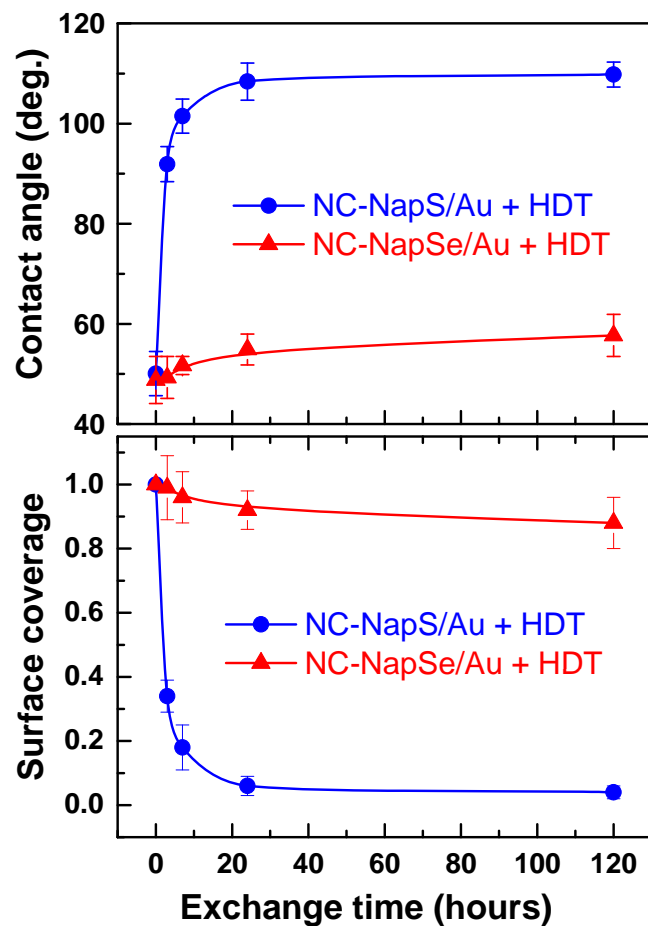


similar packing motif & molecular orientation; similar packing densities

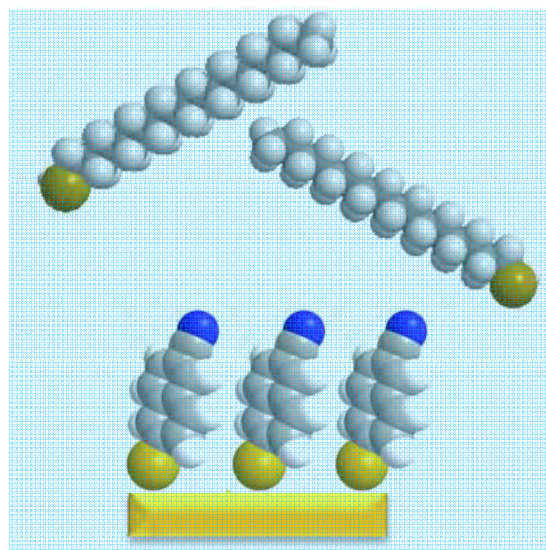


J. Ossowski, MZ, et al. ACS Nano 9, 4508 (2015)

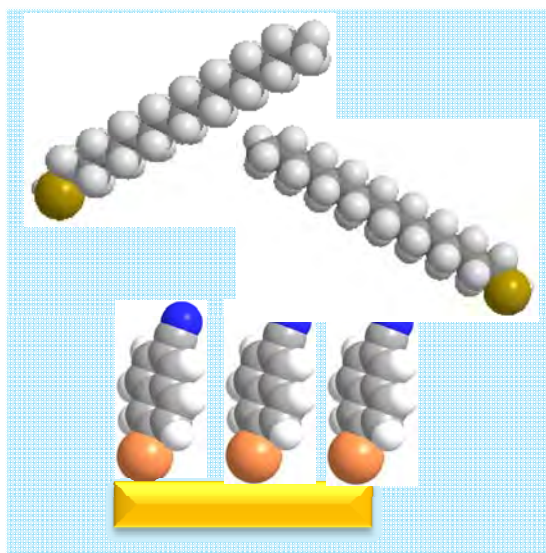
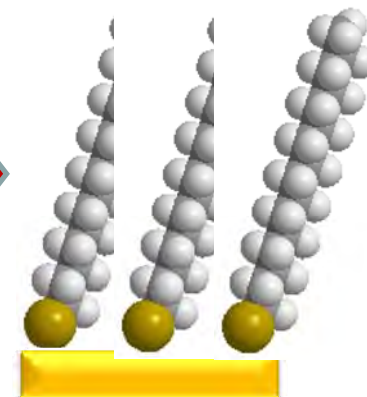
# Strength of the anchoring: exchange experiments



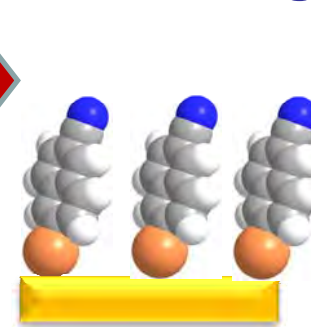
Se-Au bond is stronger than S-Au one



nearly complete exchange

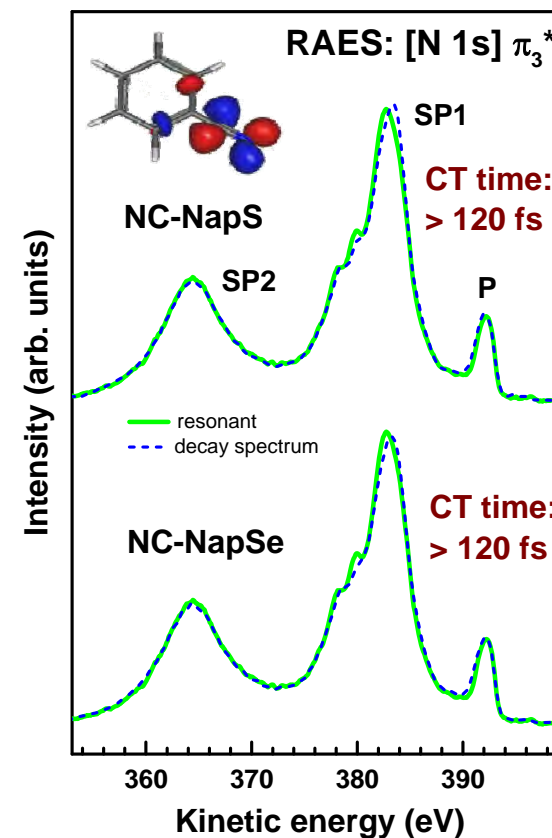
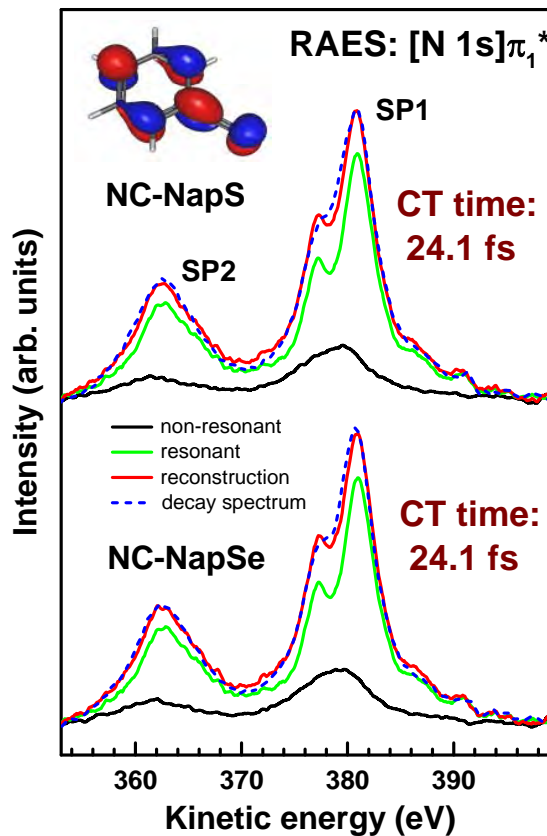
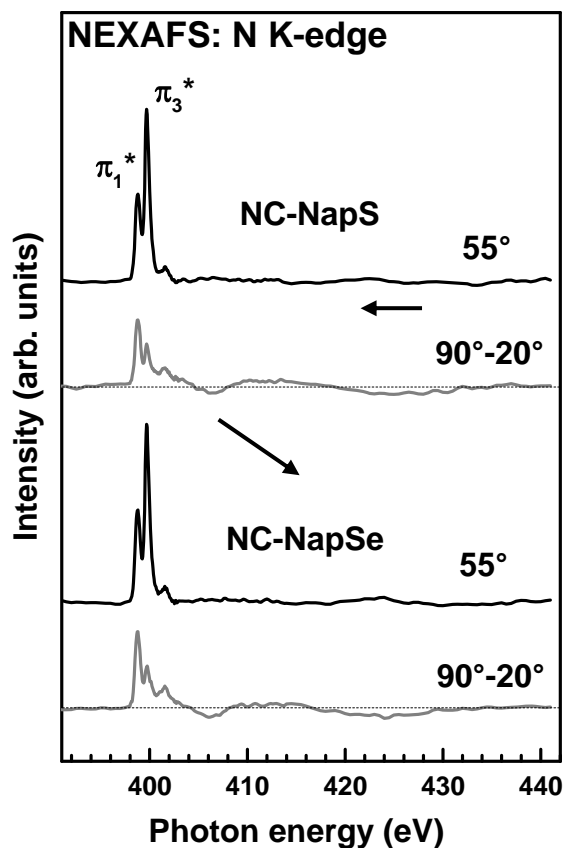


nearly no exchange



# S versus Se: nearly identical ET times

no contact problems; individual molecules are addressed



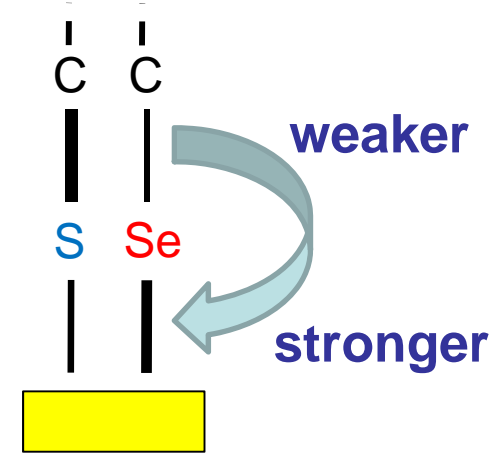
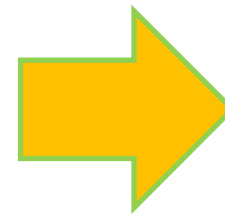
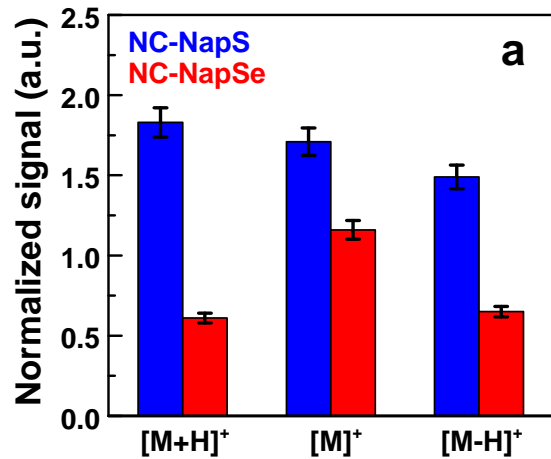
**similar ET properties**

(in spite of the stronger bond to the substrate in the case of Se!)

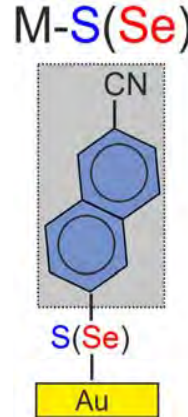
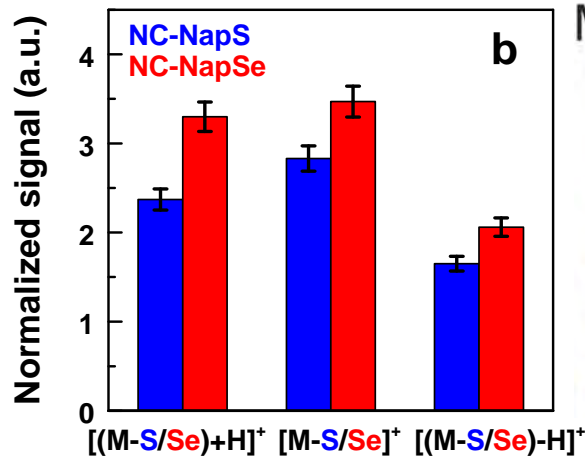
J. Ossowski, MZ, *et al.* *ACS Nano* **9**, 4508 (2015)

analogous result for NC-AnthS & NC-AnthSe (JPCC 2018)

# Static SIMS: redistribution of the electron density between the adjacent bonds

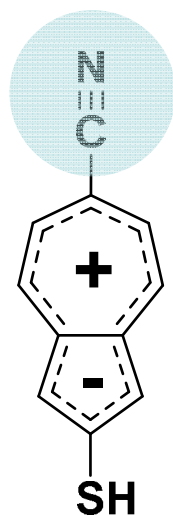


bond strength as a tentative fingerprint for the involvement of the electronic states

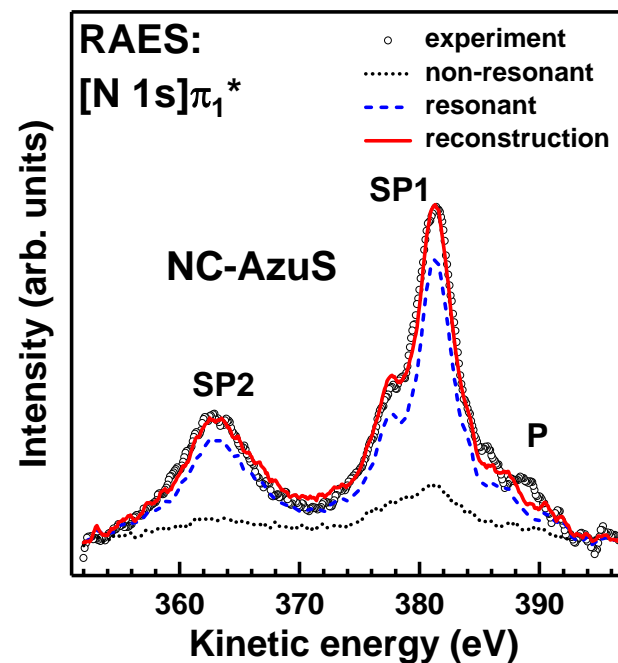
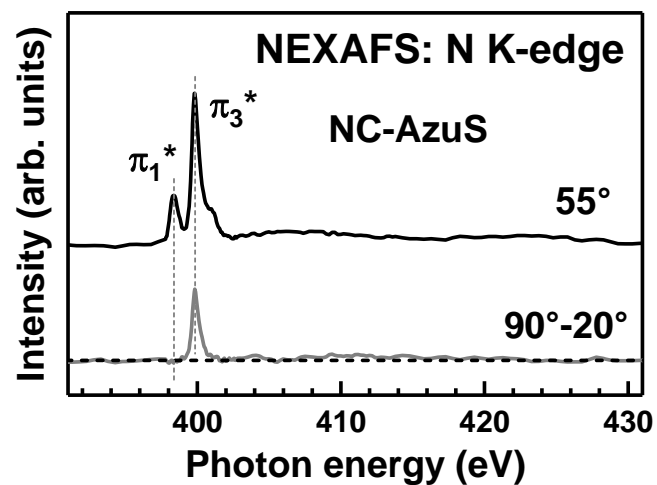


A possible reason for the similar transport properties: a stronger Se-Au bond is accompanied by a weaker Se-ring bond, bringing no gain for the total conductance

# Effect of molecular dipole



1 D



$$\tau_{\text{ET}} = 23.5 \text{ fs}$$

very similar to the value for the naphthalene backbone (no dipole) – **24.1 fs**

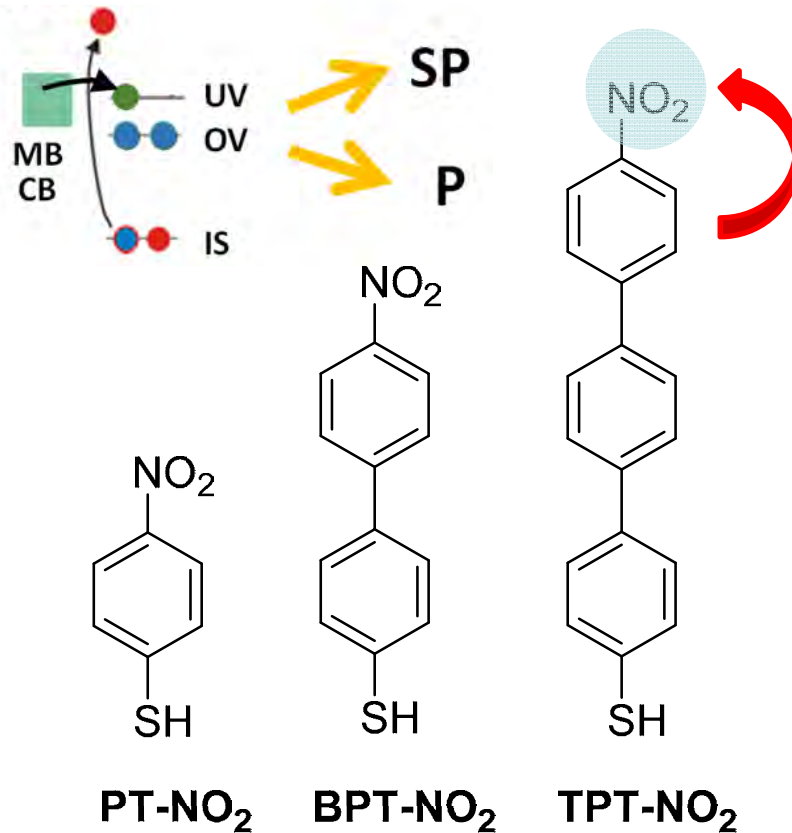
**no perceptible effect of molecular dipole**

T. Wächter, MZ *et al.*, *J. Phys. Chem. C* **121**, 13777 (2017)

confirmed by the dedicated experiments on other systems (not published yet)

# Other functional groups for site-specific excitation

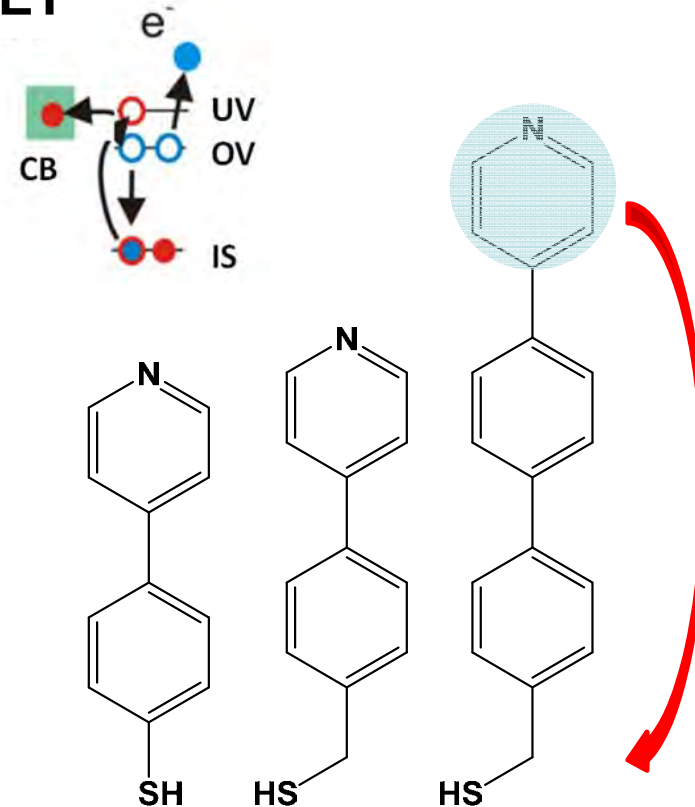
**A+IET**



- strongly electronegative group
- traces of RAES features in AES spectra
- only the adjacent ring is involved

T. Wächter, MZ *et al.*, *J. Phys. Chem. C* **118**, 26049 (2014)

**ET**

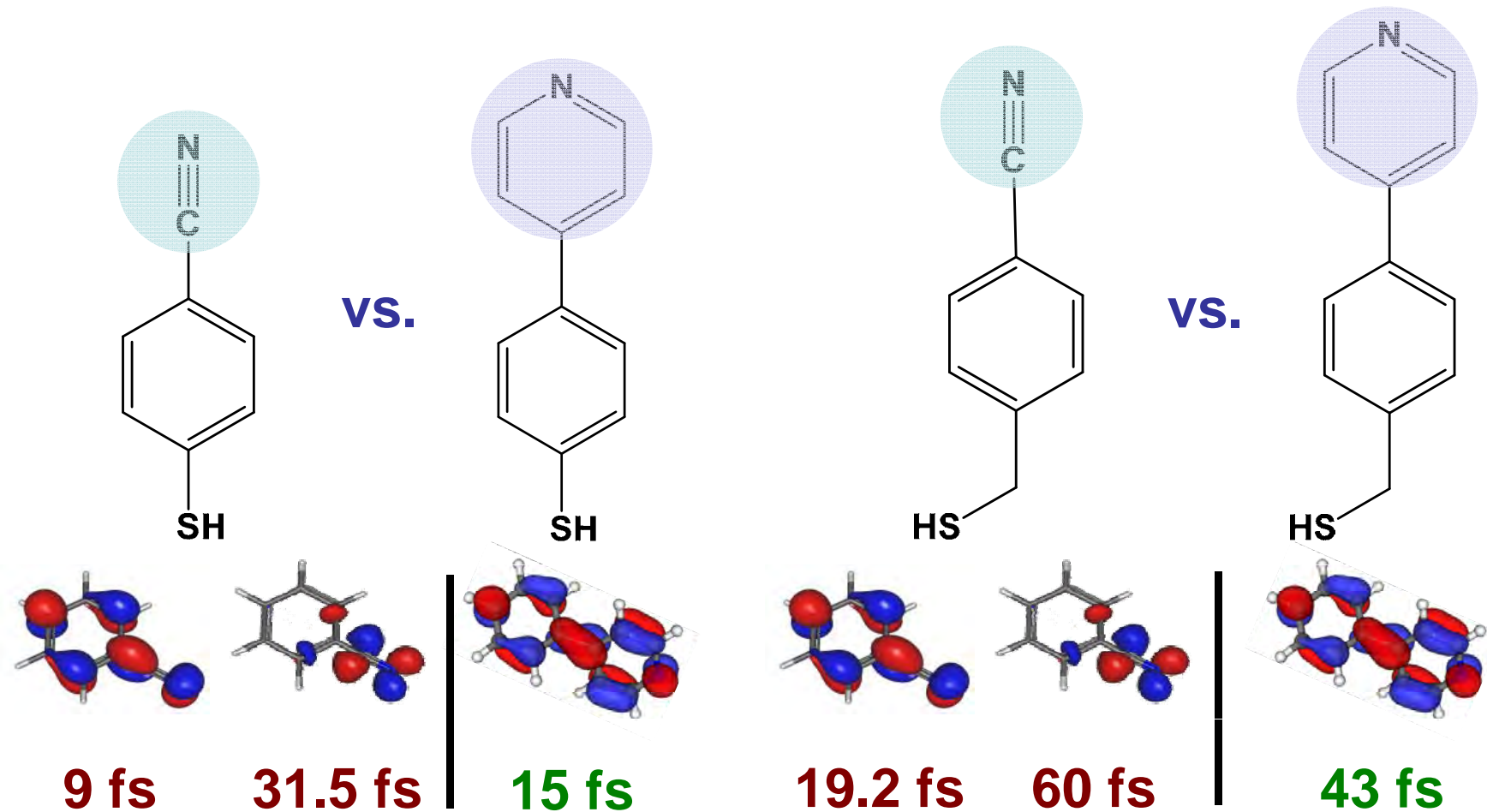


- pyridil is well-suited for CHC on SAMs
- perceptible traces of ET in RAES
- reasonable  $\tau_{ET}$

T. Wächter, MZ *et al.*, *J. Phys. Chem. C* **122**, 12534 (2018)



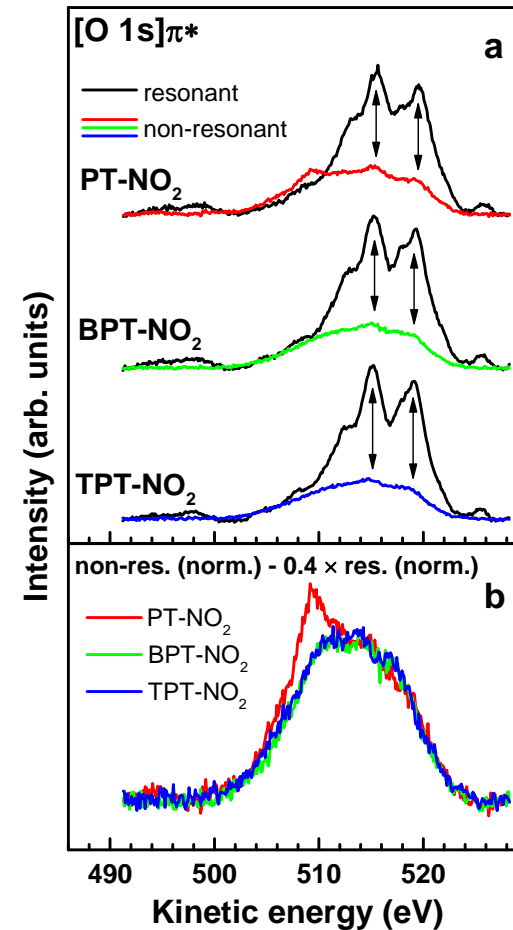
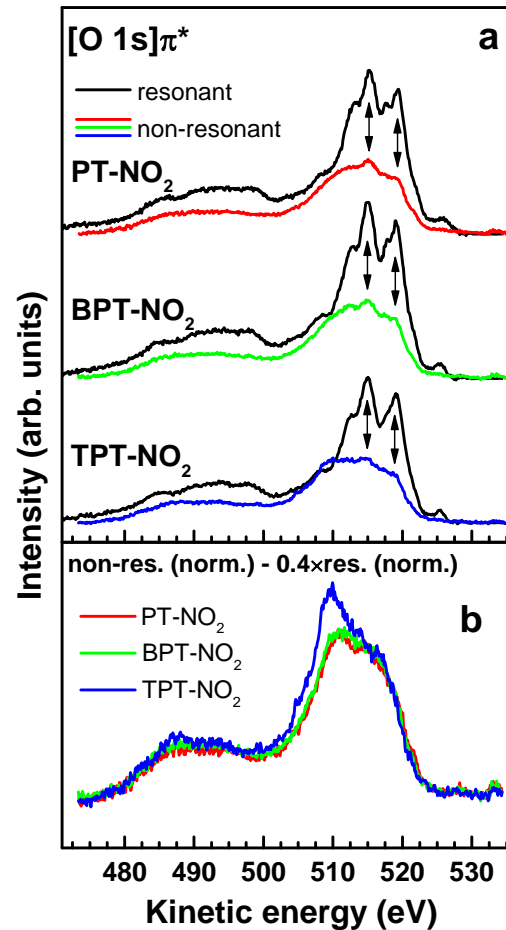
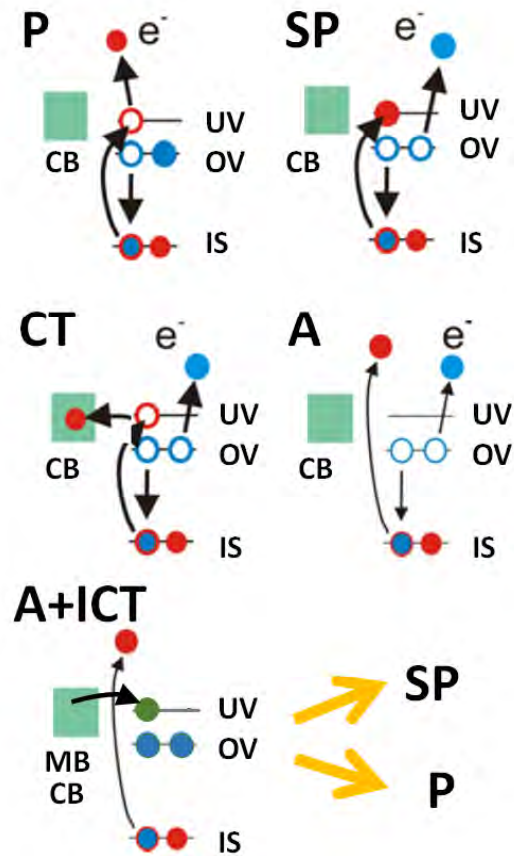
# Pyridine versus nitrile



H. Hamoudi, MZ *et al.*, *Phys. Rev. Lett.* **107**, 027801 (2011)

T. Wächter, MZ *et al.*, *J. Phys. Chem. C* **122**, 12534 (2018)

# Inverse electron transport



The presence of the resonant features in the non-resonant spectra suggests the inverse electron transfer. Similar extent of these features – only the adjacent ring is involved.

## **Take-home message**

**static conductance and ET dynamics are strongly related**

## **RAES-CHC**

**can be indeed considered as complementary to static conductance**

**fs time domain, individual molecules, ideal top contact,  
orbital-dependent ET**

## **Results**

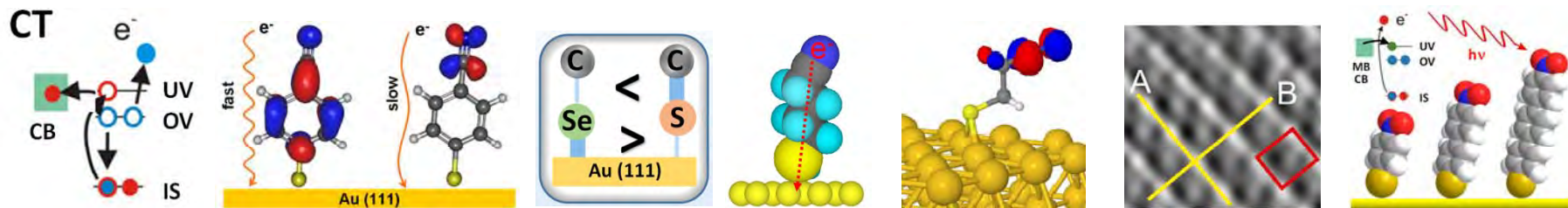
- numerical data ( $\beta_{\text{dynamics}}$ ,  $\tau_{\text{coupling}}$ , etc.)**
- effect of the anchoring group**
- effect of the top electrode**
- effect of molecular dipole, etc.**

# Co-authors & partners

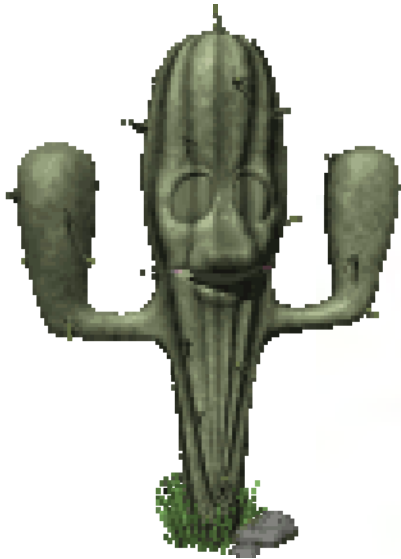
T. Wächter, A. Shaporenko, H. Hamoudi and P. Waske (Heidelberg)  
S. Neppi, F. Blobner, D. Menzel & P. Feulner (Munich, Germany) – general  
P. Kao & D. L. Allara (PennState, USA) – synthesis (aliphatic/OPE)  
A. Terfort et al. (Frankfurt, Germany) – synthesis (aromatic)  
P. Cyganik et al. (Krakow, Poland) – STM, SIMS (naphthalene)  
A. Guttentag & P. Weiss (UCLA, USA) – STM, IR, Raman (NC/Au)  
M. V. Barubin et al. (University of Kansas, USA) – synthesis (azulene)  
M. Thoss et al. (Erlangen-Nürnberg, Germany) – theory (symmetry)  
M. Buck et al. (University of St Andrews, UK) – STM (NC-TP1)

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**Thank you for your  
attention!**



Speedy Gonzales - "The Fastest Mouse in all Mexico"

courtesy of Warner Bros.