Ultrafast charge injection at complex interfaces: organic-organic, organic-inorganic and organic-graphene.

A.Morgante, Dean Cvetko, Albano Cossaro, Luca Floreano, Martina Dell'Angela, Gregor Kladnik

Istituto Officina dei Materiali

IOM-CNR TASC Laboratory Trieste Italy

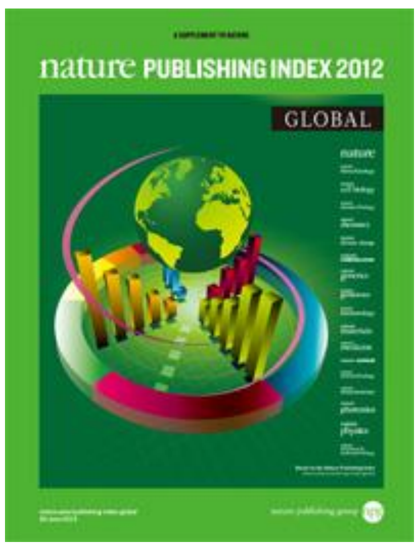
University of Trieste Italy, University of Ljubljana, Slovenia, Elettra Trieste

Milano Bicocca University

Guido Fratesi, Gian Paolo Brivio

Columbia University

Latha Venkataraman, John Kymissis, Alon Gorodetsky



IOM

Headquarters in Trieste
90 CNR permanent
100 associated permanent staff
Phd students, post docs etc

IOM@ Trieste Basovizza
IOM@ SISSA Trieste (theory)
Neutrons and X-rays @ Grenoble research activities at synchrotron and neutron european sources
IOM@Perugia
IOM@ Cagliari (Theory)

Nature publishing index – 2012 - 2019 global 200
CNR only italian Institution IOM top

Nanoscience and material facility

•Fine analysis

Synchrotron radiation

Electron microscopy center

Scanning probe microscopies

•MICRO and NANO FABRICATION

Lithography (electronic, optic, X-rays, ionic)

Nano imprinting

Nano manipulation

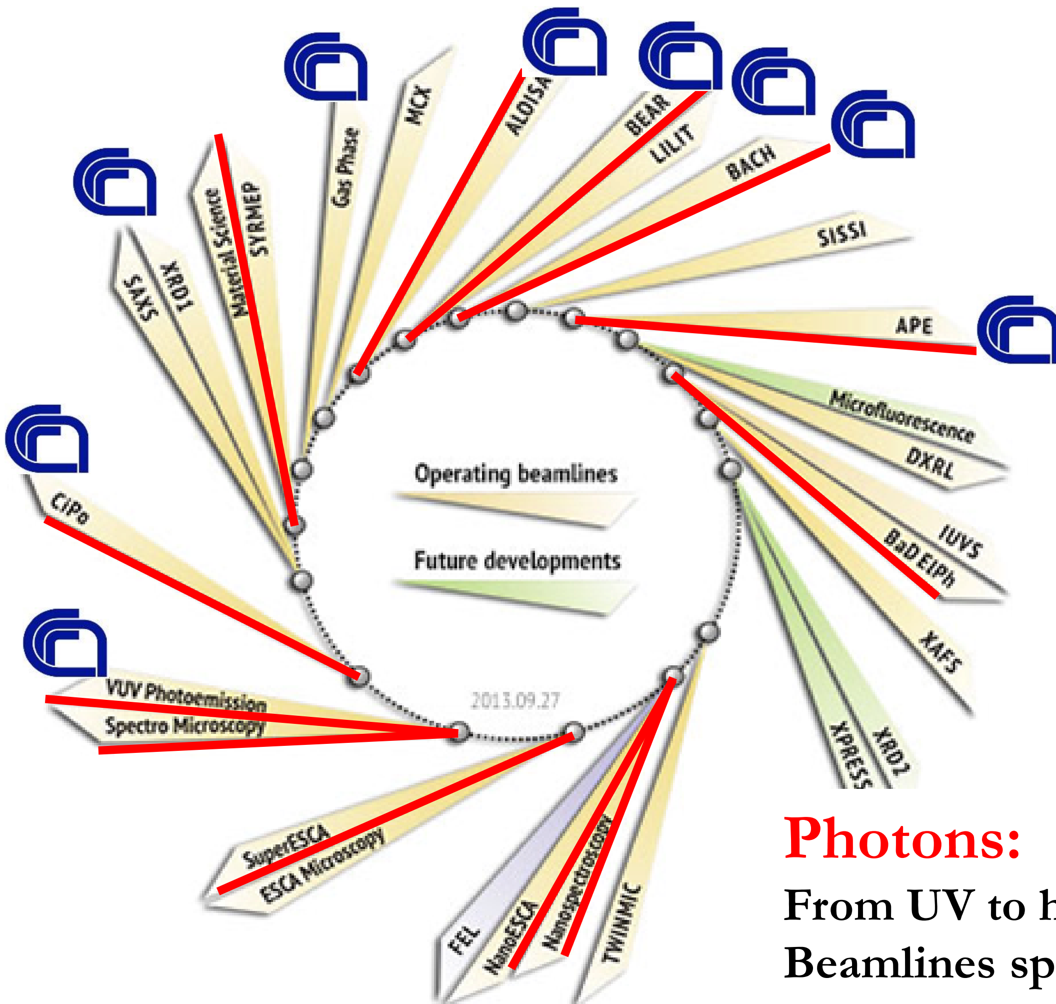
•NANOSTRUCTURED MATERIALS SYNTHESIS

Growth of nanowires, nanotubes, thin films

CNR beamlines at Elettra

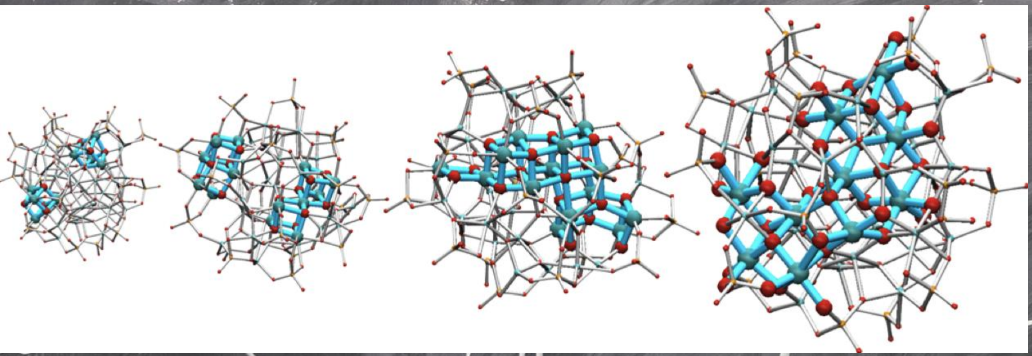
IOM beamlines

ALOISA
APE
BACH
BEAR
CIPO
GasPhase
Lilit
XRD1
VUV
SISSI



Photons:
From UV to hard X-rays
Beamlines specialised for different fine analysis tecniques.

IOM @ SISSA and Cagliari



First principle simulations

Atomic-level numerical modelling applied to materials, biologic systems and physics of highly correlated systems

New methods development

Quantum ESPRESSO project, a high-level software platform for the simulation of materials first-principles and nanoscale modelling

AN OPEN ACCESS RESOURCE

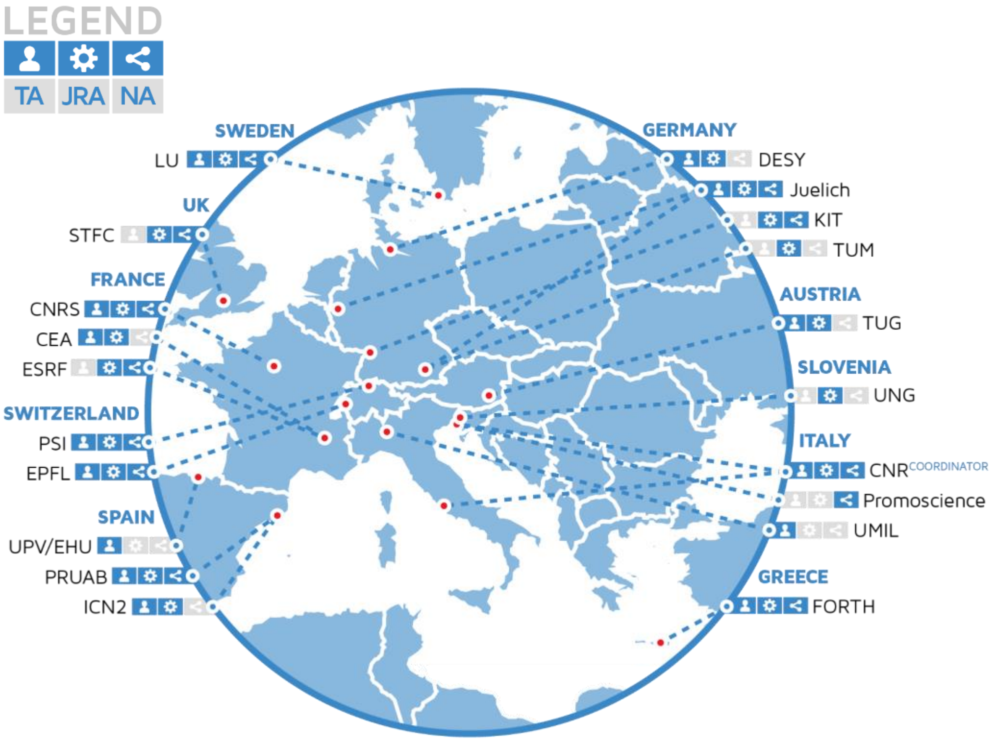
for experimental & theoretical nanoscience

CNR – IOM

Istituto Officina dei Materiali

The consortium

Istituto Officina dei Materiali



1	CNR	[IT]	Consiglio Nazionale delle Ricerche
		LABORATORIES	IOM Istituto Officina dei Materiali
			ISM Istituto di Struttura della Materia
2	CEA	[FR]	Commissariat à l'énergie atomique et aux énergies alternatives
		LABORATORY	LETI Laboratoire d'Electronique de Technologie de l'Information
3	CNRS	[FR]	Centre National de la Recherche Scientifique
		LABORATORIES	LPN Laboratoire de Photonique et de Nanostructures
			IEF Institut d'Electronique Fondamentale
4	DESY	[DE]	Stiftung Deutsches Elektronen-Synchrotron Desy
		LABORATORY	NanoLab DESY Nanolaboratory
5	EPFL	[CH]	École polytechnique fédérale de Lausanne
6	ESRF	[EU]	Installation Européenne de Rayonnement Synchrotron
7	FORTH	[EL]	Foundation for Research and Technology Hellas
		LABORATORY	IESL Institute of Electronic Structure and Laser
8	ICN2	[ES]	Fundacio Institut Català de Nanociència i Nanotecnologia
9	Juelich	[DE]	Forschungszentrum Juelich GmbH
		LABORATORIES	PGI Peter Grünberg Institute
			JCNS Juelich Centre for Neutron Science
10	KIT	[DE]	Karlsruher Institut für Technologie
11	LU	[SE]	Lunds Universitet
		LABORATORIES	LNL Lund Nano Lab
			nCHREM National Center for High Resolution Electron Microscopy
12	Promoscience	[IT]	Promoscience S.r.l.
13	PRUAB	[ES]	Parc de Recerca Universitat Autònoma de Barcelona
		LABORATORIES	CSIC-CNM Agencia Estatal Consejo Superior De Investigaciones Cientificas-National Centre of Microelectronics
			CSIC-ICMAB Agencia Estatal Consejo Superior De Investigaciones Cientificas-Institute of Materials
			UAB Universitat Autonoma De Barcelona
14	PSI	[CH]	Paul Scherrer Institute
		LABORATORY	LMN Laboratory for Micro- and Nanotechnology
15	STFC	[UK]	Science and Technology Facilities Council
16	TUG	[AT]	Technische Universität Graz
17	TUM	[DE]	Technische Universität München
18	UMIL	[IT]	Università degli Studi di Milano
19	UNG	[SI]	Univerza v Novi Gorici
20	UPV/EHU	[ES]	Universidad del País Vasco /Euskal Herriko Unibertsitatea

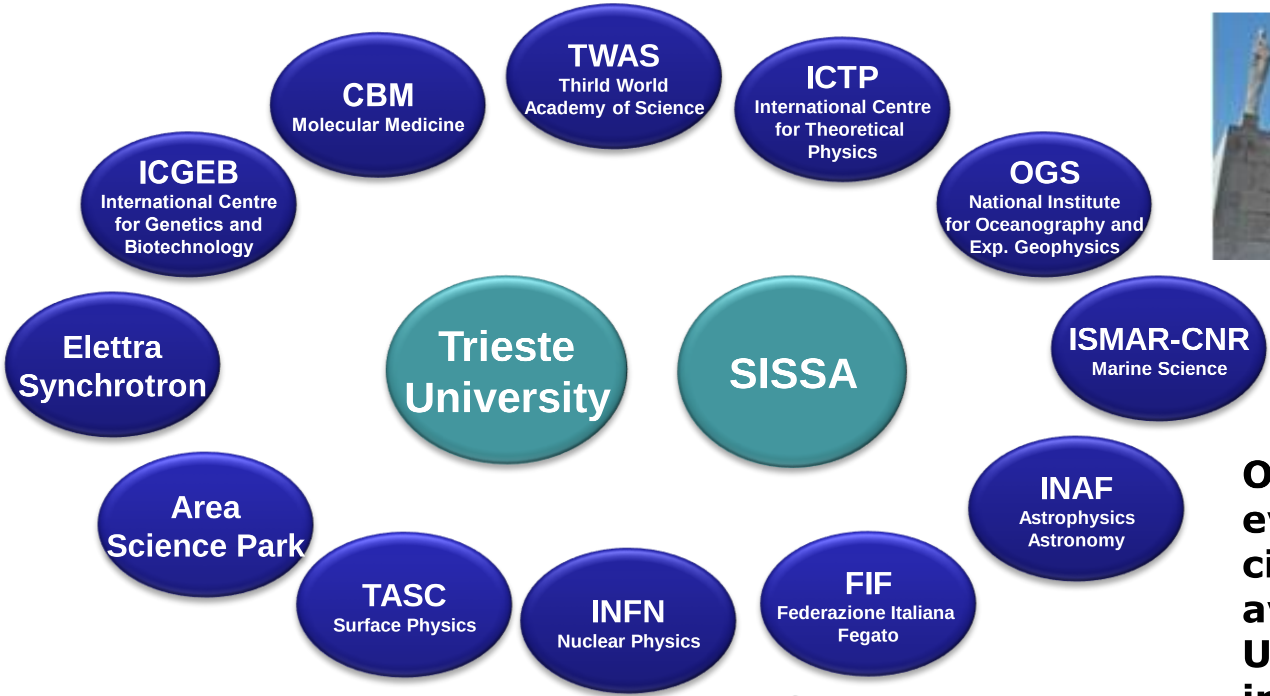
20 partners of which **10 nanofoundries**
colocated with Analytical Large Scale facilities.

PhD Program in Nanotechnology

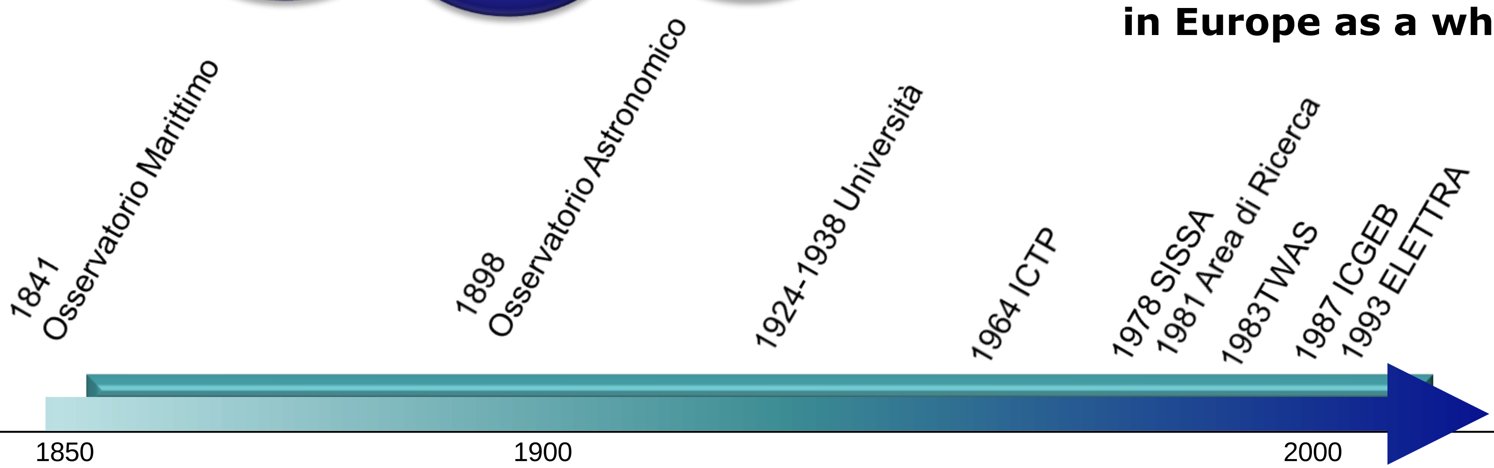
University of Trieste

www.units.it/do= orato/nanotecnologie/en

Trieste System

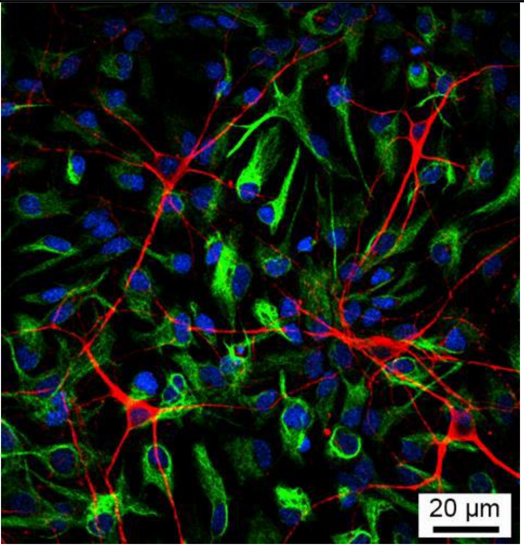


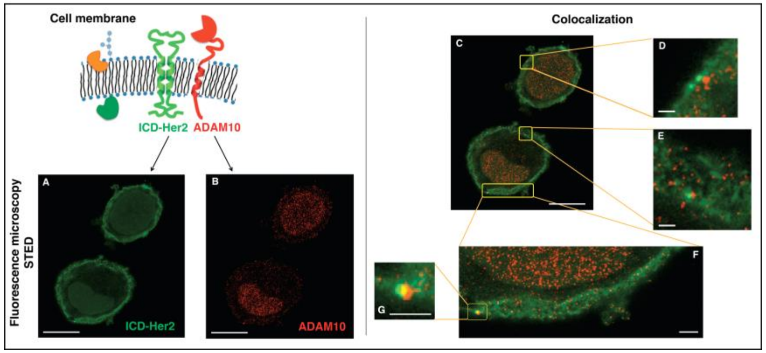
Over 30 researchers every 1,000 active citizens (compared to an average of 8.1 in the USA, 9.1 in Japan, and 5.7 in Europe as a whole)

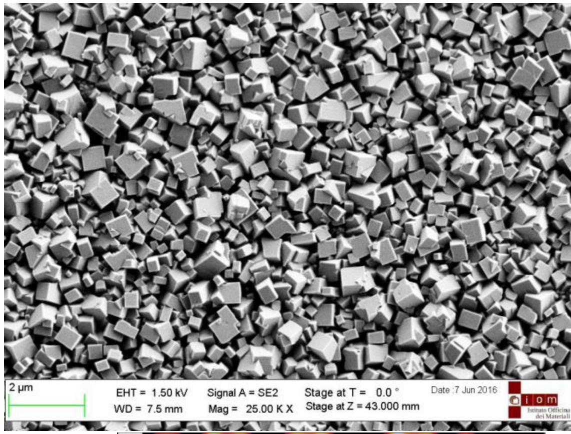


UNIVERSITÀ DEGLI STUDI DI TRIESTE

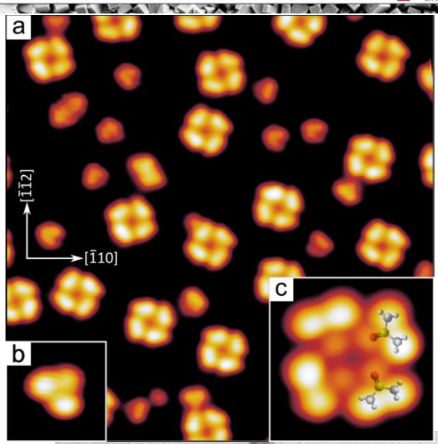
Mission

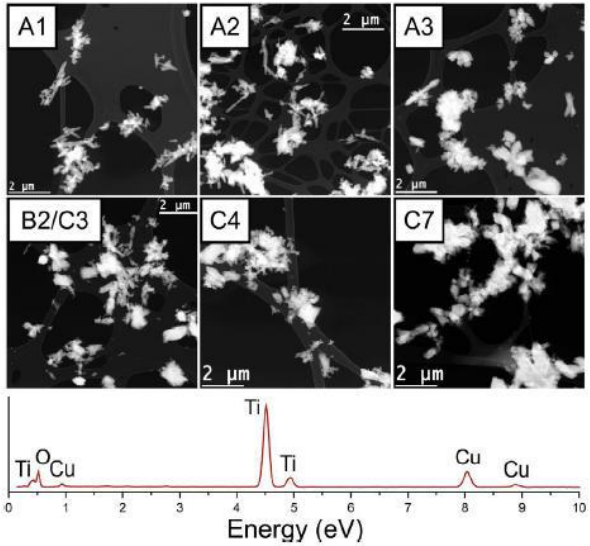


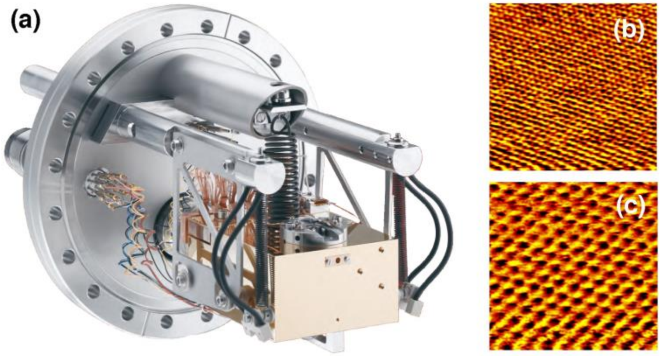


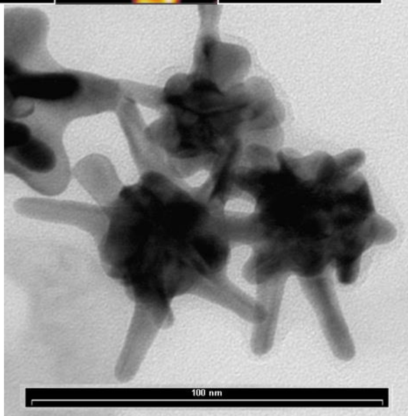


- to provide students with knowledge and training in the field of nanotechnology
- to provide the necessary background to become 21st century scien<sts and technicians.









UNIVERSITÀ DEGLI STUDI DI TRIESTE

Research Activity

Methods and Techniques:

Nanomodeling:

Multiscale molecular modeling

Ab initio molecular modeling

Development of new theory / methods

Nanocharacterization:

Single molecules detection

Living cells characterization

Characterization techniques/ instruments

Imaging & diagnostics

Toxicity

Investigations of dynamical processes

Novel characterization techniques

Nano characterization of materials

Low-dimensional systems

Electronic and geometric structure of solid surfaces

Research Ac*vity

UNIVERSITÀ DEGLI STUDI DI TRIESTE

Methods and Techniques:

Nanofabrica*on:

Nanofabrica, on bo- om up

Nanofabrica, on top down

Nanopar, cles fabrica, on and characteriza, on

Self assembly

Development of MEMS and NEMS

Development of new nanofabrica, on techniques/instruments

Templated growth/deposi, on

Applications of Nanotechnology:

Micro, Nano and Opto electronics

Advanced Materials & biomaterials

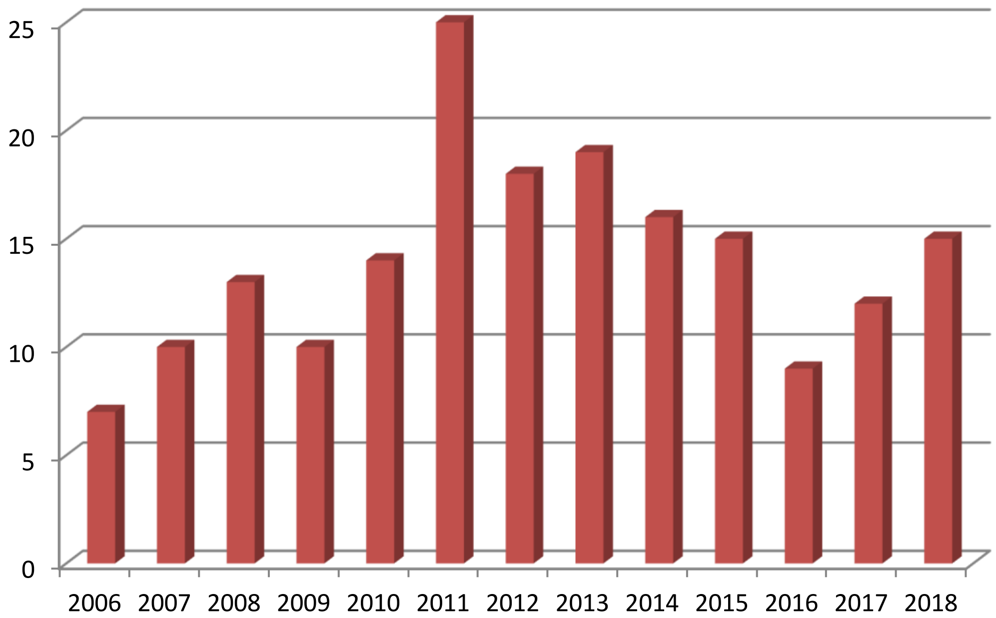
Therapy & Diagnosis

Medicine & Life Sciences

Energy & Environment

Some numbers….

- Number of students from 2006 (XXII ciclo) to 2018 (XXXIV ciclo): 183



Some numbers….

UNIVERSITÀ DEGLI STUDI DI TRIESTE

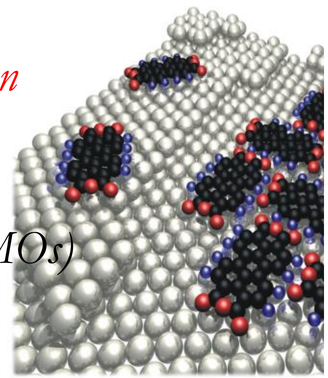
- Entities involved:
  - Departments of UNITS: 5
    - Dep. of Physics,
    - Dep. of Ingenieering and Architecture
    - Dep. of Chemistry and Pharmaceutical Sciences
    - Dep. of Medicine
    - Dep. of Life Science
  - Research agencies/companies: 10
    - IOM – CNR, Trieste
    - Elettra Sincrotrone Trieste
    - IRCCS CRO, Aviano
    - IRCCS Burlo Garofalo, Trieste
    - ICCOM – CNR, Trieste and Firenze
    - ISTEC – CNR, Faenza
    - ICGEB - Trieste
    - IRCCS Istituto dei Tumori di Milano
    - Industrie Bracco
    - Industrie Electrolux

Organic Thin Films are topic of intense research due to technological potential

- *Organic solar cells*
- *flexible OTFTs*
- *color OLEDs*
- many more ...

Tunable photon energy, variable polarization

- *X-ray photoemission*
  (Core & valence band structure, filled MOs)



Research issues :

- *Near edge X ray absorption Fine structure (NEXAFS) empty MOs*

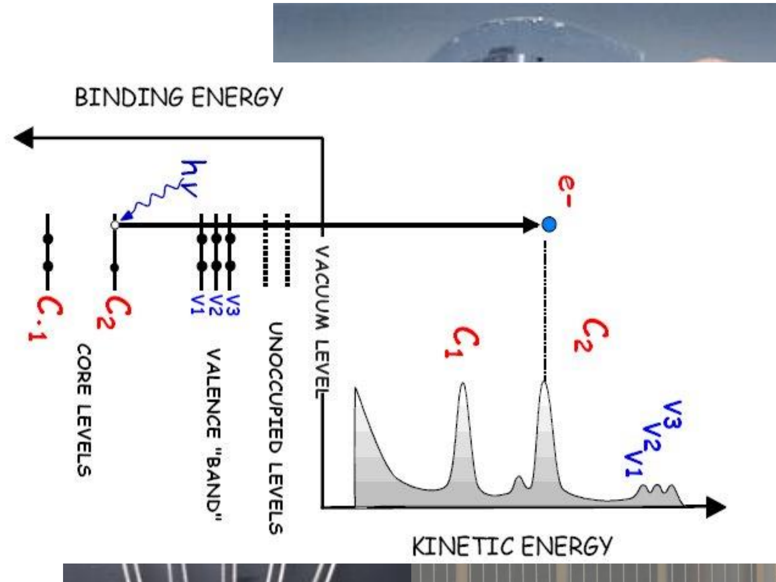
- *Structure and morphology at hybrid interfaces*
- *Coupling of organic molecules at interfaces*
- *Electronic structure & transport phenomena*

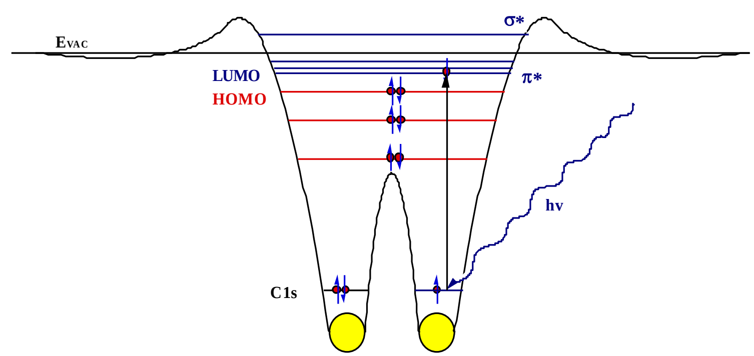
However :

- *Molecular interface - low signal ?*
- *Distinguish molecular VB from the substrate ?*

@ Synchrotron spectroscopies:
NEXAFS, XPS, VB photoemission, Resonant Photoem.

- *Resonant photoemission*

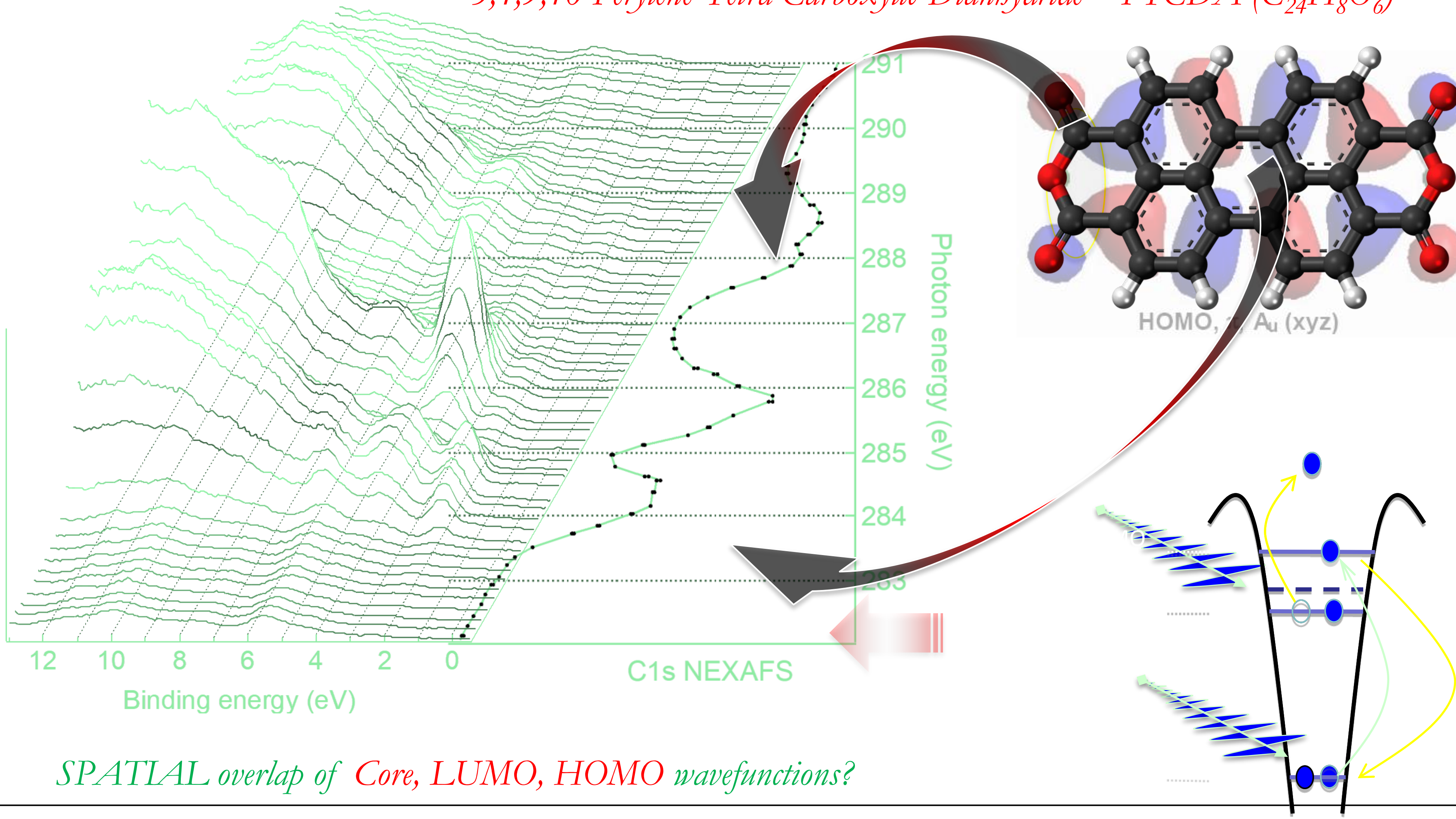




Resonant Photoemission – RPES overview

In RPES we measure XPS spectra with photon energy tuned across absorption edge
VB resonances occur ➔ Absorption & Hole decay via Autoionization.

3,4,9,10-Perylene Tetra Carboxylic Dianhydride – PTCDA ($C_{24}H_8O_6$)



SPATIAL overlap of Core, LUMO, HOMO wavefunctions?

Atomic Clock for Femtosecond Timing

iom Istituto Officina dei Materiali

Dynamics of the intermediate state?
Core-hole lifetime exploited to measure ultrafast delocalization of electron from the intermediate LUMO (CT) state.

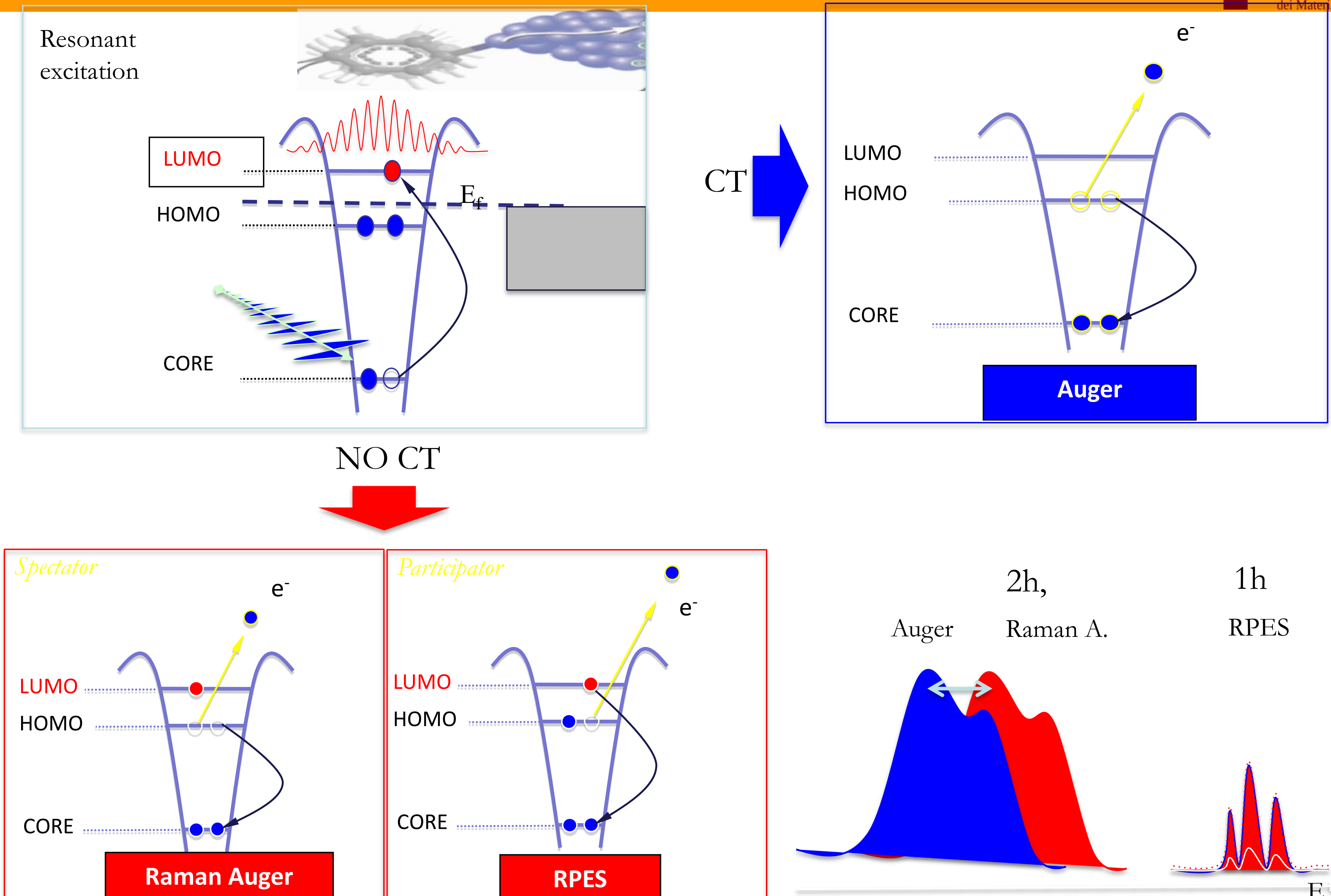
By measuring branching ratio of CT vs No CT decay channels femtosecond timing with atomic clock.

Typical core-hole lifetimes of inner shell vacancies for

- *Oxygen* KLL: *T= 4 fs.*
- *Nitrogen* KLL: *T= 5 fs,*
- *Carbon* KLL: *T=6 fs, M. Coville et al., Phys. Rev. A (1991),*
- *Argon* $L_3M_{4/5}M_{4/5}$: *T=6 fs; Fohlisch et al, Chem. Phys. (2003).*

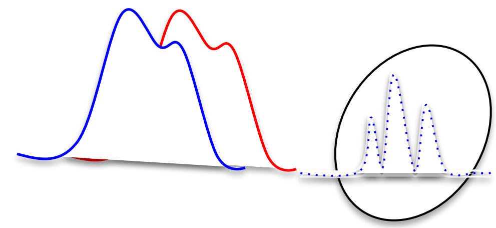
- *Chemical environment little influence on hole lifetime*
- *How do we measure CT vs No CT decay channels ? …*

"Core Hole Clock" method

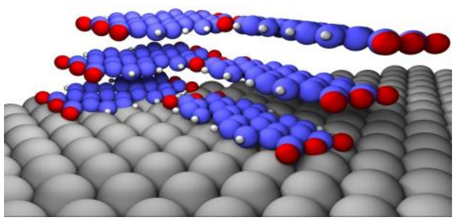


Organic films: C, N, O Auger -Raman → *Quenching of RPES*

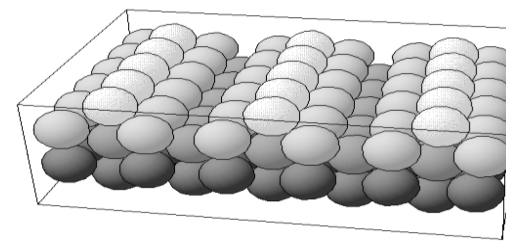
Coupled & Isolated system (e.g. gas, v.d.W. solid) with $\tau = \infty$.
RPES attenuation in coupled gives CT time.



- *Thick PTCDA film*

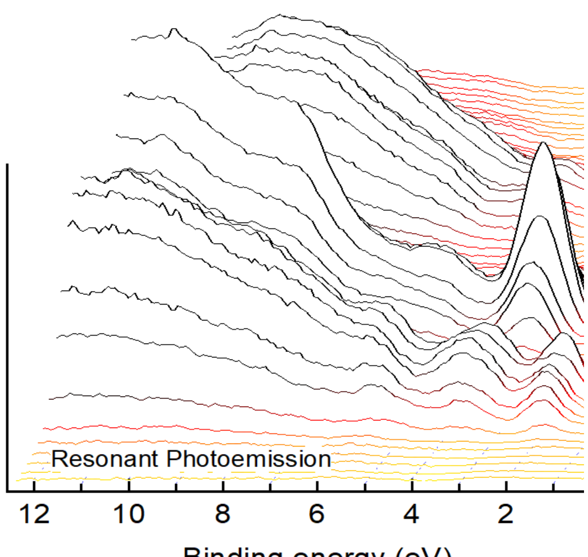


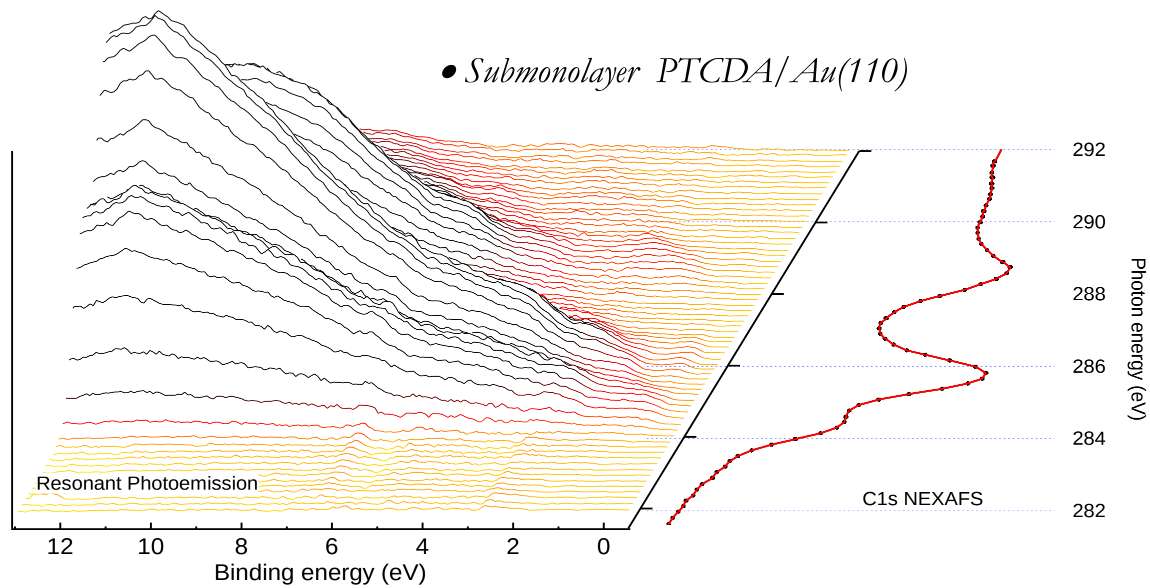
$$t_{CT} = t_{core} \frac{I_{coupled}}{I_{Iso} - I_{coupled}}$$



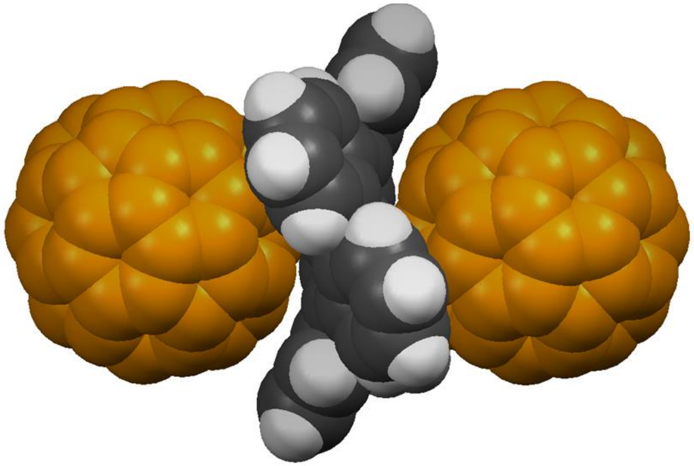
fcc(110)-(1x2) missing row reconstruction

- *Submonolayer PTCDA/Au(110)*

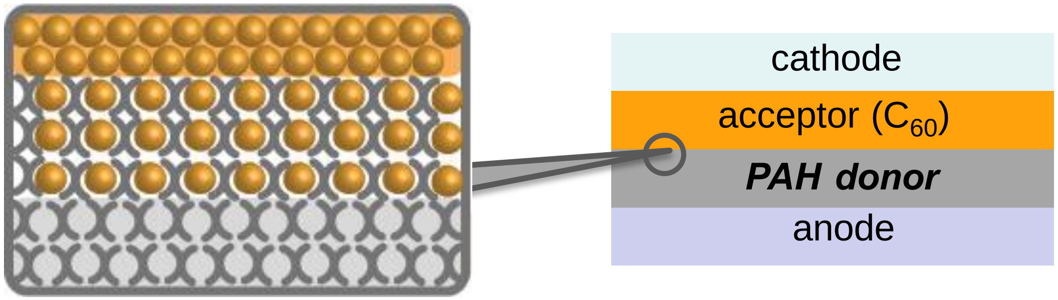




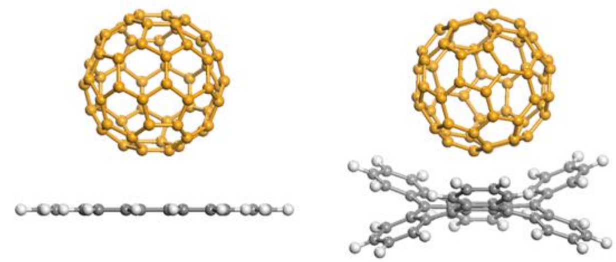
Donor-acceptor shape-complementarity drives performance in photovoltaics



Self-assembled D/A interfaces: HBC and DBTTC



ball and socket joints
Tremblay *et al*. ChemPhysChem 11 (2010) 799

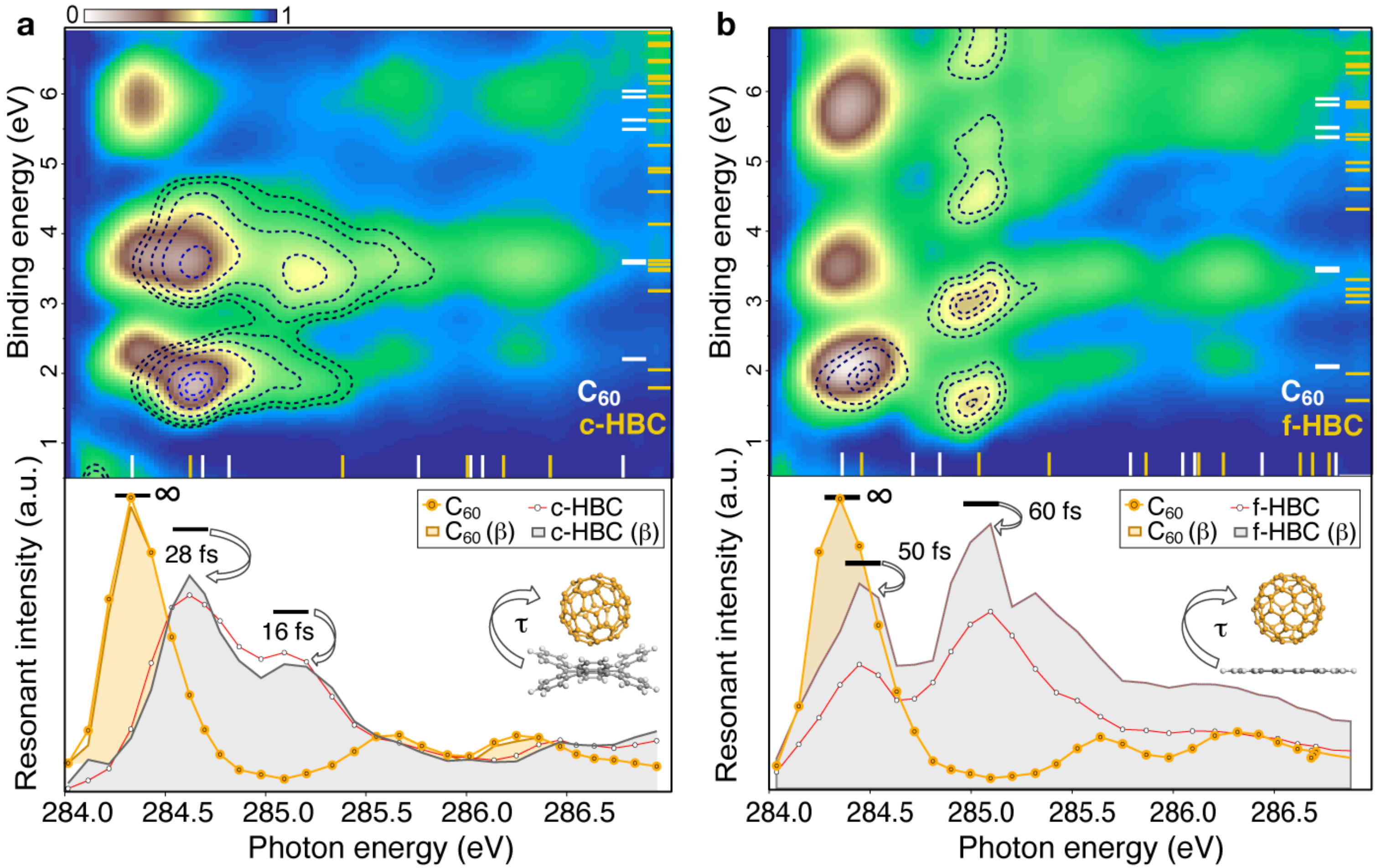


V_{oc} within 10% of theoretical max, 10xs higher efficiency than flat HBC

x-rays reveal an extended *shape-complementary D/A interface* which can be modeled by the co-crystal structure

Origin of improved performance of shape-complementary OPVs?

Influence of contortion on D/A charge transfer rates (RPES)



D/A electron transfer (exciton dissociation) rate increases with shape-complementarity

Conclusions I

- Molecular shape-complementarity between donor and acceptor drives higher efficiency in OPV devices.

- Shape-complementarity increases the D/A coupling and drives self-assembly into an intermixed morphology with a “ball-and-socket” interface.

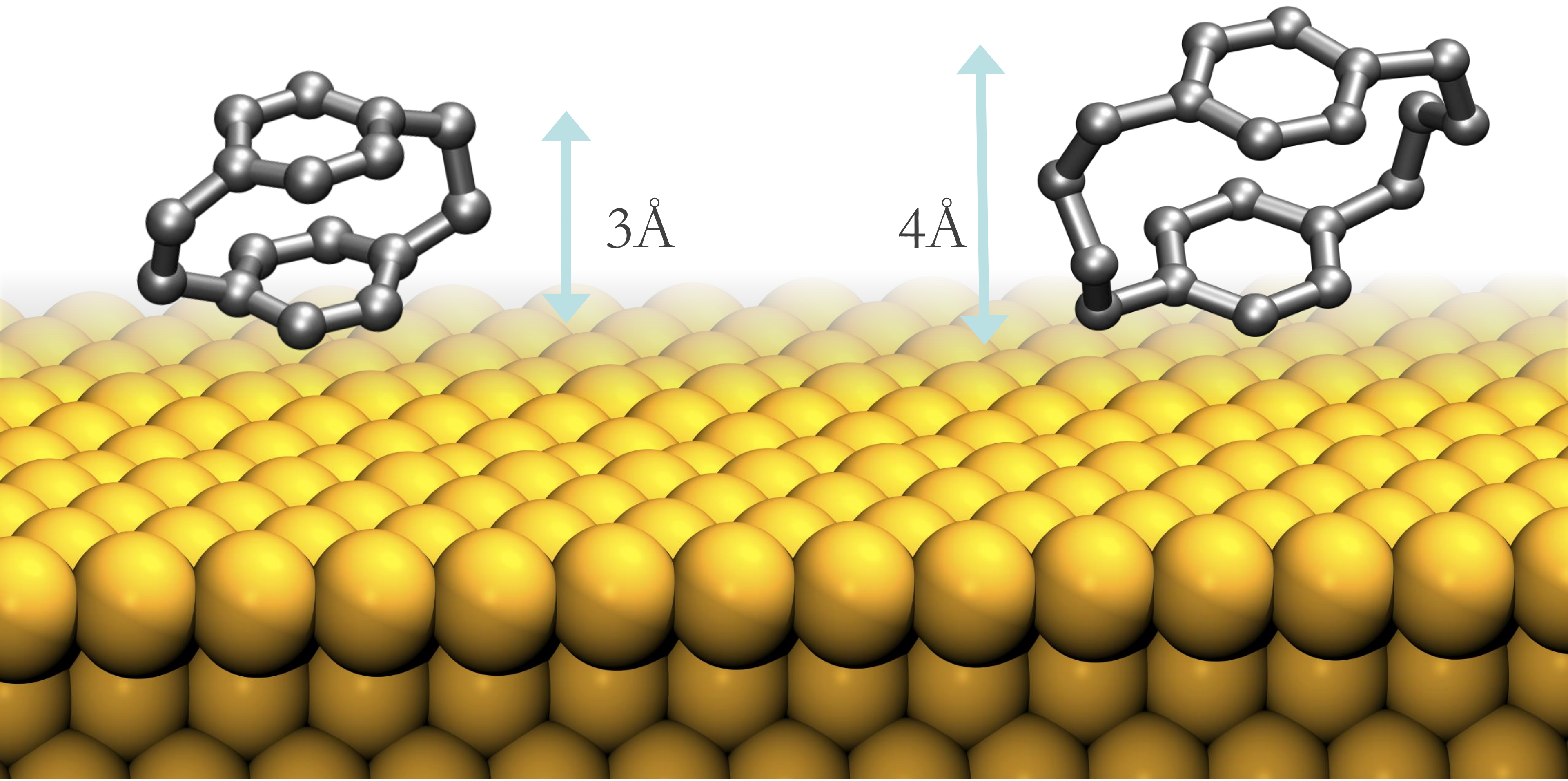
- The extended, shape-complementary interface results in:
  - a larger active volume => higher EQE.
  - optimal charge transfer efficiency (faster exciton dissociation) => higher IQE.
  - an order of magnitude increase in PCE of the bilayer OPV device.

- Shape-complementarity represents a new direction in the molecular scale design of interfaces for optimal exciton dissociation and charge transport to enable higher efficiency OPV devices.

Molecular systems

[2,2]Paracyclophane (22PCP) // Au(111)

[4,4]Paracyclophane (44PCP) //Au(111)



CT from each Benzene ring

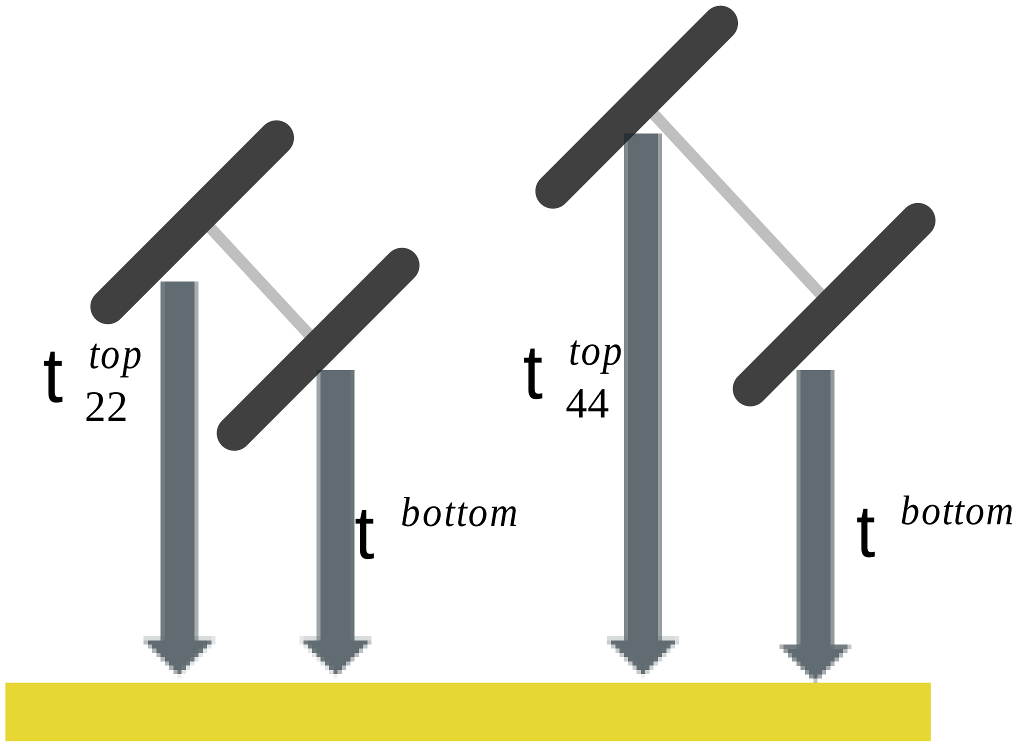
$$t_{22}^{top} = 2.3 \pm 0.6\, fs$$

$$t^{bottom} = 0.7 \pm 0.3\, fs$$

$$t_{44}^{top} > 50\, fs$$

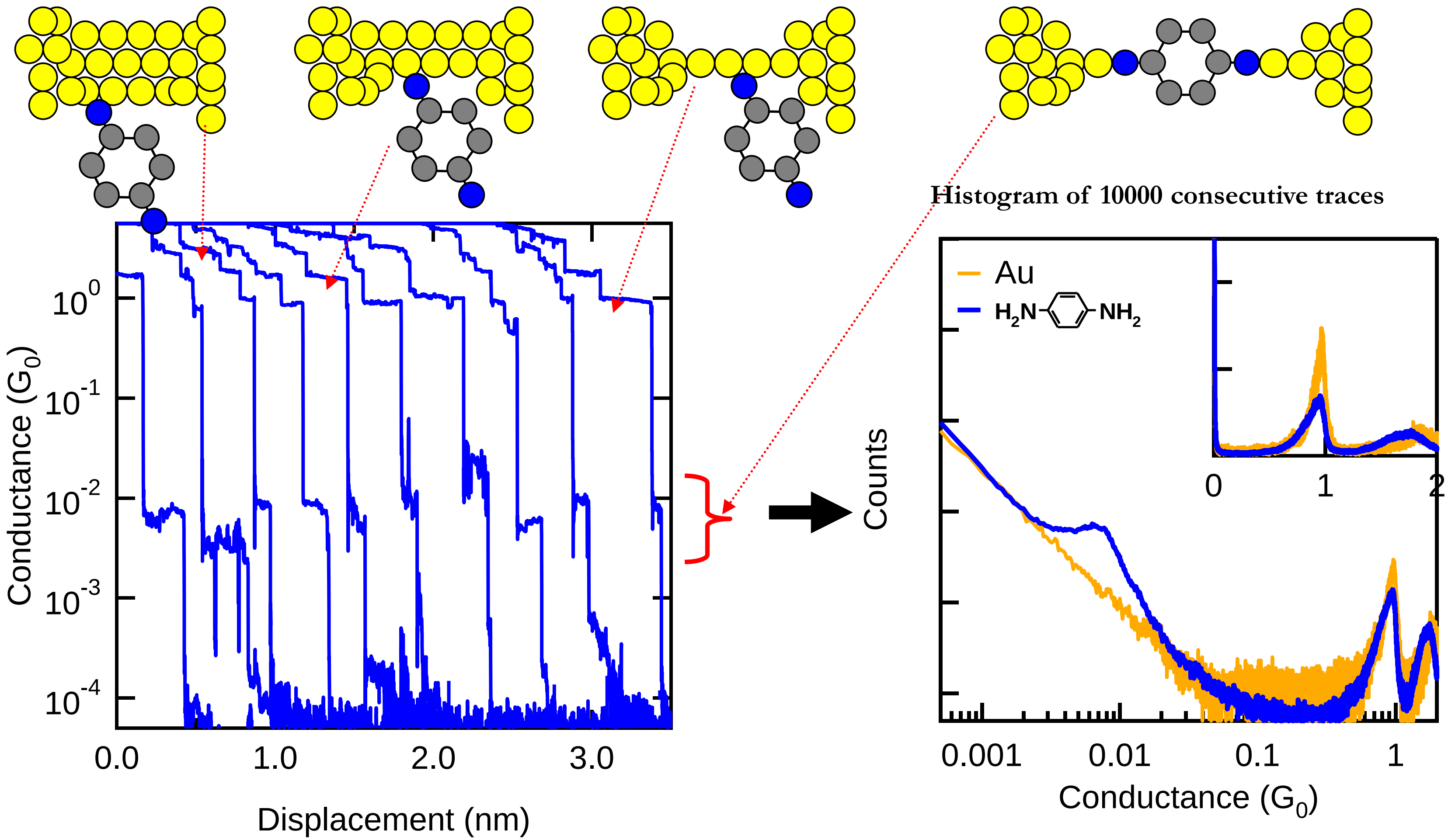
$$t^{bottom} = 0.7 \pm 0.3\, fs$$

22PCP is >20X faster



Changing Link-Group: Amines (NH_2 Group)

1,4 Benzenediamine



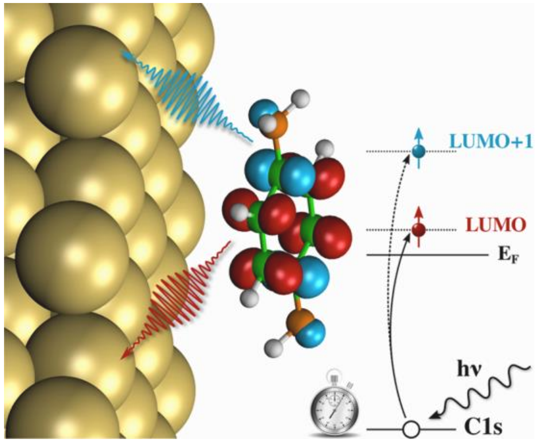
Bias = 25 mV

Steps visible over a very limited range!

We study 1,4 BDA in four systems with different coupling strength

- *Gas molecules*
- *Solid thick film*
- *Monolayer on Au substrate with FLAT geometry*
- *Monolayer on Au with TILTED geometry*

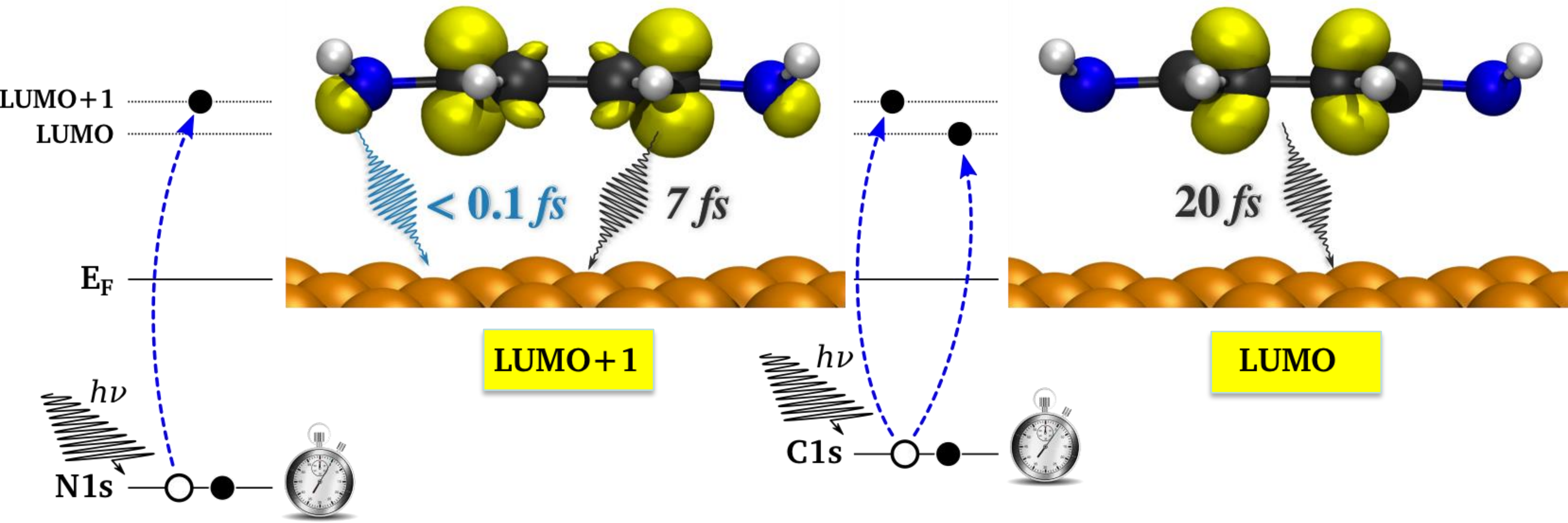
UHV deposition at -60C, RT, -20C



Experimentally "tune" the BDA coupling strength (gas, solid, interface,…)

Study carrier dynamics from RESPES & Core Hole clock …

Fast Charge Transfer Due to Amine-Au link ?



We can “populate” empty orbitals on different atomic sites (N, $C_{1,4}$, $C_{2,3}$) and measure CT dynamics …

Conclusions II

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With RPES & NEXAFS

- *Spatially Identify filled & unoccupied molecular wavefunctions of 1,4-BDA*
- *Verified for 4FBDA-BDA-TMBDA closer HOMO to E_F the higher G*

With core hole clock

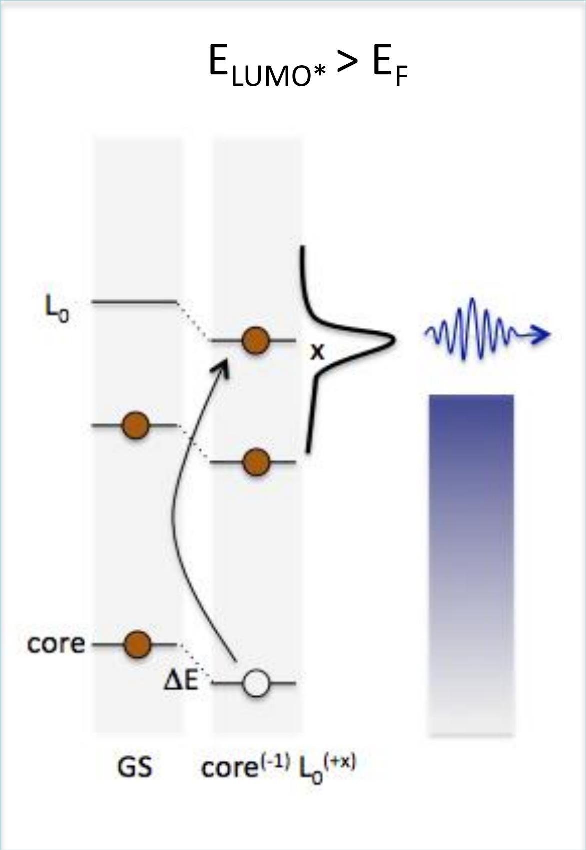
Measured CT dynamics with atomic resolution

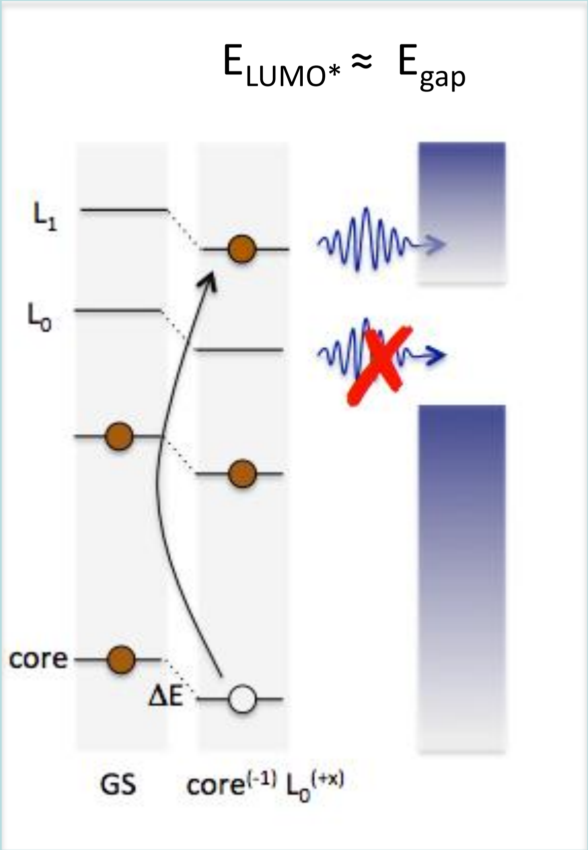
Evidence the role of Au-amine link in molecular conductance:

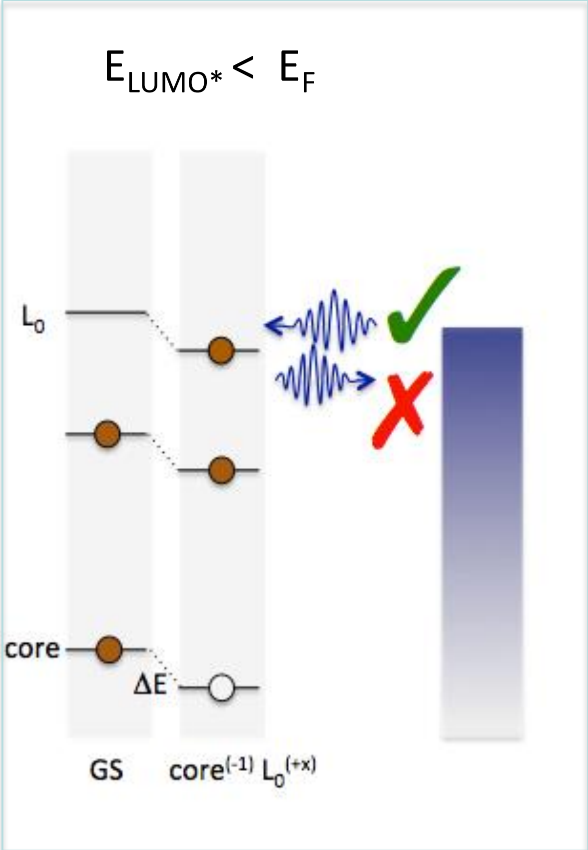
- *fast CT from N sites linked to Au (< 0.1 fs)*
- *but also from adjacent C1,4 sites of the aromatic ring (7 fs vs 20 fs)*
- *Non linked N of the tilted phase is essentially isolated (>10 fs)*

In H-bonded BDA solid phase

- *fast electron delocalization on N (≈1fs)*



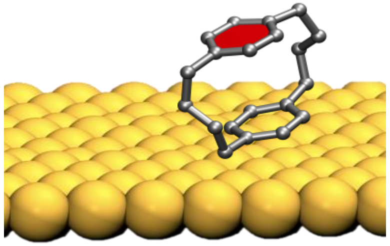




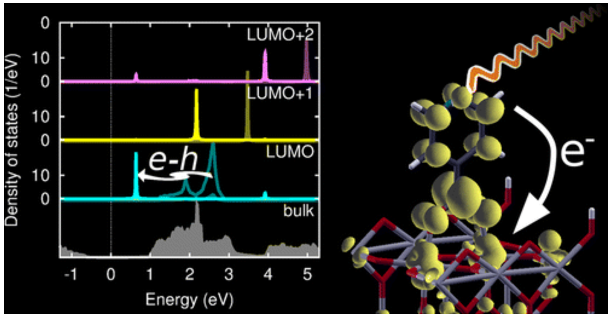
2,2 PCP /Au(111)

Isonicotinic acid / TiO_2

Pyridines / Au



Nature Communications, 3, 1086 (2012)

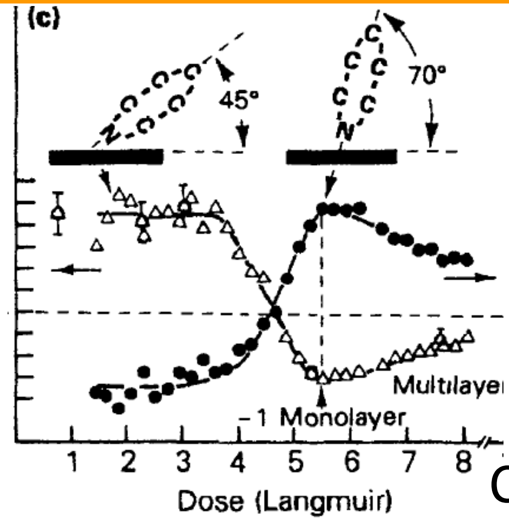


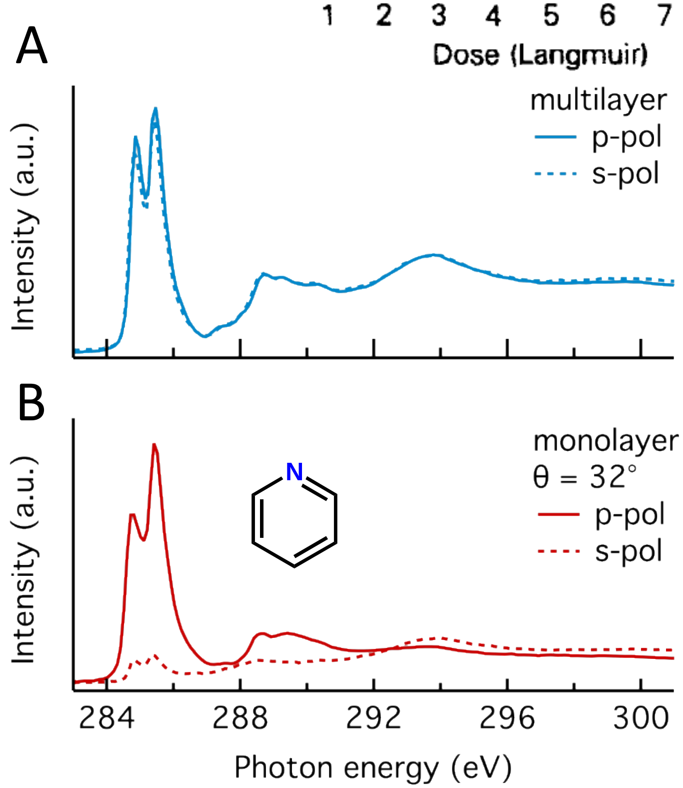
?

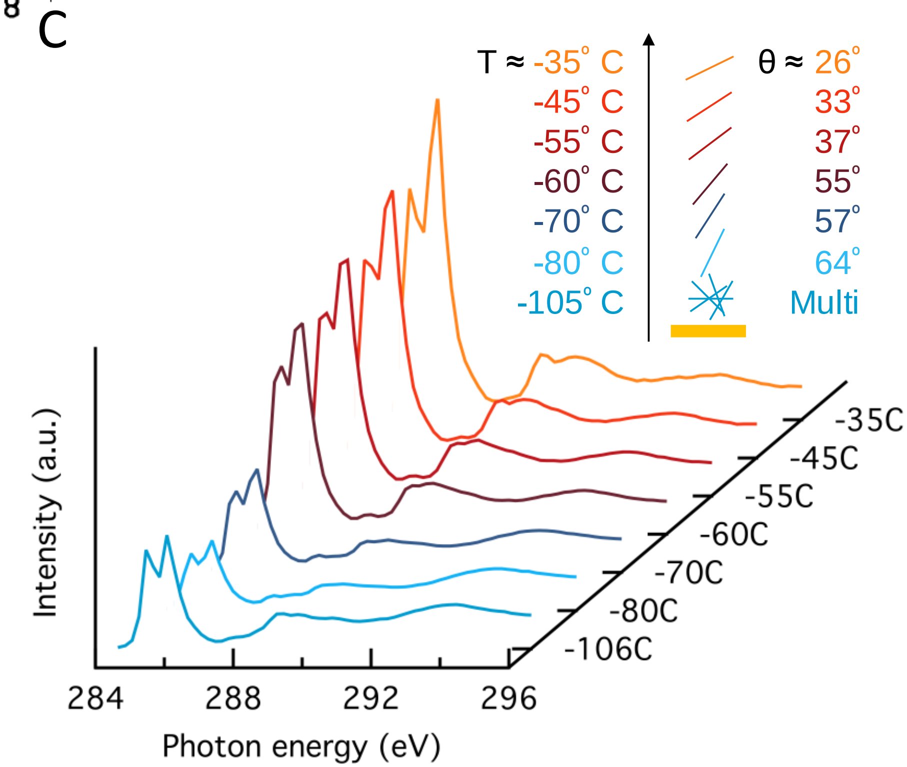
G.Fratesi et al., JPCC, 2014

- Bind through the N lone-pair (N-Au) and/or π-Au interaction

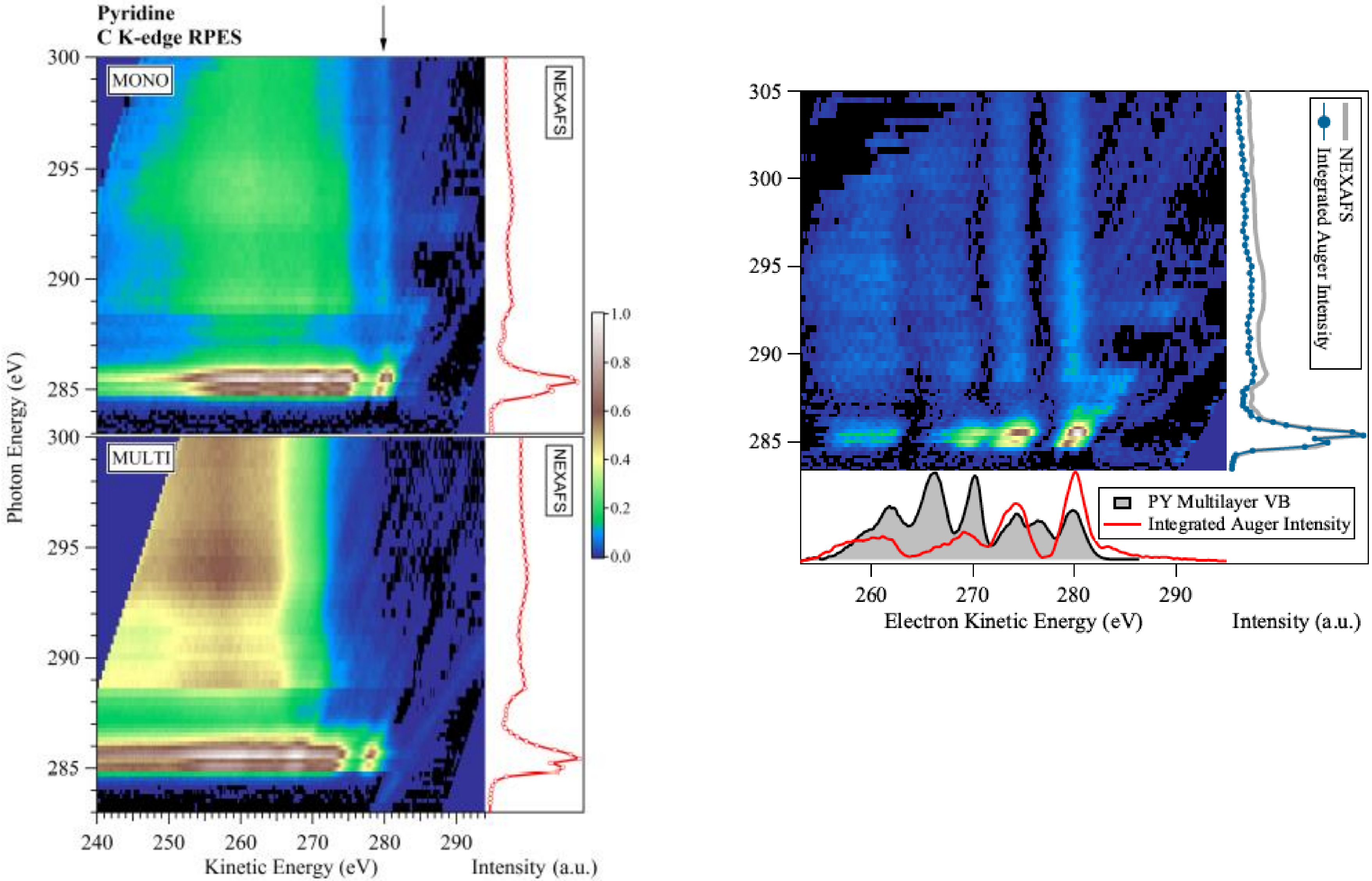
Stohr –Springer, Pyr/Ag(111), "selected systems", p.326

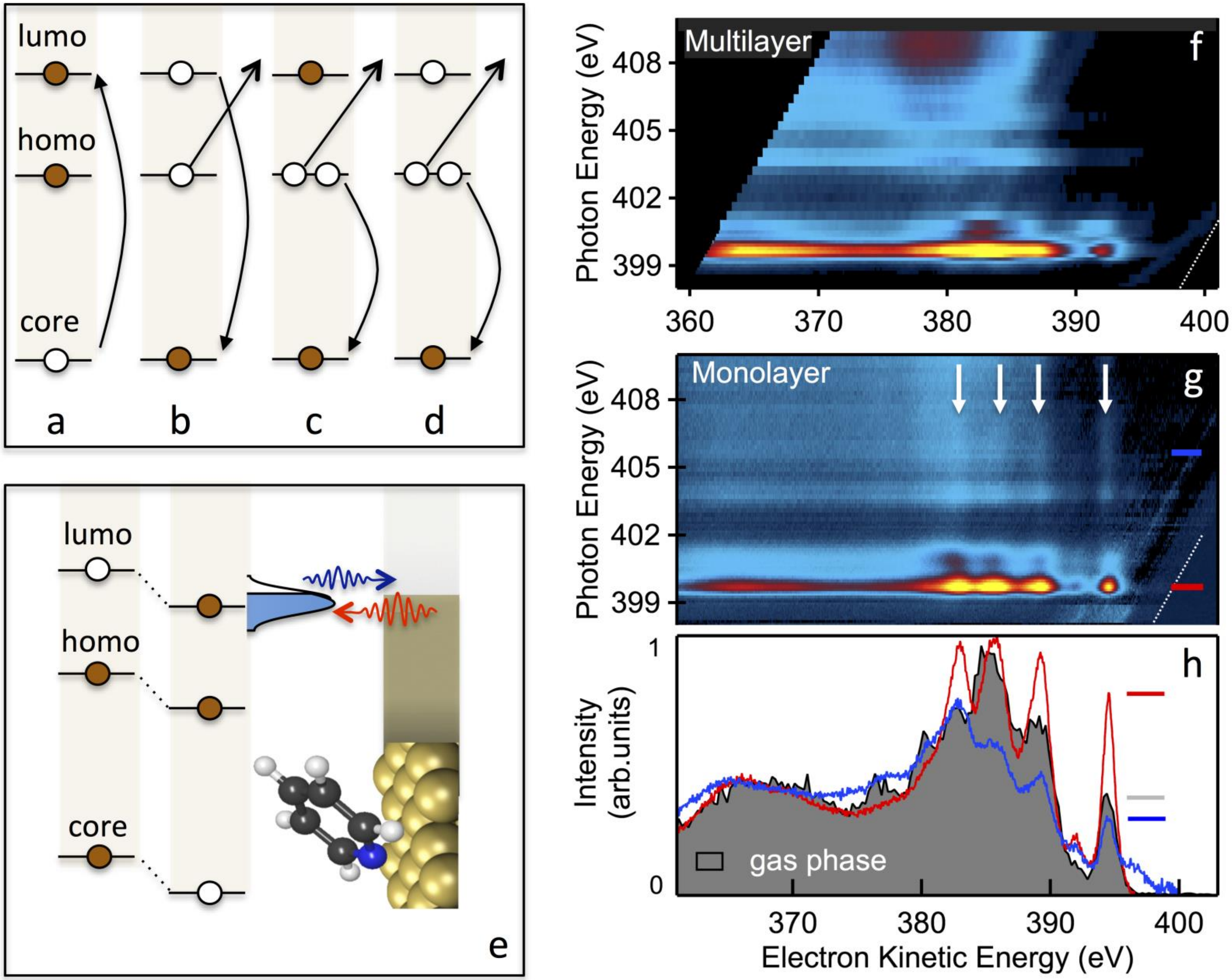






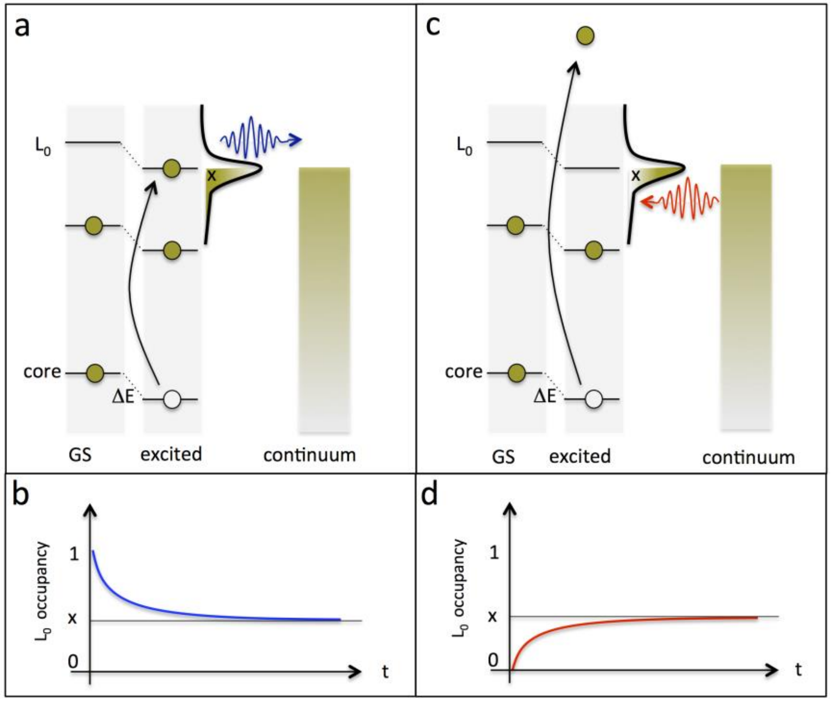
Additional core-hole decay channels – Superparticipator Auger – not present in gas/multilayer

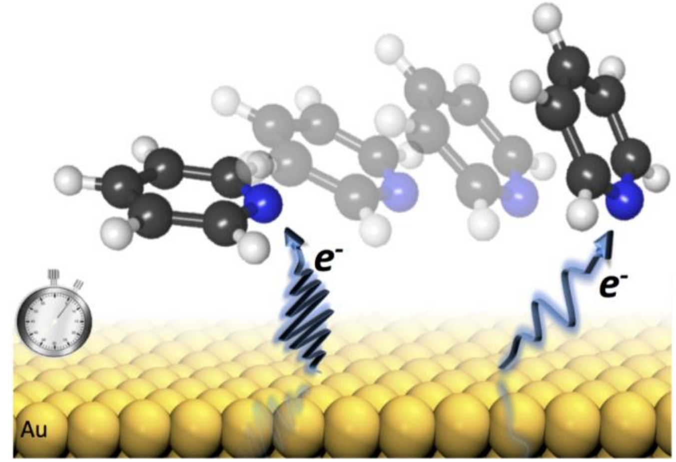


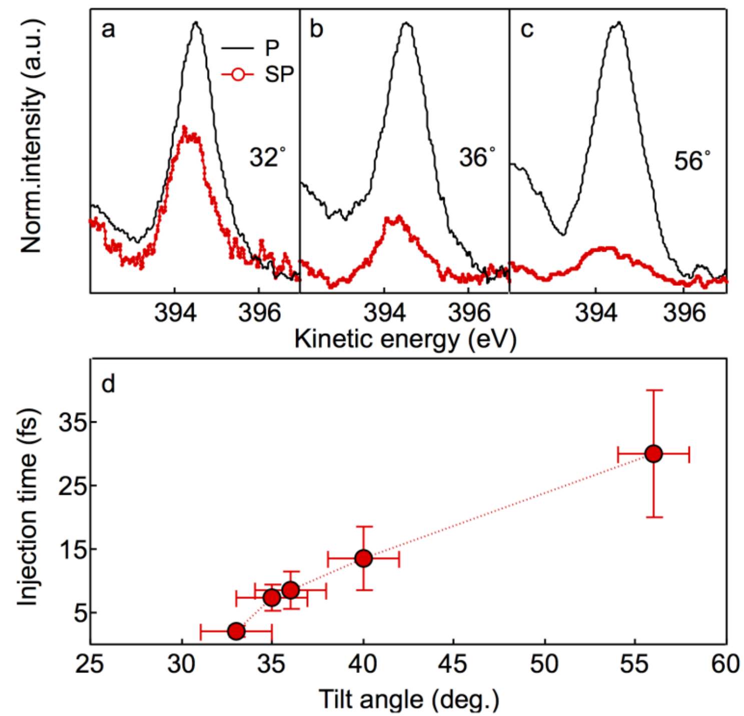


lumo
homo
core
a
b
c
d
e
Multilayer
f
Monolayer
g
h
Photon Energy (eV)
408
405
402
399
360
370
380
390
400
Intensity (arb.units)
1
0
gas phase
Electron Kinetic Energy (eV)

CHC analysis of Super-participator peak intensity:







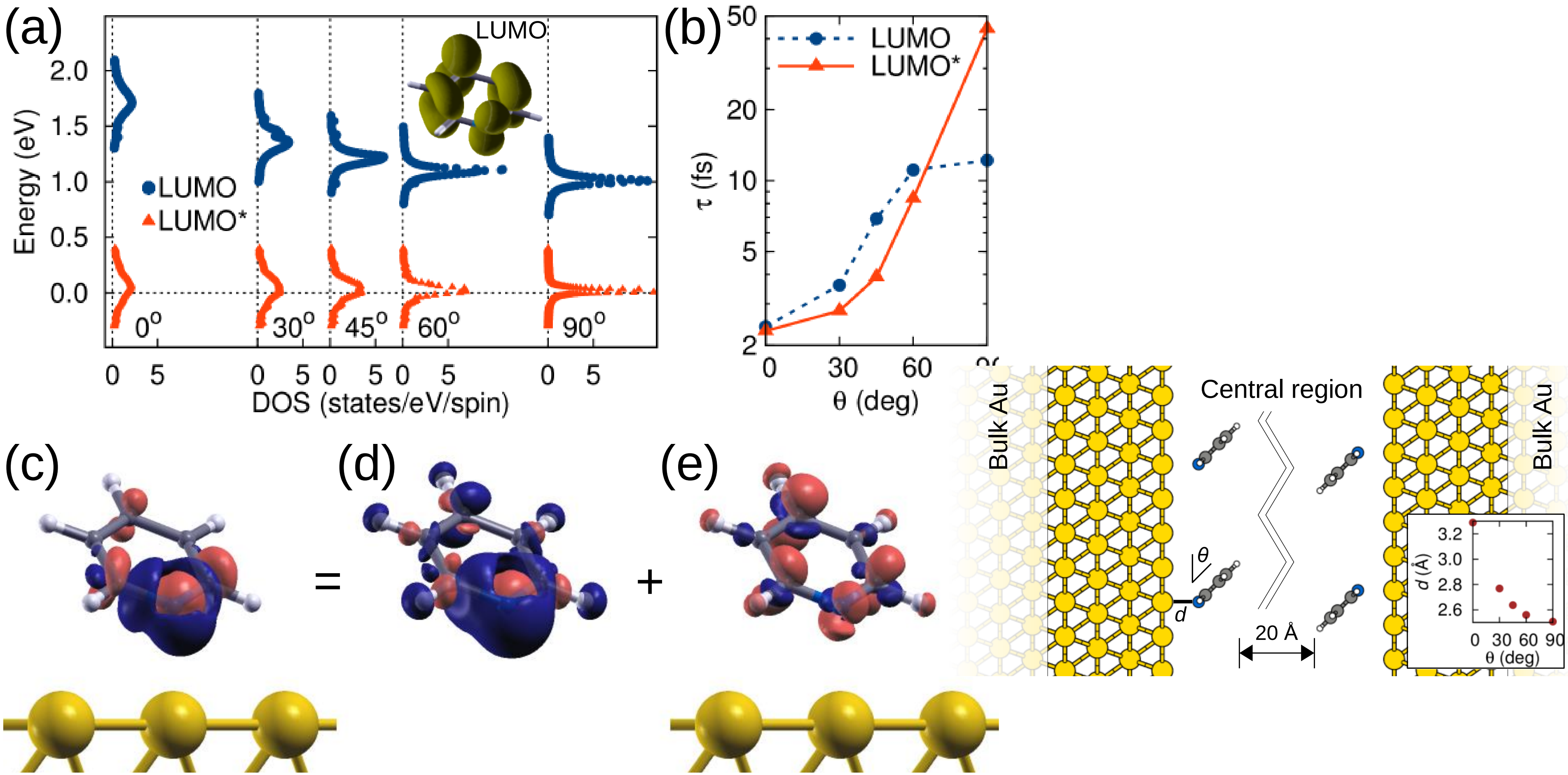
$$f = I_p / I_p^0$$

$$\beta = I_{sp} / I_p$$

$$\tilde{\tau} = \frac{f(1-\beta)}{1 - f(1-\beta)}$$

$$x = \frac{\beta f}{1 - f(1-\beta)}$$

- *DFT -> LUMO* pinned at Fermi*
- *LUMO* coupling to Au continuum decreases*
- *With increasing tilt angle Δρ with LUMO symmetry -> charge BT to LUMO* => ultrafast el.injection from Au.*



In Conclusion:

Evidence of ultrafast injection of Au electrons to LUMO* of the molecule.

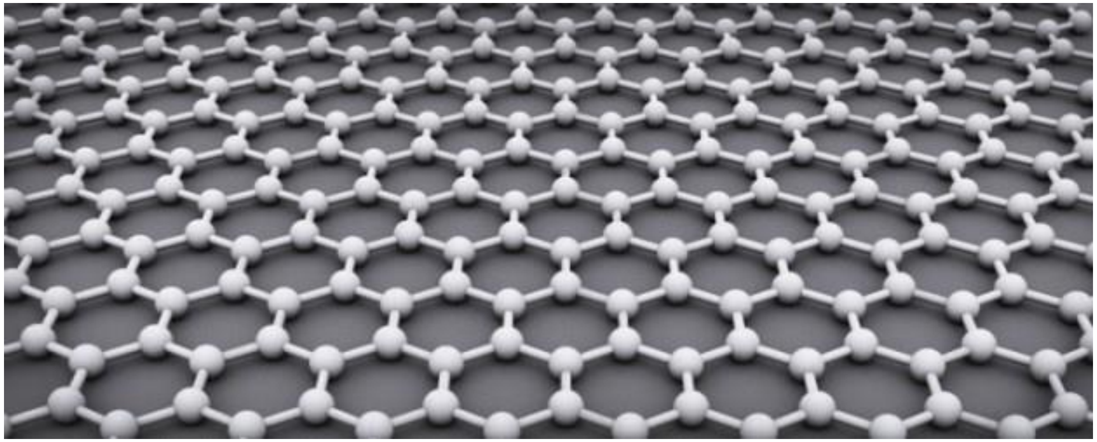
Localization of Au electron on the molecule enabled by:

⇒ LUMO* pinned at Fermi & spatial overlap of orbital with Au band
⇒ Strong angular dependence due to wavefunction overlap dependence

Acknowledgement also to:

Dr.Guido Fratesi, Prof.Dr.Gian Paolo Brivio, *University of Milano, Italy*

Graphene: single layer of sp^2 hybridized C atoms

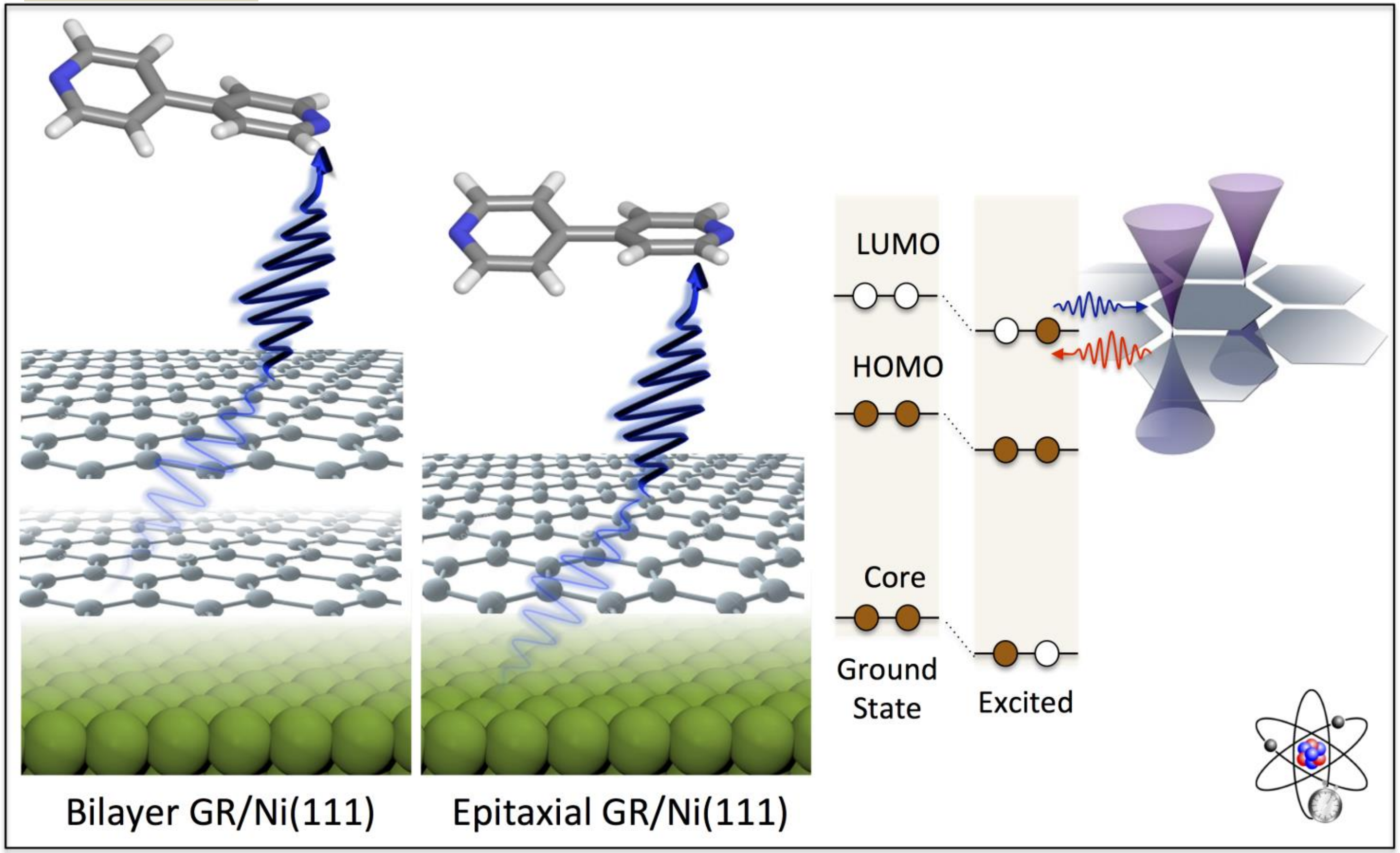


2D material with remarkable properties:

- high electric conductivity
- thermal stability
- mechanical strength
- unusuall band structure
- transparent electrode

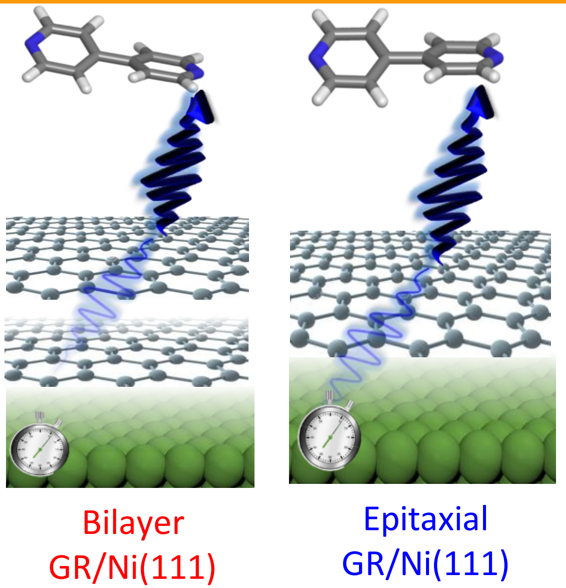
Core-hole-clock of ultrafast charge injection at GR/organic interface

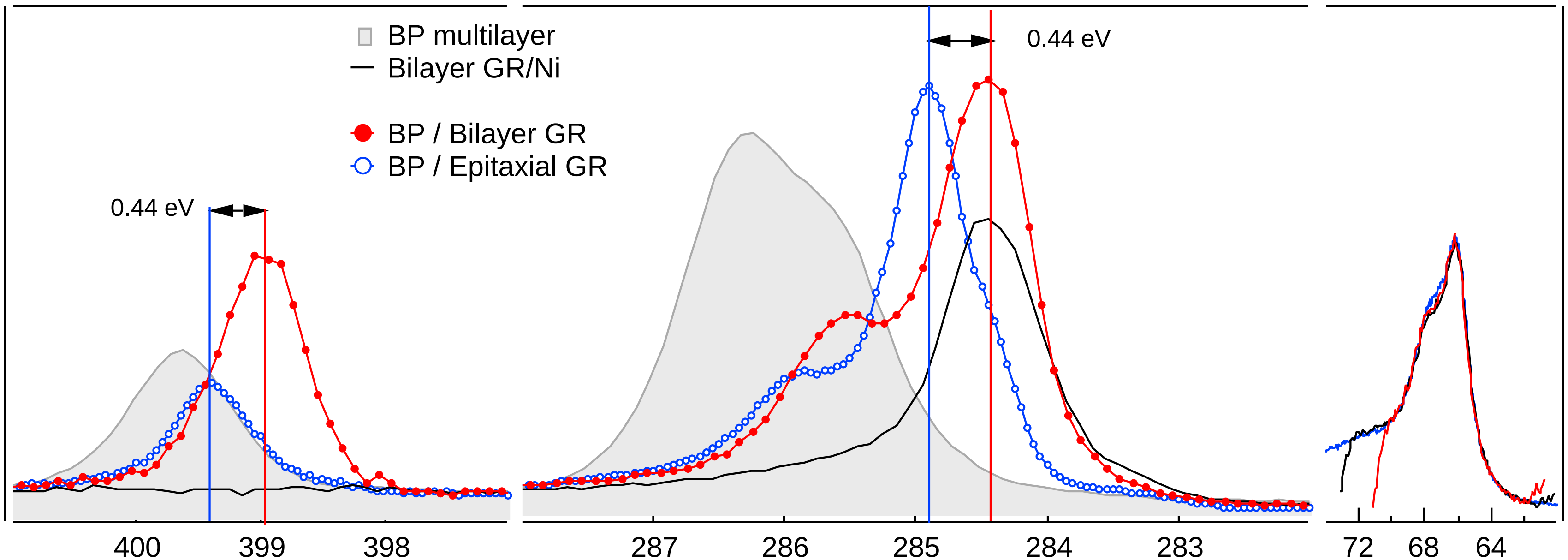
Bipyridine

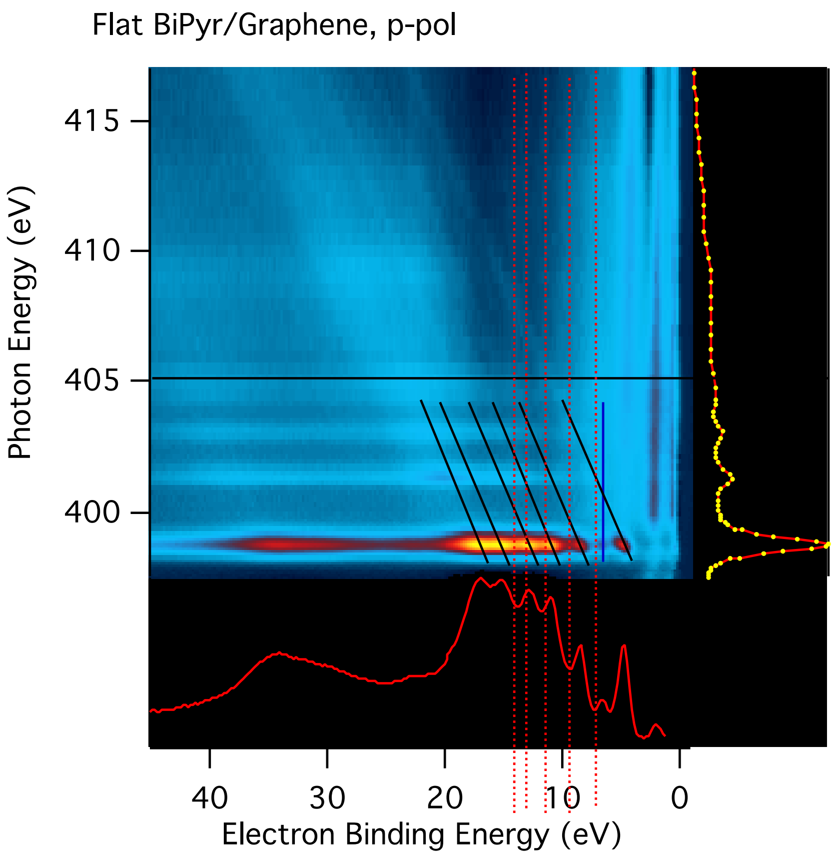


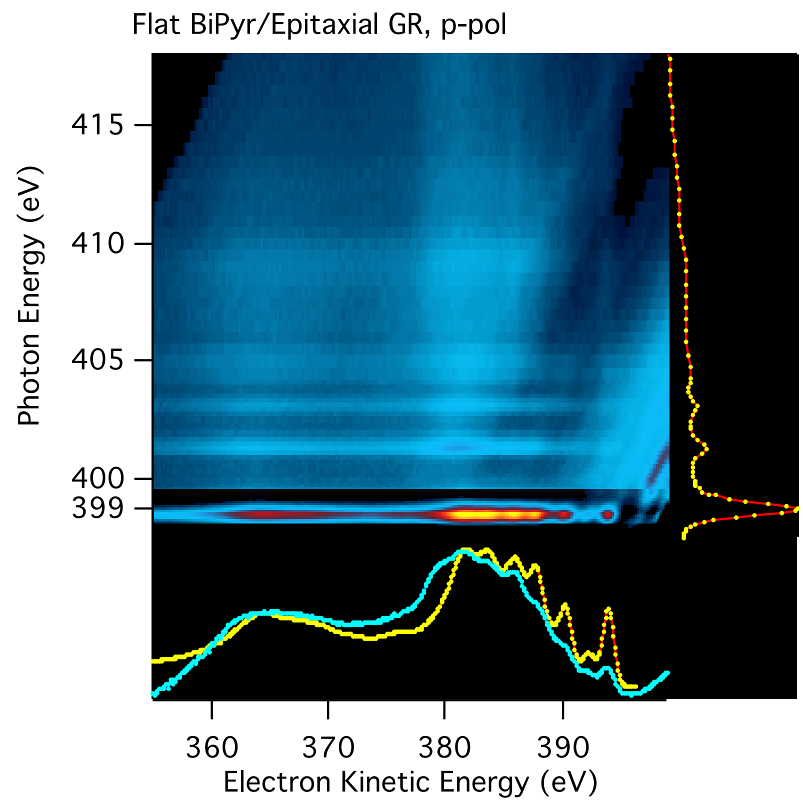
BiPyridine Adsorption on GR

We measured also BP/Au, BP/Ag
For comparison (not shown)



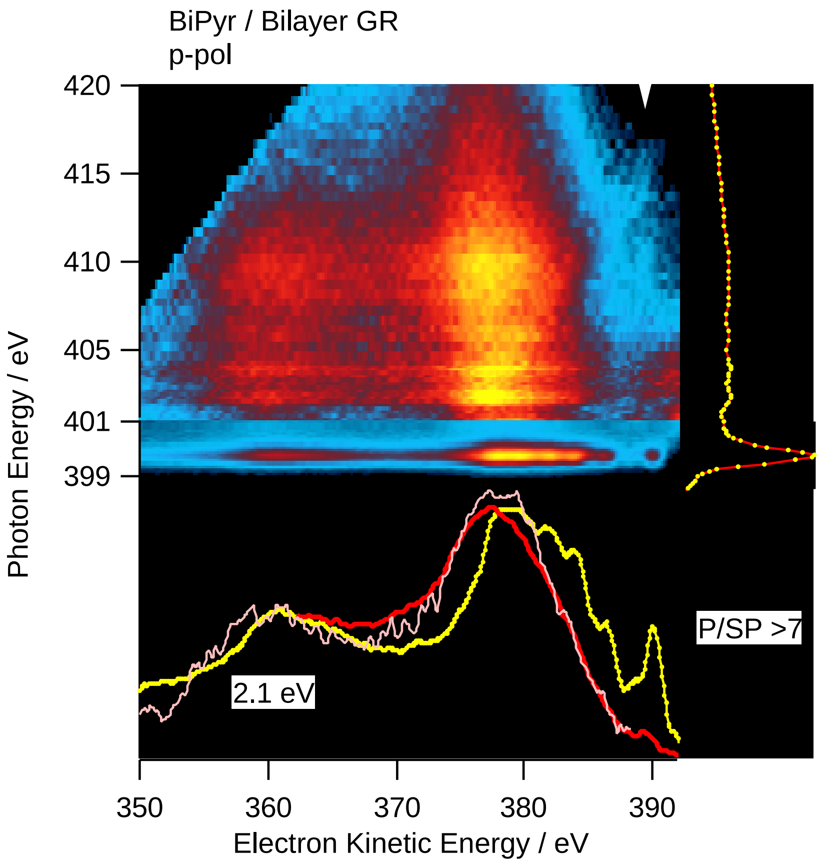




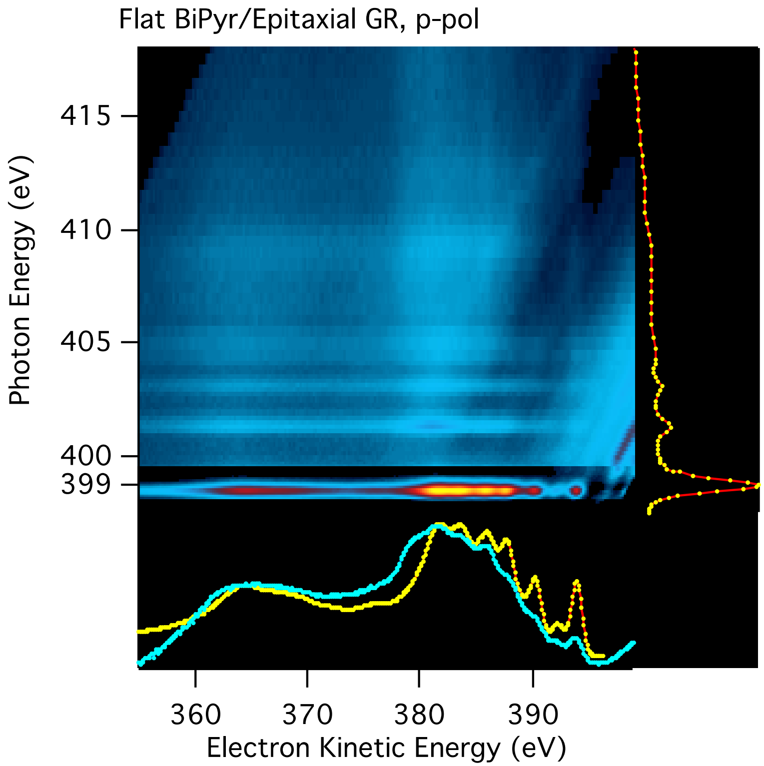


Intensity of SP resonances in epitaxial comparable to Au and Ag.
Evidence of strong coupling BP coupling and LUMO* at Fermi.

Bilayer GR



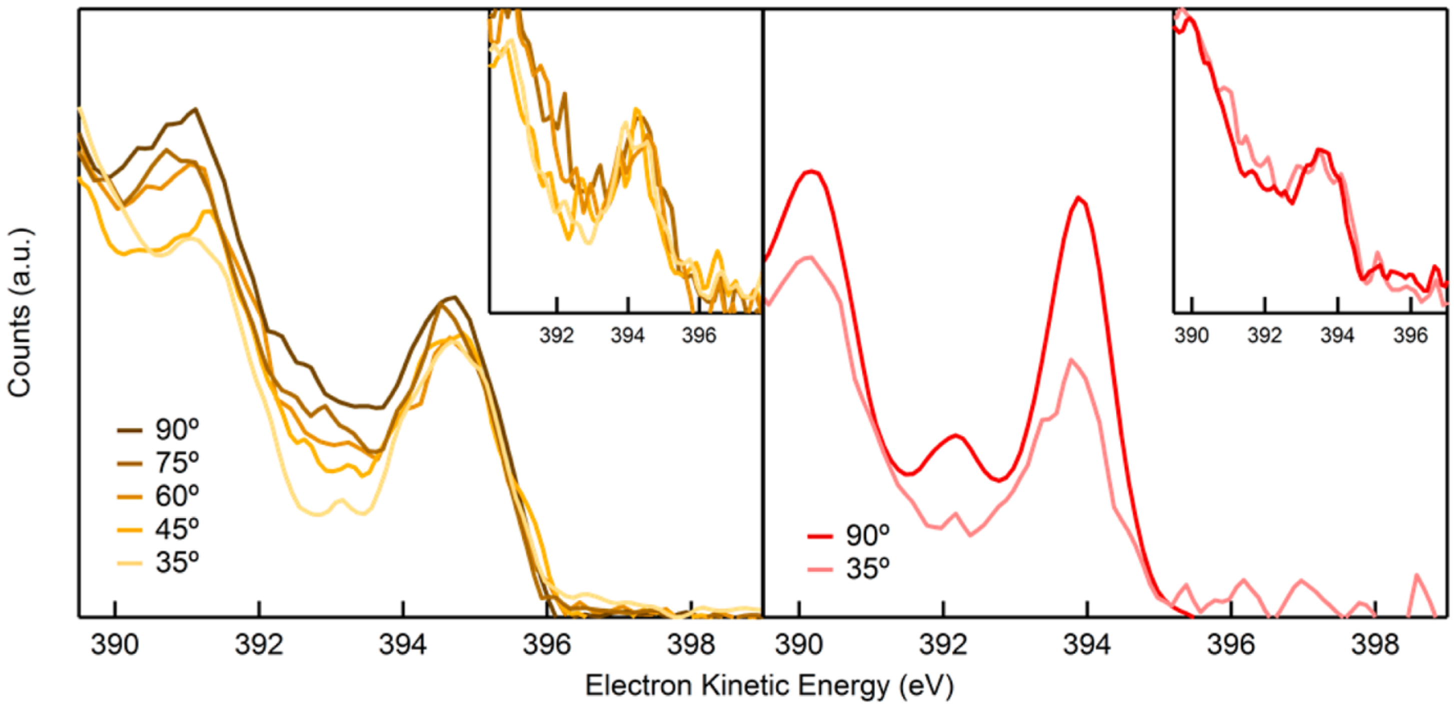
Epitaxial GR



Electron injection Time : T = 10 fs

T = 3 fs

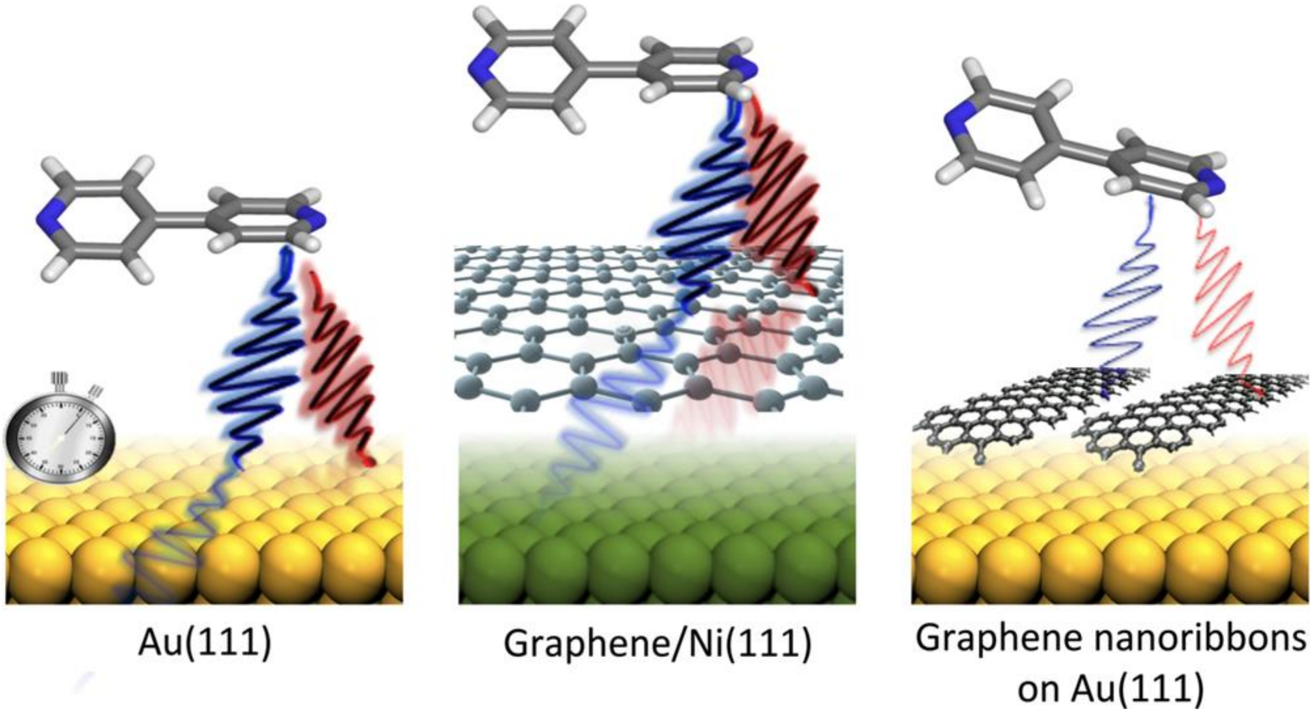
Nitrogen K-edge RPES at the LUMO* energy



BP on Au(111) polarization angles 90°, 75°, 60°, 45°, and 35°

BP on epitaxial GR polarization angles 90° and 35°

Inset: Nitrogen K-edge RPES line scans taken at 416 eV showing the superparticipator peaks



τ_c=2.0 ± 0.5 fs

EG τ_c=4.0 ± 1 fs
DLG τ_c=10.0 ± 5 fs

τ_c=10 ± 2 fs

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We obtain a charge transfer time of 2.0 ± 0.5 fs for the BP/Au(111) system, 4 ± 1 fs for the BP/epitaxial graphene system, 20 ± 5 fs for the DLG and 10 ± 2 fs for the BP/GNR/Au(111) system

Conclusions

Fastest charge transfer to Au

Decoherence in participator channel on Au

Slower to epitaxial graphene

Even slower to GRN probably due to band gap

Slowest to non interacting graphene

Graphene hinders charge transfer from molecule to substrate

Collaborators

ALOISA beamline @ Elettra synchrotron, Laboratorio TASC CNR IOM:
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Ljubljana University

Dean Cvetko, Gregor Bavdek, Gregor Kladnik

Columbia University

Latha Venkataraman, Arun Batra, Masha Kamenetska (charge tranport in single molecule conductance measurements)

John Kymissis, Alon Gorodetsky, Theanne Schiros, (devices based on organic thin films, materials for photovoltaics)

Milano Bicocca University

Guido Fratesi, Gian Paolo Brivio, (charge transfer calculations)

Thank you for you attention.