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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
ALOISA
APE
BACH
BEAR
CIPO
GasPhase
Lilit
XRD1
VUV
SISSI

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

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
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)
Mission

• to provide students with knowledge and training in the field of nanotechnology
• to provide the necessary background to become 21st century scientists and technicians.
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
Methods and Techniques:

Nanofabrication:
- Nanofabrica, on bottom-up
- Nanofabrica, on top-down
- Nanoparticles fabrication, on and characterisation, on
- Self assembly
- Development of MEMS and NEMS
- Development of new nanofabrication, on techniques/instruments
- Templated growth/deposition, on

Applications of Nanotechnology:
- Micro, Nano and Optoelectronics
- 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....

- **Entities involved:**
  - Departments of UNITS: 5
    - Dep. of Physics,
    - Dep. of Engineering 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...

**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
- 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_{8}O_{6})

SPATIAL overlap of Core, LUMO, HOMO wavefunctions?
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: \( T = 4 \text{ fs} \).
- **Nitrogen** KLL: \( T = 5 \text{ fs} \).
- **Argon** L\(_3\)M\(_{4/5}\)M\(_{4/5}\): \( T = 6 \text{ fs} \); 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

Resonant excitation

LUMO
HOMO
CORE

NO CT

CT

LUMO
HOMO
CORE

Auger

Spectator

Participator

2h, 1h
Auger Raman A. RPES

Raman Auger RPES
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

$CT = \frac{I_{\text{coupled}}}{I_{\text{core}}} \frac{I_{\text{iso}}}{I_{\text{coupled}}}$

- Submonolayer PTCDA/Au(110)
Donor-acceptor shape-complementarity drives performance in photovoltaics
**Self-assembled D/A interfaces: HBC and DBTTC**

![Diagram of D/A interfaces with ball and socket joints]

**cathode**

**acceptor (C<sub>60</sub>)**

**PAH donor**

**anode**

**ball and socket joints**


**V<sub>oc</sub>** 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**
• 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:
  o a larger active volume => higher EQE.
  o optimal charge transfer efficiency (faster exciton dissociation) => higher IQE.
  o 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

\[
top_{22} = 2.3 \pm 0.6 \text{fs} \\
bottom = 0.7 \pm 0.3 \text{fs}
\]

\[
top_{44} > 50 \text{fs} \\
bottom = 0.7 \pm 0.3 \text{fs}
\]

22PCP is >20X faster
Changing Link-Group: Amines (NH$_2$ Group)

1,4 Benzenediamine

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?
"Core hole clock” with atomic resolution

We can “populate” empty orbitals on different atomic sites ($N, C_{1,4}, C_{2,3}$) and measure CT dynamics ...
**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 ($\approx 1$ fs)
Beyond the standard Core-Hole-Clock approach

\[ E_{\text{LUMO}}^* > E_F \]

\[ E_{\text{LUMO}}^* \approx E_{\text{gap}} \]

\[ E_{\text{LUMO}}^* < E_F \]

2,2 PCP / Au(111)

Isonicotinic acid / TiO\(_2\)

Pyridines / Au

Nature Communications, 3, 1086 (2012)

G. Fratesi et al., JPCC, 2014
Pyridine on Au: angular dependent coupling

Stohr –Springer, Pyr/Ag(111), “selected systems”, p.326
Superparticipator Auger, reverse charge transfer

Additional core-hole decay channels – Superparticipator Auger – not present in gas/multilayer
**CHC analysis of Super-participator peak intensity:**

\[
f = \frac{I_p}{I_p^0}, \quad \beta = \frac{I_{sp}}{I_p}
\]

\[
\tau = \frac{f(1-\beta)}{1-f(1-\beta)}
\]

\[
x = \frac{\beta f}{1-f(1-\beta)}
\]
• **DFT -> LUMO* pinned at Fermi**
• **LUMO* coupling to Au continuum decreases**
• **With increasing tilt angle $\Delta \rho$ with LUMO symmetry -> charge BT to LUMO* =⇒ ultrafast el. injection from Au.**

(a) ![Energy vs. DOS](image)
(b) ![Charge transfer vs. $\theta$](image)
(c) ![Molecule representation](image)
(d) ![Molecule representation](image)
(e) ![Molecule representation](image)
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

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Why graphene?

Graphene: single layer of sp² hybridized C atoms

2D material with remarkable properties:
- high electric conductivity
- thermal stability
- mechanical strength
- unusual band structure
- transparent electrode
Core-hole-clock of ultrafast charge injection at GR/organic interface

Bipyridine

Bilayer GR/Ni(111)  Epitaxial GR/Ni(111)
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.
Electron injection Time: $T = 10\,\text{fs}$
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
We obtain a charge transfer time of $2.0 \pm 0.5$ fs for the BP/Au(111) system, $4 \pm 1$ fs for the BP/epitaxial graphene system, $20 \pm 5$ fs for the DLG and $10 \pm 2$ 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
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Dean Cvetko, Gregor Bavdek, Gregor Kladnik

Columbia University
Latha Venkataraman, Arun Batra, Masha Kamenetska (charge transport 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 your attention.