Magnetic molecular networks

Maria Grazia BETTI*

Dipartimento di Fisica, CNISM, Università di Roma La Sapienza

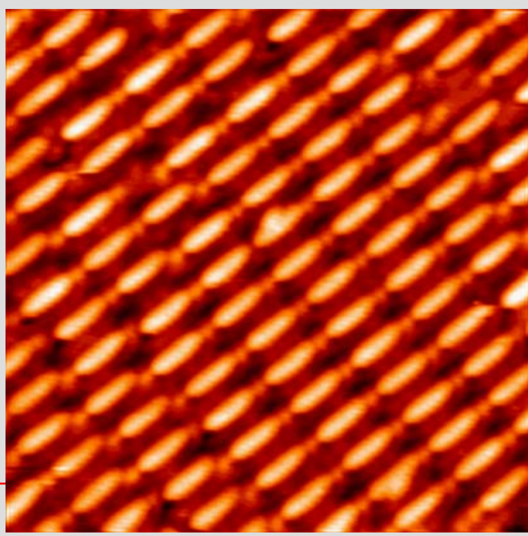
http://server2.phys.uniroma1.it/gr/lotus/index.htm

*with Pierluigi GARGIANI (post-doc)

Simone LISI (PhD student)

Sara FATALE (laureanda)

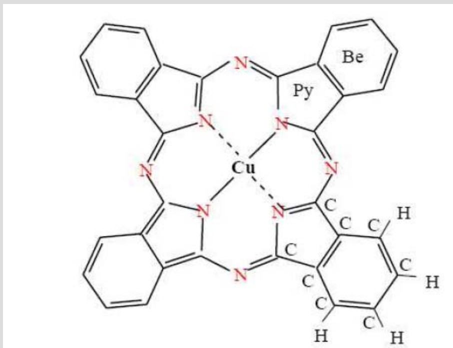
15 nm



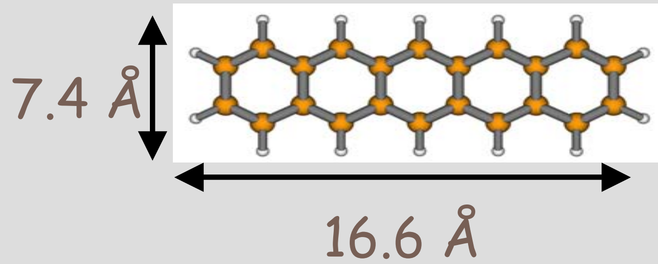
Roma, CNISM, 13 giugno 2012

molecular model systems

Cu-phthalocyanine, CuPc:
Cu-$C_{32}H_{18}N_8$

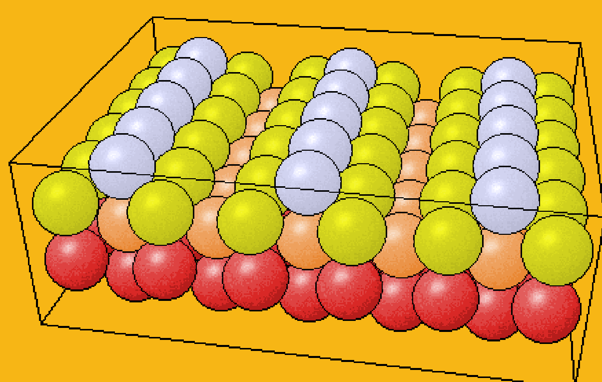


pentacene: $C_{22}H_{14}$

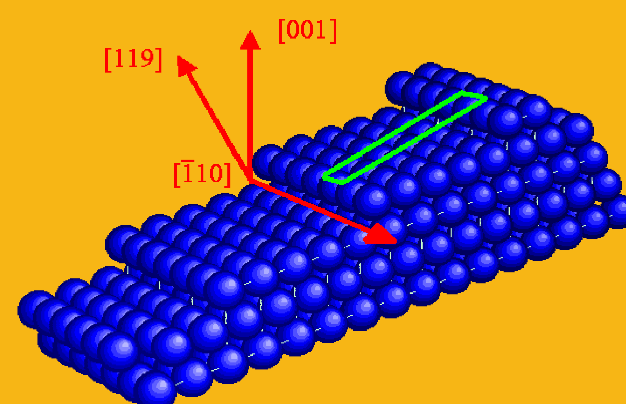


naturally patterned substrates

Au(110)-(1x2)



Cu(119)

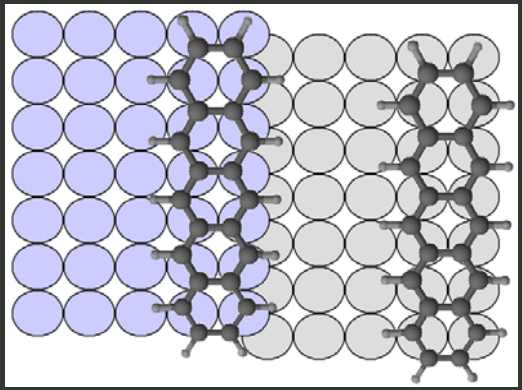


changing the molecular orientation and interaction

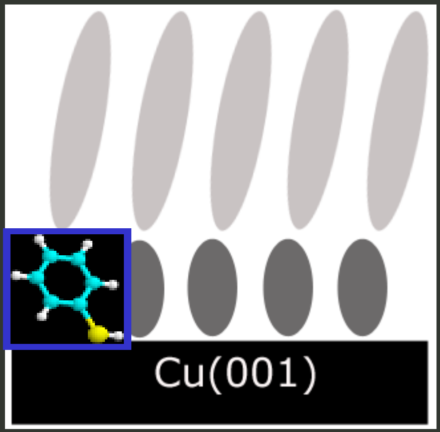
organic-metal interface (OM)

organic-organic interface (OO)

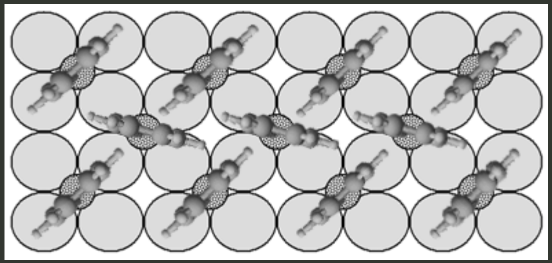
side view



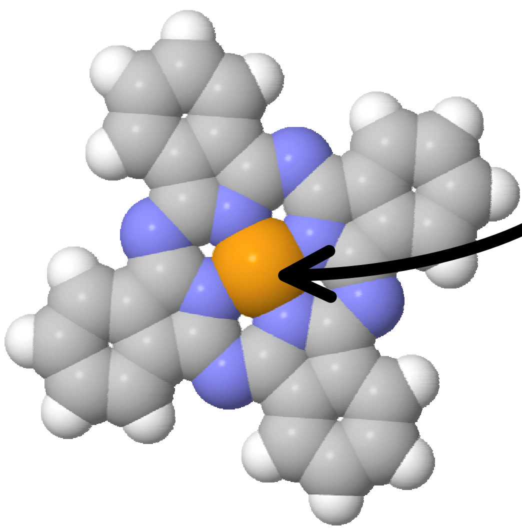
top view



C_6H_5S-SAM buffer layer



Baldacchini et al., Phys. Rev. B **76**, 245430 (2007); **Ferretti et al.**., *Phys. Rev.Lett.* **99**, 046802 (2007);
Betti et alii, Physical Review Letters **100**, 027601 (2008); J. Phys. Chem. A **111**, 12454 (2007)



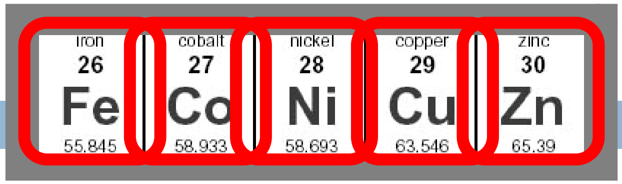
Structural configuration, ordering

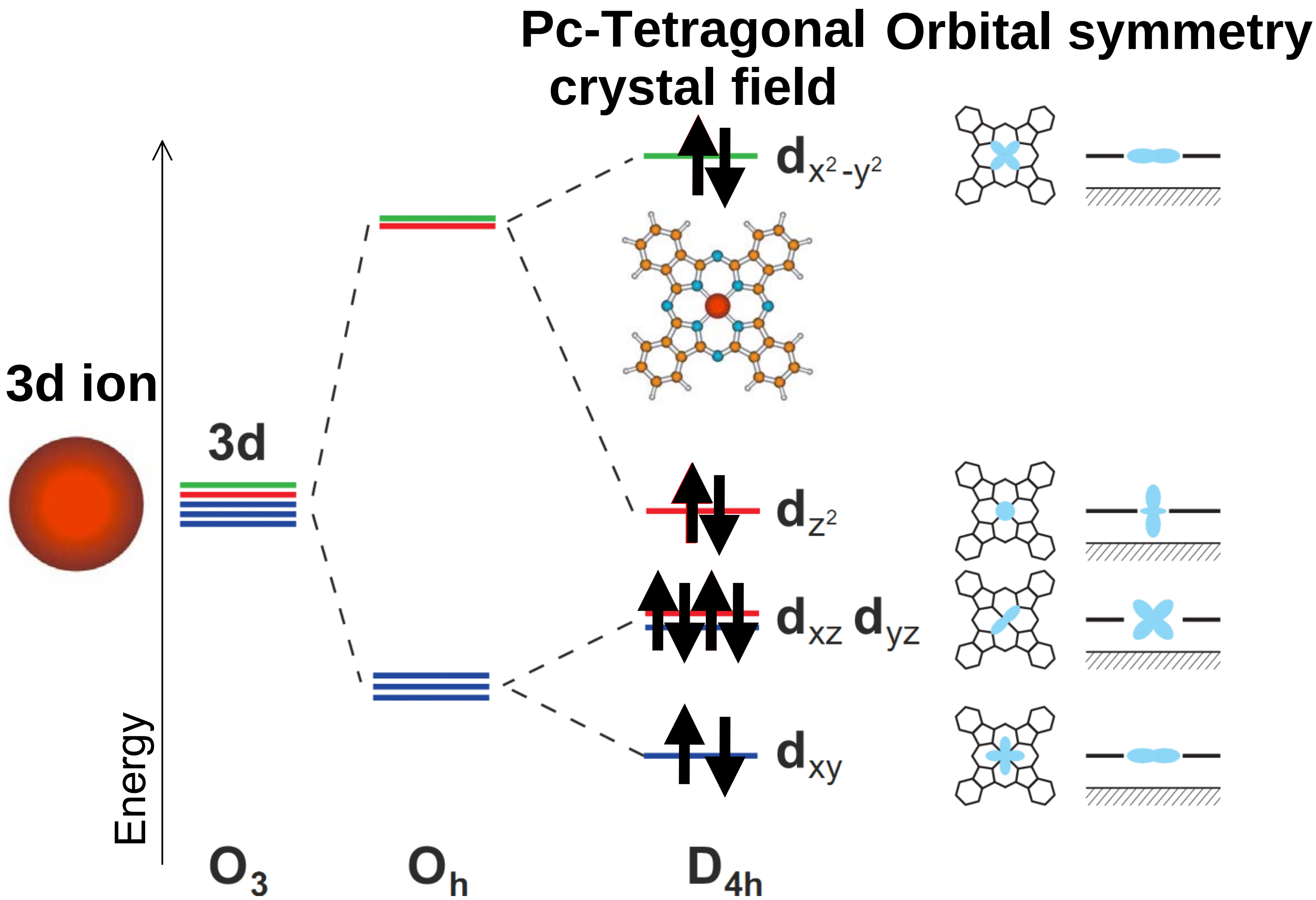
Metal ion configuration

Molecule/substrate coupling

Charge injection into molecular orbitals

Spin configuration of metal-phthalocyanines

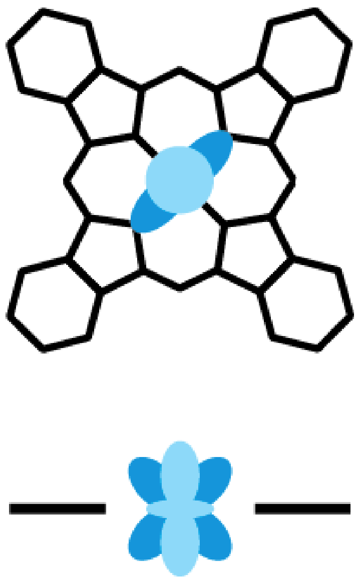




Three paradigmatic systems

MPcs spin-carrying orbitals spatial distribution:

FePc

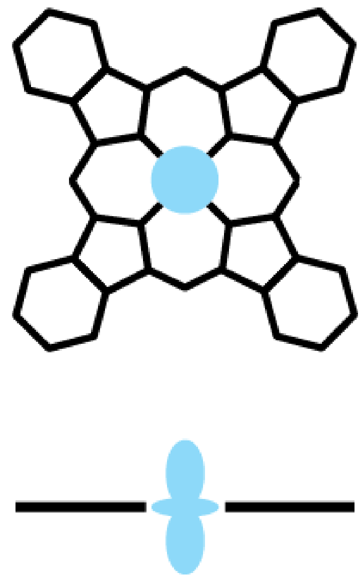


S=1

Semi-occupied levels: a_{1g}, e_g

mostly out-of-plane

CoPc

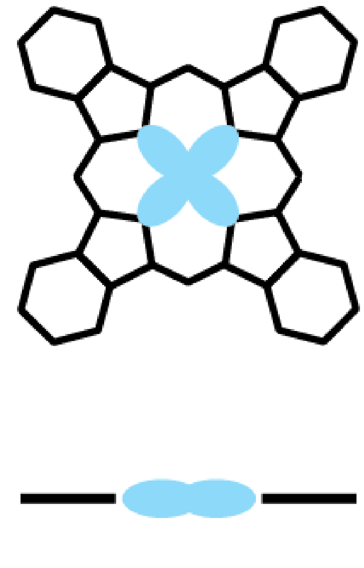


S=1/2

Semi-occupied levels: a_{1g}

out-of-plane

CuPc



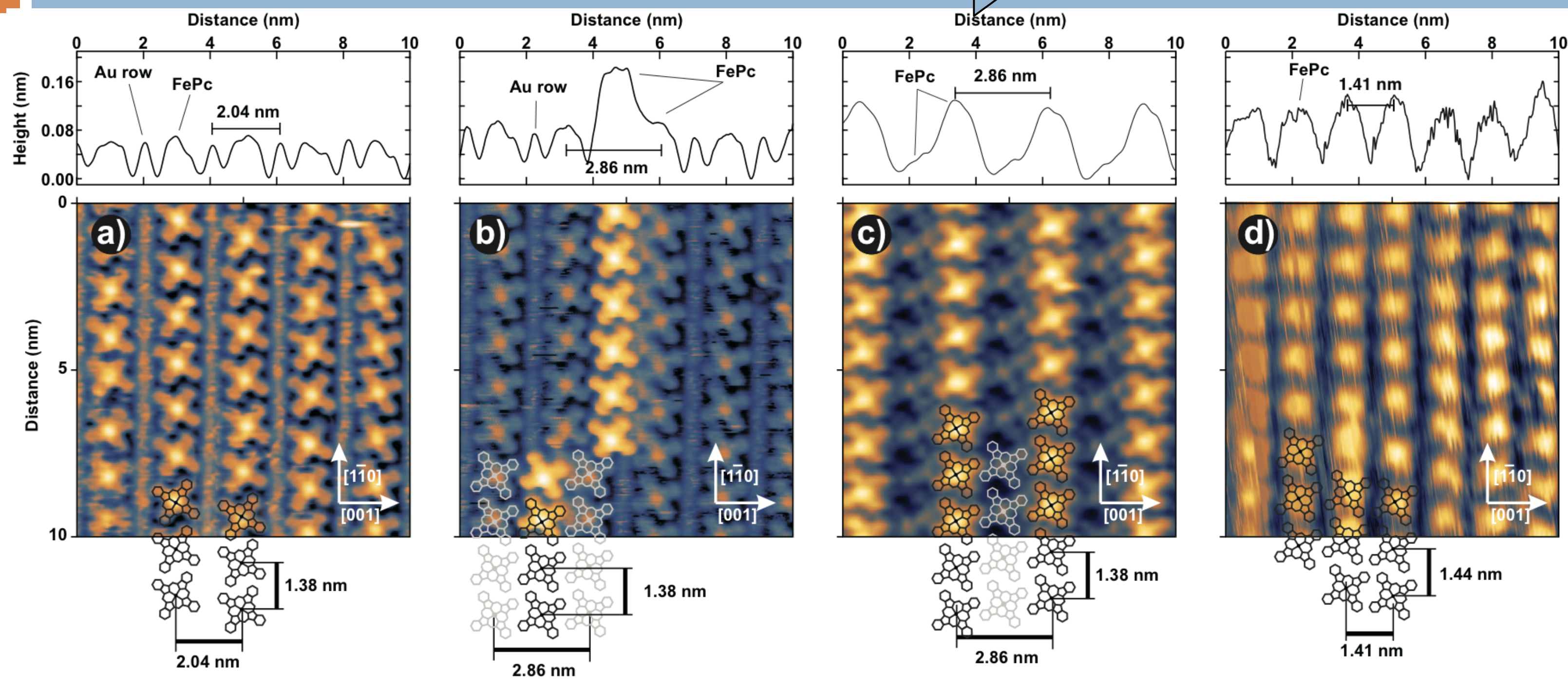
S=1/2

Semi-occupied levels: b_{1g}

in-plane

FePc/Au(110): molecular ordering

FePc coverage

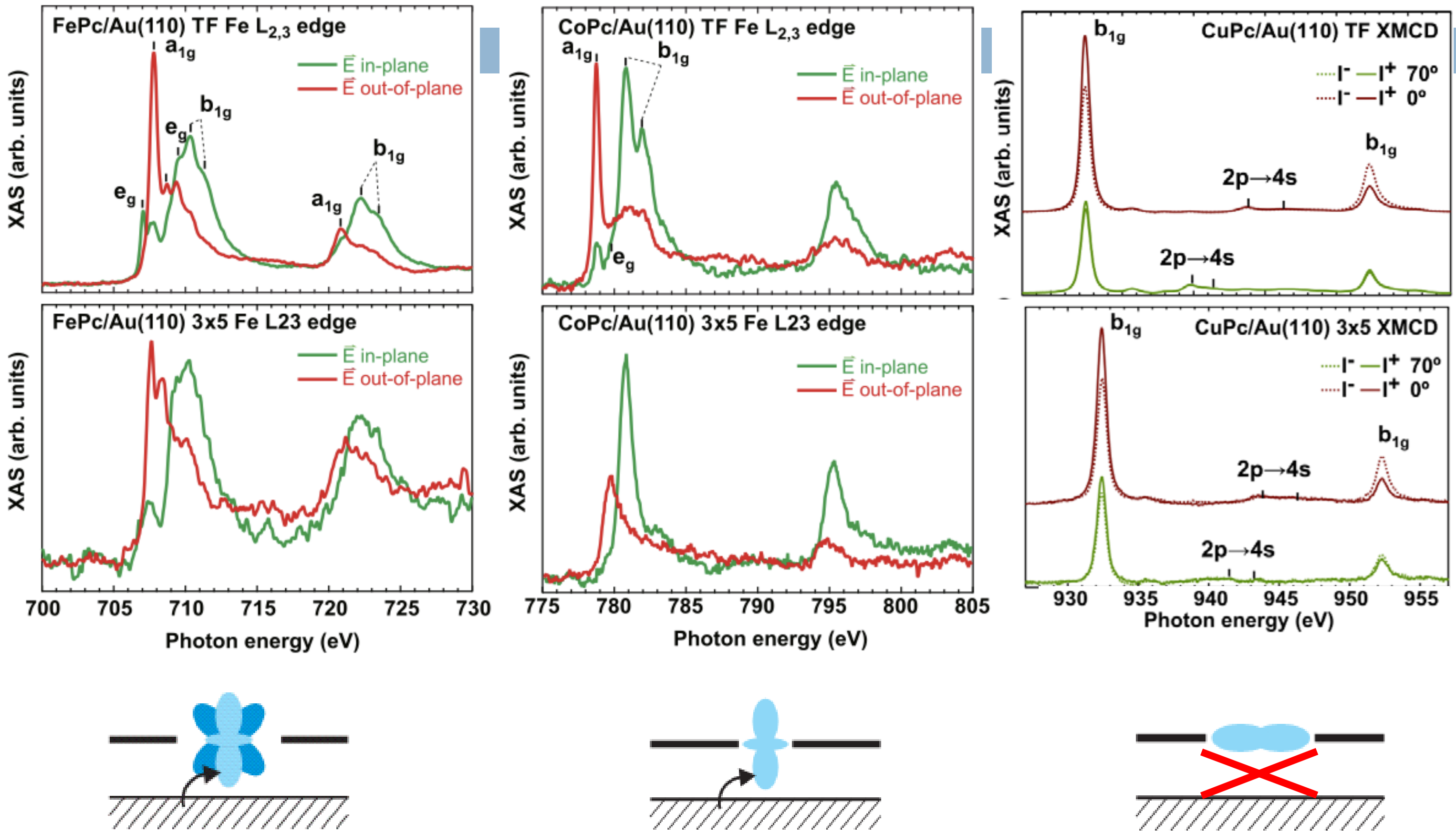


Formation of MPc molecular chains

Sara Fortuna et al., J. Phys. Chem. C **116**, 6251 (2012);
Maria Grazie Betti et al., J. Phys. Chem. C **116**, 8657 (2012)

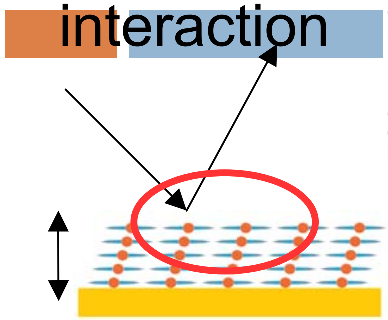
3d metal interaction with Au(110): XAS (NEXAFS)

FePc CoPc CuPc

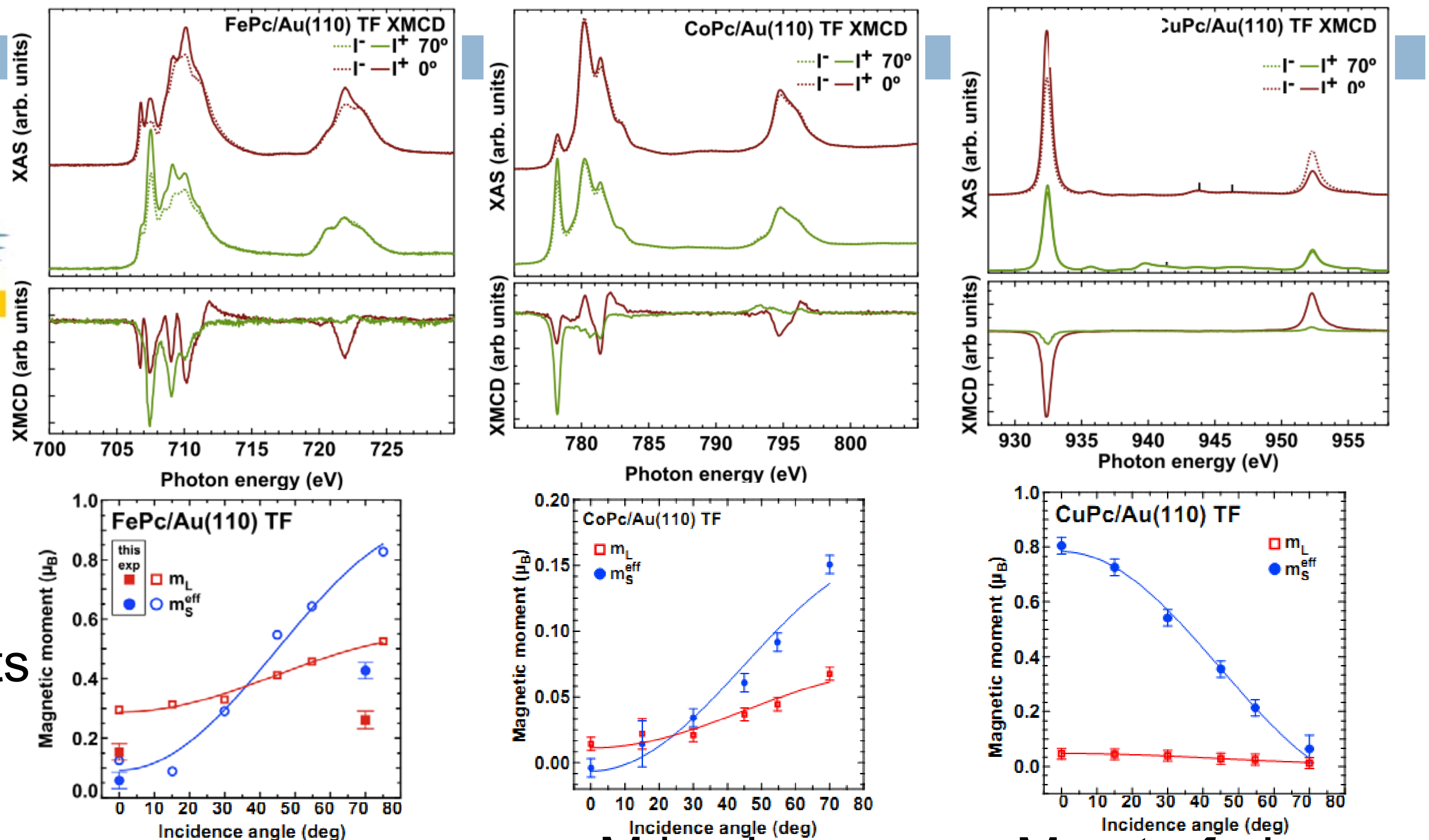


XMCD on Mpcs thin films

no substrate interaction



FePc S=1 | CoPc S=1/2 | CuPc S=1/2



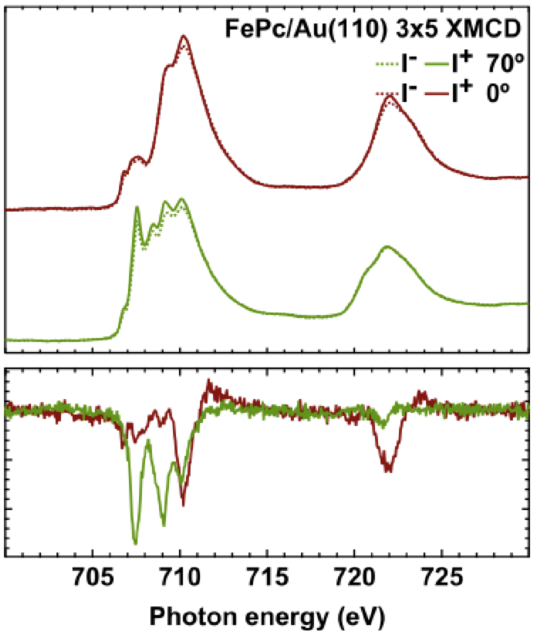
M in plane | M in plane | M out-of-plane

Orbital and **Spin** moments vs angle

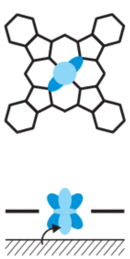
- Magnetic moment ≠0 for Fe, Co and CuPc
- Magnetization easy axis dependent on orbital configuration

XMCD on MPc single-layers / Au(110)

FePc

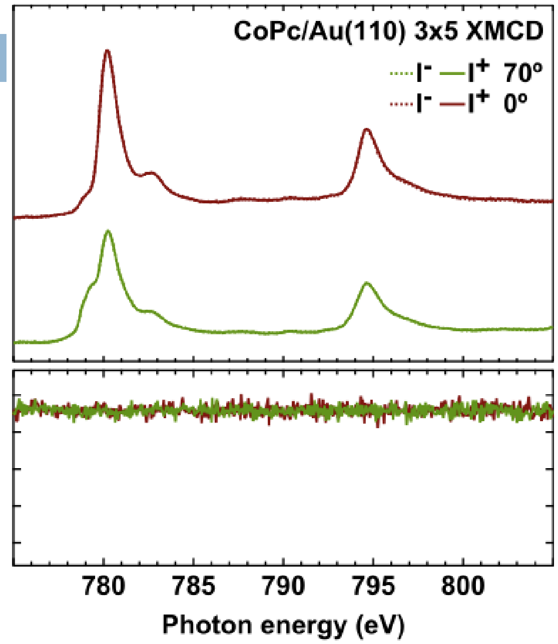


- **FePc: reduced moment**

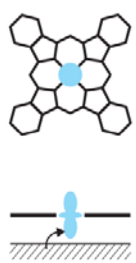


- **Out-of-plane 3d metal orbitals**
- **Fe/substrate hybridiziation**

CoPc

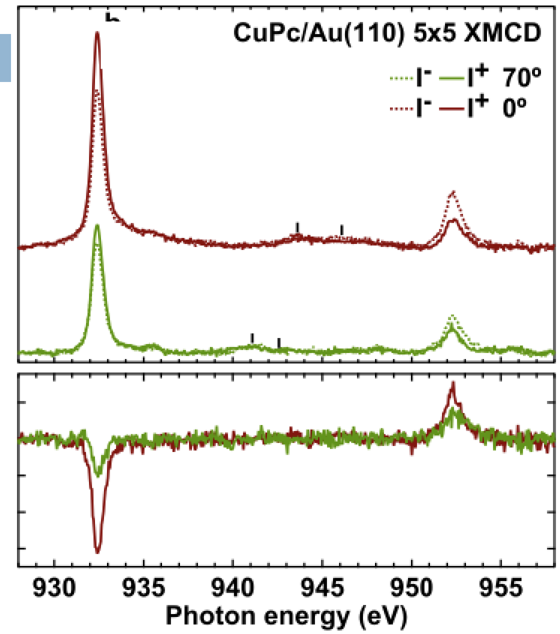


- **CoPc: quenched moment**



- **Out-of- plane 3d metal orbitals**
- **Strong Co/substrate hybridization**

CuPc



- **CuPc: unaffected moment**

- **In-plane 3d metal orbitals**
- **No Cu/substrate hybridization**

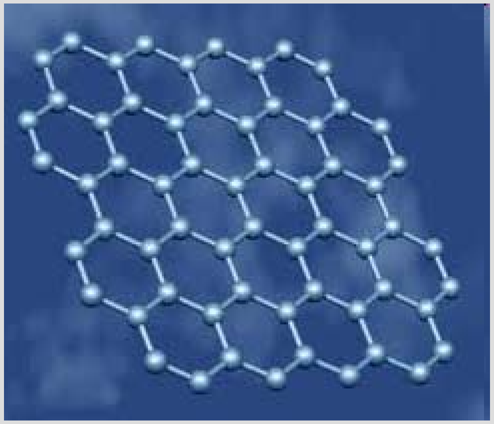
Graphene and its functionalisation

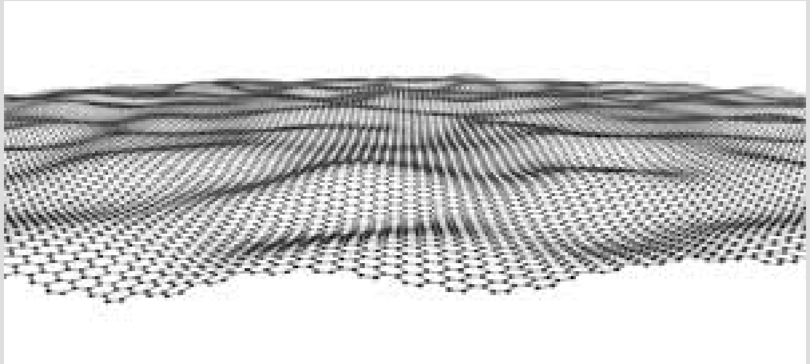
Carlo MARIANI*

Dipartimento di Fisica, CNISM, Università di Roma La Sapienza

http://server2.phys.uniroma1.it/gr/lotus/index.htm

*with Mattia SCARDAMAGLIA (PhD student)
Simone LISI (PhD student)
Marco ANGELUCCI (PhD student)
Lorenzo MASSIMI (laureando)

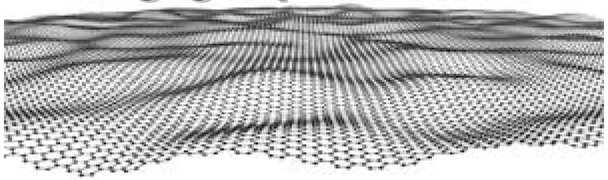




Roma, CNISM, 13 giugno 2012

Come lo facciamo crescere per utilizzarlo?

Quasi –free standing graphene



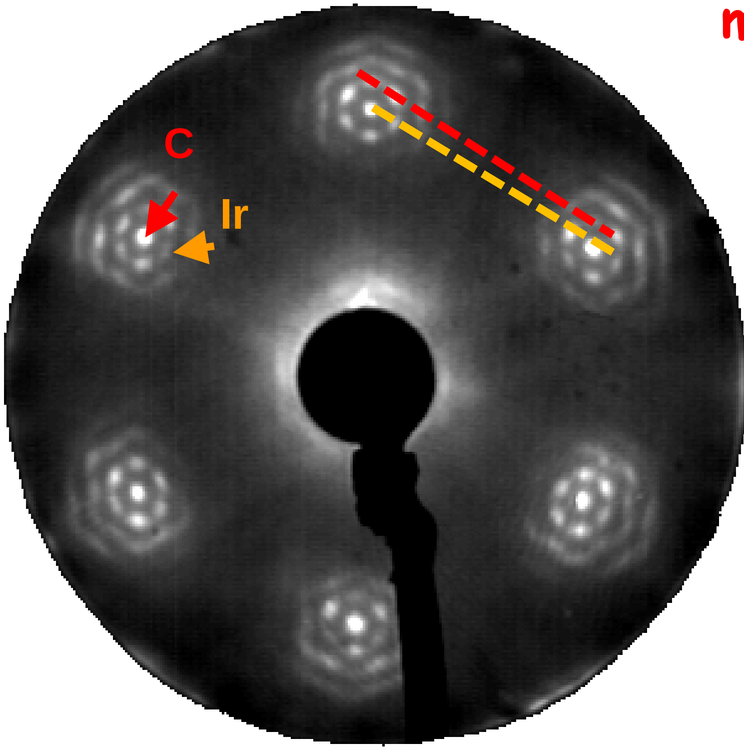
Epitaxial growth on transition metal surfaces:
5d - **Ir(111),** Pt(111)
4d - Ru(0001), Rh(111)
3d - Ni(111)

Increase of the interaction strength:
- more graphene corrugation
- less C / TM distance
- gap opening at K (as SiC)
- hybridization π - d

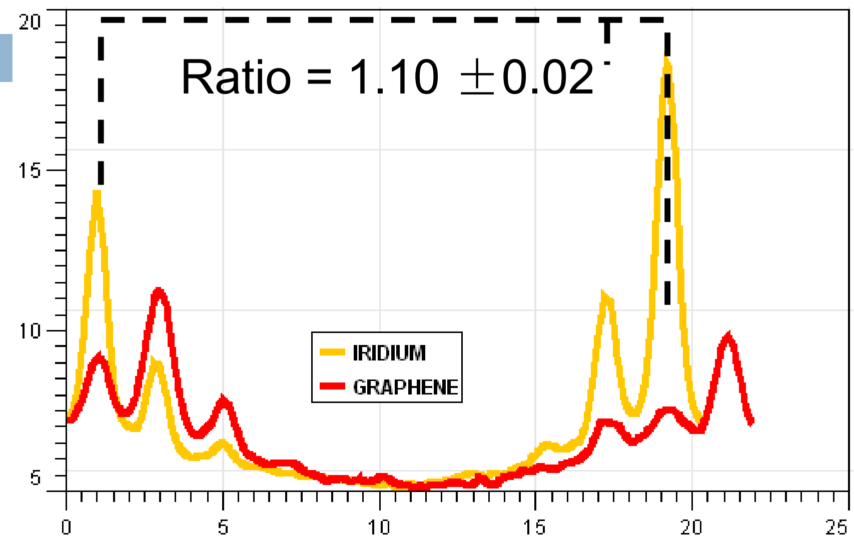
Preobrajenski et al., *Phys. Rev. B* 78, 073401 (2008)
Lacovig et al., *Phys. Rev. Lett*., 103, 166101 (2009)

Ir(111) the best compromise between quasi-free standing and use

Long-range order (low-energy electron-diffraction, LEED)



moiré pattern



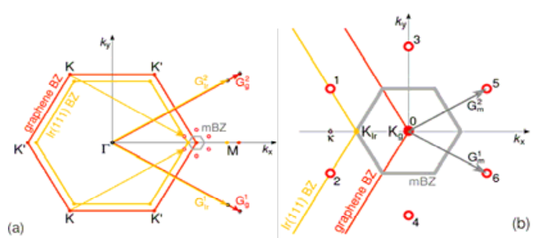
Super-periodic potential's vector: $\mathbf{G_m} = \mathbf{G_g} - \mathbf{G_i}$

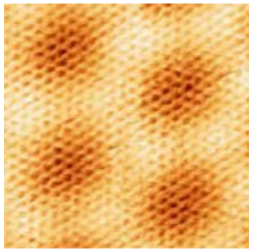
Ir: 2.71 Å
C: 2.45 Å

--> moiré: 25.2 Å

LEED, diffraction

M. Scardamaglia et al.,
J. Nanop. Res. **13**, 6013 (2011)



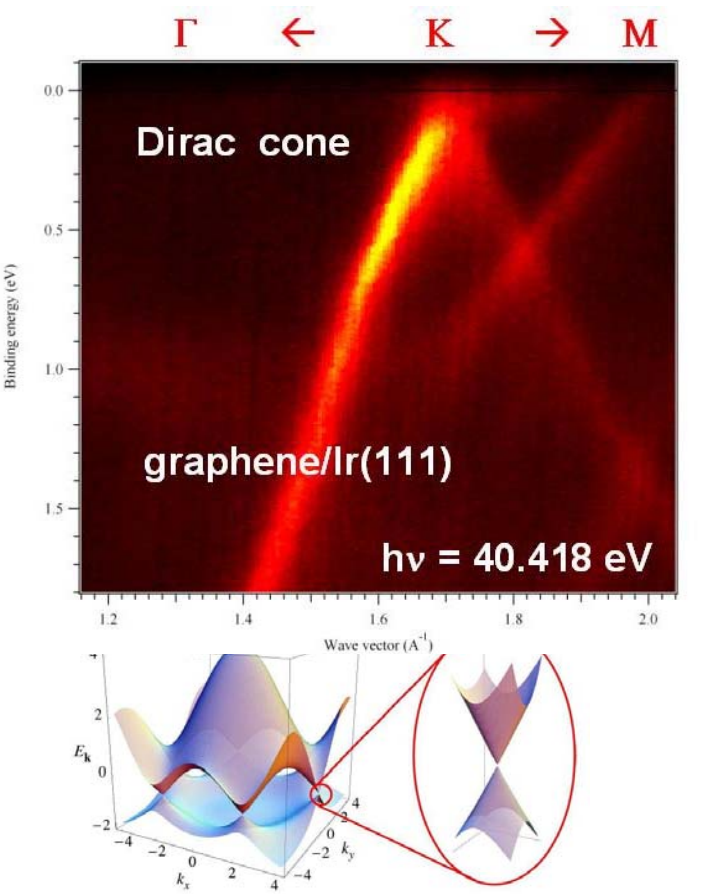


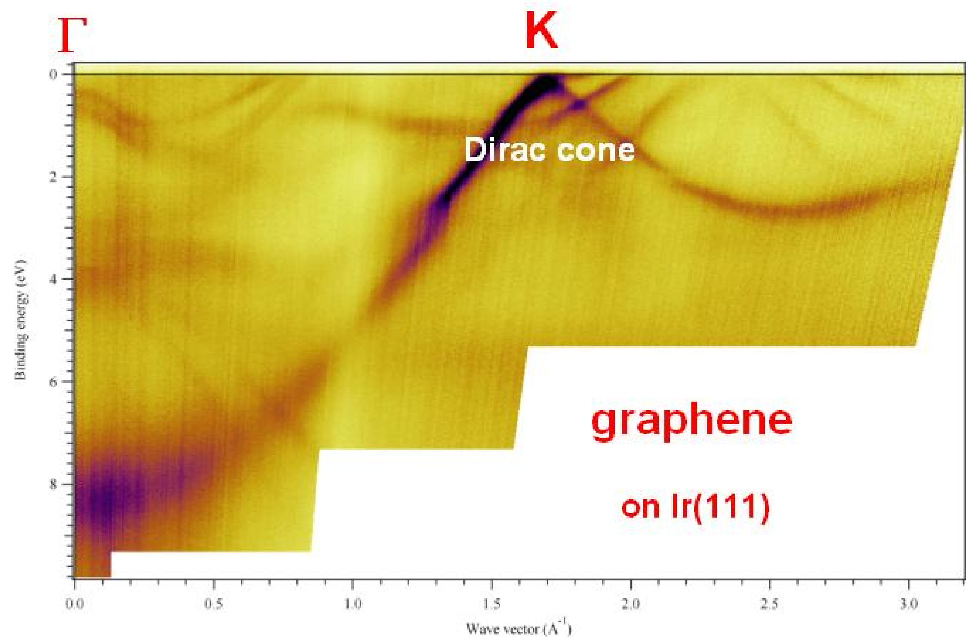
STM, local imaging

Pletikosic et al., *Phys. Rev. Lett.* 102, 056808 (2009)

il cono di Dirac sul graphene/Ir(111)

- il nostro dato misurato nel lab. LOTUS della Sapienza a Roma

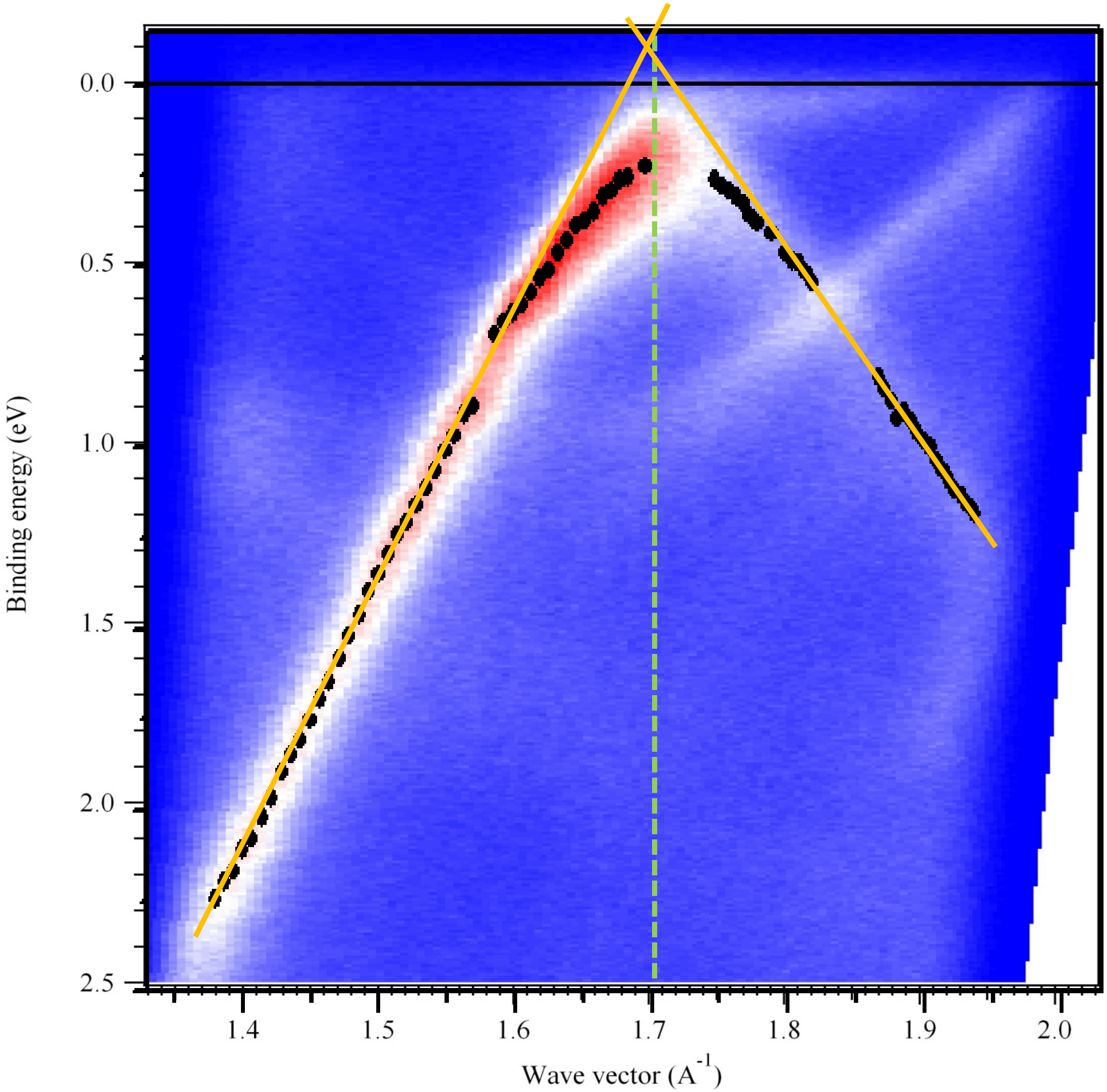




High-Resolution Angular-Resolved Ultraviolet Photoelectron Spectroscopy (HR-ARUPS)

M. Scardamaglia, P. Gargiani , M.G.Betti, and C. Mariani, to be published

il cono di Dirac a 40.8 eV di hν

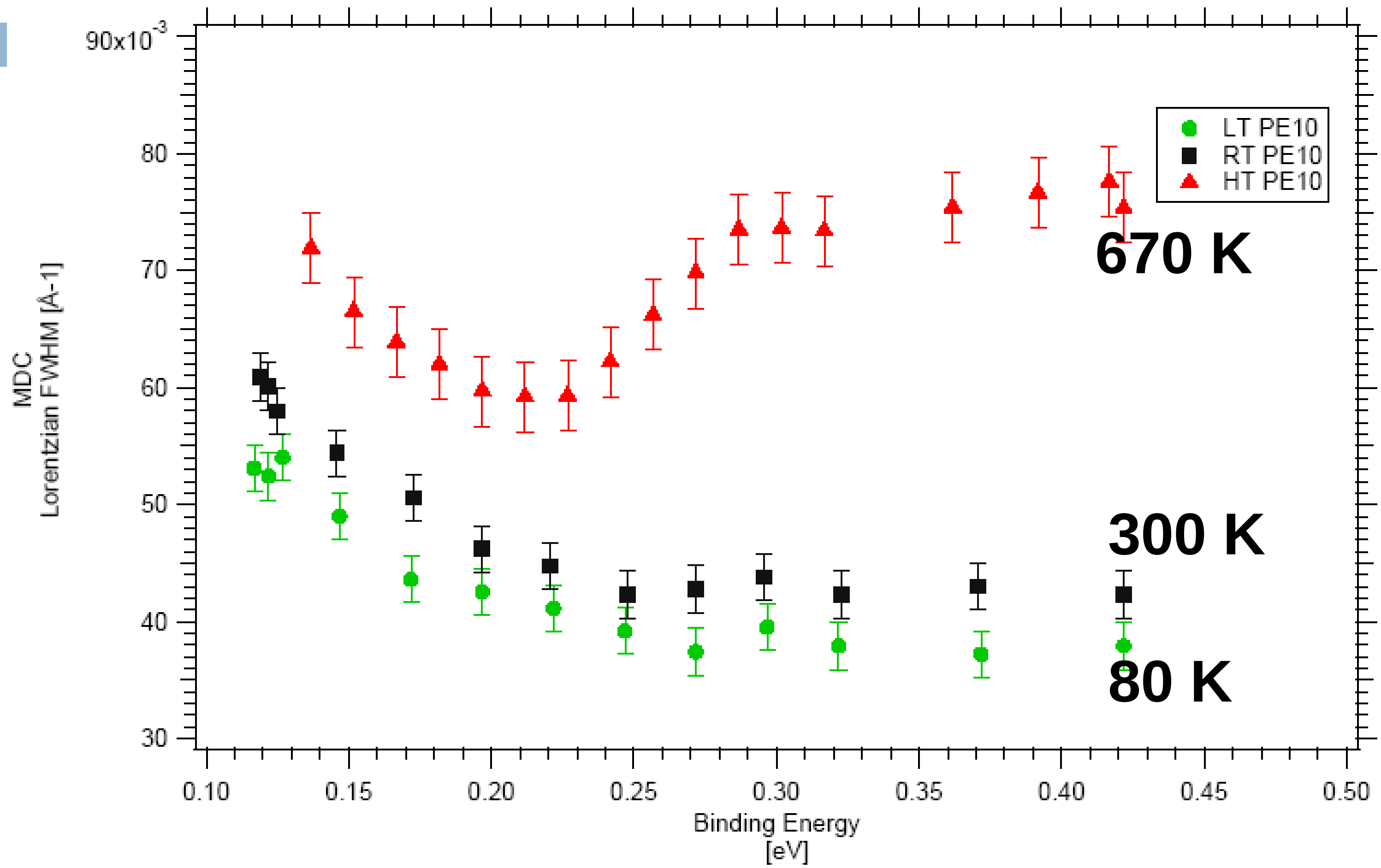


$v_{\Gamma K} = (11.6 \pm 0.5) \cdot 10^5$ m/s

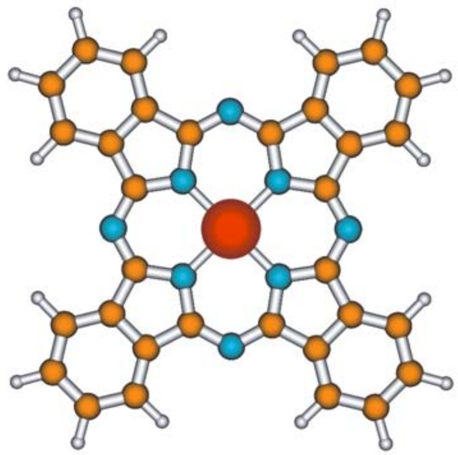
$v_{KM} = (8.4 \pm 0.9) \cdot 10^5$ m/s

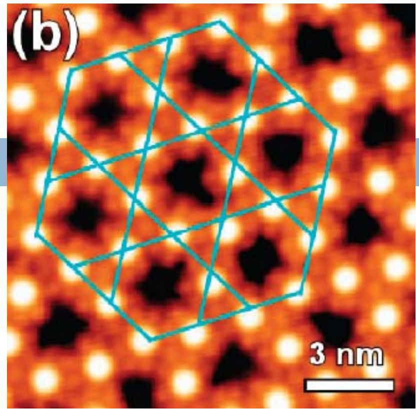
$E_D = (110 \pm 50)$ meV

il kink (minigap) a 0.2 eV BE, e-ph interaction



single-layer FePc – graphene/Ir(111)

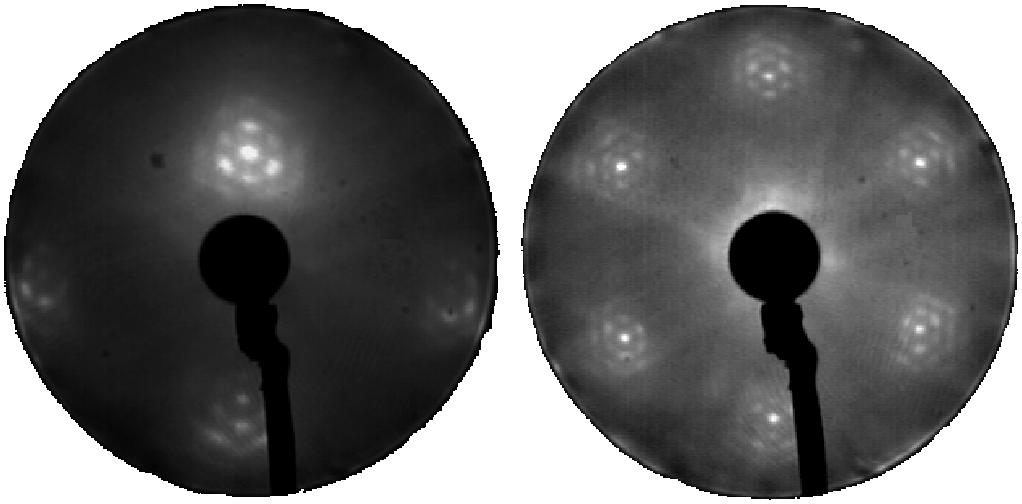


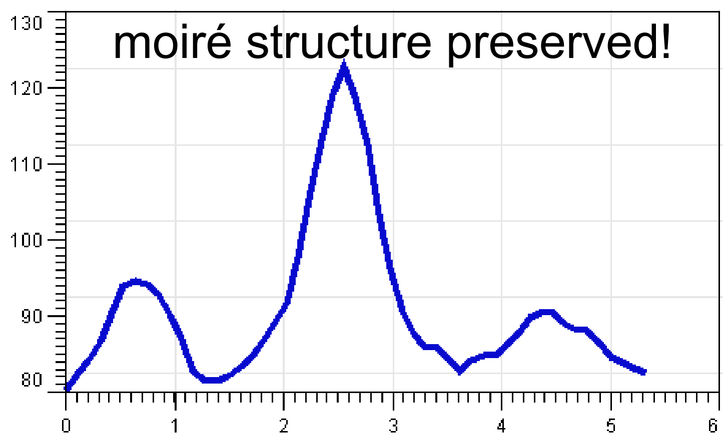


Mao et al., *JACS.* 131, 14136 (2009)

SL FePc – graphene/Ir(111)

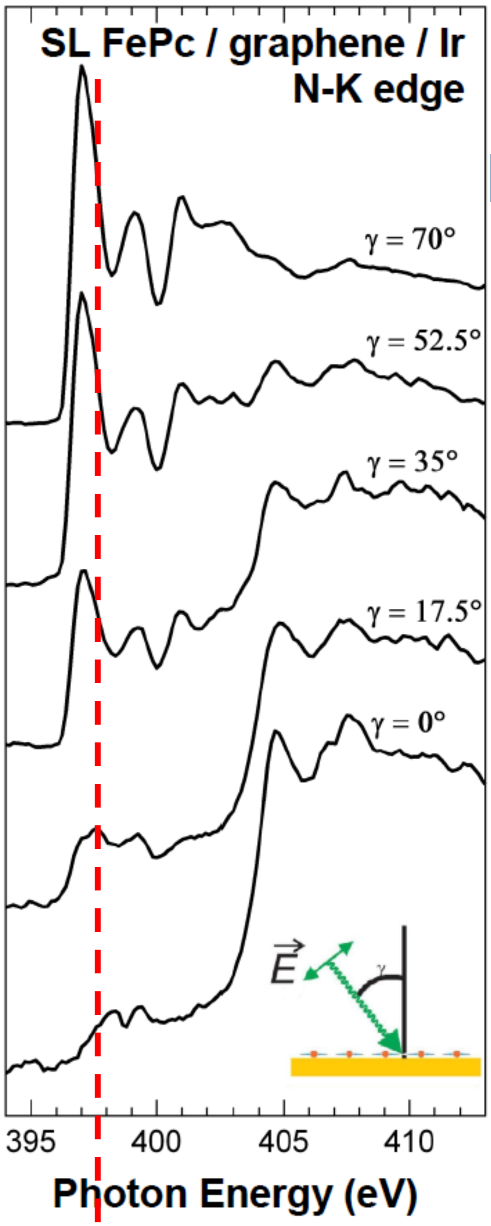
70 eV T = 70 K **141 eV**



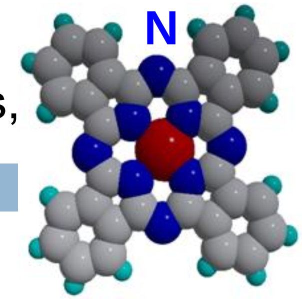


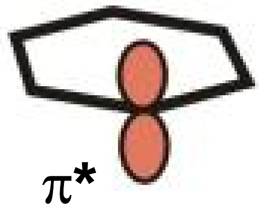
➡ the first SL of FePc takes places in the 10x10 real-space superstructure of the moiré cell

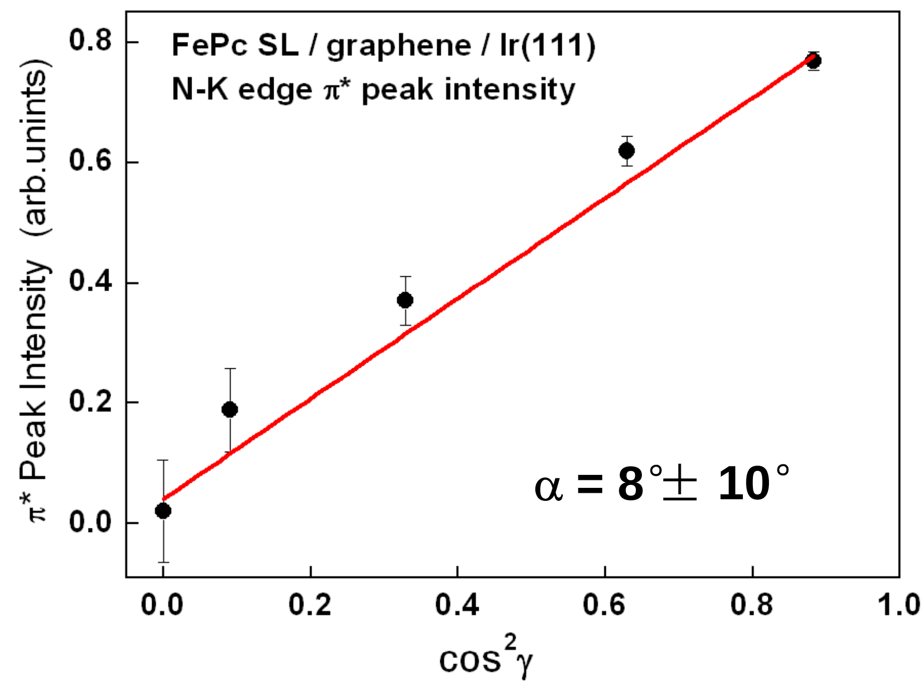
FePc MOLECULAR ORIENTATION



NEXAFS across the N K-edge, exploiting the symmetry of π^* and σ^* orbitals, by using linearly polarized radiation





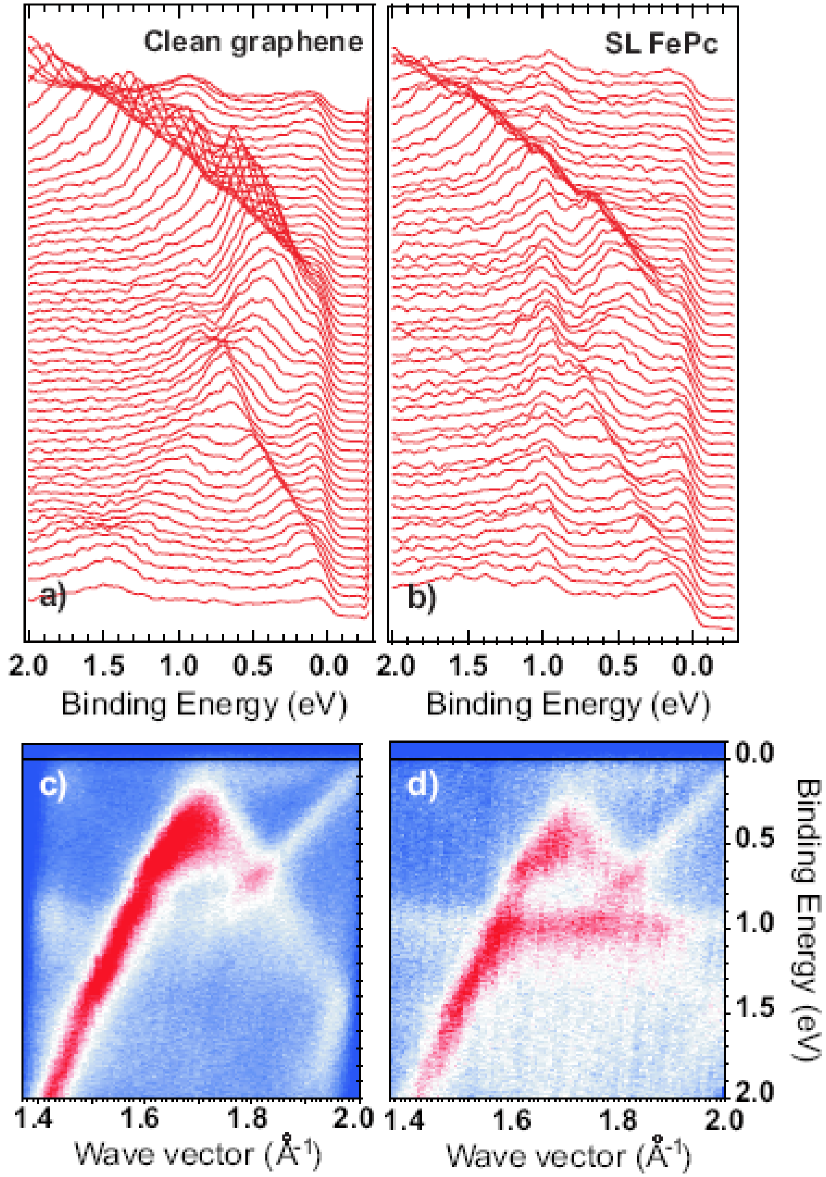


Flat lying configuration

M. Scardamaglia et al., *J. Nanop. Res*. **13**, 6013 (2011)

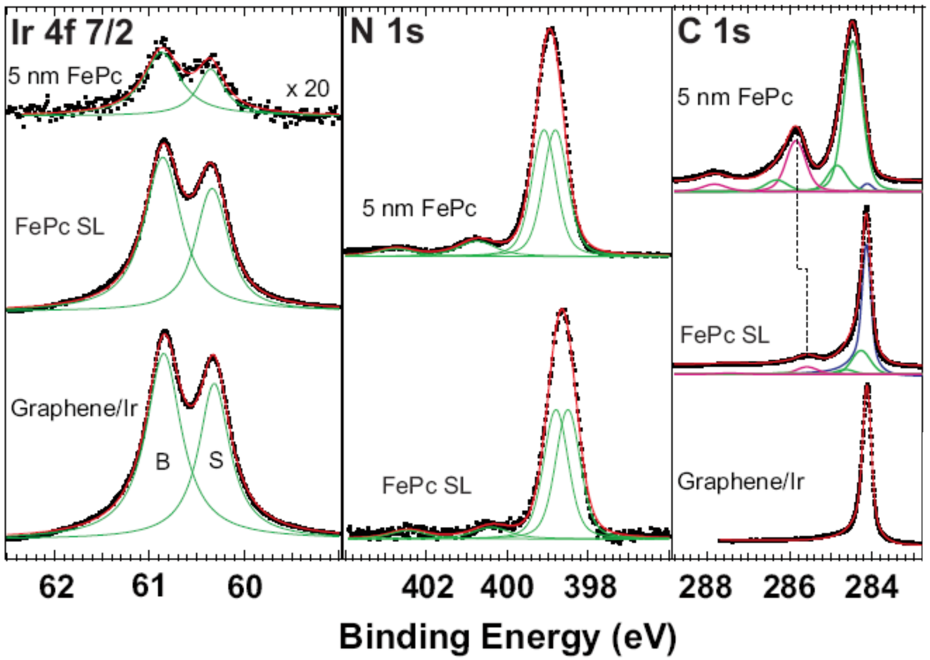
the Dirac cone?

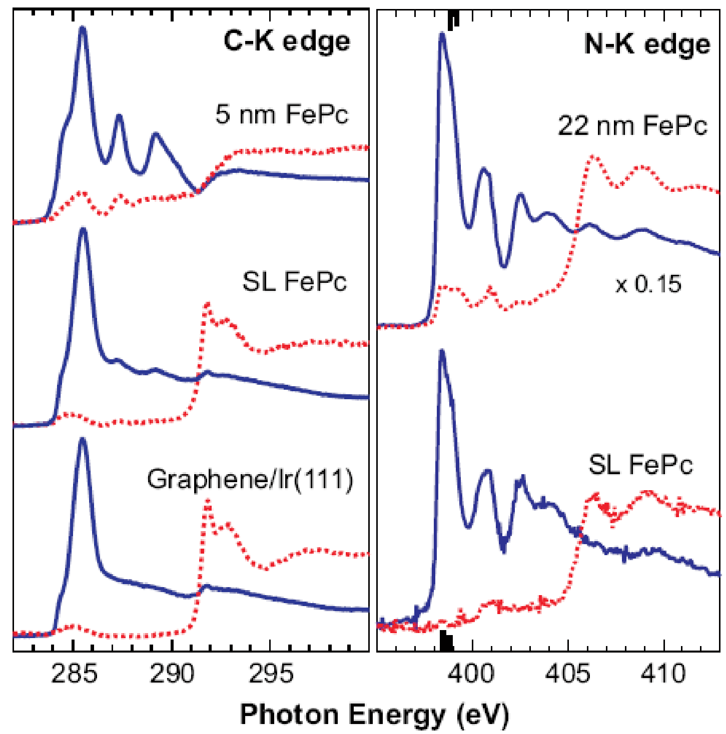
FePc causes a light n-type doping: -80 meV energy shift and a light velocity renormalization (less than 10%)
→ weak coupling



M. Scardamaglia et alii,to be published

the FePc – graphene – Ir interaction

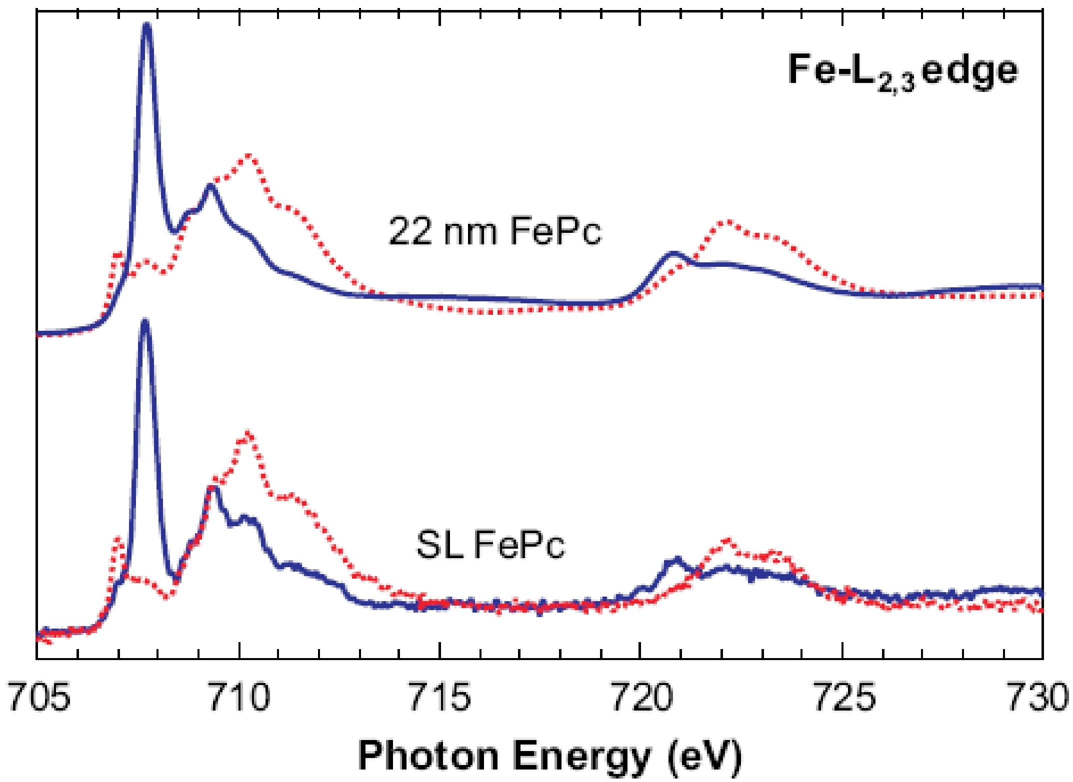




weak contribution of the organic macrocycles to the interaction

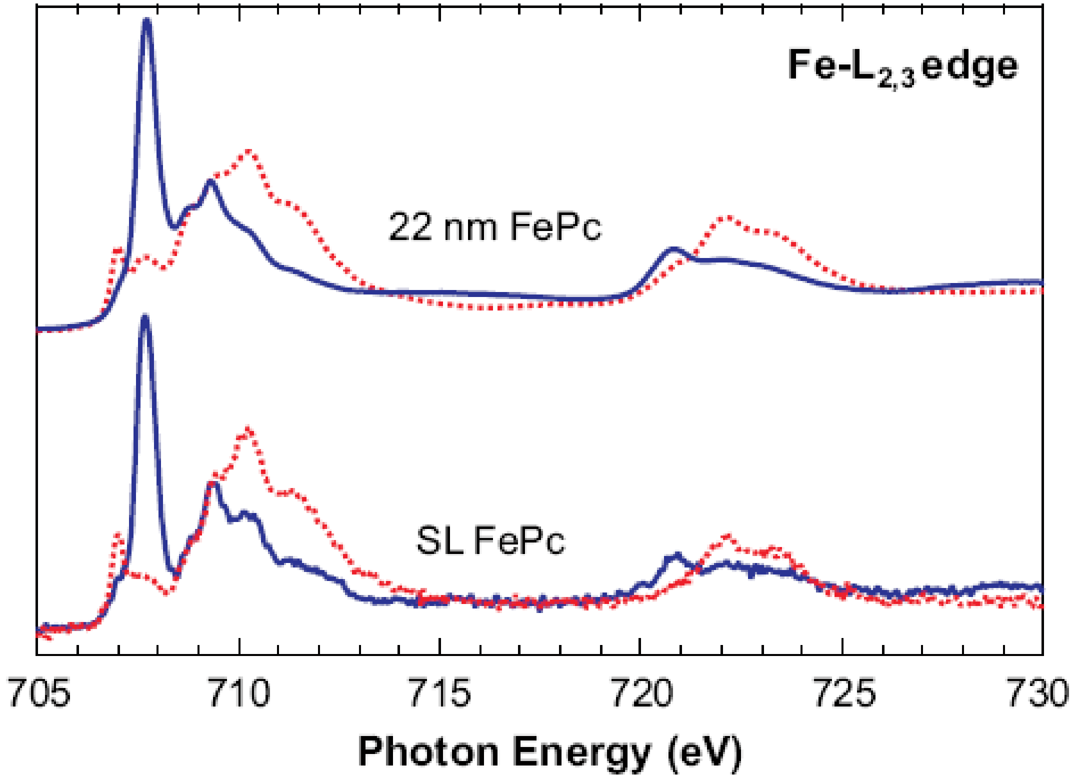
M. Scardamaglia et al., *J. Nanop. Res*. **13**, 6013 (2011); and to be published

the FePc – graphene – Ir interaction



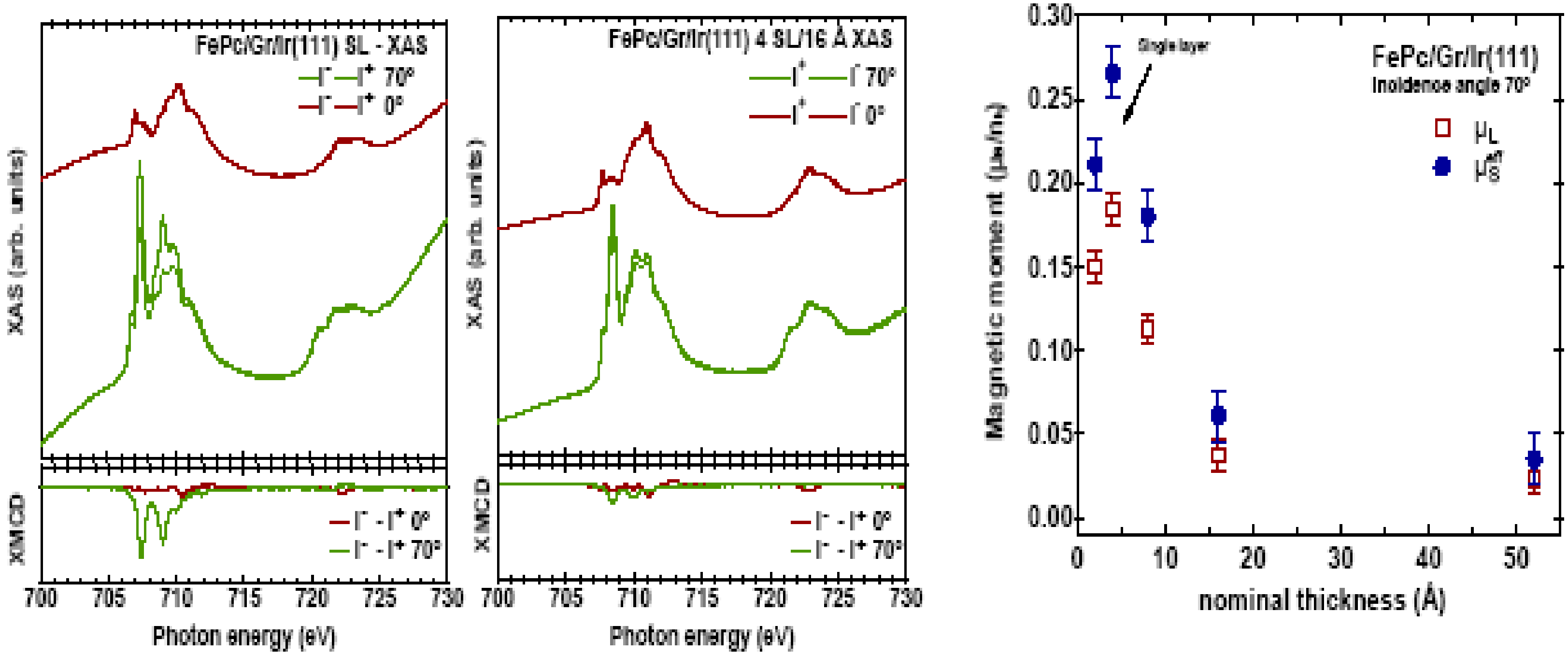
much narrower Fe-related d-orbitals at the $L_{2,3}$ edges → spin-dependent interaction ?

the FePc – graphene – Ir interaction



much narrower Fe-related d-orbitals at the $L_{2,3}$ edges → spin-dependent interaction ?

the FePc – graphene – Ir magnetic properties



<u>Giant magnetic anisotropy</u> at the FePc single-layer on graphene → functionalisation with MPc magnetic molecules, towards a spin-valve?

Experimental techniques and collaborations

Electronic structure: electron spectroscopies

- High-Resolution Angular-resolved UV Photoemission (in-situ
  LOTUS Lab. Dip. Fisica Università "La Sapienza"
- Polarization dependent X-Ray absorption (Synchrotron radiation: beamlines ID08 @ ESRF, ALOISA @ ELETTRA)
- X-ray Photoemission (Synchrotron radiation: beamlines CIPO and ALOISA @ ELETTRA)

LOTUS

Magnetic measurements

- X-Ray Magnetic Circular Dichroism (Synchrotron radiation + magnetic field: beamline ID08 @ ESRF)

elettra

Structural investigation: microscopy and diffraction

- Scanning Tunneling Microscopy (STM) in collaboration with Prof. Silvio Modesti TASC Trieste (Synchrotron radiation + magnetic field: beamline ID08 @ ESRF)
- Grazing Incidence X-ray Diffraction (Synchrotron radiation: beamline ID03 @ ESRF)
- Low Energy Electron Diffraction (LEED) (in situ)

ESRF

Theoretical calculations

- DFT (PBE-GGA), SISSA @ ELETTRA group, S. Fabris et alii