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Mesoscopic Donor-Acceptor Multilayer by Ultra-High-Vacuum Deposition of Zn-Tetraphenyl-Porphyrin and C70

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Zn-porphyrin/C_{70} complexes for solar cells: Molecular orientations, electronic properties and charge transfer time

Mesoscopic Donor-Acceptor Multilayer by Ultra-High-Vacuum deposition of Zn-Tetraphenyl-Porphyrin and C_{70}

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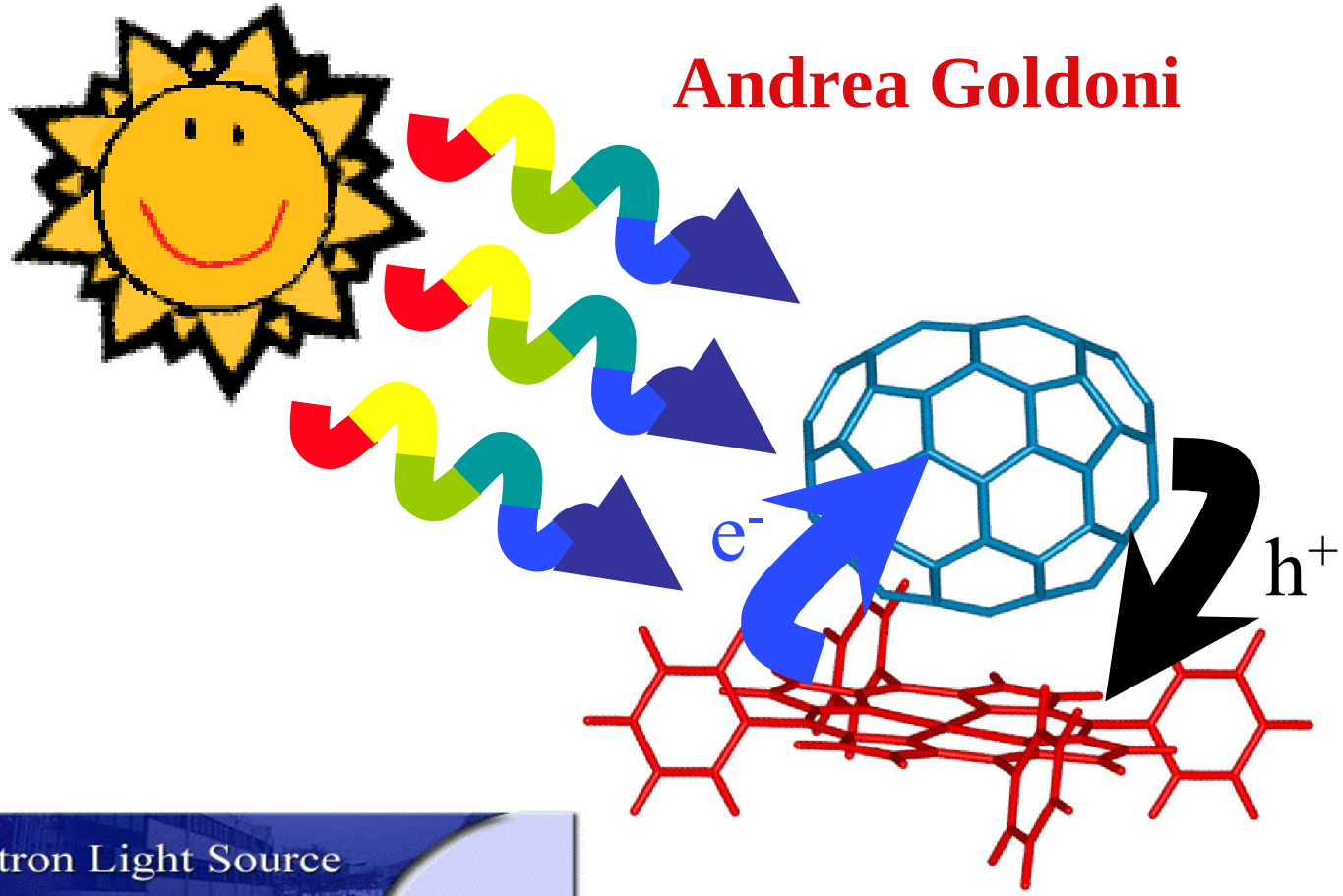

Elettra Synchrotron Light Source

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G. Zampieri, L. Petaccia, S. Lizzit
Sincrotrone Trieste S.C.p.A. (The SuperESCA people)

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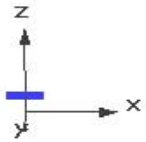
OUTLINE

Short introduction on organic photovoltaic cells then…

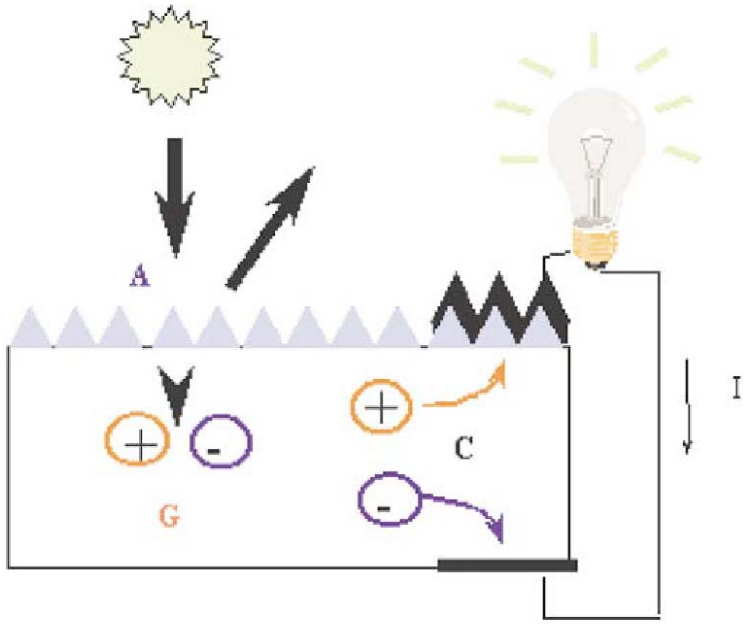
1) Growth and orientation of Zn-TPP/C_{70} films
   * Zn-TPP thick-layers on Si(111)
   * Double layer Zn-TPP/C_{70}/Si(111)
   * Multilayer co-deposited Zn-TPP/C_{70}

2) Electronic structure *via* NEXAFS and photoemission
   * Same systems as above
   * Evidence for interaction between C_{70} and Zn-TPP

3) Charge-transfer time scale with resonant photoemission
   *Same systems as above
   *In mixed systems the excited electrons are delocalized more efficiently



Photovoltaic principles



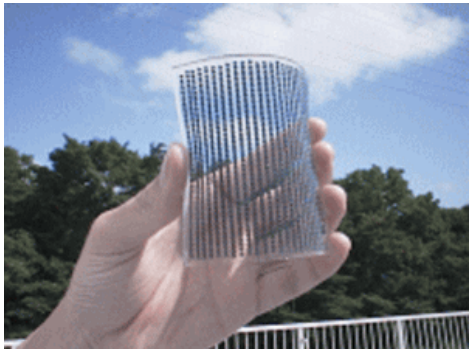
- Photovoltaic energy conversion needs:
- photon absorption across an energy gap
- charge separation
- Charge (electrons & holes) transport

Incident solar energy = Electricity + Heat

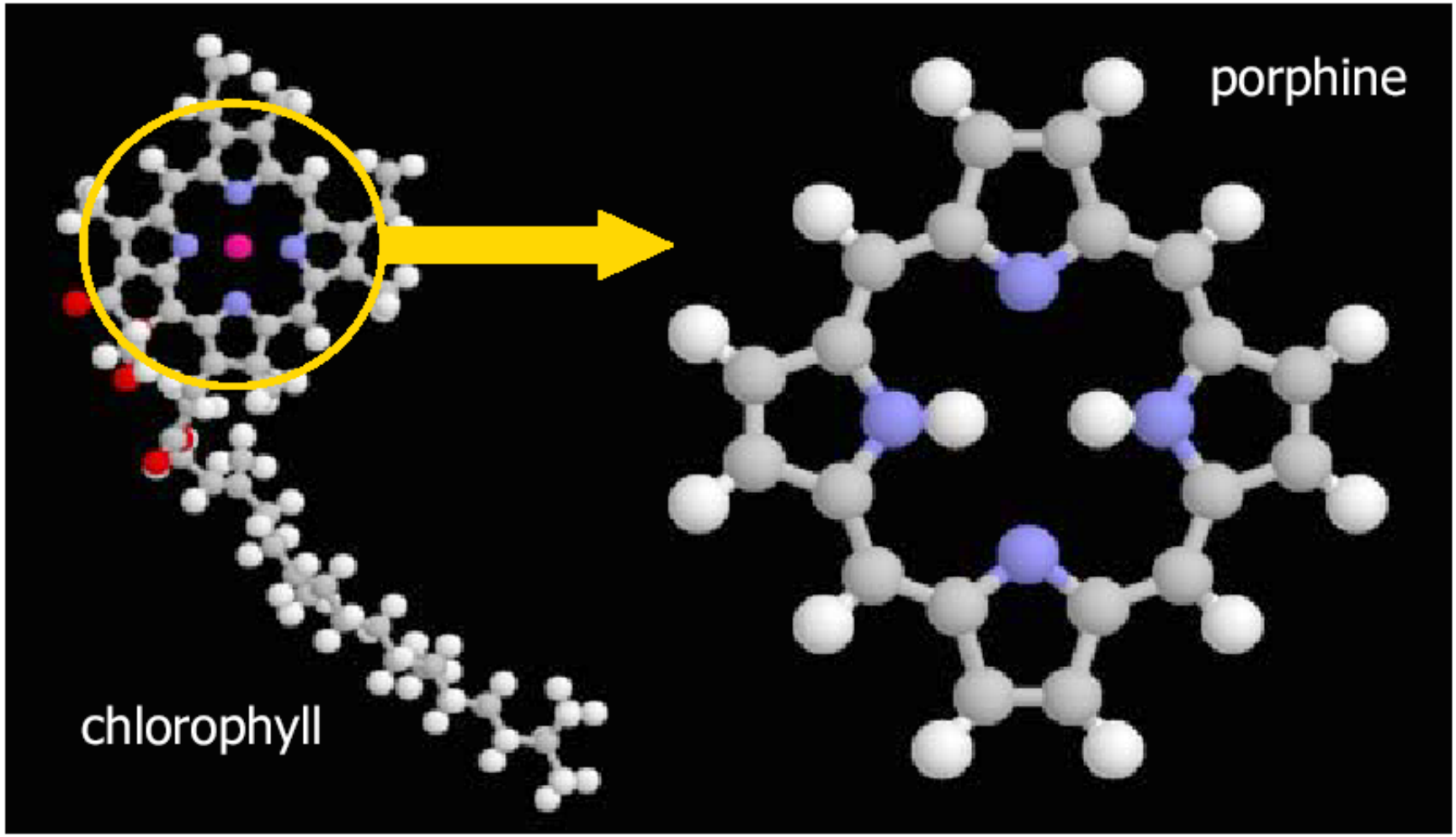
Reasons for the use of organics in solar cell applications

1) Easy processing, e.g. spin coating, sublimation.
2) Relatively small amount of organic molecules per device (100 nm of film thickness for 100% light absorption).
3) Large scale production easier than for inorganic materials.
4) Chemical tuning of band gap, charge transport and electronic properties, as well as structural properties and solubility.
5) Self assembled monolayers, layer by layer deposited films, Langmuir Blodgett films can allow the control of molecular order.
6) Can sensitize semiconductor for efficient electron-hole extraction.
7) Vast variety of materials (fullerenes, polymers, oligomers, dyes, pigments, liquid crystals, …) and structural combinations.
8) Every kind of transparent & conducting substrate (even plastic).

and…



Photovoltaic inspired to natural processes



Bio-mimetic systems

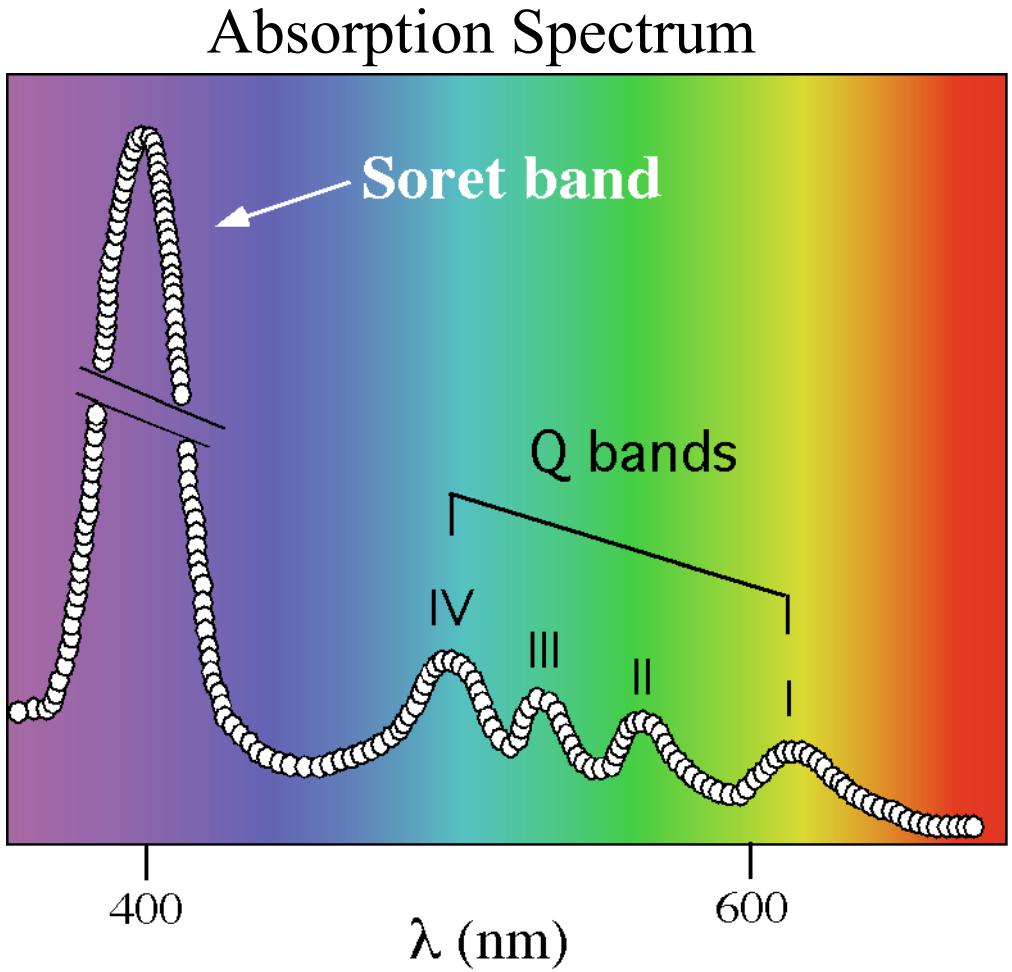
GOOD:

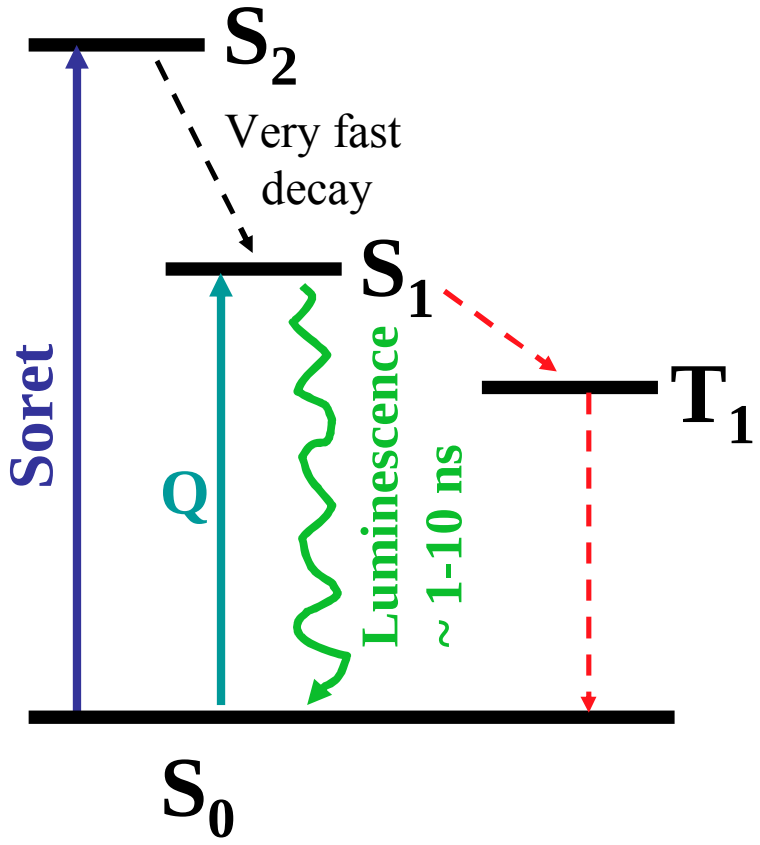
Absorption spectrum of porphyrins covers almost the whole visible range (Donors)

Hole-transport (p-type)

BAD:

No triplet state T_1 reachable (long lived excitons) in a short time: S_1-S_0 luminescence decay dominates

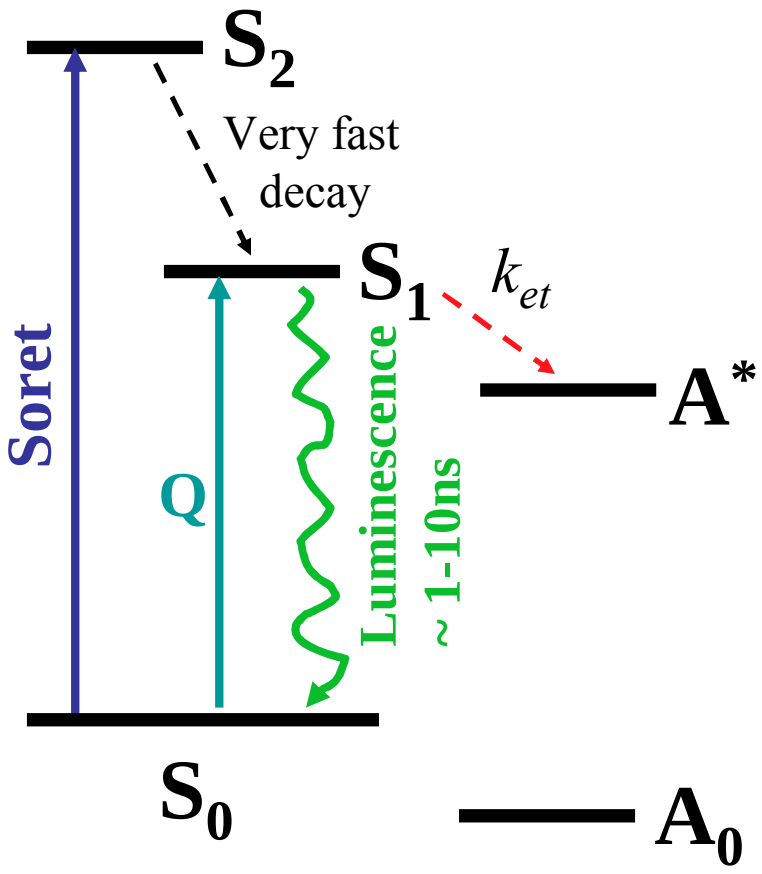




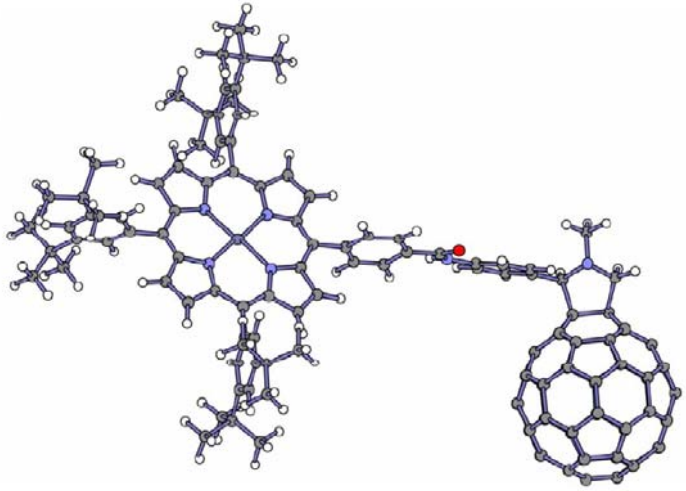
H.L. Anderson, Chem. Commun. (1999)

SOLUTION: DONOR-ACCEPTOR complexes

Fullerenes (A) covalently linked to porphyrins (D) shows the formation of relatively long lived charge separated states: promising as photoactive materials for energy conversion



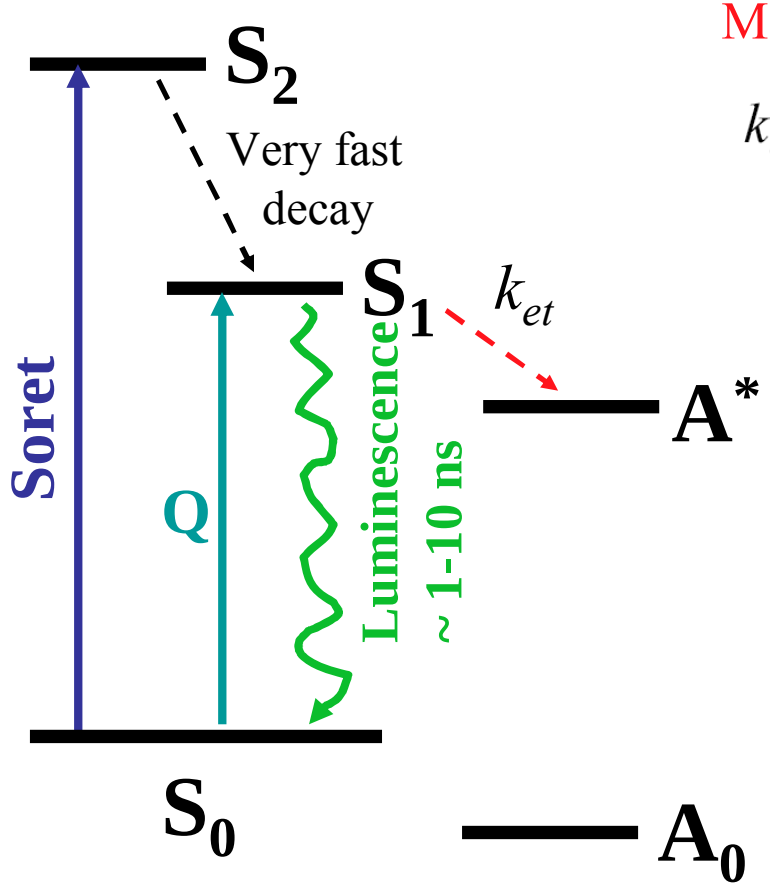
S_0 and A* should be localized on the D and A molecules, respectively, in order to have charge separation and a low probability of a radiative $A^* \rightarrow S_0$ decay: use linker molecules between D and A



1/*ket*=charge transfer time ~ 100-500 fs

N. Armaroli et al., Chem. Eur. J. (2000)

On the other hand….



Marcus equation for charge transfer rate constant:

$$k_{et} = \sqrt{(\pi / \hbar^2 \lambda k_B T)}\,|V|^2 \exp\left[-\left(\Delta G^o + \lambda\right)^2 / 4\lambda k_B T\right]$$

- Depends on D-A orbital overlap $|V|^2 \propto e^{-d}$: minimize the distance between π orbitals

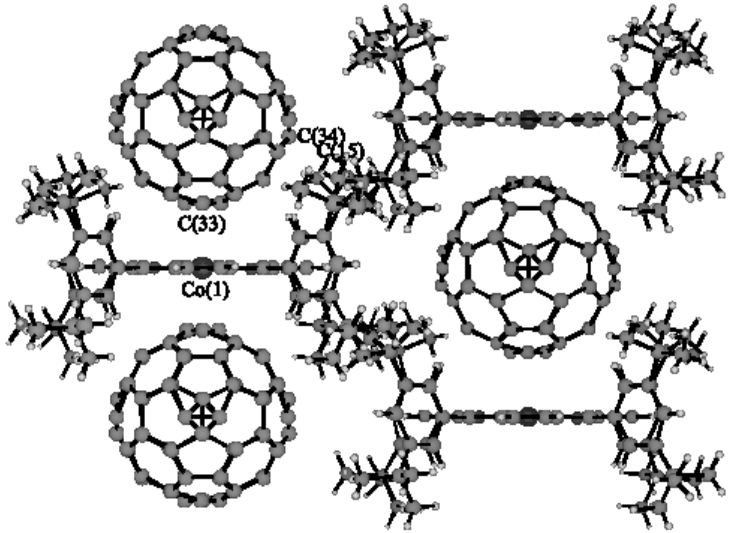


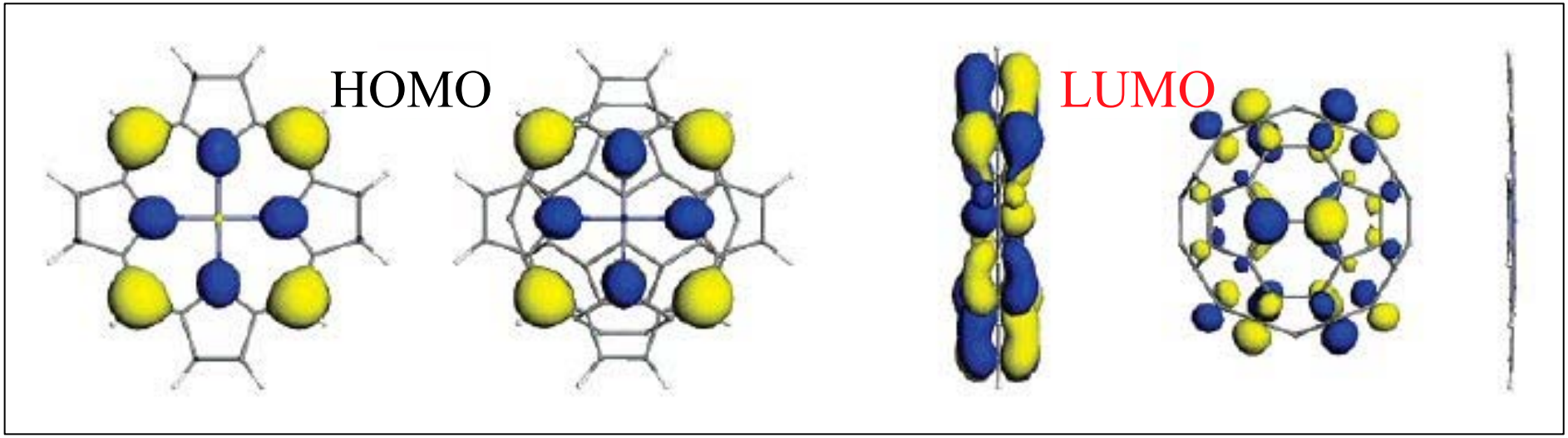
Fig. 13. Crystal Structure of Co(II)(tbp)·C_{60} viewed along the *a*-axis.

Close proximity between C_{60} and C_{70} and several kinds of porphyrins observed in cocrystals and in solution: the luminescence decay of porphyrin is strongly quenched.

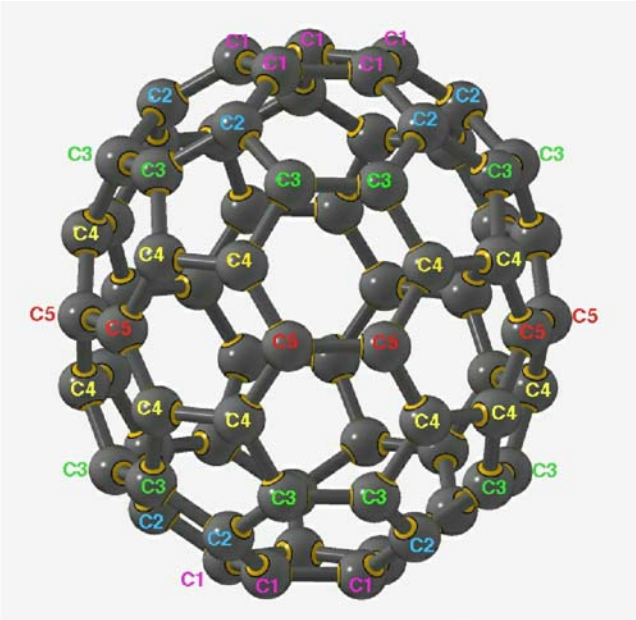
Y.P. Sun et al, J. Org. Chem. **62,** 3642 (1997); P.D.W. Boyd et al, J. Am. Chem. Soc. **121**, 10487 (1999);
T. Ishii et al, Coordination Chem. Rev. **226**, 113 (2002).
M.E. Milanesio et al, J. Phys. Org. Chem. **15**, 844 (2002).

ZnTPP/C_{60} complexes with no linker: orbital calculations

Zn-Porph Zn-Porph/C_{60} Zn-Porph Zn-Porph/C_{60}

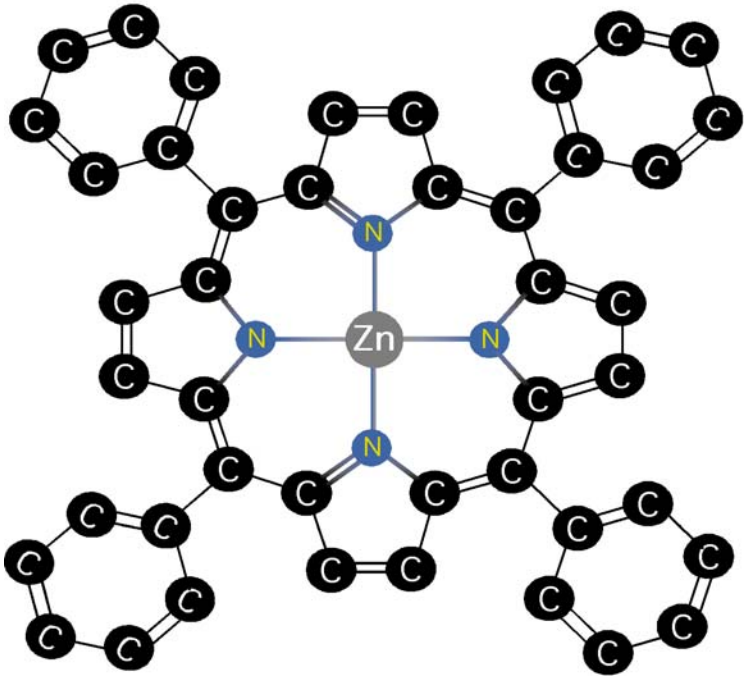


GOOD COMPROMISE: The two molecules are close, good conjungation, but the molecular orbitals are well localized (HOMO on Zn-porphyrin macrocycle and LUMO on fullerene), so the charge transfer should be facilitated.



C_{70}-fullerene

The big brother of the most famous C_{60}.
Fullerenes are highly symmetric carbon cages with very good tendency of accepting electrons.
Among the few organic materials that may behave as n-type conductors.
Small reorganization energy λ and luminescence yield (optically forbidden lowest HOMO-LUMO transition)



Porphyrins

from the Greek *porphura* = "purple"

Basic structure is the porphine macrocycle, which consists of a 16-atoms ring containing four nitrogen atoms, obtained by linking four tetrapyrrolic subunits with four methine bridges.
The macrocycle is an aromatic system containing 22 π-electrons, but only 18 of them are delocalized according to the Hückel's rule of aromaticity (4n+2 delocalized π-electrons, where n=4). The size of the macrocycle is perfect to bind almost all metal ions (e.g. Fe, Zn, Cu, Ni, and Co) which can be inserted in the center forming metal-porphyrins.

OUR GOAL

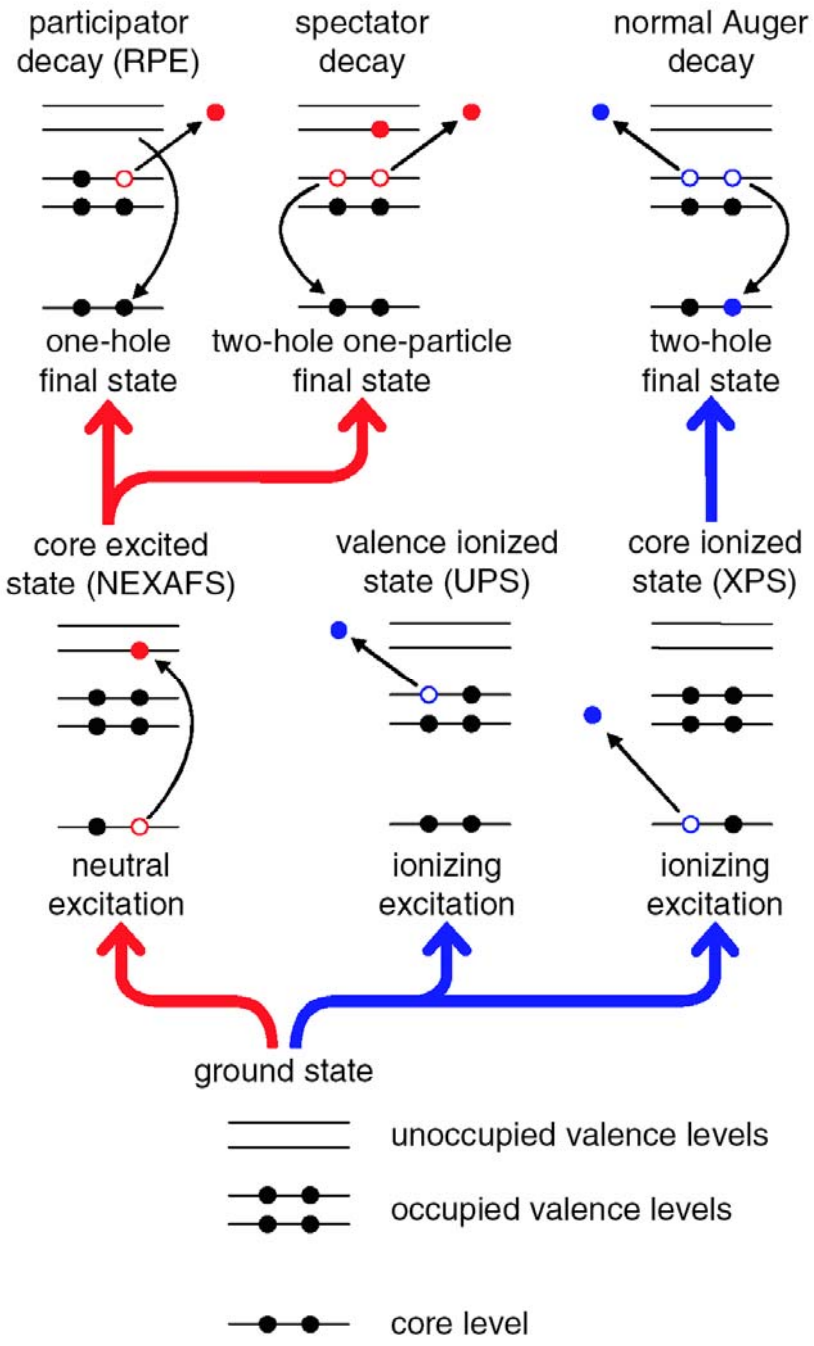
Deposition of C_{70} and Zn-TPP on substrates by UHV sublimation :

1) Formation of ordered compact films
2) Thickness control layer-by-layer
3) Sandwich structures with different molecular orientations
4) Self assembled mixed C_{70}/Zn-TPP thick films

Electronic structure, bonding formation and molecular orientations investigated using photoemission and x-ray absorption

D-A charge transfer time investigated by resonant photoemission

Note: order and molecular packing increase exciton and charges mobility by orders of magnitude (example: typical organic mobility 10^{-4} - 10^{-8} $cm^2/V{\cdot}s$, while in C_{60} single crystal ~ 2 $cm^2/ V{\cdot}s$); Relative molecular orientations influence the charge transfer time and transport.



EXPERIMENTAL

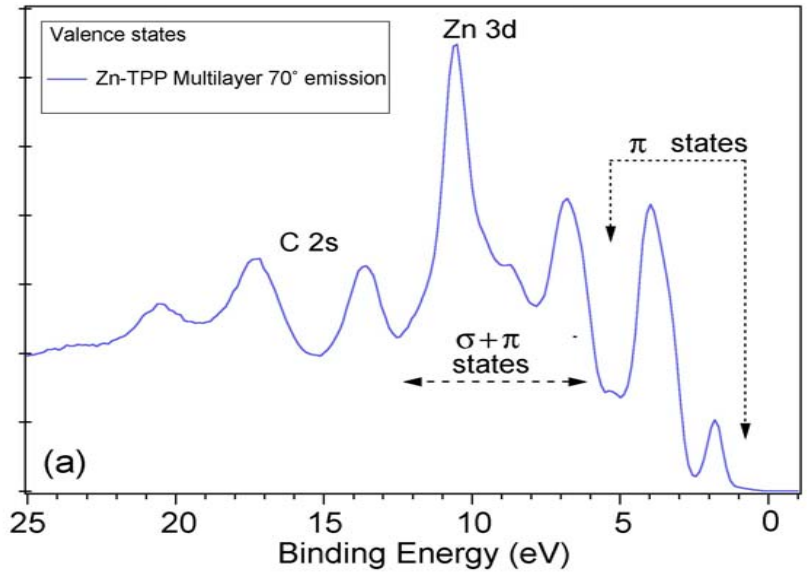
Measurements performed at elettra

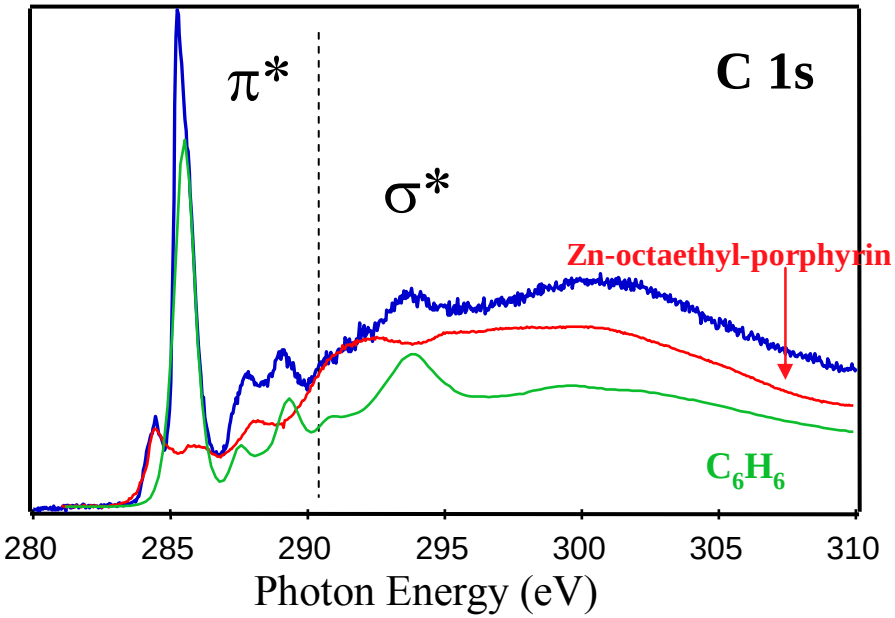
SuperESCA: XPS, NEXAFS, UPS, RESPES
ALOISA: polariz. dependent NEXAFS, XPS

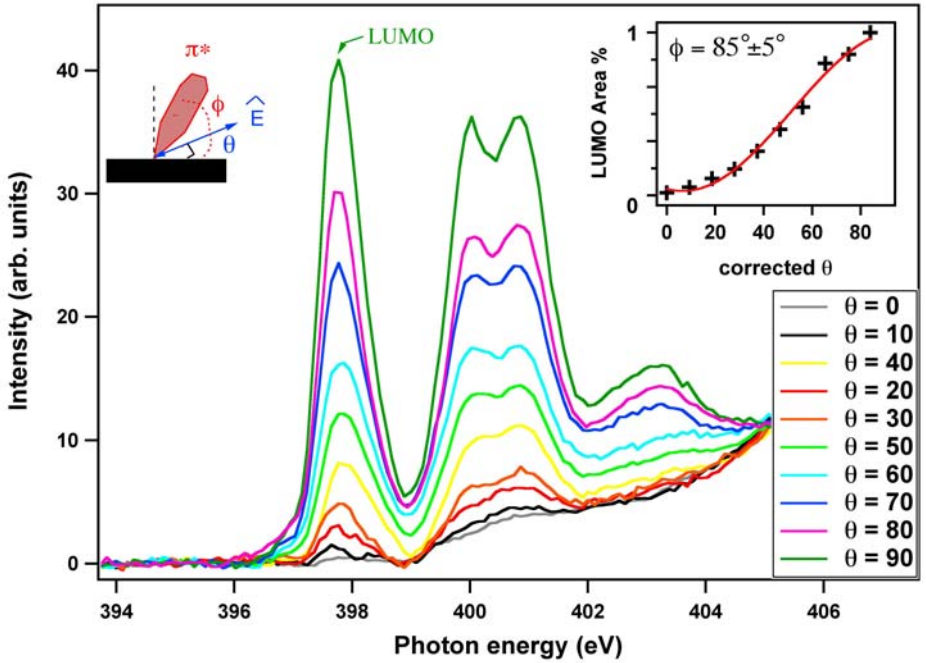
RESPES probes the charge transfer time of an excited state on the time scale of the core hole lifetime (core hole clock): pump & probe experiment in the energy domain ($\Delta E \cdot \Delta t \geq h/2\pi$)

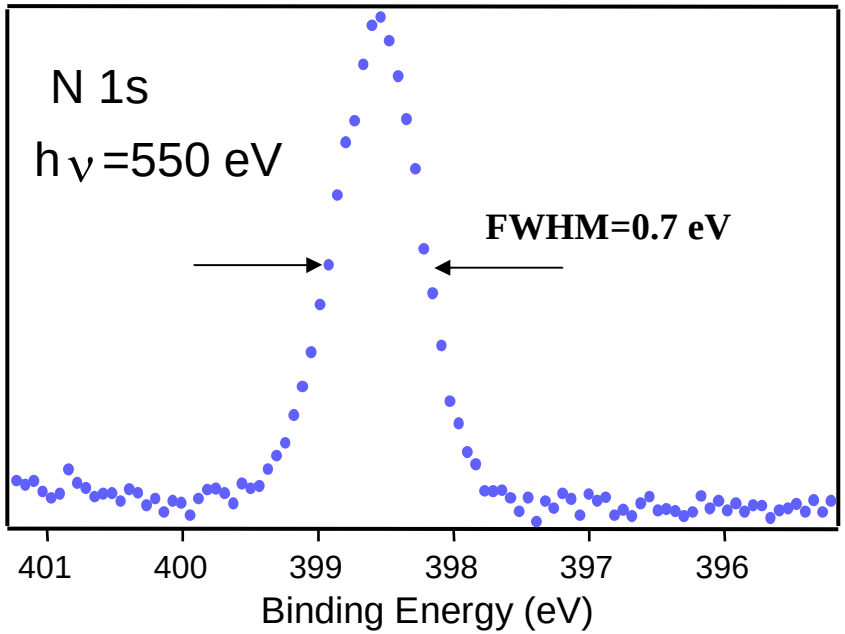
W. Wurth & D. Menzel, Chem. Phys. **251**, 141 (2000);
J. Schnadt et al, Nature **418**, 620 (2002)

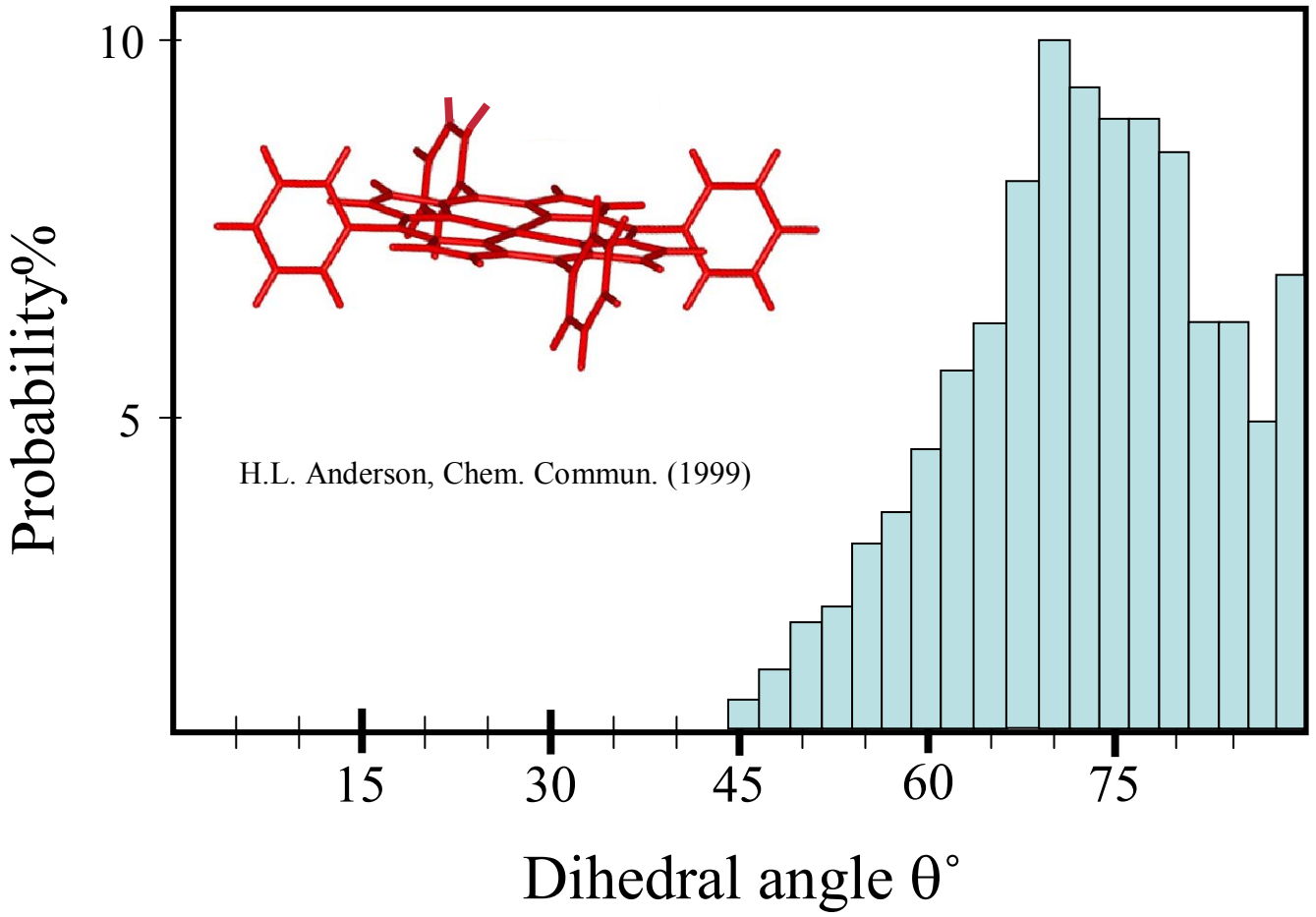
ZnTPP multilayer









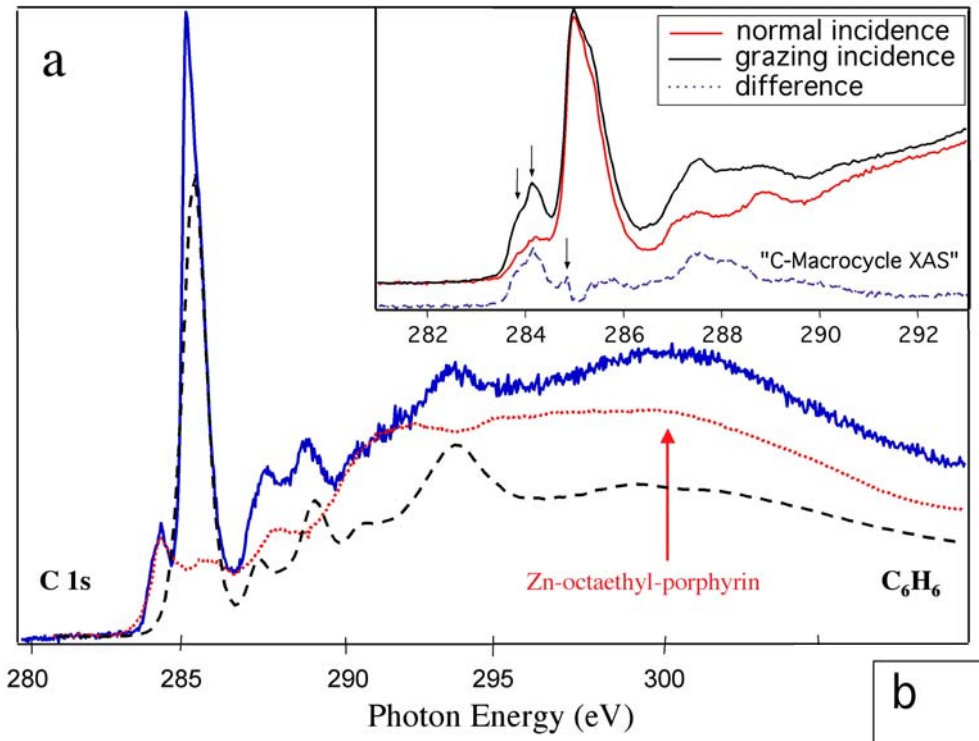


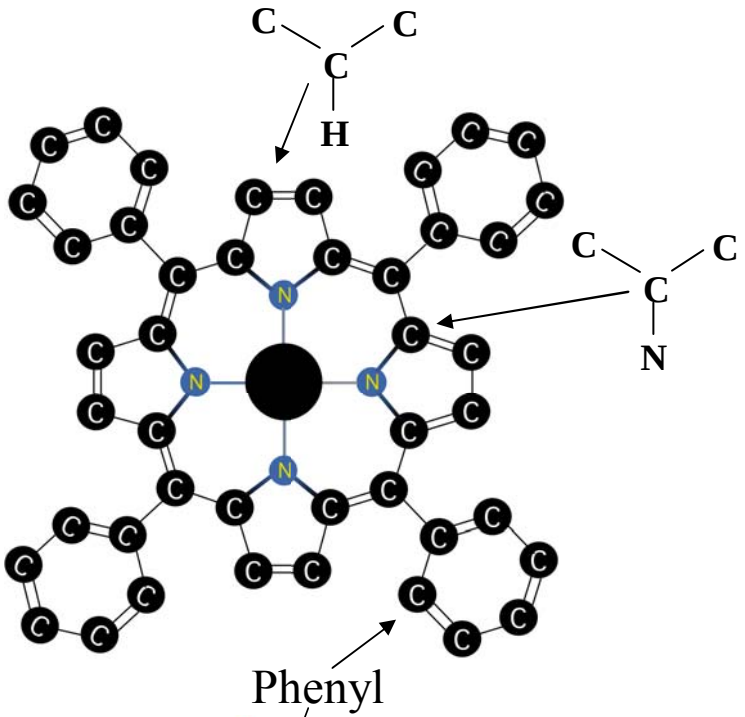
Dihedral angle: angle θ between the phenyl plane and the macrocycle

The angle is big due to the steric interactions between the hydrogen atoms:

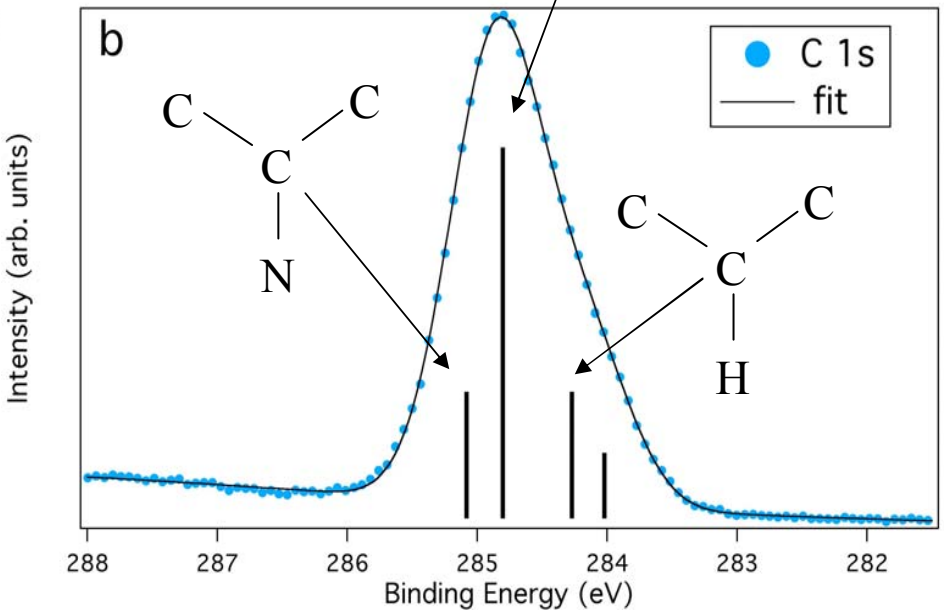
Minimal π-overlap between macrocycle and phenyl-groups

Small perturbation of the porphyrin electronic structure

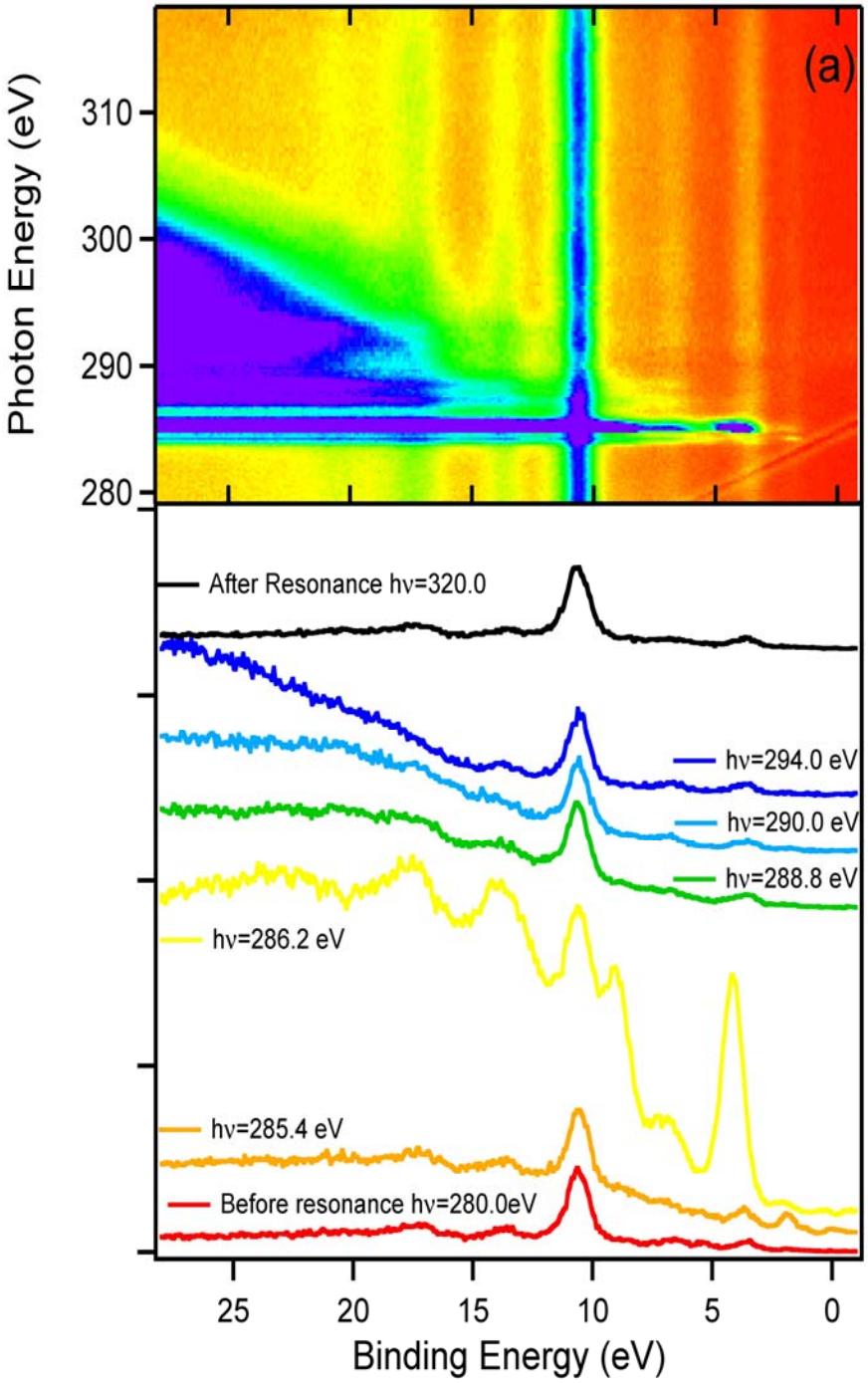


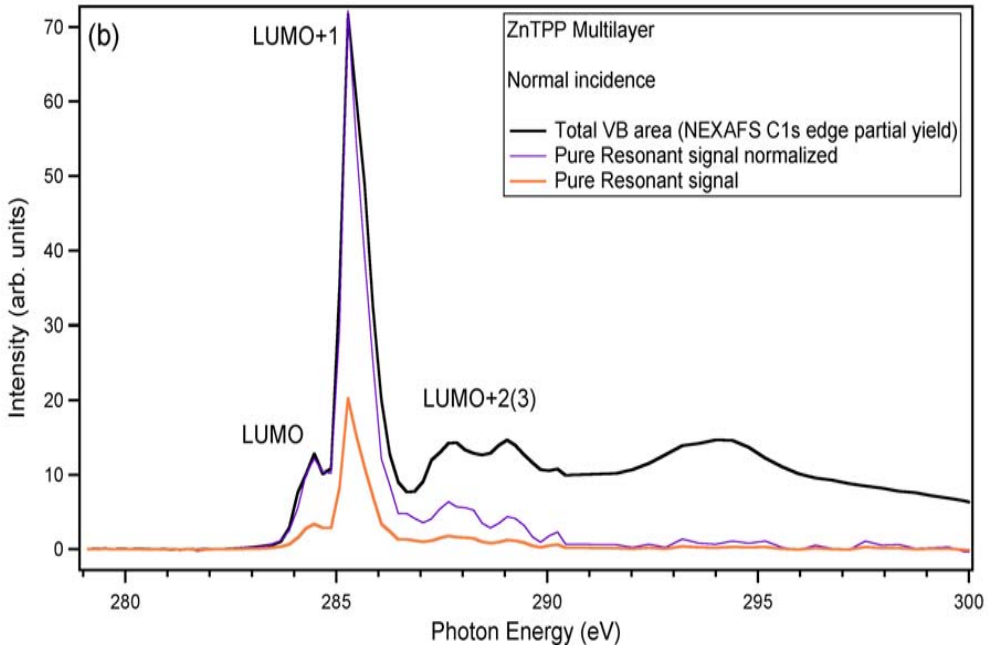


The contribution from the different carbon atoms can be highlighted



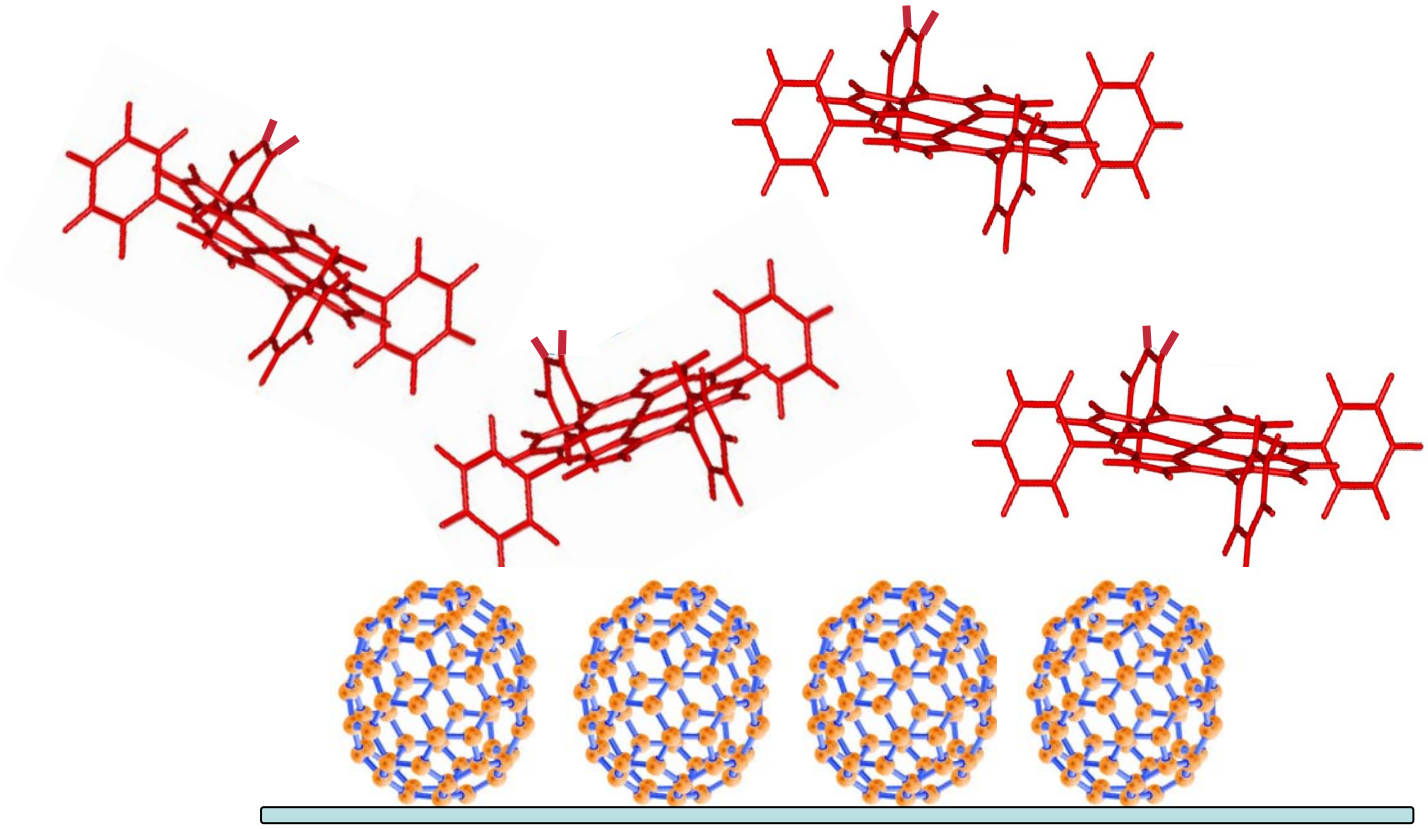
Resonant photoemission across the C1s threshold



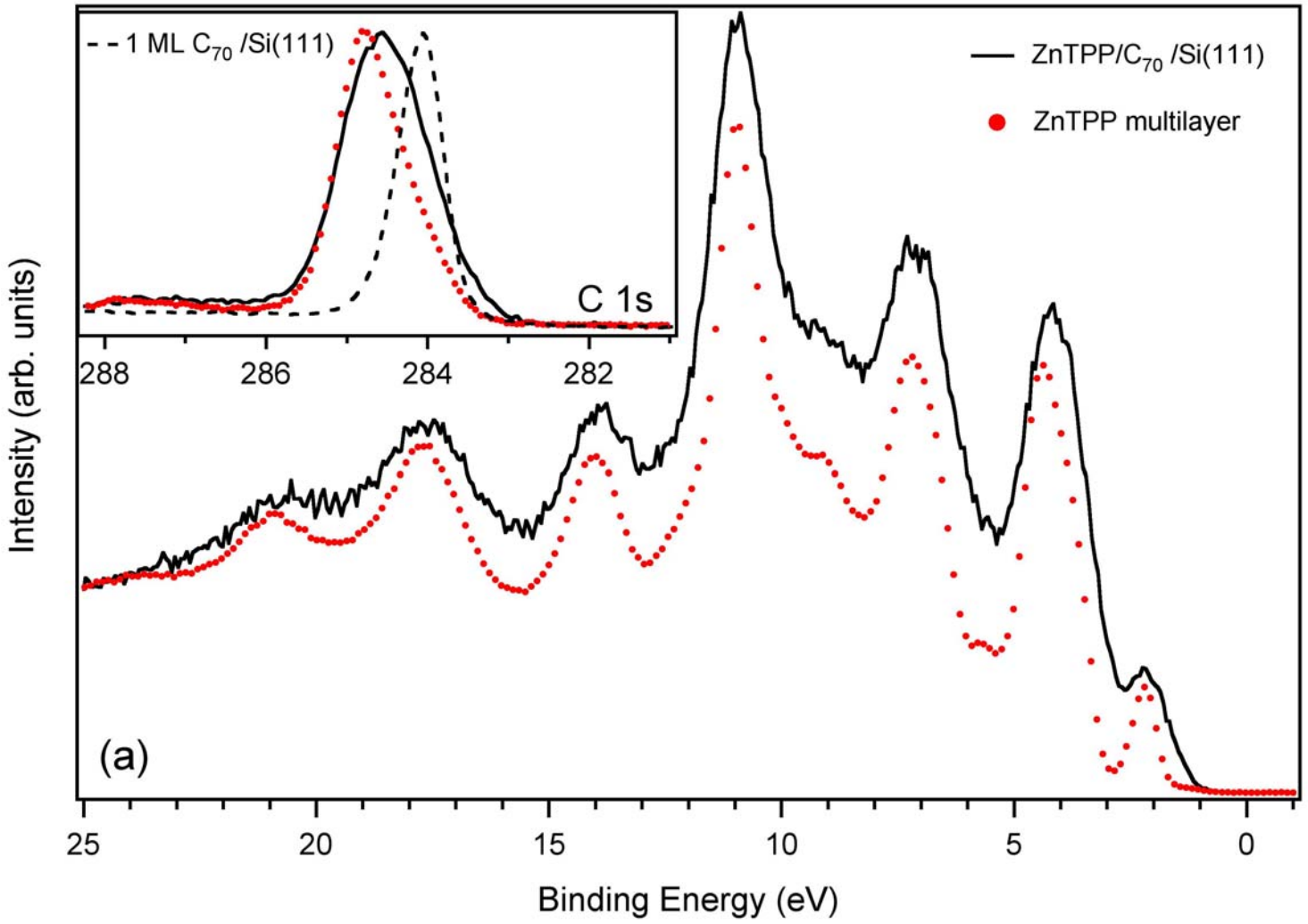


LUMO+2(3) feature is reduced. This indicates that when the electron is excited into the LUMO+2(3) states it remains localized on the molecule for a time bigger but comparable (competing) to the core-hole lifetime (~ 5 fs for the C 1s) and therefore this excited states contribute only partly to the core-hole decay as spectator state. On the contrary, in the LUMO and LUMO+1 states the electron remains localized for a time much bigger than the core-hole lifetime.

1 ML of ZnTPP/1ML C_{70}/Si(111): Double Layer Structure



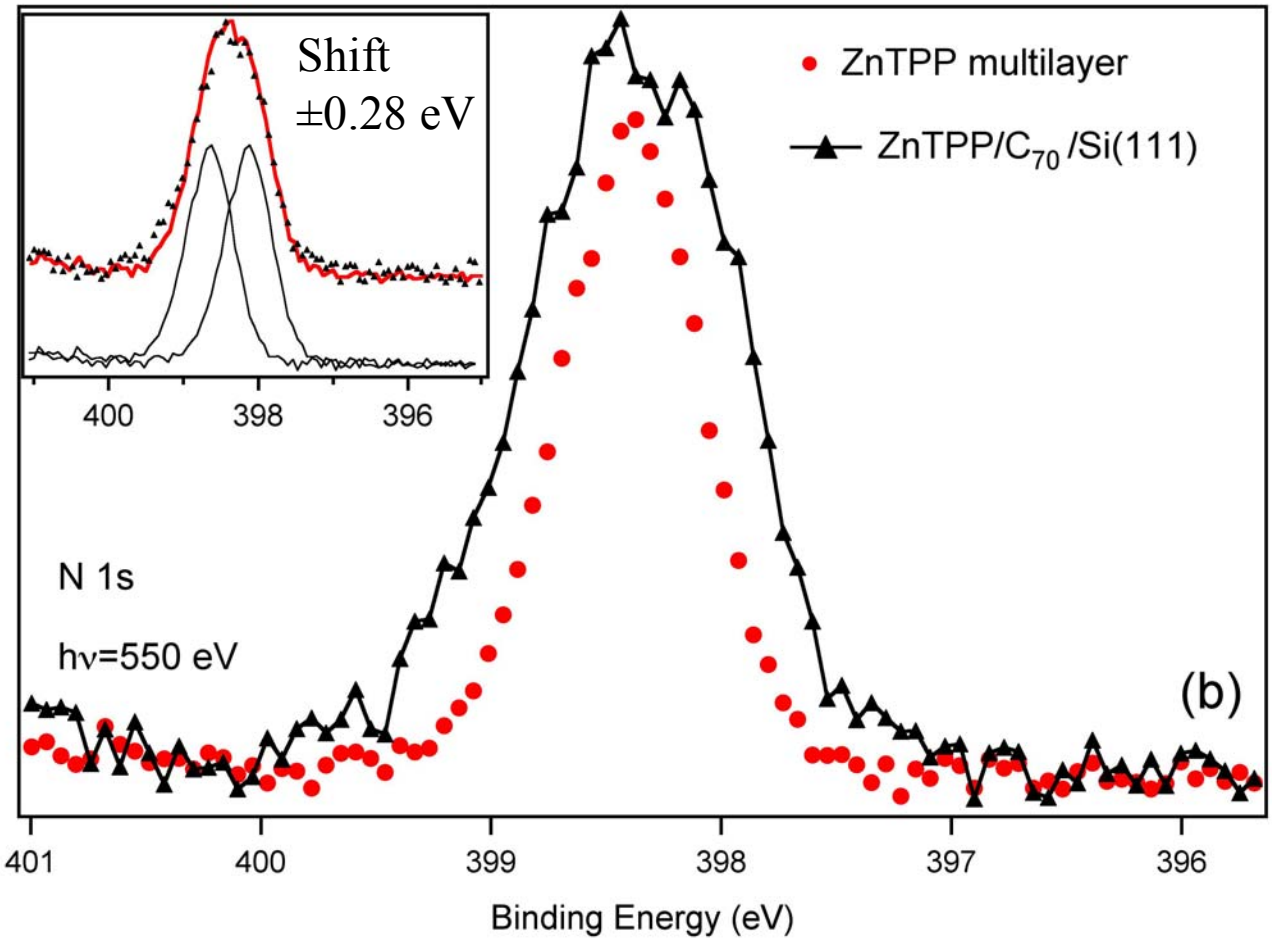
1 ML ZnTpp/1ML C_{70}/Si(111)



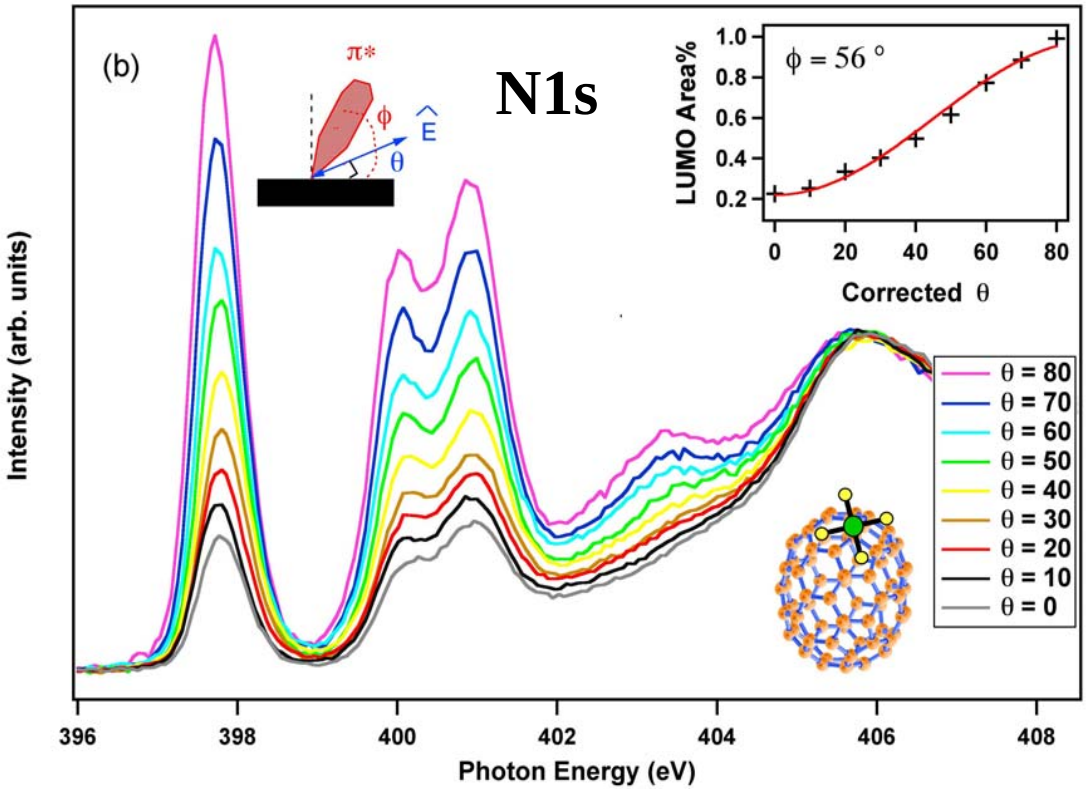
Close packed C_{70} ML are adsorbed on Si with the long axis perpendicular to the surface

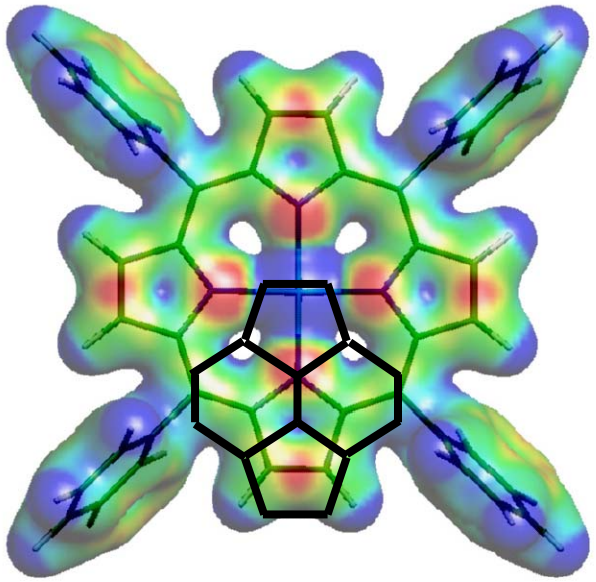
ZnTpp single layer formed on top by depositing molecules with the substrate @200 ˚C

The N equivalence is broken by the interaction with C_{70}



The N 1s XPS spectrum of the ZnTpp/C_{70} double layer can be reproduced by the superposition of two N 1s spectra of the ZnTpp multilayer (1:1)





Y.-B. Wang & Z. Lin, JACS 125, 6072 (2003)

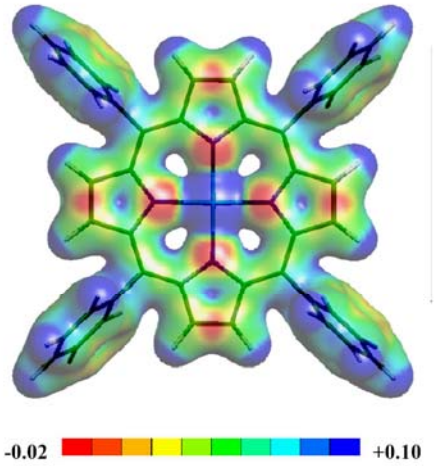


Figure S4. Molecular electrostatic potentials of 5,10,15,20-tetraphenylporphyrinato-zinc, mapped from -0.02 to +0.10 e/$4\pi\varepsilon_0 a_0$, onto 0.02 e Å^{-3}m isosurface of the electron density at the PBE/6-31G(d,p) level

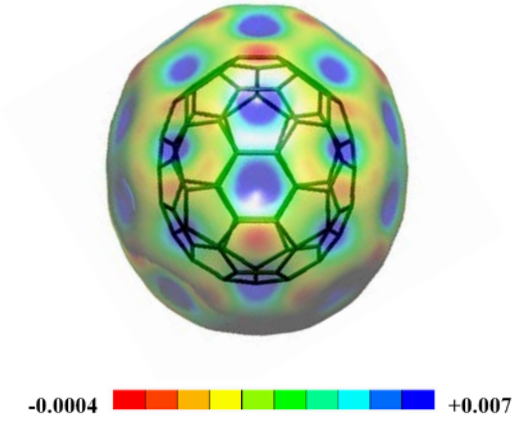
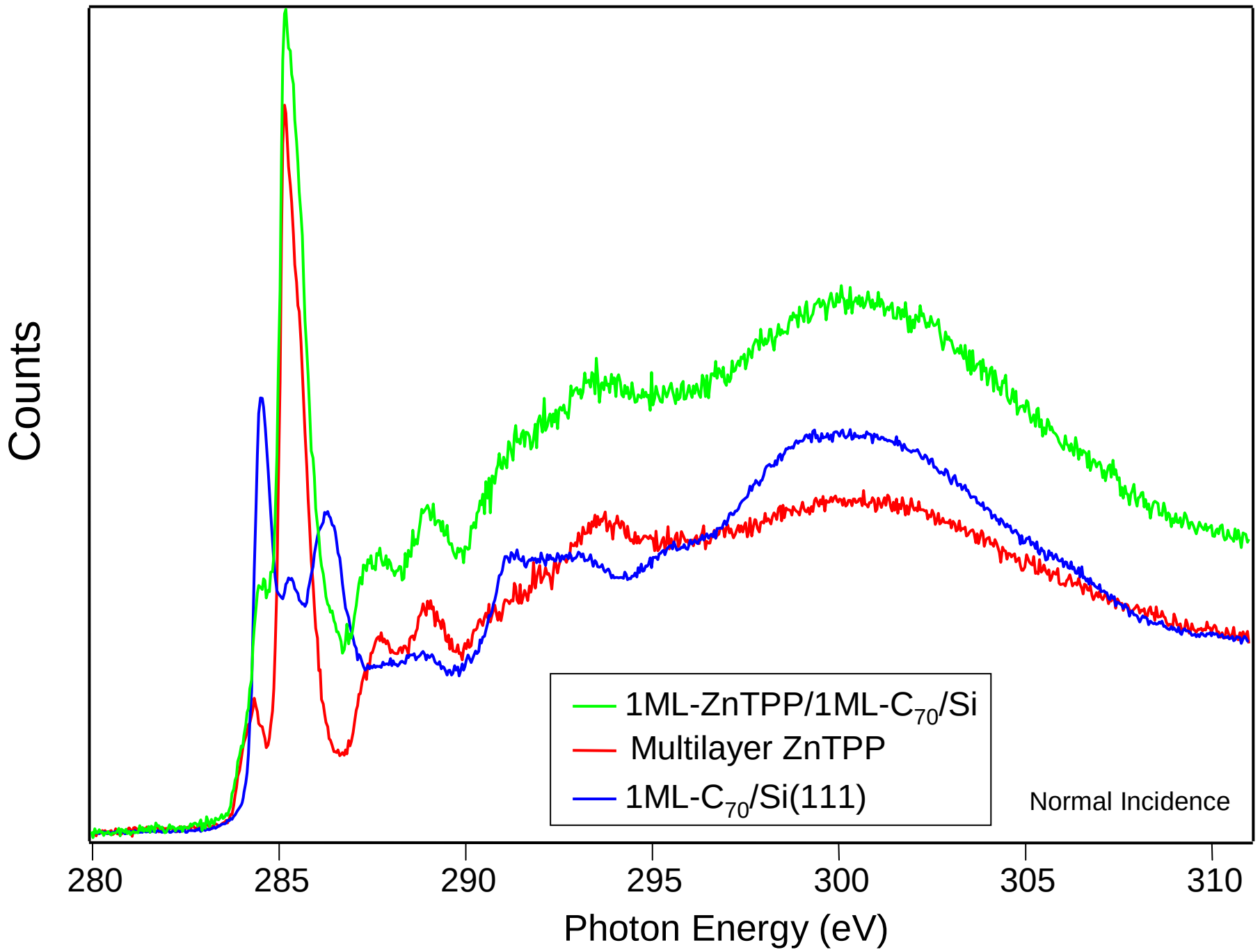
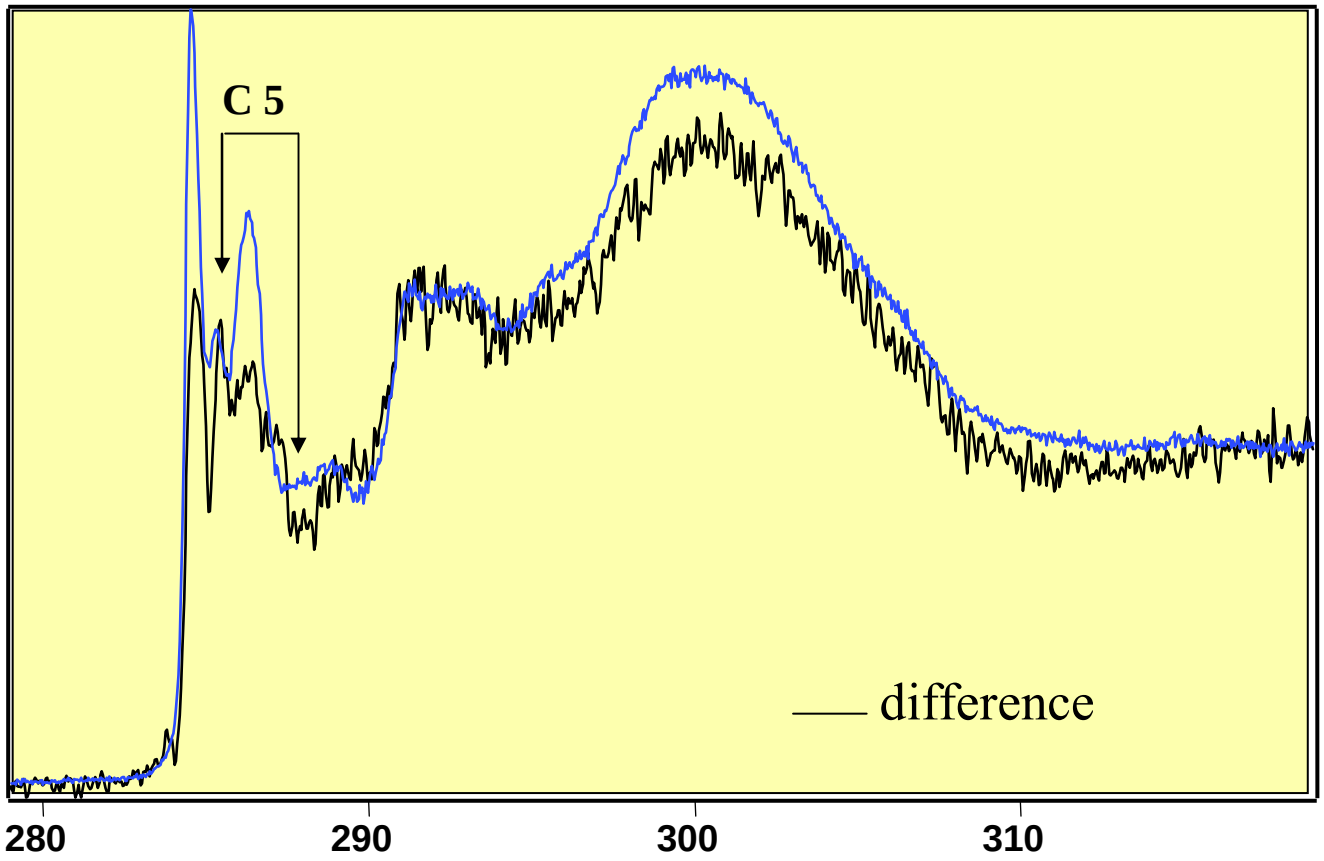
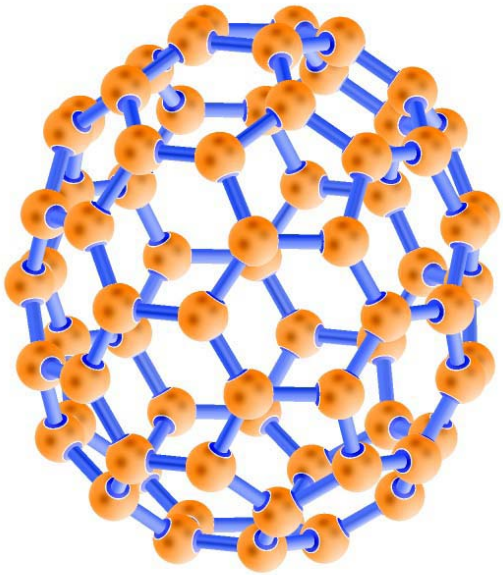
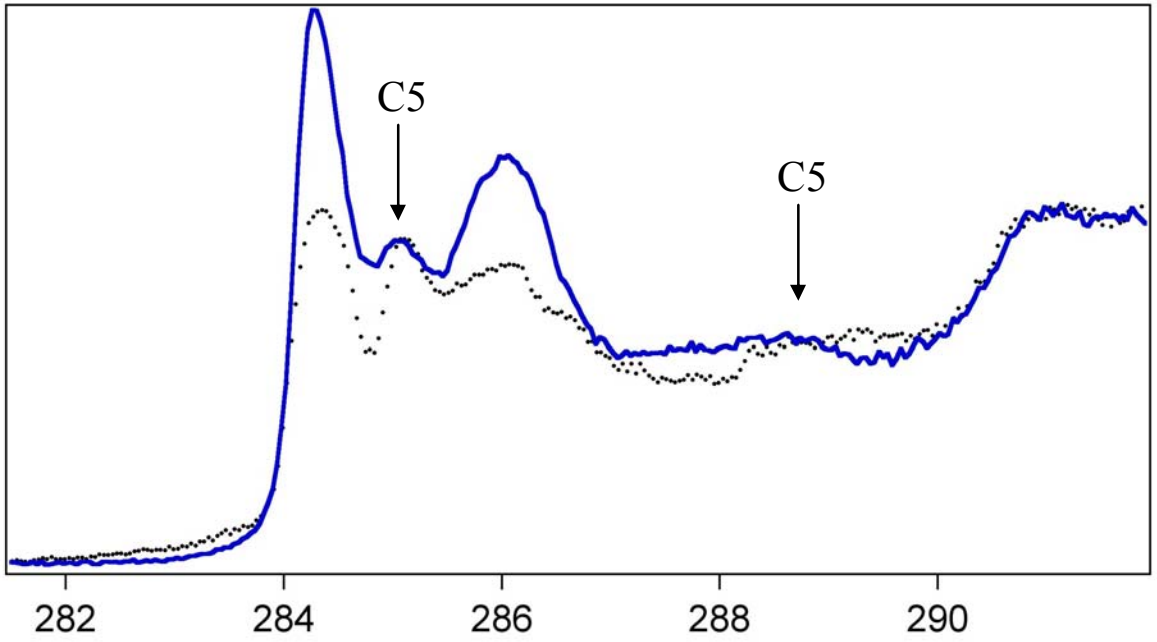


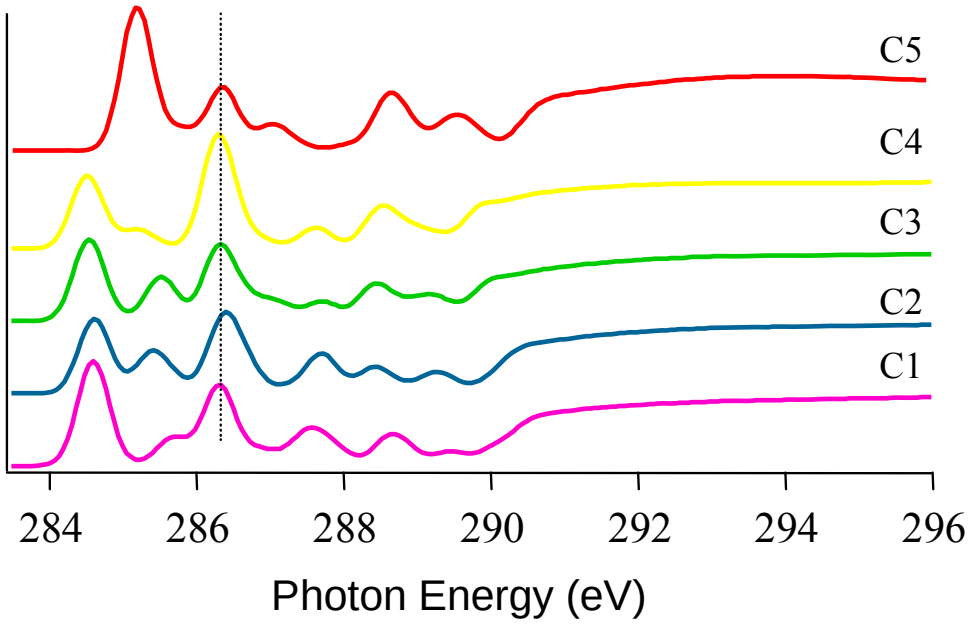
Figure S2. Molecular electrostatic potentials of C_{70} from difference perspective projections, mapped from -0.0004 to +0.007 e/$4\pi\varepsilon_0 a_0$, onto 0.001 e Å^{-3}m isosurface of the electron density at the PBE/6-31G(d,p) level


Counts
280
285
290
295
300
305
310
Photon Energy (eV)
1ML-ZnTPP/1ML-C70/Si
Multilayer ZnTPP
1ML-C70/Si(111)
Normal Incidence


C 5
difference
280
290
300
310

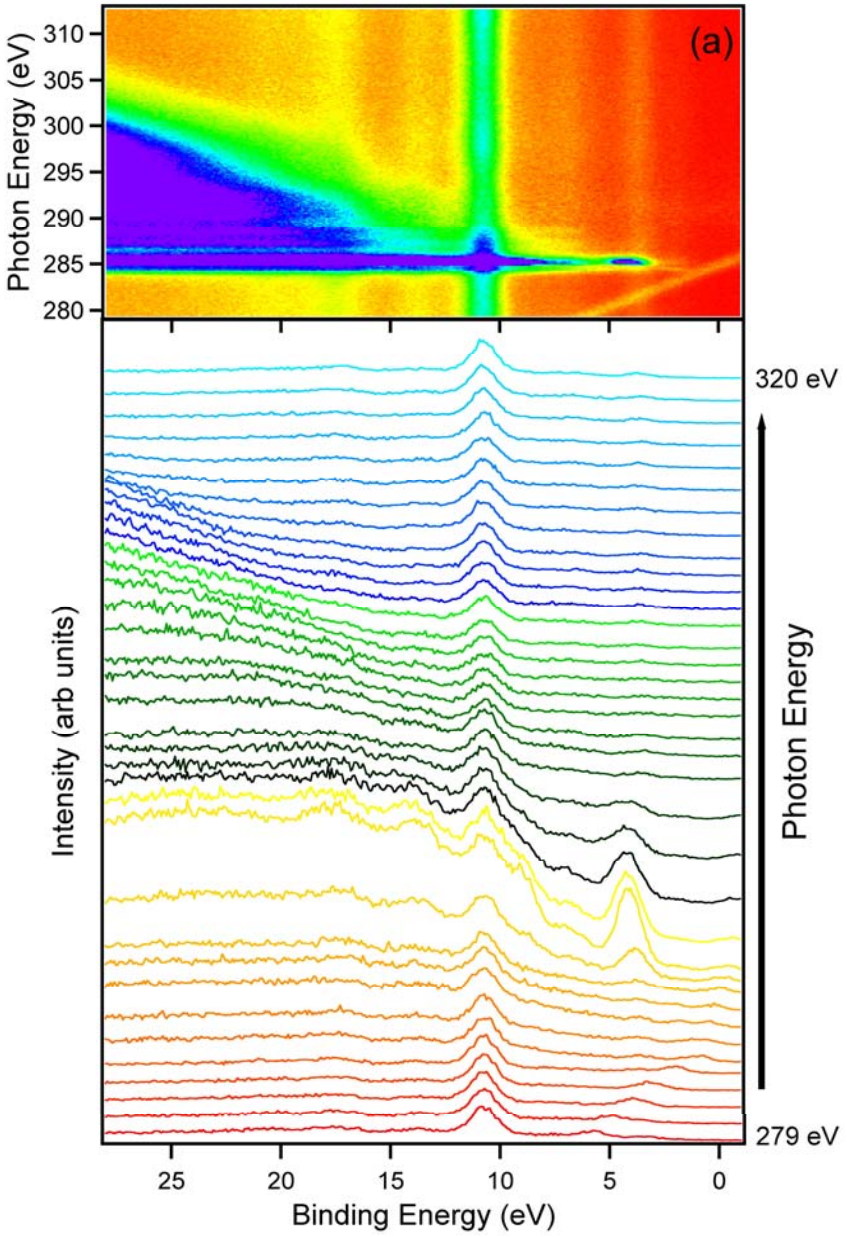






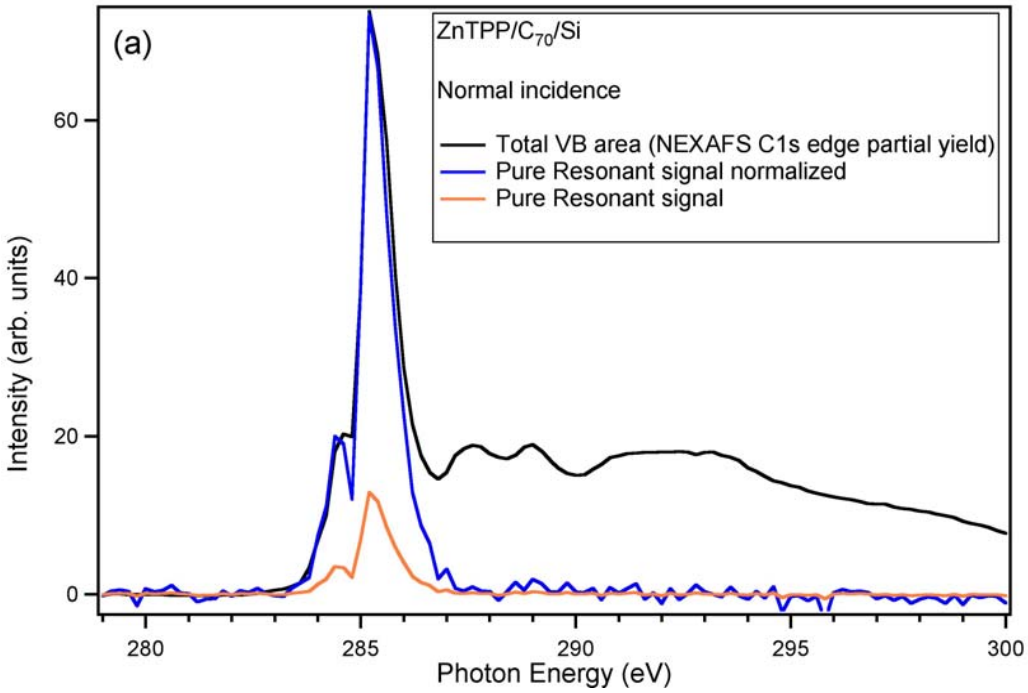
Full core hole calculations.
Contribution of the 5 different atoms to the C_{70} NEXAFS spectrum

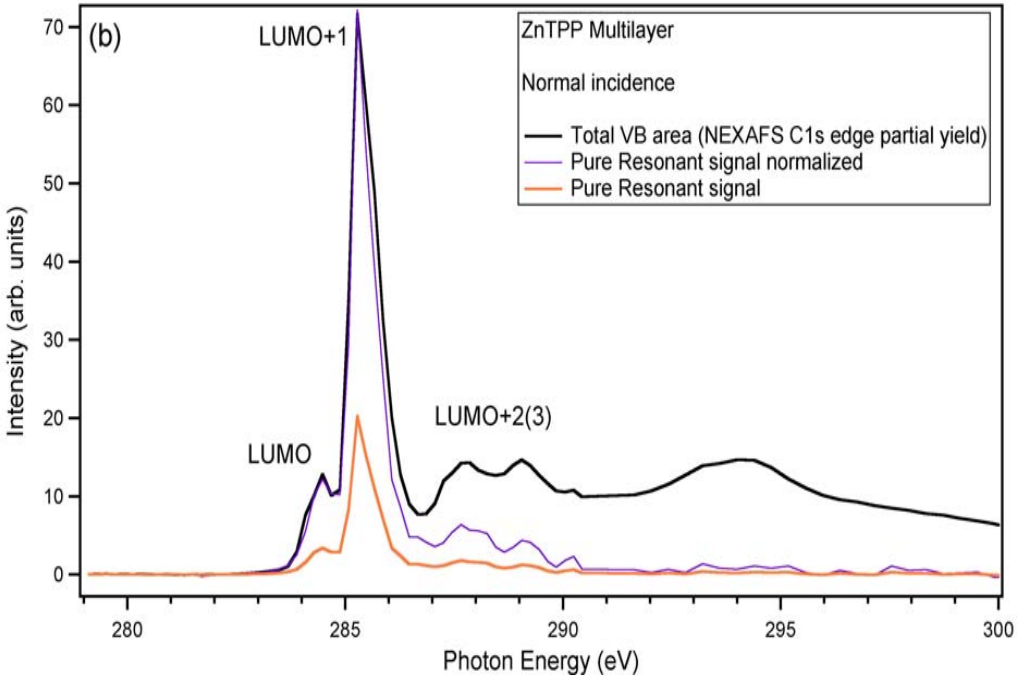
Resonant Photoemission



Already from a first sight in comparison with the ZnTPP multilayer there is a general reduction of the intensity enhancement at resonance (a factor of 1.5).

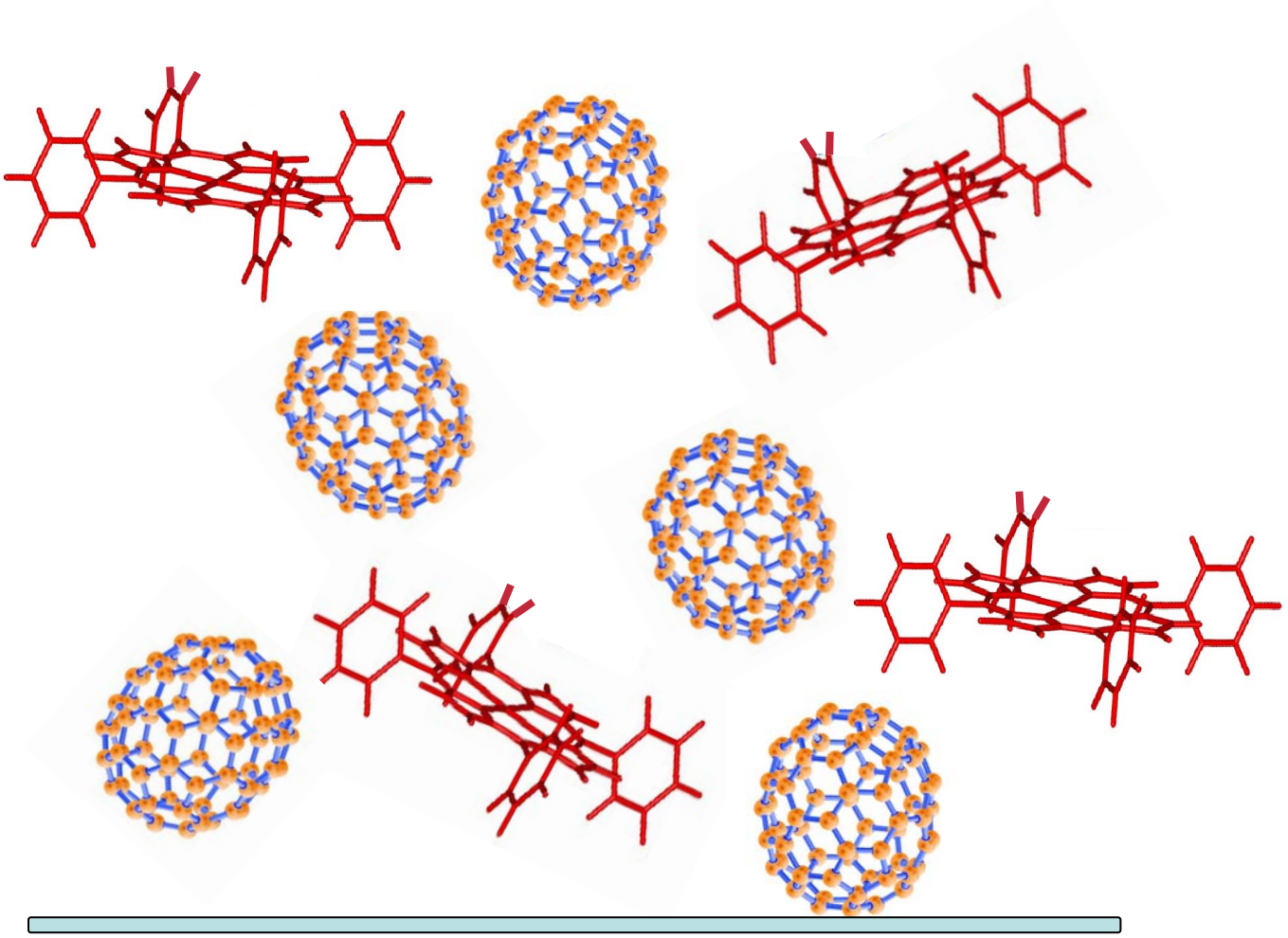
This global reduction of the resonant intensity indicates that in the ZnTPP/C_{70} double layer system the electron excited on a ZnTPP molecule is transferred away on a time scale of ~ 7 fs.

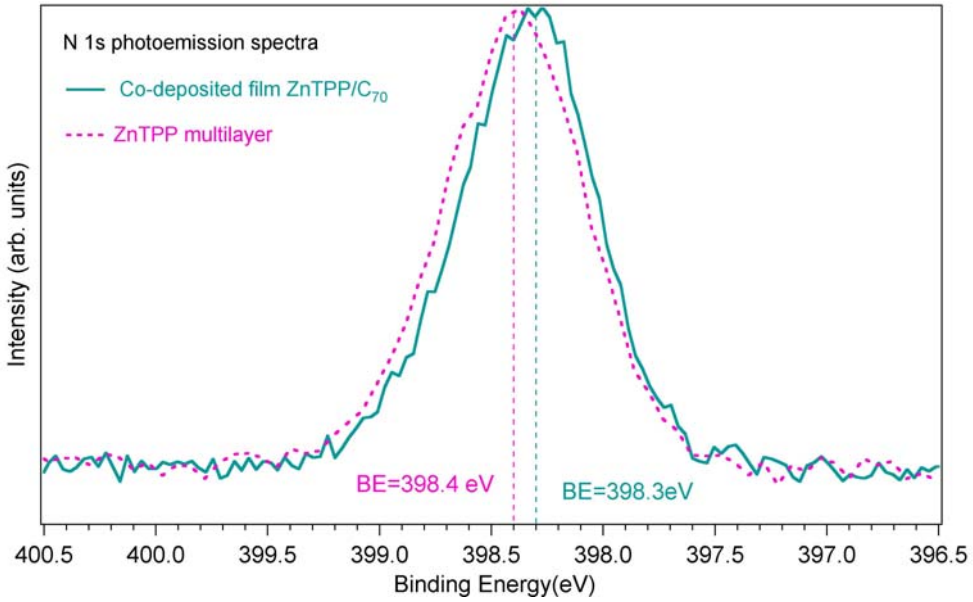


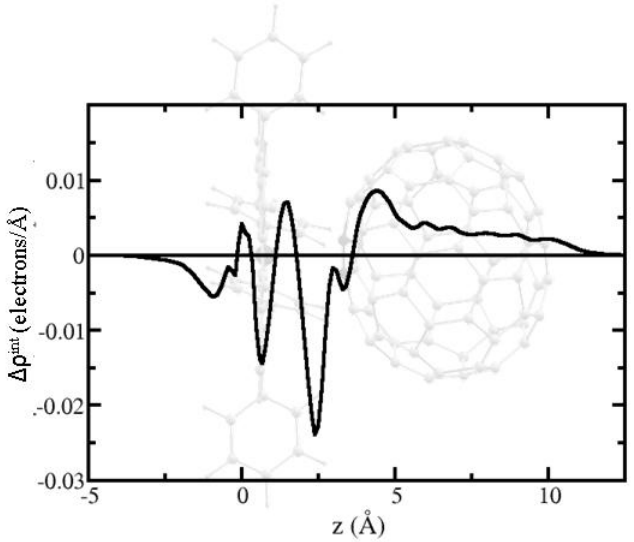


The transition to the LUMO+2(3) is completely quenched: the charge transfer from these states is much faster than the core-hole lifetime (5 fs)

Co-deposition of C_{70} and ZnTPP

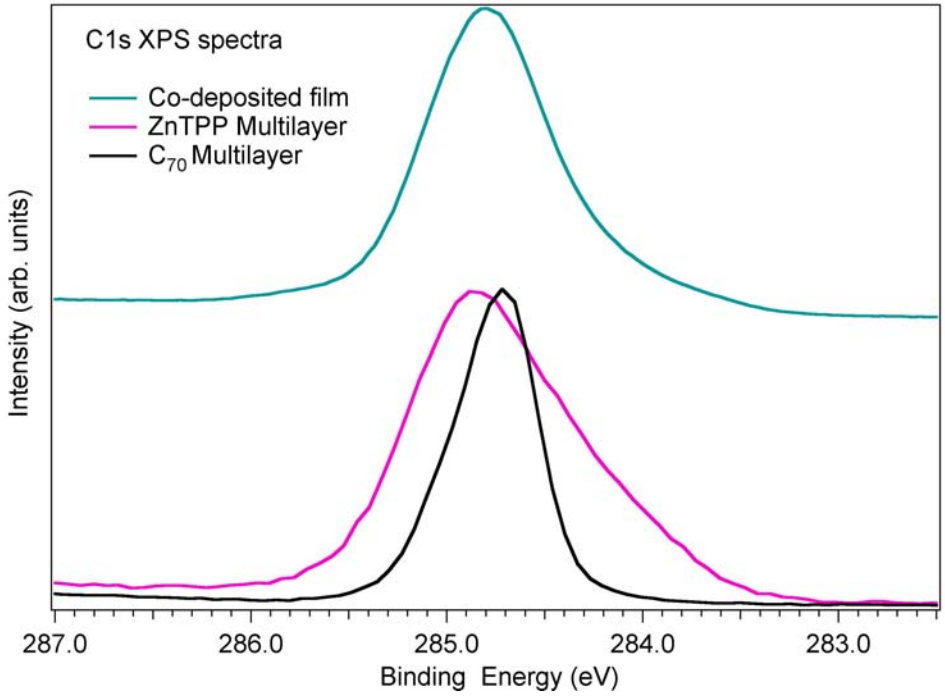


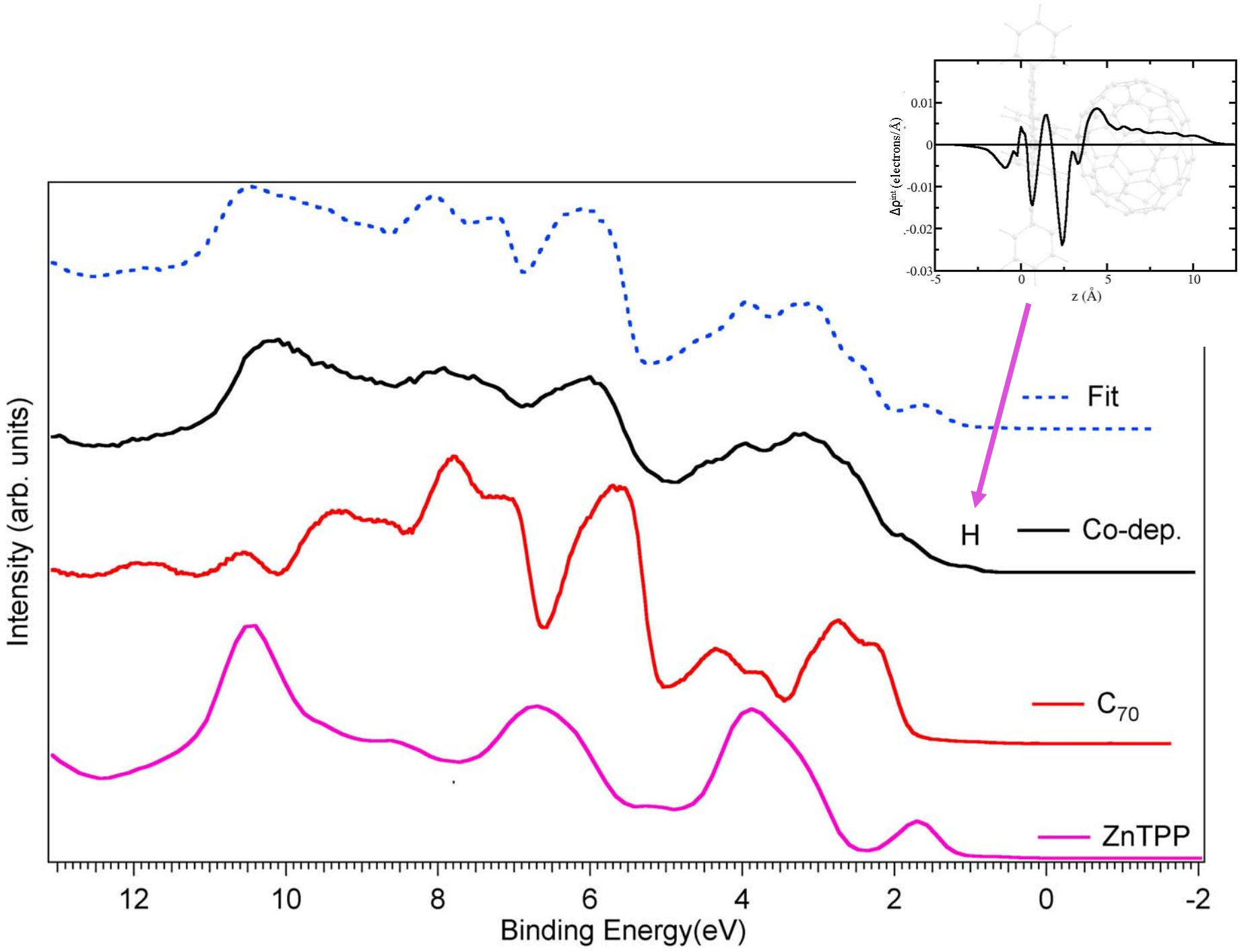




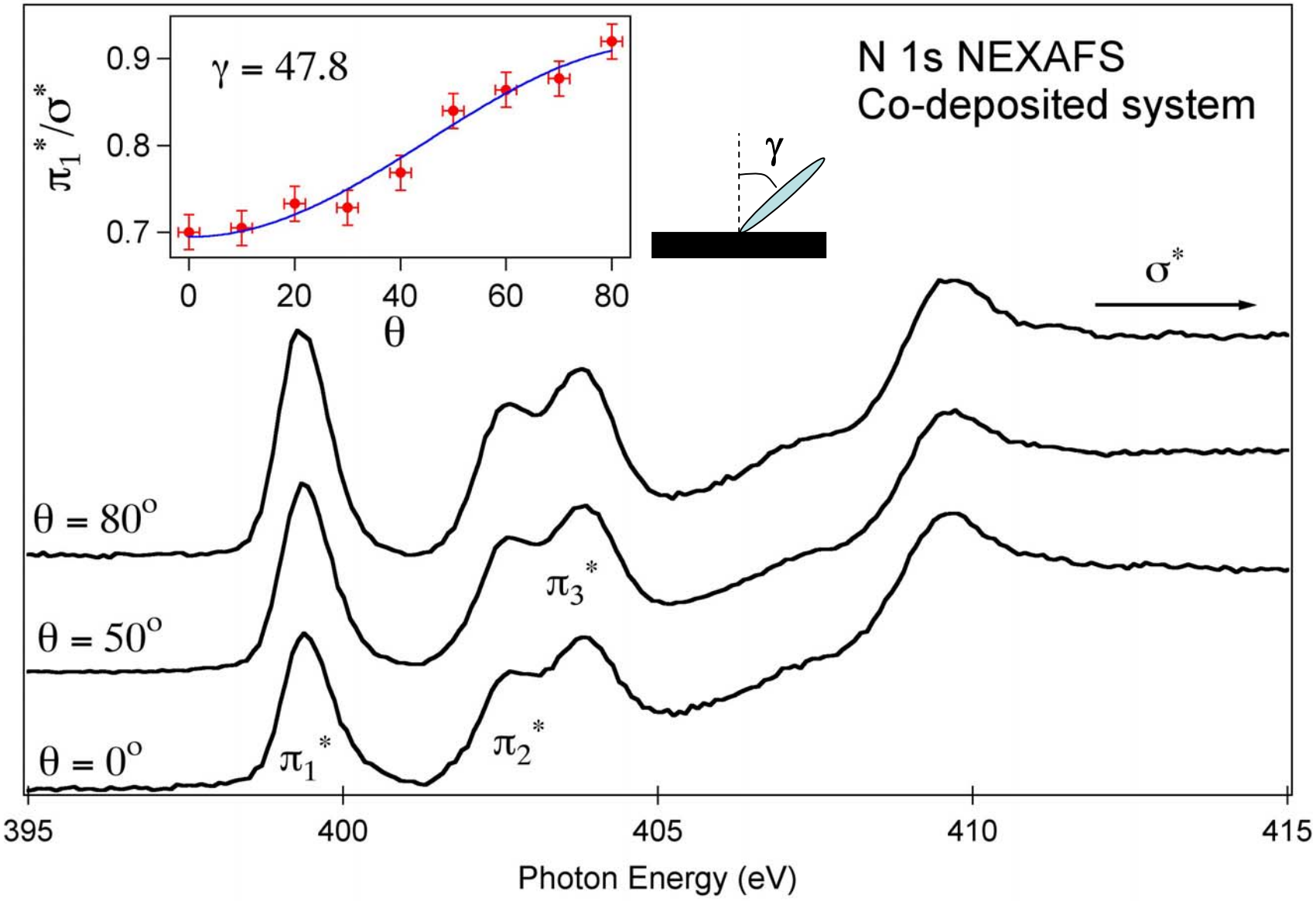
Small charge transfer from porphyrin to C_{70} ~ 0.013 el/molecule

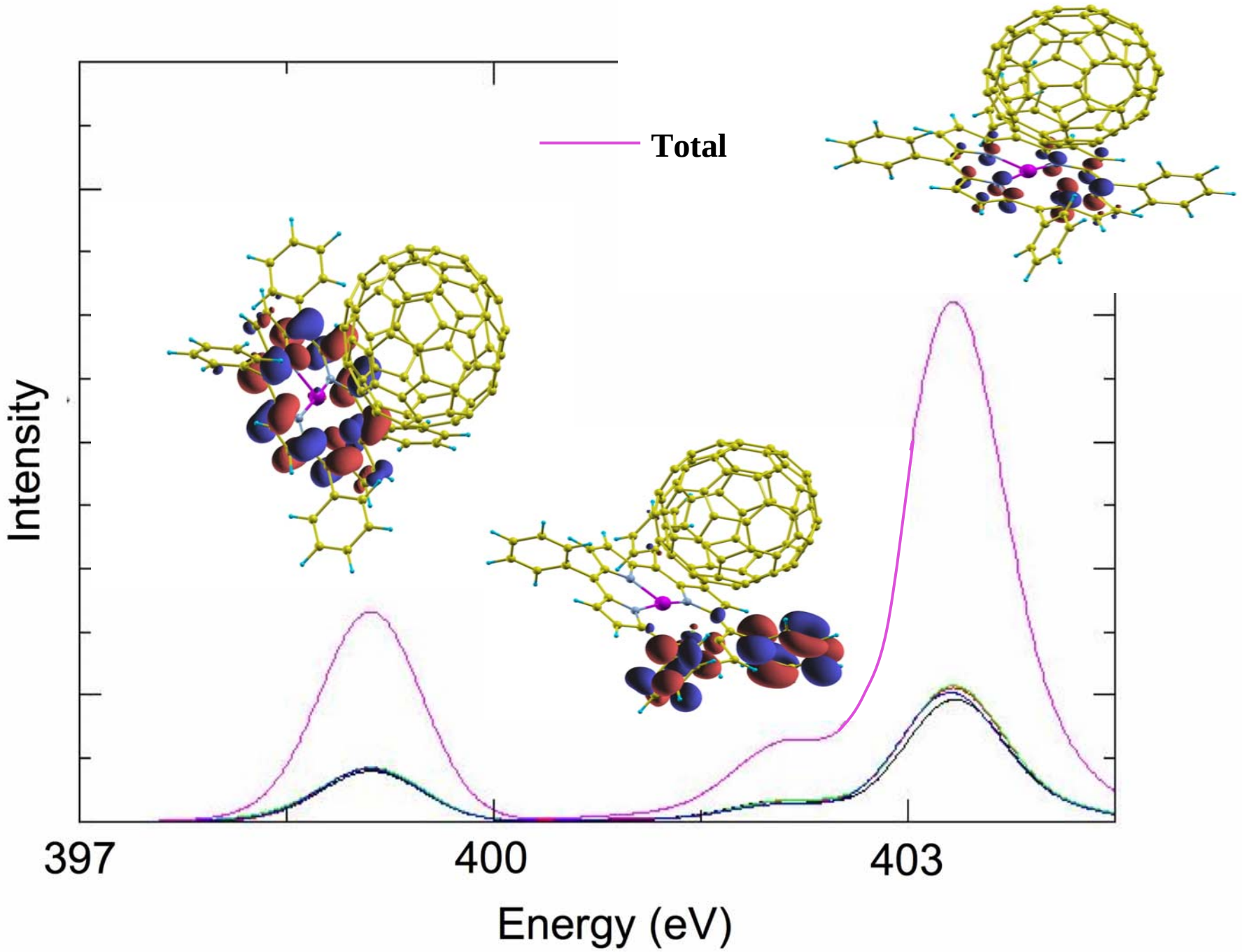
The ground state electronic spectra are a simple summation of ZnTPP and C_{70} properties

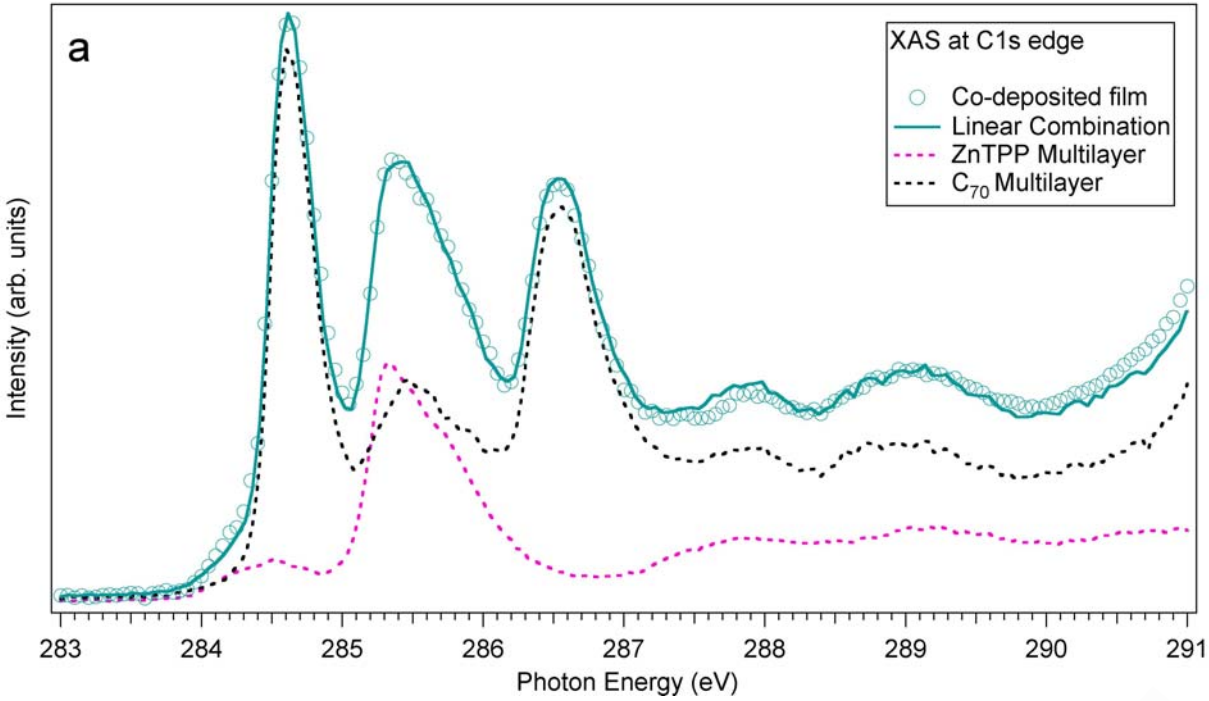


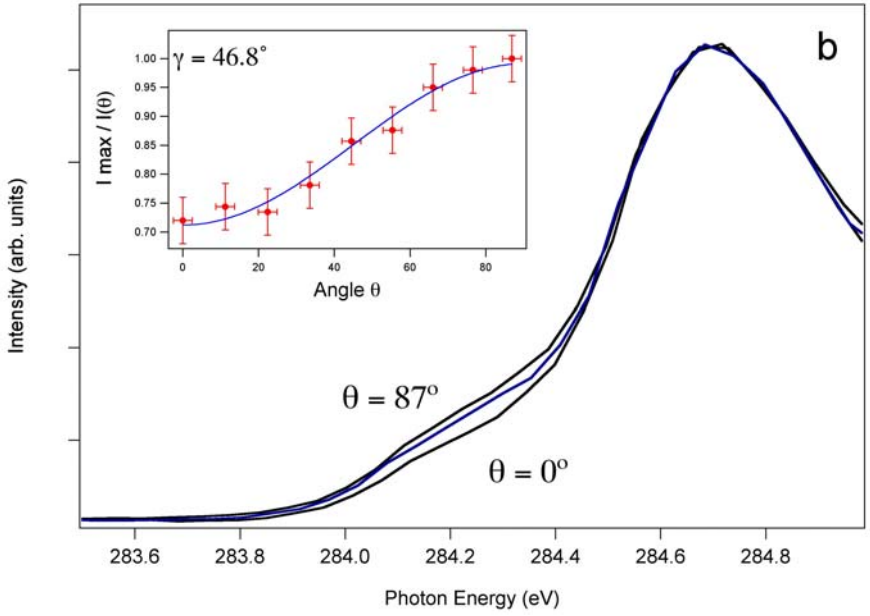

0.01
0
-0.01
-0.02
-0.03
-5
0
5
10
z (Å)
Δρ^ini (electrons/Å)
Fit
H
Co-dep.
C70
ZnTPP
Intensity (arb. units)
12
10
8
6
4
2
0
-2
Binding Energy(eV)

Orientation of ZnTPP and C_{70}




Total
Intensity
397
400
403
Energy (eV)

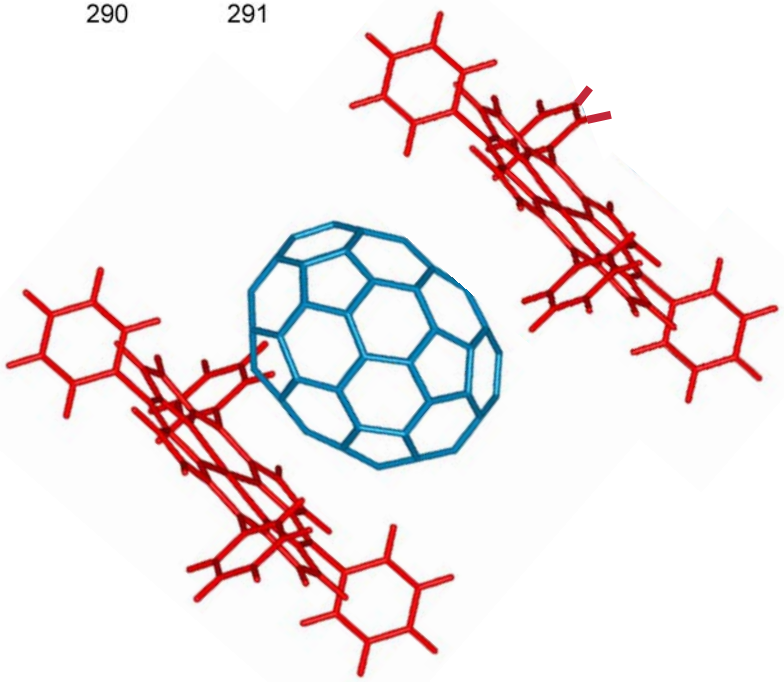


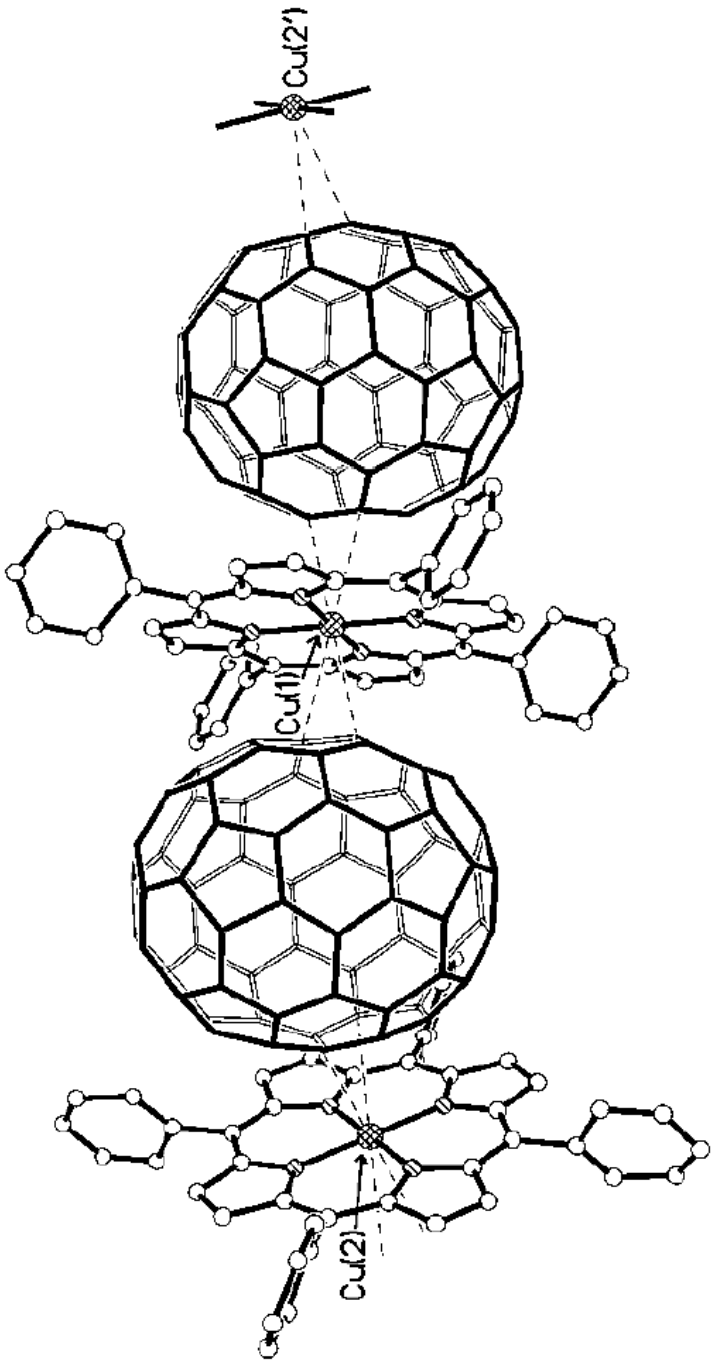


Substantial disorder, but tendency of the π* of porphyrins to stay at ~ 47˚

It turns out that C_{70} long axis is almost parallel to the ZnTPP macrocycle.

Maximization of the electrostatic interactions



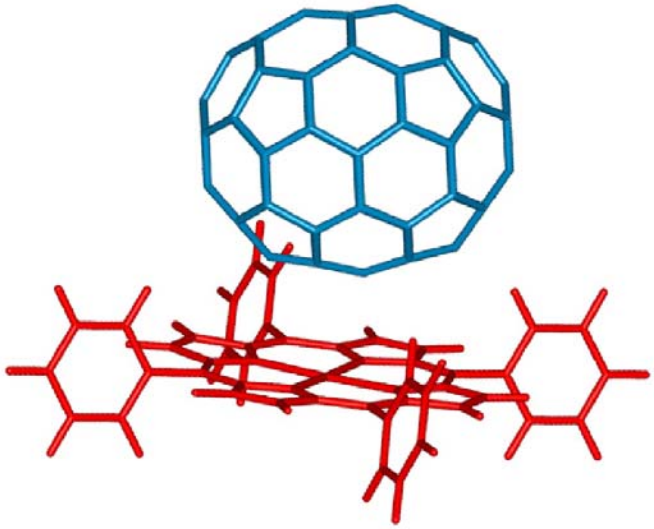


Similar molecular arrangements observed in CuTpp-C_{70}, ZnTpp-C_{70} and H_2TPP-C_{70} cocrystals precipitated from solutions

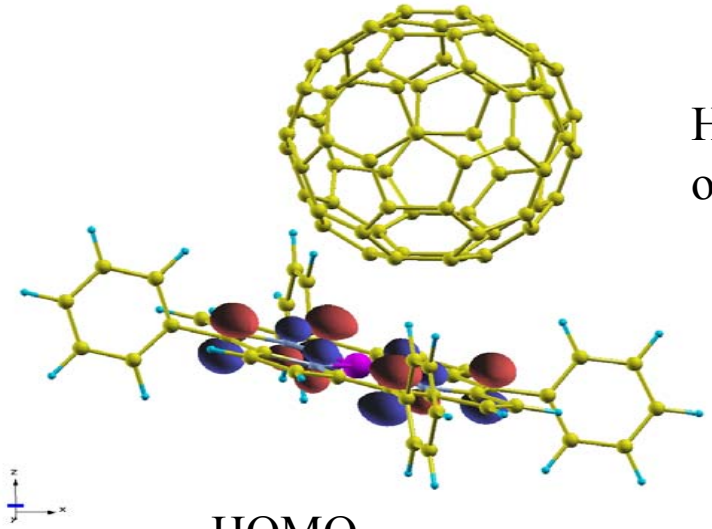
D.V. Konarev *et al*, Chem. Eur. J. **7**, 2605 (2001)
P.D.W. Boyd et al, JACS **121**, 10487 (1999)

and predicted for ZnTpp-C_{70}

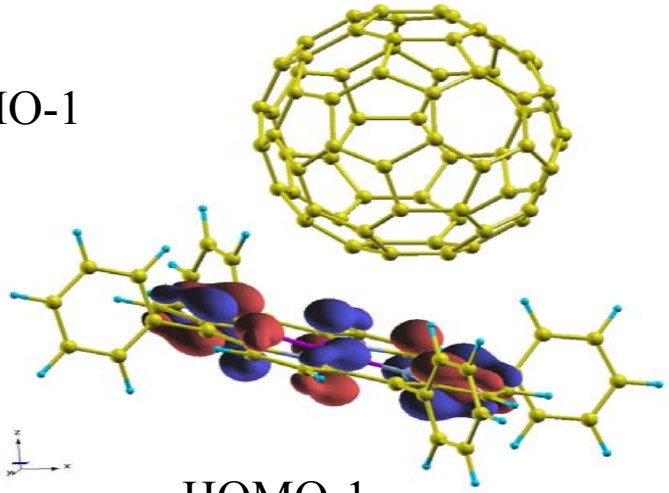
Y.-B. Wang & Z. Lin, JACS **125**, 6072 (2003)



HOMO and HOMO-1
on the porphyrin

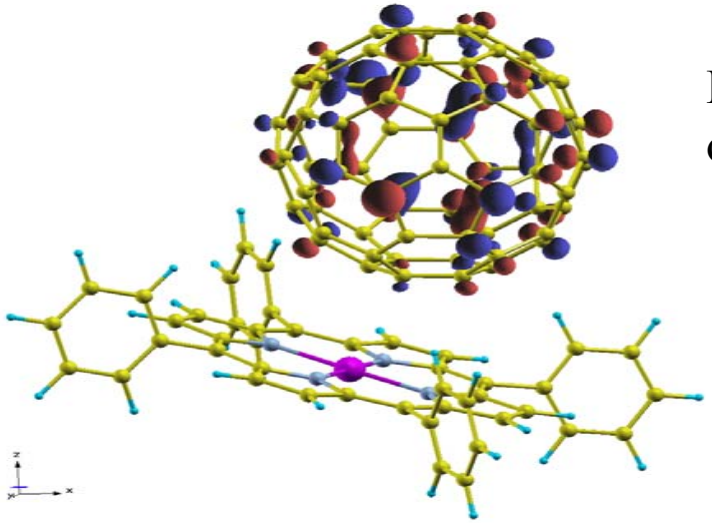


HOMO

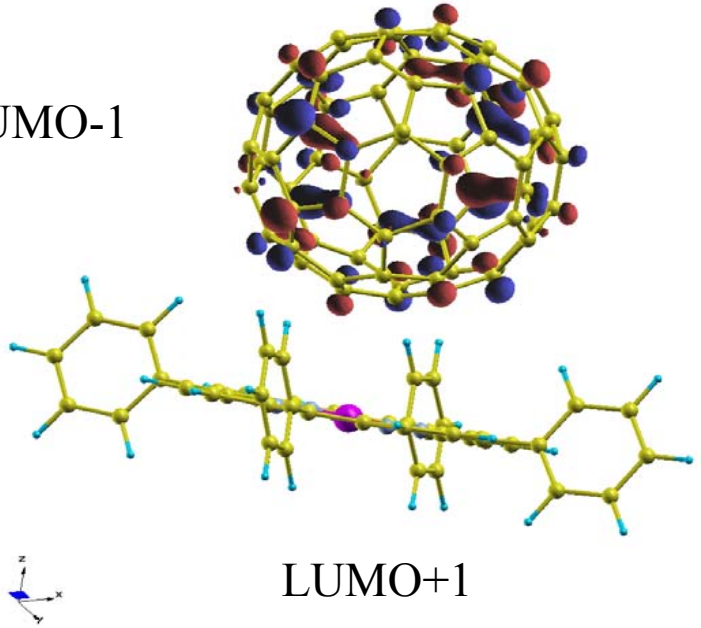


HOMO-1

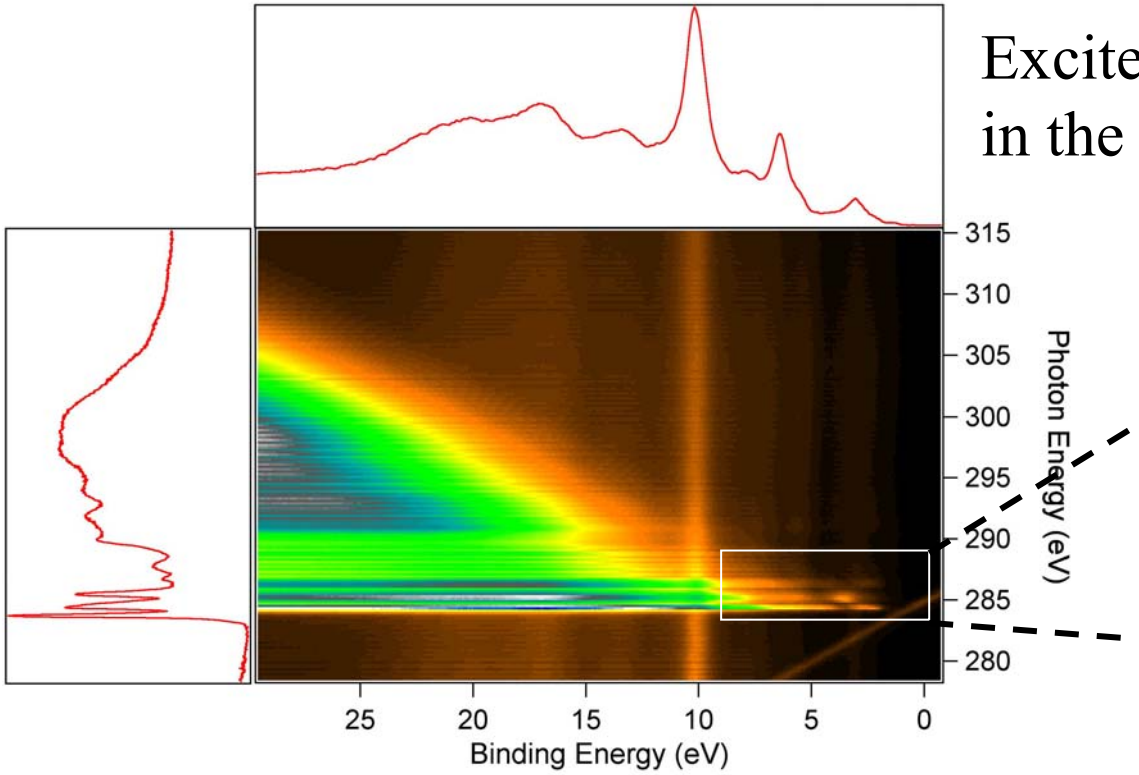
LUMO and LUMO-1
on the C_{70}



LUMO



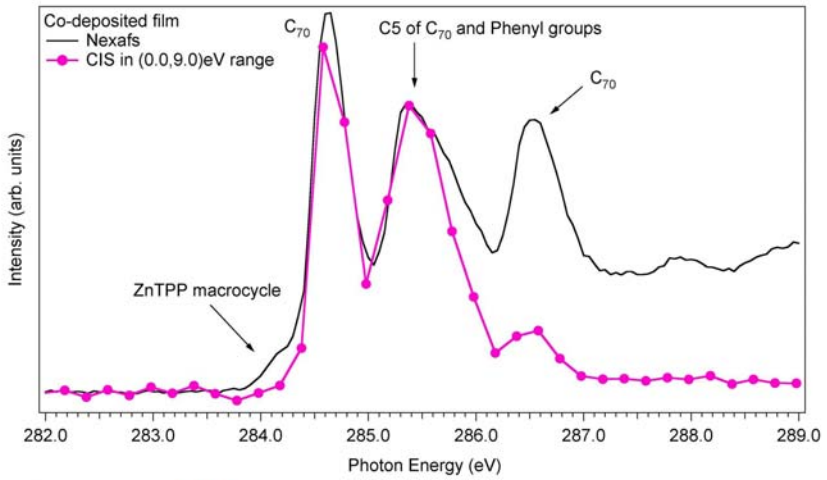
LUMO+1

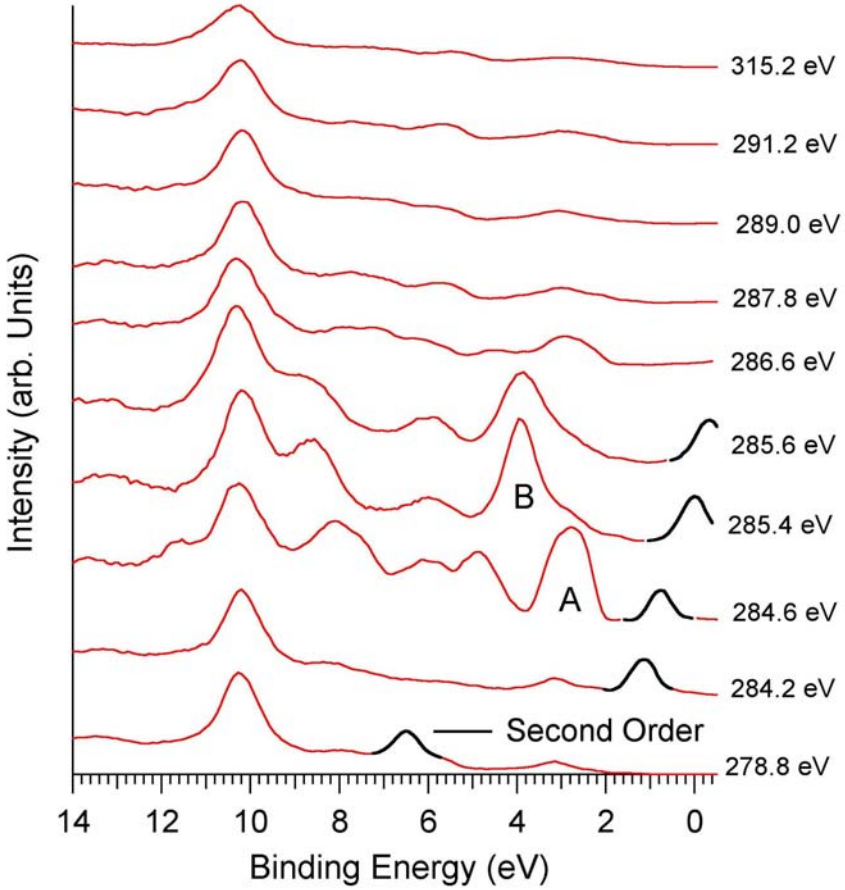


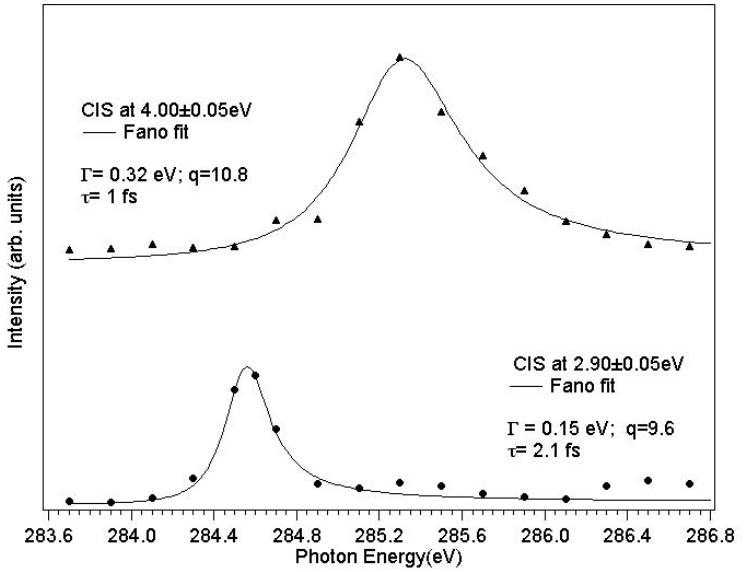
Excited state interactions in the contiguous chromophores

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

There are many resonances which, more or less, follow the NEXAFS peaks, but …







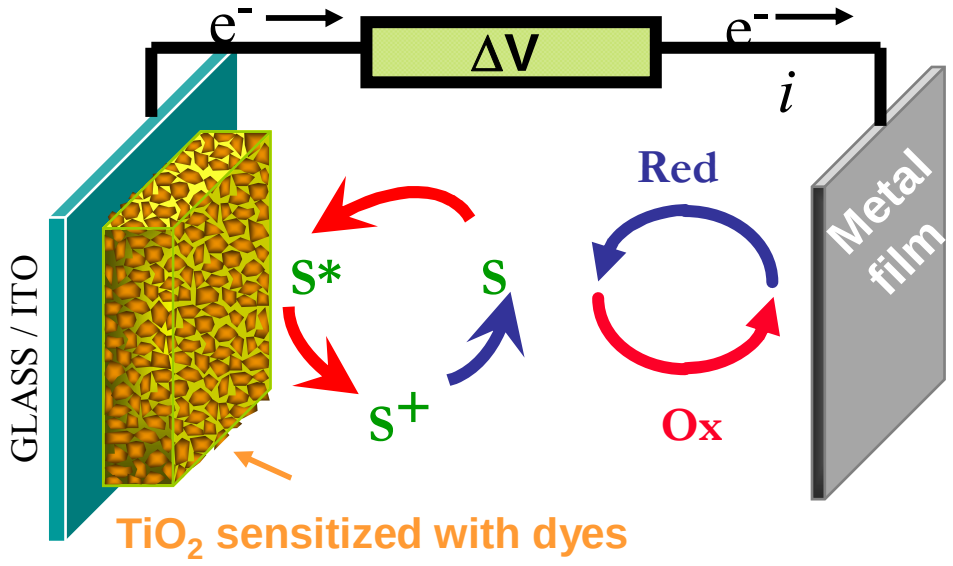
Excited state interactions are present in the contiguous chromophores and this system acts as a *donor/acceptor* junction where the excited charges at the porphyrin macrocycle can fast delocalize to the fullerene. The time scale of the ultra-fast charge transfer is smaller than 1-2 *fs*.

CONCLUSIONS

•The attraction of C_{70} and ZnTPP allows the engineering of supramolecular solids on a mesoscopic scale.

•We were able to grow in ultra-high vacuum molecular complexes of ZnTPP and C_{70} deposited on a semiconductor surface, where the two molecules assume a preferential reciprocal orientation.

•The double-layer system can fast delocalize (5-7 fs) the excited charge and could act as a dye in Gratzel cell.



B. O'Regan, M. Grätzel *Nature* **1991**, *353*, 737

•The ground state electronic spectra of our co-deposited material reflect a simple summation of components, so the ground state perturbation is weak.

•However, the excited state interactions are present in the contiguous chromophores and this system acts as a *donor/acceptor* junction where the excited charges at the porphyrin macrocycle can fast delocalize to the fullerene. The time scale of the ultra-fast charge transfer is smaller than 1-2 *fs*.