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Understanding molecular interfaces used for energy conversion

Håkan Rensmo, Uppsala University

HAXPES 2011
4th International Workshop on
Hard X-ray Photoelectron Spectroscopy



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Foto: B. Göleason

Uppsala University **Molecular and Condensed Matter Physics**

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Susana Kaufman (PhD)
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Johan Oscarsson (PhD)
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Center for Molecular Devices

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Prof. Ander Hagfeldt (Uppsala University)
Doc. Gerrit Boschloo (Uppsala University)
Prof. Lars Kloo (Royal Institute of Technology)
Prof. Lichen Sun (Royal Institute of Technology)

- Fundamental research
- Materials development
- Up-scaling and process development
- Dyenamo AB



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Dr. Elin Sondergard
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Funding

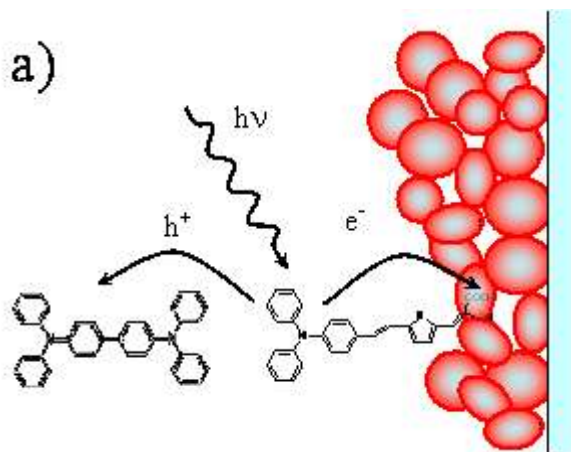
Swedish Research Council
Swedish Energy Agency
KAW



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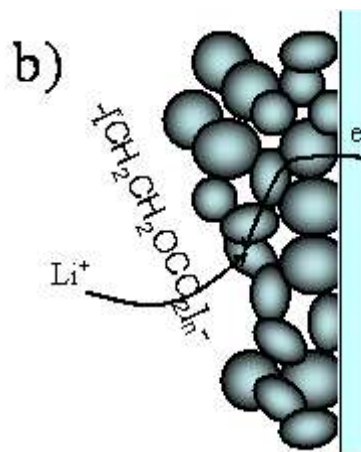
Understanding molecular interfaces used for energy conversion

Solar cells



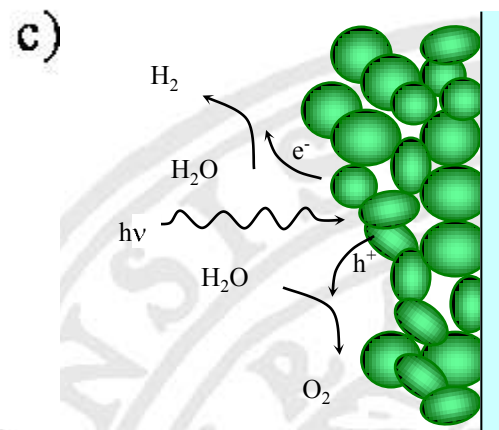
Nanostructured dye-
sensitized solar cell
Prof. Anders Hagfeldt
CMD

Batteries



Li-ion Batteries
Prof. Kristina Edström
Uppsala University, ÅABC

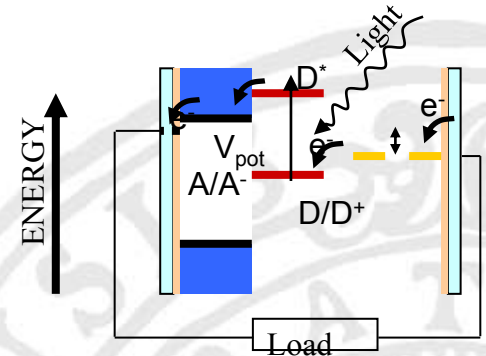
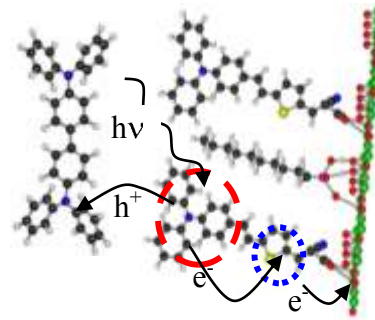
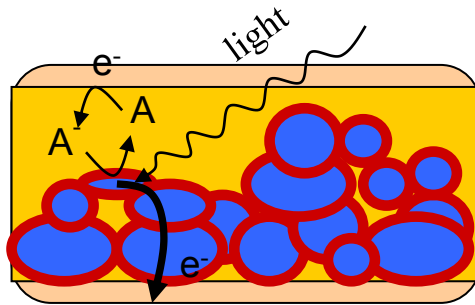
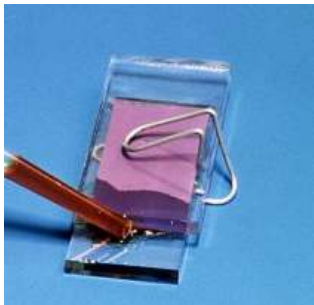
Photocatalysis



H₂O/TiO₂
Prof. Anders Sandell



Key function: Light absorption and charge separation



Different models, many questions!

Molecular functions

- Molecular units absorb light
- Charges are separated at interfaces,
- "all molecules has to work"



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DSC: Technical status

Consumer Electronics - YES

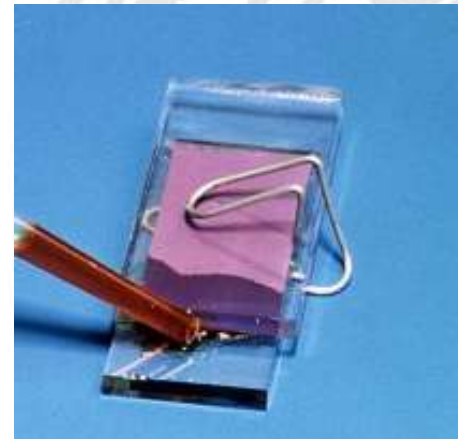
DSC in buildings – ?





Some Facts

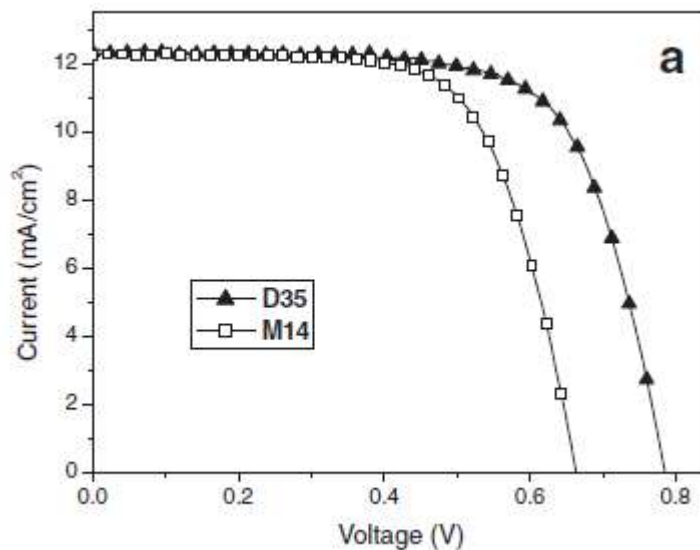
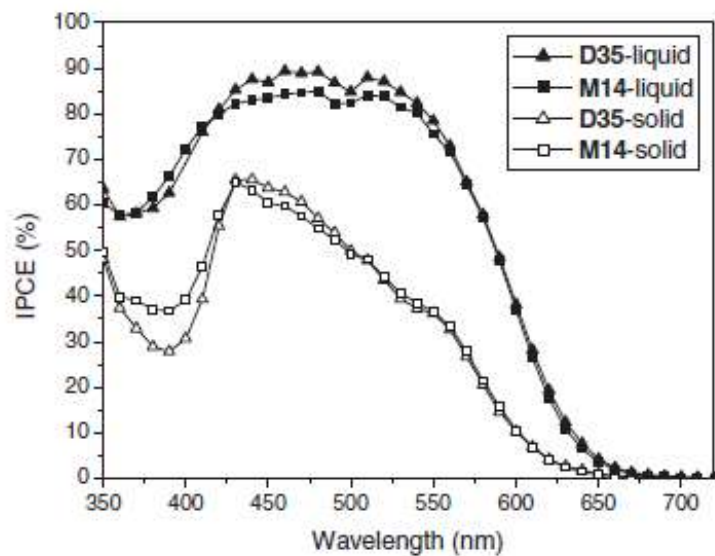
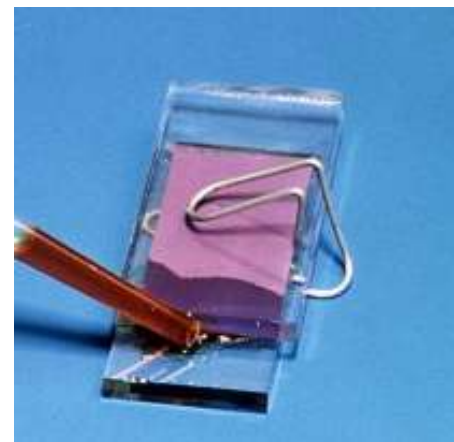
- World record efficiency 12.3 %.
- Mini-module efficiencies above 10 %
- Cells passed accelerated life-time testing at 9 %
- Solid-state DSCs above 7 %
- Big research field, more than 2-3 articles published every day





Research directions

- New organic dyes
- New redox systems
- Solid state hole-conducting systems



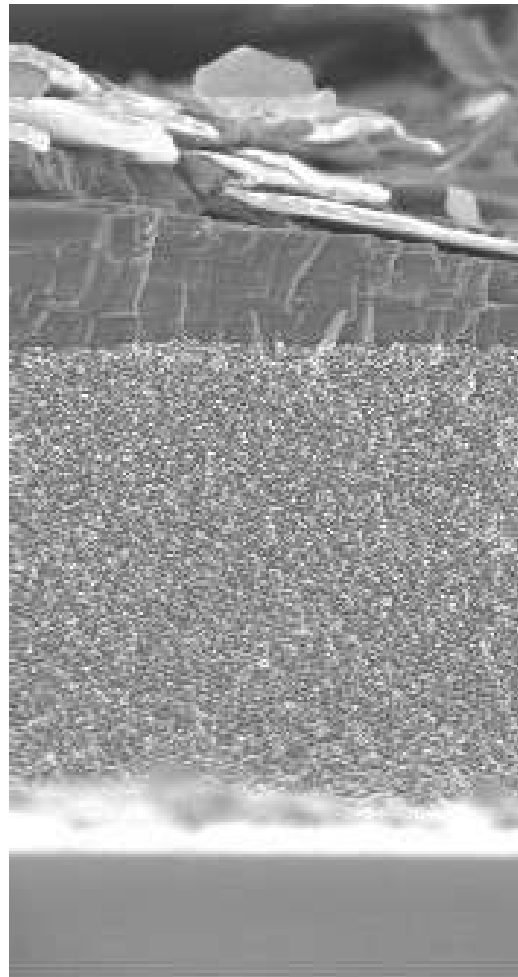
X. Jiang et al. *Adv. Funct. Mater.* **2011**, *21*, 2944–2952

Centre of Molecular Devices



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Nanostructured dye-sensitized solar cell



Metal/hole-conductor interface

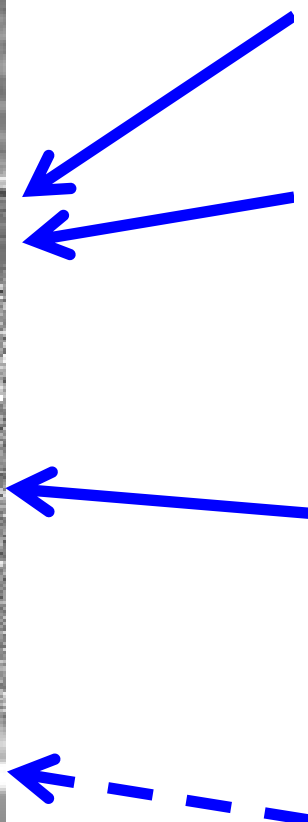
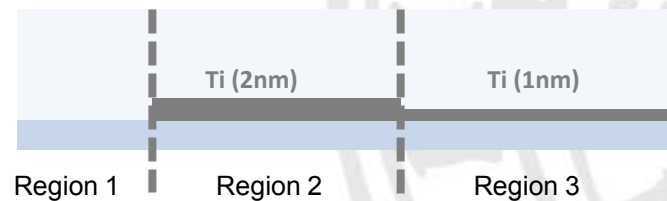
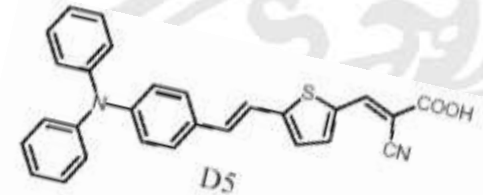
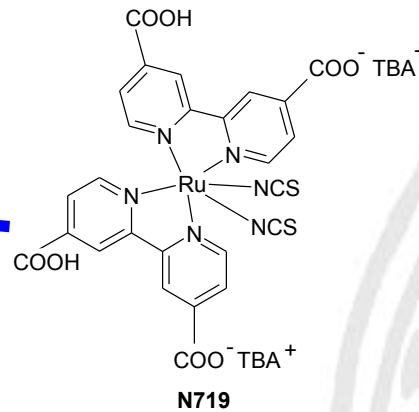
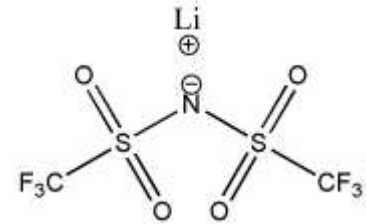
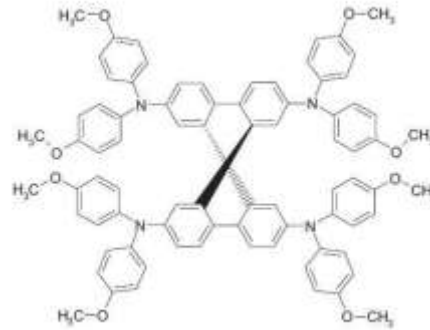
Holeconductor doping

Dye structure

Conducting glass

10 μ m*

Nanostructured dye-sensitized solar cell

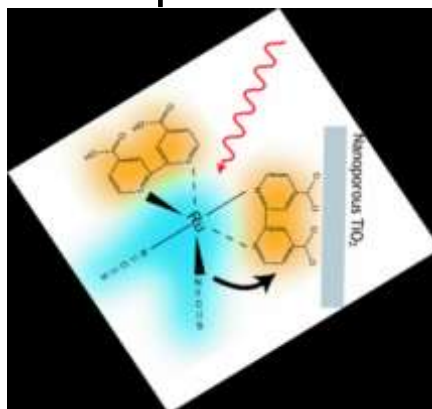
 $10\mu\text{m}^*$ 



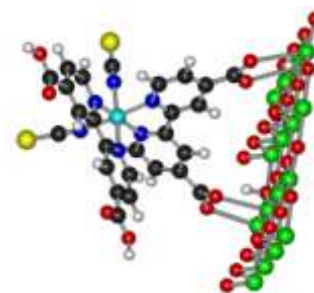
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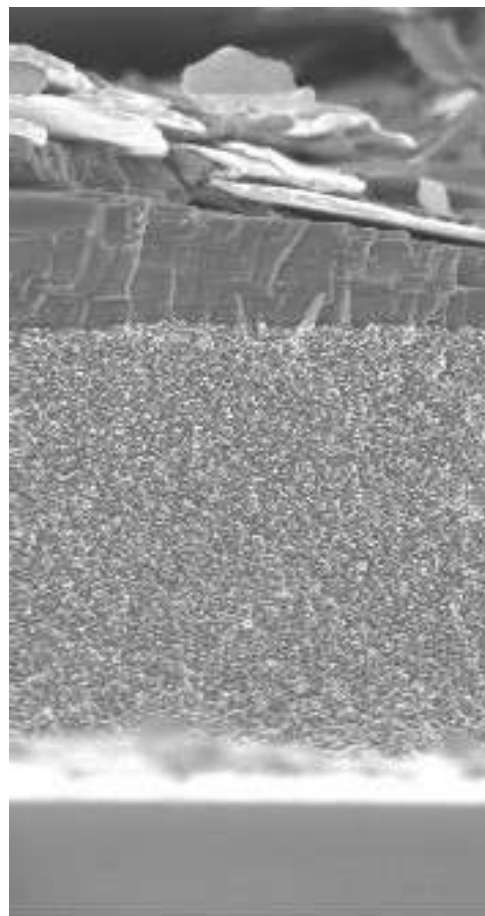
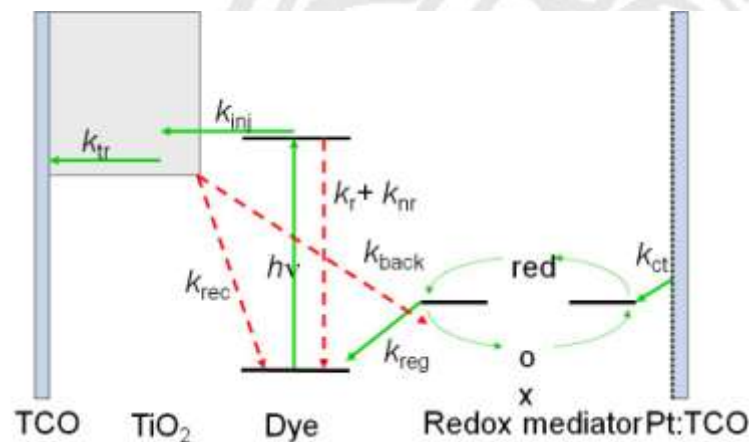
Molecular orbital Composition



Interfacial structure



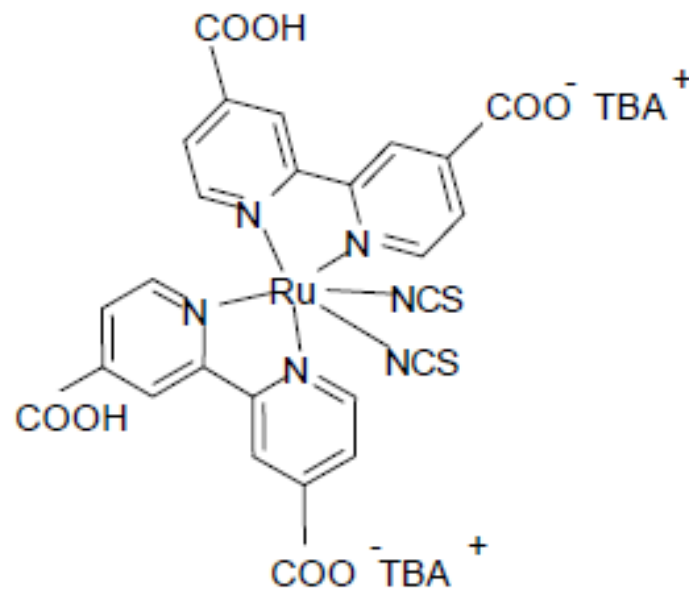
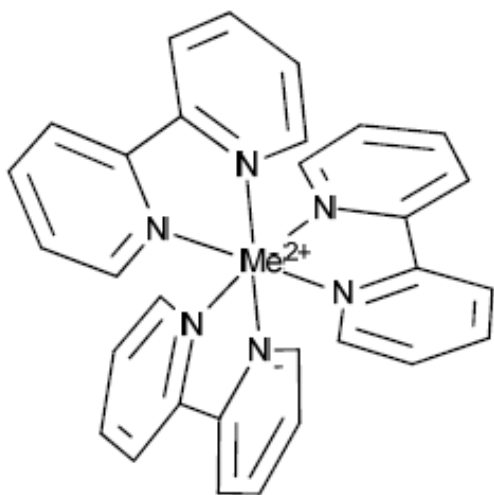
Energy Matching



$10\mu\text{m}^*$



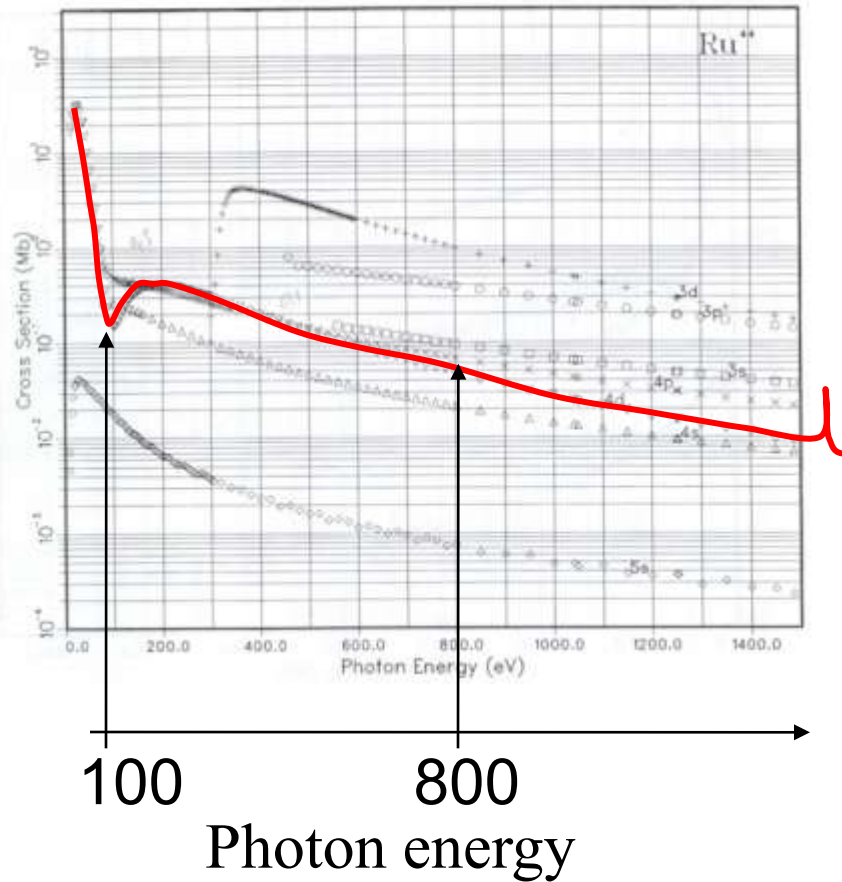
Molecular orbital composition





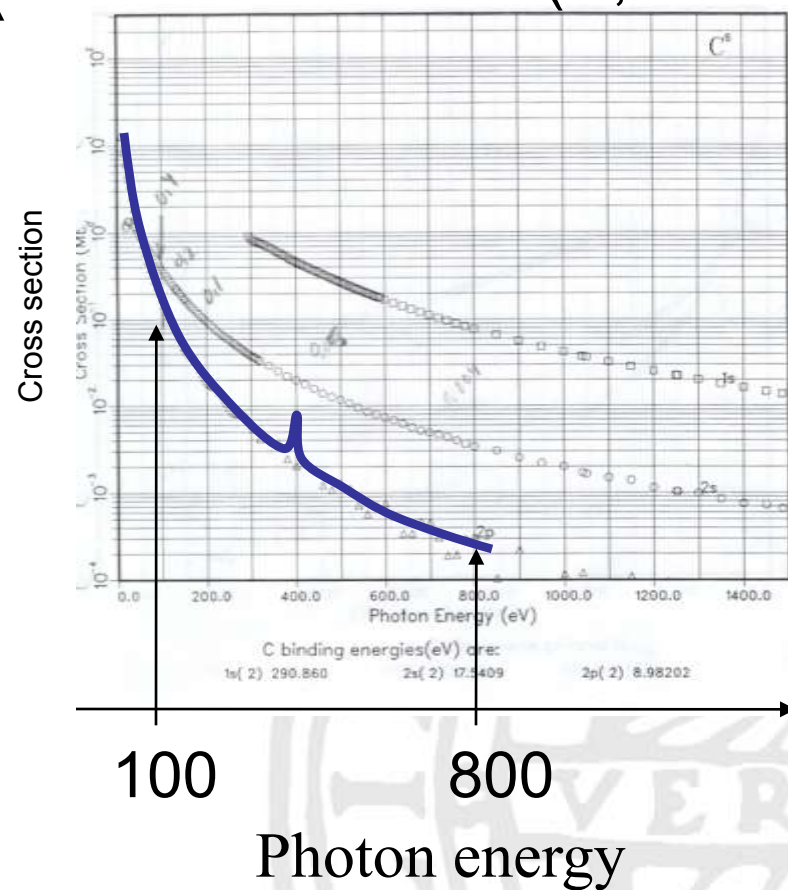
Molecular orbital composition

Ruthenium, 4d



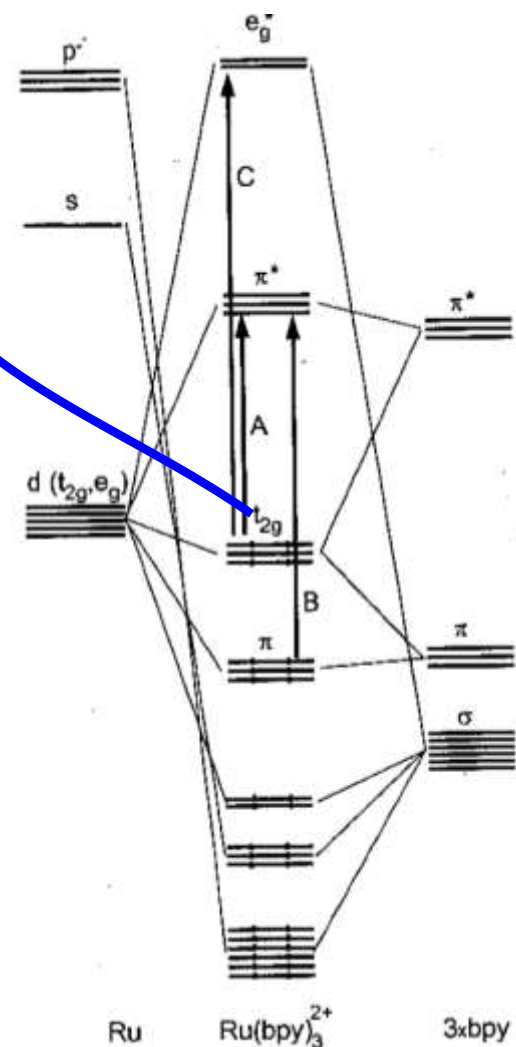
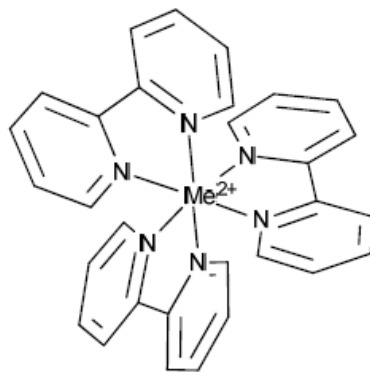
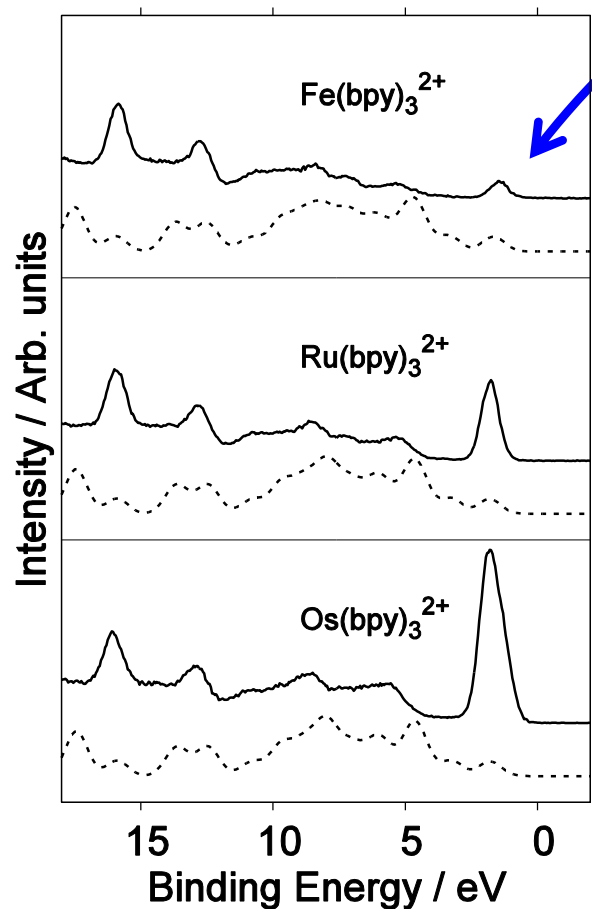
Carbon, 2p

(N,O are simila





Molecular orbital composition

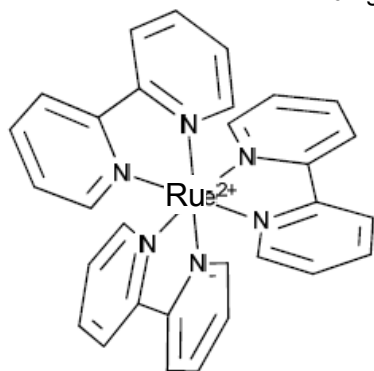
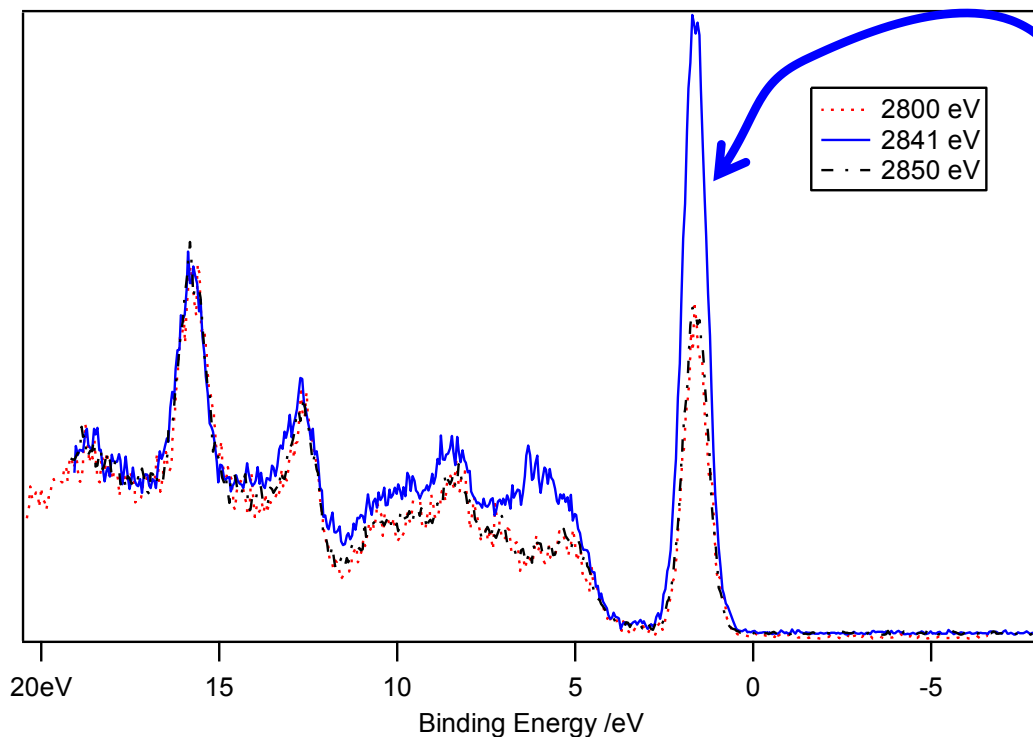




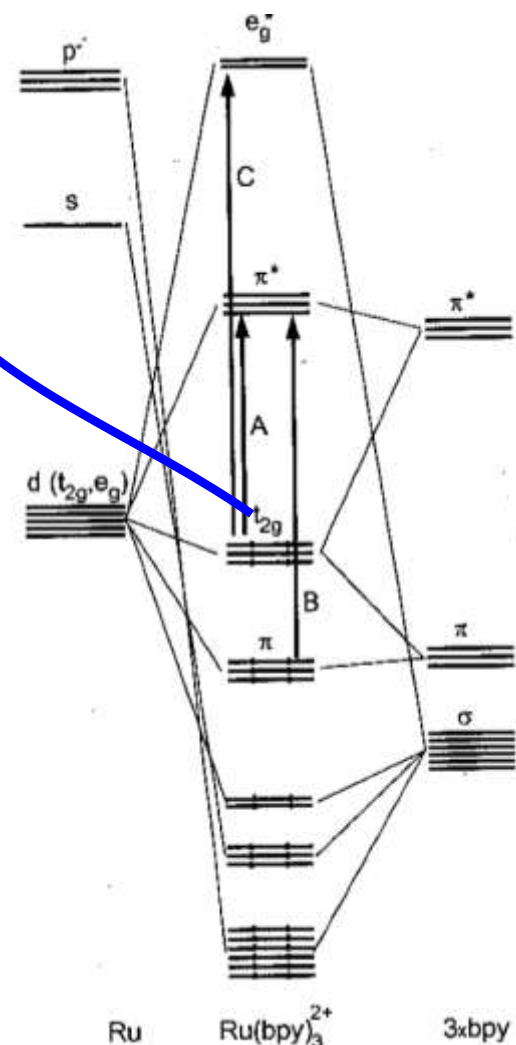
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Molecular orbital composition

Intensity /arb. units



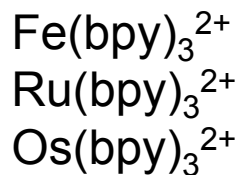
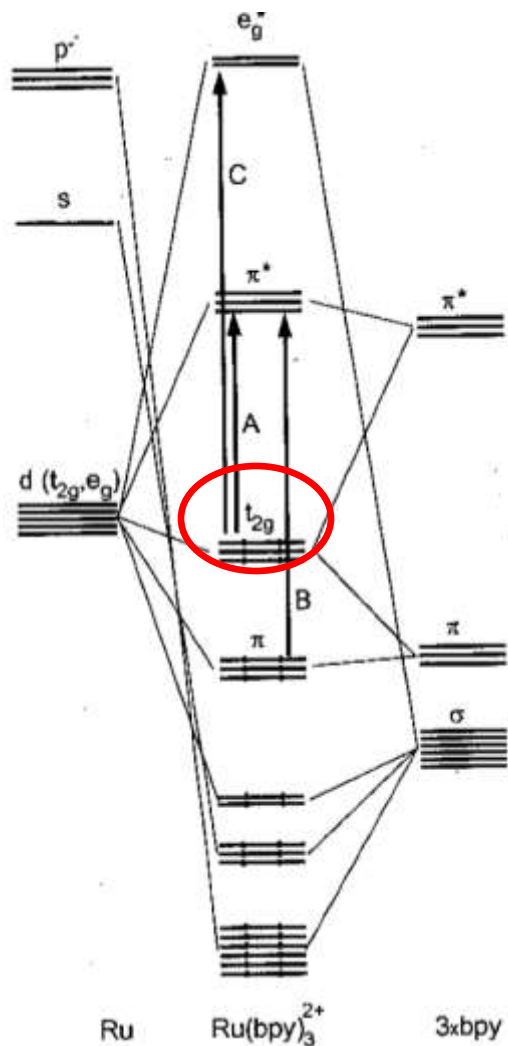
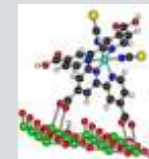
Ru 2p to Ru 4d
at about 2841 eV





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Molecular orbital composition

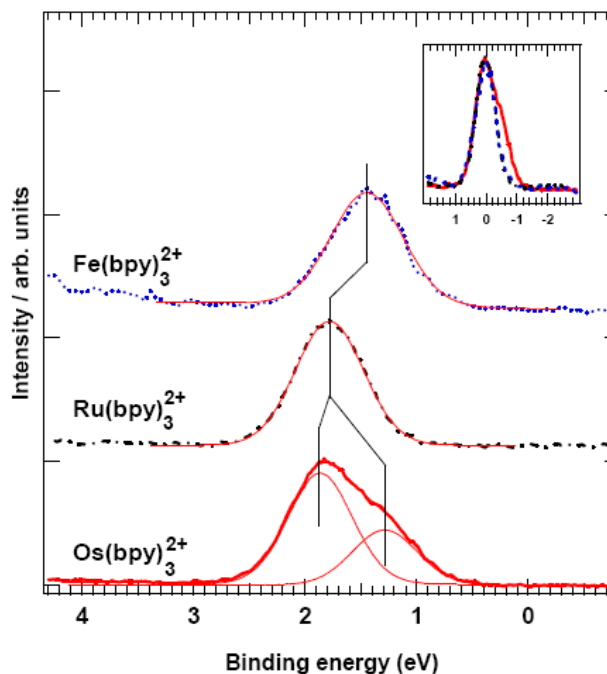
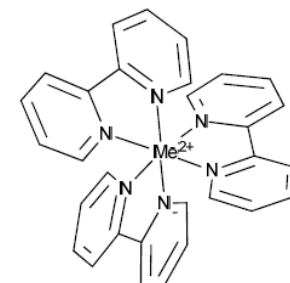


V versus SCE

1.03

1.20

0.81



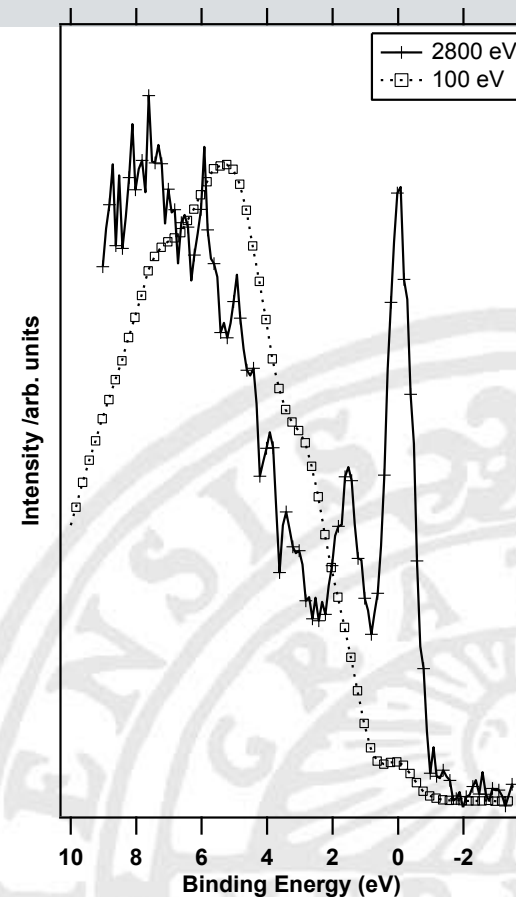
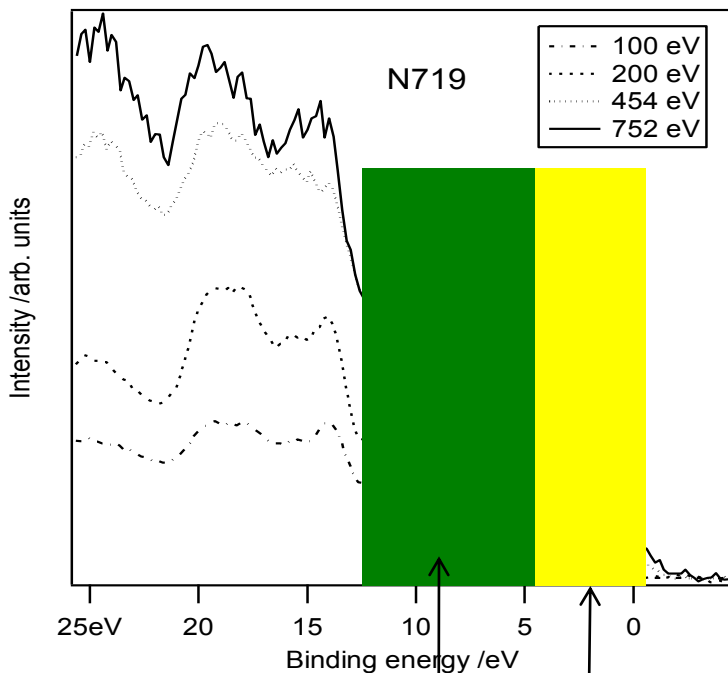
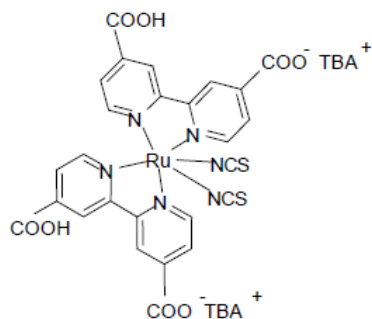
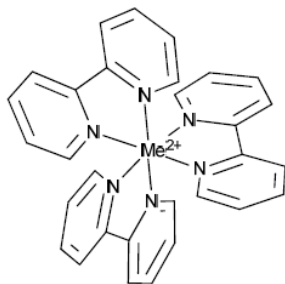
Spin orbit split 0.6 eV in $\text{Os}(\text{bpy})_3^{2+}$



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Molecular orbital composition

Multilayer



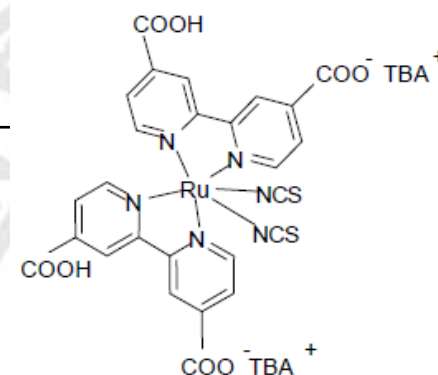
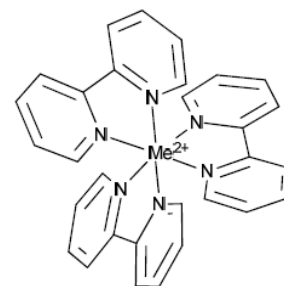
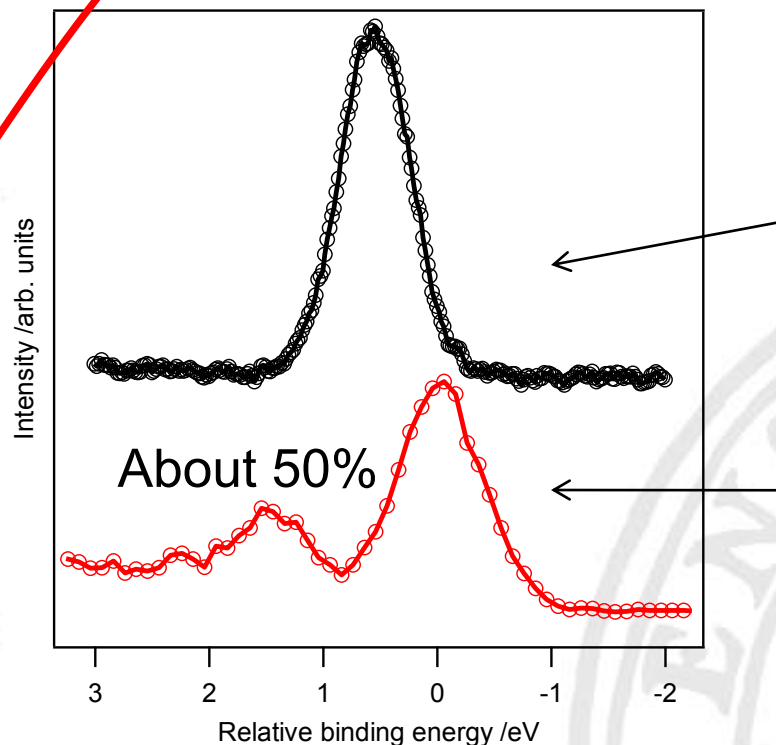
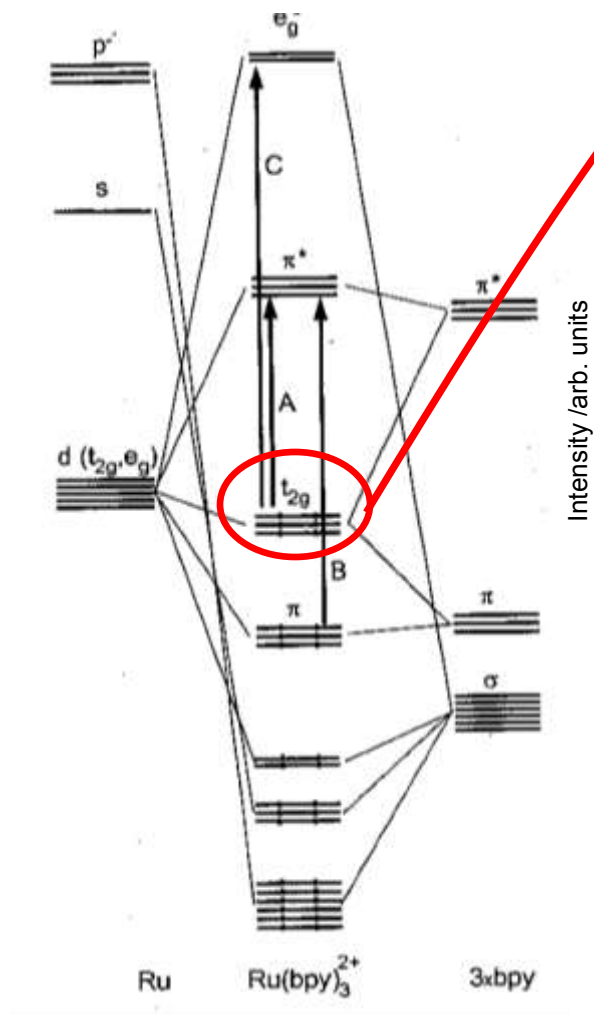
Cross-section based and resonance techniques (**NCS**)





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Molecular orbital composition



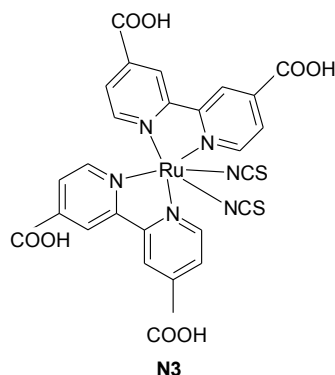
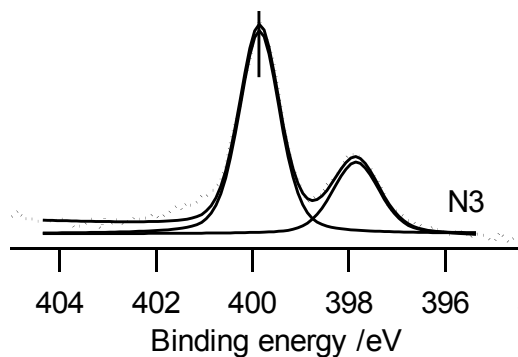
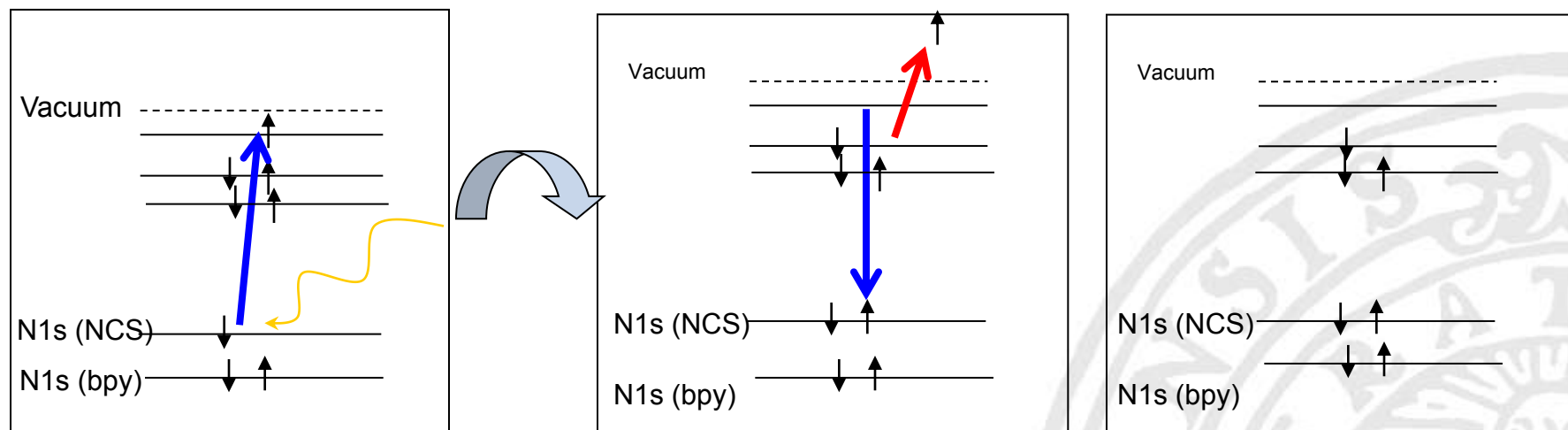
Partial DOS of Ru 4d

Valence level at 2800 eV



Molecular orbital composition

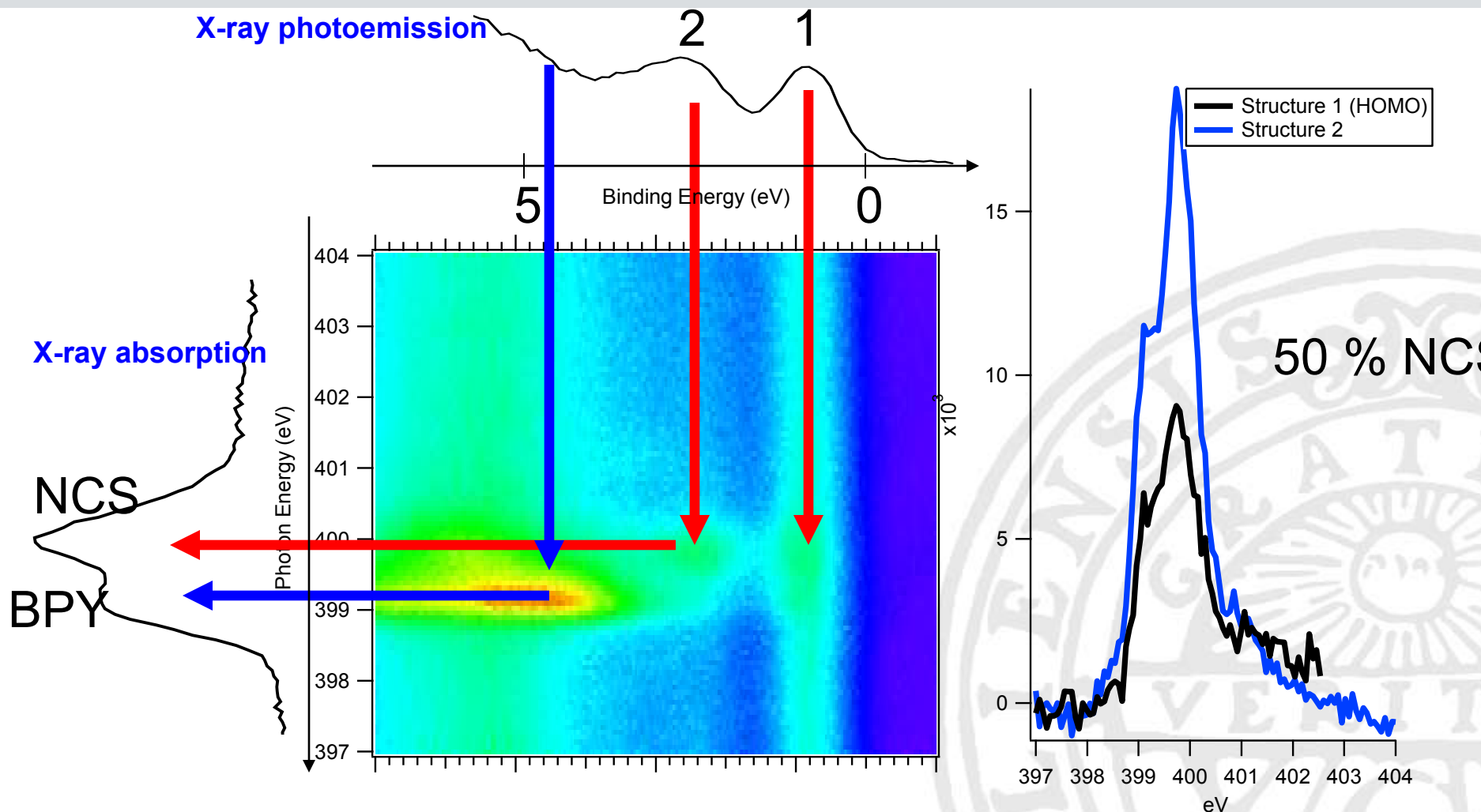
RPES - Resonant PhotoEmission Spectroscopy





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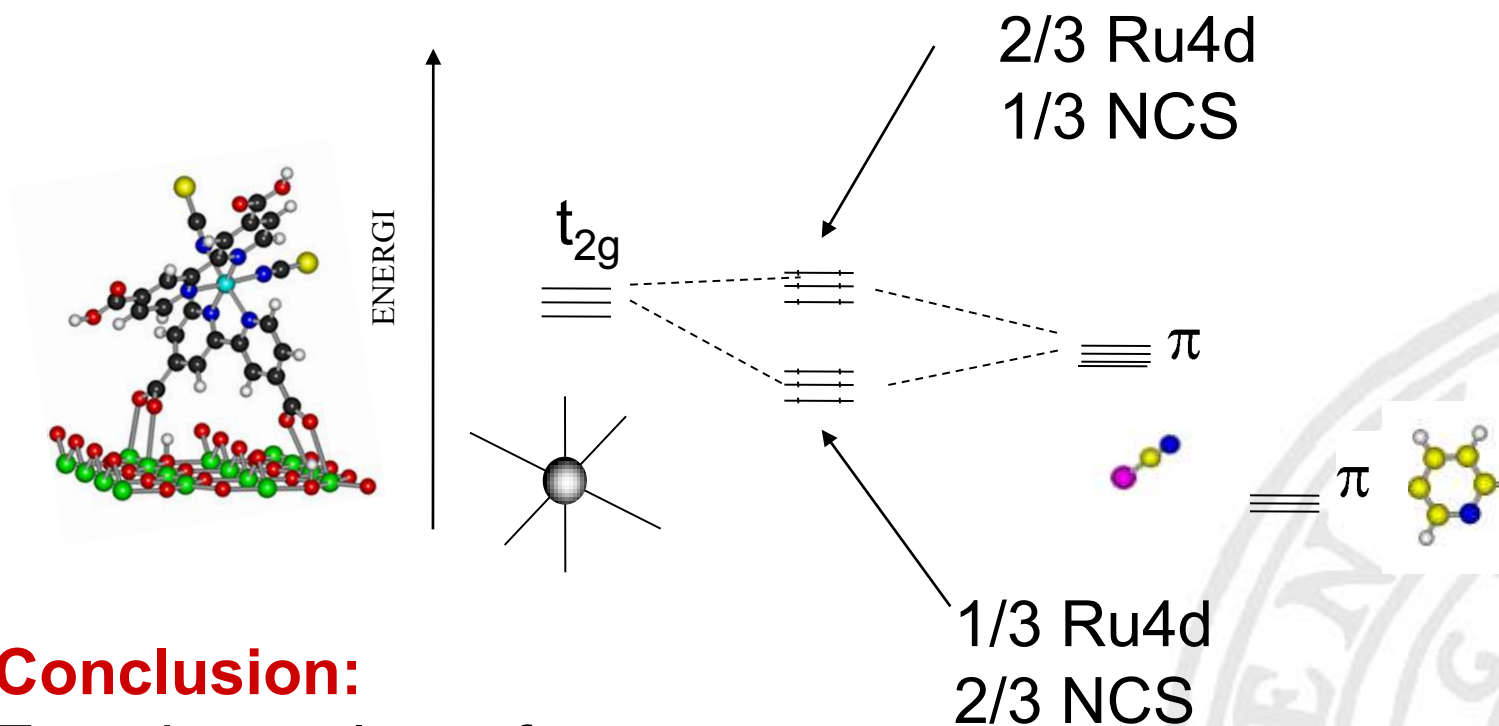
Molecular orbital composition





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Molecular orbital composition



Conclusion:

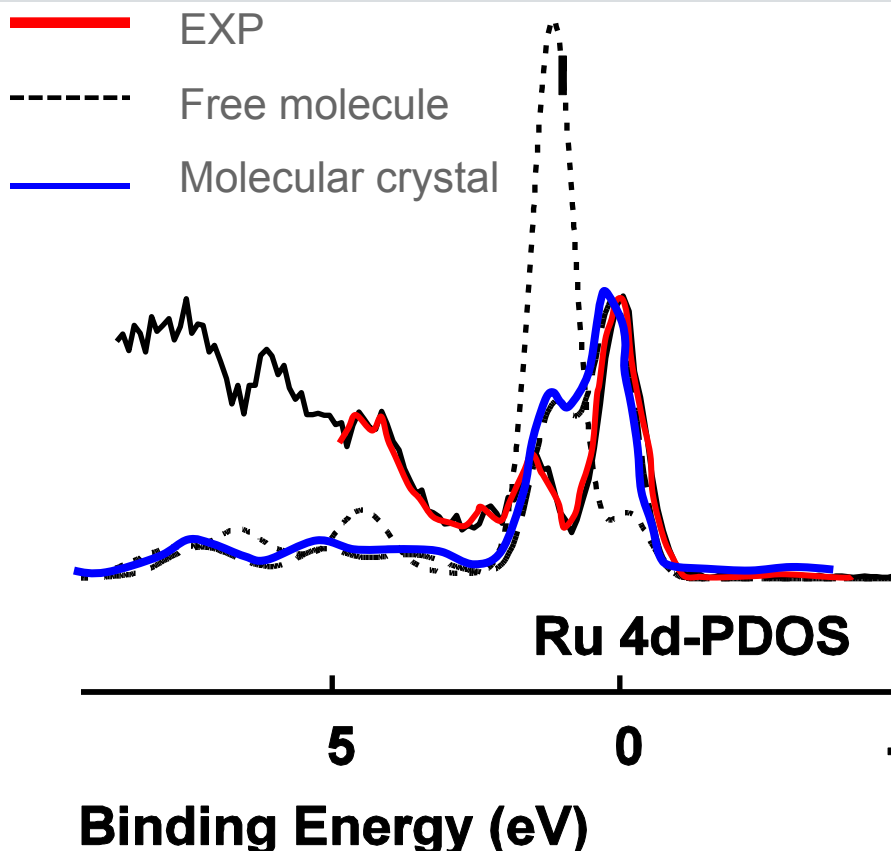
Experimental proof:
The t_{2g} set split.

Experimentally determine the relative amount of Ru4d and N(NCS) in the MO.

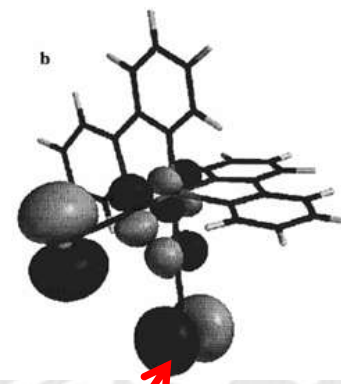


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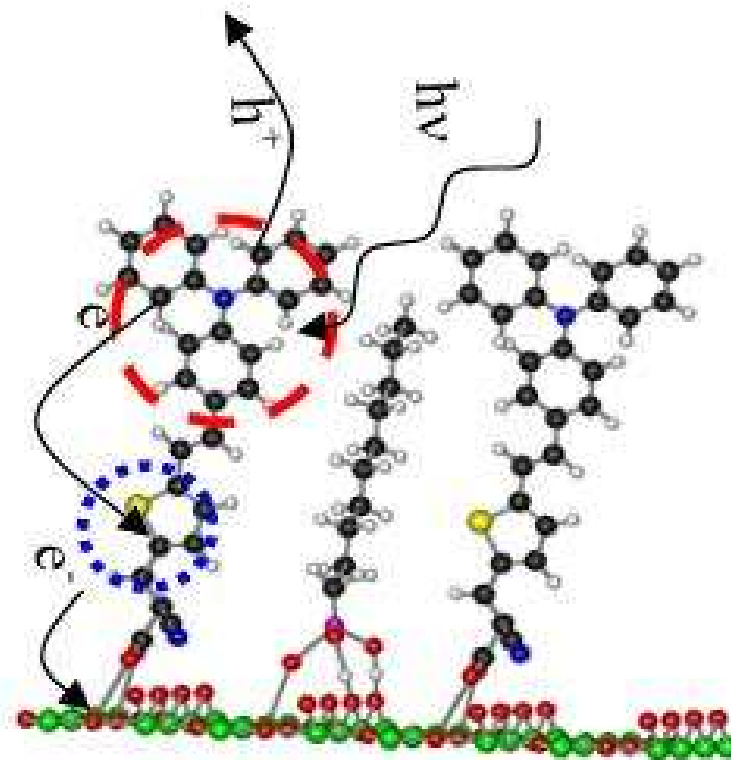
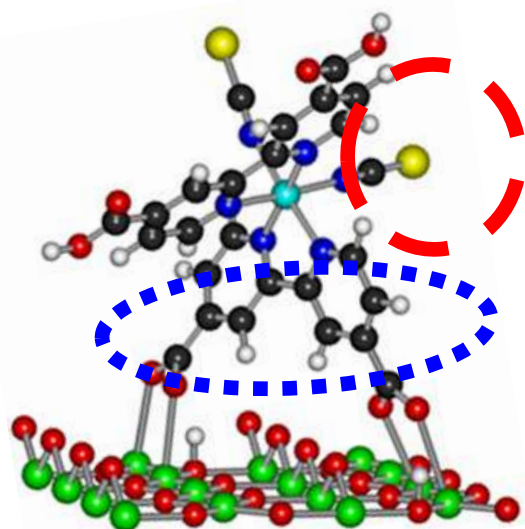
Molecular orbital composition



2/3 Ru4d
1/3 NCS



Calculations on the dye molecules require the **crystal structures** in order to model the experimental results

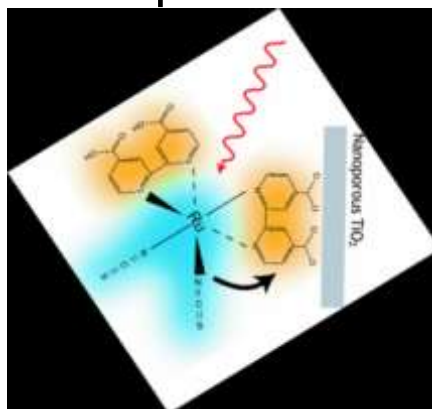




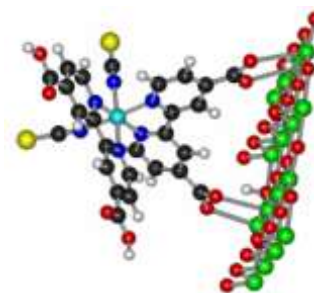
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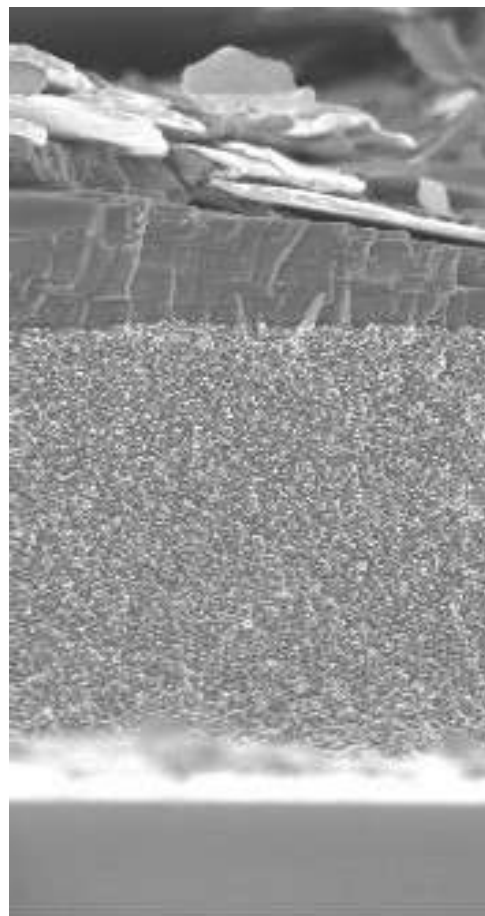
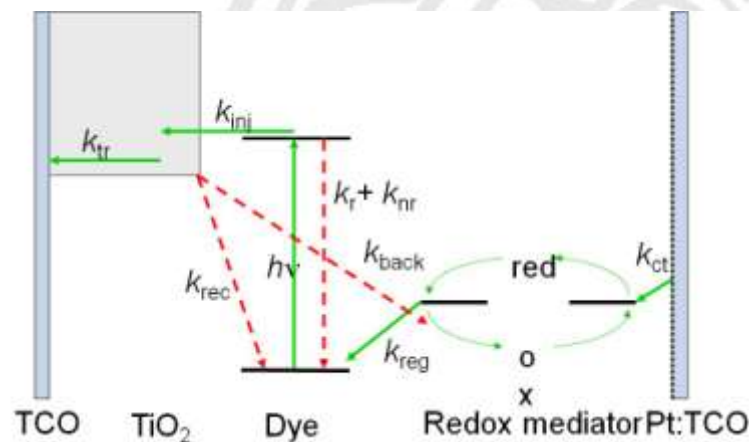
Molecular orbital Composition



Interfacial structure



Energy Matching



10 μ m*

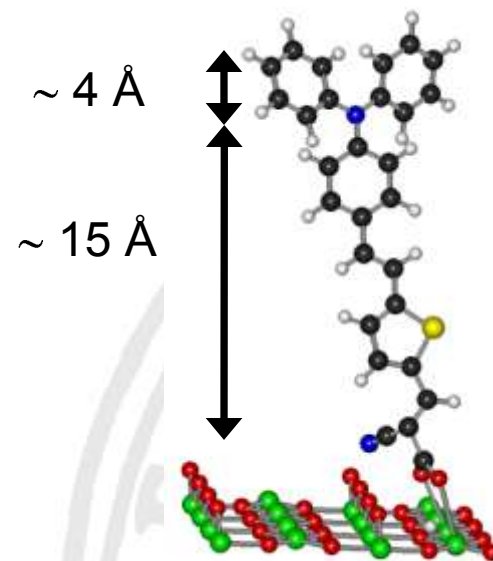
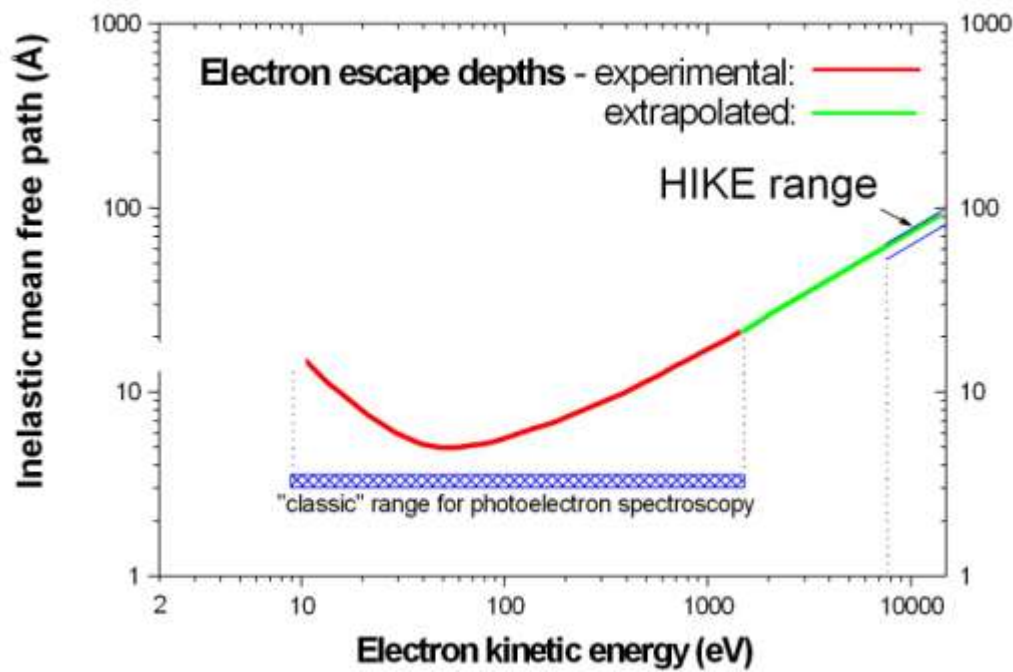


Binding configuration



Probe **NITROGEN**
atoms via the
N1s core-level

$$I_a \propto \rho_a * \sigma_a(h\nu, \theta) * \exp[-z/\Lambda(E_k)]$$

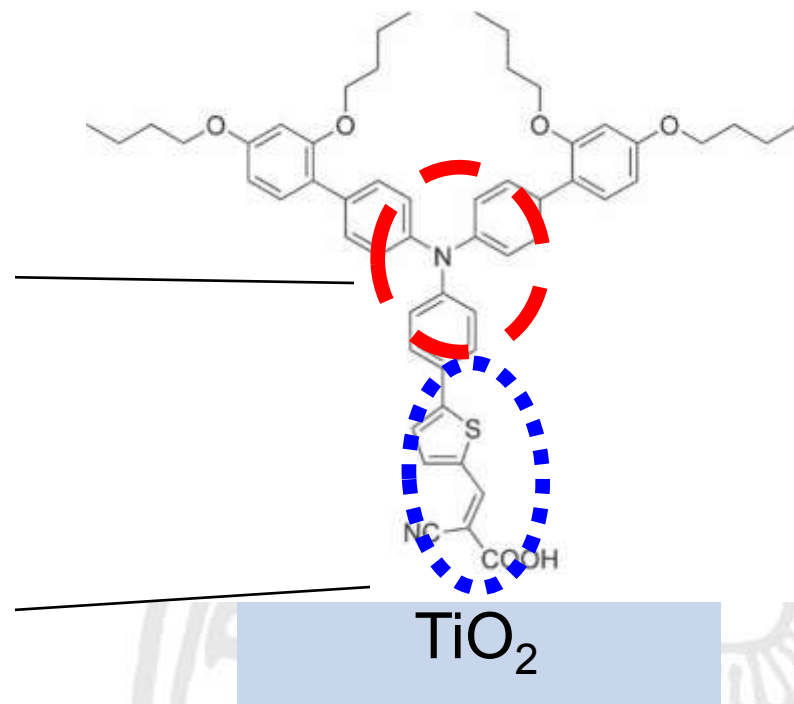
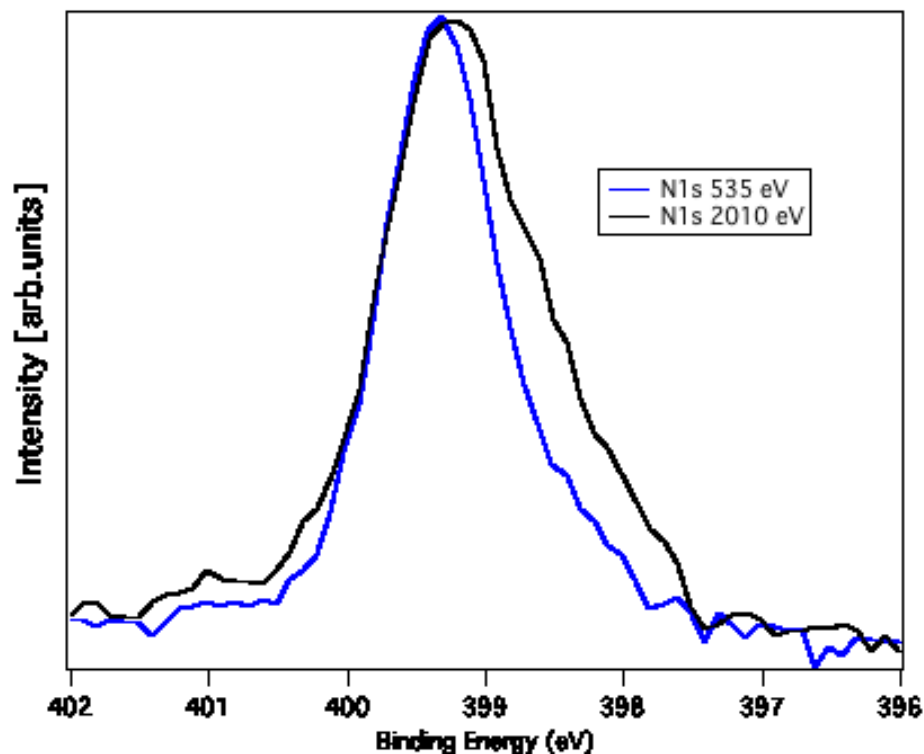




Bonding configuration

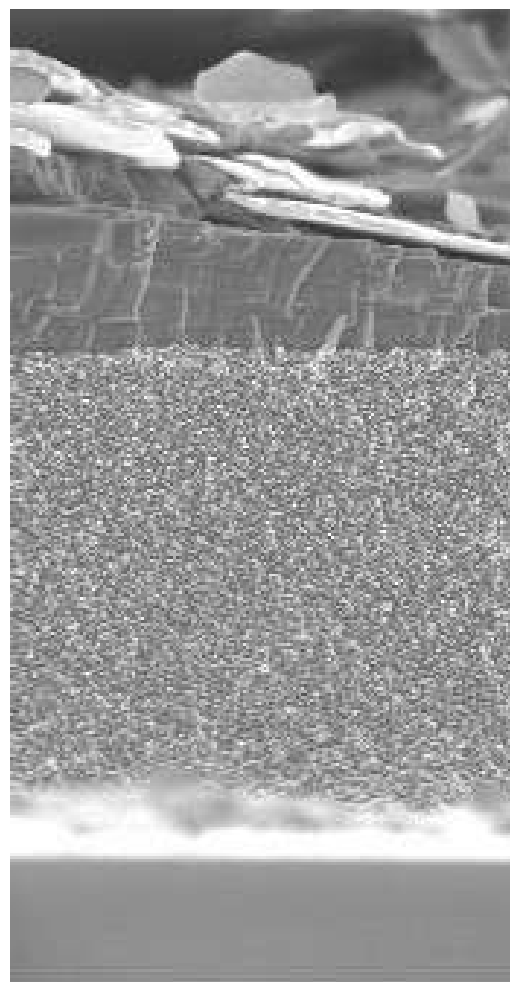
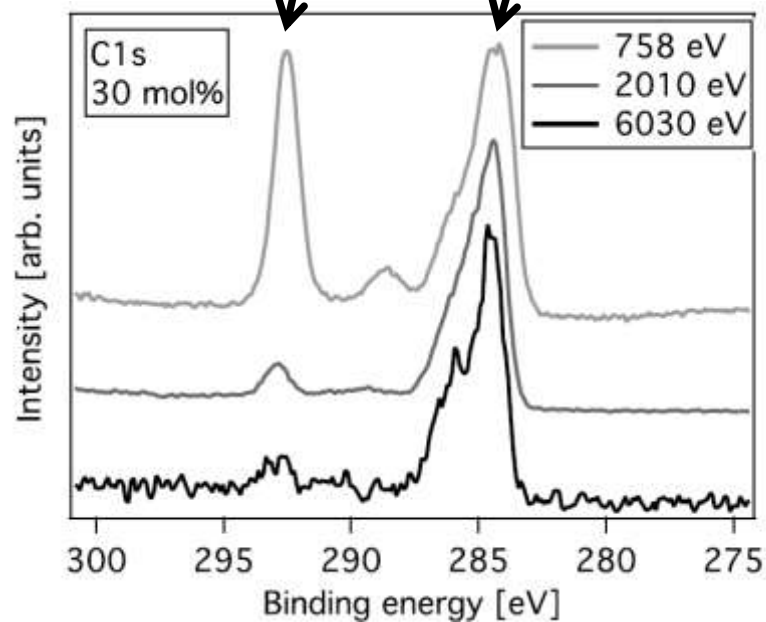
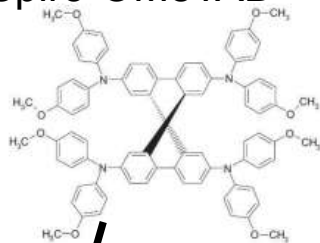
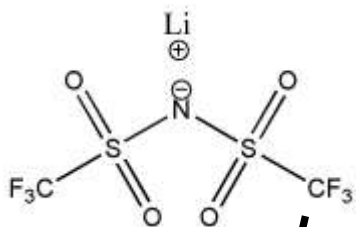
D35 on TiO_2

N1s



Some information on
surface configuration

Spiro-OMeTAD



Li-TFSI

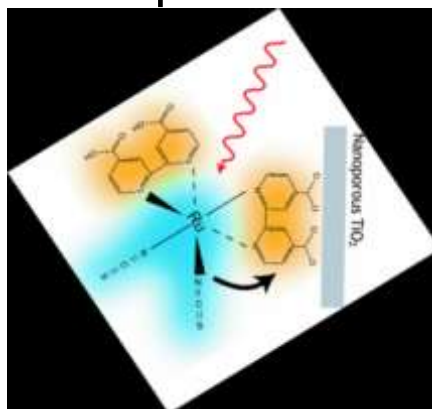
 $10\mu\text{m}^*$



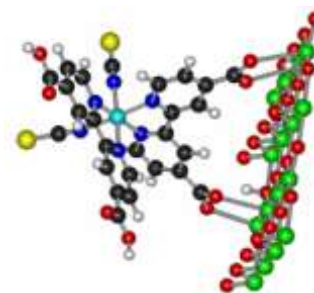
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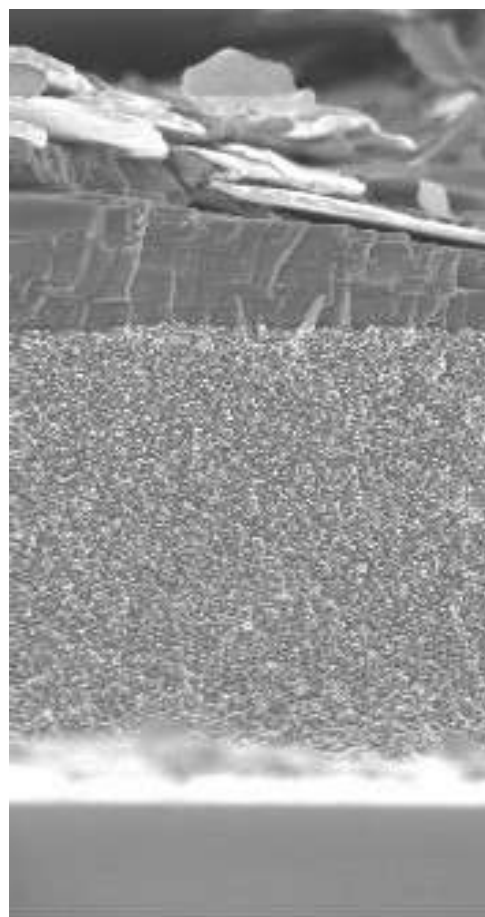
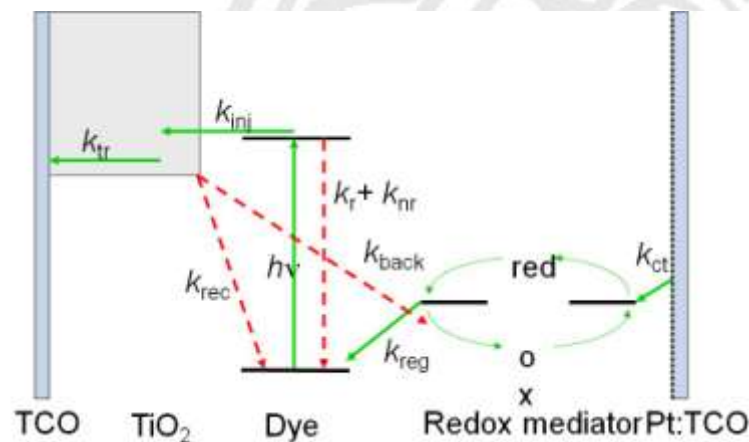
Molecular orbital Composition



Interfacial structure



Energy Matching

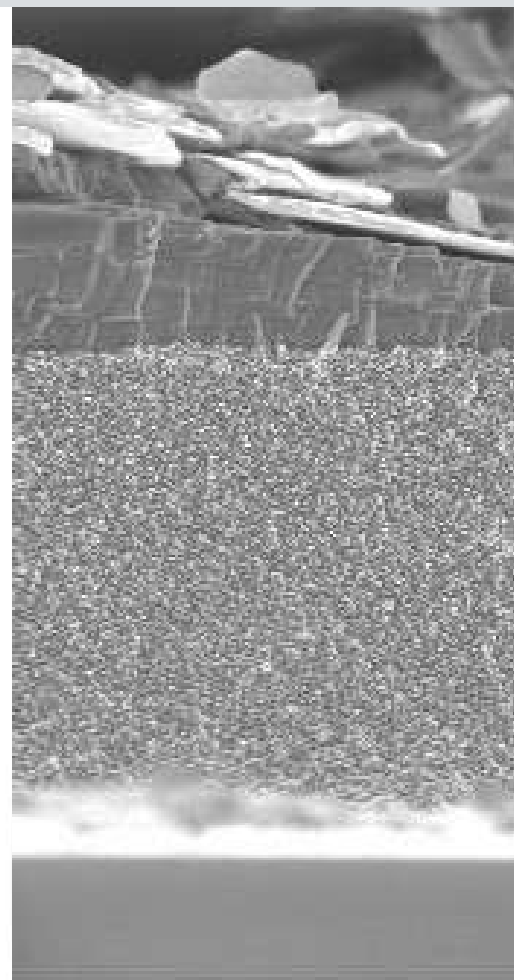
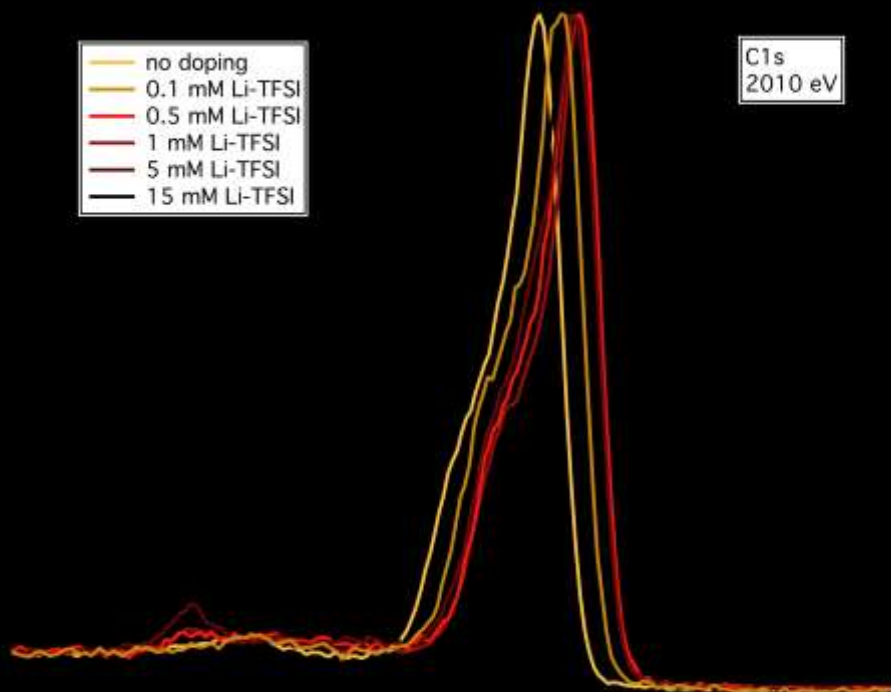
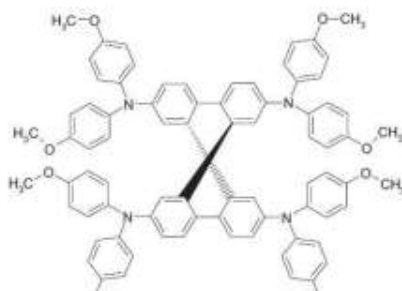
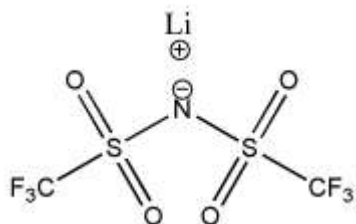


10 μm^*



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Spiro-OMeTAD - doping

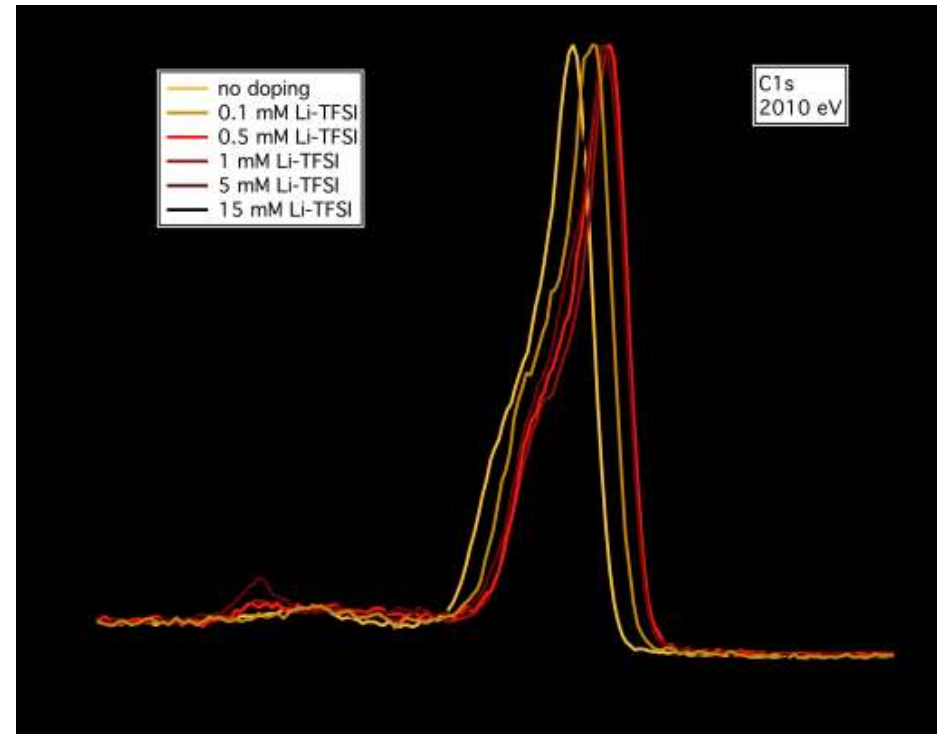
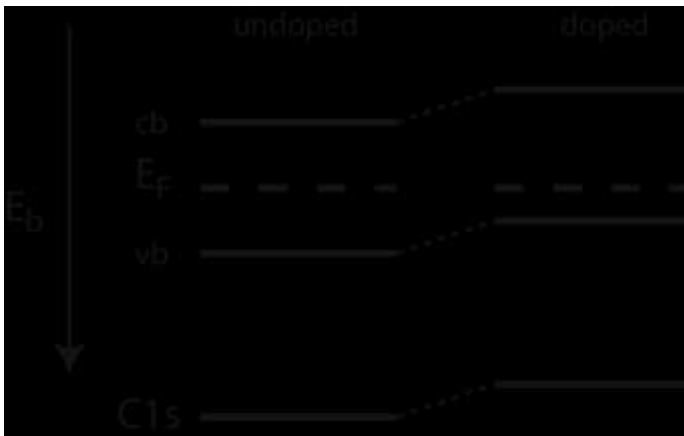


10 μm *



Spiro-OMeTAD - doping

- Doping – fermi level shift
- Shift up to 1 eV
(more doping doesn't give larger shift)

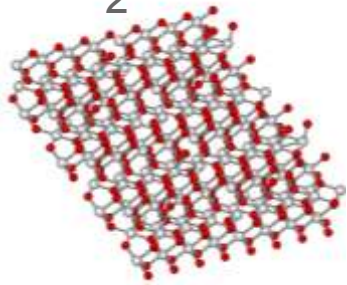




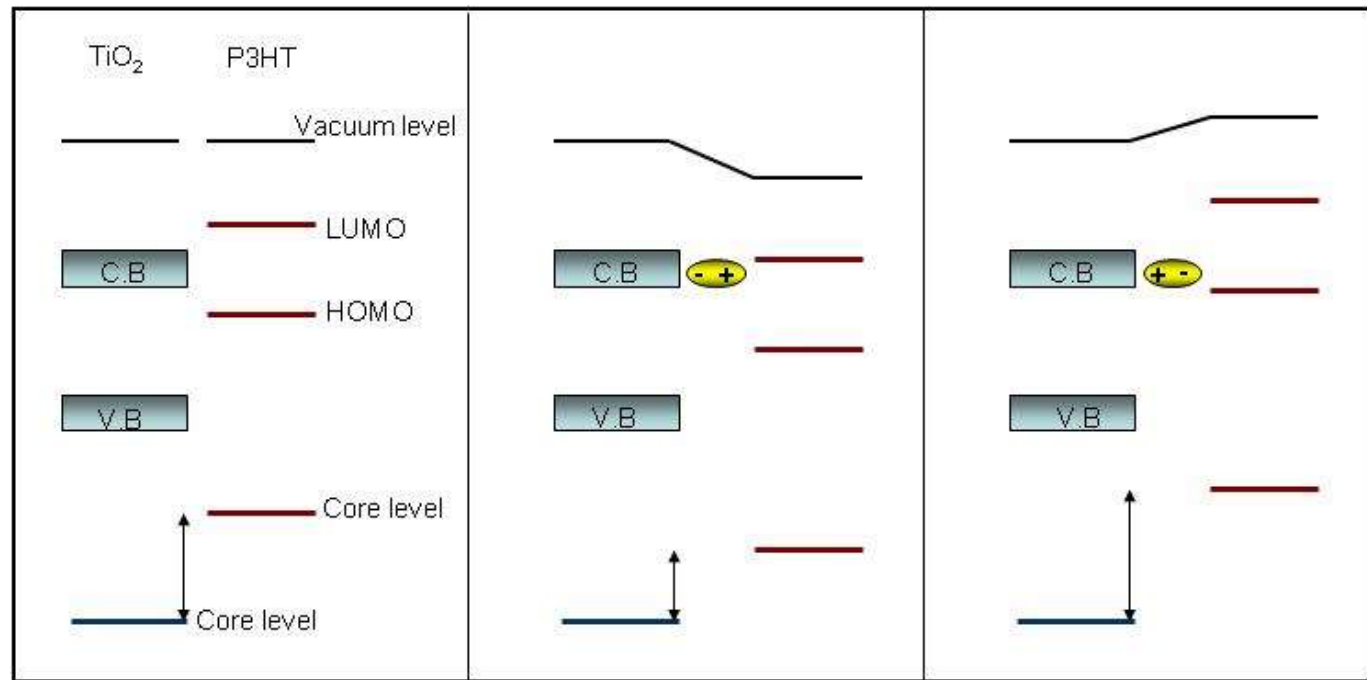
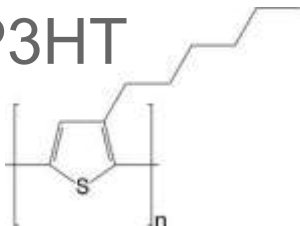
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Energy matching $\text{TiO}_2/\text{P3HT}$

TiO_2



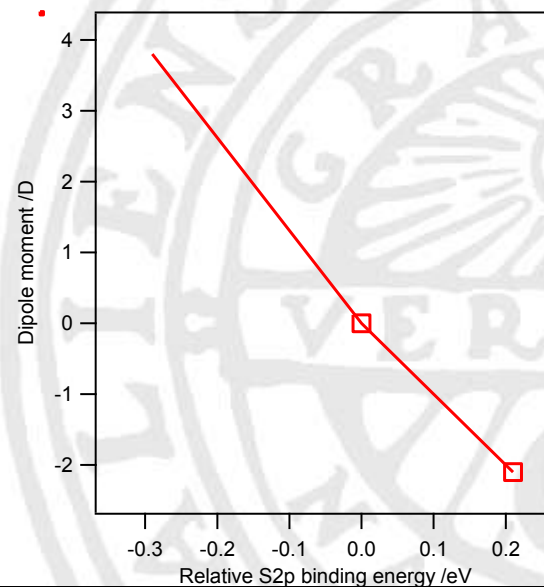
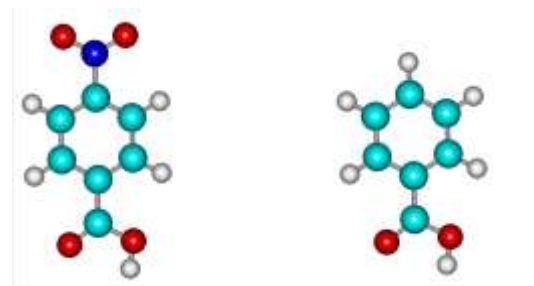
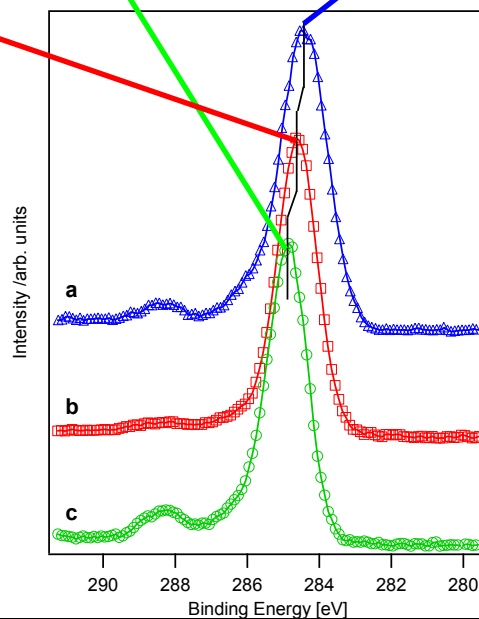
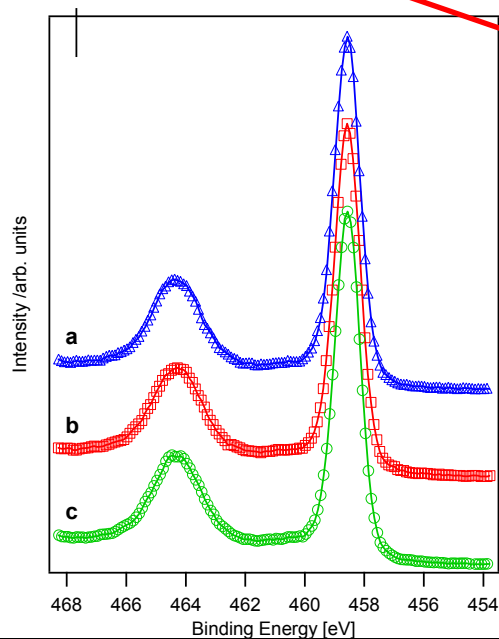
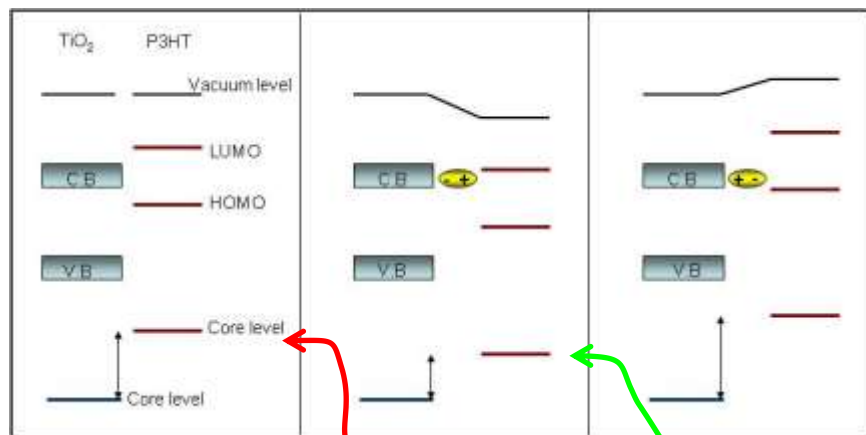
P3HT





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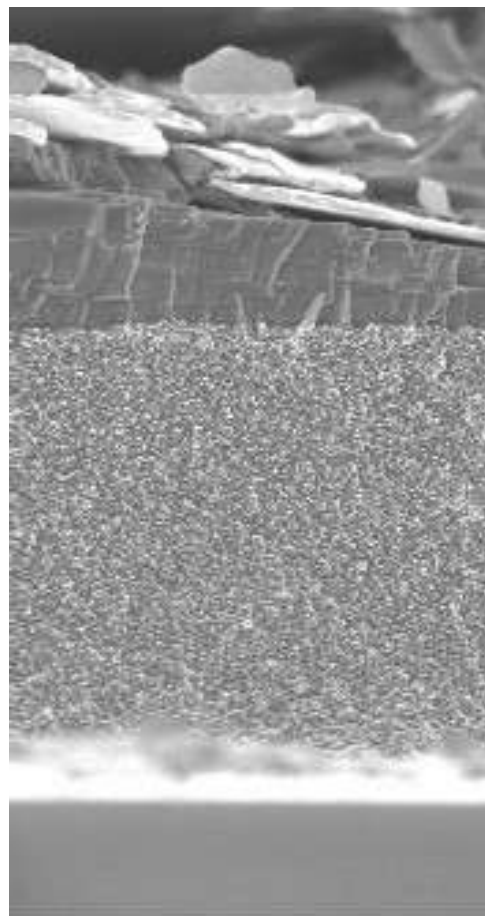
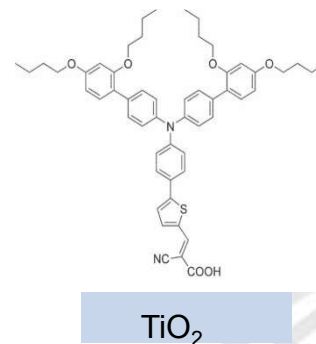
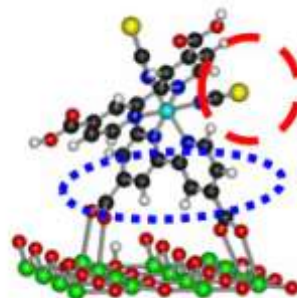
Energy matching $\text{TiO}_2/\text{P3HT}$



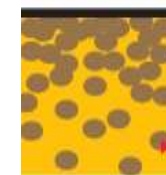
Summary

Solid-stat dye-sensitized solar cells

Molecular orbital Composition

 $10\mu\text{m}^*$ 

Interfacial structure



Li-TFSI

Energy Matching

