GDR Meeting 2022

RECENT PROGRESS IN THE DEVELOPMENT OF ECO-FRIENDLY PROCESSED ORGANIC SOLAR CELLS: EXPERIMENTS AND THEORY

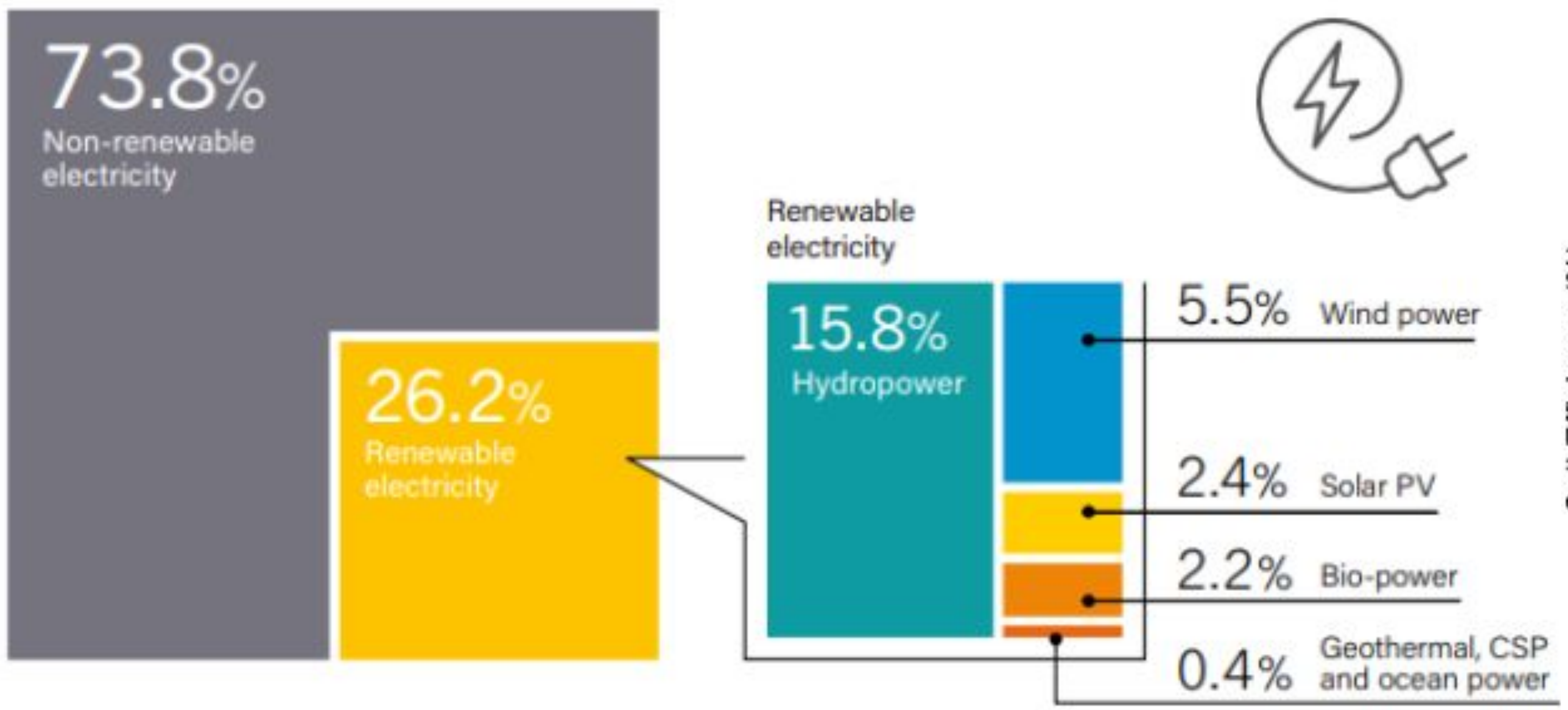
Wilken Aldair Misael

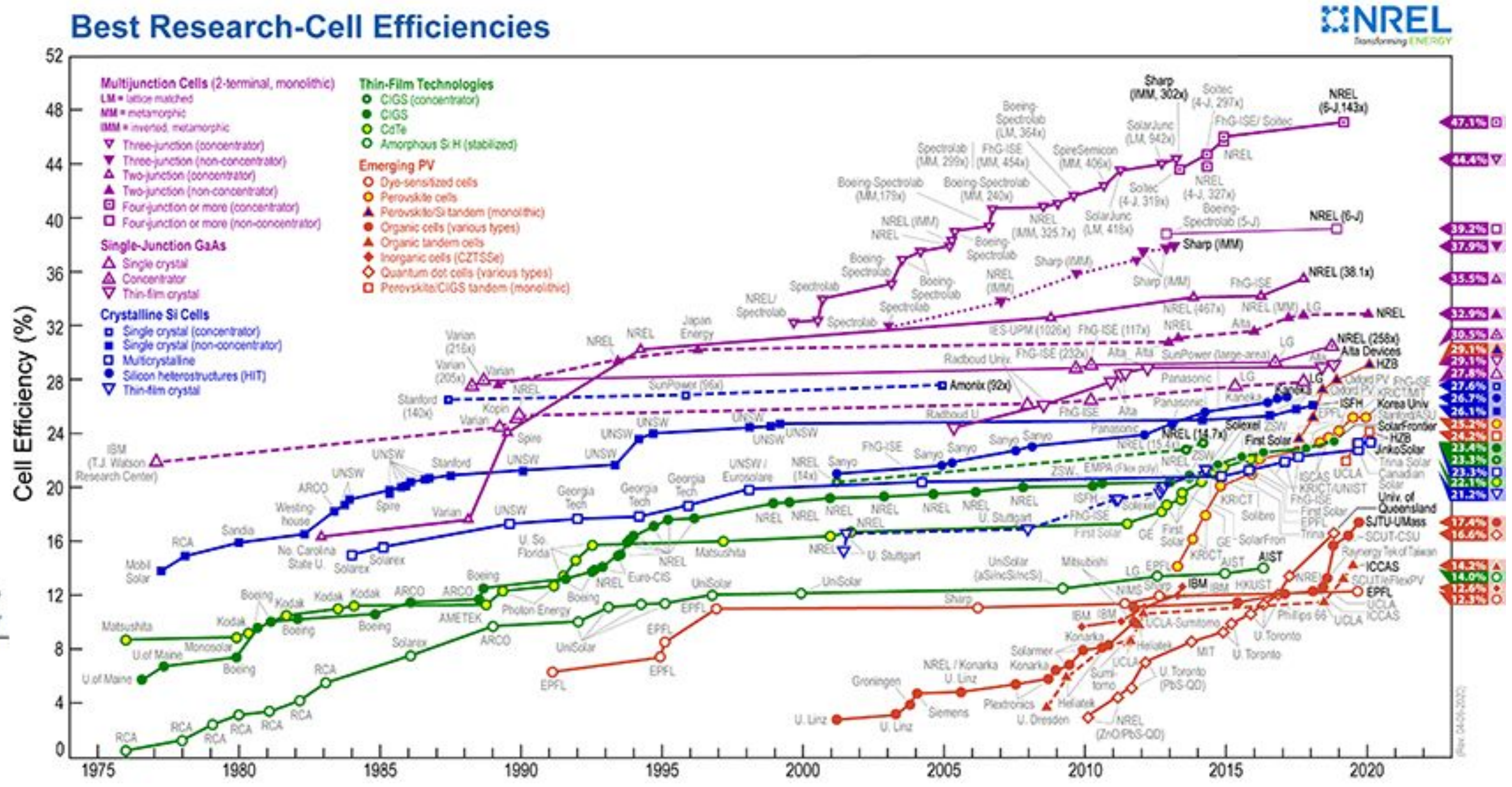
Université de Lille, France

OUTLINE

- **The Big Picture: Energy Demand & Challenges to Renewable Solutions**
- Organic Molecules and Polymers for Photovoltaic Applications
- Main Objectives
- X-ray Spectroscopies
- PTB7-Th Investigations
- ITIC Investigations
- PTB7-Th:ITIC Investigations
- Final Considerations and Future Perspectives

THE BIG PICTURE: ENERGY DEMAND & CHALLENGES TO RENEWABLE SOLUTIONS



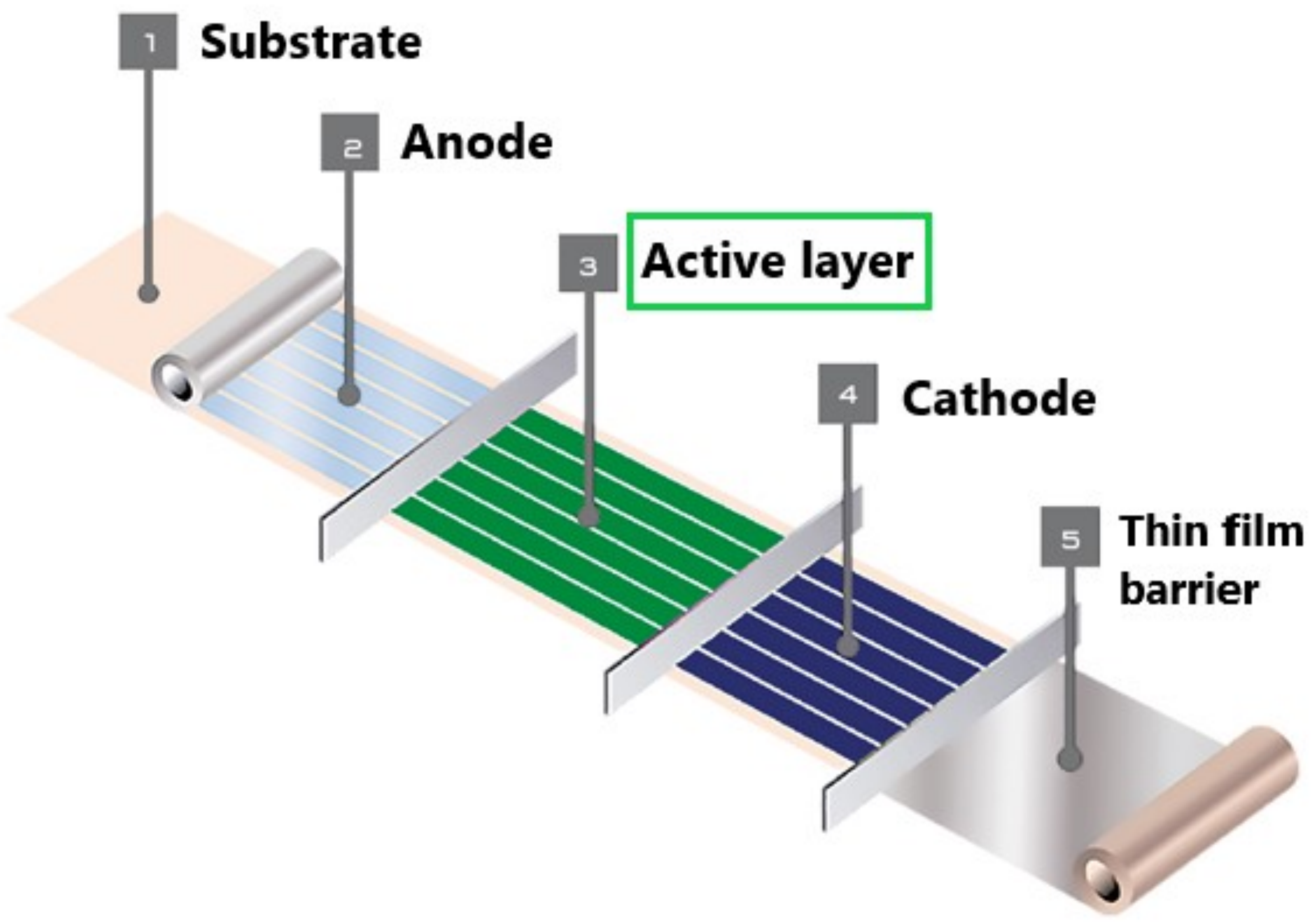


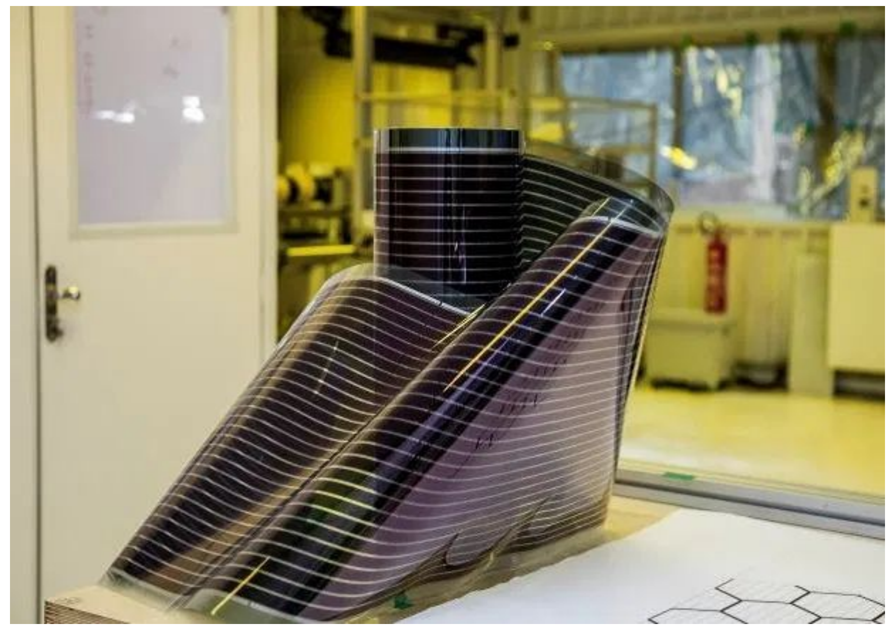
Extracted from *NREL, 2019.*

THE BIG PICTURE: ENERGY DEMAND & CHALLENGES TO RENEWABLE SOLUTIONS

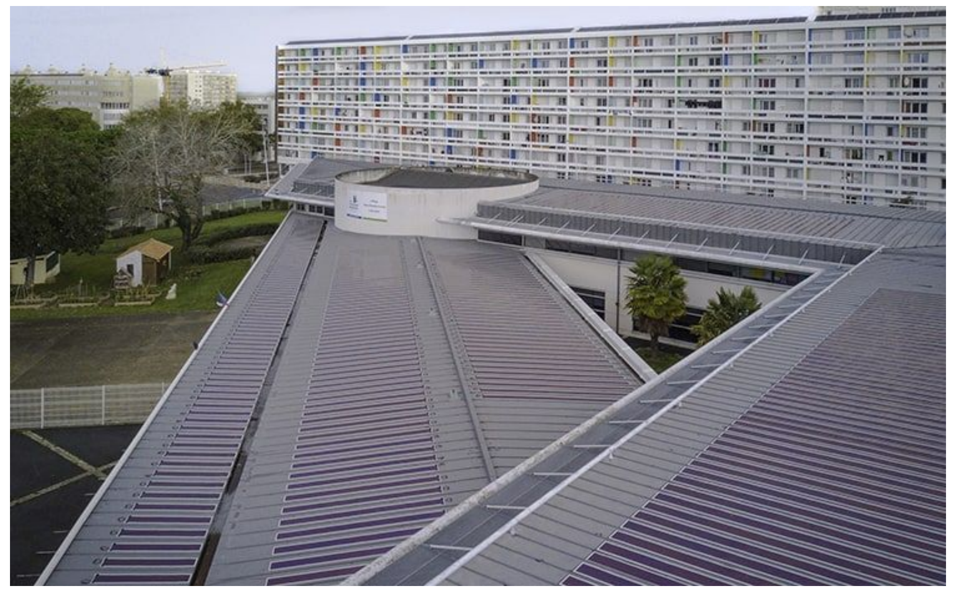
- **ORGANIC SOLAR CELLS (OSC)**

Over the past two decades OSC has been a subject widely explored due to the characteristics of their components.





Extracted from CSEM Brasil®



Extracted from Heliatek®

Extracted from SUNEW®

OUTLINE

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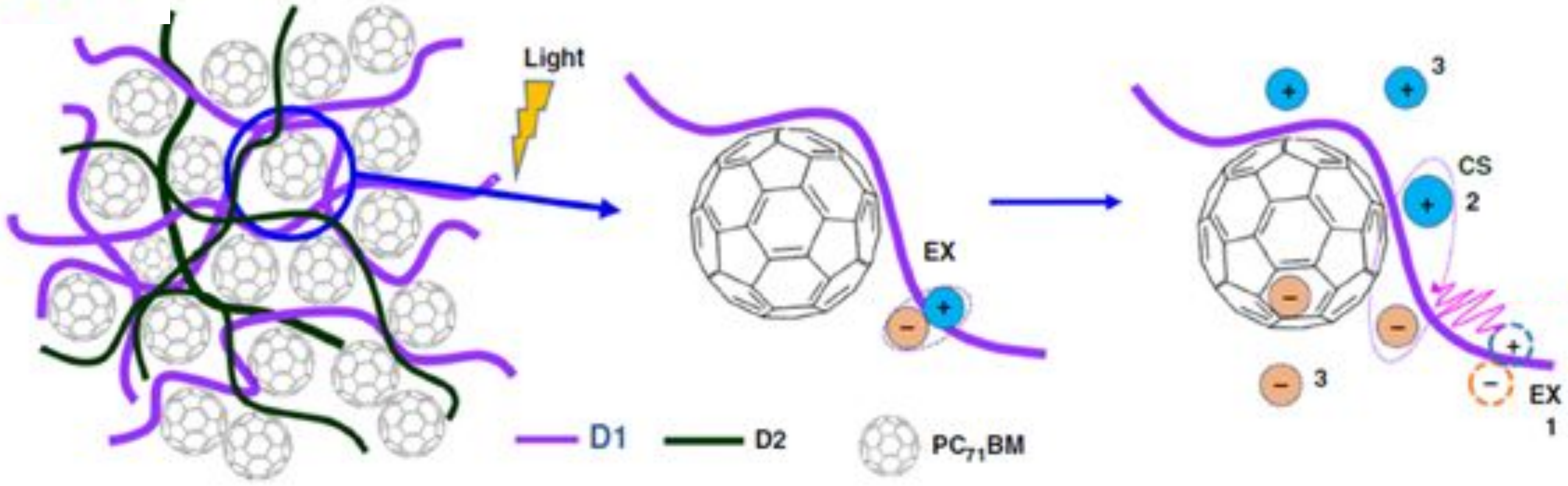
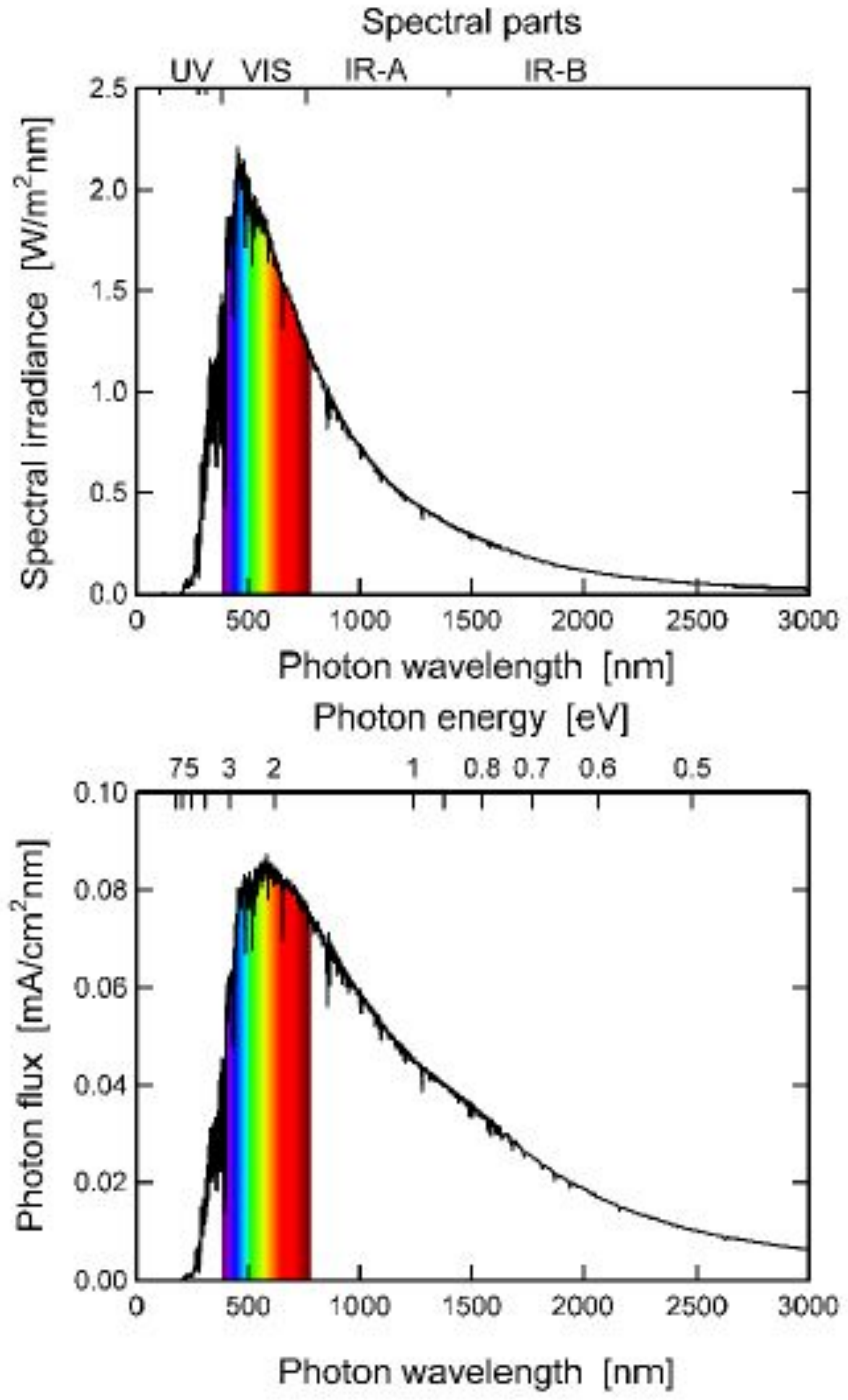
ORGANIC MOLECULES AND POLYMERS FOR PHOTOVOLTAIC APPLICATIONS

Why the allignment of the energy levels is important?

Generation of charges - an interface phenomena

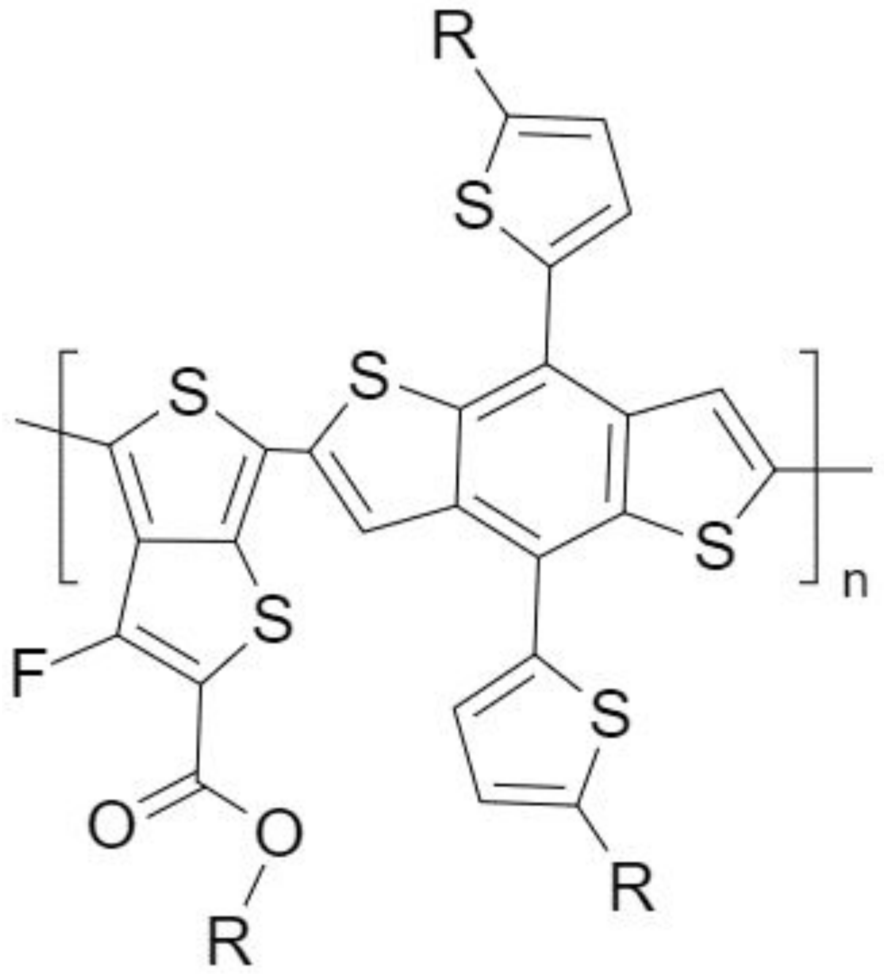


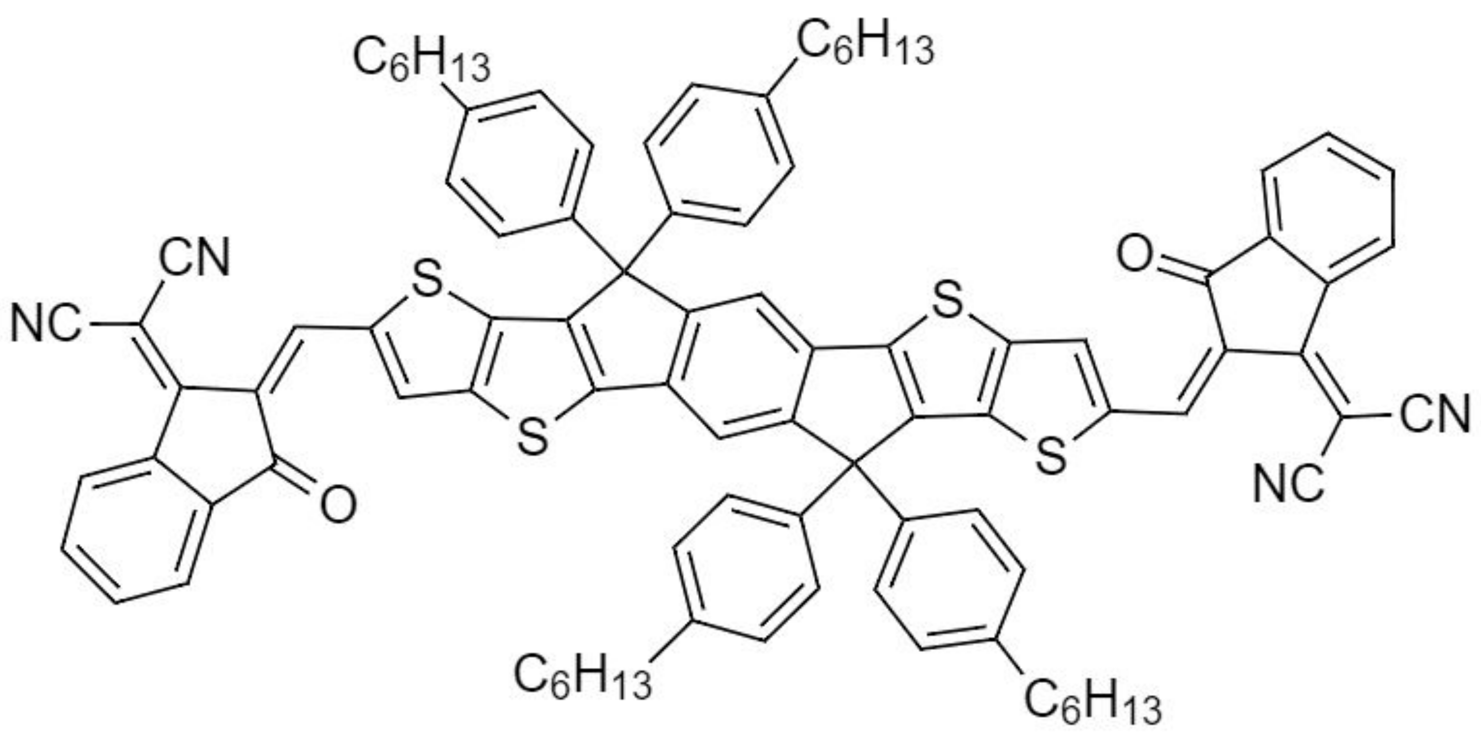
Extracted from Bronstein et. al., 2020.

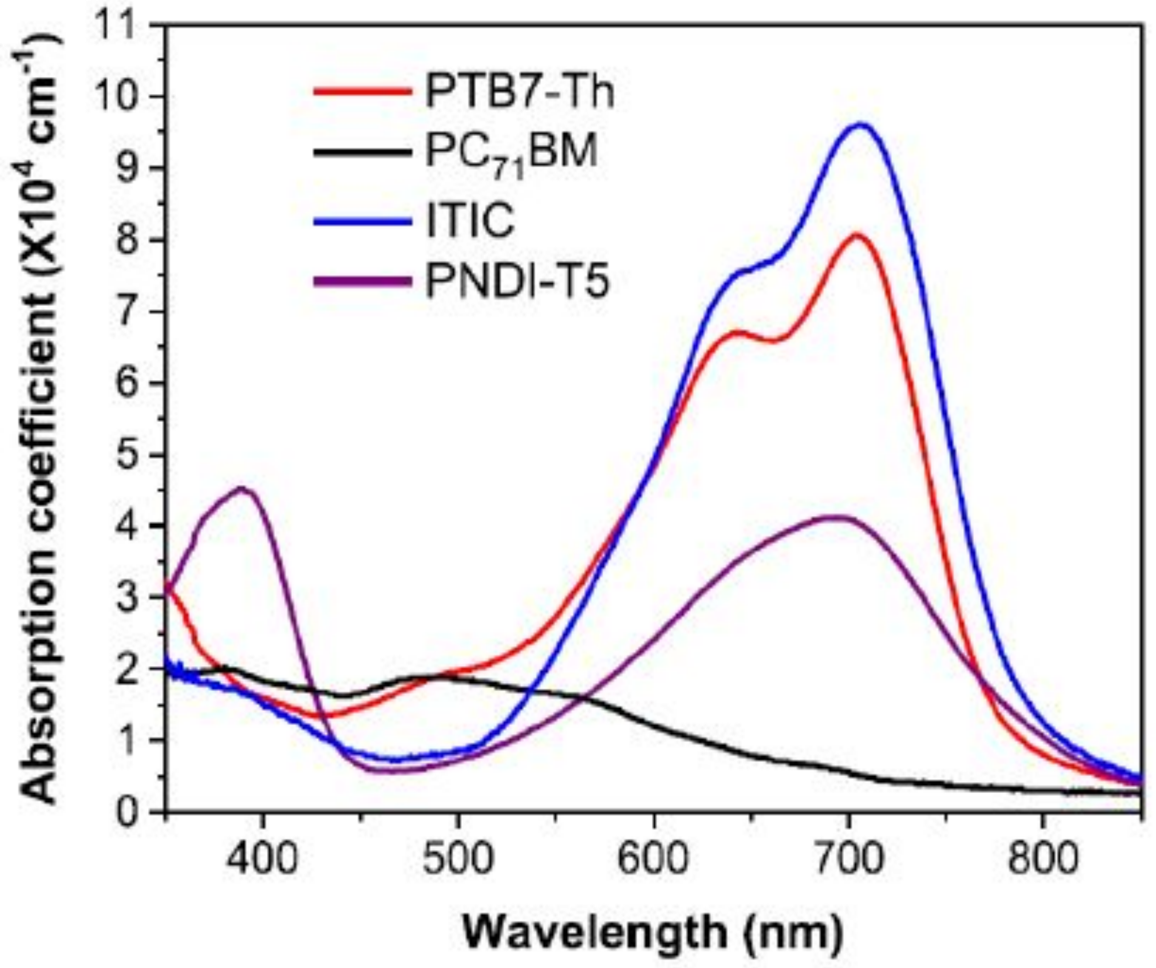


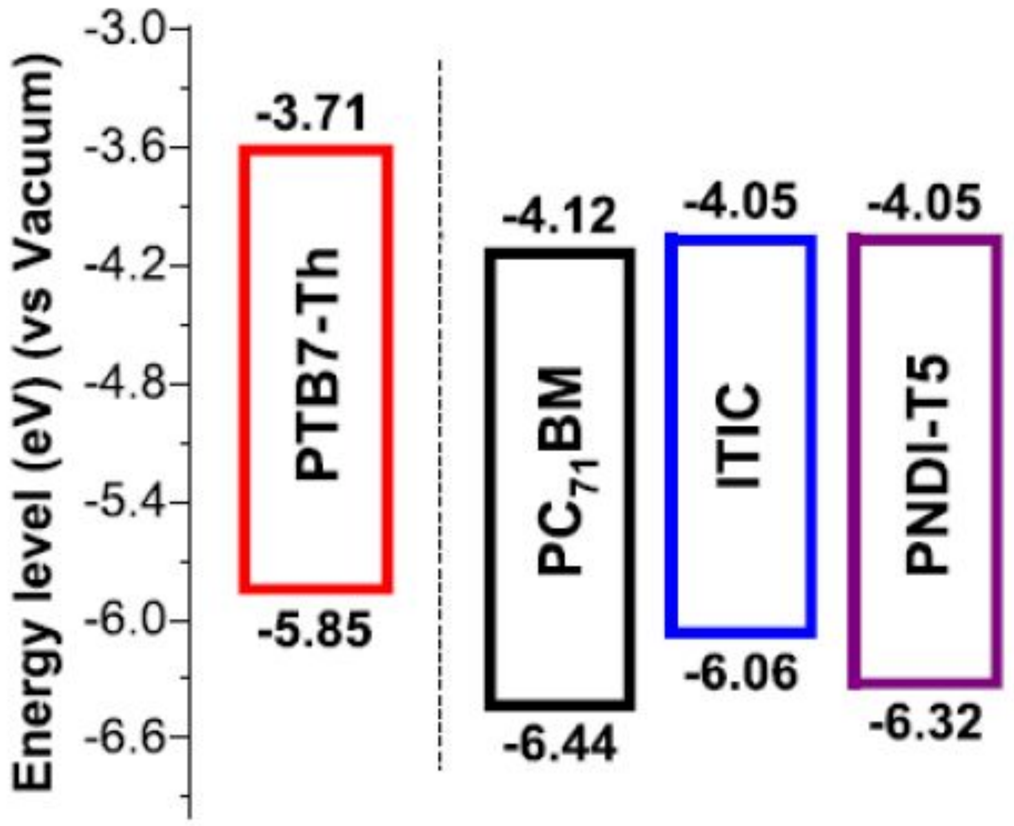
ORGANIC MOLECULES AND POLYMERS FOR PHOTOVOLTAIC APPLICATIONS

Why these two components are broadly used?







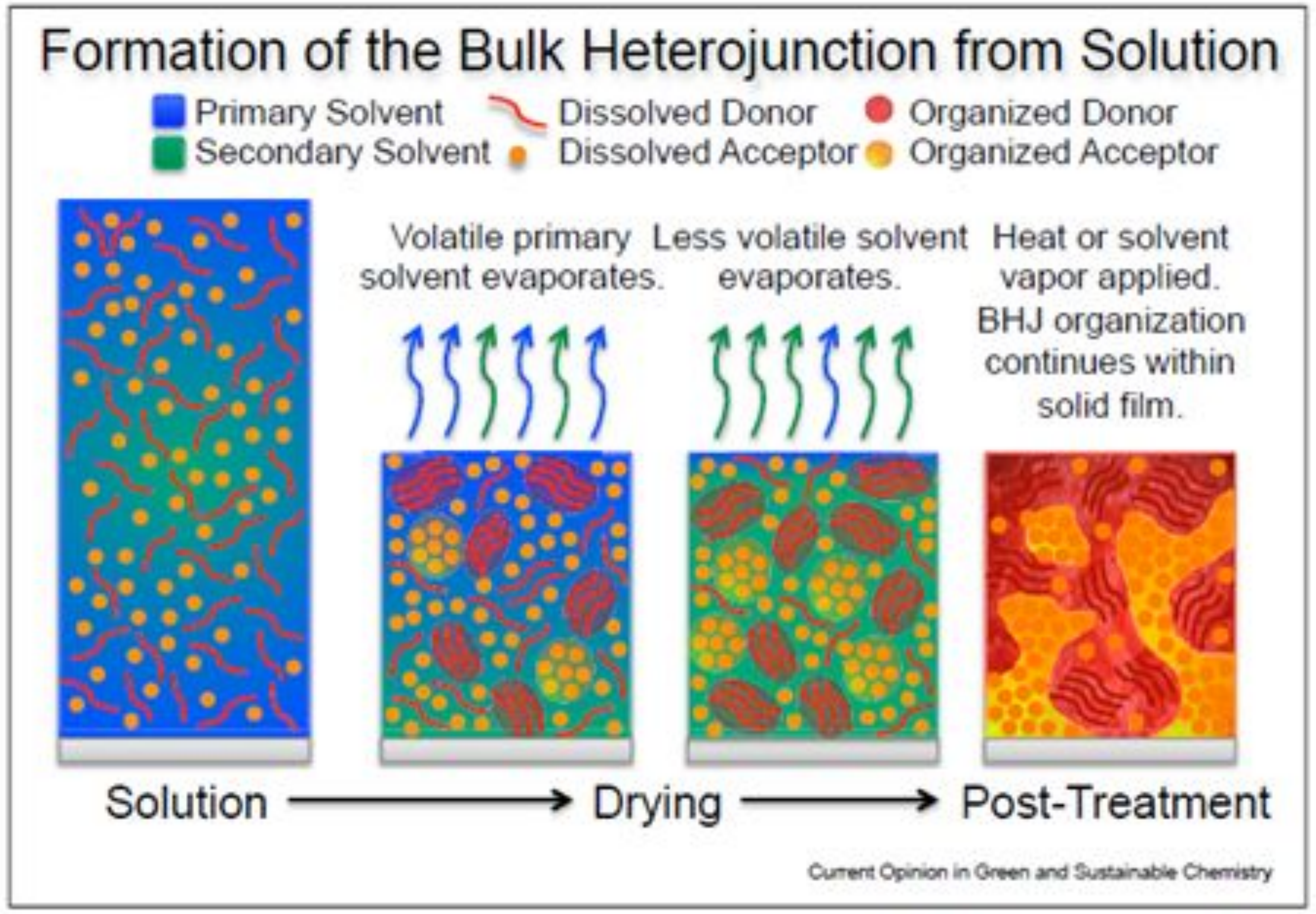


Donor: PTB7-Th

Acceptor: ITIC

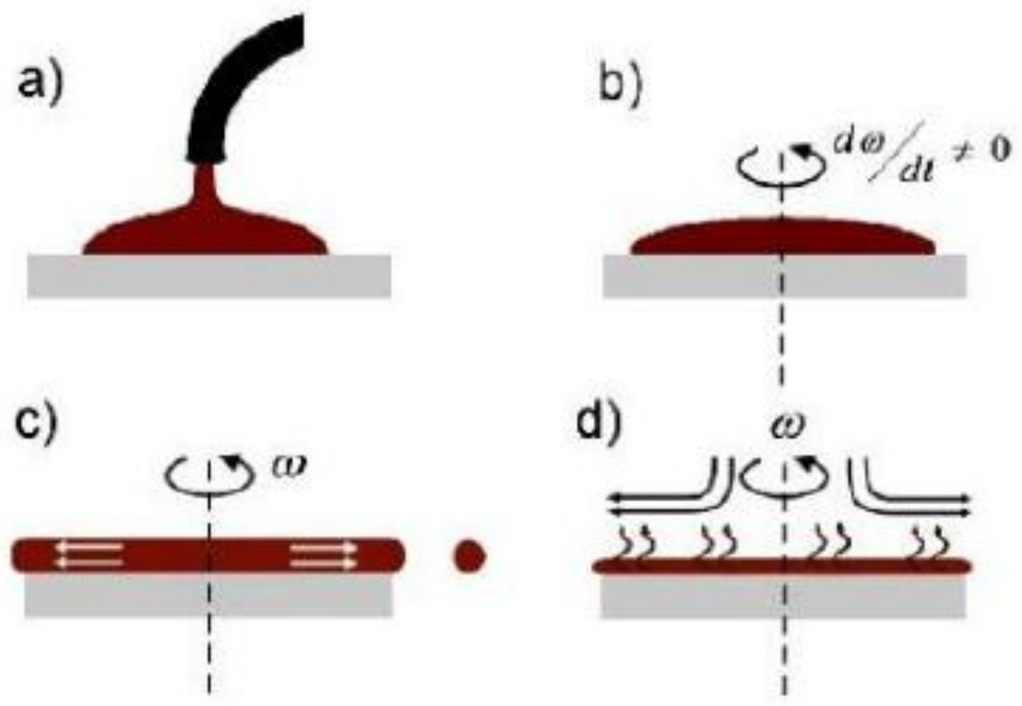
ORGANIC MOLECULES AND POLYMERS FOR PHOTOVOLTAIC APPLICATIONS

- **Processement**

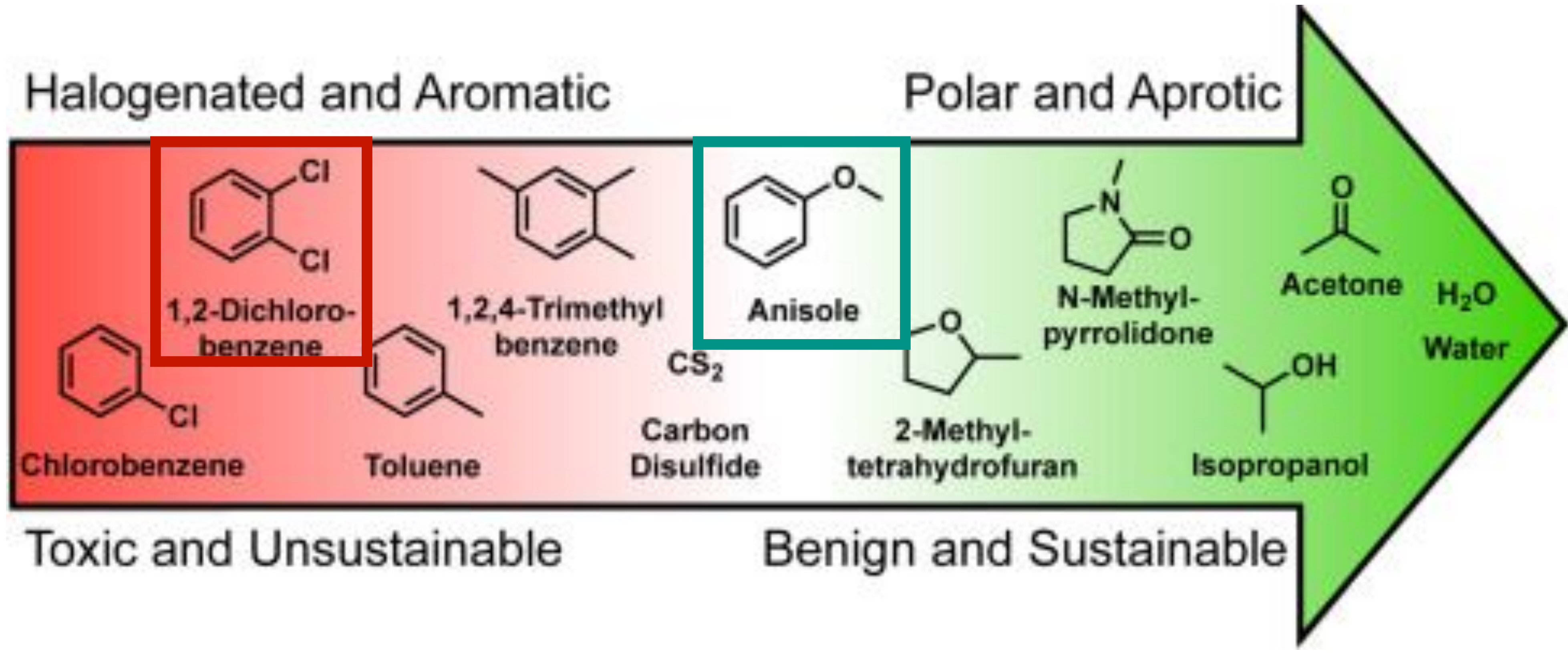


Extracted from McDowell and Bazan, 2017.

Thin film formation by Spin Coating



Solvent choice



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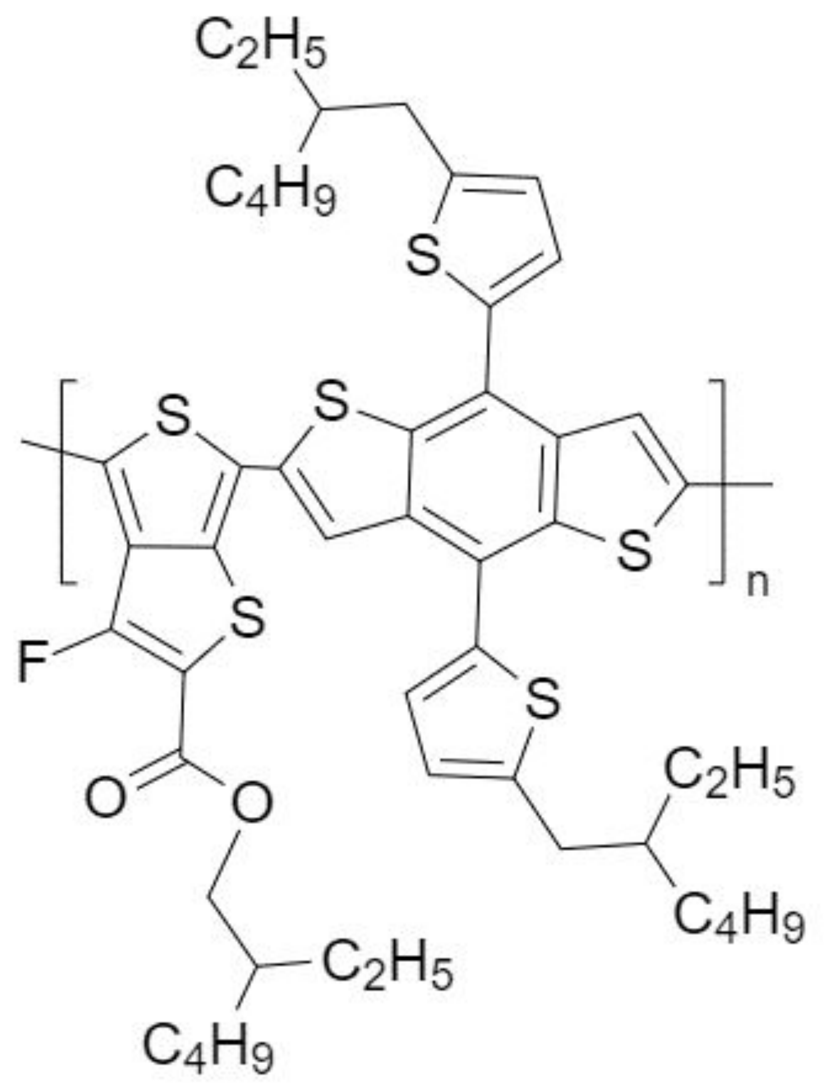
MAIN OBJECTIVES

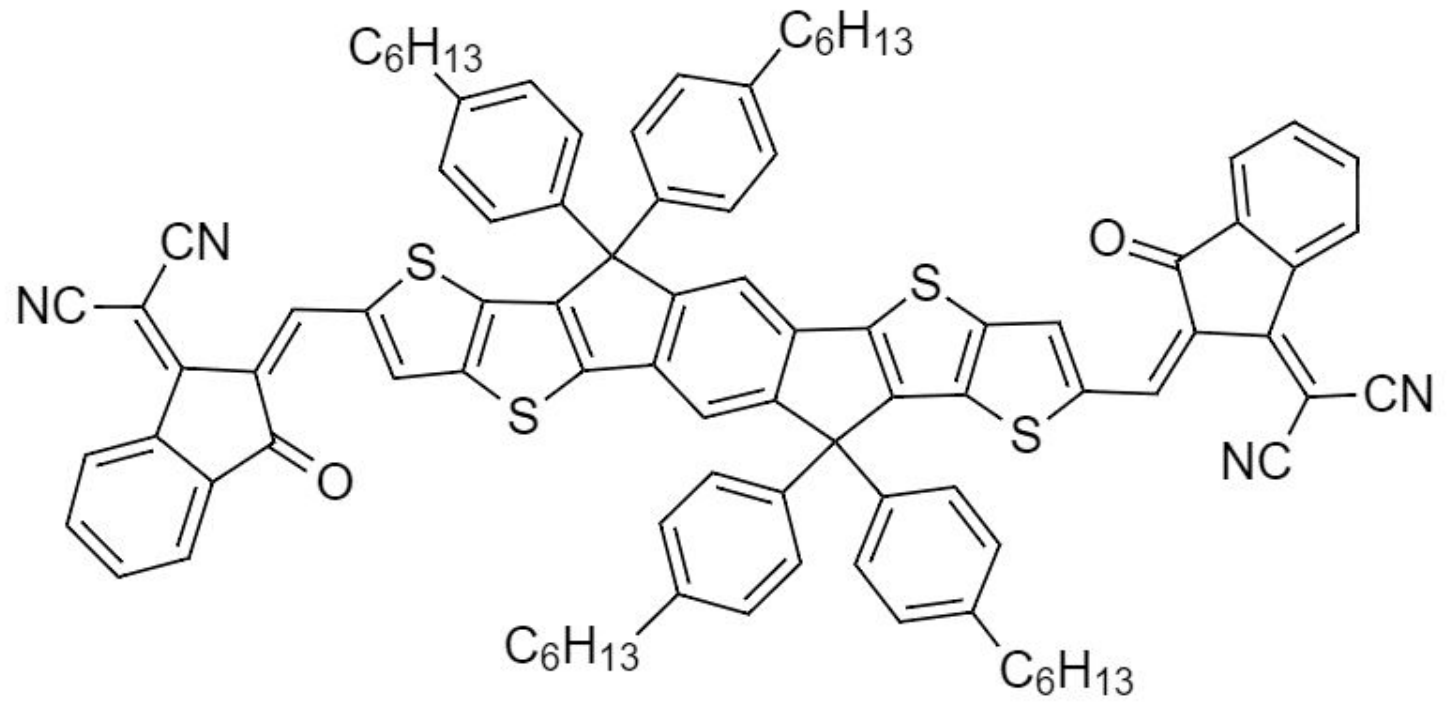
- **PTB7-Th and ITIC**

Evaluate the behaviour of the polymeric and molecular films processed in a halogenic solvent **(o-DCB)** and an environmentally friendly solvent **(o-MA)** in terms of:

- **Molecular orientation** by Angle-Resolved Near Edge X-Ray Absorption Fine Structure (**NEXAFS**);



PTB7-Th



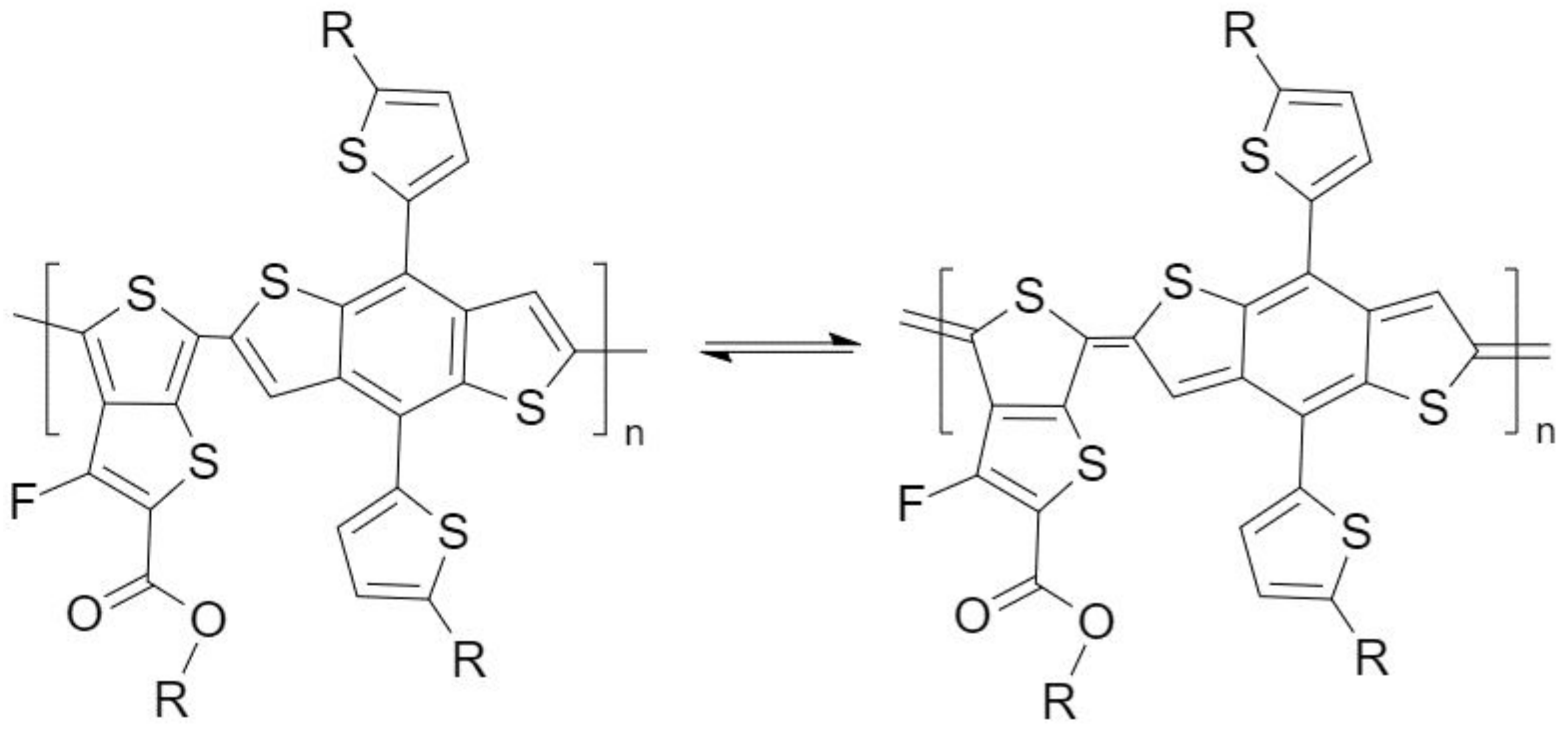
ITIC

MAIN OBJECTIVES

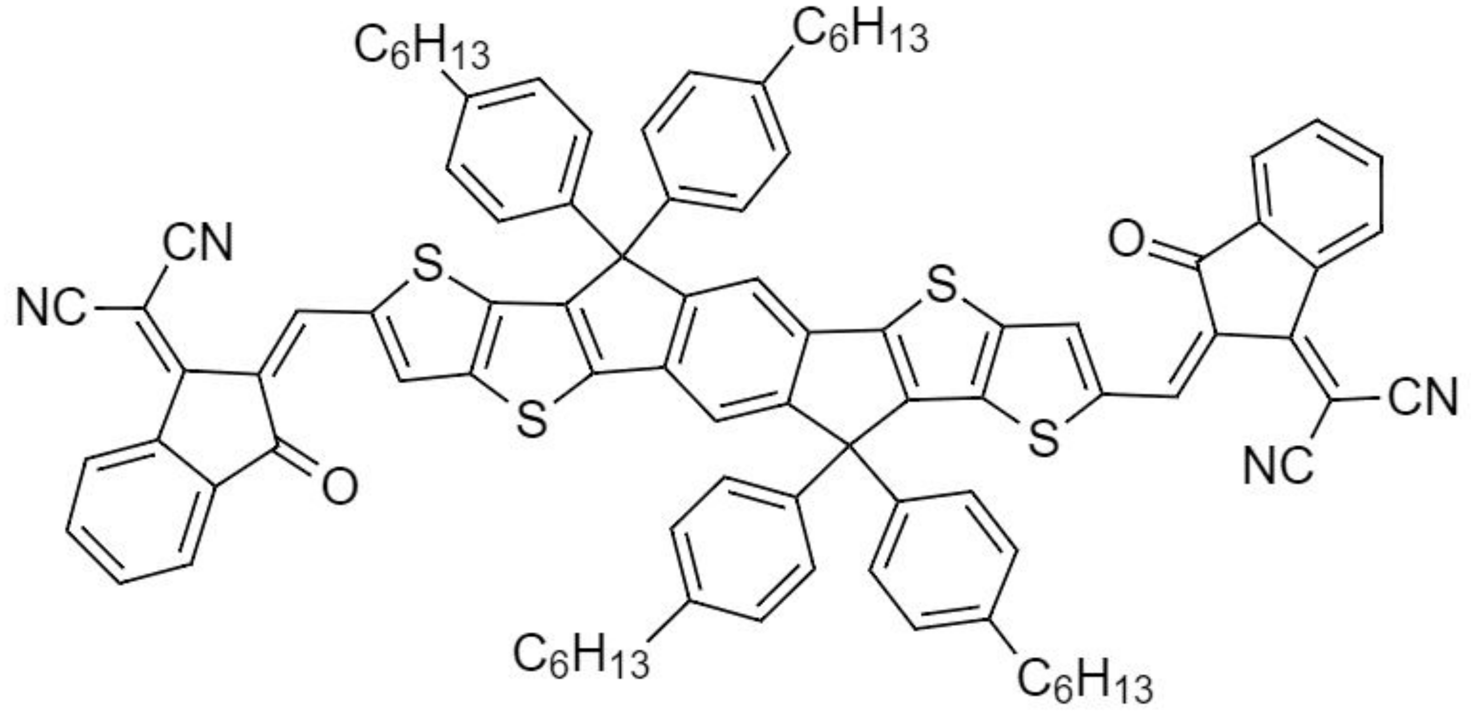
- **PTB7-Th and ITIC**

  - Obtain information about the **electronic structure** by means NBO analysis;

  - For PTB7-Th, obtain the HOMO-LUMO gap using the Donor/Acceptor approach and the Aromatic/Quinoidal approach;



The aromatic and quinoid forms of PTB7-Th



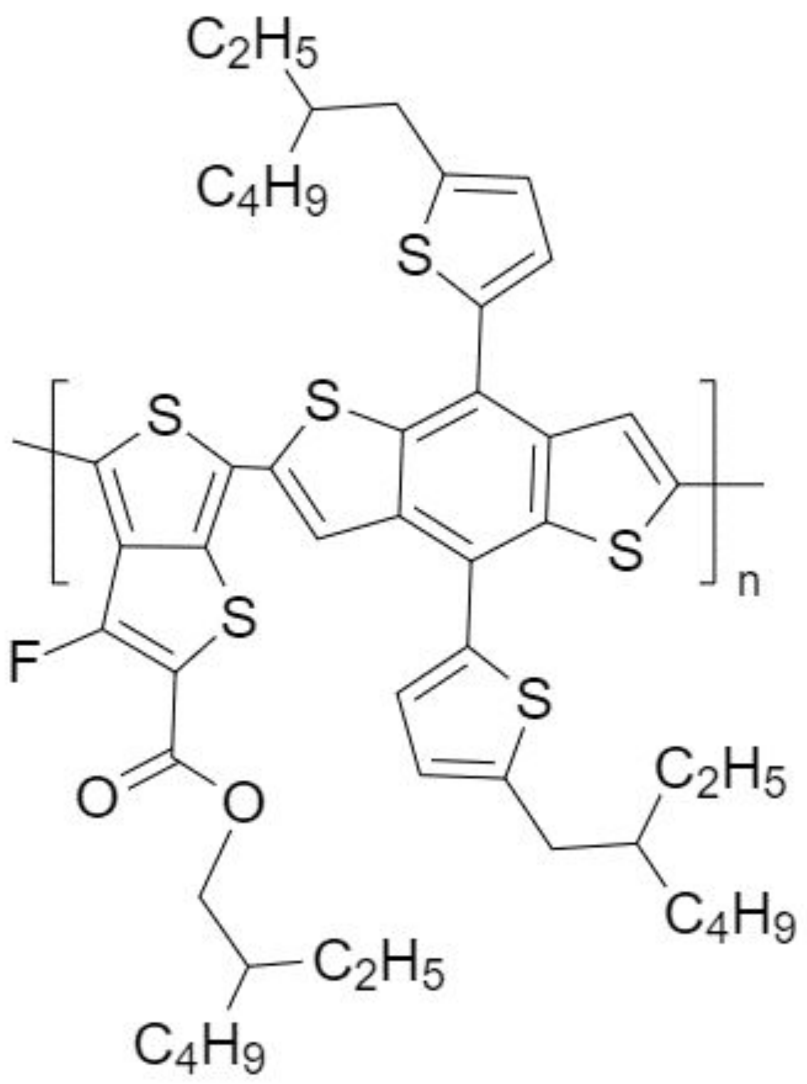
ITIC

MAIN OBJECTIVES

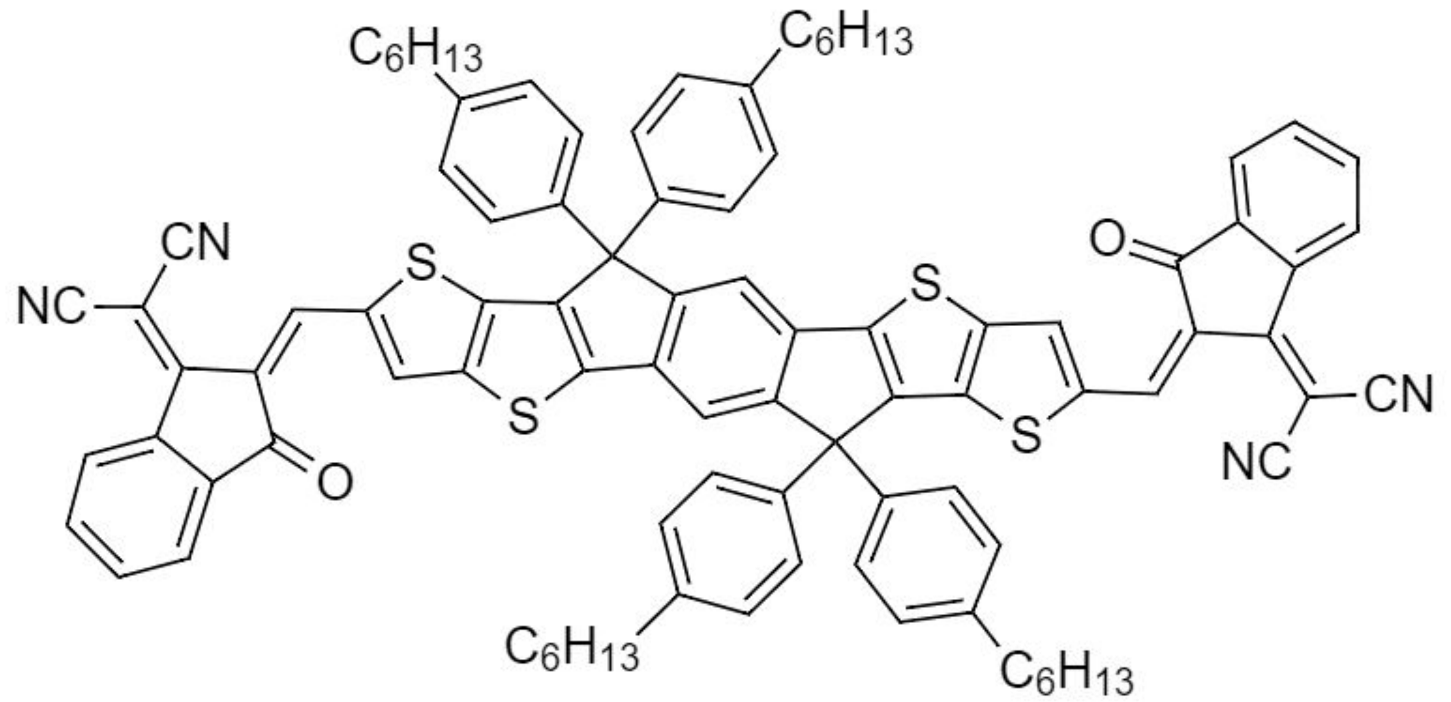
- **PTB7-Th:ITIC blend**

Evaluate the behaviour of the films processed in **o-DCB** and **o-MA** at **different temperatures** (RT, 100°C, 200°C), using the same techniques to answer:

- Does the blend film suffer significant morphological changes when a not conventional solvent is used?
- What is the influence of the annealing process in these properties?
- **In detriment of the values of charge transfer achieved, is it possible to**



PTB7-Th



ITIC

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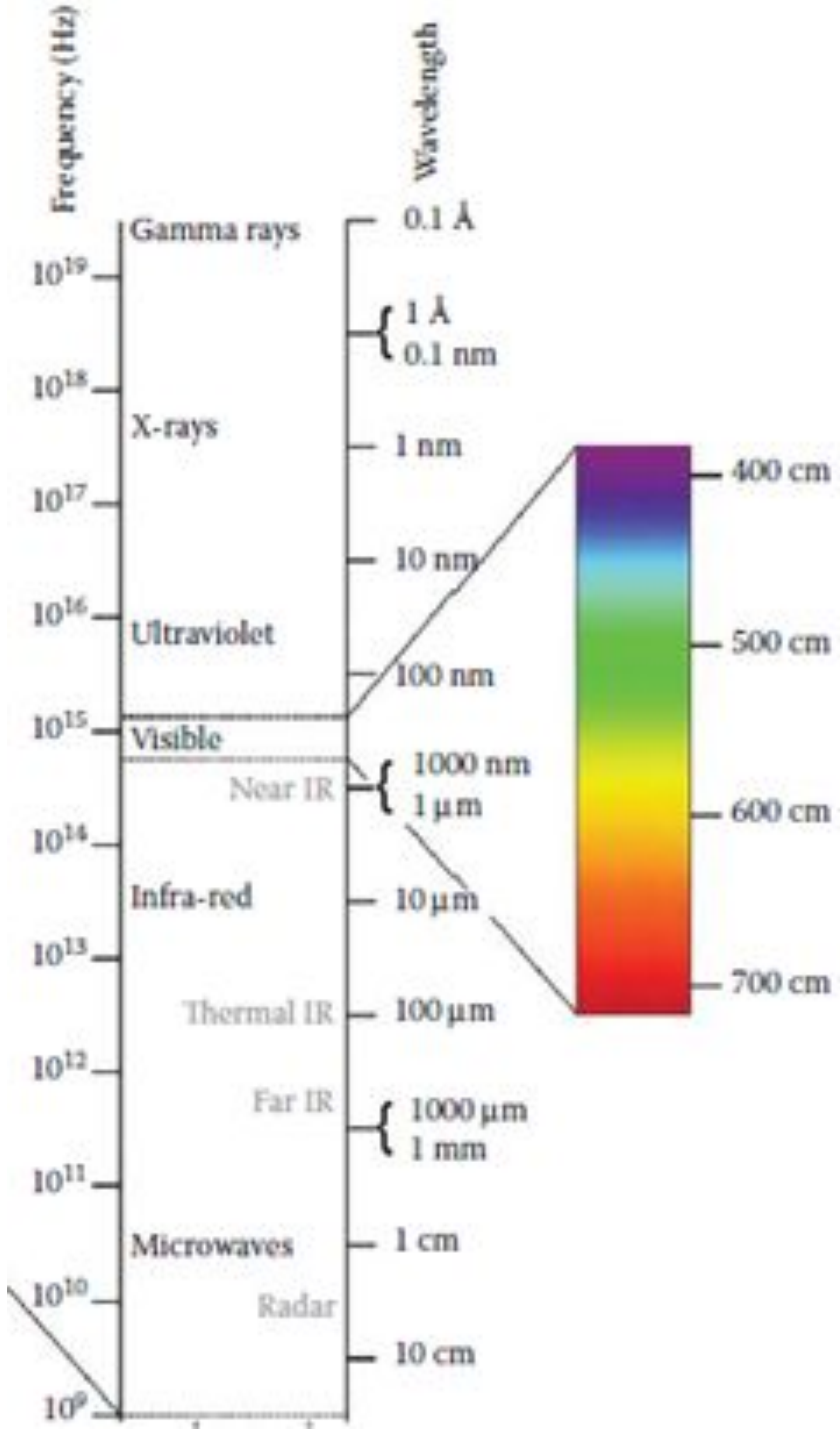
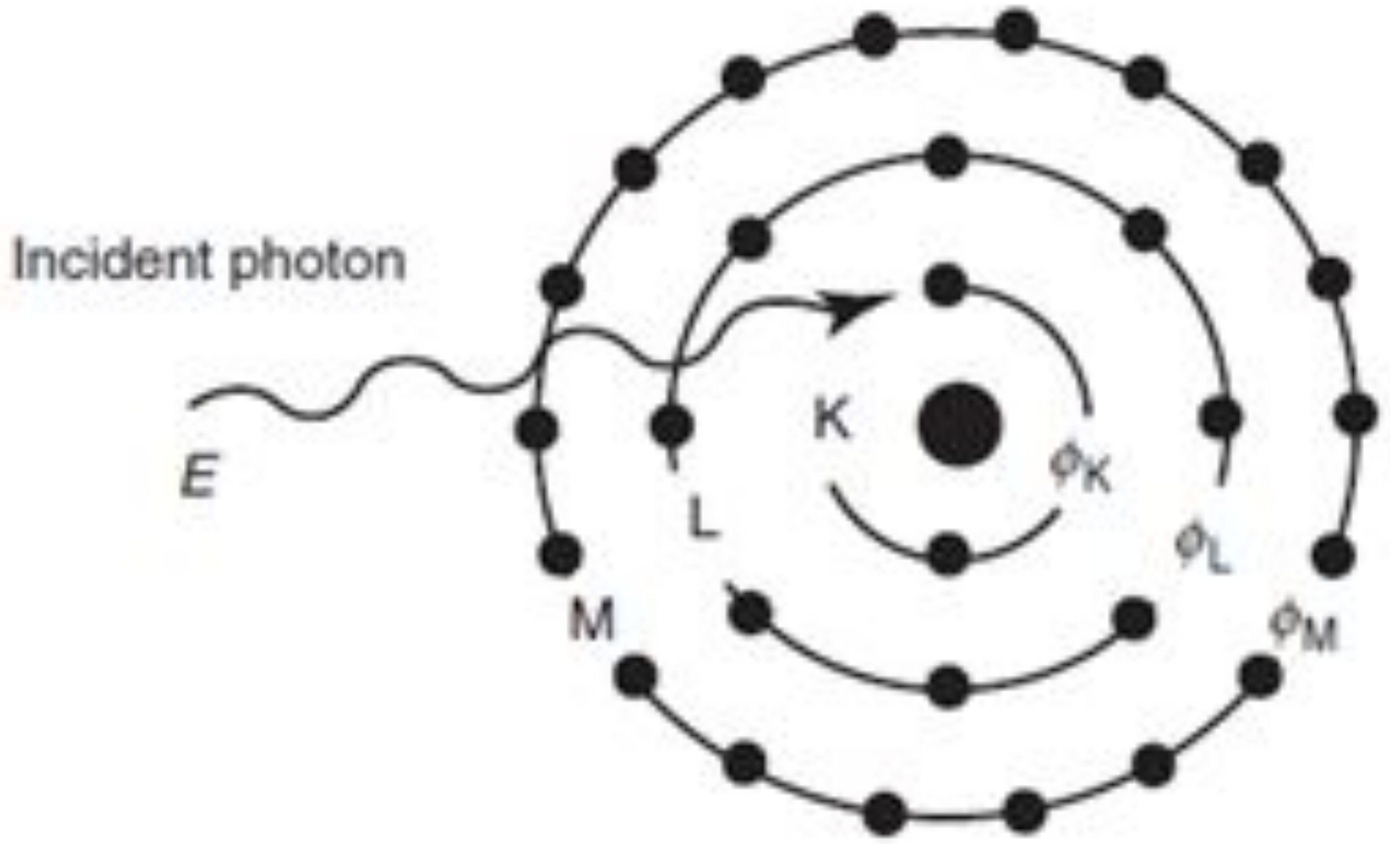
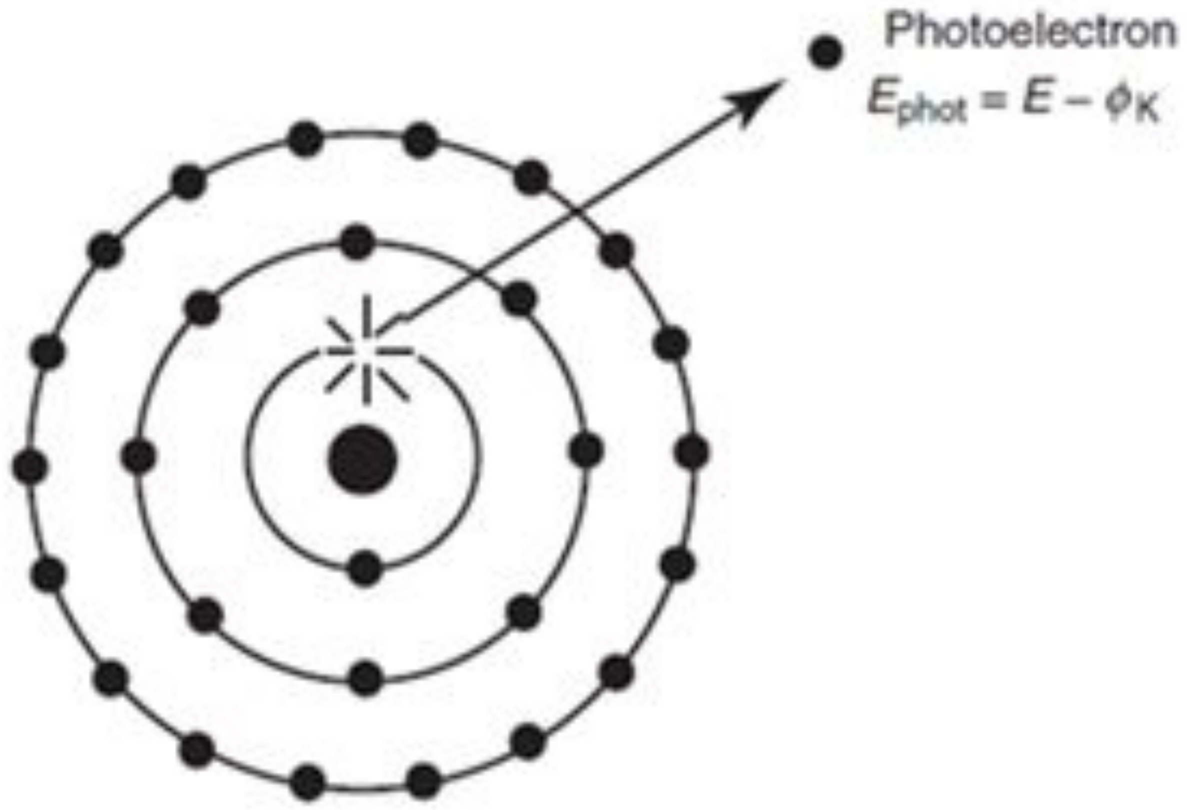
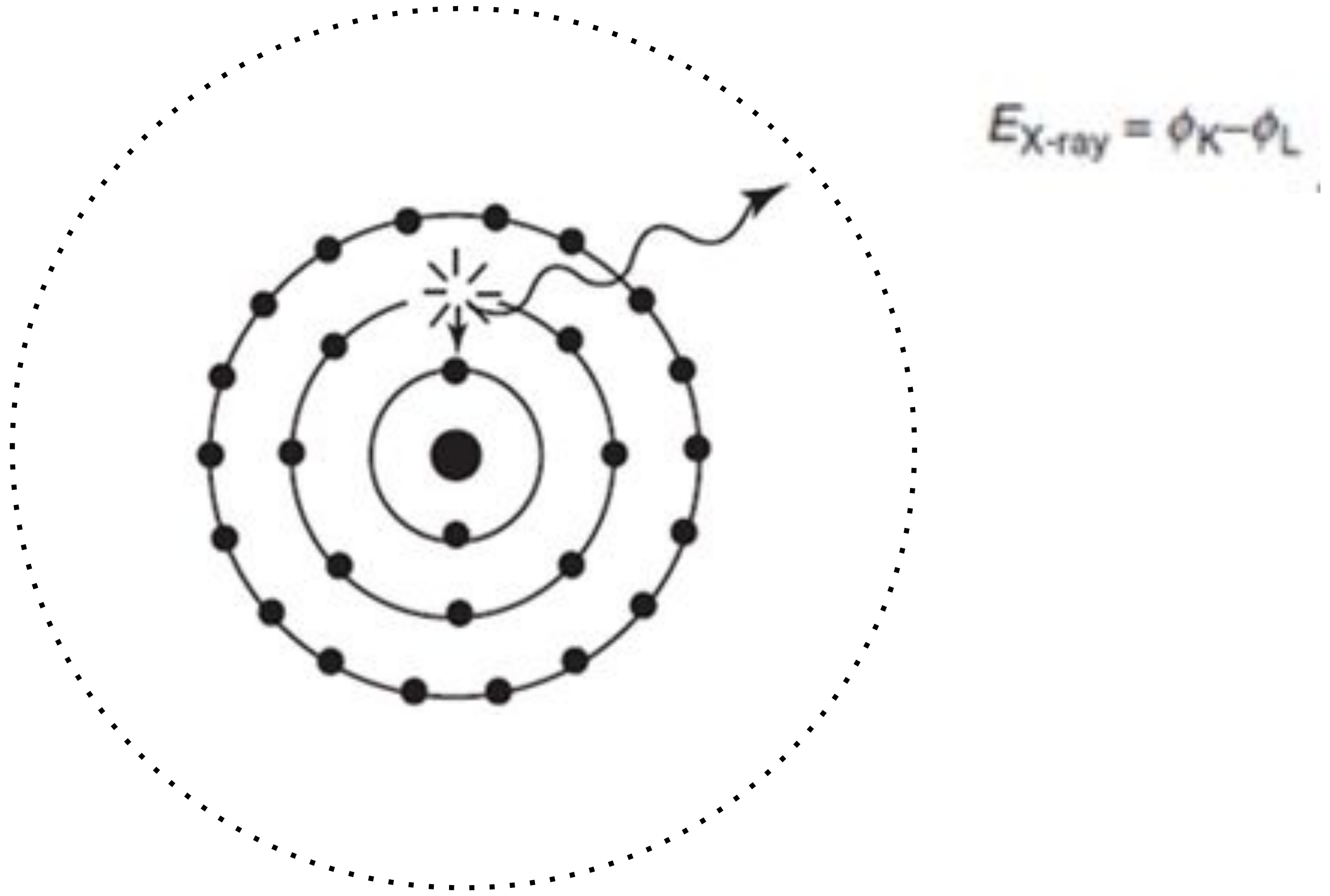
X-RAYS ABSORPTION PROCESSES







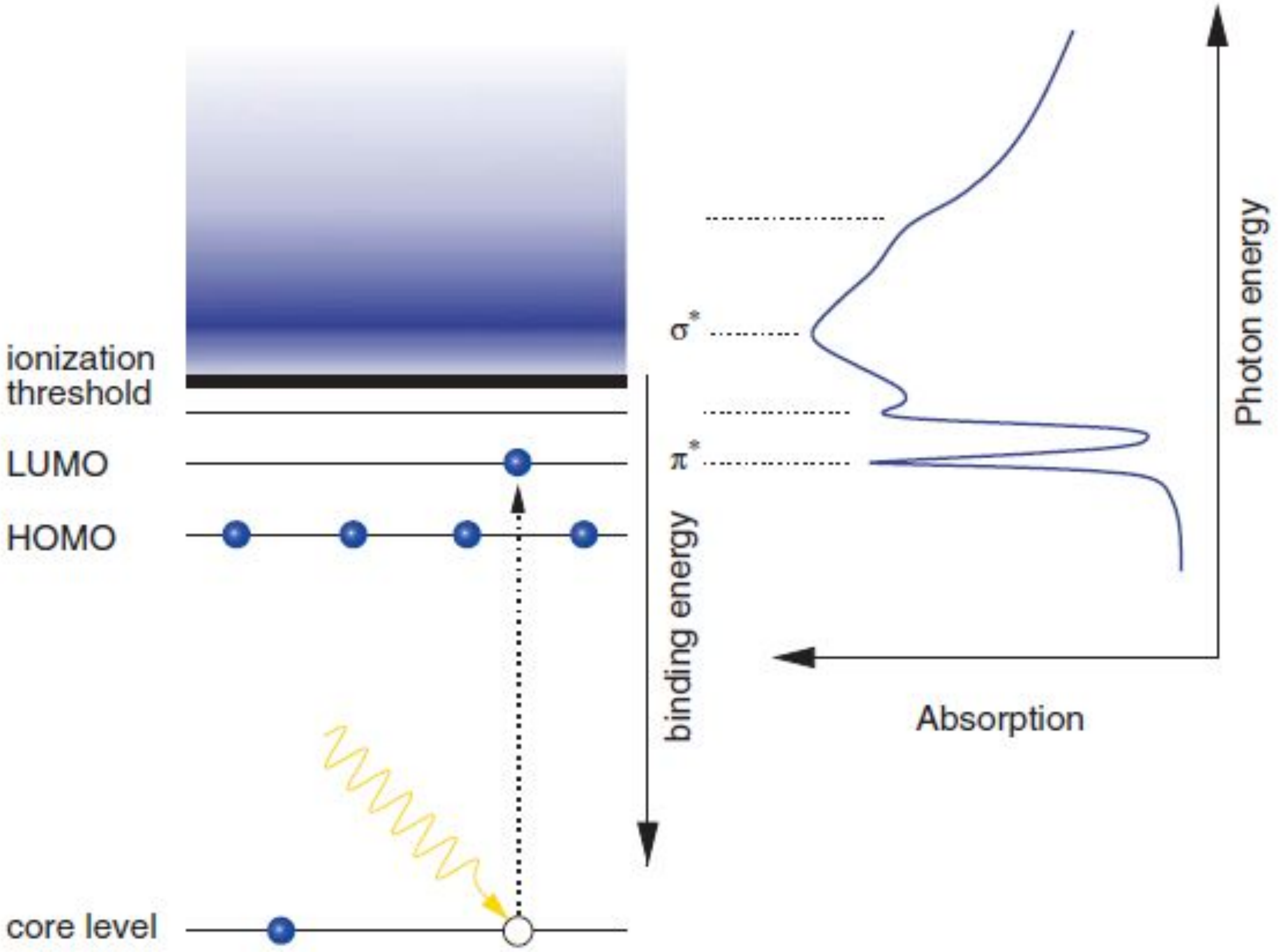
Non-Radiative processes



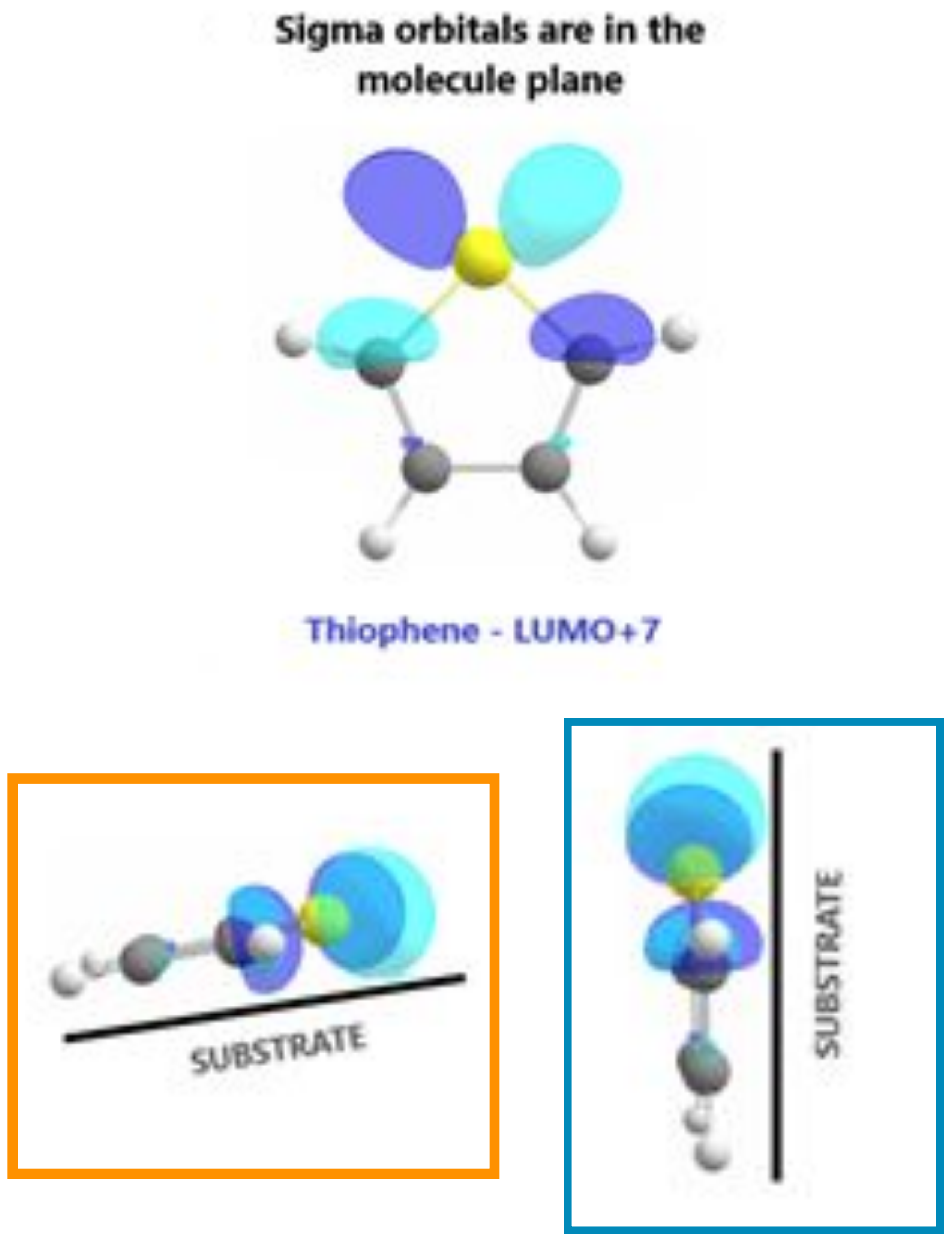
Radiative processes

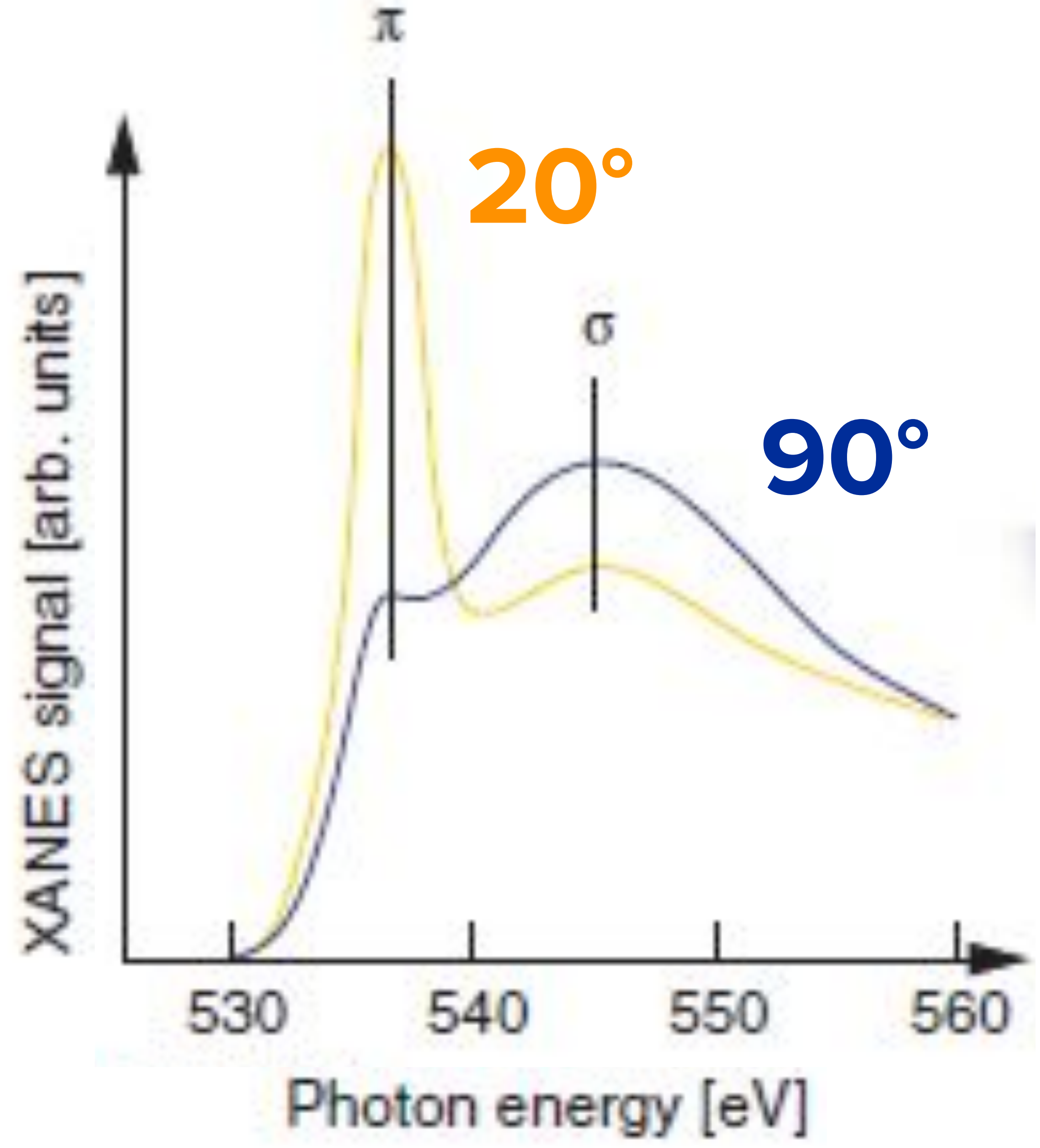
MOLECULAR ORIENTATION BY ANGLE-RESOLVED NEAR EDGE X-RAY ABSORPTION FINE STRUCTURE

$$I \; \alpha \; (\cos^2\theta \sin^2\gamma + 2 \; \sin^2\theta \cos^2\gamma)$$



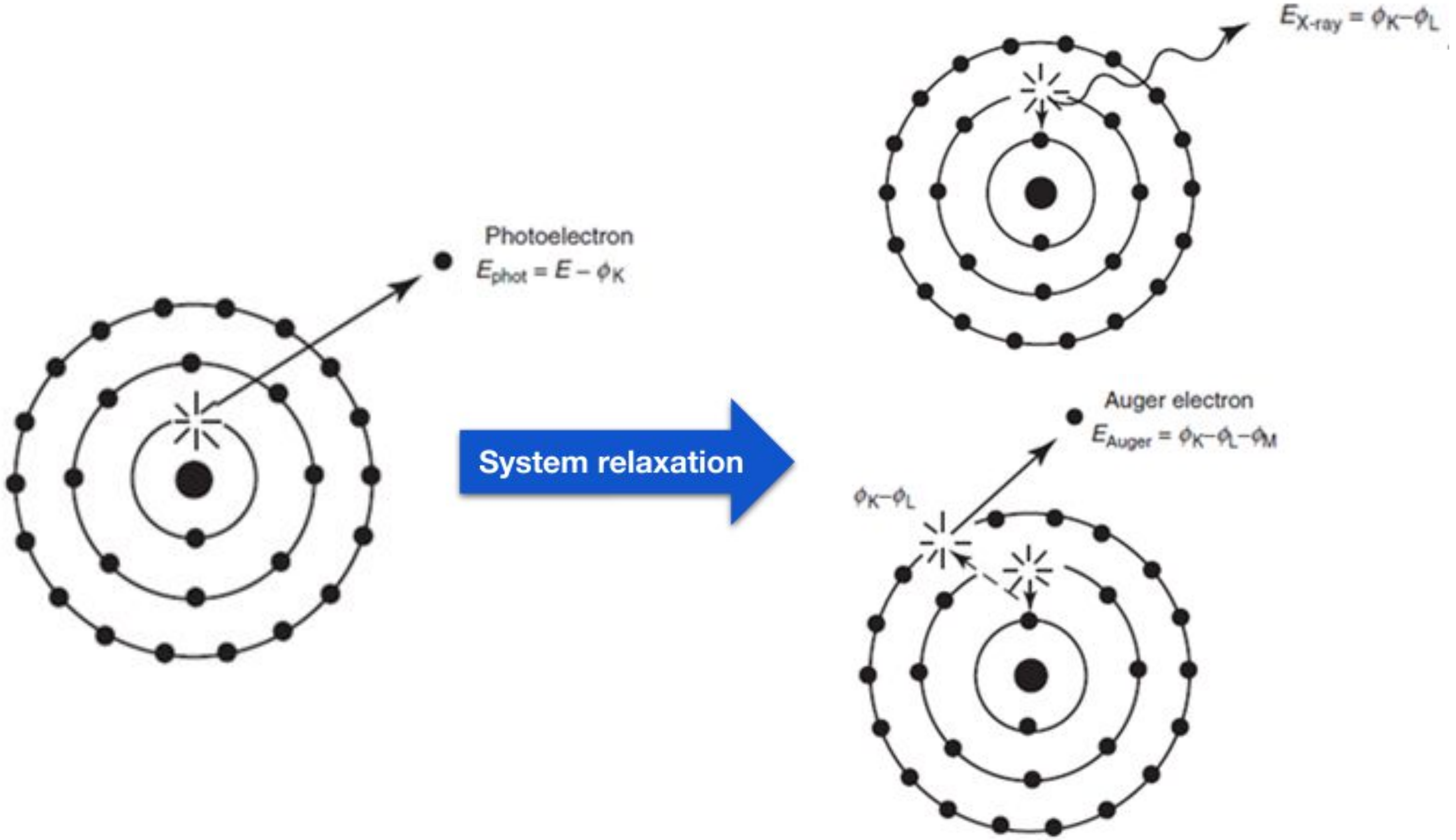
Extracted from Willmot, 2019

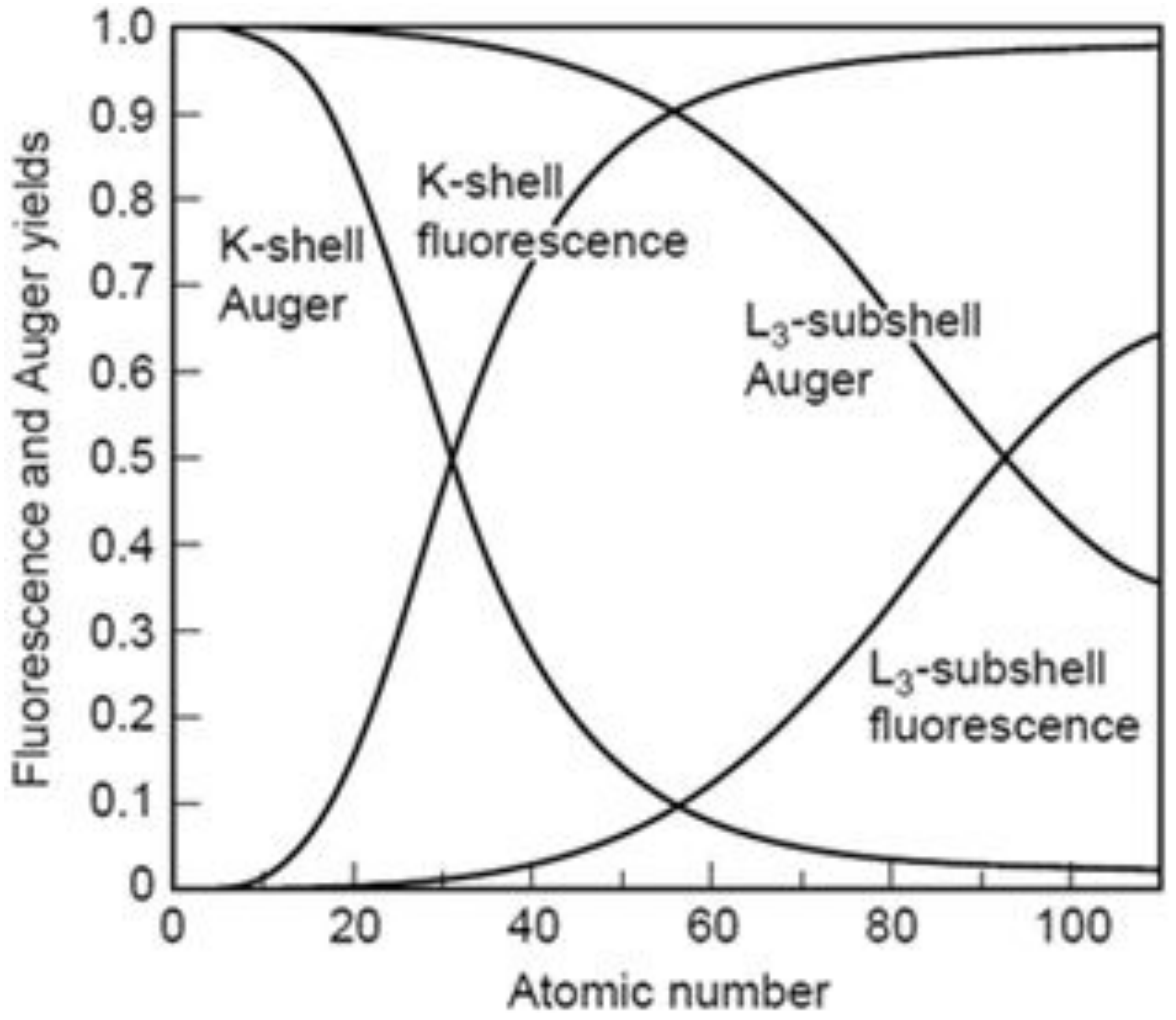




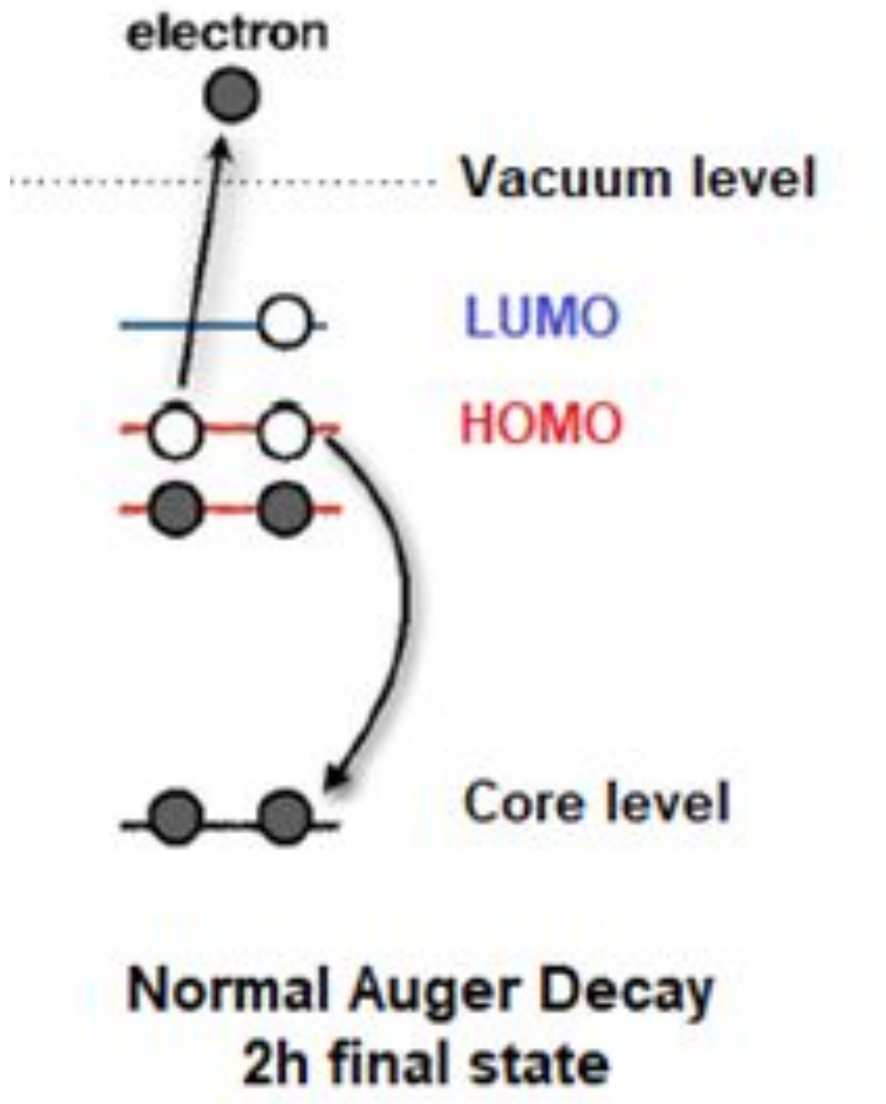
***Face-on* orientation**

X-RAYS ABSORPTION PROCESSES

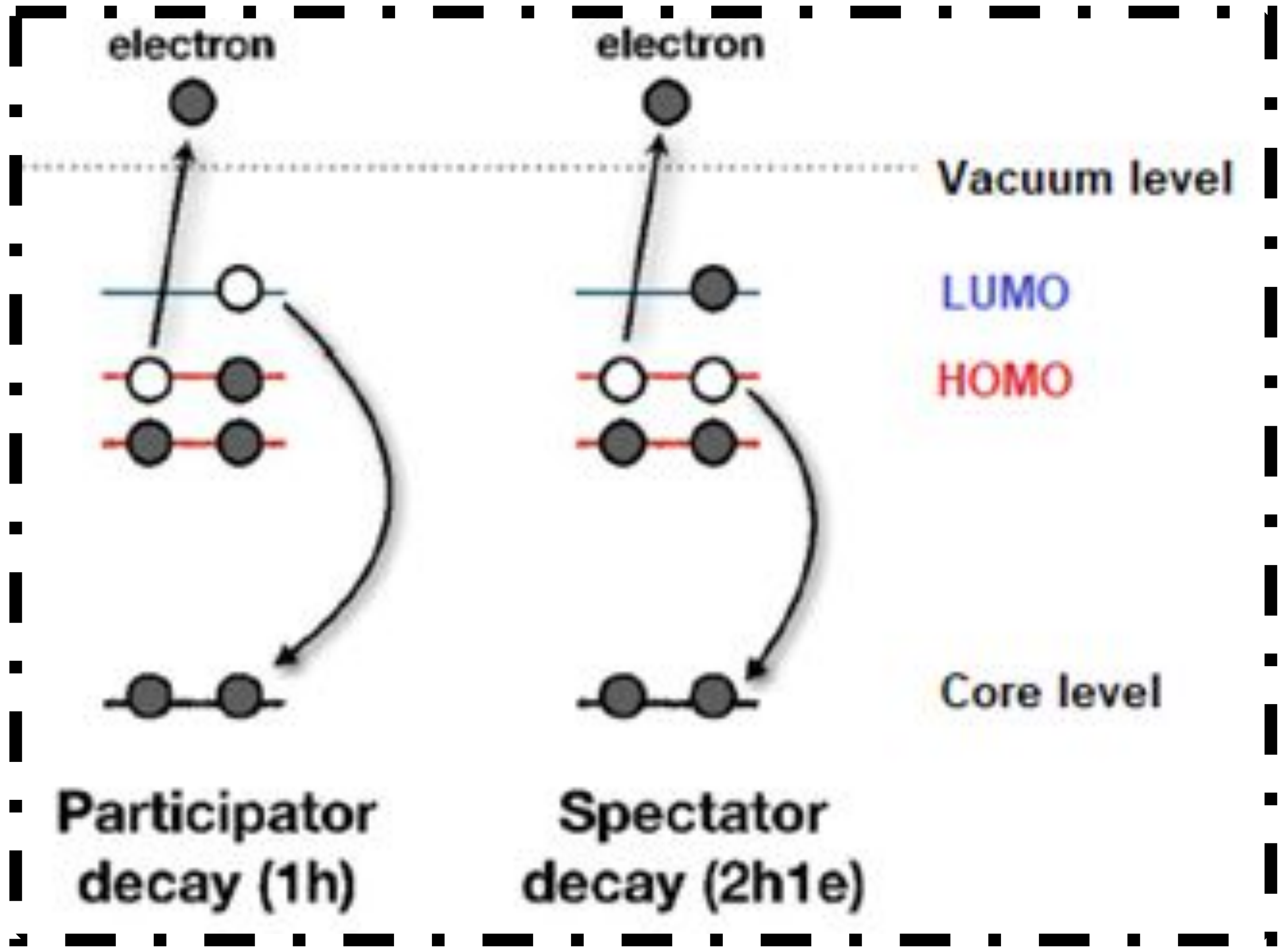


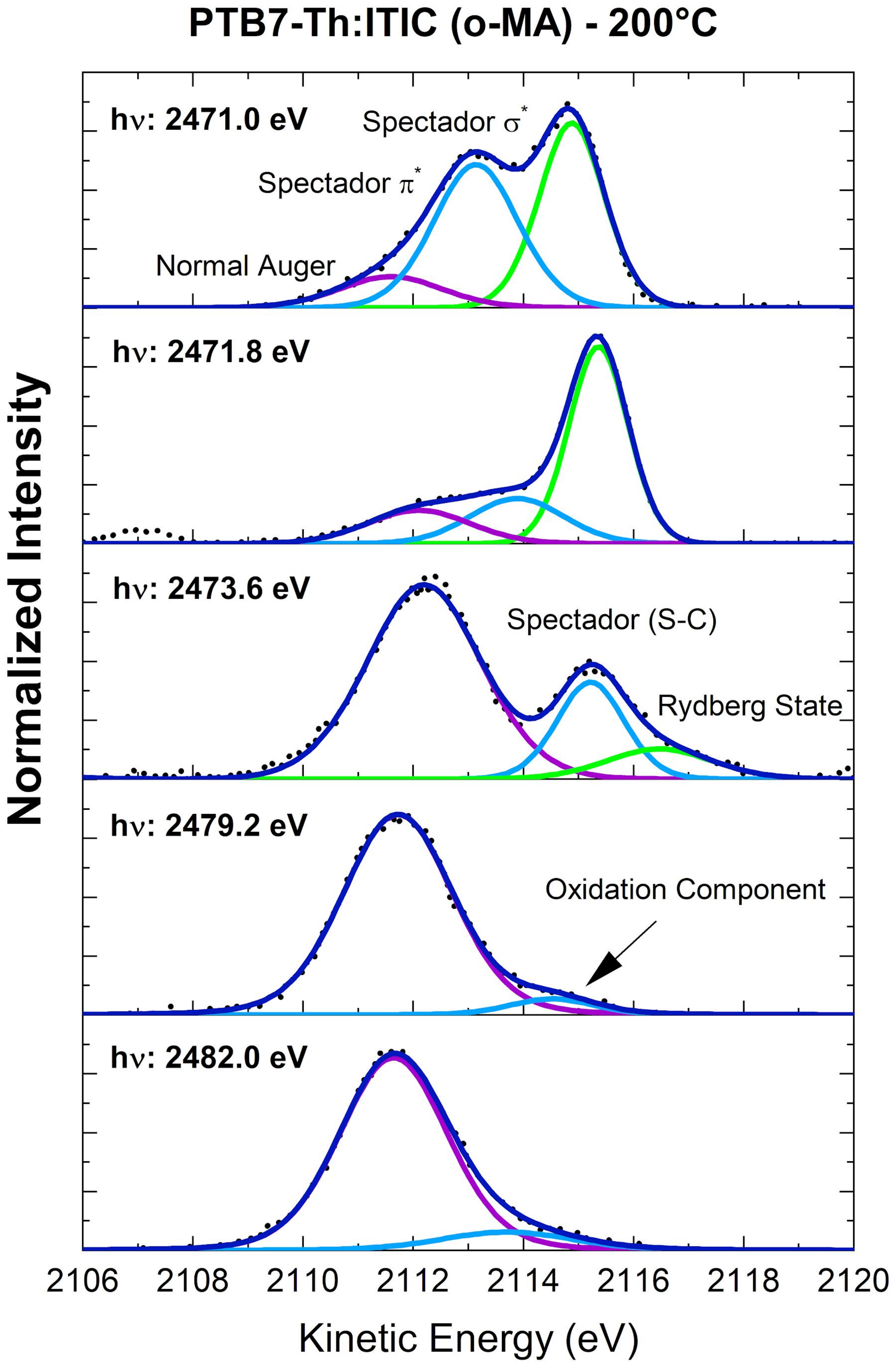


AUGER PROCESSES



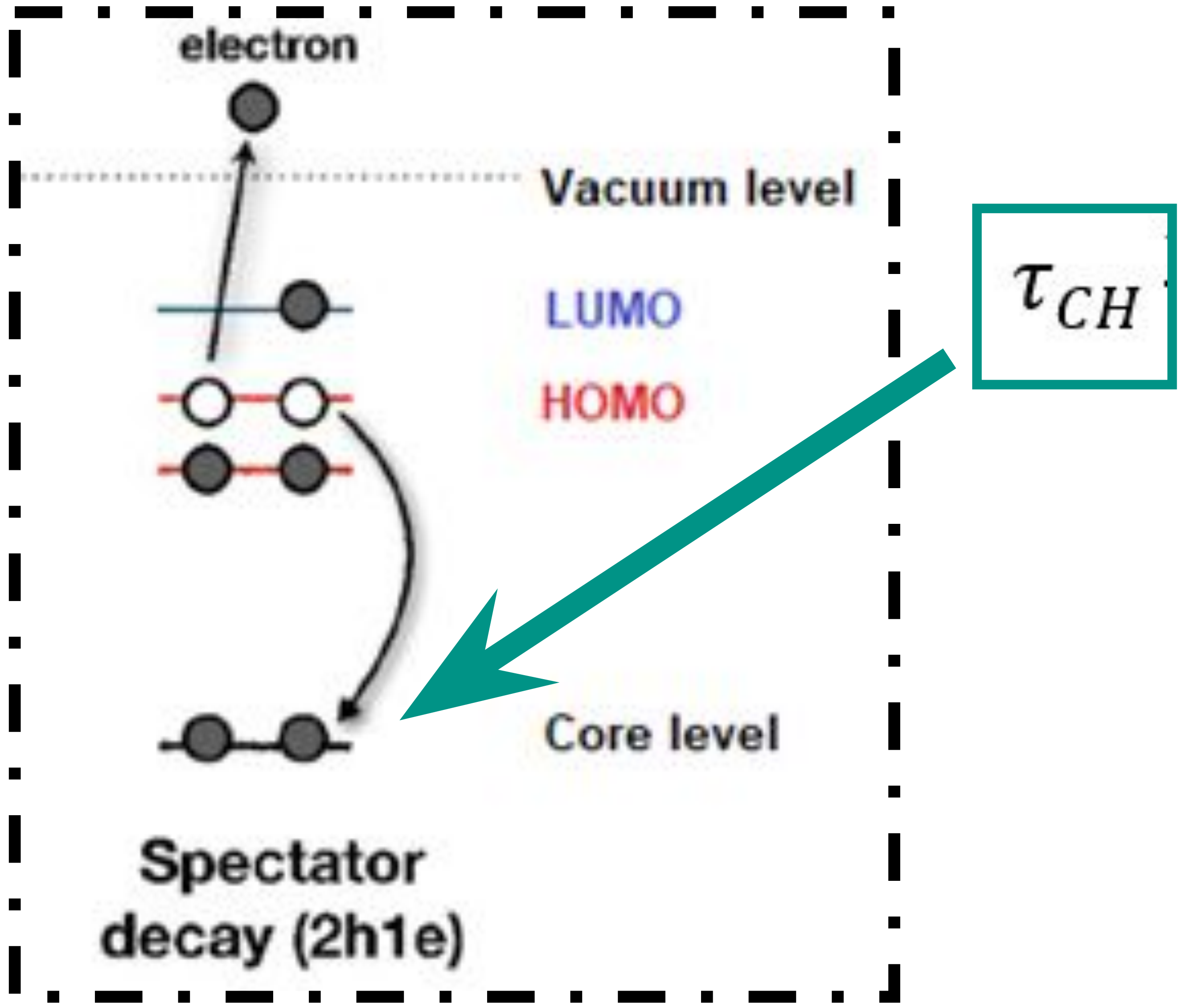
The resonant process with a **2h1e final state** can be monitored via **RAES**



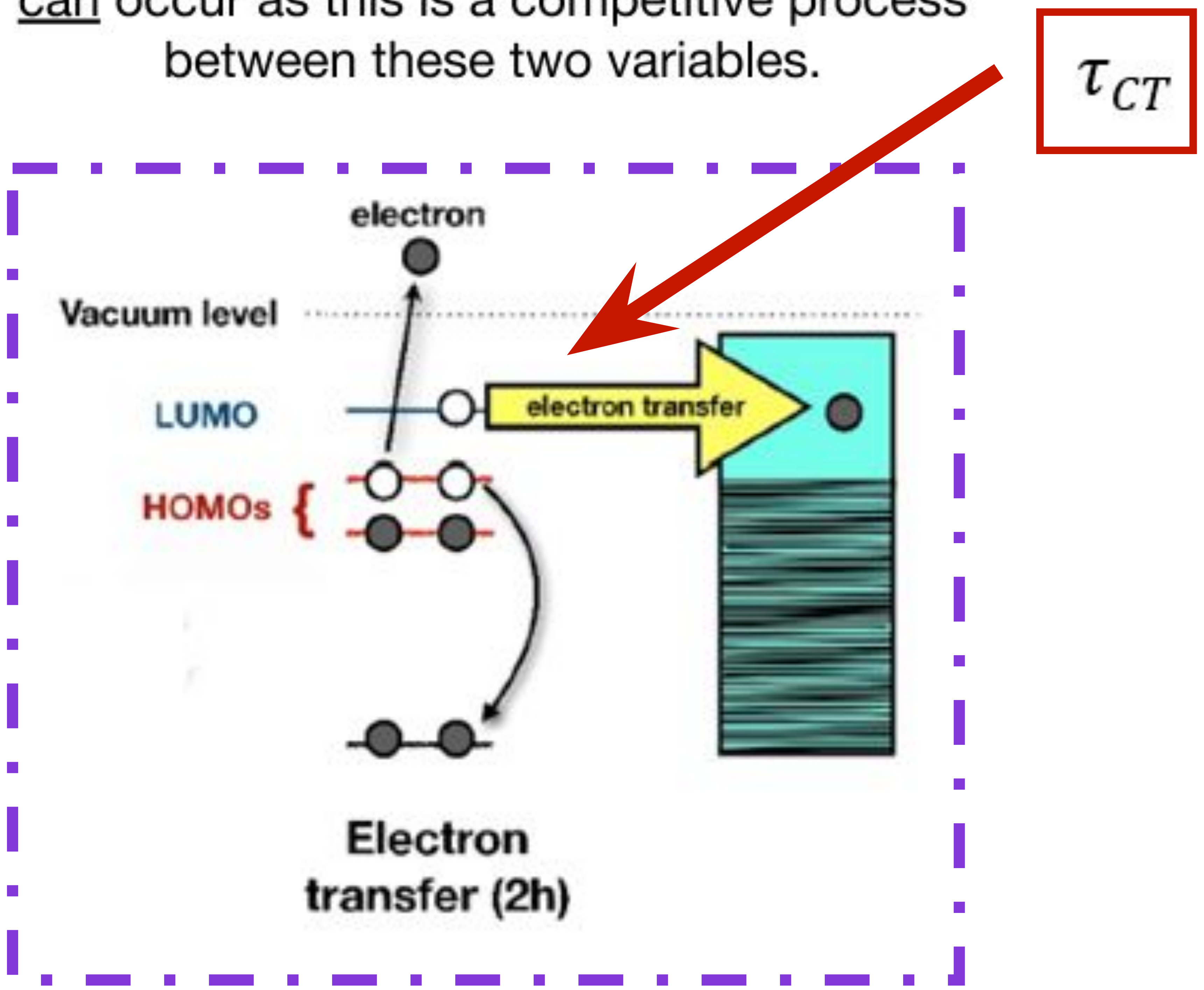


CHARGE TRANSFER DYNAMICS PROBED BY THE CORE-HOLE-CLOCK SPECTROSCOPY

The resonant process with a **2h1e final state** can be monitored via **<u>RAES</u>**



When the *core-hole* lifetime **is greater** than the time for charge transfer (**CT**) to occur, the latter <u>can</u> occur as this is a competitive process between these two variables.



CHC Expression

$$\tau_{CT} = \tau_{CH} \frac{I_{resonant}}{I_{normal}}$$

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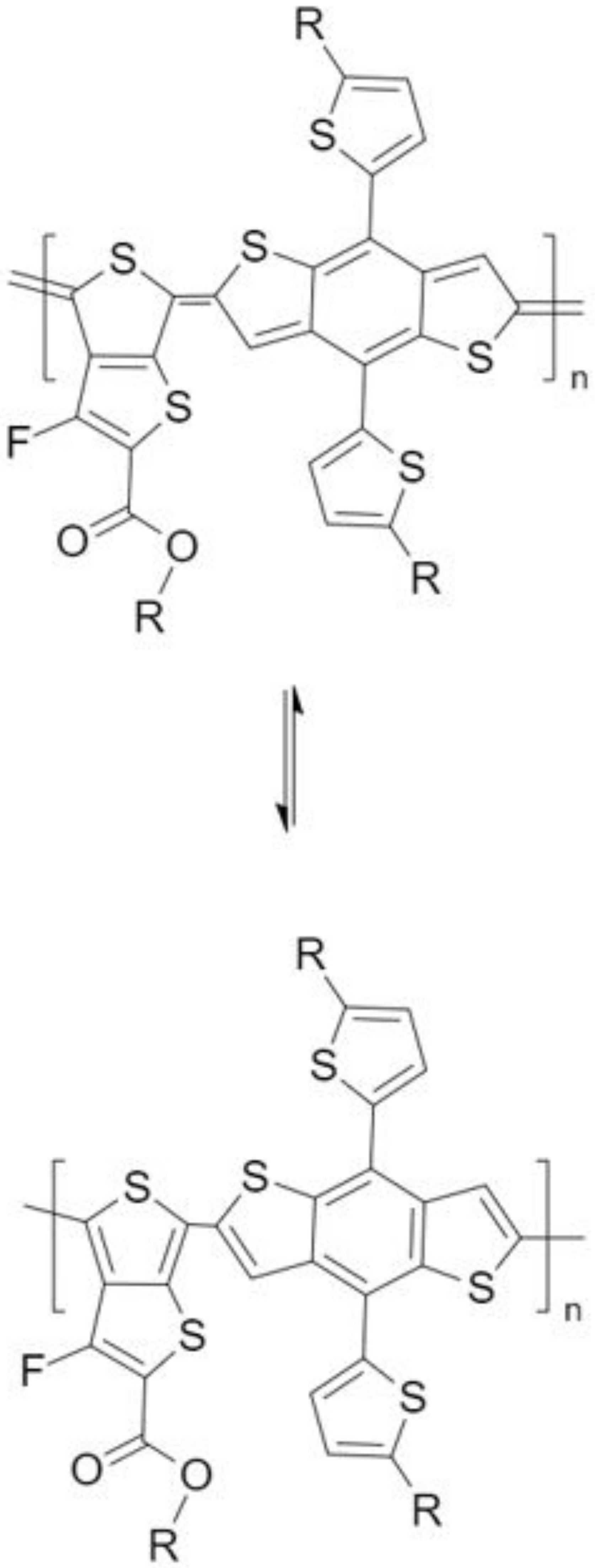
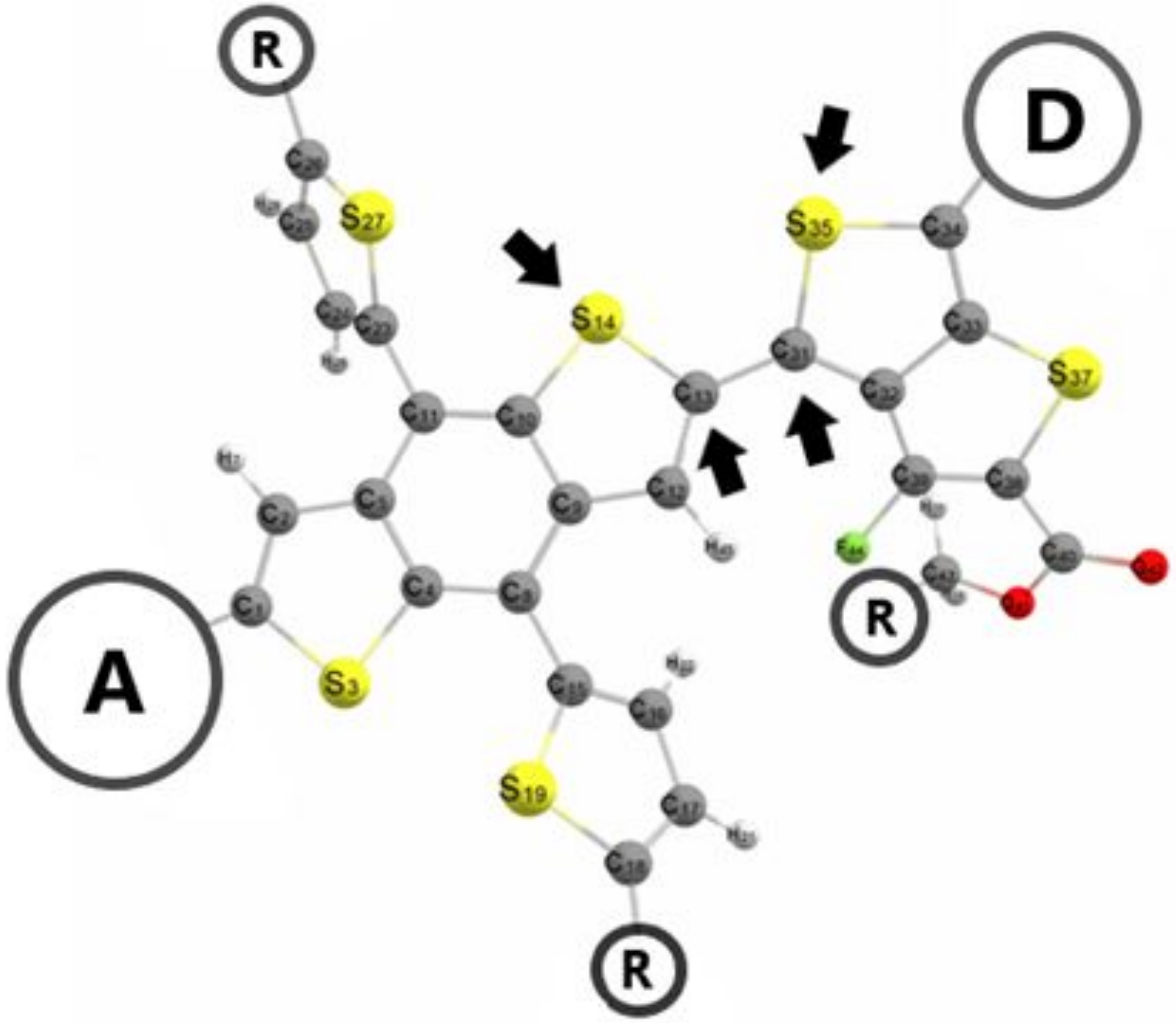
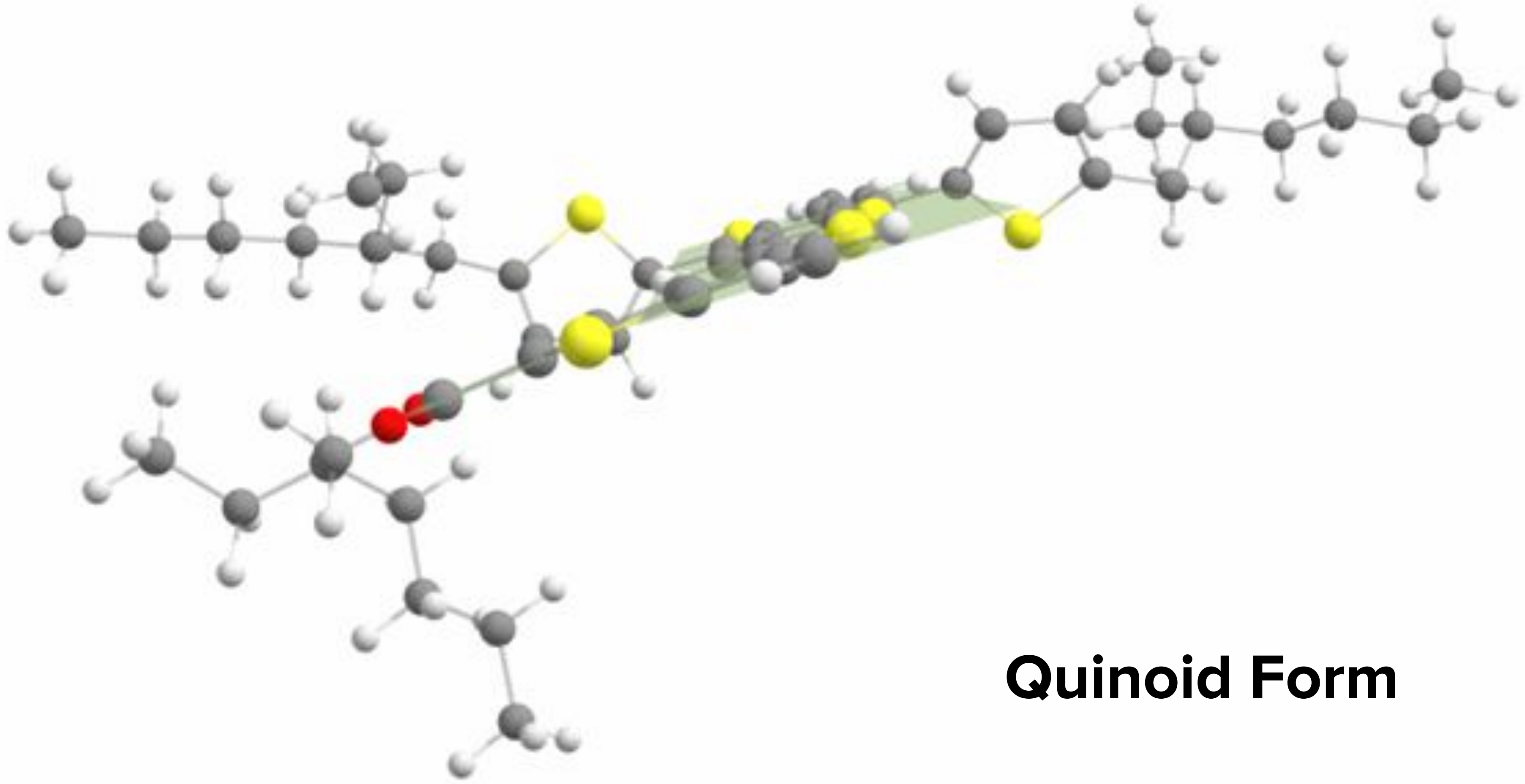
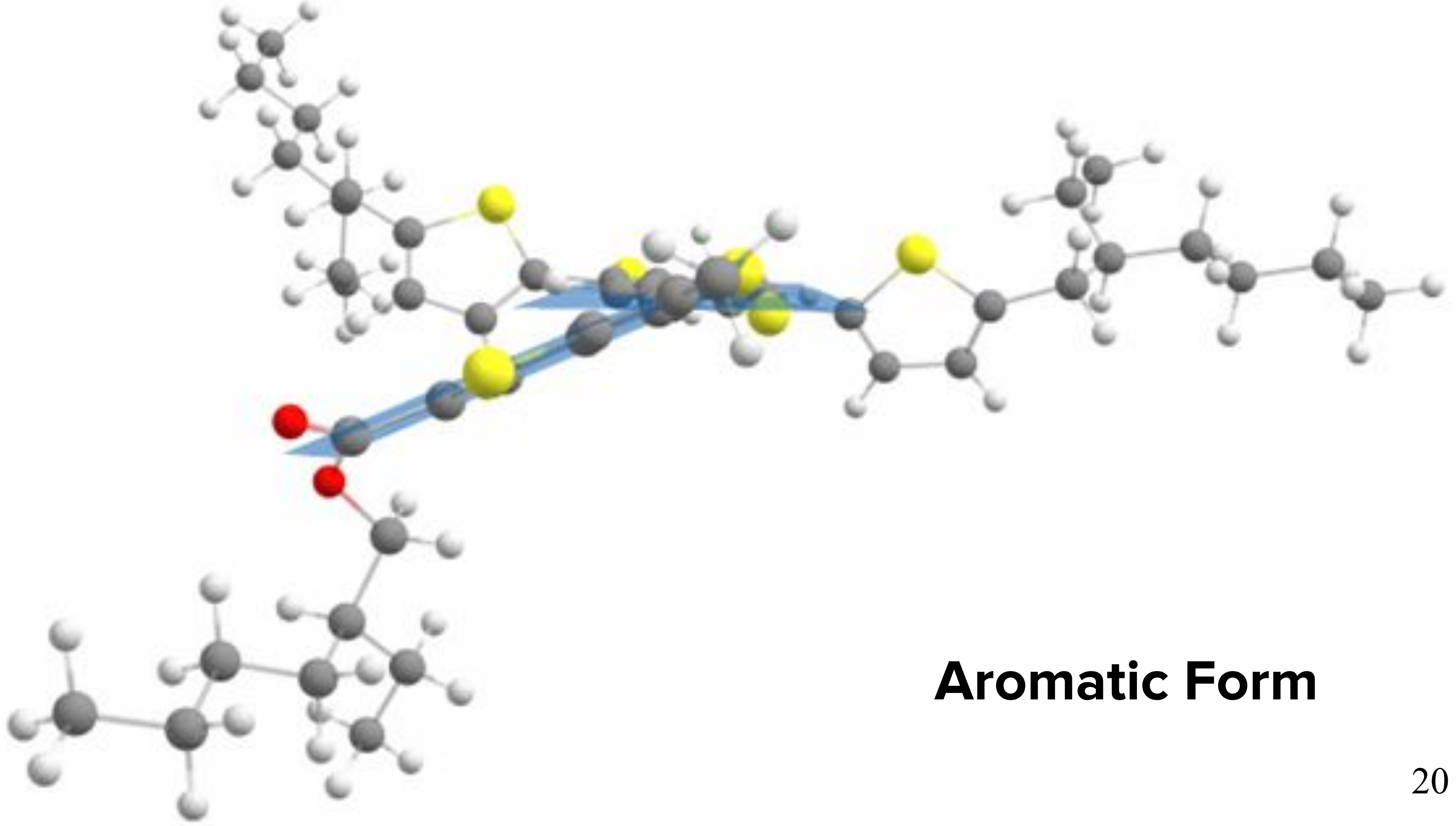
PTB7-TH INVESTIGATIONS: ELECTRONIC STRUCTURE





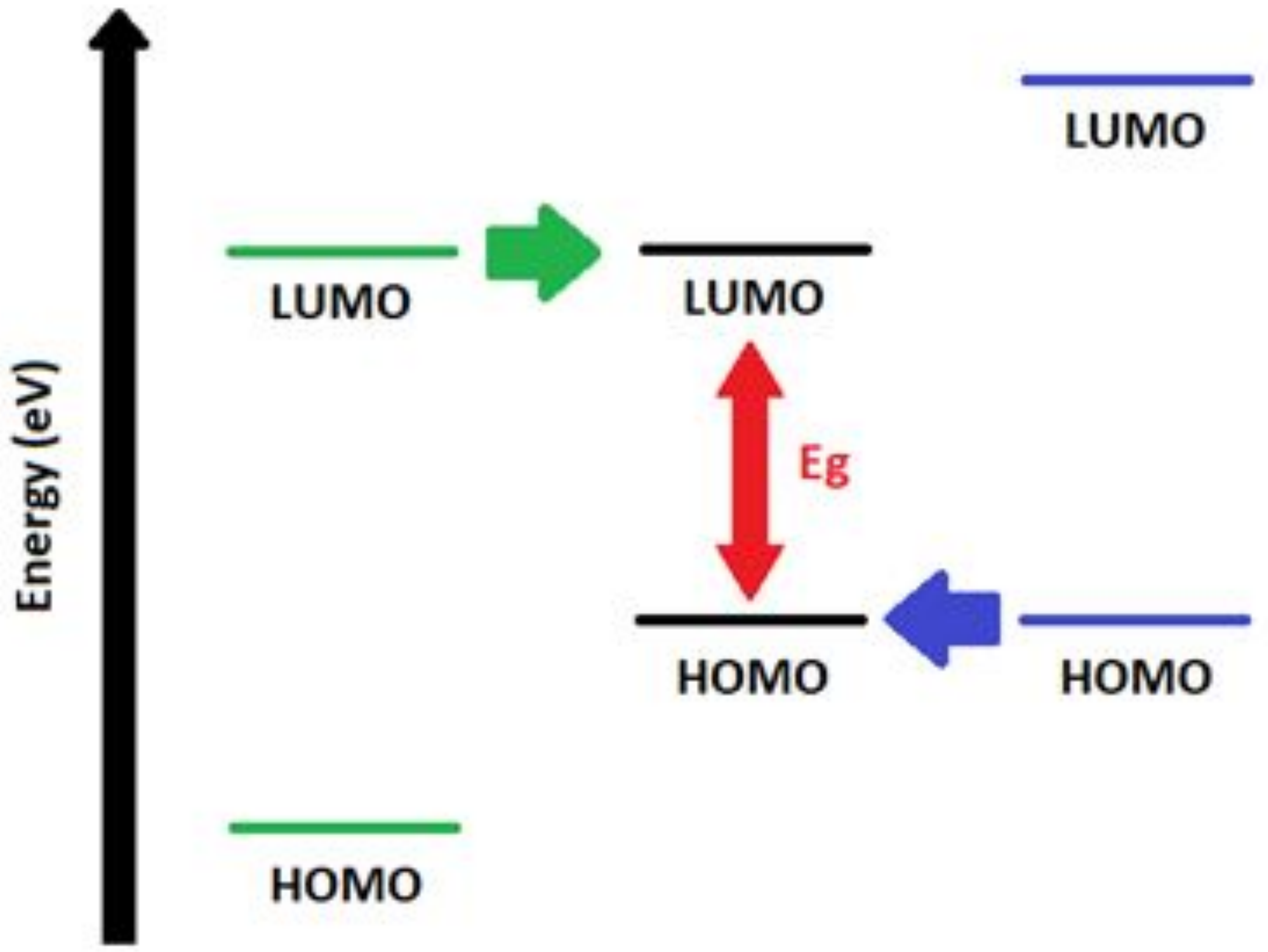


Quinoid Form



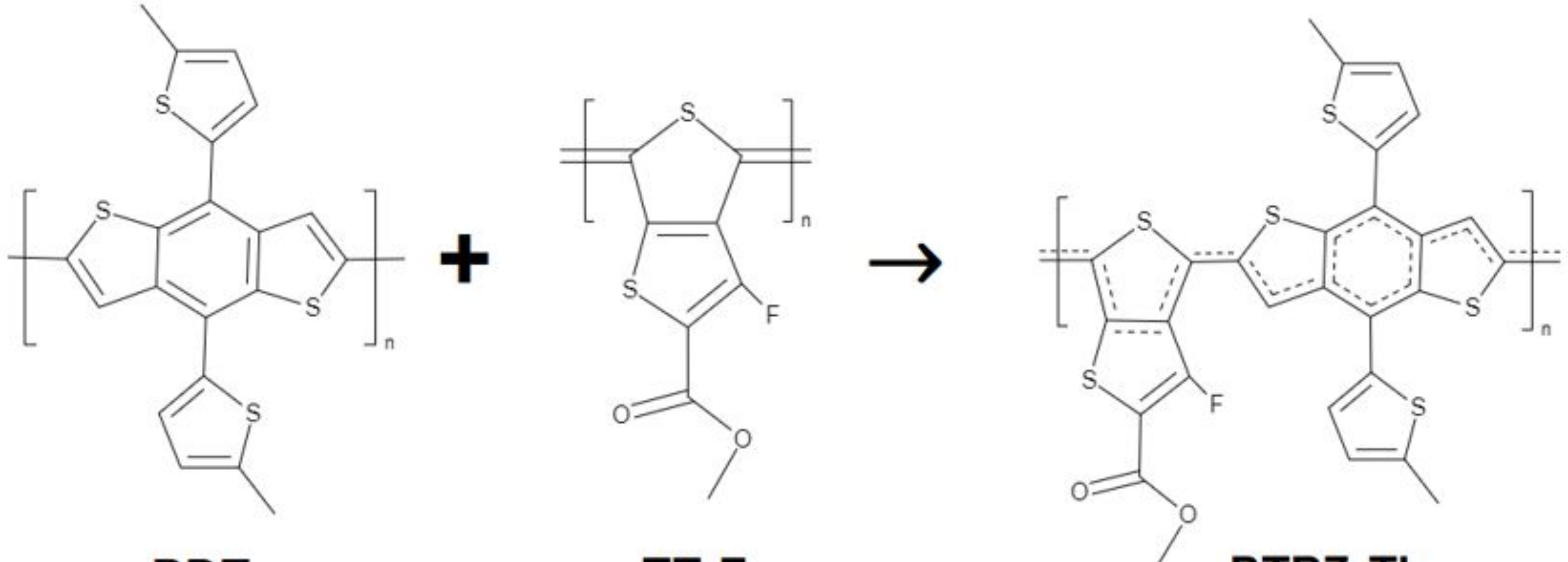
Aromatic Form

PTB7-TH INVESTIGATIONS: VISIBLE LIGHT SPECTROSCOPY



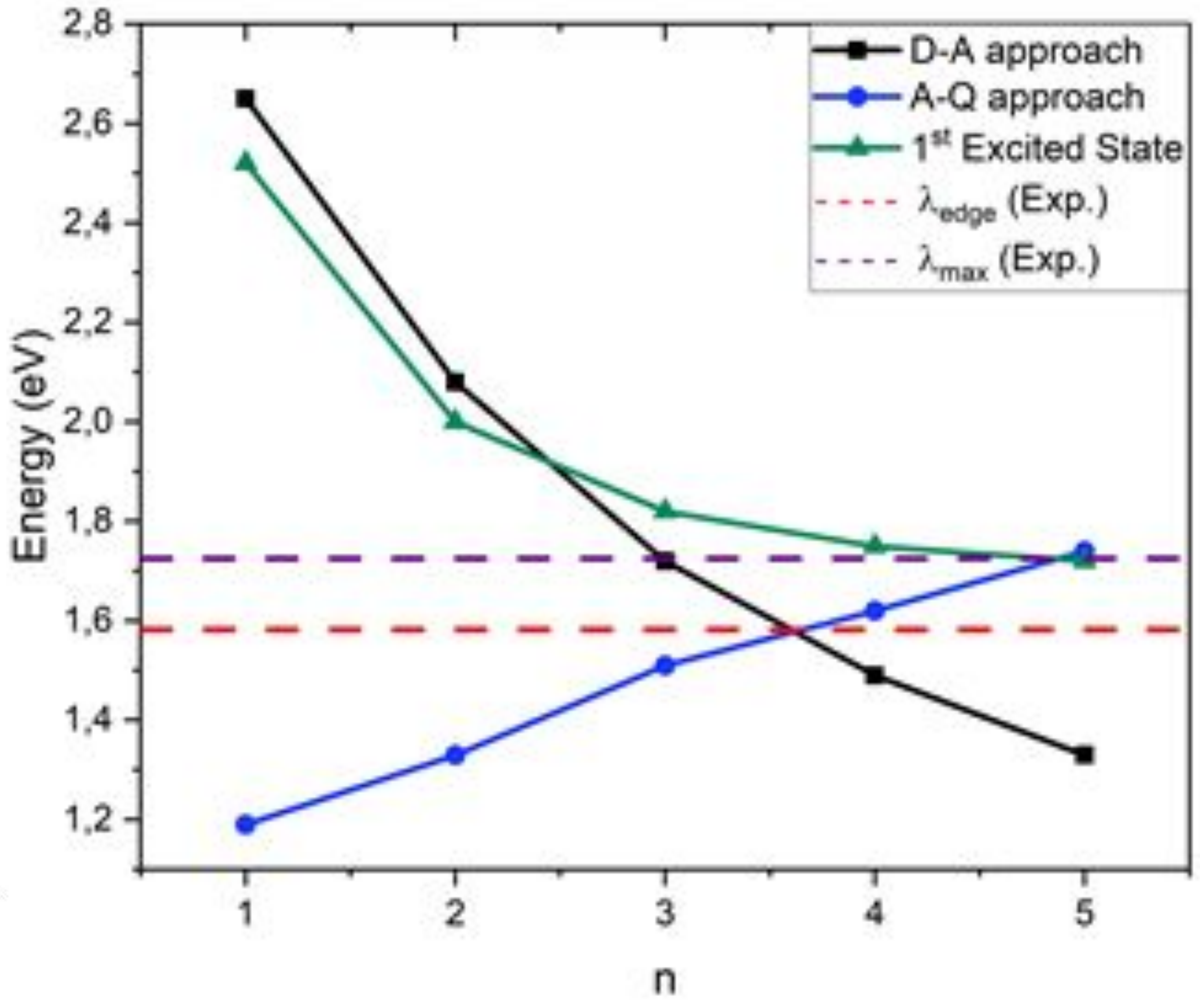
D/A Approach

$$E_g^{DA} = Lowest\ "IP" - Highest\ "EA"$$



$$E_{g,qui} = \frac{|\sum qNE_g - PMC|}{\sum N} + PMC$$

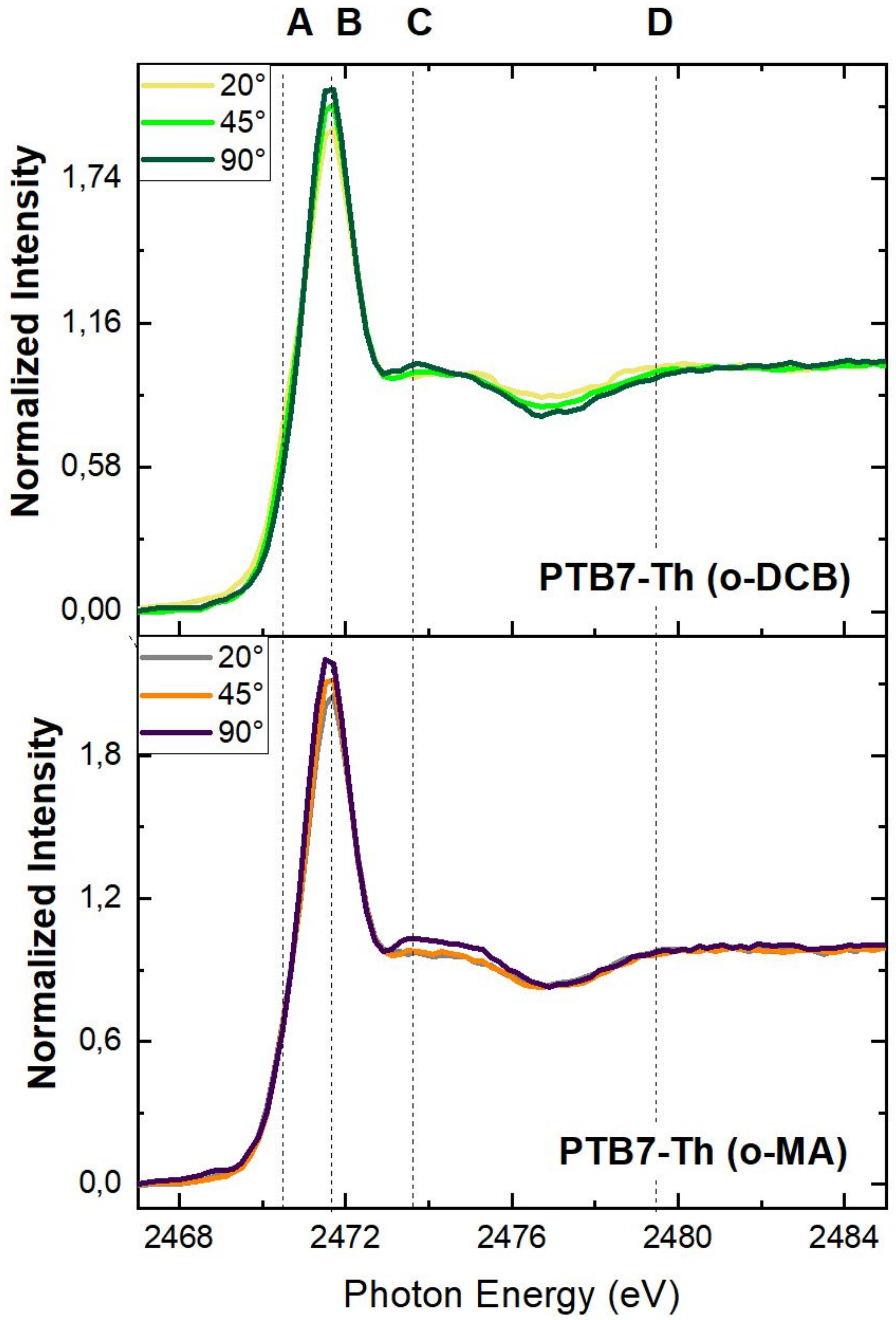
A/Q Approach

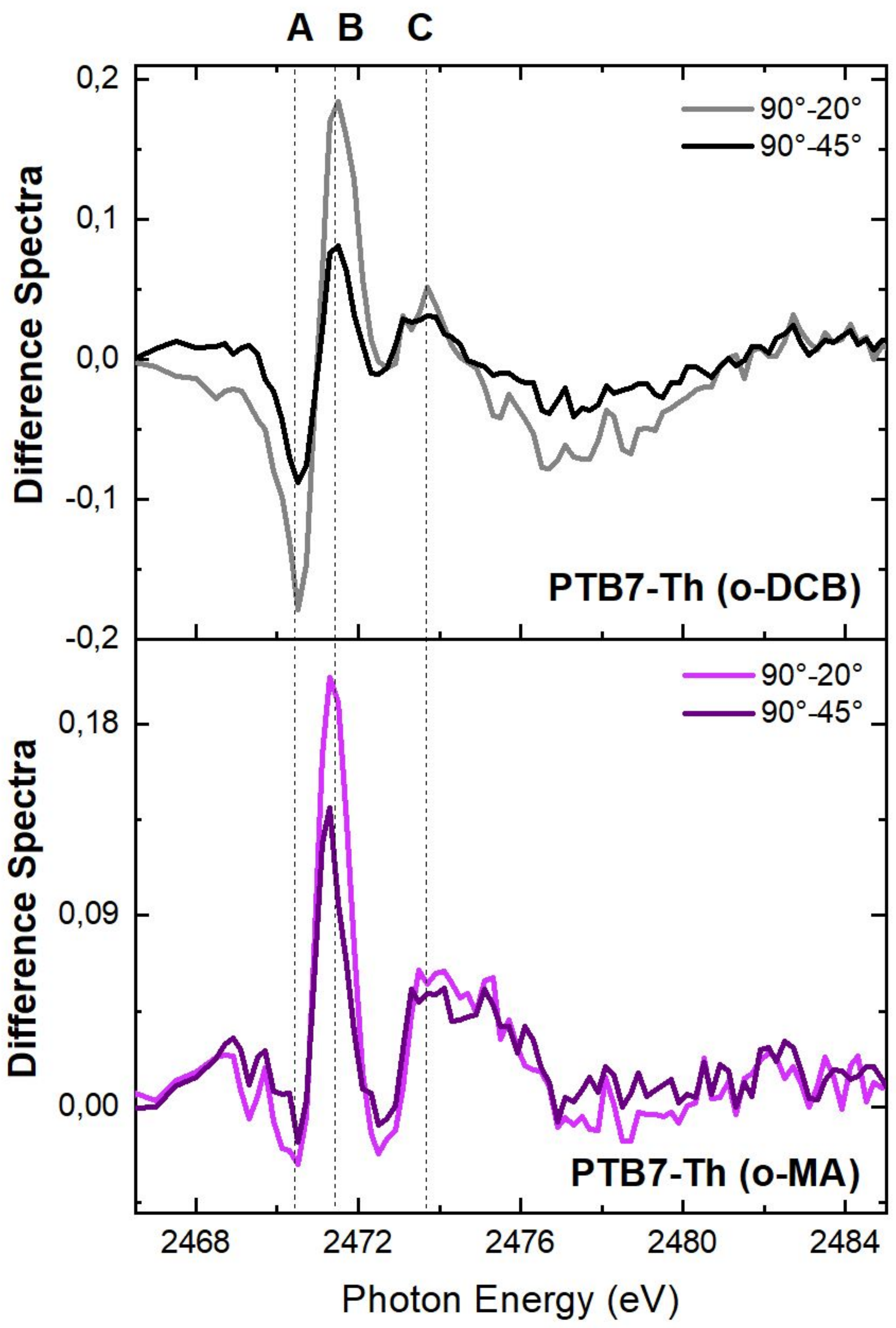


Theoretical Level: B3LYP/6-31g(d)

PTB7-TH INVESTIGATIONS

Molecular Orientation and the S 1s Excited States





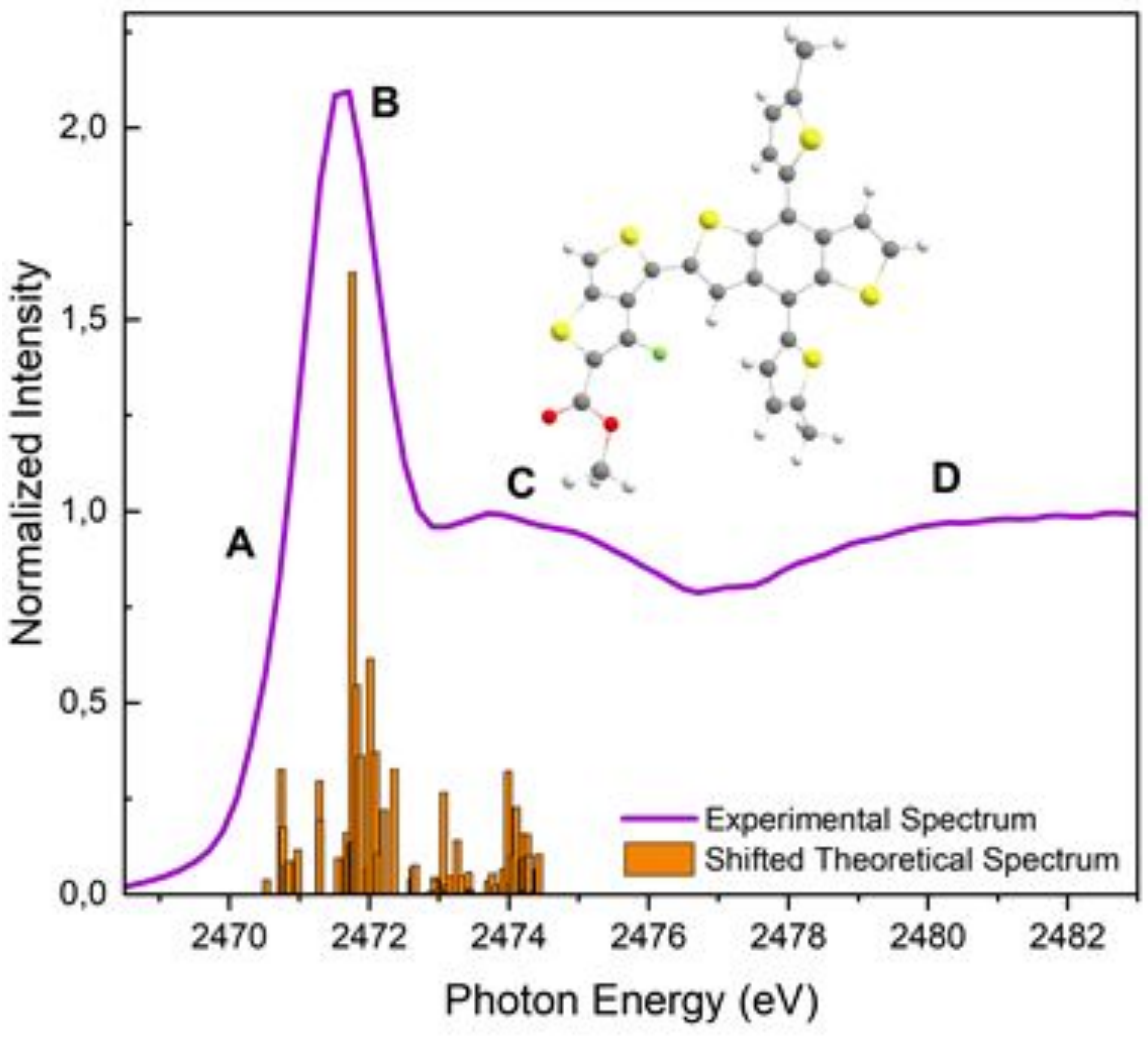
	PTB7-Th	
	Transition Energy (eV)	
	PBE0	Experimental (o-DCB)
S 1S → π^*	2469.8	2470.3
S 1S → σ^*	2470.8	2171.9
S 1S → σ^*	2472.9	2473.7

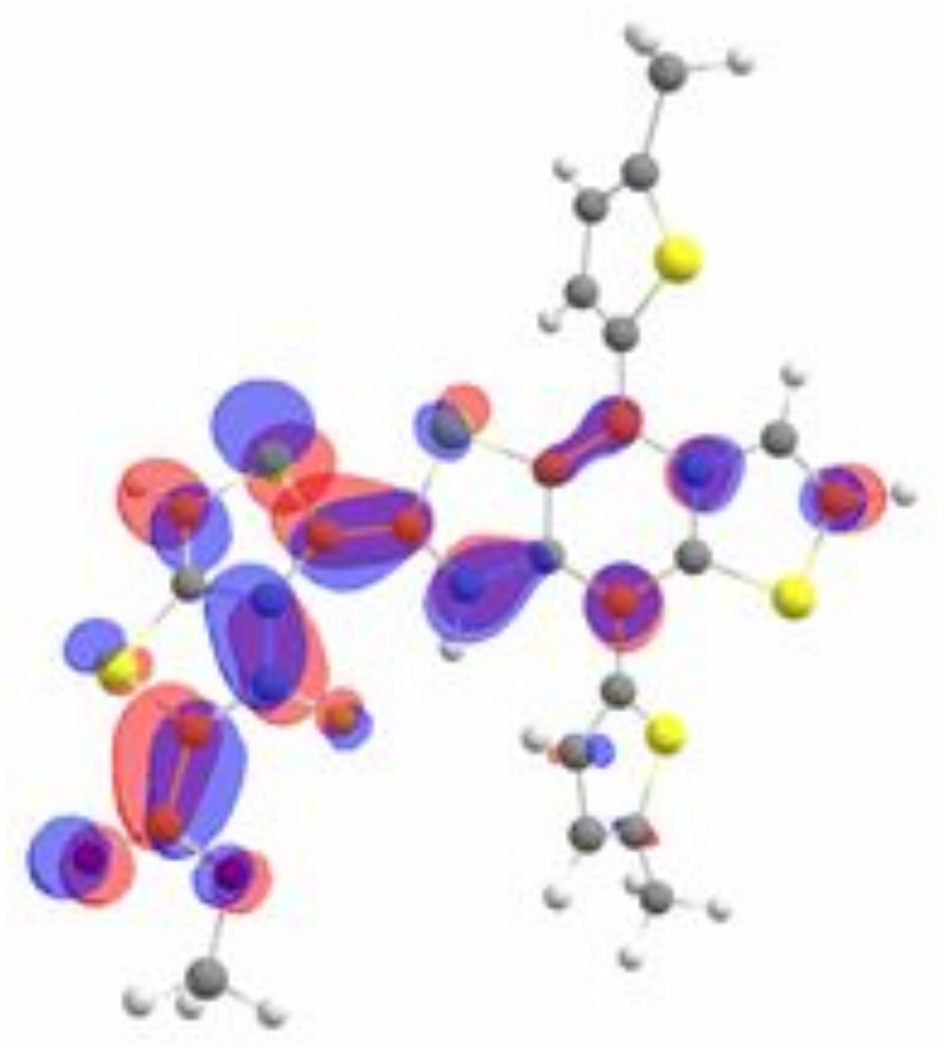
Theoretical Level:
PBE0/cc-pVDZ-DK

Incidence	S 1s → π^*	S 1s → σ^*	S 1s → σ^*	*Geometry*
Normal	*Low intensity*	*High intensity*	*High intensity*	*face − on*
Grazing	*High intensity*	*Low intensity*	*Low intensity*	

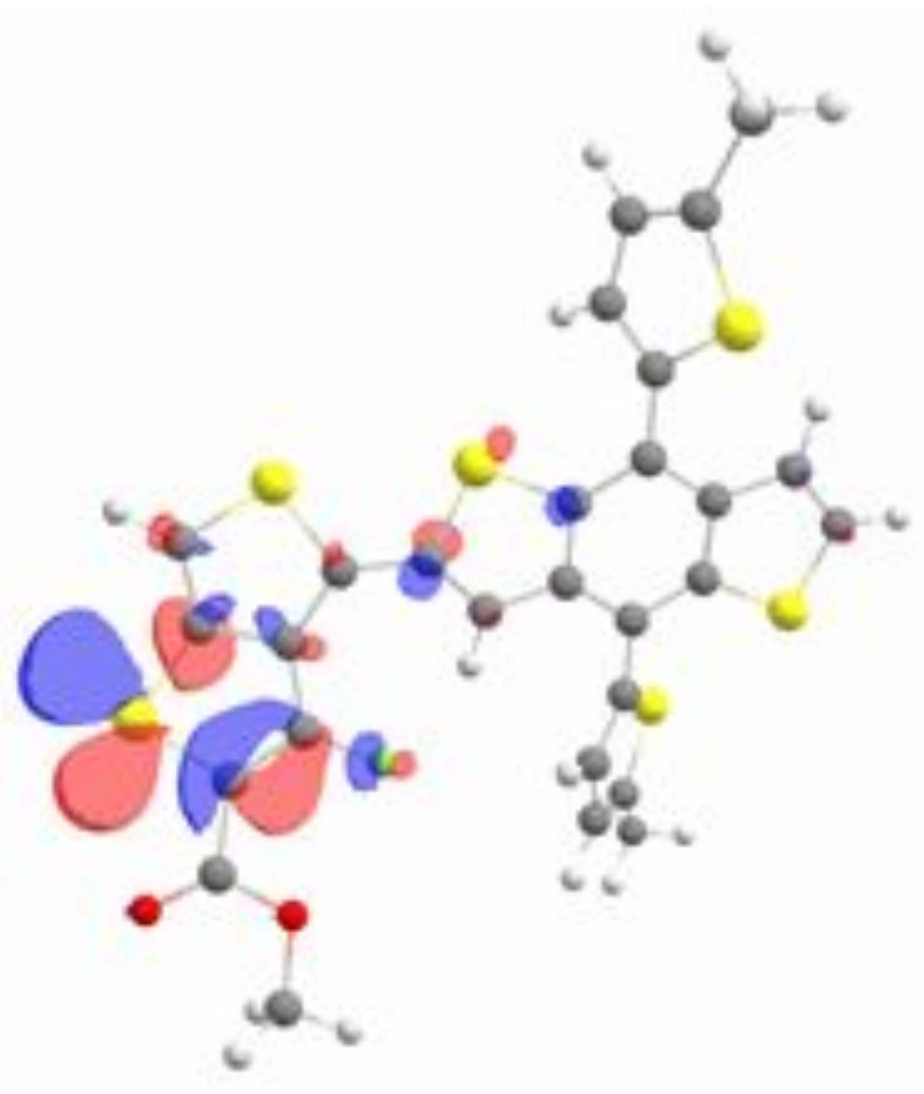
PTB7-TH INVESTIGATIONS

Molecular Orientation and the S 1s Excited States

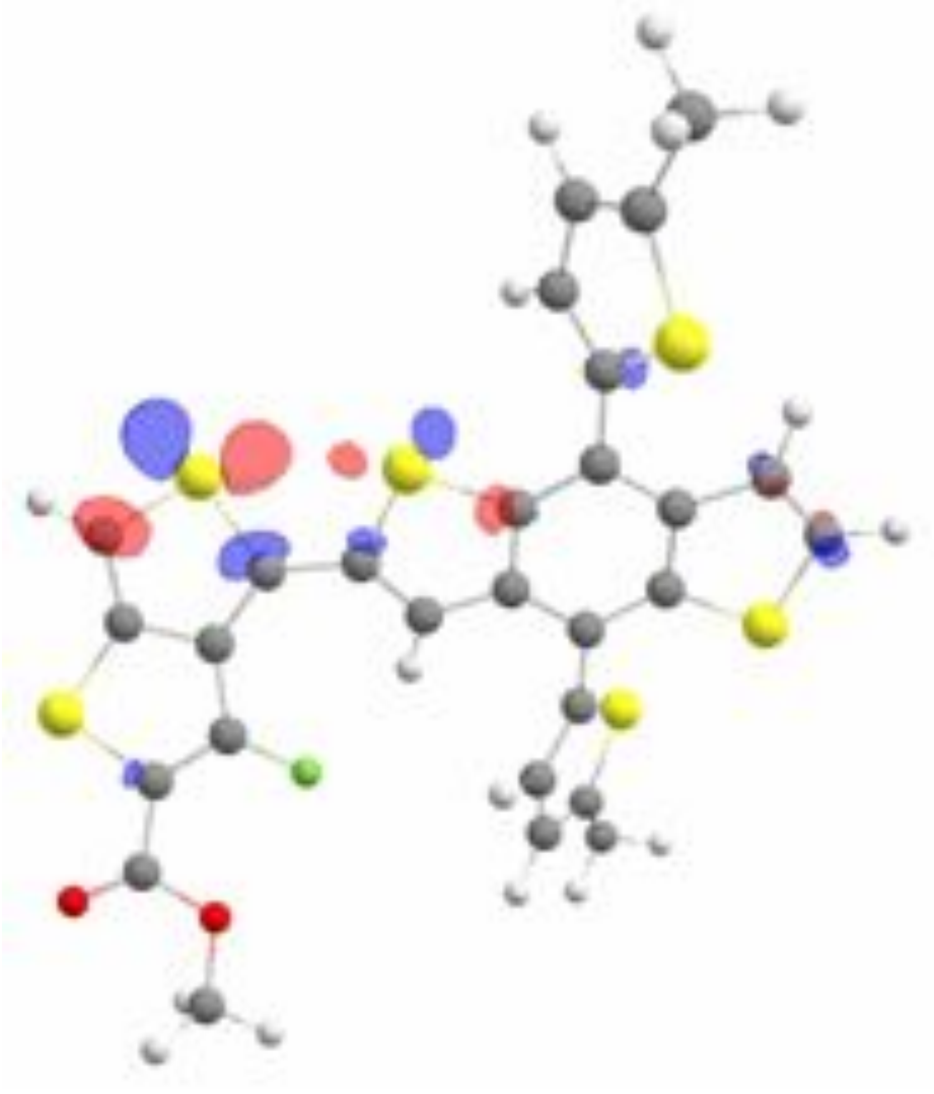




S(1) 1s → LUMO (π*)

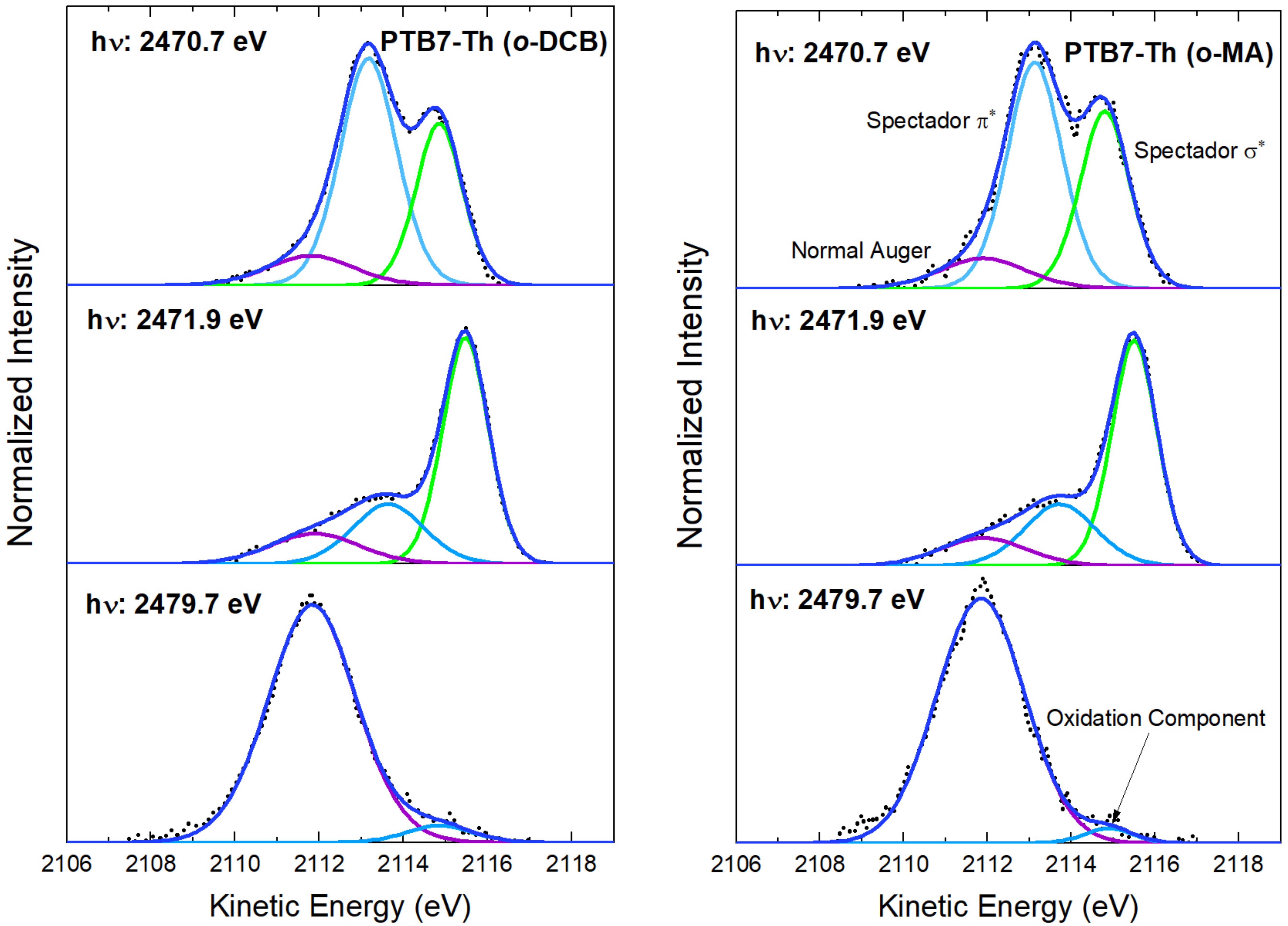


S(2) 1s → LUMO+7 (σ*)



S(1) 1s → LUMO+5 (σ*)

PTB7-TH INVESTIGATIONS



Charge Transfer Dynamics

$$\tau_{CT} = \tau_{CH} \frac{I_{resonant}}{I_{normal}}$$

PTB7-Th [τ_{CT} (fs)]			
Photon Energy (eV)	o-DCB	Photon Energy (eV)	o-MA
2470.7	10.23	2470.7	10.45
2471.9	6.83	2471.9	7.71

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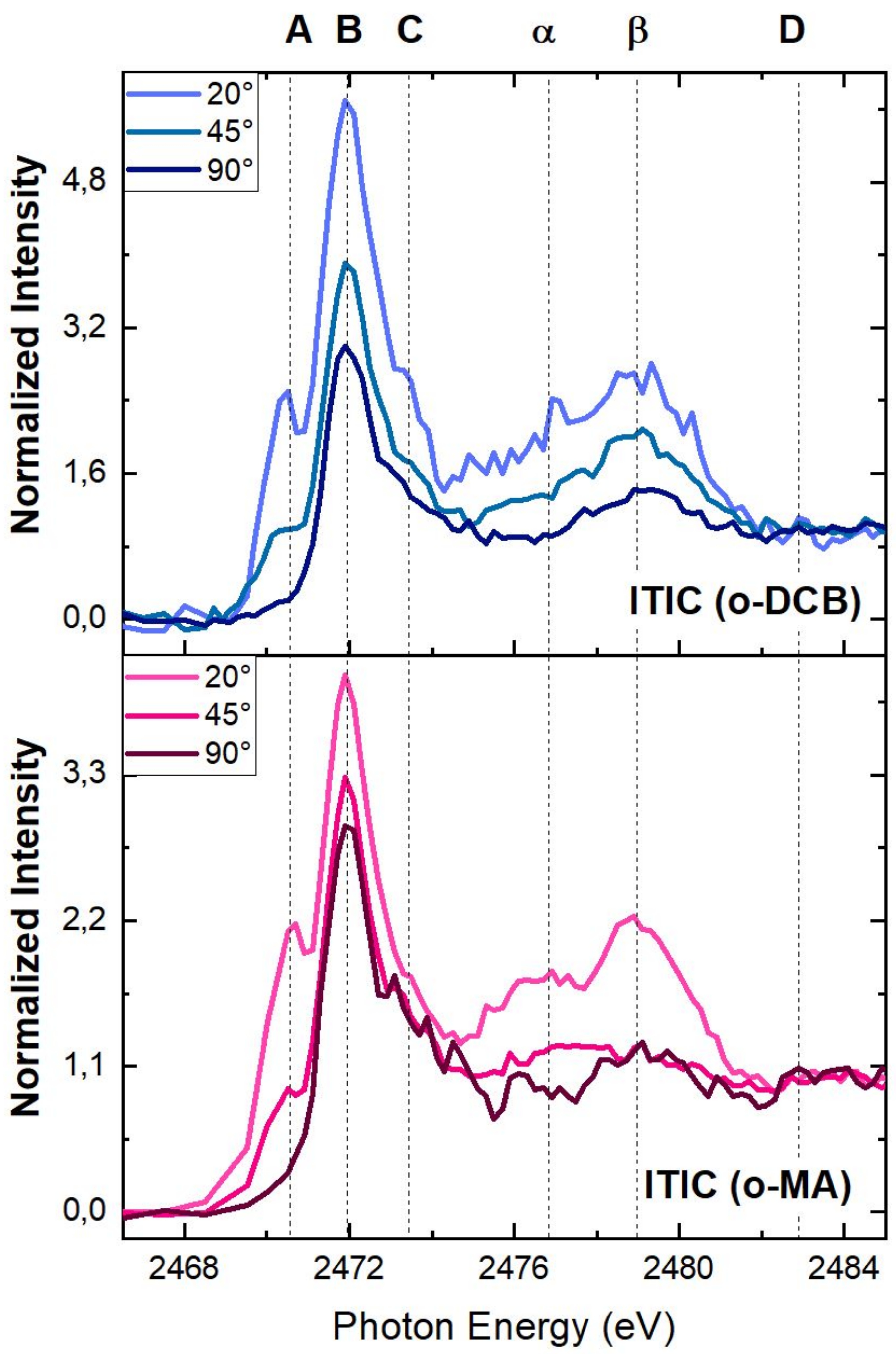
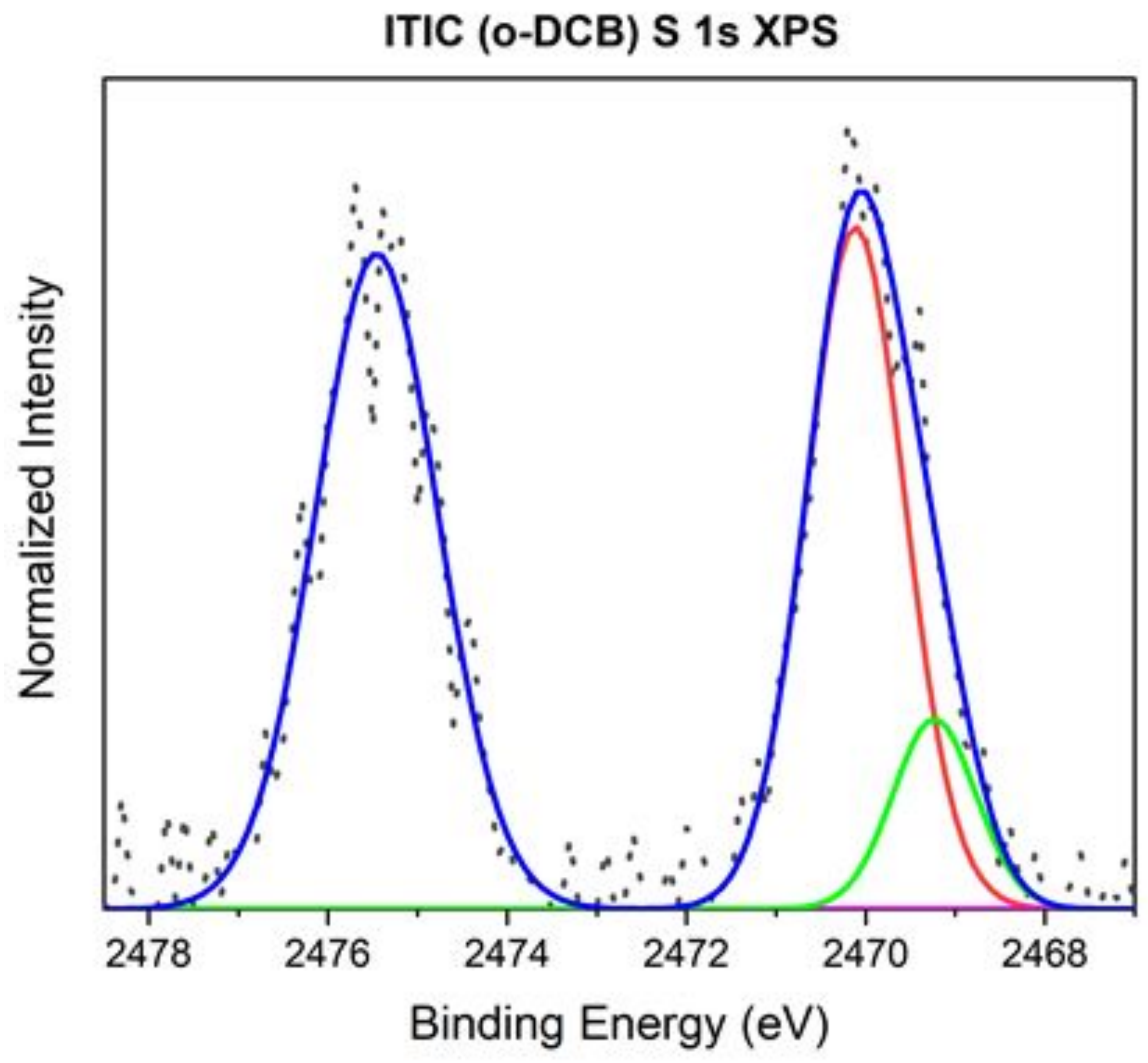
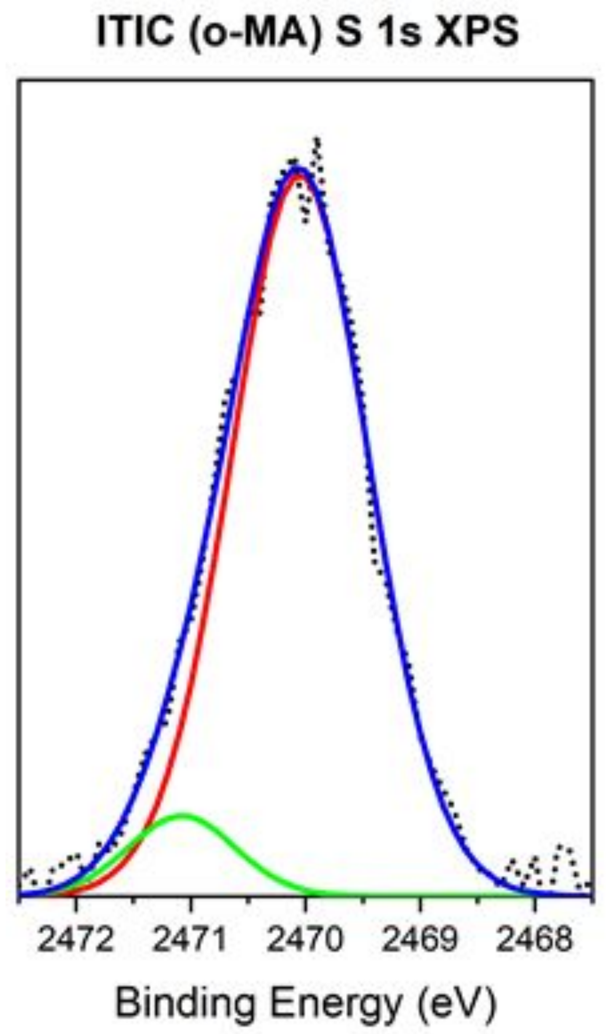
ITIC INVESTIGATIONS



Label	Transition	Transition Energy (eV) - Experimental	Transition Energy (eV) - Theoretical
A	S $1s \rightarrow \pi^*$	2470.5	2469.1
B	S $1s \rightarrow \sigma^*$	2472.1	2471.4
C	S $1s \rightarrow \pi^*$	2473.5	2472.7

	S $1s \rightarrow \pi^*$	S $1s \rightarrow \sigma^*$ $(C-S)$	S $1s \rightarrow \sigma^*$
at normal incidence	↓ *Intensity*	↑ *Intensity*	↑ *Intensity*
at grazing incidence	↑ *Intensity*	↑ *Intensity*	↑ *Intensity*





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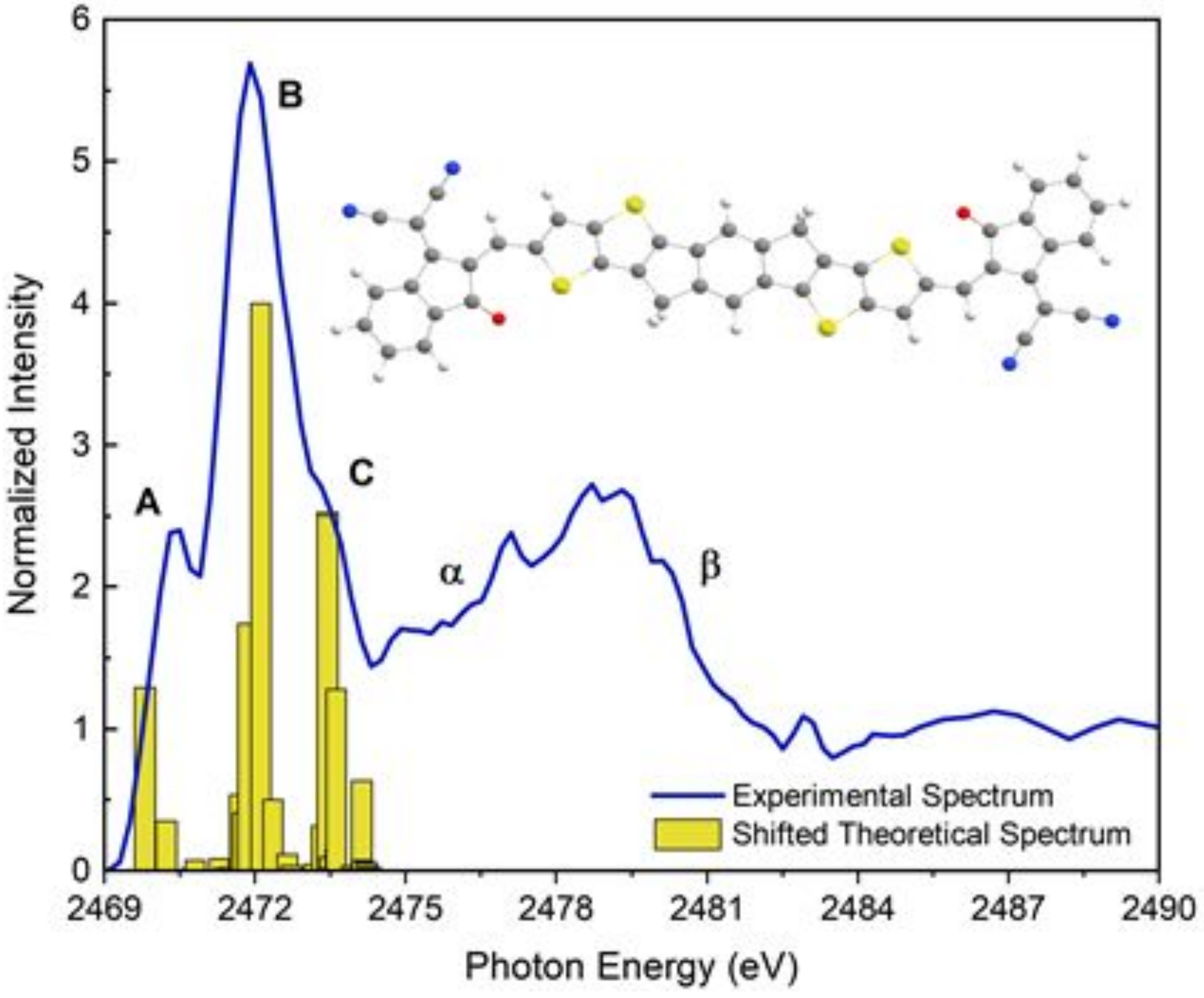
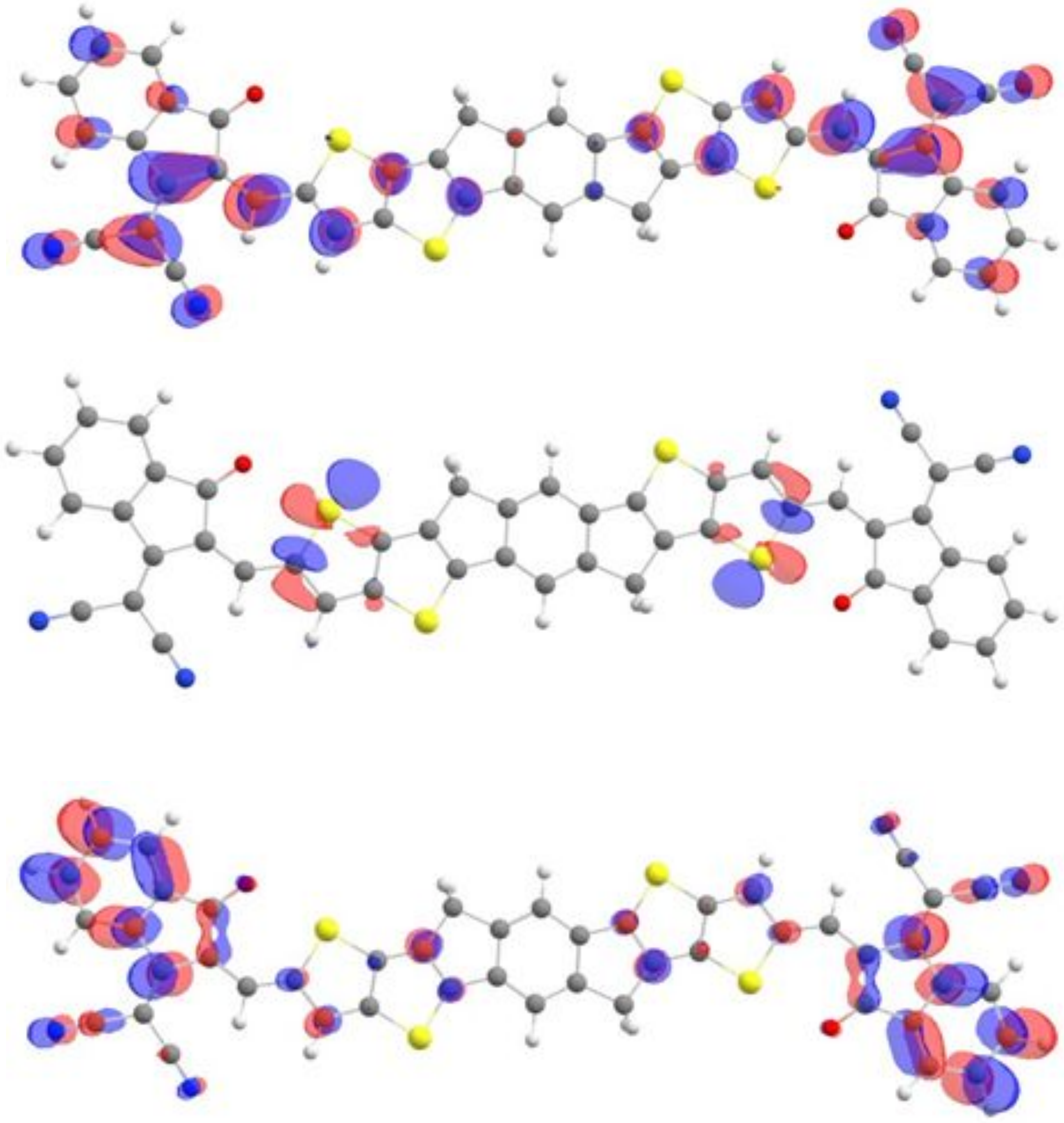


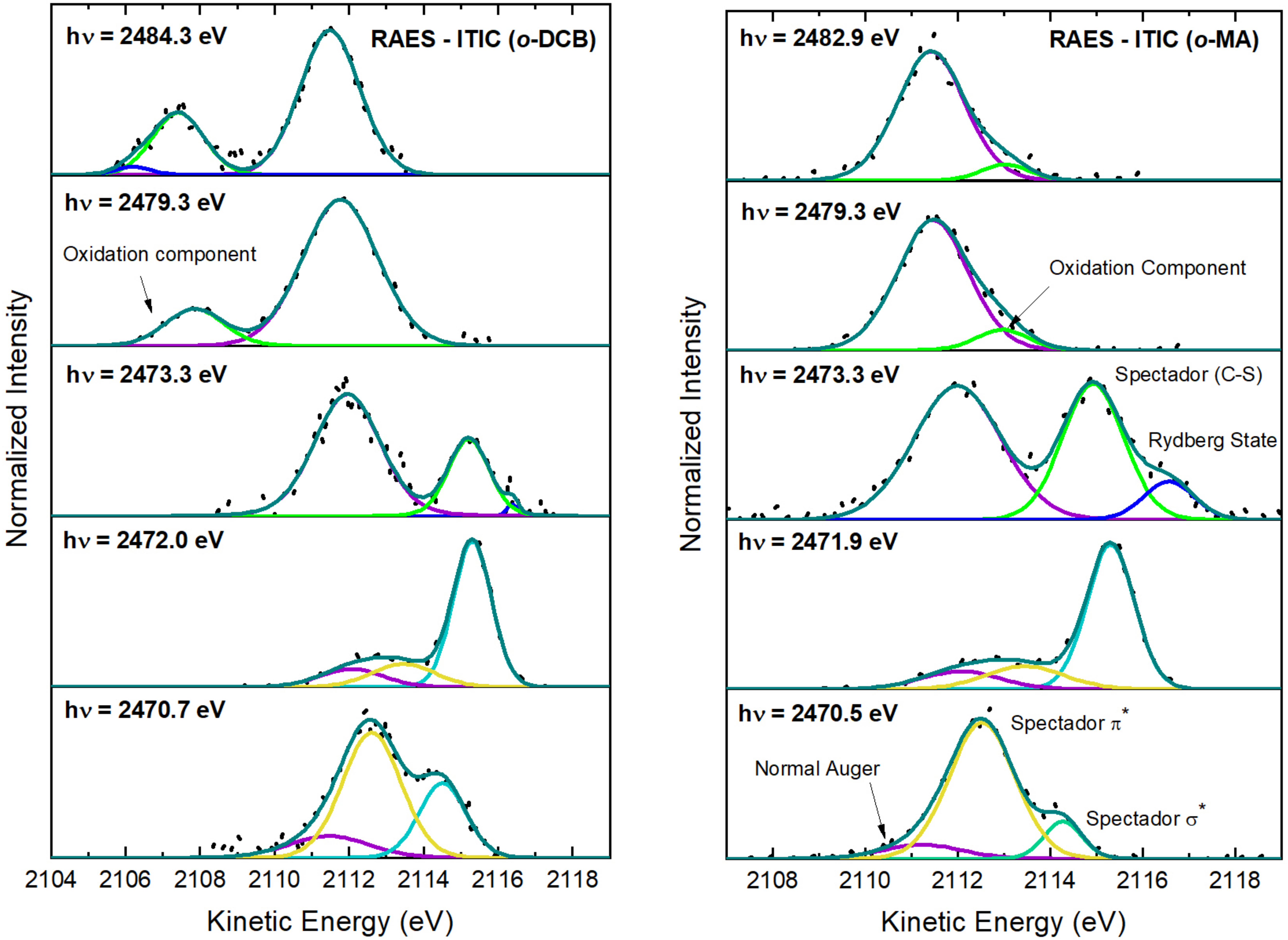


1s → LUMO+1 (π*)

1s → LUMO+17 (σ*)

1s → LUMO+12 (π*)

ITIC INVESTIGATIONS



Charge Transfer Dynamics

ITIC [τ_{CT} (fs)]			
Photon Energy (eV)	o-DCB	**Photon Energy (eV)**	o-MA
2470.7	9.34	2470.5	12.06
2472.0	7.79	2471.9	10.07
2473.7	0.51	2473.3	1.12

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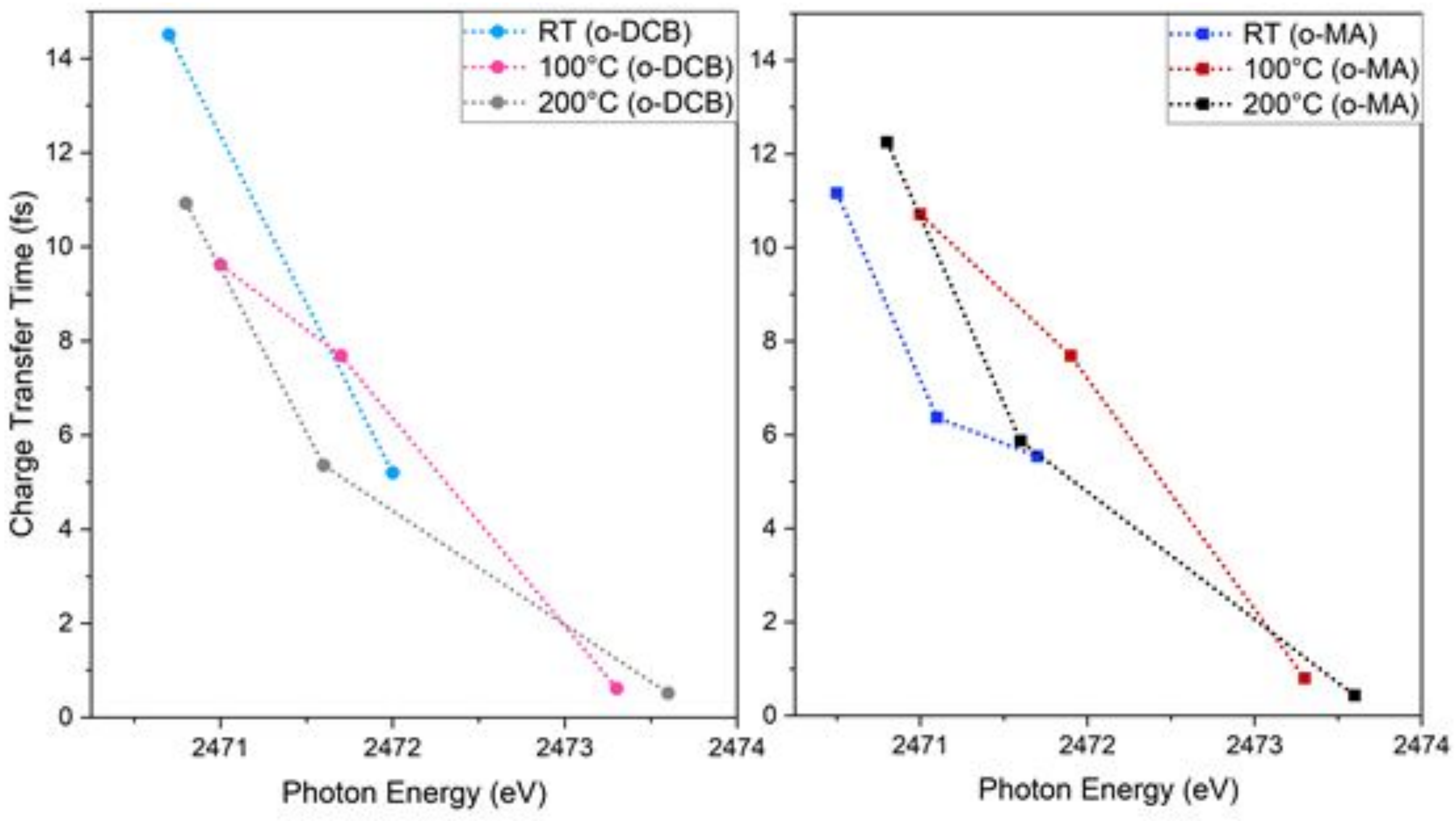
PTB7-TH:ITIC INVESTIGATIONS

Molecular Orientation Under the Solvent Effect and Thermal Annealing

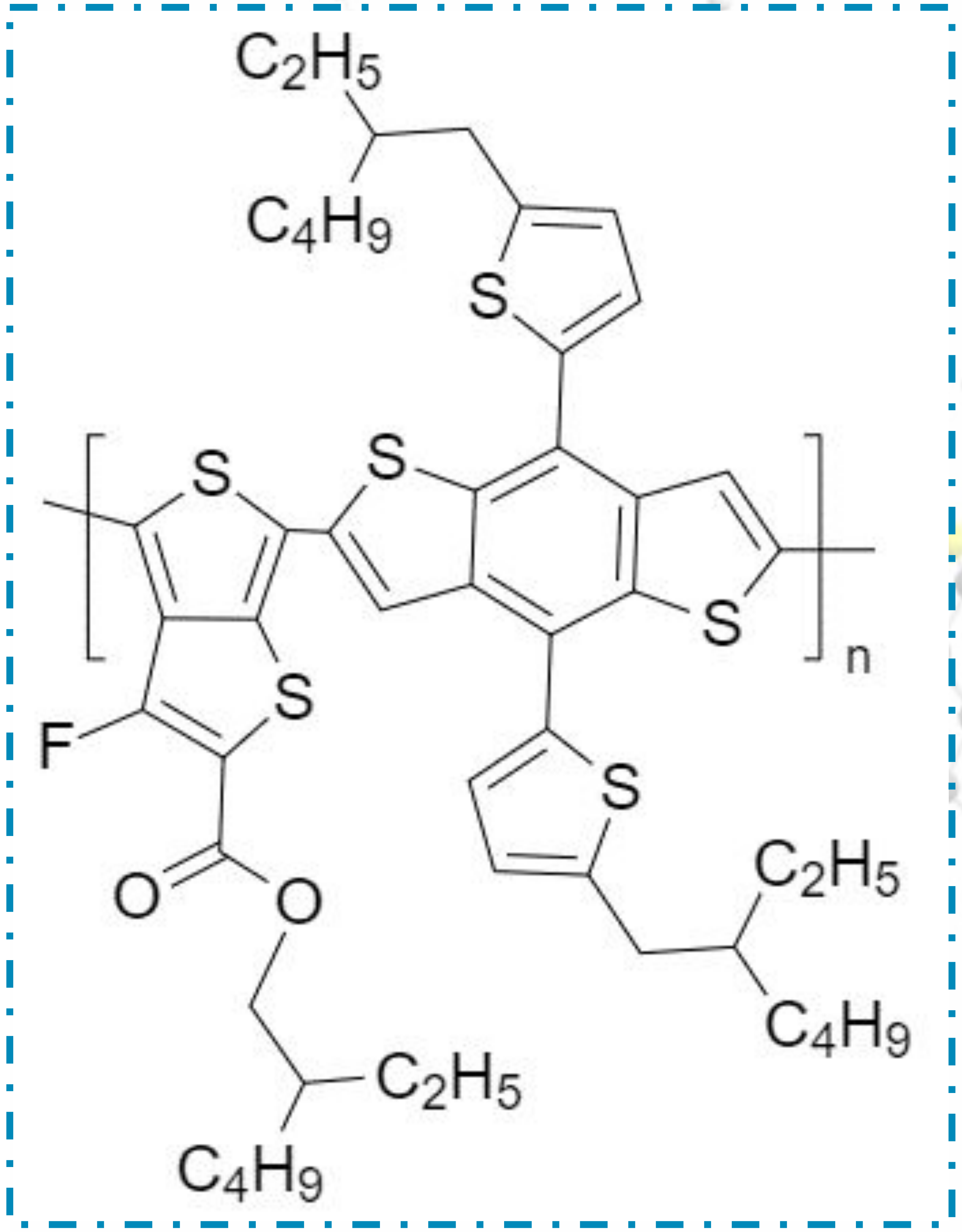
***o*-MA** **o-DCB**

PTB7-TH:ITIC INVESTIGATIONS

Charge Transfer Dynamics Under the Solvent Effect and Thermal Annealing



FINAL CONSIDERATIONS AND FUTURE PERSPECTIVES



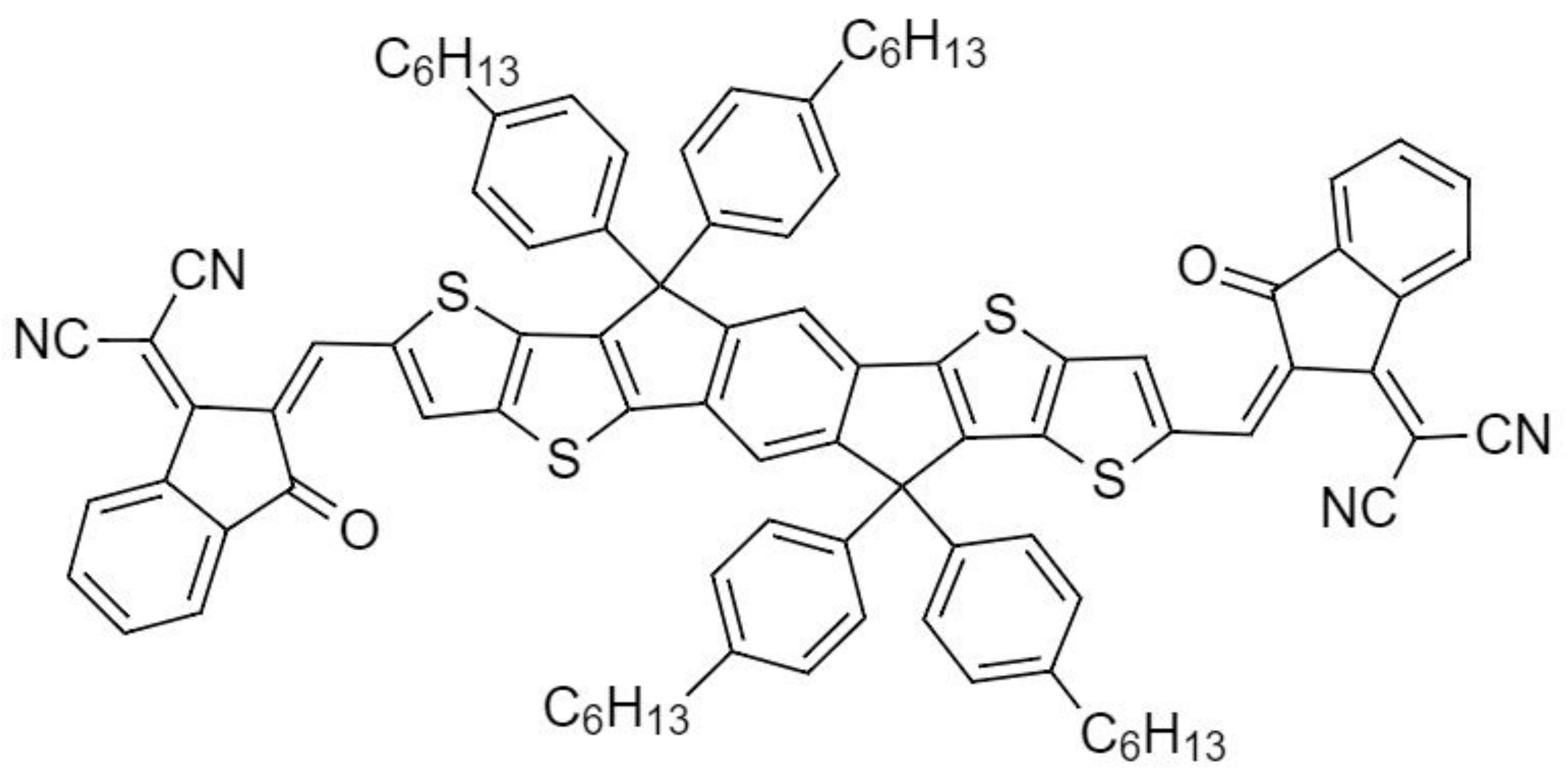
- Stable film with face-on orientation in relation to ITO substrate;

- Similar charge transfer dynamics in both solvent processing;

- The aromatic-quinoid approach helps us understand this type of polymer;

- The calculatations with the monomer helps us understand the NEXAFS spectra.

FINAL CONSIDERATIONS AND FUTURE PERSPECTIVES



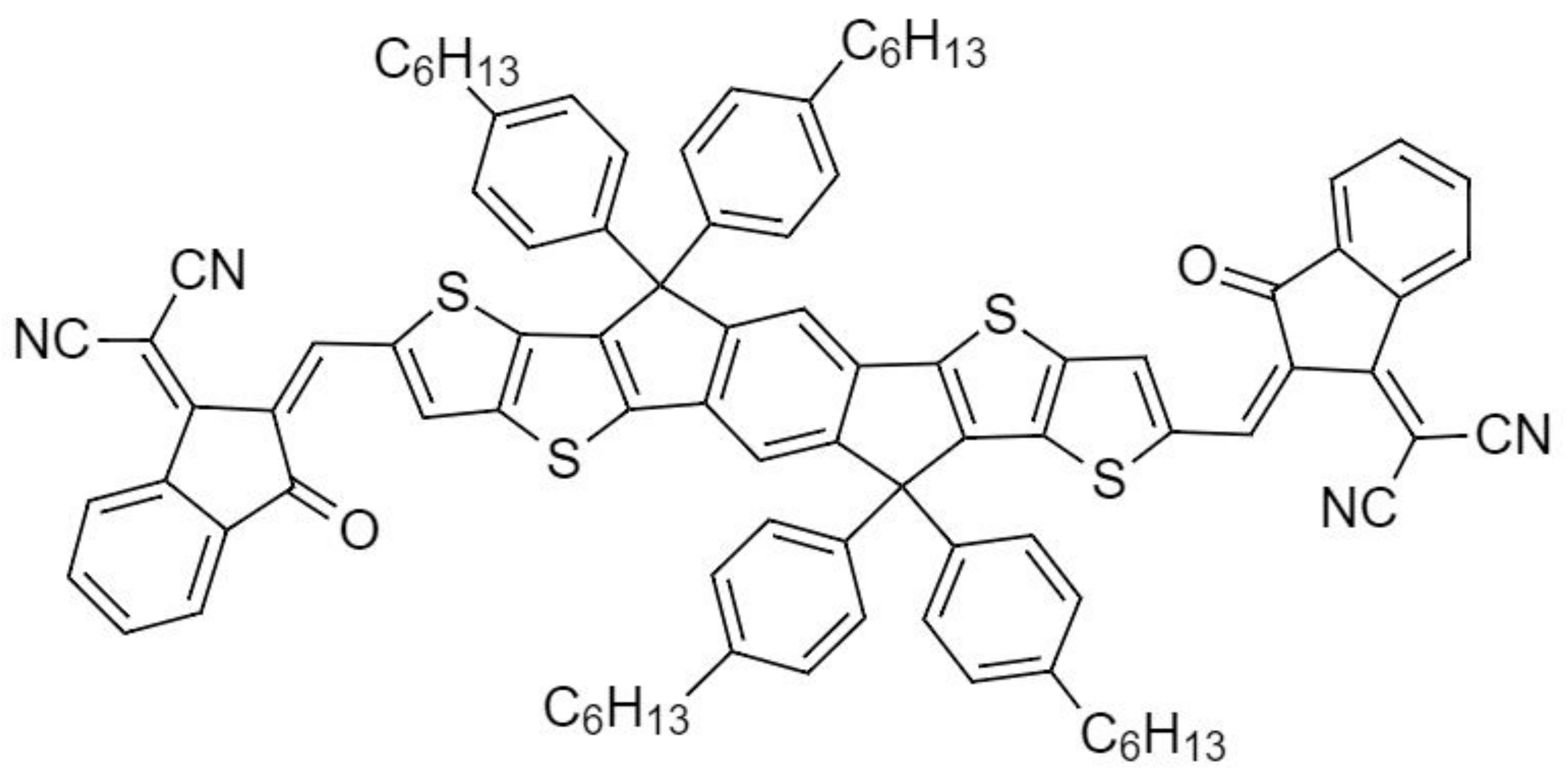
- Suffers severe degradation, principally being processed in *o-DCB;*

- Fast charge transfer dynamics in *o*-DCB, but the *o*-MA film is more stable;

- XPS measurements could help us understand more of this system;

- The calculatations with only main plane helps us understand the NEXAFS spectra.

FINAL CONSIDERATIONS AND FUTURE PERSPECTIVES



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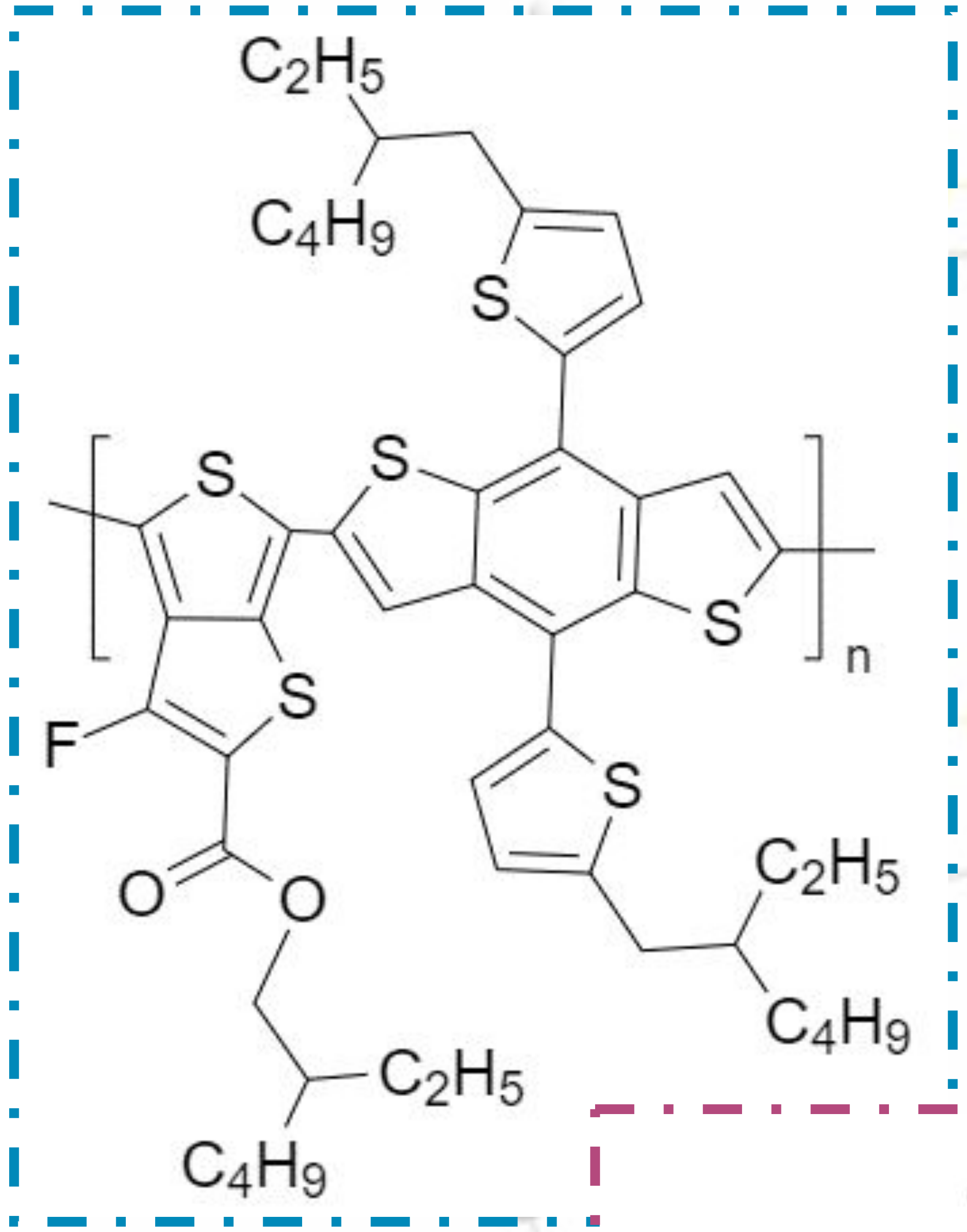
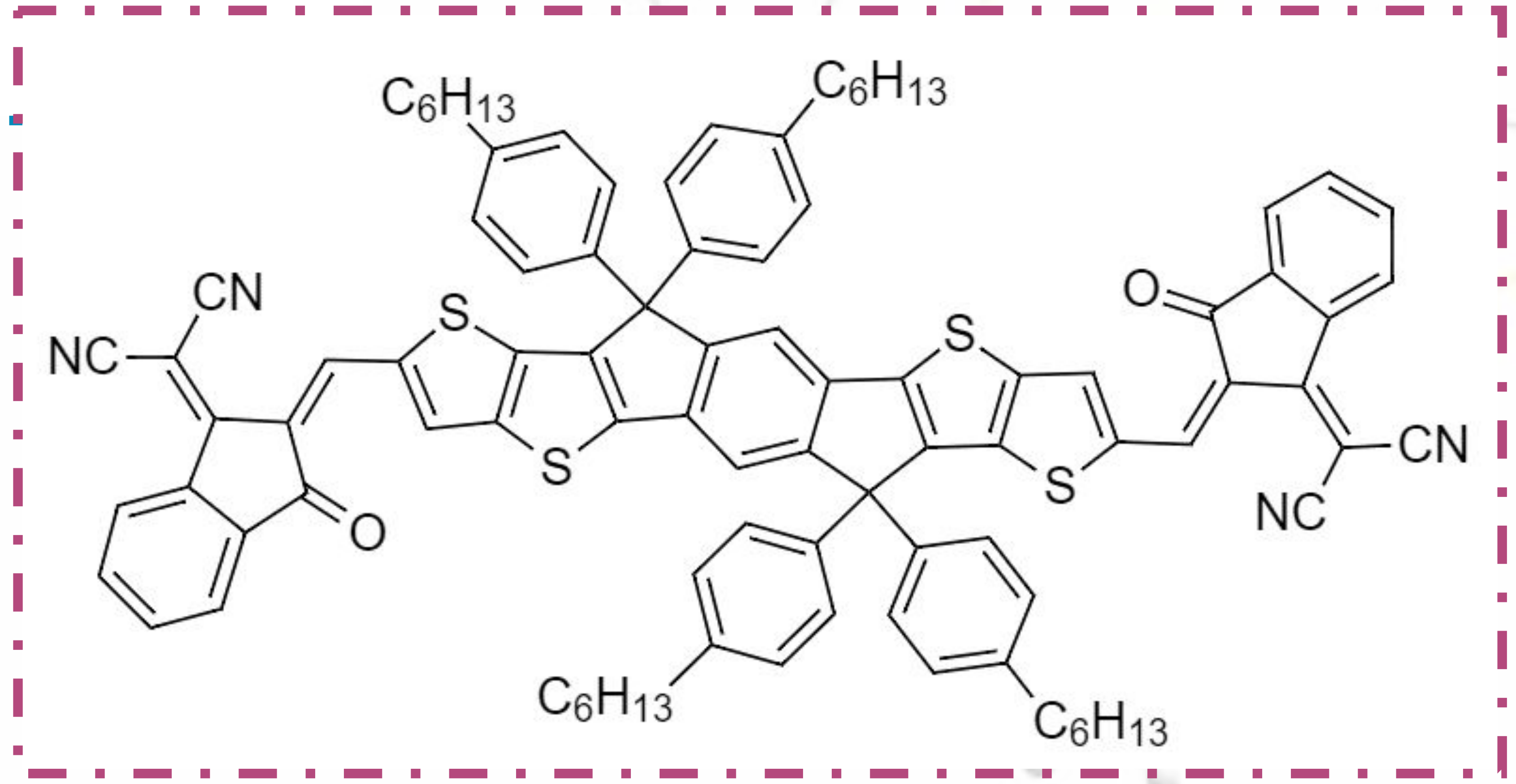
FINAL CONSIDERATIONS AND FUTURE PERSPECTIVES





- Stable film with face-on orientation in relation to ITO substrate;
- The BHJ somehow stabilizes ITIC;
- Yes, it is possible to change to a green solvent!

ACKNOWLEDGEMENTS

CAPES

LNLS

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