Energy levels in molecular doping of organic semiconductors

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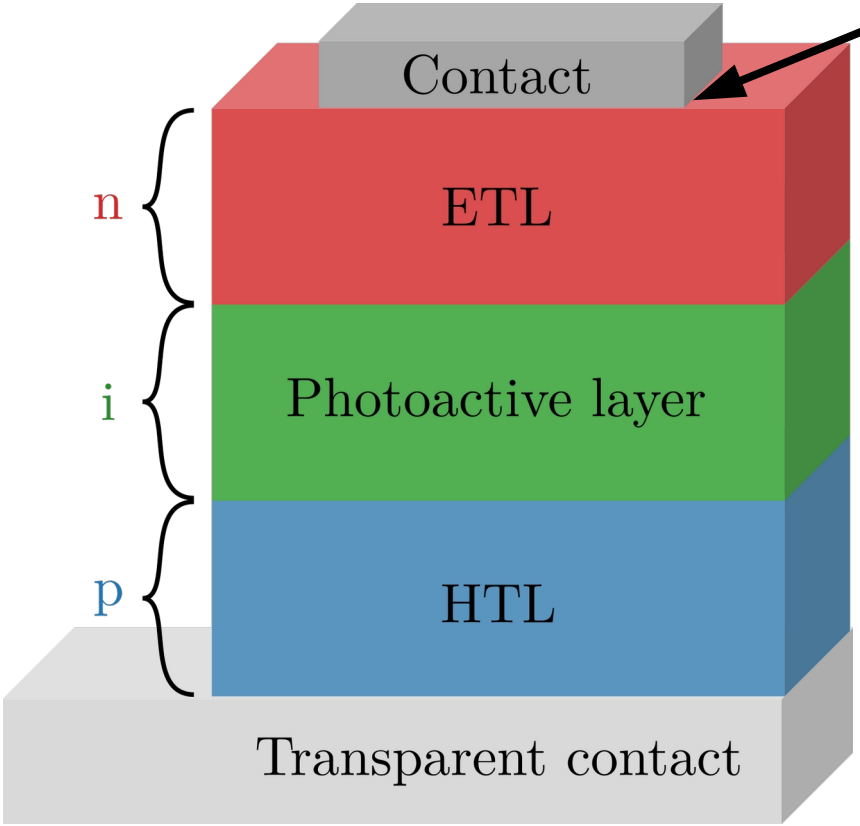
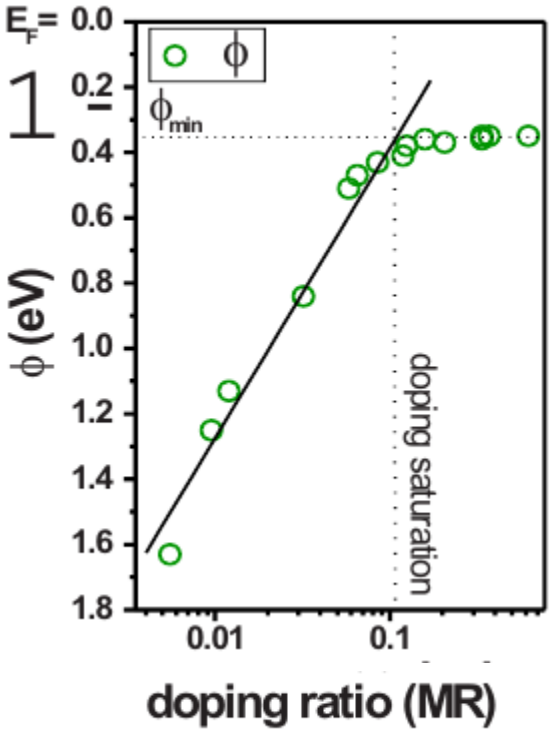
13th December 2019
MRM19, Yokohama, Japan

Motivation

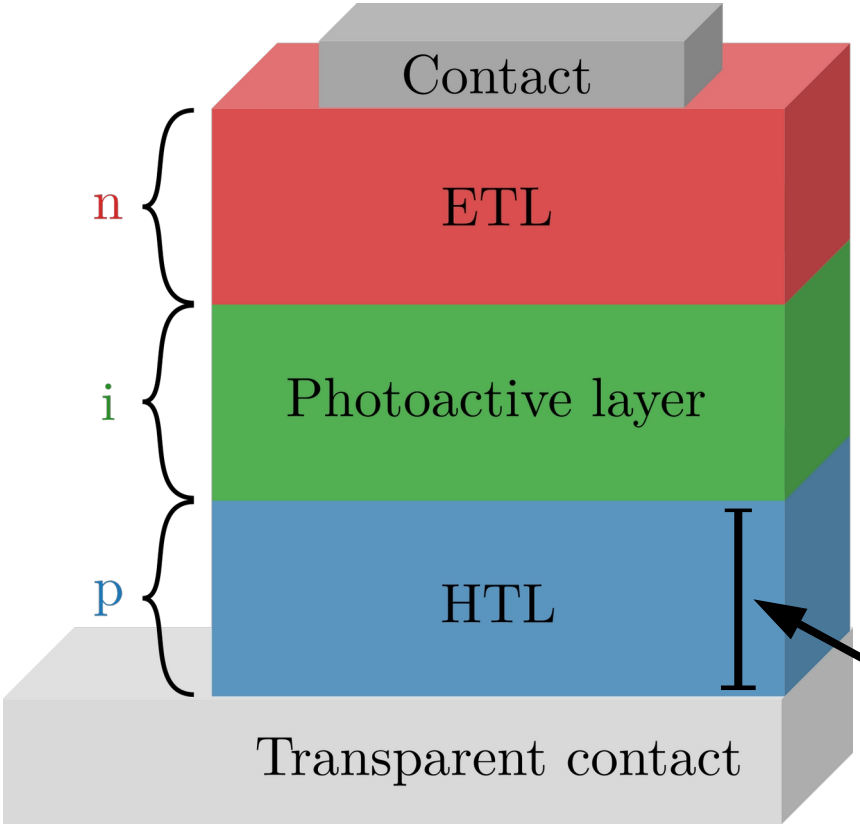
(1) Ohmic injection

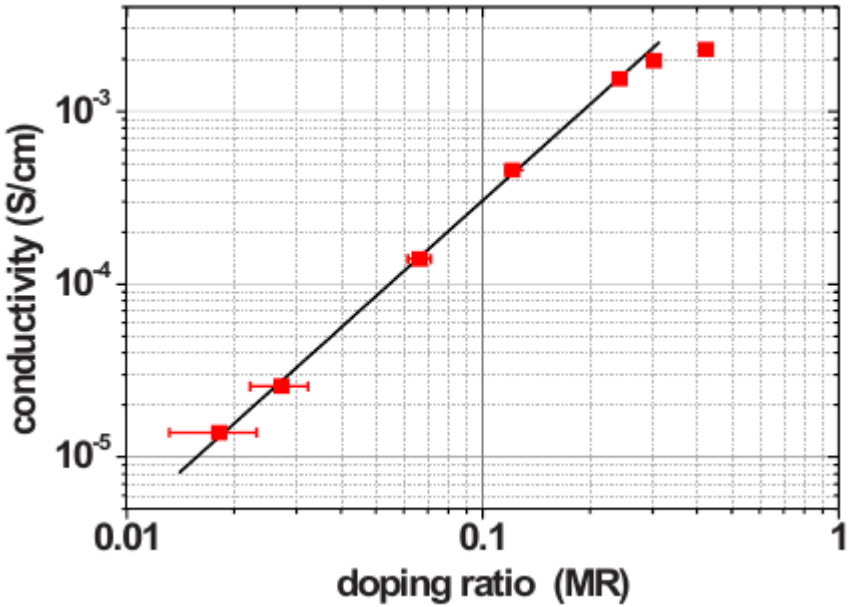




S. Olthof *et al.* J. Appl. Phys. **106,** 103711 (2009)

Motivation





(2) Reduce resistive loss

S. Olthof *et al.* J. Appl. Phys. **106,** 103711 (2009)

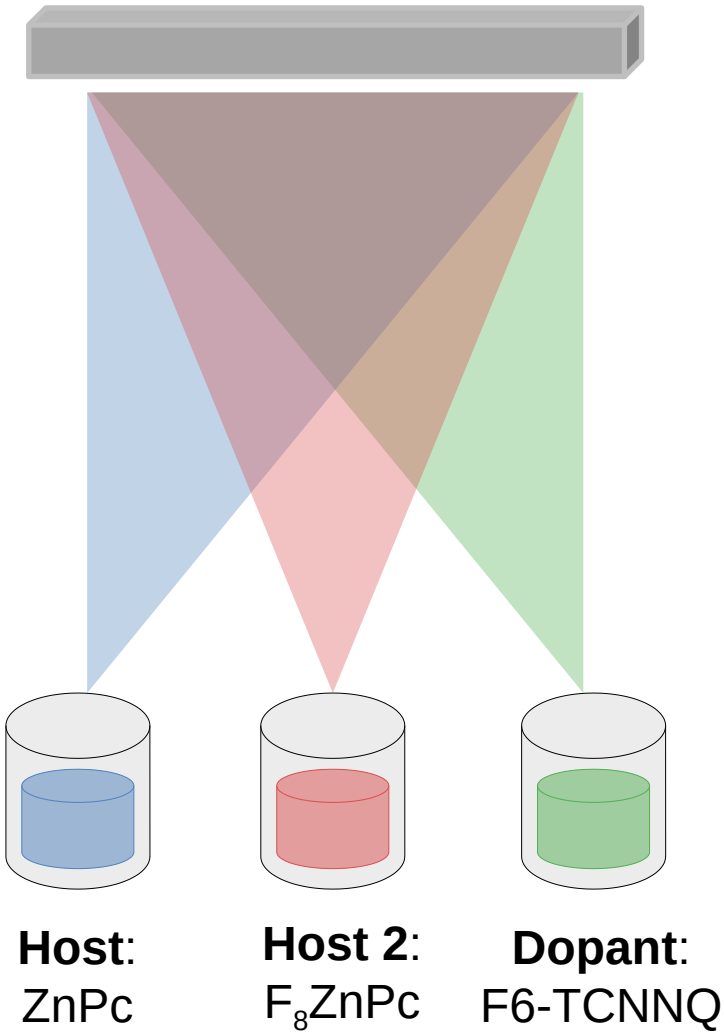
Outline

(1) Doping and energy levels

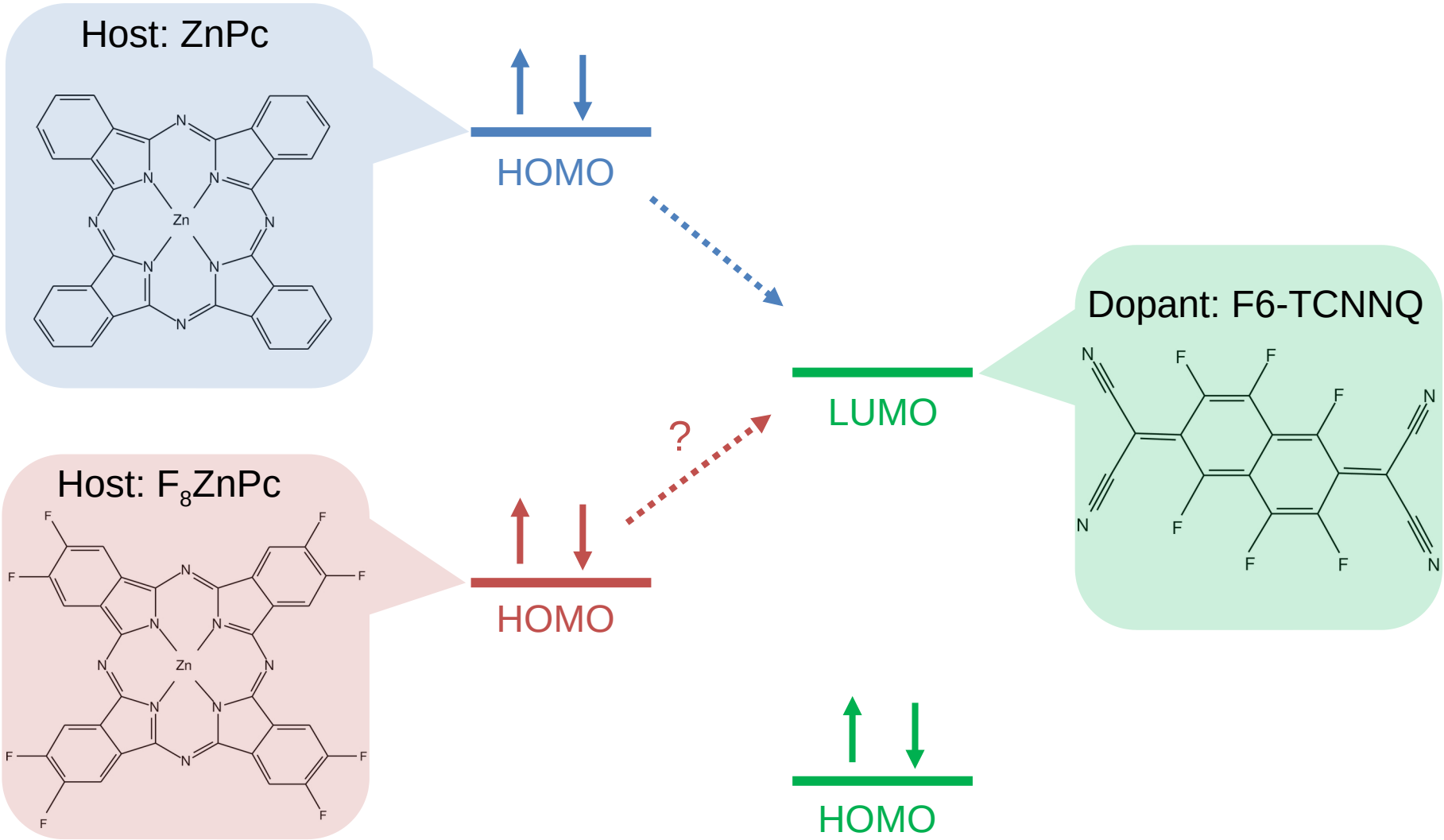
(2) Experimental results

(3) Statistical model

(4) Conclusion

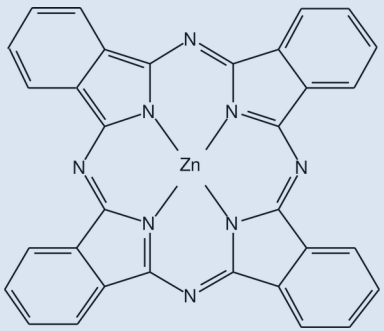


Molecular doping and energy levels

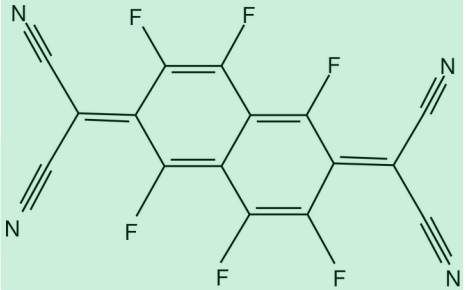


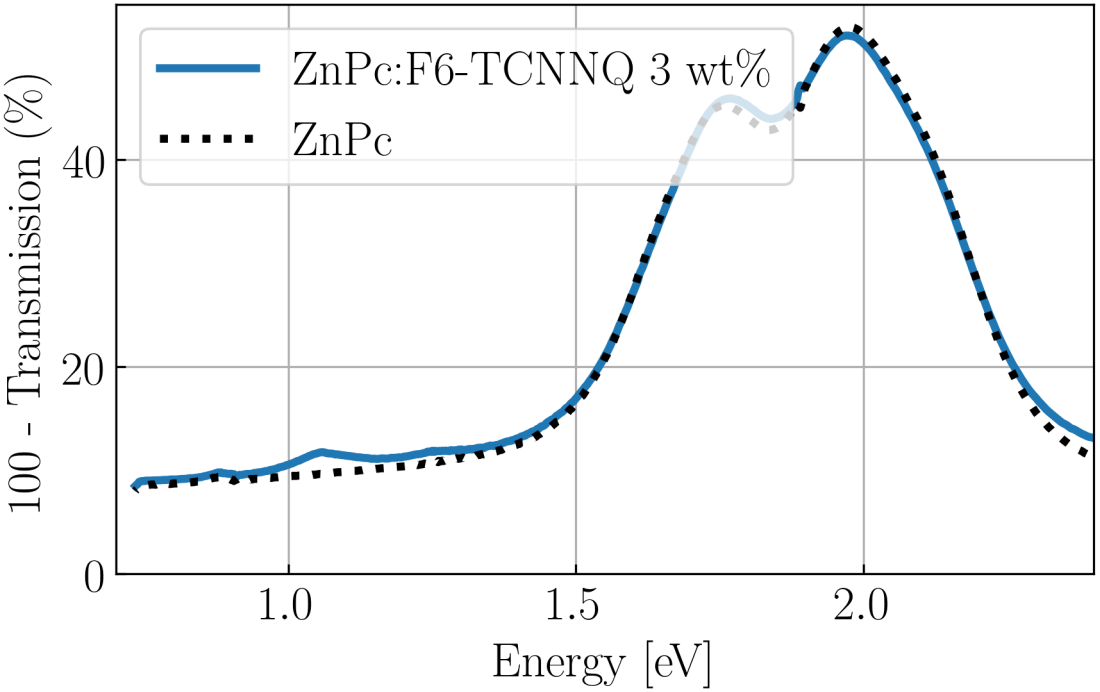
UV-vis absorption of thin films

ZnPc



F6-TCNNQ **3 wt%**





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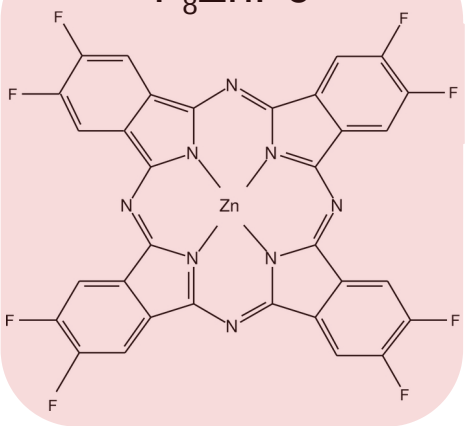

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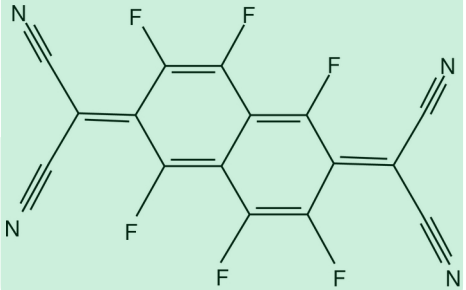
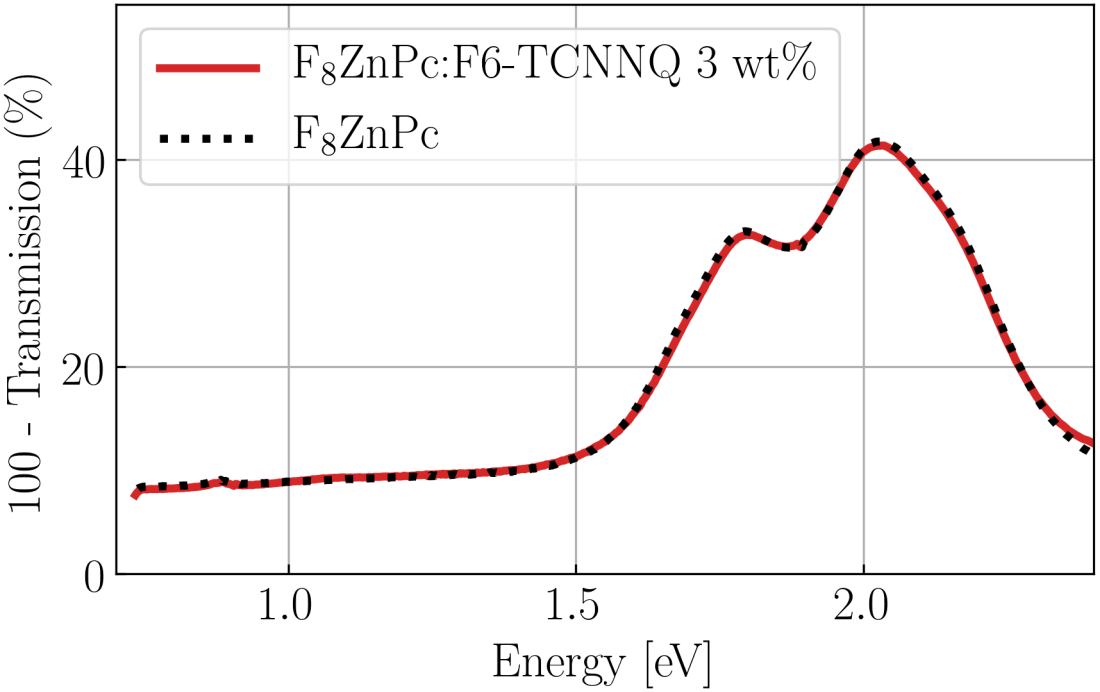
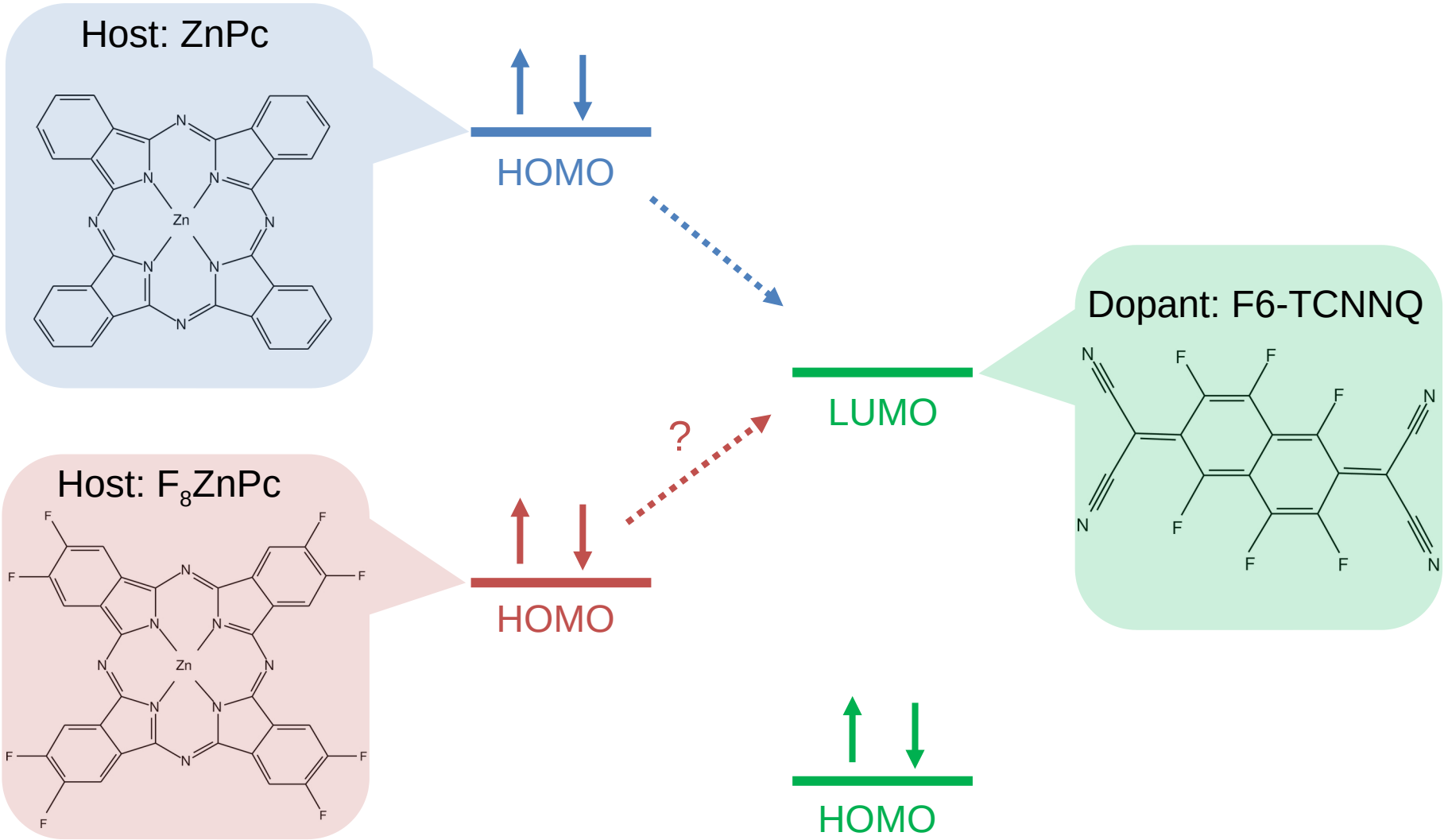




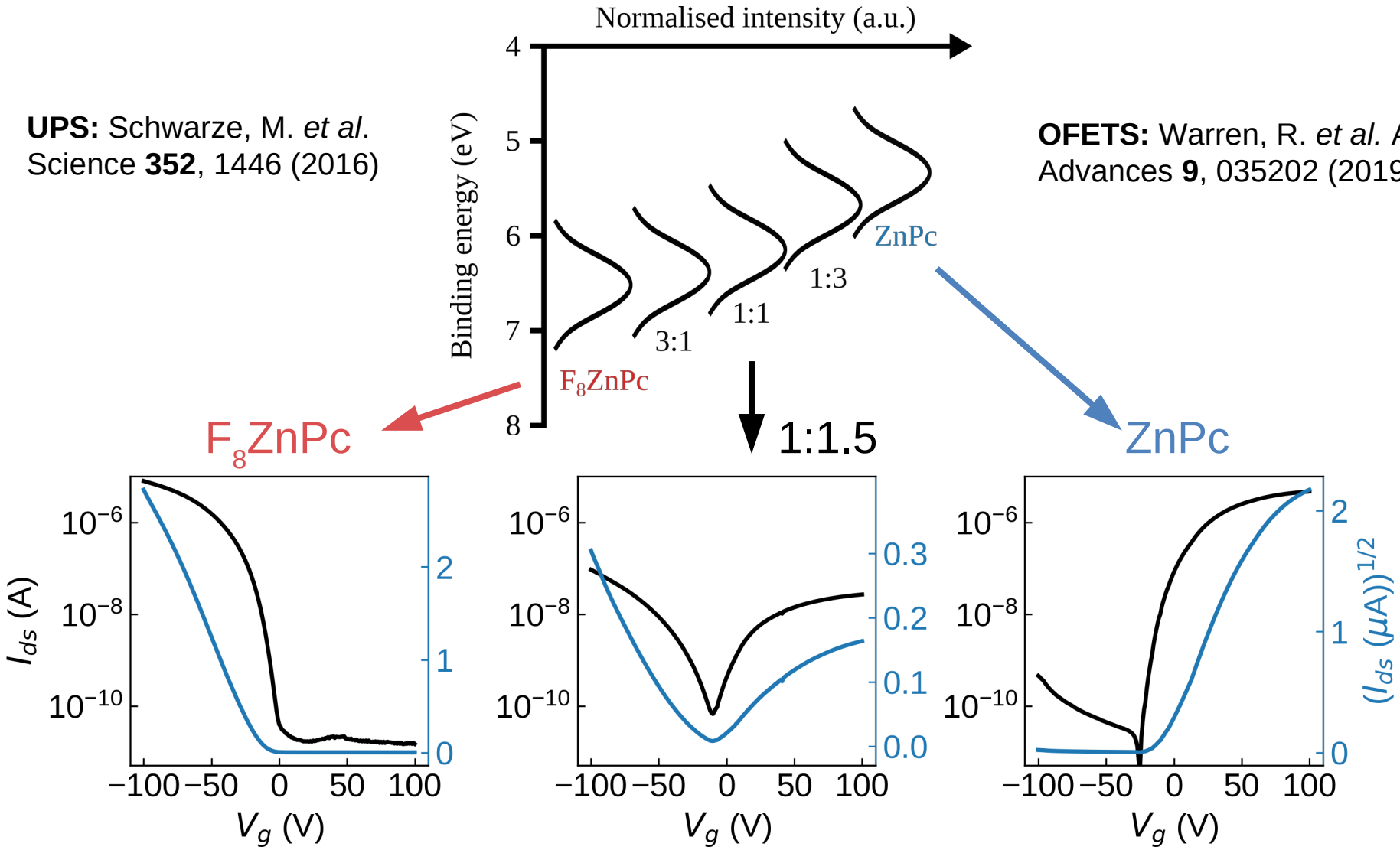
Molecular doping and energy levels



Energy level tuning

UPS: Schwarze, M. *et al.* Science **352**, 1446 (2016)

OFETS: Warren, R. *et al.* AIP Advances **9**, 035202 (2019)



Photothermal deflection spectroscopy

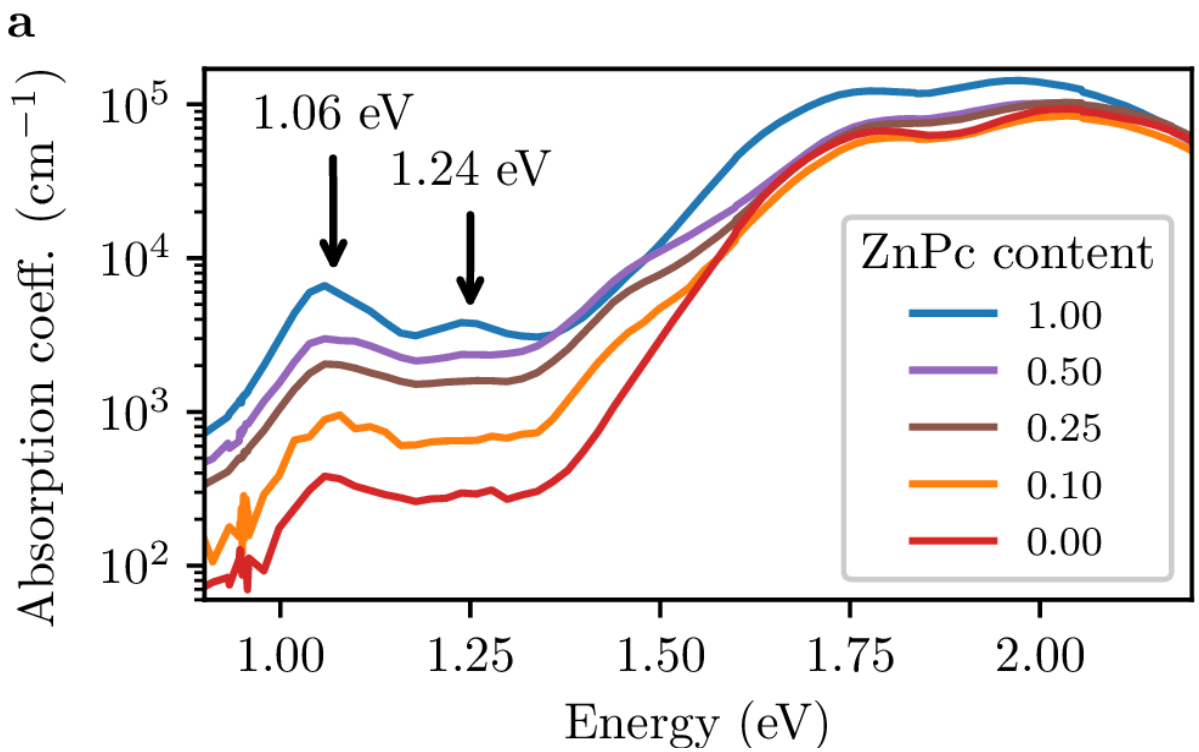
Host blend

ZnPc

F_8ZnPc

Dopant

F6-TCNNQ **3 wt%**



Warren *et al. Nat Commun* **10,** 5538 (2019)

Photothermal deflection spectroscopy

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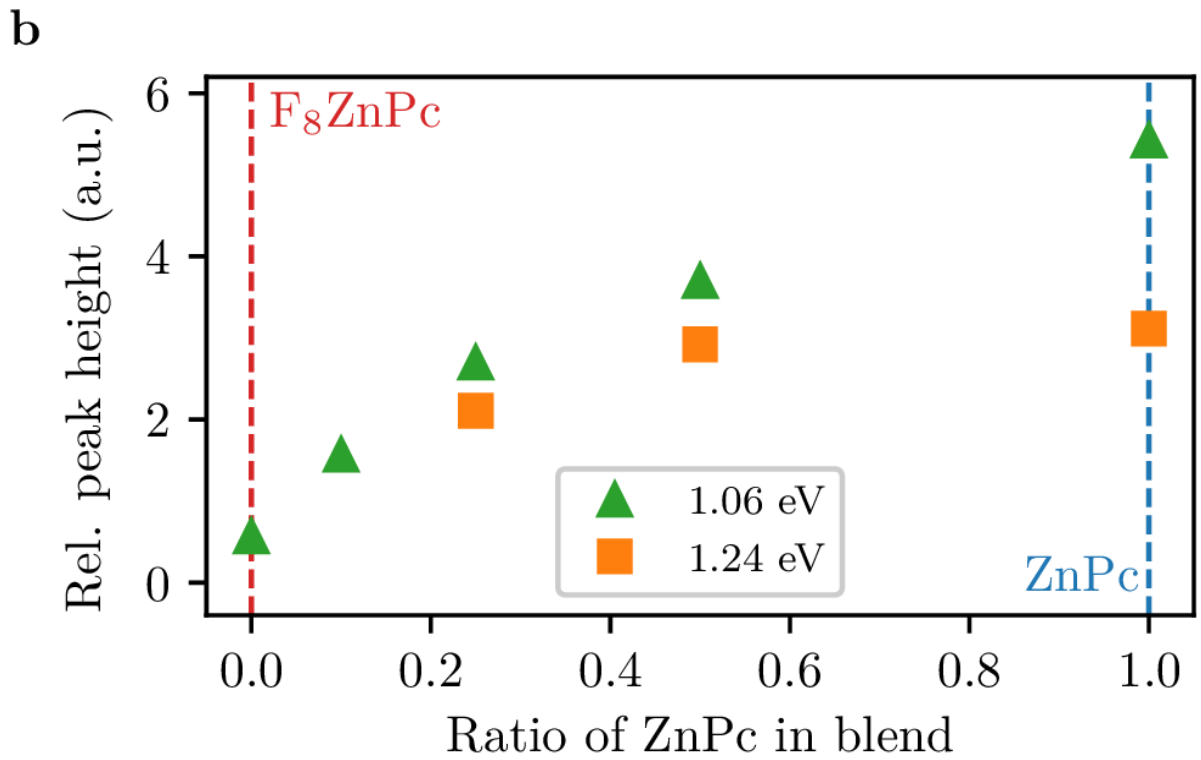

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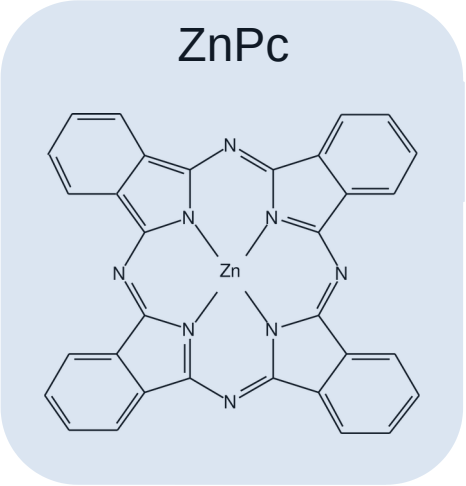
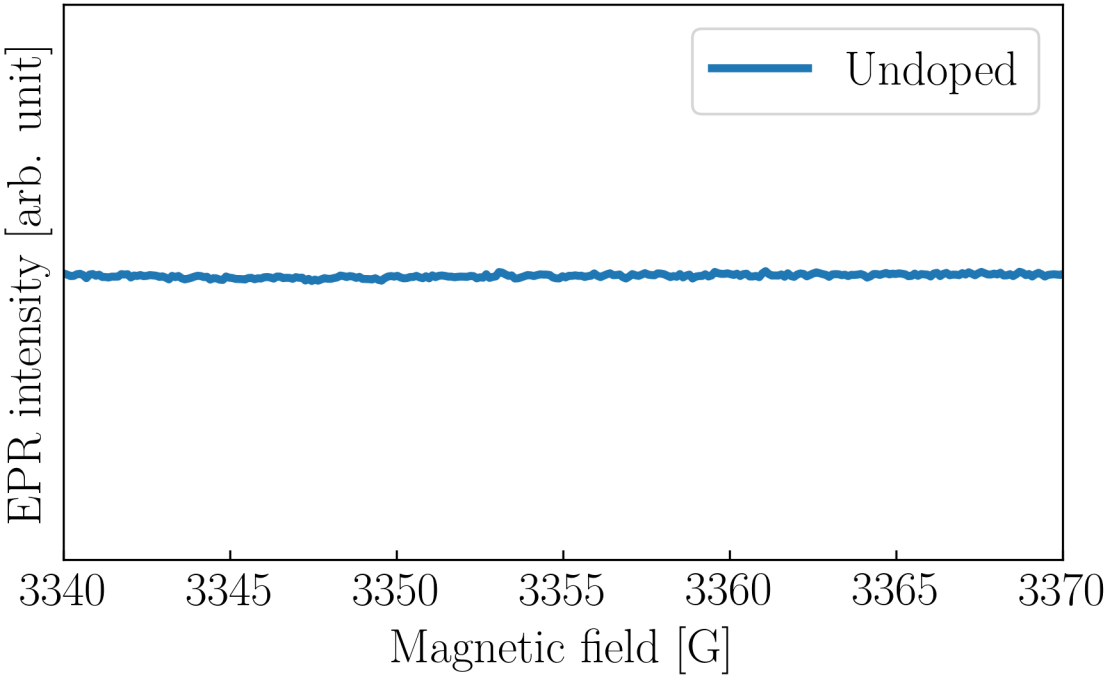
Electron paramagnetic resonance





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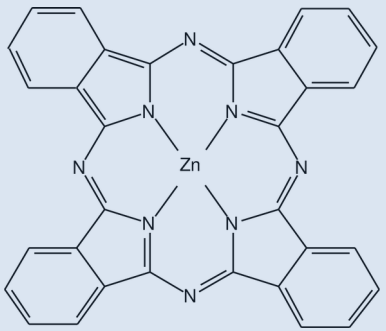

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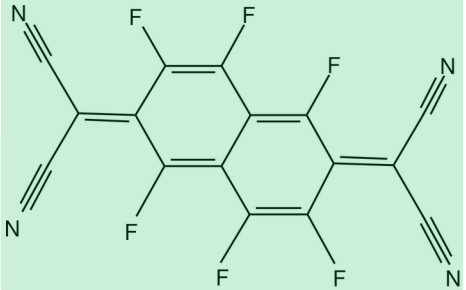
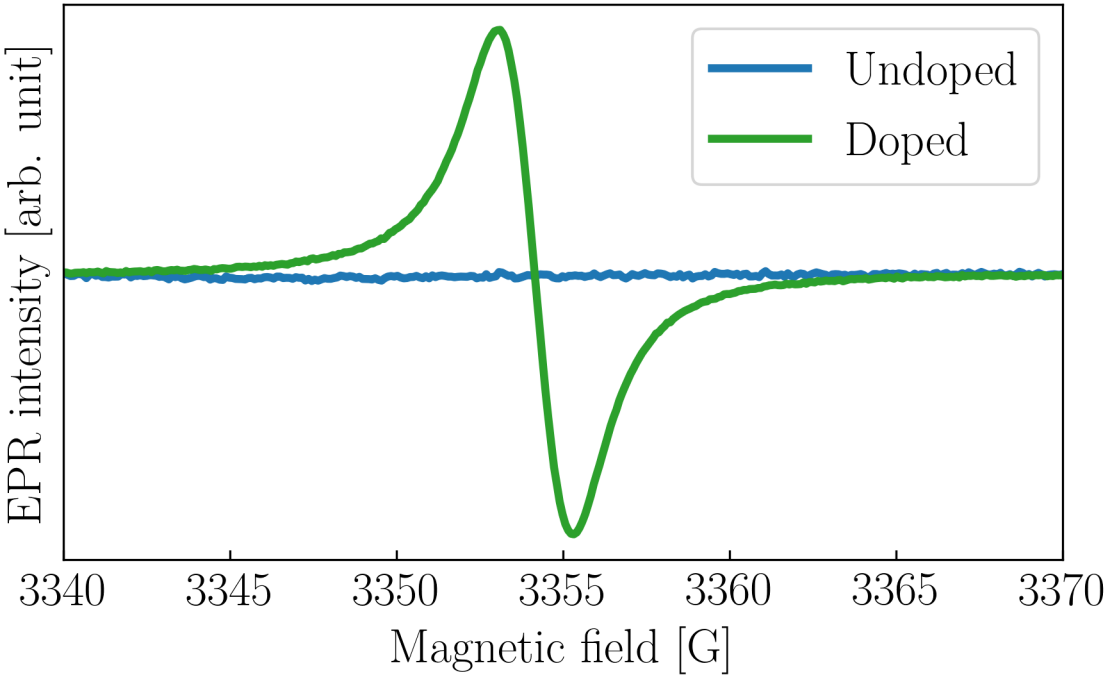




Electron paramagnetic resonance

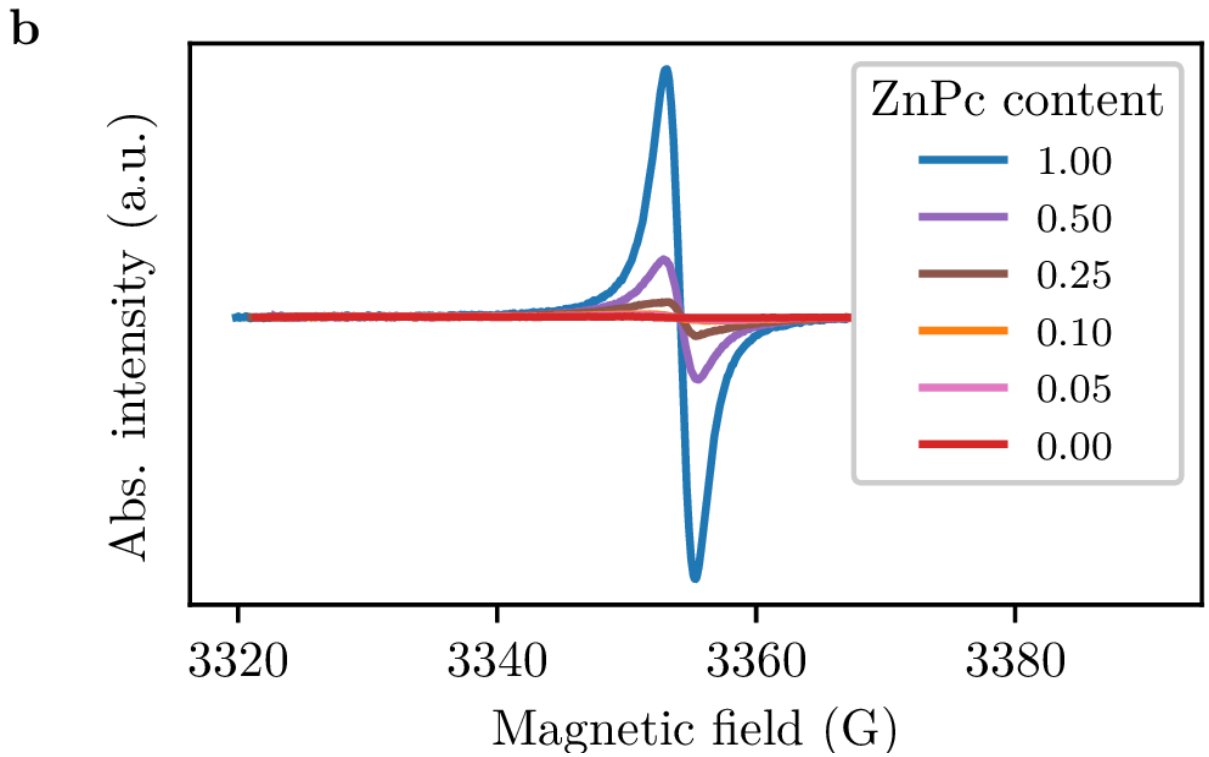
Host blend

ZnPc

F_8ZnPc

Dopant

F6-TCNNQ **3 wt%**



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Electron paramagnetic resonance

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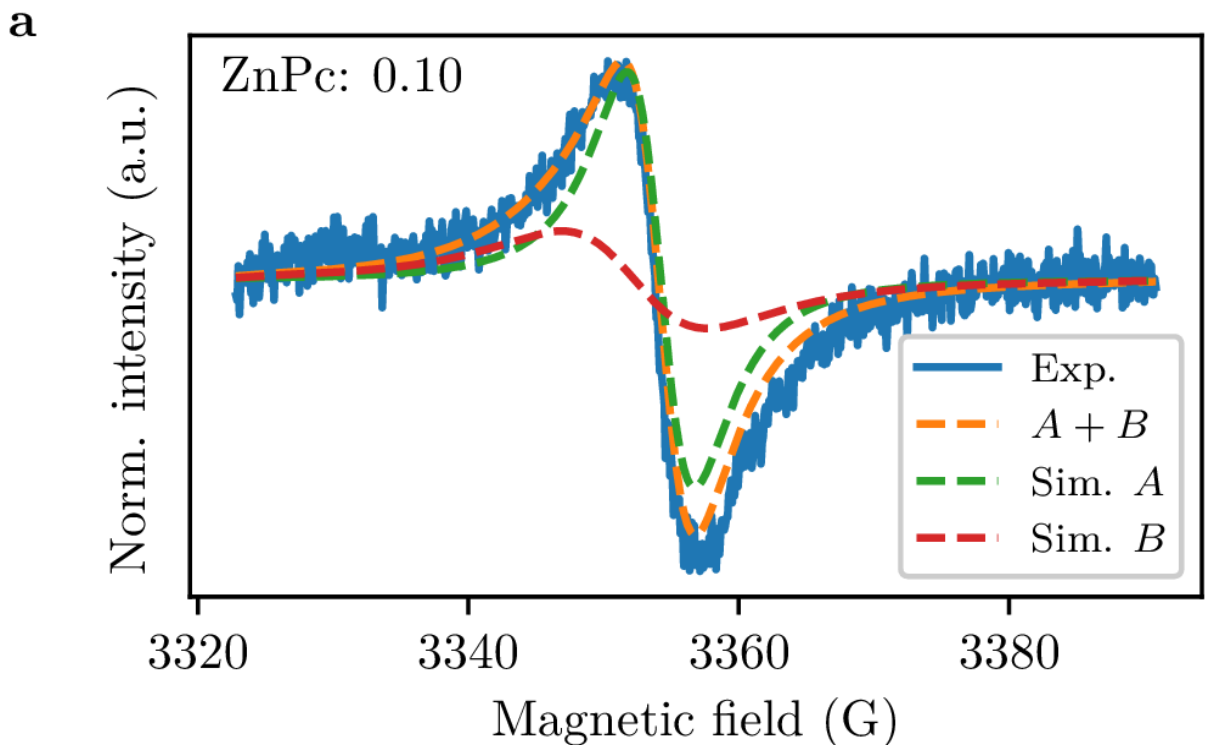

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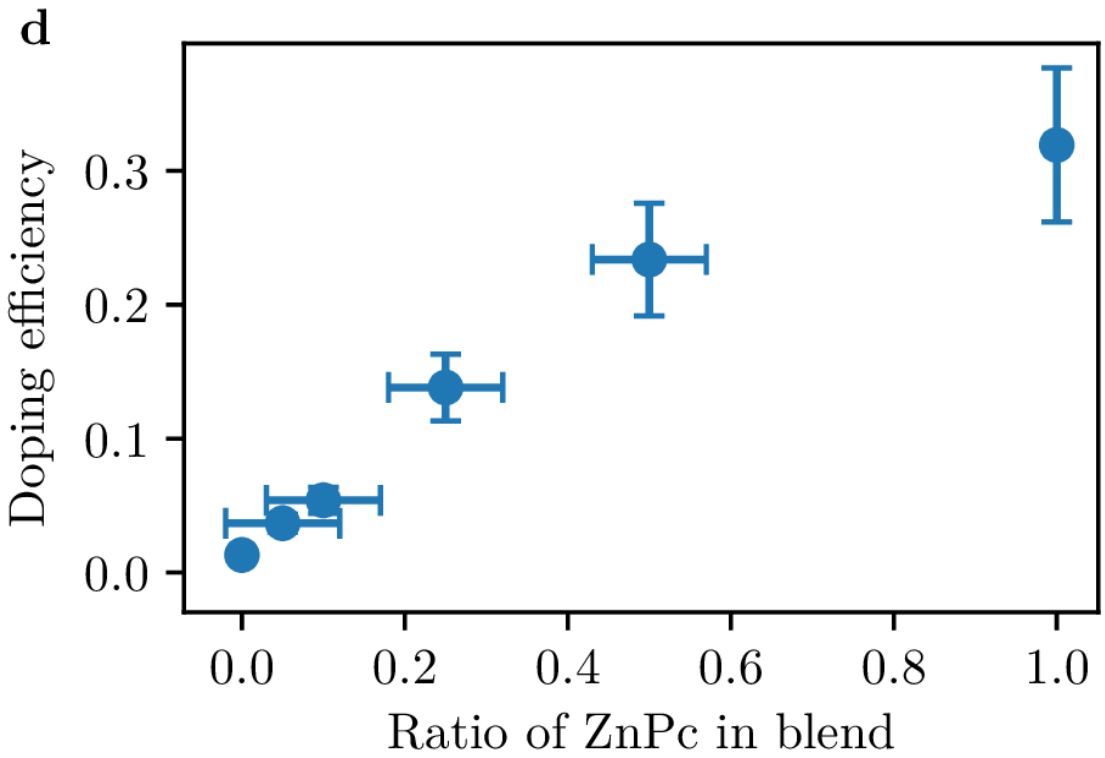

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Electron paramagnetic resonance

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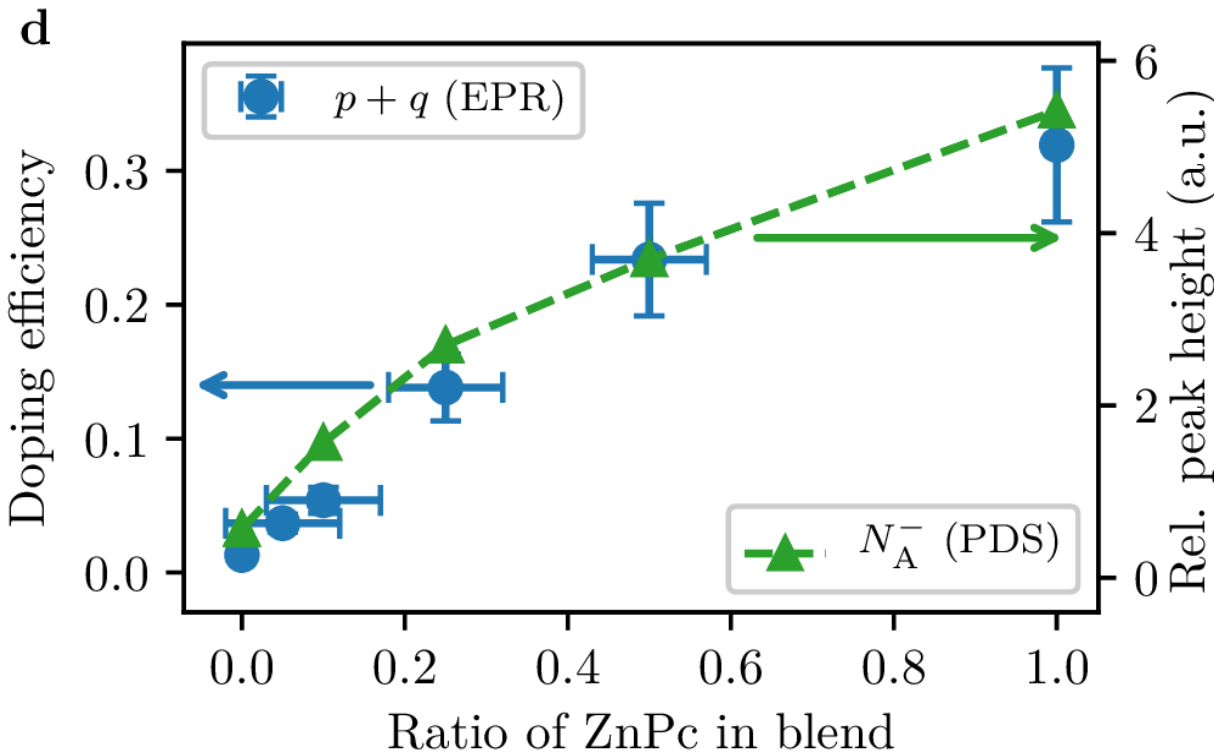

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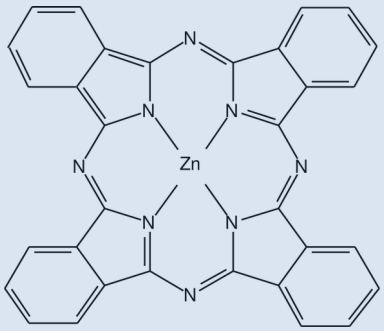
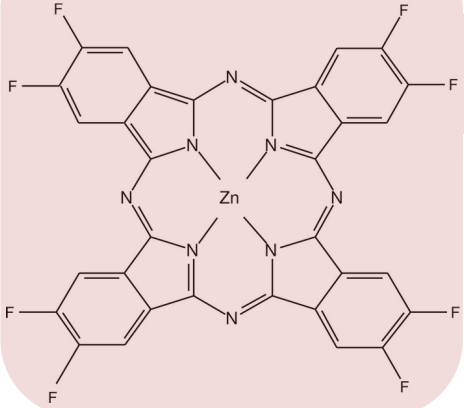
Statistical model

Host: ZnPc

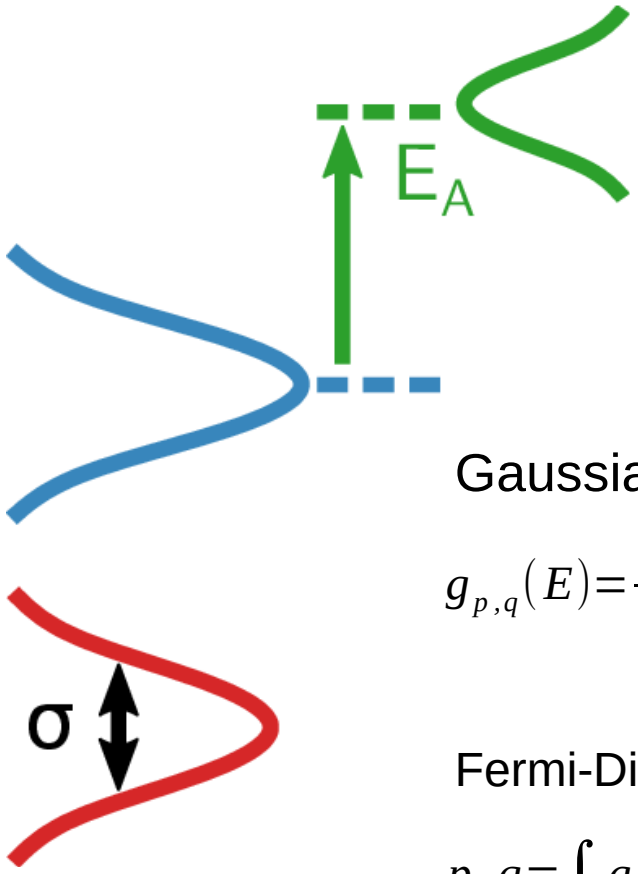


Host: F_8ZnPc

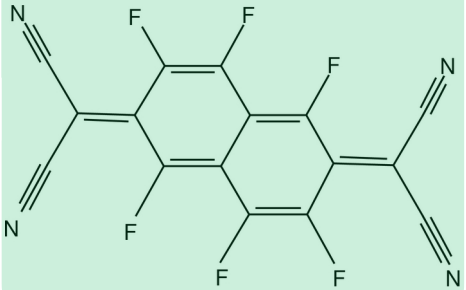


Neutrality eq.:

$$p+q=N_A^-$$



Dopant: F6-TCNNQ



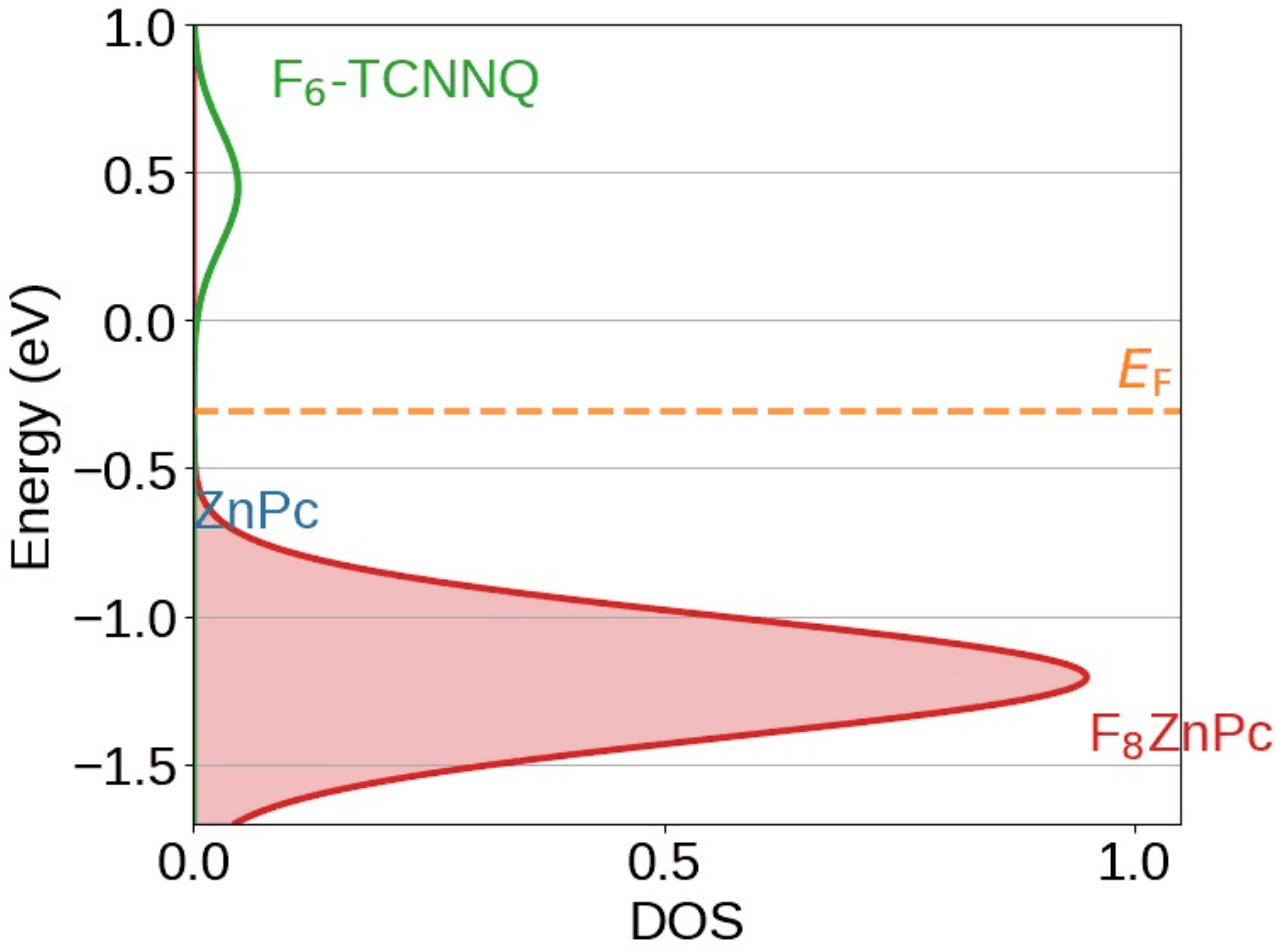
Gaussian DOS:

$$g_{p,q}(E)=\frac{N_0}{\sqrt{2\pi}\sigma}\exp\left[\frac{(E-E_{p,q})^2}{2\sigma^2}\right]$$

Fermi-Dirac statistics:

$$p,q=\int g_{p,q}(E)[1-f(e)]\ dE$$

Model 1 – dopant level fixed



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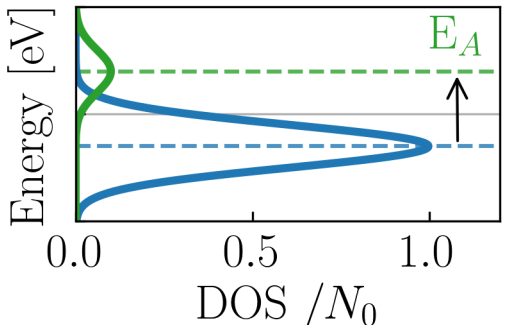

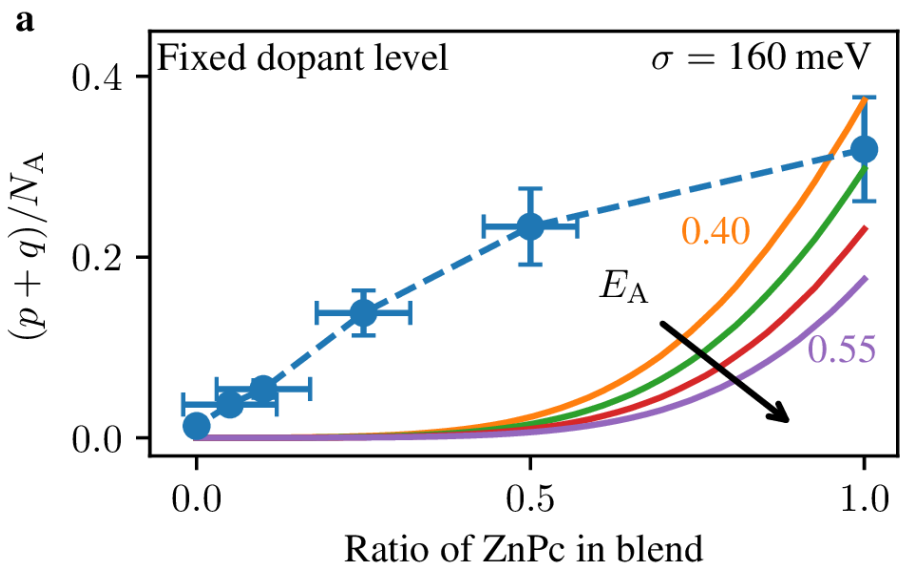

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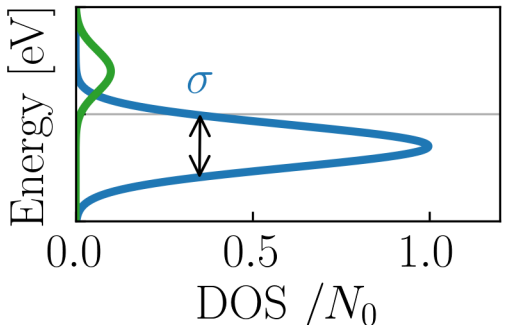

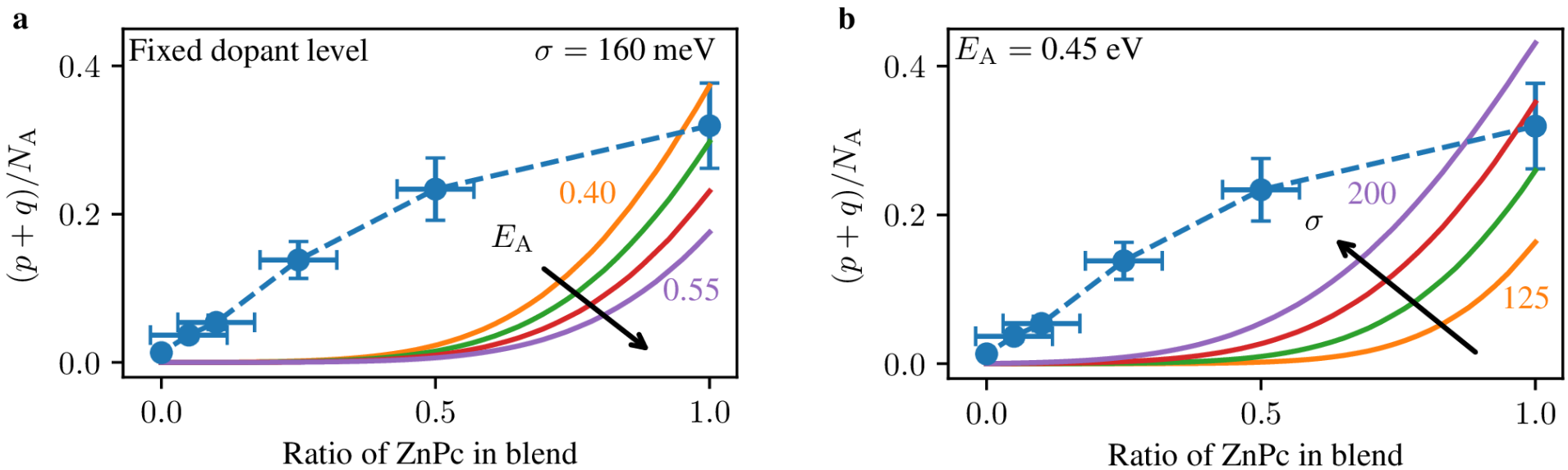

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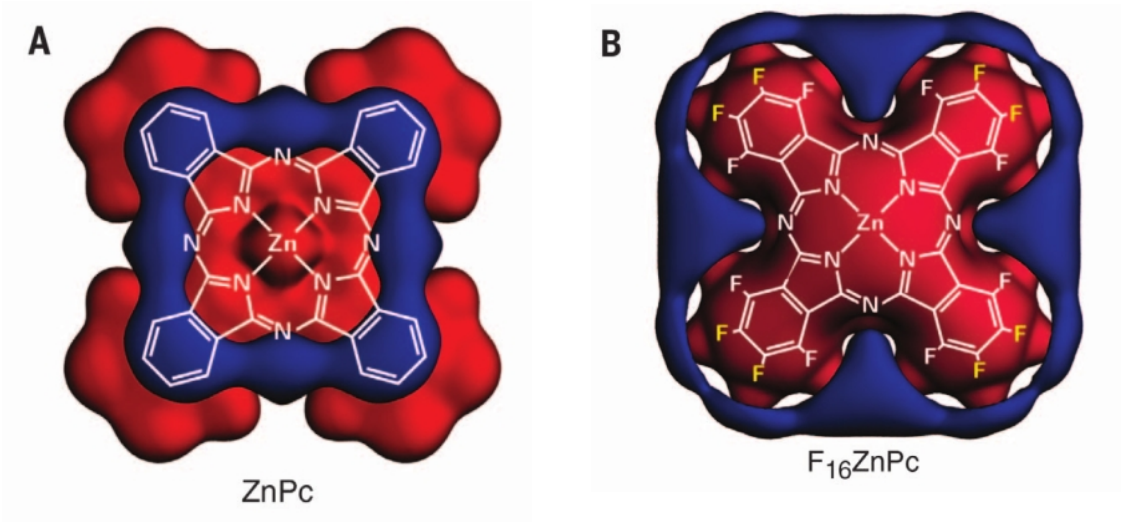
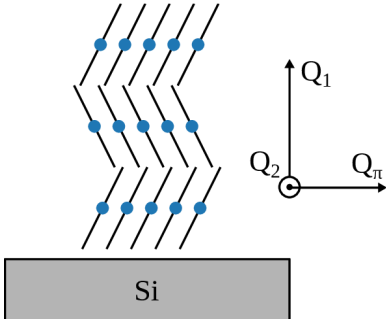
Including electrostatic interactions

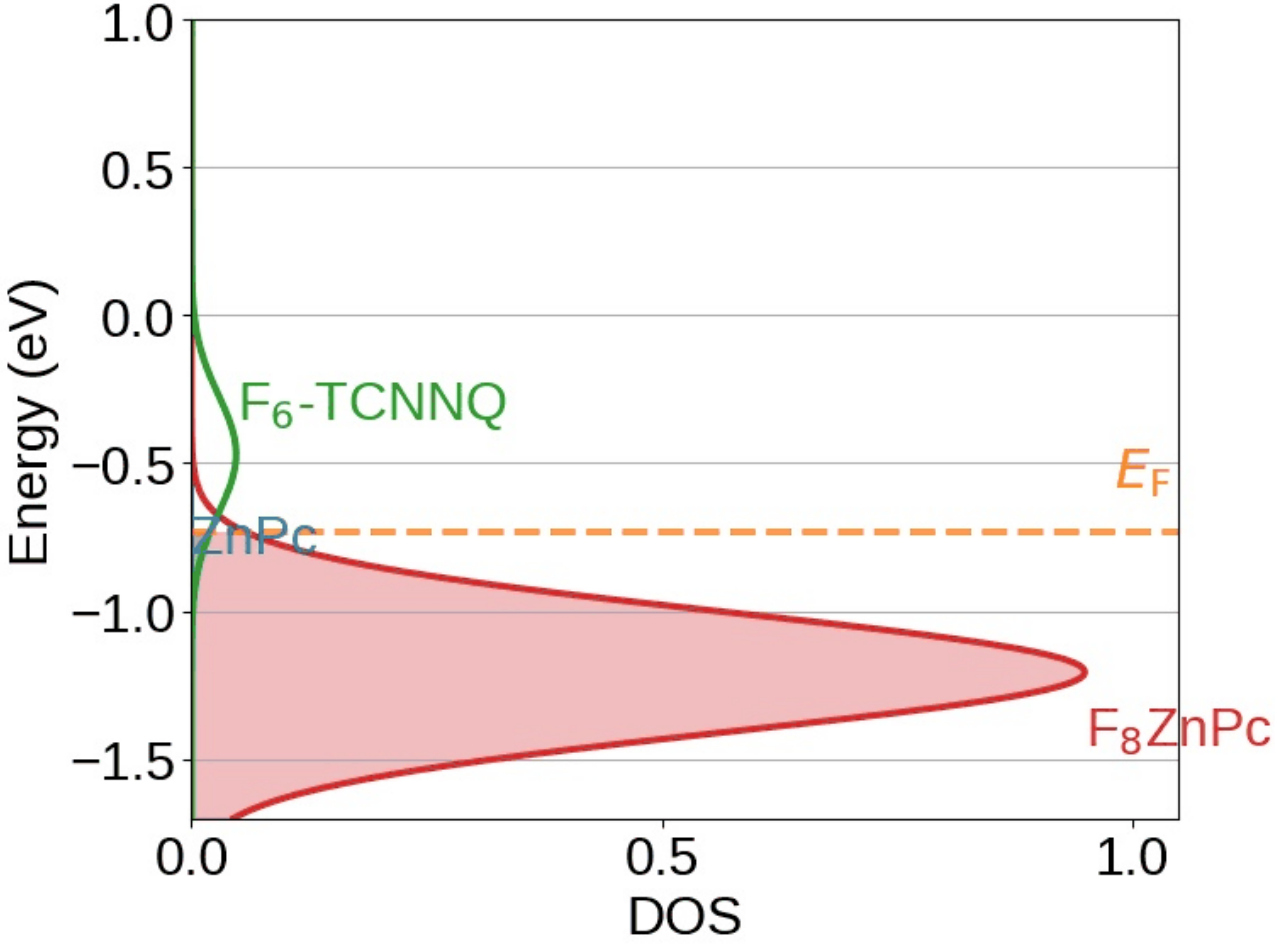


Molecule	Q_1	Q_2	Q_3
ZnPc	12.35	12.35	-24.69
F_8ZnPc	-15.31	-15.31	30.61
F6-TCNNQ	-38.91	2.08	36.83



Schwarze, M. *et al*. Science **352**, 1446 (2016)
Warren *et al. Nat Commun* **10,** 5538 (2019)

Model 2 – dopant level shifting



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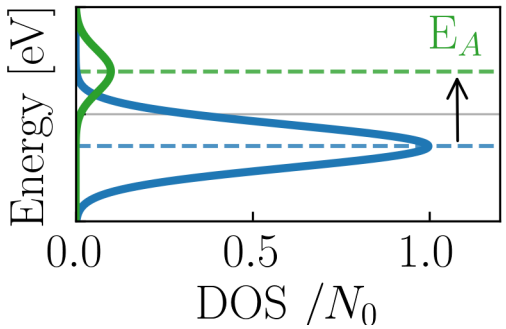

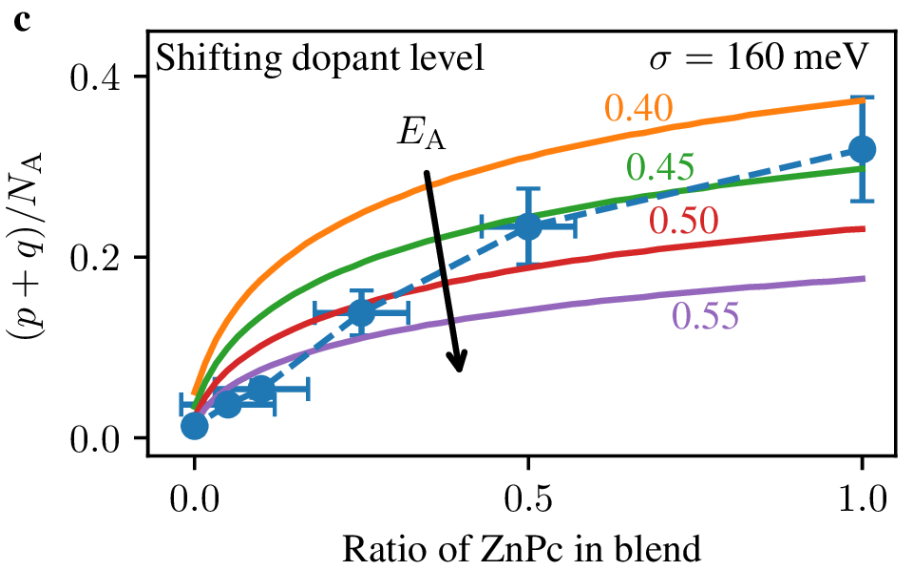

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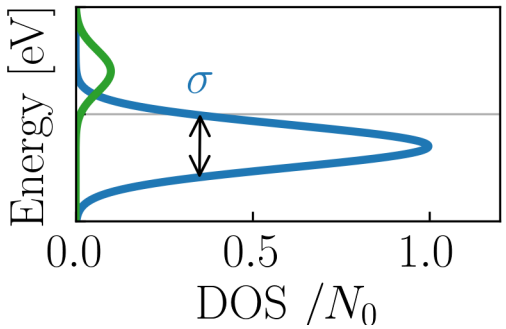

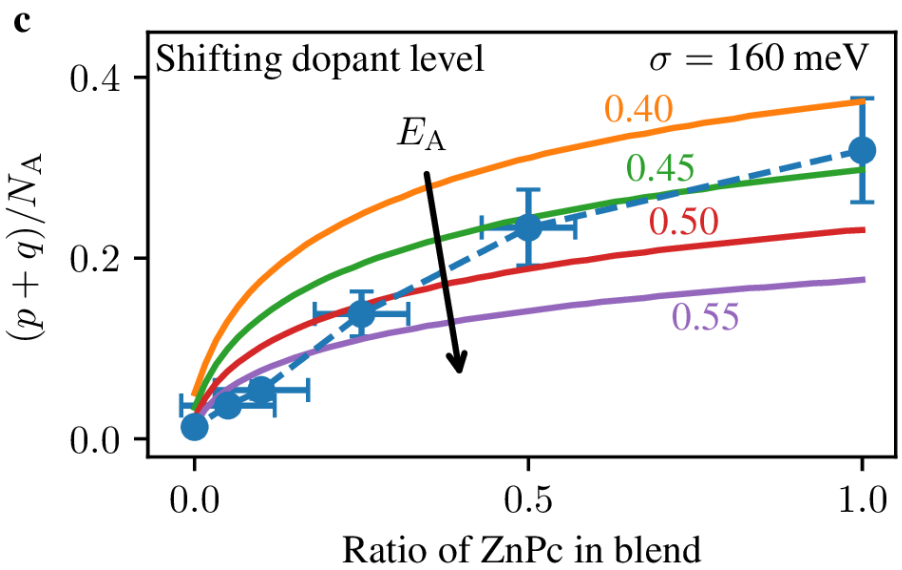

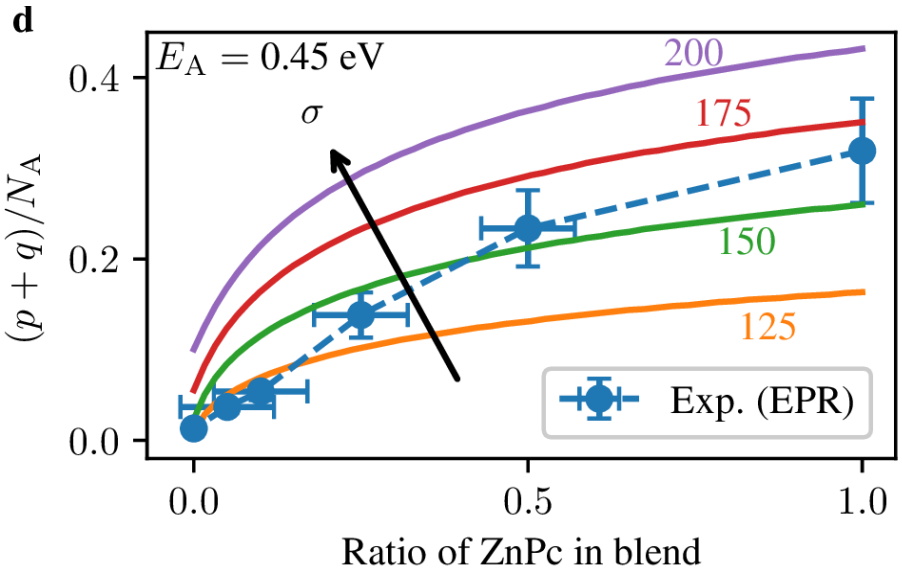

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Conclusion

- **Energy level tuning** in the doping process in ZnPc : F_8ZnPc : F6-TCNNQ using **PDS**, **EPR** and a **statistical model**.

- **Decrease** in the **doping efficiency** as the content of ZnPc in the blend of ZnPc : F_8ZnPc **decreases**.

- We present two models:
    - with a **fixed** dopant level
    - with a **shifting** dopant level
- **Energy level tuning effects** that influence the host's energy, should also be considered for the dopant's energy level.

Acknowledgements

Jenny Nelson

Pascal Kaienburg

Oliver Thimm
(FC Jülich)

Alberto Privitera

Moritz Riede

Andreas Lauritzen

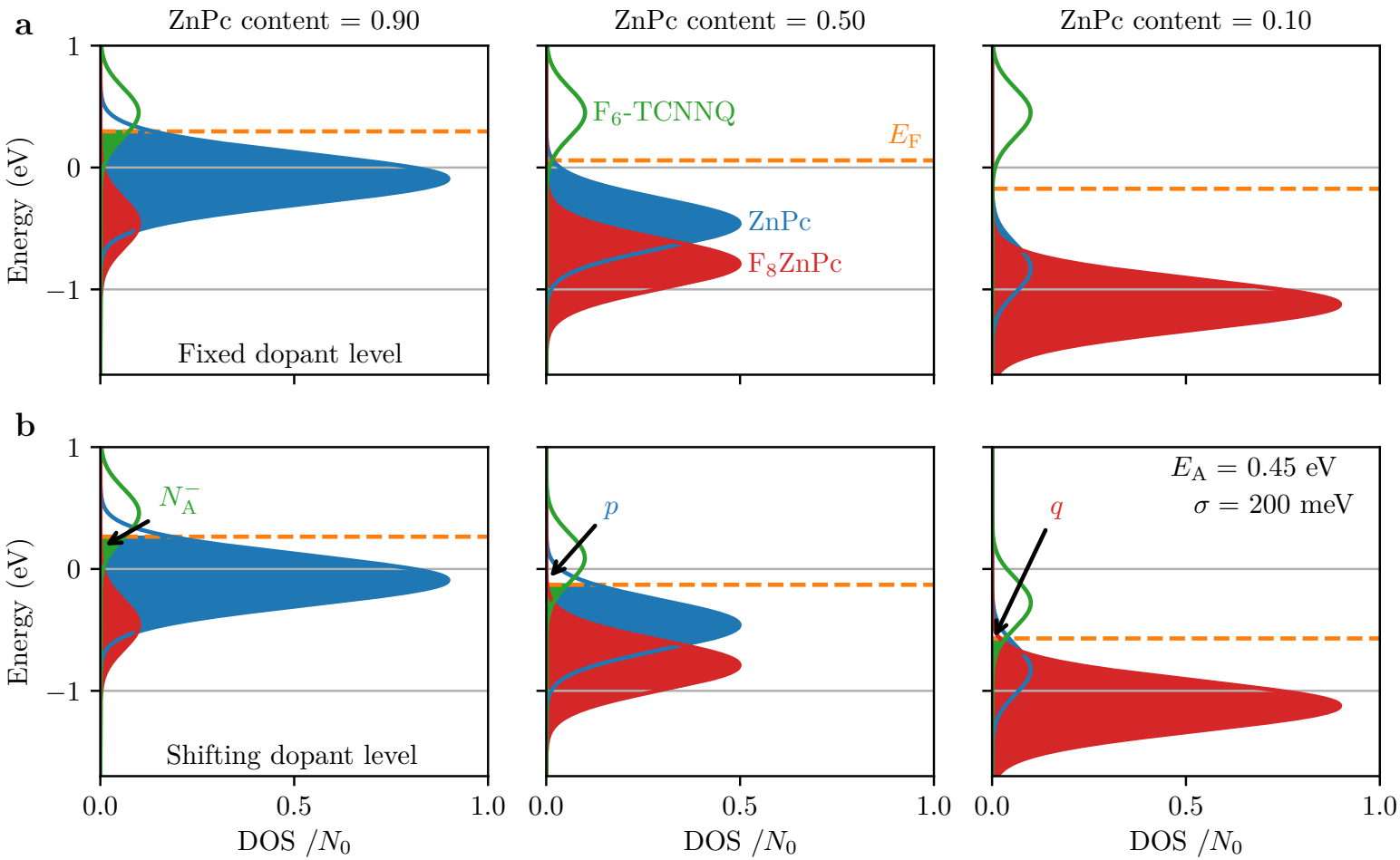
EPSRC
Pioneering research and skills

CPE

UNIVERSITY OF OXFORD

Thank you for your attention!

DOS backup slide



Further model verification

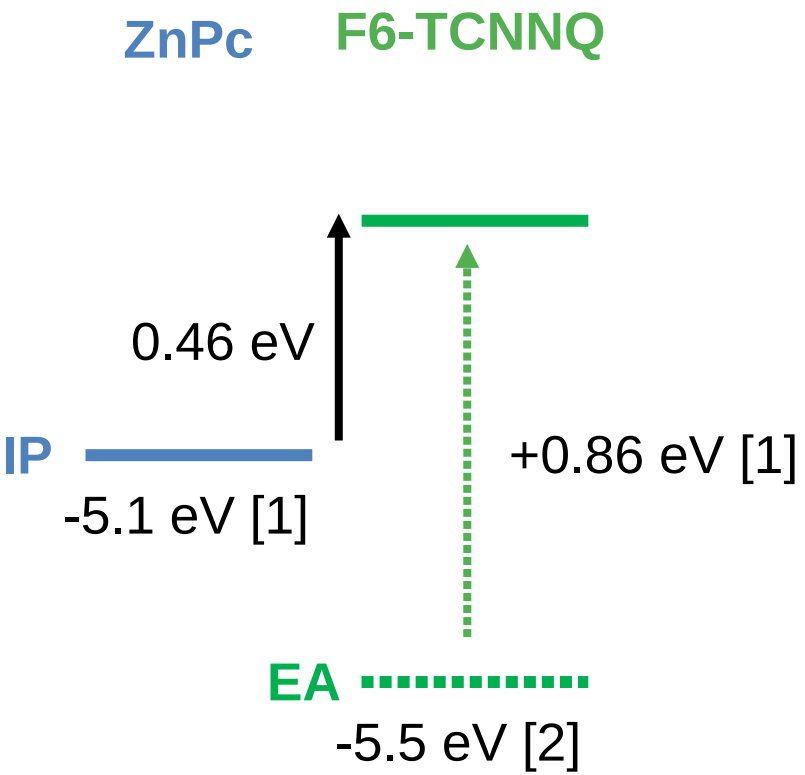
- With disorder set at [1]:

$$\sigma = 160\, meV$$

- Best fit E_A for dopant:

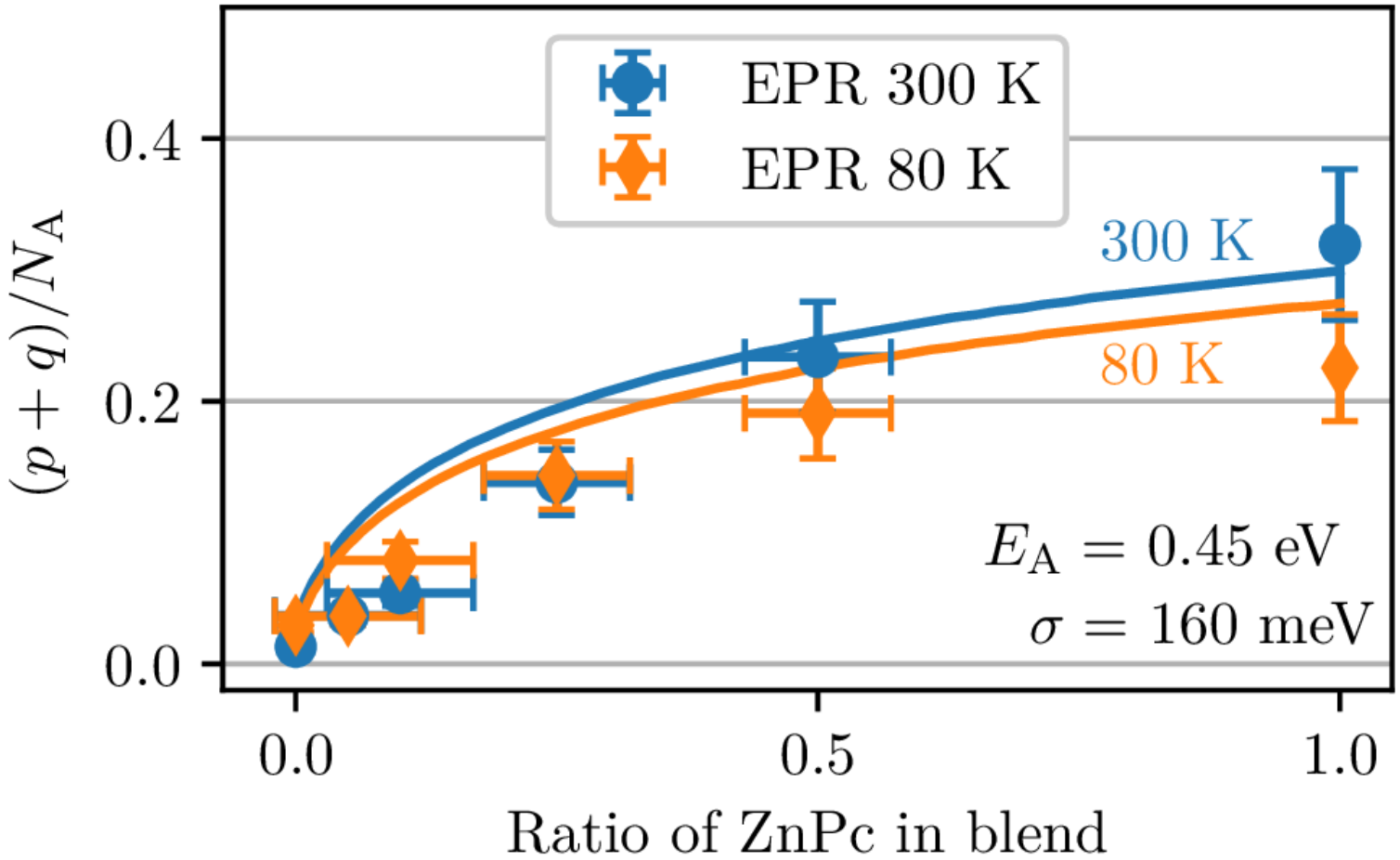
$$E_A = 0.45\, eV$$

- Matches UPS values + a shift from quadrupole interactions.

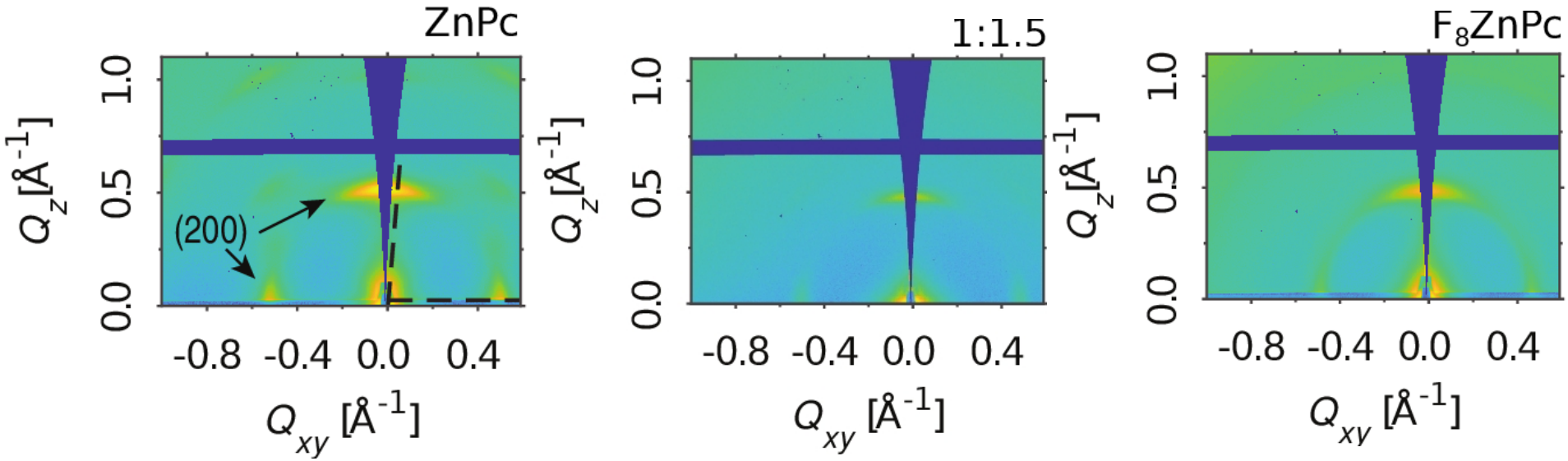


[1] Schwarze, M. *et al*. Science **352**, 1446 (2016)
[2] Waas *et al. Phys. Status Solidi B* **256,** 1800245 (2019)

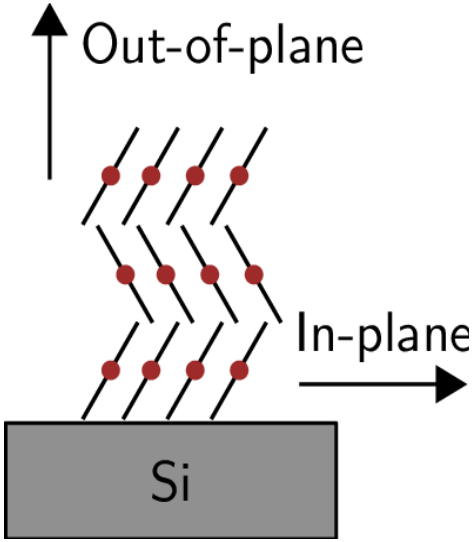
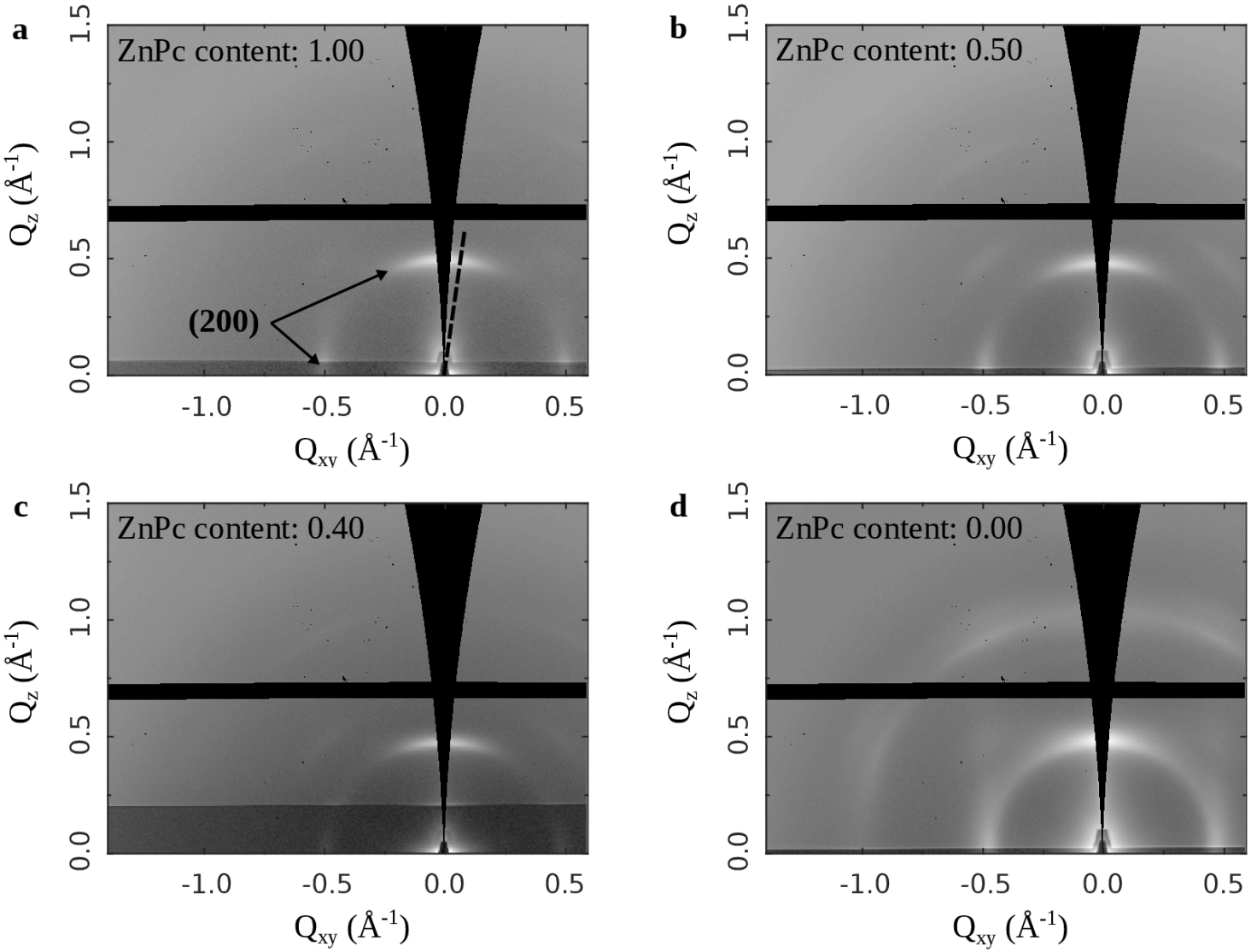
Temperature dependence



GIWAXS - undoped



- Preferred orientation of (200) peak fully in- & out-of plane
- Stronger out-of-plane peak suggests majority edge on orientation
- Higher order features in ZnPc compared to F_8ZnPc
- F_8ZnPc more powder-like - greater distribution of grain orientations



GIWAXS - doped