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TU Graz

Exploring polymorphism in molecular organic thin films

By Kaltenegger Martin

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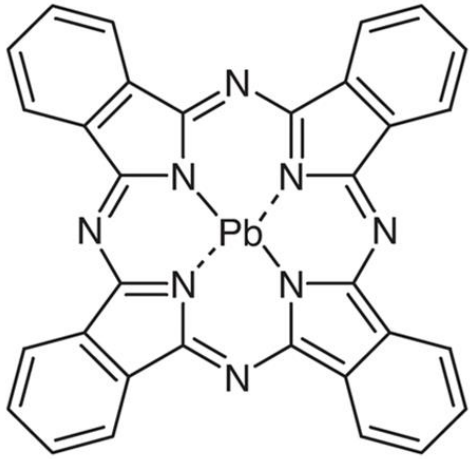
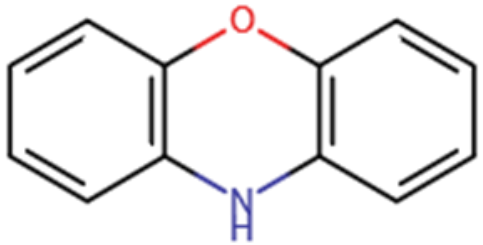
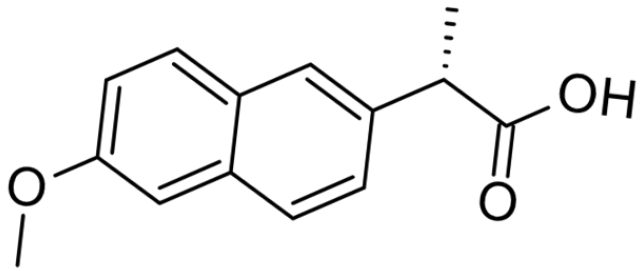


Lead-phthalocyanine



Phenoxazine



S-naproxen

What is polymorphism?

- 1 molecule exists in different crystal structures (packing)

→Impact on properties

(stability, morphology, processability, …)

Brazilian Journal of Analytical Chemistry
2020, Volume 7, Issue 26, pp 12-17
doi: 10.30744/brjac.2179-3425.letter.rmbdezena.N26

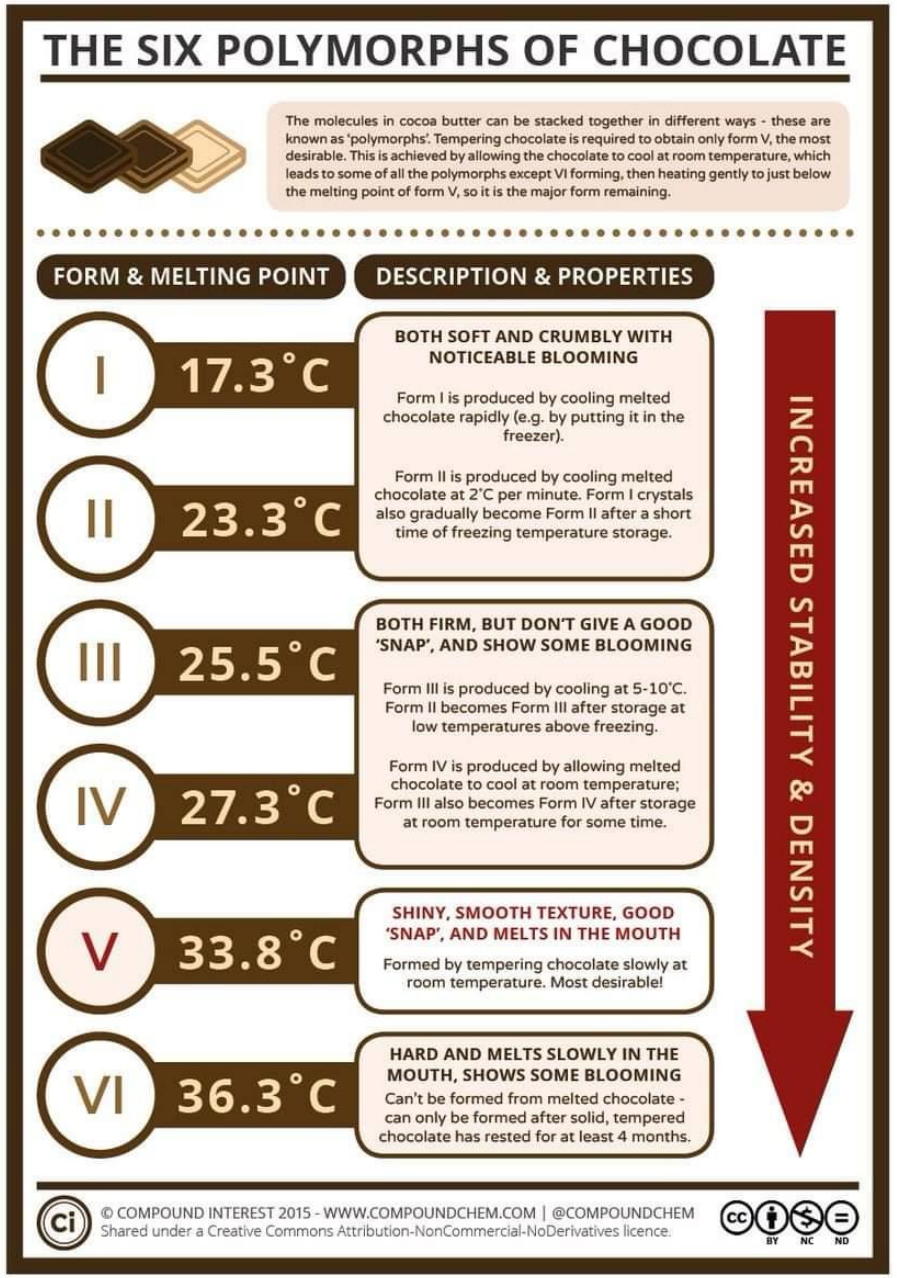
BrJAC

LETTER

Ritonavir Polymorphism: Analytical Chemistry Approach to Problem Solving in the Pharmaceutical Industry

Renan M. B. Dezena
Preformulation Specialist
Pharmaceutical Industry, Campinas, SP, Brazil

R.M.B. Dezena, Braz.J.Anal.Chem. 2020, 7 (26), 12-17



The Polymorphs of Chocolate – Compound Interest (compoundchem.com)

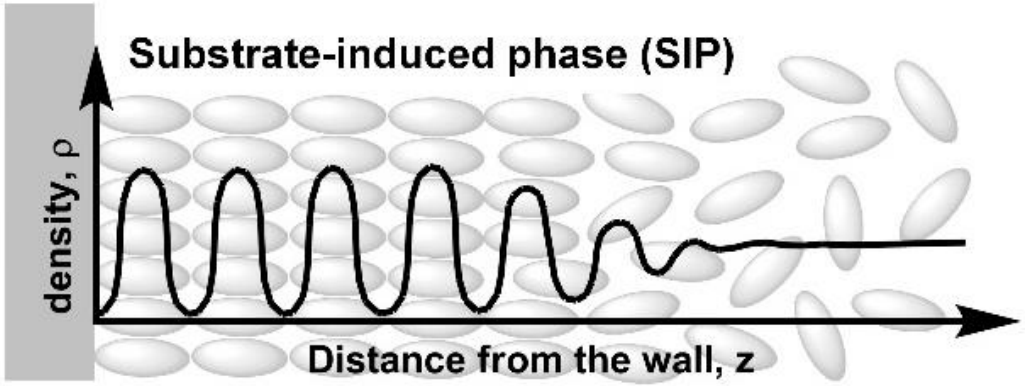
What is polymorphism?

- 1 molecule exists in different crystal forms (packing)

→Impact on different properties

(stability, morphology, processability, …)

- Limited access in bulk crystallization
- Some phase only observable on surfaces



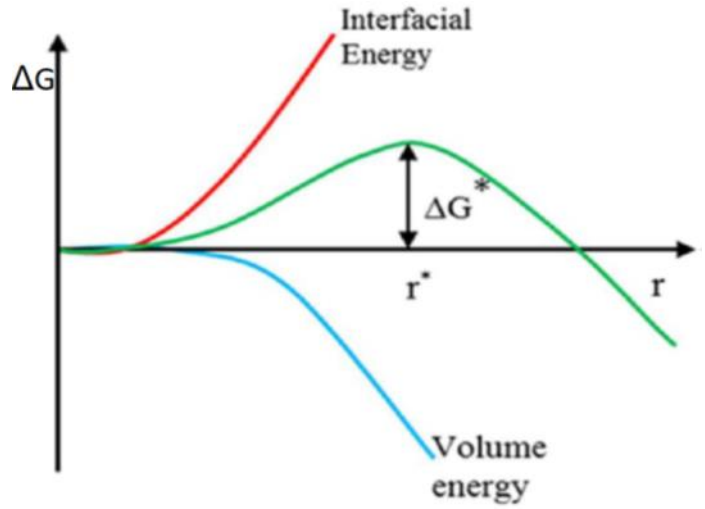
Heterogeneous nucleation

- Nucleation: 1st step of crystallization

→ Seems to determine polymorph

- Heterogeneous: on dust or surfaces

→Lowers the activation energy ΔG*



$$I_{nuc} = I_0 \exp(-\frac{\Delta G^*}{k_B T})$$

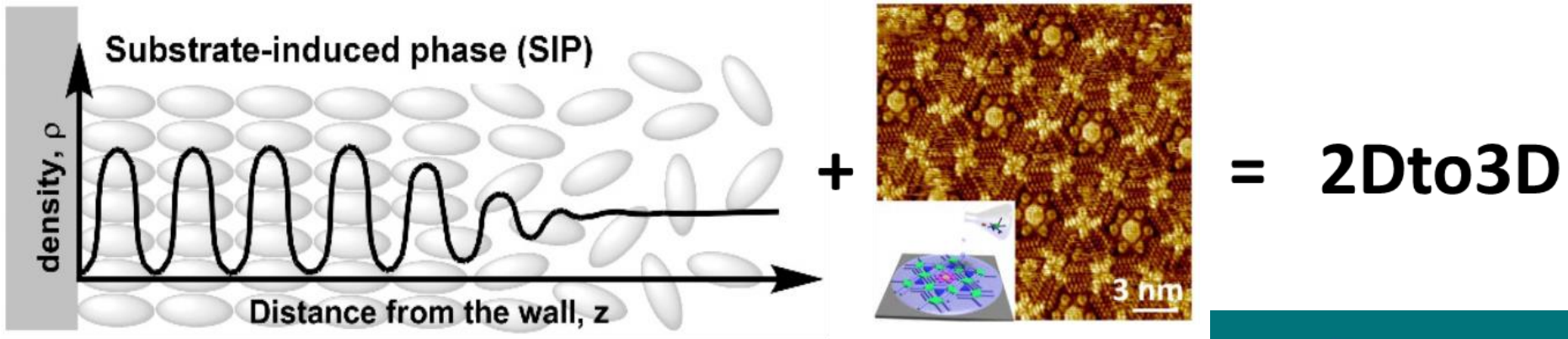
$$\Delta G^* = \Delta G_V + \Delta G_S = \frac{-4\pi r^3}{3v} k_B T ln S + 4\pi r^2 \sigma$$

S. Karthika, T. K. Radhakrishnan, P. Kalaichelvi, Crystal Growth & Design 2016, 16, 6663-6681.

EOS-Project: From 2Dto3D

- Substrate-induced-polymorphism (SIP) should be related to 2D crystallization
- For now: only a few molecular systems

→Fundamental understanding necessary



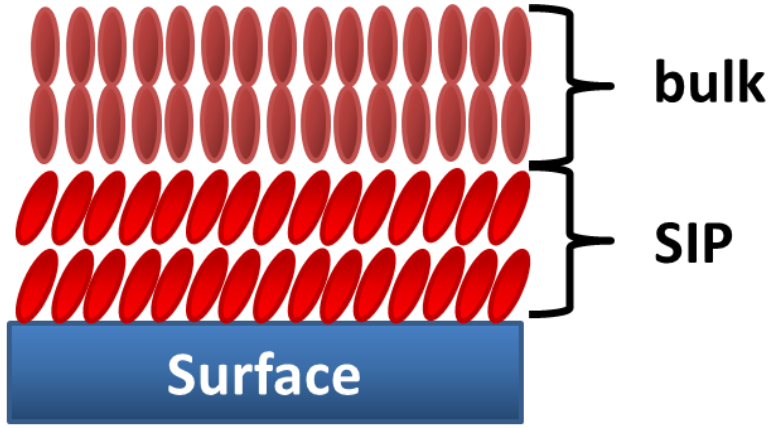
+ = 2Dto3D

Yves Geerts, kickoff meeting, 12.06.2018

Thesis subject & strategy

Subject

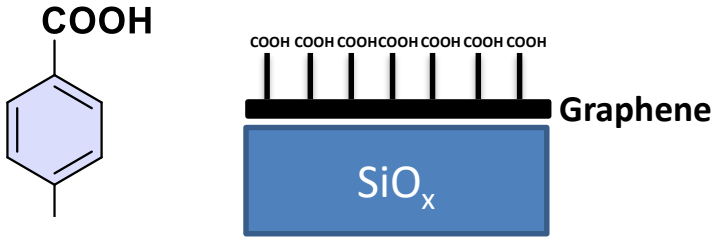
- Investigations on polymorphism
- show the influence of different substrates on thin film formation



Principals substrate-induced-polymorphism (SIP)

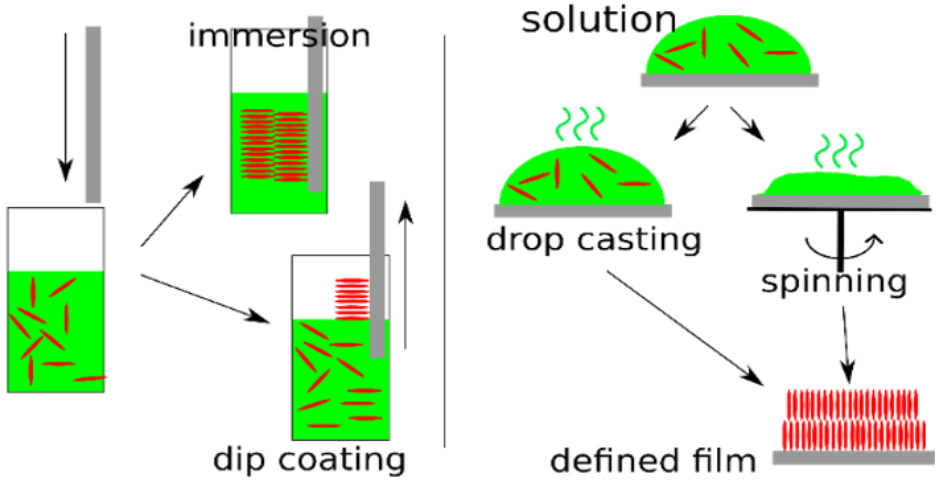
Planned Strategy

- <u>3-4 parts:</u>
  1. **SiO_x substrates**
  2. **Highly orientated pyrolytic graphite (HOPG)**
  3. **SiO_x + graphene**
  4. **SiO_x + graphene + chemisorbed molecules**

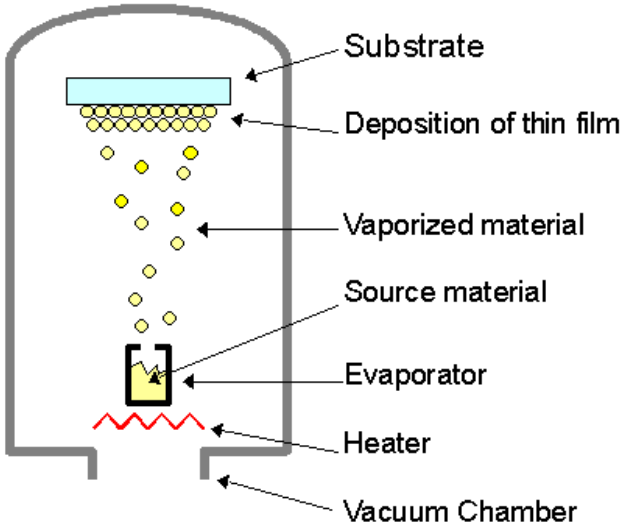


Thin film preparation

- From solutions:
  - Drop casting (covered)
  - Spin coating
  - Dip coating



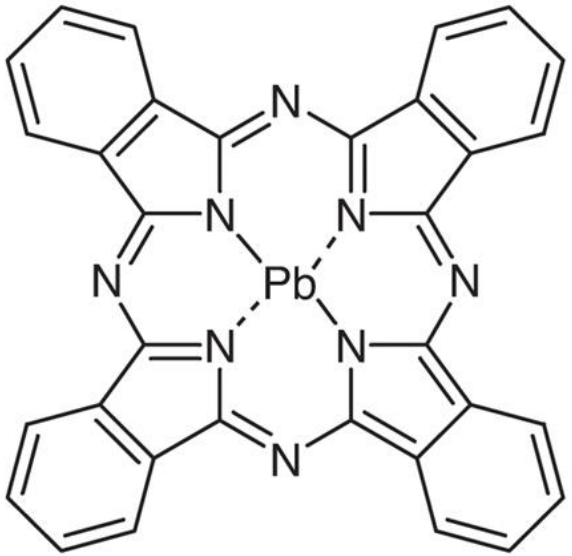
- Solution free:
  - Physical vapor deposition (PVD)

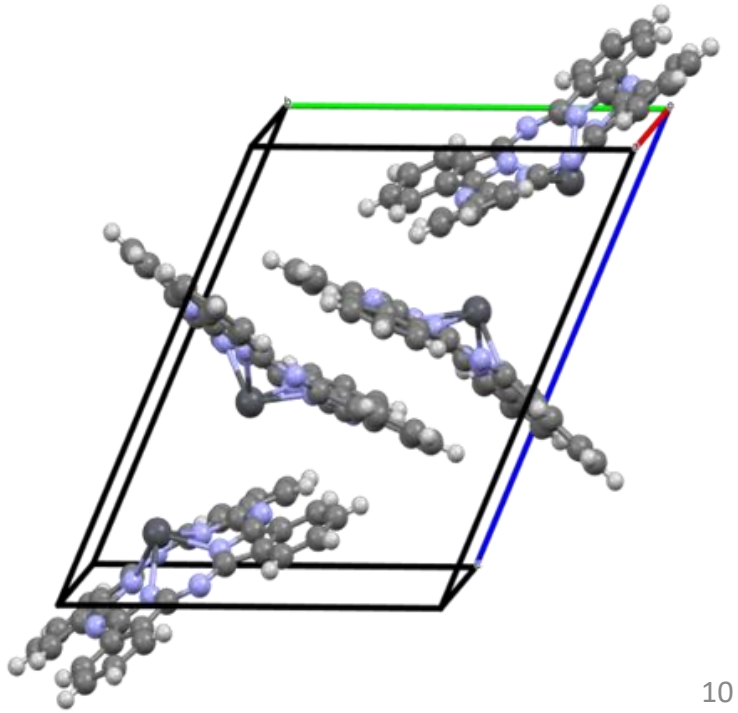


AR Coating Techniques: Thin Film Deposition Methods (findlight.net)

Lead phthalocyanine (PbPc)

- Physical vapour deposition
- Substrate: HOPG, Graphene & SiOx
- Known structure: triclinic





Substrate-induced polymorph

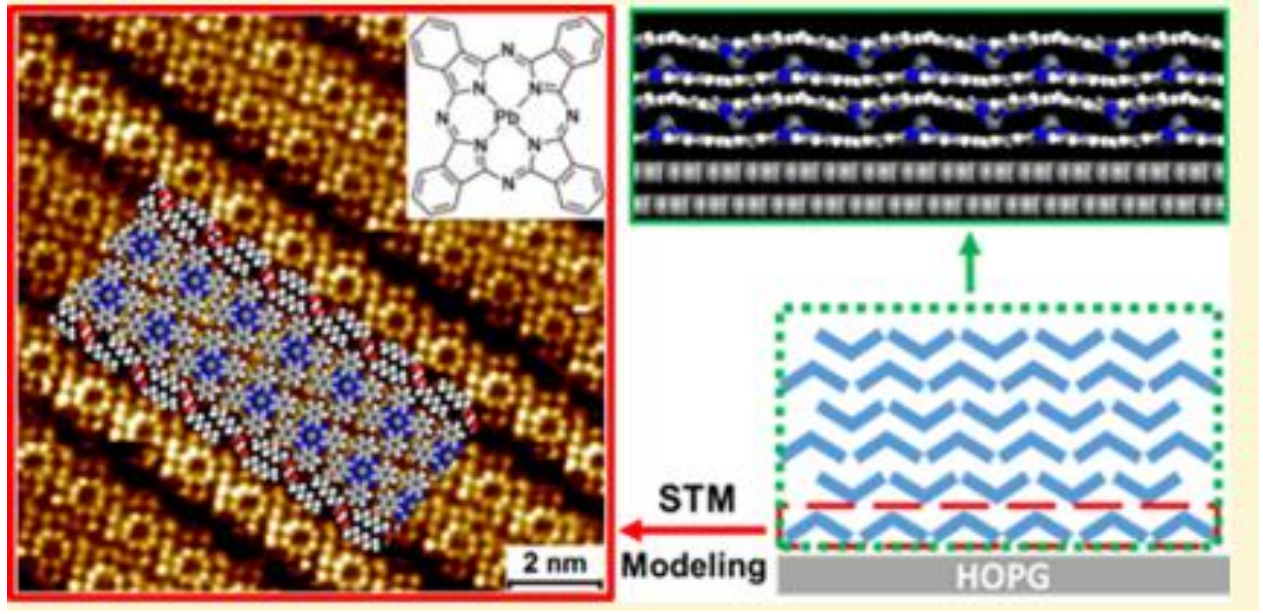
CHEMISTRY OF MATERIALS

pubs.acs.org/cm Article

From 2D to 3D: Bridging Self-Assembled Monolayers to a Substrate-Induced Polymorph in a Molecular Semiconductor

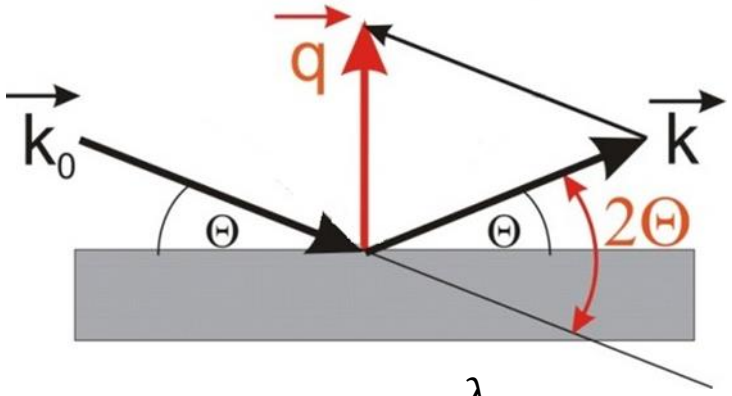
Yansong Hao, Gangamallaiah Velpula, Martin Kaltenegger, Wolfgang Rao Bodlos, François Vibert, Kunal S. Mali, Steven De Feyter, Roland Resel, Yves Henri Geerts, Sandra Van Aert, David Beljonne, and Roberto Lazzaroni*

Cite This: *Chem. Mater.* 2022, 34, 2238–2248 Read Online



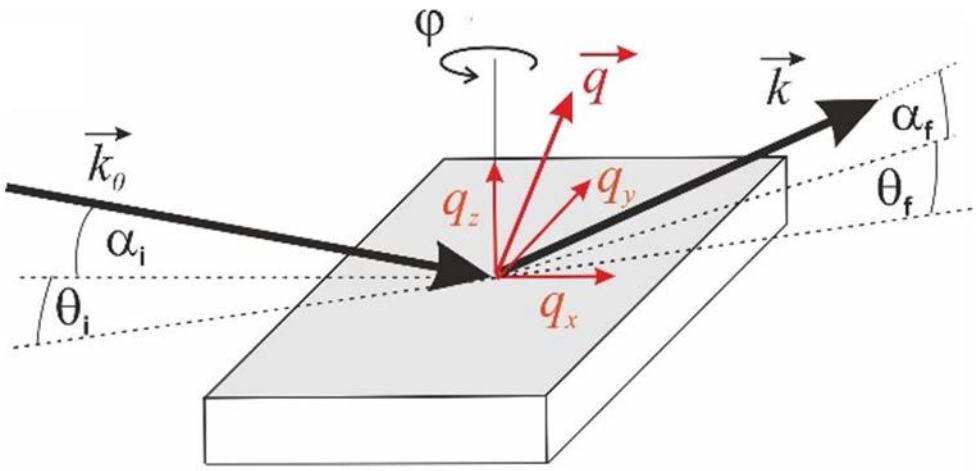
Methods of examination

- Specular X-ray diffraction:
  - Bragg condition: $\lambda = 2d_{hkl}\sin(\frac{2\theta}{2})$
  - Laue condition: $\vec{q} = \vec{G}$

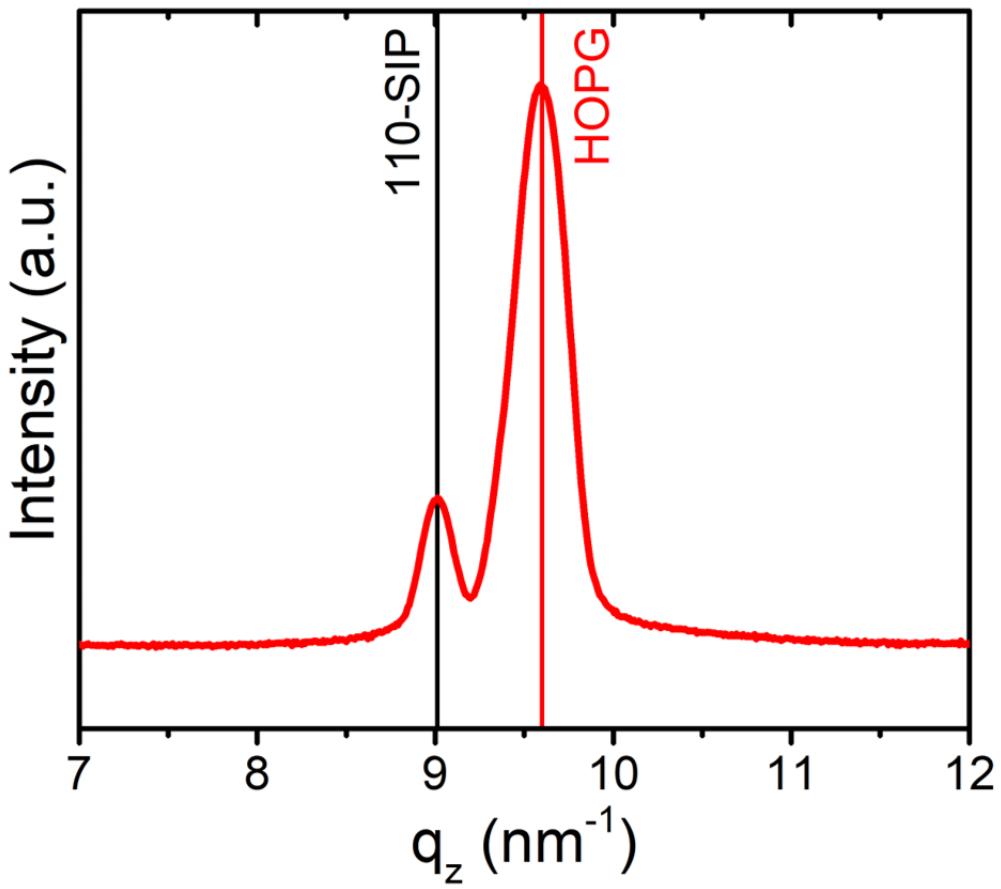


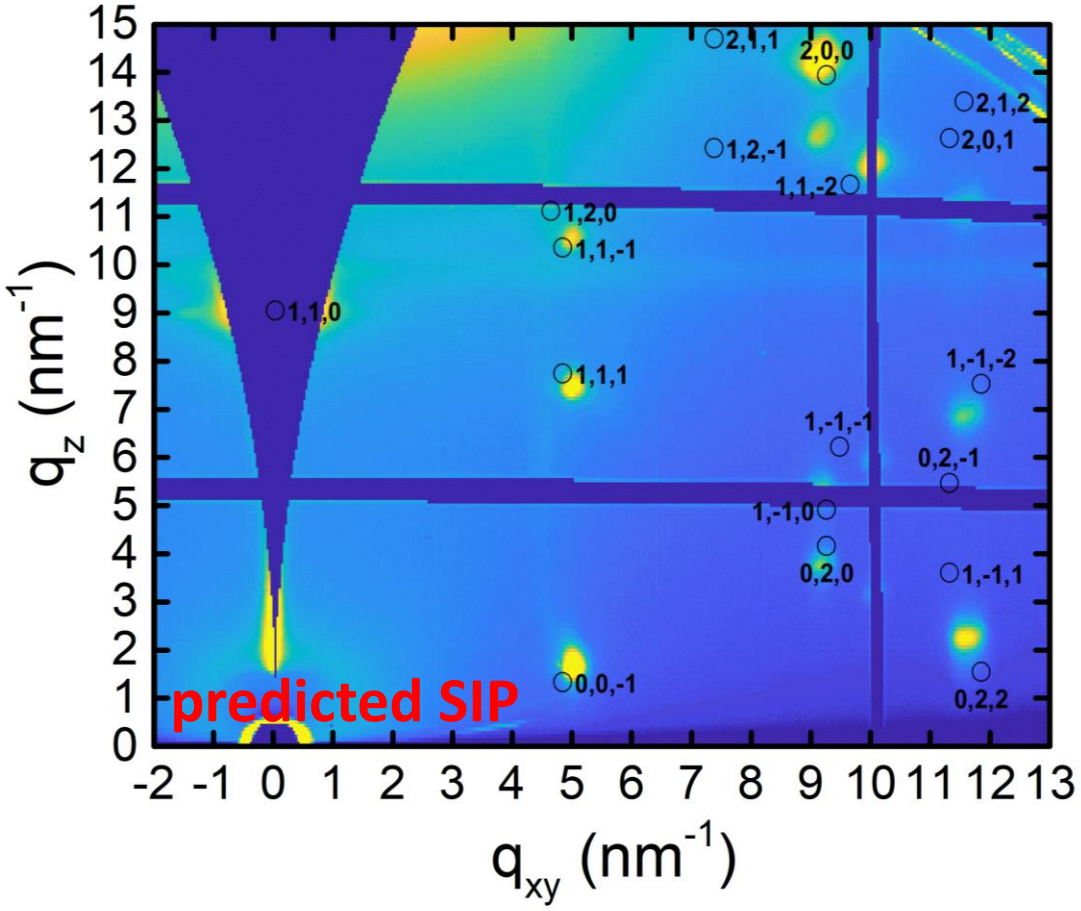
$$|\vec{k_0}| = |\vec{k}| = \frac{\lambda}{2\pi}$$

- Grazing incidence X-ray diffraction:
  - Diffraction due to evanescent waves
  - Incoming angle $\alpha_i \neq \alpha_f$
  - $\vec{q} = \begin{pmatrix} q_x \\ q_y \\ q_z \end{pmatrix} = \vec{k} - \vec{k_0}$



PbPc: 40 nm on HOPG





From GIXD to crystal structure solution

0 grazing incidence x-ray diffraction

1 determine unit cell parameters

2 extract intensities ($|F(hkl)|^2$)

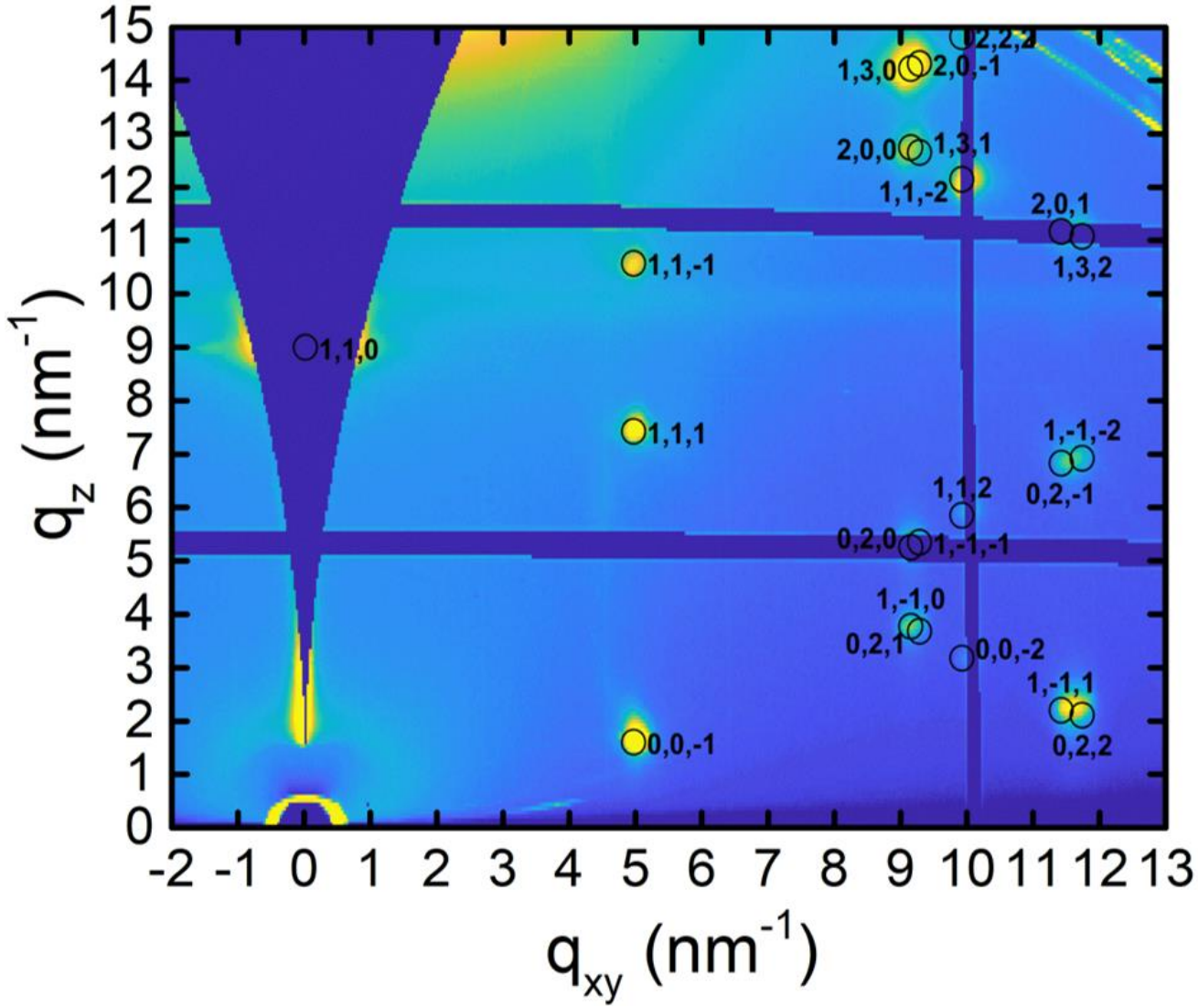
3 molecular dynamics simulations

4 compare $|F(hkl)|^2$

Indexation with GIDInd*

- refined unit cell
- 110 texture
- Energy optimization (Y. Hao, Mons)

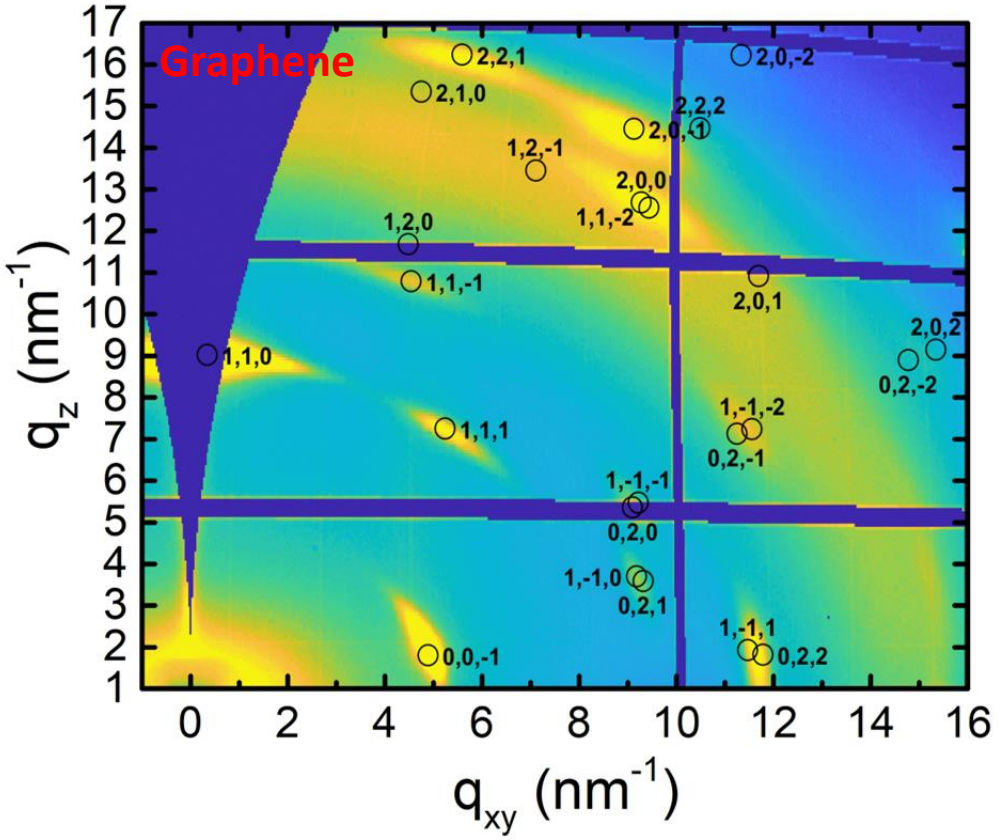
	Predicted	Refined
a [Å]	7.707	8.140
b [Å]	13.231	12.860
c [Å]	13.300	13.030
α [°]	71.39	68.41
β [°]	80.71	80.95
γ [°]	78.09	81.21
V [Å^{-3}]	1250.95	1245.79



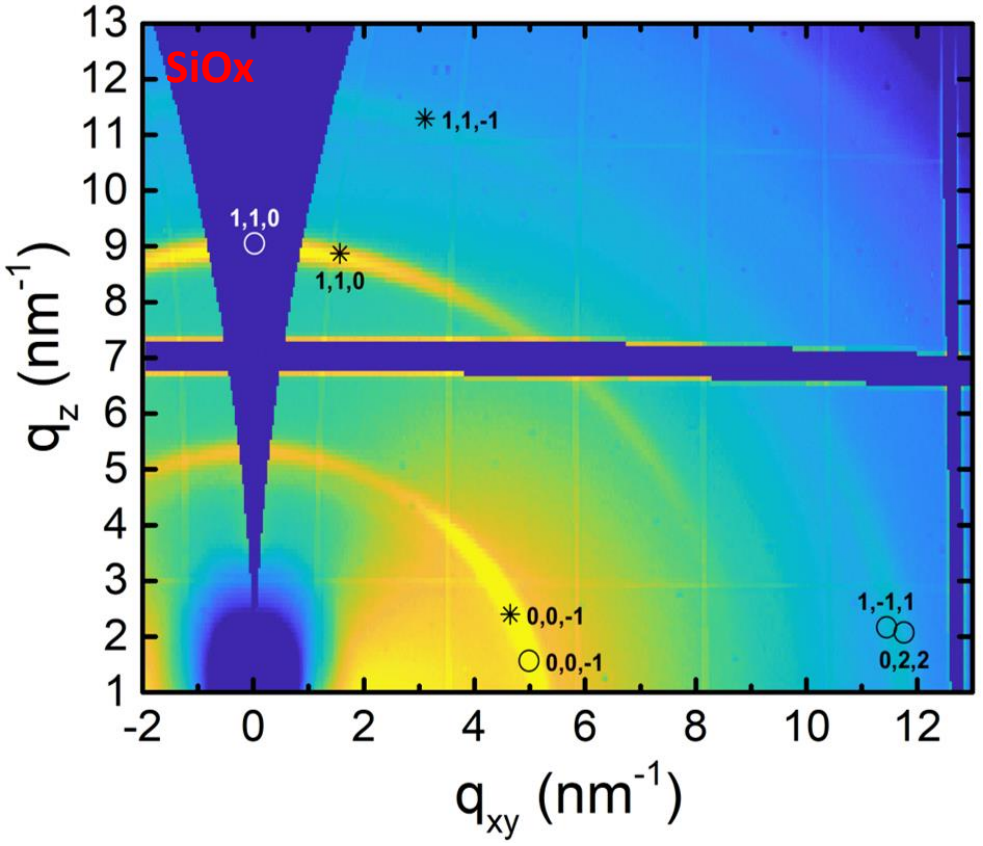
* M. P. Kainz, M. Kaltenegger et al, *Appl. Cryst.* **2021**,54, 1256-1267

PbPc on Graphene & SiOx

- (<u>14</u> <u>14</u>-1)-orientation

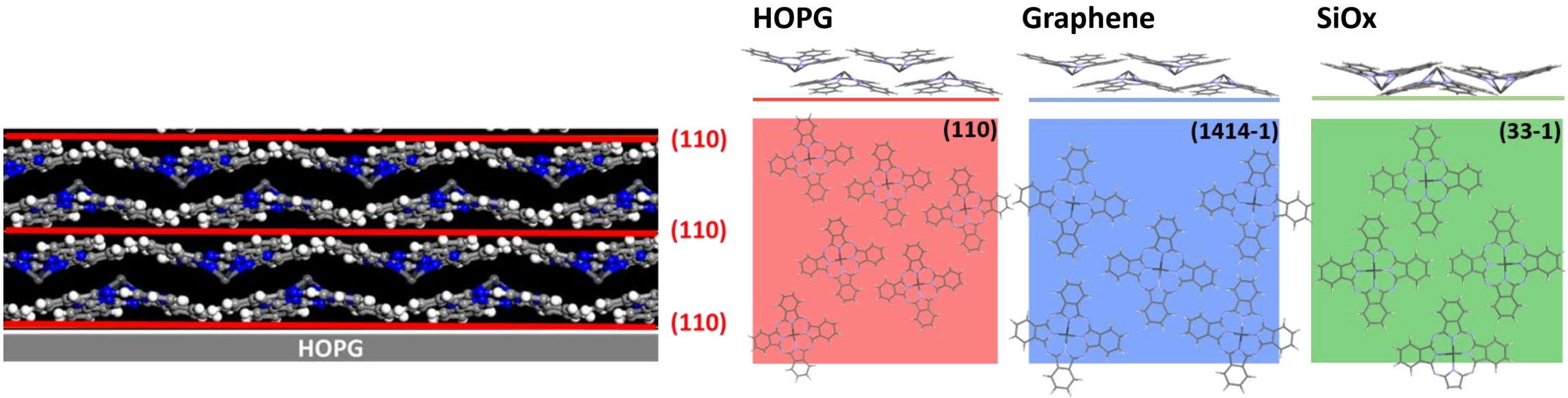


- (33-1)-orientation
- High mosaicity



Conclusion lead-phthalocyanine

- Substrate-induced polymorph confirmed
- Similar orientation on different substrates
  → flat-on



Phenoxazine

CRYSTAL GROWTH & DESIGN

pubs.acs.org/crystal

Article

Molecular Packing of Phenoxazine: A Combined Single-Crystal/ Crystal Structure Prediction Study

Martin Kaltenegger, Louis Delaive, Sai Manoj Gali, Patrick Brocorens, Oliver Werzer, Hans Riegler, Yves Henri Geerts, Roberto Lazzaroni, Roland Resel,* and Jie Liu

Cite This: https://doi.org/10.1021/acs.cgd.1c00691

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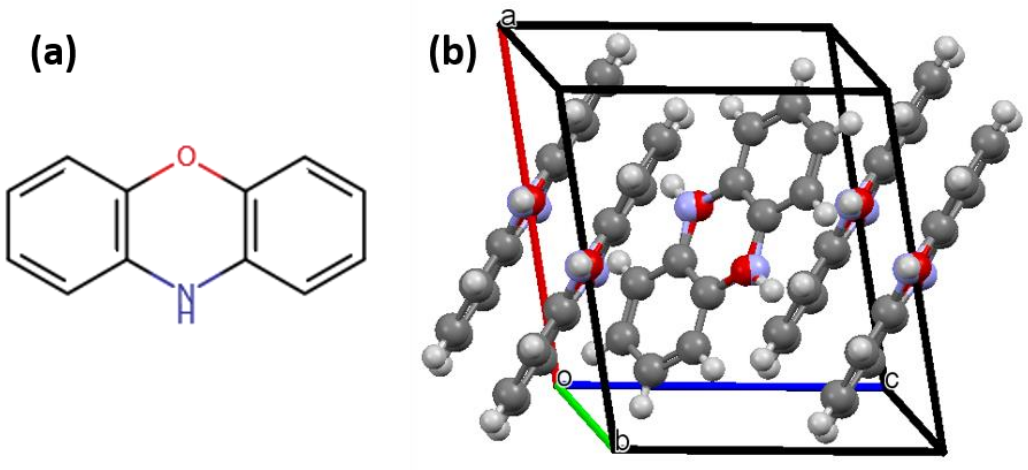
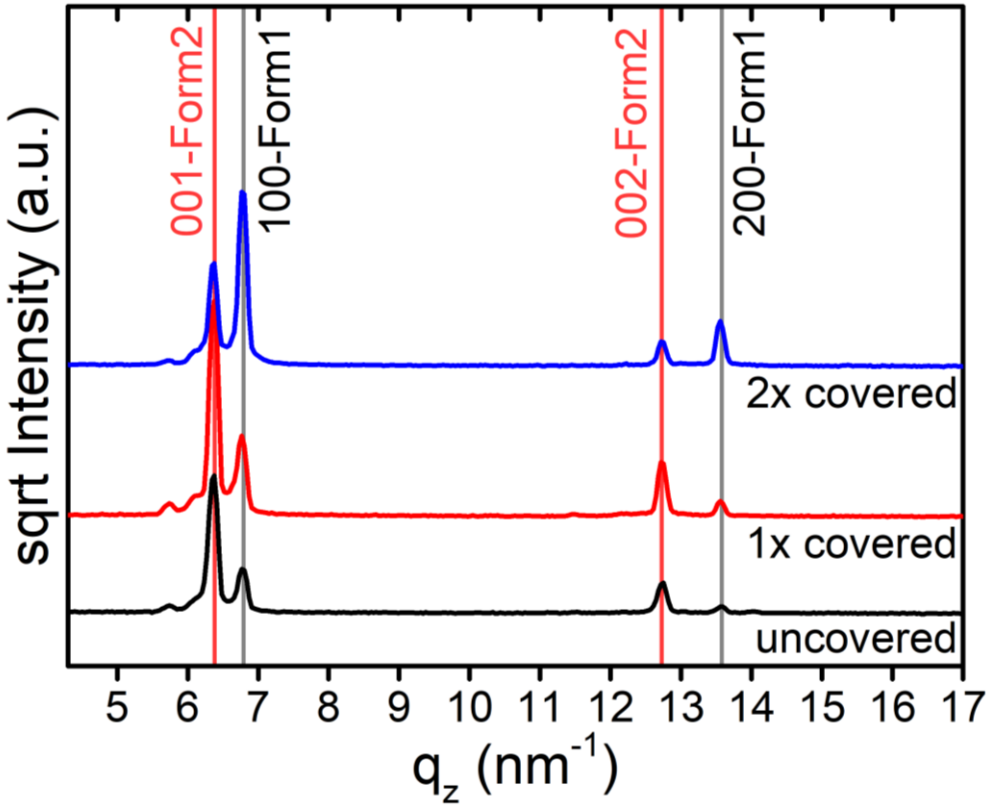
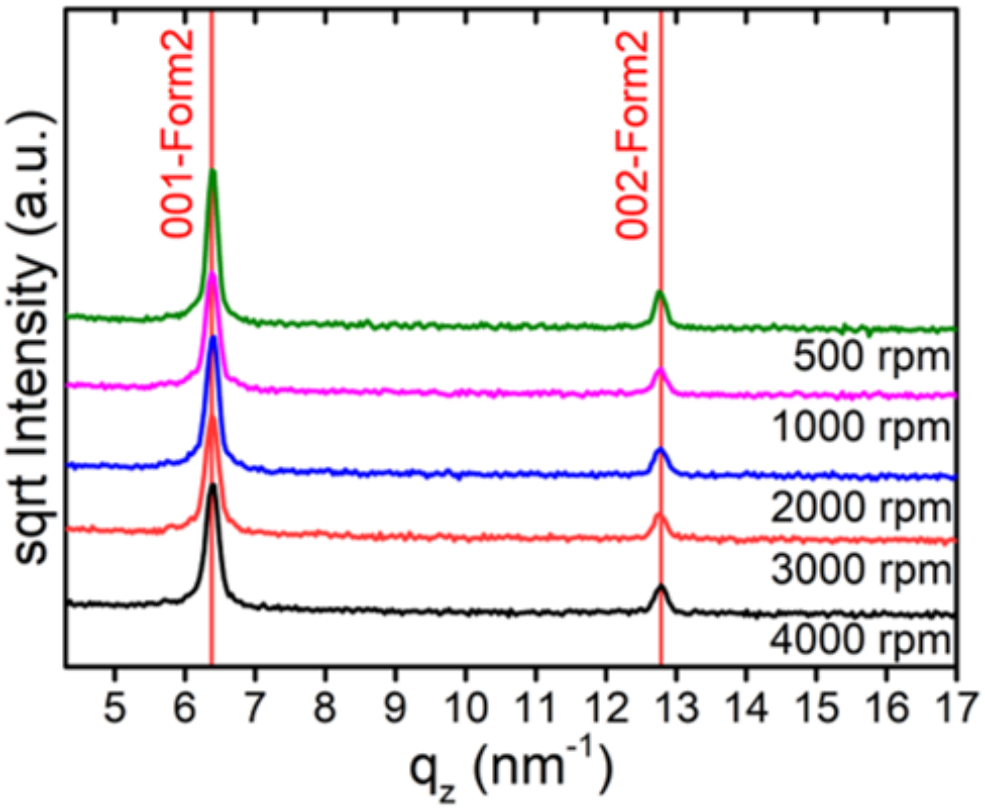


Thin film growth kinetics

Drop casting



Spin coating



Kinetically driven polymorph

CrystEngComm

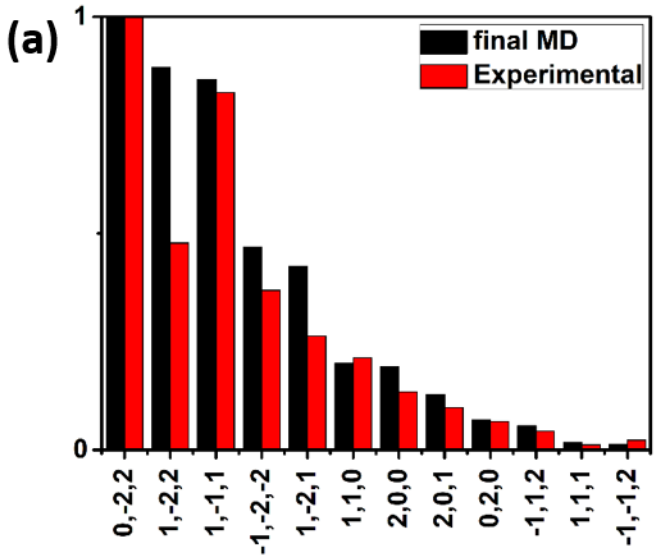
ROYAL SOCIETY OF CHEMISTRY

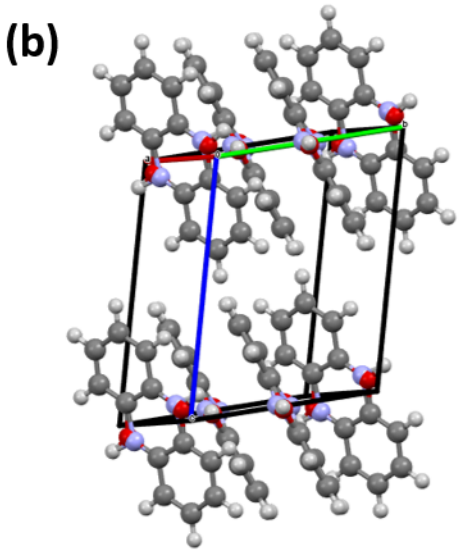
PAPER

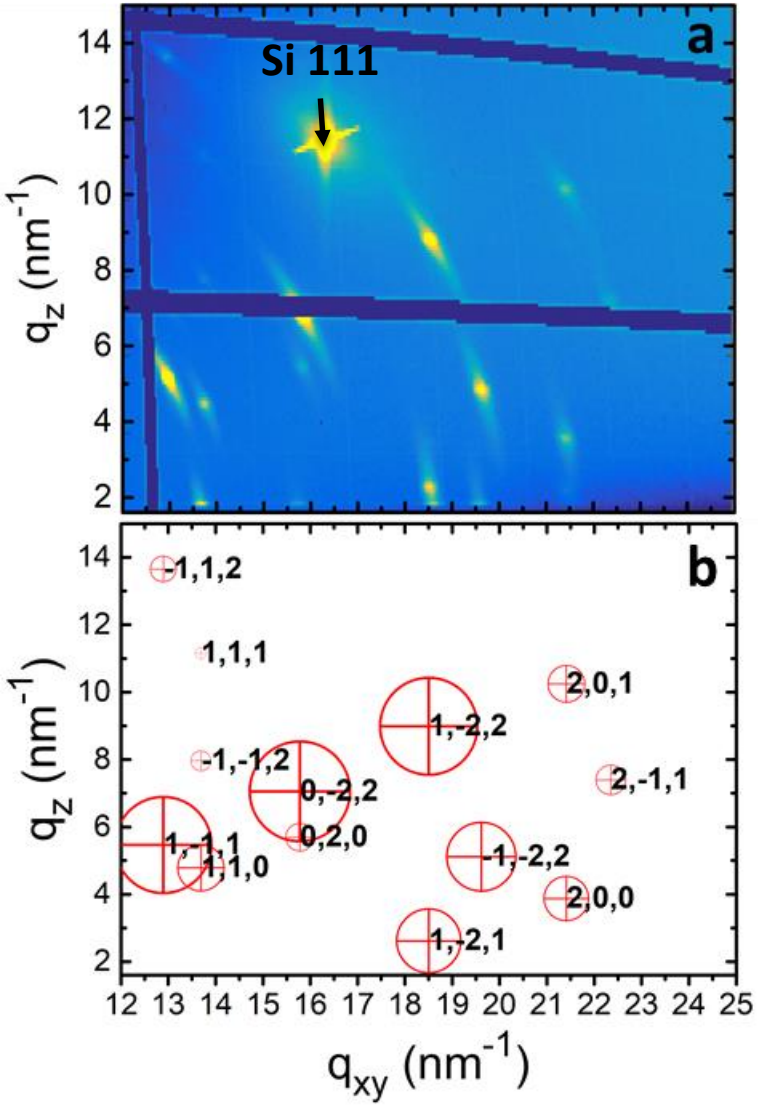
Engineering of a kinetically driven phase of phenoxazine by surface crystallisation†

Cite this: DOI: 10.1039/d2ce00479h

Martin Kaltenegger,[ab] Sebastian Hofer,[a] Roland Resel,*[a] Oliver Werzer,[cd] Hans Riegler,[c] Josef Simbrunner,[e] Christian Winkler,[a] Yves Geerts[bf] and Jie Liu[b]

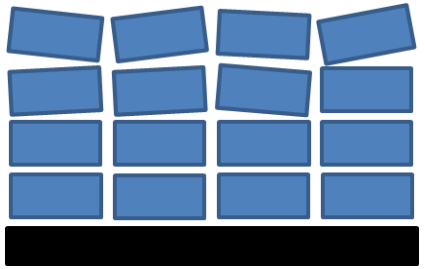


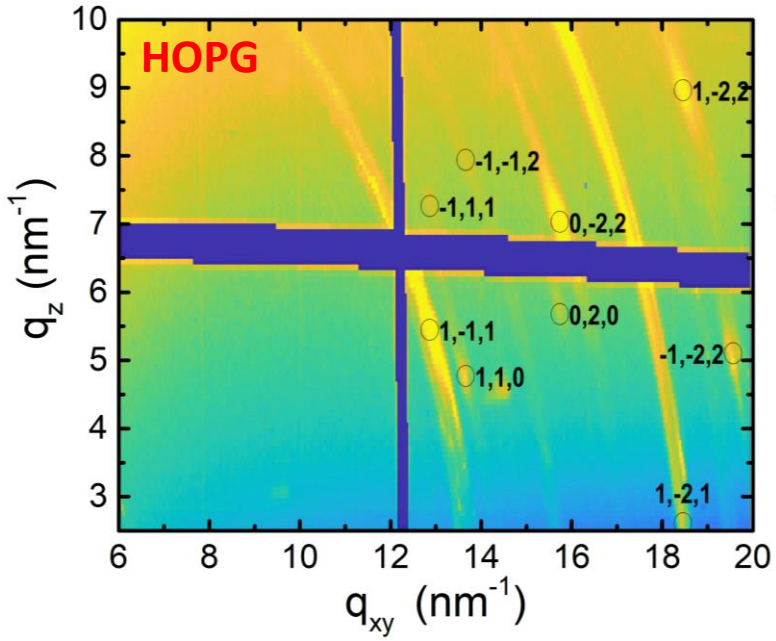


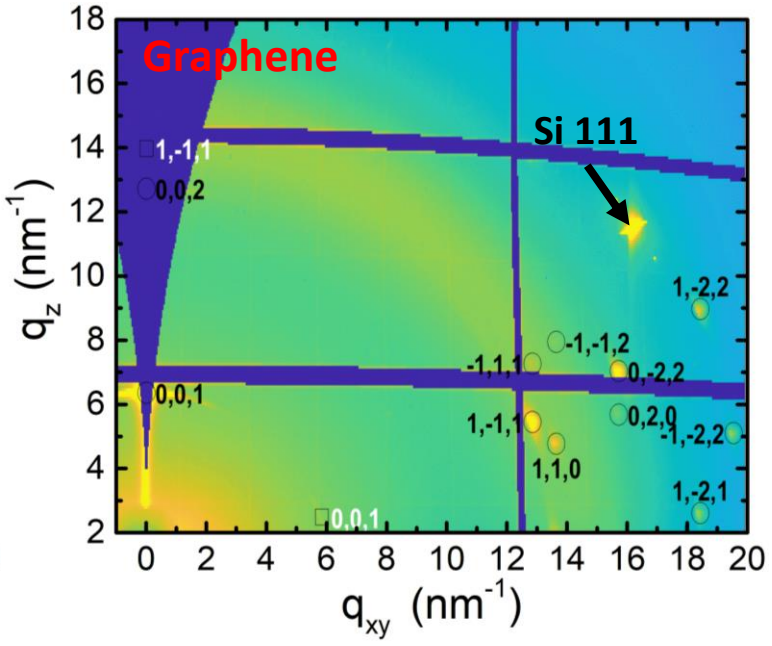


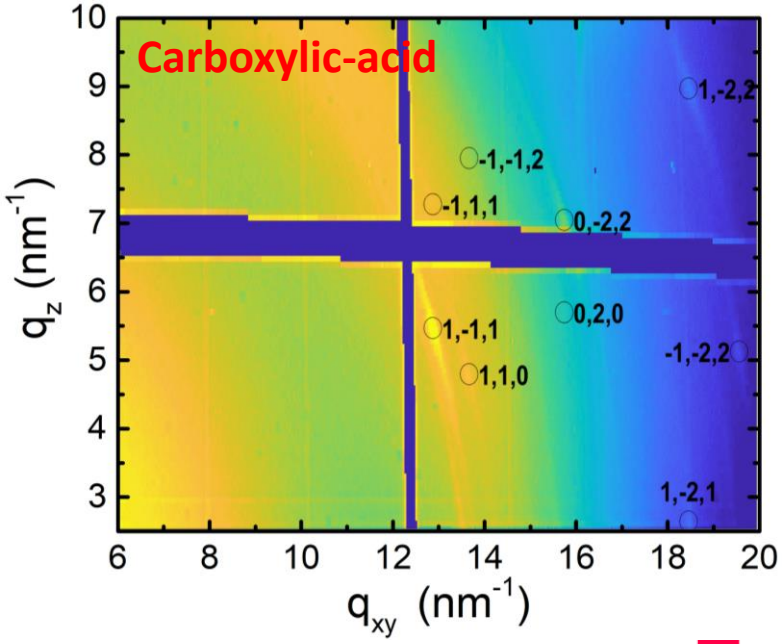
Phenoxazine on multiple substrates

All samples show kinetic driven polymorph → (001)-orientation
HOPG: smeared-out peaks → mosaicity
Graphene: clear peaks → texture
Carboxylic-acid: smeared-out peaks → mosaicity



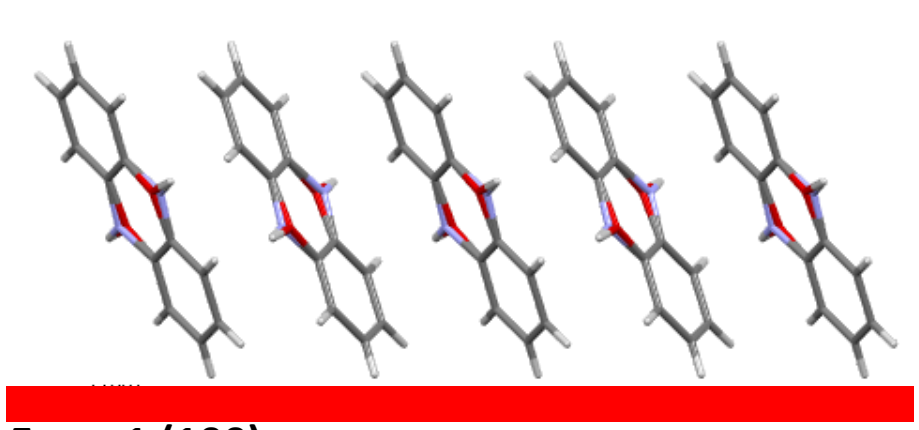




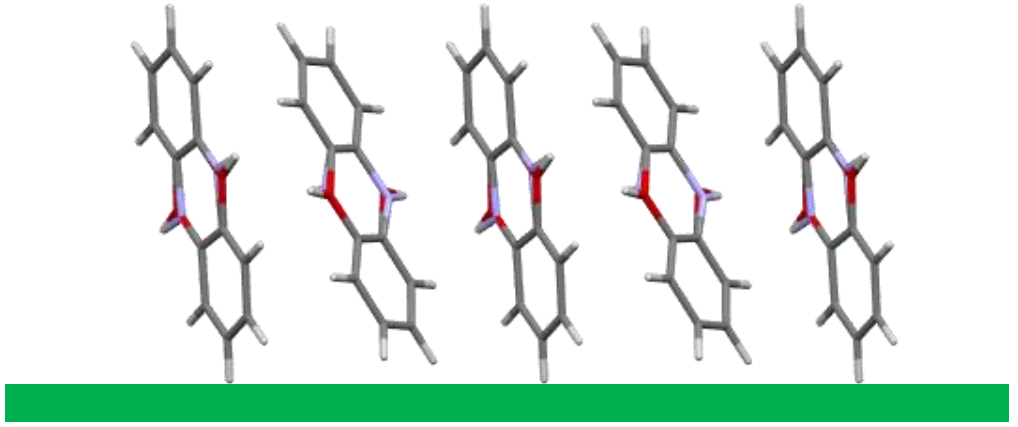


Conclusion phenoxazine

- 2 polymorphic structures solved
- End-on orientations
- Form 2: kinetic driven polymorph
  but no substrate-induced polymorph
- Varying substrates: no influence on polymorph selection



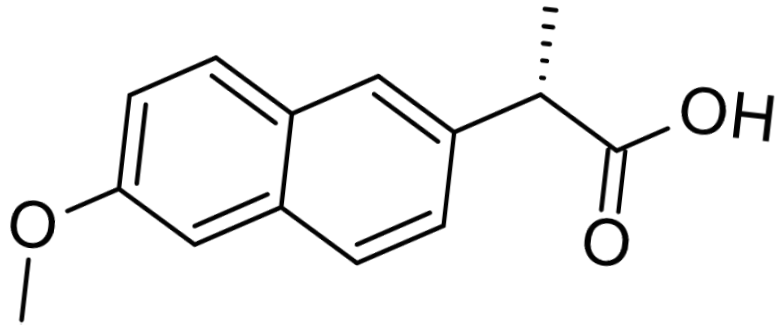
Form 1 (100)

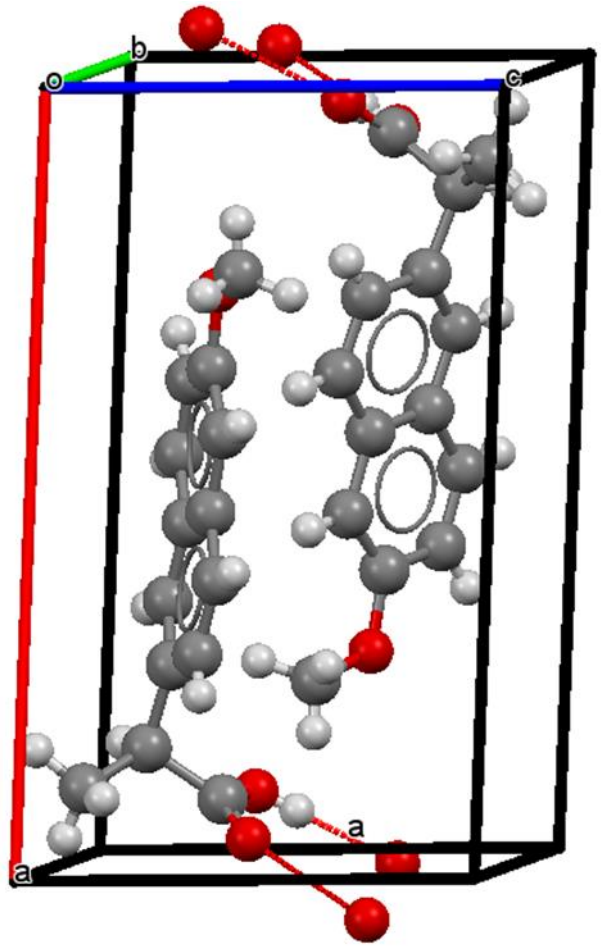


Form 2 (001)

Naproxen S-enantiomer

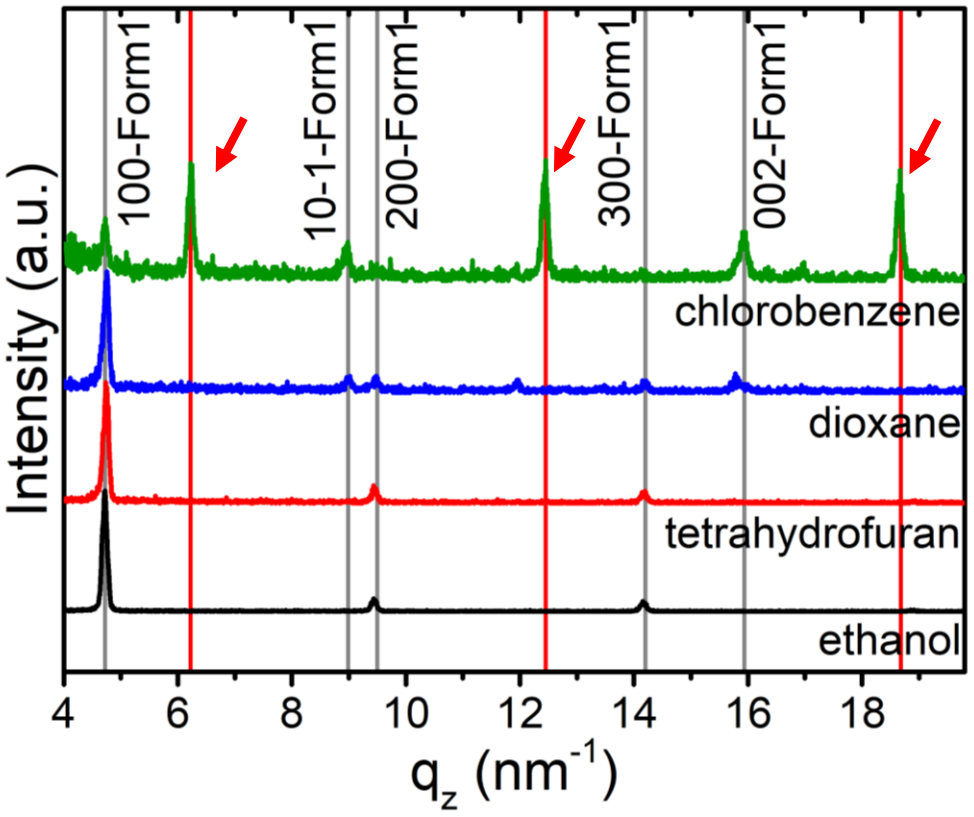
- 2-(6-Methoxy-2-naphthyl)-propionic acid
- Nonsteroidal anti-inflammatory drug
- Chiral → only S enantiomer

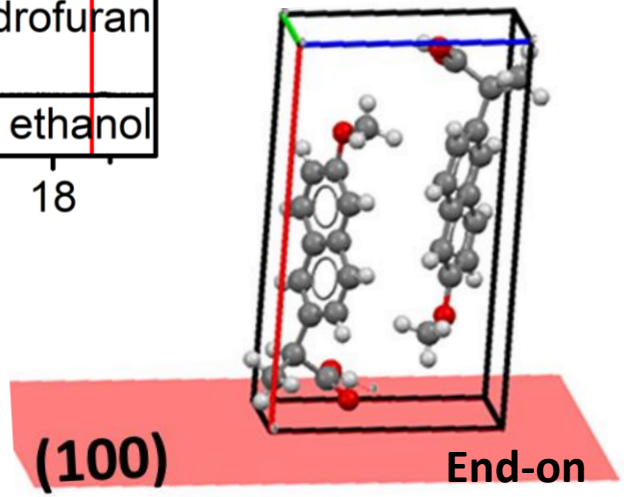




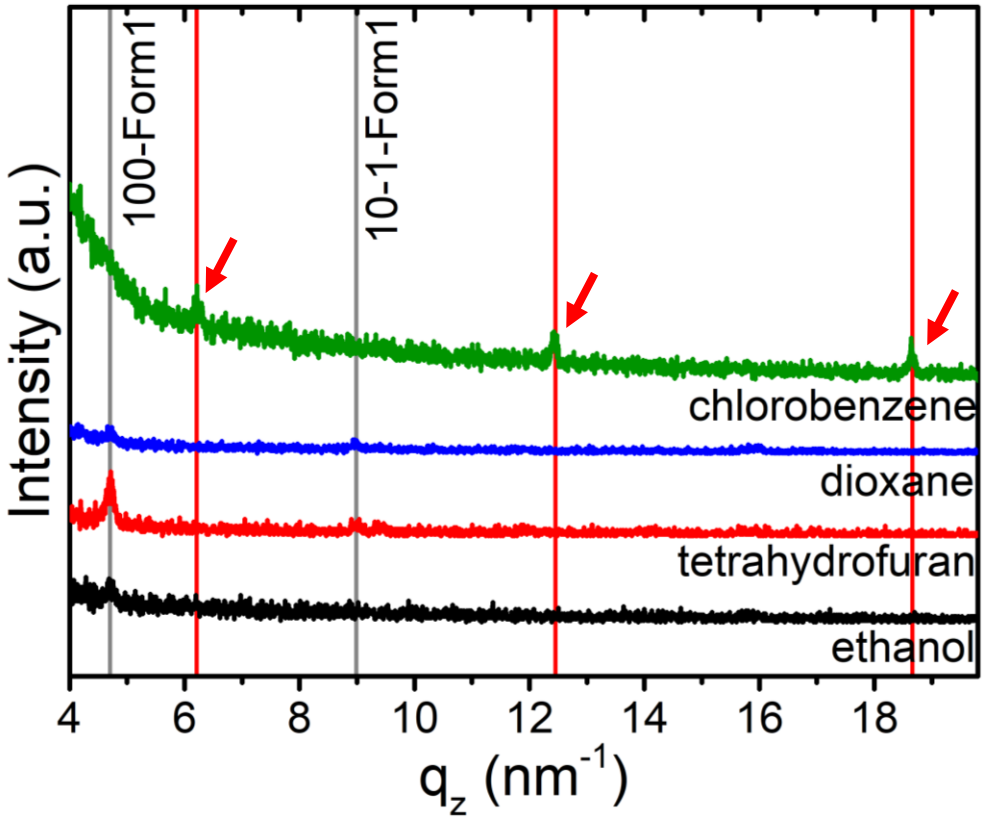
S-Naproxen on SiOx

Drop casting

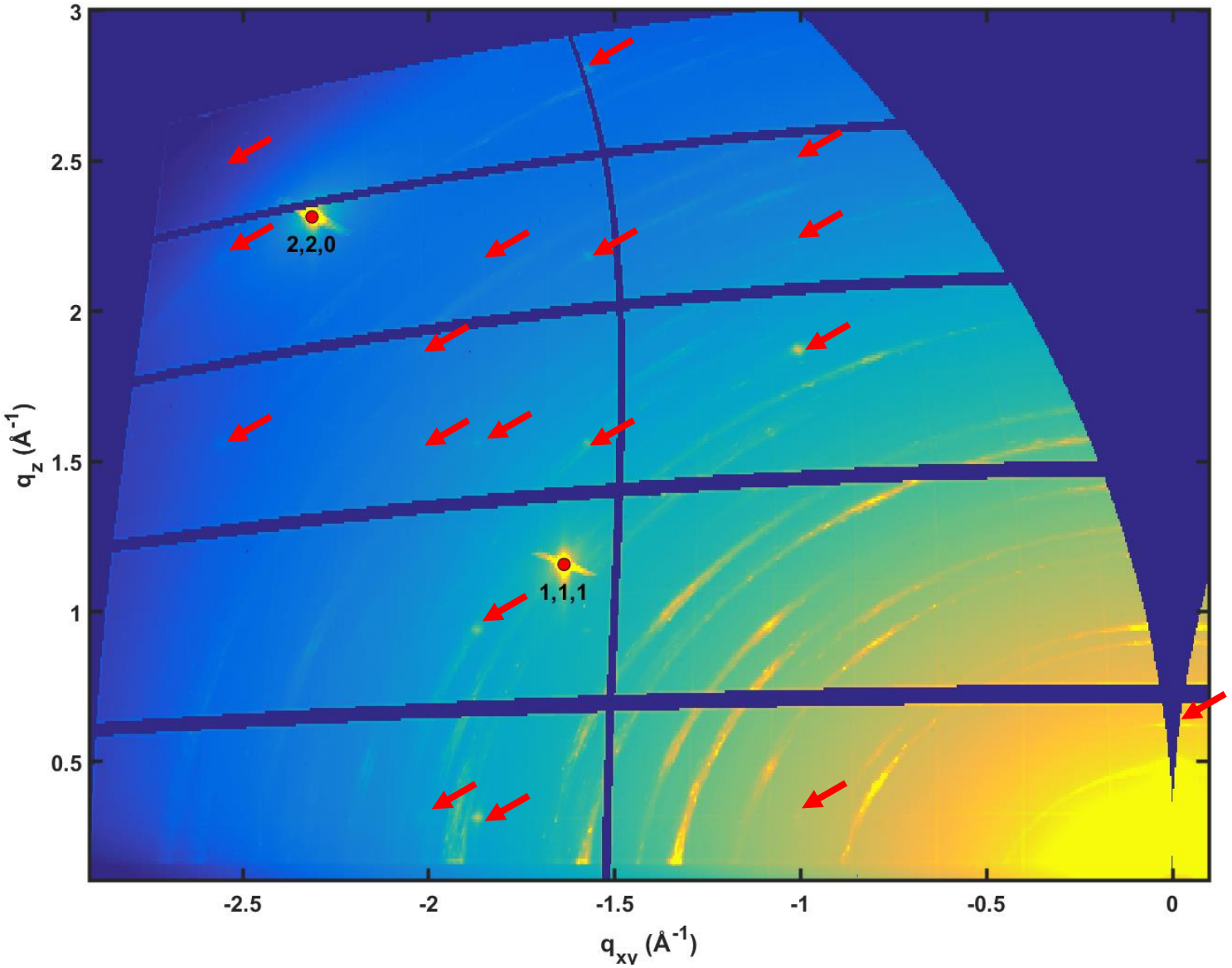




Spin coating



Indexation 2nd form (GIDInd)



- <u>GIDInd:</u>
  4 sets of in plane peaks
  23 different peaks found
  → monoclinic structure
  → 14 diff. unit cell found

  → Crystal structure prediction in process

Naproxen on various substrates

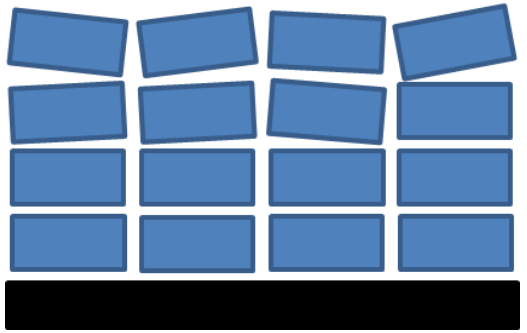
Most samples reveal Form 1 of naproxen

HOPG: clear peaks representing (002)-orientation

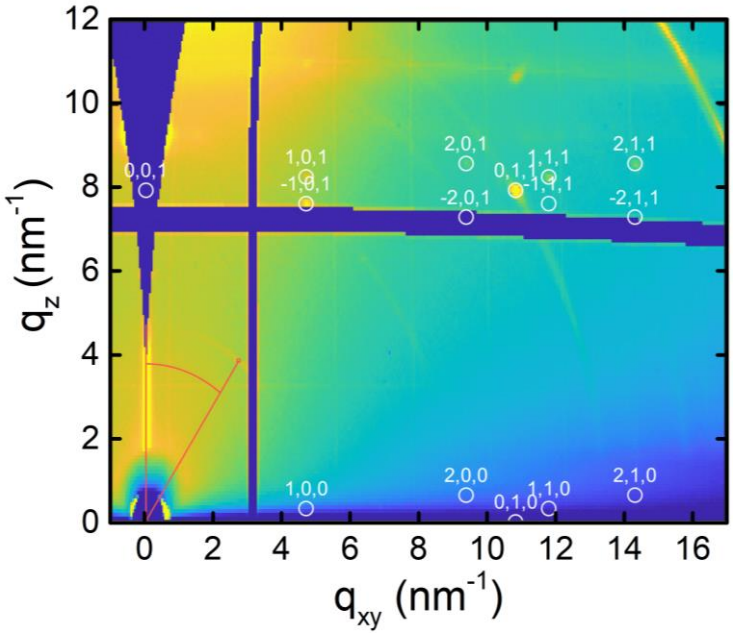
→ flat-on texture

Graphene: flat on orientation & high mosaicity

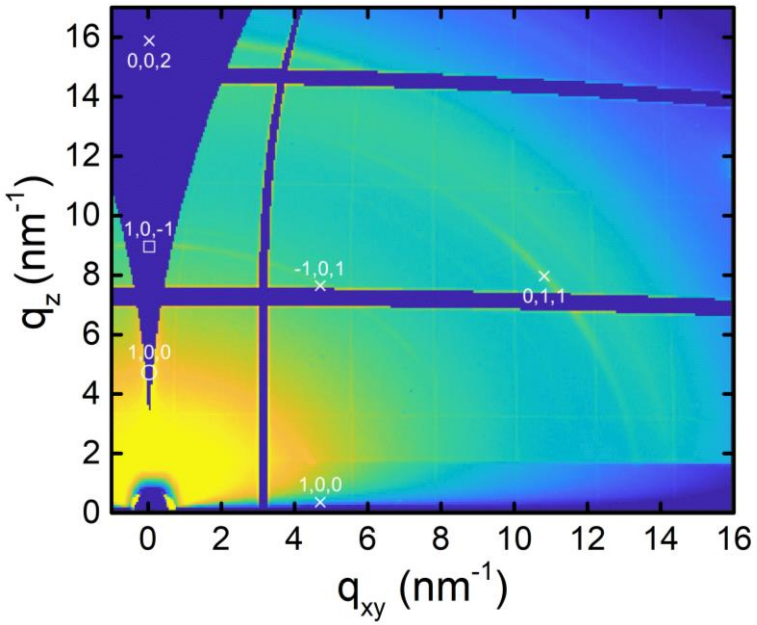
Carboxylic-acid: flat-on & end-on



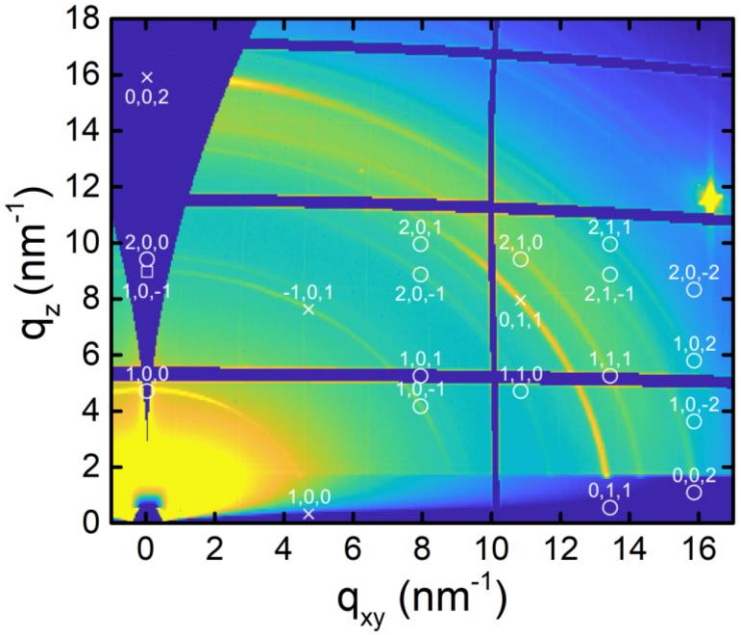
HOPG



Graphene

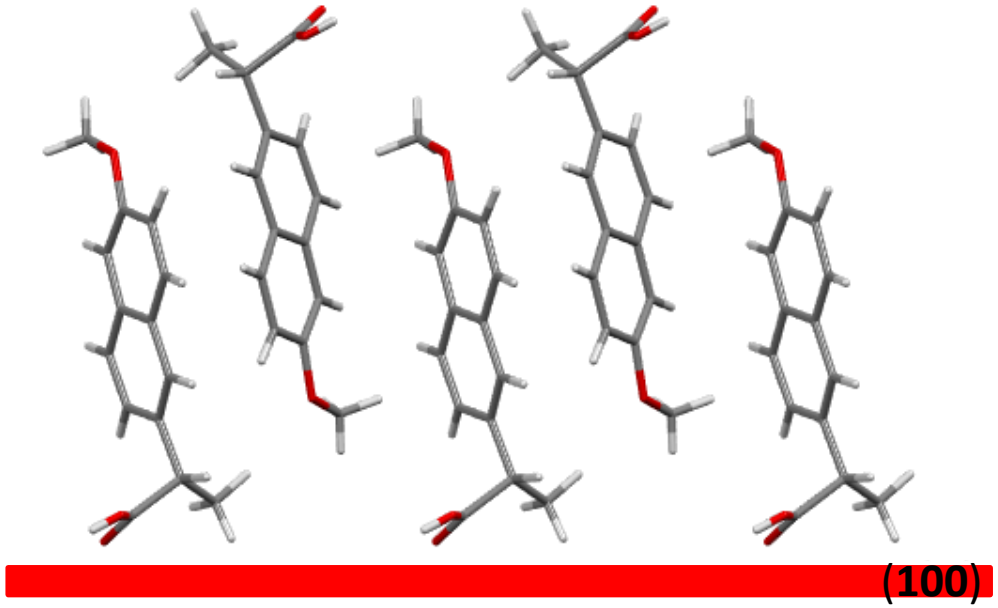


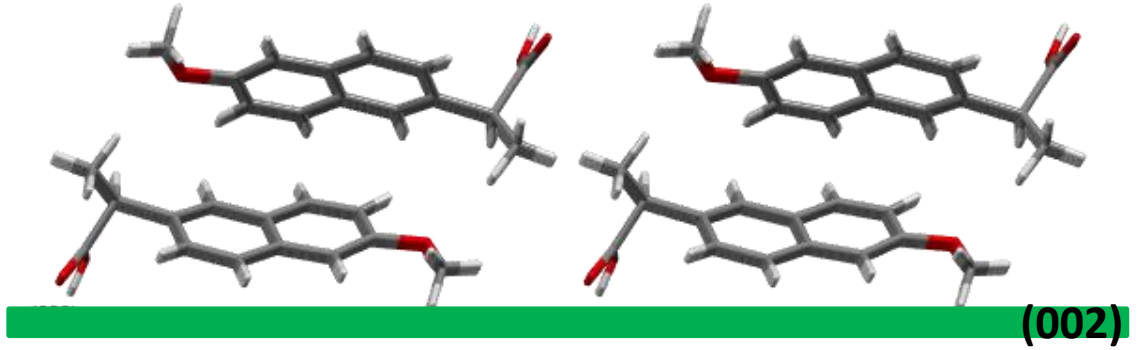
Carboxylic-acid



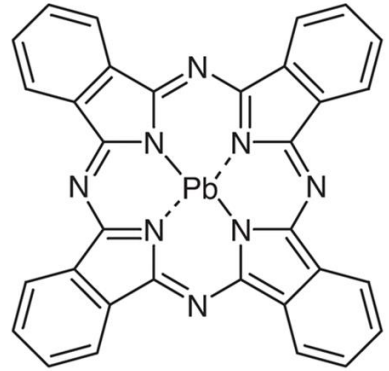
Conclusion naproxen

- 2nd Form of naproxen: set of unit cells found
  → crystal structure missing
- Change in molecular orientation:
  end-on (silica) → flat-on (HOPG, Graphene)





General Conclusion



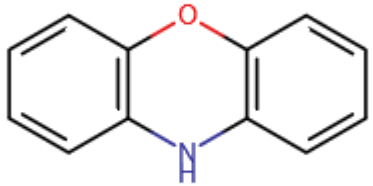
Lead-phthalocyanine

- Lead-phthalocyanine: substrate-induced polymorph
- Phenoxazine: kinetic-driven polymorph

→ molecule-molecule interaction > substrate-molecule interaction

- Naproxen: 2nd polymorph found,

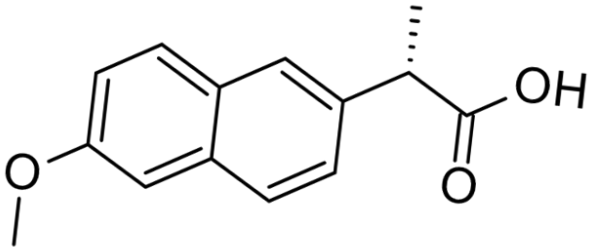
crystal structure solution is missing



phenoxazine

- Substrates: may influence molecular orientation

HOPG/graphene: flat-on (PbPc, naproxen)



naproxen

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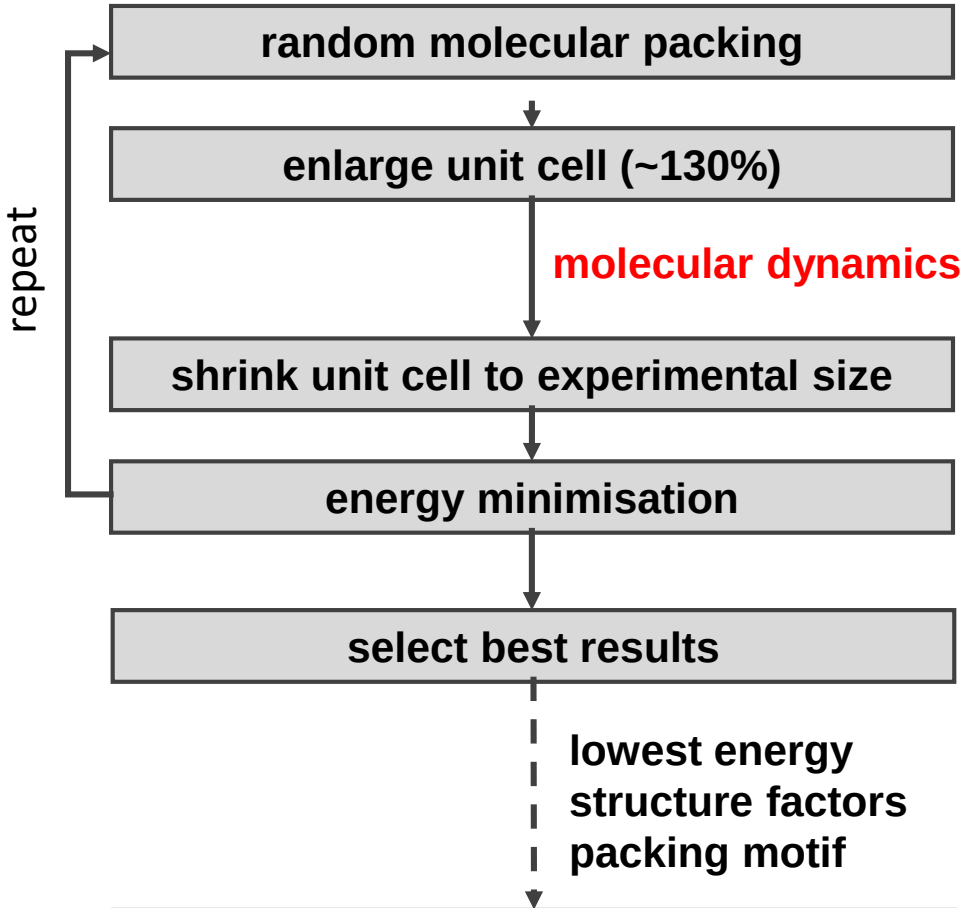
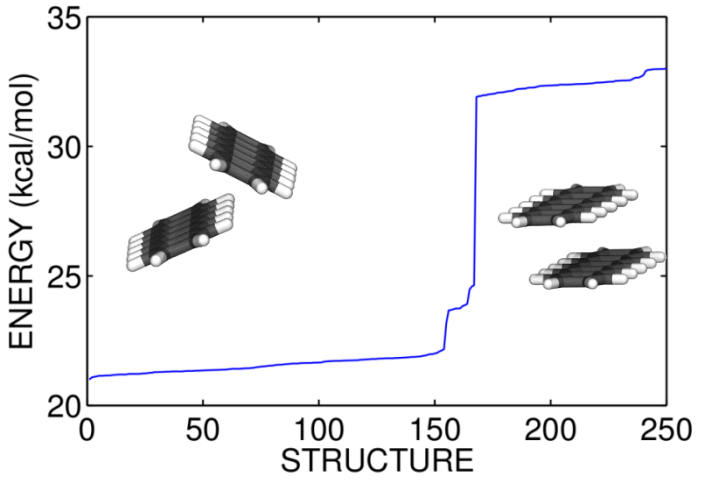
The Laboratory of Polymer Chemistry
(Université Libre de Bruxelles)

This work is part of the
EOS-Project:
From 2Dto3D
ID:30489208

Molecular packing analysis

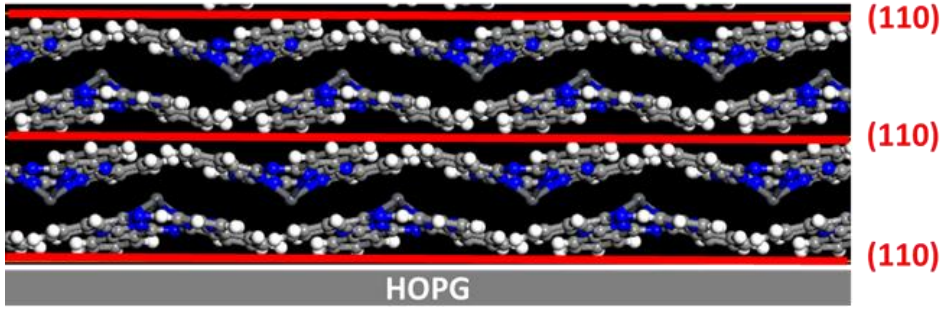
input: lattice constants from GIXD experiments

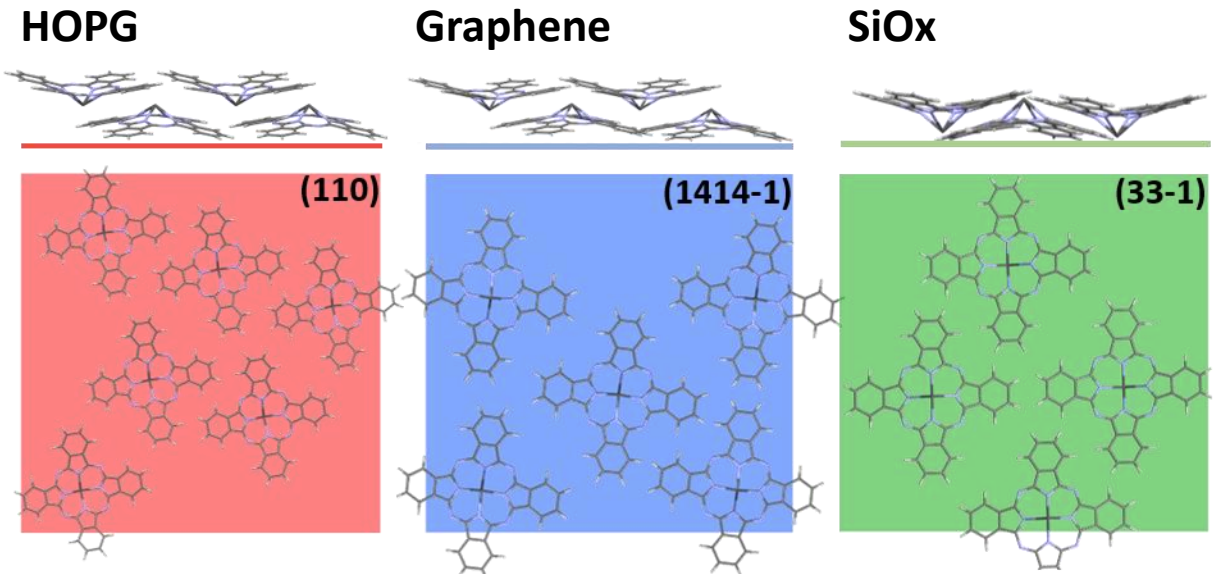




Conclusion lead-phthalocyanine

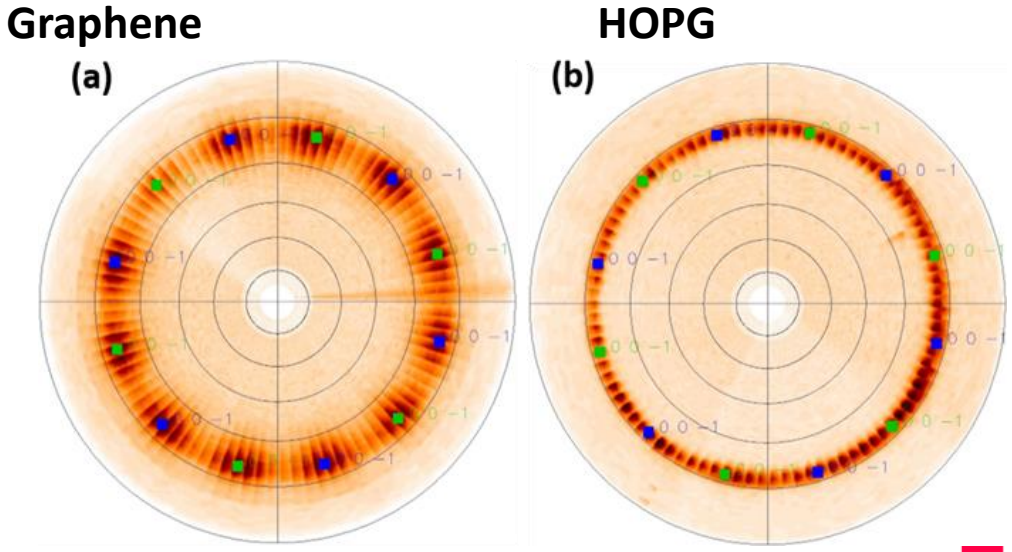
- Substrate-induced polymorph confirmed
- Similar orientation on different substrates
  → flat-on





- Epitaxy on graphene
  → 12 crystal alignments
- HOPG: graphene crystal orientations
  → 2D powder

Spatial distribution of (00-1) in real space

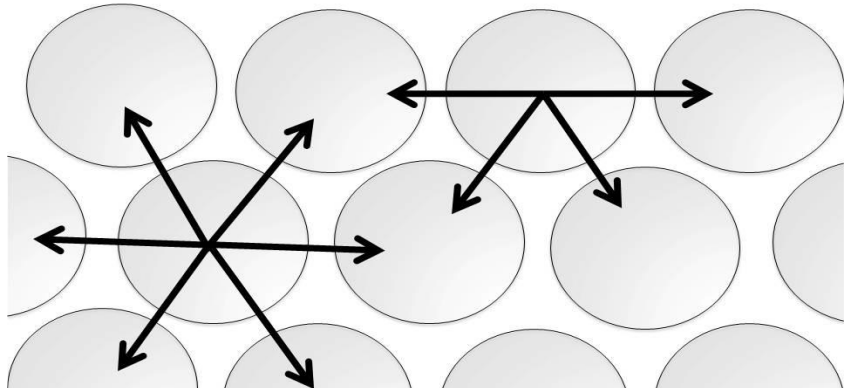


Surface energy

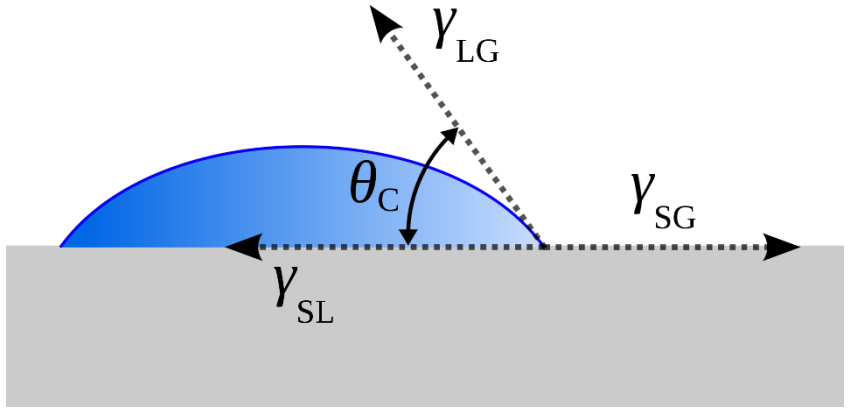
- Surface unfavourable condition
- Requires surface energy (tension) γ
- OWRK: $\gamma = \gamma^d + \gamma^p$
- γ^d: dispersive component
- γ^p: polar component

- Young equation:

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} * \cos\theta_C$$



Schematic intermolecular interaction at interfaces



Schematic derivation of the Young equation.

Surface free energies