

Thin Film Formation and Polymorphism of a Benzothieno-Benzothiophene Derivative

Presenter: Ann Maria James
Supervisor: Roland Resel

5th July 2023

Contents



- 1 Introduction
- 2 Overview
- 3 Crystal Structure Solution
- 4 Thin Film Forming/Charge Transport Properties
- 5 Polymorph Screening at Surfaces
- 6 Memory Effect from Melt Crystallisation
- 7 Conclusion

Introduction



Ultra High Charge Carrier Mobility to Elucidate
Charge Transport Mechanism in Molecular
Semiconductors



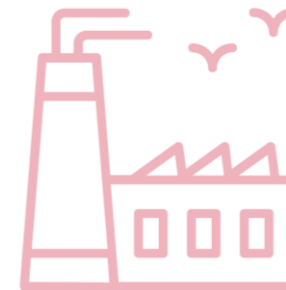
- UHMob is a European Innovative Training Network (ITN).
- Multidisciplinary and cross sectoral training & research in the field of Organic Semiconductors (OSCs).



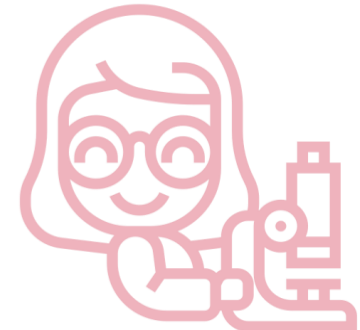
6 Universities



2 Research
Institutes



2 Industries



15 Ph.D.
Students

Organic Semiconductors

- Primarily composed of Carbon and Hydrogen
- Some times heteroatoms (e.g: Oxygen, Sulphur) are also included

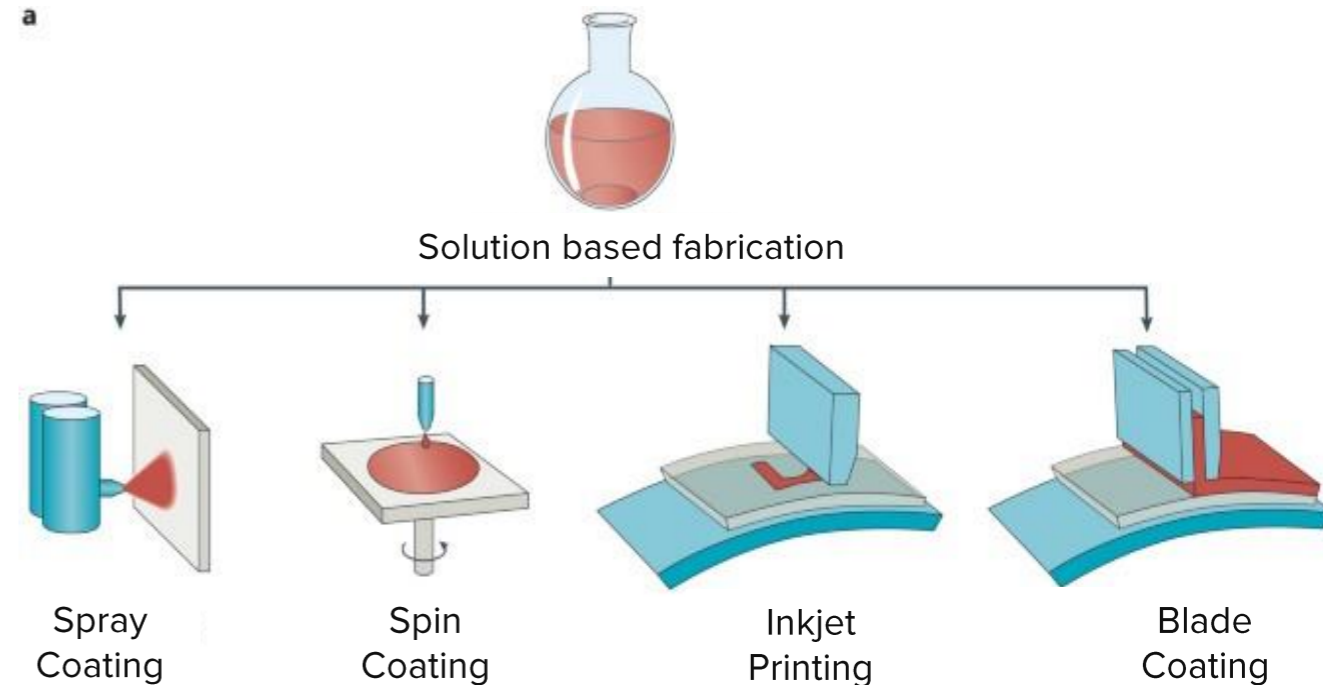
Advantages

Solution Processability

Low cost Fabrication

Flexible Devices

Tunable Properties



Srivastava, Anshika, and Brijesh Kumar. "Organic Light Emitting Diodes-Recent Advancements." *2017 14th IEEE India Council International Conference (INDICON)*. IEEE, 2017.

Ma, Qijie, et al. "Tunable optical properties of 2D materials and their applications." *Advanced Optical Materials* 9.2 (2021): 2001313.

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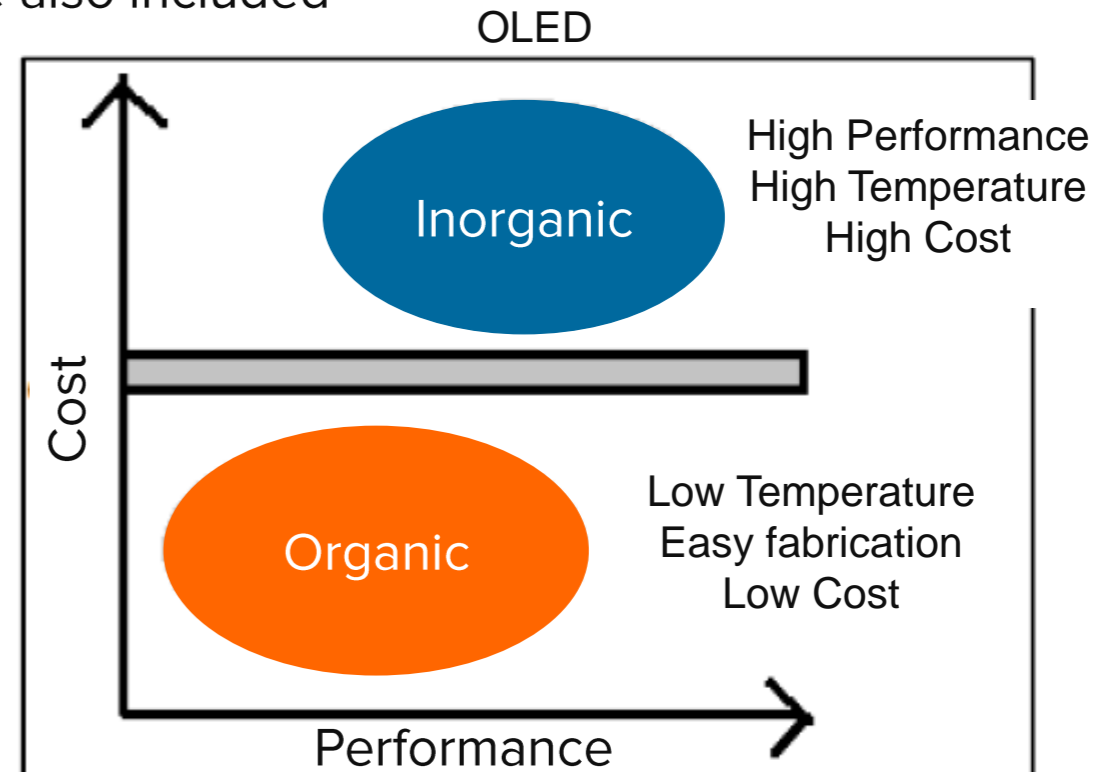
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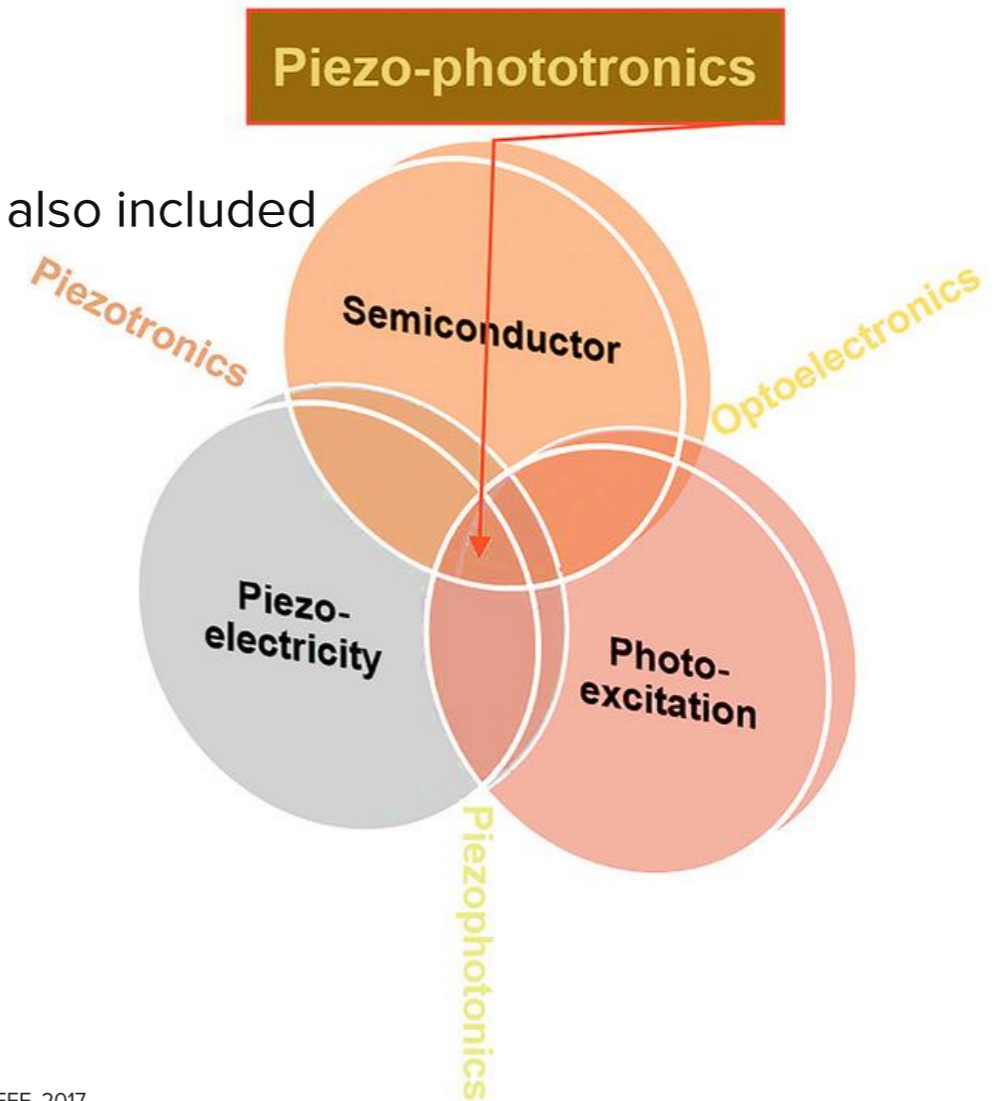
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Advantages

Solution Processability

Low cost Fabrication

Flexible Devices

Tunable Properties

Disadvantages

Poor Performance

Low Stability

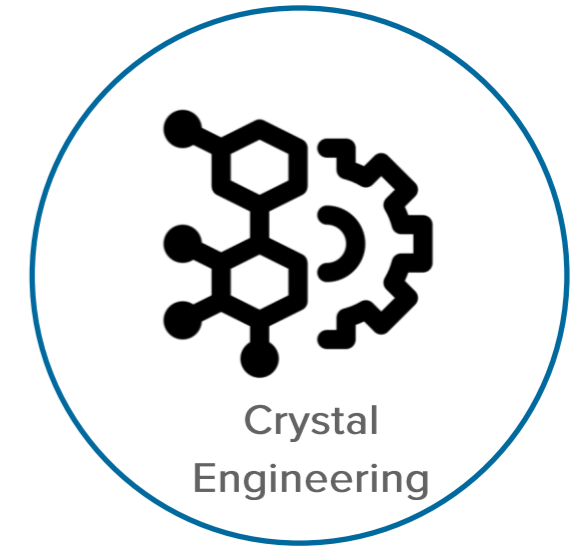
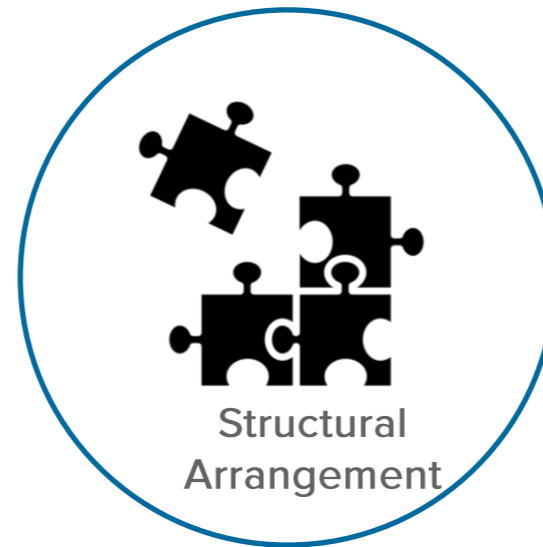
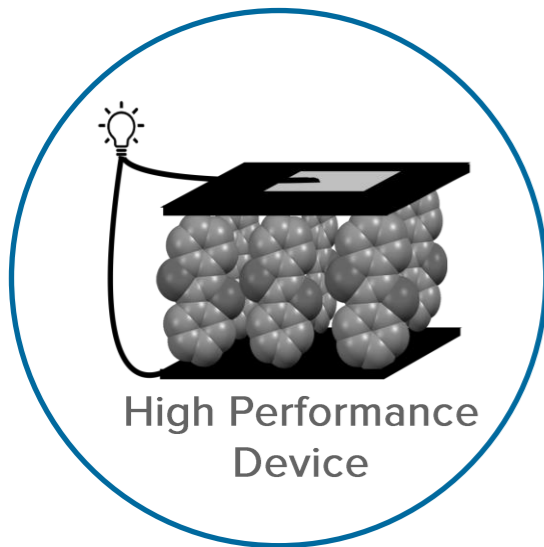
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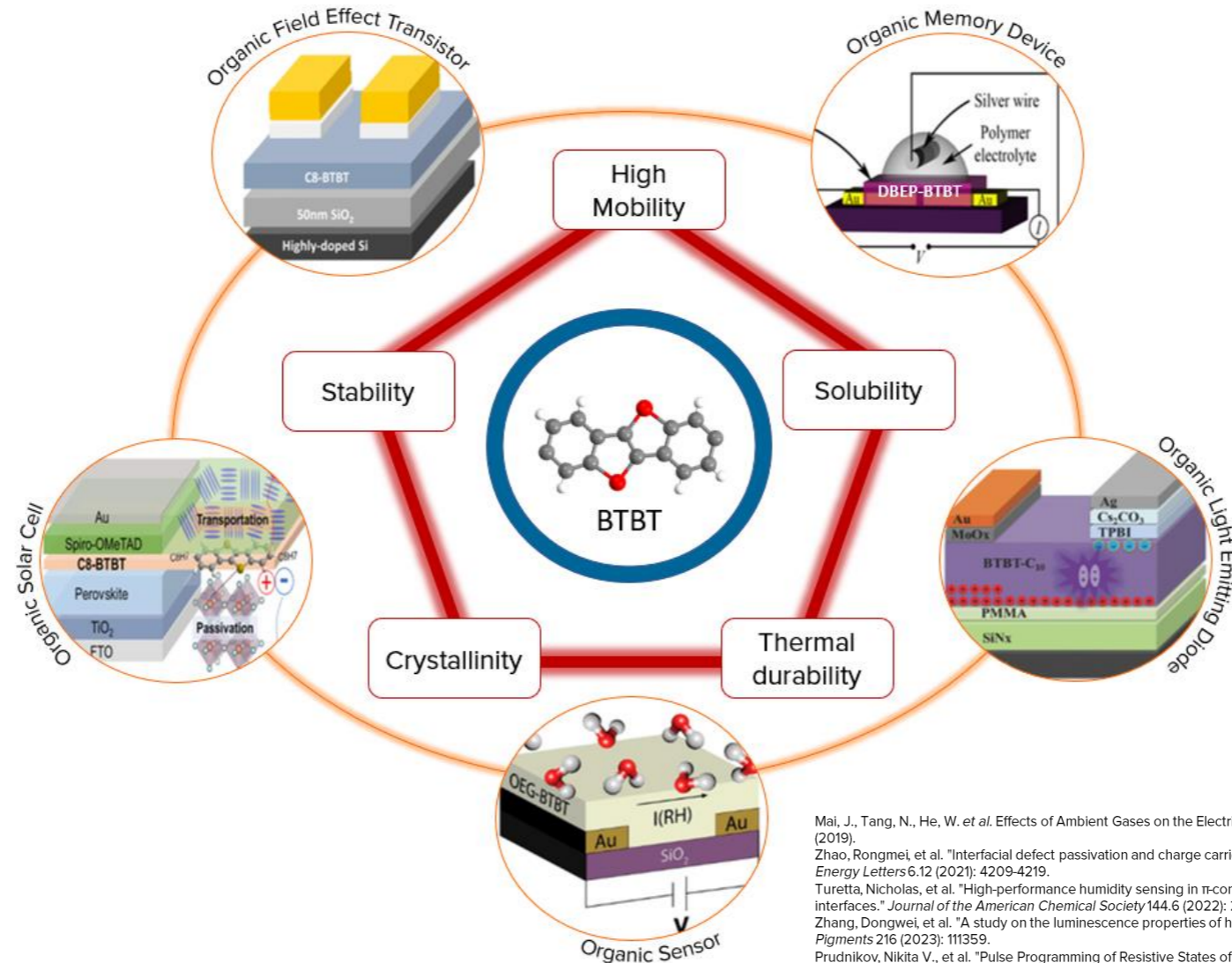
García de Arquer, F. Pelayo, et al. "Solution-processed semiconductors for next-generation photodetectors." *Nature Reviews Materials* 2.3 (2017): 1-17.

OSCs: Tunable Properties

Design Strategy → Bottom-Top approach



Benzothieno Benzothiophene (BTBT) Based Devices



Mai, J., Tang, N., He, W. et al. Effects of Ambient Gases on the Electrical Performance of Solution-Processed C8-BTBT Thin-Film Transistors. *Nanoscale Res Lett* 14, 169 (2019).

Zhao, Rongmei, et al. "Interfacial defect passivation and charge carrier management for efficient perovskite solar cells via a highly crystalline small molecule." *ACS Energy Letters* 6.12 (2021): 4209-4219.

Turetta, Nicholas, et al. "High-performance humidity sensing in π -conjugated molecular assemblies through the engineering of electron/Proton transport and device interfaces." *Journal of the American Chemical Society* 144.6 (2022): 2546-2555.

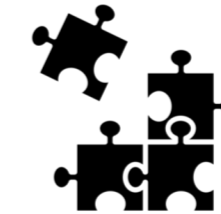
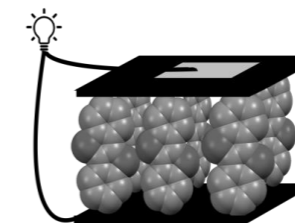
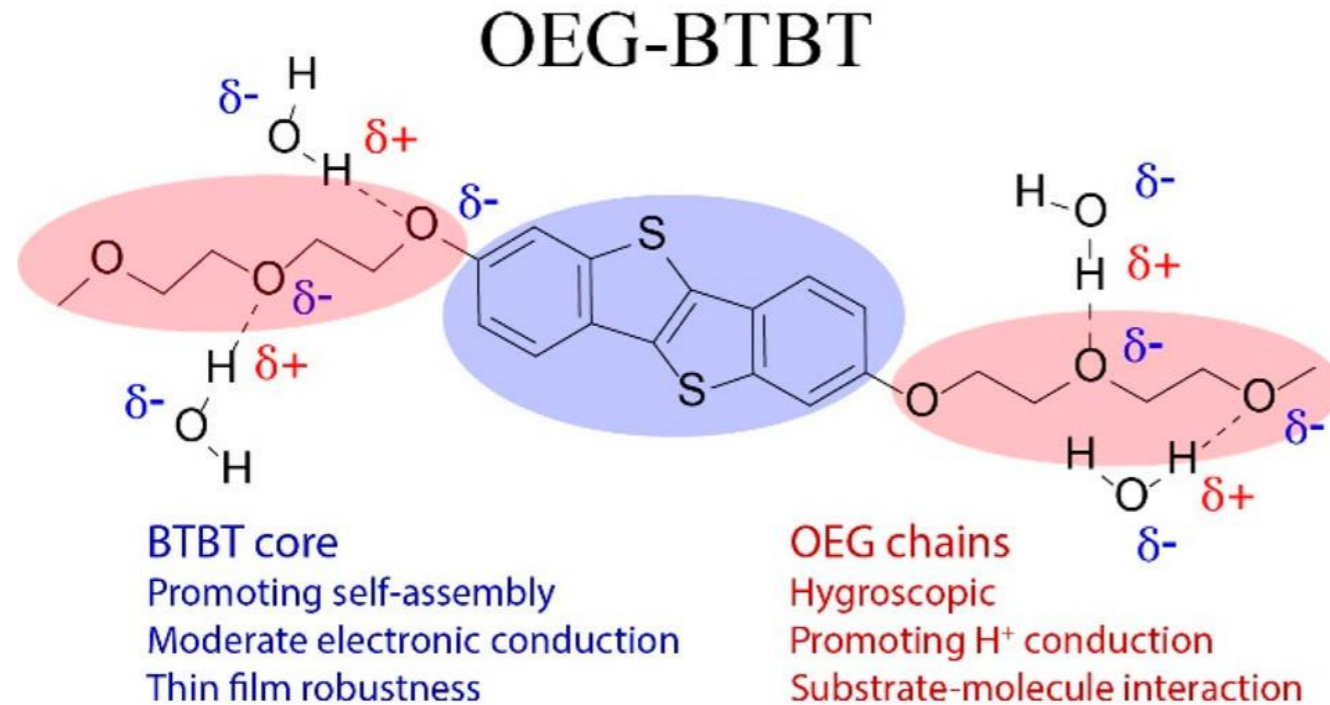
Zhang, Dongwei, et al. "A study on the luminescence properties of high-performance benzothieno [3, 2-b][1] benzothiophene based organic semiconductors." *Dyes and Pigments* 216 (2023): 111359.

Prudnikov, Nikita V., et al. "Pulse Programming of Resistive States of a Benzothieno [3, 2-B][1]-Benzothiophene-Based Organic Memristive Device with High Endurance." *physicstatus solidi (RRL)—Rapid Research Letters* 16.2 (2022): 2100471.

Molecule of Interest: OEG-BTBT

Design &
Synthesis

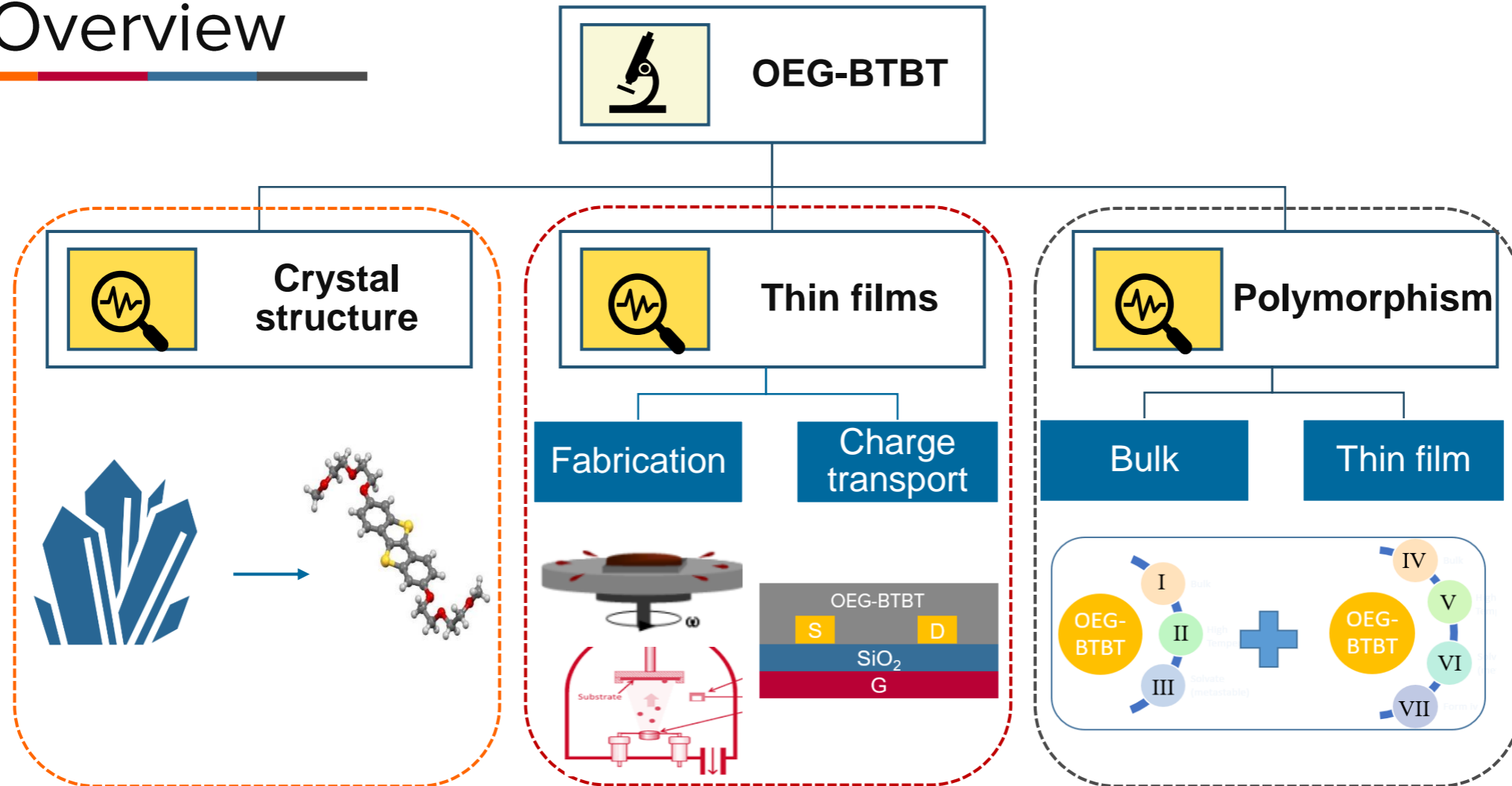
ULB

Structural
InvestigationsDevice
Performance

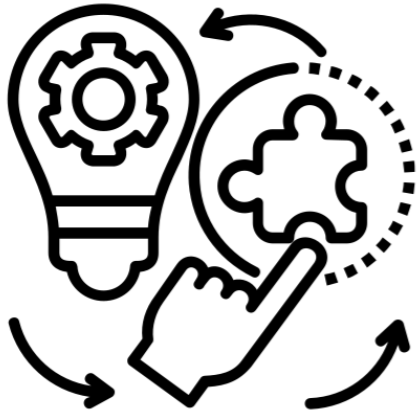
Note: OEG → Oligo Ethylene Glycol

TU
GrazUniversité
de Strasbourg

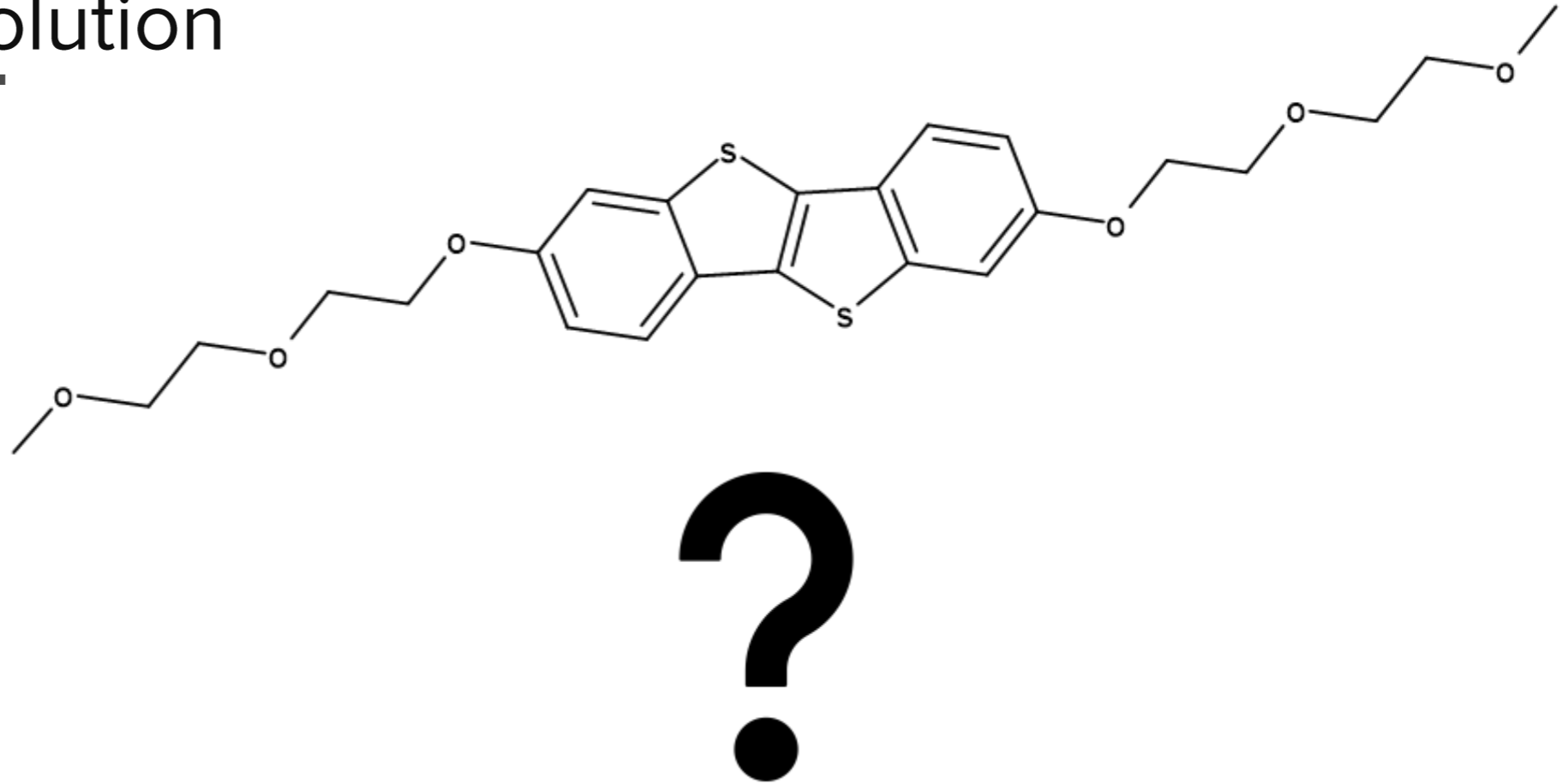
Overview

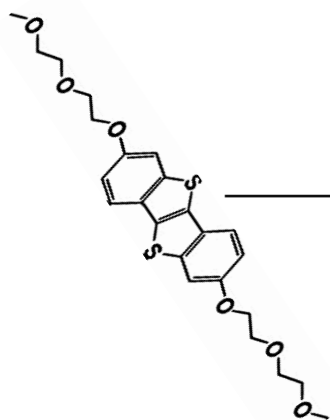


Crystal Structure Solution

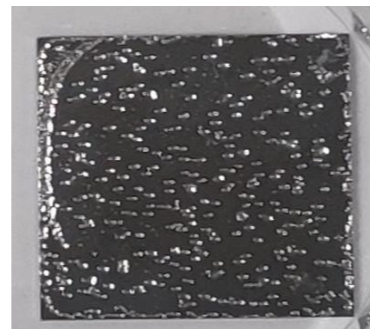


“ It is fascinating, right?
Sometimes all you need to solve
a puzzle is a beam of X-rays”

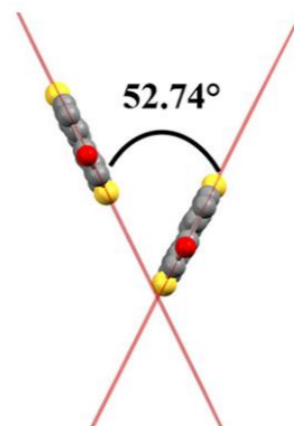
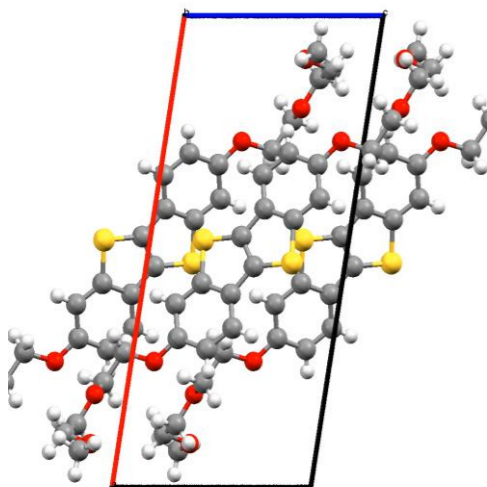
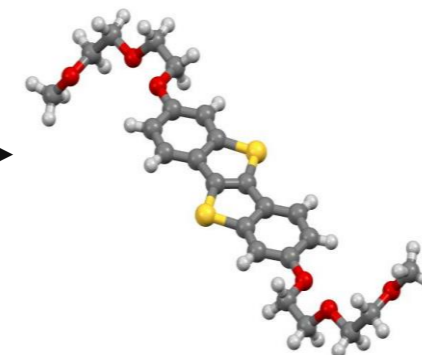




Drop Casting (Slow)
Cyclohexanone



Single Crystal
XRD



Herringbone angle 52°

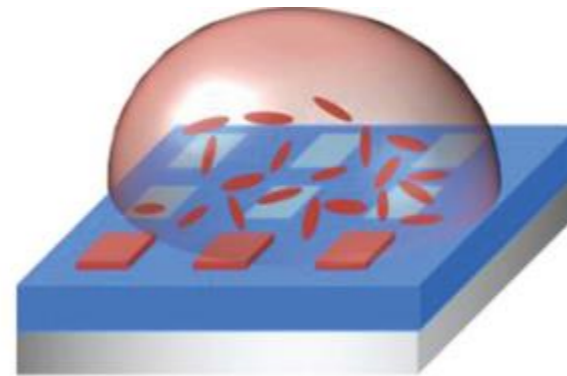
a	18.635
b	7.6670
c	8.2930
α	90
β	99.35
γ	90
Volume	1169.14

Thin Film Forming Properties

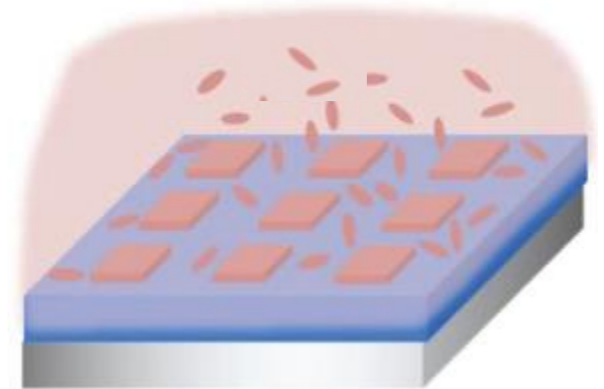


Thin Films

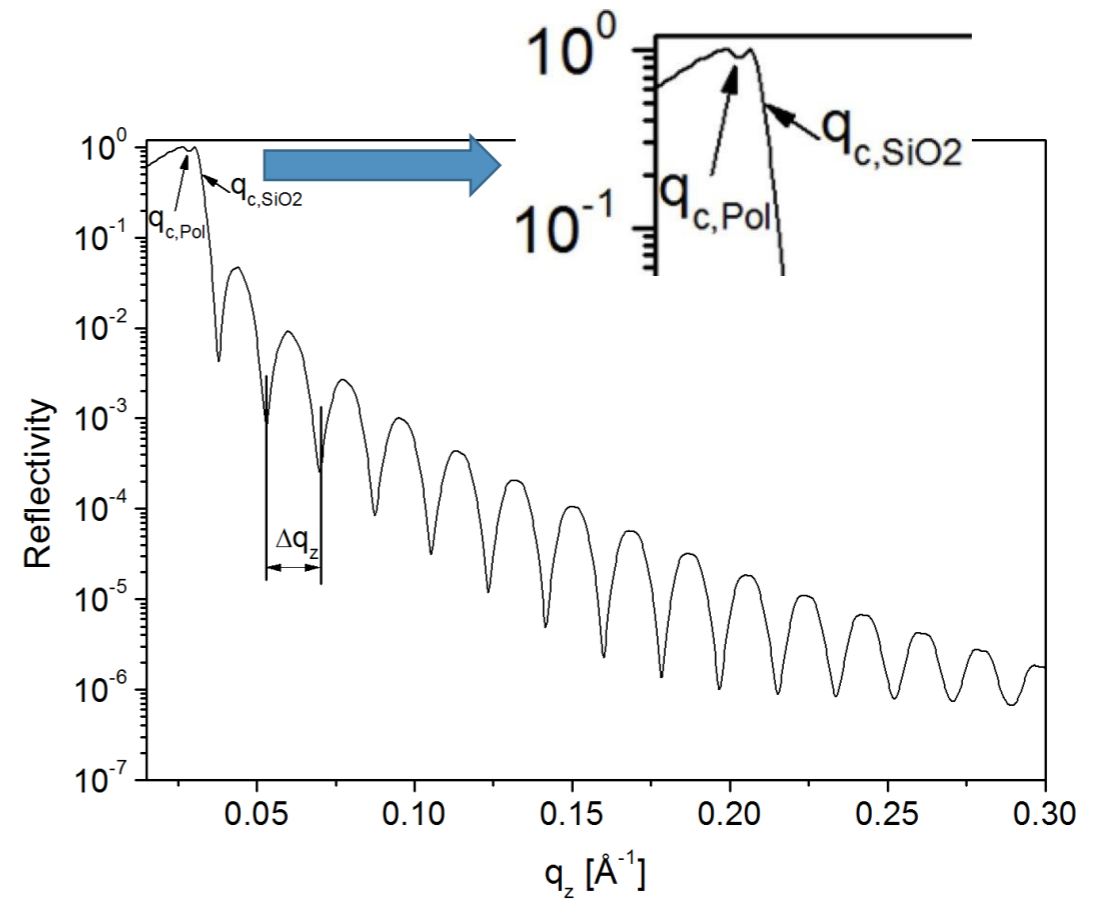
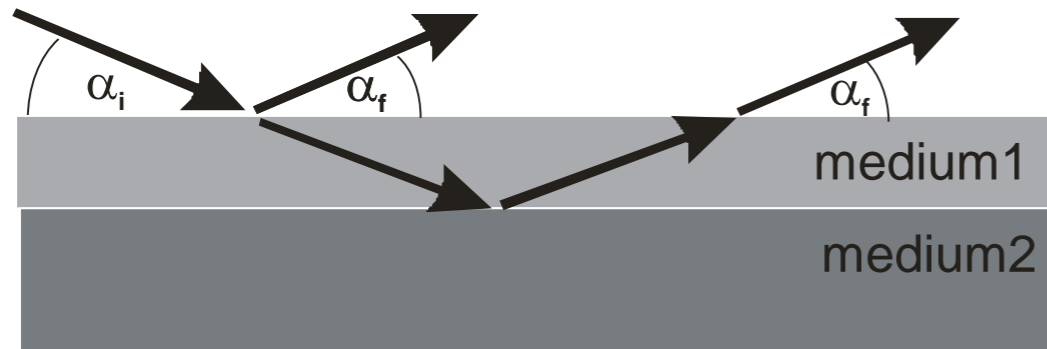
Solution
Processing



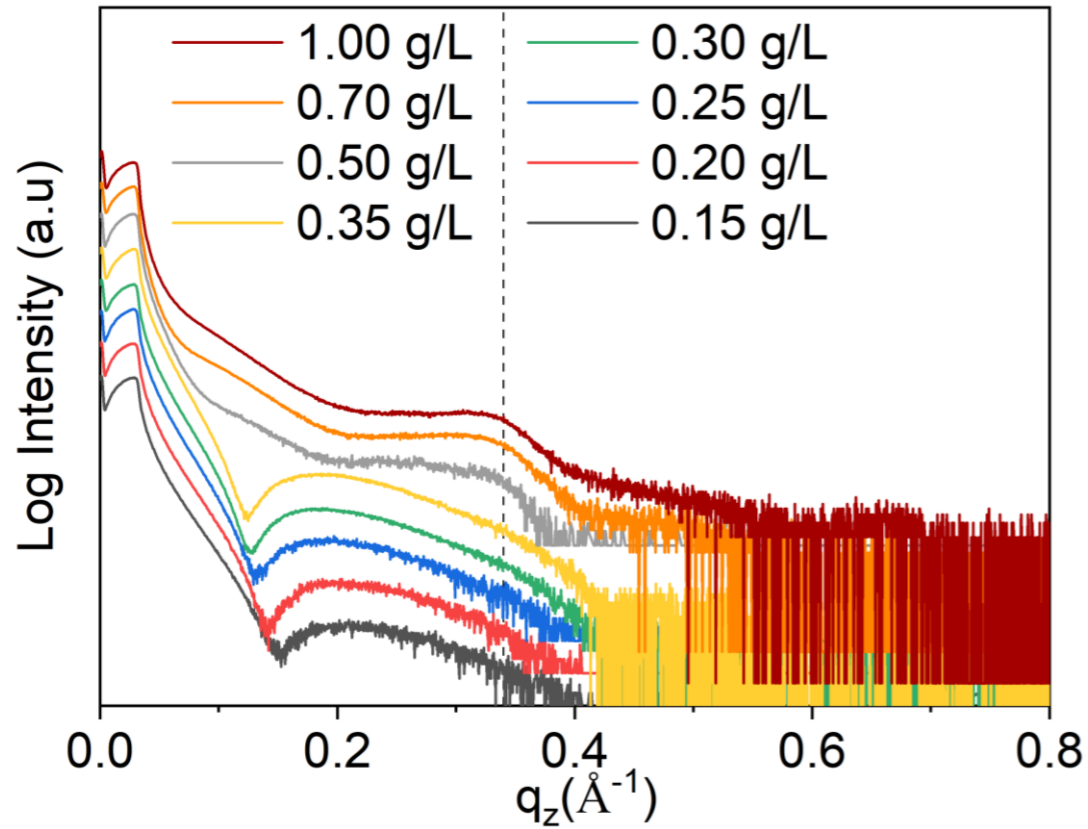
Physical
Vapor
Deposition



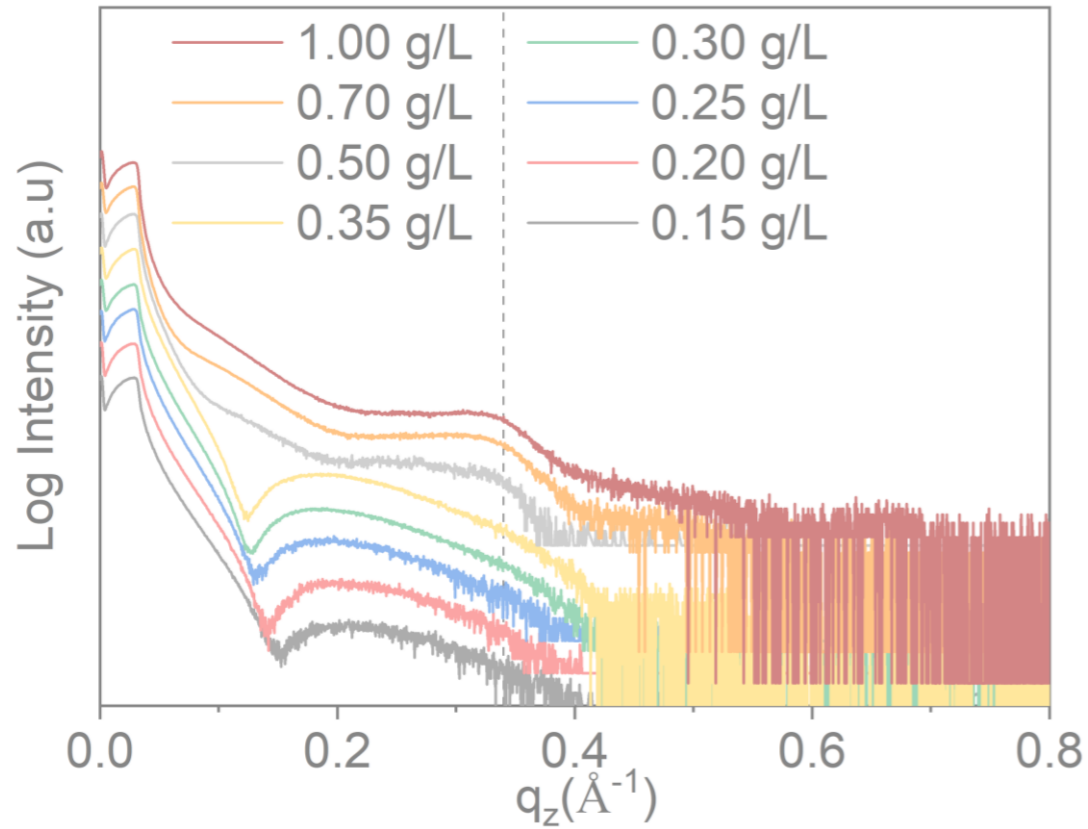
- Contrast in electron density
- interference between the surface reflected and the interface reflected beams



- mono to bulk layer formation

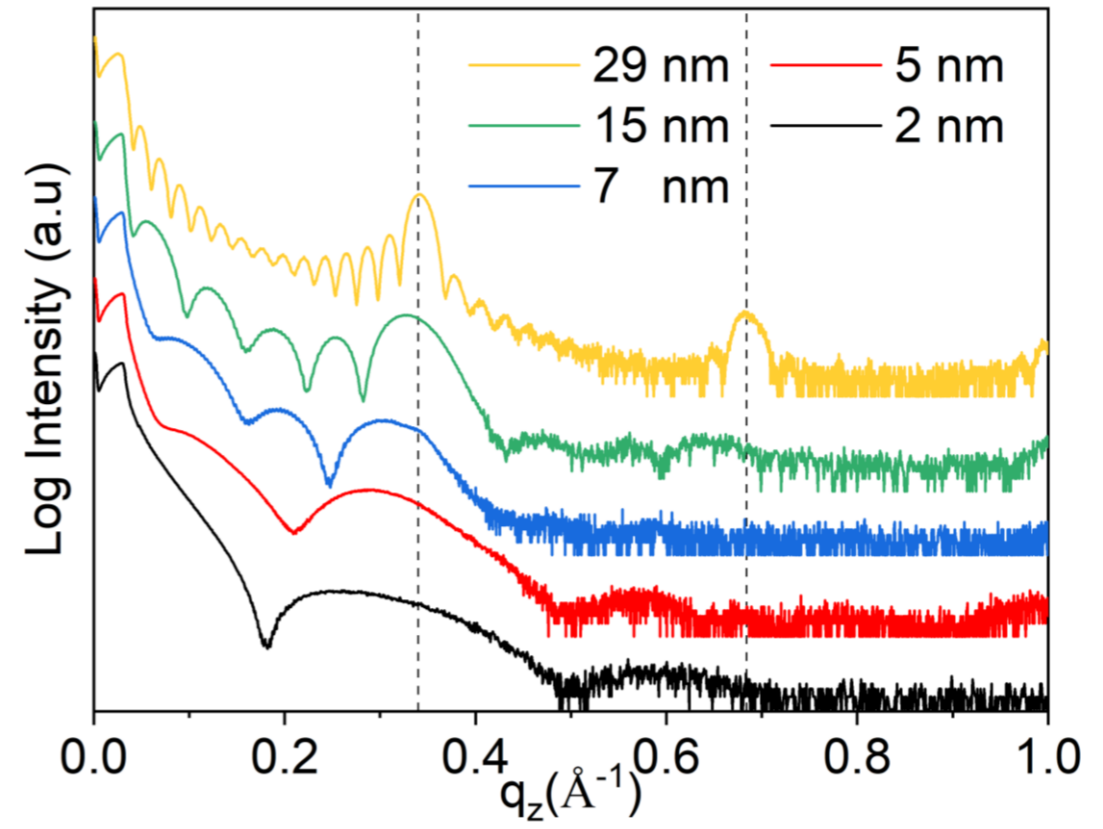


- mono to bulk layer formation



Solution Processed

Spin Coating (Chloroform)



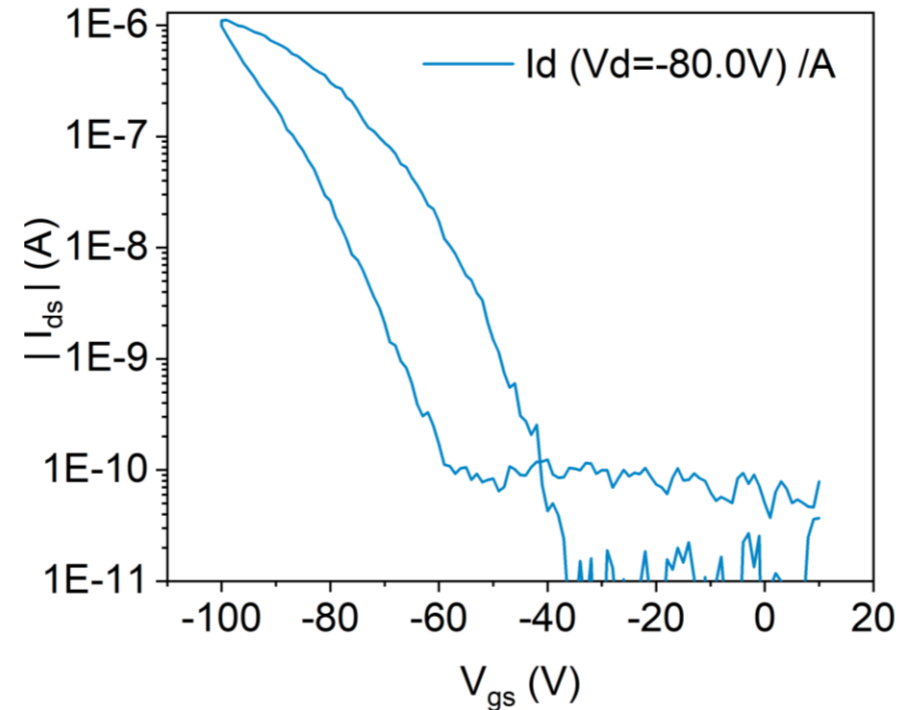
Physical Vapor Deposition

Thermal Evaporation

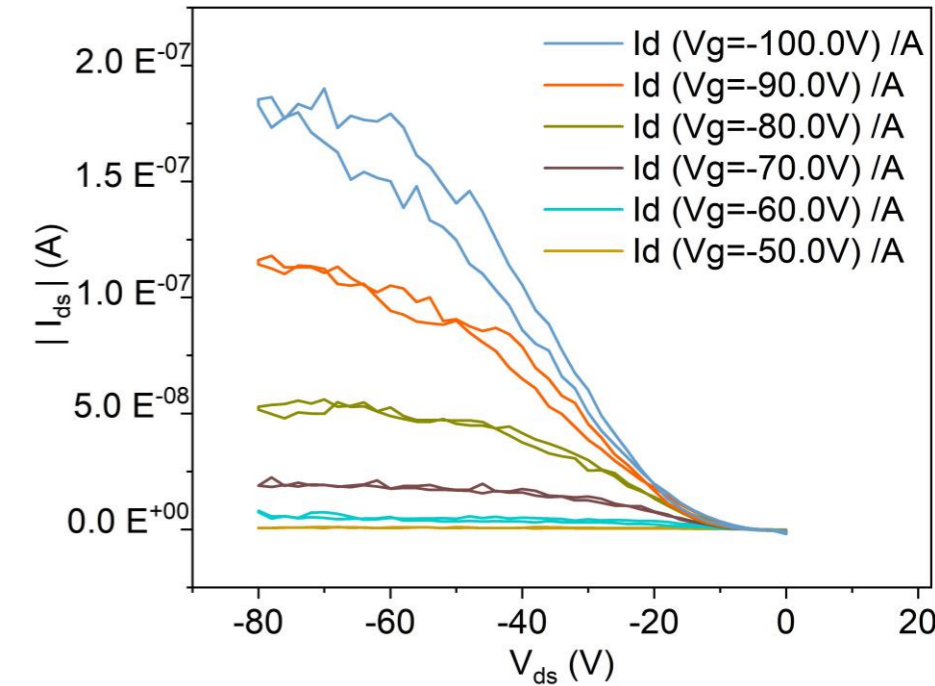
Charge Transport Properties



Transfer characteristic



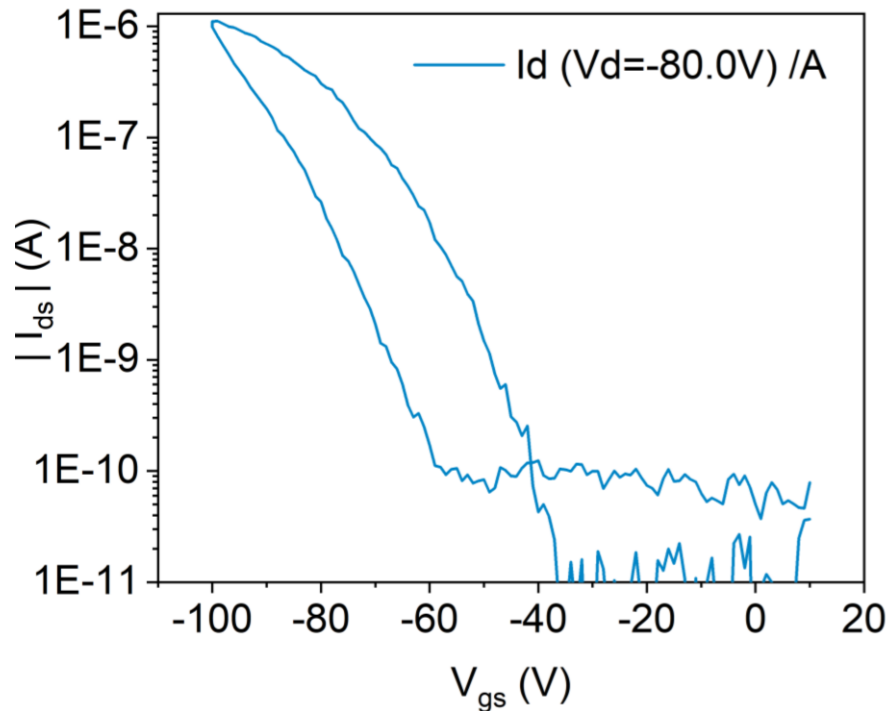
Output characteristic



- threshold voltage $V_{th} = -64 \text{ V}$
- I_{on}/I_{off} ratio = 10^4
- charge carrier mobility $\mu_{sat} = 6.2 \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$

Charge Transport Properties

Transfer characteristic



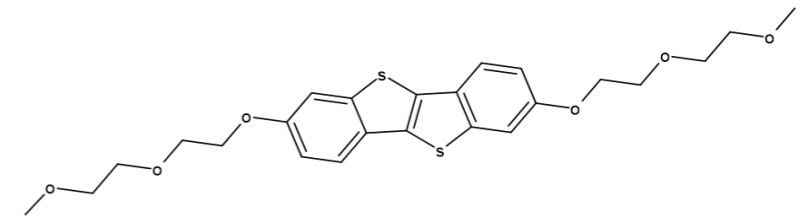
- Large turn on volage → -64 V



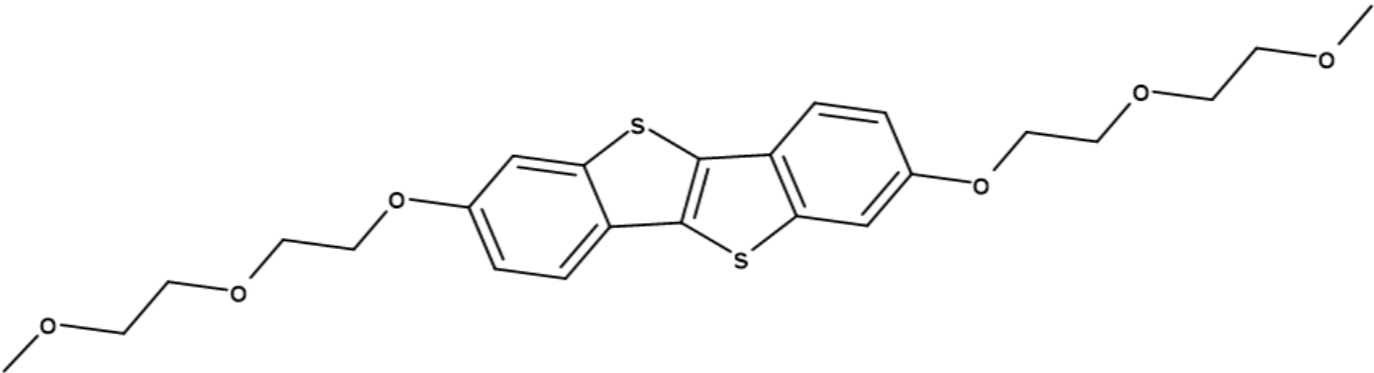
Improved Performance ?

Optimisation

- Deposition of active channel layer at different temperature
- Surface Modification
→ self assembled monolayer
- Different metals for electrodes



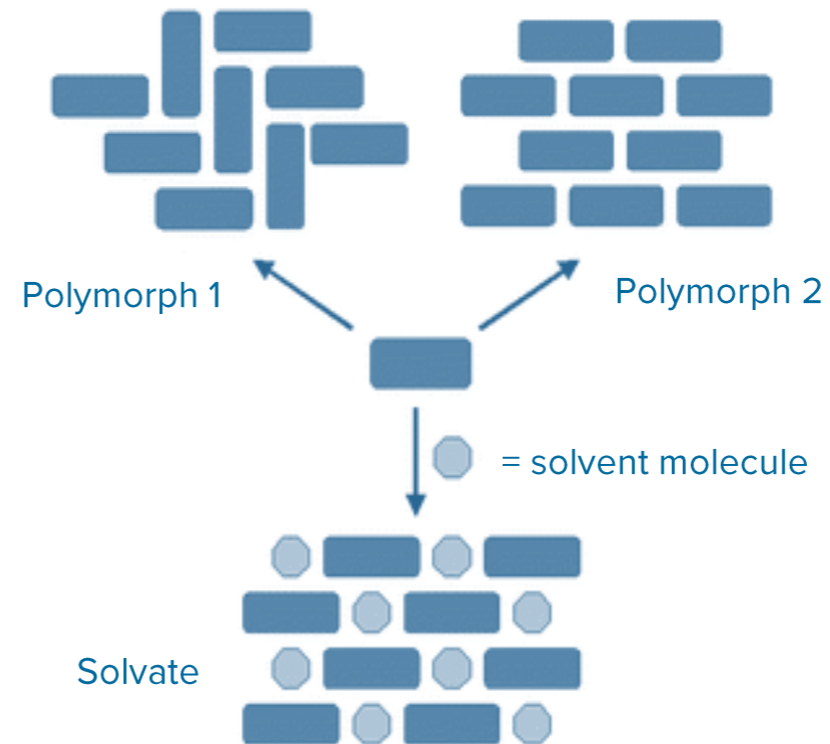
Polymorphism



Polymorphism → ability of a molecular compound to possess different crystal structures with same molecular composition.

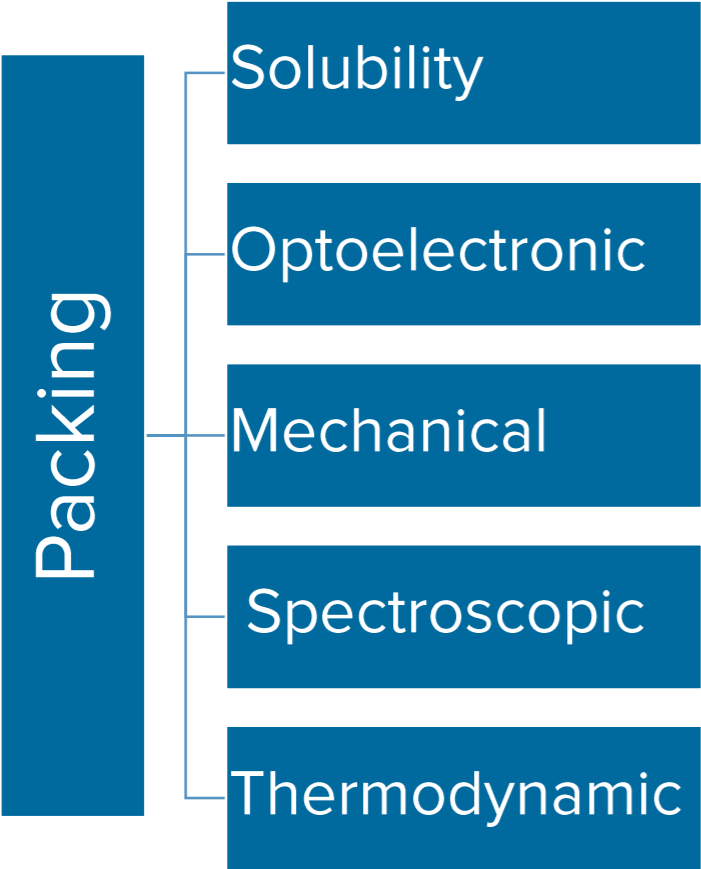


“Catch me, if you can.”

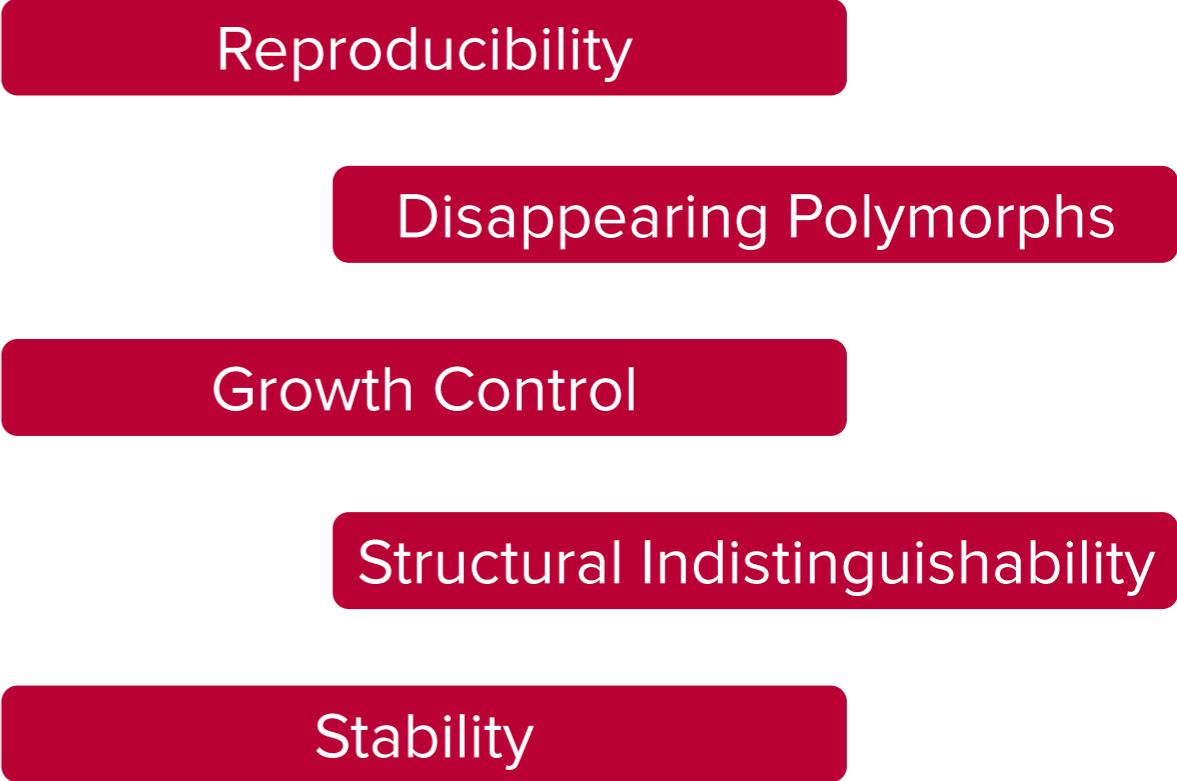


→ formed due to complex interplay between thermodynamics & kinetics during the crystallisation process.

Interesting ?

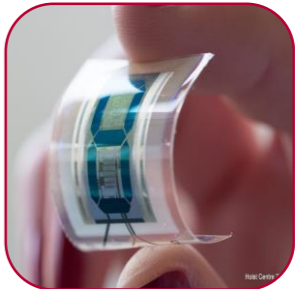


Challenging ?





Applications



Pharmaceuticals

Organic semiconductors

■ Mebendazol → 3

Clinically favoured

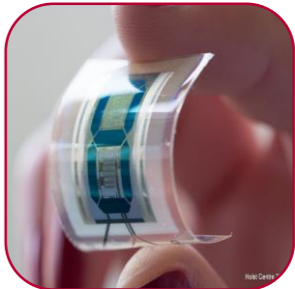


Least soluble
Not efficient

More side effects
More soluble
(risk of high dosage)



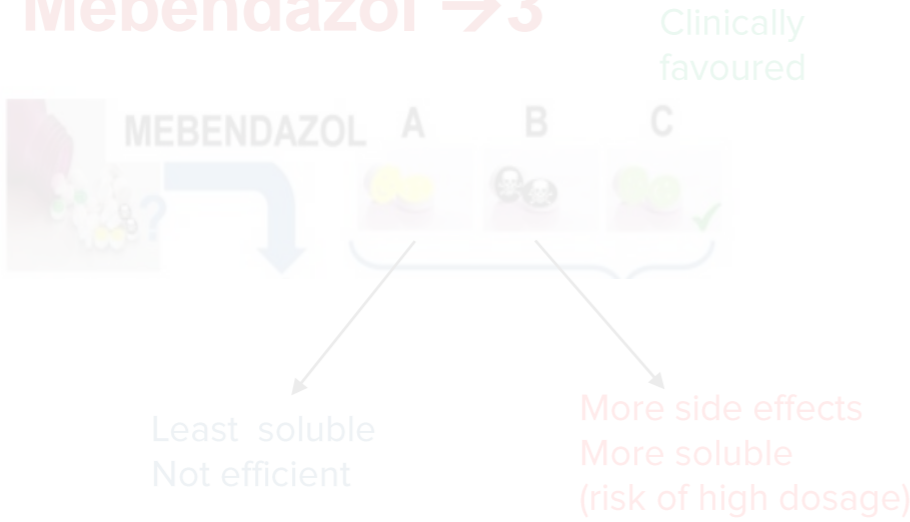
Applications



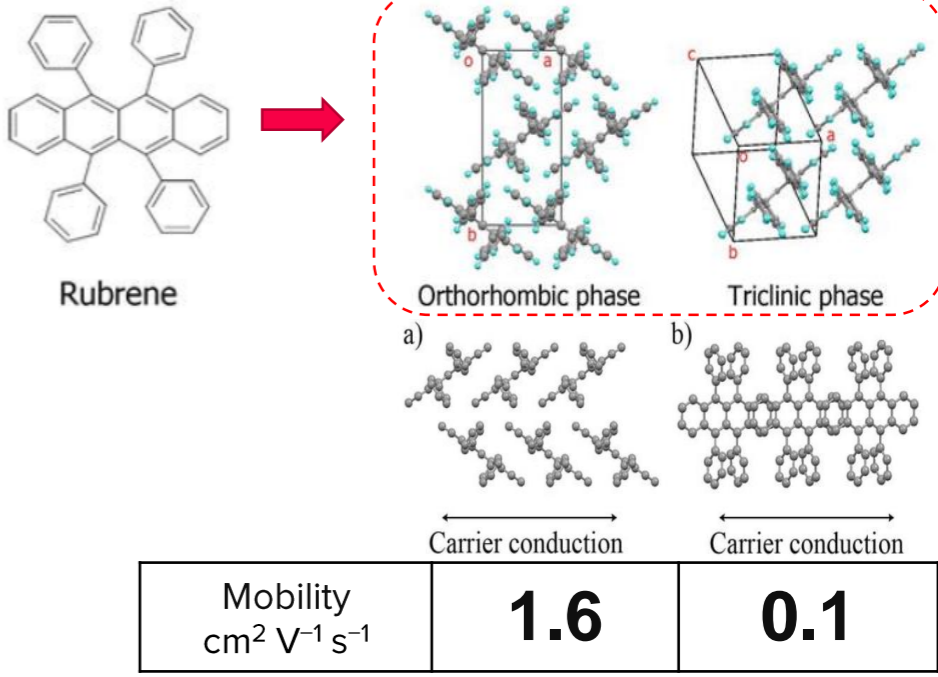
Pharmaceuticals

Organic semiconductors

▪ Mebendazol → 3



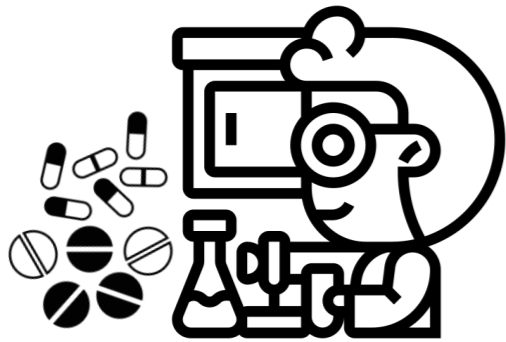
▪ Rubrene → 4



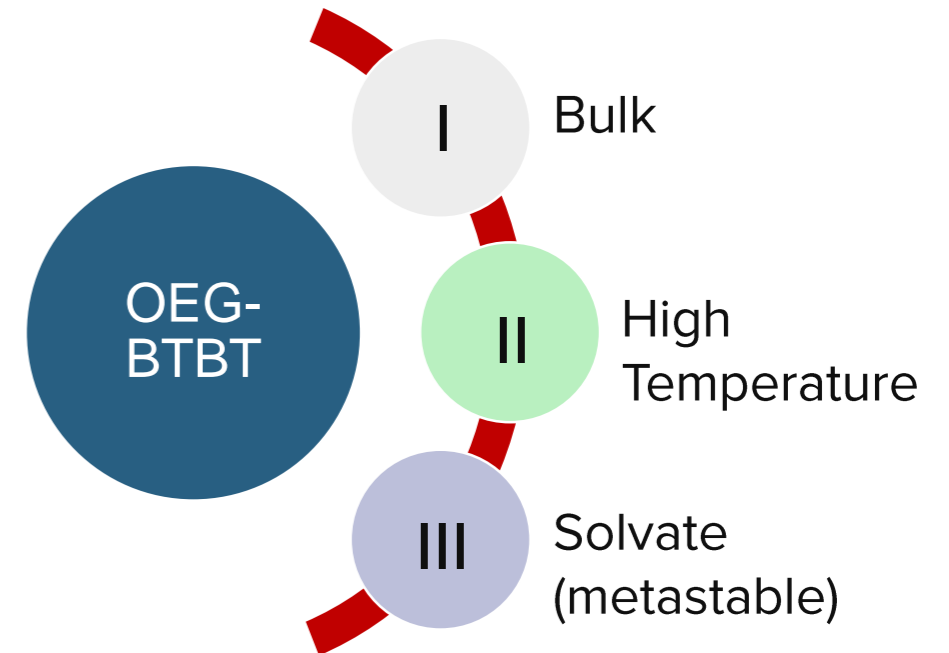
Calvo, Natalia L., Teodoro S. Kaufman, and Rubén M. Maggio. "Mebendazole crystal forms in tablet formulations. An ATR-FTIR/chemometrics approach to polymorph assignment." *Journal of Pharmaceutical and Biomedical Analysis* 122 (2016): 157-165 ■

Polymorph Screening → Bulk → 3

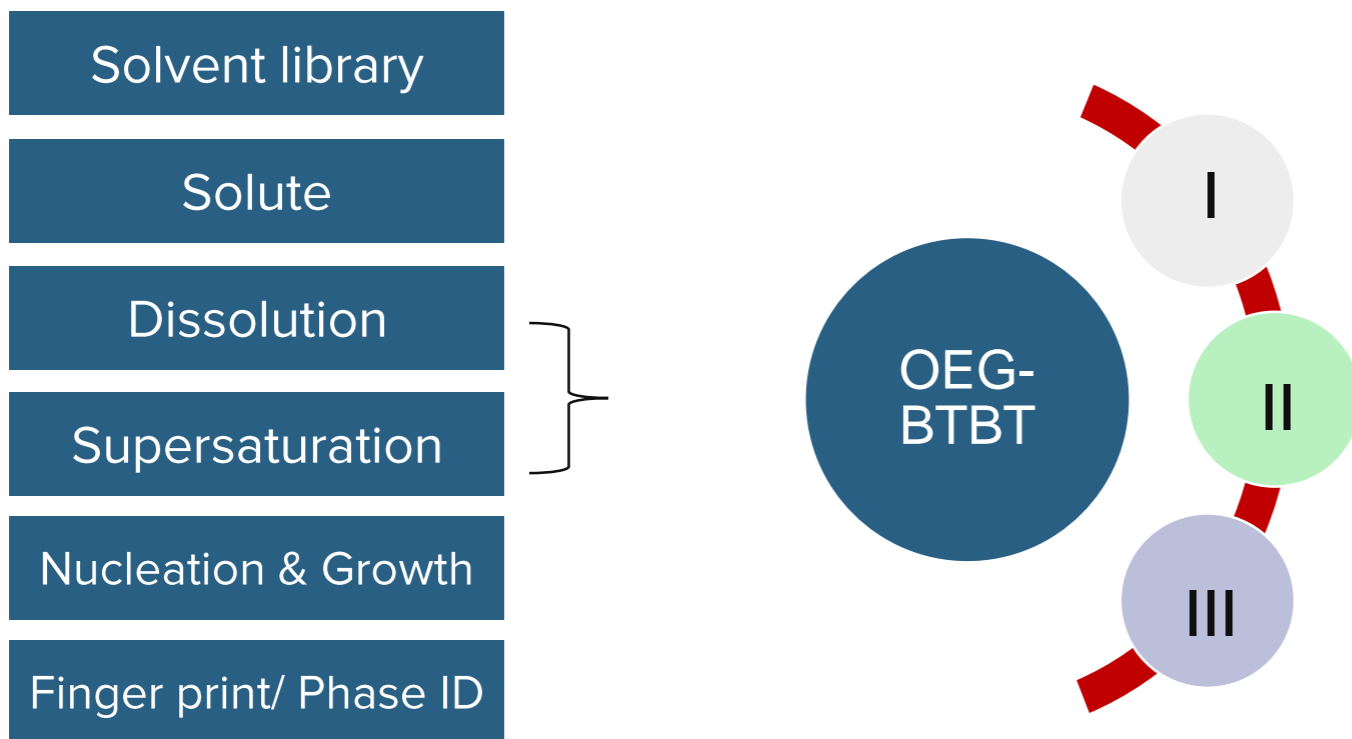
-Set of experimental protocols designed for discovering new polymorphs.



- Solvent library
- Solute
- Dissolution
- Supersaturation
- Nucleation & Growth
- Finger print/ Phase ID

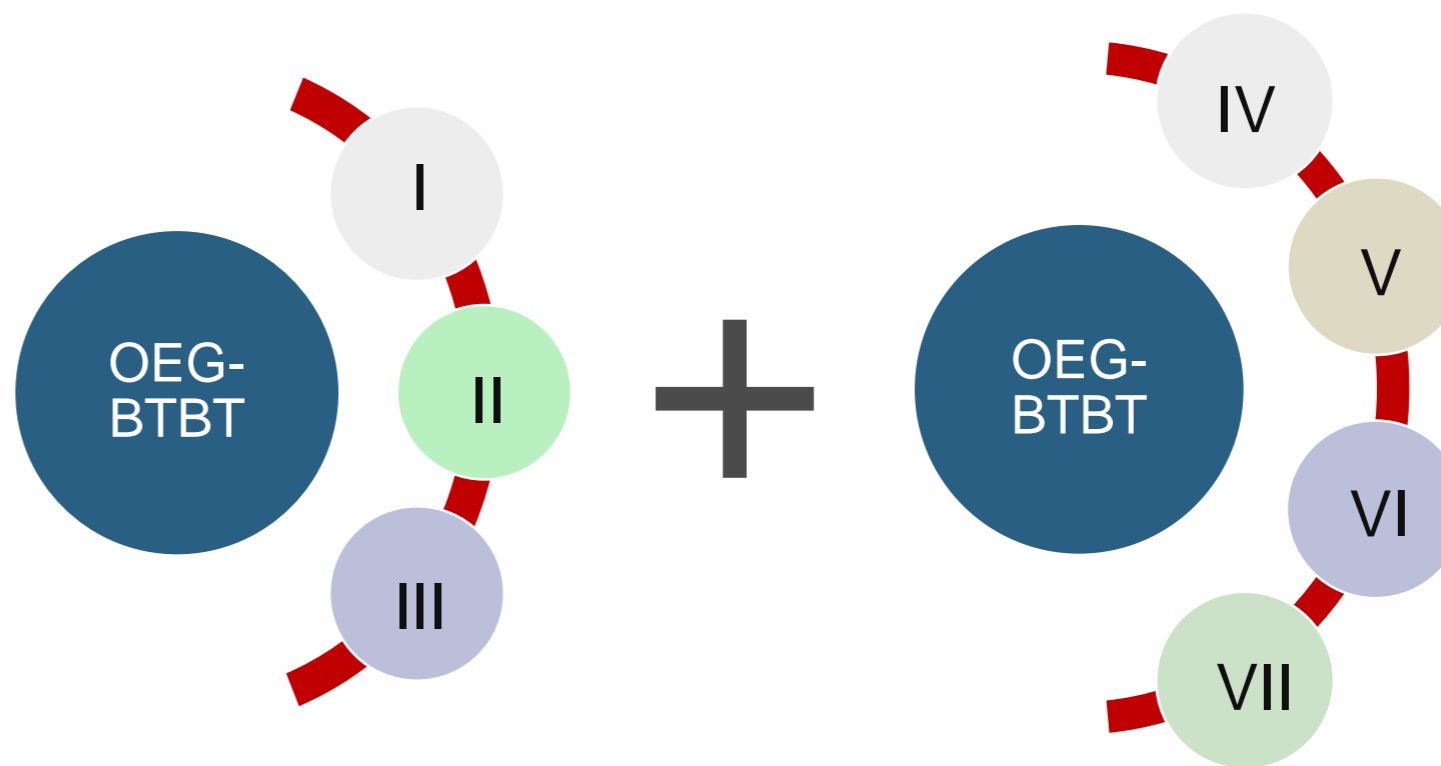


Polymorph Screening → Surfaces



Polymorph Screening → Surfaces → 4

- Solvent library
- Solute
- Dissolution
- Substrate
- Supersaturation
- Nucleation & Growth
- Finger print/ Phase ID





- Discovery of new surface exclusive phases

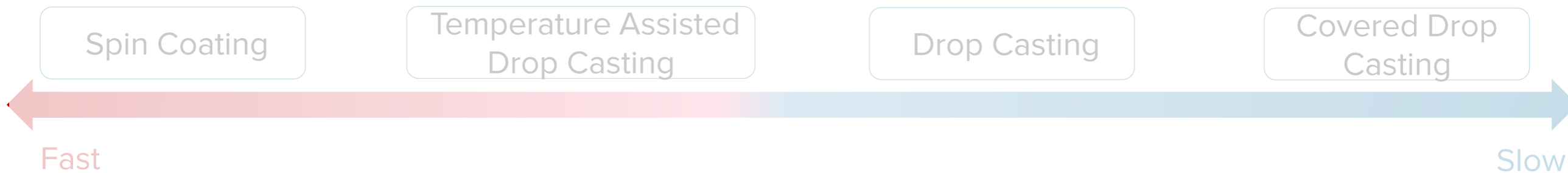
↳ Crystallisation kinetics can be broadly varied.





- Discovery of new surface exclusive phases

↳ Crystallisation kinetics can be broadly varied.



↳ “Stabilisation” of metastable phases at surfaces.



Surface Mediated Structures: Stabilization of Metastable Polymorphs on the Example of Paracetamol

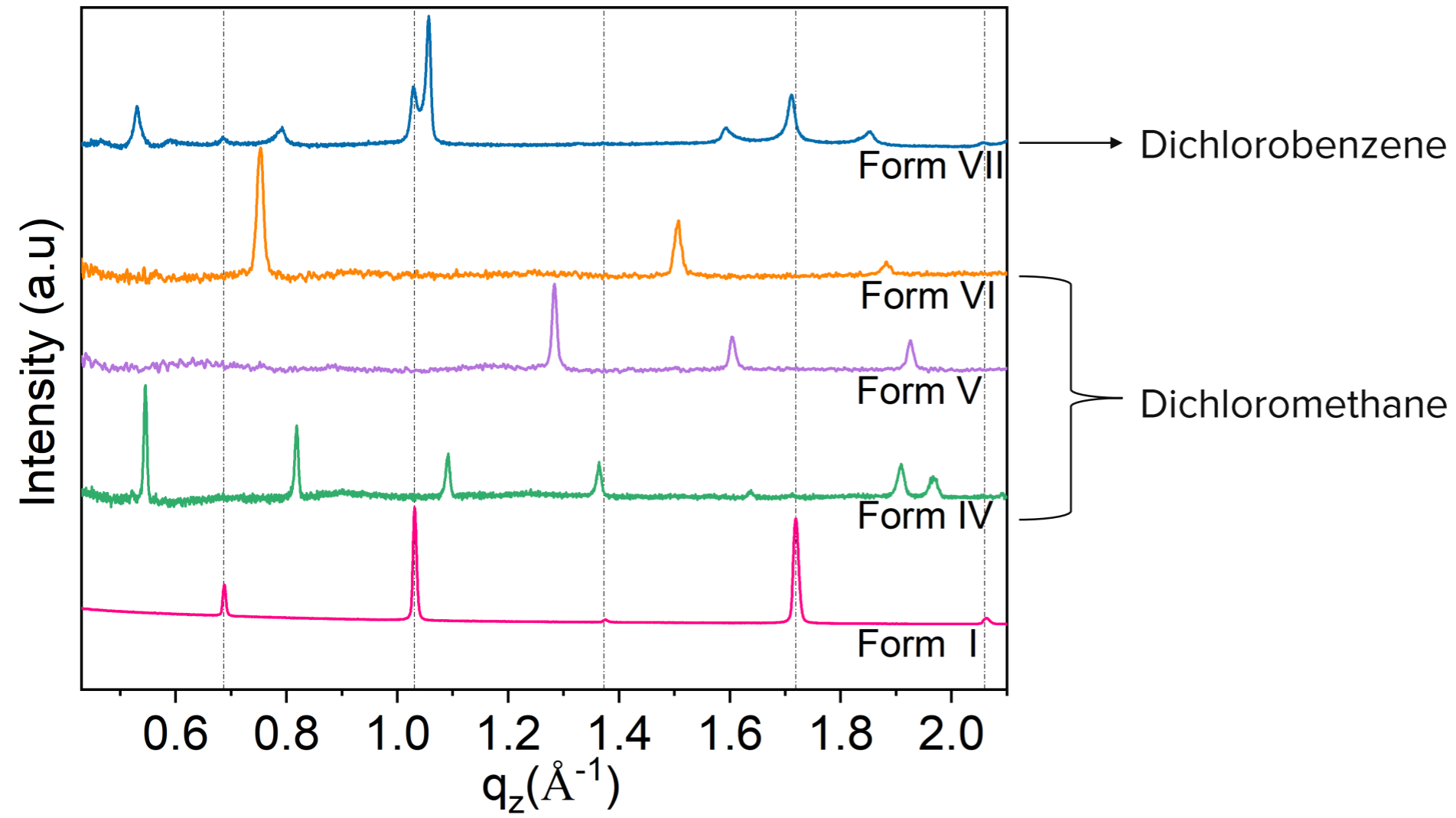
Heike M. A. Ehm^{*} and Oliver Werzer

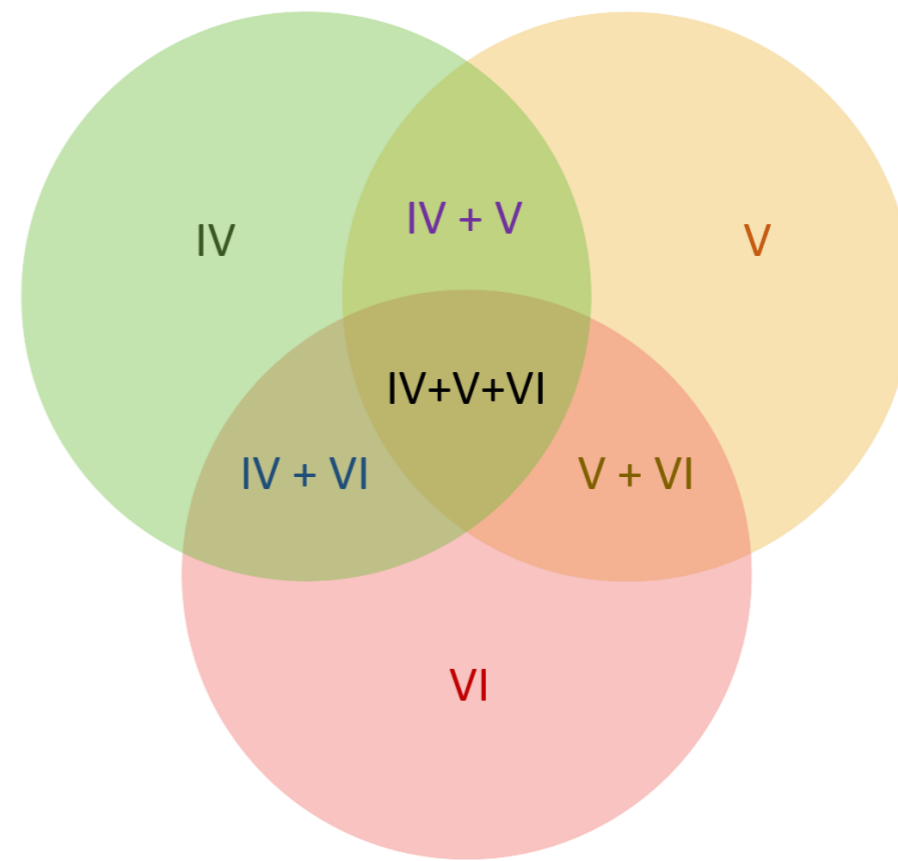
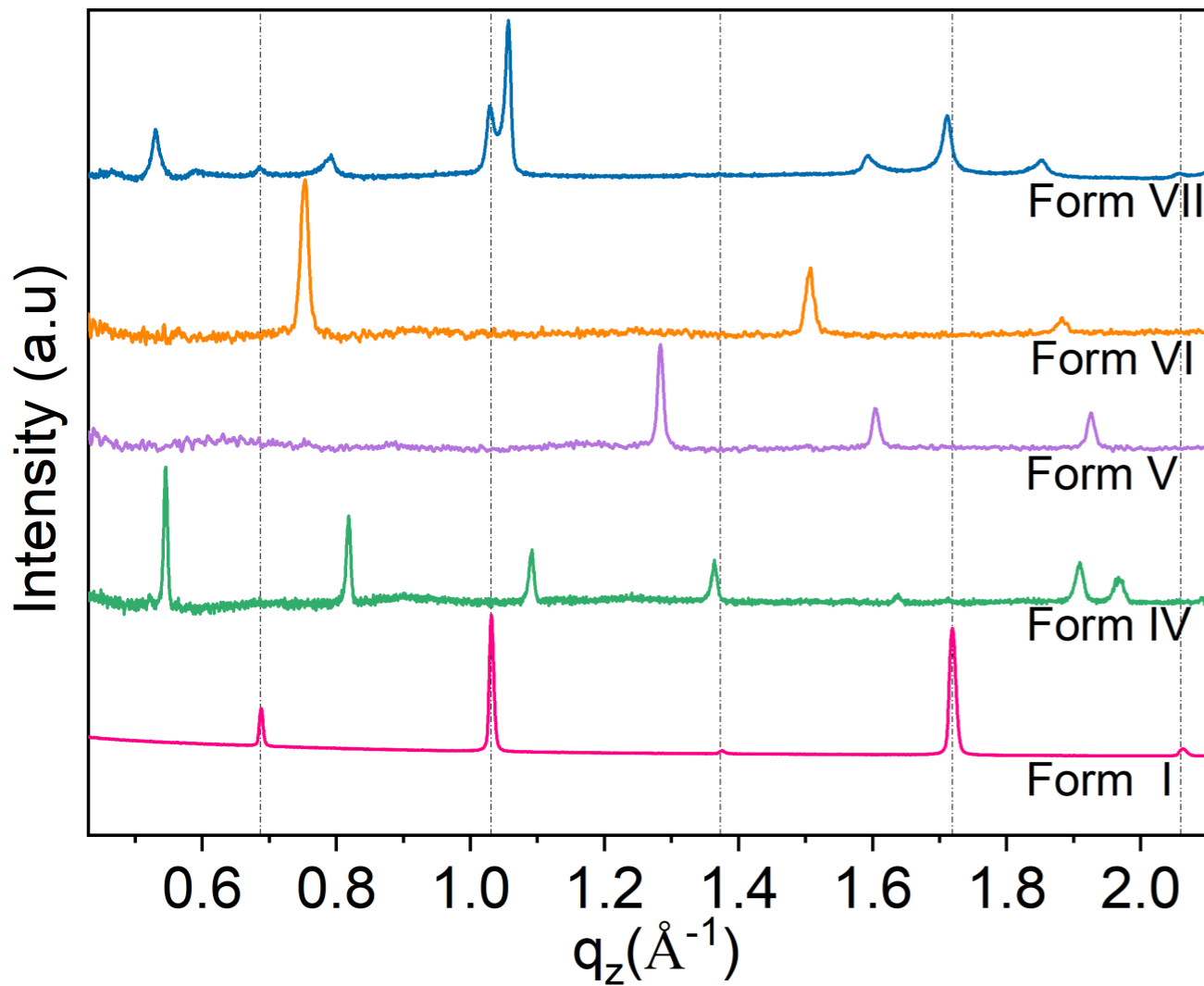


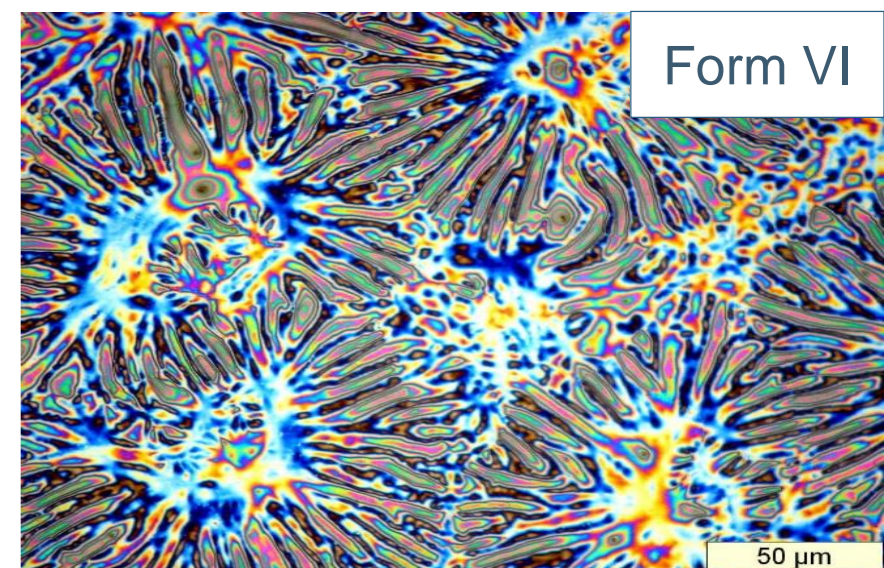
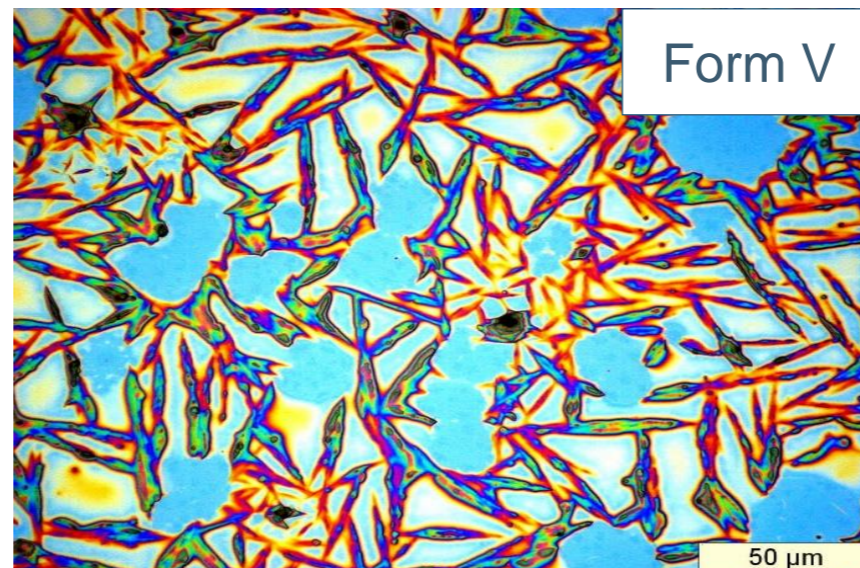
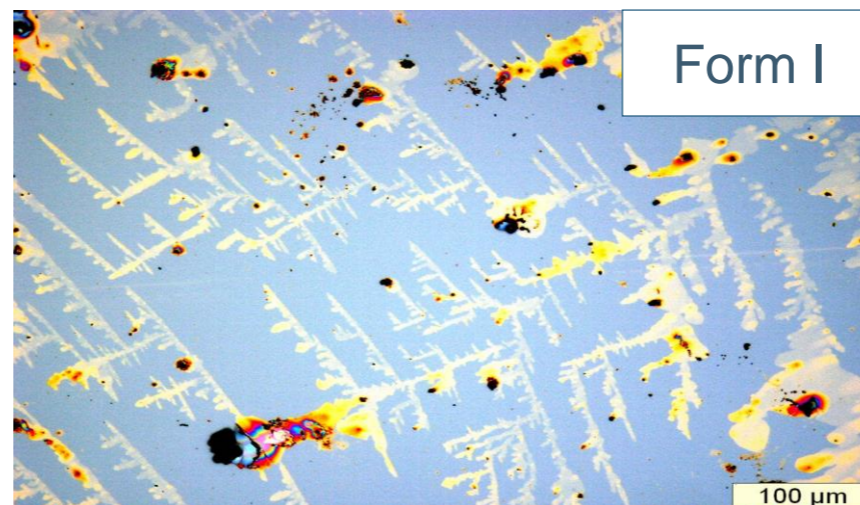
Communication

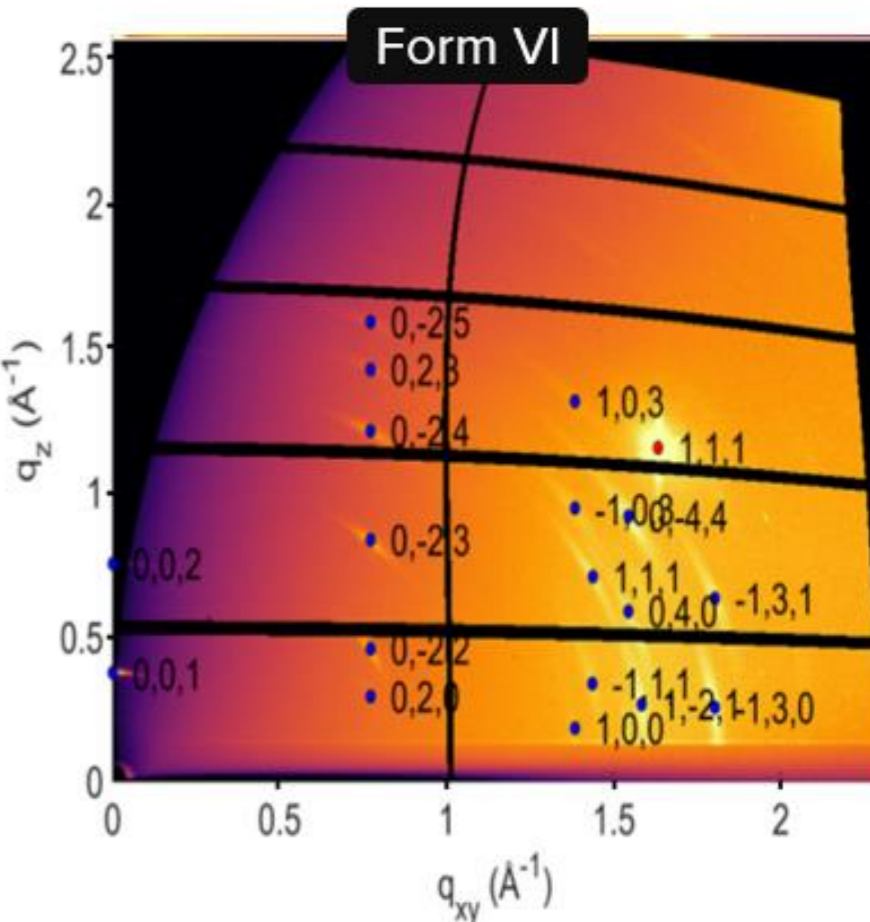
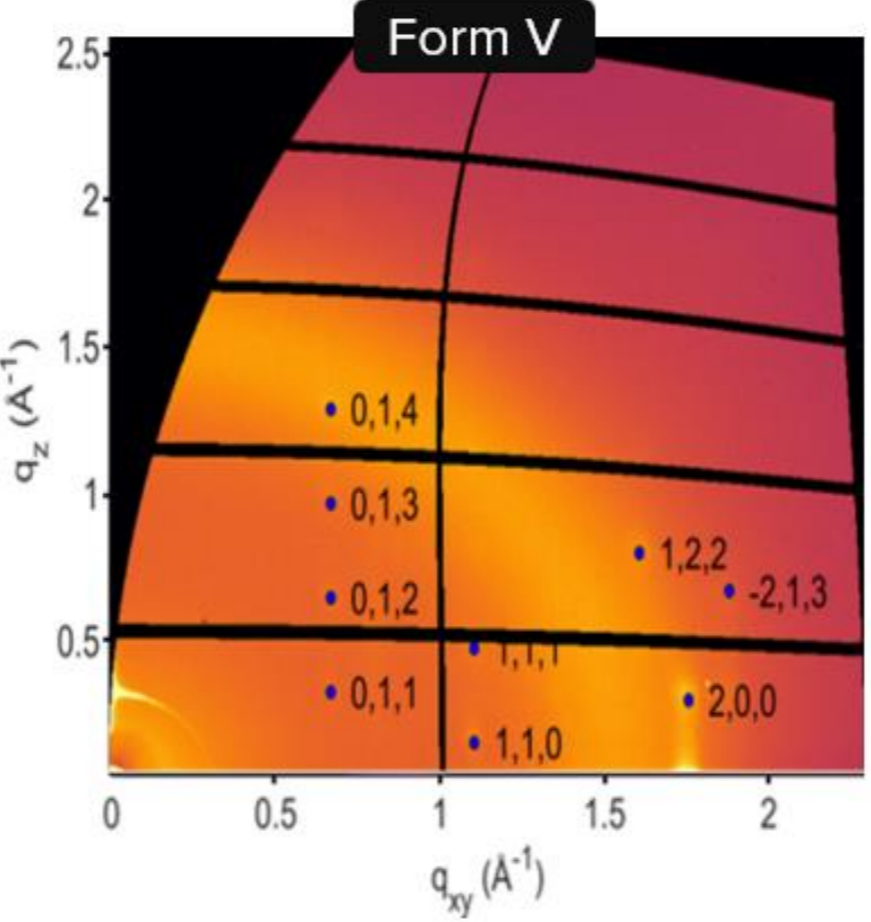
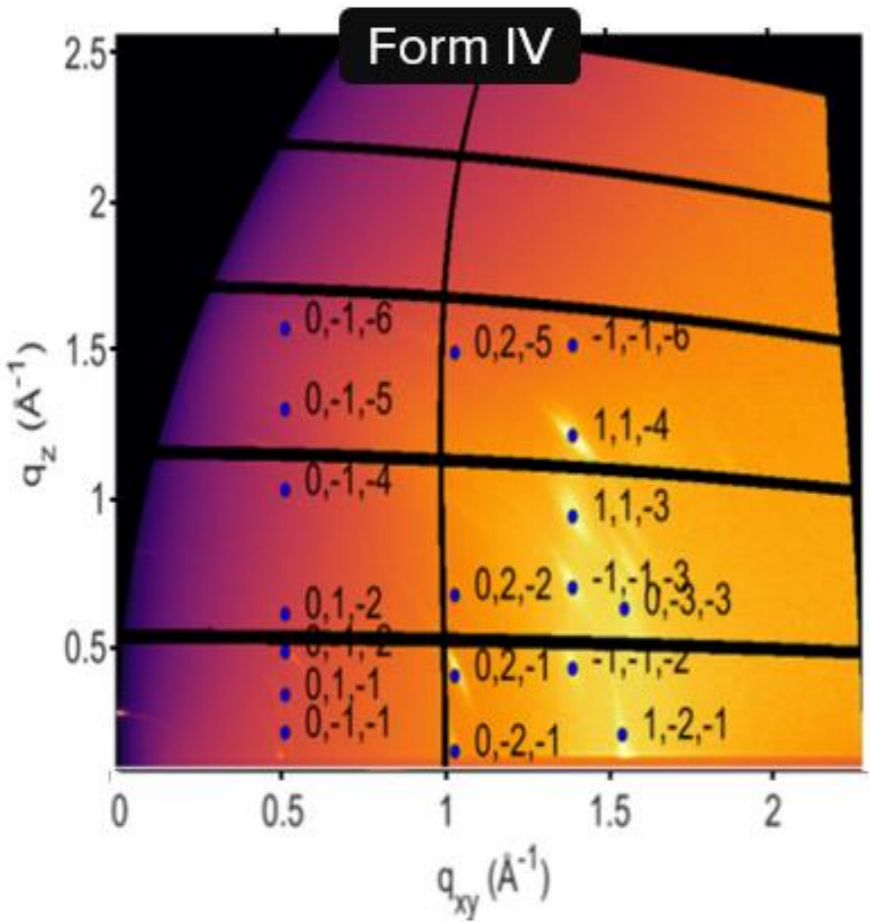
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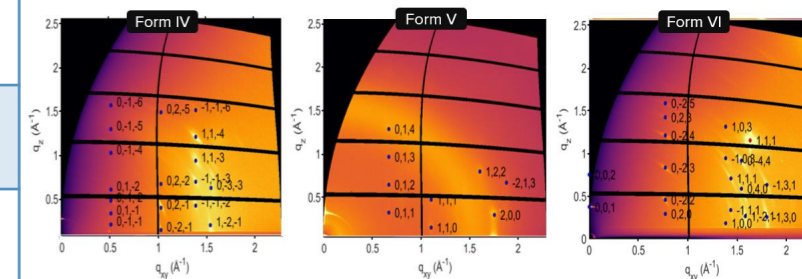


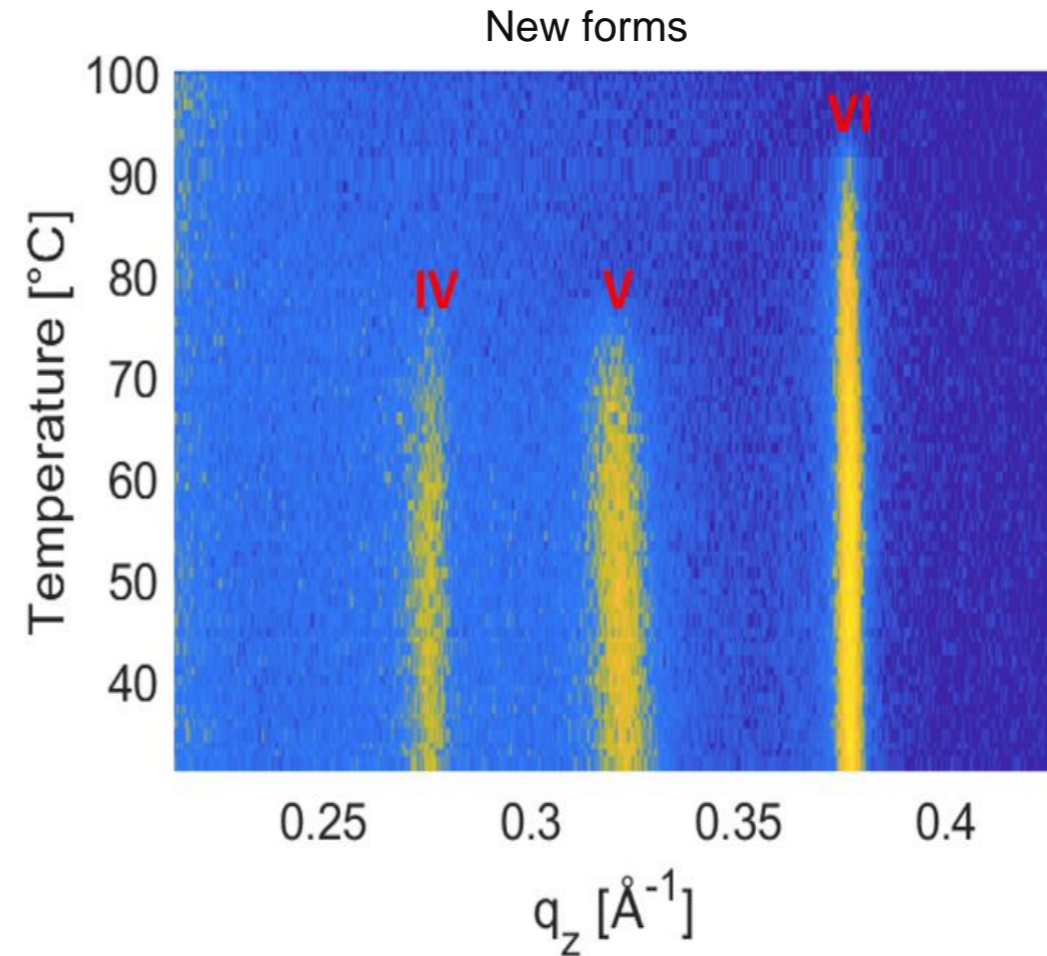
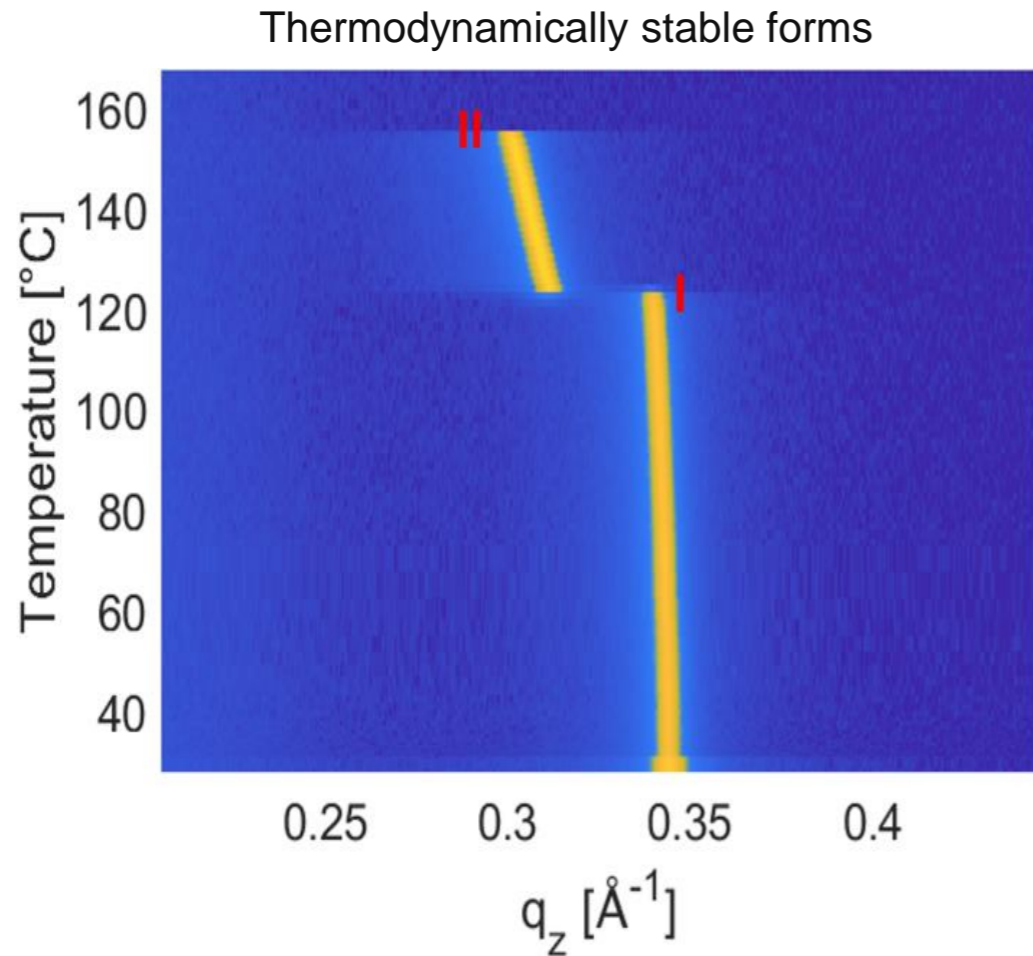






	Form I	Form IV	Form V	Form VI
temperature [°C]	25	25	25	25
contact plane [hkl]	100	00-1	001	001
a [Å]	18.63	5.03	7.15	4.54
b [Å]	7.66	12.13	9.34	16.28
c [Å]	8.29	23.16	19.87	17.99
α [deg]	90	96.16	90.29	110.7
β [deg]	99.35	91.92	99.60	97.07
γ [deg]	90	95.30	90.08	90.12
volume [Å ³]	1169	1399	1312	1236
Z	2	2	2	2





Large difference in melting temperature → Solvates ?!

- Formed due to strong solute-solvent interactions

CrystEngComm



PAPER


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Cite this: *CrystEngComm*, 2021, 23, 1555

Organic solvates in the Cambridge Structural Database

Jen E. Werner and Jennifer A. Swift *

- Formed due to strong solute-solvent interactions

CrystEngComm



PAPER

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View Journal | View Issue

Check for updates

Cite this: CrystEngComm, 2021, 23,
1555Organic solvates in the Cambridge Structural
Database

Jen E. Werner and Jennifer A. Swift*

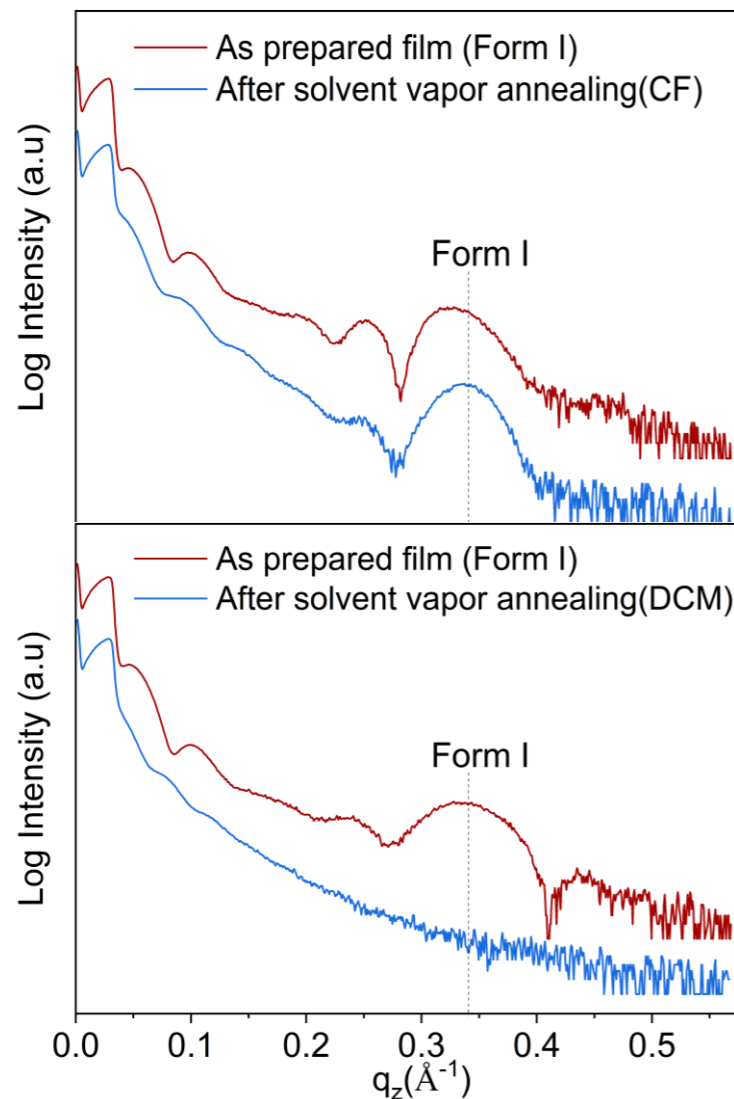
Table 1 The top 50 organic solvates in the 2020 CSD (V 5.41) ranked according to their frequencies. Numbers in the all solvates column correspond to the total number (and %) of structures containing each solvent. Solvate-hydrate and hetero-solvates list the number of entries (and %) as determined from the total number of solvates for a given solvent molecule. The far right column reproduces numbers from ref. 5

	2020 rank	All solvates (% of total)	Solvate-hydrates (% of that solvent)	Hetero-solvates (% of that solvent)	2000 rank ⁵
Methanol	1	5007 (15.79%)	924 (18.5%)	372 (7.4%)	1
Dichloromethane	2	4349 (13.71%)	298 (6.9%)	406 (9.3%)	2
Chloroform	3	4142 (13.06%)	301 (7.3%)	392 (9.5%)	5
Acetonitrile	4	2834 (8.94%)	415 (14.6%)	226 (8.0%)	6
Ethanol	5	1984 (6.26%)	392 (19.8%)	134 (6.8%)	4
Dimethyl sulfoxide	6	1738 (5.48%)	205 (11.8%)	79 (4.5%)	13
Acetone	7	1616 (5.10%)	221 (13.7%)	99 (6.1%)	7
<i>N,N</i> -Dimethylformamide	8	1384 (4.36%)	178 (12.9%)	57 (4.1%)	14
Benzene	9	1346 (4.24%)	63 (4.7%)	106 (7.9%)	3
Toluene	10	1171 (3.69%)	58 (5.0%)	97 (8.3%)	8

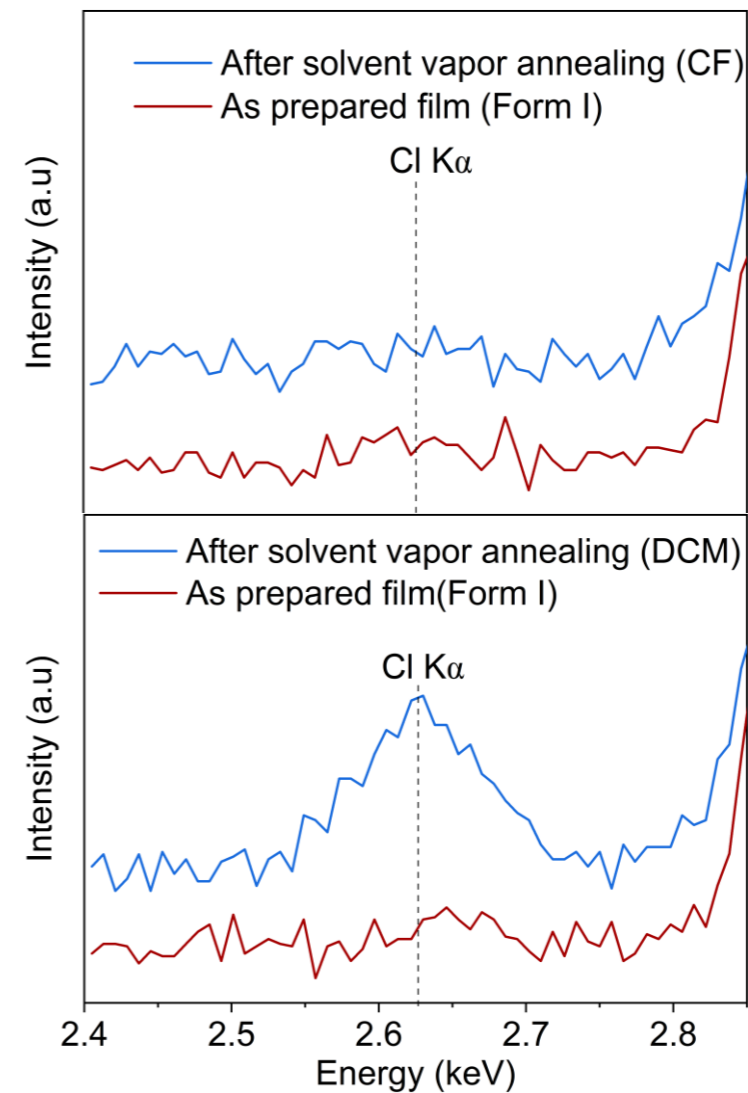
Chloroform

Dichloromethane

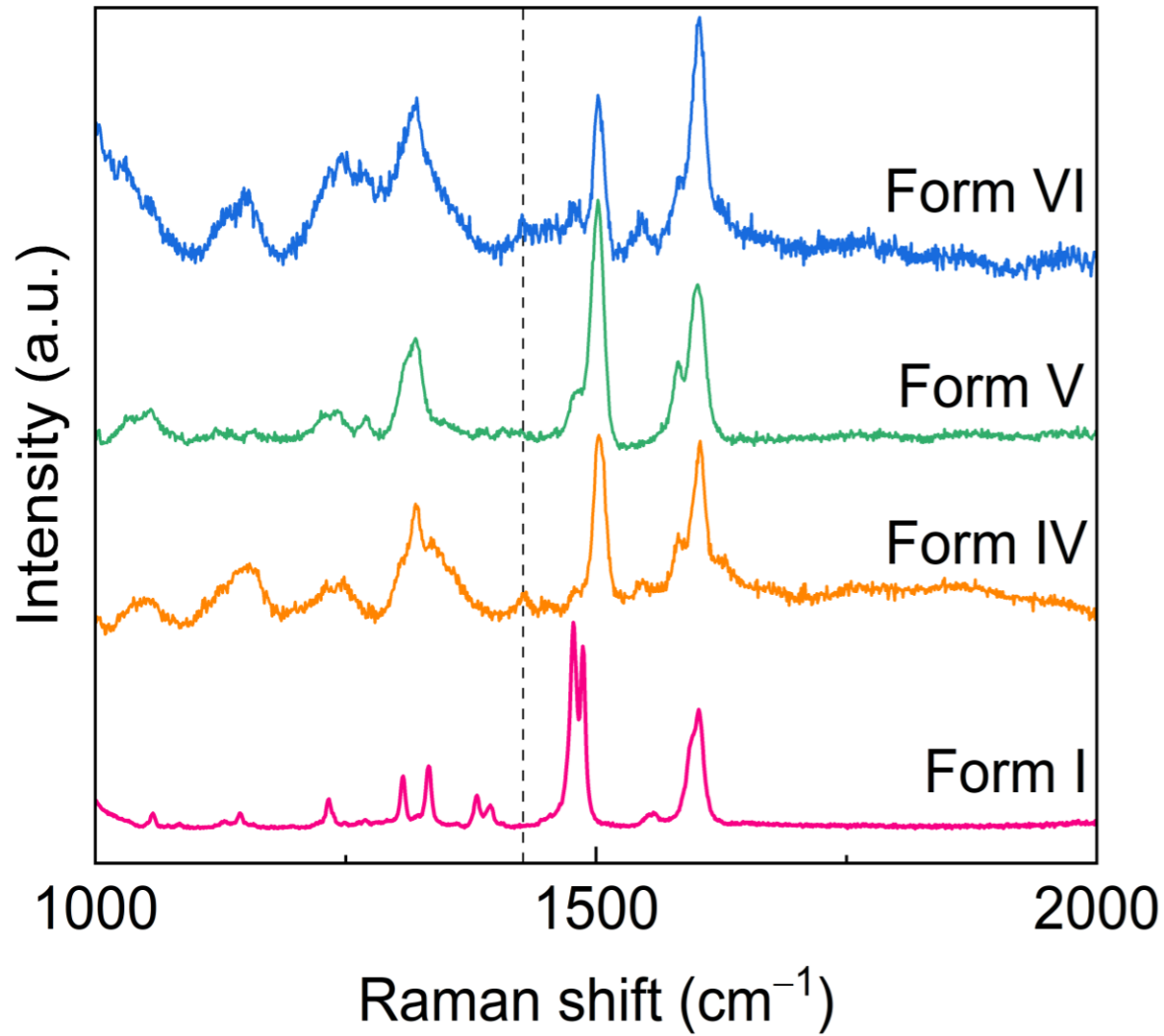
X-ray Reflectivity



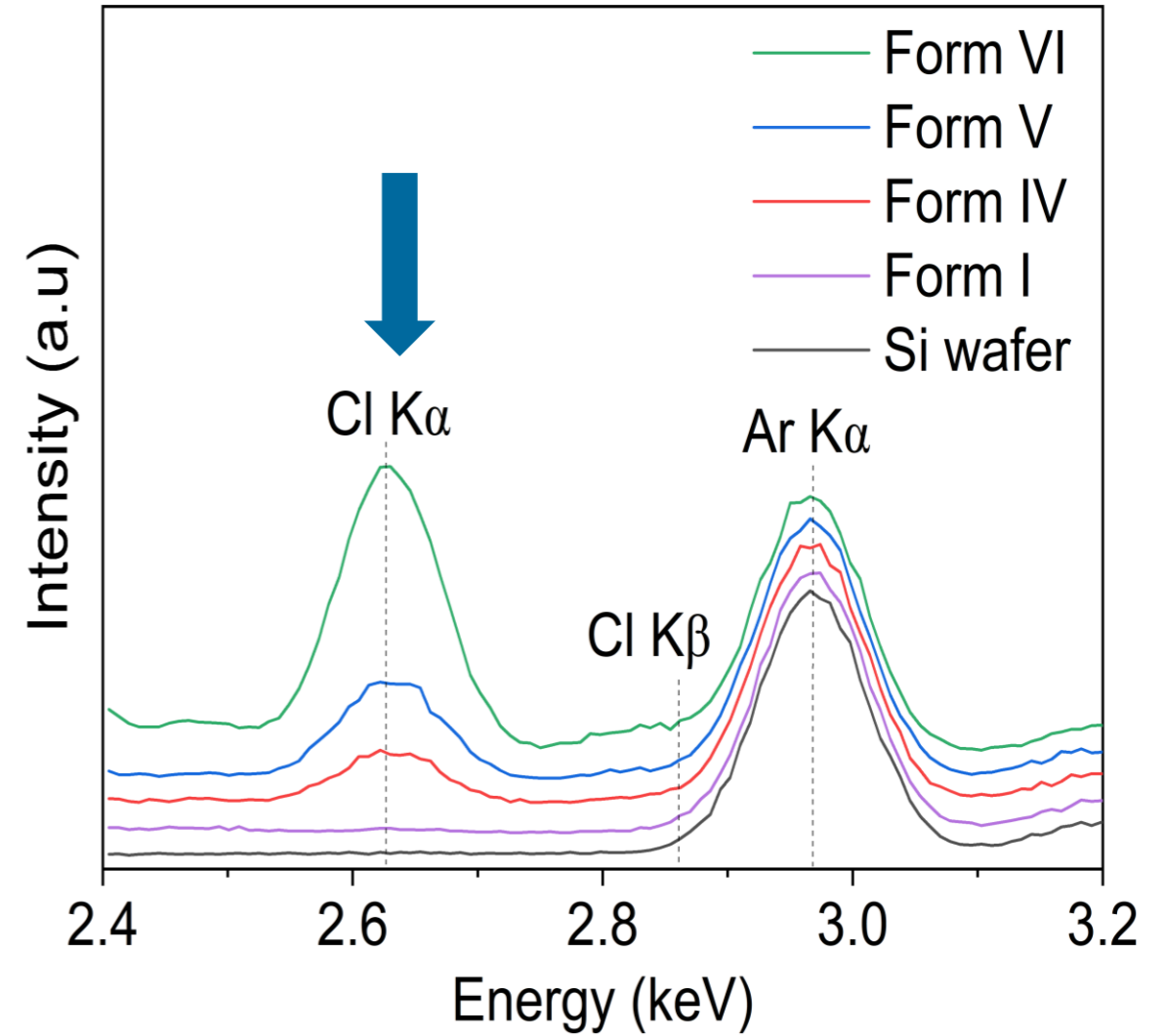
X-ray Fluorescence



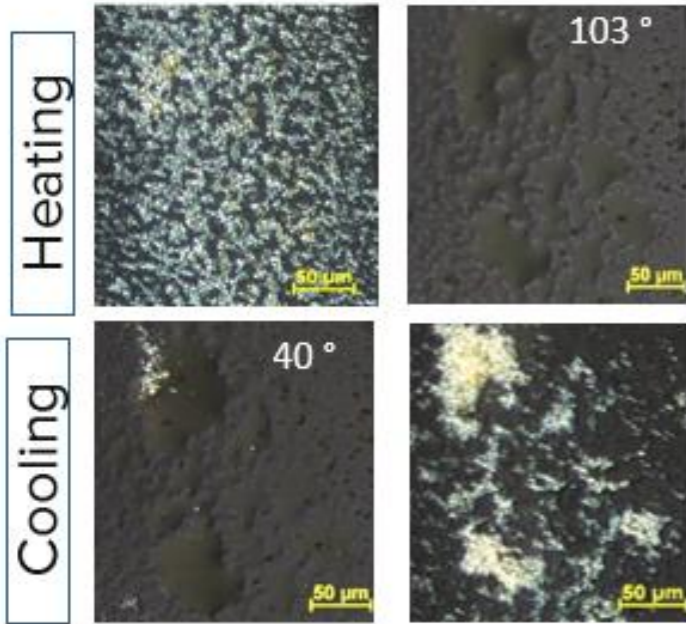
Raman Spectra



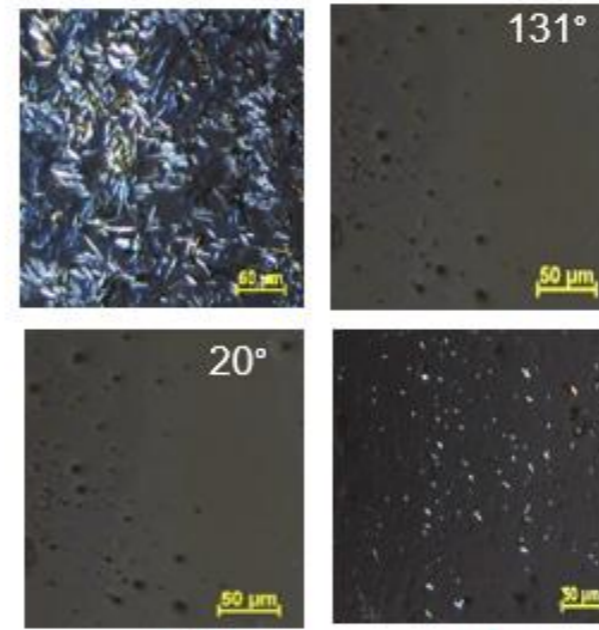
X-ray Fluorescence Spectra



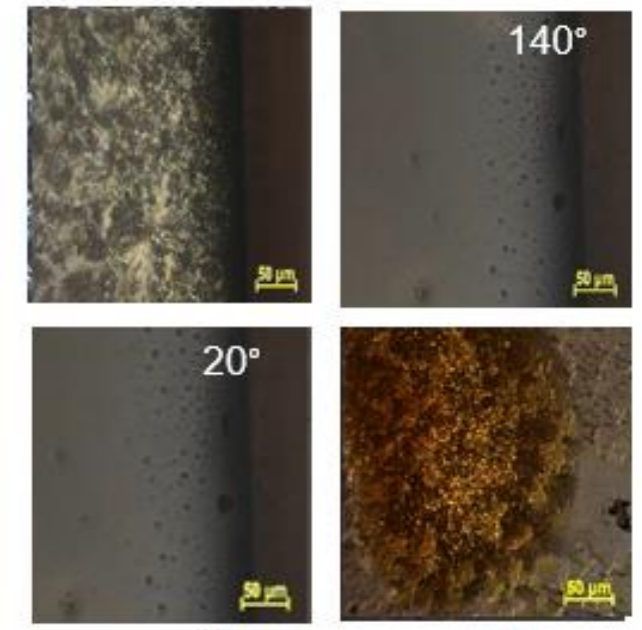
Form IV



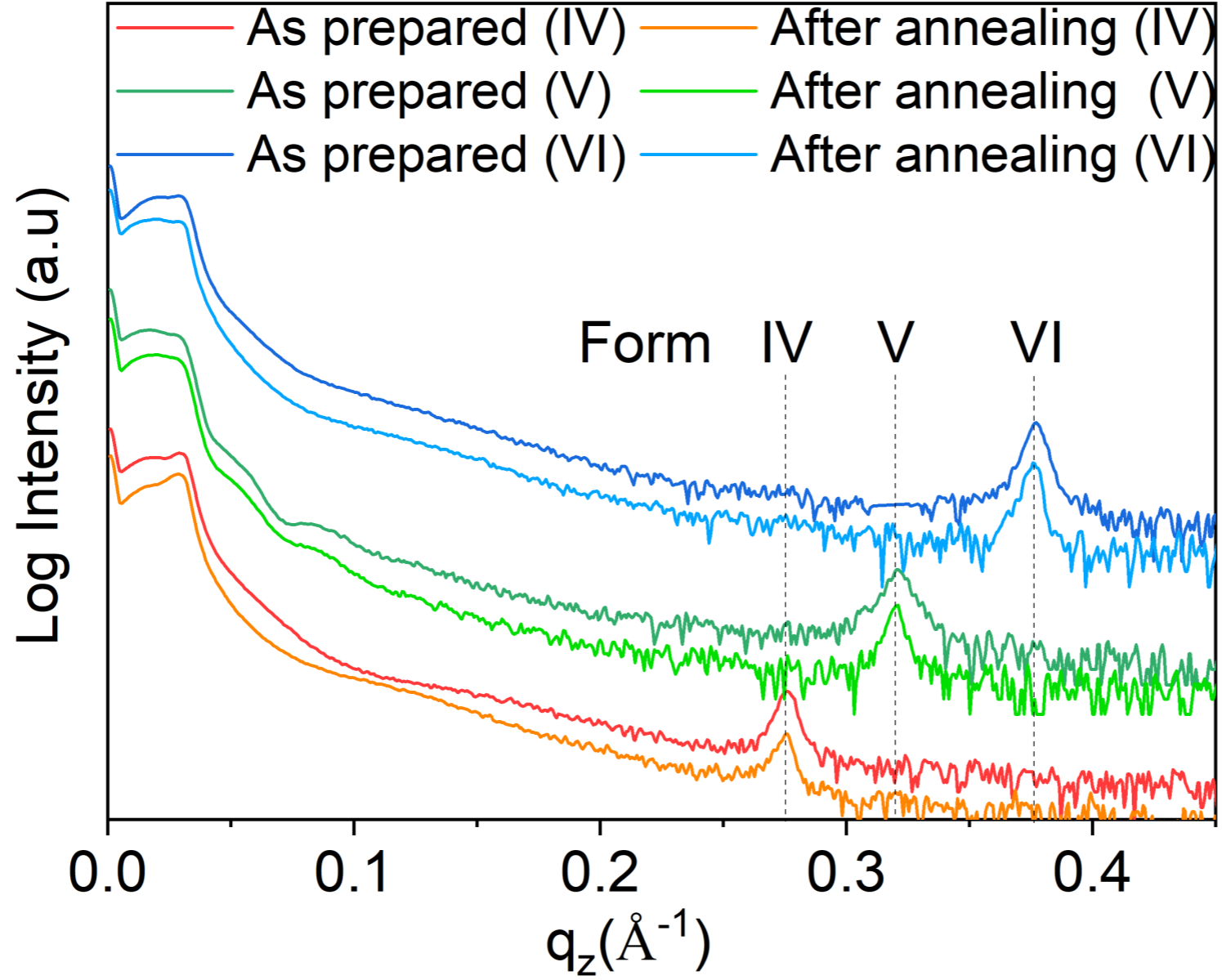
Form V

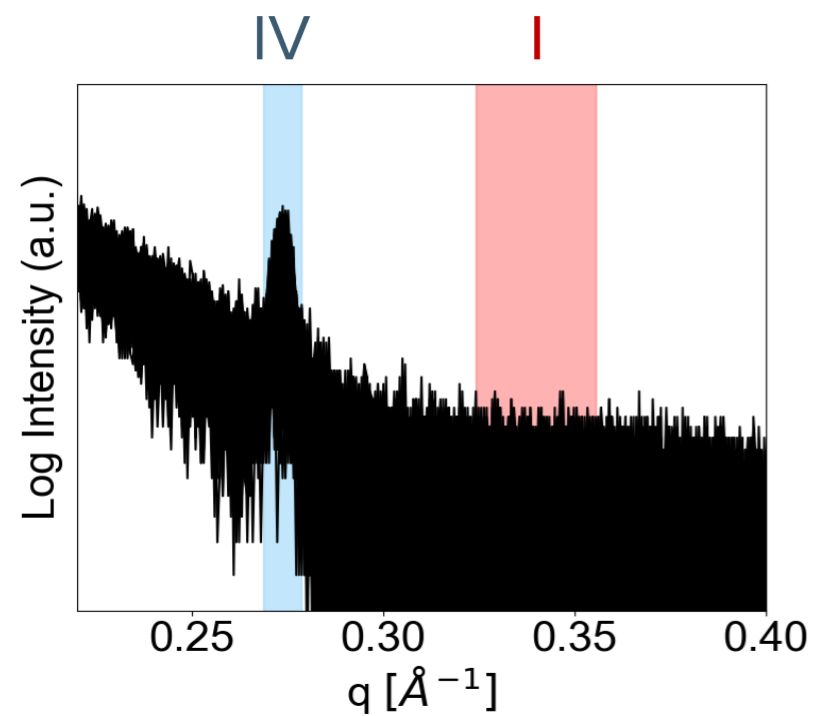


Form VI

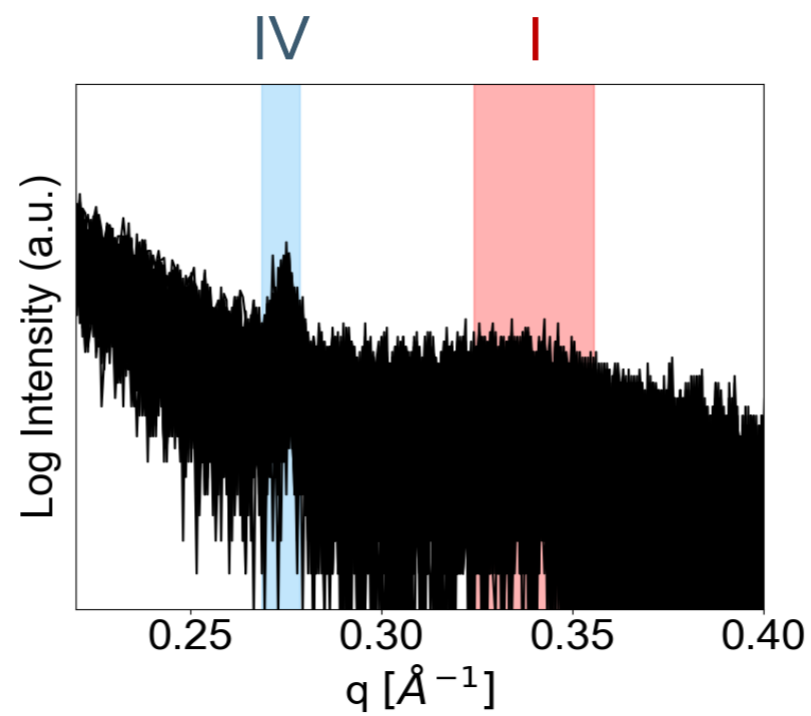


Form	I	IV	V	VI
Melting (°C)	156	103	131	140
Re-crystallisation (°C)	140	40	after 24 hrs	after 24 hrs

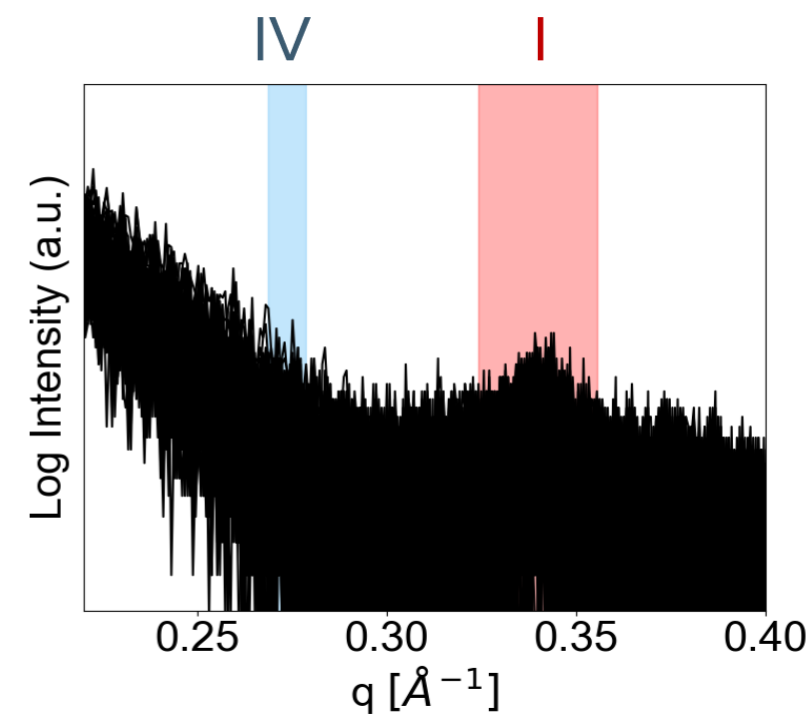




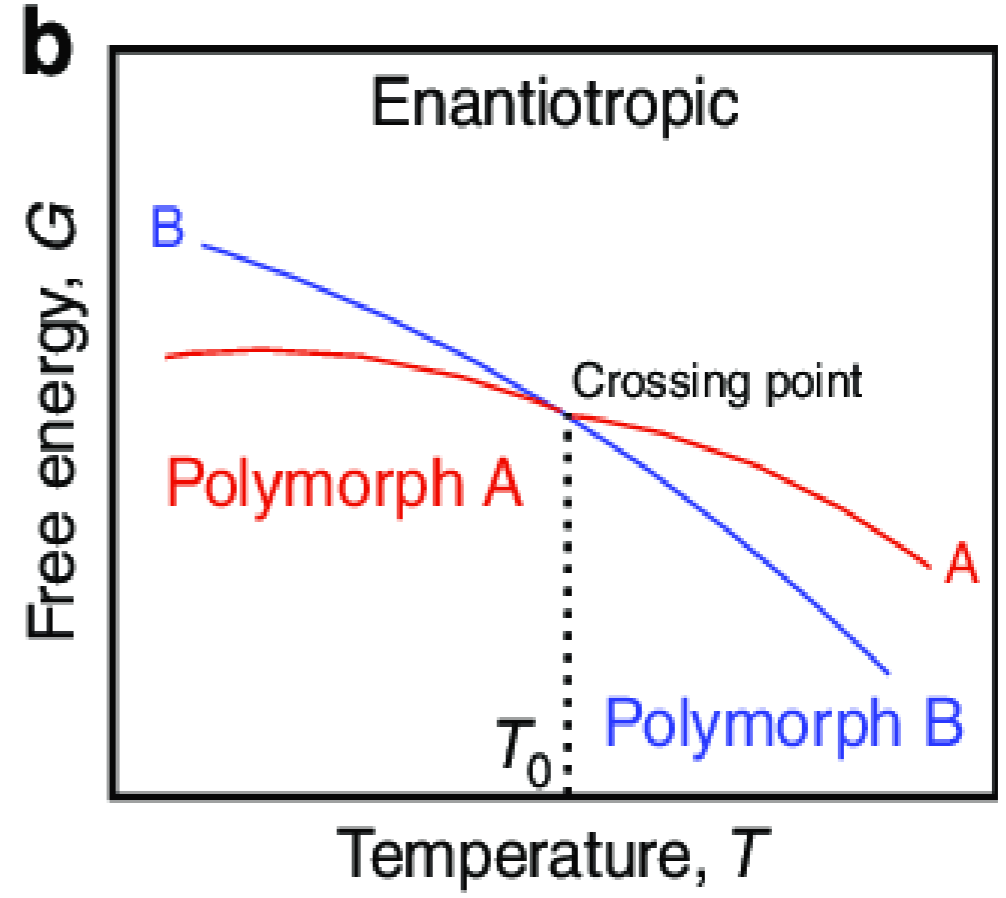
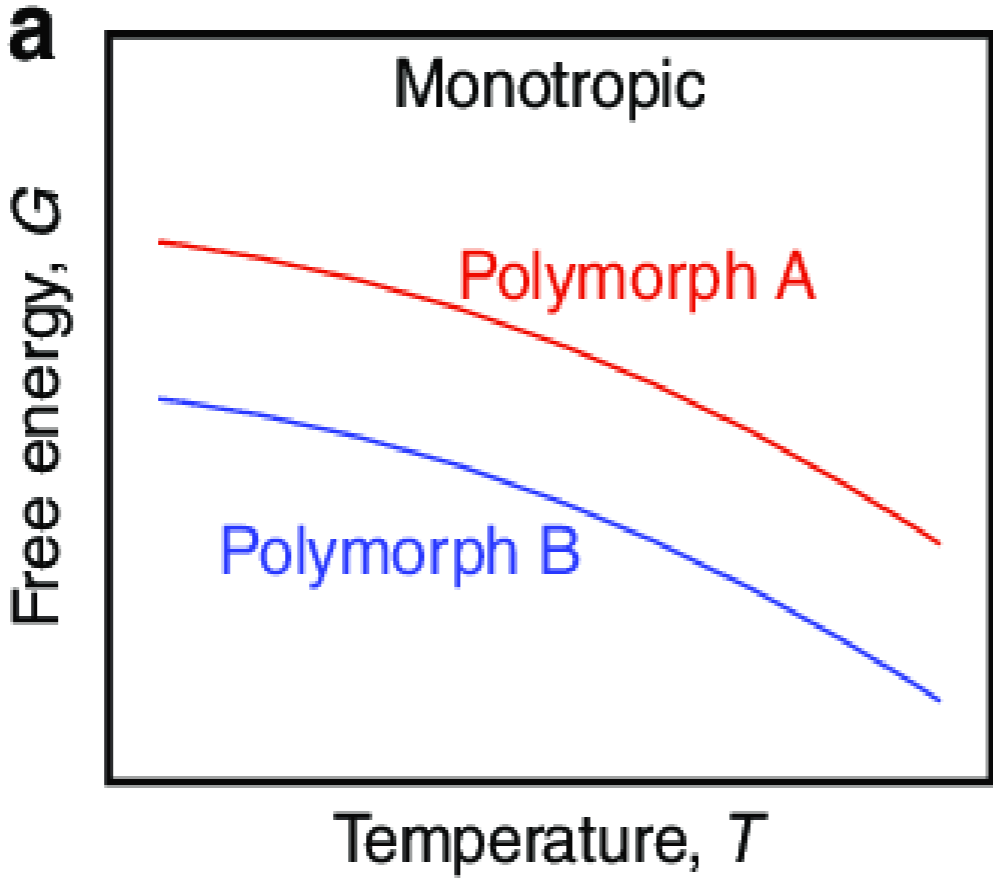
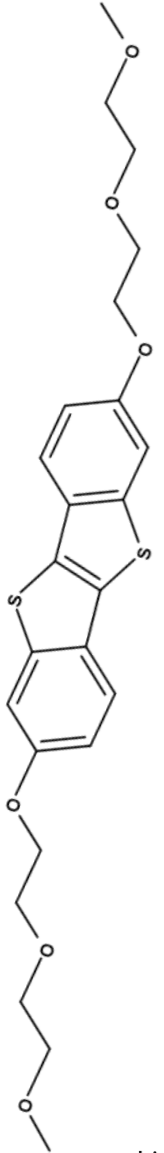
$T_0 = 100^\circ\text{C}$



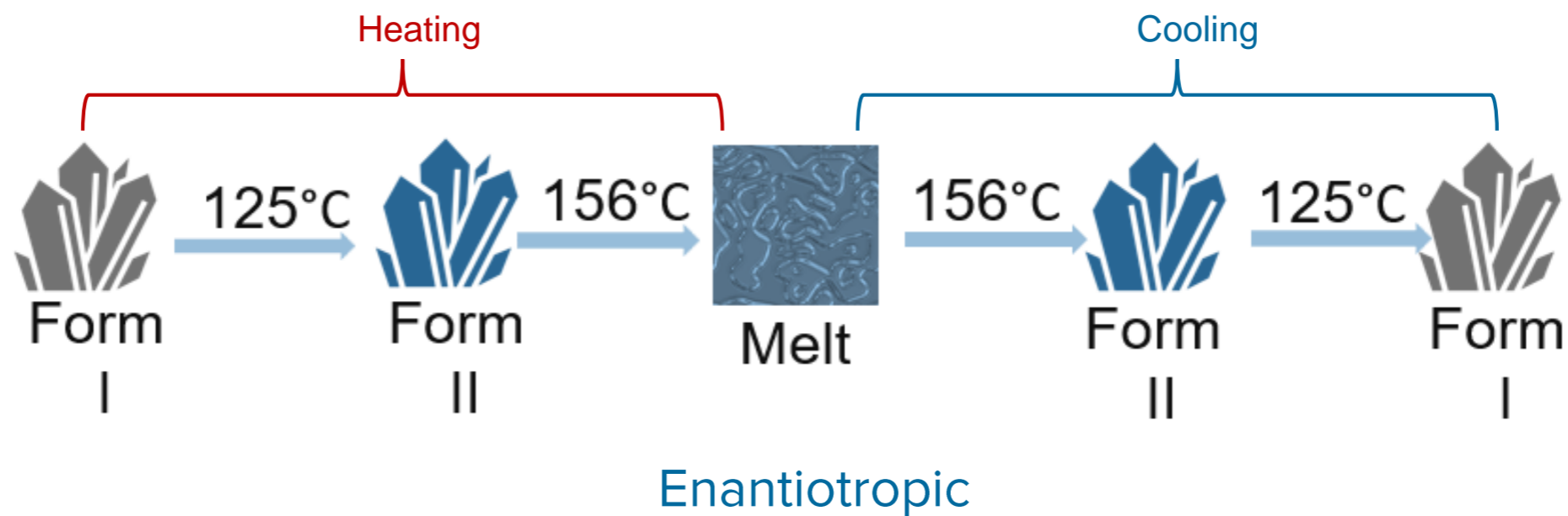
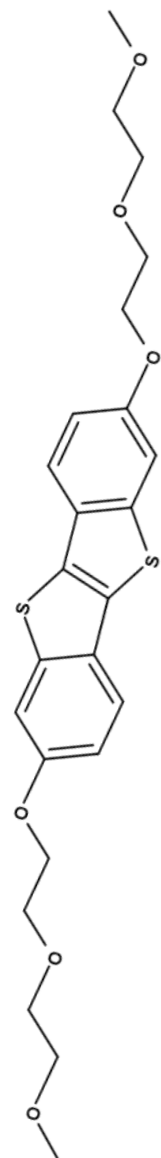
$T_0 = 120^\circ\text{C}$



$T_0 = 140^\circ\text{C}$

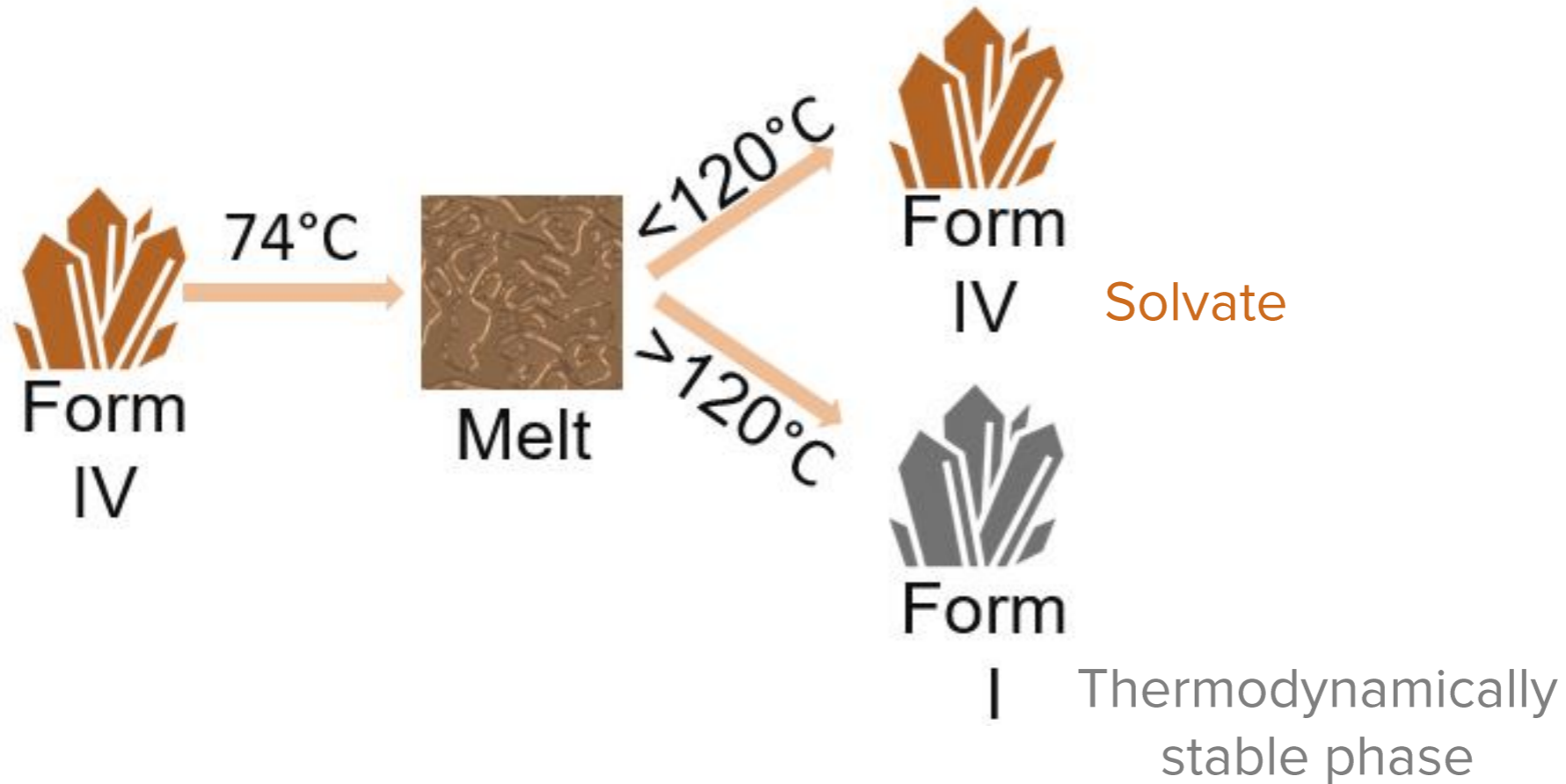
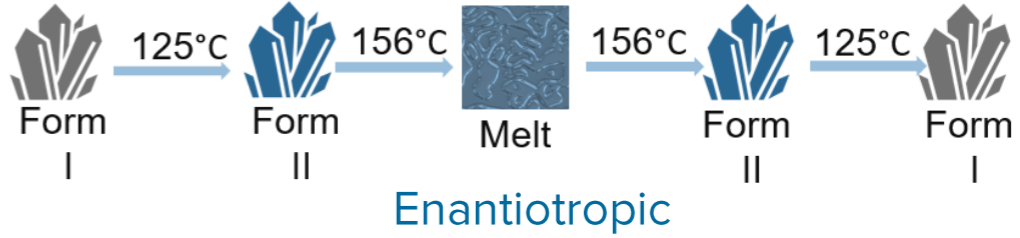


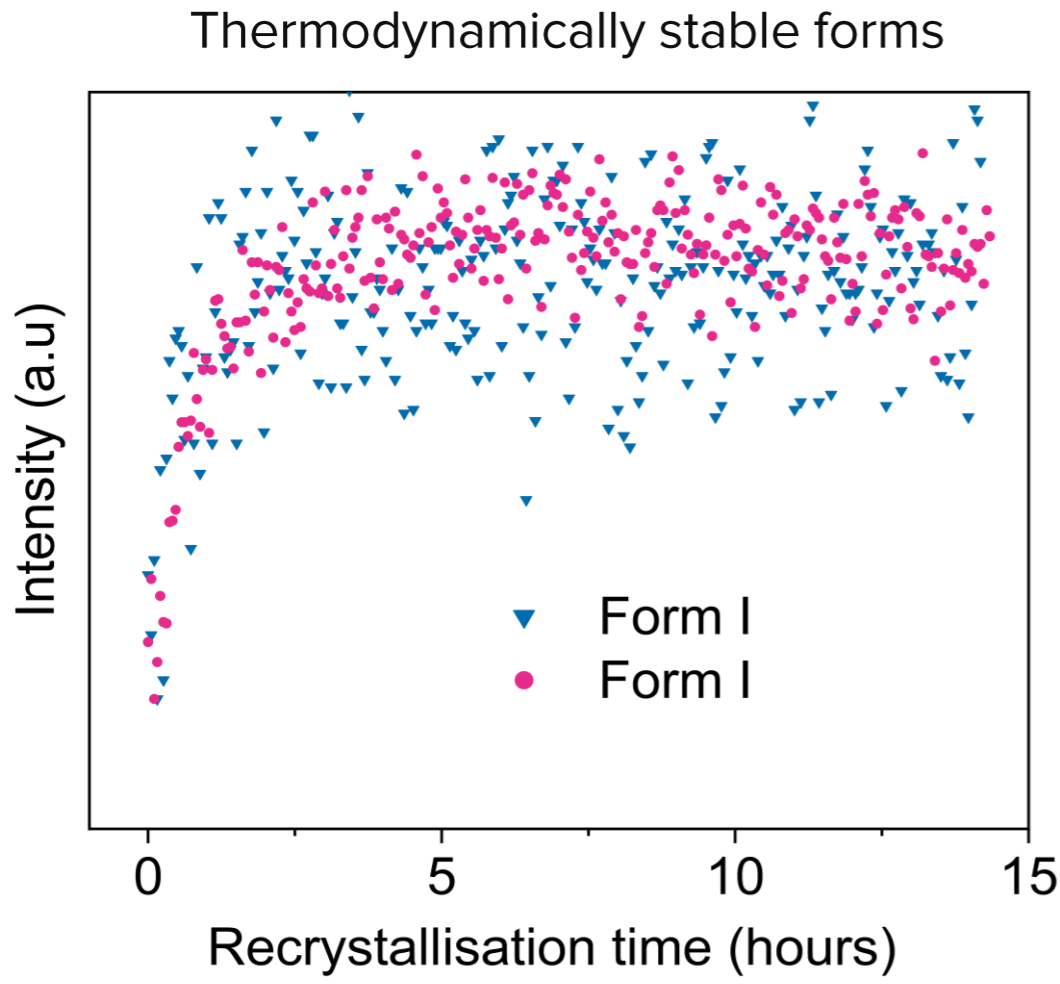
Li, Lin, et al. "An unusual type of polymorphism in a liquid crystal." *Nature communications* 9.1 (2018): 714.



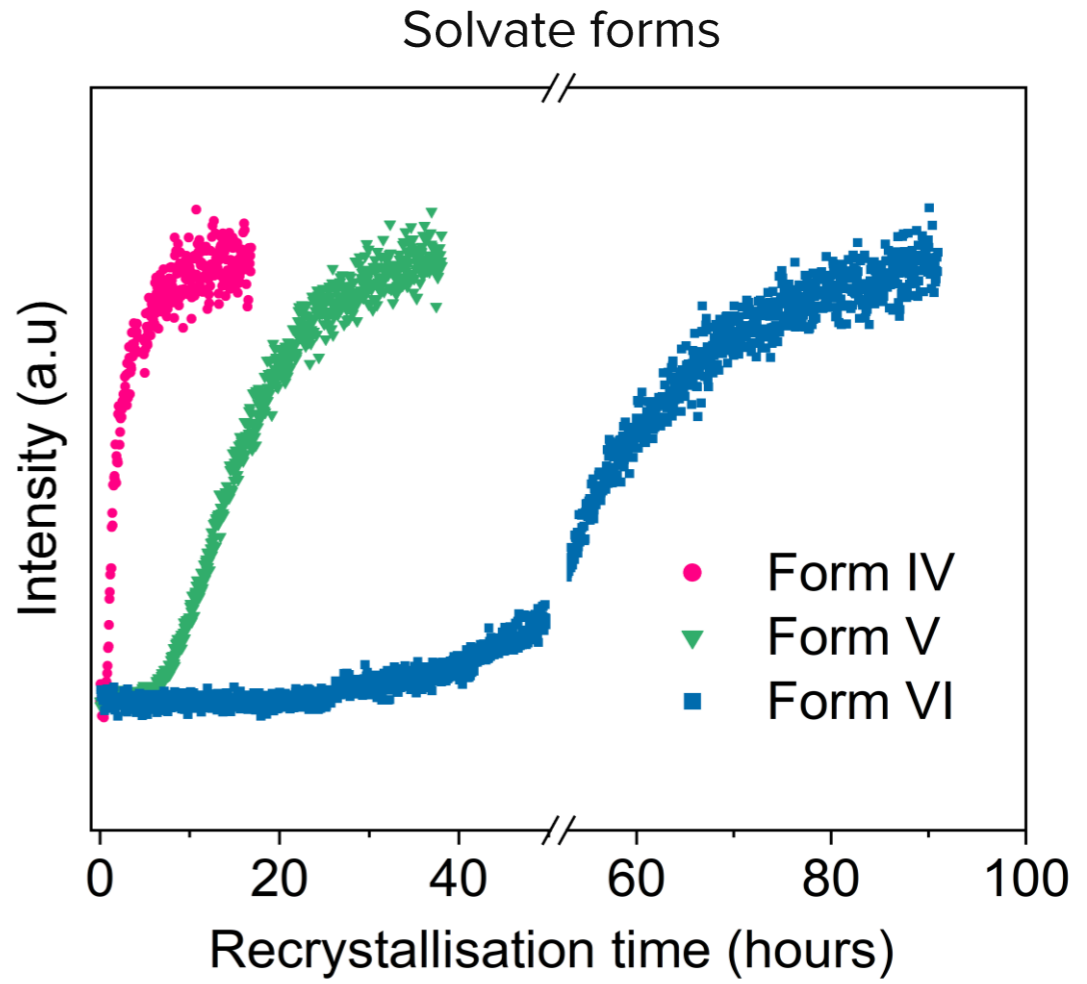
Li, Lin, et al. "An unusual type of polymorphism in a liquid crystal." *Nature communications* 9.1 (2018): 714.

Memory Effect from Melt

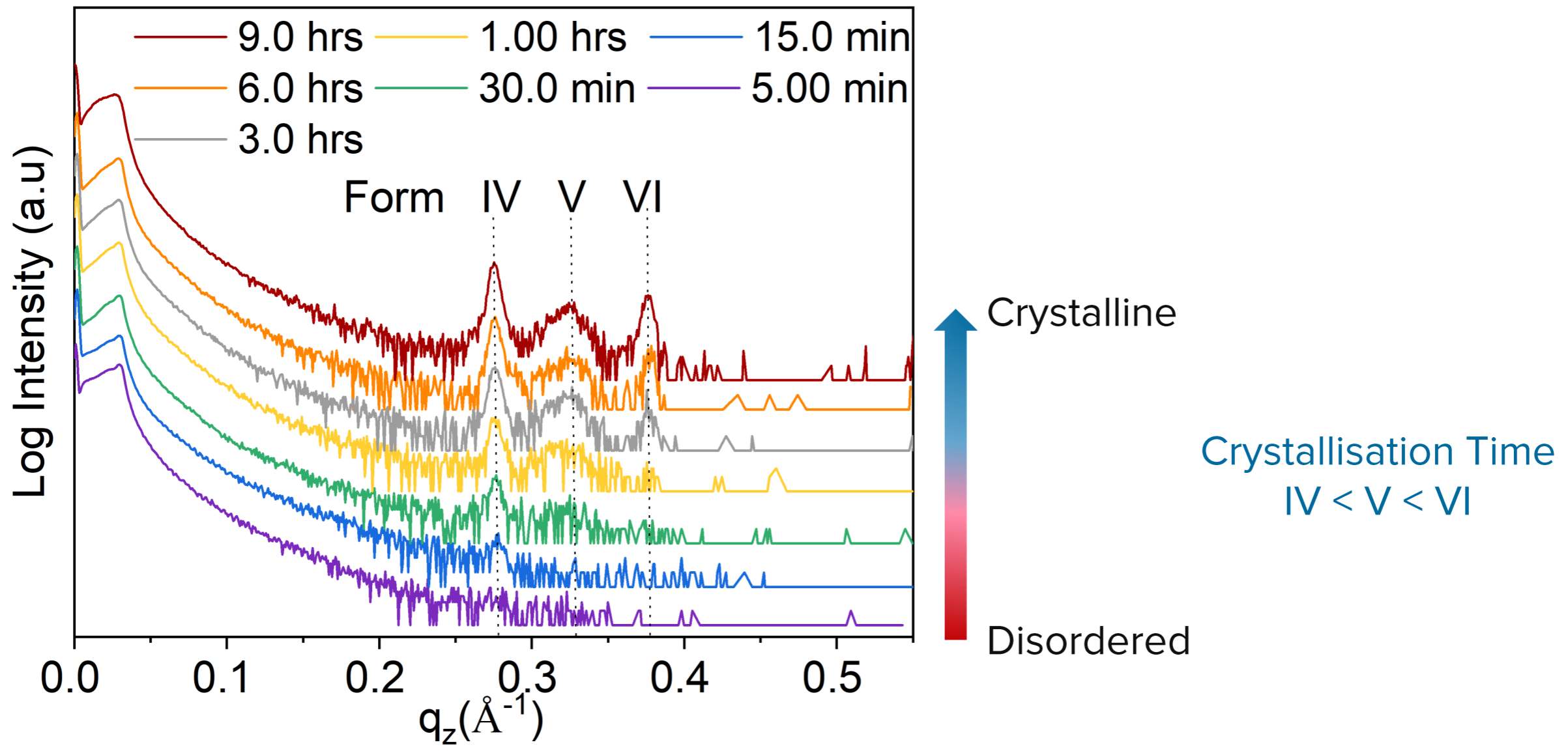




Form I

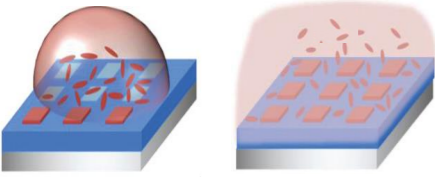


Form IV, V, VI

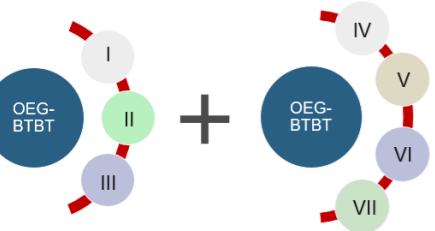


Conclusion

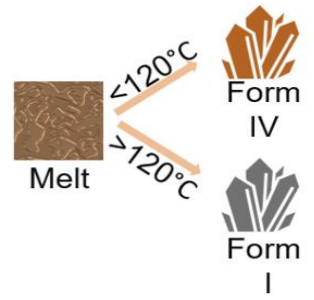
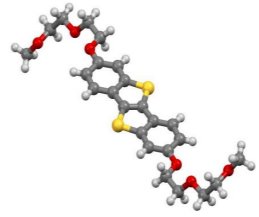
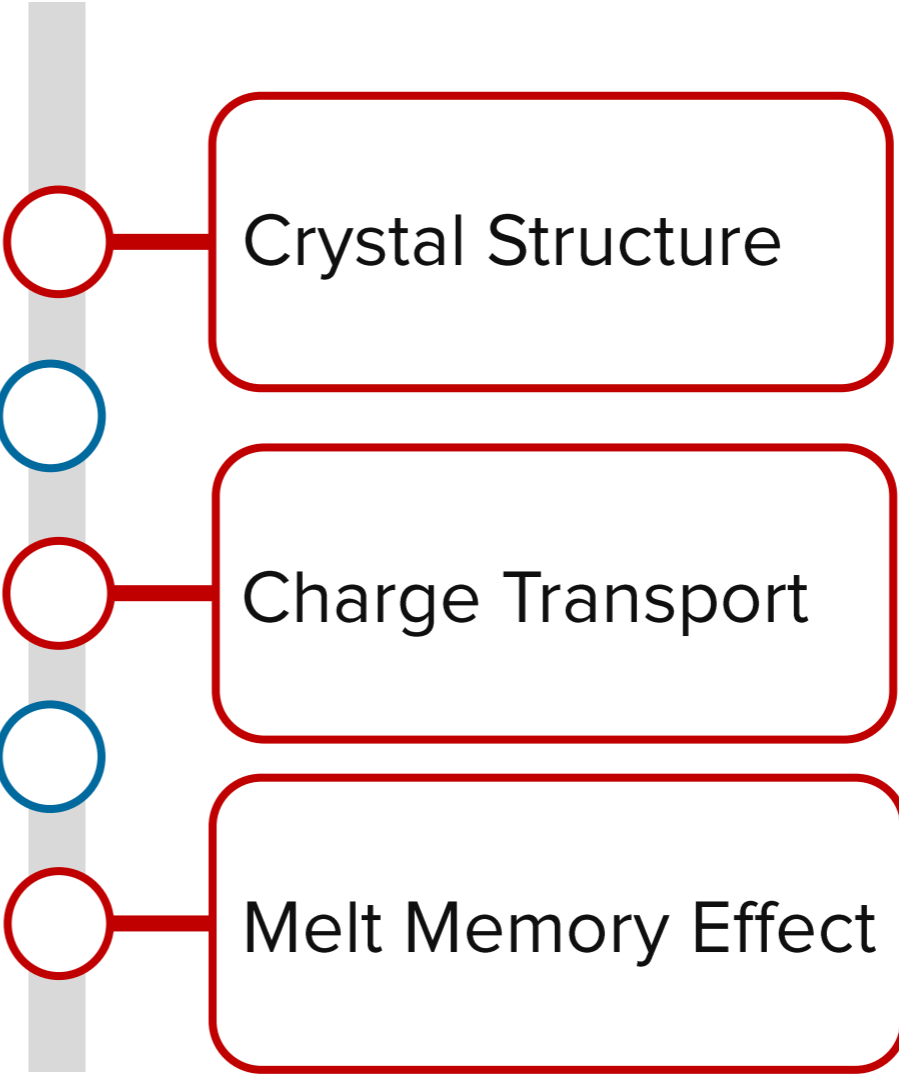
OEG-BTBT



Thin Film Fabrication

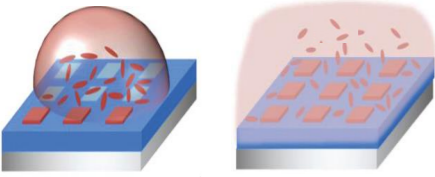


Polymorph Screening



Conclusion

OEG-BTBT



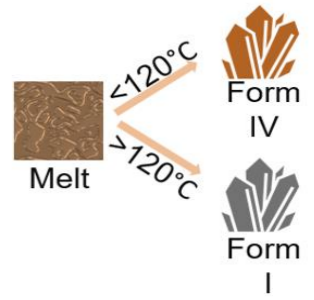
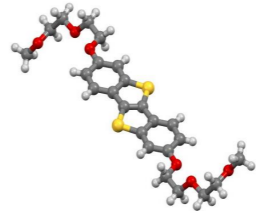
Thin Film Fabrication
 JOURNAL OF **CRYSTAL GROWTH** → Soon to be Submitted

Polymorph Screening
 Materials Horizons → Under Review

Crystal Structure
 CRYSTAL GROWTH & DESIGN → Published

Charge Transport
 → Under Drafting

Melt Memory Effect
 CRYSTAL GROWTH & DESIGN → Under Review



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