Monitoring the structural transformation on thin films of an Asymmetric Benzothieno[3,2-b][1]-benzothiophene Derivative

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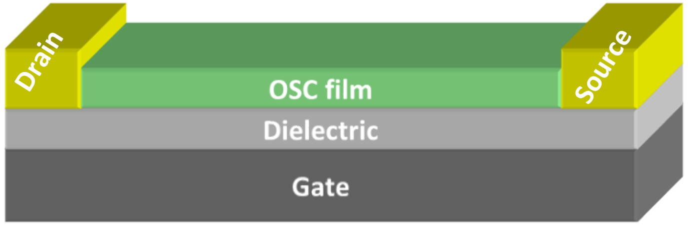
ALBA

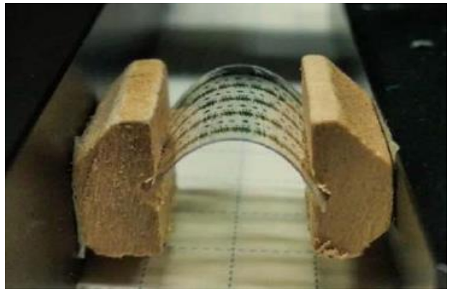
02/09/2024

Organic Semiconductor (OSCs) Devices

- Low-temperature processing
- Low-cost production
- Mechanical flexibility
- Light weight
- Large range of tunability

Organic-field-effect transistors
OFETs





Debdatta Panigrahi *et al* 2021 *Appl. Phys. Express* **14** 081004

Mobility critically determined by the **crystal structure and crystalline order**, particularly at the interface

Thermal treatment of the as-grown films is a common strategy to improve the crystalline order

Key factors in thermal behaviour

Temperature might induce:

Polymorphism

- A common phenomenon due to the **non-covalent interactions** in organic crystals.
- A large impact for the charge transport and stability of the devices: Need of characterization and control

Thermal expansion and strain have been poorly investigated in correlation with polymorphism

Inhomogeneous strain

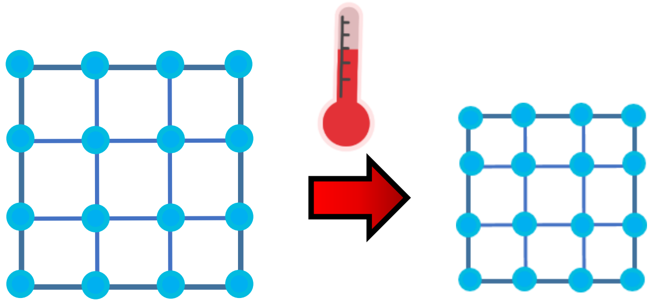
Coefficient of Thermal Expansion (CTE)

$$CTE = \frac{1}{d}\left(\frac{\Delta d}{\Delta T}\right)$$

SiO2/Al3O2 : $4 – 5 \text{ x } 10^{-6}\ K^{-1}$

OSC : $100 – 300 \text{ x } 10^{-6}\ K^{-1}$

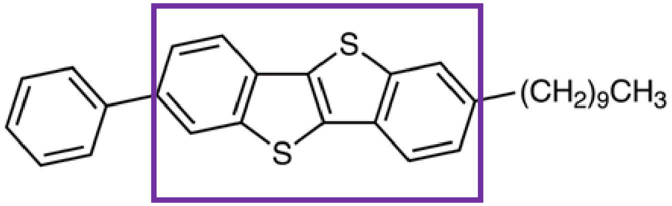
- Large CTE Mismatch at the Semiconductor–Dielectric Interface
- Anisotropy and Negative thermal expansion



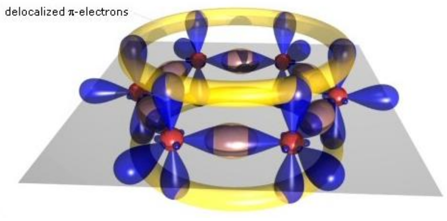
Small molecule organic semiconductors: BTBT derivatives

[1]benzothieno[3,2-b][1]- benzothiophene

Ph-BTBT-C_{10}

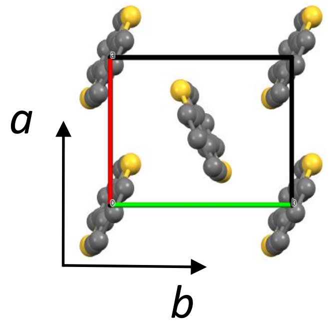


BTBT core

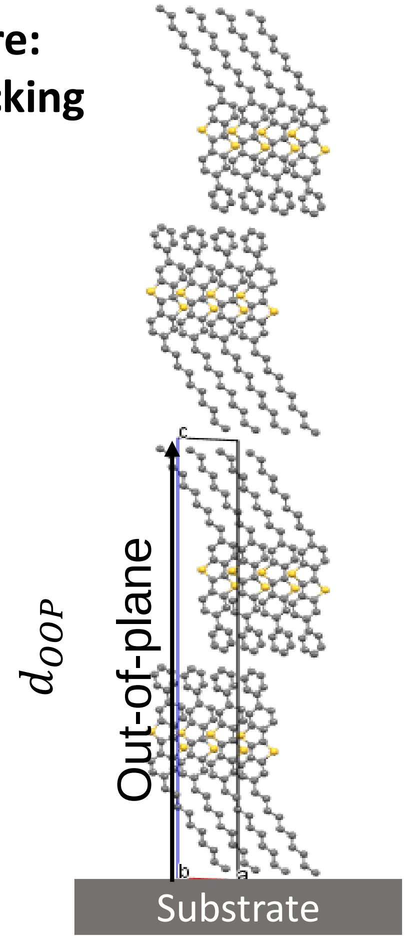


- ✓ Mobility comparable to polysilicon devices (1 cm^2 V^{-1} s^{-1})
- ✓ Highly ordered crystalline layers (lamellar structures)
- ✓ Air-stable devices

The single-crystalline structure: monoclinic with a bilayer-packing



Herringbone arrangement of BTBT core



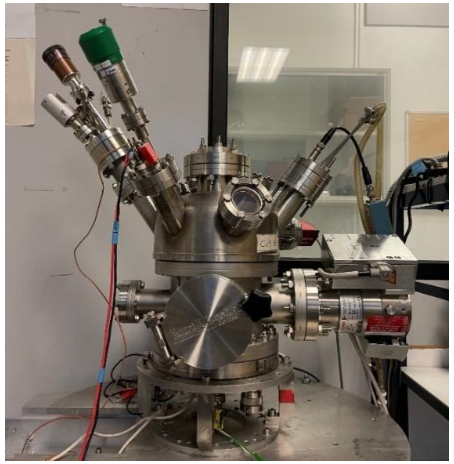
However, Ph-BTBT-C10 **thin films** exhibit **polymorphism**

Goals & Experiments

Goals :

- **Structural transformations with temperature**
- **Thermal expansion and strain for the different Ph-BTBT-C10 polymorphs**

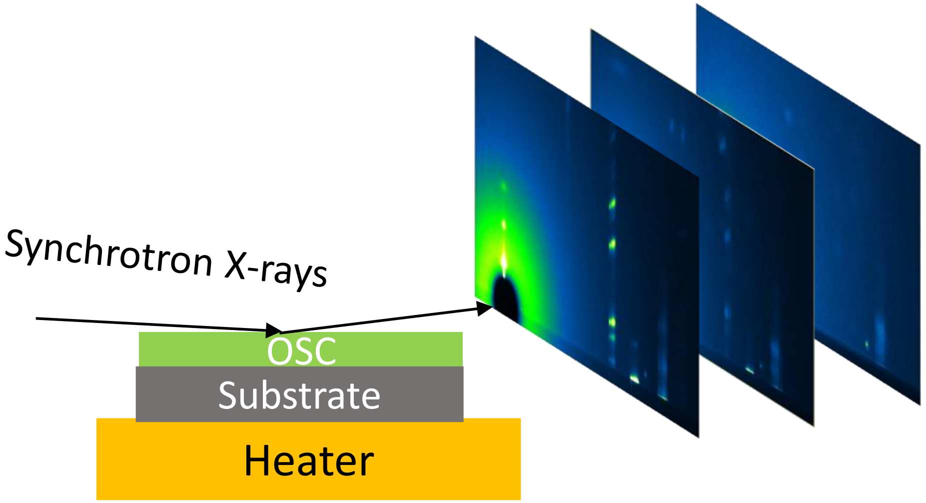
Film prepared by vacuum sublimation



The substrate is native SiO_2

Film thickness: 20 nm and 40 nm

Grazing-Incidence Wide Angle X-ray Scattering (GIWAXS)

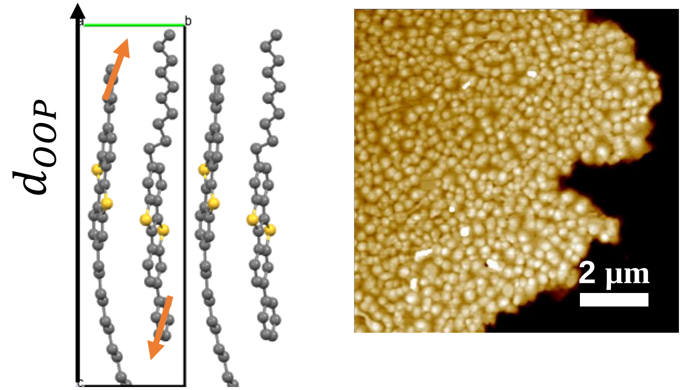


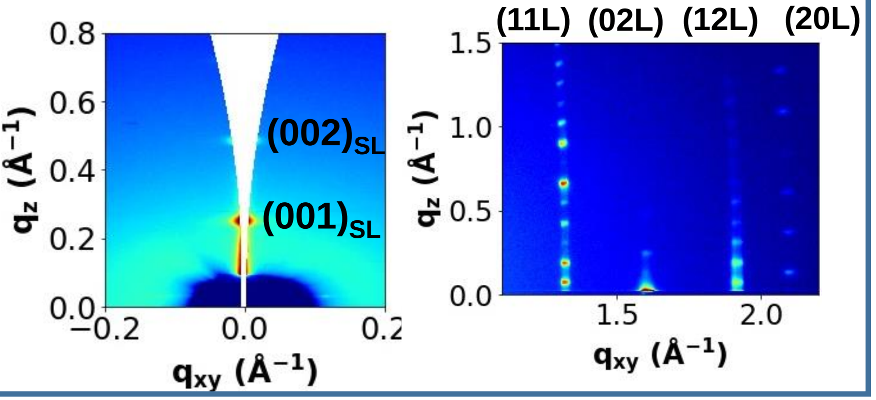
GIWAXS experiments were performed at NCD-SWEET Beamline at ALBA Synchrotron

Polymorphism of Ph-BTBT-C10 thin-films

Same herringbone arrangement of BTBT cores in the in-plane

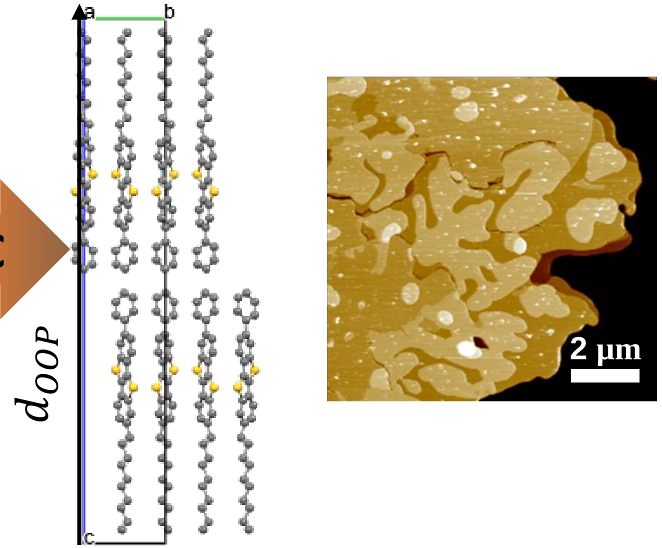
Single-layer metastable phase

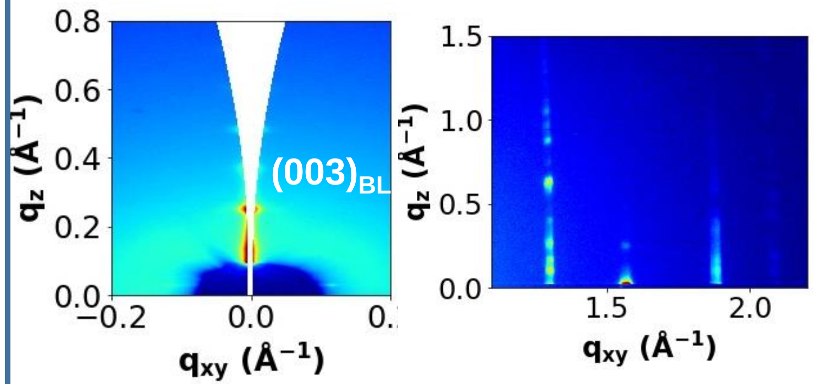




120°C

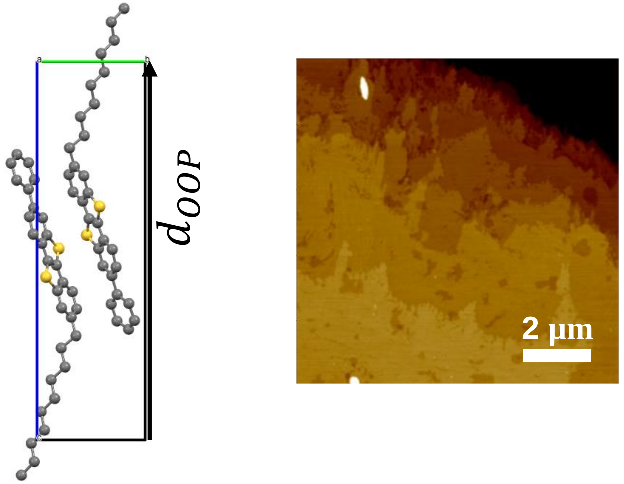
Bilayer Head to head

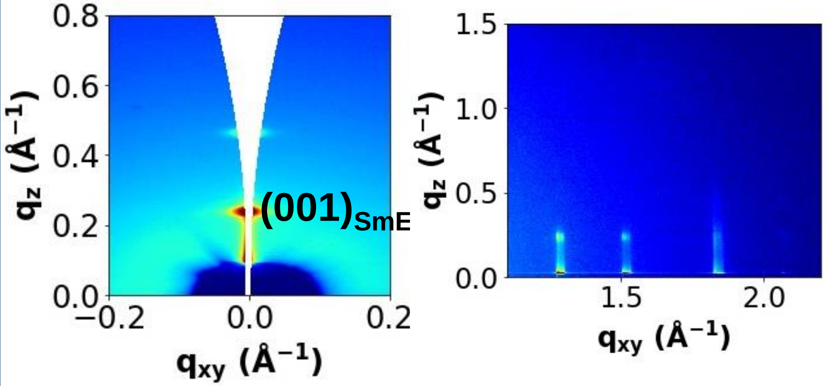




150°C

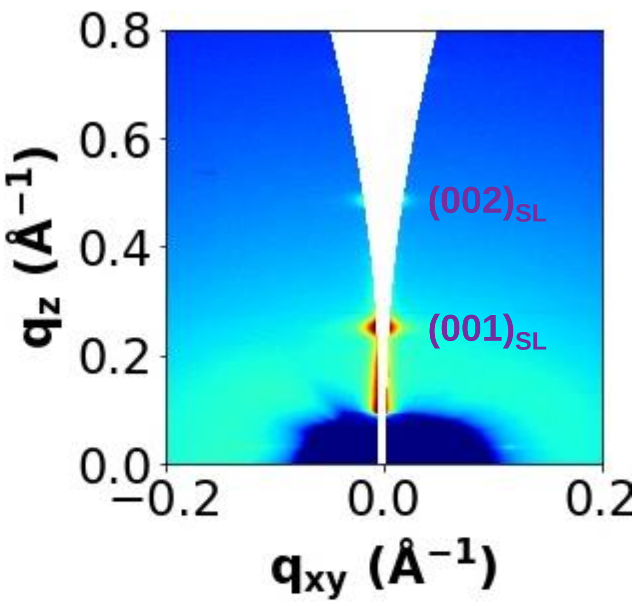
Single-layer Liquid Crystal - Smetic E

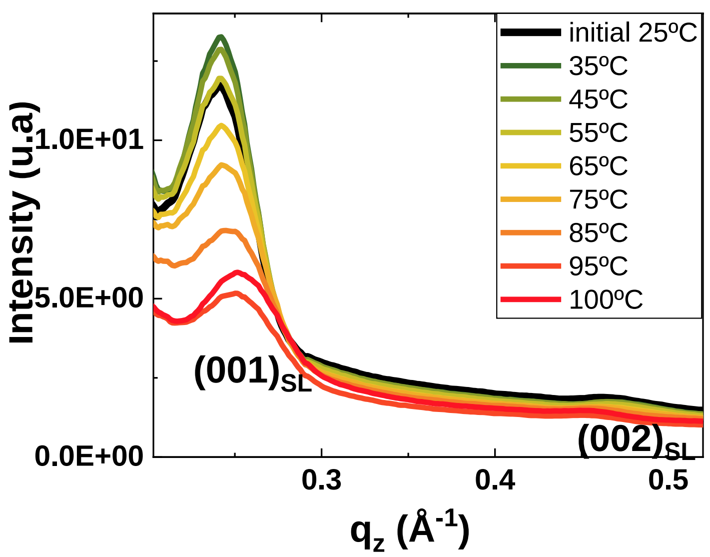


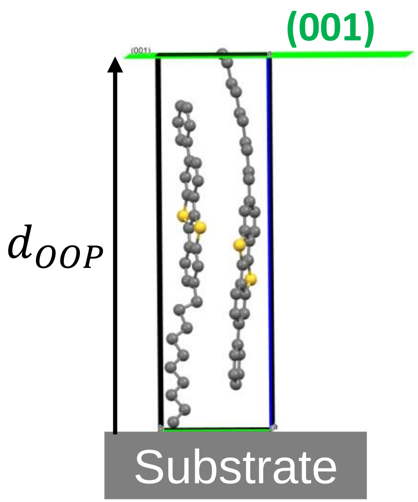


Single-Layer structure

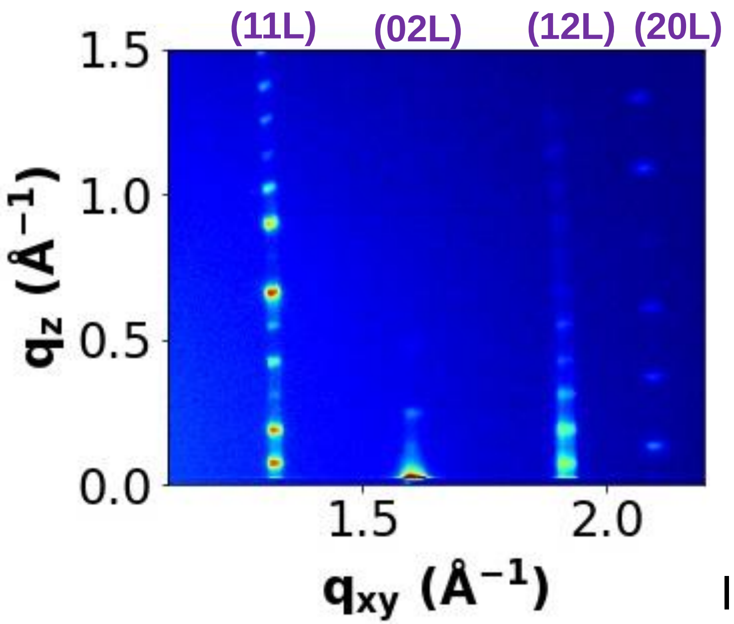
Out-of-plane (OOP)

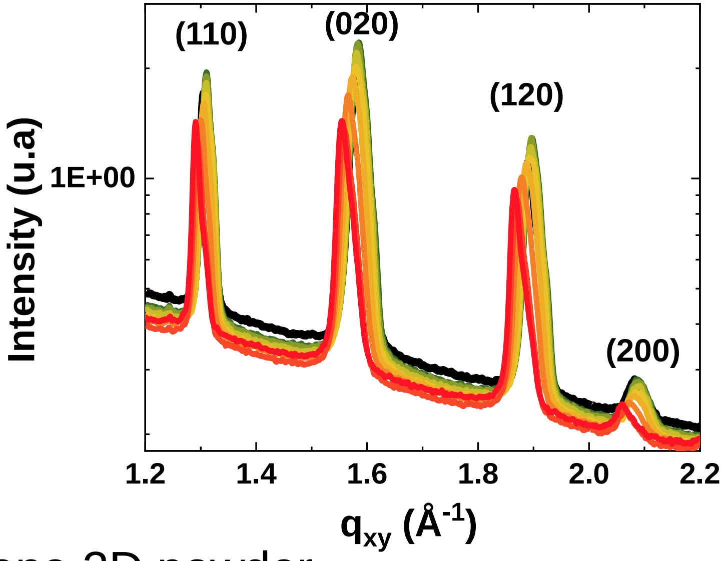


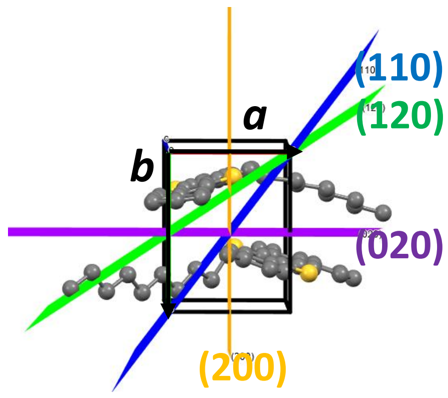




In-plane (IP)

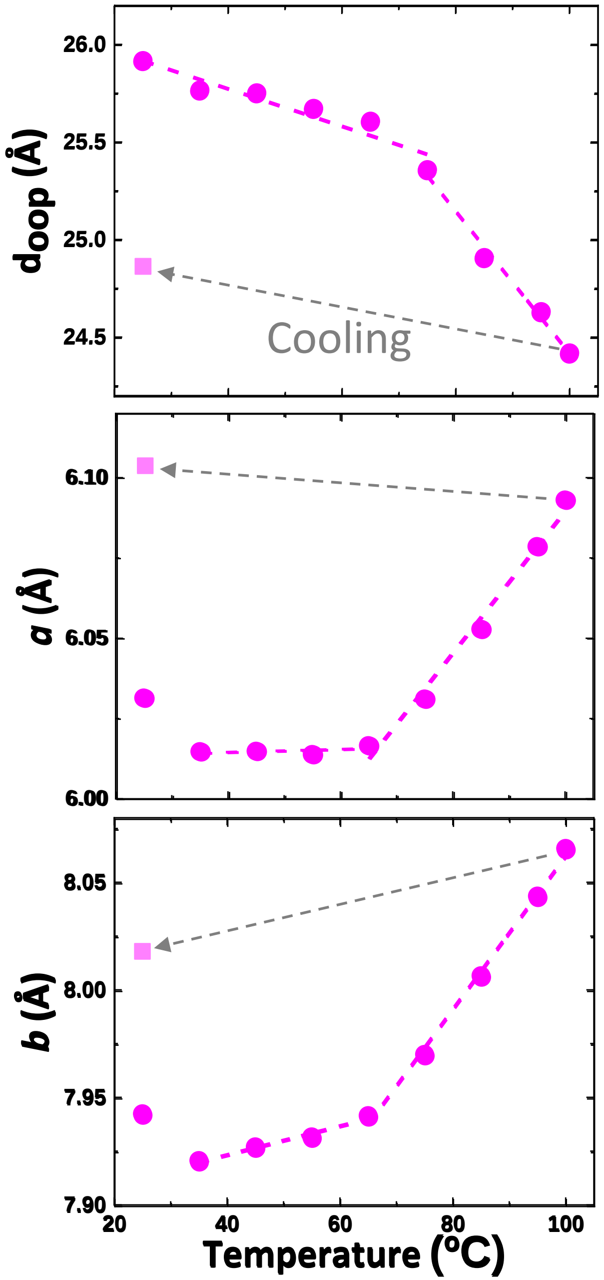






In-plane 2D powder

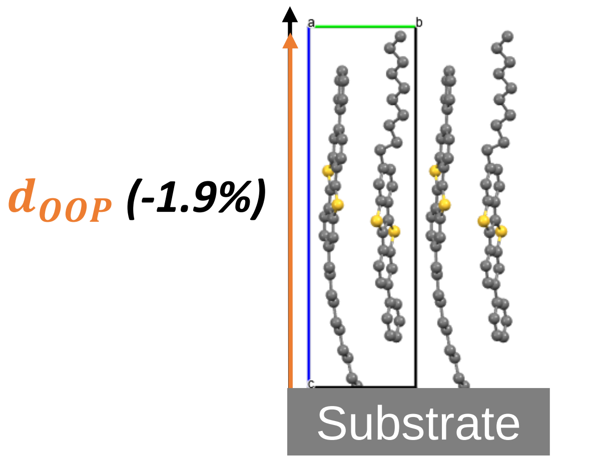
Strain on Single-Layer structure

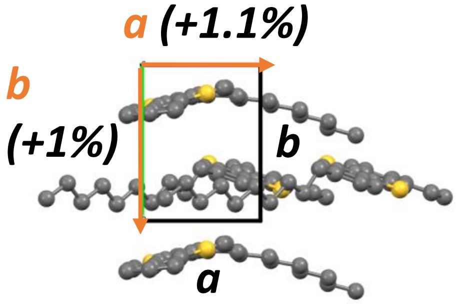


Out-of-plane

In-plane

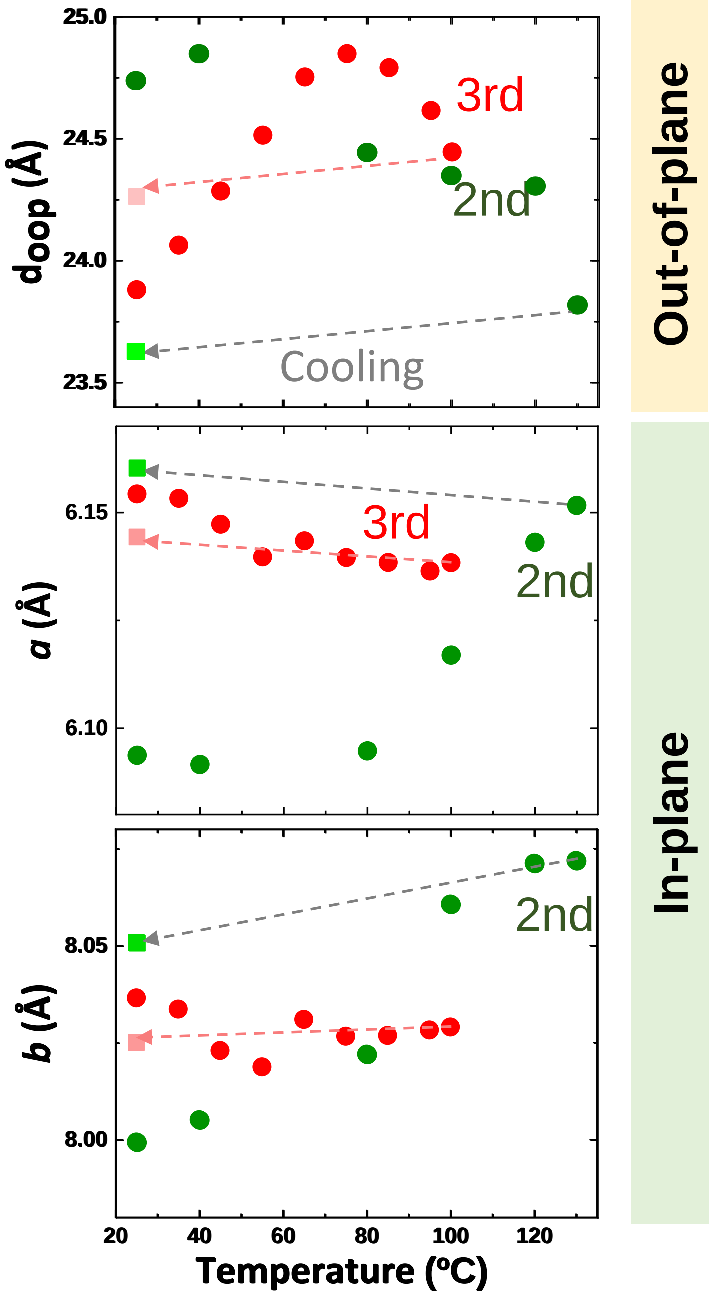
With thermal annealing

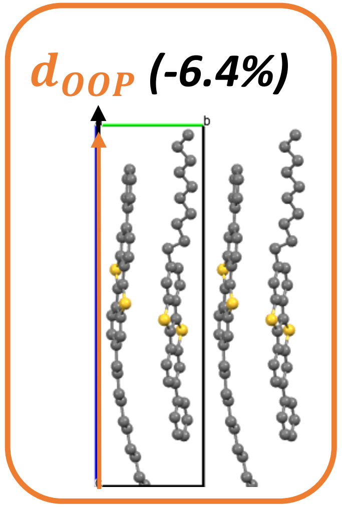




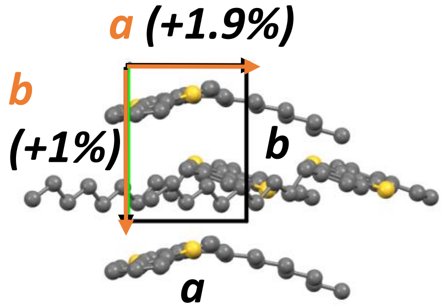
- ❑ **Anisotropic and non-linear expansion with temperature.**
- ❑ Irreversible changes: Reduction of the out-of-plane direction and expansion of in-plane unit cell.

Thermal Cycling

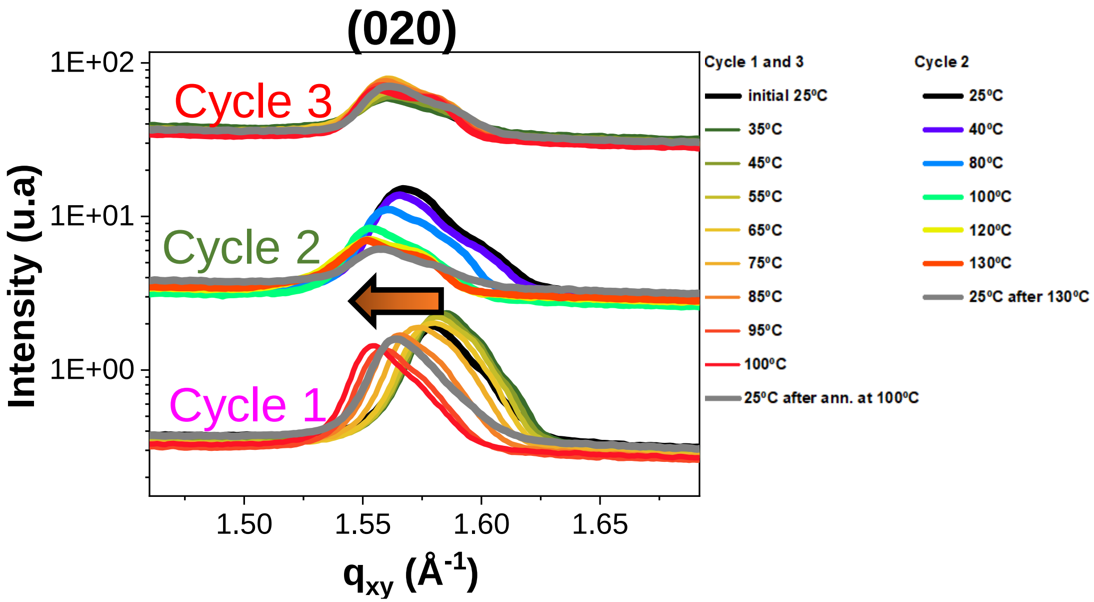




After 3 annealing cycles

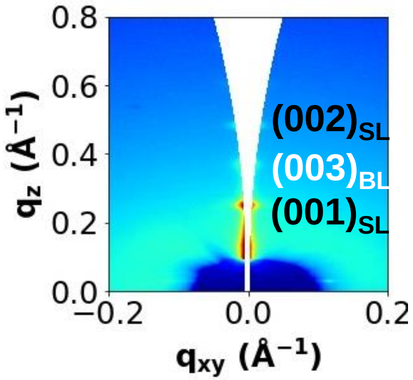


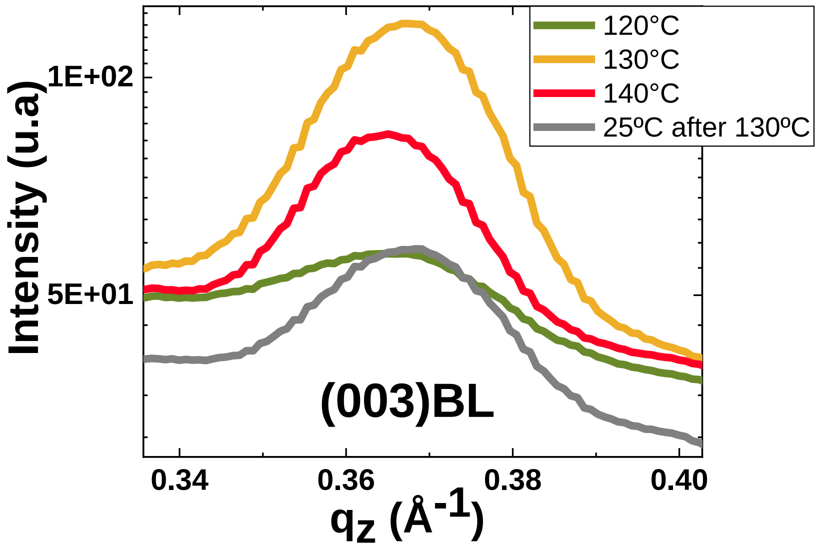
- The in-plane strain is released after 2 annealing cycles

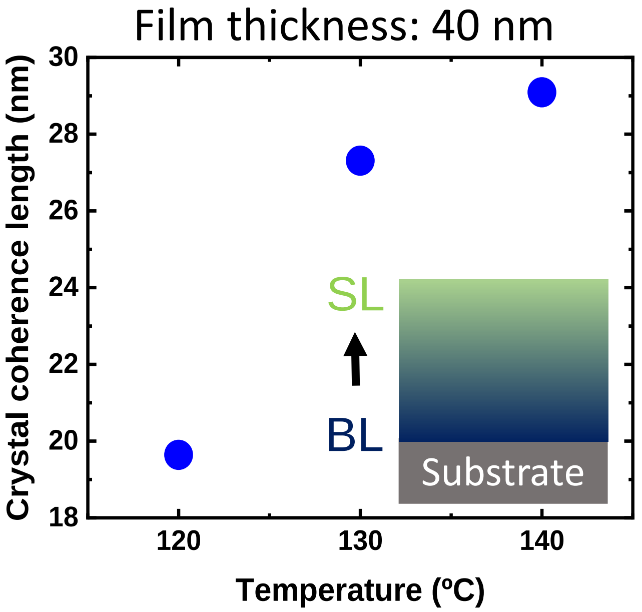


Bilayer structure

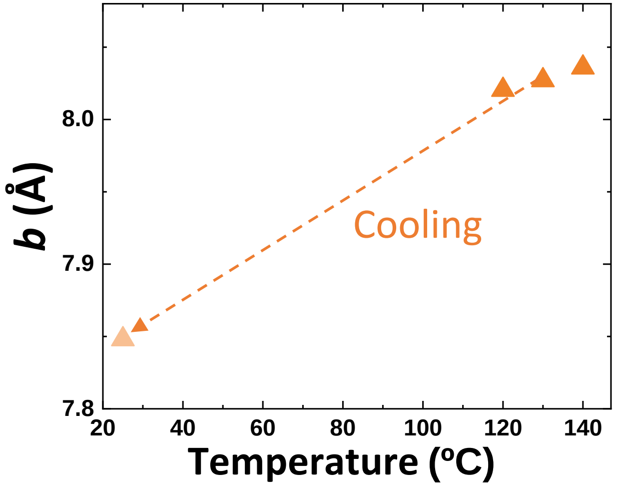
Out-of-plane







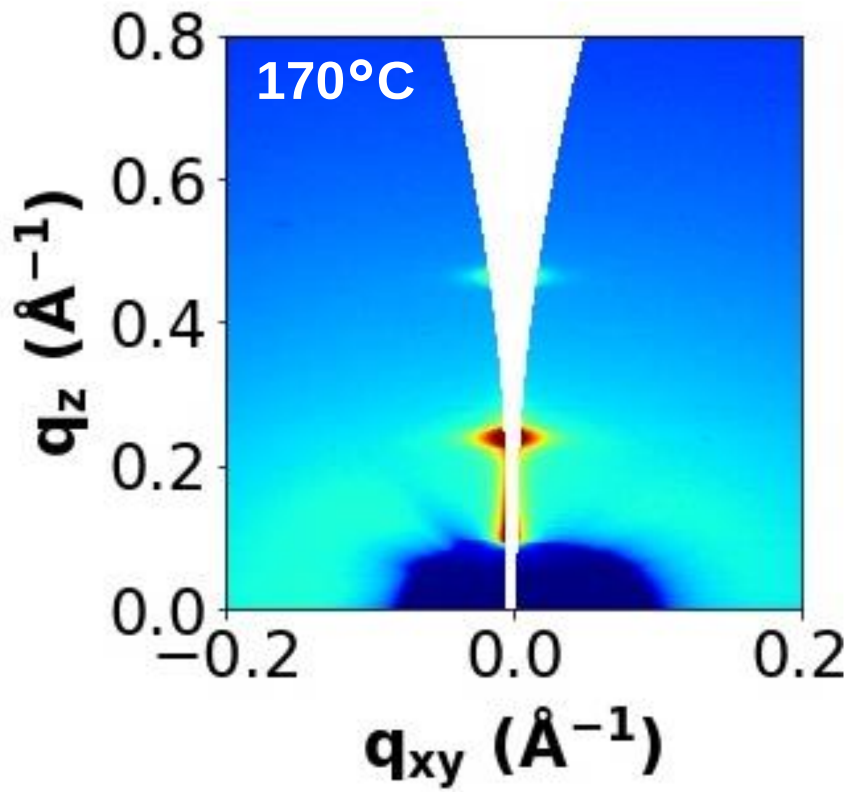
In-plane

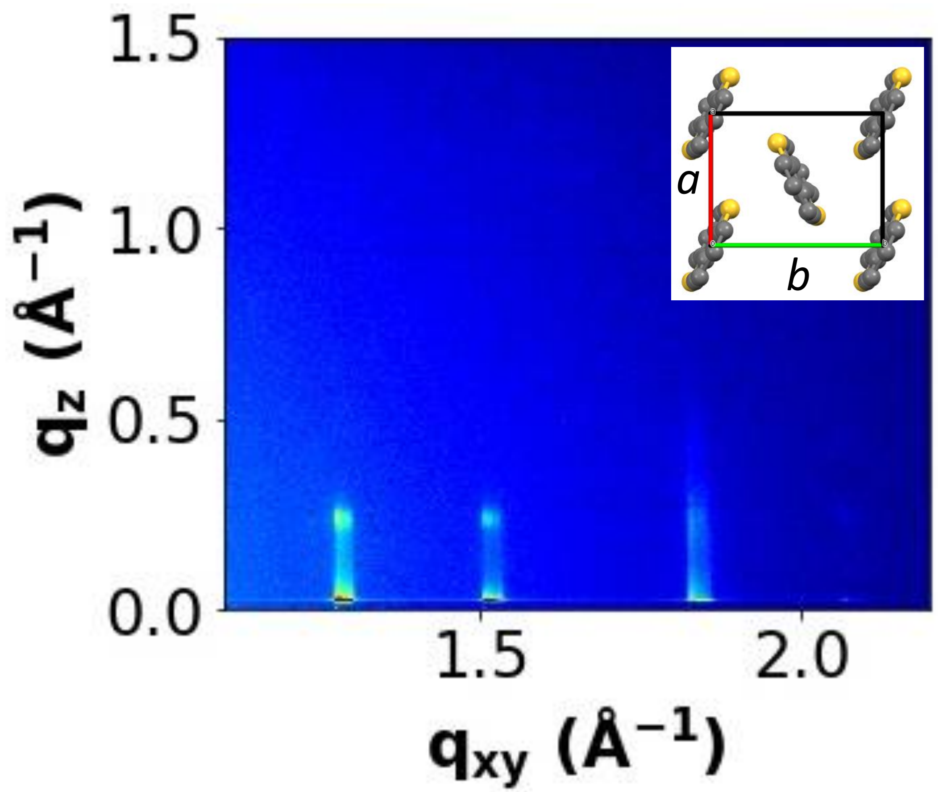


- Bilayer emerges above 120°C and develops with further annealing: SL-BL transformation occurs in the vertical direction
- No thermal expansion along the out-of-plane direction (stronger interlayer interaction for the bilayer packing)
- Expansion between room temperature and 140 °C along *b*-axis (CTE_b = 17 x 10^{-6} K^{-1})

SmE Single-Layer structure

It forms for T>150ºC

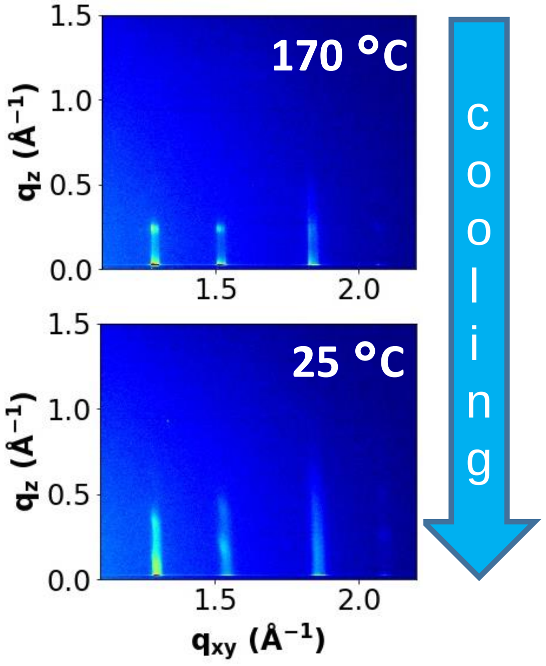




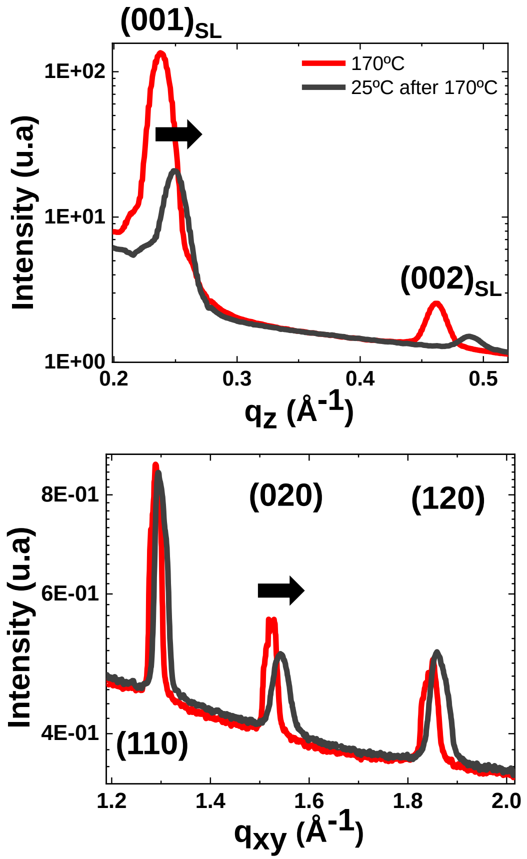
- In-plane: Herringbone BTBT packing
- OOP: Short-range order
- Recently proposed: molten alkyl chains

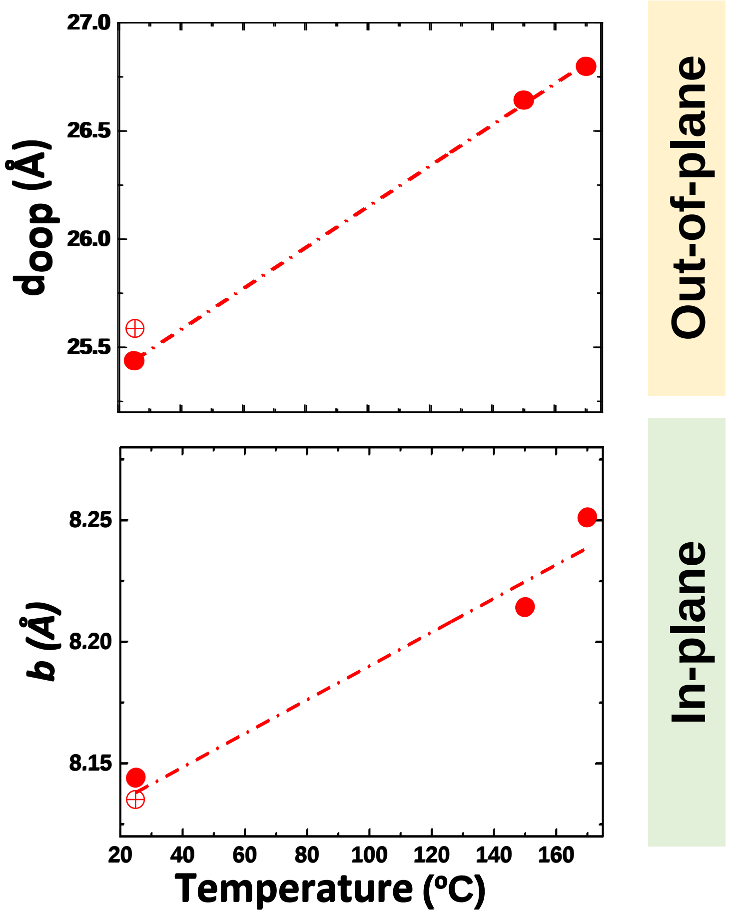
[Saito et al., Journal of Chemical physics, vol.139, p.114902, 2013]

Thermal expansion on Smetic E structure



Cooling rate: 150 °C/min



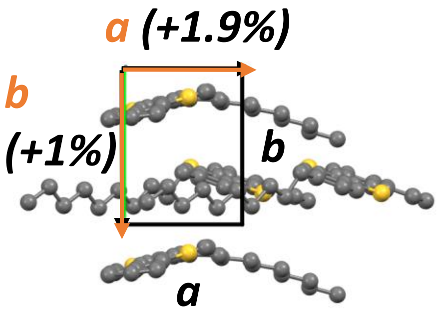


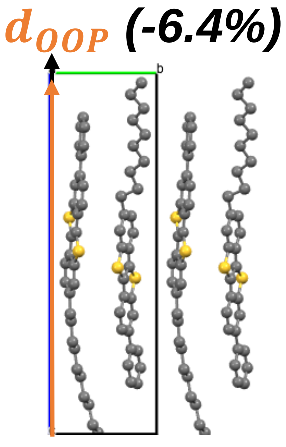
- ❑ Liquid crystalline phase smE remains at room temperature (after cooling down)
- ❑ **Anisotropic 'colossal' thermal expansion on smetic E phase.** Largest expansion along the out-of-plane direction

Parameter	CTE ($10^{-6}K^{-1}$)
d_{OOP}	350
b	89

Summary

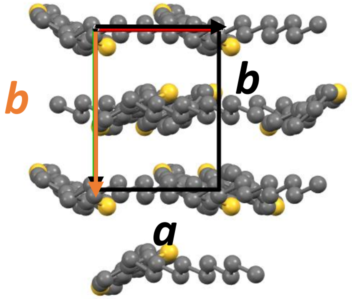
Single Layer

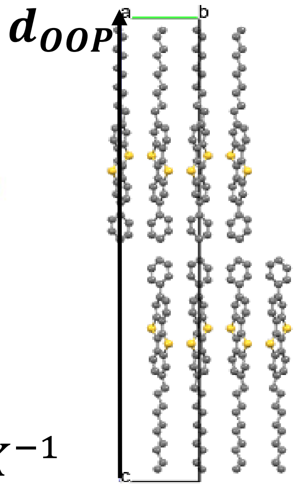




- ❑ STRAIN: Anisotropic and non linear changes with temperature.
- ❑ In-plane structure stabilized after 3 annealing cycles

Bilayer

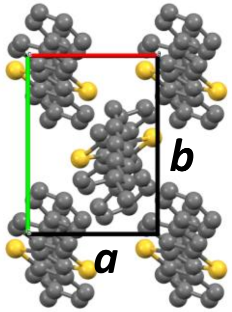


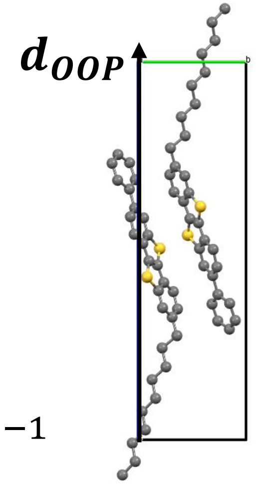


CTE_b = 17 x 10^{-6} K^{-1}

- ❑ Stable phase
- ❑ Anisotropic **thermal expansion**: only along *b*-axis.

SmeticE





CTE_b = 89 x 10^{-6} K^{-1}

$CTE_{d_{OOP}}$ = 350 x 10^{-6} K^{-1}

- ❑ Anisotropic and ‘colossal’ **thermal expansion**, largest along out-of-plane direction.

Implication in OFETs

Lack of reproducibility

Tightest packing, highest mobility

Cracks on the film

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Dr. Eduardo Solano

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In situ Correlative Facility for Advanced Energy Materials (InCAEM) project

Crystal structure of asymmetric organic semiconductor 7-decyl-2-phenyl[1]benzothieno[3,2-*b*][1]benzothiophene

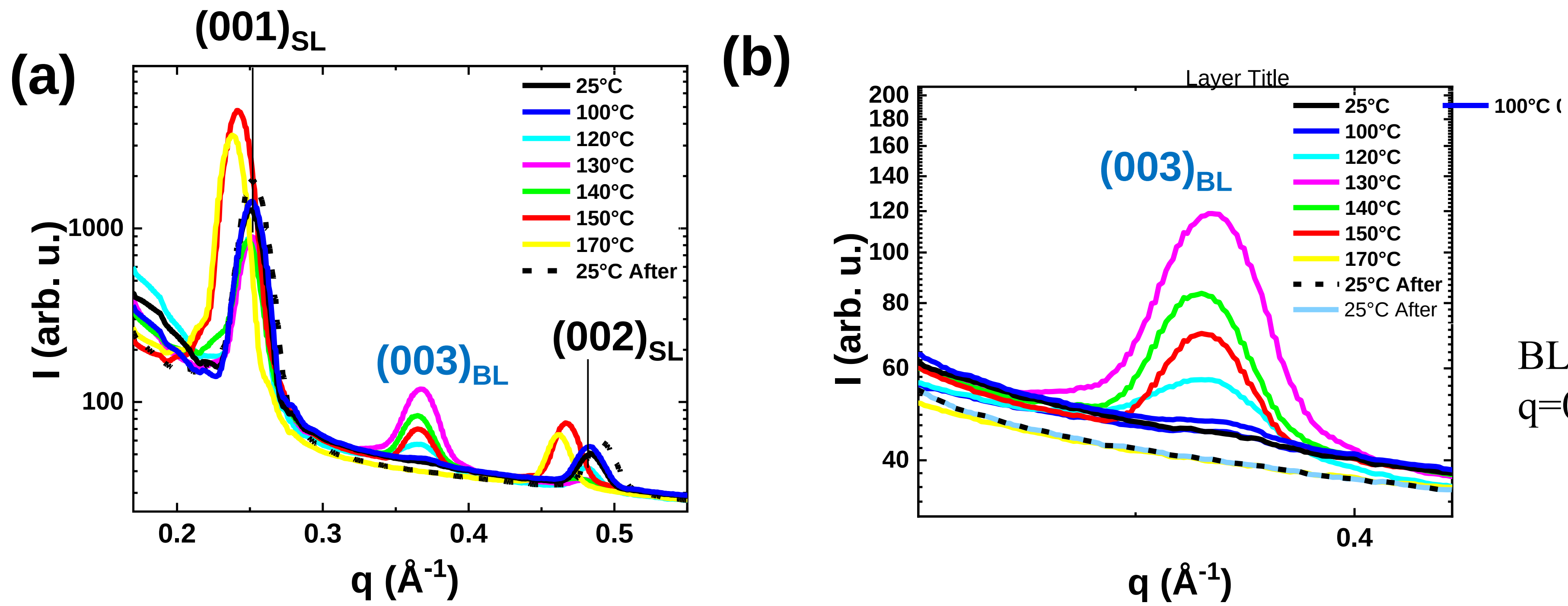
Hiromi Minemawari[1*], Jun'ya Tsutsumi[1], Satoru Inoue[1], Toshikazu Yamada[1], Reiji Kumai[2], and Tatsuo Hasegawa[1,3]

Single crystal of Ph-BTBT-C10 present the BL packing

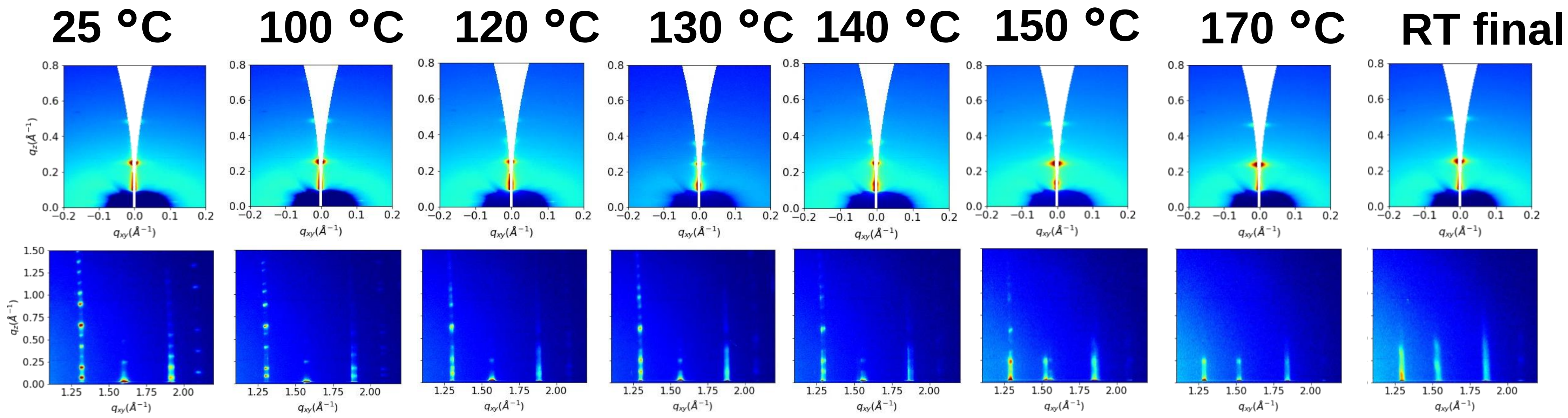
For a sample of 40 nm (L1) the unit cell parameters of the different polymorphs at room temperature are:

	a	b	doop monolayer
SL	5.97	7.82	25.4
BL	6.03	7.85	25.6
smE	6.02	**8.15**	25.2
Single crystal (BL)	6.04	7.76	26.56

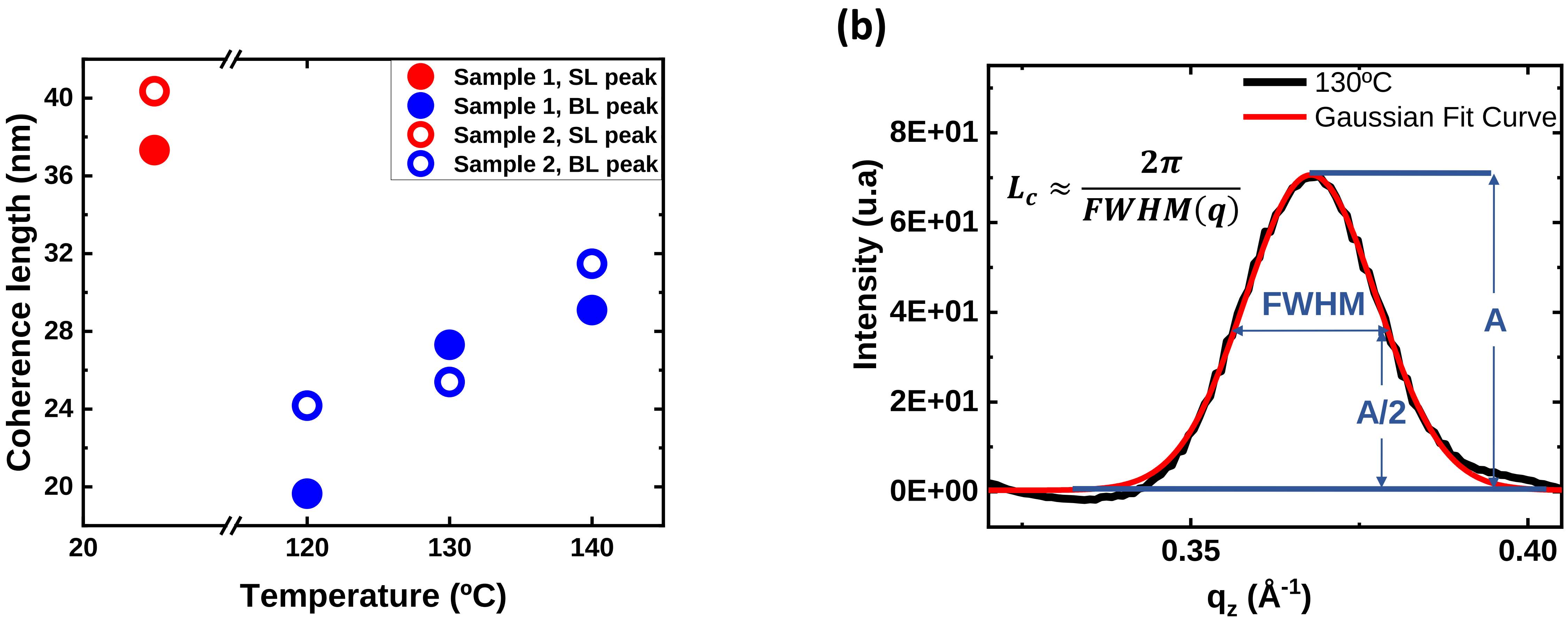
For SL is the value at initial RT
For BL is the value at RT after annealing at 130ºC
For smE is the value at RT after annealing at 170ºC



BL observed at q=0.366 $Å^{-1}$



2D GIWAXS images for all the measured temperatures



Crystal coherence length calculated from the FWHM values of the (001) SL peak at initial 25°C and of (003) BL peak at certain temperatures.

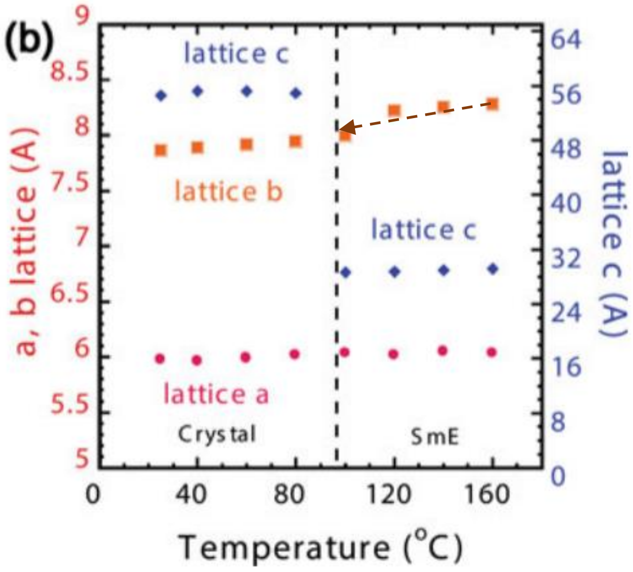
smE as a precursos for crystalline films

Liquid crystal and crystal structures of a phenyl-benzothienobenzothiophene derivative

Hiroaki Iino and Jun-ichi Hanna

They prepare the crystal phase (Bilayer) from the smE pase upon cooling. A thick (10 um) and thin (50 nm) films are prepared on **glass substrates**.

Parameters evolution during the cooling process on the 10 um bulk film:

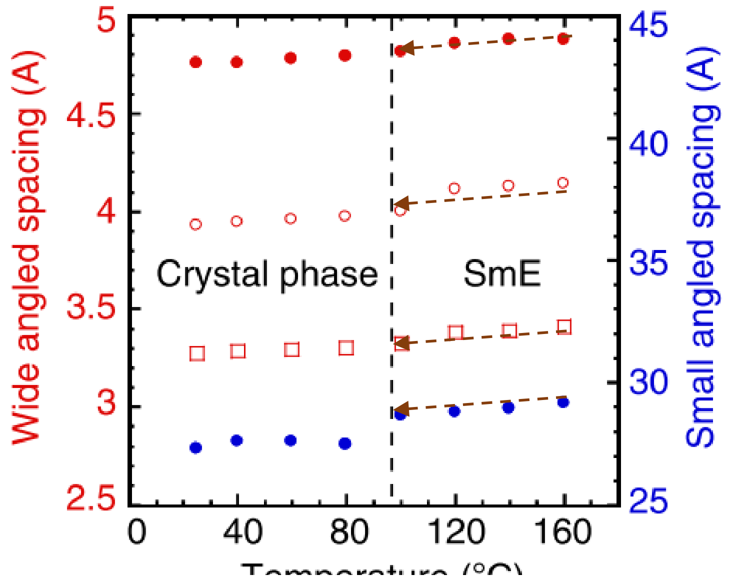


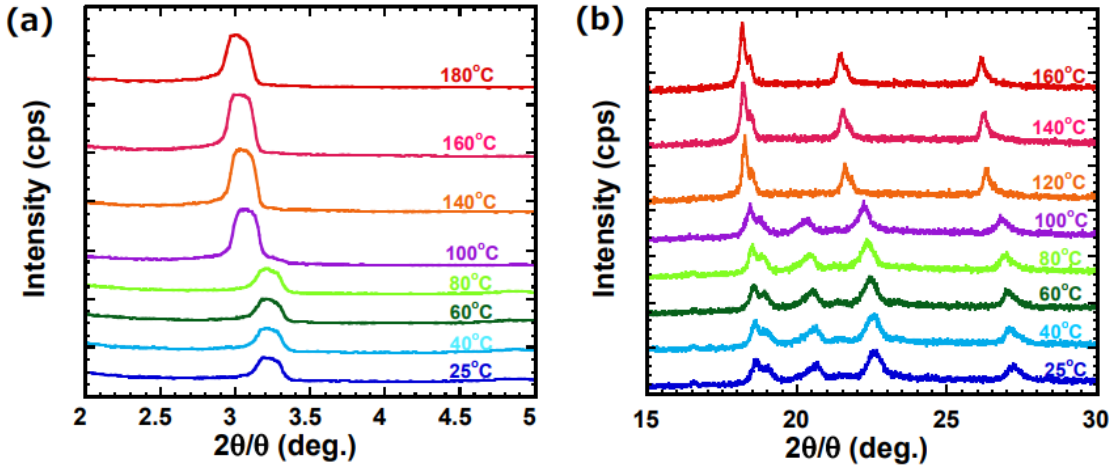
Comparison BL-smE:
Shorter b in BL
Doubled c in BL
Same a

Evolution of smE parameters with temperature:
Decrease of b with cooling temperaturas
No change on a or c in the temperaturas o smE

Liquid crystals for organic thin-film transistors

Hiroaki Iino[1,2], Takayuki Usui[1,2] & Jun-ichi Hanna[1,2]





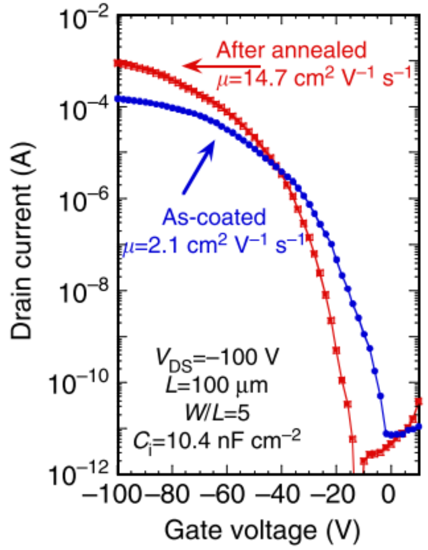
Supplementary Figure 2 | XRD patterns of Ph-BTBT-10 at several temperatures

Liquid crystals for organic thin-film transistors

Hiroaki Iino[1,2], Takayuki Usui[1,2] & Jun-ichi Hanna[1,2]

Top contact – bottom gate OFETs

b



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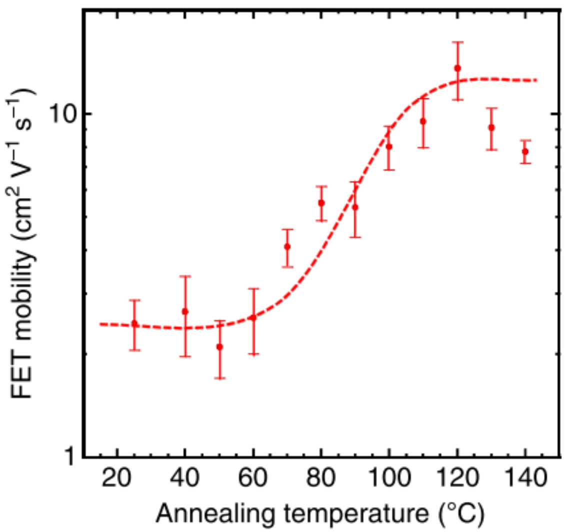
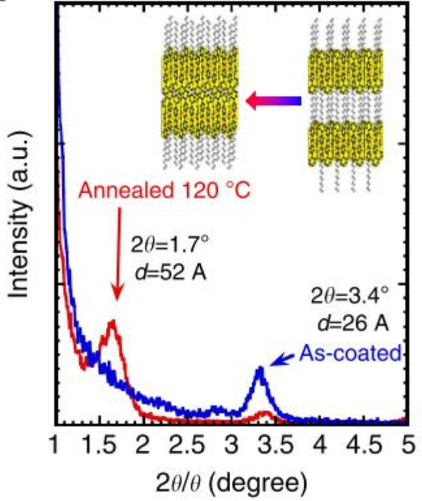


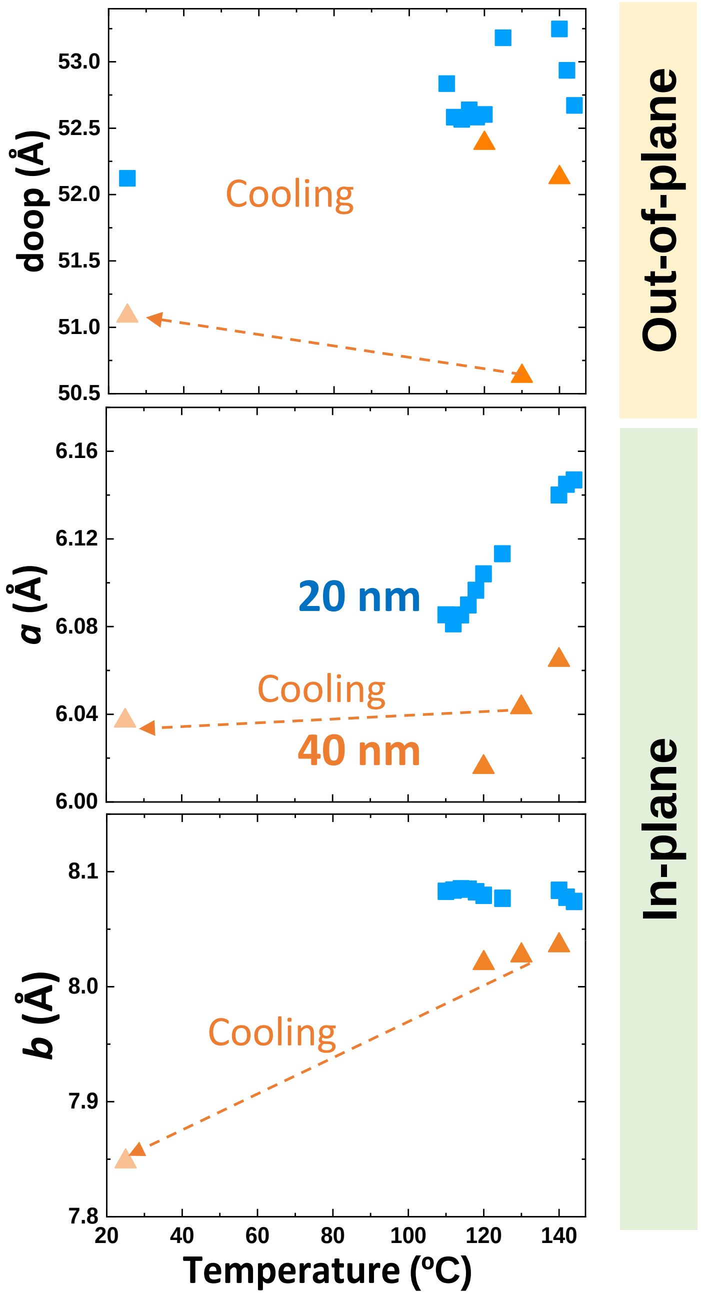
f

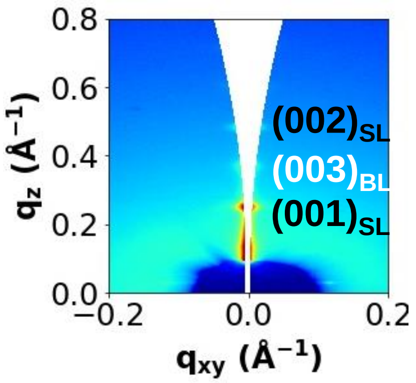


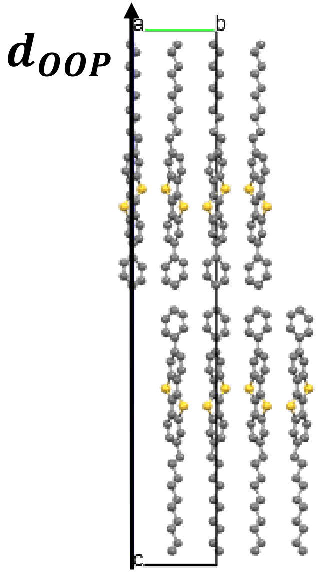
FET mobility improved after thermal annealing at 120 °C for 5 min from 2.1 cm2V-1s-1 up to 14.7 cm2V-1s-1 due to the transition from monolayer to bilayer phase

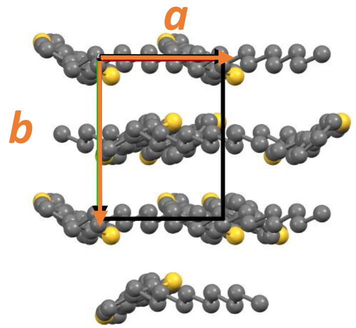
*Prepared from solution

Thermal expansion on Bilayer structure









- ❑ No thermal expansion along the out-of-plane direction (stronger interlayer interaction for the bilayer packing)
- ❑ Largest expansion between room temperature and 140 °C is along *b*-axis (CTE_b = 17 x 10^{-6} K^{-1})

Outlook

- Measure in situ the OFETs while annealing. See if the strain have an impact on the charge trapping. See if it is possible to minimize by thermal treatment.

- Strain effects with different substrates (different mismatch between the coefficient of thermal expansion)

- Role of the side groups (alkyl chain length, phenyl groups..) on the strain effects