

**9<sup>th</sup> Workshop on Substrate-Mediated Polymorphism  
in Organic Thin Films (SMP9)**

# **Book of Abstracts**



**25<sup>th</sup> - 27<sup>th</sup> of September 2017**

**University of Graz, Schubertstraße 1, Austria**

**<http://www.if.tugraz.at/smp/>**



**Anton Paar**



**NAWI  
Graz**



**TU  
Graz**





| MONDAY            |               | TUESDAY           |              | WEDNESDAY         |                  |
|-------------------|---------------|-------------------|--------------|-------------------|------------------|
| 25 September 2017 |               | 26 September 2017 |              | 27 September 2017 |                  |
|                   |               | 9:00 - 10:00      | Ward         | 9:00 - 10:00      | Todorovic        |
|                   |               | 10:00 - 10:30     | Mali         | 10:00 - 10:30     | Scherbela        |
|                   |               | 10:30 - 11:00     | Balzer       | 10:30 - 11:00     | Breuer           |
|                   |               |                   | coffee break |                   | coffee break     |
|                   |               | 11:30 - 12:30     | Tkatchenko   | 11:30 - 12:30     | Myerson          |
|                   |               | 12:30 - 13:00     | Poster       | 12:30 - 13:00     | Chattopadhyay    |
|                   |               |                   | lunch        |                   | CONCLUSION       |
|                   |               | 13:00 - 14:30     | Poster       |                   |                  |
|                   |               | 14:30 - 15:30     | Forker       |                   |                  |
|                   |               | 15:30 - 16:00     | Roese        | 15:00             | excursion        |
|                   | 16:00 - 16:30 | Th. Wagner        |              |                   |                  |
|                   | 16:30 - 17:00 | Matkovic          |              |                   |                  |
|                   |               | coffee break      |              |                   |                  |
| 16:00 - 17:00     | Ocko          |                   | coffee break |                   |                  |
| 17:00 - 17:30     | Smilgies      | 17:30 - 18:30     | Sugden       |                   |                  |
| 17:30 - 18:00     | Schiek        | 18:30 - 19:00     | Rozboril     |                   | Invited talk     |
| 18:00 - 18:30     | Rivalta       |                   |              |                   | Contributed talk |
|                   |               | 20:00             | dinner       |                   | Poster           |





# Program of the Workshop

**Monday**  
**25<sup>th</sup> September 2017**

12:45 – 13:00                  Welcome

## SESSION 1:

**Chairman: A. Daniel Boese, Graz University**

13:00 – 14:00                  **Ulrich Griesser** (University of Innsbruck, Austria)  
Pathways to polymorphs in molecular crystals

14:00 – 15:00                  **Lynn Loo** (Princeton University, NJ, USA)  
Polymorphic accessibility and stability in molecular semiconductor thin films

15:00 – 15:30                  **Gabin Gbabode** (Normandie University, Rouen, France)  
Preliminary results on the polymorphic behavior in thin films of a small organic model molecule: n-methylurea

15:30 – 16:00                  **Coffee Break**

## SESSION 2:

**Chairman: Oliver Werzer, Graz University**

16:00 – 17:00                  **Ben Ocko** (Brookhaven National Laboratory, NY, USA)  
Surface freezing

17:00 – 17:30                  **Detlef-M. Smilgies** (Cornell University, NY, USA)  
Transient polymorphs during processing of organic semiconductors

17:30 – 18:00                  **Manuela Schiek** (University of Oldenburg, Germany)  
Polymorphic phases of an aniline-squaraine in spin casted and vapor deposited thin films

18:00 – 18:30                  **Ariana Rivalta** (University of Bologna, Italy)  
Polymorphs and Surface Induced Structures in drug thin films investigated by Raman spectroscopy

# Tuesday

## 26<sup>th</sup> September 2017

### SESSION 3:

**Chairman: Oliver Hofmann, Graz University of Technology**

- 9:00 – 10:00      **Michael D. Ward** (New York University, NY, USA)  
The role of epitaxy and confined interfaces in thin film and crystal polymorphism
- 10:00 – 10:30      **Kunal S. Mali** (Leuven Chem and Tech, Belgium)  
Surface-supported multicomponent supramolecular architecture: interactions and stimulus responsive behaviour
- 10:30 – 11:00      **Frank Balzer** (South Danish University, Sonderborg, Denmark)  
Formation and electrostatic surface potential of functionalized quarter-phenylene nanofibers
- 11:00 – 11:30      **Coffee Break**

### SESSION 4:

**Chairman: Oliver Hofmann, Graz University of Technology**

- 11:30 – 12:30      **Alexandre Tkatchenko** (University of Luxembourg, Luxembourg)  
First-principles modeling of molecular polymorphism in crystals and on surfaces
- 12:30 – 14:30      **Poster Session including Lunch**

### SESSION 5:

**Chairman: Andrew O. F. Jones, Anton Paar, Graz**

- 14:30 – 15:30      **Roman Forker** (Friedrich Schiller University Jena, Germany)  
Physisorbed molecular adlayer exhibiting temperature- and coverage-dependent polymorphism
- 15:30 – 16:00      **Peter Roes** (Technische Universität Dortmund, Germany)  
XPS/XPD measurements of self-assembled caffeine monolayers on Ag(110)
- 16:00 – 16:30      **Thorsten Wagner** (Johannes Kepler University Linz, Austria)  
The growth of  $\alpha$ -sexithiophene on different silver surfaces
- 16:30 – 17:00      **Aleksandar Matković** (Montanuniversität Leoben, Austria)  
Contact planes of small rod-like molecules on graphene and hexagonal boron nitride
- 17:00 – 17:30      **Coffee Break**

SESSION 6:

**Chairman: Andrew O. F. Jones, Anton Paar, Graz**

- |               |  |
|---------------|--|
| 17:30 – 18:30 | <b>Isaac Sudgen</b> (Imperial College London, UK)<br>Recent advances in <i>ab initio</i> crystal structure prediction                            |
| 18:30 – 19:00 | <b>Jakub Rozbořil</b> (Masaryk University, Brno, Czech Republic)<br>In-situ X-ray diffraction annealing study on an anthradithiophene derivative |
| 20:00         | <b>Workshop dinner “Meerscheinschlössl”</b>  |

# Wednesday

## 27<sup>th</sup> September 2017

SESSION 7:

**Chairman: Roland Resel, Graz University of Technology**

- |               |   |
|---------------|---|
| 9:00 – 10:00  | <b>Milica Todorović</b> (Aalto University, Finland)<br>Efficient Bayesian inference of surface adsorption   |
| 10:00 – 10:30 | <b>Michael Scherbela</b> (Graz University of Technology, Austria)<br>Computational polymorph prediction for organic/inorganic interfaces using machine learning |
| 10:30 – 11:00 | <b>Tobias Breuer</b> (Philipps-University Marburg, Germany)<br>Influence of surface roughness on polymorph formation in organic thin films                      |
| 11:00 – 11:30 | <b>Coffee Break</b>   |

SESSION 8:

**Chairman: Roland Resel, Graz University of Technology**

- |               |   |
|---------------|---|
| 11:30 – 12:30 | <b>Allan S. Myerson</b> (Massachusetts Institute of Technology, MA, USA)<br>Nucleation of organic molecular crystals on surfaces and in nanopores |
| 12:30 – 13:00 | <b>Basab Chattopadhyay</b> (Université Libre de Bruxelles, Belgium)<br>A thermal gradient approach towards polymorph selection                    |
| 15:00 –       | <b>Excursion</b>  |

# Posters

**(1) Selective, temperature-induced F4TCNQ desorption from p-doped P3HT films**

H. Hase, A. Opitz, N. Koch, I. Salzmann

**(2) Epitaxially ordered Metal-Organic-Frameworks based on copper-benzenedioic acid**

S. Hofer, A. Jones, R. Resel, K. Okada, R. Ricco, P. Falcaro

**(3) First-principles molecular crystal structure prediction: The importance of collective van der Waals interactions and free energies**

J. Hoja, H.-Yu Ko, R. Car, R. A. DiStasio Jr., A. Tkatchenko

**(4) Computational phase diagram prediction for organic monolayers on metal substrates**

L. Hörmann, M. Scherbela, V. Obersteiner, O.T. Hofmann

**(5) Photochemical switching of azobenzene derivatives on an insulating surface**

S. Jaekel, A. Richter, R. Lindner, R. Bechstein, A. Kühnle, St. Hecht, L. Grill

**(6) Understanding polymorph selection in nabumentone thin films at surfaces**

M. Kaltenegger, O. Werzer, Ch. Röthel

**(7) Biaxial oriented growth of pentacene on rippled glass surfaces**

S. Pachmajer, O. Werzer, A. Perrotta, R. Resel

**(8) Appearance of a surface induced crystal structure of 6,6'-dibromoindigo**

M. Truger, C. Röthel, D. Kriegner, I. Salzmann, J. Simbrunner, R. Resel

**(9) Complex behaviour of caffeine crystallites on solid surfaces**

C. Röthel, M. Radziown, C. Simbrunner, R. Resel, O. Werzer

**(10) The substrate-induced phase of C<sub>8</sub>O-BTBT-OC<sub>8</sub> detected by mid-infrared and lattice phonon Raman spectroscopy**

B. Schrode, A.O.F. Jones, R. Resel, R. Schennach, A. Brillante, T. Salzillo, E. Venuti

**(11) Photoluminescence as a probe of molecular organization in PDI8-CN2 ultra-thin films**

A. Brillante, T. Salzillo, R.G. Della Valle, E. Venuti, F. Borgatti, E. Lunedei, F. Liscio, S. Milita, C. Albonetti

**(12) Accurate calculations of molecular crystals**

O. A. Loboda, G. A. Dolgonos, A. D. Boese

**(13) Addressing conformational and vibrational entropy in bio-organic systems**

M. Rossi, D. Makismov, C. Baldauf

**(14) *In-situ* crystallization and gel formation of thermodynamically unstable polymorphs: a SWAXS study of caffeine in isopropanol**

A. O. F. Jones, H. M. A. Ehmman, A. Keilbach, A. Moser, C. Röthel, O. Werzer

**(15) A fast alternative to periodic DFT calculations: DFT embedded into DFTB**

G. A. Dolgonos, O. A. Loboda, A. D. Boese



# **Oral presentations**





## PATHWAYS TO POLYMORPHS IN MOLECULAR CRYSTALS

U. J. Griesser

*Institute of Pharmacy, University of Innsbruck, Innrain 52c, 6020 Innsbruck, Austria*

Today, gaining sound knowledge about the existence ranges and properties of different solid state forms of molecular compounds is a mandatory task in lucrative industrial areas such as pharmaceutical industry. Driven by regulatory requirements, economic reasons and intellectual property rights, great efforts are undertaken to achieve a better understanding about the nature of molecular aggregations and how to design supramolecular construct with advantageous or functional material properties. Such “crystal engineering” efforts have become popular in many other disciplines dealing with the material properties of small organic crystals, of which only a small fraction has been thoroughly examined concerning their solid state phenomena. Theoretically every molecular compound may exist in different solid state forms (one-component polymorphs or multi-component crystals such as hydrates or “co-crystals”) and computational crystal structure prediction (CSP) can generate nearly an infinitive number of metastable phases of which only a few show a sufficiently high kinetic stability to be observable or used as an alternative material to the thermodynamically stable form. However, computational methods cannot replace sophisticated experimental screens and studies but the combination of both provides the confidence that the desired forms have been identified and also the necessary understanding of the molecular and thermodynamic features of a molecular compound. This presentation gives an overview of concepts for generating solid state forms and discusses intriguing cases of polymorphic systems and less common pathways including concepts based on heterogeneous seeding using isomorphic or non-isomorphic additives or templates.

## POLYMORPHIC ACCESSIBILITY AND STABILITY IN MOLECULAR SEMICONDUCTOR THIN FILMS

G.E. Purdum<sup>(a)</sup>, Y.-L. Loo<sup>(a,b)</sup>

<sup>(a)</sup> *Department of Chemical and Biological Engineering, Princeton University, USA*

<sup>(b)</sup> *Andlinger Center for Energy and the Environment, Princeton University, USA*

We investigated the polymorphic stability and reversibility of thin films of a series of naphthalene diimides (NTCDIs) with varying alkyl substitutions. Each derivative adopts its  $\beta$ -phase upon thermal evaporation; post-deposition processing via solvent-vapor annealing converts the  $\beta$ -phase to the  $\alpha$ -phase in two of the four derivatives. NTCDIs adopt layered structures driven by strong intralayer  $\pi$ - $\pi$  interactions and weaker interlayer van der Waals interactions. The presence of interlayer short contacts effectively locks the structure in place, preventing any molecular reorganization. The absence of such short interlayer contacts is instead correlated with reversible access of both polymorphs; judicious selection of post-deposition processing conditions tunes the polymorph that is accessed. This finding is generalizable across a wide range of molecular semiconductors that adopt layered structures, including derivatives of benzothiophene and functionalized acenes. Beyond organic electronics, this finding has implications on pharmaceuticals and the food industry as polymorphic stability governs bioavailability and solubility.

## Preliminary results on the polymorphic behavior in thin films of a small organic model molecule: n-methylurea

G. Gbabode<sup>1(a)</sup>, R. Simon<sup>(a)</sup>, and G. Coquerel<sup>(a)</sup>

<sup>(a)</sup>Normandie Univ, Laboratoire SMS – EA3233, Univ Rouen, 76821 Mont Saint Aignan, France

N-methylurea (NMU, hereafter), of formula  $C_2H_6N_2O_2$ , is principally used for its non-linear optical properties [1]. This compound was first studied in our laboratory due to its peculiarity to not being a chiral molecule which anyway crystallizes in a chiral space group (form I with space group  $P2_12_12_1$ ) [2]. Until our study, only form I, the crystal structure of which have been determined in 1933 [3], has been reported in the literature. This crystal structure consists in an efficient 3D hydrogen bonding network involving hydrogen bonds between the oxygen receptor and the N-H receptors composing the urea moiety. However, it appears that upon quenching from the melt, two new polymorphs are revealed depending on the quenching temperature: form II (at temperatures above  $-120^\circ\text{C}$ ) and form III (at temperatures below  $-120^\circ\text{C}$ ) [4]. The crystal structures of these forms have been determined from X-ray powder diffraction data collected at the appropriate temperatures and show a much loosely packed hydrogen bond network in which  $O\cdots H-N$  (hydrogen bonded) and methyl – methyl (nto hydrogen bonded) intermolecular contacts alternate periodically [4]. Forms II and III are monotropically related towards form I, and are metastable so that when kept at room temperature at ambient conditions, they rapidly convert back to stable form I.

Due to its interesting polymorphic behavior, NMU is a good model compound to investigate the influence of the lowering of dimensionality on the polymorphism, notably by fabricating thin films. Moreover, as the crystal packing of NMU is essentially dictating by hydrogen bonds it is a good candidate to investigate the influence of two-dimensional confinement (e.g. thin and ultrathin films) on the directionality of hydrogen bond interactions and thus help to gain some understanding on polymorphic selection in thin films in more complex compounds presenting these kind of interactions.

We will then show our preliminary results on thin films of NMU, encompassing the difficulties encountered to obtain thin films of sufficient uniformity and most importantly the lack of reproducibility of our attempts. Furthermore, we will show our first results from specular X-ray diffraction that show that either form I or II could be stabilized in thin films (still with lack of predictability). Interestingly, for some samples, a new form could be revealed as proven by the presence of reflections which could not be indexed using the unit cell parameters of the known forms (I, II and III).

[1] E. E. A. Shepherd, J. N. Sherwood, G. S. Simpson, *J. Cryst. Growth* **167**, 709 (1996).

[2] C. Huiszoon, G. W. M. Tiemessen, *Acta Crystallogr.* **B32**, 1604 (1976).

[3] R. B. Corey, R. W. Wyckoff, *Zeitschrift für Kristallographie* **85**, 132 (1933).

[4] G. Baaklini, G. Gbabode, S. Clevers, P. Négrier, D. Mondieig, G. Coquerel, *CrystEngComm* **18**, 4772 (2016).

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<sup>1</sup> Gabin.gbabode@univ-rouen.fr

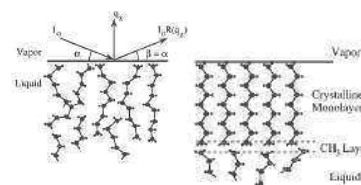
## SURFACE FREEZING

B.M. Ocko<sup>1(a)</sup>, S. Guttman<sup>(b)</sup>, E. Sloutskin<sup>(b)</sup> and M. Deutsch<sup>(b)</sup>

<sup>(a)</sup> Brookhaven National Laboratory, Upton, NY 11973, USA

<sup>(b)</sup> Bar Ilan University, Ramat Gan, 52900 Israel

Surface freezing (SF), the formation of a frozen interfacial monolayer in contact with its bulk liquid phase, is a property of simple chain molecules. These monolayers are among the simplest examples of self-assembly found in nature since they represent equilibrium behavior in a single component system.

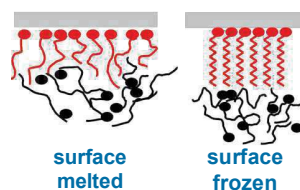


surface liquid    surface frozen

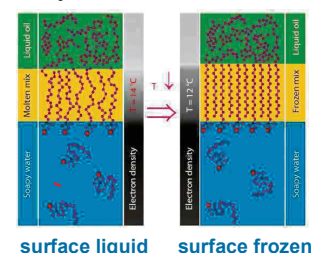
SF was first observed at the vapor interface of n-alkane molecules in 1992, and measured by our group for  $16 < n < 50$  using surface x-ray scattering and tensiometry methods [1]. The frozen monolayers consists of a rotator phase of densely packed, extended, interface-normal molecules for  $n < 28$ , and tilted ones for longer chains [2]. The SF layer exists over a (n-dependent) temperature range of up to 3°C above the bulk melting temperature. SF has also been observed for other alkyl terminated molecules including n-alkanols (long chain alcohols) and diols, for polymers, and for liquid metal alloys.

SF also occurs at solid/liquid [3] and liquid/liquid [4] interfaces.

For bulk n-alkanols melts in contact with a crystalline sapphire or amorphous silicon oxide surface, the SF monolayer comprises densely packed, extended, interface-normal molecules. It exists over a 10-30°C range. When melted, the monolayer has an unusual



structure of a “stretched liquid” where the molecules are significantly more extended than in the bulk liquid. This, and the SF behavior, are explained within a thermodynamic model combining interfacial hydrogen bonding and entropic effects. SF at the oil/liquid interface of surfactant-stabilized emulsion droplets was shown recently to induce a sequence of spherical-to-polyhedral droplet shape transitions, keeping the droplets liquid[5]. A temperature-driven self-emulsification of the droplets was also found. These and other related effects will be discussed in the talk.



[1] XZ Wu, EB Sirota, SK Sinha, BM Ocko, M Deutsch, PRL 70, 958 (1993)

[2] BM Ocko, XZ Wu, EB Sirota, SK Sinha, O Gang, M Deutsch, PRE 55, 3164 (1997)

[3] J Haddad et al., JPC 119, 17648 (2015)

[4] L Tamam et al., PNAS 108, 5522 (2011)

[5] S Guttman, Z Sapir, M Schultz, AV Butenko, B Ocko, M Deutsch, E Sloutskin, PNAS 113, 5522 (2016)

We gratefully acknowledge the US Department of Energy/NSLS, grant AC02-98CH10886, and contributions from many colleagues over the years. A full list will be given in the talk.

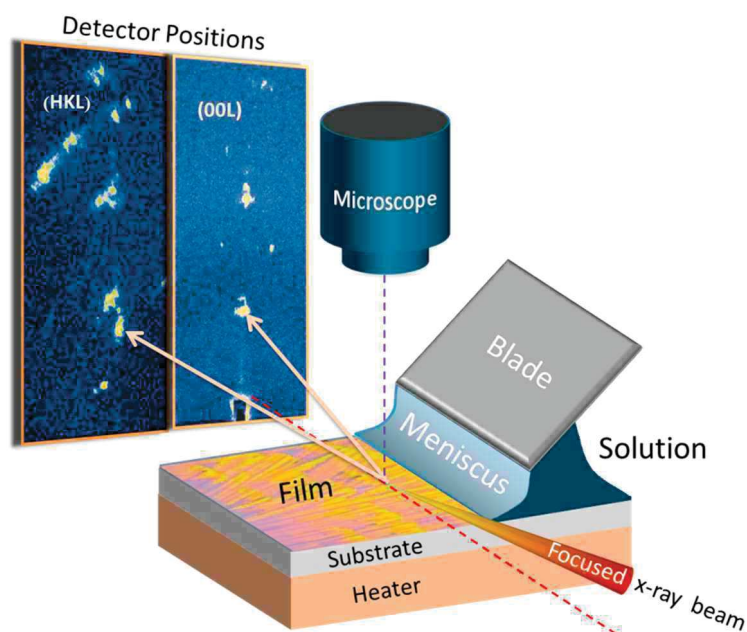
<sup>1</sup> ocko@bnl.gov

## TRANSIENT POLYMORPHS DURING PROCESSING OF ORGANIC SEMICONDUCTORS

D.-M. Smilgies

*Cornell High Energy Synchrotron Source (CHESS), Cornell University, Ithaca, NY, United States*

An overview will be given on experiments at CHESS D1 station, in which transient phases were observed. Processing involved a variety of coating techniques such as spin coating [1], blade coating [2], and pen writing [3]. High speed detection of scattering images using modern pixel array detectors has allowed to follow crystallization events with down to 10 msec resolution.



*Figure 1: In-situ blade coating set-up at CHESS D1 station with high spatial and temporal resolution [2].*

[1] Louis A. Perez, Kang Wei Chou, John A. Love, Thomas S. van der Poll, Detlef-M. Smilgies, Thuc-Quyen Nguyen, Edward J. Kramer, Aram Amassian, and Guillermo C. Bazan, *Adv. Mater.* **25**, 638 (2013).

[2] Detlef-M. Smilgies, Ruipeng Li, Gaurav Giri, Kang Wei Chou, Ying Diao, Zhenan Bao, and Aram Amassian, *Phys. Status Solidi - Rapid Research Letter* **7**, 177 (2013).

[3] Jing Wan, Yang Li, Jeffrey G. Ulbrandt, Detlef-M. Smilgies, Jonathan Hollin, Adam C. Whalley, and Randall L. Headrick, *APL Mater.* **4**, 016103 (2016).

## POLYMORPHIC PHASES OF AN ANILINO-SQUARAINES IN SPIN-CASTED AND VAPOR DEPOSITED THIN FILMS

M. Schiek<sup>(a)</sup>, T. Breuer<sup>(b)</sup>, F. Balzer<sup>(c)</sup>, M. Schulz<sup>(d)</sup>, A. Lützen<sup>(d)</sup>, and G. Witte<sup>(b)</sup>

<sup>(a)</sup> *Institute of Physics, University of Oldenburg, Germany*

<sup>(b)</sup> *Molecular Solids, University of Marburg, Germany*

<sup>(c)</sup> *Mads Clausen Institute, Sonderborg, University of Southern Denmark*

<sup>(d)</sup> *Kekulé Institute for Organic Chemistry and Biochemistry, University of Bonn, Germany*

Squaraines are small molecular quadrupolar donor-acceptor-donor (D-A-D) chromophores absorbing in the red spectral range. They are considered as photovoltaic materials in solar cells [1] and artificial photoreceptors [2]. The prototypical 2,4-bis[4-(*N,N*-diisobutylamino)-2,6-dihydroxyphenyl]-squaraine, shortly named SQIB, crystallizes at least into two polymorphic bulk structures [3], a monoclinic phase, space group P21/c, and an orthorhombic phase, space group Pbcn.

Spin-casted thin films are, depending on the annealing temperature, highly textured with two distinct morphological features, Figure 1, which can be assigned to the polymorphic forms via exclusion principle by means of X-ray diffraction.

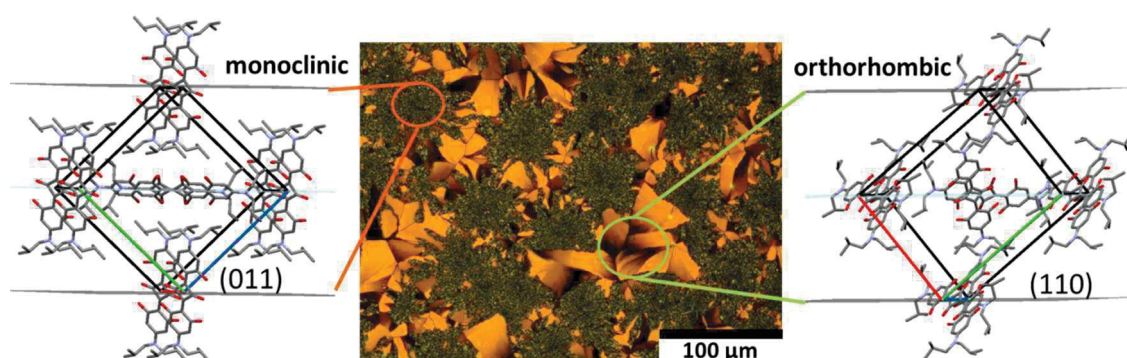


Figure 1: Microscopy image between crossed polarizers of spin-casted, at 120°C annealed SQIB layer on glass shows the “green” monoclinic phase with (011) and the “golden” orthorhombic phase with (110) parallel to the substrate.

Complementarily, we study the polymorph formation of SQIB films processed by organic molecular beam deposition on different substrates and correlate the observed polymorphs to the substrate properties, such as lattice geometry, symmetry and reactivity.

[1] G. Chen, H. Sasabe, T. Igarashi, Z. Hong, J. Kido, *J. Mater. Chem. A* **3**, 14517 (2015).

[2] O.S. Abdullaeva, M. Schulz, F. Balzer, J. Parisi, A. Lützen, K. Dedek, M. Schiek, *Langmuir* **32**, 8533 (2016).

[3] A. Viterisi, N.F. Montacada, C.V. Kumar, F. Gispert-Guirado, E. Martin, E. Escudero, E. Palomares, *J. Mater. Chem. A* **2**, 3536 (2014).



## POLYMORPHS AND SURFACE INDUCED STRUCTURES IN DRUG THIN FILMS INVESTIGATED BY RAMAN SPECTROSCOPY.

A. Rivalta<sup>1(a)</sup>, T. Salzillo<sup>(a)</sup>, O. Werzer<sup>(b)</sup>, E. Venuti<sup>(a)</sup>, R.G. Della Valle<sup>(a)</sup> and A. Brillante<sup>(a)</sup>

<sup>(a)</sup> Department of Industrial Chemistry "Toso Montanari" e INSTM-Udr Bologna, University of Bologna, Viale del Risorgimento 4, 40136 Bologna (Italy)

<sup>(b)</sup> Institute of Pharmaceutical Sciences, Department of Pharmaceutical Technology, University of Graz, Universitätsplatz 1, 8010 Graz, Austria

The study of polymorphism plays an important role in several fields of materials science, with relevant applications in technology and pharmaceuticals. This contribution aims to show how the polymorph phenomenon can be studied by means of confocal Raman microscopy in the *lattice phonons* region (Figure 1). Using this approach allows for an effective *in situ* phase recognition,<sup>[1]</sup> with the possibility of obtaining a topography of the chemical purity and polymorphism of the sample by mapping the Raman signal at a micrometric resolution.<sup>[2]</sup> Recently, there is a growing interest in a new generation of crystalline forms obtained in thin films, which are defined as surface-induced polymorphs (SIPs). In pharmaceutical science it has been demonstrated that SIPs might indeed exhibit different performances like enhanced dissolution rates for drug release. A full characterization of the SIPs is still challenging and a number of experimental and computational tools are necessary to unambiguously identify their nature and characteristics.<sup>[3]</sup>

In the model case of *phenytoin* (5,5-diphenylimidazolidine-2,4-dione) Raman spectroscopy has turned out to be a valuable support to the structural characterization of a SIP.<sup>[3]</sup> By a careful evaluation of different Raman bands, together with the morphological differences observed in the microscope, regions of distinct polymorphs could be identified. This very information was recently inaccessible, as morphologies could not directly be connected to any morphology.

As a further example of the application of the Raman technique, we also report on the investigation of the relative stability of the *paracetamol* (N-(4-hydroxyphenyl)ethanamide) phases in spin coated films on different substrates over a wide temperature range. In particular, the metastable form III has been found to show the longest lifetime on record when obtained in the film form on suitable substrates.

[1] A. Brillante, I. Bilotti, R. G. Della Valle, E. Venuti, M. Mas-Torrent, C. Rovira, Y. Yamashita, Chem. Phys. Lett., **523**, 74 (2012).

[2] A. Brillante, I. Bilotti, R. G. Della Valle, E. Venuti, A. Girlando, Cryst. Eng. Comm., **10**, 937 (2008).

[3] Daniela Reischl, Christian Röthel, Paul Christian, Eva Roblegg, Heike M. A. Ehmman, Ingo Salzmann, Oliver Werzer. Cryst. Growth Des. **15**, 4687 (2015).

### Acknowledgement:

Part of the work was funded by the Austrian Science Fund (FWF): [P25541-N19].

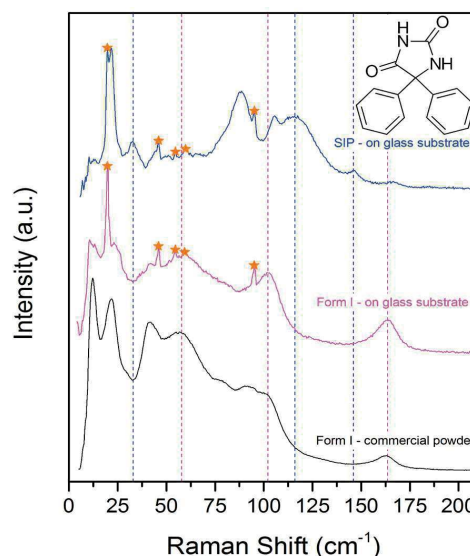


Figure 1: Lattice phonon of phenytoin (and molecular structure) in the bulk and different forms found on substrate. Markers show the peaks of the substrate.

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## THE ROLE OF EPITAXY AND CONFINED INTERFACES IN THIN FILM AND CRYSTAL POLYMORPHISM

M. D. Ward<sup>1</sup>

*Department of Chemistry and Molecular Design Institute, New York University, 100 Washington Square East, New York, New York 10003-6688, United States*

*E-mail: [mdw3@nyu.edu](mailto:mdw3@nyu.edu)*

Classical crystal growth models posit that crystallization outcomes are determined by nuclei that resemble mature crystal phases, but at a critical size where the volume free energy of nuclei begins to offset the unfavorable surface free energy arising from the interface with the growth medium, and where crystallization outcomes, including polymorphism, are deterministic. These models often ignore the role of surfaces with respect to the overall surface energy, a combination of substrate-nucleus, substrate-liquid, and nucleus-liquid interfacial energies. Moreover, molecular crystals are inherently anisotropic, adding further complexity to the interfacial energy terms. One particular approach to substrate design for regulating polymorphism involves the use of epitaxy on crystalline or conformational substrates to regulate the structure and orientation of the first molecular layer, the quintessential thin film. The various kinds of epitaxy possible beyond simple commensurism – from coincident interfaces to static distortion waves – are often not widely appreciated. Moreover, recent advances exploring crystallization under nanoscale confinement and surprising effects of size on polymorphism have opened questions of the role of pore surfaces and interfacial energetics on heterogeneous nucleation in these unique environments where surface dominates volume, particularly when crystallization is confined to length scales near the critical size where kinetics and thermodynamics of nucleation and growth intersect. This presentation will explore the contributions of epitaxy and surface effects under confinement to nucleation, crystal growth and polymorphism.

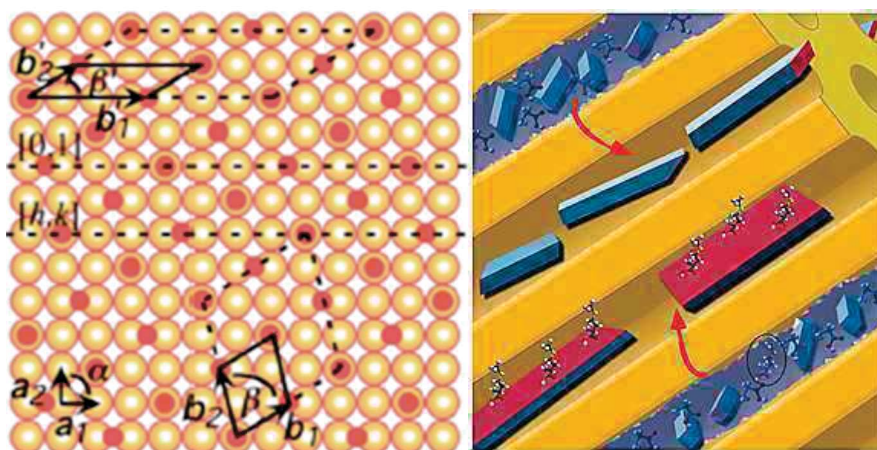


Figure 1: (left) Simple coincident epitaxial relationships for a low-symmetry crystal on a high-symmetry interface. (right) Schematic of different polymorphs forming in nanopores.

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# SURFACE-SUPPORTED MULTICOMPONENT SUPRAMOLECULAR ARCHITECTURES: INTERACTIONS AND STIMULUS RESPONSIVE BEHAVIOR

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Monolayer-thick supramolecular networks supported by solid substrates have garnered significant attention in the recent past. The complexity of self-assembly increases exponentially with increasing number of self-assembling components. Over the past few years however, we have been able to achieve self-assembly of two-, three- and four-component systems into crystalline two-dimensional lattices by using a combination of molecular design, synthetic chemistry and surface based supramolecular chemistry. The structure and constitution of the as-formed networks are characterized using sub-molecular resolution scanning tunneling microscopy (STM). In this contribution, I will discuss the evolution of ideas that lead to the design and fabrication of such complex multicomponent nanostructures. The critical contribution of molecule-substrate interactions in such multicomponent self-assembly experiments will be discussed.

The self-assembled networks supported by solid substrates also respond to external stimuli such as light, heat and electric field. Influence of strong local electric fields on the mixing behavior of molecules within such 2D supramolecular networks will be discussed. We demonstrate that whether the two molecules mix to yield an ordered crystalline network, or phase separate into an amorphous network, or show preferential adsorption of only one component can be controlled by applying an electric field in a certain orientation.<sup>1</sup>

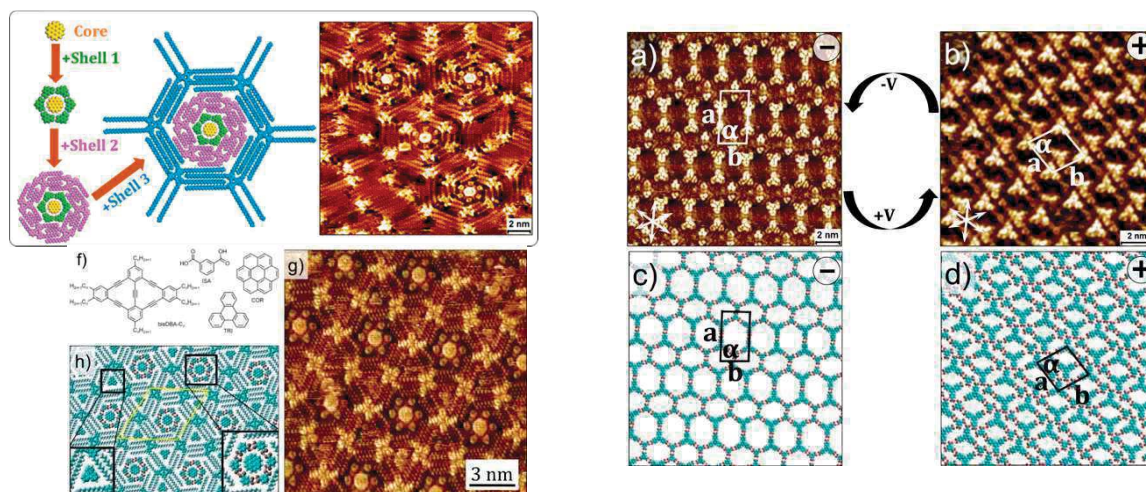


Figure 1: Left: Complex assembly of four different components. Right: Electric field-induced mixing behavior.

<sup>1</sup> K. S. Mali, C. N. Pearce, S. De Feyter, N. R. Champness *Chem. Soc. Rev.*, 2017,46, 2520-2542

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# FORMATION AND ELECTROSTATIC SURFACE POTENTIAL OF FUNCTIONALIZED QUARTER-PHENYLENE NANOFIBERS

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Self-assembled nanofibers from semiconducting organic molecules such as the *para*-phenylenes and thiophene/phenylene co-oligomers have many possible applications in organic electronics [1]. In this paper, uni- and triaxially aligned epitaxial nanofibers from functionalized *para*-quaterphenylenes formed during vacuum deposition are investigated. Functionalization controls many of their properties [2-4]. Cyano- and methoxy-functionalization are of special interest due to the asymmetric charge distribution. Here, nanofibers from in the 4,4'' positions cyano- and methoxy-functionalized *para*-quaterphenylenes (CNP4, CNHP4, MOP4) on muscovite mica are studied. Thin-film phases are identified by X-ray diffraction. Their optical properties, their morphology, and their electric surface potential with and without illumination differ, reflecting different polymorphs, facets, and contact faces.

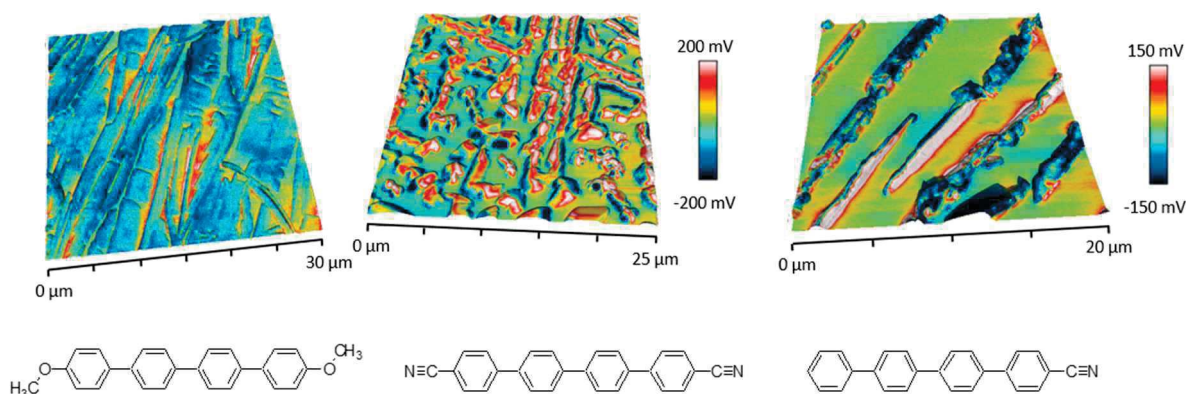


Figure 1: Kelvin Probe Force Microscopy (KPFM) images of organic nanofibers from various functionalized *para*-quaterphenylenes: MPOP4, CNP4, and CNHP4 (from left to right). The value of the surface potential is projected onto the fiber topography. In all cases the nominal film thickness is of the order of 50-100 nm.

- [1] E.M. Garcia-Frutos, *J. Mater. Chem. C* **1**, 3633 (2013).
- [2] F. Balzer, Ch. Röthel, H.-G. Rubahn, A. Lützen, J. Parisi, R. Resel, M. Schiek, *J. Phys. Chem. C* **120**, 7653 (2016).
- [3] F. Balzer, M. Schulz, A. Lützen, M. Schiek, *Soft Matter* **12**, 9297 (2016).
- [2] F. Balzer, R. Resel, A. Lützen, M. Schiek, *J. Chem. Phys.* **120**, 134704 (2017).

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## First-Principles Modeling of Molecular Polymorphism in Crystals and on Surfaces

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Molecules can assemble in many different polymorphic arrangements depending on the environment and crystallization conditions. Modeling such polymorphic assembly provides a plethora of challenges and opportunities for developing novel theoretical methods. In this talk, I will describe recent advances in predictive modeling of pervasive van der Waals (vdW) interactions in complex organic and inorganic systems [1]. I will demonstrate that newly developed many-body methods that correctly treat the quantum-mechanical nature of vdW interactions [2] are often able to achieve predictive accuracy in the description of polymorphism in molecular crystals [3,4], when combined with non-empirical density functionals. Furthermore, applications to molecular interactions on metal surfaces yield new discoveries that transform our fundamental understanding of vdW interactions, i.e. their ubiquitous cohesiveness [5].

[1] J. Hermann, R. A. DiStasio Jr., and A. Tkatchenko, *Chem. Rev.* 117, 4714 (2017).

[2] A. Ambrosetti, N. Ferri, R. A. DiStasio Jr., and A. Tkatchenko, *Science* 351, 1171 (2016).

[3] J. Hoja, A. M. Reilly, and A. Tkatchenko, *WIREs: Comput. Mol. Sci.* 7, e1294 (2017).

[4] A. M. Reilly et al., *Acta Cryst. B* 72, 439 (2016).

[5] M. Sadhukhan and A. Tkatchenko, *Phys. Rev. Lett.* 118, 210402 (2017).

## PHYSISORBED MOLECULAR ADLAYERS EXHIBITING TEMPERATURE- AND COVERAGE-DEPENDENT POLYMORPHISM

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The self assembly of molecules at surfaces is governed by the balance between molecule-molecule and molecule-substrate interactions. For certain cases each molecule within densely packed domains may adopt the energetically most favorable adsorption site of a single molecule on a given substrate. Those would be examples of commensurate epitaxial relations as depicted in numerous textbooks. In other quite frequent cases, however, the global energetic minimum may be achieved through a different type of epitaxy, namely a so-called on-line coincidence, where the surface unit cells of the adsorbate and the substrate have a common periodicity in one direction only [1]. Recently, a room-temperature stable monolayer of hexa-*peri*-hexa-benzocoronene (HBC) on graphene was structurally characterized by means of low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) [2]. The surprising result there was that the substrate and the adsorbate have no coincidence at all, and hence the concept of lattice epitaxy fails to explain the evident energy gain in this particular system. Instead, we found that the HBC adlayer is stabilized by so-called static distortion waves that manifest in measurable sub-Ångström lateral shifts away from the positions of a translationally symmetric lattice (which itself is incommensurate). We further discuss adlayers of coronene on graphene which exhibit a pronounced polymorphism. In fact, the lattice parameters of coronene films (and thus the type of epitaxy) vary as a function of (i) temperature, (ii) surface coverage, and even (iii) time. The structural relaxation of an as-deposited commensurate coronene layer is shown in Figure 1. We have developed model calculations to describe this phenomenon.

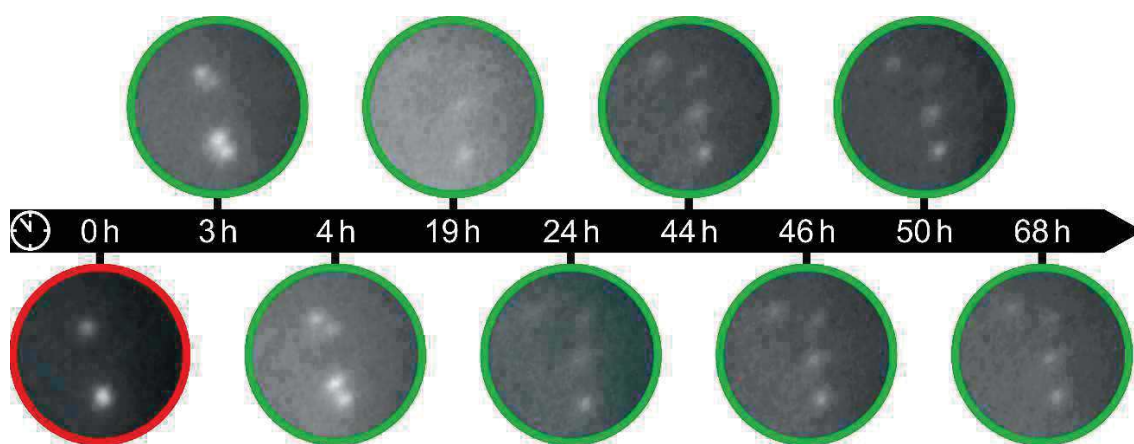


Figure 1: LEED images (300 K, 30.8 eV) of a coronene adlayer on epitaxial graphene. The same selected area of the LEED screen is depicted in each panel in order to focus on a particular set of four spots. The initial structure is commensurate, as clearly evidenced by the pairwise coincidence of spots (red outline). These pairs of spots split as a function of time which proves that non-commensurate epitaxial relations with the substrate are formed.

[1] R. Forker *et al.*, *Soft Matter* **13**, 1748 (2017).

[2] M. Meissner *et al.*, *ACS Nano* **10**, 6474 (2016).

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## XPS/XPD measurements of self-assembled caffeine monolayers on Ag(110)

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In the last years there has been progress in the self-assembly of organic compounds on different surfaces. Beside the exact knowledge of the electronic and chemical properties of such systems, the structural information is of great interest. In this context polymorphism of organic compounds plays an important role in their electronic properties [1, 2] or bio-availability [3]. An example for such a molecule is caffeine. A few publications analyzed the growth of caffeine on different substrates, but they always used multilayers of caffeine on non-metallic substrates [4, 5, 6, 7, 8]. Therefore we analyzed a monolayer of caffeine on an Ag(110) crystal surface. Because of its flat, well reconstructed and inert surface, no strong molecule-surface interaction influences the molecule-molecule interaction during deposition. Most organic-inorganic systems are analyzed by STM or AFM, but those techniques provide neither chemical information about the atomic bonds nor information about the interface. Photoelectron diffraction (XPD) easily provides that information. By comparison of a measured XPD pattern with calculated XPD pattern, the local emitter environment of each atom in the molecule can be analyzed. We present first results for photoelectron spectroscopy (XPS) and photoelectron diffraction of Caffeine on Ag(110).

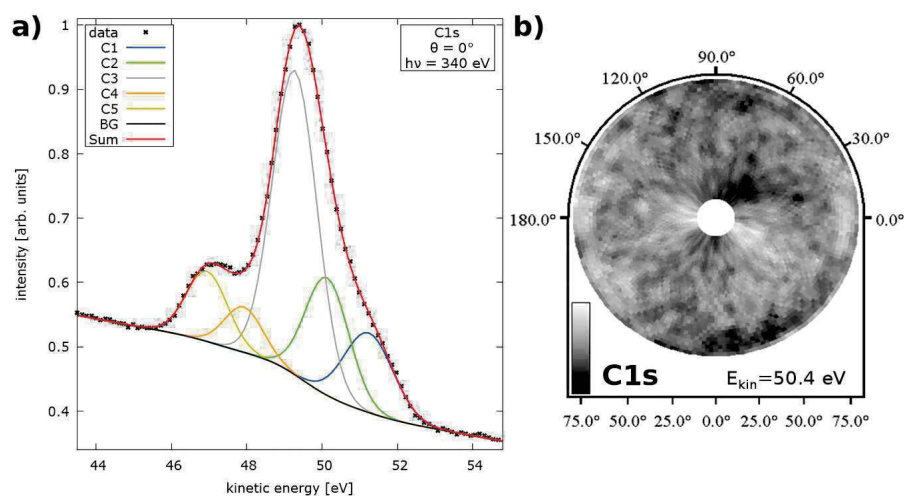


Figure 1: Fitted Carbon 1s XP spectrum of IML Caffeine on Ag(110) with 5 components (a)), corresponding XPD pattern (b))

- [1] A. O. F. Jones, ACS Appl. Mater. Interfaces **7**, 1868 (2015).
- [2] H. Wang, Org. Electron. **15**, 1586 (2014).
- [3] D. Singhal, Adv. Drug Delivery Rev. **56**, 335 (2004).
- [4] A. Safraz, Cryst. Growth Des. **12**, 583 (2012).
- [5] O. Werzer, Cryst. Growth Des. **13**, 1322 (2013).
- [6] J. Leiterer, Langmuir **24**, 7970 (2008).
- [7] C. Röthel, Cryst. Growth Des. **15**, 4563 (2015).
- [8] C. Röthel, CrystEngComm **19**, 2936 (2017).

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## THE GROWTH OF $\alpha$ -SEXITHIOPHENE ON DIFFERENT SILVER SURFACES

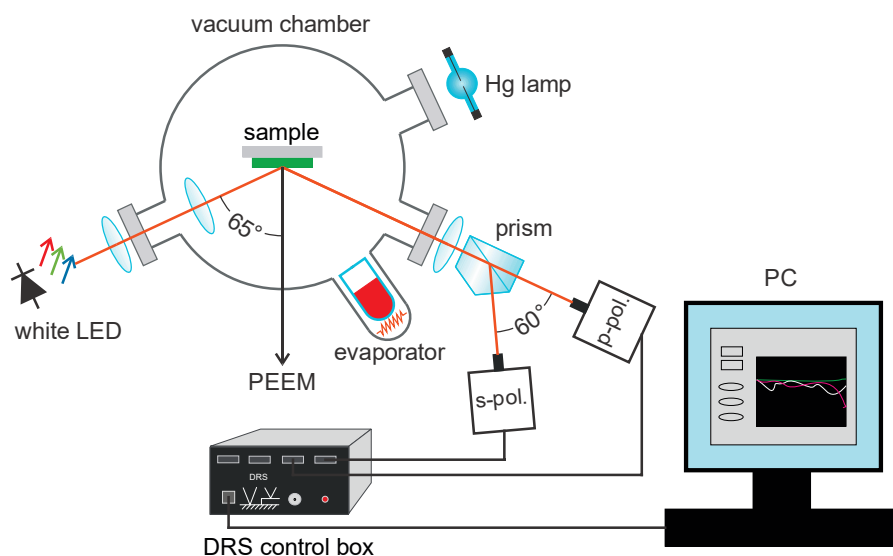
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The combination of photoelectron emission microscopy (PEEM) and differential (optical) reflectance spectroscopy (DRS) [1] is used to compare the growth of the prototype organic semiconductor  $\alpha$ -sexithiophene ( $\alpha$ -6T) on different silver surfaces, namely the Ag(111), the Ag(110), and the vicinal Ag(441) [2] surface.

A non-polarized Hg lamp was used as excitation source for the photoelectrons. For all three substrates, the transient of the mean intensity obtained with PEEM follows the same trend: The first layer decreases the emission barrier for the photoelectrons and, hence, increases the electron yield. The deposition of additional molecules just decreases the electron yield, because the electron exclusively excited from the silver substrate have to pass through the molecular layers, which do not further alter the emission barrier. In all three cases, at least an equivalent of two monolayers has to be deposited before nucleation of 3D crystallites is observed in PEEM.

After being reflected at the sample surface, the light of a white LED was split by a prism into its two linearly polarized components (pol-DRS). For the isotropic Ag(111) surface, the spectra obtained for s and p polarized light do not differ qualitatively. For the Ag(110) surface, the optical spectra indicate an orientation of the  $\alpha$ -6T molecules along the [001] direction. On the Ag(441) surface, the molecules align parallel to the steps, i.e., along the [1-10] direction.



*Figure 1: Experimental setup to monitor the growth of organic thin films simultaneously and in real-time by photoelectron emission microscopy (PEEM) and differential reflectance spectroscopy (DRS).*

[1] A. Navarro-Quezada, M. Aiglinger, E. Ghanbari, Th. Wagner, and P. Zeppenfeld, *Rev. Sci. Instr.* 86, 113108 (2015)

[2] Th. Wagner, D. R. Fritz, R. Zimmerleiter, P. Zeppenfeld, *Surf. Sci.* 661, 77 (2017)

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# CONTACT PLANES OF SMALL ROD-LIKE MOLECULES ON GRAPHENE AND HEXAGONAL BORON NITRIDE

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In this study we investigate growth morphologies and epitaxial relations of small molecule organic semiconductor crystallites on the surface of graphene (Gr) and hexagonal boron nitride (hBN). The molecules under consideration in our study are the rod-like oligophenylene para-hexaphenyl (6P) and dihydrotetraaza-heptacene (DHTA7) – Fig. 1a. 6P is a model molecule for understanding growth and interfacial phenomena in organic electronics, which is known to form needle-like crystallites (with flat lying molecules) on the surfaces of both Gr and hBN [1,2]. As a contrast to 6P, DHTA7 is not expected to form a herringbone structure due to dipolar interactions and hydrogen bonding between neighboring molecules. Nonetheless, needle-like crystallites of DHTA7 – in some cases over 500  $\mu\text{m}$  long – have been observed both on Gr, and on hBN. By atomic force microscopy (AFM) analysis (Fig. 1b) of the preferred growth directions (Fig. 1b-c) and knowing the preferred adsorption sites of individual molecules obtained from density functional theory calculations, contact planes could be revealed (Fig. 1d), as  $(\bar{6}29)$  6P plane in the case of 6P/hBN interface [2], or  $(11\bar{1})$  for 6P/Gr [1].

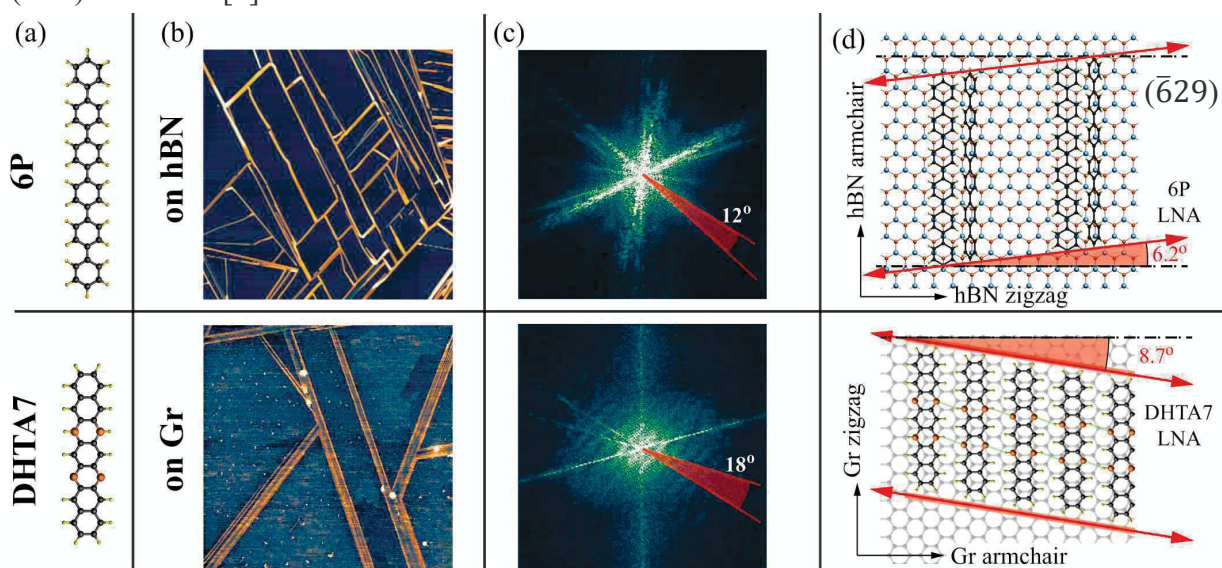


Figure 1: 6P on hBN (top) and DHTA7 on Gr (bottom). (a) ball-and-stick models of 6P and DHTA7. (b)  $16 \times 16 \mu\text{m}^2$  AFM topography images, (c) corresponding 2DFFT, and (d) epitaxial relation of the needles with the substrate. LNA – long needle axis.

[1] M. Kratzer, C. Teichert., Nanotechnology **27**, 292001 (2016).

[2] A. Matković, J. Genser, D. Lüftner, M. Kratzer, R. Gajić, P. Puschnig, C. Teichert, Sci. Rep. **6**, 38519 (2016).

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## Recent advances in *ab initio* crystal structure prediction

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The CrystalPredictor I and II<sup>1</sup> codes have been used to explore the space of crystal structures successfully in several crystal structure prediction (CSP) investigations in recent years<sup>2</sup>, including in the series of blind tests organised by the Cambridge Crystallographic Data Centre and in the prediction of the crystal structures of pharmaceutically-relevant molecules<sup>3,4</sup>. We present a summary of CrystalPredictor, focussing on improvements to the lattice energy evaluation that the most recent blind test<sup>5</sup>, as well as our own investigations into a variety of flexible polymorphic molecules, has prompted. These improvements aim to achieve greater accuracy in the initial ranking of potential crystal structures, while managing computational cost so that a thorough exploration of the search space is possible<sup>6</sup>.

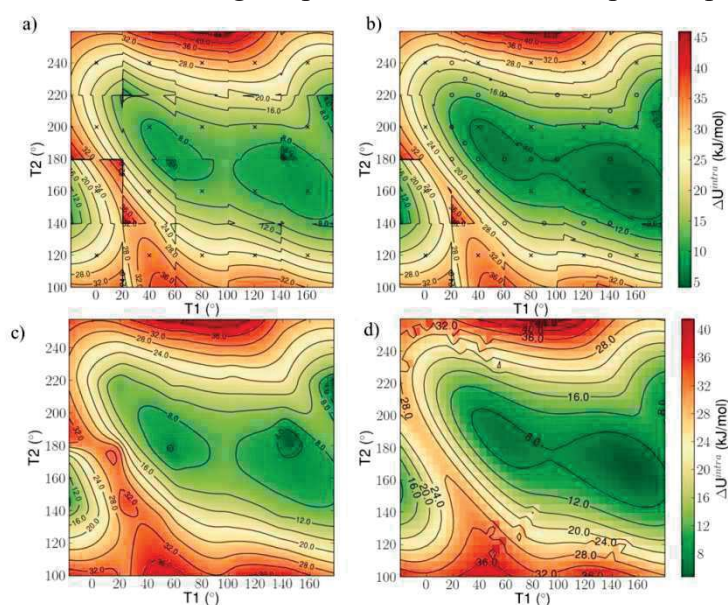


Figure 1: Intramolecular energy (in  $\text{kJ mol}^{-1}$ ) as predicted by LAMs in  $0.5^\circ$  scan across conformational space; (a) under a regular coarse grid ( $= 20$ ), (b) using the adaptive LAM scheme, (c) Under the smoothed intramolecular potential scheme, and (d) *ab initio* intramolecular energy based on a  $5^\circ$  scan. Crosses represent regular LAMs, circles non-uniform/adaptive LAMs

- [1] M. Habgood, I. J. Sugden, A. V. Kazantsev, C. S. Adjiman, and C. C. Pantelides, *J Chem Theory Comput* **11**, 1957 (2015).
- [2] C. C. Pantelides, C. S. Adjiman, and A. V. Kazantsev, *Top Curr Chem* **345**, 25 (2014).
- [3] M. Vasileiadis, C. C. Pantelides, and C. S. Adjiman, *Chem Eng Sci* **121**, 60 (2015).
- [4] M. Vasileiadis, A. V. Kazantsev, P. G. Karamertzanis, C. S. Adjiman, and C. C. Pantelides, *Acta Crystallographica Section B-Structural Science* **68**, 677 (2012).
- [5] A. M. Reilly *et al.*, *Acta Crystallographica Section B: Structural Science, Crystal Engineering and Materials* (2016).
- [6] I. Sugden, C. S. Adjiman, and C. C. Pantelides, *Acta Crystallogr B* **72**, 864 (2016).

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## IN-SITU X-RAY DIFFRACTION ANNEALING STUDY ON AN ANTHRADITHIOPHENE DERIVATIVE

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One of the promising materials in the field of small molecule organic semiconductors is 5,11-bis(triethyl silylethynyl) anthradithiophene (TES-ADT), mostly because of its high charge-carrier mobility [1], which is, however, strongly dependant on crystal quality and crystal phase of TES-ADT. Several crystal phases of TES-ADT were already reported [3], but their crystal structure and phase kinetics is still not fully understood.

We used X-ray reflectivity and grazing incidence X-ray diffraction to investigate phase transformation dynamics in spin-coated TES-ADT thin films during post growth heating, cooling and quenching. The measurements were performed on a Rigaku SmartLab home-lab diffractometer equipped with an Anton Paar domed heating stage. We show that previously reported phases may coexist at room temperature (RT) (Fig. 1, left). Particularly, the alpha phase of TES-ADT appears to be the most stable phase at RT and it is formed out of the amorphous phase with the progress of the time after an annealing treatment. Additionally, we show that the gamma phase may form during cooling the amorphous melt and we demonstrate previously not reported gamma to beta phase transition (Fig. 1, right).

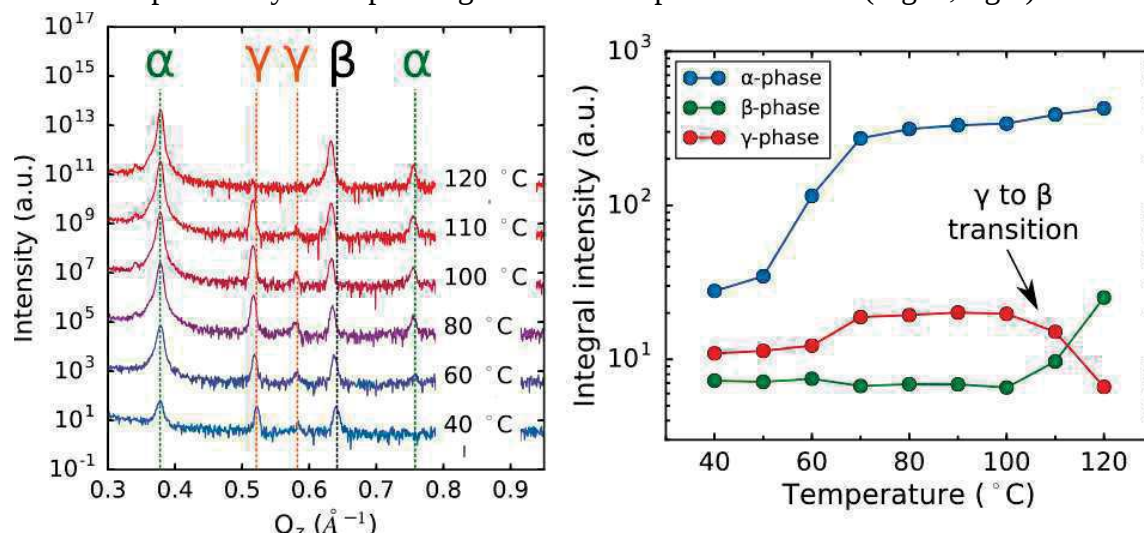


Figure 1: X-ray diffraction during TES-ADT heating (left); temperature dependence of integral intensities of diffraction peaks corresponding to individual phases (right).

[1] M. M. Payne et al., *J. Am. Chem. Soc.*, **127**, 4986 (2005).

[2] J. Chen et al., *Nanoscale*, **6**, 449 (2014).

[3] L. Yu, et al., *Chem. Mater.* **25** (9), 1823-1828 (2013).

## EFFICIENT BAYESIAN INFERENCE OF SURFACE ADSORPTION

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The adsorption and self-organisation of molecules at inorganic surfaces is central to many industrial processes from catalysis and coatings, to organic electronics and solar cells. Computer simulations can help identify interface morphology and functionality, but sampling many atomic configurations over large length scales is prohibitively costly. We combined Bayesian optimisation [1] with accurate atomistic simulations in our efficient structure search tool BOSS, designed for intelligent probabilistic sampling of atomic configurations. The nearly parameter-free framework relies on Gaussian processes (GPs) to construct a probable potential energy surface (PES), which is then iteratively refined by input of energy data points from selected configurations.

The BOSS framework was employed in up to six dimensions to identify the optimal adsorption structures of large organic molecules on functional oxide substrates (see Figure 1). We report a dramatic speed-up in identifying optimal configurations, compared to the traditional chemical intuition technique, without significant loss of accuracy. Thanks to the clever Bayesian sampling scheme (balancing exploitation and exploration steps) and a streamlined "building block" approach to molecular structure, even complex interface problems can be solved for relevant global and local minima structures [2].

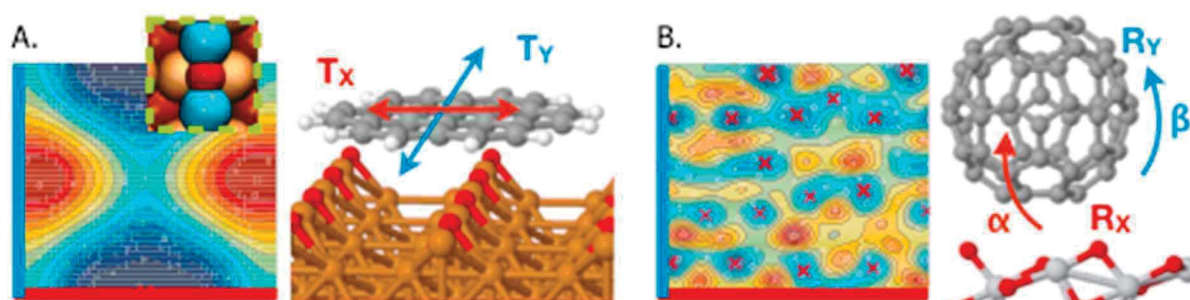


Figure 1: BOSS application to A) adsorption registry of coronene/Cu(110)-O  $p(2 \times 1)$ , B) molecular orientation of fullerene/TiO<sub>2</sub>(101).

[1] M. U. Gutmann, J. Corander, J. Mach. Learn. Res. **17**, 1 (2016).

[2] M. Todorović, M. U. Gutmann, J. Corander and P. Rinke, *in preparation*.

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## Computational Polymorph Prediction for Organic/Inorganic Interfaces using Machine Learning

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A major step towards designing new materials is understanding and predicting the crystal structures that form at interfaces. Finding thermodynamically stable phases could in principle be done by calculating the enthalpy of all possible structures. However, the rich polymorphism exhibited by these systems prohibits an exhaustive search for the global minimum using expensive ab-initio calculations. This configurational explosion is particularly problematic for crystal structures that contain many molecules per unit cell, due to the many degrees of freedom. In this work it is shown on the example of tetracyanoethylene (TCNE) on Ag(100) that this challenge can be tackled with a combination of coarse-graining and machine learning:

First the adsorption geometries that isolated molecules would adopt on the substrate are found. Supercells with multiple molecules per unit cell are built by combining these isolated adsorption geometries to generate a set of possible “guess polymorphs”. This discretizes the configurational space to a finite, but still huge size. Using optimal design methods, a small, representative subset is selected and its energies are calculated using Density Functional Theory (DFT). By training a Gaussian Process Regression model on these DFT calculations, effective interactions between adsorbates are obtained. These provide an efficient and accurate energy prediction for all remaining guess polymorphs, which is exploited by sampling the energetically most promising structures and iterated relearning.

We show that the Machine Learning model achieves the accuracy of DFT, and can even reach this accuracy using very few training calculations.

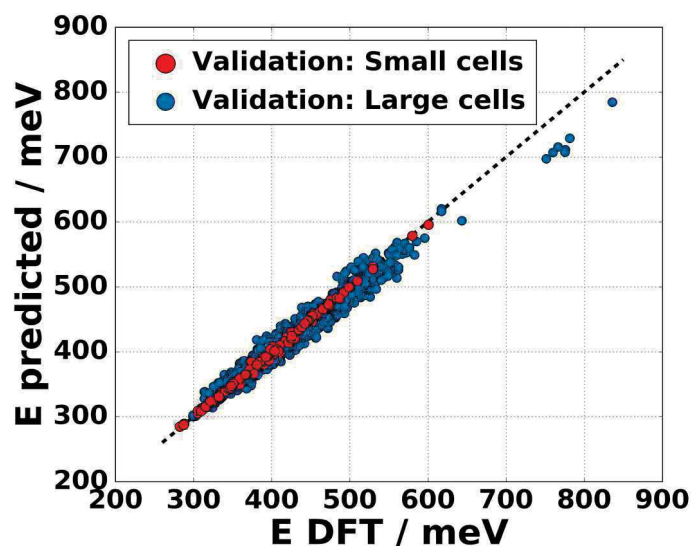


Fig 1: Comparison of Machine Learning model to DFT results

## INFLUENCE OF SURFACE ROUGHNESS ON POLYMORPH FORMATION IN ORGANIC THIN FILMS

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The properties of molecular thin films such as their morphology, orientation, crystallinity and their crystal polymorph are crucially influenced by the supporting substrate during film preparation, even enabling the crystallization in polymorphs which are not found in freestanding crystals. Several examples have been reported for such substrate-mediated polymorph formation, in many cases mediated by metal substrates. Interestingly, however, also weakly interacting substrates like graphite are capable of controlling the polymorph formation. In this case, the quality of the substrate such as the surface crystallinity and roughness directly determines the adopted polymorph.

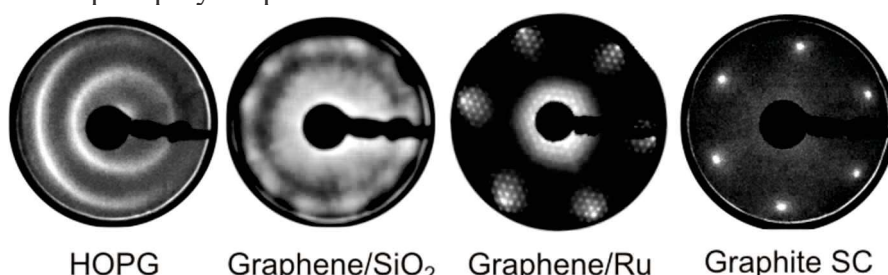


Figure 1: Comparison of LEED patterns observed for different graphite / graphene samples revealing their different surface crystallinities.

By systematic variation of the surface roughness of graphite substrates, we investigate its interrelation with the polymorphism formation for thin films of the organic semiconductors pentacene and perfluoropentacene [1]. Moreover, we study the utilization of further, emerging substrate materials such as two-dimensional TMDC surfaces for polymorphism control in TMDC-organic hybrid systems [2]. Performing temperature-dependent measurements, e.g. using X-ray diffraction techniques, the stability of different polymorphs and their anisotropic thermal expansion, which again crucially depends on the utilized substrates, are compared [3].

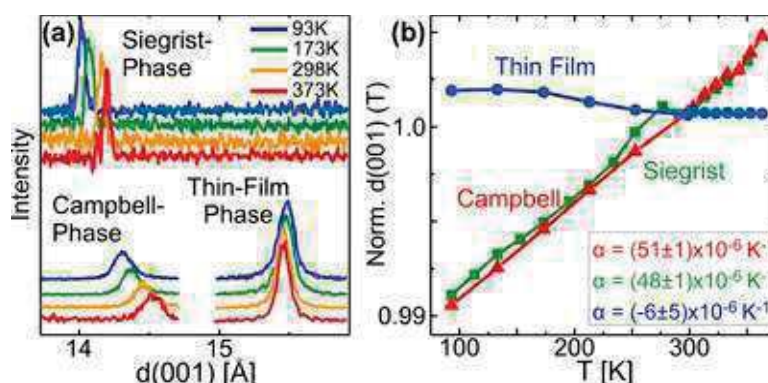


Figure 2: Thermal expansion characteristics of different pentacene polymorphs [3]

[1] T. Breuer, I. Salzmann, J. Götzen, M. Oehzelt, A. Morherr, N. Koch, G. Witte, *Cryst. Growth. Des.* 11, 4996-5001 (2011).

[2] T. Breuer, T. Maßmeyer, A. Mänz, S. Zoerb, B. Harbrecht, G. Witte, *Phys. Stat. Sol. - RRL* 10, 905 (2016).

[3] L. von Helden, T. Breuer, G. Witte, *Appl. Phys. Lett.* 110, 141904 (2017).

## Nucleation of Organic Molecular Crystals on Surfaces and in Nanopores

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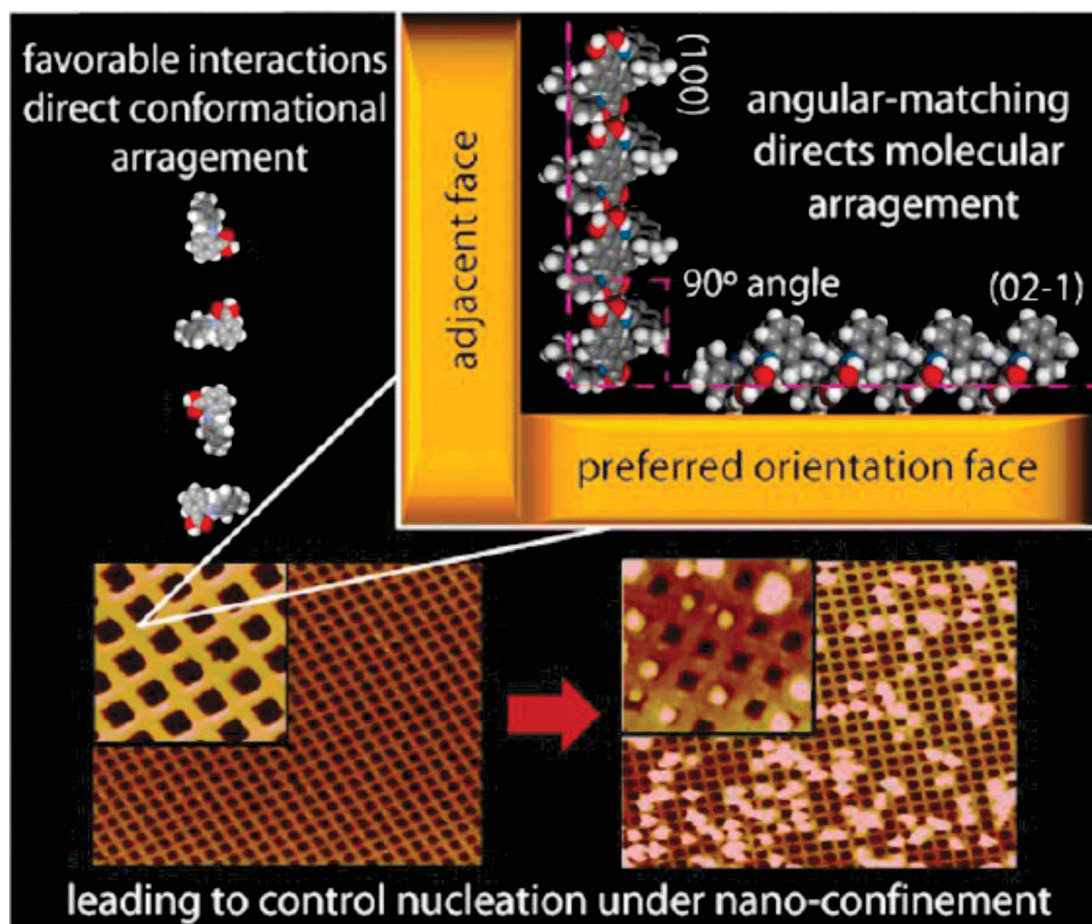
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Crystallization is vital to many processes occurring in nature and manufacturing. In chemical, pharmaceutical and food industries, crystallization from solution is widely used for a variety of materials. It is an attractive isolation step during manufacturing as particle formation and purification are combined within a single process. Almost all of the products based on fine chemicals, such as dyes, explosives and photographic materials, require crystallization in their manufacture and over 90% of all pharmaceutical products contain bioactive drug substances and excipients in the crystalline solid state. Hence it is necessary to control the crystallization process in order to obtain products with desired and reproducible properties. The quality of a crystalline product is usually judged by four main properties: size, purity, and morphology (shape) and crystal structure. It is vital in pharmaceutical industry to produce the desired crystal form (polymorph) to assure the bioavailability and stability of the drug substance. It is also important to produce the desired particle shape and size distribution to allow mixing of API with excipient and the formation of the final drug product.

Nucleation is the first step of the crystallization process and control of nucleation is crucial in forming crystals of the desired properties and of the desired polymorphic form. Surfaces are well known to influence nucleation and polymorphism. In this talk we will present work on the role of crystalline and polymer surfaces on nucleation and polymorphism of organic molecular crystals. In addition, recent work on biocompatible polymer surfaces imprinted with nanopores of various geometries which are used as heteronucleants will be presented as will work on the nucleation within nanopores of silicon dioxide.





## A THERMAL GRADIENT APPROACH TOWARDS POLYMORPH SELECTION

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Polymorphism can be defined as the intrinsic ability of a solid material to exist in two or more crystal forms which may differ in the molecular conformation and/or crystal packing. It is linked to the unpredictability of crystal structures from the first principles as polymorphs differ only in energy  $\leq 10$  KJ/mol. The phenomenon is generally understood in terms of nucleation, i.e. once a nucleus of a given phase has appeared, growth continues in the same phase without any subsequent phase transition. Although an extensive body of research is available in this topic, some elements key to the understanding of polymorphism are still missing. To this extent we sought to understand the role of heat flux in polymorphic control and phase transitions.<sup>1</sup> This is experimentally facilitated by a temperature gradient heating stage which essentially consists of two independent heating elements separated by a distance of 2.5 mm. Structural evolution is then followed as thin films of model systems are translated across the thermal gradient. In this presentation, we report on the crystallization of polymorphs of acetaminophen as a function of thermal gradient parameters (magnitude of the gradient, sample velocity) in a thin film geometry. The thin film samples were displaced at a given rate ( $1 \leq v \leq 75$   $\mu\text{m/s}$ ) to control direction and the rate of crystal growth. This allows to decouple nucleation and growth.<sup>2</sup> A detailed structural analysis combining polarized optical microscopy (POM) and X-ray diffraction (out-of-plane, in-plane) has been carried out to characterize different crystalline forms produced by the thermal gradient technique. The resulting polymorphic forms have been found to have high phase purity and exhibit remarkable stability over time

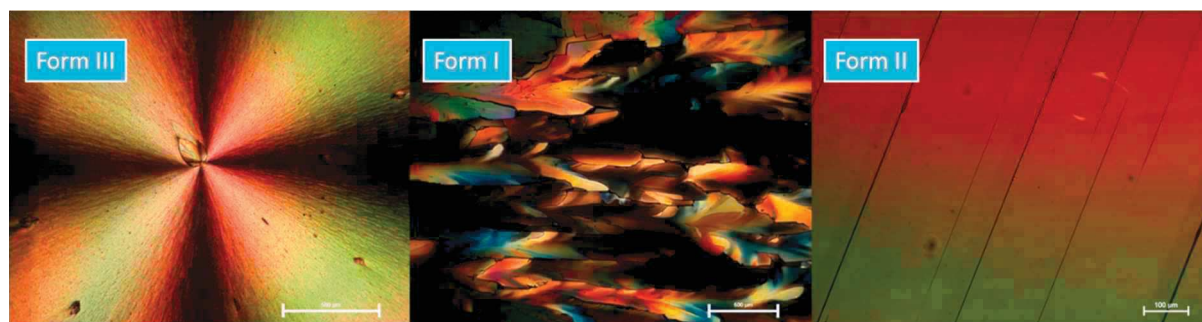


Figure 1. POM images of a) Form III as obtained from melt; b) Form I and c) Form II obtained with the thermal gradient with translation velocity of  $10\mu\text{m/s}$ .

[1] G. Schweicher, *et al.* Cryst. Growth Des. **11**, 3663 (2011).

[2] G. Schweicher, (2012). PhD thesis, Université Libre de Bruxelles, Brussels, Belgium.

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# **Poster presentations**



## Selective, temperature-induced F4TCNQ desorption from p-doped P3HT films

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Typically, after solution processing, functional conjugated polymer (CP) films are thermally treated with great application-related success, e.g., in organic photovoltaic cells. In a number of studies, the same approach is being followed also for *p-doped* CPs, where doping by strong electron acceptors aims at improving the electrical properties of the films. Typical molecular dopants are conjugated organic molecules of low-molecular weight like, e.g., tetrafluoro-tetracyanoquinodimethane (F4TCNQ). Such materials must, however, be expected to be prone to diffusion caused by the thermal annealing. Interestingly, the temperature-dependent diffusion/desorption behavior of molecular dopants from CP films has hitherto been largely disregarded in pertinent literature.

In the present study, we explore to which extent different annealing temperatures (at constant annealing times) influence poly(3-hexylthiophene-2,5-diyl) (P3HT) thin films doped with F4TCNQ, where integer-charge transfer between the *p*-dopant and the CP occurs as fundamental doping process. We investigated, inter alia, the amount and the nature of the remaining dopants (anionic or neutral) by Fourier-transform infrared spectroscopy (FTIR). Annealing-induced changes in the structure of the films were assessed by grazing-incidence X-ray diffraction (GIXRD).

We found that thermal annealing at a sample temperature of 60 °C leaves the concentration of ionized dopants unchanged. However, with further increased treatment temperature, a significant reduction in the dopant concentration occurs.

Importantly, based on the combination of above experimental techniques, our thermal annealing study further reveals indications for different preferential positions of the dopants relative to the polymer matrix, as deduced from their different desorption temperature. Therefore, the systematic use of heat-induced desorption can help pronouncing certain microstructural phases.

## EPITAXIALLY ORDERED METAL-ORGANIC-FRAMEWORKS BASED ON COPPER - BENZENEDIOIC ACID

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Aligned Metal-Organic Frameworks (MOFs) are interesting for usage in optical, sensor and microelectronic application. Recently it is shown that MOFs can be prepared epitaxially on copper hydroxide ( $\text{Cu}(\text{OH})_2$ ) [1]. In this work, MOFs, consisting of copper ions, linked in 2 dimensions by 1,4-benzenedioic acid (BDC), as well as 3D-MOFs, consisting of copper, BDC and 1,4-Diazabicyclo[2.2.2]octan (DABCO) are grown on  $\text{Cu}(\text{OH})_2$  nanobelts. The nanobelts with dimensions of several  $\mu\text{m}$  in length and 20 nm in width are deposited on silicon surfaces by solution processing. It is apparent that the alignment of the  $\text{Cu}(\text{OH})_2$  nanobelt substrate is an important parameter for the controlled, oriented growth of MOFs. The degree of alignment is studied by X-ray diffraction using pole figure techniques. The nanobelts are aligned uniaxially with the [100] axis along the silicon surfaces. The MOF follow the orientation of the underlying nanobelts. Interestingly, the formed crystal structures of the MOFs are not known in detail. Further work has to be performed to figure out details of the MOF structure. In a subsequent step a study on the functionalization of grown MOFs by exchanging the ligands is undertaken.

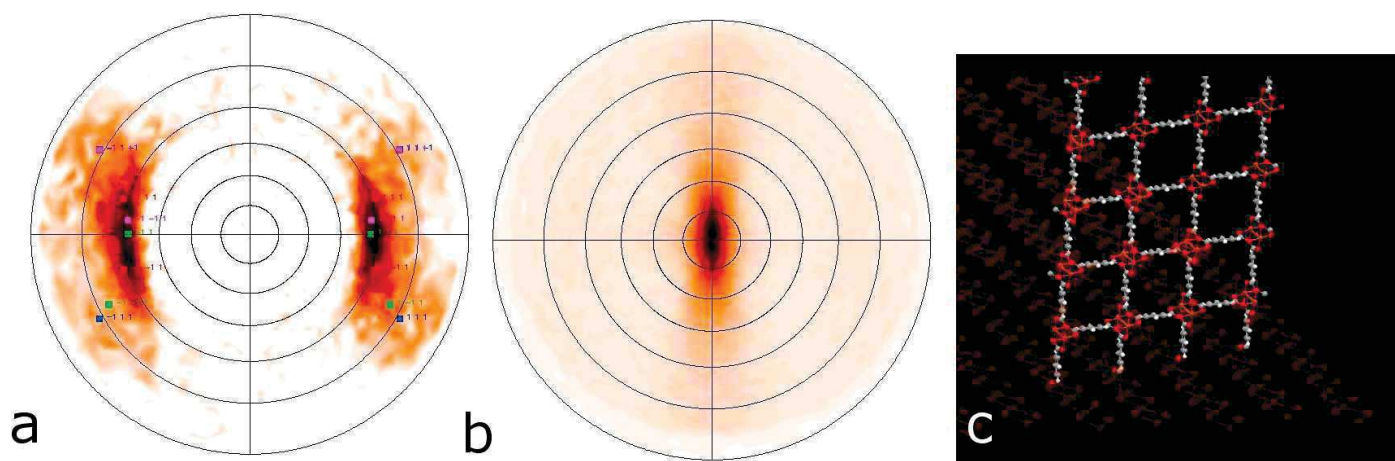


Figure 1 a) Polefigure on the [111] Cu Nanobelts peak. b) Polefigure on the [200] 2D-MOF peak. c) Possible schematically drawn model of the 2D MOF on Cu Nanobelt substrate.

[1] P. Falcaro, K. Okada, T. Hara et al. Nature Materials, 2, 1-26 (2016)

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## First-Principles Molecular Crystal Structure Prediction: The Importance of Collective van der Waals Interactions and Free Energies

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For meaningful crystal structure predictions (CSP) of practically relevant molecular crystals, it is imperative to calculate relative lattice energies with an accuracy of about 1 kJ/mol since it is necessary to correctly rank the stabilities of numerous low-energy polymorphs. Accurate results can be obtained by utilizing density-functional theory (DFT) supplemented by a high-level van der Waals (vdW) model, such as the many-body dispersion (MBD) method [1, 2]. Since relative stabilities have to be determined at finite temperatures, vibrational free energies have to be considered as well [3]. Furthermore, vdW interactions are not only important for lattice energies but also crucial for the actual structure of molecular crystals and all related response properties [4]. The importance of an accurate treatment of vdW interactions and free energies is discussed in terms of the systems studied in the most recent CSP blind test of the Cambridge Crystallographic Data Centre [5], with a particular focus on a challenging case of a highly polymorphic system (see Figure 1). It is shown that collective many-body vdW interactions completely change the relative stabilities of the studied polymorphs in comparison to a pairwise-additive approach. Furthermore, the inclusion of thermal fluctuations also leads to a significant improvement of the relative stabilities. Overall, the CSP approach based on DFT+MBD provides remarkably accurate structures and stability rankings for relevant molecular crystals.

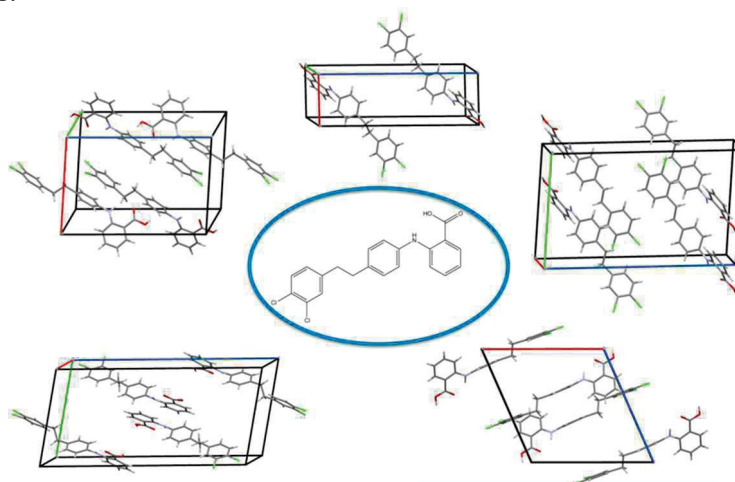


Figure 1: Polymorphs of a studied molecular crystal

- [1] A. Tkatchenko, R.A. DiStasio Jr., R. Car, and M. Scheffler, *Phys. Rev. Lett.* **108**, 236402 (2012).
- [2] A.M. Reilly, A. Tkatchenko, *J. Chem. Phys.* **139**, 024705 (2013).<sup>[SEP]</sup>
- [3] A.M. Reilly, A. Tkatchenko, *Phys. Rev. Lett.* **113**, 055701 (2014).<sup>[SEP]</sup>
- [4] J. Hoja, A.M. Reilly, A. Tkatchenko, *WIREs Comput. Mol. Sci.* **7**, 1294 (2017).<sup>[SEP]</sup>
- [5] A.M. Reilly et al., *Acta Cryst.* **B72**, 439 (2016).

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## Computational Phase Diagram Prediction for Organic Monolayers on Metal Substrates

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Monolayers of organic molecules on inorganic substrates often show rich polymorphism with diverse structures in differently shaped unit cells. Determining the different commensurate structures and their epitaxy matrices from first principles is far from trivial due to the large number of possible polymorphs.

We pursue a novel approach based on coarse-graining the potential energy surface and applying machine learning to efficiently determine the energetically most stable structures. First the adsorption geometries of isolated molecules as well as all possible unique super cells of the substrate are determined. Then all configurations are generated by combining each adsorption geometry with every super cell. For a subset of configurations adsorption energies are determined using dispersion-corrected DFT. This subset serves as training data for a machine learning algorithm, that allows us to predict the adsorption energies for all configurations. Configurations with an adsorption energy below predefined energy threshold are then probed using DFT.

We demonstrate the capability of our approach for TCNE (tetracyanoethene) on Cu(100) and Naphtalene on Cu(111). We determine the adsorption energies for a large number of polymorphs and compare the results to the experimentally obtained phase diagram.

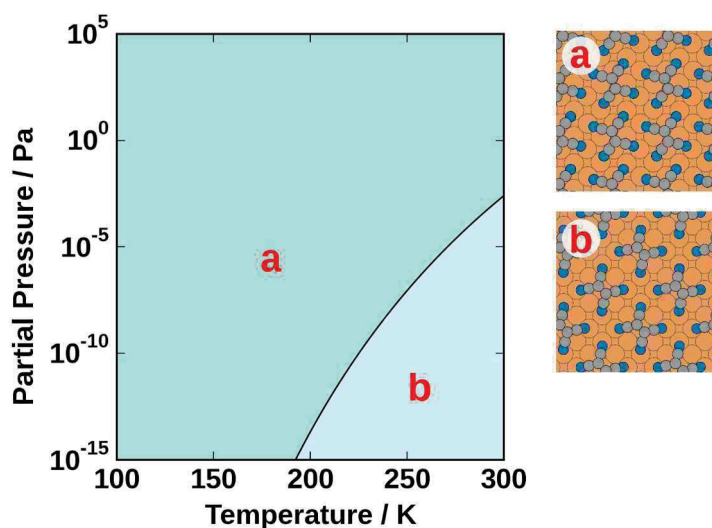


Figure 1: Phase diagram of TCNE on Cu(100)

## Photochemical switching of azobenzene derivatives on an insulating surface

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Studying single molecular switches is of interest for a better understanding of fundamental physical and chemical processes, but also in view of their possible use in molecular nanotechnology [1]. A prototypical conformational switch is azobenzene, which changes between *trans* and *cis* isomers at the central N=N bond upon an external stimulus, showing efficient photochemical activation. In the past years, various studies have shown that adsorption on metal substrates strongly influences the switching properties [2,3], especially for activation by light [4]. We present non-contact atomic force microscopy (nc-AFM) results on the switching of individual azobenzene molecules on a calcite surface where the molecules retain their photochemical activity.

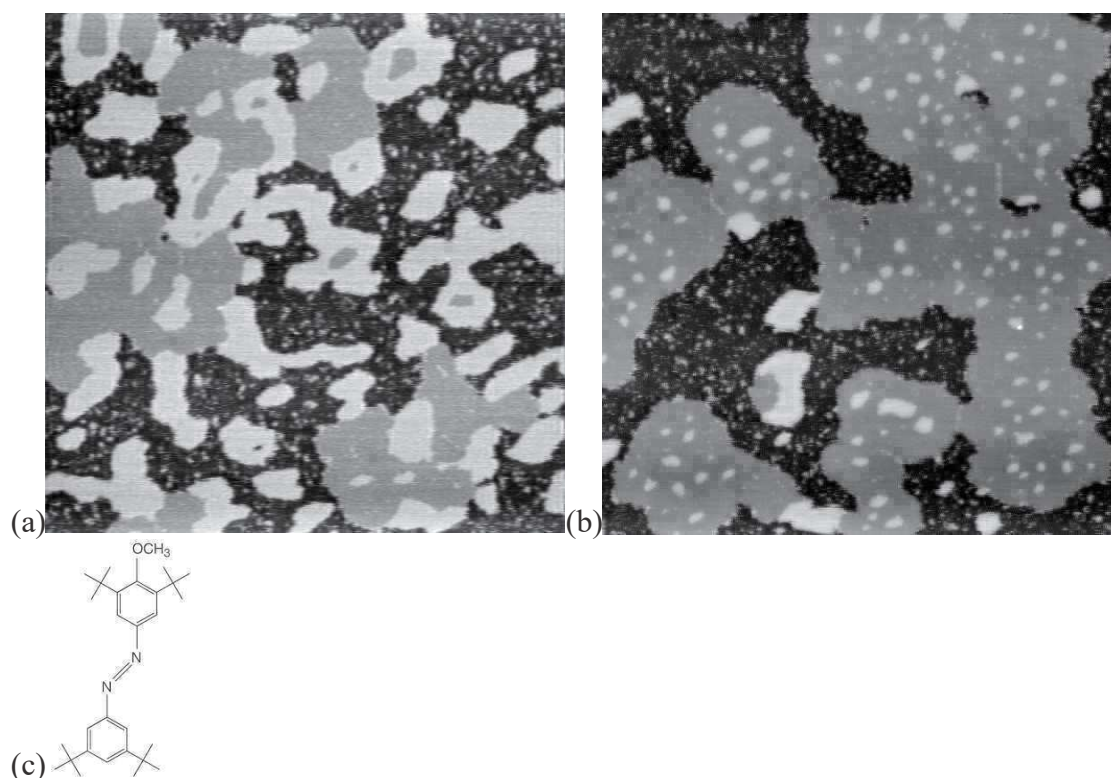


Figure 1:  $1 \times 1 \mu\text{m}^2$  nc-AFM images of Methoxy-tertbutyl-Azobenzene (c) on Calcite(104) before (a) and after (b) Illumination with a 450nm laser.

[1] C. Joachim et al., Nature 506, 651 (2000); [2] Choi et al., Phys. Rev. Lett. 96, 156106 (2006); [3] Dri et al., Nature Nanotechnology 3, 649 (2008); [4] Comstock et al., Phys. Rev. Lett 99, 038301 (2007)



## Understanding polymorph selection in nabumentone thin films at surfaces

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Polymorphs have a strong influence on many different properties including thermodynamic and chemical stability, processibility or dissolution which in turn directly impact pharmaceutical formulation and therapeutic actions. As such the preparation of specific polymorphs as well as their reproducibility is of crucial importance. In this work the polymorphic phase behaviour of nabumetone is studied. This model substance is a non-steroidal anti-inflammatory drug which has two known polymorphs. By employing various thin film fabrication techniques like spin coating, drop casting or dip coating homogenous layers form at substrate surfaces. Nabumetone was dissolved in different solutions like ethanol, toluene and tetrahydrofuran (THF) at different amounts. The thin film properties were examined using microscopy and X-ray diffraction. The experimental results show that often form I results when films are prepared using slow techniques while spin coating induced the form II more frequently. Nevertheless, the substrate surface is unable to stabilize the form II of nabumetone so that a solid – solid phase transition into form I over time takes place. In many cases the thin film formation results in the presence of the two forms simultaneously which also is reflected in the morphological appearance consisting of spherulites and clusters. For sake of increase of surface area, nabumetone is processed together with a matrix forming substance, polystyrene. In such co-processed samples a homogenous mixture of the two species is achieved while at relatively larger nabumetone content a phase separation exists. Here form II is developing only in small crystals while form I seems to be less affected. The results allow now draw conclusion on the polymorph selection during thin film fabrication as well as being hosted in a matrix which will be further investigated towards application relevant surfaces and matrices.

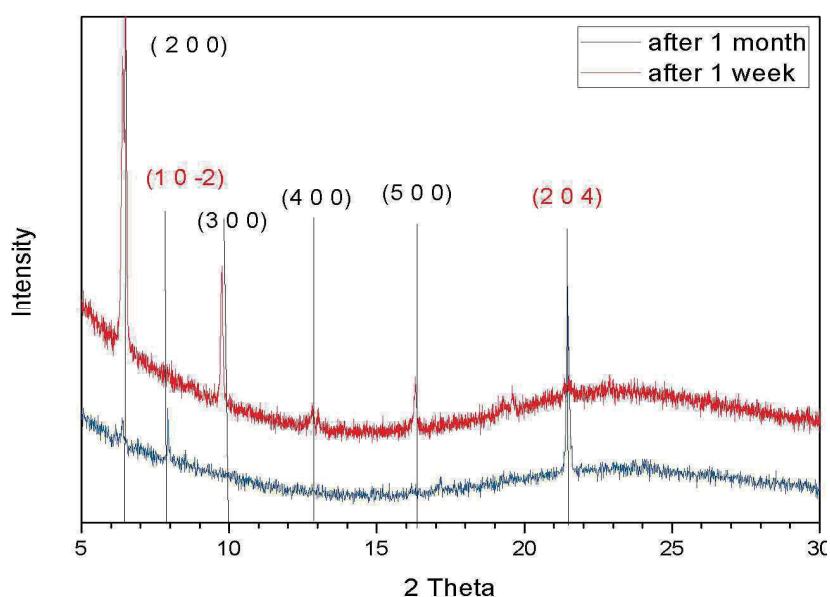


Figure 1: Stability test of form II (red curve) and during phase transition (blue curve)

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## BIAXIAL ORIENTED GROWTH OF PENTACENE ON RIPPLED GLASS SURFACES

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Pentacene is known to grow on isotropic surfaces like  $\text{SiO}_x$  in a uniaxial oriented surface induced phase [1]. This recent growth study is investigating the molecules behavior on patterned surfaces without changing the surface chemistry. Therefore, pure glass substrates have been patterned with ripples via ion beam sputtering and pentacene in thicknesses up to 300 nm nominal has been deposited on top. Using grazing incidence x-ray diffraction, atomic force microscopy and ellipsometry, a biaxial oriented growth of pentacene in the thin-film phase and the bulk phase, relative to the ripples orientation, is observed. A growth model (cf. Figure 1) gives one possible explanation for the oriented growth. While the molecules keep the preferred 001 orientations to the surface, the grooves on the surface open the possibility to a certain in-plane orientation by alignment of molecules in different phases.

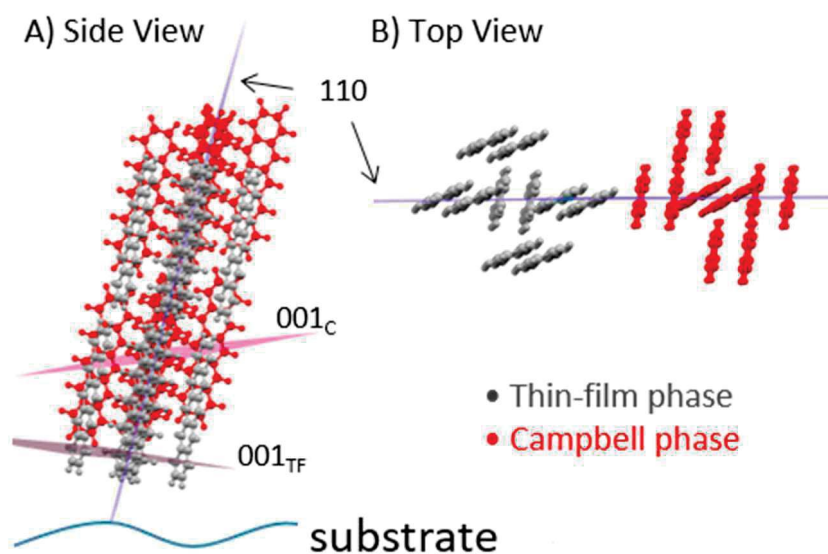


Figure 1: Pentacene molecules in their thin-film phase (grey) and Campbell phase (red) aligning on a rippled substrate. The 001 planes, aligning with the substrate (Side view), and the conjunct 110 plane due to alignment of molecules in different phases (Top View), are given respectively.

[1] Self-Limited Growth in Pentacene Thin Films, S. Pachmajer et al., *ACS Appl. Mater. Interfaces* **2017** 9 (13), 11977-11984

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## APPEARANCE OF A SURFACE INDUCED CRYSTAL STRUCTURE OF 6,6'-DIBROMOINDIGO

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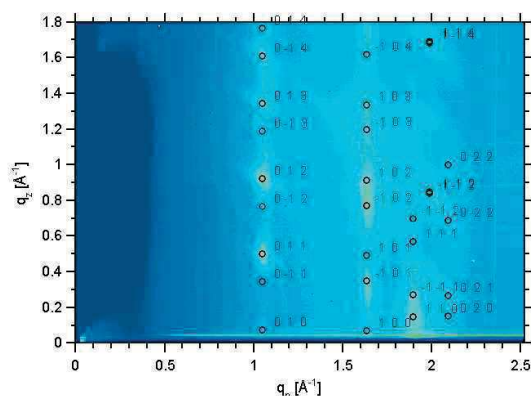
<sup>2</sup> Institute of Pharmaceutical Sciences, University of Graz, Austria

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Tyrian Purple (6,6'-dibromoindigo) can be used as organic semiconductors for a cheap and sustainable way to build electronic devices. Due to the intra- and intermolecular hydrogen bonding Tyrian Purple (TP) shows good charge transport properties and forms highly crystalline films. The crystal bulk phase was solved in 1979 having lattice constants  $a = 11.50$  Å,  $b = 4.85$  Å,  $c = 12.60$  Å and  $\beta = 104.0^\circ$  (space group P21/a) and two molecules per unit cell. Within this work thin films of TP were prepared by thermal evaporation onto substrates with different surface energies and roughnesses. The substrates were kept at room temperature during evaporation, which is the reason for the appearance of the surface induced crystal phase, whereas at elevated temperatures the known bulk phase appears. The crystal structure of the new polymorph were solved based on an combined experimental / theoretical approach. Grazing incidence x-ray diffraction (GIXD) experiments were performed at the ESRF, beamline ID10B, using a 2D detector and exposure times between 10 s and 30 s. The reciprocal space maps were analyzed using the software *xrayutilities* and PyGid. They all show similar diffraction patterns which result from a triclinic unit cell with one molecule per cell. The molecular packing was obtained by molecular dynamics simulations and geometry optimization by density functional theory [1,2]. Finally it could be concluded that the crystal structure is formed by columns of parallel stacks of aromatic planes, which is significantly different from the bulk phase.



## COMPLEX BEHAVIOUR OF CAFFEINE CRYSTALLITES ON SOLID SURFACES

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Defined fabrication of organic thin films by physical vapour deposition (PVD) are highly desired in applications allowing adjustments of polymorphic and morphological properties. Most PVD studies on organic films focus on conjugated molecules, as these promise a direct application in electronics. However, for other molecules, especially drug molecules, such studies are rare. Anyway, drug molecules are very interesting as they feature asymmetric chemical structures with somehow ambipolar character. This ensures aqueous solubility and penetration abilities to the living cell. Furthermore, such molecules might allow fundamental information of heterogeneous crystal growth to be obtained.

Within this work, the growth of a prototype asymmetric, disk-like molecule (caffeine) on silica, muscovite mica and NaCl surfaces is studied. Microscopy reveals, independent of the substrate, the presence of needle-like crystallites after the PVD process in a Hot-Wall-Epitaxy setup (HWE). X-ray diffraction reveals, that for all samples a unique polymorph,  $\beta$ -form, is present with caffeine arranging in an edge-on conformation. Depending on the surface, the azimuthal arrangement, however, is different. A random distribution is present on silica, while mica as well as NaCl induce defined azimuthal needle directions during growth (see Figure 1). This agrees with their different surface properties, i.e. isotropic properties are present on silica while the others have regular surfaces. Thus, the caffeine needles (or molecules) adapt arrangements on account of the specific surface properties which is further concluded from X-ray diffraction pole figure measurements.<sup>1</sup>

Defined variation of the HWE process parameters and the surfaces reveal that the quality of needle alignment is strongly affected by the surface indicating a route for high quality heterogenous crystallisation. Comparison of previous studies,<sup>2</sup> on solution cast caffeine show that the needle quality is higher for the HWE process. Solution casting also allows for azimuthal alignment but due to different environmental conditions, needles align along different directions compared to the HWE processed needles.

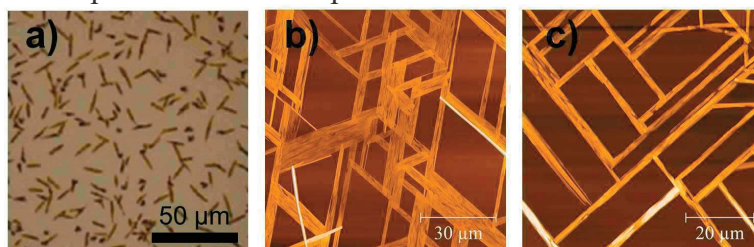


Figure 1: a) Optical micrograph showing azimuthally randomly distributed caffeine needles on silica and atomic force microscopy height images of bi-axially aligned needles on muscovite mica (b) and NaCl (c).

[1] Röthel, C. et al. CrystEngComm **9**, 2936–2945 (2017).

[2] Werzer, O. et al. Cryst. Growth Des. **13**, 1322–1328 (2013).

## THE SUBSTRATE-INDUCED PHASE OF C<sub>8</sub>O-BTBT-OC<sub>8</sub> DETECTED BY MID-INFRARED AND LATTICE PHONON RAMAN SPECTROSCOPY

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Organic molecules show a pronounced tendency to form polymorphic phases, requiring simple and fast techniques to relate the type of polymorphic phase to the appropriate crystallization conditions. In this work, the appearance of the previously reported substrate-induced phase of C<sub>8</sub>O-BTBT-OC<sub>8</sub> [1] is investigated using mid-infrared and lattice phonon Raman microscopy. Samples investigated include thin films prepared by solution processing with varying deposition parameters and single crystals grown from different solvents. Lattice phonon Raman microscopy shows clear differences for the crystallographic phases of the single crystals (Figure 1), but is only applicable to thicker films. Mid-infrared spectroscopy, probing intramolecular vibrations, allows differentiation of the phases even for thinner films. The results show that as-prepared films crystallize predominantly in the substrate-induced phase, while post treatment by solvent vapor annealing transforms the sample to the bulk form. This work demonstrates that the phase behavior of C<sub>8</sub>O-BTBT-OC<sub>8</sub> can be detected by a fast and easy access to the crystal structure using infrared and lattice phonon Raman spectroscopy.

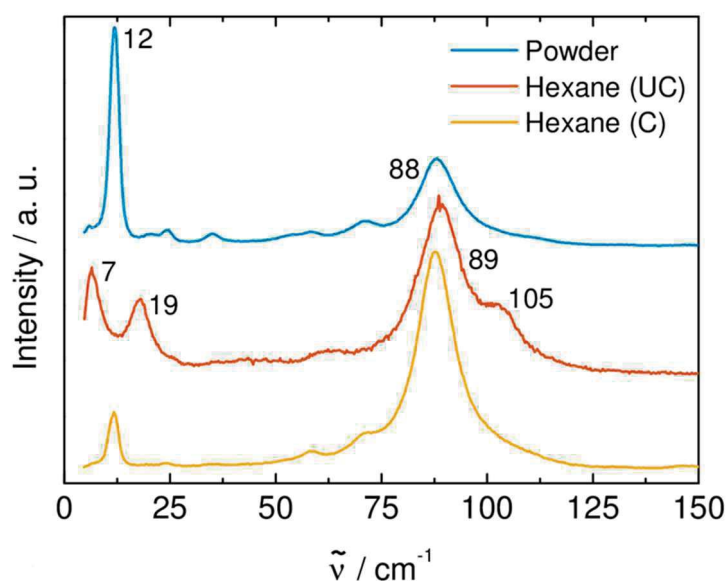


Figure 1: Lattice phonon Raman spectra of the polycrystalline C<sub>8</sub>O-BTBT-OC<sub>8</sub> powder compared to the spectra of the crystals grown from hexane solution in an uncovered (UC) and a partially covered vial (C).

[1] A. O. F. Jones, Y. H. Geerts, J. Karpinska, A. R. Kennedy, R. Resel, C. Röthel, C. Ruzié, O. Werzer, M. Sferrazza, ACS Applied Material & Interfaces **2015** 7 (3)

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## PHOTOLUMINESCENCE AS A PROBE OF MOLECULAR ORGANIZATION IN PDI8-CN2 ULTRA-THIN FILMS

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Photoexcited ultra-thin films of the organic semiconductor N,N'-bis(n-octyl)-dicyanoperylene-3,4:9,10-bis dicarboximide (PDI8-CN2), grown on thermal Si/SiO<sub>2</sub>, exhibit an intense room temperature emission, strongly dependent on molecular coverage, even for sub-monolayer thicknesses. The luminescence spectra are characterized by a highly structured, isolated molecule emission in the sub-monolayer regime (coverage < 30%) and by a condensed-state singlet exciton fluorescence temporally evolving (within 0.5 ns) toward an unstructured, energetically relaxed, excimer-like emission, for thicker films. Once a complete monolayer is formed, only the unstructured excimer emission can be detected. The experimental findings are interpreted in terms of progressive deposition of nearly not interacting molecules, followed by islands formation where a strong dimeric coupling takes place, upon increasing the coverage. A thorough investigation by means of AFM and in-situ X-ray diffraction confirms the proposed picture.

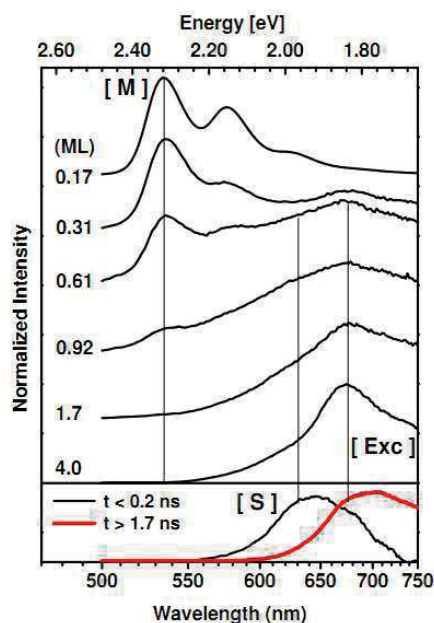


Figure 1: Upper panel: steady-state PL spectra of PDI8-CN2 ultra-thin films deposited on Si/SiO<sub>2</sub> at  $T_{\text{sub}}=120^{\circ}\text{C}$ . Lower panel: sub-ns time-resolved PL spectra of a 2 ML film

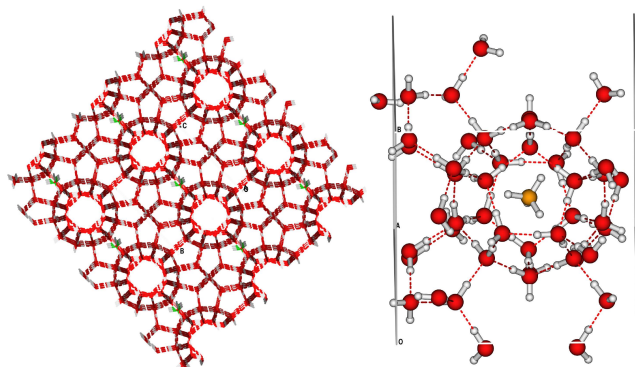
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## ACCURATE CALCULATIONS OF MOLECULAR CRYSTALS

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During the last decade, advances in method development have been leading to increasingly accurate predictions of molecular crystals. Thus, nowadays it is possible to accurately predict crystal structures of organic molecules and, in particular, organic salts and gas hydrates.



*Figure 1: The methane hydrate crystal structure*

Much of this progress can be attributed to the increased application of density-functional theory including dispersion correction (DFT+D) using periodic boundary conditions. Such computations are very time demanding and require the calculation of large number of different molecular crystals/polymorphs in each crystal structure prediction (CSP). Therefore, faster methods than DFT+D are also necessary for CSP.

Recently, a QM:QM scheme has been proposed<sup>1</sup>. The QM:QM approach relies on embedding calculations of molecular crystals, for example, by embedding MP2 into PBE+D2. The method works along the lines of several already established QM:MM schemes<sup>2,3</sup>. However, it does not use a force field for the periodic model, but rather PBE+D2 as the embedded functional.

To get the fully relaxed structure, the optimisation of atom positions and cell lattice parameters is required. In this work, we report the implementation of a cell optimisation within the QM:QM approach, whereas only geometry optimisation of atoms in the unit cell have been performed earlier. Here, we combine the analytical stress tensor from periodic calculations with the corresponding stress originating from the cluster contributions involving one periodic image fragment.

[1] A.D. Boese, J. Sauer, *Cryst. Growth Des.* **17**, 1636 (2017).

[2] S. Wen, G.J.O. Beran, *J. Chem. Theory Comput.* **7**, 3733 (2011).

[3] P. Mörschel, M.U. Schmidt, *Acta Crystallogr., Sect. A: Found. Adv.* **71**, 26 (2015)



## Addressing conformational and vibrational entropy in bio-organic systems

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Bio-organic components and materials are desirable tools for the use in technological and medicinal applications due to their abundance, low cost, low toxicity, and ease of fabrication. However, from a theoretical point of view, these systems present an immense challenge due to the large conformational space they can explore at finite temperatures, leading to many sorts of polymorphism, and the inherent anharmonicity of their intra and intermolecular interactions. Moreover, the presence of light atoms and frequently the interaction with water increases the importance of nuclear quantum effects in these systems. In this work we discuss our advances to address the challenges mentioned above.

For molecular crystals, that are notorious due to their high polymorphism, we present a comprehensive approach based on different flavors of thermodynamic integration in order to estimate all contributions to the free energies of these systems with density-functional theory, including the oft-neglected anharmonic contributions and nuclear quantum effects. We take the two main stable forms of paracetamol as a paradigmatic example. We find that anharmonic contributions, different descriptions of van der Waals interactions, and nuclear quantum effects all matter to quantitatively determine the stability of different phases. Our analysis highlights the many challenges inherent in the development of a quantitative and predictive framework to model molecular crystals. We also show calculations of anharmonic Raman spectra for different crystal structure polymorphs that can aid the characterization of different polymorphs and the quantitative analysis of anharmonic signatures.

For the structure search of flexible bio-organic molecules, also in contact with inorganic interfaces, we have extended the Fafoom code [2] (a genetic algorithm code that works on internal degrees of freedom) to include orientations and translations of flexible molecules with respect to one another and to fixed frames, like surfaces. I will show results obtained from density-functional theory for the case of the Arginine peptide in different protonation states, that is known to adopt isolated or dimeric conformations on metallic surfaces. From our data we can show how the conformational space of the molecule is reduced upon adsorption and make considerations on how to obtain simpler energy functions for an initial pre-screening of these systems. These first steps pave the way for the study of self-organization of different structures on surfaces and their polymorphs when intramolecular degrees of freedom play an important role.

[1] M. Rossi, P. Gasparotto, M. Ceriotti, *Phys. Rev. Lett.* **117**, 115702 (2016).

[2] A. Supady, V. Blum, C. Baldauf, *J. Chem. Inf. Model.* **55**, 2338 (2015).

## ***In-situ* crystallization and gel formation of thermodynamically unstable polymorphs: a SWAXS study of caffeine in isopropanol**

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The preparation of typically thermodynamically unstable polymorphs is a challenge which has gained significant interest in recent years. This is especially true for pharmaceutical small molecule systems where less stable polymorphs may have enhanced properties (e.g. solubility) compared with more stable forms. In this work, caffeine is used as a model system to study the formation of different polymorphs (the more stable  $\beta$  form, and the less stable  $\alpha$  form) during heating and cooling using combined small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) measurements.

It is shown that heating caffeine in isopropanol results in the recrystallization of the thermodynamically stable  $\beta$  form to the less stable  $\alpha$  form during subsequent cooling. The formation of a small molecule gel is also observed during heating and cooling. *In-situ* monitoring of the phase changes, made possible by the use of a temperature controlled SAXS/WAXS sample stage, is important for a better understanding of how to control which polymorph forms and of the relationships between different phases.

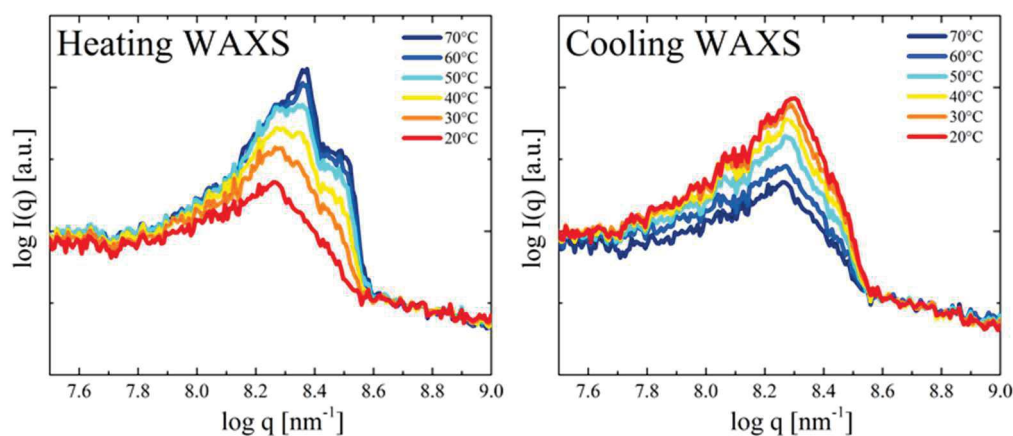


Figure 1: WAXS curves of caffeine in isopropanol during heating and cooling.

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## A FAST ALTERNATIVE TO PERIODIC DFT CALCULATIONS: DFT EMBEDDED INTO DFTB

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It is commonly accepted that weakly bound molecular and periodic systems require a proper treatment of nonbonded interactions which is known to be problematic within the standard Hartree-Fock and density-functional theory (DFT). Further developments in dispersion-corrected algorithms to DFT (DFT-D) improved the overall description of weakly bound systems by either introducing empirical dispersion coefficients with almost no additional computational cost or by using more costly nonlocal, density-dependent dispersion corrections. Despite these efforts, typical calculations for different crystal structures with these approaches are still rather time-consuming and require further elaboration of much faster methods than DFT-D without significant loss in accuracy.

In the last twenty years, with the advent of hybrid methodologies allowing one to incorporate a high-level calculation into a low-level one, it became possible to approach the high-level reference value for the property of interest and to systematically improve the accuracy of performed calculations.

Recently [1], a hybrid quantum mechanical : quantum mechanical (QM:QM) method which relies on the embedding of cluster models (at a high level) into a periodic system (at a low level) has been proposed. In a similar manner, the current approach consists in choosing DFT-D as a high-level method and the density-functional tight-binding (DFTB) for the low-level calculations [2].

In this contribution, the main features of the DFT-D:DFTB embedding scheme and the details of implementation will be presented with a particular emphasis on the main properties (sublimation enthalpies and lattice parameters) of molecular crystals. The performance of this embedding scheme in terms of accuracy and possible gain in speed with respect to standard periodic DFT calculations will be discussed.

[1] A. D. Boese, J. Sauer, *Cryst. Growth Des.* **17**, 1636 (2017).

[2] O. A. Loboda, G. A. Dolgonos, A. D. Boese, in preparation.

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