

## Various approaches to control solid/solid wetting self-assembly of organic semiconductors with STM

Frank Trixler<sup>\*,1</sup> and Wolfgang M. Heckl<sup>1,2</sup>

<sup>1</sup>Dept. für Geo- und Umweltwissenschaften, Ludwig-Maximilians-Universität München (LMU) and Center for NanoScience (CeNS), Theresienstrasse 41, 80333 München, Germany

<sup>2</sup>Deutsches Museum, Museumsinsel 1, 80538 München, Germany

Organic solid/solid wetting deposition (OSWD) is an easy, low cost method to prepare epitaxial monolayers of organic semiconductors under ambient conditions. This chapter describes various approaches to induce complexity into highly ordered monolayers with Scanning Tunnelling Microscopy (STM): nanomanipulated self-assembly aiming towards molecular data storage, directed local guided self-assembly to achieve complex nanowire arrays, and dip-pen induced coadsorption to achieve mixed domains of different semiconductors. These approaches demonstrate the potential of OSWD for the development of supramolecular nanoelectronics and photonics.

**Keywords** scanning tunnelling microscopy, organic semiconductor, adsorption, self-assembly, nanomanipulation

### Introduction

When approaching the length scale of molecules, conventional top-down strategies for microfabrication such as lithographic techniques encounter fundamental physical [1] and economical [2] limitations. Nanomanipulation and self-assembly processes [3] to generate nano-scale structures on substrate surfaces without such limitations are being widely explored [4]. The characteristic of these processes is the assembly of elementary building blocks such as atoms or molecules into larger, functional structures – a strategy which is termed “bottom-up approach” (Figure 1).

In the context of Scanning Probe Microscopy, nanomanipulation is an operation mode in which a tip is used as a tool to locally modify the sample structure instead of acting as a probe for imaging. In case of imaging, tip-sample interactions are minimized in order to leave the sample surface unmodified. The closer the sample is approached by the tip, the stronger repulsive forces become. This allows e.g. to push single building blocks adsorbed at substrate surfaces [5,6]. Thus, nanomanipulation enables a high degree of positional control of building blocks on substrates. However, this type of bottom-up approach is a typical serial process and thus extremely time-consuming when structures are to be built unit by unit.

In contrast to nanomanipulation, supramolecular self-assembly [7-12] is based on a highly parallel and automatic process: non-covalent chemical interactions between adsorbed building blocks lead to the spontaneous growth of highly ordered structures. Hence, supramolecular self-assembly is a means for easy, low-cost fabrication of epitaxial layers even under ambient conditions. Moreover, the reversibility of non-covalent bonds offers the possibility of going beyond simple miniaturisation by introducing dynamic features to surface supported devices such as reconfiguration, self-contacting and self-repairing [13]. However, the self-assembly of monolayers usually produces highly periodic structures, apart from domain boundaries and defects [8-10]. This characteristic of self-assembly is disadvantageous for the fabrication of nanostructures with structural complexity.

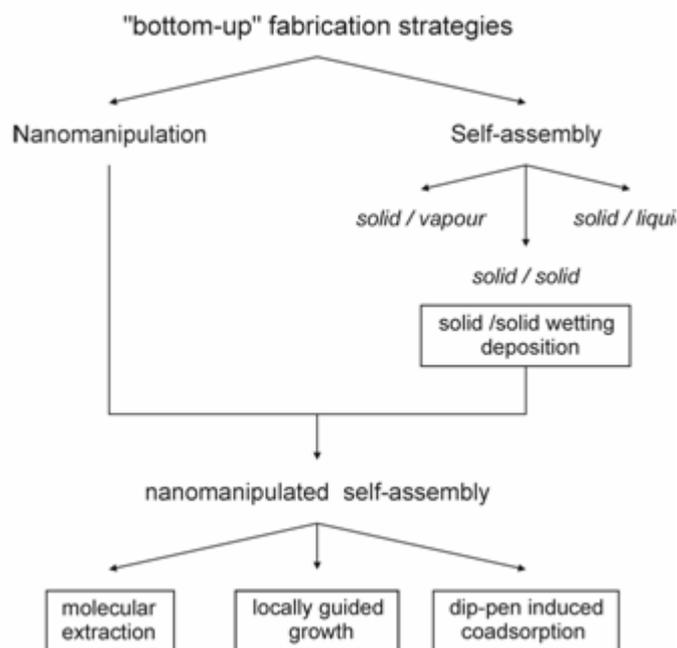
Attempts to combine the advantages of locally controlled assembly and parallel processing encounter various obstacles. These arise when applying conventional strategies in order to induce epitaxial growth of monolayers. For instance, a commonly used method to grow supramolecular monolayers on crystal substrates is the deposition of molecules at the solid/vapour interface by vacuum sublimation, referred to

---

\* Corresponding author: e-mail: trixler@lmu.de, Phone/Fax: (+49)89-2180-4331

as “Organic Molecular Beam Deposition” (OMBD) [14]. A clear disadvantage of this method, particularly in light of future applications of low-cost molecular electronics, is the enormous instrumental effort. Furthermore, this approach is limited to molecules which are sufficiently stable for sublimation. In addition, locally controlled self-assembly and nanomanipulations based on re-adsorption and self-contacting of supramolecular nanostructures (as described below) require a constant supply of molecules - a criterion that can not be met by standard OMBE techniques or the so called “precursor method” [15]. Several alternative techniques are based on dissolving the molecules. These techniques utilize the solution as a carrier to supply molecules to the interface [16-18]. However, molecular adsorption and self-assembly at the solid/liquid interface suffers a severe disadvantage when the compound of interest is virtually insoluble. This is the case for many organic semiconductors and pigments [19,20] – compounds which are of high relevance for the development of nanoelectronics and photonics. In addition, a serious drawback for nanomanipulation of self-assembled monolayers at the solid/liquid interface arises by the fact that normally, when molecules are removed from the substrate, the periodic structures immediately grow back. This limits the freedom for actively influencing the outcome of the self-assembly process.

In this contribution we show that these drawbacks can easily be overcome by a process applicable under ambient conditions which we term “Organic Solid/Solid Wetting Deposition” (OSWD) [21]. We demonstrate that our approach to induce the growth of organic semiconductor monolayers enables the realization of different concepts of nanomanipulated self-assembly (Figure 1) in order to create desired nanostructures.



**Fig. 1** Context of solid/solid wetting induced self-assembly and the discussed approaches of nanomanipulated self-assembly within the bottom-up fabrication concept.

### Organic solid/solid wetting deposition (OSWD)

The OSWD process enables to grow epitaxial monolayers of virtually insoluble organic semiconductors and pigments under ambient conditions. The basic idea behind this approach can be described as follows.

Regard the case of a liquid droplet in contact to a solid surface: it will spread on the solid and wet its surface if the adhesion energy between the surface molecules of the droplet and the surface atoms of the substrate exceeds the cohesion energy between the molecules of the droplet. Now, regard some properties of crystals of organic semiconductors and pigments: the organic molecules are assembled into solid crystals via noncovalent bonds such as van-der-Waals interactions and hydrogen bonds. Such bonds are weak compared to covalent or metallic bonds of inorganic substrate crystals. Thus, it could be possible for some organic compounds that, if a direct contact between the surface of organic nanocrystals and the surface of inorganic substrates is established, the binding energy of surface molecules in the nanocrystal is exceeded by the binding energy of the molecules to the substrate (adsorption energy). In this case, molecules should detach from the nanocrystal, adsorb on the substrate surface and form monolayers via diffusion, if the molecule-substrate interaction is not too strong.

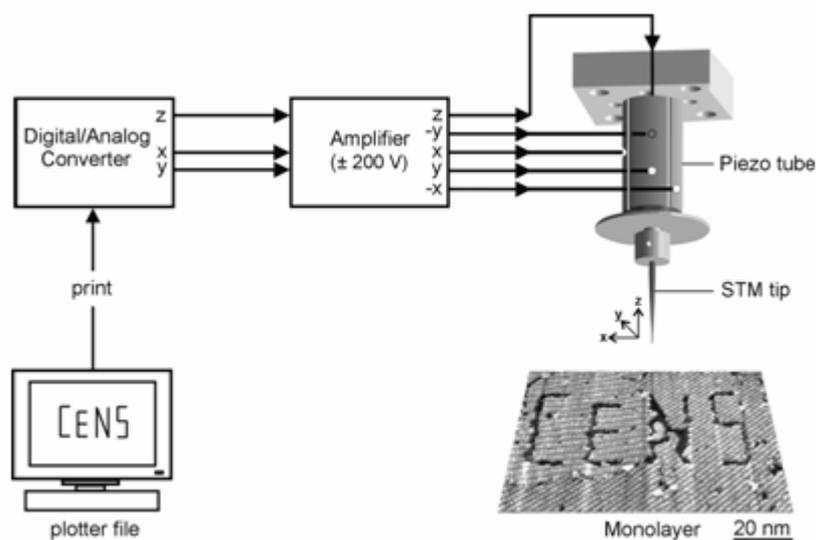
We tested various molecules including Indigo, Quinacridone (QAC) [19,21] and Perylene-tetracarboxylicdianhydride (PTCDA) [22] for their ability to adsorb on graphite based on a subtle balance of binding energies as discussed above. The tests were performed both experimentally and with force-field calculations. For the experiments, we established a direct contact between organic nanocrystals and the substrate surface in different ways. One approach is to simply deposit pure nanoparticle powder of the respective compound onto the substrate surface and subsequently remove the powder by using a stream of compressed dry air or using adhesive tapes. Alternatively, nanoparticle powder is mixed up with a viscous compound such as alkyd resin or the liquid crystal 8CB (Octylcyanobiphenyl) [23] and applied under ambient conditions as a small droplet to the substrate. Centrifugation experiments revealed that the solubility of the semiconductor pigments in such mixtures is below 1 ppm. Based on our calculations, this amount is not sufficient to generate the dense molecular coverages e.g. of QAC on graphite as observed by STM [21]. Thus, the viscous compound is acting as a binder which suspends the nanocrystals rather than being a solvent for molecules.

Both methods to establish a direct contact between nanocrystals and substrate produced the same results: STM measurements revealed that monolayers of the organic semiconductors QAC and PTCDA grow instantly after applying nanocrystals to a graphite surface, while Indigo monolayers were not detected despite numerous attempts. Force-field calculations of the relative binding energies, performed with the Cerius2 software package employing a Dreiding II force field [24], revealed that for QAC and PTCDA molecules embedded within specific crystal surfaces there is a preference for the graphite substrate while for Indigo this is not the case [21]. Due to the coincidence of experimental and theoretical results as well as other observations (see section “molecular extraction”), we conclude that the behaviour of QAC and PTCDA nanocrystals at the graphite surface can be discussed as being analogue to the above mentioned classical case of wetting - the spreading of a liquid on a solid. Thus, we refer to this process as “Organic Solid/Solid Wetting”. The term “solid/solid wetting” is already been used in the literature [25]. However, the occurrence of this effect has only been reported in the special context of inorganic oxide catalysts in a high temperature and time regime [25, 26], but not for solid nanoparticles of organic compounds.

We developed various approaches to influence the outcome of OSWD induced self-assembly. These approaches will be described in the following.

### **Molecular extraction**

The approach of molecular extraction from self-assembled monolayers under ambient conditions is based on two subsequent steps: After solid/solid wetting induced self-assembly of a monolayer, the STM tip is used to desorb molecules from the monolayer along predefined vectors via repulsive tip-sample interactions.



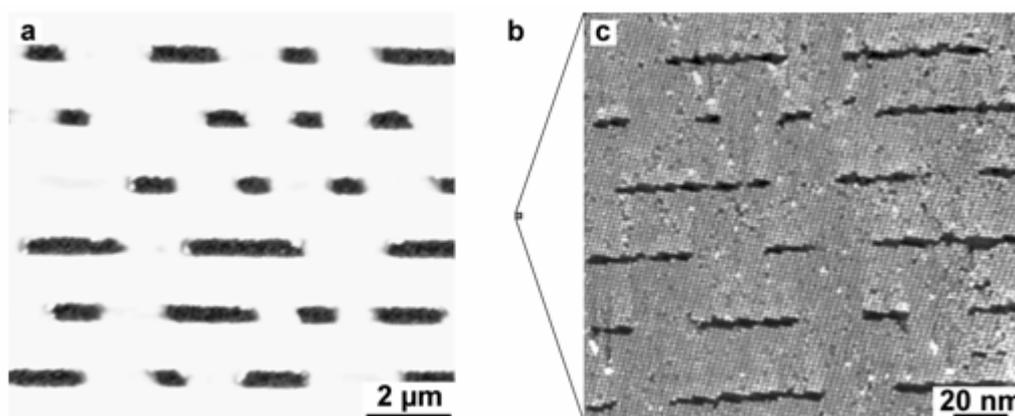
**Fig. 2** Operation principle of the used nanomanipulator. The manipulation is exemplified with the logo of CeNS (Center for NanoScience), which was written via molecular extraction into a PTCDA monolayer self-assembled on graphite.

The basic operation principle of the nanomanipulator used for our molecular extraction and data storage approach can be described as follows: Extraction lines are defined by drawing a set of vectors with a commercial vector graphic program. The graphic is then stored as a plotter file, which is usually destined for printing vector graphics with plotters. However, instead of a plotter, the print job is executed by a pocket size STM. The STM tip performs the same movements as the drawing pen of a plotter would do. However, STM and plotters are working at very different scales, since vertical and lateral movements of the STM tip are within a few nanometres (Figure 2).

Molecules from the self-assembled monolayer are extracted when the tip moves along predefined vectors with a decreased tip-sample distance of about 0.5 nm with respect to the imaging mode distance. The lower tip-sample distance increases the repulsive interaction between the tip and adsorbed molecules to an extent which leads to a desorption of molecules along the manipulation vectors. A high degree of control over the result of nanoextractions can be achieved if the following two basic requirements are complied: Firstly, the adsorbate compound may not be forced into relatively strong supramolecular networks by hydrogen bonds in order to prevent the collateral desorption of adjacent molecules within the network. Secondly, relatively strong non-covalent bonds between an adsorbed molecule and the substrate (e.g.  $\pi$ - $\pi$  interactions between large, flat aromatic molecules and the graphite substrate) should be present in order to prevent unintended extractions/desorptions when the tip-sample distance is only slightly decreased with respect to the imaging mode. This combination can be achieved by using compounds such as the organic semiconductor PTCDA (Perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride) [22].

Usually, no modifications are detected after nanomanipulation of monolayers at the solid/liquid interface (e.g. pure 8CB on graphite), since the periodic structure heals out immediately by filling the gaps with molecules from the liquid. In contrast, modifications within self-assembled PTCDA monolayers grown by OSWD via suspended nanoparticles (Figures 2, 3) are by far more stable: long-term STM experiments under ambient conditions with control scans executed every 5 hours revealed, that even after 54 hours generated gaps could be identified in STM scans. This degree of stability can be explained by the characteristic of OSWD: a precondition for the adsorption of molecules via OSWD is a direct, physical contact between organic nanocrystals and the substrate. However, the gaps, which are usually below 4 nm, are too small to incorporate suspended PTCDA nanocrystals, because the average

size of primary particles of commercially available PTCDA is about 50 nm. Thus, the nanocrystals cannot achieve a contact with the substrate surface exposed by the gap. This prevents the direct resupply of molecules to fill up the gaps. The model predicts that increasing the gap width should decrease the stability of the modifications. This is due to the increasing fraction of suspended particles with sizes suitable for a direct contact with the exposed substrate increases. In fact, this behaviour can be observed in our experiments.



**Fig. 3** Molecular data storage. (a) AFM image of the surface of a standard compact disc (CD). (b) STM image of a PTCDA monolayer after nanoextraction vectors were executed in the nanomanipulation mode. The STM image is displayed in the same scale as the AFM image of (a) (c) enlarged image of (b).  $I_T=250$  pA,  $U_T=0.55$  V.

Additional experiments revealed that thin graphite layers, stripped away from a graphite block with a commercial adhesive tape, are suitable substrates for OSWD generated monolayers. This enables a very low cost substrate fabrication for such devices.

Results as depicted in Figure 3 indicate that this approach may in principal open up the way for devices which offers a data storage density in the regime of 1 Tbit/in<sup>2</sup> and, at the same time, can both be fabricated and written totally under ambient conditions with a low preparational effort.

### Locally guided growth

In the above described concept of molecular extraction, self-assembly and nanomanipulation are applied one after another. In a different approach which we term “locally guided growth”, self-assembly and nanomanipulation occur simultaneously. In this case, the nanomanipulation induces information into a self-assembly process concerning the direction of growth.

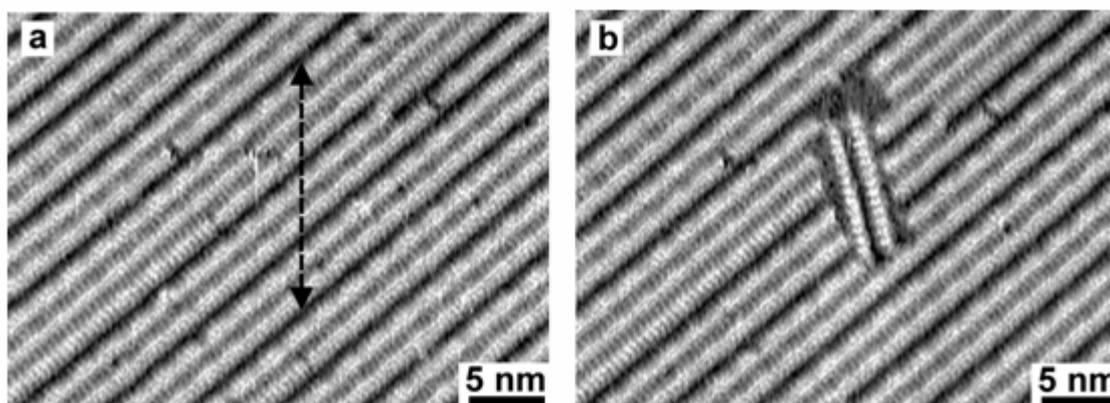
Locally guided growth utilizes the anisotropic stability of supramolecular networks. For example, QAC molecules adsorbed on graphite assemble into linear chains. In these chains, molecules are interconnected by two O...NH hydrogen bonds with each neighbour [21]. We calculated the energy needed to displace a QAC molecule within a chain for two perpendicular directions using force-field simulations. The results reveal a highly anisotropic behaviour: displacing a molecule along the H-bond axis (compression and extension) by a certain amount requires considerably more force than shearing [21].

The anisotropic stability can be utilized to locally steer the growth direction of nano-chains by applying the following procedure: After creating gaps/areas which are free of molecules by applying nanomanipulation induced desorption, the repulsive tip-sample interactions are decreased to a degree which allows the formation of wire nuclei at the exposed substrate. As a consequence to the anisotropic stability of chains, wire-nuclei with the H-bond direction aligned nearly parallel to the manipulation direction (or fast scan direction respectively) are more resistant against disruption by the scanning probe,

thus can continue to grow. In the case of non-parallel alignments with respect to the direction of tip movement, wire nuclei are again desorbed and replaced. Thus, in contrast to STM tip induced mechanical reorientations of already adsorbed wires [27], the rearrangement can be described as the result of re-adsorption and direction selective growth. Since the growth is actually influenced by the probe, its time constant must be in the same order as the scanning process. Molecules for the re-adsorption are again supplied by the nano-crystals, which are still present or monomers might originate directly from the tip.

The effect of guided self-assembly can be observed on length scales down to the regime of  $\sim 10$  nm. Figure 4b shows that the STM tip generates a gap in the nano-chain assembly along a vertical manipulation path. The orientation of the re-grown and stabilised self-assembled chains is related to the scanning direction.

Locally guided growth enables to steer the self-assembly of nanostructure without relying on external templates. This allows repeated changes of structural complexity of self-assembled monolayers.



**Fig. 4** Locally guided growth of supramolecular QAC chains. (a) Initial configuration of parallel QAC chains grown on graphite. (b) The result of locally guided self-assembly. The initial gap within the monolayer was generated by moving the STM tip in 0.1 s along the path indicated by the dashed line in (a). The tip moved with a decreased sample distance of  $\sim 0.5$  nm with respect to the imaging mode. After generating the gap by extracting the molecules, the area was repeatedly scanned with the fast scan direction being vertical.  $I_T=600$  pA,  $U_T=0.90$  V (a) (b).

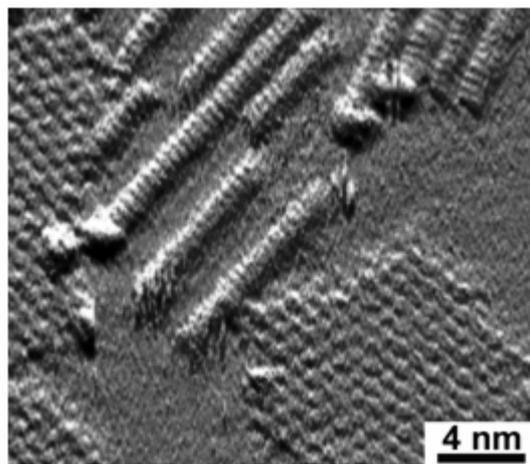
### Dip-pen STM induced coadsorption

The approaches described above were developed in order to induce structural complexity into homomolecular assemblies, in which all adsorbate domains consist of the same molecular species. In this section we demonstrate that complexity in OSWD monolayers can also be achieved by an approach which results in the growth of adjacent domains of different compounds.

The local coadsorption process described here can be divided into two subsequent steps: Initially, a monolayer is grown by OSWD at the interface between a substrate and suspended nanocrystals of one compound. Then, the STM tip is dipped into a suspension of nanocrystals of another compound. The tip, covered with a thin film of the dipped suspension is then penetrated into the substrate-supported suspension of the first compound for encountering the substrate surface. After a short and very slight physical contact of the scanning tip with the monolayer/substrate, the tip is retracted to the imaging mode distance and images are aquired.

The approach is exemplified with the organic semiconductors QAC and PTCDA. Figure 5 shows domains of coadsorbed QAC within a monolayer of PTCDA. We choose QAC and PTCDA as their monolayer structures can easily be distinguished (QAC: nano-chains [21], PTCDA: herringbone structure [22]). This enables to clearly identify the coadsorption of chemically different adsorbate molecules with STM. The result indicates that suspended QAC nanocrystals are transferred from the thin

film covering the STM tip to the substrate surface at the contact area and induce the self-assembly of QAC monolayers via OSDW.



**Fig. 5** Dip-pen induced coadsorption of QAC and PTCDA monolayers. The nano-chains can be assigned to QAC according to [21] while the 2-D pattern can be attributed to PTCDA [22].  $I_T=500$  pA,  $U_T=0.90$  V.

Our dip-pen approach contributes to the set of coadsorption strategies such as host-guest self-assembly [28] or the growth of noncovalently bound complexes [29]. In contrast to these approaches which create uniform monolayers from mixed solutions, dip-pen STM coadsorption can be achieved at selected sites locally at the nanoscale to create monolayers of chemically different domains. The advance of this method to comparable approaches [30] is the fact that it requires neither UHV conditions for OMBE deposition nor a solubility of molecules. This is relevant for the low-cost fabrication of nanostructures using virtually insoluble organic semiconductors.

## Conclusion

We have shown that our concept of growing monolayers of virtually insoluble organic semiconductors under ambient conditions via “organic solid/solid wetting deposition” enables the realization of various approaches of nanomanipulated self-assembly. These approaches allow to steer the outcome of self-assembly in order to deliberately create desired supramolecular structures. This may open up the way to the development of very low-cost bottom-up fabricated organic semiconductor devices with complex nanostructures.

**Acknowledgements** This project was partly supported by the Deutsche Forschungsgemeinschaft within the Sonderforschungsbereich 486. We thank A. Gigler and P. Hix for helpful discussions and the Clariant GmbH for supplying Quinacridone samples.

## References

- [1] P. A. Packan, *Science* **285**, 2079 (1999).
- [2] E. S. Meieran, *Intel Tech. J.* **Q4**, 1 (1998).
- [3] G. M. Whitesides and B. Grzybowski, *Science* **295**, 2418 (2002).
- [4] R. F. Service, *Science* **294**, 2442 (2001).
- [5] T. A. Jung, R. R. Schlittler, J. K. Gimzewski, H. Tang and C. Joachim, *Science* **271**, 181 (1996).
- [6] S.-W. Hla, K.-F. Braun and K.-H. Rieder, *Physical Review B* **67**, 201402(R) (2003).
- [7] J.-M. Lehn, *Supramolecular chemistry: Concepts and Perspectives*. VCH, Weinheim (1995).

- [8] S. De Feyter, A. Gesquière, F. C. De Schryver, U. Keller and K. Müllen, *Chem. Mater.* **14**, 989 (2002).
- [9] A. P. H. J. Schenning, P. Jonkheijm, E. Peeters and E. W. Meijer, *J. Am. Chem. Soc.* **123**, 409 (2001).
- [10] V. Percec, M. Glodde, T. K. Bera, Y. Miura, I. Shiyonovskaya, K. D. Singer, V. S. K. Balagurusamy, P. A. Heiney, I. Schnell, A. Rapp, H.-W. Spiess, S. D. Hudson and H. Duan, *Nature* **419**, 384 (2002).
- [11] S. De Feyter and F. J. De Schryver, *J. Phys. Chem. B* **109**, 4290 (2005).
- [12] J. A. Theobald, N. S. Oxtoby, M. A. Phillips, N. R. Champness and P. H. Beton, *Nature* **424**, 1029 (2003).
- [13] J.-M. Lehn, *Science* **295**, 2400 (2002).
- [14] S. De Feyter and F. C. De Schryver, *Chem. Soc. Rev.* **32(3)**, 139 (2003).
- [15] P. T. Herwig and K. Müllen, *Adv. Mater.* **11**, 480 (1999).
- [16] D. G. Yablon, J. Guo, D. Knapp, H. Fang and G. W. Flynn, *J. Phys. Chem. B* **105**, 4313 (2001).
- [17] B. J. Gyarfas, B. Wiggins, M. Zosel and K. W. Hipps, *Langmuir* **21**, 919 (2005).
- [18] W. Mamdouh, H. Uji-i, J. S. Ladislaw, A. E. Dulcey, V. Percec, F. C. De Schryver and S. De Feyter, *J. Am. Chem. Soc.* **128**, 317 (2006).
- [19] E. F. Paulus, F. J. J. Leusen and M. U. Schmidt, *CrystEngComm* **9**, 131 (2007).
- [20] W. Herbst and K. Hunger, *Industrial organic pigments: production, properties, applications*. VCH, Weinheim (2003).
- [21] F. Trixler, T. Markert, M. Lackinger, F. Jamitzky and W.M. Heckl, *Chem. Eur. J.* **13**, (2007), in press.
- [22] C. Kendrick, A. Kahn and S. R. Forrest, *Applied Surface Science* **104/105**, 586 (1996).
- [23] D. P. E. Smith, J. K. H. Hörber, G. Binnig and H. Nejo, *Nature* **344**, 641 (1990).
- [24] S. L. Mayo, B. D. Olafson and W. A. III. Goddard, *J. Phys. Chem.* **94**, 8897 (1990).
- [25] E. I. Ko, Role of solid/solid wetting in catalysis, in: Berg, J. C. (ed.): *Wettability*. Dekker, New York (1993).
- [26] S. Günther, M. Marsi, A. Kolmakov, M. Kiskinova, M. Noeske, E. Taglauer, U. A. Schubert, G. Mestl and H. Knozinger, *J. Phys. Chem. B* **101 (48)**, 10004 (1997).
- [27] D. L. Keeling, N. S. Oxtoby, C. Wilson, M. J. Humphry, N. R. Champness and P. H. Beton, *Nano Letters* **3**, 9 (2003).
- [28] S. J. H. Griessl, M. Lackinger, F. Jamitzky, T. Markert, M. Hietschold and W. M. Heckl, *Langmuir* **20**, 9403 (2004).
- [29] L. Kampschulte, S. Griessl, W. M. Heckl, M. Lackinger, *J. Phys. Chem. B* **109**, 14074 (2005).
- [30] D. Takajo, T. Nemoto, O. Franco, H. Kurata and S. Isoda, *Japanese Journal of Applied Physics* **45 (3B)**, 2091 (2006).