

# The Epitaxial Growth of Self-Assembled Ternaphthalene Fibers on Muscovite Mica

## Supplementary Information

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### Experimental Details Synthesis 2,2':6',2''-Ternaphthalene (NNN)

2,2':6',2''-Ternaphthalene (NNN) was prepared using standard Suzuki cross-coupling procedures as shown below.<sup>1-3</sup> This all-aromatic compound could be obtained in high yield by coupling 2 equivalents of 2-naphthaleneboronic acid (1) with 1 equivalent of 2,6-dibromonaphthalene (2), as shown in scheme 1. The final product, 2,2':6',2''-ternaphthalene (NNN), was obtained as a colorless product, which appears to be highly insoluble in common solvents and could only be recrystallized from 1,2,4-trichlorobenzene (colorless platelets).

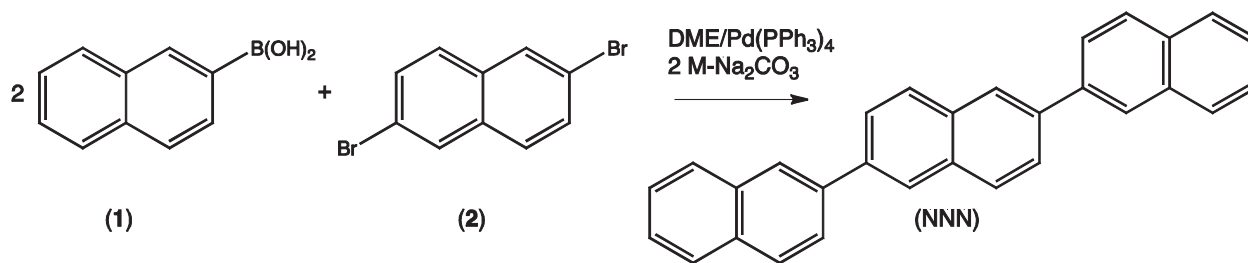
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Scheme 1: The synthetic route to 2,2':6',2''-ternaphthalene (NNN)

General. All intermediates and reagents were purchased from Sigma-Aldrich and were used without further purification. Mass spectra (MS) were obtained using a Shimadzu GCMS-QP2010S (direct inlet mode);  $M^+$  represents the molecular ion. Infrared spectra were obtained with a PerkinElmer Spectrum 100 FT-IR spectrometer in ATR mode. The melt temperature was determined using a Perkin-Elmer Sapphire differential scanning calorimeter, which was calibrated with indium (99.99%) (m.p., 156.5 °C,  $\Delta H=28.315$  J/g) and tin (99.99%) (m.p., 232.0 °C,  $\Delta H=54.824$  J/g). The sample (5 mg) was encapsulated in a hermetically sealed aluminum pan and the melting point was determined using a heating rate of 10°C min<sup>-1</sup> under an inert (nitrogen) atmosphere.

Synthesis of 2,2':6',2''-Ternaphthalene (NNN). A 100 ml 2-neck flask equipped with magnetic stir bar, reflux condenser, and argon inlet was charged (under argon atmosphere) with 2,6-dibromonaphthalene (2) (0.74 g, 2.6 mmol) and 6 mol% tetrakis(triphenylphosphine)palladium(0) (0.2 g, 0.17 mmol). 20 ml Dimethoxyethane (DME) was added and this yellow solution was stirred for 10 min at room temperature. 2-naphthaleneboronic acid (1) (1.1 g, 6.6 mmol) and 20 ml 2M-Na<sub>2</sub>CO<sub>3</sub> were added and this mixture was refluxed under argon atmosphere for 24 h. After cooling to room temperature the reaction mixture was diluted with 50 ml water and filtered. The solids were washed with acetone and dichloromethane and dried overnight at 60°C under vacuum. Pure 2,2':6',2''-Ternaphthalene (NNN), 0.89 g (91%) was obtained as colorless platelets after three recrystallizations from hot 1,2,4-trichlorobenzene. IR  $\nu_{max}$ : 3054, 1590, 1391, 1277, 963, 878, 855, 806, 741, 676, 628 cm<sup>-1</sup>; MS: 380 ( $M^+$ ), 252, 190, 126, 32 (purity >99%); Differential Scanning Calorimetry: T<sub>m</sub> (peak maximum) = 294°C,  $\Delta H_f = 61.6$  kJ.mol<sup>-1</sup>.

# X-ray diffraction

X-ray diffraction (XRD) has been chosen to study the structural properties of the organic crystallites. In order to obtain sufficient diffraction intensity a sample has been chosen where NNN has been deposited for 60 min at 80°C substrate temperature. Fig. 1 reports the acquired specular XRD spectrum (solid line) which is dominated by a series of {00n} diffraction peaks. These peaks are characteristic for island shaped crystal morphologies, built up by approximately standing NNN molecules and are consequently abbreviated by S-orientations. The corresponding reciprocal lattice vector  $q_{001}=0.324 \text{ \AA}^{-1}$  and surface unit cell parameters are listed in tab. 1. A graphical sketch of molecular alignment within the discussed crystal geometries is provided by fig. 2. Arrows in the upper part of fig. 1 indicate the positions of (00.2n) diffraction peaks stemming from the muscovite mica (001) substrate.

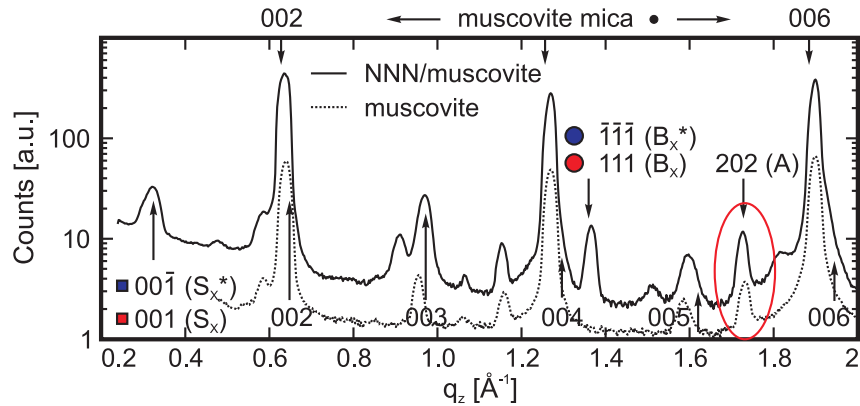


Figure 1: Specular x-ray diffraction (XRD) spectrum acquired on a sample where NNN (solid line) has been deposited for 60 min on muscovite mica (001). The spectrum is dominated by a series of S (001) diffractions peaks which are representative for island like morphologies. Additionally, contributions which could originate from A (101) and B (111) orientations are indicated. As the spectrum which has been acquired on plain muscovite mica (dotted line) indicates an analogous diffraction pattern at  $q_z=1.724 \text{ \AA}^{-1}$ , only the presence of B (111) orientations are verified by XRD.

Additionally, diffraction peaks arise at  $q_z=1.724 \text{ \AA}^{-1}$  and  $q_z=1.36 \text{ \AA}^{-1}$ . These peaks nicely correlate with A (101) and B (111) orientated NNN crystallites. Both orientations are characteristic for nearly flat lying molecular configurations and thus would explain the presence of needle like crystallites as revealed by SFM analysis. Again, characteristic parameters are listed in tab. 1

Table 1: Crystal Contact Planes observed for NNN crystallites. The corresponding reciprocal lattice vector ( $|q_z|$ ), crystal orientation of the long needle axis (LNA) and surface unit cell (a, b,  $\gamma$ ) are listed in the table. The tilt of the crystal side wall is also listed representing the enclosing angle between contact- and low energy-plane.

NNN Type	Plane	$ q $ [ $\text{\AA}^{-1}$ ]	LNA	Tilt [ $^\circ$ ]	a [ $\text{\AA}$ ]	b [ $\text{\AA}$ ]	$\gamma$ [ $^\circ$ ]
S	(001)	0.324	-	-	5.98	8.15	90.00
A	(101)	0.862	[010]	63.42	5.98	21.68	90.00
B	(111)	1.360	[1 $\bar{1}$ 0]	73.51	10.11	20.35	96.44

including additionally the crystallographic orientation of the long needle axis which is defined by the zone axis of the low energy plane (001) and corresponding contact plane.<sup>4</sup> Additionally, fig. 1 reports a specular scan which was acquired on a plain muscovite mica substrate (dotted line). By comparing both spectra (red marked region), it can be concluded that the peak located at  $q_z=1.724 \text{ \AA}^{-1}$  must be related to the mica substrate which is consistent with XRD pole figure (XRD-PF) measurements, where no traces of A (101) crystallites could be verified. Consequently, x-ray diffraction analysis verifies only the presence of B and S type crystallites when depositing NNN on a muscovite mica (001) substrates.

## References

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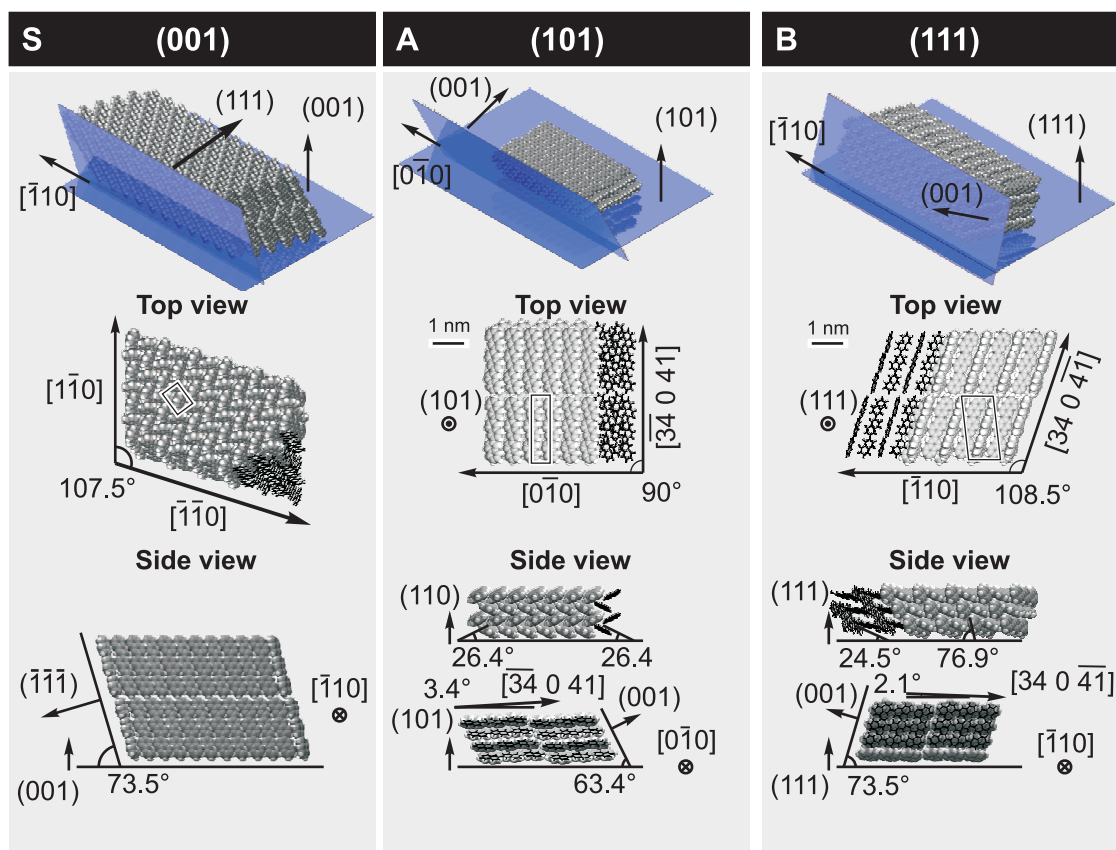


Figure 2: Graphical sketch of the discussed NNN contact planes S (001), A (101) and B (111). The top panel depicts a 3D representation of the molecular stack. Blue areas represent the alignment of the (001) low energy plane and the chosen contact planes. The centre panel shows a top view onto the corresponding molecular stack. A black polygon represents the surface unit cell. A side view (bottom) onto the stack visualizes the herring bone stacking angles relative to the substrate surface and the orientation of the long molecular axis (LMA). The LMA has been approximated by the  $[34.0\bar{4}1]$  orientation.