Electronic Supplementary Information (ESI)

Substrate Steered Crystallization of Naphthyl End-Capped Oligothiophenes into Nanofibers: The Influence of Methoxy-Functionalization

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Morphology and growth

In Fig. S1 the dependence of sample morphology on the nominal thickness at elevated deposition temperature is demonstrated for the case of NaT3. First, Fig. S1(a) for a nominal thickness of $d = 0.75\,\mathrm{nm}$, only clusters are observed. By increasing the thickness to $d = 1.5\,\mathrm{nm}$, Fig. S1(b), fibers and flat islands form, resulting in a network of fibers for even larger thicknesses of $d = 7.5\,\mathrm{nm}$, Fig. S1(c). The flat islands increasingly fill out the areas in between the fibers and consume the clusters. For even higher thicknesses only flat islands and fibers remain.

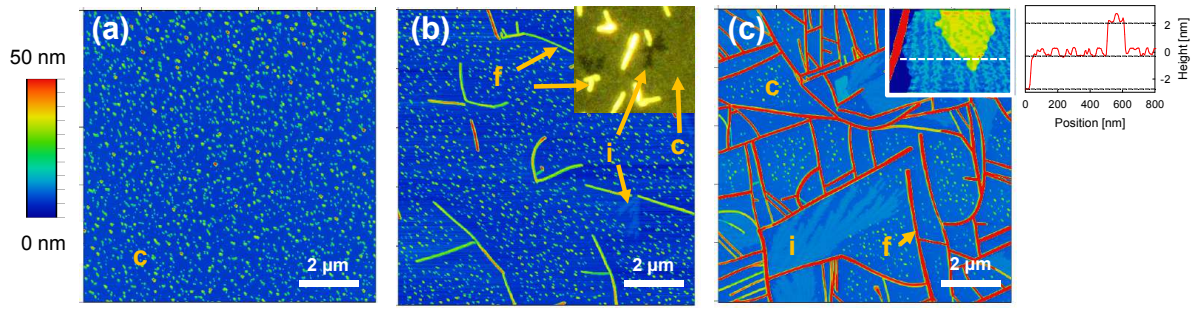

Figure S1: AFM images of NaT3 deposited on muscovite mica at an elevated temperature of $T_{\mathrm{sub}} = 377\,\mathrm{K}$ consisting of clusters ("c"), flat islands ("i") and fibers ("f"). The nominal thickness is increasing from left to right: $d = 0.75\,\mathrm{nm}$, $1.5\,\mathrm{nm}$, and $7.5\,\mathrm{nm}$. The fluorescence microscope inset in (b) demonstrates that flat islands appear as dark areas and are thus consisting of upright standing molecules. Note the 0.5 nm tall branch-like structures on the flat islands, visible in the inset in (c) together with a height profile along the red, solid line. The dashed horizontal lines denote the distance between NaT3 (3 0 0) planes.

For flat islands sub-nanometer step heights have been observed in previous work for, e.g., α-sexithiophene[1]. Here they are observed for all molecules. For NaT3 in the inset in Fig. S1(c) they are visible as branchlike structures on top of the flat islands, having a height of 0.5 nm. Several elementary step heights are observed for NaT3 islands: 0.5 nm, 1.9 nm, and 2.4 nm. The minimum step height for standing molecules in the bulk crystal structure is the distance between NaT3 (3 0 0) planes, i.e. 2.464 nm. This corresponds to the horizontal lines in the cross section in Fig. S1(c) and suggests a mixture of upright and lying molecules on the surface since patches of 0.5 nm height are even found on the bare substrate.

Polarization analysis

Angles for maximum polarization, local fiber orientation, and local orientational angles for all six investigated molecules are collected in Tab. S1.

Table S1: Orientation and polarization angles of naphthyl-thiophene nanofibers and of their methoxy-functionalized siblings on muscovite mica, and for NaT3 on phlogopite mica (P). The orientational angle θ_{orient} and the polarization angle ϕ_{pol} are measured with respect to muscovite $\langle 1\,1\,0\rangle_{\text{g}}$ or with respect to one of the hs-directions for phlogopite. The error bars are deduced from measurements on several samples.

molecule	θ_{orient} [°]	ϕ_{pol} [°]	β_{mol} [°]
NaT	$\pm 30 \pm 3$	$\mp 60 \pm 3$	90 ± 2
NaT2	$\pm 8 \pm 2$	$\mp 58 \pm 5$	66 ± 4
	$\pm 55 \pm 2$	$\mp 68 \pm 5$	59 ± 5
NaT3	$\pm 14 \pm 4$	$\mp 60 \pm 6$	74 ± 5
	$\pm 47 \pm 3$	$\mp 68 \pm 4$	66 ± 5
MONaT	$\pm 17 \pm 3$	$\mp 67 \pm 3$	85 ± 3
MONaT2	$\pm 20 \pm 3$	$\mp 67 \pm 5$	90 ± 4
	$\pm 22 \pm 5$	$\mp 67 \pm 5$	45 ± 5
	$\pm 65 \pm 9$	$\mp 67 \pm 5$	45 ± 5
MONaT3	$\pm 0 \pm 4$	$\mp 90 \pm 4$	90 ± 3
	$\pm 25 \pm 4$	$\mp 64 \pm 6$	90 ± 4
NaT3/P	$\pm 12 \pm 5$	$\mp 60 \pm 6$	70 ± 5
	$\pm 48 \pm 5$	$\mp 60 \pm 6$	70 ± 5
	$\pm 73 \pm 5$	0 ± 6	70 ± 5
	$\pm 30 \pm 5$	$\mp 60 \pm 6$	90 ± 5

Phlogopite is a trioctahedral mica, missing the grooves along the $\langle 1\,1\,0\rangle$ directions. Because of this no reason exists that the molecules align just along two of the hs-directions. This is in fact demonstrated in Fig. S2. Six peaks in the orientational distribution within 180° are observed, but also three peaks for the polarization maxima. These peaks are along the three phlogopite hs-directions, showing that the molecules also align along these directions. The correlation plots reveal that the orientational angle is $\beta_{\text{mol}} = 70° \pm 5°$, i.e. between the two orientations on muscovite. Whether this is an averaging effect of the two different fiber types observed on muscovite obscured by the experimental error, or whether really fibers with a slightly different contact plane are observed cannot be decided due to

the experimental error.

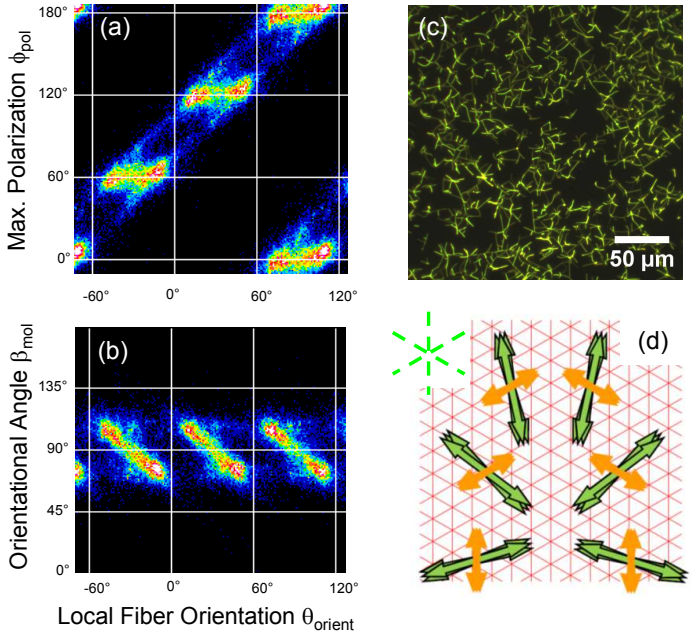

Figure S2: Correlation plots for NaT3 on phlogopite mica. The fluorescence microscope image is presented in (c). In (a) the correlation between the polarization angle ϕ_{pol} and the local fiber orientation θ_{orient} is shown. The brighter the color (black $\rightarrow$ blue $\rightarrow$ red $\rightarrow$ white), the more pixels from the analyzed polarization image sequence apply to this combination of parameters. The vertical and horizontal lines denote the substrate high-symmetry directions. In (b) the correlation between the orientational angle β_{mol} and the local fiber orientation is shown. Again, vertical lines depict substrate high-symmetry directions. In (d) a sketch of the transition dipoles (thin orange arrows) and fiber directions (bold green arrows) is presented. Experimental errors are denoted by tripled arrows. The substrate hs-directions are marked in the upper left corner.

Fluorescence spectroscopy

The peaks in the fluorescence spectra are labeled (00), (01), (02), etc., relating to the excitonic notation for transitions between the vibrational ground state of the S_1 electronic state and different vibrational states of the electronic ground state S_0. Their positions are given in Tabs. S2 and S3.

Table S2: Band positions for emission spectra of the different observed components of thin films of naphthyl end-capped oligothiophene aggregates. Error bars for the transition energies are ±0.015 eV.

molecule	E_{00} [eV]	E_{01} [eV]	E_{02} [eV]	E_{03} [eV]	E_{04} [eV]	E_{05} [eV]
NaT-I	2.96	2.80	2.62	2.45	2.27	2.09
NaT-II	2.92	2.73	2.55	2.37	2.20	
NaT2-I	2.60	2.41	2.23	2.04	1.86	
NaT2-II	2.53	2.32	2.14	1.96		
NaT2-III	2.48	2.28	2.09			
NaT3-I	2.40	2.23	2.05	1.88		
NaT3-II	2.36	2.18	2.01			
NaT3-III	2.28	2.10	1.93			

Table S3: Band positions for emission spectra of the different observed components of thin films of methoxy-functionalized naphthyl end-capped oligothiophene aggregates. Error bars for the transition energies are ±0.015 eV.

molecule	E_{00} [eV]	E_{01} [eV]	E_{02} [eV]	E_{03} [eV]
MONaT-I	2.63	2.46	2.27	2.08
MONaT-II	2.56	2.36	2.18	
MONaT2-I	2.47	2.31	2.12	1.94
MONaT2-II	2.51	2.35	2.18	2.00
MONaT2-III	2.58	2.42	2.24	2.06
MONaT3-I	2.41	2.21	2.04	1.86
MONaT3-II	2.28	2.10	1.93	

Experimental

Scheme S3 depicts the synthesis of NaT3 and MONaT3.

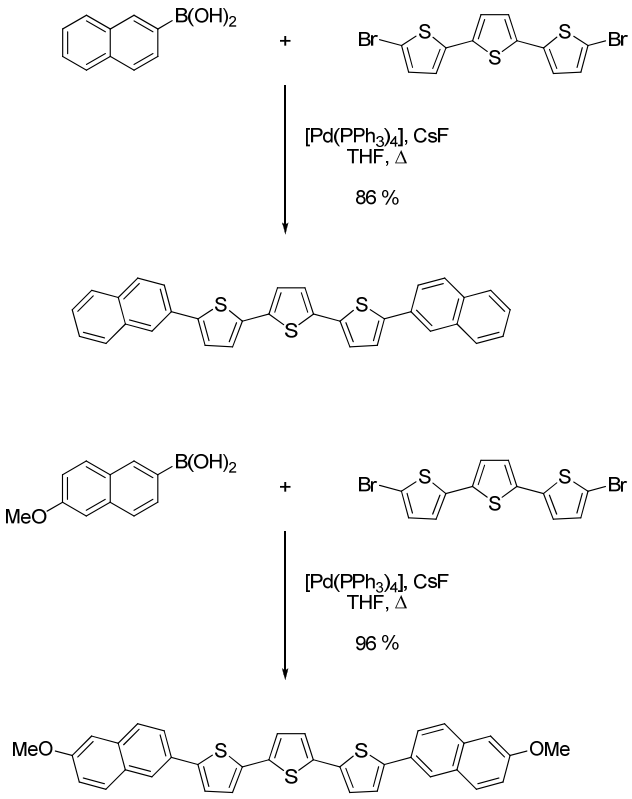

Figure S3: Synthesis of NaT3 and of MONaT3.

References

(1) Kankate, L.; Balzer, F.; Niehus, H.; Rubahn, H.-G. Organic nanofibers from thiophene oligomers. *Thin Solid Films* **2009**, *518*, 130 – 137.