Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supplementary Information. Assembly of Diverse Molecular Aggregates With a Single, Substrate-Directed Molecule Orientation

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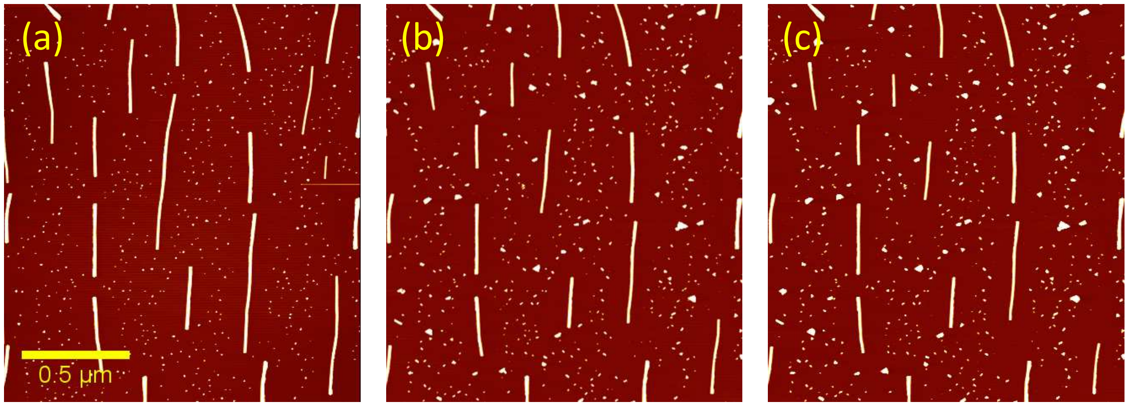

Figure S1: Aging of CNP4 fibers and clusters (nominal film thickness $d = 1.6\,\mathrm{nm}$) grown on muscovite mica at $T_s = 323\,\mathrm{K}$. The AFM images show the same sample area (a) 67 minutes, (b) 4505 minutes, and (c) 8143 minutes after transfer from vacuum to ambient conditions.

Fibers are less stable than wings under ambient conditions, especially fibers representing a sample with a small nominal thickness. In Figure S1 AFM images are shown for a CNP4 sample (nominal thickness 1.6 nm, mean fiber hight 25 nm) grown on muscovite mica, after transfer from the deposition system to ambient conditions. A few minutes (a) after transfer only fibers and many clusters are visible. Within days, (b) and (c), the clusters become larger but decrease in umber, and wings start to form, whereas the fibers shorten. Fibers are more stable for thicker samples, but the disappearance of clusters together with the growth of wings is still observed. A movie of this aging process is provided.[1] Here, the length of the white bar in the upper left is proportional to the time after removal of the sample from the vacuum chamber. The total timespan is 136 hours.

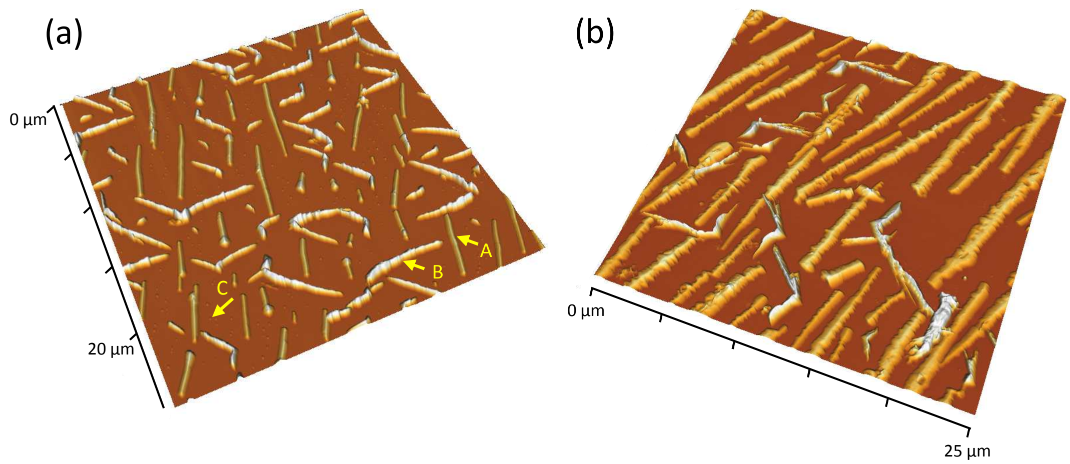

Figure S2: AFM images of CNP4 aggregates grown on muscovite mica. (a) The height of the triangular shaped fibers is about 100 nm, the nominal film thickness 10 nm. Letters mark different aggregate types. (b) After contact with water, fibers have facetted. The nominal thickness of the film is 70 nm.

In a three-dimensional representation of an AFM image of CNP4 deposited on muscovite mica, the different morphologies of aggregates growing along $\langle 1\,1\,0\rangle_{g}$ ("A"), and along the other two directions [1 0 0] and $\langle 1\,1\,0\rangle_{ng}$ ("B") are visible, Figure S2(a). In addition, small clusters "C" are observed in between. Contact with water for wet-transfer leads to an increased facetting of the fibers, Figure S2(b). The width of the fibers in (b) is larger than in (a) due to the larger nominal thickness of the sample.

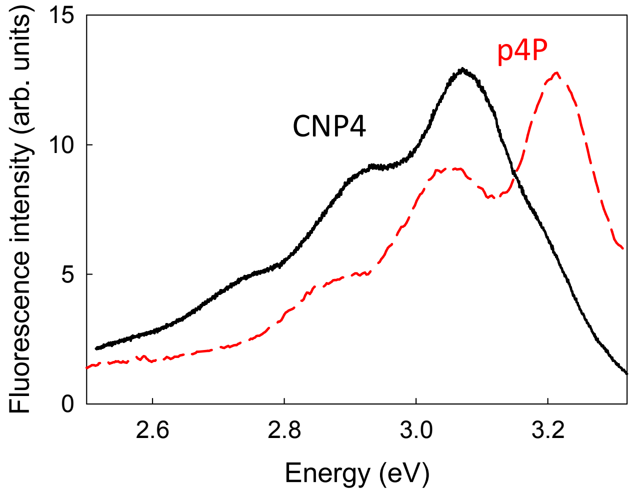

Figure S3: Fluorescence spectra of CNP4 aggregates (black solid line) and *p*-4P fibers (red dashed line) deposited on muscovite mica. Excitation wavelengths are $\lambda_{\text{exc}} = 325\,\text{nm}$ and $365\,\text{nm}$, respectively.

A typical fluorescence spectrum after UV excitation of a thin CNP4 film, deposited on muscovite mica, is shown as a solid line in Figure S3. It is dominated by several excitonic transitions between the first excited state S_1 and the electronic ground state S_0. Compared to the fluorescence spectrum from *para*-quaterphenylene (p4P) fibers grown on muscovite mica, the fluorescence is red-shifted by about 140 meV. Note that both fibers and wings contribute to the spectrum, although the contribution from the wings is stronger due to their brighter fluorescence.

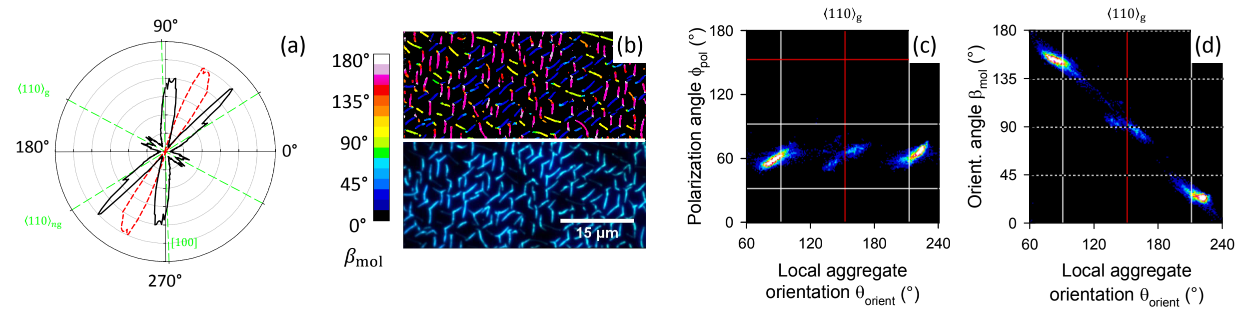

Figure S4: (a) Orientational (solid black line) and polarization (dashed red line) analysis of CNP4 aggregates grown on muscovite mica. The lower part of (b) shows an unpolarized fluorescence microscope image of CNP4 aggregates; in the upper part the molecular angle β_{mol} is superimposed. Correlation plots (c) and (d) demonstrate the relations between the quantities. Solid white lines mark muscovite high-symmetry directions, red lines the grooved muscovite direction. The nominal sample thickness is $d = 8\,\mathrm{nm}$, deposition temperature $T_s = 320\,\mathrm{K}$.

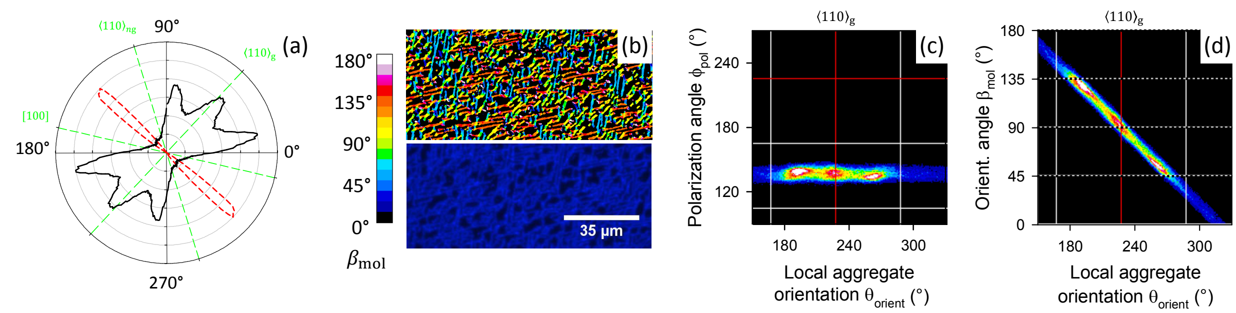

Figure S5: The same as Figure S4, but for a sample with a nominal thickness of 100 nm and deposition temperature $T_s = 320\,\mathrm{K}$.

Polarization and orientational analysis together with correlation plots of a thin (nominal thickness $d = 8\,\mathrm{nm}$, Figure S4) and a thick (nominal thickness $d = 100\,\mathrm{nm}$, Figure S5) CNP4 sample reveals similar results as for the one presented in the main text, Figures 4 and 5. The angle of the wings with respect to $\langle 1\,1\,0\rangle_{\mathrm{g}}$ varies in between the samples, whereas the emitted fluorescence is always polarized perpendicular to $\langle 1\,1\,0\rangle_{\mathrm{g}}$.

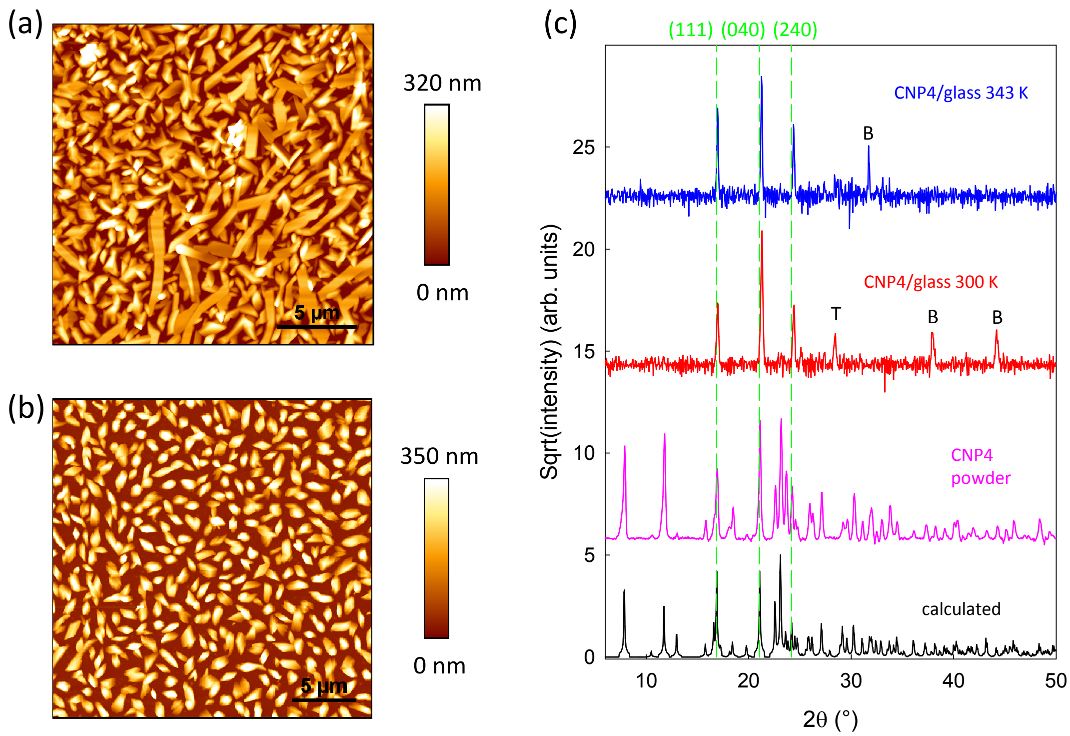

Figure S6: AFM images of CNP4 crystallites grown on glass at (a) room temperature (nominal thickness $d = 80\,\mathrm{nm}$) and (b) at 343 K (nominal thickness $d = 100\,\mathrm{nm}$). The X-ray diffractogram (c) compares measurements on CNP4 powder as well as on the CNP4 films from (a) and (b) with a calculated diffractogram. The three dominant contact planes (1 1 1), (0 4 0), and (2 4 0) are identified; their calculated positions are denoted by dashed vertical lines. Note that the for each of the diffractograms the background from the glass substrate has been subtracted for the ease of comparison. The peak marked as "T" cannot be assigned to any of the bulk diffraction peaks. The peaks marked as "B" are artifacts and stem from different sample holders.

Vacuum deposition of CNP4 on glass does not lead to the formation of aligned fibers and wings, but to a disordered growth of crystallites with the occasional appearance of fibers, Figures S6(a) and (b). Such a behavior is in contrast to the growth of, e.g., MOP4, where mainly islands and films from upright standing molecules form. Higher deposition temperatures lead to taller but more separated crystallites. The X-ray diffractograms presented in Figure S6(c) allow the identification of three main phases, i.e. crystallites with either (1 1 1), (0 4 0), or (2 4 0) as contact planes. All these three contact planes correspond to lying CNP4 molecules on the glass surface. Several small peaks between $2\theta = 27°$ and $30°$, observed for samples deposited at various temperatures such as the one shown at $2\theta = 28.4°$ and marked by a "T", cannot be assigned to any of the bulk CNP4 planes.

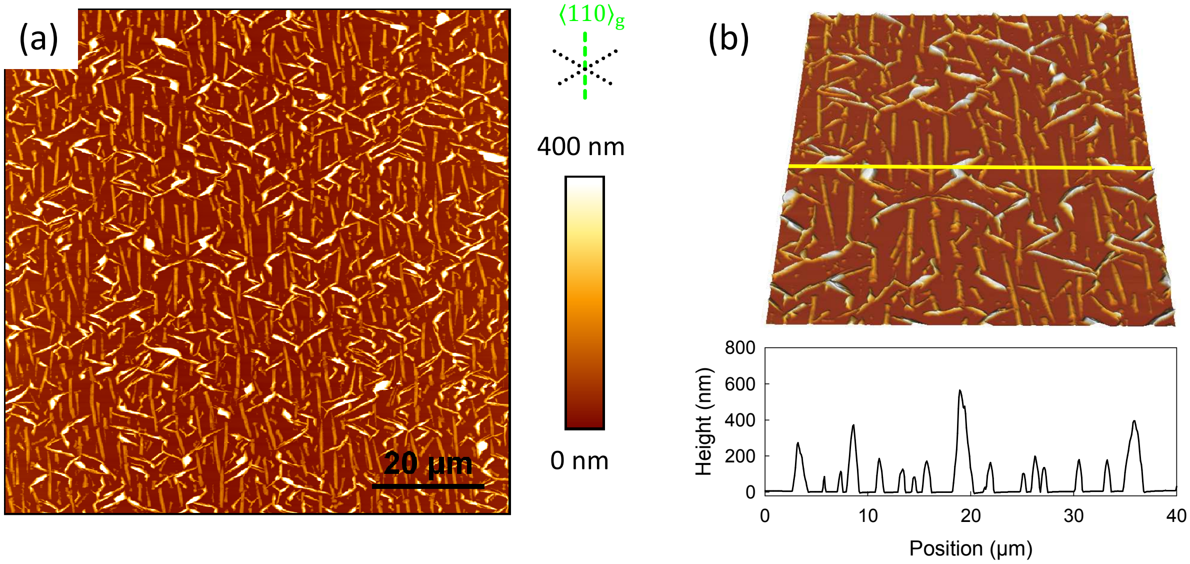

Figure S7: AFM images of CNP4 aggregates from a 60 nm thick sample. The cross section in (b) along the thick yellow line documents the different heights of fibers and wings. Muscovite mica directions are given.

AFM images of nominally 60 nm thick CNP4 samples deposited at 317 K in Figure S7(a) also show the occurrence of fibers and wings. The $\langle 1\,1\,0 \rangle_g$ direction is vertical. In the three-dimensional view as well as in the cross-section along the thick, yellow line triangular shape of the fibers is visible. The average height of the fibers is less than 200 nm, and of the wings of about 400 nm ± 200 nm.

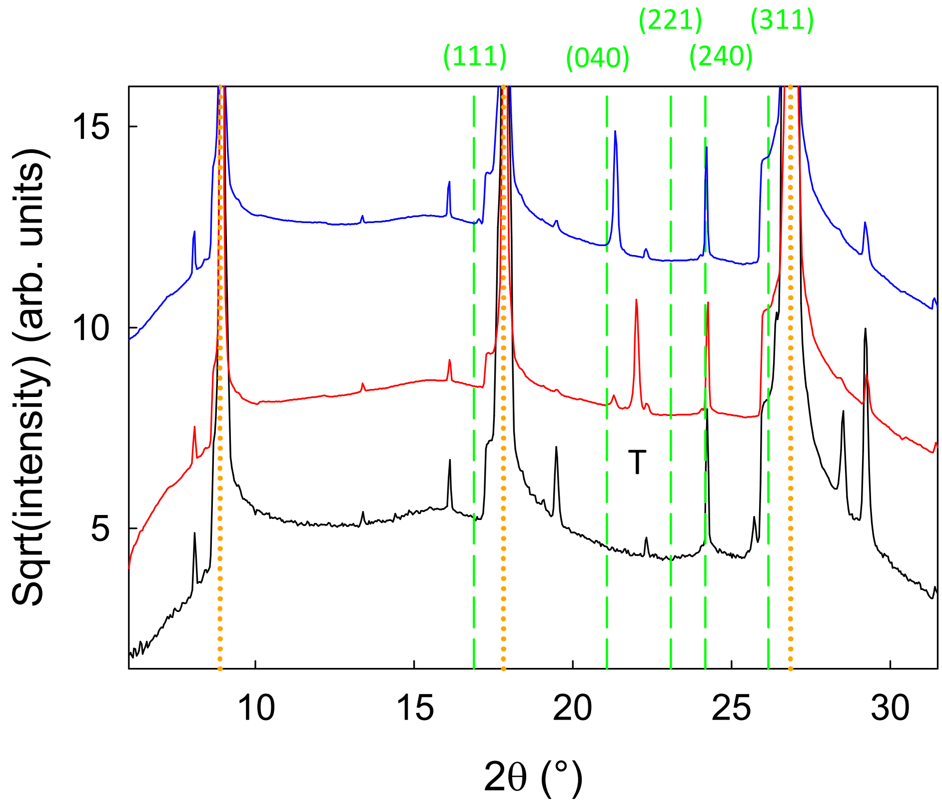

Figure S8: X-ray diffractograms for clean muscovite mica (lower black curve) and for CNP4 deposited on muscovite mica (middle red curve, $d = 50\,\mathrm{nm}, T_\mathrm{s} = 320\,\mathrm{K}$ and upper blue curve, $d = 80\,\mathrm{nm}, T_\mathrm{s} = 340\,\mathrm{K}$). Vertical dashed green lines mark the positions of some of the CNP4 bulk reflections. The "X" denotes a reflection which cannot be related to the CNP4 bulk structure. Dotted orange vertical lines finally mark strong reflections from muscovite mica.

Muscovite mica (0 0 1) shows strong X-ray diffraction peaks, marked by dotted orange lines. Because of this, Cu-K$_\beta$ peaks are also clearly visible, their height being similar to the diffraction peaks from CNP4.

References

(1) Horcas, I.; Fernandez, R.; Gomez-Rodriguez, J.; Colchero, J.; Gomez-Herrero, J.; Baro, A. WSXM: A Software for Scanning Probe Microscopy and a Tool for Nanotechnology. *Rev. Sci. Instrum.* **2007**, *78*, 013705.