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Supporting Information for

Novel Highly Substituted Thiophene-based n-type Organic Semiconductor: Structural Study, Optical Anisotropy and Molecular Control

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Contents

1. Synthesis and molecular structure characterization

All chemicals were purchased from commercial sources and used without further purification. 1-(2,2′-Bithiophen-5-yl)hexane-1-one was prepared by the reported procedure.[1] ^1H and ^{13}C NMR spectra were recorded on Varian VNMRS (600 MHz for ^1H, 151 MHz for ^{13}C) in chloroform-d_1 ($CDCl_3$), with $SiMe_4$ as an internal standard. IR spectra were determined with Agilent Cary 630 FTIR spectrometer. HRMS analysis was recorded on an Orbitrap Elite (Thermo Scientific) with ESI ionization and melting points were obtained with a Melting Point M-656 Büchi apparatus and are reported uncorrected.

1-[5'-(Naphthalen-2-yl)-2,2'-bithiophen-5-yl]hexan-1-one (NCOH)

1-(5'-Bromo-2,2'-bithiophen-5-yl)hexan-1-one (664 mg, 1.94 mmol), 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene (590 mg, 2.32 mmol, 1.2 equiv.) and $Pd(PPh_3)_4$ (224 mg, 0.194 mmol, 0.1 equiv.) were placed into two-necked flask and degassed toluene (19 mL) was added. Then, 1 M solution of Na_2CO_3 (19 mL, 10 equiv.) was added and the reaction mixture was stirred under reflux for 24 hours. After cooling, the precipitate was formed. Precipitate was filtered off and washed with water and hexanes. Precipitate was dissolved in chloroform and filtered through a silica pad. Solvent was evaporated and the product was obtained as yellow solid (610 mg, 81%). M. p. = 190.8–192.1 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.87 (d, J = 8.3 Hz, 2H), 7.83 (d, J = 7.9 Hz, 1H), 7.74 (dd, J = 8.5, 1.7 Hz, 1H), 7.63 (d, J = 3.9 Hz, 1H), 7.50 (ddd, J = 14.8, 13.5, 6.7 Hz, 2H), 7.39 (d, J = 3.8 Hz, 1H), 7.34 (d, J = 3.8 Hz, 1H), 7.22 (d, J = 3.9 Hz, 1H), 2.88 (t, J = 7.5 Hz, 2H), 1.81–1.74 (m, 2H), 1.43–1.35 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 193.2, 145.4, 145.3, 142.3, 135.7, 133.5, 133.0, 132.6, 131.0, 128.7, 128.1, 127.7, 126.8, 126.6, 126.3, 124.4, 124.3, 123.9, 123.9, 39.0, 31.5, 24.7, 22.5, 13.9 ppm. FTIR (solid): υ 2956, 2927, 1649, 1436, 794 cm^{-1}. HRMS (pESI): m/z $[M + H]^+$ for $C_{24}H_{23}OS_2H$: calculated 391.1192, found 391.1185.

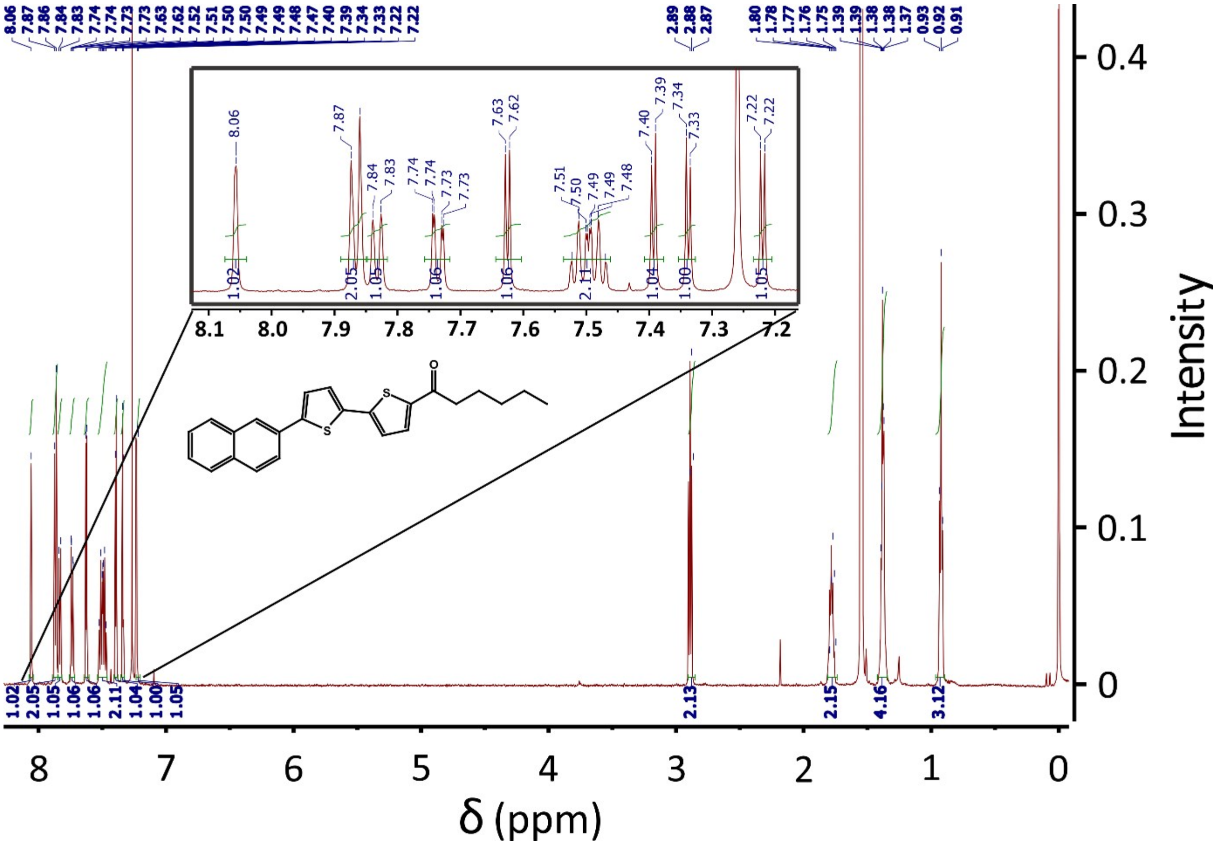

Figure S1. ^{1}H NMR (600 MHz, $CDCl_3$) of 1-[5'-(naphthalen-2-yl)-2,2'-bithiophen-5-yl]hexan-1-one (NCOH).

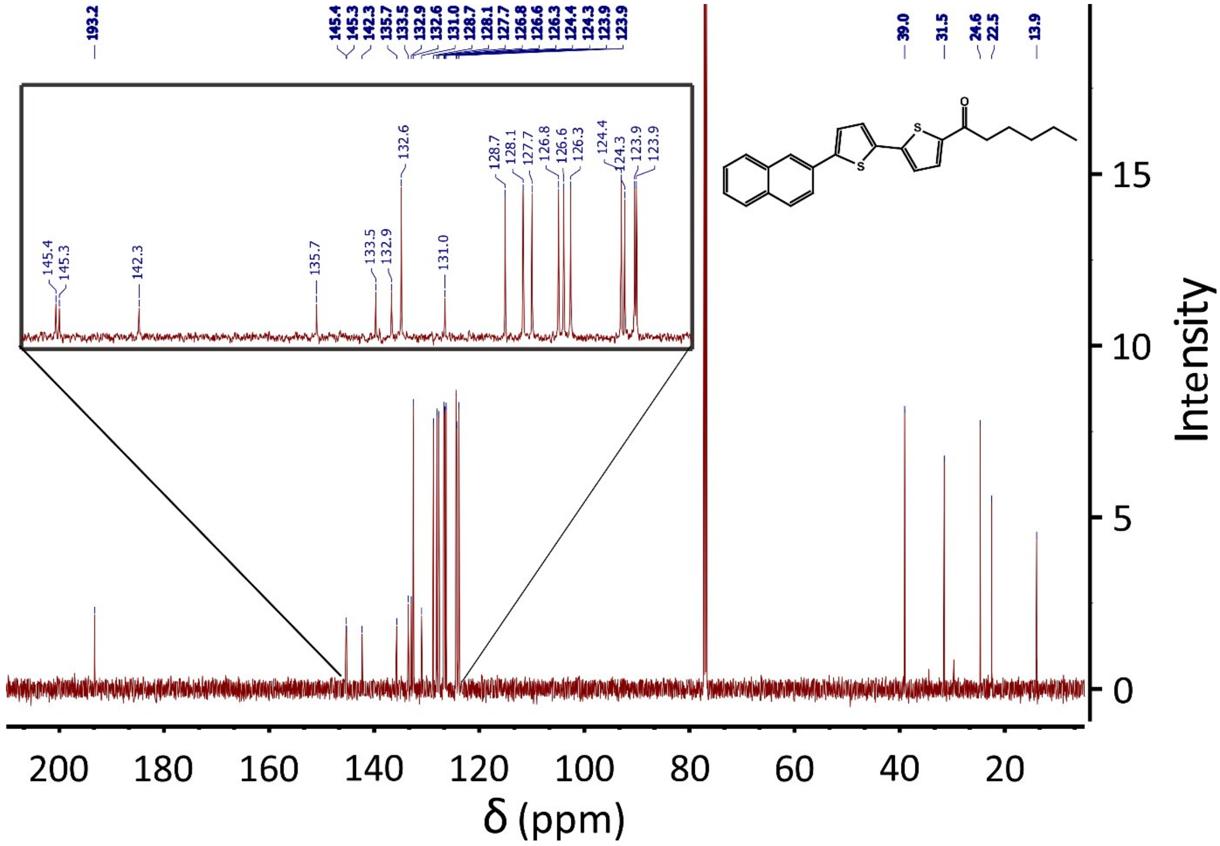

Figure S2. ^{13}C NMR (151 MHz, $CDCl_3$) of 1-[5'-(naphthalen-2-yl)-2,2'-bithiophen-5-yl]hexan-1-one (NCOH).

1-(5'-Bromo-2,2'-bithiophen-5-yl)hexan-1-one (precursor)

To solution of 1-(2,2'-bithiophen-5-yl)hexan-1-one (2.00 g, 7.56 mmol) in dry DMF (15 mL), NBS (7.56 mmol, 1.35 g) was added portionwise at 0 °C. The reaction mixture was stirred at room temperature for 4 hours. Then, the reaction mixture was poured into a cold water and extracted twice with dichloromethane. Combined organic phases were washed with brine and dried over Na$_2$SO$_4$. After evaporation, the product was obtained as yellow solid (2.10 g, 82%). The product was used in the subsequent synthesis without further purification. M. p. = 95.8–97.5 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.57 (d, J = 4.0 Hz, 1H), 7.09 (d, J = 3.9 Hz, 1H), 7.05 (d, J = 3.9 Hz, 1H), 7.01 (d, J = 3.9 Hz, 1H), 2.87–2.83 (m, 2H), 1.75 (dq, J = 14.8, 7.4 Hz, 2H), 1.39–1.32 (m, 4H), 0.94–0.88 (m, 3H) ppm. ^{13}C NMR (151 MHz, CDCl$_3$): δ 193.2, 144.0, 142.8, 137.8, 132.4, 131.0, 125.5, 124.2, 113.3, 39.0, 31.5, 24.6, 22.5, 13.9 ppm. FTIR (solid): v 2926, 2866, 1648, 1421, 789 cm^{-1}. HRMS (pESI): m/z [M + H]$^+$ for C$_{14}$H$_{15}$BrOS$_2$H: calculated 342.9826, found 342.9821.

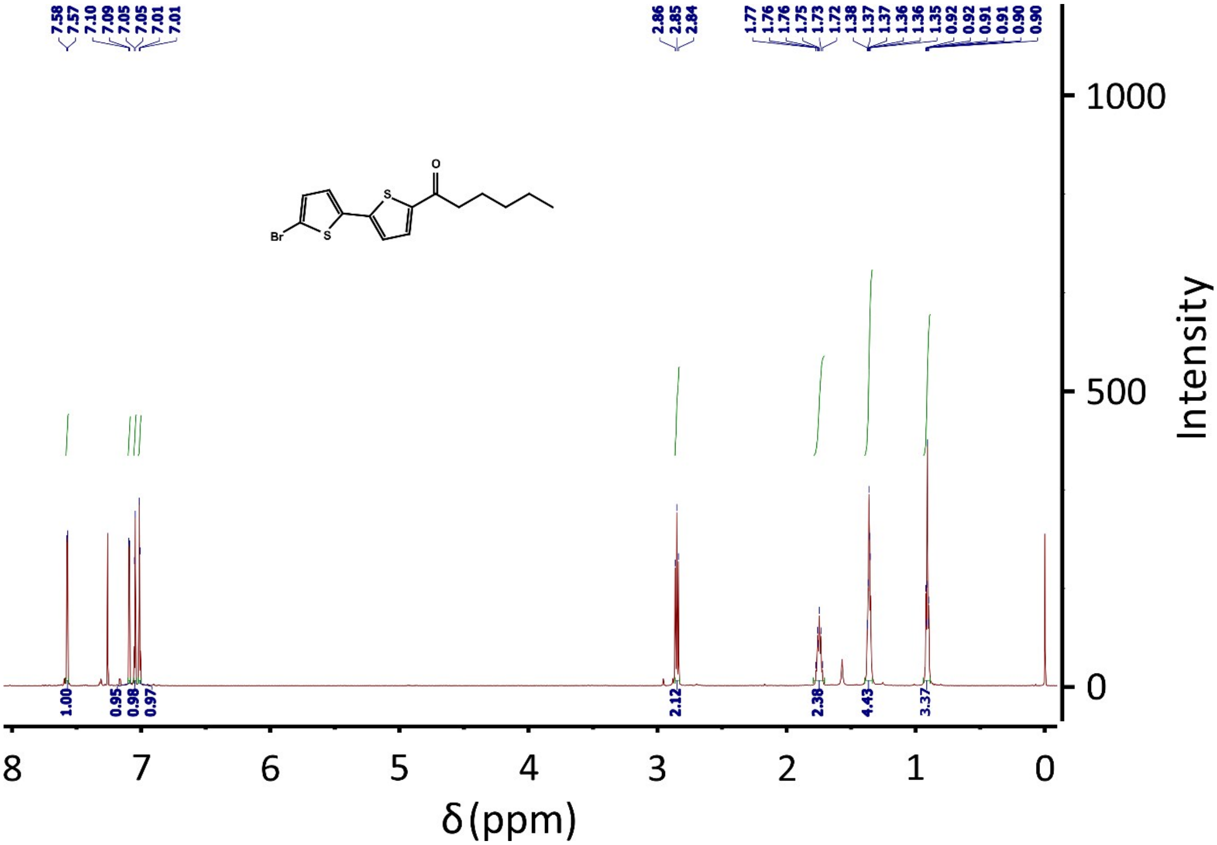

Figure S3. ^{1}H NMR (600 MHz, CDCl$_3$) of 1-(5'-bromo-2,2'-bithiophen-5-yl)hexan-1-one.

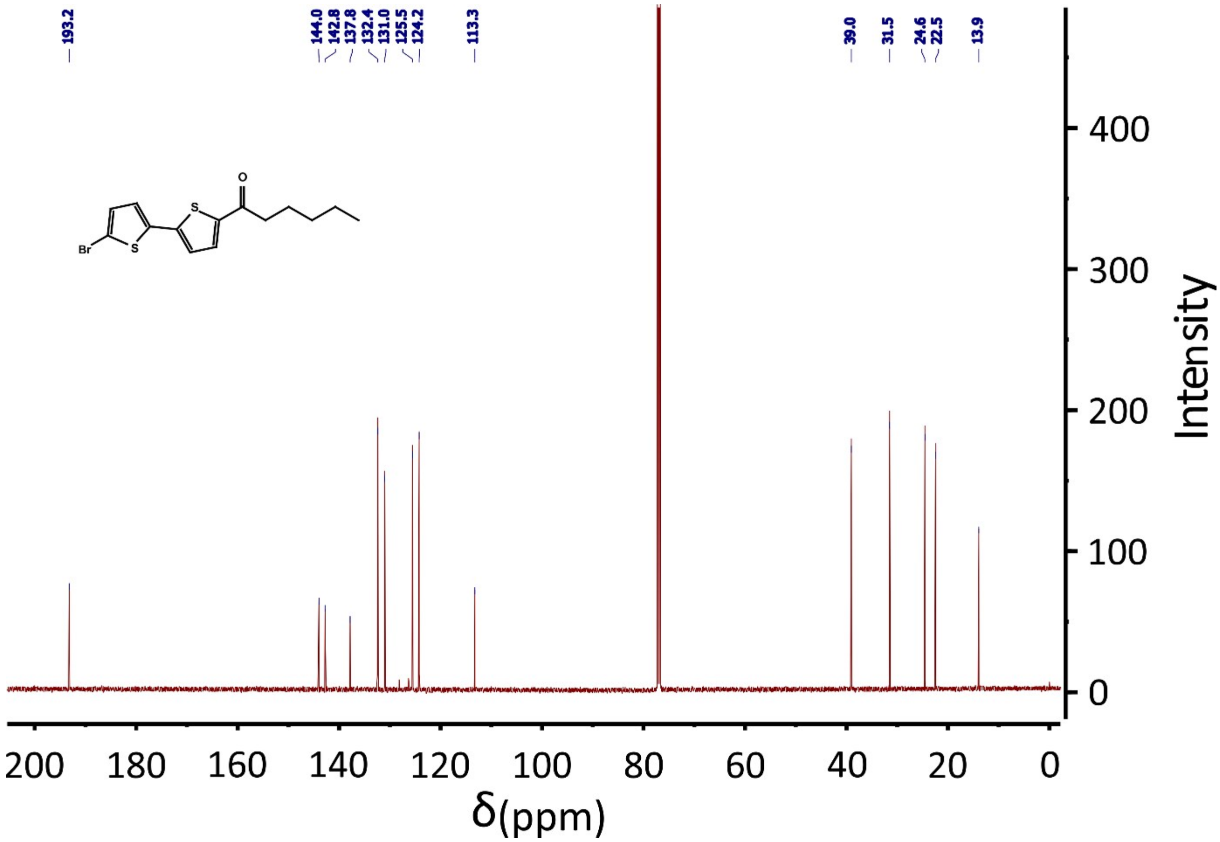

Figure S4. ^{13}C NMR (151 MHz, $CDCl_3$) of 1-(5'-bromo-2,2'-bithiophen-5-yl)hexan-1-one.

In order to confirm the n-type conductivity of the NCOH molecule, we performed the electrochemical impedance spectroscopy (EIS) measurement, in which the electronic density of states (DOS) was mapped,[2] see Fig. S5. From the electronic DOS layout, we were able to determine the position of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), being (-5.9 ± 0.1) eV and (-3.2 ± 0.1) eV, respectively.

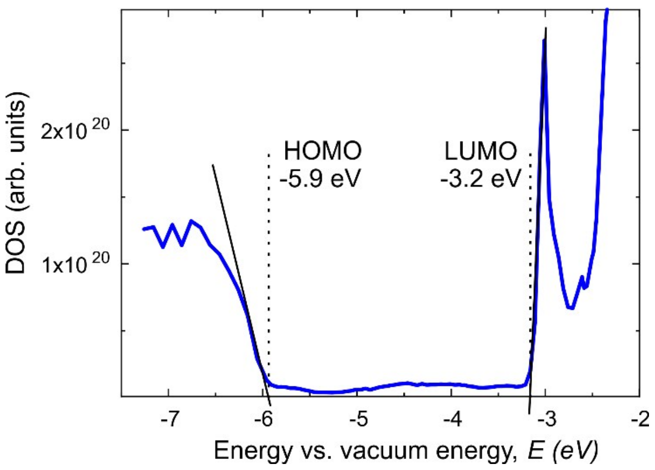

Figure S5. DOS function of NCOH film measured by EIS.

2. GIWAXS of NCOH on Si substrate

Figure S6a shows the same reciprocal space map as in the main text (Fig. 1). Figure 6b shows a reciprocal segment with 110, 111, 201, and 202 diffraction peaks in more detail and without the calculated positions of the diffractions. The shape and the intensity of the measured Bragg peaks are thus clearly visible.

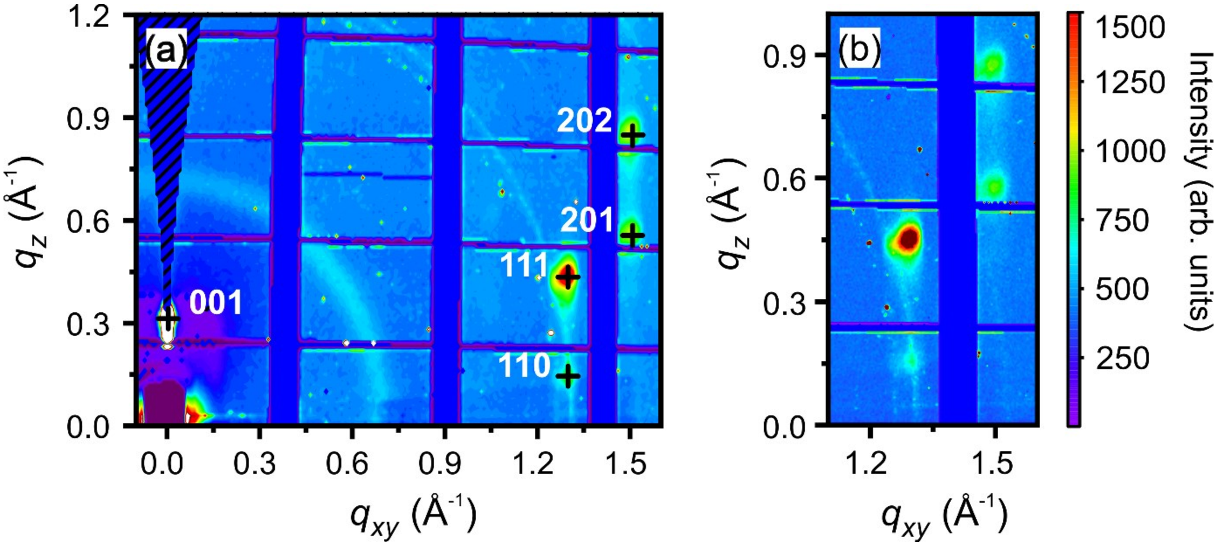

Figure S6: (a) Reciprocal space map of 15 nm thick NCOH thin film on Si substrate. Black crosses indicate the Bragg peak positions calculated from experimentally determined unit cell parameters. (b) A magnified segment of the reciprocal space map in (a), showing the intensity and shapes of the observed Bragg reflections.

3. AFM of NCOH layers on Si substrate

Figure S7 shows the height distribution that was calculated from the AFM image of 25 nm thick NCOH layer on Si substrate (see Fig. 3c in the main text). From the height distribution, we determined the distance between the planar molecular terraces (~ 2 ± 0.6) nm. We note that the error was calculated based on the propagation error theorem)

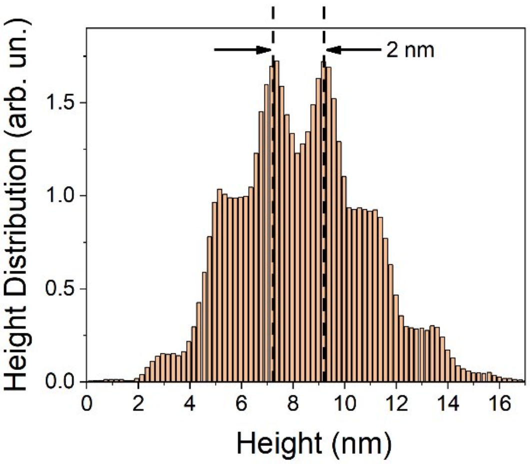

Figure S7. Height distribution obtained from the AFM measured on the 25 nm thick NCOH layer on Si substrate. The distance between the two planar molecular terraces (~ 2 ± 0.6) nm.

4. AFM of NCOH layers on MoS_2 substrates

AFM images of the 30 nm thick NCOH layers deposited on vertically and horizontally aligned MoS_2 substrates are shown in Fig. S8a and Fig. S8b, respectively. In the case of vertically aligned MoS_2 layers, we assume that the molecules grow in the Stranski-Krastanov[3] (layer-plus-island) growth mode, similarly to the growth on Si substrate (see Fig. 3 in the main text). The individual NCOH layers are hard to distinguish because of the grainy surface structure. The surface roughness is in the order of several nanometers.[4] On the other hand, for the molecules deposited on the horizontally aligned MoS_2, we observed an island-type growth, *i.e.*, the Volmer-Weber[3] growth mode.

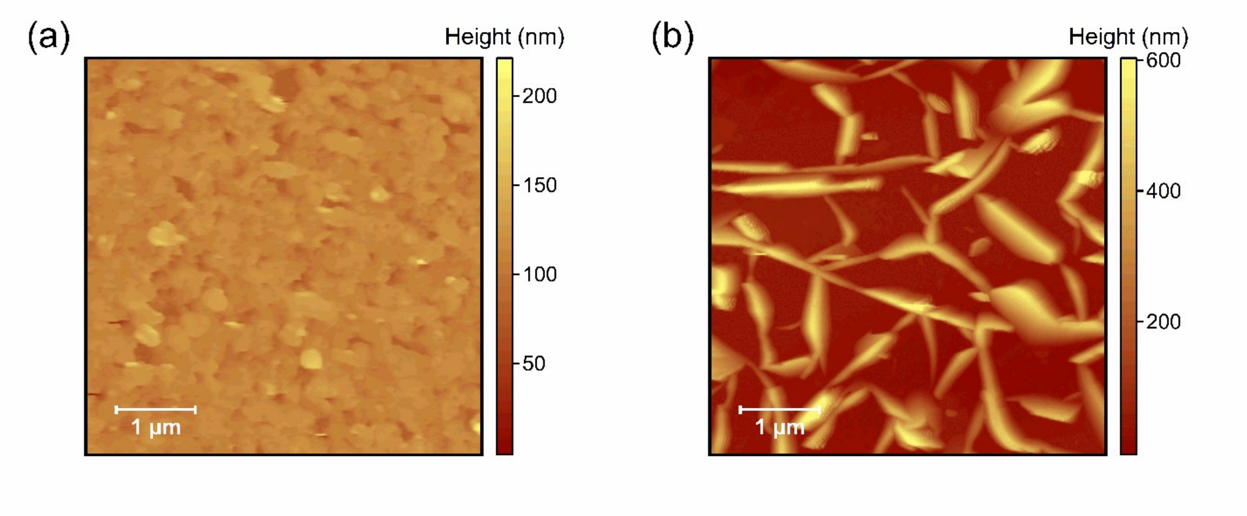

Figure S8. AFM images of 30 nm thick NCOH thin film grown on (a) vertically aligned (b) horizontally aligned MoS_2 substrate.

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