ADVANCED FUNCTIONAL MATERIALS

# Supporting Information

for *Adv. Funct. Mater.*, DOI: 10.1002/adfm.201001940

Uniform π-System Alignment in Thin Films of Template-Grown Dicarbonitrile-Oligophenyls

Florian Klappenberger, * Dirk Kühne, Matthias Marschall, Stefan Neppl, Wolfgang Krenner, Alexei Nefedov, Thomas Strunskus, Karin Fink, Christof Wöll, Svetlana Klyatskaya, Olaf Fuhr, Mario Ruben, and Johannes V. Barth

Submitted to ADVANCED FUNCTIONAL MATERIALS

**Supporting Information**

# Uniform π-system Alignment in Thin Films of Template-Grown Dicarbonitrile-Oligophenyls

*By* Florian Klappenberger*, Dirk Kühne, Matthias Marschall, Stefan Neppl, Wolfgang Krenner, Alexei Nefedov, Thomas Strunskus, Karin Fink, Christof Wöll, Svetlana Klyatskaya, Olaf Fuhr, Mario Ruben, and Johannes V. Barth

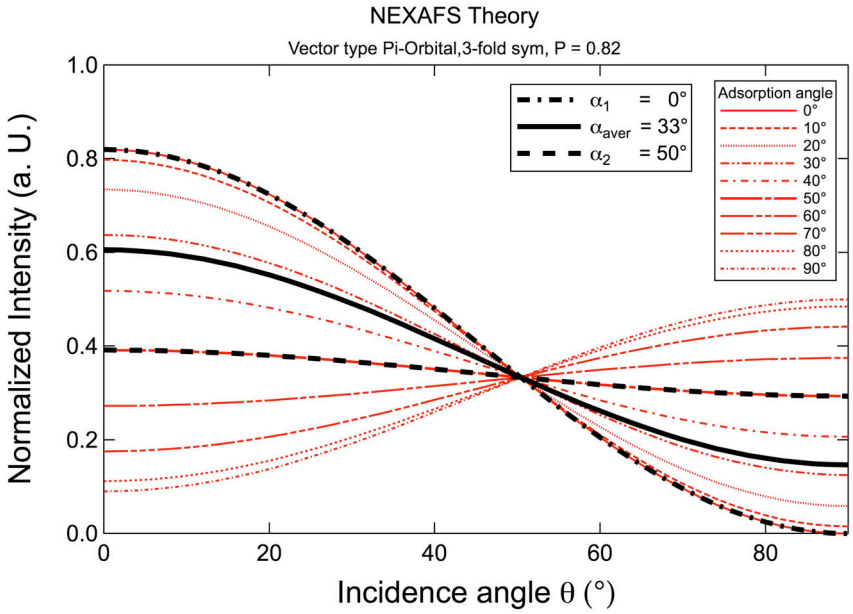


**Figure SI1.** Theoretic curves (red lines) for NEXAFS intensities for a π*-resonance with an adsorption angle α as defined in Scheme 3 and given in the legend. Due to the three-fold (or higher) symmetry all curves cross at a single point defining the magic angle. With the present polarization (P = 0.82) of the X-ray beam the magic angle amounts to ~ 50°. The line expected for the situation in which half of the phenyl rings feature $\alpha_1 = 0°$ and the other half features $\alpha_2 = 50°$ indicates $\alpha_{aver} = 33°$. It was obtained by averaging the corresponding intensities $I_{aver}(\theta) = 0.5\,[I_1(\theta) + I_2(\theta)]$.

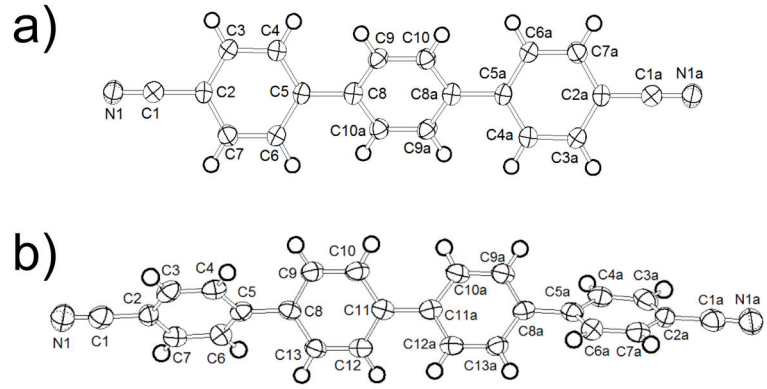


**Figure SI2.** a) Atomic labeling and displacement ellipsoids of NC-$Ph_3$-CN (Compound **1**) as obtained by X-ray structure analysis. b) Atomic labeling and displacement ellipsoids of NC-$Ph_4$-CN (Compound **2**) as obtained by X-ray structure analysis.

**Table SI1.** Overview of bulk properties of NC-$Ph_3$-CN (Compound **1**) measured at T = 180 K and NC-$Ph_4$-CN (Compound **2**) measured at T = 180 K and T = 293 K and parameters of X-ray crystal structure analysis.

| Data | Compound **1** | Compound **2** (low temp) | Compound **2** (room temp) |
|---|---|---|---|
| empirical formula | $C_{20}H_{12}N_2$ | $C_{26}H_{16}N_2$ | $C_{26}H_{16}N_2$ |
| formula weight | 280.32 g/mol | 356.41 g/mol | 356.41 g/mol |
| Temperature | 180 K | 180 K | 293 K |
| crystal system | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/n$ (14) | $C2/c$ (15) | $C2/c$ (15) |
| unit cell dimensions | a=389.3(1) pm<br>b=1195.5(2) pm<br>c=1497.5(3) pm<br>β=97.02(3)° | a=1628.9(3) pm<br>b=1674.9(3) pm<br>c=743.9 (2) pm<br>β=113.20(3)° | a=1633.7(3) pm<br>b=1685.5(3) pm<br>c=748.45 (15) pm<br>β=112.20(3)° |
| Volume | 691.7(2) · $10^6$ $pm^3$ | 1865.4(6) · $10^6$ $pm^3$ | 1901.5(7) · $10^6$ $pm^3$ |
| number of molecules per unit cell *Z* | 2 | 4 | 4 |
| calculated density | 1.346 g/$cm^3$ | 1.269 g/$cm^3$ | 1.245 g/$cm^3$ |
| $\mu$ | 0.080 $mm^{-1}$ | 0.075 $mm^{-1}$ | 0.073 mm^-1 |
| *F*(000) | 292 | 744 | 744 |
| crystal size | 0.28 × 0.03 × 0.02 $mm^3$ | 0.29 × 0.04 × 0.03 $mm^3$ | 0.15 × 0.03 × 0.02 $mm^3$ |
| $\theta$ range for data collection | 2.19° – 25.70° | 2.43° – 25.79° | 1.81° – 25.61° |
| reflections collected/unique | 2827 / 1287 [$R_{int}$ = 0.0745] | 3307 / 1671 [$R_{int}$ = 0.1169] | 3679 / 1768 [$R_{int}$ = 0.0649] |
| restraints/parameters | 0 / 101 | 0 / 128 | 0 / 128 |
| reflections with I > 2$\sigma$(I) | 702 | 800 | 1117 |
| Extinction coefficient | 0.027(5) | 0.0043(14) | 0.012(2) |
| largest diff. peak and hole | 0.210/–0.179 e $Å^{-3}$ | 0.179/–0.179 e $Å^{-3}$ | 0.137/–0.134 e $Å^{-3}$ |
| goodness-of-fit on $F^2$ | 0.991 | 0.999 | 0.916 |
| final R indices [$I > 2\sigma(I)$] | R1 = 0.0637, wR2 = 0.1071 | R1 = 0.0830, wR2 = 0.1539 | R1 = 0.0436, wR2 = 0.1085 |
| *R* indices (all data) | R1 = 0.1311, wR2 = 0.1274 | R1 = 0.1696, wR2 = 0.1892 | R1 = 0.0769, wR2 = 0.1214 |
| CCDC number | 752434 | 752435 | |

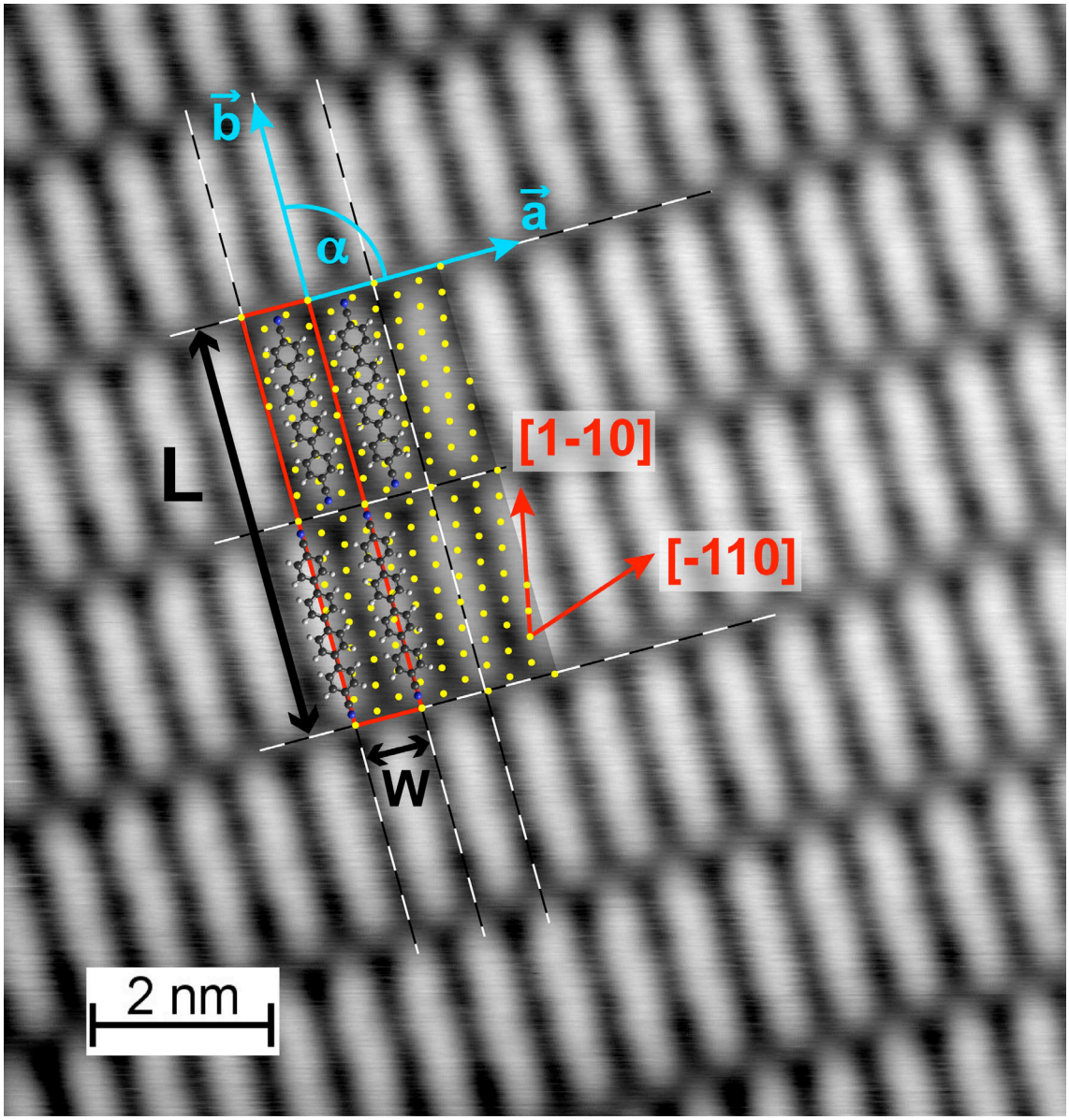


**Figure SI3.** STM image of the saturated monolayer of **2** grown at RT and imaged at 8 K. Molecules appear as bright stick-like features of approximately 2.1 nm. The tentative epitaxy model is shown with the unit cell (red) and the atoms (yellow) of the underlying Ag(111) substrate.

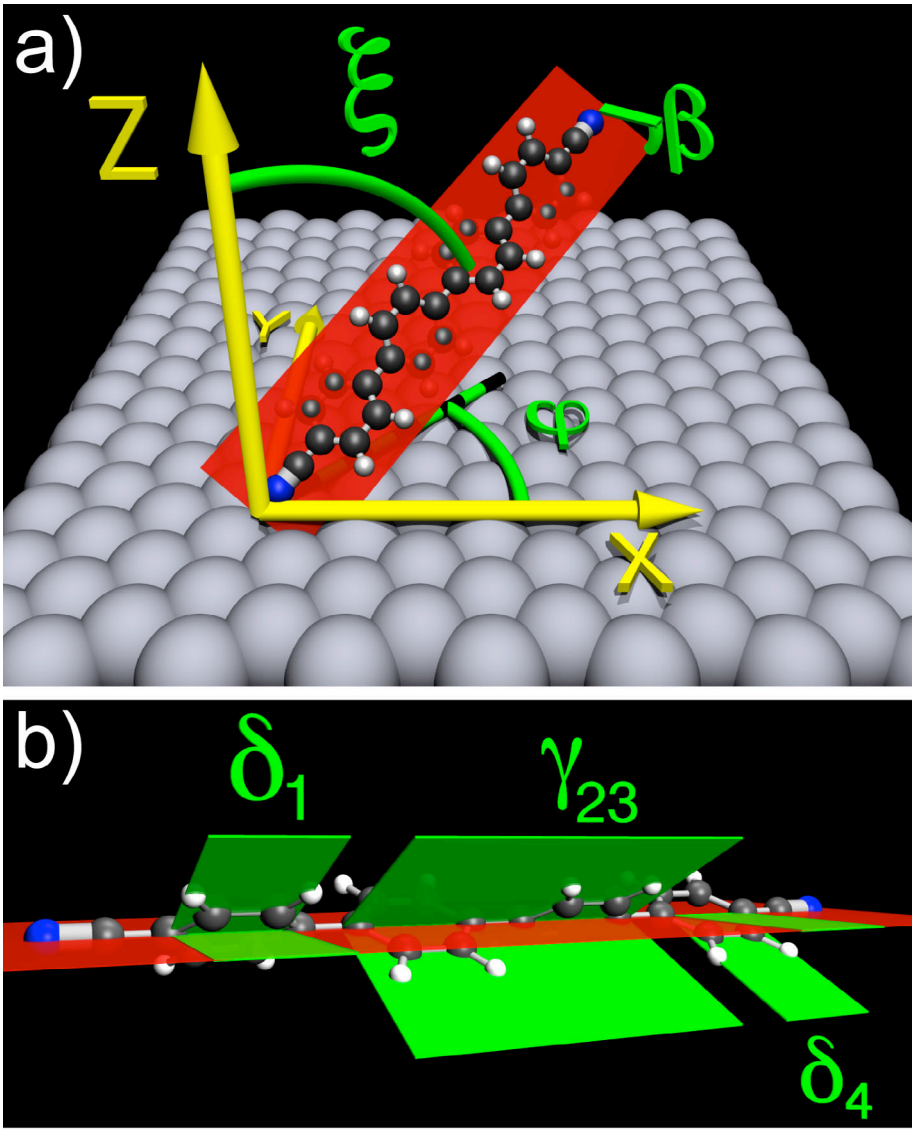


**Figure SI4.** Color version of Scheme 2.

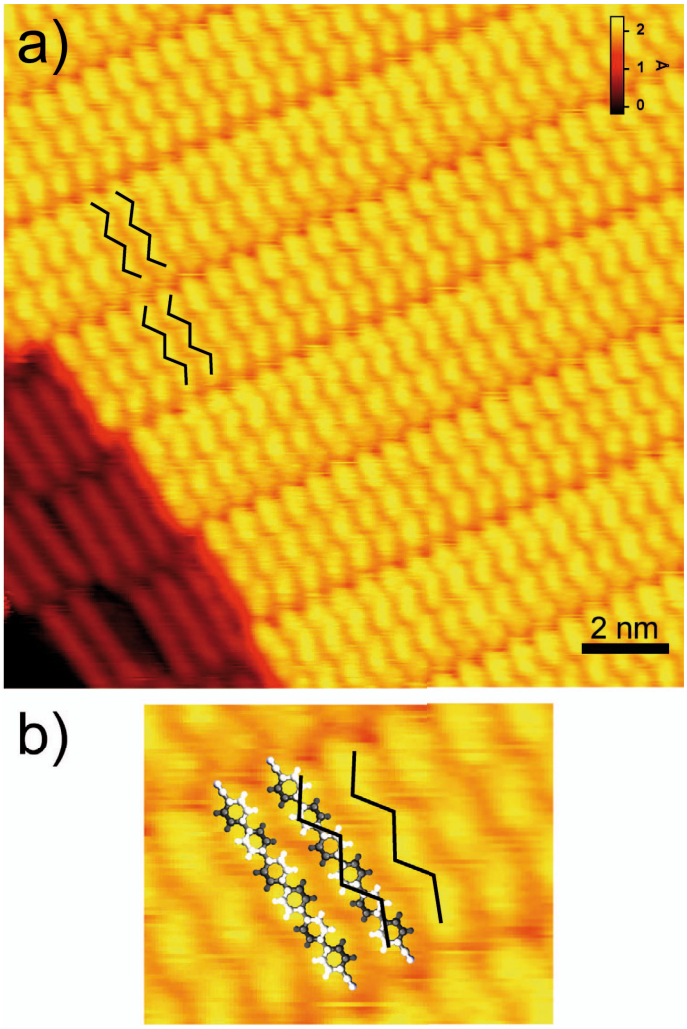


**Figure SI5.** Color version of Figure 11.