

Influence of Molecular Geometry on Adsorption Orientation for Oligo-phenylene-ethynelenes on Au(111)

Sigrid Weigelt[†], Carsten Busse^{†,§}, Morten Nielsen[‡], Kurt V. Gothelf[‡], Flemming Besenbacher[†], and Trolle R. Linderoth^{*,†}

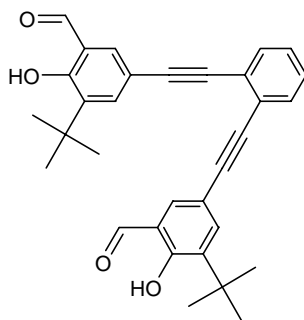
Interdisciplinary Nanoscience Center (iNANO) and [†]Department of Physics and Astronomy or [‡]Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark.

[§] Present address: II. Physikalisches Institut, Universität zu Köln, D-50937 Köln, Germany.

SUPPORTING INFORMATION

ORGANIC SYNTHESIS FOR THE ORTHO-MOLECULE

1,2-Bis[(5-*t*-butyl-3-formyl-4-hydroxyphenyl)ethynyl]benzene



Standard Schlenk and vacuum line techniques were employed using argon as the inert atmosphere for all manipulations of air- or moisture-sensitive compounds. Yields refer to isolated chromatographically and spectroscopically homogeneous materials, unless otherwise stated. Commercially available starting materials were used without further purification. Solvents were dried according to standard procedures. Purification of the products was carried out by flash chromatography (FC) using Merck silica gel 60 (230-400 mesh). ¹H and ¹³C NMR spectra were recorded at 400 and 100 MHz, respectively, using CDCl₃ as the solvent and were reported in ppm downfield from TMS (δ = 0) for ¹H NMR and relative to the central CDCl₃ resonance (δ = 77.00) for ¹³C NMR. Mass spectra and high resolution mass spectra were obtained on an LC-TOF spectrometer (Micromass).

Triethylamine was distilled from CaH₂ under argon prior to use. Bis(triphenylphosphine)palladium(II) chloride (Aldrich) were purchased from commercial sources. 1,2-Diethynylbenzene (Boydston *et al. J. Org. Chem.* **2002**, 67, 8812) were synthesized according to literature procedures.

Bis(triphenylphosphine)palladium(II)chloride (50 mg, 0.07 mmol) and copperiodide (15 mg, 0.08 mmol) were stirred in a Schlenk flask under vacuum for 30 min. 5-Iodo-3-*tert*-butylsalicylaldehyde (1.00g, 3.29 mmol), 1,2-diethynylbenzene (200 mg, 1.59 mmol) and NEt₃ (8 mL) and THF (12 mL) were added and the reaction mixture was stirred under argon at room temperature for 18 h. The reaction mixture was poured into 10% aqueous NH₄Cl (25 mL) and extracted with CH₂Cl₂ (3 x 15 mL). The combined organic fractions were washed with water, dried over Na₂SO₄ and concentrated. The crude product was purified by flash chromatography on silica gel (CH₂Cl₂/pentane, 1:1 → 2:1) to yield the product as yellow crystals (756 mg, 97%): mp = 126-127 °C; ¹H NMR (CDCl₃, 400 MHz) δ 1.36 (s, 18H), 7.33 (dd, J = 6.0 Hz, J = 3.2 Hz, 2H), 7.56 (dd, J = 6.0 Hz, J = 3.2 Hz, 2H), 7.62 (d, J = 2.0 Hz, 2H), 7.66 (d, J = 2.0 Hz, 2H), 9.80 (s, 2H), 11.94 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 29.3, 35.2, 87.5, 92.7, 114.5, 120.7, 125.8, 128.4, 132.0, 135.3, 137.3, 139.3, 161.7, 196.8; HRMS (ES) m/z : [M+Na]⁺ calcd for C₃₂H₃₀O₄Na, 501.2042; found, 501.2050.

SUPPLEMENTARY STM IMAGE:

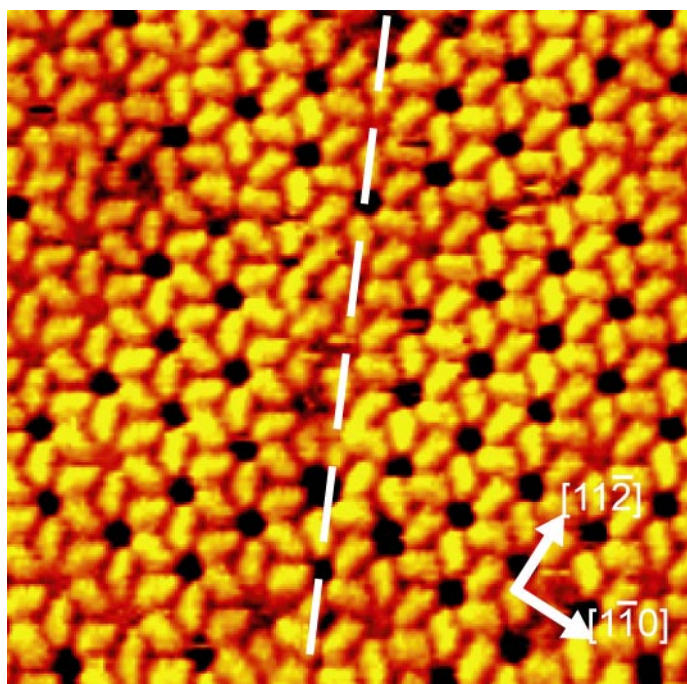


Figure S1: STM image of the hexagonal phase with a boundary between two mirror domains (size $170 \times 170 \text{ \AA}^2$, $I_t=0.97 \text{ nA}$, $V_t=1.25 \text{ V}$).