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Protecting-Group-Controlled Surface Chemistry - Organization and Heat-Induced Coupling of 4,4'-Di(tert-butoxycarbonylamino)biphenyl on Metal Surfaces

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Supporting Information

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Supporting Information for

Protection group controlled surface chemistry – organization and heat induced coupling of 4,4'-di(BOC-amino)biphenyl on metal surfaces

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1. Synthesis and characterization of model compounds and their precursors

General: All chemicals were directly used for the synthesis without purification if nothing else is remarked. The solvents for chromatography and extractions were distilled once before use. Dry THF was distilled over sodium and potassium. Reaction vessels were flame dried and kept under a protection gas atmosphere. The following instruments have been used: ¹H-Nuclear Magnetic Resonance (¹H-NMR): Bruker DPX-NMR (400 MHz), Bruker BZH-NMR (250 MHz) instruments were used to record the spectra. Chemical shifts (δ) are reported in ppm relative to residual solvent peaks, and coupling constants, *J* are in Hertz (Hz). NMR solvents were obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). The measurements were done at room temperature unless temperatures are given. The multiplicity's are written as: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *quin* = quintet, *m* = multiplet and *b* = broad. ¹³C-Nuclear Magnetic Resonance (¹³C-NMR): Bruker DPX-NMR (400 MHz) was used to record the spectra. Chemical shifts (δ) are reported in ppm relative to residual solvent peaks. The measurements were done at room temperature. Electron impact massspectrometry (EI-MS) was performed with a Finnigan MAT 95Q massspectrometer. Elementary analysis (EA): The elementary analysis were measured on a Analysator 240 from Perkin-Elmer. Melting points (MP) have been measured with a Stuart SMP3

melting point apparatus and are uncorrected. Column chromatography (CC): For column chromatography silica gel 60 (40-63 μm) from Merck was used. Thin layer chromatography (TLC): Silica gel 60 F254 glass plates with a thickness of 0.25 mm from Merck were used. The detection was observed with a UV-lamp at 254 nm. Analytical reversed phase HPLC (RP-HPLC) was performed on Lichorspher® 100 RP-18 silica gel from Merck (5 μm particle size, 4x250 mm column) with HPLC-grade MeCN.

Synthesis: The model compounds **1**, **2**, **7**, **9** and **11** are labeled according to the manuscript text and their synthesis is displayed in scheme 1.

Scheme 1: Synthesis of the monomer **1**, the dimer **2** and the model compounds **7**, **9** and **11**.

***tert*.Butyl biphenyl-4,4'-diylldicarbamate (**1**):**

tert-Butyl biphenyl-4,4'-diylldicarbamate (**1**) was synthesized according to a reported procedure.^[SI-1] In a 250 ml tree neck flask benzidine (0.41 g, 2.2 mmol, 1eq) was dissolved in THF (100 ml) and triethylamine (0.9 ml, 6.5 mmol, 3 eq.). A solution of di-

tert.-butyl dicarbonate (1.37 g, 6.3 mmol, 2.9 eq.) in THF (75 ml) was added slowly to the reaction mixture. After stirring for 16 h at RT, the solvents were removed under reduced pressure. Purification by CC (Hexane/EtOAc:1/1) provided **1** as white solid (0.5 g, 1.3 mmol, 59%). MP: decomposition; ¹H-NMR (400 MHz, d₆-DMSO): δ = 9.38 (*s*, 2H, -NH), 7.49 (*s*, 8H, phenyl), 1.46 (*s*, 18H, -CH₃); ¹³C-NMR (100 MHz, d₆-DMSO) δ = 153.61 (NH-CO₂), 139.35, 134.31, 127.12, 119.26 (phenyl); 79.90 (C(Me₃)), 28.99 (CH₃); EI-MS: 384.1 [M⁺]; E.A. calcd. for C₂₂H₂₈N₂O₄ (384.47 g/mol): C 68.73, H 7.34, N 7.29, found: C 68.48, H 7.19, N 7.22.

1,2-bis(4-iodophenyl)diazene was synthesized following a reported procedure:^[SI-3]

4-Iodo-aniline (1.1 g, 5 mmol, 1eq.) was dissolved in CH₂Cl₂ (50 ml). Equal amounts of oxidants KMnO₄ (2.5 g, 15.8 mmol) and FeSO₄·7H₂O (2.5 g, 9 mmol) were prepared by grinding in a mortar and added to the solution. The mixture was refluxed for 6 h and subsequently filtered through cellite. After washing with water and brine, the organic layer was dried over Na₂SO₄. After evaporation of the solvent CC (Hexane/CH₂Cl₂: 3/1) provided 1,2-bis(4-iodophenyl)diazene as orange solid (0.39 g, 0.9 mmol, 18%). MP: 242-244°C; ¹H-NMR (400 MHz, CDCl₃): δ = 7.87 (*d*, 2H, phenyl, *J* = 8.6 Hz); 7.64 (*d*, 2H, phenyl, *J* = 8.6 Hz); ¹³C-NMR (100 MHz, CDCl₃): δ = 152.13 (I-C_{phenyl}); 138.84 (C_{phenyl}); 124.94 (C_{phenyl}); 98.55 (N-C_{phenyl}); EI-MS: 433.8 [M⁺].

***tert.*Butyl 4',4''-(diazene-1,2-diyl)bis(biphenyl-4',4-diyl)dicarbamate (2):**

A 25 ml flask was charged with a toluene/ethanol: 6/1 mixture (14 ml) and a 2M aqueous Na₂CO₃ solution (1 ml). The solution was degassed by bubbling with argon while 1,2-bis(4-iodophenyl)diazene (86.95 mg, 0.2 mmol, 1 eq), 4-(Boc-amino)benzeneboronic acid pinacol ester **12** (143.8 mg, 0.44 mmol, 2.2 eq) and tetrakis(triphenylphosphine)-palladium (26 mg, 0.02 mmol, 10 mol%) were added. The reaction mixture was refluxed for 16 h. After cooling down to RT the solvents were removed and the crude dissolved in CH₂Cl₂, washed with water and brine and dried over Na₂SO₄. After evaporation of the solvent CC (CH₂Cl₂) provided the azo derivative **2** as orange solid (75.7 mg, 0.13 mmol, 67%). MP: decomposition; ¹H-NMR (400 MHz, d₆-DMSO): δ = 9.54 (*s*, 2H, NH-CO₂R), 7.98 (*d*, *J* = 8.4 Hz, 4H, phenyl), 7.88 (*d*, *J* = 8.4 Hz, 4H, phenyl), 7.72 (*d*, *J* = 8.4 Hz, 4H, phenyl), 7.60 (*d*, *J* = 8.4 Hz, 4H, phenyl), 1.50 (*s*, 18H, -CH₃); The limited solubility of **2** did not allow to record a ¹³C-NMR spectrum; EI-MS: 564.3 [M⁺], 464.2 [M⁺-BOC], 364.1 [M⁺-2BOC]; EA calcd. for C₃₄H₃₆N₄O₄ (564.67 g/mol): C 72.32, H 6.43, N 9.92, found: C 71.67, H 6.43, N 9.53.

1,3-Bis(4-iodophenyl)urea (6) was synthesized according to a reported procedure:^[SI-4]

4-Biphenylamine (113.3 mg, 0.67 mmol, 6 eq.) and 4-(Dimethylamino)-pyridin (109.13 mg, 0.89 mmol, 8 eq.) in CH_2Cl_2 (2 ml) were kept under argon in a 25 ml flask. Triphosgene (32.64 mg, 0.11 mmol, 1 eq.) dissolved in CH_2Cl_2 (2 ml) was added dropwise at RT and the reaction mixture was stirred for additional 15 min. while the precipitation of a white solid was observed. The solid was collected by filtration, washed extensively with CH_2Cl_2 and dried at reduced pressure to provide **6** as white solid (103.07 mg, 0.28 mmol, 85 %). MP: decomposition; ^1H -NMR (400 MHz, d_6 -DMSO): δ = 8.85 (*s*, 2H, -NH), 7.67-7.58 (*m*, 12H), 7.45 (*bt*, 4 H, J = 8 Hz); 7.32 (*bt*, 2 H, J = 7.6 Hz); The limited solubility of **6** did not allow to record a ^{13}C -NMR spectrum; MALDI-ToF-MS: 364.82 [M^+]; RP-HPLC (MeCN) R_t = 7.6 min, purity 99%.

***tert*.Butyl biphenyl-4-ylcarbamate (7)**

tert.Butyl biphenyl-4-ylcarbamate (**7**) was synthesized according to a reported procedure.^[SI-2] In a 100 ml flask a mixture of toluene/ethanol: 6/1 (35 ml) and an aqueous Na_2CO_3 solution (2 M, 1 ml) were bubbled with argon while bromobenzene (0.11 ml, 1 mmol, 1 eq.), 4-(Boc-amino)benzeneboronic acid pinacol ester (0.32 g, 1 mmol, 1 eq.) and tetrakis(triphenylphosphine)palladium (0.06 g, 0.05 mmol, 5 mol%) were added. The reaction mixture was refluxed for 16 h. The solvents were removed under reduced pressure and the crude dissolved in CH_2Cl_2 and washed with water and brine and dried over Na_2SO_4 . After evaporation of the solvent, purification by CC (hexane/EtOAc: 6/1) provided **7** as white solid (0.23 g, 0.85 mmol, 85%). MP: 148-150°C; ^1H -NMR (400 MHz, CDCl_3): δ = 7.57-7.52 (*m*, 4H, phenyl), 7.44-7.40 (*m*, 4H, phenyl), 7.31 (*tt*, 1 H, J_1 = 7.6 Hz, J_2 = 1.2 Hz, phenyl), 6.52 (*s*, 1H, -NH), 1.52 (*s*, 9H, -CH₃); ^{13}C -NMR (100 MHz, CDCl_3) δ = 153.13, 141.04, 138.06, 136.35, 129.14, 128.03, 127.33, 127.18, 119.21, 81.05, 28.76; EI-MS: 269.2 [M^+]; EA calcd. for $\text{C}_{17}\text{H}_{19}\text{NO}_2$ (269.34 g/mol): C 75.81, H 7.11, N 5.20, found: C 75.56, H 7.17, N 5.14.

1,2-di(biphenyl-4-yl)diazene (9)

In a 25 ml flask a mixture of toluene/ethanol: 6/1 (14 ml) and an aqueous Na₂CO₃ solution (2 M, 1 ml) were bubbled with argon while 1,2-bis(4-iodophenyl)diazene (108.5 mg, 0.25 mmol, 1 eq.), phenylboronic acid pinacol ester (112.2 mg, 0.55 mmol, 2.2 eq) and tetrakis(triphenylphosphine)palladium (28.9 mg, 0.025 mmol, 10 mol%) were added. The reaction mixture was refluxed for 16 h. The solvents were removed under reduced pressure and the crude dissolved in CH₂Cl₂ (50 ml) and washed with water and brine and dried over Na₂SO₄. After evaporation of the solvent, purification by CC (CH₂Cl₂) provided **9** as orange solid (40.5 mg, 0.12 mmol, 48%). MP: 253-255°C; ¹H-NMR (250 MHz, d₄-THF): δ = 8.03 (*d*, *J* = 8.5 Hz, 4 H), 7.84 (*d*, *J* = 8.5 Hz, 4 H), 7.74 (*d*, *J* = 7 Hz, 4 H), 7.46 (*t*, *J* = 7 Hz, 4 H), 7.38 (*t*, *J* = 7 Hz, 2 H); The limited solubility of **9** did not allow to record a ¹³C-NMR spectrum; EI-MS: 334.2 [M⁺]; EA calcd. for C₂₄H₁₈N₂ (334.41 g/mol): C 86.20, H 5.43, N 8.38, found: C 85.79, H 5.66, N 8.25. RP-HPLC (MeCN) Rt = 18.7 min, purity 99%.

2. Experimental

Surface deposition: The experiments were carried out in an UHV system consisting of several chambers for sample preparation and characterization (base pressure of 1×10^{-10} mbar). STM (scanning tunneling microscopy) measurements were carried out both at room temperature with a home-built microscope and at 77 K with a commercially available microscope (Omicron NanoTechnology GmbH). As substrate for the molecular films both a (111)-oriented Cu single-crystal and a (111)-oriented Ag single-crystal were used which were cleaned by cycles of sputtering with Ar⁺ ions and subsequent annealing. The molecular compounds were deposited by thermal evaporation onto the substrate which was held at room temperature. The deposition rate was controlled by a quartz crystal microbalance.

Simulation of the surface reaction: The reaction conditions were mimicked by adsorbing **7** (5 mg, 0.0186 mMol) dissolved in dichloromethane on Ag nanoparticles with a diameter of about (2±1) μm (1.01g) by evaporation of the solvent at the rotavap. Subsequently, the surface functionalized particles were treated at 200°C and 0.1 mbar for 6h in a glass reaction vessel. To analyze the emerging organic compounds, the particles were extracted extensively with CH₂Cl₂. After concentration of the eluent and preparative TLC three new compounds have been isolated together with considerable amounts of unreacted starting material **7**. Analysis by MALDI-ToF displayed their molecular weights of 321.12, 334.11 and 471.22 suggesting the structures **8** - **10** displayed in Scheme 2 as reaction products.

In a similar procedure the urea derivative **11** (5 mg, 0.0137 mMol) was dissolved in DMF and immobilized on Ag nanoparticles with a diameter of about (2±1) μm (1.01g) by evaporation of the solvent at reduced pressure. After similar treatment of the particles as described above, the cooled down particles were extracted with DMF. The solvent of the extract was removed under reduced pressure and the remaining material was redissolved in acetonitrile for subsequent analysis by reversed phase HPLC. The analysis

of the extract displayed three main compounds: unreacted starting material **11**, an unknown reaction product and the expected azo derivative **9** (see figure SI 1).

Figure SI 1: Reversed phase HPLC (CH_3CN , flow 0.4ml/min, $\lambda_{\text{det}} = 362 \text{ nm}$, $t = 25^\circ\text{C}$) of the azo derivative **9** (top), the DMF extract of the Ag nanoparticles (middle in red) and of the urea derivative **11** (bottom). Due to the poor adsorption at $\lambda_{\text{det}} = 362 \text{ nm}$ the signal of the urea derivative **11** after 7.6 min. is weak. However, a strong signal can be recorded at $\lambda_{\text{det}} = 284 \text{ nm}$.

3. STM-Measurements for **1** adsorbed on Ag(111) / Cu(111)

1 adsorbed on Ag(111)

For **1** adsorbed on Ag(111) a molecular arrangement similar to the one of **1** adsorbed on Cu(111) was observed. Additionally, after annealing the samples at temperatures around 200°C, chainlike structures were found which indicates that a chemical reaction occurred: the BOC groups are released and such, the remaining biphenyl units can interlink.

Figure SI 2: STM image ($5.2 \times 4.8 \text{ nm}^2$; $U_{\text{gap}} = 2 \text{ V}$, $I_{\text{tunnel}} = 20 \text{ pA}$, room temperature) of **1** on Ag(111). As for Cu(111) as substrate, again the molecules assemble in a herringbone arrangement.

Figure SI 3. STM images of **1** on Ag(111) annealed at 200°C. Both images show the same area on the surface. Since the tip conditions were different during acquiring the images, in a) the tert-butyl groups are mainly imaged ($15 \times 15 \text{ nm}^2$; $U_{\text{gap}} = -2.18 \text{ V}$, $I_{\text{tunnel}} = 6 \text{ pA}$, room temperature) while in b) primarily the π -system is observed ($15 \times 15 \text{ nm}^2$; $U_{\text{gap}} = -1.18 \text{ V}$, $I_{\text{tunnel}} = 6 \text{ pA}$, room temperature). Because of thermal and piezoelectric drift the imaged sample area shifted toward the bottom. The same position on the sample is marked by a blue arrow.

1 adsorbed on Cu(111)

Figure SI 4. For submonolayer coverage of **1** on Cu(111) both the parallel and the herringbone arrangements can be seen ($16 \times 16 \text{ nm}^2$; $U_{\text{gap}} = 1.6\text{V}$, $I_{\text{tunnel}} = 10\text{pA}$, 77K). The position of the individual molecules is indicated by the blue lines.

Figure SI 5. STM image for submonolayer coverage of **1** on Cu(111) ($10.8 \times 10.5 \text{ nm}^2$; $U_{\text{gap}} = 1.21\text{V}$, $I_{\text{tunnel}} = 10\text{pA}$, 77K). In the middle part of the image, a single row of **1** can be seen (the orientation of the individual molecules is indicated by a blue line). Such a molecular row can be considered as the building block for both the parallel and the herringbone arrangements. In the upper and the lower part of the image the molecules are arranged in double rows in the parallel pattern.

Figure SI 6: Large scale STM image ($100 \times 93 \text{ nm}^2$, $U_{\text{gap}} = 1.6 \text{ V}$, $I_{\text{tunnel}} = 10 \text{ pA}$, 77 K) for submonolayer coverage of **1** on Cu(111). Molecular double and triple rows are visible which are aligned along the three principle directions of the underlying Cu substrate.

Figure SI 7: STM image ($12 \times 7.5 \text{ nm}^2$, $U_{\text{gap}} = 1.4 \text{ V}$, $I_{\text{tunnel}} = 16 \text{ pA}$, room temperature) of **1** adsorbed on Cu(111) after annealing at 196°C .

Figure SI 8: Time lapse series of STM images ($34 \text{ nm} \times 17 \text{ nm}$, V , pA) of **1** on Cu(111) annealed at 198°C . The green arrow points to representative cross shaped structures, which did not move during the acquisition of the series of STM images, while the blue arrow denotes a moving cross-type structure. In contrast, the encircled structures show two representative areas in which emerging and vanishing aggregated structures can be observed. We thus conclude that the cross-type structures are covalently interlinked biphenyl building blocks forming large macromolecules while the aggregated structures

consist of modified monomers or dimers which have lost either one or both BOC protection groups.

Figure SI 9: STM image (28nm x 28nm, pA, V, 77 K) of **1** on Cu(111) annealed at 200°C.

Atomic resolution on Cu(111)

Figure SI 10: STM image ($4.7 \times 4 \text{ nm}^2$, $U_{\text{gap}} = 0.9\text{V}$, $I_{\text{tunnel}} = 10\text{pA}$, 77 K) of Cu(111) showing atomic resolution which was possible at the given tunnelling parameters because a molecule was picked up with the STM tip.

Since the orientation of the substrate was maintained during all experiments done at the LT STM the orientation of the molecules with regard to the principle directions of the Cu substrate can be determined.

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