Supporting Information

Azo bond formation on metal surfaces

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1. Methods

**STM:** STM measurements are carried out with a low-temperature STM (Createc, LT-STM) under ultrahigh vacuum condition at base pressure \(~4 \times 10^{-10}\) mbar. STM images are recorded at 77 K. Single crystal surfaces, Ag(111) and Au(111), are cleaned by cycles of \(\text{Ar}^+\) ion sputtering and high temperature annealing. Molecules used in this work are deposited from quartz crucibles onto metal surfaces. After deposition (3-5 min), the sample was quickly transferred into cold STM (77K). Annealing of samples is operated on the heater (typically 30 min) in the preparation chamber. The annealing temperature is monitored by one infrared thermometer (Optris, 3MLCF3, 50-400 °C). After evaporation from the crucible at 423 K, intact NTPA molecules were detected by in situ mass spectrometry (Hiden Analytical, EPIC system) before XPS experiments.

**XPS:** Before XPS measurements, the coverage of the precursors was checked by a low-temperature scanning probe microscopy (Scienta Omicron, LT-STM/AFM) under ultrahigh-vacuum conditions and at 77 K. XPS experiments were carried out under UHV conditions at a base pressure of \(2 \times 10^{-10}\) mbar. The UHV system of XPS is connected to the LT-STM/AFM chamber, allowing in situ sample transfer. The XPS experiments were carried out with a monochromated Al K\(\alpha\) X-ray source. Photoelectron detection was conducted in normal emission with a SPECS PHOIBOS 100 hemispherical analyzer and a 2D delay-line detector. The binding energies were calibrated with the Au 4f peak of the substrate.\(^{[1]}\) Samples for cold deposition experiments were held at 170 K. All other samples were held at RT. The peaks in all spectra are fitted using CasaXPS (http://www.casaxps.com). The envelope on clean Ag(111) surface is fitted by two components, whose peak positions and full width at half maximums (FWHMs) were used in other spectra to simulate the contribution from silver surface (with flexible covering area). The XP spectrum on multilayer/Ag(111) shows an
obvious peak around 397.7 eV. Therefore, this component is also considered when analyzing XP spectra recorded on monolayer samples on Ag(111).
2. Azo chains of DNTP on Ag(111)

DNTP molecules, which carry nitro groups at both ends, were studied separately on Ag(111) surface. The DNTP molecules formed close-packed structures after deposition onto Ag(111) surface held at room temperature (Fig. S1a and b). The azo formation by nitro-nitro coupling only produced short azo chains (Fig. S1c). The short molecular chains usually mixed with DNTP monomers (Fig. S1d). These results also confirm the low efficiency of azo formation from nitro-nitro coupling (reaction path 2) in comparison with the amino-nitro crossing coupling (reaction path 1).

![Figure S1. Azo chains via DNTP on Ag(111). (a, b) self-assembly of DNTP after adsorption. (c, d) STM image recorded after annealing the sample at 440 K. (a, b) $V = -1.2 \text{ V}, I = 62 \text{ pA};$ (c) $V = -0.7 \text{ V}, I = 110 \text{ pA};$ (d) $V = -1.1 \text{ V}, I = 110 \text{ pA}.$]
3. Azo formation by dimerization of monofunctional arenes

Fig. S2. Nitro-amino coupling on Ag(111) surface. (a) chemical structures of molecules ARA and NQP. (b, c) STM images of co-adsorption on Ag(111). Black arrows denote the protrusions on NQP. White arrow denotes the amino dimers by N-Ag coordination bonds. (d, e) STM images recorded after annealing the sample at 395 K for 30 min. Red and green arrows represent the azo dimers formed by reaction path 1 and 2 in Scheme 1a, respectively. Set point: (b and c) \( V = -1 \, \text{V}, \, I = 60 \, \text{pA}; \) (d and e) \( V = -2 \, \text{V}, \, I = 60 \, \text{pA}.

Fig. S2a shows the chemical structures of two organic molecules, anthracen-2-amine (ARA) and 3-nitro-\( p \)-quaterphenyl (NQP), carrying one amino and one nitro group individually. Fig. S2b and c show the STM images of co-adsorption of both molecules with ratio \( \sim 1:1 \). The dehydrogenation of the amine groups has already occurred and yielded amine dimers connected with Ag adatoms (white arrow in Fig. S2c), similar to the case on Cu surface.\(^{[2,3]} \) The annealing process leads to the formation of azo dimers (red arrow in Fig. S2e) through nitro-amino coupling (path 1 in Scheme 1a). The products of path 2 were also observed (green arrow in Fig. S2e). The azo groups by path 3 have not been seen on the surface.
As a new system possibly capable to undergo dimerization reactions, NTP and ARA were tested together on Ag(111). Upon desorption at RT, NTP was found to form short self-assembled chains and disordered clusters. No ordered structures were found for ARA (Fig. S3b and c). After annealing at 420 K, the ordered structures of NTP disappeared and only mixed structures with some dimers were observed (Fig. S3d and e). Similarly, selectivity toward redox coupling was still low at 420 K and 440 K (Fig. S3f and g).

Figure S3. Cross-coupling between NTP and ARA. (a) Chemical structures of NTP and ARA. (b-g) STM images recorded after depositing NTP and ARA onto Ag(111) kept at room temperature (b, c), annealing the sample at 420 K (d, e) and annealing at 440 K (f, g). Set point: (b) $V = -1.0 \, V$, $I = 100 \, pA$; (c) $V = -0.4 \, V$, $I = 220 \, pA$; (d) $V = -1.0 \, V$, $I = 100 \, pA$; (e) $V = -2.0 \, V$, $I = 67 \, pA$; (f, g) $V = -2.5 \, V$, $I = 53 \, pA$. 
Next, (4-aminophenyl)-biphenyl-4-ylmethanone (BYM) were tested with NTP on Ag(111). These two molecules formed separate islands after deposition on Ag(111) at RT (Fig. S4b and c). After annealing at 420 K, dimers from both path 1 and 2 were observed (Fig. S4d and e). Also at 440 K, no enhanced selectivity was observed (Fig. S4f and g).

As a next system, NTP and 5’-(4-aminophenyl)-m-terphenyl (PTA) were co-adsorbed on Ag(111). After annealing at 420 K, dimers formed through redox coupling were observed on the surface (Fig. S5e). Similarly, the products obtained
on the surface were formed with low selectivity towards the redox coupling and NTP homocoupling.

Figure S5. Cross-coupling between NTP and PTA. (a) Chemical structures of NTP and PTA. (b-g) STM images recorded after depositing NTP and PTA onto Ag(111) kept at room temperature (b, c), annealing the sample at 420 K (d, e) and annealing at 440 K (f, g). Set point: (b) $V = -1.0 \, \text{V}$, $I = 90 \, \text{pA}$; (c) $V = -0.25 \, \text{V}$, $I = 250 \, \text{pA}$; (d) $V = -1.7 \, \text{V}$, $I = 60 \, \text{pA}$; (e) $V = -1.0 \, \text{V}$, $I = 62 \, \text{pA}$; (f, g) $V = -1.1 \, \text{V}$, $I = 63 \, \text{pA}$.
4. Statistical analysis of azo formation events following path 1 and path 2

Figure S6 shows azo formation of five different systems. The statistics were carried out on samples where the ratio of amino groups and nitro groups is approximate 1:1. The density of each functional group on the surface for all three samples was about 0.1 nm\(^{-2}\). The low reaction efficiency of the four systems reacting intermolecularly (NQP+ARA, NTP+ARA, NTP+BYM and NTP+PTA) might be related to different aromatic backbones of the precursors leading to different mobility, adsorption structures and electronic states. It’s worth noting that the amino molecules have shown very high mobility on the surface as they led to blurred STM images throughout all of our experiments.

Throughout the experiments, we were able to show that two aspects are important for the reaction. (i) the monomers should combine both groups in one molecule, as the selectivity for redox coupling is by far much better for NBPA. It is speculated that the introduction of nitro groups onto the amines reduces the mobility to an appropriate level for the reaction. (ii) a planar arrangement and a fixed conformation are necessary to achieve a better selectivity, as shown by the dimerization of NTP and ARA which proceeds with better selectivity in comparison to NTP and BYM.

![Figure S6. Comparision of amino-nitro cross-coupling and nitro-nitro homocoupling on Ag(111).](image-url)
5. **Experiment towards amino-amino coupling on Ag(111)**

Fig. S7 shows ARA molecules on Ag(111) surface. Azo coupling reaction of path 3 in Scheme 1a was not observed on the surface even when the surface temperature increased to 400 K. Most of the precursor monomers only formed dimers connected by N-Ag-N coordination bond (White arrow and the inset in Fig. S7b), which is consistent with Fig. S2 as well as previous works.[2,3] The molecules desorbed from the surface when the temperature was further increased to 440 K.

![Figure S7](image)

**Figure S7.** Molecule ARA on Ag(111) surface. (a) Adsorption of ARA on Ag(111) surface. (b, c) STM images recorded after the sample was annealed at 400 K and 440 K, respectively. White arrow: coordination dimers (inset). Red and black arrows: clusters formed by three and four molecules, respectively. Set point: (a, b) $V = -1 V, I = 80 \text{ pA}$; (c) $V = -1.5 V, I = 80 \text{ pA}$. 


6. **Azo dimers as model compounds in theoretical and experimental studies**

The TURBOMOLE V6.3 program package (*a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com*) was employed for all calculations of the structural properties of the molecular system. The geometry optimizations were performed using the BLYP functional[4–6] together with the TZVPP basis set[7] and the RI approximation.[8] In addition the D3-dispersion correction was applied.[9,10]

![Figure S8. DFT calculation of azo dimer. The distance between the center benzene ring is 15.06 Å, consistent with STM results.](image)

The distance of azo dimers formed by DNTP was calculated (Fig. S8). The distance between two central benzene rings is 15.06 Å, which agrees well with the experimental results (1.51 ± 0.03 nm).

We further want to give experimental evidence for the azo formation on surface. Therefore, **EBD** (Fig. S9a) was synthesized ex situ and deposited from a crucible at 445 K onto Ag(111) surface which was held at RT.
The molecules assembled into a well-ordered structure after adsorption on Ag(111) (Fig. S9b), which shows the same topography as the azo groups formed on surface. The zoom-in STM topography of EBD marked by a black square in Fig. S9b is shown in Fig. S9c. The distance measured between the centers of the biphenyl moieties was found to be $1.52 \pm 0.03 \text{ nm}$, in good agreement with the experimental and theoretical results.
7. Tip manipulation of azo chains on Ag(111)

Tip manipulation experiment is carried out on the azo chains obtained using NTPA and NBPA on Ag(111) surface. The white arrows (Fig. S10) show the manipulation routes and directions (set point $V = 8$ mV and $I = 20$ nA). The performance of the chain indicates the strong coupling between each unit.

![ STM images before and after tip manipulation on azo chains obtained by NTPA and NBPA.](image)

**Figure S10.** Tip manipulation on the azo chains. (a, b) STM images recorded before and after tip manipulation on azo chains obtained by NTPA. (c, d) STM images recorded before and after tip manipulation on azo chains obtained by NBPA. White arrows: tip routes with set point: $V = 8$ mV, $I = 20$ nA. Set point: (a,b) $V = -0.95$ V, $I = 63$ pA; (c, d) $V = -1.4$ V, $I = 70$ pA.
8. NTPA on varied surfaces

On the Ag(110) surface, NTPA assembles into long 1D chains in which the molecules are probably connected via hydrogen bonding (Fig. S11a and b). Upon annealing, polymers are observed that tend to align along the [11̅0] direction of the surface, but many defects were identified (Fig. S11c). Some chains are found...
in the surface hollows (Fig. S11d). Fig. S11 e-h show the performance of NTPA on Au(111). The NTPA molecules assemble into very long chains, with the nearest units probably linked by hydrogen bonds (Fig. S11e). The regular sieve structures on Ag(111) were also observed on Au(111) surface (Fig. S11f). However, the azo formation reaction by NTPA is also very difficult on gold surface. It is found that only hydrogen bonding is observed between the monomers even after annealing at 420 K. This rather weak interaction is confirmed by tip manipulation (Fig. S11g and h). The distance between the centers of nearest units is measured to be 1.74 nm, agreeing with the hydrogen bond in length of 2.55 Å. On the Au(110) surface, the formation of the (1x3) reconstruction was observed upon deposition of NTPA molecules (Fig. S11i and j). While some molecules are adsorbed on the surface perpendicular to the channels, some molecules are found inside the reconstructed channels (Fig. S11j). After annealing, polymerization takes place inside the channels (Fig. S11k and l), and molecules exhibiting a similar topography as observed on Ag(111) were formed. As a last step of our study on the effect of the surface, NTPA was tested on Cu(111) (Fig. S11m-p). Azo group formation was not observed. Only disordered structures connected via hydrogen bonds or coordination bonds were observed on the surface.
9. **Azo formation at RT**

Azo group formation can also be performed at room temperature. Fig. S12 shows the STM images after annealing of a NBPA-covered Ag(111) surface at RT for 24 hours. Similar oligomers as after high temperature annealing of NBPA were obtained on the surface (Fig. S12b).

![Figure S12](image1.png)

**Figure S12.** Azo coupling on Ag(111) surface after annealing NBPA/Ag(111) at RT for 24 h. (a) Overview STM image recorded on Ag(111) surface. (b) Zoomed-in STM image. Set point: (a, b) $V = -1.1 \text{ V}$, $I = 74 \text{ pA}$.

Also, NTPA was found to oligomerize upon long time annealing at RT (Fig. S13a and b). After 10 h oligomers with similar lengths of the recurring motif as in the case of thermal oligomerization were observed. These results indicate the easy reduction of nitroarenes as well as the dehydrogenation of amino groups, which is consistent with the following XPS study.

![Figure S13](image2.png)

**Figure S13.** (a) STM image after deposition of close to one monolayer NTPA on Ag(111). (b) STM image after RT annealing for 10 h. (c) Line profile taken along the white dashed line in (b). Set point: (a, b) $V = -1 \text{ V}$, $I = 100 \text{ pA}$.
10. N 1s of multilayers and O 1s spectrum on different samples

On Au(111) surface, two N 1s peaks are observed at binding energy of 406 eV and 399 eV, which are assigned to intact nitro[11–13] and intact amino,[14–17] respectively. On Au(111) surface, the O 1s peak at binding energy around 533 eV in spectrum (Fig. S14 b) is due to intact nitro groups,[18] consistent with N 1s spectrum.

On Ag(111), besides the nitro peak (533 eV), a shoulder peak (between 530 eV and 531 eV) was observed in the O 1s spectra, which could be assigned to the reduced nitro groups, in which one N–O bond is cleaved or oxygen bonded to metal atoms.[18] On the NTPA monolayer adsorbed on cold Ag(111) surface, the higher intensity of reduced nitro implies the easy reduction of nitro below RT. As expected, the O 1s peaks almost vanished on the annealed monolayer sample.

Figure S14. XP spectra of N 1s (a) and O 1s (b) on different samples.
The N 1s peaks on different samples are summarized in Table S1. On Ag(111) and Au(111), the test molecule is NTPA. For the XPS data of the powder samples, the experiments were carried out using 5'-((4-nitrophenyl)-m-terphenyl, 5'-((4-aminophenyl)-m-terphenyl and 4,4'-di(4-butylphenyl)azobenzene. The structures of these molecules can be found below.

**Table S1, binding energy shown in the N 1s spectra on different samples.**

|        | On Ag(111) | On Au(111) | Powder | Previous works |
|--------|------------|------------|--------|----------------|
| Nitro  | 406.3      | 406.1      | 406.2  | 406.0,[12][13] 405.6[11] |
| Amino  | 399.6      | 399.3      | 399.6  | 399.6,[11][19] 399.3,[16] 400.2[20] |
| Azo    | 400.1      | ------     | 399.9  | 400.1,[21] 399.9[22] |
11. Dimerization of hydroxylamines and nitrosoarenes

As both groups, nitro and amino group, should be metalated stepwise at the surface ultimately leading to reactive intermediates coordinating to the surface or surface adatoms, we proposed that the net comproportionation of amino and nitro group should also be possible with \(N\)-arylhydroxylamines. \(N\)-(naphthalene-1-yl)hydroxylamine was chosen as a possible reference molecule for this. The molecule can be deposited on the Ag(111) surface after evaporation at RT but a self-assembled structure is not observed (Fig. S15a). In the STM image it can be seen that the molecule is already activated at RT, since some molecules appear bigger and might be coordinating to adatoms. Unfortunately, the molecule is very mobile during scanning resulting in blurred STM images. After annealing at 383 K a clean dimerization is observed and azo formation can be assumed judging from the STM image (Fig. S15b).

![Figure S15. Azo formation from \(N\)-arylhydroxylamines. (a) STM image of \(N\)-(naphthalene-1-yl)hydroxylamine after deposition on Ag(111) at RT. (b) STM image recorded after annealing at 383 K. Set point: (a) \(V = -0.35 \text{ V, } I = 70 \text{ pA; (b) } V = 0.37 \text{ V, } I = 130 \text{ pA.}\)](image)

Furthermore, nitrosoarenes could be intermediates of the redox coupling reaction as a partially reduced nitro group. To test this hypothesis, \(p\)-decyloxy-nitrosobenzene (DNB) was prepared ex situ and deposited on Ag(111) held at RT
(Fig. S16b and c). The molecules were found to self-assemble into well-ordered porous structures. After annealing the sample at 420 K, the molecules form big islands of highly ordered dimers (Fig. S16d and e).

**Figure S16.** Homocoupling of DNB. (a) Chemical structure of DNB. (b-e) STM images recorded after deposition of DNB on Ag(111) held at RT (b, c) and after annealing the sample at 420 K (d, e). Set point: (b) $V = -1.4$ V, $I = 80$ pA; (c) $V = -0.3$ V, $I = 40$ pA; (d) $V = -1.5$ V, $I = 120$ pA; (e) $V = -0.3$ V, $I = 97$ pA.
12. Chemical Synthesis

General part:

Reactions containing air- or moisture-sensitive compounds were performed under argon atmosphere in oven-dried glassware using Schlenk techniques.

Chemicals were purchased from ABCR, Acros Organics, Alfa Aesar, Fluka, TCI, Fluorochem and Sigma Aldrich and used as received. Degassed K$_2$CO$_3$ solution (2N) was prepared by sonicating K$_2$CO$_3$ (13.8 g, 100 mmol) in H$_2$O (50 ml) for 10 min, 3 subsequent freeze-and-thaw cycles and bubbling argon into the solution for 1 h. 2-Aminoanthracene (ARA) was purchased from Alfa Aesar and used as received for on-surface reaction.

Solvents for extraction or flash chromatography (FC) were distilled before use. THF was freshly distilled from K and CH$_2$Cl$_2$ from P$_2$O$_5$. EtOH (for analysis) and MeCN (extra pure) were purchased from Acros Organics.

Flash chromatography was performed on Merck silica gel 60 (40-63 μm) or Acros Organics silica gel (35-70 μm) with an excess argon pressure up to 0.5 bar applied. Merck silica gel 60 F254 plates were used for thin layer chromatography (TLC) using UV light (254/366 nm) for detection.

$^1$H-NMR (300 MHz, 400 MHz and 500 MHz) and $^{13}$C-NMR (75 MHz, 101 MHz and 126 MHz) measurements were carried out on a Bruker DPX 300, a Bruker Avance II 400 and an Agilent DD2 500 spectrometer respectively. The chemical shifts were referred to the solvent residual peak ($^1$H: δ = 7.26 ppm, $^{13}$C: δ = 77.16 ppm (CDCl$_3$) or $^1$H: δ = 2.50 ppm, $^{13}$C: δ = 39.52 ppm (DMSO-$d_6$)).
The multiplicity was described as *s* (singlet), *d* (doublet), *t* (triplet), *br* (broad), and *m* (multiplet) as well as its combinations.

All melting points (MP) were determined by a *Stuart SMP10* and are uncorrected.

Infrared spectra (IR) were recorded by a *Digilab 3100 FT-IR Excalibur Series* spectrometer. The IR signals are listed as *br* (broad), *s* (strong), *m* (medium) and *w* (weak) in cm\(^{-1}\).

**HR-ESI-MS** (*m/z*) spectra were measured on a *Bruker MicroTof* or a *Thermo Fisher Scientific Orbitrap LTQ XL*, **HR-EI-MS** on a *Thermo Fisher Scientific Exactive GC-MS* and **EI-MS** chromatograms were recorded on an *Agilent Technologies 7820A GC-system* equipped with an *Agilent 5977B MSD(EI)* detector and a *HP-5MS* column with helium as carrier gas.

**General procedure for Suzuki-coupling of aryl boronic acid with aryl halides (GP1)**

The aryl halide (1.00-3.04 eq.), the according aryl boronic acid or aryl boronic acid ester (1.0-2.2 eq.) and Pd(PPh\(_3\))\(_4\) (5.0-10.0 mol%) were dissolved in THF (1-20 ml) and aqueous K\(_2\)CO\(_3\) solution (2 M, 0.1-2 ml) was added dropwise. The reaction mixture was stirred at 80 °C for 24-69 h: After cooling to RT it was added to water and the aqueous layer was extracted with CH\(_2\)Cl\(_2\) (3x). The combined organic layers were washed with brine and dried over MgSO\(_4\). After removing the solvents *in vacuo*, the crude product was purified by FC or recrystallization.
**4’-Nitrobiophenyl-3-amine (NBPA)**

![Structure of 4’-Nitrobiophenyl-3-amine](image)

According to GP1 with 1-bromo-4-nitrobenezene (404 mg, 2.00 mmol, 1.00 eq.), 3-aminophenylboronic acid (411 mg, 3.00 mmol, 1.50 eq.) and Pd(PPh₃)₄ (185 mg, 160 µmol, 8.00 mol%) in THF (20 ml) and aqueous K₂CO₃ (2 ml) at 80 °C for 88 h. Recrystallization (EtOAc:pentane) yielded the product as an orange solid (428 mg, 2.00 mmol, >99%).

**¹H NMR** (300 MHz, DMSO-d₆, 293 K): δ = 8.28 (d, J = 8.8 Hz, 2H, Aryl-H), 7.83 (d, J = 8.8 Hz, 2H, Aryl-H), 7.16 (t, J = 7.8 Hz, 1H, Aryl-H), 6.92 (t, J = 2.1 Hz, 1H, Aryl-H), 6.90-6.84 (m, 1H, Aryl-H), 6.66 (dd, J = 8.1, 2.0 Hz, 1H, Aryl-H), 5.30 (s, 2H, NH₂). **¹³C NMR** (75 MHz, DMSO-d₆, 293 K): δ = 149.4 (C), 147.6 (C), 146.4 (C), 138.5 (C), 129.8 (CH), 127.5 (CH), 124.1 (CH), 114.7 (2xCH), 112.2 (CH). **HRMS** (ESI): m/z calculated for [M+Na]+: 215.0815, found: 215.0828.

Spectroscopic data are in accordance with those described in the literature.[23]

**4’-Bromo-3-nitrobiophenyl**

![Structure of 4’-Bromo-3-nitrobiophenyl](image)

According to GP1 with 1-iodo-3-nitrobenezene (125 mg, 502 µmol, 1.00 eq.), 4-bromophenylboronic acid (150 mg, 747 µmol, 1.49 eq.) and Pd(PPh₃)₄ (46 mg, 40 µmol, 7.9 mol%) in THF (5 ml) and aqueous K₂CO₃ (0.5 ml) at 80 °C for 69 h. FC (pentane:CH₂Cl₂ 10:1) yielded the product as a colorless solid (118 mg, 424 µmol, 85%).
¹H NMR (300 MHz, CDCl₃, 293 K): δ = 8.42 (t, J = 2.0 Hz, 1H, Aryl-H), 8.22 (ddd, J = 8.2, 2.2, 0.9 Hz, 1H, Aryl-H), 7.88 (ddd, J = 7.8, 1.7, 1.0 Hz, 1H, Aryl-H), 7.71-7.55 (m, 3H, Aryl-H), 7.52-7.43 (m, 2H, Aryl-H). ¹³C NMR (75 MHz, CDCl₃, 293 K): δ = 141.9 (C), 137.8 (C), 133.3 (C), 132.9 (CH), 132.5 (CH), 130.1 (CH), 128.9 (CH), 123.2 (C), 122.6 (CH), 121.9 (CH). MS (EI): m/z {277.1 (100), 278.1 (13), 279.2 (98), 280.1 (13)} [M]+, {231.1 (10), 233.1 (9)} [M-NO₂]+, 152.2 (74) [M-Br-NO₂]+.

Spectroscopic data are in accordance with those described in the literature.[24]

3-Nitro-p-quarterphenyl

[Diagram]

According to GP1 with 4'-bromo-3-nitrobiphenyl (74 mg, 0.27 mmol, 1.0 eq.), p-biphenylboronic acid (79 mg, 0.40 mmol, 1.5 eq.) and Pd(PPh₃)₄ (25 mg, 22 µmol, 8.1 mol%) in THF (3 ml) and aqueous K₂CO₃ (0.3 ml) at 80 °C for 64 h. Instead of hydrolysis, the crude mixture was filtrated through a silica pad (EtOAc) and the solvent was removed in vacuo. RC (EtOAc:pentane) yielded quarterphenyl 2 as a colorless solid (63 mg, 0.18 mmol, 67%).

¹H NMR (500 MHz, CDCl₃, 293 K): δ = 8.53 (t, J = 2.0 Hz, 1H, Aryl-H), 8.22 (ddd, J = 8.2, 2.3, 1.0 Hz, 1H, Aryl-H), 7.98 (ddd, J = 7.7, 1.8, 1.1 Hz, 1H, Aryl-H), 7.83-7.77 (m, 2H, Aryl-H), 7.77-7.70 (m, 6H, Aryl-H), 7.69-7.59 (m, 3H, Aryl-H), 7.52-7.42 (m, 2H, Aryl-H), 7.41-7.34 (m, 1H, Aryl-H). ¹³C NMR (126 MHz, CDCl₃, 293 K): δ = 149.0 (C), 142.6 (C), 141.1 (C), 140.8 (C), 140.7 (C), 139.2 (C), 137.7 (C), 133.0 (CH), 129.9 (CH), 129.0 (CH), 127.9 (CH), 127.8 (CH), 127.8 (CH), 127.6 (CH), 127.6 (CH), 127.2 (CH), 122.3 (CH), 122.0 (CH). HRMS (EI): m/z calculated for [M]+: 351.12538, found: 351.12562. IR (neat):
3038w, 1531w, 1521m, 1487w, 1402w, 1346m, 1289w, 899w, 876w, 827s, 806m, 768s, 744s, 690m, 670w. **MP**: 271-273 °C.

4,4''-Dinitro-p-terphenyl (DNTP)

According to GP1 with 1-bromo-4-nitrobenzene (152 mg, 752 µmol, 3.04 eq.), 1,4-phenylene-diboronic acid (41 mg, 0.25 mmol, 1.0 eq.) and Pd(PPh₃)₄ (23 mg, 20 µmol, 8.0 mol%) in THF (2 ml) and aqueous K₂CO₃ (0.2 ml) at 80 °C for 65 h. Recrystallization (CH₂Cl₂:pentane) yielded the products as an orange solid (43 mg, 0.13 mmol, 54%).

**¹H NMR** (300 MHz, DMSO-d₆, 293 K): δ = 8.39-8.31 (m, 4H, Aryl-H), 8.12-8.02 (m, 4H, Aryl-H), 7.98 (s, 4H, Aryl-H). **¹³C NMR** (75 MHz, DMSO-d₆, 293 K): δ = 146.9 (C), 145.6 (C), 138.2 (C), 128.1 (CH), 127.9 (CH), 124.1 (CH).

**HRMS** (EI): m/z calculated for [M]⁺: 320.07916, found: 320.07907.

Spectroscopic data are in accordance with those described in the literature.[25]

4-Bromo-4’-nitrobiphenyl

According to GP1 with 1-iodo-4-nitrobenzene (249 mg, 1.00 mmol, 1.00 eq.), 4-bromophenylboronic acid (201 mg, 1.00 mmol, 1.00 eq.) and Pd(PPh₃)₄ (92 mg, 80 µmol, 8.0 mol%) in THF (1 ml) and aqueous K₂CO₃ (0.1 ml) at 80 °C for 64 h. FC (pentane:EtOAc 10:1) yielded the product as a colorless solid (42 mg, 0.15 mmol, 15%).

**¹H NMR** (300 MHz, DMSO-d₆, 293 K): δ = 8.31 (dt, J = 8.9, 2.5 Hz, 2H, Aryl-H), 7.97 (dt, J = 8.9, 2.5 Hz, 2H, Aryl-H), 7.78-7.71 (m, 4H, Aryl-H). **¹³C NMR** (75 MHz, DMSO-d₆, 293 K): δ = 146.9 (C), 145.3 (C), 137.0 (C), 132.1 (CH),
129.3 (CH), 127.8 (CH), 124.1 (CH), 122.7 (C). **HRMS** (ESI): m/z calculated for [M+Ag]$^+$: 383.87839, found: 383.87902. **IR** (neat): 2923w, 2850w, 1596w, 1508s, 1476w, 1345m, 1108w, 1003w, 863w, 821m, 754w. **MP.**: 176 °C.[26]

4''-Nitro-p-terphenyl-4-amin (NTPA)

According to GP1 with 4-Bromo-4’-nitrobiphenyl (20 mg, 72 µmol, 1.0 eq.), 4-aminophenylboronic acid hydrochloride (19 mg, 0.11 mmol, 1.5 eq.) and Pd(PPh$_3$)$_4$ (6.6 mg, 5.7 µmol, 7.9 mol%) in THF (1 ml) and aqueous K$_2$CO$_3$ (0.2 ml) at 80 °C for 41 h. After hydrolysis, the aqueous layer was extracted with CH$_2$Cl$_2$ (7x15 ml) and the combined organic layers were diluted with CH$_2$Cl$_2$ (50 ml) before drying over MgSO$_4$ to dissolve suspended particles. RC (CH$_2$Cl$_2$:pentane) yielded nitro amino terphenyl 3 as an orange solid (18 mg, 62 µmol, 86%).

$^1$H NMR (400 MHz, DMSO-$d_6$, 293 K): $\delta$ = 8.30 ($d$, $J$ = 8.9 Hz, 2H, Aryl-H), 8.00 ($d$, $J$ = 8.9 Hz, 2H, Aryl-H), 7.82 ($d$, $J$ = 8.4 Hz, 2H, Aryl-H), 7.71 ($d$, $J$ = 8.4 Hz, 2H, Aryl-H), 7.46 ($d$, $J$ = 8.5 Hz, 2H, Aryl-H), 6.67 ($d$, $J$ = 8.5 Hz, 2H, Aryl-H), 5.34 ($brs$, 2H, NH$_2$). $^{13}$C NMR (101 MHz, DMSO-$d_6$, 293 K): $\delta$ = 148.9 (C), 146.4 (C), 146.3 (C), 141.3 (C), 134.7 (C), 127.6 (CH), 127.3 (CH), 127.3 (CH), 126.1 (C), 125.9 (CH), 124.2 (CH), 114.2 (CH). **HRMS** (ESI): m/z calculated for [M+H]$^+$: 291.11280, found: 291.11232.

Spectroscopic data are in accordance with those described in the literature.[27]
Biphenyl-4,4’-diamine (BPDA)

According to a procedure from the literature,[28] hydrazobenzene (1.00 g, 5.43 mmol, 1.00 eq.) was suspended in aqueous HCl (10%, 60 mL) and heated at reflux for 3 h. The solution was treated with aqueous NaOH (1 N) until the pH was >8 and then extracted with MTBE (3x200 mL). The combined organic layers were dried over MgSO₄ and the solvent removed in vacuo. RC (PhMe:pentane) followed by FC (MTBE:Pentan 3:1 → 4:1 → 6:1) yielded benzidine 5 as an orange solid (0.67 g, 67%)

**¹H NMR** (300 MHz, CDCl₃, 293 K): δ = 7.40-7.29 (m, 4H, Aryl-H), 6.76-6.70 (m, 4H, Aryl-H), 3.66 (brs, 4H, NH₂). **¹³C NMR** (75 MHz, CDCl₃, 293 K): δ = 145.0 (C), 131.9 (C), 127.3 (CH), 115.5 (CH). **HRMS** (ESI): m/z calculated for [M+H]⁺: 185.1073, found: 185.1080.

Spectroscopic data are in accordance with those described in the literature.[29]

N-(naphthalene-1-yl)hydroxylamine

According to procedure from the literature,[30] 1-nitronaphthalene (346 mg, 2.00 mmol, 1.00 eq.) was dissolved in THF (10 ml) and 5% Rh/C (12 mg, 5.8 µmol, 0.29 mol%) was added. The suspension was cooled to 0 °C and hydrazine monohydrate (0.12 ml, 2.4 mmol, 1.2 eq.) was added dropwise. The resulting mixture was stirred for 2 h at 0 °C, warmed to RT and stirred for 2 h at that temperature. Afterwards, the crude mixture was filtrated through a cellite pad and the solvent was removed in vacuo. The residue was recrystallized (CH₂Cl₂:pentane) at –20 °C yielding the product as a yellow solid (230 mg, 1.44 mmol, 72%).
**1H NMR** (300 MHz, DMSO-\(d_6\), 293 K): \(\delta = 8.95\) (s, 1H, OH), 8.40 (d, \(J = 1.9\) Hz, 1H, NH), 8.02-7.89 (m, 1H, Aryl-H), 7.89-7.74 (m, 1H, Aryl-H), 7.60-7.22 (m, 4H, Aryl-H), 7.13 (dt, \(J = 7.3, 1.3\) Hz, 1H, Aryl-H).

**\(^{13}\)C NMR** (75 MHz, DMSO-\(d_6\), 293 K): \(\delta = 146.8\) (C), 133.3 (C), 127.8 (CH), 126.3 (CH), 125.6 (CH), 124.3 (CH), 122.0 (CH), 121.6 (CH), 118.7 (CH), 106.5 (C).

**HRMS** (ESI): \(m/z\) calculated for [M+H]\(^+\): 160.0757, found: 160.0753.

**IR** (neat): 3274br, 3057w, 2927w, 1628w, 1597w, 1580w, 1514w, 1462w, 1400m, 1344w, 1270w, 1170w, 1086w, 1059w, 995w, 900w, 857w, 789m, 767s, 705w, 613w, 561w.

**MP.:** decomp. >74 °C.

1,3-Dibromo-5-nitrobenzene

According to a procedure from the literature,\(^{[31]}\) 2,6-dibromo-4-nitroaniline (296 mg, 1.00 mmol, 1.00 eq.) was dissolved in EtOH (7 ml) and concentrated sulfuric acid (0.5 ml) was added dropwise at 0 °C. The resulting mixture was warmed to 60 °C and NaNO\(_2\) (207 mg, 3.00 mmol, 3.00 eq.) was added. Afterwards, the reaction mixture was warmed to 90 °C and refluxed at this temperature for 3 h. After cooling to RT, the mixture was poured onto ice water (20 ml). The resulting solid was filtrated and washed with H\(_2\)O (2x10 ml). The product was yielded as a brown powder (219 mg, 0.780 mmol, 78%) after drying in HV.

**1H NMR** (300 MHz, CDCl\(_3\), 298 K): \(\delta = 8.32\) (d, \(J = 1.7\) Hz, 2H, Aryl-H), 8.00 (t, \(J = 1.7\) Hz, 1H, Aryl-H). **\(^{13}\)C NMR** (75 MHz, CDCl\(_3\), 298 K): \(\delta = 149.3\) (C), 140.2 (CH), 125.8 (C), 123.7 (CH). **MS** (EI): \(m/z\) 281.0 (100) [M]\(^+\), 235.0 (55) [M-NO\(_2\)]\(^+\), 223.0 (10) [M-C-NO\(_2\)]\(^+\), 154.0 (5) [M-NO\(_2\)-Br]\(^+\), 75.1 (8) [M-NO\(_2\)-2Br]\(^+\).
The analytical data are in accordance with the literature.[31]

5′-Nitro-m-terphenyl (NTP)

According to GP1 with 1,3-dibromo-5-nitrobenzene (200 mg, 0.71 mmol, 1.00 eq.), phenylboronic acid (191 mg, 1.57 mmol, 2.20 eq.) and Pd(PPh\(_3\))\(_4\) (41 mg, 35 mmol, 5.0 mol%) in THF (10 ml) and aqueous K\(_2\)CO\(_3\) (1 ml) at 80 °C for 24 h. FC (pentane:EtOAc 20:1) yielded the product as a yellow solid (185 mg, 0.671 mmol, 94%).

\(^1\)H NMR (300 MHz, CDCl\(_3\), 298 K): \(\delta = 8.42 \ (d, J = 1.6 \text{ Hz}, 2\text{H}, \text{Aryl-H}), 8.11 \ (t, J = 1.7 \text{ Hz}, 1\text{H}, \text{Aryl-H}), 7.73-7.63 \ (m, 4\text{H}, \text{Aryl-H}), 7.58-7.40 \ (m, 6\text{H}, \text{Aryl-H}).\)

\(^{13}\)C NMR (75 MHz, CDCl\(_3\), 298 K): \(\delta = 149.4 \ (C), 143.5 \ (C), 139.0 \ (C), 131.8 \ (CH), 129.4 \ (CH), 128.8 \ (CH), 127.4 \ (CH), 120.8 \ (CH).\) MS (EI): \(m/z 275.1 \ (100) [M]^+, 228.2 \ (50), 202.1 \ (15), 152.2 \ (3) [M-NO\(_2\)-C\(_6\)H\(_6\)]^+, 113.0 \ (5) [M-NO\(_2\)C\(_6\)H\(_6\)-C\(_3\)H\(_3\)]^+, 101.1 \ (2).\)

The analytical data are in accordance with the literature.[32]

4-Amino-4′-phenyl-benzophenone (BYM)

According to a known procedure,[33] \(p\)-aminobenzoic acid (274 mg, 2.00 mmol, 1.00 eq.) was dissolved in CH\(_2\)Cl\(_2\) (4 ml) and polyphosphoric acid (6.0 g, 61 mmol, 31 eq.) and biphenyl (617 mg, 4.00 mmol, 2.00 eq.) were added. After stirring at 180 °C for 4 h, the reaction mixture was poured onto crushed ice and was basified with aqueous ammonia solution (25%). The aqueous layer was extracted with CH\(_2\)Cl\(_2\) (3x10 ml) and the combined
organic layers were dried over MgSO$_4$. The solvent was removed in vacuo. FC (pentane:EtOAc 10:1) yielded the product as a yellow solid (54 mg, 0.20 mmol, 10%).

$^1$H NMR (300 MHz, CDCl$_3$, 298 K): $\delta$ = 7.86-7.74 (m, 4H, Aryl-H), 7.72-7.62 (m, 4H, Aryl-H), 7.53-7.35 (m, 3H, Aryl-H), 6.70 (dd, $J$ = 8.6, 1.2 Hz, 2H, Aryl-H), 4.15 (s, 2H, NH). $^{13}$C NMR (75 MHz, CDCl$_3$, 298 K): $\delta$ = 195.05 (C), 151.03 (C), 144.39 (C), 140.37 (C), 137.67 (C), 133.04 (CH), 130.35 (CH), 129.06 (C), 128.10 (CH), 127.72 (CH), 127.41 (CH), 126.93 (CH), 113.82 (CH). HRMS (ESI-pos): Calculated mass for [M+Na]$^+$: 296.10513, found: 296.10432.

The analytical data are in accordance with the literature.$^{[33]}$

**2-(4-Butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (136)**

1-Brom-4-butylbenzene (4.9 ml, 28 mmol, 1.0 eq.) was dissolved in THF (50 ml) and nBuLi (1.6 M in hexane, 21 ml, 34 mmol, 1.2 eq.) was added dropwise at $-78^\circ$C. After stirring at this temperature for 1.5 h, B(OMe)$_3$ (6.3 ml, 56 mmol, 2.0 eq.) was added. The resulting mixture was stirred at RT for 17 h. The reaction was quenched upon addition of aqueous HCl (2 M, 30 ml) and stirring for 2 h. the phases were separated and the aqueous layer was extracted with Et$_2$O (2x30 ml). The combined organic layers were washed with H$_2$O (40 ml) and dried over MgSO$_4$. The solvent was removed in vacuo, the residue was dissolved in pentane (60 ml) and after addition of pinacol (3.47 g, 29.4 mmol, 1.06 eq.) at 0 $^\circ$C the resulting mixture was stirred for 24 h at RT. The reaction was quenched upon addition of H$_2$O (50 ml) and after phase separation, the aqueous layer was extracted with Et$_2$O (50 ml). The combined organic layers were dried over MgSO$_4$
and the solvent was removed in vacuo. FC (pentane/Et₂O 40:1) yielded the product as a colorless liquid (3.28 g, 12.6 mmol, 46%).

**¹H NMR** (300 MHz, CDCl₃, 293 K): \( \delta = 7.73 \) (d, \( J = 7.9 \) Hz, 2H, Aryl-H), 7.20 (d, \( J = 7.9 \) Hz, 2H, Aryl-H), 2.76-2.44 (m, 2H, CH₂), 1.69-1.52 (m, 2H, CH₂), 1.41-1.29 (m, 14H, CH₂+CH₃), 0.92 (t, \( J = 7.3 \) Hz, 3H, CH₃). **¹³C NMR** (75 MHz, CDCl₃, 293 K): \( \delta = 146.4 \) (C), 134.8 (CH), 127.9 (CH), 83.6 (C), 35.9 (CH₂), 33.5 (CH₂), 24.9 (CH₃), 22.4 (CH₂), 13.9 (CH₃). **¹¹B NMR** (96 MHz, CDCl₃, 293 K): \( \delta = 29.9 \).

**HRMS** (ESI): \( m/z \) calculated for [M+Na]+: 283.1843, found: 283.1857.

**IR** (film): 2979w, 2960w, 2930w, 2860w, 1612m, 1516w, 1467w, 1398m, 1359s, 1319m, 1270w, 1214w, 1144s, 1089s, 1022w, 963w, 860m, 825w, 738w, 658m.

The **¹³C**-signal of quartenary carbon binding to C–Bpin was not detected.

**4-Butyl-4'-nitro biphenyl**

According to GP1 with 1-bromo-4-nitrobenzol (404 mg, 2.00 mmol, 1.00 eq.), 2-(4-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (572 mg, 2.20 mmol, 1.10 eq.) and Pd(PPh₃)₄ (185 mg, 160 mmol, 8.0 mol%) in THF (20 ml) and aqueous K₂CO₃ (2 mL) at 80 °C for 24 h. FC (pentane:EtOAc 10:1) yielded the product as a brown solid (393 mg, 1.54 mmol, 77%).

**¹H NMR** (300 MHz, CDCl₃, 298 K): \( \delta = 8.35-8.23 \) (m, 2H, Aryl-H), 7.75-7.69 (m, 2H, Aryl-H), 7.59-7.52 (m, 2H, Aryl-H), 7.36-7.29 (m, 2H, Aryl-H), 2.72-2.65 (m, 2H, CH₂O), 1.65 (tt, \( J = 8.9, 6.9 \) Hz, 2H, CH₂), 1.47-1.33 (m, 2H, CH₂), 0.96 (t, \( J = 7.3 \) Hz, 3H, CH₃). **¹³C NMR** (75 MHz, CDCl₃, 298 K): \( \delta = 147.8 \) (C), 147.0 (C), 144.3 (C), 136.2 (C), 129.4 (CH), 127.6 (CH), 127.4 (CH), 124.2 (CH), 35.5 (CH₂), 33.7 (CH₂), 22.5 (CH₂), 14.1 (CH₃). **MS** (EI): \( m/z \) 281.0 (7), 255.0 (8)
[M]^+, 225.1 (45), 207.0 (30), 182.0 (100), 165.0 (12), 133.1 (4) [M-C₆H₄NO₂]^+, 115.0 (5), 91.0 (4), 73.0 (3), 51.1 (2).

The analytical data are in accordance with the literature.[34]

**4,4’-Di(4-butylphenyl)azobenzene (EBD)**

According to procedure from the literature,[35] 4-butyl-4’-nitro biphenyl (370 mg, 1.45 mmol, 1.00 eq.) was dissolved in ethylenediamine (1 ml) and stirred at 150 °C for 45 h. After cooling to RT, volatiles were removed *in vacuo*. FC (pentane:EtOAc 20:1) yielded the product as a red solid (81 mg, 180 mmol, 25%).

**1H NMR** (300 MHz, CDCl₃, 298 K): δ = 8.06-7.95 (m, 4H, Aryl-H), 7.79-7.71 (m, 4H, Aryl-H), 7.64-7.57 (m, 4H, Aryl-H), 7.29 (d, J = 8.1 Hz, 4H, Aryl-H), 2.68 (t, J = 7.7 Hz, 4H, Aryl-CH₂), 1.74-1.58 (m, 4H, CH₂), 1.50-1.32 (m, 4H, CH₂), 0.96 (t, J = 7.3 Hz, 6H, CH₃). **13C NMR** (75 MHz, CDCl₃, 298 K): δ = 151.9 (C), 143.8 (C), 143.0 (C), 137.7 (C), 129.2 (CH), 127.7 (CH), 127.2 (CH), 123.5 (CH), 35.5 (CH₂), 33.8 (CH₂), 22.6 (CH₂), 14.1 (CH₃). **HRMS** (ESI-pos): Calculated mass for [M+Na]^+: 447.27882, found: 447.28002. **IR** (neat): 1381w, 903s, 723s, 650m, 628w. **MP**: 240-242 °C.

**1-Bromo-4-(decyloxy)benzene**

According to a known procedure,[36] 4-bromophenol (865 mg, 5.00 mmol, 1.00 eq)
was dissolved in MeCN (7.5 ml) and K$_2$CO$_3$ (1.73 g, 12.5 mmol, 2.50 eq.) and 1-bromodecane (1.1 ml, 5.3 mmol, 1.1 eq.) were added. The resulting mixture was stirred at 80 °C for 17 h and afterwards poured into an aqueous NaOH solution (1 M, 30 ml). The layers were separated and the aqueous layer was extracted with pentane (2x30 mL). The combined organic layers were washed with H$_2$O (20 ml) and saturated, aqueous NaCl solution (20 ml) and were dried over MgSO$_4$. The solvent was removed \textit{in vacuo}. FC (pentane) yielded the product as a colourless oil (1.56 g, 4.98 mmol, >99%).

$^1$H NMR (300 MHz, CDCl$_3$, 298 K): $\delta = 7.40$-7.32 ($m$, 2H, Aryl-H), 6.82-6.73 ($m$, 2H, Aryl-H), 3.91 ($t$, $J = 6.6$ Hz, 2H, CH$_2$O), 1.89-1.69 ($m$, 2H, CH$_2$), 1.59-1.19 ($m$, 14H, CH$_2$), 0.97-0.85 ($m$, 3H, CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$, 298 K): $\delta = 158.4$ (C), 132.3 (CH), 116.5 (CH), 112.7 (C), 68.5 (CH$_2$O) 32.1 (CH$_2$), 29.7 (CH$_2$), 29.7 (CH$_2$), 29.5 (CH$_2$), 29.5 (CH$_2$), 29.3 (CH$_2$), 26.2 (CH$_2$), 22.8 (CH$_2$), 14.3 (CH$_3$). MS (EI): $m/z$ 312.1 (23) [M]$^+$, 281.0 (<1), 256.0 (<1), 240.0 (<1), 214.0 (<1), 187.0, 172.0 (100), 157.0 (6), 143.0 (4), 119.0 (2), 991. (<1), 85.1 (6), 71.1 (6), 55.1 (17).

The analytical data are in accordance with the literature.$^{[36]}$

**4-Decyloxyphenylboronic acid**

According to a known procedure,$^{[37]}$ 1-bromo-4-(decyloxy)benzene (1.56 g, 4.98 mmol, 1.00 eq.) was dissolved in THF (10 ml) and nBuLi (1.6 M in hexane, 3.3 ml, 5.3 mmol, 1.1 eq.) was added dropwise at $-78$ °C. After the reaction mixture was stirred at $-78$ °C for 2 h, B(OMe)$_3$ (2.2 ml, 20 mmol, 3.9 eq.) was added. The resulting mixture was warmed to RT and stirred for 16 h at this temperature. Afterwards, aqueous HCl
solution (4 M, 15 ml) was added and the mixture was stirred for another hour. The layers were separated and the aqueous layer was extracted with Et₂O (3x20 ml). The combined organic layers were dried over MgSO₄ and the solvent was removed in vacuo. FC (Et₂O) yielded the product as a colourless solid (451 mg, 1.62 mmol, 33%).

**1H NMR** (300 MHz, CDCl₃, 298 K): δ = 8.15 (d, J = 8.3 Hz, 2H, Aryl-H), 7.00 (d, J = 8.4 Hz, 2H, Aryl-H), 4.04 (t, J = 6.5 Hz, 2H, CH₂O), 1.91-1.75 (m, 2H, CH₂), 1.66-1.18 (m, 14H, CH₂), 0.93-0.84 (m, 3H, CH₃). **13C NMR** (75 MHz, CDCl₃, 298 K): δ = 163.0 (C), 137.6 (CH), 135.4 (C), 114.2 (CH), 68.1 (CH₂), 32.1 (CH₂), 29.7 (CH₂), 29.7 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 26.2 (CH₂), 22.8 (CH₂), 14.3 (CH₃). **MS** (EI): m/z 122 (100) [M-C₁₆H₂₁O]⁺, 109.0 (50), 96.0 (5), 79.0 (10), 63.0 (3), 50.9 (<1).

The analytical data are in accordance with the literature.⁴⁸

**4-Decyloxy nitrosobenzene (DNB)**

According to a known procedure,⁴⁸ NaNO₂ (76 mg, 1.1 mmol, 2.2 eq.) and TMSCl (0.14 ml, 1.1 mmol, 2.2 eq.) were added to CH₂Cl₂ (5 ml). After stirring at RT for 5 min, 4-decyloxyphenylboronic acid (139 mg, 500 µmol, 1.00 eq.) was added under air. The reaction mixture was stirred at RT for 48 h, whereas the flask was flushed with argon after 10 min. Afterwards, the mixture was filtrated. The filtrate was dried over MgSO₄ and the solvent was removed in vacuo. FC (pentane:Et₂O 10:1) yielded the product as a green oil (56 mg, 0.21 mmol, 43%).
**$^1$H NMR** (300 MHz, CDCl₃, 298 K): $\delta = 7.90$ ($d, J = 8.6$ Hz, 2H, Aryl-H), 7.00 ($d, J = 8.8$ Hz, 2H, Aryl-H), 4.10 ($t, J = 6.5$ Hz, 2H, CH₂O), 1.90-1.76 ($m$, 2H, CH₂), 1.58-1.19 ($m$, 14H, CH₂), 0.88 ($t, J = 6.3$ Hz, 3H, CH₃). **$^{13}$C NMR** (75 MHz, CDCl₃, 298 K): $\delta = 165.5$ (C), 164.2 (C), 124.6 (CH), 114.4 (CH), 69.1 (CH₂), 32.0 (CH₂), 29.7 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.1 (CH₂), 26.1 (CH₂), 22.8 (CH₂), 14.2 (CH₃). **HRMS** (ESI-pos): Calculated mass for [M+H]$^+$: 264.19635, found: 264.19594. **IR** (neat): 2925m, 2854m, 1600m, 1590m, 1504s, 1467m, 1414m, 1390m, 1358m, 1326m, 1296w, 1144m, 1112s, 1089s, 1038w, 1012m, 961w, 904w, 858m, 838m, 756w, 723m, 662m, 649m, 578w, 562w.
5′-(4-Nitrophenyl)-m-terphenyl

According to GP1 with 5′-bromo-m-terphenyl (618 mg, 2.00 mmol, 1.00 eq.), 4-nitrophenylboronic acid (401 mg, 2.40 mmol, 1.20 eq.) and Pd(PPh₃)₄ (231 mg, 200 mmol, 10.0 mol%) in THF (20 ml) and aqueous K₂CO₃ (2 ml) at 80 °C for 48 h. FC (pentane:EtOAc 10:1 → 5:1) yielded the product as a yellow solid (628 mg, 1.79 mmol, 89%).

**1H NMR** (300 MHz, CDCl₃, 298 K): δ = 8.41-8.30 (m, 2H, Aryl-H), 7.92-7.77 (m, 5H, Aryl-H), 7.76-7.65 (m, 4H, Aryl-H), 7.58-7.36 (m, 6H, Aryl-H).

**13C-NMR** (75 MHz, CDCl₃, 298 K): δ = 147.7 (C), 143.1 (C), 141.7 (C), 140.8 (C), 140.1 (C), 129.1 (CH), 128.2 (CH), 128.1 (CH), 127.5 (CH), 126.9 (CH), 125.4 (CH), 124.3 (CH). **HRMS** (ESI-pos): Calculated for [M+Na]⁺: 374.11570, found: 374.11509.

The analytical data are in accordance with the literature.[39]

5′-(4-Aminophenyl)-m-terphenyl

5′-(4-Nitrophenyl)-m-terphenyl (176 mg, 0.501 mmol, 1.00 eq.) was dissolved in EtOH (6 ml) and Pd/C (5.5 mg, 52 mmol, 10 mol%) was added. The atmosphere was exchanged by a H₂ atmosphere and the resulting mixture was stirred for 22 h at RT. Afterwards, the crude mixture was filtrated through a celite pad and the solvent was removed in vacuo. FC (pentane:EtOAc 3:2) yielded the product as a yellow solid (153 mg, 476 µmol, 95%).
$^1$H NMR (300 MHz, CDCl$_3$, 298 K): $\delta = 7.78$-$7.66$ ($m$, 8H, Aryl-H), 7.60-$7.33$ ($m$, 7H, Aryl-H), 6.93-$6.79$ ($m$, 2H, Aryl-H), 4.12 ($brs$, 2H, NH$_2$). $^{13}$C NMR (75 MHz, CDCl$_3$, 298 K): $\delta = 146.1$ (C), 142.4 (C), 142.4 (C), 141.6 (C), 131.7 (C), 128.9 (CH), 128.4 (CH), 127.6 (CH), 127.5 (CH), 124.6 (CH), 124.4 (CH), 115.7 (CH). HRMS (ESI-pos): Calculated mass for [M+H]$^+$: 322.15957, found: 322.15894.

The analytical data are in accordance with the literature.$^{[40]}$
13. $^1$H- and $^{13}$C-NMR spectra of new compounds

$^1$H NMR (500 MHz, CDCl$_3$, 293 K) of 3-nitro-$p$-quarterphenyl

$^{13}$C NMR (126 MHz, CDCl$_3$, 293 K) of 3-nitro-$p$-quarterphenyl
$^1$H NMR (300 MHz, DMSO-$d_6$, 293 K) of 4-bromo-4’-nitrobiphenyl

$^{13}$C NMR (75 MHz, DMSO-$d_6$, 293 K) of 4-bromo-4’-nitrobiphenyl
$^1$H NMR (300 MHz, DMSO-$d_6$, 293 K) of $N$-(1-naphthyl)-hydroxylamine

$^{13}$C NMR (75 MHz, DMSO-$d_6$, 293 K) of $N$-(1-naphthyl)-hydroxylamine
$^1$H NMR (300 MHz, CDCl$_3$, 293 K) of 5'-nitro-m-terphenyl

$^{13}$C NMR (75 MHz, CDCl$_3$, 293 K) of 5'-nitro-m-terphenyl
$^1$H NMR (300 MHz, CDCl$_3$, 293 K) of 2-(4-Butylphenyl)-4,4,5,5-tetramethyl-1,3,2-
dioxaborolan



$^{13}$C NMR (300 MHz, CDCl$_3$, 293 K) of 2-(4-Butylphenyl)-4,4,5,5-tetramethyl-1,3,2-
dioxaborolan



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\(^1\)H NMR (300 MHz, CDCl\(_3\), 293 K) of 4,4'-di(4-butylphenyl)azobenzol

\(^13\)C NMR (75 MHz, CDCl\(_3\), 293 K) of 4,4'-di(4-butylphenyl)azobenzol
$^1$H NMR (300 MHz, CDCl$_3$, 293 K) of 4-decyloxynitrosobenzol

$^{13}$C NMR (75 MHz, CDCl$_3$, 293 K) of 4-decyloxynitrosobenzol
14. Mechanistic investigations by means of periodic DFT calculations

Computational Details

The Vienna Ab-initio Simulation Package\(^{[41,42]}\) (VASP, version 5.4.4), was used to perform periodic DFT calculations with the PBE\(^{[43,44]}\) exchange–correlation functional and PAW-based\(^{[45,46]}\) pseudopotentials. The self-consistent field (SCF) convergence criterion was set to \(10^{-6}\) eV for the total energy. Geometries were optimized until the maximum force component was smaller than 0.01 eV/Å. The Methfessel-Paxton electron smearing scheme\(^{[47]}\) was applied (\(\sigma = 0.2\) eV), and the calculated energies were subsequently extrapolated to \(\sigma = 0\). A dipole correction along the surface normal\(^{[48]}\) was included and the first Brillouin Zone was sampled using a 3x3x1 Monkhorst-Pack k-point mesh.\(^{[49]}\) The wave functions were expanded in a plane-wave basis set up to an energy cutoff of 500 eV. In order to take into account long-range dispersion interactions, the D3 dispersion correction\(^{[9]}\) with Becke–Johnson damping\(^{[10,50-52]}\) was applied. Prior to all production calculations, the convergence of the total energy with respect to the energy cutoff and the numbers of k-points was carefully assessed.

The Ag(111) surface was modelled with an asymmetric slab geometry including four atomic layers. The upper two layers were allowed to relax during the optimization, while atoms in the remaining two layers were kept fixed at their bulk positions. In order to avoid erroneous interactions between periodic images, the size of the slab model was chosen such that the distance between the periodic images of the adsorbates exceeded 8.00 Å, and the height of the supercell was set large enough to ensure that the thickness of the vacuum layer above the adsorbates is at least 15.00 Å. The slab model was built with the ASE package\(^{[53,54]}\) using a calculated Ag lattice constant of 4.07 Å, which is in good agreement with the value found in literature (4.09 Å\(^{[55]}\)).

The molecular structures investigated in this work were generated with Avogadro\(^{[56,57]}\) and pre-optimized using the Turbomole program\(^{[58]}\) (version
7.4.1), before they were employed in the periodic calculations. The preoptimizations were performed with the def2-SVP basis set\textsuperscript{[59]} and the PBE-GGA\textsuperscript{[43,44]} exchange–correlation functional. Structures that were not used for periodic calculations were calculated with the def2-TZVP basis set\textsuperscript{[7]} and the TPSS functional.\textsuperscript{[60]} In all calculations, the resolution-of-identity (RI) approximation was employed\textsuperscript{[8,61]} and the DFT-D3 approach\textsuperscript{[9]} with Becke-Johnson damping\textsuperscript{[10,50-52]} was utilized. Geometries were regarded as converged when the change in energy between two iterations was smaller than $10^{-6}$ a. u. and the maximum norm of the cartesian gradients was below $10^{-3}$ a. u.

Adsorption energies $E_{\text{ads.}}$ were calculated according to the below equation, where $E_{\text{slab+X}}$ denotes the total energy of the adsorbate-adsorbent system, and $E_{\text{slab}}$ and $E_X$ are the total energies of the clean slab and the adsorbate $X$ in vacuum, respectively. These energies were always obtained employing identical calculation parameters, including the unit cell size and shape. Note that a negative $E_{\text{ads.}}$ corresponds to exothermic adsorption and that a more negative adsorption energy means stronger adsorption.

$$E_{\text{ads.}} = E_{\text{slab+X}} - E_{\text{slab}} - E_X$$

The images showing the adsorption geometries were generated with VMD 1.9.4.\textsuperscript{[62]}

**Computational study of the reaction of arylamines and nitroarenes on Ag(111)**

As a first step towards the calculation of polymerization pathways, the preferred adsorption geometries of all possible reactants, intermediates and products involved in the model reaction under study were carefully determined. As described in the main manuscript, we used aniline and nitrobenzene as smallest possible model reactants. For each adsorbate, several geometry optimizations starting from different orientations of the relaxed (molecular) structures on the
Ag(111) surface were performed. The most favorable structures were then used as initial geometries of the respective adsorbates in the later mechanistic studies. This procedure is important because (relative) energies of adsorbates on surfaces can be strongly sensitive to the position and orientation on the substrate. Even though there is no guarantee that the best possible adsorption geometry, i.e. the global minimum on the potential energy surface, was found for each adsorbate, this procedure ensures a high degree of comparability between calculated stages in the mechanistic pathways. The most favorable adsorption geometries of all considered reactants, intermediates and (by-)products are shown in Fig. S17 – S19. In the following mechanistic calculations, all adsorbates associated with an intermediate structure were calculated together in the same unit cell.

**Figure S17.** Converged adsorption geometries (tilted view and top view) of proposed (intermediate) by-products of the on-surface polymerization reaction of arylamines and nitroarenes on Ag(111). a Adsorbed H atom on Ag(111). b Adsorbed H2 molecule on Ag(111). c Adsorbed O atom on Ag(111).
Figure S18. Converged adsorption geometries (side view and top view) of monomeric structures involved in the investigated on-surface reaction of aniline and nitrobenzene on Ag(111).  

Figure S19. Converged adsorption geometries (side view and top view) of dimeric structures involved in the investigated on-surface reaction of aniline and nitrobenzene on Ag(111).

Please note that no reaction barriers or transition states were calculated to obtain the data shown in Fig. 6 in the main article, merely the relative total energies of the reactants, the possible intermediates and the proposed product are compared. Such calculations require a large amount of computation time and the calculation of transition states was out of reach with our resources. The geometry optimizations of the intermediate structures already required approximately three to four weeks each (the calculations were performed on a 72-core Intel Xeon Gold 6140 machine running at 2.30 GHz), and transition-state optimizations can be expected to be considerably more demanding. We stress that the knowledge of transition states would be essential for the unambiguous determination of the most
favorable reaction pathway.\textsuperscript{[63]} The Hammond postulate\textsuperscript{[64]} links product stability and barrier height for simple reactions, but its applicability for complex on-surface reactions must be considered questionable. If we make the - somewhat drastic - assumption that Hammond’s postulate is also valid for the reaction under study, we may assume that the pathways connecting the intermediates with the lowest energies will be predominantly pursued. Considering the lack of accessible alternatives to obtain information about the different pathways, this seems to be the most plausible assumption.

In order to back up our XPS assignments, we calculated the N1s XPS data for the 9 species shown in Fig. S18 and S19 using Teplyakov's method\textsuperscript{[65]}. The converged geometries from the periodic DFT calculations were utilized and the entire Ag slab was deleted except for the 1-3 Ag atoms directly underneath the nitrogen atoms. As Teplyakov and coworkers point out, this is an admittedly oversimplified approach, especially for adsorbates strongly interacting with the metal surface (which is the case for essentially all species investigated in this work). Hence, no perfect correlation between experimental and calculated N1s energies can be expected, but the results may still be qualitatively useful.\textsuperscript{[65]} The Turbomole program\textsuperscript{[58]} (version 7.4.1) was employed for these single-point calculations, along with the B3LYP\textsuperscript{[66-68]} exchange–correlation functional, the LANL2DZ ECP\textsuperscript{[69]} basis set for Ag atoms and the 6-311G(2df,2pd)\textsuperscript{[70]} basis set for all other atoms. The results are shown in Table S2. As expected, the magnitude of the calculated negative N1s orbital energies (second column) is much smaller than the experimental XPS data (also see Fig. 5). Note that due to the model setup, most of the calculations have been carried out as unrestricted Kohn-Sham calculations, which leads to different orbital energies for $\alpha$ - and $\beta$ -spin components (with a maximum difference of 0.26 eV). A correction of the calculated negative N1s orbital energies according to Teplyakov's method, which suggests simply adding $+10.03$ eV to the negative N1s orbital energies,\textsuperscript{[65]} (third
column) still results in a deviation of approximately 0.8 eV between the experimental and theoretical -NH$_2$ peaks.

**Table S2.** Calculated negative N1s orbital energies for the investigated nitrogen compounds on Ag(111). Column 2 shows the calculated negative orbital energies ($-\epsilon_{N1s}$) while column 3 shows the corrected energies after applying Teplyakov’s formula.$^{[65]}$ The last column shows the relative energies with respect to the calculated Ph-NH$_2$ N1s $\alpha$ orbital energy. The XPS spectra shown in Fig. 5 is used for comparisons, the peaks at 399.6 eV and 400.1 eV correspond to the amino and azo groups, respectively, while the peak at 397.7 eV can be ascribed to the deoxygenated nitro and dehydrogenated amino groups. For multilayers, a peak at 406 eV arises from the nitro groups (also see the discussion below Fig. 5).

|                  | $-\epsilon_{N1s}$ calc. [eV] | $-\epsilon_{N1s}$ calc. corr. [eV] | rel. energy [eV] |
|------------------|-------------------------------|-----------------------------------|-----------------|
| Ph-NH$_2$ $\alpha$ | 390.36                        | 400.39                            | 0.00            |
| Ph-NH$_2$ $\beta$  | 390.32                        | 400.35                            | -0.04           |
| Ph-NO$_2$ $\alpha$ | 393.87                        | 403.90                            | 3.51            |
| Ph-NO$_2$ $\beta$  | 393.69                        | 403.72                            | 3.33            |
| Ph-NH              | 388.63                        | 398.66                            | -1.73           |
| Ph-NO $\alpha$     | 390.77                        | 400.80                            | 0.41            |
| Ph-NO $\beta$      | 390.51                        | 400.54                            | 0.15            |
| Ph-N $\alpha$      | 389.00                        | 399.03                            | -1.36           |
| Ph-N $\beta$       | 388.74                        | 398.77                            | -1.62           |
| Ph-NH-NO-Ph $\alpha$ | 393.02                      | 403.05                            | 2.67            |
| Ph-NH-NO-Ph $\beta$ | 392.83                      | 402.86                            | 2.47            |
| Ph-NH-NO-Ph $\alpha$ | 391.02                      | 401.05                            | 0.66            |
| Ph-NH-NO-Ph $\beta$ | 390.98                      | 401.01                            | 0.63            |
| Ph-NH-N-Ph         | 389.53                        | 399.56                            | -0.83           |
| Ph-NH-N-Ph         | 390.97                        | 401.00                            | 0.61            |
| Ph-N-NO-Ph $\alpha$ | 393.71                        | 403.74                            | 3.35            |
| Ph-N-NO-Ph $\beta$ | 393.65                        | 403.68                            | 3.29            |
| Ph-N-NO-Ph $\alpha$ | 390.02                        | 400.05                            | -0.33           |
| Ph-N-NO-Ph $\beta$ | 389.92                        | 399.95                            | -0.44           |
| Ph-N=N-Ph          | 390.85                        | 400.88                            | 0.50            |
| Ph-N=N-Ph          | 390.76                        | 400.79                            | 0.41            |

Considering that Teplyakov’s formula$^{[65]}$ was developed for molecules on silicon, copper and nickel surfaces, a weaker correlation on silver surfaces is hardly surprising. We therefore decided to focus on the relative negative N1s orbital energies, using the Ph-NH$_2$ N1s $\alpha$ orbital energy as internal reference (fourth column). According to experiment (see Fig.5 and the discussion below this figure), the peak ascribed to the azo group (-N=N-) is expected 0.5 eV higher in energy than the amino (-NH$_2$) peak, which indeed fits the calculated energy differences very well. Yet, the calculated nitro (-NO$_2$) peak is no more than approximately 3.4 eV higher in energy than the amino peak, whereas the experiment suggests a relative energy of +6.7 eV. However, this may relate to the fact that the nitro peak
is observed for multilayers only, suggesting a different interaction with the surface compared to the calculated geometry. The peak ascribed to the reduced nitro or dehydrogenated amino groups is observed to have a relative energy of $-1.9 \text{ eV}$. The theoretical results indicate that both, the Ph-NH compound ($-1.73 \text{ eV}$) and the Ph-N compound ($-1.36 \text{ eV}$ and $-1.62 \text{ eV}$ for $\alpha$ and $\beta$ orbitals, respectively) could contribute to this XPS signal.
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