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Supporting Information

In Situ Coupling of Single Molecules Driven by Gold-Catalyzed Electrooxidation

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Supporting Information

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1. Synthetic Details

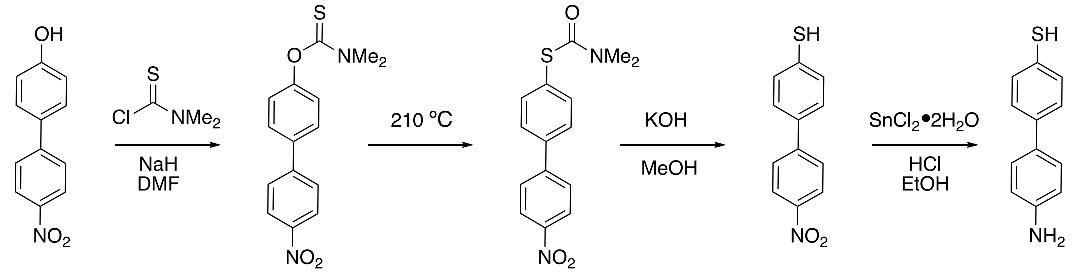
General Information

All reactions were performed open to atmosphere with magnetic stirring, unless otherwise noted. All commercial reagents and solvents were used as provided. All final products were dried *in vacuo* prior to reporting yields.

$AlCl_3$ was purchased from Acros Organics. $SnCl_2 \cdot 2\ H_2O$ and diazabicyclo[5.4.0]undec-7-ene (DBU) were obtained from Alfa Aesar. 4-hydroxy-4'-nitrophenyl was purchased from TCI Chemicals. Zn dust was purchased from Honeywell Riedel-deHaen. Di-*tert*-butyl dicarbonate was obtained from Oakwood Chemical. $CDCl_3$ was purchased from Cambridge Isotope Laboratories. Dichloromethane (DCM), ethyl acetate, ethanol, hexanes, methanol, tetrahydrofuran (THF) and toluene were obtained from Fisher Scientific. Anhydrous *N*,*N*-Dimethylformamide (DMF) was purchased from Sigma-Aldrich. Silica gel was obtained from Silicycle. **A1** and all other reagents and solvents were purchased from Sigma-Aldrich.

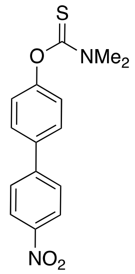
Synthesis of A2

A2 was prepared according to the sequence shown in Scheme S1. Individual steps are modified literature procedures.[1,2]



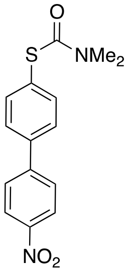
1 **2** **3** **A2**

Scheme S1: Synthetic scheme for synthesis of **A2**.



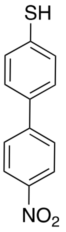
1. **1** was prepared according to a modified literature procedure.[1] An oven-dried 50 mL three-neck round bottom flask equipped with a Teflon coated stir bar under Ar atmosphere was charged with 4-hydroxy-4'-nitrophenyl (530 mg, 2.5 mmol) and anhydrous DMF (15 mL) and was cooled to 0 ºC in an ice bath. Sodium hydride (152 mg, 3.8 mmol) was added in three portions. After hydrogen evolution stopped, the dark red solution was warmed to room temperature and stirred for an additional 15 min. N,N-dimethylthiocarbamoyl chloride (461 mg, 3.7 mmol) was then added and the solution was stirred for another 15 min at room temperature. The solution was then heated to 60 ºC and stirred for 1 h during which time the color turned yellow. The solution was then cooled to room temperature and quenched with slow addition of water (10 mL). The mixture was extracted with DCM (3 x 10 mL), and the combined organic layers were washed with water (5 x 10 mL) and brine (2 x 10 mL), dried with Na_2SO_4 and the solvent was removed via rotary evaporation. The solid was purified by sequential recrystallizations in ethanol/ethyl acetate (1:1 v/v) to afford **1** as a fluffy yellow solid. Yield: 597 mg, 81%.

The characterization data is consistent with what has been previously reported.[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.30 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 3.49 (s, 3H), 3.38 (s, 3H).



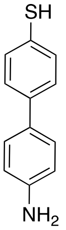
2. **2** was prepared according to a modified literature procedure.[1] **1** (120 mg, 0.4 mmol) was flame-sealed in a glass tube under vacuum. The tube was heated to 230 °C in a box furnace for 18 h and then quenched in air. The resulting orange solid was purified by recrystallization in ethanol to afford **2** as an orange powder. Yield: 90 mg, 75%.

The characterization data is consistent with what has been previously reported.[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.31 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.63 (s, 4H), 3.09 (s, 6H).



3. **3** was prepared according to a modified literature procedure.[1] An oven-dried 50 mL three-neck round bottom flask fitted with a reflux condenser and equipped with a Teflon coated stir bar under Ar atmosphere was charged with **2** (90 mg, 0.3 mmol), potassium hydroxide (145 mg, 2.6 mmol) and methanol (3 mL) and sparged for 20 minutes. The reaction mixture was then refluxed for 14 hours. The reaction was allowed to cool to room temperature before it was acidified with dropwise addition of 6 M HCl. A precipitate formed. Water (3 mL) was added and the brown-orange solid was collected by filtration, washed with water and dried under vacuum. The solid was then heated in toluene to dissolve an orange phase leaving a dark brown solid. This solid was removed by gravity filtration. The filtrate was collected and the solvent was removed via rotary evaporation to afford **3** as an orange powder. Yield: 40 mg, 59%.

The characterization data is consistent with what has been previously reported.[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.29 (d, *J* = 8.9 Hz, 2H), 7.70 (d, *J* = 8.9 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 3.55 (s, 1H).

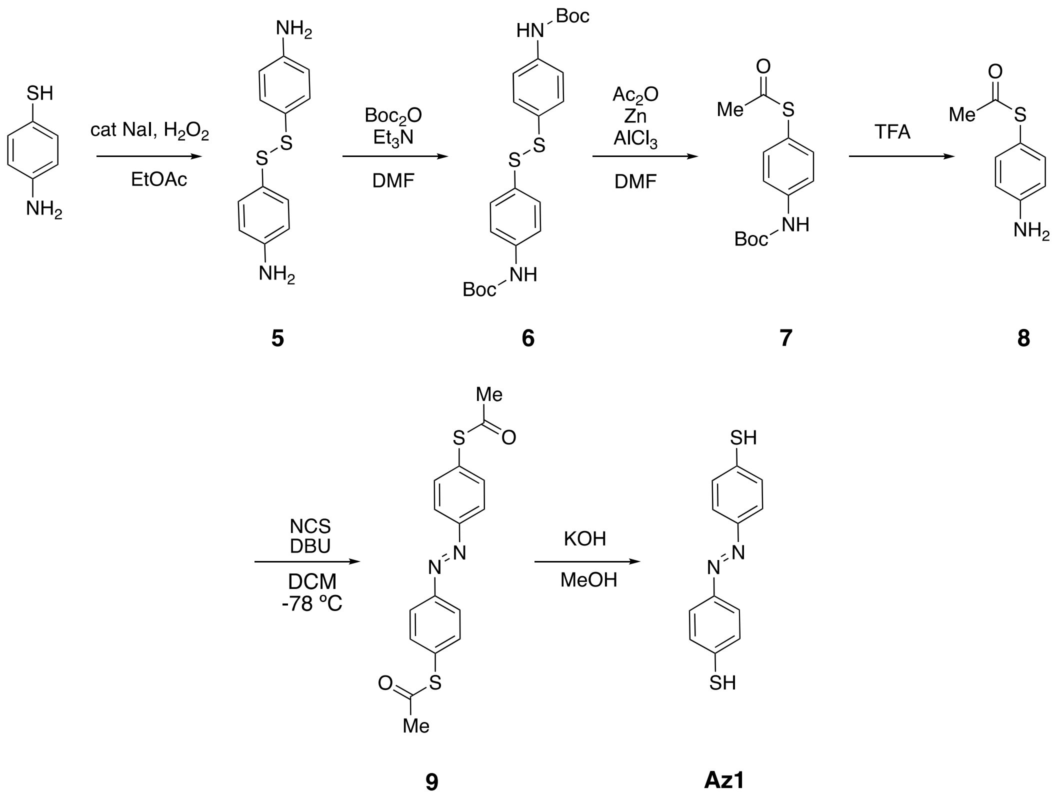


4. **A2** was prepared according to a modified literature procedure.[2] An oven-dried 50 mL three-neck round bottom flask fitted with a reflux condenser and equipped with a Teflon coated stir bar under Ar atmosphere was charged with **3** (40 mg, 0.2 mmol), $SnCl_2 \cdot 2\,H_2O$ (135 mg, 0.6 mmol) and ethanol (4 mL). The solution was sparged with Ar for 20 minutes. Concentrated aqueous HCl (0.2 mL) was then added and the solution was refluxed for 6 hours. The mixture was allowed to cool to room temperature and was then poured into 5 mL of ice cold water. The solution was basified by careful addition of 2 M aqueous NaOH until the pH reached ~10. The aqueous solution was then extracted with DCM (3 x 10 mL), dried with Na_2SO_4 and the solvent was removed via rotary evaporation to afford **4** as a yellow-orange powder. Yield: 9 mg, 26%.

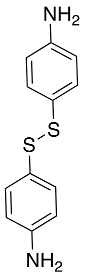
The characterization data is consistent with what has been previously reported.[2] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.44 – 7.34 (m, 4H), 7.31 (d, *J* = 8.3 Hz, 2H), 6.74 (d, *J* = 8.5 Hz, 2H), 3.72 (s, 2H), 3.44 (s, 1H).

Synthesis of Az1

Az1 was prepared in the sequence shown in Scheme S2. Individual steps are modified literature procedures.[3,4,5,6,7]

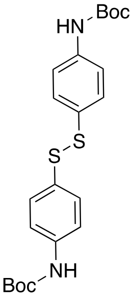


Scheme S2: Synthetic scheme for synthesis of **Az1**.



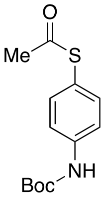
5. **5** was prepared according to a modified literature procedure.[3] A 50 mL round bottom flask was charged with 4-aminothiophenol (600 mg, 4.8 mmol), NaI (10 mg, 0.1 mmol), 30% H_2O_2 aqueous solution (0.55 mL, 5.0 mmol of H_2O_2) and ethyl acetate (15 mL). The reaction mixture was stirred open to atmosphere at room temperature for 24 h. The reaction was then diluted with ethyl acetate (60 mL) and washed with saturated $Na_2S_2O_3$ solution (30 mL). The aqueous layer was further extracted with ethyl acetate (2 x 25 mL) and the combined organic layers were washed with brine (75 mL), dried with Na_2SO_4 and the solvent was removed via rotary evaporation to afford **5** as a red oil that could be used without further purification. Yield; 596 mg, 99%.

The characterization data is consistent with what has been previously reported.[8] ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.28 (d, J = 3.0 Hz, 4H), 6.60 (d, J = 8.4 Hz, 4H), 3.78 (s, 4H).



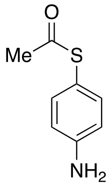
6. **6** was prepared according to a modified literature procedure.[4] A 50 mL three-neck round bottom flask under Ar atmosphere was charged with **5** (596 mg, 2.4 mmol), triethylamine (1.4 mL, 9.7 mmol), and THF (10 mL). A solution of di-tertbutyl-dicarbonate (2.095 g, 9.6 mmol) in THF (2 mL) was added dropwise to the disulfide solution and the reaction mixture was then stirred at room temperature for 2 days. The solvent was removed via rotary evaporation, and the waxy solid residue was purified using silica gel flash column chromatography, eluting with 10% ethyl acetate in hexanes to afford **6** as a red solid. Yield: 270 mg, 25%.

The characterization data is consistent with what has been previously reported.[4] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39 (d, *J* = 8.1 Hz, 4H), 7.29 (d, *J* = 9.0 Hz, 4H), 6.45 (s, 2H), 1.51 (s, 18H).



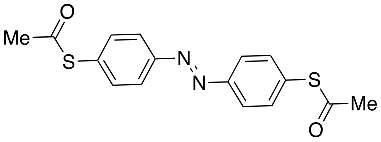
7. **7** was prepared according to a modified literature procedure.[4] An oven-dried 50 mL three-necked round bottom flask equipped with a Teflon coated stir bar under Ar atmosphere was charged with Zn dust (130 mg, 2.0 mmol) and anhydrous $AlCl_3$ (400 mg, 3.0 mmol). Degassed, anhydrous DMF (5 mL) was added, which caused the flask to heat up. When the flask cooled to room temperature, a solution of **6** (208 mg, 0.5 mmol) in degassed anhydrous DMF (2 mL) was added and the reaction mixture was stirred at 65 °C for 30 minutes, during which time most of the Zn dissolved. Acetic anhydride (0.14 mL, 1.5 mmol) was then added and the reaction stirred for an additional 18 h. The yellow/grey solution was cooled to 0 °C in an ice bath and quenched with careful addition of 5% w/w aqueous $NaHCO_3$ (25 mL). The reaction mixture was diluted with ethyl acetate (100 mL) and washed with 5% w/w aqueous $NaHCO_3$ (100 mL). The aqueous layer was further extracted with ethyl acetate (2 x 50 mL) and the combined organic layers were washed with water (5 x 50 mL) and brine (1 x 50 mL), dried with Na_2SO_4. The solvent was removed via rotary evaporation to afford **7** as a yellow solid. Yield: 230 mg, 94%.

The characterization data is consistent with what has been previously reported.[4] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 9.8 Hz, 2H), 6.54 (s, 1H), 2.39 (s, 3H), 1.52 (s, 9H).



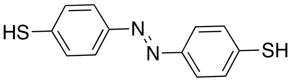
8. 8 was prepared according to a modified literature procedure[6]. A 25 mL round bottom flask equipped with a Teflon coated stir bar was charged with **7** (230 mg, 0.86 mmol) and trifluoroacetic acid (1.5 mL). The reaction was stirred at room temperature for 30 min, then diluted with DCM (25 mL) and washed with 1 M aqueous NaOH (25 mL). The aqueous layer was further extracted with DCM (2 x 15 mL), dried with Na_2SO_4. The solvent was removed via rotary evaporation to afford **8** as a yellow/brown solid. Yield: 130 mg, 90%.

The characterization data is consistent with what has been previously reported.[9] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.20 (d, *J* = 8.5 Hz, 2H), 6.71 (d, *J* = 8.5 Hz, 2H), 3.88 (bs, 2H), 2.39 (s, 3H).



9. 9 was prepared according to a modified literature procedure.[5] A 50 mL round bottom flask equipped with a Teflon coated stir bar was charged with **8** (130 mg, 0.8 mmol) and DCM (12 mL). 1,8-Diazabicyclo[5.4.0]undec-7-ene (0.24 mL, 1.6 mmol) was added and the solution was stirred for 5 min open to atmosphere before cooling to -78 °C in a dry ice/acetone bath. N-chlorosuccinimide (208 mg, 1.6 mmol) was added and the solution immediately turned bright red. After 10 minutes the flask was removed from the bath and the reaction was quenched with slow addition of saturated aqueous $NaHCO_3$ solution (5 mL). The solution was then diluted with DCM (35 mL), washed sequentially with water (1 x 50 mL) and 1 M aqueous HCl (1 x 50 mL), dried with Na_2SO_4 and the solvent was removed via rotary evaporation. The bright orange/red residue was purified using silica gel flash column chromatography, eluting with DCM in hexanes (0-70%) to afford **9** as a yellow/orange solid. Yield: 16 mg, 12%.

The characterization data is consistent with what has been previously reported.[10] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.98 (d, *J* = 8.6 Hz, 4H), 7.60 (dd, *J* = 8.2, 1.2 Hz, 4H), 2.49 (s, 6H).

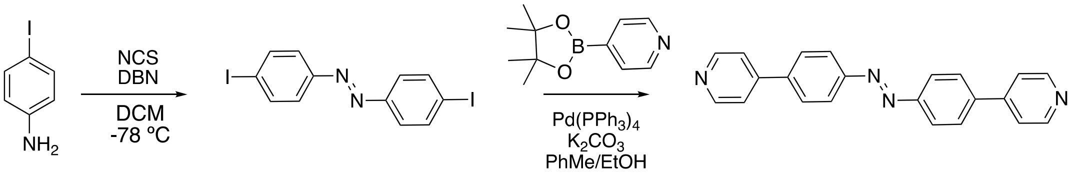


Az1. Az1 was prepared according to a modified literature procedure.[7] A 25 mL round bottom flask equipped with a Teflon coated stir bar was charged with **9** (11 mg, 0.03 mmol), 2 M KOH (0.2 mL) and methanol (5 mL). The reaction mixture was stirred at room temperature for 6 h during which time it turned red. The reaction was then cooled to 0 °C and acidified with dropwise addition of 1 M aqueous HCl (1 mL) and immediately turned yellow. The solution was diluted with DCM (20 mL), washed with additional 1 M aqueous HCl (20 mL), and the aqueous layer was further extracted with DCM (2 x 10 mL), dried with Na_2SO_4. The solvent was removed via rotary evaporation to afford **10** as a bright yellow solid. Yield: 12 mg, 99%.

Az1 has been previously reported.[11] While most of our characterization matches this report, we note that the thiol peak in our ^{1}H NMR does not match. Here we include additional characterization to support our synthesis. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.78 (d, J = 8.6 Hz, 4H), 7.37 (d, J = 8.6 Hz, 4H), 3.62 (s, 2H). IR: (cm^{-1}) 2929, 2857, 2270, 1589, 1481, 1263, 1095, 1011, 912, 840, 738. High-Res MS (ASAP-): calculated *m/z* for $[C_{12}H_9N_2S_2]^-$ 245.0207, found 245.0206.

Synthesis of Az5

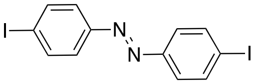
***trans*-Az5** was prepared in the sequence shown in Scheme S3. Individual steps are modified literature procedures.[5,12]



11

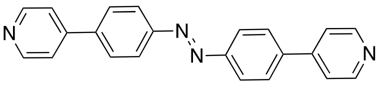
Az5

Scheme S3: Synthetic scheme for synthesis of **Az5.**



11. 11 was prepared according to a modified literature procedure.[5] A 50 mL round bottom flask equipped with a Teflon coated stir bar was charged with 4-iodoaniline (264 mg, 1.2 mmol) and DCM (18 mL). 1,5-Diazabicyclo[4.3.0]non-5-ene (0.3 mL, 2.4 mmol) was added and the solution was stirred for 5 min open to atmosphere before cooling to -78 °C in a dry ice/acetone bath. N-chlorosuccinimide (319 mg, 2.4 mmol) was added and the solution immediately turned bright red. After 10 min, the flask was removed from the bath and quenched with slow addition of saturated aqueous $NaHCO_3$ (5 mL). The solution was then diluted with DCM (35 mL), washed sequentially with water (50 mL) and 1 M aqueous HCl (50 mL), dried with Na_2SO_4 and the solvent was removed via rotary evaporation. The bright orange/red residue was purified using silica gel flash column chromatography, eluting with DCM in hexanes (0-100%) to afford **11** as a bright orange solid. Yield: 158 mg, 58%.

The characterization data is consistent with what has been previously reported.[5] ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.87 (d, *J* = 10.4 Hz, 4H), 7.65 (d, *J* = 10.2 Hz, 4H).



Az5. *trans*-**Az5** was prepared according to a modified literature procedure.[12] A 50 mL three-necked round bottom flask fitted with a reflux condenser and equipped with a Teflon coated stir bar under Ar atmosphere was charged with **11** (108 mg, 0.3 mmol), 4-pyridine boronic acid pinacol ester (112 mg, 0.6 mmol) and tetrakis(triphenylphosphine)palladium(0) (30 mg, 0.03 mmol). A separate 50 mL round bottom flask equipped with a Teflon stir bar under Ar atmosphere was charged with $KHCO_3$ (304 mg, 2.2 mmol), toluene (12 mL), ethanol (2 mL) and water (1 mL) and sparged with Ar for 20 min. The basic solution was then added to the mixture of solids resulting in a bright yellow cloudy solution. The reaction mixture was refluxed for 36 h. After cooling to room temperature, the solvent was removed via rotary evaporation. The solid residue was dissolved in ethyl acetate (50 mL), washed with water (2 x 50 mL) and brine (1 x 50 mL), dried with Na_2SO_4 and the solvent was removed via rotary evaporation. The red/brown residue was purified using silica gel flash column chromatography, eluting with 2.5-10% ethyl acetate in hexanes to afford *trans*-**Az5** as a bright orange solid. Yield: 60 mg, 72%.

This compound has been previously reported,[13] but only electronic absorption spectra were provided. Here we include additional characterization to support our synthesis.

^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.73 (d, *J* = 6.2 Hz, 4H), 8.09 (d, *J* = 8.7 Hz, 4H), 7.84 (d, *J* = 8.6 Hz, 4H), 7.65 (d, *J* = 5.3 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.7, 150.1, 147.3, 140.6, 127.8, 123.6, 121.5. IR: (cm^{-1}) 3050, 1596, 1490. 1404, 1265, 819, 730. High-Res MS (ASAP+): calculated *m/z* for $[C_{22}H_{17}N_4]^+$ 337.1453, found 337.1452.

cis-**Az5** was prepared by photoisomerization of *trans*-**Az5** according to a previous procedure.[13] A solution of *trans*-**Az5** in propylene carbonate (1 mL, 0.1 mM) was irradiated under UV light (365 nm) for 2 h. Conversion of *trans*-**Az5** to *cis*-**Az5** was monitored by electronic absorption spectroscopy (Figure S1) and the resulting spectra match the reported data.[13]

We also include ^{1}H NMR of *cis*-**Az5**. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.72 (d, *J* = 6.2 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.60 (d, *J* = 6.2 Hz, 1H).

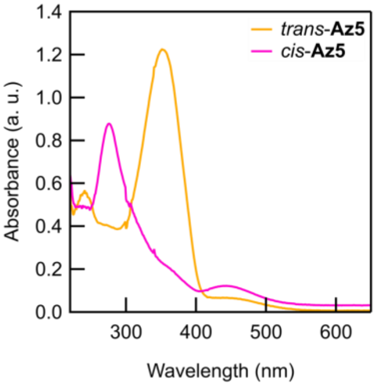
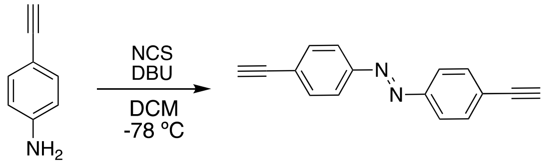


Figure S1. Electronic absorption spectra of *trans*-**Az5**, and *cis*-**Az5** generated by photoisomerization.

Synthesis of Az4

Az4 was prepared in the sequence shown in Scheme S4.



Scheme 4: Synthesis of **Az4.**

Az4. Az4 was prepared according to a modified literature procedure.[5] A 50 mL round bottom flask equipped with a Teflon coated stir bar was charged with 4-ethynyl aniline (113 mg, 1.0 mmol) and DCM (15 mL). 1,8-Diazabicyclo[5.4.0]undec-7-ene (0.3 mL, 2.0 mmol) was added and the solution was stirred for 5 min open to atmosphere before cooling to -78 °C in a dry ice/acetone bath. N-chlorosuccinimide (261 mg, 2.0 mmol) was added and the solution immediately turned bright red. After 10 minutes the flask was removed from the bath and quenched with slow addition of saturated aqueous $NaHCO_3$ (5 mL). The solution was then diluted with DCM (35 mL), washed sequentially with water (50 mL) and 1 M HCl (50 mL), dried with Na_2SO_4 and the solvent was removed via rotary evaporation. The bright orange/red residue was purified using silica gel flash column chromatography, eluting with DCM in hexanes (0-70%) to yield **Az4**. Yield: 60 mg, 55%.

The characterization data is consistent with what has been previously reported.[5] ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.89 (d, *J* = 8.6 Hz, 4H), 7.64 (d, *J* = 8.5 Hz, 4H), 3.24 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.5, 133.4, 125.4, 123.3, 83.6, 80.1. IR: (cm^{-1}) 3268, 1408, 1264, 1104, 1046, 847, 808, 763, 676, 636. High-Res MS (ASAP+): calculated *m/z* for $[C_{16}H_{11}N_2]^+$ 231.0922, found 231.0926.

2. Instrumentation

^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX400 and DMX500 spectrometers in $CDCl_3$ and at frequencies as noted. Data for ^{1}H NMR are reported as follows: chemical shift (δ, in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (*J*, in Hz), and integration (b = broad). Data for ^{13}C NMR are reported in terms of chemical shift. High-resolution mass spectrometry (High-Res MS) was performed at the Columbia University Mass Spectrometry Facility on a Waters XEVO G2XS QToF mass spectrometer equipped with a UPC2 SFC inlet and atmospheric solids analysis probe (ASAP). Electronic absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer using a 1.0 cm quartz cell. Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum400 FTIR spectrometer using a PIKE ATR attachment.

3. STM-BJ Method

Conductance measurements were made using a custom-built scanning tunneling microscope that has been described in detail before.[14] Conductance measurements were performed in dilute solutions (10-100 µM) of the molecules in propylene carbonate with tetrabutylammonium perchlorate as a supporting electrolyte. The insulated tips were created by driving a mechanically cut gold tip through Apiezon wax.[15] One-dimensional conductance histograms are constructed using logarithmic bins (100/decade), and two-dimensional histograms use logarithmic bins along the conductance axis (100/decade) and linear bins (1000/nm) along the displacement axis. The junction length is determined from the length profile of the molecular conductance plateau in the two-dimensional histograms.

4. Additional Data

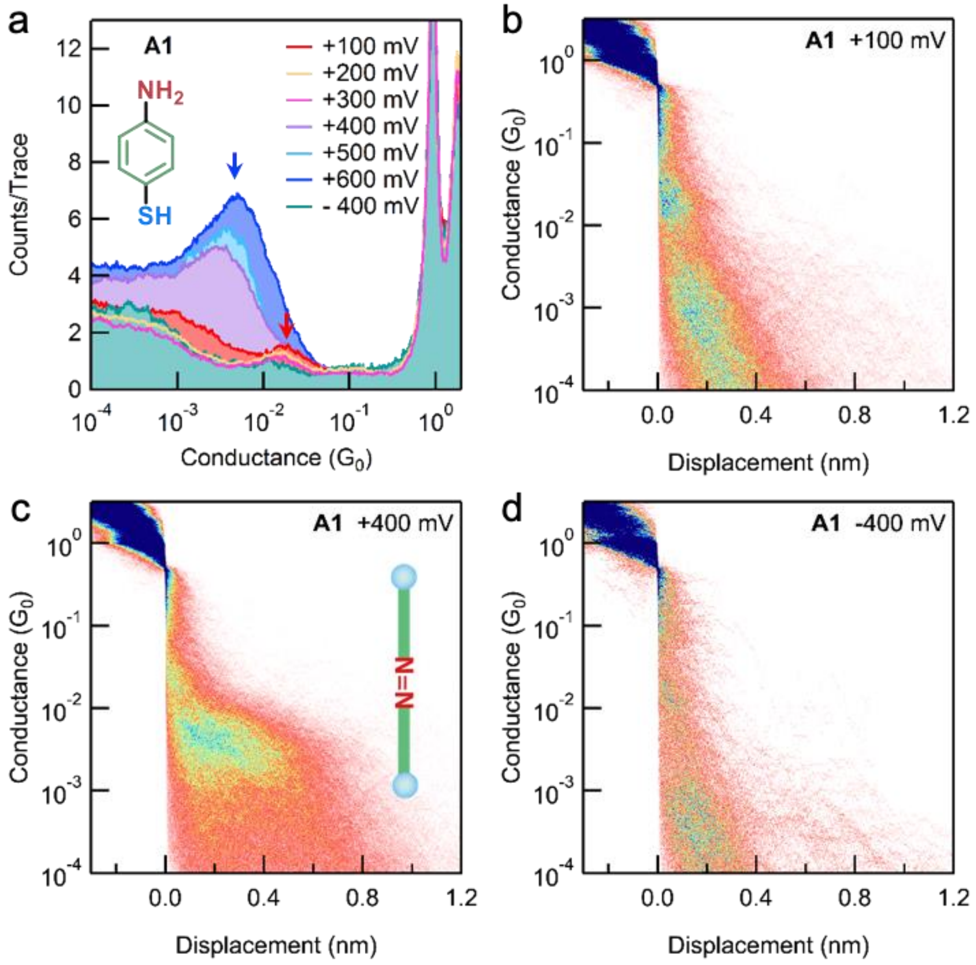


Figure S2. (a) Logarithm-binned 1D histograms of **A1** measured at different biases. Arrows indicate peak positions. (b-d) 2D conductance-displacement histogram of **A1** measured at +100 mV, +400 mV and -400 mV respectively. A new feature with a lower conductance and a longer plateau is observed at ~5×10^{-3} G_0 with a high positive tip bias (> +400 mV), indicating the formation of **Az1** junctions.

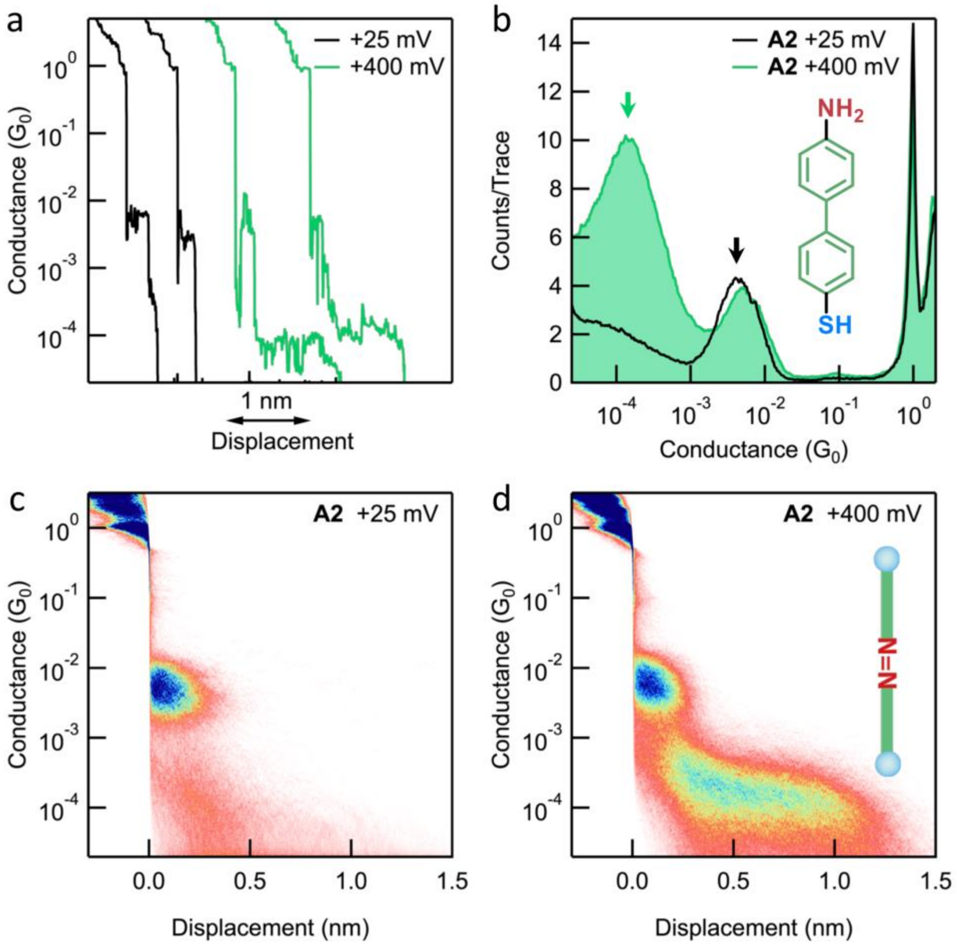


Figure S3. (a) Sample conductance traces of **A2** measured at a tip bias of +25 mV (black) and +400 mV (green). (b) Logarithm-binned 1D histograms of **A2** measured at +25 mV (black) and +400 mV (green). Inset: structure of **A2**. Arrows indicate peak positions. (c) 2D conductance-displacement histogram of **A2** measured at +25 mV. (d) 2D conductance-displacement histogram of **A2** measured at +400 mV. Inset: schematic of **Az2** formed *in situ*. A new feature with lower conductance and longer average plateau length is visible at ~2x10^{-4} G_0 using a high tip bias of +400 mV signifying the formation of **Az2** junctions.

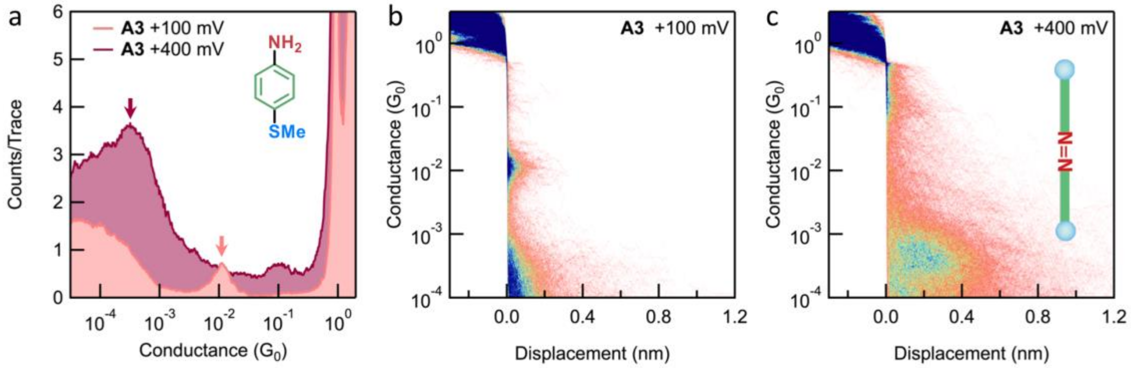


Figure S4. (a) Logarithm-binned 1D histograms of **A3** measured at a tip bias of +100 mV (pink) and +400 mV (dark pink). Inset: structure of **A3**. Arrows indicate peak positions. (b) 2D conductance-displacement histogram of **A3** measured at +100 mV. (c) 2D conductance-displacement histogram of **A3** measured at +400 mV. Inset: schematic of **Az3** formed *in situ*. A new feature with lower conductance and longer plateau length is visible at ~3x10^{-4} G_0 using a high tip bias of +400 mV, signifying the formation of **Az3** junctions.

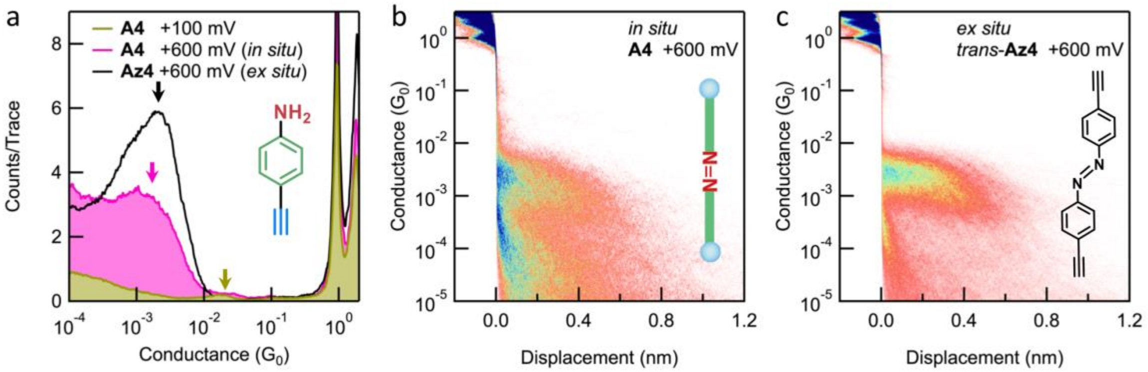


Figure S5. (a) Logarithm-binned 1D histograms of **A4** measured at a tip bias of +100 mV (green) and +600 mV (pink), and **Az4** prepared *ex situ* and measured at +600 mV (black). Inset: structure of **A3**. Arrows indicate peak positions. (b) 2D conductance-displacement histogram of **A4** measured at +600 mV. Inset: schematic of **Az4** formed *in situ*. (c) 2D conductance-displacement histogram of **Az4** prepared *ex situ* and measured at +600 mV. Inset: structure of *trans*-**Az4**.

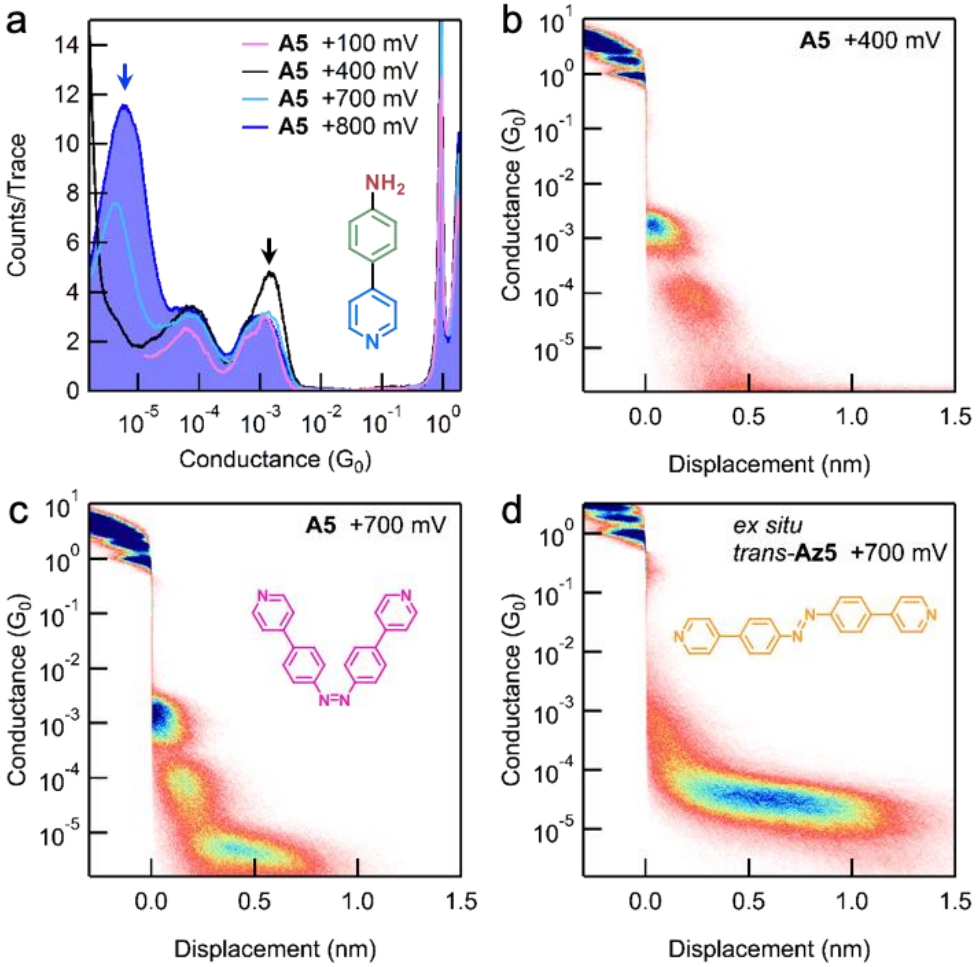


Figure S6. Logarithm-binned 1D histograms of **A5** measured at a tip bias of +100 mV (pink), +400 mV (black) +700 mV (light blue), and +800 mV (filled blue). Inset: structure of **A5**. Arrows indicate peak positions. (b) 2D conductance-displacement histogram of **A5** measured at +400 mV. (c) 2D conductance-displacement histogram of **A5** measured at +700 mV. Inset: structure of *cis*-**Az4**. (d) 2D conductance-displacement histogram of trans-**Az5** prepared *ex situ* and measured at +700 mV. Inset: structure of *trans*-**Az4**.

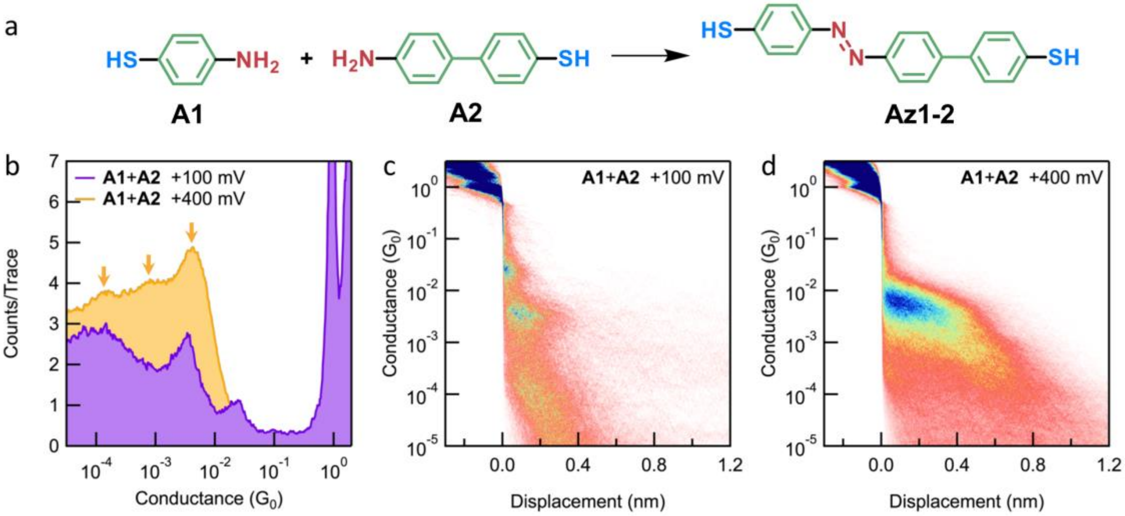


Figure S7. (a) Reaction that couples **A1** and **A2** to form **Az1-2.** (b) Logarithm-binned 1D histograms for the mixture of **A1** and **A2** measured at a tip bias of +100 mV (purple) and +400 mV (orange). At the high tip bias of +400 mV, three peaks corresponding to the coupling of **A1**+**A1**, **A2**+**A2**, and **A1**+**A2** leads to the formation of **Az1**, **Az2** and **Az1-2**, resulting in three peaks, indicated by arrows. (c) 2D conductance-displacement histogram for the mixture of **A1** and **A2** measured at a tip bias of +100 mV. (d) 2D conductance-displacement histogram for the mixture of **A1** and **A2** measured at a tip bias of +400 mV.

5. References

1. Waske, P., Wächter, T., Terfort, A. & Zharnikov, M. Nitro-Substituted Aromatic Thiolate Self-Assembled Monolayers: Structural Properties and Electron Transfer upon Resonant Excitation of the Tail Group. *J. Phys. Chem. C* **118**, 26049-26060 (2014).
2. Meyerbroeker, N., Waske, P. & Zharnikov, M. Amino-Terminated Biphenylthiol Self-Assembled Monolayers as Highly Reactive Molecular Templates. *J. Chem. Phys.* **142,** 101919 (2015).
3. Kirihara, M., Asai, Y., Ogawa, S., Noguchi, T., Hatano, A. & Hirai, Y. A Mild and Environmentally Benign Oxidation of Thiols to Disulfides. *Synthesis* **2007,** 3286-3289 (2007).
4. Kitagawa, K., Morita, T. & Kimura, S. A Helical Molecule That Exhibits Two Lengths in Response to an Applied Potential. *Angew. Chem. Int. Ed.* **44**, 6330-6333 (2005).
5. Antoine John, A. & Lin, Q. Synthesis of Azobenzenes Using N-Chlorosuccinimide and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU). *J. Org. Chem.* **82**, 9873-9876 (2017).
6. Lundt, B. F., Johansen, N. L., Vølund, A. & Markussen, J. Removal of *t*-butyl and *t*-butoxycarbonyl Protecting Groups with Trifluoroacetic Acid. *Int. J. Pept. Protein Res.* **12**, 258-268 (1978).
7. Zervas, L., Photaki, I. & Ghelis, N. On Cysteine and Cystein Peptides. II. S-Acylcysteines in Peptide Synthesis. *J. Amer. Chem. Soc.* **85**, 1337-134 (1963).
8. Li, X.-B., Li, Z.-J., Gao, Y.-J., Meng, Q.-Y., Yu, S., Weiss, R. G., Tung, C.-H. & Wu, L.-Z. Mechanistic Insights into the Interface-Directed Transformation of Thiols into Disulfides and Molecular Hydrogen by Visible-Light Irradiation of Quantum Dots. *Angew. Chem. Int. Ed.* **53**, 2085-2089 (2014).
9. Vibert, F., Marque, S. R. A., Bloch, E., Queyroy, S., Bertrand, M. P. Gastaldi, S. & Besson, E. Arylsulfanyl radical lifetime in nanostructured silica: dramatic effect of the organic monolayer structure. *Chem. Sci.* **5**, 4716-4723 (2014).
10. Flatt, A. K., Dirk, S. M., Henderson, J. C., Shen, D. E., Su, J., Reed, M. A. & Tour, J. M. Synthesis and testing of new end-functionalized oligomers for molecular electronics. *Tetrahedron* **59**, 8555-8570 (2003).
11. Huang, Y.-F., Zhu, H.-P., Liu, G.-K., Wu, D.-Y., Ben, B. & Tian, Z.-Q. When the Signal Is Not from the Original Molecule To Be Detected: Chemical Transformation of para-Aminothiophenol on Ag during the SERS Measurement *J. Amer. Chem. Soc.* **132**, 9244-9246 (2010).
12. Boz, S.; Stöhr, M., Soydaner, U. & Mayor, M. Protecting-Group-Controlled Surface Chemistry—Organization and Heat-Induced Coupling of 4,4′-Di(*tert*-butoxycarbonylamino)biphenyl on Metal Surfaces. *Angew. Chem. Int. Ed.* **48**, 3179-3183 (2009).
13. Zhang, D. Synthesis and photophysical properties of square and triangular organoplatinum(II) metallacycles. *Dyes and Pigments* **127**, 128-132 (2016).

14. Venkataraman, L., Klare, J. E., Nuckolls, C., Hybertsen, M. S. & Steigerwald, M. L. Dependence of Single-Molecule Junction Conductance on Molecular Conformation. *Nature* **442**, 904-907 (2006).
15. Nagahara, L. A., Thundat, T. & Lindsay, S. M. Preparation and Characterization of STM Tips for Electrochemical Studies. *Rev. Sci. Inst.* **60**, 3128-3130 (1989).