Supporting Information

Gold-Carbon Contacts from Oxidative Addition of Aryl Iodides

Rachel L. Starr[1], Tianren Fu[1], Evan A. Doud[1], Ilana Stone,[1] Xavier Roy[1*], Latha Venkataraman[1,2*]

[1]Department of Chemistry and [2]Department of Applied Physics, Columbia University, New York, New York, 10027, United States

* e-mail: (L.V.) lv2117@columbia.edu; (X.R.) xr2114@columbia.edu

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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.

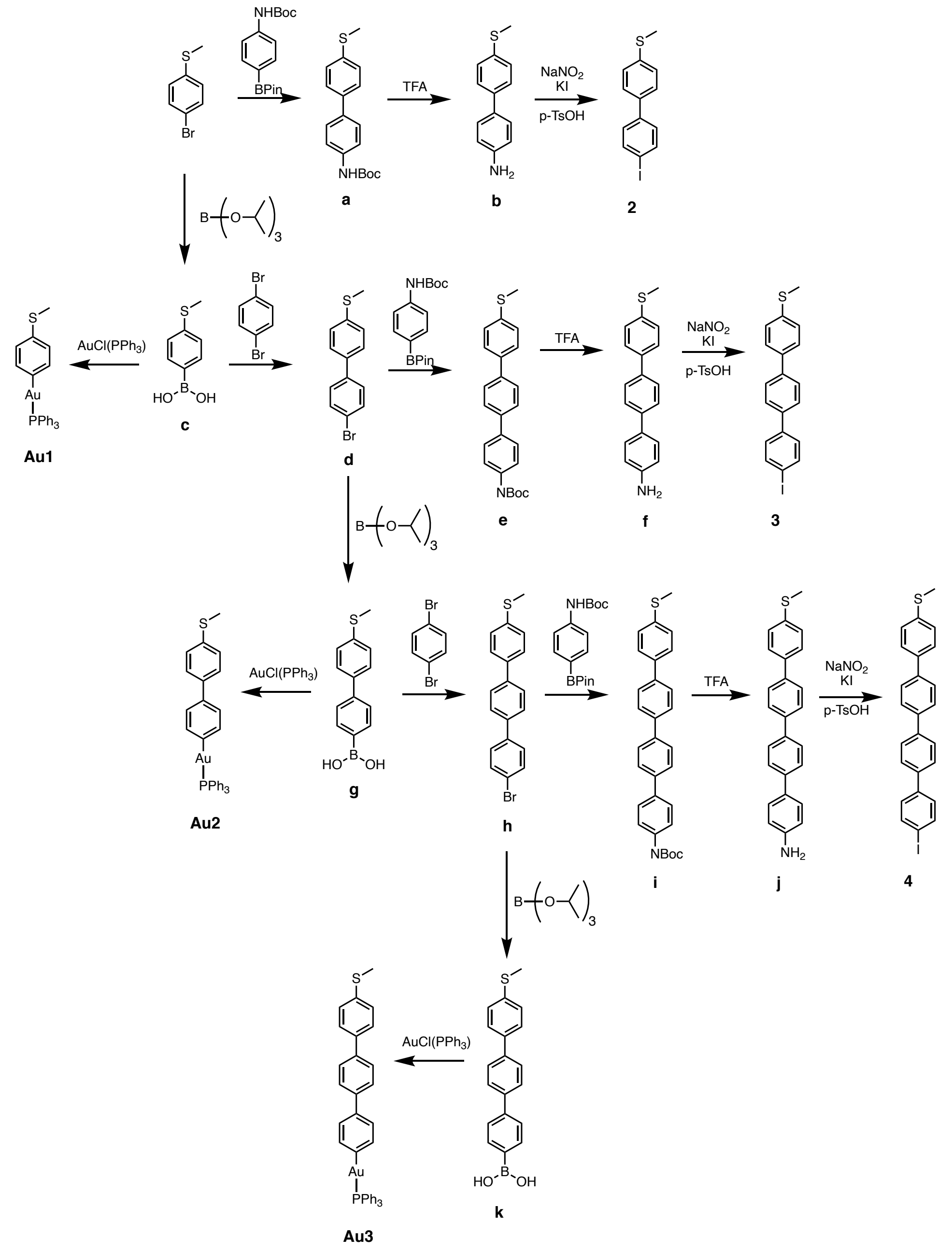
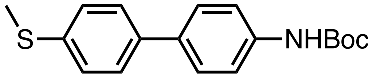


Figure S1: Synthetic scheme for the synthesis of asymmetrical iodides (**2-4**) and gold analogs (**Au1-Au3**).

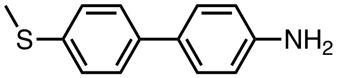
4-bromothioanisole was purchased from Acros Organics. Trifluoroacetic acid (TFA), benzene, and chloro(triphenylphosphine)gold(I) were obtained from Alfa Aesar. Triisopropyl borate was purchased from Strem Chemicals. $CDCl_3$, CD_2Cl_2, and DMSO-d_6 were purchased from Cambridge Isotope Laboratories. Dichloromethane (DCM), ethyl acetate, ethanol, hexanes, acetonitrile, tetrahydrofuran (THF), and toluene were obtained from Fisher Scientific. Dry and deoxygenated solvents were prepared by elution through a dual-column solvent system (MBraun SPS). Silica gel was obtained from Silicycle. All other reagents were purchased from Sigma-Aldrich.



a

a. Synthesized following a modified literature procedure.[1] A 250 mL three-necked round bottom flask fitted with a reflux condenser and equipped with a Teflon coated stir bar under N_2 atmosphere was charged with 4-bromothioanisole (500 mg, 2.46 mmol), 4-(N-boc-amino)phenyl boronic acid pinacol ester (864 mg, 2.71 mmol) and tetrakis(triphenylphosphine)palladium(0) (228 mg, 0.197 mmol). A separate 100 mL round bottom flask equipped with a Teflon stir bar under N_2 atmosphere was charged with potassium bicarbonate (1700 mg, 12.3 mmol), toluene (60 mL), ethanol (9 mL) and water (6 mL) and sparged with N_2 for 20 minutes. The basic solution was then added to the solids resulting in a bright yellow cloudy solution. The reaction mixture was refluxed at 110 °C for 24 h. After cooling to room temperature, the solvent was removed via rotary evaporation. The solid residue was dissolved in DCM (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 crude brown solid was purified using silica gel flash column chromatography, eluting with 5% ethyl acetate in hexanes to afford **1** as a white solid. Yield: 488 mg, 63%.

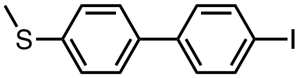
The characterization data is consistent with what has been previously reported.[1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (ddt, *J* = 6.7, 4.3, 2.2 Hz, 4H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.34 – 7.29 (m, 2H), 6.49 (s, 1H), 2.51 (s, 3H), 1.54 (s, 9H).



b

b. A vial containing protected amine **a** (163 mg, 0.517 mmol) was equipped with a Teflon coated stir bar and charged with TFA (4.0 mL, 51.7 mmol) and stirred for 30 minutes. The reaction mixture was diluted with DCM (10 mL) and washed with 1M NaOH (3 x 10 mL). The aqueous layers were combined and extracted further with DCM (2 x 10 mL). All organic layers were combined and dried with Na_2SO_4, and the solvent was removed via rotary evaporation to afford the deprotected amine. Yield: 97 mg, 87%.

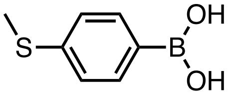
^{1}H NMR (300 MHz, DMSO-d_6) δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 6.74 (d, *J* = 8.5 Hz, 2H), 2.48 (s, 3H).



2

2. A vial containing the deprotected amine **b** (157 mg, 0.729 mmol) was equipped with a Teflon coated stir bar and charged with p-toluenesulfonic acid (377 mg, 2.19 mmol). The solids were dissolved in 10 mL MeCN and the mixture was cooled to 0 °C. In a separate vial, potassium iodide (303 mg, 1.82 mmol) and sodium nitrite (101 mg, 1.46 mmol) were dissolved in 0.3 mL water. The aqueous solution was slowly added dropwise to the organic solution (immediate color change to brown). The reaction was left to stir overnight and warm to room temperature. After 18 h, the reaction mixture was diluted with water (20 mL) and basified (pH 9) with sodium bicarbonate. Sodium thiosulfate (2 mL) was added. The mixture was extracted with ethyl acetate (3 x 30 mL). The organic layers were combined and dried with Na_2SO_4, and the solvent was removed via rotary evaporation. The crude material was purified using silica gel flash column chromatography, eluting with 5% ethyl acetate in hexanes to afford **2** as a light yellow solid. Yield: 154 mg, 65%.

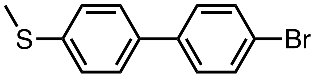
The characterization data is consistent with what has been previously reported.[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.27 (m, 4H), 2.52 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.14, 137.89, 128.97, 128.62, 127.81, 127.17, 124.28, 90.83, 15.87. HRMS (ASAP+) calculated for $C_{13}H_{11}SI^+$ $[M+H]^+$ 325.9626, observed 325.9629 $[M+H]^+$.



c

c. Boronic acids were synthesized following a modified literature procedure.[1] An oven-dried 2-neck 250 mL round bottom flask equipped with a Teflon coated stir bar, 60 mL addition funnel with a rubber septum, gas inlet adapter, and rubber septum was charged with 50 mL of THF under N_2 atmosphere. The flask was cooled to -78 °C in a dry ice/acetone bath, and *n*-BuLi (2.5 M in hexanes, 9.63 mL, 24.1 mmol) was added to the cooled THF and allowed to stir for 10 minutes. A solution of 4-bromothioanisole (3.00 g, 14.8 mmol) in 50 mL of THF was added to the addition funnel via a N_2 flushed syringe. The 4-bromothioanisole solution was then added dropwise to the *n*-BuLi solution and the reaction was stirred for 1 h, forming a white slurry. A solution of triisopropyl borate (3.78 g, 20.1 mmol) in 20 mL of THF was then added to the addition funnel using a N_2 flushed syringe. The triisopropyl borate solution was added dropwise; the reaction was warmed to room temperature after the addition finished and was stirred for an additional 3 h. The reaction was then opened to air, 100 mL of water was added dropwise through the addition funnel, and allowed to stir for an additional 30 min. 1M aqueous HCl was slowly added until a pH of 1 was obtained, and the mixture was stirred for 30 min. THF was then removed in vacuo. The resulting solid was then filtered and washed with water (3 x 50 mL), hexanes (3 X 50 mL), and dried overnight in vacuo to yield 3 as a white fluffy powder. Yield: 1.53 g, 62%.

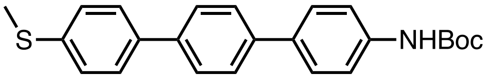
The characterization data is consistent with what has been previously reported.[1] ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.94 (s, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 2.47 (s, 3H).



d

d. Synthesized following a modified literature procedure.[1] A 250 mL three-necked round bottom flask fitted with a reflux condenser and equipped with a Teflon coated stir bar under N_2 atmosphere was charged with **c** (1500 mg, 8.93 mmol), 1,4-dibromobenzene (4630 mg, 19.6 mmol) and tetrakis(triphenylphosphine)palladium(0) (310 mg, 0.268 mmol). A separate 250 mL round bottom flask equipped with a Teflon stir bar under N_2 atmosphere was charged with potassium bicarbonate (6170 mg, 44.6 mmol), dioxane (60 mL), and water (30 mL) and sparged for 20 minutes. The basic solution was then added to the solid resulting in a yellow solution. The reaction mixture was refluxed at 95 °C for 24 hours. 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 (3 x 50 mL) and brine (2 x 50 mL), dried with Na_2SO_4, and the solvent was removed via rotary evaporation. The light yellow solid was purified using silica gel flash column chromatography, eluting with hexanes to afford **d** as an off-white solid. Yield: 1555 mg, 62%.

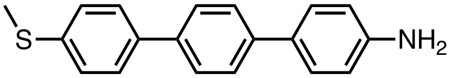
The characterization data is consistent with what has been previously reported.[1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.9 Hz, 2H), 7.51 – 7.39 (m, 4H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.52 (s, 3H).



e

e. Prepared by the same procedure as **a**, but using **d** (140 mg, 0.501 mmol) as the starting bromide. Yield: 133 g, 68%.

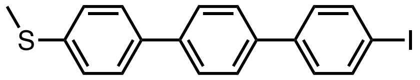
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 4H), 7.57 (dd, *J* = 8.5, 3.6 Hz, 4H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 6.51 (s, 1H), 2.53 (s, 3H), 1.54 (s, 9H).



f

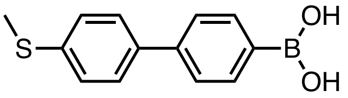
f. Prepared by the same procedure as **b**, but using **e** (133 mg, 0.341 mmol) as the starting protected amine. Yield: 79 mg, 79%.

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.70 – 7.58 (m, 6H), 7.38 (dd, J = 18.2, 8.5 Hz, 4H), 6.65 (d, J = 8.5 Hz, 2H), 5.23 (s, 2H), 2.51 (s, 3H).


3

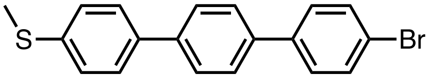
3. Prepared by the same procedure as **2**, but using **f** (79 mg, 0.269 mmol) as the deprotected amine. Yield: 13 mg, 12%.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.83 (d, J = 8.4 Hz, 1H), 7.76 (s, 4H), 7.70 (ddd, J = 13.4, 8.6, 1.3 Hz, 3H), 7.55 – 7.46 (m, 2H), 7.38 – 7.36 (m, 2H), 2.52 (s, 3H). Insolubility of the compound precluded ^{13}C NMR characterization. HRMS (ASAP+) calculated for $C_{19}H_{15}SI^+$ $[M+H]^+$ 401.9939, observed 401.9954 $[M+H]^+$.


g

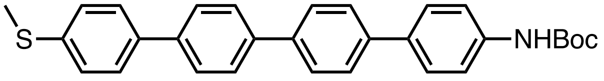
g. Prepared via the same procedure as **c**, but using **d** (1.00 g, 3.58 mmol) as the starting bromide. Yield: 720 mg, 82%.

The characterization data is consistent with what has been previously reported.[1] ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.03 (s, 2H), 7.86 (d, J = 8.2 Hz, 2H), 7.63 (t, J = 8.4 Hz, 4H), 7.35 (d, J = 8.5 Hz, 2H), 2.51 (s, 3H).


h

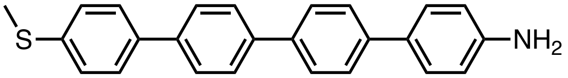
h. Prepared in a similar manner to **d**, with some modifications. **c** (1.0 g, 5.95 mmol) was used as the starting boronic acid, and 4,4'-dibromobiphenyl (2.3 g, 7.37 mmol) was used as the starting bromide. The reaction was run in a 1:4 H_2O/THF solvent mixture at 85 °C for 2 days. The product was obtained as a white powder. Yield: 1.58 g, 75%.

The characterization data is consistent with what has been previously reported.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 4.6 Hz, 4H), 7.60 – 7.48 (m, 6H), 7.35 (d, J = 8.5 Hz, 2H), 2.54 (s, 3H).


i

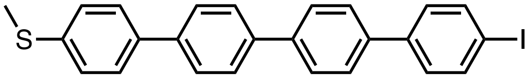
i. Synthesized following a modified literature procedure.[4] A 3-necked round bottom flask was charged with **h** (150 mg, 0.422 mmol), 4-(N-boc-amino)phenyl boronic acid pinacol ester (142 mg, 0.443 mmol), tetrakis(triphenylphosphine)palladium(0) (15 mg, 0.0127 mmol), and CsF (192 mg, 1.27 mmol) under N_2 atmosphere. The solids were dissolved in anhydrous THF (12.5 mL) and refluxed for 3 days. The reaction mixture was cooled to room temperature, and the Boc-protected product precipitated from the reaction mixture and was collected by filtration. The solid was washed repeatedly with THF and H_2O to give a gray solid. Yield: 70 mg, 35%.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 – 7.67 (m, 12H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 6.56 (s, 1H), 2.52 (s, 3H), 1.54 (s, 9H). Insolubility of the compound precluded ^{13}C NMR characterization.



j

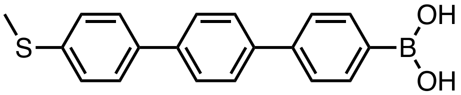
j. Synthesized following a modified literature procedure.[4] Protected amine **i** (70 mg, 0.150 mmol) was suspended in 0.5 mL DCM and cooled to 0 °C. TFA (1.0 mL) was added dropwise and the resulting solution was stirred for 24 h. Upon treatment with aqueous NaOH (2 M, ~1.5 mL) the product precipitated from the solution and was collected by filtration. Repeated washing with H_2O and DCM gave **j**. Yield: 19 mg, 34%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.82 – 7.62 (m, 10H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 6.69 (d, *J* = 7.6 Hz, 2H), 5.15 (s, 1H), 4.75 (s, 1H), 2.52 (s, 3H). Insolubility of the compound precluded ^{13}C NMR characterization.



4

4. Prepared by the same procedure as **2** and **3**, but using **j** (19 mg, 0.0517 mmol) as the deprotected amine. Yield: 6 mg, 24%.

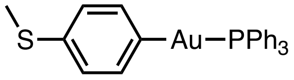
^{1}H NMR (300 MHz, DMSO-d_6) δ 7.72 (d, *J* = 30.4 Hz, 8H), 7.37 (d, *J* = 8.0 Hz, 3H), 6.68 (m, 1H), 5.07 (d, *J* = 4.8 Hz, 2H), 4.95 (s, 2H), 2.52 (s, 3H). Insolubility of the compound precluded ^{13}C NMR characterization. HRMS (ASAP+) calculated for $C_{25}H_{20}SI^+$ $[M+H]^+$ 479.0330, observed 479.0327 $[M+H]^+$.



k

k. Prepared via the same procedure as **c** and **g**, but using **h** (1.0 g, 2.81 mmol) as the starting bromide. Isolated as a light tan powder. Yield: 800 mg, 89%.

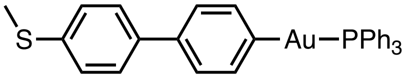
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.06 (s, 2H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.76 (dd, *J* = 3.5, 1.9 Hz, 4H), 7.69 (d, *J* = 8.1 Hz, 5H), 7.38 (s, 2H), 2.52 (s, 3H).



Au1

Au1. Synthesized following a modified literature procedure.[5] An oven-dried round bottom flask was charged with boronic acid **c** (50 mg, 0.298 mmol) and cesium carbonate (88.1 mg, 0.271 mmol) under a N_2 atmosphere. The solids were dissolved in 5 mL of isopropanol. Chloro(triphenylphosphine)gold(I) (66.9 mg, 0.135 mmol) was added and the reaction mixture was sparged with N_2 for 20 minutes. The reaction was then stirred at 50 °C for 24 h. After cooling to room temperature, the solvent was removed via rotary evaporation. The solid residue was dissolved in benzene, filtered through celite, and concentrated again to yield a white solid. To recrystallize, a solution of **Au1** in benzene was layered with an equal volume of hexanes and placed in a 5 °C refrigerator overnight. Yield: 31 mg, 18%.

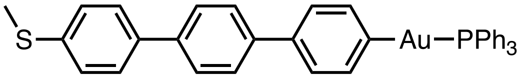
The characterization data is consistent with what has been previously reported.[6] ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.64 – 7.58 (m, 6H), 7.51 (ddd, J = 14.4, 7.4, 2.1 Hz, 9H), 7.46 – 7.43 (m, 2H), 7.19 – 7.15 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 139.64, 134.37, 134.26, 131.19, 131.17, 129.09, 129.00, 126.08, 126.03, 16.08; ^{31}P NMR (202 MHz, CD_2Cl_2) δ 43.55. HRMS (ESI+) calculated for $C_{25}H_{23}AuPS^+$ $[M+H]^+$ 583.0924, observed 583.0933 $[M+H]^+$.



Au2

Au2. Prepared via the same procedure as **Au1**, but using **g** (22 mg, 0.0950 mmol) as the starting boronic acid. Isolated as a white solid. Yield: 15 mg, 25%.

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.68 – 7.46 (m, 22H), 7.31 (d, J = 8.4 Hz, 2H), 2.51 (s, 3H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 140.05, 134.78, 134.67, 131.60, 131.58, 129.50, 129.41, 126.49, 126.44, 16.49.; ^{31}P NMR (121 MHz, CD_2Cl_2) δ 43.47. HRMS (ESI+) calculated for $C_{31}H_{27}AuPS^+$ $[M+H]^+$ 659.1237, observed 659.1246 $[M+H]^+$.



Au3

Au3. Prepared via the same procedure as **Au1** and **Au2**, but using **k** (50 mg, 0.156 mmol) as the starting boronic acid. Isolated as a light brown solid. Yield: 27 mg, 24%.

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.73 – 7.44 (m, 26H), 7.33 (d, J = 1.9 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 140.37, 134.99, 134.89, 132.55, 132.47, 132.31, 131.74, 129.66, 129.58, 129.05, 128.95, 127.74, 127.68, 127.60, 127.43, 54.27, 54.06, 53.84, 53.62, 53.41, 16.30; ^{31}P NMR (121 MHz, CD_2Cl_2) δ 43.47. HRMS (ESI+) calculated for $C_{37}H_{31}AuPS^+$ $[M+H]^+$ 735.1550, observed 735.1559 $[M+H]^+$.

2. Instrumentation

^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX300, DRX400 and DMX500 spectrometers in solvents as specified 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 and ^{31}P NMR are reported in terms of chemical shift. Accurate mass measurements/high resolution mass spectra (HRMS) were obtained from the Columbia University Chemistry Department Mass Spectrometry Facility on a Waters XEVO G2-XS QToF mass spectrometer equipped with UPLC inlet and a LockSpray source with one of three probes: electrospray ionization (ESI) probe, atmospheric pressure chemical ionization (APCI) probe, or atmospheric pressure solids analysis probe (ASAP). Electrochemical measurements were performed on a Bio-Logic VMP-3 potentiostat/galvanostat.

3. DFT Calculation Details

For transmission function calculations, the relaxed geometry of each molecule in the junction is found using density functional theory (DFT). The target molecule is first relaxed with Au atoms bound to each linker. For **Au1**-**Au4**, two Au atoms are placed on the Au linker, and one Au atom on the S linker. For **1**-**4**, one Au atom is placed on the S linker, but a Au_{19} cluster is put on the I linker, to better simulate the Au–I bond. The geometry is relaxed until the maximum residue force component per atom is below 10^{-2} eV·Å^{-1}. Once the geometry is optimized, two Au_{60} tetrahedral clusters are appended to each linker, replacing the Au atoms used during the geometry optimization. For B3LYP calculations, smaller Au_{18} clusters are used to decrease the time of each calculation. Within the clusters, the neighboring Au–Au distance is 2.88 Å. The clusters represent the (111) lattice surface of gold. Figure S5 demonstrates the geometry of Au_{60}-species-Au_{60} cluster used in the calculation for **Au2** and **2**, respectively. The structures are illustrated using VESTA 3.[7]

4. STM-BJ Method

Conductance measurements were made using a custom-built scanning tunneling microscope that has been described in detail before.[8] Conductance measurements were performed in dilute solutions (100 µM) of the molecules in either 1,2,4-trichlorobenzene (TCB), or propylene carbonate (PC) with 0.1 M tetrabutylammonium perchlorate ($TBAPF_6$) as a supporting electrolyte.[9] The insulated tips used with PC were created by driving a mechanically cut gold tip through Apiezon wax.[9] One-dimensional (1D) conductance histograms are constructed using logarithmic bins (100/decade), and two-dimensional (2D) histograms use logarithmic bins along the conductance axis (100/decade) and linear bins (1000/nm) along the displacement axis. The junction length is determined by displacement profiling of the molecular conductance feature in the two-dimensional histograms.

5. Additional Data

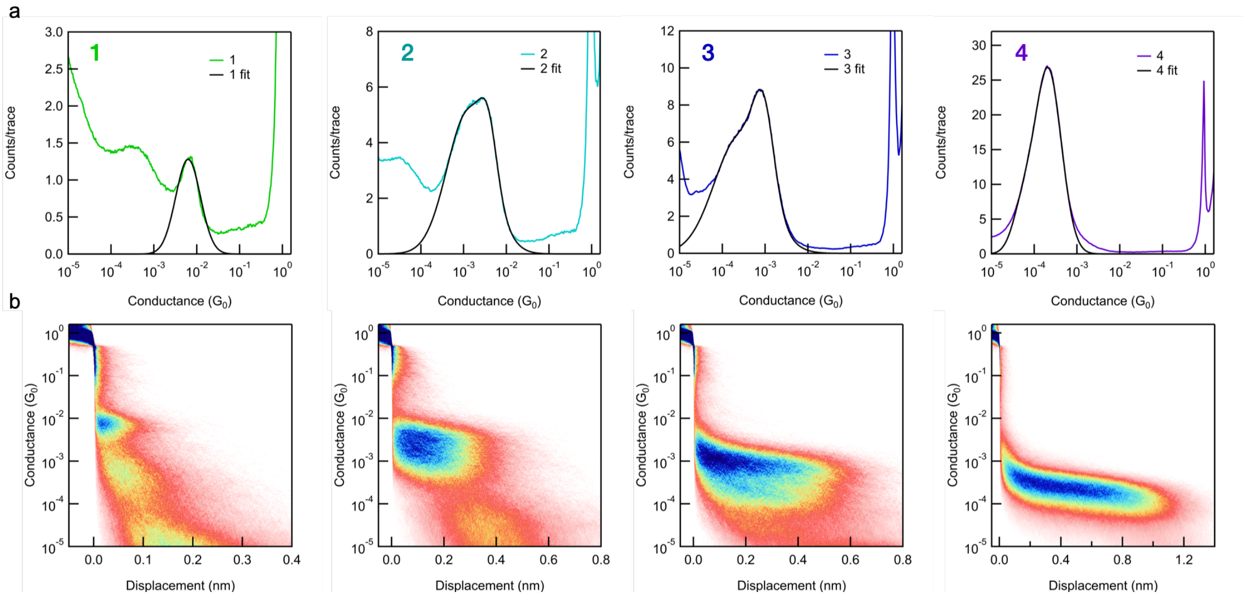


Figure S2. (a) Logarithm-binned 1D and (b) and (b) 2D conductance-displacement histograms of **1-4** measured in TCB at 100 mV. Double Gaussian fits in (a) are shown in black. Peak splitting is most clearly observed in **2** and **3**.

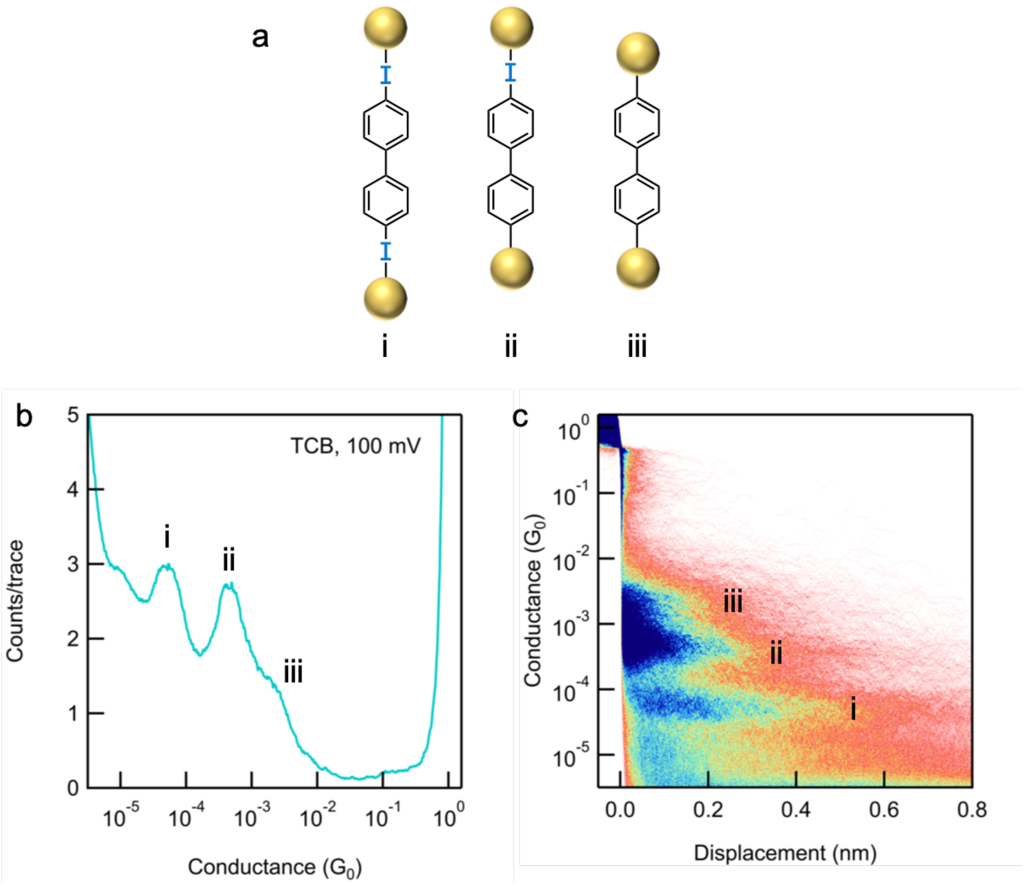


Figure S3. Oxidative addition via iodide linker is observed for the symmetric molecule diiodobiphenyl. (a) Schematic of diiodobiphenyl in the junction showing the three expected binding modes: two Au-I contacts, one Au–I and one Au–C contact, and two Au–C contacts. (b) Logarithm-binned 1D histograms of diiodobiphenyl measured in TCB at 100 mV. Three peaks are visible; we assign the highest peak to junction type **iii** and the lowest one type **i**. (c) 2D conductance-displacement histogram generated from the data used to create the 1D histogram. Three distinct peaks are clearly visible, with the length increasing as conductance decreases. This is consistent with our hypothesis; the shortest junction has two Au–C contacts while the longest one has two Au–I contacts.

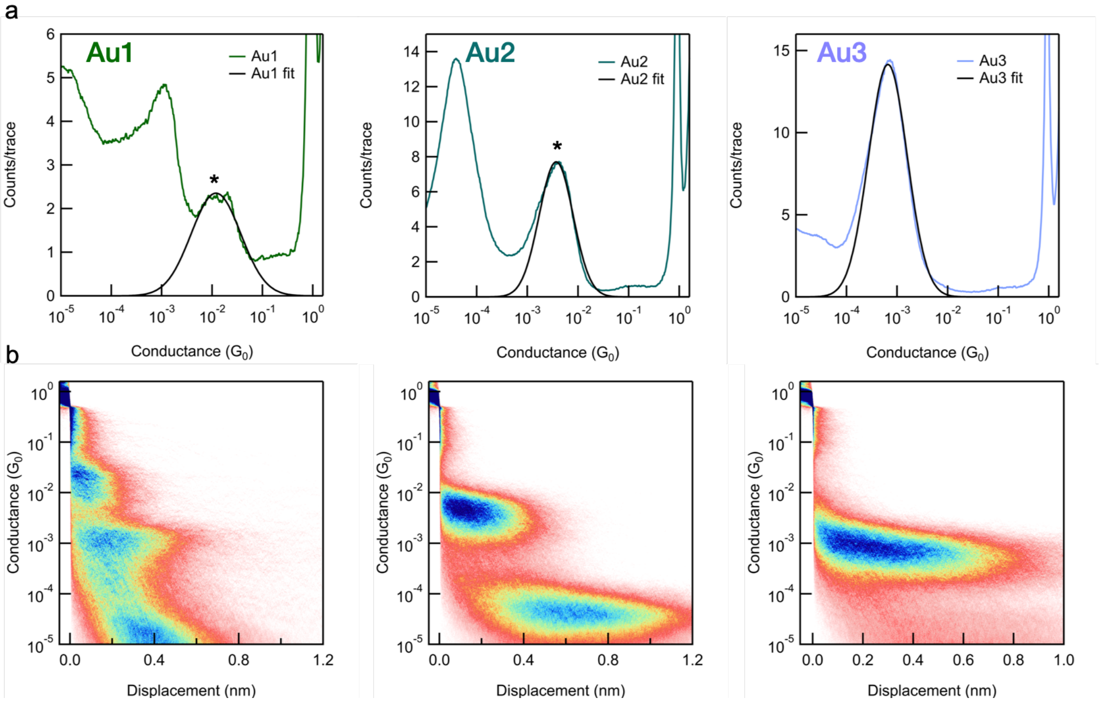


Figure S4. (a) Logarithm-binned 1D and (b) 2D conductance-displacement histograms of **Au1-3** measured in TCB at 100 mV. Gaussian fits in (a) are shown in black. Note that the higher conducting junction corresponds to the Au–(Ph)$_n$–SMe–Au junction. The lower conducting peaks with longer plateaus are due to Au–SMe–(Ph)$_{2n}$–SMe–Au dimers formed in situ.

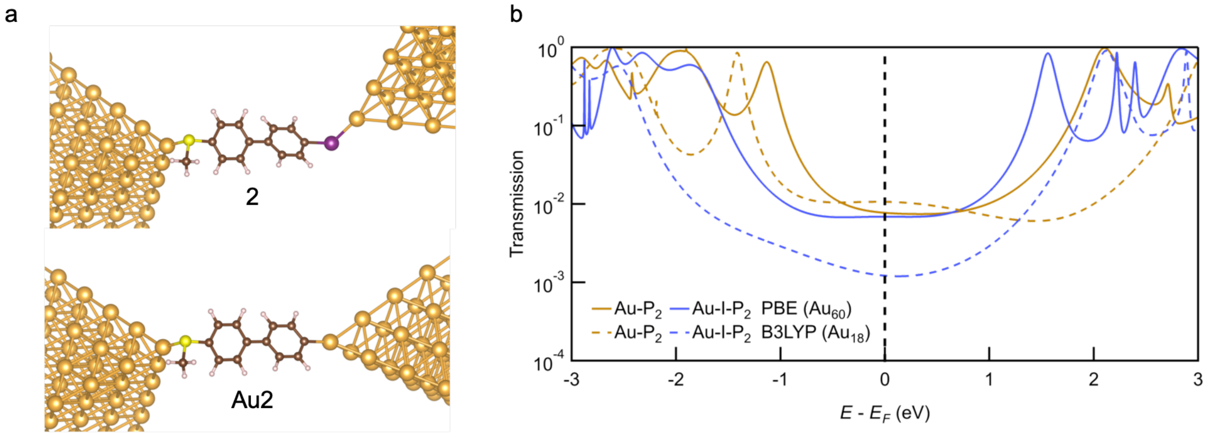


Figure S5. (a) Relaxed junction geometries of **2** and **Au2** attached to Au$_{60}$ clusters. (b) Comparison of the transmission functions of **2** and **Au2** calculated using PBE (solid) and B3LYP (dashed). The PBE and B3LYP results provide upper and lower bounds of the transmission at Fermi.

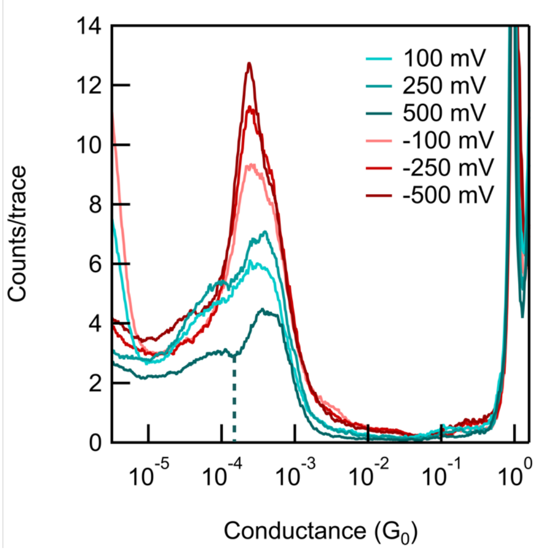


Figure S6. Logarithm-binned 1D histograms of **3** measured in PC at different biases. To quantify the effect of the applied bias, we divided the 1D histograms at every bias into a high-G and low-G window (dotted line represents an example cutoff for the +500 mV data). The number of data points within each window was counted to obtain the percentage of points per the trace corresponding to the high-G peak. This was iterated over thousands of traces at each bias. The analysis was repeated with multiple data sets.

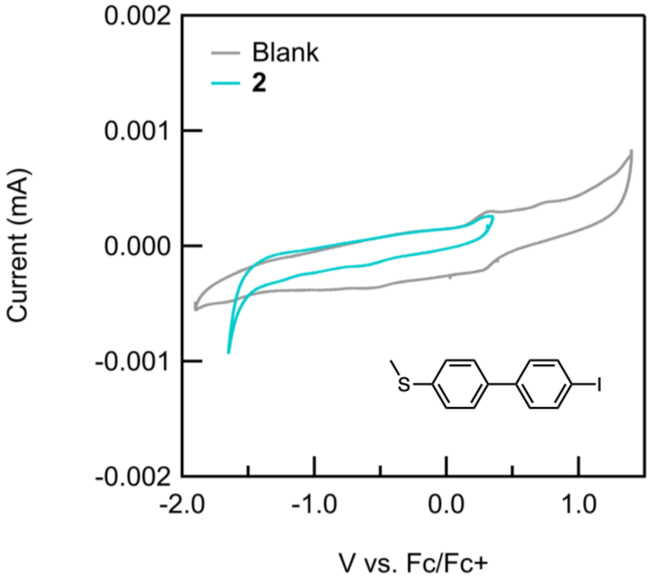


Figure S7. Cyclic voltammogram of **2**. No reductive peak is visible. CVs were taken in PC with $TBAPF_6$ as a supporting electrolyte, using a gold electrode and a scan rate of 50 mV/s.

6. References

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