Supporting Information

Assembly, structure and thermoelectric properties of 1,1'dialkynylferrocene 'hinges'

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1. Theoretical Calculations

1.1. Geometry Calculations

A ferrocene molecule has a low energy barrier for rotation of the cyclopentadiene rings, with a value of approximately 0.04 eV.¹ In the case of molecules **1-4**. This means that the arms of the molecule attached to one side of the ferrocene are free to rotate at room temperature. Using the SIESTA DFT code, the ground state energy of the molecules is calculated as a function of the rotation angle θ through 360°.² The calculations use a double zeta polarized basis set (defined by an energy cut off of 0.001 Rydbergs), norm conserving pseudopotentials, a mesh cut-off of 150 Rydbergs and the calculation is carried out for two types of exchange correlation functional, GGA³ and VDW.^{4,5} The optimum geometry of the molecules is then calculated by relaxing the geometry for the open system ($\theta = 0^{\circ}$) and the closed system ($\theta = 144^{\circ}$) as defined in Figure S1.

1.1.1. Molecule 1



Figure S1. Definition of the rotation angle θ for molecule **1** for angles of $\theta=0^\circ$, $\theta=72^\circ$ and $\theta=144^\circ$.



Figure S2. Ground state energy of molecule **1** as a function of rotation angle θ calculated using a GGA functional (left) and VdW functional (right).



Figure S3. SIESTA relaxed geometry of molecule **1** *in the open configuration (left) and closed (right).*

Table S1 Energy difference between the open and closed optimum geometries of molecule 1
calculated using SIESTA for GGA and VDW functionals.

Functional	E _{open} - E _{closed} (eV)
GGA	-0.03
VDW	0.19

1.1.2. <u>Molecule 2</u>



Figure S4. Ground state energy of molecule **2** as a function of rotation angle θ calculated using a GGA functional (left) and VdW functional (right).



Figure S5. SIESTA relaxed geometry of molecule 2 in the open configuration (left) and closed (right).

Table S2 Energy difference between the open and closed optimum geometries of molecule 2

 calculated using SIESTA for GGA and VDW functionals.

Functional	E _{open} - E _{closed} (eV)
GGA	-0.042
VDW	0.21

1.1.3. Molecule 3



Figure S6. Ground state energy of molecule **3** as a function of rotation angle θ calculated using a GGA functional (left) and VdW functional (right).



Figure S7. SIESTA relaxed geometry of molecule 3 in the open configuration (left) and closed (right).

Table S3 Energy difference between the open and closed optimum geometries of molecule **3**calculated using SIESTA for GGA and VDW functionals.

Functional	E _{open} - E _{closed} (eV)
GGA	-0.027
VDW	0.185

1.1.4. Molecule 4



Figure S8. Ground state energy of molecule **4** as a function of rotation angle θ calculated using a GGA functional (left) and VdW functional (right).



Figure S9. SIESTA relaxed geometry of molecule 4 in the open configuration (left) and closed (right).

Table S4 Energy difference between the open and closed optimum geometries of molecule **3**calculated using SIESTA for GGA and VDW functionals.

Functional	E _{open} - E _{closed} (eV)
GGA	0.083
VDW	0.22

1.1.5. <u>Molecule 5</u>



Figure S10. SIESTA relaxed geometry of molecule 5.

1.1.6. Electronic Structure of Molecules 1-5

The ionization potential is evaluated using the formula IP = E(N-1) - E(N) and the electron affinity by EA = E(N) - E(N+1). Where E is the total energy of the molecule and N is the number of electrons on the molecule.

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Molecule	HOMO (eV)	LUMO (eV)	IP (eV)	EA (eV)
1	-5.13	-3.05	7.26	1.45
2	-5.05	-2.96	7.13	1.36
3	4.99	-2.86	7.05	1.27
4	-4.87	-2.83	6.70	1.22
5	-4.94	-2.71	7.33	0.67

Table S5. Electronic properties of molecules **1-5** *in the open configuration using a VDW functional.*

Table S6. Electronic properties of molecules 1-5 in the closed configuration using a VDW functional

Molecule	HOMO (eV)	LUMO (eV)	IP (eV)	EA (eV)
1	-5.04	-2.94	7.21	1.19
2	-4.97	-2.88	7.12	1.11
3	-4.89	-2.77	7.02	1.04
4	-4.78	-2.72	6.63	0.98
5	-4.94	-2.71	7.33	0.67

1.1.7. Gaussian calculation

To test the robustness of the SIESTA calculations in predicting the geometry of these molecules, additional calculations were carried out using the GAUSSIAN 09 package.⁶ Different functionals and basis sets were used to compare the energy difference between the open and closed configurations for molecule **1** and molecule **4**. The empirical dispersion correction of Grimme⁷ was used to describe the vdW effect.

The closed and open configurations of molecule **1** are shown in Figure S11, after relaxation, and their energy differences are summarized in Table S7. Using the B3LYP functional and LANL2DZ pseudopotential for Fe and the 6-311G(d,p) basis sets for other elements, without dispersion, the open configuration has a slightly lower energy (0.035 eV) than the closed. Including the dispersion correction, the closed configuration is more stable, with an energy 0.185 eV smaller than the open configuration. With dispersion, when we change the basis sets of Fe to 6-311G(d,p), we observed a similar energy difference 0.179 eV. For completeness, the M06-2X functional, successful describing non-covalent interactions was also used to explore the energy difference of these two configurations.⁸ It was found that the closed configuration has a lower energy, 0.161 eV and 0.139 eV separately with or without dispersion correction, consistent with that which was found using the B3LYP functional.

A similar trend is also observed for molecule **4**. For this system, the open and closed configurations are shown in Figure S12, and energy differences are summarized in Table S8. With the B3LYP functional including a dispersion correction, the energy of the closed configuration is 0.34 eV lower than the open one which is about 2 times that of molecule 1, while their energy is almost same without taking dispersion into account. The dispersion-corrected wB97xD functional is also used to compare which gives a consistent value 0.37 eV.



Figure S11. Optimum geometry of molecule **1** in a closed (left) and open (right) configuration calculated using GAUSSIAN.

Table S7. GAUSSIAN calculated Energy difference between closed and open configurations formolecule 1.

Functional/Basis set	Dispersion correction	E _{open} -E _{close} (eV)
B3LYP/6-311G(d,p)+LANL2DZ	Yes	0.185
B3LYP/6-311G(d,p)+LANL2DZ	No	-0.035
M062X/Def2TZVP	Yes	0.161
M062X/Def2TZVP	No	0.139
B3LYP/6-311G(d,p)	Yes	0.179



Figure S12. Optimum geometry of molecule **4** in a closed (left) and open (right) configuration calculated using Gaussian.

molecule 4 .				
Functional/Basis set	Dispersion correction	E _{open} -E _{close} (eV)		
B3LYP/6-311G(d,p)+LANL2DZ	Yes	0.35		
B3LYP/6-311G(d,p)+LANL2DZ	No	0.0046		
M062X/Def2TZVP	Yes	0.28		
M062X/Def2TZVP	No	0.25		
B3LYP/6-311G(d,p)	Yes	0.34		
B3LYP/6-311+G(d,p)	Yes	0.308		
B3LYP/6-311G(d,p)	No	-0.0048		
wB97XD/6-311G(d,p)	Yes	0.37		

 Table S8. GAUSSIAN calculated Energy difference between closed and open configurations for

1.2. Investigating the Binding Geometry (of Molecule 5)

The optimum binding distance d_{TOP} was calculated between the ferrocene unit and the gold electrode, which forms the top contact in the junction (Figure S13). This was achieved by evaluating the binding energy as a function of d_{TOP} . Here the system was treated as a two-component object, where the gold electrode is A and the molecule is B. Due to basis set superposition errors (BSSE), when using a localized basis set we used a counterpoise method to evaluate the binding energy. This is given by the following equation:

Binding Energy = $E_{AB}^{AB} - (E_{A}^{AB} + E_{B}^{AB})$

where E_{AB}^{AB} is the ground state energy of the gold electrode (A) and molecule (B), E_{A}^{AB} is the energy of the gold (A) in the basis of the dimer AB and E_{B}^{AB} is the energy of the molecule in the basis of the dimer AB. Figure S13 shows that the optimum binding distance d_{TOP} is 3.2 Å and the magnitude of the binding energy is 0.34 eV, using a VdW functional. The calculation is repeated for a geometry where the molecule is tilted 60° away from the normal (Figure S14), in this case the binding distance and energy give similar values.



Figure S13. Binding geometry for molecule **5** for the ferrocene group on a gold (111) surface defined by the binding distance d_{TOP} at a tilt angle (ϕ) of 0°.



Figure S14. Binding geometry for molecule **5** for the ferrocene group on a gold (111) surface defined by the binding distance d_{TOP} at a tilt angle (ϕ) of 60°.

1.3. Quantum Transport Calculations for SAMs

The transmission coefficient (T(E)), conductance (G) and the Seebeck coefficient (S) were calculated using the GOLLUM code for molecules **1**, **3**, **4** and **5**. To simulate the SAM, the junction geometry is formed of gold electrodes consisting of 6 layers of (111) gold each containing 20 atoms. This gives a unit cell size of 14.4 Å by 9.996 Å. The optimum binding location for the pyridine anchor group is found to be a top site with a binding distance of 2.55 Å. The top binding distance is then taken to be 3.2 Å. A range of possible geometries of the molecules within the SAM were explored, and in each case a Hamiltonian was calculated using the SIESTA code with the parameterization utilized for the gas phase calculations and a VdW functional. However, a single zeta basis set is used for the gold atoms to reduce the computational expense.



Figure S15. Transmission coefficient (left) and Seebeck coefficient (right) as a function of energy for molecule $\mathbf{1}$ ($\phi = 0^{\circ}$) at different arm rotation angles θ .

1.3.2. <u>Molecule 3</u>



Figure S16. Junction geometry for molecule **3** ($\phi = 0^{\circ}$).



1.3.3. Molecule 4

Figure S17. SAM geometry for molecule **4** for two arm rotation angles, $\theta = 72^{\circ}$, and $\theta = 108^{\circ}$ (left). Conductance and thermopower as function of θ at three different values of Fermi energy E_{F} .



Figure S18. Transmission coefficient versus energy for molecule **4** for different values of rotation angle θ .



1.3.4. <u>Molecule 5</u>

Figure S19. Junction geometry for molecule **5** at three different values of ϕ , $\phi = 0^{\circ}$ (left), $\phi = 40^{\circ}$ (middle) and $\phi = 60^{\circ}$ (right).



1.3.5. Junction separation – molecule tilt angle (ϕ)

Figure S20. Transmission coefficient T(E) and Seebeck coefficient S as a function of energy for molecules **1**,**3**,**4** and **5** for a tilt angle $\phi=0^{\circ}$.



Figure S21. Transmission coefficient T(E) and Seebeck coefficient S as a function of energy for molecules **1**,**3**,**4** and **5** for a tilt angle ϕ =40°.



2. Further Analysis of the Single-Molecule Charge Transport Data

Figure S22. 2D conductance-displacement histogram (a), 1D conductance histogram (b), and breakoff distance histogram of 11166 traces of **2**. (d-g) 2D conductance histograms of traces of **2** clustered into 4 classes. Coloured lines in (a-c) are corresponding histograms of cluster 1 (blue, 3188 traces), 2 (purple, 3152 traces), 3 (orange, 2679 traces), and 4 (red, 2247 traces). (h) Representation of all traces, colour coded according to cluster, represented in a 3D vector space generated by PCA. Vector space has been rotated to depict significant separation of classes; data along PC 1 is predominately uniform, though C1 tilts below the plane formed by the PC 2 and PC3 axes, while C4 tilts above.

A larger data set of 16000 traces was used for further clustering analysis of **2**. Of this data set ~5000 traces were removed during a pre-filtering step which removed traces which never formed a Au-Au contact, or did not reach a lower threshold value of $10^{-5.5}$ G₀ within 8 nm. The data shown in the main text is a complete subset (subset #7 of 8 total) of the 16000 traces. Figure S22 shows the entire ~11000 trace data set.

Clustering proceeding following Ref. [9]. The 1D conductance histogram divided the conductance range from $10^{0.5}$ G₀ to $10^{-5.8}$ G₀ into the usual 128 bins. A 2D conductance-displacement histogram divided the displacement from -0.5 to 3.0 nm into 28 bins, and divided the conductance range from $10^{0.5}$ G₀ to $10^{-5.8}$ G₀ into 28 bins. The 2D conductance histogram was then straightened into a 1D array. This 28 * 28 = 784 dimensional array was assembled into a data matrix of all traces. k-means clustering was then applied to the data matrix, with a user-defined number of four clusters in the data. This choice is to some extent arbitrary, but our reasoning was that the presence of significant sub-populations in the data may lead to systematic differences between (some of) the imposed clusters. For the same reason, we also performed PCA on the dataset and plotted the first three PCA components in Figure S22(h). However, neither of the two analyses provided evidence for the presence of separate sub-populations in the data and observed differences between the (imposed) clusters merely reflected different sections of an overall distribution of molecular characteristics. With a view on the different ferrocene configurations formed during junction elongation, this finding is in line with a rather continuous transition from one to the other, rather than the formation of distinct states with significant activation barriers between them.¹⁰

On a final note, within the larger data set in Figure S22, more so than in Figure 2 of the main text, a shoulder at $\sim 10^{-3}$ G₀ is observed. This shoulder is apparent in all classes, i.e. does not appear to form a separate event class, and is best interpreted as a metastable geometry present in all traces before the junction elongates to the final geometry prior to rupture. In this case, clustering is helpful in emphasizing that the presence of this feature is universally present in all traces.

3. Formation and Thermoelectric Characterisation of SAMs

3.1. Au Preparation

Template stripped (TS) gold preparation: The ultra-flat gold was prepared by modifying the template stripped (TS) method of Whitesides.¹¹ 150 nm gold film was deposited on a Si substrate by thermal evaporation. Another Si wafer (5 mm x 5 mm) was ultra-sonicated and cleaned in acetone, methanol and isopropanol in series, and then cleaned with oxygen plasma for 10 minutes. The Si wafer, after cleaning, was glued onto a gold substrate using Epotek 353nd epoxy to form a Si (up)/Glue/Au/Si (bottom) sandwich structure. The epoxy was cured at 150 °C for 40 minutes, and the atomic flat gold was obtained by cleaving off the Si (bottom) part using a surgery blade.

The prepared gold was scanned by AFM at several random spots for quality control, and only substrates with average roughness below 0.2 nm were used for SAMs growth.

3.2. SAMs Growth

All molecules were dissolved in toluene with 1 mM concentration, followed by 15 minutes of ultrasonication. The solutions were bubbled with nitrogen for 15 minutes for deoxygenation. The Au^{TS} was then immersed into each solution, without any further treatment, for SAMs growth. The SAMs growing process was conducted under a nitrogen atmosphere for 48 hours. The substrate, after SAMs growth, was rinsed with toluene, ethanol and iso-propanol, in sequence, to wash off physisorbed molecules. Finally, the SAMs were then incubated in a vacuum chamber for 2 hours, to allow for solvent evaporation.

3.3. SAMs Structural Characterisation

A multi-mode 8 AFM (Brucker) system was used for SAMs characterization. Peak force (peak force setpoint at 500 pN, peak force frequency at 2kHz) supplied by Brucker was used for obtaining the topographic images of prepared SAMs. The roughness of the surface of each of the SAMs was obtained with gwyddion software on several 500 nm x 500 nm scans taken at different spots of the SAM surface.

SAMs thickness was obtained by a nano-scratching technique. For this, a probe with force constant 3 N/m was used for the nano-scratching. The probe was scanning in a 300 nm x 300 nm area in contact mode with high loading force (~30 nN) for several cycle for to scratch the surface and remove the molecule and would then be set to scan in a large area (1 μ m x 1 μ m), in a peak force mode with low peak force setpoint (~0.5 nN) to characterize the scratched window. The height difference between a scratched area and an un-scratched area then indicated the thickness of the film. Figure S23 shows a

typical image of a SAM following performance of a nanoscratching analysis, as well as the height distributions of SAMs of **1-4**, gained from this analysis.



Figure S23. An example of sample SAMs 1 topography after nano-scratching (top), and thickness distributions of SAMs 1-4 obtained from a nano-scratching analysis (bottom).

3.4. Electric Characterisation

The electrical conductivity of the films was characterized by a conductive AFM setup based on a Multimode 8 AFM instrument (Bruker Nano Surfaces). The bottom gold substrate was used as the source, and a Pt/Cr coated probe (Multi75 E, BugetSensors) was used as the drain. The force between probe and molecule was controlled by the deflection error set point. The triangular shape AC bias was added between the source and drain by a voltage generator (Aglient 33500B), the source to drain current was acquired by a current pre-amplifier (DLPCA200, Femto) providing current-to-voltage conversion. The I-V characteristics were obtained using a Nanoscope 8 controller simultaneously collecting drive bias and current, with subsequent correlation of these values at each time point.

The contact area between probe and sample was estimated via RKJ model^{12,13}, where the contact radius, r, is calculated from the following equation:

$$r = (F \times R \times \frac{1}{Y})^{\frac{1}{3}}$$
$$\frac{1}{Y} = \frac{3}{4} \times (\frac{1 - v_1^2}{E_1} + \frac{1 - v_2^2}{E_2})$$

Here, r is the contact radius, F is the loading force from probe to sample, R is the radius of the probe, v1 and v2 are the Poisson ratio of the material, and E1 and E2 are the Young's Modulus for probe and SAMs. The radius of the probe was obtained from SEM image and estimated to be 25 nm. The Young's modulus was obtained from AFM in peakforce mode.



Figure S24. (a-d) Statistics of IV curves obtained from SAMs 1-4. (e-h) Statistics of conductance obtained from SAMs 1-4.

3.5. Seebeck Measurements

The Seebeck coefficient of the SAMs were obtained by Thermal-Electrical Atomic Force Microscopy (THEFM), a modified version of the cAFM for electrical transport measurement. For this, the probe was coated with 100 nm Au by thermal evaporation for voltage stabilization. A Peltier stage controlled by a voltage generator (Agilent 33500B with broad-band amplifier) was used for substrate temperature control, to allow for a temperature difference between sample and probe, ΔT , to be created. A Type T thermal couple was used to quantify this ΔT . The thermal voltage between sample and probe, ΔV_{Therm} , was amplified by a high impedance differential pre-amplifier (SR551, Stanford Research System). The signal was passed through a low pass filter and recorded by the computer. The linear regression of ΔV_{Therm} vs. ΔT was plotted, and the slope of the linear curve was the Seebeck coefficient of the system.



Figure S25. (a-d) histogram plots of measured thermovoltage at a range of temperature differences for SAMs of molecules **1-4**.

4. X-ray Photoelectron Spectroscopy

4.1. Methods

XPS measurements were taken using a Kratos Axis Supra instrument using a monochromatic Al K α 1486.7 eV source operating at 15 kV and 15 mA. All binding energies were referenced to the Au 4f peak at 84 eV and spectra analysed using CasaXPS software. Samples were introduced into the XPS system immediately following preparation.

4.2. Representative Scan

A representative overview scan is shown in Figure S26 for the SAM of molecule $\mathbf{1}$, with key peaks related to the ferrocene molecule and Au substrate labelled. A small number of additional peaks can be observed, which are believed to originate from small amounts of lodine arising from the copper iodide co-catalyst and the initial 1,1'-diiodoferrocene used in the preparation of the molecules.



Figure S26. A representative overview XPS scan of a SAM of molecule 1.

4.3. Angle Resolved XPS

ARXPS was performed on a SAM of molecule **1** in order to gain greater insight into the position of the nitrogen atoms within this material. ARXPS data was collected at angles of emission of 0° and 70° and the data obtained from this are shown in Figure S27.



Figure S27. ARXPS data of a SAM of molecule **1**, collected at two angles of emission, 0° (a), and 70°(b).

5. <u>References</u>

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