Electronic Supplementary Information

Adsorption of a Dihydro-TTF Derivative on Au(111) via a Thiolate Bonding Complex to Gold Adatoms.

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ESI 1. Synthetic Procedure



Figure S1. Synthetic scheme for preparation of TAT-TTF 3.

The synthesis of the precursor compound, tetramethyl 2,6-exo-8,12-exo-4,10-bis(1,3-dithiol-2-ylidene)-3,5,9,11-tetrathiatetracyclo $[5.5.1.0^{2,6}.0^{8,12}]$ tridecane-4',5',4'',5''-tetracarb-oxylate **1**, has been described fully in [1].

Preparation of 2,6-exo-8,12-exo-4,10-bis(4',5'-bis(hydroxymethyl)-1',3'-dithiol-2'ylidene)-3,5,9,11-tetrathiatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridecane 2.



Compound 1 (0.25 g, 0.37 mmol) was dissolved in dry THF (15 cm³) to give a dark red solution. To this sodium borohydride (0.14 g, 3.70 mmol) and zinc chloride (0.50 g, 3.70 mmol) were added and the mixture heated under reflux for 3 hours, after which the mixture had turned dark yellow. The mixture was cooled to 0 °C and ethyl acetate (10 cm³) added, followed by a dropwise addition of saturated aqueous ammonium chloride (5 cm³). The mixture was then filtered, and dichloromethane added to the filtrate causing the immediate formation of a precipitate that was filtered off and washed with water to leave the product **2**

as a yellow solid (0.20 g, 95 %), mp 159–161 °C (dec.), (HRMS: Found M+H 569.9229, $C_{19}H_{21}O_4S_8$ requires 569.9205), δ_H (d₆-DMSO) 5.46 (4H, t, *J* 6, -OH), 4.18 (8H, d, *J* 6, CH₂OH), 4.06 (4H, s, 2,6,8,12-H), 2.45 (2H, s, 1,7-H) and 1.63 (2H, s, 13-H), δ_C 131.2 (C-4', C-5'), 118.5 (C-4), 112.1 (C-2'), 59.6 (C-2, C-6, C-8, C-12), 56.6 (-CH₂OH), 53.4 (1,7-H) and 26.8 (13-H), *m*/*z* 570 (M+H, 80 %), 551 (15), 330 (12), 303 (25), 289 (20), 264 (53) and 210 (100).

Preparation of 2,6-exo-8,12-exo-4,10-bis(4',5'-bis(acetylthiomethyl)-1',3'-dithiol-2'ylidene)-3,5,9,11-tetrathiatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridecane 3



Triphenylphosphine (1.18 g, 4.50 mmol) was dissolved in dry THF (10 cm³). The solution was cooled to 0 °C and diisopropyl azodicarboxylate (DIAD) (0.91 g, 0.89 cm³, 4.50 mmol) added which immediately formed a white suspension. Compound **2** (0.16 g, 0.28 mmol) and thioacetic acid (0.34g, 0.32 cm³, 4.50 mmol) were dissolved in dry THF (20 cm³) and added dropwise to the suspension. The mixture was then stirred at 0 °C for 30 minutes, warmed up to room temperature and stirred for 24 hours. The mixture gradually turned dark green before finally forming a yellow solution. The solvent was removed under reduced pressure to yield a yellow solid. The solid was pre-adsorbed onto silica before being subjected to flash column chromatography (SiO₂, diethyl ether). The eluting solvent was then changed to pure CH₂Cl₂ which the yielded the product **3** as a yellow solid (0.02 g, 15 %), mp 270–275°C (HRMS: Found M+Na, 822.8519, C₂₇H₂₈O₄NaS₁₂ requires 822.8534), $\delta_{\rm H}$ (d₆-DMSO) 4.09 (4H, s, 2,6,8,12-H), 3.99 (8H, s, CH₂S), 2.45 (2H, s, 1,7-H), 2.38 (12H, s, CH₃) and 1.62 (2H, s, 13-H); $\delta_{\rm C}$ 194.7 (C=O), 128.3 (C-4', C-5'), 119.9 (C-4, C-10), 113.9 (C-2'), 59.8 (C-2, C-6, C-8, C-12), 53.2 (C-1, C-7), 30.4 (CH₃), 26.8 (C-13) and 25.7 (CH₂S); *m/z* 825 (M+Na, 7 %), 823 (14), 429 (70), 401 (53), 245 (100) and 201 (49).

SI 2. Spectroscopic characterisation data



Figure S2(a). ¹H NMR spectrum of 2 in DMSO.



Figure S2(b). DEPTQ ¹³C NMR spectrum of 2 in DMSO.



Figure S3(a). ¹H NMR spectrum of 3 in DMSO.



Figure S3(b). DEPTQ ¹³C NMR spectrum of 3 in DMSO.



Figure S4. (a) Combined experimental transmission infrared spectrum of TAT-TTF (blue) and Gaussian DFT calculated infrared spectrum (green) of TAT-TTF in the gas-phase. **(b)** Table of infrared vibrational assignments.

DFT calculations of TAT-TTF in the gas-phase were performed by the Gaussian DFT package [2] in order to simulate the infrared spectrum of the molecule. The Becke three-parameter Lee-Yang-Paar (BY3LP) [3] functional was used in the optimisation process. For all calculations the 6-311G basis set [4] was used with an additional diffuse function. The Gaussview package was used for visualisation. Calculated infrared frequencies are scaled using a correction factor proposed by Yoshida *et al* [5]. The experimental transmission infrared spectrum of TAT-TTF and the DFT simulated spectrum are shown in **Figure S4(a)**. A table of the principal infrared vibrational frequencies is shown in **Figure S4(b)**.

ESI 3. X-ray structure of compound 1

An X-ray structure of TAT-TTF **3** could not be obtained. Therefore the X-ray structure of the methoxycarbonyl precursor **1**, previously published in [1], is shown in **Figure S5** to illustrate that the measured length between the two highlighted carbon atoms of 17.3 Å is comparable to the peak-to-peak distance of 17.6 Å as measured in the line-profile taken along the TAT-TTF molecules in **Figure 3(d)** main. The separation of the $-CH_2S$ - carbon atoms between ligands on either side of the TAT-TTF molecule should also be similar, given the identical dihydro-TTF skeleton of compounds **1** and **3**.



Figure S5. X-ray structure of **1** previously published in [1]. Separation between carbonyl carbons = 17.3 Å.

ESI 4. Experimental procedure

STM measurements were carried out using a commercially available system (Createc GmbH, Germany). The STM is housed in a UHV chamber adjacent to a sample preparation chamber, both with base pressure $< 1 \times 10^{-10}$ mbar. The Au(111) single crystal (MaTeck GmbH, Germany) was cleaned in the preparation chamber using repeated cycles of argon ion sputtering (1.5 keV, 1×10^6 mbar of Ar⁺, 10 minutes) followed by annealing (800 K, 15 minutes). The condition of the gold surface was assessed using STM prior to deposition of molecules. The TAT-TTF molecules were dosed on the cleaned surface by sublimation from a modified ion gauge, consisting of a quartz capillary tube containing the sample heated by a filament. The TAT-TTF sample was degassed at 341 K for 24 hours prior to deposition. The

TAT-TTF molecules were then sublimed at 420 K onto the Au(111) surface. The prepared sample was transferred to a liquid nitrogen cooled STM and allowed to thermally equilibrate. Tungsten STM tips were used for all measurements and were prepared from tungsten filament by electrochemical etching using KOH solution. A Nicolet 760 Fourier Transform mid-IR spectrometer was used to take measurements in the mid infrared region between 4000–800 cm⁻¹ under UHV conditions.

ESI 5. Further STM data

The Au(111) surface, kept at 298 K and exposed to TAT-TTF sublimed at 420 K from the molecular doser is shown in Figure S6(a). The following STM images were taken at 77 K. The STM images are presented using the WSxM software package [6]. Prior to any surface annealing treatment, large areas of disordered organic material can be seen on the surface. However, dim spherical features, approximately 4.0 Å in diameter are visible in isolated groups that are highlighted by the green arrows. Further clusters of such features are visible in Figure S6(b). These are identified as acetyl radicals that have formed following cleavage of the sulfur-acetyl bond in the TAT-TTF molecules. Such acetyl species of identical diameter were previously identified on Ag(100) using STM by Vaughan et al. [7], following cleavage of the sulfur-acetyl bond in acetylthio functionalised porphyrins. However, Vaughan et al. [7] only observed such features after annealing the adlayer to 473 K, and thus advocate a surface mediated cleavage of the sulfur-acetyl bond. The appearance of acetyl groups on the Au(111) surface in the current study, prior to any annealing treatment higher than 298 K, indicates that cleavage of the sulfur-acetyl bond in the TAT-TTF molecule may be thermally activated during the sublimation process, rather than surface mediated as in the case of Vaughan et al. [7].

After annealing the surface to 333 K, the acetyl species are observed to coexist with the ordered TAT-TTF ribbon structures as shown in **Figure S7(a)**. A line profile, taken across one of the spherical features displayed in the inset, is shown in **Figure S7(b)** confirms the diameter as 4.0 Å.



Figure S6 Au(111) exposed to TAT-TTF sublimed at 420 K, acetyl species highlighted by green arrows (a) -1.34 V, 0.06 nA, 37×37 nm² (b) -0.99 V, 0.05 nA, 19×19 nm².



Figure. SI.7 Surface annealed to 333 K for 1 hour:(**a**) -1.34 V, 0.06 nA, 37×37 nm²; inset 4×4 nm² area in green square magnified, (**b**) Line-profile taken across single acetyl species along dashed red line in inset.

Annealing the adlayer to 373 K appear to result in desorption of the TAT-TTF complexes from the surface as shown in **Figur. S8(a)**. However, the acetyl species remain in large clusters on the Au(111) surface as shown in **Figure S8(b)**.



Figure S8. Surface annealed to 373 K for 1 hour (a) -1.23 V, 0.02 nA, 55×55 nm² (b) Area in green square magnified 24×24 nm². Acetyl species indicated by green arrows.

The lateral spacing of the TAT-TTF molecules in the ribbon structure is detailed in **Figure S9(a)**. As demonstrated in the line-profile shown in **Figure S9(b)**, the peak-to-peak separations as measured along the $[-2 \ 3 \ -1]$ direction are 5.8 Å and 8.3 Å, illustrating the skew in electron density caused by the weak C-H. S hydrogen bonding between neighbouring molecules. However, the actual separation between atoms of adjacent molecules is likely to be much shorter, and not accurately represented by the peak-to-peak separation. Therefore the atoms are likely to be separated by $\approx 2.0-3.0$ Å as indicated in the line-profile. These separations are within the limits for C-H. S hydrogen bonding (≤ 3.15 Å) and S. S van der Waals interactions (≤ 4.0 Å) [8], and demonstrate that these forces play a key role in the formation of the TAT-TTF ribbons.



Figure S9. (a) TAT-TTF ribbon shown in **Figure 3(c)** main; -0.90 V, 0.08 nA, 6×6 nm² (b) Line-profile taken across TAT-TTF molecules as indicated by white line in (a).

ESI 6. Periodic DFT Simulations

Calculation details and discussion

Periodic DFT calculations were carried out using the VASP program [9-11], using the PBE functional [12], a plane-wave basis set with an energy cut-off of 400 eV, PAW (Projector Augmented Wave [13]) treatment of core electrons and the VASP-supplied pseudopotentials for this method [14]. Unless stated otherwise, the empirical D2 Van-der-Waals correction [15] was included.

The surface was modelled by a three-layer gold slab. These slabs were separated by 22.3 Å of vacuum in the z direction. The uppermost Au layer, as well as the adsorbed molecule and any adatoms, was allowed to relax during optimisations, while the lower two layers were frozen at the optimised bulk geometry. Dipole correction [16] was applied to the direction orthogonal to the surface.

The geometry was optimized from a starting structure based on the STM images, with a gas-phase optimised TTF structure placed on the $(15\times3\times3)$ surface unit cell and the terminal sulfur atoms close to adatoms placed in a hollow site. **Figure S10** shows the optimised structure from above and from the side. The large distance between the central group and the surface (3.92 Å from the lowest H atoms in the norbornane group) seems to indicate that

there is no chemical interaction between adsorbate and surface other than through the adatoms.



Figure S10. Top and side-views of DFT optimised geometry of TAT-TTF bound via two gold adatoms (red) to a $(15 \times 3 \times 3)$ gold slab (beige).

To test for charge transfer between the surface and adsorbate, AIM charges [17] were determined from the VASP CHGCAR using the Bader program [18]. A Bader analysis was conducted for the combined TAT-TTF molecule bound via two Au adatoms to a $(15\times3\times3)$ Au slab (**Figure S11**). The same was repeated for an isolated TAT-TTF molecule with only the two Au adatoms bound to the terminal sulfur atoms present (**Figure S12**). The total charge of the molecule without gold atoms remains virtually unchanged (-0.38 vs. -0.33 a. u.), which demonstrates that there is no significant charge transfer other than between the terminal S atoms and the Au adatoms they bind to.

Element	Cartesi	an Coor	Charge	
	х	у	Z	
S	33.171	0.796	8.596	-0.25
S	32.292	-3.161	7.525	-0.23
S	15.590	3.574	8.275	-0.22
S	15.310	-0.623	7.470	-0.21
S	30.274	0.149	10.767	0.22
S	29.690	-2.621	10.072	0.29
S	17.889	-0.699	9.994	0.24
S	18.241	2.148	10.510	0.22
S	27.017	0.731	11.030	0.10
S	26.539	-2.099	10.344	0.17
S	21.065	-1.211	10.383	0.12
S	21.489	1.642	10.930	0.10
Н	33.081	0.580	10.992	0.08
Н	33.764	-0.887	10.274	0.11
Н	32.108	-4.127	9.729	0.06
Н	33.355	-2.851	9.717	0.11
Н	15.793	3.509	10.671	-0.01
Н	14.610	2.298	10.126	0.09
Н	14.339	0.191	9.599	0.07
Н	15.148	-1.393	9.787	0.04
Н	24.338	1.767	11.654	0.07
Н	23.692	-2.408	10.764	0.04
Н	25.445	1.095	9.250	0.05
Н	25.032	-1.165	8.745	0.04

Element	Cartesi	an Coor	Charge	
	х	у	z	
Н	23.077	-0.438	12.472	-0.03
Н	24.857	-0.717	12.480	0.04
Н	23.149	1.428	9.203	0.11
Н	22.781	-0.841	8.744	0.06
С	32.956	-0.149	10.173	-0.10
С	32.335	-3.102	9.396	-0.06
С	15.608	2.713	9.929	0.00
С	15.238	-0.386	9.348	-0.08
С	31.628	-0.819	10.260	0.00
С	16.640	1.642	10.043	-0.32
С	16.471	0.303	9.807	0.12
С	31.356	-2.119	9.930	-0.29
С	29.047	-1.059	10.506	-0.27
С	19.009	0.590	10.357	-0.28
С	27.691	-0.823	10.608	-0.20
С	20.360	0.378	10.511	-0.17
С	25.410	0.489	10.167	-0.06
С	25.155	-1.019	9.827	-0.03
С	23.989	-0.453	11.858	0.00
С	22.957	0.874	10.134	-0.13
С	24.199	0.848	11.069	0.00
С	23.856	-1.336	10.607	0.05
С	22.719	-0.645	9.824	-0.06
	Total Charge on TAT-TTF			-0.38
Au	32.926	-0.899	6.982	0.13
Au	15.123	1.713	6.952	0.11

Figure S11. Bader charges for TAT-TTF molecule bound via two Au adatoms to a $(15 \times 3 \times 3)$ Au slab. Charge on the two Au adatoms also given.

Element	Cartesian Coordinates			Charge
	x	у	z	
S	33.170	0.795	8.596	-0.26
S	32.289	-3.161	7.523	-0.24
S	15.577	3.577	8.281	-0.21
S	15.310	-0.622	7.467	-0.22
S	30.276	0.149	10.768	0.21
S	29.690	-2.621	10.070	0.30
S	17.892	-0.699	9.990	0.27
S	18.242	2.148	10.510	0.22
S	27.019	0.731	11.031	0.10
S	26.542	-2.098	10.344	0.17
S	21.067	-1.209	10.381	0.12
S	21.491	1.645	10.930	0.12
Н	33.088	0.571	10.992	0.08
Н	33.765	-0.895	10.266	0.10
Н	32.101	-4.130	9.723	0.14
Н	33.352	-2.859	9.715	0.04
Н	15.795	3.506	10.674	-0.01
Н	14.611	2.295	10.129	0.09
Н	14.342	0.188	9.599	0.07
Н	15.152	-1.395	9.782	0.04
Н	24.341	1.767	11.657	0.07
Н	23.693	-2.408	10.763	0.04
Н	25.447	1.096	9.251	0.08
Н	25.034	-1.164	8.746	0.05

Element	Cartesian Coordinates Charge			
	x	у	z	
Н	23.079	-0.440	12.473	0.00
Н	24.859	-0.719	12.480	0.04
Н	23.152	1.430	9.205	0.11
Н	22.784	-0.838	8.744	0.11
С	32.959	-0.154	10.170	-0.09
С	32.332	-3.105	9.393	-0.05
С	15.608	2.713	9.931	0.00
С	15.241	-0.387	9.346	-0.06
С	31.629	-0.821	10.258	0.00
С	16.641	1.641	10.041	-0.37
С	16.474	0.302	9.805	0.13
С	31.356	-2.120	9.927	-0.29
С	29.049	-1.059	10.505	-0.26
С	19.011	0.590	10.355	-0.27
С	27.694	-0.822	10.608	-0.21
С	20.362	0.380	10.510	-0.18
С	25.412	0.490	10.169	-0.08
С	25.157	-1.018	9.828	-0.03
С	23.991	-0.454	11.858	-0.02
С	22.960	0.875	10.136	-0.13
С	24.202	0.848	11.071	-0.01
С	23.858	-1.336	10.607	0.04
С	22.721	-0.643	9.824	-0.11
	Total Charge on TAT-TTF			-0.33
Au	32.926	-0.899	6.982	0.17
Au	15.122	1.715	6.952	0.16

Figure S12. Bader charges for isolated TAT-TTF molecule bound to two Au gold adatoms. Charge on the two Au adatoms also given.

ESI 7. References

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