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Reference:

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The journal of physical chemistry: C : nanomaterials and interfaces - ISSN 1932-7455 - 127:47(2023), p. 23023-23033
Full text (Publisher's DOI): <https://doi.org/10.1021/ACS.JPCC.3C04913>
To cite this reference: <https://hdl.handle.net/10067/2016710151162165141>

Conformation-Dependent Monolayer and Bilayer Structures of an Alkylated TTF Derivative Revealed using STM and Molecular Modelling

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#Equal contribution

ABSTRACT

In this study, the multi-layer self-assembled molecular network formation of an alkylated tetrathiafulvalene compound is studied at the liquid-solid interface between 1-phenyloctane and graphite. A combined theoretical/experimental approach associating force-field and quantum-chemical calculations with scanning tunnelling microscopy is used to determine the two-dimensional self-assembly beyond the monolayer, but also to further the understanding of the molecular adsorption conformation and its impact on the molecular packing within the assemblies at the monolayer and bilayer level.

1. INTRODUCTION

Two-dimensional (2D) self-assembled molecular networks (SAMNs) of organic molecules on atomically flat, and often conductive, surfaces have been studied extensively over the past decades due to their potential applicability in different areas ranging from organic photonic or electronic devices to single-molecule switches.¹⁻⁶ In these reports, it has been demonstrated that during their formation, the surface interacts with molecules and acts as a template facilitating the formation of highly ordered supramolecular networks. Combined with other non-covalent intermolecular forces, such as hydrogen bonding,^{7, 8} van der Waals (vdW),⁹⁻¹¹ electrostatic,¹²⁻¹⁴ dipolar^{15, 16} and π - π interactions,^{17, 18} molecular assemblies with complex architectures have been built. Therefore, building on the relationship between the structure of the SAMNs and their properties, by unravelling the role and influence of those forces on the packing, the ambition is to predict, understand and control those properties.

Amongst the techniques used to understand the structure of SAMNs, scanning tunnelling microscopy (STM) has become a powerful tool as it allows direct observation of SAMNs on solid surfaces at (sub-)molecular resolution. This high-spatial resolution brings insight into the adsorption conformations of molecules¹⁹⁻²¹ and enables the measurement of the 2D lattice parameters, in some cases elucidating the self-assembly mechanism of the studied systems.^{22, 23}

Few studies have aimed to unravel the correlation between the surface confined SAMNs and the substrate induced phases (SIPs) which may be templated by the SAMNs. SIPs are polymorphic phases that form when the material crystallizes near the substrate as a thin film (~few tens of nm in thickness). SIPs can have polymorphic structures that differ from those observed in the corresponding single crystals ("bulk" structure), and in some cases from the SAMN in contact with the substrate.²⁴⁻²⁶ SIPs may lead to enhanced charge transport mobility in the field of organic semiconductors^{27, 28} and solubility in pharmaceuticals.^{29, 30}

SAMNs and SIPs are conceptually related as a SAMN can be seen as the thinnest SIP with only one-molecular layer thickness. Efforts have been made to investigate molecular self-assembly beyond monolayers,^{31, 32} but there are still some challenges. One of the bottlenecks for the characterization of thin SIPs with techniques such as X-ray diffraction is the low signal-to-noise ratio posing constraints on the detection limit.³³⁻³⁵ On conductive substrates, techniques like STM may provide valuable input and allow the characterization of up till few-layer-thin structures with submolecular resolution.³¹ However, relying only on STM for the structural characterization of thin films on conductive substrates has its limitations as well, and often complementary atomistic simulations^{36, 37} are required to achieve deep understanding. A good starting point is the study of the molecular conformation and structural organization of multilayer SAMNs, which acts as bridging stage between monolayer SAMNs and SIPs.

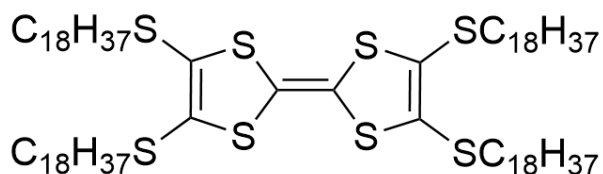


Figure 1. Molecular structure of tetrakis(octadecylthio)-tetrathiafulvalene, **1**.

Bearing this in mind, in this study we use a combined experimental and theoretical approach, where the self-assembly of an alkylated tetrathiafulvalene (TTF) derivative, *i.e.*, tetrakis(octadecylthio) tetrathiafulvalene (**1**, Figure 1), is investigated at the solution/graphite interface. The choice of this molecule is based on its versatile properties, which allows it to be used for a wide range of applications,³⁸⁻⁴¹ as well as its compatibility with STM⁴² as thin-film characterization tool. Studying the self-assembly behaviour of **1** *in-situ* with STM together with DFT and forcefield calculations not only allows the visualisation of the 2D assembly beyond the monolayer level, but also brings insight into the importance of molecular conformation on the multilayer packing.

2. METHODS

2.1 Synthesis of **1**.

4,4',5,5'-tetrakis(octadecylthio)-2,2'-bi(1,3-dithiolylidene) or **1** was synthesized in two steps from commercially available [1,3]dithiolo[4,5-d][1,3]dithiole-2,5-dione. Initially, [1,3]dithiolo[4,5-d][1,3]dithiole-2,5-dione was treated with NaOMe in methanol (0.5 M, 9.6 ml, 2 equiv.) to generate disodium dithiolate which was trapped by octadecyl bromide in the presence of DMF as a solvent at 65 °C. The obtained dialkylated compounds underwent dimerization in presence of triethyl phosphite (10 equiv. excess) at 120 °C for overnight, resulted in formation of the dimeric product **1**, which was purified by repeated washing with cold methanol (> 99% purity by NMR) (see section 1 in the supporting information).

2.2 Preparation of self-assembled layers and STM characterization.

A stock solution of **1**, ($C = 7.5 \times 10^{-4}$ M) was prepared by dispersing 1 mg of the compound per 1 ml of 1-phenyloctane (1-PO) followed by sonication for one hour. 1-PO was obtained from Sigma-Aldrich (>99%) and used without further purification. The stock solution was diluted further with 1-PO to prepare a concentration series. One should note that the actual solubility of **1** at room temperature is only in the order of 3.7×10^{-5} to 4.2×10^{-5} M (*vide infra*). All solutions, where the formal concentration of **1** exceeds this limit, are dispersions. All solutions were sonicated for 5 minutes before use. This procedure homogenized and stabilized the dispersions, possibly by decreasing the size of particles of dispersed solid **1**. All STM experiments were performed at room temperature (21–23°C), using a PicoLE (Agilent) machine operating in constant-current mode with the tip immersed in the liquid. STM tips were prepared by mechanically cutting a Pt/Ir wire (80%/20%, diameter 0.2 mm). Prior to imaging, a drop of solution was placed onto a freshly cleaved surface of HOPG. The

images were corrected for drift *via* scanning probe image processor (SPIP) software, using the recorded graphite images for calibration purposes, allowing accurate unit cell determination. The unit cell parameters were determined by examining several images. The imaging parameters, tunnelling current (I_{set}) and sample bias (V_{bias}), are indicated in each figure caption.

2.3 UV-Vis spectroscopy characterization.

The UV-Vis absorption spectra were recorded using a Lambda 950 spectrophotometer with blocked beam and blank corrections. To record UV-Vis spectra as a function of the temperature, a temperature controller was used and every time that the required temperature was stabilized, a UV-visible spectrum was recorded.

2.4 DFT geometry optimizations and STM simulations.

All DFT calculations were performed using the 4.1 version of the SIESTA package.⁴³ The exchange-correlation functional was described by the PBE functional⁴⁴ within the general gradient approximation. The valence electrons were described by a numerical double-zeta polarized (DZP) basis set with a reasonable mesh-cutoff of 250Ry, while the core electrons were treated by the Troullier-Martins pseudopotentials.⁴⁵ The Brillouin zone was sampled using a Monkhorst-Pack grid⁴⁶ of $(1 \times 1 \times 1)$. A single point is sufficient for sampling as the dimension of the smallest unit cell employed in the calculations is already relatively large: around 25Å and 30Å in X and Y direction, respectively. Along the Z direction, a distance of 60Å was used to avoid the artificial interactions due to periodic boundary conditions. van der Waals interactions were incorporated in the calculations through the Grimme corrections.⁴⁷ For geometry optimizations, the atomic positions of the adsorbed molecules were relaxed until the interatomic forces are smaller than 0.04 eV/Å. All simulated STM images were generated based on the force-field-optimized geometries. In this study, the geometry optimizations and STM image simulations were carried out on adsorption systems that involve TTF molecules having alkyl chains with different lengths. In SIESTA, the integration of the local density of states (LDOS) was calculated over an energy window that is determined by the experimental bias voltage used for recording the STM images. The simulated STM images were then generated from this integrated LDOS, based on the Tersoff-Hamann approximation using the WSxM software.⁴⁸

2.5 Molecular mechanics (MM) and dynamics (MD) simulations.

All force-field calculations were carried out in the Forcite module as implemented in the BIOVIA Materials Studio 2018.⁴⁹ The Universal Force Field^{50, 51} was employed in all MM and MD simulations described in this paper, which has been validated by previous studies.⁵² ESP charges calculated at the DFT level with the Gaussian 16 simulation package⁵³ and Gasteiger charges were combined and used as the atomic charges in the force-field calculations. For the calculation of ESP charges, the B3LYP⁵⁴⁻⁵⁸ functional was employed with the 6-31+G(d,p) basis set. MD simulations for the assemblies of TTFs

were performed in the NVT ensemble (constant number of particles, volume, and temperature) with the Nosé-Hoover-Langevin (NHL)⁵⁹ thermostat. The HOPG substrate was represented by a single graphene layer whose atoms are frozen during the simulations, since the physisorption of TTFs on HOPG is not expected to change the geometry of the substrate underneath. The quench-MD approach (Figure S1 in supporting information), where the structures are optimized periodically during the MD run, was used to refine the initially optimized structures, thus enabling a better convergence towards the most stable structure.

3. RESULTS AND DISCUSSION

3.1 Self-assembly of **1** at the 1-phenyloctane/HOPG interface: STM

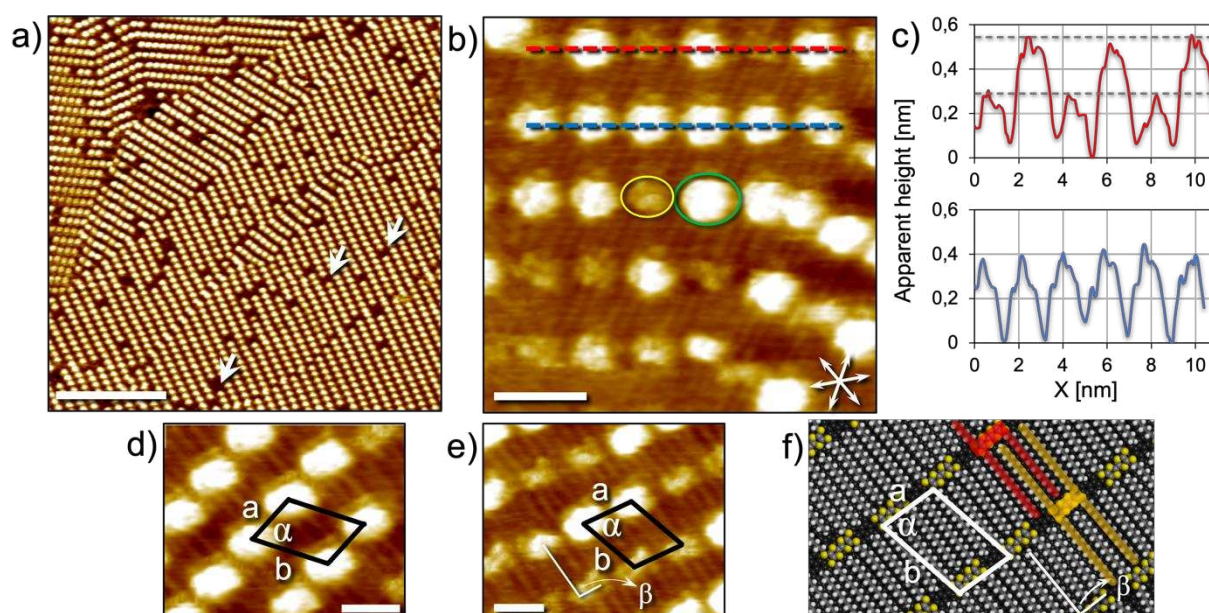


Figure 2. Self-assembly of **1** ($C = 7.5 \times 10^{-4}$ M) at the 1PO/graphite interface. (a) Large scale STM image (scale bar = 20 nm) showing the overall morphology of the physisorbed SAMN formed by **1**. The white arrows highlight the defects in the SAMN. (b) Smaller scale STM image (scale bar = 3 nm) showing variable STM contrast within the SAMN which we ascribe to the formation of a bilayer. (c) Profiles corresponding to the red and blue dashed lines in panel (b) highlighting the differences in the apparent heights of molecules in the upper and lower layers. (d, e) Small scale images showing the unit cells within the upper (d) and lower (e) layers. Imaging parameters (a, b, d, e): $I_{set} = 70$ pA to 90 pA, $V_{bias} = -0.750$ V to -1.000 V. (f) A molecular model depicting the packing arrangement of **1** in the first layer adsorbed on the graphite surface. Two molecules, one in red, and one in orange highlight the interdigitation of the alkyl chains.

SAMNs of **1** were obtained by drop casting a 1-PO solution onto freshly cleaved HOPG and the STM imaging was carried out at the 1-PO/HOPG interface. **1** promptly forms a highly ordered SAMN upon physisorption at the 1-phenyloctane/HOPG interface. Figure 2a shows a typical large scale STM image of the SAMN where it is possible to distinguish the bright TTF moieties from the alkyl substituents,

which are adsorbed in the darker regions. The higher tunnelling current recorded over the TTF moieties is in line with their electron-rich nature, whereas the darker areas corresponding to lower tunnelling current indicate the regions where the alkyl chains are adsorbed. The rows of bright features and dark regions alternate. The STM images show defects (white arrows, Figure 2a) which we ascribe to missing TTF molecules.

Smaller scale STM images such as the one presented in Figure 2b highlight a peculiar feature of the SAMNs of **1** formed at the 1-PO/HOPG interface. The bright features within the SAMN appear with different levels of contrast. Two different levels can be identified within the STM image provided in Figure 2b wherein the brighter features (green oval) also appear slightly larger than the dimmer features (yellow oval). Based on the variable contrast within the SAMN, we conclude that **1** forms a bilayer at the 1-PO/graphite interface under these experimental conditions with the bright features corresponding the molecules adsorbed in the second layer whereas the darker moieties are the molecules adsorbed directly on the HOPG surface. Besides the difference in the STM contrast, the formation of the bilayer can also be inferred from the difference in the measured apparent height of the TTF cores as depicted in the line profiles presented in Figure 2c. We conclude that the defects observed in large scale images (white arrows, Figure 2a) are thus missing molecules in the second layer and the smaller scale images allow the observation of the layer beneath the top layer.

Table 1. Unit cell parameters for the SAMNs of **1**.

	Unit cell (exp)			Packing density
	a (nm)	b (nm)	$\alpha(^{\circ})$	Molecules/nm ²
Bilayer	1.8 ± 0.1	2.9 ± 0.2	69.0 ± 4.0	0.209
Bottom layer (sim)	1.8	2.9	71.7	0.202
Monolayer (exp)	2.2 ± 0.2	3.8 ± 0.2	74.0 ± 4.0	0.122
Monolayer (sim)	2.1	3.7	73.4	0.134

Figures 2d, e show STM images highlighting the unit cells of the top and the (partially visible) bottom layers, respectively. The unit cells are comparable (Table 1). The striped features running in between the rows of TTF cores are ascribed to the alkyl chains. Based on the average distance between the adjacent rows of TTF cores (2.6 ± 0.2 nm), we conclude that the octadecyl chains are fully extended and adsorbed on the HOPG surface. All four chains per molecule are adsorbed on the surface which are always oriented along one of the main symmetry axes of the graphite lattice and make an angle of $\beta = 102 \pm 5^{\circ}$ with respect to the row of TTF cores (Figure 2e). We hypothesize that the bilayer SAMN is governed by π - π stacking between TTF cores and is stabilized by the interdigitation of the alkyl chains between the first layer at the surface. A molecular model of the first layer in contact with

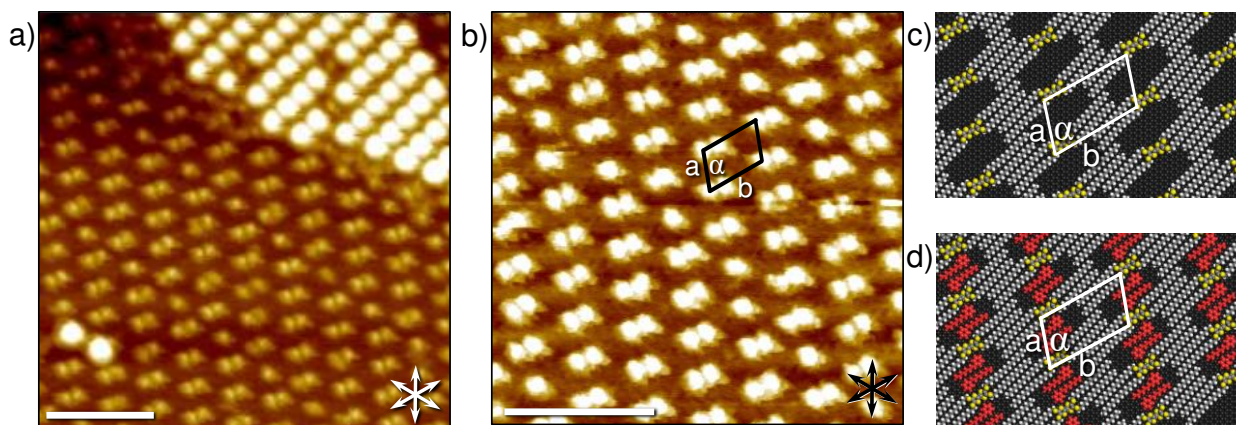


Figure 3. Self-assembly of **1** at the 1-PO/graphite interface a few hours after deposition of the solution. (a) STM image showing the coexistence of the monolayer and the bilayer structures (scale bar = 10 nm). (b) STM image of the monolayer structure with overlaid unit cell (scale bar = 10 nm). Graphite symmetry axes are presented in the lower left corner of the STM images. Imaging parameters (a, b): $I_{set} = 70\text{ pA}$ to 90 pA , $V_{bias} = -0.750\text{ V}$ to -1.000 V . (c) A forcefield-optimized structural model for the molecular arrangement of the monolayer considering the experimentally measured unit cell. (d) The same model as in (c) but considering the co-adsorption of the solvent molecules (red).

the surface was built using these considerations and then further refined using MM/MD simulations (*vide infra*) and is presented in Figure 2f. The model depicts close-packed assembly of **1** where pairs of alkyl chains on either side of the TTF core are interdigitated with those of molecules in the neighboring rows. The lattice parameters obtained from simulations are in close agreement with those obtained experimentally (Table 1).

In addition to the bilayer assembly, which is the dominant pattern observed under these experimental conditions, another molecular packing was also observed. This new structure was observed a few hours after deposition of the solution of **1**. Figure 3a shows the STM image of the second network coexisting with the previously described bilayer structure. In contrast to the bilayer, here the network structure is dominated by double lobed bright features. Single lobed features are also observed albeit to a lesser extent (29%). Much like in the bilayer assembly, the molecules organize in rows. In areas with exclusive double-lobed features, the average double-lobe to double-lobe distance is $2.2 \pm 0.2\text{ nm}$. The average orthogonal intermolecular distance between adjacent rows is $3.4 \pm 0.1\text{ nm}$. A characteristic unit cell for the assembly is represented in Figure 3b which exhibits lattice parameters distinctly larger than those for the bilayer (Table 1) making this a rather loosely packed assembly. The darker regions do not exhibit any specific contrast which could be unambiguously ascribed to the alkyl chains. The absence of point defects and the fact that scanning at high currents (scanning at shorter tip sample distances) revealed graphite lattice indicates that the new structure can be ascribed to a monolayer.

Assuming that the bright features correspond to the TTF core of **1**, a molecular model was built which is presented in Figure 3c. The model depicts a rather open structure where the molecules are arranged in rows with the alkyl chains fully extended and arranged in pairs instead of interdigitation. This leaves quite some open areas in between the molecules which are mostly occupied by solvent molecules, providing additional stability to the network. A molecular model presented in Figure 3d shows this possibility where pairs of 1-PO molecules are co-adsorbed between the molecules of **1**. We hypothesize that such packing is stabilized by interactions between aromatic-CH group on the phenyl ring of 1-PO and the sulfur atoms on the core of the neighboring molecule of **1** (see Figure S2 in the supporting information). Invoking such stabilization is not unreasonable as existence of hydrogen-bond-like interactions between -CH donors and sulfur acceptors has been reported earlier.⁶⁰ Furthermore, the coadsorption of the solvent molecules does not distort the unit cell of the network which remains the same after co-adsorption of 1-PO. To understand the origin of the contrast difference in the features observed in the STM images for the two structures and to shed light on the composition of the new structure, we resorted to MM/MD simulations.

3.2 Adsorption conformation of single molecule and STM contrast: MM/MD and STM simulations

The striking contrast difference between the features observed in the bilayer (oval or rectangular) and the monolayer (single and double lobed) structures can be traced back to the conformation of TTF cores. Previous theoretical studies on TTF derivatives have revealed that for the simplest alkylated TTF, (*tetrakis*(methylthio)tetrathiafulvalene (TTF-(SC₁)₄), the TTF core is boat-shaped,⁶¹⁻⁶³ which is also confirmed by our DFT calculations (Figure S3 in the supporting information). We hypothesize that the nonplanar geometry of the TTF core and in turn its adsorption geometry on the graphite surface is a key aspect towards understanding the experimentally observed STM contrast. To understand the factors contributing to the peculiar STM contrast of the features observed in the monolayer and to determine the adsorption conformation of **1** within the experimentally observed assembly, elaborate DFT and force-field simulations were performed. Harmonic restraints were applied on **1** in all the force-field calculations to reproduce the boat-shaped conformation of the TTF core. To have a better consistency with the molecular geometry optimized at DFT-level, extra harmonic restraints were applied to the torsion angle φ and its three equivalents (Figure S4 in the supporting information) in all force-field calculations. The equilibrium angle for these restraints is set at 160 degrees. In this way, an energy penalty is applied when the molecule geometry deviates from the boat-like shape as revealed by the DFT optimizations. Force constants of such restraints are determined to be 25 kcal/mol/°, at which the DFT-optimized adsorption conformation of TTF-(SC₁)₄ on HOPG is successfully reproduced by the forcefield simulations (Figure S4b in the supporting information).

In previously reported STM data on TTF derivatives,⁵² TTF cores were imaged as featureless rectangular bright features similar to the STM images recorded in this study for the bilayer. In this previous study, the STM contrast was attributed to a planar TTF core adsorbed on the surface, held together by interdigitated alkyl chains. However, this hypothesis was not examined thoroughly using atomistic simulations. Figure 4a shows the adsorption conformation of **1** on the graphite surface with the TTF core initially in a boat-like conformation resembling that calculated for TTF-(SC₁)₄. Upon minimization, the TTF core of **1** clearly goes through planarization (Figure 4a, b) in the same way as proposed in earlier report.⁵² This planarization, which is also found in the DFT calculations (see Figure S4 in the supporting information), is probably due to increased π - π interactions between the TTF core and the graphite surface. Given its planar geometry, we will refer to this conformation as the *core-flat* conformation in the following text. To understand the STM contrast of the *core-flat* conformation, STM simulations were carried out on this adsorption geometry. A simulated STM image is also depicted in Figure 4b together with the corresponding STM image. The TTF core appears as a rectangle with uniform brightness in the simulated STM image, closely matching the contrast in the experimental STM image of the bilayer assembly.

If the core planarization does not occur, the inherent boat-like shape of the TTF core allows for two additional adsorption geometries for **1**, which are not equivalent, namely *core-down* (Figure 4c, d, 'the boat is afloat') and *core-up* (Figure 4e, f, 'the boat has capsized'). For these two conformations, the octadecyl chains are tentatively paired into two groups. The arguments in favor of this arrangement are: (1) the lack of any experimental evidence for the interdigitation of alkyl chains in the monolayer, in contrast to what observed in the bilayer assembly, and (2) the unit cell of the monolayer assembly is larger than that of the bilayer assembly. Considering these possibilities, alkyl chain pairing is presumed as a reasonable packing arrangement for the alkyl chains adsorbed on the substrate.

Force-field-optimized structures for *core-down* (Figure 4c) and *core-up* (Figure 4d) adsorption geometries show that, after optimization, (i) the alkyl chains remain paired and (ii) the boat-like TTF core is preserved in both conformations (Figure 4d, f). STM simulations were also performed on these geometries and are presented in (Figure 4d, f). For the *core-down* geometry, the simulated STM image shows an overall rectangular shape with brighter regions at both ends of the TTF core (Figure 4d, green dashed ovals) and a less bright region at the center of the molecule. We attribute the two brighter regions to the protruding sulfur atoms of the bent TTF core. The appearance of this simulated image is consistent with the double-lobed features in the monolayer assembly. On the contrary, the simulated STM image for the *core-up* conformation shows higher brightness at the center of the molecule (Figure 4d, green circle). This is directly related to the *core-up* adsorption geometry where the central part of the TTF core stays at a higher elevation with respect to the surface of graphite. This simulated image corresponds to the single-lobed features in the experimentally observed STM image of the monolayer of **1**. It is therefore likely that the single- and double-lobed

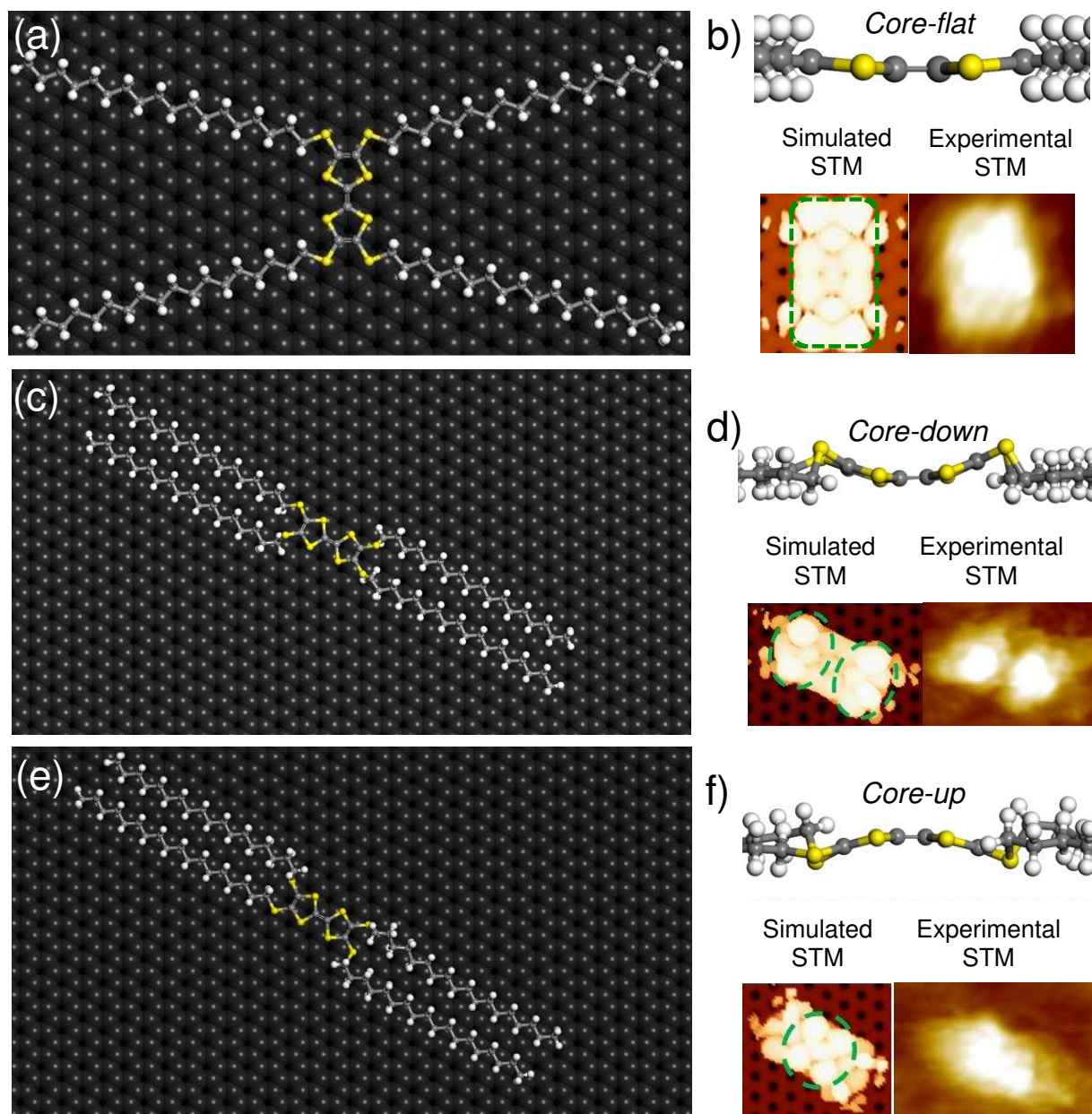


Figure 4. Force-field-optimized molecular models for the adsorption of **1** in *core-flat* (a, b), *core-down* (c, d) and *core-up* (e, f) conformation. Panels (b, d and f) show zoomed-in side-view of the TTF core for each conformation and the simulated STM image at the experimental bias voltage, $V_{bias} = -1.000V$, respectively. The experimental STM images are also shown at the right side of each simulated image for the sake of comparison. The green dashed shapes correspond to the brightest areas in the simulated STM images.

features observed in the monolayer of **1** correspond to TTF molecules with dissimilar adsorption geometries, namely *core-up* and *core-down*, respectively. Furthermore, both *core-up* and *core-down* conformations show excellent ability to self-assemble at the monolayer level. Thus, a monolayer consisting of molecules with *core-up* and *core-down* is feasible. This was verified by constructing a molecular model of the monolayer made up of *core-down* geometries and inserting a few molecules

with *core-up* geometry. Both overall packing and the lattice parameters were found to be well-preserved after optimization, which indicates that mixing between the two geometries occurs without causing any significant distortion to the original lattice and hence supports the experimental observation of the monolayer with mixed adsorption geometries (Figure S5 in the supporting information).

Another peculiar aspect of the experimentally observed monolayer is that the surface coverage of the double-lobed species is significantly higher than its single-lobed counterpart. To understand the discrepancy in the surface coverage of the *core-up* and *core-down* adsorption geometries, we estimated their potential energy and correlated it to their relative stabilities. In the optimized structures, the potential energy for *core-down* geometry is -141.8 kcal/mol while it is only -125.3 kcal/mol for the *core-up* geometry. Thus, the *core-down* geometry of **1** (Figure 4c,d) is the preferred adsorption geometry in the monolayer, which explains the higher surface coverage of double-lobed features in the experimentally observed monolayer. The *core-flat* conformation in Figure 4a,b shows an intermediate stability with a potential energy of -136.0 kcal/mol. We believe that the superior stability of the *core-down* geometry is due to the stronger interaction between the paired alkyl chains. On the contrary, the *core-up* geometry (Figure 4e, f) shows the poorest stability, despite similar pairing of alkyl chains. This could be explained by its weaker interactions with the substrate owing to the adsorption geometry of the core. For the *core-up* geometry, in fact, the TTF core of the molecule does not adsorb in the most favourable way on the substrate (Figure S6 in the supporting information). Based on the experimental STM data, STM simulations and energetic calculations, we can conclude that the three types of contrast we see in the experimental STM images can be attributed to three different adsorption geometries of **1** within the assembly. The rectangular, double-lobed, and single-lobed features are successfully correlated with *core-flat*, *core-down* and *core-up* conformations, respectively.

It is worth noting here that, as demonstrated by the experimental data and the STM simulations, the arrangement of the alkyl chains plays a crucial role in determining the adsorption conformation of alkylated-TTFs on the surface. The *core-flat* conformation is only stable when the alkyl chains are perpendicular to the long axis of the TTF core, while the *core-down* and *core-up* conformations are obtained only when the alkyl chains of molecules are paired and are oriented along the long axis of the TTF core. To demonstrate that this is the case, we performed a systematic study on how the length of the alkyl chains affects the geometry of the TTF core once the molecules adsorb on graphite. Figure 5 shows the optimized geometries for TTF-(SC₃)₄ adsorbed on the HOPG surface in *core-flat* (Figure 5a, b), *core-down* (Figure 5c, d) and *core-up* (Figure 5e, f) conformation. Their input structures have the same geometry as that for **1** adsorbed on the graphite surface, except for the shorter length of the alkyl chains.

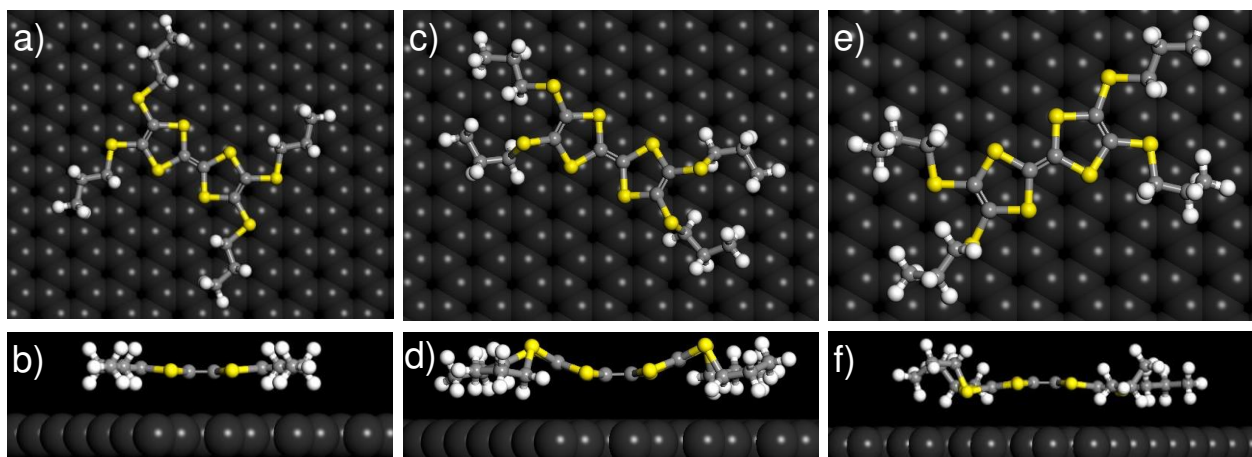


Figure 5. Force-field optimized atomistic model of TTF-(SC₃)₄ in (a, b) *core-flat*, (c, d) *core-down* and (e, f) *core-up* conformation.

In contrast to that in the case of **1**, after optimization, it is the *core-flat* conformation that shows the best stability instead of the *core-down* conformation. The potential energy of the *core-down* and *core-up* conformation is 24.3 kcal/mol and 27.4 kcal/mol higher, respectively. Using the same input structures, identical stability ranking, and geometries were obtained from optimizations at the DFT level, which confirms the appropriate description of the adsorption geometry by the force-field. The propyl side chains are roughly paired in the *core-down* and *core-up* conformations of TTF-(SC₃)₄ although a much weaker interaction is expected, due to the shortened length. For this reason, a lower stability is gained from the alkyl chains for TTF-(SC₃)₄, making the relative energetic stability reversed between the *core-flat* and *core-down* conformation, compared to **1**. The *core-up* conformation still suffers from the less favored geometry and is again the least stable structure.

A 100ps-long MD simulation at 298K was then performed on the three optimized structures of TTF-(SC₃)₄. At the end of these simulations, both *core-down* and *core-up* geometries converted into the *core-flat* geometry (Figure S7 in the supporting information), which is not the case for molecule **1**. This structural conversion and the change in the relative energetic stabilities indicates that the core conformation of the adsorbed alkylated-TTFs is very sensitive to the arrangement of the alkyl chains. When adsorbed on the substrate, the presence of long and paired alkyl chains preserves the original boat-like conformation existing in the isolated molecule. The long and paired alkyl chains interact strongly between themselves and with the substrate. They therefore act as anchors, hindering the planarization of the molecule. This is not the case for the *core-flat* conformation, where the planarization of the molecule is easier since the hindrance from paired alkyl chains is absent.

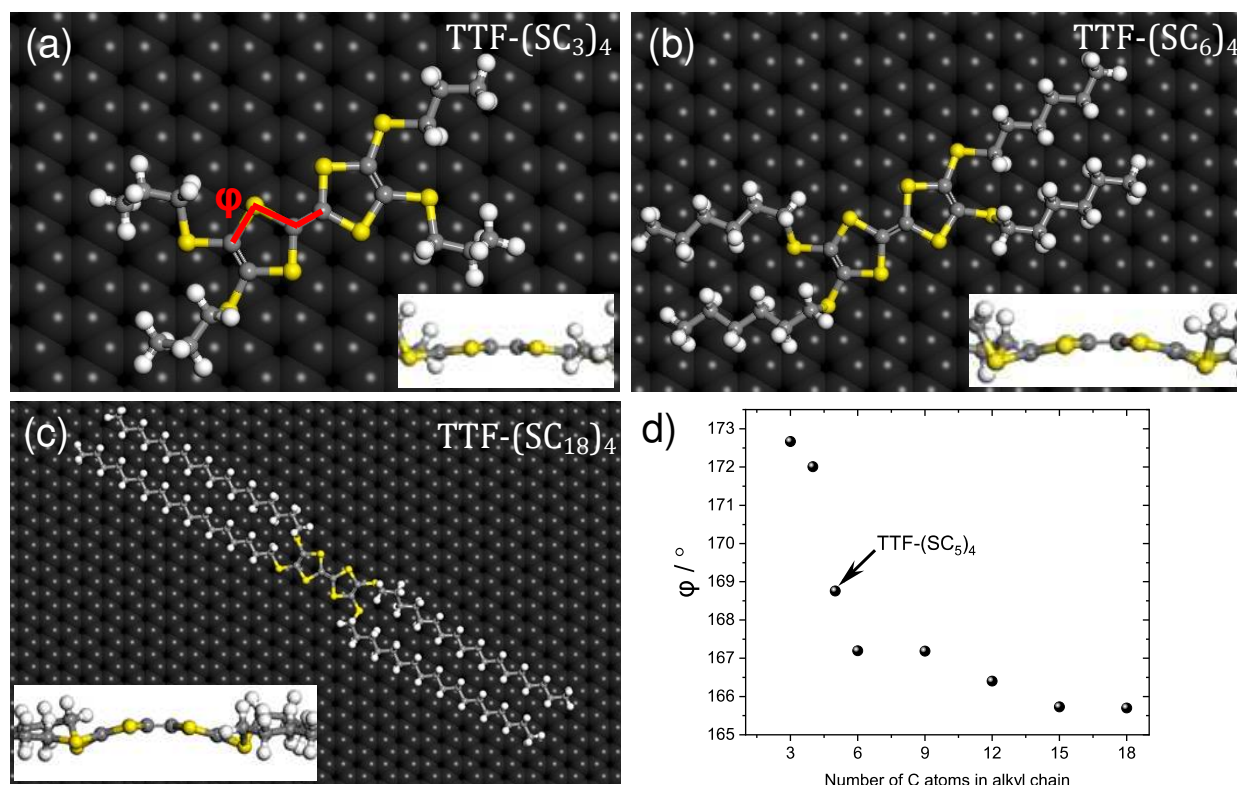


Figure 6. Force-field optimized adsorption geometries of (a) TTF-(SC₃)₄, (b) TTF-(SC₆)₄ and (c) TTF-(SC₁₈)₄ in *core-up* conformation. The insets are side views of the TTF core to better visualize the molecular planarization. The torsion angle φ associated with molecular planarization is labelled in (a). There are four equivalent torsion angles in the TTF core. Only one is shown here for the sake of clarity. (d) A plot showing the changes in the torsion angle φ as a function of chain length.

Finally, the effect of the alkyl chains on the planarization of the molecule was further investigated by modelling the adsorption of alkylated TTFs having chains with different lengths in the same *core-up* conformation. The optimized geometries of TTF-(SC₃)₄, TTF-(SC₆)₄ and TTF-(SC₁₈)₄ (= compound **1**) are shown in Figure 6. The torsion angle (φ , Figure 6a) associated with the planarization of the molecule was measured. With this exercise, the effects of the alkyl side chains on the conformation of the core can be discerned in a more quantitative way. The average values of this torsion angle increase gradually from 165.5° for TTF-(SC₁₈)₄ to 172.3° TTF-(SC₃)₄, which corresponds to the most planarized conformation (φ closest to 180°). Increase of torsion angle φ (more planarization) as a function of decreasing alkyl chain length is observed for a broad coverage of alkylated TTFs (Figure 6d). The planarization is suppressed for TTFs with longer alkyl chains because the pairing of those chains and the subsequent van der Waals interactions between them prevails over the interactions between the TTF core and the graphite surface.

While the discussion provided above rationalizes the structure and constitution of the experimentally observed self-assembled monolayer and the bilayer, it does not necessarily explain the driving force for the formation of the two structures. To shed light on this aspect, we undertook a

systematic concentration dependent STM study. Considering the difference in the packing density of the bilayer and the monolayer, increasing the concentration of **1** should favor the bilayer structure for concentrations below the solubility limit of **1**, which was estimated to be situated in the range of 3.7 to 4.2×10^{-5} M (*vide infra*). When the amount of **1** added to 1-PO exceeds the solubility limit, solid **1** is present besides dissolved **1** at a concentration equal to the solubility limit and a potential equilibrium between the monolayer and bilayer structure is no longer expected to shift upon adding more **1** to the 1-PO solution. Contrary to our expectation though, upon decreasing the formal concentration of **1** by diluting the solution, the bilayer network remains the dominant structure. In fact, for the lowest concentrations used, only a fraction of the HOPG surface was found to be covered by the bilayer of adsorbed **1** (Figure S8 in the supporting information). This unexpected behaviour can be attributed to a packing of the adsorbed **1** that is determined by kinetic rather than thermodynamic control or to the formation of aggregates of **1** in solution.⁶⁴ To further understand the behavior of **1** in solution we carried out UV-Vis spectroscopy measurements in 1-PO.

3.3 Behaviour of **1** dissolved in solution: UV-Vis spectroscopy

We probed the concentration (7.5×10^{-5} M to 9.0×10^{-4} M) and temperature (25 °C to 65 °C) dependence of the UV-Vis spectra of **1** in 1-PO. Figure 7a shows an apparent concentration dependence of the normalized UV-Vis spectra of **1**, which even at the lowest concentration differ from those of dilute solutions of alkyl- or thioalkyl- substituted TTF derivatives in several solvents.⁶⁵⁻⁶⁹ However the normalized spectra recorded for the same concentration range at 65 °C are identical over the concentration range used (Figure 7b). Their features, consisting of a maximum at 307 nm, a shoulder at 329 and 380 nm, and a long wavelength tail extending to 500 nm, match those of tetra-thioalkyl substituted TTF derivatives in dilute solution, as well as calculated spectra of tetramethyl-bis(ethylenedithio)-tetrathiafulvalene.⁶⁷⁻⁶⁹ Long wavelength tails, extending sometimes to 1400 nm was reported for thin layers TTF derivatives.⁷⁰⁻⁷⁴ For UV-Vis spectra obtained at higher temperatures (Figure 7b), the short wavelength maximum and shoulder become more prominent, while at longer wavelengths the transmittance (above 350 nm) is increased systematically, and the weak bands at 374 and 446 nm disappear in favor of the 380 nm species. The maximum at 307 nm and the shoulder at 329 nm are characteristic for monomers as upon aggregation these transitions shift to 297 and 317 nm, respectively.⁶⁸ From the absorbance at the maximum at 307 nm and the shoulder at 380 nm, molar extinction coefficients of respectively 1.6×10^4 M⁻¹cm⁻¹ and 3.6×10^3 M⁻¹cm⁻¹ can be obtained, which are close to the molar extinction coefficients found for TTF or alkyl substituted TTFs.^{65, 66} Also in the long wavelength tail the absorbance is compatible with molar extinction coefficients reported for TTF.⁶⁵ Therefore the spectra obtained at 65 °C allow us to conclude that up to a formal concentration of 9.0×10^{-4} M a solution of **1** in 1-PO only contains monomers of **1** at 65 °C.

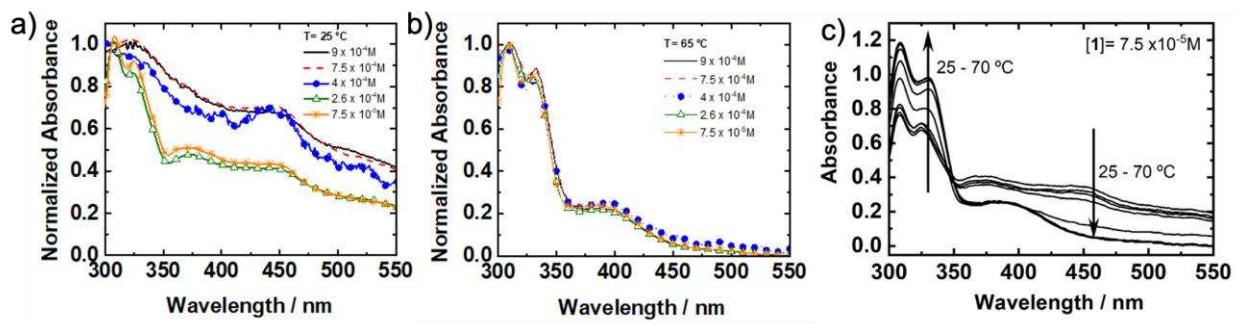


Figure 7. UV-Vis absorption spectra of **1** in 1-PO (normalized at the maximum) as a function of concentration recorded at (a) 25 °C and (b) 65 °C. (c) Temperature dependence of the UV-Vis absorption spectra of **1** in 1-PO for 7.5×10^{-5} M.

At lower temperatures (Figure 7a, c), the transmittance systematically increases below 350 nm while above 350 nm the opposite occurs. Furthermore, the shoulder around 380 nm splits into a weak band around 374 nm and 446 nm while a long wavelength tail extending beyond 550 nm develops. The increase of the absorption at 400 nm is too large to be attributed to the low oscillator strength of $1^1A_1 \rightarrow 2^1A_1$ transition or to transitions to a triplet state.^{63,69,75} At first sight, the absorbance close to 450 nm could be ascribed to molecular aggregates. However, the outsized shift for J-type or H-type aggregates (from 380 nm to 446 nm or 3590 cm^{-1}),⁷⁶⁻⁷⁹ together with the absence of a blue shift of the 307 nm band and the 329 nm shoulder at 25 °C⁶⁹ when comparing spectra at 65 °C and 25 °C, make it highly unlikely that an equilibrium between monomers and small aggregates explains the temperature and concentration dependence of the spectra. Another plausible explanation is the formation of the $\text{TTF}^{\circ+}$ radical cation since TTF and its derivatives are easily oxidized. The absorption bands of the radical cation of TTF and thio-alkyl substituted TTFs are situated at 430 nm, 495 nm, 580 nm between 750 and 850 nm which could explain the increased absorption at wavelengths longer than 400 nm.^{73,74,80-83} However, the reversible nature of the temperature dependence would indicate that the $\text{TTF}^{\circ+}$ radical cation is reduced back to TTF which is improbable in the absence of a reducing agent.

As there is no plausible explanation for an increased absorbance above 400 nm at room temperature compared to 65 °C, the observed loss of transmittance above 400 nm at room temperature is most likely related to light scattering by particles of undissolved TTF, as was previously observed for a vapor deposited film of dimethyl-TTF.⁷¹ Since at 25 °C part of the added **1** is present in the solid state, the actual concentration of dissolved **1** is lower than the formal concentration of 7.5×10^{-5} M. This explains why the absorbance at 307 nm and 329 nm has been reduced from respectively 1.20 and 1.00 at 70 °C to 0.61 and 0.48 at 25 °C. The values for the absorbance at 25 °C are corrected for light scattering because at 500 nm there is no absorption at 65 °C, and hence the apparent absorption at 500 nm at 25 °C (0.21) is attributed to light scattering. When we make the conservative estimate that the light scattering at 307 and 329 nm is identical to

that at 500 nm, the apparent absorbance at 307 and 329 nm, which amounts to respectively 0.82 and 0.69, has to be reduced to 0.61 and 0.48. Hence at 25 °C the concentration of dissolved **1** is reduced from 7.5×10^{-5} M to $3.7 \pm 0.1 \times 10^{-5}$ M. As our correction for light scattering at 25 °C is probably a conservative one, the actual absorbance at 307 and 329 nm and the corresponding solubility limit should be considered as an upper limit. The UV-Vis spectra of **1** recorded as a function of concentration and temperature allow to conclude that: (1) At 25 °C, the solubility limit of **1** is somewhere between 3.7×10^{-5} M to 4.2×10^{-5} M. (2) At 25 °C, the solutions of **1** with a formal concentration of 7.5×10^{-5} M or higher are a heterogeneous mixture of a saturated solution of **1** and solid **1**, possibly present in the form of microcrystals. (3) In 1-PO, there is no evidence for aggregation of **1** to dimers or trimers between 25 °C and 70 °C (also see Figure S9 in the supporting information).

Even though the UV-Vis absorption spectroscopy does not show strong evidence for pre-aggregation of **1** in 1-PO solution, it is clear is that there is a fraction of undissolved material at room temperature for a formal concentration of **1** of 4×10^{-5} M and higher. This could affect the free monomer concentration at the liquid-solid interface. Also, micro- or nanoparticles of **1** present in solution may dissociate upon coming in contact with the substrate, as previously reported.⁸⁴ Furthermore, kinetic effects may play a role in affecting the on-surface monolayer to bilayer ratio; the monolayer being the kinetically controlled structure and the bilayer the thermodynamically one.

While the formation of bilayer is not expected in the low concentration regime, one can rationalize such behavior by considering the binding energies of molecules adsorbed in the monolayer and those adsorbed in the second layer of the bilayer. Such binding energy estimates the energy gained by the molecules when incorporated in a self-assembly with respect to an isolated molecule adsorbed on the substrate. The binding energy was calculated as:

$$E_{bind} = \frac{E_{sam} - N * E_{mol}}{N}$$

where E_{bind} is the binding energy, E_{sam} is the potential energy of free-standing self-assembly, E_{mol} represents the potential energy of individual molecule when adsorbed on the substrate and N is the total number of the molecules in the self-assembly (note that by freezing the surface, its energy is 0 and can be ignored for the calculation of E_{bind}). The resulting binding energy for TTF-(SC₁₈)₄ in the monolayer and in the 2nd layer of the bilayer assembly was found to be -8.6 kcal/mol and -53.8 kcal/mol, respectively. The much higher stability for the 2nd layer of the bilayer comes from the more compact packing of the molecules as well as the fully interdigitated organization of the alkyl chains. Such higher binding energy indicates that the molecules have a strong preference to form the bilayer structure, which can therefore persist even at low-concentration regime.

4. CONCLUSIONS

This combined experimental (STM) and modelling approach (molecular mechanics, molecular dynamics, DFT) brings insight into the self-assembly of a TTF derivative at the solution/graphite interface. Two assembly structures are found. A bilayer network, governed by π - π stacking, is the predominant structure. Additionally, a more loosely packed monolayer network, sustained by the co-adsorption of solvent molecules, is also observed. The latter is counterintuitively observed only at higher concentrations, which may find its origin in the presence of TTF particles in solution, as revealed by UV/Vis spectroscopy. We also found that the conformation of the TTF core, which can be linked to the experimental contrast seen in the two networks, is strongly affected by the length and the organization of the alkyl chains. This work is yet another testimony highlighting the often-complex nature of self-assembly at the liquid-solid interface, and the value of a combined experimental and theoretical approach to unveil factors impacting the self-assembly.

Associated content

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/>

Experimental materials and methods, details of the molecular mechanics and molecular dynamics simulations, additional and supporting STM data as well as supporting data from the simulations. (PDF)

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Notes

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Acknowledgments

Financial support from the Research Foundation-Flanders (FWO G081518N, G0A3220N) and KU Leuven-Internal Funds (C14/19/079) is acknowledged. This work was in part supported by FWO and F. R. S.-FNRS under the Excellence of Science EOS program (project 30489208 and 40007495). C.M. acknowledges the financial support: Grants PID2021-1287610A-C22 and CNS2022-136052 funded by MCIN/AEI/10.13039/501100011033 by the “European Union” and SBPLY/21/180501/000127 funded by JCCM and by the EU through “Fondo Europeo de Desarrollo Regional” (FEDER). Research in Mons is also supported by the Belgian National Fund for Scientific Research (FRS-FNRS) within the Consortium des Équipements de Calcul Intensif – CÉCI, under Grant 2.5020.11, and by the Walloon Region (ZENOBÉ Tier-1 supercomputer, under grant 1117545).

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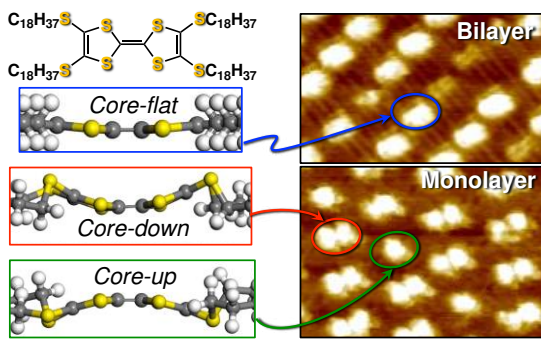
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TOC graphic



Supporting Information

Conformation-Dependent Monolayer and Bilayer Structures of an Alkylated TTF Derivative Revealed using STM and Molecular Modelling

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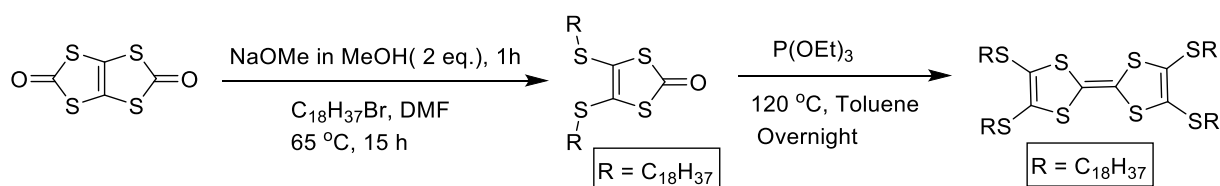
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#Equal contribution

Contents:

1. Synthesis and characterization of **1**.
2. Molecular modelling (additional/supporting data on MM/MD simulations).
3. STM data showing the self-assembled molecular network of **1** at the 1-phenyloctane/graphite interface at low concentration.
4. Supporting data for UV-Vis spectroscopy measurements.

1. Synthesis and characterization of tetrakis-(octadecylthio)-tetrathiafulvalene, 1.

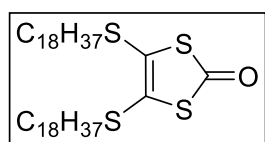


Scheme S1. Synthesis of tetrakis-(octadecylthio)-tetrathiafulvalene, 1.

The synthesis of compounds 4,5-bis(octadecylthio)-1,3-dithiol-2-one and 4,4',5,5'-tetrakis(octadecylthio)-2,2'-bi(1,3-dithiolylidene) has been reported previously.¹

Synthetic procedure

4,5-Bis(octadecylthio)-1,3-dithiol-2-one: [1,3] dithiolo[4,5-d] [1,3] dithiole-2,5-dione (500

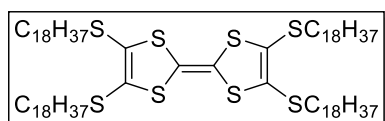


mg, 1 equiv.) was added to a solution of NaOMe in methanol (0.5 M, 9.6 ml, 2 equiv.) and stirred for 1 h under Argon atmosphere. Then, 1-bromooctadecane (2 equiv. 1.6 g) and 10 ml dimethylformamide (DMF) were added to the solution and stirred for 15 h at 65 °C. After the

reaction, the crude reaction mixture was evaporated and extracted with water and ethyl acetate.

The ethyl acetate layer was evaporated and directly purified by silica gel column chromatography with gradual eluting with ethyl acetate and heptane (1:9), which afforded the product as a white solid (462 mg, 56% yield). ¹H NMR (400 MHz, CDCl₃) δ 2.84 (t, *J* = 7.3 Hz, 4H), 1.68–1.61 (m, 8H), 1.43–1.37 (m, 8H), 1.26 (m, 56H), 0.88 (t, *J* = 6.8 Hz 6H). ¹³C NMR (100 MHz, CDCl₃) δ 190.41, 127.44, 36.88, 32.12, 29.94, 29.92, 29.90, 29.88, 29.86, 29.83, 29.79, 29.77, 29.68, 29.56, 29.30, 28.72, 22.89, 14.31. LRMS: (TOF MS EI+) *m/z*: found 686.5 (M^{•+}), 687.5 (MH⁺).

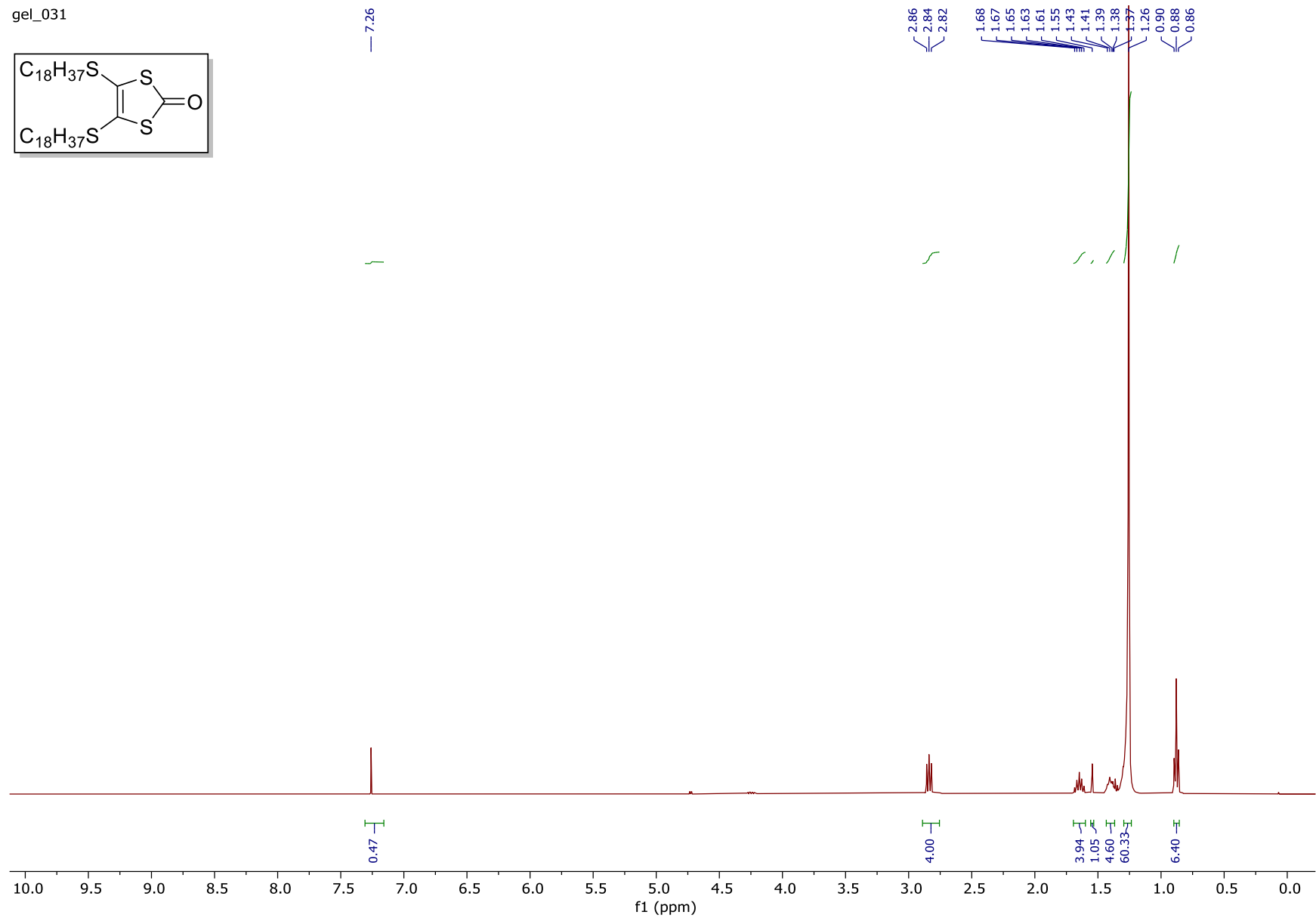
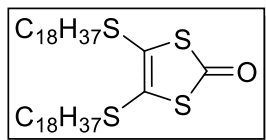
4,4',5,5'-tetrakis(octadecylthio)-2,2'-bi(1,3-dithiolylidene): To a stirred solution of the



dialkylated compound (100 mg, 1 equiv.) triethoxyphosphene (10 equiv. excess) in toluene (5 ml) was added and the reaction mixture refluxed overnight. After completion of the reaction,

the reaction mixture was allowed to cool to room temperature and cold methanol (10 ml) was added to reaction mixture to precipitate the product from reaction mixture and the precipitate was filtered and washed with cold methanol (5 × 5ml) for several times and the obtained solid compound was dried under vacuum to get the pure tetraalkylated TTF derivatives as a yellow solid (66 mg, 68% yield). ¹H NMR (400 MHz, CDCl₃) δ 2.82 (t, *J* = 7.3 Hz, 8H), 1.68–1.61 (m, 8H), 1.44–1.38 (m, 8H), 1.30–1.24 (m, 112H), 0.89 (t, *J* = 6.8 Hz, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 128.11, 110.31, 36.56, 32.14, 30.02, 29.94, 29.92, 29.89, 29.87, 29.82, 29.73, 29.55, 29.35, 28.78, 22.87, 14.23. HRMS: (TOF MS EI+) *m/z*: found 1340.9292 (M^{•+}), C₇₈H₁₄₈S₈^{•+} requires 1340.9347.

gel_031



gel_031
13C BBD

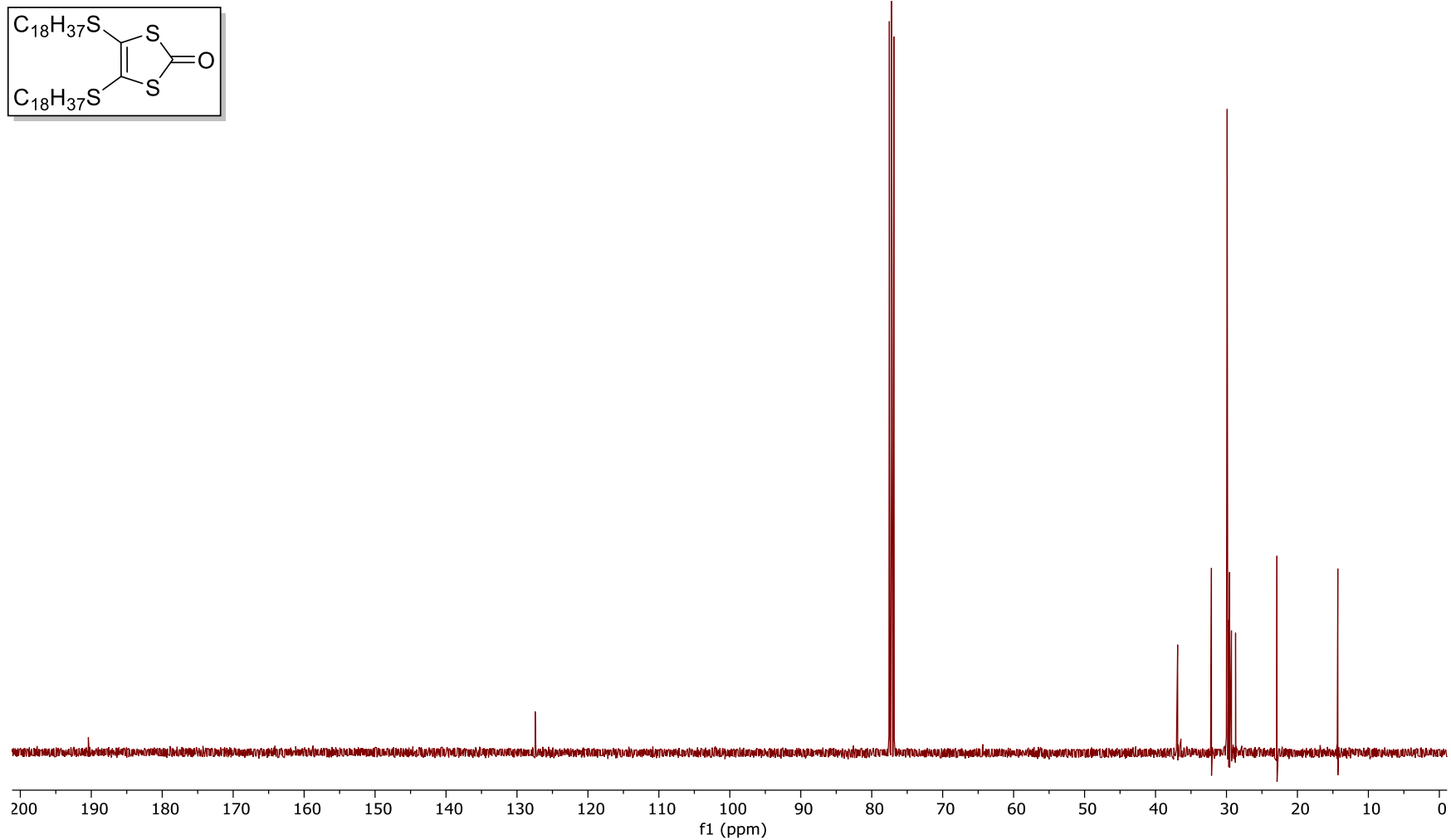
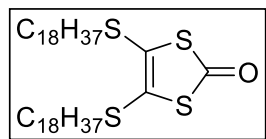
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127.44

77.52
77.20
76.88

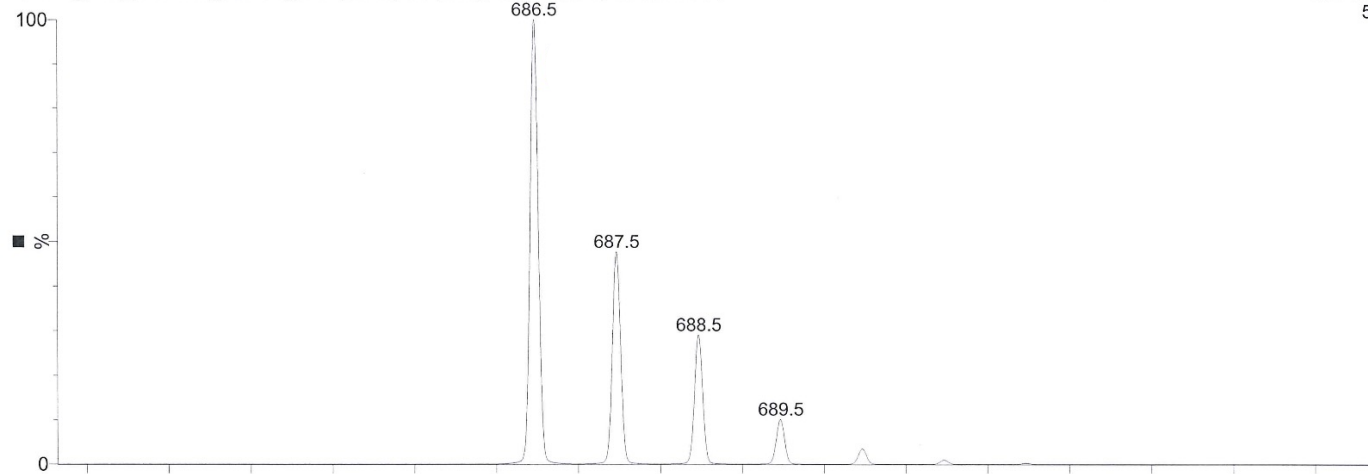
36.88
32.12
29.94
29.92
29.90
29.88
29.86
29.83
29.79
29.77
29.68
29.56
29.30
28.72
22.89

14.31



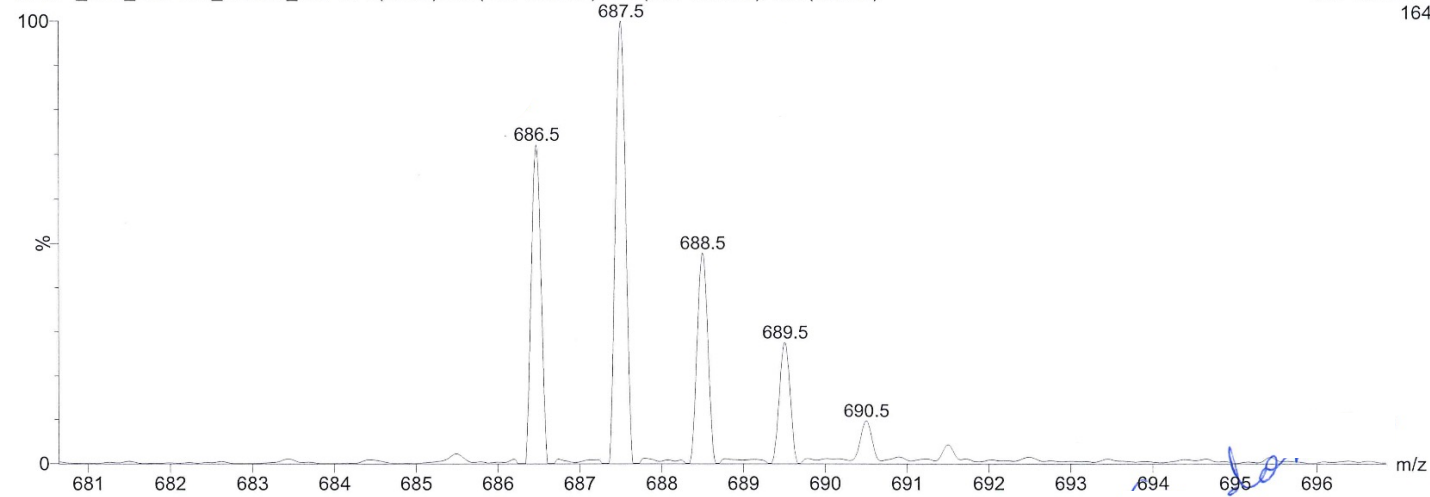
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TOF MS LD+
5.22e12

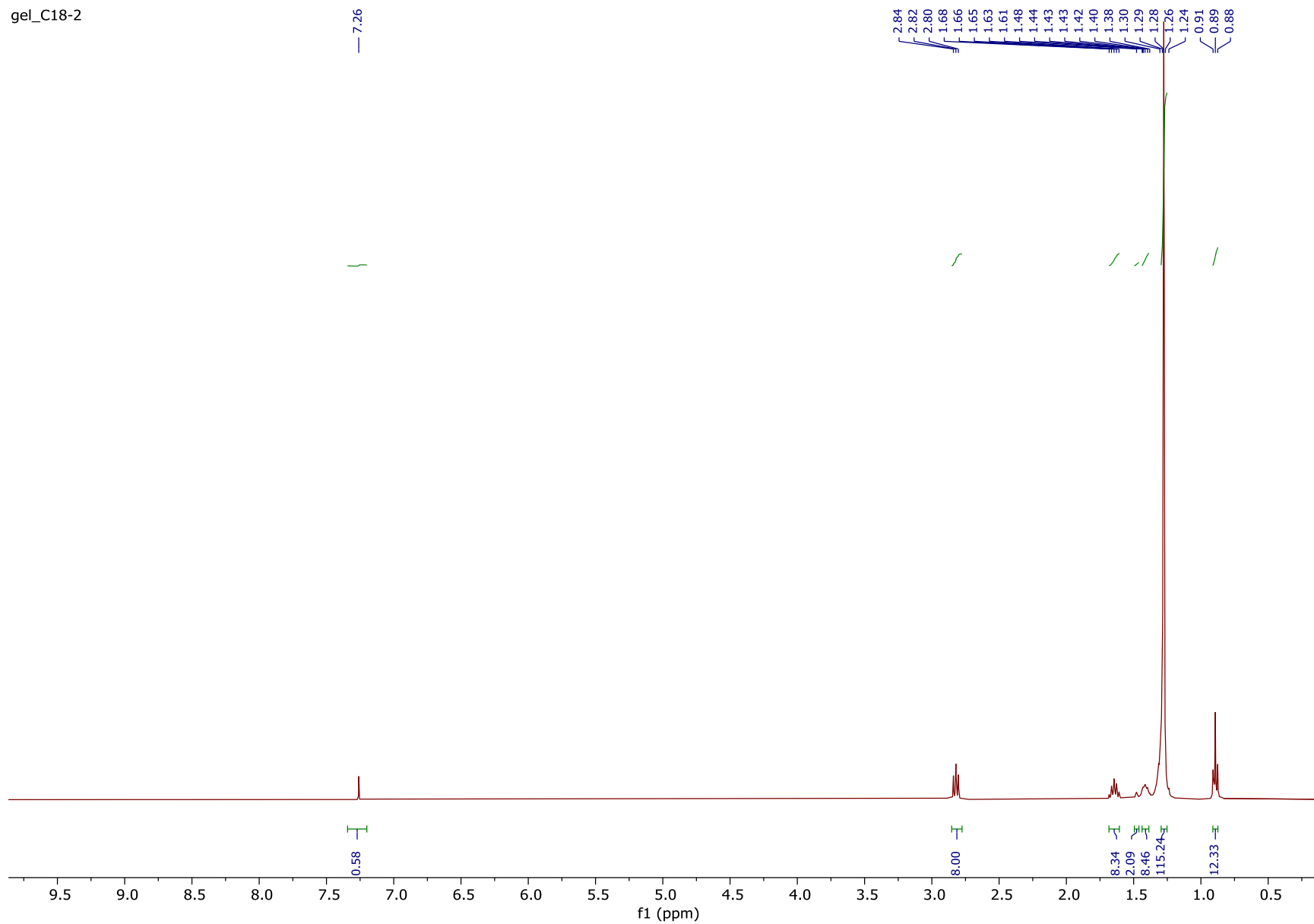


QTOF1_ULB_GEL-031_120220_002 214 (3.962) Sm (SG, 10x6.00); Sm (SG, 10x6.00); Cm (93:243)

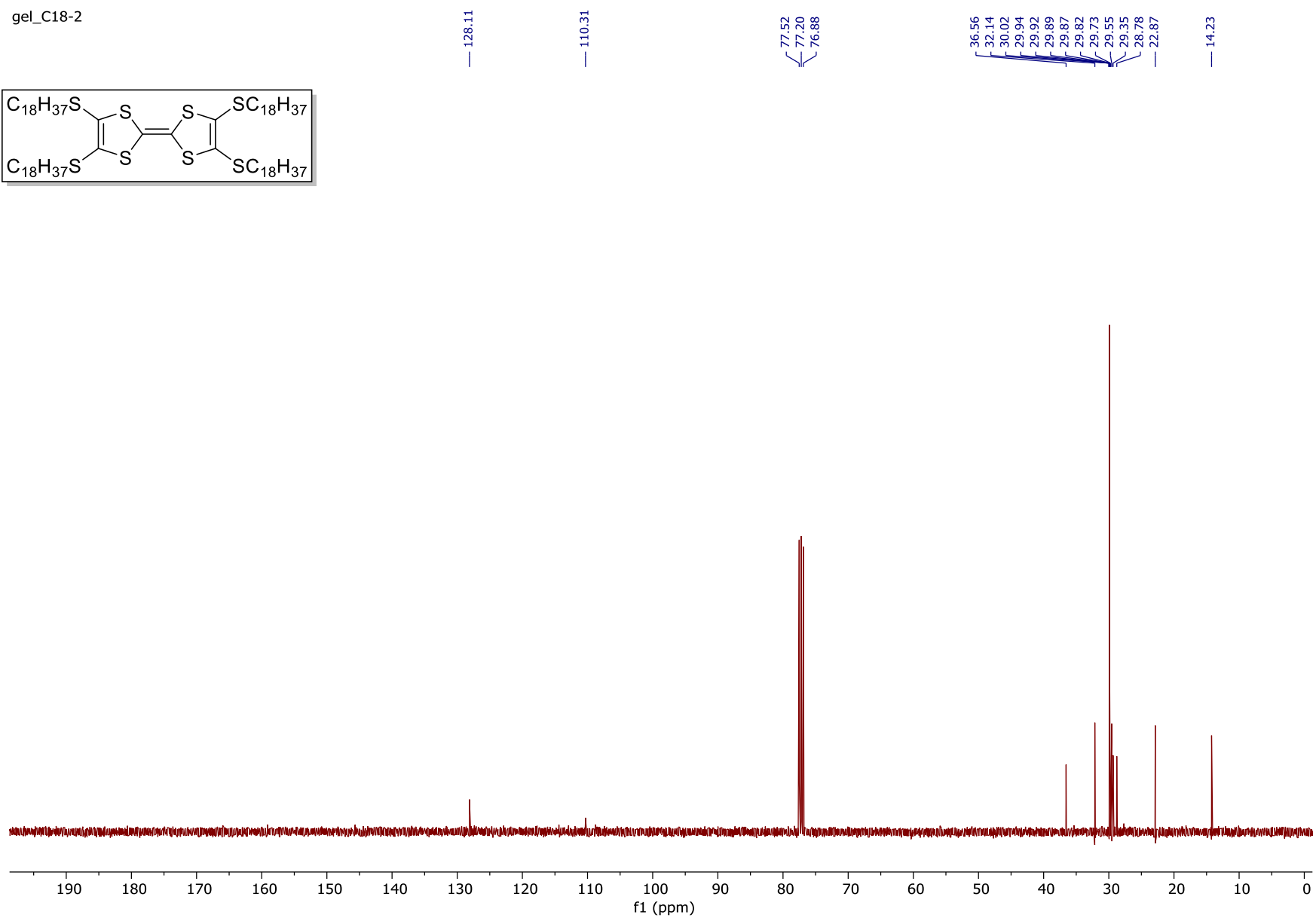
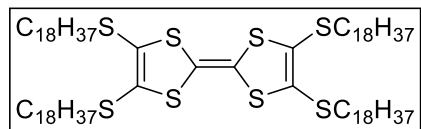
TOF MS LD+
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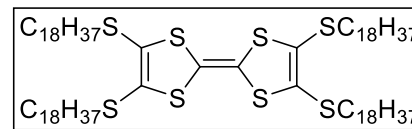
gel_C18-2



gel_C18-2



Elemental Composition Report



Single Mass Analysis

Tolerance = 25.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions

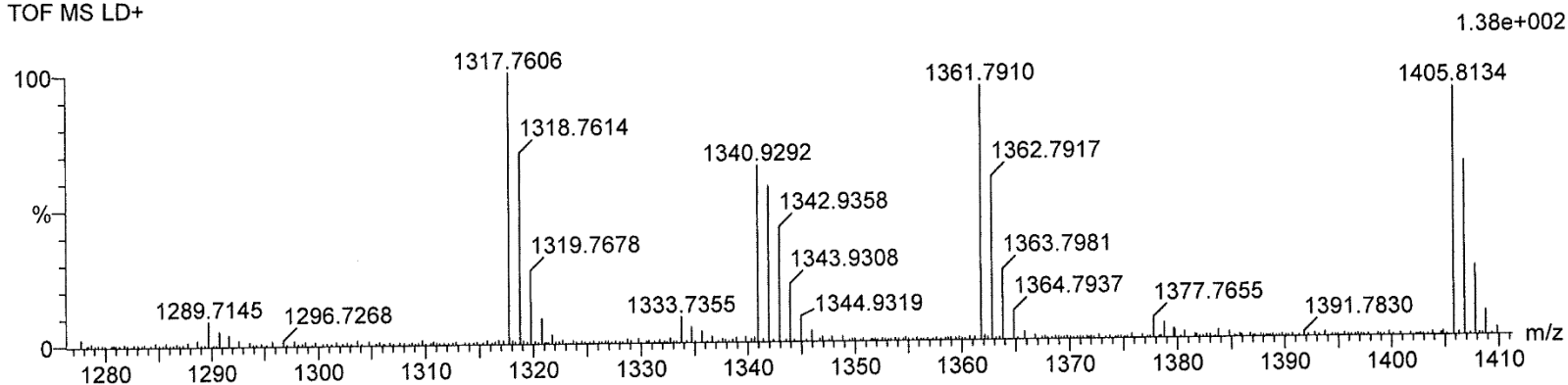
14 formula(e) evaluated with 1 results within limits (up to 10 closest results for each mass)

Elements Used:

C: 0-100 H: 0-200 S: 8-8

QTOF1_ULB_200901_GEL-C18-2_002 79 (1.463) AM (Cen,6, 80.00, Ht,9000.0,1317.76,1.00); Sm (SG, 10x6.00); Cm (76:131)

TOF MS LD+



Minimum: -1.5
Maximum: 5.0 25.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
1340.9292	1340.9347	-5.5	-4.1	5.0	11.1	n/a	n/a	C78 H148 S8

2. Molecular modelling (additional/supporting data on MM/MD simulations)

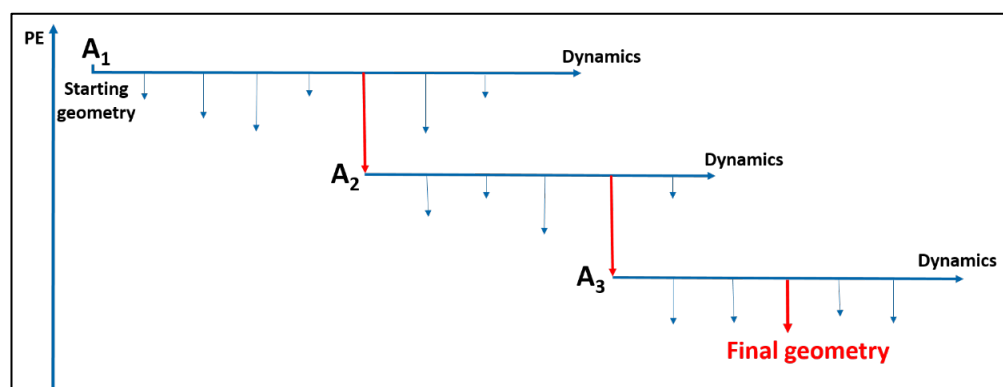


Figure S1. Principle of the quench MD protocol. Additional geometry optimizations (vertical blue arrows) are performed periodically during the normal MD run. The most stable structure (red arrow) is then employed as the starting point for the next round of quench MD. This process is iterated until all optimized structures from the same MD run have a very similar energy. In this way, the potential energy surface of the target system could be sampled better without being trapped in a local minimum. In this study, this quench MD refinement was carried out on the initially optimized molecular assemblies. A 100ps-long quench MD simulations was performed at 50 K and the structure was optimized every 1ps.

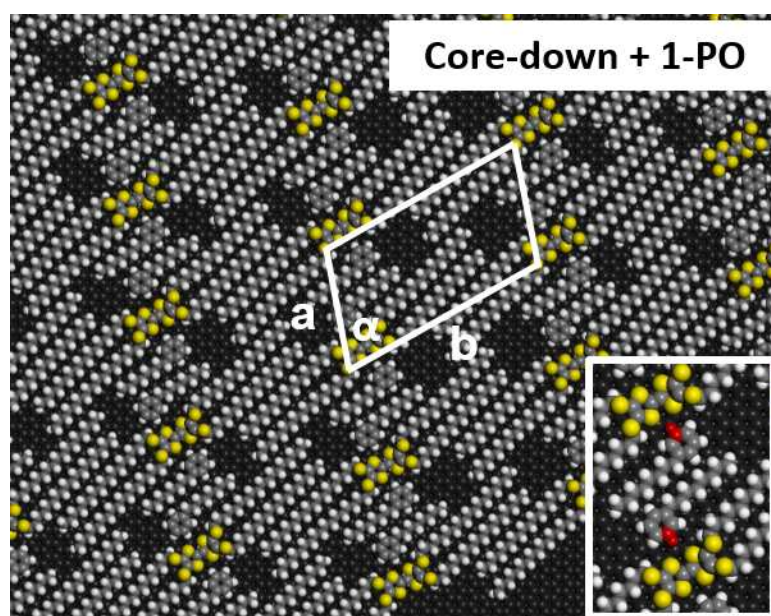


Figure S2. Force field-optimized structures for the co-assembled structure of **1** and the solvent, 1-PO. Here, **1** is adsorbed in *core-down* geometry.

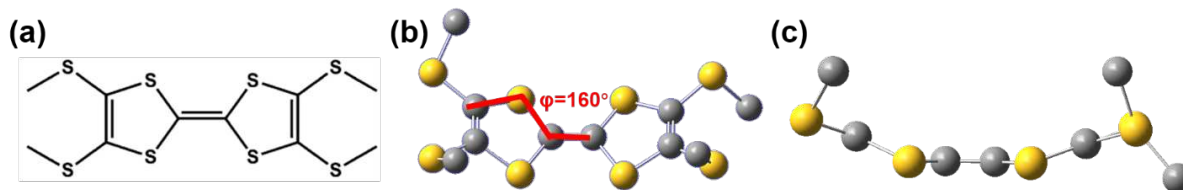


Figure S3. (a) Molecular structure of TTF-(SC₁)₄. (b) DFT-optimized TTF-(SC₁)₄ molecule with nonplanarity shown by the torsion angle φ . (c) Side view of the optimized structure. These simulations confirm the previously reported boat-like geometry of TTF-(SC₁)₄.

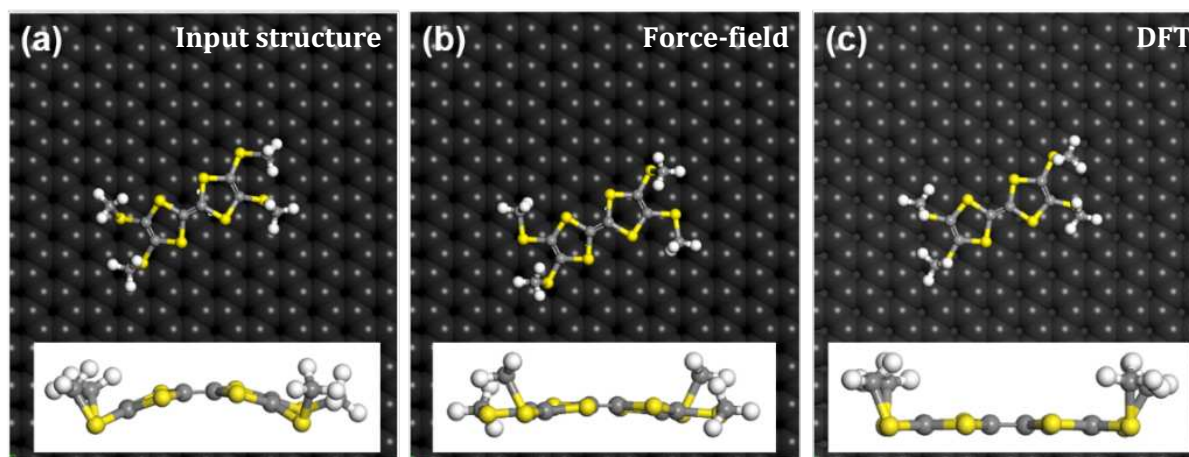


Figure S4. Adsorption of TTF-(SC₁)₄ on HOPG: (a) Input structure, (b) Force-field optimized structure and (c) DFT-optimized structure. With a force constant of 25 kcal/mol/° for the harmonic restraints applied on the torsion angle φ , the planarization of the molecule in the DFT-optimized structure can be successfully reproduced by the force-field simulations (Figure S4b). Stiffer restraints were also tested in the force-field calculations; in those cases, the molecules could not planarize upon adsorption, indicating that too stiff restraints are applied.

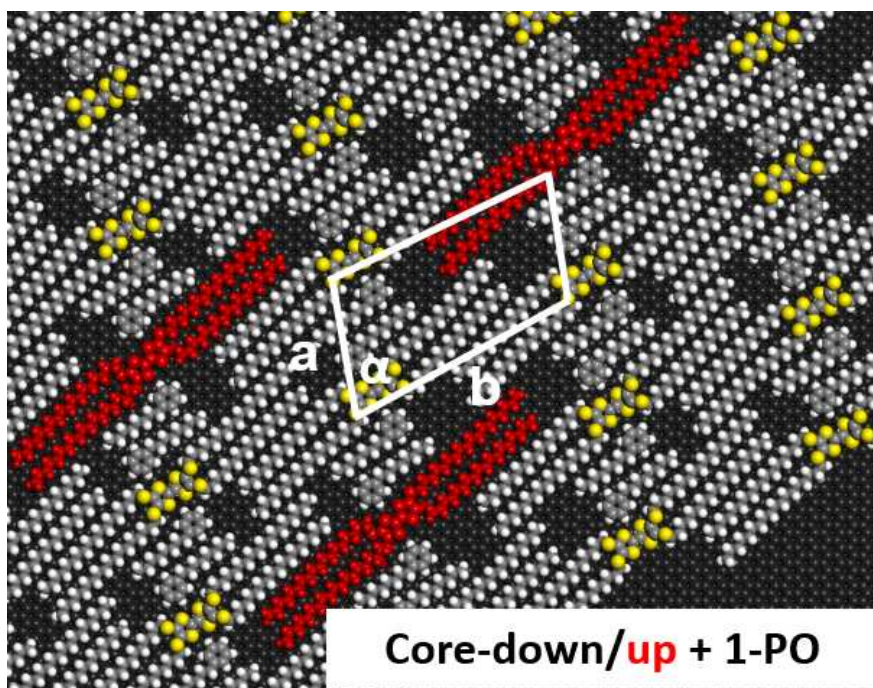


Figure S5. Force field-optimized structure for the co-assembled network of **1** and the solvent, 1-PO. Here, the molecules of **1** highlighted in red are flipped around so that they are in core-up geometry whereas rest of the molecules within the network are adsorbed in core-down geometry. Lattice parameters: $a = 2.2$ nm, $b = 3.9$ nm and $\alpha = 71.2^\circ$.

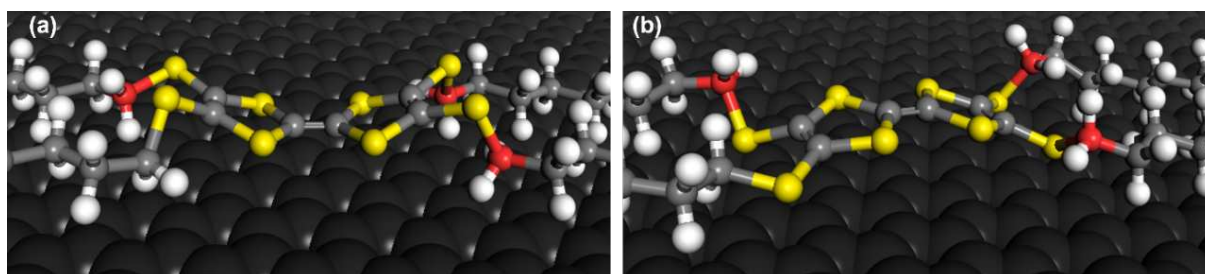


Figure S6. Molecular core configuration of TTF-(SC₁₈)₄ in the optimized core-down (a) and core-up (b) conformation. When TTF-(SC₁₈)₄ is adsorbed in the core-down conformation, the part of alkyl chains near the molecular core interacts with the substrate in a stronger way. The first carbon atom in each alkyl chain (three of four are highlighted in red for clearer visualization) point towards the substrate, which favors a stronger interaction between the alkyl chains and the substrate. Instead, these carbon atoms point away from the substrate in the core-up conformation, leading to a less favored interaction.

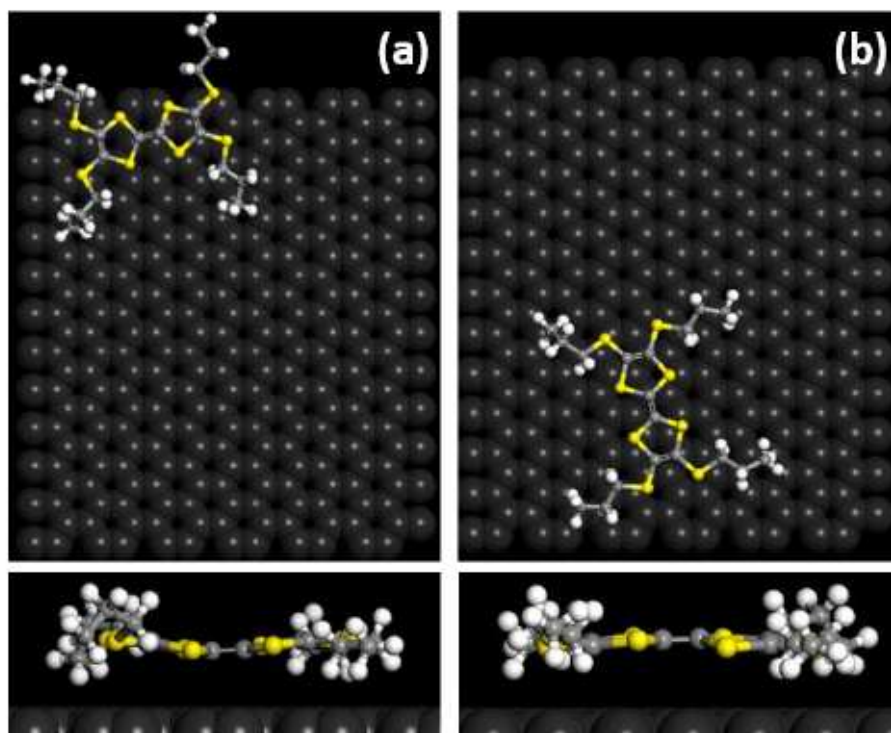


Figure S7. Adsorption geometry at the end of MD simulations for the initial *core-down* (a) and *core-up* (b) conformations of TTF-(SC₃)₄. Top panel: top views showing the arrangement of the alkyl chains; Bottom panel: side views showing the geometry of the molecular core. In both cases, the TTF core planarizes during the simulation. The HOPG substrate is shown underneath the adsorbed molecule.

3. STM data of the self-assembly of TTF-(SC₁₈)₄ on HOPG at the solid–liquid interface for low concentration

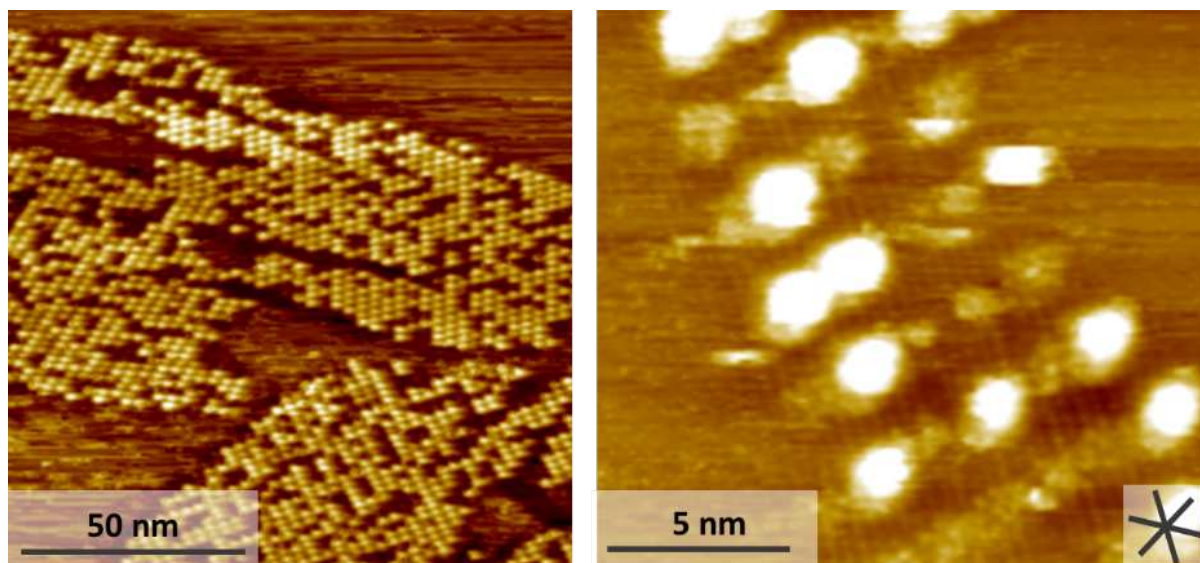


Figure S8. Self-assembly of **1** at the 1-PO/HOPG interface. Concentration is 4.6×10^{-6} M. Large (a) and small scale (b) STM images of the bilayer islands. It is clear from these images that at lower concentration, the bilayer structure dominates even the surface coverage is not complete revealing large, uncovered areas of the substrate. Graphite symmetry axes are indicated at the bottom right corner of STM images. *Imaging parameters:* $I_{set} = 70$ pA to 90 pA, $V_{bias} = -0.750$ V to -1.000 V.

We also note that a wide variety of concentrations ranging from 7.5×10^{-4} M to 4.0×10^{-6} M were tested for STM experiments. At the lowest concentration, we could not observe any self-assembled network formation. Throughout the range, where we could observe self-assembly at the solution/solid interface, only bilayer network was observed predominantly. Counterintuitively, the monolayer was only observed at higher concentrations. In order to understand the adsorption behavior from another solvent, we also carried out STM experiments at the 1, 2, 4-trichlorobenzene (TCB)/graphite interface. The adsorption behavior remained the same, with predominant bilayer formation at the TCB graphite interface, while no monolayer network was observed at this interface. Annealing of the sample was also tested for the possibility of formation of monolayers. This was tested for two different concentrations: 7.5×10^{-4} M and 4×10^{-6} M in 1-PO. Only the bilayer conformation was observed after annealing. Samples were annealed at 80°C for 20 minutes.

4. UV-Vis spectroscopy

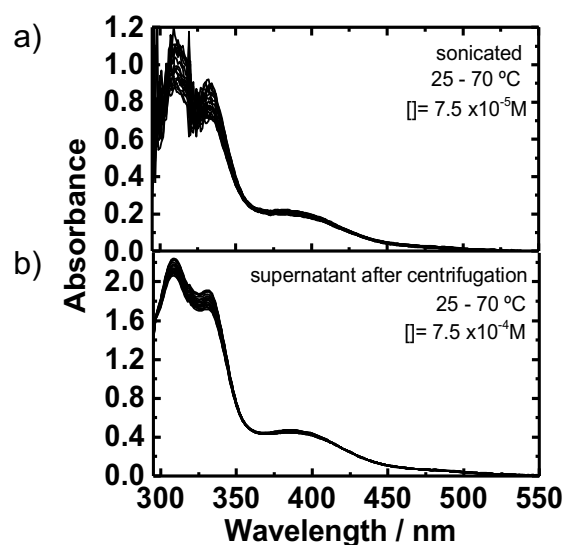


Figure S9. (a) Absorption spectrum of a sonicated dispersion of $7.5 \times 10^{-5} \text{ M}$ of **1** in 1-PO. (b) Absorption spectrum of the supernatant of a centrifugated $7.5 \times 10^{-4} \text{ M}$ suspension of TTF-(SC₁₈)₄ in 1-PO.

To confirm the role of the undissolved TTF, a sample with a high formal concentration ($7.5 \times 10^{-4} \text{ M}$) was centrifugated while the sample with a low formal concentration ($7.5 \times 10^{-5} \text{ M}$) was sonicated (Figure S9) in order to remove the particles from the solution. For both the supernatant of the centrifuged $7.5 \times 10^{-4} \text{ M}$ solution and the sonicated $7.5 \times 10^{-5} \text{ M}$ solution changing the temperature from 25 to 70 °C did not lead to changes in the absorption spectra, which continues to correspond to the absorption spectrum of monomers of **1**. This indicates that in the supernatant and the sonicated solution, light absorption can only be attributed to monomers. While sonication breaks up microcrystals of **1** and therefore reduces their light-scattering properties, it is not expected to have a lasting effect on solution equilibria between monomers and aggregates. Hence also before sonication the only dissolved species present are monomers of **1**. Consequently, the data in Figure S9 also support the hypothesis that the 450 nm maximum is only due to the presence of solid particles, such as microcrystals of **1**.

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