Supplementary information

Where are the counterions gone? Tip-induced dissociation of self-assembled triazatriangulenium–based molecules on Au(111)

S. Snegir[*,1], Y. J. Dappe[2], D. Sysoiev[3,4], O. Pluchery[5], T. Huhn[3], E. Scheer[1]

[1]Department of Physics, University of Konstanz, Universitätsstraße 10, 78464 Konstanz, Germany

[2]SPEC, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France

[3]Department of Chemistry, University of Konstanz, Universitätsstraße 10, 78464 Konstanz, Germany

[4] Current address: Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences Flemingovo nam. 2, 16610 Prague (Czech Republic).

[5]Sorbonne Université, CNRS, Institut des NanoSciences de Paris (INSP), 4 place Jussieu, 75005 Paris, France.

* corresponding author,

SAMPLE PREPARATION

The synthesis of the TATA–BF$_4$ molecule functionalized with –[CH$_2$]$_8$ groups has already been reported elsewhere.[1] The ^{1}H and ^{13}C MNR spectra (**Figure S1,S2**) of the synthesized compound were recorded to verify it purity. For the deposition of the molecules on Au(111) surface, a freshly prepared solution of TATA–BF$_4$ molecules in 1,2,4–dichlorobenzene (TCI, p.a., used as received) with concentration 1.3×10^{-7} mL^{-1} was prepared. The preparation of the self-assembled monolayers (SAMs) was performed by deposition of 2µL of the solution onto the freshly flamed gold substrates.
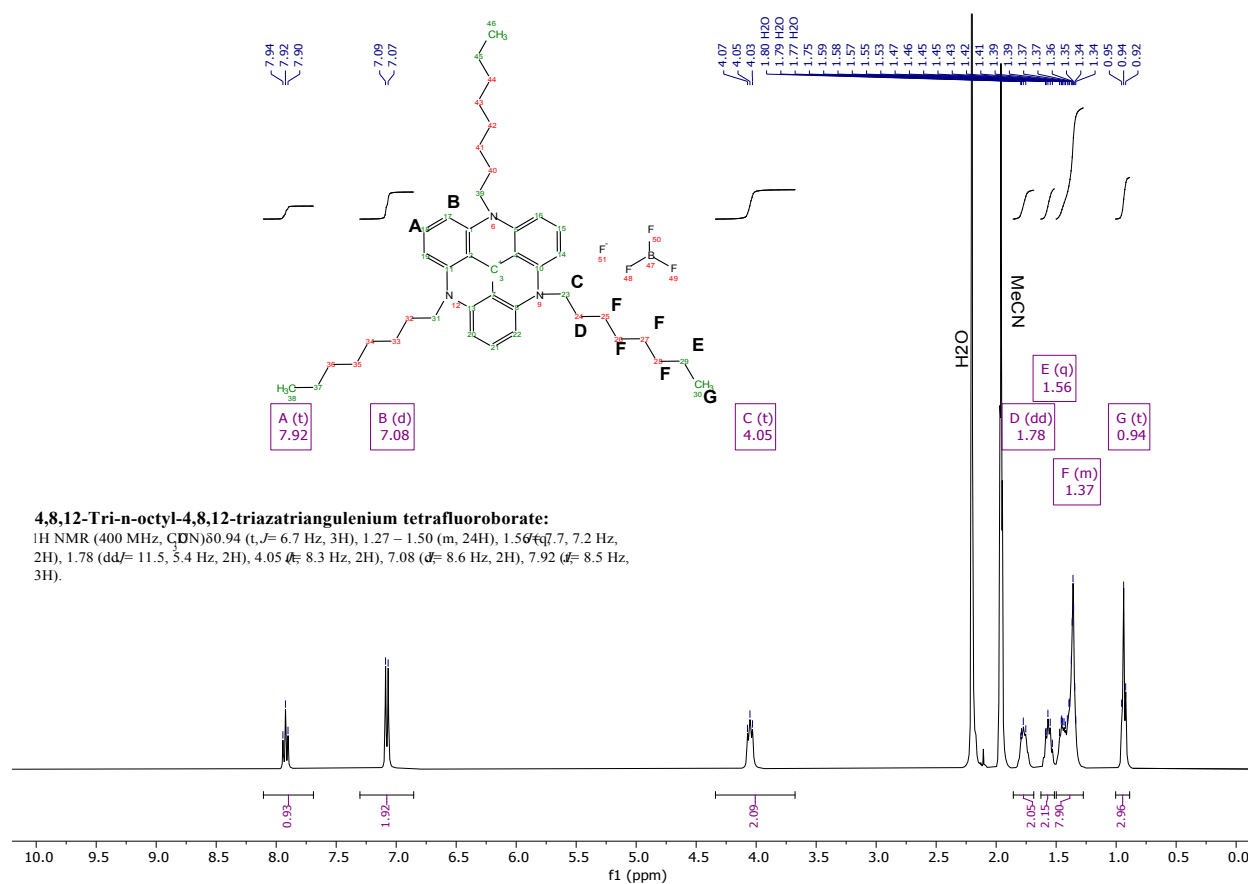

4,8,12-Tri-n-octyl-4,8,12-triazatriangulenium tetrafluoroborate:
1H NMR (400 MHz, CD$_3$CN) δ 0.94 (t, J = 6.7 Hz, 3H), 1.27 – 1.50 (m, 24H), 1.56 (q, J = 7.7, 7.2 Hz, 2H), 1.78 (dd, J = 11.5, 5.4 Hz, 2H), 4.05 (t, J = 8.3 Hz, 2H), 7.08 (d, J = 8.6 Hz, 2H), 7.92 (t, J = 8.5 Hz, 3H).

Figure S1 ^{1}H NMR spectrum of TATA–BF$_4$ in [D3]-MeCN
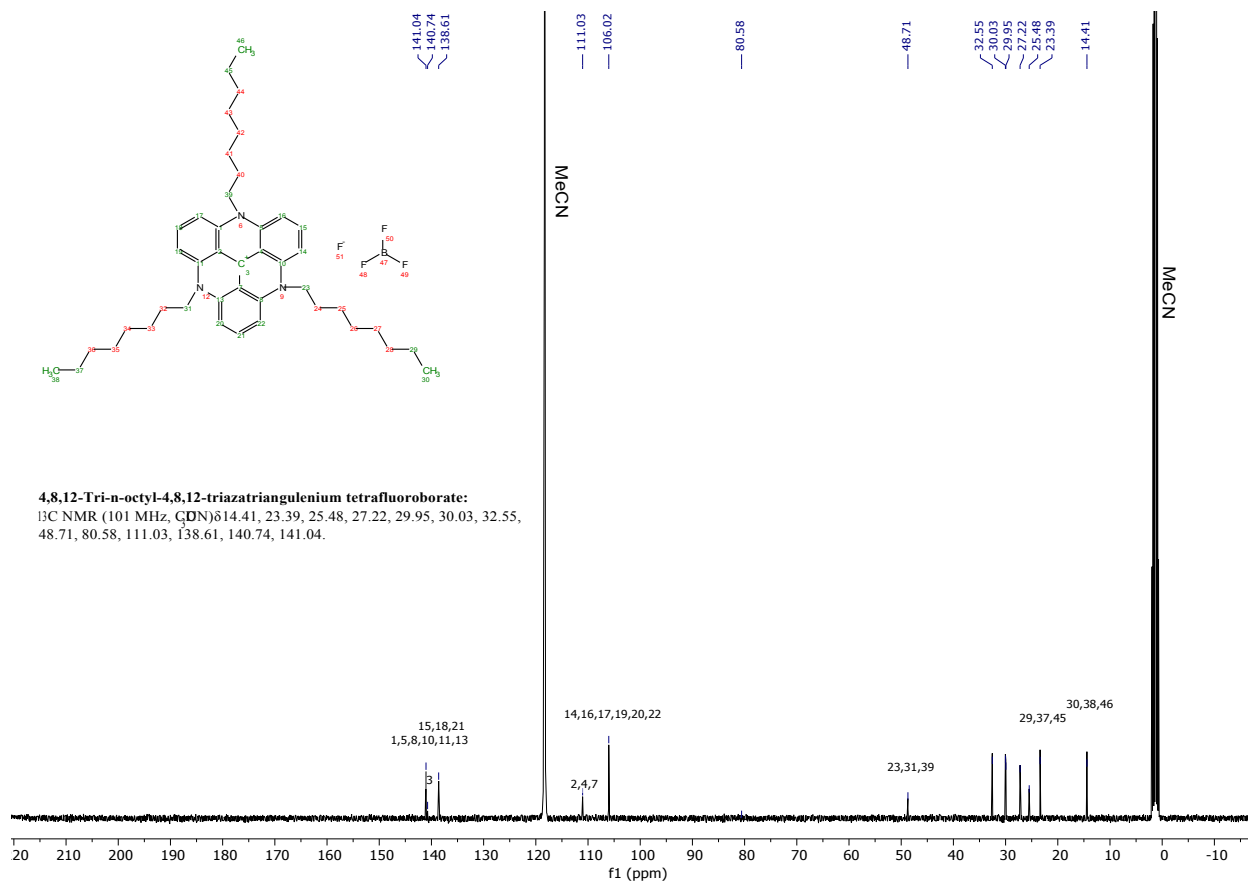
Figure S2 ^{13}C NMR spectrum of TATA−BF$_4$ in [D3]-MeCN.

4,8,12-Tri-n-octyl-4,8,12-triazatriangulenium tetrafluoroborate:
13C NMR (101 MHz, C$_3$DN) δ14.41, 23.39, 25.48, 27.22, 29.95, 30.03, 32.55, 48.71, 80.58, 111.03, 138.61, 140.74, 141.04.

The use of different solvents for SAM formation

Direct sample preparation by drop-casting and drying TATA solutions of either ethanol, chloroform or 1,2,4-trichlorobenzene on Au(111) surfaces did not result in SAM formation judged by STM. Warming the samples for 2h at 50°C after solvent evaporation resulted in SAM formation only for samples prepared from 1,2,4-trichlorobenzene, which then was used throughout the whole study. We conclude that a thermally driven diffusion process is essential for the SAM formation of the molecules with an extensive aromatic core and three alkyl-chain side groups.

Verification of the molecular position within a SAM

While measuring STM, different molecular orbitals (MO) can be probed by changing the tunneling parameters. In the case of a SAM of TATA−BF$_4$, a small change of the tunneling bias leads to a significant STM contrast modification

(**Figure S3a**). Initially, the SAM had a 2D pattern (**Figure S3a** bottom part) without the possibility to identify the position of the molecules, their orientation, and separation distance. When the bias is modified from 0.3 to 0.45 V, the 2D pattern changes to the one with well-separated quasi-round spots with a dark region inside (**Figure S3b**). Raising the bias further to the $U_t = 0.6$ V leads to the change of the spot shape from rounded to triangle-like (**Figure 3** in the main manuscript). Taking into account DFT calculations of the form of the MO of TATA–BF$_4$ on Au(111) (**Figure 6b**), each spot can be associated with the position of a single TATA platform.
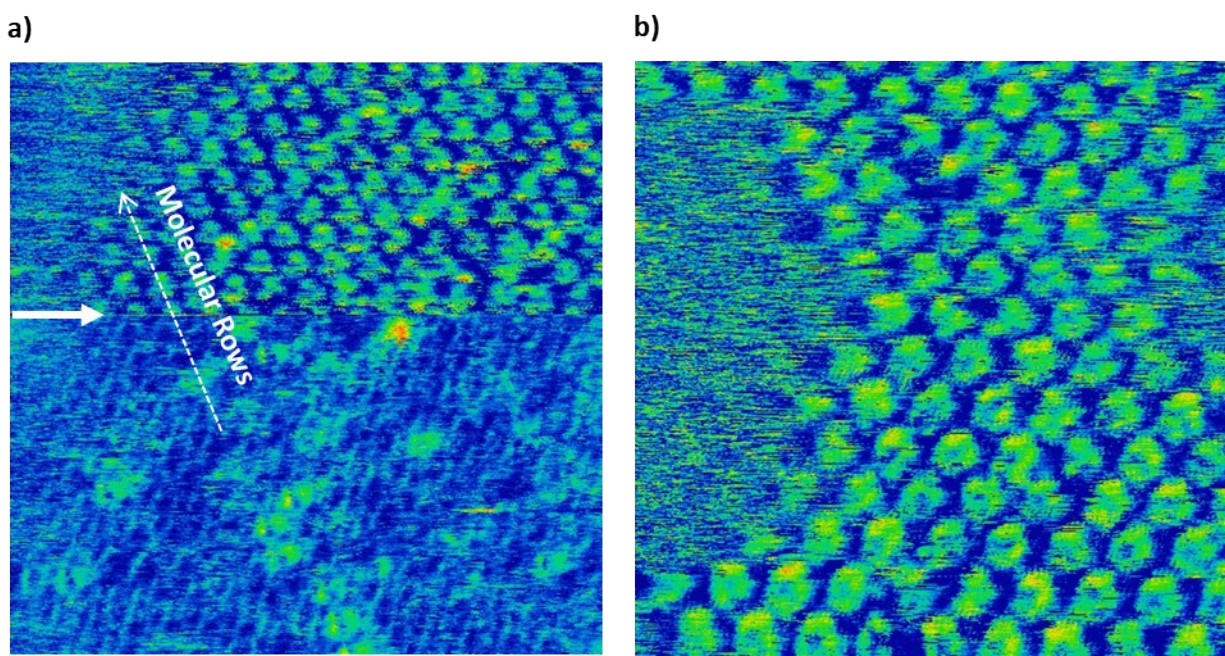

Figure S3. a) The lower part of the STM image (23×23 nm^2) is recorded using different tunneling parameters ($U_t = 0.3$ V, $I_t = 15$ pA) than for the upper part ($U_t = 0.45$ V, $I_t = 15$ pA); scan direction bottom to top. The white solid arrow in **a)** shows the position where the bias was intentionally switched. **b**) STM recorded image with higher magnification (7.7×7.7 nm^2) ($U_t = 0.45$ V, $I_t = 15$ pA).

2D-FFT analysis of the domains

In the STM image (**Figure S4)** four domains can be observed. The 2D-FFT analysis of each domain was made to verify the packing structure and molecular row orientation on the substrate. The analysis of the surface was performed for the

areas inside the black squares. The resulting 2D-FFT images contain the first order frequencies mainly (bright spots) that reflect the packing structure of each domain with a corresponding in-plane orientation of the rows.[2] Comparison of the 2D-FFT images revealed the coexistence of two pairs of equivalent patterns, suggesting that the analyzed domains in **Figure 4** have two types of molecular packing, namely α and β. The β domain has hexagonal packing, while the α has a slightly distorted hexagonal arrangement of the molecules.
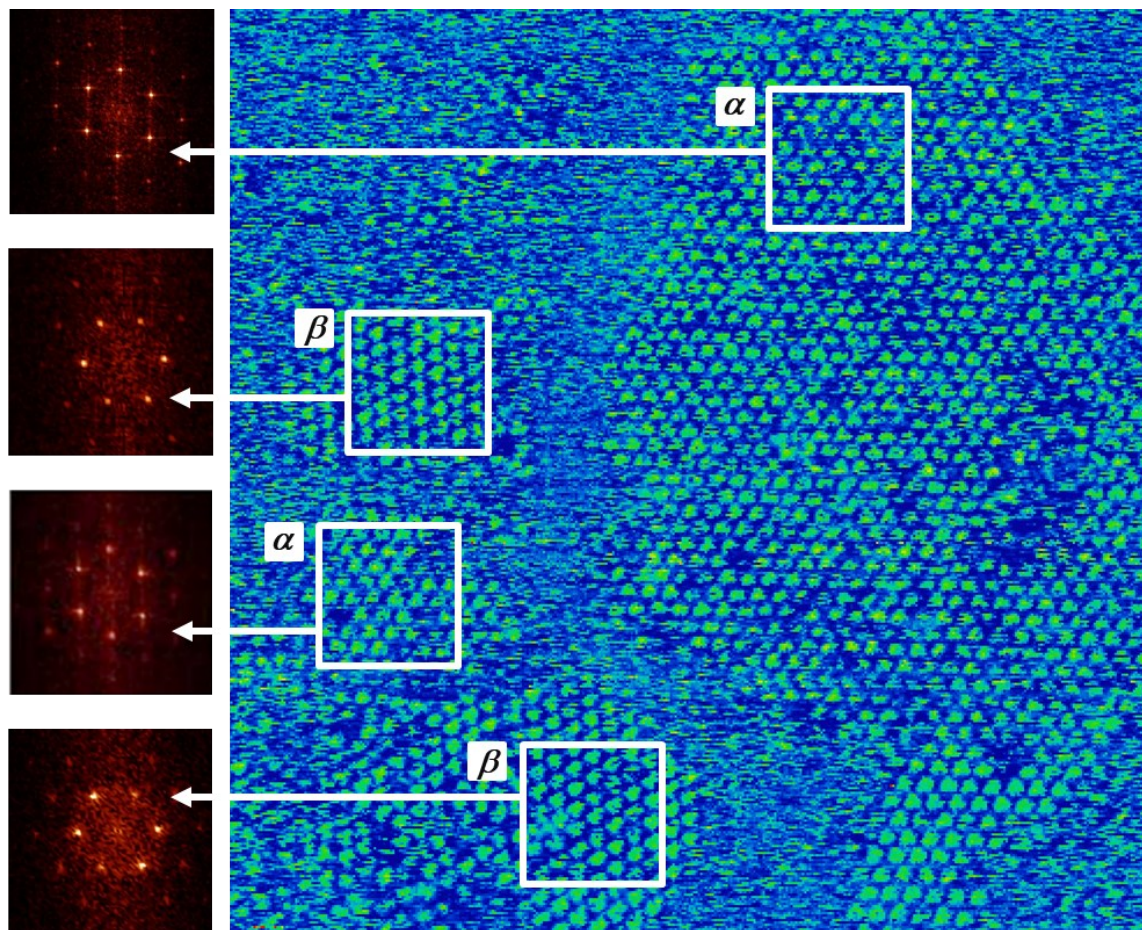

Figure S4. The STM image(60.8×60.8 nm²) of α and β domains with related 2D-FFT frequencies that display differences in packing of molecules in domain α (elongated hexagons) and β (normal hexagons). The STM parameters are Ut = 0.6 V, It = 20 pA.

STRUCTURE OF MOLECULAR PACKING

Defining the packing structures of the molecules within the α and β domains is currently possible only as a hypothesis since the STM studies do not allow to visualize the orientation of the alkyl chains of the molecules. However, on the basis of the orientation of the triangular-shaped STM contrast of the molecules within the domains (**Figure 3**) and using the measured distance between the molecules, we propose the following packing models, in which the structure of the TATA aromatic core is presented as a triangle (**Figure S6**). The ratio of the core size and alkyl chains is similar to the one in real chemical structure.

In both models, we adjusted the orientations of the alkyl chains to omit steric hindrance. Using this approach in the α domain, we orient one alkyl chain of each molecule in parallel to the alkyl chain of the neighboring molecule. In such geometry, the resulted packing has an elongated hexagonal structure in accordance with the experimental observations. Moreover, the parallel orientation of the alkyl chains can appear due to chain-chain interactions that can effectively drive the self-organization of liquid crystals.[3] In the β domain, all TATA platforms are separated from each other by the same distance (**Figure 3**). Therefore, we placed alkyl chains in the equivalent orientation to the platforms. With this packing structure, the intermolecular distance corresponds to the experimentally measured one without evident steric hindrance.
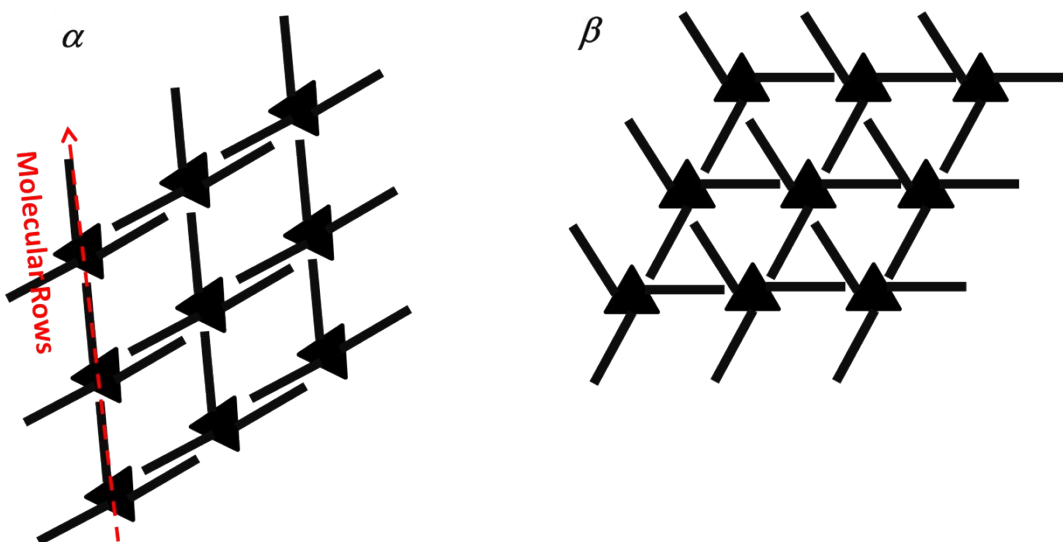

Figure S5. The structure of TATA packing in the domains α and β.

DOS CALCULATIONS

DFT calculations have been performed using the localized-orbital code Fireball.[4] In this approach, a self-consistent version of the Harris-Foulkes LDA functional[3,5] is used, instead of the traditional Kohn-Sham functional based on the electronic density. More details are given in Experimental section of the manuscript.

The structure of the isolated TATA–BF$_4$ molecule (**Figure S6**) has been optimized until the forces went below 0.1 eVÅ^{-1}.From the obtained equilibrium structure, we have determined the density of states (DOS).
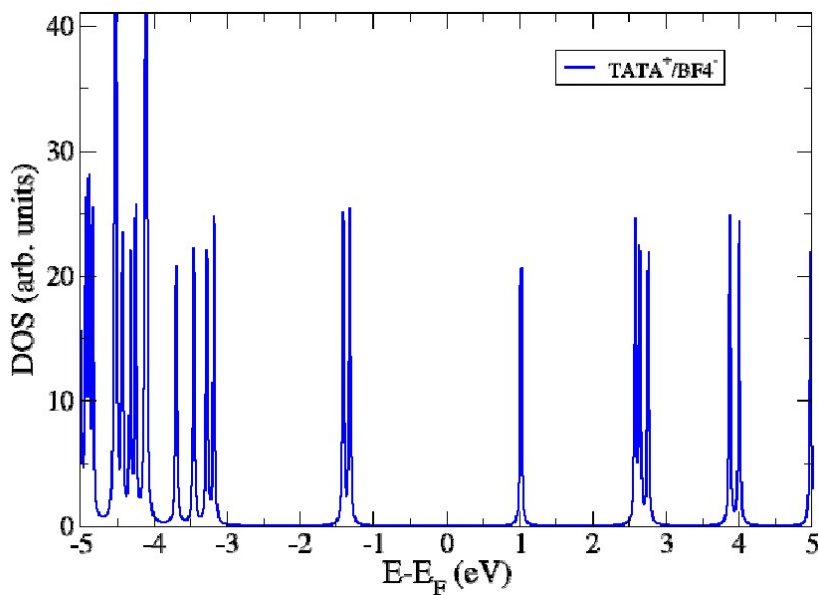

Figure S6. Calculated DOS of the isolated TATA–BF$_4$ molecule.

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