Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Material:
Two-dimensional soft supramolecular networks

Carlos-Andres Palma*[a], Artur Ciesielski*[b], Murat Anil Öner[a], Gaël Schaeffer[b], Jean-Marie Lehn[b], Johannes V. Barth[a] and Paolo Samorì*[b]

[a] Physik-Department E20, Technische Universität München, D-85748 Garching, Germany.

E-mail: c.a.palma@tum.de

[b] ISIS & icFRC, Université de Strasbourg & CNRS, 8 allée Gaspard Monge, 67000 Strasbourg, France.

E-mail : ciesielski@unistra.fr, samori@unistra.fr

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1. Scanning tunneling microscopy (STM)

STM measurements were carried out by using a Veeco scanning tunneling microscope (multimode Nanoscope III, Veeco) at the interface between highly oriented pyrolytic graphite (HOPG) and a supernatant solution. Diluted solutions of molecule **1** were applied to the basal plane of the surface. The STM tips were mechanically cut from a Pt/Ir wire (90/10, diameter 0.25 mm). The raw STM data are processed by the application of background flattening and the drift is corrected using the underlying graphite hexagonal lattice as a reference. The latter lattice is imaged underneath the molecules by lowering the bias voltage to 20 mV and raising the current to 65 pA. Molecule **1** was dissolved in dimethyl sulfoxide (DMSO) to afford a 3mM solution and diluted with 1,2,4-trichlorobenzene (TCB) to give 30±1 μM and 5±1 μM TCB solutions with <1% volume in DMSO. Monolayer pattern formation was achieved by applying 4μL of a warm (30-40ºC) solution onto freshly cleaved HOPG. The same protocol was applied to molecule **2**. **Figures S1a** and **S1b** depict STM constant height images of **2** and **1** respectively.

In the range of concentrations that were investigated for **1** (44, 4.4 and 0.4 μM), a concentration of 0.4±0.1 μM afforded a polymorphic tight-packed pattern in coexistence with the honeycomb pattern. **Figure S2** depicts the second polymorph structure along side the previously crystalline honeycomb domain. The tight-packed oblique lattice features an unit cell a = (7.2 ± 0.2) nm, b = (2.6 ± 0.2) nm and α = (58 ± 3)°, corresponding to an area A = (15.87 ± 0.79) nm^2, where each unit cell contains two molecules **1.**

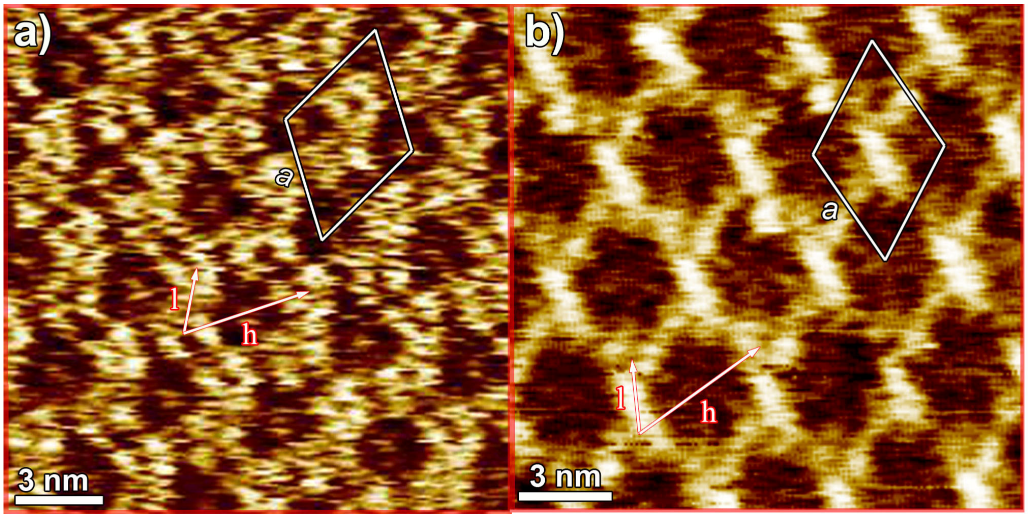


Figure S1. STM constant current data comparison between **a)** self-assembled soft-matter network of **2** and **b)** of **1**. I_t = 5 pA, V_t = 350 mV.

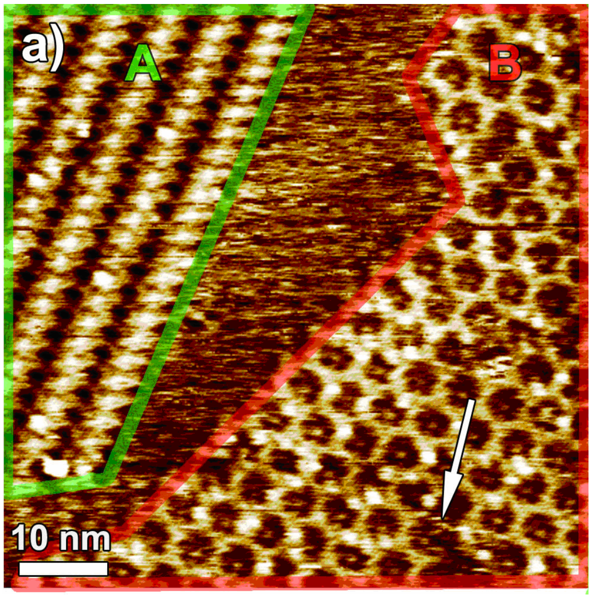


Figure S2. STM constant current data of polymorphism observed in the self-assembled soft network of **1**. I_t = 5 pA, V_t = 350 mV. Arrow indicates open pore.

2. Molecular Dynamics (MD)

All simulations were performed with the general force field MMFF [1] as implemented in the package CHARMM 36b1 [2]. Details about the different calculation setups are given in the following sub-sections. Explicit graphene was setup as described elsewhere [3] which has been shown to describe very well adsorption energies of polyaromatics unto HOPG substrates. Before the MD simulations, it is important to diagnose the molecular force field used in the parameterization of **1**. We do this by comparing the energies of dissociation of the H-bonds in the MMFF parameterization and in the DFT B3LYP/6-311G++(d,p) level of theory (see below). We treat non-bonded interactions in the CHARMM-program as follows: NBONDS ELEC ATOM RDIE SHIFT VDW VATOM VSHIFT CUTNB 26. Notice that a distance dependent r-dielectric (RDIE) was used in every energy computation. A Langevin thermostat with friction coefficient 1 ps^{-1} was employed in all simulations. An integration timestep of 0.002 ps with SHAKE BONH was employed for the simulation of STM footprints and 0.007 ps with SHAKE BOND (and hydrogen mass of 7 a.m.u.) for the dissociation simulations. For the simulation of the STM footprints periodic boundary conditions and an implicit substrate were used (see below).

3. Density functional theory (DFT)

Density Functional Theory calculations were performed with the commercial package Gaussian 03. Calculated ΔE for conformational change and association energies (ΔE) in vacuum were performed at the B3LYP/6-311G++(d,p) level of approximation on optimized geometries. When minimizing molecular geometries through DFT B3LYP/6-311G++(d,p) level of theory without the presence of a substrate, we find four hydrogen bonds with an energy of interaction of -23 kcal mol^{-1} for the dimer in **Fig. 2b** and two hydrogen bonds with an energy of -13 kcal mol^{-1} for the dimer in **Fig. 2a**. This data has not been corrected for the basis set superposition error typical of atom-centered basis sets, but stands as a good approximation for relative energy differences between two dimers with similar structural overlap. When considering the absolute DFT energy between **Fig. 2a** and **Fig. 2b**, the dimer in **Fig. 2b** is only favored by 0.4 kcal mol^{-1}. This is partly due to the highly strained CO-NHR bond in the *cis* conformer (**Fig. S3**). The result explains the very similar stability of both conformations and, again, points out to a reasonable parameterization in the MMFF force field.

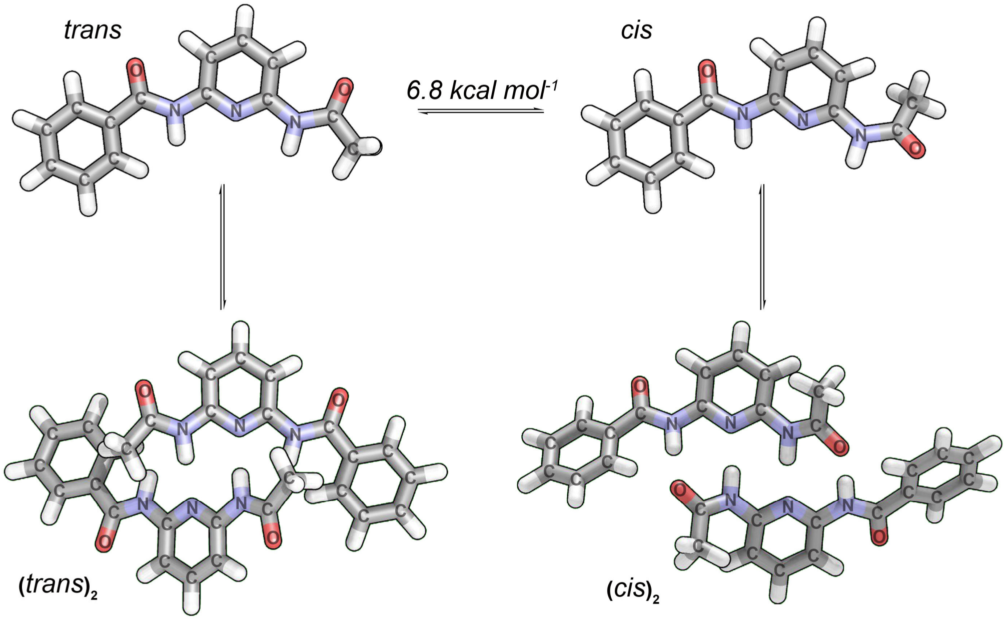


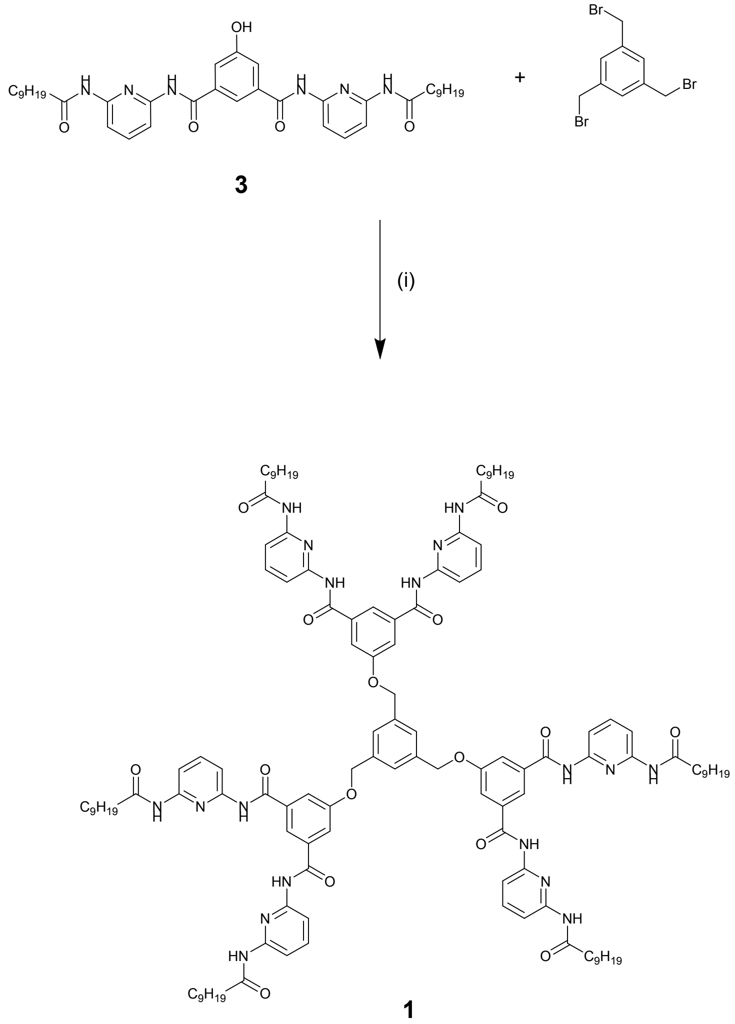
Figure S3. Self-association of two acetamido terminal groups in the *trans* and *cis* conformation (around CO-NHR bond) *via* two and four strong H-bonds, respectively. The calculated ΔE for conformational changes in vacuum using B3LYP/6-311G++(d,p) level of approximation on optimized geometries is shown.

4. Tunneling current time average patterns (TC-TAP)

Simulation of STM images proceeded through averaging 1000 snapshots of the MD simulations, each snapshot corresponding to 20 ps of molecular dynamics simulation time. The factor $\langle \beta(x,y)\cdot z \rangle$ was obtained by multiplying the MMFF polarizable atomic radii by the corresponding β factor for aromatic or non-aromatic atoms (main text). For overlapping atomic radii, the $\langle \beta(x,y)\cdot z \rangle$ factor is added together. The simulation is set up to reproduce a crystalline pattern of **1** through periodic boundary conditions. An eight-molecule unit cell is constructed and minimized. Due to the arbitrary size of the substrate super cell which can be made commensurable with the molecular unit cell, we chose to perform minimization with periodic boundaries with only an implicit substrate, after which the best-fit rectangular unit cell is found to be a= 87Å, b= 76Å. The primitive unit cell of this assembly is found to be a = 4.4 nm , (a,b) = 60°; i.e. a featuring a 10% discrepancy with the experimental unit cell. (See main text **Figure 2i**). The implicit harmonic 2D potential was implemented through the CHARMM command: GEO PLAN ZDIR 1 FORCE 0.001 DROF 0 SELECT ALL END.

5 . Methods and Synthesis

All commercially available products were used without further purification. Flash chromatography was performed using silica gel (Geduran, SI60, 40-63 µm, Merck). All the reactions were carried out under inert atmosphere. 400 MHz ^{1}H NMR and 100 MHz ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. ES mass spectrometric measurements were performed by the Service de Spectrométrie de Masse, ISIS, UDS. The synthesis of **2** has been described previously.[4]



(i) K_2CO_3, DMF, 50 °C, 3 days

Figure S4: Synthesis of **1**

5,5',5''-(benzene-1,3,5-triyltris(methylene))tris(oxy)tris(*N*1,*N*3-bis(6-decanamidopyridin-2-yl)isophthalamide) **2**:

Compound **3** was prepared using a procedure developed previously in our group.[5] A mixture of **3** (100 mg, 0.15 mmol, 5 eq.), K_2CO_3 (20 mg, 0.15 mmol, 5 eq.) and 1,3,5- tris(bromomethyl)benzene (10.6 mg, 0.03 mmol, 1 eq.) in 5 mL of anhydrous DMF was left to stir at 50 °C for 3 days. After evaporation of the majority of the solvent, 10 mL of ethyl acetate and 10 mL of water were added. The organic phase was dried over $MgSO_4$, filtered, evaporated to dryness and purified by column chromatography (SiO_2, AcOEt/CH_2Cl_2 1:9) to afford **1** as a white powder (19 mg, 30 %). ^{1}H NMR (400 MHz, DMSO-d_6) : δ = 10.48 (s, 6H), 10.06 (s, 6H), 8.16 (s, 3H), 7.80 (m, 24H), 7.66 (s, 3H), 5.38 (s, 6H), 2.37 (m, 12H), 1.56 (m, 12H), 1.23 (m, 72H), 0.83 (m, 18H). ^{13}C NMR (400 MHz, DMSO-d_6) : δ = 172.08, 164.73, 158.33, 150.47, 149.95, 139.90, 137.31, 135.56, 131.38, 128.72, 117.48, 110.28, 109.87, 65.54, 36.03, 31.18, 28.79, 28.71, 28.59, 24.89, 22.22, 13.83 HRMS (ESI): *m/z* $[M+H]^+$: 2132,2602; calculated for $[C_{123}H_{162}N_{18}O_{15}+H]$: 2132,264.

6 . References

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