A self assembled molecular zipper based on a perfluorophenyl-phenyl diacetylene motif

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The synthesis and characterization of a molecular rod consisting of a pentafluorophenyl and a *para*-dodecylphenyl subunit linked by a diacetylene and its large area self assembly into perfect parallel lines consisting of interlocked molecular rods are reported and discussed.

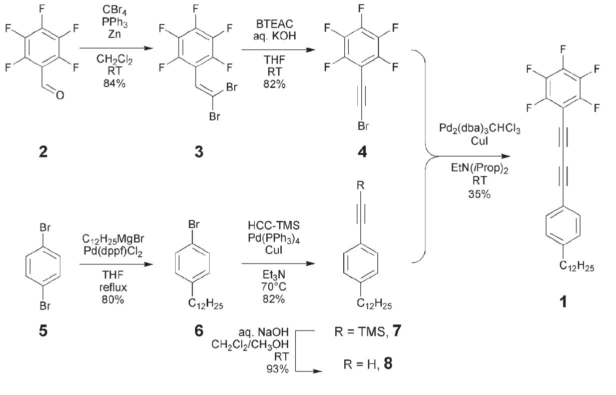
Perfluorophenyl and phenyl substituted diacetylenes attracted our attention as the first reported example of a supramolecular stacked diacetylene was said to result in a *cis*-polybutadiyne upon photopolymerization in the solid state.[1] The π–π stacking interaction between benzene and hexafluorobenzene has already been reported in 1960 by Patrick and Prosser.[2] The supramolecular synthon has meanwhile been investigated in detail and has been applied successfully in crystal engineering,[3] topochemistry[4] and even to preorganize reactants.[5] Furthermore, the synthon allowed the tuning of the material properties of liquid crystals,[6] polymers,[6] hydrogels[7] and even biomolecules like DNA duplexes.[8] To investigate the properties of the supramolecular synthon on the surface, we further functionalized a 1-pentafluorophenyl-4-phenylbutadiyne rod with a dodecyl alkyl chain to increase solubility, processability and also surface packing properties.

Here we report the synthesis and the self assembly properties on a graphite (HOPG) surface of the molecular rod **1**, consisting of a diacetylene linked pentafluorophenyl and *para*-dodecylphenyl subunit.

As displayed in Scheme 1, the synthesis of **1** is based on a Cadiot–Chodkiewicz[9] coupling between the bromoacetylene **4** and the acetylene **8**.† Starting from commercial pentafluorobenzaldehyde **2**, a Corey–Fuchs[10] reaction sequence gave the bromoacetylene **4** in good yield. To assemble **8**, 1,4-dibromobenzene **5** was first functionalized with a dodecyl chain in a Grignard reaction to afford **6**. A subsequent Sonogashira reaction[11] gave the trimethylsilyl (TMS)-protected acetylene **7**, which was deprotected to afford **8** in good yield. A Pd/Cu catalyzed variation[12] of the Cadiot–Chodkiewicz coupling in *N*-ethyldiisopropylamine at room temperature gave the desired rod **1** in 35% yield, after column chromatography, as a white solid.† All compounds have been characterized by ^{1}H-NMR and ^{13}C-NMR spectroscopy, electron impact mass spectroscopy and elemental analysis.

To investigate the self assembly properties of **1** on HOPG, a droplet of solution **1** (concentration near saturation) in phenyloctane was applied to a freshly cleaved HOPG surface. Subsequent investigation of the surface by STM displayed perfectly ordered parallel stripes consisting of alternating bright and dark regions covering the whole observed surface. To demonstrate the extent of the surface structuring effect, Fig. 1 displays a typical 210 × 210 nm large area completely covered with the stripe pattern.

The dimensions of the observed stripes are a width of about 19 Å for the brighter ribbons and 12 Å for the darker lines clearly in the range of the size of the molecules. The first hypothesis was the formation of stripes due to the aryl-perfluoroaryl stacking synthon. However, higher resolution of the STM pictures enabled a closer inspection of the self assembly properties of **1** on the graphite surface. As displayed in Fig. 2, the bright ribbons consist of dumbbell shaped bright spots with the size of the rigid molecular rod substructure of **1**. These dumbbell structures consist of a brighter outside unit and a less intense inside unit. These inside units interlock like a zipper and combine two rows of dumbbell structures to form the bright ribbons. The periodicity of the structure has been measured along the white line in Fig. 2. Calibration with the underlaying graphite gave a periodic distance between two bright spots of 10.6 Å. The spacing is much too large to explain the self assembly pattern with an aryl-perfluoroaryl stacking synthon, which displays a spacing in the solid state of about 3.7 Å.[1] The relatively large spacing between two dumbbell structures rather points at a flat arrangement of the rigid rod on the graphite substrate. As fluor-atoms are known to appear less visible in an STM experiment,[13] the less intense center parts of the self assembled ribbons consist of the pentafluoroaryl subunits.



Scheme 1 Synthesis of the molecular rod **1**.

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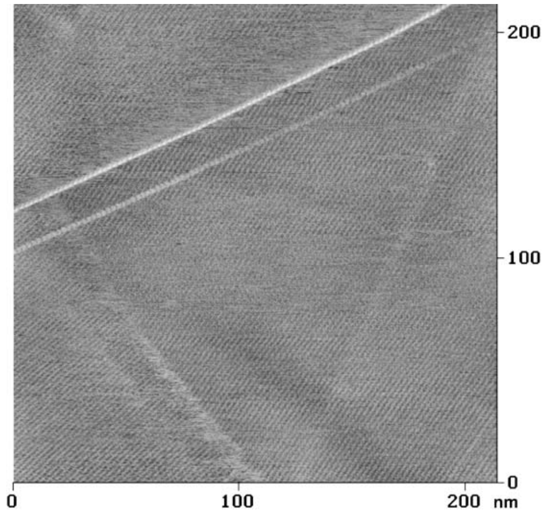

Fig. 1 Pattern of parallel stripes on an HOPG surface covered with **1**.

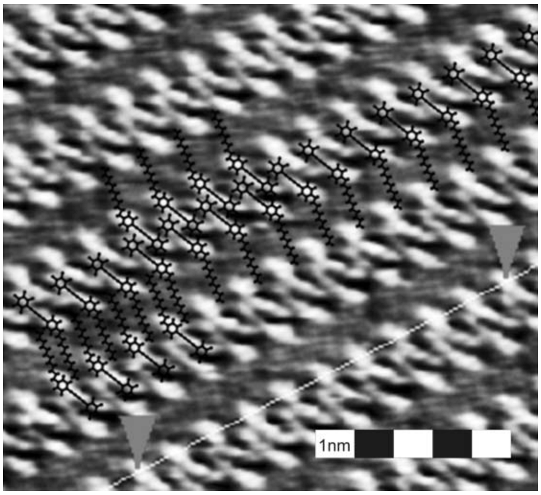

Fig. 2 STM image of the self assembled ribbons consisting of **1**. A model of the molecular structure of **1** is overlaid to illustrate the packing.

A model of the molecular rod **1** has been overlayed onto the STM image (Fig. 2). The excellent fit between the STM picture and the molecular model further confirms and illustrates the self assembled molecule as the origin of the surface pattern. Obviously the dark regions separating two parallel bright ribbons by about 12 Å are due to the intercalating dodecyl chains. However, the STM picture does not allow individual dodecyl chains to be resolved and hence, two arrangements differing in the direction of the kink between the rod and the dodecyl chain are possible. The perfectly parallel aligned dodecyl chains favour the packing displayed in Fig. 2. To our surprise, neither the aryl-perfluoroaryl stacking synthon nor C–H···F hydrogen bonds[3e,14] are dominating the self assembly of **1** on the HOPG surface. The dense arrangement of the pentafluoroaryl subunits in the centre of the bright ribbon rather support F···F interactions together with C–F···π interactions as potential intermolecular forces. Furthermore the packing suggests a stabilizing interaction between the electronegative fluorine atoms and the electron rich diethynyl linkers.

In conclusion we have synthesized a pentafluorophenyl and phenyl substituted diacetylene with an additional dodecyl chain to investigate self assembly properties on surfaces. Upon wet deposition on HOPG, huge areas of perfectly ordered patterns of parallel bright stripes are observed. A closer inspection of the structure unravels a zipper like interlocked pattern of the molecular rod as the origin of the bright stripes. The intercalating dodecyl chain results in the separate dark regions between the bright stripes. Packing parameters leading to the surface patterns are supported by intermolecular interactions, in particular of the pentafluorophenyl and diacetylene subunits and of the alkyl chains.

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Notes and references

† Bromoacetylene **4** (0.7 g; 2.6 mmol), acetylene **8** (0.7 g; 2.6 mmol), $Pd_2(dba)_3CHCl_3$ (0.08 g; 0.08 mmol; 3 mol%), CuI (0.02 g; 0.1 mmol; 4 mol%) and *N*-ethyldiisopropylamine (0.5 ml) in toluene (25 ml) was degassed with nitrogen and stirred at room temperature for 10 hours. After evaporation of the solvent, column chromatography on SiO_2 with hexane as the eluent gave 1-pentafluorophenyl-4-(4′-dodecylphenyl)butadiyne **1** (0.42 g; 0.91 mmol; 35%) as a white solid. Mp: 38 °C. ^1H NMR ($CDCl_3$) δ_H: 0.94 (t, 3H), 1.31 (br, 18H), 1.35 (m, 2H), 1.66 (q, 2H), 2.67 (t, 2H), 7.20 (d, 2H), 7.49 (d, 2H). ^{13}C NMR ($CDCl_3$) δ_C: 14.00, 22.72, 29.31, 29.40, 29.50, 29.62, 29.69 (br), 29.72, 31.08, 31.98, 36.10, 64.27 (q, J = 4.0 Hz), 72.30, 85.63, 85.82 (q, J = 3.2 Hz), 99.60 (td, J = 17.8 Hz, J = 4.0 Hz), 117.88, 128.67, 132.67, 137.75 (dm (doublet of multiplet), J = 255 Hz), 142.00 (dm, J = 255 Hz), 145.69, 148.30 (dm, J = 255 Hz). EI-MS *m*/*z* 460.3 [M^+]. Anal. calcd for $C_{28}H_{29}F_5$: C, 73.03; H, 6.35. Found: C, 73.14; H, 6.07%.

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