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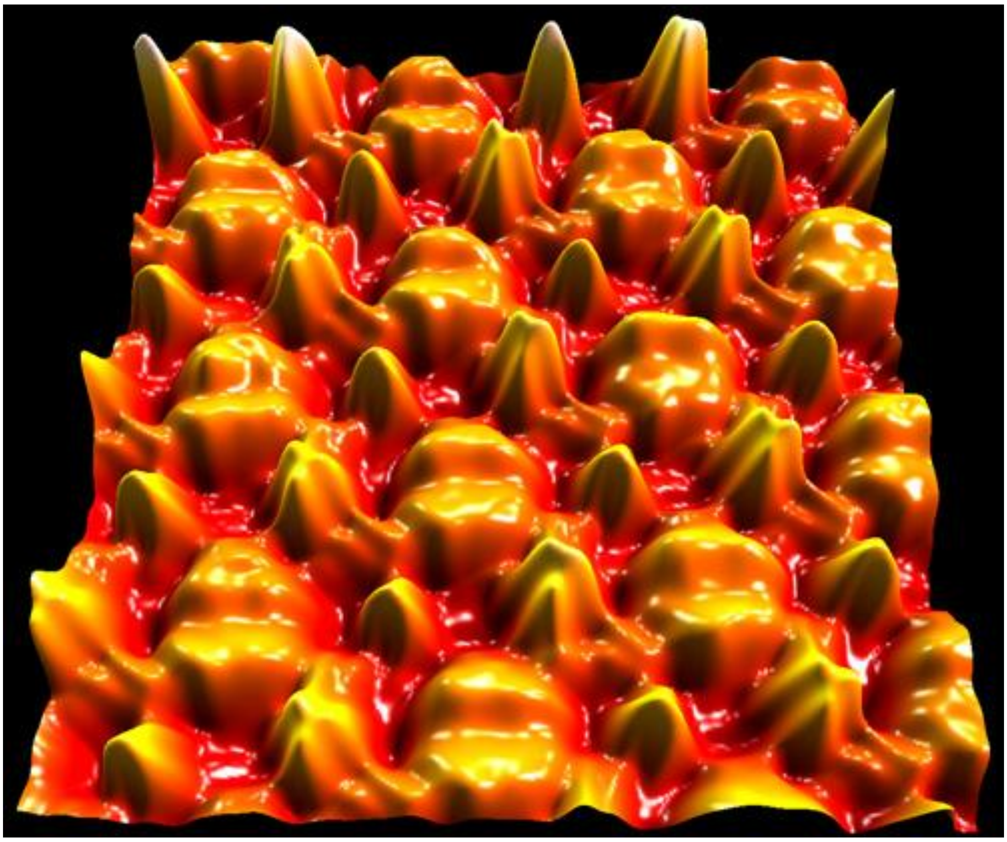

ChemComm

Cite this: *Chem. Commun.*, 2011, **47**, 9333–9335

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COMMUNICATION

On the transfer of cooperative self-assembled π-conjugated fibrils to a gold substrate†‡

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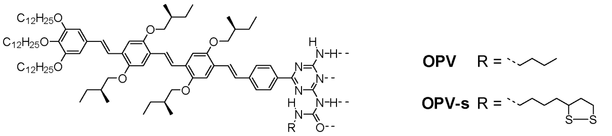
Received 12th May 2011, Accepted 30th June 2011

DOI: 10.1039/c1cc12799c

The transfer of the cooperative self-assembled fibrils to a gold substrate has been studied by means of scanning probe microscopy techniques revealing the crucial role of the early formation of a monolayer.

The development of plastic electronics as an alternative to the common silicon based electronic circuitry is currently receiving much attention, where the first applications have become commercially available.[1] This impressive progress has stimulated the fabrication of electronic devices in the nanometer range by using self-assembled structures consisting of π-conjugated oligomers, a research area generally referred to as nanosized or supramolecular electronics.[2] In solution, examples about the self-assembly of π-conjugated molecules are ubiquitous,[3] however, reports dealing with functional devices are scarce.[1,4–6] Especially transferring self-assembled fibrils from the solution to device-relevant substrates such as gold or SiO_2 while retaining the self-assembled structure limits the development of nanoelectronics. This process is shown to be a delicate balance between the solvent, surface and deposition technique.[7–9] In the past, we have shown the disruptive influence of gold on the deposition of π-conjugated self-assembled oligo(*p*-phenylenevinylene) (**OPV**, Scheme 1) fibers on the surface.[8] Recently, the groups of Müllen and Fichou have reported on the utilization of the gold–sulfur bond to prepare highly stable nanocolumns of self-assembled hexa-*peri*hexabenzocoronenes equipped with a thiol unit on a gold surface in which the orientation of the molecules could be directed.[10] Hence this approach could be a promising method to obtain stable self-assembled fibers of π-conjugated oligomers on a gold surface which are otherwise disrupted.



Scheme 1 Molecular structures of **OPV** and **OPV–s**.

In the past, we have reported on the self-assembly of chiral **OPV** derivatives bearing the self-complementary quadruple hydrogen bonding ureidotriazine unit. In chlorinated solvents like chloroform and 1,2,4-trichlorobenzene (TCB) an equilibrium exists between monomers and their hydrogen-bonded dimers (**OPV**, Scheme 1).[8] In alkane solvents, such as methylcyclohexane (MCH), the hydrogen-bonded dimers are self-assembled into helical fibrils according to the cooperative mechanism.[11] The helical handedness of the assembly is biased by the enantiomeric purity of the side tails that are attached to the **OPV** chromophore.[3] The presence of fibril-like assemblies has been observed, which are visualized on the surface with Atomic Force Microscopy (AFM) after dropcasting a dilute alkane solution onto highly ordered pyrolytic graphite (HOPG).[8,11] Remarkably, the π-conjugated fibrils were destroyed on a gold surface.[8]

In this report, we aim to transfer the supramolecular fibrils from the solution to a gold surface in such a manner that the one-dimensional fibrillar structure is maintained. For this reason, we have equipped an oligo(*p*-phenylene vinylene) ureidotriazine oligomer (**OPV**, Fig. 1) with a dithiol bridge (**OPV–s**, Scheme 1). We show that the structure of the self-assembled fibrils formed by **OPV–s** on gold is maintained. Interestingly, the presence of a monolayer on a gold substrate has been revealed which is shown to be the crucial factor for retaining the fibrillar nature of the assemblies on the gold surface.

While the synthesis of **OPV** has been described,[8] the synthesis of **OPV–s** is described in the ESI.‡ Similar chemical shifts in ^{1}H-NMR for **OPV–s** are observed when compared to **OPV**,

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† This article is part of the *ChemComm* 'Molecule-based surface chemistry' web themed issue.

‡ Electronic supplementary information (ESI) available: Synthesis, CD Spectra, AFM data. See DOI: 10.1039/c1cc12799c

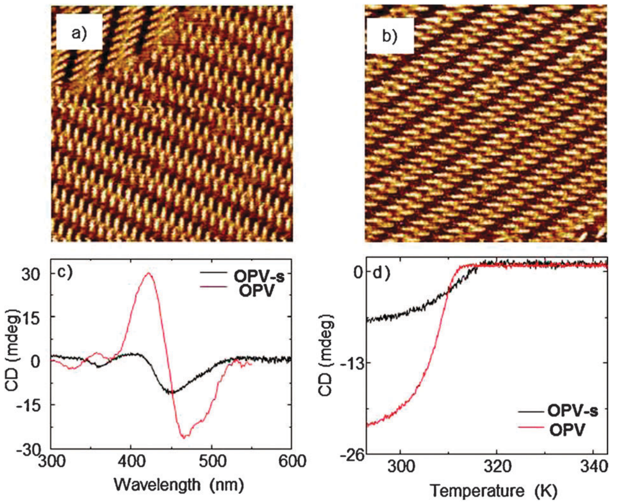

Fig. 1 STM images of **OPV** (a) and **OPV–s** (b) on HOPG in TCB, scan sizes are 42.3 × 42.3 nm^2 and 31.2 × 31.2 nm^2, respectively (I_{set} = 39 pA; V_{set} = −680 mV and I_{set} = 33 pA; V_{set} = −480 mV, respectively). (c) CD spectroscopy of a MCH solution of **OPV** (red) and **OPV–s** (black) (c = 1 × 10^{-5} M, T = 298 K). (d) Temperature-dependent CD measurements of **OPV** (red) and **OPV–s** (black) (c = 1 × 10^{-5} M, $\Delta T/\Delta t$ = −60 K h^{-1}, λ = 460 nm).

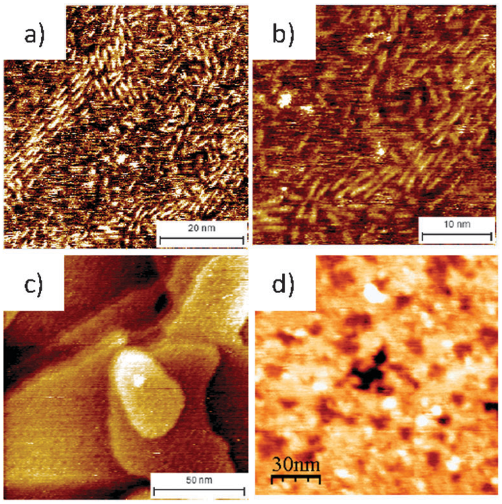

Fig. 2 STM images of **OPV** (a, b) and **OPV–s** (c) on gold in TCB, where (b) is an enlargement of (a) (I_{set} = 161 pA; V_{set} = −412 mV and I_{set} = 67 pA; V_{set} = −520 mV, respectively). (d) FM-AFM image of a monolayer of **OPV–s** on a gold substrate.

thereby showing the ability to form hydrogen-bonded dimers in chloroform. Also in the case of monolayer formation from TCB as studied with Scanning Tunneling Microscopy (STM) at the liquid/solid (HOPG) interface similar results for **OPV** and **OPV–s** have been revealed (Fig. 1a and b). For both molecules, the formation of highly organized monolayers on HOPG is observed, where the images show the presence of hydrogen-bonded dimers that are arranged with the π-conjugated plane of the molecules parallel to the surface while following the three-fold symmetry axis of HOPG. Next the self-assembly of **OPV–s** in MCH is investigated with circular dichroism (CD) and UV/Vis spectroscopy and compared to **OPV**. **OPV–s** assembles into preferential left-handed helical structures, similar to the previously reported **OPV**. However, the lower CD intensity and shape indicate that the packing of **OPV–s** in the self-assembled fibril is different with respect to **OPV**. The non-sigmoidal shape of the temperature-dependent CD curves indicates a cooperative self-assembly mechanism, implying an equilibrium between supramolecular fibrils and monomers only.[11] These **OPV–s** and **OPV** fibrils are successfully transferred to a HOPG surface (ESI‡). Hence, the self-assembly characteristics in solution, as well as monolayer formation and transfer of the supramolecular fibrils on a HOPG substrate, are largely unaffected by the sulfur functionality.

As mentioned above, in the past the self-assembled structures of **OPV** could not be observed on a gold substrate.[8] In sharp contrast, dropcasting **OPV–s** from a MCH solution on a gold substrate, followed by slow evaporation of the solvent in a saturated MCH atmosphere, leads to the formation of thick fibril-like assemblies composed of a multitude of single stacks (see ESI‡). This result shows the important role of the sulfur moiety in retaining the fibrillar nature of the assemblies on the gold surface.

In order to shed light on the different behaviour of **OPV** and **OPV–s** we have carried out a detailed analysis of the self-assembly behaviour of the two compounds on a gold surface by scanning probe techniques. In order to elucidate the possibility of monolayer formation on the gold surface by **OPV** and **OPV–s** we performed STM measurements using TCB as the solvent. The presence of a monolayer on a gold substrate has been revealed for **OPV** where the molecules are adsorbed as hydrogen bonded dimers and it has been showed that the molecules are arranged parallel to the substrate (Fig. 2a and b). These results are analogous to the results obtained on HOPG (Fig. 1a), except for some lower degree of ordering. In the case of **OPV–s** the STM results do not show any well-organized **OPV** molecules at all on the surface and thus prove to be inconclusive for the formation of a monolayer on the gold terraces (Fig. 2c). Instead, we employ Frequency Modulation AFM (FM-AFM) in ultra-high vacuum to confirm the presence of the monolayer.[12] In this case the monolayer has been prepared by dropcasting a chloroform solution on a gold substrate after which the solvent is evaporated. Features having a height of ~1 nm can be observed. This height corresponds to the width of the molecules (1.0 nm), and therefore it can be concluded that the molecules are forming a monolayer where the molecules are standing upright on the surface (Fig. 2d). Furthermore, the image shows objects of 50 nm in diameter, where a zoom in on these structures reveals that they consist of clusters of single molecules that are either directly on top of the gold surface or are present on the monolayer of the **OPV–s** molecules (see ESI‡). Although the FM-AFM measurements reveal the presence of a monolayer, the molecules are not as clearly visualized by the STM as in the case of **OPV** on gold. This could be the result of a different orientation of the molecules with respect to the surface resulting from the gold–sulfur attachment.

Since the STM and the FM-AFM results show that the molecules form a monolayer on gold, the next step is to analyze if this monolayer is crucial for fibril formation and/or transfer. Therefore, monolayer formation is achieved by treating the surface with a solution of **OPV** or **OPV–s** prior to dropcasting the solution containing the self-assembled structures of either **OPV** or **OPV–s** (Fig. 3). Dropcasting a chloroform solution of **OPV–s** (c = 1 × 10^{-5} M) on the substrate is followed by

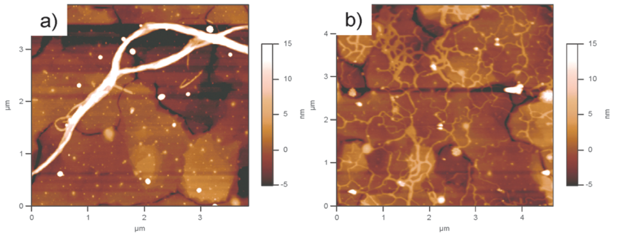

Fig. 3 TM-AFM images on a gold substrate after dropcasting a MCH solution of either **OPV–s** (a) or **OPV** (b) on a substrate having a monolayer of **OPV–s**.

evaporation of the solvent to yield the monolayers. Subsequently the supramolecular assemblies have been transferred to the surface by dropcasting the MCH solution. Irrespective of the underlying monolayer, the TM-AFM images show in all cases the presence of self-assembled fibrils on the surface. However, the morphology differs for the two systems at hand, where micrometer sized thick bundles of fibrils are observed for **OPV–s**, **OPV** yields much shorter fibril-like structures that are less high (Fig. 3a *versus* 3b). These results show that the presence of a monolayer is crucial for retaining the fibrils at the surface, while the orientation of the molecules in the monolayer seems to be less important (see ESI‡).

In order to establish the strength of the monolayers formed by either **OPV** or **OPV–s**, the surface containing the monolayer was placed back in chloroform for either 10, 20 or 30 seconds and dried. Subsequently a MCH solution having self-assembled structures of **OPV** is dropcast to transfer the self-assembled structures on the surface. Irrespective of the residence time in chloroform, fibril-like assemblies are observed when the monolayer consists of **OPV–s**. However, when the **OPV** monolayer is used, already 10 seconds submerged in a chloroform solution is enough to remove the **OPV** monolayer to such an extent that fibril formation is severely hampered (ESI‡). The removal of this monolayer has been confirmed by FM-AFM. This shows that the stability of the **OPV–s** monolayer is significantly enhanced with respect to the **OPV** monolayer.

Based on these results, we propose the following mechanism for the deposition of the fibrils on a gold surface (Fig. 4). Due to the cooperative nature of the self-assembly process an equilibrium between supramolecular fibrils and monomers exists in solution. It is likely that the stronger interaction of the **OPV–s** monomers with the gold surface leads to a faster formation of a stable monolayer, thereby counteracting the destructive influence of gold for the fibers, while monolayer formation is probably too slow for **OPV** monomers.

In conclusion we have shown that the presence of a monolayer can be a crucial factor for retaining the solution morphology and connectivity of fibrils on a surface. For cooperative self-assembled systems, the remaining monomers, inherently present in the solution, significantly influence the organization of the self-assembled structures on the surface. It can be anticipated that electronic (nano)devices made from π-conjugated systems could have a monolayer that is arranged differently than the bulk of the active layer, thus potentially influencing the performance of the device.

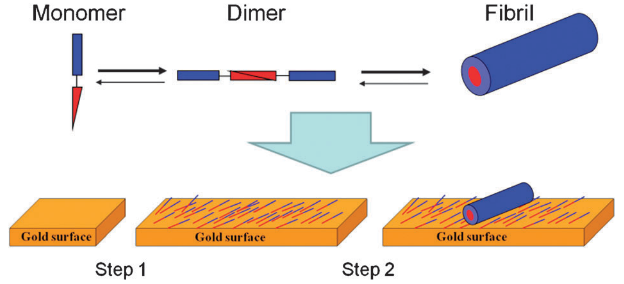

Fig. 4 Proposed model for the transfer of self-assembled π-conjugated fibrils on a gold substrate.

The collaboration between Mons and Grenoble has been carried out in the frame of a joint bilateral research program (FNRS-CGRI/CNRS 20182). Ph.L. is a Research Associate of the FRS-FNRS (Belgium). The Dutch team acknowledges the Netherlands Foundation for Scientific Research (NWO). I.D.C. and S.D.F. acknowledge the Fund of Scientific Research—Flanders (FWO), K.U.Leuven (GOA), the Belgian Federal Science Policy Office through IAP-6/27. I.D.C. is grateful to the Agency for Innovation by Science and Technology in Flanders (IWT).

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