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Electric-Field-Assisted Alignment of Supramolecular Fibers**

By Laura Sardone, Vincenzo Palermo, Eloïse Devaux, Dan Credgington, Maaïke de Loos, Giovanni Marletta, Franco Cacialli, Jan van Esch,* and Paolo Samorì*

Dedicated to Professor Vincenzo Balzani on the occasion of his 70th birthday

A molecular wire consisting of a metal/molecule/metal junction can be regarded as the basic building block for future nanoelectronics applications. Alongside the great effort expended in the last ten years on the use of single molecules as electroactive components,^[1–3] there is also a growing interest centered on the use of supramolecular architectures as electroactive species to bridge metallic electrodes.^[4] The supramolecular approach can enhance the mechanical and electronic properties of the wire, which should improve the performance of electronic devices.^[5–10]

One major challenge in the study of charge transfer across organic molecules is achieving reproducible attachment between metallic electrodes. Although different electrode pairs have been employed, including break junctions,^[3] lithographically tailored nanoelectrodes,^[11] and a solid substrate and a

conductive tip of an atomic force microscope^[12–14] or a mercury drop,^[15] new, scalable routes to the controlled incorporation of nanometer-scale objects in the gap between nanoelectrodes are required.

The manipulation and alignment of an anisotropic object using dielectrophoretic forces in an electric field has been successfully accomplished with a variety of different structures including metal and semiconducting nanoparticles^[11] and nanowires,^[16] DNA molecules,^[17] carbon nanotubes,^[18,19] block copolymers,^[20] ZnO–organic complexes,^[21] and dendron rod–coil ribbons.^[22] This has recently led, for example, to improved emission properties of single conjugated polymer molecules.^[23] The possibility of applying this technique to supramolecularly engineered nanostructures is thus of major interest in view of their reversible self-assembling properties under external stimuli such as temperature and chemical environment.^[24] We provide here the first direct quantitative determination of the electric-field-assisted alignment of single organic supramolecular fibers self-assembled at a surface.

We have chosen a gel-forming functionalized 1,3,5-triamide *cis,cis*-cyclohexane derivative (cyclohexane trisamide gelator (CTG), Fig. 1a) that is known to self-assemble into supramolecular fibers in aqueous solution through the formation of hydrogen bonds.^[25,26] Due to its wider applicability for electronic applications, we present here attempts to form similar fibers in an organic solvent. Fibers were deposited from solution onto two gold electrodes arranged in a source–drain geometry with micrometer-scale separation. During deposition, a DC voltage was applied between the two electrodes and the system was cooled below its sol–gel transition temperature ($T_{\text{sol-gel}}$).

In the gel, the three intermolecular hydrogen bonds among the amide moieties of CTGs are both parallel to one another and perpendicular to the plane of the cyclohexane ring (see Fig. 1a inset), endowing strong, self-complementary, and uniaxial intermolecular interactions that are necessary to enforce quasi-1D self-assembly.^[27] Since each hydrogen bond has a dipolar nature, the identical orientation of at least two of the three H-bonded networks provides the columnar architecture with a large dipole moment, making the CTG fibers excellent candidates to study the effect of applied electric fields.

Micrometer-length CTG fibers were observed preferentially on the top of the negatively charged electrode and tended to align with the local electric field, which has been calculated for our system geometry using finite element analysis. Given

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Figure 1. a) Chemical structure of the cyclohexane trisamide gelator, CTG, highlighting in red the NH groups acting as hydrogen-bonding donors and in blue the carbonyl moieties behaving as acceptors. Inset: Schematic drawing of the hydrogen-bonded stack characterized by a large dipole moment. b,c) Scanning force microscopy images of the fibers arranged as b) a densely packed network and c) isolated fibrils. Z-scales: (b) 40 nm, (c) 25 nm. d) Scanning electron microscopy image highlighting the selective adsorption on the input electrode of preferentially oriented fibers that occurred on applying 2 V between two electrodes for 1 h while decreasing the temperature. A is the output electrode and B is the input electrode. e) Electric-field stream lines over the electrodes calculated using finite element analysis.

the notable synthetic versatility of CTGs, which can be covalently functionalized in their peripheral positions with electroactive moieties, one can foresee their use as a scaffold for the bottom-up fabrication of supramolecular wires for nanoelectronics applications, providing an alternative to single-molecule multichromophoric wires.^[28]

Figures 1b and c show scanning force microscopy (SFM) images of a CTG gel adsorbed onto muscovite mica. Some areas of the sample are coated by densely packed intercoiled fibers, forming a network, while other parts exhibit isolated fibrils. The fibers display effective widths of 41 ± 14 nm and average heights of 12 ± 4 nm. Given the 3.4 nm diameter of the single molecules when their side chains adopt a fully extended conformation, the fibers are likely to be about four molecules thick and twelve molecules wide.

A solution of CTG in 1-octanol kept at $T_{\text{sol-gel}} = 80^\circ\text{C}$ was cast onto a SiO_x/Si surface overlaid with two facing Au electrodes separated by a 5 μm gap. While applying a 2 V DC bias across the two electrodes, the substrate temperature was

reduced from 80°C to room temperature in steps of 20°C every 15 min for 1 h, initiating the formation of a gel film on the surface. These gel films, shown in Figure 1d, reveal a preferential adsorption of the CTG architectures on the Au, while the SiO_x/Si remains almost uncoated. The CTG formed intercoiled fibers that are preferentially adsorbed on the input (i.e., negative) electrode. This behavior appears similar to the observed preferential adsorption of carbon nanotubes onto positive electrodes, which has been explained in terms of an induced charged character of the nanotubes triggering site-selective adsorption.^[18] In this case, it is likely that, by using an AC voltage, one could prevent the charging of the fibers, thereby hindering the preliminary selective adsorption onto the input electrode.^[29,30] Alternatively, the preferential adsorption onto the input electrode could be due to an oxidation of the positive Au electrode, which acquires a poor affinity for the more hydrophobic CTG fibers as it becomes more hydrophilic.

On top of the input electrode shown in Figure 1d, the bundles of fibers do not adopt a random orientation; instead, they align with the local electric field (Fig. 2a), as confirmed by the sharp signals in the fast Fourier transform (FFT) spectra (Fig. 2a, insets).

To support this assertion, we modeled the electrode system using a finite element method and evaluated the electric field throughout. Figure 1e shows the electric field stream lines immediately above (i.e.,

within 500 nm of) the electrodes, assuming a liquid conductivity of 100 S m^{-1} . This field is weak, of about 1 V cm^{-1} , and, as shown in Figure 2b, it exhibits a component in the plane of the input electrode with structure strongly reminiscent of that displayed by the CTG fibers in Figure 2a. Calculated FFT spectra of the electric field lines, shown by the insets in Figure 2b, are in good qualitative agreement with FFTs calculated for the corresponding real electrode areas.

To rule out other causes that could lead to the alignment, the fibers were simultaneously deposited on another electrode pair, located hundreds of micrometers away from the first and across which no bias was applied. The same drop of solution covered both the biased and unbiased pairs, providing identical experimental conditions. Figure 2c shows that the fibers deposited on the unbiased electrodes exhibit random orientations, demonstrating that the alignment displayed in Figure 2a is driven solely by the applied electric field.

The mean fiber orientation within any given area of the SFM image can be characterized statistically using standard

Figure 2. a) SFM image of the biased Au electrode coated by CTG intercoiled fibers. A 2 V bias was applied to the electrode for 1 h immediately after solution deposition to drive the orientation of the fibers. The electrode apex (not shown) is in the center-left of the visible area. The insets display the 2D FFTs calculated for a $5\ \mu\text{m} \times 5\ \mu\text{m}$ area centered on two representative points (i.e., I and II) of the SFM image. The white arrows show the main fiber's orientation ($a_{\text{max}} + 90^\circ$) in each point calculated using 2D FFT image analysis. b) Electric field lines calculated over the same area of (a). The insets display the 2D FFTs calculated on a $5\ \mu\text{m} \times 5\ \mu\text{m}$ area centered on two representative points (i.e., I and II) of the calculated image. c) Scanning electron microscopy (SEM) image of fibers deposited on an unbiased electrode showing an isotropic orientation of the fibrils. As the fibers look dark in raw SEM images, the contrast of the image has been inverted to facilitate their identification. The insets display the 2D FFTs calculated on random $5\ \mu\text{m} \times 5\ \mu\text{m}$ areas.

2D FFT-based image processing. For each orientation angle a in the plane, the amplitude A of the radial Fourier spectrum may be calculated as

$$A(a) = \sum_{r=1}^{N/2-1} |F(N/2 + r \cos(a), N/2 + r \sin(a))| \quad (1)$$

where $F(u,v)$ is the Fourier transform for vector (u,v) in reciprocal space, N is the number of pixels comprising the area in question, the DC component of the spectrum is at $u = N/2$, $v = N/2$, and r is an index running through all the wavelengths present in the FFT image. The angle a_{max} having the highest amplitude A_{max} in reciprocal space will therefore be perpendicular to the dominant orientation of the fibers in the chosen region.

To quantify the fiber alignment in a given location on the sample surface, an empirical parameter, the texture direction index S , was calculated from a weighted average of A_{max} , such that

$$S = \frac{\sum_{t=0}^{M-1} A(t\pi/M)}{M A_{\text{max}}} \quad (2)$$

where t is an index running through all angles on the surface. S tends to 0 for fibers perfectly aligned along one axis and tends to 1 for a perfectly isotropic distribution. These parameters are typically employed for surface roughness characterization.^[31]

Table 1 summarizes the values of a_{max} and S calculated in different positions on the input electrode (Fig. 2a) and simulated electrode (Fig. 2b), and compares them to the S values determined at random locations of the unbiased electrode (Fig. 2c).

The comparison of the a_{max} and S values provides unambiguous evidence for the electric-field-induced alignment of the fibrils. These anisotropic architectures adopt orientations that are preferentially parallel to the field lines. The orientation of the fibers is not perfect, as confirmed by comparing the experimental data with the electric-field angles calculated by the simulation. Moreover, the simulated values of S are notably smaller than those determined experimentally. This is most likely due to the presence in the real experimental case of noise in the system, including thermal fluctuations and dissolved solute and solvent effects. The behavior for intermediate values of the electric field (between the points reported here), including their interpretation, will be detailed elsewhere.^[32]

The electrostatic field is not needed for the supramolecular fibers' formation, as proven by the presence of fibers even on the unbiased electrode (Fig. 2c), and thus it only influences the fibers' orientation.

The electric-field-induced orientation found here to act on fiber bundles can be expected to be even more pronounced on single-molecule-wide fibers, which possess a well-defined intrinsic dipole moment. Single-molecule-wide fibers could be

Table 1. Fiber-orientation angles ($a_{\text{max}} + 90^\circ$) and order parameters (S) quantifying the preferential orientation of the fibers, as measured on $5\ \mu\text{m} \times 5\ \mu\text{m}$ zones centered on points I to V, compared with values predicted by the model. The average texture direction indexes S for the unbiased electrode has been averaged on ten different areas of $5\ \mu\text{m} \times 5\ \mu\text{m}$ each.

	Zone	I	II	III	IV	V	Average unbiased electrode
Experiment	$a_{\text{max}} + 90^\circ$	246°	186°	215°	184°	185°	—
	S	0.78	0.69	0.77	0.71	0.72	0.88
Model	$a_{\text{max}} + 90^\circ$	225°	186°	195°	182°	168°	—
	S	0.456	0.457	0.389	0.356	0.398	—

obtained by grafting side groups that hinder the fibers' lateral attractive interactions without affecting the tendency to pack face-to-face. Such substitutions in the bay positions could be tuned to allow a higher affinity between the molecule and SiO_x/Si , favoring the adsorption of the fibers between the two electrodes. Moreover, the alignment effect could be further amplified by using a solvent which is less polar than 1-octanol. Ongoing work in our laboratories is along these two lines.

In summary, we have successfully manipulated supramolecular fibers with a DC electric field triggering their alignment in preferred directions on a patterned surface made of Au electrodes supported on an insulating SiO_x/Si substrate. The triggered alignment was determined quantitatively and compared to the stream-line orientation of an electric field simulated using a finite element approach. This result represents the first step towards the controlled connection of metallic nanoelectrodes by self-assembled fibers.

Experimental

The synthesis of the CTG has been described elsewhere [25,26,33]. Given the known critical gelation concentration and temperature of the sol-gel transition ($T_{\text{sol-gel}}$) of 2 g L^{-1} and 80°C , respectively, we have prepared a 2 g L^{-1} solution of CTG in 1-octanol by heating at 80°C . A solution drop was cast on the SiO_x/Si sample supporting the nanopatterned electrodes, while applying 2 V between the electrodes for one hour and decreasing of the temperature from 80°C (T_{sol}) to room temperature (T_{gel}). After the deposition, the drops were immediately blown off the substrate with a gentle stream of N_2 to remove the residual gel from the gap between the two electrodes. The DC voltage was applied with a Keithley 6517A high-resistance electrometer. Prolonged application of a DC voltage also led to the presence of the fibers on the SiO_x/Si surface located in the gap between the two Au electrodes.

Thin CTG films supported on mica were prepared on the freshly cleaved substrate by drop-casting a $50 \mu\text{L}$ drop of gel obtained by cooling the above solution to room temperature, followed by a dry-up process of 1 h under a gentle stream of N_2 .

The polycrystalline Au electrodes were nanofabricated by focused ion beam milling (FEI Dual Beam Strata 235 system, using Ga ions, 5 nm nominal beam diameter) of a 20 nm thick Au (99%) or Pt (99%) layer deposited by sputter coating (Emitech K575X Turbo Sputter Coater) on an insulating Si wafer bearing a 85 nm thick thermally grown layer of SiO_x . The substrate was washed before the deposition with ethanol in an ultrasonic bath.

Samples were studied by both SEM (FEI Dual Beam Strata 235) and tapping-mode SFM using a Digital Instruments Dimension 3100 (Veeco USA) operating at room temperature in air. Measurements were executed with microfabricated silicon nanoprobe (length $125 \mu\text{m}$ and width $30 \mu\text{m}$) having a spring constant between 17 and 64 N m^{-1} , using scan rates of $1\text{--}3 \text{ lines s}^{-1}$ and a resolution of $512 \text{ pixels} \times 512 \text{ pixels}$. The off-line analysis of the images was performed using "Scanning Probe Image Processor" (SPIP) software (version 2.000, Image Metrology A/S). The effective width of the fibers was estimated taking into account the tip-broadening effect [34]. To understand the observed local alignment of CTG fibers seen in Figure 2a, we modeled the DC electric field in the vicinity of the electrodes using the COMSOL Multiphysics finite element analysis package (COMSOL Inc, USA). The model comprises two 20 nm thick gold electrodes overlaid on a $100 \mu\text{m} \times 110 \mu\text{m}$ slab of insulating substrate and submerged in 500 nm of weakly conducting liquid, representing the CTG in 1-octanol solution. The electrodes are separated by a $5 \mu\text{m}$ gap and a total bias of 2 V was applied across them. Current flowing

through the system leads to a potential drop across the gold, giving rise to a small electric field component in the vicinity of the electrodes. To determine the structure of this field, we first quantified the conductive properties of the materials in the system. Detailed modeling of the conductivity of sputtered gold is difficult without knowing its polycrystalline structure. However, previous work [35] suggests that the conductivity of a 20 nm sputtered gold film will be 5–10 orders of magnitude less than that of the bulk metal, which has a typical conductivity of $4.5\text{--}5.0 \times 10^7 \text{ S m}^{-1}$. We therefore modeled the electrodes as a metal with conductivity $\sigma_{\text{gold}} = 5 \times 10^6 \text{ S m}^{-1}$, and considered an arbitrary solvent conductivity (σ_{sol}) much lower than the σ_{gold} , ranging between 10^2 to 10^6 S m^{-1} . Under such conditions, the structure of the electric field present around the electrodes was found to be largely invariant.

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