Biomolecular nanowires decorated by organic electronic polymers

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We demonstrate the shaping and forming of organic electronic polymers into designer nanostructures using biomacromolecules. In order to create nanowires, nanohelixes and assemblies of these, we coordinate semiconducting or metallic polymers to biomolecular polymers in the form of DNA and misfolded proteins. Optoelectronic and electrochemical devices utilizing these shaped materials are discussed.

Introduction

As electronics has moved into the nanoelectronic age, with recent production facilities using technology at the 45 nm node, pursuit of alternative patterning methods to reach even smaller structures is highly topical. Self-assembly of nanostructures is a major effort in this direction, with activities spanning many classes of materials and functions.[1] Even conversion of classical semiconductors to thin wires, for the purpose of processing and patterning, is a route of interest.[2] The choice of electronic polymers for giving electronic functions is better motivated by the possibilities of fluidic self-assembly than by any advantage in transport capacity, as these materials show disorder limited charge transport and low mobilities. If organization at the nanoscale could reduce disorder, this may have an influence on electronic transport, and improve mobilities. The control of electronic structure by chemical design of electronic polymers is, however, well demonstrated, and bandgaps are easily tuned for applications. The processability of electronic polymers is therefore the main advantage, but the importance of novel functions must be emphasized. The vicissitudes of self-assembly methods to reach complex geometries and combinations will always require a considerable redundancy in elements, and the selective wiring and connection of these overpowering numbers of devices is critical for obtaining relevant systems function. Contacting such self-assembling systems on the nanolevel in fluid environments, to make three dimensional circuits or systems, is a very considerable problem to be solved. This is the task of joining self-assembly from the nanometre level up to reach micro and nanopatterning efforts coming from the micro dimensions. Combining micro- and nanopatterning with bridging structures named micro–nanocouplers somewhat helps to bridge the micro to nano gap,[3] and requires assembly from fluids.

To make molecular wires into stiffer wires, mimicking the cables for electrons in electronics, electronic polymers in the form of conjugated polymers require extensive substitution and special choice of main chain structures in order to obtain long

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Per Björk has an MSc in Engineering Biology from Linköping University (2003), and did his PhD studies in the Biomolecular and Organic Electronics group at Linköping University. He graduated in 2007 with a thesis focusing on utilizing conjugated polymers for the construction of biomolecular templated electronics and as reporter molecules for biological sensing on DNA chip and in primary cell cultures. Per has continued to combine the areas of biology and physics in his present joint postdoc position at Acreo AB and Clinical Neuroscience, Karolinska Institutet. The current focus is on BioMEMS in both soft and hard materials for organized neural culturing.

Anna Herland

Anna Herland has a background as MSc in Engineering Biology (Linköping University 2003) and a PhD in Biomolecular and Organic Electronics (Linköping University 2007). Her thesis work combined biological macromolecules and conjugated polymers for biosensing and organic electronic applications. Anna joined the company BioChromix 2008–2009 as a project leader. In 2009 she received a PostDoc scholarship within regenerative medicine and tumor suppression at the Department of Neuroscience, Karolinska Institutet, funded by the Swedish research council. Anna is currently pursuing her research interest to develop active, functional materials for biomedical and biochemical applications.

persistence lengths. The reward would be to use a single polymer chain, with transport limited by the high mobilities detected by transient electromagnetic methods.[4] Though the rewards of making a single polymer chain extend from one junction to the next are presumably quite small, the effort necessary to reach this geometry is very extensive. For chains spanning the necessary length from junction to junction, we would require a persistence length of $\approx$50 nm, if the target is to span distances in circuits defined with geometries below 45 nm line widths. While electronic polymers are narrow, they seldom have the persistence length necessary and will therefore organise according to the statistical principles of polymer physics. This would prevail in the absence of some novel ordering principle.

Spontaneous self-organisation on a low level is found in liquid crystals, where collective effects in self-organisation give media rich in function for optics. Conjugated polymers may be ordered in non-conjugated liquid crystal hosts.[5,6] The nematic state is often found in conjugated polymers,[7] and is one primitive level giving attractive functions for macroelectronics, if not for nanoelectronics. Alignment of liquid crystalline polymers give polarised photoluminescence and electroluminescence;[8] effects on the transport of charges are visible in field effect transistors. These effects are valuable in some optoelectronic functions, and therefore means to organise polymer chains into oriented geometries have been searched for. The brute force approach of chain stretching through elongation of polymer films was reported,[9] and does not require spontaneous self-organisation; nematic liquid crystals of electronic polymers today give the best polarisation properties in light emitting devices[10] also extending to the infrared emission range.[11] To induce global ordering over large areas, necessary for lighting and signage devices generating polarised light, the means to orient the chains locally is required. This can be done by influence from a patterned substrate.[8] Other means are of interest, if we could only orient the polymer chains by alternative methods.

We introduce novel possibilities with conjugated polymer chains decorated on highly anisotropic biomolecular nanowires which allow fluidic ordering and orientation methods. This topic of development comes from studies of the interaction of conjugated polyelectrolytes (CPE) and biological polyelectrolytes (Fig. 1), also useful in detection of biomolecular identity, structural state and activity. We can detect in optical emission and absorption the geometrical changes of CPEs complexed with DNA,[12] RNA, proteins[13,14] and synthetic polypeptides,[15,16] where the biomacromolecule is the master and the CPE is the slave to geometrical changes. We have pushed these studies also to the single molecule level, with the help of the molecular combing method. DNA can be stretched and elongated in a liquid flow, as found at the edge of a moving drop of solution on a solid surface.[17] By this method we can stretch and orient long chains of λ-DNA, spanning $\approx$25 μm in length and therefore visible in the luminescence microscope. By decoration with a CPE, we can detect the DNA chains through the emission of the CPE, and use emission from small lengths along the molecule to follow the varying conditions for complexing. As the DNA chain is narrow (1–2 nm) and very long, an aspect ratio of 10 000 is possible in these studies. In addition, we retain the possibility of using the base pair hybridization of the DNA chain for addressing functions. Hybridisation of DNA chains can be detected in the optical emission of the CPE, giving us the tool to use the DNA chain as an address label.

An alternative biomolecular nanowire is found in the misfolded protein nanowires, known as amyloid fibrils. These are ubiquitous materials found in many neurological diseases, and one expression of the manifold geometries found in the folding of one dimensional protein chains, out of which a small minority gives the function, but where many folding patterns lead to formation of biologically inactive, or at worst, toxic forms. The amyloid fibril is found in primary geometries of 7–10 nm thickness and extends up to 1–10 microns in length; therefore a smaller aspect ratio of 1000 is obtained. We have found that CPEs interact strongly with amyloid fibrils *in vitro*[14] and with amyloid deposits in tissue.[18] This interaction has been monitored also on the single fibril level and is displayed by the clear changes in optical characteristics of the CPE, which distinctively differs from that found in the presence of non- amyloidal protein.[64]

Mahiar Hamedi

Mahiar Hamedi holds a MSc in Applied Physics from Chalmer's Technical University (2001), and he finished his PhD studies in the Biomolecular and Organic Electronics group at Linköping University in 2008. The focus of his research has been on self-assembled organic nano electronics and electronic textiles. Here he has explored the use of non-conventional patterning methods, including biomolecular template assembly and soft lithography in combination with the unique electrochemical properties of organic electronics to achieve functional devices/systems.

Olle Inganäs

Olle Inganäs is professor of biomolecular and organic electronics, IFM, Linköpings Universitet, Sweden. He has received a MSc in engineering physics from Chalmers University of Technology (1977), a BSc in philosophy and economics from Göteborg University (1978), and a PhD in applied physics at Linköping University (1984). He was appointed professor in 1999, and is presently director of a Center of Organic Electronics in Sweden. He has focused on studies of the class of conjugated polymers throughout areas of polymer physics, electrochemistry, electronics and optics. The use of electronic polymers as interfaces to biological systems is a present topic of research.

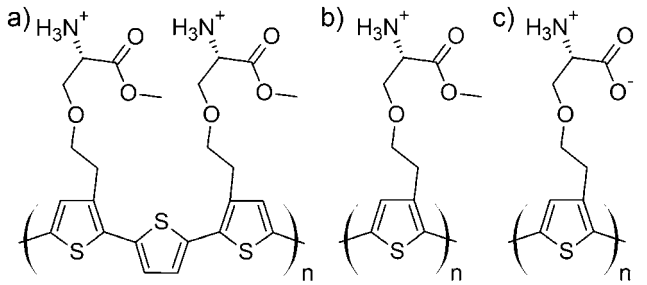

Fig. 1 Examples of conjugated polyelectrolytes (CPEs). (a) tPOMT, (b) POMT, (c) POWT.

The single molecule spectroscopy (SMS) methods have been developed to also handle polarised light, and in the more elaborate experiments, a full characterisation of emission and polarisation properties is possible, under polarised excitation and polarised emission. With this combination SMS becomes a powerful tool to determine the organization of absorbing and emitting dipoles of conjugated polymer chains in and along single nanowire geometries.[19]

DNA templated electronics

DNA has been the most extensively used biomolecular template in the last decades. Even though the built in recognition sequence offers the possibility for complex geometries such as networks[20] crossings[21] and 3D structures,[22] the main work when it comes to functionalisation with electronically active materials has been done on the less complex stretched wire geometry. From its native random coiled state in solution, single or double stranded DNA can by different methods be stretched out to linear and aligned geometries. The most straightforward method is molecular combing where the DNA molecules are stretched by the force rendered from a receding meniscus of a liquid (Fig. 2). Bensimon *et al.* were the first to report DNA stretching[17] and used this fluid-flow assisted molecular combing technique. Some of the other methods to stretch molecules include electrophoretic stretching[23–29] and hydrodynamic stretching[30–34] DNA needs to be functionalized with electronic materials to achieve a functional electronic device, as intrinsic conduction in DNA does not give the basis for electronics. Though a considerable effort to use the DNA chain as conductor is found in the literature, there are many problems with these concepts and the electronic conduction on the DNA chain may have little relevance for materials or nanoelectronic systems.[35–37] To utilize DNA with other electronic materials, various functionalization methods have been suggested in the literature. The DNA chains have been complexed with metal ions which then are reduced to metal particles[38,39] Sometimes, this is also followed by further metallization to improve the conduction.[21,40,41] The drawback is the thickening of the resulting wire, and a final thickness of 50 nm or more is not unusual. Other possibilities are to decorate DNA with semiconducting,[42] surface-functionalized metal nanoparticles[43,44] or physically sputter of the low temperature, superconductor $Me_{19}Ge_{79}$.[45] Keren *et al.* have shown that a more advanced structure, such as a field effect transistor, can be fabricated by direct assembling of carbon nanotubes to DNA in combination with a metallization technique.[46]

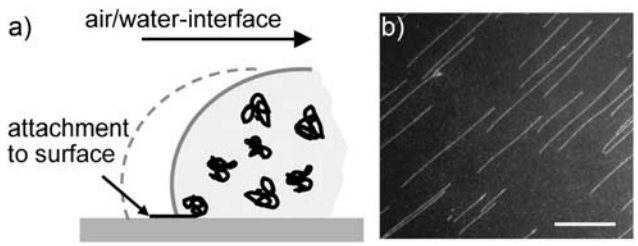

Fig. 2 Molecular combing. (a) The ends of DNA chains are attached to the surface usually *via* hydrophobic interaction, and the DNA is stretched in parallel direction to the receding meniscus. (b) Molecular combed λ-DNA stained with the intercalating dye YOYO-1. Scale bar: 12 μm.

Immobilization of aniline monomers to a DNA chain followed by polymerization to the conjugated polymer polyaniline has been demonstrated by Ma *et al.*[47] The polyaniline decorated DNA network stretching between two gold electrodes gives a measurable conductance. In further work, both carbon nanotubes and DNA have been combined with polyaniline.[48]

We have shown that decoration with conjugated oligo/polyelectrolytes (CPEs) is a highly interesting alternative for functionalisation of biomolecular nanowires. The complexation of CPE with biological polyelectrolytes offers an attractive approach for building devices and materials where the scale of a few nanometres thickness is conserved. The assembly of the electronic polymers can by this approach be controlled by the interactions with macromolecular assemblers such as DNA and amyloid fibrils.

Our approach is to use zwitterionic and positively charged conjugated poly- and oligoelectrolytes with a chain length of 9–20 repeating thiophene rings to decorate λ-DNA, derived from a bacteriophage (Fig. 2 and Fig. 3). Electrostatic and hydrogen bonding are probably the most important binding forces for DNA/CPEs complexes. The complex can be formed in solution and then stretched into aligned photoluminescent arrays by the molecular combing techniques described above.[49] Compared to DNA stretching with bare DNA, the CPEs introduce some new phenomena to take into account. The first is that during the mixing of CPE and DNA, crosslinking can occur. In solution, DNA has a random coil structure and the polycationic CPEs can therefore cross link within the same DNA chain, but also between different DNA molecules. Furthermore, the CPEs themselves can induce polymer aggregation. The result is therefore often observed as stretched bundles of DNA (Fig. 3). The continuous coverage along the DNA can also be an issue. It is a balance between having enough CPE for continuous decoration, but not any excess that may create a background of surface bound CPEs and may induce undesired aggregation. As an alternative, decoration of the DNA after stretching is an interesting possibility, to avoid DNA bundles. However, so far the liquid environment and the CPE interaction tend to make the DNA detach from the surface during the decoration process.[49]

In understanding the CPE interactions, measurements on single or few polymer chains can be very rewarding. The single molecule spectroscopy technique makes it possible to follow the alteration in fluorescence properties of CPEs along a DNA chain. The polydisperse POMT shows a large variation of emission maximum with a tendency for a red shift for brighter spots.[49] The brighter spots are probably characterized by more inter-chain phenomena allowing energy transfer to lower energy sites, while the less bright spots to a larger degree have

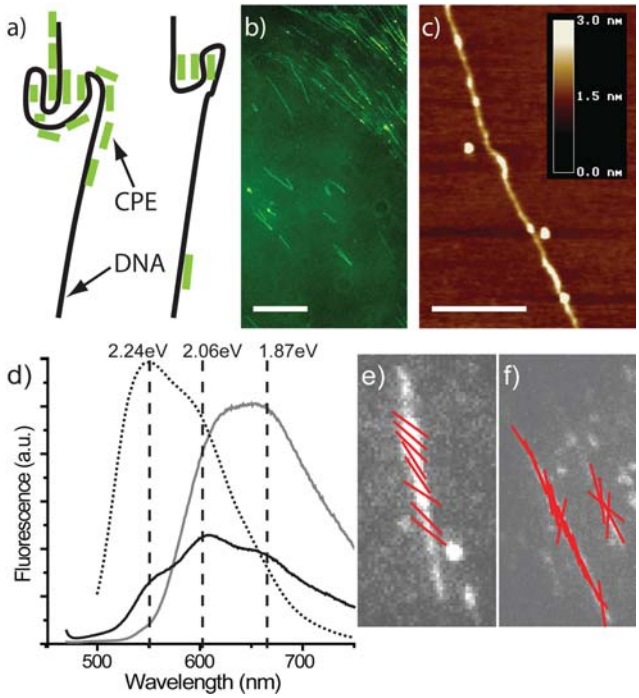

Fig. 3 (a) Cartoon showing possible organization of the DNA/CPE complexes; a middle size cluster (left) and a small cluster or an individual chain that can show fluorescence blinking (right). Fluorescence image (b) and AFM image (c) of stretched DNA decorated with POMT. (d) Fluorescence spectra of tPOMT in MES buffer (gray), tPOMT in ethanol (dot), tPOMT + 20 bp dsDNA in MES buffer (black). (e, f) Direction of each red line shows the orientation of the maximal excitation cross section for tPOMT decorated on stretched DNA. Scale bars: 10 μm (b), 500 nm (c). Figures adopted from ref. 49 and 50 (copyright Wiley and ACS).

intra-chain processes (Fig. 3). AFM (atomic force microscopy) images also confirm the variation in size distribution of CPE molecules/clusters along the DNA chain (Fig. 3c).[49] However, for the more monodisperse tPOMT chains (Fig. 2a), which to 80% are nonamers of thiophene rings, no clear relation between spectral shifts and intensity is found, most likely because they form more well-defined clusters that do not differ too much in size.[50] The more defined tPOMT also give better possibilities to understand the processes in the CPEs (Fig. 3). This has helped us to assign the spectral shape and the peak position in the fluorescence spectra of tPOMT to vibronic structure. The spacing, *ca.* 0.18 eV, between peaks agrees with the C=C stretching vibration typically found in conjugated polymers. Enhancement of the structures in the emission spectra of tPOMT can be seen when cooling down the samples to 77 K. Using anisotropy measurements, recorded simultaneously in absorption and emission, we can observe that tPOMT in liquid solution forms a weakly-coupled H-aggregate that is disrupted upon binding to DNA. This powerful 2D polarization technique, developed by Scheblykin and collaborators in Lund University,[51] also confirms energy transfer between CPE's, and show that CPE chains in complexes with λ-DNA have orientation differences of at least 15° within the energy transfer range (5–10 nm).

The decoration process is one element in realizing an electronic component based on biomolecules and conjugated polymers. Another important aspect is positioning of the nanostructures in

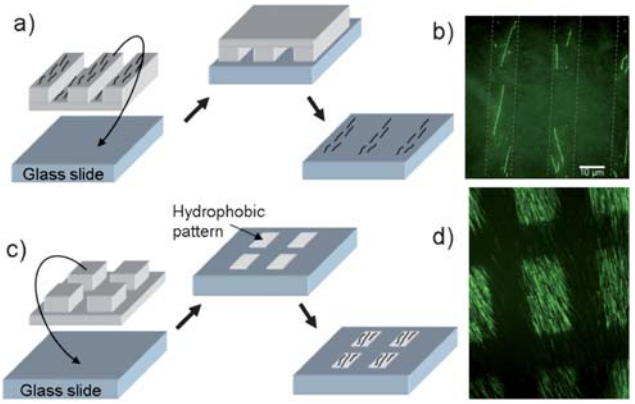

Fig. 4 (a, b) Transfer printing of stretched DNA. The dashed lines indicate the structure of the stamp. (c, d) Positioning of stretched DNA by surface energy modification. Scale bars: 10 μm (b), 25 μm (d). Figures adopted from ref. 53 (copyright Wiley).

such ways that a functional geometry can be achieved. Molecular combing results in straight DNA wires aligned parallel to the receding meniscus. For a more precise localization, constraints have to be added. Soft lithography offers tools for achieving good positioning of molecules.[52] We have used elastomeric stamps to transfer print stretched DNA with and without CPE decoration to defined areas on a surface[53] (Fig. 4). The stamps can also be used to create surface modified areas on a substrate to where DNA can selectively be stretched.[53] In this process, we utilize the transfer of hydrophobic low molecular weight species from a bare PDMS stamp to create a pattern to where the DNA can attach during the combing process. Control of the positioning on electrodes or the formation of crossings can be obtained by these methods.

Amyloid fibril templated electronics

Nature uses protein fibers or fibrils in numerous ways as highly dynamic elements for protection, scaffolding, stabilization and motility.[54] The functionality of the more complex biological protein fibers demands a well-controlled environment. A much more stable protein structural element is the pleated β-sheet structure of an amyloid fibril. Compared to native protein fibrils and DNA, mature amyloid fibrils can withstand much rougher conditions in both dry and wet states, such as high temperatures and exposure to some organic solvents.[55] The ability to form the stable β-sheet structure is found in many proteins and peptides, and it is even suggested that it can be the fundamental structure of all proteins.[56,57] It may be that minor perturbations of the conformation of native proteins inside the body is the trigger for amyloid deposition with associated diseases like Alzheimers.[56] Peptide derived amyloid has been pointed out as a major element in protein nanotechnology in a recent review.[57]

Despite the amazing inherent functionalities of protein and peptide fibrils the combinations of them with electronic materials are limited to coating with metal,[58,59] often *via* recombinant proteins and the stable gold–sulfur bond, and the attachment of redox-active heme groups.[60] Also synthetic peptides have been used to create nanowires for metal decoration.[59,61]

As in the case of DNA, metallization of the biopolymer nanostructure not only gives considerable broadening, but more

importantly, buries the biochemical information, such as the sequence of the nucleotide bases or easily modified amino acid side chain, of the biological wire forming material. Another issue is the material mismatch between the soft, water-containing biological material and a metal coating. This causes constraints on the complexity of the possible geometries generated with this combination, and on the methods to assemble the formed objects into functional devices. By letting organic polymeric materials deliver the electronic function to objects where biological structures define shape and specific identity, our aim is to generate toolkits for bioorganic nanoelectronics.

Our first effort in the combination of amyloid fibrils and organic electronic material was to create a material where the two components were interwoven into a new hybrid material. However the harsh conditions necessary for some proteins to initialize the amyloid fibrillation process *in vitro*, *i.e.* acidic

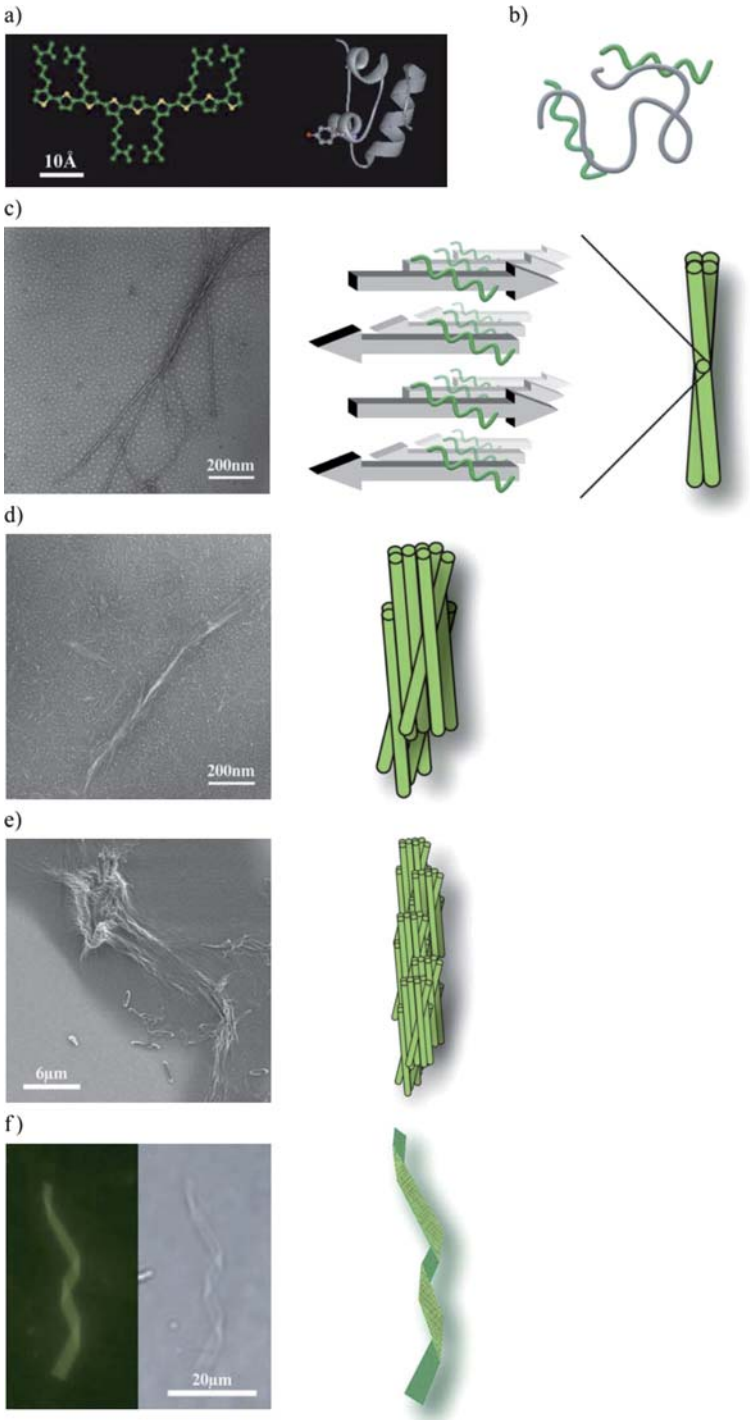

Fig. 5 Assembly of luminescent amyloid wires from the oligoelectrolyte tPONT with insulin (a) coassembled with tPONT (b) followed by transmission electron microscopy (c), scanning electron microscopy (d and e), and finally optical microscopy (f) in luminescence and in transmission mode. Symbolic models of the assembly process are given to the left. Reprinted from ref. 62 with permission.

water-based solutions incubated at high temperatures, are likely to degrade an organic electronic oligomer or polymer. To our surprise we found that when we incorporated a defined water-soluble conjugated oligomer in the amyloid fibril formation process of insulin its semiconducting, luminescent properties was kept only if the protein was present.[62] The defined length of the oligomer minimized diversity in the protein–electronic material interaction, due to the single conjugation length, in the different state of fibrillation pictured in Fig. 5, from protein oligomers to protofibrils and finally to a helical superstructure of assembled fibrils. To demonstrate the electroactivity of the final structures we used electrochemical induced photoluminescence quenching where we could reversibly dope and de-dope the material. This demonstrates that the density of the organic electronic oligomer is above the percolation limit enabling charge transport in the hybrid material.

Conjugated polymers with ionic or polar side chains have been shown to have high affinity for amyloid structures both *in vitro*[14,63,64] and in much more complex tissue samples for histological staining[18,65] The strong interaction between the ordered β-sheets in the amyloid fibrils and the conjugated polymers is likely to be dependent on the hydrophobic backbone of the polymer, similar to the aromatic small dyes such as Congo Red and Thioflavine T that traditionally have been used to stain amyloid. The ionic and polar conjugated polymers have furthermore the possibility of multiple interaction points with amyloid fibrils similarly to what has been shown in natural polyelectrolytes[66] giving avidity effects resulting in very strong binding. We have studied the interaction between conjugated polymer and amyloid fibrils on the single fibril scale using both an ionic electronic polymer[67] and a polar electronic polymer.[68] In both cases the fibrils are aligned using molecular combing on hydrophobic surfaces (Fig. 6). We have also shown how soft lithography can be used to transfer fibrils to surfaces in desired patterns. This technique has been used with other materials to print highly sophisticated nano-circuits out of inorganic nanowires.[2] Important for generation of functional nano-circuits, the polymer decorated amyloid fibrils are highly stable in the generated patterns on surface and can withstand extensive rinsing. To elucidate the organization of the polymer chains on the amyloid fibrils single molecular spectroscopy tools were used. By using rotating polarizers in emission and/or excitation we could conclude that both polymers orient preferentially with the polymer backbone along the fibrillar axis. In the case of fibrils decorated with the water soluble ionic polymer polythiophene acetic acid PTAA (Fig. 6a and c) the G-value, a ratio of emitted maximum intensity divided with the emitted minimum intensity, was varying from 2.5 to 17 when exciting with circularly polarized light. Even though this value, which reflects the orientation of the emitting dipoles in the polymer, is higher than the value we reported for polymer decorated DNA, *vide supra*, it is still lower than for the fibrils decorated with a polar but more hydrophobic alternating fluorene copolymer APFO-12 polymer (Fig. 6d). We used a mixture of THF (tetrahydrofuran) and water to create a solvent mixture for both the APFO polymer and the insulin fibrils and could after molecular combing measure a G-value varying from 5 to 38. The higher order of the APFO polymer might origin from the higher stiffness in the polymer backbone, alternating polyfluorene, compared to the polythiophene backbone of the ionic polymer.

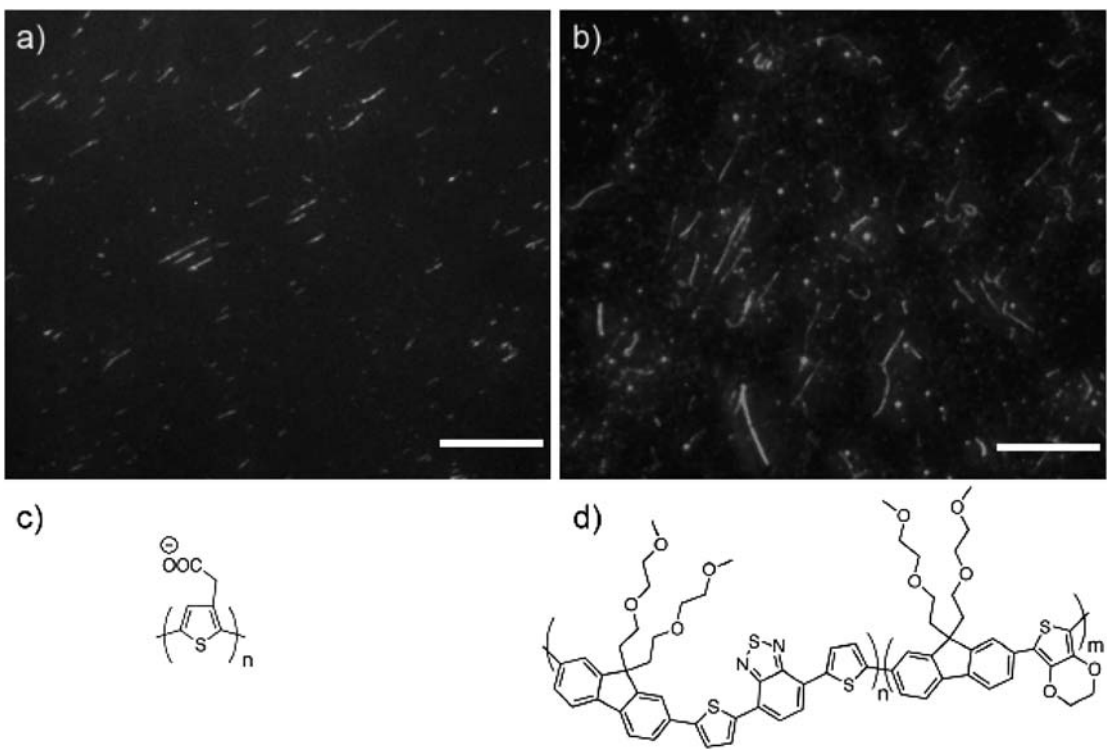

Fig. 6 (a) Fluorescence micrograph of PTAA/insulin fibril complexes aligned on surfaces with molecular combing. The scale bar represents 2 μm. (b) Fluorescence micrograph of APFO12/insulin fibril complexes partially aligned on surfaces with molecular combing. (c) PTAA structure; (d) APFO-12 structure. Reprinted from ref. 67 with permission.

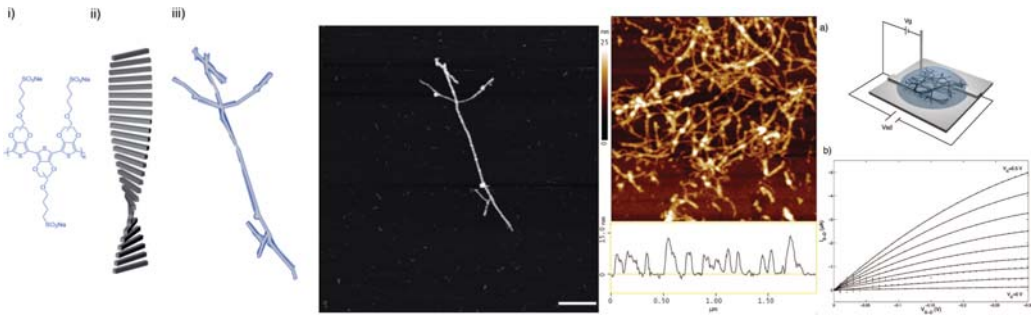

Fig. 7 (left) Structure of (i) PEDOT-S, (ii) amyloid, (iii) decorated structure. (middle left) An AFM image of the decorated structure (scale bar 1 μm). These nanowires are utilized in an electrochemical transistor (a), where a random network of wires (middle right, AFM image 2 μm^2) are in contact with an electrolyte and with drain and source electrodes (a), which allow modulation of current between drain and source (b). Reprinted from ref. 70 with permission.

Semiconducting, and possibly optically active, electronic components are fundamental, but for the construction of electronic circuits more conducting elements are essential. There are very few examples of single species organic materials with high conductivity and good solubility. The commercially most successful electronic polymer is the polythiophene PEDOT, which is sold in a dispersion with excess polystyrene sulfonate (PSS). Recently we synthesized an ionic version of PEDOT (PEDOT-S) with an alkoxysulfonate side chain giving good solubility in water.[69] This material is easy processable and can be spin coated into even films with a conductivity of 12 S cm^{-1}. Sulfate groups are known to associate with amyloid[66] which together with the mentioned studies of conjugated polymers and amyloid fibrils indicated that PEDOT-S might be suitable for the formation of an amyloid fibril with a truly conducting organic coating. Recently we demonstrated the formation of networks of insulin amyloid fibrils decorated with PEDOT-S.[70] This is done through spontaneous self-assembly of PEDOT-S onto amyloid fibrils in water at room temperature (Fig. 7). The polyelectrolyte character of PEDOT-S contributes to the possibility of interaction with biomolecules which often carry net charges, in contrast to PEDOT:PSS. The ionic interactions of the side groups can also, together with other weak interaction forces such as hydrogen binding/hydrophobic interactions, be the mechanisms of binding between this CPE and positively charged amyloid fibrils. One of the weaknesses of the commercial material PEDOT:PSS is that the excess of the large PSS ions create dispersions of micellar structures resulting in domains with non-conducting islands[71] that can cause problems when defining geometries in the nano domain. It is believed that PEDOT-S chains assemble around amyloid fibrils until the majority of assembly sites are filled. The remaining PEDOT-S is then filtered away since these molecules are smaller than the coated fibrils. The microscopic characterization of the networks formed by the coated fibrils reveals a thickness of around 15 nm to be compared with 10 nm for these amyloid fibrils in pure form.

From ordering to materials and devices

The use of nanostructural elements derived from a biopolymer to influence electronic processes in electronic solids is rather new, with only a few examples. We have included amyloid elements in the assembly of light emitting devices[72] and in organic photovoltaics,[73] and shown that these inclusions can influence transport properties. In a blue organic light emitting device (OLED), light output is increased by an order of magnitude compared to the neat polymer.[72] Electrochemical nanotransistors can be obtained on nanofibers,[70] which could potentially lead to 3D connected electrochemical/electronic systems, as has already been demonstrated with electrochemical transistors on microwires.[74,75] The combined function of field effect transistors and of electrochemical transistors has recently been presented.[70] Though these demonstrations indicate that improved performance can be obtained in devices incorporating electronic polymers nanostructured on biomolecular nanowires, there is a long way to go in order to get the best integration of the elements in standard electronic solids.

Conclusions

Ordering of electronic polymers through interactions with biological macromolecules is possible, and can give highly aligned nanostructures, which can also be positioned on a surface. Biomacromolecular nanostructures can also be used as templates for ordering and organizing electronic polymers to make possible macro and nanodevices.

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