

Supramolecular electronics; nanowires from self-assembled π -conjugated systems

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The conditions required for supramolecular electronics, *e.g.* nano-sized optoelectronic devices, will be illustrated on the basis of the programmed self-assembly of π -conjugated systems into individual nanosized wires. Using the supramolecular design rules nanowires can be created from almost any polymeric and oligomeric π -conjugated system. In the case of oligomers it is even possible to construct individual wires having a uniform diameter of one molecule thickness. The construction of wires on a substrate is possible by self-assembly in solution or during the deposition. The transfer of the supramolecular stacks from solution to a solid support is a very delicate process. A comprehensive knowledge of all intermolecular interactions gives rise to controlled transfer of π -conjugated assemblies to specific surfaces. There are a large number of very appealing targets that should be reached before supramolecular electronics can serve as an attractive alternative in between single molecule electronics and bulk devices. Nevertheless, the combination of exciting scientific results and intriguing technological challenges creates an interesting future for supramolecular electronics.

Introduction

The construction of supramolecular assemblies of π -conjugated systems on the 5–100 nm length scale offers an excellent tool to construct wires of electronic components in the nanometer range. We have proposed to call this field of research “supramolecular electronics”.¹ Supramolecular electronics bridges the gap between molecular electronics and bulk, ‘plastic’ electronics (Fig. 1). The latter is well established and the first polymer-based light-emitting diodes are now commercially available.² In the research field of molecular electronics, the properties of single molecules are investigated on the Ångstrom length scale and simple device structures have been demonstrated.³ Applications of single molecule devices are, however, hampered by orientational and conformational

motion of the molecule (thermal noise) and contact problems exist between molecule and electrode. Self-assembly is an attractive and efficient bottom-up strategy to position well-defined shape-persistent objects under thermodynamic control at predefined locations. Where bulk materials have limitations in the size of the “crystalline” domains which are typically smaller than 100 nm and single molecules have limitations in shape selectivity, it is proposed that self-assembled structures with the dimensions of 5–100 nm are the ideal building blocks. They combine smallest dimensions with 100% “crystalline” organization in the object. Bottom-up approaches have been reported for inorganic nanowires⁴ and carbon nanotubes⁵ and both show promising electrical characteristics.

In the self-assembly of π -conjugated systems, different specific interactions work simultaneously and the strength of the overall binding is the result of many cooperative processes.⁶ In most cases, combined secondary interactions are required to

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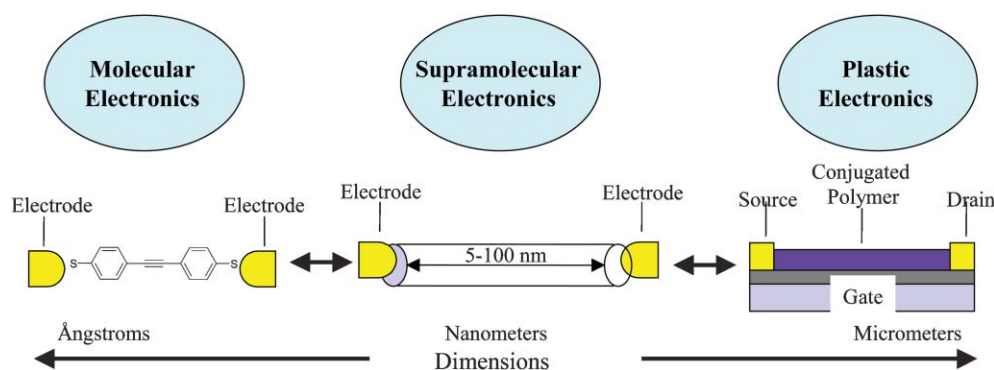


Fig. 1 Schematic representation illustrating the gap between molecular electronics and plastic electronics. Supramolecular electronics is an unexplored field with the aim of constructing and investigating supramolecular optoelectronic nanoarchitectures that are hooked up to electrodes.

obtain nanosized objects. Programmed self-assembly has mainly been controlled by using rod-coil block copolymers⁷ and supramolecular design rules.⁸ This feature article will focus on the most significant developments on how π -conjugated systems can be programmed to self-assemble into individual nanosized wires and what is required to use them in supramolecular electronics, *e.g.* (nanosized) field effect transistors (FETs), photovoltaic devices, light-emitting diodes (LEDs) and logic gates. The π -conjugated systems that will be discussed are π -conjugated polymers and their related oligomers. Polymers are polydisperse and often contain defects while oligomers have a monodisperse, well-defined chemical structure and can be purified relatively easily. This feature article starts with polydisperse π -conjugated segments and ends with monodisperse systems while examples will be given on how both systems have been organized into nanowires. Wires based on dyes,^{9,10} charge transfer salts,¹¹ and crystalline fibers from π -conjugated oligomers by physical vapor deposition¹² are beyond the scope of this article and the reader is referred to other reviews.

Self-assembled fibers based on polydisperse π -conjugated segments

Polyaniline (Fig. 2, 1) is unique among the family of conjugated polymers since it can be doped in a controlled way through reversible acid/base doping/dedoping processes. Polyaniline nanofibers have been constructed using

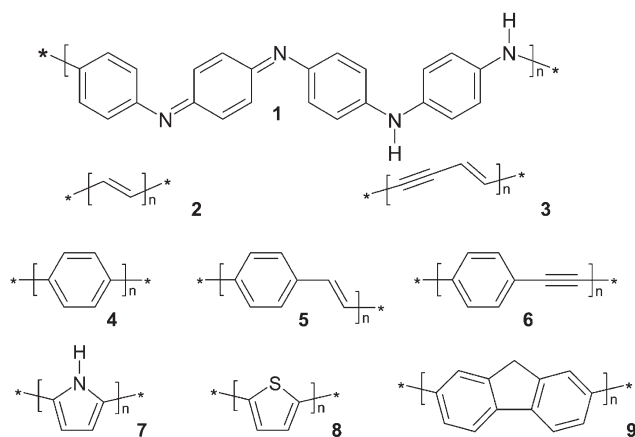


Fig. 2 π -Conjugated polymers that can form nanowires.

surfactants,^{13,14} or organogels¹⁵ as template¹⁶ for guiding the shape of the objects yielding micrometer long wires with diameters in some cases smaller than 100 nanometers. Electrospinning^{17,18} is another method to obtain fibers and can be applied to a variety of π -conjugated polymers.¹⁹ Electrochemical polymerisation,²⁰ interfacial polymerisation²¹ and flash welding,²² in the absence of a template have also been reported. These fibers could be used as chemical sensors.^{23–25} Interestingly, seeding the polymerisation of aniline with even very small amounts of (in)organic fibers could change the morphology to almost exclusively fibers.²⁶ Helical fibers have been obtained using camphor sulfonic acid, an oxidant and aniline oligomers to accelerate the polymerisation reaction.²⁷ In most of the examples described above, however, wires with a diameter larger than 100 nanometers were obtained.

Polyacetylene (PA, Fig. 2, 2) wires have been prepared by exposure of acetylene to a Ziegler–Natta catalyst.²⁸ After several treatments, single PA wires were obtained that were deposited on an electrode pattern having AuPd or Pt electrodes with 100 nm distance. After doping with iodine, a hole mobility of 10^{-5} cm²/Vs was measured for a single PA nanofiber. Helical PA could be produced using a chiral nematic liquid crystal as a template.²⁹ Well-dispersed helical fibers were obtained after soaking a small piece of a PA film in a non-ionic surfactant in DMF.³⁰ One isolated fiber could be deposited on top of 2 mm spaced Pt electrodes. After doping with iodine a conductance of 8×10^{-7} S/cm was measured at room temperature.

Polydiacetylene (Fig. 2, 3) wires have been drawn on a surface using a scanning tunneling microscope (STM) tip (Fig. 3).³¹ A self-assembling diacetylene compound was adsorbed on graphite and subsequently polymerized by a probe tip allowing spatial precision of about 1 nm. This method is very promising for the construction of interconnecting nanostructures and circuits.

In another very attractive approach, Electrochemical Dip-Pen Nanolithography (E-DPN) has been used to fabricate polyaniline, polypyrrole, oligothiophene,³² polyphenylenevinylene³³ and polythiophene (Fig. 2, 1, 5, 7, 8) wires on semiconducting and insulating surfaces in the sub-100 nm regime.^{34,35} PolyEDOT (PEDOT, Fig. 5, 11) wires could be constructed having less than 100 nm dimensions by electrochemical polymerization of 3,4-ethylenedioxythiophene

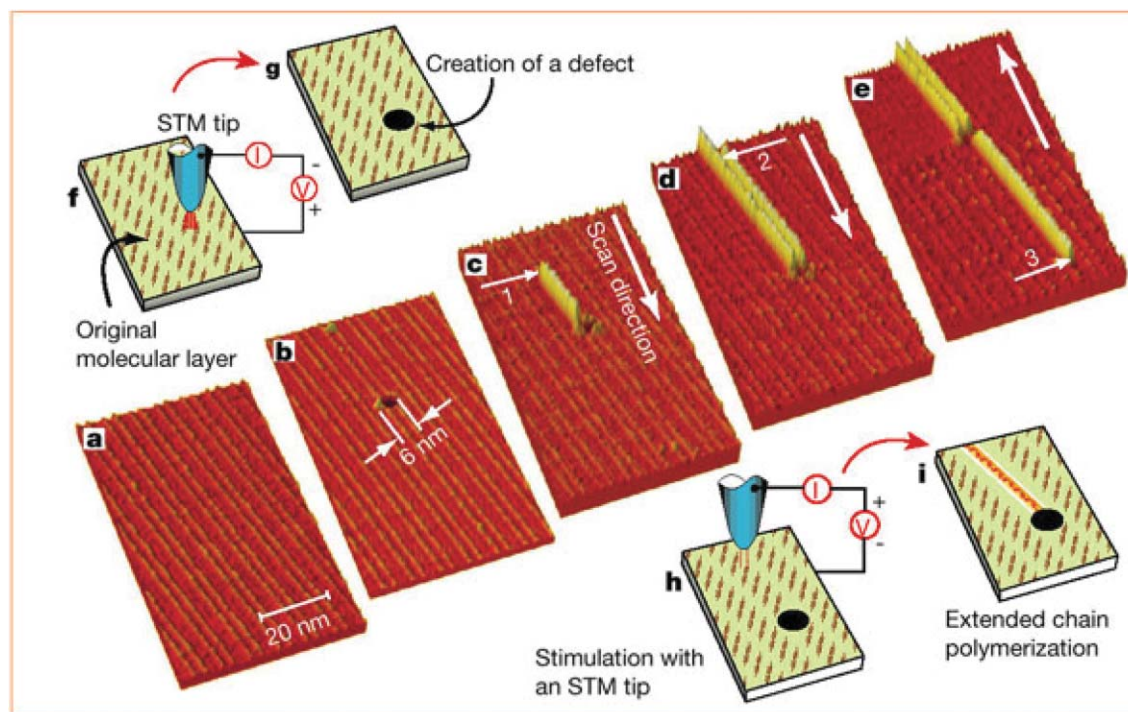


Fig. 3 Creation of polyacetylene fibers using an STM tip. (Reprinted with permission from Ref. 31. Copyright 2001 Nature.)

(EDOT) at the AFM tip/substrate (Fig. 4).³⁶ This fabrication technique could be very useful for the creation of complicated structures using multiple inks.

Self-assembled polydiacetylenes have been formed in silica as a template and a polymerizable diacetylene surfactant as monomer while polypyrrole (Fig. 2, 7) nanowires bundles have been fabricated using a pyrrole surfactant in a silicate template, synthesized using tetramethoxysilane in the sol-gel process.³⁷ After silicate formation, pyrrole was polymerised in one-dimensional silicate nanochannels by FeCl_3 , yielding polypyrrole nanofibers. Similar approaches have been used for creating polydiacetylenes,^{38,39} and polythiophene⁴⁰ wires and interestingly, the polymer chains could be liberated by dissolving the silicate in HF. Templates like the track-etched membranes⁴¹ or surfactants⁴² can also be used to construct π -conjugated wires.

Poly(3-hexylthiophene) (P3HT, Fig. 5, 13) has been copolymerized with polystyrene by McCullough and co-workers.⁴³ Nanowires, in which the P3HT wires are embedded in the polystyrene matrix, could be obtained from block-copolymer **10** (Fig. 5) by slow evaporation from toluene due to

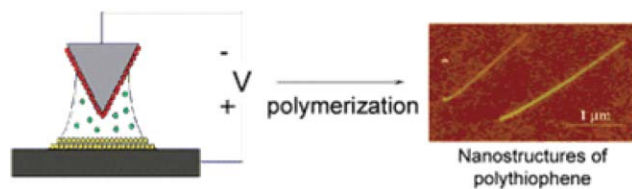


Fig. 4 Polythiophene wires constructed by Electrochemical Dip-Pen Nanolithography. (Reprinted with permission from Ref. 36. Copyright 2002 American Chemical Society.)

the immiscibility of the blocks. Under accelerated evaporation conditions, using chloroform as solvent or casting from toluene under a stream of nitrogen, nanowire formation was suppressed. Oxidized films obtained *via* I_2 doping showed a drop in conductivity when the ratio between the P3HT and polystyrene block was decreased.

Bjørnholm and coworkers have constructed polythiophene nanowires from amphiphilic thiophene polymer **12** (Fig. 5).⁴⁴ These polymers are able to form Langmuir films, which fold into wire-like structures when compressed beyond the collapse point. Bundles of wires could be placed between gold

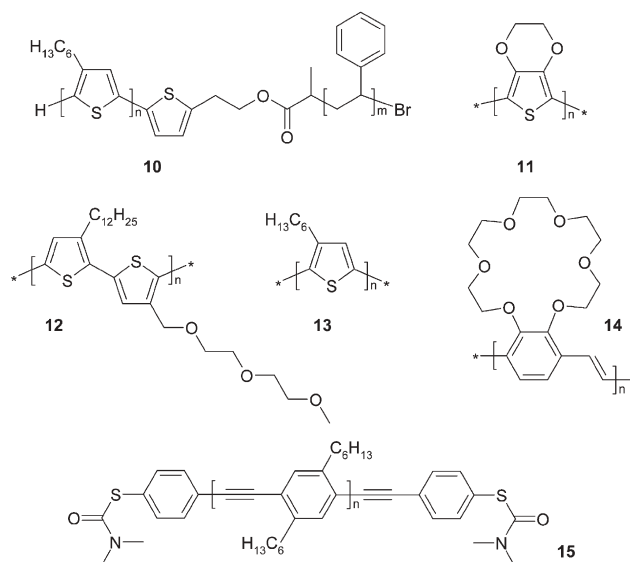


Fig. 5 Functionalized π -conjugated polymers that can form nanowires.

electrodes, separated by a 50 μm gap. The room-temperature conductivity of the undoped wires was less than 10^{-5} S/cm, while in the doped state a value of 40 S/cm was reached.

Leclère, Lazzaroni and coworkers have studied the self-assembly properties of a variety of π -conjugated polymers⁴⁵ and copolymers⁴⁶ including poly(phenylene) (PP, Fig. 2, 4), poly(phenylene ethynylene) (PPE, Fig. 2, 6), polyfluorene (PF, Fig. 2, 9) or poly(indenofluorene) as the rod segment and polydimethylsiloxane, poly(ethylene oxide) or polystyrene as the coil segment. In most cases, fibrillar objects were obtained after deposition from solvents in which the compounds are molecularly dissolved. Commonly, the fibers are ribbon-like as their width is significantly larger than their height. In the case of PPE–polydimethylsiloxane copolymers, nanowires were obtained having a constant height and width in which the chains are packed in a head to tail fashion with their rod segments parallel to each other.⁴⁷ Copolymers of polyfluorene with low molecular weight poly(ethylene oxide) (PEO) segments (16, Fig. 6) formed nanoribbons from tetrahydrofuran (THF), having constant width of 11 nm and a height of 1 nm on mica as a possible result of π – π interactions between the conjugated segments and the interaction of the PEO with the mica (Fig. 6).⁴⁸ Copolymers with higher average volume of PEO lead to untextured aggregates. When toluene was used instead of THF, ribbons were observed for these co-polymers. In both solvents the block copolymers are highly soluble, indicating that slow evaporation in the case of toluene (higher boiling point) favors the formation of organized assemblies while rapid evaporation in the case of THF leads to kinetically trapped aggregates. Remarkably, nanoribbons were formed on graphite, a more apolar substrate, while in the case of the triblock copolymer a completely different morphology was obtained.

Poly(phenylenevinylene) (PPV, Fig. 2, 5) with crown-ether substituents (14, Fig. 5) can be organized into nanoribbons on carbon coated copper grids by complexation of potassium.⁴⁹ The length of the ribbons increased with time. End-functionalised poly(phenyleneethynylene) polymer 15 (Fig. 5) can be organized in ribbons on mica from a THF solution.^{50,51} The polymers are fully extended and oriented with the conjugated backbone parallel to the substrate and perpendicular to the

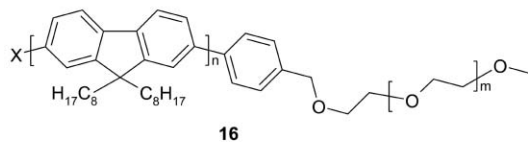


Fig. 6 AFM image of a thin deposit of polyfluorene–poly(ethylene oxide) block copolymer **16** on mica from THF. (Reprinted with permission from Ref. 48. Copyright 2004 Wiley VCH.)

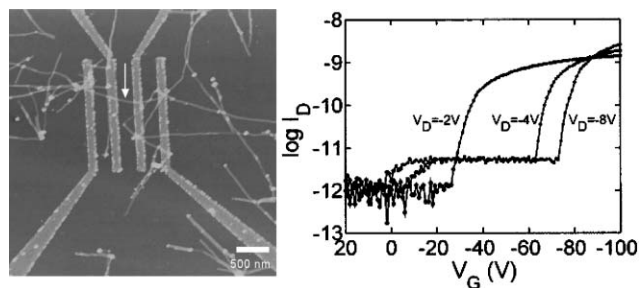
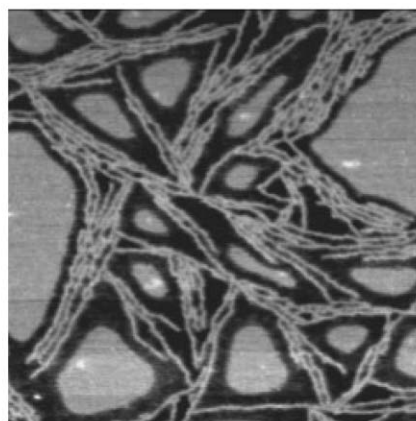


Fig. 7 AFM image of a single P3HT (**13**) fiber (indicated by the arrow) across four electrodes (left panel) and the semilog plot of the drain current *versus* the gate voltage at different drain voltages (right panel) for the single nanofiber transistor. (Reprinted with permission from Ref. 54. Copyright 2003 Wiley-VCH.)

long axis of the ribbons. On graphite, these polymers form nematic-like molecularly-ordered monolayers.⁵² Templated self-assembly of poly(phenyleneethynylene) (PPE, Fig. 2, 6) is possible by drop-casting a dilute solution of a PPE polymer into the pores of anodiscs.⁵³ After removal of the template nanosized towers, wires and tubes were obtained which have a high aspect ratio.

Although all these block copolymers can create nano-sized wires, the isolation of the individual wires and placing them between electrodes remain an enormous challenge. So far, single nanowires are only tested in devices when prepared from well-defined homopolymers.

Merlo and Frisbie have reported the electrical conductance of nanofibers of P3HT (Fig. 5, 13) as a function of the gated-induced charge (Fig. 7).⁵⁴ The nanofibers were deposited on SiO₂/Si substrates by casting from dilute *p*-xylene solutions in which the polymer is self-assembled. Analysis of the micrometers long nanofibers revealed height of 3–7 nm and widths of approximately 15 nm. A field effect transistor geometry having gold electrodes as source and drain contacts with a gap of typically 1 μm and hexamethyldisilazane (HMDS) SiO₂/Si as the gate yielded hole mobilities as high as 0.06 cm²/Vs with on/off current ratios greater than 10³. The dependency of the charge mobility of devices of P3HT prepared from chloroform solution with electrode spacings from 5 nm to 20 nm was



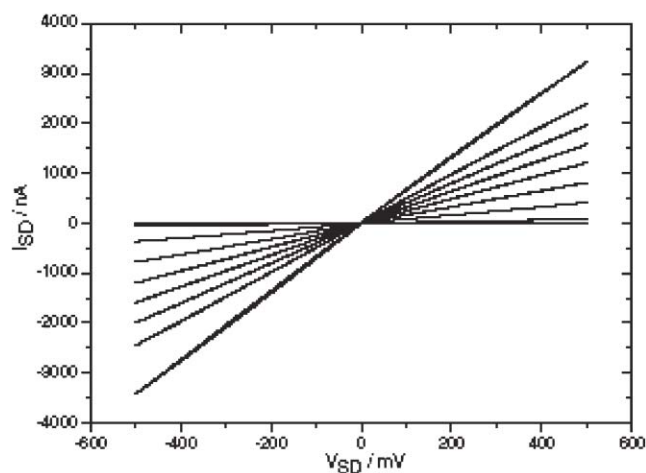
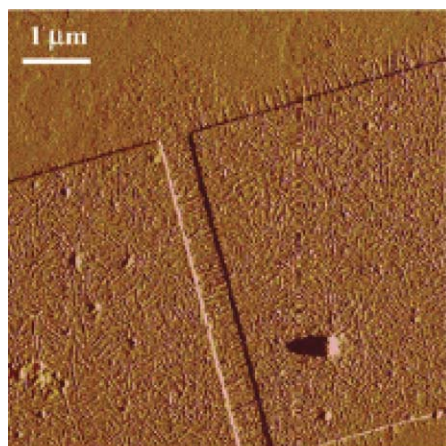


Fig. 8 AFM image of a device prepared by dropcasting a solution of P3HT (**13**) in *p*-xylene applying an ac voltage (2 V, 102 kHz) resulting in aligned nanofibers (left panel). Source drain current versus source drain voltage at different gate voltages for the aligned fibers (right panel). (Reprinted with permission from Ref. 55. Copyright 2004 Institute of Physics.)

studied by Mas-Torrent and coworkers (Fig. 8).⁵⁵ The mobility decreased as the electrode spacing was made smaller, which probably indicates that the transport properties on closely spaced electrodes are dominated by the contacts. Interestingly P3HT fibers in *p*-xylene could be aligned between the electrodes by applying an ac field. Films of aligned fibers showed mobilities as high as 0.04 cm²/Vs.

As can be concluded from this section, polydisperse π -conjugated segments are able to form self-assembled nanowires that have often a relatively large and irregular diameter. Some wires have already been sandwiched between electrodes resulting in the first prototype nanosized field effect transistors. The use of probe tips for connecting such nanosized devices is a very promising approach in making logic gates, however, the properties of the constructed wires have not yet been measured.

Self-assembled fibers based on monodisperse π -conjugated segments

In contrast to polydisperse π -conjugated polymers, well-defined oligomers can serve as ideal building blocks of stacked aggregates with perfectly tuned π - π interactions. These molecules are often liquid-crystalline in the bulk, but self-assemble into individual stacks in dilute solution. The solubilizing side chains act as an insulating layer, yielding, in principle, single cables ready to be used as supramolecular electronic wires. This section describes two classes of self-assembled oligomers. First, molecules that are stacked by

hydrogen bonding and π - π interactions are discussed and secondly, systems that self-assemble by solely π - π interactions or in combination with hydrophobic interactions will be presented.

Self-assembly by π - π and hydrogen bonding interactions

Bisurea appended oligothiophenes (**17**–**18**) have been prepared and in tetralin and 1,2-dichloroethane these compounds self-assemble into elongated fibers by hydrogen bonding (Fig. 9).⁵⁶ Electron microscopy and X-ray diffraction studies revealed that the fibers have a lamellar structure, in which the molecules are arranged as 1D ribbons with their long molecular axes parallel to each other and they make a small angle with the normal of the lamella. Pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) experiments showed high charge carrier mobility of at least 0.001 cm²/Vs for **17** and 0.005 cm²/Vs for **18**, due to the H-bond assisted π -stacking of adjacent thiophene oligomers. The two-dimensional self-assembly of these bisurea-*n*-thiophene oligomers has also been studied on solid substrates.⁵⁷ On SiO₂, micrometer-sized fibers are present, in which the thiophenes adopt an upright orientation whereas they lie down flat on graphite. Scanning tunneling spectroscopy (STS) and scanning tunneling microscopy (STM) showed that the thiophenes were π -stacked on a solution/graphite interface, indicating that the observed zero conductance gap is considerably smaller than for an isolated oligothiophene.⁵⁸ It will be of interest to test such fibers from molecules with a longer π -fragment.

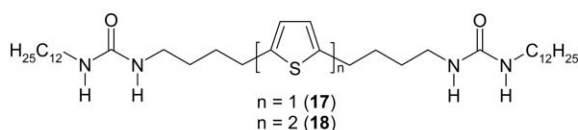


Fig. 9 Structure of bisurea appended thiophene oligomers and electron micrographs of the lamellar fibers of **17** (A) and **18** (B). (Reprinted with permission from Ref. 56. Copyright 1999 Wiley-VCH.)

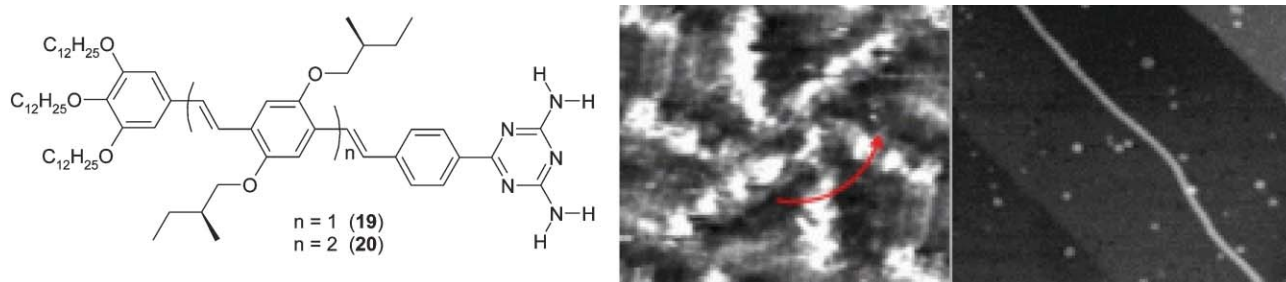


Fig. 10 Molecular structures of **19** and **20** (left hand side), STM image of **20** ($18.4 \times 18.4 \text{ nm}^2$, $V_{\text{set}} = -0.50 \text{ V}$, $I_{\text{set}} = 0.45 \text{ nA}$) monolayers (picture in the middle) and AFM image of drop cast **20** solution in heptane ($5 \times 10^{-5} \text{ M}$) on HOPG (right hand side picture, size $604 \times 604 \text{ nm}^2$). (Reprinted with permission from Ref. 59. Copyright Wiley-VCH.)

We studied oligo(*p*-phenylenevinylene) (OPV) derivatives bearing a hydrogen-bonding diaminotriazine headgroup. These molecules can form hexameric π -conjugated rosettes that self-assemble into chiral tubular objects (Fig. 10).⁵⁹ The OPV trimer and tetramer (**19** and **20**) are equipped with a tridodecyloxy wedge as end group and substituted with two or four enantiomerically pure (*S*)-2-methylbutoxy side chains on the OPV backbone. Scanning tunneling microscopy (STM) experiments in collaboration with the group of S. De Feyter and F. De Schryver show that hydrogen bond formation exerted by the diaminotriazine moieties leads to chiral hexameric macrocycles at the solid-liquid interface (Fig. 10).

These cycles further organize into aggregates in solution as is demonstrated by UV-vis, fluorescence and circular dichroism (CD) spectroscopy. On a graphite surface micrometer long tubules were formed with heights of 6.4 nm (Fig. 10). This thickness is in agreement with the Small Angle Neutron Scattering (SANS) data and corresponds well to the diameter of the hydrogen bonded hexamers found by STM, pointing to fibers consisting of stacked rosettes.⁵⁹

The complementarity of the hydrogen bonding unit in perylenebisimide, which is an electron acceptor, with the diaminotriazine OPV units, which are electron donors, yielded supramolecular donor-acceptor-donor triads **21** (Fig. 11).

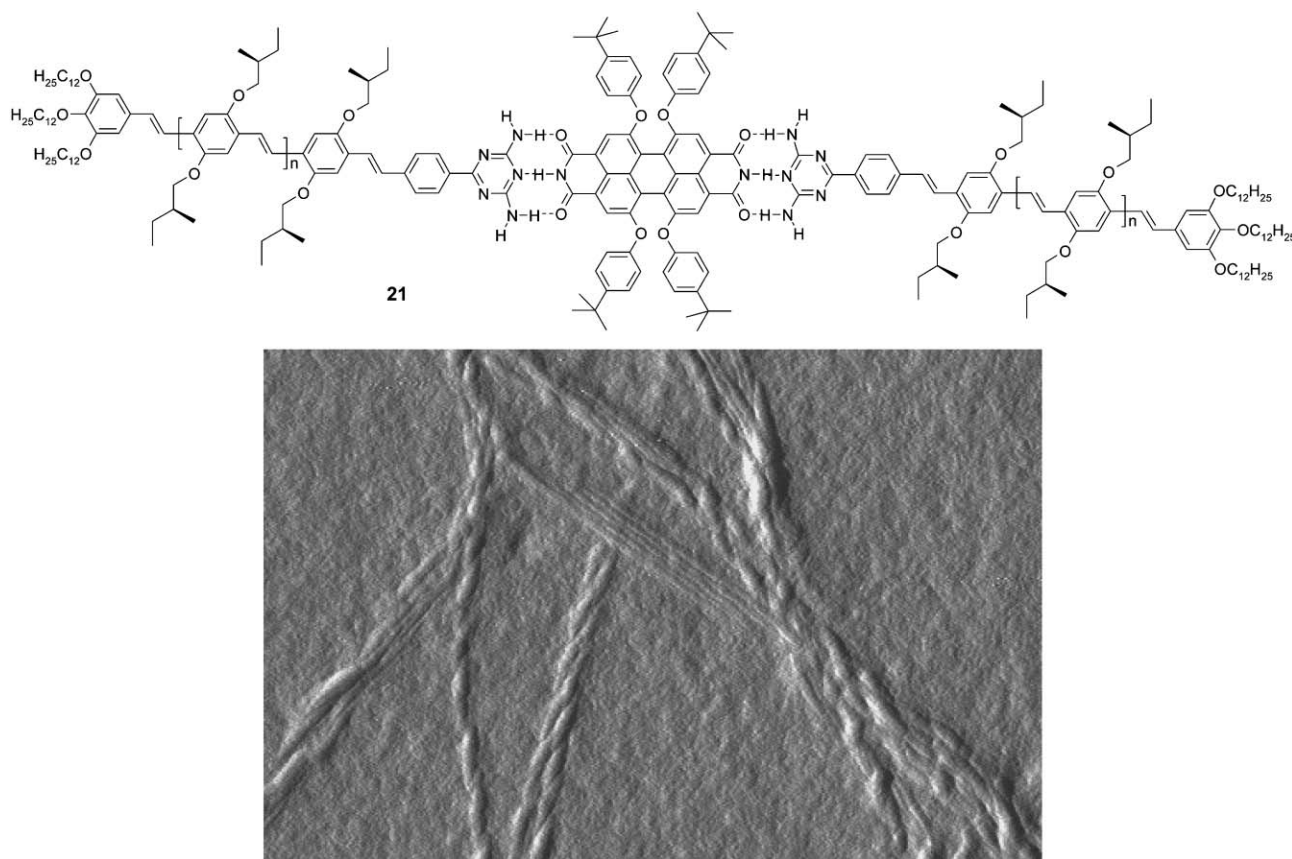


Fig. 11 Hydrogen-bonded triad consisting of one perylenebisimide electron acceptor sandwiched between two OPV electron donors and tapping mode AFM image ($715 \times 475 \text{ nm}$) of hydrogen bonded triad **21** upon spin-coating from MCH ($c = 1 \text{ wt } \%$) on a glass slide. (Reprinted with permission from Ref. 60. Copyright American Chemical Society).

These p–n–p type junctions were created and studied in collaboration with the group of F. Würthner.^{60,61} The hydrogen-bonded triads form helical columnar stacks in apolar solvent as shown by UV-vis, fluorescence and CD titration experiments.⁶⁰ Efficient electron transfer takes place from the electron donor (OPV) to the electron acceptor (perylenebisimide) in the aggregates. AFM measurements showed the appearance of chiral, rod-like aggregates with a length of several micrometers and a width of the smallest resolved fibers of about 7 nm. The large fibers are presumably composed of multilayers having a width of multiples of 7 nm that coil into chiral aggregates (Fig. 11). This concept was extended to a series of OPVs of different length.⁶² Temperature and concentration dependent results clearly indicate that the stability of the donor–acceptor aggregates increases with OPV conjugation length, due to the possibility of having more π – π stacking interactions between the building blocks.

The supramolecular interactions were strengthened by increasing the number of hydrogen-bond interactions. Three hydrogen-bonded oligo(*p*-phenylenevinylene)s equipped with self-complementary ureido-triazazine units that differ in conjugation length (an OPV trimer, tetramer **22** and pentamer) have been synthesized (Fig. 12).⁶³

¹H-NMR and photophysical measurements show that these OPV oligomers grow hierarchically in an apolar solvent; initially dimers are formed by hydrogen bonds that subsequently develop into stacks by π – π interactions of the phenylenevinylene backbone with induced helicity *via* the chiral side chains. SANS measurements show the formation of rigid cylindrical objects. Stacks of **22** have a persistence length of 150 nm and a diameter of 6 nm. The trimer analogue of **22** shows rigid columnar domains of 60 nm with a diameter of 5 nm. Temperature and concentration variable measurements show that the stability of the stacks increases with the conjugation length as a result of more favorable π – π interactions. The stability of the stacks is probably the consequence of many reinforcing bonds each of which is relatively weak. The formation of any of these stabilizing bonds very much depends on whether adjacent bonds are also made. Mixed columnar stacks of hydrogen-bonded oligo(*p*-phenylenevinylene) oligomers were formed, where oligomers of longer conjugation length were incorporated into

stacks to act as energy acceptors. Ultra-fast energy transfer from the shorter oligomers to the longer oligomer in these stacks in solution was observed in collaboration with the group of R. Friend.⁶⁴ This concept could be used in light emitting color tuning to show that the recognition sites are electro- and photochemically inert. The transfer of the single OPV cylinders from solution to a solid support as isolated objects is only possible when specific concentrations and specific solid supports are used as investigated by AFM.⁶³ Numerous micrometers single long fibers are found in cast films of this OPV on graphite (Fig. 13) with a uniform height of 5.2 nm and a persistence length of 125 nm. At higher concentrations an intertwined network is formed while at low concentrations ill-defined globular objects are observed. Molecule–surface interactions are also crucial to successfully transfer the supramolecular stack present in solution to a solid support (inert surfaces: graphite and silicon oxide). When the molecule–molecule interactions present in the supramolecular stacks in solution are perturbed by stronger molecule–surface interactions (attractive surfaces: gold), the stacks cannot be transferred to the surface. Repulsive surfaces (mica and glass) give rise to clustering of stacks due to the minimization of the contact area between the stack and the support, resulting in lamellar arrays of stacks. Because the concentration and the temperature of the cast solution also determine the equilibrium between individual molecules and the supramolecular stack, it is obvious that many variables control the successful transfer of stacks from solution to surfaces. Currently, the performance of the wires in nanosized electronics is under investigation.

Ajayaghosh and coworkers have reported OPV derivatives that thermoreversibly self-assemble in a series of hydrocarbon solvents from single OPV molecules into fibers and ultimately into an entangled network structure (Fig. 14).⁶⁵ In a comparative study, it was shown that the gelation was cooperative and strongly dependent on the choice of hydrogen bonding motif, alkoxy side chain length and the conjugation length. SEM, X-ray diffraction and IR on the gel revealed an entangled network filament up to micrometer lengths and 100–150 nm in width consisting of well-ordered lamellae of stacked molecules positioned by hydrogen bonds (Fig. 14).

OPVs bearing chiral side chains provided gels with helical morphologies.⁶⁶ Detailed SEM and AFM analyses showed the

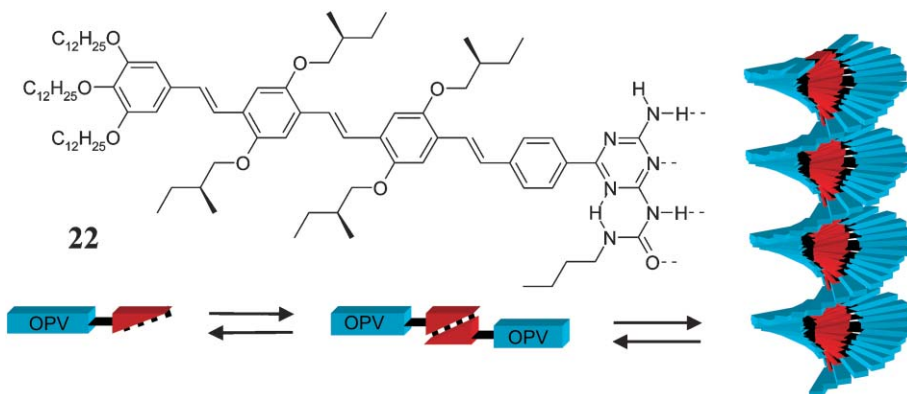


Fig. 12 OPV tetramer functionalised with a hydrogen-bonding ureidotriazine unit **22** and a schematic representation of a helical stack formed by this molecule. Bars represent the oligo(*p*-phenylenevinylene)s and triangles represent the hydrogen-bonding ureidotriazine units.

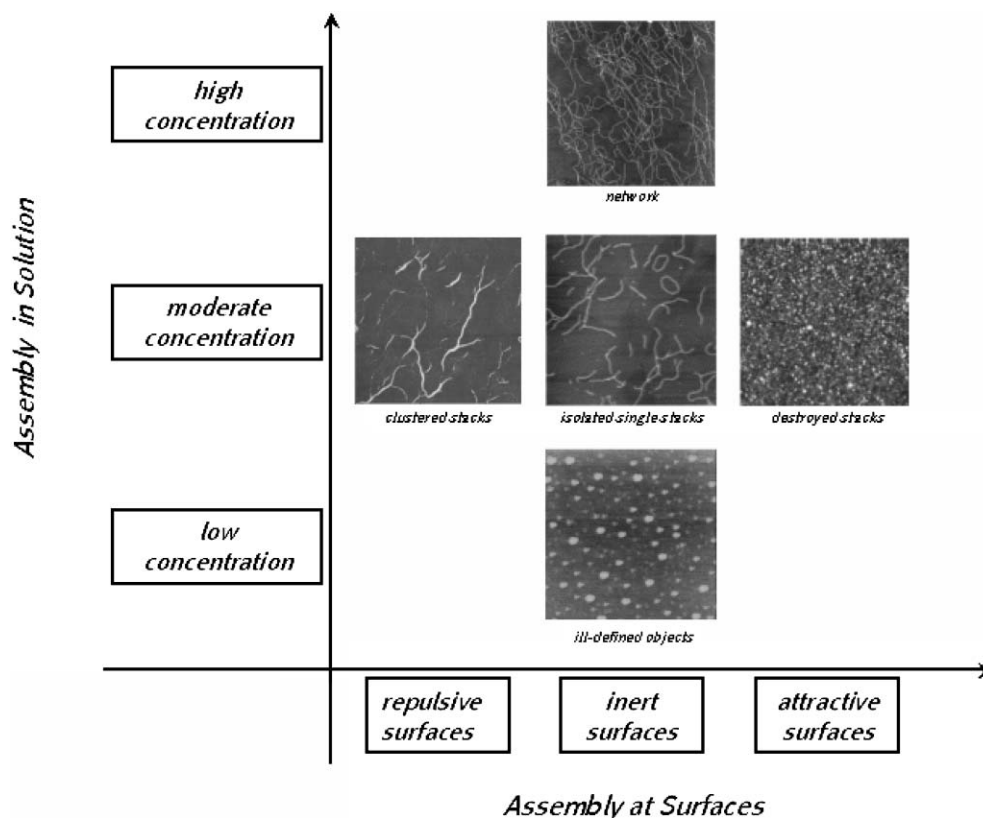


Fig. 13 Plot showing the dependence of morphology on both the solution concentration and surface type. Depicted are tapping mode AFM images on glass (repulsive surface), graphite (inert surface) and gold (attractive surface). (Reprinted with permission from Ref. 63. Copyright American Chemical Society.)

hierarchical growth of helical nanotapes and coiled-coil ropes (Fig. 14). The assemblies could be used for light-harvesting applications and energy transfer to an incorporated dye.⁶⁷ Efficient energy transfer was observed in a xerogel film, doped with a Rhodamine B dye, in which OPV fluorescence was almost completely quenched. The crucial role of the supramolecular OPV organization in energy transfer was illustrated with a temperature-dependent study on a mixed xerogel, in which the reversible gel formation with temperature was used to switch the energy transfer process on and off.

Self-assembly by π - π interactions only

We studied the self-assembly of chiral thiophenes **24**⁶⁸ containing ethylene oxide side chains in solution and in the solid state in collaboration with the group of R. Lazaronni and the group of W. Feast (Fig. 15).⁶⁹ Based on circular dichroism studies, in polar solvents like n-butanol and water chiral aggregates are formed which are not fiber-like.⁷⁰ Remarkably, when deposited from molecularly dissolved solutions like THF or toluene helical fibers were obtained. On graphite nanowires were formed while on mica platelets were generated. Surprisingly both thiophene enantiomers formed left-handed helices on silicon while the CD measurements on these drop-cast films revealed mirror images for both enantiomers. This observation was dependent on the hydrophilicity of the silicon. Furthermore, the achiral sexithiophene, lacking the methyl

group at the asymmetric center, did not form helical aggregates.

Diblock molecules containing an OPV trimer as the rod segment and a poly(ethylene oxide) as the coil segment have been reported by Wu and coworkers (**25**, Fig. 16).⁷¹ These polymers form island-like morphologies on mica when cast for several hours. Remarkably, when the cast films were kept in a saturated atmosphere of water at room temperature for 3 weeks, ribbons were obtained. The authors propose that this morphology alteration is caused by the change of the hydrophilicity of the mica PEO interface.

Yu and co-workers have synthesized similar copolymers with different lengths of OPVs as the rod-block and poly(propylene oxide) and poly(ethylene oxide) as the coil-block (**26–28**, Fig. 16).^{72,73} These polymers self-assemble into cylindrical micelles in solution and in cast films. The micelles have a cylindrical OPV core surrounded by the coil-block corona and readily align with each other to form parallel packed structures when mica is used as the substrate. The same group also reported a new class of rod-rod diblock copolymers of oligothiophenes-co-oligo(phenylenevinylene)s.⁷⁴ Because of the expected difference in the Flory-Huggins χ parameter, which determines the degree of microphase separation, these polymers phase separate and layered stripes were observed when a hexane/chloroform mixture was placed on a carbon-coated copper or SiN grid. When pure chloroform was used as the solvent an intertwined network was obtained. Small Angle X-ray Scattering (SAXS) measurements indicate a layered

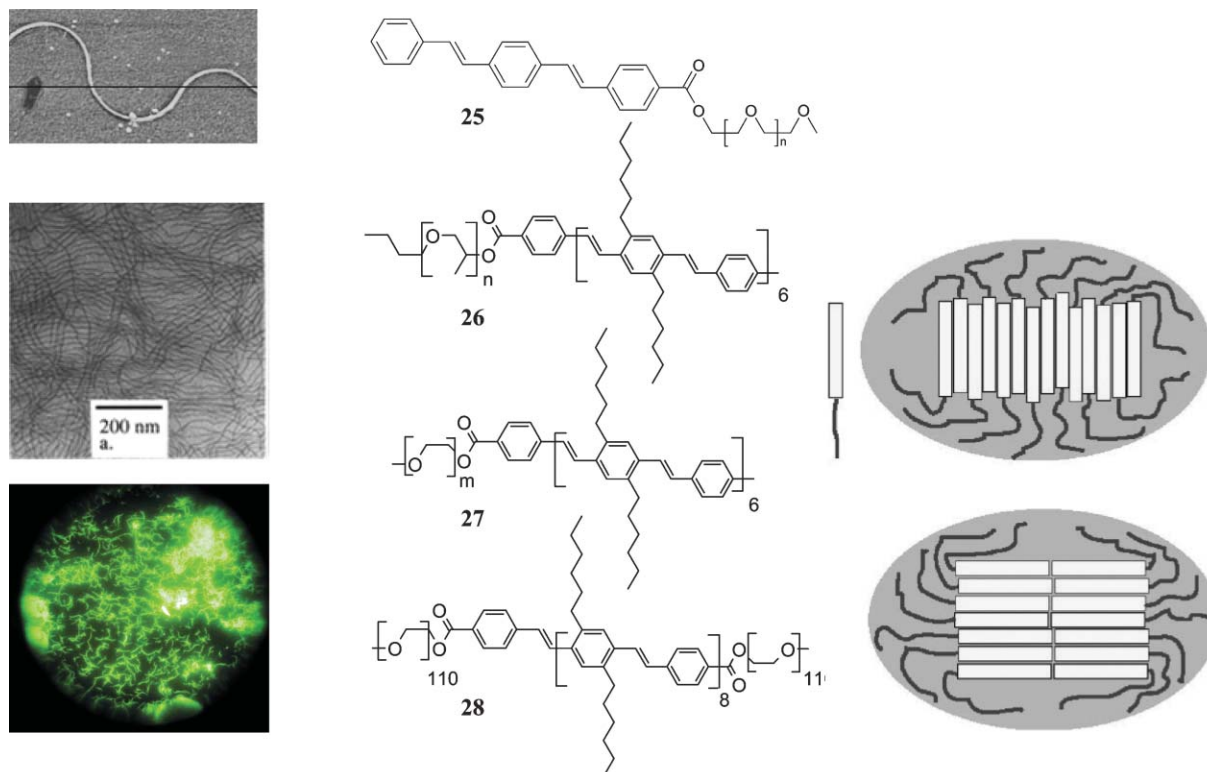


Fig. 16 Chemical structure of diblock molecule **25** that forms nanoribbon on mica in which the molecules form a bilayer (Reproduced with permission from Ref. 71. Copyright 2003 Chemical Society of Japan) and the fiber formation by rod-coil copolymers **26–28** based on OPVs. (Reprinted with permission from Ref. 73. Copyright 2004 Wiley-VCH.)

same group has also synthesized dendron rod-coil molecules that contain a conjugated segment of oligothiophene, OPV and oligo(phenylene). Despite the structural difference all three molecules self-assemble into high aspect ratio ribbon-like nanostructures on mica.⁷⁶ The authors proposed that the ribbons consist of two molecules held together by hydrogen bond interactions in the hydroxyl rich dendrons that further self-assemble in ribbons by π - π stacking of the conjugated segments. Interestingly, in the case of an oligothiophene segment a 3 orders of magnitude increase in the conductivity of iodine doped films was observed. Furthermore, electric field

alignment of the assemblies was possible, creating arrays of self-assembled nanowires on a device substrate.

Müllen and coworkers synthesized polyphenylene dendrimers with various cores such as tetraphenylmethane or biphenyl. In collaboration with the group of S. De Feyter and F. De Schryver, they found that different generation dendrimers can self-assemble into micrometer long fiber nanofibers on HOPG when dropcast from dichloromethane in which the dendrimers are highly soluble.^{77,78} When the solvent evaporation was extended over several days, monolayers were observed on HOPG while on mica, globular

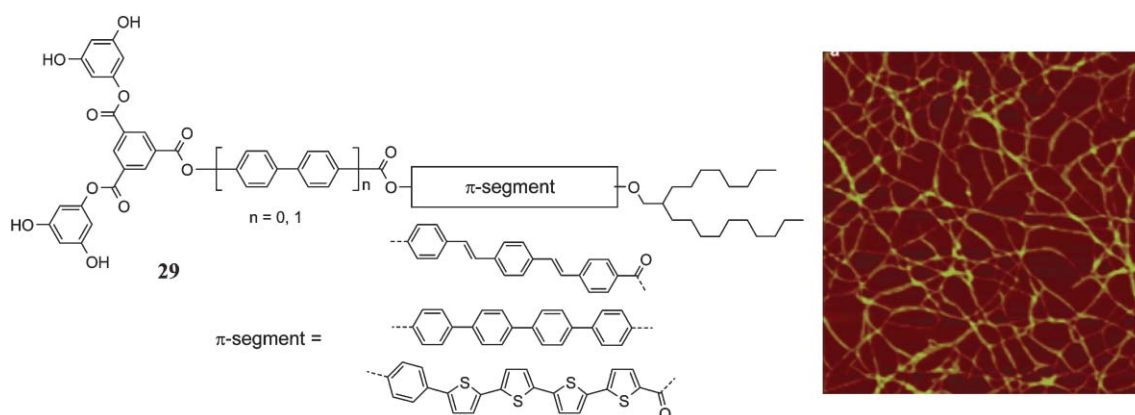


Fig. 17 Chemical structure of the dendron rod-coil molecules **29** and the formation of nanoribbons. (Reprinted with permission from Ref. 76. Copyright 2004 American Chemical Society.)

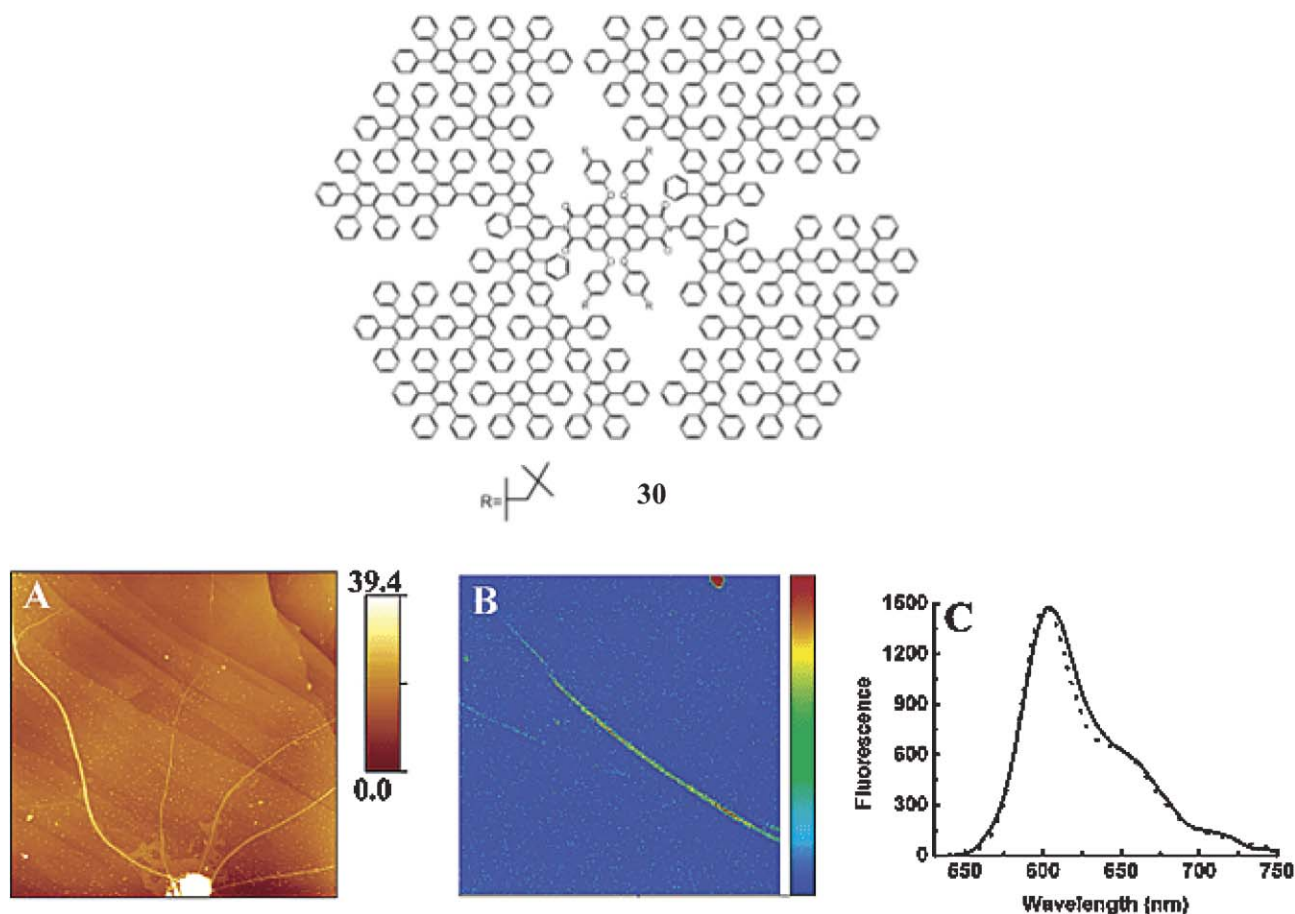


Fig. 18 AFM image and confocal fluorescence image and the emission spectrum of dendrimer **30**. (Reprinted with permission from Ref. 79. Copyright 2003 American Chemical Society.)

aggregates were formed. The authors propose two possibilities for the nanofiber formation. Dendrimer aggregates preform in solution, deposit and grow into nanofibers on the substrate, or dendrimer molecules could nucleate and grow directly. When the dendrimers were functionalized with one or multiple peryleneimide chromophores, fluorescent nanofibers could be constructed (**30**, Fig. 18).⁷⁹ The morphology of the fibers highly depends on the substrate, solvent and preparation method. Depending on the chromophore position in the dendrimer, isolated or dimer like chromophore emission was detected. Furthermore, fibers of mixed dendrimers could be constructed having a homogeneous composition.

Fukushima, Aida and coworkers have reported an amphiphilic hexa-peri-hexabenzocoronene that self-assembles in THF into nanotubes that have an aspect ratio greater than 1000 and are 14 nanometers wide (**31**, Fig. 19).⁸⁰ The walls of the tubes consist of helical arrays of π -stacked coronenes covered by hydrophilic glycol chains. Interestingly, an individual nanotube could be positioned across Pt nanogap electrodes (180 nm) on a SiO₂ substrate. The tube was essentially insulating, however, after oxidation with NOBF₄ it revealed an I–V profile with an ohmic behavior having a resistance of 2.5 megaohm at 285 K. This value is comparable to inorganic semiconductor tubes.

Conclusions and perspectives

This work demonstrates that it is possible to program π -conjugated molecules into self-assembled nanowires in solution and in the solid state. All π -conjugated molecules belong to the class of p-type semiconductors, showing that it remains a challenge to develop n-type wires. Using the supramolecular design rules nanowires can be created from almost any polymeric and oligomeric π -conjugated system. In the case of oligomers it is even possible to construct individual wires having a uniform diameter of one molecule thickness. The construction of wires on a substrate is possible by self-assembly in solution or during the deposition. The latter approach has the disadvantage that there is no control over size and orientation. The transfer of the supramolecular stacks from solution to a solid support is a very delicate process. A comprehensive knowledge of all intermolecular interactions gives rise to controlled transfer of π -conjugated assemblies to specific surfaces. As can be concluded from this review, there is no methodology to connect nanowires to electrodes. However, in some cases wires could be hooked up between electrodes and a current was measured for doped wires and wires based on polymers.

There are a large number of very appealing targets that should be reached before supramolecular electronics can serve

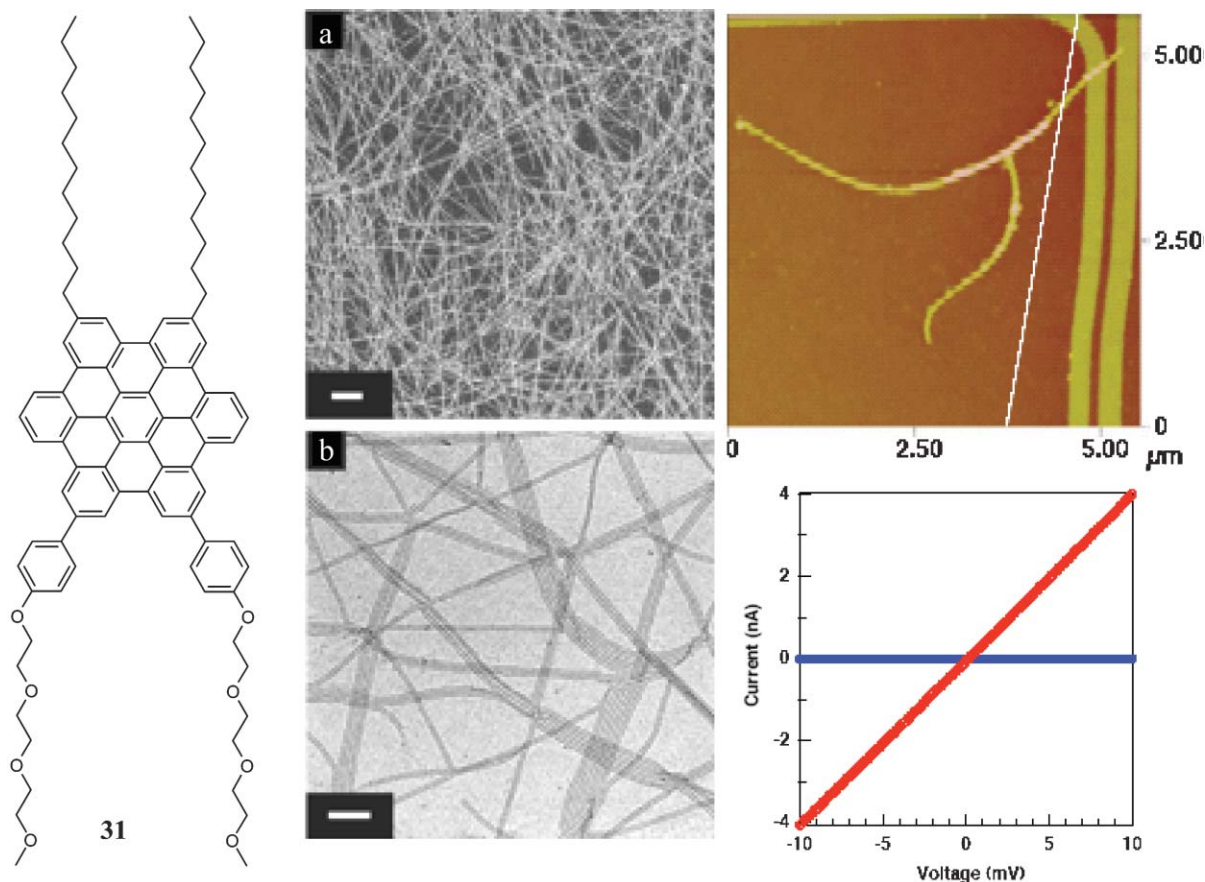


Fig. 19 Amphiphilic hexa-peri-hexabenzocoronene **31** which forms tubes that can be placed between two electrodes. (Reprinted with permission from Ref. 80. Copyright 2004 American Association for the Advancement of Science.)

as an attractive alternative for carbon nanotubes and inorganic wires. The lack of control to exactly position chromophores with nanometer precision and the difficulty in controlling the dimensions of supramolecular nanostructures will be the challenges to tackle to improve this relatively new discipline. The use of templates like biomolecules could be one attractive approach to solve these problems since these molecules are monodispersed and the position of units is well defined.⁸¹ Another issue is the robustness of non-covalent interactions, which are often temperature and solvent sensitive. Recently, several new approaches have been reported to fixate, polymerise self-organized π -conjugated systems to obtain more robust nano-objects.^{82,83} Finally, the bottom-up approach does not produce designed, interconnected patterns that are necessary for building electronic devices. This problem exists also for carbon nanotubes and inorganic wires and at a certain point this approach has to be linked with the top-down approach. As shown in this review, soft lithography or dip-pen lithography in combination with self-assembly can overcome this problem. Ideally it would be a dream to self-assemble all components at once like nature does in the case of, for example, living cells. Recently, the first step in this direction was reported in the orthogonal self-assembly of p- and n-type fibers.⁸⁴

This work shows that self-assembled π -conjugated systems can serve as a beautiful starting point in the search for

supramolecular electronics, but as in the case of carbon nanotubes and inorganic wires a number of challenging problems have to be resolved first.

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