

Towards supramolecular electronics

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Abstract

We have demonstrated that it is possible to program π -conjugated molecules to self-assemble into cylindrical aggregates in solution. By incorporating energy or electron traps in our stacks, energy and electron transfer processes in these one-dimensional assemblies have been studied in solution. The transfer of the single OPV cylinders from solution to a solid support as isolated objects was only possible when specific concentrations and specific solid supports were used. So far, however, we have not been able to measure any current through our fibers.

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1. Introduction

In this paper, we will summarize our results on the construction of supramolecular assemblies in the 10–100 nm length scale that act as optoelectronic components. In the future, we would like to connect these assemblies to electrodes to construct supramolecular electronic devices (Fig. 1) [1]. Such systems could serve as an alternative for devices based on carbon nanotubes [2] or inorganic wires [3]. At the moment, there is no methodology to connect supramolecular structures to electrodes. However, this will be crucial for the success of supramolecular chemistry

in the field of nanotechnology [4]. The construction and properties of supramolecular nanosized optoelectronic devices is of industrial and scientific importance. With such architectures, scientifically interesting processes like energy transfer and solar energy conversion and storage can be investigated while industrial applications can be foreseen in the nanofabrication of smaller and less expensive (optoelectronic) devices concurrent to silicon technology. In addition, the field of plastic electronics [5] could benefit from this research since we are combining the advantages of small molecules (no defects) with that of polymers (easy to process) resulting eventually in improved performance properties [6].

For the fabrication of these supramolecular electronic devices, π -conjugated (chiral) oligo(*p*-phenylenevinylene)s

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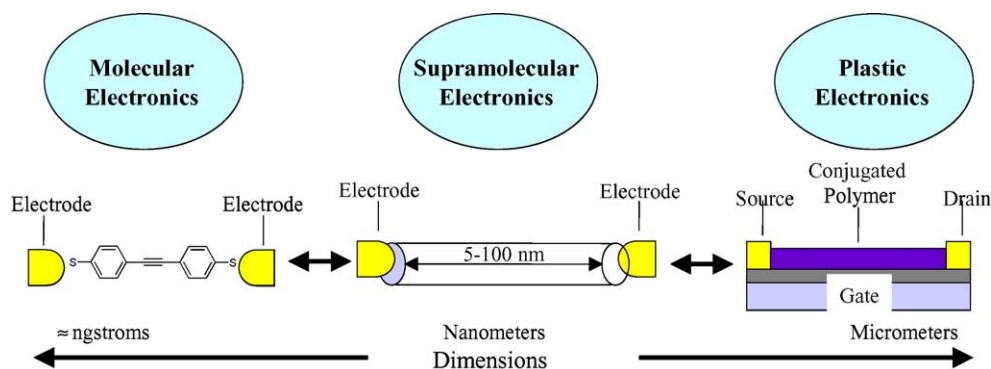


Fig. 1. Schematic representation illustrating the gap, with respect to length scale, between molecular electronics [7], where single molecules are studied, and plastic electronics [8], which relies on bulk properties of π -conjugated polymers. Supramolecular electronics is an unexplored field with the aim to construct and investigate supramolecular optoelectronic nanoarchitectures that are hooked up to electrodes.

(OPVs) oligomers were synthesized, which self-assemble in a controlled fashion into (helical) wires in solution. In these stacks, energy and electron traps were incorporated to investigate fundamental issues like light harvesting, exciton diffusion lengths, and energy and electron transfer processes within the nanometer dimensions. The structures in solution were transformed to a solid support and will be sandwiched between electrodes in future work. The sandwiched architectures can have potential applications in (nanosized) field effect transistors (FETs), photovoltaic devices, light-emitting diodes (LEDs) and logic gates.

2. Result and discussion

2.1. Self-assembly in solution

We have found that an OPV derivative bearing a hydrogen bonding diaminotriazine headgroup can form hexameric π -conjugated rosettes that self-assemble into chiral tubular objects [9]. The OPV trimer and tetramer (**OPVT3** and **OPVT4**, Fig. 2) 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) shows that hydrogen

bond formation exerted by the diaminotriazine moieties leads to chiral hexameric macrocycles at the solid–liquid interface (Fig. 2). These cycles further organize into aggregates in solution as is demonstrated by UV–vis, fluorescence and circular dichroism (CD) spectroscopy (data not shown). Disordered OPV molecules self-assemble hierarchically; first forming hexameric rosettes by hydrogen bond formation, which subsequently develop into stacks aided by π – π interactions of the phenylenevinylenes. The chiral side chains induce supramolecular helicity. It is proposed that the cyclic hexameric rosettes are not fully planar at the triazine end, resulting in a propeller arrangement allowing interplanar hydrogen bond interactions from rosette to rosette, hereby locking the rosettes within the tubules. The tubules of 7 nm in diameter and 180 nm in length and with perfect space filling are still soluble due to the apolar shell that surrounds the stacks as revealed with small-angle neutron scattering (SANS). Atomic force microscopy (AFM) measurements of **OPVT4** assemblies was used to study the shape of the supramolecular aggregates in solution when transferred from solution to a graphite surface with heights of the stacks around 6.4 nm (Fig. 2). This thickness is in agreement with the SANS data and corresponds well to the diameter of the hydrogen-bonded hexamers found by STM pointing to fibers consisting of stacked rosettes.

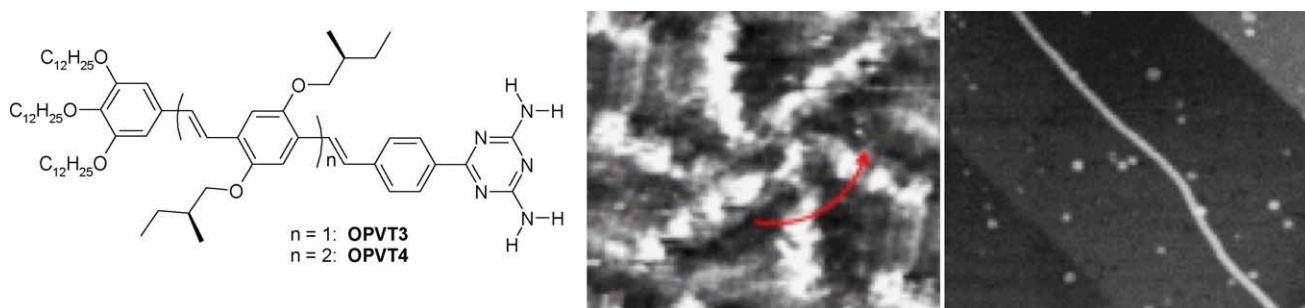


Fig. 2. Molecular structures of **OPVT3** and **OPVT4** (left-hand side), STM image of **OPVT4** (18.4 nm $\times$ 18.4 nm, $V_{\text{set}} = -0.50$ V, $I_{\text{set}} = 0.45$ nA) monolayers (picture in the middle) and AFM image of drop cast **OPVT4** solution in heptane (5×10^{-5} M) on HOPG (right-hand side picture, size 604 nm $\times$ 604 nm).

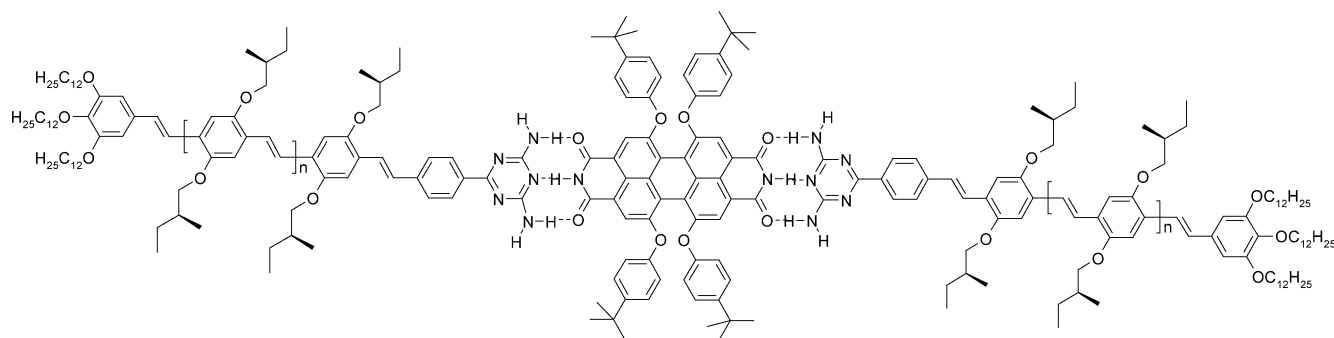


Fig. 3. Hydrogen-bonded triad consisting of one perylenebisimide electron acceptor sandwiched between two OPV electron donors.

As a result of the complementarity of the hydrogen bonding unit in perylenebisimide, which is an electron acceptor, with the diaminotriazine OPV units, supramolecular donor–acceptor–donor triads, i.e. a p–n–p type junction could also be created (Fig. 3) [10]. The covalent analogue of this triad could be visualized by STM (Fig. 4) [11]. Bias-dependent measurements show an electron-acceptor core sandwiched between two electron donors. The hydrogen-bonded triads form helical columnar stacks in apolar solvent as shown by UV–vis, fluorescence and CD titration experiments [10]. The three techniques prove the existence of two phases for the triad in solution; aggregates at low temperatures and molecularly dissolved monomeric species at high temperatures. Very efficient electron transfer takes places from the electron donor (OPV, p-type) to the electron acceptor (perylenebisimide, n-type) 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. 5).

The hydrogen bonding strength in our OPV systems could be increased by increasing the number of hydrogen bond interactions. Three hydrogen-bonded oligo(*p*-phenylenevinylene)s of this type that differ in conjugation length (an OPV trimer, tetramer and pentamer) have been synthesized (Fig. 6), only the OPV tetramer is shown [12].

All three compounds contain chiral side chains, long aliphatic chains and a ureido-*s*-triazine hydrogen bonding

unit. ^1H NMR and photophysical measurements show that the 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 that rigid cylindrical objects are formed. Stacks of OPV4 have a persistence length of 150 nm and a diameter of 6 nm. OPV3 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. When the fraction of aggregated species (ϕ) versus the temperature (T) is plotted for the three different photophysical techniques, fairly equivalent transition curves are obtained (data not shown). The melting of the stacks takes place in a relatively narrow temperature range indicating that the thermal denaturation of the stacks is a cooperative process. 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. The melting of the stacks depends similarly on concentration as found for the denaturation of DNA in nature. The melting temperature and the persistence length of the stacks increases with elongation of the π -system of the OPV oligomers.

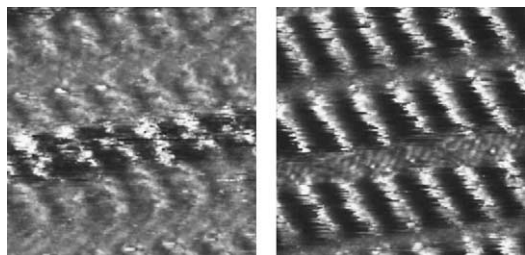


Fig. 4. Bias-dependent STM imaging of a D–A–D triad (left-hand side picture: $V_{\text{bias}} = +1.43$ V, right-hand side image $V_{\text{bias}} = -1.19$ V, image size is $10.1 \text{ nm} \times 10.1 \text{ nm}$, $I_{\text{set}} = 0.40 \text{ nA}$).

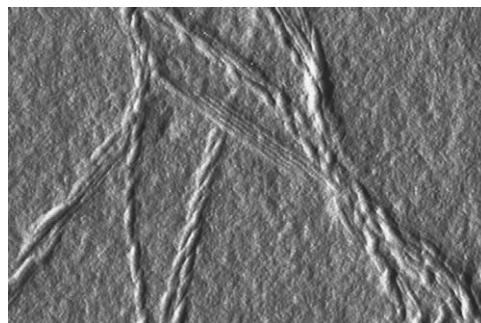


Fig. 5. Tapping mode AFM image ($715 \text{ nm} \times 475 \text{ nm}$) of the hydrogen-bonded triad (Fig. 3) upon spin-coating from MCH ($c = 1 \text{ wt.}\%$) on a glass slide.

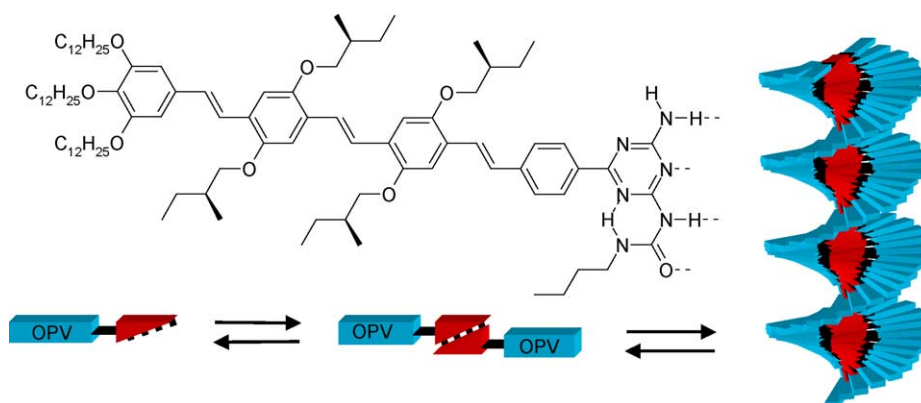


Fig. 6. An OPV tetramer functionalized with a hydrogen-bonding ureidotriazine unit and a schematic representation of a helical stack formed by this molecule. Bars represent the oligo(*p*-phenylenevinylene)s and triangles represent the hydrogen-bonding ureidotriazine units.

We have investigated mixed columnar stacks of hydrogen-bonded oligo(*p*-phenylenevinylene) oligomers, where oligomers of longer conjugation length were incorporated into stacks to act as energy acceptors (Fig. 7). Ultrafast energy transfer from the shorter oligomers to the longer oligomer in these stacks in solution was observed [13]. Such an efficient energy transfer is normally only seen in adsorbed monolayers or thin films. This concept could be used in light-emitting color tuning (data not shown).

2.2. Self-assembly in the solid state

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 [12]. Numerous single micrometers long fibers are found in cast films of OPV on graphite (Fig. 8) with a uniform height of 5.2 nm and a persistence length of 125 nm. At higher concentrations, an intertwined network is

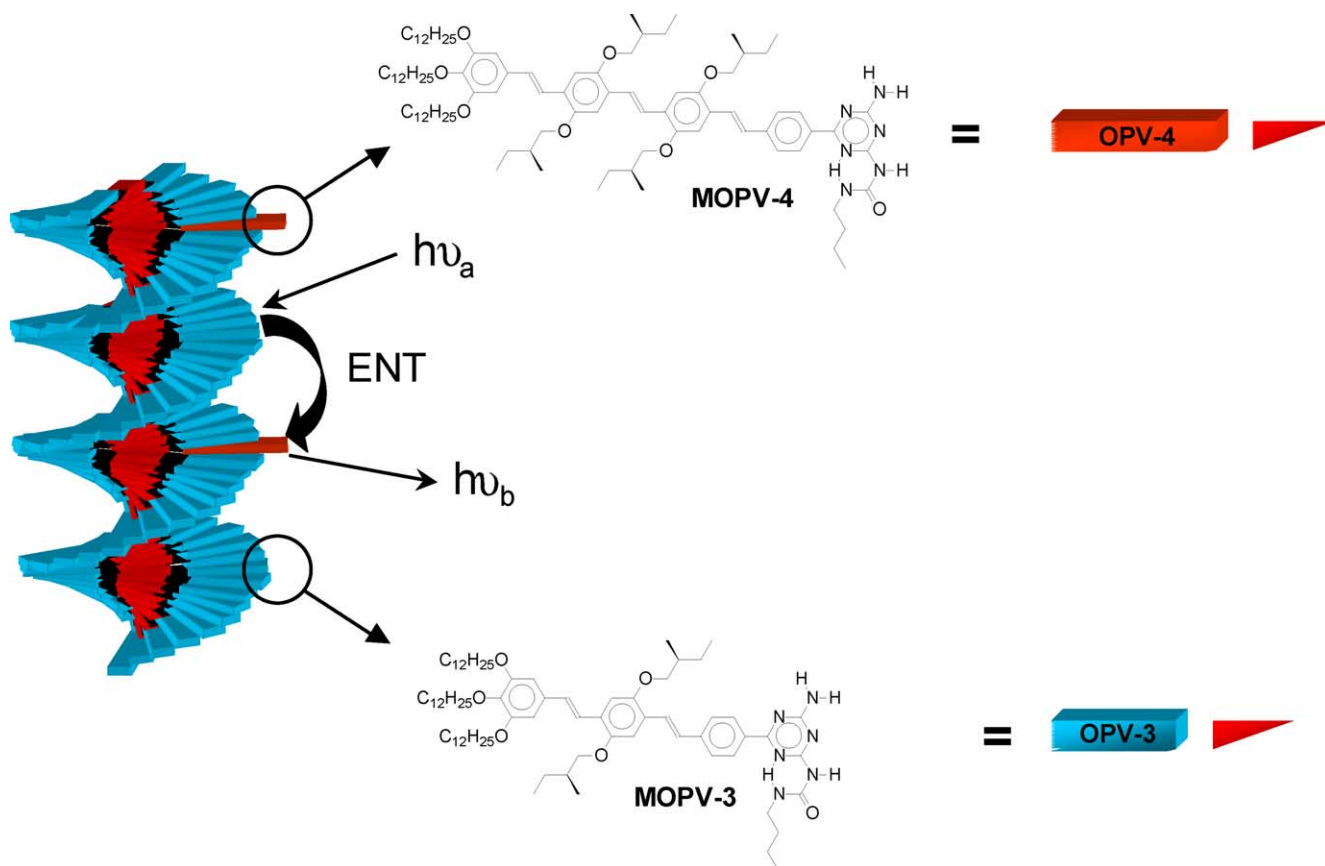


Fig. 7. Mixed columnar stacks of OPV dimers in an apolar environment. The formation of mixed stacks is enabled by the identical hydrogen-bonded motif of both molecules. Within mixed stacks energy transfer (ENT) occurs from MOPV3 to MOPV4.

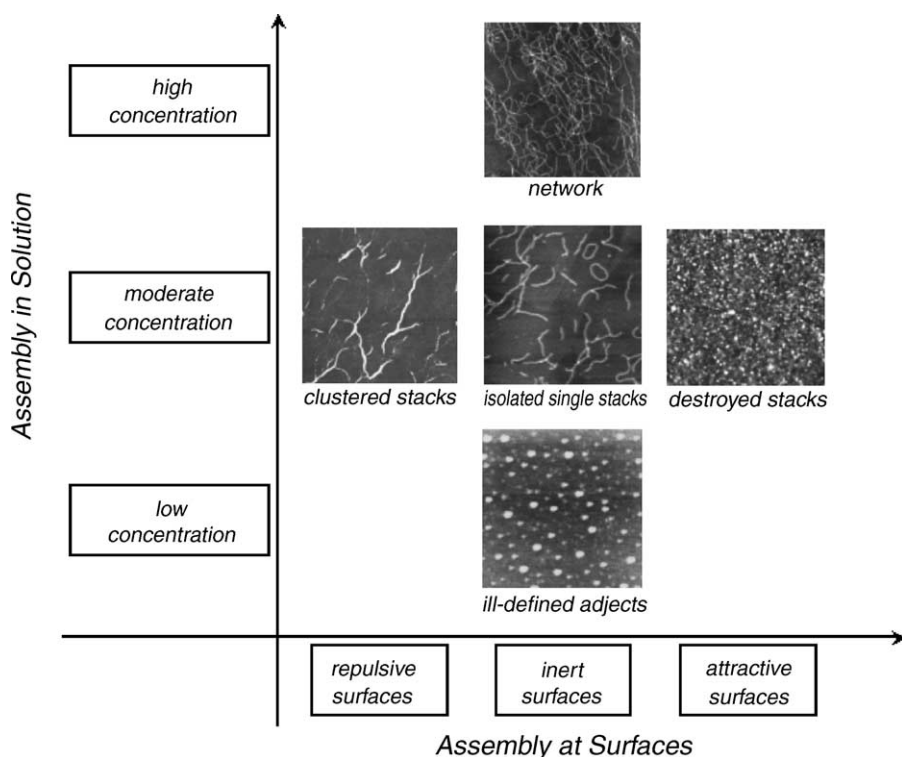


Fig. 8. Plot showing the dependence of morphology on both the solution concentration and surface type. Depicted are tapping mode AFM images on glass (repulsive surface), graphite (inert surface) and gold (attractive surface).

formed while at low concentration ill-defined globular objects are observed. Molecule–surface interactions are also crucial to transfer successfully 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.

2.3. Electronic devices

Plastic electronic devices have been made from the supramolecular hydrogen-bonded OPV systems to show that the recognition sites are electro- and photochemically inert. The morphology of the active layer was controlled by programmed self-assembly of π -conjugated oligomers in solution. The soluble columnar stacks present in solution could be easily processed by spin-coating resulting in films in which the organization present in solution is retained with uniform aligned domains with sizes of hundreds of nanome-

ters. The optical characteristics are also retained as shown by photoluminescence and time-resolved photoluminescence measurements. Stable light-emitting diodes, field effect transistor and photovoltaic devices can be constructed [14]. The concept of controlling the supramolecular organization of the active layer is, in principle, applicable to all kinds of π -conjugated oligomers and will probably improve the performance of opto-electronic devices.

We also investigated isolated OPV fibers as nanosized wires. A solution containing self-assembled structures was drop-cast on electrode patterns in order to obtain some stacks that are oriented across two electrodes. The electrode patterns were produced by electron-beam lithography in which the electrodes are separated by less than 100 nm from each other [15]. However, so far no current has been measured [16]. To solve this problem, an electric field will be applied to align the fibers between the electrodes similar as has been done with polythiophene fibers [15] carbon nanotubes [17] and inorganic wires [18].

3. Conclusions

This work demonstrates that it is possible to program π -conjugated molecules into self-assembled cylindrical aggregates in solution and in the solid state [19]. Ultra-fast energy transfer has been observed in mixed supramolecular stacks of oligo(phenylenevinylene)s (OPVs) in solution. We

also observed collectively and hierarchically self-assemble of oligo(*p*-phenylenevinylene) with perylenebisimide to construct chiral fibers that show photo-induced electron transfer. It demonstrates that control of nanoscale order provides a strategy for tailoring macroscopic electronic properties of organic semiconductor systems.

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. Understanding the interactions in this transfer process will be crucial for the success of applying these semiconducting stacks in the field of nanotechnology. The design of such nanodevices must be such that all components behave as an inert surface toward self-assembled stacks.

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