

## ORGANIC ELECTRONICS

## Supra solutions

Supramolecular interactions between organic molecules not only enable them to self-organize into large regular assemblies, but also enhance their electronic and luminescent properties, which should help to improve the performance of organic devices.

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Supramolecular chemistry has been around for several decades, but never has it been so close to delivering materials of technological relevance for organic electronics. The recent European Materials Research Society symposium on *Supramolecular Approaches to Organic Electronics and Nanotechnology* in Strasbourg, France (24–28 May, 2004) featured a number of important advances towards the development of electronic devices. There are two distinct approaches that scientists are pursuing, and both are giving interesting results. One approach is based on exploiting electron transfer through single molecules. The other aims to exploit extensive non-covalent interactions to prepare large (several hundreds of nanometres) domains by supramolecular organization.

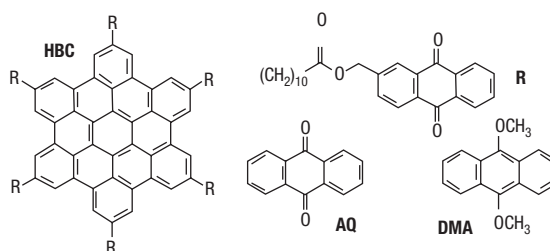
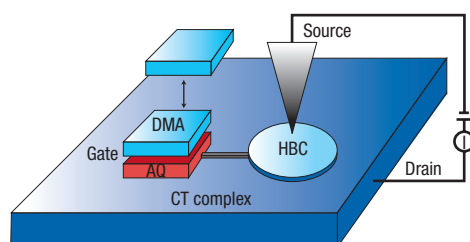
To make molecules perform the function of an electronic device it is essential to orient them on a substrate and put them in electrical contact with nanosize wires as electrodes. The possibility to form extended ordered arrays (two-dimensional crystals) of these functional molecules through adsorption on graphite was demonstrated using scanning tunnelling microscopy (STM). More recently, several groups showed that when assembling molecules combining electron-donating and electron-accepting moieties, the STM micrograph could show either the donor or acceptor group, depending on the applied bias. For hexa-*peri*-hexabenzocoronene (HBC), which is a

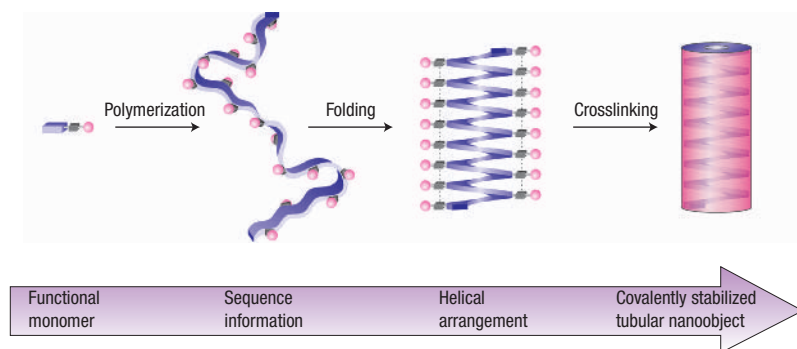
large electron-rich polycyclic aromatic hydrocarbon, linked covalently to anthraquinone (AQ) — an electron-withdrawing group — through an alkyl chain (Fig. 1), scanning tunnelling spectroscopy (STS) showed different current–voltage plots for a tip placed above the HBC, the linking alkyl chains or the AQ (J. P. Rabe, Humboldt University, Germany). This represents the construction and addressing of a diode with submolecular resolution. Furthermore, complexation of the AQ moiety with 9,10-dimethoxyanthracene (DMA) — an electron-donor molecule — resulted in a 0.12 V shift of the STS-curve of the HBC moiety to less-positive values of the substrate potential. This was attributed to the field of the dipole moment of the DMA–AQ charge-transfer complex, which downshifted the energy levels of the graphite substrate versus those of the tip, and in this way yielded a single-molecule chemical field-effect transistor<sup>1</sup> (FET).

An ordered array of molecular diodes was also obtained by the consecutive adsorption of cyclo[12]thiophene (C12T) and C<sub>60</sub>-fullerenes on a substrate (E. Mena-Osteritz, Ulm University, Germany). C<sub>60</sub> formed a layer on top of the C12T and, although the fullerene molecules are not complexed inside the macrocycle cavity, both C12T and fullerene formed a perfect hexagonal array where the large spacing between fullerenes was dictated by the underlying C12T arrangement. When the STM tip was placed on a C<sub>60</sub> molecule, an asymmetric current–voltage plot was obtained — a hallmark of a current rectifier.

Whereas HBC and C12T need a substrate for forming electronically active assemblies, triazine-substituted chiral oligo(*p*-phenylenevinylene)s (OPV) use hydrogen bonds to form hexamer ‘rosettes’, which

**Figure 1** A monomolecular device. On the left, a schematic representation of a prototypical single-molecule chemical FET. On the right, the structures of chemicals used: anthraquinone (AQ), 9,10-dimethoxyanthracene (DMA), and hexa-*peri*-hexabenzocoronene (HBC) decorated with six functionalized anthraquinones (R). The current–voltage characteristics of a single molecule in an STM junction can be modified by charge-transfer (CT) complexation of the AQ moiety with DMA. This CT complex generates an electric field that decreases the positive voltage that has to be applied to the substrate in order to obtain the same current between the tip and the HBC moiety. Reprinted with permission from ref. 1. Copyright (2004) American Physical Society.





**Figure 2** Folding and fixing. From left to right: monomers with suitable side groups are polymerized to obtain a chain that spontaneously folds into a helix (stabilized by  $\pi$ - $\pi$  interactions) when placed in polar solvents. This helix can be stabilized through covalent bonds formed by photochemical or thermal crosslinking reactions, leading to the formation of stable synthetic nanotubes. Reprinted with permission from ref. 4.

assemble with a combination of  $\pi$ -interactions and hydrogen bonds into helices several hundreds of nanometres long (A. Schenning, Eindhoven Technology University, The Netherlands). Combining the triazine-substituted OPVs with perylene diimide — an electron-accepting aromatic polycycle — yielded helices consisting of donor-acceptor-donor structures. The assemblies showed large exciton diffusion length<sup>2</sup> (the distance that a neutral exciton can travel before decaying) and efficient photo-induced charge separation. Both these factors increase the probability that an absorbed photon creates a pair of charge carriers that survives until the hole and electron reach the electrodes. Those helical assemblies — spin-coated as a thin film with uniform aligned domains several hundreds of nanometres in size — were used to build light-emitting diodes, FETs and photovoltaic devices.

HBC and its larger homologues don't just form two-dimensional crystals, but can take many other shapes. Spin- or drop-casting form randomly oriented fibrils and ribbons several hundreds of micrometres long. However, deposition of the solution from a stationary nozzle onto a moving substrate (zone casting) can produce regular (often hexagonal) columnar crystalline phases or discotic mesophases<sup>3</sup>, where the columns can be considered as insulating 'nanowires' (K. Müllen, Max-Planck Institute, Mainz, Germany). When these aligned columns, lying parallel to the substrate, are incorporated in an organic FET, relatively high mobility values between 0.1 and 1 cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup> were obtained (for organics these values come close or equal to single-crystal values). In addition to a large charge-carrier mobility, photovoltaic devices also require columnar order in the direction perpendicular to the substrate (homeotropic alignment, that is, the columns must be standing on the substrate). This arrangement, which up to now can only be obtained by cooling from the melt or annealing just below the isotropization temperature, seems to be limited to discotic mesogens (molecules forming discotic liquid-crystalline phases). The increased photocurrent in homeotropic aligned areas compared to non-aligned areas demonstrates the

importance of the alignment of the insulating 'nanowires'. On spin-coating a mixture of an HBC and a perylene diimide derivative, vertical phase-separation occurs, yielding two parallel layers of HBC and perylene columns connected electronically by a partially interpenetrating network. The vertical separation at the nanoscale combines efficient generation of electron-hole pairs with increased transport to the electrodes and a lesser chance of recombination. These discotic mesogens offer great versatility in terms of ease of chemical functionalization, a broad window of processing conditions, and diverse two- and three-dimensional ordering possibilities, which can be optimized according to the requirements of a specific function. They have therefore become a popular means to produce single crystals of linear polycyclic aromatic hydrocarbons.

In general, the molecules interact with each other only through relatively weak van der Waals forces. Although such interactions proved useful to guide self-assembly, further stabilization is required to maintain these structures under conditions where self-assembly is not thermodynamically favoured. For example, poly(*m*-phenyleneethynylene) with hydrophilic side-groups folded spontaneously to form regular helices that could be stabilized in a tubular structure by photochemical crosslinking<sup>4</sup>, ring-closing metathesis or acrylate polymerization (S. Hecht Free University Berlin, Germany) (Fig. 2). Alternating copolycondensation of phenylethyne with different side groups leads to tubular structures with different reactive groups inside and outside. These could be transformed in insulated wires by internal metal complexation followed by reduction. Alternatively, functionalization with other external groups allows those 'organic nanotubes' to pack into larger arrays.

The judicious use of supramolecular interactions has allowed us to prepare organic materials that combine a lower density of charge-carrier and exciton traps with strong and anisotropic intermolecular electronic coupling, which in turn lead to higher charge-carrier mobility and larger luminescence efficiencies. As for the possibility of scaling down electronic components to the molecular level, we are still very far from a molecular Pentium V. We now have components ('wires' and 'switches') of molecular size with which in principle we could build a computer. But progress towards the development of an efficient way to (self) assemble these elements in a non-periodic way to form a processor has proved to be a more challenging task. Whether this is just a question of developing more sophisticated technologies, or if some more fundamental hurdles are in the way, remains a riddle for many a scientist at this stage.

#### References

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