

Subject line: Organic Electronics

Title: **Supra solutions**

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Engineering of non covalent interactions organizes organic molecules in regular assemblies for improved electronic device properties and permits the addressing of single molecules by an STM-tip.

Supramolecular chemistry has been around for several decades. But never has this discipline based on the non covalent interaction between organic molecules been so close to delivering materials of technological relevance for organic electronics. Supramolecular scientists at the recent European Materials Research Society symposium on “Supramolecular approaches to organic electronics and nanotechnology” in Strasbourg (France) revealed 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 nm) domains by supramolecular organization.

To make molecules perform the function of an electronic device, such as a diode or a transistor, it is essential to orient them on a substrate and put them in electrical contact with nanosize wires or electrodes. The possibility to form extended ordered arrays (two-dimensional crystals) of these functional molecules upon adsorption on graphite was

demonstrated using scanning tunneling microscopy (STM). More recently several groups showed that when assembling molecules combining electron donating and electron accepting moieties the STM micrograph could represent either the donor or acceptor group depending upon the applied bias. For hexa-*peri*-hexabenzocoronene (HBC) – a large electron rich polycyclic aromatic hydrocarbon - linked covalently to anthraquinone (AQ) – an electron withdrawing group - through an alkyl chain (figure 1) scanning tunneling 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, complexing the AQ moiety with 9,10-dimethoxyanthracene (DMA) – an electron donor molecule - resulted in a shift of the STS-curve of the HBC moiety by 0.12 V to less positive values of the potential of the substrate. This shift 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 yielded in this way a single molecule chemical-field-effect transistor<sup>1</sup>.

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). Although the fullerene was complexed rather than inside the C12T cavities, both C12T and fullerene formed a perfectly packed array with hexagonal symmetry where the fullerenes were a large spacing between fullerenes was dictated by the underlying C12T arrangement. When the tip was placed on a C<sub>60</sub> molecule an asymmetric current-voltage plot was obtained, a hallmark of a current rectifier.

While 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 assemble with a combination of  $\pi$ -interactions and hydrogen bonds into helices several hundreds of nanometers long (A. Schenning, Eindhoven Technology University, The Netherlands) . Combining the triazine substituted OPV’s with perylene diimide – an electron accepting aromatic polycycle - yielded helices consisting of donor-acceptor-donor structures. The assemblies showed a large exciton diffusion length<sup>2</sup> (the distance that a neutral exciton can travel before decaying) as well as an efficient photo-induced electron charge separation. Both factors will increase the probability that an absorbed photon creates a pair of charge carriers that survives until the hole and electron reach the electrodes. Those supramolecular helical assemblies can be cast either as single helices or spin coated as a thin film and form uniform aligned domains several hundreds of nm in size. The latter domains were used to construct light emitting diodes, field effect transistors and photovoltaic devices.

HBC and larger homologues of HBC (graphenes) 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 microns long. Instead, deposition of the solution from a stationary nozzle onto a moving substrate (zone casting)<sup>3</sup> 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 are incorporated in an organic FET device, where a large in plane charge carrier mobility is required, mobilities between 0.1 and 1 cm<sup>2</sup>/Vs were obtained. In addition to a large charge carrier mobility, photovoltaic devices also require columnar order in the direction perpendicular to the substrate (homeotropic alignment) While for the FET’s the columns must be lying they must be standing for the photovoltaic device. 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”. Upon spin coating a mixture of a HBC and a perylene diimide derivative vertical phase separation yielding 2 parallel layers of HBC and perylene columns connected electronically by a partially interpenetrating network occurs. The vertical separation at the nanoscale combines efficient generation of electron-hole pairs with increased transport to the electrodes and lesser chance of recombination. These discotic mesogens offer great versatility in terms of ease of chemical functionalization, broad window of processing conditions, 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 polyacene (polyacenes are linear polycyclic aromatic hydrocarbons or polycyclic aromatic hydrocarbons where all rings lie on one line) single crystals.

In several examples above the molecules cast adsorbed to the substrate are in dynamic equilibrium with molecules in solution and interact with each other only through relatively weak van der Waals forces. While such interactions proved to be 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 which could be stabilized in a tubular structure by photochemical cross-linking<sup>4</sup>, ring closing metathesis or acrylate polymerization (S. Hecht Free University Berlin, Germany) (Figure 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. Other functional groups allow those “organic nanotubes” to pack in larger arrays.

Using supramolecular interactions allows us to prepare organic materials that combine a lower density of charge carrier and exciton traps with strong and anisotropic intermolecular electronic coupling. This has led to materials with higher charge carrier mobilities (for organic materials) 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. But molecules acting as diodes or FETs can be addressed individually with limited cross interference. Moreover, supramolecular interactions can be used to form large regular arrays of molecules on a substrate. Despite the achievement of collectively addressable micrometer size assemblies of molecular diodes, our molecular diodes and FETs are still characterized by a small ratio of the current in the ‘on’ and the ‘off’ state. Supramolecular interactions help us to further develop insulated wires of nanoscopic dimensions. Now we have in principle components (“wires” and “switches”) of molecular size to 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 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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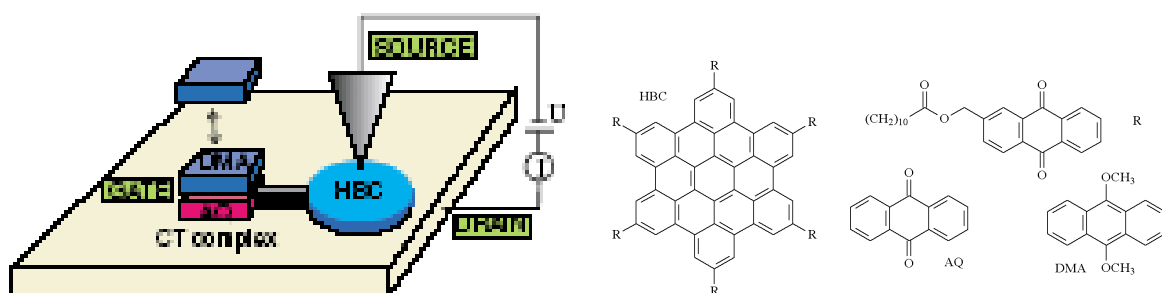


Figure 1, left: Schematic representation of a prototypical single-molecule CFET; right: chemical formulas of the employed materials: hexa-*peri*-hexabenzocoronene (HBC) decorated with six anthraquinones, anthraquinone (AQ), 9,10-dimethoxy-anthracene (DMA). Due to involvement of the HOMO of HBC, the tunneling current between the tip (placed on top of the HBC moiety) and the substrate increases much faster when a negative voltage is applied to the substrate versus a positive one. Upon complexing AQ with DMA the charge transfer complex between DMA and AQ generates an electric field that decreases the positive voltage that has to be applied to the substrate (in order to obtain the same current).

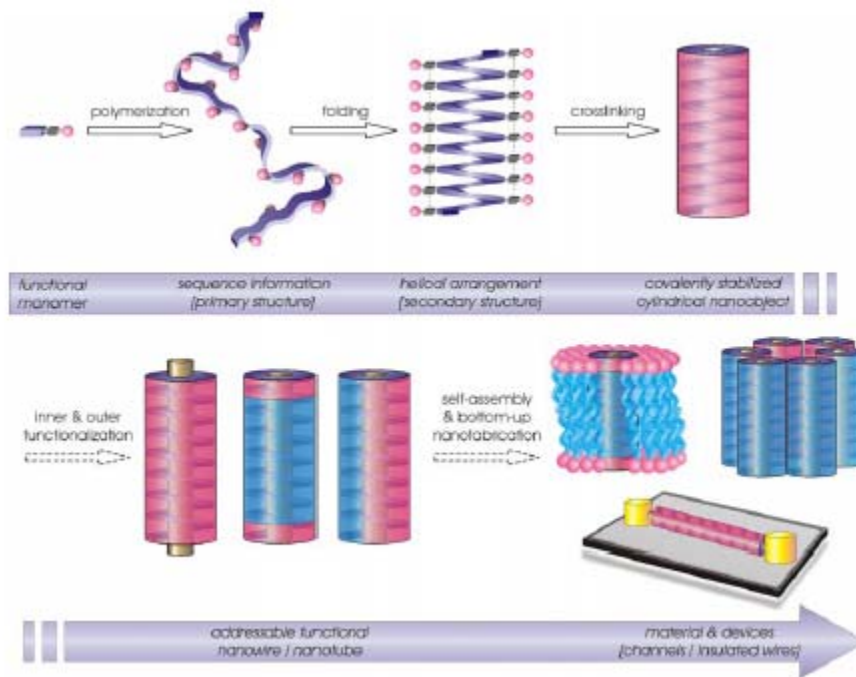


Figure 2: Polycondensation or polymerization of monomers with suitable side groups (left) results in a polymer that spontaneously organizes in a helix (stabilized by  $\pi$ - $\pi$ -interactions) in polar solvents (center). This helix can be stabilized by the formation of covalent bonds between the side groups by photochemical or thermal cross linking reactions (right) leading to the formation of stable synthetic nanotubes.