

# Nanochemistry

## From single molecules to functional supramolecular nanomaterials and devices

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### Résumé

#### Nanochimie : de molécules individuelles à des nanomatériaux et dispositifs supramoléculaires

L'auto-assemblage moléculaire est une stratégie très puissante pour développer des nanostructures supramoléculaires fonctionnelles dont les propriétés peuvent être étudiées sur plusieurs échelles de longueur à l'aide de microscopies à sonde locale. À travers cinq exemples de notre laboratoire, cet article va mettre en lumière la formation, l'exploration et l'exploitation de nanostructures organiques et polymères composées ordonnées en vue d'applications en optoélectronique. Le premier exemple décrit le développement de nouvelles méthodes de traitement et de post-traitement permettant de former des nanostructures supramoléculaires hautement organisées sur des surfaces à partir de composés électroactifs. Une attention particulière est portée à la compréhension du mécanisme d'auto-assemblage. Dans le deuxième exemple, la microscopie à effet tunnel (STM) est utilisée pour étudier la cinétique et la thermodynamique de l'auto-assemblage multicomposant à l'interface solide-liquide. Le troisième exemple illustre la manière dont l'autorecognition de bases nucléiques peut être utilisée pour construire des architectures supramoléculaires dynamiques dont le processus d'assemblage/réassemblage réversible sur des surfaces peut être suivi en temps réel à l'échelle subnanométrique. Le quatrième décrit le potentiel de différentes techniques à sonde locale comme la microscopie à force atomique à sonde conductrice (C-AFM) et la microscopie à sonde de Kelvin (KPFM) pour étudier quantitativement les propriétés des nanostructures. Enfin, deux exemples de composants électroniques supramoléculaires obtenus par auto-assemblage multicomposant contrôlé sont présentés. Ces exemples donnent un aperçu des différentes approches permettant de révéler la relation structure-fonction des nanomatériaux supramoléculaires fonctionnels pour l'électronique organique. L'extension de ces stratégies à la conception de matériaux composites à la complexité croissante destinés à la fabrication de composants aux fonctions complexes, multiples et indépendantes est prévisible.

### Mots-clés

**Auto-assemblage, chimie supramoléculaire, dynamères, microscopie à sonde locale, électronique supramoléculaire, transistors à effet de champ.**

### Abstract

Molecular self-assembly is a very powerful strategy to develop functional supramolecular nanostructures whose properties can be explored across multiple length scales by means of scanning probe microscopies. This paper highlights five examples from our laboratory on the formation, exploration and exploitation of ordered multicomponent organic and polymeric nanostructures of interest for opto-electronics applications. In the first example, the development of new processing and post-processing methods to form highly ordered supramolecular nanostructures at surfaces starting from electroactive building blocks is described with a particular focus on the unveiling of the mechanism of self-assembly. In the second example, scanning tunneling microscopy is exploited to study the kinetics and thermodynamics of multicomponent self-assembly at the solid-liquid interface. The third example shows how self-recognition among nucleobases can be used to construct dynamic supramolecular scaffolds whose reversible assembly/reassembly process occurring at surfaces can be monitored on the sub-nanometric scale in real-time. In the fourth example, the capability of different scanning probe techniques such as conducting-atomic force microscopy and Kelvin probe force microscopy to explore nanostructure's properties in a quantitative way is described. Finally, by mastering controlled multicomponent self-assembly, two examples of supramolecularly engineered electronic devices are presented. While the described examples provide a glimpse of different approaches towards the unravelling of the architecture vs. function relationship in supramolecularly engineered functional nanomaterials for organic electronics, one can foresee the extension of these strategies to the design of ever more complex multicomponent materials to fabricate devices that can express multiple yet independent complex functions.

### Keywords

**Self-assembly, supramolecular chemistry, dynamers, scanning probe microscopies, supramolecular electronics, field-effect transistors.**

The properties of molecular materials are known to depend on the way the components are organized at the supramolecular level. This is because there is a stringent relationship between architecture and function in materials based on one or more molecular component interacting *via*

non-covalent forces. Achieving a control over such a relationship opens the door towards the application of molecular systems in various technologically relevant areas including (opto)electronics, photonics and catalysis as well as biomedicine [1]. Such endeavours will also make it possible to

ultimately fabricate prototypes of (supra)molecular and multifunctional nanodevices operating at surfaces. Supramolecular chemistry is a well-established field of chemistry that has been attracting more and more interest in the last three decades. Most of the researches in this field have been conducted in liquid media, *i.e.* an environment in which the chemistry of molecules can be best exploited. By profiting from such a deep knowledge, *i.e.* the well-established capacity of supramolecular approaches to form complex architectures in solution, an increasing research activity during the last decade has addressed different aspects of nano- and supramolecular chemistry at surfaces and interfaces ranging from fundamental chemical studies to technologically more relevant explorations, towards new functions at the nanoscale [2]. I highlight here some of our recent works on the molecular self-assembly at surface to form ordered supramolecular architectures, whose properties are investigated across multiple length scales, in particular by using scanning probe microscopy (SPM) based approaches beyond imaging [3]. The quantitative information on the physico-chemical properties on these architectures has been instrumental to the fabrication and characterization of multicomponent organic electronic device prototypes, like field-effect transistors.

### Processing and post-processing methods to produce highly ordered supramolecular electroactive architectures at surfaces

The processability of giant (macro)molecules into highly ordered supramolecular structures at surfaces is of fundamental importance for studying chemical, physical and biological phenomena, as well as for their exploitation as active units in the fabrication of hybrid devices. Organic thin films prepared from solution typically suffers from the limited long-range molecular ordering in the deposited structures, the latter being a factor which plays a pivotal role in the performance of organic devices. As a result, post-treatment procedures like thermal annealing [4] and solvent vapour annealing [5] can be successfully employed to increase the degree of order within the self-organized films and improve the performance of the associated devices. While the former annealing approach is not very mild, the latter is more friendly and tunable.

Solvent vapour annealing (SVA) post-treatment is a simple and versatile approach allowing macroscopic healing of molecular assemblies at surfaces. Through a careful balance of all the interactions arising among the involved components (molecule, solvent and substrate surface), the morphology and crystalline character of the material can be finely tuned, as a result of long-range reorganization by a high mass transport of the material adsorbed at surfaces. For example, we have used this approach on spin-coated films of a commercial semiconducting molecule, *i.e.* perylene-bis-dicarboximide (PDI), on SiO<sub>x</sub>. The initial films exhibit ribbons adsorbed on the substrate. These ribbons have a length of ca. 200 nm, a width and height of a few tens of nm (*figure 1b*). By exposing these films in a sealed environment saturated with the vapour of tetrahydrofuran at room temperature, a notable change in the morphology is observed resulting in the formation of macroscopic fibers having lengths up to 3 mm (*figure 1c-e*). The fiber cross sections, in the sub-micrometre range, remain constant over lengths of several tens of microns yielding aspect ratios surpassing 10<sup>3</sup>. These structures feature an anisotropic crystalline nature as

evidenced by its birefringence and polarized fluorescence emission (*figure 1f-g*), which in turn suggest the alignment of the transition dipole moment of a whole PDI fiber to the direction of the 1D molecular packing. Real-time optical microscopy provides evidence for a sigmoidal kinetics of the fiber length during the SVA process in a nucleation-governed growth. The observed phenomena comply with an Avrami growth mechanism, and can be described as a homogeneous crystallization characterized by continuous nucleation and growth of rod-like structures. The extent of reorganization is striking: a typical fiber consumes the PDI material which has been deposited through spin-coating on ca. 16 mm<sup>2</sup> of the substrate per second, confirming that a very long-range mass transport is achieved by SVA [6]. By modulating the temperature of the set-up during the SVA process it has been possible to increase the molecular reorganization on the microscopic scale [7].

On the other hand, thermal sublimation under vacuum environment is a common method used in particular by physicists to deposit molecules on surfaces. This method cannot be used to process ultra large organic molecules because of their limited thermal stability. To circumvent this problem, we devised a new general approach to process giant (macro) molecules into ultra-pure and highly ordered structures at surfaces. This method relies on the soft-landing of ions generated by solvent-free matrix assisted laser desorption/ionization (MALDI) [8]. Being poorly invasive, this procedure is of general interest for deposition of organic, inorganic and biological multicomponent materials into highly ordered two- and three-dimensional (2D and 3D) architectures.

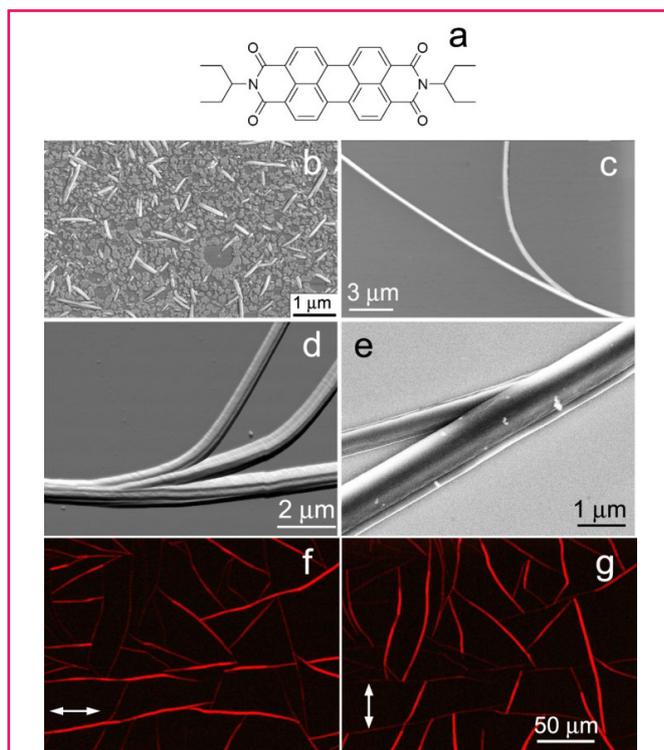


Figure 1 - (a) Chemical formula of the PDI derivative used as a model system in ref. [6]. (b) AFM phase image of PDI nanostructures obtained by spin-coating a 10<sup>-3</sup> M solution in CHCl<sub>3</sub> on s SiO<sub>x</sub> substrate. (c-e) AFM topography (c), AFM topography gradient (d), and SEM images (e) of PDI fibers obtained after SVA in THF of spun samples. (f-g) Polarized fluorescence microscopy images; the same area of the sample is observed with different orientations of the polarizer. White arrows show the direction of the excitation polarization. Z-ranges: (c) 345 nm; (d) 3 290 nm/nm.

Image reproduced from [6] with permission from Wiley-VCH.

## Unravelling and controlling the kinetics vs. thermodynamics of multicomponent self-assembly at the solid-liquid interface

While three-dimensional crystal engineering is a well established field, in the past decade there has been an increasing effort towards the fabrication of two-dimensional patterns. In particular, the need for engineering of functional materials with sub-nm precision has triggered research on the development of perfectly ordered architectures exploiting weak yet highly directional interactions, such as metal-ligand or H-bonding [9]. Scanning tunneling microscopy (STM) operating both under UHV and at the solid-liquid interface makes it possible to characterize on the nanoscale supramolecular 2D architectures providing a detailed insight into the structural motifs at the sub-molecular level. The solid-liquid interface is of special interest because of its analogy to biological processes: upon adsorption at interfaces, (supra)molecules are subjected to complex thermodynamic equilibrium to produce functional architectures.

The controlled formation of ordered multicomponent architectures at the solid-liquid interface from a concentrated solution is thermodynamically unfavored. In fact, among the various components present in the supernatant solution, the component with a higher affinity for the substrate, *i.e.* featuring a minimization of the free interface energy per unit area, will assemble on its surface, whereas the others will remain in the supernatant solution. To immobilize all the components on the basal plane of the surface, thus to achieve a complete physisorption of all the components at the solid-liquid interface, it is necessary to control the stoichiometry of the molecules adsorbed at surfaces. The number of molecules in the solution applied to the surface should be lower than that required to form a monolayer of physisorbed molecules lying flat on the basal plane of the substrate [10]. By using very low concentrations, we have been able to physisorb a bi-component solution of properly designed molecular modules on the basal plane of graphite, and prove by STM that both components can be immobilized at surfaces forming self-assembled discrete architectures [11] or extended networks [12]. This result was truly important since, upon operating in the conventional high concentration regime at the solid-liquid interface, only one component is typically observed on the surface. The general applicability of this approach to form discrete and multicomponent assemblies has been established on a library of different linear molecular modules (linkers) bridging melamine *via* triple hydrogen-bonds, leading to tunable porous supramolecular 2D arrays [13]. This made it possible also to explore at the nanoscale the phenomena of polymorphism and phase segregation which rule the generation of highly crystalline nanoporous patterns self-assembled at the solid-liquid interface, thereby paving the way towards predictive 2D self-assembly (*figure 2*). By employing the same “low concentration regime” strategy, we have visualized for the first time by STM at the solid-liquid interface a main-chain bi-component supramolecular polymer built up from ditopic molecular components bearing complementary H-bonding recognition groups. By making use of two different types of the wedge molecules featuring a different conformational rigidity, we were able to control the geometry of linear supramolecular polymer, leading to the controlled formation of either perfectly linear architectures or zig-zag motifs [14].

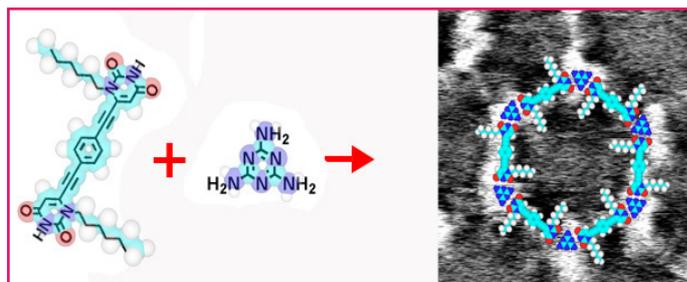


Figure 2 - The recognition of a di-uracyl module by melamine through three hydrogen bonds leads to the formation of a 2D porous network as visualized by STM at the graphite-solution interface.

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## From supramolecular scaffolding to dynamers operating at surfaces

The properties of materials incorporating functional units strongly depend on their position in space. Some supramolecular interactions such as H-bonding and metallo-ligand interactions are highly directional, thus they can be used to develop scaffolds for positioning functional units in space.

Recently we have shown that of linear coordination supra-polymers can be formed at the solid-liquid interface using palladium(II) ions. The metallo-organic framework was formed by using a rigid anthracene derivative bearing two units (pyridine and terpyridine) at the extremities, and palladium(II) or cobalt(I) ions as metal centers. 1D arrays were obtained only when using Pd(II), whereas 2D arrays were observed when  $\text{CoCl}_2 \times \text{H}_2\text{O}$  salt was added. Because of the di-cationic nature of palladium, its interaction with the neutral anthracene derivative generates a charged square-planar complex formed by the palladium center and one terpyridine and one pyridine unit belonging to consecutive anthracene derivatives. The lateral correlation between the 1D networks forming the crystalline layer suggests a cooperative process that takes place during their assembly on graphite. Depending on the overall charge of the network and thus on the nature of the tectons used, it is possible to obtain either 1D or 2D arrays [15]. The versatility of such an approach was proven by further adding a control at the nanoscale of both the geometry and the directionality of supramolecular 1D arrays. Such a control was attained through the proper design of the organic tectons and the choice of metal. In particular by differing only in the position of the nitrogen atom on the pyridine ring (from *para* to *meta*), we have demonstrated that the geometry of the directional network may be shifted from linear to zig-zaged [16]. These results showed that it is possible to pattern the surface with functional groups like optically active anthracene units or metal centers with a precision of a few ångströms.

To explore the potential of H-bonding to form ordered supramolecular networks on surfaces, we have focussed our attention since over a decade to lipophilic guanosines [17] and guanine derivatives [18], because they are very versatile building blocks. Depending on the experimental conditions, they can undergo different self-assembly pathways, leading to the formation of either H-bonded ribbons or quartet-based columnar structures. Given the possibility to functionalize the guanosines in the side-chains, they appear as ideal building blocks for the fabrication of complex architectures with a controlled high rigidity, thus opening perspectives towards their future use as scaffolds to locate functional units in pre-programmed positions. We have shown that guanosine

derivatives can form H-bonded ribbon-like or quartet-based supramolecular architectures in solution, depending on the conditions. By decorating the side group of the guanosine with an electrically active oligothiophene, we showed that it is possible to use the nucleobase recognition forming H-bonded ribbons to achieve a control over the position of the oligothiophene units in space, ultimately forming 1D conjugated arrays that may be employed as prototypes of supramolecular nanowires (figure 3) [19].

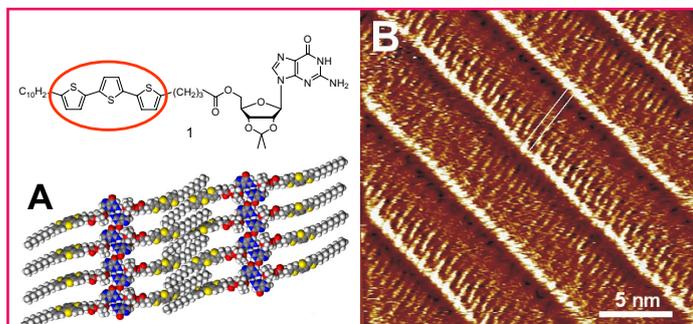


Figure 3 - Guanosine-oligothiophene molecule. (B) STM image of the H-bonded network based on self-association of the guanosines, leading to controlled positioning of the ter-thiophene moiety in the 2D space. The model of packing is shown in (A).

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On the other hand, small organic molecules, capable of undergoing efficient and reversible transformations between (at least) two (meta)stable states associated with markedly different properties, continue to impact the materials world. Among various stimuli, metal complexation and release is a rather versatile approach that can be operated in liquid media.

Recently we have monitored on the sub-nanometer scale the metal-templated reversible assembly/reassembly process of an octadecyl substituted guanine into highly ordered ribbons and quartets (G4) (figure 4a) [20]. The self-assembly

of octadecyl guanines alone on HOPG has been studied, and, upon subsequent addition of [2.2.2]cryptand, potassium picrate ( $K^+(\text{pic}^-)$ ), and trifluoromethanesulfonic acid (HTf), the reversible interconversion between two different highly ordered supramolecular motifs was induced. In the absence of metal ions, the obtained monolayer shows ribbon-like motifs (figure 4b). Upon *in-situ* addition of 10 mM potassium picrate solution in 1,2,4 trichlorobenzene, the initial ribbons disappeared and tetrameric (G4) structures were observed on the surface (figure 4c). Upon subsequent *in-situ* addition of a 10 mM solution of [2.2.2]cryptand in TCB, the guanine reassembled into the original ribbon (figure 4d). By adding a 10 mM solution of HTf in 1,2,4 trichlorobenzene, the potassium ions were released from the cryptate and the G4 assembly was regenerated (figure 4e). Upon further addition of a [2.2.2]cryptand solution, the ribbon structure was observed again (figure 4f). This result represents the first dynamer operating at surfaces which was monitored on the sub-nm scale. The visualization of such supramolecular interconversion at the solid-liquid interface opens new avenues towards understanding the mechanism of formation and functioning of complex nucleobase architectures like DNA or RNA. Furthermore, the *in-situ* reversible assembly and reassembly between two highly ordered supramolecular structures at surfaces represents the first step towards the generation of nanopatterned responsive architectures [21].

Change in pH can be used as external stimulus to activate large conformational variations in self-assembled structures. We recently showed that upon addition of trifluoroacetic acid, a highly ordered self-assembled monolayer of 2,6-bis(1-aryl-1,2,3-triazol-4-yl)pyridine (BTP) molecules at the solid-liquid interface underwent significant conformational changes from a “rosette” to a “tetragon” structure, as reflected in dramatically altered 2D self-assembly over large areas extending over hundreds of nanometers. This result represents the first and crucial step towards the development of reversible pH triggered switches at the solid-liquid interface [22].

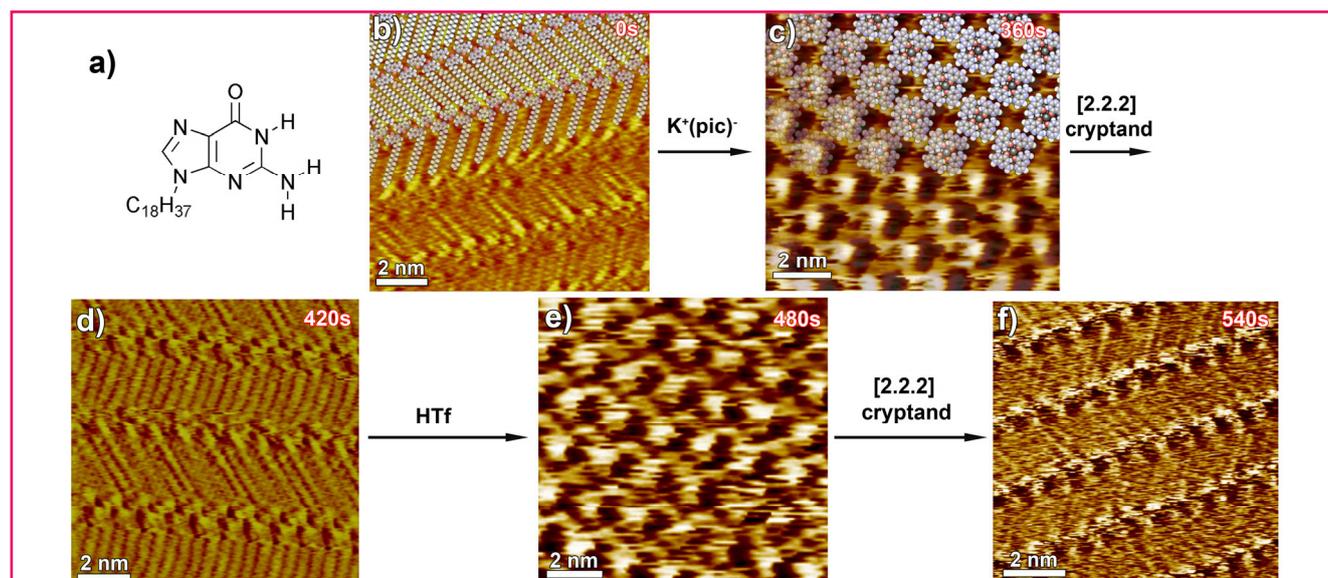


Figure 4 - (a) Chemical structure of octadecyl guanine; (b-f) consecutive STM images showing the structural evolution of a monolayer of 1 over a 9 min time scale (time range displays in the upper right part of the images correspond to the time that was needed to reach the equilibrium after addition of reacting agents). Images (b), (d) and (f) show ribbon-like structure, whereas (c) and (e) exhibit G4-based architectures.

Images (b-f) adapted from [20], with permission from Wiley-VCH.

## Scanning probe microscopies (SPMs) beyond imaging

SPM are very powerful local techniques that make it possible to quantitatively study numerous physico-chemical properties of multicomponent nanostructured architectures with a sub-nm precision, as well as to nanomanipulate surfaces with a nanoscale precision. In this regard, conductive atomic force microscopy (C-AFM) [23] has been used to correlate the detailed structural and electrical characteristics of graphene [24] derived from graphene oxide. Uniform large currents were measured over areas exceeding tens of micrometers in reduced graphene oxide few-layer thick films obtained *via* thermal reduction of graphene oxide spin coated film upon exposure to 750 °C in an inert environment. This process is known to restore ~ 80% of the  $sp^2$  network, yielding a conductive film, albeit with a lower conductivity than pristine graphene. These findings indicate that graphene can be used as a transparent electrode material. The electrical measurements by C-AFM provided evidence for the presence of defects such as electrical discontinuities. Multilayer films were found to have a higher conductivity per layer than single layers. This can be due to a more modest charge trapping occurring because of the interactions with the substrate and to an increased number of percolation pathways around defects.

In presence of water, acting as electrolyte, the AFM-tip could be exploited to locally trigger an electrochemical reduction thereby to pattern conductive pathways on otherwise-insulating graphene oxide (GO). By using the AFM tip to induce reduction of GO physisorbed in the microscopic channel of transistors, devices featuring an ambipolar transport and an 8 order of magnitude increase in current density upon local reduction were successfully fabricated (*figure 5*) [25]. Such an electrochemical reduction of GO was also accomplished macroscopically by using the source and drain electrodes of a transistor first to trigger the electrochemical reduction of the GO in the channel, and later to characterize the ambipolar transistor based on a semiconducting reduced GO filling the interelectrode channel [26]. These results are important in the frame of the use of simple upscalable approaches for the generation of either graphene based transistors or transparent graphitic electrodes for organic opto-electronics.

Kelvin probe force microscopy (KPFM) technique [27] allows the quantitative investigation of charges at surfaces. This is particularly interesting since in microelectronics and biology, many fundamental processes involve the exchange of charges between small objects, such as nanocrystals in photovoltaic blends or individual proteins in photosynthetic reactions. Hence, KPFM is the ideal technique to map of the photovoltaic activity in organic bulk-heterojunctions consisting of electron acceptor/donor blends. We have employed

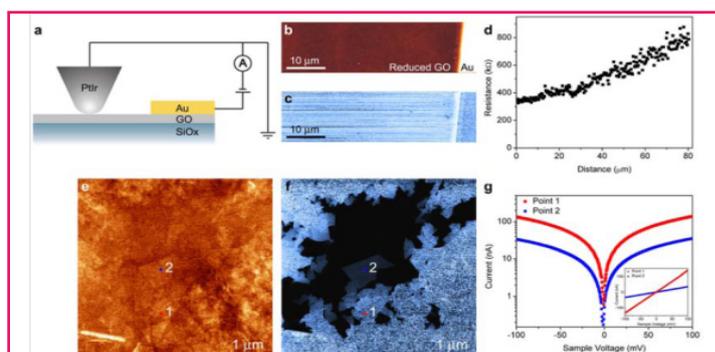


Figure 5 - (a) Schematics of the setup employed for C-AFM current mapping and current-voltage acquisition, (b) a contact mode topographic AFM image of a few layers reduced GO film with a top-contact Au electrode, and (c) the simultaneously recorded current map obtained using a 100 mV sample voltage. (d) The dependence of the electrical resistance as a function of tip to counter-electrode separation. Each data point represents an average of 20 measurements. (e) Contact mode image of a defect region of a reduced GO film, along with the corresponding current image (f) showing the absence of current over electrically disconnected segments, and differences in the current over regions of different thickness (current range = 200 nA). (g) Current-voltage traces measured at points 1 and 2 marked in (e) and (f). The inset shows the same data on a linear scale.

Image reproduced from [25] with permission from the American Chemical Society.

such a method to monitor such a photovoltaic activity on the hundreds of nanometers [28] and, for the first time, on the few nanometers scale (*figure 6*) [29]. In the latter case, we provided direct evidence of the electronic cross-talk in nanoscale phase segregated photovoltaic blends. The obtained results are crucial to gain a deeper understanding in the correlation between structural, compositional and electronic processes in multicomponent architectures, and for the optimization of organic solar cells.

## Supramolecular electronics

Achieving a full control over the order of functional building blocks at the ensemble level is crucial as it rules various physico-chemical properties of the system such as charge transport. By taking advantage of the capacity of supramolecular chemistry to develop architectures at will, we have exploited supramolecular strategies, through the self-assembly of multicomponent architectures at surfaces, to fabricate prototypes of nanoscopic and macroscopic devices. By attaining a control over the architecture vs. function relationship, we aim at improving the performance of organic electronic devices.

In particular, the use of solution-deposited polymers featuring semiconducting properties represents a valid alternative to amorphous silicon, with the advantage of a versatile processability using ink-jet printing/roll-to-roll techniques which are suitable for the mass production of low-cost electronics.

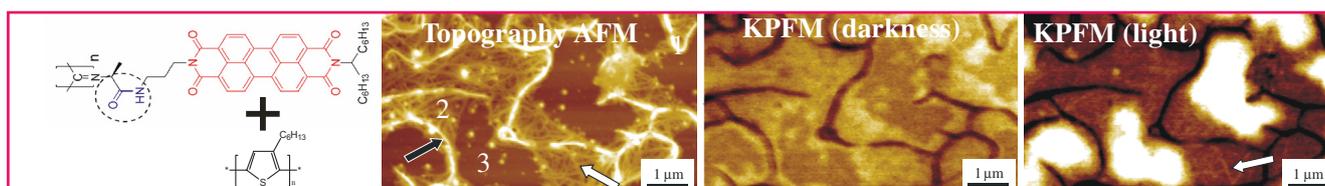


Figure 6 - Blends of poly(3-alkylthiophene) with polyisocyanide exposing PDI in the periphery. The two polymers both form fibers that can be visualized by topographical AFM imaging. The Kelvin probe force microscopy measurement of the surface potential in the dark reveals that the thicker fibers can be ascribed to the electron acceptor phase. Upon light irradiation with white light, the KPFM quantitative estimate of the surface potential reveals that the acceptor fibers get negatively charged and the donor ones get positively charged.

Image reproduced from [29b] with permission from the American Chemical Society.

When processed in these films, small molecules typically exhibit extremely high charge carrier mobilities, but suffer from problems related to their tendency to aggregate forming microscopic crystals. These crystals cannot be easily interfaced with metallic electrodes, limiting charge injection at metal-semiconductor interfaces, and are characterized by grain boundaries, which negatively affect the charge transport within the film. On the other hand, conjugated polymers combine a good solubility in organic solvents with large field-effect mobilities in thin films. However the semicrystalline nature of the polymer based assemblies limits the electrical characteristics of the films. For this reason, blends of polymer/small molecule are used in all those applications where multiple requirements are necessary and cannot be fulfilled by employing a single component. Mobilities measured upon blending two p-type components exhibited improved charge transport characteristics over the starting mobilities of the polymer based film or ideally also that of both single components.

In this frame we have focused our attention both to n-type and to p-type systems. In the former, we have co-deposited on insulating surfaces the monomeric perylenebis(dicarboximides) PDI derivative (M-PDI) with the polymeric P-PDI. We found conditions for producing crystals of M-PDI which are bridged by fibers of P-PDI, the latter architectures behaving as percolation pathways for charge transport. Compared to pure M-PDI, the bicomponent films (P-PDI + M-PDI) that feature polymer interconnections between crystallites of the monomer display a significant improvement in electrical connectivity and a 2 orders of magnitude increase in charge carrier mobility within the film, as measured in FETs device prototypes (figure 7) [30].

In the latter, we have co-deposited a prototypical polymeric semiconductor, *i.e.* poly(3-hexylthiophene) (P3HT), with a small conjugated molecule, *viz.* an alkyl-substituted bisphenyl-bithiophene (dH-PTTP). We observed final hole mobility as high as  $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  in 1:1 blends transistor, which corresponds to an enhancement of over 10-fold with respect to the mobility of the two starting components. Notably, the charge transport of the polymer is improved by the presence of oligomeric crystalline assemblies bridging conducting polymer domains. This remarkable improvement was achieved without introduction of any further surface functionalization or annealing step. Hence, it is highly

suitable for real device fabrication processes [31]. This blending method can be applied also by combining polymeric semiconductors with nanostructures possessing extraordinary electrical properties like grapheme [32].

Other supramolecular approaches to improve the performance of 2-, 3- and 4-terminal devices are being explored in our lab. Among them, the tailoring of electrodes-semiconductor interfaces using self-assembled monolayers is a key in order to control and optimize various properties of electrodes such as surface energies, work functions (WFs), etc. In this regard we developed a novel bottom-up approach to fabricate asymmetric (nano)electrodes using the electrochemical reductive desorption of a previously coated Au source electrode in a transistor. The uncoated electrode was then coated with a second thiolated molecule. The selective modification of electrode WF is demonstrated by Kelvin probe force microscopy and IV characterization of OFETs. The asymmetric FET devices showed controlled and independent charge injection and extraction at the interfaces with the source and drain electrodes as well as ambipolar behaviour in the OFET based on polythiophene (figure 8) [33]. This result is of paramount importance for applications in (opto)electronics in which asymmetric electrodes, *i.e.* electrode pairs in which each electrode has a different WF, can be a key for optimizing charge injection and extraction, *e.g.*, in ambipolar FETs, planar light-emitting diodes and solar cells. Moreover, such a bottom-up fabrication method can be employed to covalently tether functional groups to individual electrodes, towards multi-responsive devices [34].

## Conclusions

The different examples I have highlighted in this review article provide evidence for the significant improvements to the chemists' ability to control the transition from supramolecular structures to supramolecular functions, paving the way towards the fabrication of supramolecular nanodevices operating at surfaces. The challenges ahead are connected with the transition from mono-functional to multi-functional materials and devices, which are characteristics that can be achieved by using multicomponent systems, each one imparting a given property to be integrated in a multi-gating or multi-responsive device, *i.e.* a device that is capable of responding to various independent external stimuli [35].

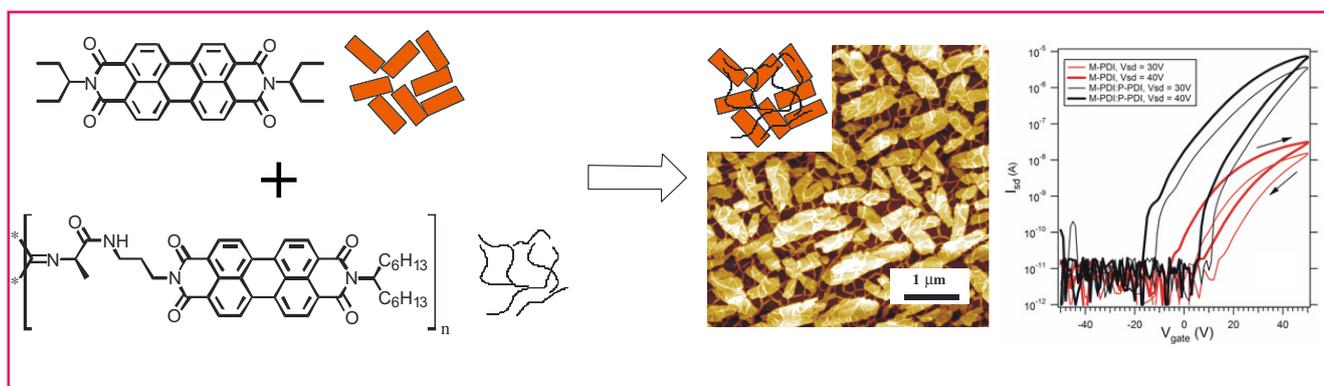


Figure 7 - Upon blending M-PDI (forming crystals) with P-PDI (forming fibers), it is possible to have the latter connecting the semiconducting crystals of the monomer, thereby acting as percolation pathways for charge transport (see AFM image for the binary morphology of the crystals linked by the fibers). Through the fabrication of prototypes of FETs, it was possible to measure the improved electrical properties of the bi-component film.

Image reproduced from [30] with permission from the American Chemical Society.

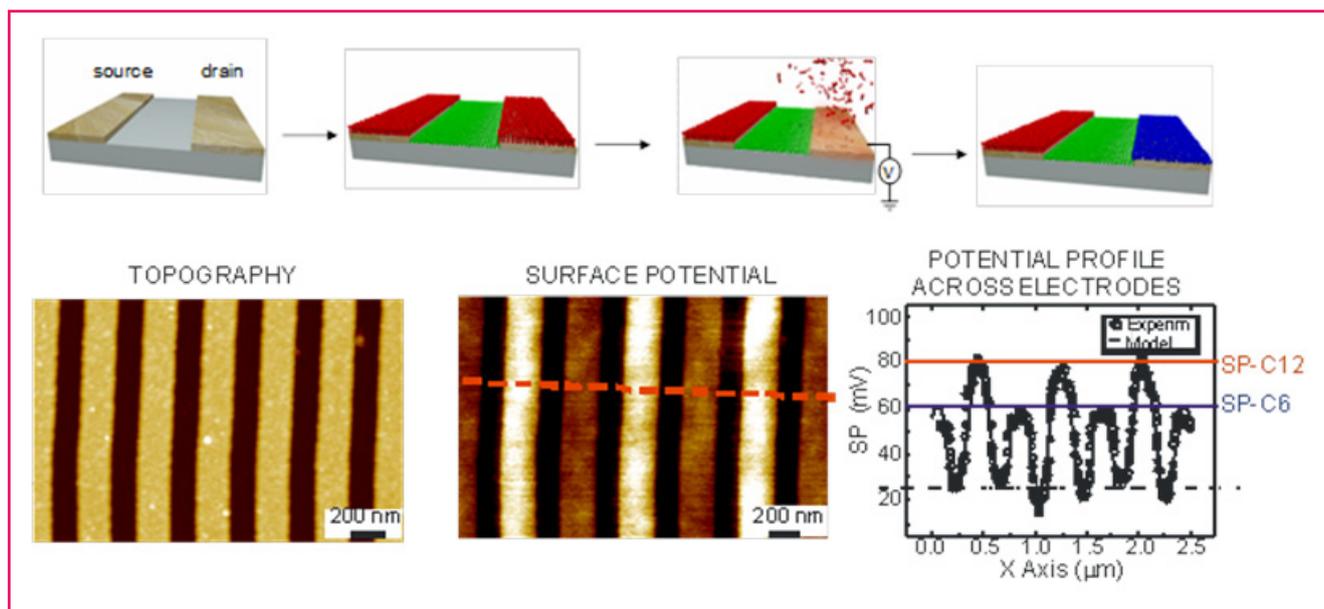


Figure 8 - Top: preparation of asymmetric electrodes: dodecanethiol (red) is chemisorbed on the uncoated Au supported on  $\text{SiO}_2$ ; the selective SAM reductive desorption from the drain electrode is followed by the chemisorption of a hexanethiol SAM (blue). Bottom: topography and KPFM potential image of nanometric source-drain interdigitated electrodes covered by alternating dodecanethiol and hexanethiol SAMs. The surface potential profile (○) recorded along the red dashed line. Image reproduced from [34] with permission from Wiley-VCH.

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