Conducting Nanomaterials

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Highly Conductive Supramolecular Nanostructures of a Covalently Linked Phthalocyanine–C_{60} Fullerene Conjugate**

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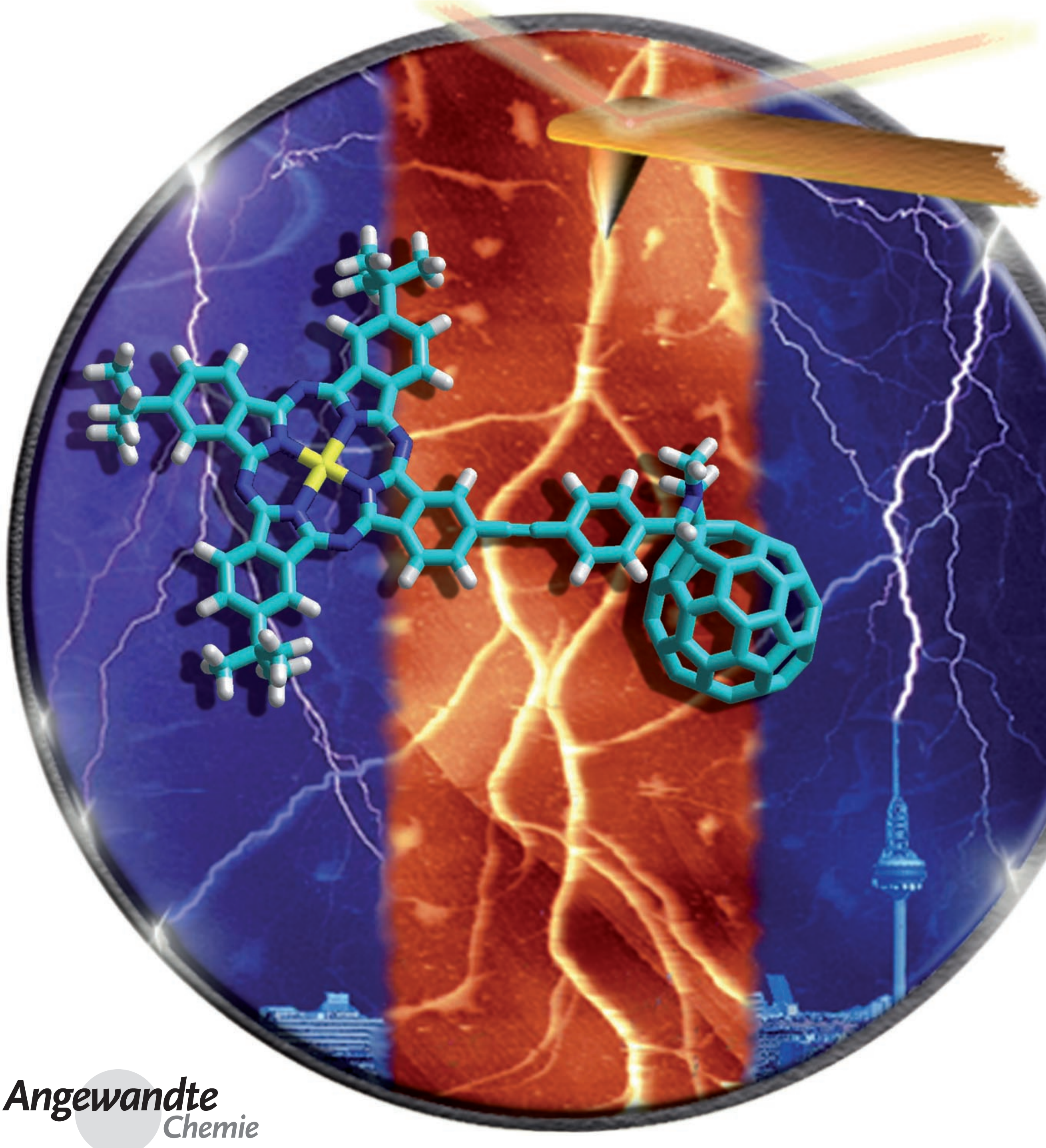
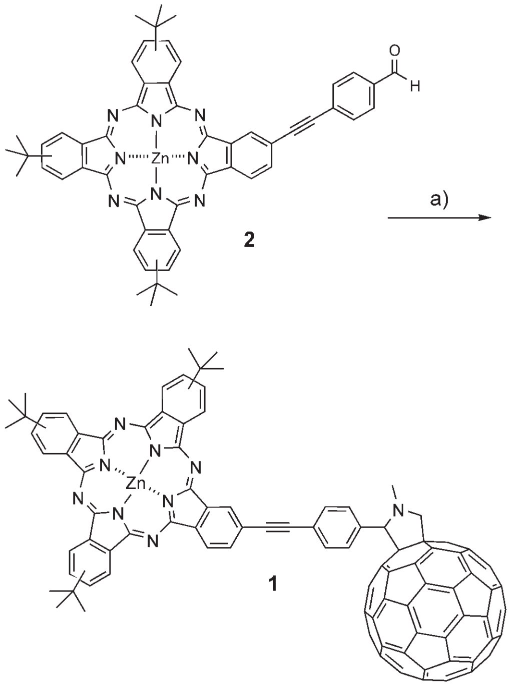


The construction of highly ordered supramolecular architectures in which organic molecules are organized on surfaces across multiple length scales represents a key issue within the fast-growing field of supramolecular electronics.[1] In this context, self-assembly appears as an attractive and efficient bottom-up approach for the construction of such molecular systems where enhanced electrical properties are sought, as it allows the preparation of complex functional systems through the use of weak, noncovalent interactions. One of the most promising methods for the construction of these supramolecular assemblies relies on the self-organization ability of π-conjugated systems.[2]

Phthalocyanines (Pcs)[3,4] are planar, two-dimensional aromatic molecules able to self-assemble into stacks through π–π supramolecular interactions.[5] These macrocycles possess electrical[6] and outstanding optical[7] properties that make them perfect building blocks for incorporation into multifunctional materials.[3] Similarly, the excellent electron-accepting property of the C_{60} fullerene,[8] together with its low reorganization energy,[9] renders this spherical carbon cage a perfect partner for photo- and electroactive molecular systems, such as Pcs.

To date, a few molecular and supramolecular architectures incorporating a Pc macrocycle and a C_{60} fullerene moiety (that is, a Pc-C_{60} dyad) have been prepared and their photophysical properties studied both in solution and in the solid state, which give rise to the formation of long-lived charge-separated species.[5g,10–12] However, to the best of our knowledge, the electrical properties of Pc-C_{60} dyads organized on surfaces at the nanoscale have not yet been investigated. Herein, we report a covalently linked Pc-C_{60} fullerene conjugate **1** (Scheme 1) that is able to self-organize on graphite and graphite-like surfaces to form fibers and films that possess outstanding nanoscale electrical conductivity.



Scheme 1. Synthesis of the Pc-C_{60} conjugate **1**. a) *N*-methylglycine, C_{60} fullerene, dry toluene, reflux, 24 h, 36 %.

The Pc-C_{60} dyad **1** was prepared by a three-step synthesis starting from the unsymmetrical tri-*tert*-butyl iodo Pc,[13] which was subjected to a Sonogashira coupling reaction with 4-ethynylbenzaldehyde to give the benzaldehyde-substituted Pc **2** in 92 % yield. Reaction of the latter compound with C_{60} fullerene in the presence of *N*-methylglycine afforded the dyad **1** in 36 % yield as a racemic mixture at the methine pyrrolidine carbon atom (Scheme 1). All the compounds were fully characterized by using different analytical and spectroscopic techniques (see the Supporting Information for details).

The organization property of the donor–acceptor (D-A) Pc-C_{60} dyad **1** on highly oriented pyrolytic graphite (HOPG) was investigated by atomic force microscopy (AFM). A freshly prepared solution of dyad **1** in toluene was deposited by a drop-casting technique on HOPG and allowed to evaporate (see the Supporting Information for details). AFM studies on drop-cast graphitic surfaces revealed the formation of layers and micrometer-long fibers (Figure 1 a,b), the height and density of the latter being strongly dependent on the concentration of the drop-cast solution (see Supporting Information).

The coexistence of layers and fibers on the drop-cast substrate is probably a result of two competitive, concentration-dependent organization processes. These processes probably occur simultaneously, as confirmed by the presence of some supramolecular fibers "sandwiched" between dyad layers on the film surface (Figure 1 a, box area).

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

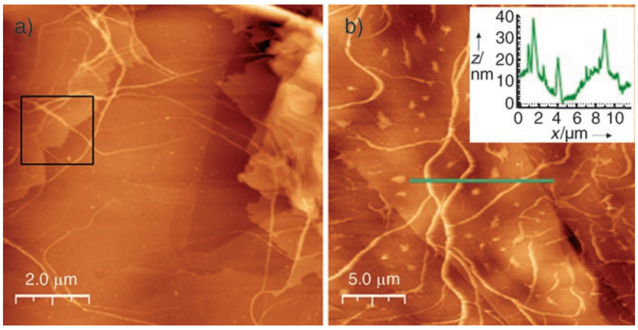

Figure 1. a,b) AFM topographic images of the Pc-C_{60} dyad **1** drop-cast on HOPG ([**1**]: a) = 10^{-5} M, b) = 10^{-6} M). The box in (a) shows a region of the substrate where supramolecular fibers of **1** are sandwiched between dyad layers. The inset in (b) shows the AFM topographic profile of the green line in that image.

The supramolecular nanostructures are not hard and could be mechanically "pierced" by using the AFM tip in contact mode at high load force, thus generating nanometer-deep holes on the film surface (see Supporting Information). As expected, the film thickness strongly depends on the concentration of the drop-cast solution although it varies within the same drop-cast substrate, probably because of the nonuniform evaporation of the cast solution on the substrate as well as the steps of the HOPG surface (see Supporting Information).

In an attempt to shed light on the key factors influencing the supramolecular organization of the Pc-C_{60} conjugate **1**, solutions of two dyad components in toluene, namely the ethynylbenzaldehyde-substituted Pc **2** and the *N*-methyl-3,4-fulleropyrrolidine **3** (see Supporting Information for details; [**2**] and [**3**] = 10^{-5} M), were prepared, separately drop-cast on HOPG substrates, and studied by AFM. We reckon that because of their strong tendency to self-aggregate, these two dyad moieties (that is, the Pc and C_{60} units) should be responsible, probably each to a different extent, for the supramolecular organization of the dyad. Interestingly, the AFM studies showed no signs of supramolecular organization (see Supporting Information). These findings suggest that in the structurally rigid Pc-C_{60} dyad **1**, which has the Pc and the fulleropyrrolidine moieties connected by a stiff ethynylphenyl spacer (see Supporting Information), both the Pc and the C_{60} moieties act cooperatively as strong elements of ordering giving rise to the observed mesoscopic organization.

Further AFM studies on the organization property of the conjugate **1** on HOPG were carried out in the presence of pyridine. Pyridine is a molecule known to promote deaggregation in Zn^{II}Pcs through the axial coordination of its nitrogen atom to the metal center of the Pc macrocycle.[14] The presence of this nitrogenated ligand in a drop-cast dyad solution ([**1**] = 10^{-5} M) suppressed the formation of fibers and induced a high degree of disorder within the nanostructures (see Supporting Information). This last experiment shows the importance of the π–π stacking intermolecular interactions between the Pc units as one of the key factors responsible for the supramolecular organization of the Pc-C_{60} conjugate **1** on HOPG, while the possibility of other intermolecular interactions, such as C_{60}–C_{60} and/or Pc–C_{60}, cannot be ruled out.

It was not possible to unambiguously assess whether the supramolecular organization of dyad **1** takes place in solution [that is, concentration-dependent UV/Vis studies did not show any evidence of supramolecular interactions of the dyad in the concentration range investigated (10^{-4}–10^{-7} M; see Supporting Information)] or is induced by the graphitic surface, or both. However, it would be reasonable to suggest that molecule-to-molecule as well as molecule-to-surface interactions should play an important role in the organization displayed by dyad **1** on HOPG.

Considering that self-organized π-electron systems have already been incorporated as building blocks for the construction of electrically conductive molecular structures,[15] we decided to investigate the potential electrical transport properties of the D-A Pc-C_{60} nanostructures by using conductive AFM (C-AFM). C-AFM is a powerful tool for measuring electrical properties in nanostructured architectures.[16] In fact, this technique allows the electrical mapping (usually with a spatial resolution of the order of the C-AFM tip radius, ca. 30 nm) of a sample as a metal-coated AFM tip is passed over it.

Initially, a region of the drop-cast HOPG substrate is scanned with a highly doped, conductive diamond AFM tip in dynamic mode. Once the AFM topographic image has been recorded, the C-AFM tip is driven to contact a chosen point of the surface and at a desired tip indentation a current–voltage (*I*–*V*) characteristic is acquired (see the Supporting Information for details).[17] In such an experiment, the electrical current measured during the voltage ramp corresponds to the charges that flow through the nanometer-thick dyad material which is sandwiched between the C-AFM tip and the HOPG surface ("out-of-plane" conductivity). Figure 2d shows the *I*–*V* curves obtained by contacting the C-AFM tip to a 20-nm-high Pc-C_{60} fiber (Figure 2a, point I), to a few-nanometer-thick dyad plaque (Figure 2b, point II), and to a bare HOPG substrate used as reference (Figure 2c, point III).

Surprisingly, the *I*–*V* values obtained for the fiber (Figure 2d, black curve) and the plaque (Figure 2d, red curve) saturate the preamplifier at 30 µA for bias voltages ranging from 0.30 to 0.55 V. Notably, these *I*–*V* values are very close to that of HOPG, which is an excellent electrical conductor with a very low resistivity (Figure 2d, blue curve), and are among the highest measured in supramolecular nanostructures.

The C-AFM experiments were repeated several times on different drop-cast substrates, and in all cases comparable *I*–*V* values were obtained for both layers and fibers. (No signs of any morphological change at the contact point of the C-AFM tip with the plaques and the fibers were observed after each of the *I*–*V* experiments.) The slightly lower current values recorded for the Pc-C_{60} fibers compared to the values obtained for the plaques are probably a result of the different supramolecular organization adopted by dyad **1** in the two supramolecular structures, which in the case of the fibers leads to a lower efficiency in electrical transport. The benzaldehyde-substituted Pc **2** and the fulleropyrrolidine

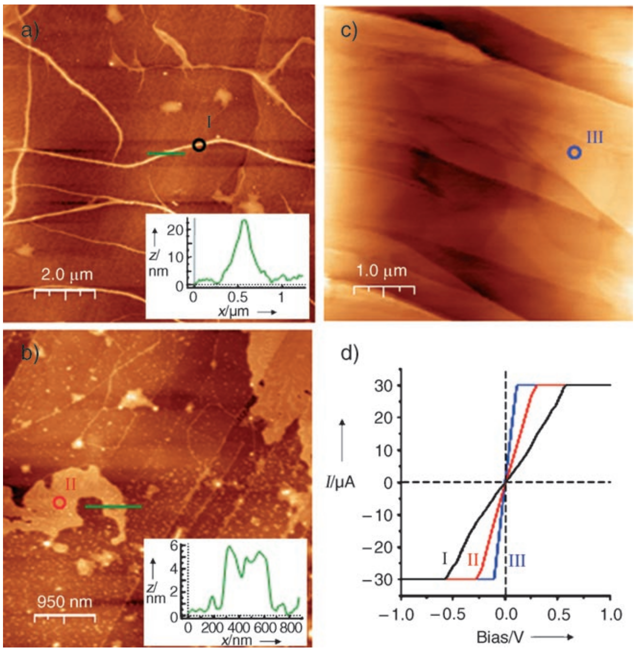

Figure 2. a–c) AFM topographic images of a,b) Pc-C_{60} dyad **1** drop-cast on HOPG ([**1**]: a) $=10^{-6}$ M, b) $=10^{-7}$ M) and c) bare HOPG. The insets in (a) and (b) show the AFM topographic profiles of the green lines in the corresponding images. After acquisition of the images, a metal-doped AFM tip was connected to a Pc-C_{60} fiber (a, point I), a Pc-C_{60} plaque (b, point II), and bare HOPG (c, point III) to measure their *I*–*V* characteristics. d) *I*–*V* curves at points I (black), II (red), and III (blue) measured by C-AFM. A dc bias was applied from −1 to +1 V.

derivative **3**, which do not organize when separately drop-cast on HOPG (see above), did not show any electrical conductivity in C-AFM experiments (see Supporting Information).

In an attempt to unravel whether the high electrical conductivity values observed for the drop-cast Pc-C_{60} samples were a result of the high degree of organization adopted by the conjugates within the nanostructures, C-AFM experiments were carried out on 1) a spin-coated sample of Pc-C_{60} **1** and 2) a drop-cast sample of Pc-C_{60} **1**/pyridine (1:1). The spin-coated sample of the dyad showed a morphology that was quite distinct from the drop-cast material, as no fibers were observed throughout the rough surface (see Supporting Information). The marked change in the morphology on going from the drop-cast to the spin-coated substrates could be explained by considering the extremely fast evaporation process experienced by the cast Pc-C_{60} dyad solution in the spin-coating process, which resulted in the formation of highly unorganized structures.

The *I*–*V* characteristics of the spin-coated sample of dyad **1** revealed a complete loss of the excellent electrical properties observed for the drop-cast samples (see Supporting Information). In the other experiment, a 1:1 solution of Pc-C_{60} **1**/pyridine was drop-cast on HOPG to obtain poorly organized structures (see above), which were electrically characterized by C-AFM. As in the case of the spin-coated sample, electrical conductivity values several orders of magnitude lower than those observed for the dyad sample drop-cast in the absence of the pyridine ligand were obtained (see Supporting Information).

These findings suggest that the high conductivity values observed for the Pc-C_{60} dyad **1** must be related to the nanostructure organization adopted by the dyad in the drop-cast samples, as when this organization is somehow altered (that is, adding pyridine or spin-coating the sample) a dramatic drop in the electrical conductivity is observed.

The remarkable out-of-plane electrical conductivity showed by the Pc-C_{60} nanostructures prompted us to investigate the electrical transport of the dyad along the plane ("in-plane" conductivity). This proved to be a nontrivial task because unfortunately dyad **1** did not form fibers or layers on some of the most common insulating surfaces, such as silica or mica (see Supporting Information). In the quest for alternative insulating surfaces over which dyad **1** could organize, we selected graphite oxide (GO) flakes.

GO flakes are electrically insulating, polyoxygenated graphene sheets with heights that range from one to a few atomic layers.[18] GO-physisorbed HOPG substrates (hereafter referred to as GO@HOPG substrates) could be readily prepared by drop-casting a water dispersion of the GO flakes on HOPG (see the Supporting Information for details). Figure 3a shows the AFM topographic image of some nanometer-high GO flakes on a GO@HOPG substrate.

A C-AFM experiment was carried out by contacting the C-AFM tip to a micrometer-square GO flake (hereafter referred to as the "reference" GO flake) on the GO@HOPG

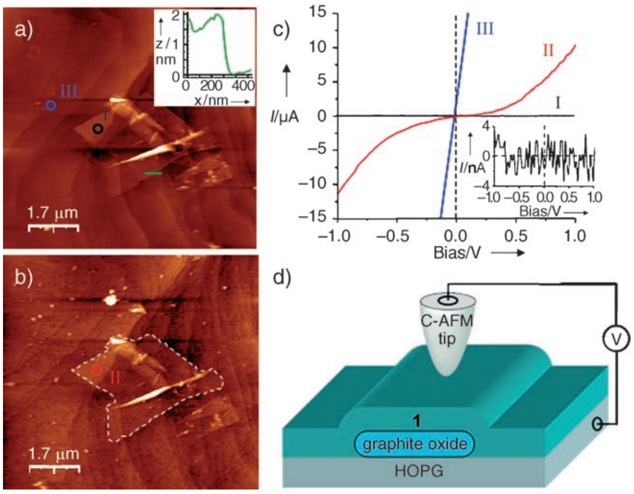

Figure 3. a,b) AFM topographic images of a) micrometer-sized GO flakes deposited on a HOPG substrate (GO@HOPG) and b) Pc-C_{60} dyad **1** drop-cast on GO@HOPG ([**1**] $=10^{-8}$ M). The inset in (a) shows the AFM topographic profile of the green line in that image. After acquisition of the images, a metal-doped AFM tip was connected to the uncovered HOPG surface (a, point III), to a GO flake in the pristine GO@HOPG substrate (a, point I), and to the same GO flake from (a) after drop-casting of dyad **1** over the GO@HOPG substrate (b, point II) to measure their *I*–*V* characteristics. In (b) a white dashed line is drawn around the GO flake investigated to facilitate its visualization. c) *I*–*V* curves at points I (black), II (red), and III (blue) measured by C-AFM. Inset: magnification of the black curve. A dc bias was applied from −1 to +1 V. d) Schematic representation of the C-AFM experiment carried out in (b). The objects are not to scale.

substrate (Figure 3a, point I). The recorded *I–V* curve showed the features typical of a material with a high electrical resistance (Figure 3c, black curve), with a current intensity in the nanoamp range (Figure 3c, inset), thus confirming the electrically insulating nature of the GO flakes. (These *I–V* values are within the electronic noise of the preamplifier used.) A C-AFM experiment was also carried out on an "uncovered" HOPG area on the same GO@HOPG substrate (Figure 3a, point III), which as expected revealed a metallic behavior in the *I–V* profile (Figure 3c, blue curve).

A solution of dyad **1** in toluene ($[\mathbf{1}]=10^{-8}\,\text{M}$) was then drop-cast on the same GO@HOPG substrate previously studied and the reference GO flake of Figure 3a was located again (see Supporting Information). The concentration of the dyad solution drop-cast onto the substrate is crucial, as at dyad concentrations higher than $10^{-7}\,\text{M}$ the GO flakes would be completely hidden below the dyad film, thus making their detection unfeasible.

A C-AFM measurement was carried out on the reference GO flake of the drop-cast GO@HOPG substrate (Figure 3b, point II). Surprisingly, the *I–V* curve obtained was now in the microamp range (Figure 3c, red curve). Notably, the electrical conductivity measured above the reference GO flake increased by almost four orders of magnitude for a bias of 1 V on going from the pristine to the drop-cast GO@HOPG substrate. We repeated the C-AFM measurements at distinct positions on the reference GO flake in the drop-cast GO@HOPG substrate and on different GO flakes of several drop-cast GO@HOPG substrates, and similar *I–V* curves were recorded in all cases.

The remarkable increase in the electrical conductivity observed above the GO flakes upon drop-casting of a dyad solution on the GO@HOPG substrates could be explained by assuming that in these substrates, the Pc-C_{60} dyad **1** is able to form highly organized supramolecular films on both the uncovered HOPG surface and on top of the electrically insulating, oxygen-rich graphene sheets of the GO flakes. Thus, when a bias voltage is applied between the C-AFM tip and the HOPG surface an electrical current flows "through" the electrically conductive dyad film (in-plane conductivity) which lies above the GO flakes (Figure 3d). AFM tip indentation experiments were carried out to determine the thickness of the dyad film organized above the GO flakes; values of about 3 nm were obtained, in agreement with observations for the dyad drop-cast at the same concentration ($10^{-8}\,\text{M}$) on HOPG (see Supporting Information).

Currently, we do not have an exact model that could account for the remarkable electrical transport properties of the dyad nanostructures. However, it seems reasonable to suggest that efficient inter- and intramolecular electronic communication between the Pc donor and the C_{60} fullerene acceptor moieties takes place within the dyad assembly, as a result of the supramolecular organization adopted by the Pc-C_{60} conjugates in the film (inter-) as well as some intrinsic structural features of the dyad (intra-), thus resulting in efficient electrical pathways for charge transport.

In conclusion, self-assembled films and fibers of a covalently linked Pc-C_{60} conjugate have been prepared by simple solution-processing steps on graphite and graphite-like substrates. These nanostructures were electrically characterized by a C-AFM technique, and show outstanding out-of-plane and in-plane electrical conductivity values that reflect an extremely high degree of molecular order of the Pc-C_{60} conjugate within the nanostructures.

The preparation of highly conductive, easy-to-assemble supramolecular nanostructures in which photo- and redox-active units, such as Pcs and C_{60} fullerenes which are excellent donor and acceptor moieties, respectively, are molecularly assembled on graphitic surfaces is extremely promising. The technique may lead to molecular materials with possible applications in the fields of nano-optoelectronics and photovoltaics,[19] such as the active layer in fully transparent graphene-based silica composites.[20]

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