

Connecting Organic Nanowires

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In this work we report on a universal methodology for connecting organic nanowires and nanosheets formed by π -conjugated molecules via metal nanoparticles. We present a brief study on the electrical characteristics of the thus connected nanowires carried out in a four-tip-STM manipulation and measurement system (4TMMS; STM = scanning tunneling microscopy) under ultra-high vacuum (UHV) conditions.

The recent developments in organic semiconducting nanostructures have permitted important advances in the fabrication of low-cost, large-area, flexible optic and microelectronic devices.^[1] In fact, over the last few years the use of π -conjugated molecules as building blocks for such organic nanostructures has received special attention and interest.^[1] Within the class of π -conjugated molecules, the families of metallo porphyrins, metallo phthalocyanines, and perylenes are promising materials for varying applications such as vapor (gas) nanosensors and as active components for photonic devices, organic field effect transistors (OFETs), phototransistors, and solar cells.^[2] It has been realized that the fabrication of hybrid organic/inorganic materials comprising semiconducting organic nanowires and metal particles opens new routes in the design of devices' functionality.^[3] Such hybrid materials may provide a ideal model system for the study of organic/inorganic nanomaterials. Despite this promising prospect, only very few works exist regarding the formation of organic semiconducting nanofibers/metal particles hybrid systems.^[3b-d,f]

In this Communication, we present a significant step forward in the fabrication of nanowire–metal–nanowire junctions by using metal nanoparticle-decorated organic nanowires as a base for the growth of secondary nanowires in such a way that a new route for the fabrication of connected organic single-crystal nanowires is demonstrated.

First, we describe the organic/inorganic hybrid nanostructures prepared by decorating single-crystal organic nanowires with metal particles in a one-step dry process at room temperature. In a second step we demonstrate an unprecedented class of heterostructured nanowires formed by connection through metal nanoparticles of different organic nanostructures. Finally, the electrical conductivity of these connected nanowires is studied in a 4TMMS.^[4]

Preparation of Hybrid and Connected Nanowires: Recently, we have reported a universal method for the growth of squared nanowires and nanobelts formed by π -conjugated molecules on

metal and non-metal substrates.^[5] This protocol is based on physical vapor deposition (PVD) of the organic molecules on substrates at controlled temperatures. A high density of supported single-crystalline organic nanowires can be obtained by this methodology.^[5]

The preparation of the silver-decorated organic nanowires is carried out by direct current (DC) sputtering of silver at room temperature on the as-grown nanowires. DC sputtering is a versatile technique for producing metal thin films and nanoparticles (silver, gold, copper, etc.).^[6] To the best of our knowledge, this is the first time that this method is applied for the formation of metal nanoparticles on organic nanowires. The main parameter controlling the metal particle size distribution along the organic nanowires is the deposition time. Further improvements in the morphology and crystal homogeneity can be achieved by different post-treatments.^[6] Figure S1 of the Supporting Information shows different examples of the formation of silver particles on phthalocyanine nanowires where the randomly oriented collection of crystalline Ag nanoparticles are readily detectable by selected-area electron diffraction (SAED). Unlike hybrid materials studied in the references^[3b-d,f], the metal nanoparticles deposited by this dry method are formed exclusively on the surface of the organic nanowires. It is very important to stress that the transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) analyses have revealed that the deposition of the metal particles by this DC method does not affect the composition, crystalline structure, and morphology of the organic nanowires.

As we have shown, the single-crystalline nanowire grows by a crystallization process from the nucleation site at its basis. Such nucleation sites can be nanoparticles, grains resulting from the roughness or morphology of the substrate, defects, etc.^[5b] The main idea behind the growth of connected nanowires is the formation of secondary organic nanowires on a substrate previously coated with primary hybrid organic/inorganic nanowires. Figure 1 presents the growth of cobalt-phthalocyanine (CoPc) molecules on silver-decorated iron-phthalocyanine (FePc) nanowires. Figure 1a clearly shows the formation of the CoPc nanowires (secondary nanowires) from the silver nanoparticles attached to the FePc nanowires (Ag-FePc primary nanowires). This method provides a high density of these connected nanowires (Fig. 1b). Besides, the protocol can be repeated in order to get a complex network of connected nanowires. It is noteworthy that the size distribution of the silver particles along the nanowire and their percolation level determine the morphology of the secondary nanowires. By adjusting the amount and size of the metal nanoparticles, a diverse variety of nanostructures such as squared nanowires (Fig. 1a, on the left side), nanobelts (Fig. 1a, on the right side), and nanosheets can be fabricated (Fig. 2, and Fig. S2 and S3 of the Supporting Information). The origin of the nanosheets in Figure 2 can be the merging of several nanobelts or squared nanowires growing from

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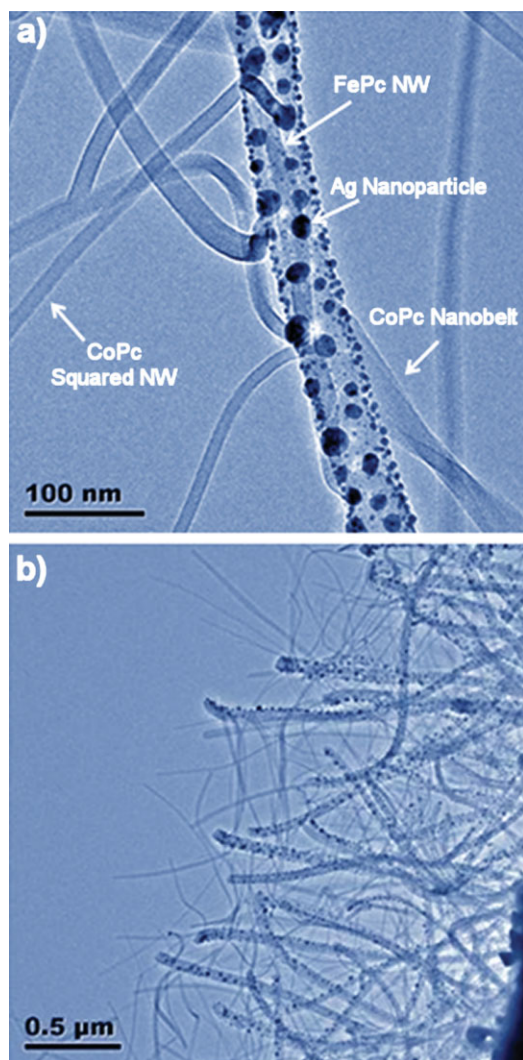


Figure 1. Organic nanowires connected by Ag nanoparticles. a) TEM image showing the growth of several CoPc nanowires from an Ag/FePc nanowire. b) Lower-magnification TEM image, where a high density of the heterostructured CoPc/Ag-FePc nanowires can be observed.

neighboring nucleation sites. Such nanosheets present just one dimension in the ~ 100 nm range. This formation results in a clear lamellar microstructure that is not present in the primary nanowires. It is interesting to note that the squared nanowires and nanobelts are 1D nanostructures whereas the nanosheets can be considered 2D nanostructures. Figure S4 of the Supporting Information shows a high density of palladium octaethyl porphyrins (PdOEP) nanosheets growing from perylene nanowires. These new architectures may be very interesting in light-harvesting applications of such organic semiconducting molecules.

Since the metal particles act as nucleation sites for nanowires formed by a wide variety of π -conjugated molecules, our protocol is readily extendable to the connection of nanowires of different composition. Figure 2 shows an example of Pd-porphyrin and perylene nanofibers connected by Ag. The protocol is not restricted to the presence of silver particles and other metal as non-metal nanoparticles can also provide the formation of

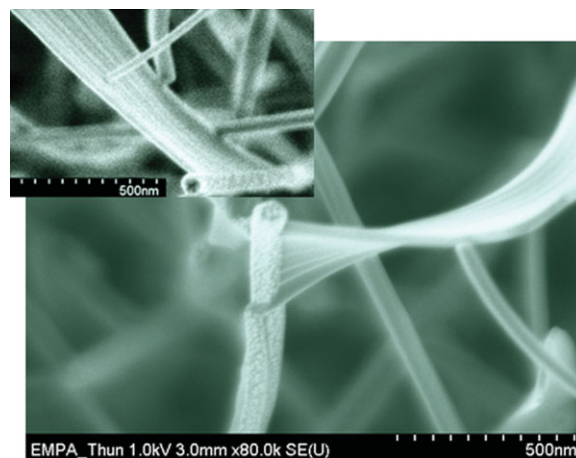


Figure 2. PdOEP nanosheets and nanowires growing from a perylene nanowire decorated with Ag particles.

organic nanostructures. In fact, other methods of nanoparticle formation can be applied to the formation of the new nucleation sites.^[3,7] The nanowires grown by this PVD method are single-crystalline. This has been established by HRTEM and electron diffraction (see Fig. S5 in the Supporting Information).^[5] Therefore, this methodology provides a facile route for the connection of single-crystalline nanowires.

Electrical Conductivity of the Nanowires: One of the most important advantages of this dry growth process is the straightforward formation of organic nanowire heterojunctions into prefabricated device architectures. In this context, we here present a first electrical characterization of individual connected nanowires in a 4TMMS.^[4] This system consists of a tunneling microscope with four tips, where each tip can be positioned independently in three dimensions. In addition, a field-emission scanning electron microscopy (FESEM) instrument is attached to the STM system in such a manner that the resolution provided by the FESEM permits to localize the organic nanowires and navigate the STM tips to a specific region. Figure 3 displays two of the I - V curves characteristic of the CoPc-NW/Ag-FePc-NW system. The sketches in Figure 3 show that these curves were measured between two tips (see Fig. S6 for the in-situ SEM images). These experiments were carried out at room temperature and at a residual vacuum pressure of $\sim 10^{-10}$ mbar. The I - V curve in Figure 3a was acquired on a ~ 10 -nm-thick CoPc nanowire. The two STM tips were placed at a distance of ~ 230 nm along the nanowire axis. The smooth and low noise I - V characteristic indicates that the two tips made stable contact to the nanowire. This was also verified by driving the voltage ramp in forward and reverse direction. Figure 3b shows the connection of two CoPc-NWs similar to the previous one through a ~ 50 -nm-thick FePc nanowire decorated with Ag particles. The CoPc-NWs are of square morphology connected to the FePc-NW by a single silver nanoparticle (c.f. Fig. 1a and Fig. S3 in the Supporting Information).

All the I - V curves acquired for individual and connected nanowires are symmetrical and show no rectification effect. The symmetry of the curves is remarkable and confirms that there is good electrical contact between the nanowires and the tips. For the different situations presented in Figure 3 (see also Fig. S7 in the

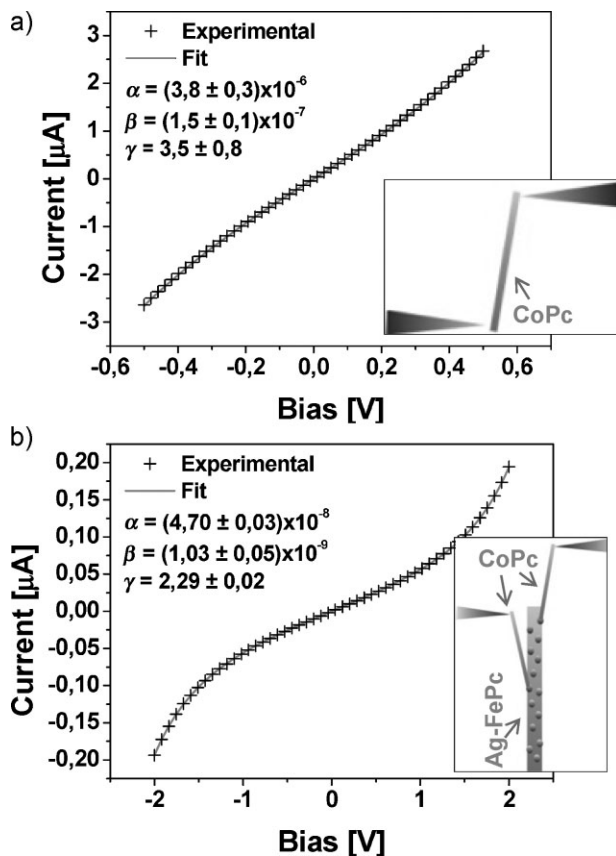


Figure 3. I - V characteristic curves measured between two tips for a CoPc nanowire (a) and two CoPc nanowires connected by the decorated Ag/FePc nanowire (b).

Supporting Information) the I - V curves fit in a very good agreement with the combination of an ohmic behavior at small voltage range and a variable range hopping (VRH)^[8] regime (see Eq. 1).

$$I(V) = aV + \text{sign}(V) \beta [\exp(\gamma|V|) - 1] \quad (1)$$

where I is the current, V is the applied voltage, and α , β , and γ are constants.

It is worth noticing that the single CoPc nanowire shows high conductivity values in comparison with other nanowires based on phthalocyanines and phthalocyanine derivatives.^[1] From the fit parameter α we estimate a specific electrical resistance of $\rho \sim 90 \Omega \text{ mm}^2 \text{ m}^{-1}$. This value represents the upper limit as the contribution of the contact resistance is included. This low resistivity confirms the high quality of the nanowires grown by this protocol in both their crystal structure and purity (see Fig. S5). Higher current values could be expected for a thicker nanowire. However, the resistivity corresponding to a $\sim 50 \text{ nm}$ Ag-FePc nanowire is much larger: $\rho \sim 10^4 \Omega \text{ mm}^2 \text{ m}^{-1}$ (see Fig. S7). Such variations can be explained by several reasons; the first one is the type of metal cation that is used for the semiconducting molecule. The specific resistivity values in the literature for FePc molecules are slightly higher than those for CoPc.^[9] Secondly, the lower conductivity of hybrid organic/inorganic nanostructures comprising metal particles and organic

nanowires has been very recently reported in a few works. Metal nanoparticles have recently been used to modify the dielectric-organic interface of organic field-effect transistors.^[3,10] In these publications it was shown that the presence of the metal nanoparticles reduced the mobility on the different studied devices. One of the possible reasons for such a decrease in device performance is the induction of carrier traps on the metal nanoparticles. In our case, the steric form and complete symmetry of the I - V plots presented in Figure 3b and S7 very likely indicate that the metal particles are not acting as carrier traps. The formation of silver particles exclusively on the surface of the nanowires supports this assumption as well. Moreover, it has to be taken into account that the conductivity through the cross section might play a key role in a thicker nanowire. This is supported by the observation that the molecular arrangement along the wire results in a herringbone-like stacking (see Fig. S5). Such a structure is produced by molecules that build columns along the wire axis via strong π - π interactions and form an angle with respect to the surrounding columns.^[5b)] This π - π stacking is expected to enhance the charge-carrier mobility, which is believed to be favored along the nanowire length.^[1,8] However, the energy barrier between two neighboring molecular columns may induce a lower conductance along the cross section of the nanowires.^[1,11] This energy barrier is eventually skipped by increasing the bias voltage. Above a certain bias, an electron can tunnel across the columns, which increases the conductance of the nanowire. In fact, the presence of an energy barrier across the Ag-FePc nanowire together with the possible bottle-neck effect due to the changes in nanowire thickness in the system CoPc/AgFePc/CoPc might be responsible for the lower current values achieved for the two CoPc connected nanowires (c.f., Fig. 3b).

Finally, the analysis of the I - V plots obtained in the CoPc/AgFePc and CoPc/AgFePc/CoPc systems (see Fig. 3 and S7) shows that a Schottky barrier is not formed at the connection between the semiconducting nanowires and the metal particles. This result also indicates that the decoration of organic nanowires by this DC method can be applied in the formation of electrodes along the nanowires for those device performances where an ohmic connection is required.

We have demonstrated a one-step dry method for the fabrication of high-quality supported organic nanowires formed by π -conjugated molecules.^[5] Metal nanoparticles can be deposited along these nanowires by simple DC sputtering at room temperature without modifying the nanowire structure. The nanoparticles act as nucleation sites for the new organic nanowires. The silver nanoparticles also operate as ohmic connectors between the nanowires. Very low values of resistivity have been measured in the nanowires as a result of their high crystallinity and purity. The high density of connected nanowires achieved by this protocol opens new possibilities for the integration of the semiconducting organic nanowires into dense arrays for electronic, sensing, and catalytic applications. In addition, this methodology is fully compatible with the present microelectronic and optoelectronic technology.

Experimental

Nanowires Deposition: The sublimation of the molecules for the nanowires deposition was carried out in a 10-mL OLED Knudsen cell (Lesker) placed in a

high vacuum chamber. The system was pumped to 5×10^{-6} mbar base pressure before the deposition. The distance between the substrate and the sublimation source was 8 cm. During the experiments Ar was dosed using a calibrated mass flow controller (MKS). The pressure in the system during deposition was fixed at 0.020 mbar. The growth rate was controlled by a quartz crystal microbalance located in the same plane as the substrates. Deposition rates were between 0.30 and 0.50 s^{-1} considering a density in the balance of 0.5 g cm^{-3} . These experimental parameters were common for both the primary nanowire and the secondary nanowire growth. Perylene (MePTCDI: 2,9-dimethyl-anthra-(2,1,9-def,6,5,10-d'ef)diisoquinoline-1,3,8,10-tetraone, from Sensient Imaging Technologies.), porphyrins (Frontier Sci.), and phthalocyanines (Aldrich) were used as purchased. The temperatures of the substrates were $(150 \pm 5)^\circ\text{C}$ for PdOEP, $(180 \pm 5)^\circ\text{C}$ for perylene, $(240 \pm 5)^\circ\text{C}$ for FePc and $(260 \pm 5)^\circ\text{C}$ for CoPc.

Silver Particles: Silver was deposited by DC sputtering in Ar at ~ 0.35 mbar applying a voltage of 450 V to a silver thread sited 3 cm above the substrates. The different distributions of silver particles along the nanowires were obtained through the control of the deposition time. The substrate temperature for the secondary growth also affects to the silver distribution.

Sample Characterization: For transmission electron microscopy (TEM) analysis the nanowires were grown on copper grids previously cover with silver. The microscope was a Tecnai F30 TEM operating at an acceleration voltage of 300 kV and equipped with a Schottky field emission electron source and Super Twin lens. Planar view and cross sectional images on Si (100) substrates were obtained in a Hitachi S4800 SEM. The *I*-*V* characteristics were measured in a 4TMMS (Nanoprobe stage from Omicron Nanotechnology GmbH). The experimental setup also includes a MATRIX control system for probe fine positioning and STM feedback, a programmable Keithley 2601 source meter to measure the IV curves, and a CSW-4G remote-controlled current switches for signal re-direction from the STM pre-amplifier to the source meter.

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- [1] a) S. R. Forrest, *Nature* **2004**, 428, 911. b) A. L. Briseno, S. C. B. Mannsfeld, S. A. Jenekhe, Z. Bao, Y. Xia, *Mater. Today* **2008**, 11, 38.
- [2] a) W. Wang, J. Han, L.-Q. Wang, L.-S. Li, W. J. Shaw, A. D. Q. Li, *Nano Lett.* **2003**, 3, 455. b) M. D. Curtis, J. Cao, J. W. Kampf, *J. Amer. Chem. Soc.* **2004**, 126, 4318. c) K. Xiao, I. N. Ivanov, A. A. Puzos, Z. Liu, D. B. Geohegan, *Adv. Mater.* **2006**, 18, 2184. d) P. A. Troshin, R. Koeppel, A. S. Peregudov, S. M. Peregudova, M. Egginger, R. N. Lyubovskaya, N. S. Sariciftci, *Chem. Mater.* **2007**, 19, 5363. e) J. W. Lee, H.-S. Kang, M.-K. Kim, K. Kim, M.-Y. Cho, Y.-W. Kwon, J. Joo, J.-I. Kim, C.-S. Hong, *J. Appl. Phys.* **2007**, 102, 124104. f) C. G. Claessens, U. Hahn, T. Torres, *Chem. Records* **2008**, 8, 75. g) C. G. Claessens, U. Hahn, T. Torres, *Chem. Rec.* **2008**, 8, 75.
- [3] a) L. Ma, S. Pyo, J. Ouyang, Q. Xu, Y. Yang, *Appl. Phys. Lett.* **2003**, 82, 1419. b) Z. Wang, C. J. Medforth, J. A. J. Shelnut, *Am. Chem. Soc.* **2004**, 126, 16720. c) D. J. Milliron, I. Gur, A. P. Alivisatos, *MRS Bull.* **2005**, 30, 41. d) R. J. Tseng, J. Huang, J. Ouyang, R. B. Kaner, Y. Yang, *Nano Lett.* **2005**, 5, 1077. e) Z. Wang, K. J. Ho, C. J. Medforth, J. A. Shelnut, *Adv. Mater.* **2006**, 18, 2557. f) A. L. Briseno, S. C. B. Mannsfeld, E. Formo, Y. Xiong, X. Lu, Z. Bao, S. A. Jenekhe, Y. J. Xia, *Mater. Chem.* **2008**, 18, 5395.
- [4] a) X. Lin, X. He, J. Lu, L. Gao, Q. Huan, Z. Deng, Z. Cheng, D. Shi, D. Gao, *Surf. Interf. Anal.* **2006**, 38, 1096. b) Omicron website, <http://www.omicron.de/nanoprobe/> (last accessed August 4, 2009).
- [5] a) A. Borras, M. Aguirre, O. Groening, C. Lopez-Cartes, P. Groening, *Chem. Mater.* **2008**, 20, 7371. b) A. Borras, O. Groening, M. Aguirre, F. Gramm, P. Groening, unpublished.
- [6] a) D. R. Sahu, C. Y. Chen, S. Y. Lin, J.-L. Huang, *Thin Sol. Films* **2006**, 515, 932. b) A. Borras, A. Barranco, J. P. Espinos, J. Cotrino, J. P. Holgado, A. R. Gonzalez-Elipe, *Plasma Process Polym.* **2007**, 4, 515. c) A. K. Chawla, R. J. Chandra, *Nanopart. Research* **2009**, 11, 297.
- [7] a) T. Girardeau, S. Camelio, D. Babonneau, J. Toudert, A. Barranco, *Thin Sol. Films* **2004**, 455, 313. b) J. H.-G. Ng, M. P. Y. Desmulliez, K. A. Prior, D. P. Hand, *Micro Nano Lett.* **2008**, 3, 82. c) D. W. H. Fama, A. I. Y. Tok, Al. Palaniappana, P. Nopphawana, A. Lohania, S. G. Mhaisalkara, *Sensors Actuators B* **2009**, 138, 189.
- [8] a) V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey, J.-L. Bredas, *Chem. Rev.* **2007**, 107, 926. b) S. Liu, W. M. Wang, A. L. Briseno, S. C. B. Mannsfeld, Z. Bao, *Adv. Mater.* **2009**, 21, 1.
- [9] H. S. J. Nalwa, *Elec. Mater.* **1988**, 17, 291.
- [10] M. Nishioka, Y. Chen, A. M. Goldman, *Appl. Phys. Lett.* **2008**, 93, 153308.
- [11] H. Liu, J. Li, C. Lao, C. Huang, Y. Li, Z. L. Wang, D. Zhu, *Nanotechnology* **2007**, 18, 495704.