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LETTER

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Ultralong Single Organic Semiconducting Nano/Microwires Based on Spiro-Substituted Perylenetetracarboxylic Diimide

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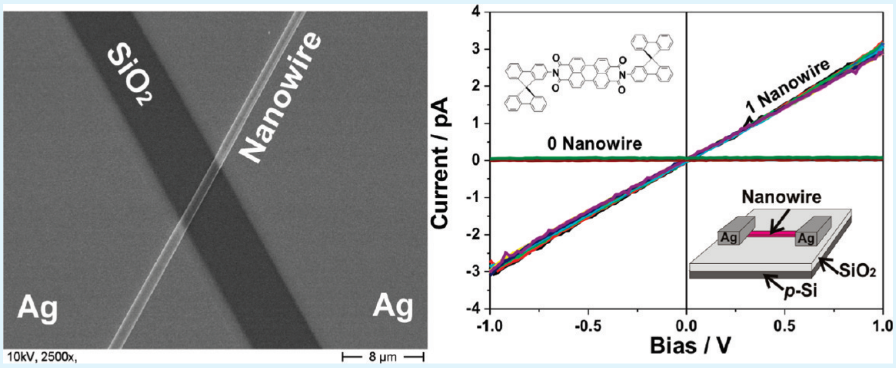
S Supporting Information

ABSTRACT:



An ultralong single organic semiconducting nano/microwire (NMW) is difficult to obtain. Here we show that this NMW can easily be prepared by using drying under solvent atmosphere method. This technique is not only unique, but also very compatible with our active material, spiro-substituted perylenetetracarboxylic diimide. A single NMW with a length of up to ~5.5 mm and an aspect ratio of ~9200 can be obtained. Finally, we succeeded to measure the electrical resistivity of a single NMW with values between 1×10^2 and 1×10^4 Ω m and the growth direction can be controlled as well by using a prestructured substrate.

KEYWORDS: self-assembly, ultralong, organic semiconductors, nano/microwires, spirobifluorene, perylenetetracarboxylic diimide

Nano/microwires (NMWs) are becoming an interesting topic in the scientific research community, especially in the field of micro- and nanoelectronics because the small dimension of the wires enables us to optimize, for example, the device density on a given substrate area. Besides inorganic semiconductors and metallic nanowires,[1,2] organic semiconductors have also attracted much attention in the scientific and industrial community because of their low-cost potential applications such as for light-emitting devices, field-effect transistors, and solar cells. Therefore, the scientific interest grows to fabricate NMWs based on organic materials as well. Such semiconducting NMWs can generally be fabricated through several methods, for example, electrospinning,[3] vapor condensation system,[4] solvent-vapor annealing technique,[5] or self-assembly approach from solution.[6−15] The latter technique is very interesting because the simplicity of fabrication implicates minimized processing costs.

Organic semiconductors based on the spiro concept have been used in order to improve the corresponding morphological stability of functional organic glasses while retaining their functionality.[16] Connecting two functional moieties with a spiro carbon atom achieves the task of raising the glass temperature (T_g) because the increased steric demand effectively hinders crystallization. Generally, spiro-linked compounds based on the 9,9′-spirobifluorene core are known as good glass formers with high T_g and good morphological stability, making them well suitable for organic electronic applications like solar cells, light-emitting devices, field-effect transistors, and lasers.[16] Beside these known and widely used properties of such compounds, the spiro moiety and its related steric hindrance in connection with an also established dye moiety, the perylenetetracarboxylic diimide, leads to a molecule with new and quite unexpected aggregation properties.

In this communication, we report self-assembly of ultralong organic semiconducting NMWs by using a new spirobifluorene-substituted perylenetetracarboxylic diimide, *N*,*N*′-bis(9,9′-spirobifluorene-2yl)-3,4,9,10-perylenetetracarboxylic diimide (Spiro-PDI), as shown in Figure 1a.[17] We found that drying under solvent atmosphere technique is a way to obtain an ultralong single NMW, allowing self-assembly process of the wires on the surface. The growth direction of NMWs can also be controlled by using a prestructured substrate. Finally, the electrical resistivity of a single NMW can be estimated.

Received: March 23, 2011
Accepted: May 16, 2011
Published: May 16, 2011

dx.doi.org/10.1021/am2003685 | ACS Appl. Mater. Interfaces 2011, 3, 1809–1812

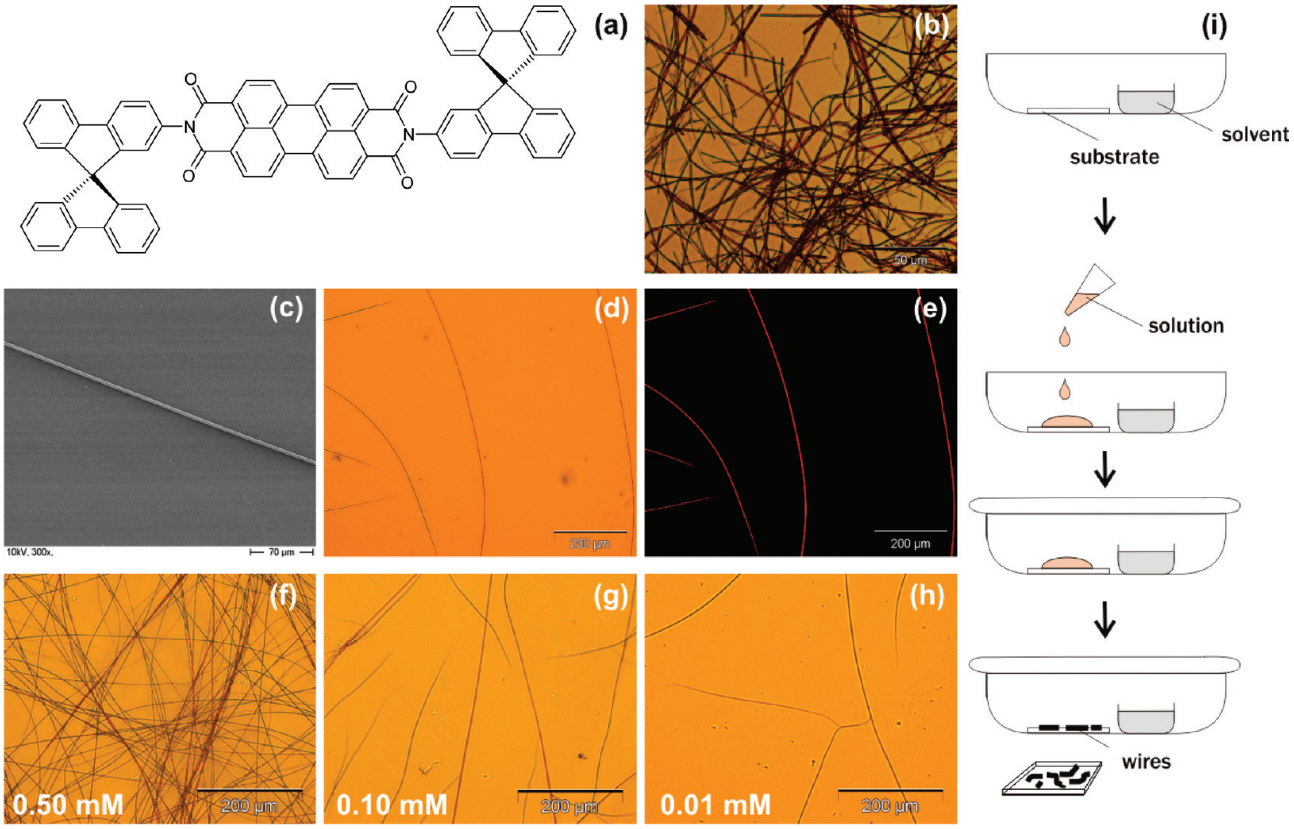


Figure 1. (a) Chemical structure of *N*,*N*′-bis(9,9′-spirobifluorene-2yl)-3,4,9,10-perylenetetracarboxylic diimide (Spiro-PDI); (b) optical micrograph of Spiro-PDI NMWs obtained from bisolvent phase transfer method (chloroform solution 0.25 mM/poor solvent methanol); (c−e) scanning electron microscopy, optical microscopy, and fluorescence microscopy images of wires obtained from drying under solvent atmosphere technique (0.01 mM chloroform solution); (f−h) optical micrographs of wires obtained from drying under chloroform atmosphere with different concentration of Spiro-PDI chloroform solution; (i) schema of self-assembly process via drying under solvent atmosphere (for further experimental details see the Supporting Information).

For low-cost, solution-based wire fabrication there are two well-known methods, namely (a) bisolvent phase transfer[7] and (b) rapid dispersion.[8] In both techniques, the wires are created in the volume-phase of the solution, and, subsequently, they can be transferred on a desired substrate by drop casting process. Figure 1b shows an optical micrograph of obtained Spiro-PDI wires from bisolvent phase transfer method (for experimental details, see the Supporting Information: experimental section and Figure S1). Applying rapid dispersion technique leads to similar results. The examination of the structure reveals a "belt" or a "wire" morphology, which is similar as observed for other materials.[9,18] The width of the resulting fibers ranges from several hundreds of nanometers to several micrometers. The maximum length cannot be determined because the wires break during the transfer pipetting process. Both methods work with the combination of a good and a poor solvent and the crystallization process takes place at the interface or in the mixture of these two solvents, respectively. Monitoring the absorption during the wire formation indicates the existence of *J*-type aggregation for Spiro-PDI (see Figure S2 in the Supporting Information).

Despite the common usage of the two established methods for fabricating wires from perylenetetracarboxylic diimides there is a considerable disadvantage. After the transfer process on a given substrate, the wires are very dense deposited on the surface and a kind of wire network is obtained. This arrangement is not very suitable for studying the electrical or optical properties of a single organic wire. For this reason, we adopted another technique, namely drying under solvent atmosphere. In this case, wires can be directly generated on a desired substrate. First, Spiro-PDI is dissolved in the good solvent chloroform and, then, this solution is dropped on the substrate and, subsequently, is dried under solvent atmosphere. The use of poor solvent as solvent atmosphere is already known,[9] but in our case, the arrangement of resulting wires is similar as obtained for bisolvent phase transfer method. For obtaining a better control on wire growth, we adopted using the good solvent chloroform as vapor atmosphere. The crystallization can thus be adapted into a slower and more controlled process. Figure 1c−e shows the resulting NMWs. We observed that growing wires this way results in different quality of NMWs with respect to the first two methods. Lacking a transfer process, the resulting structures are ultralong (in our case several millimeters), uniform, and well-separated. This is an advantage if we want to study the properties of a single wire. Moreover, varying the concentration of Spiro-PDI solution provides the opportunity to influence the wire density on the substrate (Figure 1f−h). In general, the wire width ranges from 0.2 to 3 μm.

The method we use here is similar as reported by Kim et al. in growing polythiophene microwires.[19] We conjecture that the spirobifluorene moiety in Spiro-PDI with its steric hindrance, gives a significant effect in aggregation process. By slowing down the evaporation of drop-casted solution by drying in solvent

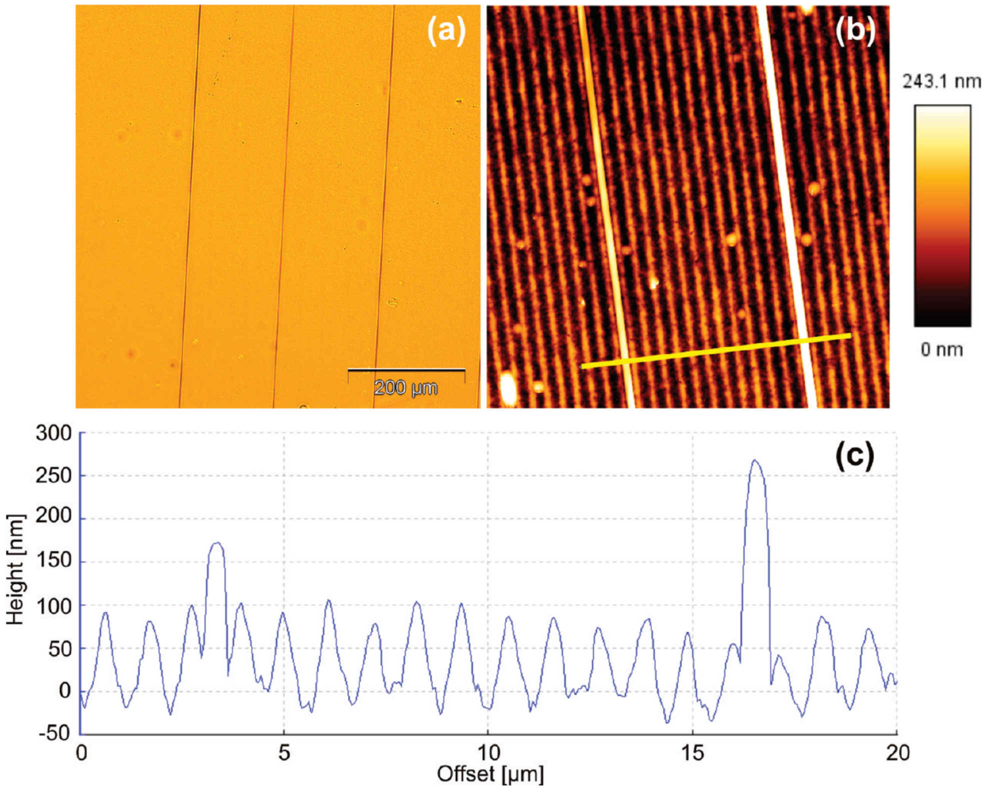


Figure 2. (a) Optical micrograph of self-assembled Spiro-PDI NMWs on the structured plastic substrate, grown by drying under chloroform atmosphere. (b) AFM image (30 μm × 30 μm) of two wires and (c) cross-sectional line profile aquired along the yellow line (wire width between 600 and 800 nm, wire height between 150 and 300 nm).

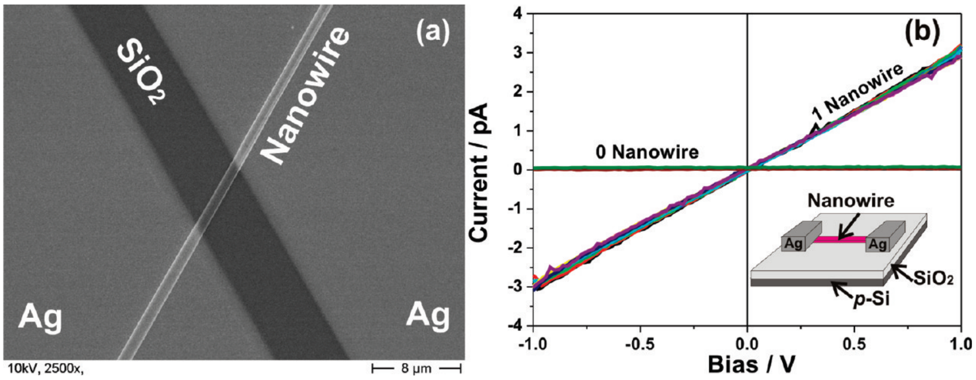


Figure 3. (a) SEM image of a typical single Spiro-PDI NMW device contacted with silver electrodes, and (b) *I*—*V* characteristics of a top-contacted single Spiro-PDI NMW acquired in the dark and under ambient atmosphere. The device was measured as the voltage being swept from −1 to 1 V in step of 0.02 V and vice versa. The graphic shows five sequences of measurement. A control device without wires showed a current as low as 5×10^{-14} A. Inset: Schematic diagram of the electrical measurement of single Spiro-PDI NMW.

vapor the molecules have sufficient time for arranging in a way favorable for the stacking in high order. This allows an effective self-assembly, giving rise to ultralong NMWs with high uniformity. With this method, we can even achieve a single wire with a length of 4 mm on glass substrate.

To further control the wire forming process, control of growth direction is a challenging task. To achieve this, we adopted a prestructured substrate. Figure 2 displays an optical micrograph and atomic force microscopy (AFM) image with cross-section analysis of the self-assembled Spiro-PDI NMWs on a plastic substrate with prestructured lines. The direction of the growing wires is driven by the direction of the grating. This directed growth is presumed to be a combination of favored crystal nucleation on surface kinks with the fact that solution is guided in the channels through capillary forces.

However, we cannot control the distance between the wires. The longest wire that can be observed in our experiment is 5.5 mm long, which means that the maximum aspect ratio of ~9200 (considering the diameter of wire ~600 nm) can be obtained. The real time dynamic of the directed self-assembly process on the structured plastic substrate can be watched in video (in the Supporting Information).

Investigating charge transport properties of single NMWs is our main interest. We have shown that the two volume-based wire fabrication methods cannot be used to prepare single separated wires. In contrast, drying under solvent atmosphere technique enabled us to fabricate ultralong single Spiro-PDI NMW and, therefore, it allows us to study the corresponding electrical properties. Figure 3a shows the SEM image of a single wire contacted with silver electrodes. The wire dimensions of one here exemplarily analyzed device were measured by AFM technique (width 880 nm, thickness 252 nm, see Figure S3 in the Supporting Information). Figure 3b shows the measured current−voltage ($I-V$) characteristics and the data are linear for bias voltages in the range of -1 to 1 V without any hysteresis. We also observed that the devices still show linearity in the range of ± 5 V. We extracted the resistance of a single Spiro-PDI NMW to be $R \approx 3.125 \times 10^{11}$ Ω. By taking into account the wire length of $L \approx 7$ μm, and the cross section of the wire A to be $\approx$880 nm (width) × 252 nm (height) one can calculate the wire resistivity ρ to be: $\rho = RA/L = 9.9 \times 10^3$ Ωm. The extracted resistivity values for 12 devices are in the range of 1×10^2 Ωm $< \rho < 1 \times 10^4$ Ωm. The variation in resistivity can be attributed to different quality of NMWs or contact behavior between silver and organic wires and the uncertainty in measuring the cross section of wires. Nevertheless, our result is similar as observed for other perylenetetracarboxylic diimide-derivative nanobelts[10,11] like *N,N*′-di(propoxyethyl)-perylene-3,4,9,10-tetracarboxylic diimide with a resistivity of 10^3 Ωm and also similar as for poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(bithiophene)] nanowires.[20] But it is much lower than the resistivity of condensed benzothiophene compound[21] and CdS−polypyrrole heterojunction nanowires.[22] We also tested the shown device configuration for functionality as field-effect transistor. However, no field-effect on the measured current could be observed. We conjecture that problems with thickness of dielectric or interface between wires and dielectric could be the reasons.

In summary, we have shown the simple processes in fabricating Spiro-PDI NMWs by using self-assembly approach drying under solvent atmosphere. This method resulted in a controllable number of NMWs on a desired substrate, enabling the fabrication of single Spiro-PDI NMW device. Furthermore, we were able to control the direction of NMWs by using a prestructured substrate. An aspect ratio as high as ~9200 could be obtained in our experiment and the longest wire was determined to be 5.5 mm. The resistivity of the single Spiro-PDI NMW was characterized and the value is in the range of 1×10^2 Ω m $< \rho < 1 \times 10^4$ Ω m.

■ ASSOCIATED CONTENT

Supporting Information. Experimental details and additional characterization data (PDF, movie file). This material is availible free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

The University of Kassel scholarship is gratefully acknowledged for support to J.L. and we thank N. Anspach, A. Schöne, and A. Deing for AFM measurements.

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