Supporting Information

High-performance phototransistors based on PDIF-CN_2 solution-processed single fiber and multi-fiber assembly

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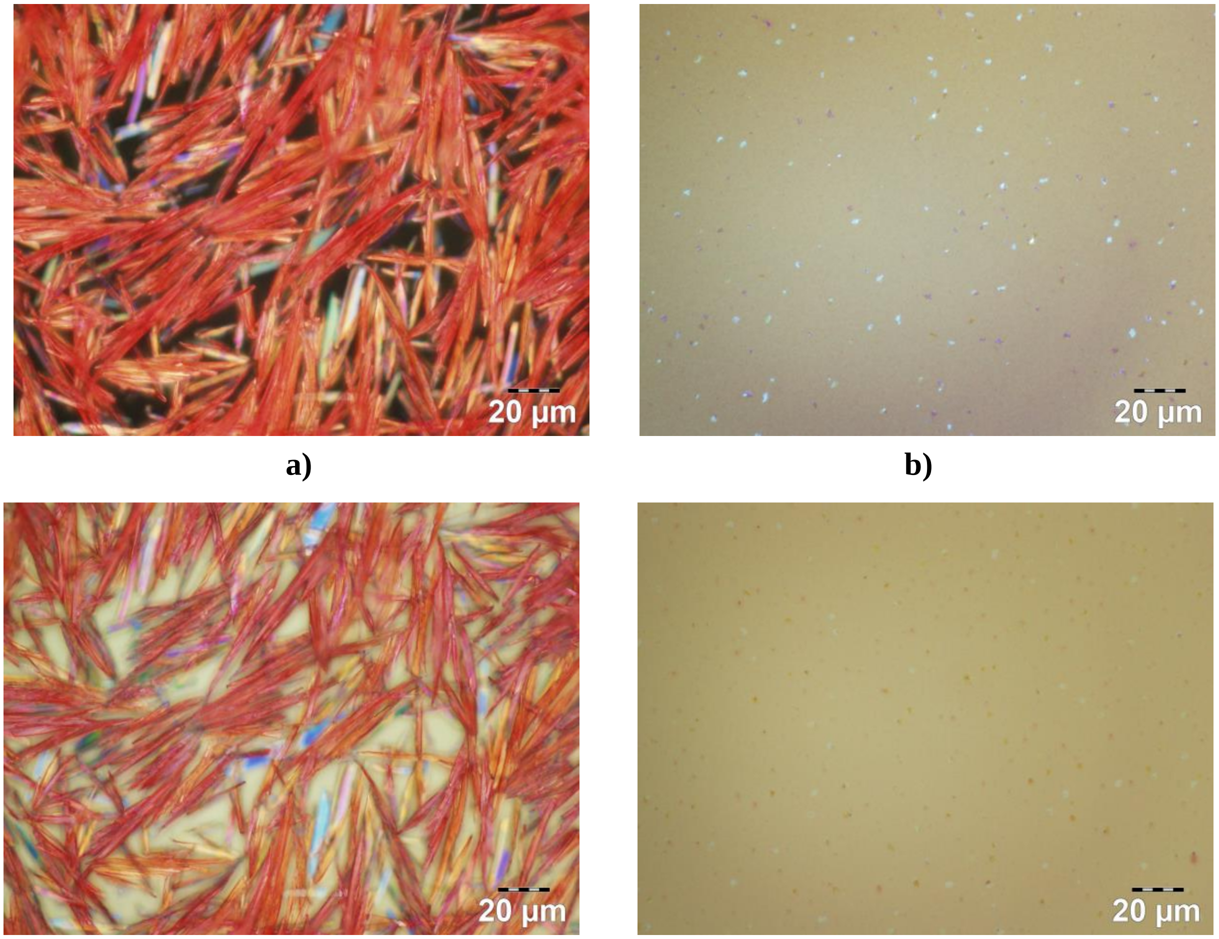
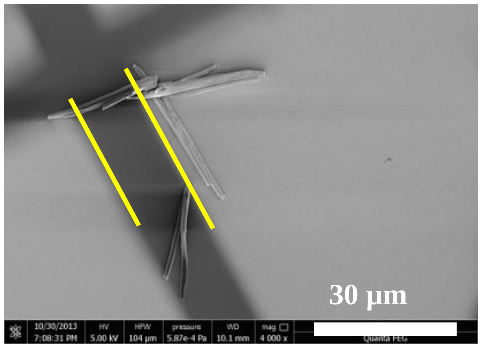


Figure S1 Polarized optical microscopic images of a), c) multifibers and b), d) amorphous spin-coated film-based devises.

Table S1. Summary of thin-film based FET parameters.

Spin-coated thin-film based FET		
devices treatment	**V_{th} (V)**	**μ ($cm^2V^{-1}s^{-1}$)**
Untreated SiO_2	(41 ± 9)	(6.3 ± 0.4) × 10^{-6}
OTS	(13 ± 8)	(3.9 ± 0.1) × 10^{-4}
OTS annealed devices at 60°C for 1h	(-23 ± 2)	(2.8 ± 0.2) × 10^{-2}



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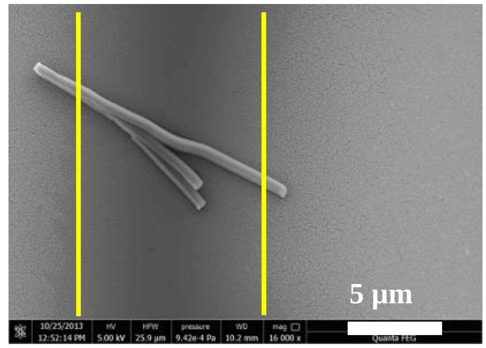
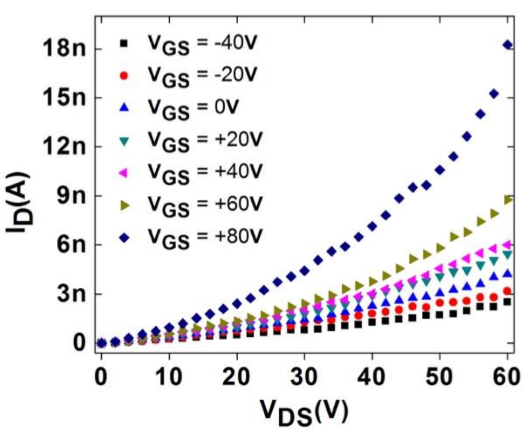
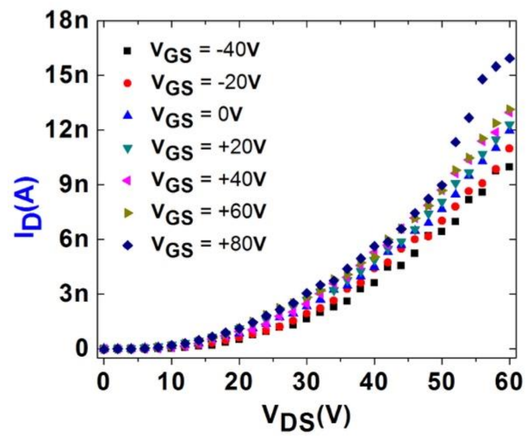


(b)



(c)



(d)

Figure S2. (a-b) SEM images and **(c-d)** output characteristics of FET devices treated with OTS based on: **(a,c)** two interconnected fibers, **(b,d)** superposed-fibers. The yellow lines in the SEM images serve as a guide to the eyes and indicate the source and drain electrode edges.

Table S2. Summary of multifiber-based and spin-coated FET parameters measured in dry nitrogen and ambient air in dark.

FET Devices		μ($cm^2V^{-1}s^{-1}$)	V_{th}(V)	Δμ($\mu_{Air}/\mu_{Nitrogen}$)	Δ_{Vth}|($V_{th\ air}$ -$V_{th\ Nitrogen}$)|
Multifiber	Dry nitrogen	2.0 × 10^{-3}	+ 10.8	no variation (1)	9.4
	Ambient air	2.0 × 10^{-3}	+ 20.2		
Spin-coated films	Dry nitrogen	5.3 × 10^{-4}	+ 3.3	0.09	56.4
	Ambient air	4.9 × 10^{-5}	-59.7		

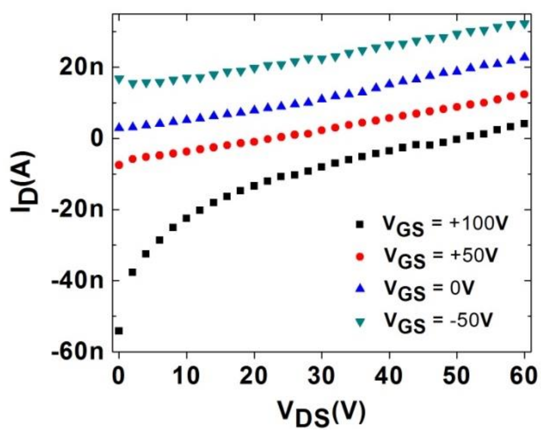


Figure S3. Typical output curve recorded on top-contact FETs in case of devices with 150 nm of Au electrodes thickness reveals non-functioning devices. Device dimensions are L = 60 µm and W = 10 mm.

Table S3. Summary of multifiber-based FET parameters measured in dark and under light irradiation in dry nitrogen and ambient air.

Multifiber devices	μ ($cm^2V^{-1}s^{-1}$)	V_{th}(V)	$\Delta\mu(\mu_{light}/\mu_{dark})$	$\Delta_{Vth}\lvert(V_{th\text{-}light}\text{-}V_{th\text{-}dark})\rvert$
Dry nitrogen_Dark	2.0×10^{-3}	+10.8	no variation (1)	13.8
Dry nitrogen_Light	2.0×10^{-3}	-2.9		
Ambient air_Dark	1.9×10^{-3}	+20.2	no variation (1)	32.5
Ambient air_Light	1.9×10^{-3}	-12.3		

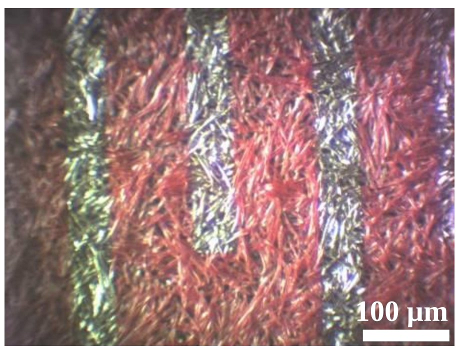
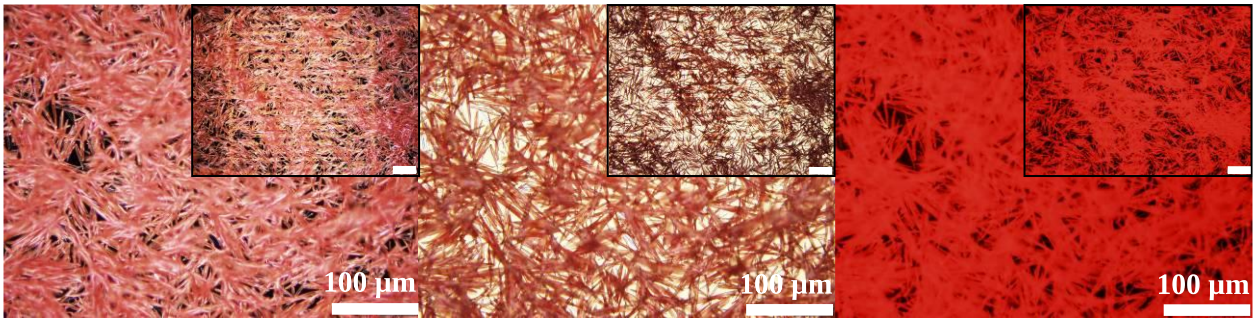


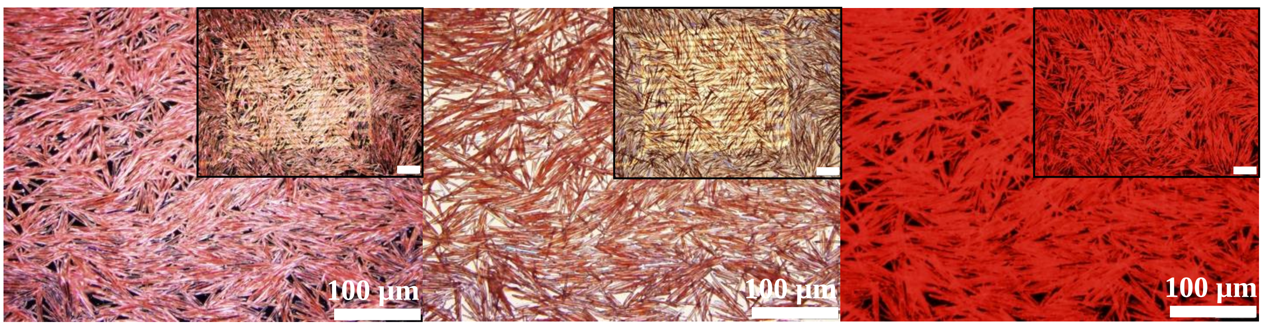
Figure S4. Optical microscopic image (bright field) of a top-contact device based on SIP fibers.

Table S4. Summary of spin-coated-based FET parameters measured in dark and under light irradiation in dry nitrogen and ambient air.

Spin-coated devices	μ ($cm^2V^{-1}s^{-1}$)	V_{th}(V)	$\Delta\mu(\mu_{light}/\mu_{dark})$	$\Delta_{Vth}\lvert(V_{th\text{-}light}\text{-}V_{th\text{-}dark})\rvert$
Dry nitrogen_Dark	5.3×10^{-4}	+3.3	0.96	26.8
Dry nitrogen_Light	5.1×10^{-4}	-23.5		
Ambient air_Dark	7.6×10^{-5}	-65.8	0.76	2.2
Ambient air_Light	5.8×10^{-5}	-68		



(a)



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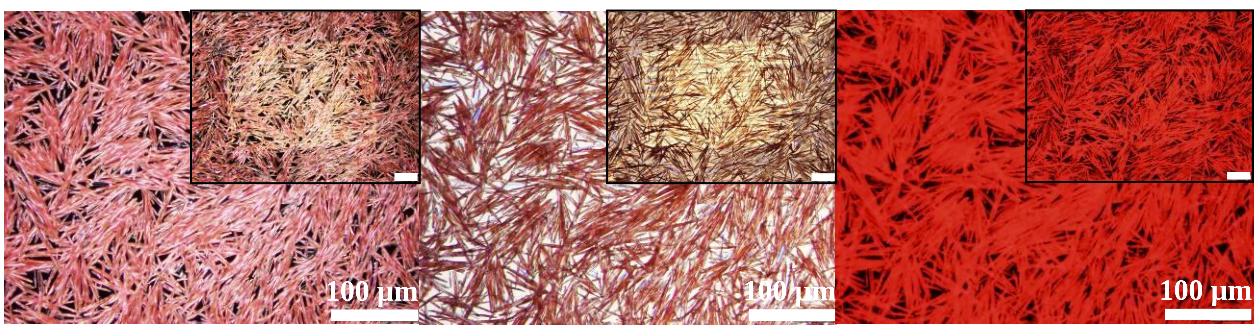


(c)

Figure S5. Optical microscopic and fluorescence images of multifiber deposited on **(a)** untreated SiO_2, **(b)** OTS or **(c)** HMDS treated SiO_2. Inset scale bar is 100 µm.

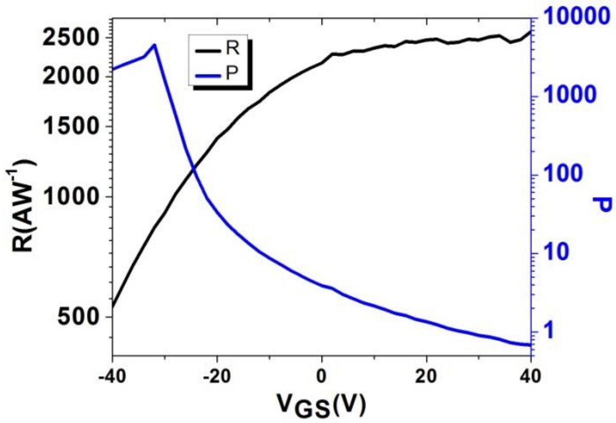


Figure S6. Variation of responsivity (R) and photosensivity (P) with V_G at V_D = 60 V for single-fiber OPT (L = 14 µm) under green light irradiation, for device treated with OTS.

Effect of light intensity on OPTs electrical performances

Different light sources of illumination were used including white light and monochromatic green light at λ = 525 nm. Such a wavelength was chosen in view of the absorption characteristics of PDIF-CN2 (see **Figure S9**). Transfer curves are illustrated in **Figure S7**; green light irradiation at λ = 525 nm with high intensity (4.84 mWcm^{-2} as measured using an analog optical power meter, PM100A, Thorlabs) yielded the largest enhancement in the drain current (I_{DS}) due to the larger absorption of incoming photons. However, it is noteworthy that white light illumination (5.06 mWcm^{-2}) exhibited similarly high I_{DS} obtained under green light with high intensity as the photocurrent/dark-current ratio is strongly dependent upon the incident optical power density, while the green light with low intensity (7.24 µWcm^{-2}) exhibited the smaller enhancement in the drain current due to the smaller optical power intensity than the two other light sources.

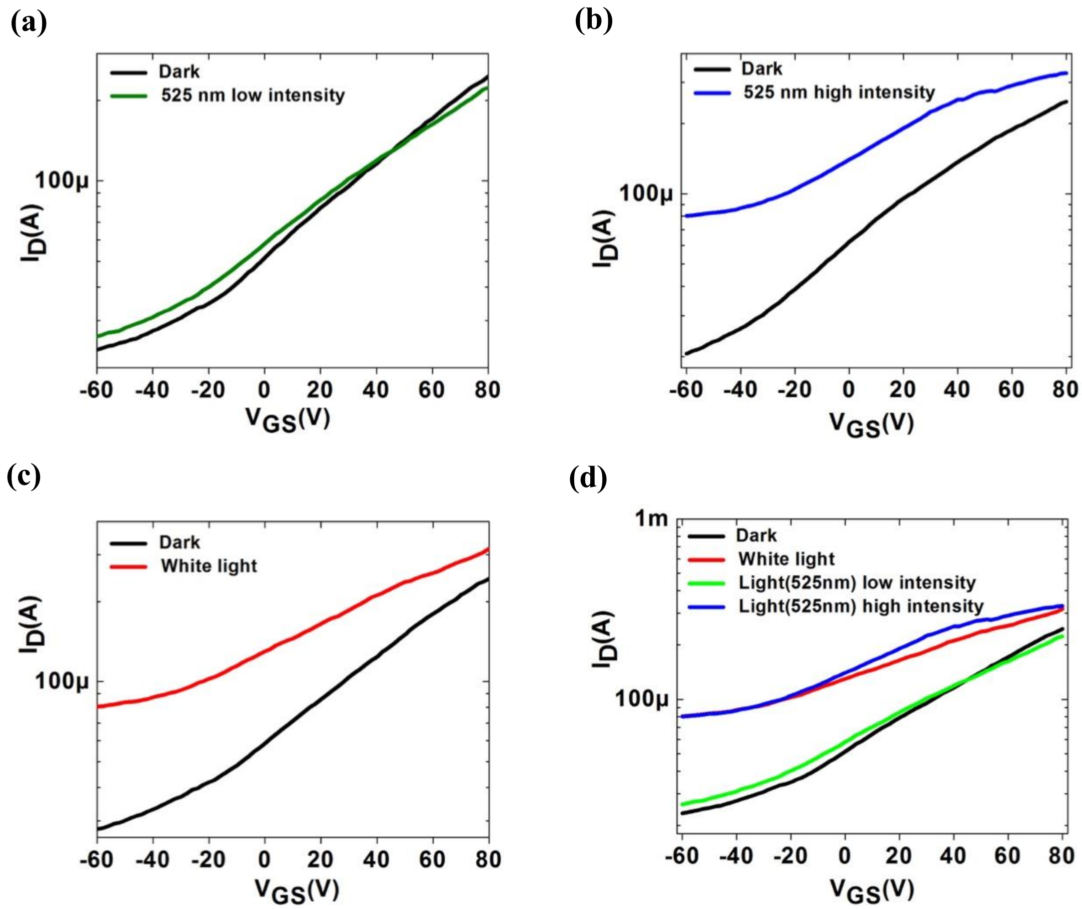
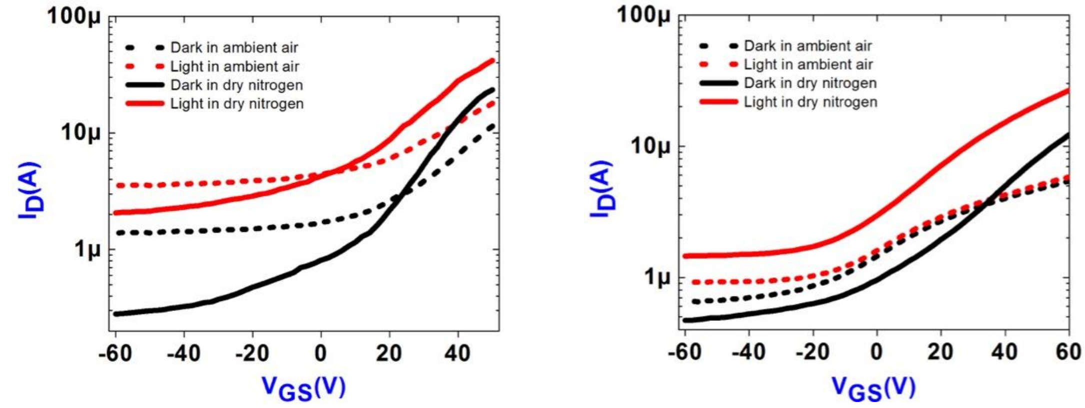


Figure S7. Transfer characteristics recorded on multifiber OPT device treated with OTS and undecanethiol self-assembly monolayers, measured in dark and under different irradiation conditions; **(a)** under green light at 'low intensity', **(b)** green light at 'high intensity', **(c)** white light, **(d)** comparison between I_D current in dark and under three different illumination conditions. [V_{DS} = +60 V, L = 2.5 μm]



(a) **(b)**

Figure S8. Transfer characteristics of **(a)** multifiber OPT and **(b)** thin-film devices in dark and under white light irradiation measured in dry nitrogen and air atmosphere. [V_{DS} = +60 V, L = 2.5 μm].

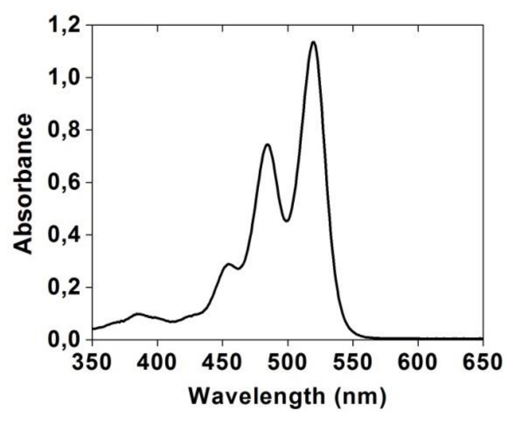


Figure S9. Absorption spectra of PDIF-CN2 from solution (2.1 × 10^{-5} M in $CHCl_3$).

Effect of the channel length on OFETs electrical performances

Another important aspect one has to consider is also the dependence of the electrical characteristics on the channel length. Upon variation of the channel length the channel resistance decreases and as a result, the effect of the electrodes becomes more important as a voltage drop constantly occurs. If one looks at the relationship $R_{TOT} = R_{ch} + R_{contact}$, it is evident that the total resistive contribution (R_{TOT}) estimated by measuring the current flowing across the device channel is composed of two different components. A voltage drop at the electrode is normally called contact resistance ($R_{contact}$) and is constant with changing the channel length as it only depends on the energetic misalignment between the work function of the source-drain metal and the HOMO (LUMO) of the p-type (n-type) system employed. The resistive contribution given by the channel resistance (R_{ch}) depends on the channel length, instead, as it varies as $R_{ch} = \rho \times (L/A)$, where ρ is the film resistivity, L is the distance between the electrodes and A is the film section.

However, in our system (fiber-based FETs) the variation of the mobility properties with the channel length showed an increase in shorter channels (see **Figure S10**) which reflects the fact that the longer the channel the more grain boundaries between fibers are encountered by the charges. Such inter-fiber transport can be correlated to the fibers sizes as measured by AFM (atomic force microscopy) revealing lengths of about 20 μm, widths of 1-3 μm and thicknesses of hundreds of nanometers (see **Figure S11**).

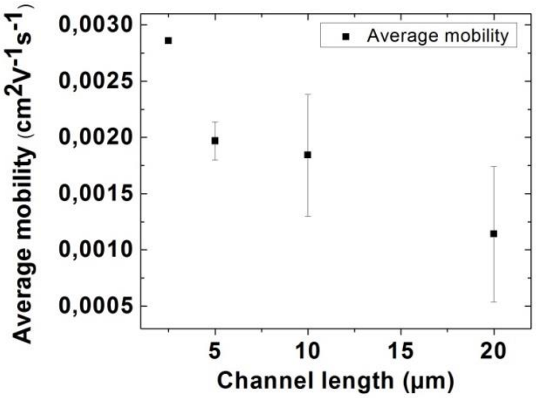


Figure S10. Average mobility (μ_{av}) values measured on fiber-based FETs device treated with OTS. The error bars correspond to the standard deviations.

Atomic Force Microscopy

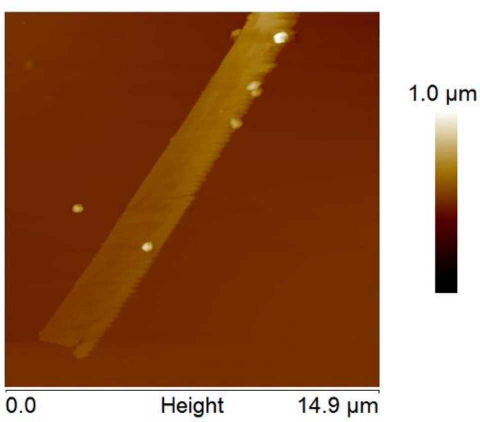


Figure S11 Topographical tapping mode AFM image of PDIF-CN2 fiber.