

# Electronic Supplementary Information (ESI †)

## All-Organic Coaxial Nanocables with Interfacial Charge-Transfer Layers: Electrical Conductivity and Light-Emitting-Transistor Behavior

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### Experimental section

#### MATERIALS

Regioregular P3HT ( $M_w = 87,000$ ) was purchased from Aldrich Company and used as received. CN-TFMBE was synthesized by the Suzuki coupling reaction and the Knoevenagel reaction, following previously published procedures,<sup>5</sup> and was then purified by vacuum sublimation.

Coaxial nanocables were prepared by dissolving binary mixtures of CN-TFMBE and P3HT in *o*-dichlorobenzene with gentle heating. Several samples with different ratios of CN-TFMBE (i.e., 0, 50, 100, and 200%) with respect to P3HT, keeping the concentration of the latter as 0.1 wt.% in solution were prepared and investigated. All solutions were coated by the drop-casting method, evaporated at room temperature, and then annealed on a hot plate at 85°C for one hour.

#### DEVICE FABRICATION

Bottom-contact devices were prepared to measure the electrical conductivity and the transistor properties of the coaxial nanocables. Before fabrication, Si/SiO<sub>2</sub> substrates were cleaned by sonication in acetone and isopropyl alcohol. Ultraviolet ozone (UVO) was only applied to those substrates prepared for measuring the electrical conductivity. The deposition of two 50 nm-thick gold electrodes onto the clean substrates by thermal evaporation was

carried out in a nitrogen-filled glove box under a vacuum of  $3 \times 10^{-6}$  Torr. The deposition rate was 0.2–0.3 nm/s and the channel length and width between the two electrodes was 50  $\mu\text{m}$  and 1 mm, respectively. After cooling, the active layers of pristine P3HT (0.1 wt.%) and the blended solutions (200% CN-TFMBE with respect to P3HT, keeping the concentration of the latter as 0.1 wt.% in solution) were drop-cast. After evaporation of the solvent, the samples were annealed on a heating plate at 85°C for one hour in a nitrogen-filled glove box to remove any effects due to solvent residues. All the coaxial nanocables with different blending ratios between P3HT and CN-TFMBE showed enhanced electrical characteristics with different degrees depending on the uniformity of the coaxial structures.

Interdigital heteroelectrodes for evaluating the light-emitting transistors were fabricated on the same  $\text{SiO}_2/\text{Si}$  substrates using photolithography and lift-off processes. Firstly, Au (30 nm)/Cr (10 nm) source electrodes were formed on the  $\text{SiO}_2$  layer. Guiding lines for the succeeding processes were also formed on the substrates. A photomask was then placed at the exact position referring to the guiding lines to prepare the Al drain electrodes (30 nm). The channel length ( $L$ ) and width ( $W$ ) of the electrodes were 5  $\mu\text{m}$  and 38 mm, respectively. After fabricating the heteroelectrodes, the same cleaning and device-preparation methods as those described above were applied.

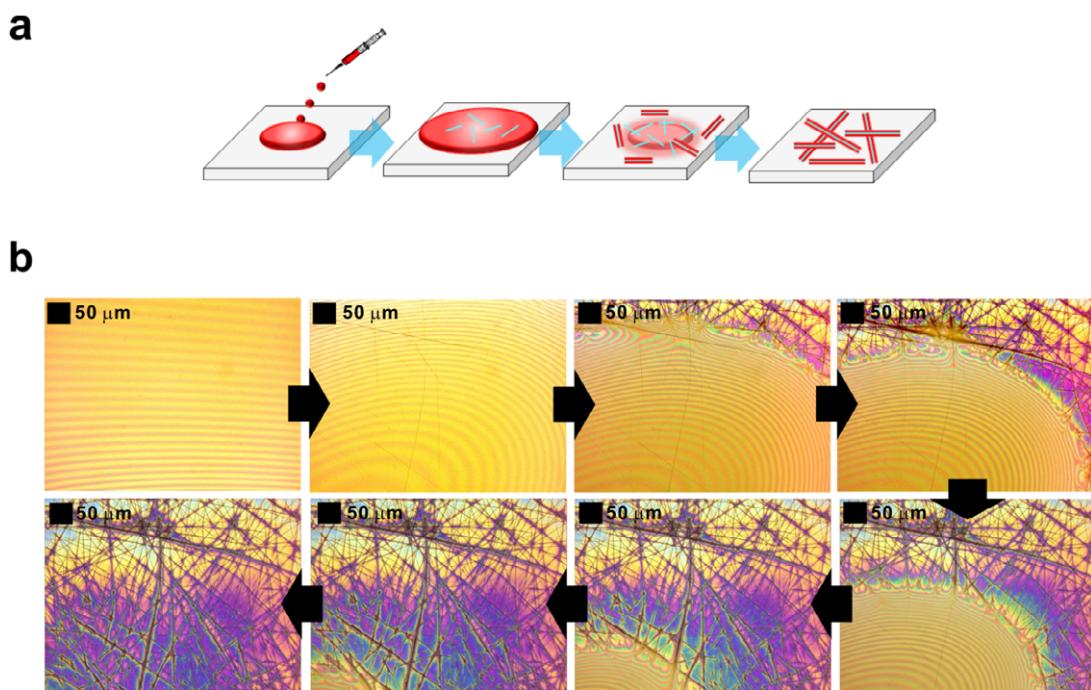
## ELECTRICAL MEASUREMENTS

The current–voltage characteristics for investigating the electrical conductivities and transistor properties were measured using Keithley 2400 and Keithley 6517 equipments connected to a probe station. In the case of the light-emitting-transistor measurements, the electrical characteristics were measured using Keithley 6487 and Keithley 487 instruments. The light intensity was detected with a Si photodiode placed just above the device, through a glass window of the vacuum chamber (at a vacuum of  $5 \times 10^{-6}$  Torr at room temperature).

Magnifying the sample under the optical microscope which is attached to the probe-station, we were able to cut the individual coaxial nanocable using the sharp tip of the probe. I-V measurements were repeated after disconnecting the individual nanocables. Before proceeding to the next cutting or I-V measurement, we have thoroughly cleaned the tip using solvent (acetone) to remove any residuals attached to the tip.

## S1

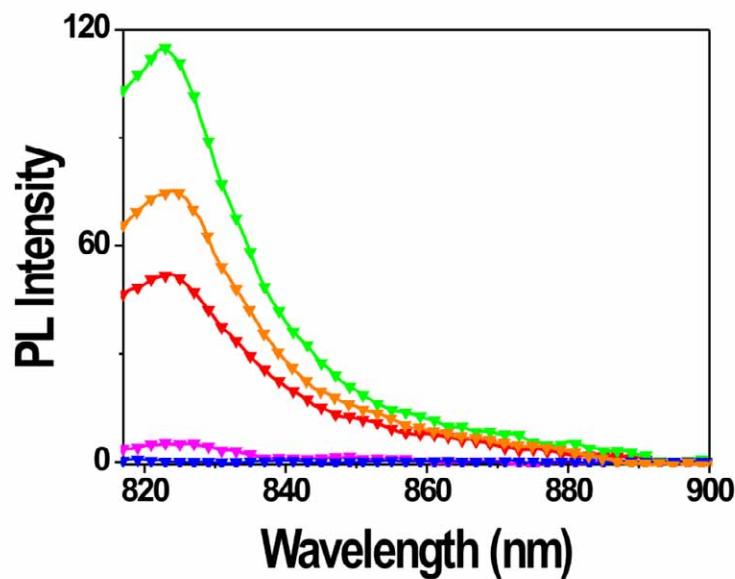
We observed morphology change during coaxial nanocable formation. After drop casting of blended solution onto the substrate, we measured optical microscopy images with time. CN-TFMBE nanowires are slowly formed and floating on the solution due to its high self-assembling power in 30 minutes after drop casting. Then nanowires go down to the bottom of substrate, P3HT covers them with solvent evaporation and coaxial nanocables are fabricated as shown in Fig S1.



**Fig. S1.** Schematic diagram (a) and optical microscopy images (b) explaining a process of coaxial nanocable growth.

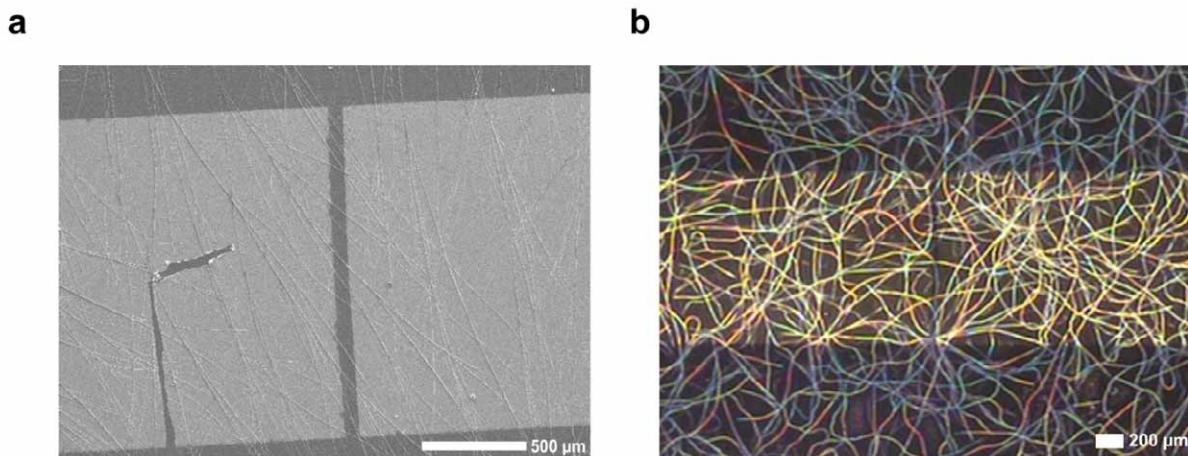
**S2**

In order to investigate emission from a charge-transfer complex, we measured the photoluminescence (PL) spectra of solution P3HT and the coaxial nanocables from clear solution state to the solution state containing CN-TFMBE nanowires with time (Fig. S2) at a fixed excitation wavelength of charge-transfer absorption (755 nm) indicated in Fig. 2a. No emission signals are detected at pure P3HT solution and clear solution of coaxial nanocable's. As CN-TFMBE nanowires grow, emission peak at 824 nm is observed and its intensity increased with time. From these PL spectra, we confirm that at first clear solution state, no charge-transfer can be occurred due to the absence of nanowires, however, with increased amount of grown CN-TFMBE nanowires, a charge-transfer complex at the interface between P3HT and CN-TFMBE is formed.



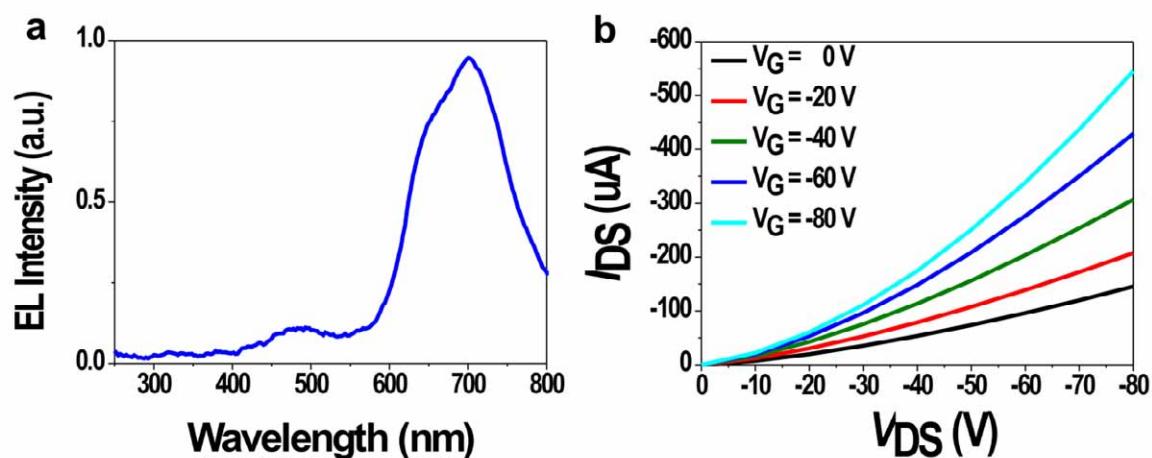
**Fig. S2.** Photoluminescence spectra (excited by 755 nm corresponding to the charge-transfer band absorption wavelength) measured from clear solution state (blue line) to the solution state containing coaxial nanocables (green line).

S3



**Fig. S3.** Scanning electron microscopy (a) and optical microscopy (b) images of fabricated devices based on coaxial nanocables.

S4



**Fig. S4.** Electroluminescence (EL) spectrum (a) and output curve (b) of light emitting organic transistors based on coaxial nanocables during operation.