Electronic Supplementary Information:

Charge transport in fiber-based perylene-diimide transistors: effect of the alkyl substitution and processing technique

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1. Synthesis and Analysis

The five perylene-diimide derivatives are presented in Fig. 1. Derivatives **2-4** were synthesised via imidization of perylenedianhydride (PDA) with alkyl amines, whereas system **1** was purchased from Sigma Aldrich (assay 98%) and compound **5** was purchased from Sensient Technologies.

FD mass spectra were obtained on a VG Instruments ZAB 2-SE-FPD spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded in deuterated dichloromethane on a Bruker Avance 300 spectrometer. The deuterated solvent was used as an internal standard. Elemental analysis was carried out on a Foss Heraeus Vario EL as a service of the Institute for Organic Chemistry, Johannes-Gutenberg-Universität of Mainz. Solution UV/vis spectra were recorded at room temperature on a Perkin-Elmer Lambda 900 spectrophotometer. Fluorescence spectra were measured on a T&D TIDAS diodearray spectrometer. IR-spectra were obtained on a Nicolet 730 FT-IR SPECTROMETER with Endurance Diamant ATR unit.

*N,N'-Dioctyl-3,4,9,10-perylenedicarboxIimide (**2**)*[1]

0.51 mmol perylene tetracarboxylicacid dianhydride, 5.1 mmol 1-octylamine and 25 mg zinc acetate were suspended in 10 mL of N-methylpyrolidone (NMP). The reaction mixture was stirred under argon at 140°C for 16 hours. After cooling to room temperature, the reaction mixture was poured into 50 mL of 2 N HCl. The precipitate was filtered, washed with water and dried *in vacuo*. The raw product was purified utilizing preparative column chromatography (silica gel, eluent: dichloromethane). The product was obtained as red-orange solid.

Yield: 221 mg (0.36 mmol), 71 %

*N,N'-Di-(2-octyl)-3,4,9,10-perylenedicarboximide (**3**)*

0.51 mmol perylene tetracarboxylicacid dianhydride, 5.1 mmol 2-octylamine and 25 mg zinc acetate were suspended in 10 mL of N-methylpyrolidone (NMP). The reaction mixture was stirred under argon at 140°C for 16 hours. After cooling to room temperature, the reaction mixture was poured into 50 mL of 2 N HCl. The precipitate was filtered, washed with water and dried *in vacuo*. The raw product was purified utilizing preparative column chromatography (silica gel, eluent: dichloromethane). The product was obtained as red-orange solid.

yield: 261 mg (0.42 mmol), 83%

^{1}H-NMR (300 MHz, CD_2Cl_2, 298 K): δ [ppm] 8.52 (d, ^3J=8.0 Hz, 4H), 8.42 (d, ^3J=8.1 Hz, 4H), 5.30–5.12 (m, 2H), 2.30–2.11 (m, 2H), 2.02–1.84 (m, 2H), 1.60 (d, ^3J=6.9 Hz, 6H), 1.45–1.13 (m, 16H), 0.84 (t, ^3J=6.7 Hz, 6H).

^{13}C-NMR (75 MHz, CD_2Cl_2, 293 K): δ [ppm] 163.98, 134.52, 131.26, 129.58, 126.48, 124.03, 123.25, 50.21, 33.90, 32.18, 29.57, 27.47, 23.00, 18.39, 14.21.

FD-MS (8 kV): m/z = 612.8 (100%) [M+](calc. for $C_{40}H_{42}N_2O_4$: 614.8)

IR: ν [cm^{-1}] 2921, 2855, 1697, 1650, 1593, 1434, 1403, 1340, 1257, 1178, 848, 808, 796, 744, 625.

Elemental analysis

calc.: 78.17% C 6.89% H 4.56% N

found: 78.10% C 6.34% H 4.57% N

UV-VIS: λ_{max} (ε in M^{-1}cm^{-1}):527 (38037), 490 (22897), 459 (8574)

Fluorescence (excitation 480 nm): λ_{max}(nm) 535, 575

N,N'-Di-[2-(6-methylheptyl)]-3,4,9,10-perylenedicarboximide (**4**)

0.51 mmol perylene tetracarboxylicacid dianhydride, 5.1 mmol 6-Methylheptyl-2-amine and 25 mg zinc acetate were suspended in 10 mL of N-methylpyrolidone (NMP). The reaction mixture was stirred under argon at 140°C for 16 hours. After cooling to room temperature, the reaction mixture was poured into 50 mL of 2 N HCl. The precipitate was filtered, washed with water and dried *in vacuo*. The raw product was purified utilizing preparative column chromatography (silica gel, eluent: dichloromethane). The product was obtained as red-orange solid.

yield: 235 mg (0.38 mmol), 75%

^{1}H-NMR (300 MHz, CD_2Cl_2, 298 K):δ [ppm] 8.61 (d, ^{3}J=8.0 Hz, 4H), 8.54 (d, ^{3}J=8.1 Hz, 4H), 5.35–5.23 (m, 2H), 2.32–2.11 (m, 2H), 2.02–1.83 (m, 2H), 1.63 (d, ^{3}J=6.9 Hz, 6H), 1.59–1.19 (m, 10H), 0.87 (d, ^{3}J=6.0 Hz, 6H), 0.86 (d, ^{3}J=6.0 Hz, 6H).
^{13}C-NMR (75 MHz, CD_2Cl_2, 293 K): δ [ppm] 164.06, 164.06, 134.67, 131.37, 129.69, 129.69, 126.63, 124.10, 123.35,50.18, 39.12, 34.07, 28.24, 25.24, 22.78, 22.63, 18.38.
FD-MS (8 kV): m/z = 613.6 (100%) [M+](calc. for $C_{40}H_{42}N_2O_4$: 614.8)
IR: ν [cm^{-1}] 2954, 2922, 2869, 1700, 1646, 1594, 1577, 1466, 1404, 1342, 1259, 1179, 861, 808, 745, 625.

Elemental analysis
calc.: 78.17% C 6.89% H 4.56% N
found: 77.90% C 6.88% H 4.52% N
UV-VIS: λ_{max} (ε in M^{-1}cm^{-1}): 526 (24156), 490 (15021), 458 (6140)
Fluorescence (excitation 480 nm): λ_{max}(nm) 535, 575

2. Experimental Methods

2.1 Device preparation and characterization. All devices were prepared on interdigitated electrodes supplied by the Fraunhofer Institute for Photonic Microsystems, with pre-patterned Au contacts and 230 nm thermally grown SiO_x as dielectric, in a bottom-gate bottom-contact configuration. The channel-widths were 10 mm, and the lengths 2.5, 5, 10 and 20 µm. Prior preparation of the organic layer, the Au contacts were functionalized with an undecanethiol SAM in order to lower the energy mismatch between the gold work function and the PDIs' LUMO and allow for a more efficient charge injection/extraction from the electrodes to the semiconductor. Afterwards the SiO_x dielectric was treated with hexamethyldisilazane (HMDS). During preparation of the latter the annealing step was limited to 80°C in order to avoid desorption of the thiolated species. All sample preparation was performed in a glove-box with a nitrogen atmosphere. The preparation of the undecanethiol SAMs was performed outside the glove-box, and immediately transferred after removal from the solution and rinsing. Electrical characterization was carried out in the glove-box using a Cascade Microtech M150 probe station with a dual channel Keithley 2636A SourceMeter® and associated software.

a. Field-effect mobility

All mobility values were extracted from the transfer characteristic curves (Id-Vg) in saturation regime (V_D = +80V).

	film	***SVA*** (Chloroform)	***SVA*** (TetrahydroFuran)	***SIP***
1	$(2.6 \pm 2.1) \times 10^{-3}$	$(7.6 \pm 5.4) \times 10^{-5}$	$(3.7 \pm 0.8) \times 10^{-5}$	$(1.4 \pm 0.1) \times 10^{-3}$
2	$(3.2 \pm 0.6) \times 10^{-3}$	$(1.8 \pm 0.8) \times 10^{-5}$	$(5.5 \pm 2.7) \times 10^{-6}$	$(9.9 \pm 2.0) \times 10^{-4}$
3	$(5.7 \pm 3.1) \times 10^{-4}$	$(4.4 \pm 2.1) \times 10^{-5}$	$(8.7 \pm 5.6) \times 10^{-7}$	$(2.1 \pm 0.3) \times 10^{-5}$
4	$(1.0 \pm 0.9) \times 10^{-3}$	$(6.0 \pm 5.2) \times 10^{-6}$	$(6.9 \pm 7.5) \times 10^{-7}$	$(1.0 \pm 0.8) \times 10^{-4}$
5	$(2.7 \pm 0.4) \times 10^{-5}$	$(1.6 \pm 1.4) \times 10^{-5}$	$(1.7 \pm 0.8) \times 10^{-5}$	

Mobilities (cm^2/Vs) of all sample types, averaged over two to six devices with 5 μm channel length. The uncorrected device-mobilities are presented for all the deposition techniques but the spin-coating which does not need it because it implies full channel coverage. For consistency with all the other values, the field-effect mobility referred to devices based on spin-coated films are presented without standard deviation in Table 2. In some cases the device mobilities spanned several orders of magnitude, and in these cases the standard deviation could surpass the average value.

b. Turn-on Voltage

The turn-on voltages were all extracted from the trans-characteristic curves (Id-Vg) in linear regime (V_D = +10V).

	film	***SVA*** (Chloroform)	***SVA*** (TetrahydroFuran)	***SIP***
1	(-10 ÷ -12)V	(-30 ÷ -35)V	(0 ÷ +14)V	(-20 ÷ -40)V
2	(-10 ÷ -30)V	(-15 ÷ -20)V	(-5 ÷ -12)V	> -40V
3	(0 ÷ +5)V	(0 ÷ -10)V	(+8 ÷ +10)V	> -35V
4	(-10 ÷ -20)V	(-10 ÷ -15)V	(-10 ÷ -20)V	> -40V
5	(-4 ÷ +2)V	(-10 ÷ -15)V	(+8 ÷ +13)V	

2.2. Films and fibers preparation. The solutions of systems **1-5** were made in $CHCl_3$ to a concentration of 0.25 mg / ml. The molecules employed were found to be soluble in $CHCl_3$ up to the following concentrations: **1**: 0.7 mg / ml, **2**: 1.0 mg / ml, **3**: 9.7 mg / ml, **4**: 10.6 mg / ml, **5**: 18.0 mg / ml, and in THF up to the following concentrations: **1**: 0.14 mg / ml, **2**: 0.18 mg / ml, **3**: 5.0 mg / ml, **4**: 7.5 mg / ml, **5**: 18.6 mg / ml.

Three types of device preparation were used: spin-coating, solvent-vapour annealing (SVA) and solvent-induced precipitation (SIP). During preparation of the spin-coated films, 50 μl of solution was spun onto the pre-patterned substrates at 700 rpm for 60 sec until dry. Films used for SVA treatment were first prepared the same way, and subsequently placed in a sealed container with a saturated $CHCl_3$ or THF atmosphere. The substrates were elevated 2~5 mm above the surface of the solvent on an up-turned Petri dish (Fig S1a). During the treatment a tight-fitting lid ensured that the atmosphere inside the bottle was saturated with solvent vapors. The jars were left at room temperature for at least 24 h, after which they were removed and any excess solvent allowed to evaporate before characterization. SIP structures were prepared by injecting a small amount of solution into a larger quantity of non-solvent (methanol) at a volume-ratio of 1:5 (Fig. S1b).

The vials were then left undisturbed overnight, to allow the precipitation of supramolecular assemblies. These were subsequently deposited in 20 drops of 50 µl each into the prepared electrodes, allowing each drop to dry before the deposition of the next, and agitating the vials before each deposition to ensure an even distribution of material in the liquid. Thus we could deposit an equal amount of material on each chip, despite the structures' tendency to settle to the top of the liquid. It was not possible to induce precipitation of the **5**-system, either in methanol nor hexane, using volume-ratios of up to 1:15.

2.3 Atomic Force Microscopy (AFM) and X-ray Diffraction (XRD) characterizations.

Following electrical characterization samples were transferred to the AFM and scanned under ambient conditions. Topographic AFM was performed in tapping (intermittent-contact) mode, using a Digital Instruments Dimension 3100 AFM with a Nanoscope IV controller. Silicon cantilevers tips were used (Veeco MPP-11120) with a nominal spring constant of 40 N/m, resonance frequency of circa 300 kHz, nominal tip-radius of 10 nm and side-angle of around 18°. The widths of structures were measured from the full width half maximum (FWHM) of the edges, with no correction to account for tip broadening.

A θ-θ Siemens D500 Kristalloflex with a graphite-monochromatized CuK_α X-ray beam was used for the investigation of the structure in the thin films.

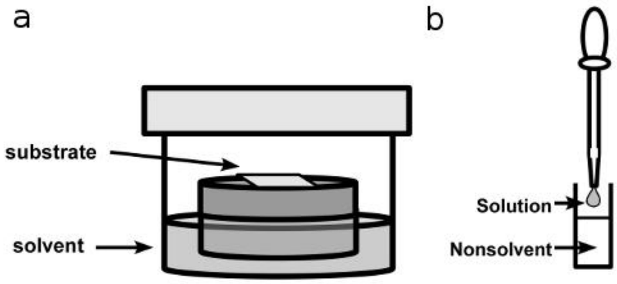

Figure S1: Schematic of the preparation of (a) SVA- and (b) SIP-supramolecular assemblies.

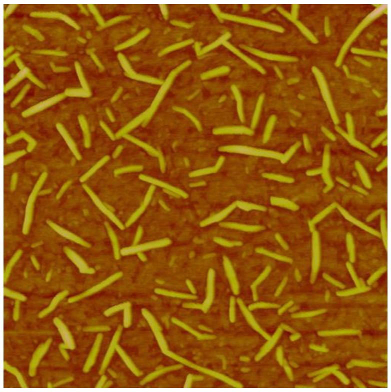

Figure S2: Topography-AFM image of spin-coated film of **5**, using a solution of 1 mg/ml in $CHCl_3$. Image width 5 μm, z-scale 100 nm.

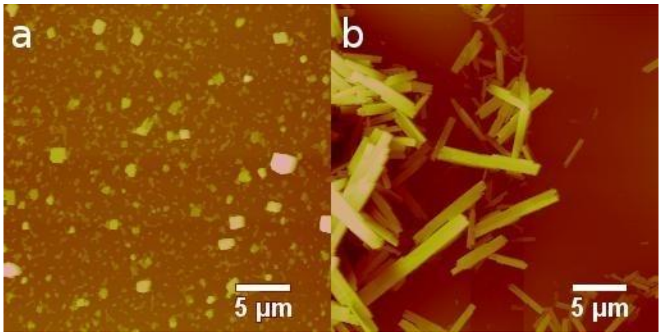

Figure S3: Topography AFM images of films of **4**, after SVA-treatement in (a) $CHCl_3$ and (b) THF. z-scale of (a) is 300 nm and of (b) is 1000 nm.

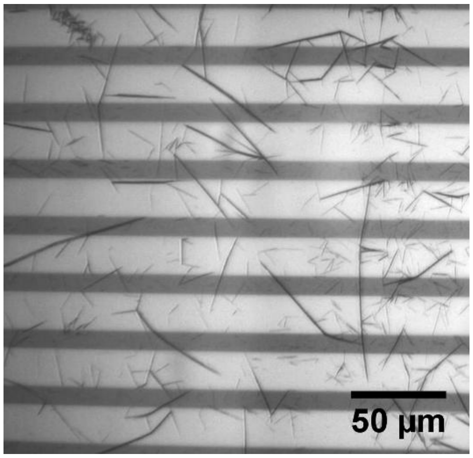

Figure S4: Optical microscopy image of high-aspect ratio needles of **5** formed after SVA-treatment in THF. Films were formed on undecanethiol-treated Au electrodes and HMDS-treated SiO_x.

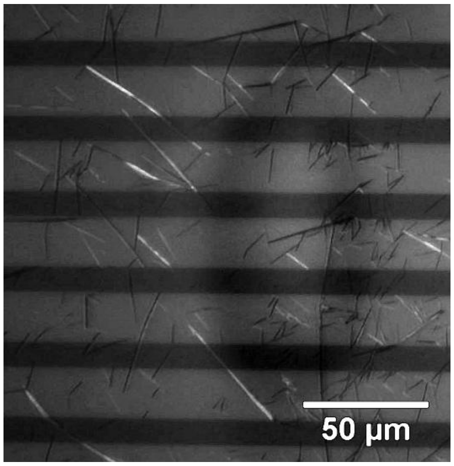

Figure S5: Optical microscopy under crossed (↔↕) polarizers showing birefringence in needles formed form films of molecule **5** after SVA-treatment in THF.

In some exceptional cases, after SVA in $CHCl_3$ systems **1** and **3** formed crystals with a thickness ranging from tens to hundreds of nanometers, a width of several microns, and featuring a very strong birefringence.

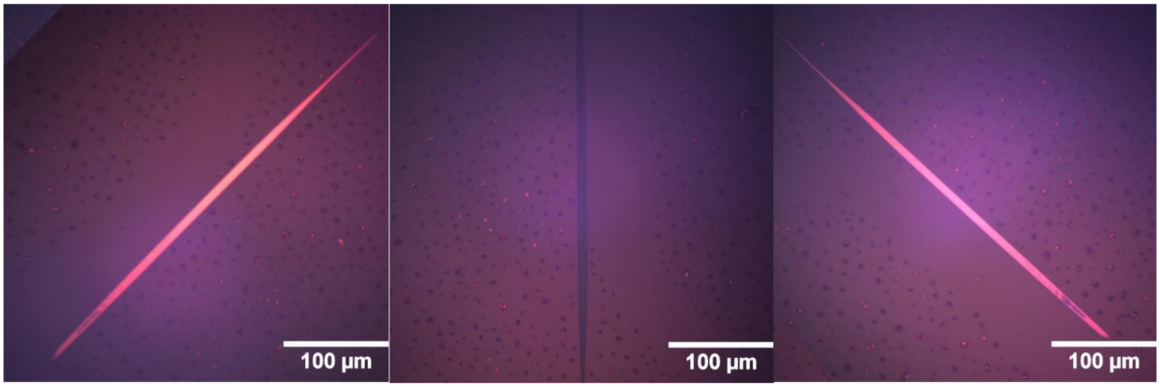

Figure S6: Optical microscopy images observed under crossed (↔↕)polarizers of molecule **1** after SVA-treatment in THF. The strong birefringence is evident when the same needle is observed at different orientations relative to the polarizers

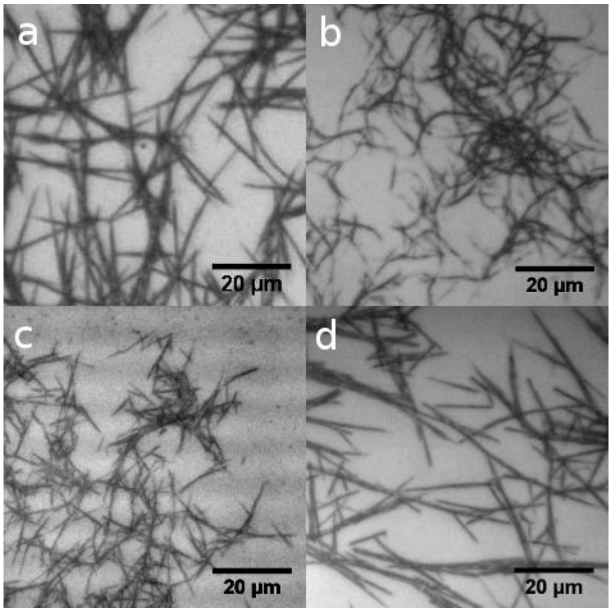

Figure S7: Optical microscopy images of SIP-samples of (a) **1** (b) **2** (c) **3** and (d) **4** on SiO_x.

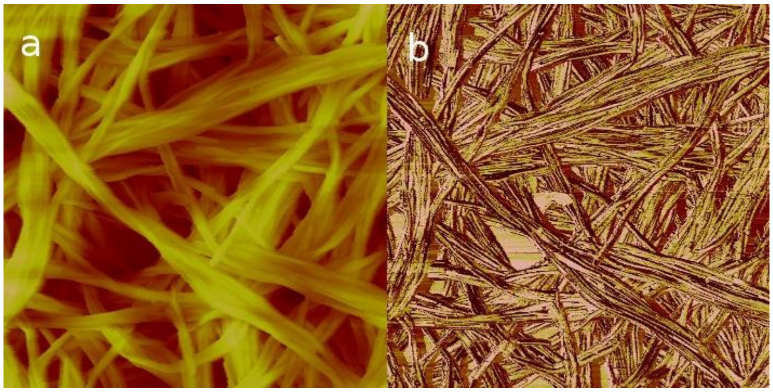

Figure S8: AFM image from the (a) topographic and (b) phase-channel, showing a mesh of **2**-SIP fibres on SiO_x, and the smaller fibrils they seem to be composed of. Images are 5 µm wide, z-scale of (a) is 800 nm.

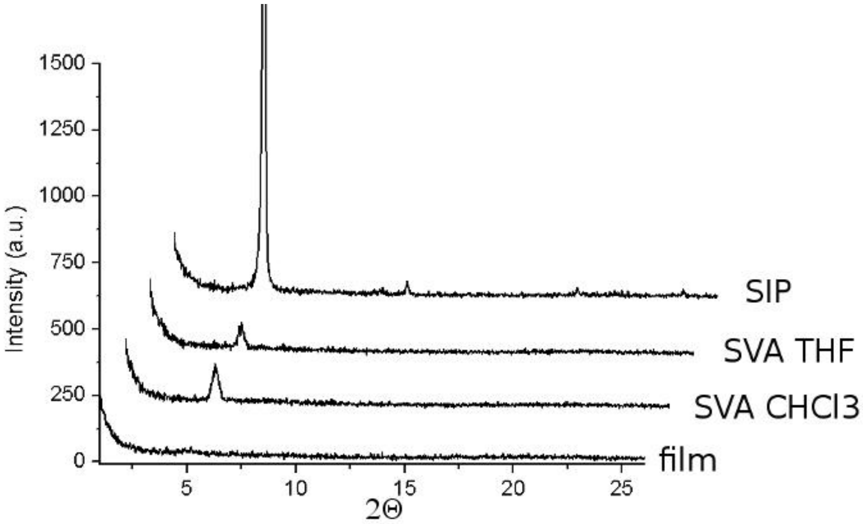

Figure S9: XRD meaurements of the various **1**-samples. Plots have been shifted for clarity.

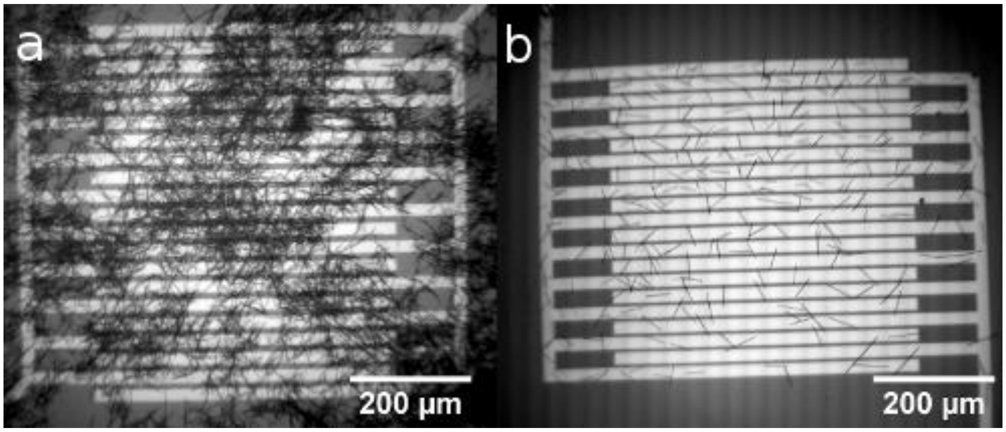

Figure S10: Optical microscopy images of devices obtained from molecule **1** devices with (a) SIP fibres and (b) needles from SVA in $CHCl_3$.

References

[1]: T. Sakamoto, C. Pac, *J. Org. Chem.*, 2001, **66**, 94-98