Electronic Supplementary Information:

Photoconductive and supramolecularly engineered organic field-effect transistors based on fibres from donor-acceptor dyads

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Table of contents

1. Experimental methods

The synthesis of HBC-PMI is described elsewhere.[1]

HBC-PMI has been dissolved in 1-phenyloctane (Aldrich) with concentrations ranging from 0.02mM to 0.2mM. Solutions have then been mixed with 2-propanol (Carlo Erba) in a 1:1 volume ratio and left to precipitate. Precipitation was slow for this combination of solvents with fibres only becoming visible by eye after more than one day. Additional 2-propanol has been added after more than 2 days to complete precipitation. Bundles of precipitated fibres have been carefully picked up with a pipette and cast on mica/SiO_x. Samples have then been dried at 70°C in air for at least 12hours.

AFM measurements have been performed in air using a Veeco Dimension 3100 AFM in tapping mode.

KPFM (and the corresponding AFM) images has been recorded using a Multimode IIIA (Veeco) scanning probe microscope with Extender Electronics module. Imaging was done in tapping mode using a conductive SCM-PIT probe (Veeco, Pt/Ir coated Si with frequency f_0 = 79 KHz and nominal tip radius ≤ 20 nm). All images were collected under ambient conditions at 10% relative humidity and RT with a scanning raster rate of 1 Hz. The humidity has been measured with a commercial RH meter (Honeywell, HIH-4000-001) having an operating range from 0% to 100% RH with an accuracy of ±3.5%. KPFM measurements has been acquired in lift mode (lift height = 20 nm, V_{AC} = 1000 mV).

Au electrodes (120nm) have been deposited using TEM grids (Ted Paella Inc, gilder grid 200 Mesh) as a shadow mask. Deposition has been performed in a high vacuum chamber (Plassys, p<10^{-6}mbar) using resistively heated boat evaporators with the sample being kept at room temperature. The deposition rate (1nm/s) has been monitored using a quartz microbalance. After electrode deposition, samples were immediately transferred inside a glovebox operated under nitrogen atmosphere (O_2<10ppm) for electrical characterization. To exclude any effects of the air exposure on the device properties, some devices have been annealed at 80ºC inside the glovebox which did however not lead to a measurable change in the electronic properties.

Devices have been characterized using a Keithley 2636A sourcemeter with biases applied to gate and drain while the source was being connected to the ground. n++-doped silicon

serves as a gate covered with a 230nm thermally grown oxide (Frauenhofer Institute, capacitance $1.5x10^{-8}$ F/cm^2).

The light intensity during measurements has been determined using a Thorlabs slim power sensor (S130A). A black curtain was used to reduce stray light inside the glovebox for measurements in the dark (total light intensity <0.1μW/cm^2). For measurements under illumination, a Leica LED1000 white light OLED ring with 40 white OLEDs was used as a white light source (7mW/cm^2 at sample position).

2. Photoresponse of an OFET based on a spin-coated thin film of HBC-PMI

Figure S1 shows the output characteristics under illumination with white light and in the dark of an OFET based on a spin-coated thin film of HBC-PMI. The device has been prepared on commercial electrodes purchased from the Fraunhofer Institute (www.ipms.fraunhofer.de). Devices have been prepared inside a glovebox by i) spin coating 100 μl drop of 0.1mM chloroform solution (500 rpm) on pre-patterned samples (i.e. micro-electrodes on SiOx substrates) and ii) annealing at 80°C for 15 hours. The distance between electrodes and channel width amount to 5μm and 10mm, respectively.

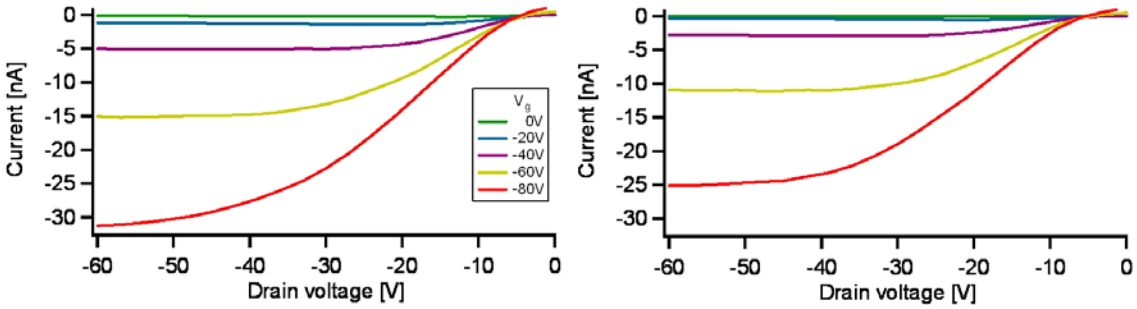

Figure S1: Output characteristics of an OFET based on a spin-coated thin film of HBC-PMI under white light illumination (left) and in the dark (right).

Bibliography

[1] J. M. Mativetsky, M. Kastler, R. C. Savage, D. Gentilini, M. Palma, W. Pisula, K. Müllen, P. Samorì, *Advanced Functional Materials* **2009**, *19*, 2486.