Electronic supplementary information for the manuscript:

"Towards understanding the behavior of indigo thin films in organic field-effect transistors: a template effect of the aliphatic hydrocarbon dielectric on the crystal structure and electrical performance of the semiconductor"

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Experimental procedures

Materials and solvents

Indigo, tetracontane, paraffin wax (m.p. 70-80 °C), polyvinyl alcohol (PVA) and solvents were purchased from Sigma-Aldrich. Indigo was purified four times using temperature gradient vacuum sublimation. Toluene and chlorobenzene were purified using standard distillation. Tetracontane, paraffin and mesitylene were used as received. The dielectric BCB was obtained under the trade name CYCLOTENE 4024 resin as a product of The Dow Chemical Company.

OFET fabrication

A 1 mm wide and 200 nm thick aluminum gate electrode was deposited by thermal evaporation onto 1.5×1.5 cm² glass slides. It was subsequently anodized by immersing in a citric acid solution (0.2 g per 100 mL) in a potentiostatic regime at 10 V to achive a formation of uniform AlO_x coating. Afterwards, the samples were rinsed with deionized water and dried in an oven at 80 °C for 30 min. Organic dielectric coatings were deposited immediately after taking the samples out from the oven.

<u>*Tetracontane TC*</u> (Aldrich) was dissolved in a mixture of toluene with chlorobenzene (2:1 v/v ratio) to achieve a total material concentration of 1,7 mg/ml. The resulting solution was spin-coated onto the dried Al/AlO_x electrodes at 3000 rpm.

<u>Polyvinyl alcohol PVA</u> was dissolved in a deionized water to achieve a material concentration of 50 mg/mL. This solution was spin-coated on the Al/AlO_x substrates at 3000 rpm. The obtained samples were annealed overnight on a hot plate at 58 °C inside argon glove box.

<u>Benzocyclobutene derivative BCB</u> was deposited from a commercial CYCLOTENE 4024 resin solution diluted with mesitylene in 1:100 v/v ratio. The obtained solution was spin-coated onto the the Al/AlO_x substrates at 1500 rpm. The resulting coatings were annealed overnight on a hot plate at 280 °C inside argon glove box.

<u>*Paraffin PF*</u> was dissolved in a toluene to achieve a concentration of 4 mg/ml. The resulting solution was spin-coated onto the dried Al/AlO_x electrodes at 3000 rpm.

Semiconductor indigo films were grown on the organic dielectric coating by thermal evaporation from a resistively heated quartz crucible at a pressure of 2×10^{-6} mbar at the rate of 0,6 Å/s. The typical thickness of the indigo films was 70 nm. Silver or gold source and drain electrodes (typically 100 nm) were evaporated through a shadow mask ($L = 50 \mu m$, W = 2 mm) at a pressure of 2×10^{-6} mbar. Transistor characterization was carried out inside an argon glove box with <1 ppm O₂ and < 1 ppm H₂O. The transfer and output characteristics were recorded using Kethley 2612A instrument with LabTracer software.

GIWAXS measurements

The samples were prepared in the same way as in the case of OFET fabrication using silicon slides as substrates. Silicon has a very flat surface and does not produce intense amorphous halo on GIWAXS patterns like a normal glass. A set of samples with the thickness of indigo films varied between 70 nm and 500 nm was prepared for every investigated dielectric coating. Bare silicon (passivated with a native SiO_2 layer) and glass were applied as substrates in additional experiments aimed to study the structure of thin indigo films grown without using organic dielectric coatings.

GIWAXS measurements were performed using XeuSS SAXS/WAXS (Xenocs, France) machine coupled to GeniX3D generator ($\lambda = 1.54$ Å). The incidence angle was 0.2°. The 2D data were collected with the incidence angle 0.2° using Pilatus 300k detector with sample to detector distance approx. 9cm. The modulus of the scattering vector s (s = $2\sin\theta/\lambda$, where θ is the Bragg angle) was calibrated using seven diffraction orders of silver behenate powder.

AFM and SEM microscopy and optical spectroscopy

Atomic force microscopy (AFM) and scanning electron microscopy (SEM) images were typically measured from the channels of the fabricated OFETs after electrical I-V characterization. NTEGRA PRIMA instrument (NT MDT, Russia) was used to obtain the AFM images. SEM images were obtained on a Zeiss LEO SUPRA 25 instrument.

The optical spectroscopy studies were performed for 40 nm thick indigo films grown on the PVA, PF, BCB and TC dielectrics covered on borosilicate glass slides. The absorption spectra were measured using Avantes 2048 dual-channel fiber spectrometer equipped with a sample holder installed inside an argon glove box.

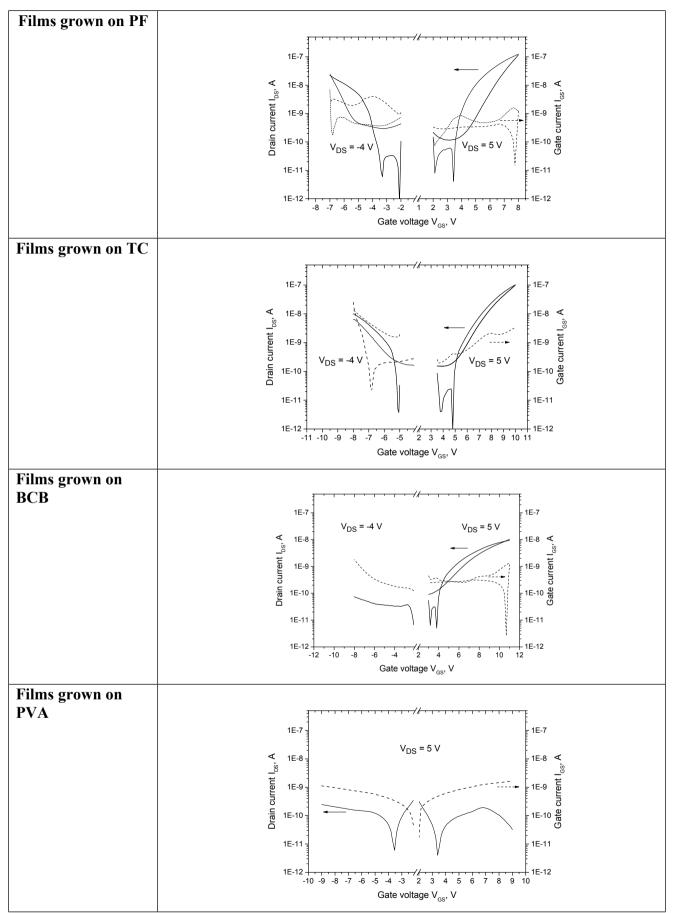


Fig. S1 Transfer characteristics of ambipolar indigo-based OFETs with gold source and drain electrodes

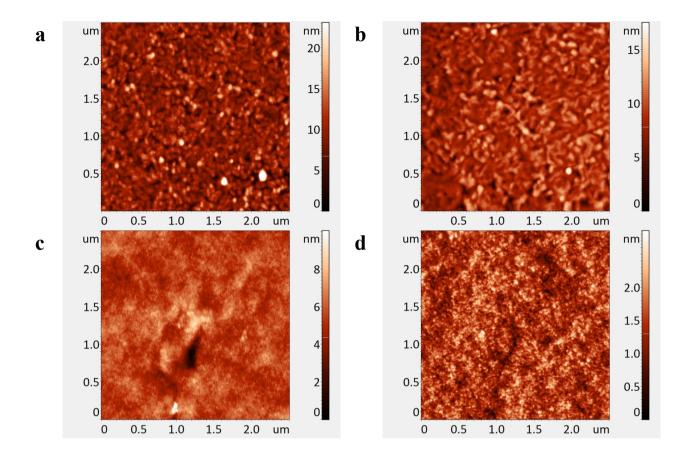


Fig. S2 AFM images of the films of TC (a), PF (b), BCB (c) and PVA (d) dielectrics spin-coated on the Al/AlO_x gate electrodes

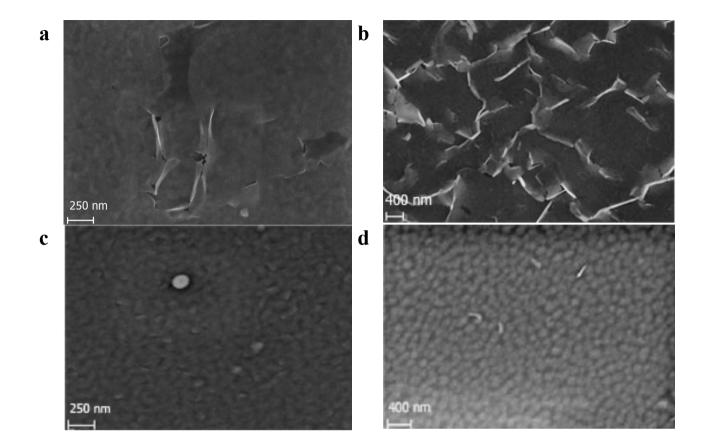


Fig. S3 SEM images of indigo thin films thermally evaporated on TC (a), PF (b), BCB (c) and PVA (d) underlayer dielectrics

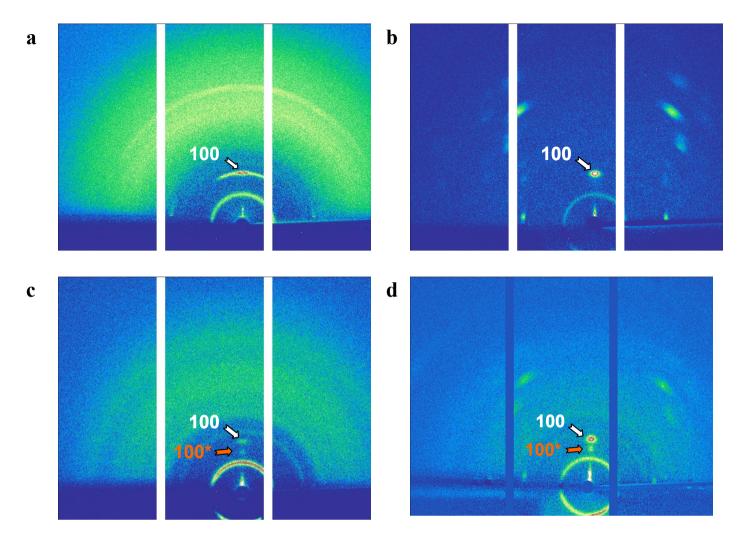


Fig. S4 GIWAXS patterns of indigo films deposited on glass (a), SiO_2 -passivated silicon (b), evaporated TC (c) and solution-processed TC (d)