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Electronic Supplementary Information (ESI)

Dramatic role of the annealing temperature and dielectric functionalization on the electron mobility of Indene-C_{60} Bis-Adduct thin films.

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1. Sample preparation details

ICBA was purchased by Sigma-Aldrich and used without further purification. The powder was handled in air but the solutions were all prepared in a nitrogen environment (O_2 < 5ppm and H_2O < 3ppm) by addition of anhydrous chloroform (10 mg/ml). The spin-cast films were then transferred on a hot-plate were they all underwent annealing at different temperature except for the not annealed ones which dried up at room temperature.

The substrates with pre-patterned gold electrodes were purchased by IPMS Fraunhofer Institut. They were rinsed with raw acetone and successively sonicated in acetone (15'), isopropanol (15') and then dried with a nitrogen flow.

The OTS functionalization procedure started by first cleaning the silicon oxide surface with a UV-Ozone cleaner. The samples were then transferred in a glass jar (in glovebox) containing a 5 mM solution of OTS in toluene. The sealed jar containing the samples immersed in the toluene/OTS solution was then heated at 60°C for 30' and then the samples were left undisturbed overnight and thoroughly rinsed in a pure toluene bath the day after.

2. Atomic Force Microscopy study

The film morphology was imaged by Atomic Force Microscopy (AFM), Digital Instruments Dimension 3100 AFM running with Nanoscope IV controller, under ambient conditions in tapping mode. To ensure full consistency, the films were realized by spin-coating following the same experimental conditions of those prepared for the devices, including the silicon oxide treatment.

The surface roughness, R_{rms}, was measured by AFM. R_{rms} represents the surface roughness. Mathematically it is the variance of the height values acquired in the image (M,N) and is calculated as follows on the images in Figure 2:

$$R_{rms} = \sqrt{\frac{1}{MN} \sum_{(i,j)}^{(M,N)} \left[z_{i,j} - \bar{z} \right]^2} \qquad \text{(Equation S1)}$$

where $z(i,j)$ is the matrix element and $\bar{z}$ the average value.

	No annealed	90°C	140°C	200°C	
OTS	0.504 nm	0.791 nm	0.431 nm	1.2 nm (21.2 nm all image)	Roughness (R_{rms})
HMDS	0.313 nm	0.428 nm	0.331 nm	2.20 nm (26.4 nm all image)	Roughness (R_{rms})
	37.1 nm	*41.6 nm*	*45.3 nm*	*30 nm*	*thickness*

Table S1: Film root mean square roughness (R_{rms}) measured by Atomic Force Microscopy on ICBA films, supported on either OTS or HMDS, annealed at different temperature. The roughness measurements are performed on the images reported within the main manuscript in Figure 2.

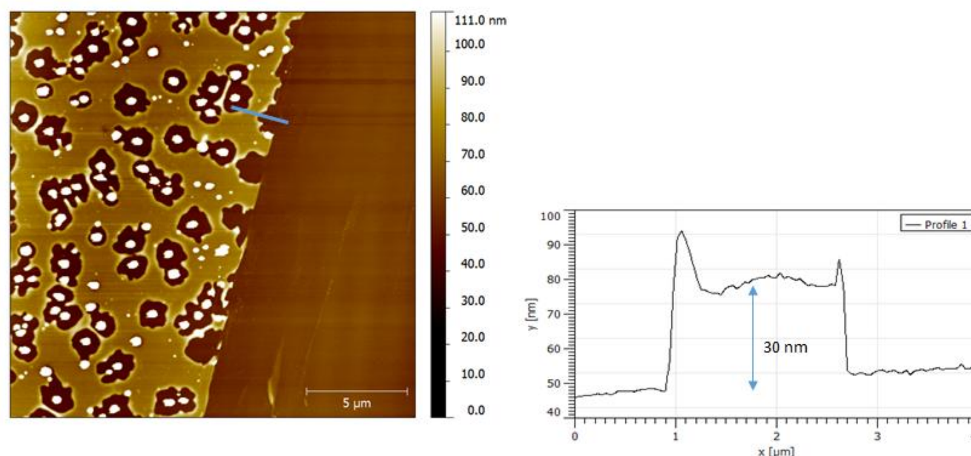


Figure S1: Topography Atomic Force Microscopy image showing the step-height of a typical hollow within the ICBA film.

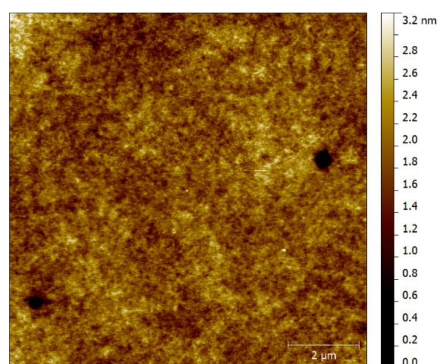


Figure S2: Topography Atomic Force Microscopy image of an ICBA film on OTS-treated SiO_2 after annealing at 170°C for 1h. Roughness (R_{rms}) = 0.37 nm.

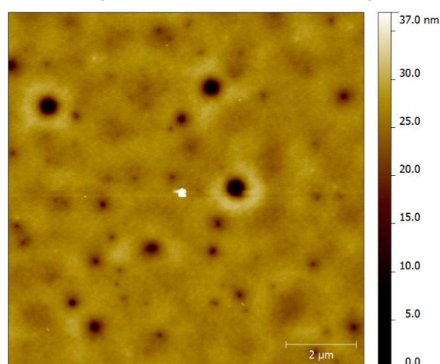


Figure S3: Topography Atomic Force Microscopy image of an ICBA film on OTS-treated SiO_2 after annealing at 200°C for 10 minutes. Roughness (R_{rms}) = 2.1 nm.

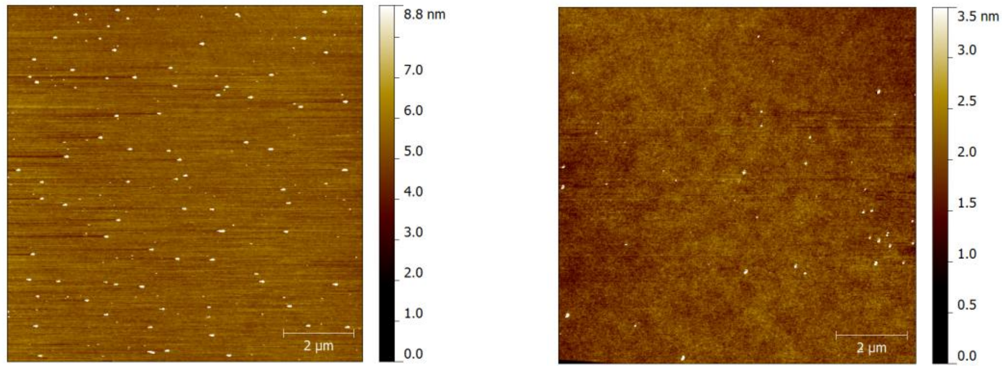


Figure S4: Topography Atomic Force Microscopy image of (left) an OTS-treated SiO_2 sample (R_{rms} = 0.3 nm) and (right) a HMDS-treated silicon oxide sample (R_{rms} = 0.2 nm).

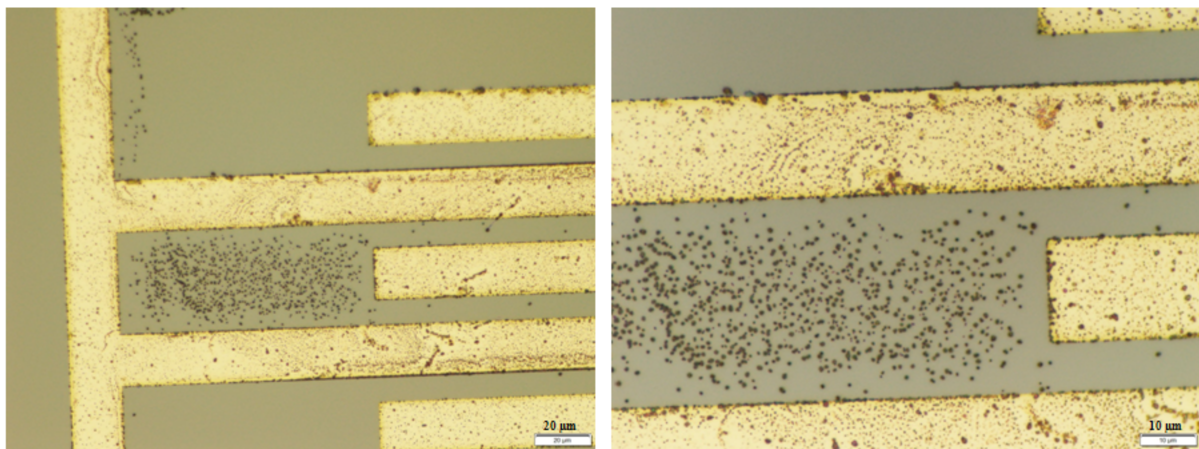


Figure S5: Optical Microscope images showing the morphology of an ICBA film deposited on OTS/SiO_2 upon annealing for 4 days at 200°C. (left image) 20 µm scale bar; (right image) 10 µm scale bar.

3. Water Contact Angle

The wettability of the modified surfaces was determined by static water contact angle (CA) measurements.
The experimental values were:
HMDS: (62.5 ± 2.9)°
OTS: (95.5 ± 0.5)°

4. Electrical parameters extraction

Organic thin-film transistors were prepared starting from n^{++}-Si/SiO_2 substrates exposing pre-patterned interdigitated gold source and drain electrodes (IPMS Fraunhofer). After an accurate cleaning of the substrates, the solutions (in different ratios) were spin-cast onto the

substrates. Electrical characterization was performed in an inert environment by means of an electrometer, Keithley 2636A, interfaced by LabTracer™ software.

The following equations, S2 and S3, correlate the saturated drain current of a n-type thin-film transistor with the applied bias voltages to the gate and the drain electrode respectively while the source electrode is grounded.

In particular considering the following equation

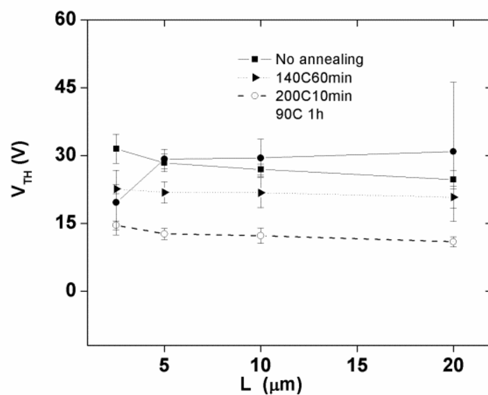
$$I_D = \frac{1}{2}\mu_{SAT,n} C_i \frac{W}{L}(V_G - V_{TH})^2 \qquad \text{(equation S2)}$$

which holds in the **saturation regime**, where $V_D \geq (V_G - V_{TH})$,

(I_D is the drain current, V_G is the gate voltage, V_D is the drain voltage, L is the channel length, and $C_i = 1.5 \cdot 10^{-8}$ F·cm^{-2} is the capacitance of the gate dielectric per unit area) the field-effect mobility for electrons in the saturation regime can be extracted from

$$\mu_{SAT,n} = \frac{2 \cdot \left(\frac{\partial \sqrt{I_D, sat}}{\partial V_G} \right)^2}{C_i \frac{W}{L}} \qquad \text{(equation S3)}$$

then the threshold voltage values can be extracted by plotting the sqrt(I_D) vs. V_G curve and then extracting the intercept with the voltage axis of the line which fits the linear part of the curve.



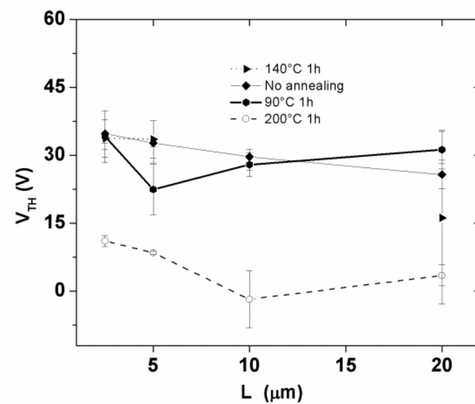


Figure S6: (left) Threshold voltage (V_{TH}) measured in HMDS-treated devices; (right) Threshold voltage (V_{TH}) measured in OTS-treated devices at different channel lengths and annealing temperature. [Error bars indicate the standard deviation over >4 devices].

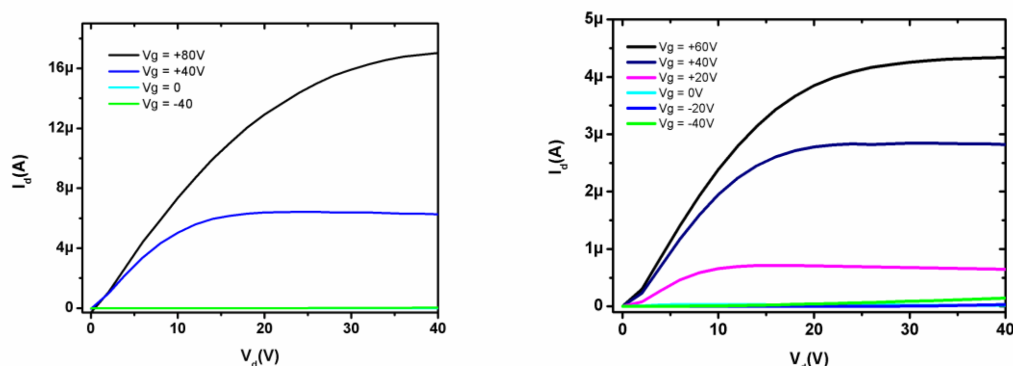


Figure S7: Output characteristics (I_d-V_d) of ICBA-based transistors upon 1h annealing at 200°C Threshold voltage (V_{TH}) measured in HMDS-treated (left) and OTS-treated devices (right).

5. Structural Characterization of ICBA films

The crystallinity of ICBA films was investigated by Grazing Incidence X-Ray Diffraction (GIXRD) measurements performed at the ELETTRA-XRD1 beamline at Trieste's synchrotron facility (Italy) using a monochromatic beam with a wavelength (λ) of 1.542 Å and a dimension of 0.2×0.2 (H×V) mm^2. The incident angle of the X-ray beam, α_i, was chosen equals and slightly larger than the critical angle for total reflection of the organic film (~0.18° and 0.22°), in order to control the penetration through the full film depth. The diffraction patterns were recorded using a 2D camera (Pilatus detector) placed normal to the incident beam direction at 300mm from the sample. Several images were collected translating the sample 0.5 mm in a direction perpendicular to the beam to probe the sample homogeneity.

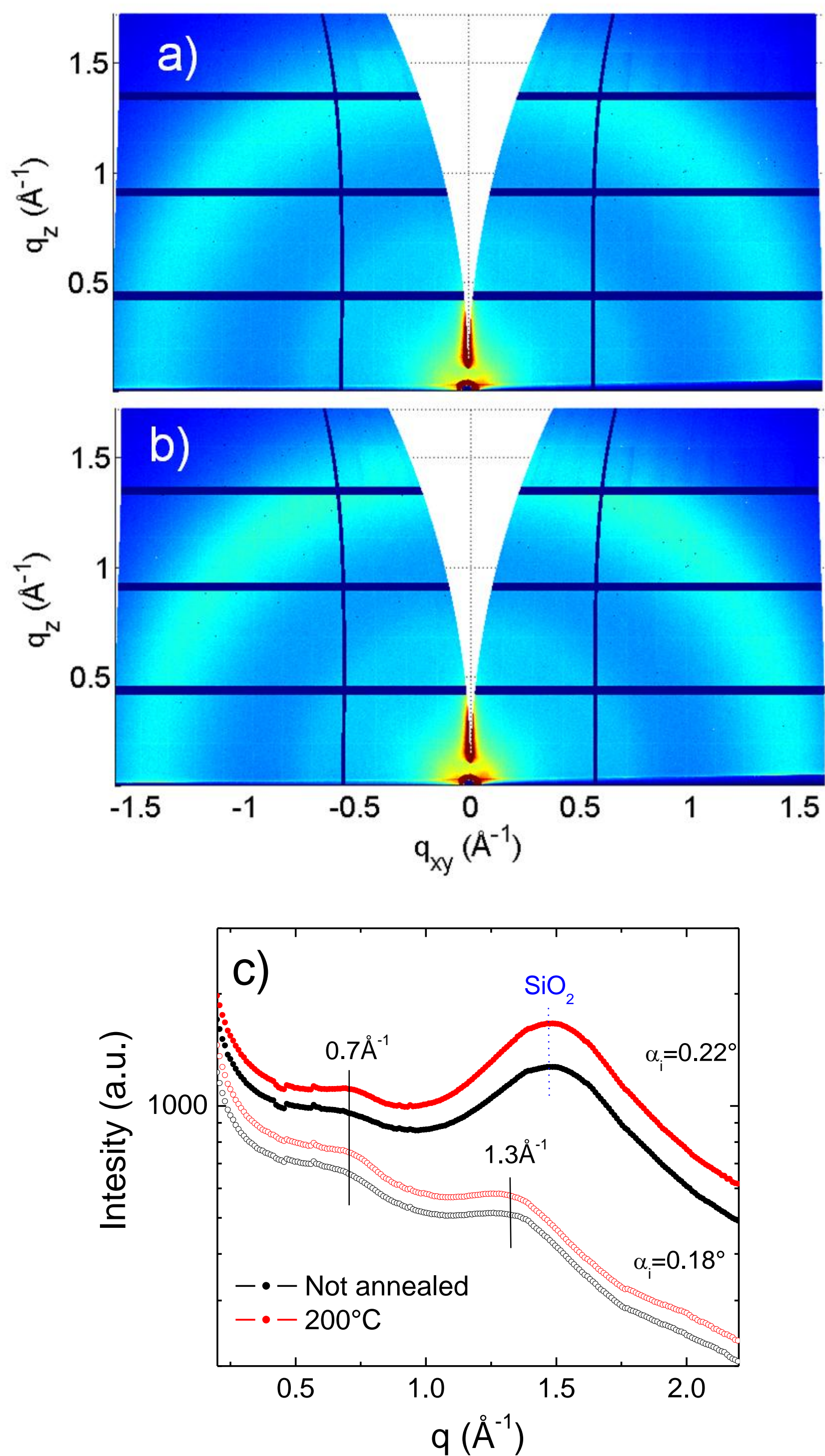


Figure S8: 2D-GIXRD patterns of (a) not annealed ICBA film and (b) after thermal treatment at 200°C for 1h collected at α_i=0.22°. c) Radially integrated scattering intensity of 2D-GIXRD images collected at α_i=0.22° (full dots) and at α_i=0.18° (open dots).

Figure S8 a and **b** report the 2D-GIXRD patterns collected for ICBA films without annealing and with annealing at 200°C (1h), respectively. Isotropic rings are visible at q~0.71 Å^{-1} and

1.32 $Å^{-1}$ when the 2D-GIXRD images, collected at different incidence angles, are radially integrated (**Figure S8c**). The peak width is typical for amorphous films but after annealing at 200°C, the peaks become slightly narrower which is indicative of an early stage of crystallization.