

## **A solvent-free and vacuum-free melt-processing method to fabricate organic semiconducting layers with large crystal size for organic electronic applications**

Jean-Charles Ribierre<sup>ab\*</sup>, Li Zhao,<sup>a</sup> Xiao Liu,<sup>cd</sup> Emmanuelle Lacaze,<sup>d</sup> Benoît Heinrich,<sup>e</sup> Stéphane Méry,<sup>e</sup> Piotr Sleczkowski,<sup>f</sup> Yiming Xiao,<sup>f</sup> Frédéric Lafalet,<sup>gh</sup> Daisuke Hashizume,<sup>i</sup> Tetsuya Aoyama,<sup>j</sup> Masanobu Uchiyama,<sup>jk</sup> Jeong Weon Wu,<sup>fl</sup> Elena Zaborova,<sup>m</sup> Frederic Fages,<sup>m</sup> Anthony D'Aléo,<sup>fmn\*</sup> Fabrice Mathevet<sup>ac\*</sup> and Chihaya Adachi<sup>abo\*</sup>

<sup>a</sup> Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan

<sup>b</sup> Japan Science and Technology Agency (JST), ERATO, Adachi Molecular Exciton Engineering Project, c/o Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan

<sup>c</sup> Sorbonne Universités, Faculté des Sciences, CNRS, Institut Parisien de Chimie Moléculaire (IPCM), UMR 8232, Chimie des Polymères, 4 Place Jussieu, 75005 Paris, France

<sup>d</sup> Sorbonne Universités, Faculté des Sciences, CNRS, Institut des NanoSciences de Paris (INSP), UMR 7588, 4 Place Jussieu, 75252 Paris Cedex 05, France

<sup>e</sup> Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504, CNRS-Université de Strasbourg, 23 Rue du Loess, 67034 Strasbourg Cedex 2, France

<sup>f</sup> Department of Physics, Ewha Womans University, Seoul 03760, South Korea

<sup>g</sup> Univ. Grenoble Alpes, DCM UMR 5250, F-38000 Grenoble, France

<sup>h</sup> Univ. Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR 7086 CNRS, 15 rue Jean-Antoine de Baïf, 75205 Paris Cedex 13, France

<sup>i</sup> RIKEN Center for Emergent Matter Science (CEMS), 2-1 Hirosawa, Wako, Japan

<sup>j</sup> Elements Chemistry Laboratory, RIKEN Cluster for Pioneering Research (CPR), 2-1 Hirosawa, Wako, Japan

<sup>k</sup> Graduate School of Pharmaceutical Sciences, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

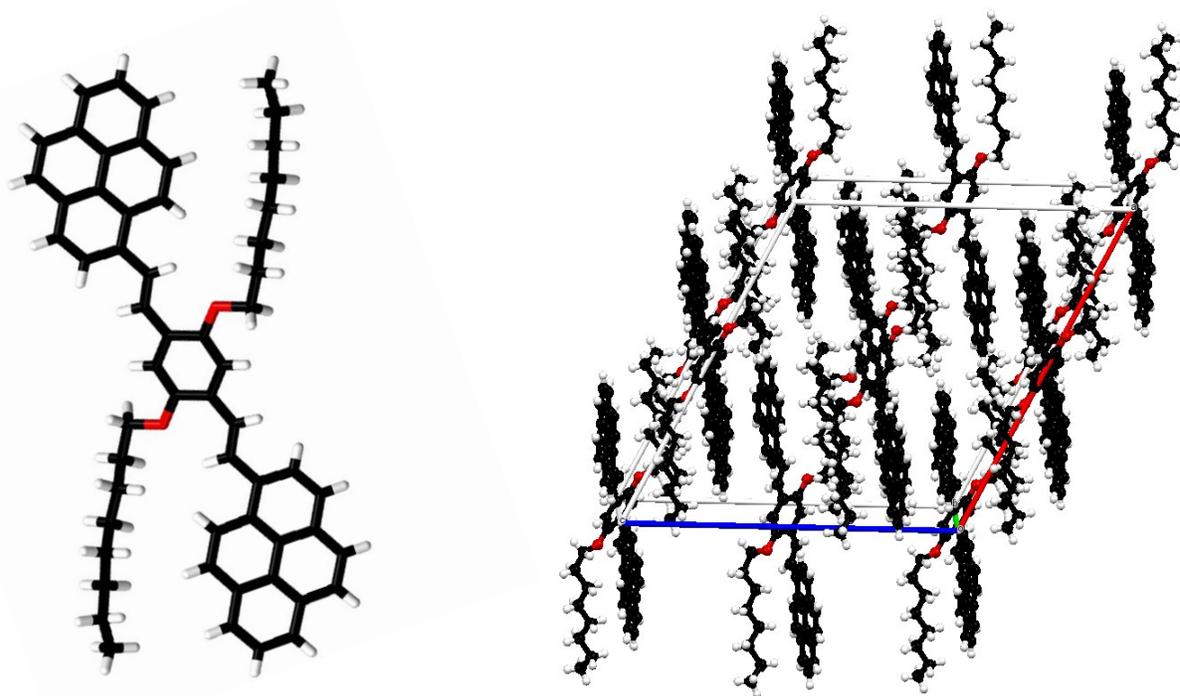
<sup>l</sup> Building Blocks for Future Electronics Laboratory (2-B FUEL), The joint CNRS-Ewha-Yonsei Laboratory, UMI 2002, Seoul, Republic of Korea

<sup>m</sup> Aix Marseille Univ, CNRS, CINaM UMR 7325, Campus de Luminy, Case 913, 13288 Marseille, France

<sup>n</sup> International Institute for Carbon Neutral Energy Research (WPII2CNER), Kyushu University 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

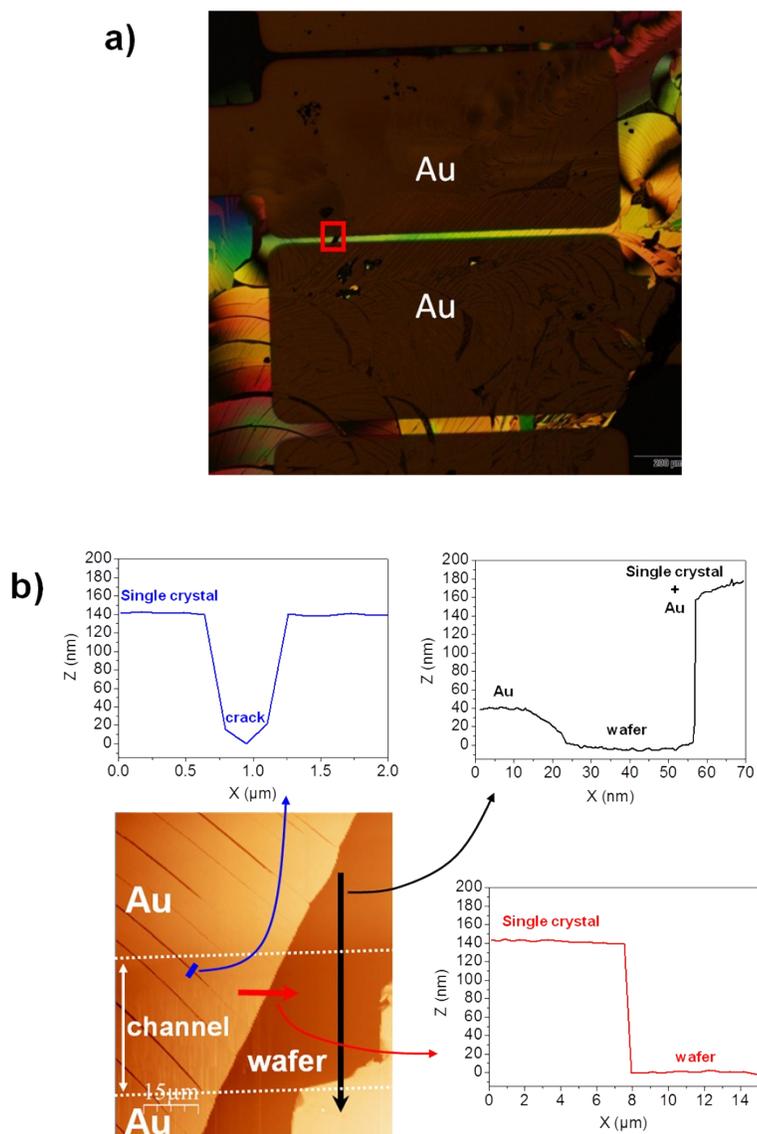
### Single crystal structure of bis-styryl-pyren.

X-ray quality single-crystals of bis-styryl-pyren were grown by slow evaporation of dichloromethane in a mixture of dichloromethane/methanol. A single crystal was mounted on a glass fiber and diffraction data were acquired using a Mo K $\alpha$  radiation source ( $\lambda = 0.71073 \text{ \AA}$ ). Detailed crystallographic parameters are included in **Table S1**. This dye crystallizes in a monoclinic crystal system (C2/c, Z = 4). The molecule is non-planar with a tilt of the pyrene units of  $35.57^\circ$  compared to the central phenyl unit (see below and animation of structure in **Supporting Information**).



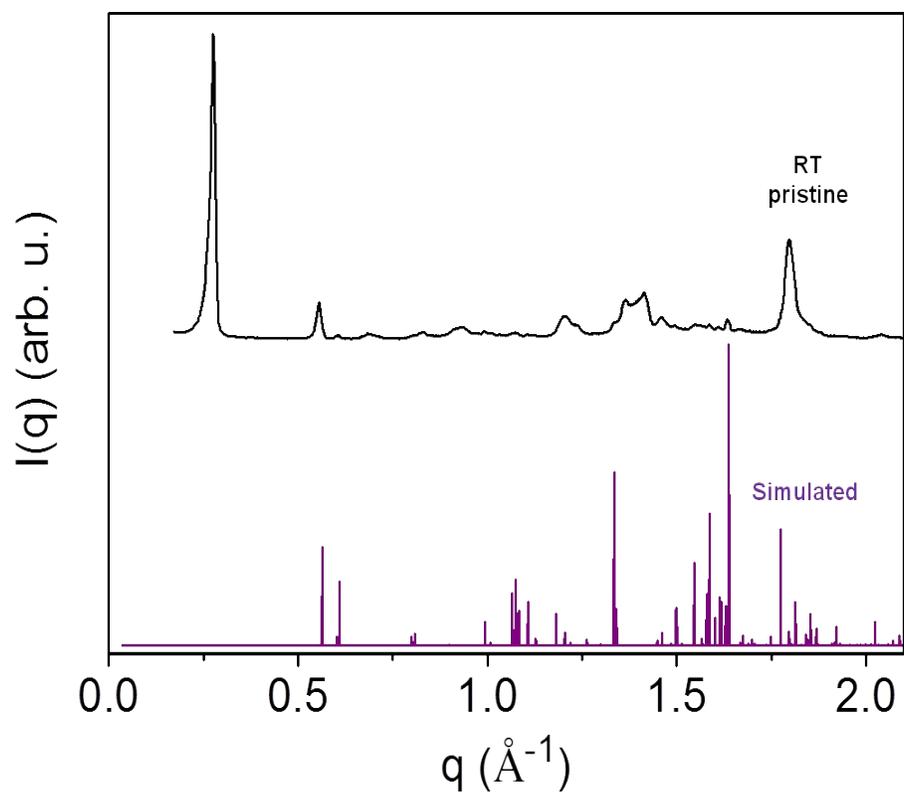
**Table S1.** Crystal structure data for single crystal of bis-styryl-pyren prepared by slow solvent evaporation.

Compound	
Formula	C58 H58 O2
Molecular weight (g mol <sup>-1</sup> )	787.04
Size (mm)	0.3 x 0.24 x 0.06
Crystal lattice	monoclinic
Space group	C2/c
a [Å]	25.0499(5)
b [Å]	8.3917(2)
c [Å]	23.4363(6)
β	116.997(2)
V [Å <sup>3</sup> ]	4389.73(19)
ρ <sub>calcd</sub> (g cm <sup>-3</sup> )	1.191
Z	4
λ(Mo/Kα) / Å	0.71073
T / K	293(2)
θrange / deg	1.825-27.483
<i>hkl</i> ranges	0 < h < 32 0 < k < 10 -30 < l < 26
Variable	289
Refln measured	34085
Refln <i>I</i> > 2σ( <i>I</i> )	4995
R1 <i>I</i> > 2σ( <i>I</i> )	0.057
R1 all data	0.1241
wR2 <i>I</i> > 2σ( <i>I</i> )	0.1585
wR2 all data	0.1977
Δρ (+/-) / e. Å <sup>-3</sup>	0.473 / -0.396



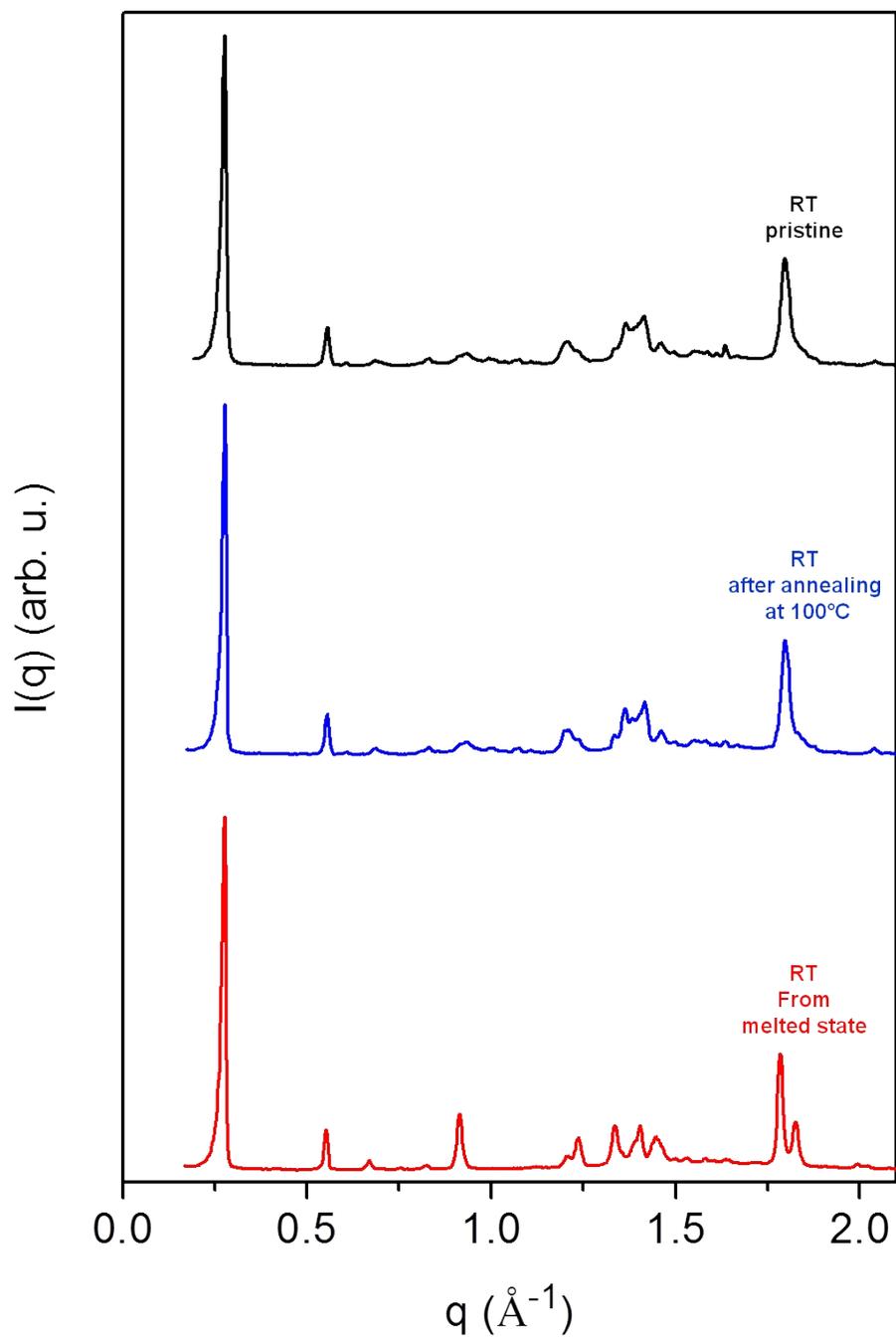
**Figure S1**

a) Picture of a transistor prepared with a melt-processed thin film of bis-styryl-pyren. b) AFM image of the transistor channel area surrounded by the red square in a), and height profiles along the red, black and blue lines showing the typical melt-processed thin film thickness and the crack depth.



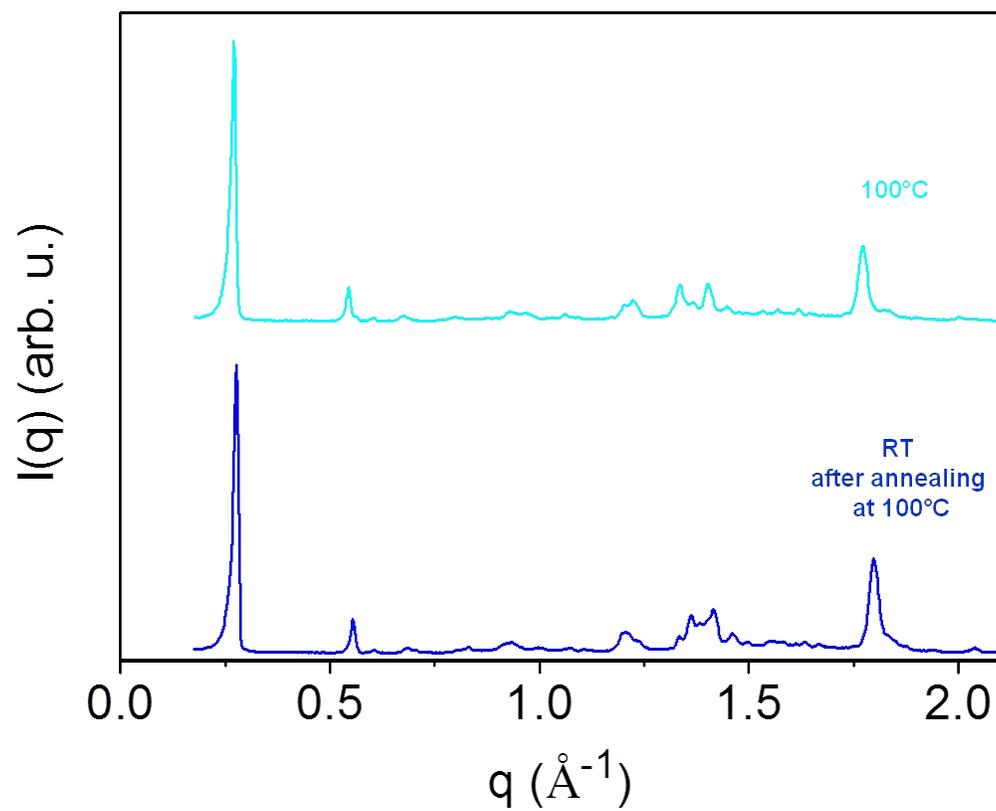
**Figure S2**

SAXS pattern of bis-styryl-pyren pristine powder and simulated SAXS pattern calculated from crystal structure resolved from single-crystals prepared by slow solvent evaporation.



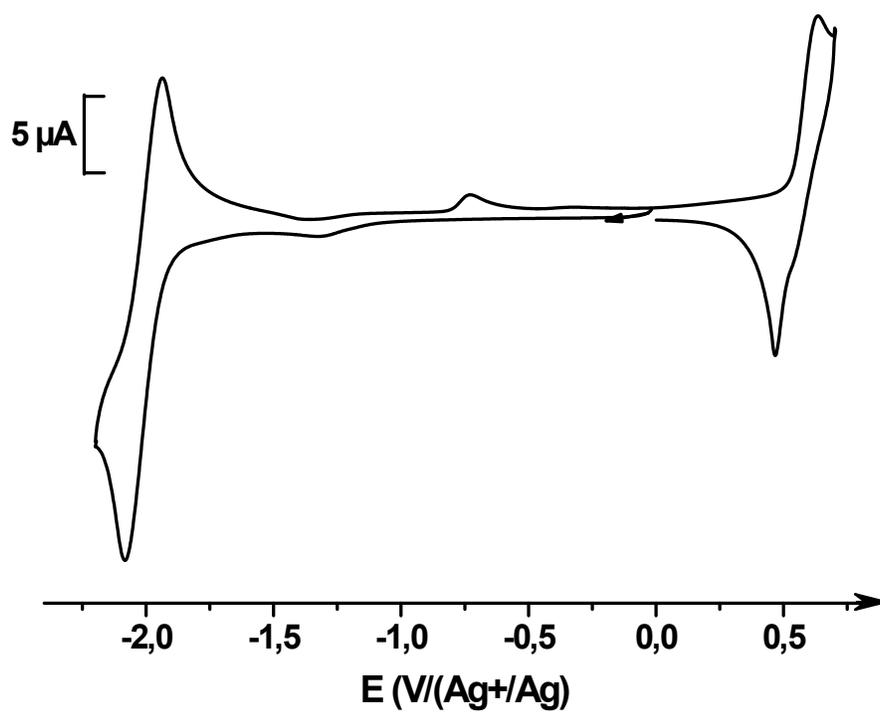
**Figure S3**

SAXS patterns of bis-styryl-pyren at Room Temperature in the pristine powder state (black), after annealing at 100°C (blue) and after melting in the isotropic liquid phase and cooling (red).



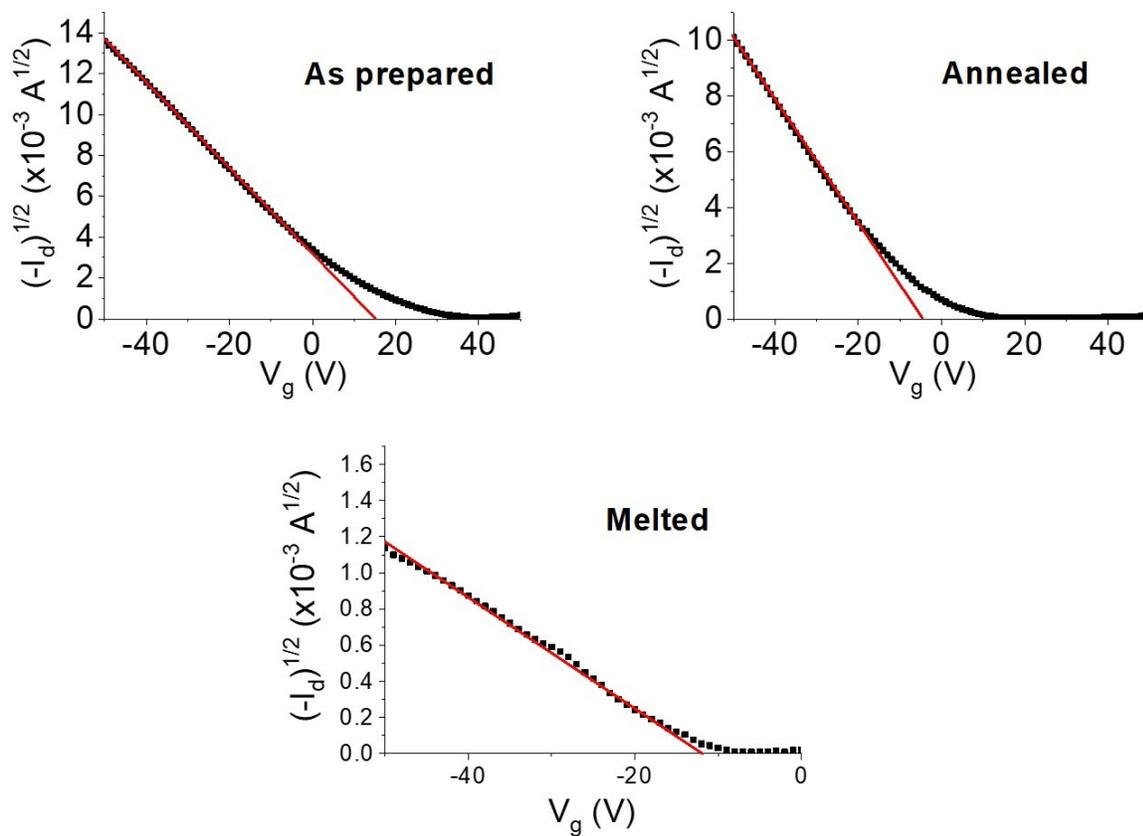
**Figure S4**

SAXS patterns of bis-styryl-pyren powder at 100°C (sky blue) and at Room Temperature after the annealing at 100°C (blue).



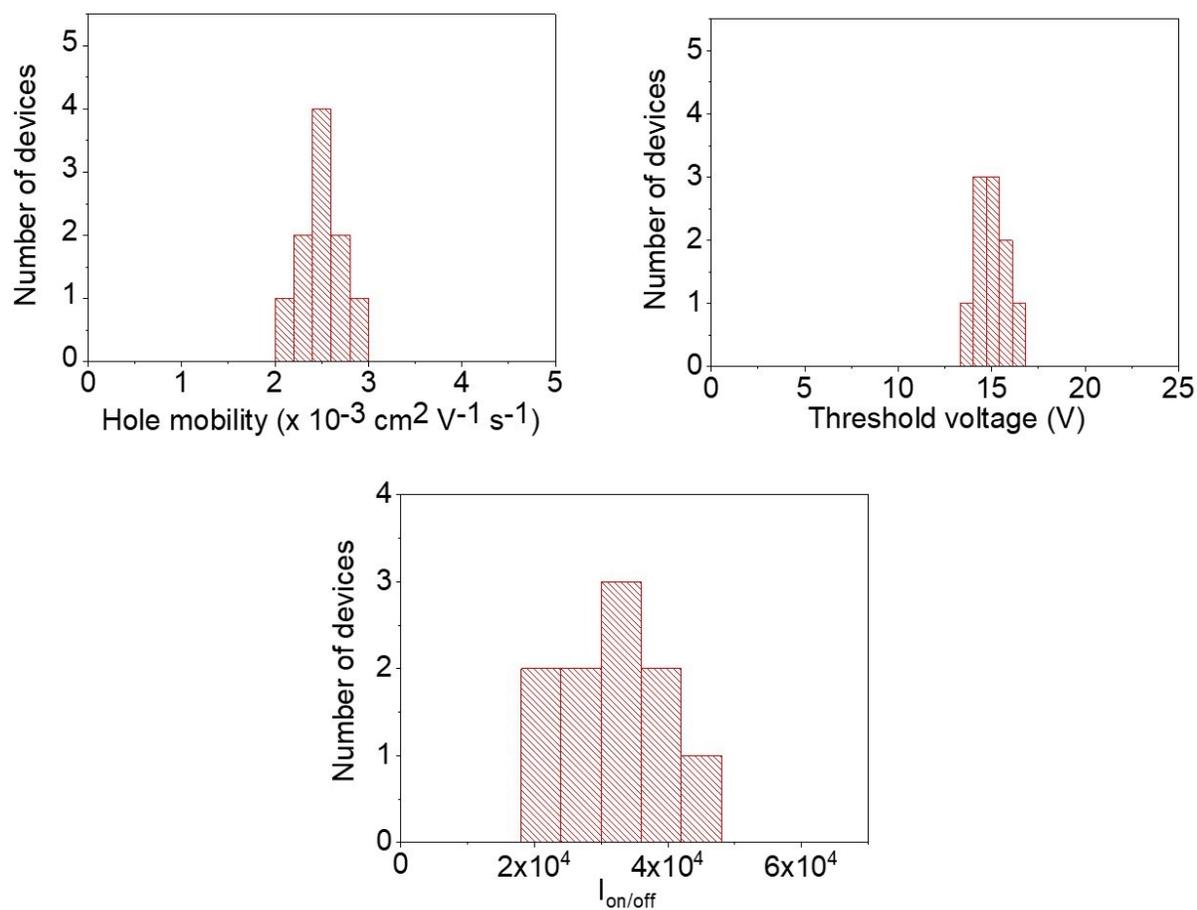
**Figure S5**

Cyclic voltammogram of a 1M solution of bis-styryl-pyren in THF using TBAPF<sub>6</sub> as the supporting electrolyte and a vitreous carbon working electrodes at a rate of 50 mV.s<sup>-1</sup>.



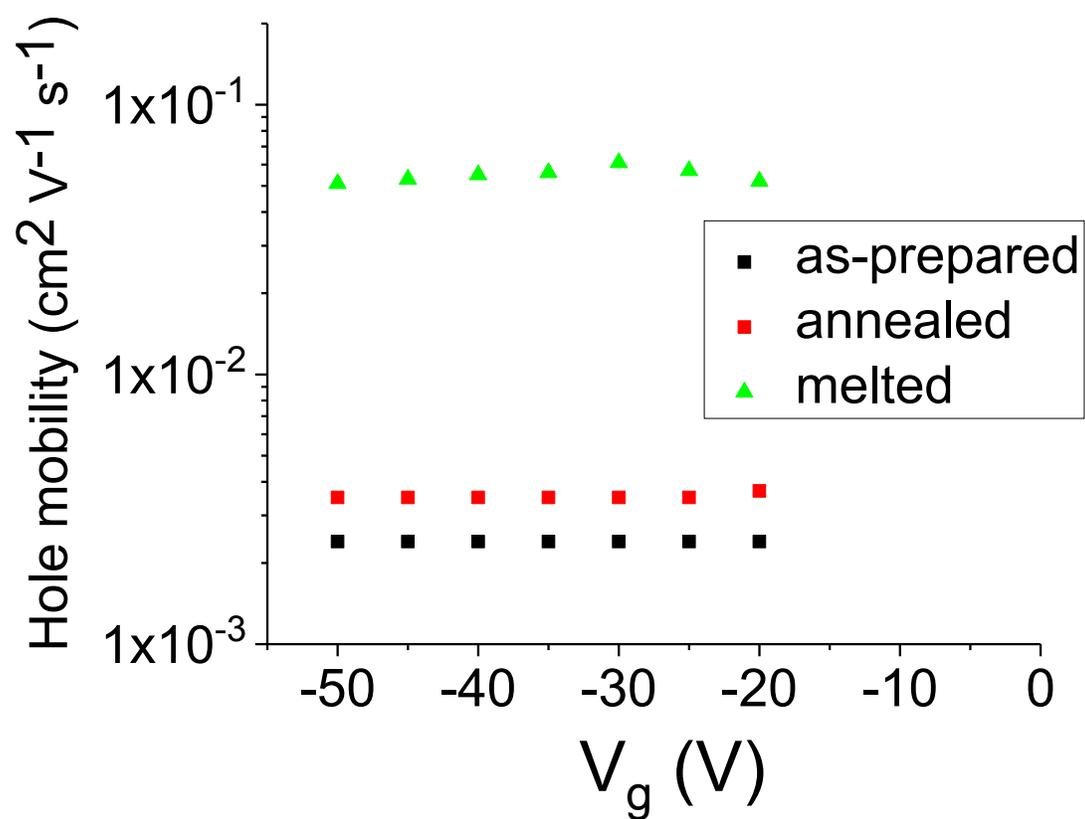
**Figure S6**

Square root of the s/d current versus the gate voltage in as-prepared, annealed, and melted OFETs.



**Figure S7**

Summary of the OFET properties measured in the as-prepared device. These data show the excellent repeatability of the device performance.



**Figure S8**

Gate voltage dependence of the hole mobility in representative as-prepared, annealed and melted OFETs. These data indicate that the influence of the contact resistance of the samples on the field-effect mobility determined in the saturation regime is negligible.