Supporting Information:

Late Stage Crystallization and Healing During Spin-Coating Enhance Carrier Transport in Small-Molecule Organic Semiconductors

Kang Wei Chou[†], Hadayat Ullah Khan[†], Muhammad R. Niazi[†], Buyi Yan[†], Ruipeng Li[†], Marcia M. Payne[ϟ], John E. Anthony[ϟ], Detlef-M. Smilgies[‡], and Aram Amassian[†,]*

[†] Physical Sciences and Engineering Division, Solar and Photovoltaic Engineering Research Center, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

[ϟ]Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506, United States

[‡]Cornell High Energy Synchrotron Source, Cornell University, Ithaca, New York 14853, United States

*Email: aram.amassian@kaust.edu.sa

Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS)

The GIWAXS experiments were performed at the D1 station at the Cornell High Energy Synchrotron Source (CHESS, Ithaca, NY) and a Pilatus 100k detector was used to record the scattering patterns. For the static studies, an exposure time of 1 sec was used while an exposure time of 0.09 sec was used during the time-resolved experiments. A scattering pattern of the bare substrate was recorded prior to the in situ spin coating measurements, and was used as reference for the background subtraction. Figures S1 and S2 show the radially integrated and azimuthally integrated intensity, respectively, of the TIPS pentacene thin films, right after they were spin coated.

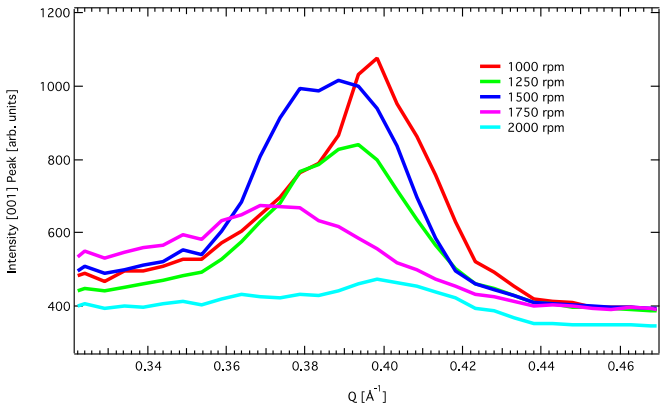

Figure S1: Radially integrated intensity curves around the (001) Bragg sheet in the <001> orientation of TIPS-pentacene thin films prepared at 5 different spinning speeds (1000, 1250, 1500, 1750 and 2000 rpm).

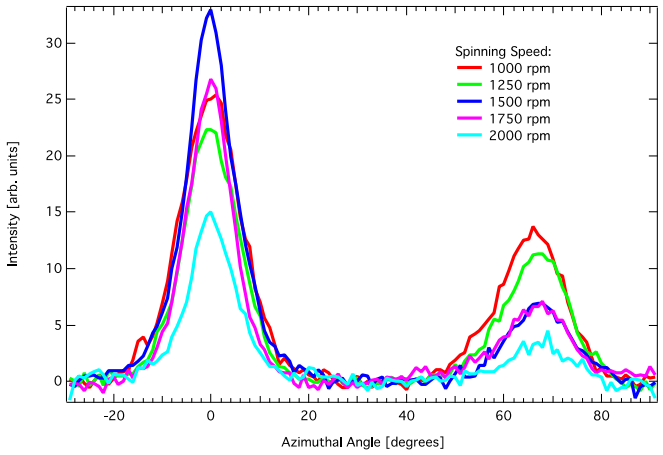

Figure S2: Azimuthally integrated intensity curves around the (001) Bragg sheet and peak in the <001> and <111> orientations, respectively, for TIPS-pentacene thin films prepared at 5 different spinning speeds (1000, 1250, 1500, 1750 and 2000 rpm).

Table S1 summarizes the dimension of the lamellar stacking d, the domains size D_z and the mosaicity of the different films prepared at different spinning speeds.

	<001>			<111>
Spin Speed [rpm]	d-spacing [nm]	D_z [nm]	$FWHM_{az}$	$FWHM_{az}$
1000	1.589	16.3	14.8°	16.0°
1250	1.616	14.7	13.5°	15.6°
1500	1.628	14.7	12.3°	14.2°
1750	1.708	7.7	11.3°	14.1°
2000	1.606	12.5	11.0°	13.3°

Table S1: Values extracted from the GIWAXS data from TIPS-pentacene thin films produced at five different spinning speeds (1000, 1250, 1500, 1750 and 2000 rpm). The d-spacing, domain size D_z and the full width at half maximum (FWHM) of the azimuthal spread was determined for the first order peak in the <001> orientation. For the first order peak in the <111> direction, only the FWHM of the azimuthal spread was calculated.

The evolution of the (001) peak in the <001> orientation (full lines) and <111> orientation (dotted lines) during the spin coating of the TIPS pentacene solution at the different spinning speeds are shown in Figure S3. The characteristic times and durations of crystallization were extracted and are summarized in Table S2.

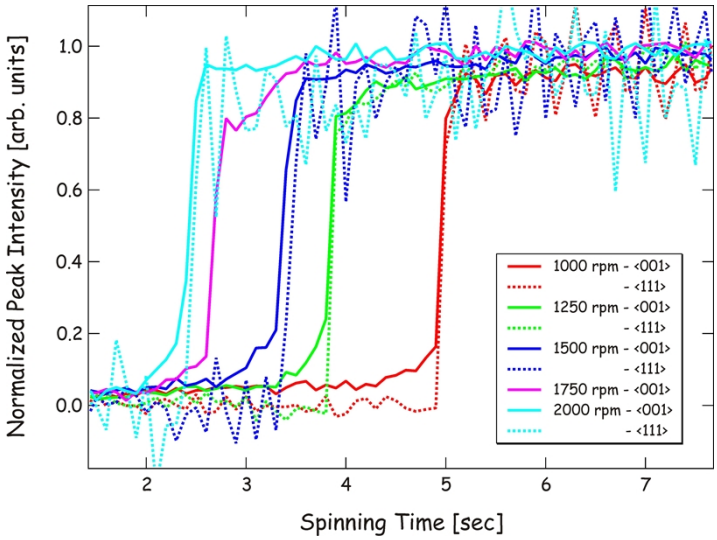

Figure S3: Normalized peak intensities of the (001) peak in the <001> orientation (full lines) and <111> orientation (dotted lines) as a function of the spinning time during the spin-coating of TIPS-pentacene at 5 different spinning speeds (1000, 1250, 1500, 1750 and 2000 rpm). The 1750 rpm, <111> orientation data is missing due to too high noise in the data.

Spinning Speed [rpm]	Onset Crystallization [sec]	Duration Fast Crystallization [sec]	Duration Slow Crystallization [sec]
1000	**4.953 ± 0.005**	**0.116 ± 0.003**	**8.6 ± 0.1**
1250	**3.640 ± 0.006**	**0.140 ± 0.004**	**5.5 ± 0.1**
1500	**3.068 ± 0.006**	**0.231 ± 0.005**	**4.5 ± 0.1**
1750	**2.787 ± 0.013**	**0.278 ± 0.011**	**2.8 ± 0.1**
2000	**2.325 ± 0.006**	**0.204 ± 0.005**	**2.5 ± 0.1**

Table S2: Overview of the timing and duration of the different processes during the film formation of TIPS-pentacene, extracted from in situ GIWAXS measurements.

Bottom gate, top contact organic thin film transistors (OTFTs) were fabricated under the same conditions as the in situ GIWAXS experiments. The average saturation hole mobility, the threshold voltage and the current on/off ratio were extracted from the transfer curves and are shown in Figure S4.

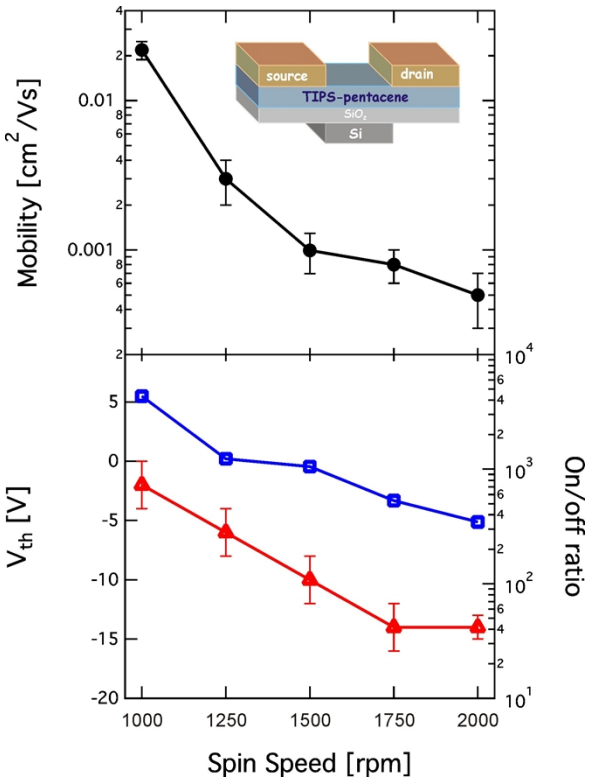

Figure S4: The saturation hole mobility, threshold voltage (red) and current on/off ratio (blue) are plotted for OTFT devices prepared from films deposited at five different spinning speeds (1000, 1250, 1500, 1750 and 2000 rpm).