Supporting Information for

Probing interfacial molecular packing in TIPS-pentacene organic semiconductors by Surface enhanced Raman Scattering

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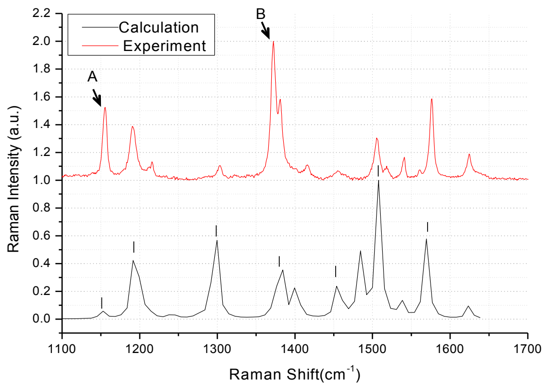
a



b

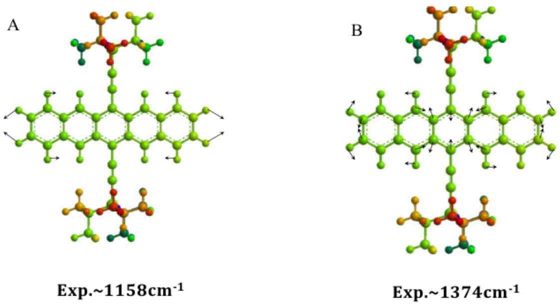


Figure S1. **(a) Comparison between the Raman spectrum of TIPS-Pentacene film (red), and calculated vibrational spectrum of gas-phase TIPS-Pentacene single molecule (black).** The vibrational spectrum was calculated using Density Functional Theory at the B3LYP level of theory and a basis set of 6-31G*. An empirical scaling factor of 0.9613 was applied to the calculated wavenumbers. **(b) Selected C-H bending mode and aromatic C-C stretching modes of a TIPS-**

pentacene that calculated form DFT B3LYP/6-31G (d). Modes (A) and (B) correspond to C-H bending vibrations localized at the ends of the pentacene backbone, C-C stretching vibrations in the conjugated pentacene backbone, primarily oriented along the short-. This bending modes assigned here are in good agreement with others work.[1]

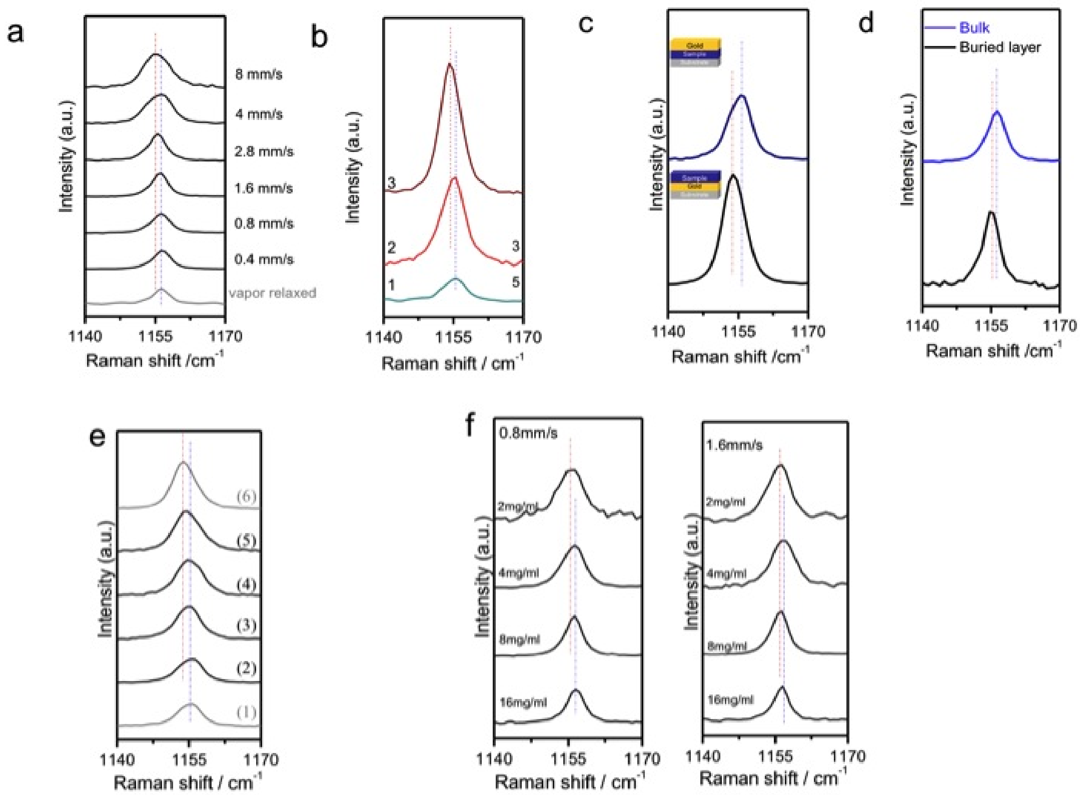


Figure S2. The enlarge region of 1140-1170 cm^{-1} (C-H in-plane bending region) in each spectra: (a) Raman spectra of TIPS-pentacene film solution sheared at different speeds with 8mg/ml solution concentration. (b) Raman (1), surface SERS spectra (2) and interface SERS spectra (3) of TIPS-pentacene film solution-sheared at 2.8 mm/s with 8mg/ml solution concentration. (c) SERS spectra of TIPS-pentacene film with gold layer on the film sample surface (gray) and beneath the film (navy). (d): Raman spectra of bulk (black) and the buried layer of TIPS-pentacene film (blue). (e): (1) SERS spectra of vapor relaxed TIPS-pentacene film; 2)-4) Surface SERS spectra of TIPS-pentacene film solution sheared at 0.8mm/s, 2.8 mm/s, 4 mm/s and 8.0 mm/s, respectively; (5) Interface SERS spectra of TIPS-pentacene film solution sheared at 8.0mm/s. (f) Raman spectra of TIPS-pentacene film solution sheared at 0.8 mm/s (left) and 1.6 mm/s (right) with different solution concentrations. Theses spectra were normalized to the intensity of the strongest C-C band at 1374 cm^{-1}. Spectra are offset for clarity. The dashed lines serve as guidelines.

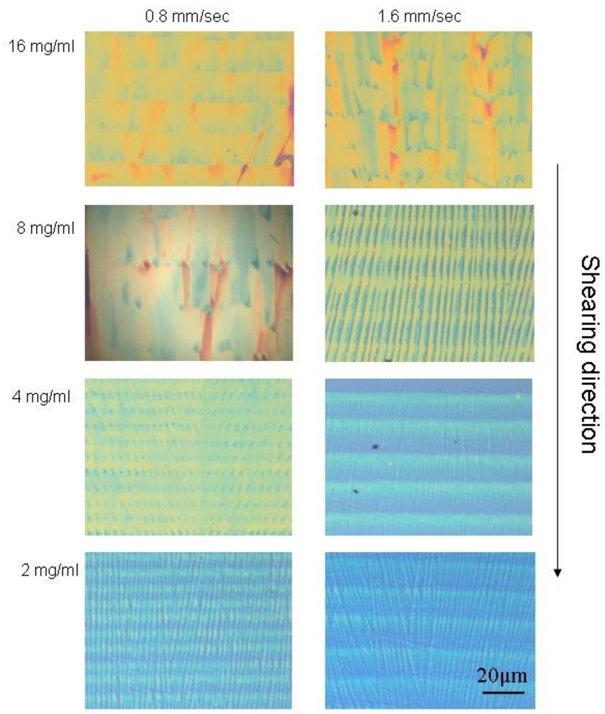


Figure S3: Optical image of TIPS-pentacene films deposited from different concentration solutions.

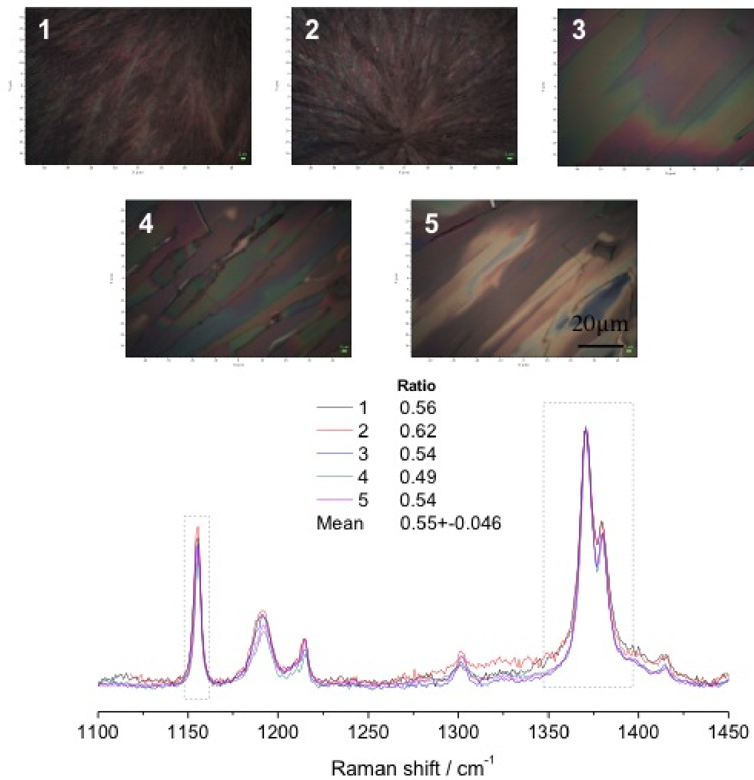


Figure S4: Optical images and Raman spectra of TIPS-pentacene drop-casted films at different locations.

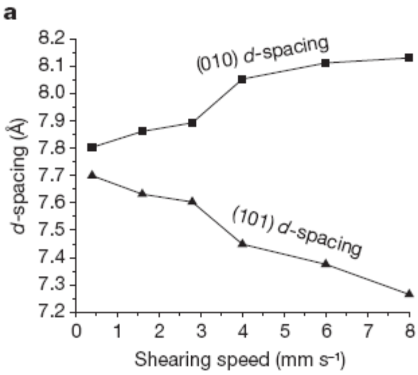


Table S1: d-spacing parameters and unit cell parameters of sheared TIPS-pentacene thin films

Speed	a	b	c	α	β	γ	Cell Volume	d-spacing (100)	d-spacing (010)	Mobility	On/Off	Vt
(mm/s)	(Å)	(Å)	(Å)	(deg)	(deg)	(deg)	(Å)	(Å)	(Å)	(cm /Vs)		(V)
Evaporated[31]	7.70	7.83	16.78	103.5	88.0	99.0	972.0	-	-	-	-	-
0.4	7.79	7.76	17.10	104.4	88.2	97.8	991.1 (14.3)	7.70 (0.07)	7.80 (0.11)	0.33	1.8E+04	39.3
1.6	7.75	7.96	17.02	104.3	87.4	99.6	1002.8 (7.5)	7.65 (0.05)	7.86 (0.07)	0.78	2.1E+05	30.2
2.8	7.70	8.03	17.18	104.3	87.5	99.8	1013.5 (8.2)	7.60 (0.03)	7.89 (0.03)	1.49	8.2E+06	-16.5
4	7.59	8.13	17.02	104.8	86.9	100.4	998.9 (19.5)	7.45 (0.07)	8.05 (0.06)	0.81	1.0E+07	-27.4
8	7.56	8.56	16.83	102.6	88.1	108.0	1009.8 (6.7)	7.26 (0.08)	8.13 (0.06)	0.47	1.2E+07	-35.7
8*	7.80	7.82	17.00	103.3	88.1	98.7	998.1 (3.6)	-	-	-	-	-

b

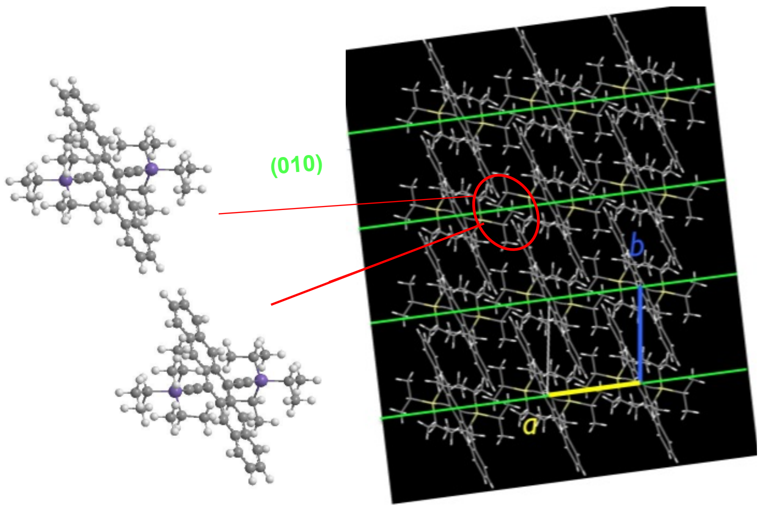


Figure S5. a (101) and (010) d-spacing of TIPS-pentacene thin films sheared at different speeds.[2] Supplementary Table S1: d-spacing parameters and unit cell parameters of sheared TIPS-pentacene thin films.[2] Average values of (101) d-spacing and (010) d-spacing of solution sheared TIPS-pentacene thin films, and the TIPS-pentacene unit cell parameters as a function of shearing speeds. Standard deviation is shown in parentheses. * Sample was annealed in toluene vapor for 1hr. **b. Schematic of the enlarged spacing between two TIPS-pentacene molecular ends.** According to Giri's work, the nonequilibrium TIPS-pentacene in-plane unit cell geometry becomes more oblique with an increased (010) d-spacing, which in turn weakens the intermolecular interactions along this direction.

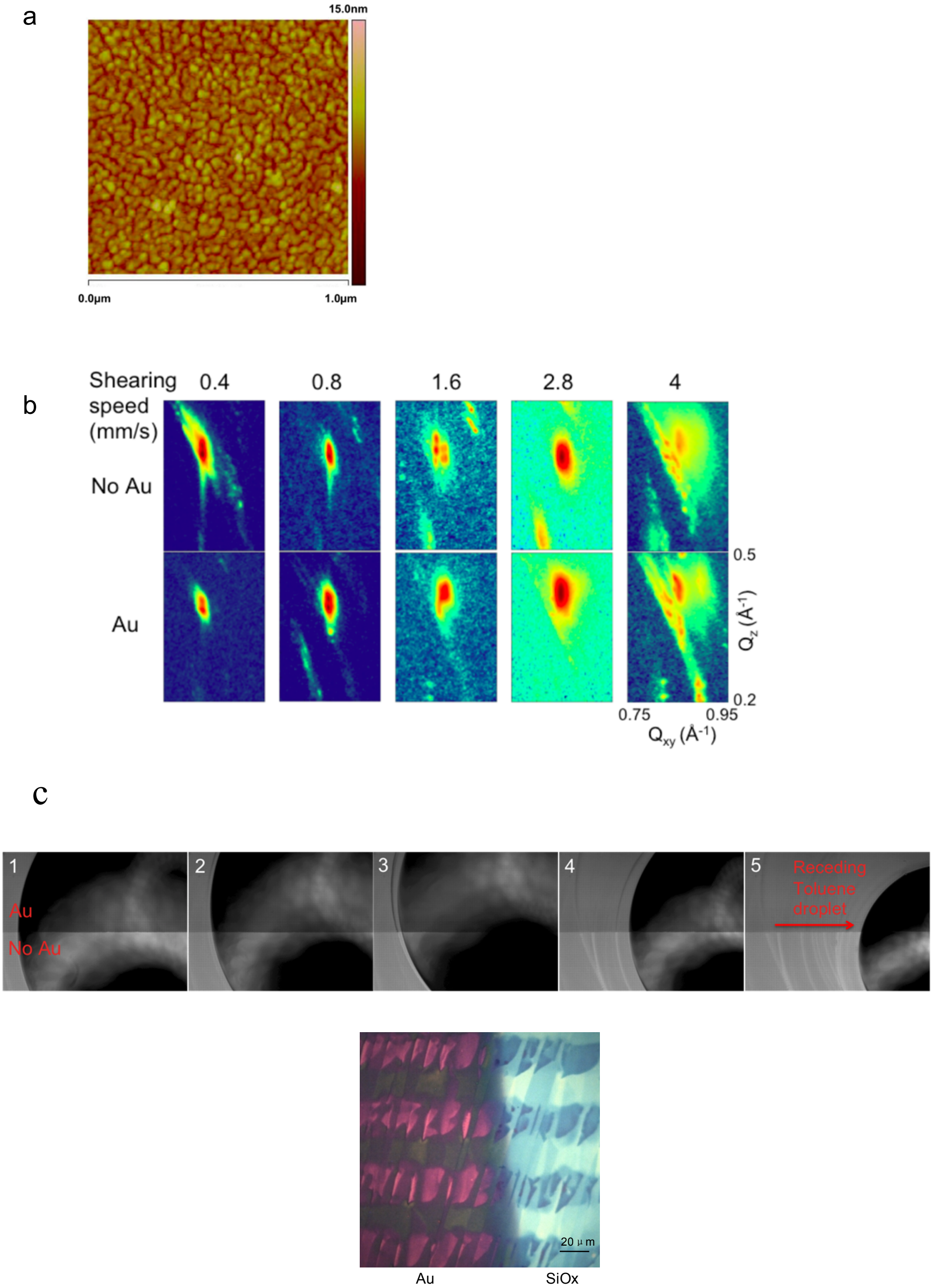


Figure S6. a. AFM image of 9nm Au layer on the substrate. This image shows that the gold covers the majority of the surface, and the surface roughness is around 0.796 nm, which demonstrate that the gold film is smooth. (As a reference, the surface roughness of a PTS modified Si wafer is ~0.5 nm.[2]) **b. comparison of GIXD images of (101) peak of TIPS-pentacene sheared on substrates with 9nm Au layer vs.**

without at various shearing speeds. The (101) peak is chosen to indicate the extent of lattice deviation from equilibrium packing. The films were made from 8 mg/ml TIPS-pentacene/Toluene solution at 90 °C. The peak positions did not change on the substrate with thin Au layer, indicating that this Au layer did not affect the overall molecular packing. **c. dynamic contact angle video.** The supporting video shows that the thin gold layer evaporated onto the PTS substrate has little effect on the receding contact angle of toluene, and therefore the solvent evaporate rate during solution shearing.The bottom image shows the film morphology is not affected by the presence of Au.

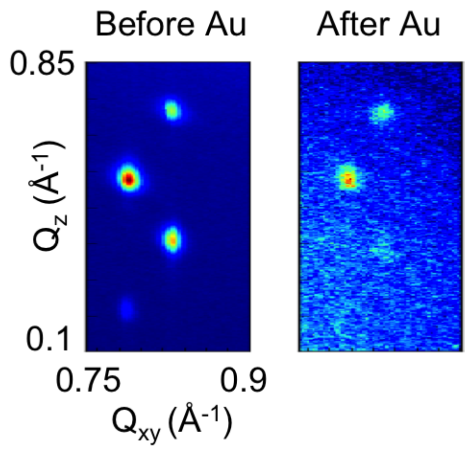


Figure S7. GIXD images showing (010) and (101) peak positions before and after deposition of 9nm Au on the film top surface. Thin films were prepared by shearing at 90°C from 2mg/ml toluene solution at 0.8mm/s. The GIXD was taken with sample in-plane rotation (phi scan). After depositing Au layer, the peak intensities decrease because of X-ray scattering from Au. The peak positions did not change after Au deposition, indicating that the molecular packing was not affected by Au deposition.

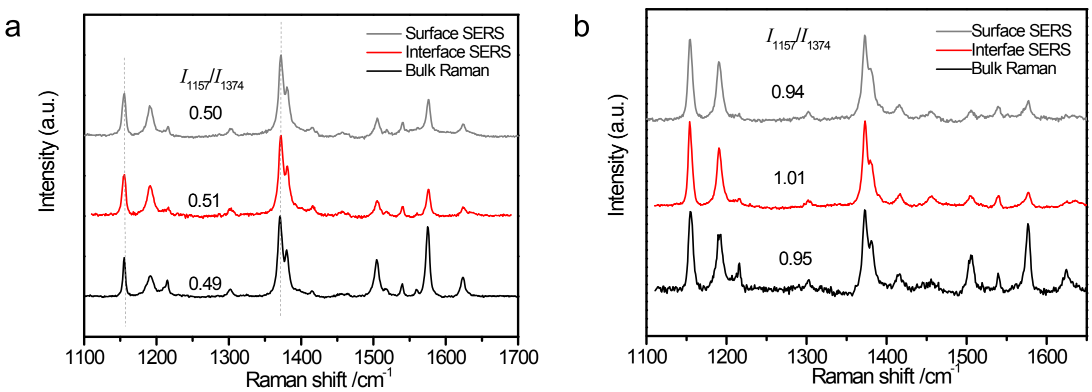


Figure S8. (a) Raman and SERS spectra of film with equilibrium packing. This film was annealed by toluene vapor for more than 1h, which could sufficiently relieve the nonequilibrium packing throughout the film.[2] Comparing the Raman and SERS spectra, we observed that the ratio I_{1157}/I_{1374} is identical within experimental error. **(b) Raman and SERS spectra of highly nonequilibrium TIPS-pentacene film.** Thin films were prepared by shearing at 8 mm/s from 8mg/ml toluene solution. The thickness is around 15nm. We observed that the ratio I_{1157}/I_{1374} are comparable for the Raman and SERS spectra. Therefore, we infer the SERS effect contributes little to the changing of relative ratio I_{1157}/I_{1374}. (All spectra were normalized to the intensity of the strongest C-C band at 1374 cm^{-1}. Spectra are offset for clarity.)

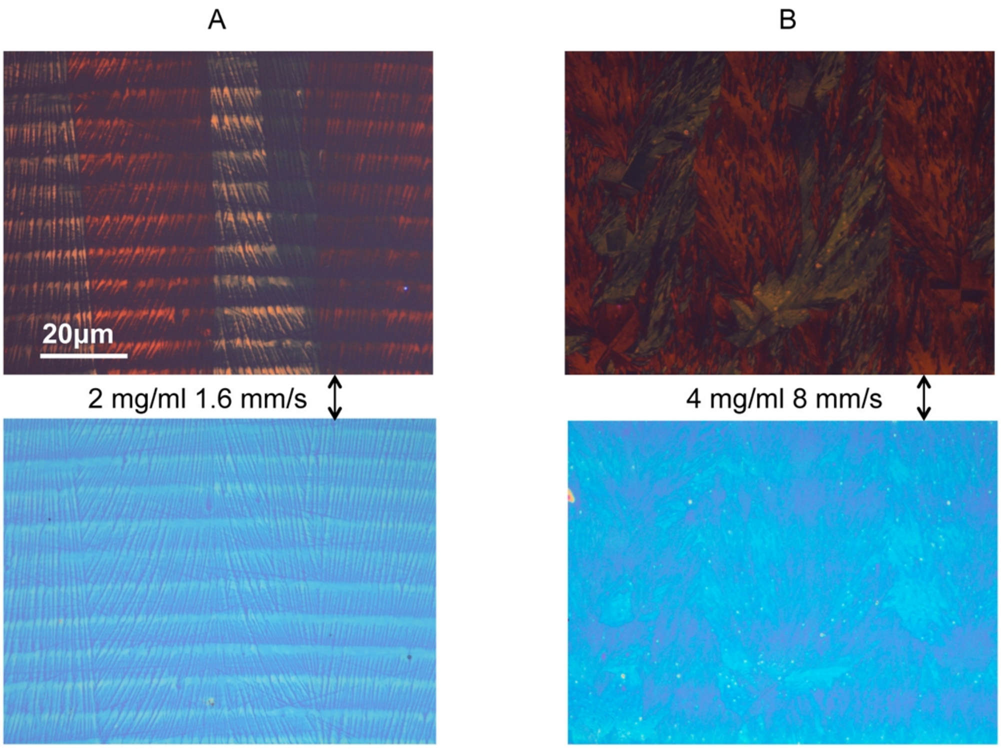


Figure S9. Morphology comparision of TIPS-pentacene films with similar thickness prepared either with low concentration (A) or high shearing speed (B). Upper images are taken under cross-polarized optica microscope. All imgages are of the same scale. These optical images show that the film prepared with low concentration and low speed has a better crystalline alignment.

(1) James, D. T.; Kjellander, B. K. C.; Smaal, W. T. T.; Gelinck, G. H.; Combe, C.; McCulloch, I.; Wilson, R.; Burroughes, J. H.; Bradley, D. D. C.; Kim, J. S. *ACS Nano*, 2011, *5*, 9824.

(2) Giri, G.; Verploegen, E.; Mannsfeld, S. C. B.; Atahan-Evrenk, S.; Kim, D. H.; Lee, S. Y.; Becerril, H. A.; Aspuru-Guzik, A.; Toney, M. F.; Bao, Z. A. *Nature*, 2011, *480*, 504.