

[Electronic Supplementary Information](#)

Electrical stability study of polymer-based organic transistors in ambient air using active semiconducting/insulating polyblend-based pseudo-bilayer

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Outline

1. **Supplementary experimental details of analytical methods**
2. **Current decay analysis**
3. **Absorption and Raman spectroscopy**
4. **In-situ absorption spectroscopy**
5. **A cartoon illustration of structural model**

1. Supplementary experimental details of analytical methods

Analytical methods. The absorption spectrum was recorded using a GBC Cintra 202 UV/Vis spectrophotometer (scanning rate of 1000 nm/min, resolution of the spectrometer was 0.9 nm). The Raman spectrum was obtained using a iHR550 imaging spectrometer. A 633 nm He–Ne laser served as the excitation light source and was kept below 0.5 mW to prevent thermal damage of the polymer film. The spectral resolution is approximately 0.4 cm⁻¹ for 633 nm excitation source.

Absorption spectra and theoretical fitting procedure. According to theoretical predictions,^{s1} the absorption from crystalline regions and the magnitude of the exciton bandwidth (W) of P3HT can be estimated by fitting the absorption spectrum through a modified Frank-Condon analysis:^{s2}

$$A \propto \sum_{m=0} \left(\frac{e^{-S} S^m}{m!} \right) \left(1 - \frac{W e^{-S}}{2E_p} G_m \right)^2 \Gamma(\hbar\omega - E_{0-0} - mE_p) \quad (\text{S1})$$

where A is the relative absorption intensity of the individual bands, m is the vibrational level, S is the Huang-Rhys factor, E_p is the energy of the main vibrational mode, G_m is equal to $\sum_{n(\neq m)} S^n/n!(n-m)$ (n is the vibrational quantum number), Γ is assumed as a Gaussian function, ω is the vibrational frequency, and E_{0-0} is the energy of the 0-0 electronic transition. During the curve-fitting procedure, S is assumed to be 1 and a refractive index ratio of 0.97 between the A_0 and A_1 bands was used.^{s1,s3}

2. Current decay analysis

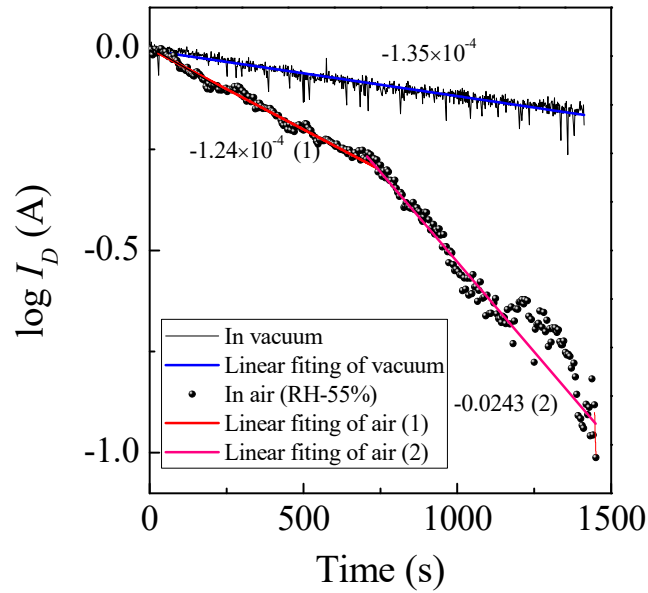


Figure S1. Comparison of normalized I_D as a function of time of neat P3HT-based OTFTs in semi-logarithmic scale. The data was the same as in Figure 2a. In vacuum condition, the curve shows a monotonic relationship. In ambient air condition, the curve shows a superlinear decay behavior. The solid line with slopes were obtained by fitting the data with the first order least square method.

3. Absorption and Raman spectroscopy

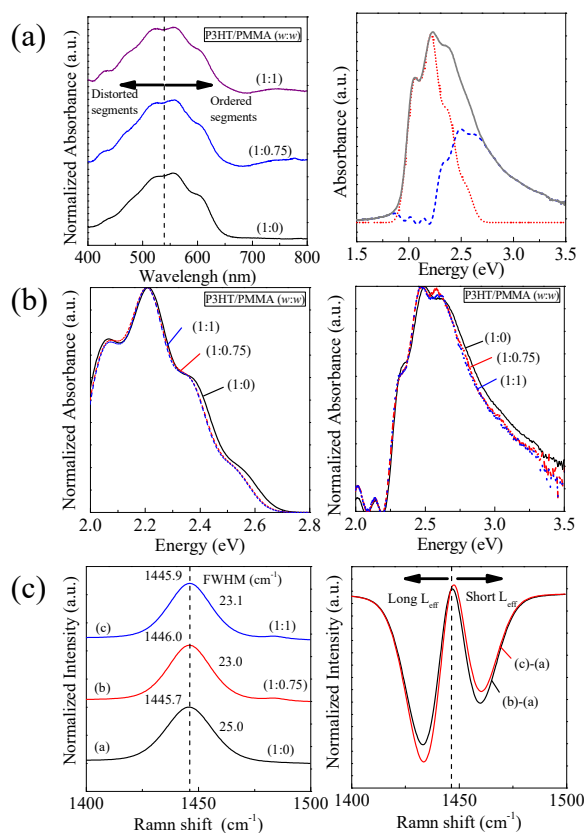


Figure S2. (a) Absorption spectra of the neat P3HT-based and P3HT/PMMA blend-based films (left panel), and (right panel) experimental (solid line) and simulated absorption spectra of the neat P3HT film. The dashed line represents the theoretical fit of crystalline portions, while the dotted line represents the amorphous portions. Comparison of absorption spectra of (b) crystalline (left panel) and amorphous (right panel) portions of P3HT in the neat P3HT-based and P3HT/PMMA blend-based films. Note: The weight ratio of P3HT/PMMA in the blend films is shown. (c) Raman spectra of the neat P3HT (trace a) and P3HT/PMMA blend (trace b and c) films. The weight ratio of P3HT/PMMA in the blend films is shown. Trace (b-a) and (c-a) represent the difference spectra, obtained by subtracting the spectra of (a) from (b) and (c), respectively. The dashed line serve as guideline. Note: The best-fit spectra are used to obtain the difference spectra.

4. In-situ absorption spectroscopy

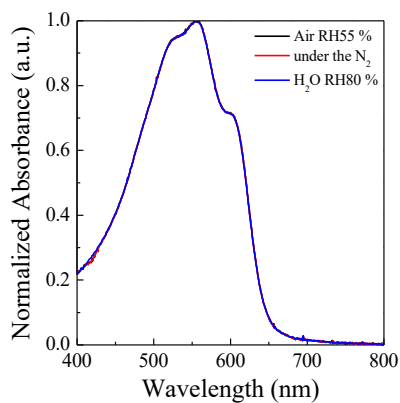


Figure S3. Comparison of normalized absorption spectra of P3HT/PMMA (1:0.75) blend-based films in ambient air with different relative humidity and when exposed to N₂ gas. Note: No significant shape differences of these in-situ absorption spectra were observed when the P3HT/PMMA (1:0.75) blend-based active layer was exposed to N₂ or even in a high humidity condition (above 80% RH). Thus, the ground-state association between the P3HT chains and gases (N₂ gas and/or H₂O molecules) is not sufficiently large to be detected. Therefore, we avoid tentative discussions of the results.

5. A cartoon illustration of structural model

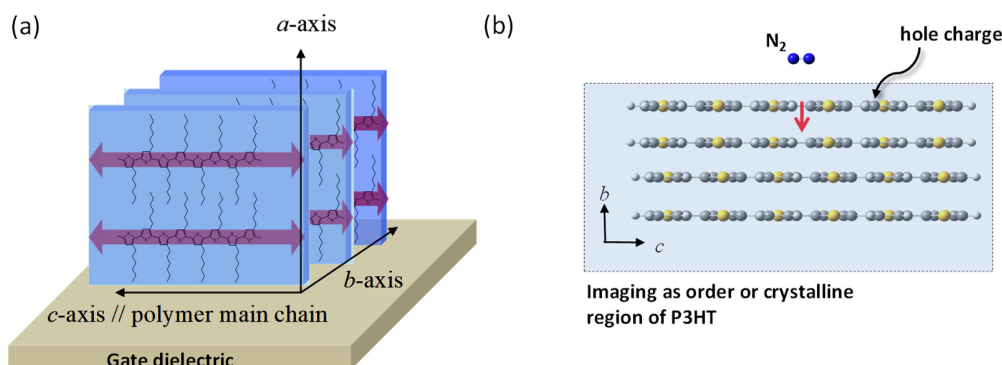


Figure S4. (a) Schematic illustration of edge-on P3HT crystals grown on the gate dielectric surface. (b) A cartoon illustration of the presence of incoming N_2 gas can help P3HT chains maintain the extended conformation. Red arrow indicates the calculated net dipole moment vector of hole charged P3HT- N_2 complex. The dipole moment vector is parallel to the b -axis and toward the P3HT chains. This would help P3HT chains to keep their extended conformation. In other words, there is possible that the dipole-dipole interaction (or induced dipole-dipole interaction) between N_2 gas and P3HT can pull the polymer chains closer together.

Reference

- (s1). F. C. Spano, Modeling disorder in polymer aggregates: the optical spectroscopy of regioregular poly(3-hexylthiophene) thin films, *J. Chem. Phys.*, 2005, **122**, 234701.
- (s2). J. Clark, C. Silva, R. H. Friend, F. C. Spano, Role of intermolecular coupling in the photophysics of disordered organic semiconductors: aggregate emission in regioregular polythiophene, *Phys. Rev. Lett.*, 2007, **98**, 206406.
- (s3). H. L. Cheng, J. W. Lin, F. C. Wu, W. R. She, W. Y. Chou, W. J. Shih, H. S. Sheu, Reformation of conjugated polymer chains toward maximum effective conjugation lengths by quasi-swelling and recrystallization approach, *Soft Matter*, 2011, **7**, 351.