Supporting Information

A. Estimation of the charge density and dipole density

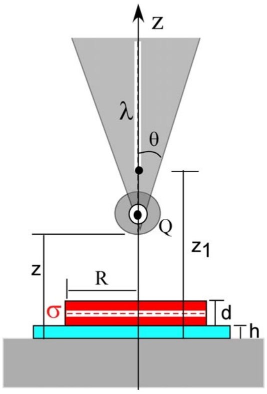

Figure S1. Illustration of the charge distribution model in EFM tip and the pentacene islands with relevant geometric parameters.

The EFM probe is modeled as a sphere attached to the end of a cone[1] and the pentacene islands are modeled as circular discs of charge density σ as illustrated in Figure S1. The electric field and potential at a distance z away from the center of the charge disc are

$$E_z = \frac{\sigma}{2\varepsilon_0}\left(1-\frac{z}{\sqrt{R^2+z^2}}\right) \qquad \text{(S-1)}$$

$$V_z = \frac{\sigma}{2\varepsilon_0}\left(\sqrt{R^2+z^2}-z\right) \qquad \text{(S-2)}$$

The Coulombic forces for the point charge and the line charge are $F_{sphere} = E_z C_{sphere} V_{ac}$ and $F_{cone} = \int_{z_1}^{\infty} E_z \lambda dz = \int_{z_1}^{\infty} -\frac{dV_z}{dz}\lambda dz = V_z(z_1)\lambda$, respectively. The total force is the sum of the two and the forces from image charges.

$$\begin{aligned} F_{EFM} &= F_{cone} + F_{sphere} + F_{cone}^{img} + F_{sphere}^{img} \\ &= V(z_2)\lambda + E(z_1)C_{sphere}V_{ac} - V(z_4)\lambda - E(z_3)C_{sphere}V_{ac} \end{aligned} \qquad \text{(S-3)}$$

with the $C_{sphere} = 4\pi\varepsilon_0\rho\sum_{n=1}^{20}\frac{\sinh(\alpha)}{\sinh(n\alpha)}$ where $\alpha = \ln(1+\sqrt{\frac{z^2}{\rho^2}+\frac{2z}{\rho}}+\frac{z}{\rho})$,

and $\lambda = \frac{4\pi\varepsilon_0 V_{ac}}{\beta}$ where $\beta = \ln(\frac{1+\cos\theta}{1-\cos\theta})$.

Z_1 through Z_4 are adjusted distance parameters:

$z_1 = z+\rho-\frac{1}{2}d-\frac{h}{\varepsilon_h}$;

$z_2 = z\sqrt{1+\tan^2\theta}-\frac{1}{2}d-\frac{h}{\varepsilon_h}$;

$z_3 = z+\rho+\frac{1}{2}d+\frac{h}{\varepsilon_h}$;

$z_2 = z\sqrt{1+\tan^2\theta}+\frac{1}{2}d+\frac{h}{\varepsilon_h}$

Finally, the equation $\frac{\partial F_{EFM}}{\partial z} = \frac{2k|\Delta\nu|}{\nu}$ is numerically solved in Mathematica 4 (Wolfram Research Inc., Champaign, IL). For a 300 nm disc with E-force gradient of 0.0005 N/m, a charge density of 0.0024 C/m^2 is obtained.

If the observed E-field results from electric dipole in the sample, the model above is modified to include spatially separated charges of opposite signs as well as their image charges. For a dipole with the negative charge located at the pentacene/SiO$_2$ interface and the positive end at the middle of the disk, Mathematica calculation yields a 1×10^{18} Debye/m^2 for an E-force gradient of 0.0005 N/m.

B. Calculation of Coulombic repulsion in a dielectric disk with a charge density.

For a uniform charge disc of radius R and total charge Q, the charge density is $\sigma = \frac{Q}{\pi R^2}$. The potential at point (r,θ,z) in a cylindrical coordinate with the origin located at the center of the disc is[2]

$$V(r,z)=\frac{Q}{2\pi\varepsilon\varepsilon_0 R}\int_0^\infty J_0(mr)J_1(mR)e^{-m|z|}\frac{dm}{m} \tag{S-4}$$

in which J_0 and J_1 are Bessel functions.

For the plane of the disc, z=0, thus the potential becomes

$$V(r,0)=\frac{\sigma R}{2\varepsilon\varepsilon_0}\int_0^\infty J_0(mr)J_1(mR)\frac{dm}{m} \tag{S-5}$$

Total work needed to assemble the charge distribution is

$$W=\tfrac{1}{2}\int \sigma\cdot V\cdot da=\tfrac{1}{2}\int_0^{2\pi}\int_0^R \sigma\cdot V(r,0)\cdot r\,d\theta dr \tag{S-6}$$

Combine equations S-5 and S-6, we obtain:

$$W=\frac{\pi\sigma^2 R}{2\varepsilon\varepsilon_0}\int_0^R r\int_0^\infty J_0(mr)J_1(mR)\frac{dm}{m}dr \tag{S-7}$$

For a charge density of $0.012 C/m^2$ in a 300 nm diameter disc, numerical integration using Mathmatica yields a work of 1.5×10^{-14} J.

C. Effect of the bias voltage-induced lateral field.

The AC modulation voltage applied to the tip creates a lateral AC field that may disturb the charges in the sample. The upper limit of the lateral field is estimated considering the field produced by the charge at the probe tip, CV_{ac}, in the pentacene dielectric. The real field has to include the contribution from partial image charges in Si, therefore, be lower than the estimate. For a tip radius of 20 nm at a lift height of 10 nm, the capacitance is 3×10^{-18} F; at a V_{ac} of 3V, it produces a lateral electric field as shown in Figure S2. The maximum lateral field of about 4×10^{7} V/m appears at about 12 nm away from the tip apex. If trap states are spatially confined within 1nm range (> one unit cell dimension), this field is able to push holes out of traps shallower than 40 meV. Previous experiments in UHV suggest that pentacene induces in-gap states at about 0.3-0.5 eV above the pentacene valence band maximum. These gap states are occupied by the photo-induced holes after laser excitation and quick relaxation. Because of the deep energy gap between the traps and the valence band, the lateral AC field induced by the bias voltage does not affect the trapped holes. In principle, the local probing capability of EFM shall be able to tell the spatial confinement of these states. However, in these large scale scans, the physical size of each pixel is typically 12 nm; so the lateral resolution of these EFM images are not equipped to detect the spatial extension of the photo-induced holes.

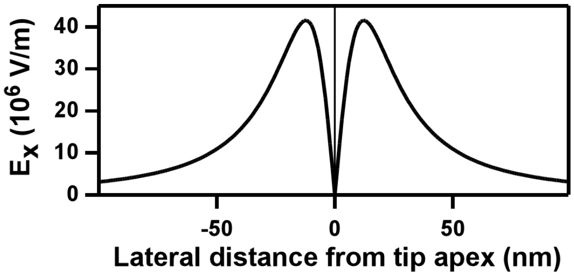

Figure S2. Lateral field caused by the AC modulation voltage on EFM probe. The magnitude of the field is estimated for a 20 nm radius tip lifted 10 nm above the substrate.

D. E-force and capacitive gradients anti-correlation.

The capacitive force gradient above pentacene islands is simultaneously measured using a lock-in amplifier at the double frequency of the AC modulation voltage along with the E-force gradient.[1] The samples experienced Coulomb explosion show an interesting anti-correlation between the E-force gradient signal and the capacitive signal in the region without the particles (Figure S3). The anti-correlation is not in the presence before the illumination.

Pentacene molecules form metastable crystalline domains on SiO_2 surface with a tilt angle higher than that in bulk crystal.[3] We speculate the tilt angle between the long axis of pentacene molecules and the substrate could respond to the strong vertical AC field between the tip and the surface and thus contribute to the dielectric force gradient. Highly charged islands are less likely to be pushed by the same AC field because of the stronger attraction with the image charges in the substrate.

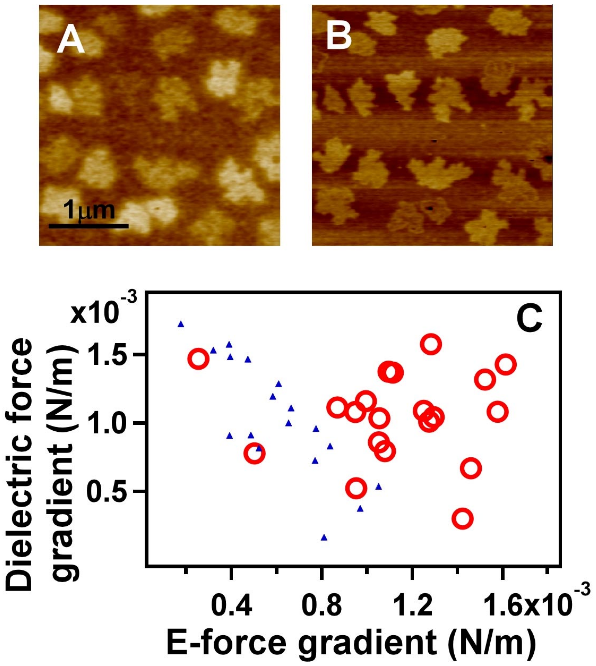

Figure S3. Anti-correlation in E-force and capacitive force in n-type sample after strong illumination. (A) E-force image (B) capacitive image. (C) anti-correlation; red circle: in dark; blue triangle: after strong illumination.

Reference:

S1. Cherniavskaya, O.; Chen, L. W.; Weng, V.; Yuditsky, L.; Brus, L. E. *Journal of Physical Chemistry B* **2003,** 107: 1525-1531.

S2. Durand, E., *electrostatique et magnetostatique*. ed.; Masson et Cie: Paris, 1953

S3. Dimitrakopoulos, C. D.; Brown, A. R.; Pomp, A. *Journal of Applied Physics* **1996,** 80: 2501-2508.