

SUPPORTING INFORMATION

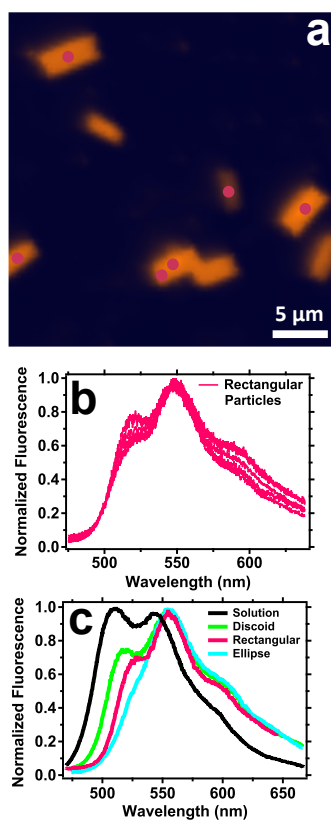


Figure S1: **a)** Total fluorescence image of rectangular particles found in the THF:MeOH solvent combination; intensity scale is from 0 to 55,000 counts. **b)** Emission spectra collected from the individual particles at the points marked in (a). **c)** Comparison of the averaged rectangular, discoid and ellipse particle emission spectra, along with spectra of O6T in THF solution.

The rectangular particle emission spectrum shows a 0-0 vibronic band intensity in between that of the discoid and ellipse particles. The amount of suppression is closer to that of the discoid particles than it is to that of the ellipse particles.

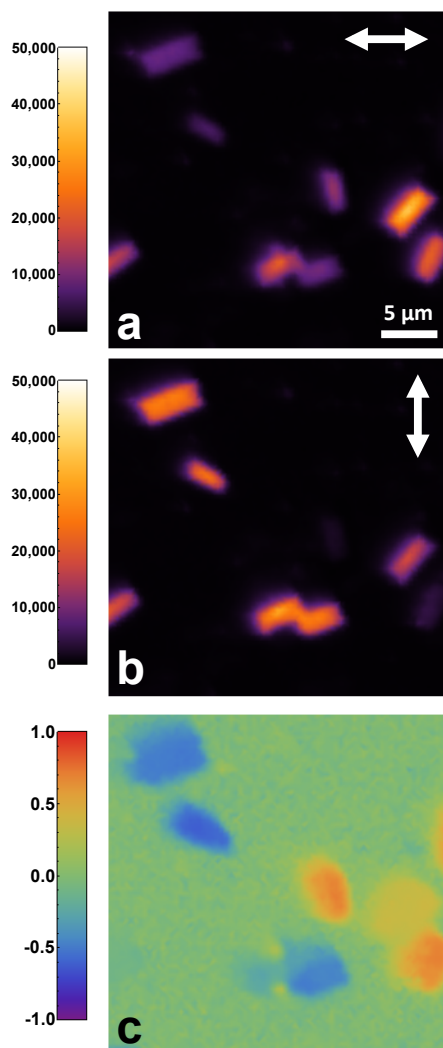


Figure S2: **a)** Horizontally and **b)** vertically polarized fluorescence images, defined in terms of the lab plane. **c)** The fluorescence dichroism (FD) image calculated from the fluorescence images shown in (a) and (b).

The FD of ~ 0.8 for rectangular particles shows that the molecular transition dipole moments within these particles are geometrically well-aligned. Thus the variable energetic disorder, gauged by the 0-0 vibronic band suppression in the different particle shapes, is not a result of geometric molecular order, as the FD values for all particle shapes (discoid, rectangular and ellipse) are similar.

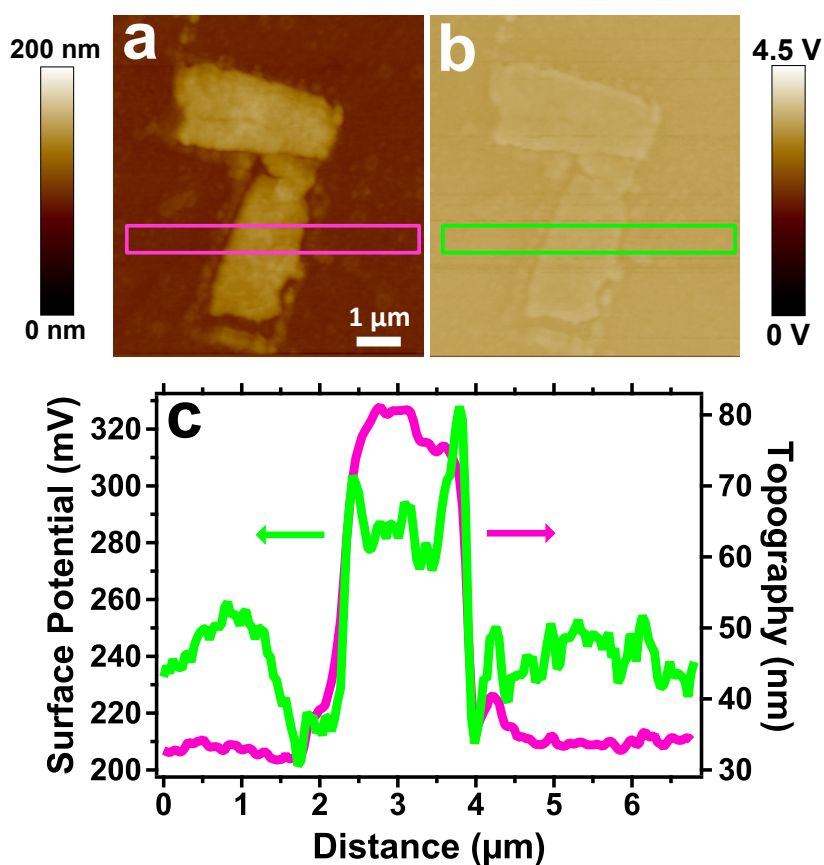


Figure S3: **a)** Topography and **b)** LCP images of the rectangular morphology from the THF:MeOH solvent combination deposited on glass. **c)** The cross-sectional plot from the region of interest marked in images (a) and (b).

The LCP values for the rectangular morphology were found to be 23 ± 14 mV higher than the discoid particles and 50 ± 30 mV lower than ellipse particles. This is where the surface potential of the rectangular particles is expected to fall based on the optical properties, as the 0-0 vibronic band suppression is in between that of discoid and ellipse particles.

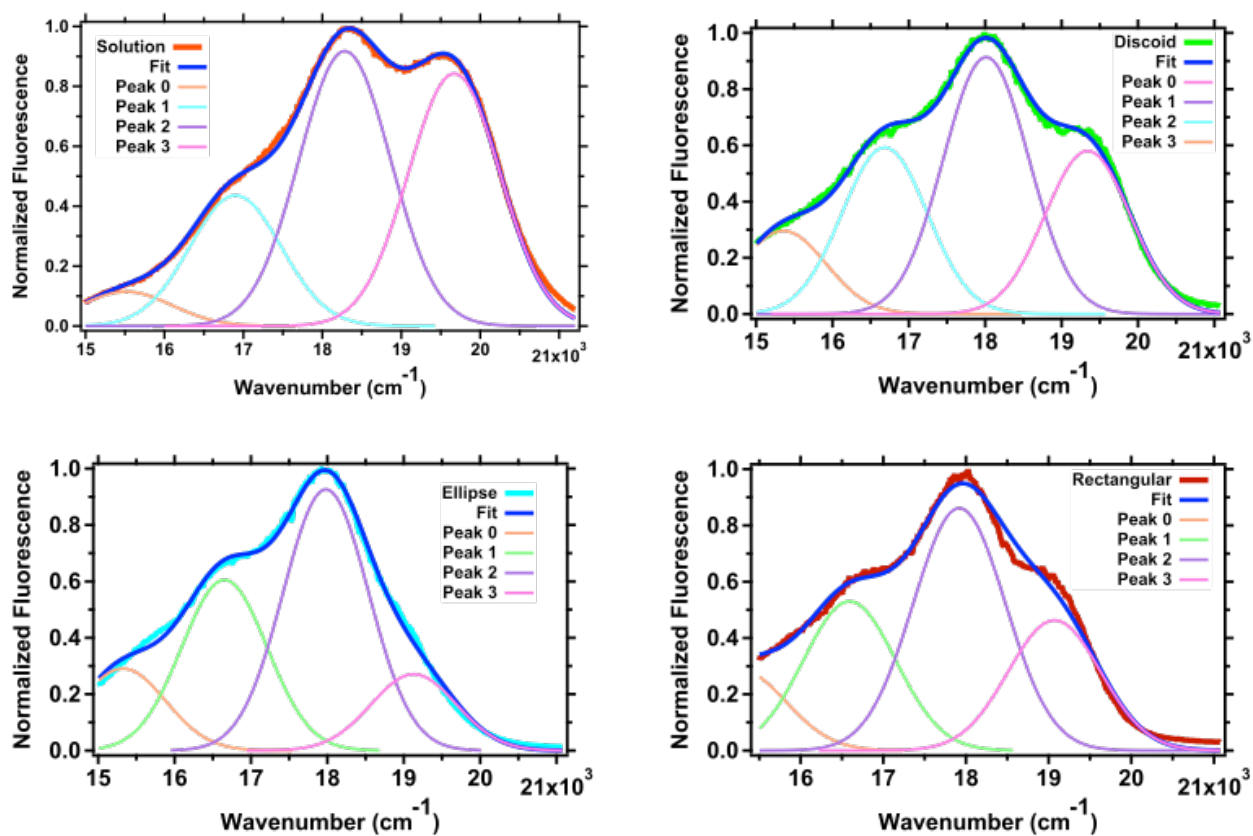


Figure S4: Overlay of each emission spectrum with the fit for the spectrum and the four Gaussian peaks composing each fit. **Top left)** O6T in THF solution. **Top right)** discoid particles. **Bottom left)** ellipse particles. **Bottom right)** rectangular particles.

As mentioned in the main text, to better quantify the extent to which the 0-0 vibronic band is suppressed, all the emission spectra were fit to a series of four Gaussian peaks. In order to remain consistent with a vibronic progression model where each vibrational level is energetically separated by the same amount, the peaks were kept at a constant energy spacing of 1328 cm^{-1} . The only exceptions to this were in the spectra where the 0-0 vibronic band was most suppressed, the ellipse and rectangular particle spectra. For these spectra, the spacing was constant at 1328 cm^{-1} as well, except the spacing between the 0-0 and 0-1 bands was decreased by shifting the 0-0 band to lower energy by 178 cm^{-1} . The solution spectrum in THF and the particle spectra from Figure 2c were all collected with the same instrumental setup so direct comparison between peak intensities are possible without instrument correction. For a consistent model, the widths of the Gaussian peaks were held constant for a particular spectrum. Also, all particle spectra were fit using the same peak width. The full-width-half-max and energetic spacing used to fit the solution spectra were 1365 cm^{-1} and 1385 cm^{-1} , respectively. This was slightly different than the full-width-half-max and energetic spacing used for the particle spectra fits of 1315 cm^{-1} and 1328 cm^{-1} , respectively. These differences are attributed to solvent effects.

Frank Spano has developed models for correlating the spectral properties of weakly coupled aggregates with energetic disorder and electronic coupling parameters.¹⁻⁶ For strongly coupled H-aggregates, the 0-0 vibronic band should be completely suppressed, as it is a symmetrically forbidden transition. However, when energetic disorder is added to the system, the symmetry is broken and the 0-0 vibronic band may be

observed to a varying extent. It is also true that even in the presence of energetic disorder, if the disorder is spatially correlated enough, the 0-0 vibronic band may be completely suppressed as well.³ The character β is the amount of spatial correlation to the energetic disorder of the aggregate and can range from 0 to 1. The energetic disorder, denoted as σ , is estimated from the standard deviation multiplied by $\sqrt{2}$ of the Gaussian peaks used to fit the spectra. It is possible that some motional narrowing occurs in the peak width.² However, it holds that the σ from experimental spectra is the minimal possible value and is used in further calculations. Another parameter used in the models is the free exciton bandwidth (W). For determination of W from these models, the absorbance spectrum of the aggregate is needed.¹ However, due to the large extent of optical scattering off of the particle aggregates deposited on glass and no setup for localized absorbance measurements, absorbance spectra of the different particle shapes was unattainable. Thus, for these aggregates, W could not be calculated from this model. As an approximation of W for these O6T particles, a value of 2000 cm^{-1} was used. This was determined based on the results of previous studies. One study where W for a poly(3-hexylthiophene) (P3HT) film spun from chloroform was found to be $\sim 968\text{ cm}^{-1}$ and another study where a 6 unit oligothiophene molecule was shown to have around double the electronic coupling value of the polymer at the same intermolecular distance of 4 angstroms.^{5, 7}

Since the same value of σ was used to fit the spectra of all the targeted particle shapes, the suppression in the vibronic 0-0 band must be a result of variation in another parameter. As previously mentioned, the other parameters that affect the intensity of the 0-0 vibronic band are β and W.^{2, 3} Here, we estimated the range β could vary between particles to obtain the experimentally determined intensity ratio of 0-0 to 0-1 bands for

each particle shape. For this, the σ from the fit spectra was used along with Equations 1 and 2.³

$$I_{0-0} \approx \frac{(1-\beta)}{(1+\beta)} \frac{\sigma^2}{2e^{-1}W^2} \left(1 - \frac{0.24W}{\omega_0}\right)^2 \quad (1)$$

$$I_{0-1} \approx e^{-1} \left(1 - \frac{0.39W}{\omega_0}\right)^2 \quad (2)$$

I_{0-0} and I_{0-1} are the intensities of the 0-0 and 0-1 vibronic bands, respectively. The Huang-Rhys factor (λ^2) is calculated from the ratio of I_{0-0}/I_{0-1} from the solution (non-interacting molecular) spectrum, with $I_{0-0}/I_{0-1} = 1/\lambda^2$. Equations 1 and 2 apply only when the Huang-Rhys factor is 1; therefore, 1 has been inserted in place of λ^2 in the $e^{-\lambda^2}$ term of both equations shown above. The Huang-Rhys factor for this molecule was determined to be 1.07; for simplicity, the equations were used as written with an assumed value for the Huang-Rhys factor of 1, which was very close to the measured value. With a constant value for W (2000 cm^{-1}), β was determined to be 0.37, 0.44 and 0.65 for discoid, rectangular and ellipse particles, respectively. These β values were then used to calculate the spatial correlation length (ℓ_0), in dimensionless units, of lattice spacing, as determined through the relationship $\ell_0 = -1/\ln(\beta)$.² The spatial correlation lengths were determined to be 1.0, 1.2 and 2.3 for discoid, rectangular and ellipse particles, respectively.

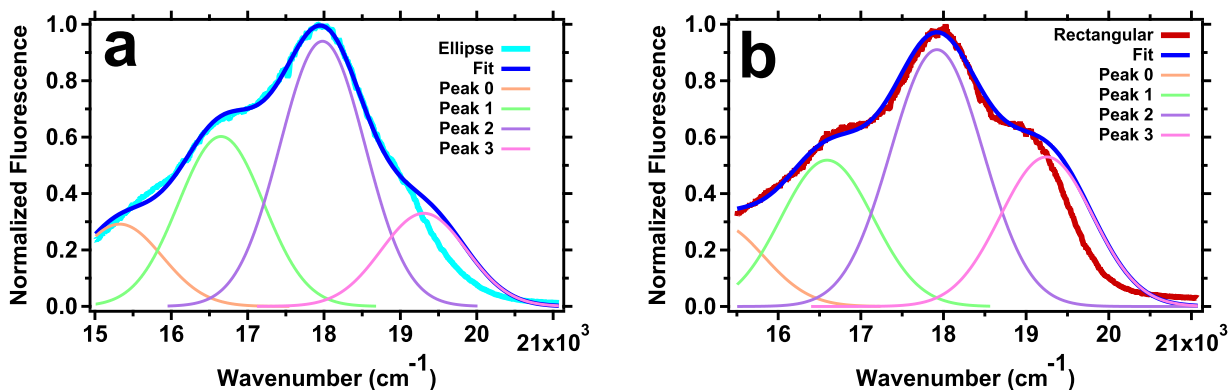


Figure S5: A modified version (from Figure S4) of the fit and four Gaussian peaks composing each fit to the emission spectra of **a)** ellipse and **b)** rectangular particles. These fits purposefully miss the high energy edge of the spectra to exaggerate any possible effect of self-absorption.

As discussed earlier in the original fits shown in Figure S4, the energy spacing between the peaks in the particle spectra was kept at a constant 1328 cm⁻¹. However, the energy spacing between the 0-0 and 0-1 vibronic peaks in the ellipse and rectangular particle spectra fits was decreased by 178 cm⁻¹. This shift in energy spacing could be hypothesized to be the result of self-absorption of the particles, with more self-absorption resulting in decreased 0-0 band intensity. Other reasons disproving self-absorption have been discussed in the main text. However, to test what effect, if any, this shift in energetic spacing would have on the 0-0/0-1 intensity ratio, the ellipse and rectangular particle spectra were refit with a constant energy spacing of 1328 cm⁻¹. These fits are shown in Figure S5; the fit purposefully misses the high energy edge of the spectra to exaggerate

any possible effect from self-absorption. From these modified fits, the 0-0/0-1 intensity ratio was determined to be 0.35 and 0.58 for ellipse and rectangular particles, respectively. These values are very similar to those deduced from the original fits shown in Figure S4: values of 0.29 for ellipse particles and 0.54 for rectangular particles. The discoid particle fit was not modified keeping the 0.64 value for the 0-0/0-1 intensity ratio. This shows that even with constant vibronic energy spacing in the fits of all the particles, the resulting 0-0/0-1 intensity ratios are essentially the same as the original fits discussed in the text, and more importantly the trend in the data is unaffected.

Calculation of surface charge density (σ_{cd}) from KPFM results.

The surface charge density was calculated from the LCP measurement and equation 3.^{8,9}

$$LCP = \frac{\sigma_{cd}d}{\epsilon_r\epsilon_0} \quad (3)$$

where ϵ_r and ϵ_0 are the relative and vacuum permittivity respectively and d is the distance between the two plates of the theoretical capacitor. For this calculation ϵ_r was estimated to be 3 from the value for un-substituted α -sexithiophene.¹⁰ The value for d was estimated to be 1 nm based on the approximate size of the O6T molecule.

Supporting Information References:

1. Spano, F. C., The Spectral Signatures of Frenkel Polarons in H- and J-Aggregates. *Acc. Chem. Res.* **2010**, *43*, 429-439.
2. Spano, F. C., Modeling Disorder in Polymer Aggregates: The Optical Spectroscopy of Regioregular Poly(3-hexylthiophene) Thin Films. *J. Chem. Phys.* **2005**, *122*, 234701.
3. Spano, F. C.; Clark, J.; Silva, C.; Friend, R. H., Determining Exciton Coherence from the Photoluminescence Spectral Line Shape in Poly(3-hexylthiophene) Thin Films. *J. Chem. Phys.* **2009**, *130*, 074904.
4. Spano, F. C.; Yamagata, H., Vibronic Coupling in J-Aggregates and Beyond: A Direct Means of Determining the Exciton Coherence Length from the Photoluminescence Spectrum. *J. Phys. Chem. B* **2011**, *115*, 5133-5143.
5. Clark, J.; Chang, J. F.; Spano, F. C.; Friend, R. H.; Silva, C., Determining Exciton Bandwidth and Film Microstructure in Polythiophene Films Using Linear Absorption Spectroscopy. *Appl. Phys. Lett.* **2009**, *94*, 163306.
6. Clark, J.; Silva, C.; Friend, R. H.; Spano, F. C., Role of Intermolecular Coupling in the Photophysics of Disordered Organic Semiconductors: Aggregate Emission in Regioregular Polythiophene. *Phys. Rev. Lett.* **2007**, *98*, 206406.
7. Gierschner, J.; Huang, Y. S.; Van Averbeke, B.; Cornil, J.; Friend, R. H.; Beljonne, D., Excitonic *Versus* Electronic Couplings in Molecular Assemblies: The Importance of Non-Nearest Neighbor Interactions. *J. Chem. Phys.* **2009**, *130*, 044105.
8. Taylor, D. M.; Bayes, G. F., Calculating the Surface-Potential of Unionized Monolayers. *Phys. Rev. E* **1994**, *49*, 1439-1449.
9. Maldonado, S.; Smith, T. J.; Williams, R. D.; Morin, S.; Barton, E.; Stevenson, K. J., Surface Modification of Indium Tin Oxide Via Electrochemical Reduction of Aryldiazonium Cations. *Langmuir* **2006**, *22*, 2884-2891.
10. Aruta, C.; D'Angelo, P.; Barra, M.; Ausanio, G.; Cassinese, A., Improved Structural Ordering in Sexithiophene Thick Films Grown on Single Crystal Oxide Substrates. *Appl. Phys. A: Mater. Sci. Process* **2009**, *97*, 387-394.