Supporting Information

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SI Text

Universal Single-Chromophore Transitions

Fig. S1 plots the 115 single-chromophore spectra from Fig. 1*B* in a waterfall representation (Fig. S1*A*), and with all spectra normalized and shifted to a common origin (*Inset*). The spectra are coded from red to blue, corresponding to low and high transition energy. Fig. S1 *B–D* show representative single-chromophore transitions from poly[2-methoxy-5-(2′-ethylhexyloxy)-*p*-phenylene vinylene] (MEH-PPV) (1), ladder-type poly(*para*-phenylene) (1), and β-phase polyfluorene (2), shifted along the *x* axis to the same origin. The transition characteristics of single chromophores in these very different materials are universal (1).

Histogram of Single-Chromophore Peak Positions

Fig. S2 plots the histogram of peak positions of the 115 single-chromophore spectra reported in Fig. 1*B*. Note that this histogram is in no way weighted by peak intensity, but simply reports peak occurrence. It is not possible to extrapolate this histogram to the ensemble spectrum of isolated polymer chains, or even to the bulk film, because the histogram is always weighted by the brightest, most stable chromophores. These units may or may not contribute to the majority of the emission in the ensemble. It is worth noting that the histogram appears to resemble a trimodal distribution. Other conjugated polymers such as polyfluorene (2) or MEH-PPV (3) exhibit bimodal distributions.

It is crucial to distinguish between chromophore conformation and overall chain conformation (4, 5). The two may be interrelated but are revealed in different functions. Chromophore conformation controls spectral shape [vibronic coupling and spectral diffusion (6)] and transition energy, whereas chain shape controls the coupling between chromophores (e.g., by energy transfer) (3, 4). In polyfluorene, a bimodal distribution of photoluminescence (PL) peak positions arises due to the fact that the chromophore (and often the entire chain) can exist in twisted or planarized conformation (2, 4). Planarization, referred to as formation of the β-phase, leads to a spectral red shift in emission as well as a narrowing of the peak energy distribution. In MEH-PPV, the peak distribution appears to be bimodal, too (3). The bluer distribution of peaks corresponds to stretched phenylene-vinylene units, as can be resolved by polarization anisotropy measurements, whereas the red distribution arises due to bent chromophores (6). Overall, there are therefore (at least) three distinct chain conformations that can impact the spectroscopy: bending, twisting, and planarization. At present, we do not have compelling evidence to correlate single-chain spectroscopy of poly(3-hexylthiophene) (P3HT) with chain conformation, other than observing that, at room temperature, the most extended units (i.e., the polymer chains with the highest *M* values) appear to correspond to the most red-shifted spectra (Fig. 4*A*, *Inset*). We tentatively propose that the three peaks in the histogram of peak positions correspond to the three conformational species illustrated in Fig. S2: bending, as revealed in scanning tunneling microscopy measurements (7), resulting in high energy transitions; twisting at intermediate energies (6); and planarization at low energies (2). We stress that this tentative assignment remains entirely speculative at the present time.

Random Variations in Single-Chromophore Vibronic Intensity and Structural Relaxation

Fig. 1*D* shows a substantial scatter in vibronic intensity of the single-chromophore PL spectra. This peak ratio is known to vary strongly between different single chromophores (8) due to slight changes in conformation and the resulting modifications in structural relaxation energy. This variation is illustrated for P3HT in Fig. S3*A*. Structural relaxation (the shift between ground and excited-state potential surfaces) controls the intensity of the vibronic sidebands in luminescence as sketched in Fig. S3*B*. The strength of vibronic coupling is not constant from chromophore to chromophore, implying that microscopic models of excitonic coherence cannot necessarily be applied to describe the macroscopic spectrum with an averaged relaxation energy.

Dynamic Disorder in Single Chromophores

Dynamic disorder (i.e., the spectral jitter of single chromophores, also referred to as spectral diffusion) occurs in all single emitters, implying that the measured transition line width exceeds the homogeneous electronic line width. The effect can be particularly pronounced in conjugated polymers (1): it has been shown that it can account for most of the conformation-dependent spectral broadening (>0.1 eV) found in ensemble MEH-PPV (6). Spectral diffusion is clearly seen in single P3HT chromophores, providing unambiguous evidence for the detection of single chromophores (1) and posing important limitations on the concept of the fundamental transition width of single chromophores in models of excitonic coupling. Fig. S4*A* shows example fluorescence traces of single P3HT chromophores as a function of time, exhibiting spectral meandering that will contribute to spectral broadening in the ensemble and bulk film. The implication of these observations is that the longer the single-molecule measurement lasts, the broader the spectrum becomes.

An understanding of spectral broadening mechanisms is crucial to developing models of interchromophoric interactions. Homogeneous line width controls both coherent coupling in aggregates (9) and incoherent FRET (10). Both microscopic coupling mechanisms can strongly impact the ensemble emission spectrum. Single-molecule fluorescence spectroscopy typically provides an upper estimate of homogeneous line width because the transitions will be broadened artificially by spectral meandering during the measurement process. In MEH-PPV, for example, the homogeneous line width is so small (<10 μeV) (11), that FRET relaxation pathways are frozen out at very low temperatures (5), leading to a blue shift in emission at low temperature. There is no obvious reason why the homogeneous line width of chromophores in P3HT should be much broader than those in MEH-PPV. Fig. S4*B* provides two examples of single-chromophore spectra with transition line widths as narrow as 3 meV. Because spectral diffusion occurs, broadening of this transition line is simply an artifact of the measurement: the faster the measurement, the narrower the transition. It is crucial to realize this phenomenon in theoretical descriptions that compute instantaneous couplings through an effective Hamiltonian.

Examples of Single-Molecule Fluorescence Polarization Measurements

The polymer chain conformation is assessed by performing fluorescence polarization modulation spectroscopy. A molecule with a single linear transition dipole will modulate its fluorescence as the plane of excitation polarization is rotated through an angle θ following a cosine-squared law. Deviations from a linear dipole result in a modification of fluorescence modulation following $I(\theta) \propto 1 + M\cos(2\theta)$, where θ is the angle of excitation polarization and M the modulation depth, a value of 1 signifying a linear dipole and 0 an unpolarized absorber. In this terminology, it is also equivalent to

note that M is defined by the ratio of maximum to minimum emission intensities through $M = \frac{I_{max} - I_{min}}{I_{max} + I_{min}}$. To illustrate the data quality, Fig. S5 plots three fluorescence intensity traces, along with fits, for single P3HT chains in PMMA and Zeonex, respectively.

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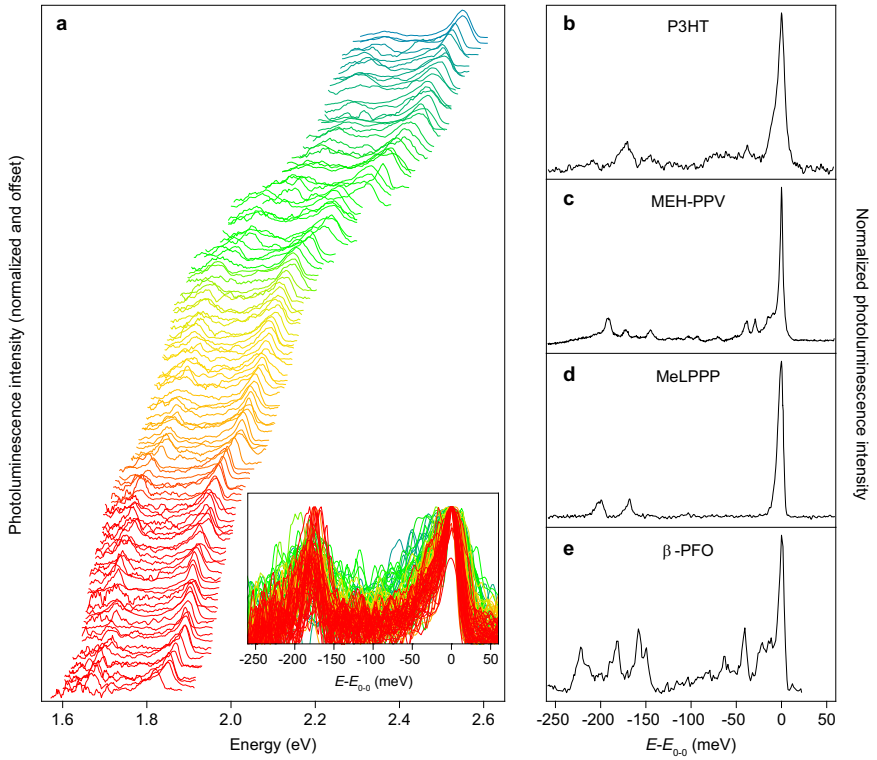

Fig. S1. Universal shape of single-chromophore spectra of P3HT at 4 K. (*A*) Waterfall plot of 115 single spectra, smoothed for clarity and sorted by transition energy. The *Inset* shows the superposition of all spectra, shifted to a common origin. The spectra are color-coded from blue to red according to their transition energy. (*B*–*E*) Representative single-chromophore spectra of P3HT, MEH-PPV, methyl-substituted ladder-type poly(*para*-phenylene) (MeLPPP), and β-phase poly (9,9-dioctylfluorene) (PFO). The spectral characteristics of these different materials are universal, displaying a dominant asymmetric zero-phonon line at the origin and a distinct vibronic progression that is determined by the chemical structure.

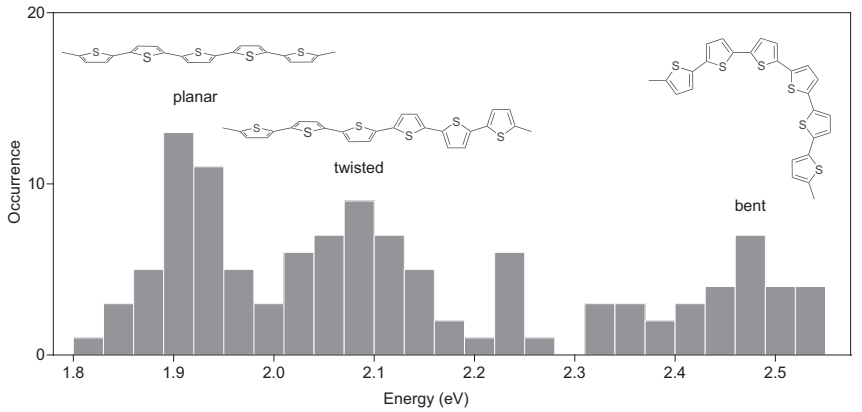

Fig. S2. Histogram of the 0–0 emission peaks of the P3HT single-chromophore spectra shown in Fig. S1. The histogram may be interpreted as being trimodal. In analogy to other conjugated polymer materials, where distinct chromophore conformations have been identified, possible chromophore conformations of P3HT are sketched.

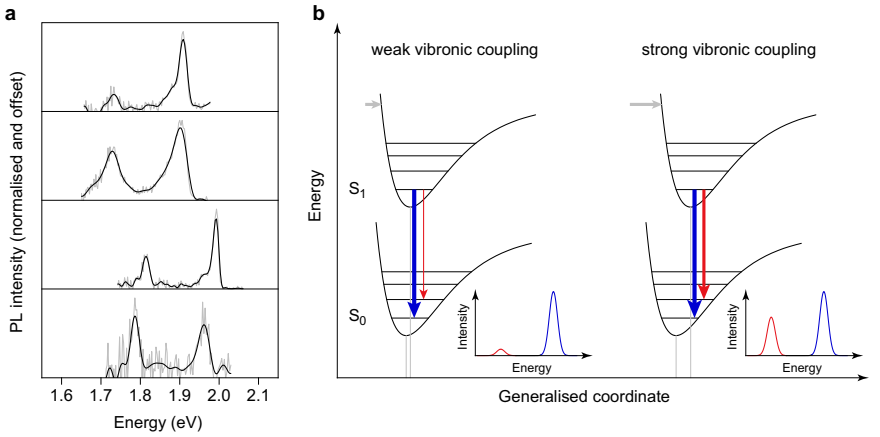

Fig. S3. Variation of the intensity of the vibronic sideband in single-chromophore PL between different chromophores. (*A*) Four spectra showing different ratios of 0–0 and 0–1 bands. The ratio varies randomly by a factor of 4. (*B*) This variation can be rationalized by a simple Franck–Condon diagram in which the structural relaxation energy (gray arrow) differs between chromophores due to slight differences in ground-state conformation.

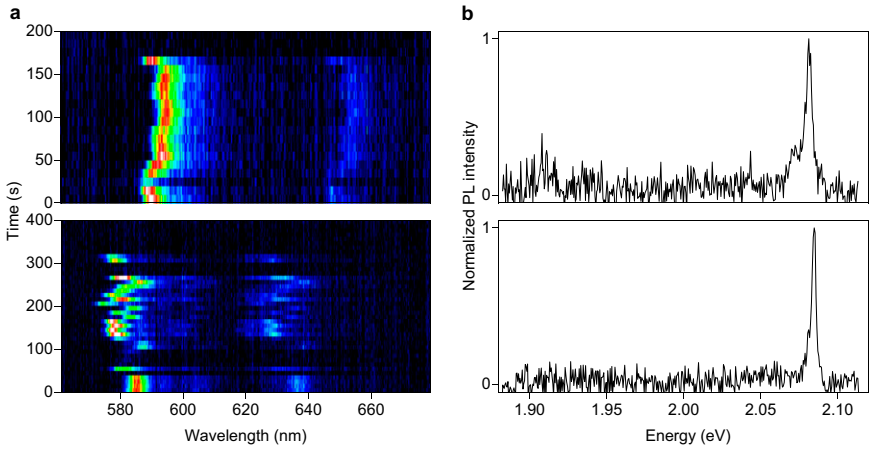

Fig. S4. Influence of random spectral diffusion of single-chromophore emission on spectral line width in two representative chromophores. (*A*) Temporal evolution of the emission. Each spectrum was integrated for 10 s. The spectra drift over 20 meV (*Upper*) and 36 meV (*Lower*). (*B*) A single time slice from the traces. The upper panel exhibits a chromophore of spectral width 5 meV, and the lower panel, a narrower chromophore of width 3 meV.

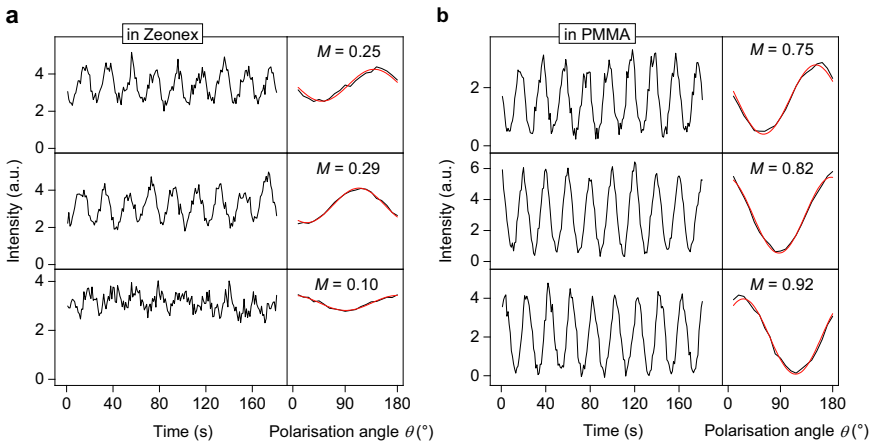

Fig. S5. Example excitation polarization modulation traces of three single P3HT chains at room temperature (*A*) in Zeonex and (*B*) in PMMA. The averaged PL intensity is plotted as a function of polarization angle on the right-hand side of the panels (black line), with a cosine-square fit superimposed (red line).