Supplementary information

Single chain versus single aggregate spectroscopy of conjugated polymers. Where is the border?

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1. GPC data for MEH-PPV

![Graph showing molecular weight distribution function of MEH-PPV](image)

**Figure SI-1.** Molecular weight distribution function of MEH-PPV, determined by gel permeation chromatography (GPC) using chloroform as an eluent and polystyrene as a standard.

2. Fluorescence brightness analysis for MEH-PPV doped PMMA films

\[ F_{\text{ensemble}} = D \sum \frac{\sigma_i^{\text{chr}} \Phi_i I_{ex}^{i}}{h \nu_{ex}} \]  

(SI-1)

where \( D \) – detection efficiency of the microscope, \( \sigma_i^{\text{chr}} \) and \( \Phi_i \) – absorption cross section and fluorescence quantum yield of the chromophore \( i \), and \( I_{ex}^{i} \) – excitation power density (W/cm\(^2\)) for the chromophore \( i \), and \( h \nu_{ex} \) – excitation photon energy. The local
excitation power density $I^e(x,y)$ can be seen as uniform in a the very small area $(x, x+dx; y, y+dy)$ of the sample plane, so we can write:

$$dF_{ensemble}(x,y) = \frac{D}{h\nu_{ex}} d(\sum_i \sigma_i^{chr} \Phi_i I^e_{i}) = \frac{D}{h\nu_{ex}} I^e(x,y) d(\sum_i \sigma_i^{chr} \Phi_i)$$  \hspace{1cm} (SI-2)

where $d(\sum_i \sigma_i^{chr} \Phi_i)$ is the sum of $\sigma_i^{chr} \Phi$ for all chromophores within $(x, x+dx; y, y+dy)$ area. If the sample is uniform, we have:

$$d(\sum_i \sigma_i^{chr} \Phi_i) = \sum_{i\text{over}} \sigma_i^{chr} \Phi_i = \langle \sigma^{chr} \Phi \rangle dN_{chr,indxy} = \langle \sigma^{chr} \Phi \rangle \frac{N_A \cdot C \cdot l \cdot dx dy}{M_{chr}}$$

$$= \langle \sigma^{chr} \Phi \rangle \frac{N_A \cdot C \cdot l \cdot dx dy}{n_{chr}M_{monomer}}$$  \hspace{1cm} (SI-3)

Combining (SI-2) and (SI-3) together and integrating $dF_{ensemble}$ over the whole sample area, we get:

$$F_{ensemble} = \frac{D}{h\nu_{ex}} \int_I^e(x,y) d(\sum_i \sigma_i^{chr} \Phi_i) = \frac{D}{h\nu_{ex}} \langle \sigma^{chr} \Phi \rangle C \cdot l \cdot N_A \int_I^e(x,y) dx dy$$

$$= \frac{D}{h\nu_{ex}} \langle \sigma^{chr} \Phi \rangle C \cdot l \cdot N_A \frac{P}{n_{chr}M_{monomer}}$$  \hspace{1cm} (SI-4)

where $P = \int I^e(x,y) dx dy$, i.e. the total excitation power (W) exerted on the sample.

During the experiments, the parameter $D$, $h\nu_{ex}$, and $l$ are all fixed. Therefore, we have:

$$F_{ensemble} \propto \frac{\langle \sigma^{chr} \Phi \rangle CP}{n_{chr}}$$  \hspace{1cm} (SI-5)

When the mass (g) of MEH-PPV is much less than that of PMMA,

$$C = \frac{\text{Mass}_{MEH-PPV}}{\text{V}} = \frac{\text{Mass}_{MEH-PPV}}{\text{Mass}_{PMMA} / \rho} = \rho C_{mass}$$  \hspace{1cm} (SI-6)

where $\rho$ is the density of PMMA film (ca 1g/cm$^3$), and $C_{mass}$ is the weight-to-weight ratio of MEH-PPV/PMMA.
\[ F_{ensemble} \propto \frac{\langle \sigma_{chr} \Phi \rangle \rho C_{mass} P}{\langle n_{chr} \rangle} \] (SI-6)

density of PMMA is a constant, thus:

\[ \frac{\langle \sigma_{chr} \Phi \rangle}{\langle n_{chr} \rangle} \propto \frac{F_{ensemble}}{C_{mass} P} \] (SI-7)

\[ \frac{\langle \sigma_{chr} \Phi \rangle}{\langle n_{chr} \rangle} \] is the intrinsic property of MEH-PPV. Let us assume for a moment that \( \Phi \) is constant. Then \( \frac{\langle \sigma_{chr} \Phi \rangle}{\langle n_{chr} \rangle} \) is actually just proportional to the absorption of the sample at the excitation wavelength. The absorption spectrum of a pristine MEH-PV film and e.g. low concentration MEH-PPV solution in chromophore possess their maxima at different wavelength, however the shift is much smaller than the width of the spectra. Therefore, \( \frac{\langle \sigma_{chr} \Phi \rangle}{\langle n_{chr} \rangle} \) (or the experimentally measured \( \frac{F_{ensemble}}{C_{mass} P} \)) should stay approximately constant for PMMA films doped with different concentration of MEH-PPV because we excited fluorescence in the middle of the broad absorption band (458 nm). (Figure 1)

3. Examples of 2D polarization plots

![Figure SI-2. Examples of 2D polarization plots for four different conjugated polymer chains. Each plot shows the fluorescence intensity (colour scale) as a function orientation of the excitation polarization plane (x) and the orientation of the analyser (y). Top plots – experimental data. Bottom plots – fitting by the formal model.](image)
See more details in http://www.chemphys.lu.se/research/techniques/polarsms/

and the reference below:

O. Mirzov, R. Bloem, P. R. Hania, D. Thomsson, H. Lin, and I. G. Scheblykin, "2D polarisation single molecule imaging of multichromophoric systems with energy transfer", Small, 2009, 5, 1877; http://dx.doi.org/10.1002/smll.200801168