

## Supplementary information

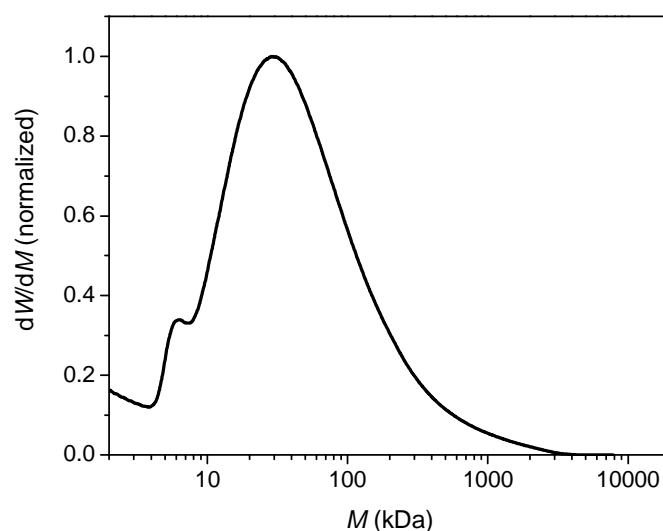
### Single chain versus single aggregate spectroscopy of conjugated polymers. Where is the border?

Hongzhen Lin, Ralph P. Hania, Robert Bloem, Oleg Mirzov, Daniel Thomsson, Ivan G. Scheblykin\*

*Chemical Physics, Lund University, Box 124, 22100, Lund, Sweden*

\* Corresponding author. Email address: ivan.scheblykin@chemphys.lu.se

#### 1. GPC data for MEH-PPV



**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

$F_{\text{ensemble}}$  (photons/s) is a sum of the fluorescence intensities of all the MEH-PPV chromophores excited by the laser:

$$F_{\text{ensemble}} = D \sum \frac{\sigma_i^{\text{chr}} \Phi_i I_i^{\text{ex}}}{h\nu_{\text{ex}}} \quad (\text{SI-1})$$

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  $I_i^{\text{ex}}$  – excitation power density ( $\text{W}/\text{cm}^2$ ) for the chromophore  $i$ , and  $h\nu_{\text{ex}}$  – excitation photon energy. The local

excitation power density  $I^{ex}(x,y)$  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:

$$dF_{ensemble}(x,y) = \frac{D}{h\nu_{ex}} d(\sum \sigma_i^{chr} \Phi_i I_i^{ex}) = \frac{D}{h\nu_{ex}} I^{ex}(x,y) d(\sum \sigma_i^{chr} \Phi_i) \quad (SI-2)$$

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

$$\begin{aligned} d(\sum \sigma_i^{chr} \Phi_i) &= \sum_{over dx dy} \sigma_i^{chr} \Phi_i = \langle \sigma^{chr} \Phi \rangle dN_{chr.in dx dy} = \langle \sigma^{chr} \Phi \rangle \frac{N_A \cdot C \cdot l \cdot dx dy}{\langle M_{chr} \rangle} \\ &= \langle \sigma^{chr} \Phi \rangle \frac{N_A \cdot C \cdot l \cdot dx dy}{\langle n_{chr} \rangle M_{monomer}} \end{aligned} \quad (SI-3)$$

where  $\langle \sigma^{chr} \Phi \rangle$  is the average  $\sigma^{chr} \Phi$  over all the chromophores in the sample,  $dN_{chr.in dx dy}$  is the number of chromophores in the area ( $x, x+dx; y, y+dy$ ),  $N_A$  – Avogadro constant,  $C$  – concentration of MEH-PPV ( $g/cm^3$ ),  $l$  – thickness of the film,  $M_{chr}$  – the molecular weight of a chromophore,  $n_{chr}$  – the number of the polymer monomer units in a chromophore, and  $M_{monomer}$  – the molecular weight of a monomer units.

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

$$\begin{aligned} F_{ensemble} &= \frac{D}{h\nu_{ex}} \int I^{ex}(x,y) d(\sum \sigma_i^{chr} \Phi_i) = \frac{D}{h\nu_{ex}} \frac{\langle \sigma_{chr} \Phi \rangle C \cdot l \cdot N_A}{\langle n_{chr} \rangle M_{monomer}} \int I^{ex}(x,y) dx dy \\ &= \frac{D}{h\nu_{ex}} \frac{\langle \sigma_{chr} \Phi \rangle C \cdot l \cdot N_A}{\langle n_{chr} \rangle M_{monomer}} P \end{aligned} \quad (SI-4)$$

where  $P = \int I^{ex}(x,y) dx dy$ , 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:

$$F_{ensemble} \propto \frac{\langle \sigma_{chr} \Phi \rangle CP}{\langle n_{chr} \rangle} \quad (SI-5)$$

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

$$C = \frac{Mass_{MEH-PPV}}{V} \approx \frac{Mass_{MEH-PPV}}{Mass_{PMMA} / \rho} = \rho C_{mass} \quad (SI-6)$$

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.

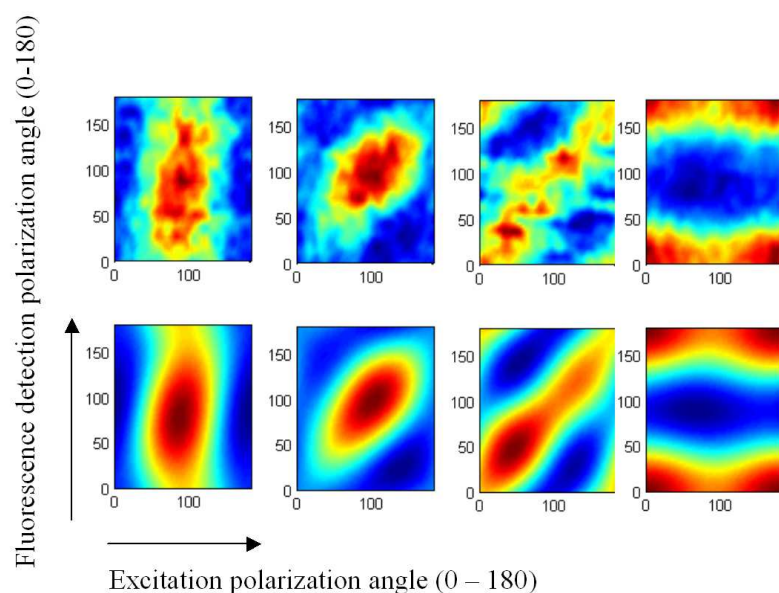
$$F_{ensemble} \propto \frac{\langle \sigma_{chr} \Phi \rangle \rho C_{mass} P}{\langle n_{chr} \rangle} \quad (\text{SI-6})$$

density of PMMA is a constant, thus:

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

$\frac{\langle \sigma_{chr} \Phi \rangle}{\langle n_{chr} \rangle}$  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.

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/sml.200801168>