

Supplementary Materials: Determination of the Best Empiric Method to Quantify the Amplified Spontaneous Emission Threshold in Polymeric Active Waveguides

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1. Determination of the spectral Full Width at Half Maximum

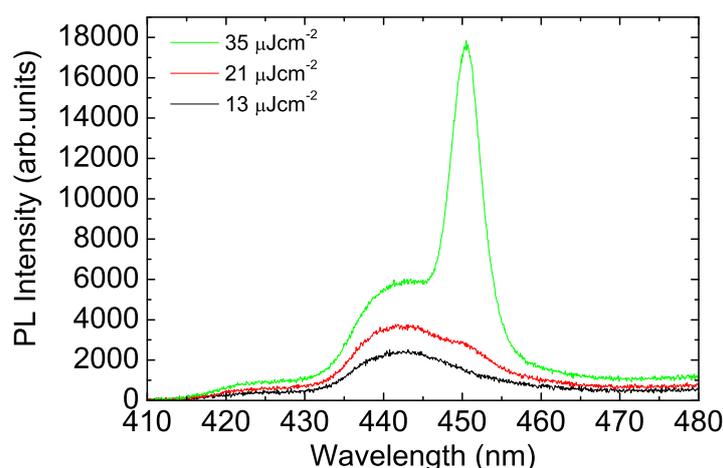


Figure S1. Example of the variation of the peak wavelength with the excitation density for the PFO film.

The FWHM has been determined, at each excitation density, as the spectral interval in which the emission intensity is above 50% of the peak one, detected at the wavelength of maximum emission. In order to obtain the FWHM value we took into account that the ASE band, as typical of materials showing light amplification, is at higher wavelength than the spontaneous emission peak. This result is due to the decrease of self absorption when the wavelength increase, leading to the best compromise between high gain and low losses at a wavelength higher than the spontaneous emission peak one.

At low excitation density, when ASE is not present, the spectral lineshape is independent of the excitation density and the peak wavelength is also constant. When the ASE appears in the spectra the wavelength of maximum emission changes, and the peak intensity has to be detected at the correct peak wavelength. For example, with reference to the PFO spectra shown in Fig. S1, we observe that the spectra at $13 \mu\text{Jcm}^{-2}$ and $21 \mu\text{Jcm}^{-2}$ have a linewidth determined by the 0-1 line one, thus we considered as peak wavelength 443 nm, while the spectrum at $35 \mu\text{Jcm}^{-2}$ is already dominated by ASE, thus we considered as peak wavelength the ASE peak one (about 451 nm).

Considering that the emission spectra of polymers often show the contribution of the 0-0 line and of different vibronic replicas the FWHM below threshold will reflect the linewidth of the peak that generates ASE only if this peak also dominates the spontaneous emission as it is well resolved. Otherwise the FWHM values below the threshold will be affected by the contribution of different peaks.

For the samples investigated in this experiment we observe a well resolved vibronic progression only for PFO, with a spontaneous emission dominated by the 0-1 line, that also gives the ASE peak. In this case our procedure allows to determine the 0-1 FWHM in the whole excitation density range. For the other two samples the vibronic peaks are not resolved, thus leading to higher values of the FWHM at low excitation density. We anyway observe that this effect only affects the FWHM value below the

25 threshold, but it does not modify the FWHM excitation density dependence due to the narrower ASE
26 band appearance, resulting in a FWHM decrease in all the samples.

27 2. Determination of the ASE integrated intensity and of the net gain

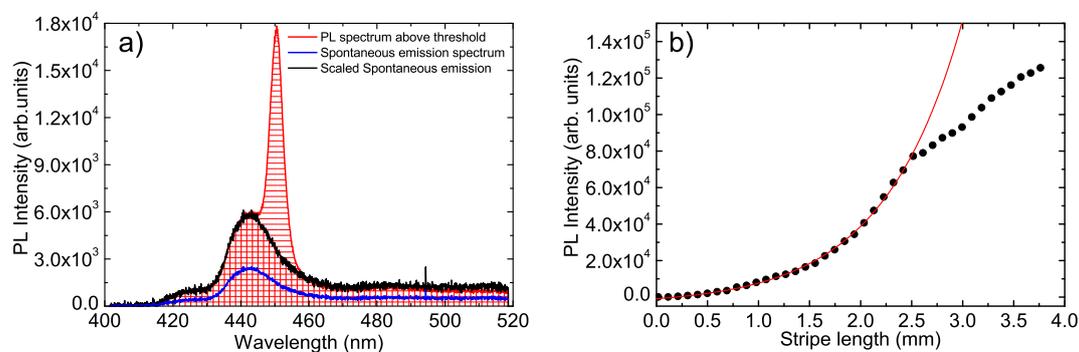


Figure S2. a: Example of the determination of the ASE integrated intensity for the PFO film. The ASE integrated intensity is evidenced by the region with horizontal red line pattern, while the contribution of the spontaneous emission to the total intensity is evidenced by the squared patterned region. b: Intensity increase with the stripe length for the PFO film (dots), the red line is the best fit function with Equation 1.

28 In order to determine the ASE integrated intensity at any given excitation density we plotted
29 the corresponding PL spectrum (see red line in Fig. S2 a) and we initially determined the integrated
30 emission intensity. We then separated the ASE contribution to the total integrated intensity by
31 exploiting the lack of excitation density dependence of the spontaneous emission lineshape. We thus
32 plotted a PL spectrum below the visual ASE threshold (blue line in Fig. S2 a) and we rescaled it in
33 order to match the intensity of the spontaneous emission contribution to the total spectrum (black line
34 in Fig. S2 a). We finally determined the total spontaneous emission intensity by numerical integration
35 of the rescaled spectrum below threshold, and the integrated ASE intensity as difference between the
36 total intensity and the spontaneous emission integrated intensity.

37 The net gain values have been instead determined taking care to exclude in the fitting procedure
38 the data showing effects of gain saturation. For example the data shown in Fig. S2 b, relative to the
39 PFO film, show an almost exponential increase up to a stripe length of 2.5 mm, while a sublinear
40 increase is observed at higher values of the stripe length. In this case only the data up to a stripe length
41 of 2.5 mm have been included in the fitting procedure.

42 3. Film thickness

43 The thickness of the investigated films has been determined by SEM measurements in cross
44 section. The obtained images show (see Fig. S3 a and b) a uniform thickness for the PFO and F8BT
45 films, of about 150 nm and 170 nm, respectively. On the contrary the thickness of the F8BT:rrP3HT film
46 is clearly not uniform, with a lower thickness of about 340 nm in the central part and a progressive
47 increase toward the sample edges up to about 1.25 μm (see Fig. S3 c and d).

48 4. Working time estimate

49 In order to estimate the time required to obtain the threshold value with the different methods
50 we took into account the net time necessary for the measurements, for the data extraction and for the
51 fitting procedures (see Tab. S1).

52 In particular we considered that the visual determination of the threshold simply requires to
53 observe the PL spectra evolution while continuously increasing the excitation density, by running the
54 acquisition CCD in real time. This procedure can be completed in about 1 minute and we typically

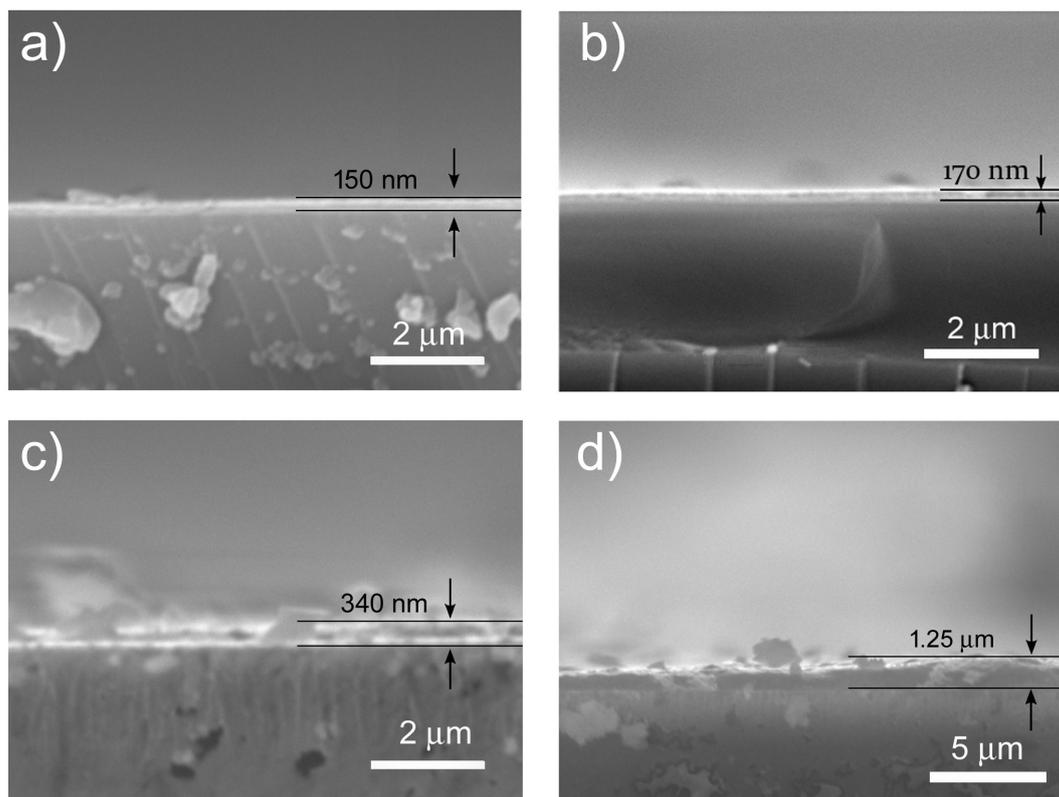


Figure S3. SEM image in cross section of a: the PFO film; b: the F8BT film; c: the central part of the F8BT:rrP3HT film and d: the F8BT:rrP3HT film close to the substrate edge, evidencing the progressive thickness increase.

55 repeat it 4-5 times, in order to safely determine the minimum excitation density that leads to a lineshape
 56 variation. We thus estimated that the determination of the visual threshold can take about 5 minutes.

57 For the other methods we first of all estimated the time to acquire each spectrum in about 1 minute,
 58 considering that the integration time is typically of few seconds, and that every measurement just
 59 needs to add the time for the setting of the acquisition parameter (excitation density in VPI experiments
 60 and stripe length in VSL ones) and for the file saving. The methods based on the VPI methods thus
 61 need about 25 minutes for the measurements. This limited time further evidences that the acquisition
 62 of a high number of spectra has a very limited impact on the total experiment working time and thus,
 63 on the contrary, there are not real reasons to limit the VPI experiment to the collection of a low number
 64 of spectra, as often done in literature.

65 The times for the VLS are instead much higher as we collected, at each excitation density, the PL
 66 spectra at 40 different values of the stripe length and we performed the whole experiment using at
 67 least 5 different values of the excitation density. Thus overall 200 measurements have been done for
 68 each sample.

69 Concerning the time for the data extraction we considered that the FWHM is estimated from the
 70 PL spectra plot. This work has been done with Origin 8 from OriginLab and it simply requires to select
 71 the data column, to press the plot command, to determine the PL peak value and then the FWHM.
 72 Overall, starting from fully imported data, this procedure requires about 1 minute for each value (thus
 73 overall 25 minutes).

74 The times needed for the calculation of the intensity value are instead different for I_{TOT} , I_{ASE}
 75 and I_{peak} . In particular each value of I_{TOT} is obtained by plotting the PL spectrum and numerically
 76 integrating it, requiring about 1 minute. The estimate of I_{ASE} is instead longer, as it requires the
 77 spectrum plotting and integration, but also the rescaling of the spectrum below threshold to match the
 78 spontaneous emission band, its integration and, finally, the subtraction of the two integrated intensities

Table S1. Estimated working time in minutes for the determination of the ASE threshold values for each method.

| Method | Measurements | Data extraction | Best fit | Total |
|---------------|--------------|-----------------|----------|-------|
| Visual | 5 | - | - | 5 |
| I_{TOT} | 25 | 25 | 20 | 70 |
| I_{ASE} | 25 | 60 | 20 | 105 |
| I_{peak} | 25 | 5 | 20 | 50 |
| $FWHM_{nar}$ | 25 | 25 | 10 | 60 |
| $FWHM_{cros}$ | 25 | 25 | 20 | 70 |
| $FWHM/2$ | 25 | 25 | 20 | 70 |
| $FWHM_{ave}$ | 25 | 25 | 30 | 80 |
| Gain | 200 | 50 | 50 | 300 |

79 to obtain the integrated ASE intensity. Overall this procedure can be completed in a bit more than 2
80 minutes.

81 On the contrary the extraction of the I_{peak} value is much faster, as it simply requires to copy the
82 intensity value at the ASE peak wavelength for each spectrum (we estimated about 10 seconds).

83 A similar assumption was made for the time needed to have the PL intensity at a given wavelength
84 and stripe length in the VSL experiment.

85 Furthermore, we assumed that each best fit requires about 10 minutes.

86 We observe that the estimated time reported in the table for the VLS method corresponds to the
87 determination of the net gain dependence on the excitation density at a single wavelength. In our
88 experiment we determined the whole net gain spectrum by repeating the procedure for 75 different
89 wavelength, thus increasing of 75 times the real working time.

90 Finally, we highlight that the total times in the last column of the table represent only a lower
91 limit of the overall time taken by the experiment.