# Supporting information for:

# Tuning photophysical properties of semiconducting polymer nanoparticles for improved photocatalytic activity.

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### **DLS** measurements:

In DLS, correlograms are obtained that are described by correlation functions. These functions give information about the fluctuations in the intensity of scattered light, which is directly related to the diffusion coefficients, and then to the size, and have the following expression<sup>1</sup>:

$$g^{(2)}(\tau) = B + b [g^{(1)}(\tau)]^2$$
 (SI.1)

This equation includes baseline B, and the intersection of the correlation function b, related to the system optics and detector alignment, and  $g^{(1)}(\tau)$ , which is defined as the correlation function of the electric field. Figure S1 shows the correlograms obtained for different sets of measurements on miniemulsion NPs and flash NPs.

The correlation functions can be used to determine the particle size. There are several approaches. One approach is the cumulant analysis, which considers that  $Ln(g^{(2)}(\tau) - B)$  can be approached as a power series of  $\tau$ :

$$Ln(g^{(2)}(\tau) - B) \approx \mu_0 + \mu_1 \tau + \mu_2 \tau^2 + \dots$$
(SI.2)

In the cumulant analysis, the coefficient  $\mu_1$  can be related to the effective diffusion coefficient  $(D_{\text{eff}})^2$  by

$$D_{eff} = \frac{\mu_1}{2q^2} \tag{SI.3}$$

Where q is the modulus of the scattering vector. The coefficient  $\mu_2$  describes the deviation of the particle population from a monodisperse distribution (polydispersity).

 $D_{eff}$  can be directly related to the hydrodynamic radius  $R_{\rm H}$  of the particles, by the Stokes-Einstein relationship:  $^3$ 

$$D_{eff} = \frac{k_B T}{6\pi\eta R_H} \tag{SI.4}$$

where  $k_B$  is Boltzmann's constant, T is the temperature,  $\eta$  is the viscosity and  $D_{eff}$  is the diffusion coefficient. Polydispersity index can be obtained as:

$$Q = \frac{\mu_2}{{\mu_1}^2}$$
(SI.5)

However, from a physical point of view, it is more appropriate to obtain the numerical average of the size distribution ( $R_n$ ), since it can be compared with the values obtained by alternative experimental techniques such as AFM. Assuming a log normal distribution of sizes, there is a simple relationship between the numerical average and the polydispersity factor, Q, given by the expression:<sup>4</sup>

$$R_n = \frac{R_h}{\left(1+Q\right)^5}$$

(SI.6)



**Figure SI.1.** DLS correlograms obtained from NPs suspensions: Miniemulsion nanoparticles (blue colors) and Flash nanoparticles (red colors).

#### Methylene Blue Absorbance coefficient

100 mL of a 15 mg/L solution of MB was prepared. The UV-Vis absorbance of this solution was obtained using a 0.5 cm optical path quartz couvette. From this initial solution, different dilutions were performed to obtain MB solutions with different known concentrations. UV-Vis spectra were obtained. The value of the absorbance at the main MB band (<del>634</del>-<u>664</u> nm) is plotted against the concentration. From the slope of the linear fit, using the Lambert Beer equation (eq. S7), the absorbance coefficient is obtained.



Optical path: 0.5 cm



**Figure SI.2.** Calibration curve to obtain MB absorbance coefficient. The value of the measured absorbance at  $\lambda = 634$ -664 nm is presented against the concentration. Linear fit is presented as a red line.

$$A = \varepsilon_{64} \cdot c \cdot l \tag{SI.7}$$

From that fitting, a value of  $\epsilon_{6\underline{6}\underline{3}4}$  = 0.194 mg^-1 L cm^-1

#### X ray scattering analysis

To deconvolute the WAXS curves in terms of amorphous and semicrystalline contributions, the methodology followed was inspired by reference <sup>5</sup> and it is described here. The experimental results were fitted with simulated curves composed of an amorphous contribution whose shape has two broad maxima, as it has been revealed by X ray patterns of a melted P3HT <sup>6</sup> and the Bragg peaks corresponding to the reflections associated with a monoclinic crystalline phase according to the equation:

$$q = 2\pi \sqrt{\frac{\frac{h^2}{a^2} + \frac{k^2}{b^2} \cos}{(\sin \gamma)^2} + \frac{l^2}{c^2}}$$
 S.8

Where  $h_{k}$  and l are the Miller indexes and a, b, c and  $\gamma$  are the dimensions of the unit cell and the angle between the b and c axes.

Initially, an amorphous halo described by two Gaussians located approximately at q=5.55 nm<sup>-1</sup> and 14.8 nm<sup>-1</sup> is selected to fit the regions where no crystalline peaks are expected. The shape of the amorphous halo is inspired by that obtained from previous results on molten P3HT<sup>6</sup>.

In an initial step, the region from 3.34 to 8.18 nm<sup>-1</sup> is fitted to obtain the relevant parameters corresponding to the *100*, *200* and amorphous halo. The 100 and 200 reflections are described by Lorentzian functions with fitting parameters being their center, their width and their area. The center positions of the Lorentzian functions are related to the lattice parameter *a* and the angle of the monoclinic cell  $\gamma$ .

Once *a* and  $\gamma$  are obtained, they are fixed and the whole measured range from 3.34 nm<sup>-1</sup> to 21.5 nm<sup>-1</sup> is fitted considering the sum of Lorentzian functions to describe the reflections were-, (300), (111), (211), (020), (120), (012) (plus the fixed peaks (100),(200) and amorphous halo at 5.55 nm<sup>-1</sup> previously fitted). The position of each Lorentzian function is related to the lattice parameters *b* and *c* that are obtained from the fittings and on *a* and  $\gamma$ , previously obtained.

From this protocol, the crystallite size, the degree of crystallinity and the unit cell volume are obtained. To obtain the crystalline size, the Scherrer equation is used (eq. SI.11).<sup>7</sup> The degree of crystallinity,  $X_c$ , is calculated as  $A_c/(A_c+A_{am})$ , where  $A_c$  and  $A_{am}$  are the areas below the crystalline reflections and the amorphous contribution, respectively. Finally, the unit cell volume is calculated as  $V=a\cdot b\cdot c\cdot sin(\gamma)$ .

$$D = \frac{K\lambda}{\beta\cos\theta}$$
SI.9

Where K is a dimensionless factor close to 1,  $\lambda$  is the wavelength,  $\beta$  is the width of the peak at half intensity and  $\theta$  is the scattering angle.

The whole set of obtained results is presented in table SI.3

**Table SI.1**: Unit cell parameters and crystallite size obtained from the fittings of the diffractograms to eq. S10 and S.11

	<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)	γ ? <b>9</b> ?	V(nm <sup>3</sup> )	Xc	D <sub>100</sub> (nm)	D <sub>020</sub> (nm)
Miniemulsion	1.66	0.76	0.77	88.0	<u>1.000.97</u>	0.77	19.6	13.0
Flash	1.68	0.77	0.79	88.9	<del>0.97<u>1.00</u></del>	0.44	13.6	18.0



**Figure SI.3:** UV Vis spectra from water dispersion of nanoparticles prepared by flash (a) and from miniemulsion (b). Continuous lines correspond to the best fit to a Frank-Condon fit, as described below.

The absorption spectra can be described by the modified Frank–Condon approximation, which takes into account the effect of crystalline aggregates on the relative vibronic intensities

$$A \propto \sum_{m=0}^{\infty} \left(\frac{e^{-S}S^m}{m!}\right) \left(1 - \frac{We^{-S}}{2E_p}G_m\right)^2 \Gamma(\hbar\omega - E_{0-0} - mE_p, \sigma_m)$$
Eq. SI.10

In eq. SI9. *m* denotes the vibrational level, and  $G_m$  depends on *m* as:  $G_m = \sum_{n \ (\neq m)} S^n/n!(n-m)$  where the sum is over the vibrational quantum number n, and S is the

 $n \ (\neq m)$  where the sum is over the vibrational quantum number n, and S is the Huang Rhys factor, W is the bandwidth,  $E_{0.0}$  is the energy of the 0-0 vibronic transition and  $E_p$  takes a value of 0.18 eV and is the phonon energy of the main oscillator coupled to the electronic transition. For each vibronic transition, we have used a Gaussian line shape  $\Gamma$ , with specific width  $\sigma_n$  following Clark et al. <sup>8</sup>. The absorption fit also takes into account the amorphous component, which is obtained from the absorption of the solved polymer. In this way, the absorption from the NPs dispersion is fitted considering a linear combination of the amorphous absorption and of the aggregate absorption, represented by equation S.9

The fit parameters for both types of NPs are presented in table SI.1. and table SI.2

	E <sub>0</sub>	W	σ1 (eV)	σ <sub>2</sub> (eV)	<b>σ</b> <sub>3</sub> (eV)	σ <sub>4</sub> (eV)
	(eV)	(meV)				
Miniemulsion	2.03	44	6.43·10 <sup>-2</sup>	8.37.10-2	9.16.10-2	1.15.10-1
	±	±	±	±	±	±
	0.01	3	0.02.10-2	0.03.10-2	0.06.10-2	$0.01 \cdot 10^{-1}$
Flash	2.05	341	6.64·10 <sup>-2</sup>	9.21·10 <sup>-2</sup>	1.03.10-1	1.20.10-1
	±	±	±	±	±	±
	0.01	2	0.02.10-2	0.01.10-2	$0.01 \cdot 10^{-1}$	$0.01 \cdot 10^{-1}$

**Table SI.2**: Parameters obtained from fitting the aggregate part of the UV-Vis absorbances to eq. SI.9.

Table SI.3: Amorphous and aggregate contributions to the UV-Vis spectra

	Amorphous	Aggregate	Others (%)	
	fraction	component		
	(%)	(%)		
Miniemulsion	24.8	72.8	2.4	
Flash	36.8	59.8	3.4	

#### TauC Plot:

The Tauc plot method is a technique commonly used in solid-state physics to determine the band gap of semiconductor materials from their optical absorption spectra. This fitting is based on the relationship between the absorption coefficient of the material and the energy of the incident photons and allows the band gap value to be estimated indirectly.

The band gap ( $E_g$ ) is the minimum energy required for an electron to pass from the valence band to the conduction band. According to the semiconductor theory, the relationship between the absorption coefficient ( $\alpha$ ) and the photon energy (hv) is expressed by the following equation:

$$(\alpha h\nu)^{n} = A (h\nu - E_{g})$$
(SI.8)

#### $2.303 \cdot A$

where alpha is the absorption coefficient ( $\alpha = d$ , being A absorption and d the thickness of the sample), h is the Planck constant in eV, v is the light frequency, A is a material-dependent constant, and n is a number that depends on the type of electronic transition (n=2 for allowed indirect transitions and n=1/2 for allowed direct transitions).

To obtain  ${\rm E}_{\rm g}$  from this equation, we assume that  $\alpha$  is directly proportional to absorption and hc

calculate the photon energy in eV (hv =  $\lambda$ ) and (Ahv)<sup>n</sup>, using a value of n=2 for the type of transitions presented by P3HT. We plot (Ahv)<sup>2</sup> as a function of hv. From this representation, the linear region of the curve obtained is identified, and a linear fit is performed to extrapolate to the intersection of the hv axis. The energy value at this intersection corresponds to E<sub>g</sub>.

The linear part of the Tauc plot indicates the region where the absorption is dominated by electronic transitions involving the creation of electron-hole pairs. The intersection of this line with the energy axis represents the minimum energy required to excite an electron from the valence band to the conduction band.



**Figure SI.4.** Tauc plot for both types of NPs; Miniemulsion NPs (blue) and Flash NPs (red).

## **FLIM Fits**



**Figure SI.5:** Details on the fitting of the FLIM decays for both types of NPs. In the residuals plot, the blue represents the contribution to the negative log likelihood (always positive) used for optimization. The orange residuals are standard least squares residuals used to visualize positive and negative deviations between the data and model.

Flash NPs					
Name	value	standard error	relative error		
tau_1	0.013	0.002	(17.96%)		
amp_1	2.83	1.845	(65.16%)		
tau_2	0.095	0.004	(4.41%)		
amp_2	0.085	0.005	(5.55%)		
tau_3	0.255	0.008	(3.09%)		
amp_3	0.020	0.002	(8.66%)		
tau_4	0.959	0.070	(7.25%)		
amp_4	2.751e-04	5.861e-05	(21.30%)		
Bck	1.140	0.032	(2.78%)		
Shift	5.620	0.126	(2.24%)		

Table SI.4. Fitting parameters of the FLIM experiments for flash NPs.

Miniemulsion NPs						
Name	value	standard error	relative error			
tau_1	0.007	6.114e-04	(8.95%)			
amp_1	107.027	58.700	(54.85%)			
tau_2	0.072	0.005	(7.18%)			
amp_2	0.108	0.012	(11.32%)			
tau_3	0.221	0.018	(8.05%)			
amp_3	0.009	0.002	(22.98%)			
tau_4	0.899	0.127	(14.10%)			
amp_4	1.431e-04	5.579e-05	(39.00%)			
Bck	1.194	0.0347	(2.91%)			
Shift	2.896	0.0814	(2.81%)			

Table SI.5. Fitting parameters of the FLIM experiments for miniemulsion NPs.

# **LC-MS Results**



**Figure SI.6.** LC-MS profiles obtained for the initial MB solution and for the MB solution, MB with flash NPs and MB with miniemulsion NPs after 4 h of lamp irradiation.



Figure SI.7. Chemical formulas of MB and the intermediate products observed in LC-MS analysis

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