Supporting Information

# Mechanically Induced Conformation Change, Fluorescence Modulation and Mechanically Assisted Photodegradation in Single Nanoparticles of the Conjugated Polymer Poly(9,9-dioctylfluorene)

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**Contents**

*Numerical simulation of β-phase segment orientation inside the PFO NPs*

β-phase is an ordered and straight conformation segment and is often observed in bulk films after annealing by thermal treatment or solvent vapor. Therefore, it is an interesting question how is β-phase incorporated and oriented in PFO NPs. To reveal this, we measured modulation depth of fluorescence polarization traces on individual PFO NPs without applying force. Although β-phase is three-dimensionally oriented in the PFO NPs, this orientation can be observed only projected into the two dimensions of the sample plane because PFO NPs are much smaller than diffraction limit of light and the emitting components cannot be distinguished. Therefore, we performed numerical simulation of polarization modulation depth to reveal the angles between individual β-phase segments within 1 NP. The projected angle in the sample plane will be changed by 3-dimensional orientation change (rotation). It can increase or decrease depending on the direction of rotation. In the numerical simulation, we started with two β-phase segments but found out that a minimum of three β-phase segments are required to reproduce the results. The angle between molecules 1 and 2 (θ), the angle between molecules 1 and 3 (φ), the angle between a common plane formed by molecules 1 and 2 and molecule 3 (χ) were decided and rotated around x and y axis in random steps. For each step modulation depth $M_F$ was calculated as $(I_{max} - I_{min})/(I_{max} + I_{min})$. This process was repeated for 10000 steps and a histogram of $M_F$ was constructed. The combination of the angles (θ, φ, χ) which resulted in best reproduced experimental histogram of $M$ was (29º, 9º, 63º). The relatively small values of the angles θ and φ cause a degree of orientation of the β-phase segments in the PFO NPs.

The numerical simulations of the absorption (excitation) polarization anisotropy were carried out in a similar way, using three effective glass-phase segments to reproduce the distribution of the absorption modulation depth $M_A$. The results shown in Fig. S1 confirm the random nature of the glass phase, with the angles (θ, φ, χ) of (106º, 72º, 26º).

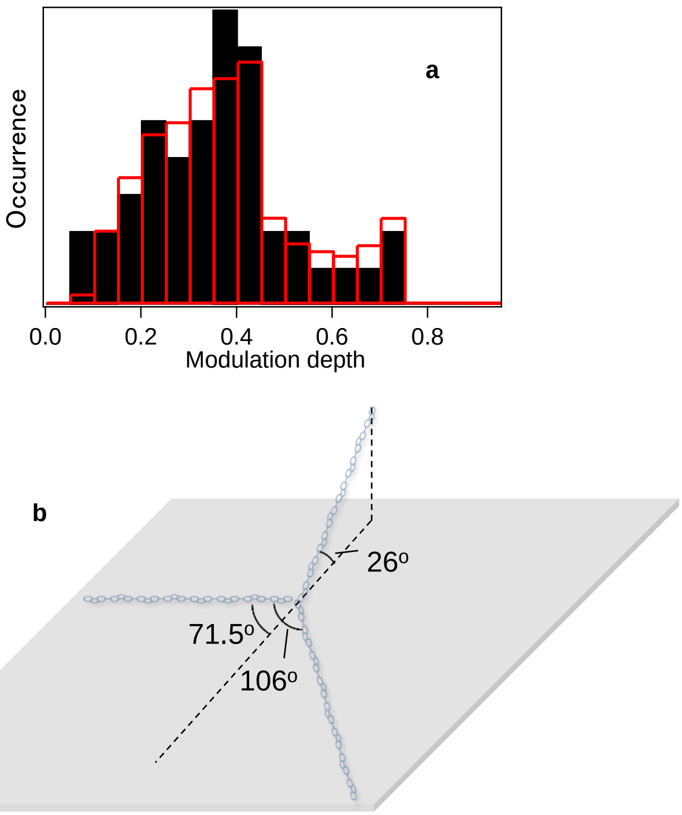


**Figure S1**. a) Measured (full black bars, 45 NPs) and simulated (open red bars, 50,000 data points) modulation depth of absorption (excitation) polarization traces; b) An example of spatial arrangement of three glass-phase segments that represent the overall measured modulation depth distribution in a).

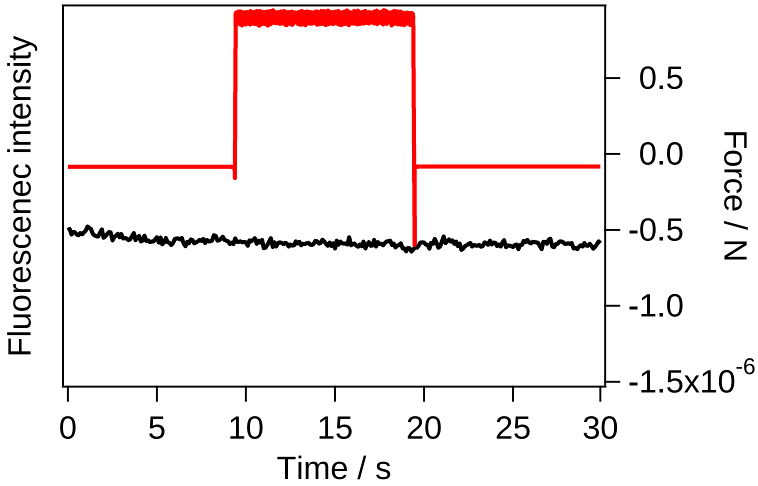


**Figure S2.** Force curve (red) and simultaneously measured fluorescence intensity (black) from a single fluorescent bead Envy Green.

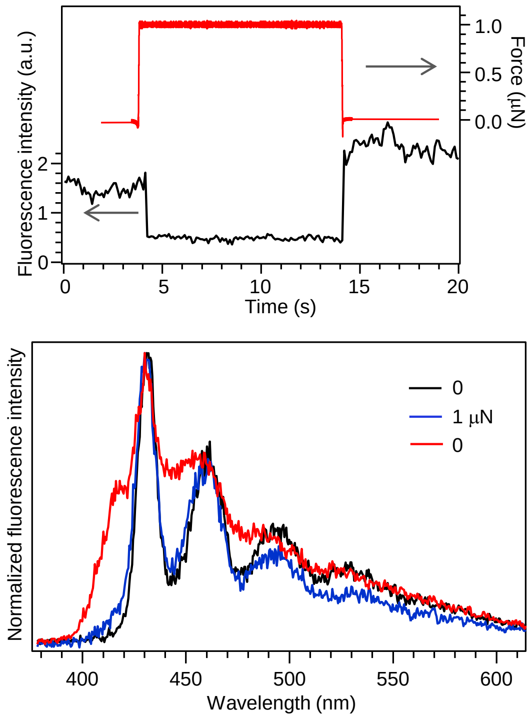


**Figure S3**. Top: Force curve (red) and simultaneously measured fluorescence intensity (black) from a single PFO nanoparticle; Bottom: Fluorescence spectra taken before (black), during (blue) and after (red) applying the force.

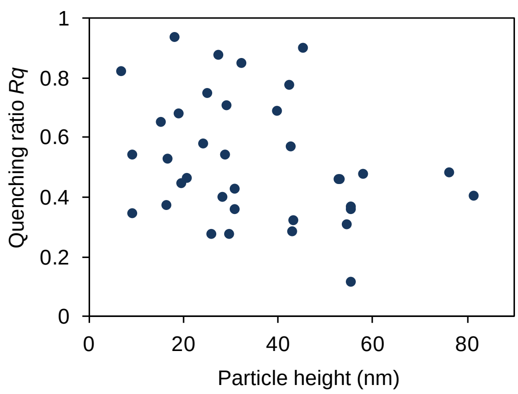


**Figure S4.** Quenching ratio *Rq* as a function of the nanoparticle height measured by AFM.

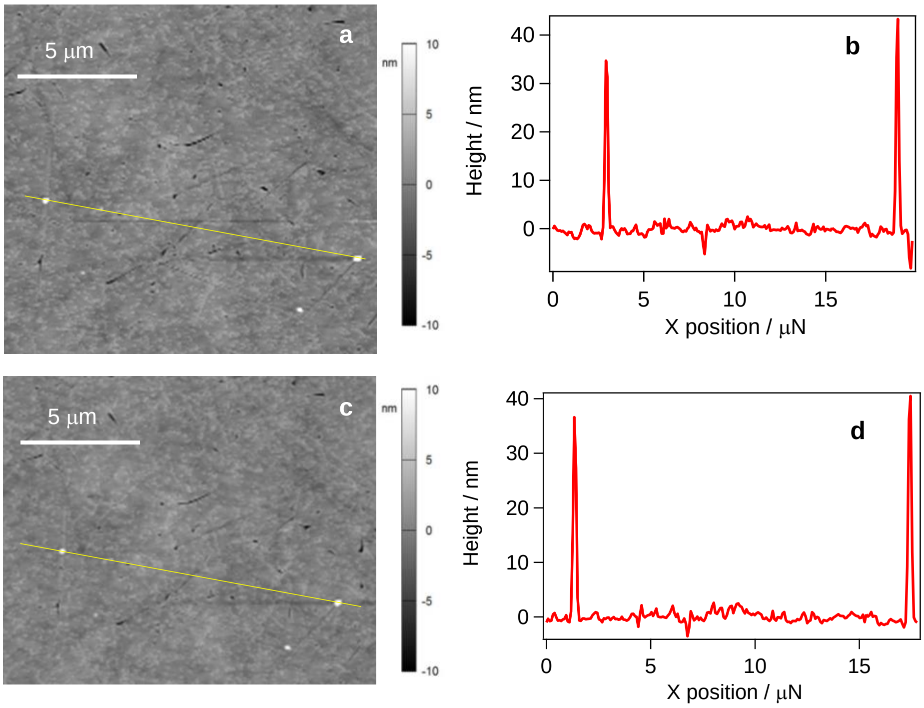


**Figure S5**. AFM images (a, c) of 3 NPs before (a) and after (b) applying the force of 5 µN. The profiles of the top two NPs are shown in b) before and in d) after applying the force.

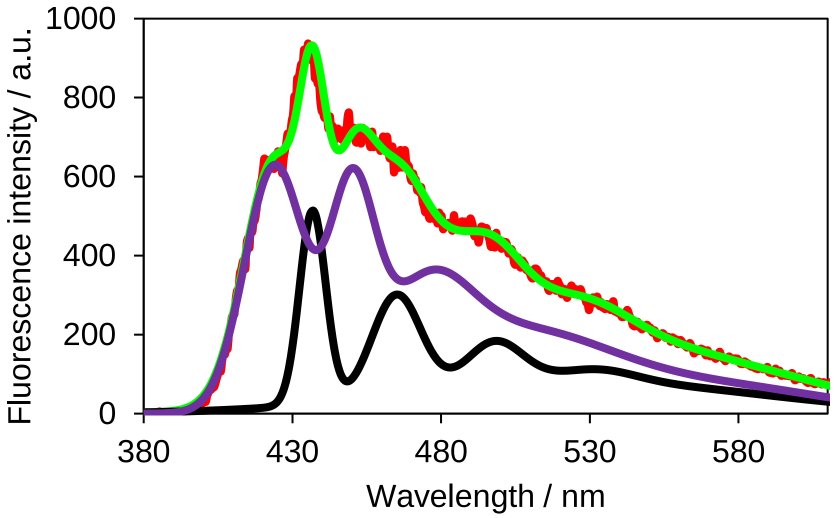


**Figure S6.** Red: Fluorescence spectrum of a single PFO NP measured after applying the force of 5μN; Black: Multiple-Gaussian fit of a spectrum before applying the force; Purple: Multiple Gaussian fit of a difference spectrum obtained by subtracting the spectrum before applying the force from the one after applying the force. Green: Sum of the black and purple curves.

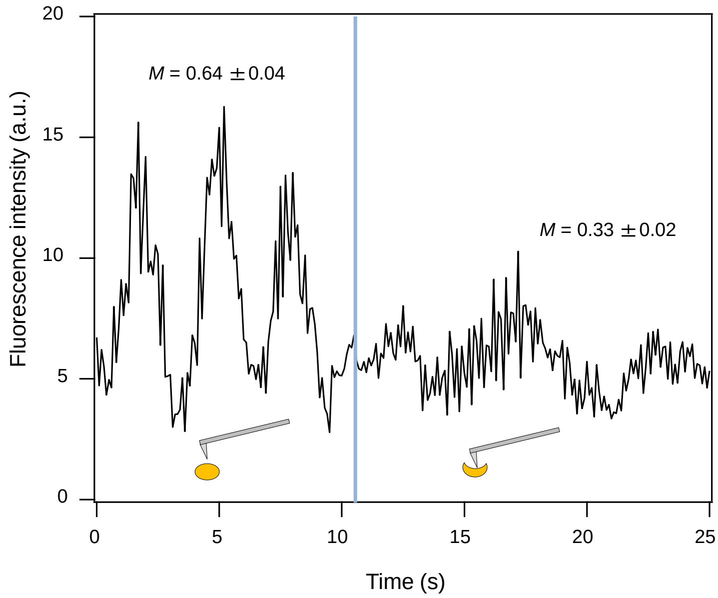


**Figure S7.** Polarization modulation of fluorescence from a single PFO NP before (left) and during (right) application of a force of 5 μM. The curve was measured by continuously rotating an analyzer placed in front of the CCD detector.

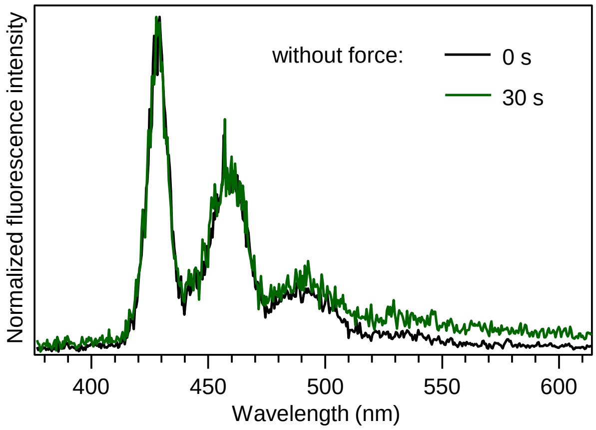


**Figure S8.** Fluorescence spectra from a single PFO NP measured in air without an applied force at the start (0 s, black) and end (30 s, green) of the measurement interval, normalized at the 0-0 band.

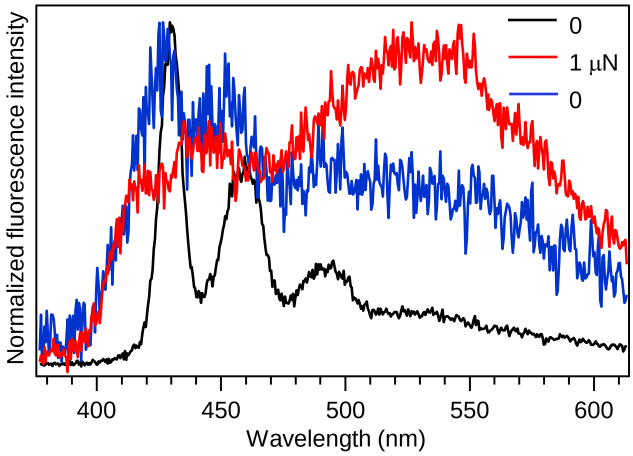


**Figure S9.** Fluorescence spectra from a single PFO NP before (black), during (blue) and after (red) applying a force of 1 μN. The spectra are normalized at their respective maxima.

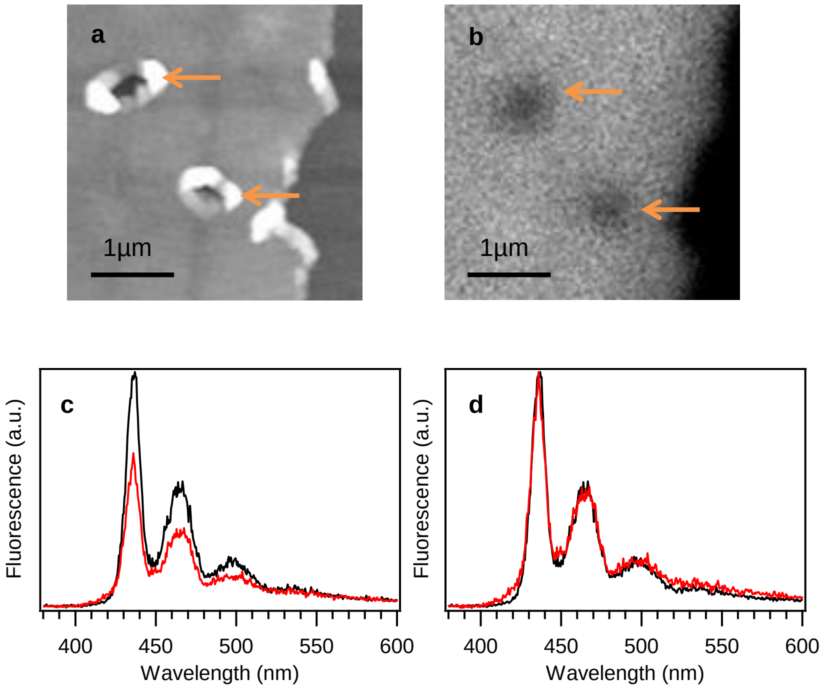


**Figure S10**. a) AFM and b) fluorescence images of a bulk film of PFO spin-coated on a substrate. The arrows indicate locations that were mechanically pressed by the AFM tip with a force of 5 μN; c) Fluorescence spectra from an intact part of the film (black) and from the pressed part (red); d) Same spectra as in c) normalized at the 0-0 band.

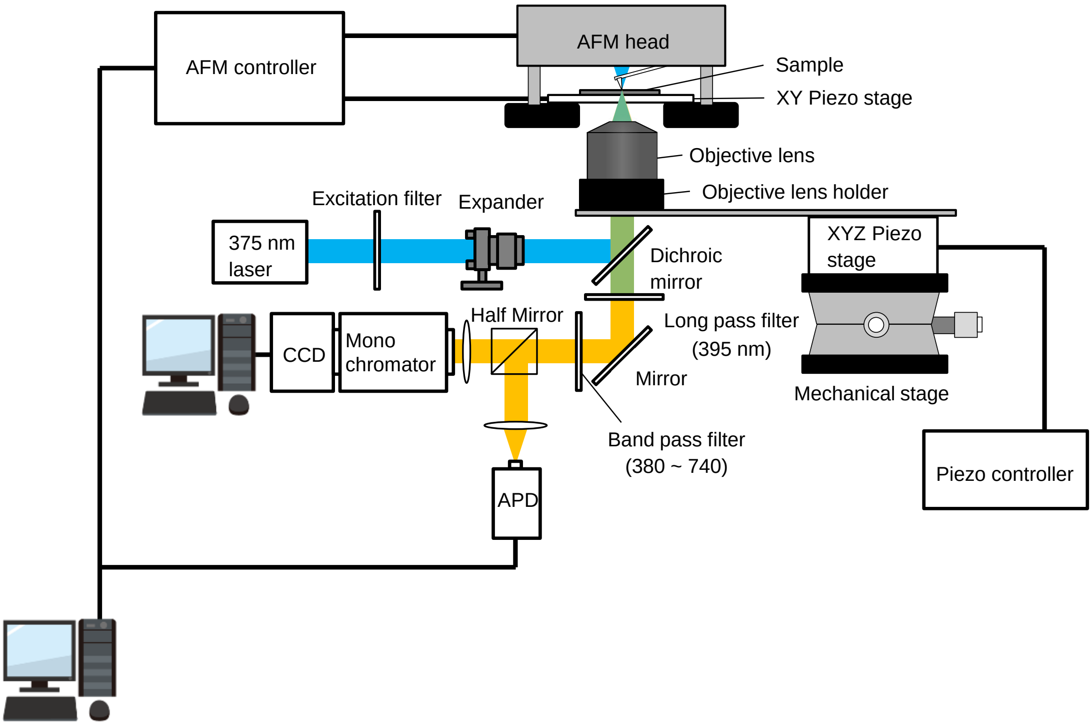


**Figure S11.** Scheme of the experimental setup.