

Supporting Information

Highly Ordered Single Conjugated Polymer Chain Rod Morphologies

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FITTING PROCEDURE

The single molecule polarization anisotropy, A , histograms were calculated by a best-fit procedure of the observed modulation depth values, M , using a program which convolutes the molecular orientation with anisotropy distribution. As mentioned in the main text, M is a projection of molecular anisotropy onto the x-y plane. Therefore, M values can be lower than A values depending on the tilt angle of each molecule (see Figure S1). Polarization distortion due to the high NA objective lens was also included in the program. The program generates an arbitrary A distribution and converts it to an M histogram. Then a fitting routine finds the best A distribution to reproduce the experimental result. The calculation employed Forkey's *et al.* equations for the fluorescence intensity of a single dipole as a function of orientation angle in a laboratory frame.¹ In order to calculate the modulation depth, M , of a multi-chromophoric system, the expressions were modified as described in the following text. MEH-PPV was assumed to be well-modeled by multiple local chromophores along the polymer chain. An absorption spheroid, representing a continuous distribution of chromophores, was

used to describe the absorption rate of a single MEH-PPV chain as a function of chain orientation in the laboratory frame. An absorption dipole moment vector at the angle (θ' , ϕ') in a molecular frame is described as follows.

$$\mu_x(\theta', \phi') = a \cos \phi' \cos \theta' \quad (\text{S1})$$

$$\mu_y(\theta', \phi') = a \cos \phi' \sin \theta' \quad (\text{S2})$$

$$\mu_z(\theta', \phi') = c \sin \phi' \quad (\text{S3})$$

where a is the minor axis, c is the major axis, θ' is the azimuthal angle and ϕ' is the elevation angle. When the spheroid is tilted at angle ζ from the z-axis around the x-axis of a laboratory frame, the following vector is derived.

$$\mu_x(\theta', \phi') = a \cos \phi' \cos \theta' \quad (\text{S4})$$

$$\mu_y(\theta', \phi') = a \cos \phi' \sin \theta' \cos \zeta - c \sin \phi' \sin \zeta \quad (\text{S5})$$

$$\mu_z(\theta', \phi') = a \cos \phi' \sin \theta' \sin \zeta + c \sin \phi' \cos \zeta \quad (\text{S6})$$

The observed fluorescence intensity at a detector can be described as follows.

$$I_x = C_{ex1}(C_{em1} + C_{em2})\mu_{ex}^2 + C_{ex2}(C_{em1} + C_{em2})\mu_{ey}^2 + C_{ex3}C_{em3}\mu_{ez}^2 \quad (\text{S7})$$

$$I_y = C_{ex2}(C_{em1} + C_{em2})\mu_{ex}^2 + C_{ex1}(C_{em1} + C_{em2})\mu_{ey}^2 + C_{ex3}C_{em3}\mu_{ez}^2 \quad (\text{S8})$$

Here, a spheroid is tilted at angle ζ only around the x-axis, so I_x and I_y are the minimum and maximum values, respectively. μ_{ex}^2 , μ_{ey}^2 , μ_{ez}^2 are the x, y, z component of the absorption dipole integrated over the surface of the spheroid, and C_{ex1} , C_{ex2} and C_{ex3} are

the coefficients which take the numerical aperture of the objective lens into account for the excitation and C_{em1} , C_{em2} and C_{em3} for the emission.

$$\mu_{ex}^2 = \int_{-\pi}^{\pi} \int_{-\pi/2}^{\pi/2} d\phi' d\theta' \cos \phi' \{a \cos \phi' \cos \theta'\}^2 \quad (S9)$$

$$\mu_{ey}^2 = \int_{-\pi}^{\pi} \int_{-\pi/2}^{\pi/2} d\phi' d\theta' \cos \phi' \{a \cos \phi' \sin \theta' \cos t - c \sin \phi' \sin t\}^2 \quad (S10)$$

$$\mu_{ez}^2 = \int_{-\pi}^{\pi} \int_{-\pi/2}^{\pi/2} d\phi' d\theta' \cos \phi' \{a \cos \phi' \sin \theta' \sin t + c \sin \phi' \cos t\}^2 \quad (S11)$$

$$C_1 = \frac{1}{8} (5 - 3 \cos \delta - \cos^2 \delta - \cos^3 \delta) (1 - \cos \delta)^{-1} \quad (S12)$$

$$C_2 = \frac{1}{24} (1 - 3 \cos \delta + 3 \cos^2 \delta - \cos^3 \delta) (1 - \cos \delta)^{-1} \quad (S13)$$

$$C_3 = \frac{1}{6} (2 - 3 \cos \delta + \cos^3 \delta) (1 - \cos \delta)^{-1} \quad (S14)$$

$$\delta = \sin^{-1} \frac{NA}{n} \quad (S15)$$

where NA is the numerical aperture of the objective lens and n is the refractive index of the media.

From I_x and I_y , the modulation depth M for a single molecule with an angle ζ was calculated as follows.

$$M = \frac{I_y - I_x}{I_y + I_x} \quad (S16)$$

A log-normal distribution was used to generate an arbitrary A distribution.²

A least square procedure was used to fit the calculated histogram to the experimental data, and the results are shown in the main text.

SINGLE CHAIN SIMULATION

To simulate the folding of a semiflexible chain from an elongated, disordered coil state at high temperature to the collapsed, low temperature state, we used the Langevin dynamics simulation for a coarse-grained chain. The motion of an individual bead in the beads on a chain model is governed by the Langevin equation³:

$$\ddot{\mathbf{r}}_i = \Gamma \dot{\mathbf{r}}_i - \nabla U - \mathbf{W}_i(t) \quad (\text{S17})$$

where subscript $i=1,...,N$ represents the bead index, N being the total number of beads. The left-hand side is the inertial term and the right-hand side consists of the dissipative frictional force ($\Gamma \dot{\mathbf{r}}_i$), the conservative interaction force (∇U) and the random noise force ($\mathbf{W}_i(t)$) which captures the dynamical effects of the implicit solvent molecules. The equation above is written in reduced units where the distance is scaled with r_0 , the equilibrium segment length, the time is scaled with $\sqrt{mr_0^2/k_B T}$ and the energy is described in the units of $k_B T$. In these units, the dimensionless friction coefficient Γ is chosen to be unity³. The random noise has following properties:

$$\begin{aligned} \langle \mathbf{W}_i(t) \rangle &= 0 \\ \langle \mathbf{W}_i(t) \cdot \mathbf{W}_j(t') \rangle &= 6\Gamma \delta_{ij} \delta(t-t') \end{aligned} \quad (\text{S18})$$

Starting with random initial chain conformations, equation (S18) is integrated in time using the velocity Verlet finite difference scheme.⁴ The time step in our simulations was kept as 0.01. Even though the simulated chains are allowed to evolve over a very long time, it might be possible that the chains at equilibrium may be trapped in a

non-stationary state separated from the global minimum by an energy barrier. However, the histograms, generated for an ensemble of around 400 chains, are believed to capture the representative probability distribution of multiple crystalline states.

FIGURES

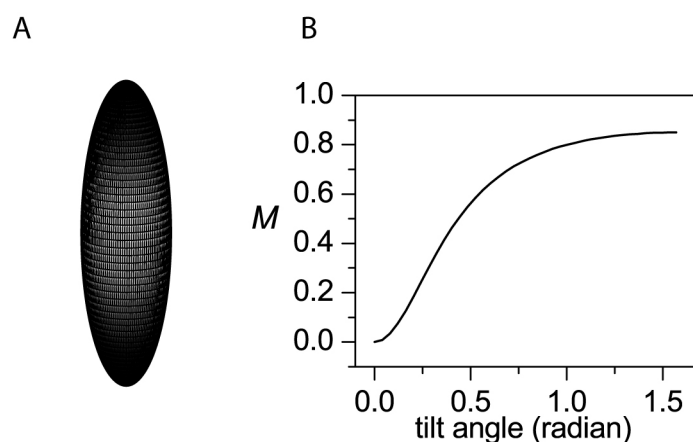


Figure S1. (A) A spheroid with anisotropy of 0.85. (B) Calculated modulation depth in the x-y plane of the laboratory frame as a function of the tilt angle. A major axis of the spheroid is in the z-axis when the tilt angle is 0.

REFERENCES

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