Transformation Process and Mechanism between the $\alpha$-Conformation and $\beta$-Conformation of Conjugated Polymer PFO in Precursor Solution

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Supporting Information

1. The calculation method of the proportion of β-conformation in PFO solution

The proportion of β-conformation in PFO solution can be calculated according to Lambert-Beer's law (Eq. S2), where \( c_\alpha \) and \( c_\beta \) are the concentrations of α-conformation and β-conformation, respectively, \( A \) (obtained from experiments) is the absorbency and \( \varepsilon \) is the absorption coefficient. In UV-vis absorption spectra of PFO solutions, it is difficult to obtain the \( \varepsilon \) for α-conformation and β-conformation. Thus we used the method of molecular simulation to the absorption spectra to calculate the proportion of \( \varepsilon_\beta / \varepsilon_\alpha \).\(^2\)

\[
\alpha\% + \beta\% = 1 \tag{S1}
\]

\[
\beta\% = \frac{c_\beta}{c_\beta + c_\alpha} = \frac{A_\beta \times \varepsilon_\alpha}{A_\beta \times \varepsilon_\alpha + A_\alpha \times \varepsilon_\beta} \tag{S2}
\]

By defining six monomer units as the conjugation length,\(^3\) we optimized the symmetry geometries of PFO chains for the approximate calculation of \( \varepsilon \) using Density Functional Theory (DFT).\(^4\) To calculate the oscillator strengths (f), Time-Dependent Density Functional Theory (TD-DFT) was used,\(^5\) as this method has been found to give reliable results.\(^6\) DFT and TD-DFT are both with a B3LYP hybrid functional basis set level of 6-31G*.\(^7\) All calculations were performed using the Gaussian 03 package.\(^6\) The oscillator strengths (f) of the two conformations are 4.46 for α-conformation at 386 nm and 4.83 for β-conformation at 437 nm. Thus, the proportion of \( \varepsilon_\beta / \varepsilon_\alpha \) can be obtained from Eq. S3 and Eq. S4, where \( k \) is a constant and \( \nu \) is the vibration frequency of two conformations. We can calculate the proportion of β-conformation in each UV-vis absorption spectra of PFO solutions using Eq. S2 and Eq. S4.

\[
f = k \int \varepsilon dv, \quad \text{and} \quad f \propto \varepsilon \tag{S3}
\]
\[ \frac{\varepsilon_\beta}{\varepsilon_\alpha} = \frac{f_\beta}{f_\alpha} = 4.83 \div 4.46 = 1.08 \]  

(S4)

REFERENCES


2. Light emission spectra of the transformation process from \( \alpha \)-conformation to \( \beta \)-conformation

![Light emission spectra](image)
Fig.S1 Normalized light emission spectra of five PFO samples with different toluene/ethanol ratios: 32:1, 16:1, 8:1, 4:1, 2:1. All the five curves were normalized at the 415 nm.

From Fig.S1, it can be seen that the corresponding light emission spectra is well consistent with the UV-vis absorption spectra Fig.2 (a) in the transformation process from α-conformation to β-conformation.