Quantitative Study on β-Phase Heredity Based on Poly(9,9-dioctylfluorene) from Solutions to Films and the Effect on Hole Mobility

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Supporting Information

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

The proportion of β-conformation in PFO solution can be calculated according to Lambert-Beer's law (Eq. S2), where c_α and c_β are the concentrations of α-conformation and β-conformation, respectively, A (obtained from experiments) is the absorbency and ε is the absorption coefficient. In UV-vis absorption spectra of PFO solutions, it is difficult to obtain the ε 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 ε 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 ν 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.

$$f = k \int \varepsilon \, dv, \qquad f \propto \varepsilon \tag{S3}$$

$$\frac{\varepsilon_\beta}{\varepsilon_\alpha} = \frac{f_\beta}{f_\alpha} = \frac{4.83}{4.46} = 1.08 \qquad\qquad\qquad\qquad (S4)$$

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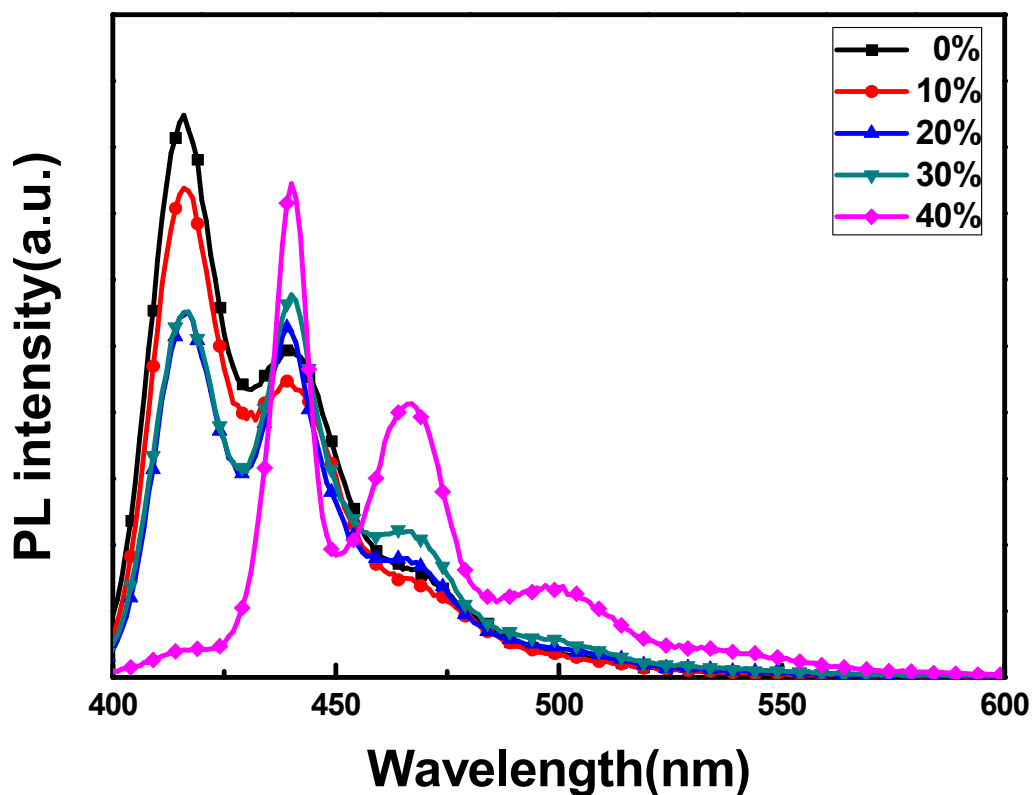## 2. The fluorescence spectra of PFO with different β-conformation in PFO contents

Figure S1 fluorescence spectra of five PFO samples with different percent of ethanol (0% to 40%) spin-casting from original solution (10mg/ml)

From Fig.S1, it can be seen that the corresponding fluorescence spectra is well consistent with the UV-vis absorption spectra Fig.2 (a) and (b) in the β phase of PFO transfer from solutions to films. However, the fluorescence spectra of PFO is same no matter in solutions or films.

When the ethanol increased from 0% to 30%, a fluorescence self-absorption phenomenon has resulted in a decrease in the PL intensity in the range of 400nm to 450nm.(as the absorption peak of PFO is in the range of 300-500 nm).The change of peak intensity also means the polymer conformation changes.Nevertheless, the ethanol content exceeds 30%, the red shift of the PL spectrum occurred,

meanwhile, energy transfer occurs.The emission peak becomes 442,464,496nm, these three are the emission peaks of the PFO β conformation. The predominantly chromophore that produces fluorescence emission is β conformation,442nm is the 0-0 emission peak, 464,496nm is the 0-1 and 0-2 emission peak, respectively. It is shown that the effective conjugated length of the PFO grows, and the energy decreases to form a more stable conformation, but also indirectly explain the β-conformation of the conjugate length growth and low energy stability.