Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Chain Structure and β Conformation of Poly (9,9-dioctylfluorene) (PFO) with Different Molecular Weight Delivering from Solution to Film in Drop-casting Process

*Tao Li,[a,b] Qilong He,[a] Yanan Guo,[c] Yijia Guan,[*a] Yuhua Zhang,[a] Weijie Cao,[a] Jieyi Qin,[a] Jianguo Liao,[a] Xuemao Guan,[a] and Dan Lu[*c]*

[a] School of Materials Science and Engineering, Henan Polytechnic University, Henan, Jiaozuo 454000, China.

[b] SDU NanoSYD, Mads Clausen Institute, University of Southern Denmark, Alsion 2, Sønderborg DK-6400, Denmark.

[c] State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, 2699 Qianjin Avenue, Changchun, China.

Supporting information

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

The proportion of β conformation in PFO film can be calculated according to Lambert-Beer's law (Eq. S1), 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 films, 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].

$$\alpha\% + \beta\% = 1 \qquad (S1)$$

$$\beta\% = \frac{c_\beta}{c_\beta + c_\alpha} = \frac{A_\beta \times \varepsilon_\alpha}{A_\beta \times \varepsilon_\alpha + A_\alpha \times \varepsilon_\beta} \qquad (S2)$$

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[7].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 v is the vibration frequency of two conformations. We can approximately calculate the proportion of β conformation in each UV-vis absorption spectra of PFO films using Eq. S2 and Eq. S4. Then the proportion of α conformation can be easily got by Eq. S1.

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

$$\frac{\varepsilon_\beta}{\varepsilon_\alpha} = \frac{f_\beta}{f_\alpha} = \frac{4.83}{4.46} = 1.08 \tag{S4}$$

2. Calculation method of the aggregates of fractal dimension (d_f) in solution by static light scattering (SLS)

In solution, the scattering intensity of polymer aggregates has the following power relationship with the test angle:

$$I(q)=(K/R_s)\ C\ M_{app}\ (q\ R_{app})^{-d_f}$$

Where $I(q)$ is the scattering light intensity, K is a constant factor, R_s is the solvent Rayleigh ratio, C is the polymer concentration, q is the scattering vector and M_{app} and R_{app} are the apparent mass and apparent radius, respectively. The fractal dimension d_f of the aggregation can be obtained from $I(q)$ and q^{-d_f}.

3. Influence of Concentration on the β Conformation Formation of PFO in pure THF solvent.

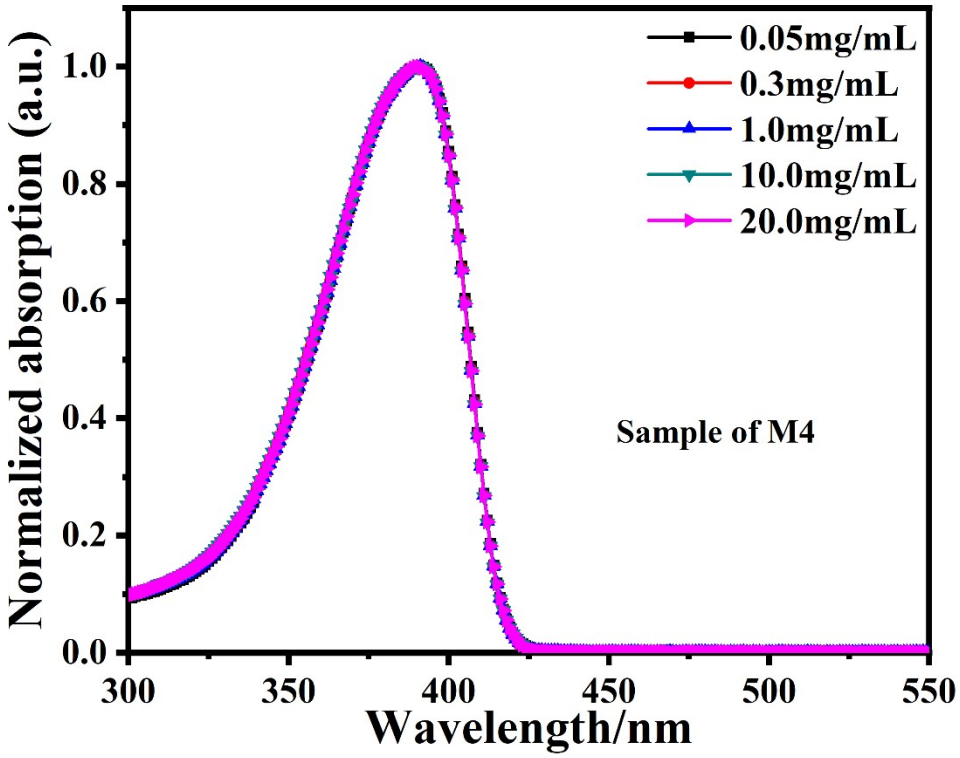

Figure S1. Normalized UV-vis absorption spectra of sample of M4 at different concentrations of THF solutions

4. Relationship between the volatilization time and the β conformation contents which were calculated from Figure 9a and Figure 9c.

Table S1. the β conformation contents which were calculated from the normalized UV-vis absorption spectra of the films with the change of volatilization time when the initial concentration was 10 mg/mL and 20 mg/mL.

	Volatilization time												
	0s	30s	60s	90s	120s	150s	180s	210s	240s	270s	300s	330s	360s
10mg/mL	0	4.5%	21.0%	29.0	32.8	34.5%	35.4%	35.9%	36.2%	36.3%	36.4%	36.5%	36.5%
20mg/mL	0	8.6%	26.3%	34.8	36.7	37.0%	37.2%	37.3%	37.3%	37.4%	37.4%	37.5%	37.5%

REFERENCES

(1) Huang, L.; Huang, X. N.; Sun, G. N.; Gu, C.; Lu D.; Ma, Y. G. *J. Phys. Chem. C* **2012,** *116,* 7993-7999.

(2) Gu, C.; Tang, S.; Yang, B.; Liu, S. J.; Lv, Y.; Wang, H.; Yang, S. M.; Hanif, M.; Lu, D.; Shen, F.Z.; Ma, Y. G. *Electrochim. Acta* **2009,** *54,* 7006-7011.

(3) Ng, M. F.; Sun, S. L.; Zhang, R. Q. *J. Appl. Phys.* **2005,** *97*, 103513.

(4) Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864-871.

(5) Runge, E.; Gross, E. K. U. *Phys. Rev. Lett.* **1984**, *52*, 997-1000.

(6) Hirata, S.; Lee, T. J.; Gordon, M. H. *J. Chem. Phys.* **1999**, *111*, 8904-8912.

(7) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.