

## Supporting Information

# $C_{\beta}$ Conformer Formation of Poly(9,9-dioctylfluorene) Single Chain Facilitated by Endcapping with Electron Deficiency Moiety

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## 1. Sample Preparation for Ensemble-Average Spectroscopic Measurements

The PFO samples were dissolved in the THF (Spectroscopic Grade, SIGMA) and the solutions were stirred overnight to ensure that the polymer chains were well dissolved. The concentrations of all polymer solutions were 100  $\mu\text{M}$ . The freshly-prepared solutions were subsequently used for preparing the thin films with 95 – 100 nm in thickness on quartz substrate by spin casting. The UV-vis absorption of the polymer thin films were measured by means of a Jobin-Yvon FluoroMax-3 spectrophotometer. All the measurements were performed at room temperature.

## 2. Single Molecule Spectroscopy Measurements

For the SMS experiments, the PFO solutions with the concentration of  $10^{-9}$  M were prepared in a mixture of THF with polystyrene ( $M_w = 250$  kDa; concentration = 7.0 mg/ml). The solutions were sonicated and subsequently heated to 50  $^{\circ}\text{C}$  to avoid polymer aggregation. The polymers remained chemically stable after all treatments. The samples for SMS measurements were prepared by spin casting (at the speed of 2000 rpm) the solutions containing PFO and polystyrene on clean cover glasses using a spin coater. The films were sealed in the sample holders before measurements. All the sample preparation processes were conducted in a glove box filled with pure nitrogen gas to avoid oxygen-induced photo-bleaching of the polymer.

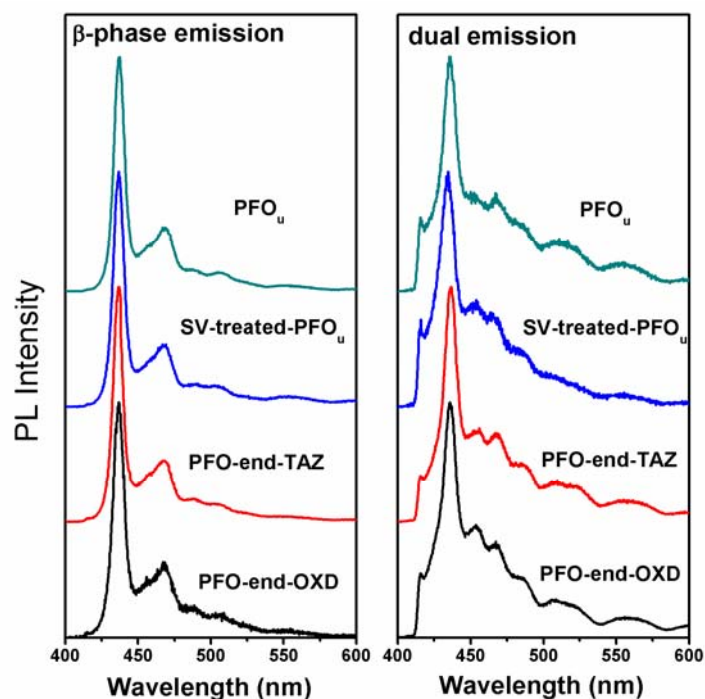
Spectroscopic measurements of isolated PFO chains dispersed in polystyrene matrix were performed using a home-built confocal microscope system which was excited using a 375 nm pulsed laser (80 MHz repetition rate). The details of the setup of the SMS system used have been described in our previous work.<sup>1</sup>

In order to assess the chromophore alignment within the isolated chains, excitation polarization modulation measurement was performed.<sup>2-4</sup> The emission intensity ( $I(t)$ ) from each absorption dipole ( $\vec{\mu}$ ) of an individual segment is given by the following expression<sup>5</sup>

$$I(t) \propto |\vec{\mu} \cdot \vec{E}(t)|^2, \quad (1)$$

where  $\vec{E}(t)$  is the time-dependent excitation electric field vector. If the absorption dipole of the segment is perpendicular to the electric field vector, no emission light will be observed. The maximum emission intensity is obtained when the absorption dipole is aligned parallel to the electric field vector. A polymer chain contains a number of emissive segments with distributed conjugation lengths and alignments. Therefore, a number of absorption dipoles with various orientations along a certain director (e.g. the end-to-end distance vector) are expected. By using the lights with various rotation polarization angles to illuminate the polymer, the modulating emission intensity from the polymer can be used to assess the degree of segmental alignment within the polymer chain. In practice, the fixed polymer chain was excited by the light with the rotation polarization angles adjusted by an electro-optical modulator (Con-Optic, Model 350-5) with the frequency of 3.0 Hz. The oscillated emission intensity from the molecule was then monitor as a function of time and polarization angle using photon-counting photodetector (MPD).

### 3. Typical single-chain PL spectra of PFOs



**Figure S1.** Typical single-chain PL spectra of the four PFO samples. Two types of spectra were identified, namely, dominant  $C_\beta$  conformer emission and dual emission from  $C_\beta$  and amorphous chromophores.

### 4. Single-Molecule PL Spectrum of the Completely Amorphous Chain

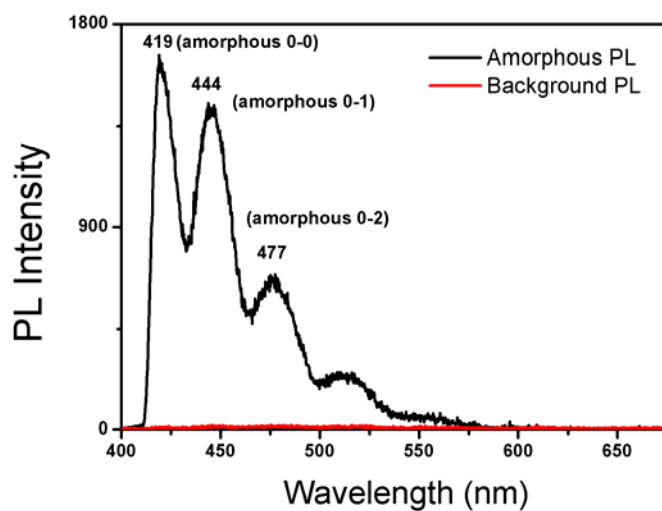
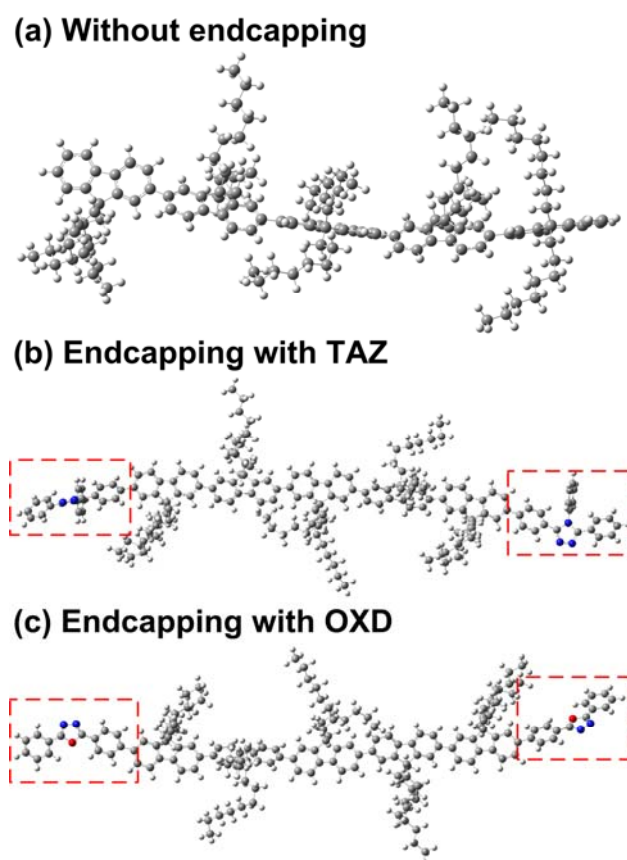


Figure S2. Typical single-molecule PL spectrum associated with amorphous emission in PFO<sub>u</sub> cast from chloroform. The emission peak positions are labeled in the figure. The red curve is the background signal. It can be seen that the background intensity is much lower than the PL intensity of the polymer chain.

### 5. Quantum chemical calculations for the conformation of oligofluorenes.

The calculation was performed using Gaussian 09 program package.<sup>6</sup> The molecular geometries of five monomers of oligofluorene including octyl side chains and the endgroups were optimized by a semi-empirical method called “Austin Model 1 (AM1)”.<sup>6</sup> The optimized conformational structures of the oligofluorene without endcapping and the endcapped oligofluorenes are displayed in Figure S3.



**Figure S3.** Optimized structures of oligofluorenes composed of five monomer units.

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