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ARTICLE TYPE

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

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**Using single molecule spectroscopy, we demonstrated the enhancement of $C_\beta$ conformer formation in poly(9,9-dioctylfluorene) (PFO) at the single chain level by endcapping with the electron deficient moiety, triazole (TAZ) or oxadiazole (OXD). The single-chain photoemission spectra of PFO without endcapping ($PFO_u$) and the endcappers contained mixed contribution from disordered and $C_\beta$ conformation. The as-cast endcappers were found to exhibit significantly larger amount of $C_\beta$ emission than as-cast $PFO_u$. The higher population of $C_\beta$ conformer led to better alignment of the chromophores in the polymer backbone, as demonstrated by the polarization modulation depth measurement. Our finding is consistent with the higher β-phase content in the thin films cast from the endcapped PFOs, which means that the intra-chain interaction mediated by EDM dominates the β-phase formation. The present study offers an important basis for a useful approach of increasing β-phase content based on endcapping PFO with TAZ or OXD without the need of further sample treatment.**

Conjugated polymers constitute an important class of active materials for organic opto-electronic devices such as light-emitting diodes (LED), photovoltaics and thin-film transistors. The performance of these devices is strongly influenced by the conformational and supramolecular structure of the polymer in the active layer. The present study is centered on one of the most important conjugated polymers, poly(9,9-dioctylfluorene) (PFO), for LED applications. PFO is a highly efficient blue-emitting polymer due to its high quantum yield, high hole mobility, trap-free charge transport, and good thermal and electrochemical stability.[1, 2] In the bulk and thin-film state, PFO may form various types of supramolecular structure characterized by different packing order and chain conformation manifested by the coplanarity of the fluorene rings along the backbone. The PFO chains in α phase are crystalline with a helical conformation of the average torsional angle 135°.[3] The mesomorphic *β*-phase may develop in the polymer films cast from appropriate solvent[4] or by treating with solvent vapor.[5] The PFO chains in *β*-phase exhibit a larger torsional angle between the monomer units (near 167°), which results in a more extended conformation (called $C_\beta$) and a longer conjugation length up to 30 ± 12 monomer units.[6, 7]

The β-phase of PFO has received particular attention due to various advantages of its associated photophysical properties for improving the device performance, including reduced photobleaching,[8] reduced triplet exciton formation,[9] and pure blue light emission.[10] Therefore, different methods have been developed to induce or promote the formation of β-phase in PFO, including dissolution of PFO in solvents with relatively poor quality and high boiling point,[10, 11, 12] exposure of the film to solvent vapor,[13] cyclic thermal annealing,[13]and dipping the film into a solvent/non-solvent mixture.[14] However, these treatments usually result in inhomogeneous film morphology, which in turn affects the efficiency and leads to short lifetime of the LED devices.[15] Consequently, developing the strategy of promoting the formation of β-phase without the need of further treatment of the film is important for enhancing the performance of LED devices based on PFO.

In a previous work, Huang et al. have reported that the use of the PFO endcapped with triazole (TAZ) electron-deficient moiety (EDM) offered deep blue emission and improved the LED device efficiency without further sample treatment.[5] The deep blue emission was proposed to arise from the incomplete energy transfer from the amorphous matrix to the β-phase regions, whose content was enhanced by the presence of the endcapper, and the improvement of the device efficiency was driven by the alignment of the endcapped EDM relative to the backbone.[5]

The promotion of β-phase formation by endcapping with EDM could occur at the inter-chain or intra-chain level; that is, the endgroup might facilitate the packing of the PFO chains to form the β-phase or the incorporation of EDM group favors the segments constituting the individual chains to adopt $C_\beta$ conformation. In this study, we intend to reveal that intra-chain effect is strongly operative by studying the conformation and the photoemission spectra of the isolated PFO chains endcapped with TAZ or oxadiazole (OXD) (denoted as PFO-end-TAZ and PFO-end-OXD) using single molecule spectroscopy (SMS). We will demonstrate that the single chains of both endcappers as cast from tetrahydrofuran (THF) exhibit significantly higher extent of photoemission from the $C_\beta$ conformer than the as-cast PFO without endcapping (denoted as $PFO_u$). The modulation depth measurement further reveals that the segments in the isolated chains of the endcappers show better relative alignment, which is consistent with the higher population of $C_\beta$ conformer displaying better coplanarity of the fluorene rings.

The synthetic routes of PFO-end-TAZ and PFO-end-OXD (chemical structures are shown in the inset of Figure 1) have been

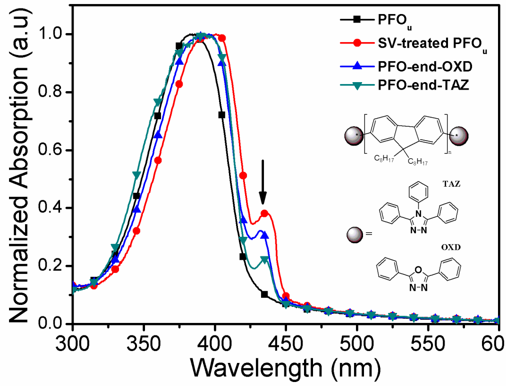

**Figure 1**. Ensemble-average UV-vis spectra of the THF-cast thin films of the four PFO samples. The chemical structures of PFO-end-TAZ and PFO-end-OXD are shown in the inset.

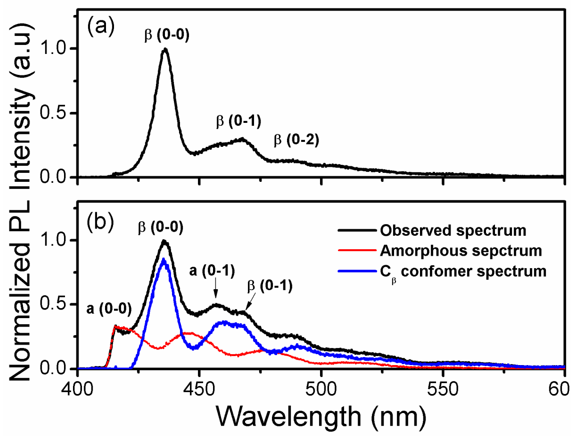

**Figure 2.** Representative single-chain PL spectra of PFO-end-TAZ with (a) dominant $C_\beta$ conformer emission and (b) dual emission from $C_\beta$ and amorphous chromophores. The observed spectrum in (b) is considered to be the sum of the β-dominant spectrum and amorphous spectrum, and the percentage of amorphous emission is estimated from the scale factors of these two types of spectrum that yield the best fit to the observed one .

described in the previous work.[5] The weight-average molecular weights ($M_w$) of PFO$_u$, PFO-end-TAZ and PFO-end-OXD are 141000, 277000 , and 182000, respectively. Da Como et al. have studied the oligofluorenes with different number of monomer units and concluded that the isolated molecules of oligofluorene could form $C_\beta$ conformer when they contained more than nine repeating units.[16] The number of the monomer units in all the PFO samples studied here exceeds this critical value.

Preparations of the samples for ensemble-average spectroscopic characterizations and for SMS measurement are presented in the Supporting Information (SI). The isolated chains of PFO were embedded in the fluorescence-free polystyrene matrix with 100 nm of thickness. A 375 nm laser was used as an excitation source with ~140 W/cm$^2$ in power. A sample treated by the solvent vapor was also prepared by exposing a PFO$_u$ film to saturated toluene vapor for 24 hours followed by removing the adsorbed solvent in nitrogen environment. This sample is denoted as "SV-treated PFO$_u$".

Figure 1 displays the ensemble-average UV-vis spectra of the PFO thin films. The primary peak locating at 375 nm is associated with the absorption of the segments in the amorphous phase.[9] The presence of β-phase in the film can be manifested by the existence of the lower-energy peak locating at ca. 430 nm (marked by the arrow). It can be seen that the absorption spectrum of PFO$_u$ thin film shows only the primary peak without the β-phase absorption. The β-phase peak becomes observable for the thin films of SV-treated PFO$_u$, PFO-end-TAZ and PFO-end-OXD, with the solvent vapor-treated film exhibiting the highest content of β-phase. The UV-vis spectra thus confirm that endcapping with OXD or TAZ moiety promotes the formation of the β-phase in PFO thin films without the need of further sample treatment. It should be noted that the difference in molecular weight between PFO$_u$ and PFO-end-OXD is only 3%; therefore, the enhancement of β-phase formation in the later should not stem from their difference in molecular weight, but is rather due to the effect of the endgroup.

The PL spectra of the isolated chains cast from THF were measured by SMS. Two types of PL spectra are identified among the single chains in all PFO samples, as displayed in Figure 2. The first type shown in Figure 2(a) consists of the vibronic transition peaks locating at 435, 466 and 490 nm. The PL peak positions closely agree with those of the β-phase of PFO reported previously[5]; therefore, this type of spectrum is called "β-dominant spectrum" to signify that the emission is contributed mainly by the $C_\beta$ conformer. It is noted that Lupton et al. have identified the 0-0 transition band of the $C_\beta$ conformer of PFO single molecules at ca. 440 nm, [16-18] which is slightly longer in wavelength than that observed here. The difference may arise from the different measuring temperature, where the PL spectra in the studies of Lupton et al. were collected at 4 ~ 5 K, while the measuring temperature in the present study is ca. 298 K. Due to the existence of some degree of freedom in backbone torsion at room temperature, the $C_\beta$ conformer studied here may possess shorter conjugation length and hence gives rise to the emission peak at shorter wavelength.

The second type of spectrum composes of an additional peak at 416 nm, which is contributed by the disordered conformer, according to the reported PL spectrum of the amorphous phase of PFO.[13] Consequently, the polymer chain showing this type of spectrum contains both $C_\beta$ and disordered segments, and the incomplete energy transfer from the amorphous segments to the $C_\beta$ segments leads to the overlap of the PL spectra from both conformers. The number fraction of the chains exhibiting the β-dominant spectrum is 48%, 54%, 56% and 58% in PFO$_u$, SV-treated PFO$_u$, PFO-end-TAZ and PFO-end-OXD, respectively, implying that the isolated chains of the endcappers contain a greater population of $C_\beta$ conformer than the PFO$_u$ chains.

The spectrum of completely amorphous chains was not identified among all the single chains cast from THF; however, such a spectrum was observable for several chains cast from chloroform (Figure S2). We then used this amorphous spectrum to estimate the amount of amorphous emission from the single-chains cast from THF according to the following way. First, the amorphous spectrum in Figure S2 was multiplied by a scale factor, such that the intensity of its first peak matches that of the 416 nm peak in the observed spectrum (see the red dashed curve in Figure 2b.). The amorphous spectrum thus obtained is considered to stem from the photoemission from the disordered conformer in the polymer chain. Then this amorphous spectrum is subtracted from the observed spectrum to yield to spectrum associated with the $C_\beta$ conformer in the chain (see the blue curve in Figure 2b). The relative fractions of the disordered and $C_\beta$ conformer are then estimated from the ratios of the areas of the corresponding spectra to the total area.

Figure 3 displays the histograms of the content of amorphous emission estimated over the single-chain spectra of 300 isolated chains. The average values are labeled in the Figure. It can be seen that the average amount of amorphous emission reduces to 15% and 14% in PFO-end-TAZ and PFO-end-OXD, respectively, comparing to 25% in $PFO_u$. The average content of amorphous emission in $PFO_u$ also decreases to 15% after solvent vapor treatment. The results attest that the population of $C_\beta$ conformer in the endcappers is significantly higher than that in the freshly cast PFO chains without the EDM endcapping. Among the conformers of PFO chains, $C_\beta$ conformer displays the largest torsional angle of 167°;[6, 7, 19] therefore, the polymer chain with higher population of $C_\beta$ conformer should become more extended. The coplanarity of chromophores in the isolated PFO chains can be elucidated by measuring their single-molecule polarization excitation modulation.[18, 20] The average orientation of the chromophores in a given chain is characterized by a parameter called "modulation depth (*M*)".[20] Its value is close to unity when most of absorption chromophores within the chain are aligned parallel to each other. The value of *M* approaches zero when the chromophores in the chain are more randomly oriented.[1, 10]

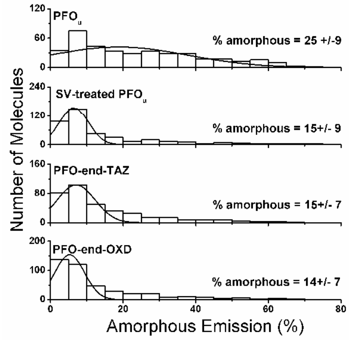

**Figure 3.** Histograms of the percentages of amorphous emission of the single chains in the four PFO samples. The solid curves are the fits by the Gaussian functions. The mean values of the amounts of amorphous emission are displayed in the plots.

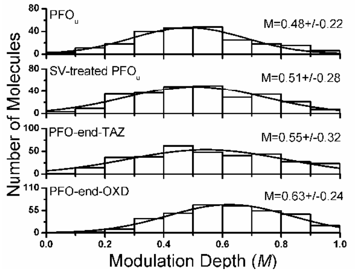

**Figure 4.** Modulation depth histograms of the single chains in the four PFO samples. The solid curves are the fits by the Gaussian functions. The mean values of the modulation depth, <*M*>, are displayed in the plots.

Figure 4 show the histogram of the modulation depths of four PFO samples. The mean values of the modulation depth, <*M*>, obtained by fitting the histograms by Gaussian functions for $PFO_u$, SV treated-$PFO_u$, PFO-end-TAZ and P3HT-end-OXD are 0.48, 0.51, 0.55 and 0.63, respectively. The corresponding number fractions of molecules having *M* greater than 0.5 are 48%, 52%, 54% and 74%, respectively. The results show that endcapping with EDM tends to enhance the coplanarity of the chromophore in the chain comparing to $PFO_u$, which is consistent with the greater population of $C_\beta$ conformer in the endcappers.

The enhancement of intra-chain coplanarity by endcapping is verified by the quantum chemical calculation for the oligofluorenes (see Supporting Information). The fluorene rings in the oligofluorene without endcapping are found to display poorer coplanarity than those in the endcappers, which is qualitatively consistent with the promotion of $C_\beta$ conformer formation observed experimentally. The increase of $C_\beta$ conformer population in the EDM-endcapped chains is attributed to the electron withdrawing capability of the endgroups, which causes the delocalization of the electrons at the fluorene units next to the EDM. Such an effect further induces the electrons at the other fluorine monomer units within a certain correlation length to be delocalized. Since the electron delocalization is accomplished by increasing the coplanarity between the successive fluorene rings, the $C_\beta$ conformer formation is promoted.

Our photophysical characterization of the single chains demonstrates that the incorporation of EDM at the chain ends of PFO facilitates the formation of $C_\beta$ conformer. That is, the promotion of the β-phase behavior is already operative at the single-chain or intra-chain level. The enhancement of the population of $C_\beta$ conformer in the single chains favors the formation of β-phase in the thin films of the EDM-endcapped PFO and consequently improves the purity of blue-light emission relative to that associated with the PFO with the endgroup of para-tert-butyl phenyl (TBP).[5]

## Conclusions

We have identified a strategy to induce the formation of $C_\beta$ conformer in PFO single chains by endcapping with TAZ or OXD group. Using SMS, we demonstrated that endcapping PFO with these two EDMs promoted the population of $C_\beta$ conformer in the individual polymer chains, and such an effect led to higher coplanarity of the chromophores or segmental anisotropy. The presence of higher content of $C_\beta$ conformer in the individual chains may favor the packing or assembly of the PFO chains to form the β-phase in the films. Therefore, the use of the EDM-endcapped PFO offers an effective strategy to promote the β-phase formation without the need of applying further sample treatment, considering that the presence of β-phase has the advantages of improving the device performance.

## Notes and references

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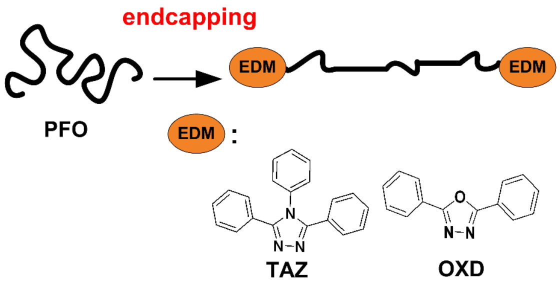
# TOC GRAPHICS



Using single molecule spectroscopy, we reveal that endcapping poly(9,9-dioctylfluorene) (PFO) with electron deficient moiety (EDM) can promote the population of $C_\beta$ conformer at the intra-chain level. The enhancement of $C_\beta$ conformer formation is caused by the electron withdrawing capability of the EDMs. Therefore, the use of the EDM-endcapped PFO offers an effective strategy to promote the β-phase formation without the need of applying further sample treatment, considering that β-phase is advantageous for improving the performance of the relevant opto-electronic devices.