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A Rational Molecular Design of β -Phase Polydiarylfluorenes: Synthesis, Morphology, and Organic Lasers

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Supporting Information

ABSTRACT: Rational molecular design allows for manipulating the chain conformations of polymer semiconductors by cooperative arrangement of bulky groups with steric hindrance effect and supramolecular groups with noncovalent attractions. Herein, a model polyfluorene with β -phase, poly[4-(octyloxy)-9,9-diphenylfluoren-2,7-diyl]-*co*-[5-(octyloxy)-9,9-diphenylfluoren-2,7-diyl] (PODPF), has been synthesized successfully via key Baeyer–Villiger rearrangement reaction. Its thin film exhibited excellent spectral stability without green band emission after thermal annealing at 200 °C under air and nitrogen ambients. The β -phases of PODPF in the concentrated toluene solution, organogels, and films have



been characterized and confirmed by UV absorption and PL spectra as well as grazing-incidence X-ray scattering. The results suggest that the octyloxy substituents enable backbone planarization via van der Waals forces of the in-plane alkyl chains to overcome intrachain repulsion between fluorene monomers. Organic lasers using β -phase PODPF exhibit lower threshold than those of poly(9,9-dioctylfluorene), suggesting promising optical gain media. This observation suggested that supramolecular steric hindrance (SSH) is a promising molecular design of polymer semiconductors, and supramolecular steric polymers are one kind of model to get insight into the structure-function relationships for electrically pumped organic lasers in organic electronic and photonics.

■ INTRODUCTION

Thin-film morphology of π -conjugated polymers is of great importance to govern the fundamental exciton and carrier behaviors, device performance, and stability in printed plastic electronics.^{1–3} However, it is thorny task to control over their morphologies owing to the conformation diversity, complex interchain interactions, and polymorphism phenomena.^{1,4,5} Polymorphic behaviors are strongly dependent on film fabrication procedures such as film-processing methods, ink formulations, substrate types, and rheological kinetics.^{6–9} As one typical example, poly(dialkylfluorenes) (PDAFs) exhibit various morphologies, including amorphous phase,^{10,11} β -phase,¹² liquid crystalline,¹³ semicrystalline α - and α' -phases,^{14,15} and networking gel states.¹⁶ Among them, β -phase showed a series of the appealing features such as improved charge-carrier mobility,¹⁷ high current efficiency (CE), and excellent spectral stability in polymer light-emitting diodes (PLEDs),^{9,18} efficient amplified spontaneous emission (ASE), and low threshold lasers.^{19–21} In addition, β -phase morphology provides an opportunity to create patterned thin films.^{19,22}

PDAFs' β -phase, especially poly(9,9-dioctylfluorene) (PFO), stemmed from an intriguing "planar zigzag" (2₁ helix) chain conformation,²³ resulting in an enhanced effective conjugation length,¹² close molecular chain packing, and larger Förster radius of excitation transfer. The β -phase of PDAFs were widely observed in solutions,^{4,24,25} thin films,^{26–28} nanostructures (nanoparticles²⁹ and nanowires^{30,31}), and gels.^{16,32–35} Such β phase morphology was also achieved in PDAFs by variations of external conditions, such as film postprocessing,²⁸ and adding a small amount of high-boiling-point 1,8-diiodooctane (DIO),⁸ nonvolatile polyphenyl ether,³⁶ or liposome phospholipid bilayers into precursory solution.³⁷ However, PDAFs have the inherent drawback with poor environmental stability, in which the generation of ketone defects not only deteriorate the color purification but also decrease the lifetime of devices.¹ Therefore, it is significant to explore the novel β -phase polyfluorenes via molecular design.

Up to date, many efforts have been made to investigate the effects of molecular structure, such as molecular weight, alkyl substituent, and copolymerization, on the formation of β -phase

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Scheme 1. (a) Schematic Two-Side Molecular Design Model of PODPF, (b) Fluorescent Photograph of Diluted (left) and β (right) Phase Contained PODPF Solution, and (c) Synthetic Routes of PODPF



in polyfluorenes.^{4,17,38-48} It has been confirmed that the prerequisite to achieve β -phase of PDAFs is the van der Waals forces of side chains stronger enough to overcome the steric repulsion and polarize polymer backbone.²³ Furthermore, an optimal chain length of PDAFs for the formation of β -phase is regarded as an octyl side chain in PFO which is easier to form the interdigitation packing than any other length and substituted style.⁴ To date, most of examples show that the low-content β phase of PDAFs only keep after the introduction of chiral groups,⁴⁶ cross-linking networks,⁴² and surfactant zwitterion groups.⁴⁷ The delicate balances are easily destroyed by the introduction of molecular segments. As a result, morphologydirected molecular designs face severe challenge to achieve β phase homopolyfluorenes beyond PDAFs. In our previous works, the attractive $\pi - \pi$ stacking interactions at the cruciformshaped spirofluorenes have been proved to modulate the luminescence and manipulate molecular assembly effectively.⁴⁹⁻⁵² Supramolecular steric hindrance (SSH)^{49,50} would become one molecular design principle to control over molecular conformation and thin film morphology in conjugated polymers. In this work, we explored the conformational stabilization of β chains in polyfluorenes via the noncovalent forces at steric hindrance. A molecular building block was designed where bulky groups with the feature of steric repulsions and alkyl groups with the van der Waals attractive forces are arranged into two side of fluorene monomer, respectively (Scheme 1a). In consideration of bulky groups with the merits of high thermal and chemical stability, poly(diarylfluorenes) have the obvious advantages with the more environmental stability against aggregation and oxidation over PFO. One model polyfluorene, poly[4-(octyloxy)-9,9- diphenylfluoren-2,7-diyl]-co-[5-(octyloxy)-9,9diphenylfluoren-2,7-diyl] (PODPF), has been synthesized in which diphenyl moieties lied at the 9-positon of fluorene and the alkyl side chains substituted at 4-position of fluorene. The β phase of PODPF has been obtained in solutions (Scheme 1b),

organogels, and films. It has been characterized by UV–vis electronic absorption, photoluminescence (PL) spectra, and grazing incidence X-ray diffraction (GIXD). Lasers from β -phase PODPF exhibited lower threshold with respect to PFO-based laser.

RESULTS AND DISCUSSION

Synthesis and Characterization of PODPF. As a model polymer, PODPF was prepared via Yamamoto-type polymerization of key monomer that was synthesized by the Baeyer-Villiger rearrangement reaction (Scheme 1c). Concretely, dibromofluorenone was transformed into 3,8-dibromobenzochromen-6-one (1) after the Baeyer-Villiger rearrangement reaction at the yield of 75%. The Grignard reaction of 1 gave the tertiary alcohol 2,4'-dibromo-2'-(hydroxydiphenylmethyl)biphenyl-2-ol, followed by nucleophilic substitution of 1bromooctane to obtain (4,4'-dibromo-2'-(octyloxy)biphenyl-2yl)diphenylmethanol (3). The monomers 4 were prepared by BF3·Et2O-catalysted Friedel-Crafts reaction according to our previous work.⁵³ The chemical structure was fully characterized and confirmed by nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC) (Figures S1 and S2). GPC measurement revealed the molecular weight (M_n) of PODPF to be 5.60×10^4 (PDI = 1.33). PODPF exhibited good solubility in common organic solvents, such as chloroform (CHCl₃) and tetrahydrofuran (THF). The decomposition temperature (T_d) is up to 405 °C, and glassy transition temperatures (T_{σ}) is 108 °C (Figures S3 and S4). Cyclic voltammetry (CV) study shows the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of PODPF are -2.38 and -5.55 eV, respectively (Figure S5).

Optical Properties of PODPF. We investigated the optical properties of PODPF solution and films and uncovered the effects of film thermal postprocessing on the formation of PODPF β -phase to examine the capability of conformational



Figure 1. Optical properties of PODPF in various states. UV–vis (a) and PL spectra (b) of PODPF in toluene solution (0.01 mg/mL), organogels, and films (films A and B were spin-coated from toluene and CHCl₃, 10 mg/mL). UV–vis and PL spectra of PODPF film spin-coated from CHCl₃ solution after thermal annealing at 200 °C in N₂ (c) and in air (d) for 0, 6, and 12 h. PL and transient decay spectra of PODPF film drop-coated from CHCl₃ (e) and toluene (f) solution (3 mg/mL).

planarization. PODPF adapted β -phase structures in solvents such as toluene (>0.01 mg/mL), rather than in dichloromethane, CHCl₃, and THF (Figure S6), and PODPF exhibited β -phase conformation in films spin-coated from toluene or mixed solvents of CHCl₃ and methylcyclohexane (1:2) but not in the film spin-coated from CHCl₃. Meanwhile, β -phase can also be observed in PODPF organogels in toluene or toluene/ methylcyclohexane, which were formed using the heatingcooling method at the concentration of 15 mg/mL at -20 °C in toluene or 10 mg/mL in toluene/methylcyclohexane (1:1) at room temperature (Figure S7). In addition, PODPF films adapt the β -chain conformation and phase through thermal annealing, as shown in Figure 1c,d. Furthermore, similar to PFO, PODPF would self-assemble into nanowires or nanoribbons by dropcoating from dilute toluene solution (0.01 mg/mL) (Figure S8). These results suggested that synergic induction occur that are favorable for β -chain conformations via the two-side balanced introduction of bulky groups with steric repulsion and alkyl chains with the van der Waals forces.⁵⁴

Optical analyses were employed here to probe the formation of β -phase in various states (Figure 1). The maximum absorption peak of PODPF in various states located at 390 nm is attributed to main-chain backbones of polyfluorenes.⁵⁵ Previous study suggested that the small peak at ~436 nm in absorption spectra indicated the formation of polyfluorenes β -chain phase.¹² The appearance of the shoulder peaks at 444 nm (similar position to the 436 nm peak at the absorption spectra of polyfluorenes) in the absorption spectra in Figure 1a,c confirms the formation of PODPF β -phase in concentrated toluene solutions (>0.01 mg/ mL), organogels, and films. It is easy to find that the content of β phase in the drop-coated film is higher than those in spin-coated films and organogels. However, this shoulder peak was absent in the absorption spectra of pristine films spin-coated (Figure 1a, film B, and Figure 1c,d) or drop-coated (not shown) from CHCl₃ solution, suggesting no β -phase formed in film spin- and dropcoated from CHCl₃ solution. PL spectra of PODPF in diluted toluene solution (<0.01 mg/mL) exhibited three well-resolved emission bands at 432, 456, and 483 nm that are assigned to the 0-0, 0-1, and 0-2 interaction singlet transition in an isotropic phase, according to the literature (Figure S6).¹⁶ For the formation of β -phase in organogel, there are four emission bands at 432, 458, 486, and 515 nm. However, the peak at 432 nm was slightly guenched than those of PODPF diluted solution (Figure 1b and Figure S7), implying energy transfer from isotropic phase to β -phase, similar to PFO/toluene gels.^{16,33} Figure 1b shows that this energy transfer was significantly stronger in the PODPF film spin-coated from toluene solution, of which the PL spectra consisted of three peaks at 456, 486, and 518 nm similar to emission of β -phase PFO according to the reports by Khan et al.,⁵⁶ corresponding to 0-0, 0-1, and 0-2 vibration transition of β -phase. For PODPF drop-coated films from toluene solution, there are three featured emission peaks at 486, 515, and 555 nm. With regard to low-content β -phased films, the 0–0 vibration transition at ~456 nm of β -phase becomes very weak. A peak profile at 486 nm is similar to the emission spectra of PFO/DCE gel according to our previous report.¹⁶ The excitation spectra of PODPF β -phase films spin- or drop-coated from toluene presented an excitation peak at 446 nm below the π – π * edge, further confirming the classical well-resolved sharp feature of β -phase polyfluorenes (Figure S9).²⁸

From Figure 1c,d, there was no shoulder peak at 444 nm in absorbance spectra of the pristine PODPF film spin-coated from CHCl₃ suggesting not β -phase in the film. But the films exhibited the featuring shoulder peak at 444 nm in the absorption spectra and emission peaks at 458, 483, and 515 nm after thermal annealing (either in N₂ or in air), suggesting the formation of β phase. Moreover, the low-energy green bands at the center of 530–550 nm have no obvious changes in PL profile of PODPF films after samples annealed at 200 °C for 12 h in air or in nitrogen. These results suggest that PODPF have advantages over PFO in terms of high spectral stability and antioxidation (Figure S10). It has been observed that the β -phase conformation gives rise to orders of magnitude enhancement in photophysical stability in terms of increased lifetime.⁵⁷ Timeresolved PL (Figure 1e,f and Table 1) showed that the

 Table 1. Photophysical Data of PODPF in Solution and Thin

 Films

polymer	solvent	states	$\lambda_{abs} \ (nm)$	$\lambda_{ m PL}~(m nm)$	T (ps)	$\Phi_{ ext{pLQY}}^{d}_{(\%)}^{d}$
PODPF	toluene	solution ^a	390	432, 456, 483	412	81
		film ^b	395, 444	438, 456, 482, 518	500	39 (30 ^c)
	CHCl ₃	solution ^a	390	430, 452, 481	396	80
		film ^b	390	445, 465, 502	300	46 (33 ^c)

^{*a*}Concentration of 0.01 mg/mL. ^{*b*}Spin-coated thin films. ^{*c*}Drop-coated thin films. ^{*d*}PFO amorphous film with Φ_{PLQY} of about 43% at the same conditions.

fluorescent longevity is longer for β -phased film (500 ps) than that of the pristine film (300 ps). The PL quantum yields (Φ_{PLQY}) of PODPF are ~80% in solution, ~46% in amorphous films, ~39% in β -phase films, and 30% in drop-coated film, which are equivalent to those of PFO at the same states.

Molecular Arrangements of PODPF Films. Grazing incidence wide-angle X-ray diffraction (GIXD) was carried out to characterize the molecular ordering and orientation of PODPF film on Si substrates. Figures 2a,c,e display 2D GIXD patterns of the PODPF films spin-coated from CHCl₃ solution, and spin-coated and drop-coated from toluene solution, respectively, while Figures 2b,d,f show their corresponding outof-plane (q_z) and in-plane (q_{xy}) profiles. The diffusive ring with a broad peak at $Q = 1.45 \text{ A}^{-1}$ (d = 4.33 Å, according to $d = 2\pi/q$) in Figure 2a is ascribed to the $\pi - \pi$ stacking distances from adjacent polymer chains. This value is much larger than the prototype P3HT layer stacking distance.⁵⁸ In fact, the value is close to the highly branching side chain substituted poly[N-9"-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) (1.42 A⁻¹).⁵⁹ The larger $\pi - \pi$ distance can be explained by the steric hindrance of 9,9-diphenyl moieties at the 9-position of fluorene, which block the interchain interaction. The angular dependence of this scattering peak (Figure 2b) is

very broad, with a slight enhancement of intensity in the out-ofplane direction, indicating that the π - π stacking is weakly faceon orientated. A weak hump at 0.85 A^{-1} (corresponding to 7.4 Å) in the in-plane line cut profile. This most probably comes from the alkyl chain spacing along the polymer backbone as indicated from Figure 3g or simply the spacing of main chain repeat unit. By using an all trans-conformation, the alkyl chain spacing was calculated to be about 8.0 Å, the same as the length of fluorene along the backbone,¹² corresponding with GIXD results. For the case of PODPF films spin-coated from toluene (Figure 2c,d), there are a broad peak at $Q = 1.46 \text{ A}^{-1} (d = 4.30 \text{ Å})$ in out-ofplane profiles, a peak at $Q = 1.36 \text{ A}^{-1}$ (d = 4.62 Å), and a peak at Q = 0.85 A^{-1} (d = 7.39 Å) in in-plane profiles. The peak at 1.36 A^{-1} comes from the amorphous average chain spacing of the polymer resulting from bulky diphenyl groups and distributes randomly and overlaps with the $\pi - \pi$ peak. For the PODPF films dropcoated from toluene (Figure 2e,f), the structure of the material becomes even more complicated. In the out-of-plane direction, there is a small 0.48 A^{-1} lamellae spacing peak. In the high angle region, there are peaks at 1.36 and 1.51 A^{-1} . The 0.48 A^{-1} lamellae spacing enhances significantly and shows as a sharp peak in the in-plane direction, suggesting the crystal form in face-on orientation. The peak at $Q = 0.48 \text{ A}^{-1} (d = 13.09 \text{ Å})$ in the dropcoated sample is very similar to the distinguished " β -phase" reflection mode of PFO, showing a reduced lamellar spacing in the crystal. The new peak of 1.51 A^{-1} (4.16 Å) with high intensity in the in-plane direction is from a better stacked $\pi - \pi$ plane. This peak also arises from the β -phase as observed in PFO β -phase system a distinctive 1.50 \AA^{-1} is shown. The angular distribution of this peak enhances in mainly in-plane direction with also a trace of enhancement in out-of-plane direction, as shown in the color coding in the diffratogram. These results indicate this ordered structure takes place in both face-on and edge-on orientation. Compared to the drop-coated sample, spin-coated film exhibits less order of the PODPF chain. This is due to the formation of the film being too fast in a spin-coated film, which does not give the polymer chains enough time to dewell and order, thus reducing the crystalline structure. The rich scattering peaks and humps in both in-plane and out-of-plane direction indicate there are more than one ordered structure in the toluene drop-casted sample. It contains a weak aggregated structure similar to β -phase. On the basis of these structural analyses, we proposed a schematic model of PODPF with a face-on arrangement of polyfluorene backbones in β -domain (Figure 2g,h). It should be noted that PODPF spin-coated films have β phase, as observed by optical characterizations, but no featuring peak at $Q = 0.48 \text{ A}^{-1}$, indicating a ribbon type of assemblies made up of enhanced $\pi - \pi$ stacking similar to β -phase. The alky side chains are frustrated under the fast drying process and cannot form a good order.

Lasing Properties of PODPF β -**Phase.** It has been reported that the β -phase of PFO exhibited efficient amplified spontaneous emission (ASE) as a gain medium for polymer laser. Therefore, β -phase contained PODPF film was studied to explore its suitability as optical gain media. In order to investigate the optical gain properties, slab waveguide samples were fabricated and excited with the 355 nm beam from a Q-switched Nd:YAG laser pumped optical parametric amplifier (Spectron SL450), 10 Hz, 4.2 ns pulsed excitation. A rectangular spot of dimensions was about 4 mm × 0.4 mm stripe for ASE measurement. By increasing the excitation energy, we observed ASE centered at 461 nm with a spectral half-width below 4.6 nm as shown in Figure 3a, which is near the 0–0 vibronic transition

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Figure 2. Grazing-incidence-X-ray scattering (GIXD) images, X-ray profiles, and schematic models of PODPF films on the Si substrates deposited via different method at room temperature: (a, b) spin-coated from CHCl₃ solution; (c, d) spin-coated from toluene solution; (e, f) drop-coated from toluene solution; (g) schematic model of in-plane chain arrangements of and (h) face-on orientation in the out-of-plane in the β -phase domain. The regioregular structure is shown for the sake of drawing in (g) and (h), but the real structure is regiorandom.



Figure 3. (a) Amplified spontaneous emission (ASE, 461 nm) and laser spectra of a one-dimensional DFB laser comprising PODPF films. (b) Inputoutput characteristics of the 1D DFB lasers at lasing wavelengths of 461 nm.

of the β -phase PODPF. In order to better quantify the ASE behavior, we defined a threshold pulse energy (EASEth) at which the fwhm of the emission spectrum drops to half its low excitation pulse energy PL value. This energy is usually accompanied by a kink in the input versus output intensity graphs of the ASE. The ASE thresholds of PODPF for 461 nm is 251 nJ/pulse (15.69 μ J/cm²), lower than reported thresholds for PFO film⁶⁰ measured on the same experimental apparatus. Distributed feedback (DFB) lasers were also fabricated by spin-coating the polymer film on the grating-patterned fused silica substrates. For a grating with period 290 nm, fill factor 25%, and etch depth 90 nm, the lowest lasing threshold of 41.9 nJ/pulse was achieved for a laser operating at 462 nm using a 160 nm thickness PODPF film (Figure 3b). The results suggest that

PODPF is a promising optical gain media for using in solid state amplifiers and lasers.

CONCLUSIONS

In conclusion, we demonstrated the rational molecular design of supramolecular steric hindrance (SSH) to achieve β -phase polyfluorene by means of the introduction of hydrophobic interactions of the in-plane alkyl chains cross the steric hindrance. PODPF as a model with the alkyloxy side chains at the 4-position of fluorene was synthesized via key Baeyer–Villiger rearrangement. Its β -phase morphology was achieved in toluene solution, organogels, and films by spin- or drop-coating from toluene solution as well as in amorphous thin films by the

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annealing process. PODPF thin film exhibited excellent spectral stability without green band emission under thermal annealing in air and N₂ at 200 °C. GIXD analysis suggested the featuring peak at Q = 0.48 A⁻¹ corresponds to the interdigitation distance of 13.09 Å, suggesting a possible chain arrangement of face-on packing style relative to the silicon substrates. Organic lasers of PODPF exhibited low threshold that will be potential optical gain media toward electrical injection lasers. Supramolecular steric hindrance will be a promising molecular design principle in conjugated polymer semiconductors.

ASSOCIATED CONTENT

S Supporting Information

Full experimental section, including detailed synthesis of monomer and PODPF, together with their NMR spectra, GPC, DSC, and TGA curve, cyclic voltammetry (CV) curve, absorption and PL spectra, SEM image of self-assembled nanowires. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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