Macromolecules

Poly(spirobifluorene)s Containing Nonconjugated Diphenylsulfone Moiety: Toward Blue Emission Through a Weak Charge Transfer Effect

Xuchao Wang,^{†,‡} Lei Zhao,^{†,‡} Shiyang Shao,[†] Junqiao Ding,^{*,†} Lixiang Wang,^{*,†} Xiabin Jing,[†] and Fosong Wang[†]

[†]State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, P. R. China

[‡]University of Chinese Academy of Sciences, Beijing, 100049, P. R. China

Supporting Information

ABSTRACT: Instead of conjugated dibenzothiophene-*S*,*S*-dioxide (DBTSO), we have introduced nonconjugated diphenylsulfone (DPSO) as the electrondeficient unit into the main chain of poly(spirobifluorene)s (PSFs). Because of the weaker electron affinity of DPSO relative to DBTSO, the charge transfer from the pendant 2,3,6,7-tetraoctyloxyfluorene to the main chain can be effectively prevented. Consequently, the resultant polymers containing DPSO moiety show pure blue emissions, which is different from DBTSO-based PSFs that exhibit undesired green emissions. With a single-layer device configuration, a peak luminous efficiency of 2.90 cd/A and a maximum luminescence of 14130 cd/m² have been realized for the polymer PSFDPSO03. The corresponding CIE coordinates are (0.17, 0.18), nearly independent of the applied current density from 2 to 592 mA/cm². These results indicate that tuning the electron affinity of the incorporated electron-deficient units is a very promising strategy



to control the charge transfer strength for the development of blue-emitting PSFs with high efficiency and stability.

1. INTRODUCTION

Polymer light-emitting diodes (PLEDs) have attracted lots of industrial and scientific interests due to their low-cost wetprocessing capability for display and illumination applications.¹ To realize full-color displays, three primary color emitting polymers, i.e., blue, green, and red, are highly desirable.² Among them, it is a great challenge to produce blue-emitting polyfluorenes (PFs) have been recognized as the most promising blue emitters because of their high solid-state quantum yields.⁴ Unfortunately, a blue to greenish blue color change is often observed for PFs associated with the appearance of a novel low energy green band emission during device operation or thermal annealing in air. The origin of this green emission is generally believed to be from the aggregation or keto-defects in PFs according to the literatures.⁵

To solve this problem, spirobifluorene is adopted as a building block to design blue-emitting polymers.⁶ Through a spiro linkage at the 9-position of fluorene, the possibility of the fluorene repeat unit into fluorenone is avoided, and thus the chemical stability of poly(spirobifluorene)s (PSFs) is enhanced. Meanwhile, the orthogonal configuration between backbone and side groups in PSFs can bring about a large steric hindrance of the individual polymer chains, and further prevent their aggregation in the solid state. As a result, different from PFs, PSFs have excellent spectral stability. For example, poly(2'- octyloxy-9-spirobifluorene) reported by Bo Z. et al. reveals no green emission even after annealed at 200 °C for 3 h in air.⁷ However, PSFs still suffer from poorer device efficiency compared with PFs.⁸

It is believed that the hypervalent sulfur atom obtained by oxidation can lead to an electron deficiency of the *S*,*S*-dioxide based backbones.⁹ Particularly, dibenzothiophene-*S*,*S*-dioxide (DBTSO) has been recently demonstrated as an excellent electron-deficient moiety by the Cao group to improve the luminous efficiency and stability of PFs.¹⁰ In view of this, we decided to introduce the same DBTSO unit into the main chain of PSFs. Nevertheless, our initial attempt failed because an undesired green emission was obtained with Commission Internationale de L'Eclairage (CIE) coordinates of (0.27, 0.46) for PSFDBTSO05 (Figure 1).¹¹ This was caused by the strong charge transfer (CT) from pendant 2,3,6,7-tetraoctyloxyfluorene to DBTSO in the main chain. Therefore, aiming at blue emitters, it is necessary to weaken the strong CT effect observed in PSFs containing DBTSO.

In this paper, by finely tailoring the structure of the electrondeficient moiety, we have realized blue-emitting PSFs with high efficiency and stability. As depicted in Figure 1, in place of

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Figure 1. Molecular design of PSFs with different electron-deficient units.

Scheme 1. Synthetic Route of the Polymers^a



"Reagents and conditions: (a) $C_8H_{17}Br$, Bu_4NBr , NaOH, THF/H₂O, 80 °C, 84%; (b) NBS, DMF, 94%; (c) Mg, LiCl, FeCl₃, 1,2-dibromoethane, THF, 57%; (d) NBS, DMF/CHCl₃, 60%; (e) Mg, LiCl, 2,7-dibromofluorenone, THF, 62%; (f) HCl, CH₃COOH, 60%; (g) PdCl₂(dppf), bis(pinacolato)diboron, KOAc, DMF, 80 °C, 75%; (h) CuI, Na₂S·9H₂O, K₂CO₃, DMF, 60%; (i) H₂O₂, CH₃COOH, 90%; (j) Pd₂(dba)₃, 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl, Aliquat 336, K₂CO₃, H₂O, toluene, 85–95%.

DBTSO whose electron cloud could be delocalized into the whole conjugated backbone through 3,7-linkage, a nonconjugated analogue, diphenylsulfone (DPSO), is incorporated into the main chain of PSFs. Unlike PSFDBTSO05, the CT strength can be effectively inhibited because of the lower electron affinity energy of DPSO relative to DBTSO, and pure blue emissions are achieved for the DPSO-based polymers including PSFDPSO01, PSFDPSO03, PSFDPSO05, PSFDPSO07, and PSFDPSO10 (Figure 1). Additionally, their electron injection barriers are reduced by about 0.1–0.4 eV after the introduction of DPSO. On the basis of a simple single-layer device structure, PSFDPSO03 gives a promising luminous efficiency of 2.90 cd/A together with CIE coordinates of (0.17, 0.18), which is almost independent of the applied current density.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization. Scheme 1 shows the synthetic route of the polymers. Starting from 1,2-benzenediol, alkylation, bromination, and iron-catalyzed homocoupling reactions¹² were performed in sequence to give the intermediate **3.** After bromination of **3**, the corresponding Grignard reagent was prepared in the presence of magnesium power and LiCl,¹³ followed by quenching with

2,7-dibromofluorenone to afford the tertiary alcohol **5**. Further treatment of **5** with HCl/HOAc gave the key monomer **6**, which was further converted to the desired boronic ester 7 in a yield of 75% via a palladium-catalyzed cross-coupling reaction. On the other hand, another comonomer, di(4-bromophenyl) sulfone (**9**), was easily obtained after the oxidation of di(4-bromophenyl) sulfide that was derived from 4-bromoiodobenzene under Na₂S·9H₂O and CuI catalyst. With **6**, 7 and **9** in hand and simultaneously tuning the feed ratio of **9**, the blueemitting polymers, PSFDPSO00, PSFDPSO01, PSFDPSO03, PSFDPSO05, PSFDPSO07, and PSFDPSO10 were finally synthesized via the Suzuki polycondensation. The actual content of DPSO in the polymers could be estimated according to their ¹H NMR spectra. As shown in Figure 2, the peaks at



Figure 2. ¹H NMR spectra of the polymers.

7.67 ppm are assigned to the protons of the homopolymer PSFDPSO00, while the signals at 7.83 and 7.49 ppm are attributed to the protons of DPSO. By comparing the integral of these two sets of signals, the DPSO loading is calculated, and the data are listed in Table 1. It is found that the actual content

Table 1. Physical Properties of the Polymers

	DPSO o polym	content in the ers (mol %)			
polymer	feed ratio	actual content ^a	$M_{\rm n}^{\ b}$ (kDa)	PDI^b	$T_{\rm d}^{\ c}$ (°C)
PSFDPSO00	0	0	101	4.0	360
PSFDPSO01	1	1.23	147	4.8	360
PSFDPSO03	3	3.61	105	4.5	360
PSFDPSO05	5	4.76	89	4.0	360
PSFDPSO07	7	6.98	155	4.5	360
PSFDPSO10	10	10.11	107	3.7	360

^{*a*}Calculated from the ¹H NMR spectra. ^{*b*}Determined by GPC in THF using polystyrene standards. ^{*c*}5% weight loss temperature determined by TGA in N_2 .

of DPSO is very close to the feed ratio, suggesting that DPSO has been fully incorporated into the main chain of the polymers during polymerization.

The number-average molecular weight (M_n) and polydispersity index (PDI) of these polymers, determined by gel permeation chromatography (GPC), are in the range of 89– 155 kDa and 3.7–4.8, respectively (Table 1). Furthermore, in the presence of four octyloxy chains, all the polymers are readily soluble in common organic solvents, such as toluene, xylene, chloroform, THF, etc., ensuring the formation of their high quality films by spin-coating. Their thermal properties were also studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The polymers PSFDPSO00–PSFDPSO10 exhibit the same decomposition temperature of 360 $^{\circ}$ C, corresponding to a 5% weight loss (Figure 3). And in the range of 25 to 280 $^{\circ}$ C, no glass transition



Figure 3. TGA curves of the polymers.

or melting is detected for all polymers (Figure S1, Supporting Information). According to the literature reports, ^{6g,7} the glass transition temperatures are reported to be 121 and 293 °C for PSFs that contain one and two alkyloxy groups, respectively. Hence we can speculate that the glass transition temperatures of PSFDPSO00–PSFDPSO10 with four octyloxy chains may be close to or even higher than the decomposition temperature, indicative of the good thermal stability of their formed films.¹⁴

2.2. Electrochemical Properties. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were used to explore the electrochemical properties of the polymers PSFDPSO00–PSFDPSO10. With regard to the energy level of the ferrocene reference (4.8 eV below the vacuum level), their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels are estimated according to the equations of HOMO = $-e(E_{ox} + 4.8 \text{ V})$ and LUMO = $-e(E_{red} + 4.8 \text{ V})$, where E_{ox} and E_{red} are taken from the first oxidation and reduction peak in DPV curves, respectively (Figure 4). All the polymers display nearly the same HOMO level of about -5.40 eV, independent of the DPSO content.



Figure 4. Cyclic voltammograms (a) and differential pulse voltammetry (b) of the polymers in films.

In striking contrast, the LUMO level gradually decreases as the content of DPSO rises. For instance, PSFDPSO10 has a LUMO level of -2.65 eV, which is 0.43 eV lower than that of PSFDPSO00 (-2.22 eV), implying that the electron injection barrier can be effectively modulated to facilitate the electron injection/transport with the insertion of DPSO into the



Figure 5. Absorption and PL spectra of the polymers in toluene (a) and PL spectra of the polymers in films (b).

polymeric backbone. Noticeably, the LUMO level of PSFDPSO10 is still higher than that of PFs copolymer containing the planar conjugated DBTSO fragment (-2.82 eV).^{10a} The result further verifies that the nonconjugated DPSO unit possesses much weaker electron-withdrawing capability compared with DBTSO,¹⁵ which may be favorable for the tuning of CT degree as will be discussed later.

2.3. Optical Properties. Figure 5a depicts the UV-vis and photoluminescence (PL) spectra of the polymers PSFDPSO00–PSFDPSO10 in dilute toluene solutions (data are given in Table 2). As can be clearly seen, all the polymers

Table 2. Optical and Electronic Properties of the Polymers

polymer	${\lambda_{ m abs} \over (m nm)^a}$	$\lambda_{ m em} \ ({ m nm})^a$	$(nm)^{b}$	$\Phi_{ m em}{}^c$	$_{\rm (eV)^{d}}^{\rm HOMO}$	$(eV)^d$
PSFDPSO00	344, 383, 399	452	437, 455	0.20	-5.39	-2.22
PSFDPSO01	344, 383, 399	452	456	0.33	-5.40	-2.33
PSFDPSO03	344, 383, 399	452	457	0.24	-5.40	-2.45
PSFDPSO05	343, 383, 396	453	464	0.24	-5.38	-2.58
PSFDPSO07	343, 383, 396	455	465, 480	0.22	-5.39	-2.62
PSFDPSO10	343, 381, 395	456	468, 481	0.20	-5.38	-2.65

^{*a*}Measured in toluene solution of 10^{-6} M at 298 K. ^{*b*}Measured in solid film at 298 K and the excitation wavelength is 360 nm. ^{*c*}Solid state fluorescence quantum yield measured by integrating-sphere method. ^{*d*}HOMO = $-e(E_{ox} + 4.8 \text{ V})$ and LUMO = $-e(E_{red} + 4.8 \text{ V})$, where E_{ox} and E_{red} are the first oxidation and reduction peak taken from the DPV curves, respectively.

exhibit two similar absorption bands in the ranges 360-430 and 310-360 nm. The former absorption originates from the $\pi - \pi^*$ transition of the polymeric backbone and the latter is related to the spiro-conjugated system between the backbone and side fluorene attached with four alkoxyl groups.¹⁶ However, their PL spectra are obviously influenced by the DPSO content, as indicated in Figure 5a. The homopolymer PSFDPSO00 with no DPSO unit shows an emission maxima at 452 nm accompanied by a shoulder at 425 nm, corresponding to the 0-1 and 0-0 transitions, respectively.¹⁶ While for the copolymers PSFDPSO01, PSFDPSO03, PSFDPSO05, PSFDPSO07, and PSFDPSO10, a discernible 0-2 vibronic peak at around 481 nm appears in their PL spectra, and its intensity increases with the increasing DPSO content. Owing to the existence of the spiro-conjugation in PSFs, the observed spectral changes may be reasonably ascribed to the intramolecular CT from the electron-donating 2,3,6,7-tetraoctyloxyfluorene unit to the electron-withdrawing DPSO unit. To confirm this CT effect, the PL spectra with different solvent polarity were recorded for these copolymers. Taking PSFDPSO05 as an example, the emission maxima is slightly red-shifted from 452 nm in toluene to 478 nm in THF, and correspondingly the full width at half-maximum (fwhm) is increased from 78 to 100 nm (Figure S2).

On going from solution to solid state, the 0-2 emission is further intensified (Figure 5b). Consequently, its intensity is comparable to that of the 0-1 counterparts for PSFDPSO07 and PSFDPSO10. Taking into account that PSFDPSO00 has similar PL spectra in solution and film, aggregation could be excluded due to the inherent orthogonal configuration. Therefore, in this case both the intra- and intermolecular CT are proposed for the enhancement of 0-2 emission. It is worthy noting that, the developed copolymers are basically blue emissive even for PSFDPSO10 with high content of DPSO, for they all show well-defined vibronic peaks including 0-0, 0-1, and 0-2 transitions. This is quite different from green-emitting PSFDBTSO05, where a structureless CT emission dominates the whole spectrum (Figure 5b).¹¹ The significant difference correlates well with the theoretical calculations performed on the pentamers DSBF-DPSO-DSBF and DSBF-DBTSO-DSBF, where two spirobifluorene dimers are bridged by DPSO and DBTSO, respectively, and the octyloxy side chains are truncated into methoxy groups. In DSBF-DBTSO-DSBF, as shown in Figure S3, the LUMO is mainly distributed on the central DBTSO moiety. However, due to the weaker electronwithdrawing ability of DPSO relative to DBTSO, the LUMO further extends into the neighboring spirobifluorene backbones at both ends of DPSO for DSBF-DPSO-DSBF. The less separation between HOMO and LUMO means a weak CT character in DPSO-containing polymers, which results in their pure blue emissions.

2.4. Electroluminescent Properties. PLEDs with a singlelayer device structure of ITO/PEDOT:PSS (40 nm)/EML (80 nm)/Ca (20 nm)/Al (100 nm) were fabricated to investigate the electroluminescent (EL) properties of the polymers PSFDPSO00-PSFDPSO10. The EL spectra for all the polymers are shown in Figure 6 and the corresponding device data are summarized in Table 3. After the inclusion of DPSO in the backbone, the CIE coordinates gradually red-shift from (0.16, 0.14) of PSFDPSO00 to (0.18, 0.22) of PSFDPSO10. Interestingly, compared with the film PL counterparts (Figure 5b), the 0-2 emissions are greatly alleviated under electric excitation. The reason is not very clear now, but we believe that PL and EL spectra are measured under different environments, and the lower radiative decay constant of CT states relative to local excited states may contribute to the suppression of 0-2emissions.17



Figure 6. EL spectra of the polymers at 5 V.

Table 3. Devices Characteristic of PLEDs Based on the Polymers

polymer	$\begin{pmatrix} V_{\mathrm{on}}^{a} \\ \mathrm{(V)} \end{pmatrix}$	$L_{\rm max} \over ({\rm cd/m}^2)$	$\eta_{ m l,max} \ (m cd/A)$	$\eta_{ m p,\ max} \ (m lm/W)$	$\eta_{ m ext,max} \ (\%)$	$CIE^b (x, y)$
PSFDPSO00	3.4	7749	1.12	0.37	0.76	(0.16, 0.14)
PSFDPSO01	3.0	13 425	2.74	1.79	1.82	(0.16, 0.16)
PSFDPSO03	3.0	14 130	2.90	1.80	1.78	(0.17, 0.18)
PSFDPSO05	3.0	11 555	2.35	1.71	1.48	(0.17, 0.18)
PSFDPSO07	3.0	8442	1.70	1.27	1.03	(0.17, 0.19)
PSFDPSO10	2.8	3914	0.77	0.62	0.43	(0.18, 0.22)

^aTurn-on voltage at a brightness of 1 cd/m². ^bMeasured at a brightness of 1000 cd/m². L_{max} : maximum brightness; $\eta_{\text{l, max}}$: maximum luminous efficiency; $\eta_{\text{p, max}}$: maximum power efficiency; $\eta_{\text{ext, max}}$: maximum external quantum efficiency.

Parts a and b of Figure 7 show the current densityvoltage-luminescence characteristics of the polymers PSFDPSO00-PSFDPSO10, and their current density dependence of luminous efficiency, respectively. Except for PSFDPSO00, the current density at the same driving voltage seems to substantially increase from PSFDPSO01 to PSFDPSO10. With the increasing DPSO loading, the abovementioned LUMO levels of the polymers can be efficiently tuned to facilitate electron injection, and thus lead to the enhanced current density. In addition, when the feed ratio of DPSO increases from 0% to 3% (Figure 7b and Table 3), the luminous efficiency is first increased from 1.12 cd/A of PSFDPSO00 to 2.90 cd/A of PSFDPSO03, which comes from the much more balanced carriers in PSFDPSO03 induced by the improved electron injection. The further enhancement of the DPSO content would interrupt the obtained charge balance, resulting in lower efficiency of 0.77 cd/A for

PSFDPSO10. Correspondingly, the brightness goes initially from 7749 cd/m² of PSFDPSO00 upward to 14130 cd/m² of PSFDPSO03, and then downward to 3914 cd/m² of PSFDPSO10. As a consequence, among the polymers PSFDPSO00–PSFDPSO10, PSFDPSO01 and PSFDPSO03 show the best device performance with a maximum luminous efficiency of 2.74 cd/A (1.79 lm/W, 1.82%) and 2.90 cd/A (1.80 lm/W, 1.78%), respectively. These values are very promising and are comparable to those of state-of-art blue-emitting PSFs.^{1c}

To evaluate the spectral stability of these polymers, PSFDPSO03 is taken as an example, and its EL spectra are recorded driving at different applied current densities (Figure 8). With the increasing current density from 2 to 592 mA/cm^2



Figure 8. EL spectra of PSFSO03 under different applied current densities.

(corresponding to the brightness from 54 cd/m^2 to 12169 cd/m^2), the EL spectra remain nearly unchanged, and only a slight variation of CIE coordinates is observed from (0.17, 0.18) to (0.16, 0.16). Most importantly, no long wavelength emission that is usually detected for PFs appears during device operation. These observations indicate that the DPSO-based polymers do have good color stability.

3. CONCLUSION

A series of blue-emitting PSFs have been successfully designed and synthesized by incorporating a nonconjugated DPSO moiety into the polymer backbone rather than the conjugated DBTSO. The relative weaker electron affinity of DPSO to DBTSO is demonstrated to contribute to the prevention of the strong CT effect, thereby leading to pure blue emissions for DPSO-based PSFs. At the same time, their electron injection abilities are improved with the loading of DPSO. In comparison to the homopolymer PSFDPSO00, a more than 2-fold enhancement of the device efficiency is attained for PSFDPSO03. Under different applied current densities, moreover, such DPSO-based PSFs display nearly unchanged



Figure 7. Current density-voltage-luminance curves of the devices (a) and their current density dependence of luminous efficiency (b).

EL spectra without long wavelength emissions. In terms of the pure blue emission, high color stability, and promising device performance, we believe that, the PSFs containing DPSO moiety would have great potential applications for full-color displays.

4. EXPERIMENTAL SECTION

4.1. Characterization. ¹H and ¹³C NMR spectra were recorded with a Bruker Avance 400 NMR spectrometer. Molecular weight of the polymers were determined by gel permeation chromatography (GPC) on a Waters 410 instrument with polystyrene as a standard and THF as the eluent. Elemental analysis was performed on a Vario EL elemental analyzer. MALDI/TOF (matrix-assisted laser desorption ionization/time-of-flight) mass spectra were performed on AXIMA CFR MS apparatus (COMPACT). GC-MS was recorded on an Agilent 5975 GC-MS spectrometer. Melting point was measured with Beijing Tech X-4 digital melting-point apparatus with optical microscope. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed under a flow of nitrogen with PerkinElmer-TGA 7 and PerkinElmer-DSC 7 system, respectively. UV-visible absorption and photoluminescent spectra were measured with a PerkinElmer Lambda 35 UV-vis spectrometer and a PerkinElmer LS 50B spectrofluorometer, respectively. The PL quantum yields of solid state films on the quartz plate were measured using a quantum yield measurement system (C10027, Hamamatsu Photonics) excited at 360 nm. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were measured in anhydrous acetonitrile with Bu_4NClO_4 (0.1 mol/L) as the electrolyte on a CHI660a electrochemical analyzer at a scan rate of 100 mV/s. A glass carbon electrode, a saturated calomel electrode, and a Pt wire were used as the working electrode, the reference electrode, and the counter electrode, respectively. The polymers were spin-coated on the working electrode for the measurement. Theoretical calculations were performed using the Gaussian 09 package, and the model geometries of oligomers were fully optimized by density functional theory (DFT) using Beck's three-parametrized Lee-Yang-Parr exchange functional (B3LYP) with 6-31G* basis sets.

4.2. Device Fabrication and Measurements. The device structure was ITO/PEDOT:PSS (35 nm)/polymer (80 nm)/Ca (20 nm) /Al (100 nm). The indium tin oxide (ITO) (20 Ω per square) samples were cleaned with acetone, detergent, and distilled water and then were cleaned in an ultrasonic solvent bath. After baking in a heating chamber at 130 °C for 2 h, the ITO-glass substrates were treated with O₂ plasma for 25 min. Subsequently, poly(3,4ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Batron-P4083, Bayer AG) was spin-coated on top of the ITO at a speed of 5000 rpm for 60 s and then baked at 120 °C for 45 min. Then, solutions of the polymers in toluene were filtered through a filter (0.45 μ m) and spin-coated on PEDOT:PSS as the emissive layer (EML) at a speed of 1500 rpm for 60 s. Successively, the substrate was annealed at 100 °C for 0.5 h inside a nitrogen-filled glovebox and then transferred to a vacuum thermal evaporator. On top of the EML, the calcium was thermally deposited the cathode through a shadow mask with an array of 70 mm² openings at a pressure of 4.0×10^{-4} Pa. Finally, aluminum was deposited subsequently as the protective layer for calcium at a pressure of 1.0×10^{-3} Pa. The EL spectra and CIE coordinates were measured using a PR650 spectra colorimeter. The current-voltage and brightness-voltage curves of devices were measured using a Keithley 2400/2000 source meter and a calibrated silicon photodiode. All the measurements were carried out at room temperature under ambient conditions.

4.3. Materials. All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to the standard procedures.

1,2-Bis(octyloxy)benzene (1). 1,2-Benzenediol (17.0 g, 154.00 mmol), NaOH (37.0 g, 924.00 mmol), Bu₄NBr (5.0 g, 15.40 mmol), and 1-bromootane (73 mL, 273.00 mmol) were dissolved in 300 mL of THF and 100 mL of water under nitrogen. Then the solution was stirred at 80 °C. After 3 h, the resulting mixture was

poured into 500 mL water and extracted with dichloromethane three times. The organic layer was combined and dried over Na₂SO₄. After removal of the solvent, the product was separated by column chromatography to have colorless liquid (43.0 g, yield 84%). ¹H NMR (400 MHz, CDCl₃, δ): 6.88 (s, 4 H), 3.99 (t, *J* = 6.7 Hz, 4 H), 1.86–1.75 (m, 4 H), 1.51–1.42 (m, 4 H), 1.40–1.22 (m, 16 H), 0.88 (t, *J* = 6.8 Hz, 6 H).

4-Bromo-1,2-bis(octyloxy)benzene (2). 1,2-Bis(octyloxy)benzene (43.0 g, 120.00 mmol) was dissolved in 150 mL of CHCl₃ at 0 °C. NBS (23.0 g, 130.00 mmol) dissolved in 250 mL of DMF was added dropwise at 0 °C. After that, the resulting mixture was stirred at room temperature for 12 h. Then the solution was poured into 2000 mL of water and extracted with dichloromethane three times. The organic layer was combined and dried over Na₂SO₄. After removal of the solvent the product was separated by column chromatography to afford colorless liquid (50 g, yield 94%). ¹H NMR (400 MHz, CDCl₃, δ): 7.02–6.94 (m, 2 H), 6.76–6.69 (m, 1 H), 3.95 (m, 4 H), 1.80 (m, 4 H), 1.51–1.39 (m, 4 H), 1.38–1.23 (m, 16 H), 0.96–0.83 (m, 6 H).

3,4,3',4'-Tetrakis(octyloxy)biphenyl (3). The compound 2 (33.1 g, 80.00 mmol) in 150 mL of THF was slowly added dropwise to 15 mL of THF containing anhydrous LiCl (3.7 g, 86.40 mmol), iodide, and magnesium turnings (2.9 g, 120.00 mmol) at room temperature. Then the solution was stirred for 12 h at 50 °C. The solution then added dropwise to a 20 mL THF, containing FeCl₃ (389.0 mg, 2.40 mmol) and 1,2-dibromoethane (15.0 g, 80.00 mmol) at room temperature. The whole procedure was carried under an argon atmosphere. The resulting mixture was stirred at room temperature for 12 h and then hydrolyzed with a 1 M aqueous HCl solution (100 mL). After extraction with dichloromethane three times, the organic layer was combined and dried over Na2SO4. After removal of the solvent, the white solid product was obtained by recrystallization from petroleum ether (15.0 g, yield 57%). ¹H NMR (400 MHz, CDCl₃, δ): 7.09–7.02 (m, 4 H), 6.92 (d, J = 8.9 Hz, 2 H), 4.16-3.87 (m, 8 H), 1.97-1.74 (m, 8 H), 1.58–1.43 (m, 8 H), 1.38–1.19 (m, 32 H), 0.89 (m, 12 H).

2-Bromo-4,5,3',4'-tetrakis(octyloxy)biphenyl (4). The compound 3 (17.0 g, 26.00 mmol) was dissolved in 200 mL CHCl₃ at 0 °C. NBS (5.0 g, 28.00 mmol) dissolved in 70 mL of DMF was slowly added dropwise at 0 °C. After that, the solution was stirred at room temperature for 12 h. Then the resulting mixture was poured into 700 mL of water and extracted with dichloromethane three times. The organic layer was combined and dried over Na₂SO₄. After removal of the solvent, the white solid of product was obtained by recrystallization from petroleum ether (16 g, yield 60%). ¹H NMR (400 MHz, CDCl₃, δ): 7.10 (s, 1 H), 6.95 (s, 1 H), 6.90 (s, 2 H), 6.84 (s, 1 H), 4.15–3.88 (m, 8 H), 1.94–1.73 (m, 8 H), 1.53–1.41 (m, 8 H), 1.39–1.20 (m, 32 H), 1.02–0.77 (m, 12 H).

2,7-Dibromo-9-(4,5,3',4'-tertrakis(octyloxy)biphenyl-2-yl)-9H-flu-oren-9-ol (5).¹⁸ The compound 4 (16.4 g, 20.00 mmol) in 200 mL of THF was slowly added dropwise to 20 mL of THF containing anhydrous LiCl (924.0 mg, 22.00 mmol), iodide, and magnesium turnings (528.0 mg, 22.00 mmol) at room temperature. Then the solution was stirred for 8 h at 50 °C. The solution then added dropwise to a 30 mL of THF, containing 2,7-dibromofluorenone (7.4 g, 20.00 mmol) at room temperature. The reaction mixture was stirred for 8 h. The whole procedure was carried under an argon atmosphere. At last, the resulting mixture was poured into 300 mL of water and extracted with dichloromethane three times, the organic layer was combined and washed with water and dried over Na2SO4. After removal of the solvent, the product was separated by column chromatography to afford a colorless liquid (12.4 g, yield 62%). ¹H NMR (400 MHz, $CDCl_3$, δ): 7.10 (s, 1 H), 6.95 (s, 1 H), 6.90 (s, 2 H), 6.84 (s, 1 H), 4.15-3.88 (m, 8 H), 1.94-1.73 (m, 8 H), 1.53-1.41 (m, 8 H), 1.39–1.20 (m, 32 H), 1.02–0.77 (m, 12 H).

2,7-Dibromo-2',3',6',7'-tertrakis(octyloxy)-9,9'-spirobifluorene (6). The compound 5 (9.0 g, 8.80 mmol) was dissolved in acetic acid (200 mL) at 10 °C. And then 10 mL of HCl was added slowly. The solution was stirred for 10 h at room temperature. After the reaction was complete, the mixture was poured into 2000 mL of water and extracted with dichloromethane three times. The organic layer was combined and dried over Na_2SO_4 . After removal of the solvent, the

product was purified by column chromatography and recrystallized from ethanol there times to produce a white solid (5.0 g, yield 60%). ¹H NMR (400 MHz, CDCl₃, δ): 7.64 (d, *J* = 8.1 Hz, 2 H), 7.47 (d, *J* = 6.8 Hz, 2 H), 7.20 (s, 2 H), 6.85 (d, *J* = 1.4 Hz, 2 H), 6.14 (s, 2 H), 4.12 (s, 4 H), 3.72 (s, 4 H), 1.93–1.83 (m, 4 H), 1.71–1.62 (m, 4 H), 1.58–1.19 (m, 40 H), 0.93–0.82 (m, 12 H). ¹³C NMR (101 MHz, CDCl₃, δ): 150.7, 149.5, 148.4, 138.9, 138.8, 134.6, 130.4, 126.9, 121.3, 120.7, 109.4, 104.6, 69.1, 31.3, 31,2, 29.0, 28.9, 28.8, 28.7, 25.6, 25.5, 22.2, 22.1, 13.6. Anal. Calcd for 6 (%): C, 69.36; H, 7.97. Found: C, 69.74; H, 7.88. MALDI–TOF MS: *m*/*z* 984.4. Melting point: 76–78 °C.

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-2',3',6',7'tertrakis(octyloxy)-9,9'-spirobifluorene (7). The compound 6 (7.0 g, 7.10 mmol), PdCl₂(dppf) (350.0 mg, 0.43 mmol), KOAc (2.0 g, 20.40 mmol), and bis(pinacolato)diboron (4.0 g, 15.80 mmol) were dissolved in 40 mL of dry DMF and then stirred at 80 °C for 24 h under an argon atmosphere. After the reaction was complete, the mixture was poured into 200 mL of water and extracted with dichloromethane three times. The organic layer was combined and dried over Na2SO4. After removal of the solvent, the product was separated by column chromatography and recrystallized from ethanol to give a white solid (5.8 g, yield 75%). ¹H NMR (400 MHz, CDCl₃, δ): 7.84 (s, 4 H), 7.17 (d, J = 12.5 Hz, 4 H), 6.12 (s, 2 H), 4.12 (s, 4 H), 3.66 (s, 4 H), 1.96–1.79 (m, 4 H), 1.69–1.46 (m, 8 H), 1.42–1.15 (m, 60 H), 0.94–0.79 (m, 12 H). ¹³C NMR (101 MHz, CDCl₃, δ): 149.0, 148.7, 148.1, 143.7, 140.3, 135.0, 133.8, 129.9, 128.3, 118.9, 109.8, 104.5, 83.2, 69.1, 31.3, 31,2, 29.0, 28.9, 28.8, 28.7, 25.6, 25.4, 24.3, 22.2, 22.1, 13.6, 13.5. Anal. Calcd for 7 (%): C, 76.65; H, 9.51. Found: C, 77.15; H, 9.18. MALDI-TOF MS: m/z 1080.8. Melting point: 142-144 °C.

Di(4-bromophenyl) Sulfide (8).¹⁵ 4-Bromoiodobenzene (11.3 g, 40.00 mmol), Na₂S·9H₂O (5.8 g, 24.00 mmol), CuI (760.0 mg, 4.00 mmol), and K₂CO₃ (5.5 g, 40.00 mmol) in 80 mL of DMF under argon were stirred at 120 °C for 18 h. Then the resulting mixture was poured into 200 mL of water and extracted with dichloromethane. The combined organic layer was dried with Na₂SO₄ and then concentrated under vacuum. The residue was purified by column chromatography to give a white solid (4.1 g, yield 60%). ¹H NMR (400 MHz, CDCl₃, δ): 7.43 (d, *J* = 8.3 Hz, 4 H), 7.19 (d, *J* = 8.3 Hz, 4 H).

Di(4-bromophenyl) Sulfone (9). Di(4-bromophenyl)sulfide (3.4 g, 9.88 mmol), 30% hydrogen peroxide (50 mL), and CH₃COOH (100 mL) were stirred continuously at 100 °C for 10 h. Then the resulting mixture was poured into 500 mL of water and extracted with dichloromethane. The combined organic layer was dried with Na₂SO₄. After removal of the solvent, the product was purified by column chromatography and recrystallized from hexane to give a white solid (3.4 g, yield 90%). ¹H NMR (400 MHz, CDCl₃, δ): 7.78 (d, *J* = 8.0 Hz, 4 H), 7.65 (d, *J* = 8.0 Hz, 4 H). ¹³C NMR (101 MHz, CDCl₃, δ): 139.7, 132.2, 128.7, 128.3. Anal. Calcd for 9 (%): C, 38.33; H, 2.14. Found: C, 38.50; H, 2.45. GC–MS: *m*/*z* 374, 376, 378. Melting point: 171–172 °C.

General Procedures of Suzuki Polycondensation Taking PSFDPSO01 as an Example. A mixture of monomer 7 (270.3 mg, 0.25 mmol), monomer 6 (241.8 mg, 0.245 mmol), monomer 9 (1.9 mg, 0.005 mmol), Pd₂(dba)₃ (0.9 mg), Aliquat 336 (20.0 mg), and 2dicyclohexylphosphino-2',6'-dimethoxybiphenyl (3.2 mg) were dissolved in a mixture of toluene (6 mL) and water (2 mL) under an argon atmosphere. The mixture was heated to 95 °C and stirred for 2 h. Benzeneboronic acid (15 mg) in 3 mL of toluene was subsequently added and the mixture was refluxed for 5 h. Finally, 1 mL of bromobenzene was added, and the mixture was refluxed for 5 h. Then sodium diethyldithiocarbamate trihydrate (1.0 g) and deionized water (20 mL) were added into the mixture. The solution was kept at 80 °C with vigorous stirring under argon for 24 h. After cooling, the resulting polymer was resolved in dichloromethane, and then washed three times with deionized water. After removal of the solvent, the resulting polymers were received by precipitation in methanol. The final purification was carried out by Soxhlet extraction with acetone for about 24 h and then precipitated in methanol (370.0 mg, yield 90%). ¹H NMR (400 MHz, CDCl₃, δ): 7.86–7.79 (br, 0.3 H), 7.66 (br, 1.8

H), 7.20 (s, 2.4 H), 6.83 (s, 2.4 H), 6.12 (s, 2.6 H), 4.09 (s, 4.0 H), 3.61 (s, 3.7 H), 1.85 (s, 5.6 H), 1.60–1.46 (br, 11.9 H), 1.38–1.13 (br, 51.3 H), 0.94–0.86 (m, 8.8 H), 0.85–0.78 (m, 8.1 H). ¹³C NMR (101 MHz, CDCl₃, δ): 150.2, 149.3, 148.6, 140.9, 140.6, 140.3, 135.0, 126.9, 122.2, 119.9, 109.6, 104.9, 69.5, 69.3, 31.9, 31,7, 29.5, 29.3, 29.2, 26.2, 25.9, 22.7, 22.6, 14.1, 14.0. Anal. Calcd for PSFSO01 (%): C, 82.56; H, 9.72; S, 0.04. Found: C, 82.71; H, 9.25; S, 0.11.

PSFDPSO00. Green fiber, 370 mg. Yield: 90%. Monomer 7 (270.3 mg, 0.25 mmol) and monomer **6** (246.8 mg, 0.25 mmol) were used. ¹H NMR (400 MHz, CDCl₃, δ): 7.65 (br, 2.6 H), 7.19 (s, 2.9 H), 6.82 (s, 3.2 H), 6.11 (s, 2.8 H), 4.08 (s, 4.0 H), 3.60 (s, 3.7 H), 1.84 (s, 5.8 H), 1.58–1.45 (br, 14.6 H), 1.39–1.11 (br, 63.2 H), 0.92–0.85 (m, 10.4 H), 0.84–0.77 (m, 10.9 H). ¹³C NMR (101 MHz, CDCl₃, δ): 149.7, 148.9, 148.1, 140.1, 134.5, 126.4, 121.7, 119.4, 108.9, 104.5, 69.1, 68.8, 31.4, 31.3, 29.0, 28.8, 28.7, 25.7, 25.4, 22.2, 22.1, 13.6. Anal. Calcd for PSF (%): C, 82.56; H, 9.72. Found: C, 82.81; H, 9.62.

PSFDPSO03. Green fiber, 385 mg. Yield: 95%. Monomer 7 (270.3 mg, 0.25 mmol), monomer **6** (232.0 mg, 0.235 mmol), and monomer **9** (5.6 mg, 0.015 mmol) were used. ¹H NMR (400 MHz, CDCl₃, δ): 7.81 (br, 0.4 H), 7.66 (br, 1.8 H), 7.48 (br, 0.3 H), 7.19 (s, 2.5 H), 6.83 (s, 2.3 H), 6.11 (s, 2.4 H), 4.08 (s, 4.0 H), 3.61 (s, 3.6 H), 1.85 (s, 5.0 H), 1.63–1.46 (br, 11.4 H), 1.42–1.10 (br, 48.8 H), 0.95–0.85 (m, 8.2 H), 0.84–0.76 (m, 7.9 H). ¹³C NMR (101 MHz, CDCl₃, δ): 150.2, 149.3, 148.6, 140.8, 140.5, 140.2, 135.0, 127.7, 126.9, 122.1, 119.8, 109.5, 104.9, 69.5, 69.3, 31.8, 31,7, 29.4, 29.3, 29.1, 26.1, 25.9, 22.7, 22.6, 14.1, 14.0. Anal. Calcd for PSFSO03 (%): C, 82.43; H, 9.68; S, 0.12. Found: C, 82.70; H, 9.32; S, 0.18.

PSFDPSO05. Green fiber, 357 mg. Yield: 90%. Monomer 7 (270.3 mg, 0.25 mmol), monomer **6** (222.1 mg, 0.225 mmol), and monomer **9** (9.4 mg, 0.025 mmol) were used. ¹H NMR (400 MHz, CDCl₃, δ): 7.82 (br, 0.5 H), 7.66 (br, 1.6 H), 7.52–7.45 (br, 0.5 H), 7.19 (br, 2.4 H), 6.83 (br, 2.3 H), 6.11 (s, 2.3 H), 4.09 (s, 4.0 H), 3.61 (s, 3.8 H), 1.85 (s, 4.8 H), 1.61–1.46 (br, 11.2 H), 1.38–1.10 (br, 46.2 H), 0.92–0.86 (m, 7.8 H), 0.84–0.77 (m, 7.5 H). ¹³C NMR (101 MHz, CDCl₃, δ): 150.2, 149.3, 148.6, 140.8, 140.5, 140.4, 135.0, 127.8, 126.9, 122.2, 119.9, 109.6, 104.9, 69.5, 69.3, 31.8, 31,7, 29.4, 29.3, 29.1, 26.1, 25.9, 22.7, 22.6, 14.1, 14.0. Anal. Calcd for PSFSO05 (%): C, 82.33; H, 9.65; S, 0.20. Found: C, 82.98; H, 9.33; S, 0.23.

PSFDPSO07. Green fiber, 344 mg. Yield: 88%. Monomer 7 (270.3 mg, 0.25 mmol), monomer **6** (212.2 mg, 0.215 mmol), and monomer **9** (13.2 mg, 0.035 mmol) were used. ¹H NMR (400 MHz, CDCl₃, δ): 7.82 (br, 0.7 H), 7.66 (br, 1.5 H), 7.52–7.45 (br, 0.6 H), 7.19 (br, 2.4 H), 6.95–6.77 (br, 2.3 H), 6.16–6.09 (br, 2.3 H), 4.08 (s, 4.0 H), 3.61 (s, 3.8 H), 1.85 (s, 5.3 H), 1.67–1.45 (br, 12.2 H), 1.42–1.12 (br, 53.6 H), 0.91–0.86 (m, 10.2 H), 0.84–0.79 (m, 8.6 H). ¹³C NMR (101 MHz, CDCl₃, δ): 150.2, 149.3, 148.6, 141.0, 140.6, 140.3, 135.0, 127.9, 126.9, 122.2, 119.9, 109.6, 104.9, 69.5, 69.3, 31.8, 31,7, 29.5, 29.3, 29.2, 26.2, 25.9, 22.7, 22.6, 14.1, 14.0. Anal. Calcd for PSFSO07 (%): C, 82.24; H, 9.62; S, 0.29. Found: C, 82.58; H, 9.40; S, 0.33.

PSFDPSO10. Green fiber, 324 mg. Yield: 85%. Monomer 7 (270.3 mg, 0.25 mmol), monomer 6 (197.4 mg, 0.20 mmol), and monomer 9 (18.8 mg, 0.05 mmol) were used. ¹H NMR (400 MHz, CDCl₃, δ): 7.82 (br, 0.8 H), 7.71–7.63 (br, 1.6 H), 7.53–7.47 (br, 0.8 H), 7.19 (br, 2.3 H), 6.98–6.77 (br, 2.3 H), 6.11 (br, 2.3 H), 4.09 (s, 4.0 H), 3.61 (s, 3.9 H), 1.85 (s, 4.7 H), 1.66–1.45 (br, 10.9 H), 1.37–1.10 (br, 44.6 H), 0.91–0.86 (m, 7.4 H), 0.84–0.79 (m, 7.1 H). ¹³C NMR (101 MHz, CDCl₃, δ): 150.2, 149.3, 148.6, 140.9, 140.5, 140.3, 135.0, 127.7, 126.9, 122.2, 119.9, 109.6, 104.9, 69.5, 69.3, 31.8, 31,7, 29.4, 29.3, 29.1, 26.1, 25.9, 22.7, 22.6, 14.1, 14.0. Anal. Calcd for PSFSO10 (%): C, 82.09; H, 9.58; S, 0.42. Found: C, 82.34; H, 9.25; S, 0.44.

ASSOCIATED CONTENT

S Supporting Information

DSC curves of the polymers, solution PL spectra, HOMO and LUMO distributions, and ¹H NMR and ¹³C NMR spectra. This material is available free of charge via the Internet at http:// pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

*(J.D.) E-mail: junqiaod@ciac.ac.cn. *(L.W.) E-mail: lixiang@ciac.ac.cn.

Notes

The authors declare no competing financial interest.

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