# "One-Pot" Synthesis of a Thermally Stable Blue Emitter: Poly[spiro(fluorene-9,9′-(2′-phenoxyxanthene)]

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*Introduction.* Luminescent organic materials have long been the focus of intense academic and industrial research and are currently being investigated in applications ranging from organic light-emitting diodes, organic photovoltaics, organic thin-film transistors, lasers, and sensors. To meet these demands, high-molecular-weight blue-emitting poly(*p*-phenylene) (PPP) materials including, ladder-type PPPs, polyfluorenes (PF), polyindenofluorenes (PIFs), and polytetrahydrophenanthrene (PTHP) are being extensively studied.[1] Alkyl-substituted PFs are promising materials, in particular, the dioctyl-substituted polymer (polydioctylfluorene, PFO) is the "workhorse" material in this field.[1] While PF materials are strong candidates for optoelectronic applications, their spectral instability or their tendency to exhibit green emission upon thermal stress remains a significant challenge and could limit the realization of their full potential.

The origin of PFs spectral instability has been attributed to morphological and/or oxidative instability, resulting in low-energy excimer or fluorenone-based emission, respectively.[2] A variety of approaches toward achieving color purity have appeared in the literature and include, but are not limited to, monomer purification,[3] polymer blending,[4] nanoparticle doping,[5−9] copolymerization,[10,11] incorporation of sterically demanding groups,[12] and functionalization with thermally stable[13−17] and spiro moieties.[18−20]

Spiro-containing materials, in which a common $sp^3$-hybridized atom links two orthogonally oriented $\pi$-systems, have been shown to stabilize blue emission in low-molecular-weight spirobifluorene (SBF) compounds by blocking efficient crystallization from the amorphous state.[21] This success has led to the incorporation of spiro moieties into polymeric systems such as polyspirobifluorene[22−29] (PSBF) and polyspiroanthracenefluorene[18,30,31] (PSAF), resulting in increased spectral stability. In addition to PSBF and PSAF polymers, a new class of blue-emitting low-molecular-weight spirofluorenexanthene[19] (SFX) and high-molecular-weight polyspirofluorenexanthene[20] (PSFX) materials, prepared through one-pot methodologies, have recently appeared in the literature. These xanthene-containing materials have only recently appeared due to a limited number of reports outlining their efficient synthesis. Consequently, detailed studies of SFX and PSFX material properties are limited.[19,20] Xie et al. reported a one-pot synthesis in which a one-step condensation reaction of 2,7-dibromo-9-fluorenone in the presence of phenol and methanesulfonic acid at high temperatures (ca. 150 °C) yielded spiro[fluorene-9,9′-xanthene], SFX.[19] A low-molecular-weight blue-emitting material prepared from SFX displayed good oxidative stability after annealing for 12 h at 150 °C. However, no high-molecular-weight polymers were reported. Consequently, it remains unknown if the oxidative stability of the low-molecular-weight material will be manifested in the polymer.[19] In another recent report, Tseng et al. were able to prepare alkyl-substituted high-molecular-weight poly[spiro(fluorene-9,9′-xanthene)], PSFX. They conducted a one-step condensation reaction of 2,7-dibromo-9-fluorenone with resorcinol in the presence of $ZnCl_2$/HCl to prepare the monomer. Subsequent polymerization yielded polymers of limited solubility in common organic solvents.[20] Thermal properties were investigated by thermogravimetric analysis (TGA) revealing 5 and 10% weight losses of 411 and 433 °C, respectively. Thermal annealing studies conducted under a nitrogen environment showed no long wavelength emission. However, ambient studies were not reported; therefore, their oxidative stability is unknown.[20]

In an effort to prepare PFs with increased oxidative stability and consequently increased spectral stability, we sought to introduce aromatic ethers (AE) at the 9,9′-position. AEs are well-known engineering thermoplastics that find applications wherever high thermal, chemical, irradiative, and oxidative stability are required.[32] In an effort to prepare AE-containing PFs utilizing a methodology developed for preparing phenol substituted fluorenes,[33] we discovered that combining 2,7-dibromo-9-fluoreneone with 1,3-diphenoxybenzene in the presence of methanesulfonic acid and a catalytic amount of 3-mercaptopropionic acid led directly to an AE-substituted SFX species 2,7-dibromo-spiro(fluorene-9,9′-(2′-phenoxyxanthene)) AE-SFX (Scheme 1). Subsequent polymerization afforded an AE-substituted PSFX material, poly[spiro(fluorene-9,9′-xanthene)] AE-PSFX, possessing excellent solubility in common organic solvents and excellent thermal and oxidative stability.

*Results and Discussion. Synthesis and Characterization of AE-SFX.* As illustrated in Scheme 1, reacting 2,7-dibromofluorene-9-one[34] with a 10-fold excess of 1,3-diphenoxybenzene allowed for the preparation of AE-SFX. After isolating a white powder, we were able to grow suitable single crystals for single-crystal X-ray diffraction (Figure SI-1 of the Supporting Information). Of particular note, the orthogonal disposition of the fluorene and xanthene ring systems, along with the asymmetry generated by the lone aromatic ether group, should lead to increased solubility of the polymer. The structure was also confirmed with $^1$H NMR and $^{13}$C NMR spectroscopy. The aromatic hydrogen and carbon atoms were readily assigned by analysis of the $^1$H (Figure SI-2) and $^{13}$C NMR (Figure SI-3) spectra as well as 2D NMR experiments, including $^1$H−$^1$H correlation spectroscopy ($^1$H-COSY) (Figure SI-4) and long-range (HMBC) (Figure SI-5) and short-range (HMQC) (Figure SI-6) $^1$H−$^{13}$C heteronuclear correlation spectroscopy. In addition, high-resolution mass spectrometric data (Figure SI-7) and elemental analysis support the structure.

*Synthesis and Characterization of AE-PSFX.* Subsequent polymerization of AE-SFX under Yamamoto coupling conditions[35] produced blue-emitting poly[spiro(fluorene-9,9′-(2′-phenoxyxanthene)], AE-PSFX, polymers, as shown in Scheme 1. In contrast to other reports of PSFX materials,[19,20] AE-PSFX is very soluble at room temperature in common organic solvents such as chloroform, toluene, and THF. Gel-permeation chromatography (GPC) (Figure SI-8) of AE-PSFX shows a monomodal molecular weight distribution with a number-average molecular weight ($M_n$) of 34 000 and weight-average molecular

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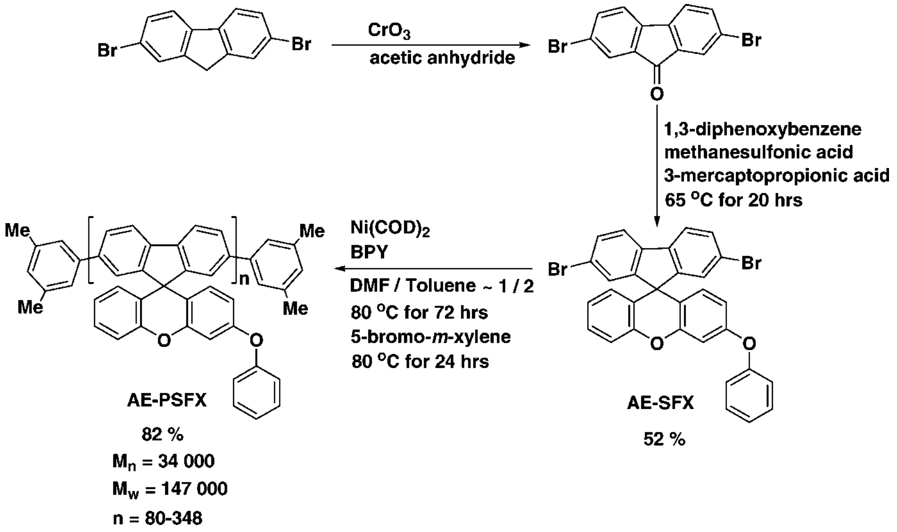
**Scheme 1. Synthetic Route to AE-PSFX**



weight ($M_w$) of 147 000. This corresponds to $M_n$ and $M_w$ degree of polymerizations of approximately 80 and 348, respectively, and a polydispersity index (PDI) of 4.3. The high polydispersity may play a role in our observation of increased solubility in common organic solvents. The polymer was also characterized by $^1$H NMR (Figure SI-9) and $^{13}$C NMR (Figure SI-10) spectroscopy.

*Optical and Thermal/Oxidative Properties of AE-PSFX. UV−Vis Absorption and Photoluminescence of AE-PSFX.* The absorption and photoluminescence (PL) spectra of a 0.0005% w/v toluene solution of AE-PSFX are consistent with PF-type materials; the absorption maximum and the 0−0 PL vibronic transition occur at 396 and 419 nm, respectively (Figure SI-11).

*Thermal Stability of AE-PSFX.* The thermal stability of AE-PSFX was investigated by TGA under a nitrogen atmosphere at a heating rate of 10 °C/min, as shown in Figure 1. AE-PSFX exhibits greater thermal stability, with 5 and 10% weight loss values of 536 and 577 °C, respectively, in comparison to PFO, with 5 and 10% weight loss values of 404 and 420 °C, respectively.

*Photoluminescence Stability of AE-PSFX under Thermal Stress.* To investigate the spectral stability of AE-PSFX when thermally stressed, we conducted studies in an argon-filled glovebox and followed the evolution of its photoluminescence spectra when heated to 200 °C. Figure 2 illustrates the normalized PL spectra of an AE-PSFX film drop-coated from a 0.5% w/v toluene solution onto a quartz disk. Thermal annealing of the film for 20, 40, 60, and 80 h in an argon-filled glovebox demonstrates its spectral stability. As expected, thermal processing leads to small spectral variations in the region of 400−500 nm. The stable blue emission and the absence of a green emission band after prolonged heating highlight the stability of AE-PSFX to excimer formation. We applied identical thermal stresses to PFO to directly compare the two materials. A film of PFO subjected to the same conditions clearly illustrates its spectral instability; exhibiting an increase in intensity at ~550 nm which we attribute to excimer formation (Figure SI-12).[36,37] Therefore, thermal annealing under an argon atmosphere demonstrates the improved spectral stability of AE-PSFX in contrast to PFO.

*Photoluminescence Stability of AE-PSFX under Thermal Oxidative Stress.* To investigate the oxidative stability of AE-PSFX when thermally stressed, we heated a drop-coated film of AE-PSFX on a hot plate at 150 °C, under ambient conditions, for predetermined periods of time and followed the evolution of its photoluminescence spectra. As illustrated in Figure 3, AE-PSFX continues to display a strong blue emission after 3 h of annealing and a substantially smaller increase in green emission at ~550 nm, in contrast to PFO (Figure SI-13). On the basis of the present observation that no green emission arises upon thermal stressing in inert atmosphere (vide supra), we propose

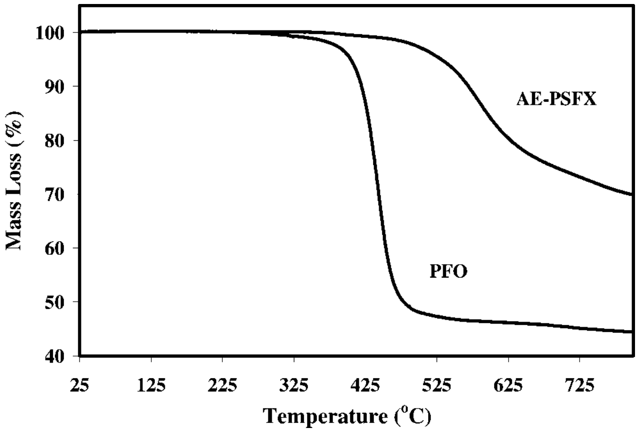


**Figure 1.** TGA curves of AE-PSFX and PFO under a $N_2$ atmosphere at a heating rate of 10 °C/min.

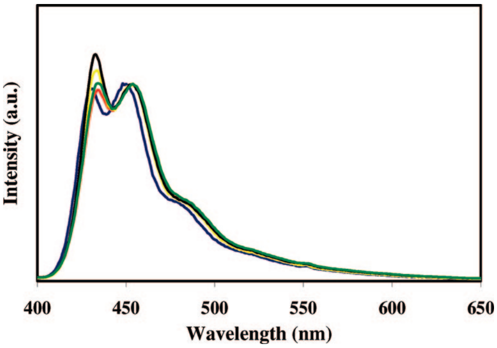


**Figure 2.** PL spectra ($\lambda_{ex}$ = 350 nm) of a AE-PSFX film before (blue) and after annealing at 200 °C for 20 h (red), 40 h (yellow), 60 h (black), and 80 h (green) under an argon atmosphere.

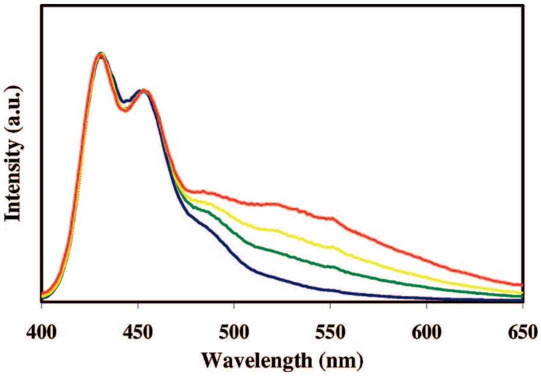


**Figure 3.** PL spectra of a AE-PSFX film before (blue) and after annealing for 1 h (green), 2 h (yellow), and 3 h (red) at 150 °C under ambient conditions.

this spectral change does not arise solely from excimer formation and that an as-of-yet unidentified oxidized species gives rise to this emission. Of particular note and for comparison purposes, the present AE-PSFX shows a weak green emission after 1 h, whereas PFO shows an intense green emission (ca. 550 nm) after only 20 min of annealing.

*Conclusions.* The direct incorporation of AE functionality into SFX-containing materials from readily available starting materials has allowed for the preparation of a high-molecular-weight, room-temperature soluble, thermally stable material with good oxidative stability. This is the first report of a highly soluble SFX material exhibiting excellent thermal and oxidative stability. We are currently exploring the scope of the above chemistry in an effort to prepare other PSFX materials with improved thermal and oxidative properties. In addition, we are currently investigating the solution and solid-state properties of AE-PSFX to gain detailed structure/property relationships on this minimally studied class of PSFX materials.

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**Supporting Information Available:** Experimental procedure for AE-SFX and AE-PSFX and $^{1}$H and $^{13}$C NMR spectra, 2D NMR spectra, MS data, GPC, and X-ray crystallographic file (CIF) for AE-SFX. This material is available free of charge via the Internet at http://pubs.acs.org.

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