# Macromolecules

# On the Degradation Process Involving Polyfluorenes and the Factors Governing Their Spectral Stability

Roberto Grisorio, Giovanni Allegretta, Piero Mastrorilli,\* and Gian Paolo Suranna

Department of Water Engineering and of Chemistry, Polytechnic of Bari, Campus Universitario, via Orabona 4, 70125 Bari, Italy

**ABSTRACT:** This study deals with an investigation of the spectral stability of differently structured polyfluorenes (**PFs**), deprived of 9-H defects, embodying 9,9-dialkylfluorene (**P1**), 9,9-diarylfluorene (**P2**), or 9,9-diarylfluorene/9,9-dibenzylfluorene units in a 1:1 alternating fashion (**P3**). Thermal annealing or UV irradiation carried out on films of **P1**–**P3** in air revealed that their typical blue photoluminescence is invariably stained, independently of their 9-substitution, by the appearance of the low-energy band (g-band) pointing out a remarkable effect of light on the degradation pathway is proposed, including as key



step a light-promoted formation of a PF radical cation generated by aerobic oxidation (photoluminescence test) or p-doping (cyclic voltammetry test). The blue emission of P1–P3 could successfully be preserved by dispersing them into a higher band gap matrix, such as polyvinylcarbazole (PVK), indicating a fundamental role of the intermolecular interactions between PF chains in the appearance of the low-energy emission band. Comparison between the optical behavior of suitably prepared **PFs** containing either fluorenone moieties (**PFK**) or 9-(bis-methylsulfanyl-methylene)fluorene moieties (**PFS**) holds regions of planarity within the PF backbone (inducing local intermolecular interactions) and not the fluorenone charge-transfer emission as responsible of the g-band of degraded **PFs**.

## ■ INTRODUCTION

During the past years, the research interest concerning polyfluorenes (**PFs**)<sup>1</sup> has produced numerous studies focused on the appearance, under oxidative conditions, of an unwanted green emission (the so-called "g-band") at 520-535 nm accompanying their typical blue emission. An intense research impulse has therefore been directed to understand the origin of this spectral instability of fluorene-based materials, with the aim of suppressing it to successfully employ PFs as blue emitters in OLED devices. After a decade-long debate, it is now generally accepted that the appearance of the g-band is correlated with the formation of 9-fluorenone units in the polymer backbone,<sup>2</sup> though the exact role of these units, named keto defects, remains so far not completely clear. The hypothesis according to which the fluorenone unit constitutes a potential green-emitting site (on-chain emission) has been supported by theoretical calculations<sup>3</sup> associating the low-energy emission band to a charge-transfer (CT) state deriving from the presence of carbonyl moieties.<sup>4</sup> On the basis of these assumptions, the g-band emission intensity would mainly be governed by the ease with which the fluorenone excited states can be populated by energy transfer. However, the sole formation of fluorenone units in the course of an oxidative degradation of a PF is not sufficient to cause the appearance of the g-band. For instance, it has been noted that the g-band is suppressed in fluorenone-containing polymers bearing bulky substituents. This observation was attributed to the frustration of the interchain packing between PF units, hindering an efficient energy transfer toward fluorenone emitters.<sup>5</sup> Thus, a lively research

has concentrated on the synthesis of **PFs** functionalized with bulky substituents in order to hamper intermolecular interactions, thereby limiting the evolution of the g-band.<sup>6</sup> It is worth noting that the PF functionalization with bulky substituents can be successful also under the alternative hypothesis explaining the g-band emergence in terms of an emission from fluorenone-based excimers,<sup>7</sup> rather than from on-chain defects.

Parallel to the search for the origin of the g-band, the mechanisms of PFs oxidative degradation, which are equally important in order to rationalize the spectral instability of this class of polymers, have also been extensively studied. Oxidation to 9-fluorenone is a favorable process due to the resonance stabilization deriving from the extension of the  $\pi$ -conjugated system. The preferred sites of oxidation in PFs have been individuated in their 9-H defects (i.e., the fluorene units embodying a hydrogen atom at the C-9 position) invariably present in the polymer as a consequence of an incomplete purification of the dialkylfluorene monomer feed.<sup>8</sup> To circumvent this drawback, two main strategies have been proposed: (i) the thorough purification of the fluorene monomers<sup>9</sup> or (ii) the employment of specifically designed synthetic approaches that avoid any fluorene alkylation step to obtain fully C-9 disubstituted fluorene units.<sup>10</sup> However, the appearance of the g-band has been recently reported also for defect-free oligofluorenes,<sup>11</sup> highlighting that the great advantages

Received:	July 1, 2011
Revised:	August 30, 2011
Published:	September 26, 2011

associated with the presence of the highly reactive C-9 on fluorene (e.g., its easy functionalization) unfortunately also represent the weakness point of **PFs**, indicating the necessity of an ultimate effort for the rationalization of the degradation mechanisms involving fluorene-based materials.

In the course of the years, the original motivation for the studies on **PFs** spectral instability (their use as blue OLEDs) has gradually shifted toward the mandatory need to explore more generally the fate of an organic semiconductor under p-doping conditions which, in perspective, is of transversal interest for any organic electronics application, including solar cells and field effect transistors. On these basis, we decided to study the spectral stability of suitably chosen **PFs** endowed with different C-9 functionalization focusing on the degradation mechanisms and on the role of intermolecular interactions in **PFs** spectral instability.

We have addressed our attention on three **PFs** embodying 9,9dialkyl-, 9,9-diaryl-, or 9,9-dibenzylfluorene units. The polymers were prepared starting from dibromofluorene monomers thoroughly purified from their 9-H defects, in order to correlate the spectral behavior solely to the fluorene C-9 substitution. This study allowed us to sketch new pathways for the degradation of **PFs** and to suggest a pivotal role of intermolecular interactions between adjacent backbones in the appearance of the low-energy emission band.

### EXPERIMENTAL SECTION

All syntheses were carried out under an inert nitrogen atmosphere using Schlenk techniques. All solvents were carefully dried and freshly distilled. All reactants were purchased by commercial sources and used without further purifications. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded at 295 K on a Bruker Avance 400 MHz spectrometer; chemical shifts are reported in ppm referenced to SiMe<sub>4</sub>. UV-vis spectra were recorded on a Jasco V-670 instrument, and fluorescence spectra were obtained on a Varian Cary Eclipse spectrofluorimeter. To prepare the polymer films submitted to spectral stability test in the solid state, the materials were deposited on quartz substrates by spin-coating (2000 rpm) a drop of 5 a mg/mL solution of the polymer in CHCl<sub>3</sub>. UV-photodecomposition experiments were carried out by irradiating the sample with a 150 W high-pressure Hg lamp for 30 min. Thermogravimetric analyses (TGA) were carried out on a Perkin-Elmer Pyris TGA 6 thermobalance. GPC analyses were carried out on an Agilent Series 1100 instrument equipped with a Pl-gel 5  $\mu$ m mixed-C column. THF solutions for GPC analysis were eluted at 25 °C at a flow rate of 1.0 mL/min and analyzed using a multiple wave detector. Molecular weights and molecular weight distributions are relative to polystyrene. Cyclic voltammetry (CV) was carried out under an inert nitrogen atmosphere with an Autolab PGSTAT 100 potentiostat using a three-electrode cell consisting of a platinum disk as a working electrode, a platinum wire as counter electrode, and a Ag/Ag<sup>+</sup> electrode as pseudoreference electrode. The CV measurements were carried out in dry acetonitrile solutions of tetrabutylammonium tetrafluoroborate (0.10 M).

**2,7-Dibromo-9,9-dihexylfluorene (1).** A suspension of 2,7-dibromofluorene (10.93 g, 33.73 mmol) and tetrabutylammonium bromide (3.62 g, 11.25 mmol) in a 50 wt % NaOH aqueous solution (75 mL) was stirred for 15 min at 60 °C. To the red suspension, *n*-hexyl bromide (11.69 g, 70.84 mmol) was added, and the mixture was kept under stirring overnight. After cooling the solution, the product was extracted with diethyl ether ( $3 \times 75$  mL) and the organic layer dried over Na<sub>2</sub>SO<sub>4</sub>. After removing the solvent under vacuum, the crude product was submitted to flash chromatography (SiO<sub>2</sub>, petroleum ether 40–60 °C) to afford 1 in 92% yield as white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.54 (d, *J* = 8.9 Hz, 2H), 7.50–7.45 (m, 4H), 1.99–1.91 (m, 4H), 1.21–1.02 (m, 12H), 0.83 (t, *J* = 7.0 Hz, 6H), 0.68–0.58 (m, 4H). <sup>13</sup>C{<sup>1</sup>H}

NMR (101 MHz, CDCl<sub>3</sub>): δ 152.6, 139.1, 130.2, 126.2, 121.5, 121.1, 55.7, 40.2, 31.5, 29.6, 23.7, 22.6, 14.0.

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-9,9dihexylfluorene (2). To a solution of 1 (4.00 g, 8.12 mmol) in THF (80 mL) kept at -80 °C, a solution of n-BuLi (1.6 M in hexanes, 15.2 mL, 24.36 mmol) was added dropwise. The obtained mixture was vigorously stirred for 1 h at -80 °C before the addition of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.53 g, 24.36 mmol) in one portion. The resulting solution was then allowed to reach room temperature and to react for further 4 h. After removing the solvent under vacuum,  $CH_2Cl_2$  (50 mL) was added, and the obtained solution was washed with water  $(3 \times 50 \text{ mL})$  and dried over Na<sub>2</sub>SO<sub>4</sub>. After removing the solvent under vacuum, the obtained crude product was purified by flash column chromatography (SiO<sub>2</sub>, petroleum ether  $40-60 \text{ °C/CH}_2\text{Cl}_2 = 2/1$ ) to give 2 (3.55 g, 74%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.85–7.79 (m, 2H), 7.78–7.70 (m, 4H), 2.06-1.97 (m, 4H), 1.40 (s, 24H), 1.15-0.95 (m, 12H), 0.76 (t, J = 7.3 Hz, 6H), 0.61–0.50 (m, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) 150.5, 143.9, 133.7, 128.9, 119.4, 83.8, 55.2, 40.1, 31.5, 29.7, 24.9, 23.6, 22.6, 14.1.

**2,7-Dibromo-9,9-dibenzylfluorene (3).** A suspension of 2,7-dibromofluorene (1.00 g, 3.09 mmol) and tetrabutylammonium bromide (1.61 g, 5.00 mmol) in a 50 wt % NaOH aqueous solution (20 mL) was stirred for 15 min at 60 °C. To the red suspension, benzyl bromide (6.18 g, 32.00 mmol) was added, and the mixture was kept under stirring overnight. After cooling the solution, the product was extracted with diethyl ether (3 × 75 mL) and the organic layer dried over Na<sub>2</sub>SO<sub>4</sub>. After removing the solvent under vacuum, the crude product was submitted to flash chromatography (SiO<sub>2</sub>, petroleum ether 40–60 °C) to afford 3 (1.12 g, 72%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.53 (s, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.06–6.95 (m, 6H), 6.68 (d, *J* = 6.3 Hz, 4H), 3.34 (s, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 150.2, 138.8, 136.1, 130.4, 130.2, 128.0, 127.4, 126.3, 121.2, 120.6, 57.2, 45.2.

**2,7-Dibromo-9,9-bis(4-hydroxyphenyl)fluorene (4).** A mixture of 2,7-dibromofluoren-9-one<sup>12</sup> (7.05 g, 20.9 mmol), phenol (19.7 g, 0.209 mol), and methansulfonic acid (30 mL) was heated to 50 °C overnight. After cooling to room temperature, the mixture was poured into water. The obtained solid was filtered and washed with water several times. The desired product 4 (9.63 g, 91%) was obtained by precipitation from ethyl acetate into petroleum ether as a brownish solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.71 (d, 2H), 7.49 (dd, 2H), 7.44 (d, 2H), 6.94 (m, 4H), 6.68 (m, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 158.2, 153.8, 137.9, 136.3, 130.7, 129.3, 129.0, 121.8, 121.6, 114.3, 64.4.

**2,7-Dibromo-9,9-bis(4-hexyloxyphenyl)fluorene (5).** A mixture of 4 (8.40 g, 16.5 mmol), NaOH (1.44 g, 36.3 mmol), 1-bromohexane (6.00 g, 36.3 mmol), and THF (30 mL) was stirred at 50 °C overnight. After cooling the solution down to room temperature, diethyl ether (60 mL) was added. The organic phase was washed with water (3 × 60 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. After solvent removal, the crude product was purified by flash chromatography (SiO<sub>2</sub>, petroleum ether 40–60 °C/CH<sub>2</sub>Cl<sub>2</sub> = 4/1 v/v) yielding **5** (4.20 g, 38%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.56 (d, *J* = 8.5 Hz, 2H), 7.48–7.43 (m, 4H), 7.05 (d, *J* = 8.5 Hz, 4H), 6.77 (d, *J* = 8.5 Hz, 4H), 3.90 (t, *J* = 6.7 Hz, 4H), 1.75 (m, *J* = 6.7 Hz, 4H), 1.48–1.27 (m, 12H), 0.93–0.86 (m, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 158.2, 153.8, 137.9, 136.3, 130.7, 129.3, 129.0, 121.8, 121.6, 114.3, 68.0, 64.4, 31.6, 29.2, 25.8, 22.6, 14.1.

**2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-9,9-bis(4-hexyloxyphenyl)fluorene (6).** To a solution of **5** (2.97 g, 4.39 mmol) in THF (80 mL) kept at -80 °C, a solution of *n*-BuLi (1.6 M in hexanes, 8.2 mL, 13.17 mmol) was added dropwise. The obtained mixture was vigorously stirred for 1 h at -80 °C before the addition of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.45 g, 13.17 mmol) in one portion. The resulting solution was then allowed to reach room

#### Scheme 1. Synthesis of $P1-P3^a$



<sup>*a*</sup> Reagents and conditions: (i) NaOH<sub>aq</sub> (50 wt %), TBAB, *n*-hexyl bromide, 60 °C; (ii) *n*-BuLi, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, -80 °C; (iii) NaOH<sub>(aq)</sub> (50 wt %), TBAB, benzyl bromide, 60 °C; (iv) phenol, CH<sub>3</sub>SO<sub>3</sub>H, 80 °C; (v) *n*-hexyl bromide, NaOH, 50 °C; (vi) Pd(PPh<sub>3</sub>)<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub> 2 M, reflux.

temperature and to react for further 4 h. After removing the solvent under vacuum, CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added, and the obtained solution was washed with water (3 × 50 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. After removing the solvent under vacuum, the obtained crude product was purified by flash column chromatography (SiO<sub>2</sub>, petroleum ether 40– 60 °C/CH<sub>2</sub>Cl<sub>2</sub> = 1/1 v/v) to give 6 (1.05 g, 31%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.78–7.74 (m, 6H), 7.14 (d, *J* = 8.5 Hz, 4H), 6.75 (d, *J* = 9.5 Hz, 4H), 3.90 (t, *J* = 6.7 Hz, 4H), 1.50–1.25 (m, 36H), 0.91 (t, *J* = 7.3 Hz, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 157.7, 151.9, 142.6, 137.7, 134.1, 132.2, 129.4, 119.8, 114.0, 83.7, 67.9, 64.2, 31.6, 29.3, 25.8, 24.9, 22.6, 14.1.

**Poly**[2,7-(9,9-dihexylfluorene)] (P1). A mixture of 1 (123 mg, 0.25 mmol), 2 (147 mg, 0.25 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (6 mg,  $0.5 \times 10^{-2}$  mmol) in a 2.0 M Na<sub>2</sub>CO<sub>3</sub> aqueous solution (2.5 mL) and toluene (4.5 mL) was refluxed for 72 h. After cooling the solution, the reaction mixture was poured into a beaker containing methanol (200 mL), causing the precipitation of the polymer which was filtered off, washed with methanol, and reprecipitated with methanol. The obtained solid was then dried under vacuum at 60 °C for 24 h to give P1 as an off-white powder in 69% yield. GPC (THF):  $M_n = 12\,600$  Da,  $M_w = 24\,300$  Da, D = 1.9. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.91–7.81 (m, 2H), 7.77–7.62 (m, 4H), 2.25–1.99 (m, 4H), 1.25–1.05 (m, 12H), 0.92–0.72 (m, 10H).

**Poly**{2,7-[9,9-bis(4-hexyloxyphenyl)fluorene]} (P2). Following the procedure reported for P1, this polymer was synthesized

starting from **5** and **6** in 71% yield as an off-white solid. GPC (THF):  $M_n = 12\ 000\ Da, M_w = 28\ 400\ Da, D = 2.4.$ <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.81–7.71 (m, 2H), 7.63–7.47 (m, 4H), 7.24–7.11 (m, 4H), 6.82–6.72 (m, 4H), 3.98–3.87 (m, 4H), 1.81–1.70 (m, 4H), 1.49–1.38 (m, 4H), 1.37–1.26 (m, 8H), 0.94–0.85 (m, 6H).

Poly{2,7-[9,9-bis(4-hexyloxyphenyl)fluorene]-*alt*-2,7-(9,9dibenzylfluorene)} (P3). Following the procedure reported for P1, this polymer was synthesized starting from 6 and 3 in 46% yield as an offwhite solid. GPC (THF):  $M_n = 15\,000\,Da$ ,  $M_w = 36\,000\,Da$ , D = 2.4. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.95 (m, 2H), 7.75–7.63 (m, 4H), 7.57–7.45 (m, 6H), 7.36–7.29 (m, 4H), 7.01–6.78 (m, 14H), 3.98–3.87 (m, 4H), 3.60–3.43 (m, 4H), 1.81–1.70 (m, 4H), 1.49–1.38 (m, 4H), 1.37–1.26 (m, 8H), 0.94–0.85 (m, 6H).

**Poly[2,7-(9,9-dihexylfluorene)**-*co*-2,7-(fluoren-9-one)] (PFK). Following the procedure reported for P1, this polymer was synthesized starting from 2 (mole fraction = 0.50), 1 (mole fraction = 0.45), and 2,7-dibromofluoren-9-one (mole fraction = 0.05) in 69% yield as a pale yellow powder. GPC (THF):  $M_n$  = 16 000 Da,  $M_w$  = 38 000 Da, D = 2.4) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.91–7.81 (m, 2H), 7.77–7.62 (m, 4H), 2.25–1.99 (m, 4H), 1.25–1.05 (m, 12H), 0.92–0.72 (m, 10H).

Poly{2,7-(9,9-dihexylfluorene)-*co*-2,7-[9-(bis-methylsulfanylmethylene)fluorene]} (PFS). Following the procedure reported for P1, this polymer was synthesized starting from 2 (mole fraction = 0.50), 1 (mole fraction = 0.45), and 2,7-dibromo-9-(bis-methylsulfanylmethylene)fluorene (mole fraction = 0.05) in 51% yield as a pale yellow powder. GPC (THF):  $M_n = 10500$  Da,  $M_w = 23500$  Da, D = 2.2. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.96–7.83 (m, 2H), 7.77–7.49 (m, 10H), 7.22–6.67 (m, 10H), 3.60–3.43 (m, 4H), 2.28–2.11 (m, 4H), 1.30–1.13 (m, 12H), 0.91–0.73 (m, 10H).

#### RESULTS AND DISCUSSION

Polymer Synthesis and Characterization. The polymers chosen to compare the effect of different C-9 substitutions on the spectral behavior embodied (i) *n*-hexyl chains, which are easily subject to radical degradation that ends up in fluorene C-9 oxidation; (ii) 4-hexyloxyphenyl chains, as bulky substituents which also constitute a barrier to the radical C-9 oxidation; (iii) 4-hexyloxyphenyl and benzyl chains, the latter of which are bulky substituents albeit easily subject to radical degradation. The three PFs (Scheme 1) were thus the homopolymers poly[2,7-(9,9-di*n*-hexylfluorene)] (P1) and poly{2,7-[9,9-bis(4-hexyloxyphenyl)fluorene]  $\{P2\}$  as well as the alternating copolymer poly  $\{2,7-[9,9$ bis(4-hexyloxyphenyl)fluorene]-*alt*-2,7-(9,9-dibenzylfluorene)} (P3). The obtainment of 2,7-dibromo-9,9-di-*n*-hexylfluorene (1) and 2,7-dibromo-9,9-dibenzylfluorene (3) was achieved by a straightforward alkylation of 2,7-dibromofluorene with n-hexyl bromide or benzyl bromide, respectively. In order to evaluate the effect of the C-9 substitution on the spectral stability of P1-P3 excluding any possible contribution of 9-H defects, care was taken to obtain the above-mentioned polymers deprived of such defects. To this purpose, monomers 1 and 3 were thoroughly purified following Meijer procedure.9 After the standard column chromatography, treatment of a dry THF solution of 1 and 3 (0.10 g/mL) with an excess of a strong base (potassium tertbutoxide) promoted the abstraction of the 9-H of monoalkylated fluorenes, testified by the strongly red coloration of the solution due to the formation of the fluorenyl anions. The obtained mixture was then purified by column chromatography using neutral alumina as stationary phase. This procedure was repeated until the color of the solution after the addition of the base remained unaltered, which can be considered as a qualitative test for the absence of 9-H fluorene defects in the monomer feed.<sup>13</sup>

The monomer 2,7-dibromo-9,9-bis(4-hexyloxyphenyl)fluorene (5) was prepared starting from 2,7-dibromofluorenone by a double Friedel—Crafts reaction with phenol (Scheme 1) followed by an alkylation with *n*-hexyl bromide. The synthetic procedure followed for the introduction of the aryl groups at the fluorene C-9 position did not leave 9-H defects in the target monomer 5, as confirmed by the negative result of the "*tert*butoxide test" on this compound. The boronic esters 2 and 6 were prepared by metalation of the corresponding 2,7-dibromo derivatives, followed by reaction with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

The polymers P1-P3 were obtained by a Suzuki polycondensation in 46–71% yields starting from the suitable diboronic esters and dibromofluorenes, as shown in Scheme 1. Their number-average molecular weights were estimated by GPC in the range 12 000–15 000 Da with polydispersities ranging from 1.9 to 2.4.

The thermal stability of the polymers was investigated by thermogravimetric analysis (TGA) carried out under a nitrogen atmosphere. The incipient decomposition temperature, corresponding to the 5% weight loss, was recorded at 413, 423, and 361 °C for P1, P2, and P3, respectively (Figure 1). The lower thermal stability observed for P3 with respect to P1 and P2 suggests that the presence of the benzyl groups at the C-9



Figure 1. TGA plots of P1-P3.



Figure 2. UV-vis spectra of P1-P3 recorded in chloroform and as thin film on quartz.

position accelerates the thermal degradation of the corresponding polymer, which is likely triggered by the homolitic  $C^9-CH_2Ph$  bond cleavage.

The optical properties of the polymers were studied both in solution and in the solid state. In chloroform solution, the UV–vis spectra of P1-P3 exhibited a maximum in the range 379–390 nm (Figure 2) while, in the solid state, their absorption maxima are slightly blue-shifted (in the range 378–381 nm) with respect to those observed in solution seemingly due to a backbone torsion, limiting the conjugation extension, or as the result of aggregation.

Concerning their photoluminescence (PL), CHCl<sub>3</sub> solutions of **P1**–**P3** showed emission wavelengths ranging between 415 and 417 nm, independently of their structure (Figure 3). In the solid state, their emission relevant to the  $S_1$ – $S_0$  transitions (421–425 nm) were not remarkably red-shifted with respect to those recorded in solution.

Spectral Stability of the Polymers. The spectral behavior toward aerobic thermal stress was investigated by studying the solid-state PL spectra of P1-P3 after a thermal annealing in air at 130 °C for 2 h (Figure 4). After the annealing, the emission profile of the dialkylfluorene P1 was only slightly modified by the appearance of a g-band of very low intensity, while the thermal annealing in air did not modify the emission profile of the fully arylated P2. On the contrary, in the case of P3 a quite intense



Figure 3. PL spectra of P1-P3 recorded in chloroform solution and as thin film on quartz.



**Figure 4.** PL spectra of **P1**–**P3** after thermal annealing in air (130 °C, 2 h) in daylight.

g-band was observed. The same thermal annealing carried out under a nitrogen atmosphere did not determine any change of the absorption and emission profiles of the annealed films. As stated above, since **P1**–**P3** are deprived of 9-H defects, the difference in behavior between **P1** and **P2** must be explained invoking that the different C-9 substitution controls the evolution of the g-band for the corresponding polymer. In fact, while for **P1** the presence of alkyl side chains susceptible of oxidation could favor the formation of fluorenones through well-established degradation pathways,<sup>13,14</sup> in the case of **P2** the steric hindrance of the aryl pendant groups at the C-9 position may exert an influence in frustrating the intermolecular packing, thereby limiting the efficiency of the energy transfer toward fluorenone defects possibly formed during the aerobic oxidative stress.

Interestingly, the appearance of the g-band observed for P3 after annealing points out that the presence of benzyl substituents (which are bulky but, differently from 4-hexyloxyphenyl ones, susceptible of radical attack) results in a rapid degradation of the emission profile, suggesting that the steric hindrance of the substituents does not play a central role in the issue of spectral stability of **PFs**.

The spectral stability observed for P2 was not indefinite: in fact, by prolonging the thermal annealing at 130  $^{\circ}$ C in air, the



**Figure 5.** PL spectra of **P2** after thermal annealing in air at 130 °C for 24 and 48 h in daylight.



Figure 6. PL spectra of P1-P3 after UV exposure in air for 30 min.

spectral degradation of **P2** started after 24 h and became evident after 48 h (Figure 5). This result points out an important conclusion: notwithstanding a scale of stability can be sketched for differently substituted fluorene units (9,9-diarylfluorene > 9,9-dialkyfluorene > 9,9-dibenzylfluorene), the results collected so far point out that **PFs** are intrinsically susceptible of aerobic oxidation, albeit with different rate, whatever the substitution at the C-9 sites.

In order to study the influence of light on the degradation of the **PFs**, the spectral stability of **P1**–**P3** was also investigated by submitting polymer films to UV photodecomposition in air for 30 min. The corresponding PL spectra (Figure 6) showed the formation of a g-band of equal intensity for **P1** and **P2**, suggesting that under these conditions the kinetics of degradation is independent of the alkyl or aryl substitution. Under these conditions, a more intense g-band was again exhibited by **P3**.

Furthermore, since the g-band intensity shown by the polymers after a UV irradiation was invariably higher with respect to that caused by a thermal annealing, it can be stated that UV irradiation accelerates the degradation processes of the fluorene units. To gain insight into the influence of light on the PF degradation, a thermal annealing (130 °C, 2 h) in air was carried out on P3 (the material that exhibited the most intense g-band under the same conditions) either in the dark or in daylight.

Figure 7 shows that when the aerobic thermal annealing was carried out in daylight, a strong g-band was present in the PL spectrum, while such a g-band was almost completely suppressed when the same aerobic thermal annealing was carried out in the absence of a light source. This finding confirms a strong influence of light on the PF degradation.

Mechanisms of the Degradation Process. The following preliminary considerations on the degradation process of PFs can be formulated: (i) the similar behavior of P1 and P2 upon UV irradiation suggests that the mechanism should consider an initiation step which takes place independently of the type of substituent at the fluorene C-9 position; (ii) the aerobic degradation of PFs is strongly influenced by the presence of a light source.

In the case of **P1**, the polymer functionalized with aliphatic side chains, a radical mechanism for the degradation of 9,9-



Figure 7. PL spectra of P3 after thermal annealing in air at 130 °C for 2 h in the dark and in daylight.

dialkylfluorene units can be hypothesized as described in the literature.<sup>13,14</sup>

Under the harsh conditions of the aerobic thermal or radiative stress, the generation of radical species initiates the mechanism responsible for the degradation of the aliphatic side chains of the fluorene units, as shown in pathway A of Scheme 2. Although a radical could be able to attack any C-H bond of the hexyl chain of P1, causing its step-by-step degradation,<sup>11</sup> the formation of a radical at the  $C_{\alpha}$  position followed by reaction with dioxygen can rapidly lead to fluorenone units. The attack of radicals to the  $C_{\alpha}$ position of the side chains may also explain the fact that P3 is more degradable with respect to P1 and P2 due to the mesomeric stabilization of the formed benzylic radical (pathway B of Scheme 2). However, this degradation pathway could not explain the appearance of the g-band in polymers deprived of sidedegradable chains such as P2, for which the cleavage of the C(9) $sp^3-C sp^2$  bond can be the only possible starting point for the generation of fluorenones.

A plausible degradation route for **P2** which takes into account the effect of light is reported in pathway C of Scheme 2. After the absorption of light, at the excited state and in the presence of hydrated dioxygen,<sup>15</sup> the conjugated segment undergoes an electron abstraction, forming a radical cation. The conjugated system then rearranges to form the more stable benzyl radical species by elimination of the C-9 substituent as a cation. The fluorenyl radical, endowed with a high mesomeric stabilization for the presence of an aryl substituent at the C-9 position of the fluorene group, can be involved in a further oxidation to fluorenone.

A similar rearrangement of a radical cation onto a  $\pi$ -conjugated system has been proposed for thiophene-based materials.<sup>16</sup>



Scheme 2. Proposed Degradation Pathways of Polyfluorenes



Figure 8. Cyclic voltammetry of P1–P3. For each sample, two consecutive oxidation cycles are reported.



Figure 9. Cyclic voltammetry of P1. Five consecutive oxidation cycles are reported.

It is worth remarking that the degradation pathway described so far for **P2** can occur also for **P1** and **P3**. Since these findings may be of considerable importance in order to rationalize possible degradation routes of functionalized **PFs** upon positive charging (p-doping), we have carried out an electrochemical investigation aimed at gaining more insight into the behavior of the materials upon p-doping.

To this purpose, we carried out cyclic voltammetry (CV) measurements on P1-P3 under an inert atmosphere. The anodic scans recorded for the three materials are shown in Figure 8.

The samples were analyzed as thin films obtained by dropcasting from a 1.0 mg/mL chloroform solution onto a Pt disk used as a working electrode. In the case of P1, two electrochemical events were clearly observed in the range of the applied potential (0–2 V): the first event at  $E_{\text{peak}} = 1.59$  V and the second one at  $E_{\text{peak}} = 1.87$  V. The irreversible character of the latter event (indicated by the absence of an electrochemical response in the second CV scan) suggests that further p-doping of the conjugated backbone results in the loss of its conductive properties probably by  $\sigma$ -bond cleavage.<sup>17</sup> In fact, if the scan is stopped at 1.70 V (Figure 9), the only anodic event was clearly reversibile, suggesting that under these conditions the sole electrochemical process is the polaron formation by a one-electron abstraction from the  $\pi$ -conjugated backbone of the polymer.



Figure 10. UV—vis spectra of a film of P1 on ITO before and after five anodic scans in acetonitrile.



**Figure 11.** PL spectra of **P1**–**P3** in blend with PVK (10 wt %) after UV treatment in air for 30 min.

By contrast, in the case of **P2** and **P3**, only an irreversible anodic event was observed and the oxidation process completely degraded the two polymers, since no electrochemical events were observed during the second scan on the same sample. It is reasonable to suppose that the anodic scan causes several consecutive electrochemical processes, inducing irreversible chemical modifications, one of which is a  $\sigma$ -bond cleavage involving the C-9 position of the arylated fluorene units. A further investigation on the electrochemical behavior of **P1** was performed by carrying out the same voltammetric scans at potentials lower than 1.70 V, using as working electrode an ITO sheet on which **P1** was dropcasted, in order to measure the UV—vis spectrum before and after the scans, as shown in Figure 10.

This experiment allowed us to draw some conclusions about the fate of the formed radical cation. In fact, the recovered films of **P1** after the voltammetry cycles were almost completely insoluble in chloroform. Furthermore, the UV—vis spectrum of the film showed a remarkable ( $\sim 20$  nm) blue shift of the absorption maximum. From these observations, it can reasonably be hypothesized that after the formation of a radical at the C-9 position, in the absence of dioxygen, this radical attacks the p-conjugated backbone (pathway D of Scheme 2) resulting in a cross-linking of the polymer chains, leading to a backbone distortion (causing the blue shift of the absorption maximum) and to the formation of an insoluble film. Furthermore, no solid-state PL of the resulting

#### Scheme 3. Synthetic Approach for the Obtainment of PFK and PFS<sup>a</sup>



<sup>a</sup> Reagents and conditions: (i) Pd(PPh<sub>3</sub>)<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub> 2.0 M, reflux.

film could be measured, suggesting that a higher packing degree of the **PFs** cross-linked backbones may favor nonradiative decay pathways for the excited state.

On the Origin of the g-Band. Although **PFs** have shown to be intrinsically susceptible of aerobic oxidation, the synthesis of **PFs** for which the appearance of the g-band is retarded as much as possible is all the same highly desirable, and it would very much benefit from a continuous investigation on the physical origin of the onset of the g-band. Recalling that no consensus has been reached on this issue and that the origin of the g-band has been explained either by a favorable energy transfer toward the low-energy luminophors (the so-called on-chain defect emission hypothesis) or by the formation of fluorenone-based excimers, the following experiment was set up to discriminate between the two assumptions.

The spectral stability of the synthesized **PFs** was studied submitting dispersions (10 wt %) of **P1–P3** into polyvinylcarbazole (PVK) to the same UV treatment in air described above. The use of a semiconducting higher energy gap matrix such as PVK was conceived to ensure a three-dimensional energy transfer toward the low-energy luminophors. Thus, the eventual appearance of the g-band for the UV-treated PF/PVK blends could be taken as a clue of the occurrence of the on-chain defect emission hypothesis, whereas a response of spectral stability would favor the fluorenone-based excimers assumption.

Since the results of this experiment are significant to our purpose only if a complete energy transfer occurs from PVK toward the polyfluorene emitters, preliminary tests were carried out by recording the PL spectra of blends of P1-P3 in PVK obtained by exciting at 320 nm, the absorption maximum of PVK. Under these conditions, only the polyfluorene emission was observed, without residual emission from PVK, thereby confirming the occurrence of a complete energy transfer. It should be noted that, due to the amorphous nature of the polymers used in this study and to the low concentration of PFs in the blend, the degree of oxygen penetration in the blend films (a possible variable influencing the extent and/or the kinetics of the aerobic degradation) can be thought as independent from the PFs primary structure. As is apparent from Figure 11, all of the P1-P3 polymers in blend with PVK show an excellent spectral stability upon UV irradiation in air for 30 min. After this treatment, no g-band could be recorded either at  $\lambda_{ex} = 320$  nm (i.e., exciting the donor PVK and promoting a three-dimensional energy transfer) or at  $\lambda_{ex} = 380$  nm, thus directly exciting the polyfluorene emitters. This result can be interpreted by admitting that the isolation of the polymeric chains drastically frustrates the appearance of the low-energy emission.

In order to further clarify the role of the interchain interactions in the appearance of the g-band, we deemed it worthwhile



**Figure 12.** PL spectra of PFK in chloroform solution, as neat film and as a 3 wt % blend with PVK.



Figure 13. PL spectra of **PFS** in chloroform solution, as neat film and as a 3 wt % blend with PVK.

to investigate the PL behavior of a fluorenone-containing polymer PFK, as neat film or in blend with PVK. The polymer PFK was synthesized starting from 1 (mole fraction = 0.45), 2 (mole fraction = 0.50), and 2,7-dibromofluorenone (mole fraction = 0.05) by a Suzuki polycondensation, as shown in Scheme 3.

As already observed for similar fluorenone-containing polymers, while in chloroform solution only the blue emission was observed, the PL of **PFK** in the solid state was almost completely dominated by the g-band with an  $I_g/I_b$  ratio ( $I_b$  and  $I_g$ : maximum intensity emission in the blue and green regions) independent of the excitation wavelength (320 or 380 nm). The complete absence of the g-band in a chloroform solution of **PFK** can be explained, according to the on-chain defect emission scenario, by the fact that the population of the excited states of fluorenone luminophors is hindered due to a poorly efficient energy transfer operating along the polyfluorene chain.

To improve the energy transfer toward the fluorenones while simultaneously preserving the isolation of the polymeric chains, we dispersed **PFK** (3 wt %) in PVK. Interestingly, in this case, **PFK** exhibited the g-band (Figure 12) when the blend was excited at 380 nm. However, the emission of the blend showed a lower  $I_g/I_b$  ratio, when excited at 320 nm. The observation that the  $I_g/I_b$  ratio remarkably changes as a function of the excitation wavelength indicates the possible formation of an inhomogeneous blend, comprising both isolated and aggregated chains.

The PL emission of an inhomogeneous blend is the sum of the photoluminescence of isolated polymeric chains (the contribution of which is higher at  $\lambda_{ex}$ = 320 nm, since they can accept also energy from the PVK host) and aggregated polymeric chains, the contribution of which is higher at  $\lambda_{ex}$ = 380 nm, since the energy transfer from PVK is less efficient toward the aggregated chains. This explains why the excitation at 380 nm increased the  $I_g/I_b$ ratio. The cause of the formation of an inhomogeneous blend may reside in the dipolar interactions between keto-groups, inducing strong intermolecular interactions between adjacent polymer chains.<sup>18</sup> The entity of these interactions may depend on several parameters including the polymer architecture and the preparation of the films, thus explaining the variability reported in the literature concerning the emission properties of fluorenone-containing model systems. At the same time our results prove the on-chain defect model as definitely insufficient to interpret the results obtained for an inhomogeneous blend of a fluorenone-containing PF in PVK as host.

The reproduction of the same behavior of fluorenone-containing polymers with a different planar moiety introduced into the polymer chain could be useful to reinforce the hypothesis on the excimeric nature of the g-band (Figure 13). To this purpose, a poly(9,9-di-n-hexylfluorene) containing a 5% mol/mol of 9-(bismethylsulfanylmethylene)fluorene units (PFS) was prepared, as reported in Scheme 3. The 9-(bis-methylsulfanylmethylene)fluorene was chosen as comonomer to warrant the presence, within the PF backbone, of planar units devoid of carbonyl moieties.<sup>19</sup> The fluorescence behavior of PFS strictly resembles that of PFK, since in chloroform solution PFS solely emits in the blue region ( $\lambda_{max}$  = 415 nm) while as film its fluorescence is dominated by a lower energy ( $\lambda_{max} = 537 \text{ nm}$ ) band. In the case of the 3 wt % PFS/PVK blend, however, the low-energy emission band is completely suppressed, exciting both at 320 and at 380 nm (Figure 13). It can tentatively be stated that the absence of the strong dipolar interactions between the polymeric chains facilitates the homogeneous dispersion of PFS in PVK. The fact that the g-band emerges only under conditions promoting the aggregation of PF chains is an indication that the interchain interactions play a pivotal role in the appearance of the lowenergy emission band. By this line of reasoning, it is worth noting that the oxidative degradation of PFs introduces not only the keto-defects but also, through the fluorenone formation, regions of planarity in the polymer backbone that can favor local interchain interactions strongly influencing the optical behavior in the solid state.

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The spectral stability of three differently structured **PFs** under aerobic oxidative stress was studied as a function of the C-9 substitution. The degradation of the **PFs** was studied in air either by thermal annealing or by UV photodecomposition and allowed us to support the following conclusions: (i) **PFs** show an intrinsic tendency toward fluorenone formation independently of their 9-substitution and from the presence of 9-H defects; (ii) the degradation pathways of **PFs** are greatly influenced by the presence or the absence of a light source.

These experiments also allowed us to add additional pathways to the known degradation mechanism of these materials, the most important of which is the formation of a radical cation which can occur by aerobic oxidation or by p-doping. Furthermore, this study contributed to the elucidation of the origin of the g-band emission. By studying the behavior of the synthesized PFs, our investigation points out that the sole on-chain defect emission hypothesis is insufficient to explain the origin of the g-band for fluorenone containing PFs. In this regard the fundamental role of the interchain interactions was clearly established. The formation, in the course of the PF degradation, of fluorenone defects so close in space to cofacially interact with each other is unlikely because it would imply a massive aerobic degradation under thermal or photochemical stress. Conversely, it is safe to assume that the generation of regions of planarity accompanying the fluorenone formation along the polymer backbone can favor local intermolecular interactions (aggregate and/or excimer formation) on which the spectral stability of the polymer depend. The opinion matured on the matter of the stability of fluorene-based materials is that the great advantages associated with the presence of the highly reactive C-9 on fluorene (e.g., its easy functionalization) unfortunately also represent the Achille's heel of PFs. The research on alternative to the fluorene building block seems to be a more promising approach to warrant material stability under oxidative or, in general, under p-doping exercise conditions.

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: p.mastrorilli@poliba.it.

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