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Nejmeddine Jaballah, Khaled Hriz, Mustapha Majdoub, Mohamed Jouini, Jean-Louis Fave. New Blue-Photoluminescent Semi-Conducting Polymer Derived from Fluorinated Bisphenol A. High Performance Polymers, 2010, 22 (4), pp.483-497. 10.1177/0954008309348664 . hal-01236810

HAL Id: hal-01236810

<https://hal.science/hal-01236810>

Submitted on 14 Aug 2020

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New Blue-Photoluminescent Semi-Conducting Polymer Derived from Fluorinated Bisphenol A

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Abstract: A new confined *p*-phenylenevinylene (PPV)-type polymer (**BPAF-PPV**) has been synthesized using Wittig condensation. The chemical structure of the polymer was well defined by ¹H-NMR, ¹³C-NMR, and FT-IR spectroscopic analysis. **BPAF-PPV** contains oligomeric PPV units separated by hexafluoroisopropylidene groups in the main chain; it is fully soluble in common organic solvents and has a number-average molecular weight of 4570 g mol⁻¹. Differential scanning calorimetry indicates that **BPAF-PPV** is amorphous and displays a glass transition temperature of 114 °C. The optical properties of the polymer were investigated by UV-visible absorption and photoluminescence spectroscopies. Its thin film showed a blue photoluminescence with a narrow emission spectrum. A high photoluminescence quantum efficiency of about 83% was determined in dilute solution. From the cyclic voltammetry analysis, the electrochemical bandgap was estimated to be 3.08 eV. A single-layer diode device of the configuration indium-tin oxide/**BPAF-PPV**/aluminium has been fabricated and has a relatively low turn-on voltage of 3.0 V.

Key Words: Conjugated semi-conducting polymers, confined *p*-phenylenevinylene, blue photoluminescence, fluorinated bisphenol A

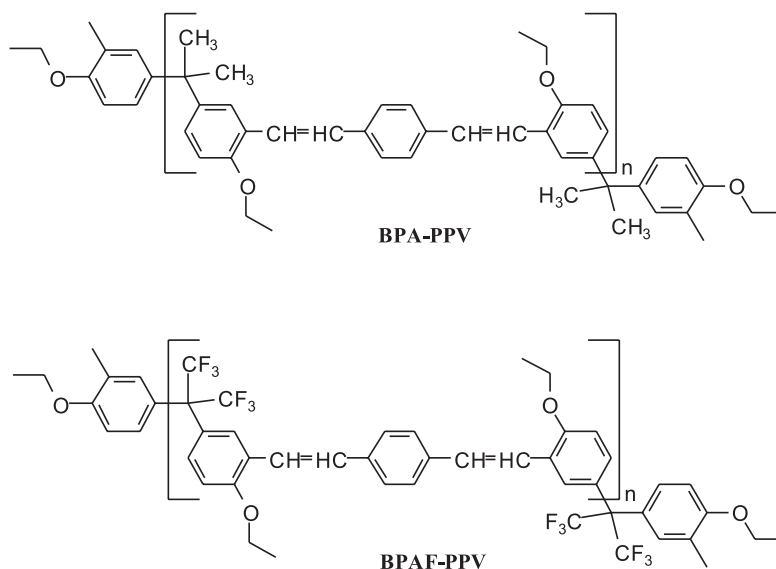
1. INTRODUCTION

The discovery of electroluminescence in poly(*p*-phenylenevinylene) (PPV), in 1990 [1], has produced a new area in polymer sciences: the π -conjugated semi-conducting polymers. Since then, a tremendous progress has been made in the molecular engineering of conjugated polymers and in their uses as active components in polymeric light-emitting diodes (PLEDs) [2–4]. These organic materials are currently expanding their applications to others devices, such as light-emitting electrochemical cells [5, 6], thin-film transistors [7], solar cells [8, 9] and chemical sensors [10, 11]. Such light-emitting polymers have several potential advantages over electroluminescent inorganic materials in that single-polymer-layer devices can be fabricated that exhibit low operating voltage, high emission quantum yield, mechanical strength, low weight, large display area and color tunability. Moreover, device fabrication can be simplified by the use of spin-coating or ink-jet printing techniques.

Full color display applications require red, green, and blue emission and while all three colors have been demonstrated there are relatively few blue-emitting polymers [12]. The first blue-LED was made using poly(9,9-dihexylfluorene) [13]. Other blue-electroluminescent polymers have since been demonstrated, including 9,9-disubstituted polyfluorenes [14], polyphenylene derivatives [15], 3,4-disubstituted polythiophenes [16] and poly(*m*-phenylenevinylene) derivatives [17]. PPV-type blue-emitting polymers can be obtained by a partial conversion of the precursor polymer in the sulfonium route to PPV, giving a high concentration of interruptions in the conjugated chain [18, 19]. In a second way, introducing co-monomers with flexible linker groups into a step growth condensation route to PPV, can lead to blue-emitting copolymer [20]. However, these two methods only allow limited control of the length and the distribution of conjugated segments. Hence, the emission occurs usually from the more highly conjugated segments, and the emission spectrum is therefore broadened and red-shifted.

To solve this problem, the confinement of the conjugation into a well-defined length is one of the most successful developed strategies [3]. Some blue-emitting polymers, containing well-defined oligomeric PPV units separated with non-conjugated aliphatic spacer units in the polymer backbone, were reported [21, 22]. Such polymers usually exhibit good solubility. They are homogeneous in terms of conjugation length and show narrow emission spectra and high photoluminescence quantum yields in the solid state, due to exciton confinement and reduction of luminescence loss via the quenching processes caused by π - π stacking of the conjugated moieties [23]. Nevertheless, the relatively long aliphatic segments, used as spacers in these polymers, can act as a barrier to injection and mobility of the charge carriers, resulting in higher turn-on voltages [2].

In our contribution in molecular engineering of blue-emitting PPVs, we follow the same confined-conjugation strategy, but using shorter spacer groups. In previously work, we have reported a PPV-type confined polymer derived from bisphenol A (scheme 1, **BPA-PPV**) [24]. This polymer, which contains the isopropylidene group as spacer, showed a low operating voltage. A blue emission and a narrow photoluminescence spectrum were obtained in **BPA-PPV**/chloroform solution. However, in thin film the emission was red-



Scheme 1. **BPA-PPV** and **BPAF-PPV** structures.

shifted and the spectre was significantly broadened, due to π - π stacking of the PPV segments. Introduction of bulky moieties in polymer backbone or as side groups, is one of the more useful methodologies to prevent π - π stacking in conjugated polymer films [25, 26]. Herein, we follow the same approach. We report on the design, synthesis and characterization of a **BPA-PPV** fluorinated analogue. The new polymer has the same PPV-type conjugated unit, but contains the bulky hexafluoroisopropylidene group as spacer and π - π interaction preventing moiety (scheme 1, **BPAF-PPV**).

2. EXPERIMENTAL

2.1. Materials and measurements

4,4'-(Hexafluoroisopropylidene)diphenol (fluorinated bisphenol A, **BPAF**) (Acros, 97%), bromoethane (Acros, 98%), potassium carbonate (Acros, 99%), paraformaldehyde (Acros, 96%), triphenylphosphine (Acros, 99%), terephthalaldehyde (Aldrich, 99%) and potassium *tert*-butoxide (Acros, 98%) were used as received. Tetrahydrofuran (THF) was dried over Na/benzophenone and freshly distilled before use. Acetone was stirred over and distilled from potassium carbonate under argon. Other solvents were commercially available and were used without further purification. Melting points (mp) were determined on an Electrothermal Mode 9100 digital analyzer and were not corrected. NMR spectral

data were obtained on a Bruker AV 300 spectrometer. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ chemical shifts are referenced to CHCl_3 signal (7.26 ppm for ^1H , 77.16 ppm for ^{13}C). For $^{19}\text{F-NMR}$ spectrum, CFCl_3 was used as an external standard (0 ppm), and upfield shifts are reported as negative values. Signals associated with the CF_3 groups and proximal quaternary center were not reported in the $^{13}\text{C-NMR}$ data due to C–F coupling and low signal-to-noise ratios. FTIR spectra were acquired on a Perkin-Elmer BX FTIR system spectrometer by dispersing samples in KBr disks. Thermogravimetric analysis (TGA) was carried out on a Setaram TG-DTA 92-10 thermal analyzer under ambient atmospheric conditions at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. DSC was performed on a Setaram instrumentation-regulation DSC 131 system with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. UV-vis absorption spectra were recorded on a Cary 5000 UV-Vis-NIR spectrophotometer. Photoluminescence (PL) spectra were obtained on a Jobin-Yvon spectrometer HR460 coupled to a nitrogen-cooled Si charged-coupled device (CCD) detector. Samples were excited with a 450 W Xenon lamp at the corresponding absorption maximum. For solid state measurements, the films were spin coated onto a silica substrate from a $2 \times 10^{-2}\text{ mol L}^{-1}$ chloroform solution. All measurements were performed at room temperature ($25\text{ }^\circ\text{C}$). Cyclic voltammetry (CV) was performed on an EG&G model 273 potentiostat/galvanostat (Princeton Applied Research) in a three-electrode cell using polymer films that were drop-cast onto an indium tin oxide (ITO) as working electrode. The measurements were carried out at a scanning rate of 50 mV s^{-1} against a saturated calomel reference electrode (SCE) and using the tetrabutylammonium perchlorate ($(\text{n-Bu})_4\text{ClO}$) in acetonitrile (0.1 mol L^{-1}) as supporting electrolyte. The electrochemical cell was externally calibrated by a ferrocene standard. The measurements were performed at $25\text{ }^\circ\text{C}$ and the cell was deoxygenated with argon before each scan.

2.2. Synthesis of 2,2-bis(4-ethoxyphenyl)hexafluoropropane (BPAFEt)

To a stirred mixture of **BPAF** (3.46 g, 10 mmol) and potassium carbonate (3.48 g, 25 mmol) in 20 mL of dimethylformamide, was added dropwise bromoethane (2 mL, 26 mmol). After stirring for 8 h at room temperature ($25\text{ }^\circ\text{C}$), the reaction mixture was poured into distilled water and extracted with diethyl ether. The extract was washed with distilled water, dried over anhydrous magnesium sulfate, and then evaporated. The resultant crude product was purified by recrystallization from ethanol/water (3/1) to afford **BPAFEt** as white crystals. Yield: 92%; mp: $44\text{ }^\circ\text{C}$; $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 7.31 (d, $J = 8.7\text{ Hz}$, 4H, Ar-H), 6.87 (d, $J = 8.7\text{ Hz}$, 4H, Ar-H), 4.05 (q, $J = 6.9\text{ Hz}$, 4H, OCH_2), 1.43 (t, $J = 6.9\text{ Hz}$, 6H, CH_3); $^{13}\text{C-NMR}$ (75.5 MHz, CDCl_3 , δ): 159.2, 131.6, 125.4, 114.0, 63.6, 14.9; FTIR (cm^{-1}): 3093, 3059 (w, aromatic C–H stretching), 2979, 2924, 2879 (w, aliphatic C–H stretching), 1613, 1519 (s, C=C stretching), 1252 (s, C–O–C asymmetric stretching), 1049 (m, C–O–C symmetric stretching), 832 (s, aromatic C–H out-of-plane bending).

2.3. Synthesis of 2,2-bis(3-chloromethyl-4-ethoxyphenyl)hexafluoropropane (BPAFCI)

A mixture of **BPAFEt** (3.92 g, 10 mmol), paraformaldehyde (2.50 g, 80 mmol of CH₂O), and 37% aqueous HCl (8.5 mL, 102 mmol) in acetic acid (30 mL) was stirred at 80 °C for 22 h. The resulting mixture was then poured into distilled water and extracted with diethyl ether. The organic layer was washed several times with distilled water and dried over anhydrous magnesium sulfate. After solvent removal, **BPAFCI** was obtained as a colorless viscous liquid. Yield: 54%; ¹H-NMR (300 MHz, CDCl₃, δ): 7.40–7.30 (m, 4H, Ar-H), 6.85 (d, J = 9.0 Hz, 2H, Ar-H), 4.61 (s, 4H, CH₂Cl), 4.13 (q, J = 6.9 Hz, 4H, OCH₂), 1.47 (t, J = 6.9 Hz, 6H, CH₃); ¹³C-NMR (75.5 MHz, CDCl₃, δ): 157.2, 132.6, 131.7, 126.0, 125.1, 111.3, 64.2, 41.3, 14.8; FT-IR (cm⁻¹): 3084, 3056 (w, aromatic C–H stretching), 2984, 2939, 2888 (w, aliphatic C–H stretching), 1614, 1509 (s, C=C stretching), 1250 (s, C–O–C asymmetric stretching + CH₂Cl out-of-plane bending), 1044 (s, C–O–C symmetric stretching), 810 (s, aromatic C–H out-of-plane bending), 686 (s, C–Cl stretching).

2.4. Synthesis of 2,2-bis(4-ethoxy-3-triphenylphosphoniomethylphenyl)hexafluoropropane dichloride (BPAFP)

A solution of **BPAFCI** (3.81 g, 10 mmol) and triphenylphosphine (5.82 g, 22 mmol) in anhydrous acetone (50 mL) was stirred and heated at reflux for 6 h in an argon atmosphere. After cooling the reaction mixture, the resulting white precipitate was filtered off, washed with diethyl ether several times and dried under vacuum. Yield: 90%; mp: 220 °C; ¹H-NMR (300 MHz, CDCl₃, δ): 7.78–7.40 (m, 30H, P(Ph)₃), 7.25 (d, J = 9.0 Hz, 2H, Ar-H), 6.84 (s, 2H, Ar-H), 6.65 (d, J = 9.0 Hz, 2H, Ar-H), 5.27 (d, ²J_{H-P} = 13.8 Hz, 4H, CH₂P), 3.57 (q, J = 6.9 Hz, 4H, OCH₂), 1.03 (t, J = 6.9 Hz, 6H, CH₃); ¹³C-NMR (75.5 MHz, CDCl₃, δ): 157.3, 135.1, 133.8 (d, J = 9.7 Hz), 131.4, 130.1 (d, J = 12.5 Hz), 128.7, 117.8 (d, J = 85.8 Hz), 116.3 (d, J = 8.3 Hz), 111.2, 64.0, 24.3 (d, ¹J_{C-P} = 49.1 Hz, CH₂P), 14.4; FT-IR (cm⁻¹): 3052 (w, aromatic C–H stretching), 2984, 2845, 2772 (w, aliphatic C–H stretching), 1611, 1507 (s, C=C stretching), 1249 (m, C–O–C asymmetric stretching), 1115 (s, P–C stretching), 1039 (s, C–O–C symmetric stretching), 743, 721, 691 (s, aromatic C–H out-of-plane bending), 507 (s, P–Cl stretching).

2.5. Synthesis of poly[2,2-bis(4-ethoxyphenyl)hexafluoropropane-alt-1,4-divinylbenzene] (BPAF-PPV)

To a stirred mixture of an equimolar amount of a **BPAFP** (0.913 g, 1 mmol) and terephthalaldehyde (0.135 g, 1 mmol) in 10 mL of anhydrous THF, 10 mL of a 0.5 mol L⁻¹ *t*-BuOK solution in THF (5 mmol) was added dropwise at room temperature under a nitrogen atmosphere. The reaction mixture was stirred for 24 h after the addition and then acidified with 3% aqueous hydrochloric acid, poured into water and extracted with chloroform. The organic phase was washed with water, concentrated and then precipitated into methanol. A pale yellow powder was obtained, filtered and dried

under vacuum for 24 h. Yield: 58%; $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 7.70–6.40 (br m, aromatic and vinylic H), 4.20–3.80 (br m, OCH_2), 2.19 (s, Ar- CH_3 end-group), 1.55–1.10 (br m, CH_3); $^{13}\text{C-NMR}$ (75.5 MHz, CDCl_3 , δ): 157.5, 156.6, 137.2, 136.4, 132.3, 132.2, 130.8, 131.9, 131.6, 130.6, 129.7, 129.8, 129.6, 129.2, 129.0, 128.7, 128.6, 127.0, 126.4, 126.2, 125.7, 125.5, 125.4, 125.0, 124.9, 124.8, 123.4, 114.1, 111.2, 110.1, 64.1, 63.6, 16.6, 15.0, 14.9; $^{19}\text{F-NMR}$ (282 MHz, CDCl_3 , δ): -64.4; FTIR (cm^{-1}): 3053 (w, aromatic and vinylic C–H stretching), 2982, 2932, 2881 (w, aliphatic C–H stretching), 1607, 1504 (w-m, C=C stretching), 1253 (s, C–O–C asymmetric stretching), 1044 (m, C–O–C symmetric stretching), 806 (s, aromatic C–H out-of-plane bending), 965 (m, *trans*-HC=CH out-of-plane bending), 865 (w, *cis*-HC=CH out-of-plane bending).

2.6. Fabrication and characterization of diode

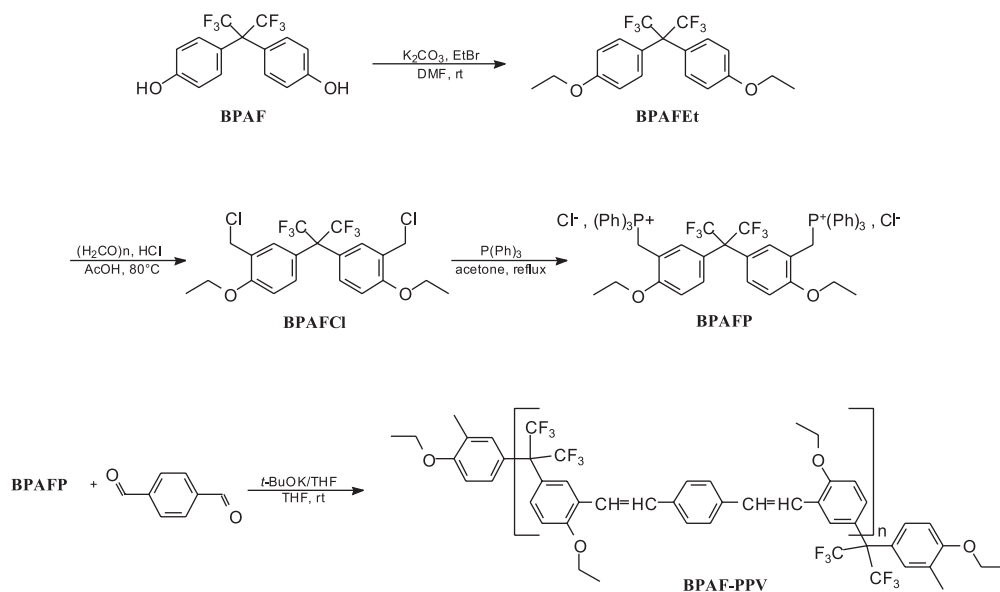
The single-layer device was fabricated as a sandwich structure between aluminium (Al) cathode and indium tin oxide (ITO) anode. Polymer solution (10 mg mL^{-1} in chloroform) was spin-cast (2000 rpm) onto ITO glass to obtain a film with a thickness of about 60 nm after annealing at 40 °C for 1 h. The thin aluminium layer (150 nm) was deposited as the cathode by thermal evaporation under 3×10^{-6} Torr. The current–voltage (I–V) characteristic of the device was recorded with a digital oscilloscope Tektronix 5034.

3. RESULTS AND DISCUSSION

3.1. Synthesis and structural characterization

The polymer was obtained according to a four steps synthetic route as showed in scheme 2. A new bischloromethyl aromatic derivative (**BPAFCI**) was synthesized from **BPAF** by direct chloromethylation of the benzene ring of the corresponding ethylated ether (**BPAFet**) in a HCl/paraformaldehyde/acetic acid system following a conventional described procedure [27]. Then, the bis(triphenylphosphonium) salt (**BPAFP**) was prepared by acetone reflux of **BPAFCI** in presence of triphenylphosphine. The synthesis of the polymer was carried out via a conventional Wittig reaction [28]. Thus, the addition of *t*-BuOK/THF solution to a suspension of **BPAFP** and terephthalaldehyde produced **BPAF-PPV** which was isolated and purified by precipitation from methanol. The polymer was found to have good solubility in common organic solvents such as THF, chloroform, methylene chloride and so forth.

The polymer structure was well confirmed by NMR and FT-IR spectroscopic analysis. The $^1\text{H-NMR}$ spectrum (figure 1) showed a broad peak between 7.70 and 6.40 ppm assigned to phenylene and vinylic protons. The CH_2O group and the methyl group appear in the ranges 4.20–3.80 ppm and 1.55–1.10 ppm, respectively. The absence of the aldehyde terminal groups was supported by the absence of the corresponding peak from the $^1\text{H-NMR}$ spectrum (10 ppm). On the other hand, the appearance of a signal at 2.10 ppm



Scheme 2. Synthetic route to **BPAF-PPV**.

suggests a toluene methyl end-group (Ar-CH₃). In fact, regarding the quantum efficiency, this feature is very significant knowing that carbonyl is a fluorescence-quencher group [29]. The FT-IR spectrum (figure 2) showed absorption bands due to aromatic and vinylic C–H stretching at 3053 cm⁻¹. The valence bands of the aliphatic C–H groups are seen between 3000 and 2880 cm⁻¹. The aromatic ring and vinylic C=C stretching vibrations appear between 1610 and 1500 cm⁻¹. The strong band at 1253 cm⁻¹ is attributed to the asymmetric C–O–C vibration. The band at 1044 cm⁻¹ is attributed to the symmetric C–O–C vibration. The out-of-plane vibration of the aromatic hydrogen shows a strong absorption at 806 cm⁻¹. The spectrum showed the presence of both *cis* (865 cm⁻¹) and *trans* (965 cm⁻¹) vinylic absorptions [30]. Indeed, according to its chemical structure, the ylide used in this work can be classified as semi-stabilized ylide, and its normal Wittig reaction with aldehydes produces mixtures of *Z*- and *E*- configurations nonstereospecifically [31].

By comparing the ¹H-NMR signal integration for toluene methyl terminal groups and OCH₂ units, the degree of polymerization was estimated to be 8, which gives a number-average molecular weight of 4570 g mol⁻¹. The thermal stability of **BPAF-PPV** was investigated by TGA (figure 3) and DSC under ambient atmospheric conditions. The results showed a glass transition temperature (*T*_g) at 114 °C and an onset thermal decomposition temperature at 263 °C. No melting or other thermal events were seen before thermal decomposition, which suggested that the polymer was completely amorphous.

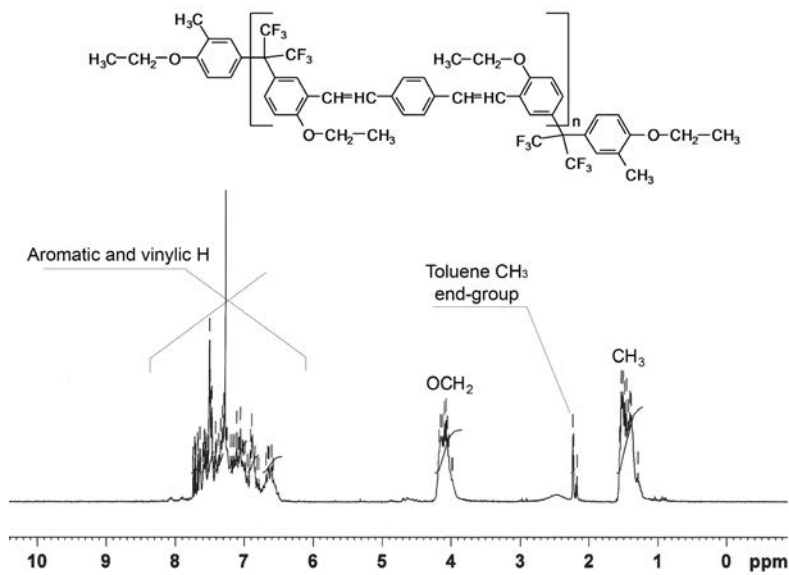


Figure 1. $^1\text{H-NMR}$ spectrum of **BPAF-PPV**.

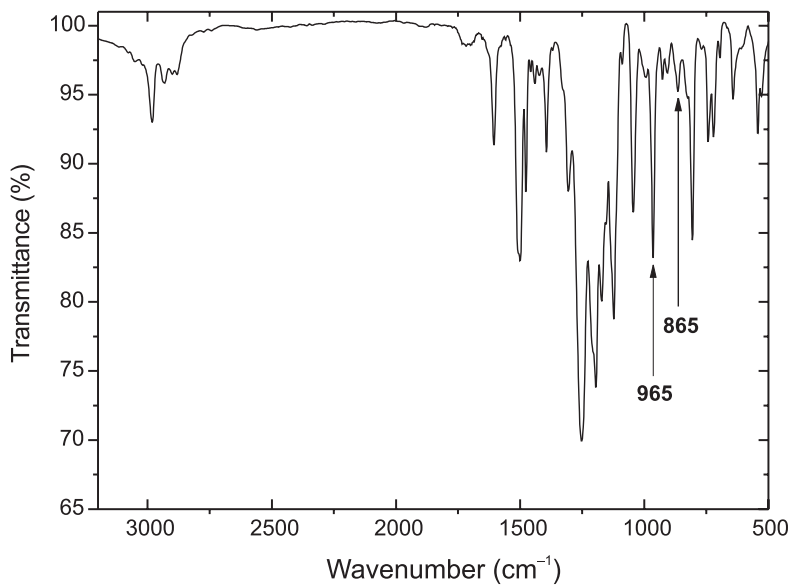


Figure 2. FT-IR spectrum of **BPAF-PPV**.

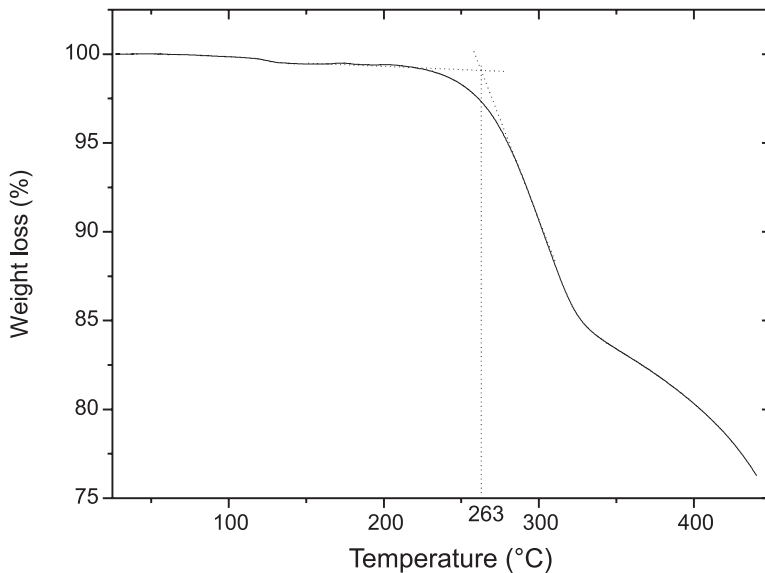


Figure 3. TGA thermogram of **BPAF-PPV**.

3.2. Optical properties

The UV-vis absorption and PL spectra of **BPAF-PPV** in dilute chloroform solution and as thin film are depicted in figure 4. The polymer solution exhibits an unstructured absorption spectrum with a maximum at 364 nm and an absorption coefficient of $2.18 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. It emits in the blue region with a narrow PPV-type emission spectrum [32] comprising two well-resolved bands at 412 and 437 nm. The PL quantum efficiency (ϕ_{PL}) of the polymer was determined in dilute chloroform solution by a relative method using quinine sulfate as standard [33] and its value was 83%.

In comparison with **BPA-PPV** (table 1), **BPAF-PPV** showed slightly blue-shifted absorption and emission spectra. This is mainly caused by the inductive electronic effect of the trifluoromethyl withdrawing groups. We also noticed narrower UV-vis and PL spectra in the case of the fluorinated polymer. Such behavior is probably due to the steric hindrance of the bulky fluoromethyl groups which block the spacer segment conformational changes and reduce consequently the available vibrational and rotational freedom degrees [34]. This relatively important rigidity is probably the origin of the high PL efficiency observed for **BPAF-PPV**. In fact, the polymer **BPA-PPV**, containing the isopropylidene group as spacer, showed a significantly lower PL efficiency (44%).

In the solid state, **BPAF-PPV** showed an absorption maximum at 353 nm with an absorption coefficient of about $6.34 \times 10^4 \text{ cm}^{-1}$. From the onset of film absorption (416 nm), the optical bandgap is calculated to be 2.98 eV. In comparison with the dilute solution, the UV-visible spectrum of the film was broader and the absorption onset was

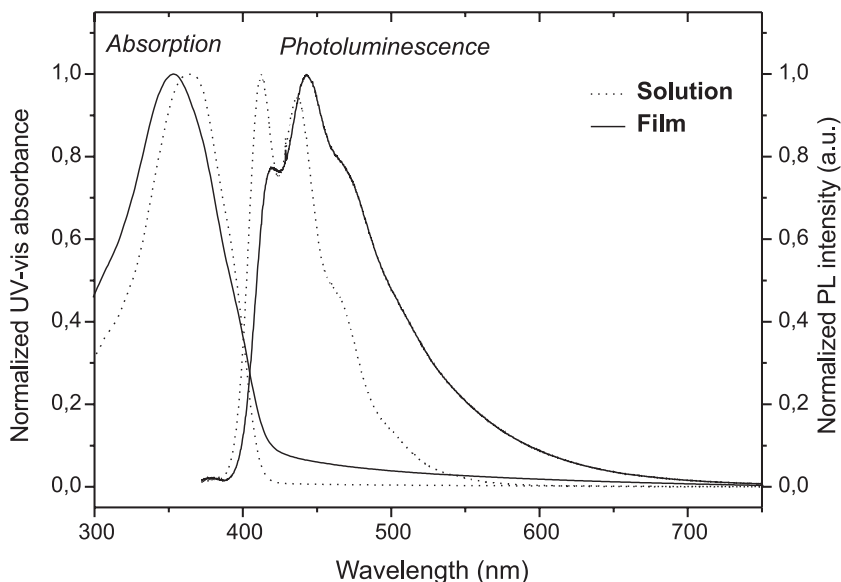


Figure 4. UV-vis absorption and PL spectra of **BPAF-PPV** in chloroform solution ($5 \times 10^{-5} \text{ mol L}^{-1}$ in absorption; $2 \times 10^{-7} \text{ mol L}^{-1}$ in PL) and as thin film (60 nm).

slightly red-shifted. Such behavior is in fact generally observed in π -conjugated polymers and was attributed to the π - π stacking of conjugated segments and aggregates formation in the solid state [35]. These interactions also influence the film emission and a broad red-shifted PL spectrum was obtained as consequence to excimers formation [36].

In comparison with **BPA-PPV**, we noted lower red-shift and broadening values upon going from solution absorption and PL spectra to corresponding film spectra (table 1). These results suggest weaker π - π interactions in **BPAF-PPV** film. The restriction of PPV units stacking is probably due to the steric repulsion of the bulky hexafluoroisopropylidene groups. Such solid state behavior limit the loss of film PL via π - π stacking quenching processes [23] and makes **BPAF-PPV** a good candidate for high-efficiency PLEDs.

3.3. HOMO and LUMO energy levels

To investigate the redox behavior of **BPAF-PPV** and to estimate its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, CV was applied to the polymer film. In fact, the knowledge of the HOMO and LUMO energy levels is of crucial importance to the selection of cathode and anode materials for PLED devices [37]. The use of CV analysis is of good reliability as the electrochemical processes probed thereby are similar to those involved in charge injection and transport processes in PLEDs [38]. **BPAF-PPV** was drop-coated onto ITO glass substrate and

Table 1. Optical data of **BPAF-PPV** and **BPA-PPV**.

In chloroform dilute solution							
Absorption			Photoluminescence				
	λ_{\max} (nm)	ϵ_{\max} ($10^4 \text{ M}^{-1} \text{ cm}^{-1}$)	FWHM ^a (nm)	λ_{onset} (nm)	λ_{\max} (nm)	FWHM ^a (nm)	ϕ_{PL} ^b (%)
BPAF-PPV	364	2.18	70	411	412; 437; 465 ^c	55	83
BPA-PPV	369	2.48	79	419	420; 445; 478 ^c	63	44
As thin film							
Absorption			Photoluminescence				
	λ_{\max} (nm)	ϵ_{\max} (10^4 cm^{-1})	FWHM ^a (nm)	λ_{onset} (nm)	λ_{\max} (nm)	FWHM ^a (nm)	
BPAF-PPV	353	6.34	97	416	420; 443; 473 ^(c)	88	
BPA-PPV	364	7.78	109	428	428; 453; 484; 510 ^(c)	161	

^a Spectrum full width half maximum.

^b PL quantum yield measured using quinine sulfate as the standard ($\phi_{\text{PL}} = 0.546$ in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$).

^c Shoulder.

scanned both positively and negatively in (n-Bu)₄NCIO/acetonitrile solution. As shown in the cyclic voltammogram depicted in figure 5, the onset of oxidation ($V_{\text{onset-ox}}$) was found to occur at 1.17 V and the onset of reduction ($V_{\text{onset-red}}$) was at -1.91 V (vs SCE). According to an empirical method [39] and by assuming that the energy level of the ferrocene/ferrocenium is 4.8 V below the vacuum level, the HOMO and LUMO energy levels can be calculated as follows:

$$E_{\text{HOMO}} (\text{IP, ionization potential}) = -(V_{\text{onset-ox}} - V_{\text{FOC}} + 4.8) \text{ eV}$$

$$E_{\text{LUMO}} (\text{EA, electron affinity}) = -(V_{\text{onset-red}} - V_{\text{FOC}} + 4.8) \text{ eV}$$

where V_{FOC} is a 0.55 V, the ferrocene half-wave potential measured versus SCE. Thus, E_{HOMO} , E_{LUMO} and the electrochemical bandgap values were estimated to be -5.42, -2.34 and 3.08 eV, respectively. The slight difference between the bandgaps obtained from the optical method and from electrochemical analysis has been previously reported in some other conjugated polymers and was attributed to the interface barrier between the polymer film and the electrode surface [38]. In fact, the optical value corresponds to the pure bandgap between the valence band and the conduction band, while the electrochemical value may be the results of the optical bandgap coupled with the interface barrier for charge injection, which makes it larger.

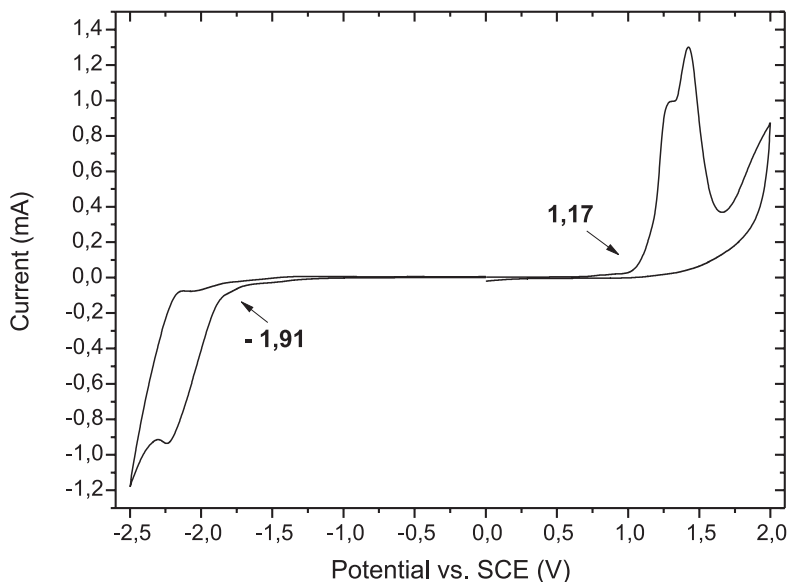


Figure 5. Cyclic voltammogram of **BPAF-PPV** film coated on an ITO electrode in 0.1 mol L⁻¹ (n-Bu)₄ClO/acetonitrile at scanning rate of 50 mV s⁻¹.

3.4. Electrical properties

A single-layer device with the configuration ITO/**BPAF-PPV**/Al has been fabricated to investigate the current–voltage (I–V) characteristic of the polymer. As shown in figure 6, the I–V curve indicates typical diode behavior with a relatively low turn-on voltage of 3.0 V. Nevertheless, no electroluminescence could be recorded for this simple device. The reason is probably the unbalanced charge injection which increases the probability of excitons radiationless quenching at the electrode/polymer interface [40]. Indeed, the energy barrier for hole injection from ITO (work function: -4.60 eV) into **BPAF-PPV** film (E_{HOMO} : -5.42 eV) was 0.82 eV. In return, the barrier for electron injection from Al (work function: -4.20 eV) into the polymer (E_{LUMO} : -2.34 eV) was 1.86 eV. Thus, we guess that the device turn-on voltage indicates the threshold of a hole-governed unipolar injection. Work is in progress to build electroluminescent multilayer devices.

4. CONCLUSION

A new soluble confined PPV-type polymer (**BPAF-PPV**) has been synthesized and characterized. The well-defined degree of conjugation in the oligomeric PPV segment results in a chromophore that exhibits blue photoluminescence in thin film. Limited interchain interactions were observed in the solid state, due to presence of bulky packing disrupting

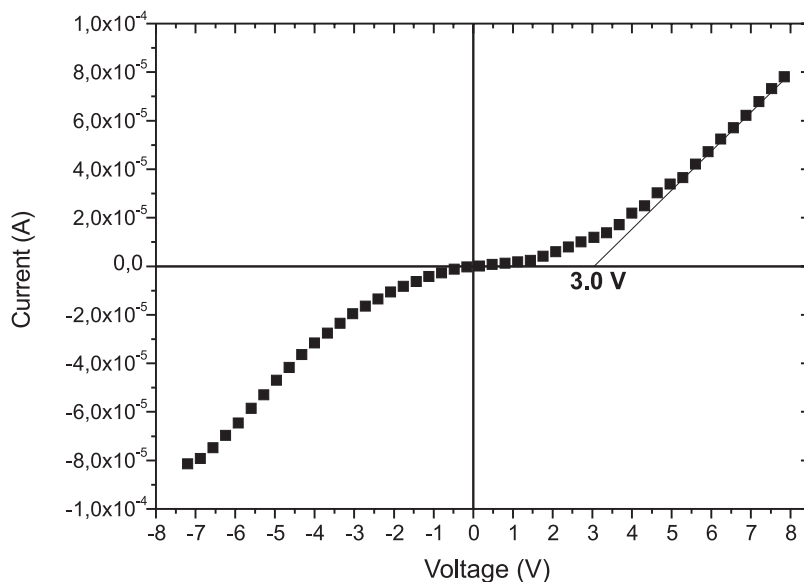


Figure 6. Current-voltage curve of ITO/BPAF-PPV/Al diode.

trifluoromethyl groups, and a narrow emission spectrum was obtained. The photoluminescence quantum efficiency was determined in dilute solution and was about 83%. The I–V characteristic of the device with an ITO/BPAF-PPV/Al configuration demonstrates typical diode behavior and a relatively low turn-on voltage of 3.0 V. In further work, this new blue-photoluminescent semi-conducting polymer will be characterized in different light-emitting-device configurations.

Acknowledgements. This work was partially supported by the contact CMCU code 05S1304. The authors thank Dr Rafik Ben Chaâbane (Laboratoire de Physique et Chimie des Interfaces, Faculty of Sciences, Monastir) for the electrical measurements and Madam Anna Debbebi (Faculty of Sciences, Monastir) for NMR measurements.

NOTE

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