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Characterization and Side Chain Manipulation in Violet-Blue Poly-[(9,9-dialkylfluoren-2,7-diyl)-*alt*-co-(benzen-1,4-diyl)] Backbones

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ABSTRACT: In this work, conditions of Suzuki condensation and polymer modification of polymers of benzene and fluorene units have been studied. A new polymer was prepared with statistical equimolecular amounts of two 2,7-dibromo-9,9-bis(6′-susbtituted-hexyl)fluorene as starting monomers. The C9 position of the poly[9,9-bis(6′-bromohexylfluoren-2,7-diyl)-*alt-co*-(benzen-1,4-diyl has been substituted yielding poly-[9,9-bis(6′-cyanohexylfluoren-2,7-diyl)-*alt-co*-(benzen-1,4-diyl)] with a high degree of conversion. All polymers were completely soluble in THF and chloroform and were characterized by NMR, FTIR, and elemental analysis. Molecular weights measured by gel permeation chromatography coupled with light scattering detector results in polydispersity values between 3.3 and 1.2. Their glass transitions temperature were over 90 and 99 °C by DSC. Comparative studies of optical properties in solution and solid state show similar values indicating that the remote substitution of functional group maintains the spectroscopic characteristics of the backbone. Cyclic voltammetry studies and preliminary results in bias potentials of electroluminiscent devices reveal that these polymers may be promising candidates to be used as hole and electron transporting materials.

Introduction

Fluorene-based polymers have been receiving significant attention as promising components in luminescent optoelectronic devices.[1−9] The great synthetic versatility of organic polymers makes them excellent candidates for studying the effects of structural modifications in the material properties.[10] Fluorene derivatives are interesting since they contain a rigidly planar biphenyl unit and due to the facile substitution at the remote C9 site that provides the possibility of improving the solubility and processability of polymers without significant increase of the steric interactions in the polymer backbone. Remote substitution also offers the possibility of controlling the interchain interactions, that can lead to excimer formation in excited state.[11−14] Problems with unspecified interactions between biomolecules or metals and conjugated polymers also make their study difficult and thus hinder the viable development of such materials. Other challenges to be solved are the dispersity of polymer molecular weights and the batch to batch variability.[15]

The advantage of polymer analogue reaction approach is that the transformation can be controlled, or at least, modifications depend on the degree of substitution of good leaving group, yielding a tunable polymer. By means of the interconversion of the functional group, different solubilities can be obtained in organic solvents or water. This effect was applied to different buffer layers in the inkjet printing process that takes place in the fabrication of devices such as PLED's and transistors.[2,16−19] It could also be used for specific applications as sensory materials to detect chemical[20] or bioactive species.[21,22]

In this work, we propose a versatile synthetic route that allows for facile functional group conversion and an alternative strategy for preparing conjugated polymers by Suzuki coupling. Taking advantage of this feature enables preparation of new polyelectrolytes with different charge (anionic or cationic), which have molecular weight distributions identical to the neutral polymer precursor. Optical and electrochemical characterizations of these polymers in solution and solid films have been performed in order to check the influence of the side chain in the specific properties of the backbone structure.

Experimental Section

Characterization. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 500 spectrometer, with tetramethylsilane as an internal reference and chloroform-*d* ($CDCl_3$) as solvent. FTIR spectra were obtained using a Nicolet model 520P spectrometer with samples prepared as KBr pellets. Elemental analyses were conducted on a Carlo Erba analyzer. Coupled gel permeation chromatography and light scattering measurements were carried out using a HP-1090 liquid chromatograph with autosampler, autoinjector and light scattering detector; ELSD 2000 Alltec (conditions evaporated at 60 °C and nitrogen flow 1.7 L/min). The GPC data were calibrated using Polymer Laboratories EasiCal PS standards and THF as eluent. A flow rate was maintained at 1.0 $mL\cdot min^{-1}$ through a linear column PLGel 5 μm MIXED-C at constant temperature (30 °C). Samples were prepared at 5−10 mg/mL in THF and filtered through nylon 0.22 μm. Differential scanning calorimetry (DSC) was performed using purged nitrogen atmosphere at a heating/cooling rate of 10 °C/min using a Perkin-Elmer Pyris model 6. Samples were scanned from 30 up to 350 °C. and the glass transition temperature (T_g) was recorded during the second heating curve. The absorption and photoluminescence emission spectra of the

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polymers were measured in different solvents using a spectrophotometer Shimadzu 1673 and a SLM8000C spectrofluorimeter, respectively. The fluorescence analysis was performed using absorption solutions less than 0.05 au. Quantum yields were calculated by triplicate probes, comparing the emission to that of a standard solution of quinine sulfate in sulfuric acid 0.1 M ($\Phi_{PL} = 54.6\%$) at 25 °C.[23] Cyclic voltammograms were performed with a HQ Instruments potentiostat and an EG&G Parc 175 wave generator. The solvent employed for electrochemical measurements was acetonitrile, and tetrabutylammonium tetraborate (TBA) was used as supporting electrolyte. A platinum wire was employed as the auxiliary electrode, and the potentials are referred to an Ag/AgCl (3 M KCl) electrode immersed in the same solution. Cyclic voltammograms were obtained at a constant sweep rate of 100 mV s^{-1}.

Materials. For chemical reaction and electrochemical analysis, all solvents were used as received, without further purification, and were HPLC grade. For optical measurements the solvents were spectroscopy graded (Merck). All starting materials and reagents were purchased from Aldrich corporation: salts of potassium carbonate (99%) and potassium cyanide (>98%), 2,7-dibromofluorene (97%), 1,6-dibromohexane (96%), 1,4-phenyldiboronic acid, and a catalyst of palladium(II), [$PdCl_2$(dppf)] complex with dichloromethane (1:1), were used without purification. Poly(9,9-di-*n*-hexylfluoren-2,7-diyl), PFC6 [201807-75-2], was used as a reference for a conjugated light-emitting polymer.

Synthesis. 2,7-Dibromo-9,9-bis(6′-bromohexyl)fluorene (**1**) was obtained by transfer catalysts reaction in two phases (1:1, water and 1,6-dibromohexane), according to previous procedure.[24,25]

2,7-Dibromo-9,9-bis(6′-cyanohexyl)fluorene (2). To a mixture of 2,7-Dibromo-9,9-bis(6′-bromohexyl)fluorene (7.5 mmol) and potassium cyanide (20.5 mmol) in 25 mL of DMSO. The reaction mixture was then heated at 80 °C for 4 h. The cooled mixture was extracted workup in chloroform. The organic phase was dried over $MgSO_4$ and the solvent was evaporated. The crude was repurified from with hexane to afford white solid (86%). ^1H NMR ($CDCl_3$, ppm): δ 7.53 (d, J = 8,0 Hz, 2H), 7.47 (d, J = 8,0 Hz, 2H), 7.43 (s, 2H), 2.22 (t, J = 7.1 Hz, 4H, $2\times -C\mathbf{H}_2-CN$), 1.93 (br, m, 4H, $2 \times$ fluorene$-C\mathbf{H}_2-$), 1.46 (q, 4H, J = 7.3 Hz, $2\times -C\mathbf{H}_2-CH_2-CN$), 1.21, 1.09 (2br, m, 8H, $2\times -C\mathbf{H}_2-(CH_2)_2-CN$, $2\times -C\mathbf{H}_2-(CH_2)_3-CN$, respectively) and 0.58 (br, m, 4H, $2\times -C\mathbf{H}_2-(CH_2)_4-CN$). ^{13}C NMR ($CDCl_3$, ppm): δ 152.12, 139.18, 130.53, 126.15, 121.72, 121.43, 119.87, 55.61, 29.02, 28.33, 25.28, 23.43, 17.11. IR (KBr disk, cm^{-1}): 3430, 2930, 2855, 2243, 1464, 1259, 1058, 1005, 882, 826, 752, and 664.

Poly(9,9-bis(alkyl)fluorene phenylene) Synthesis. Monomers (1 mmol), 1,4-phenyldiboronic acid (0.9 mmol), $PdCl_2(dppf)_2$ (15 mg), and potassium carbonate (10 mmol) were placed in a round-bottom flask with THF (10 mL) and water (10 mL). The mixture was degassed (three times, argon, vacuum) and stirred at 80 °C (reflux) in dark conditions. After 3 days, the reaction was precipitated into methanol, and the crude product was filtered and washed with abundant water and acetone. The polymer was reprecipitated upon addition of methanol to yield a purified white grayish solid.

Poly{[(9,9-bis(6′-(bromohexyl)fluoren-2,7-diyl)-*alt*-co-(benzen-1,4-diyl)]} (3). Anal. Calcd for [$C_{31}H_{34}Br_2$]: C, 65.74; H, 6.05; Found: C, 65.54 H, 6.09. ^1H NMR ($CDCl_3$, ppm): δ 7.82 (br, m, 5H), 7.71−7.59 (m, 5H), 3.30 (t, J = 7 Hz, 4H, $2\times -C\mathbf{H}_2-Br$), 2.11 (br, m, 4H, $2\times$ fluorene$-C\mathbf{H}_2-$), 1.69 (br, m, 4H, $2\times -C\mathbf{H}_2-CH_2-Br$), 1.25, 1.14 (2br, m, 8H, $2\times -C\mathbf{H}_2-(CH_2)_2-Br$, $2\times -C\mathbf{H}_2-(CH_2)_3-Br$, respectively) and 0.79 (br, m, 4H, $2\times -C\mathbf{H}_2-(CH_2)_4-Br$). ^{13}C NMR ($CDCl_3$, ppm): δ 151.68, 140.67, 140.43, 139.96, 127.85, 126.37, 121.59, 120.48, 55.46, 40.56, 34.20, 32.89, 29.34, 28.02, 23.91. IR (KBr disk, cm^{-1}): 3435, 3020, 2928, 2850, 1461, 1244, 890, 811, 742, 642, and 560.

Poly{[(9,9-bis(6′-(cyanohexyl)-fluoren-2,7-diyl)-*alt*-co-(benzen-1,4-diyl)]} (4). Anal. Calcd for [$C_{33}H_{34}N_2$]: C, 86.42; H, 7.47; N, 6.11; Found: C, 85.95 H, 7.63, N, 5.90. ^1H NMR ($CDCl_3$, ppm): δ 7.82 (br, m, 5H), 7.71−7.49 (m, 5H), 2.21 (t, J = 7,2 Hz, 4H, $2\times -C\mathbf{H}_2-CN$), 2.11 (br, m, 4H, $2\times$ fluorene$-C\mathbf{H}_2-$), 1.48 (br, m, 4H, $2\times -C\mathbf{H}_2-CH_2-CN$), 1.27, 1.15 (2br, m, 8H, $2\times -C\mathbf{H}_2-(CH_2)_2-CN$, $2\times -C\mathbf{H}_2-(CH_2)_3-CN$, respectively) and 0.78 (br, m, 4H, $2\times -C\mathbf{H}_2-(CH_2)_4-CN$). ^{13}C NMR ($CDCl_3$, ppm): δ 151.41, 140.54, 140.35, 139.90, 127.76, 126.35, 121.42, 120.45, 119,96, 55.33, 40.46, 29.24, 28.40, 25.34, 23.71, 17.16. IR (KBr disk, cm^{-1}): 3436, 3028, 2932, 2858, 2243, 1515,1462, 1257, 895, 814, 746, and 506.

Poly{[(9,9-bis(6′-(bromohexyl)-fluoren-2,7-diyl)-*alt*-(benzen-1,4-diyl)-*co*-(9,9-bis(6′-(cyanohexyl)-fluoren-2,7-diyl)-*alt*-(benzen-1,4-diyl)]} (5). Anal. Calcd for [$C_{64}H_{68}Br_2N_2$]: C, 74.99; H, 6.69; N, 2.73; Found: C, 74,58; H, 6.63; N, 2.64. ^1H NMR ($CDCl_3$, ppm): δ 7.83 (br, m, 10H), 7.71−7.36 (m, 10H), 3.30 (t, J = 7 Hz, 4H, $2\times -C\mathbf{H}_2-Br$), 2.21 (t, J = 7,1 Hz, 4H, $2\times -C\mathbf{H}_2-CN$), 2.19 (br, m, 8H, $2\times -C\mathbf{H}_2-CH_2-CN$ and $2\times -C\mathbf{H}_2-CH_2-Br$), 1.68, 1.48 (br, m, 8H, $4\times$ fluorene$-C\mathbf{H}_2-$), 1.25, 1.15 (2br, m, 16H, $2\times -C\mathbf{H}_2-(CH_2)_{2,3}-CN$ and $2\times -C\mathbf{H}_2-(CH_2)_{2,3}-Br$) and 0.79 (br, m, 8H, fluorene$-C\mathbf{H}_2-$). ^{13}C NMR ($CDCl_3$, ppm): δ 151.58, 151.41, 140.61, 140.49, 140.34, 139.91, 139.89, 127.76, 127.73, 126.35, 126.27, 121.49, 121.42, 120.45, 120.38, 119,95, 55.37, 55.32, 40.47, 40.34, 34.15, 32.79, 29.25, 28.40, 27.92, 25.34, 25.30, 23.81, 23.71, 17.15. IR (KBr disk, cm^{-1}): 3465, 3026, 2931, 2853, 2244, 1522, 1462, 1263, 893, 813, 743, 639, 560, and 506.

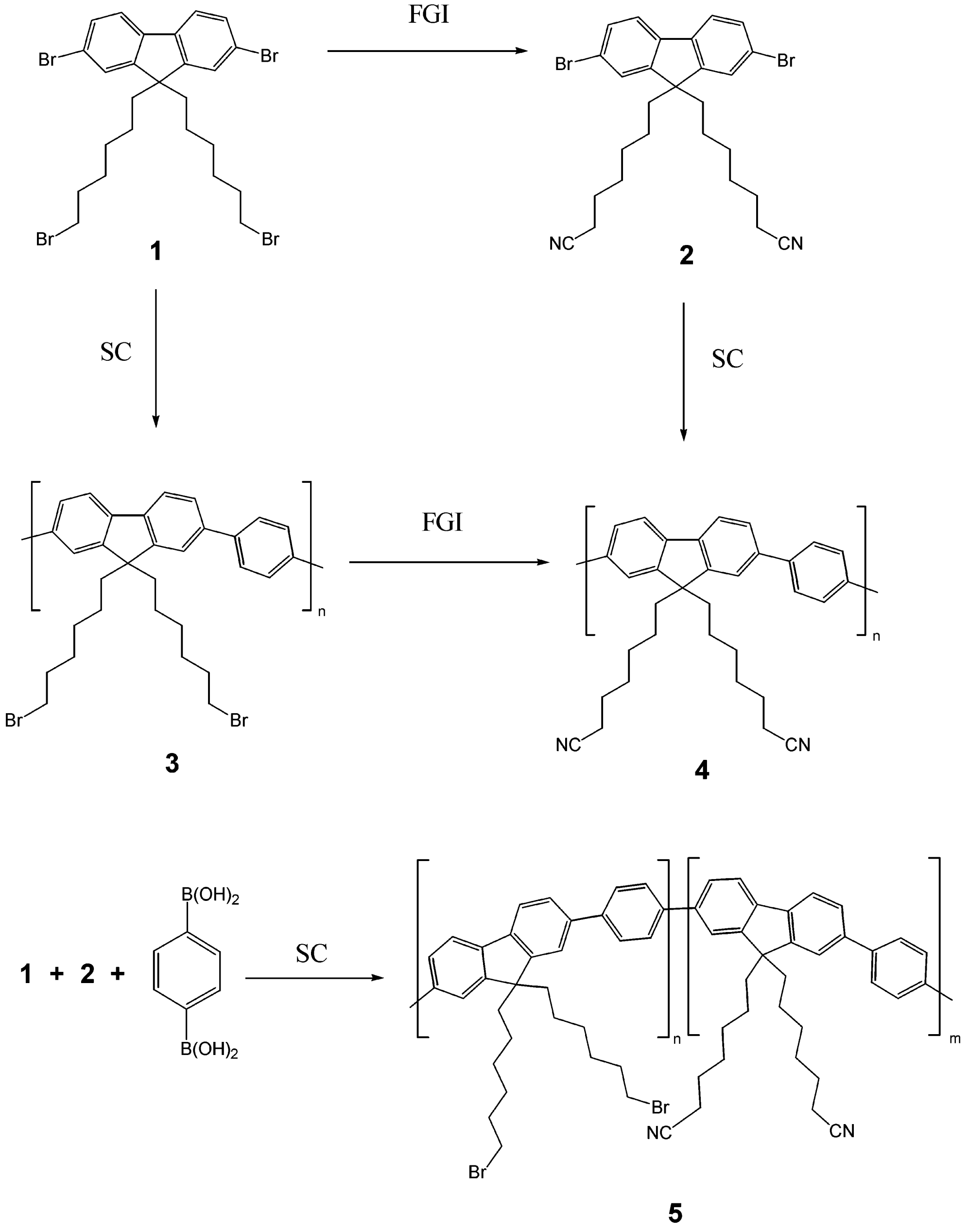
Thin Film Preparation. Thin films were prepared with a SMA spin-coater model AC6000. Polymer solutions (2.25 wt %), prepared in THF, were previously filtered through 0.22 μm nylon, and placed onto 1 cm^2 area quartz or ITO glasses (60 $\Omega^{-1}\cdot cm^{-1}$). The substrates were spin-coated at 80 Hz for 30 s and acceleration of 0.3 s. The thickness of the films was measured on a contact profilometer, Alpha step 200 (Tenkor Inst.).

Device Fabrication Process and Characterization. Patterned indium−tin−oxide (ITO) coated glass was used as substrate for organic EL devices. Prior to film deposition, the substrates were cleaned using a soap-based solution placed in an ultrasound field. The photoresistant film was then spin-coated at 4500 rpm and then annealed at 100 °C for 30 min. These samples, having on the top a mask consisting of 16 circles with diameters <2 mm, were placed under UV exposure for a typical period of 30 s. Next, the photoresistant film was removed in a NaOH solution, leaving round-shaped wells above the ITO contacts. The already patterned samples were cleaned using distilled water and nitrogen and annealed at 110 °C for 2 h to remove residual solvent. Subsequently, a hole injection layer, (PEDOT:PSS), was spin-coated at 6000 rpm and dried in an oven at 110 °C for 30 min. The measured thickness for this layer was 75 nm. The polymer solution was spin-coated at 6000 rpm and then heated at 110 °C for 30 min, resulting in an active layer thickness of 100 nm. Thus, this film will not suffer effects from UV exposure or wet etching. Finally, the Al cathode was vacuum evaporated on the organic layer surface under an atmosphere of 10^{-7} Torr. The insulating properties of the photoresist prevent from leakage current away from the diodes. The device current−voltage characteristics were measured using a pulse train as input signal. The duty cycle was set to be 10%, thus having a pulse width of 2 ms for a period of 20 ms. The refresh time between two consecutive pulses ensures long time operation without significant device degradation. Furthermore, the $I-V$ curve stability was achieved by gradually increasing the pulse amplitude up to observe reproducible measurements. EL spectra were performed using the linear CCDs detector arrays of 2048 pixels together with the monochromator of ORIEL MS257 spectrometer provided with an appropriate grating of 150 lines/mm.

Results and Discussion

Synthesis and Characterization of the Polymers. As shown in Scheme 1, the neutral poly[9,9-bis-(6′-substitutedhexylfluoren-2,7-diyl)-*alt-co*-(benzen-1,4-diyl)] **3**−**5** was synthesized via Suzuki coupling reaction using 1,4-phenyldiboronic acid and the corresponding monomer bromide: 2,7-dibromo-9,9-bis(6′-bromohexyl)-

Scheme 1. Synthetic Route of Polymers 3, 4, and 5[a]



[a] Abbreviations: FGI, functional group interconversion; SC, Suzuki coupling.

fluorene (**1**) and/or 2,7-dibromo-9,9-bis(6′-cyanohexyl)-fluorene (**2**). The polymer 9,9-bromohexyl **3** was obtained according to the previous method.[24,25] Different molecular weights, batch to batch, under different conditions were observed, depending on the time coupling reaction (Table 1). A similar correspondence with batch for polymer **4** was found. Optimal time reaction of Suzuki polymerization using this *cis*-Pd catalyst is 60 h. An increase in the reaction time to 72 h results in a reduction of the yield. It is likely that the time necessary to follow Suzuki mechanism was reduced due to the introduction of a *cis*-Pd(II) with respect to the Pd(0) catalyst used in others methodologies.[26,27] Employing the same procedure, we have obtained a new statistical poly[[9,9-bis-(6′-bromohexylfluoren-2,7-diyl)-*alt*-*co*-(benzen-1,4-diyl)]-9,9-bis(6′-cyanohexylfluoren-2,7-diyl)-*alt*-*co*-(benzen-1,4-diyl)] (**5**) from a coupling reaction between the 2,7-dibromo monomers **1** and **2** and acid diphenylboronic with a mole ratio (1:1:2). Polymer **5** presents a regular alternating structure, and the molecular weight obtained has a similar value to the corresponding polymers **3** and **4**.[28]

Alternatively, polymer **4** was prepared successfully by modification over polymer **3**, using the same conditions to obtain monomer **2** by reaction with monomer **1**. In this case, we showed that each method guarantees a way to obtain the desired polymer. Usually, the characteristics of the polymer are dependent on the batch obtained as well as on the manipulation of the specific monomer. In our case, the modification was performed over 9,9-bis(6′-bromohexyl) fluorene unity in order to obtain different derivatives of polymer with the same molecular distribution. The synthetic procedure is carried out in the same reaction conditions as those described for monomer synthesis but with the advantage that purification of bromohexyl monomer **2** is easy and controllable. Availability of the polymer **3** enables access to a wide range of functional polymers, for

Table 1. Reaction Conditions and Molecular Weight Characteristics of Polymers Compared to Commercial Poly(9,9-dihexylfluoren-2,7-diyl)

polymer	batch[a]	polymerization conditions	yield (%)	$M_w \times 10^{-3}$ (g/mol)	PDI	$M_p \times 10^{-3}$ (g/mol)	n[d]
$PFPBr_2$; **3**	1S	80 °C; Ar, 48 h	62	6.9	1.2	5.96	10
	2S	80 °C; Ar, 60 h	75	95.6	3.3	59.91	105
	3S	80 °C; Ar, 72 h	35	70.3	2.6	54.13	95
	4S	80 °C; Ar, 60h+end-cap,12 h[b]	89	25.7	2.4	19.68	35
$PFPCN_2$; **4**	1S	80 °C; Ar, 48 h	59	2.5	1.3	2.51	5
	2S	80 °C; Ar, 72 h	34	28.0	2.0	18.14	39
	1M-2S	THF, 24 h.	NR[c]				
	2M-2S	DMSO/THF (3:1),4 h	80	92.1	3.1	51.05	111
	3M-3S	DMSO/THF (1:1), 24 h	21	42.3	2.5	28.34	62
	4M-3S	DMSO/THF (3:1), 24 h	83	40.5	3.0	24.00	52
	5M-3S	DMSO/THF (3:1), 4 h	86	39.9	2.7	22.65	49
$PFPBr_2CN_2$; **5**	1S	80 °C; Ar, 72 h	32	22.9	2.2	11.03	11[e]
PFC6 (ref)	Aldrich		–	4.2	1.5	3.39	10

[a] Batch number. Abbreviations: S, Suzuki coupling; M, polymer modification following starting batch. [b] End-capping used was 6% molar of 2-bromofluorene. [c] No reaction. [d] Unity of polymers calculated over M_p. [e] The unity of **5** was considered as each monomer addition ($n + m$).

example, the reaction of substitution of trimethylamine in THF/water was conducted to the desired polycation,[24] and now, the polyanion is being synthesized and characterized by facile group conversion of polymer **4**.

Obtained polymers have polydispersities (PDI) and molecular weights typical of Suzuki coupling polymerization (Table 1). These results were determined by GPC/LS, and precise molecular weights varied from batch to batch. Monomer units (n) were calculated using the molecular weight in peak (M_p), and the values of n ranged from 10 to 105 in starting polymer bromide **3**. A modification was introduced in batch 4S to obtain polymer **3** (after 60 h), and 6% (molar) 2-bromofluorene was added as end-capping. In this case, we obtained a good PDI and excellent yield with respect to the batch 2S, and we used batch 4S to compare the optical and electrochemical properties with similar number of chains (see Table 1). Finally, we performed the modification of **3** to obtain poly[9,9-bis-(6′-cyanohexylfluoren-2,7-diyl)-*alt-co*-(benzen-1,4-diyl)] (**4**). A key factor of elevated degree of conversion was the mixture of solvents DMSO/THF (3:1) used that would keep the reactants in solution and preserved the molecular weight respect to the starting polymer batch (see Table 1).

The solubility of the synthesized polymers was checked using 2.5 mg of polymer in 5 mL of different solvents. All synthesized polymers are readily soluble in organic solvents with intermediate polarity (for $E_T(30)$, polarity[29] between 0.285 and 0.222), such as dichloromethane, tetrahydrofuran and chloroform, moderately soluble in toluene (0.111), dioxane (0.178), and dimethylformamide (0.379) and insoluble in water (1.107) and DMSO (0.443). Poor solubility in other solvents as acetonitrile or cyclohexane is caused by the aggregation of the polymer and results in a precipitate in these media.[30]

The structure of polymers and conversion degree in modification were confirmed by ^1H and ^{13}C NMR spectroscopy. Bidimensional experiments of NMR corroborate the correct assignments of each proton and carbon. The spectral data of the polymers **3**–**5** are similar to those of the other fluorene polymer derivatives, including the commercial polymer. Figure 1 shows the ^1H NMR spectra of these polymers in deuterated chloroform. Identification was possible due to the shift of the triplet peak assigned to the methylene group joints, centered at 3.31 ppm corresponding to a bromide group in **3**, and at 2.40 ppm the shift of the triplet by cyanide group in **4**. Both triplet signals in polymer **5** present related area integrals with the corresponding feed ratio. The ^{13}C NMR spectra of the polymers **3**–**5** are similar to those of poly(fluoren-2,7-dyil) synthesized by Suzuki coupling, with a regioregular and well-defined polymer indicated by analysis of the aromatic region of ^{13}C NMR spectra, where only six peaks appear (polymers **3** and **4**), with one more corresponding to polymer **5**. Secondary products derived of the possible elimination of the bromine or alkyl coupling were not detected. The appearance of the characteristic band of nitrile group at 2243 cm^{-1} in **4** and **5**, confirmed the structure of the new polymer and the IR band assigned to the group CH_2Br (640 cm^{-1}) in the region of identification of alkyl halides for **3** and **5** (see Figure 2). Both techniques (NMR and IR) are complementary and have been useful tools to calculate the conversion percentages degrees, with low experimental error (estimated 2%), when the characteristics peaks of starting materials cannot be found.

Thermal properties of polymers **3**–**5** were investigated by DSC (see Table 2) and the glass transition temperature was around 90–99 °C for polymers with molecular weight lower than 30 000 g/mol. The transition for polymers with higher molecular mass was very difficult to observe in second heating rate.

Optical Characterization. Solution phase absorbance spectra of polymers **3**–**5** have similar bandwidths, absorption maximum, and intensity in chloroform and tetrahydrofuran (figure not shown). Polymers exhibit a maximum absorption at 368–370 nm, in THF solution, due to a $\pi\pi^*$ transition derived from the conjugated fluorene-phenylene structure of the backbone (Table 2). No changes are observed for THF or chloroform solutions stored under room temperature for more than 1 week, such the formation aggregates mediated by the solvent quality.[30] The most important difference in the case of the polymer **5** is the higher absorption coefficient since this polymer has a number of cromophore groups twice its molecular mass. The quantum yield (Φ_{PL}) was registered by triplicating in solution and was around 80%, the same order as other conjugated polyfluorenes, like the reference PFC6. Note that the quantum yield for polymer **5** has an intermediate value with respect

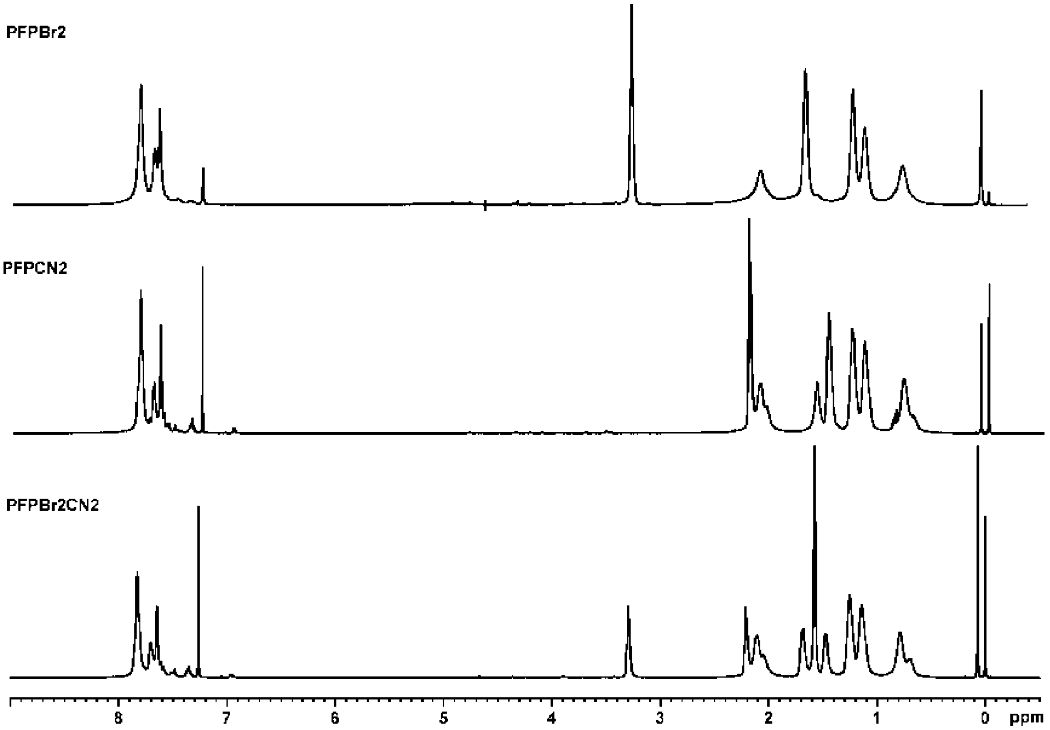


Figure 1. ^{1}H NMR spectra of synthesized polymers **3**, **4**, and **5** (500 MHz, in $CDCl_3$).

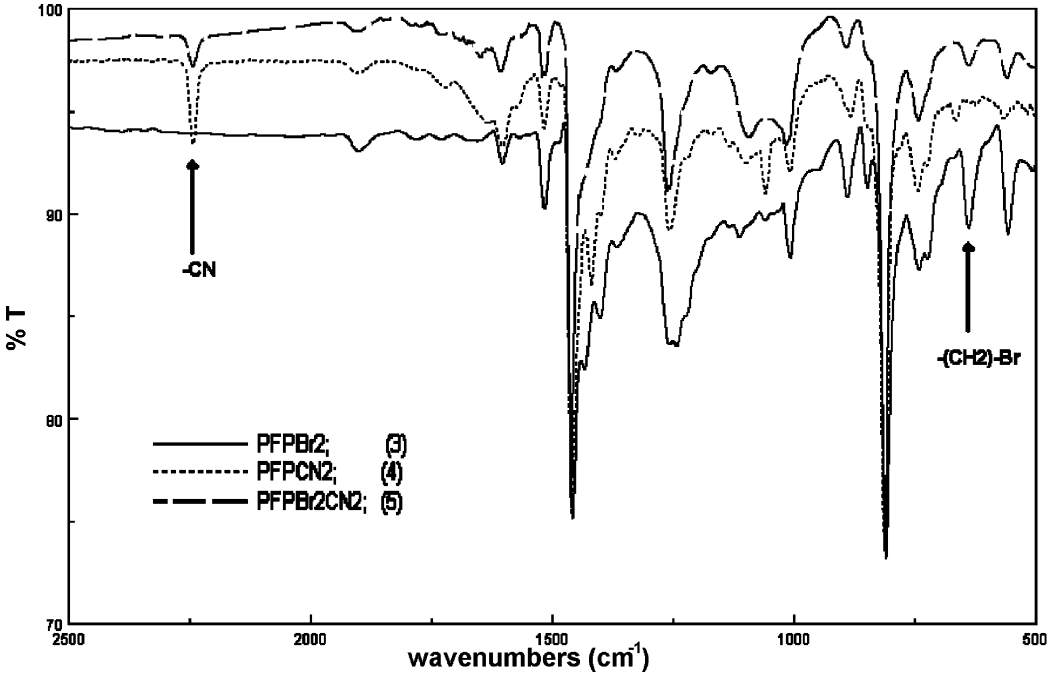


Figure 2. Normalized transmission infrared spectra of polymers **3**, **4**, and **5** in KBr pellets. Arrows indicate the specific band of functional group.

to the corresponding polymers **3** and **4**, as if polymer **5** was a physic mixture of both (Table 2). It is also remarkable that the bromide group has not observable quenching of fluorescence due to heavy atom.[31]

Transparent and uniform films of polymers **3**−**5** were prepared by spin-casting of THF solution filtered on a quartz substrate. Figure 3 shows the representative UV−visible absorption and fluorescence (PL) spectra for three synthesized polymers **3**−**5** and the reference polymer. The optical band gaps were around 2.9 eV (absorption onset) for all the polymers. The emission peaks in the blue polymers present a maximum at 420−422 nm with a well-defined vibronic feature at 442 nm, and they are very similar to those of PFC6. Again, the band related properties (bandwidth, absorption maximum, and intensity) for studied polymers in solid state give identical results among themselves. All values are summarized in Table 2. A slight red-shift (around 10−12 nm) in emission of the solid phase was observed comparing to the solution phase polymers. Usually, this effect in disordered films is attributed to a chain aggregation of the polymer main chain.[32] This is the reason the functional group in the side chain does not affect the excited-state surface of the polymer solution.

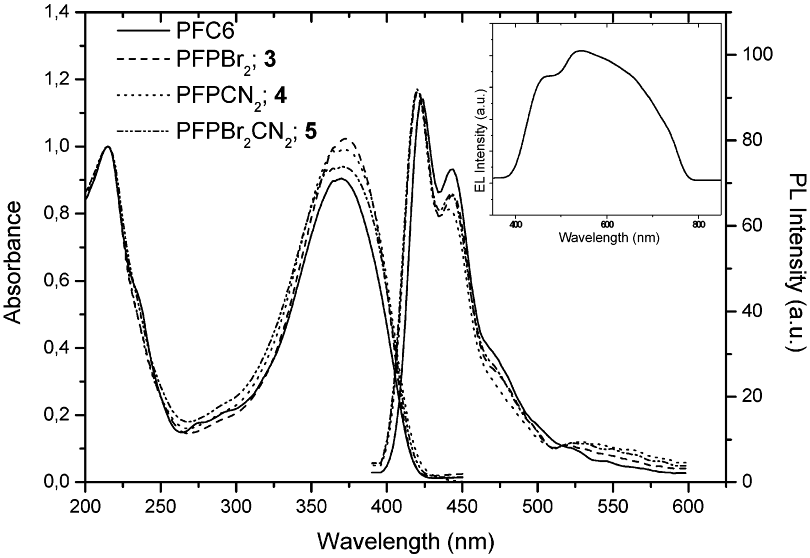


Figure 3. Normalized absorption and fluorescence spectra of synthesized polymers **3** (- - -), **4** (···), **5** (—··—··) and reference PFC6 (solid), in film prepared on quartz. The inset shows evolution of EL spectrum of ITO/PEDOT/PFPBr$_2$ (**3**)/Al device at 15 V.

Table 2. Glass Transition Temperature and Optical Measurements in Solution and Film, for Polymer Batches 3, 4, and 5 with Similar Molecular Masses

polymer; no.-batch	T_g[a] (°C)	THF solution λ_{max}^{Abs} (nm)	ϵ_{max} (M^{-1} cm^{-1})	λ_{max}^{PL} (nm)	Φ_{PL}[b]	quartz film λ_{max}^{Abs} (nm)	λ_{max}^{PL} (nm)	E_g[c] (eV)
PFPBr$_2$; **3**-4S	99	368	53 500	410/430	82	373	422/442	2.94
PFPCN$_2$; **4**-2S	90	370	50 850	410/432	70	370	420/442	2.87
PFPBr$_2$CN$_2$; **5**-1S	93	368	107 950	410/432	75	371	422/442	2.92
PFC6 (ref)	104	369	36 000	414/438	83	372	424/446	2.92

[a] Calculated on second heating scan. [b] Quinine sulfate (0.1 M H_2SO_4), at λ_{ex} = 370 nm, and data were repeated three times. [c] Energy gap measurements by onset of absorption spectra.

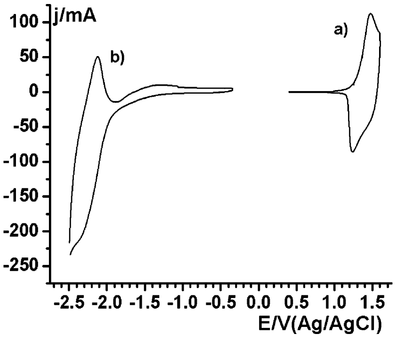


Figure 4. Stabilized cyclic voltammograms of ITO electrode covered by the polymer **5** in an acetonitrile solution 0.1 M TBA: (a) anodic branch; (b) cathodic branch.

Moreover, the PL shoulder band around 540 nm is caused by the increased face to face π-stack between aromatic rings in the adjacent chain. The longer wavelength emission is common in 9,9-disubstituted polyfluorenes and it has been attributed to interchain excimer formation.[33] Efficient exciton energy transfer occurs from the bulk, and these latter states of aggregated chains have lower-lying excited-state energy that produces intermediates band gaps.

Electrochemical Characterization. Figure 4 shows the stabilized cyclic voltammograms of an ITO electrode coated by polymer **5**. The electrode was rinsed with acetonitrile and immersed in the electrochemical cell at a controlled potential of +0.4 V. In the zone of positive potentials (right side, a), the polymer oxidation related current (oxidation onset 1.11 V) can be observed with the oxidation peak centered at 1.48 V. In the backward scan, the corresponding observed reduction is centered at 1.22 V. This behavior can be related to the polymer p-doping process. After the acquisition of the anodic branch of the voltammogram, an experiment was performed with a fresh polymer electrode scanning directly toward less positive potentials. Figure 4b shows the stabilized voltammogram obtained in the exploration of the cathodic branch. In this potential zone, a cathodic current can be observed due to the polymer reduction. The onset of the reduction peak begins at −1.76 V and the reduction peak is centered at −2.25 V. In the successive forward scan the corresponding oxidation process (dedoping) is observed with an oxidation peak centered at −2.14 V. Voltammograms are stable in successive voltammetric scans indicating that this polymer is stable for hole and electron injection.

Similar voltammetric behavior was obtained with polymers **3** and **4**. Both electrodes are stable for hole and electron injection, since stabilized voltammograms are obtained (not shown). The cyclic voltammogram of an ITO glass covered by the reference polymer PFC6 has some differences with respect to the other polymers. During successive voltammetric cycles in the zone of *p*-doping process, a constant decrease of the intensity of the oxidation and reduction peaks can be observed. This voltammetric behavior indicates a low stability of the reference polymer for hole injection. The oxidation of the polymer at potentials lower than 1.63 V produces the solubilization of the layer. On the other hand, the cathodic behavior of this polymer is similar to that obtained with the other polymers, indicating an n-doping reversible process. This polymer is stable for electron injection.

Data obtained from voltammetric analysis are summarized in Table 3. The oxidation and reduction onsets can be related with HOMO and LUMO levels assuming a value for the absolute potential of the reference electrode (Ag/AgCl) in acetonitrile solution[34] of 4.39 eV below the vacuum level. These values are also reported in Table 3. The values of E_g obtained with electrochemical methods are very similar to those obtained by means of optical measurements, within the margins of experi-

Table 3. Data Obtained from the Stabilized Voltammograms of Synthesized Polymers

						anodic branch			cathodic branch		
polymer	E^{onset}_{ox} (V)	E^{onset}_{red} (V)	HOMO (eV)	LUMO (eV)	E_g (eV)	E_{ox}/V	E_{red}/V	ΔE/V	E_{ox}/V	E_{red}/V	ΔE/V
3-4S	1.14	−1.69	−5.53	−2.70	2.83	1.47	1.22	0.25	−1.83	−2.00	0.17
4-2S	1.14	−1.76	−5.53	−2.63	2.90	1.42	1.27	0.15	−2.12	−2.27	0.15
5-S	1.11	−1.76	−5.50	−2.63	2.87	1.48	1.24	0.24	−2.14	−2.25	0.11
PFC6	1.31[a]	−1.90[a]	−5.70	−2.49	3.21	1.53[a]	1.28[a]	0.25	−2.23	−2.36	0.13

[a] Data measured in the first voltammetric scan.

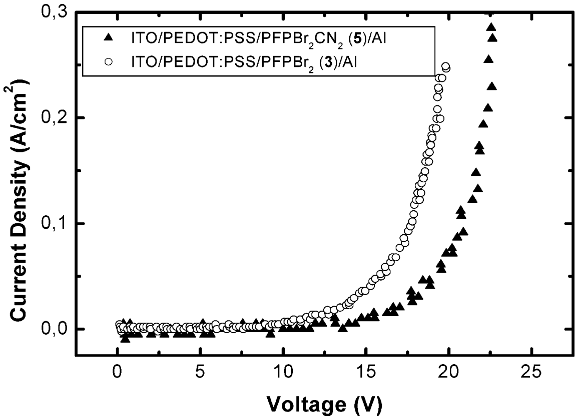


Figure 5. Current−voltage characteristic curves of the EL devices for two different active layers: **3** (circles) and **5** (triangles).

mental error. The voltammetric charge for both processes is similar and indicates a reversible doping and dedoping process. The reversibility of both processes is evaluated attending to the potential difference between the oxidation and reduction processes in each branch (ΔE). From the analysis of the anodic branch, it can be concluded that the polymer **4** has the highest reversibility for hole injection, while the polymer **3** has a poorer behavior similar to that of the reference polymer. The polymer **5** has a similar behavior to polymer **3** for p-doping with a slightly higher reversibility with respect to **3**. Polymers **3** and **4** have a similar reversibility for the electron injection process, but polymer **5** has a better performance for electron transfer across the polymer film.

Electroluminescence and Current—Voltage Characteristics. Preliminary results of electroluminescence (EL) and current−voltage ($I-V$) characteristics of the synthesized polymers into luminescent devices are encouraging. Devices were fabricated using the following configuration: ITO/PEDOT (75 nm)/polymer (100 nm)/Al. EL spectrum of polymer **3** shows a significantly broadened emission (inset in Figure 3). A vibronic shoulder appears at around 475 nm, and a new broad peak is centered at 543 nm. This difference between PL and EL emissions implies that the recombination zones are different. Red-shift emission is a common phenomenon observed in these devices, and no clear explanation was given in the literature.[35] We believe that the new emission band shown in the EL spectrum has its origin in the excimer found by aggregation (or between molecular chains) in the solid state. In addition, defects in the fabrication process during application of electric field may produce an effective degradation of emission by electrooxidation.[10]

Finally, Figure 5 shows a comparative $I-V$ curves obtained in devices for polymers **3** and **5**. Potential threshold has not a clear dependence with diode area for different samples. The preliminary study shows a dispersion of results with different diodes belonging to the same polymer sample. The onset potential obtained for polymer **3** was lower to that for polymer **5**. This result agrees with the corresponding HOMO levels determined by cyclic voltammetry, thus confirming the improved hole affinity of polyfluorenes derivatives.

Conclusion

Suzuki condensations present a disadvantage for obtaining the different and desired polymers because of the variability of the lots, since an appropriate treatment is necessary in each monomer, namely the purification of derivatives 2,7-dibromofluorene. The polymer analogue reaction appears as a new divergent route in order to manipulate the lateral chain in conjugated polymer having total reactivity of functional group of starting batch polymer. Furthermore, it was shown that the molecular weight of the polymer analogue reaction yields a derivative polymer similar to the corresponding precursor.

Polymer band gaps obtained by optical and electrochemical properties exhibit similar values. In addition, no significant differences were observed in optical and electrochemical band gaps between synthesized polymers due to the modification of the lateral chain. Bromide-containing polymers show a lower reversibility for the p-doping processes than the corresponding polymers with CN groups. Synthesized polymers show high electrochemical stability toward electron and hole injection as checked by cyclic voltammetry. Future work will be focused on the electroluminescence properties in combination with electrochemical techniques in new polyelectrolytes synthesized by neutral precursors and their use in specific applications, such as organic electronic devices, paying special attention to polarized EL and thin-film transistors.

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Supporting Information Available: Figure S1, ^{13}C NMR spectra of polymers **3**, **4**, and **5** obtained by Suzuki coupling reaction in CDCl$_3$ (125 MHz), and Figure S2, ^{13}C NMR spectra of polymer **4** in CDCl$_3$ (125 MHz). This material is available free of charge via the Internet at http://pubs.acs.org.

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