From Block Copolymers to End-Capped Polymers: A Suitable Method To Control the Electro-Optical Properties of Polymeric Materials

A. Bolognesi,* P. Betti, C. Botta, S. Destri, U. Giovanella, J. Moreau,[†] M. Pasini, and W. Porzio

Istituto per lo Studio delle Macromolecole, CNR, Via Bassini 15, 20133 Milano, Italy, and Polo Scientifico e Tecnologico del CNR, via Fantoli 16, 20138 Milano, Italy.

ABSTRACT: New block copolymers constituted by different molar ratios of two semiconducting macromolecules, namely alternated copolymer of triphenylammino disubstituted fluorene with dialkylsubstituted fluorene (PFTPA) and alternated copolymer between benzothiadiazole with dialkylfluorene (PF8BT), have been synthesized and characterized. The copolymers formation was checked by gel permeation chromatography and photoluminescence (PL) measurements in solution. By controlling such a molar ratio the electro-optical properties can be tuned, reaching a PL quantum yield (QY) value higher than the one measured for each component alone. We show that both intra and interchain interactions determine the emission properties of block copolymers, that behave differently from homopolymer blends. By a proper chemical tailoring of a block copolymer structure, the emission can be addressed in terms of both emission spectral region and PLQY. The results suggest that the chance given by properly designed copolymers, has some advantages with respect to the approach of reaching the desired emission either by blending two polymers or by randomly polymerizing different amounts of chromophores with the desired emission.

Introduction

The preparation of block copolymers[1] has attracted much attention mainly because of the ordered nanophase separation occurring in these systems in the solid state as a results of the interchain interactions between the constituting blocks.

Most of the studies have been focused on two linear polymers linked together and on the possibility to tailor the morphologies in the solid state by a proper choice of both the annealing temperature and the relative length of the two blocks. Many examples have been reported on the nanophase separation occurring in polystyrene− (PS−) polymethylmethacrylate (PMMA) block copolymers,[2] PS−polyisoprene[3] and many others.[4]

The interest in these materials has recently increased because of the envisaged chance to use the ordered morphology generated by nanophase separation to create submicrometric patterns. This approach is particularly attractive for electronic applications both in traditional and organic microelectronics without the use of nanolithography. As an example Park et al.[5] showed how the use of RIE (reactive ion etching) can lead to a regular pattern on silicon as a result of an original self-organization due to nanophase separation occurring in a copolymeric film.

A further development in the use of block copolymers has been reached by synthesizing block copolymers formed by a semiconducting block and by an insulating block. Segalman et al. have shown[6] that the kind of structure reached by the active film prepared with a block copolymer with a block formed by a semiconducting polymer, strongly influences the electro-optical properties of organic light-emitting device (OLED).

Besides the morphological control achievable with copolymeric structures in the solid state, linking together, on the same macromolecule, two semiconducting blocks with different electronic properties, represents a new tool for reaching innovative materials which can undergo a fine-tuning of the electro-optical properties essentially through nanophase separation.

Relatively few examples appeared in literature describing the electro-optical properties of diblock semiconducting copolymers.[7,8] Recently Scherf et al.[9] reported on the synthesis and characterization of diblock copolymers formed by poly(9,9-dialkylfluorene) (PF) and poly(3-alkylthiophene): most of the work had been addressed to the solution properties of that copolymer.

In this work we have focused our attention on a series of semiconducting diblock copolymers (generally called Cop in the text, Scheme 1c); each block is formed by an alternated copolymer of triphenylammino disubstituted fluorene with dialkylsubstituted fluorene (hereafter PFTPA, Scheme 1a) and an alternated copolymer between benzothiadiazole with dialkyl-fluorene (hereafter PF8BT, Scheme 1b). We report on a description of the synthetic procedure and on the electro-optical properties of the synthesized copolymers both in solution and in solid state by varying the length of the two constituting blocks.

Experimental Section

**Characterization.** ^{1}H NMR spectra were recorded with a Bruker ARX400 spectrometer.

Gel permeation chromatography (GPC) measurements were carried out on Waters SEC system consisting of a pump, a 410 differential refractometer, and a 490 UV spectrophotometer as detectors. The column was a Ultrastyragel Waters; THF as solvent and polystyrene as standard were used.

Cyclovoltammetric (CV) measurements were performed at room temperature under nitrogen in a three electrode cell. The counter electrode was platinum; reference electrode was a silver/0.1 M silver perchlorate in AN (0.34 V vs SCE). The working electrode was a platinum minidisc electrode (0.003 cm²). The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator.

* Address correspondence to this author at the Istituto per lo Studio delle Macromolecole. E-mail: bolognesi@ismac.cnr.it.
† Present address: Groupe de Chimie de Coordination, ICMR-UMR CNRS 6229, UFR Sciences Exactes et Naturelles, Moulin de la Housse-BP 1039, 51687 Reims cedex 2-France.

Scheme 1. Synthesis Route of the Block Copolymers: (a) PFTPA1, PFTPA2, and PFTPA3 (Borolane Terminated); (b) PF8BT1 and PF8BT2 (Br Terminated); (c) Copolymers PFTPA−PF8BT:Cop1 and Cop2
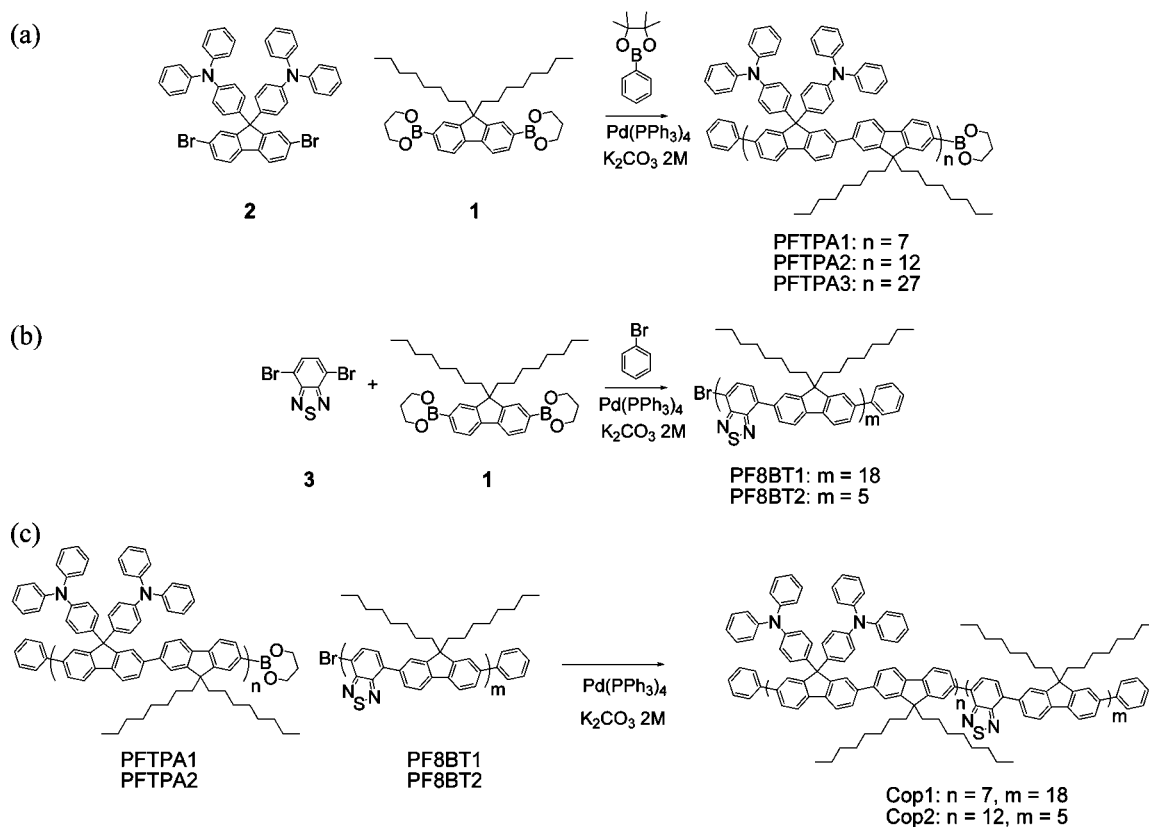
Photoluminescence (PL) was obtained with a spectrometer equipped with a CCD detector, by exciting with a monochromated Xenon lamp.

Solid-state PL quantum yield (QY) was obtained by using a homemade integrating sphere.

AFM investigations were performed using a NT-MDT NTEGRA instrument in noncontact mode.

All chemicals used were reagent grade and used as received. All solvents (Aldrich) used for the chemical reactions were dried by standard procedures.

Butyllithium (BuLi), bromohexane, 2-isopropoxy-(4,4,5,5-tetramethyl)-1,3,2-dioxoborolane, N-bromosuccinimide (NBS), 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (**1**), phenylboronic acid pinacol ester, bromobenzene, tetrakis(triphenylphosphine)palladium ((Ph3P)4Pd), and Aliquat 336 available from Aldrich or Acros were used as received. Flash chromatography purifications were carried out using silica gel (200−300 mesh ASTM). Suzuki reactions with conventional heating were carried out under nitrogen atmosphere.

The compounds: 9,9-bis(4-diphenylaminophenyl)-2,7-dibromofluorene[10] (**2**), 4,7-dibromo-2,1,3-benzothiadiazole[11] (**3**), 9,9-dioctyl-2-bromofluorene[12] (**4**) were prepared following the same procedure reported in literature. 2-(4,4,5,5-tetramethyl-1,3,2-dioxoborolane)-9,9-dioctylfluorene (**5**) was synthesized from **4** as reported in ref 13.

4-Bromo-2,1,3-benzothiadiazole-7-(9,9-dioctylfluorene) (6). Under inert atmosphere, 250 mg (0.853 mmol) of **5** and 440 mg (0.853 mmol) of **5** were dissolved in 10 mL of dry toluene, and then 1.6 mL of a degassed aqueous solution of 2 M K2CO3, the phase transfer catalyst Aliquat, and 21 mg (0.02 mmol) of (Ph3P)4Pd were added. The reaction mixture was stirred and heated at reflux under nitrogen for 24 h. The mixture was poured into water and extracted four times with diethyl ether. The combined organic phases were washed with brine, then dried over anhydrous MgSO4. The solvent was removed by rotary evaporation. The product was purified by column

chromatography (heptane/CH2Cl2 8/2). The yield was 45% (231 mg).

^{1}H NMR (CDCl3, 298 K) δ (ppm): 7.82 (d, 1H, J = 7.6 Hz, BT), 7.79 (dd, 1H, J = 1.37 Hz, J = 7.88 Hz, fluorenyl), 7.73 (s, 1H, fluorenyl), 7.70 (d, 1H, J = 7.89 Hz, fluorenyl), 7.63 (dd br, 1H, fluorenyl), 7.51 (d, 1H, J = 7.61 Hz, BT), 7.27−7.19 (br, 3H, fluorenyl), 1.9 (m, 4H, CH2), 1.06−0.94 (m, 20H, CH2), 0.66 (m, 10H, CH3, CH2).

PFTPA−Borolane Terminated. In a Schlenk tube 100 mg (0.123 mmol) of **2**, 69 mg (0.123 mmol) of **1** and 6 mg (5 μmol) of (Ph3P)4Pd were dissolved in 2 mL of anhydrous toluene. A 260 μL aliquot of of K2CO3 2 M and a catalytic amount of Aliquat were added to the solution. The reaction was stirred at 90 °C under nitrogen for 12 h. The end groups were terminated by adding 25 mg (0.123 mmol) of phenylboronic acid pinacol ester and stirring for 12 h at 90 °C. Then the reaction mixture was filtered on Celite and precipitated into methanol (100 mL). The precipitate was collected and extracted with acetone using a Soxhlet apparatus to give 53 mg, 41% yield. This compound, soluble in heptane, has been referred to as PFTPA1 in the text.

Ph-(C78H74N2)7-*borolane*^{1}H NMR (CDCl3, 298 K) δ (ppm): 7.89 (br, 2H, fluorenyl), 7.76 (br, 4H, fluorenyl), 7.71 (br, 2H, fluorenyl), 7.59 (br, 4H, fluorenyl), 7.23−7.17 (m, 12H, N−Ph), 7.11−7.08 (br, 8H, N−Ph), 7.01−6.96 (br, 8H, N−Ph), 2.05 (br, 4H, αCH2 alkyl chain), 1.08 (br, 24H, CH2), 0.77 (m, 6H, CH3).

GPC: M_n = 7700, polydispersity index (PDI) = 2.2.

Anal. Calcd for C78H74N2: C 89.95; H, 7.36.; N, 2.69%. Found: C 90.01; H, 7.89; N, 2.1%.

With a similar procedure, but with a polymerization time of 24 h, a PFPTA−borolane terminated was obtained with M_n = 12900 and PDI = 3.2. This polymer has been referred in the text as PFTPA2 (55 mg, 43% yield). With a polymerization time of 48 h, PFTPA3 (57 mg, 44% yield) was obtained with M_n = 28640 and PDI = 3.2.

PF8BT−Br Terminated. To a solution of 150 mg (0.510 mmol) of **3**, 294 mg (0.510 mmol) of **1**, 12 mg (10.2 μmol) of (Ph3P)4Pd,
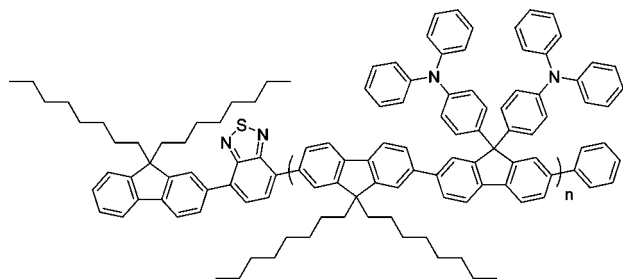
Figure 1. End1 and End2 polymer structures.

and a catalytic amount of Aliquat in 4 mL of toluene, 1 mL (2.2 mmol) of 2 M aqueous solution of K_2CO_3 was added. The reaction was stirred at 100 °C for 24 h then was capped by refluxing for 12 h with an excess of bromobenzene 81 μL (0.76 mmol). The reaction mixture was filtered on Celite and precipitated into methanol (100 mL). The precipitate was collected and extracted with acetone using a Soxhlet apparatus to give a PF8BT–bromine terminated polymer (153 mg, 57% yield). This polymer, soluble in cyclohexane, has been referred to as PF8BT1.

Ph-$(C_{35}H_{44}N_2S)_{18}$(Br) ^{1}H NMR (CDCl$_3$, 298 K) δ (ppm): 8.09−7.92 (m, fluorenyl + BT), 7.71−7.46 (m, Ph), 2.13 (br, CH$_2$), 1.16 (br, CH$_2$), 0.80 (br, CH$_3$).

GPC: M_n = 9700, PDI = 1.6.

With a similar procedure, but with a polymerization time of 3 h, a PF8BT–Br terminated compound was obtained with a M_n value of 2900 and PDI =2.1. This polymer has been referred to in the text as PF8BT2 (170 mg, 63% yield).

Copolymer PFTPA−PF8BT. PFTPA−borolane, an excess of PF8BT−Br and 2% molar ratio of (Ph$_3$P)$_4$Pd with respect to bromine derivative homopolymer, were dissolved in a solution of degassed toluene and aqueous 2 M potassium carbonate with a drop of Aliquat. The mixture was stirred at 85 °C for 24 h. The solution was filtered on Celite to remove the palladium then precipitated in methanol and extracted with acetone, cyclohexane, and heptane subsequently using a Soxhlet apparatus to remove the excess of PF8BT−Br, PFTPA homopolymer, and other impurities. In Scheme 1, the general synthetic route followed for this coupling has been reported.

Two different copolymeric materials were obtained as result of the coupling between PFTPA1 + PF8BT1 and PFTPA2 + PF8BT2. The two copolymers will be called in the text as Cop1 and Cop2 where the number 1 and 2 are related to the starting homopolymers.

Cop2= *Ph*-$(C_{78}H_{74}N_2)_{12}(C_{35}H_{44}N_2S)_5$-*Ph*: reagents PFTPA-boro-lane 39 mg (0.032mmol), PF8BT−Br 44.1 mg (0.065mmol), (Ph$_3$P)$_4$Pd 1.5 mg (1.3 μmol) in 3 mL of toluene, yield 24 mg ∼ 40% (w); ^{1}H NMR (toluene-d_6, 298 K) δ (ppm): 8.11 (s, fluorenyl), 7.8−7.6 (m, fluorenyl + BT), 7.42 (m, fluorenyl), 7.2−6.8 (m, N−Ph), 2.07 (br, αCH$_2$ alkyl chain), 1.05 (br, CH$_2$), 0.81 (m, CH$_3$).

GPC: Cop1, M_n = 16840, PDI = 2.6; Cop2, M_n =19800, PDI = 2.1.

End-Capped Copolymer. 50 mg PFTPA1, 20 mg of **6** (0.033 mmol), 3 mg of (Ph$_3$P)$_4$Pd (2.6 μmol) in 2 mL toluene, were reacted together in the presence of 400 μL K$_2$CO$_3$ 2 M in degassed water at 85 °C for 24 h. The solution was filtered on Celite and subsequently was precipitated in methanol. The resulting powder was dissolved in toluene and precipitated in an excess of methanol and dried. A further Soxlet extraction with acetone was performed in order to remove the excess of **6**. This polymer has been called in the text End1 (43 mg, 86% yield), while the same kind of polymer was obtained starting from PFTPA2 and capped with **6** following the same procedure above-described has been called in the text End2 (40 mg, 80% yield). See Figure 1 for the structures of End1 and End2.

Ph-$(C_{78}H_{74}N_2)_{27}(C_{35}H_{45}N_2S)$ ^{1}H NMR (CDCl$_3$, 298 K) δ (ppm): 8.02 (m, fluorenyl + BT), 7.86 (m, fluorenyl), 7.73 (m, fluorenyl),

7.56 (m, fluorenyl), 7.33 (m, Ph-end), 7.20−6.9 (m, N−Ph), 1.91 (br, αCH$_2$ alkyl chain), 1.04 (br, CH$_2$), 0.72 (m, CH$_3$).

GPC: End1, M_n = 8000, PDI = 1.8; End2, M_n = 29000, PDI = 3.3.

PFTPA-Capped. 30 mg PFTPA1, 13 μL of bromobenzene (0.127 mmol), 3 mg of (Ph$_3$P)$_4$Pd (2.6 μmol) in 2 mL toluene, were reacted together in the presence of 400 μL K$_2$CO$_3$ 2 M in degassed water and a catalytic amount of Aliquat at 85 °C for 18 h. The mixture was filtered on Celite and subsequently was precipitated in methanol. The resulting powder was dissolved in toluene and precipitated in an excess of methanol and dried. A further Soxhlet extraction with acetone was performed in order to remove the excess of bromobenzene. This polymer has been called in the text PFTPA1-capped (22 mg, 73% yield), while the same kind of polymer obtained starting from PFTPA2 has been called in the text capped-PFTPA2 (26 mg, 86% yield).

Ph-$(C_{78}H_{74}N_2)_7$-*Ph* ^{1}H NMR (CDCl$_3$, 298 K) δ (ppm): 8.01 (m, fluorenyl + BT), 7.86 (m, fluorenyl), 7.72 (m, fluorenyl), 7.56 (m, fluorenyl), 7.34 (m, Ph-end), 7.20−6.9 (m, N−Ph), 1.91 (br, αCH$_2$ alkyl chain), 1.04 (br, CH$_2$), 0.71 (m, CH$_3$).

PF8BT-Capped. 30 mg of PF8BT1, 20 mg (0.098 mmol) of phenylboronic acid pinacol ester, 3 mg (2.6 μmol) of (Ph$_3$P)$_4$Pd in 2 mL of toluene were reacted together in the presence of 400 μL K$_2$CO$_3$ 2 M in degassed water and a catalytic amount of Aliquat at 85 °C for 18 h. The reaction mixture was filtered on Celite and precipitated into methanol (100 mL). The precipitate was collected, extracted with acetone and toluene subsequently using a Soxhlet apparatus. This polymer has been called in the text PF8BT1-capped (27 mg, 90% yield), while the same kind of polymer obtained starting from PF8BT2 has been called in the text capped-PF8BT2 (25 mg, 83% yield).

Ph-$(C_{35}H_{44}N_2S)_{18}$-*Ph* ^{1}H NMR (CDCl$_3$, 298 K) δ (ppm): 8.09−7.92 (m, fluorenyl + BT), 7.71−7.46 (m, Ph), 2.13 (br, CH$_2$), 1.16 (br, CH$_2$), 0.80 (br, CH$_3$).

Results and Discussion

Synthesis and Copolymer Composition. We have chosen the polymer structures shown in Scheme 1 because they absorb and emit in two different regions of the visible range, i.e. blue region for PFTPA and green for PF8BT, moreover the emission spectrum of the former partially overlaps the absorption spectrum of the latter allowing both intra- and interchain energy transfer (ET) processes. PFTPA has been preferred to conventional dialkylsubstituted poly(fluorene)s because it does not show fluorenone luminescence even after exposition to both air and light,[14] displaying a stable amorphous phase.

Our general synthetic approach is based on the chance to get the two blocks, PFTPA and PF8BT, end capped with a boronic ester and a bromine respectively. The homopolymers have been synthesized in two different steps following the synthetic procedures reported in literature: see Scheme 1a for PFTPA[13] and Scheme 1b for PF8BT.[15] In Scheme 1c the synthetic method to obtain block-copolymers formed by PFTPA and PF8BT (Cop in the text) is outlined. Following this procedure PFTPA-*borolane terminated* further reacted with an excess of PF8BT−Br *terminated* under Suzuki cross-coupling in degassed toluene and aqueous 2 M potassium carbonate using 2% molar ratio of (Ph$_3$P)$_4$Pd and transfer catalyst to give the final copolymeric structures. We checked carefully in all steps the molar percentage of the catalyst in order to avoid deboronation reactions which prevent the final Suzuki coupling. The separation of block-copolymers from homopolymers side products was accomplished by solvent extraction using Soxhlet apparatus since the constituting homopolymers are soluble either in heptane or in cyclohexane. However, we do not exclude that some PFTPA homopolymer still remain in the polymeric reaction media. GPC provides the way to determine the average molar mass (M_n) of the copolymers and attests the efficient formation of a link between the two constituting blocks. The data obtained from
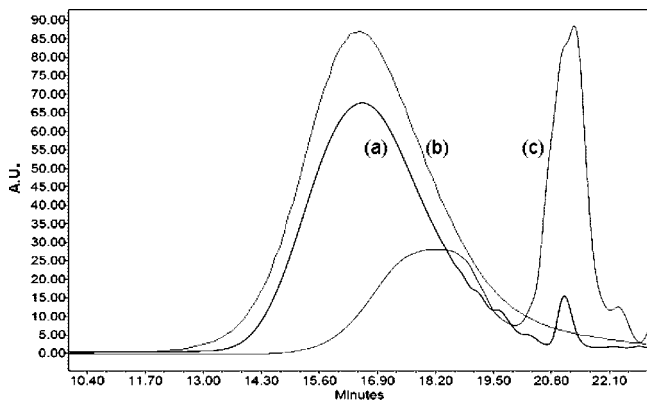
Figure 2. GPC traces of Cop1 before ciclohexane extraction (a), after (b) and of a mixture (c) of the starting homopolymers constituting Cop1 (PFTPA1-capped and PF8BT1-capped) in the feed molar ratio.

Table 1. GPC Data for PFTPAs and PF8BTs Homopolymers, Block Copolymers, and End Copolymers

	M_n	M_w/M_n	
PFTPA1	7700	2.2	$Ph\text{-}(C_{78}H_{74}N_2)_7\text{-}borolane$
PFTPA2	12900	3.2	$Ph\text{-}(C_{78}H_{74}N_2)_{12}\text{-}borolane$
PFTPA3	28640	3.2	$Ph\text{-}(C_{78}H_{74}N_2)_{27}\text{-}borolane$
PF8BT1	9700	1.6	$Ph\text{-}(C_{35}H_{44}N_2S)_{18}(Br)$
PF8BT2	2900	2.1	$Ph\text{-}(C_{35}H_{44}N_2S)_5(Br)$
Cop1	16840	2.6	(PFTPA1)-(PF8BT1)
Cop2	19800	2.2	(PFTPA2)-(PF8BT2)
End1	8000	1.85	(PFTPA1)-$(C_{35}H_{45}N_2S)$
End2	29000	3.3	(PFTPA3)-$(C_{35}H_{45}N_2S)$

this technique using both Refraction index and UV−vis absorption detections, clearly indicate that the M_n values for the copolymers result to be higher than those of the starting homopolymers. In Figure 2 a GPC chromatogram of the PFTPA−PF8BT copolymer (Cop1) is reported as an example and compared with a chromatogram of the mixture of the two homopolymers (PFTPA1-capped and PF8BT1-capped) in the same molar ratio used for the copolymer preparation.

It is evident that the copolymer elution time is shorter than those of both mixture components. Moreover it can be seen that a small amount of the PF8BT homopolymer exhibiting an elution time at 21 min, still remains as impurity in the copolymeric system. A selective extraction of this impurity by using cyclohexane as solvent was possible as evidenced in the chromatogram which shows a monomodal symmetric trace and no peaks at 21 min.

Using the same synthetic procedure we have also prepared some PFTPAs ending with a green cromophore formed by benzothiadiazole linked to dioctylsubstituted fluorene residue (**6**), which means one monomeric unit of PF8BT homopolymer (End1 and End2).

In Table 1 the average molecular mass and the polydispersity values of the starting homopolymers PFTPA1, PTFPA2, PTFA3, PF8BT1 and PF8BT2 and of the resulting block copolymers Cop1 and Cop2 and end-polymers End1 and End2 are reported. We have verified the success of this synthetic approach also in the case of a block copolymer obtained from polyfluorene and poly(3-alkylthiophenes)blocks. In that case also the M_n value of the block copolymer is higher than the M_n of the two starting homopolymers.[16]

According to the M_n values obtained from GPC, which have been referred to standard of polystyrene, a very rough estimation of the length of the blocks constituting both Cop1 and Cop2 can be attempted. Due to the strict chemical difference between the two conjugated segments is not possible the extrapolation of the relative intensity of their ^1H NMR signals to calculate the ratio of the two blocks.

Table 2. Polymer Oxidation and Reduction Potentials (Onsets in Brackets)

polymer	E_{ox}/V^a	E_{red}/V^b
PFTPA2-capped	0.47, 0.57, 0.97 (0.3)	−2.8 (−2.40)
Cop2	0.46, 0.55, 0.98 (0.3)	−2.8 (−2.40)
Cop1	0.44, 0.57, 1.05 (1.0)	−2.39 (−2.54)
PF8BT2-capped	1.0 (1.1)	−2.4 (−2.45)

^{a} Redox values. ^{b} Peak values.

CV Characterization. CV characterizations of Cop1, Cop2, PFTPA2, and PF8BT2 were performed. The polymers were cast on glass carbon electrode from 1% solution in toluene. The redox patterns, particularly the oxidation, of PFTPA2 and Cop2 are very similar as well as the electrochemical parameters, as expected for a system in which PFTPA2 block is prevailing. Conversely PF8BT2 and Cop1 resemble each other in the reduction trace as expected for a block copolymer mainly constituted by fluorenbenzothiadiazole segments. The polymer films of Cop2 and PFTPA2 are oxidized with reversibility in a twin process with redox potentials $E^0 = $ ca. 0.47 and 0.56 V, followed by a further oxidation process at $E^0 = $ ca. 1.0 V, which involves roughly 50% of the charge used in the previous one. The first twin process is due to oxidation of the two triphenylamine moieties, the second to the polyfluorene backbone. These two peaks probe the antioxidant effect of the triphenylammine moiety.

The polymers Cop2 and PFTPA2 are also reversibly reduced at $E^0 = $ ca. −2.80 V, though the reversibility is scarce and lost at low scan rates due to dissolution of the produced anions. The values of redox potential of PF8BT2 block and Cop1 are also reported in Table 2, the polymers are reversibly reduced at lower voltages, −2.4 V and shows an oxidation pattern similar to a standard PF ($E^0 = $ ca. 1 V).[17] The contribution of the two constituting homopolymers is evident both in the peak shape of the oxidation zone of Cop1 and, even in less extent, in the profile due to the reduction process of Cop2. Cyclic voltammogram of polymer films in acetonitrile + 0.1 M Bu₄NClO₄ are reported in Figure 3.

Optical Characterization. UV visible absorption and PL spectra obtained by exciting at 390 nm PFTPAs, PF8BTs, Cops and Ends polymers in solution are reported in Figure 4. It is clear from the absorption spectra that by changing the copolymer composition, the spectrum shapes change accordingly, i.e. increasing the PF8BT content the intensity of the peak associated to this polymer increases.

The main peaks at 388 and 450 nm in the absorption spectra, are attributed to $\pi\text{-}\pi^*$ transition of the homopolymers PFTPA and PF8BT respectively, the peak at 310 nm is due to TPA groups. In the absorption spectrum of Cop1 and Cop2, being formed by different amount of the two homopolymers, the components of both the constituent blocks are present. Both End1 and End2 exhibit the same absorption spectra of the PFTPA homopolymer with a weak tail only around 450 nm in addition.

The PL spectra of the solutions show spectral features of both components. The emission peaks are 417 and 441 nm for PFTPA and 525 nm for PF8BT.

UV visible absorption and PL spectra of homopolymers and copolymers in solid-state are reported in Figure 5. The main peak in the absorption spectra of PFTPA is at 388 nm and at 470 nm for PF8BT, while peaks in PL emission spectra are at 426, 448, 483 nm for PFTPA and 544 nm for PF8BT, respectively.

A complete spectral overlap between the absorption of PF8BT and the emission of PFTPA is attained. This condition satisfies the request for an efficient Förster resonant energy transfer[18]
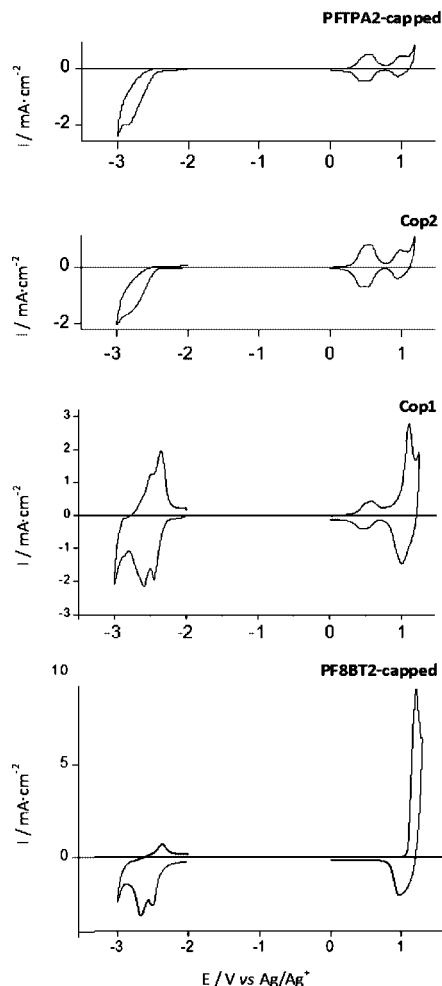
Figure 3. Cyclic voltammograms of polymer films in acetonitrile + 0.1 M Bu₄NClO₄. Scan rate: 0.02 V s⁻¹.

(FRET) from PFTPA, the excitation donor, to the PF8BT, that behaves as acceptor.

It is evident that beyond the bathocromic shift, PL spectra dramatically change in the solid state with respect to the solution. In fact, while in diluted solutions the interchain FRET is absent, both intra and intermolecular FRET processes take place in solid state resulting in an enhancement of the contribution of the PF8BT emission with respect to PFTPA. PL emission occurs in the blue region (PFTPA) only when the PFTPA/PF8BT ratio between the two blocks is high (End2) while PF8BT emission dominates in Cop2. For lower ratio (End1 and Cop1), only emission from the lower energy gap material, i.e., PF8BT, occurs as a result of the FRET process and the emission spectra progressively shifts from a solution-like spectrum (peak centered at 525 nm) to a solid-state one (peak centered at 544 nm).

In order to investigate the FRET process, we calculated the Förster radius (or critical radius) R_0, defined as the average distance between donor and acceptor when the FRET rate is equal to the sum of all other relaxation rates of the donor, following the method reported elsewhere.[15] A value of $R_0 = 3.1$ nm in agreement with those reported in literature for standard PF and PF8BT blends[19,20] has been obtained.

The evidence of the formation of the diblock structures is also confirmed by a spectroscopical study of the copolymer diluted solutions and those of corresponding blends with the same molar ratio by exploiting FRET mechanism. The plot reported in Figure 6 as example, shows the PL spectra of diluted solutions (concentration less than 10^{-5} M) of Cop2 and corresponding blend of the two blocks capped-PFTPA2 and

capped-PF8BT with the same molar ratio of the copolymer. Cop2 shows the spectral features of both PFTPA and PF8BT, while no emission from PF8BT was detected in the blend by direct excitation of PFTPA ($\lambda = 390$ nm). This is an indication that an intramolecular FRET process, occurring between PFTPA and PF8BT blocks, takes place in Cop2 only, proving that PFTPA and PF8BT are chemically linked together.

The PLQY of neat PFTPA and PF8BT film results to be $(45 \pm 5)\%$ and $(50 \pm 5)\%$, respectively. The PLQY value of PFTPA is in good agreement with standard PF.[21] As reported by Cadby et al.,[22] there is a range of ratios where the recorded PLQY of the blend is higher than that of its individual components, reaching a maximum value of $70 \pm 3\%$ at a relative PF8BT concentration of 5 wt %. The same trend is observed for the copolymers as shown in Table 3 and the optimal ratio PFTPA/PF8BT of 12/5 mol (=4/1 w/w) between the two components is found (Cop2).

In fact, PLQY of Cop2 is $(74 \pm 6)\%$, while for the other copolymer compositions it is comparable with PLQY of neat blocks.

Previous studies of PF and PF8BT polymers in devices have been focused on blends ranging from 5 wt % to 25 wt % of PF8BT into PF. LEDs having as active layer a thin film formed by blends with 5 wt % PF8BT in PF show good performances.[23]

Preliminary measurements of optoelectronic properties of Cop2-based OLED devices showed improved performances, i.e. quantum efficiency and luminance, with respect to the other devices based on copolymers reported both here and in literature. Cop2's EQE is at least three times greater than Cop1 and End copolymers and slightly better if compared with blend of commercial PFO and F8BT with the same molar ratio. Performances of block copolymers and end-capped polymers-based OLEDs are object of a forthcoming publication.

No changes in copolymers optical characteristics upon thermal treatment are observed by heating at 160 °C for 30 min under nitrogen atmosphere, as already reported for PFTPA homopolymer.[13]

Morphology. Tapping mode AFM investigation reveals strong differences in morphology of Cop1 with respect to both the end-capped polymers and Cop2, behaving essentially as PFTPA, i.e. mainly amorphous. In Figure 7 we report AFM height (left) and phase (right) images of Cop1 film on quarz; a phase separation occurs with domain size comparable to the length of the two blocks ($\sim$10nm). The root-mean-square roughness is 0.44 nm.

Moreover, the thermal analysis of Cop1 reveals strict similarities with PF8BT1 one (more crystalline homopolymer) showing a T_g at around 120 °C, consistent with the results reported by Donley et al.,[24] hence pointing out a relevant role of PF8BT in determining the segregation/aggregation in the copolymers.

Although the technique can not univocally address toward a copolymer formation, the results are compatible with such an indication.

Conclusions

We have synthesized and characterized several diblock copolymers PFTPA−PF8BT. They exhibit different electro-optical properties according to the relative length of the two blocks. The maximum in the PLQY (0.74 ± 6) has been reached with a ratio between PFTPA and PF8BT of 4/1 w/w. This value is much higher than the PLQY of the PFTPA and PF8BT homopolymers. A similar increase in PLQY has been reported also for blends of PF and PF8BT, but the ratio between the two homopolymers was 19/1 w/w. The different ratio is a neat
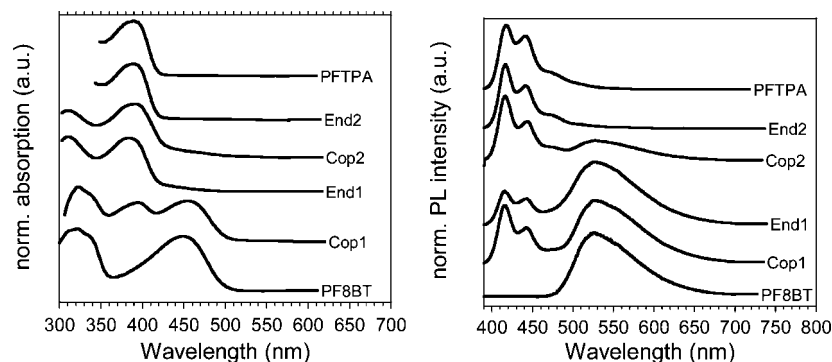
Figure 4. Normalized absorption (left) and PL spectra (right) of homo- and copolymers in solution. Spectra are shifted for clarity. Excitation wavelength of PL spectra is 390 nm.
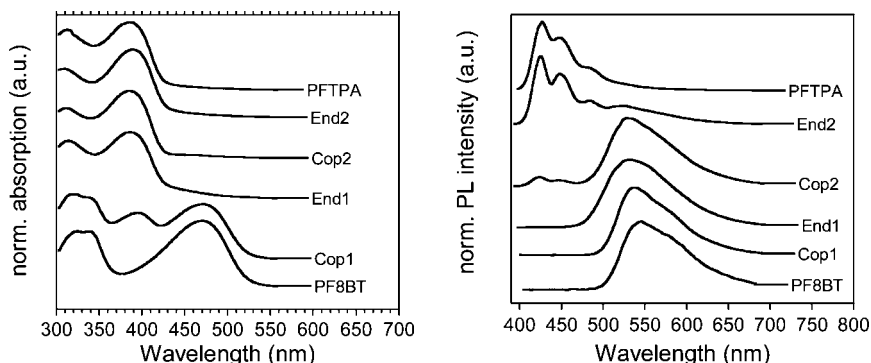

Figure 5. Normalized absorption (left) and PL spectra (right) of homo- and copolymers in solid-state. Spectra are shifted for clarity. The excitation wavelength of PL spectra is 390 nm.
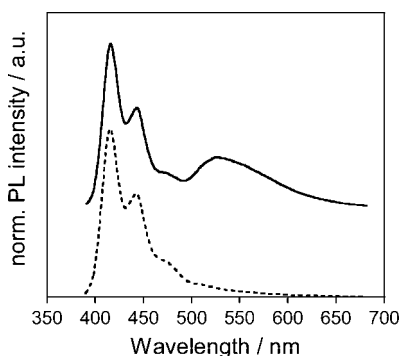

Figure 6. Solution PL spectra of Cop2 (solid line) and corresponding blend (dotted line) by exciting at 390 nm. Spectra are shifted for clarity.

Figure 7. AFM tapping mode height (left) and phase (right) images of Cop1 film on quarz; the bar is 100 nm.

Table 3. PLQY of the Compounds in the Solid State

compound	solid-state PLQY
PFTPA1-capped	0.45 ± 5
Cop1	0.48 ± 5
Cop2	0.74 ± 6
PF8BT1-capped	0.50 ± 3
End1	0.45 ± 4
End2	0.48 ± 5

indication that the interaction between the homopolymers in a blend is extremely different with respect to the block copolymers.

Our study indicates that the emission in a block copolymer where two semiconducting blocks are chemically linked is a process dominated by intrachain processes in diluted solutions. In the solid state however both intra and interchain interactions control of the emission from the homopolymer blocks. As a result, in order to obtain emission from both the blocks of the copolymeric structur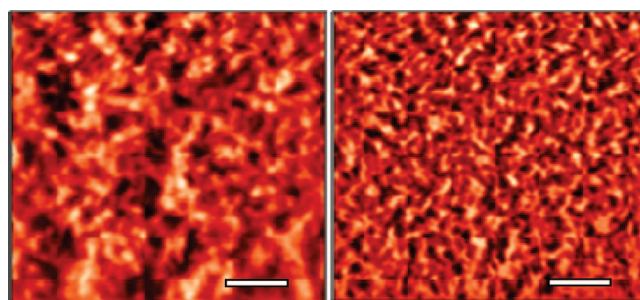e one should avoid that all the energy absorbed by the block having higher energy gap is transferred to the lower energy gap block. Hence the length of the two blocks, their relative PLQY, and the structural and morphological properties of the material are key steps in the determining the overall emission.

By proper chemical tailoring we have shown that the control and the reproducibility of the emission in a copolymeric structure can be achieved easier than by randomly polymerization of different chromophores. We believe that the chance given by conjugated block copolymers, with known composition and structure, has the advantage to simplify and make highly reproducible the procedures for the preparation of active materials thin films for devices. Such benefits make these block copolymers a valuable alternative to the standard approach of blending two different polymers.

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