

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231240769>

All-Conjugated Diblock Copolymer Approach To Improve Single Layer Green Electroluminescent Devices

ARTICLE in CHEMISTRY OF MATERIALS · OCTOBER 2010

Impact Factor: 8.35 · DOI: 10.1021/cm102154q

CITATIONS

17

READS

21

9 AUTHORS, INCLUDING:



Chiara Botta

Italian National Research Council

193 PUBLICATIONS 2,022 CITATIONS

SEE PROFILE



Silvia Destri

Italian National Research Council

175 PUBLICATIONS 1,957 CITATIONS

SEE PROFILE



Mariacecilia Pasini

Italian National Research Council

66 PUBLICATIONS 879 CITATIONS

SEE PROFILE



W. Porzio

Italian National Research Council

228 PUBLICATIONS 3,027 CITATIONS

SEE PROFILE

All-Conjugated Diblock Copolymer Approach To Improve Single Layer Green Electroluminescent Devices[†]

Umberto Giovannella,^{*,‡} Paolo Betti,[‡] Chiara Botta,[‡] Silvia Destri,[‡] Juliette Moreau,^{‡,§} Mariacecilia Pasini,[‡] William Porzio,[‡] Barbara Vercelli,^{||} and Alberto Bolognesi[‡]

[‡]*Istituto per lo Studio delle Macromolecole, Consiglio Nazionale delle Ricerche via Bassini 15, 20133 Milano (Italy)*, [§]*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.*, and ^{||}*Istituto per l'Energetica e le Interfasi, Consiglio Nazionale delle Ricerche c.o Stati Uniti 4, 35127 Padova (Italy)*

Received July 31, 2010. Revised Manuscript Received September 21, 2010

To improve both the stability and the efficiency of single spin-coatable active-layer polymer light emitting devices based on fluorene (F) and benzothiadiazole (BT), that is, two of the monomers employed as building units in the most efficient electroluminescent polymers commonly used in organic electronics, we carry out a dual strategy. We prepare a triphenylamino (TPA) disubstituted F in order to improve hole injection, prevent oxidation and aggregation and we exploit the mechanism of resonant energy transfer through the macromolecular approach of a rod–rod-type all conjugated diblock copolymer formed by an alternated copolymer of TPA disubstituted F with dialkylsubstituted F (poly[(9,9-di-*n*-hexylfluorene)-*alt*-(9,9-bis(4-diphenylaminophenyl)-fluorene)] and an alternated copolymer between BT and F (poly(9,9'-dioctylfluorene-*alt*-benzothiadiazole)). We show that, by changing the relative length of the two blocks, we are able to address the electrooptical properties thanks to a different supramolecular organization, which can be governed by a proper chemical design, and the energy transfer mechanism tunability. The device performance and color coordinates are controlled by both the suppression of oxidation processes and the high thermal stability of the copolymers which allow stable green HDTV standard-matching electroluminescence to be obtained at ambient conditions for several hours. Two different copolymers are studied: a diblock amorphous copolymer and a more crystalline one. A further increase of the external quantum efficiency up to 5.5%, a luminous efficiency of 22.5 cd/A with a luminance of above 50 000 cd/m², is obtained by the improvement of the cathode/polymer interfacial adhesion in the former copolymer upon thermal treatment above the glass transition temperature of PF8BT. On the contrary, the same treatment on the latter compound is detrimental (charge carrier unbalancing) due to a further increase of the crystallinity. The insertion of a poly(*N*-vinylcarbazole) interlayer prevents exciton quenching at the PEDOT:PSS interface.

1. Introduction

The fine-tuning of the electrooptical properties is one of the main advantages of the organic semiconductors with respect to the inorganic ones. Absorption, emission, and charge transport are the results of many different factors that chemists are able to manage with the aim of optimizing a structure in view of the final application. Polymers are particularly suitable to undergo fine-tuning because of the chance given by many synthetic actions onto the same starting backbone: change in side chain length and structure, presence of groups with different polarities, and stiffness of the substituents. Besides this approach, which is already a common procedure, we have shown that combining together two semiconducting polymers, giving a diblock semiconducting macromolecule, offers the further advantage to address morphological features and allows the electrical properties to be tuned by controlling

inter- and intrachain interactions.¹ The tuning of the chemical structure of diblock copolymers together with the choice of the proper film deposition procedure allow the suitable supramolecular organization to be reached to address the physical processes at the base of device performances.²

Among the wide class of conjugated polymers for organic light emitting device (OLED) fabrication, the most used for blue and green emission are polymers based on fluorene and benzothiadiazole, respectively. Very efficient, but still far from phosphorescence emitters,³ green emitting devices have been prepared using the state-of-the-art alternated

[†] Accepted as part of the "Special Issue on π -Functional Materials".

*Corresponding author. E-mail: u.giovannella@ismac.cnr.it.

- (1) Scherf, U.; Gütacker, A.; Koenen, N. *Acc. Chem. Res.* **2008**, *41*, 1086–1097.
- (2) (a) Segalman, R. A.; McCulloch, B.; Kirmayer, S.; Urban, J. J. *Macromolecules* **2009**, *42*, 9205–9210. (b) Sommer, M.; Hutter, S.; Wunder, S.; Thelakkat, M. *Adv. Mater.* **2008**, *20*, 2523–2527. (c) Liang, Y.; Wang, H.; Yuan, S.; Lee, Y.; Gan, L.; Yu, L. *J. Mater. Chem.* **2007**, *17*, 2183–2194.
- (3) Lai, S. L.; Tao, S. L.; Chan, M. Y.; Ng, T. W.; Lo, M. F.; Lee, C. S.; Zhang, X. H.; Lee, S. T. *Org. Electron.*, doi: 10.1016/j.orgel.2010.06.011.

poly(9,9'-dioctylfluorene-co-benzo-thiadiazole) (PF8BT),^{4,5} random copolymers between fluorene and benzothiadiazole,⁶ or blends between a small percentage of PF8BT and polyfluorene.^{7,8} To improve the performance of these green emitting OLEDs, we have focused the attention on semiconducting diblock copolymers formed by an alternated copolymer of triphenylamino (TPA) disubstituted fluorene with dialkylsubstituted fluorene (hereafter PFTPA) and an alternated copolymer between benzothiadiazole with dialkylfluorene (hereafter PF8BT). We showed that the introduction of TPA as lateral substituents in polyfluorenes greatly improves their performances since it leads simultaneously to (i) improved hole injection, (ii) strong antioxidant action, (iii) reduced energy transfer (ET) toward residual defect sites, and (iv) nano-encapsulation environment of the polymer chains, leading to OLED devices with deep blue color stability.^{9,10}

In this paper we report on the behavior of optical and electrooptical properties of two all-conjugated diblock copolymers obtained by varying the length of the PFTPA and PF8BT constituting blocks. We show that the peculiar supramolecular organization of the diblock copolymers allows us to prepare single emitting layer devices with improved green emission, in terms of efficiency, color purity, and stability.

2. Experimental Section

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 an Ultrastaygel Waters; THF as solvent and polystyrene as standard were used. Cyclic voltammetric measurements were performed at room temperature under nitrogen in a three electrode cell. The counter electrode was platinum; the 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. AFM investigations were performed using a NT-MDT NTEGRA instrument in noncontact mode in ambient conditions. Differential scanning calorimetry (DSC) measurements were carried out on a Perkin-Elmer Pyris 1 instrument calibrated with indium standard. Photoluminescence (PL) and electroluminescence (EL) were obtained with monochromator equipped with a CCD detector, by exciting with a monochromated Xenon lamp, or by applying a constant bias, respectively.

Solid-state PL quantum yields (QY) were obtained by using a homemade integrating sphere.¹¹ Current–voltage (*I*–*V*) characteristics were recorded with a Keithley 2602 source meter. The luminance of the device was measured with a calibrated photodiode. The external quantum efficiency (EQE) in the forward direction was derived, by supposing a lambertian source behavior, according to the expression¹² $\eta_{\text{EXT}} = \pi r^2 e P_{\text{DET}} \lambda / (A_{\text{DET}} h c I_{\text{OLED}})$, where *r* is the distance between OLED and the detector, *e* the charge of an electron, *P*_{DET} the power that the detector measures, λ the emission wavelength, *A*_{DET} the area of the detector, *h* Planck's constant, *c* the speed of light in vacuum, and *I*_{OLED} the current injected.

All chemicals used were reagent grade and used as received. All solvents (Aldrich) used for the chemical reactions were dried by standard procedures. Each segment and the final block-copolymers were obtained via Suzuki reactions carried out under nitrogen atmosphere in toluene using Pd(PPh₃)₄ as catalyst and conventional heating.¹³

Film and OLED Fabrication. Polymers were dissolved in 15 mg/mL toluene. Indium tin oxide (ITO; 15 Ω per square) substrates were cleaned by sonication in distilled water, acetone, and isopropyl alcohol. After treatment with nitrogen plasma, a thin film (50 nm) of filtered (nylon 0.45 μm) poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonic acid) (PEDOT:PSS) (Clevios P VP AI 4083, H.C. Starck) used as a hole-injection layer at the anode interface was spin-coated onto the ITO substrate and then dried under nitrogen atmosphere at 100 °C for 15 min. A thin film (50 nm) of poly(vinylcarbazole) (PVK; Aldrich, MW 1 000 000) from chlorobenzene solution was subsequently deposited on top of the PEDOT:PSS layer and treated at 150 °C for 30 min. A thin film of emitting compound (100–120 nm) was then spin-coated inside a nitrogen-filled M-Braun drybox. A thin layer of Calcium (30 nm) or Barium (5 nm) and subsequently a 100 nm layer of Aluminium were deposited on the top by vacuum (10^{−7} mbar) thermoevaporation. All device preparation steps were carried out inside the drybox system.

3. Results and Discussion

A. Synthesis. We have chosen the diblock copolymer structure shown in Scheme 1 because the two blocks emit in two different regions of the visible range, that is, blue region for PFTPA and green for PF8BT, and the emission spectrum of the former almost completely overlaps the absorption spectrum of the latter allowing both intra- and interchain energy transfer (ET) processes. The two blocks have different morphological and structural properties: PFTPA shows a stable amorphous phase,⁵ while PF8BT, accordingly to its molecular weight and polydispersity, can achieve a noticeable degree of order.

The details of the synthesis route of the block copolymers were reported elsewhere.¹³ Our general synthetic approach is based on the chance to get the two blocks,

- (4) He, Y.; Gong, S.; Hattori, R.; Kaniki, J. *Appl. Phys. Lett.* **1999**, *74*, 2265.
- (5) Kabra, D.; Lu, L. P.; Song, M. H.; Snaith, H. J.; Friend, R. H. *Adv. Mater.* **2010**, *22*, 3194–3198.
- (6) (a) Herguth, P.; Jiang, X.; Liu, M. S.; Jen, A. K.-Y. *Macromolecules* **2002**, *35*, 6094. (b) Liu, J.; Bu, L.; Dong, J.; Zhou, Q.; Geng, Y.; Ma, D.; Wang, L.; Jing, X.; Wang, F. *J. Mater. Chem.* **2007**, *17*, 2832.
- (7) Xu, Q.; Ouyang, J.; Yang, Y.; Ito, T.; Kido, J. *Appl. Phys. Lett.* **2003**, *83*, 4695.
- (8) Morgado, J.; Friend, R. H.; Cacialli, F. *Appl. Phys. Lett.* **2002**, *80*, 2436.
- (9) Giovanella, U.; Pasini, M.; Destri, S.; Porzio, W.; Botta, C. *Synth. Met.* **2008**, *158*, 113.
- (10) Pasini, M.; Giovanella, U.; Betti, P.; Bolognesi, A.; Botta, C.; Destri, S.; Porzio, W.; Vercelli, B.; Zotti, G. *Chem. Phys. Chem.* **2009**, *10*, 2143–2149.

- (11) Moreau, J.; Giovanella, U.; Bombenger, J.-P.; Porzio, W.; Vohra, V.; Spadacini, L.; Di Silvestro, G.; Barba, L.; Arrighetti, G.; Destri, S.; Pasini, M.; Saba, M.; Quochi, F.; Mura, A.; Bongiovanni, G.; Fiorini, M.; Uslenghi, M.; Botta, C. *Chem. Phys. Chem.* **2009**, *10*, 647 and references therein.
- (12) Gong, X.; Robinson, M. R.; Ostrowski, J. C.; Moses, D.; Bazan, G. C.; Heeger, A. J. *Adv. Mater.* **2002**, *14*, 581–585. Chen, Z.-Q.; Ding, F.; Bian, Z.-Q.; Huang, C.-H. *Org. Electron.* **2010**, *11*, 369–376.
- (13) Bolognesi, A.; Betti, P.; Botta, C.; Destri, S.; Giovanella, U.; Moreau, J.; Pasini, M.; Porzio, W. *Macromolecules* **2009**, *42*, 1107.

Scheme 1. Synthesis Route of the PFTPA-PF8BT Diblock Copolymers

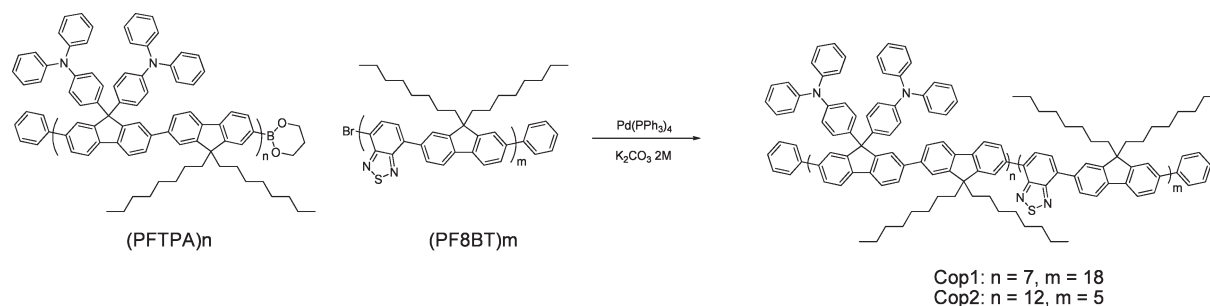


Table 1. GPC Data of PFTPA and PF8BT Homopolymers and Diblock Copolymers

compound		M_n	M_w/M_n	chemical formula
(PFTPA) _n	$n = 7$	7700	2.2	Ph-(C ₇₈ H ₇₄ N ₂) _n -borolane
	$n = 12$	12900	3.2	
(PF8BT) _m	$m = 18$	9700	1.6	Ph-(C ₃₅ H ₄₄ N ₂ S) _m Br
	$m = 5$	2900	2.1	
Cop1	$n = 7, m = 18$	16840	2.6	Ph-(C ₇₈ H ₇₄ N ₂) _n -(C ₃₅ H ₄₄ N ₂ S) _m -Ph
Cop2	$n = 12, m = 5$	19800	2.2	

PFTPA and PF8BT, end-capped with a boronic ester and a bromine, respectively, and so, thanks to their complementary functionality, be able to react with each other. These precursor homopolymers have been synthesized in two different steps following the synthetic procedures reported in the literature.¹⁴ The two different diblock copolymers were obtained as result of the coupling between the a short segment (PFTPA)₇ and a long segment (PF8BT)₁₈, yielding blockcopolymer Cop1, while the longer segment (PFTPA)₁₂ reacts with the shorter (PF8BT)₅, producing Cop2. The data obtained from the gel permeation chromatography (GPC) technique using both the refraction index and UV-vis absorption detections clearly indicate that the M_n values for the diblock copolymers are higher than those of the starting homopolymers, as reported in Table 1 together with the polydispersity values.

A rough estimation of the length of the blocks constituting Cop1 and Cop2, deduced from the M_n values as obtained from GPC referred to polystyrene standard, are 16 840 (polydispersity 2.6) and 19 800 (2.2), respectively. The block copolymers are compared with the homopolymers obtained by capping at both ends the precursor polymers, as reported elsewhere,¹³ giving PFTPA-capped and PF8BT-capped (hereinafter PFTPA and PF8BT, respectively).

B. Optical Characterization. UV visible absorption and PL spectra of capped homopolymers and block copolymers in solid-state are reported in Figure 1. In the absorption spectra, the main peaks of PFTPA are at 310 and 388 nm, and those of PF8BT are at 340 and 470 nm. Peaks in the PL emission spectra are at 426, 448, and 483 nm for PFTPA, while the peaks at 536 nm and 525 nm dominate in the Cop1 and Cop2 spectra, respectively. For PF8BT the peak is at 545 nm. A residual blue emission

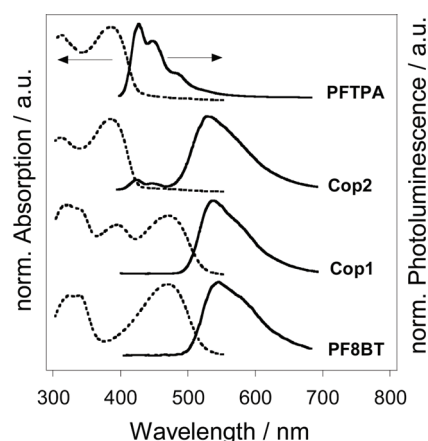


Figure 1. Normalized absorption (dotted line) and PL spectra (solid line) of homopolymers and diblock-copolymers in the solid state. Spectra are vertically shifted for clarity. The excitation wavelength for PL spectra is 390 nm.

from the PFTPA moiety is observed in the Cop2 PL spectrum.

An almost 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 ET¹⁵ (FRET) from PFTPA, the excitation donor, to PF8BT that behaves as the acceptor.

PL spectra of homopolymers and block copolymers were recorded using an excitation wavelength of 390 nm, which corresponds to the absorption peak of PFTPA. 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 the PFTPA one.

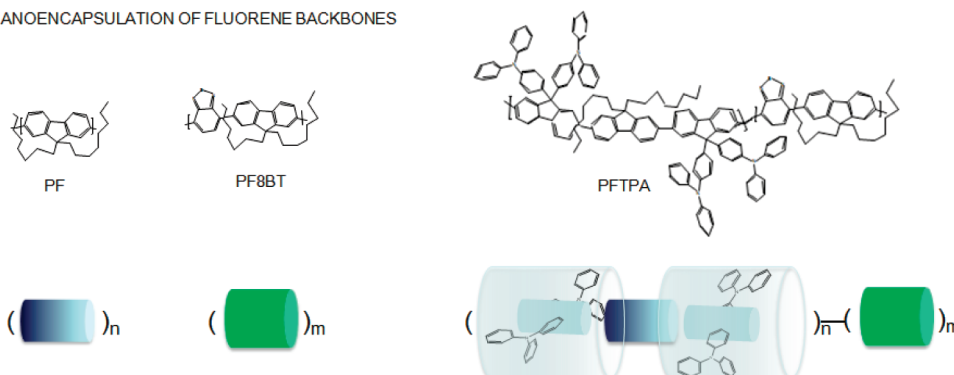
The value of the Förster radius (or critical radius) R_0 , defined as the average distance between donor and acceptor when the FRET rate is equal to the sum of all other

(14) (a) Banach, M. J.; Friend, R. H.; Sirringhaus, H. *Macromolecules* **2003**, *36*, 2838. (b) Snaith, H. J.; Friend, R. H. *Thin Solid Films* **2004**, *451–52*, 567.

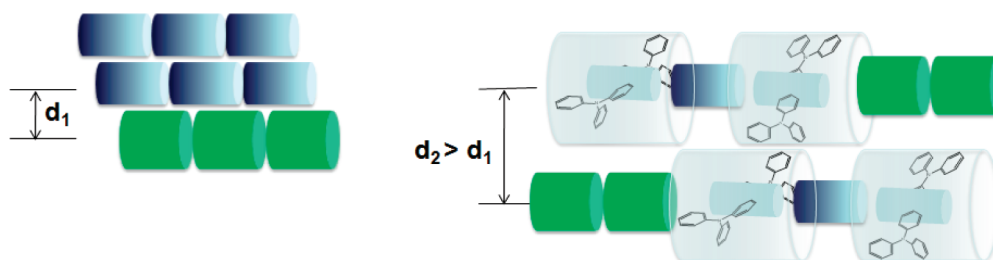
(15) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer Academic Plenum Publishers: New York, 1999.

Scheme 2. Representation of the Nano-Encapsulation Role of the TPA Groups that Increase the Interchain Distances, thus Reducing FRET Efficiency from PF8BT to PF8BT Segments

a) NANOENCAPSULATION OF FLUORENE BACKBONES



b) INCREASING THE INTERMOLECULAR DISTANCES



relaxation rates of the donor,¹⁵ is $R_0 = 3.1$ nm, in agreement with those reported in literature for standard polydiocylfluorene (PF) and standard PF8BT blends.^{16,17} When the average distance among donor–acceptor chromophores is shorter than the Förster radius, a complete energy transfer is expected, and only the green emission should be visible. Indeed, in bulk materials the presence of donor–donor hopping processes generally increases the value of the theoretical donor–acceptor Förster radius, thus increasing the rate of energy transfer.¹⁸ Although the intensity of the PF8BT emission band is dominant in Cop1 and Cop2 spectra and far stronger than the emission from a directly excited block of PF8BT, blue emission from PFTPA is still present in Cop2 spectrum.¹⁹ This fact clearly indicates that the nanoencapsulation environment of the polymer chains, played here by TPA bulky groups and recently explored also with cyclodextrins,²⁰ hampers hopping processes among donors¹⁸ by increasing donor–donor intermolecular distances (Scheme 2), hence reducing FRET efficiency toward PF8BT segments.

The PLQY of neat PFTPA and PF8BT film is $52\% \pm 5\%$ and $50\% \pm 3\%$, respectively, as shown in Table 2. These values are in good agreement with those of standard PF²¹ and commercial PF8BT,²² while that of the block copolymers varies with block length ratio. We find that the composition of 20 wt % of PF8BT (Cop2) gives the highest PLQY of $74\% \pm 6\%$. Interestingly, Cadby et al.²³ found that in polymer blends of PF and standard PF8BT a maximum PLQY of $70\% \pm 3\%$ was reached at a relative PF8BT concentration of 5 wt %. The quite different PF8BT concentration requested for the best PL performance indicates that the encapsulation property of TPAs and the different supramolecular organization of block copolymers (see Scheme 2) plays a role in the photophysics of these systems.

Indeed a direct comparison between block copolymers and blend of homopolymers is quite difficult. In fact, in the block copolymers, on one hand the encapsulation reduces the efficiency of exciton hopping, while, on the other hand, both interchain and intrachain FRET contributes to the excitation of the green emitting sites. However, we believe that the main contribution determining the optimal composition in block copolymers and homopolymer blends for high PLQY is the different tendency to chain aggregation and the degree of crystallinity of the two systems (see above) and therefore depends also on the film preparation procedure. These considerations

- (16) Buckley, A. R.; Rahn, M. D.; Hill, J.; Cabanillas-Gonzalez, J.; Fox, A. M.; Bradley, D. D. C. *Chem. Phys. Lett.* **2001**, *339*, 331.
- (17) Hill, J.; Heriot, S. Y.; Worsfold, O.; Richardson, T. H.; Fox, A. M.; Bradley, D. D. C. *Synth. Met.* **2003**, *139*, 787.
- (18) (a) List, E. J. W.; Creely, C.; Leising, G.; Schulte, N.; Schluter, A. D.; Scherf, U.; Mullen, K.; Graupner, W. *Chem. Phys. Lett.* **2000**, *325*, 132. (b) Giovanella, U.; Botta, C.; Gurioli, M.; Papagni, A.; Tubino, R.; Maiorana, S.; Del Buttero, P.; Alderighi, D.; Kudrna, J. *J. Appl. Phys.* **2002**, *91*, 6511.
- (19) Morgado, J.; Moons, E.; Friend, R. H.; Cacialli, F. *Adv. Mater.* **2001**, *13*, 810.
- (20) Brovelli, S.; Meinardi, F.; Winroth, G.; Fenwick, O.; Sforazzini, G.; Frampton, M. J.; Zalewski, L.; Lewitt, J. A.; Marinello, F.; Schiavuta, P.; Suhling, K.; Anderson, H. L.; Cacialli, F. *Adv. Funct. Mater.* **2010**, *20*, 272–280.

- (21) Su, H.-J.; Wu, F.-I.; Tzeng, Y.-H.; Shu, C.-F. *Adv. Funct. Mater.* **2005**, *15*, 1209.
- (22) Kim, Y.; Bradley, D. D. C. *Curr. Appl. Phys.* **2005**, *5*, 222–226.
- (23) Cadby, A. J.; Dean, R.; Elliott, C.; Jones, R. A. L.; Fox, A. M.; Lidzey, D. G. *Adv. Mater.* **2007**, *19*, 107.

Table 2. PLQY of the Compounds in Solid-State (Spin-Coated on Glass Substrate) Together with Details of OLED Prepared with the Compounds

compound	solid-state PLQY [%]	EQE [%]	L [cd/m ²]/at bias [V]	EL CIE (1931)	
				x	y
PFTPA	52 ± 5	0.5 ± 0.1 ^a 1.5 ± 0.2 ^d	411/10 295/10	0.20	0.16
Cop1	48 ± 5	0.3 ± 0.05 ^a 0.1 ± 0.05 ^{b,d} 0.3 ± 0.05 ^c 0.1 ± 0.05 ^{c,e}	7000/5 4100/5 6600/5 6000/5	0.39	0.58
Cop2	74 ± 6	0.9 ± 0.1 ^a 1.2 ± 0.2 ^b 0.8 ± 0.1 ^{b,d} 3.9 ± 0.3 ^c 5.5 ± 0.3 ^{c,e}	40000/10 54200/13 35700/13 11000/10 10000/10	0.36	0.59
PF8BT	50 ± 3	0.7 ± 0.1 ^b	20000/10	0.43	0.55

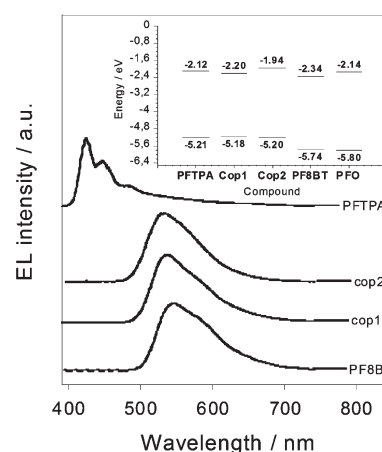
^a ITO/PEDOT:PSS/copolymer/Ca/Al. ^b ITO/PEDOT:PSS/emissive-layer/Ba/Al. ^c ITO/PEDOT:PSS/PVK/emissive-layer/Ba/Al. ^d Thermal treated before cathode deposition. ^e Thermal treated after cathode deposition.

should be taken into account for the design of new copolymer systems.

C. Electroluminescence. Devices were prepared with the standard architecture ITO/PEDOT:PSS/emissive-layer/Ca/Al and the bilayer ITO/PEDOT:PSS/PVK/emissive-layer/Ba/Al one. The energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the compounds have been derived from cyclovoltammetric measurements^{13,24} and are reported in the inset of Figure 2. For PVK we measured only the oxidation potential, from which the HOMO is derived, while the LUMO value is obtained by using the optical energy gap of the polymer. EL spectra (Figure 2) have been measured together with their current density–voltage and luminance–voltage curves.

By using a thin conductive polymeric interlayer between PEDOT:PSS and the emitting layer, the efficiency²⁵ and lifetime can be improved.²⁶ In fact, the PEDOT:PSS acidic nature may contribute to the active polymer degradation,²⁷ and its poor electron blocking capability does not favor a good charge balancing.²⁸ Moreover, we measured a reduction of the PLQY of PFTPA homopolymer (see Table 3) when it is deposited on PEDOT:PSS.

We observed that, after annealing treatment, the solubility of the high molecular weight PVK layer is lowered, and this allows us to fabricate multilayer architecture by successive solution deposition (see AFM topographic section profile in the Supporting Information). We performed a deeper investigation to elucidate the role of such an interlayer. In our opinion, the PVK film, thanks to its HOMO and LUMO energy level positions (−5.44 and −1.84 eV, respectively), is able to block the radiative

**Figure 2.** Normalized EL spectra devices based on the compounds. Spectra are vertically shifted for clarity. In the inset, HOMO and LUMO energy levels of the compounds; PF is reported as reference.**Table 3.** PLQY of PFTPA Films Deposited on Different Substrates

substrate	PLQY [%]
glass	52 ± 5
glass/ITO/PEDOT:PSS	26 ± 3
glass/PVK	59 ± 5

excitons from direct quenching by PEDOT:PSS and thus remove a nonradiative decay channel introduced by PEDOT:PSS itself. In fact, the PL-QY of a PFTPA film directly spin-coated on PVK is comparable to the one on glass (see Table 3). A similar role is played by other semiconducting polymer interlayers.²⁹ Moreover, an electron confinement into the emissive layer produced by the energy barrier between PVK and active layer LUMO levels that reduces hole injection from anode is feasible.³⁰

Previous studies on green emitting devices based on the standard PF and PF8BT polymers have been focused on blends ranging from 5 wt % to 25 wt % of PF8BT into PF. EQE is always significantly higher in the case of the blends compared to the neat PF8BT.⁸ OLEDs having as

- (24) Janietz, S.; Bradley, D. D. C.; Grell, M.; Giebeler, M.; Inbasekaran, M.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 2453.
 (25) Giovannella, U.; Betti, P.; Bolognesi, A.; Destri, S.; Melucci, M.; Pasini, M.; Porzio, P.; Botta, C. *Org. Electron.* **2010**, *11*, 2012–2018.
 (26) (a) Shakutsui, M.; Matsuura, H.; Fujita, K. *Org. Electron.* **2009**, *10*, 834–842. (b) Yang, N. C.; Suh, M. C. *Curr. Appl. Phys.* **2009**, *9*, 505–509. (c) Duan, L.; Chin, B. D.; Yang, N. C.; Kim, M.-H.; Kim, H. D.; Lee, S. T.; Chung, H. K. *Synth. Met.* **2007**, *157*, 343–346.
 (27) Wong, K. W.; Yip, H. L.; Luo, Y.; Wong, K. Y.; Lau, W. M.; Low, K. H.; Chow, H. F.; Gao, Z. Q.; Yeung, W. L.; Chang, C. C. *Appl. Phys. Lett.* **2002**, *80*, 2788.
 (28) Yan, H.; Scott, B. J.; Huang, Q.; Marks, T. J. *Adv. Mater.* **2004**, *16*, 1948.

- (29) Kim, J.-S.; Friend, R. h.; Grizzi, I.; Burroughs, J. H. *Appl. Phys. Lett.* **2005**, *87*, 0235061–0235063.
 (30) Joo-Won, L.; Jai-Kyeong, K.; Young-Soo, Y. *Chin. J. Chem.* **2010**, *28*, 115–118.

active layer a thin film formed by a blend with 5 wt % PF8BT in PF showed the best performances (EQE 2.5%).³¹

In agreement with its highest PLQY, Cop2-based OLED devices show improved performances, that is, quantum efficiency and luminance, with respect to the other devices based on copolymers reported both here and in literature. All the details of OLED performances are reported in Table 2.

The lack of residual PFTP emission in the EL spectrum of Cop2 as compared with its corresponding PL is due to the fact that two simultaneous processes contribute to the low-energy emission: (i) FRET from singlet excitons on the PFTP main chain to PF8BT and (ii) trapping of charge carriers at the 9,9'-dioctylfluorene-co-benzothiadiazole sites followed by a subsequent emissive recombination event. The second process occurs only in EL and increases the contribution of the PF8BT EL band.

The color of the emission can be represented in the Commission International d'Eclairage CIE (1931) chromaticity diagram by two coordinates (x ; y). The evident blue-shift of the emission maximum going from PF8BT (544 nm) to Cop1 (536 nm) and Cop2 (525 nm) greatly improves the color purity of the materials addressing the standard green emission demanded in the Rec709 triangle used worldwide as High Definition Television (HDTV) color triangle,³² better than alternated and random fluorene-benzothiadiazole based copolymers.^{6b}

The thermal analysis of Cop1 reveals strict similarities with that of the PF8BT homopolymer showing the T_g peak at around 140 °C, consistently with the results reported by Donley et al.³³ This observation points out a relevant role of PF8BT in determining the segregation/aggregation in the copolymers. Specifically, differential scanning calorimetry analysis performed on PF8BT blocks of Cop1 and Cop2 consistently indicates a crystalline character for the former, while the latter displays an amorphous character, which is fully confirmed in the corresponding Cop2 material (see Supporting Information).

Recently, heat treatment has been used to increase the efficiency of polymer-based OLEDs. Heat treatment of a polymeric thin film not only can improve the interfacial adhesion³⁴ between the polymer and the electrodes but also can modify the intrinsic properties of the organic film itself.³⁵ Higher brightness and higher EQE have been achieved in this way, as reported by Han et al.,³⁶ Niu et al.,³⁷ and Lee and Park.³⁸ We therefore performed the thermal treatment both before and after electrode

deposition for the different compounds. All the details on the device performances are listed in Table 2. The PVK buffer layer in the optimized device architectures is not affected by the annealing process, due to its high molecular weight and T_g above 200 °C.

We heated the active layers in nitrogen atmosphere at a temperature of 150 °C (above the glass transition temperature of PF8BT) for 2 h followed by a slow cooling. After the thermal treatment, before electrode deposition, we did not observe any relevant change in the optical spectra of Cop2, while a decreasing in the EL intensity of low-energy shoulder of the green emission band is noticeable in the device with Cop1 (see Supporting Information). This variation in the EL spectral shape might indicate a crystallization of the PF8BT³³ component of Cop1. The morphological investigations support this interpretation. Tapping mode AFM shows that thermal treatment of Cop1 results in a reorganization of the polymer chains, giving rise to a phase segregation between PFTP-rich and PF8BT-rich domains at the nanometric scale, that is, domain size comparable to the length of the two blocks (~ 10 nm).¹³ On the contrary, the same treatment performed on Cop2 causes no change, the block-copolymer behaving as PFTP, that is, essentially amorphous in agreement with thermal analysis results.

Van Vooren et al.³⁹ reported that device annealing over the glass transition temperature of PF8BT-based active layer could bring about an improvement of EL efficiency to more than twice. This improvement was attributed to a better balance of electron and hole carriers due to a reduction of the dominant electron conduction of PF8BT. Differently for Cop1, thermal treatment of the OLED active layer both before and after cathode deposition shows only weak improvements or even a decrease of performance of the devices. Therefore for Cop1, the thermal treatments alter carrier balancing leading to a hole conduction predominance that reduces device performance. On the contrary, even if annealing Cop2-based devices before cathode deposition does not provoke relevant changes in electrooptical properties, the best performance device is achieved with the postdeposition treatment. After this treatment devices based on Cop2 give EQE of 5.5% (ph/el) measured in the forward direction, luminous efficiency (LE)⁴⁰ of 22.5 cd/A, power efficiency⁴¹ of 19.6 lm/W (roughly equivalent to a total EQE of 9.3%, LE of 38, and PE of 33 lm/W),⁴² and CIE coordinates of (0.36; 0.59). Since Cop2 thermal analysis does not show any indication of copolymer reorganization, we believe that this increase in efficiency is mainly related to the optimization of the cathode/polymer interfacial adhesion.

(31) Wilkinson, C. I.; Lidzey, D. G.; Palilis, L. C.; Fletcher, R. B.; Martin, S. J.; Wang, X. H.; Bradley, D. D. C. *Appl. Phys. Lett.* **2001**, *79*, 171.

(32) International Telecommunication Union. <http://www.itu.int/>.

(33) Donley, C. L.; Zaumseil, J.; Andreasen, J. W.; Nielsen, M. M.; Sirringhaus, H.; Friend, R. H.; Kim, J.-S. *J. Am. Chem. Soc.* **2005**, *127*, 12890.

(34) Luo, J.; Li, X.; Hou, Q.; Peng, J.; Yang, W.; Cao, Y. *Adv. Mater.* **2007**, *19*, 1113.

(35) Kreuzis, T.; Bradley, D. D. C.; Campbell, A. J. *Proc. SPIE* **2004**, *5214*, 197.

(36) Ahn, T.; Lee, H.; Han, S. H. *Appl. Phys. Lett.* **2002**, *80*, 392.

(37) Niu, H.; Hou, Q.; Cao, Y. *Appl. Phys. Lett.* **2002**, *81*, 634.

(38) Lee, T. W.; Park, O. O. *Adv. Mater.* **2000**, *12*, 801.

(39) (a) Van Vooren, A.; Kim, J.-S.; Cornil, J. *Chem. Phys. Chem.* **2008**, *9*, 989–993. (b) Xiong, Y.; Peng, J.-B.; Wu, H. B.; Wang, J. *Chin. Phys. Lett.* **2009**, *26*, 097801.

(40) (a) Luminous efficiency is defined as $\eta_L = L/J_{\text{OLED}}$. (b) Gong, X.; Robinson, M. R.; Ostrowski, J. C.; Moses, D.; Bazan, G. C.; Heeger, A. J. *Adv. Mater.* **2002**, *14*, 581–585.

(41) Power efficiency is defined as $\eta_P = \pi L/J_{\text{OLED}} V$.

(42) D'Andrade, B. W.; Holmes, R. J.; Forrest, S. R. *Adv. Mater.* **2004**, *16*, 624.

Therefore, thanks to the suppression of oxidation obtained through the TPA substitution, efficient OLEDs with EL spectra essentially unchanged after several operating hours under ambient conditions are obtained. Devices based on Cop2 show extremely high performances thanks to the strong morphological stability of this copolymer that allows the device to be optimized by increasing the interfacial adhesion of the active layer with the electrodes.

4. Conclusion

A new highly efficient polymeric green emitting OLED is fabricated thanks to a dual chemical and physical approach in designing and synthesizing all-conjugated rod-rod diblock copolymers PFTP A-PF8BT. The copolymers exhibit different electrooptical properties according to the relative length of the two blocks. The maximum in the PLQY (0.74 ± 0.06) is reached for the block copolymer possessing a ratio between PFTP A and PF8BT segments of 4/1 by weight (Cop2). This PLQY value is much higher than that of the PFTP A and PF8BT homopolymers. The nanoencapsulation role of the TPA groups prevents oxidation and increases interchain distances, controlling FRET processes from PFTP A to PF8BT segments.

An EQE of 5.5% (ph/el), luminance above 50 000 cd/m², luminance efficiency of 22.5 cd/A, and high color purity

CIE coordinates of (0.36; 0.59) are achieved by thermally treating Cop2-based devices, thanks to cathode/polymer interfacial adhesion optimization. The role of the PVK is fundamental for device performance improvement with deeper implications on films of organic materials as a protective barrier against PEDOT:PSS.

By a proper chemical tailoring using a grafting-on copolymerization process and by a tuning energy transfer mechanism, a more efficient, stable, purer, and reproducible green emission than by alternated or random polymerization of two chromophores can be achieved. Such benefits, together with the lack of any demixing during operation time, make these block copolymers a valuable alternative to the standard approach of blending two different polymers.

Acknowledgment. This work was partially supported by Italian project MIUR-PRIN 2007PBWN44, FIRB-RBIP06JWBH NODIS, FIRB-RBIP0642YL LUCI. The authors wish to thank to Ing. R. Mendichi and A. Giacometti-Schieroni for GPC analysis and Dr. Fabio Bertini for thermal characterization.

Supporting Information Available: AFM of bilayer device architecture, thermal analysis of PF8BT blocks, and PL and EL spectra of thermal treated copolymer film and device, respectively (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.