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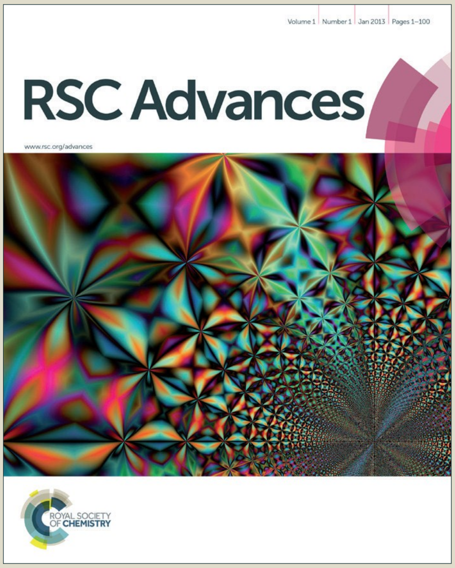

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Side Chain Engineering in π-Stacked Polybenzofulvene Derivatives Bearing Electron-Rich Chromophores for OLED Applications

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ABSTRACT

In order to obtain new polymeric materials endowed with improved optoelectronic performances, a suitable side chain engineering was designed to insert different chromophores showing electron donating ability [*i. e.* triphenylamine (TPA) and 9-methylcarbazole (MCBZ) residues] in two different key positions (*i. e.* 6 and 4') of the 3-phenylindene scaffold of the polybenzofulvene monomeric units. Among the four newly-synthesized polybenzofulvene derivatives, those bearing triphenylamine moieties were found to show higher emissive properties with respect to the corresponding carbazole derivatives. Moreover, the preliminary OLED devices prepared with the triphenylamine-based polymers showed promising features, but the role of the aggregation process in affecting the emission properties of poly-6-TPA-**BF3k** suggested that extensive device development studies are required in order to maximize polybenzofulvene performances in OLED applications.

INTRODUCTION

The development of organic light emitting diodes (OLEDs) based on polymeric materials is becoming a matter of increasing interest owing to the intriguing scenario offered by multilayer OLEDs in terms of efficiency.[1] OLEDs can be generally produced by two routes: the wet-chemical deposition of polymers onto the substrate or the sublimation of small molecules under reduced pressure.[1]

Poly(*N*-vinylcarbazole) (**PVK**, Figure 1) is the most commonly used π-stacked polymer in the fabrication of optoelectronic devices such as OLEDs, field effect transistors (FETs), and non-volatile memory.[2,3]

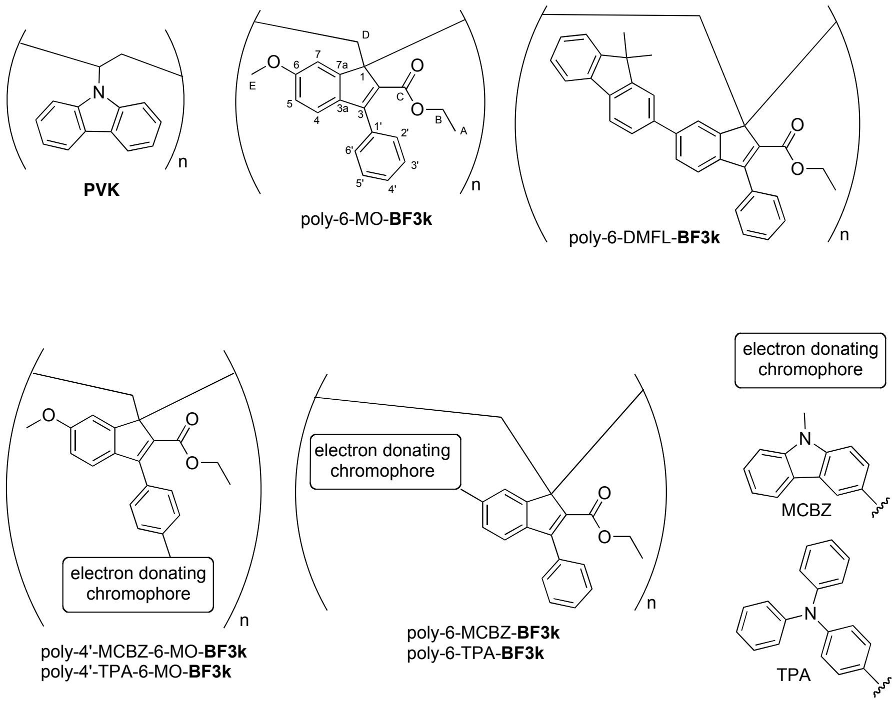


Figure 1. Structures of **PVK**, poly-6-MO-**BF3k**, poly-6-DMFL-**BF3k**, and of the newly designed polybenzofulvene derivatives bearing electron-donating chromophores.

PVK shows electroluminescence, photoconductive, photorefractive, energy-donating, carrier-switching and hole-transporting properties due to intrachain stacked orbitals that result from face-to-face conformation of the carbazole moieties.[2,4] Since the discovery of the spontaneous polymerization of some benzofulvene monomers, polybenzofulvene derivatives represent a new family of π-stacked polymers showing peculiar features such as the prompt and quantitative formation by spontaneous thermoreversible polymerization and the tunable solubility both in organic and aqueous media combined with interesting hole-mobility features.[5-11] Polybenzofulvenes are through-space conjugated polymers formed by stacked arrays of π-electron systems along a single polymer chain, as suggested by the observation that the absorption and emission features of these polymers do not vary significantly from the solid state to diluted solutions, both characterized by quite large Stokes shifts. This characteristics was explained in terms of monomeric chromophore stacking leading to excimer emission induced by interactions among the monomeric units of the polymeric chain.[7]

We recently reported that the replacement of the methoxy group in position 6 of the 3-phenylindene structure of poly-6-MO-**BF3k** with a 9,9-dimethylfluorene (DMFL) residue, as in poly-6-DMFL-**BF3k**, led to the design of highly emissive polymeric supramolecular assemblies useful in optoelectronic applications.[10,12,13] The promising results obtained with poly-6-DMFL-**BF3k** led us to envision a systematic approach in the exploration of different chromophores in substitution of the previously employed fluorene moiety. This approach could afford polybenzofulvene derivatives provided with improved optoelectronic features, which, combined with the peculiar spontaneous polymerization process could provide additional tools to the armamentarium for the development of multilayer devices, offering a third route in assembling the layers of the device.

The present paper describes the synthesis and the spontaneous polymerization of four newly designed benzofulvene derivatives bearing, in the two different key positions (6 and 4’) of the 3-phenylindene scaffold, different chromophores [*i. e.* 9-methylcarbazole (MCBZ) and triphenylamine (TPA)] showing electron donating ability in principle superior than that of fluorene moiety. The corresponding homopolymers were characterized from the point of view of their macromolecular and optoelectronic properties.

EXPERIMENTAL SECTION

Synthesis. The experimental procedures for the synthesis of the new benzofulvene derivatives and their spontaneous polymerization are described in Electronic Supplementary Information (ESI). NMR spectra were recorded with a Varian Mercury-300, a Bruker DRX-400 AVANCE, a Bruker DRX-500 AVANCE, or a Bruker DRX-600 AVANCE spectrometer in the indicated solvents (TMS as internal standard): the values of the chemical shifts are expressed in ppm and the coupling constants (J) in Hz. An Agilent 1100 LC/MSD operating with an electrospray source was used in mass spectrometry experiments.

Photophysical properties. UV-vis absorption spectra are obtained with a Perkin Elmer Lambda 900 spectrometer. PL spectra are obtained with a SPEX 270 M monochromator equipped with a N_2 cooled charge-coupled device exciting with a monochromated 450W Xe lamp. The spectra are corrected for the instrument response. PL QY values of solutions were obtained by using quinine sulfate as the reference. PL QY of solid powders and casted films were measured with a home-made integrating sphere according to the procedure reported elsewhere.[14] These results are not reported for spin coated films due to the low intensity of the emission for thin film samples.

Device preparation and characterization. PVK was obtained from Aldrich. (25,000-50,000 g/mol) Glass substrates with ITO pattern were cleaned ultrasonically in distilled water, acetone and isopropanol. Subsequently, a 50 nm film of poly(3,4-ethylene-dioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS, Clevios PVP.AI 4083, H. C. Starck) was spincoated from water solution through nylon filter (pore size 0.45 μm) and annealed at 100° C for 10 min. On such prepared substrates, appropriate active layers were spincoated in a nitrogen filled glovebox. Emissive layers of all devices were prepared from THF solutions showing a concentration of about 15 mg/mL and rotations in the range 1200-2500 rpm. After the deposition of emissive layer, cathode consisting of 8 nm of barium and 70 nm of aluminum was thermally evaporated at pressure 10^{-6} mbar. Electrical characterization of devices was performed with

Keithley 2602 combined with calibrated photodiode under nitrogen atmosphere. External quantum efficiency (EQE) was obtained using Lambertian source assumption, by placing an OLED on photodiode surface and collecting the light emitted in half sphere solid angle as reported elsewhere.[15] Thickness of organic layers was about 160-215 nm, as measured with a Bruker Dektak XT profilometer.

SEC-MALS. The MWD characterization of the newly prepared polybenzofulvene derivates was performed by a MALS light scattering photometer on-line to a SEC chromatographic system. The multi-detector chromatographic system was composed of an absolute multi-angle laser light scattering detector (MALS) and a differential refractometer (DRI) used as concentration detector. The SEC-MALS system and the corresponding experimental conditions were identical to those used in our previous studies[5,6] and are not reported in detail here. The dn/dc values of the polymers were measured off-line in THF at 35 °C using a Chromatix KMX-16 differential refractometer. The introduction of different chromophore in the repeating unit of the polybenzofulvene derivatives produced slight changes (increase) in dn/dc value. In particular the measured values are the following: 0.252 mL/g for poly-6-MCBZ-**BF3k**; 0.210 mL/g for poly-4'-MCBZ-6-MO-**BF3k**; 0.270 mL/g for poly-6-TPA-**BF3k**; 0.240 mL/g for poly-4'-TPA-6-MO-**BF3k**; 0.195 mL/g for poly-**BF3k**; 0.192 mL/g for poly-6-MO-**BF3k**.

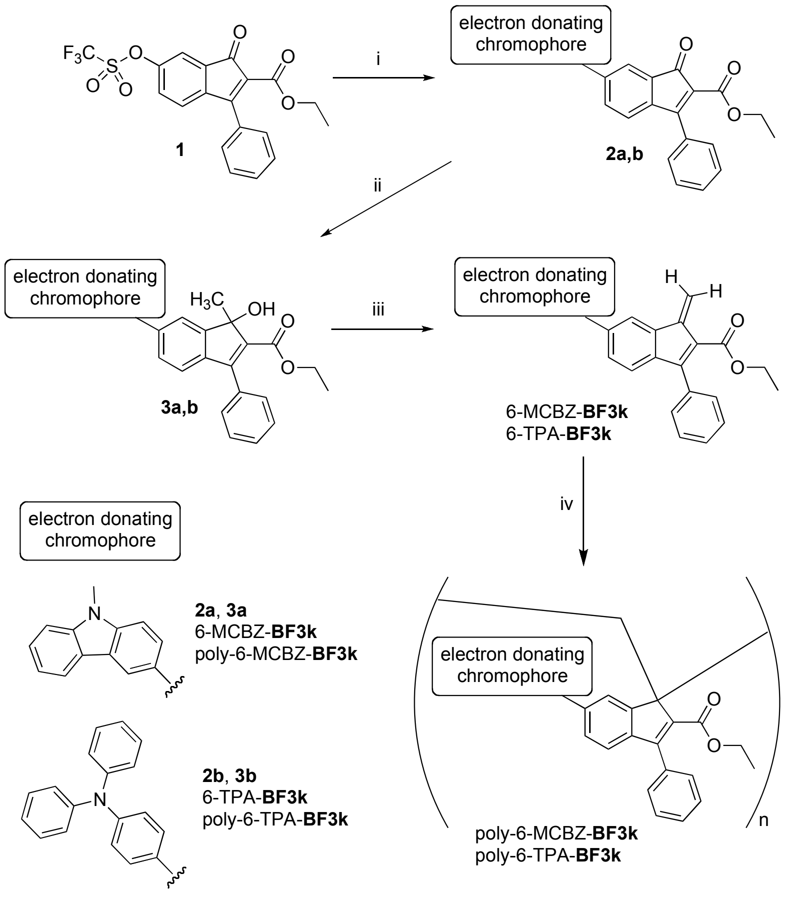
X-Ray crystallography. Single crystals of compounds **2a,b** and **5b** were submitted to X-ray data collection on an Oxford-Diffraction Xcalibur Sapphire 3 diffractometer with a graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293 K. The structures were solved by direct methods implemented in SHELXS-97 program.[16] The refinements were carried out by full-matrix anisotropic least-squares on F^2 for all reflections for non-H atoms by means of the SHELXL-97 program.[17] Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1062833 (**2a**), 1062836 (**2b**)**,** and 1062837 (**5b**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; (fax: + 44 (0) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Synthesis and spontaneous polymerization of the newly designed benzofulvene derivatives.

The preparation of the polybenzofulvene derivatives bearing electron donating chromophores [*i. e*. 9-methylcarbazole (MCBZ) and triphenylamine (TPA)] was based on the chemistry developed for the preparation of the previously published fluorene members of this sub-series of polybenzofulvenes. In particular, triflate derivative **1** (see ref 10) was used as starting material in the multistep procedure described in Scheme 1 to obtain polybenzofulvene derivatives poly-6-MCBZ-**BF3k** and poly-6-TPA-**BF3k**.

Scheme 1. Preparation of poly-6-MCBZ-**BF3k** and poly-6-TPA-**BF3k**.

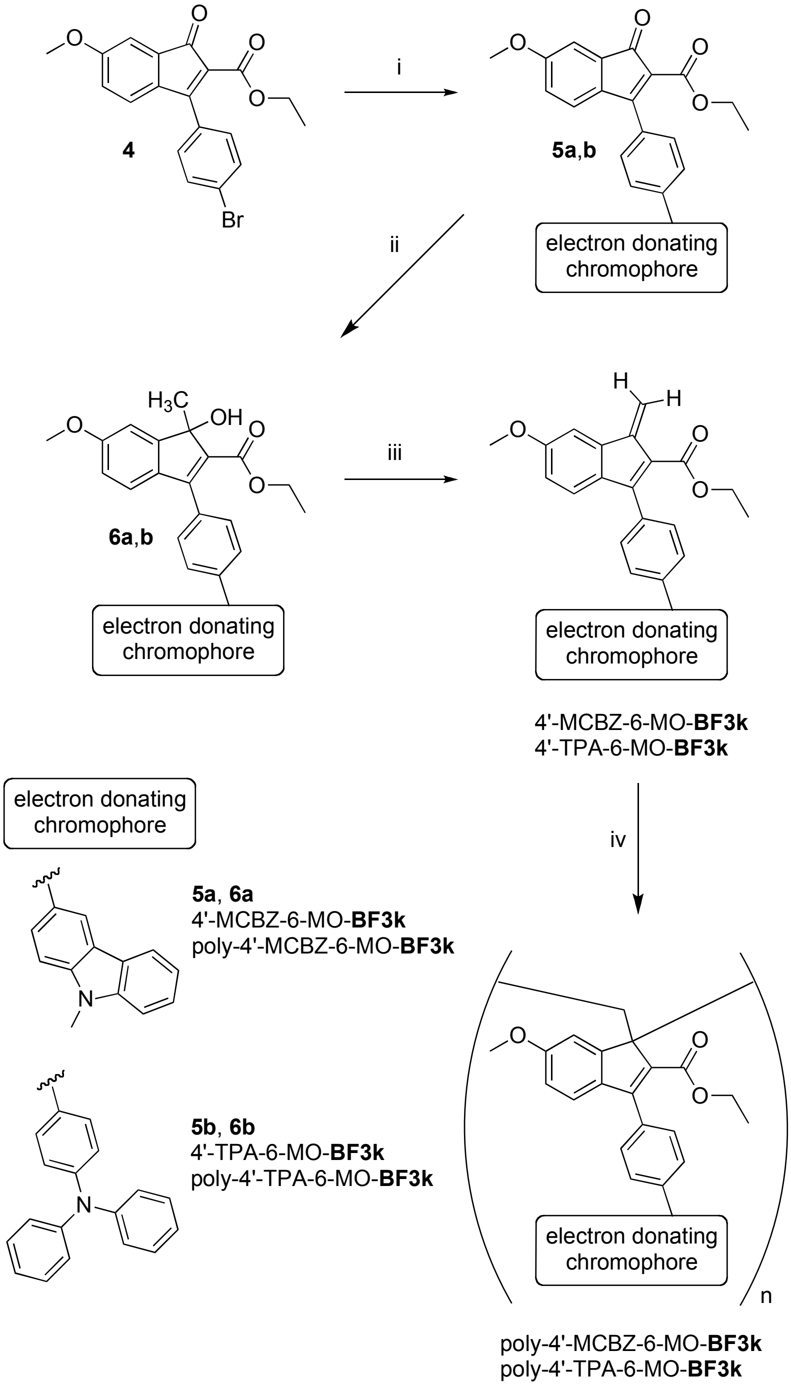


Reagents: (i) 9-methyl-9*H*-carbazole-3-boronic acid (for **2a**) or 4-(diphenylamino)phenylboronic acid (for **2b**) pinacol esters, $Pd(PPh_3)_2Cl_2$, PPh_3, Cs_2CO_3, CH_3OH, THF; (ii) $Al(CH_3)_3$, CH_2Cl_2; (iii) PTSA, $CHCl_3$; (iv) solvent evaporation.

Suzuki-Miyaura cross-coupling of **1** with the commercially available pinacol esters of the suitable boronic acids gave indenones **2a**,**b**, which were submitted to the methylation/dehydration procedure[5-11] to obtain benzofulvene monomers 6-MCBZ-**BF3k** and 6-TPA-**BF3k**. Interestingly, we observed that the preparation of carbazole-substituted polybenzofulvene derivative poly-6-MCBZ-**BF3k** required to carry out the dehydration reaction with diluted solutions of indenol **3a** in order to maximize both the yield and purity of the benzofulvene monomer 6-MCBZ-**BF3k**. As expected, benzofulvene monomers 6-MCBZ-**BF3k** and 6-TPA-**BF3k** polymerized in the apparent absence of catalysts, upon solvent removal, to give the corresponding polymers poly-6-MCBZ-**BF3k** and poly-6-TPA-**BF3k**, respectively.

The polybenzofulvene derivatives bearing the electron donating chromophores in positions 4’ of the phenylindene scaffold were prepared by applying the synthetic procedure shown in Scheme 2.

Scheme 2. Synthesis of polybenzofulvene derivatives bearing the electron donating chromophores in positions 4’ of the phenylindene scaffold.



Reagents: (i) 9-methyl-9*H*-carbazole-3-boronic acid (for **5a**) or 4-(diphenylamino)phenylboronic acid (for **5b**) pinacol esters, Pd(PPh$_3$)$_2$Cl$_2$, PPh$_3$, Cs$_2$CO$_3$, CH$_3$OH, THF; (ii) Al(CH$_3$)$_3$, CH$_2$Cl$_2$; (iii) PTSA, CHCl$_3$; (iv) solvent evaporation.

The Suzuki-Miyaura cross-coupling was applied to bromophenylindenone **4** (see ref 10) to afford indenones **5a**,**b**, which were used in the methylation/dehydration procedure[5-11] leading to benzofulvene monomers 4’-MCBZ-6-MO-**BF3k** and 4’-TPA-6-MO-**BF3k** and, after spontaneous polymerization, to the corresponding polymers poly-4’-MCBZ-6-MO-**BF3k** and poly-4’-TPA-6-MO-**BF3k**.

Molecular Characterization

The molecular weight distribution (MWD) and the conformation plot of poly-6-MCBZ-**BF3k**, poly-6-TPA-**BF3k**, and poly-4’-TPA-6-MO-**BF3k** samples were characterized by means of a SEC-MALS system (*i. e.* a multi-angle laser light scattering detector on-line to a size exclusion chromatography apparatus) with THF as mobile phase (Table 1). The MWD results summarized in Table 1 suggested that the new polymers showed high molecular weight values and quite broad dispersity (M_w/M_n) similar to those shown by parent polybenzofulvenes. This result confirmed that the presence of bulky chromophores is compatible with the spontaneous polymerization mechanism leading to high molecular mass polybenzofulvene derivatives. Unfortunately, poly-4’-MCBZ-6-MO-**BF3k** sample appeared to be only partially soluble in THF mobile phase (about 33%, as estimated from the area of the DRI concentration detector); consequently, the whole MWD of this sample could be not determined with sufficient accuracy. Thus, for poly-4’-MCBZ-6-MO-**BF3k** sample, Table 1 reports only the peak molecular weight M_p of the soluble fraction in THF. Probably, the polymeric fractions with higher molecular weight were insoluble in THF.

Table 1. Macromolecular features of the newly synthesized polybenzofulvene derivatives compared with those shown by parent polymers poly-**BF3k** and poly-6-MO-**BF3k**.

polymer	M_p (kg/mol)	M_w [a] (kg/mol)	M_w/M_n [b]	R_g [c] (nm)	K [d] (nm)	α [d]
poly-6-MCBZ-**BF3k**	774	891	3.0	28.1	$1.18\cdot10^{-2}$	0.55
poly-4'-MCBZ-6-MO-**BF3k** [e]	324					
poly-6-TPA-**BF3k**	550	607	2.6	23.5	$1.23\cdot10^{-3}$	0.71
poly-4'-TPA-6-MO-**BF3k**	997	953	2.7	32.7	$2.70\cdot10^{-3}$	0.66
poly-**BF3k**	1,900	1,506	3.4	49.9	$6.63\cdot10^{-3}$	0.60
poly-6-MO-**BF3k**	312	347	4.3	19.4	$5.75\cdot10^{-3}$	0.61

[a] M_w: weight-average molecular weight; [b] M_w/M_n: dispersity where M_n denotes the numeric-average molecular weight; [c] R_g: radius of gyration i.e. dimension of the macromolecules; [d] K, α: intercept and slope of conformation plot; [e] sample showing low solubility (≈33%) in THF mobile phase.

NMR characterization of the spontaneous polymerization of the newly designed benzofulvene derivatives.

The spontaneous polymerization of the newly-designed benzofulvene derivatives was followed by NMR spectroscopy by comparing the spectra of polymers with those of the corresponding monomers according to a well-established protocol.[5-11]

First, the ^{1}H and ^{13}C NMR spectra of the monomers were carefully assigned by means of 2D correlation experiments and then the spectra of the newly-synthesized polybenzofulvene derivatives were compared with the assigned ones of the corresponding monomers (see for example Figures ESI-2, ESI-3, ESI-5, ESI-6, ESI-8, ESI-9, ESI-12, and ESI-13) and of the parent macromolecules in order to ascertain the retention of the original vinyl (1,2) polymerization mechanism and to exclude the eventual 1,4-addition mode. In particular, the enchainment of the new polymers was evaluated on the basis of the chemical shift values of the peaks, which were considered diagnostic of this structural feature: the one attributed to the aliphatic quaternary carbon of the 1,2-repeating indene unit at around 57 ppm (C-1, the carbon adjacent to the exo-methylene group of benzofulvene monomer), the one attributed to the carbon of the methylene bridge among the monomeric units along polybenzofulvene backbone (C-D), and the ones attributed to the indene carbon atoms, which may be affected by the competing 1,4-polymerization (C-1' and C-3).[5,6,9,18] All these comparisons allowed us to propose the 1,2-enchainment as the fundamental structural motif also for the backbones of TPA- and MCBZ-based polybenzofulvenes.

Moreover, the assignment studies showed that the chemical shift value of carbon atom C-6 bearing the chromophore moiety was quite sensitive to the variation its stereoelectronic features. In particular, the C-6 chemical shift values ranged from 140.9 ppm (6-TPA-**BF3k**) to 141.8 ppm (6-DMFL-**BF3k**) and 142.5 ppm (6-MCBZ-**BF3k**) symptomatic of the existence of a certain degree of π-overlap between the benzofulvene moiety and the chromophore, as suggested by the planar arrangements observed in the solid state structures of indenones **2a**,**b** (see ESI). Thus, we assumed that the highest electron density in 6-TPA-**BF3k** indene moiety could affect the optoelectronic properties of the corresponding polymer. Furthermore, the comparison of the ^{13}C NMR spectra of the four polybenzofulvene derivatives confirmed that the presence of the chromophore in position 6 of the indene nucleus produced a significant broadening of the signal in the spectra of both poly-6-MCBZ-**BF3k** and poly-6-TPA-**BF3k** (Figure 2).

As previously proposed for poly-6-DMFL-**BF3k** (see ref 10), the presence of the chromophore residues in position 6 of the 3-phenylindene monomeric units of poly-6-MCBZ-**BF3k** and poly-6-TPA-**BF3k** produced a high degree of π-stacking interactions among the aromatic moieties, which was assumed to decrease the mobility of the monomeric unities in polybenzofulvene backbone, showing anyway significant symptoms of local mobility in the distal phenyl rings of the triphenylamine chromophore groups of poly-6-TPA-**BF3k**.[19]

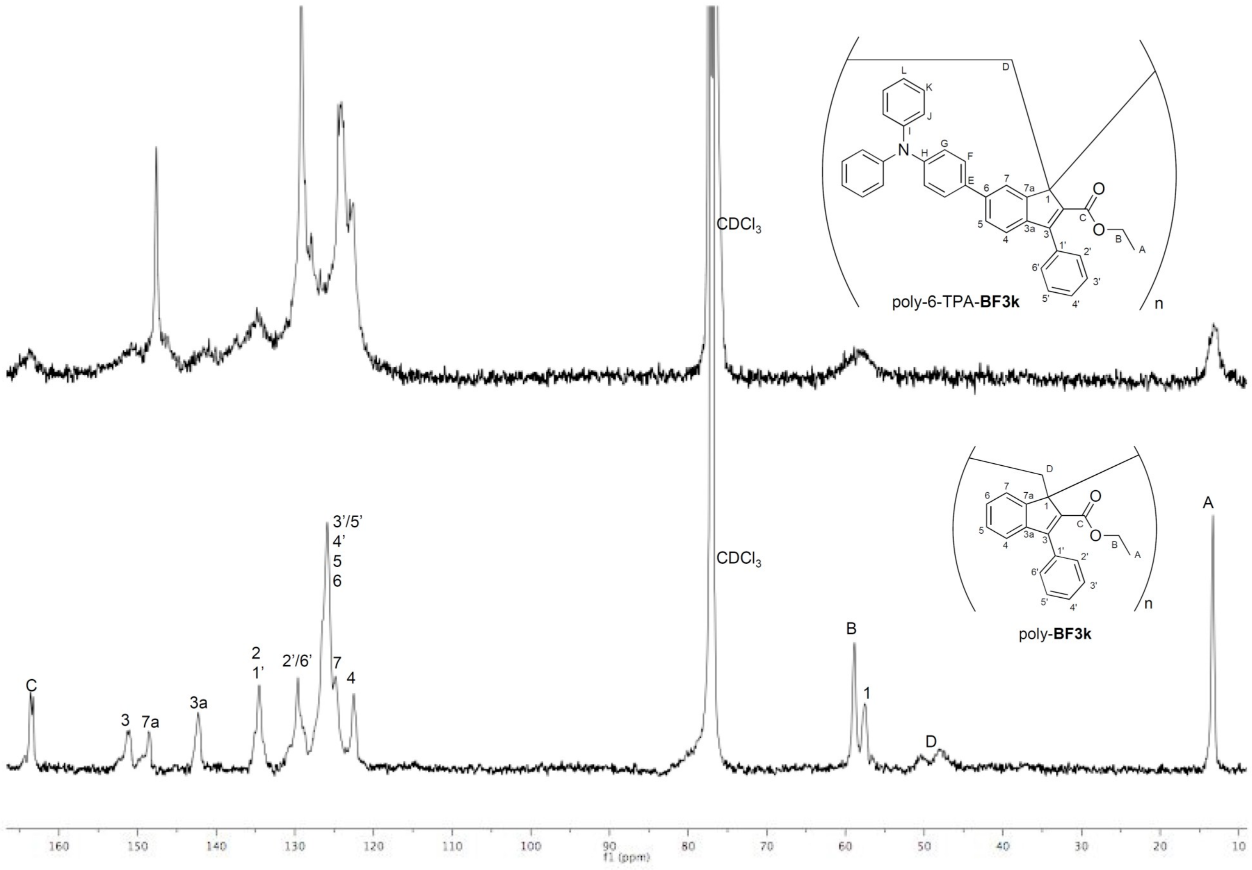


Figure 2. Comparison of the ^{13}C NMR spectrum of poly-6-TPA-**BF3k** with that of the parent macromolecule poly-**BF3k**.

Optoelectronic properties of polybenzofulvene derivatives bearing the electron donating chromophores.

The photophysical characteristics of the newly-designed polybenzofulvenes are summarized in Table 2 for both the solid state and the solution (Figures 3 and 4) and compared with those of the previously reported fluorene-based polybenzofulvene derivatives poly-6-DMFL-**BF3k** and poly-4'-DMFL-6-MO-**BF3k**.[10]

Table 2. Optical properties of the new polybenzofulvene derivatives bearing electron donating chromophores as compared with the fluorene-based polybenzofulvene derivatives.

	solution[a]			solid		
polymer	λ_{ab} (nm)	λ_{em} (nm)	QY (%)	λ_{ab}[b] (nm)	λ_{em}[c] (nm)	QY[c] (%)
poly-6-DMFL-**BF3k**	295, 319, 345	465	21	295, 345	486	24
poly-6-MCBZ-**BF3k**	290, 350	497	17	243, 300, 358	509	14
poly-6-TPA-**BF3k**	305, 377	495	46	318, 388	542	23
poly-4'-DMFL-6-MO-**BF3k**	295, 316	455	6	295, 318	480	9
poly-4'-MCBZ-6-MO- **BF3k**	285, 320, 350[sh]	470	12	243, 295, 355[sh]	488	8
poly-4'-TPA-6- MO-**BF3k**	314	482	14	325	478	9

[a] dichloromethane, [b] spin coated films, [c] cast films from dichloromethane solutions, [sh] shoulder.

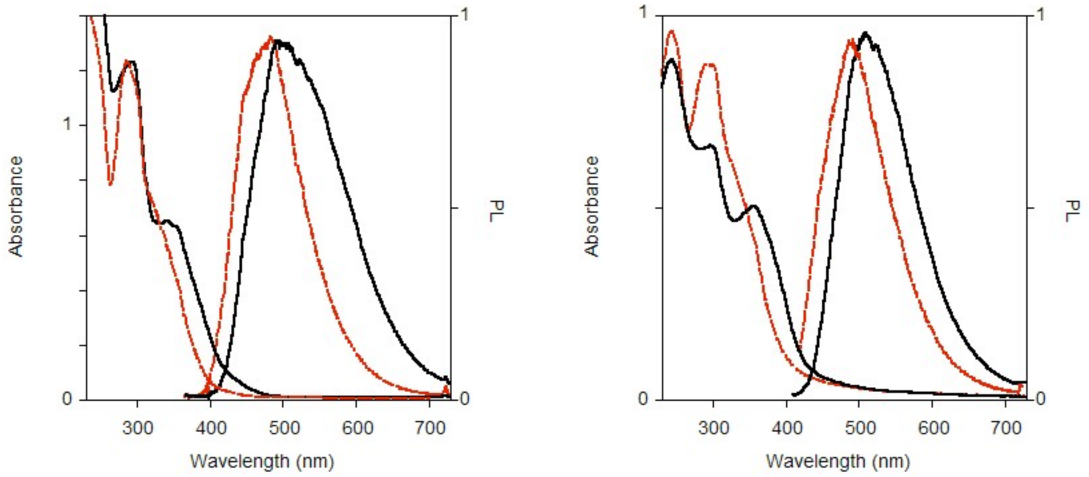


Figure 3. Optical absorption and emission spectra of poly-6-MCBZ-**BF3k (**black solid lines)**,** and poly-4'-MCBZ-6-MO-**BF3k** (red dotted lines) in dichloromethane solutions (left panel) and in the solid state (film, right panel).

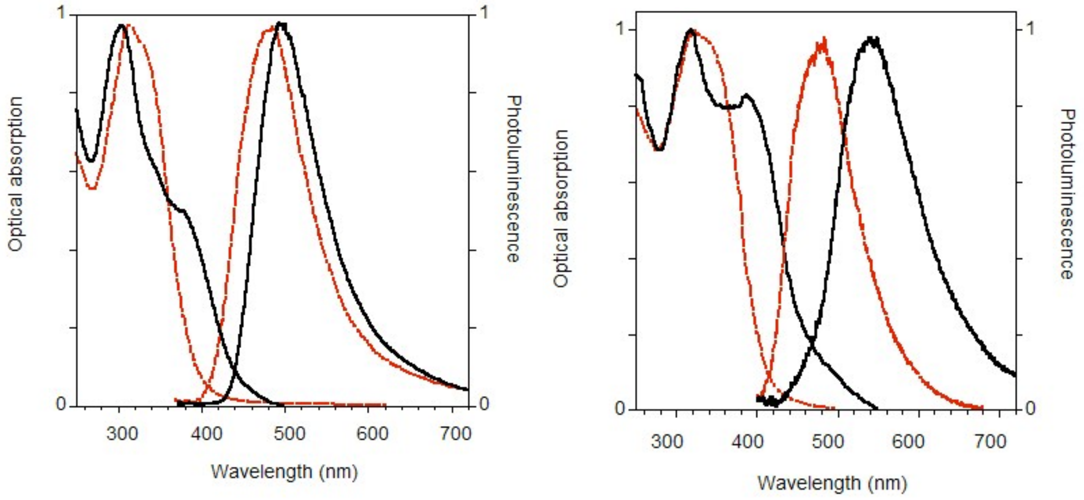


Figure 4. Optical absorption and emission spectra of poly-6-TPA-**BF3k (**black solid lines)**,** and poly-4'-TPA-6-MO-**BF3k** (red dotted lines) in dichloromethane solutions (left panel) and in the solid state (film, right panel).

The absorption spectra of all the polymers with the attachment of the chromophore in position 6 display a low energy peak at about 350 nm for the MCBZ and 400 nm for TPA derivative, whose intensity increases in the solid state with respect to the solution. This contribution, indicative of the presence of π-stacked chromophores, is apparent as a weak shoulder in the polymer with substitution in the position 4' only for the MCBZ chromophore. As already observed in the polymers bearing the DMFL chromophore,[10] the substitution in position 6 induces higher stacking among the monomeric unities both in solution and in the solid state that could enhance PL efficiency by restriction of the intramolecular rotations.[20]

The most remarkable result obtained with the new polymers is that poly-6-TPA-**BF3k** bearing a triphenylamine substituent in position 6 of the 3-phenylindene scaffold shows a high quantum yield (QY = 46%) in dichloromethane solution that is an unprecedented value in the polybenzofulvene derivatives studied so far. Indeed as observed for most conjugated polymers, the polybenzofulvene derivatives bearing the MCBZ and TPA chromophores show a decrease of the emission efficiency upon aggregation in the solid state. This observation was suggestive of the existence of significant differences in poly-6-TPA-**BF3k** conformation between the solid state and the solution and stimulated the investigation of the influence of the aggregation process in the emission features.[21] In Table 3 we report the PL properties of cast films and spin-coated films obtained from dichloromethane solutions of the new polybenzofulvene derivatives as compared with the properties of the corresponding powders obtained by the precipitation-based purification procedure (see ESI).

Table 3. Solid-state emissive features of the new polybenzofulvene derivatives bearing electron donating chromophores.

	spin coated films [a]	casted films [a]		powder [b]	
polymer	λ_{em} (nm)	λ_{em} (nm)	QY (%)	λ_{em} (nm)	QY (%)
poly-6-MCBZ-**BF3k**	544	509	14	535	19
poly-6-TPA-**BF3k**	501	542	23	530	35
poly-4’-MCBZ-6-MO-**BF3k**	507	488	8	494	5
poly-4’-TPA-6-MO-**BF3k**	475	478	9	486	13

[a] from dichloromethane solutions, [b] powders obtained by precipitation in the excess of a bad solvent.

Quite surprisingly, the powder obtained by precipitation of poly-6-TPA-**BF3k** in the excess of a bad solvent such as ethanol showed an emission efficiency (QY = 35%) higher than the one obtained in cast films from dichloromethane solutions (QY = 23%), but lower than the corresponding value obtained with the dichloromethane solution (QY = 46%). Furthermore, the QY decrease observed passing from the solution to the cast film was paralleled by a red shift as in a typical aggregation caused quenching (ACQ) effect.[22] We assumed that the emission properties of poly-6-TPA-**BF3k** are the result of a complex equilibrium between the electronic structure and the dynamic of its monomeric unit within the polymeric backbone, so that little changes in the intrachain and interchain interactions promoted by aggregation could result into dramatic changes in the emission properties. When the good solvent (*i. e.* dichloromethane or chloroform) is rapidly eliminated from the polymer matrix, precipitated poly-6-TPA-**BF3k** could be trapped in a conformation close to the one present in solution with a partial retention of the emission efficiency. On the other hand, the evaporation of the solvent in the film formation appears to drive the polymer toward the formation of detrimental (interchain and intrachain) stacking interactions leading to ACQ. The different behavior of closely related poly-6-MCBZ-**BF3k** suggests that the emission properties may depend on the structure of the chromophore. In fact, the propeller-like geometry[23] of

TPA moiety could affect the intrachain and interchain interactions in poly-6-TPA-**BF3k** with different modalities with respect to the planar bicyclic moieties of poly-6-MCBZ-**BF3k**.

By virtue of its very promising emissive features, poly-6-TPA-**BF3k** was evaluated along with its close congener poly-4'-TPA-6-MO-**BF3k** in the assembling of optoelectronic devices such as OLED showing simple architectures in order to obtain information on the intrinsic optoelectronic features of this polybenzofulvene derivatives. Thus, the performances of single layer OLED structures ITO/PEDOT:PSS/EML/Ba/Al were compared for the two polymers and the standard **PVK** polymer, widely used in the literature for its good hole transporting properties combined with emission in the blue region.[24,25] The results for different emitting layer (EML) are reported in Table 4.

Table 4. Optoelectronic properties of the OLED devices prepared with poly-6-TPA-**BF3k**, poly-4’-TPA-6- MO-**BF3k**, or with **PVK**.

EML	thickness [nm]	V_{on} [V]	EQE_{max} [%]	LE_{max} [cd/A]	L_{max} [cd/m^2]	PE_{max} [lm/W]
poly-6-TPA-**BF3k**	210	11	0.008	0.022	20	0.004
poly-4’-TPA-6-MO-**BF3k**	214	15	0.0015	0.0035	3	0.0005
PVK	161	14	0.012	0.013	16	0.002

The results obtained in these preliminary studies confirmed the good optoelectronic features of the polybenzofulvene derivatives, that in the polymer bearing the triphenylamine chromophore in the position 6 of the phenylindene moiety (poly-6-TPA-**BF3k**) are comparable (or superior) to those shown by **PVK** and about one order of magnitude higher than those shown by the corresponding polybenzofulvene derivative bearing the triphenylamine chromophore in the position 4’ of the phenylindene moiety (poly-4’-TPA-6- MO-**BF3k**) in agreement with the high degree of π-stacking interactions among the aromatic moieties of poly-6-TPA-**BF3k** as suggested by NMR studies.

However, the role played by the aggregation process (*i. e.* in the formation of the emitting layer) in affecting the emission properties of poly-6-TPA-**BF3k** stressed the importance of development studies in order to obtain the suitable device configuration for the use of polybenzofulvenes in OLED applications.

Conclusion

New polybenzofulvene derivatives were designed and synthesized by introducing, in two different key positions of the 3-phenylindene scaffold, different chromophores showing electron donating ability in order to obtain polymers endowed with improved optoelectronic performances. Among the newly-synthesized polybenzofulvenes, poly-6-TPA-**BF3k** bearing a triphenylamine substituent in position 6 of the 3-phenylindene scaffold showed a high quantum yield in dichloromethane solution that was an unprecedented value in the polybenzofulvene derivatives studied so far. This successful accomplishment accounted for the power of rational design in the obtainment of polybenzofulvenes endowed with the desired optoelectronic properties. Moreover, the photophysical features (*i. e.* the emissive efficiency) of the new polymers were affected by the chromophore type, the position of the attachment, and the aggregation state. Finally, the preliminary devices prepared with the newly-synthesized polymers showed promising features, but the role played by the aggregation process (*i. e.* in the formation of the emitting layer) in affecting the emission properties of poly-6-TPA-**BF3k** stressed the importance of development studies in order to obtain the suitable device configurations for the use of polybenzofulvenes in OLED applications.

Electronic supplementary information (ESI) available: Experimental details for the synthesis and the characterization of poly-6-MCBZ-**BF3k**, poly-4'-MCBZ-6-MO-**BF3k**, poly-6-TPA-**BF3k**, poly-4'-TPA-6-MO-**BF3k** and their intermediates.

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Side Chain Engineering in π-Stacked Polybenzofulvene Derivatives Bearing Electron-Rich Chromophores for OLED Applications

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A side chain engineering designed to introduce electron donating chromophores in the 3-phenylindene scaffold led to the discovery of an highly emissive polybenzofulvene derivative for OLED applications.