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Bithiophene-Based Polybenzofulvene Derivatives with High Stacking and Hole Mobility

Andrea Cappelli,,a Vincenzo Razzano,a Marco Paolino,a Giorgio Grisci,a,b Germano Giuliani,a Alessandro Donati,a Raniero Mendichi,b Filippo Samperi,c Salvatore Battiato,c Antonella Caterina Boccia,b Andrea Mura,d Giovanni Bongiovanni,d Wojciech Mróz,b Chiara Botta.b*

aDipartimento di Biotecnologie, Chimica e Farmacia and European Research Centre for Drug Discovery and Development, Università degli Studi di Siena, Via Aldo Moro 2, 53100 Siena, Italy

bIstituto per lo Studio delle Macromolecole (CNR), Via E. Bassini 15, 20133 Milano, Italy

cIstituto per i Polimeri, Compositi e Biomateriali (IPCB) U.O.S. di Catania, CNR, Via Gaifami 18, 95126 Catania, Italy

dDipartimento di Fisica, Università degli Studi di Cagliari, S. P. Monserrato-Sestu Km 0.700, 09042 Monserrato, Cagliari, Italy

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ABSTRACT

Four new benzofulvene derivatives bearing bithiophene chromophores in two different key positions of the phenylindene scaffold were prepared in order to evaluate the role of different chromophores in the optoelectronic features of polybenzofulvene derivatives. The results of the photophysical studies showed that the optical properties of the newly-synthesized bithiophene-functionalized polymers were affected by both the polymer enchainment and the substitution topology of the monomeric units. On the other hand, the hole-mobility appeared to be affected to a lower extent, but the best performances were obtained in poly-6-HBT-**BF3k** showing the strongest bithiophene side chain packing. This work demonstrates that the optoelectronic properties of polybenzofulvene derivatives can be optimized by a targeted chemical design such as side chain engineering.

INTRODUCTION

The development of high performance π-conjugated polymers has allowed the fabrication of optoelectronic devices [e. g. organic light-emitting diodes (OLEDs), field effect transistors (FETs), and photovoltaic cells] showing appealing properties.[1-3] In this field, π-stacked polymers, such as polydibenfofulvene derivatives[4-6] and ciclophanes,[7,8] may offer an alternative macromolecular platform with novel photophysical and photoelectronic characteristics, due to through-space non covalent interactions among the pendant chromophore residues aligned along polymer backbone. These peculiar spatial arrangements account for a new promising way to transport both charge and energy[9] and allow to tune the electronic properties of the polymer system by modifying the geometry of π-packing[10,11] (*e. g.* the distance and the spatial orientation of the interacting chromophores planes). However, the potential optoelectronic applications of these materials have been poorly investigated in the past years. We recently demonstrated that π-stacked polybenzofulvene derivatives (i. e. poly-6-DMFL-**BF3k** in Figure 1) can be considered intriguing materials for the production of optoelectronic devices such as OLEDs.[12,13] Polybenzofulvenes are through-space conjugated polymers formed by arrays of π-electron systems stacked along a single polymer chain.[14] The most studied π-stacked polymer is poly(*N*-vinylcarbazole) (**PVK**, Figure 1), which has been shown to transfer charge via intrachain stacked orbitals resulting from face-to-face conformation of the carbazole moieties, and show photoconductive, photorefractive, hole-transporting, energy-donating, and carrier-switching properties.[15]
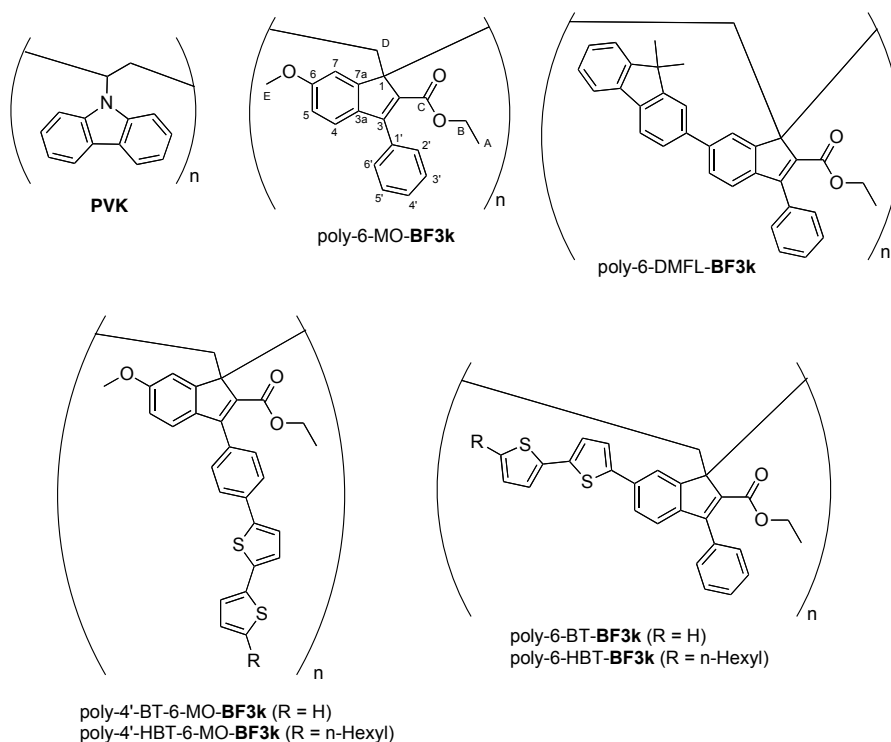
Figure 1. Structures of **PVK**, poly-6-MO-**BF3k**, poly-6-DMFL-**BF3k**, and of the newly designed polybenzofulvene derivatives bearing bithiophene chromophores.

Similarly, polybenzofulvene derivatives were found to show significant hole-transporting capabilities linked to the presence of methoxy substituents in the structure of poly-6-MO-**BF3k** (Figure 1) and combined with other peculiar features such as the prompt and almost quantitative formation by spontaneous thermoreversible polymerization, the tunable solubility and aggregation behavior, etc.[16-21] Furthermore, the replacement of the methoxy group in position 6 of the 3-phenylindene structure of poly-6-MO-**BF3k** with a 9,9-dimethylfluorene residue (as in poly-6-DMFL-**BF3k**) was determinant in the obtainment of highly emissive polymeric supramolecular assemblies for optoelectronic applications.[12,13]

Based on the intriguing results obtained, we conceived a systematic investigation of different chromophores in substitution of the previously employed fluorene moiety in order to explore the potentialities of polybenzofulvene derivatives in providing materials for optoelectronic applications. Thus, we designed four benzofulvene derivatives bearing bithiophene chromophores in the two

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different key positions (6 and 4') of the phenylindene scaffold that were found to retain the
spontaneous polymerization mechanism. By means of spectroscopic and electrical characterizations, we show that the bithiophene chromophore substitution induces in the polybenzofulvene derivatives a quenching of the emission combined with an improvement of the hole-transporting features.

EXPERIMENTAL SECTION

Synthesis. The details of the preparation of benzofulvene derivatives and their spontaneous polymerization are described in Electronic Supplementary Information (ESI). NMR spectra were recorded with a Bruker DRX-400 AVANCE, 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.

SEC-MALS. The molecular weight distribution (MWD) characterization of the newly prepared polybenzofulvene derivates was performed by a MALS light scattering photometer on-line to a SEC chromatographic system. The SEC-MALS system and the corresponding experimental conditions were identical to those used in our previous studies[17,18] 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 functional groups in the repeating unit of the polybenzofulvene derivatives produced slight changes (increase) in dn/dc value. In particular the measured values are the following: 0.195 mL/g for poly-**BF3k**; 0.192 mL/g for poly-6-MO-**BF3k**; 0.198 mL/g for poly-6-BT-**BF3k**; 0.198 mL/g for poly-4'-BT-6-MO-**BF3k**; 0.198 mL/g for poly-6-HBT-**BF3k**; 0.225 mL/g for poly-4'-HBT-6-MO-**BF3k**.

MALDI-TOF mass spectrometry. MALDI–TOF mass spectra were recorded in reflectron or linear delayed extraction mode, using a Voyager-DE STR instrument (Perseptive Biosystem) mass spectrometer, equipped with a nitrogen laser ($\lambda = 337$ nm, pulse width = 3 ns), working in a positive ion mode. The accelerating voltage was 20 KV, grid voltage and delay time (delayed extraction, time lag), were optimized for each sample to achieve the higher mass resolution. Laser irradiance was maintained slightly above threshold. The best spectra were recorded using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) 0.1 M in THF as matrix. Samples for the MALDI analyses were prepared as follows: 10 μL of polymer solution (5 mg/mL in THF), were mixed with 10 μL or 30 μL of a matrix solution. Then 1 μL of each analyte/matrix mixture

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was spotted on the MALDI sample holder and slowly dried to allow analyte/matrix co-crystallization. For the analysis of polymer SEC fractions 1 μL of each selected concentrated SEC solution was mixed with 1 μL or 3 μL of the matrix solution (DCTB).

SEC Fractionation. The polymeric material obtained by the dehydration of indenol **3a** in the usual conditions was accurately fractionated by means of a SEC system consisted of an integrated Waters 515 apparatus (pump and injector) and a Waters R401 DRI detector, using THF as the mobile phase (1 mL/min of flow rate). The column set was composed of four Ultrastyragel HR columns (ID = 7.8 mm, L = 300 mm, 5 μm of particle size) in the order HR-4, HR-3, HR-2 and HR-1 connected in series. The SEC traces were recorded and processed using a Clarity-GPC software provided by DataApex. In a typical fractionation, 100 μL of a polymer solution in THF (ca. 5 mg/mL of concentration) was injected and fractions were taken at every prefixed interval time. In the range of elution volume (Ve) within 16 and 28 mL (peak 1 in Figure 3) the solutions were taken every 1 mL collecting 12 SEC-fractions, whereas in the Ve range within 28 and 38 mL (peak 2 in Figure 3) were taken every 0.25 mL collecting 40 ones.

Optical measurements. UV-vis absorption spectra were obtained with a Perkin Elmer Lambda 900 spectrometer. PL spectra were 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 were corrected for the instrument response. PL QY of solutions were obtained by using quinine sulfate as reference. PL QY of solid powders were measured with a home-made integrating sphere according to the procedure reported elsewhere.[22]

Time resolved measurements was performed by using a mode locked Titanium:sapphire laser system operating at 80 MHz and delivering 100 fs long pulses (FWHM) with a cw mean power of about 500 mW at 780 nm. Optical excitation around 390 nm was obtained using a lithium iodate ($LiIO_3$) crystal as a frequency doubler. Photoluminescence was spectrally dispersed in a single spectrometer and temporally resolved with a visible 2D-streak camera (Hamamatsu C5680). The

temporal resolution in the configuration we employed was of the order of 10 ps. Decay traces were extracted from streak camera spectrograms by integrating over a ~50-nm-wide spectral window.

Devices preparation and characterization. Glasses covered with indium tin oxide (ITO, 15 $\Omega/\square$) were cleaned ultrasonically in distilled water, acetone, and isopropanol. On the substrates, a water solution of poly-(3,4-ethylenedioxythiophene)-poly-(styrenesulfonic acid) (PEDOT:PSS, Clevios P VP AI 4083, H. C. Starck) was spincoated through a nylon filter (pore size 0.45 μm), creating layer with thickness of 50 nm. Subsequently, the substrates were annealed for 10 min at 100 °C in nitrogen atmosphere. On such prepared substrates, 10 nm of MoO_3 were evaporated at a pressure of 10^{-7} mbar, creating ohmic contact for hole injection. Then, inside a nitrogen filled glovebox, organic films were deposited from a chloroform solution with concentration 15 mg/mL. The obtained layers showed thicknesses values between 200 nm and 300 nm. Finally, top electrodes consisting of 7 nm of MoO_3 and 80 nm of Al were evaporated. The current density-voltage curves were measured with a Keithley 2602 source meter. All the device characterizations were performed in a nitrogen atmosphere. Thickness of organic films was evaluated by using a Dektak XT (Bruker) profilometer.

RESULTS AND DISCUSSION

Synthesis and spontaneous polymerization of the newly designed benzofulvene derivatives bearing bithiophene chromophores.

The synthesis of the newly designed polybenzofulvene derivatives was based on the chemistry developed for the preparation of the previously published fluorene members of this sub-series of polybenzofulvenes bearing pendant chromophore residues.[12] In particular, triflate **1** (ref 12) was used as starting material in the multistep procedure described in Scheme 1 to obtain polybenzofulvene derivatives poly-6-BT-**BF3k** and poly-6-HBT-**BF3k**.

Scheme 1. Synthesis and spontaneous polymerization of benzofulvene derivatives 6-BT-**BF3k** and 6-HBT-**BF3k**.
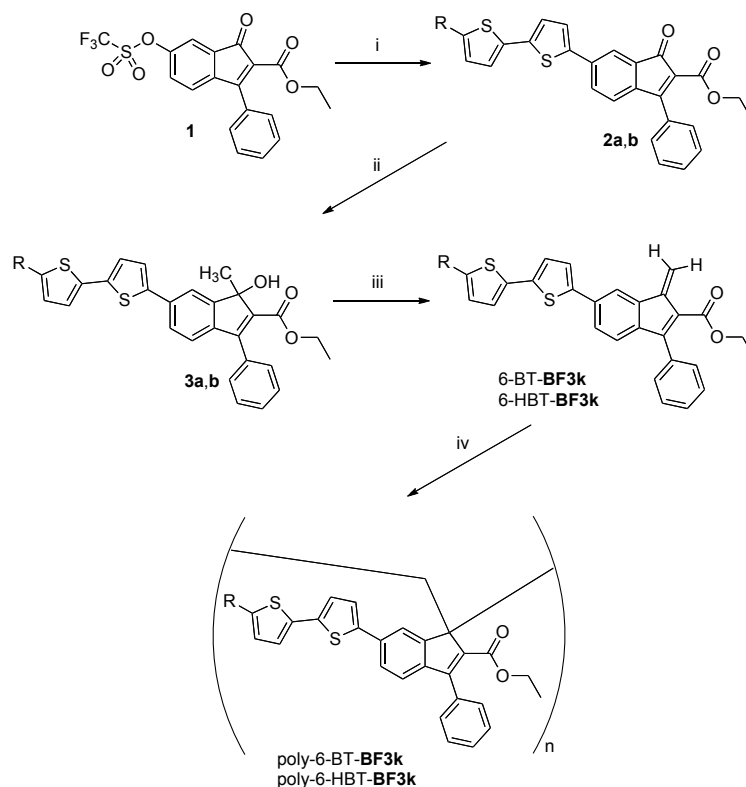
Reagents: (i) 2,2'-bithiophene-5-boronic acid pinacol ester for **2a** (or 5'-hexyl-2,2'-bithiophene-5-boronic acid pinacol ester for **2b**), Pd(PPh$_3$)$_2$Cl$_2$, PPh$_3$, Cs$_2$CO$_3$, CH$_3$OH, THF; (ii) Al(CH$_3$)$_3$, CH$_2$Cl$_2$; (iii) PTSA, CHCl$_3$ (**Method B**); (iv) solvent evaporation. **Substituents**: R = H in **2a**, **3a**, 6-BT-**BF3k**, and poly-6-BT-**BF3k**; R = n-Hexyl in **2b**, **3b**, 6-HBT-**BF3k**, and poly-6-HBT-**BF3k**.

Suzuki-Miyaura cross-coupling of **1** with the suitable bithiopheneboronic acid pinacol esters (commercially available from Aldrich) gave indenones **2a**,**b**, which were transformed into the corresponding indenols **3a**,**b** by methylation with trimethylaluminium.[17-21] The dehydration of indenol **3a** in the usual conditions (**Method A**: 0.05 M solutions of **3a** in CDCl$_3$ containing catalytic amounts of p-toluenesulfonic acid, PTSA, see ESI) led to the formation of a new polybenzofulvene derivative showing the unusual enchainment displayed in poly-**5** (Scheme 2) as suggested by SEC-MALS, SEC-MALDI, and NMR spectroscopy (see below).

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Scheme 2. Dehydration of indenol **3a** by **Method A**.
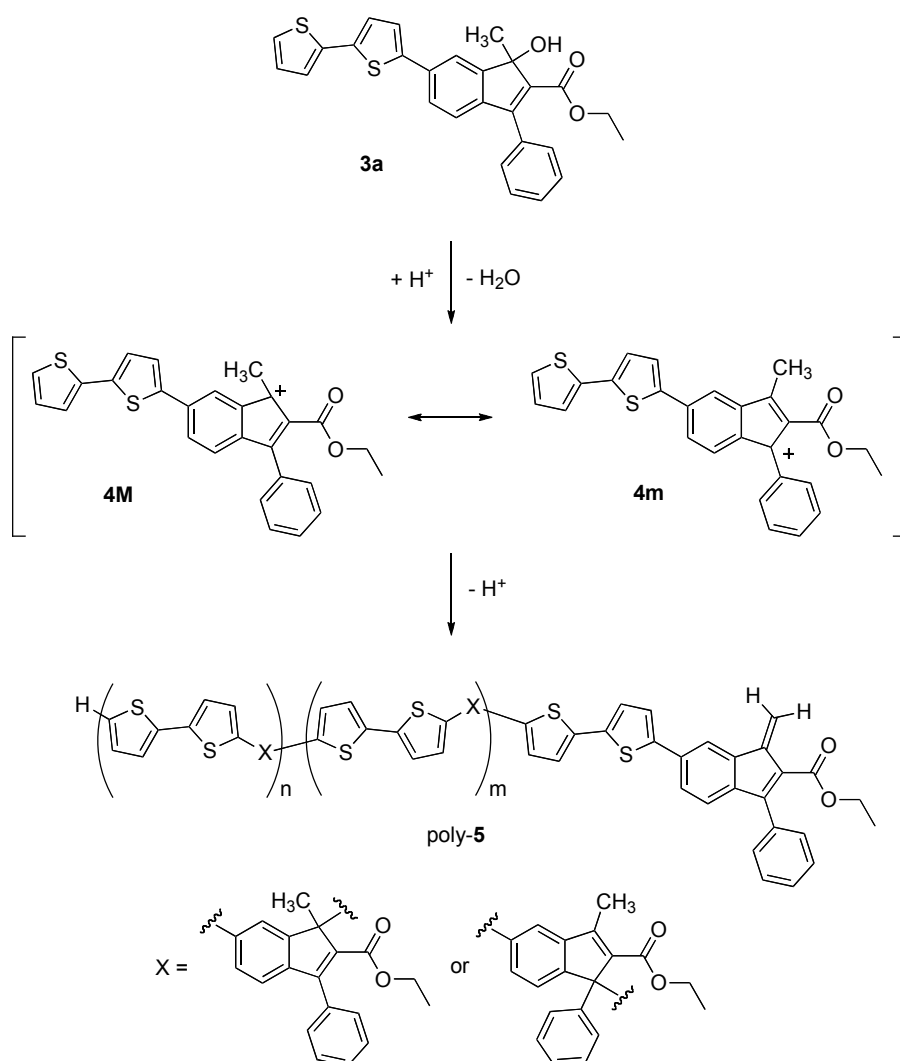
We assumed that the product of the first step of the dehydration reaction (i. e. carbonium ion **4**) was capable to perform an electrophilic attack on the distal thiophene ring of the bithiophene moiety that could be depressed in diluted conditions. In fact, monomer 6-BT-**BF3k** was obtained in good purity by carrying out the dehydration reaction of **3a** in diluted conditions (**Method B,** concentration ca. 0.001 M), which depressed the intermolecular events (i. e. the oligomerization process driving to poly-**5**) in favour of the intramolecular hydrogen ion elimination leading to 6-BT-**BF3k**. Thus, the diluted conditions of **Method B** became the standard methodology in the dehydration of indenol derivatives bearing the bithiophene chromophores. As expected, benzofulvene monomers 6-BT-**BF3k** and 6-HBT-**BF3k** polymerized in the apparent absence of catalysts, upon solvent removal, to give the corresponding polymers poly-6-BT-**BF3k** and poly-6-

HBT-**BF3k**. A similar procedure (Scheme 3) starting from bromophenylindenone **6** (ref. 12) was used for the synthesis of the polybenzofulvene derivatives bearing the bithiophene chromophores in positions 4' of the phenylindene scaffold.

Scheme 3. Synthesis of polybenzofulvene derivatives bearing the bithiophene chromophores in positions 4' of the phenylindene scaffold.

4'-BT-6-MO-**BF3k**
4'-HBT-6-MO-**BF3k**

poly-4'-BT-6-MO-**BF3k**
poly-4'-HBT-6-MO-**BF3k**
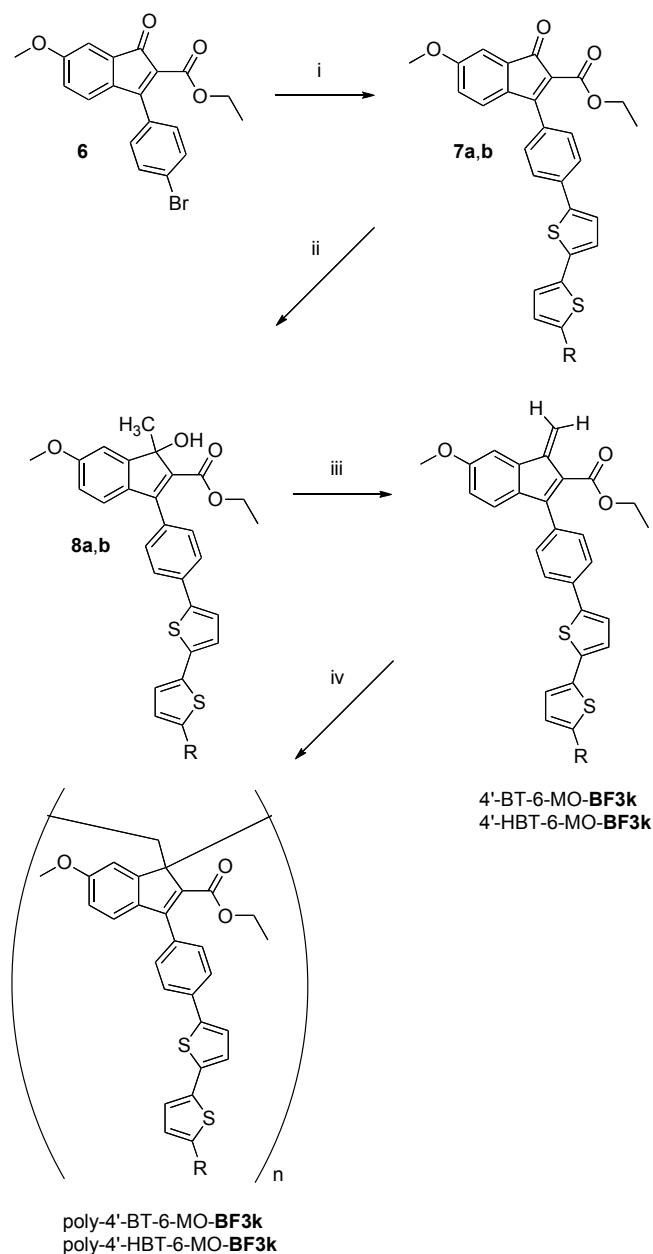
Reagents: (i) 2,2'-bithiophene-5-boronic acid pinacol ester for **7a** (or 5'-hexyl-2,2'-bithiophene-5-boronic acid pinacol ester for **7b**), Pd(PPh$_3$)$_2$Cl$_2$, PPh$_3$, Cs$_2$CO$_3$, CH$_3$OH, THF; (ii) Al(CH$_3$)$_3$, CH$_2$Cl$_2$; (iii) PTSA, CHCl$_3$; (iv) solvent evaporation. **Substituents**: R = H in **7a**, **8a**, 4'-BT-6-MO-**BF3k**, and poly-4'-BT-6-MO-**BF3k**; R = *n*-Hexyl in **7b**, **8b**, 4'-HBT-6-MO-**BF3k**, and poly-4'-HBT-6-MO-**BF3k**.

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Macromolecular characterization of polybenzofulvene derivatives bearing bithiophene chromophores.

An absolute multi-angle laser light scattering (MALS) detector on-line to a size exclusion chromatography (SEC or GPC) system (THF as the mobile phase) was employed in the characterization of molecular weight distribution (MWD), size of macromolecules (radius of gyration Rg), and conformation of the polybenzofulvene derivates bearing bithiophene chromophores.

Very interestingly, the polybenzofulvene derivatives obtained by spontaneous polymerization of the newly-designed benzofulvene derivatives (Table 1) featured particularly high average molecular weight values and broad dispersity ($D = M_w/M_n$) similar to the ones shown by parent polybenzofulvenes. These results confirmed that the presence of bithiophene chromophores in the two different key positions of the phenylindene scaffold is compatible with the spontaneous polymerization mechanism leading to ultrahigh molecular weight polybenzofulvene derivatives so that the mass values observed in the new polymers were significantly higher than those observed in the parent macromolecules poly-6-MO-**BF3k** and poly-**BF3k**. This observation could be rationalized in terms of additional stacking interactions due to bithiophene moiety stabilizing the polybenzofulvene backbone. Finally, the slope of the conformation plot was in the range (0.5-0.6) usually found for linear polymers with a random coil conformation in relatively good solvent (THF) as already observed in the parent polybenzofulvene derivatives poly-6-MO-**BF3k** and poly-**BF3k**.

Table 1. Macromolecular features of the polybenzofulvene derivatives obtained by spontaneous polymerization of the newly-designed benzofulvene derivatives bearing bithiophene chromophores compared with those shown by parent polymers poly-6-MO-**BF3k** and poly-**BF3k**.

polymer	M_p	M_w [a]	M_w/M_n [b]	R_g [c]	K [d]	α [d]
	(kg/mol)	(kg/mol)		(nm)	(nm)	
poly-6-BT-**BF3k**	2,968	2,012	3.5	43.7	1.38·E-02	0.53
poly-6-HBT-**BF3k**	4,735	4,596	2.5	72.7	2.16·E-02	0.51
poly-4'-BT-6-MO-**BF3k**	3,884	2,840	5.2	55.3	2.32·E-02	0.50
poly-4'-HBT-6-MO-**BF3k**	3,817	3,438	2.9	66.2	2.53·E-02	0.51
poly-6-MO-**BF3k**	312	347	4.3	19.4	5.75·E-03	0.61
poly-**BF3k**	1,900	1,506	3.4	49.9	6.63·E-03	0.60

[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.

On the other hand, SEC-MALS analysis of the samples obtained by dehydration of indenol **3a** by **Method A** (performed in two different runs to evaluate the reproducibility of the results) showed the presence of two components differing in molecular weight. In particular, the chromatogram obtained with a first run sample (**MA-1**) showed the presence of a dominant (about 80%) oligomeric component and a minor (about 20%) polymeric component showing a higher MW value (Figure 2).
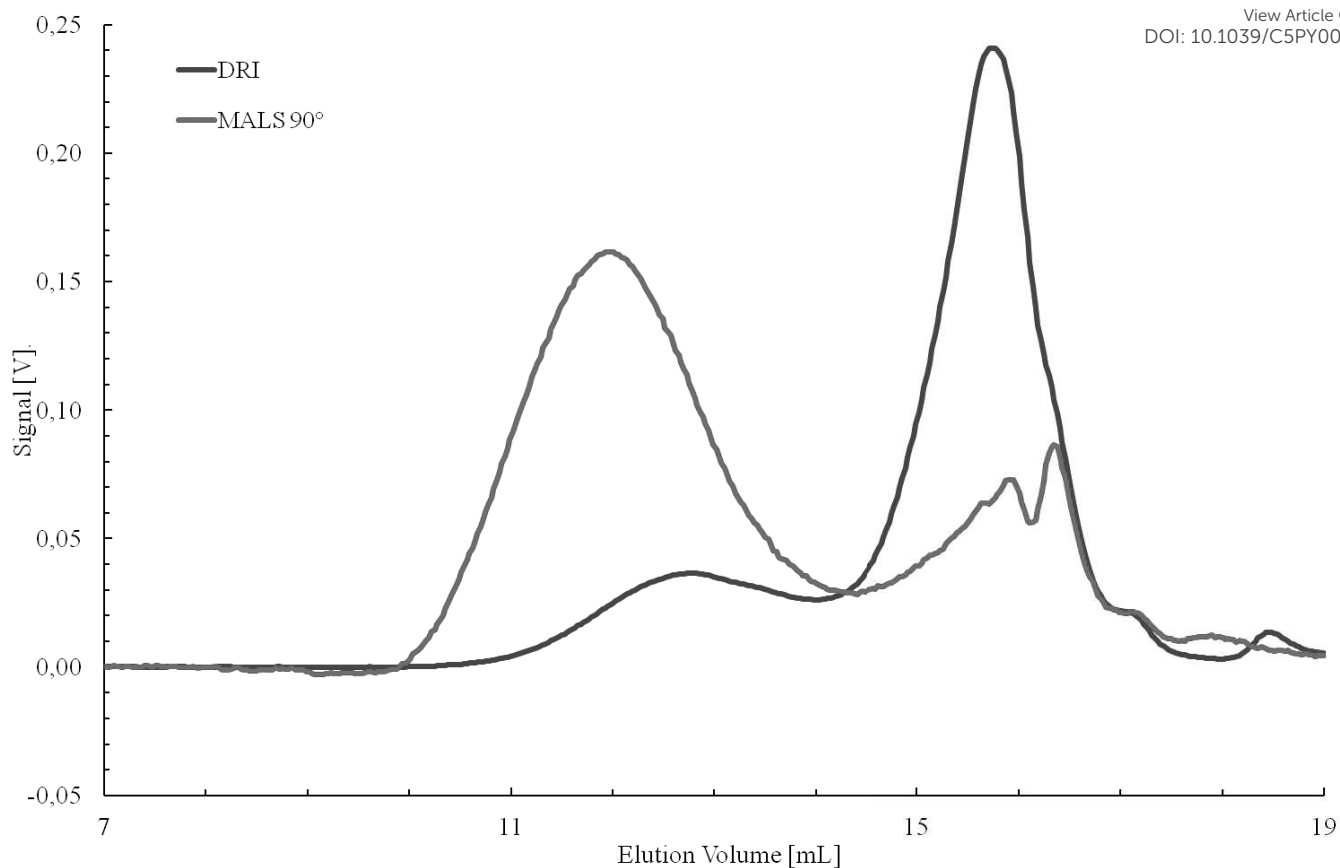
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Figure 2. SEC-MALS signals (DRI = concentration detector, MALS 90° = MALS photodiode at 90°) recorded for the first run sample (**MA-1**) obtained by the dehydration of indenol **3a** by **Method A**.

Moreover, the SEC-MALDI analysis of the second run sample (**MA-2**) showed an analogous composition (Figure 3).
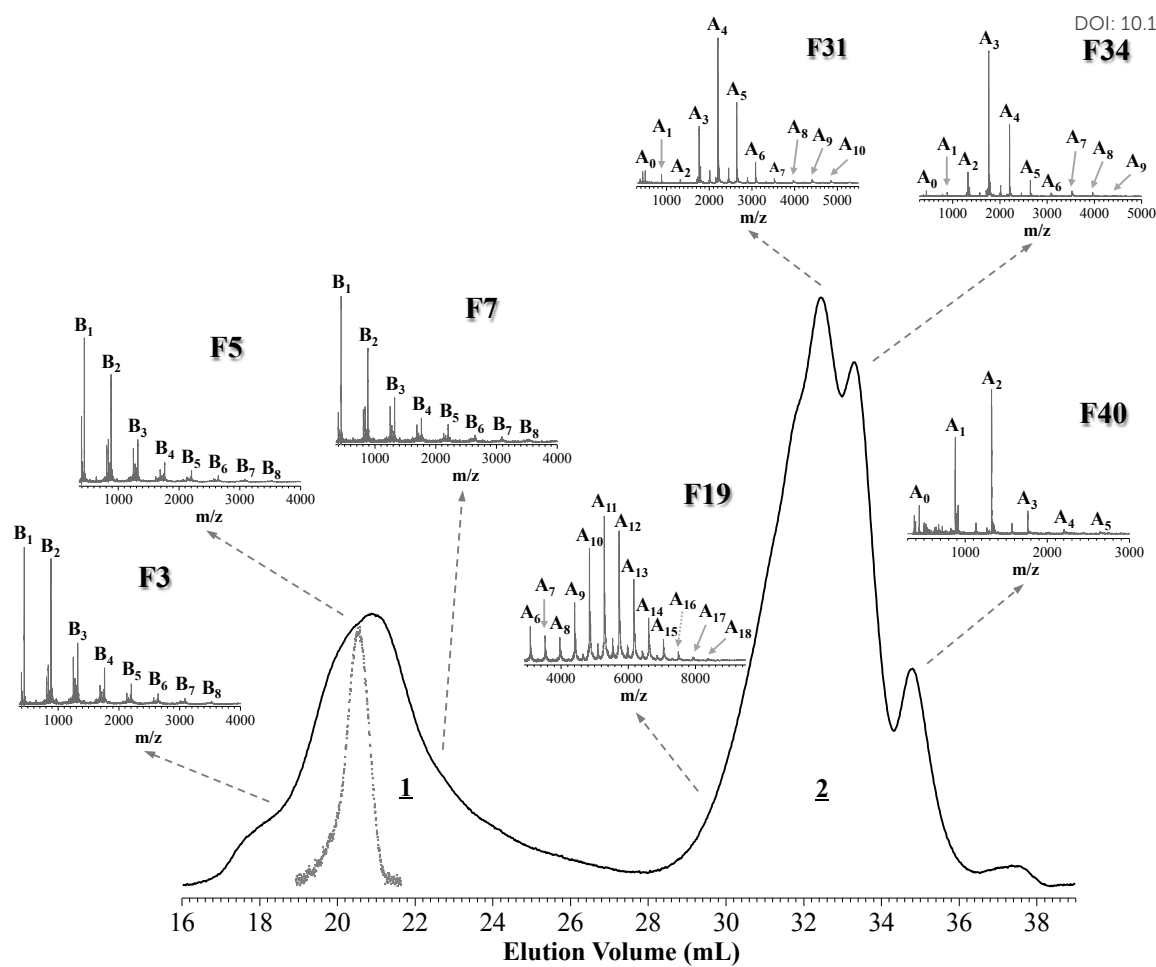
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Figure 3. SEC-MALDI chromatogram obtained with second run sample (**MA-2**) obtained by the dehydration of indenol **3a** by **Method A**. SEC curve (dotted line) of the re-injected fraction F5 is also reported.

MALDI-TOF mass spectrum of sample **MA-2** obtained the dehydration of indenol **3a** by **Method A**, recorded in linear mode using *trans*-2-[3-(4-t-butyl-phenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as the matrix, is displayed in Figure ESI-1 (ESI). The spectrum showed a series of repeating families of peaks spanning from *m/z* 400 up to *m/z* 6,000 having a 440.6 ± 0.3 Da transition, corresponding to the mass of the repeating unit (440.6 g/mol). The most intense peaks correspond to the oligomers terminated with hydrogen at both ends. Since, the SEC analysis (Figure 3) showed that the polymer sample was composed of about 60% of the oligomer component and about 40% of the polymeric component with a higher MW value, we

assumed that the mass spectrum was representative only of the oligomeric component. It is well

known that in MALDI-TOF MS analysis of polydisperse polymer, macromolecular species with

molar mass lower than 10,000 - 15,000 g/mol are detected, owing to several discrimination

effects.[23-28] To obtain more reliable information on the chemical composition on the polydisperse

polymers, the off-line SEC/MALDI-TOF MS coupling method was applied.[23,24,28,29] Thus, the

second run sample (**MA-2**) was fractionated into narrow molar mass fractions by analytical SEC

analysis, by collecting 12 fractions between 16 and 28 mL (peak 1 in Figure 3) and 40 ones within

28 and 38 mL (peak 2 in Figure 3). Figure 3 shows SEC curve and the MALDI-TOF mass spectra

of some representative fractions. The assignments of the most intense mass peaks are also reported

in Figure 3. As expected, the mass spectra of the fractions corresponding to the peak 2 shown that

they are constituted of oligomers with a narrow molar mass dispersity: the most intense peaks

belong to the protonated ions of the species formed according to Scheme 2. The average molar

masses of these fractions increased with the decrease of the corresponding elution volume, in

agreement to the SEC behaviour and the SEC-MALDI recorded for other polymers.[23,24,28,29]

However, a surprising result was obtained by analyzing the SEC fractions corresponding to peak 1,

at lower elution time. Contrary to the expectation, they gave the same mass spectra independently

of their elution volume (see mass spectra of fraction F3, F5 and F7 in Figure 3). In fact, they show

peaks only in the mass range within m/z 400 and m/z 4000, corresponding to the species formed

according to Scheme 1. This behavior could be explained by taking into account the following

hypotheses: i) aggregation phenomena could occur in the SEC conditions and the molar mass of the

component eluted at each elution volume value was apparent; ii) fragmentation processes could

occur during the MALDI-TOF MS analysis of high molar mass poly-6-BT-**BF3k**. The first

hypothesis was excluded because both the elution volume and the mass distribution of some

fractions re-injected in the SEC apparatus did not change with respect to that observed during the

analysis of neat sample, as well as the fraction F5 reported in Figure 3 (dotted line curve).

Therefore, the assumption that polybenzolfulvenes gave fragmentation in the MALDI-TOF

conditions is reasonable. This behaviour was also confirmed by the MALDI mass spectrum of the poly-6-BT-**BF3k** (Figure ESI-2)(ESI) that showed peaks due to the molecular ions of di-hydrogen ended linear oligomers from dimers (*m/z* 882) up to octamers (*m/z* 3526), together to other fragmentation products.

This finding suggests that fragmentation process could occur during the MALDI-TOF MS analysis of polybenzofulvenes already published, because generally were observed mass peaks only in the mass range of *m/z* 400÷9000. At the present, a series of studies are carried out to investigate the mechanisms of fragmentation processes occurring during the MALDI-TOF MS analysis of polybenzofulvenes.

NMR characterization of the polymerization of the newly designed benzofulvene derivatives bearing bithiophene chromophores.

The spontaneous polymerization of benzofulvene derivatives 6-BT-**BF3k**, 6-HBT-**BF3k**, 4'-BT-6-MO-**BF3k**, and 4'-HBT-6-MO-**BF3k** was studied by NMR spectroscopy by comparing the spectra of the polymers with those of the corresponding monomers after a careful assignment work. In particular, the ^{1}H and ^{13}C NMR spectra of the monomers were assigned by means of correlation experiments (see ESI for details). This work allowed the retention of the original vinyl (1,2) polymerization mechanism to be evaluated on the basis of the presence of the diagnostic peak at around 57 ppm attributed to the aliphatic quaternary carbon (C-1) of the 1,2-repeating indene unit (see for example Figures 4 and 5).[17,18,30] Based on the comparison of the ^{13}C NMR spectra of poly-4'-HBT-6-MO-**BF3k** and poly-4'-BT-6-MO-**BF3k** with that of the parent macromolecule poly-6-MO-**BF3k,** (Figure 4) the sharpest signals were assigned to the carbon atoms belonging to the bithiophene chromophores, while the phenylindene signals were as broad as in the parent macromolecule poly-6-MO-**BF3k**.

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Figure 4. Comparison of the ^{13}C NMR spectra of poly-4'-BT-6-MO-**BF3k** and poly-4'-HBT-6-MO-**BF3k** with that of the parent macromolecule poly-6-MO-**BF3k**.

Moreover, the comparison of the ^{13}C NMR spectra of the four polybenzofulvene derivatives bearing the bithiophene chromophores confirmed that the presence of the bithiophene moiety in position 6 of the indene nucleus produced a significant broadening of the signal in the spectra of both poly-6-BT-**BF3k** and poly-6-HBT-**BF3k** (Figure 5).
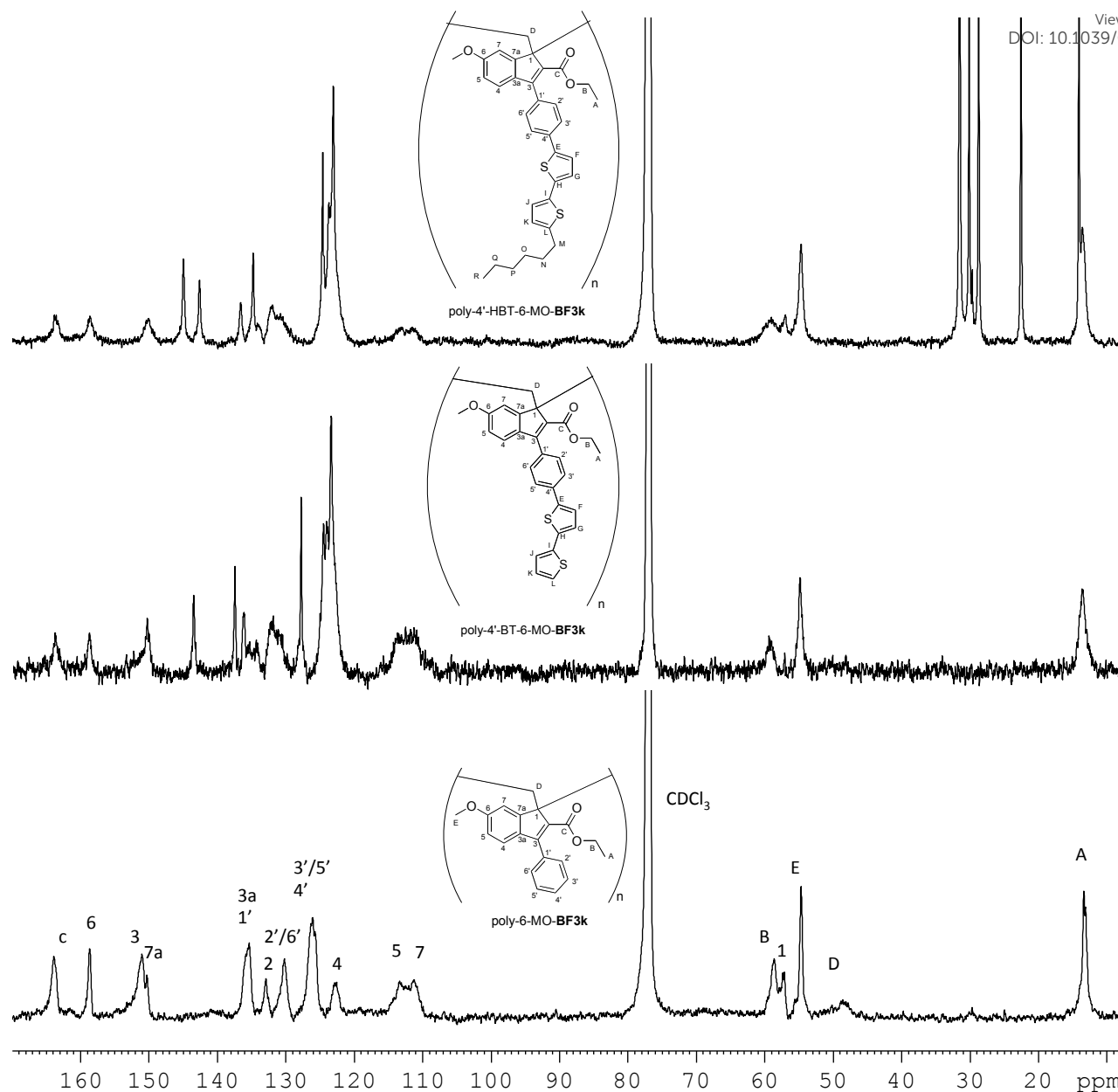
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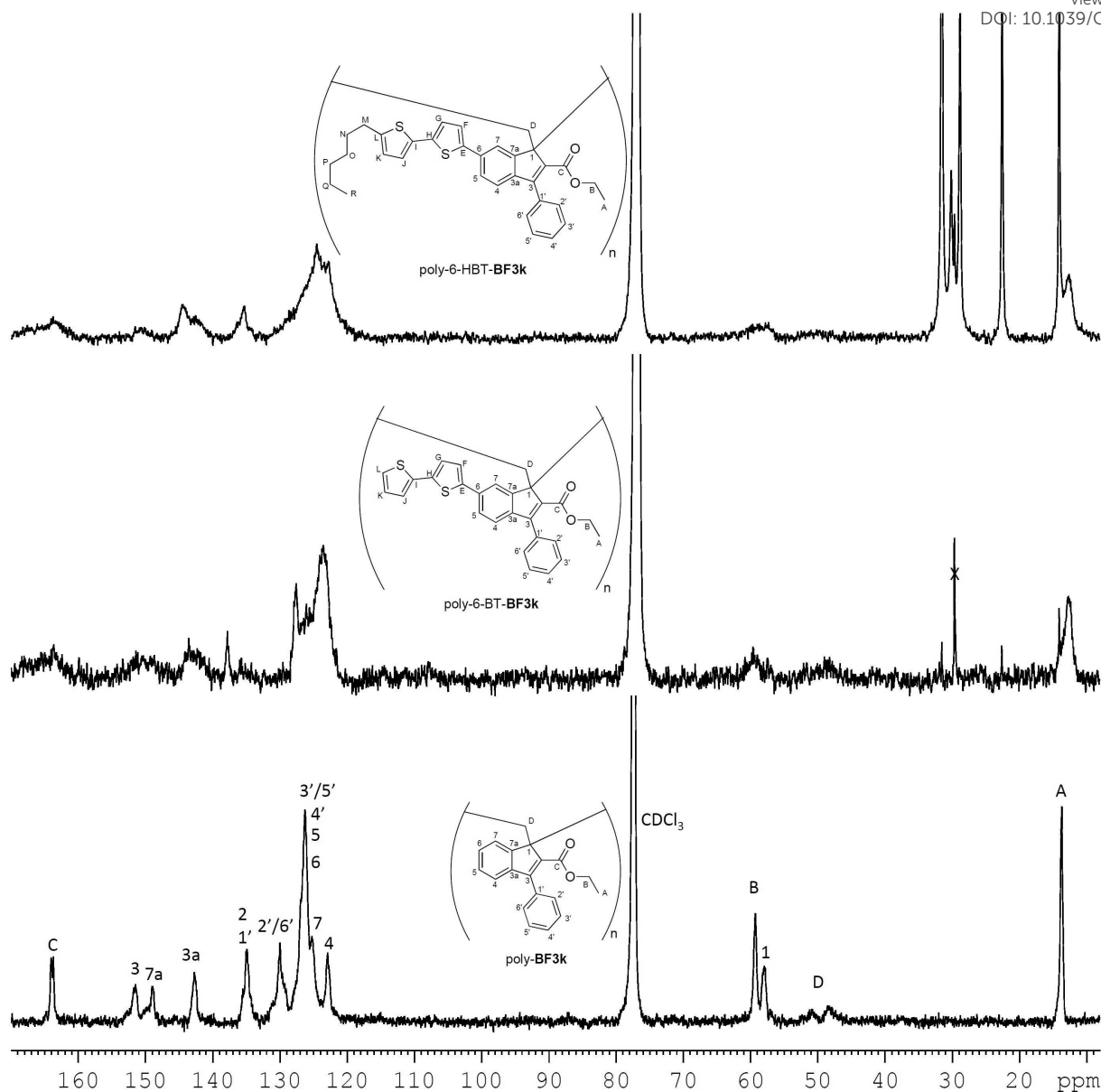
Figure 5. Comparison of the ^{13}C NMR spectra of poly-6-BT-**BF3k** and poly-6-HBT-**BF3k** with that of the parent macromolecule poly-**BF3k**.

Overall, these observations were rationalized in terms of different dynamics of the monomeric unities in the polybenzofulvene backbone, as proposed for the previously reported fluorene-based polybenzofulvenes.[12] The introduction of the bithiophene residues in position 6 of the indene nucleus enhances the degree of π-packing among the aromatic moieties of both poly-6-BT-**BF3k** and poly-6-HBT-**BF3k** resulting in a reduction of the dynamic features of the monomeric unities, although the hexyl side chains of poly-6-HBT-**BF3k** hold significant symptoms of local mobility.

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On the other hand, the bithiophene chromophores of poly-4'-BT-6-MO-**BF3k** and poly-4'-BT-6-MO-**BF3k** were assumed to freely rotate around their attachment bond at the pendent phenyl group in the apparent lack of stacking constraints.

Both the samples **MA-1** and **MA-2** obtained from the dehydration of indenol **3a** by **Method A** were studied by NMR spectroscopy in order to establish the structure and the formation mechanism of this unusual polybenzofulvene derivative. Thus, ^{1}H and ^{13}C NMR spectra of **3a** were assigned by means of homonuclear ^{1}H-^{1}H-COSY, [1]H-[1]H-NOESY and heteronuclear ^{1}H-^{13}C-HSQC, ^{1}H-^{13}C-HMBC 2D correlation experiments and the assigned spectra were used in the interpretation of the corresponding ones obtained with the unusual polybenzofulvene derivative.

Interestingly, ^{13}C NMR spectra of both the samples were characterized by the presence of sharp and well-resolved resonances, but the most significant structural information could be obtained from [1]H-^{13}C correlation experiments. The analysis of the HMBC (Heteronuclear Multiple Bond Correlation) spectrum of sample **MA-2** (Figure 6) showed the presence of three species in different proportions: a Major one (*i. e.* the Major monomeric unit, **Mmu**, Figure 6) with two minor ones (*i. e.* the minor monomeric unit, **mmu**, and the Terminal monomeric unit, **Tmu**, Figure 6)).
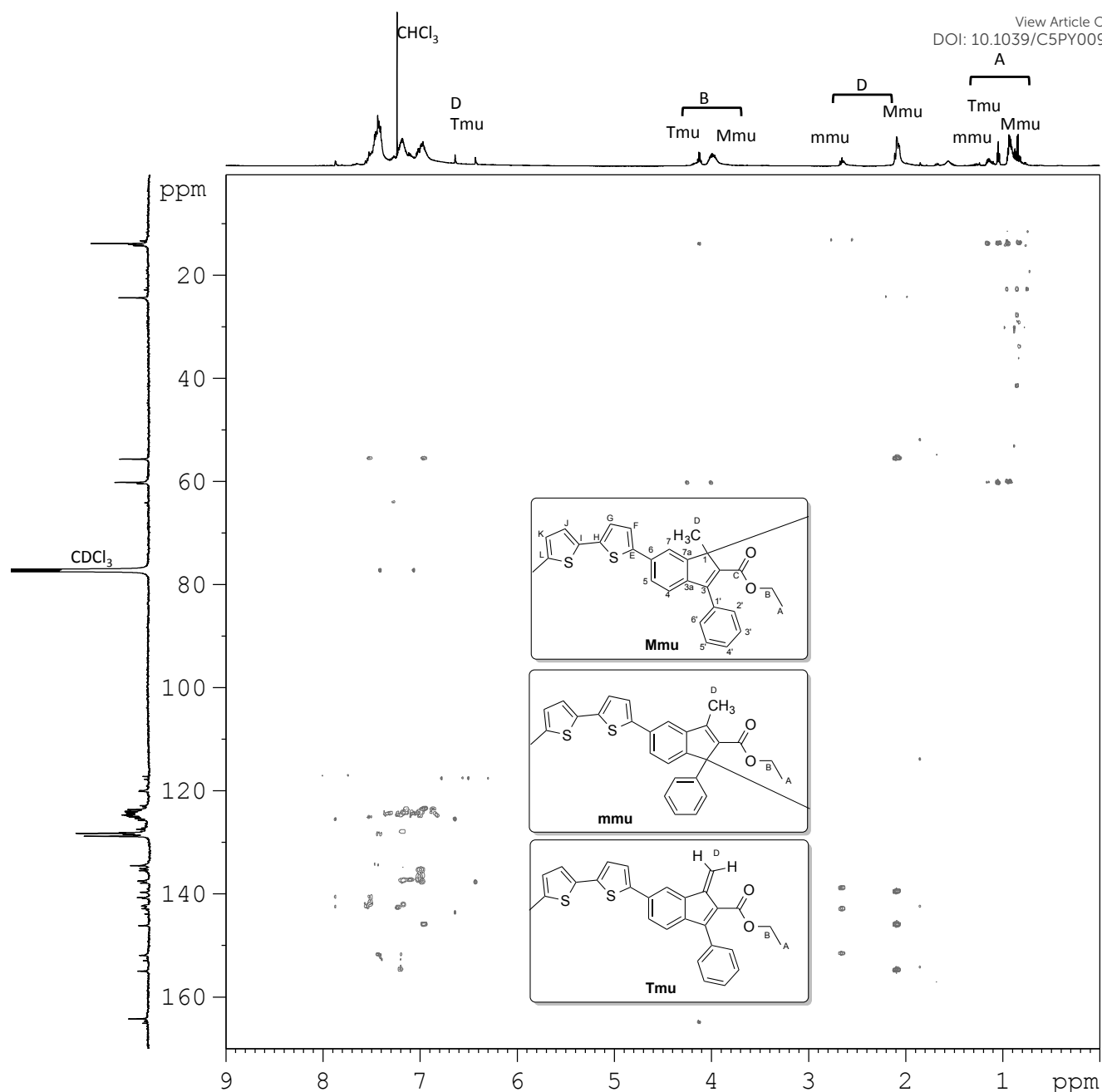
Figure 6. HMBC spectrum (CDCl₃) of sample **MA-2** obtained by the dehydration of indenol derivative **3a** by **Method A**. In the inset: the possible structures of the monomeric units assumed to compose poly-**5** obtained from the dehydration of indenol **3a** by **Method A** as determined by NMR spectroscopy. HMBC experiments were carried out with 2-fold low-pass J-filter, a delay of 100 ms for the evolution of long-range coupling, and delays corresponding to $^1J_{CH}$ = 130 and 160 Hz. 90° pulse – 8.05 ms, - 2.0 dB.

The comparison of ^{13}C NMR spectrum (Figure ESI-5 ESI) of sample **MA-2** with that of its precursor **3a** suggested that the structure of this intermediate was conserved in the Major monomeric unit (**Mmu**) with the most significant change being the loss of the indenol hydroxyl group as suggested by dramatic change in the chemical shift value of the C-1 carbon atom.

In the HMBC of sample **MA-2** (Figure 6), the signal at $\delta_H = 2.10$ ppm (directly related with the signal at 24.2 ppm in the ^{13}C dimension and assigned to methyl D of **Mmu** species) showed four cross peaks at $\delta_C = 55.5, 139.4, 145.9,$ and 154.8 ppm, respectively. This suggested that CH_3 D of **Mmu** was correlated through two bonds with C-1 ($\delta_C = 55.5$ ppm) and through three bonds with C-7a, ($\delta_C = 154.8$ ppm), C-2 ($\delta_C = 139.4$ ppm), and with a resonance at 145.9 ppm that is a quaternary carbon atom (roughly corresponding to thiophene C-E of **3a**, as chemical shift value), which correlates in the HMBC spectrum with thiophene methine group K. Therefore, the resonance at 145.9 was assigned to the carbon atom C-L of the thiophene ring, meaning that the indene group at C-1 position is directly bonded to a thiophene ring as in **Mmu** in Figure 6 and in poly-**5**. The structure elucidation of the minor species was complicated by the partial overlap and the low intensities of their signals, but the careful analysis of NMR data suggested the structures reported in Figure 6 for the Terminal monomeric unit (**Tmu**) and the minor monomeric unit (**mmu**).

Photophysical properties of polybenzofulvene derivatives bearing bithiophene chromophores.

The photophysical features of the new polybenzofulvene derivatives (Figure 7), summarized in Table 2 for both the solid state and the solution, gave information useful in evaluating their possible application as active materials in electronic devices.

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Table 2. Optoelectronic properties of the new polybenzofulvene derivatives bearing bithiophene chromophores.

polymer	Mobility (cm²/Vs)	solution			solid		
		λ_{ab} (nm)	λ_{em} (nm)	QY (%)	λ_{ab}^{a} (nm)	λ_{em}^{b} (nm)	QY[b] (%)
sample **MA-1**		380	575	5	387	640	< 0.1
						580[a]	
poly-6-BT-**BF3k**		380	490	7	386	555	< 0.1
poly-6-HBT-**BF3k**	5.81·E-05	386	493	3	394	558	< 0.1
poly-4'-BT-6-MO- **BF3k**		346	460	12	348	490	9
poly-4'-HBT-6- MO-**BF3k**	3.95·E-05	354	460	14	360	490	13

[a] spin coated films, [b] powders

The strong attitude of thiophene oligomers towards emission aggregation quenching processes (see ref 31) induced a sharp reduction of the PL efficiency in the solid state in the case of sample **MA-1** and for polymers with bithiophene moiety at position 6 (i. e. poly-6-BT-**BF3k** and poly-6-BT-**BF3k**). In particular, for sample **MA-1** the nearly vanishing emission in the solid state is accompanied by a red-shift of the emission typical of low emissive excimer states. The PL QY values observed in solution were comparable to those of the parent polymer poly-6-MO-**BF3k**.[19] Interestingly, the emission of the corresponding polymers bearing the chromophore in position 4' (poly-4'-BT-6-MO-**BF3k** and poly-4'-HBT-6-MO**BF3k**) was higher and quite independent on the aggregation state, as previously observed for other polybenzofulvene derivatives and in agreement with the assumption that emission originates from the recombination from similar excimer/aggregates states both in solution and in the solid state.

This result is suggestive of different aggregation behaviors in the solid state for polybenzofulvene derivatives showing different polymer enchainment and substitution topology of the monomeric units. Thus, the most efficient side chain packing in the solid state was obtained in poly-6-BT-**BF3k**

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and poly-6-HBT-**BF3k** bearing the bithiophene chromophore in position 6, whereas in the corresponding polymers bearing the chromophore in position 4' (poly-4'-BT-6-MO-**BF3k** and poly-4'-HBT-6-MO-**BF3k**), the packing was less strong. PL time decay of the polymers is biexponential, with a dominant fast component of about 150 ps (100 ps) and a slow one of about 1.5 ns (1 ns), in solution (in the solid state) suggestive of a complex excimer recombination pathway (see Table 3 and Figure 8)

Table 3. Lifetimes of two polybenzofulvene derivatives bearing bithiophene chromophores in dichloromethane solutions and cast films.

polymer	solution [a]				solid [b]			
	τ_1	τ_2	A_1	A_2	τ_1	τ_2	A_1	A_2
	(ps)	(ps)			(ps))	(ps)		
poly-6-HBT-**BF3k**	140	1550	0.72	0.28	90	1000	0.87	0.13
poly-4'-HBT-6- MO-**BF3k**	160	1550	0.62	0.38	110	950	0.83	0.17

[a] dichloromethane solutions; [b] cast films.

Hole mobilities were measured for the polymers with alkyl substituted bithiophene derivatives (see Table 2) and compared with that obtained for the standard hole-transporting polymer **PVK** measured in the same conditions. **PVK** is widely used in optoelectronic applications since its hole-transporting properties make this polymer an optimal matrix for emissive molecules to be used in OLEDs. Since different methods are used for the measure of the mobility of conducting polymers and the results are often quite different according to the method used, we measured the mobility of the two polybenzofulvenes and **PVK** by using a simple hole only device structure ITO/PEDOT/MoO$_3$/polymer/MoO$_3$/Al that give good ohmic contacts. Both the polybenzofulvene derivatives showed higher mobility with respect to **PVK** (4.84 x 10^{-6} cm^2/Vs) and the parent
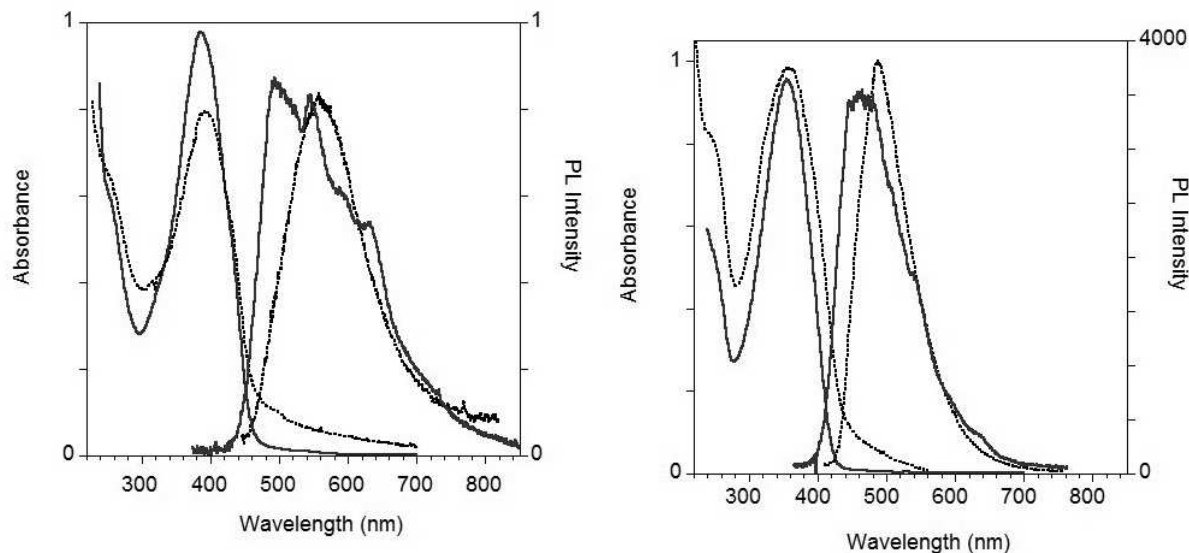
Figure 7. Optical absorption and emission spectra of poly-6-HBT-**BF3k** (left panel), and poly-4'-HBT-6-MO-**BF3k** (right panel) in dichloromethane solutions (blue lines) and in the solid state (black lines).
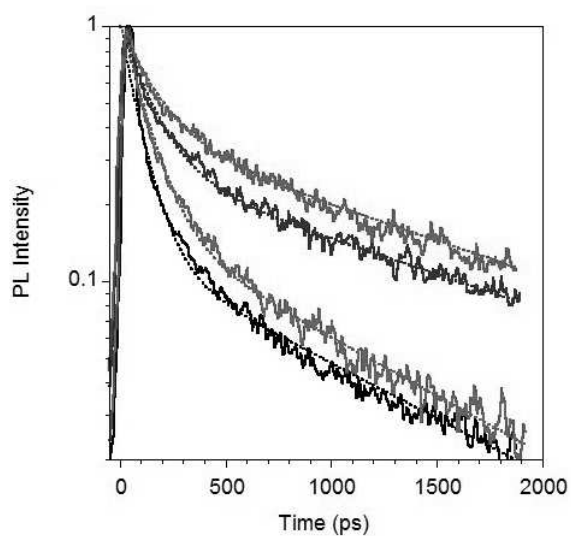

Figure 8. PL decays of poly-6-HBT-**BF3k** and poly-4'-HBT-6-MO-**BF3k** films (black and green lines) and dichloromethane solutions (blue and red lines).

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CONCLUSION

In order to evaluate the effects of different chromophores on the optoelectronic features of polybenzofulvene derivatives, four new monomers were designed to carry bithiophene chromophores in two different key positions of the phenylindene scaffold. These benzofulvene derivatives were demonstrated to retain the spontaneous polymerization propensity to produce polybenzofulvene derivatives showing hole-transporting performances higher than reference **PVK**. Moreover, the optoelectronic features of the polymers were affected by both the polymer enchainment and the substitution topology of the monomeric units, with the hole-mobility being affected to a lower extent, but with the best performances being obtained in poly-6-HBT-**BF3k** showing the strongest bithiophene side chain packing. The results of the present work suggest that the optoelectronic properties of polybenzofulvene derivatives can be optimized by an appropriate chemical design (i. e. side chain engineering). Furthermore, owing to the interesting results obtained in these exploratory approaches, the investigation of the chemical space around polybenzofulvene derivatives could afford new optoelectronic materials endowed with unprecedented features.

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Table of contents entry

Bithiophene-Based Polybenzofulvene Derivatives with High Stacking and Hole Mobility

A. Cappelli,[*] V. Razzano, M. Paolino, G. Grisci, G. Giuliani, A. Donati, R. Mendichi, F. Samperi, S. Battiato, A. C. Boccia, A. Mura, G. Bongiovanni, W. Mróz, C. Botta.

The insertion of bithiophene chromophores in two different key positions of the phenylindene scaffold produced stacked polybenzofulvene derivatives showing high hole mobility values.