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Highly Emissive Supramolecular Assemblies Based on π -Stacked Polybenzofulvene Hosts and a Benzothiadiazole Guest

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ABSTRACT

Two new benzofulvene derivatives bearing a fluorene chromophore in different positions of the phenylindene scaffold were synthesized and induced to polymerize spontaneously. The photophysical investigation evidenced the role of the substitution topology of the monomeric units on the optical properties of the corresponding polymers. In particular, the polymer emission efficiency was found to improve both in solution and in solid state when the fluorene residue enhances monomer conjugation and rigidity. The ability of this newly-synthesized class of polymers to self-organize in supramolecular structures is evidenced through a study on blends with a benzothiadiazole based dye at different concentrations. Aggregation quenching processes of the dye are sharply reduced and a complete resonant energy transfer from the polymer to the dye is reached even at 1% dye concentration. The peculiar ability of this new class of π -stacked polymers to self-assemble in such a supramolecular organization suggests their use as platforms for the design of more complex nanostructured films with enhanced optical and optoelectronic properties.

INTRODUCTION

π -Conjugated polymers have received particular attention by the scientific community because of their intriguing features, which can be exploited in the fabrication of optoelectronic devices such as organic light-emitting diodes (OLEDs), field effect transistors (FETs), and photovoltaic cells.¹⁻³ Among them, particularly appealing are soluble conjugated polymers designed with proper monomeric units, that, beside possessing highly film forming ability with low cost techniques, are able to self-organize in nanostructured films with enhanced optoelectronic properties.^{4,5}

Another promising class of polymers is represented by non-conjugated polymers able to self-organize in stacked arrays of π -conjugated small units. These polymers are through-space conjugated polymers formed by stacked arrays of π -electron systems along a single polymer chain.⁶ The most investigated π -stacked polymer is poly(N-vinylcarbazole) (**PVK**, Figure 1), which has been demonstrated to transport charge via intrachain stacked orbitals that result from face-to-face conformation of the carbazole moieties, and show photoconductive, photorefractive, hole-transporting, energy-donating, and carrier-switching properties.⁷

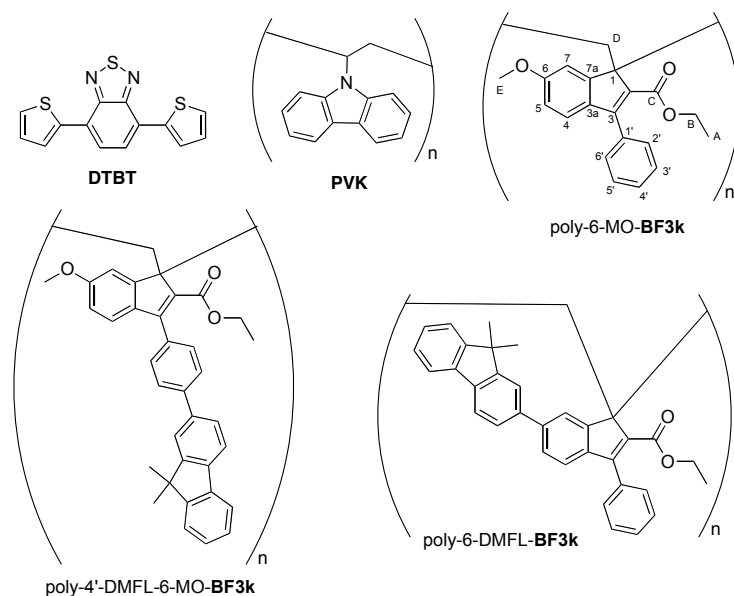


Figure 1. Structures of **DTBT**, **PVK**, **poly-6-MO-BF3k**, and **poly-4'-DMFL-6-MO-BF3k (P1)**, and **poly-6-DMFL-BF3k (P2)**.

Polybenzofulvene (poly-**BF**) derivatives constitute a new class of π -stacked polymers showing hole-mobility features related to the presence of methoxy substituents in the structure of poly-6-MO-**BF3k** (Figure 1) and combined with other distinctive features such as the rapid and almost quantitative formation by spontaneous thermoreversible polymerization, the high solubility in the most common organic solvents, the tunable solubility and aggregation behavior, etc.⁸⁻¹² We have shown that the absorption and emission features of this class of polymers do not vary significantly from the solid state to diluted solutions, both characterized by quite large Stokes shifts. This peculiar behavior can be accounted for the presence of monomeric chromophore stacking leading to excimer emission induced by interactions among the monomeric units of the polymeric chain.¹⁰ With the aim of designing highly emissive polymeric supramolecular assemblies for optoelectronic applications, we envisioned the insertion of a 9,9-dimethylfluorene residue in two different key positions of the 3-phenylindene structure of poly-6-MO-**BF3k**. The resulting π -stacked polymers should be potentially able to establish π -stacking interactions with small conjugated molecules and therefore to behave as hosts capable to accommodate guest molecules in their π -stacked architecture. Among the different emissive small molecules we considered a dye based on benzothiadiazole, namely 4,7-di(2-thienyl)-benzo[2,1,3]thiadiazole (**DTBT**). Benzothiadiazoles have been introduced in the monomers of different conjugated polymers, copolymers and block copolymers in order to modulate their energy gap, electrical conductivity, emissive properties and charge separation.¹³⁻¹⁵ The introduction of this unit in conjugated polymers through chemical bond, rather than by a simple blending, has been dictated by the need to avoid phase segregation between the polymer and the dye, that in most cases becomes detrimental for concentrations higher than 0.1%. In fact dye microaggregation introduces unwanted emission aggregation quenching in OLEDs and reduces donor-acceptor interface areas in photovoltaics, thus reducing the performances of optoelectronic devices.¹⁶ Transparent polymers, as PMMA or polycarbonate, are widely employed as hosts in many applications requiring emissive and homogeneous film, as luminescent solar concentrators.^{17,18} The possibility to obtain good dispersion of dyes at concentrations above

1% in a polymer matrix possessing good electrical properties and film forming ability, by simply blending polymer and dye from solution, would open new perspectives in the field of solution processable materials for smart applications.

The present paper describes the synthesis of two novel benzofulvene derivatives bearing a fluorene chromophore in two different positions of the phenylindene scaffold, their spontaneous polymerization in the two homopolymers poly-4'-DMFL-6-MO-**BF3k** (**P1**) and poly-6-DMFL-**BF3k** (**P2**), and the analysis of their ability to behave as polymeric hosts for the small molecule **DTBT**. By a photophysical study of blends of **DTBT** with the new homopolymers, compared with a standard non conjugated polymer (**PMMA**) or a standard π -stacked polymer (**PVK**), we demonstrate the ability of poly-6-DMFL-**BF3k** (**P2**) to envelope the organic chromophore in a supramolecular organization thus enhancing its emissive properties in films of concentrated blends.

EXPERIMENTAL SECTION

Synthesis. The details of the preparation of benzofulvene derivatives and their spontaneous polymerization are described in Electronic Supplementary Information (ESI). 4,7-di(2-thienyl)-benzo[2,1,3]thiadiazole (**DTBT**) was synthesised as reported elsewhere.¹⁹ NMR spectra were recorded with a Varian Mercury-300, a Bruker DRX-400 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 N₂ cooled charge-coupled device exciting with a monochromated 450W Xe lamp. The spectra are corrected for the instrument response. PL QY of solutions are obtained by using quinine sulfate as reference. PL QY of solid powders are measured with a home-made integrating sphere according to the procedure reported elsewhere.²⁰ PL excitation profiles are obtained by measuring the PL

intensity as a function of the exciting wavelength and correcting for the variation of the lamp intensity with a Rhodamine B solution standard.

SEC-MALS. The MWD characterization of polybenzofulvene derivatives poly-6-DMFL-**BF3k** and poly-4'-DMFL-6-**MO-BF3k** samples 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^{8,9} 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 a fluorene 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: 0.195 mL/g for poly-**BF3k**; 0.192 mL/g for poly-6-**MO-BF3k**; 0.228 mL/g for poly-6-DMFL-**BF3k**; 0.210 mL/g for poly-4'-DMFL-6-**MO-BF3k**.

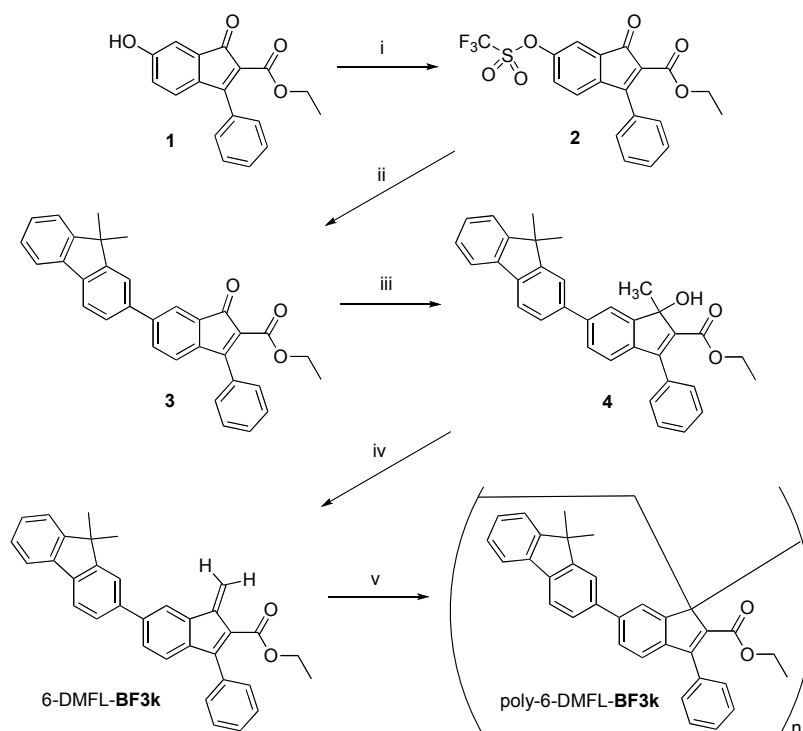
X-Ray Crystallography. Single crystals of compounds **2**, **3**, **7**, and **8** were submitted to X-ray data collection on an Oxford-Diffraction Xcalibur Sapphire 3 diffractometer with a graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. The structures were solved by direct methods implemented in SHELXS-97 program.²¹ 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.²² 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 1005464 (**2**), 1005465 (**3**), 1005462 (**7**), 1005463 (**8**). 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 Benzofulvene Derivatives 6-DMFL-BF3k** and 4'-DMFL-6-**MO-BF3k**.**

Benzofulvene derivative 6-DMFL-BF3k was synthesized from indenone **1** (ref 11) by following the multistep procedure described in Scheme 1.

Scheme 1. Synthesis and Spontaneous Polymerization of Benzofulvene Derivative 6-DMFL-BF3k.

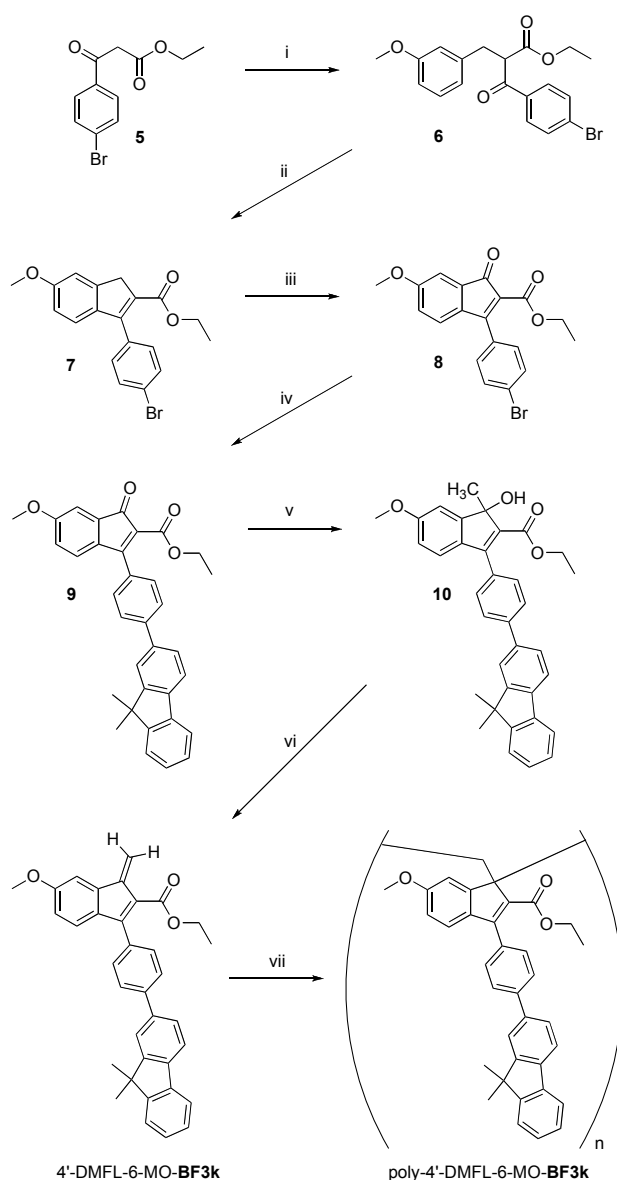


Reagents: (i) $\text{ Tf}_2\text{O}$, TEA, CH_2Cl_2 ; (ii) 9,9-dimethylfluorene-2-boronic acid pinacol ester, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, PPh_3 , Cs_2CO_3 , CH_3OH , THF; (iii) $\text{Al}(\text{CH}_3)_3$, CH_2Cl_2 ; (iv) PTSA, CHCl_3 ; (v) solvent evaporation.

The phenol hydroxyl group of indenone derivative **1**¹¹ was esterified with triflic anhydride to obtain trifluoromethanesulfonate ester **2**, which was readily used in the Suzuki-Miyaura cross-coupling with commercially available 9,9-dimethylfluorene-2-boronic acid pinacol ester (Aldrich). After a careful optimization work, the palladium catalyzed cross-coupling reaction afforded indenone derivative **3** in good yield (56%), and the structure of this important intermediate was confirmed by crystallography (see ESI). The usual methylation/dehydration procedure⁸⁻¹² was

applied to indenone derivative **3** to afford benzofulvene monomer 6-DMFL-**BF3k**. This benzofulvene derivative polymerized in the apparent absence of catalysts, upon solvent removal, to give the corresponding polymer. A similar procedure was used for the preparation of poly-4'-DMFL-6-MO-**BF3k** (Scheme 2).

Scheme 2. Synthesis and Spontaneous Polymerization of 4'-DMFL-6-MO-**BF3k**.



Reagents: (i) 3-methoxybenzyl chloride, NaHCO₃, NaI, DMF; (ii) PPA; (iii) SeO₂, 1,4-dioxane
 (iv) 9,9-dimethylfluorene-2-boronic acid pinacol ester, Pd(PPh₃)₂Cl₂, PPh₃, Cs₂CO₃, CH₃OH, THF;
 (v) Al(CH₃)₃, CH₂Cl₂; (vi) PTSA, CHCl₃; (vii) solvent evaporation.

The required bromophenylindenone **8** was prepared from ethyl 3-(4-bromophenyl)-3-oxopropanoate (**5** from Aldrich), which was alkylated with 3-methoxybenzyl chloride (Aldrich) to produce intermediate **6** prone to be cyclized in polyphosphoric acid (PPA) to afford indene derivative **7**. Oxidation of this latter compound with selenium dioxide in refluxing 1,4-dioxane gave indenone **8**, which was submitted to the same reaction sequence described for the synthesis of poly-6-DMFL-**BF3k** to obtain poly-4'-DMFL-6-MO-**BF3k**.

NMR Characterization of the Spontaneous Polymerization of Benzofulvene Derivatives 6-DMFL-**BF3k** and 4'-DMFL-6-MO-**BF3k**.

The spontaneous polymerization of 6-DMFL-**BF3k** was followed by ^1H NMR spectroscopy by comparing the spectrum of monomer 6-DMFL-**BF3k** with that of the corresponding polymer poly-6-DMFL-**BF3k** (Figure ESI-4 in the ESI). The sharp signals of monomer 6-DMFL-**BF3k** become very broad multiplets in the spectrum of the corresponding polymer. Thus, ^1H NMR spectrum of poly-6-DMFL-**BF3k** provided little information about the polymer structure. On the other hand, the ^{13}C NMR spectrum of poly-6-DMFL-**BF3k** shows a more significant signal pattern, which could be valuably compared with the corresponding spectrum of monomer 6-DMFL-**BF3k** (Figure ESI-5 in the ESI, the ^1H and ^{13}C NMR spectra of this monomer were assigned by means of homonuclear ^1H - ^1H -COSY, ^1H - ^1H -NOESY and heteronuclear ^1H - ^{13}C -HSQC, ^1H - ^{13}C -HMBC 2D correlation experiments).

Most importantly, the ^{13}C NMR spectrum of poly-6-DMFL-**BF3k** could be compared with the corresponding spectrum of parent macromolecule poly-**BF3k** (Figure 2).

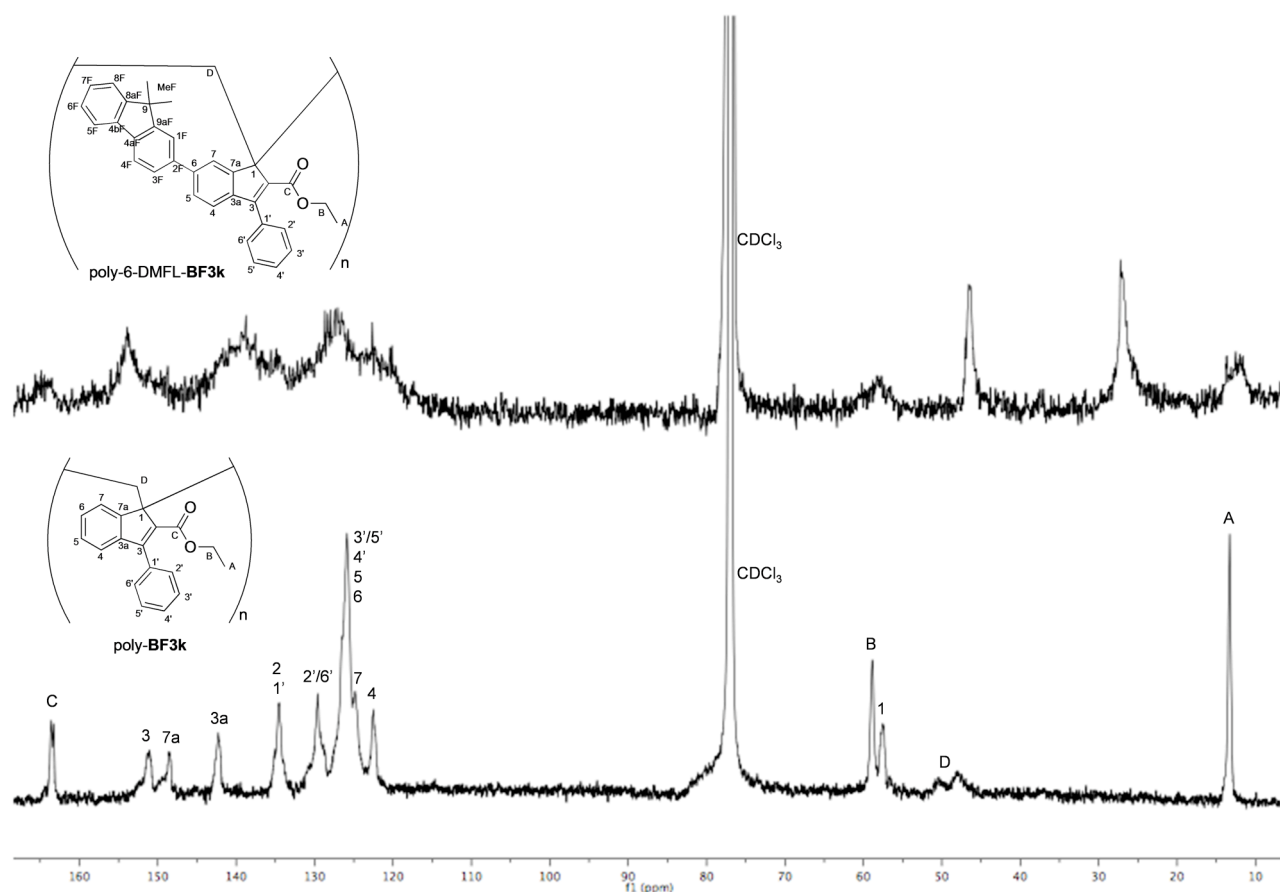


Figure 2. Comparison of the ^{13}C NMR spectrum of poly-6-DMFL-BF3k with that of the parent macromolecule poly-BF3k.

In fact, the comparison shown in Figure 2 suggests that the presence of the fluorene system in position 6 of the indene nucleus produces a significant broadening of the signals in the spectrum of poly-6-DMFL-BF3k. Probably, the high degree of π -stacking interactions among the aromatic moieties in this polymer is capable of decreasing the mobility of the monomeric unities in the backbone of poly-6-DMFL-BF3k, without any significant symptom of local mobility within the monomeric unit.²³

Also the spontaneous polymerization of benzofulvene monomer 4'-DMFL-6-MO-BF3k was followed by ^1H NMR spectroscopy (Figure ESI-8 in the ESI), which shows that the sharp signal of monomer 6-DMFL-BF3k progressively disappeared to leave the place to broad multiplets of the corresponding polymer.

Relevant structural information was obtained from the ^{13}C NMR spectrum of poly-4'-DMFL-6-MO-BF3k (Figure 3).

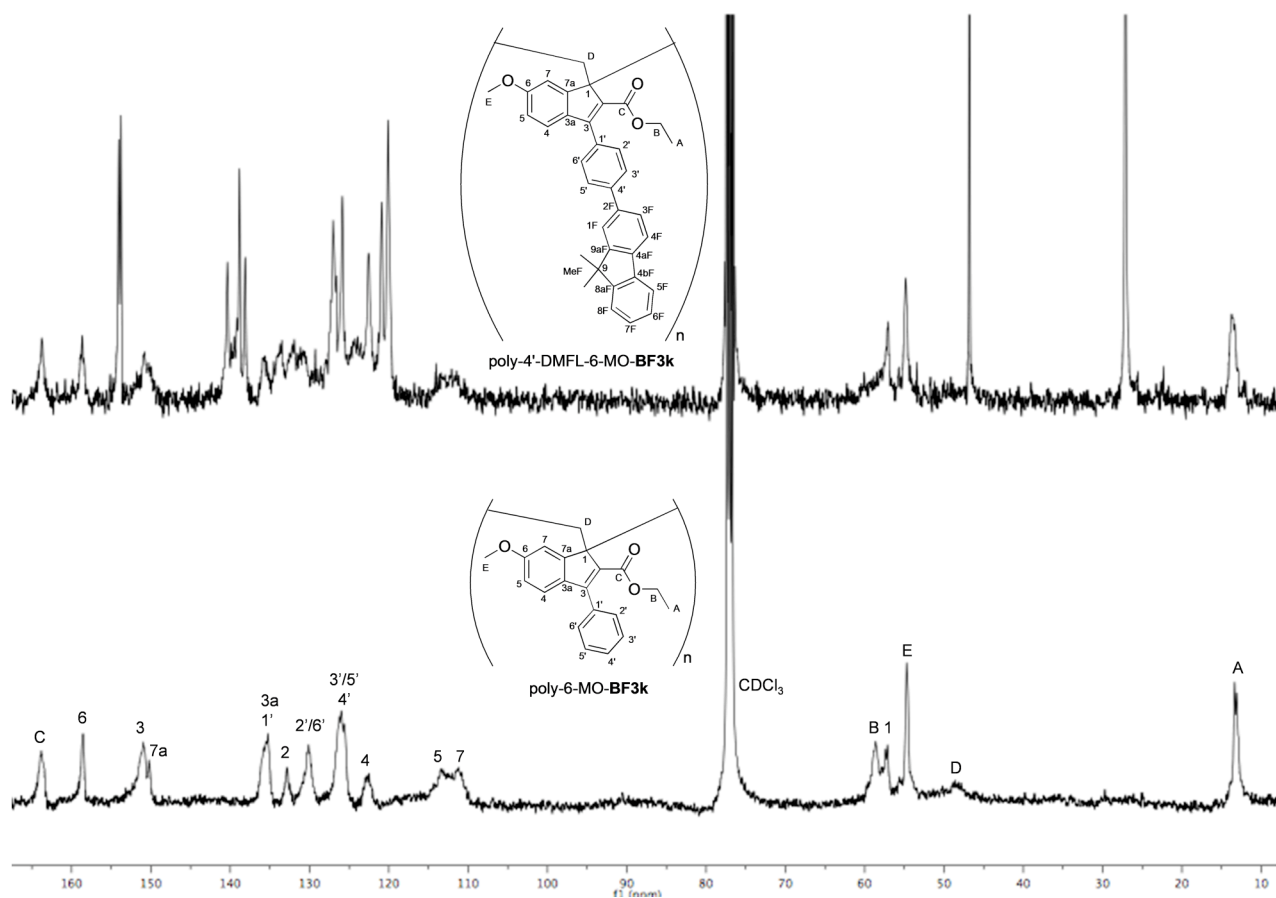


Figure 3. Comparison of the ^{13}C NMR spectrum of poly-4'-DMFL-6-MO-BF3k with that of the parent macromolecule poly-6-MO-BF3k.

Interestingly, the ^{13}C NMR spectrum of poly-4'-DMFL-6-MO-BF3k shows two signal patterns differing in their apparent broadness. The comparison shown in Figure 3 demonstrates that the sharpest signals can be assigned to the carbon atoms belonging to the fluorene moiety, whereas the broadness of the phenylindene signals is comparable to that of the parent macromolecule poly-6-MO-BF3k. This result suggests that the introduction of the fluorene system in *para*-position of the pendent phenyl group does not alter the dynamics of the monomeric unities in the backbone of poly-4'-DMFL-6-MO-BF3k with respect to the parent macromolecule poly-6-MO-BF3k. Furthermore, a local mobility can be assumed for the fluorene moieties that can be interpreted in

terms of a lower degree of π -stacking interactions in poly-4'-DMFL-6-MO-**BF3k** with respect to poly-6-DMFL-**BF3k**.

In conclusion, poly-6-DMFL-**BF3k** shows a high degree of π -stacking interactions among the aromatic moieties able to decrease the mobility of the monomeric unities, while the fluorene systems of poly-4'-DMFL-6-MO-**BF3k** appears to freely rotate around their attachment bond at the pendent phenyl group because of the lack of stacking constraints.

Molecular Characterization.

The molecular weight distribution (MWD) and the conformation plot of polybenzofulvene derivatives poly-6-DMFL-**BF3k** and poly-4'-DMFL-6-MO-**BF3k** samples was determined by means of a multi-angle laser light scattering (MALS) detector on-line to a size exclusion chromatography (SEC) system with tetrahydrofuran (THF) as mobile phase. The results are reported in Table 1 along with those previously reported for parent macromolecules poly-6-MO-**BF3k** and poly-**BF3k** that are included for the sake of comparison. Both the newly-synthesized polybenzofulvene derivatives showed ultrahigh molecular mass values and quite broad dispersity similar to those shown by parent polybenzofulvenes. This result suggests that the presence of bulky fluorene chromophores is compatible with the spontaneous polymerization mechanism leading to ultrahigh molecular mass polybenzofulvene derivatives.

Table 1. Macromolecular Features of the Newly-Synthesized Poly-6-DMFL-**BF3k** and poly-4'-DMFL-6-MO-**BF3k** Compared with Those Shown by Previously Reported Poly-6-MO-**BF3k** and Poly-**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-DMFL- BF3k	1,967	1,471	3.0	43.1	1.18·E-02	0.55
poly-4'-DMFL-6-MO- BF3k	2,365	1,635	2.1	42.2	9.84·E-03	0.57
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.

Photophysical Properties of poly-6-DMFL-**BF3k** and poly-4'-DMFL-6-MO-**BF3k**.

The photophysical properties of the newly-synthesized polymers in solution and in the solid state were studied in order to evaluate their potential use as active materials in electronic devices. The absorption spectra of the polymers in dichloromethane are reported in Figure 4a. The peak at 315-320 nm, related to the absorption of poly-6-MO-**BF3k** monomeric unit,¹⁰ is the main absorption component of poly-4'-DMFL-6-MO-**BF3k** (**P1**), showing that the addition of a fluorene residue to the pendent phenyl ring does not affect polymer absorption giving rise only to a weak shoulder at 290 nm. In poly-6-DMFL-**BF3k** (**P2**) the 290 nm shoulder becomes more evident and an additional red-shifted band at 360 nm grows up, suggesting an extended conjugation of the phenylindene group upon fluorene introduction at the position 6 of the indene nucleus. This observation is consistent with the NMR analysis of these polymers in solution highlighting a lower mobility of the

monomeric unities in the backbone of **P2**, with respect to **P1** and the parent polymers poly-6-MO-BF3k and poly-BF3k.

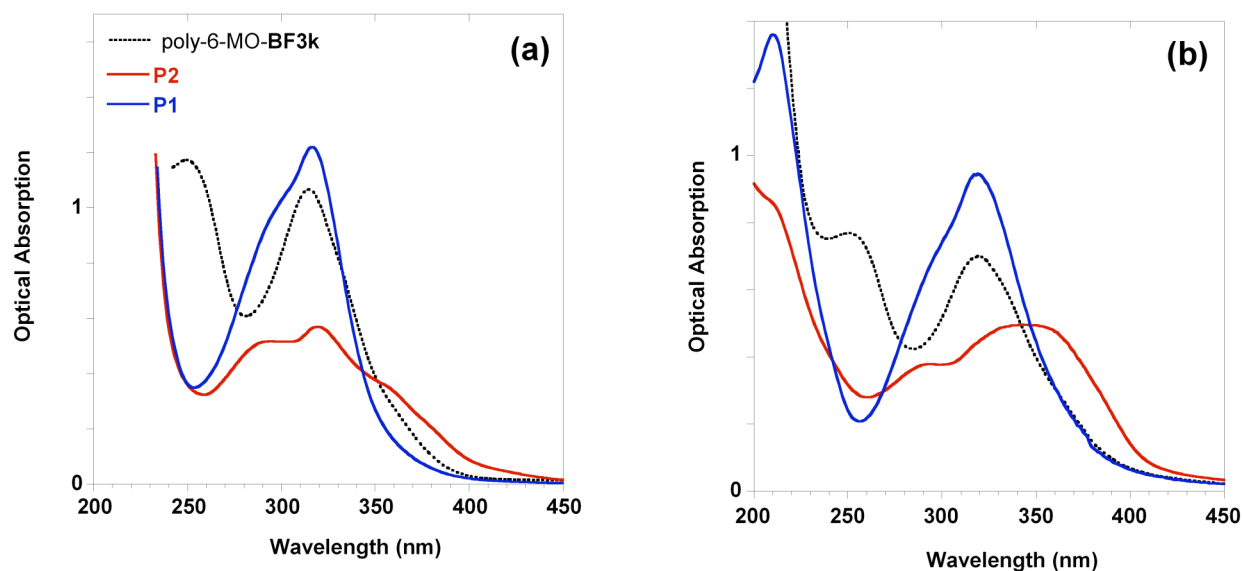


Figure 4. Optical absorption spectra of **P1**, **P2**, and poly-6-MO-BF3k in dichloromethane solution (a) and in the solid state (spin coated films) (b).

The analysis of the absorption spectra in the solid state (Figure 4b) also evidences a large difference in the behaviour of the two newly-synthesized polybenzofulvene derivatives. The absorption spectrum of the **P1**, similarly to the parent polymer poly-6-MO-BF3k, does not show any variation from solid state to solution. This behavior, already observed in this class of polymers,¹⁰ indicates that the π -stacking of the benzofulvene units in solution is not modified by inter-chain interactions in the solid state. Differently, the absorption spectrum of the **P2** in the solid state shows a strong enhancement of the 360 nm shoulder of the solution, leading to a main broad absorption at about 345 nm. Since this band is associated to the increased conjugation of the phenylindene group, induced by the fluorene unit, its enhancement in the solid state envisages a tighter π -stacking of these bulky monomers. Therefore the reduced conformational mobility of **P2** π -stacked monomers in solution favors supramolecular organizations with higher π -stacking in the solid state.

The PL emission is at about 460-480 nm for both the newly-synthesized polybenzofulvene derivatives, similarly to poly-6-MO-**BF3k**, with a slight red-shifted emission for the solid state with respect to the solution (see Table 2). Interestingly, as observed in other polybenzofulvene derivatives, the PL QY does not change in the solid state with respect to the solutions, in agreement with the hypothesis that emission originates from the recombination from similar excimer/aggregates states both in solution and in the solid state. The **P1** PL QY is similar to that of the polymers without the fluorene unit (about 6%),¹⁰ while the PL QY of **P2** is much higher. The fluorene contribution in the polymer PL properties appears therefore to be relevant only when the fluorene residue contributes to the conjugation of the phenylindene monomeric unit.

Table 2. Optical properties of the newly-synthesized polybenzofulvene derivatives in dichloromethane diluted solution and in the solid state.

polymer	solution			film		
	λ_{ab} (nm)	λ_{em} (nm)	QY (%)	λ_{ab}^a (nm)	λ_{em}^b (nm)	QY ^b (%)
P2	295, 319, 345	465	21	295, 345	484	24
P1	295, 316	455	6	295, 318	480	9

^a spin coated films, ^b cast films from dichloromethane solution.

We assume that in these polybenzofulvene derivatives, the macromolecular conformation leading to the formation of emissive arrays of π -stacked monomeric units even in diluted solutions is probably characterized by a helical organization^{24,25} of single polymeric chains that can be exploited as a platform for more complex supramolecular organizations. To test this hypothesis, we mixed the newly-synthesized polybenzofulvene derivatives with the highly emitting dye **DTBT**. The emissive properties of this dye strongly depends on its aggregation state, being red-shifted (from 570 to 610

nm) and quenched upon aggregation in the solid state, with respect to its molecular dispersions in the appropriate solvents or in nanostructured hosts capable of suppressing intermolecular interactions (i. e. PL QY drops from 100% in solution to 12% in the aggregated state).²⁶

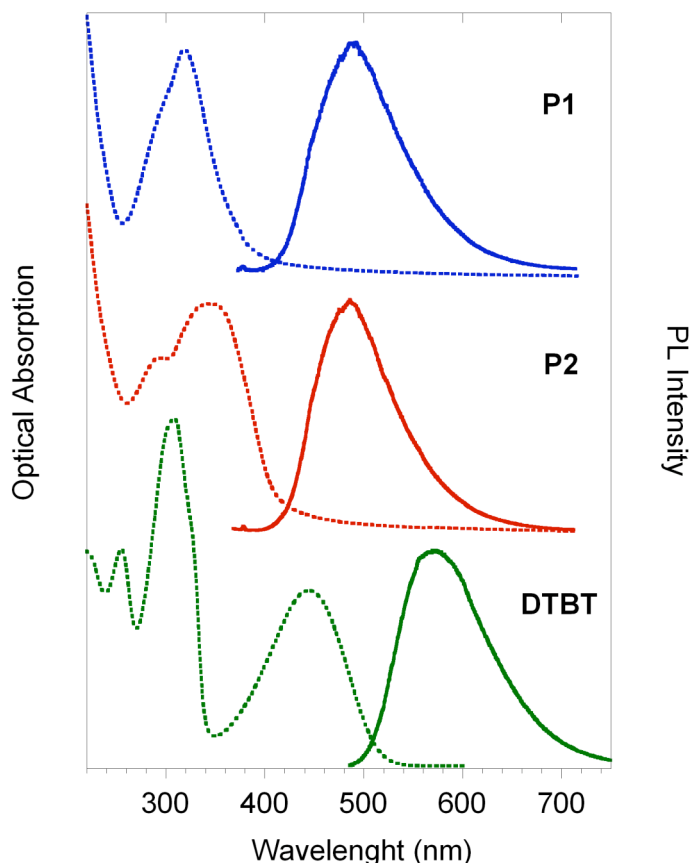


Figure 5. Optical absorption (dotted lines) and PL spectra (solid lines) of **P1** and **P2** films and **DTBT** in THF solution.

In Figure 5 the optical properties of the films obtained with the newly-synthesized polybenzofulvene derivatives are reported together with those of **DTBT** dye in THF solution. Due to the overlap of the polymer emission spectra with the 445 nm absorption band of the dye, Resonant Energy Transfer (RET) is expected from the polymers to the dye if their distance is of the order (or below) the Foerster radius²⁷ in blends. In order to study the ability of the polymers to embed the dye and therefore their potentiality as hosts for organic dyes in optoelectronic

applications, we compared the efficiency of resonant energy transfer from the polymers to **DTBT** dye at low (1% w/w) dye concentration with that of a standard **PVK** sample (see Figure 6). The films are excited at the maximum of the polymer absorptions, where dye direct excitation is negligible both due to its low concentration and to its optical absorption properties. As it can be seen, the polymer emission is completely suppressed in the **P2** blend and only a weak emission, at 460-480 nm, is observed from **P1**. This is a consequence of complete (or nearly complete) RET from **P2** (**P1**) to the dye. Differently, for the **PVK** blend, only a weak emission is observed for the dye, being most of the PL from the excited polymer. PL excitation (PLE) spectra of the polybenzofulvene blends show a close correspondence with the PLE and absorption spectra of the polymers, in agreement with the presence of an efficient RET from the polymer to the dye (see Figure ESI-1 in the ESI). This huge difference in the ability to transfer energy from the polybenzofulvene derivatives to the dye, with respect to the standard **PVK** polymer, is not ascribable to their different spectroscopic properties [Foerster radius for the **PVK** blend is 24 Å, comparable with that of **P1** and **P2** of 24 Å and 28 Å, respectively, as obtained from the spectroscopic data, see Table ESI-1 in the ESI], but has to be related to a different ability of the polymers to envelop the emitting dye by entrapping it among the helical structure of the polymer chain, through the π -stacked monomeric unities. In fact, when dye microaggregation is present in a blend, RET from the polymer matrix to the dye is less efficient as it only can occur near the polymer-aggregate interfaces. We believe that the different ability of the new polymers to embed the **DTBT** dye, with respect to the standard **PVK** polymer, might be related to the larger dimension of their monomeric units and/or to their higher affinity with the **DTBT** dye, that enhance the tendency to form π -stacking with the guest chromophore.

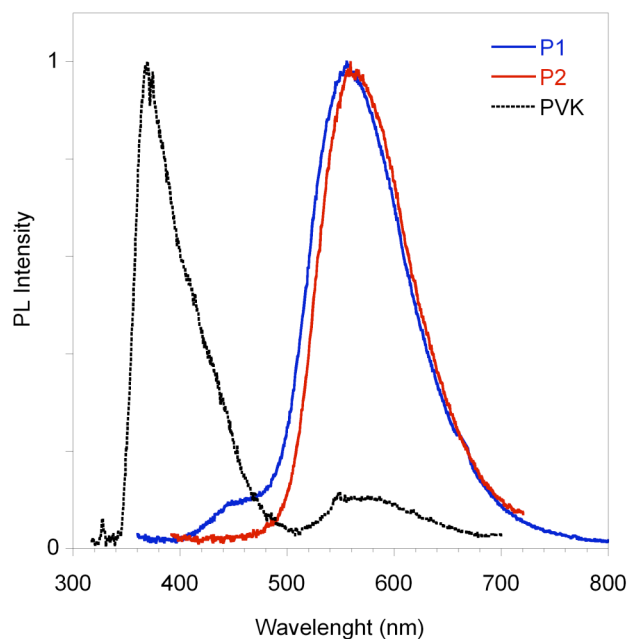


Figure 6. PL spectra of blends of **P2**, **P1**, and **PVK** with **DTBT** at 1% (w/w) concentration. Excitation at the absorption maxima of the polymers (365, 330, and 340 nm for **P2**, **P1**, and **PVK**, respectively).

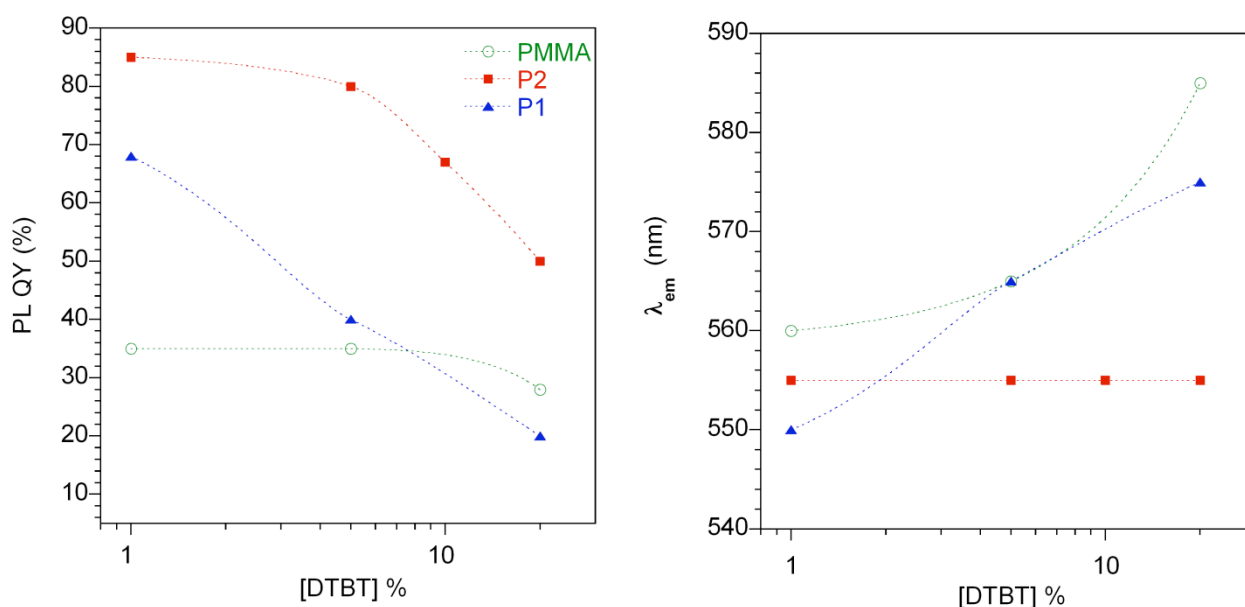


Figure 7. PL QYs (left) and PL peak position (right) of blends of **P2**, **P1**, and **PMMA** as a function of **DTBT** % (w/w) concentration for films cast from solution. The lines are guide for the eye.

The ability of the polymers to efficiently separate the **DTBT** molecules avoiding their unwanted aggregation was tested by studying the optical properties of blends with dye concentrations up to 20% (w/w) and by comparing them with those of blends in the standard polymer polymethylmetacrylate (PMMA). Figure 7 reports the PL QY and peak position as a function of **DTBT** molar concentration for the different polymers. The PLQY of the **P2** blend at 1% (w/w) of dye concentration is very high (comparable to that of **DTBT** in host-guest systems) and slowly decreases by increasing the dye concentration, suggesting only a minor aggregation of the dye at concentration as high as 10% (w/w). Differently, **P1** shows a sharp decrease of the PL QY at 5% (w/w) of dye concentration while the standard PMMA polymer displays a quite low QY value even at 1% (w/w) concentration. Accordingly, **DTBT** aggregation in the **P1** and PMMA blends is envisaged by the red-shift of the PL emission observed upon increasing dye concentration, while for the **P2** blend no shift is observed in the same range of **DTBT** concentration.

This analysis shows that **P2** is more efficient than **P1** in terms of dye incorporation, suggesting that conformational mobility of the chain plays an important role in the host-guest interactions leading to solid-state supramolecular organization with efficient dye incorporation.

CONCLUSIONS

In conclusion, we have synthesized a new class of π -stacked poly-BF by inserting a 9,9-dimethylfluorene residue in two different key positions of the 3-phenylindene structure of poly-6-MO-**BF3k**. The introduction of the fluorene chromophore in the benzofulvene monomer in position 6 of the indene nucleus increases its conjugation and rigidity thus improving the polymer emission both in solution and in the solid state. We show that the ability of the newly-synthesized polybenzofulvene derivatives to embed a benzothiadiazole based dye allows to obtain highly emissive polymer blends at dye concentrations up to 10%, reducing unwanted dye microaggregation typical of standard polymeric blends. The impressive efficiencies of emission (up

to 85%) and complete resonant energy transfer observed for the poly-6-DMFL-**BF3k** (**P2**) blends are consistent with a self-organized complex supramolecular organization where π -stacking of the monomeric units with **DTBT** suppresses the dye microaggregation. The peculiar ability of this new class of π -stacked polymers to self-assemble in such a supramolecular organization suggests their use as platforms for the design of more complex nanostructured films with enhanced optical and optoelectronic properties.

Electronic supplementary information (ESI) available: Experimental details for the synthesis and the characterization of poly-6-DMFL-**BF3k** (**P2**), poly-4'-DMFL-6-**MO-BF3k** (**P1**) and their intermediates.

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Table of contents entry

Highly Emissive Supramolecular Assemblies Based on π -Stacked Polybenzofulvene Hosts and a Benzothiadiazole Guest

A. Cappelli, F. Villaflorita-Monteleone, G. Grisci, M. Paolino, V. Razzano, G. Fabio, G. Giuliani, A. Donati, R. Mendichi, A. C. Boccia, M. Pasini, C. Botta.**

Two new polymers envelop a benzothiadiazole dye by π -stacking interactions and a complete resonant energy transfer from the polymer to the dye is obtained

