



Spontaneous polymerization of benzofulvene monomers bearing a 4-Pyridylacetylene substituent in different positions of the benzofulvene scaffold

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ARTICLE INFO

Keywords:

Spontaneous polymerization
Topochemical polymerization
 π -stacked polymers
Hole mobility

ABSTRACT

Two benzofulvene derivatives bearing a 4-pyridylacetylene substituent in different positions (i. e. 2 and 6) of the benzofulvene scaffold are designed and synthesized to evaluate the effects on the spontaneous solid-state polymerization of the presence of the same substituent in two different key positions of the 3-phenylbenzofulvene moiety. Both the benzofulvene derivatives showed the tendency to polymerize spontaneously in the consequence of solvent removal under reduced pressure without the addition of catalysts or initiators. The macromolecular structure of the stemming polymeric materials was investigated by NMR spectroscopy and MALDI-TOF mass spectrometry. Both NMR and MALDI-TOF studies confirmed the polymeric nature of the materials and suggested for the polybenzofulvene derivative bearing the 4-pyridylacetylene substituent in positions 6 a higher structural homogeneity with respect to the one bearing the same substituent in position 2. The photophysical characterization of the most homogeneous polybenzofulvene derivative led to the discovery of its outstanding hole mobility value, which was found to be around one order of magnitude higher than that previously measured for two oligothiophene-based polybenzofulvene derivatives and almost two orders of magnitude higher than that of poly(vinylcarbazole), commonly used as hole-transporter matrix. This result places the new polybenzofulvene derivative in an outstanding position as a promising material for field-effect transistor (FET) device applications.

1. Introduction

The synthesis of large-size polymer single crystals has recently received a great deal of attention [1–7]. Topochemical polymerization techniques are grounded on monomers capable of organizing themselves into ordered structures (in solid-state and/or in solution) by the establishment of weak intermolecular non-covalent interactions such as π - π stacking, CH- π , hydrophobic, and hydrogen bonding interactions [8–12].

In our laboratories, the concept of topochemical polymerization has been translated into the so-called “affinity polymerization” in which 3-phenylbenzofulvene derivatives (i. e. BF3 compounds in Fig. 1) represented interesting examples of monomers capable of polymerizing spontaneously in the solid-state and in highly concentrated solutions

without the addition of any catalysts and/or initiators [13–16].

The results of extensive structure–property studies advocated the key role of π - π -stacking interactions among the monomers as driving force in the initial process of affinity recognition, which was assumed to prelude the spontaneous polymerization leading to polybenzofulvene derivatives [15,17–20]. These polymers were endowed with interesting optoelectronic properties [17,21–29], along with some other intriguing features such as the very fast and almost quantitative formation [13,16,19,30,31], the thermoreversibility of the polymerization process [13,15,19,32–34], and the tunable solubility in both organic and aqueous solvents [33–41]. Similarly to poly(vinylcarbazole) (PVK), polybenzofulvene derivatives are π -stacked polymers formed by stacked arrays of π -electron systems conjugated through-space along a single polymer chain [15–17,21,22,25,33].

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<https://doi.org/10.1016/j.eurpolymj.2023.111957>

Received 9 December 2022; Received in revised form 17 February 2023; Accepted 23 February 2023

Available online 27 February 2023

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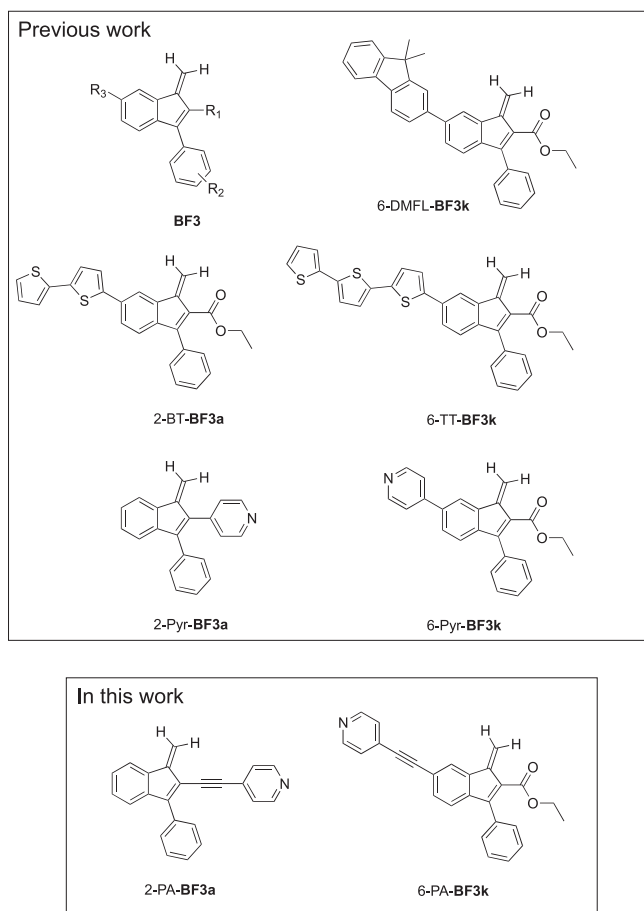


Fig. 1. Structures of some benzofulvene derivatives bearing different substituents in key positions of their 3-phenylindene nucleus.

Our studies demonstrated that the presence of relatively bulky substituents such as 4-pyridyl group (but also dimethylaminocarbonyl and *t*-butyl) depress the spontaneous polymerization process of benzofulvene derivatives when these groups are positioned in the close proximity (i. e. in position 2) of the polymerization center as in the case of 2-Pyr-BF3a derivative [15,42,43]. On the contrary, the polymerization mechanism appeared to be operative when bulky substituents were located far from the polymerization center as in the case of 6-Pyr-BF3k or 6-DMFL-BF3k monomers [21,44]. Intriguingly, *poly*-6-DMFL-BF3k was employed in the production of highly emissive polymeric supramolecular assemblies potentially useful in optoelectronic applications

[21,23,26,27].

In the present work, a 4-pyridylacetylene substituent was introduced in position 2 of the 3-phenylbenzofulvene scaffold as in compound 2-PA-BF3a (Fig. 1) in order to shift the steric bulk a step from the polymerization centre with respect to 2-Pyr-BF3a derivative. Moreover, the same 4-pyridylacetylene substituent was introduced in position 6 of the 3-phenylbenzofulvene scaffold as in compound 6-PA-BF3k. These studies were finalized to evaluate the effects of the presence of relatively bulky substituents in some key positions (i. e. 2 and 6) of the 3-phenylbenzofulvene moiety on both the spontaneous polymerization mechanism and the polymer features. Finally, the hole mobility of the *poly*-6-PA-BF3k was evaluated revealing promising results.

2. Experimental section

Synthesis. All chemicals used were of reagent grade. Yields refer to purified products and are not optimized. Melting points were determined in open capillaries on a Gallenkamp apparatus and are uncorrected. Merck silica gel 60 (230–400 mesh) was used for column chromatography. Merck TLC plates, silica gel 60 F₂₅₄ were used for TLC. NMR spectra were recorded with a Bruker DRX-400 AVANCE or a Bruker DRX-500 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.

2.1. 3-Phenyl-2-(pyridin-4-ylethynyl)-1H-inden-1-one (2)

A degassed mixture of bromoindenone derivative **1** [45] (200 mg, 0.70 mmol) in 15 mL of dry THF-TEA (2:1) containing the commercially available 4-ethynylpyridine hydrochloride (Aldrich, purity 97 %, 127 mg, 0.91 mmol) and CuI (Aldrich, purity 98 %, 6.0 mg, 0.032 mmol) was stirred at room temperature for 10 min. Subsequently, Pd(PPh₃)₂Cl₂ (Aldrich, purity 98 %, 21 mg, 0.030 mmol) was added and the resulting mixture was refluxed for 3 h. The reaction mixture was concentrated under reduced pressure, the residue was dissolved into ethyl acetate-dichloromethane (2:1) and washed with a saturated solution of NaHCO₃. The organic layer was dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography with petroleum ether-ethyl acetate-dichloromethane (7:2:1) as the eluent gave indenone derivative **2** as a red solid (163 mg, yield 76 %, mp 161–162 °C). ¹H NMR (400 MHz, CDCl₃): 7.31 (d, *J* = 5.8, 2H), 7.33–7.48 (m, 3H), 7.53–7.63 (m, 4H), 7.85 (dd, *J* = 7.5, 1.9, 2H), 8.57 (s, 2H). MS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₂H₁₄NO 308.1; Found 308.0.

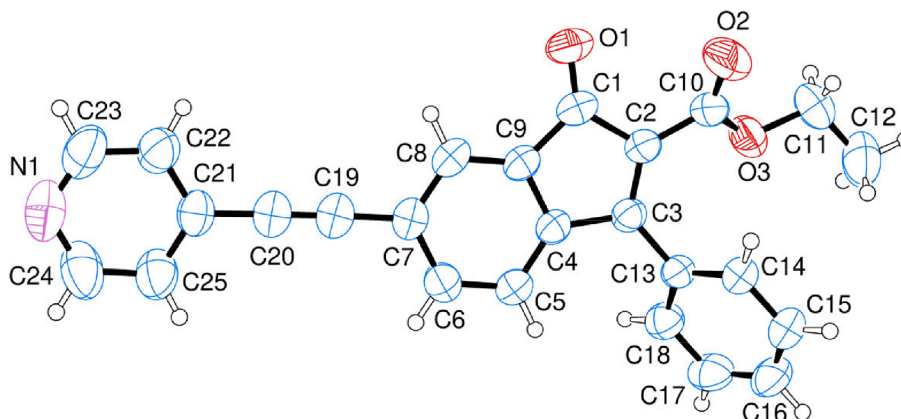


Fig. 2. Structure of indenone intermediate **5** as determined by crystallography. Ellipsoids enclose 50% probability.

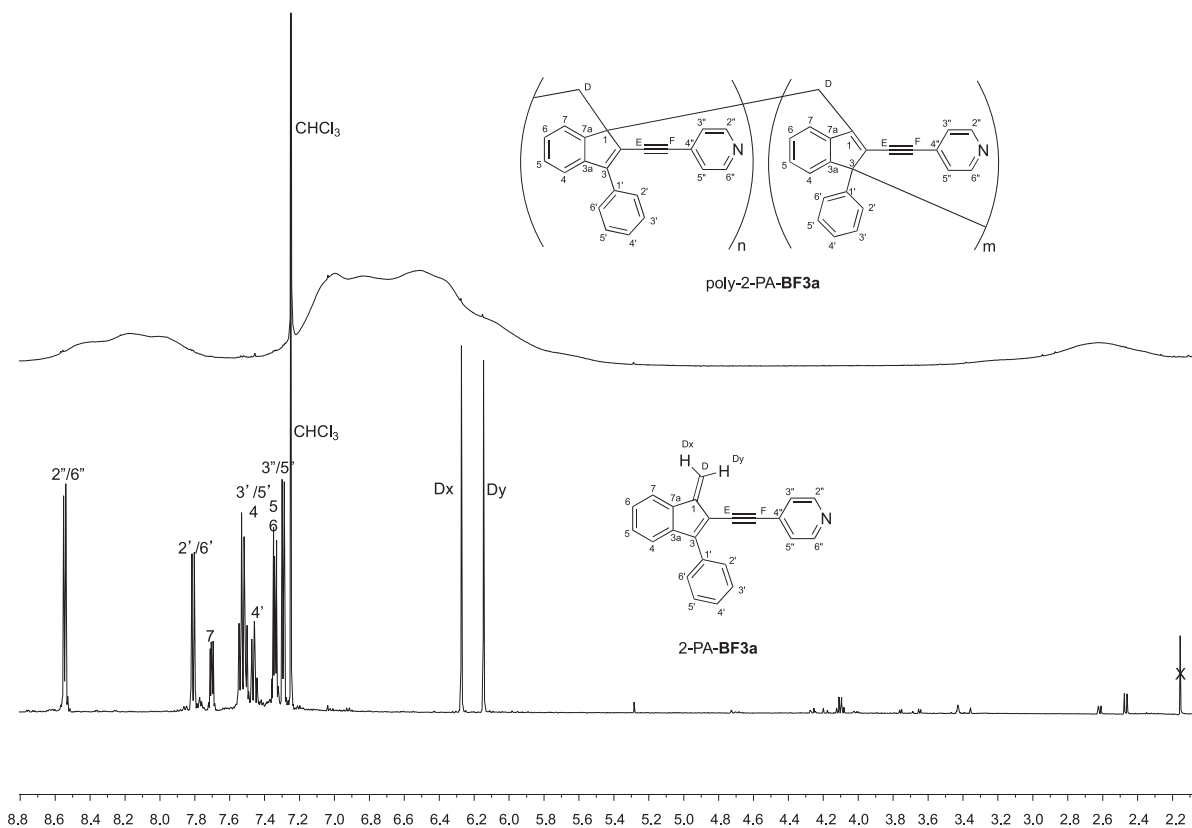


Fig. 3. Comparison of ^1H NMR spectrum (CDCl_3 , 500 MHz) of *poly-2-PA-BF3a* with that of corresponding benzofulvene derivative *2-PA-BF3a* (CDCl_3 , 500 MHz).

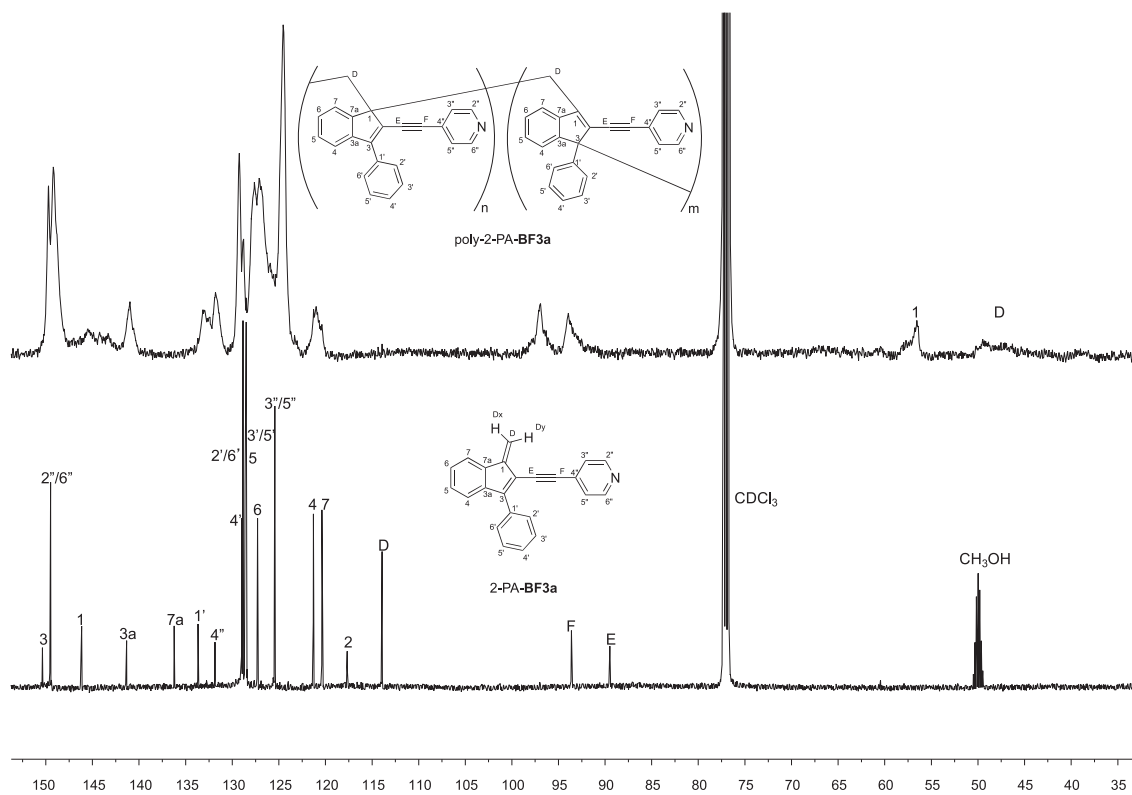


Fig. 4. Comparison of ^{13}C NMR spectrum (CDCl_3 , 125 MHz) of *poly-2-PA-BF3a* with that of corresponding benzofulvene derivative *2-PA-BF3a* (CDCl_3 , 125 MHz).

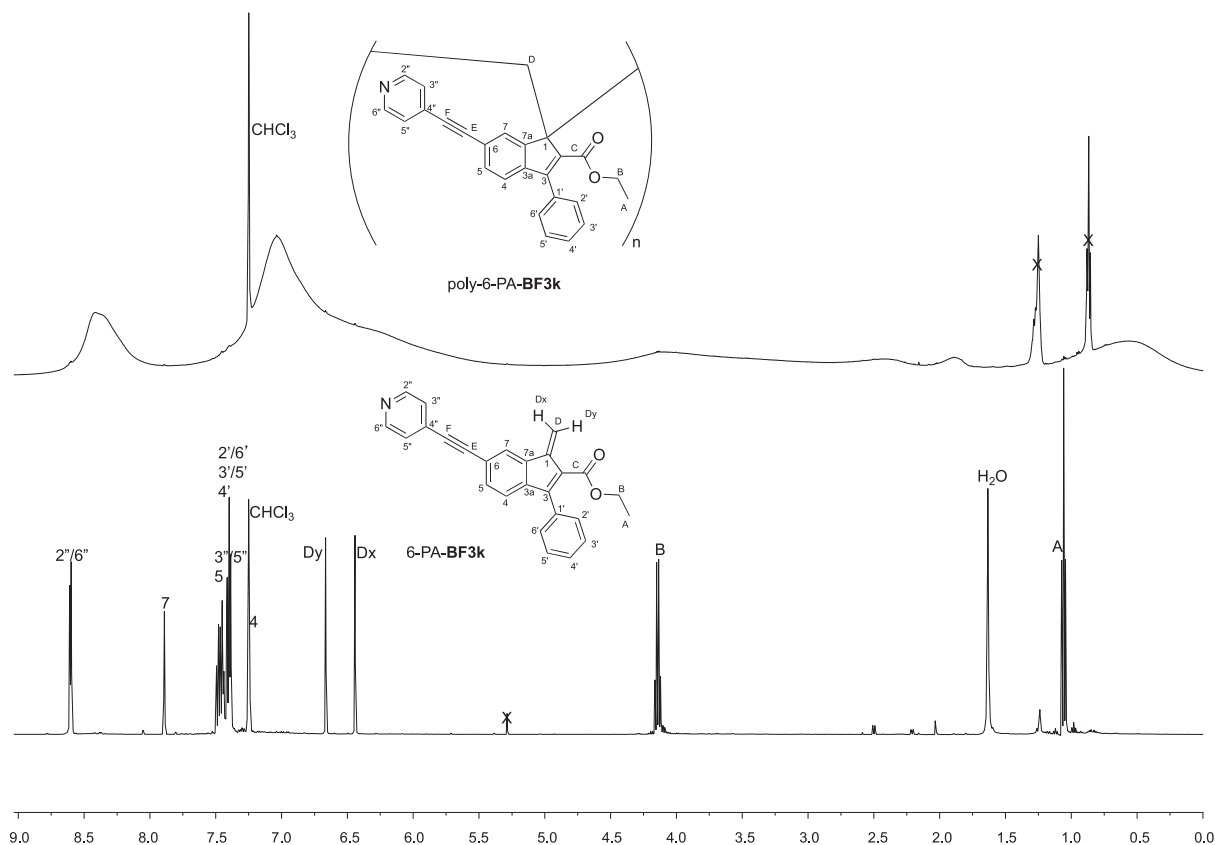


Fig. 5. Comparison of ^1H NMR spectrum (CDCl_3 , 500 MHz) of *poly-6-PA-BF3k* with that of corresponding benzofulvene derivative *6-PA-BF3k* (CDCl_3 , 500 MHz).

2.2. 1-Methyl-3-phenyl-2-(pyridin-4-ylethynyl)-1H-inden-1-ol (3)

To a solution of compound **2** (100 mg, 0.325 mmol) in dichloromethane (10 mL), a 2 M solution of $\text{Al}(\text{CH}_3)_3$ (Aldrich, purity 1.90–2.20 M, 0.66 mL, 1.32 mmol) in toluene was added, and the reaction mixture was stirred at room temperature for 30 min. Subsequently, the $\text{Al}(\text{CH}_3)_3$ excess was decomposed with a 1 N solution of NaOH and the solid was filtered off. The organic phase was dried over sodium sulfate and concentrated under reduced pressure. The resulting residue was purified by flash chromatography with petroleum ether-ethyl acetate (6:4) as the eluent to obtain indenol derivative **3** as a pale-yellow solid (102 mg, yield 97 %). ^1H NMR (400 MHz, CDCl_3): 1.75 (s, 3H), 2.73 (br s, 1H), 7.23–7.26 (m, 2H), 7.29–7.38 (m, 2H), 7.39–7.60 (m, 5H), 7.70–7.76 (m, 2H), 8.48 (d, $J = 5.8$, 2H). MS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{18}\text{NO}$ 324.1; Found 324.0.

2.3. 4-((1-Methylene-3-phenyl-1H-inden-2-yl)ethynyl)pyridine (2-PA-BF3a)

A mixture of indenol derivative **3** (50 mg, 0.155 mmol) in HCOOH (Aldrich, purity 98 %, 5.0 mL) was heated to 50°C for 5 h. The reaction mixture was then diluted with chloroform and washed with water. The organic layer was dried over sodium sulfate and concentrated under reduced pressure to a volume of 5 mL. The resulting residue was purified by flash chromatography with CDCl_3 - CD_3OD (98:2) as the eluent to obtain a solution of benzofulvene monomer **2-PA-BF3a**. ^1H NMR (500 MHz, CDCl_3): 6.15 (s, 1H), 6.27 (s, 1H), 7.29 (m, 2H), 7.32–7.36 (m, 2H), 7.43–7.47 (m, 1H), 7.49–7.56 (m, 3H), 7.68–7.73 (m, 1H), 7.80–7.83 (m, 2H), 8.55 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3): 89.5, 93.6, 113.9, 117.7, 120.4, 121.3, 125.4, 127.3, 128.5, 128.6, 128.9, 129.0, 131.9, 133.7, 136.2, 141.3, 146.1, 149.5, 150.4.

2.4. Poly[4-((1-methylene-3-phenyl-1H-inden-2-yl)ethynyl)pyridine] (poly-2-PA-BF3a)

The solution of benzofulvene monomer **2-PA-BF3a** in CDCl_3 was concentrated under reduced pressure. The resulting residue was dissolved into chloroform and again evaporated (this process of dissolution/evaporation was repeated three times). The last residue was purified by precipitation with *n*-hexane (8.0 mL) from a solution of the polymer in chloroform (2.0 mL) and dried under reduced pressure to obtain *poly-2-PA-BF3a* as a pale-yellow solid (70 mg, yield 32 % in monomeric unit). ^1H NMR (500 MHz, CDCl_3): see Fig. 3. ^{13}C NMR (125 MHz, CDCl_3): see Fig. 4.

2.5. Ethyl 1-oxo-3-phenyl-6-(pyridin-4-ylethynyl)-1H-indene-2-carboxylate (5)

A degassed mixture of triflate **4** (100 mg, 0.235 mmol) in 6.0 mL di DMF-TEA (5:1 v/v) containing the commercially available 4-ethynylpyridine hydrochloride (Aldrich, purity 97 %, 65 mg, 0.47 mmol), CuI (Aldrich, purity 98 %, 6.0 mg 0.03 mmol), and tetrabutylammonium iodide (Aldrich, purity 98 %, 260 mg, 0.70 mmol), was stirred at room temperature for 10 min. Subsequently, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (Aldrich, purity 98 %, 21 mg, 0.030 mmol) was added and the resulting mixture was stirred at 50°C for 1.5 h. The reaction mixture was concentrated under reduced pressure, the residue was dissolved into dichloromethane and washed with water. The organic layer was dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography with petroleum ether-ethyl acetate (6:4) as the eluent gave indenone derivative **5** as a red solid (63 mg, yield 71 %). An analytical sample was obtained by recrystallization from ethyl acetate by slow evaporation (mp 143 – 144°C). ^1H NMR (400 MHz, CDCl_3): 1.16 (t, $J = 7.2$, 3H), 4.21 (q, $J = 7.2$, 2H), 7.22 (d, $J = 7.6$, 1H), 7.42 (d, $J =$

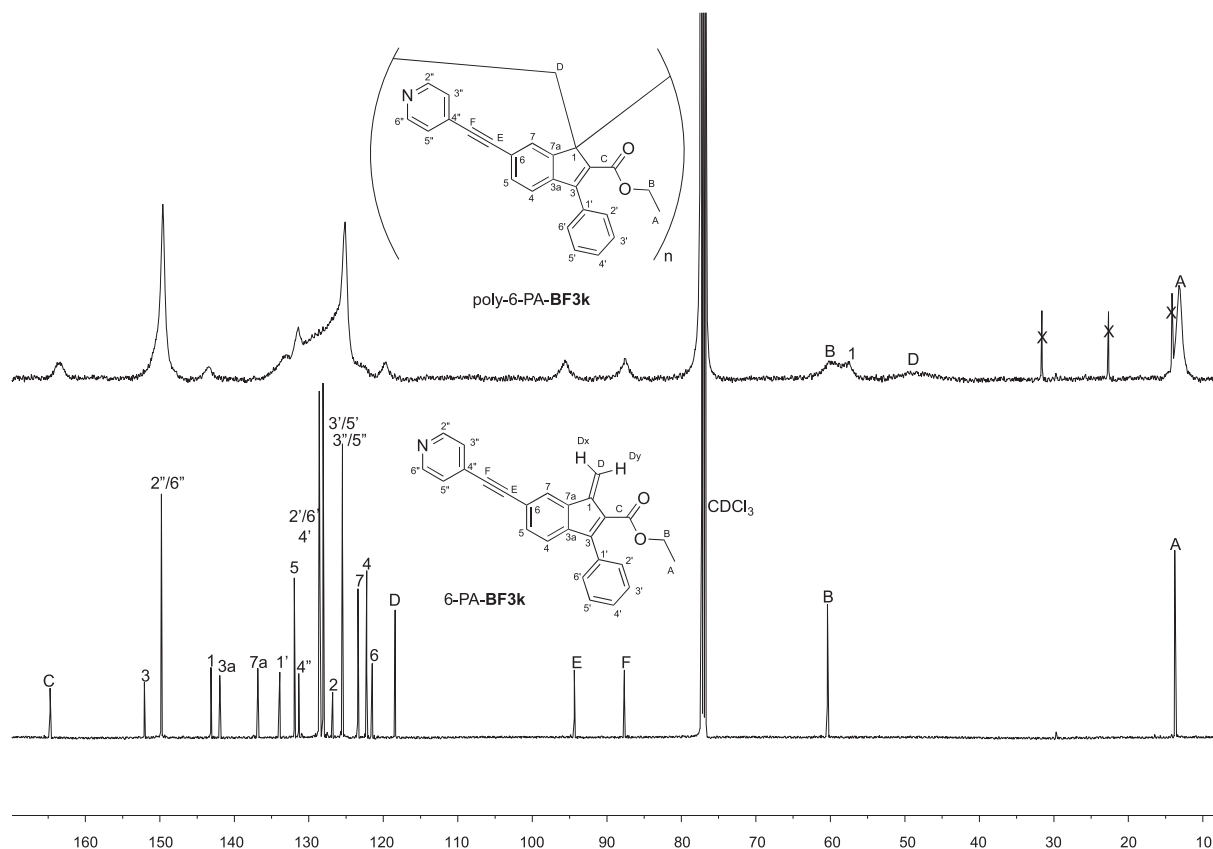
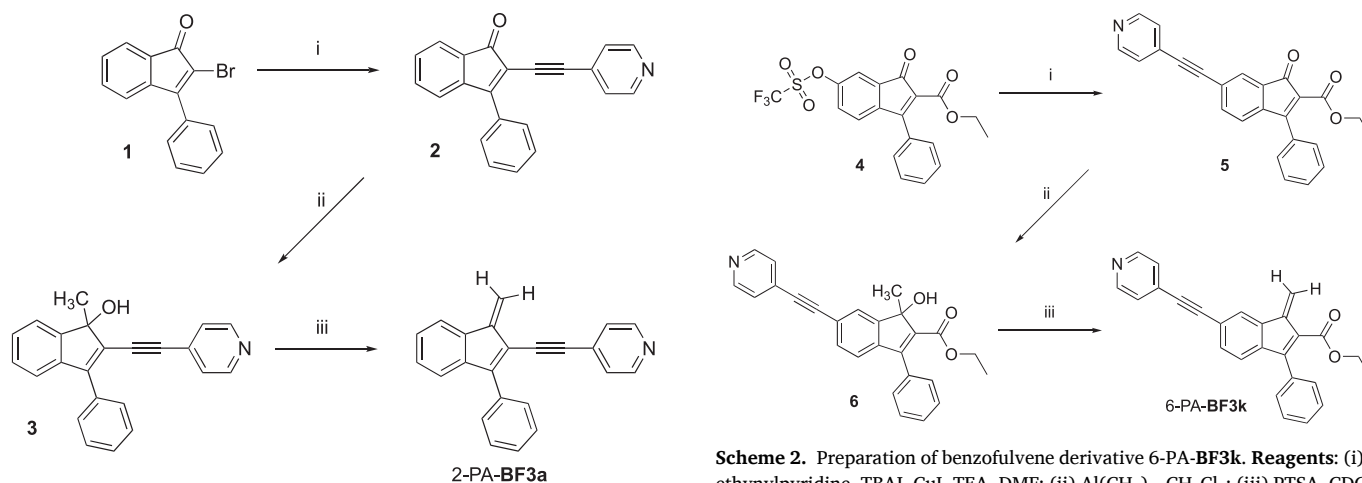


Fig. 6. Comparison of ^{13}C NMR spectrum (CDCl_3 , 125 MHz) of *poly*-6-PA-BF3k with that of corresponding benzofulvene derivative 6-PA-BF3k (CDCl_3 , 125 MHz).



Scheme 1. Preparation of benzofulvene derivative 2-PA-BF3a. Reagents: (i) 4-ethynylpyridine, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI, TEA, THF; (ii) $\text{Al}(\text{CH}_3)_3$, CH_2Cl_2 ; (iii) HCOOH.

6.2, 2H), 7.49–7.53 (m, 5H), 7.60 (dd, $J = 7.6, 1.6$, 1H), 7.76 (d, $J = 1.6$, 1H), 8.63 (d, $J = 6.2$, 2H). MS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{25}\text{H}_{17}\text{NNaO}_3$ 402.1; Found 402.1.

2.6. Ethyl 1-hydroxy-1-methyl-3-phenyl-6-(pyridin-4-ylethynyl)-1H-indene-2-carboxylate (6)

To a solution of compound 5 (440 mg, 1.16 mmol) in dichloromethane (20 mL), a 2 M solution of $\text{Al}(\text{CH}_3)_3$ (Aldrich, purity 1.90–2.20 M, 2.32 mL, 4.64 mmol) in toluene was added, and the reaction mixture

Scheme 2. Preparation of benzofulvene derivative 6-PA-BF3k. Reagents: (i) 4-ethynylpyridine, TBAI, CuI, TEA, DMF; (ii) $\text{Al}(\text{CH}_3)_3$, CH_2Cl_2 ; (iii) PTSA, CDCl_3 .

was stirred at room temperature for 30 min. Subsequently, the $\text{Al}(\text{CH}_3)_3$ excess was decomposed with a 1 N solution of NaOH and the solid was filtered off. The organic phase was dried over sodium sulfate and concentrated under reduced pressure. The resulting residue was purified by flash chromatography with petroleum ether-ethyl acetate (6:4) as the eluent to obtain indenol derivative 6 as an off-white solid (326 mg, yield 71 %). Recrystallization of 6 from ethyl acetate by slow evaporation afforded pale-yellow crystals melting at 184–185 °C. ^1H NMR (400 MHz, CDCl_3): 1.05 (t, $J = 7.2$, 3H), 1.79 (s, 3H), 3.66 (s, 1H), 4.07–4.20 (m, 2H), 7.15 (d, $J = 8.0$, 1H), 7.35–7.45 (m, 7H), 7.48 (dd, $J = 8.0, 1.6$, 1H), 7.74 (d, $J = 1.6$, 1H), 8.60 (m, 2H). MS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{22}\text{NO}_3$ 396.2; Found 396.1.

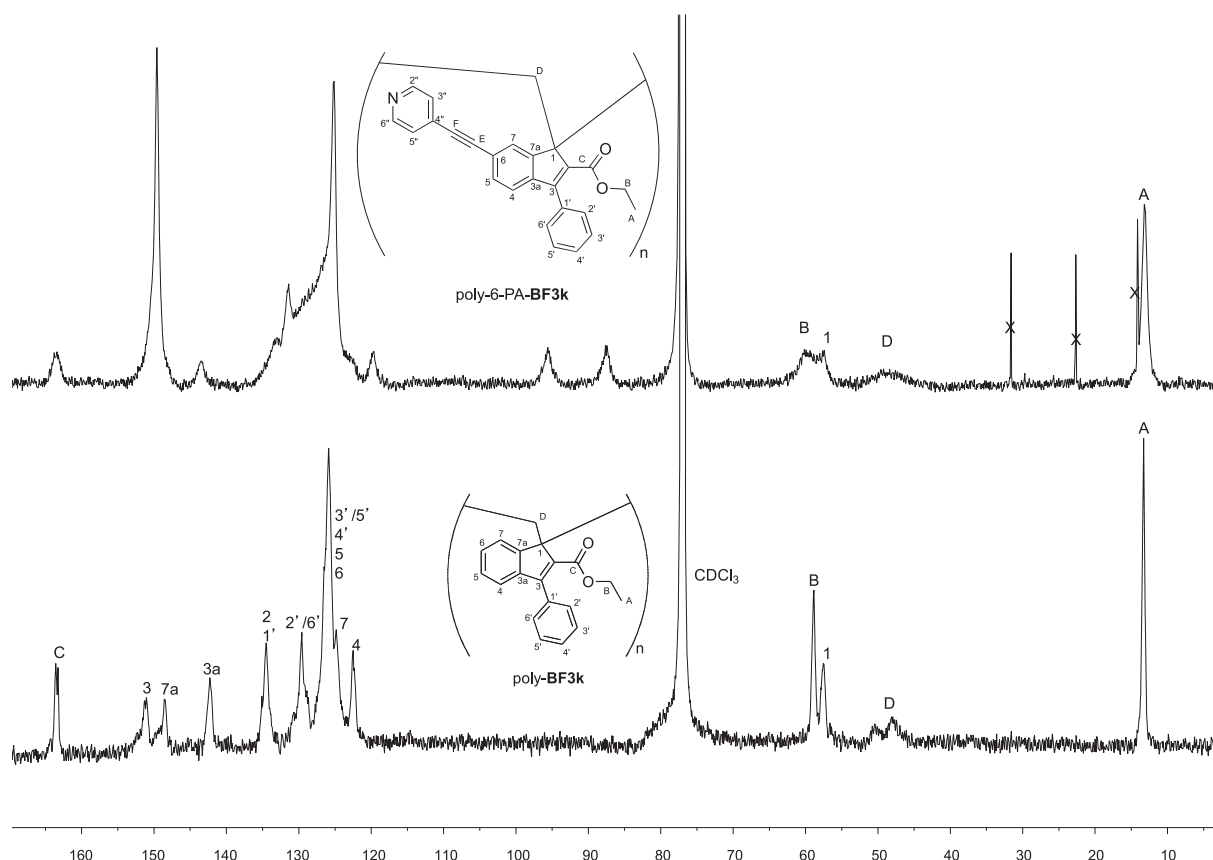


Fig. 7. Comparison of ^{13}C NMR spectra of *poly-6-PA-BF3k* with that of closely related *poly-BF3k*.

2.7. Ethyl 1-methylene-3-phenyl-6-(pyridin-4-ylethynyl)-1H-indene-2-carboxylate (6-PA-BF3k)

A mixture of indenol derivative **6** (10 mg, 0.025 mmol) in CDCl_3 (3.0 mL) containing *p*-toluenesulfonic acid monohydrate (Aldrich, purity 98.5 %, 15 mg, 0.079 mmol) was heated to reflux for 2 h. The reaction mixture was then washed with a saturated solution of NaHCO_3 and dried over sodium sulfate to obtain a solution of benzofulvene monomer 6-PA-BF3k. ^1H NMR (400 MHz, CDCl_3): 1.05 (t, $J = 7.2$, 3H), 4.13 (q, $J = 7.2$, 2H), 6.43 (s, 1H), 6.65 (s, 1H), 7.24 (d, $J = 7.6$, 1H), 7.35–7.49 (m, 8H), 7.88 (d, $J = 1.6$, 1H), 8.59–8.64 (m, 2H).

2.8. Poly[ethyl 1-methylene-3-phenyl-6-(pyridin-4-ylethynyl)-1H-indene-2-carboxylate] (*poly-6-PA-BF3k*)

The solution of benzofulvene monomer 6-PA-BF3k in CDCl_3 was concentrated under reduced pressure. The resulting residue was dissolved into chloroform and again evaporated (this process of dissolution/evaporation was repeated three times). The last residue was purified by precipitation with *n*-hexane (40 mL) from a solution of the polymer in chloroform-ethanol (1:1) and dried under reduced pressure to obtain *poly-6-PA-BF3k* as a pale-yellow solid (220 mg, yield 75 % in monomeric unit). ^1H NMR (500 MHz, CDCl_3): see Fig. 5. ^{13}C NMR (125 MHz, CDCl_3): see Fig. 6.

2.9. X-ray crystallography

Single crystals of indenone derivative **5** were submitted to X-ray data collection on an Oxford-Diffraction Xcalibur Sapphire 3 diffractometer with a graphite monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. The structures were solved by direct methods implemented in SHELXS-97 program [46]. The refinements were carried out by full-

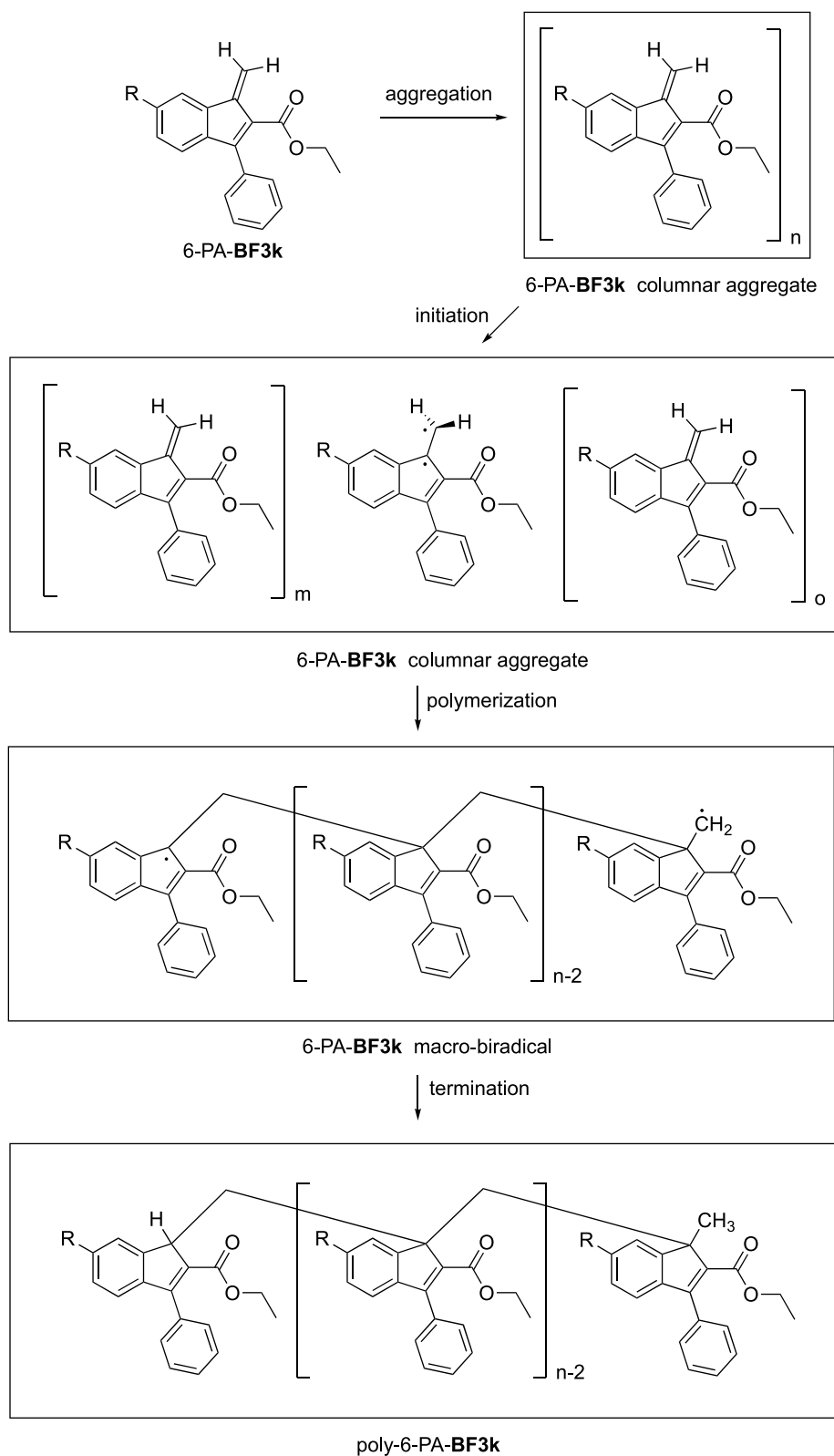
matrix anisotropic least-squares on F^2 for all reflections for non-H atoms by means of the SHELXL-97 program [47]. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2213739 (5). 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).

2.10. Matrix assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS)

MALDI-TOF mass spectra were recorded in reflectron mode by means of a 4800 Proteomic Analyzer (Applied Biosystems) MALDI-TOF/TOF instrument equipped with a Nd:YAG laser at a wavelength of 355 nm with <500 ps pulse and 200 Hz firing rate. The accelerating voltage was 15 kV. External calibration was performed using an Applied Biosystems calibration mixture consisting of polypeptides with different molar mass values. The irradiance was maintained slightly above the threshold, to obtain a mass resolution of about 8000–10000 fwhm. Mass accuracy was about 50 ppm. The best mass spectra were recorded using 3-indoleacrylic acid (IAA) or trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix.

2.11. Differential scanning calorimetry (DSC)

DSC measurements of both polymers were performed by a TA Instrument Q100 DSC, calibrated with melt purity indium standard (156.6 °C and 28.45 J/g). Each sample (2–2.5 mg) was analyzed under nitrogen atmosphere (flow rate of 50 mL/min) using the following runs: (a) heating at 10 °C/min from –90 to 160 °C; (b) cooling at 50 °C/min from 160 to –90 °C; (c) heating at 10 °C/min from –90 to 140 °C. Three



Scheme 3. Hypothetical mechanism for the spontaneous polymerization (Affinity Polymerization) of benzofulvene derivative 6-PA-BF3k.

repeated cycles were performed to verify the reproducibility of thermal transitions. The glass-transition (T_g) temperatures measured in the first and second heating run were computed by the midpoint.

2.12. Thermogravimetric analysis (TGA)

The thermogravimetric analyses of both polymers were carried out by a thermogravimetric apparatus (TGA, TA Instruments Q500) under a nitrogen atmosphere (flow rate 60 mL/min) at 10 °C/min heating rate, from 40 °C to 800 °C. The weight loss percent and its derivate (DTG)

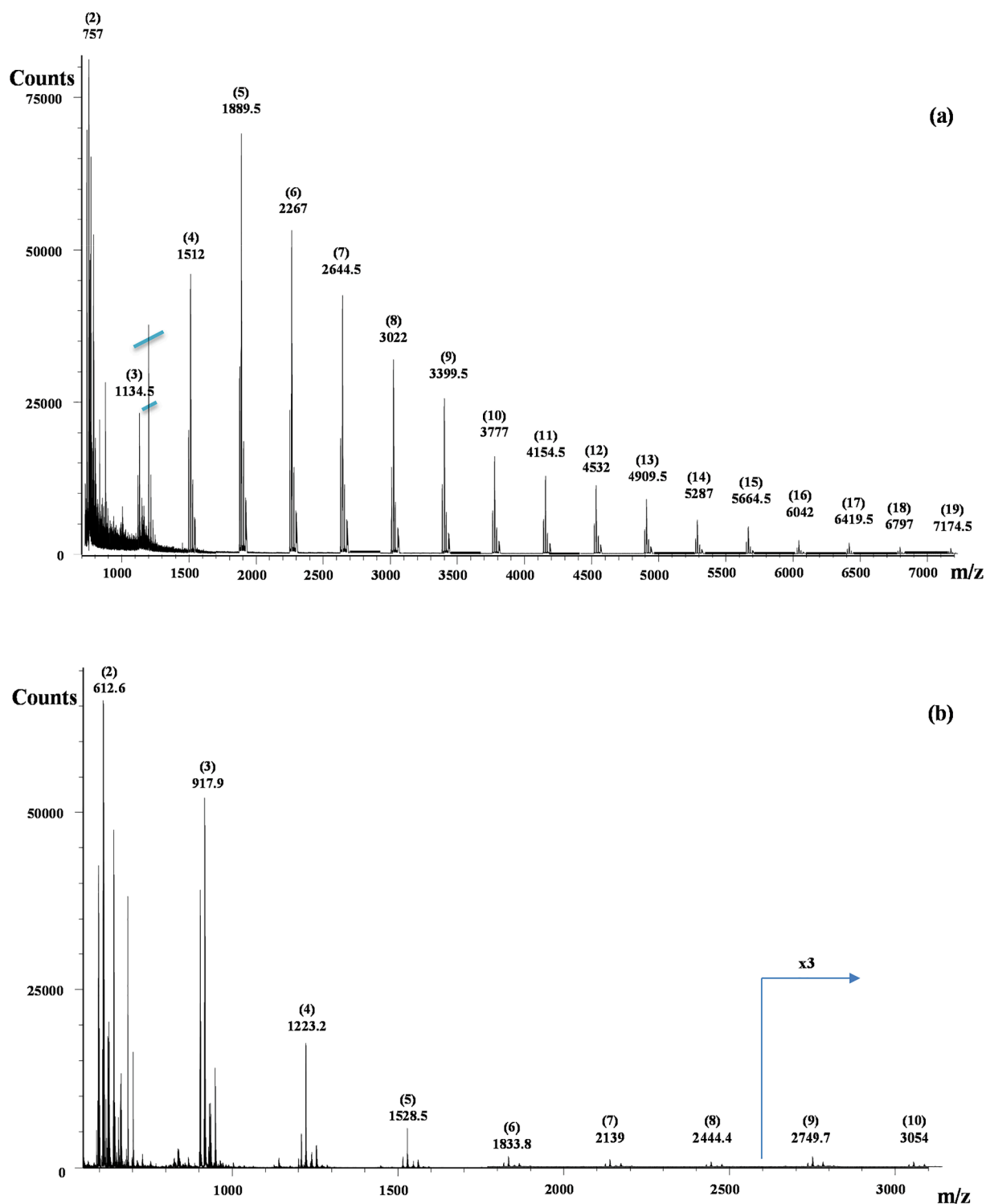


Fig. 8. MALDI-TOF mass spectrum of (a) *poly-6-PA-BF3k* and (b) *poly-2-PA-BF3a* recorded in reflectron mode using 3-indoleacrylic acid (IAA) as the matrix.

were recorded as a function of temperature. Sample weights were approximately 1.5–2 mg.

2.13. Photophysical characterization

Photoluminescence (PL) and PL excitation spectra (PLE) are obtained with a NanoLog composed by a iH320 spectrograph equipped with a Synapse QExtra charge-coupled device by exciting with a monochromated 450 W Xe lamp. The spectra are corrected for the instrument

response. PL QY in solution were measured by using quinine sulfate as a reference and for solids with a home-made integrating sphere according to the procedure reported elsewhere [48].

2.14. Hole mobility measurements

Glass substrates with indium tin oxide (ITO, sheet resistance 15 Ω /sq) patterns were cleaned ultrasonically in deionized water, acetone and isopropanol. After 10 min oxygen plasma treatment, poly(3,4-

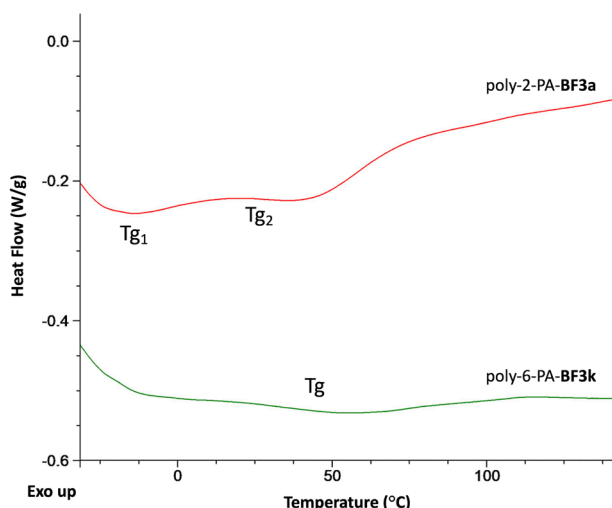


Fig. 9. Thermograms of the first heating run of (red trace) poly-2-PA-BF3a and (green trace) poly-6-PA-BF3k samples in the temperature range from -40 to 140 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ethylene-dioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS, Heraeus Clevios AI 4083) was deposited through nylon filter (0.45 μm) on the substrates at rotation 2000 rpm. Subsequently, the substrates were annealed for 10 min at 100 °C. On the PEDOT:PSS films 10 nm of MoO_3 layer was deposited in vacuum evaporation system. A solution of poly-6-PA-BF3k in CHCl_3 at concentration 15 mg/mL was sonicated for 4 h, treated by a heat gun and left for 12 h under stirring before deposition at 1000 rpm rotation. On such prepared samples, 10 nm of MoO_3 and 90 nm of Al were deposited by thermal evaporation. The final architecture of the device was ITO / PEDOT:PSS / MoO_3 / poly-6-PA-BF3k / MoO_3 / Al and the active area was equal to 5.7 mm^2 .

Current density of holes as a function of applied voltage was registered with Keithley 2602 source meter and home developed LabVIEW software. Negative bias was applied to ITO while positive one to the Al electrode in order to create optimal conditions for holes transport. Thicknesses of the devices were measured with Bruker Dektak XT profilometer.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis of benzofulvene monomer 2-PA-BF3a is shown in Scheme 1.

Sonogashira reaction [49] of bromoindenone derivative 1 [45] with the commercially available 4-ethynylpyridine (Aldrich) afforded indenone derivative 2 by the insertion of the 4-pyridylacetylene group in position 2 of the 3-phenyl-1-indenone nucleus.

Intermediate 2 was then submitted to the already described methylation procedure [13,17,18] to obtain indenol derivative 3, which was dehydrated with formic acid to give benzofulvene monomer 2-PA-BF3a.

On the other hand, when Sonogashira reaction with 4-ethynylpyridine (Aldrich) was performed on triflate derivative 4 [21], indenone 5 was obtained in good yield as described in Scheme 2.

The structure of this indenone intermediate was confirmed by crystallography (Fig. 2).

Then, the usual methylation-dehydration procedure [13,17,18] was applied to indenone derivative 5 to obtain benzofulvene monomer 6-PA-BF3k.

Interestingly, both benzofulvene derivatives 2-PA-BF3a and 6-PA-BF3k demonstrated the tendency to polymerize spontaneously in

similarity with many structurally-related benzofulvene derivatives. In fact, the concentration of the respective monomer solutions (in CHCl_3 or CDCl_3) at reduced pressure into a rotary evaporation apparatus gave the corresponding polybenzofulvene derivatives, which were purified by re-precipitation as described in the Experimental section.

The macromolecular structure of 2-PA-BF3a and 6-PA-BF3k was investigated by NMR spectroscopy, which showed evident analogies, but also some significant differences. In these studies, we adopted the usual protocol based on the comparison of ^1H and ^{13}C NMR spectra of the polymer with the corresponding spectra of the relevant monomer (Figs. 3–5). As expected, the ^1H NMR spectra of the polymers (Figs. 3 and 5) showed very broad signals that were up-field shifted with respect to those appearing in the spectra of the corresponding monomers. This result supported the polymeric nature of both poly-2-PA-BF3a and poly-6-PA-BF3k.

Moreover, the comparison shown in Fig. 3 allowed us to assume for poly-2-PA-BF3a a significant structural inhomogeneity because the presence of very broad signals attributed to pyridine hydrogen atoms $2''/6''$ that suggested the occurrence of monomeric unities showing significant differences in their structures. The comparison of the corresponding ^{13}C NMR spectra (Fig. 4) showing a sufficient resolution strongly supported our assumption.

In the ^{13}C NMR spectra of benzofulvene monomer 2-PA-BF3a, the signal at 113.9 ppm was assigned to the exocyclic methylene carbon (C-D) and the one at 146.1 ppm was assigned to the other vinylidene carbon (C-1). These two signals were up-field shifted in the corresponding polymer poly-2-PA-BF3a spectrum because of the change in hybridization produced by the polymerization according to the results obtained with related polybenzofulvene derivatives [15,32].

However, we estimate the existence of about five peaks in the aliphatic region comprised from 37 and 51 ppm (i. e. 39.0 , 42.7 , 44.7 , 47.1 , 49.5 ppm) that could be attributed to methylene carbon (C-D). On the other hand, the analysis of the region from 52 to 61 ppm showed the presence a big complex peak at around 56.6 ppm and a small one at 60.6 ppm. These observation supports the presence of different monomeric units representing enchainment isomers deriving from either vinyl (1,2) or diene (1,4) polymerizations, as previously suggested by us [14,15] and confirmed by Ishizone and co-workers [50,51]. Thus, monomeric unities in the 1,4-enchainment could be responsible for the peaks at 60.6 ppm (aliphatic quaternary carbon atom) and at 39 ppm (C-D). However, the small intensity of these peaks with respect to the other peaks in the same aliphatic regions suggested that the diene (1,4) polymerization mechanism appeared to be disfavoured with respect to the vinyl (1,2) one.

Interestingly, in the ^1H NMR spectrum of poly-2-PA-BF3a (Fig. 3), the signals in the aromatic region are significantly broader with respect to the corresponding ones of poly-6-PA-BF3k (Fig. 5).

In particular, the peak at 8.41 ppm in the ^1H NMR spectrum of poly-6-PA-BF3k (Fig. 5) assigned to pyridine hydrogen atoms $2''/6''$ appeared to be constituted by two relatively sharp components, whereas the corresponding peak in the ^1H NMR spectrum of poly-2-PA-BF3a (Fig. 3) is composed at the least by three broad components. This observation appeared to be in full agreement with the assumption of a higher structural homogeneity of poly-6-PA-BF3k with respect to poly-2-PA-BF3a.

This assumption was also supported by ^{13}C NMR spectroscopy analysis (Figs. 6 and 7).

In fact, some key correspondences were observed between the ^{13}C NMR spectra shown in Fig. 7, particularly in the peaks attributed to C-1 and C-D, which were assumed to be diagnostic of the structure of the monomeric unit and supported the consistency of the vinyl (i.e. 1,2) polymerization mechanism in poly-6-PA-BF3k as already observed in poly-BF3k [32,33].

In conclusion, the presence of the 4-pyridylacetylene substituent in different positions of the 3-phenylindene nucleus appears to be compatible with the spontaneous vinyl (1,2) polymerization

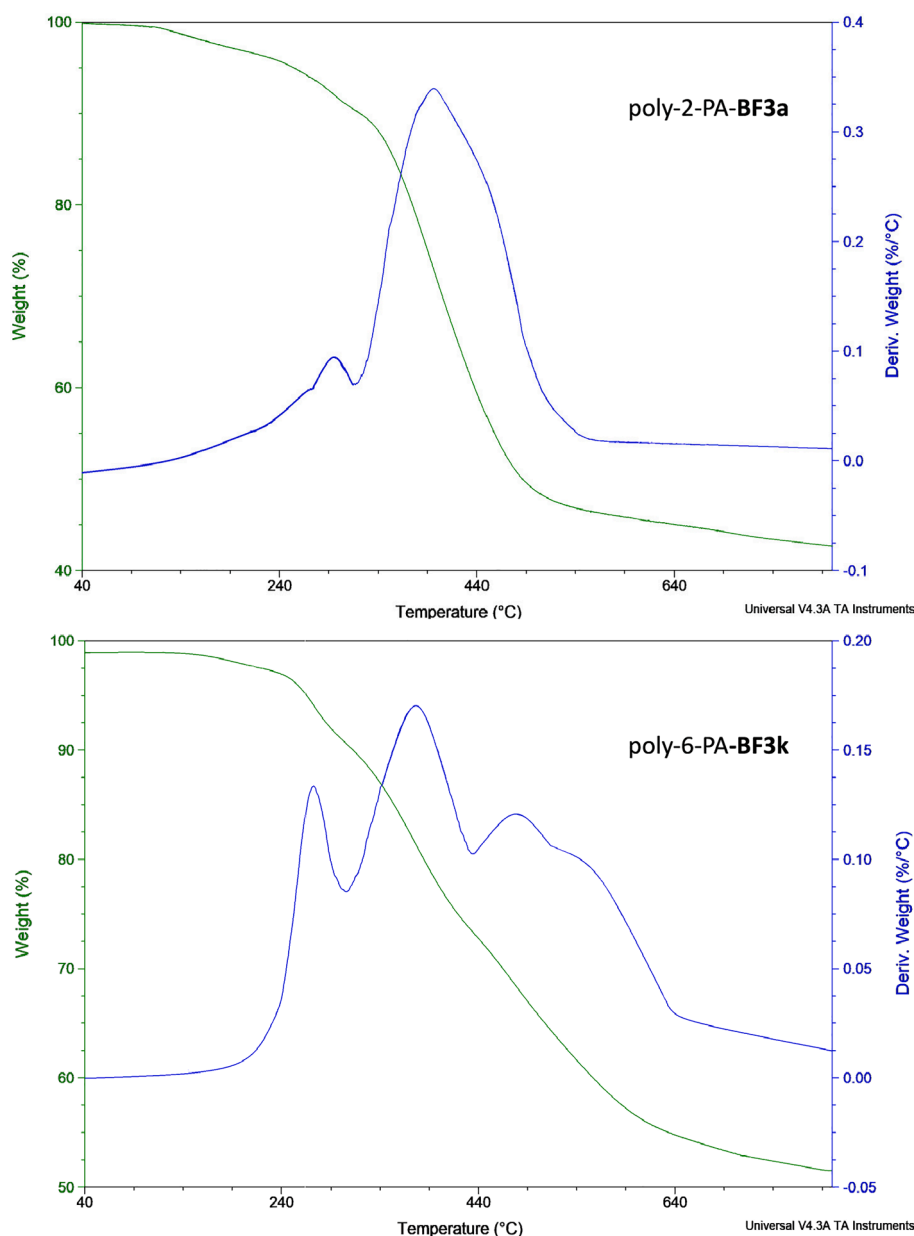


Fig. 10. Weight loss and DTG curves of poly-2-PA-BF3a and poly-6-PA-BF3k samples recorded by TGA analyses under nitrogen atmosphere.

mechanism, but the best results from the point of view of the structural homogeneity were assured by the presence of the ester group in position 2, as already observed [15,18,32].

From the mechanistic perspective, the ester group can be assumed to play a dual role of stabilizing the position of the double bond to preserve the conjugation with the electron-donating phenyl group and of pre-organizing the structure of the monomer towards the formation of columnar aggregates precluding the polymerization step (Scheme 3). In fact, the presence of the ester group was assumed to constrain the phenyl group in conformations capable of stimulate the establishment of *T*-shaped interactions, which could play a pivotal role in the formation of the columnar aggregates.

Within the concept of “Affinity Polymerization”, the mutual recognition and interaction among the benzofulvene monomers (as in a crystallization process) lead to the formation of relatively ordered supramolecular systems such as columnar aggregates. When the intermolecular distance and the orientation of the monomers is suitable, the polymerization mechanism becomes operative and starts as a domino reaction within the columnar aggregates. If this mechanistic hypothesis

is correct, the ordered orientation of the monomers within the columnar aggregate should affect the enchainment of the resulting poly-benzofulvene derivatives.

Finally, the polymeric nature of benzofulvene derivatives 2-PA-BF3a and 6-PA-BF3k was further evaluated by MALDI-TOF mass spectrometry experiments, and the spectra recorded in reflectron mode using 3-indoleacrylic acid (IAA) as the matrix are displayed in Fig. 8. The mass spectrum of the poly-6-PA-BF3k (Fig. 8a) indeed showed a series of repeating peak families from m/z 700 up to about m/z 7200 showing 377.5 ± 0.1 Da intervals corresponding to the mass of the repeating unit of the poly-6-PA-BF3k (*i. e.* 377.4 Da). The most intense peaks corresponded to the molecular ions of the expected oligomers terminated with hydrogen at both ends from the dimer up to the nonadecamer. The mass spectrum of poly-2-PA-BF3a sample (Fig. 8b) showed a series of repeating peak families from m/z 600 Da up to about m/z 3100 Da showing 305.3 ± 0.1 Da intervals corresponding to the mass of the repeating unit of this polymer (*i. e.* 305.3 Da). Likely to the poly-6-PA-BF3k sample, the most intense peaks correspond to the macromolecular chains terminated with hydrogen at both ends. In this case the most

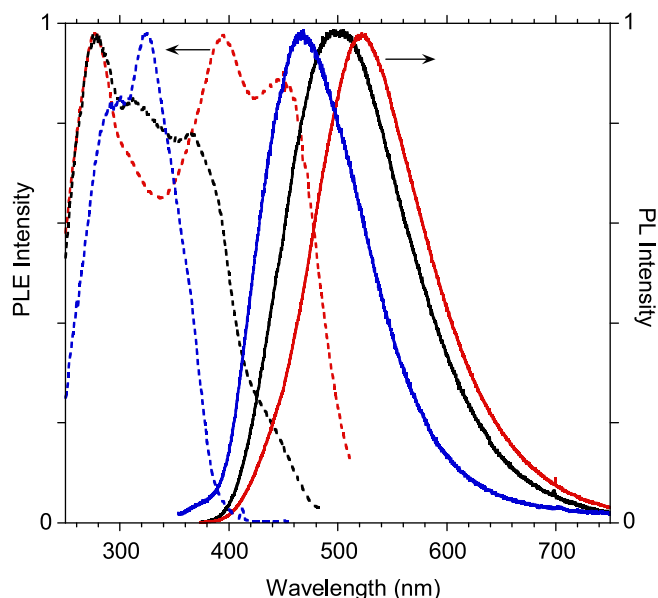


Fig. 11. PLE (dashed line) and PL (solid lines) spectra of *poly-6-PA-BF3k* in THF solution (blue lines, $\lambda_{em} = 468$ nm, $\lambda_{ex} = 350$ nm), cast-film (black lines, $\lambda_{em} = 468$ nm, $\lambda_{ex} = 350$ nm) and powders (red lines, $\lambda_{em} = 525$ nm, $\lambda_{ex} = 350$ nm). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Optoelectronic properties of *poly-6-PA-BF3k*, compared with those of *poly-6-Pyr-BF3k* [44], *poly-6-TT-BF3k* [25], and *poly-6-BT-BF3k* [22].

Polymer	Hole mobility (cm ² /Vs)	Solution			Solid		
		λ_{ab} (nm)	λ_{em} (nm)	QY (%)	λ_{ab}^a (nm)	λ_{em}^b (nm)	QY ^b (%)
<i>poly-6-PA-BF3k</i>	$7.7 \cdot 10^{-4}$	325 ^c	470	5	350 ^c	525	11
<i>poly-6-Pyr-BF3k</i>					370 ^c	485	13
<i>poly-6-TT-BF3k</i>	$5.9 \cdot 10^{-5}$	405	560	10	420	573	1
<i>poly-6-BT-BF3k</i>	$7.3 \cdot 10^{-5}$	380	490	7	386	555	< 0.1
PVK	$9.8 \cdot 10^{-6}$						

^a Spin coated films, ^b powders; ^c PLE maximum.

intense peaks correspond to the low molar mass oligomers from dimer up to pentamer, while the oligomers from hexamer up to octamer appear with very low intensity.

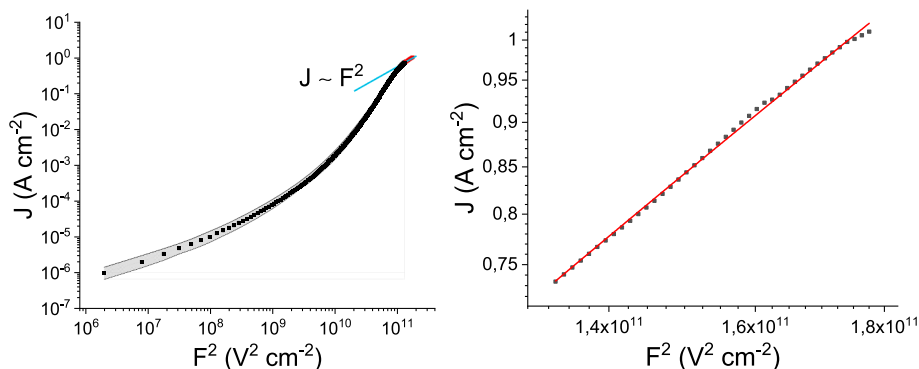


Fig. 12. Hole current density as a function of square applied electric field, the gray area shows the range within which all curves were registered while the points are the average of all measurements (left); hole current density in the electric field range where space charge limited current was recorded ($J \sim F^2$) and its best fit within the Mott-Gurney law (right).

The thermal properties of both polybenzofulvene derivatives were investigated by differential scanning calorimetry (DSC) by heating from -90 to 140 °C using a heating rate of 10 °C/min under nitrogen flow (50 mL/min). The thermograms recorded in the first heating run in the range -40 up to 140 °C are shown in Fig. 9.

Both polymers showed only the glass transition temperature (T_g), indicating their amorphous structure. In particular, *poly-6-PA-BF3k* showed only a single T_g at about 46 °C, whereas *poly-2-PA-BF3a* presented two T_g values at about -11 °C and 39 °C. This result is consistent with the copolymeric composition (two different monomeric units) of *poly-2-PA-BF3a* as suggested by the results of NMR characterization (see above). Therefore, the DSC analysis supports that both 1,2 (vinyl) and 1,4 (diene) mechanisms occur during the polymerization of *2-PA-BF3a*.

The thermal stability of both polymers was also investigated by thermogravimetric analysis (TGA) in inert atmosphere. Fig. 10 shows the weight loss percent and its derivative (DTG) curves as a function of the heating temperature. *Poly-2-PA-BF3a* degraded in a temperature range from 120 °C up to 560 °C with a maximum rate of thermal degradation at about 280 °C and 400 °C and with a char residue of about 40 %. In the first thermal degradation step we observed a weight loss of 11 %, which can be due to the degradation or the volatilization of oligomers with very low molar mass (monomers or dimers). In the second step, a weight loss of about 40 % was recorded that may be due to the degradation of *poly-2-PA-BF3a* macromolecular chains. On the other hand, *poly-6-PA-BF3k* degraded in the temperature range from 190 °C to 640 °C forming a char residue of about 60 %. It showed three thermal degradation steps with maxima at 270 °C, 370 °C and 480 °C. The differences in the thermal degradation profiles of polybenzofulvene derivatives *poly-6-PA-BF3k* and *poly-2-PA-BF3a* confirmed their different chemical structures.

3.2. Photophysical features of polybenzofulvene derivative *poly-6-PA-BF3k*

The optoelectronic features of the most structurally homogeneous polybenzofulvene derivative *poly-6-PA-BF3k* (Fig. 11) are summarized in Table 1 for both the solid state and the solution in comparison with those previously reported for the corresponding polybenzofulvene derivatives bearing pyridine (i. e. *poly-6-Pyr-BF3k*) [44], terthiophene (i. e. *poly-6-TT-BF3k*) [25], and bithiophene (i. e. *poly-6-BT-BF3k*) [22,25] moieties in position 6 of the indene nucleus of the monomeric unit.

We previously reported that polybenzofulvene derivative *poly-6-Pyr-BF3k* displays an intense fluorescent blue emission centered at 485 nm, average lifetime of 8.5 ns, and quantum yield (QY) of 13 % (Table 1) in the solid state (i. e. powder samples). As expected, the insertion of an acetylene spacer between the pyridine moiety and the indene scaffold produced a red shift in the emission maxima of *poly-6-PA-BF3k* in the solid state. Interestingly, the photoluminescence (PL) QY of the powders

is retained to 11 %.

Previously, we observed that the presence of thiophene moieties in position 6 of the indene nucleus of polybenzofulvene derivatives poly-6-TT-BF3k, and poly-6-BT-BF3k produced a strong reduction of the PL-QY, accompanied by a sharp red-shift of the emission. Thiophene oligomers are recognized to display a high aggregation liability leading to aggregation-caused PL quenching (ACQ) processes, which are induced by the strong intermolecular interactions established by this class of molecules in the solid state [52]. Thus, the efficient side chain packing in the solid state of poly-6-TT-BF3k and poly-6-BT-BF3k was considered to be responsible for the interesting hole mobility values measured in their films.

The hole mobility was measured also for the newly-synthesized poly-6-PA-BF3k by using the same experimental methodology previously used for poly-6-TT-BF3k and poly-6-BT-BF3k, and with poly(*N*-vinylcarbazole) (PVK) as a standard hole-transporting polymer. In particular, we used a simple hole-only device structure ITO/PEDOT:PSS/MoO₃/polymer/MoO₃/Al that gives good ohmic contacts. Fig. 12 shows results of holes mobilities measurements extracted from the Mott-Gurney law

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_h \frac{F^2}{d}$$

where ε_0 is the vacuum permittivity, ε_r denotes the relative permittivity of the material, μ_h stands for the hole mobility and the electric field is $F = U/d$, where d denotes the distance between the electrodes and U is the applied voltage.

Graph on the left presents current density of holes as a function of the square of applied electric field. The gray area shows the range within which all curves were registered while the points are the average of all measurements. Plot on the right presents current density for the field range where space charge limited current (SCLC) was recorded ($J \sim F^2$) and its best fit with the Mott-Gurney law; the relative permittivity (ε_r) was assumed to be equal to 3.

Very interestingly, the hole mobility of newly-synthesized poly-6-PA-BF3k (Table 1) was found to be around one order of magnitude higher than that previously measured for both the two oligothiophene-based polybenzofulvene derivatives poly-6-TT-BF3k and poly-6-BT-BF3k and almost two orders of magnitude higher than that of PVK ($9.8 \times 10^{-6} \text{ cm}^2/\text{Vs}$). This result appears to improve the already good transporting features of this class of polybenzofulvene derivatives possessing chromophore π -stacking [17], and places poly-6-PA-BF3k among the most promising polybenzofulvene derivatives for field-effect transistor (FET) device applications.

4. Conclusion

In conclusion, two benzofulvene derivatives bearing the 4-pyridylacetylene substituent in the two different key positions (i. e. 2 and 6) of the 3-phenylbenzofulvene scaffold were designed and synthesized to evaluate the effects on the spontaneous solid-state polymerization. Both the benzofulvene monomers were easily prepared and proven to polymerize spontaneously by removing the solvent at reduced pressure in the apparent absence of catalysts or initiators. The structure of the stemming polybenzofulvene derivatives was studied by NMR spectroscopy, MALDI-TOF mass spectrometry. The results of the NMR studies supported for 6-PA-BF3k the occurrence of a vinyl (i.e. 1,2) thermoreversible polymerization mechanism as already observed in several structurally related polybenzofulvene derivatives. On the other hand, NMR measurements suggested a significant structural inhomogeneity for poly-2-PA-BF3a. Thus, the most homogeneous polybenzofulvene derivative poly-6-PA-BF3k was characterized from the point of view of its photophysical and optoelectronic features. Significant fluorescent emissions were measured at variable wavelength values depending on the aggregation state with aggregation induced enhancement of the emission. Finally, the hole mobility of poly-6-PA-BF3k was evaluated

revealing a very interesting value, which was around one order of magnitude higher than that previously measured for both the two oligothiophene-based polybenzofulvene derivatives poly-6-TT-BF3k and poly-6-BT-BF3k and almost two orders of magnitude higher than that of PVK. The hole mobility of poly-6-PA-BF3k is particularly interesting due to the lack of aggregation caused quenching with respect to the corresponding thiophene based polymers, and therefore, places poly-6-PA-BF3k as an outstanding polybenzofulvene derivatives for field-effect transistor (FET) device applications.

Data availability:

The raw/processed data required to reproduce these findings are available from the corresponding author by request.

Author Contributions

Marco Paolino, Mario Saletti, Annalisa Reale, Vincenzo Razzano, and Germano Giuliani were involved in the synthesis and the preliminary characterization; Alessandro Donati and Claudia Bonechi performed the NMR studies; Gianluca Giorgi was involved in the crystallographic studies; Giuseppa Mercorillo and Filippo Samperi performed the MALDI-TOF, DSC and TGA experiments; Wojciech Mróz performed the hole mobility studies; Chiara Botta performed the photophysical characterization; Andrea Cappelli designed the compounds and organized the research activities.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

The authors are grateful to Dr. Francesco Berrettini (CIADS, Università di Siena) for the X-ray data collection.

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